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Buckling Instabilities in Polymer Brush Surfaces via ² Postpolymerization Modification

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10 Supporting Information

ABSTRACT: We report a simple route to engineer ultrathin 11 polymer brush surfaces with wrinkled morphologies using 12 postpolymerization modification (PPM), where the length 13 scale of the buckled features can be tuned from hundreds of 14 nanometers to one micrometer using PPM reaction time. We 15 show that partial cross-linking of the outer layer of the polymer 16 brush under poor solvent conditions is critical to obtain wrinkled 17 morphologies upon swelling. Characterization of the PPM 18 kinetics and swelling behavior via ellipsometry and the through 19 thickness composition profile via time-of-flight secondary ion 20



mass spectroscopy (ToF-SIMS) provided key insight into parameters influencing the buckling behavior. 21

22 INTRODUCTION

23 Buckling instabilities are ubiquitous in soft materials and can be 24 exploited to define the shape, morphology, and function of 25 complex systems—as exemplified by nature in the wrinkling of 26 skin¹ or folding of brain tissue.² Following nature's lead, strain-27 induced wrinkling of polymer thin films has emerged as a 28 powerful bottom-up approach to engineer surfaces that exhibit 29 complex ordered and disordered patterns at multiple length 30 scales.³ Recently, significant efforts have focused on exploiting 31 this approach to create surfaces suitable for a range of 32 applications, including advanced adhesion,⁴⁻⁷ tunable wett-33 ability,^{8,9} antifouling,^{10,11} particle assembly,¹² stem cell growth/ ³⁴ differentiation, ¹³ ultrasensitive pressure sensor, ¹⁴ stretchable ³⁵ electronics, ^{15,16} microlens arrays, ¹⁷ diffraction gratings, ^{18,19} 36 microcontact printing,²⁰ maskless lithography,²¹ open-channel 37 microfluidics,²² and many others.^{23–25}

Buckling instabilities in polymer films can be engineered 38 39 using three primary film structures: layered, homogeneous, and 40 gradient systems.^{3,23} In the prototypical example, surface 41 wrinkling can occur from an in-plane compression (i.e., 42 mechanical, thermal, or osmotic) of a bilayer composed of a 43 thin, high modulus film bonded to a semi-infinite, low modulus 44 substrate. The onset and wavelength of the wrinkles are 45 dictated by the thickness of the top film and the film/substrate 46 modulus ratio, whereas the wrinkle amplitude is related to 47 applied strain. Researchers have demonstrated numerous 48 methods to create thin film structure profiles that can buckle, 49 including metal deposition,^{18,26} UV/ozone oxidation,²⁷ photoinduced cross-linking,^{28,29} and surface-grafting techniques;³⁰ 50 however, these methods have focused primarily on the 51 fabrication of thin films with microscale morphologies on 52 soft, deformable substrates (e.g., elastomers). Relatively few 53 studies have focused on methods to induce buckling 54 instabilities in ultrathin (i.e., <100 nm) polymer films attached 55 to rigid substrates.³¹⁻³³

Postpolymerization modification (PPM) of polymer 57 brushes—ultrathin assemblies of polymer chains densely 58 grafted to a surface such that chains experience strong 59 segmental repulsion and stretch perpendicular to the 60 substrate—is a powerful platform for tailoring the chemical 61 and mechanical properties of surfaces.³⁴ The extended chain 62 conformation of brushes has specific implications for the PPM 63 process, where the high osmotic pressure and reduced chain 64 conformational entropy disfavor the penetration of reactive 65 modifiers into the brush.^{35,36} Thus, the penetration depth and 66 the through thickness compositional homogeneity of the brush 67 resulting from the PPM process are ultimately dependent on (i) 68 the reaction conditions (solvent quality, reaction efficiency, and 69 reaction time), (ii) the tethered brush parameters (grafting 70 density and thickness), and (iii) the physical properties of the 71 reactive modifier (molecular mass and steric bulk). Indeed, 72 Klok et al. showed via neutron reflectometry³⁶ and X-ray 73



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Scheme 1. Postpolymerization Modification of pSMA Brushes with Cystamine under Poor Solvent (Aqueous) Conditions^a





74 photoelectron spectroscopy (XPS)³⁷ that increases in brush 75 thickness, grafting density, and molecular mass of the modifier 76 result in decreased depths of penetration and increased vertical 77 heterogeneity. Intentional manipulation of PPM parameters 78 provides an opportunity to design brush structures with 79 through thickness material properties profiles that fulfill the 80 requirements for nanoscale buckling within ultrathin films on 81 rigid substrates but has rarely been reported.

