Nanostructured Films of Oppositely Charged Domains from Self-Assembled Block Copolymers

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ABSTRACT

Exploration of poly(tert-butyl methacrylate)-block-poly(4-vinylpyridine), PtBMA-b-P4VP, as a precursor material for the creation of nanostructured films with oppositely charged domains is reported. Thin films of hexagonally-packed P4VP cylinders were self-assembled perpendicular to the surface and subsequently treated with bromoethane vapor at various times to quaternize pyridinyl nitrogens. The PtBMA matrix was then partially hydrolyzed to poly(methacrylic acid), PMAA, through HCl vapor treatment followed by neutralization by brief submersion in KOH solution. Under optimal treatment conditions, atomic force microscopy and contact angle
measurements confirm that the film morphologies remain intact and become more hydrophilic. Time of flight secondary ion mass spectrometry confirms the presence and location of specific anions and cations within each domain throughout the block copolymer film and corroborates successful ionization during each treatment step. These results bolster the viability of PtBMA-\textit{b}-P4VP as a suitable material for creating self-assembled nanostructures bearing oppositely charged domains under relatively facile conditions and opens the door to future investigations for their potential application in charged mosaic membranes.

**INTRODUCTION**

Charged mosaics are systems with coexisting yet separate domains of positive and negative charge that were first conceptualized by Söllner over 80 years ago.\textsuperscript{1, 2} As a membrane, they are predicted to have unique transport properties over typical ion exchange membranes comprised of one type of single ion conductor (positive or negative) used in many nanofiltration processes. For example, membranes with channels of only polycations would allow preferential permeation of anions over cations in a solution, leading to a loss of electroneutrality and the problem of salt rejection. A membrane with coexisting “zones” rich in either polyanions or polycations will theoretically allow the simultaneous transport of both cations and anions, respectively, without violation of macroscopic electroneutrality.\textsuperscript{3-5} Therefore an ion current could be established between the individual exchange elements that would increase salt transport and deter permeation of neutral species of similar size.\textsuperscript{6-8} Ion transport through charged mosaic membranes is poorly understood, including the effects of morphology and the size of the mosaic pattern morphology and size of the mosaic pattern,\textsuperscript{11-14 9, 10} and chemistries and methods to create charged mosaics are lacking.
Successful charged mosaic membranes to date have shown promise for the selective transport or rejection of dissolved salts, piezodialysis, and negative osmosis.\textsuperscript{7,15-17} These systems also have viability for other applications, such as the creation of cell patterned sensors and antifouling surfaces.\textsuperscript{18,19} Recent work by Phillip and co-workers utilized ink jet patterning of random copolymers containing azido moieties to create functionalized nanopores and demonstrate that these materials have great promise for micro-scale controlled patterning.\textsuperscript{18} The same group also reported the creation of charge mosaic membranes through the use of layer-by-layer assembly process.\textsuperscript{8} Chen et al. recently reported the first use of conjugate electrospinning with P4VP and sodium polystyrene sulfonate (PNaSS) to create a charge mosaic membrane.\textsuperscript{20}

Autonomous block copolymer (BCP) self-assembly is an advantageous tool for many applications due to the creation of large area nanoscale templates with tunable size and morphology.\textsuperscript{9,21-31} To our knowledge, the synthesis of charged mosaics from self-assembled BCPs was last attempted more than 30 years ago.\textsuperscript{3,9,32} Since BCPs with segments of opposite charge, also termed block polyampholytes,\textsuperscript{33} have a propensity to form coacervates from electrostatic attraction, the prevailing strategy to create charge mosaics from BCPs involves self-assembly of immiscible neutral segments followed by ionization of targeted domains with chemical treatments. Complications with early systems were evident due to the use of aggressive reaction conditions, such as sulfonation of polystyrene (PS) to polystyrene sulfonate (PSS), and required the installation of a support matrix to prevent deterioration of films and morphologies.\textsuperscript{3,32} With modern advances in BCP synthesis and directed self-assembly techniques, such as solvent annealing, we envisioned exploration of new segment chemistries susceptible to ionization to create ordered BCPs in which both domains are perpendicular to the substrate.\textsuperscript{34-36}
Poly(2-vinylpyridine) (P2VP) and poly(4-vinylpyridine) (P4VP) are low cost monomers which have demonstrated high levels of versatility when incorporated as a BCP segment due to the basicity and coordinative ability of the pyridinyl nitrogen. P4VP has a pyridinyl nitrogen that is more accessible to quaternization and allows the creation of stable polycations at varying pH. Arges, Nealey, and co-workers have shown that quaternization of P4VP through alkyl halide vapor treatments following BCP directed self-assembly does not disrupt the alignment of morphology orientation. Poly(tert-butyl methacrylate) (PtBMA), is an intriguing option for use as a polyanion that undergoes hydrolysis in HCl vapor to produce poly(methacrylic acid) (PMAA) that can be subsequently neutralized in basic conditions. With this segment, the need for solution submersion for long durations, as was done for sulfonation of PS, can be avoided. A number of BCPs utilizing P2VP or P4VP together with PtBMA have been reported and can be largely divided into two categories: Those that study the bulk self-assembly without ionization treatment and those that study solution self-assemblies with ionization treatements. Surprisingly, no reports were found where bulk self assembly of BCPs containing these segments were used for the creation of charged mosaics. It also bears mentioning that nanostructured design of oppositely charged surfaces using different types of materials is also an active field, and new developments in these materials can lead to applications in selective bind of guests, such as multi-layers or nanoparticles. Herein we describe the first creation of nanostructured charge mosaic surfaces through thin film directed self-assembly of neutral P4VP-b-PtBMA followed by selective vapor treatments that ionize each segment domain. Below, we describe the synthesis and processing of these materials and demonstrate the formation of self-assembled, charged mosaic films through a combination of atomic forcemicroscopy (AFM) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS).
EXPERIMENTAL METHODS

