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Understanding the Role of Polymer Sequence and Chemistry on Lithographic Patterning

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy
in Chemical Engineering

by

Cameron Patrick Adams

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June 2026

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Understanding the Role of Polymer Sequence and Chemistry on Lithographic Patterning

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by

Cameron Patrick Adams

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- 3) Yuan, C.; Lüttgenau, B.; Im, H.; Zhang, Q.; **Adams, C. P.**; Segalman, R. A.; Kostko, O.; Ober, C. K. “Sequence-defined polypeptoid resists for molecularly precise stochastic control and mechanistic innovation in EUV lithography.” In *Proc.SPIE*, 2026; Vol. 13983, p 139830V. DOI: 10.1117/12.3090186.
- 4) **Adams, C. P.**; Henein, C.; Yuan, C.; Ober, C. K.; Segalman, R. A. “Polymer sequence alters sensitivity and resolution in chemically amplified polypeptoid photoresists.” *ACS Macro Letters* 2025, 14, 1055-1059. DOI: 10.1021/acsmacrolett.5c00320
- 5) Yuan, C.; Marui, R.; **Adams, C. P.**; Segalman, R. A.; Ober, C. K. Sequence-defined polypeptoids facilitating stochastics control and EUV patterning study. In *Proc.SPIE*, 2025; Vol. 13428, p 134281K. DOI: 10.1117/12.3050582.
- 6) Kaefer, F.; Yuan, C.; **Adams, C. P.**; Segalman, R. A.; Ober, C. K. “Photoresist Design to Address Stochastics Issues in EUV Resists.” *J. Photopolym. Sci. Tech.* 2023, 36 (1), 61-66. DOI: 10.2494/photopolymer.36.61

- 7) Zhu, C.; Burkey, A. A.; **Adams, C. P.**; Uruchurtu Patino, D.; Lynd, N. A. “Concurrent ring-opening/ring-closing polymerization of glycidyl acetate to acid-degradable poly(ether-co-orthoester) materials using a mono(μ -alkoxo)bis(alkylaluminum) initiator.” *Macromolecules* 2022, 55 (7), 2797-2805. DOI: 10.1021/acs.macromol.2c00009

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ABSTRACT

Understanding the Role of Polymer Sequence and Chemistry on Patterning

by

Cameron Patrick Adams

Microelectronics underpin virtually every aspect of modern technology, and continued advances in their performance and miniaturization depend critically on the ability to fabricate increasingly smaller features on semiconductor devices. The continued scaling of these devices has placed increasing demands on photoresist materials, exposing fundamental limitations in the chemically amplified resists (CARs) that have long underpinned semiconductor lithography. These issues primarily stem from chemical heterogeneity imparted by conventional polymer synthesis and formulation which, along with insufficient absorption of extreme ultraviolet (EUV) radiation, contributes to degraded patterning resolution and process reliability at the nanoscale. Sequence-defined polymers are an emerging class of materials that offers a possible solution to these problems. By precisely controlling chain length, monomer sequence, and sidechain identity, these materials are uniquely suited to isolate and interrogate the molecular-level factors governing resist performance that are otherwise obscured by the heterogeneity of conventional materials. However, much remains unknown about how these structural properties influence patterning.

This work utilizes sequence-defined polypeptoids as a model platform for understanding the roles of sequence and chemistry on patterning performance. First, systematic studies of sequence and chain length effects revealed that monomer arrangement significantly influences patterning resolution, establishing sequence as an actionable design variable in resist development. Second, iodine-bearing sidechains were incorporated into polypeptoid photoresists to understand the impacts of strongly EUV-absorbing elements on electron generation and sensitivity. Finally, the monodisperse nature of polypeptoids was leveraged to investigate the critical ionization (CI) model for resist dissolution and gain insight into the mechanisms governing development. Collectively, these results demonstrate that synthetic precision is a powerful and underutilized lever in photoresist design, and that sequence-defined polymers offer a compelling platform for both advancing next-generation lithographic materials and deepening fundamental understanding of the polymer physics that governs them.

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Chapter 1: Introduction

Microelectronic electronic devices are ubiquitous in everyday life and are one of the defining technologies of the 20th and 21st centuries. Over the past 20 years the world has become more connected than ever, and the introduction of portable electronic devices such as smartphones and laptop computers has provided a previously unattainable amount of information at our fingertips. The average American household now contains between 17 and 21 connected devices, and global estimates place per-capita device ownership at roughly 9 connected devices per person.^{2, 3} Smartphones alone are now present in 90% of US households. Beyond personal electronics, microelectronics are present in countless industries. In healthcare, they are found in pacemakers, MRIs, continuous glucose monitors, and a wide range of other critical technologies. In the transportation industry, thousands of microchips control everything in a vehicle from the stereo to the ignition, and this number will only

increase with the continued transition to automated transport. They also provide the basis for communications including the internet, data centers, and satellites. This incredible societal demand for microchips means that the semiconductor industry that manufactures these devices has become a massive operation. Global semiconductor sales reached over \$630 billion in 2024 and are expected to clear \$1 trillion in the next few years.⁴ As annual production continues to increase, so does the drive to improve the speed and power efficiency of these devices, especially in the budding age of artificial intelligence.

1.1 Photolithography

In order to manufacture the billions of transistors that make up the microelectronic chips used throughout the modern world, the semiconductor industry has relied upon a patterning technique known as photolithography. Rather than fabricating individual transistors one by one at the nanometer scale, photolithography allows semiconductor fabrication plants to build a chip by effectively printing a series of interconnected layers onto a substrate, enabling modern microchips to contain billions of transistors. In this process, a substrate (typically a silicon wafer) is first coated with a light-sensitive material known as a photoresist, or simply a resist. The coated wafer is then illuminated through a patterned template that selectively blocks or transmits light, known as a photomask, exposing the resist in a precisely defined pattern. The interaction between light and the resist induces a change in the material's solubility, which allows either the exposed region (in what's known as a positive tone resist) or the unexposed region (known as a negative tone resist) to be selectively dissolved by a solvent known as a developer while leaving the complementary region intact. This process is depicted in **Figure 1.1**. The wafer then undergoes an etching step where the pattern is

transferred into the underlying substrate. Here, the patterned resist acts as a protective barrier, allowing material to be removed only where resist has been cleared away. This is followed by a deposition step in which metal (frequently copper) or dopants are introduced into the etched regions to form the transistors and interconnecting wires that constitute the functional chip. Any remaining resist is then stripped away, and the entire sequence is repeated to build the next layer. Through this iterative process, a complete chip comprising billions of transistors can be constructed layer by layer, with hundreds of individual chips patterned simultaneously across a single wafer.

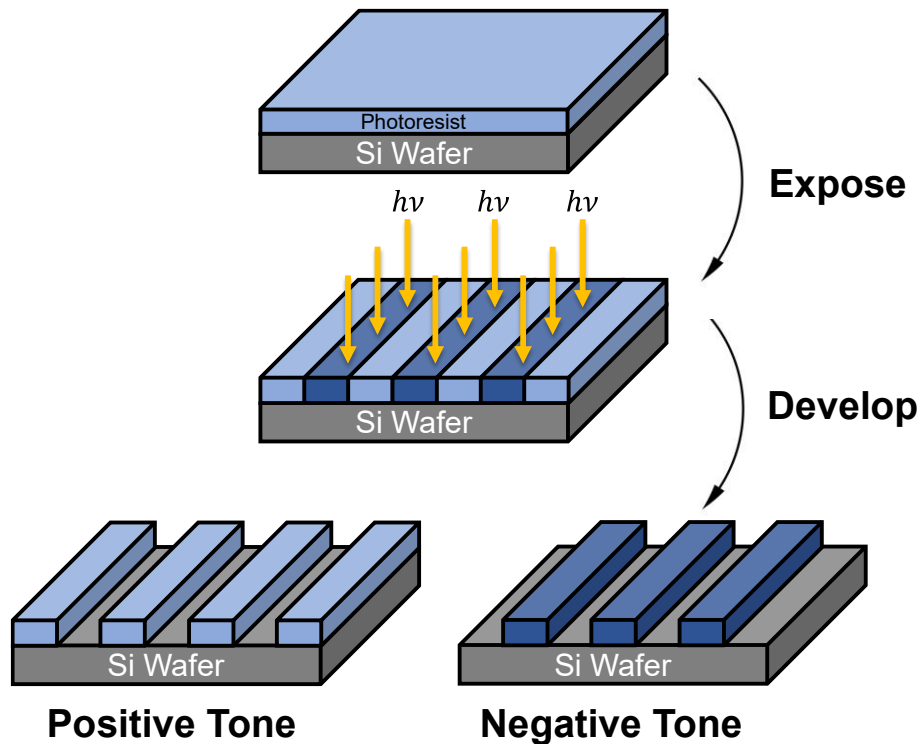


Figure 1.1. Simplified schematic of the lithographic process. In the first step, a coated silicon wafer is exposed to light or other radiation, causing a chemical change to occur in exposed regions of the photoresist film. This chemical change results in a solubility change, allowing one of the two regions to be selectively removed with a developer.

For decades, the semiconductor industry has driven towards packing more transistors on a chip through a process of feature miniaturization according to Moore's Law. In a 1965 paper, Intel co-founder Gordon Moore observed that the number of transistors on an integrated circuit had been doubling approximately every two years, and he extrapolated this trend to continue years into the future.⁵ This observation quickly transformed into both a roadmap and a benchmark, with manufacturers and equipment suppliers aligning their development cycles to sustain the cadence. This exponential increase in transistor count has resulted in dramatic performance improvements over the years. As transistors shrink and more are packed into a given area of silicon, chips become simultaneously faster, more power-efficient, and cheaper to produce on a per-transistor basis. A modern high-end processor contains upwards of 100 billion transistors, a number that would have been impossible even two decades ago. While the pace of purely geometric scaling has slowed in recent years, the spirit of Moore's Law continues to drive the industry through advances in three-dimensional chip architectures, novel materials, and new patterning technologies.

The length scales involved in photolithography have evolved dramatically in step with this miniaturization. Early processes in the 1960s began with feature sizes on the order of 10 microns. Today, state-of-the-art patterning can resolve features below 10 nanometers; a

reduction of more than three orders of magnitude. The theoretical basis for understanding this progress is given by the Rayleigh criterion:

$$CD = k_1 \frac{\lambda}{NA}$$

Equation 1. The Rayleigh Criterion

Here, CD refers to the critical dimension, which is the smallest feature that can be reliably resolved. It is directly proportional to the wavelength of light (λ) used for exposure, and inversely proportional to the numerical aperture (NA) of the optical system. The prefactor k_1 is a dimensionless process constant that captures the contributions of resist chemistry, illumination conditions, and pattern fidelity, with a theoretical minimum of 0.25 for conventional single-exposure imaging. It follows that the most direct route to smaller features is a shorter exposure wavelength, and the history of lithography is largely a history of that pursuit.

After an initial period of broadband illumination using white light in the early 1970s, mercury arc lamps served as the dominant light source for lithographic exposure for approximately two decades. These lamps emit at several discrete wavelengths, and the industry successively migrated to shorter ones: first the g-line at 438 nm, then the i-line at 365 nm. The development of excimer lasers then enabled a transition to far shorter wavelengths: KrF lasers provided 248 nm illumination through much of the 1990s, followed by ArF lasers operating at 193 nm in the 2000s. A subsequent effort to extend this trajectory to 157 nm using molecular fluorine (F_2) lasers ultimately proved unworkable, largely due to the strong absorption of 157 nm radiation by both atmospheric oxygen and the fused silica optics used

in conventional exposure tools, which would have required a complete redesign of the optical train. Rather than abandoning 193 nm, the industry instead found new ways to continue reducing patternable feature sizes. Immersion lithography replaced the air gap between the final projection lens and the wafer with purified water, which has a refractive index of approximately 1.44 at 193 nm compared to 1.00 in air. Since the effective wavelength in a medium scales inversely with its refractive index, this substitution provided a substantial increase in NA without requiring a new light source. Later, multi-patterning techniques allowed for further reduction in feature size at 193 nm. By performing two or more sequential patterning and etch cycles with slightly offset masks, or by using spacer-based self-alignment approaches, manufacturers could effectively multiply the spatial frequency of features beyond the single-exposure diffraction limit, enabling the continued scaling of logic nodes through the 2010s.

The most recent and consequential development in lithographic light sources has been the introduction of “extreme ultraviolet” (EUV) lithography, which has decreased the exposure wavelength all the way down to 13.5 nm radiation. Generating EUV light at useful intensities requires a fundamentally different approach: a high-power CO₂ laser is fired in two pulses at a stream of free-falling molten tin droplets, first deforming each droplet into a disk and then vaporizing it into a plasma. This plasma emits strongly at 13.5 nm, and the radiation is collected and directed to the wafer by a series of multilayer reflective mirrors, as conventional refractive optics are entirely opaque at EUV wavelengths. The dramatic reduction in wavelength allows EUV to pattern features that would require three or four multi-patterning steps with 193 nm immersion lithography in a single exposure, substantially simplifying the process flow and improving pattern placement accuracy. EUV has been in high-volume

manufacturing since around 2019, and next-generation high-NA EUV tools with an NA of 0.55 (compared to 0.33 for conventional EUV) are currently being introduced to push resolution further still. Further improvements to EUV exposure tools in hyper-NA systems (NA of 0.75-0.85) are in development for introduction around 2030, demonstrating that EUV will likely be the predominant patterning technology for the foreseeable future.

1.2 History of Photoresists

The first documented use of a photoresist occurred in France during the 1820s, over a century before the invention of the transistor in 1947. This material, an asphalt known as bitumen of Judea, was used by inventor Nicéphore Niépce to create the first known photograph. Niépce coated a layer of this tar on a polished pewter plate and exposed it to an image of his courtyard through a camera obscura. After eight hours, the regions that were exposed to sunlight were rendered less soluble in a mixture of lavender oil and light petroleum. The plate was then developed, leaving behind an image in the bare pewter where the bitumen had been rinsed away.⁶ While this was a foundational discovery, bitumen of Judea was clearly lacking in sensitivity to light and would not be the predominant photosensitive material platform for long.

The next major breakthrough in photoresists came in the form of dichromated gelatin (DCG). These materials were made by combining gelatin with either sodium, potassium, or ammonium dichromate salts in water. After casting a film on a substrate, exposure to light causes a photochemical reduction in chromium from Cr^{6+} to Cr^{3+} , which forms a crosslinked complex with the carboxylate functional groups in gelatin.⁷ This dramatically increases the exposed region's resistance to dissolution, functioning as a negative tone resist where a raised

image is remain behind after the unexposed regions are washed away. DCG was pioneered in the 1850s in England by William Henry Fox Talbot, who used a DCG with ammonium dichromate for printing plate production. While DCGs were orders of magnitude more sensitive than bitumen of Judea and effectively spawned the photolithography industry,⁶ they were not without faults. Primarily, they were plagued by an issue known as dark reaction. Upon mixing ammonium dichromate and gelatin, a slow crosslinking reaction begins that occurs even in the dark. This meant that the materials had to be combined immediately before use and could not be commercialized as pre-coated sheets. Additionally, the gelatin protein does not provide substantial resistance to strong acids or bases, which hinders its use in post-patterning etch processes used in the semiconductor industry. These issues ultimately led to the first generation of photoresists designed explicitly for use in semiconductor manufacturing.

The first photoresist designed specifically for semiconductor use was poly(vinylcinnamate), a negative tone material that sought to mimic the patterning mechanism of DCG without its key drawbacks. Upon exposure to light, pendant cinnamoyl groups along adjacent polymer chains dimerize to form crosslinks that render the material insoluble in organic solvents. While this material was able to form good images and solved the two main problems with DCG, adhesion issues between poly(vinylcinnamate) and the underlying substrate ultimately led to the need for further iteration.⁶ Its successor was a photoresist that blended a cyclized poly(cis-isoprene) matrix that imparted great adhesive properties with a bis-azide compound. Upon UV irradiation, the bis-azides formed an incredibly reactive intermediate which reacted with adjacent polymer chains to form an insoluble crosslinked network. This resulting material was known as Kodak Thin Film Resist (KTFR),⁸ and it

became the primary photoresist for the entire semiconductor industry from 1957 until 1972 when it finally reached its resolution limit of 2 microns.⁶

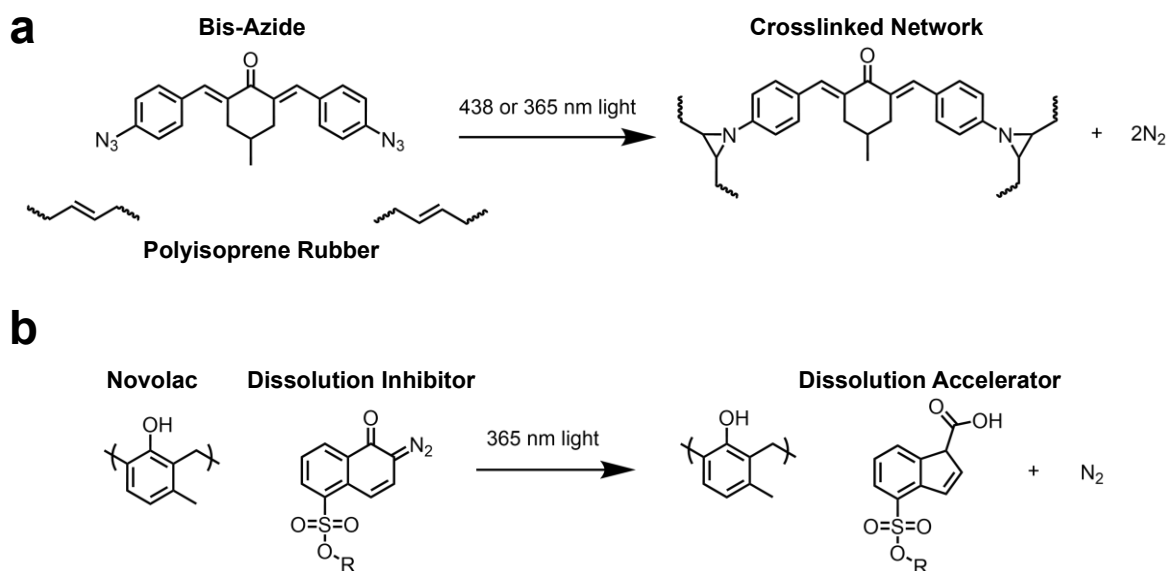


Figure 1.2. (a) KTFR photoresists operated through a crosslinking mechanism where a bis-azide reacted with two separate polyisoprene chains. (b) Novolac/DNQ operated via the change in solubility caused by DNQ turning from a dissolution inhibitor in aqueous base into a dissolution accelerator after exposure.

The transition to positive-tone imaging represented the critical step that enabled the industry to push below the 2 μm barrier. Novolac/diazonaphthoquinone (novolac/DNQ) resists, originally developed for the printing industry and adopted for semiconductor use from the late 1960s onward, operate through a fundamentally different mechanism from the crosslinking-based systems that preceded them. Novolac, a material formed by the polymerization of formaldehyde and phenol, is inherently soluble in aqueous base developer, but the DNQ component acts as a dissolution inhibitor in the unexposed film, suppressing this solubility through interactions with the phenolic groups of the resin.⁹ Upon UV exposure,

DNQ undergoes a photochemical rearrangement into a carboxylic acid, transforming the dissolution-inhibiting additive into a base-solubilizing one and dramatically increasing the dissolution rate of the exposed regions relative to the unexposed film.¹⁰ Because development occurs in aqueous rather than organic solvent, the unexposed resist does not swell during processing, enabling substantially higher resolution than the rubber-based systems. Novolac/DNQ resists served as the workhorse of the semiconductor industry through the g-line and i-line era, supporting manufacturing from feature sizes of several microns down to approximately 250 nm.⁶

As the semiconductor industry pushed below 250 nm feature sizes and transitioned to 248 nm KrF excimer laser exposure sources, the DNQ/novolac platform reached the limit of its patterning capabilities. Novolac resin absorbs strongly at 248 nm, preventing light from penetrating to the bottom of the resist film and producing poorly defined, sloped pattern profiles. More fundamentally, DNQ-based resists are non-amplified systems in which each absorbed photon drives exactly one chemical event, meaning that the limited number of photons delivered at practical exposure doses was insufficient to generate adequate solubility contrast at shorter wavelengths. A solution to both problems was developed by Ito, Willson, and Fréchet in the early 1980s in the form of the chemically amplified resist (CAR).¹¹⁻¹³ Rather than relying on a stoichiometric photochemical reaction, CARs incorporate a photoacid generator (PAG) that produces a strong acid upon exposure to radiation. This acid then acts as a catalyst during a subsequent post-exposure bake (PEB), driving the deprotection of many acid-labile groups along the polymer backbone from a single photon event. In positive-tone CARs, the most widely adopted design uses acid-catalyzed cleavage of hydrophobic protecting groups such as tert-butoxycarbonyl (t-BOC) from a poly(hydroxystyrene)

backbone,¹⁴ generating a hydrophilic carboxylic acid that is readily soluble in aqueous base developer. Because a single acid molecule can catalyze numerous deprotection events before being consumed or quenched, CARs dramatically lowered exposure doses compared to their non-amplified predecessors, directly addressing the sensitivity demands of short-wavelength lithography. This led to their rapid adoption for 248 nm lithography in the 1990s, and their later extension to 193 nm lithography. Here, materials were modified to use the deprotection of a protected acrylate or methacrylate instead of styrenic materials due to opacity issues with poly(hydrostyrene) at 193 nm and the increased stability of the protecting group.¹⁵

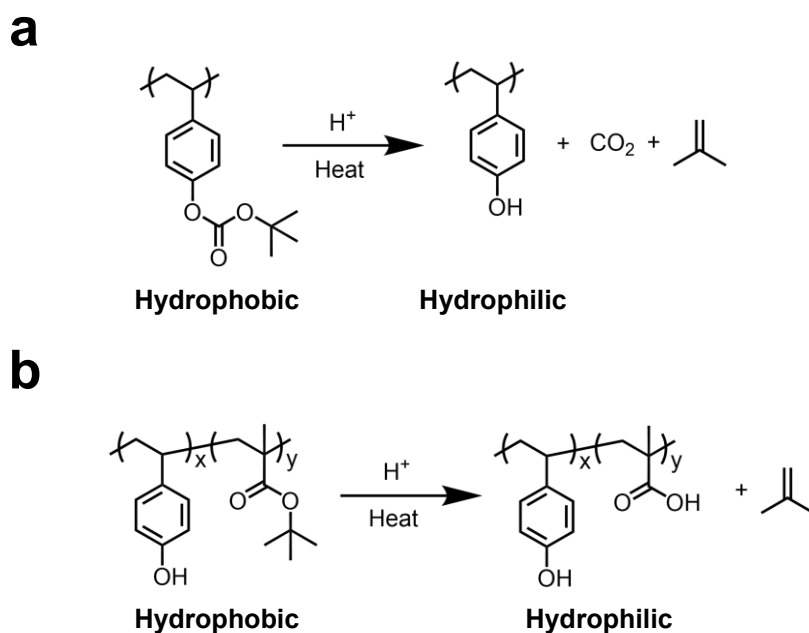


Figure 1.3. Early chemically amplified resists utilized the deprotection of a protected phenol as their solubility switch. (b) Later iterations for 193 nm resists changed to acrylates and methacrylate solubility switches to improve patterning.

1.3 Challenges with Modern Photoresists

The transition from 193 nm ArF immersion lithography to EUV lithography at 13.5 nm represents an extraordinarily large change in exposure wavelength. As 13.5 nm radiation is effectively in the soft X-ray regime, it marks a fundamental shift in the physics governing how light interacts with a resist film. At 193 nm, photons carry approximately 6.4 eV of energy, enough to drive photochemical reactions directly through excitation of valence electrons. At 13.5 nm, each EUV photon carries 92 eV, well above the ionization potential of most organic materials. Rather than driving photochemistry directly, EUV photons initiate a cascade where absorption ejects a primary photoelectron, which in turn generates numerous lower-energy secondary electrons through inelastic scattering events, and it is these secondary electrons that are thought to drive the chemistry in the resist film.^{16, 17} While this electron cascade increases the number of electrons available to perform chemical reactions, the exact mechanisms of many of these reactions remain poorly understood. In many cases, photoresists for EUV lithography were ported over from DUV and empirically tuned to perform under EUV, but development of EUV-specific resists has remained comparatively underexplored.

Compounding this is a severe reduction in the number of photons available to drive resist chemistry. Because EUV photons carry roughly 14 times more energy than 193 nm photons, a given EUV exposure dose contains roughly 14 times fewer photons than an equivalent dose under DUV exposure.¹⁸ Photon absorption is a discrete, probabilistic event, in which the

number of absorbed photons within an area of the resist follows Poisson statistics, with a standard deviation equal to the square root of the mean photon count.¹⁹ As EUV-relevant feature sizes shrink to the order of only tens of square nanometers, the number of photons involved is small enough that this statistical fluctuation, known as shot noise, becomes a significant fraction of the signal itself.^{20, 21} Because of this, even a perfectly uniform, chemically ideal resist will produce patterns with line edge roughness (LER) simply because of the granular nature of light. This photon shot noise contribution to LER has been estimated to account for approximately 60% of total pattern roughness in optimized EUV CAR systems.²² Increasing exposure dose reduces shot noise by increasing the photon count, but this directly reduces wafer throughput, making it undesirable from a manufacturing standpoint. These considerations place significant demands on resist materials to absorb EUV photons efficiently and convert that energy into productive chemistry and motivate the two classes of materials challenges discussed in the following sections: poor EUV absorptivity in conventional organic resists, and stochastic variation arising from chemical heterogeneity in the resist film.

