The Design and Synthesis of Aromatic Ion-Based Polyelectrolytes for Divergent Applications

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ABSTRACT

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Versatile polyelectrolytes with tunable physical properties have the potential to be transformative in applications ranging from medicine to energy storage. To expand the design space for innovative cationic polymeric materials, I describe herein the development of a new class of functional polyelectrolyte based on the aromatic trisaminocyclopropenium (TAC) ion. The facile synthesis of a series of cyclopropenium-based macromolecules via either the direct polymerization of functional monomers or a post-polymerization click reaction is demonstrated. To probe fundamental structure-property relationships and understand technological implications of cyclopropenium polymers, a variety of materials were evaluated as gene delivery agents for cellular transfection and as ion conducting membranes. It was found that certain cyclopropenium polymers are biocompatible and efficient transfection agents, and that post polymerization functionalization chemistry enabled the straightforward screening of polymeric TAC derivatives. Furthermore, the thermal properties, local morphology, and dielectric response of a series of monomeric and polymeric TAC ionic liquids with different counter ions were characterized. It was found that the mechanism for ion transport depends on the nature of the ion pair, which can promote anomalously high conductivity at the calorimetric glass transition temperature. Finally, the synthesis of a new class of polyelectrolyte based on the cyclopentadienyl aromatic anion is described.
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**Chapter One: The Design and Synthesis of Tris(aminocyclopropenium) Polymers**


**Chapter Two: Biomedical applications of cyclopropenium-based polyelectrolytes**

Chapter Three: Nanoscale morphology and ion transport properties of cyclopropenium materials

The evaluation of cyclopropenium materials as ion exchange membranes was adapted from two publications. The evaluation of polymerized ionic liquids with various counter ions was adapted from the publication: Griffin, P. J.; Freyer, J. L.; Han, N.; Geller, N.; Yin, X.; Gheewala, C. D.; Lambert, T. H.; Campos, L. M.; Winey, K. I., Ion Transport in Cyclopropenium-Based Polymerized Ionic Liquids. *Macromolecules* **2018**, *51* (5), 1681-1687., where P. J. Griffin and J. L. Freyer contributed equally to the work. J. L. Freyer synthesized the mono- and poly-ionic liquids and P. J. Griffin measured the nanoscale morphology by multi-angle X-ray scattering and ionic transport of the materials. Both J. L. Freyer and P. J. Griffin wrote the manuscript.


Chapter Four: Polyelectrolytes based on aromatic anions

The synthesis of polyelectrolytes based on aromatic anions is unpublished, but was carried out by J. L. Freyer with the help and advice of Alex Radtke and Dr. Chirag Gheewala.
Introduction

It is difficult to overstate the importance of polymers to our world and the critical role they play in everyday life. Since polymers were first developed by Baekeland\textsuperscript{1} over a century ago, our understanding of and ability to manipulate macromolecules has revolutionized nearly every facet of the human experience. Recognizing DNA as a biological polymer comprising four different repeat-units has enabled a quantitative approach to understanding evolution. The polymeric nature of gluten is directly responsible for the delicious chewiness of bagels. Cellulose is the polymer that allows cotton to be spun into the textiles we wear as clothing. Yoga pants and bulletproof vests owe their incredible properties, ranging from flexibility to tensile strength, to the polymers that make them up. Polymers can be made into comfy foam mattresses, incorporated into processed foods to improve texture, and are often found in the noses of sea turtles.\textsuperscript{2}

The ubiquity of natural and synthetic polymers is the direct result of the nearly limitless design space of organic chemistry and the inherent processability that arises from these long, reptating molecules.\textsuperscript{3} Depending on the molecular structure, polymers can conduct or insulate heat, or radiate or absorb light. They can deliver drugs and help diagnose disease. The promise of materials science is that by cleverly designing molecules, systems, and processes, we can engineer almost any desirable property into a material.\textsuperscript{4}

Materials science thus has significant implications for all kinds of technology, but as countless researchers have discovered, dialing desired capabilities into a material is neither easy nor straightforward. It takes lots of trial and error, and many PhDs are spent attempting to deconvolute the unexpected relationships between molecular structure, macromolecular architecture, and material properties and function. This has been the case with my own PhD,
during which I have developed a new family of polymers, outlined straightforward synthetic pathways to elaborate the molecular structure, assessed and characterized their physiochemical properties, and explored technological applications for which these materials will add value.

The research presented in this thesis concerns a subclass of polymers called polyelectrolytes, where the polymer repeat units contain ion pairs. There are many natural and synthetic polyelectrolytes, and significant research has been performed to investigate the fundamental properties of and potential uses for these multivalent materials. Of particular relevance to my work are synthetic cationic polyelectrolytes, which have had a profound impact on many facets of materials science, from electrochemical devices for energy storage to gene delivery biotechnologies.\textsuperscript{5-7} Synthetic cationic macromolecular systems, like many polymers, benefit from facile processability and can be engineered to display remarkable properties, such as high ionic conductivity, alkaline stability, antimicrobial activity, and biocompatibility, among others.\textsuperscript{7-8} These properties are installed via rational manipulation of chemical handles that tune material structure. Most functional units investigated to date for polyelectrolytes are heteroatom-based (charges on nitrogen, phosphorus, oxygen, etc.),\textsuperscript{9} with polymers containing ammonium, phosphonium, or imidazolium groups being particularly common (Figure 1).\textsuperscript{10-14} This is likely due to the stability of these cationic species and their ease of synthesis via post polymerization reaction of alkyl halide-containing polymers (e.g polyvinylbenzylchloride) with amines, phosphines, and imidazoles, respectively. In general, the principal strategies to modulate properties for these commonly reported systems are varying substituent alkyl chain length, tuning spacer chemistry from the polymer backbone, and copolymerizing charged monomers with neutral monomers. However, few systematic studies have been performed for these types of
cationic polymers, leaving a limited understanding of how the specific nature of ionic structure and molecular geometry influences material properties.\textsuperscript{12,14}

![Hard ion - Soft ion](tetrahedral-planar.png)

**Figure 1.** Structures of cationic polyelectrolytes: phosphonium, ammonium, imidazolium, and cyclopropenium (left to right). Common handles to modify chemical structure highlighted in blue, and tether to polymer backbone shown in orange. Both groups can be used to tune functionality. The nature of the charge diffusivity and molecular geometries are noted.

In order to expand the repertoire of cationic functional groups for polymers, we sought to develop a polyelectrolyte based on the trisaminocyclopropenium (TAC) ion and characterize its distinct structural and electronic properties (Figure 2). Unlike other polycations reported in the literature, TAC’s positive charge is formally localized on carbon atoms. Owing to its aromaticity and the resonant electron donation of its nitrogen substituents, the TAC ion is highly stable despite its charge and ring strain. The $\pi$-orbital overlap of the conjugated C$_3$ ring system with the nitrogen lone pairs provides TAC derivatives with an exceptionally high HOMO, which helps explain unique observations of halide repulsion,\textsuperscript{15-16} dimer formation,\textsuperscript{17} and a relatively low oxidation potential.\textsuperscript{18-20} Aromaticity and bulky substituents render TAC a rigid, planar, and relatively large molecule. With a physiochemical profile so unlike other cations described in the literature, we were eager to begin our studies of TAC but first had to verify they were sufficiently accessibly via straightforward and scalable synthesis.
In 1994, Taylor and co-workers outlined an efficient synthesis for TAC derivatives, whereby they were prepared in large quantities simply by treating pentachlorocyclopropane with an excess of a nucleophilic secondary amine. In this procedure, the proton is eliminated, forming the activated tetrachlorocyclopropene, and subsequent nucleophilic substitutions of the amines yields the corresponding tris(dialkylamino)cyclopropenium. When sterically hindered secondary amines are used (e.g. dicyclohexyl amine), two amino groups are substituted onto the ring to yield the chlorobis(dialkylamino)cyclopropenium. The 4 to 6 alkyl groups on the resulting molecule provide ample opportunity to modulate properties and impart functionality. The facile synthesis, high stability, and promising behavior of TACs have promoted its successful employment as enantioselective Brønsted base catalysts, ionic liquids, catholytes for redox flow batteries, and ligands for metal complexes. The conception of polymeric-TAC challenged us to imagine how, through rational design, this new family of materials could be leveraged to overcome challenges in various fields and advanced technologies.

Before investigating potential applications, a feasible and scalable synthesis towards well-defined TAC polymers was developed. The field of polymer chemistry is vast, and the polymerization method of interest informs monomer design. One of the most commonly employed classes of polymerization is reversible-deactivation radical polymerization (RDRP) because this provides polymers with a high degree of control over molecular weight, a low
dispersity, high tolerance to water and functional groups, and a straightforward synthetic procedure.\textsuperscript{3, 28-29} Radical polymerizations involve the rapid initiation of a radical species followed by propagation of successive additions of vinyl monomers with a reactive radical on the chain end. Introducing a “reversible-deactivation” capability to conventional radical polymerizations is a powerful way to impart uniformity in molecular weight distributions across different polymer chains: continually terminating and re-activating the radical chain carriers has been shown to slow the reaction kinetics (Figure 3). This causes the propagation of polymer chains to be longer lived, the distribution of molecular weight much narrower, and reduces unwanted termination reactions such as chain-chain coupling and disproportionation. These polymerizations are classified as “living” due to the absence of termination events; thus, it is relatively straightforward to synthesize block copolymers and other nonconventional macromolecular topologies.\textsuperscript{30} Different RDRP techniques diverge in how they mediate the active and dormant states of radicals and in their tolerance to various functional groups. Two common types of RDRP reactions that we employed in this work are reversible addition-fragmentation chain transfer (RAFT, Figure 3A) polymerization, and atom transfer radical polymerization (ATRP, Figure 3B). In the case of RAFT, a reversible chain transfer process promoted by the extremely rapid exchange of the dithioester grants control of polymer growth.\textsuperscript{31} ATRP, on the other hand, accomplishes reversible radical termination via ligand transfer to a transition metal complex.\textsuperscript{32} The living nature of both of these methods is

\[
A. \quad P^* \quad + \quad S \quad S \quad R \quad \xleftrightarrow{M} \quad P^* \quad S \quad S \quad R \quad \xleftrightarrow{Z} \quad P^* \quad S \quad S \quad R \quad + \quad R^* \\
B. \quad P-Br \quad + \quad Cu(I)Br/L \quad \xleftrightarrow{M} \quad P^* \quad + \quad Cu(II)Br_2/L
\]
Figure 3. Schematic of the reversibility of radical deactivation for (A) RAFT, and (B) ATRP.

evidenced by the resulting polymer’s narrow molecular weight distribution and the linear increase in molecular weight with respect to reaction time and monomer conversion. Because of the many benefits of these RDRP polymerizations, we elected to use a styrenic moiety as our polymerizable handle to form most of the TAC-based polymers. Styrene and its derivatives are commercially available and there are numerous reports of functionalized styrenic monomers that successfully underwent polymerization via these methods.33-35