Recently, Brooks et al.³⁸ reported the fabrication of nanoscale creases in ultrathin poly(pentafluorophenyl acrylate) (pPFPA) brushes on silicon substrates following PPM of the pPFPA with an amine-terminated polymer under the confinement of microcontact printing (μ CP). The PPM process increased the molecular mass of the brush resulting in osmotic swelling normal to the substrate surface. Confinement of the swollen brush under the μ CP stamp led to a critical in-plane stress, which was relieved via formation of creases. Brooks et al. demonstrated simple control over the crease morphology by varying the stamping pressure and recently extended this approach using droplets of amine-terminated polymer solution of to provide confinement.³⁹

Herein, we report a simple PPM approach to engineer 95 96 ultrathin poly(styrene-alt-maleic anhydride) (pSMA) brush 97 surfaces with tunable wrinkled morphologies. We cross-link 98 pSMA brushes under poor solvent conditions to limit the 99 postmodification reaction to the near surface region of the 100 brush, where reaction time dictates the ultimate thickness of the 101 cross-linked surface region. Subsequent exposure of the 102 selectively cross-linked brush surface to good solvent conditions generates an in-plane compressive stress arising from a 103 104 mismatch between lateral and perpendicular swelling directions within the brush. The compressive stress causes an out-of-plane 105 106 deformation of the untethered surface resulting in wrinkled 107 morphologies. Characterization of the PPM kinetics via 108 ellipsometry and through thickness composition profile via 109 time-of-flight secondary ion mass spectroscopy (ToF-SIMS) 110 provided key insight into parameters influencing the buckling 111 behavior.

112 **RESULTS AND DISCUSSION**

Synthesis of pSMA Polymer Brush. For this work, we remployed pSMA as a reactive polymer brush scaffold. pSMA is reactive toward amines for facile postpolymerization modrification. Alternating pSMA brushes were synthesized via surface-initiated polymerization of a 54:46 styrene:maleic reactive monomer feed from silicon substrates modified

with an asymmetric trichlorosilane azo-based initiator. Exper- 120 imental details are provided in the Supporting Information. It is 121 well-known that styrene and maleic anhydride monomers form 122 nearly perfect alternating copolymers under most free-radical 123 polymerization conditions. Polymerizations were carried out at 124 95 °C to generate pSMA brushes with consistent thickness (H_0 125 \approx 80 nm). Following extraction, the surfaces displayed a typical 126 featureless brush morphology with 6.6 nm root-mean-squared 127 (RMS) roughness, as determined via atomic force microscopy 128 (AFM) (Figure S1). The chemical composition and hydrolytic 129 stability of the pSMA brush were measured by grazing angle 130 attenuated total reflection Fourier transform infrared spectros- 131 copy (gATR-FTIR). Peaks at 1781 and 1857 cm^{-1} are 132 attributed to the five-membered anhydride ring,^{40,41} whereas 133 peaks at 1454 and 1494 cm⁻¹ are indicative of the aromatic 134 styrene unit. As shown in Figure S2, the anhydride was found 135 to be sufficiently stable in air at room temperature (i.e., minimal 136 hydrolysis of the anhydride) and surprisingly stable when 137 immersed in deionized water at 60 °C for 60 min. The 138 hydrophobicity of the pSMA brush surfaces (92° water contact 139 angle, Figure S1) likely contributes to the observed stability by 140 limiting diffusion of water into the brush—an important point 141 that we exploited for controlled PPM of the brush surface. 142