1.3.1 Issues with EUV Sensitivity

A central challenge in designing resist materials for EUV lithography is that the organic polymers used in conventional CARs absorb EUV radiation very weakly. The photoabsorption cross section of a material at a given wavelength determines the probability that an incident photon will be absorbed and initiate chemistry. At 92 eV, the photoabsorption cross section of carbon, hydrogen, and oxygen — the primary constituents of organic resists — is very low, as depicted in Figure X.¹ Quantitatively, a typical organic polymer resist film

of 50 nm thickness absorbs only 15–20% of incident EUV photons, meaning that the majority of incident EUV photons pass through the film without being absorbed by the material.²¹ This directly increases the required exposure dose, limiting throughput and exacerbating shot noise.²³

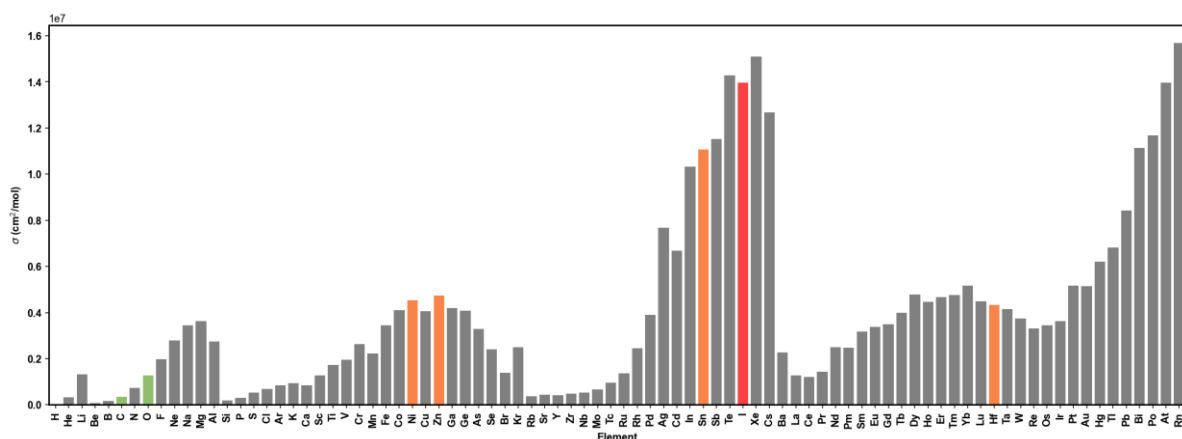


Figure 1.4. EUV photoabsorption cross section from elements with atomic numbers 1-86. Typical organic elements are highlighted in green, relevant metals used in photoresists are in orange, and relevant halogens are highlighted red. Plotted using data from Ref 1.¹

The photoabsorption cross section of an element at EUV energies is determined largely by the availability of accessible inner-shell or semi-core electron levels near 92 eV. For light elements such as carbon and oxygen, no such levels exist at this energy and absorption is entirely valence-dominated. For heavier elements, deep valence or shallow core electrons can be directly ionized by 92 eV photons, giving rise to dramatically higher cross sections that are largely independent of the element's broader molecular structure.²³ This principle motivates two broad strategies for improving the EUV sensitivity of resist materials: incorporation of heavy metals, and incorporation of halogens.

Due in large part to their high EUV absorption cross sections, metal-containing materials have attracted significant interest as photoresist platforms. These systems most commonly take the form of inorganic-organic hybrid materials, in which an inorganic metal-oxide nanoparticle or nanocluster core is surrounded by a shell of organic ligands. Upon EUV exposure, the metal core efficiently absorbs incident photons and generates secondary electrons that drive chemistry in the surrounding ligand shell, inducing either crosslinking or ligand loss depending on the system. This allows the tone of the resist to be tuned through the choice of ligand chemistry, with both negative- and positive-tone imaging having been demonstrated.¹⁰ These metal-organic resist (MOR) platforms were originally developed around hafnium oxide nanoparticles,²⁴⁻²⁶ and they have since been extended to smaller nanoclusters utilizing a broad range of metals including hafnium,^{27, 28} zirconium,²⁹ zinc,³⁰ nickel,³¹ and tin.³² Tin-based systems have been particularly heavily explored, owing to an EUV absorption cross section approximately ten times greater than that of carbon, and organotin resists have emerged as one of the leading MOR platforms currently under evaluation for high-volume EUV manufacturing.³³ Beyond cluster-based systems, hybrid approaches that incorporate discrete metal sensitizer molecules or metal-containing monomers directly into organic polymer matrices have been explored as a route to combining the absorption advantages of strongly absorbing elements with the compositional flexibility and processing compatibility of conventional polymer resists.³⁴⁻³⁶ While MOR platforms offer compelling sensitivity, questions around etch tool contamination, metal ion diffusion into the device stack, and the limited tunability of inorganic cluster systems relative to polymeric alternatives remain active areas of investigation.

Halogens, and iodine in particular, represent a complementary strategy for improving the EUV sensitivity of organic resist materials. Due to the electronic structure of iodine, iodine-containing compounds have EUV absorption cross sections orders of magnitude greater than comparable all-organic materials,^{23, 37} making iodinated monomers an attractive route to improving photon capture without fundamentally departing from a polymer-based resist architecture. Bromine and other halogens show a similar but less pronounced enhancement. Because halogenated monomers can be incorporated into polymer chains through standard synthetic methods, this approach retains the compositional flexibility and processing compatibility that make polymeric resists appealing relative to MOR platforms. To this end, fluorine³⁸ and iodine³⁹ have both been incorporated into CAR systems to improve their EUV absorption properties. Iodine-containing radiosensitizers have also been incorporated into CAR formulations to demonstrate measurable improvements in both sensitivity and LER, which was attributed to the enhanced generation of secondary electrons from iodine sites that more efficiently drive PAG decomposition.⁴⁰

1.3.2 Material Stochastics

Even setting aside photon shot noise, the materials themselves introduce a second, independent source of stochastic variation. In a conventional CAR film, the polymer matrix, PAG molecules, and base quenchers are physically blended rather than covalently integrated, and the spatial distribution of each component within the film is inherently non-uniform. PAG molecules, in particular, have been shown through nanoscale secondary ion mass spectrometry and atomistic simulation to aggregate into domains on the order of several nanometers, driven by the tendency of the bulky PAG counterion to preferentially partition

into hydrophobic regions of the polymer matrix.⁴¹⁻⁴⁶ At 193 nm feature sizes, where a printed line may span hundreds of nanometers and sample thousands of PAG molecules, this heterogeneity is averaged out and has little practical consequence. At EUV dimensions below 20 nm, the number of PAG molecules within a resolution element drops to tens or fewer, and local fluctuations in their concentration become a dominant factor controlling where and how efficiently acid is generated. This chemical stochasticity compounds photon shot noise to produce stochastic defects, including microbridges, line breaks, and edge roughness, that represent one of the primary yield-limiting challenges in EUV manufacturing.^{47, 48}

A key challenge in CAR systems at EUV scales is that the acid molecules central to chemical amplification actively contribute to pattern blur through diffusion. A photogenerated acid molecule may diffuse tens of nanometers during the post-exposure bake, deprotecting polymer chains well beyond the original exposure boundary. Base quenchers are typically included in CAR formulations to limit this diffusion. However, as small molecules dispersed within the film they are also subject to the same stochastic variations as the PAG, and the combined heterogeneity of PAG and quencher distributions contributes significantly to LER.²² One widely explored strategy to address this is the covalent attachment of the PAG, base quencher, or both directly to the polymer backbone, effectively consolidating the photoresist into a single-component material.⁴⁹⁻⁵⁴ By fixing the spatial relationship between acid generator and quencher within the polymer chain, this approach aims to reduce PAG aggregation, limit acid diffusion length, and narrow the distribution of quencher concentrations throughout the film. These materials have shown to improve patterning resolution: one study reported a reduction in the minimum resolvable feature size from 60 nm line/space patterns with a free PAG to 30 nm with a bound equivalent,⁵⁵ and separate work

has demonstrated improvements in both resolution and sensitivity alongside reduced blur when using anion-bound PAGs relative to conventional resist blends.⁵² In addition to attaching PAGs and quenchers to the polymer, covalent attachment of the PAG and base quencher to each other has been shown to reduce unintended acid diffusion by constraining the spatial relationship between acid generator and quencher within a single molecular unit.⁵⁶ Despite these improvements, covalent PAG attachment introduces its own challenges. Tethering ionic groups to the polymer backbone can substantially alter resist solubility in organic solvents, complicating film processing. Furthermore, the range of chemistries compatible with backbone attachment is limited, increasing synthetic complexity and constraining the design space available to resist developers.⁵⁷

From a stochastic standpoint, the single-component cluster architecture of metal-organic resists offers an additional and distinct advantage over conventional CAR blends. Rather than relying on a physically mixed polymer, PAG, and quencher system prone to nanoscale phase segregation, MOR films are significantly more uniform by construction. These generally have a well-defined cluster size of 2 nm or less³⁰ which limits compositional heterogeneity and eliminates the PAG distribution and acid diffusion problems that limit CAR performance at EUV dimensions. The dense inorganic core also provides substantially higher etch resistance than organic polymer systems,²⁶ which is an increasingly important consideration as the resist film thicknesses used in EUV lithography continue to shrink.⁵⁸ As previously mentioned, the disadvantages of MORs primarily stem from concerns about metal contamination during the manufacturing process. In addition, the patterning mechanisms of these materials are still not adequately understood¹⁶ and are the subject of continued research. These remaining limitations of both CARs and MORs motivate continued interest in polymeric resist platforms

that can achieve the molecular uniformity needed to reduce stochastic variation while retaining the synthetic versatility to incorporate diverse functional groups.

1.4 Sequence Control and Polypeptoids

While a wide range of materials have been explored to reduce heterogeneity within photoresists, polymeric systems remain advantageous due to their ease of processing and the broad range of functional groups that can be incorporated into their design. In recent years, sequence control has emerged as a source of increasing interest within the polymer science field, motivated largely by the remarkable functional precision observed in biological macromolecules.⁵⁹ In living systems, polymer chains are constructed with exact monomer sequences to serve diverse roles including information storage,⁶⁰ signaling,⁶¹ hierarchical self-assembly,⁶² and the templating of biomineralization.⁶³ While synthetic techniques for producing polypeptides, DNA, and RNA are well-established,^{64, 65} these biologically derived materials lack the chemical diversity, stability, and scalability of traditional synthetic polymers. Sequence-controlled synthetic polymers represent an effort to find a middle ground between these extremes. Broadly, the methods for achieving sequence control can be classified either as iterative exponential growth (IEG) or iterative sequential growth (ISG). In IEG, sequences are built through repeated coupling reactions — first forming a dimer, then a tetramer, and so on — allowing large molecular weights to be reached relatively quickly.^{66, 67} However, IEG requires stepwise purification after each doubling to remove unreacted oligomers,⁶⁸ and orthogonal chemistries must be used at each stage to ensure selective coupling.^{67, 69} ISG instead adds a single monomer at a time to a growing chain, typically anchored to a solid support matrix. This configuration allows for repeated high-concentration

monomer additions followed by solvent washes, enabling near-quantitative coupling efficiencies at each step without the need for orthogonal chemistry.^{70, 71} The primary drawback of ISG is the large excess of reagents and solvents consumed per synthesis due to the tens to hundreds of injections that occur for each material. Both approaches are ultimately limited in accessible molecular weight by the cumulative effect of imperfect coupling reactions, and post-synthetic purification is generally required to isolate the target sequence.⁵⁹ Despite these limitations, sequence-defined synthetic polymers represent a significant opportunity to systematically study the effects of monomer arrangement on material properties in a controlled and scalable manner.

One particularly attractive sequence-defined polymer platform is the polypeptoid. These bioinspired materials are structurally analogous to polypeptides, with the key distinction that the functional side chain is appended to the backbone nitrogen rather than the α -carbon. This shift eliminates the chiral center inherent to amino acids and removes the hydrogen-bond donor capacity of the amide bond, giving polypeptoids greater conformational flexibility and rendering them fully resistant to proteolytic degradation, which can be advantageous for both biological and materials applications.⁷² Polypeptoids are synthesized via a solid-phase submonomer ISG approach, in which chain growth proceeds through iterative two-step cycles.⁷⁰ First, acylation of a resin-bound functional group is done with a haloacetic acid in the presence of a coupling agent such as N,N'-diisopropylcarbodiimide (DIC). This is followed by nucleophilic displacement of the halide by a primary amine that introduces the desired side chain. Each step proceeds in near-quantitative yield, and because nearly any primary amine can serve as a submonomer (hundreds of which are commercially available), the accessible side chain chemical space is exceptionally broad.⁷³ Importantly, the

submonomer approach eliminates the protection and deprotection steps required in traditional solid-phase peptide synthesis, both simplifying monomer preparation and dramatically increasing accessible scale. While polypeptides are typically synthesized on the order of 10–100 mg per reaction, polypeptoids can readily be produced at gram scale. Additionally, the iterative synthesis is well-suited to robotic automation, reducing both synthesis time and the need for manual oversight.

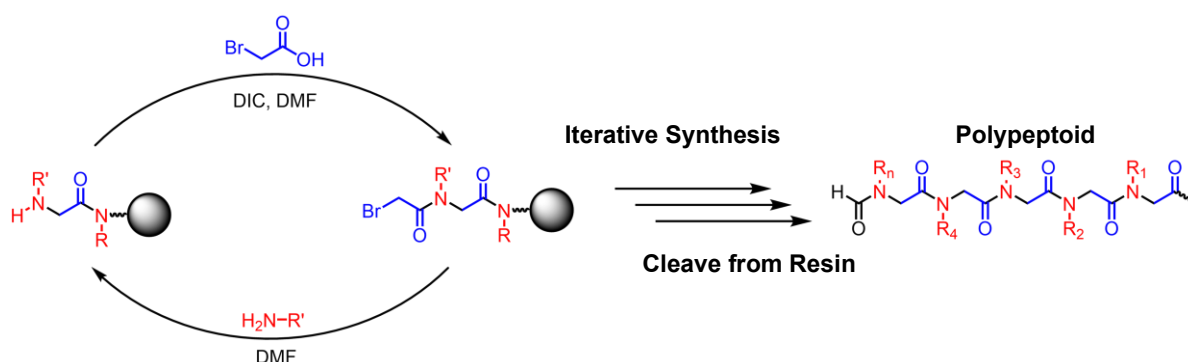


Figure 1.5. Polypeptoids are synthesized via the solid-phase submonomer method through repeated acylation steps with a haloacetic acid followed by a halogen displacement reaction with a primary amine. The N-terminus (left) of the final polypeptoid is frequently capped to improve stability, while the C-terminus (right) is dependent on the resin used in the synthesis.

Polypeptoids have been employed as a platform for studying the effects of sequence and functional group placement across a broad range of applications. In efforts to understand self-assembly and push synthetic polymers toward protein-like structural complexity, polypeptoids have been designed to form two-dimensional crystalline nanosheets,⁷⁴ superhelices,⁷⁵ and ribbons,⁷⁶ with the specific monomer sequence governing the geometry and order of the resulting structures. At the bulk level, monomer identity and placement have been shown to control crystallization behavior and melting in both homopolymers and

copolymers.⁷⁷ Polypeptoids have also been studied extensively as model systems for antifouling materials: zwitterionic polypeptoid brushes have been used to probe the effects of charge placement and ionic strength on protein resistance in biomedical contexts,⁷⁸ while related studies in marine antifouling coatings have revealed sequence-dependent effects of hydrogen bonding capacity and backbone chemistry on antifouling and fouling-release performance.⁷⁹⁻⁸² These examples, among others, demonstrate that monomer sequence is a meaningful and designable materials variable, not merely a synthetic detail. This insight provides motivation for the use of polypeptoids in photoresist applications. Unlike conventional polymer resists, where dispersity in molecular weight, composition, and sequence exacerbates other sources of film heterogeneity to produce patterning defects and edge roughness, polypeptoids can be synthesized in effectively monodisperse form with precise control over the placement of a wide range of functionalities, including solubility switches, etch-resistant groups, and strongly EUV-absorbing species. Early work demonstrated the patterning of polypeptoid photoresists under DUV (248 nm) radiation using a variety of acid-labile protecting groups,⁸³⁻⁸⁵ and subsequent studies have extended this to EUV exposure conditions.⁸⁶ The work presented in this thesis builds on these foundations to investigate the effects of polymer sequence and halogenated EUV-absorbing groups on patterning resolution, sensitivity, and dissolution behavior.

1.5 Dissertation Outline

In this dissertation, sequence-defined polypeptoids are leveraged as a unique polymer platform for the next generation of chemically amplified resists. Their monodispersity and

precise sequence control directly address the heterogeneity limitations of conventional CAR systems, while their broad side chain chemical space enables the independent incorporation of functional groups targeting sensitivity, etch resistance, and dissolution behavior, enabling exploration of properties that are difficult to decouple in traditional multicomponent resist formulations.

To motivate the relevance of precise sequence control to photoresists, **Chapter 2** studies the effects of changing both polypeptoid sequence and molecular weight in polymers of otherwise identical monomer composition on both patterning resolution and sensitivity under Deep Ultraviolet lithography. **Chapter 3** then seeks to understand patterning behavior under state-of-the-art EUV conditions. Specifically, iodine is examined as a means to potentially improve EUV sensitivity in polymeric photoresists due to its high EUV absorption cross section. **Chapter 4** then utilizes the precise sequence control enabled by polypeptoids to better understand the critical ionization model for photoresist dissolution.

Chapter 2: Imparting Sequence Control into Polymeric Photoresists

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2.1 Introduction

The ability to pattern transistors at sub-10 nm length scales is essential for sustaining improvements in microelectronics device performance. Achieving this goal has driven the transition to extreme ultraviolet (EUV, 13.5 nm) lithography and the development of new chemically amplified resists (CARs) optimized for this wavelength.^{10, 16} CARs typically consist of an acid-sensitive polymer matrix, photoacid generators (PAGs), base quenchers, and other components.^{11-13, 87, 88} Upon exposure to radiation, the PAG photodissociates, producing a strong acid that eliminates hydrophobic protecting groups along the polymer chain, yielding a much more hydrophilic material that can then be selectively dissolved using an aqueous base. This process is catalytic, as a single acid molecule can deprotect multiple polymer side groups, effectively amplifying the initial photon exposure and enabling lower dose requirements. The efficiency and sensitivity of CARs have made them a cornerstone of high-resolution lithography for decades.

However, as EUV lithography pushes resolution limits below 10 nm, the inherent complexity and multicomponent nature of CARs introduce new challenges. Intermolecular interactions between polymers, PAGs, and quenchers lead to nanosegregated domains on a length scale comparable to the printed features, leading to both inconsistencies in feature size and the presence of line edge roughness (LER). These structural variations exist even before exposure and thermal processing, as demonstrated both experimentally and through simulation.⁴¹⁻⁴³ To address these limitations, low-stochastic materials have emerged as a promising strategy for improving film homogeneity, reducing LER, and minimizing defect formation. For instance, photoresists made up of metalorganic clusters have been shown to

enhance uniformity by decreasing the size of molecular building blocks and reducing reliance on reactive additives such as PAGs.^{24, 32} However, polymers remain attractive due to their diverse monomer compositions and straightforward processing. Efforts have been made to improve homogeneity in CARs by tethering PAGs to the polymer itself, which has been shown to improve patterning resolution.^{51, 55} Additionally, covalently linking the PAG and quencher can limit acid diffusion into unexposed areas, further improving feature fidelity.⁵⁶ Despite these advances, traditional synthetic polymers inherently exhibit dispersity in molecular weight, composition, and sequence, posing a fundamental barrier to achieving a unimolecular resist material.

Polypeptoids (N-substituted glycines), a class of bioinspired materials,^{59, 72, 89} offer a versatile platform for developing the next generation of low-stochasticity CARs due to their ability to incorporate a wide range of functionalities along a single polymer backbone with precise monomer sequence control. Unlike conventional polymers, polypeptoids are synthesized via a highly efficient solid-phase synthesis route, yielding monodisperse materials with uniform molecular weight, composition, and sequence.^{70, 90} Unlike polypeptides whose yields are limited by significant protection/deprotection chemical steps in solid-phase synthetic routes, polypeptoids are commonly synthesized at gram scale and sequence-specificity up to 50 monomers in length.⁷² This inherent precision significantly reduces nanoscale variability. Additionally, polypeptoids provide broad functionalization potential, allowing for the incorporation of diverse side chains tailored to optimize critical performance parameters such as solubility, sensitivity, and etch-resistance. Polypeptoid photoresists have previously been patterned under deep ultraviolet (DUV, 248 nm) radiation using various acid-labile solubility switches,⁸³⁻⁸⁵ and more recent studies have demonstrated their viability under

EUV radiation.⁸⁶ Interestingly, it has been suggested that for polypeptoid copolymers, an even spacing of functional monomers along the polypeptoid chain improves pattern quality in short, 10-mer materials.⁸⁶ This observation is particularly striking given that traditional models of photoresist dissolution do not account for sequence or proximity of specific functional groups in any meaningful way, instead assuming an average over both compositional and sequence dispersity across many chains.^{91, 92}

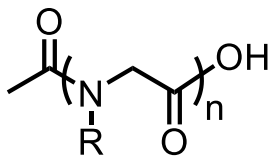
2.2 Methods

All solvents and reagents were purchased from commercial suppliers and used without additional purification. HPLC grade dimethylformamide (DMF) was used for all peptoid synthesis.

2.2.1 Polypeptoid Synthesis

Prior to the polypeptoid synthesis, β -alanine t-butyl ester hydrochloride (Nce·HCl) was freebased to remove the hydrochloride salt. 100 g of Nce·HCl was dissolved in 80 mL of water and placed in an ice bath. While stirring, 240 mL of 2.5M NaOH was added dropwise using an addition funnel. Upon completion, the freebased Nce was extracted into ethyl acetate and dried with sodium sulfate. The solution was then filtered to remove the sodium sulfate, and the ethyl acetate was removed with a rotary evaporator. The product was then stored in a freezer for up to one week. All other solvents and reagents were purchased from suppliers and used without further purification.

Polypeptoids were synthesized using an automated Symphony X synthesizer at BioPACIFIC MIP facilities using previously reported protocols.^{90, 93} 2-Chlorotrityl chloride (CTC) resin (0.91 mmol/g loading, 800 μ mol scale, purchased from Aapptec), was swollen in dichloromethane at 0.02 mL/mg of resin overnight at room temperature. Swollen resin was then transferred into a reaction vessel on the Symphony X and drained. To activate the resin, solutions of 1.2 M bromoacetic acid (BrAA) in dimethylformamide (DMF) and 1.2 M *N,N*-diisopropylethylamine (DIPEA) in dichloromethane (DCM) were added at 0.01 mL/mg of resin and mixed for 2 hours. The solution was then drained, and the resin was rinsed with DMF. Alternating steps of amine displacement (1.5 hours) and bromoacetylation (1 hour) were then performed to synthesize the desired sequences. Amine solutions of phenethylamine and 4-(2-aminoethyl)benzenesulfonamide were prepared at 1M concentration in *N*-methyl-2-pyrrolidone (NMP), while the freebased β -alanine *t*-butyl ester was made in a concentration of 1.5M in NMP. 1.2M BrAA and 2.4M *N,N'*-diisopropylcarbodiimide (DIC) in DMF were used for bromoacetylation steps in a volume ratio of 2:1 BrAA solution to DIC solution, yielding an effective concentration of 0.8M for each. Bromoacetylation steps were repeated an additional time for monomers 11-30 in each sequence to push conversion. Sequences were then acetylated with a mixture of 0.4M acetic anhydride and 0.4M pyridine in DMF for 45 minutes to cap reactive chain ends. A schematic of the final polypeptoid chain ends is shown below.



Scheme 2.1. General structure of a polypeptoid and its chain ends.

Polypeptoids were cleaved in a solution of 30% v/v hexafluoroisopropanol (HFIP) in DCM for 45 minutes. The resulting peptoid solution was drained into vials, and the cleavage was repeated with fresh HFIP for another 45 minutes. After draining, the resin was rinsed with DCM, and once again drained into the same vials. Solvent was then removed under vacuum, and the peptoids were lyophilized overnight to form a powder.

2.2.2 Polypeptoid Purification

Crude polypeptoids products were purified by preparative high-performance liquid chromatography (HPLC) using a Shimadzu Nexera Hybrid chromatography instrument paired with a single quad MS detector at NSF BioPACIFIC MIP facilities. Crude materials were dissolved at 60 mg/mL in a mixture of 70:30 v/v acetonitrile and water and filtered through a 0.45 μ m PVDF syringe filter to remove any particulates or undissolved material. These peptoid solutions were injected into a reverse phase C4 column (XBridge Protein BEH C4 OBD Column, 300 $^{\circ}$ A, 5 μ m, 19 mm x 150 mm) and separated on a 55-90% solvent B gradient over 15 minutes. Solvent A was composed of water with 0.1% v/v formic acid, while solvent B consisted of acetonitrile with 0.1% v/v formic acid. Collected fractions were dried with a rotary evaporator and then lyophilized to remove excess solvent.

Purified polypeptoid sequences were verified by analytical HPLC mass spectrometry. The purified samples were injected into a C4 column (XBridge Protein BEH C4 Column, 300°A, 3.5 μ m, 4.6 mm x 100 mm) with a 5-95% solvent B gradient over 30 minutes, using the same solvents as in preparative HPLC.

Table 2.1. Polypeptoid samples and molecular weights from analytical HPLC-MS.

Sample name	Theoretical MW (g/mol)	Exp. m/z	Ion type
Alt. 10-mer	1950.33	1949.92	$[M+H]^+$
Alt. 20-mer	3840.61	1920.40	$[M+2H]^{2+}$
Alt. 30-mer	5730.90	1909.90	$[M+3H]^{3+}$
Int. 20-mer	3840.61	1920.40	$[M+2H]^{2+}$
Blocky 20-mer	3854.64	1926.91	$[M+2H]^{2+}$

2.2.3 Polypeptoid Photoresist Sample Preparation

All procedures in sections 2.2.3 – 2.2.5 were performed in the UCSB Nanofabrication Facility. Polypeptoid photoresists were made by first making a 20 mg/mL solution of polypeptoid in propylene glycol methyl ether (PGME). Separately, a 4 mg/mL solution of triphenylsulfonium nonafluorobutanesulfonate (TPS nonaflate) was made, and each were sonicated on low power for three minutes. The two solutions were then combined in a 1:1 v/v ratio and sonicated for another 3 minutes. All work with TPS nonaflate was conducted in areas with UV-filtered lighting to avoid premature activation of the photoacid generator.

