

SUPPORTING INFORMATION

Surface-Grafted Polymeric Ionic Liquids with Tunable Morphology via *In/Ex Situ* Cross-linking Methods

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MATERIALS AND GENERAL METHODS

All chemicals were analytical reagent grade and obtained from Sigma-Aldrich and used as purchased unless otherwise specified. Deionized water (18.2 MΩ.cm) was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

NMR Spectroscopy: ¹H NMR spectra for all compounds were acquired in deuterated solvents (as indicated) on a Bruker Avance III at 600 MHz. The chemical shift data are reported in units of δ (ppm) relative to the residual solvent.

X-ray photoelectron spectroscopy (XPS): The chemical composition information of the samples was obtained by XPS; the measurement was carried out on a Thermo Scientific K-Alpha spectrometer using a monochromatic Al K-α X-ray source ($h\nu = 1486.6$ eV). Charging neutralizing equipment was used to compensate sample charging, and the binding scale was referenced to the aliphatic component of C 1s spectra at 285.0 eV.

Contact Angle Analysis: The water contact angle measurements were conducted at room temperature using a goniometer (DSA 100, Krüss) equipped with a microliter syringe. Deionized water (5.0 μL) was used as the wetting liquid.

Atomic Force Microscopy (AFM): The morphology of the silicon wafers was recorded on a Park Systems XE70 SPM Controller LSF-100 HS. A triangular-shaped Si₃N₄ cantilever with integrated tips (Olympus) was used to acquire the images in the non-contact mode. The normal spring constant of the cantilever was 0.02 N/m. The force between the tip and the sample was 0.87 nN.

Ellipsometry: The ellipsometric measurements were performed under ambient conditions using an ellipsometer (model DRE, EL X20C) equipped with a He-Ne laser ($\lambda = 632.8$ nm) at a constant incident angle of 75°. The average dry and wet thickness of polymer brushes on silicon substrate was determined by fitting the data with a three-layer model (native silicon [refractive index, $n = 3.86$] + silicon oxide layer [$n = 1.46$] + organic layer [$n = 1.47$]).

Size exclusion chromatography (SEC): *N,N*-Dimethylformamide at room temperature was used as the solvent at 1 mL/min. An RI detector (Wyatt Technology, Optilab T-rEX) and a dual detector assembly with light scattering and viscometer (Malvern, Viscotek 270 Dual Detector) were used to characterize the eluent. Molecular weight calibration was achieved through polystyrene standards. The free polymers were filtered through 0.45 μm polytetrafluoroethylene membrane filter before injection.

Grafting Density of Ea-c: The grafting density (σ) and average distance between grafting points, D of the polymer brushes were calculated from the dry polymer thickness, h and the number-average molar weight, M_n (the molecular weight of the grafted polymer chains is assumed to be similar to that of the free polymer in solution) values using eqs (1), (2),

$$\sigma = h\rho N_A / M_n \quad (1)$$

$$D = (4/\pi\sigma)^{1/2} \quad (2)$$

where ρ is the density of polymer (1.4136 g/mL) and N_A is Avogadro's number. The expected polymer chain conformation in good solvent was deduced from the comparison of D with the corresponding gyration radius (R_g) of the unperturbed chains calculated from eq (3),

$$R_g = b \cdot (DP/6)^{1/2} \quad (3)$$

where DP is the degree of polymerization and b is the segment length (0.6 nm).

Swelling ratio and Durability of PILs layers: The thickness swelling ratio, α , is defined:

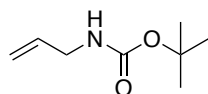
$$\alpha = h_s / h_d \quad (4)$$

where h_s is the thickness of the swollen brush, and h_d is the thickness of the dry brush. To examine the durability of PILs layers, a homemade rotary flow system was used (Figure S1). PILs grafted silicon wafers were placed in a silicon tube (inner diameter: 10 mm, length: 310 mm) with PBS solution (10 mL). The homemade rotary flow system was connected to the evaporator (Heidolph Hei-VAP), was rotated at 37 °C for 72 h. The substrates were washed with PBS and water dried under a stream of nitrogen.

