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Manipulation of the Asymmetric Swelling Fronts of Photoresist Polyelectrolyte Gradient Thin Films

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The depth profile of swelling polyelectrolyte layers is characterized by a static bulk layer and an asymmetric profile with position and shape parameters that describe the intermediate and solution side of the interfacial region. The characteristic width in the solution-side region exceeds the dimensions of the individual chains and therefore is comprised of weakly associated polymers. Contrary to that observed for polyelectrolyte gels and brushes stabilized by cross-links or by covalent bonds to the substrate, respectively, these swelling layers exhibit a more complex response to monovalent and divalent salts. Salt causes an initial contraction of the solution-side interface; layer expansion and polymer dissolution follow at higher salt concentration. The swelling layers measured by neutron reflectivity with mass change verified by quartz crystal microbalance exhibit nonequilibrium responses to the salt concentration, as observed through this interplay between swelling and dissolution. Further, the asymmetric profiles approach, but do not reach, symmetric shapes as expected by mean field equilibrium interfaces. These measurements, motivated by technological needs of photoresist materials, highlight the significance of hydrophobic interactions in determining the structure of associating polymer molecules at the lithographic feature edge.

Introduction

The persistent drive to manufacture smaller features by photolithography requires highly tuned photoresist imaging materials.¹ Recent attention has shifted toward understanding the limits^{2–9} of this top-down nanofabrication technology as the desired feature sizes approach the macromolecular dimensions of the photoresist polymers. The polymer–polymer interfaces formed by the in situ acid-catalyzed reaction–diffusion process are controlled on the nanometer scale to provide^{8–10} a chemical latent image with regions that differs in solubility in an aqueous hydroxide developer solution. The origin of the solubility difference arises from the acid catalyzed cleavage of a hydrophobic protecting group to the weakly acidic form.

A polymer–developer interface is formed during the dissolution (development) process. At this interface, the weakly acidic polymers rapidly dissolve until a soluble to insoluble transition region is reached. At this new interface a large chemical mismatch is present between hydrophobic and hydrophilic polymer segments as well as between hydrophobic groups and aqueous base solution. The response of the polymers is dynamic and not static. Recently, we discovered that an associating polyelectrolyte swelling layer remains at this feature edge after development and subsequent water rinse due to the weakly acidic polymer content.¹¹ However, upon drying, this swelling layer of nominal width ≈ 10 nm collapses leading to the final feature. This interfacial swelling becomes increasingly important as the swelling dimensions approach the intended lithographic feature dimensions. Additionally, the mechanism of swelling and swelling-layer collapse on roughness are critical problems for this technology as line edge or line-width roughness^{1,12} may limit future performance to feature size gains.

The thickness and stability of this swelling layer are dependent upon local compositional heterogeneity created by the image-forming process.^{13,14} Neutron reflectivity provides a general methodology to probe these diffuse interfaces with nanometer resolution. By exploiting the difference in scattering length density between the polymer film and deuterium oxide solvent, we find that the swollen interface has an asymmetric composition profile with multiple length scales and a highly diffuse structure at the solution-side layer. Additionally, salt concentration and charge valence were probed to manipulate these length scales expecting to induce contraction. However, the results favor a partial dissolution of the most water-soluble chains, rather than a swelling-layer collapse for these unentangled, uncross-linked films. This behavior is in stark contrast to polymer chain contraction by screening of the polymer segment–segment repulsive electrostatic interactions as observed in polyelectrolyte solutions,¹⁵ brushes,¹⁶ and gels.¹⁷ We expect these measurements will stimulate new approaches, both experimental and theoretical, to understanding the structure of swollen gradient polyelectrolyte interfaces.

Experimental Section

Materials and Sample Preparation. A well-defined composition gradient was prepared by chemical reaction between a photoacid generator feeder layer upon an acid-sensitive photoresist polymer. A thin wafer-adhesion promoting layer was added leading to the trilayer structure as shown in Figure 1b upon the silicon substrate. As described previously, this approach provides a sharp initial photoacid step profile and subsequent acid-catalyzed deprotection of the underlying photoresist polymer.^{8,9} The adhesion layer (ARC) was a diluted form of a commercial antireflective coating CD2326 (Brewer Science Inc.) spin-cast onto the cleaned silicon wafer with regrown native oxide and postapply baked at 200 °C for 5 min under a N₂ purge. The model photoresist polymer, poly(methyladamantyl meth-