By incorporating a styrenic moiety onto the cyclopropenium scaffold, we were able to demonstrate the facile synthesis of a series of polymers and nanoparticles based on monomeric cyclopropenium building blocks incorporating various functional groups that affect physical properties. Homopolymers, statistical copolymers, and block copolymers based on styrenic TAC monomers were formed using RAFT polymerization methods.36 Furthermore, we demonstrated that a post-polymerization click reaction provides access to versatile TAC-functionalized macromolecules of various architectures. Protected amine-containing styrene monomers were polymerized by ATRP, deprotected, and functionalized with TAC groups resulting in a strategy that is highly tolerant of functional groups. Quantitative conversions of polymers comprising pendent or main-chain secondary amines were observed for an array of TAC derivatives in three hours using near equimolar quantities of cyclopropenium chlorides.37

Our control of TAC functionality coupled with our use of living radical polymerization techniques allowed us to probe elements of structure, architecture, and behavior in a highly precise and methodical way. Facile chemical transformations enabled a divergent approach to application discovery, with our aim to engineer TAC-based materials for disparate applications, from gene delivery agents to ion exchange membranes for alkaline fuel cells.38 In the course of
this work, our observations of significant differences in materials’ properties (e.g. toxicity, transfection efficiency, ion transport) corresponding to seemingly minor structural changes begin to inform the rapid engineering and re-engineering of TAC polymers for a variety of applications, as well as a platform to shed light on how structural motifs impact materials systems. Synthetic routes, experiments, results, and discussion of the significance of this work are detailed in the chapters that follow.
References


Chapter One

The Design and Synthesis of Tris(aminocyclopropenium) Polymers

Modularly designed polymeric materials can be engineered to suit a broad range of applications, representing an attractive platform for technological advancement.¹ Materials that possess both inherent compositional versatility and facile accessibility via robust and scalable synthetic pathways are of particular importance to the field of materials science.²-³ In this regard, cationic polyelectrolytes have emerged as a versatile class of materials that have been exploited in a broad array of applications,⁴-⁶ ranging from gene delivery⁷-⁸ to the formation of ion-conducting membranes.⁹-¹¹ Development in the area of cationic polyelectrolytes has thus far focused on a limited menu of monomeric functionalities, including ammonium, phosphonium, imidazolium, pyridinium, and guanidinium ions.¹²-¹⁴ These heteroatomic structures have been successfully incorporated into many technological systems, but suffer from limitations in terms of the ability to finely tune their physical properties. Thus, the identification of new modular cationic polyelectrolytes with superior characteristics for processing, controllable self-assembly, and function represents an important goal for this field.¹⁵-¹⁶

In developing a new family of polyelectrolytes, certain criteria must be met:¹¹,¹⁷,¹⁵ (1) thermodynamic stability, (2) ease and scalability of polymerizations using controlled methods, (3) incorporation of accessible chemical handles to allow for diversity and intimate control of physical properties, and (4) tunable Coulombic interactions. We postulated that polyelectrolytes based on the cyclopropenium ion would satisfy these design criteria while offering highly distinct structural architectures and electronic properties. Furthermore, cyclopropenium-based systems possess unique characteristics that distinguish them from existing cationic polyelectrolytes, namely an enhanced dispersion of the positive charge (compared to ammonium,
phosphonium, and guanidinium systems) and weaker H-bond donor capacity (compared to imidazolium and pyridinium ions).\(^{18}\)

As the smallest of the Hückel aromatics,\(^{19}\) the trisaminocyclopropenium (TAC) ion possesses significant stability despite its traditionally unstable carbocationic nature (Figure 1A).\(^{20,21}\) This remarkable degree of stability is further enhanced through incorporation of electron-donating amino substituents onto the cyclopropenium ring.\(^{22}\) With pK\(_{R+}\) values estimated at >13, aminocyclopropenium ions are stable even in strongly alkaline aqueous solutions.\(^{23-24}\) Moreover, the thermal decomposition temperature (T\(_{\text{dec}}\)) of the tris(dialkylamino)cyclopropenium chloride salts has been measured to be >300 °C,\(^{18}\) exceeding that of dialkylimidazolium chloride salts (T\(_d\) ~ 250 °C).\(^{25}\) These unique structural features have already inspired the development of aminocyclopropenium ions for a range of applications, including as metal ligands,\(^{26}\) organocatalysts,\(^{27-29}\) and ionic liquids,\(^{18}\) however, the incorporation of these cations into a polymeric backbone has only led to polymers with unstable cyclopropenium ions as intermediates.\(^{30}\) Given the tunable functionality and robust, efficient, and orthogonal chemistry characterizing cyclopropenium ions, we herein describe the synthesis and evaluation of a new family of cationic polyelectrolytes.
Figure 1. Routes to synthesize TAC-containing macromolecules. A) Structure of the cyclopropenium ion, including the dialkylamino groups that can be used to stabilize and vary the application of this diverse building block. B) Types of polyelectrolytes that can be synthesized from cyclopropenium monomers by reversible-deactivation radical polymerization (RDRP) strategies and emulsion polymerization. C) Modification of a neutral polymer backbone with a bis(dialkylamino)cyclopropenium chloride yields a TAC-based polyelectrolyte.
Design of material platform

As outlined in Figure 1B, our initial vision for the design of cyclopropenium polymers began with the synthesis of a TAC-based monomer. This functional monomer includes a polymerizable unit, a spectator group (which could also serve as a functional handle), and four additional groups that provide the means to tune the physical properties of the resulting macromolecules. Due to the ease of synthesis and commercial availability of styrene derivatives, we focused on styrenic TAC monomers (termed, TAC(R)) bearing a series of dialkylamino (NR₂) substituents. Styrene-based monomers can be subjected to various reversible-deactivation radical polymerization (RDRP) strategies.\textsuperscript{31-33} For the initial synthesis, we utilized reversible-addition fragmentation chain-transfer (RAFT) polymerization\textsuperscript{33} to assemble homopolymers, statistical copolymers, and diblock copolymers of different compositions ranging from 20 to 50 mol % of TAC functionality.

While direct polymerization of functional TAC monomers reliably delivers TAC-polymers, we also proposed a post-polymerization route, which offered more modularity and the potential to clearly evaluate substituent effects. The modification of polymer backbones with functional groups by efficient and inexpensive chemistries, especially via “click” reactions, is particularly desirable for the commercialization of polymeric materials.\textsuperscript{34} The limited tolerance of myriad functional groups in controlled polymerization techniques (Figure 1B) renders post-polymerization functionalizations (PPF, Figure 1C) an attractive route to form complex macromolecular structures of polyelectrolytes.\textsuperscript{35-36} PPF is especially attractive for PILs, as charged groups are incompatible with most size exclusion chromatography (SEC) columns. As a result, many studies of PILs ignore effects of molecular weight and dispersity ($D$), correlating physical properties solely to the structure of the repeat units.\textsuperscript{37} A more complete understanding
of macromolecular systems can be achieved in materials with well-defined and narrow molecular weight distributions.\textsuperscript{38-39} A new type of click reaction between bis(dialkylamino)cyclopropenium chloride (BACCl) ILs\textsuperscript{18, 40} and polymers containing secondary amines enabled the facile synthesis of TAC-polymers via a PPF route. While many literature procedures to obtain other cationic PILs via PPF have reported reactions with large excesses of the quaternizing agent (3-10 eq) and long reaction times (up to three days),\textsuperscript{41-42} we found that this conjugation reaction proceeded in ca. 3 h under mild conditions, with near stoichiometric amounts of reactants. Therefore, we designate these reactions as “click” in the context of polymer chemistry,\textsuperscript{43} establishing the BACCl ion as a clickable ionic liquid, or ClickabIL. Both synthetic schemes outlined above provide value: one is streamlined and one allows for facile derivatization.

\textit{Synthesis of functional monomers}

The exploration of the cyclopropenium functional group in the context of cationic polyelectrolytes was originally inspired by its unique ionic liquid properties\textsuperscript{18} and the straightforward elaboration of the TAC ion with various functional groups. At the inception of this study, however, there had been no reports on the incorporation of this thermodynamically stable carbocation into macromolecules; TAC derivatives have only appeared in polymers as transient species.\textsuperscript{30, 44} Derivatives of the TAC ion are synthesized from inexpensive reagents and can be easily prepared on a multi-gram scale under ambient conditions.\textsuperscript{27} As robust chemistry is required for large-scale production of materials, we devised a viable synthetic strategy \textit{en route} to the polymerizable TAC ion monomers. The general approach to synthesize TAC ion-containing monomers is based on the facile preparation of asymmetric amino-substituted TAC ions (e.g. TAC(R), Figure 1).\textsuperscript{40} This procedure allowed us to change functionality in a straightforward manner while maintaining cationic properties and thermal stability. Notably,
synthetic routes to aminocyclopropenium derivatives are modular and highly scalable,\textsuperscript{21} with efficiency levels approaching those attained via click chemistry.\textsuperscript{45}

Figure 2. Synthesis of TAC(R) monomers for RAFT polymerizations. The monomers TAC(Cy) and TAC(iP) were synthesized by addition of dicyclohexylamine (73\%) and diisopropylamine (85\%) to 1, followed by substitution of styrenic-type amine 5 under basic conditions (86\% and 88\%, respectively). TAC(Mo) was similarly synthesized. After addition of morpholine to 1, subsequent hydrolysis, and treatment with oxalyl chloride (42\%, 3 steps), 5 was substituted to yield TAC(Mo) (59\%).

The preparation of the TAC(R) monomers begins with pentachlorocyclopropane 1, which is commercially available or can be inexpensively synthesized in hundred-gram quantities.\textsuperscript{46} Reaction of 1 with a secondary amine leads to near-quantitative yields of a corresponding TAC cation (2 or 3). Amines with high steric hindrance like dicyclohexylamine (Cy) and diisopropylamine (iP) add twice to 1, preventing addition of a third bulky amine and leading directly to compound 2. Conversely, less sterically hindered amines, such as morpholine (Mo),
add thrice to 1, resulting in an undesired \textit{tris}-amino TAC 3. However, the latter is readily hydrolyzed to its corresponding cyclopropenone in hot, aqueous base, which can subsequently be chlorinated to obtain 2. To underscore the accessibility of these materials, we note that the monomers are obtained by simple purification techniques (see Chapter 1 Supplementary Information for details). Using this process, we prepared multigram quantities of 2 incorporating three different secondary amines, as depicted in Figure 2 (bottom). Importantly, the chemistry depicted in Fig. 2 is highly amenable to a wide range of nucleophilic secondary amines incorporating a variety of functional groups, including elements of asymmetry. We specifically chose to examine dicyclohexylamine, diisopropylamine, and morpholine given that they differ significantly in their degrees of hydrophilicity and steric hindrance.

