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Buckling Instabilities in Polymer Brush Surfaces via Postpolymerization Modification

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Abstract

We report a simple route to engineer ultrathin polymer brush surfaces with wrinkled morphologies using post-polymerization modification (PPM), where the length scale of the buckled features can be tuned from hundreds of nanometers to one micrometer using PPM reaction time. We show that partial crosslinking of the outer layer of the polymer brush under poor solvent conditions is critical to obtain wrinkled morphologies upon swelling. Characterization of the PPM kinetics and swelling behavior via ellipsometry and the through-thickness composition profile via time-of-flight secondary ion mass spectroscopy (ToF-SIMS) provided keys insight into parameters influencing the buckling behavior.

Graphical Abstract

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at DOI: Synthesis and characterization details, FTIR and conversion, additional AFM. (PDF)

Introduction

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

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

Post-polymerization modification (PPM) of polymer brushes – ultrathin assemblies of polymer chains densely grafted to a surface such that chains experience strong segmental repulsion and stretch perpendicular to the substrate – is a powerful platform for tailoring the chemical and mechanical properties of surfaces.³⁴ The extended chain conformation of brushes has specific implications for the PPM process, where the high osmotic pressure and reduced chain conformational entropy disfavor the penetration of reactive modifiers into the brush.^{35, 36} Thus, the penetration depth and the through-thickness compositional homogeneity of the brush resulting from the PPM process are ultimately dependent on i) the reaction conditions (solvent quality, reaction efficiency, and reaction time), ii) the tethered brush parameters (grafting density and thickness), and iii) the physical properties of the reactive modifier (molecular mass and steric bulk). Indeed, Klok *et al.* showed *via* neutron reflectometry³⁶ and XPS³⁷ that increases in brush thickness, grafting density, and molecular mass of the modifier result in decreased depths of penetration and increased vertical heterogeneity. Intentional manipulation of PPM parameters provides an opportunity to design brush structures with through-thickness material properties profiles that fulfill the requirements for nanoscale buckling within ultrathin films on 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 to provide confinement.³⁹

Herein, we report a simple PPM approach to engineer ultrathin poly(styrene-alt-maleic anhydride) (pSMA) brush surfaces with tuneable wrinkled morphologies. We crosslink pSMA brushes under poor solvent conditions to limit the postmodification reaction to the near surface region of the brush, where reaction time dictates the ultimate thickness of the crosslinked surface region. Exposure of the selectively crosslinked brush surface to good solvent conditions generates an in-plane compressive stress arising from a mismatch between lateral and perpendicular swelling directions within the brush. The compressive stress causes an out of plane deformation of the untethered surface resulting in wrinkled morphologies. Characterization of the PPM kinetics via ellipsometry and through-thickness composition profile via time-of-flight secondary ion mass spectroscopy (ToF-SIMS) provided keys insight into parameters influencing the buckling behavior.

Results and Discussion

Synthesis of pSMA Polymer Brush

For this work, we employed pSMA as a reactive polymer brush scaffold. pSMA is easily obtained from commodity monomers and is highly reactive towards amines for facile post-polymerization modification. Alternating pSMA brushes were synthesized via surface-initiated polymerization of a 54:46 styrene:maleic anhydride monomer feed from silicon substrates modified with an asymmetric trichlorosilane azo-based initiator. Experimental details are provided in the supporting information. It is well known that styrene and maleic anhydride monomers form nearly perfect alternating copolymers under most free-radical polymerization conditions. Polymerizations were carried out at 95 °C to generate pSMA brushes with consistent thickness ($H_o \approx 80$ nm). Following extraction, the surfaces displayed a typical featureless brush morphology with 6.6 nm root-mean-squared (RMS) roughness, as determined via atomic force microscopy (AFM) (Figure S1). The chemical composition and hydrolytic stability of the pSMA brush were measured by grazing angle attenuated total reflection Fourier transform infrared spectroscopy (gATR-FTIR). Peaks at 1781 cm^{-1} and 1857 cm^{-1} are attributed to the five-membered anhydride ring,^{40, 41} whereas peaks at 1454 cm^{-1} and 1494 cm^{-1} are indicative of the aromatic styrene unit. As shown in Figure S2, the anhydride was found to be sufficiently stable in air at room temperature (i.e. minimal hydrolysis of the anhydride), and surprisingly stable when immersed in deionized water at 60 °C for 60 min. The hydrophobicity of the pSMA brush surfaces (92° water contact angle, Figure S1) likely contributes to the observed stability by limiting diffusion of water into the brush – an important point that we exploited for controlled PPM of the brush surface.