To prepare for DUV exposure, DUV42P-6 (Brewer Science), an underlayer used for improving adhesion and reducing reflections during patterning, was spin coated onto a 4-inch wafer at 3500 rpm with a 700 rpm/s ramp. This was then heated to 205°C for 1 minute to crosslink the material, yielding a film of approximately 60 nm. The peptoid photoresist was

then spin coated onto the same wafer at 1000 rpm for 45 seconds, with a 200 rpm/s ramp. A post-apply bake (PAB) was then performed at 110°C for 1 minute, yielding a film of approximately 55 nm in thickness. Film thickness was characterized by a Woolam M-2000DI Variable Angle Spectroscopic Ellipsometer after each of these steps.

2.2.4 248 nm Exposure and Development of Patterns

After coating, wafers were then loaded into an ASML 5500 248 nm (KrF) DUV stepper, where they were exposed through one of two reticles. The first was a resolution chart containing both bright- and dark-field line-space patterns from 2 μm half-pitch down to 130 nm half-pitch, which was used to evaluate photoresist performance at a variety of sizes at a constant exposure dosage of 100 mJ/cm². The second was a blank reticle that was used to create contrast curves of normalized thickness vs dose. Wafers then underwent a post-exposure bake (PEB) for 1 minute at 105°C unless otherwise stated. Wafers were then developed for 15 seconds in a solution of tetramethylammonium hydroxide (TMAH) in water at a concentration of 0.238% by weight. A simplified version of this process is depicted in **Figure 2a**.

2.2.5 Characterization of Patterns

Patterns were characterized by a combination of atomic force microscopy (AFM) and scanning electron microscopy (SEM). AFM measurements were performed on a Bruker ICON instrument using PeakForce Tapping® at a rate of 0.1 Hz over 8-10 μm to obtain depth profiles of patterns for polypeptoid photoresists at both 1.4 μm and 400 nm half-pitch. A JEOL IT800SHL Field Emission SEM was used to obtain arial images of the patterns obtained by

each sequence. Images were taken in the standard imaging mode using a secondary electron detector. An accelerating voltage of 5 kV was used across all samples. Prior to SEM measurements, approximately 3 nm of AuPd was deposited onto each sample with a Hummer® sputtering system to reduce charging and prevent sample degradation under the electron beam.

2.3 Results and Discussion

Solid-phase synthesis of polypeptoids enables the creation of monodisperse polymeric photoresists with diverse functionalities. This work utilizes polypeptoids that incorporate three key functional groups, shown in **Figure 2.1a**. The first is a tert-butyl ester (**Nce**), which functions as a solubility switch similar to poly(tert-butyl methacrylate) (PtBMA) in traditional polymeric photoresists. Upon exposure to acid and heat, the t-butyl group cleaves, forming a carboxylic acid that increases solubility in aqueous base developer. The second functionality, an aromatic phenethyl group (**Npe**) enhances hydrophobicity and raises the glass transition temperature (T_g) of the material, reducing the solubility of unexposed material. Aromatic groups also improve etch-resistance in polymeric photoresists.⁹⁴ The third monomer, an aromatic sulfonamide (**Nsf**), modulates sequence polarity and further increases T_g by hydrogen bonding with carbonyl groups on **Nce** side chains and the polypeptoid backbone. To maintain consistency, all polypeptoids in this study contained 50% **Nce**, approximating the PtBMA content in conventional polymeric photoresists.

The sequence specificity of polypeptoids enables a systematic investigation of photoresist behavior across varying chain lengths and architectures, resulting in the model sequences shown in **Figure 2.1b**. Since solubility scales inversely with molecular weight, chain length is expected to influence dark loss (the amount of unexposed film removed in the developer), motivating the synthesis of polypeptoids ranging from 10 to 30 monomers. To examine the impact of monomer sequence on photoresist performance, 20-mer polypeptoid sequences were designed with architectures ranging from fully alternating—where **Nce** units are evenly distributed—to fully blocky, as illustrated in **Figure 2.1b**. Since polypeptoids with phenethyl-rich blocks tend to crystallize,⁷⁷ a single phenylpropyl group was incorporated into the blocky sequence to disrupt potential π - π stacking and maintain an amorphous material. All three sequences exhibited similar glass transition temperatures (73-75°C), as shown in **Figure S7**.

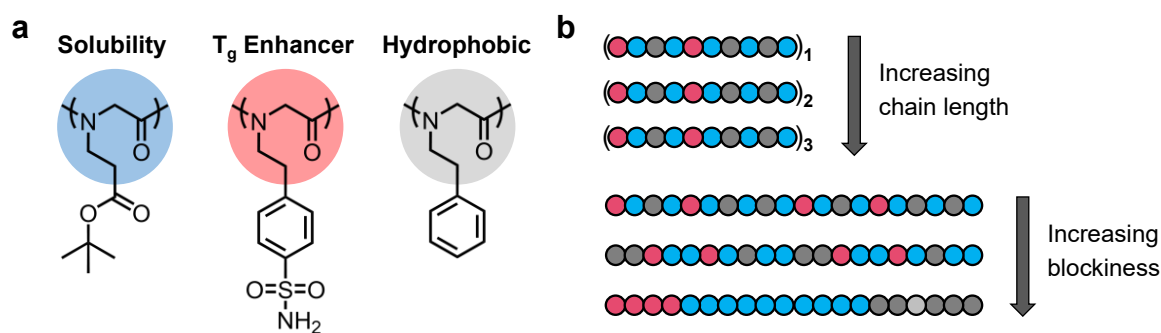


Figure 2.1. (a) Polypeptoid photoresists were composed of an acid-sensitive solubility switch, aryl sulfonamides, and aromatic side chains. (b) Polypeptoid sequences were designed to vary chain length and sequence at constant composition. One phenylpropyl group, denoted by the light grey circle, was included to avoid crystallization in the blocky sequence.

Upon DUV exposure, all polypeptoid photoresists successfully formed positive tone patterns when formulated with a triphenylsulfonium nonafluorobutanesulfonate (TPS nonaflate) PAG, with exposed areas dissolving in aqueous tetramethylammonium hydroxide (TMAH) developer as shown in **Figure 2.2a**. The exposure dose, post-exposure bake (PEB), and development conditions were optimized for the alternating 20-mer polypeptoid sequence and applied uniformly across all samples. While patterns formed on bare silicon wafers, poor adhesion led to delamination. To address this, a crosslinkable polymer underlayer (DUV42P-6, Brewer Science) was introduced, improving adhesion and pattern fidelity. A detailed summary of all processing procedures can be found beginning in **Section S1.3** of the Supplementary Information.

Increasing polypeptoid chain length enabled successful pattern formation by decreasing the solubility of unexposed regions in the aqueous base developer. The critical polymer concentration for dissolution is inversely proportional to $\sqrt{N}$, where N is the polymer chain length.⁹⁵ The 10-mer polypeptoid (**Figure 2.2b**) lacked sufficient resistance to the basic TMAH developer and dissolved or washed off completely in both exposed and unexposed regions. In comparison, the unexposed 20- and 30-mer polypeptoids remained intact, enabling clear differentiation between exposed and unexposed regions after development. An additional factor influencing solubility is the carboxylic acid C-terminus (**Scheme S1**), which increased polypeptoid solubility in aqueous base. This effect is more pronounced in shorter polypeptoids, where terminal groups constitute a larger fraction of the overall structure, contributing to the increased solubility of the 10-mer. SEM and AFM images (**Figure 2.2c-d**) show qualitatively similar patterns for the 20- and 30-mer polypeptoids at a 400 nm half-pitch, indicating that beyond 20 repeat units, extended chain length provides no significant

patterning advantage while increasing synthetic reaction time linearly with monomer count. As a result, the 20-mer polypeptoid represents an optimum in performance with synthetic ease for these materials whose monomers are added sequentially via the robotic synthetic procedure.

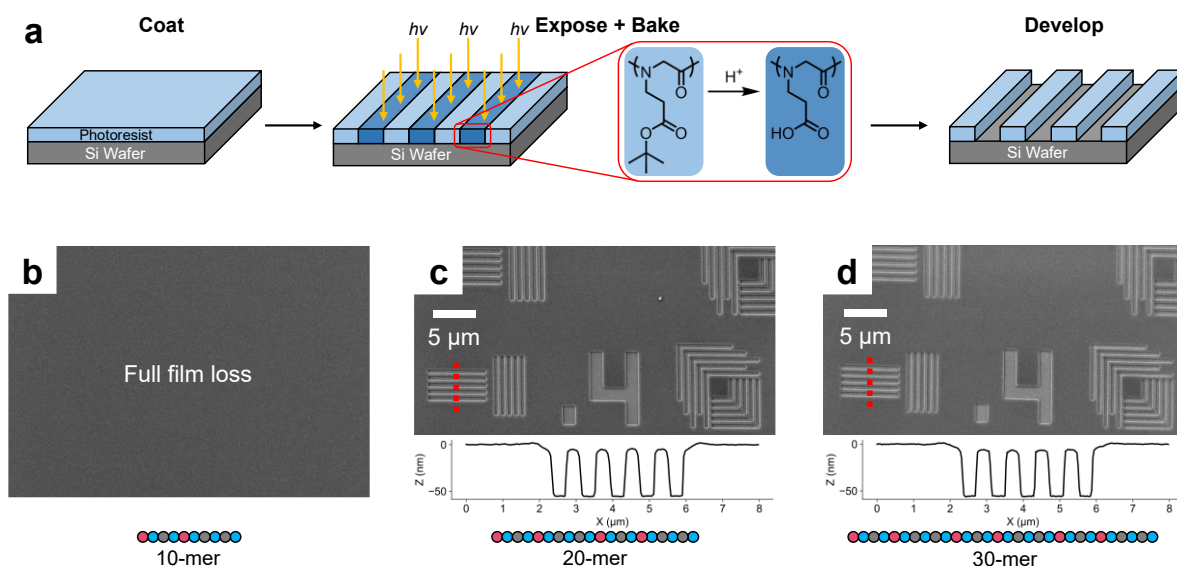


Figure 2.2. (a) Simplified workflow of photoresist processing. DUV patterns from alternating (b) 10-mer, (c) 20-mer, and (d) 30-mer polypeptoids after equivalent exposure, post-exposure bake (PEB), and development conditions. Both exposed and unexposed regions of the 10-mers fully dissolve away. 20- and 30-mers show qualitatively similar performance, and AFM traces (taken along the red dotted lines) show that the original 55 nm film thickness remains in unexposed areas.

Contrary to what would be predicted by conventional dissolution models, patterning results for the three different 20-mers demonstrate that polymer sequence affects photoresist sensitivity and resolution. As shown in **Figure 2.3a-c**, increasingly blocky sequences exhibit

reduced patterning resolution under identical exposure, bake, and development conditions. This degradation in pattern quality may stem from differences in either sensitivity—where each sequence requires a different exposure dose for sufficient deprotection—or acid diffusion, with higher diffusion rates in the blockier sequences potentially causing a higher number of deprotection events over a larger area than initially exposed resulting in more diffuse patterns.

To investigate sequence-dependent sensitivity, DUV contrast curves were measured for all three materials. As shown in **Figure 2.3d**, the exposure dose required for solubilization increases from blocky to alternating sequences, suggesting more acid-catalyzed deprotection occurs in blockier sequences. It has been reported that triphenylsulfonium (TPS) nonaflate PAGs are better solvated by side chains that can undergo hydrogen bonding, and that they tend to aggregate in hydrophobic environments akin to polystyrene.⁴³ It is therefore possible that the blocky polypeptoid sequence impacts the distribution of PAG molecules in the photoresist film, perhaps preferentially settling in areas containing higher concentrations of the sulfonamide and t-Bu ester. This, combined with the close proximity of t-Bu ester solubility switches to one another, then enables deprotection at lower doses. In comparison, we hypothesize that the alternating sequence results in a more homogeneous film due to the even spacing of functional groups along the polymer backbone.

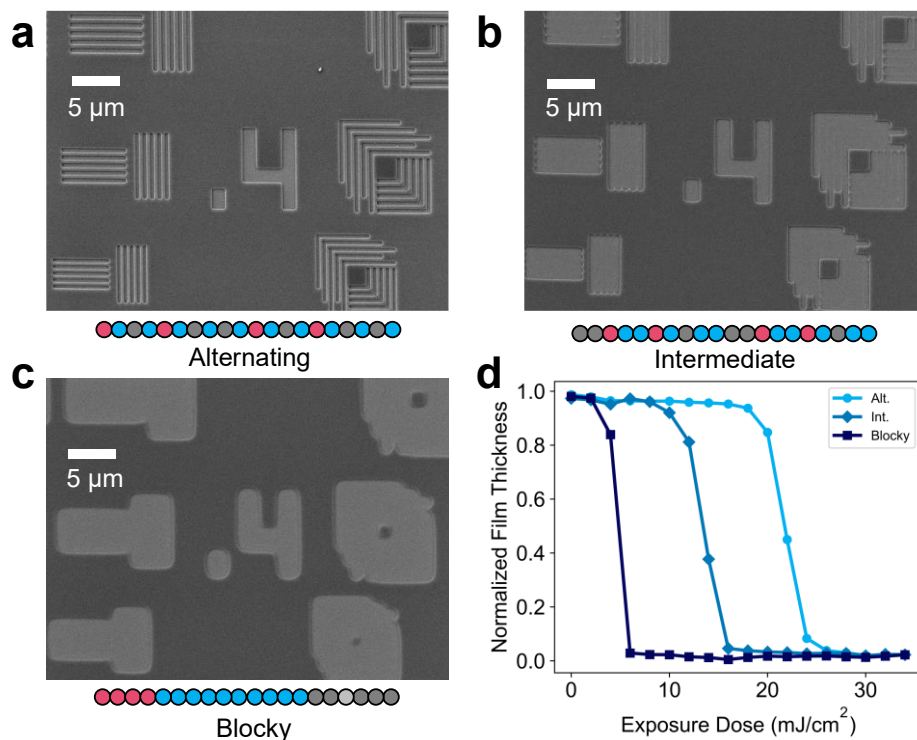


Figure 2.3. DUV patterns appear increasingly overexposed when moving from (a) alternating to (b) intermediate to (c) blocky polypeptoid 20-mers after equivalent exposure and processing conditions (d) DUV contrast curves show increasing sensitivity for 20-mer polypeptoid sequences as blockiness increases.

While patterning results vary significantly across the different polypeptoid sequences under identical processing conditions, none of the sequences were inherently unpatternable. Instead, each required unique optimization to achieve satisfactory results. As shown in **Figure 2.4**, simply lowering the post-exposure bake (PEB) temperature by 15°C dramatically improved the pattern quality of the blocky sequence, whereas the same adjustment rendered the alternating sequence undevelopable. Indeed, this difference can be used to understand the difference in susceptibility to acid-catalyzed deprotection between the two systems. The

reaction rate constant for acid-catalyzed deprotection in chemically amplified resists follows an Arrhenius dependence on temperature.⁹⁶ The fact that lowering the PEB temperature reduces the extent of development in both sequences is indicative of a decrease in deprotection rates. However, the line-thinning observed in both sequences at lower temperatures suggests that acid diffusion also plays a role in the observed patterning differences, as diffusion coefficients also scale with temperature. At the lower PEB temperature, while the blocky sequence was patternable, the exposed regions were still 30% wider than the unexposed regions despite a symmetric expected pattern, indicating that lateral acid diffusion was still very high in these systems. This resulted in deprotection occurring significantly beyond the regions of exposure. This lateral diffusion appears to occur to a lesser extent in the alternating sequence, as the pattern spread is significantly decreased compared to the blocky version at both temperatures. While it is well understood that each new photoresist formulation requires co-optimization between chemistry and processing conditions, these results indicate that not only does sequence directly control patternability in a way not predicted by conventional models, but also that this effect means that each sequence may require a different process optimization in terms of exposure times and post-exposure bake which affect reactive chemistry.

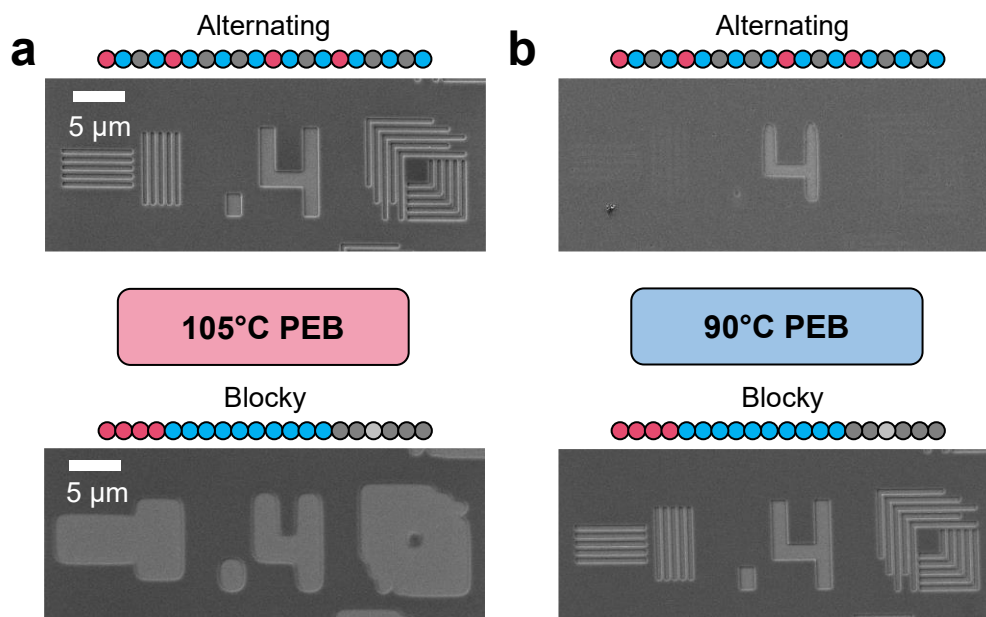


Figure 2.4. Reducing post-exposure bake temperature from (a) 105°C to (b) 90°C reduces reaction rates and limits diffusion, enabling realization of patterns in the blocky polypeptoid sequence while rendering the alternating sequence severely underdeveloped.

2.4 Conclusions

In conclusion, this study demonstrates that polymer sequence and chain length significantly influence the patterning performance of photoresists, alongside standard process variables such as dose and bake conditions. Sequence-defined polypeptoids were designed to mimic the composition and functionality of traditional photoresists while eliminating the dispersity inherent to conventional polymer synthesis. Chain length comparisons revealed a critical threshold necessary to prevent the dissolution of unexposed regions and achieve successful pattern formation. Surprisingly, monomer sequence had a pronounced effect on both sensitivity and resolution. Blocky sequences required lower exposure doses but produced more diffuse patterns under identical processing conditions. However, resolution improved

by lowering processing temperatures to slow both deprotection kinetics and acid diffusion, suggesting that optimal conditions may vary depending on sequence architecture. These findings highlight polymer sequence as a powerful yet underexplored tool for tuning resist performance and reducing material inhomogeneities—an increasingly important consideration as next-generation photoresists push the limits of nanoscale patterning.

2.5 Acknowledgements

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2.6 Appendix

Analytical HPLC Chromatograms

All mass spectra presented in the figures below are averaged over the product peaks in the chromatograms. Note that the relative intensities of the mass spectra are not quantitative, and only the chromatograms are used to evaluate sample purities. Multiple peaks show up in the spectra due to different ions (i.e. $[M+2H]^{2+}$ and $[M+3H]^{3+}$) being formed by the same polypeptoid during mass spectrometry.

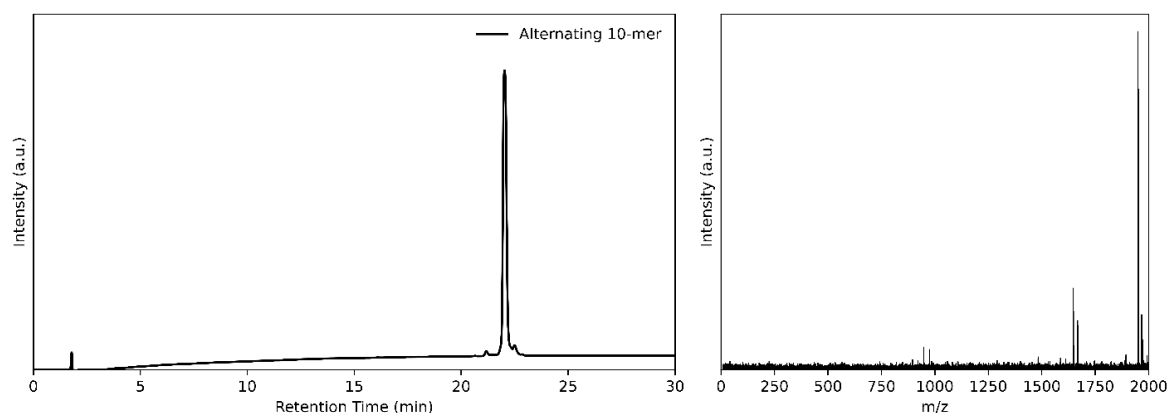


Figure 2.5. HPLC-MS chromatogram and mass spectra of the alternating 10-mer polypeptoid.

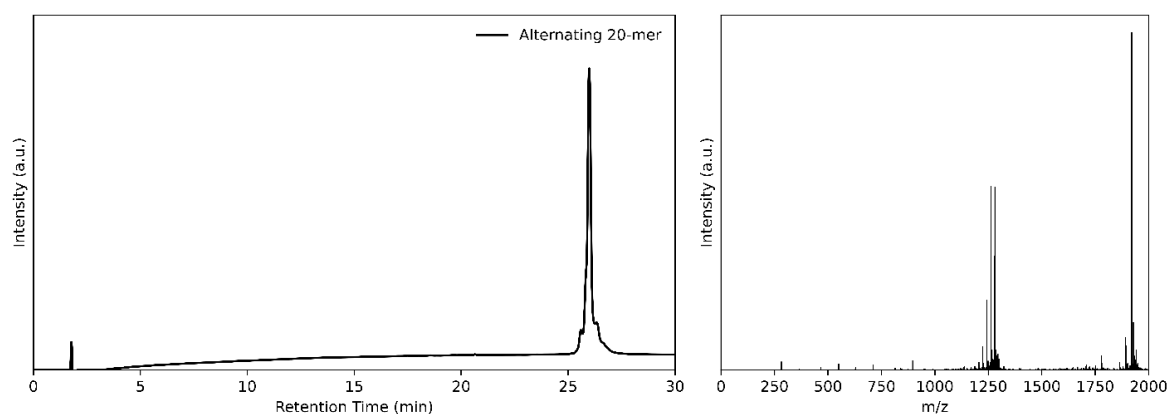


Figure 2.6. HPLC-MS chromatogram and mass spectra of the alternating 20-mer polypeptoid.

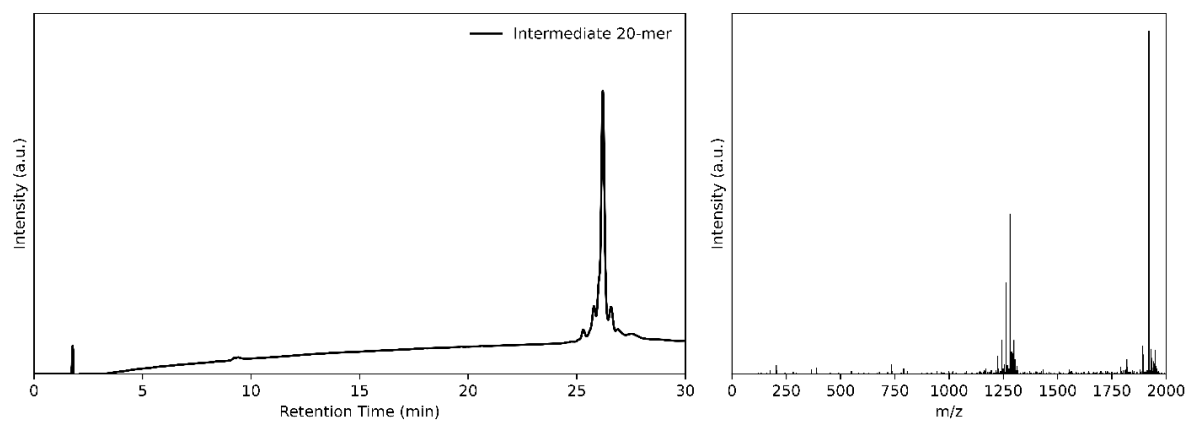


Figure 2.7. HPLC-MS chromatogram and mass spectra of the intermediate 20-mer polypeptoid.

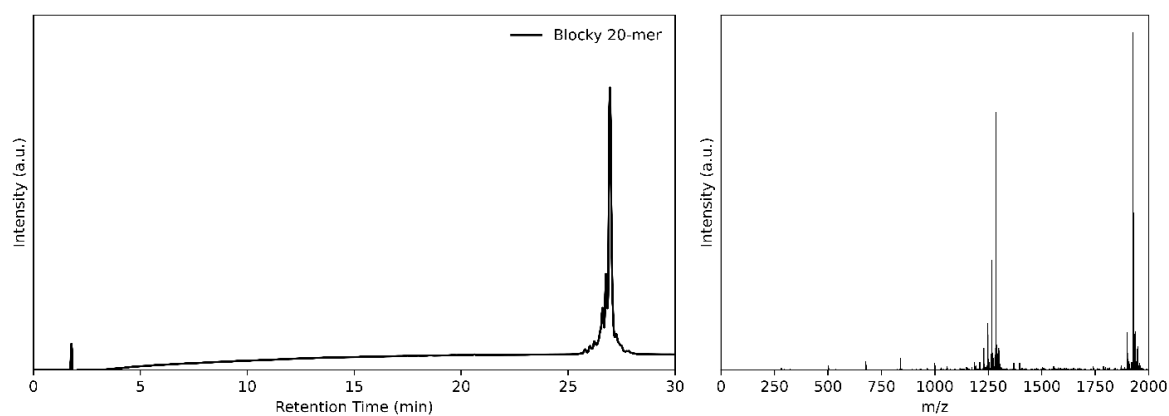


Figure 2.8. HPLC-MS chromatogram and mass spectra of the blocky 20-mer polypeptoid.