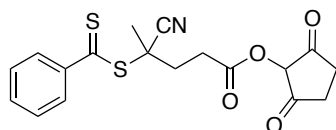


Figure S1. Photographs of the homemade rotary flow system (taken by Dr. Demirci) which was connected evaporator (a), the flow system (b), and PILs grafted silicon wafer (c) in a silicone tube.

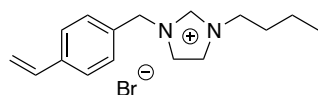
SYNTHETIC PROCEDURES



Synthesis of *t*-butyloxycarbonyl (*t*-BOC) protected allylamine: Allylamine (2.5 mL, 42.3 mmol) and chloroform (75 mL) were charged into a 250 mL flask. A solution of 3.75 g NaHCO₃ in 75 mL of water was added to the reaction solution. Next, sodium chloride (8.06 g, 0.14 mol) was added along with 9.24 g (42.3 mmol) of di-*tert*-butyl dicarbonate dissolved in a few milliliters of chloroform. This mixture was refluxed for 90 min and extracted twice with 62.5 mL of diethyl ether. The organic extracts were combined and dried over anhydrous magnesium sulfate, filtered, and evaporated to remove the solvent. The concentrated liquid was purified by vacuum distillation to yield *t*-butyloxycarbonyl protected allylamine (81% yield). ¹H-NMR (600 MHz, CDCl₃) δ (ppm) = 7.9 (s, 1H), 5.8 (m, 1H), ~5.2–5.0 (d, 2H), 4.2 (d, 2H), 1.4 (s, 9H). Physical and spectroscopic data were in agreement with literature reports.¹



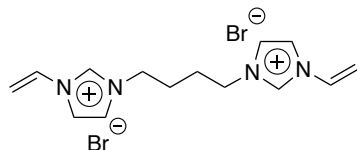
Synthesis of 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid *N*-succinimidyl ester: 4-Cyano-4-(phenylcarbonothioylthio)pentanoic, 2.79 g, 10.0 mmol) and *N*-hydroxysuccinimide (1.15 g, 10.0 mmol) were dissolved in 20 mL of anhydrous dichloromethane. *N,N'*-Dicyclohexylcarbodiimide (2.06 g, 10.0 mmol) was added to the solution. Then the mixture was stirred at room temperature in the dark for 24 h. A white product was filtrated out, and the filtrate was concentrated. The concentrated liquid was purified through a gel column with EtOAc/hexane (1:3, v/v) to yield 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid *N*-succinimidyl ester (69% yield). ¹H NMR (600 MHz, CDCl₃) δ (ppm) = 7.9 (d, 2H), 7.6 (t, 1H), 7.4 (t, 2H), 3.1 (s, 4H), ~2.8–2.3 (m, 4H), 1.9 (s, 3 H). Physical and spectroscopic data were in agreement with literature reports.^{1,2}



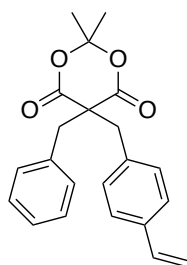
Synthesis of 1-vinylbenzyl-3-butylimidazolium bromide (VBIC): *N*-Butylimidazole was synthesized following the procedure of literature:³ Imidazole (6 g, 88 mmol), 1-bromobutane (12.33 g, 90 mmol), acetonitrile (50 mL) and

potassium hydroxide (9.9 g, 177 mmol), were added in sequence to a flask. The reaction mixture was refluxed for 4 hours and then cooled down to room temperature. The reaction mixture was concentrated, the residue was purified by column chromatography with ethyl acetate:methanol (25:1). Yield 8.65 g, 79%. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ (ppm) = 7.49 (s, 1H), 7.06 (s, 1H), 6.91 (s, 1H), 3.93 (t, 2H), 1.77 (m, 2H), 1.34 (m, 2H), 0.95 (t, 3H).