Materials

All chemicals were used as received unless otherwise noted. n-dodecanethiol (≥98%), azobisisobutyronitrile (AIBN) recrystallized from methanol, carbon disulfide (99.9%), iodine chips (≥99%), magnesium sulfate (99.8%), 4,4’-azobis(4-cyanovaleric acid) (≥98.0%), 1,4-dioxane, N,N-dimethylacetamide (DMAC) (>99.8%), and potassium hydroxide pellets (≥85%) were purchased from Sigma-Aldrich. Ethyl acetate, sodium thiosulfate solution (0.10 N aqueous), hexanes, toluene, chloroform, methanol, and HCl (36-38% ACS) were purchased from VWR. tert-Butyl methacrylate (tBMA) (≥98%) (inhibitor removed via passage through basic alumina prior to use) and bromoethane (99%) were purchased from TCI chemicals. Sodium hydride (NaH, 60% in mineral oil), 4-vinyl pyridine (4VP, 95%, distilled under reduced pressure before use) was purchased from Alfa-Aesar. Aluminum oxide (basic Brockman grade I) was purchased from Beantown chemical. Diethyl ether (DEE) (anhydrous stabilized with BHT) and tetrahydrofuran (THF) (unstabilized) were obtained from an SG Waters glass contour solvent purification system that was packed with neutral alumina and the solvents were passed through a 2 µm filter prior to being dispensed.

Characterization

$^1$H NMR experiments were conducted on a Bruker Advance III 400 or 600 MHz spectrometer in the FSU Department of Chemistry and Biochemistry NMR Laboratory. Number average molar mass ($M_n$) and dispersity ($D$) of polymer samples were determined by size exclusion chromatography (SEC) on an Agilent–Wyatt combination triple detection system (THF mobile phase) containing 3 successive Agilent PLgel Mixed-C columns, an Agilent 1260 infinity series...
pump, degasser, autosampler, and thermostatted column chamber. The Wyatt triple detection unit hosts a mini-Dawn TREOS 3-angle light scattering detector, Optilab TrEX refractive index detector, and a Viscostar II differential viscometer. Molar mass and dispersities were determined by light scattering using literature $dn/dc$ values. Atomic Force Microscopy (AFM) images were obtained using an MFP-3D AFM equipped with an ARC2 controller (Asylum Research) using Nanoworld ARROW-NCR Al-coated silicon tips, 10 nm nominal radius, and force constant between 27 and 80 N m$^{-1}$. AFM tips were calibrated under air and cantilever was tuned to 10% below the resonance frequency using the thermal fluctuation technique. Images were collected using a 1.0 Hz scan rate with 256 points and lines in tapping mode. Water contact angles were measured using a dynamic contact angle instrument (Cahn instruments). Thermogravimetric analysis (TGA) was performed on a TA instruments TGA 550 by heating samples at a rate of 10 °C min$^{-1}$ under Ar (40 mL min$^{-1}$ flow rate) using an HT platinum pan. Differential scanning calorimetry (DSC) was performed on a TA Instruments Model Q2000 with a model RCS90 refrigerated cooling system. Samples were cycled from 40 °C to 165 °C under N$_2$ (40 mL min$^{-1}$ flow rate) at a ramp rate of 10 °C min$^{-1}$