Post-polymerization Modification (PPM) of pSMA with Cystamine Dihydrochloride

Poly(styrene-alt-maleic anhydride) brushes were post-modified with cystamine dihydrochloride in the presence of triethylamine under aqueous conditions. Alswieleh and coworkers recently demonstrated the use of solvent quality to spatially control crosslinking within a brush surface; crosslinking in good solvent provided homogeneous crosslinking throughout the brush, whereas poor solvents resulted in crosslinking primarily in the surface region of the brush.⁴² Similarly, in our system, poor solvent conditions for the postmodification are postulated to collapse the brush structure and initially limit the cystamine crosslinking reaction to the exposed brush interface. If the amine-anhydride reaction is fast relative to diffusion of the cystamine into the brush (a good assumption under poor solvent conditions), then the postmodification may be expected to proceed in a front-like process as depicted in Scheme 1. Under such conditions, reaction time would serve as a facile parameter to control the penetration depth of the cystamine, and consequently, the depth of the crosslinked surface region within the brush. This hypothesis can be easily investigated by monitoring the PPM reaction kinetics and the resulting through-thickness compositional brush profiles, as discussed in the following section.

pSMA brushes with an initial dry thickness of 80 nm were post-modified with cystamine dihydrochloride in the presence of triethylamine under aqueous conditions at discrete reaction times per Scheme 1. The diamine-anhydride reaction serves to partially crosslink the brush and results in the formation of amide-acid moieties along the backbone (see FTIR, Figure S3). An increase in molecular mass of repeat units modified with cystamine results in an increase in the overall brush thickness.⁴³ The difference in brush thickness before and after PPM was used to calculate the anhydride conversion according to the equation: $H_f/H_o = (M_2\rho_1)/(M_1\rho_2)$, where H represents dry brush thickness, ρ is bulk density, and M is the molecular mass of the repeat unit. The subscripts denote the unmodified (o) and cystamine-modified (f) states of the pSMA brush. Here, we assume that the grafting density of chains before and after modification remains constant and the change in bulk density is negligible.⁴³ Anhydride conversion was also determined using FTIR based on the change in area of the anhydride peak absorption (Figure S4). Figure 1 shows the anhydride conversion versus time for the cystamine postmodification obtained by ellipsometry and FTIR under aqueous conditions. As shown, both methods are in good agreement. Under aqueous conditions, the amine-anhydride modification was relatively slow with conversion plateauing at approximately 90% at 3600s. Under poor solvent conditions, one can assume that the pSMA brush exists in a collapsed state posing a barrier to the diffusion of cystamine into the brush. Consequently, the number of accessible anhydrides to cystamine is limited by the rate of cystamine diffusion into the polymer brush. Under these conditions, the PPM reaction rate is independent of the total number of unreacted anhydride groups within the polymer brush, thus the PPM process would be expected to follow pseudo-zero-order kinetics. The linear region (0 s to 1200 s, Figure 1) in the conversion versus time plot suggests that the PPM reaction indeed proceeds with pseudo-zero-order kinetics under poor solvent conditions. In contrast, >96% anhydride conversion was achieved within 60s with PPM under good solvent conditions as shown in Figure S5. With the pSMA brush well-solvated, the PPM reaction follows pseudo-first-order kinetics (Figure S5). Similar kinetic trends have been well described by others for PPM of polymer brushes under good solvent conditions.^{44, 45}