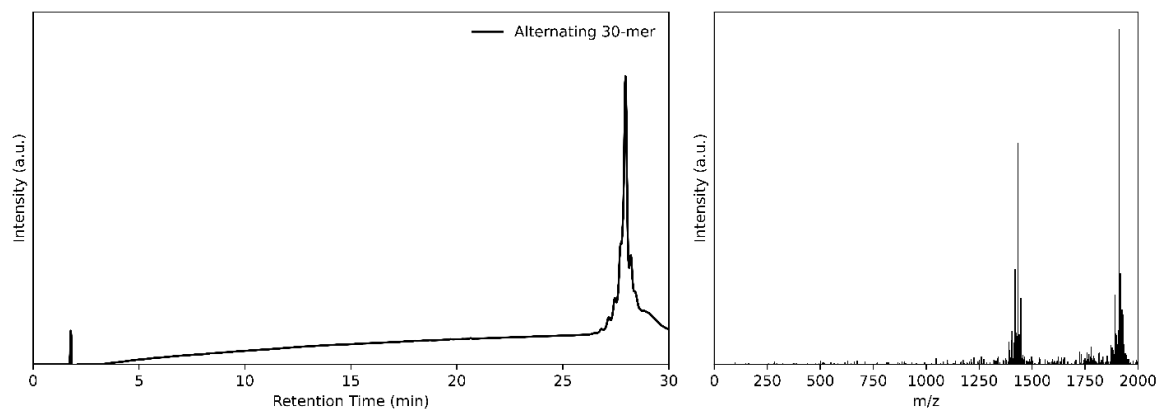


Figure 2.9. HPLC-MS chromatogram and mass spectra of the alternating 30-mer polypeptoid.

Polypeptoid Glass Transition Temperatures

Differential scanning calorimetry (DSC) measurements were performed on a TA Instruments DSC 250 at a heating rate of 10°C/min over a temperature range of 0-120°C. The reported DSC traces were each taken from the third heating cycle.

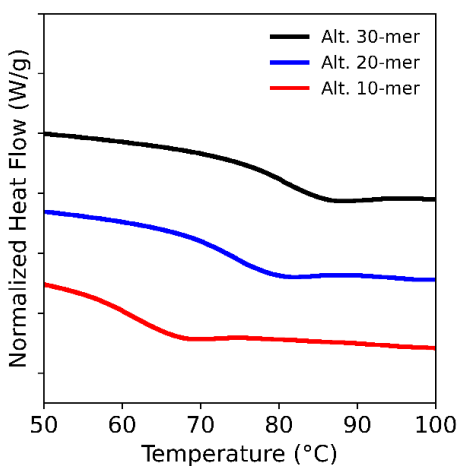


Figure 2.10. DSC traces (exo-up) for alternating polypeptoid sequences at different chain lengths.

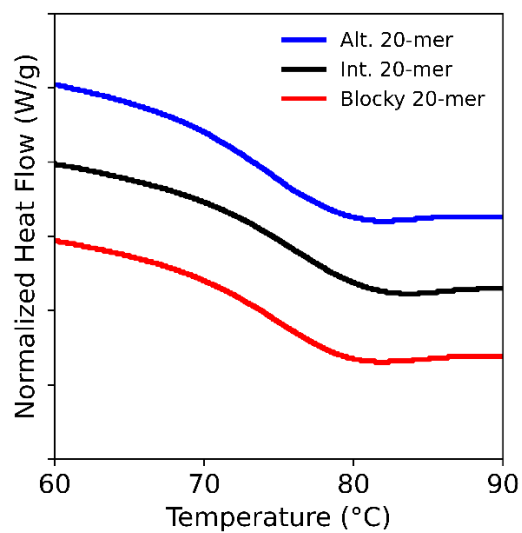


Figure 2.11. DSC traces (exo-up) for 20-mer polypeptoid sequences.

Table 2.2. Glass transition temperatures for the reported polypeptoid sequences.

Sample name	Glass Transition Temperature
Alt. 10-mer	61.7°C
Alt. 20-mer	72.8°C
Alt. 30-mer	80.5°C
Int. 20-mer	75.3°C
Blocky 20-mer	73.4°C

Chapter 3: Tuning EUV absorption and sensitivity of polypeptoid photoresists through iodine incorporation

Text and figures reprinted and adapted from:

Tuning EUV absorption and sensitivity of chemically amplified polypeptoid photoresists through iodine incorporation. **Adams, C. P.**; Kostko, O.; Yuan, C.; Zhang, Q.; Ober, C. K.; Segalman, R. A. *In preparation*. (2026)

Collaborator Contributions:

Oleg Kostko (Lawrence Berkeley National Laboratory) performed photoelectron spectroscopy, total electron yield, and outgassing measurements. Qi Zhang (Lawrence Berkeley National Laboratory) performed EUV reflectometry measurements.

3.1 Introduction

Semiconductor production around the world has long relied on a process known as photolithography to fabricate microelectronics devices. Here, light is used to pattern a photoresist in the first step to making layers of transistors. The predominant class of photoresists since its introduction in the 1980s has been the chemically amplified resist (CAR). CARs are polymeric materials composed primarily of a polymer bearing acid-labile protecting groups and a photoacid generator (PAG), among other components.^{11-13, 87, 88} Upon exposure to light, the PAG photodissociates to form a strong acid that, upon heating, causes the deprotection of the polymer matrix. This results in a solubility change of the polymer from hydrophobic to hydrophilic, enabling selective dissolution of the exposed regions in an aqueous base developer. This process is catalytic, meaning that one photon can cause multiple deprotection reactions, effectively amplifying the reactive power of each photon and lowering the required exposure dosage during patterning. This platform has been extremely effective, and CARs have been the predominant resist platform for decades.

However, some issues with CARs have arisen as the industry has shifted from “deep ultraviolet” (DUV, 248 or 193nm) to “extreme ultraviolet” (EUV, 13.5 nm) radiation in an effort to pattern smaller features.¹⁰ As opposed to DUV, where activation of the PAG is caused by the absorption of low-energy photons, PAG activation under EUV radiation is caused by secondary electrons generated from ionizing radiolysis of the film. Because of this, the intrinsically low EUV absorption of conventional CARs poses a fundamental sensitivity challenge. The photoabsorption cross section of a material at a given wavelength determines the probability that an incident photon will be absorbed and initiate chemistry. Most organic

polymers used in CARs are composed predominantly of carbon, hydrogen, and oxygen, which have relatively small photoabsorption cross sections at 13.5 nm.^{1, 19} As a result, a significant fraction of incident EUV photons pass through the resist film without being absorbed, reducing sensitivity and requiring higher exposure doses. One approach to addressing this is the incorporation of high-absorbing atoms with large photoabsorption cross sections into the resist material. Metal-containing resists, including those based on tin³² and hafnium,²⁴ have demonstrated dramatically improved EUV absorption and sensitivity,¹⁹ and have attracted considerable attention as a result. Halogenated organic resists represent an alternative approach, retaining the processability of conventional polymers while incorporating atoms with enhanced EUV absorption. In particular, fluorine has been explored as a beneficial additive, with perfluorinated and partially fluorinated polymers demonstrating improved absorption coefficients and sensitivity relative to their non-fluorinated counterparts.^{38, 97} The covalent incorporation of fluorine into the polymer backbone or sidechains avoids the compatibility and segregation issues associated with small-molecule additives, making it an attractive design strategy. However, per- and polyfluoroalkyl substances (PFAS) face increasing regulatory scrutiny due to their environmental persistence, and the long-term viability of fluorinated resist chemistries is uncertain.⁹⁸ Iodine presents a compelling alternative: it has a substantially larger photoabsorption cross section than fluorine at 13.5 nm,^{1, 19} can be incorporated covalently into organic materials, and does not carry the same regulatory concerns. Recent publications have shown increases to EUV absorption and acid generation with the inclusion of iodine in a CAR,³⁹ and improved sensitivity of a conventional CAR both when iodine was incorporated in a topcoat and when it was included in the CAR

formulation as a radiosensitizer.⁴⁰ However, iodine-containing organic photoresists remain relatively underexplored.

As EUV has enabled patterning in the sub-10 nm regime, CARs have also begun to face challenges stemming from their multicomponent nature. Intermolecular interactions between these components, which include small molecule PAGs and quenchers, and the polymer matrix lead to nanosegregated domains that exist during all stages of film processing,⁴¹⁻⁴³ leading to inconsistencies in feature size and the presence of line-edge roughness. Various strategies have been employed to improve the homogeneity of CARs, such as tethering the PAG to the polymer backbone to improve patterning resolution.^{49, 51, 52, 55} Additionally, covalently bonding the PAG and quencher has been shown to mitigate image blur due to acid diffusion into unexposed regions, enabling further control over feature definition.⁵⁶ Despite these improvements, the traditional synthetic polymers found in CARs have inherent dispersity in molecular weight, monomer composition, and sequence that prevent the realization of a truly uniform material.

Polypeptoids (N-substituted glycines)^{59, 72, 89} are a uniquely positioned polymer platform for the next generation of CARs, combining a wide range of accessible functional groups with precise control over monomer sequence and molecular weight. Unlike conventional polymers, polypeptoids can be synthesized with perfectly defined monomer sequences, compositions, and chain lengths through iterative sub-monomer solid-phase synthesis, eliminating the statistical variability inherent to free-radical and other chain-growth polymerization methods.^{70, 90} Compared to polypeptides, polypeptoids benefit from highly efficient reaction steps that avoid repeated protection and deprotection cycles, enabling gram-scale synthesis of

sequences up to 50 monomer units in length.⁷² This synthetic flexibility also provides access to a wide range of non-natural functional groups, allowing targeted incorporation of moieties that optimize key photoresist performance parameters such as resolution, sensitivity, and etch resistance. Polypeptoids have previously been reported as EUV and DUV photoresists across multiple patterning modalities, including traditional positive-tone (exposed area dissolves) CARs using acid-labile solubility switches^{83-86, 99} and negative-tone (exposed area remains) resists where hydrophobicity instead increases after exposure.^{100, 101} Critically, sequence control has been demonstrated to significantly influence patterning performance, establishing that the precision afforded by sub-monomer synthesis translates directly into practical lithographic advantages.⁹⁹ Here, we leverage this platform to systematically investigate the effects of iodine incorporation on EUV absorption, electron generation, and resist performance in a series of sequence-defined polypeptoid CARs.

3.2 Methods

All solvents and reagents were purchased from commercial suppliers and used without additional purification. HPLC grade dimethylformamide (DMF) was used for all peptoid synthesis.

3.2.1 Polypeptoid Synthesis

Prior to synthesis, β -alanine t-butyl ester hydrochloride (Nce·HCl) was freebased to remove the hydrochloride salt. 100 g of Nce·HCl was dissolved in 80 mL of water and cooled in an ice bath, and 240 mL of 2.5 M NaOH was added dropwise with stirring via addition

funnel. The freebased product was extracted into ethyl acetate, dried over sodium sulfate, filtered, and concentrated by rotary evaporation, then stored at -20°C for up to one week.

Polypeptoids were synthesized on an automated Symphony X synthesizer at BioPACIFIC MIP facilities following previously reported protocols.^{90, 93} 2-Chlorotrityl chloride (CTC) resin (0.91 mmol/g, 800 μmol scale, Aapptec) was swollen overnight in DCM at 0.02 mL/mg resin at room temperature, then transferred to the synthesis vessel and drained. The resin was activated by treatment with 1.2 M bromoacetic acid (BrAA) in DMF and 1.2 M *N,N*-diisopropylethylamine (DIPEA) in dichloromethane (DCM) (0.01 mL/mg resin) for 2 hours, then drained and rinsed with DMF. Peptoid chains were assembled through alternating bromoacetylation and amine displacement steps. Amine solutions of benzylamine, 4-iodobenzylamine, and 4-(2-aminoethyl)benzenesulfonamide were prepared at 1 M in *N*-methyl-2-pyrrolidone (NMP; freebased Nce was prepared at 1.5 M in NMP. Bromoacetylation was performed using 1.2 M BrAA and 2.4 M *N,N'*-diisopropylcarbodiimide (DIC) in DMF (2:1 v/v, 0.8 M effective concentration) for 1 hour, with a repeated coupling step for monomers 11–30 to drive complete conversion. Amine displacement steps were conducted for 1.5 hours. Chains were capped by formylation with equal amounts of 1M formic acid and 1M DIC in NMP for 45 minutes.

Peptoids were cleaved from the resin with two sequential treatments of 30% v/v hexafluoroisopropanol (HFIP) in DCM (45 minutes each). The combined cleavage solutions were drained, the resin was rinsed with DCM, and all fractions were pooled. Solvent was removed under vacuum and the crude peptoids were lyophilized overnight to yield a dry powder.

3.2.2 Polypeptoid Purification

Crude peptoids were purified by preparative reverse-phase HPLC using a Shimadzu Nexera Hybrid instrument with single-quadrupole MS detection at BioPACIFIC MIP facilities. Samples were dissolved at 60 mg/mL in 75:25 acetonitrile:water and filtered through a 0.45 μm PVDF syringe filter prior to injection. Separation was performed on a C4 column (XBridge Protein BEH C4 OBD, 300 Å, 5 μm , 19 $\times$ 150 mm) using a 65–95% solvent B gradient over 15 minutes, where solvent A was water with 0.1% formic acid and solvent B was acetonitrile with 0.1% formic acid. Collected fractions were concentrated by rotary evaporation and lyophilized to remove residual solvent.

Purified sequences were verified by analytical HPLC-MS using a C4 column (XBridge Protein BEH C4, 300 Å, 3.5 μm , 4.6 $\times$ 100 mm) with a 5–95% solvent B gradient over 30 minutes using the same solvent system.

Table 3.1. Polypeptoid samples and molecular weights from analytical HPLC-MS.

Sample name	Theoretical MW (g/mol)	Exp. m/z	Ion type
0 Iodine	3742.43	1871.86	$[\text{M}+2\text{H}]^{2+}$
2 Iodine	3994.22	1997.26	$[\text{M}+2\text{H}]^{2+}$
4 Iodine	4246.01	1416.11	$[\text{M}+3\text{H}]^{3+}$
6 Iodine	4497.80	1500.04	$[\text{M}+3\text{H}]^{3+}$

3.2.3 Polypeptoid Film Preparation

All procedures in this section were performed in the UCSB Nanofabrication Facility. Polypeptoid photoresists were prepared by dissolving polypeptoid samples in propylene glycol methyl ether (PGME) at a concentration of 20 mg/mL and triphenylsulfonium

nonafluorobutanesulfonate (TPS nonaflate) in PGME at a concentration of 4 mg/mL. Each solution was sonicated independently at low power for 3 minutes, then combined in a 1:1 v/v ratio and sonicated for an additional 3 minutes. All handling of TPS nonaflate was carried out under UV-filtered lighting to prevent premature activation of the photoacid generator. Characterization PES and TEY characterization were done in the absence of PAG, and the peptoids were dissolved at a concentration of 10 mg/mL in PGME.

For samples intended for EUV contrast curves, an adhesion-promoting antireflection underlayer (DUV42P-6, Brewer Science) was first spin-coated onto a 4-inch wafer at 3500 rpm (700 rpm/s ramp) and baked at 205°C for 1 minute to crosslink the film, yielding a thickness of approximately 60 nm. This underlayer was omitted from outgassing, PES, and TEY measurements to ensure accurate characterization of the polypeptoid samples. The peptoid solution was then spin-coated at 2000 rpm for 40 seconds (400 rpm/s ramp) and subjected to a post-apply bake (PAB) at 110°C for 1 minute, producing a film approximately 30-35 nm thick. Film thickness was measured after each deposition step by variable angle spectroscopic ellipsometry (Woolam M-2000DI).

3.2.4 Polypeptoid Film Characterization

Photoelectron spectroscopy (PES), EUV reflectometry, total electron yield (TEY), and outgassing measurements were performed according to existing procedures.^{97, 102} For EUV contrast curves, wafers underwent a post-exposure bake (PEB) for 1 minute at 105°C. Wafers were then developed for 30 seconds in a solution of tetramethylammonium hydroxide (TMAH) in water at a concentration of 0.159% by weight, which was obtained by diluted a commercial AZ300MIF developer (2.38% TMAH in water) 15x with deionized water.

3.3 Results and Discussion

The wide range of functional groups that can be incorporated into polypeptoids using sub-monomer synthesis enables a tunable photoresist platform with a variety of different monomers. The first monomer chosen for this study (shown in **Figure 3.1a**) was a *tert*-butyl ester (**Nce**) that acts as a solubility switch. In the presence of acid and heat, it undergoes a deprotection reaction to form a carboxylic acid, vastly increasing the hydrophilicity of the polypeptoid. The second monomer included is an aryl sulfonamide (**Nsf**), which helps control the overall polarity of the material, serving a similar role to 4-hydroxystyrene groups in traditional polymeric CARs. Both functionalities have been previously studied in successful polypeptoid photoresists under deep ultraviolet (DUV) radiation.⁹⁹ The final functional group included in these materials is an aromatic component, fulfilled in this case by both a 4-iodobenzyl group (**Nib**) to enable iodine incorporation and a standard benzyl group (**NPhe**) to serve as a control. This serves multiple functions: first, the bulky sidechain increases chain stiffness and therefore the glass transition temperature of the polypeptoids. Second, the amide backbone of polypeptoids is inherently more hydrophilic than traditional polymers with fully hydrocarbon backbones, making the hydrophobicity imparted by the aromatic groups critical in preventing the unexposed photoresist from dissolving in the developer solution. Lastly, aromatic groups improve the stability of incorporated iodine, as the greater s-character of sp²-hybridized carbon results in a considerably stronger C–I bond relative to sp³ aliphatic carbons.¹⁰³

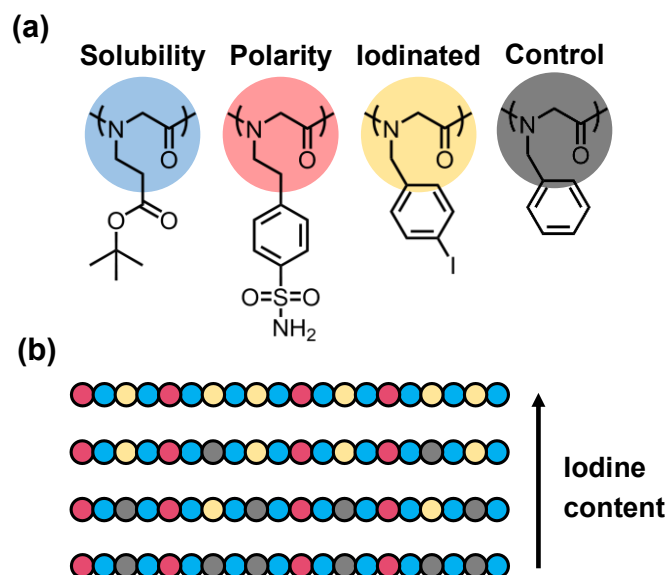


Figure 3.1. (a) Polypeptoid photoresists were comprised of an acid-sensitive solubility switch, aryl sulfonamides, and aromatic side chains with and without pendant iodine. (b) Iodine content was varied while maintaining a consistent sequence of alternating solubility switches.

The precise sequence control offered by polypeptoids enables investigation of the effects of specific monomers while holding sequence and composition constant, eliminating the statistical variations present in traditional synthetic polymers. To isolate the effects of iodine on electron generation and EUV sensitivity, the sequence of each polypeptoid was held constant while varying the number of 4-iodobenzyl groups versus benzyl control groups from zero to six iodine-containing monomers (see **Figure 3.1b**). Samples will henceforth be referred to as # **Iodine**, where # is the number of iodine-containing monomers. An alternating sequence with respect to **Nce** groups was chosen to evenly distribute all functional groups and mitigate aggregation of like moieties. Polypeptoid T_g values increased slightly with increasing iodine content, as the 4-iodobenzyl groups are more sterically hindered than their non-halogenated counterparts, though all samples fell within a similar range of 77–84°C.

Increasing iodine content significantly increased the number of both primary and secondary electrons generated within the films. Photoelectron spectroscopy (PES, shown in **Figure 2a**) was performed on films of each material during EUV exposure to directly quantify the effect of iodine on electron generation. The broad peak between 72 and 84 eV is associated with primary electrons ejected from the valence band of carbon, oxygen, and nitrogen, and thus does not vary with iodine content. However, the PES spectra show a stark increase in emitted primary electrons at 35 eV, the characteristic energy of electrons ejected from the iodine 4d core orbital. These increases above the **0 Iodine** baseline appear to be roughly linear; since primary electrons arise from collisions between EUV photons and the material, increasing iodine content should proportionally increase the number of such collisions. Once ejected into the material, primary electrons collide with surrounding atoms, which absorb energy and emit lower-energy electrons in a cascading process that ultimately produces a large quantity of low-energy electrons (LEEs, **Figure 2a** inset) capable of participating in non-ionizing chemical reactions.^{37, 104} Importantly, primary electrons stemming from iodine also boost the number of secondary LEEs, as evidenced by the growth of the low-energy peak with increasing iodine content. Taken together, the area under the PES curves serves as a proxy for the total number of electrons in the system, which increases significantly with iodine content, as shown in **Figure 3.9**. This trend was confirmed by measuring the total electron yield of each material over time (**Figure 3.10**). Separating fast and slow electrons at the 20 eV cutoff further illustrates the cascading effect: as iodine content increases, the ratio of slow to fast electrons rises before leveling off at the **6 Iodine** sample. This is significant because LEEs are expected to participate in chemical reactions such as the activation of photoacid generators in

CARs, suggesting that iodine incorporation should improve EUV sensitivity in subsequent photoresist formulations.

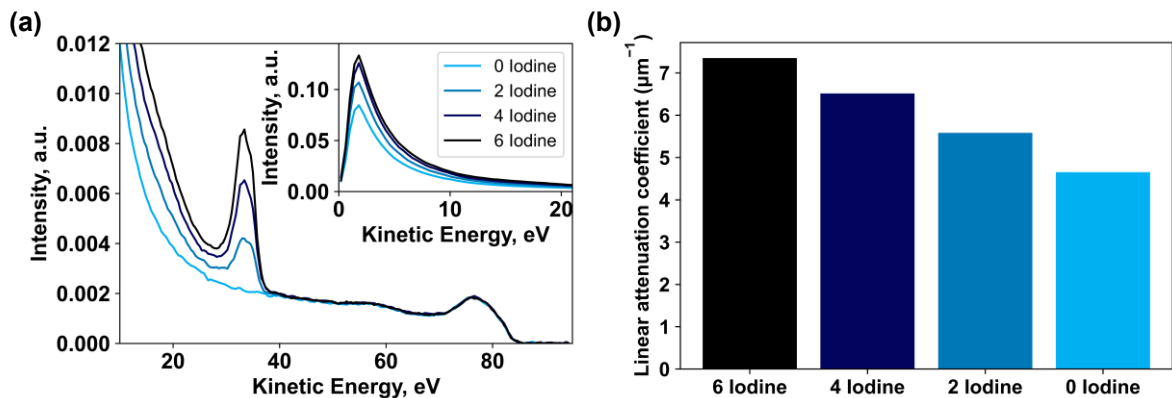


Figure 3.2. (a) Photoelectron spectroscopy reveals an increase in primary electrons at 35 eV generated from the iodine 4d core orbital as the number of iodine-containing monomers increases. This accompanies a similar trend in lower energy secondary electrons, shown in the inset plot. (b) EUV absorption coefficient increases linearly with the number of iodine-containing monomers.

In addition to increasing electron generation, iodine incorporation was also found to substantially boost the EUV absorption coefficient (μ , also referred to as the linear attenuation coefficient). **Figure 3.2b** shows a clear increase in μ with iodine content, as determined through X-ray reflectometry measurements. Even the **0 Iodine** polypeptoid exhibits a respectable value, with higher EUV absorption than many styrenic polymers⁹⁷ due to the presence of oxygen and nitrogen in the peptoid backbone. Each addition of two iodine-containing monomers improves this value further, with the **6 Iodine** material presenting a significantly higher absorption coefficient than the vast majority of non-perfluorinated polymers.⁹⁷ This is particularly notable given the relatively small amount of iodine present in these polypeptoids; even in the **6 Iodine** material, iodine accounts for only 1.2% of the overall

atomic composition, demonstrating that modest iodine additions can yield substantial gains in EUV absorption.