**Time-of-flight secondary ion mass spectrometry (ToF-SIMS)**

Negative and positive high mass resolution depth profiles were performed using a ToF-SIMS NCS instrument, which combines a ToF.SIMS$^3$ instrument (ION-TOF GmbH, Münster, Germany) and an *in-situ* scanning probe microscope (NanoScan, Switzerland). A bunched 30 keV Bi$_3^{+}$ ions (with a measured current of 0.2 pA) was used as primary probe for analysis (scanned area 90 × 90 µm$^2$), and sputtering was performed using Ar$_{1500}^{+}$ ions at 10 keV with a typical current around 0.1 nA, rastered area 500 × 500 µm$^2$. The beams were operated in non-interlaced mode, alternating 1 analysis cycle and 1 sputtering cycle (corresponding to 1.63 s) followed by a pause of 5 s for the
charge compensation with an electron flood gun. An adjustment of the charge effects has been operated using a surface potential. During the depth profiling, the cycle time was fixed to 200 µs (corresponding to m/z = 0 – 3649 a.m.u. range). The ion signals were normalized by the total ion intensity.

**Synthesis**

The synthetic procedure used to design the BCP for this study are illustrated in Scheme 1 and described below.

**Scheme 1.** RAFT synthesis of poly(4-vinylpyridine)-b-poly(tert-butyl methacrylate) (P4VP-b-PtBMA) from 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDPA).

4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanyl pentanoic acid (CDPA). Synthesis of RAFT CTA was performed according to previous literature with reiterations and modifications described here. n-Dodecanethiol (15.4 g, 76 mmol) was added via addition funnel over 10 min to a 500 mL round bottom flask (RBF) equipped with a PTFE stir bar and containing a stirring suspension of NaH (60% in mineral oil) (3.28 g, 82 mmol) in 150 mL DEE at 0 °C. The solution was stirred at 0 °C for 30 min then refluxed for 1 h. The solution was then cooled to 0 °C and the
white slurry was diluted with 150 mL of DEE. Carbon disulfide (6.03 g, 79 mmol) was added via addition funnel and allowed to stir for 30 min at 0 °C, creating a yellow slurry of sodium dodecyltrithiocarbonate. Solids were collected via vacuum filtration and dried en vacuo at 25 °C overnight. No further purifications were performed (12.6 g yield, 56%). A suspension of sodium dodecyltrithiocarbonate (12.6 g, 42 mmol) in 150 mL DEE was added to a 300 mL RBF and titrated in small portions with iodine (5.4 g, 0.21 mmol) over 2 h. The end point was observed when the solution changed from yellow to dark yellow/brown in addition to precipitation of white sodium iodide salt. After further stirring for 1 h, the salt was removed by filtration and the filtrate added to separatory funnel. Following 3 extractions with a 0.5 N sodium thiosulfate solution (aq) and 2 extractions with DI water, the organic layer was collected and dried over MgSO₄. The product oil, bis-(dodecylsulfanyltiocarbonyl) disulfide, was concentrated via rotary evaporation and dried en vacuo at 25 °C overnight. Bis-(dodecylsulfanyltiocarbonyl disulfide) (3.73 g, 6.7 mmol) and 4,4’-azobis(4-cyanopentanoic acid) (2.82 g, 10 mmol) was dissolved in 150 mL of ethyl acetate followed by refluxing for 18 h. The solution was added to a separatory funnel and washed 4 times with 50 mL of DI water and one final time with brine solution before collecting the organic layer and drying over MgSO₄. The product was concentrated via rotary evaporation followed by recrystallization from hexanes to product the pure CDPA as a yellow solid. ¹H NMR confirms the product in comparison to previous literature;⁵⁶ (¹H NMR 400 MHz, 25 °C, CDCl₃, δ (ppm) = 3.35 (t, 2H), 2.71 (m, 2H), 2.62 – 2.34 (m, 2H), 1.90 (s, 3H), 1.71 (m, 2H), 1.4 (m, 2H), 1.33 (br s, 16H), 0.89 (t, 3H) (Figure S1). (¹³C NMR 125 MHz, 25 °C, CDCl₃) δ 216.81, 177.43, 118.92, 46.20, 37.11, 33.48, 31.93, 29.64, 29.57, 29.55, 29.44, 29.36, 29.09, 28.95, 27.68, 24.87, 22.72, 14.16 (Figure S2).