ToF-SIMS analysis with argon ion cluster sputtering was employed to depth-profile the composition of the pSMA brush as a function of cystamine modification time. The intensity of the $C_3H_3^+$ ($m/z = 39$), H_3S^+ ($m/z = 35$) and Si^+ ($m/z = 28$) secondary ions – characteristic of the pSMA brush backbone, cystamine modifier, and silicon substrate, respectively – were recorded as a function of sputtering time.⁴⁶ Sputter time was converted to depth (nm) using knowledge of the overall brush thickness and sputter rate for each sample. The polymer brush/silicon substrate interface was determined using the intersection of the $C_3H_3^+$ and Si^+ profiles;⁴⁷ total brush thickness values determined from the $C_3H_3^+$ and Si^+ intersection are in good agreement with total brush thickness values obtained from ellipsometry (Table S1). The thickness of the cystamine-modified brush region (h_I) was approximated from the depth at which the H_3S^+ ion intensity reached 50% of its maximum value. Figure 2a shows the secondary ion profiles of an unmodified pSMA brush. A constant $C_3H_3^+$ intensity was observed for the full thickness of the pSMA brush. The absence of cystamine within the unmodified brush is indicated by the noise level H_3S^+ intensities observed throughout the brush thickness. The secondary ion profiles for cystamine-modified pSMA brushes post-modified under aqueous conditions with reaction times at 60 s (2.4 % conv.), 300 s (15.6 % conv.), and 600 s (30.1 % conv.) are shown in Figure 2b–e, respectively. At short PPM times, H_3S^+ ions were primarily observed near the polymer/air interface with intensities that quickly decay to noise levels with increasing depth. The H_3S^+ profiles show a progressively deeper penetration of cystamine into the pSMA brush with increasing PPM time. At extended cystamine modification times or high anhydride conversion (3600 s, 88 % conv.), a relatively constant H_3S^+ ion intensity was observed throughout the brush thickness indicating the modification reaction eventually penetrates the full thickness of the brush. In contrast, Figure 2f shows the ToF-SIMS profile for a pSMA brush modified with a low concentration cystamine solution (0.45 mmol/L) for 30 s under good solvent conditions. The anhydride conversion for this sample was ~26%. The H_3S^+ profile shows that cystamine is distributed throughout the full brush thickness despite having a much shorter cystamine modification time than any of the samples modified under poor solvent conditions. PPM under good solvent conditions swells the brush enabling rapid diffusion of the modifier into the brush and broader access to anhydride groups throughout the brush. These conditions result in a more homogeneous modified 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_I/H_f) obtained from ToF-SIMS. Figure 3a shows h_I/H_f versus PPM time. The h_I/H_f ratio scales linearly with PPM time up to 1200 s and then deviates from linearity at longer reaction times – a trend that is in qualitative agreement with PPM kinetics obtained by ellipsometry and FTIR, as previously described (Figure 1). The fractional thickness modified by cystamine shows a similar dependence on anhydride conversion (Figure 3b). With insight from kinetics and depth profiling, we return to the postulation of a front-like postmodification process under poor solvent conditions to describe an empirical relationship between anhydride conversion and brush thickness parameters (e.g., h_I , h_2 , and H_f). For example, postmodification of a pSMA brush to near quantitative conversion results, on average, in a 66 % increase in thickness ($H_o = 77.9$ nm, $H_f = 129.8$ nm, or $1.66H_o$) after modification. Assuming a frontal modification reaction, we

can now divide the brush into two distinct regions: a cystamine-modified “skin” layer of thickness h_1 , and the remaining unmodified brush layer of thickness h_2 (Scheme 1). Using this model, we can then define h_1 as $(1.66H_0)k$, h_2 as $H_0(1-k)$, and H_f as h_1+h_2 where k is conversion. Employing these 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 $H_f = 89.9$ nm. The predicted values are in good agreement with the actual measured values of $h_1 = 13.5$ nm, $h_2 = 76.5$ nm and $H_f = 90.0$ nm obtained from ToF-SIMS. These data along with additional examples are summarized in Table S2. The empirical equations proposed and the ToF-SIMS depth profile data collectively support our postulation that the cystamine modification reaction under poor solvent conditions occurs as a frontal process. Additionally, these observations provide further evidence that reaction time and anhydride conversion serve as handles to control the penetration depth of cystamine, and consequently, the depth of the crosslinked surface region within the brush.