The synthesis of the TAC(R) monomers from the precursor 2 was readily achieved in 10 to 20 gram quantities. The chlorinated 1-position of 2 is highly susceptible to addition of a secondary amine bearing a polymerizable unit, such as styrenic compound 5. A styrene-based polymerizable group was chosen as it is a well–behaved building block in polymer chemistry and its hydrophobicity relative to the TAC ion moiety could stabilize an emulsion of the type used in nanoparticle synthesis. We postulate that other polymerizable moieties, like norbornene groups for ring opening metathesis polymerization (ROMP), would yield functional monomers as well.

\textit{Polymerization of functional monomers}

The three chosen monomers (TAC(Cy), TAC(iP), and TAC(Mo), Figure 2) were polymerized in multigram quantities using RAFT and yielding linear polymers (PTAC(Cy), PTAC(iP), and PTAC(Mo) respectively, Figure 3A). PTAC(Cy) was purified through precipitation into 1,4-dioxane from CH$_2$Cl$_2$ with 88% recovered yield. PTAC(iP) was precipitated from acetone or CH$_2$Cl$_2$ into cold ethyl acetate with 70% recovered yield. Due to
their solubility in water, both PTAC(iP) and PTAC(Mo) could be purified by dialysis. Purification of PTAC(Mo) resulted in a 53% recovered yield. Each of these polymers was isolated as a powder, and PTAC(iP) and PTAC(Mo) were observed to be extremely hygroscopic. Through end-group analysis of the \(^1\)H NMR spectra, we calculated the degree of polymerization and molecular mass of each of the homopolymers (Table S2). Due to the cationic nature of the TAC groups, homopolymers and copolymers could not be characterized using size exclusion chromatography (SEC) eluted with organic solvents, as the polymers adhere to the column. We attempted to characterize the dispersity (\(\tilde{D}\)) of the hydrophilic homopolymers (PTAC(iP) and PTAC(Mo)) on an acetate buffered aqueous SEC, however only PTAC(Mo) successfully eluted owing to its greater hydrophilicity (Figure S1, Table S2). The \(\tilde{D}\) of PTAC(Mo) was determined to be 1.3, however we note that this value may not accurately reflect the degree of polymerization control, given that the polyelectrolyte may still be interacting with the column as it is eluted. The synthetic accessibility of these various TAC-based polymers is straightforward and highly efficient, rivaling that of ammonium, phosphonium, and imidazolium polymers.\(^{47-50}\)

As expected, a significant correlation was observed between the nature of the amino substituent and the physical properties of the resultant homopolymer. We observed that the decomposition temperature (\(T_{\text{dec}}\)), glass transition temperature (\(T_g\)), and solubility of the homopolymers varied as a function of substituent (Table S1, Chapter 1 Supporting Information). Through characterization by thermogravimetric analysis (TGA), we found that the \(T_{\text{dec}}\) of the homopolymers increased as the amino substituents became less sterically hindered. Of particular note, PTAC(Mo) decomposed at 310 °C, which is comparable to the decomposition temperatures of imidazolium-based polymers.\(^{42}\) Differential scanning calorimetry (DSC) was performed to identify the \(T_g\) for the homopolymers, as ion-conducting membranes are frequently formed.
through melt-processing. We observed that PTAC(Mo) exhibited a $T_g$ of 160 °C, PTAC(iP) had a $T_g$ of 82 °C, and PTAC(Cy) had a $T_g$ of 140 °C. Previous reports have revealed a connection between the nature of the counterion and the accessible temperature window; replacement of the chloride with an alternative, typically bulkier counterion is thus expected to increase the $T_{dec}$ while decreasing the $T_g$.\textsuperscript{18, 42, 51} Importantly, however, these data clearly demonstrate a similar relationship between alkyl chain identity and the observed $T_{dec}$ and $T_g$. By modifying the cyclopropenium substituents, we are able to significantly broaden the temperature-window in which these materials are processable without the need to adjust the counterion. Additionally, it was found that the solubility of PTAC(R) homopolymers is highly dependent on amino substituents, again reflecting on the influence of building block composition on macromolecular properties. Characterization of the homopolymers, including thermal data and solubility information, is summarized in Table S1.
Figure 3. Synthesis of TAC-containing polymers. (A) TAC(R) is polymerized by RAFT yielding both homopolymers, PTAC(R), (B) block copolymers PS-\textit{b}-PTAC(R) of varying styrene content and (C) statistical copolymers, P(S\textit{stat}-TAC(R)). (D) Nanoparticles are synthesized by surfactant-free emulsion polymerization with styrene using the water-soluble thermal initiator V-50.
Copolymer and nanoparticle synthesis

To augment our library of TAC-based homopolymers with block copolyelectrolytes (BCPEs), we synthesized block copolymers PS-b-PTAC(R) (TAC mol%) by growing styrene units onto the living PTAC(R) macro-chain transfer agents (macro-CTA) (Figure 3B). By varying the degree of polymerization (DP) of the polystyrene block, we effectively controlled the different mole fractions of the TAC functional block. We note that block copolymers PS-b-PTAC(R) could also be obtained by the reverse process of growing the functional monomer TAC(R) onto polystyrene macro-CTAs. Furthermore, statistical copolymers were readily synthesized by RAFT, using styrene and TAC(R) monomers to achieve PS-stat-PTAC(R) (Figure 3C). When styrene was copolymerized with each monomer in a 1:1 mole ratio, we observed some disparities in the percent incorporation of functional TAC monomers in the resulting copolymer. For TAC(Cy), TAC(iP), and TAC(Mo), the degree of incorporation was approximately 50%, 48%, and 45% respectively.

Considering our ability to copolymerize styrene and TAC(R) monomers and the amphiphilic nature of TAC(R) monomers, we sought to synthesize cationic nanoparticles based on the TAC(iP) monomer via surfactant-free emulsion polymerization (Figure 3D). Many traditional strategies rely on the use of surfactants or additional solvents\textsuperscript{52} to obtain sub-100 nm cationic particles. By simply mixing styrene and TAC(iP) at various weight percent values (1%, 2.5%, 5%, 10% and 20% of TAC(iP)) and using a thermally activated radical initiator (V-50) in aqueous solution, we were able to obtain particles ranging from 30-90 nm (as characterized by dynamic light scattering (DLS), see Supporting Information). Because the TAC ion readily dissolves in water, it is driven to the surface of styrene droplets in water to stabilize emulsions. Thus, higher loadings of TAC(iP) compared to styrene resulted in increased surface area and
smaller, albeit more disperse, particles. Figure 3D shows a scanning electron microscope (SEM) image of nanoparticles formed using 5% TAC(iP)/95% styrene. The average diameter determined by DLS was found to be 50 nm. Furthermore, the particles form stable dispersions as the zeta potential of the 5% TAC(iP) nanoparticles was found to remain above +30 mV over the range of >10 pH units (Figure S2). As a control, particles synthesized with styrene only (without any surfactants or TAC(R) monomers) were much larger and exhibited a bimodal size distribution. These data demonstrate that the TAC(R) monomer effectively stabilizes oil-in-water droplets, and that the charge is present on the particle surface. A more detailed study of this behavior followed, including the incorporation of other TAC(R) monomers into cationic nanoparticles. In general, the ability to make charged nanoparticles in a surfactant-free, large-scale process could have far-reaching potential towards interfacial additives and biological applications.53-54

**Synthesis via post polymerization functionalization**

Chemical transformations that promote a fundamental understanding of (1) structure-property relationships concerning charge density, (2) repeat unit composition, and (3) macromolecular structure in TAC-based polymeric systems was a priority research effort and could broaden the adoption of these materials in technological platforms.8, 55-57 The development of alternative synthetic routes to form TAC-polymers is valuable in the study of these materials because performing many polymerizations is cumbersome and polymers made from the different TAC monomers have batch-to-batch variations. Thus, a post polymerization functionalization (PPF) method to synthesize TAC-based polyelectrolytes is needed to simultaneously control the macromolecular architecture and molecular composition of TAC repeat units. Akin to what Coates and co-workers have demonstrated with alkaline-stable imidazolium ionic liquids (ILs),
the ability to elaborate cationic building blocks towards complex structures that are not commercially available is crucial to optimize performance for a chosen application. Therefore, straightforward access to a variety of amino substituents on the TAC scaffold could facilitate optimization, inform design principles, and elucidate chemical structure-property relationships within a single family of materials.

To obtain a well-defined neutral polymer precursor, we synthesized poly(methylaminostyrene) (PMAS, Figure 2), a polymer containing a secondary amine as a pendant group. Because monomeric PMAS is incompatible with reversible addition-fragmentation chain-transfer polymerization or atom-transfer radical-polymerization (ATRP) conditions, we elected to protect the secondary amine with a tert-butyloxy carbonyl (Boc) protecting group. The Boc-protected monomer readily polymerizes by ATRP to yield polymers of controllable molecular mass and narrow dispersity ($D$), which can be characterized by size exclusion chromatography at this step. Further details of the synthetic protocols are available in the Supporting Information.

![Figure 4](image)

Figure 4. (A) Synthesis of Boc-protected polyamine (PBoc) by ATRP; and (B) corresponding SEC trace shows high degree of control over polymer growth and narrow dispersity of 1.05.

The deprotected PMAS undergoes clean addition to BACCl salts as shown in Figure 2. The choice of BACCl can tailor the physical properties of the resulting polymers through control of solubility properties or through the introduction of functional groups via the amino
substituents (ex. diallylamine). We subjected PMAS to functionalization with six different BACCl derivatives containing isopropyl (iP), ethyl (Et), allyl (Al), cyclohexyl (Cy), morpholine (Mo), and piperidine (Pep) substituents (Figure 5). $^1$H NMR spectra of these polymers reveal that the starting material is fully converted into the corresponding TAC-containing polymer, as evidenced in the peak shifts noted in Figure 5. Notably, the positive charge is not generated by a reaction between neutral reactants in this new approach, in contrast to quaternization PPF reactions.$^{14, 60}$ Instead, cationic BACCl salts are directly coupled to neutral homopolymers containing secondary amines. While initial studies of TAC-based polymers grown from functional monomers noted differences in the solubility profiles and thermal properties of various TAC polymers,$^{61}$ this chemistry provides a direct approach to study the impact of various functional groups on macromolecular properties while keeping the effects of dispersity and degree of polymerization constant.
Figure 5. $^1$H NMR spectra of TAC polymers show complete functionalization of PMAS with BACCl ClickabILs bearing various alkyl substituents.