Poly(tert-butyl methacrylate), PtBMA, macro-CTA
Homopolymerization of tBA (6.0 g, 42 mmol) using CDPA (60 mg, 0.15 mmol) and AIBN (2.5 mg, 0.015 mmol) [280:1:0.1, respectively] in 4 mL of toluene. Contents were degassed by three freeze-pump-thaw cycles prior to heating at 65 °C for 16 h under Ar. The reaction was then cooled and quenched with air. Following additional dilution in toluene, the polymer was collected by precipitation into a 10-fold excess of MeOH at 0 °C, filtering, and solids were dried at 70 °C under vacuum for 12 h. Dry PtBMA (4.1 g, 68% yield) was confirmed by 1H NMR (Figure S1), 13C NMR (Figure S4), ATR-IR (Figure S5), and then analyzed by SEC using dn/dc = 0.065 mL/g57 in THF (Mn = 51.0 kg mol−1, D =1.04) (Figure S6).

PtBMA-b-P4VP diblock polymer

The BP was synthesized by dissolving 1.0 g of PtBMA macro-CTA (20 µmol) and 2.0 mL (18.5 mmol) of 4VP within 7 mL of DMAC in a 25 mL Schlenk flask. A 5 mg/mL stock solution of AIBN in DMAC was used to inject 0.12 mL (4 µmol) for a 5:1 ratio of CTA:AIBN. After 3 freeze-pump-thaw cycles, the flask was backfilled with Ar and submerged into a preheated bath at 70 °C. The reaction was monitored by briefly cooling the reaction to 0 °C and retrieving an aliquot via degassed syringe under Ar. The aliquots were evaluated by 1H NMR until the desired molar ratio of PtBMA:P4VP (1.5:1) respectively was achieved (~24 h) (Figure S7). The viscous orange solution was cooled and quenched by exposure to air and dilution with clean THF. The BP was purified by triplicate precipitations in 10-fold excess of MeOH/H2O mixture (80/20 v/v) and redissolutions in clean THF. The final collection by filtration and drying for 12 h at 70 °C under vacuum produced the dry pale-orange powder prior to characterizations described below.

Thin film preparation
Silicon wafers were prepared by submerging in piranha solution for 2 h at 150 °C. Wafers were removed from solution and thoroughly rinsed with DI water before drying fully under a stream of N₂. A 20 mg/mL solution of polymer in CHCl₃ was spun cast onto each wafer at 3000 RPM for 30 s. Vapor annealing treatment was performed by storing film-coated wafers in a sealed glass chamber along with 10 mL of CHCl₃ in a separate vial. The films were exposed to CHCl₃ vapor for 8 h. The chamber seal was then opened and CHCl₃ was allowed to evaporate from the chamber before removing.

**Quaternization**

Solvent annealed wafers were placed into a sealed glass chamber along with 10 mL of bromoethane in a separate vial. The chamber was sealed, and the wafers were exposed to bromoethane vapor for varying durations of 6 - 24 h. After a set duration, the wafers were removed and dried at 50 °C under vacuum for 2 h to remove excess bromoethane.

**Hydrolysis and Neutralization**

For partial hydrolysis of PtBMA domains to poly(methyl acrylic acid) (PMAA), select films were suspended in a custom-designed glass apparatus (shown in supporting information) consisting of a small glass insert within a 75 mL ChemGlass pressure flask. The films were suspended within the headspace of a vial containing ~4 mL of concentrated HCl at 60 °C for known time periods (1-4 h). Films were then removed and dried at 50 °C under vacuum for 12 h. Following drying, films were briefly submerged (~15 s) into a 0.01 M KOH solution before being submerged multiple times into a series of DI water solutions (10 dips each) to remove excess salt. Excess water was removed gently with a stream of N₂ and films were fully dried at 50 °C under vacuum.