Buckling Instability in Cystamine Modified pSMA Brush Surfaces

Figure 4a shows the tapping-mode AFM height images for pSMA brushes following PPM with cystamine dihydrochloride/TEA in water at various anhydride conversions. At each conversion point, a typical featureless brush morphology (RMS roughness: 6.6 nm) was observed that was unchanged in comparison to the unmodified pSMA brush morphology. Next, we exposed the series of cystamine modified pSMA brushes to good solvent conditions (acetonitrile) to induce swelling as illustrated in Scheme 2. Figure 4b shows the brush morphologies after swelling in acetonitrile for 60 min. The brush wrinkling patterns that developed upon swelling show a clear dependence on the anhydride conversion, transitioning from small scale random labyrinths at low conversions (7.1 %) to larger scale labyrinths at higher conversions (31.2%). In general, wrinkles were not observed in cystamine modified brush samples with anhydride conversions > 40 % (Figure S6). It is important to note that AFM imaging was conducted in the dry state after rapid evaporation of acetonitrile under a stream of nitrogen. It is expected that the pSMA polymer brush rapidly traverses the glass transition temperature (typical pSMA $T_g > 120$ °C) upon solvent evaporation, trapping the observed wrinkle morphologies in the dry state. Similar arguments have supported the observation of trapped buckled morphologies in surface-confined poly(N-isopropylacrylamide) gels.^{33, 48} The swelling response of polymer brushes relies on several interdependent parameters including grafting density, molecular mass, chemical nature of the polymer chains, and solvent quality.⁴⁹ In the present system, the brush swelling response is also influenced by the extent of crosslinking. Since the pSMA brushes were crosslinked under poor solvent conditions, subsequent exposure to a good solvent likely generates a swelling mismatch between the lateral and perpendicular directions, where the in-plane swelling constraint may be attributed to both attachment of chains to the substrate and to extent of crosslinking. As the brush expands more in the direction normal to the substrate relative to the constrained lateral direction, an in-plane compressive stress is generated. At a critical degree of swelling, the imposed compressive stress causes an out of plane deformation of the untethered surface resulting in the observed wrinkled morphologies. To define the critical degree of swelling that results in surface wrinkling, we determined the swelling ratio (α) of the cystamine-modified pSMA brushes as a function of anhydride conversion using *in situ* ellipsometry. The swelling ratio is defined as the

thickness of crosslinked brush (swollen thickness in acetonitrile) to that of the dry crosslinked brush (prior to swelling). Figure 4c shows the relationship between swelling ratio and conversion for the pSMA brushes modified with cystamine under poor solvent conditions. The swelling ratio of an unmodified pSMA brush was ~ 2.1 . At anhydride conversions $< 20\%$, an increase in the swelling ratio was observed that may be attributed to an increase in brush/solvent compatibility due to the contribution of carboxylic acid functional groups formed upon reaction of the maleic anhydride with cystamine. At anhydride conversions $> 30\%$, a gradual decrease in swelling ratio was observed as the extent of crosslinking begins to dominate the swelling behavior. The critical swelling ratio, below which the compressive stress is insufficient to induce surface buckling, was found to be ~ 1.8 ($\sim 40\%$ anhydride conversion) – a critical value that is consistent with other reports from literature.⁵⁰ Referring back to the ToF-SIMS depth profiles, the critical swelling ratio can be correlated to a h_I/H_f ratio of approximately 0.6. Additionally, we considered if the distribution or depth profile of crosslinks within the pSMA brush influenced the swelling behavior, and consequently, the propensity to undergo surface buckling. As illustrated in Figure 2f, pSMA brushes post-modified with cystamine under good solvent conditions at short reaction times resulted in distribution of cystamine throughout the full brush thickness. At comparable anhydride conversions, pSMA brushes modified under good solvent conditions exhibited lower swelling ratios (e.g., $\alpha = 1.48$ at 17% conversion, Figure 4c) than brushes modified under poor solvent conditions (e.g., $\alpha = 2.4$ at 17% conversion). When crosslinked under good solvent conditions, the swelling ratio was consistently below the critical α of 1.8, thus buckling was not observed in these samples (Figure S7). These results suggest that the crosslink profile influences the swelling ratio and the ability of the brushes to undergo buckling; however, an alternative explanation should also be considered to explain the absence of wrinkles when crosslinked under good solvent conditions. Namely, following the Flory-Rehner formalism, reswelling the crosslinked brush in the same solvent employed for crosslinking would return a zero-osmotic stress state – conditions that would not induce surface instabilities.⁵¹

