## **Electronic Supplementary Information**

# Polymer dewetting via stimuli responsive structural relaxation – Morphology and contact angle analysis

Xiumin Ma<sup>a</sup>, Rene Crombez<sup>a</sup>, Md. Ashaduzzaman<sup>b</sup>, Masashi Kunitake<sup>b</sup>, Lisa Slater<sup>c</sup>, Thomas Mourey<sup>c</sup>, and John Texter<sup>a</sup>\*,

<sup>a</sup>Coating Research Institute, School of Engineering Technology, Eastern Michigan University, Ypsilanti, MI 48197, USA

<sup>b</sup>New Frontier Science, Graduate School of Science and Technology, Kumamoto University, 39-1 Kurokami 2-chome, Kumamoto 860-8555, Japan

<sup>c</sup>Corporate Research and Engineering, Eastman, Kodak Company, Rochester, NY 14650, USA

## Materials

Acryloyl chloride (96%), 11-bromo-1-undecanol (98%), triethylamine (99.5%), 1-methylimidazole (99%), 2,6-di-tert-butyl-4-methylphenol (minimum 99% GC, powder), Methyl 4-(bromomethyl) benzoate (MBMB, 98%), potassium hexafluorphosphate (98%, KPF<sub>6</sub>), cuprous bromide (CuBr, 99.99%) 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 97%), Tetrahydrofuran (THF, anhydrous,  $\geq$  99.9%, inhibitor free), dichloromethane (anhydrous,  $\geq$ 99.8%), and neutral aluminum oxide (activated, Brockmann I, standard grade, ~ 150 mesh, 58Å) were purchased from Aldrich. Diethyl ether and Aerosol-OT (anhydrous; sodium bis[2-ethylhexyl] sulfosuccinate) were purchased from Fisher Scientific. Quartz coverslips (1.0 in\*1.0 in\*1.0mm, SPI Supplies) were purchased from Structure Probe, Inc.

## Methods

## Synthesis of 1-(11-acryloyloxyundecyl)-3-methylimidazolium bromide (ILBr)

The intermediate compound, 11-bromoundecylacrylate, was prepared by the addition of acryloyl chloride to 11-bromoundecanol in the presence of triethylamine. The reaction was carried out under a nitrogen atmosphere by stirring for 2 days at room temperature. ILBr was synthesized by stirring a small excess 1-methylimidazole with the 11-bromoundecylacrylate intermediate for 2 days at 40 °C under a nitrogen atmosphere. Greater detail is provided elsewhere.<sup>[s1, s2]</sup>

#### Synthesis of poly(ILBr)

Methanol (4.2 mL) and water (3 mL) (7:5 v/v) were taken into a reaction flask and further purged with Ar for another 10 minutes. HMTETA (0.25 mmol, 57.6 mg, 68  $\mu$ L) ligand and CuBr (0.2 mmol, 30 mg) catalyst were then charged in the flask successively. After 10 minutes purging, the solution appeared very light green in color. ILBr monomer (6.46 mmol, 2.50 g) was then added and purging continued for another 5 minutes. In this stage, additional CuBr (0.1 mmol, 15 mg) was added and the solution became bluish green. Finally, MBMB (0.2 mmol, 46 mg; a 6.4 fold excess for the solvent volume used) initiator was added and the reaction flask was then placed in a preheated oil bath at 40<sup>o</sup>C with stirring, followed by degassing with a pump and backfilling with Ar (10 minutes). The emulsified reaction mixture was run for 48 h.

After 48 h, the product reaction was cooled to room temperature and taken into a dialysis tube (SnakeSkin® pleated dialysis tubing, MWCO 3500, length 25 cm). Product adhering to the reaction flask was removed by rinsing with deionized water and adding to the dialysis tubing contents. Dialysis was performed in a 4L vessel containing a magnetic stirrer to accelerate the rate of dialysis against deionized water. Water was changed frequently during the first 12h. Almost all CuBr/HMTETA and monomer were removed from the system within this time; dialysis was continued for another 36h (changing water every 12h). Finally, a white polymer was obtained after lyophilization of the dialysis tube contents for 24h. The yield was 60%.