**RESULTS AND DISCUSSION**
**BP Design and Characterization.** The PtBMA-\(b\)-P4VP sample was characterized by \(^1\)H NMR to determine the molar ratio of each segment through comparative integration of the aryl P4VP protons (8.1 – 8.5 ppm, 2H, and 6.0 – 6.75 ppm, 2H) with the total region of the aliphatic proton peaks (0.75 – 2.25 ppm, 17H) as shown in Figures S1 and S7. The integration value of the aliphatic region was corrected to account for the 3 aliphatic protons within the P4VP repeating unit. Further characterization confirming the BCP was also performed using \(^{13}\)C NMR (Figure S8), and ATR-IR (Figure S9). The molar ratio of PtBMA:P4VP repeating units within the purified BP was determined as 1.25:1 by \(^1\)H NMR which correlates to a PtBMA volume fraction (\(f_{\text{PtBMA}}\)) of 0.65 based on the densities of PtBMA (1.02 g cm\(^{-3}\))\(^{58}\) and P4VP (1.11 g cm\(^{-3}\))\(^{59}\) at 25 °C. The asymmetry of these segments is predicted to result in hexagonally packed cylinders of P4VP within a matrix of PtBMA in accordance with a typical linear diblock polymer phase diagram.\(^{60,61}\) Based on \(M_n\) of the PtBMA macro-CTA (51.0 kg mol\(^{-1}\)), determined by MALLS-SEC, this equates to a P4VP segment of \(M_n = 30\) kg mol\(^{-1}\) and a total BP \(M_n = 81\) kg mol\(^{-1}\). SEC on the final BCP confirmed a monomodal peak shape by RI and an increase in molar mass (decrease in retention time), \(M_n = 30\) kg mol\(^{-1}\), \(D = 1.08\) based on conventional column calibration with PS standards (Figure S10). The significant difference in \(M_n\) measured by SEC (30 kg mol\(^{-1}\)) versus NMR (81 kg mol\(^{-1}\)) is caused by favorable interactions between the P4VP and the column packing that increases the BCP retention time. Therefore, the NMR determined \(M_n\) value is more rigorously justified.

A total volume-corrected degree of polymerization (\(N\)) of 1085 was calculated for the PtBMA-\(b\)-P4VP sample using the aforementioned densities of each segment and a reference volume of 118 Å\(^3\).\(^{62}\) To achieve microphase separation within the strong segregation regime (SSR) the product of \(N\) and the segment-segment effective interaction parameter, \(\chi\), needs to be well
above ~10.5 in accordance with mean field theory. Here we note ~10.5 is the limit for the order-disorder transition of $\chi N$ for a symmetric BP ($f = 0.5$), and this critical value increases when moving towards higher asymmetry of the two segments. The effective $\chi$ between PtBMA and P4VP is unknown, but for $N = 1085$ a value of $\chi$ greater than 0.05 gives $\chi N > 50$, well within the strong segregation regime. This value of $\chi$ is reasonable based on previously determined $\chi$ values of P4VP with poly(methyl methacrylate) (PMMA) ($\chi_{\text{P4VP-PMMA}} \approx 0.08$ at 150 °C). DSC analysis of PtBMA-b-P4VP reveals two glass transition temperatures ($T_g$) at 105 and 129 °C (Figure S11), which is a qualitative sign of microphase separated BCPs containing segments with dissimilar $T_g$ values. The $T_g$ of 105 °C is consistent with the PtBMA macro-CTA (Figure S12) and the higher $T_g$ value of 129 °C corresponds to P4VP (lit. ~142 °C). TGA analysis of PtBMA-b-P4VP displays a two-step decomposition with ~30% mass loss at an onset temperature of 236 °C and the remaining mass loss at 338 °C (Figure S13).

**Thin Film Assembly.** Solvent vapor annealing has proven to be an effective method to produce perpendicularly aligned morphologies on the surface of BP thin films. To determine a good solvent choice for this technique, AFM images were taken following different solvent vapor treatments (THF, DMF, CHCl$_3$) with varying exposure and evaporation times. It was determined that ~8 h of CHCl$_3$ vapor treatment followed by slow vapor purging of the chamber consistently produced a hexagonally-packed cylindrical morphology perpendicular to the air-film interface. With confidence on a solvent annealing strategy for these films, our three-step approach to transform the neutral, self-assembled, PtBMA-b-P4VP film into a charge-mosaic surface is illustrated in Scheme 2. For clarity in this discussion, we have created a two-numbered identification system with the general formula of VP-MA(#) to describe films that have been subjected to varying degrees of these treatments. The numbers within parentheses describe the
time, in hours, that the films were subjected to bromoethane and HCl vapors, respectively. All hydrolyzed samples were submerged into 0.01 M KOH (aq) to neutralize the PMAA domains.

**Scheme 2.** Synthetic route to poly(ethyl-4-vinylpyridinium bromide)-b-poly(methacrylic acid potassium salt) from poly(4-vinylpyridine)-b-poly(tert-butyl methacrylate).