Using a previously published procedure,⁴ 4-vinylbenzyl bromide (2.84 g, 14.4 mmol) and 1-butylimidazole (1.8 g, 14.4 mmol) were stirred in acetonitrile at reflux for 24 h. The reaction mixture was concentrated to form a yellow viscous oil and washed with ethyl ether (x3), dried in vacuum at rt to give a viscous liquid. Yield: 3.23 g, 70%. $^1\text{H-NMR}$ (600 MHz, $\text{DMSO}-d_6$) δ (ppm) = 7.41 (s, 1H), 6.97 (s, 1H), 6.85 (s, 1H), 3.87 (t, 2H), 1.67-1.72 (m, 2H), 1.23-1.29 (m, 2H), 0.88 (t, 3H). Physical and spectroscopic data were in agreement with literature reports.⁴



Synthesis of 1,4-di(3-vinylimidazolium)butane bisbromide (DVIMBr): 1,4-Di(vinylimidazolium) butane bisbromide (DVIMBr) was prepared by standard method.⁵ 1-Vinylimidazole (1 g, 10.6 mmol) and 1,4-dibromobutane (1.15 g, 5.3 mmol) were stirred in methanol at 60 °C for 15 h. Upon cooling, the reaction mixture was poured dropwise into diethyl ether. The white precipitate was filtered off and dried at room temperature. Yield of 59%. $^1\text{H-NMR}$ (600 MHz, $\text{DMSO}-d_6$) δ (ppm) = 9.63 (s, 2H), 8.25 (s, 2H), 7.98 (s, 2H), 7.34 (m, 2H), 5.99 (d, 2H), 5.45 (d, 2H), 4.29 (m, 4H), 1.87 (m, 4H). Physical and spectroscopic data were in agreement with literature reports.⁵



Synthesis of 5-benzyl-2,2-dimethyl-5-(4-vinylbenzyl)-[1,3]dioxane-4,6-dione: 5-Benzyl-2,2-dimethyl-5-(4-vinylbenzyl)-[1,3]dioxane-4,6-dione was synthesized according to a previously published report,⁶ with some modification. A mixture of Meldrum's acid (4.32 g, 30.0 mmol), benzaldehyde (3.18 g, 30.0 mmol), piperidine (0.129 g, 1.5 mmol), and acetic acid (0.18 g, 4.5 mmol) in DMSO (30 mL) was heated at 50 °C for 24 h. The resulting yellow solution was cooled to 0 °C, and NaBH_4 (0.6 g, 15.9 mmol) was slowly added to the solution. After stirring for 30 min at room temperature, the reaction was quenched by slowly adding water (15 mL) followed by adding 10% HCl (30 mL). The mixture was extracted with EtOAc (3 x 150 mL). The combined organic layer was washed with brine, dried over MgSO_4 , filtered, and concentrated to give yellow oil as a crude product. It was further purified by column chromatography on silica gel (Hex:EtOAc = 3:1 to 1:1) to afford the desired product 5-benzyl-2,2-dimethyl-5-(4-vinylbenzyl)-[1,3]dioxane-4,6-dione as a yellowish-white solid that matched previously reported characterization spectra.⁶ ESI-HRMS: Found: m/z 257.1. Calc. for $\text{C}_{13}\text{H}_{14}\text{O}_4\text{Na}$ [$\text{M}+\text{Na}$]: 257.1. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ (ppm) = 7.40-7.31 (m, 5H), 4.16 (m, 1H), 3.79 (m, 2H), 1.77 (s, 3H), 1.52 (s, 3H).

5-Benzyl-2,2-dimethyl-5-(4-vinylbenzyl)-[1,3]dioxane-4,6-dione (0.60 g, 2.56 mmol) and K_2CO_3 (0.53 g, 3.84 mmol) were placed in flask. After dispersing the mixture in dry DMF (2 mL), 4-vinylbenzyl chloride (0.51 g, 3.30 mmol) was dropwise added. The flask was sealed, and the mixture was stirred at room temperature for 20 h. The reaction was quenched by acidifying with 10% HCl, and it was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layer was washed with water, dried over MgSO_4 , filtered, and concentrated to afford a white solid. It was purified by column chromatography on silica gel (Hex:EtOAc = 3:1) to afford the desired product 5-benzyl-2,2-dimethyl-5-(4-vinylbenzyl)-[1,3]dioxane-4,6-dione as a white solid. ESI-HRMS: Found: m/z 373.1. Calc. for $\text{C}_{22}\text{H}_{22}\text{O}_4\text{Na}$ [$\text{M}+\text{Na}$]: 373.1. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ (ppm) = 7.36 (d, 2H), 7.32 (m, 2H), 7.25 (m, 3H), 7.20 (d, 2H), 6.68 (dd, 1H), 5.73 (d, 1H), 5.25 (d, 1H), 3.49 (s, 2H), 3.48 (s, 2H), 0.73 (s, 3H), 0.67 (s, 3H). Physical and spectroscopic data were in agreement with literature reports.⁶