#### SEC Molecular Weight Analysis<sup>[s3]</sup>

The SEC system consisted of a Waters Corporation 2695 solvent delivery system, 2487 dual wavelength spectrophotometric detector, 410 differential refractive index (DRI) detector, a Precision Detectors PD2020 two-angle light scattering (LS) detector, and a Viscotek H502 differential viscometry (DV) detector. The DV and DRI were configured with a parallel split after the spectrophotometric and LS detectors. The column set consisted of three 8 mm × 300 mm KF-806L columns from Shodex, thermostated at 40°C, calibrated with narrow-molecular-weight distribution poly(methyl methacrylate) (PMMA) standards. The eluent used was the toxic HFIP (1,1,1,3,3,3-hexafluoro-2-propanol) containing 0.01 M tetraethylammonium nitrate,

delivered at a nominal flow rate of 1.0 mL/min. The actual flow rate was determined from the retention volume of acetone added to the sample solvent as a flow marker. The specific refractive index increment dn/dc = 0.203 mL/g was obtained by integration of the differential refractive index (DRI) chromatogram.

Molecular weight averages measured by viscometry detection and Universal Calibration were  $M_n = 41,200$  Da,  $M_w = 248,000$  Da,  $M_z = 345,000$  Da with polydispersity  $M_w/M_n = 6.02$ . The SEC method for measuring  $M_n$  can be insensitive to very-low-molecular weight species, resulting in a value that is underestimated compared to the value obtained from NMR. The weight average molecular weight measured by light scattering was 291,000 Da, which is in reasonable agreement with the viscometry detection result. The whole polymer weight-average intrinsic viscosity was  $[\eta] = 0.175$  dL/g and a z-average root-mean square radius  $r_{gz}$  equal to 49.2 nm was estimated from light scattering data. The molecular weight distribution is multimodal (Figure S1) with the higher modes being slightly greater than 2x and



**Figure S1.** Differential weight fraction molecular weight distribution (primary y-axis) of poly(ILBr) (solid); viscosity-molecular weight data for linear narrow molecular weight distribution PMMA standards (symbols), poly(ILBr) (dashed) are plotted on secondary y-axis. (Reproduced bypermission from Ref. s3.)

4x multiples of the lowest mode. The polydispersity is much larger than generally obtained in a controlled ATRP process. The light-scattering molecular weight-size data were not suitable to assess conformation. The scaling exponent for intrinsic viscosity as a function of molecular weight (plotted on the secondary axis of Figure 1a) is approximately 0.45, which is indicative of a collapsed conformation such as a polymer near the theta state or a branched or other compact polymer architecture. (The preceding paragraph is reproduced by permission from Ref. s3.)

#### **Film Formation**

The Poly(ILBr) film was prepared by introducing few drops of 3 wt% of aqueous Poly(ILBr) solution on the quartz coverslips. The solution could wet the substrate spontaneously. After drying at room temperature in ambient air, a smooth and featureless film formed.

The as-deposited films were soaked in 0.1 M KPF<sub>6</sub> for 2 days. In order to remove the excess of KPF<sub>6</sub>, the films were rinsed with DI water several times. Then the films were dried in the ambient air at room temperature.

## **Scanning Electron Microscope (SEM)**

SEM analyses were performed on a Hitachi S-3400N scanning electron microscope. Energy-dispersive X-ray spectroscopy (EDAX) microanalysis was done with an IXRF 500 Analyzer. All the samples were sputter coated with Au using a Denton Vacuum Desk



**Figure S2.** Control – SEM of poly(ILBr) film on quartz coverslip before ion exchange treatment.



**Figure S3.** SEM of partially dewetted area after soaking film in 0.1 M KPF<sub>6</sub>.



**Figure S4.** SEM illustrating dewetted areas after soaking film in 0.1 M KPF<sub>6</sub>.



**Figure S5.** SEM illustrating dewetted areas after soaking film in 0.1 M KPF<sub>6</sub>.



**Figure S6.** SEM illustrating dewetted areas after soaking film in 0.1 M KPF<sub>6</sub>.



**Figure S7.** SEM illustrating dewetted areas after soaking film in 0.1 M KPF<sub>6</sub>. Notice overlap with area illustrated in Fig. S5.

IV cold sputter/etch unit to reduce charging effects in the SEM. The sputter time was 90 seconds while keeping the sputter set point at 29%.