The absorption coefficient can also be calculated through **Equation 3.1**, where ρ is the density of the film, N_A is Avogadro's number, M is the molecular weight of the material, and σ is the photoabsorption cross section at a given wavelength. The photoabsorption cross section of a molecule can be calculated by summing the individual absorption cross sections of each constituent atom. Since μ is directly proportional to the molecular photoabsorption cross section and inversely proportional to molecular weight, μ will increase provided that iodine's contribution to σ outweighs its contribution to M . Consistent with this, the increase observed in **Figure 3.2b** is not quite linear and tails off slightly at higher iodine content. Nevertheless, calculated μ values still underestimate the impact of iodine when density is held constant, indicating that an increase in film density with iodine incorporation is an additional contributing factor to the observed absorption coefficients. Film densities calculated from the true values of μ are included in **Table 3.2**. Collectively, these results confirm that iodine incorporation successfully enhances photon absorption in the polymer films, ultimately increasing the number of electrons available to engage in chemical reactions.

$$\mu = \frac{\rho N_A}{M} \sigma$$

Equation 3.1. Calculation of the linear attenuation coefficient

When formulated with a triphenylsulfonium nonafluorobutanesulfonate (TPS nonaflate) PAG, the *tert*-butyl ester sidechains of the polypeptoids undergo a deprotection reaction upon exposure to EUV light, as shown in **Figure 3.3a**. PAG activation proceeds via electron

attachment of slow electrons (~ 5 eV or less), and the clear increase in electron generation with iodine content — including nearly 60% more slow electrons in the **6 Iodine** material relative to the **0 Iodine** sequence — therefore suggested that iodine incorporation would activate the PAG at lower exposure doses, yielding a more sensitive photoresist. However, contrary to this expectation, EUV contrast curves (**Figure 3.3b**) show that increasing iodine content instead necessitates higher exposure dosages, indicating that iodine is in fact decreasing EUV sensitivity. This surprising result suggests that while the number of electrons in the system has increased, they are not solely being consumed in PAG activation. Instead, these electrons are also initiating side reactions that oppose the desired deprotection. The increase in film thickness at high dosage in the **6 Iodine** sample indicates that at least some degree of crosslinking results from these side reactions, as crosslinks can prevent dissolution even when deprotection levels would otherwise be sufficient to clear the film. While this phenomenon is observed across a range of polymeric positive-tone photoresists, it generally occurs at significantly higher dosages than seen here. These findings therefore motivated a deeper investigation into the mechanism behind these competing reactions.

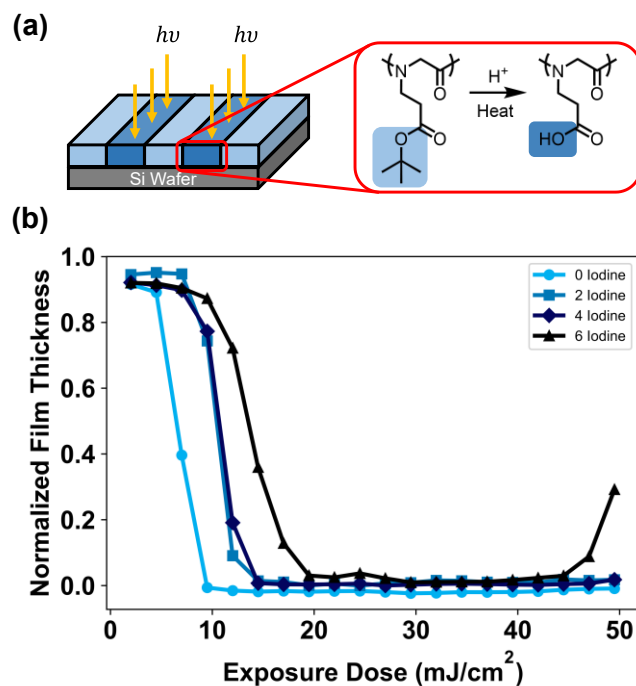


Figure 3.3. (a) Acid and heat causes deprotection to occur in exposed regions of the polypeptoid film, resulting in a solubility change. (b) EUV contrast curves show that sensitivity decreases with iodine content, contrary to what is suggested by electron generation.

Measurements of outgassed species during exposure are a powerful tool for understanding the chemistry occurring within photoresist systems. Using a residual gas analyzer on pure polypeptoid samples during EUV exposure, the most prominent outgassing was consistently observed at m/z values of 2, 28, and 44, corresponding to hydrogen gas, carbon monoxide, and carbon dioxide (**Figure 3.11**). This is unsurprising given the large number of carbonyls in the polypeptoids and the ubiquitous presence of hydrogen in any polymeric system. More revealingly, all iodine-containing samples also outgassed iodine and methyl iodide species (m/z values of 127 and 142, respectively), with methyl iodide outgassing shown in **Figure 3.4**. This outgassing begins at the onset of exposure ($t = 60$ seconds in the plot), confirming

that iodine loss occurs throughout the duration of exposure rather than only at extreme doses. The loss of iodine has two principal consequences. First, electron generation is expected to decrease as iodine is progressively removed from the material. Consistent with this, total electron yield (TEY) measurements over time (**Figure 3.10**) show a clear decline in average TEY for the **6 Iodine** and **4 Iodine samples**, while the **2 Iodine** and **0 Iodine** samples remain roughly constant. However, since the total exposure dose over the TEY measurement window is approximately 150 mJ/cm², and the dose-to-clear for these materials falls between 9.5 and 20 mJ/cm², these modest changes in electron yield are unlikely to significantly affect patterning performance. The second and more consequential effect of iodine loss is that scission of the carbon-iodine bond generates radicals that can initiate further chemical reactions, forming new bonds within the material and leading to crosslinking within the film which is consistent with the increase in normalized film thickness observed in the high-dose regions of the EUV contrast curves. Even at lower doses, these competing reactions appear to slow the transition from hydrophobic to hydrophilic, either through simultaneous deprotection and crosslinking (where crosslinks must be overcome by a greater degree of deprotection) or through radical-mediated side reactions that reduce the net level of deprotection at a given dose. In practice, both mechanisms are likely to contribute, as electrons are not especially selective when traversing a film. Disentangling their relative roles will be the subject of future study.

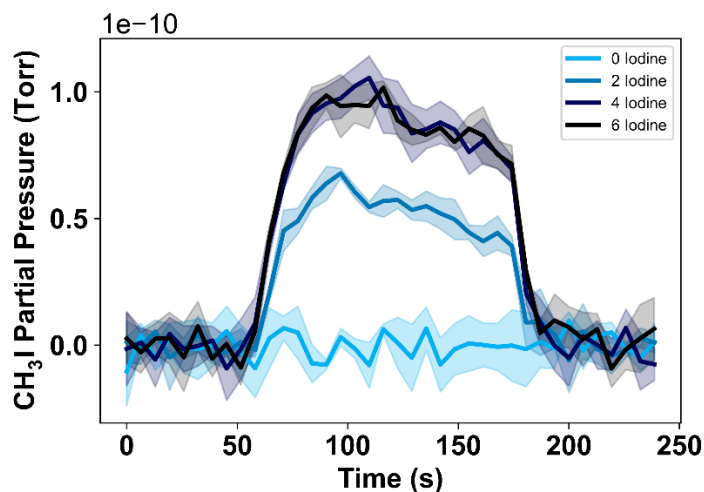


Figure 3.4. Outgassing of methyl iodide (m/z 142) increases with iodine content in the polypeptoids, potentially leaving behind reactive radical species. Shaded regions represent $\pm$ one standard deviation. Exposure begins at 50 seconds and ends at 175 seconds.

3.4 Conclusions

In conclusion, this study demonstrates that iodine incorporation into chemically amplified polypeptoid photoresists is an effective strategy for boosting EUV absorption, with as little as 1.2 atomic% iodine yielding a 58% increase in the absorption coefficient. Photoelectron spectroscopy and total electron yield measurements confirmed that this enhanced absorption translated into a corresponding increase in both primary and secondary electrons generated within the films. Despite these gains, iodine incorporation did not improve EUV sensitivity, with the highest iodine loading instead requiring roughly twice the exposure dose to clear compared to the control. Film thickness increases at high dosage in the most iodine-rich sample further indicated that crosslinking was occurring as a competing process. Outgassing measurements during EUV exposure revealed the progressive loss of iodine-containing species throughout exposure, implicating carbon-iodine bond scission and the resulting radical

species as the likely drivers of these undesired side reactions. Together, these results underscore that simply increasing electron generation is insufficient for improving resist sensitivity if the additional electrons are consumed by competing pathways. Future studies should therefore focus on identifying iodine-containing functional groups or molecular architectures that preserve the absorption and electron generation benefits of iodine while suppressing radical-mediated side reactions.

3.5 Acknowledgements

This work was supported as part of the Center for High Precision Patterning Science (CHiPPS), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences at Lawrence Berkeley National Laboratory under Contract No. DE-AC02-05CH11231. Polymer synthetic development was supported by the BioPACIFIC Materials Innovation Platform of the National Science Foundation under Award No. DMR-1933487. Polypeptoid film was performed in the UCSB Nanofabrication Facility, an open access laboratory. PES, TEY, EUV reflectometry, and EUV contrast curves were performed at the Advanced Light Source at Lawrence Berkeley National Laboratory.

3.6 Appendix

Analytical HPLC Chromatograms

All mass spectra presented in the figures below are averaged over the product peaks in the chromatograms. Note that the relative intensities of the mass spectra are not quantitative, and only the chromatograms are used to evaluate sample purities. Multiple peaks show up in the spectra due to different ions (i.e. $[M+2H]^{2+}$ and $[M+3H]^{3+}$) being formed by the same polypeptoid during mass spectrometry.

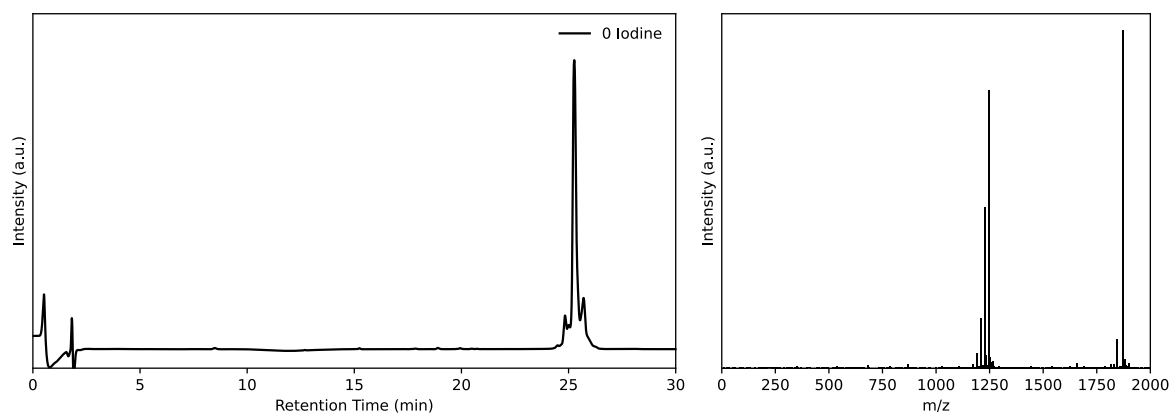


Figure 3.5. HPLC-MS chromatogram and mass spectra of the **0 Iodine** polypeptoid.

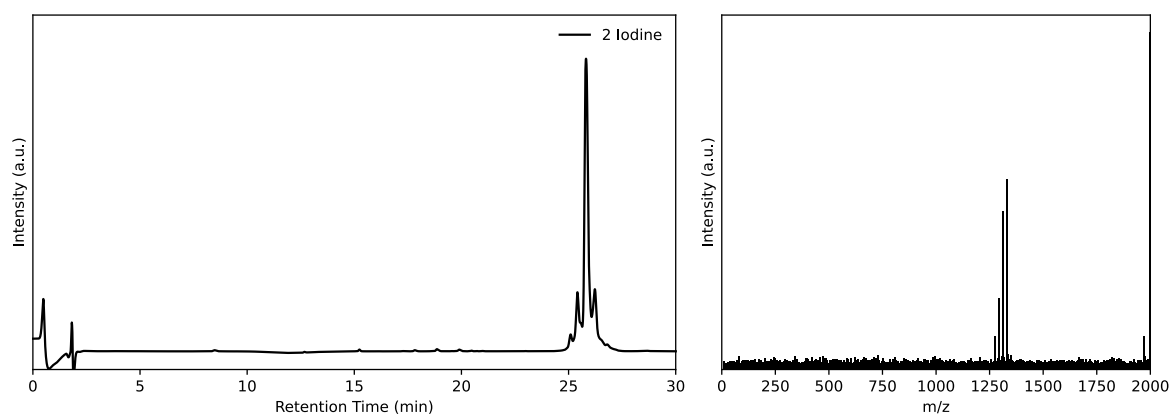


Figure 3.6. HPLC-MS chromatogram and mass spectra of the **2 Iodine** polypeptoid.

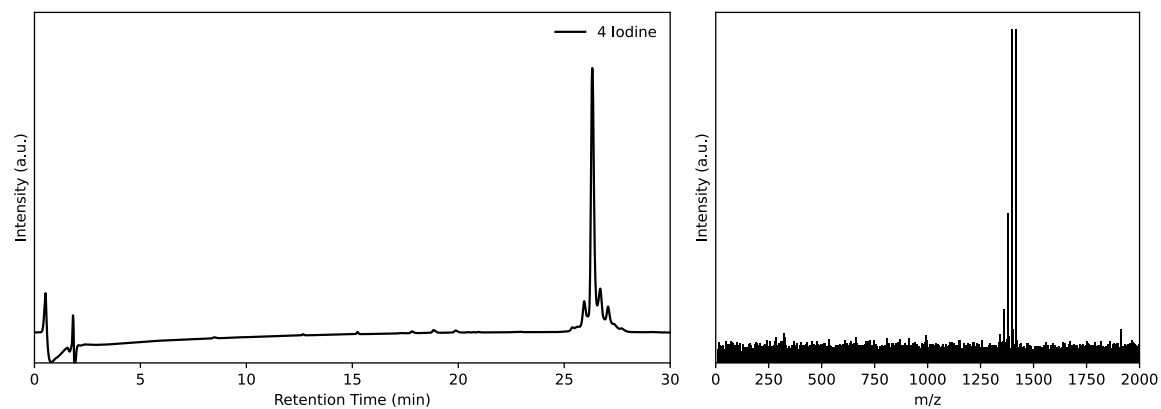


Figure 3.7. HPLC-MS chromatogram and mass spectra of the **4 Iodine** polypeptoid.

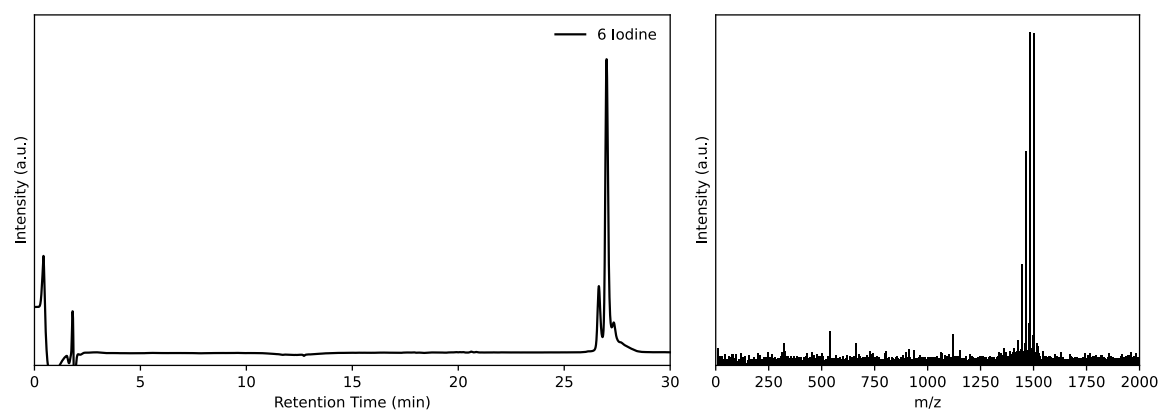


Figure 3.8. HPLC-MS chromatogram and mass spectra of the **6 Iodine** polypeptoid.

Spectroscopy Data

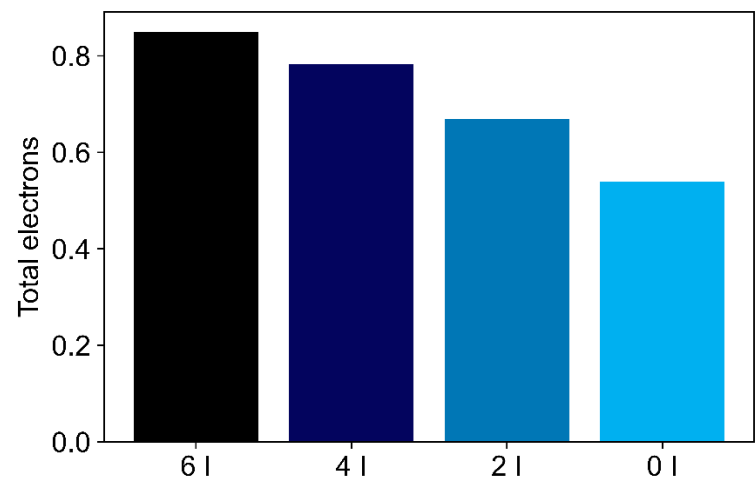


Figure 3.9. Proxy for total electrons obtained by integrating PES curves.

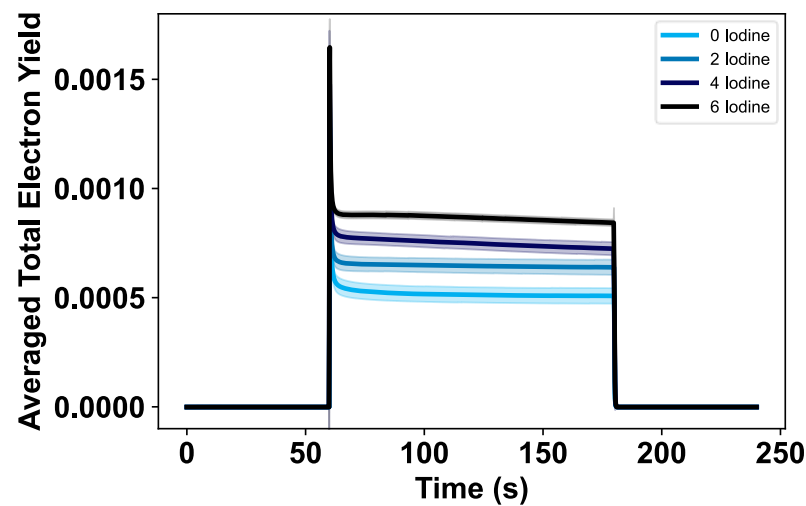


Figure 3.10. Total electron yield over time for all polypeptoid samples.

Outgassing measurements

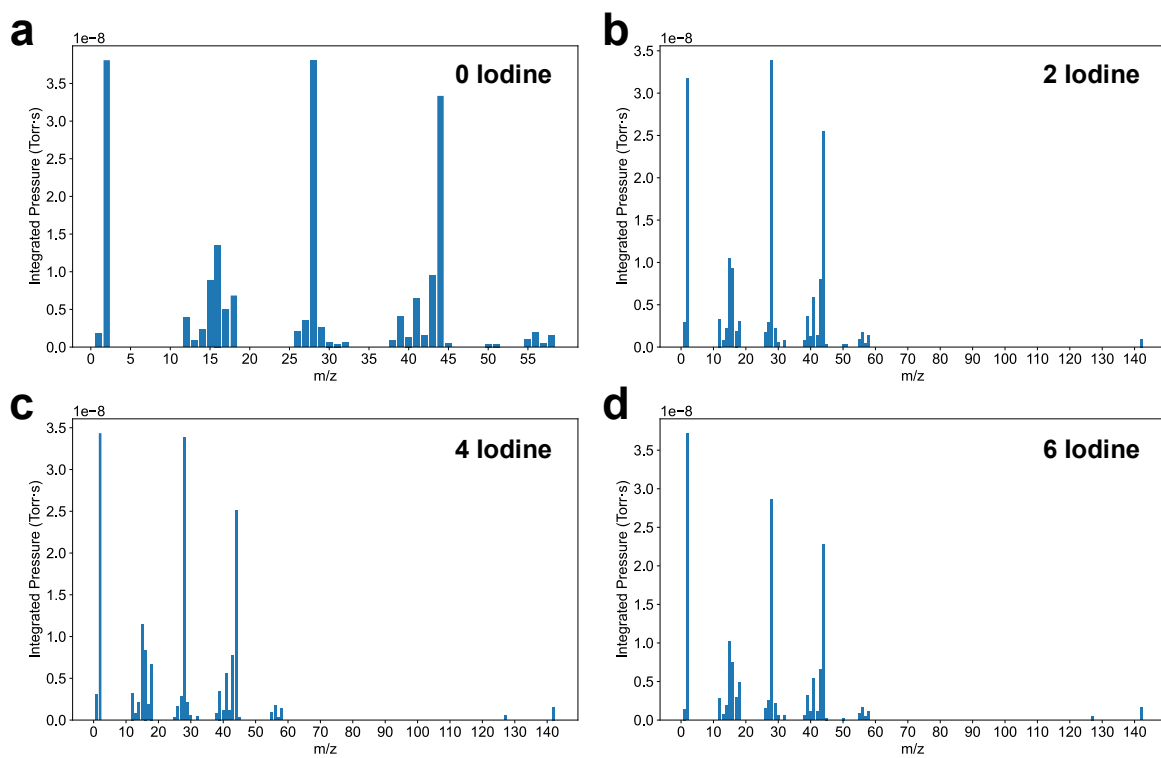


Figure 3.11. Highest 30 outgassed species for each polypeptoid sample.

Film Density Calculations

Table 3.2. Calculated film densities based on Equation 3.1

Sample Name	Molecular Weight	Abs Cross-section (Mb)	Calc. Lin. Att. Coeff (1/um)	Actual Coeff (1/um)	Calc Density (g/cm3)
6 Iodine	4497.83	389.98	6.013	7.350	1.408
4 Iodine	4246.04	343.67	5.613	6.513	1.336
2 Iodine	3994.25	297.36	5.163	5.582	1.245
0 Iodine	3742.45	251.05	4.652	4.652	1.152

Chapter 4: Evaluating the Critical Ionization Model of Dissolution through Sequence-Defined Polypeptoids

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Measurement of the Critical Ionization Level for Resist Polymer Dissolution Using a Polypeptoid Platform. Paing, A.; **Adams, C. P.**; Zhao, K.; Dilworth, B. T.; Segalman, R. A.; Oh, D.; Houle, F. A. *Macromolecules* 2026.

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Collaborator Contributions:

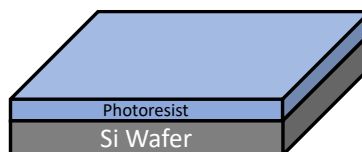
Aung Paing (Oh Lab, San Jose State University) and Kevin Zhao (Oh Lab, San Jose State University) performed quartz crystal microbalance measurements. Aung Paing developed the kinetic model used to compare with experiments.

4.1 Introduction

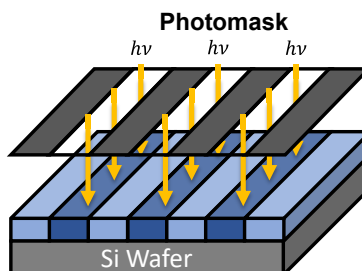
Photoresist films, commonly known as resists, are critical materials used to pattern nanoscale structures necessary for the manufacturing of semiconductor devices. Upon exposure to light, a chemical reaction is induced that results in a change in solubility, allowing either the exposed or unexposed area to be selectively washed away. One of the most prevalent classes of resists is known as chemically amplified resists, or CARs. These are polymeric materials in which a nonpolar functionality, such as a tert-butoxycarbonyl group, is used as a protecting group on an otherwise ionizable functionality such as a carboxylic acid or phenol.¹⁰⁵ Photoacid generators (PAGs) incorporated into the resist formulation generate acid upon exposure to light. During the subsequent post-exposure bake (PEB), this acid causes the deprotection of the polymer side chains, thereby altering the polymer's polarity and leaving behind a latent chemical image. This chemical change reveals ionizable functionalities and shifts the polymer from hydrophobic to hydrophilic, dramatically increasing the solubility in aqueous base developer. Most frequently, this developer is a solution of tetramethylammonium hydroxide (TMAH) because it is a strong base that is free of metal ions, which can be troublesome in device fabrication. During development, the latent image formed in the exposed resist is transformed into a visible pattern by selectively dissolving either the exposed or unexposed regions of the film (**Figure 4.1**), leaving behind features for further processing. The dissolution chemistry of the photoresist critically influences pattern resolution and quality metrics such as line-edge roughness (LER) and surface roughness.^{106,}

107

1. Film formation



2. Exposure and Bake



3. Development

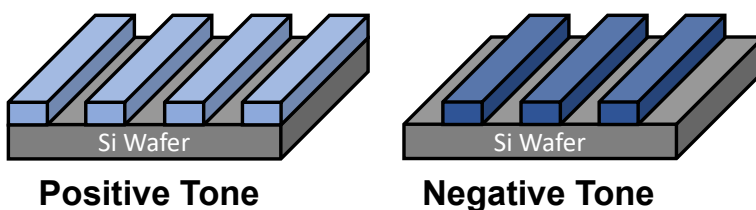


Figure 4.1. A brief description of the patterning process in photolithography. Films coated on a substrate are exposed to light, which forms a latent image of acid (protons) in the film. Chemical reactions taking place during a subsequent bake step convert the acidified regions into soluble (positive tone) or insoluble (negative tone) material, and the development step reveals the final pattern.

The dissolution of resist polymers is a reactive process in which the aqueous base developer diffuses into the polymer film, where hydroxide ions (OH^-) react with ionizable moieties on the polymer chains, altering their polarity and solubility. A minimum number of ionized moieties per chain is required for dissolution to occur. This process is often accompanied by the formation of a gel layer at the polymer–developer interface, whose thickness depends on the polymer's chemical composition.¹⁰⁸

Several physical models have been proposed to describe resist dissolution. The membrane dissolution model identifies diffusion of developer through a surface gel layer as the rate-

determining step,¹⁰⁹ while the percolation model attributes rate-limiting behavior to developer transport through microscopic channels formed by swollen polymer clusters.¹¹⁰ However, both models fail to account for observed dependencies of dissolution rate on polymer chain length and molecular weight. The most successful framework for describing dissolution across a wide range of polymer platforms is the critical ionization (CI) model, which identifies the ionization reaction between acidic polymer moieties and OH⁻ as the rate-determining step.⁹² The CI model further posits that a threshold fraction of repeat units on each chain, known as the critical ionization (CI) level, must be ionized before the chain becomes soluble.