Surface Fabrication

The silicon wafers were initially cleaned in a “piranha” solution, which is a 3:1 mixture of concentrated H₂SO₄ and H₂O₂ (30%) heated to 90 °C for 30 min (CAUTION: “piranha” solution reacts violently with organic materials and must be handled with extreme care), followed by copious rinsing with deionized water. The cleaned silicon wafers were etched for 1 min in a 2% hydrofluoric acid solution, quickly rinsed in degassed deionized water, and dried in a stream of nitrogen. *t*-butyloxycarbonyl (*t*-BOC) protected allylamine (20 µL) was introduced onto the freshly prepared Si-H wafers. The prepared sample was sandwiched between two quartz plates and a uniform thin liquid film of *t*-BOC protected allylamine formed on the Si-H wafers. The silicon wafer was placed in a N₂ purged steel reaction chamber covered with a quartz window and irradiated with a UV light (λ = 254 nm) for two hours. After irradiation, the modified silicon wafers were ultra-sonically washed with 25% TFA in methylene chloride followed by a minute rinse in 10% NH₄OH to remove the *t*-BOC protecting group and dried in a stream of nitrogen. The amine-modified silicon wafers were introduced into the solution of 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid *N*-succinimidyl ester (5.4 mmol) in 20 mL of anhydrous dichloromethane. The reaction mixture was left to react at 22 °C in the dark for 60 h. The silicon wafers were recovered from the reaction mixture and repeatedly washed with dichloromethane and acetone in an ultrasonic bath and dried under a stream of nitrogen.

RAFT agent immobilized silicon wafers were placed in a glass reactor and degassed under vacuum for 30 min. VBIC monomer (4.18 g, 21.0 mmol) and DVIMBr cross-linker (1, 5, and 10% of monomer) were added to a dry Schlenk tube along with CPDB (27.9 mg, 0.1 mmol), ACVA (14.0 mg, 0.05 mmol) and DMF (10 mL). The mixture was degassed by three freeze-pump-thaw cycles. The solution was transferred to the glass reactor just before heating the reactor to 70 °C for 24 h to allow for polymerization, and cross-linked PILs (**Ia-c**) were obtained. The modified silicon wafers were washed with acetone and dried under a stream of nitrogen. For *ex-situ* cross-linking technique, VBIC, Meldrum’s cross-linker instead of bifunctional cross-linker were polymerized under RAFT condition. After quenching the reaction in an ice bath, the modified silicon wafers were washed with acetone and dried under a stream of nitrogen. Prepared polymer brushes (**Ea-c**) were heated for 5 min at 250 °C to obtain the cross-linked polymeric films (**ECa-c**).

SURFACE CHARACTERIZATION

XPS Analysis

XPS measurements were used to monitor the surface chemical composition change of each reaction step. The identity of the amine-modified silicon wafers was confirmed by the appearance of an N 1s signal at 400 eV. Similarly, attachment of the chain-transfer agent (CTA) was confirmed by the appearance of an S 2p signal 100 eV.^{7,8} The XPS spectra of the amine and CTA modified silicon wafers include a weak Si signal originating from silicon substrate, whereas no Si signal was observed in the case of the **Ia-c**, **Ea-c** and **ECa-c**. Figure S2 shows high-resolution C 1s spectra of **Ia**, **Ea** and **ECa** with their subpeaks obtained through curve fitting. The C 1s high-resolution spectrum of **Ia**, obtained via the *in-situ* method, shows the peak components at binding energies of 286.32 eV and 284.91 eV, attributed to the C-N bonds and the C=C/C-C bonds, as shown in Figure S2a. For the *ex-situ* method, the C 1s spectrum (Figure S2b) is deconvoluted into four subpeaks assigned to C=C/C-(C-H) at 284.35 eV, C-N at 284.87 eV, O-C-O at 285.50 eV and O-C=O at 287.09 eV (**Ea**). After the thermolysis, the C 1s spectrum (Figure S2c) clearly shows the disappearance of O-C-O and O-C=O peaks and the appearance of a C=O peak at 286.95 eV due to the ketene dimerization provided by the cross-linking (**ECa**). Figure S2d and e show the O 1s XPS spectra for **Ea** and **ECa**, peaks at 530.35, 530.98 and 532.98 eV were assigned to oxygen atoms in C=O, C-O, and O-C=O, respectively. Figure S2e results showed that **ECa** contained C=O at 530.77 eV, signifying that polymer chains were cross-linked in the structure. The XPS results of the surfaces clearly confirmed the existence of the masked cross-linker and C=O on **Ea** and **ECa**, respectively.