Figure S2 illustrats and SEM of he polyILBr film prior to being treated with aqueous KPF<sub>6</sub>. Figures S3 through S7 are SEM of various regions of films after treatment with aqueous KPF<sub>6</sub>. At lower magnifications we see there are small to large areas of apparent dewetting. At higher magnification within these areas we see apparent droplets of diverse sizes, ranging from diameters of tens of microns to diamers that are sub-micron (as also shone in the text).

#### **SEM/EDAX**

EDAX analyses of a control region and a dewetted region are illustrated in Figs. S8 and S9, respectively. In the control specimen of Fig. S8 and ffrom the elemental analyses of Tables S1 to S3, we see that the film is so thick that the Si signal from the quartz substrate is very small. We also see that compared with the carbon signal, the phosphorous signal is very small (which is probably from an impurity in the sample). The C, O, Cl, and Br signals are substantial. We posit that the Cl signal is due to impurity in the bromoundecanol used to synthesize the ILBr monomer.



Figure S8. SEM illustrating thick polyILBr film before soaking film in 0.1 M KPF<sub>6</sub>.

S8.											
Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units	Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units
С	Ka	6.07	0.239	45.440	wt.%	С	Ka	6.30	0.245	46.018	wt.%
N	Ka	0.00	0.038	0.000	wt.%	N	Ka	0.00	0.038	0.000	wt.%
0	Ka	0.39	0.076	2.213	wt.%	0	Ka	0.34	0.074	1.856	wt.%
F	Ka	0.01	0.057	0.031	wt.%	F	Ka	0.00	0.063	0.013	wt.%
Si	Ka	0.00	0.118	0.010	wt.%	Si	Ka	0.13	0.124	0.297	wt.%
Р	Ka	0.23	0.126	0.598	wt.%	Р	Ka	0.25	0.127	0.654	wt.%
C1	Ka	2.13	0.177	6.292	wt.%	C1	Ka	1.95	0.175	5.666	wt.%
к	Ka	0.04	0.091	0.146	wt.%	K	Ka	0.02	0.095	0.060	wt.%
Br	La	9.44	0.314	45.271	wt.%	Br	La	9.62	0.322	45.436	wt.%
				100.000	wt.%					100.000	wt.%

**Table S1.** EDAX of Area 1 in Fig. S8.S8.

**Table S2.** EDAX of Area 2 in Fig.

Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units
С	Ka	5.72	0.215	44.467	wt.%
N	Ka	0.00	0.042	0.000	wt.%
0	Ka	0.37	0.073	2.088	wt.%
F	Ka	0.00	0.055	0.000	wt.%
Si	Ka	0.08	0.116	0.177	wt.%
Р	Ka	0.27	0.114	0.732	wt.%
C1	Ka	2.23	0.165	6.701	wt.%
к	Ka	0.04	0.084	0.148	wt.%
Br	La	9.39	0.291	45.687	wt.%
				100.000	wt.%

#### Table S3. EDAX of Area 3 in Fig. S8.

In Fig. S9 we examine regions between droplets after apparent dewetting has occurred. Carbon, phosphorous, and Si EDAX signals are given in Table S4 for the concentric rectangular regions 1 and 2 of Fig. S9. The outer region #1 exhibits a small carbon signal in Table S4, consistent with the presence of some small droplets visible in



**Figure S9.** Partially dewetted area after treatment with KPF<sub>6</sub>.

**Table S4**. EDAX elemental analyses in regions between droplets and within droplets

Regions of Figure S8	C (wt%)	P (wt%)	Si (wt%)
1	2.5	0.05	80.2
2	0.0	0.19	82.8

the field. The inner region #2 has a small carbon signal. In addition the large Si signal is consistent with ther being no overlaying film. These EDAX results effectively prove that dewetting has occurred.

## Atomic Force Microscope (AFM)

AFM images were taken using a Veeco Multi Mode Scanning Probe Microscope (MMSPM) with a Nanoscope IIIa controller. The images were taken in tapping mode using a Veeco Multi 40a probe, driven at either 42kHz or 272kHz.



Figure S10. AFM of dewetted area 5 µm wide.

## **Optical Microscopy**

The following images were obtained using the optical microscope that is integrated into a Multi-Mode Scanning Probe Microscope made by Digital Instruments (which is now a



**Figure S11.** Optical micrograph of 500  $\mu$ m wide region within a large dewetted areas after soaking film in 0.1 M KPF<sub>6</sub>.