The wavelengths of the wrinkled morphologies were measured by taking the radial average of the AFM 2D FFT power spectra. As shown in Figure 4d, the observed wrinkle wavelength (λ) scales linearly with anhydride conversion. Linear scaling relationships between wrinkle wavelength and film thickness are well-established and have been described for multiple film constructs. Here, we consider a rigid-on-soft multilayer construct consisting of a cystamine-modified “skin” layer (h_I) and an unmodified brush “substrate” layer (h_2) that is in turn covalently grafted to a rigid silicon support (h_{Si}), where $h_{Si} \gg h_2 > h_I$. For such constructs, scaling can be described as $\lambda \sim (h_I h_2)^{1/2} (E_{h1} E_{h2})^{1/6}$ where E_{h1} and E_{h2} are the Young’s moduli of the cystamine-modified “skin” layer and the unmodified “substrate” layer, respectively.^{1, 52–54} As shown in Figure 4e, the observed dependence of the wrinkle wavelength on the h_I and h_2 thicknesses is adequately described by the scaling relation $\lambda \sim (h_I h_2)^{1/2}$. Although we lack the ability to determine the modulus of the individual “skin” and “substrate” regions within the brush – values that would enable further quantitative validation to the model – our current observations are in qualitative agreement with the scaling relationship predicted by the general bilayer film model. More importantly, these observations demonstrate that wrinkle wavelength and morphology can be judiciously

tuned by controlling the brush profile via postpolymerization modification under poor solvent conditions.

The importance of employing a crosslinker such as cystamine to facilitate the formation and stabilization of the wrinkled brush surfaces was illustrated through several control experiments. First, pSMA brushes were modified with two different monofunctional amines (e.g. propylamine and hexylamine) under identical aqueous conditions as used for cystamine. Despite the similar chain length of cystamine and hexylamine, using monofunctional amines as post-modifiers did not lead to the formation of wrinkles regardless of PPM reaction time or conversion (Figure S8). Brushes modified with primary amines undergo swelling, but lack the crosslinks necessary to generate the mismatch in lateral and perpendicular swelling. Thus, the compressive stress required for buckling is absent. Additionally, we exploited the reversible nature of the disulfide linkage in the cystamine crosslinker by subjecting a wrinkled pSMA brush to reducing conditions (e.g. tris(2-carboxyethyl)phosphine (TCEP) in phosphate buffer), as illustrated in Figure 5a. Reduction resulted in release of the wrinkles and the formation of a featureless brush morphology, as shown in Figure 5b. The appearance of thiol functional groups within the brush following the TCEP reduction was confirmed by FTIR (S-H stretch, 2650 cm^{-1} , Figure 5c). This result points to an opportunity to engineer brush surfaces with dynamic buckling behavior, where wrinkle formation and release are dictated via an external stimulus. Finally, we investigated the influence of thermal treatment ($145\text{ }^{\circ}\text{C}$, 18 h) on the cystamine-modified brush surfaces prior to and after the surface was wrinkled. As shown in Figure S9a, prior to exposure to acetonitrile, thermal annealing alone does not induce the cystamine-modified brush surface to undergo wrinkling. Likewise, thermal treatment does not influence the wrinkled morphology as indicated by negligible changes in wrinkle wavelength before and after annealing, as shown in Figure S9b.

In summary, we demonstrate a simple post-polymerization modification approach to engineer ultrathin polymer brush surfaces with tunable wrinkled morphologies. Crosslinking pSMA brushes under poor solvent conditions limits the postmodification reaction to the near surface region of the brush, where reaction time dictates the ultimate thickness of the crosslinked surface region. Exposure of the selectively crosslinked brush surface to good solvent conditions generates an in-plane compressive stress arising from a mismatch between lateral and perpendicular swelling directions within the brush. Above a critical swelling ratio of 1.8, the imposed compressive stress causes an out of plane deformation of the untethered surface resulting in the observed wrinkled morphologies. The brush morphology can be tailored from nanoscale labyrinth-like wrinkles to microscale lamellar-like wrinkles simply by manipulating the crosslinking time, while wrinkle wavelength scales according to $\lambda \sim (h_1 h_2)^{1/2}$. We anticipate this simple approach will provide new routes to engineer ultrathin brush surfaces with complex functionality and morphology for a variety of applications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References