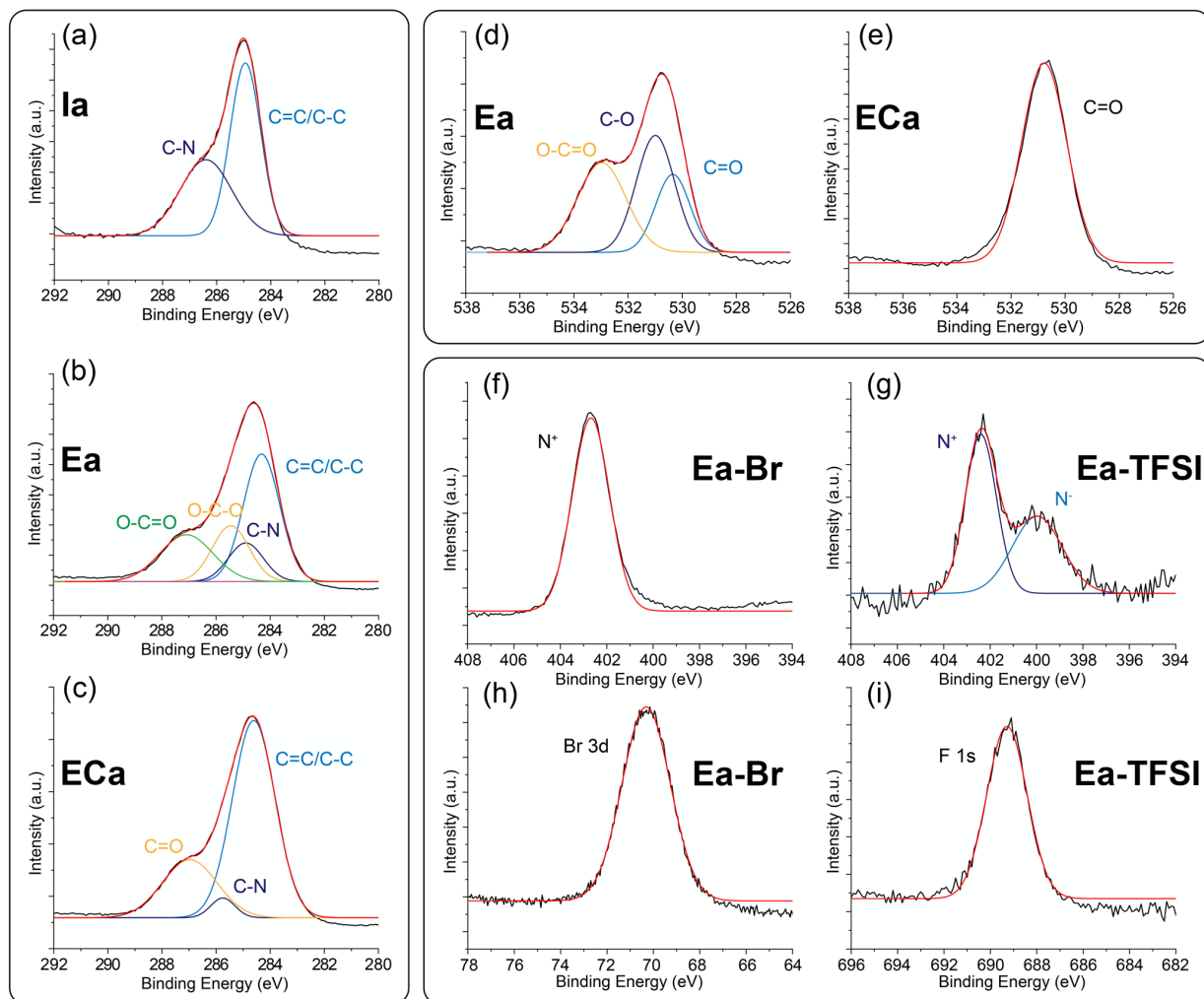


Figure S2. High resolution C 1s XPS spectra of **Ia** (a), **Ea** (b) and **ECa** (c). O 1s XPS spectra of **Ea** (d) and **ECa** (e). High resolution XPS spectra of Br salt (f, h) and TFSI (g, i) salt of **Ea**. The black solid curves represent the measured spectra, and the red solid curves represent the fitted results.