**P4VP quaternization.** Treatment of the neutral film, VP-MA(0-0), with bromoethane vapor allows selective reaction and partial quaternization of the P4VP repeating units into poly(ethyl-4-vinylpyridinium bromide), (P4VPq). Systematic bromoethane vapor treatments for varying times (6 – 24 h) were performed. To gauge the effect of these treatments on the modification of the films, a combination of AFM imaging and water contact angle measurements were initially performed (Figure 1). After 6 h of treatment, VP-MA(6-0), AFM reveals that the overall morphology of the thin film remains intact while the phase contrast between the P4VP cylinders and the PtBMA matrix is greatly increased when compared to VP-MA(0-0).
Figure 1. AFM height images (top), phase images (middle), and contact angle (bottom) of a,d,g) P4VP-\(b\)-PtBMA \text{VP-MA(0-0)}\) prior to any vapor treatments. b,e,h) P4VP-\(b\)-PtBMA \text{VP-MA(6-0)}\) after 6 hr with bromoethane vapor treatment. c,f,i) P4VP-\(b\)-PtBMA \text{VP-MA(24-0)}\) after 24 hr of bromoethane vapor treatment.

(Figure 1d and 1e). A similar contrast increase was reported by Arges et al. on block polymer thin films of PS-\(b\)-P2VP where the P2VP domains were partially quaternized with methyl iodide\(^{43}\). The
improved contrast was attributed to the presence of large halide counter-ions following quaternization, which we also conclude for our images. Interestingly, comparison of contact angle measurements on VP-MA(0-0) and VP-MA(6-0) (Figure 1g and 1h) reveals only a minor reduction in contact angle from 100° to 98°. By contrast, bromoethane vapor treatment of the film for 24 h, VP-MA(24-0) results in a substantial reduction in contact angle to 79° (Figure 1i). AFM analysis of VP-MA(24-0) reveals that the film and morphology remain intact, however, noticeable swelling of the P4VP cylinders has occurred (Figure 1c and 1f). This is explained by the increasing volume of the cylinders as P4VPq expands the domains to include ethyl groups and bromine counter anions at longer treatment times.

In order to determine the quaternization through the depth of the films, we turned to time-of-flight secondary ion mass spectrometry (ToF-SIMS) which is a useful technique for determination of sub-surface film characteristics of each block as well as associated counterions that would be present. While AFM and contact angle measurements provide qualitative conclusions on the successful quaternization of P4VP, ToF-SIMS provides an approach to detecting bromide anions within the films. ToF-SIMS measurements were initially performed on homopolymer thin films of P4VP (Figure S14) and PtBMA (Figure S15) cast on silicon wafers to determine the characteristic ion fragments for each polymer. These films were prepared identically to VP-MA(0-0) in Figure 1, and through ToF-SIMS analysis of each film we determined that CN− and C₄H₆O₂− were unique, high-intensity ion signals for P4VP and PtBMA, respectively. By tracking these ion signals during ToF-SIMS analysis, we could track the P4VP and PtBMA domains through the depth of the film. ToF-SIMS on VP-MA(0-0) revealed the CN− and C₄H₆O₂− for P4VP and PtBMA, respectively, along with a baseline bromide (Br⁻) ion signal (Figure 2a). We note that the normalized ion intensities are uncalibrated and therefore do not directly reflect
the concentrations of different species in the film but can be used to track changes in relative concentrations of molecular species. Moving from lower to higher values of argon cluster ion dose (ions/cm²) along the x-axis in Figure 2 is directly correlated with analyzing the film composition from the air interface to the silicon substrate interface, respectively. The bottom of the film was identified by a sharp increase in Si⁻ and SiO₂⁻ fragments (see, for example, Figure S14).

**Figure 2.** Normalized intensity of negative ion detection as a function of ion dose determined by ToF-SIMS in negative ion mode. a) untreated (neutral) copolymer, VP-MA(0-0). b) 6 h quaternization, VP-MA(6-0). c) 12 h quaternization, VP-MA(12-0). d) 24 h quaternization, VP-MA(24-0). Intensities were normalized with point to point method using 10 neighboring points.
ToF-SIMS analysis on **VP-MA(6-0)** revealed a large increase in the Br- ion intensity when compared to **VP-MA(0-0)** (Figure 2b). This demonstrates that quaternionization of the P4VP domains occurred thorough the depth of the film after vapor treatment. ToF-SIMS also reveals a depletion of P4VP at the film-air interface relative to PtBMA, which may explain the small change in contact angle for **VP-MA(6-0)** relative to **VP(0-0)**. Another interesting observation is that the Br⁻ intensity increased when analyzing deeper into the thin film, suggesting that quaternized P4VP was created, or migrated deeper within the film. ToF-SIMS analysis on **VP-MA(12-0)** and **VP-MA(24-0)** (Figure 2C and 2D) revealed a saturation in Br⁻ intensity through the film and an increased degree of quaternionization near the air interface. ToF-SIMS also reveals an increasing migration of PtBMA \((\text{C}_4\text{H}_6\text{O}_2^-)\) towards the film-air interface, most notably for **VP-MA(24-0)** where a large intensity of \(\text{C}_4\text{H}_6\text{O}_2^-\) near the surface is consistent with the surface swelling or “blooming” of P4VPq cylinders seen in Figure 1. The result of longer bromoethane vapor treatment for **VP-MA(24-0)** also reveals higher and more homogenous levels of P4VPq and coordinated intensity oscillations between the CN⁻ and the Br⁻ signals through the film. These matched oscillations demonstrate that the Br⁻ anions reside within the P4VP domains of the BCP.