Postpolymerization Modification (PPM) of pSMA with 143 Cystamine Dihydrochloride. Poly(styrene-alt-maleic anhy- 144 dride) brushes were postmodified with cystamine dihydro- 145 chloride in the presence of triethylamine under aqueous 146 conditions. Alswieleh and co-workers recently demonstrated 147 the use of solvent quality to spatially control cross-linking 148 within a brush surface; cross-linking in good solvent provided 149 homogeneous cross-linking throughout the brush, whereas 150 poor solvents resulted in cross-linking primarily in the surface 151 region of the brush.⁴² Similarly, in our system, poor solvent 152 conditions for the postmodification are postulated to collapse 153 the brush structure and initially limit the cystamine cross- 154 linking reaction to the exposed brush interface. If the amine- 155 anhydride reaction is fast relative to diffusion of the cystamine 156 into the brush (a good assumption under poor solvent 157 conditions), then the postmodification may be expected to 158 proceed in a front-like process as depicted in Scheme 1. Under 159 s1 such conditions, reaction time would serve as a facile parameter 160 to control the penetration depth of the cystamine and, 161 consequently, the depth of the cross-linked surface region 162 within the brush. This hypothesis can be easily investigated by 163 monitoring the PPM reaction kinetics and the resulting through 164 thickness compositional brush profiles, as discussed in the 165 following section. 166

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pSMA brushes with an initial dry thickness of 80 nm were 167 postmodified with cystamine dihydrochloride in the presence of 168 169 triethylamine under aqueous conditions at discrete reaction 170 times per Scheme 1. The diamine-anhydride reaction serves to partially cross-link the brush and results in the formation of 171 172 amide-acid moieties along the backbone (see FTIR, Figure 173 S3). An increase in molecular mass of repeat units modified with cystamine results in an increase in the overall brush 174 175 thickness.⁴³ The difference in brush thickness before and after 176 PPM was used to calculate the anhydride conversion according 177 to the equation $H_f/H_0 = (M_f \rho_0)/(M_0 \rho_f)$, where H represents dry brush thickness, ρ is bulk density, and M is the molecular mass 178 of the repeat unit. The subscripts denote the unmodified (0) 179 180 and cystamine-modified (f) states of the pSMA brush. Here, we assume that the grafting density of chains before and after 181 182 modification remains constant and the change in bulk density is 183 negligible.⁴³ Anhydride conversion was also determined using 184 FTIR based on the change in area of the anhydride peak 185 absorption (Figure S4). Figure 1 shows the anhydride



Figure 1. Anhydride conversion versus cystamine reaction time for pSMA brush under poor solvent conditions.

186 conversion versus time for the cystamine postmodification 187 obtained by ellipsometry and FTIR under aqueous conditions. 188 As shown, both methods are in good agreement. Under 189 aqueous conditions, the amine-anhydride modification was 190 relatively slow with conversion plateauing at approximately 90% at 3600 s. Under poor solvent conditions, one can assume that 191 the pSMA brush exists in a collapsed state posing a barrier to 192 the diffusion of cystamine into the brush. Consequently, the 193 number of accessible anhydrides to cystamine is limited by the 194 rate of cystamine diffusion into the polymer brush. Under these 195 conditions, the PPM reaction rate is independent of the total 196 number of unreacted anhydride groups within the polymer 197 brush; thus, the PPM process would be expected to follow 198 pseudo-zero-order kinetics. The linear region (0-1200 s,199 Figure 1) in the conversion versus time plot suggests that the 200 PPM reaction indeed proceeds with pseudo-zero-order kinetics 201 under poor solvent conditions. In contrast, >96% anhydride 202 conversion was achieved within 60 s with PPM under good 203 solvent conditions (e.g. 50:50 v/v% acetonitrile:water) as 204 shown in Figure S5. With the pSMA brush well-solvated, the 2.05 PPM reaction follows pseudo-first-order kinetics (Figure S5). 206 Similar kinetic trends have been well described by others for 207 PPM of polymer brushes under good solvent conditions.⁴ 2.08 ToF-SIMS analysis with argon ion cluster sputtering was 209