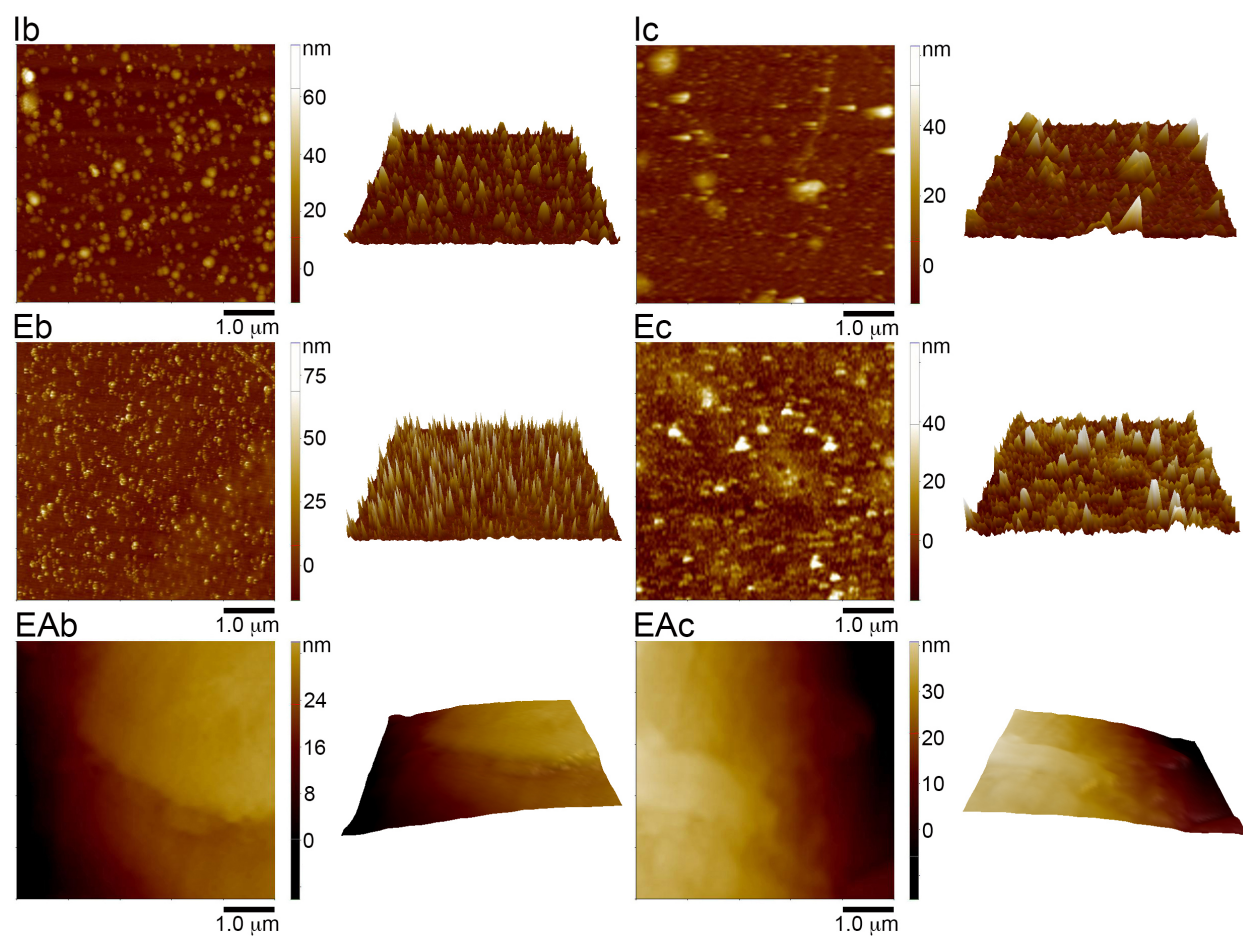


Figure S3. AFM images of PILs coatings on Si wafers prepared via *in situ* and *ex situ* methods.

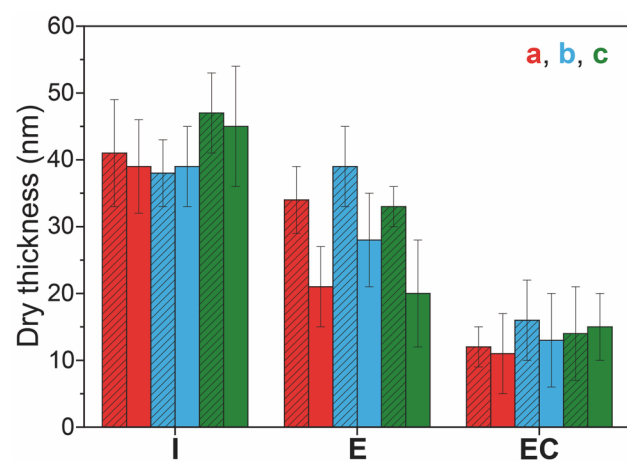


Figure S4. The dry thickness of Ia-c, Ea-c, ECa-c layers incubated before (patterned) and after 72 h in rotary flow system. The data are presented as mean \pm SD of three separate experiments. P values < 0.05 were considered statistically significant.

TABLE

Table S1. Atomic concentration of PIL-Br coatings as determined by XPS analysis.

Entry	Atomic concentration (%)			
	C	N	O	Br
Ia	62.22	18.73	11.44	7.61
Ib	57.05	19.17	14.72	9.06
Ic	54.76	19.91	13.85	11.48
Ea	64.10	12.03	16.51	5.36
Eb	63.97	11.78	19.27	4.98
Ec	64.14	11.61	20.35	4.62
ECa	62.48	13.85	16.54	7.13
ECb	62.53	13.35	17.27	6.85
ECc	63.67	12.02	17.75	6.56

Table S2. Grafting parameters of **Ea-c**.