**Figure S12.** Optical micrograph of 500  $\mu$ m wide region illustrating a large dewetted area and small dewetted areas after soaking film in 0.1 M KPF<sub>6</sub>.



**Figure S13.** Optical micrograph of 500  $\mu$ m wide region illustrating a large dewetted area after soaking film in 0.1 M KPF<sub>6</sub>. Note that this view overlaps with the image in Fig. S9.



**Figure S14.** Optical micrograph of 500  $\mu$ m wide region illustrating a large a large dewetted area and small dewetted areas after soaking film in 0.1 M KPF<sub>6</sub>.

division of Bruker). The microscope had a 10X objective made by Nikon and a color CCD camera made by Sony, model XC-999. The images illustrate various dewetted regions containing droplets of diverse sizes.



Figure S15. Calibration curve for Ag/Ag<sub>2</sub>S ion specific electrode.

## Potentiometry

Potentiometric titration was performed using a Fisher Acumet 925 pH meter and two single-channel Fisherbrand Finnpipettes with adjustable volumes from 20 to 200  $\mu$ L and

100 to  $1000\mu$ L. An Orion Ag/Ag<sub>2</sub>S ion selective electrode was used as the indicating electrode and a Ag/AgCl reference electrode was used with a salt bridge.

A series of KBr solutions at 0.1, 0.01, 0.001, and 0.0001 M aqueous KBr were prepared, and in each a small amount of AgBr powder was suspended. The Nernstian slope obtained is theoretically correct for the room temperature condition (22°C). This calibration curve, Fig. S15, was then used to convert mV readings to bromide concentrations.

In order to determine the accurate concentration of aqueous poly(ILBr) solution, 0.5740 g of aqueous Poly(ILBr) was diluted to 19.7075 g in a 50 mL beaker, then titrated with standardized AgNO<sub>3</sub> solution (0.2944 mmol/L) under stirring. The result is shown in Fig. S16. The equivalent volume for AgNO<sub>3</sub> solution is 12.75 mL, so the concentration of starting poly(ILBr) solution was 6.5394 mmol/L. The starting potential of about 55 mV corresponds to a bromide concentration of about 1.46 x  $10^{-4}$  M; the concentration of bromide in solution is 1.90 x  $10^{-4}$  M; at this dilution about 25% of the bromide is sequestered.



Figure S16. Titration of polyILBr with AgNO<sub>3</sub>.

The above poly(ILBr) solution (10.5623 g, 6.5394 mmol/L, 2.53 g/L, 6.91 x  $10^{-5}$  mol ILBr) was titrated with KPF<sub>6</sub> solution (6.1094 mmol/L) under stirring. This titration result is shown in Fig. S17a. The starting potential of 23 mV corresponds to a bromide



Figure S17a. Titration of aqueous poly(ILBr) with Aqueous KPF<sub>6</sub>.

concentration of about 0.52 mM. This concentration corresponds to less than 10% of the available bromide being free and in solution, which shows that the homopolymer exists in solution as an osmotic brush (not unusual for a polymeric micelle). The equivalence point corresponds to about 10 mL of added titrant. Turbidity (precipitation) was induced just below this point at the peak of the titration curve (8.2 mL added titrant). The titration data illustrated in Fig. S17b corresponds to the addition of about 5 mL of KPF<sub>6</sub> titrant. In Fig. S17b we show how much bromide is released as the amount of added KPF<sub>6</sub> increases



Figure S17b. Titration of aqueous poly(ILBr) with Aqueous KPF<sub>6</sub>.

#### **Bulk Stress Relaxation**

Bulk stress relaxation in poly(ILBr-*co*-MMA) hydrogel after PF<sub>6</sub><sup>-</sup> ion exchange with Br<sup>-</sup> was demonstrated by Yan and Texter in the first paper on ILBr,<sup>[s3]</sup> wherein the 15% bulk shrinkage was shown to be essentially reversible.

Here we demonstrate two examples of bulk stress relaxation in a gel of ILBr homopolymer prepared by solution polymerization at 60°C using ammonium persulfate (APS) as initiator. in a series of NMR tubes. We combined 0.624 g ILBr, 0.792 g DI water, and 4.3 mg APS in a culture tube and sonicated in an ultrasonic cleaning bath until all was dissolved (about 5 minutes). The culture tube was placed in an oil bath at 60°C overnight for 15.5 h. A transparent gel formed after a half hour, and this physica state appeared the same after 15.5 h of heating. The gel is pictured in Fig. S18.