1. Cerda E, Mahadevan L. Geometry and physics of wrinkling. *Phys Rev Lett*. 2003; 90:074302. [PubMed: 12633231]
2. Tallinen T, Chung JY, Rousseau F, Girard N, Lefèvre J, Mahadevan L. On the growth and form of cortical convolutions. *Nat Phys*. 2016; 12:588–593.
3. Genzer J, Groenewold J. Soft matter with hard skin: From skin wrinkles to templating and material characterization. *Soft Matter*. 2006; 2:310–323.
4. Chan EP, Smith EJ, Hayward RC, Crosby AJ. Surface wrinkles for smart adhesion. *Adv Mater*. 2008; 20:711.
5. Davis CS, Crosby AJ. Mechanics of wrinkled surface adhesion. *Soft Matter*. 2011; 7:5373–5381.
6. Davis CS, Martina D, Creton C, Lindner A, Crosby AJ. Enhanced Adhesion of Elastic Materials to Small-Scale Wrinkles. *Langmuir*. 2012; 28:14899–14908. [PubMed: 23025884]
7. Jeong HE, Kwak MK, Suh KY. Stretchable, Adhesion-Tunable Dry Adhesive by Surface Wrinkling. *Langmuir*. 2010; 26:2223–2226. [PubMed: 20088533]
8. Li YY, Dai SX, John J, Carter KR. Superhydrophobic Surfaces from Hierarchically Structured Wrinkled Polymers. *ACS Appl Mater Interfaces*. 2013; 5:11066–11073. [PubMed: 24131534]
9. Zhang ZQ, Zhang T, Zhang YW, Kim KS, Gao HJ. Strain-Controlled Switching of Hierarchically Wrinkled Surfaces between Superhydrophobicity and Superhydrophilicity. *Langmuir*. 2012; 28:2753–2760. [PubMed: 22176536]
10. Efimenko K, Finlay J, Callow ME, Callow JA, Genzer J. Development and Testing of Hierarchically Wrinkled Coatings for Marine Antifouling. *ACS Appl Mater Interfaces*. 2009; 1:1031–1040. [PubMed: 20355888]
11. Hoipkemeier-Wilson L, Schumacher JF, Carman ML, Gibson AL, Feinberg AW, Callow ME, Finlay JA, Callow JA, Brennan AB. Antifouling Potential of Lubricious, Micro-engineered, PDMS Elastomers against Zoospores of the Green Fouling Alga *Ulva* (Enteromorpha). *Biofouling*. 2004; 20:53–63. [PubMed: 15079893]
12. Muller M, Karg M, Fortini A, Hellweg T, Fery A. Wrinkle-assisted linear assembly of hard-core/soft-shell particles: impact of the soft shell on the local structure. *Nanoscale*. 2012; 4:2491–2499. [PubMed: 22395669]
13. Guvendiren M, Burdick JA. The control of stem cell morphology and differentiation by hydrogel surface wrinkles. *Biomaterials*. 2010; 31:6511–6518. [PubMed: 20541257]
14. Gao N, Zhang X, Liao S, Jia H, Wang Y. Polymer Swelling Induced Conductive Wrinkles for an Ultrasensitive Pressure Sensor. *ACS Macro Lett*. 2016:823–827.
15. Wagner S, Lacour SP, Jones J, Hsu PHI, Sturm JC, Li T, Suo ZG. Electronic skin: architecture and components. *Physica E*. 2004; 25:326–334.
16. Khang DY, Jiang HQ, Huang Y, Rogers JA. A stretchable form of single-crystal silicon for high-performance electronics on rubber substrates. *Science*. 2006; 311:208–212. [PubMed: 16357225]
17. Chan EP, Crosby AJ. Fabricating microlens arrays by surface wrinkling. *Adv Mater*. 2006; 18:3238.
18. Bowden N, Brittain S, Evans AG, Hutchinson JW, Whitesides GM. Spontaneous formation of ordered structures in thin films of metals supported on an elastomeric polymer. *Nature*. 1998; 393:146–149.
19. Harrison C, Stafford CM, Zhang W, Karim A. Sinusoidal phase grating created by a tunably buckled surface. *Appl Phys Lett*. 2004; 85:4016–4018.