209 10F-SIMS analysis with argon ion cluster sputtering was 210 employed to depth-profile the composition of the pSMA brush 211 as a function of cystamine modification time. The intensities of the $C_3H_3^+$ (m/z = 39), H_3S^+ (m/z = 35), and Si^+ (m/z = 28) 212 secondary ions—characteristic of the pSMA brush backbone, 213 cystamine modifier, and silicon substrate, respectively—were 214 recorded as a function of sputtering time.⁴⁶ Sputter time was 215 converted to depth (nm) using knowledge of the overall brush 216 thickness and sputter rate for each sample. The polymer brush/ 217 silicon substrate interface was determined using the intersection 218 of the $C_3H_3^+$ and Si^+ profiles;⁴⁷ total brush thickness values 219 determined from the $C_3H_3^+$ and Si^+ intersection are in good 220 agreement with total brush thickness values obtained from 221 ellipsometry (Table S1). The thickness of the cystamine- 222 modified brush region (h_1) was approximated from the depth at 223 which the H_3S^+ ion intensity reached 50% of its maximum 224 value. Figure 2a shows the secondary ion profiles of an 225 f2



Figure 2. Secondary ion intensity—sputtering time profiles of unmodified and cystamine-modified pSMA brush samples. (a) 80 nm unmodified pSMA brush, cystamine-modified pSMA under aqueous conditions for (b) 60, (c) 300, (d) 600, and (e) 3600 s. (f) Cystamine-modified pSMA brush under good solvent conditions. Anhydride conversion values are shown for each PPM time point. Vertical dashed line indicates the silicon/brush interface.

unmodified pSMA brush. A constant $C_3H_3^+$ intensity was 226 observed for the full thickness of the pSMA brush. The absence 227 of cystamine within the unmodified brush is indicated by the 228 noise level H_3S^+ intensities observed throughout the brush 229 thickness. The secondary ion profiles for cystamine-modified 230 pSMA brushes postmodified under aqueous conditions with 231 reaction times at 60 s (2.4% conversion), 300 s (15.6% 232 conversion), and 600 s (30.1% conversion) are shown in Figure 233 2b-e, respectively. At short PPM times, H_3S^+ ions were 234 primarily observed near the polymer/air interface with 235 intensities that quickly decay to noise levels with increasing 236 f3

 $_{\rm 237}$ depth. The $\rm H_3S^+$ profiles show a progressively deeper 238 penetration of cystamine into the pSMA brush with increasing 239 PPM time. At extended cystamine modification times or high 240 anhydride conversion (3600 s, 88% conversion), a relatively 241 constant H_3S^+ ion intensity was observed throughout the brush 242 thickness, indicating the modification reaction eventually 243 penetrates the full thickness of the brush. In contrast, Figure 244 2f shows the ToF-SIMS profile for a pSMA brush modified 245 with a low concentration cystamine solution (0.45 mmol/L) for 246 30 s under good solvent conditions. The anhydride conversion 247 for this sample was ~26%. The H_3S^+ profile shows that 248 cystamine is distributed throughout the full brush thickness despite having a much shorter cystamine modification time 249 than any of the samples modified under poor solvent 250 conditions. PPM under good solvent conditions swells the 251 252 brush, enabling rapid diffusion of the modifier into the brush and broader access to anhydride groups throughout the brush. 253 These conditions result in a more homogeneous modified 254 255 brush composition profile.

To further illustrate the trends for PPM of pSMA brushes with cystamine under poor solvent conditions, we generated kinetic plots using the fractional thickness of the pSMA brush penetrated by cystamine (h_1/H_f) obtained from ToF-SIMS. Figure 3a shows h_1/H_f versus PPM time. The h_1/H_f ratio scales



Figure 3. Ratio of cystamine-modified thickness (h_1) to total brush thickness (H_i) versus (a) cystamine modification time and (b) anhydride conversion.