**Figure S18.** Photograph of polyILBr hydrogel prepared at 60°C using APS thermal initiation.

The illustrated culture tube was broken by wrapping the tube in several layers of microwipe lab tissues and smashing the glass with a lead doughnut in the dead space above the hydrogel. A sharpening stone (brick shaped) was then used to fracture the glass surrounding the hydrogel, and the glass was carefully separated from the very sticky hydrogel. The hydrogel was separated into two nearly equal volume "globs".

One glob, pictured from different angles in Figs. S19(a) and S19(b), was immersed in saturated aqueous KPF<sub>6</sub> in a sealed vial and placed in an oven at 68-70°C for an hour. The glob had turned white (as a result of microscopic pore formation accompanying the ion exchange via a spinodal decomposition as explained earlier) and had shrunk.<sup>[s1,s3]</sup> The glob was removed from the vial, rinsed in DI water, and photographed from various angles, as shown in Figs. S19(c)-S19(h). The illustrated images show that the largest dimension after ion exchange is about 11.5 mm, whereas before treatment the largest dimension was about 14 mm. We see, unequivocally therefore, that this glob shrank 17-18% in largest dimension as a result of bulk stress relaxation.



**Figure S19.** PolyILBr hydrogel before (a,b) and after (c-h) immersion in saturated aqueous KPF<sub>6</sub>. The hydrogel is pictured at various angles in front of a cm ruler.

The other hydrogel glob was then compressed to a flat triangular sheet using a spatula blade to a thickness of about 1-1.5 mm and an approximately triangular wedge about 20 mm in largest dimension. This sample was then equilibrated in a Petri dish after covering it with DI water, and the sample swelled vertically (essentially one-dimensionally) as a series of contiguous "globs" as pictured in Figs. S20(a) – S20(c). This wedge-shaped sample was then placed in saturated aqueous KPF<sub>6</sub> in a deep dish when it began to whiten at the surface and transform in shape. The sample dish was then placed in an oven at 68-70°C, and after a half hour it was removed, rinsed with DI water, and photographed as illustrated in Figs. S20(d) – S20(f).



**Figure S20.** PolyILBr hydrogel swelling in DI water and before (a-c) and after (d-f) subsequent immersion in saturated aqueous KPF<sub>6</sub>. The hydrogel is pictured at various angles in front of a cm ruler.

The one dimensional swelling in DI water of the polyILBr indicates the absence of any significant surface energy component, due to the very small interfacial energy at the swollen polyILBr/water interface (see interfacial energy discussion in following section). After immersion in the aqueous  $KPF_6$  we see opacity arise from pore formation accompanying the bromide-hexafluorphosphate ion exchange process. The overall shape

also transforms from swollen wedge shape to globular, with a change in largest dimensions from 21 mm to about 13 mm. This shape change can be attributed in part to a significantly increased interfacial energy, and again unequivocally illustrates bulk stress relaxation accompanying ion exchange. This stress relaxation emanates microscopically from the spinodal decomposition accompanying pore formation.

#### Ion Exchange/Spreading Coefficient Model

The equilibrium spreading coefficient (S) for a polyelectrolyte thin film (P) on quartz (Q) immersed in an aqueous solution (W) may be written<sup>[s4]</sup>

$$\mathbf{S}_{P(W)/Q(W)} = \gamma_{Q(W)W} - \gamma_{Q(W)P(W)} - \gamma_{WP(W)}, \qquad \mathbf{Eqn \ S1}$$

where  $\gamma_{Q(W)W}$  is the interfacial quartz/water interfacial energy at equilibrium,  $\gamma_{Q(W)P(W)}$  is the interfacial quartz/polyelectrolyte interfacial energy at equilibrium in a water saturated system, and  $\gamma_{WP(W)}$  is the interfacial water/polyelectrolyte interfacial energy at equilibrium. The interfacial quartz/polyelectrolyte energy,  $\gamma_{Q(W)P(W)}$ , may be approximated by the well known Girifalco-Good equation: <sup>[s4]</sup>

$$\gamma_{Q(W)P(W)} = \gamma_{Q(W)W} + \gamma_{WP(W)} - 2\Phi(\gamma_{Q(W)W} \cdot \gamma_{WP(W)})^{1/2}$$
 Eqn S2

where  $\Phi^{[s5]}$  is a parameter reflecting the interfacial interactions of the phases in contact with one another, including interactions that deviate significantly from "regularity". These interactions include cases where<sup>[s5]</sup>

"the predominant forces within the separate phases are of

unlike types, e.g., London-van der Waals vs. metallic or

ionic or dipolar (particularly hydrogen bonding)".