20. Meitl MA, Zhu ZT, Kumar V, Lee KJ, Feng X, Huang YY, Adesida I, Nuzzo RG, Rogers JA. Transfer printing by kinetic control of adhesion to an elastomeric stamp. *Nat Mater.* 2006; 5:33–38.
21. Pretzl M, Schweikart A, Hanske C, Chiche A, Zettl U, Horn A, Boker A, Fery A. A Lithography-Free Pathway for Chemical Microstructuring of Macromolecules from Aqueous Solution Based on Wrinkling. *Langmuir.* 2008; 24:12748–12753. [PubMed: 18950207]
22. Khare K, Zhou JH, Yang S. Tunable Open-Channel Microfluidics on Soft Poly(dimethylsiloxane) (PDMS) Substrates with Sinusoidal Grooves. *Langmuir.* 2009; 25:12794–12799. [PubMed: 19572521]
23. Rodríguez-Hernández J. Wrinkled interfaces: Taking advantage of surface instabilities to pattern polymer surfaces. *Prog Polym Sci.* 2015; 42:1–41.
24. Yang S, Khare K, Lin PC. Harnessing Surface Wrinkle Patterns in Soft Matter. *Adv Funct Mater.* 2010; 20:2550–2564.
25. Chen D, Yoon J, Chandra D, Crosby AJ, Hayward RC. Stimuli-responsive buckling mechanics of polymer films. *J Polym Sci, Part B: Polym Phys.* 2014; 52:1441–1461.
26. Das A, Banerji A, Mukherjee R. Programming Feature Size in the Thermal Wrinkling of Metal Polymer Bilayer by Modulating Substrate Viscoelasticity. *ACS Appl Mater Interfaces.* 2017; 9:23255–23262. [PubMed: 28617579]
27. Bowden N, Huck WTS, Paul KE, Whitesides GM. The controlled formation of ordered, sinusoidal structures by plasma oxidation of an elastomeric polymer. *Appl Phys Lett.* 1999; 75:2557.
28. Chandra D, Crosby AJ. Self-wrinkling of UV-cured polymer films. *Adv Mater.* 2011; 23:3441–5. [PubMed: 21721055]
29. Guvendiren M, Burdick JA, Yang S. Solvent induced transition from wrinkles to creases in thin film gels with depth-wise crosslinking gradients. *Soft Matter.* 2010; 6:5795–5801.
30. Huang H, Chung JY, Nolte AJ, Stafford CM. Characterizing Polymer Brushes via Surface Wrinkling. *Chem Mater.* 2007:6555–6560.
31. Singamaneni S, McConney ME, Tsukruk VV. Spontaneous self-folding in confined ultrathin polymer gels. *Adv Mater.* 2010; 22:1263–8. [PubMed: 20437516]
32. Singamaneni S, McConney ME, Tsukruk VV. Swelling-Induced Folding in Confined Nanoscale Responsive Polymer Gels. *ACS Nano.* 2010; 4:2327–2337. [PubMed: 20232813]
33. Ortiz O, Vidyasagar A, Wang J, Toomey R. Surface Instabilities in Ultrathin, Cross-Linked Poly(N-isopropylacrylamide) Coatings. *Langmuir.* 2010; 26:17489–17494. [PubMed: 20929198]
34. Arnold RM, Patton DL, Popik VV, Locklin J. A dynamic duo: pairing click chemistry and postpolymerization modification to design complex surfaces. *Acc Chem Res.* 2014; 47:2999–3008. [PubMed: 25127014]
35. Schuh C, Rühle. Penetration of Polymer Brushes by Chemical Nonidentical Free Polymers. *Macromolecules.* 2011; 44:3502–3510.
36. Schüwer N, Geue T, Hinestroza JP, Klok HA. Neutron Reflectivity Study on the Postpolymerization Modification of Poly(2-hydroxyethyl methacrylate) Brushes. *Macromolecules.* 2011; 44:6868–6874.
37. Barbey R, Laporte V, Alnabulsi S, Klok HA. Postpolymerization Modification of Poly(glycidyl methacrylate) Brushes: An XPS Depth-Profiling Study. *Macromolecules.* 2013; 46:6151–6158.
38. Brooks K, Razavi MJ, Wang X, Locklin J. Nanoscale Surface Creasing Induced by Post-polymerization Modificatio. *ACS Nano.* 2015; 9:10961–10969. [PubMed: 26493442]
39. Brooks K, Razavi MJ, White EM, Wang X, Locklin J. The Formation and Evolution of Creased Morphologies Using Reactive Diffusion in Ultrathin Polymer Brush Platforms. *Adv Mater Interf.* 2017; doi: 10.1002/admi.201700084
40. Marquardt F-H. The intensity of carbonyl bands in the infrared spectra of cyclic anhydrides of dicarboxylic acids. *J Chem Soc B.* 1966:1242–1243.
41. Hasanazadeh R, Moghadam PN, Samadi N, Asri-Rezaei S. Removal of heavy-metal ions from aqueous solution with nanochelating resins based on poly(styrene-alt-maleic anhydride). *J Appl Polym Sci.* 2013; 127:2875–2883.