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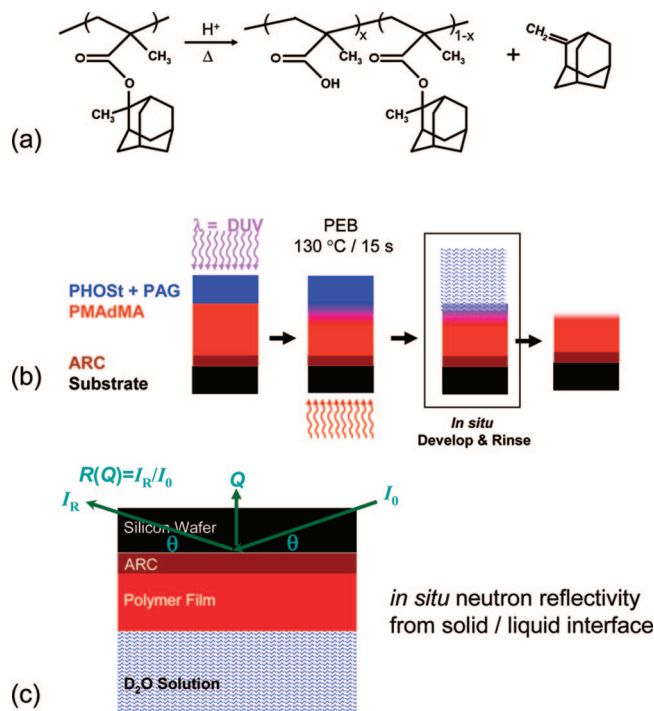


Figure 1. (a) Deprotection reaction of PMAdMA and (b) sample trilayer preparation highlighting the geometry of the thin film gradient preparation. (c) Geometry of the in situ neutron reflectivity experiment, where the neutron beam enters from the thick silicon wafer substrate.

acrylate) (PMAdMA), with number-average relative molecular mass (M_n) of 8800 g mol⁻¹ and polydispersity index of 1.18 (DuPont Electronic Polymers) was spin-cast from toluene onto this ARC layer followed by a postapply bake of 130 °C for 60 s. The acid-feeder layer consists of poly(4-hydroxystyrene) (PHOS) (DuPont Electronic Polymers, M_n = 8000 g mol⁻¹) with 5% by mass of triphenylsulfonium perfluorobutanesulfonate spin-cast from 1-butanol and postapply baked at 130 °C for 60 s.

This trilayer is then exposed to broadband ultraviolet radiation (248 nm, Oriel Instruments) and postexposure baked at 130 °C for 15 s. The deprotection reaction of PMAdMA into methacrylic acid (MAA) and residual methylene adamantane is provided in Figure 1a as characterized by infrared spectroscopy.^{8,18} This approach prepares a well-defined composition gradient in the direction normal to the film thickness suitable for neutron reflectivity measurements. For the quartz crystal microbalance (QCM) measurements, the polymer films were prepared identically, with the only difference being that the silicon wafer coated with the ARC layer was replaced by hexamethyldisilazane-treated quartz crystal.

Profilometry by Neutron Reflectivity. Neutron reflectivity measurements were performed on the NG-7 horizontal reflectometer at the National Institute of Standards and Technology (NIST) Center for Neutron Research. The reflectivity was normalized by the incident neutron beam intensity and measured as a function of the scattering wave vector (Q) normal to the film, $Q = 4\pi\lambda^{-1} \sin \theta$, where λ is the fixed incident neutron wavelength of 4.75 Å and θ is the specular angle of reflection. For studies of the solid/liquid interface the neutron beam is incident through the back-side of the supporting silicon wafer, as shown in Figure 1c. This geometry is preferred since the silicon substrate provides a high degree of transmittance. The specular reflected intensity from the solid/liquid interface provides nanometer resolution depth profile of the film due to neutron scattering length density variations between hydrogenated polymer film and deuterium oxide solution. Measurements of dry thin films are performed with the neutrons incident through air and reflecting off the silicon substrate.

The trilayer structure was characterized for unexposed and postexposure baked samples. As the deprotection reaction proceeds, the difference in hydrogen content between PHOS and PMAdMA and subsequent deprotection reaction (Figure 1a) provides sufficient neutron contrast to measure the reaction front and film profile.⁸ In situ liquid reflectivity was performed on these well-defined gradient films using a custom liquid cell with 0.065 mol/L tetramethylammonium hydroxide (TMAH,