The parameter  $\Phi$  is usually between 0.5 and 1.15 or so. When the terms under the square root are taken as the London dispersion components of the respective interfacial energies and  $\Phi$  is taken as unity, Eqn. S2 is called the Girifalco-Good-Fowkes equation.<sup>[s4]</sup> In the following we use the Girifalco-Good form, as the parameter  $\Phi$  is a useful fitting parameter and is not restricted as it is in the Girifalco-Good-Fowkes equation. Substituting Eqn S2 into Eqn S1 gives:

 $S_{P(W)/Q(W)} = \gamma_{Q(W)W} - \gamma_{Q(W)W} - \gamma_{WP(W)} + 2\Phi(\gamma_{Q(W)W} \cdot \gamma_{WP(W)})^{1/2} - \gamma_{WP(W)}$  Eqn S3 Then:

$$S_{P(W)/Q(W)} = -2\gamma_{WP(W)} + 2\Phi \left(\gamma_{Q(W)W} \cdot \gamma_{WP(W)}\right)^{1/2}$$
 Eqn S4

The change in spreading coefficient,  $\triangle S_{Br \rightarrow PF6}$  accompanying  $PF_6^-$  ion exchange for  $Br^-$  in our thin films on quartz can then be written:

$$\triangle S_{Br \rightarrow PF6} = S_{PPF6(W)/Q(W)} - S_{PBr(W)/Q(W)}$$
 Eqn S5

$$\Delta S_{Br \rightarrow PF6} = -2\gamma_{WP_{PF6}(W)} + 2\Phi \left(\gamma_{Q(W)W} \cdot \gamma_{WP_{PF6}(W)}\right)^{1/2} + 2\gamma_{WP_{Br}(W)} - 2\Phi \left(\gamma_{Q(W)W} \cdot \gamma_{WP_{Br}(W)}\right)^{1/2}$$
 Eqn S6

$$\Delta S_{Br \rightarrow PF6} = -2[\gamma_{WP^{PF6}(W)} - \gamma_{WP^{Br}(W)}] + 2\Phi(\gamma_{Q(W)W})^{1/2} [(\gamma_{WP^{PF6}(W)})^{1/2} - (\gamma_{WP^{Br}(W)})^{1/2}]$$
 Eqn S7

Here the change in spreading coefficient is expressed in terms of three quantities: the water-quartz interfacial energy, the water-poly(ILPF<sub>6</sub>) interfacial energy, and the water-poly(ILBr) interfacial energy. Examining the literature,<sup>[s6]</sup> we find that the range of water-quartz interfacial energies span a range of 93.9 to 102.6 mN/m from studies by four different groups. Therefore, we approximate  $\gamma_{Q(W)W}$  as 98 mN/m.

The water-poly(ILBr) system is one with essentially no interface since the solubility of poly(ILBr) is extremely high (a solubility limit is not known). If in fact there is no interface, the appropriate quantity to use for  $\gamma_{WPBr}(W)$  is zero. We do know from interfacial studies of seven water-poly(acrylonitrile-acrylamide-acrylic acid) hydrogels<sup>[s7]</sup> varying in acrylamide from 13 to 39.2 mol%, and varying in water content from 76 to 98 weight%. This series exhibited interfacial energies with water from 0.4 to 3.4 mN/m. In addition  $\gamma_{Poly(W)}$  for a series of polyelectrolyte brushes prepared by surface initiated ATRP and saturated with water range from 73 mN/m (PMPC; poly[2-methacryloyloxyehtyl phosphorylcholine]) to 60 mN/m (PMETAI; poly[trimethylammoniumethyl iodide methacrylate]) to 50 mN/m (PDMAEMA; poly[dimethylaminoethyl methacrylate]),<sup>[s8]</sup> and we then estimate interfacial water-polyelectrolyte energies of 0.01, 0.6, and 2 mN/m, respectively, for this series of brushes from Eqn S2a with  $\gamma_W = 72$  mN/m and  $\Phi = 1$ .