The modularity of this protocol is highlighted by the diverse set of functional groups obtained using the same parent polymer; only minor changes in procedure (e.g. use of co-solvent) are needed to accommodate structural diversity. In this vein, diblock copolymers were
synthesized by polymerization of the Boc-protected monomer onto both polyethylene oxide (PEO) and polystyrene (PS) macro-initiators using ATRP (Figure 6). SEC traces show a narrow dispersity is maintained after copolymerization in both cases (Figures S3 and S4). Following their successful deprotection, the PMAS blocks in PEO and PS diblock copolymers were fully functionalized with both hydrophobic and hydrophilic BACCl's (Cy, iP, and Mo, from most to least hydrophobic) without the need to modify the procedures used to prepare the corresponding homopolymers. The commutable nature of this chemistry will encourage systems development away from individual polymer design. Furthermore, we demonstrate the broad scope of ClickabIL chemistry by functionalizing commercially available linear polyethyleneimine (PEI) with BACCl's. PEI was subjected to the ClickabIL reaction conditions described above (Figure 6), and quantitative functionalization was observed for all BACCl's.
Figure 6. Post-polymerization functionalization of polymers containing secondary amines by addition of BACCl ClickabILs.

In conclusion, a new family of electron-rich cationic polyelectrolytes based on the cyclopropenium ion building block was assembled via direct polymerization of functional monomers and post polymerization functionalization of polyamines. Both strategies accommodate significant structural diversity of repeat units, the polymer backbone, and macromolecular architecture, which translates to widely variable physical properties. With such
modularity, this new class of cyclopropenium-based polyelectrolytes offers a wealth of functionality that translates to significant potential across a broad array of applications. Furthermore, we emphasized a novel example of macromolecular click chemistry between BACCl building blocks and polymers containing pendant and main-chain secondary amines. Linking neutral polyamines that are either commercially available or rapidly assembled with charged BACCl ClickabILs furnishes diverse classes of well-defined TAC polymers under mild conditions. The implications of the synthetic access to these materials are highlighted in upcoming chapters.
References:


Chapter One: The Design and Synthesis of Trisaminocyclopropenium Polymers

Supplementary Information

I. General notes

All materials were purchased from Sigma Aldrich and were used without further purification except as noted below. Methylene chloride (CH$_2$Cl$_2$), tetrahydrofuran (THF), and N,N-dimethylformamide (DMF) were dried using a J.C. Meyer solvent purification system. Styrene was filtered through basic alumina to remove radical inhibitor before use in polymerizations. Deuterated solvents for NMR were purchased from Cambridge Isotope Laboratories, Inc. Eluents for column chromatography were HPLC grade and purchased from Fisher Scientific.

All reactions were performed open to the atmosphere, unless otherwise noted. Organic solutions were concentrated by use of a Buchi rotary evaporator. All polymerizations were carried out with temperature control under vacuum in flame-sealed ampoules. Chemical shifts are given in ppm relative to the signal from residual non-deuterated solvent. $^1$H-NMR and $^{13}$C-NMR spectra were recorded in CDCl$_3$ (except where noted) on Bruker DRX-300, DRX-400 or DRX-500 spectrometers. Data for $^1$H NMR are reported as follows: chemical shift ($\delta$ ppm), multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, q = quartet, hept = heptet, m = multiplet), coupling constant (Hz), integration, and assignment. Data for $^{13}$C are reported in terms of chemical shift. High-resolution mass spectra were obtained from the Columbia University Mass Spectrometry Facility on a JEOL JMSHX110 HF mass spectrometer using FAB$^+$ ionization mode. Low-resolution mass spectrometry (LRMS) was performed on a JEOL JMS-LCmate liquid chromatography spectrometer system using APCI$^+$ ionization technique.
Thin layer chromatography (TLC) was performed using Teledyne Silica gel 60 F254 plates and viewed under UV light. Flash column chromatography was performed using Teledyne Ultra Pure Silica Gel (230 – 400 mesh) on a Teledyne Isco Combiflash Rf.

Size exclusion chromatography (SEC) was used to characterize PTAC(Mo) to quantify its molecular mass dispersity ($D$) on a Waters Alliance 2695 separation module equipped with a PL-aquagel-OH 8 micron Mixed-M column (300 x 7.5 mm), a Waters 2998 Photodiode Array Detector, and a Waters 2414 Refractometer Detector. Sodium acetate buffer (0.3 M) with 20 vol% methanol was used as the eluent at a flow rate of 0.7 mL min$^{-1}$. Poly(ethylene glycol) standards were used for calibration. For all other samples, a Waters GPC with a Waters 2414 refractive index detector was used for characterization of molecular mass and dispersity. Tetrahydrofuran was used as the solvent at a flow rate of 1.0 mL per minute, and the instrument was calibrated with polystyrene standards.

Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris 1 TGA from ambient temperature to 600 °C at a rate of 10 °C min$^{-1}$. Polymer samples were dried under high vacuum overnight prior to measurement, and decomposition temperatures were recorded at 5% mass loss.

Differential Scanning Calorimetry (DSC) was performed on a TA Instruments DSC Q2000 fitted with a RCS90 refrigerated cooling system to determine the glass transition temperatures. DSC measurements were taken at a sampling rate of 10 °C min$^{-1}$ in the temperature range of 0 °C to 200 °C.

Particle size, polydispersity, and electrophoretic mobility were measured using a Möbiuč dynamic light scattering instrument and Dynamics software from Wyatt Technology (Santa
Barbara, CA). Particle size and polydispersity were calculated via the Regularization fit of the correlation function of the Quasi-elastic Light Scattering (QELS) data. Each measurement contained 10 acquisitions and at least 3 measurements were performed. The reported radii or diameters are the average of those measurements. Zeta potential was calculated according to the Smoluchowski approximation and reported values are the averaged result of 5 acquisitions from each of the 31 detectors in the Massively Parallel Phase Amplitude Light Scattering (MP-PALS) detector array. Measurements were run in MilliQ water at neutral pH unless otherwise noted. Samples were passed through a 1.6 µm glass filter (Whatman) prior to measurement to remove only large aggregates and dust.

Scanning electron microscopy (SEM) was performed on a JEOL7001FLV at 3.0 to 10.0 keV. Particles were deposited on a silica wafer from solution, and imaged without sputter coating. Particle sizes measured by SEM were determined using Image-J software by manually counting at least 50 particles.

Transmission electron microscopy was performed on films of PS-\(b\)-PTAC(iP)(20) (calculated molecular mass = 33.4KDa, DP = 200), which were prepared by drop casting a 100 mg mL\(^{-1}\) solution of polymer onto a clean Teflon substrate. After allowing to dry for 24 hours, the film was sectioned with Leica UltraCut 6 ultramicrotome at \(-40 \, ^{\circ}\text{C}\), nominal thickness 70nm using a Diatome Cryo 35° diamond knife. Sections were placed on 300 mesh copper grids with homemade lacey carbon film on top. The sections were stained with RuO\(_4\) vapor for 2 minutes, which preferentially stained the PTAC(iP) block. Sections were imaged with FEI Tecnai F20 TEM operated at 200kV. Images were analyzed using ImageJ 1.48v software.
II. Supplementary Figures

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<th>Mn (Daltons)</th>
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MM = mass average molecular mass. Mn = number average molecular mass. MP = molecular mass at the peak maximum. RT = retention time.

**Figure S1.** Size exclusion chromatography (SEC) trace of PTAC(Mo). The dispersity ($\bar{D}$) was found to be 1.3.
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**Figure S2.** GPC traces of polystyrene macroinitiator and PS-\( b \)-PBoc reveal narrow dispersity is maintained after copolymerization.

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**Figure S3.** GPC traces of poly(ethylene oxide) macroinitiator and PEO-\( b \)-PBoc reveal narrow dispersity is maintained after copolymerization.
Figure S4. $^1$H-NMR spectrum of $N$-methyl-1-(2,3-bis(dicyclohexylamino)cyclopropenium)-4-vinylbenzylamine chloride (TAC(Cy))
**Figure S5.** $^{13}$C NMR spectrum of N-methyl-1-(2,3-bis(dicyclohexylamino)cyclopropenium)-4-vinylbenzylamine chloride (TAC(Cy))
Figure S6. $^1$H NMR spectrum of N-methyl-1-(2,3-bis(diisopropylamino)cyclopropenium)-4-vinylbenzylamine chloride (TAC(iP))
**Figure S7.** $^{13}$C NMR spectrum of $N$-methyl-1-(2,3-bis(diisopropylamino)cyclopropenium)-4-vinylbenzylamine chloride (TAC(iP))
Figure S8. $^1$H NMR spectrum of $N$-methyl-1-(2,3-bis(morpholino)cyclopropenium)-4-vinylbenzylamine chloride (TAC(Mo))
**Figure S9.** $^{13}$C NMR spectrum of $N$-methyl-1-(2,3-bis(morpholino)cyclopropenium)-4-vinylbenzylamine chloride (TAC(Mo))
Figure S10. $^1$H NMR spectrum of PTAC(Cy)
Figure S11. $^1$H NMR spectrum of PTAC(iP)
Figure S12. $^1$H NMR spectrum of PTAC(Mo)
Figure S13. $^1$H NMR spectrum of bis-1,2-(diallylamino)-3-chlorocyclopropenium chloride.

Figure S14. $^1$H NMR spectrum of bis-1,2-(piperidino)-3-chlorocyclopropenium chloride

Figure S15. $^1$H NMR spectrum of tert-butyl methyl(4-vinylbenzyl)carbamate.
Figure S16. $^1$H NMR spectrum of PBoc.

Figure S17. $^1$H NMR spectrum of PMAS.
Figure S18. $^1$H NMR spectrum of PTAC(Cy).

Figure S19. $^1$H NMR spectrum of PTAC(Al).
Figure S20. $^1$H NMR spectrum of PTAC(Et).

Figure S21. $^1$H NMR spectrum of PTAC(iP)
Figure S22. $^1$H NMR spectrum of PTAC(Mo)
Figure S23. $^1$H NMR spectrum of PTAC(Pip)

Figure S24. $^1$H NMR spectrum of PS-$b$-PBoc.
Figure S25. $^1$H NMR spectrum of PS-$b$-PMAS.

Figure S26. $^1$H NMR spectrum of PS-$b$-PTAC(Cy).
Figure S27. $^1$H NMR spectrum of PS-$b$-PTAC(iP).
Figure S28. $^1$H NMR spectrum of PS-$b$-PTAC(Mo).

Figure S29. $^1$H NMR spectrum of PEO-$b$-PBoc.
**Figure S30.** $^1$H NMR spectrum of PEO-$b$-PMAS.

**Figure S31.** $^1$H NMR spectrum of PEO-$b$-PTAC(Cy).
Figure S32. $^1$H NMR spectrum of PEO-$b$-PTAC(iP).

Figure S33. $^1$H NMR spectrum of PEO-$b$-PTAC(Mo).
Figure S34. $^1$H NMR spectrum of PEI(Cy).

Figure S35. $^1$H NMR spectrum of PEI(iP).
**Figure S36.** $^1$H NMR spectrum of PEI(Mo).