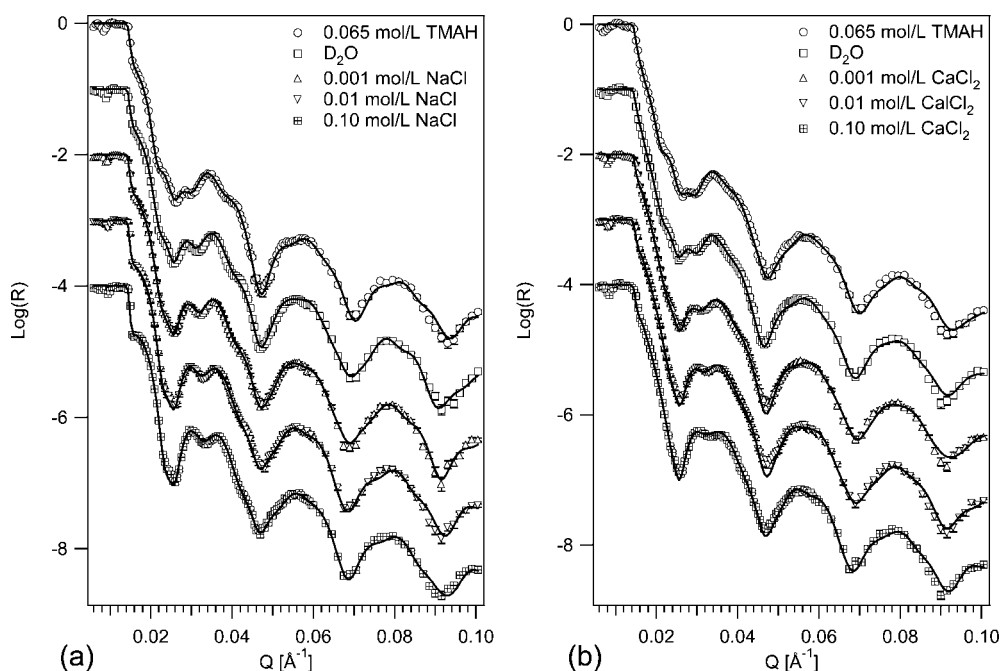


Figure 2. In situ neutron reflectivity vs wave vector as functions of aqueous base, D₂O, and three salt concentrations for (a) NaCl and (b) CaCl₂. The data have been vertically shifted down in succession by 1 decade after 0.065 mol/L TMAH. The solid lines are the model fits.

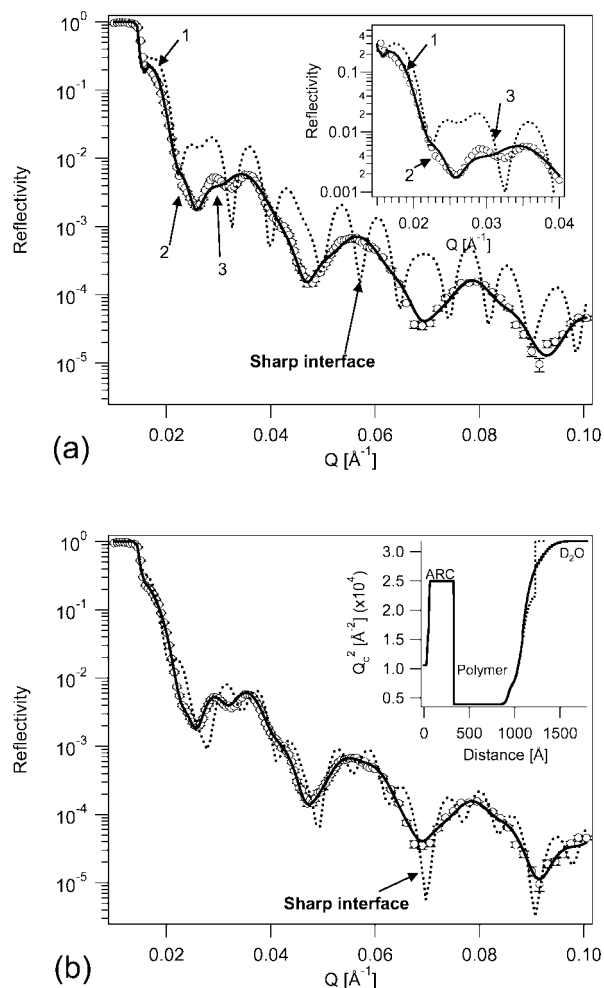


Figure 3. Model fitting of neutron reflectivity for 0.001 mol/L sodium chloride in D_2O equilibrated against swollen polymer film. In (a) a two polymer layer model for reflectivity with inset that highlights inadequate fits to features. In (b) three polymer layer model for reflectivity for a sharp (dotted line) and diffuse (solid line) solution/polymer interface along with inset that shows the corresponding Q_c^2 profiles for sharp and diffuse solution/polymer interface.

Aldrich) prepared from the salt form in D_2O (99.9% isotopic purity, Aldrich) to maximize the scattering length contrast between polymer and solvent. Once this aqueous hydroxide was introduced into the cell, the PHOST acid feeder layer and portion of the reaction front dissolved, as observed through a view port in the liquid cell. The remaining thin film in contact with developer was measured by specular neutron reflectivity (Figure 1c). Subsequently, the developer was removed from the cell, rinsed, and filled with D_2O and measured. Two different samples were used for the salt equilibration studies with sodium chloride or calcium chloride (Aldrich) dissolved in D_2O . Measurements were performed at concentrations of 0.001, 0.010, and 0.10 mol/L in order of increasing concentration on the same sample. This approach reduces sample-to-sample variability in these surface-sensitive experiments.

The reflectivity data are fit to model reflectivity calculated from scattering length density profiles ($Q_c^2 = 16\pi \sum b_i/v$) using the Parratt algorithm,¹⁹ where the scattering length of each repeat unit is determined by the sum over the atomic scattering lengths b_i within molar volume (v) leading to the absolute scattering length density.²⁰ In general, this approach uses successive layers of constant Q_c^2 with interfaces smeared by a Gaussian function. These Q_c^2 profiles can be directly converted to volume fraction profiles. Further