**PtBMA Hydrolysis and Neutralization.** For investigations on the efficacy of creating charge mosaics through the hydrolysis and neutralization of the BP thin films, samples treated with short quaternionization times (6 h) were used. The film **VP-MA(6-1)** was exposed to HCl vapor for 1 h, dried under vacuum, subsequently submerged into a 0.01 M KOH (aq) solution for ~15 sec, and finally rinsed by brief submersions into clean DI water solutions. The same is true for **VP-MA(6-2)** and **VP-MA(6-4)** with the exception of longer HCl vapor annealing times of 2 h and 4 h, respectively. Following a final drying, AFM confirmed the integrity of the films and their microphase separated morphology had remain intact throughout all treatments (Figure 3), although
some surface roughening is evident. A notable observation is the inverted contrast profiles of the height and phase image of these films compared to the films in Figure 1. For the height image, the P4VP cylinders were resolved as dark areas while the matrix was bright. The opposite was true for the phase image. An inversion of the image contrast is a strong indication that there are differences in electrostatic interactions between the piezoelectric tip of the AFM cantilever from the newly charged PMAA domains. Another consideration is that the PtBMA domains were swollen through their conversion to PMAA. Contact angle measurements revealed a gradual decrease in water droplet angle as a function of longer HCl vapor treatments, and all of the films in Figure 3 had lower contact angles than VP-MA(6-0). The results of contact angle measurements performed on various films are provided in Table 1.

Table 1. Contact angles of P4VP-b-PtBMA thin films with varying quaternization and hydrolysis conditions.

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<th>Hydrolysis rxn time (h) c</th>
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a All samples in the sample set were created from the same parent polymer. Samples are named using a binary number system to identify the varying quaternization and hydrolysis conditions. For Sample ID, numerical values (x-y), “x” is the quaternization time in h., “y” is the HCl vapor treatment time in h. b The contact angles reported are the average of both the left and right angle values obtained from the instrument measurements. c All hydrolyzed samples were subjected to KOH treatment.
Figure 3. AFM height images (top), phase images (middle), and contact angle (bottom) of films after 6 hr bromoethane vapor treatment and varying HCl vapor treatment durations. a,d,g) VP-MA(6-1), 1 hr of treatment with HCl vapor and 0.01 M KOH. b,e,h) VP-MA(6-2) after 2 hr of treatment with HCl vapor and 0.01 M KOH. c,f,i) VP-MA(6-4) after 4 hr of treatment with HCl vapor and 0.01 M KOH.

ToF-SIMS analysis of VP-MA(6-2) and VP-MA(6-4) revealed periodic oscillation in ion intensities through the depth of the film (Figure 4). The oscillations of Br\(^-\) and CN\(^-\) are in-phase and out-of-phase with C\(_4\)H\(_6\)O\(_2\)\(^-\) ions, reflecting possible microphase separation between the
quaternized P4VP and hydrolyzed PtBMA domains. Although it is difficult to specify the nature of the depth-dependent morphology, these results suggest that the various film treatments may have resulted in reorientation of the P4VP cylinders or possibly morphological transitions throughout the film.

Figure 4. Normalized intensity of negative ion detection as a function of ion dose determined by ToF-SIMS in negative ion mode. a) 6 h quaternization followed by 2 h hydrolysis and KOH treatment VP-MA(6-2). b) 6 h quaternization followed by 4 h hydrolysis and KOH treatment VP-MA(6-4). Intensities were normalized with point to point method using 10 neighboring points. The vertical dashed line is a guide to the eye to show the in-phase and out-of-phase composition fluctuations.