**Figure S37.** $^1$H NMR spectrum of PEI(Pip).
III. Supplementary Tables

**Table S1:** Characterization of PTAC(R) homopolymers. As the size and hydrophobicity of the alkyl chains decreased from Cy to Mo, conversion of the monomers became noticeably lower and $T_{\text{dec}}$ was found to increase. Solubilities also depended on the hydrophilicity of the alkyl chains.

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IV. Methods

*Procedures for synthesis of 2,3-bis(dialkylamino)-1-chlorocyclopropenium chloride*

![Chemical structure of 2,3-bis(dialkylamino)-1-chlorocyclopropenium chloride](image)

**Synthesis of 2,3-bis(dicyclohexylamino)-1-chlorocyclopropenium chloride**

Dicyclohexylamine (168 mL, 804.8 mmol, 6.0 equiv) was slowly added to a solution of pentachlorocyclopropane$^1$ (30.0 g, 140.0 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (1500 mL) in a 3L round bottom flask. A white precipitate formed as the reaction mixture was stirred for a further 48 hr at room temperature. The solution was washed with 1M HCl (3 x 500 mL), dried with anhydrous sodium sulfate, and concentrated *in vacuo* to yield an off-white solid. This solid was triturated with hot ethyl acetate to give the title product (60 g, 130 mmol, 92%). $^1$H NMR (500 MHz, CDCl$_3$) δ 3.75 (m, 2H, NCyH), 3.40 (m, 2H, NCyH), 1.10-2.20 (m, 40H, Cy). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 131.6, 93.1, 65.2, 56.3, 32.1, 30.2, 24.9, 24.7, 24.0, 23.8. HRMS (FAB+) m/z =
431.3418 calcd for C_{27}H_{44}N_{2}Cl [M]^+ 431.32.

**Synthesis of 2,3-bis(diisopropylamino)-1-chlorocyclopropenium chloride**

Pentachlorocyclopropane (5.20 g, 22.8 mmol, 1.0 equiv) was added to 230 mL of CH_2Cl_2 in a 500 mL dry round bottom flask equipped with a stir bar. To this solution, diisopropylamine (18.48 g, 182.6 mmol, 8.0 equiv) was slowly added and allowed to stir under argon at room temperature overnight. Solvent was removed from the reaction mixture leaving a crude, brown sandy-looking mixture of the desired product in quantitative yield and 3-4 equivalents of the corresponding ammonium salt. This crude mixture was used in subsequent steps without further purification. 

\[ ^1H \text{ NMR (400 MHz, CDCl}_3) \delta 4.28 \text{ (hept, } J = 6.7 \text{ Hz, 2H, C}_3(NCH(CH_3)_2CH(CH_3)_2)_2, 3.89 \text{ (hept, } J = 6.8 \text{ Hz, 2H, C}_3(NCH(CH_3)_2CH(CH_3)_2)_2, 1.45 \text{ (m, 24H, C}_3(N(CH(C_3)_2CH(CH_3)_2)_2).} \]

\[ ^{13}C \text{ NMR (125 MHz, CDCl}_3) \delta 132.0, 117.8, 93.3, 58.1, 48.6, 47.1, 22.6, 21.8, 20.9, 18.9. \]

**Synthesis of 2,3-bis(morpholino)-1-cyclopropenone**

Morpholine (58.0 g, 665.7 mmol, 7.1 equiv) was slowly added to a solution of pentachlorocyclopropane (20.0 g, 93.3 mmol, 1.0 equiv) in CH_2Cl_2 (250 mL) in a 500 mL round bottom flask. The solution turned orange, and a white precipitate formed as the reaction mixture was stirred overnight at room temperature. The white solid was filtered off and the filtrate was concentrated *in vacuo* to a crude red solid. Water (100 mL) was used to dissolve this solid. A
room temperature solution of potassium hydroxide (20 g, 356.4 mmol) in water (30 mL) was added to the solution, which was heated to 65 °C for one hr. The reaction solution was allowed to cool and water was then removed by rotary evaporation. The resulting solid was washed with CH₂Cl₂ (500 mL) and any remaining solid was filtered off. The organic solution was dried with anhydrous sodium sulfate and concentrated in vacuo to yield a crude orange solid. The crude material was purified by silica gel chromatography (10% MeOH in EtOAc) to yield the title product as an off-white solid (8.9 g, 39.7 mmol, 42% two-step yield). Note: the temperature of the rotovap was kept at 30 °C or cooler, and extended exposure to methanol will decompose the title product. ¹H NMR (400 MHz, CDCl₃) δ 3.73 (m, 8H, NCH₂CH₂O), 3.34 (m, 8H, NCH₂CH₂O). ¹³C NMR (125 MHz, CDCl₃) δ 134.8, 120.3, 66.1, 49.3. HRMS (FAB⁺) m/z = 225.1243 calcd for C₁₁H₁₇N₂O₃ [M⁺] 225.12.

Synthesis of 2,3-bis(morpholino)-1-chlorocyclopropenium chloride

Oxalyl chloride (6.86 mL, 79.4 mmol, 2.0 equiv) was slowly added to a 0 °C solution of 2,3-bis(morpholino)-1-cyclopropenone (8.9 g, 39.7 mmol, 1.0 equiv) in CH₂Cl₂ (250 mL) under argon. The solution was warmed to room temperature and left to react for one hr. The product was dried in vacuo to yield a sufficiently pure black solid in quantitative yield (11.0 g, 39.7 mmol). ¹H NMR (400 MHz, CDCl₃) δ 4.05 (m, 4H, N(HCH-CHH)₂O), 3.90 (dt, J = 20.2, 4.5 Hz, 8H, N(HCH-CHH)₂O) 3.66 (m, 4H, N(HCH-CHH)₂O).
Synthesis of N-methyl-4-vinylbenzylamine

Vinylbenzyl chloride (7.5 g, 49.3 mmol, 1 equiv) was added to a 1L round bottom flask equipped with a stir bar. Methylamine solution (8.0M in ethanol, 101.1 mL, 15 equiv) was added to the sealed flask, and an outlet was used to relieve pressure. THF (330 mL) was added to dilute the reaction mixture such that the concentration of vinylbenzyl chloride was 0.10M. The flask was filled with argon and sealed with a septum secured with copper wire. The contents of the reaction flask were allowed to stir at 45 °C for 24 hr. Solvent was subsequently removed by rotary evaporation, and the crude product was dissolved in 250 mL of CH₂Cl₂ and transferred to a 1L separatory funnel. This solution was washed 3x with 1.0M NaOH, 1x with DI water, and 1x with brine, and dried over magnesium sulfate. Removal of solvent by rotary evaporation yielded the title product as yellow oil. ¹H NMR was used to determine purity. (6.82 g, 46.4 mmol, 94% yield, 90% purity). The oil was stored at 0 ºC and was used without further purification. ¹H NMR (400 MHz, CDCl₃) δ 7.33 (m, 4H, ArH), 6.71 (dd, J = 17.6, 10.9 Hz, 1H, H₂C=CHAr), 5.73 (dd, J = 17.6, 1.0 Hz, 1H, H₂C=CHAr), 5.21 (dd, J = 10.9, 2.3 Hz, 1H, H₂C=CHAr), 3.73 (s, 2H, ArCH₂N), 2.45 (s, 3H, NCH₃).

Procedures for synthesis of TAC(R) monomers

Characterization of N-methyl-1-(2,3-bis(dicyclohexylamino)cyclopropenium)-4-vinylbenzylamine chloride (TAC(Cy)). (See main text for synthetic protocol). ¹H NMR (500
MHz, CDCl\(_3\)) \(\delta\) 7.33 (m, 4H, ArH), 6.69 (dd, \(J = 17.7, 10.9\) Hz, 1H, H\(_2\)C\(=\)CHAr), 5.74 (d, \(J = 17.6\) Hz, 1H, H\(_2\)C\(=\)CHAr), 5.25 (d, \(J = 11.0\) Hz, 1H, H\(_2\)C\(=\)CHAr), 4.80 (s, 2H, ArCH\(_2\)N), 3.35 (m, 4H, NCyH), 3.22 (s, 3H, NCH\(_3\)), 1.00-1.90 (m, 40H, CyH). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 137.4, 135.6, 133.6, 126.8, 126.6, 119.0, 117.8, 114.3, 60.3, 57.5, 39.4, 31.7, 25.2, 24.2. HRMS (FAB+) \(m/z = 542.4333\) calcd for C\(_{37}\)H\(_{56}\)N\(_3\) [M]\(^+\) 542.45.

**Synthesis of N-methyl-1-(2,3-bis(diisopropylamino)cyclopropenium)-4-vinylbenzylamine chloride (TAC(iP)).** In a 1 L round bottom flask equipped with stir bar, 2,3-bis(diisopropylamino)-1-chlorocyclopropenium chloride (26.23 g crude mixture, 38.0 mmol CP salt, 1.0 equiv) and triethylamine (11.5 g, 114.0 mmol, 3.0 equiv) were dissolved in 420 mL of CH\(_2\)Cl\(_2\) and put under an atmosphere of argon. N-Methyl-4-vinylbenzylamine (5.59 g, 38.0 mmol, 1.0 equiv) was slowly added to the solution, which was stirred for 15 hr. The reaction mixture was poured into a 1 L separatory funnel and washed with 1M HCl (3 x 200 mL), then DI water (1 x 200 mL), followed by brine (1 x 200 mL). The organic layer was collected and dried over magnesium sulfate. Rotary evaporation yielded 20.0 g of a dark brown viscous liquid. This crude product was purified by silica gel chromatography, eluted first with 100% EtOAc, followed by a mixture of 5% increasing to 20% MeOH in CH\(_2\)Cl\(_2\). Collection of pure fractions, followed by removal of solvent by rotary evaporation yielded an amber oil (13.97 g, 33.3 mmol, 88% yield) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.44 (m, 2H, ArH), 7.25 (m, 2H, ArH), 6.69 (dd, \(J = 17.6, 10.9\) Hz, 1H, H\(_2\)C\(=\)CHAr), 5.78 (dd, \(J = 17.6, 0.8\) Hz, 1H, H\(_2\)C\(=\)CHAr), 5.29 (dd, \(J = 10.9, 0.8\) Hz, 1H H\(_2\)C\(=\)CHAr), 4.82 (s, 2H, ArCH\(_2\)N), 3.90 (hept, 4H, C\(_3\)NCH(Me)\(_2\)), 3.24 (s, 3H, NCH\(_3\)), 1.00-1.90 (m, 24H, NCH(CH\(_3\))\(_2\)). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 137.7, 135.9, 134.0, 127.1, 126.9, 119.0, 116.9, 114.6, 57.9, 51.5, 39.8, 22.01. HRMS (FAB+) \(m/z = 382.3241\) calcd for C\(_{25}\)H\(_{40}\)N\(_3\) [M]\(^+\) 382.32.
Synthesis of \( N \)-methyl-1-(2,3-Bis(morpholino)cyclopropenium)-4-vinylbenzylamine chloride (TAC(Mo)). To a dry round bottom flask of 2,3-bis(morpholino)-1-chlorocyclopropenium chloride (11.08 g, 39.7 mmol, 1.0 equiv) under argon was added CH\(_2\)Cl\(_2\) (150 mL) and \(N,N\)-diethylmethylamine (5.3 mL, 43.7 mmol, 1.1 equiv). \(N\)-Methyl-4-vinylbenzylamine (5.3 g, 35.7 mmol, 0.9 equiv) was then slowly added to solution, and the reaction was left overnight. The crude product was concentrated \textit{in vacuo} and dissolved in 250 mL of CHCl\(_3\):iPrOH (2:1). The solution was extracted with water (2 x 100 mL), dried with anhydrous sodium sulfate, and concentrated \textit{in vacuo} to yield a crude solid. A portion of the product is lost in the aqueous wash. The crude product was purified with silica gel chromatography (20% MeOH in CH\(_2\)Cl\(_2\)) to yield a dark solid (10.0 g, 25.6 mmol, 59% yield).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.44 (m, 2H, ArH), 7.24 (m, 2H, ArH), 6.70 (dd, \( J = 17.7, 11.0 \) Hz, 1H, H\(_2\)C=CHAr), 5.76 (dd, \( J = 17.9, 1.7 \) Hz, 2H, H\(_2\)C=CHAr), 5.28 (dd, \( J = 10.9, 1.5 \) Hz, 2H, H\(_2\)C=CHAr), 4.65 (s, 2H, ArCH\(_2\)N), 3.81 (m, 8H, NCH\(_2\)CH\(_2\)O), 3.54 (m, 8H, NCH\(_2\)CH\(_2\)O), 3.21 (s, 3H, NCH\(_3\)). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 137.8, 135.9, 133.8, 127.0, 127.0, 118.8, 117.1, 114.7, 65.8, 58.6, 50.0, 40.8. HRMS (FAB+) m/z = 354.2171 caled for C\(_{21}\)H\(_{28}\)N\(_3\)O\(_2\) [M]\(^+\) 354.22.