$$\gamma_{WP(W)} = \gamma_W + \gamma_{P(W)} - 2\Phi(\gamma_W \cdot \gamma_{P(W)})^{1/2}$$
 Eqn S2a

1 10

The one-dimensional swelling described for Figs. S20(a) to S20(c) is also very supportive evidence for a very low  $\gamma_{WPBr(W)}$ . We think it reasonable, therefore, to approximate the water-poly(ILBr) interfacial energy as zero. This approximation then gives:

 $\Delta S_{Br \rightarrow PF6} = -2\gamma_{WP_{PF6}(W)} + 2\Phi \left(\gamma_{Q(W)W}\right)^{1/2} \left(\gamma_{WP_{PF6}(W)}\right)^{1/2}$  Eqn S8

The <u>zero</u> of Eqn S8 is given by:

$$\gamma_{WP_{PF6}(W)} = \Phi^2 \gamma_{Q(W)W} (\approx \Phi^2 98 \text{ mN/m})$$
 Eqn S9

For values of  $\gamma_{WP PF6}(W) \leq [\Phi^2 \gamma_{Q(W)W}]$  we are assured (assuming no interfacial energy between the poly(ILBr) film and water) that  $\Delta S_{Br \rightarrow PF6} > 0$ , as was originally postulated. It is safe to say that  $\gamma_{WPPF6}(W)$  could not possibly reach the level of 98 mN/m, in the case that  $\Phi = 1$ . However, it seems plausible that this ion exchange process would yield an interfacial energy significantly higher than the water-poly(ILBr) interfacial energy. This assumption is supported by the reported precipitation of nanoparticles of poly(ILPF6)<sup>[s3]</sup> upon addition of aqueous KPF6 to aqueous poly(ILBr). The water-poly(IL PF6) interfacial energy of such nanoparticles are by definition positive, and this positive free energy must be overcome by the condensation free energy in order to obtain nanoparticles that do not spontaneously re-dissolve.

We can also approximate this interfacial energy using a variant of Eqn S2a:

$$\gamma_{\text{PPF6}(\text{W})\text{W}} = \gamma_{\text{PPF6}(\text{W})} + \gamma_{\text{W}} - 2\Phi \left(\gamma_{\text{PPF6}(\text{W})} \cdot \gamma_{\text{W}}\right)^{1/2}$$
 Eqn S10

We have 72 mN/m for  $\gamma_W$ . Values of  $\gamma_{Acrylates}$  typically are in the range of 30 to 36 mN/m<sup>[s10]</sup> as similarly are values of many ionic liquids.<sup>[s11]</sup> If we then take 33 mN/m in approximation for  $\gamma_{P_{PF6}(W)}$ , Eqn S10 can be rewritten:

$$\gamma_{\rm PPF6(W)W} = 105 - 98\Phi,$$
 Eqn S11

where the units are mN/m. When we substitute this expression into Eqn S8 we obtain:

$$\Delta S_{Br \to PF6} = -210 + 196\Phi + 19.8\Phi (105 - 98\Phi)^{1/2}$$
 Eqn S12

where again the units are mN/m. The change in spreading coefficient in Eqn S12 is positive for  $\Phi \ge 0.65$  (as shown in Table S1). We next examine whether this inequality is a reasonable assumption.

Table S1				
Φ	$\Delta S_{Br \rightarrow PF6}$ (mN/m)			
1	38.4			
0.7	10.8			
0.65	0.11			
0.64	-2.1			
0.6	-11.7			
0.5	-37.9			

We note that Girifalco and Good stated:<sup>[s5]</sup>

"When there are specific interactions between the molecules forming the two phases, the energy of adhesion will be greater than the value it would have had in the absence of specific interactions. The result will be an elevated value of  $\Phi$ , and consequently values greater than one are possible."