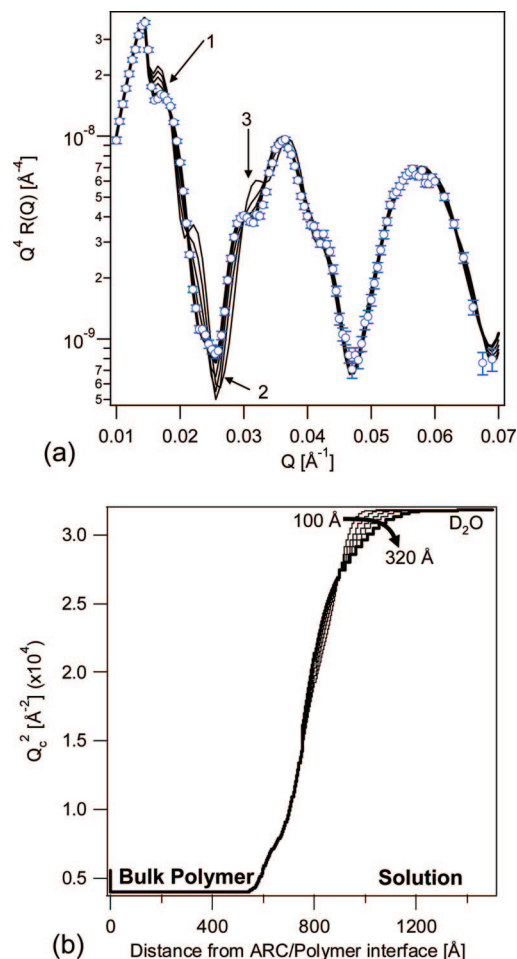


Figure 4. Model fitting of neutron reflectivity for polymer film equilibrated with 0.001 mol/L sodium chloride in D_2O : (a) Fresnel reflectivity normalized data from three polymer layer model highlighting sensitivity to asymmetry through the solution/solid interfacial width also in (b) corresponding Q_c^2 profiles highlighting polymer layer as distance from ARC/polymer interface.

experimental details regarding neutron reflectivity can be found in Thomas²¹ and Russell.²² Uncertainties are calculated as the estimated standard deviation from the mean. In the case where the limits are smaller than the plotted symbols, the limits are removed for clarity.

Quartz Crystal Microbalance. The kinetic response of the thin films to varied TMAH concentration and water and salt solutions was measured by a quartz crystal microbalance (Q-Sense) with dissipation mode (QCM-D). The QCM-D setup follows the changes in the fundamental resonance frequency, 5 MHz, as well as the overtones (15, 25, and 35 MHz) of the polymer-coated quartz crystal. The polymer films were developed in 0.065 mol/L TMAH in a temperature-controlled (298 K) flow cell. Changes in the resonance frequencies of the polymer-coated quartz crystals due to the dissolution of the PHOST acid feeder layer and a portion of the reaction front were measured as a function of time. When this change became time invariant, the hydroxide solution was replaced by D_2O (and subsequent salt solutions), and the change in the resonance frequency was measured until it again became time invariant. In order to account for the effect of different solvent density on the resonance frequencies of the crystal, a control measurement was performed on a bare quartz crystal using the aforementioned protocol. The change in resonance frequency due to a change in solvent was then subtracted from the

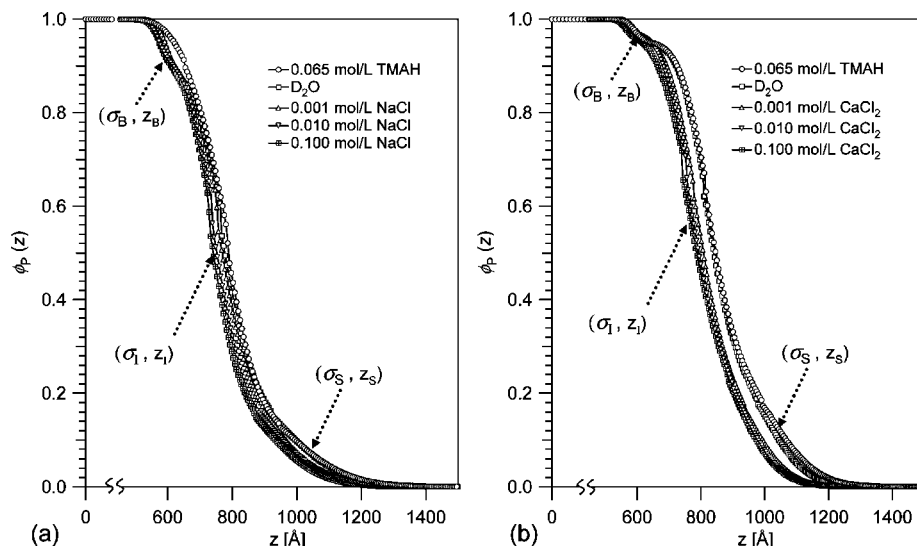


Figure 5. Effect of (a) sodium chloride and (b) calcium chloride on volume fraction of polymer segmental profiles as a function of distance from the ARC/PMAdMA interface; abscissa is broken between 0 and 600 for clarity.