\textit{Procedures for RAFT homopolymerizations of PTAC(R)}

\[
\text{CPR} + \text{AIBN, DMF} \xrightarrow{80^\circ \text{C to } 95^\circ \text{C}} \text{Homopolymer}
\]
Synthesis of PTAC(Cy). To a dry 20 mL scintillation vial, TAC(Cy) (6.0 g, 10.4 mmol, 60.0 equiv), methyl 2-(phenylcarbonothioylthio)-2-phenylacetate (52.3 mg, 1.73 mmol, 1.0 equiv), AIBN (4.3 mg, 0.26 mmol, 0.15 equiv), and DMF (6.0 mL) were added and vortexed to form a homogenous solution. This solution was transferred to a flame-dried ampule. After 4 freeze-pump-thaw cycles, the ampule was sealed under vacuum. The polymerization was run for 12 hours at 80 ºC with vigorous stirring. The reaction mixture was precipitated from CH₂Cl₂ into 1,4-dioxane 3 times to remove monomer. The polymer was then precipitated an additional 3 times into hexanes to remove residual 1,4-dioxane. Drying in vacuo yielded the pure polymer as a pink powder (5.3 g, 86% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.76-7.60 (b, 2H, -SC(ArH)S-), 7.51-6.00 (b, 240H, ArH), 5.17-4.58 (b, 120H, ArCH₂N), 3.61-2.94 (b, 420H, NCyH, NCH₃), 2.05-0.75 (b, 2580H, CyH, ArCHCH₂).

Synthesis of PTAC(iP). TAC(iP) (3.5 g, 83.1 mmol, 50.0 equiv), MCPDB (50.2 mg, 1.66 mmol, 1.0 equiv), AIBN (.54 mg, 0.033 mmol, 0.20 equiv), and N,N-dimethylformamide (DMF) (0.60 mL) were added to a flame seal ampoule and vortexed to form a homogenous solution. A stir bar was added to the ampoule, and after 4 freeze-pump-thaw cycles to remove oxygen, the ampoule was sealed under vacuum. The polymerization was run for 2 hr 15 min at 100 ºC. The reaction mixture was precipitated from CH₂Cl₂ into −78 ºC ethyl acetate 5 times to remove monomer. Drying in vacuo yielded the polymer as a pink powder (2.45 g, 70% yield). Alternatively, the reaction mixture could be transferred to a 3.5k MWCO Spectrum labs dialysis bag to dialyze for 24 hr in 1L of water. ¹H NMR (500 MHz, CDCl₃) δ 7.06-6.45 (b, 166H, ArH), 4.98-4.65 (b, 80H, ArCH₂N), 3.98-3.79 (b, 165H, C₃NCH(iPr)₂), 3.48 (s, 3H, OCH₃), 1.67-1.27 (b, 1700H, iPrH, ArCHCH₂).

Synthesis of PTAC(Mo). To a dry 20 mL scintillation vial, TAC(Mo) (7.0 g, 17.9 mmol, 700
equiv), MCPDB (54 mg, 0.179 mmol, 1.0 equiv), AIBN (4.4 mg, 0.0269 mmol, 0.15 equiv), and DMF (7.0 mL) were added and vortexed to form a homogenous solution. This solution was transferred to a flame-dried ampoule. After 4 freeze-pump-thaw cycles, the ampoule was sealed under vacuum. The polymerization was run for 12 hr at 85 °C. The reaction mixture was then transferred into a 3.5k MWCO Spectrum labs dialysis bag and left to dialyze for 24 hr in 1L of water. The water was changed five times in this time. The resulting polymer solution was freeze-dried to yield the pure polymer as a brown solid (3.6 g, 51% yield). \(^1\)H NMR (500 MHz, CD\(_3\)OD) \(\delta\) 7.90-7.74 (b, 2H, -SC(ArH)S-), 7.67-6.26 (b, 300H, ArH), 4.77-4.46 (b, 150H, ArCH\(_2\)N), 3.87-3.62 (b, 600H, NCH\(_2\)CH\(_2\)O), 3.62-3.38 (b, 600H, NCH\(_2\)CH\(_2\)O), 3.29-3.03 (b, 225H, NCH\(_3\)), 2.55-1.04 (b, 225H, ArCHCH\(_2\)).

**Procedures for RAFT Block Polymerization of PS-b-PTAC(R)**

![Diagram of homopolymer and block copolymer](image)

**Synthesis of PS-b-PTAC(Cy)(45).** To a dry 20 mL scintillation vial, PTAC(Cy) (1.0 g, 0.029 mmol, 1.0 equiv), AIBN (7.0 mg, 4.3 mmol, 0.15 equiv), styrene (0.722 g, 6.93 mmol, 4 equiv), and DMF (1.75 mL) were added and vortexed to form a homogenous solution. This solution was transferred to a flame-dried ampoule. After 4 freeze-pump-thaw cycles, the ampoule was sealed under vacuum. The polymerization was run for 12 hr at 80 °C. The reaction mixture was
precipitated from CH$_2$Cl$_2$ into hexanes 3 times. Drying in vacuo yielded the pure polymer as a pink powder (0.850 g, 70% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.90-7.78 (b, 2H, -SC(ArH)S-), 7.51-6.04 (b, 600H, ArH), 5.23-4.58 (b, 120H, ArCH$_2$N), 3.73-2.96 (b, 420H, NCyH, NCH$_3$), 2.05-0.75 (b, 2800H, CyH, ArCHCH$_2$).

**Synthesis of PS-b-PTACCy(30).** To a dry 20 mL scintillation vial, PTACCy (1.0 g, 0.029 mmol, 1.0 equiv), AIBN (7.0 mg, 4.3 mmol, 0.15 equiv), styrene (1.08 g, 10.4 mmol, 6 equiv), and DMF (1.75 mL) were added and vortexed to form a homogenous solution. This solution was transferred to a flame-dried ampoule. After 4 freeze-pump-thaw cycles, the ampoule was sealed under vacuum. The polymerization was run for 12 hr at 80 ºC. The reaction mixture was precipitated from CH$_2$Cl$_2$ into hexanes 3 times. Drying in vacuo yielded the pure polymer as a pink powder (0.850 g, 60% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.90-7.78 (b, 2H, -SC(ArH)S-), 7.51-6.04 (b, 940H, ArH), 5.23-4.58 (b, 120H, ArCH$_2$N), 3.73-2.96 (b, 420H, NCyH, NCH$_3$), 2.05-0.75 (b, 3180H, CyH, ArCHCH$_2$).

**Synthesis of PS-b-PTACiP(50).** To a dry flame-seal ampoule with stir bar, PTACiP (226.5 mg, 0.012 mmol, 1.0 equiv), AIBN (0.44 mg, 0.0027 mmol, 0.2 equiv), styrene (0.277 g, 2.66 mmol, 200 equiv), and DMF (0.130 mL) were added and vortexed to form a homogenous solution. After 4 freeze-pump-thaw cycles, the ampoule was sealed under vacuum. The polymerization was stirred vigorously for 8 hr at 100 ºC. The reaction mixture was precipitated from CH$_2$Cl$_2$ into –78 ºC ethyl acetate 3 times. Drying in vacuo yielded the pure polymer as a pale pink powder (0.240 g, 88% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.07-6.46 (b, 314H, ArH), 5.11-4.59 (b, 80H, ArCH$_2$N), 4.11-3.74 (b, 172H, C$_3$NCH(iPr)$_2$), 3.93-2.97 (b, 122H, NCH$_3$), 2.30-0.98 (b, 1600H, iPrH, ArCHCH$_2$).

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Synthesis of PS-\text{-}b\text{-}PTAC{iP}(30). To a dry flame-seal ampoule with stir bar, PTAC(iP) (271 mg, 0.014 mmol, 1.0 equiv), AIBN (0.52 mg, 0.0032 mmol, 0.2 equiv), styrene (0.414 g, 3.99 mmol, 250 equiv), and DMF (0.240 mL) were added and vortexed to form a homogenous solution. After 4 freeze-pump-thaw cycles, the ampoule was sealed under vacuum. The polymerization was stirred vigorously for 24 hr at 100 °C. The reaction mixture was precipitated from CH$_2$Cl$_2$ into $-78$ °C ethyl acetate 3 times. Drying \textit{in vacuo} yielded the pure polymer as a pale pink powder (0.310 g, 65% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.26-6.27 (b, 510H, ArH), 4.90-4.59 (b, 80H, ArCH$_2$N), 4.01-3.71 (b, 167H, C$_3$NCH(iPr)$_2$), 3.34-2.95 (b, 118H, NCH$_3$), 2.10-1.10 (b, 1690H, iPrH, ArCHCH$_2$).