261 linearly with PPM time up to 1200 s and then deviates from 262 linearity at longer reaction times—a trend that is in qualitative 263 agreement with PPM kinetics obtained by ellipsometry and 264 FTIR, as previously described (Figure 1). The fractional 265 thickness modified by cystamine shows a similar dependence 266 on anhydride conversion (Figure 3b). With insight from kinetics and depth profiling, we return to the postulation of a 267 front-like postmodification process under poor solvent 268 conditions to describe an empirical relationship between 269 270 anhydride conversion and brush thickness parameters (e.g., h_1 , h_2 , and H_f). For example, postmodification of a pSMA brush 271 to near-quantitative conversion results, on average, in a 66% 272 increase in thickness ($H_0 = 77.9 \text{ nm}, H_f = 129.8 \text{ nm}, \text{ or } 1.66H_0$) 273 after modification. Assuming a frontal modification reaction, we 274 can now divide the brush into two distinct regions: a cystamine-275 276 modified "skin" layer of thickness h_1 and the remaining 277 unmodified brush layer of thickness h_2 (Scheme 1). Using this 278 model, we can then define h_1 as $(1.66H_0)k$, h_2 as $H_0(1 - k)$, 279 and $H_{\rm f}$ as $h_1 + h_2$ where k is conversion. Employing these 280 relationships, a pSMA brush with $H_0 = 84.5$ nm and k = 9.9%results in predicted values for $h_1 = 13.8$ nm, $h_2 = 76.1$ nm, and $H_{\rm f}$ = 89.9 nm. The predicted values are in good agreement with 282 the actual measured values of h_1 = 13.5 nm, h_2 = 76.5 nm, and 283 $H_{\rm f}$ = 90.0 nm obtained from ToF-SIMS. These data along with 284 additional examples are summarized in Table S2. The empirical 285 equations proposed and the ToF-SIMS depth profile data 286 collectively support our postulation that the cystamine 287 modification reaction under poor solvent conditions occurs as 288 a frontal process. Additionally, these observations provide 289 further evidence that reaction time and anhydride conversion 290 serve as handles to control the penetration depth of cystamine 291 and, consequently, the depth of the cross-linked surface region 292 within the brush. 293

Buckling Instability in Cystamine-Modified pSMA 294 Brush Surfaces. Figure 4a shows the tapping-mode AFM 295 f4 height images for pSMA brushes following PPM with cystamine 296 dihydrochloride/TEA in water at various anhydride con- 297 versions. At each conversion point, a typical featureless brush 298 morphology (RMS roughness: 6.6 nm) was observed that was 299 unchanged in comparison to the unmodified pSMA brush 300 morphology. Next, we exposed the series of cystamine-modified 301 pSMA brushes to good solvent conditions (acetonitrile) to 302 induce swelling as illustrated in Scheme 2. Figure 4b shows the 303 s2 brush morphologies after swelling in acetonitrile for 60 min. 304 The brush wrinkling patterns that developed upon swelling 305 show a clear dependence on the anhydride conversion, 306 transitioning from small scale random labyrinths at low 307 conversions (7.1%) to larger scale labyrinths at higher 308 conversions (31.2%). In general, wrinkles were not observed 309 in cystamine-modified brush samples with anhydride con- 310 versions >40% (Figure S6). It is important to note that AFM 311 imaging was conducted in the dry state after rapid evaporation 312 of acetonitrile under a stream of nitrogen. It is expected that the 313 pSMA polymer brush rapidly traverses the glass transition 314 temperature (typical pSMA $T_g > 120$ °C) upon solvent 315 evaporation, trapping the observed wrinkle morphologies in the 316 dry state. Similar arguments have supported the observation of 317 trapped buckled morphologies in surface-confined poly(N- 318 isopropylacrylamide) gels.^{33,48} The swelling response of 319 polymer brushes relies on several interdependent parameters 320 including grafting density, molecular mass, chemical nature of 321 the polymer chains, and solvent quality.⁴⁹ In the present 322 system, the brush swelling response is also influenced by the 323 extent of cross-linking. Since the pSMA brushes were cross- 324 linked under poor solvent conditions, subsequent exposure to a 325 good solvent likely generates a swelling mismatch between the 326 lateral and perpendicular directions, where the in-plane swelling 327 constraint may be attributed to both attachment of chains to 328 the substrate and to extent of cross-linking. As the brush 329 expands more in the direction normal to the substrate relative 330 to the constrained lateral direction, an in-plane compressive 331 stress is generated. At a critical degree of swelling, the imposed 332 compressive stress causes an out of plane deformation of the 333 untethered surface, resulting in the observed wrinkled 334 morphologies. To define the critical degree of swelling that 335 results in surface wrinkling, we determined the swelling ratio 336 (α) of the cystamine-modified pSMA brushes as a function of 337 anhydride conversion using in situ ellipsometry. The swelling 338 ratio is defined as the thickness of cross-linked brush (swollen 339 thickness in acetonitrile) to that of the dry cross-linked brush 340 (prior to swelling). Figure 4c shows the relationship between 341 swelling ratio and conversion for the pSMA brushes modified 342 with cystamine under poor solvent conditions. The swelling 343 ratio of an unmodified pSMA brush was ~2.1. At anhydride 344