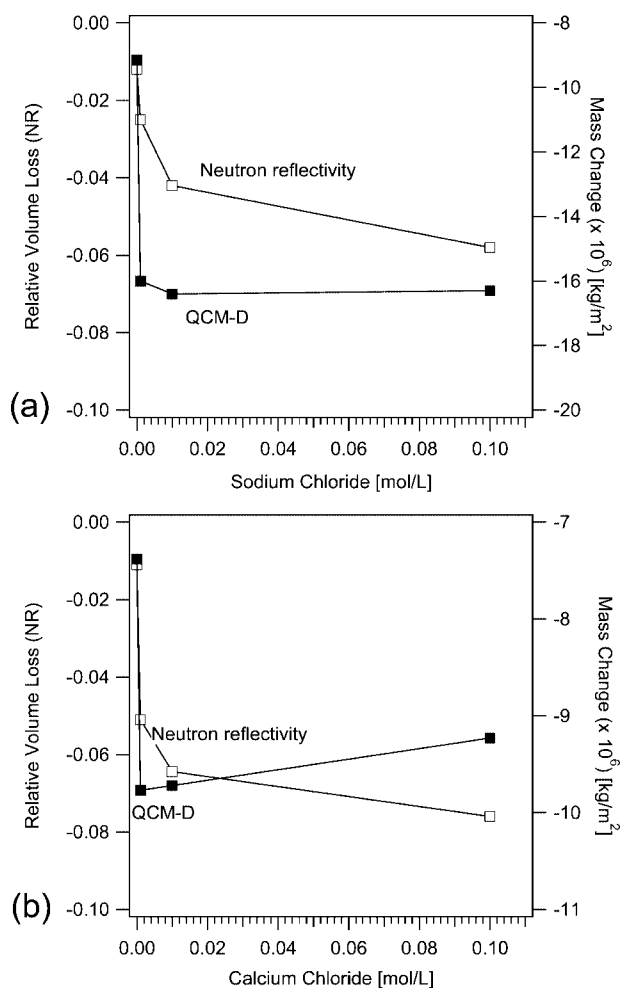


Figure 6. Relative volume loss and Sauerbrey mass change as measured by neutron reflectivity (open symbols) and QCM-D, respectively, for successive increases in salt concentration (a) sodium chloride and (b) calcium chloride.

corresponding resonance frequency of the polymer-coated crystals to obtain the density-corrected resonance frequency of the coated crystal. The mass change due to the dissolution of

the interfacial layer as a result of switching the solvent solutions was measured using the Sauerbrey equation²³

$$\Delta m = -C_q \frac{\Delta F}{n} \quad (1)$$

where C_q is $1.73 \times 10^{-7} \text{ kg}/(\text{m}^2 \text{ Hz})$, ΔF is the corrected change in the resonance frequency of the quartz crystal measured with respect to the resonance frequency of the partially developed film immersed in the hydroxide solution, and n is the number of the harmonic overtone ($n = 3, 5$, and 7).

Results and Discussion

The reaction–diffusion gradient formed by the acid feeder layer⁸ method mimics the latent image at the lithographic line edge. This acid feeder layer rapidly dissolves in 0.065 mol/L TMAH. Upon sufficient acid-catalyzed reaction into the underlying layer a portion of the gradient will dissolve. The remaining partially reacted and unreacted polymer continues to swell.¹¹

Neutron Reflectivity. Neutron reflectivity characterizes the structure of these layers with nanometer resolution and contrast from deuterium labeling. The in situ neutron reflectivity of the dissolved (developed) gradient thin film is shown in Figure 2a for the sodium chloride salt and Figure 2b for the calcium chloride salt study. The multilayer structure from the adhesion layer coating (ARC) and gradient polymer thin film gives rise to Kiessig fringes which change in amplitude and position as the polymer film thickness and composition profile shape changes in response to the 0.065 mol/L hydroxide solution, pure D_2O , and increasing salt concentrations in D_2O .

The three longest wavelength fringes, beyond the critical edge, correspond to the thin ARC layer (270 Å) due to the inverse relationship between film thickness and fringe period. However, additional fringes are convoluted near the maxima. These correspond to the total layer structure which is resolved with a multilayer stack model. The loss of higher order fringes is due to the diffuse polymer/solution interface. To provide a physical insight into the layer structure, we show, by example, the sensitivity of neutron reflectivity to these multilayer films and rationale behind the model fits. Figure 3 shows the data for the 0.001 mol/L sodium chloride system.