	Conversion (%) ^a	$M_{n,theo} \times 10^4$ (g.mol ⁻¹) ^b	$M_{n,SEC} \times 10^4$ (g.mol ⁻¹)	M_w/M_n	DP	h^c (nm)	σ (chains/nm ²)	D (nm)	R_g (nm)
Ea	62	4.73	4.00	1.27	124	34±5	0.72	2.72	0.24
Eb	64	4.60	4.23	1.33	130	39±6	0.78	2.79	0.23
Ec	61	4.60	4.32	1.41	133	33±3	0.65	2.82	0.25

^a The conversion of the polymerization was determined gravimetrically.

^b $M_{n,theo} = (\text{conversion} \times c_{\text{monomer}} \times M_{\text{monomer}} / c_{\text{RAFT agent}}) + M_{\text{RAFT agent}}$,
Monomer/RAFT agent/Initiator: 420/2/1.

^c Dry thickness of **Ea-c**.

Table S3. Water contact angle and hysteresis of PILs coated surfaces.

Entry	Water contact angle (°)		Hysteresis
	Br	TFSI	
Ia	42±6	110±6	25±7
Ib	41±8	102±9	29±6
Ic	36±9	93±8	31±9
Ea	45±6	97±9	21±5
Eb	39±8	101±8	23±6
Ec	43±8	99±6	22±8
ECa	50±5	88±4	18±5
ECb	53±4	87±5	19±4
ECc	52±5	90±5	20±5

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