Synthesis of PS-\text{-}b\text{-}PTAC{iP}(20). To a dry flame-seal ampoule with stir bar, PTAC(iP) (230 mg, 0.012 mmol, 1.0 equiv), AIBN (0.2 mg, 0.0012 mmol, 0.1 equiv), styrene (1.37 g, 13.2 mmol, 1000 equiv), and DMF (0.460 mL) were added and vortexed to form a homogenous solution. After 4 freeze-pump-thaw cycles, the ampoule was sealed under vacuum. The polymerization was stirred vigorously for 30 hr at 95 °C. Such a large excess of styrene was used so the polymer would not precipitate out of solution during the reaction. The reaction mixture was precipitated from CH$_2$Cl$_2$ into a $-78$ °C solution of 25% ethyl acetate in hexanes 3 times. Drying \textit{in vacuo} yielded the pure polymer as a pale pink powder (0.270 g, 62% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.26-6.24 (b, 900H, ArH), 4.95-4.59 (b, 80H, ArCH$_2$N), 4.01-3.77 (b, 176H, C$_3$NCH(iPr)$_2$), 3.27-3.01 (b, 126H, NCH$_3$), 2.02-0.94 (b, 1590H, iPrH, ArCHCH$_2$).

Synthesis of PS-\text{-}b\text{-}PTAC(Mo)(50). To a dry 20 mL scintillation vial, PTAC(Mo) (0.700 g, 0.024 mmol, 1.0 equiv), AIBN (0.59 mg, 0.0036 mmol, 0.15 equiv), styrene (0.75 g, 7.2 mmol, 4
equiv), and DMF (2.5 mL) were added and vortexed to form a homogenous solution. The large volume of DMF was necessary to totally dissolve PTAC(Mo). This solution was transferred to a flame-dried ampoule. After 4 freeze-pump-thaw cycles, the ampoule was sealed under vacuum. The polymerization was run for 12 hr at 85 ºC. The reaction mixture was precipitated from CH₂Cl₂ into diethyl ether 2 times. Drying in vacuo yielded the pure polymer as a pink powder (0.820 g, 90% yield). ¹H NMR (500 MHz, (CD₃)₂SO) δ 7.86-7.71 (b, 2H, -SC(ArH)S-), 7.47-6.09 (b, 760H, ArH), 4.90-4.28 (b, 150H, ArCH₂N), 3.85-3.54 (b, 600H, NCH₂CH₂O), 3.54-3.30 (b, 600H, NCH₂CH₂O), 3.22-2.86 (b, 225H, NCH₃), 2.15-1.12 (b, 500H, ArCHCH₂).

Synthesis of PS-b- PTAC(Mo)(35). To a dry 20 mL scintillation vial, PTAC(Mo) (0.900 g, 0.031 mmol, 1.0 equiv), AIBN (0.76 mg, 0.0046 mmol, 0.15 equiv), styrene (2.3 g, 22.2 mmol, 10 equiv), and DMF (8.0 mL) were added and vortexed to form a homogenous solution. The large volume of DMF was necessary to totally dissolve PTAC(Mo). This solution was transferred to a flame-dried ampoule. After 4 freeze-pump-thaw cycles, the ampoule was sealed under vacuum. The polymerization was run for 12 hr at 85 ºC. The reaction mixture was precipitated from CH₂Cl₂ into diethyl ether 2 times. Drying in vacuo yielded the pure polymer as a pink powder (1.19 g, 88% yield). ¹H NMR (500 MHz, (CD₃)₂SO) δ 7.86-7.71 (b, 2H, -SC(ArH)S-), 7.58-6.05 (b, 1000H, ArH), 5.01-4.28 (b, 150H, ArCH₂N), 3.85-3.53 (b, 600H, NCH₂CH₂O), 3.53-3.24 (b, 600H, NCH₂CH₂O), 3.21-2.57 (b, 225H, NCH₃), 2.23-1.08 (b, 640H, ArCHCH₂).

Synthesis of PS-b- PTAC(Mo)(30). To a dry 20 mL scintillation vial, PTAC(Mo) (0.900 g, 0.031 mmol, 1.0 equiv), AIBN (0.76 mg, 0.0046 mmol, 0.15 equiv), styrene (4.0 g, 38.9 mmol,
17 equiv), and DMF (11.25 mL) were added and vortexed to form a homogenous solution. The large volume of DMF was necessary to totally dissolve PTAC(Mo). This solution was transferred to a flame-dried ampoule. After 4 freeze-pump-thaw cycles, the ampoule was sealed under vacuum. The polymerization was run for 12 hr at 85 ºC. The reaction mixture was precipitated from CH$_2$Cl$_2$ into diethyl ether 2 times. Drying in vacuo yielded the pure polymer as a pink powder (1.19 g, 82% yield). $^1$H NMR (500 MHz, (CD$_3$)$_2$SO) $\delta$ 7.86-7.71 (b, 2H, -SC(Ar)H), 7.47-6.03 (b, 1175H, ArH), 4.92-4.30 (b, 150H, ArCH$_2$N), 3.81-3.54 (b, 600H, NCH$_2$CH$_2$O), 3.54-3.34 (b, 600H, NCH$_2$CH$_2$O), 3.21-2.92 (b, 225H, NCH$_3$), 2.21-0.92 (b, 750H, ArCHCH$_2$).

**Procedures for RAFT random copolymerization of P(S-stat-TAC(R))**

**Monomer**

\[
\begin{align*}
\text{Ph} & \quad \text{S} & \quad \text{S} \\
\text{Cl}^- & + & \text{Ph} & \quad \text{O} \quad \text{S} & \quad \text{Ph} \\
\text{NR}_2 & \quad \text{NR}_2 & & & \\
R_2N & & & & \\
\end{align*}
\]

**Random copolymer**

\[
\begin{align*}
\text{Ph} & \quad \text{S} & \quad \text{S} & \quad \text{Ph} \\
\text{O} & \quad \text{Me} & \quad \text{S} & \quad \text{Ph} \\
\text{R}_2N & + & \text{NR}_2 & & \\
\text{Cl}^- & & & & \\
\end{align*}
\]

80-90 ºC

AIBN, DMF

**Synthesis of P(S-stat-TAC(Cy)).** To a dry 20 mL scintillation vial, TAC(Cy) (1.00 g, 1.73 mmol, 50.0 equiv), styrene (0.180 g, 1.73 mmol, 50.0 equiv), MCPDB (10.5 mg, 0.0346 mmol, 1.0 equiv), AIBN (0.852 mg, 0.00519 mmol, 0.15 equiv), and DMF (0.500 mL) were added and vortexed to form a homogenous solution. This solution was transferred to a flame-dried ampoule. After 4 freeze-pump-thaw cycles, the ampoule was sealed under vacuum. The polymerization
was run for 12 hr at 80 °C. The reaction mixture was precipitated three times into ethyl acetate and once in hexanes. Drying in vacuo yielded the pure polymer as a pink powder (790 mg, 67% yield). Integration of the $^1$H NMR showed approximately 35 units of CPCy and 35 units of styrene (50% CPCy incorporation). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.89-7.69 (b, 2H, -SC(ArH)S-), 7.39-6.04 (b, 60H, ArH), 5.09-4.42 (b, 120H, ArCH$_2$N), 3.60-2.89 (b, 420H, NCyH, NCH$_3$), 2.09-0.77 (b, 2800H, CyH, ArCHCH$_2$).

**Synthesis of P(S-stat-TAC(iP)).** To a dry, flame-seal ampoule with stir bar, TAC(iP) (1.8 g, 4.24 mmol, 50 equiv), styrene (0.446 g, 4.29 mmol, 50 equiv), AIBN (1.4 mg, 0.0086 mmol, 0.1 equiv), 2-cyanopropan-2-yl benzodithioate (19 mg, 0.086, 1.0 equiv) and DMF (0.233 mL) were added and vortexed to form a homogenous solution. After 4 freeze-pump-thaw cycles, the ampoule was sealed under vacuum. The polymerization was stirred vigorously for 17 hr at 95 °C. The reaction mixture was precipitated from CH$_2$Cl$_2$ into a –78 °C solution of 25% ethyl acetate in hexanes 3 times. Drying in vacuo yielded a pale pink powder composed of approximately 13 units of TAC(iP) and 15 units of styrene (0.270 g, 62% yield, 47% incorporation of TAC(iP)). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.26-6.24 (b, 920H, ArH), 4.95-4.59 (b, 90H, ArCH$_2$N), 4.01-3.77 (b, 200H, C$_3$NCH(iPr)$_2$, 3.27-3.01 (b, 136H, NCH$_3$), 2.02-0.94 (b, 1750H, iPrH, ArCHCH$_2$).

**Synthesis of P(S-stat-TAC(Mo)).** To a dry 20 mL scintillation vial, TAC(Mo) (0.500 g, 1.28 mmol, 50.0 equiv), styrene (0.134 g, 1.28 mmol, 50.0 equiv), MCPDB (7.74 mg, 0.0256 mmol, 1.0 equiv), AIBN (0.632 mg, 0.00385 mmol, 0.15 equiv), and DMF (0.500 mL) were added and vortexed to form a homogenous solution. This solution was transferred to a flame-dried ampoule. After 4 freeze-pump-thaw cycles, the ampoule was sealed under vacuum. The polymerization was run for 12 hr at 90 °C. The reaction mixture was precipitated once into –78 °C ethyl acetate
to remove styrene. The precipitate was dissolved in water and transferred to a 1.0k MWCO Spectrum Labs dialysis bag and left to dialyze for 24 hr in 1L of water. The water was changed 5 times during this time. The resulting polymer was freeze-dried to yield pure polymer as a brown solid (0.190 g, 30% yield). Integration of the $^1$H NMR showed about 25 units of TAC(Mo) and 30 units of styrene (45% TAC(Mo) incorporation). $^1$H NMR (500 MHz, (CD$_3$)$_2$SO) $\delta$ 7.86-7.70 (b, 2H, -SC(ArH)S-), 7.56-6.18 (b, 1175H, ArH), 4.90-4.23 (b, 150H, ArCH$_2$N), 3.93-3.53 (b, 600H, NCH$_2$CH$_2$O), 3.53-3.17 (b, 600H, NCH$_2$CH$_2$O), 3.17-2.85 (b, 225H, NCH$_3$), 2.40-1.05 (b, 225H, ArCHCH$_2$).

Procedure for Emulsion Polymerization

**Synthesis of surfactant-free emulsion particles.** Particles were synthesized by following a general procedure that was scaled accordingly using 1-20 wt.% TAC(iP) (relative to styrene), styrene, 2,2'-azobis(2-methylpropionamide) dihydrochloride (V-50), and water. The final solution was scaled to 10 grams, with 10 wt.% monomer content. First, CPIP was dissolved in styrene and initiator was dissolved separately in 1 mL of water. The remaining volume of water was added to the monomer solution, and the V-50 solution was finally added to the monomer suspension. The mixture was vortexed for 30 seconds. The solution was added to a two-neck flask fitted with a condenser and stirbar, and was sparged with N$_2$ for 10 minutes. The solution was stirred at 70°C for 6-16 hours.