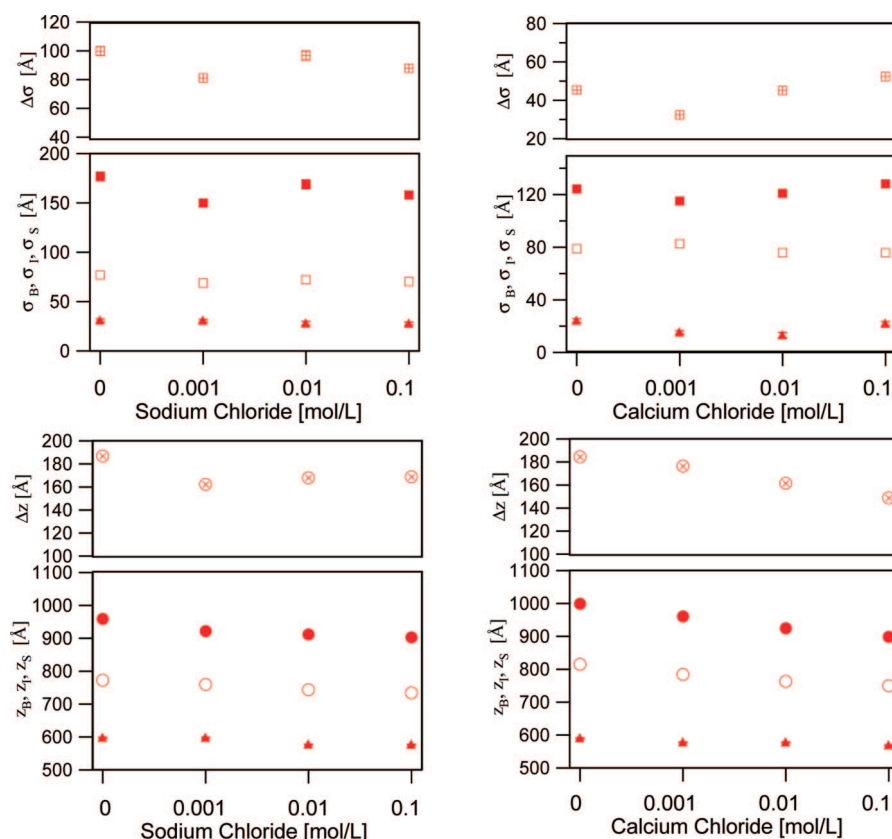


Figure 7. Profile position and shape parameters at the bulk (\blacktriangle), z_B and σ_B , intermediate (\circ), z_I and σ_I , and solution side (\bullet), z_S and σ_S , of the interfacial region for (a) sodium chloride and (b) calcium chloride solutions. The systematic shift of the position is indicative of the polymer dissolution as the swelling layer is reduced in average thickness and central position of the asymmetric profile. $\Delta z = (z_S - z_I)$ and $\Delta\sigma = (\sigma_S - \sigma_I)$ quantifies the spatial and shape asymmetry, respectively, of the interfacial region and remains several molecular sizes from the symmetric condition of $\Delta z = 0$ and $\Delta\sigma = 0$.

A simple film model comprised of a single polymer layer with average scattering length density with either sharp or diffuse interfaces was not adequate; therefore, a second layer was introduced. However, as seen in Figure 3a, this two-layer model with sharp or diffuse interfaces was unable to capture the fine structure denoted by the arrows 1, 2, and 3. Arrow 1 shows a slight maximum, where the data show only a shoulder after the drop at the critical edge; arrows 2 and 3 show a mismatch in amplitude of the shoulder before the first distinct minimum and fringe maximum, respectively. These areas are the most sensitive to the multilayer structure. The experimental data can be reconciled by adding a third layer as shown Figure 3b. This modeling strategy fits all experimental features as discussed for Figure 3a. The polymer/solution layer must be diffuse in order to eliminate the high-frequency fringes that are convoluted with the ARC layer fringes as shown by examining the diffuse layer (solid line) vs the sharp interface (dotted line) in Figure 3b. However, rather than one broad interface the polymer profile requires a slightly sharper substrate side of the interfacial region and a more diffuse solution side interfacial region. This asymmetric structure of swelling layers is indicative of a gradient in the extent of swelling at the interface.

In order to demonstrate the sensitivity to the asymmetric interface, we show in Figure 4 the same data from Figure 3 under varied interfacial width of the solution side of the interface in a Fresnel-normalized plot, $Q^4 R(Q)$. The same features of Figure 3a are marked by 1, 2, and 3. By changing the interfacial width from 100 to 320 Å, the model converges to fit the shoulder just beyond the critical edge, first minimum

and the fine structure at the first maxima. The corresponding Q_c^2 profile is shown in the polymer layer. The important point demonstrated is the sensitivity to the solution side of the interface as the thicker solid line represents the experimental data. This approach led to the fits in Figure 2 shown as the solid lines. The persistent changes to the first long wavelength maxima, in particular $0.025 \text{ \AA}^{-1} < Q < 0.045 \text{ \AA}^{-1}$, provides evidence to thin layer restructuring response to the successive increases in salt concentration. The physical meaning for requiring three layers is rationalized as well-defined composition profile from bulk unreacted polymer with a smooth transition from intermediate partially reacted, but insoluble polymer to the partially reacted surface-swollen polymer layer. We further quantify these profiles in the next section.

Composition Profiles. The scattering length density profiles are converted to polymer volume fraction (ϕ) profiles¹¹ using a mean Q_c^2 for the polymer ($Q_{c,p}^2 = 3.95 \times 10^{-5} \text{ \AA}^{-2}$) and solvent ($Q_{c,s}^2 = 3.18 \times 10^{-4} \text{ \AA}^{-2}$).

$$\phi_p(z) = \frac{Q_c^2(z) - Q_{c,s}^2}{Q_{c,p}^2 - Q_{c,s}^2} \quad (2)$$

The effect of salt on the average scattering length density of the solvent was not significant, since the D_2O subphase $Q_{c,s}^2$ had a constant critical edge. However, for the special case of characterizing the counterion profile, we demonstrated that 0.065 mol/L deuterated tetramethylammonium occupies a small, but measurable, fraction of the swollen interface with

a maximum of 5 vol %.¹¹ In the present case we determine the polymer profile without the breakdown into the salt and solvent profile.