Ionizable groups are primarily generated through acidolytic reactions during PEB, but precisely determining the CI level has remained challenging due to chemical inhomogeneities inherent to polymer synthesis, exposure, and baking. One approach estimated CI values by fitting measured dissolution rates as a function of number-average molecular weight (M_n) to a log-log linear relationship, yielding a CI level of 63% for monodisperse poly(4-hydroxystyrene) (PHS),¹¹¹ though this result lacked direct experimental verification. A complementary approach copolymerized hydroxystyrene with non-ionizable methoxystyrene at varying ratios, finding that dissolution occurred at 53 mol% PHS but not at 29 mol% — bracketing the CI level without resolving it precisely.¹¹² This ambiguity arose largely from the synthesis method (partial methylation of PHS with iodomethane), which provides limited control over comonomer sequence and chain length dispersity.¹¹²

We hypothesized that these limitations could be overcome using sequence-defined, monodisperse copolymers as a model system for directly measuring the CI level. Polypeptoids (N-substituted polyglycines) are a material that can be synthesized with complete control over

monomer sequence and chain length via iterative sub-monomer solid-phase synthesis.^{59, 70} Unlike polypeptides, polypeptoids can be synthesized on a gram scale, making them an ideal model system for experimentally studying the CI model. Additionally, they have previously been demonstrated as a viable resist platform for photolithography, where polymer sequence was found to have a significant impact on patterning results.^{86, 99} Because the exact levels of deprotection in a photoresist after exposure and bake are difficult to determine especially, and because individual chains will have variations in their individual levels of deprotection, polypeptoids were instead synthesized with defined sequences that systematically vary the fraction of ionizable phenolic monomers. This directly simulates the range of ionization states encountered during resist processing while eliminating the need for exposure and bake. All polymers were fixed at a chain length of 20 monomers and incorporated non-ionizable aromatic comonomers, including phenethylamine, 3-phenylpropylamine, and 4-methoxyphenethylamine, alongside the ionizable phenolic units (**Figure 4.2**). The inclusion of two different non-ionizable aromatic pendants was necessary to suppress crystallization, which is known to occur in phenethyl-rich polypeptoid sequences.⁷⁷

The tunable nature of polypeptoids also enables the study of other factors that could impact dissolution properties. To probe the effects of comonomer identity on dissolution behavior, pairs of samples with matched ionizable fractions but differing non-ionizable comonomers were synthesized, where a methoxyphenyl group was used to vary the hydrophilicity of the peptoid (represented as 40% and 40-S in **Figure 4.2**). The effects of chain-end chemistry were investigated through the use of identical polypeptoid chains with different end groups (carboxylic acid vs. amide; 40% vs. 40-NH₂). In this work, dissolution rates in aqueous TMAH developer were measured across the series to identify the compositional threshold for

solubility, and kinetic simulation models were developed to compare CI theory predictions against experimental dissolution data.

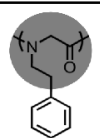
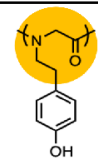
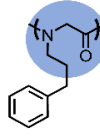
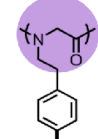
Sample Name	Structure	Symbol
0%	H-  -OH	
15%	H-  -OH	
20%	H-  -OH	
30%	H-  -OH	
40%	H-  -OH	
40-S	H-  -OH	
40- NH2	H-  -NH ₂	
50%	H-  -OH	
60%	H-  -OH	

Figure 4.2. Polypeptoids used in this study with varying amounts of ionizable phenolic groups. The sample names refer to the percentage of ionizable monomer.

4.2 Methods

This is a combined experimental-computational study. In this section and in the Supporting Information (SI) sections S1-S4, details are provided for synthesis, characterization, film casting, resist dissolution, and modeling.

4.2.1 Polypeptoid Synthesis

All solvents and reagents were purchased from commercial suppliers and used without further purification. All polypeptoid sequences were synthesized on a Symphony X automated synthesizer at the NSF BioPACIFIC MIP facilities using previously reported protocols.^{90, 93}

For polypeptoids with a carboxylic acid C-terminus, 2-chlorotrityl chloride (CTC) resin (0.91 mmol/g loading, 800 μ mol scale, Aapptec) was swollen in dichloromethane (DCM) at 0.02 mL/mg of resin at room temperature for 2–4 hours. The resulting slurry was transferred to a reaction vessel in the Symphony X and drained. The resin was then activated by adding 1.2 M *N,N'*-diisopropylethylamine (DIPEA) in DCM and 1.2 M bromoacetic acid (BrAA) in *N,N'*-dimethylformamide (DMF), and mixed for two hours. The resin was subsequently drained and rinsed with DMF.

Polypeptoids were grown through alternating amine displacement (1.5 h) and bromoacetylation (45 min) steps. Separate 1M solutions of 4-hydroxyphenethylamine (tyramine), phenethylamine, 3-phenylpropylamine, and 4-methoxyphenethylamine were prepared in *N*-methyl-2-pyrrolidone (NMP). During each bromoacetylation step, BrAA (1.2 M, DMF) and *N,N'*-diisopropylcarbodiimide (DIC, 2.4 M, DMF) were combined in a 2:1 volumetric ratio. To improve reaction conversion, the bromoacetylation was repeated for monomers 11–20. The resin was rinsed with DMF between each submonomer addition.

For polypeptoids with an amide C-terminus, Novabiochem® Rink Amide resin (0.62 mmol/g loading, 800 μ mol scale, Sigma-Aldrich) was swollen in DMF for 30 minutes. The resin was then deprotected with a 20% v/v solution of 4-methylpiperidine in DMF for 30 minutes, after which the solution was drained, and the resin was rinsed thoroughly with DMF. All subsequent bromoacetylation and amine displacement steps were carried out under the same conditions as described for the CTC resin.

Polypeptoids synthesized on CTC resin were cleaved using a 30% v/v solution of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) in DCM for 45 minutes. The resulting solution was

drained into collection vials, and the cleavage was repeated once. A final rinse with DCM was performed, after which the solvent was removed under vacuum. The cleaved polypeptoids were then lyophilized for 48 hours after being suspended in a 40% v/v acetonitrile/water solution. Polypeptoids synthesized on Rink Amide resin were cleaved using a solution of 47.5% v/v trifluoroacetic acid (TFA), 47.5% DCM, and 5% water using an otherwise identical procedure.

4.2.2 Polypeptoid Characterization

Polypeptoid products were analyzed by analytical high-performance liquid chromatography (HPLC) using a Shimadzu Nexera Hybrid chromatography system equipped with a single quadrupole mass spectrometer (MS) detector at the NSF BioPACIFIC MIP facilities. Samples were prepared at approximately 1 mg/mL in 50–70% v/v acetonitrile/water and injected into a C4 column (XBridge Protein BEH C4, 300 Å, 3.5 µm, 4.6 mm × 100 mm). Separation was achieved using a 5–95% solvent B gradient (95–5% solvent A) over 30 minutes. Solvent A consisted of water containing 0.1% v/v formic acid, and solvent B was acetonitrile containing 0.1% v/v formic acid. The characterization results are presented in SI Section S1.

4.2.3 Resist Film Preparation and Dissolution

Polypeptoid stock solutions were prepared by mixing the polypeptoid powder with propylene glycol methyl ether (PGME) (99.5%, Sigma-Aldrich) at a concentration of 100 mg/mL, except the 50% sample, which was mixed at a 150 mg/mL concentration to achieve a target film thickness of 500 nm. The solution was vortexed for 10 minutes, followed by

sonication for 20 minutes at room temperature using a bath sonicator. The solution was then spin-coated (Intras SCK-300) on a 1" AT-cut quartz crystal microbalance (QCM) crystal at 1200 RPM (1500 RPM for 50% ionizable sample) for one minute. Post-apply-bake (PAB) to drive off residual casting solvent was carried out at 110°C for one minute on a hotplate. The pre- and post-dissolution thicknesses of the film were measured by using an ellipsometer (J. A. Woollam M2000). The polypeptoid concentration used for stock solution preparation and the spin-coating RPM were selected to achieve a target film thickness of approximately 500 nm, enabling the collection of sufficient data during the subsequent dissolution experiments for further analysis. The detailed experimental procedures for film casting, the model used in the ellipsometer for the thickness measurements, and the measured thicknesses are reported in SI Section S2.

The dissolution of the polypeptoids in 0.26 N TMAH was monitored by measuring the frequency changes (ΔF) of the crystal using the QCM (SRS QCM200). The viscoelasticity of the film, an indicator of the gel layer formation, was measured by tracking the motional resistance (ΔR) in the QCM, where increasing ΔR indicates enhanced mechanical energy dissipation due to viscoelastic losses in the hydrated polymer film.¹¹³ The dissolution experiments were repeated two to three times for each sample to ensure the reproducibility of the results. The detailed experimental procedures for dissolution experiments are provided in SI Section S3. The time-dependent mass change for the coated film was obtained by using Sauerbrey's equation (Equation 1),¹¹⁴ with the assumption that the film is rigid

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q\mu_q}} \Delta m \quad (1)$$

where f_0 is the resonance frequency of the quartz crystal (Hz), A is the area of the gold electrode coated on the quartz crystal (cm^2), ρ_q is the density of the quartz crystal ($\text{g}\cdot\text{cm}^{-3}$), Δf is the change in the resonance frequency (Hz), Δm is the change in the mass of the coated film (g), and μ_q is the shear modulus of the quartz crystal ($\text{g}\cdot\text{cm}^{-1}\cdot\text{s}^{-2}$).

According to Sauerbrey's equation, the frequency change (ΔF) is inversely proportional to the mass change (Δm). An increase in ΔF corresponds to a net loss of mass due to dissolution of the coated film, whereas a decrease in ΔF indicates a net mass gain on the crystal due to the diffusion of the developer into the coated film. Because the increase in resistance ΔR reflects the increased viscoelasticity of the film, a concurrent decrease in frequency (ΔF) and increase in resistance (ΔR) is the result of the increasing viscoelasticity of the film and the increasing distance between the liquid layer and the solid layer, as developer diffusion into the polymer thickens the gel layer.¹¹³ The dissolution rates of the film in $\text{nm}\cdot\text{s}^{-1}$ were calculated by dividing the original film thickness by the time required to reach a stable ΔF after the initial increase due to dissolution. Stable ΔF was defined as the condition in which the difference between a given ΔF value and the next distinct ΔF value was less than 10 Hz.

4.2.4 Kinetic Simulation Model

A kinetic simulation model was developed using the Kinetiscope simulator (version 1.1.1328)¹¹⁵ to predict the time-dependent net mass change of the polypeptoid film dissolution in TMAH developer as a result of the polypeptoid chains dissolving into the developer. The model was based on the CI theory, which describes the dissolution process as a surface phenomenon akin to copper etching by the nitric acid.⁹¹ The criterion for the dissolution of a polypeptoid chain at the surface of the film with access to the full concentration of the

developer OH^- is that the chain be ionized to the experimentally found CI level by the developer OH^- ions in a series of ionization reactions. The series of ionization reactions is simulated using a stochastic reaction-diffusion method,¹¹⁶ a type of Kinetic Monte Carlo simulation, with the help of the Kinetiscope simulator. The derivation of the simulation algorithm employed in the simulator is available in the literature.^{116, 117}

The conversion of acidic polymer resist from an insoluble to the soluble state in the basic developer solution requires ionization reactions between the acidic moieties of the polymer and the developer OH^- ions, and the solvation of the ionized polymer chain into the developer. The kinetic simulation model is the representation of a reactive dissolution process where the dissolution is considered a surface phenomenon in which the rates of developer diffusion and solvation of the critically ionized polymer chain are much faster compared to the ionization reaction rates.¹⁰⁶ Therefore, in the simulation model, developer diffusion into the dry polymer and gel layer development during dissolution was not explicitly considered, consistent with the thinner gel layer development inferred from ΔF and ΔR measurements in the dissolution of 30%-60% polypeptoid samples. Rather, the ionization reactions are confined to a top 1 nm surface layer, in which the developer OH^- concentration is the same as in the bulk developer. The surface layer thickness of 1 nm is an assumption based on the 0.75 nm molecular size of the phenol.¹¹⁸ Additionally, in QCM measurements, the negative frequency change (ΔF) observed immediately after immersion of the crystal into the developer is influenced by three simultaneous processes- the change in the surrounding medium of the crystal from air to liquid, diffusion of the developer into the film, and some dissolution of the film and therefore does not represent an unambiguous measure of water uptake by the film. Accordingly, comparisons with the simulation results were restricted to the positive ΔF regions of the

experimental data where mass loss is dominant. Lastly, the model uses an extremely large diffusion coefficient ($1 \times 10^{36} \text{ cm}^2 \cdot \text{s}^{-1}$) to maintain a correct concentration profile of the reacting species in the surface layer. This ensured that polypeptoid chains ionized to the critical degree were instantaneously transferred from the surface layer into the developer, and that dry chains from the bulk film were simultaneously replenished at the surface. This is a modeling convenience rather than a physical parameter, and a full description of the simulation methodology is provided in the original publication and its supporting information referenced at the beginning of this chapter.

4.3 Results and Discussion

This work aims to rigorously determine the precise CI level of a resist polymer by combining experimental and simulation approaches. The ΔF and ΔR measurements using the QCM method reveal changes in solubility, dissolution rate, and viscoelasticity of the films, enabling the unambiguous determination of the CI level and providing new insights into the properties of the polymer at a solubility threshold. Simulation models identify the kinetically significant aspect of the dissolution mechanism of the resist polymer.

4.3.1 Critical Ionization (CI) Level Determination

Polypeptoid films with 0–15% ionizable monomer content did not dissolve in 0.26 N TMAH; dissolution was first observed for the 20% sample (**Figure 4.3a**). This establishes 20% ionizable monomer content as the CI level for this polypeptoid system, which is the minimum threshold required for dissolution. **Figure 4.3** shows the QCM frequency and

resistance changes due to the three peptoids used to determine the CI. In all instances, the initial drop in frequency ($\Delta F \approx -800$ Hz) and rise in resistance ($\Delta R \approx 330 \Omega$) observed within the first ~ 0.2 s reflect the change in the sensor's surrounding medium from air to liquid developer, as confirmed by the bare sensor data in **Figures 4.3a** and **4.3b**, and are not attributable to film behavior. With this baseline established, three distinct regimes of film behavior were observed across the sample series. The 0% sample showed no appreciable change in ΔF or ΔR beyond the bare sensor response, consistent with the highly hydrophobic character of the aromatic pendant groups (see **Figure 4.2**), which inhibit developer diffusion into the film. The 15% sample swelled but did not dissolve, as a simultaneous decrease in ΔF and increase in ΔR were observed until ΔR reached the instrument limit of $5,000 \Omega$. This swelling arises from the ionization of the phenolic pendants by OH^- , which increases the hydrophilicity of the film and drives water uptake. A similar mechanism has been reported for poly(norbornene ethyl carbonate-co-norbornene carboxylic acid) (P(NBCarb-NBCA)) at 30 mol% NBPA in TMAH, where deprotonation of carboxylic acid groups by diffusing OH^- ions enabled additional water diffusion into the film and the formation of a gel layer.¹⁰⁸ The 20% sample exhibited an initial increase in both ΔF and ΔR , consistent with simultaneous film swelling and gel layer formation, followed by a decline in ΔR and stabilization of ΔF upon complete dissolution. Notably, the rate of ΔR increase was substantially faster in the 20% sample than in the 15% sample, indicating that the higher ionizable monomer content accelerates OH^- diffusion into the film, initiating gel layer formation.

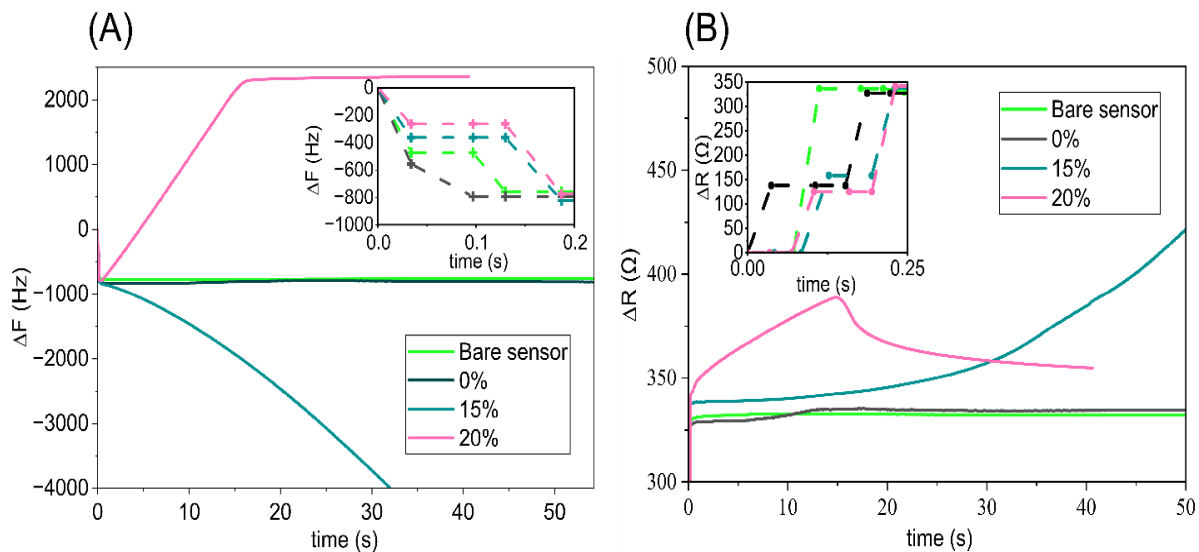


Figure 4.3. QCM measurements during dissolution to identify the CI level. (a) frequency change (ΔF) and (b) resistance change (ΔR) for the polypeptoids and the bare sensor in 0.26 N TMAH (magnified view of the first 0.25 s shown in the insets).

4.3.2 Change in Dissolution Rate with Ionizable Monomer Content

The dissolution rate increased approximately linearly with ionizable monomer content between 30% and 50% (**Figure 4.4b**), then plateaued above 50%, indicating that further increases in ionizable monomer content beyond this point do not meaningfully accelerate dissolution. At the lower boundary, the dissolution rate dropped sharply at CI level of 20% ionizable monomer content (Figure 4a), indicating that the polymer film is barely soluble at the dissolution threshold.

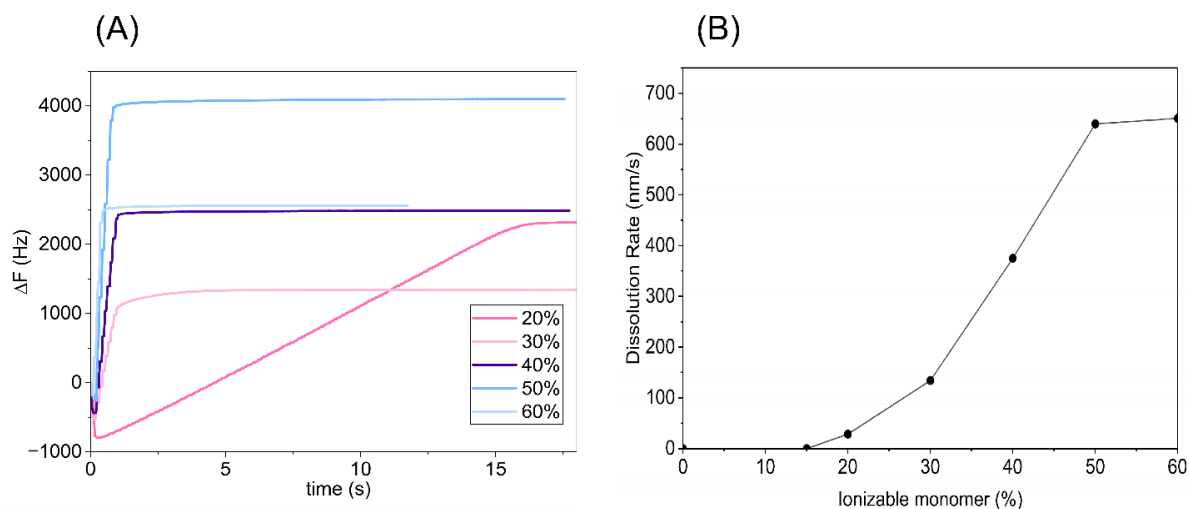


Figure 4.4. Dissolution measurements for the full range of soluble polypeptoids. (a) The experimental frequency change (ΔF) of 20%-60% ionizable polypeptoids; (b) the calculated dissolution rate of 0%-60% samples in 0.26 N TMAH.

The viscoelastic response of the dissolving films, tracked via ΔR , provides evidence for gel layer formation during dissolution (**Figure 4.5**). The largest absolute ΔR change was observed for the 50% sample, which is attributed to its greater initial film thickness (708 nm) relative to the other samples (all below 480 nm). To isolate compositional effects from thickness, comparing samples of similar thickness (~ 470 nm) is more informative. Among these, the 20% sample exhibited a substantially slower rate of ΔR increase, reflecting slower gel layer formation driven by reduced OH^- diffusion into the film. This behavior suggests that at the CI level, OH^- diffusion becomes the rate-limiting step for dissolution, rather than the ionization reaction itself. A similar transition in rate-limiting mechanism has been reported for poly(methyl methacrylate-co-methacrylic acid) (P(MMA-MAA)) at 18–21 mol% MAA,¹⁰⁸ where the ionizable fraction was comparable to the 20% polypeptoid samples studied here.

Despite its slower ΔR rate, the 20% sample ultimately reached the largest ΔR value among the thickness-matched samples, indicating formation of a thicker gel layer overall. This is consistent with the slower dissolution rate allowing extended developer water diffusion into the film before the polymer chains are fully released. In contrast, the 30%–60% samples all displayed a sharper ΔR increase followed by a rapid decline upon dissolution completion, with lower peak ΔR values, which is characteristic of thinner gel layers that form and clear quickly under faster dissolution conditions.

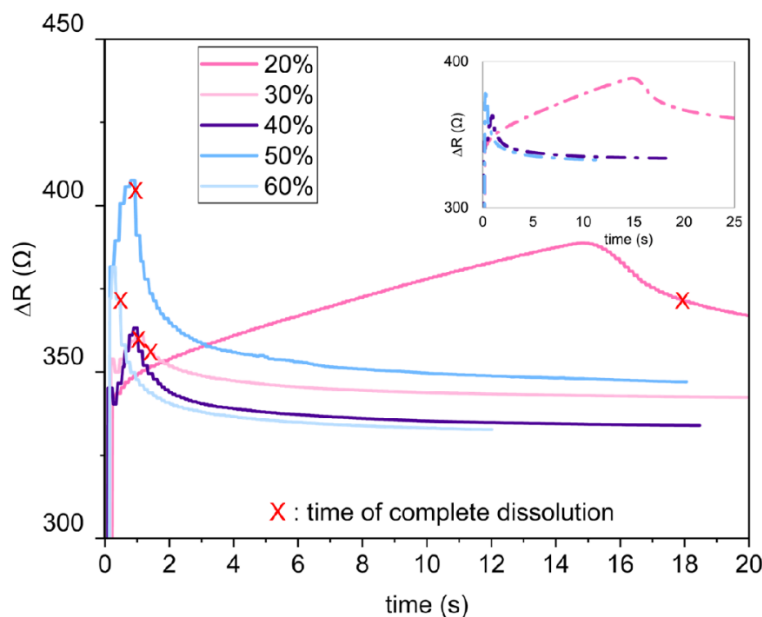


Figure 4.5. The experimental resistance change (ΔR) of 20%–60% ionizable polypeptoids samples in 0.26 N TMAH (comparison of ΔR of ~ 470 nm films in the inset).

4.3.3 Comparison to Simulation Results

Kinetic simulations enable further insights into the mechanisms behind polypeptoid dissolution. **Figure 4.6** compares simulation and experimental dissolution results for

polypeptoids with 20%–60% ionizable monomer content. Using identical prefactors in the kinetic model, the simulation reproduces the experimental dissolution behavior well for the 30%–60% samples (**Figure 4.6a**). For the 20% sample, however, the same prefactor yields a significant discrepancy, where the simulation predicts a dissolution rate substantially faster than what was measured experimentally (**Figure 4.6b**). This disagreement is consistent with a breakdown of one of the model's core assumptions at the CI level. The simulation treats OH^- diffusion as fast relative to the ionization reactions, making ionization the rate-limiting step. However, the substantially slower ΔR response relative to the other dissolving samples for the 20% polypeptoid indicates a reduced rate of OH^- diffusion into the film, since viscoelastic changes tracked by ΔR are caused by the diffusion of OH^- ions. Taken together, the slower ΔR response and the faster-than-observed simulated dissolution rate demonstrate that at the CI level, OH^- diffusion becomes the rate-limiting step, violating the assumption underlying the model and explaining its failure for the 20% sample.

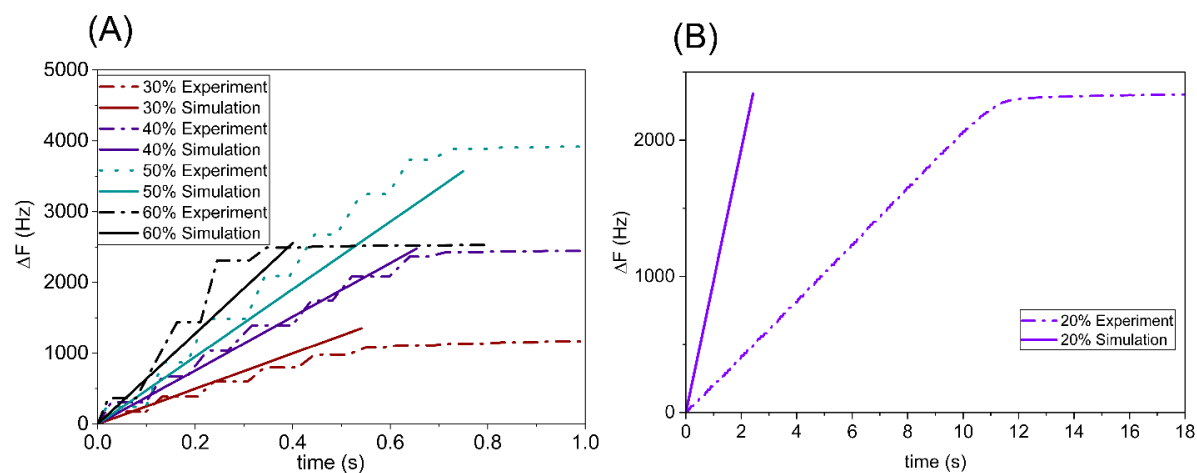


Figure 4.6. The simulated (straight lines) and the experimental (dashed lines) dissolution of (a) 30% - 60% ionizable and (b) 20% ionizable samples in 0.26 N TMAH.