Figure 4. AFM height images of pSMA brushes following (a) reaction with cystamine and (b) subsequent exposure to good solvent (acetonitrile) conditions. (c) Swelling ratio versus anhydride conversion for cystamine-modified pSMA brushes. The horizontal line represents the critical swelling ratio. (d) Wavelength versus anhydride conversion. (e) Fit of the wrinkling wavelength as a function of h_1h_2 demonstrating that the scaling relationship $\lambda \sim (h_1h_2)^{1/2}$ adequately describes the brush system.

Scheme 2. Synthetic Route to Wrinkled Polymer Brush $Surfaces^a$



"Cystamine-modified PSMA brush surfaces were exposed to good solvent conditions (acetonitrile) to induce a wrinkled brush morphology. The length scales of wrinkle wavelength and brush thickness are not drawn to scale.

345 conversions <20%, an increase in the swelling ratio was 346 observed that may be attributed to an increase in brush/solvent 347 compatibility due to the contribution of carboxylic acid 348 functional groups formed upon reaction of the maleic 349 anhydride with cystamine. At anhydride conversions >30%, a gradual decrease in swelling ratio was observed as the extent of 350 351 cross-linking begins to dominate the swelling behavior. The critical swelling ratio, below which the compressive stress is 352 insufficient to induce surface buckling, was found to be ~1.8 353 (~40% anhydride conversion)—a critical value that is 354 consistent with other reports from the literature.⁵⁰ Referring 355 356 back to the ToF-SIMS depth profiles, the critical swelling ratio 357 can be correlated to a h_1/H_f ratio of approximately 0.6. 358 Additionally, we considered if the distribution or depth profile 359 of cross-links within the pSMA brush influenced the swelling 360 behavior and, consequently, the propensity to undergo surface 361 buckling. As illustrated in Figure 2f, pSMA brushes post-362 modified with cystamine under good solvent conditions at short

reaction times resulted in distribution of cystamine throughout 363 the full brush thickness. At comparable anhydride conversions, 364 pSMA brushes modified under good solvent conditions 365 exhibited lower swelling ratios (e.g., $\alpha = 1.48$ at 17% 366 conversion, Figure 4c) than brushes modified under poor 367 solvent conditions (e.g., $\alpha = 2.4$ at 17% conversion). When 368 cross-linked under good solvent conditions, the swelling ratio 369 was consistently below the critical α of 1.8; thus, buckling was 370 not observed in these samples (Figure S7). These results 371 suggest that the cross-link profile influences the swelling ratio 372 and the ability of the brushes to undergo buckling; however, an 373 alternative explanation should also be considered to explain the 374 absence of wrinkles when cross-linked under good solvent 375 conditions. Namely, following the Flory-Rehner formalism, 376 reswelling the cross-linked brush in the same solvent employed 377 for cross-linking would return a zero-osmotic stress state- 378 conditions that would not induce surface instabilities.⁵¹

The wavelengths of the wrinkled morphologies were 380 measured by taking the radial average of the AFM 2D FFT 381 power spectra. As shown in Figure 4d, the observed wrinkle 382 wavelength (λ) scales linearly with anhydride conversion. 383 Linear scaling relationships between wrinkle wavelength and 384 film thickness are well-established and have been described for 385 multiple film constructs. Here, we consider a rigid-on-soft 386 multilayer construct consisting of a cystamine-modified "skin" 387 layer (h_1) and an unmodified brush "substrate" layer (h_2) that is 388 in turn covalently grafted to a rigid silicon support ($h_{\rm Si}$), where 389 $h_{\rm Si} \gg h_2 > h_1$. For such constructs, scaling can be described as λ 390 $\sim (h_1h_2)^{1/2}(E_{h_1}/E_{h_2})^{1/6}$, where E_{h_1} and E_{h_2} are the Young's 391 moduli of the cystamine-modified "skin" layer and the 392 unmodified "substrate" layer, respectively.^{1,52–54} As shown in 393 Figure 4e, the observed dependence of the wrinkle wavelength 394 on the h_1 and h_2 thicknesses is adequately described by the 395

396 scaling relation $\lambda \sim (h_1h_2)^{1/2}$. Although we lack the ability to 397 determine the modulus of the individual "skin" and "substrate" 398 regions within the brush—values that would enable further 399 quantitative validation to the model—our current observations 400 are in qualitative agreement with the scaling relationship 401 predicted by the general bilayer film model. More importantly, 402 these observations demonstrate that wrinkle wavelength and 403 morphology can be judiciously tuned by controlling the brush 404 profile via postpolymerization modification under poor solvent 405 conditions.