Figure 5a,b shows the diffuse polymer profiles as a function of distance (z) from the ARC substrate. The 0.065 mol/L developer data shows a swollen polymer/liquid interface. The change to pure D₂O preserves the swelling and leads to further dissolution. While the addition of 0.001 mol/L salt causes dissolution, a further increase from 0.001 to 0.10 mol/L sodium chloride or calcium chloride does not lead to a substantial collapse of the swollen layer as observed by polyelectrolyte brushes with metal ions.²⁴ Instead, the increase in salt concentration results in the dissolution of polymer chains from the swollen interfacial region. The single chain dimension (radius of gyration) will decrease as the salt concentration is increased in dilute and semidilute solutions.^{15,25} However, the combination of polymer and salt concentration at the surface layer appears to remain in the homogeneous phase far from macroscopic phase separation or precipitation at high salt.^{15,26–30} The amount of polymer dissolution was quantified by the volume change obtained by integrating the area under the curves in Figure 5a,b and also independently verified by the mass changes from QCM-D measurements. The Sauerbrey mass loss measured by QCM (Figure 6) after the TMAH dissolution step has the same trends as that deduced by neutron reflectivity. Characterization of the films before development and after the salt water rinse by Fourier transform infrared spectroscopy shows that the average methacrylic acid content decreased from 0.48 to 0.27 mole fraction MAA for the sodium chloride system and 0.50 to 0.28 mole fraction MAA for the calcium chloride system. Therefore, the most water-soluble chains are actively dissolving due to the addition of salt to the water rinse step.

These segmental profiles span the conditions of concentrated to dilute solution. At the bulk is a thin glassy layer where $\phi \approx 1$, whereas the swelling primarily occurs within the intermediate and solution side of the interface. From Figure 5, the chain segment density distribution of the swollen interface extends far into the solution even as the polymer volume fraction transitions from a value corresponding to a semidilute concentration to a dilute concentration (polymer overlap concentration, $\phi^* \approx 0.20$). The spatial distribution of the region encompassing polymer chains in the dilute state far exceeds the dimensions of a single chain, indicating the existence of associative (attractive) interactions among the polymer chains. Such an interaction would be necessary to support the ionic osmotic swelling stress and may be related to the slow mode³¹ observed in polyelectrolyte solutions. Since the polymer molecules are not chemically cross-linked and are unentangled due to the low degree of polymerization, the thermodynamic driving force for this interaction probably arises from the large chemical mismatch between protected (methyldamantyl methacrylate) and deprotected (methacrylic acid) functional groups. The nature of the latent image reaction–diffusion process must impart local spatial chemical heterogeneity with connectivity on the nanometer scale that leads to hydrophobic and hydrophilic rich regions.¹⁴ Upon exposure to the aqueous solution, these domains rearrange leading to hydrophobic domains associating to provide structural integrity to the swollen interface.

Segmental Profile Shape: Salt Valence Dependence. The locations (z_i) and widths (σ_i) of the layers composing the interface are quantified by a sum of three hyperbolic tangent functions fit to the polymer volume fraction profiles of Figure 5.

$$\phi(z) = \sum_i A_i \tanh\left(\frac{z_i - z}{\sigma_i}\right) + 0.5 \quad (3)$$

The tanh functions model the characteristic profile shape and provide a convenient comparison to mean field composition profiles between equilibrium phases.³² The indices (i) refer to the layers comprised of the bulk (B), intermediate (I), and solution (S) side of the interfacial region. The response of the above parameters to a change in the nature of the equilibrating solutions is important in the context of photolithography, since the collapse of the swollen interface during the postdevelopment rinse stage determines the fidelity of photolithography defined features.

The bulk feature at the tip of the reaction–diffusion front has a static position and shape parameters as shown by Figure 7. There is little systematic variation in the width (σ_B) with the D₂O, sodium chloride (7A) or calcium chloride (7C) solution equilibration. Additionally, the interfacial positions (z_B) do not vary by more than 20 Å. This static length scale of the local buried structure does not respond to the salt valence or concentration. A buried structure was determined by off-specular neutron reflectivity in the latent image (nondissolved film) with a different system but the same reaction–diffusion process.³³

In contrast, both z_I and z_S shift as the solution conditions vary. Since z_B is small in magnitude and static, we separate its effect by defining Δz as the difference between the layer interface positions, such that $\Delta z = (z_S - z_I)$. While the individual positions decrease with changing solution conditions, Δz remains static and does not approach the symmetric condition of $\Delta z = 0$. This response of the swelling polyelectrolyte layer supports a shift of the interface boundary due to chain dissolution such that the average degree of ionization of the layer is also changing. This position change is coupled with the width parameters σ_S and σ_I and the parameter $\Delta\sigma = (\sigma_S - \sigma_I)$ also shown in Figure 7. The bulk layer shape does not change as seen by the flat response in σ_I (open symbols); however, the solution-side parameter σ_S shows variation with D₂O and salt concentration. σ_S decreases initially at the lowest salt concentration, supported by electrostatic screening of the segment–segment repulsive interactions in the presence of either monovalent or divalent salt. In this case the Debye screening length would be reduced to 9.6 nm for 0.001 mol/L sodium chloride and 6 nm for 0.001 mol/L calcium chloride. Further increase in the salt concentration induces an increase in σ_S . If these width parameters simply reflected chain conformation, then a continuous decrease in chain radius of gyration is expected.