4.3.4 Impacts of Monomer Identity and Chain Ends

CI theory predicts that dissolution rate depends on the fraction of ionizable groups in the polymer chain but is independent of the identity or spatial arrangement of the non-ionizable moieties. This prediction, however, has been difficult to test cleanly in practice. Several studies of polypeptoids in resist formulations have reported differences in pattern resolution associated with the placement of hydrophobic monomers at chain ends versus the middle, and with blocky versus alternating monomer sequences.^{86, 99, 119} However, those materials were formulated with PAGs and underwent subsequent DUV exposure and bake steps, which each introduce a host of new variables that could contribute to the observed differences in patterning.

To isolate the effect of non-ionizable monomer identity from these confounding factors, and to better understand the dependence of dissolution on changes in hydrophilicity, we designed two polypeptoids with identical ionizable monomer content but differing non-ionizable pendant groups (samples 40% and 40-S). Here, a methoxy group was inserted non-ionizable aromatic rings to have a similar polarity to the ionizable phenols. These samples dissolved at identical rates in 0.26 N TMAH (**Figure 4.7**), consistent with CI theory's prediction that dissolution rate is independent of non-ionizable monomer identity. That said, the non-ionizable monomers in these two samples are both aromatic functionalities, and they differ in identity but not in spatial arrangement. Further studies examining a larger library of comonomers and a variety of sequences at a given composition are required to fully understand the effects of polymer sequence on dissolution.

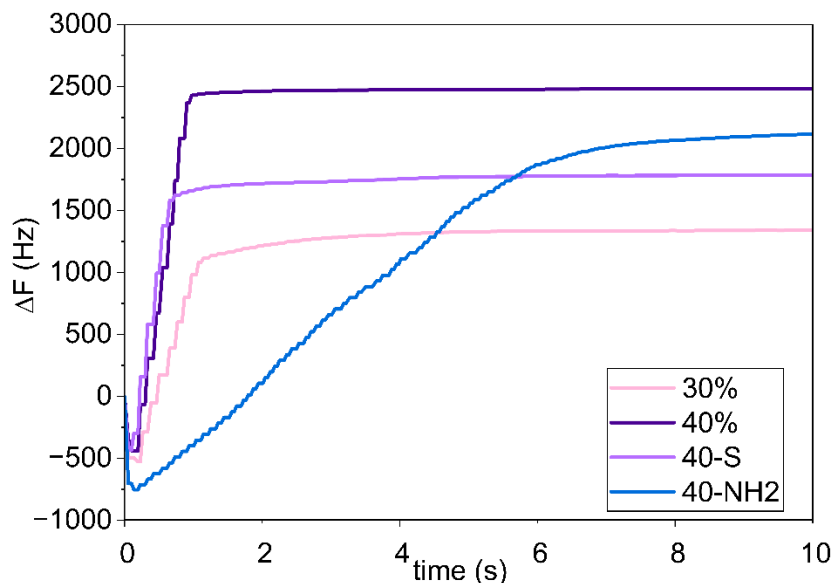


Figure 4.7. The experimental frequency change of 30% and 40% ionizable polypeptoids with varied comonomer identity and end groups in 0.26 N TMAH. Dissolution rate is shown by the initial slope prior to the plateau.

To probe the effect of chain-end chemistry, we designed an additional pair of otherwise identical polypeptoids differing only in their terminal group. In this case, the resin used during polypeptoid was changed so that one material had an ionizable carboxylic acid end (40%) and one contained a non-ionizable amide end (40-NH₂). The carboxylic end group adds one ionizable group to the 40% sample relative to 40-NH₂, which CI theory predicts should lower the stepwise pK_a and increase dissolution rate regardless of the specific chain-end identity. This was confirmed experimentally in **Figure 4.7**, where the 40% sample dissolved faster than 40-NH₂. However, 40-NH₂ also dissolved more slowly than the 30% sample containing a carboxylic acid, which carries a carboxylic chain end but one fewer total ionizable group. This result cannot be explained simply by counting ionizable groups and suggests that the influence of chain-end chemistry on dissolution is more nuanced than CI theory currently accounts for.

This could be explained by the different pKa values of the end groups used, where the carboxylic acid has a significantly lower pKa and the amide has a significantly pKa than the pendant phenols, although the CI model generally treats any ionized functionality as identical. The end groups could also be more spatially accessible to the developer solution, giving them a stronger influence on polymer solubility. Further studies examining the effects of both pendant and end group identity and pKa will be needed to fully understand the reasons for these effects.

4.4 Conclusions

Although the critical ionization model successfully predicts reactive dissolution across a wide range of photoresist polymer platforms, directly measuring the CI level has remained challenging due to the compositional and structural inhomogeneities introduced by conventional polymer synthesis, exposure, and PEB processing. To overcome these limitations, we synthesized sequence-defined, monodisperse polypeptoids as a model resist that has been fully deprotected, bypassing the exposure and bake steps entirely and instead directly encoding a controlled range of ionizable monomer fractions into precisely defined polymer chains of fixed length. This approach enabled an unambiguous experimental determination of the CI level and a clean evaluation of CI model predictions against dissolution measurements. The CI level for this polypeptoid system was identified at 20% ionizable monomer content, below which films were insoluble in 0.26 N TMAH. Above this threshold, dissolution rate increased linearly with ionizable monomer content up to 50%, beyond which it plateaued with no further gains from additional ionizable monomer.

Dissolution behavior at the CI level was qualitatively distinct from that of higher-ionizable-content samples: the 20% sample exhibited a sharp drop in dissolution rate, slower OH⁻ diffusion into the film, and formation of a thicker gel layer. This is consistent with a shift in the rate-limiting step from ionization to developer diffusion, and with a breakdown in the assumptions underlying the CI model at this boundary. For polypeptoids above the CI level, viscoelastic response followed a consistent pattern of rapid ΔR rise followed by sharp decline upon dissolution completion, reflecting thinner gel layers and faster, ionization-limited dissolution kinetics.

The precision of the polypeptoid platform also enabled two finer structural questions to be probed. Polypeptoids designed with identical ionizable fractions but differing non-ionizable pendant identities dissolved at the same rate, supporting CI theory's prediction that non-ionizable monomer identity does not significantly influence dissolution in an alkaline developer. By contrast, polypeptoids designed with differing chain-end groups revealed that an ionizable chain end accelerates dissolution beyond what would be expected from simply adding one extra ionizable group, suggesting a chain-end effect that current CI theory does not fully capture. Together, these findings demonstrate both the power of sequence-defined polypeptoids as a platform for probing dissolution mechanisms, and the open questions that remain in extending CI theory to structural features beyond bulk ionizable fraction.

4.5 Acknowledgements

This work was supported as part of the Center for High Precision Patterning Science (CHiPPS), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences at Lawrence Berkeley National Laboratory under Contract No. DE- AC02-342 05CH11231. Polymer synthetic development was supported by the BioPACIFIC Materials Innovation Platform of the National Science Foundation under Award No. DMR-1933487. The authors would like to thank Dr. Honggu Im and Dr. Finn Babbe (LBNL) for their help with the film thickness measurements, along with Dr. William Hinsberg (Columbia Hill Technical Consulting) for very helpful discussions.

4.6 Appendix

Analytical HPLC Chromatograms

Polypeptoid samples were characterized using analytical HPLC mass spectroscopy as described in Section 2.2. Expected m/z values are included in Table S1 and are characteristic of $[M+2H]^{2+}$ and $[M+3H]^{3+}$ ions, as the mass detector on the instrument has a maximum m/z of 2000.

Table 4.1. Polypeptoid samples and molecular weights from analytical HPLC-MS.

Sample Name	Exact Mass (g/mol)	$[M+2H]^{2+}$ m/z	$[M+3H]^{3+}$ m/z
0%	3295.75	1648.89	1099.59
15%	3315.71	1658.87	1106.25
20%	3331.70	1666.86	1111.58
30%	3363.69	1682.86	1122.24
40%	3395.68	1698.85	1132.90
40-S	3727.78	1864.90	1243.60
40-NH2	3394.70	1698.36	1132.58
50%	3427.67	1714.85	1143.57
60%	3459.66	1730.84	1154.23

Each HPLC chromatogram was processed by subtracting a chromatogram from a blank injection. Peaks due to pressure changes as flow begins in the HPLC appear at retention times under 5 minutes and can be ignored. All mass spectra presented in the following figures were obtained by averaging over the primary product peak and subtracting out a background from regions of time where no peaks are present in the chromatogram. Multiple peaks appear in the spectra due to the formation of both $M+2H^{2+}$ and $[M+3H]^{3+}$ ions during mass spectrometry. In some instances, noise appears in the low m/z region of the mass spectra due to low intensity of the product peaks.

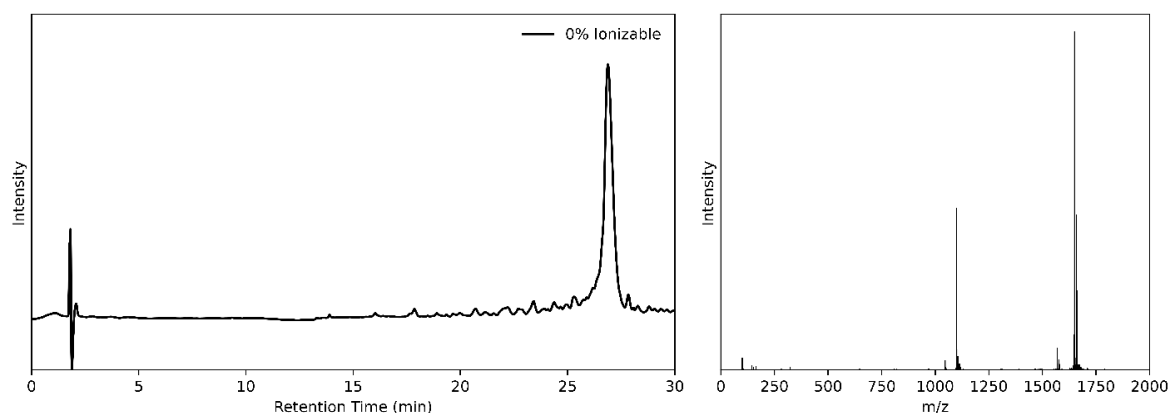


Figure 4.8. HPLC-MS chromatogram and mass spectrum of the 0% ionizable polypeptoid.

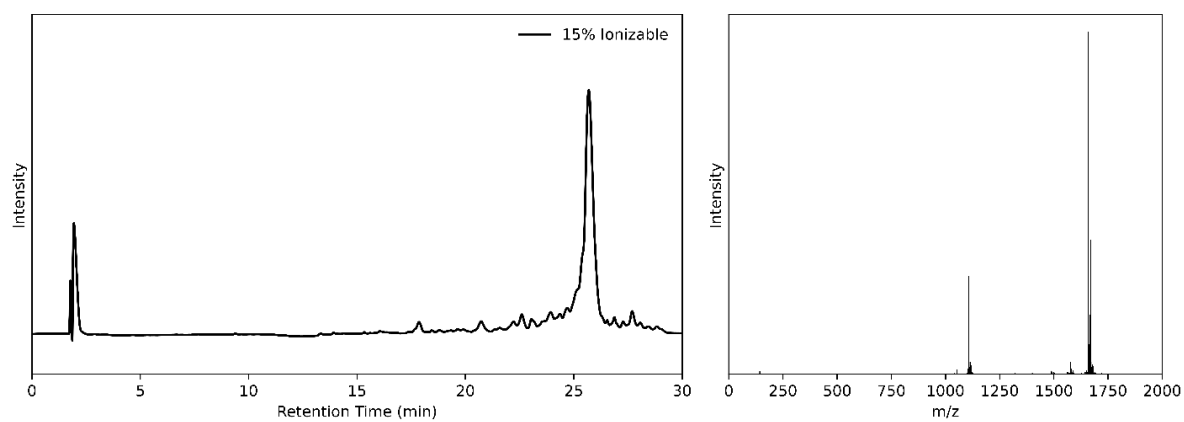


Figure 4.9. HPLC-MS chromatogram and mass spectrum of the 15% ionizable polypeptoid.

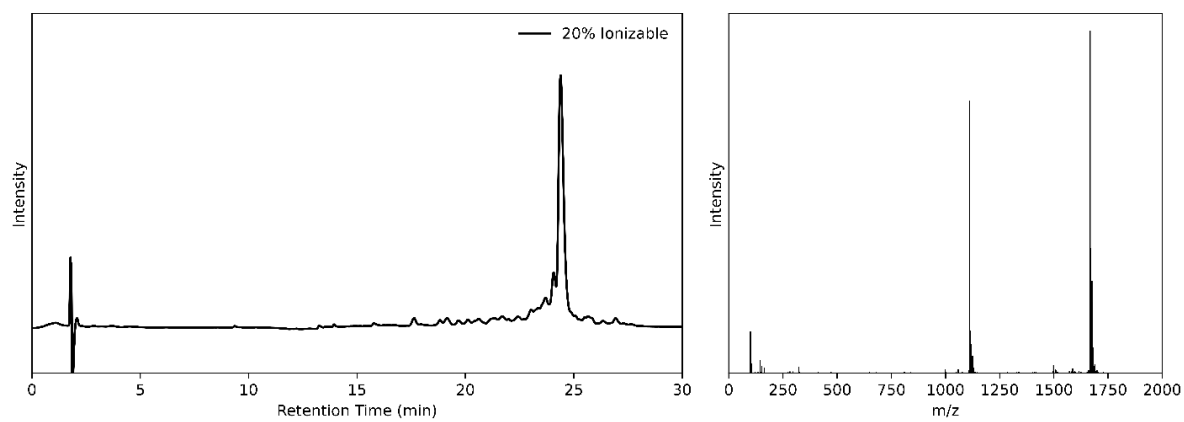


Figure 4.10. HPLC-MS chromatogram and mass spectrum of the 20% ionizable polypeptoid.

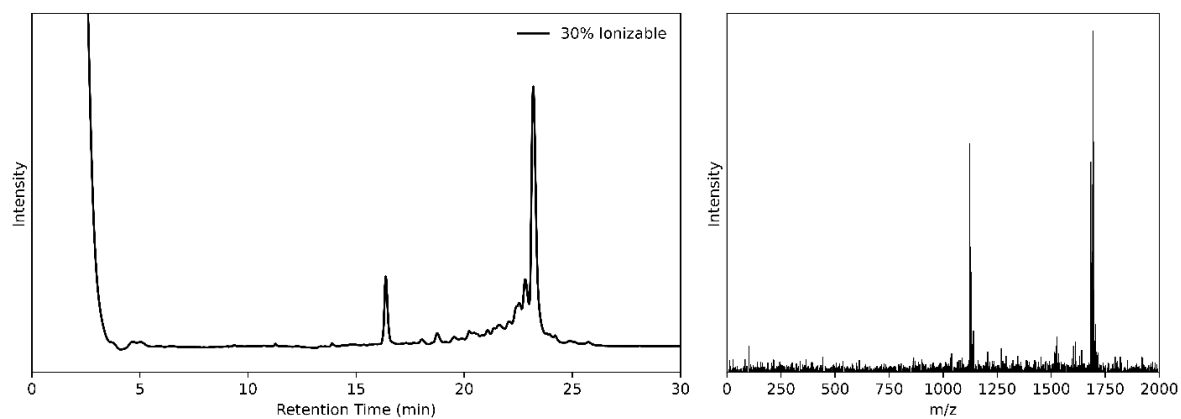


Figure 4.11. HPLC-MS chromatogram and mass spectrum of the 30% ionizable polypeptoid.

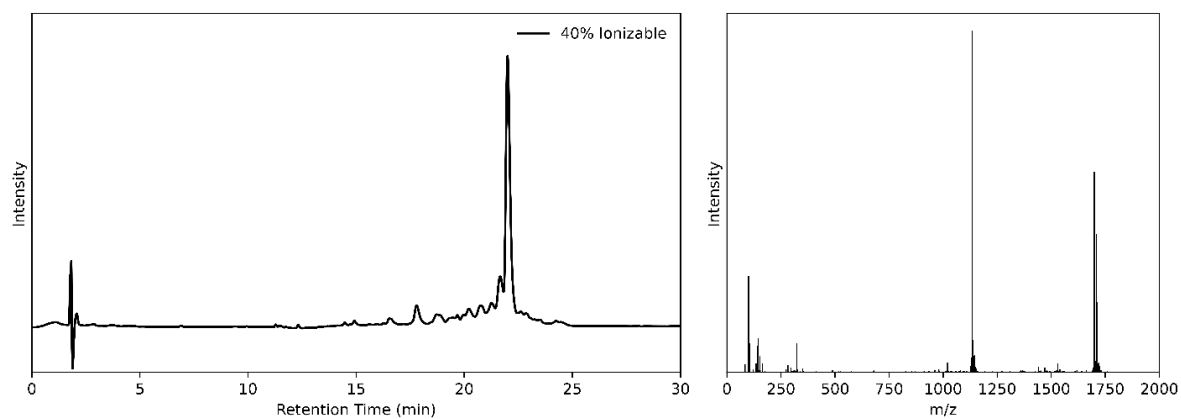


Figure 4.12. HPLC-MS chromatogram and mass spectrum of the 40% ionizable polypeptoid.

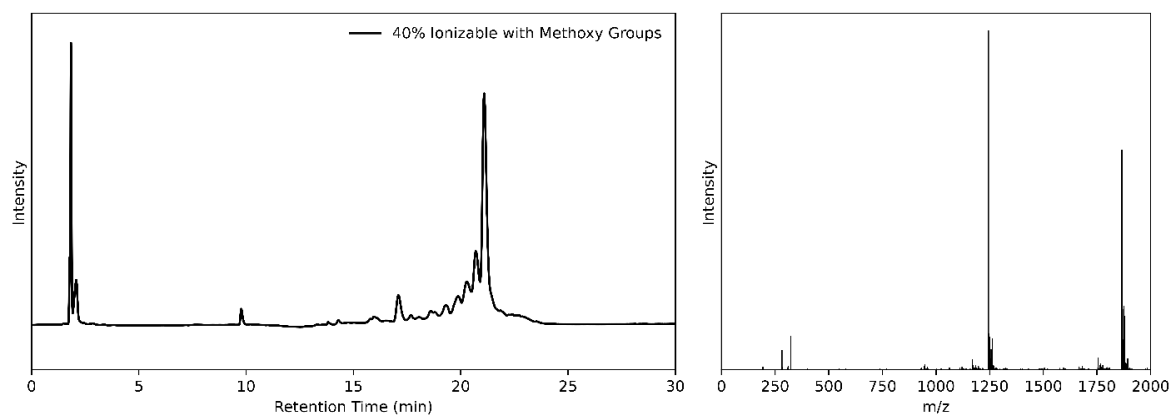


Figure 4.13. HPLC-MS chromatogram and mass spectrum of the 40-S polypeptoid sample.

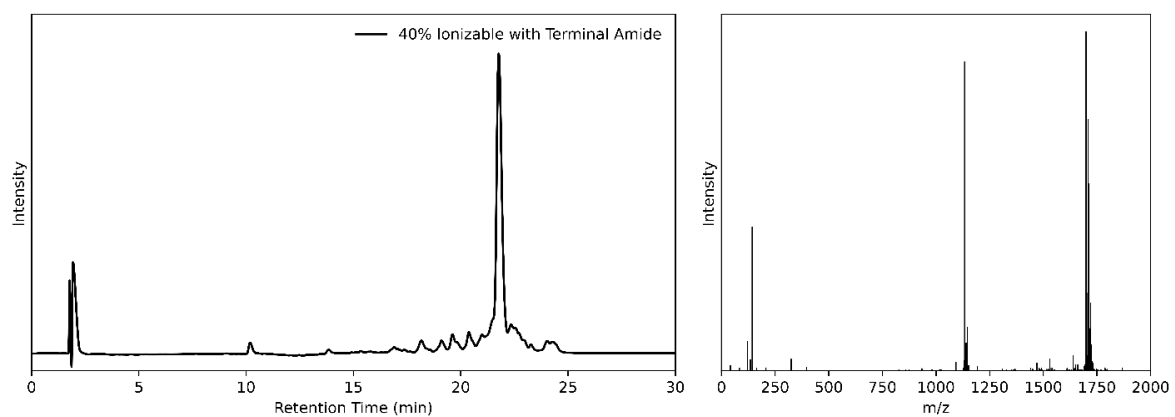


Figure 4.14. HPLC-MS chromatogram and mass spectrum of the 40-NH₂ polypeptoid sample.

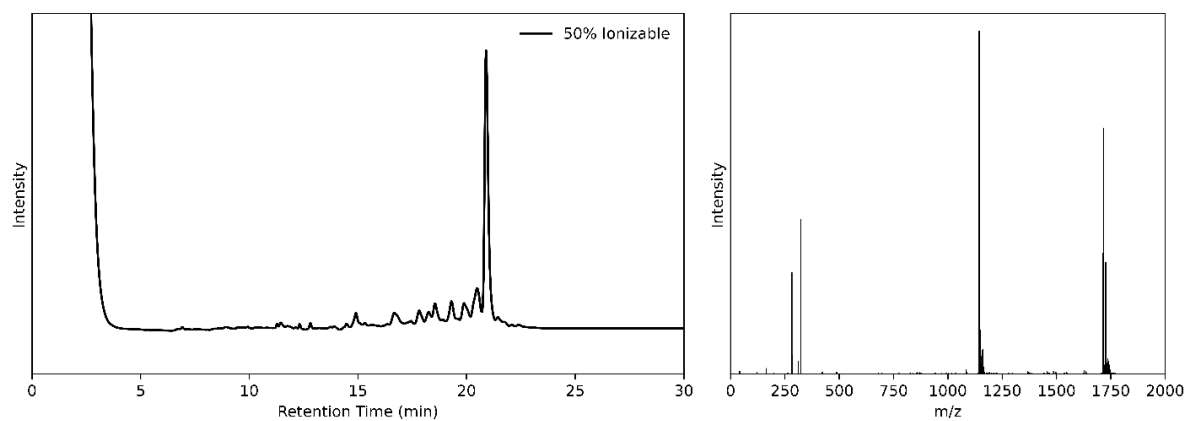


Figure 4.15. HPLC-MS chromatogram and mass spectrum of the 50% ionizable polypeptoid.

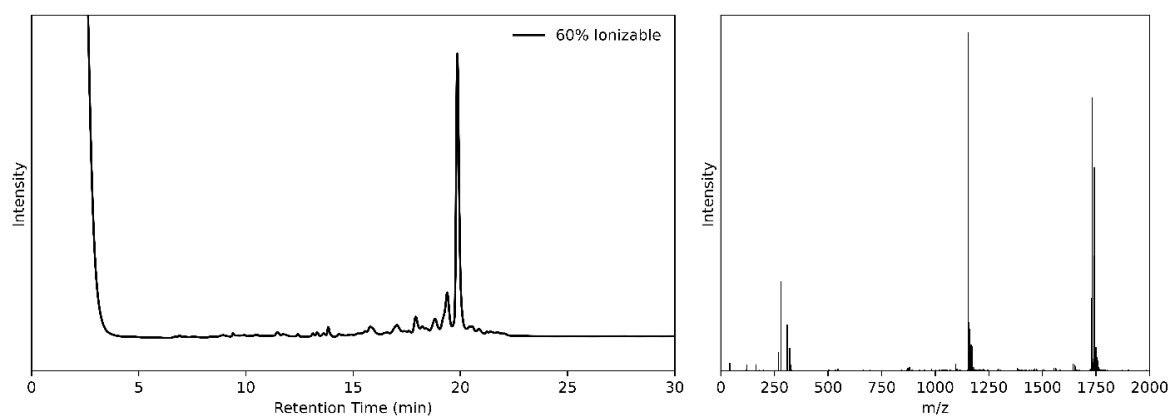


Figure 4.16. HPLC-MS chromatogram and mass spectrum of the 60% ionizable polypeptoid.

Chapter 5: Conclusions and Outlook

Polymeric chemically amplified resists (CARs) have long served as the premier patterning material for use in microelectronics fabrication. However, as necessary feature sizes have shrunk to the 10-15 nm regime with the rise of EUV lithography, new challenges with these materials have arisen. These primarily stem from two key areas: material stochastics, or chemical heterogeneity, and poor EUV absorption. This dissertation leverages polypeptoids, a bio-inspired class of sequence-defined polymers, as a model next-generation CAR platform with the potential to address both of these challenges. The precision afforded by iterative submonomer synthesis provides the unique capability to precisely control the spatial arrangement of functional groups along the polymer backbone, and **Chapter 2** exploits this to investigate the impacts of polymer sequence on patterning properties. Polypeptoids also offer access to a nearly limitless library of functional sidechains, enabling the consolidation of multiple resist components onto a single polymer scaffold. **Chapter 3** takes advantage of this to examine how strongly EUV-absorbing functional groups influence photoresist

sensitivity. Finally, the synthesis of polypeptoids enables the realization of truly monodisperse material. **Chapter 4** uses polymers of fixed chain length and precisely controlled ionizable monomer content to experimentally evaluate the critical ionization model for photoresist dissolution. While these results are promising, polypeptoids photoresists are still in their early days, and considerable opportunity exists for further exploration.