If we assume a surface energy for quartz of 225 mN/m<sup>[s6]</sup> and a water/quartz interfacial energy of 98 mN/m, the equation for the water/quartz interfacial energy analogous to Eqn S10 implies a  $\Phi$  of 0.78. We can presume attractive dispersion and polar interactions in this case due to the presence of hydroxyl groups on the quartz surface and the dipole moment of water. In the case of Teflon, were a value of about 48 mN/m has been reported in the limit of zero ionic strength from detailed contact angle studies of the water/Teflon interfacial energy,<sup>[s12]</sup> and further taking 18 mN/m for the surface energy of Teflon, we estimate a  $\Phi$  of 0.58. If we assume Teflon surfaces are apolar, all of this 0.58 can be attributed to dispersion interactions. Since the water saturated polymer exchanged with PF<sub>6</sub><sup>-</sup> will exhibit polar interactions between chain segments and the quartz surface, in addition to dispersion interactions, we believe a value of  $\Phi \ge 0.65$  is a reasonable assumption.

Another de facto estimation of  $\Phi$  was provided by the Neumann group:<sup>[s4,s13]</sup>

$$\Phi = \exp[-(\gamma_{\rm W} - \gamma_{\rm P_{\rm PF6}(W)})^2]$$
 Eqn S12

where  $\beta = 0.0001247 \text{ m}^2/\text{mN}^2$ . Taking the usual value for water and 33 mN/m for  $\gamma_{PPF6(W)}$  gives  $\Phi = 0.83$ .

Taking all of these approximations, experimental values and estimates together, we feel our conclusion that

$$\triangle S_{Br \rightarrow PF6} > 0$$

is well supported (not absolutely proven), and that the experimentally observed dewetting goes counter to generally accepted interfacial energy based dewetting, wherein the change in spreading coefficient would be negative.

#### References

- [s1] Yan F, Texter J. Solvent-reversible poration in ionic liquid copolymers. Angew. Chem. Int. Ed. **2007**;46:2440-2443.
- [s2] England D. Materials and Coatings Derived from the Polymerizable Ionic Liquid Surfactant 1-(11-Acryloyloxyundecyl)-3-methylimidazolium Bromide. MS Thesis, Eastern Michigan University, **2008.**
- [s3] Yan F, Texter J. Surfactant ionic liquid-based microemulsions for polymerization. Chem Comm 2006;2696-2698; doi: 10.1039/b605287h.
- [s4] Hiemenz P C, Rajagopalan R. *Principles of Colloid and Surface Chemistr,* Third Edition. Marcel Dekker, Inc., New York, 1997.
- [s5] Girifalco LR, Good RA. A theory for the estimation of surface and interfacial energies. I. Derivation and application to interfacial tension. J Phys Chem 1957;61:904-909
- [s6] Helmy AK, de Bussetti SG, erreiro EA. The water–silica interfacial interaction energies. Appl Surf Sci 2007;253:6878-6882.
- [s7] Hu DS-G, Tsai CE. Correlation between interfacial free energy and albumin adsorption in poly(acrylonitri1e-acrylamide-acrylic acid) hydrogels. J. Appl. Polym.Sci. 1996;59:1809-1817.
- [s8] Kobayashi M, Yamaguchi H, Terayama Y, Wang Z, Ishihara K, Hino M, Takahara A. Structure and surface properties of high-density polyelectrolyte brushes at the interface of aqueous solution. Macromol. Symp. 2009;279: 79–87.
- [s9] Ma X, Crombez R, Ashaduzaman Md, Kunitake M, Texter J, Slater L, Mourey T. Stimuli responsive poly(1-[11-acryloylundecyl]-3-methyl-imidazolium bromide) –

Dewetting and nanoparticle condensation phenomena. Langmuir 2011; doi: 10.1021/la200184c.

- [s10] Lu C-H, Su Y-C, Wang C-F, Huang C-F, Sheen Y-C, Chang F-C. Thermal properties and surface energy characteristics of interpenetrating polyacrylate and polybenzoxazine networks. Polymer 2008;49:4852–4860.
- [s11] (a) Kolbeck C, Lehmann J, Lovelock KRJ, Cremer T, Paape N, Wasserscheid P, Fröba AP, Maier F, Steinrück H-P. Density and surface tension of ionic liquids. J. Phys. Chem. B 2010;114;17025-17036; (b) Ghatee MH, Zare M, Zolghadr AR, Moosavi F. Temperature dependence of viscosity and relation with the surface tension of ionic liquids. Fluid Phase Equilibria 2010;292:188–194.
- [s12] Butkis MA, Grasso D. Impact of aqueous electrolytes on interfacial energy. J. Colloid Interface Sci. 1998;200:172-181.