The importance of employing a cross-linker such as 406 407 cystamine to facilitate the formation and stabilization of the 408 wrinkled brush surfaces was illustrated through several control 409 experiments. First, pSMA brushes were modified with two 410 different monofunctional amines (e.g., propylamine and 411 hexylamine) under identical aqueous conditions as used for 412 cystamine. Despite the similar chain length of cystamine and 413 hexvlamine, using monofunctional amines as postmodifiers did 414 not lead to the formation of wrinkles regardless of PPM 415 reaction time or conversion (Figure S8). Brushes modified with 416 primary amines undergo swelling but lack the cross-links 417 necessary to generate the mismatch in lateral and perpendicular 418 swelling. Thus, the compressive stress required for buckling is 419 absent. Additionally, we exploited the reversible nature of the 420 disulfide linkage in the cystamine cross-linker by subjecting a 421 wrinkled pSMA brush to reducing conditions (e.g., tris(2-422 carboxyethyl)phosphine (TCEP) in phosphate buffer), as 423 illustrated in Figure 5a. Reduction resulted in release of the



Figure 5. (a) Scheme illustrating disulfide reduction with TCEP and release of wrinkles. (b) AFM height images of wrinkled and reduced pSMA brushes. (c) FTIR of wrinkled and reduced pSMA brushes.

424 wrinkles and the formation of a featureless brush morphology, 425 as shown in Figure 5b. The appearance of thiol functional 426 groups within the brush following the TCEP reduction was 427 confirmed by FTIR (S–H stretch, 2650 cm⁻¹, Figure 5c). This 428 result points to an opportunity to engineer brush surfaces with 429 dynamic buckling behavior, where wrinkle formation and 430 release are dictated via an external stimulus. Finally, we 431 investigated the influence of thermal treatment (145 °C, 18 h) 432 on the cystamine-modified brush surfaces prior to and after the surface was wrinkled. As shown in Figure S9a, prior to exposure 433 to acetonitrile, thermal annealing alone does not induce the 434 cystamine-modified brush surface to undergo wrinkling. 435 Likewise, thermal treatment does not influence the wrinkled 436 morphology as indicated by negligible changes in wrinkle 437 wavelength before and after annealing, as shown in Figure S9b. 438

In summary, we demonstrate a simple postpolymerization 439 modification approach to engineer ultrathin polymer brush 440 surfaces with tunable wrinkled morphologies. Cross-linking 441 pSMA brushes under poor solvent conditions limits the 442 postmodification reaction to the near surface region of the 443 brush, where reaction time dictates the ultimate thickness of the 444 cross-linked surface region. Exposure of the selectively cross- 445 linked brush surface to good solvent conditions generates an in- 446 plane compressive stress arising from a mismatch between 447 lateral and perpendicular swelling directions within the brush. 448 Above a critical swelling ratio of 1.8, the imposed compressive 449 stress causes an out-of-plane deformation of the untethered 450 surface resulting in the observed wrinkled morphologies. The 451 brush morphology can be tailored from nanoscale labyrinth-like 452 wrinkles to microscale labyrinth-like wrinkles simply by 453 manipulating the cross-linking time, while wrinkle wavelength 454 scales according to $\lambda \sim (h_1 h_2)^{1/2}$. We anticipate this simple 455 approach will provide new routes to engineer ultrathin brush 456 surfaces with complex functionality and morphology for a 457 variety of applications. 458

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the 461 ACS Publications website at DOI: 10.1021/acs.macro- 462 mol.7b01888. 463

Synthesis and characterization details, FTIR and 464 conversion, additional AFM (PDF) 465

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