In this solution-side region σ_S is much larger than rodlike (29 Å) or globule (15 Å) estimates for the radius of gyration of these poly(methacrylic acid) chains. Therefore, the interface is not that of single adsorbed polymers, but an association of chains.³⁴ The multichain associating aspects are driven by the strong chemical mismatch between MadMA–MAA segments and MadMA–water. The local heterogeneous morphology is preformed by the reaction–diffusion process. Separating the chemical mismatch (such as hydrophobicity or excluded volume) origin from an electrostatic origin of attraction is not possible at this point. However, the associative behavior observed at this interface may be related to the slow mode observed in polyelectrolytes and electrolyte solutions.³⁵ Therefore, the associative behavior of aqueous base soluble photoresists occurs at an interface, in addition to bulk solution. Photoresist materials which perhaps minimize the bare (nonionized) chemical mismatch³⁶ between protected and deprotected polymers may reduce

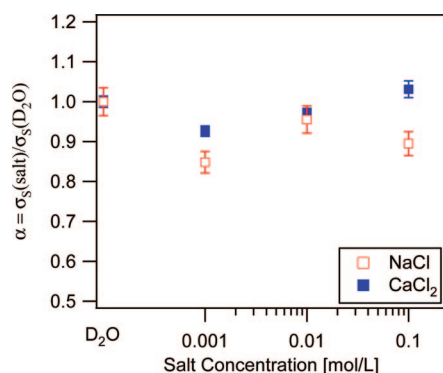


Figure 8. Expansion factor defined by the change in the solution layer width for monovalent and divalent salt concentration relative to the D₂O state.

these effects and lend the effects of electrostatics dominant. Such observations are in qualitative agreement with the studies of poly(hydroxystyrene) derivatives which show reduced swelling in single layer films¹⁰ and polyelectrolyte effects.³⁷

At 0.001 mol/L salt a larger contraction is observed for sodium chloride solutions than calcium chloride, relative to the D₂O state. Since this associated layer appears in the dilute-associated state the origin is likely initially electrostatic screening by added salt. Electrostatic screening of the charge–charge repulsion in the hydrophilic-rich regions causes coil contraction. However, an increased salt concentration, either monovalent or divalent, causes an expansion that is accompanied by (Figure 8) simultaneous partial dissolution of the most water-soluble chains. The loss of the most hydrophilic chains would be expected to lead to less swelling. However, a relative expansion appears to reflect a loosening of the network in analogy to a reduced molecular weight between cross-links or reduced polymer–substrate attractive interaction. The final stabilized network structure causes a slight expansion.

The initial deprotection heterogeneities formed by the reaction process were estimated at a length scale of 2 to 4 nm.¹⁴ However, during the swelling process a reorganization or randomization due to mobility of the polymer chains in the swollen layer may coarsen the hydrophobic domain size and contact volume. Measurements of the solvent and polymer transport within these nanometer scale swelling fronts and structural morphology would provide further insight into time scales and evolution of these weakly acidic polymer layers. Additionally, methods to characterize the coarsening process of hydrophobic groups would provide invaluable evidence toward the mechanisms of these stable swollen layers.

Conclusions

Swelling in lithographic materials is crucial to control as the desired length scales approach feature dimensions and associated roughness. Neutron reflectivity provides a general method to follow the response of the swelling layers to different external solution conditions, such as in the present study, where the ionic strength is varied. The weakly acidic compositional gradients exhibit asymmetric swelling profiles. This asymmetry is divided into a bulk region, intermediate and solution side of the polymer/liquid interface. Most strikingly, the effect of salt induces slight polymer dissolution such that the symmetric condition is approached but not reached. The role of salt appears to lower kinetic barriers to

dissolution of the most soluble hydrophilic polymers. The solution side of the interface has a characteristic length that exceeds single polyelectrolyte chain dimensions. This associated polymer layer displays an initial contraction with lowest level of added salt, consistent with screening of electrostatic segment–segment repulsions and subsequent re-expansion relative to the salt-free state. The re-expansion is hypothesized to occur due to a looser associated state at the surface. The polymers, therefore, self-assemble into a swollen structure arising due to multifunctional junctions among associated hydrophobic chain segments. Our results suggest the need to develop strategies to control this polyelectrolyte swollen structure in order to extend optical lithography to dimensions below 22 nm.

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Supporting Information Available: Neutron scattering length density profiles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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