42. Alswieleh AM, Cheng N, Leggett GJ, Armes SP. Spatial control over cross-linking dictates the pH-responsive behavior of poly(2-(tert-butylamino)ethyl methacrylate) brushes. *Langmuir*. 2014; 30:1391–400. [PubMed: 24417283]
43. Murata H, Prucker O, Ruehe J. Synthesis of functionalized polymer monolayers from active ester brushes. *Macromolecules*. 2007; 40:5497–5503.
44. Arnold RM, Sheppard GR, Locklin J. Comparative Aminolysis Kinetics of Different Active Ester Polymer Brush Platforms in Postpolymerization Modification with Primary and Aromatic Amines. *Macromolecules*. 2012; 45:5444–5450.
45. Yatvin J, Brooks K, Locklin J. SuFEx on the Surface: A Flexible Platform for Postpolymerization Modification of Polymer Brushes. *Angew Chem Int Ed*. 2015; 54:13370–13373.
46. Cyriac J, Pradeep T, Kang H, Souda R, Cooks RG. Low-Energy Ionic Collisions at Molecular Solids. *Chem Rev*. 2012; 112:5356–5411. [PubMed: 22913366]
47. Navarro M, Benetti EM, Zapotoczny S, Planell JA, Vancso GJ. Buried, covalently attached RGD peptide motifs in poly(methacrylic acid) brush layers: The effect of brush structure on cell adhesion. *Langmuir*. 2008; 24:10996–11002. [PubMed: 18767823]
48. Tirumala VR, Stafford CM, Ocola LE, Douglas JF, Mahadevan L. Geometric Control of Rippling in Supported Polymer Nanolines. *Nano Lett*. 2012; 12:1516–1521. [PubMed: 22352905]
49. Biesalski M, Rhe J. Scaling Laws for the Swelling of Neutral and Charged Polymer Brushes in Good Solvents. *Macromolecules*. 2002; 35:499–507.
50. Han Q, Li C, Guan Y, Zhu XX, Zhang Y. Swelling-induced surface instability of a hydrogen-bonded LBL film and its self-healing. *Polymer*. 2014; 55:2197–2204.
51. Flory PJ Jr. Statistical Mechanics of Cross-Linked Polymer Networks II. Swelling. *J Chem Phys*. 1943; 11:521–526.
52. Huang ZY, Hong W, Suo Z. Nonlinear analyses of wrinkles in a film bonded to a compliant substrate. *J Mech Phys Solids*. 2005; 53:2101–2118.
53. Chan EP, Lin Q, Stafford CM. Quantifying the elasticity and viscosity of geometrically confined polymer films via thermal wrinkling. *J Polym Sci B: Polym Phys*. 2012; 50:1556–1561.
54. Vandeparre H, Lopolds J, Poulard C, Desprez S, Derue G, Gay C, Damman P. Slippery or Sticky Boundary Conditions: Control of Wrinkling in Metal-Capped Thin Polymer Films by Selective Adhesion to Substrates. *Phys Rev Lett*. 2007; 99:188302. [PubMed: 17995443]

Figure 1.

(a) Anhydride conversion versus cystamine reaction time for pSMA brush under poor solvent conditions.

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) 60s, (c) 300s, (d) 600s, and (e) 3600s. (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.

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

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 $h_1 h_2$ demonstrating that the scaling relationship $\lambda \sim (h_1 h_2)^{1/2}$ adequately describes the brush system.

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.

Scheme 1.

Post-polymerization modification of pSMA brushes with cystamine under poor solvent (aqueous) conditions. Cystamine partially crosslinks the brush in a front-like process forming a cystamine-modified "skin" thickness (h_1) and an unmodified "substrate thickness" (h_2). Final brush thickness after PPM and drying is denoted as H_f .

Scheme 2.

Synthetic route to wrinkled polymer brush surfaces. 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.