ToF-SIMS analysis operated in positive-ion mode (Figure 5) allows the observation of cations through the treated films. Analysis of untreated homopolymer films revealed that C$_7$H$_8$N$^+$ and C$_8$H$_{13}$O$_2$$_{+}$ were unique and prominent ion signals for P4VP and PtBMA, respectively. Analysis of VP-MA(0-0) in Figure 5a reveals the ion signatures of both segments and provides a baseline for K$^+$ ion signals untreated films. The normalized intensities of these signals remained relatively constant when analyzing VP-MA(6-0), as expected (Figure 5b). Analysis of the films after hydrolysis, VP-MA(6-2) and VP-MA(6-4) (Figure 5c and 5d, respectively) revealed an increase in overall K$^+$ content and a higher intensity with increased hydrolysis treatment. Additionally, in-phase oscillations of K$^+$ and the C$_8$H$_{13}$O$_2$$_{+}$ ion intensity signals were clearly evident after 2 h of
hydrolysis (Figure 5c) and increased intensity and frequency after 4 hours of hydrolysis (Figure 5d). Weak out-of-phase oscillations of the $C_7H_8N^+$ are evident after 4 hours of hydrolysis. This reflects the formation of hydrolyzed PtBMA domains with $K^+$ ions segregated within the hydrolyzed PtBMA domains (Figure 5d) and $Br^-$ ions within the P4VP domains (Figure 4b).

Figure 5. Normalized intensity of positive ion detection as a function of ion dose determined by ToF-SIMS in positive ion mode. a) untreated (neutral) copolymer VP-MA(0-0). b) 6 h quaternization VP-MA(6-0). c) 6 h quaternization followed by 2 h hydrolysis and KOH treatment VP-MA(6-2). d) 6 h quaternization followed by 4 h hydrolysis and KOH treatment VP-MA(6-4). Intensities were normalized with point to point method using 10 neighboring points. The vertical dashed line is a guide to the eye to show the in-phase and out-of-phase composition fluctuations.

the creation of nanostructured charge mosaics was shown successful in films with 6 h of bromoethane vapor treatment, longer quaternization times (12 and 24 h) resulted in issues with
film dewetting after hydrolysis treatment. The “over-ionization” of the P4VP domains creates enhanced aqueous solubility and compromises film integrity when neutralized in KOH solution. After 12 h of bromoethane and hydrolysis treatment on VP-MA(12-4), noticeable holes in the film were observed by AFM and confirmed by ToF-SIMS analysis (Figure S18). Compositional analysis revealed holes through the film exposing the silicon substrate underneath. Although dewetting of polymer films can be detrimental for depth profiling of the BCP structures by ToF-SIMS, 3D reconstruction methods using AFM and ToF-SIMS is possible. As expected, film dewetting was also observed after 24 h of bromoethane vapor treatment and varying hydrolysis treatments; VP-MA(24-1), VP-MA(24-2), and VP-MA(24-4). Figure 6 shows AFM images of dewet film regions on the Si wafer surface. While the integrity of the overall film has been compromised, the morphology of the BCP is still visible even after these more aggressive conditions. We are currently investigating method to improve the film integrity, potentially through crosslinking or surface anchoring.

**Figure 6.** AFM height images of PtBMA-b-P4VP films with static bromoethane vapor treatment (24 h) and varying HCl vapor treatment durations. a) VP-MA(24-1) after 1 h of treatment with HCl vapor and 0.01 M KOH. b) VP-MA(24-2) 2 h of treatment with HCl vapor and 0.01 M KOH. c) VP-MA(24-4) after 4 h of treatment with HCl vapor and 0.01 M KOH.
CONCLUSIONS

We synthesized PtBMA-b-P4VP ($M_n = 81$ kg mol$^{-1}$, $D = 1.08$, $f_{P4VP} = 0.35$), through sequential RAFT polymerization. Solvent annealing of thin films with CHCl$_3$ produced P4VP cylinders aligned perpendicular to the substrate that were further modified through quaternization of the pyridine units through bromoethane vapor treatments. The PtBMA matrix was then hydrolyzed with HCl vapor and neutralized with brief submersion in KOH solution. At optimal conditions (6 h of bromoethane vapor treatment and 4 h of HCl treatment), it was discovered that the morphology of the film remains intact while the hydrophilicity of the films increase. ToF-SIMS analysis of the film confirmed the presence and locations of counter-ions within the nanostructured domains now comprised of polycations and the polyanions. These specific segment chemistries show great promise going forward for future development of charge mosaic membranes.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at DOI: (##).

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