Polymer sequence plays a critical role in a wide range of biological applications, yet it has remained underexplored due to synthetic limitations on traditional polymers. **Chapter 2** of this dissertation demonstrated that polymer sequence and chain length significantly influence the patterning performance of photoresists, alongside standard process variables such as dose and bake conditions. While the blocky sequence performed worse compared to the alternating material under the primary process conditions, its resolution improved by lowering processing temperatures to slow both deprotection kinetics and acid diffusion, suggesting that optimal conditions may vary depending on sequence architecture. These findings highlighted polymer sequence as a powerful tool for tuning resist performance, but much remains to be understood. The sequence space available to a polymer system scales as X^n , where X is the number of distinct monomers and n is the chain length. This number quickly becomes intractable, and it is unfeasible to experimentally test each possible outcome. Simulations will therefore play an essential role in navigating this space. While computational efforts have typically required expensive atomistic simulations, recent developments to course-grained polypeptoid models¹²⁰ should drastically improve screening capabilities when combined with high-throughput synthetic techniques. Further mechanistic studies are also needed to understand how sequence influences patterning within a fully amorphous film. One avenue for this could be secondary ion mass spectrometry (SIMS), which is a technique that can probe the spatial

distribution of PAG molecules or other additives within a film.⁴⁵ A deeper mechanistic understanding would yield new design rules to guide the future use of sequence control in photoresist development.

In **Chapter 3**, iodine incorporation into polypeptoid photoresists was explored as a strategy for improving EUV sensitivity, which is critical for increasing wafer throughput in manufacturing. This study demonstrated that iodine incorporation into chemically amplified polypeptoid photoresists is an effective strategy for boosting EUV absorption, with as little as 1.2 atomic% iodine yielding a 58% increase in the absorption coefficient. Additionally, photoelectron spectroscopy and total electron yield measurements confirmed that this enhanced absorption translated into corresponding increases in both primary and secondary electron generation. Despite these gains, iodine incorporation did not improve EUV sensitivity, with the highest iodine loading instead requiring roughly twice the exposure dose to clear compared to the control. This was attributed to crosslinking driven by carbon-iodine bond scission, as suggested by EUV contrast curves and outgassing measurements. These results underscore that increasing electron generation alone is insufficient to improve resist sensitivity if the additional electrons are consumed by competing reactions. Future studies into mitigating side reactions, either through secondary electron quenchers or more stable iodo-compounds, would be valuable for understanding the role of secondary electrons in these materials. Exploration of other EUV-absorbing functionalities such as tin and zinc would further illuminate whether the source of secondary electrons, rather than simply their quantity, meaningfully impacts patterning performance.

Chapter 4 utilized polypeptoids as a chemically defined model system to experimentally probe the critical ionization (CI) model, a widely used framework for understanding dissolution and development in polymeric photoresists. By synthesizing polypeptoids with precisely controlled quantities of ionizable groups, the ionization threshold required for dissolution in aqueous base developer was directly determined. These materials revealed two distinct dissolution mechanisms depending on proximity to the CI level: well above the threshold, dissolution was rate-limited by ionization of the pendant groups, while at the CI level it was governed by diffusion of OH^- ions into the film. Furthermore, systematic variation of polypeptoid chain-end groups produced measurable differences in dissolution rate that CI theory does not fully account for, suggesting that polymer sequence features beyond bulk ionizable fraction play a role in dissolution behavior. Looking ahead, polypeptoids will continue to serve as a powerful platform for fundamental studies of polymer dissolution and solubility due to their unique control over composition and sequence. Incorporating models that account for polymer thermodynamics and chemical identity alongside ionization will be essential for understanding how sequence influences dissolution, with implications extending beyond photoresists to the broader field of polymer physics.

The future of polypeptoid resists is promising, but further development of side-chain chemistries is required to continue pushing towards improved resolution. Tethering photoacid generators directly to the polymer backbone has been shown to improve resolution in traditional CARs by limiting acid diffusion into unexposed regions.⁵⁵ This would likely extend to polypeptoid-based materials and would open a large and exciting design space for new materials exploration through modulation of the distance between PAG molecules and acid-cleavable protecting groups along the polypeptoid chain. More broadly, this dissertation has

explored only a small subset of the functional group combinations that have been investigated in traditional CARs over decades of development. High-throughput synthetic and characterization techniques will be vital for accelerating the maturation of polypeptoid photoresists and for systematically mapping the vast design space these materials offer. Beyond polypeptoids, other sequence-defined polymer platforms represent largely unexplored territory in the context of photoresist development, and may offer complementary advantages in terms of functionality, processability, or compatibility with existing fabrication workflows.

Throughout this work, polypeptoids have proven to be a uniquely capable platform at the intersection of precision polymer chemistry and semiconductor lithography. Their sequence-defined, monodisperse nature has enabled investigations into patterning, EUV absorption, and resist dissolution that would be difficult or impossible with conventionally synthesized polymers — and the results presented here represent only an early survey of what this platform can offer. As the demands of next-generation lithography continue to intensify, materials that combine synthetic precision with functional versatility will become increasingly valuable. Polypeptoids are well positioned to meet that challenge, and the foundations established in this dissertation provide a basis for their continued development as both practical resist materials and as model systems for understanding the fundamental polymer physics that governs them.

Appendix: Zwitterionic Polypeptoids for Marine Antifouling

Collaborator Contributions:

John Finlay and Tony Clare (Newcastle University) performed *Balanus improvisus* and *Ulva linza* fouling assays.

A.1. Introduction

Marine biofouling has been a known issue since the invention of ships, but it remains a large problem to this day. The issues are largely split into (a) increased economic costs caused by increased drag and fuel consumption and (b) environmental challenges caused by increased emission of greenhouse gases and the transport of attached invasive species around the world.

Economic challenges associated with biofouling stem from increased friction and drag forces on ships caused by surface roughening. Calculations by Schultz et al. showed that in order to overcome drag and maintain a consistent speed, the required shaft power increases by 11-86% depending on the thickness of the associated biofilm.¹²¹ A high degree of fouling was shown to increase fuel consumption by over 20% compared to a ship with a perfectly smooth hull.¹²² With the majority of global trade occurring via ship, this leads to huge financial penalties not only in fuel costs, but also in the additional time and money required for more frequent docking and cleaning services. For the DDG-51 class of naval destroyers alone, which constitutes about 30% of the US fleet, fouling was estimated to cost \$1 billion over a 15-year period.¹²²

In addition to these economic driving forces, biofouling on ships causes a number of environmental issues. Increased fuel consumption naturally increases the greenhouse gas emissions, including CO₂, NO_x, and SO_x, which contributes to global warming, acid rain, and other environmental and health concerns.¹²³ International shipping accounts for about 2% of global energy-related CO₂ emissions according to the International Energy Agency (roughly 740 Mt)¹²⁴ – reducing fouling could drastically lower this. Additionally, the transport of

invasive species as part of biofilms is a major threat to indigenous species and biodiversity around the world.

Beginning in the 1960's, the biocide tributyl tin (TBT) began to see heavy use in antifouling paints and coatings. These coatings were highly effective and saw considerable use, but it was later discovered that these paints were leaching TBT into the ocean and contaminating aquatic environments. This contamination led to deformations and reproductive issues in non-target mollusks in coastal areas,¹²⁵ which was attributed to TBT interfering with the endocrine system of these animals.¹²⁶ Because of these environmental issues, the use of TBT in antifouling paints was ultimately banned by the International Maritime Organization in 2008. This decision caused a shift towards copper-based paints and coatings, which mostly use cuprous oxide (Cu_2O), cuprous thiocyanate (CuSCN), or metallic copper as biocides.¹²⁷ However, these coatings have also been shown to have negative impacts on marine life,¹²⁸ and all biocide-containing paints are facing strict regulations. The development of nontoxic, polymeric antifouling and fouling-release coatings is needed as an alternative to these toxic options moving forward.

Designing an effective antifouling coating for a marine environment is immensely challenging due to the wide variety of organisms and adhesion mechanisms. In total, over 4000 different organisms contribute to marine biofouling. These generally assemble into biofilms through four overlapping phases. First, an initial film forms from the adsorption of proteins and other macromolecules, on top of which microfoulers such as diatoms and bacteria begin to attach. This primary film then serves as a bed on which larger, multicellular

organisms such as algae can attach over the span of days. Finally, macrofouling organisms such as barnacles and mussels can be recruited to the surface.¹²⁹

A.1.1 Soft Foulers (Algae and Diatoms)

Of these, three of the most common fouling organisms are algae, diatoms, and barnacles, and together they convey the difficulty of creating a universal antifouling or fouling-release coating. To start, the adhesion strength of diatoms such as *navicula incerta* has been shown to be more sensitive to surface chemistry than mechanical properties, and they generally exhibit stronger adhesion to hydrophilic fouling-release surfaces such as poly(dimethylsiloxane) (PDMS).^{130, 131} This trend is in stark contrast to that of fouling from algae such as *ulva linza*, which exhibits preferential fouling on hydrophilic surfaces.^{132, 133} For this reason, one of the main strategies for preventing the settlement and adhesion of microfoulers has involved amphiphilic materials that can interfere with both extremes.^{79, 80, 134-136} Other strategies have involved the use of super-hydrophilic zwitterions which form a dense hydration layer of water that deters the settlement of organisms,^{137, 138} but unfortunately this strategy does not perform as well in removal studies once organisms are attached.

A.1.2 Hard Foulers (Barnacles)

Barnacles continue to add complexity to this trifecta. Unlike algae and diatoms, barnacles are “hard foulers” that excrete a cement whose binding process involves oxidative reactions and pH excursions in order to obtain strong adhesion.¹³⁹⁻¹⁴⁴ Chemical strategies for weakening or preventing the adhesion of barnacles have included the use of antioxidants to prevent

oxidative crosslinking of the cement^{145, 146} and zwitterions for the dense hydration layer previously mentioned.^{137, 147}

In the case of barnacles, both surface chemistry and mechanical properties of coatings have an impact. Like algae and diatoms, barnacles tend to initially settle on surfaces based on wettability, though the preferences vary between species.¹⁴¹ Once attached, good fouling-release properties are required for a coating to be functional. The critical stress σ_c and the critical force P_c are defined as:

$$\sigma_c = \sqrt{\left(\frac{2G_c K}{t}\right)}$$

$$P_c = \pi a^2 \sqrt{\left(\frac{2G_c K}{t}\right)}$$

where G_c , K , t , and a are the critical surface energy, bulk modulus, film thickness, and contact radius.¹⁴⁸ This suggests that a thick, soft, low surface energy film should perform best in fouling release applications. This has led to considerable research into silicones, as they are soft enough to have appreciable deformation when a force is applied to an attached object that they undergo peeling.¹⁴⁹ PDMS has been shown to perform well in these applications, though it generally requires structural or chemical modifications to make up for low resistance to mechanical damage and poor adhesion to substrates.^{149, 150}

A.1.3 Polypeptoids in Antifouling Applications

With surface chemistry playing such a large role in performance of antifouling and fouling-release coatings, polypeptoids have emerged as a promising platform for

incorporating a wide variety of functional groups. Polypeptoids are a type of N-substituted glycine analogous to polypeptides, where the functional group is shifted from the α -carbon on peptides to the nitrogen atom.⁷⁰ A wide variety of peptoids can be synthesized through an iterative submonomer solid-phase synthesis of alternating acylation with a haloacetic acid and nucleophilic substitution with almost any of the hundreds of primary amines.⁹⁰ These have higher yields per reaction than the reactions required for their peptide counterparts, allowing for polymeric chain lengths and gram-scale batch sizes. A wide variety of functionalities have been incorporated into peptoids, including hydrophilic and hydrophobic groups, charged groups,¹⁵¹ zwitterions,¹⁵² buffers,⁷⁸ and stable free-radicals.^{153, 154} Amphiphilic peptoids have previously been incorporated into marine antifouling coatings and have proven effective against algae and diatoms.^{79, 80, 82} Additionally, zwitterionic pH buffers have been incorporated into polypeptoids brushes for protein antifouling applications.⁷⁸

A.2 Methods

A.2.1 Polypeptoid Synthesis

Polypeptoids were synthesized on rink amide polymer resin beads (loading: 0.62 mmol/g) using the two-step submonomer method, consisting of alternating acylation reactions with a haloacetic acid and nucleophilic substitutions with a primary amine. Syntheses were performed on Prelude, Prelude X, and Symphony X robotic synthesizers (Gyros Protein Technologies). Upon completion, an end group modification was performed on-resin via acylation with 3-(tritylthio)propionic acid, yielding a thiol-terminated polypeptoid following

cleavage. Peptoids were then cleaved from the resin using a solution of 47.5% trifluoroacetic acid (TFA) and 47.5% dichloromethane (DCM), supplemented with either 2.5% water and 2.5% triisopropylsilane (TIPS) for peptoids bearing protecting groups, or 5% water for unprotected peptoids. Resin beads were agitated in the cleavage solution for 30 minutes, filtered, and washed with DCM. Solvent was removed under vacuum, and crude peptoids were then dissolved in a water/acetonitrile mixture and lyophilized for 1–2 days to yield the final products.

A.2.2 Triblock Copolymer Synthesis

Polystyrene-*b*-poly(dimethylsiloxane-*co*-vinylmethylsiloxane)-*b*-polystyrene, or PS-P(DMS/VMS)-PS triblock copolymers were synthesized via sequential anionic polymerization following previously reported procedures.¹⁵⁵ Prior to synthesis, benzene, tetrahydrofuran (THF), styrene, and a solution of hexamethylcyclotrisiloxane (D3) in benzene were rigorously dried and transferred into a glovebox. All reactions were conducted in septa-capped 40 mL vials under inert atmosphere. Styrene was first polymerized in benzene using sec-butyllithium as an initiator and allowed to stir overnight. The D3/benzene solution was then added and stirred for 48–72 hours, during which the reaction mixture transitioned from bright orange to pale yellow, indicating near-complete conversion of the styrene anion to the D3 anion. THF was subsequently introduced at a THF:benzene ratio of 1:3, increasing solvent polarity and initiating D3 polymerization. Concurrently, a solution of 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (V3) in THF was added via syringe pump over 24 hours to ensure uniform incorporation of the vinyl-containing monomer throughout the siloxane block. Upon

completion, dichlorodimethylsilane was added to couple the living chain ends, yielding the final PS-P(DMS/VMS)-PS triblock copolymer.

Characterization via nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC) showed successful polymerizations, resulting in a 6 kDa-60 kDa-6 kDa PS-P(DMS/VMS)-PS triblock copolymer.

A.2.3 Thiol-ene Click Reactions

Polypeptoids were attached to the PS-P(DMS/VMS)-PS triblock copolymer via thiol-ene click chemistry following previously reported procedures.¹⁵⁶ The peptoid and polymer were combined at a molar ratio of 2.5:1 (peptoid:vinyl group) and dissolved in a minimal volume of 80:20 THF:DMF containing 2,2-dimethoxy-2-phenylacetophenone as the radical photoinitiator. The solution was purged with nitrogen for 15 minutes and subsequently irradiated under UV light for 4 hours. The resulting surface-active block copolymer (SABC) was precipitated into acetonitrile and dried.

A.2.4 Coating of Microscope Slides for Antifouling Studies

Antifouling coatings were assembled on glass microscope slides following previously reported procedures.⁸⁰ Slides were first cleaned with Piranha solution (sulfuric acid and hydrogen peroxide), rinsed, and then immersed overnight in a solution of 3-aminopropyltrimethoxysilane and acetic acid in ethanol to functionalize the surface with amine groups. A maleic anhydride-functionalized Kraton styrene-ethylene-butylene-styrene (SEBS) polymer was then applied by spin coating. After annealing at 120°C overnight, the maleic anhydride reacted with the amine-functionalized glass surface to form a covalent bond

between the polymer and substrate. Three additional layers of unfunctionalized SEBS were spin-coated on top and baked overnight to yield a thick elastomeric coating in which the polystyrene domains formed physical crosslinks. Finally, the peptoid-containing SABC was dissolved in a 1:1 mixture of DCM and toluene, spray-coated onto the slides, and baked overnight to allow polystyrene domain crosslinking.

A.2.5 Characterization of Antifouling Coatings

The hydrophilicity of the coatings was assessed by underwater bubble contact angle measurements. Measurements were taken on dry coated slides and again after equilibration in water for 4 days. For each sample, three slivers per slide were measured with three bubbles each, yielding nine total measurements per sample.

Biological antifouling performance was evaluated by collaborators John Finlay and Tony Clare at Newcastle University using *Navicula incerta* diatoms, *Ulva linza* algae, and *Balanus improvisus* barnacle larvae. Fouler settlement and removal were quantified for all species using previously reported methods.^{147, 157, 158}

A.3. Preliminary Results and Discussion

The ability to precisely control the location of monomers in polypeptoids allows for unique zwitterionic structures. In this study, separate positive and negative functional groups were employed in the form of a primary amine and a carboxylic acid. This approach allows significantly more flexibility compared to attaching a traditional zwitterion with both positive and negative charges on the same molecule, as both the number and ratio of charged groups

can be varied along the polypeptoid backbone. Additionally, the chosen functional groups have previously shown success in polypeptoid brushes for antifouling, where they were hypothesized to act as buffers whose operating pH included a pH of 8,⁷⁸ which is that of seawater. For this reason, these materials were hypothesized to work well in barnacle antifouling, and a variety of sequences were synthesized. Shown in Figure A1, these materials included three different sequences where the number of charge pairs was systematically increased, along with one sequence that included an imbalance of charges to favor the more basic functionality. Also included was a purely hydrophilic polypeptoid to function as a control. In all cases, the charged functional groups were positioned at the farthest end of the polypeptoid to place them in closest proximity to the surface.

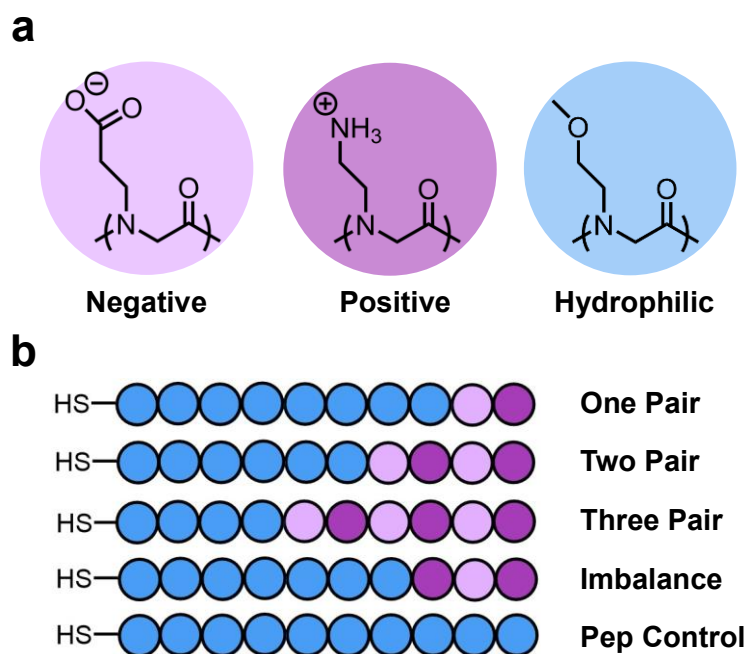


Figure A.1. (a) Polypeptoids were designed to include separate positive and negative charges, along with an uncharged hydrophilic group. (b) A variety of sequences were designed to vary charge density and charge imbalance.

After attaching polypeptoids to a PS-P(DMS/VMS)-PS triblock copolymer through thiol-ene click chemistry, the resulting surface active block copolymers (SABCs) were coated onto microscope slides and examined for barnacle antifouling properties. Barnacle settlement measurements (**Figure A2a**) showed a clear trend, where the percentage of barnacle cyprids that attached to each coating increased as the number of charged groups increased. Thus, the cyprids found the higher charge densities, irrespective of whether balanced or imbalanced, conducive to settlement, but also readily settled on the uncharged peptoid surfaces. This suggests that the interactions between cyprids and surfaces are more complex than just charge density or just surface energy and that a balance of factors is involved. In contrast, the differences in removal of juvenile barnacles from the test coatings (**Figure A2b**) were relatively small. While there seems to be a slight increase in removal with increasing charge density, the only samples from which removal was statistically different were the low charge density (One Pair) sample compared to the imbalanced sample, with removal being higher from the latter. It would therefore seem likely that the positive charge was responsible for the greater release from the unbalanced sample. In all cases, the peptoid-containing SABCs outperformed the polystyrene control.

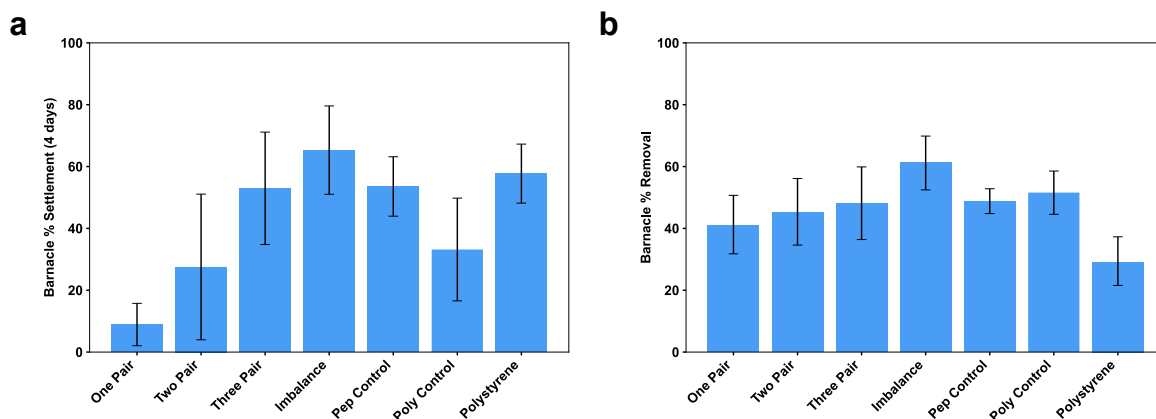


Figure A.2. (a) Percent settlement of *B. improvisus* cyprids on the test coatings after 4 days. Each point is the mean from 6 replicate slides. Bars show 95% confidence limits. (b) Percent removal of 3 to 5-day-old juvenile barnacles from test coatings. Each point is the mean from 10 replicate slides. Bars show 95% confidence limits.

While the charged polypeptoids performed well for barnacle antifouling tests, they performed poorly when transitioning to fouling tests against *Ulva linza* spores. Figure A3a shows that all charged sequences performed worse than both the hydrophilic polypeptoid SABC and the unfunctionalized triblock copolymer. If present at the surface in large enough numbers, the presence of charged groups can bind water to such an extent that spores have difficulty in sensing the coating surface and attaching. However, it doesn't appear to have happened in this case, and it looks likely that the spores were not deterred by any strong interactions between the surface and water molecules. Additionally, the removal of spores was quite poor, with all samples averaging between 0-10%. Despite this, the sample with intermediate charge density did significantly outperform the rest. However, it is unclear whether this was due to the chemistry involved or if it was due to extraneous variables such as film roughness.

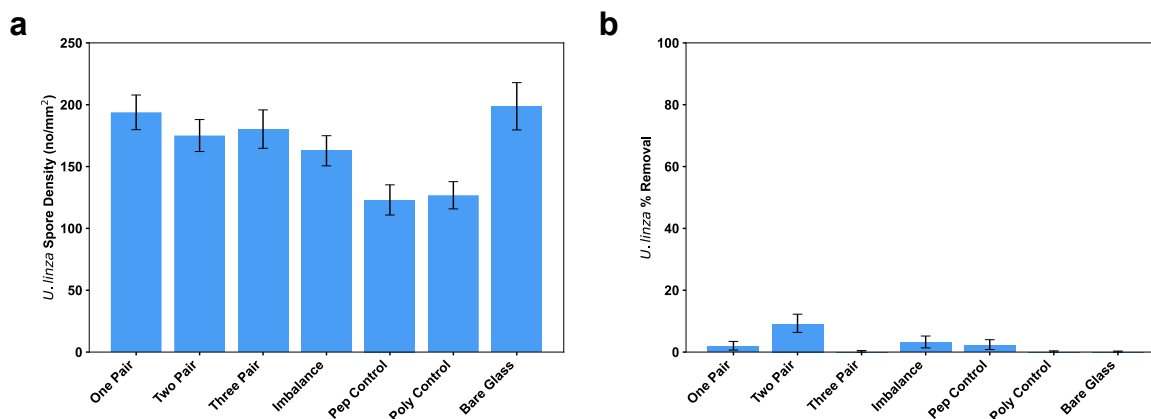


Figure A.3. (a) The density of attached spores on the coatings after 45 minutes followed by washing. Each point is the mean from 90 counts from 3 replicate slides. Bars show 95% confidence limits. (b) Percent removal of spores from the coatings due to a shear stress of 52Pa. Each point is the mean from 90 counts from 3 replicate slides. Bars show 95% confidence limits derived from arc-sine transformed data.

A.4 Conclusions and Outlook

Preliminary results from this study demonstrate that zwitterionic polypeptoids are a promising strategy for mitigating antifouling caused by barnacles. These materials provide an easily tunable ability to control both the number and ratio of charged functionalities. Polypeptoids were successfully synthesized and attached to a larger triblock copolymer that was used to form coatings. These materials outperformed controls of both a hydrophilic polypeptoid SABC and a pure polystyrene coating, with smaller amounts of charged groups showing lower barnacle settlement than peptoids with higher charge density or imbalanced charge. However, poor performance in tests with *Ulva linza* algae demonstrate that further work is required to tune these materials. In the future, experimenting with different charged groups and different charge imbalances, as well as a higher loading of peptoid in the SABC could lead to new design rules regarding antifouling materials.

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