*Post polymerization functionalization synthesis follows*

*Procedures for the synthesis of bis-1,2-(diallylamino)-3-chlorocyclopropenium chloride*
Preparations of BACCl derivatives have been reported, but briefly, their synthesis involves in situ dehydrochlorination of pentachlorocyclopropane followed by nucleophilic substitution of the resulting tetrachlorocyclopropene with a secondary amine. If the secondary amine is sterically hindered (e.g. Cy and iP), selective double addition yields the desired BACCl in a single step. However, less sterically demanding amines (e.g. Et, Al, and Mo) lead to the tris(dialkylamino)cyclopropenium products, which require hydrolysis with base to furnish the corresponding cyclopropenone, followed by chlorination with oxalyl chloride (Figure S3).

![Chemical diagram](attachment:image.png)

**Synthesis of bis-2,3-(diallylamino)-1-cyclopropenone**

This procedure was performed at ambient conditions, without deoxygenation or rigorous efforts to remove water/moisture. Diallylamine (33.0 g, 340 mmol, 7.2 equiv) was slowly added to a solution of pentachlorocyclopropane (10.0 g, 47.2 mmol, 1.0 equiv) in CHCl₃ (400 mL) in a 1L round bottom flask. The solution turned orange and, after stirring overnight at room temperature, was concentrated *in vacuo* to yield a crude solid of the same color. A room-temperature solution of water (125 mL), methanol (125 mL), and potassium hydroxide (45 g, 802 mmol) was used to dissolve this solid. The solution was heated to 65 °C and stirred for two hours. Water was removed by rotary evaporation. The resulting solid was dissolved in CH₂Cl₂ and filtered to remove salt. The organic solution was dried with anhydrous sodium sulfate, concentrated *in vacuo* yielding a crude orange solid. The crude material was purified by silica gel chromatography (20% MeOH in EtOAc) to yield the title product as an orange solid (5.26 g,
21.5 mmol, 46% two-step yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 5.80 (m, 4H, NCH$_2$CH=CH$_2$), 5.20 (dd, 8H, NCH$_2$CH=CH$_2$), 3.78 (d, 8H, NCH$_2$CH=CH$_2$). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 133.07, 132.85, 119.83, 118.26, 118.07, 117.85, 53.46. HRMS (FAB+) m/z = 245.1654 calcd for C$_{15}$H$_{20}$N$_2$Cl [M+H]$^+$ 245.16.

**Synthesis of bis-1,2-(diallylamino)-3-chlorocyclopropenium chloride (BACAl)**

Oxalyl chloride (6.86 mL, 79.4 mmol, 2.0 equiv) was slowly added to a solution of bis-2,3-(diallylamino)-1-cyclopropenone (8.9 g, 39.7 mmol, 1.0 equiv) in dry CH$_2$Cl$_2$ (250 mL) at 0 °C under argon. The solution was warmed to room temperature and left to react for one hour. The solution was concentrated in vacuo to yield the title product as a dark brown liquid in quantitative yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 5.93 (m, 1H, NCH$_2$CH=CH$_2$), 5.46 (dd, 4H, NCH$_2$CH=CH$_2$), 5.30 (dd, 4H, NCH$_2$CH=CH$_2$), 4.35 (d, 4H, NCH$_2$CH=CH$_2$), 4.10 (d, 4H, NCH$_2$CH=CH$_2$).

**Procedures for the synthesis of bis-1,2-(piperidino)-3-chlorocyclopropenium chloride**

This procedure was performed at ambient conditions, without deoxygenation or rigorous efforts to remove water/moisture. Piperidine (15.6 g, 0.183 mol, 8 equiv) was slowly added to a solution of pentachlorocyclopropane (5.0 g, 22.8 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (230 mL) in a 5000 mL
round bottom flask. The solution turned orange and was allowed to stir overnight at room temperature. The reaction mixture was washed with 1M HCl (3 x 100 mL), DI water (1 x 100 mL), and saturated NaCl solution (1 x 100 mL), dried over magnesium sulfate, and concentrated *in vacuo* to yield a crude orange/brown solid. The crude product was dissolved in room temperature DI water (50 mL), and a solution of 10 g potassium hydroxide in 15 mL DI water was added to this mixture. The solution was heated to 65 °C and left to react for one hour. Water was removed by rotary evaporation. The resulting solid was dissolved in CH$_2$Cl$_2$ and filtered to remove salt. The organic solution was dried with anhydrous sodium sulfate, concentrated *in vacuo* yielding a crude orange solid. The crude material was purified by silica gel chromatography (100% EtOAc; 5% MeOH in DCM) to yield the title product as an orange solid (1.465 g, 21.5 mmol, 30% two-step yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.28 (s, 8H, C$_3$(N(CH$_2$)$_2$(CH$_2$)$_3$)$_2$), 1.58 (s, 12H, OC$_3$(N(CH$_2$)$_2$(CH$_2$)$_3$)$_2$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 134.85, 120.40, 50.63, 25.42, 23.61. HRMS (FAB+) m/z = 221.1647 calcd for C$_{13}$H$_{20}$N$_2$O 220.16 [M+H]$^+$ 221.16.

**Synthesis of bis-1,2-(piperidino)-3-chlorocyclopropenium chloride (BACPip)**

Oxalyl chloride (0.41 mL, 4.72 mmol, 2.0 equiv) was slowly added to a solution of bis-2,3-(piperidino)-1-cyclopropenone (0.520 g, 2.36 mmol, 1.0 equiv) in dry CH$_2$Cl$_2$ (24 mL) at 0 °C under argon. The solution was warmed to room temperature and left to react for one hour. The solution was concentrated *in vacuo* to yield the title product as a dark brown liquid in quantitative yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 3.76 (t, 4H, ClC$_3$(N(CH$_2$)$_2$(CH$_2$)$_3$)$_2$), 3.62 (t, 4H, ClC$_3$(N(CH$_2$)(CH$_2$)$_2$(CH)$_3$)$_2$), 1.88-1.68 (m, 12H, ClC$_3$(N(CH$_2$)(CH$_2$)$_2$(CH)$_3$)$_2$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 132.64, 52.52, 51.32, 24.99, 22.51. HRMS (FAB+) m/z = 275.1082 calcd for C$_{15}$H$_{20}$N$_2$Cl [M+H]$^+$ 275.11.
Procedures for the synthesis of poly methylaminostyrene (PMAS)

**Synthesis of tert-butyl methyl(4-vinylbenzyl)carbamate**

*N*-methyl-4-vinylbenzylamine (10.07 g, 68.4 mmol, 1 equiv) and THF (300mL) were added to a 1L round bottom flask (RBF) and the flask was sealed with a septum secured with copper wire under argon with a gas outlet. Triethylamine (10.4 mL, 74.8 mmol, 1.1 equiv) was added to the RBF, the system was cooled to 0 ºC, and di-tert-butyl dicarbonate (16.42 g, 74.8 mmol, 1.1 equiv) was slowly injected. The RBF was warmed to room temperature and allowed to stir overnight. The solution was concentrated under vacuum, and the translucent, crude product was dissolved in 300 mL of CH$_2$Cl$_2$ and transferred to a 1L separatory funnel. The solution was washed with 1M HCl (3 x 100mL) followed by a single brine wash. The solution was then dried with magnesium sulfate, filtered, and concentrated under vacuum. The crude material was finally purified by silica gel chromatography (100% hexanes then 95% CH$_2$Cl$_2$/5% hexanes) to yield the title product as an translucent, colorless liquid (7.22 g, 29.2 mmol, 48%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37 (d, 2H, ArH), 7.18 (d, 2H, ArH), 6.71 (dd, 1H, H$_2$C=CHAr), 5.73 (dd, 1H,
H₂C=CHAr), 5.23 (dd, 1H, H₂C=CHAr), 4.41 (s, 2H, ArCH₂N), 2.81 (s, 3H, NCH₃), 1.48 (s, 9H, NC=OtBuH). ¹³C NMR (125 MHz, CDCl₃) δ 137.7, 136.6, 136.4, 128.0, 127.4, 126.4, 113.7, 79.7, 52.4, 51.7, 33.9, 28.5. HRMS (FAB+) m/z = 270.1470 calcd for C₁₅H₂₁N₁O₂ [M+Na]⁺ 270.15.

**Synthesis of PBoc** Copper (I) bromide (10 mg, 7.0E-2 mmol, 0.5 equiv) was added to a dry Schlenk flask and the material was deoxygenated via five vacuum-argon cycles. Degassed N,N,N′,N′,N′′-pentamethyldiethylenetriamine (PMDTA) (12.1 mg, 7.0e-2 mmol, 0.5 equiv) was added to the flask and allowed to stir for ten minutes to form Cu complex, a light green mixture. Degassed tert-butyl methyl(4-vinylbenzyl)carbamate (4.5 g, 18.2 mmol, 130 equiv) was then added to the mixture and three freeze-pump-thaw cycles were conducted. The Schlenk flask was closed under argon and degassed ethyl α-bromoisobutyrate (27.3 mg, 0.14 mmol, 1 equiv) was injected, and the reaction mixture was heated to 85 °C and allowed to react for 24 hours. The resulting solution was diluted with methanol and transferred to a 3.5k MWCO Spectrum Labs dialysis bag and dialyzed against methanol. The resulting solution was concentrated under vacuum to yield a fine, white powder (803.3 mg, 17.9% recovered yield). From SEC: Mₙ = 6700 g mol⁻¹, degree of polymerization ~ 65, D = 1.08. ¹H NMR (400 MHz, CDCl₃) δ 7.15-6.20 (b, 254H, ArH), 4.50-4.21 (b, 130H, ArCH₂N), 2.95-2.56 (b, 198H, NCH₃), 2.01-1.19 (b, 782H, NC=OtBuH, ArCHCH₂).

**Synthesis of PMAS** The PBoc (803.3 mg, 3.25 mmol, 1 eq) was dissolved in methanol (10 mL) in a dry round bottom flask under argon. The flask was cooled to 0 °C and trimethylsilyl chloride (2.47 g, 22.7 mmol, 7 eq) was added. The reaction solution was allowed to stir at room temperature overnight and concentrated under vacuum to yield a white powder. The powder was then re-dissolved in a 1M solution of KOH in methanol and allowed to stir for one hour.
solution was concentrated so that a minimal amount of methanol remained. To this thickened liquid, water was added until white flecks of polymer began to precipitate out. The solution was filtered and the solid white flecks were redissolved in methanol and the previous step was repeated. The resulting polymer was dried under vacuum, yielding a fluffy, white powder (440 mg, 93.6% yield). $^1$H NMR (400 MHz, CDCl3) $\delta$ 7.23-6.25 (b, 268H, ArH), 3.77-3.43 (b, 130H, ArCH$_2$N), 2.57-2.23 (b, 197H, NCH$_3$), 1.70-1.19 (b, 205H, ArCHCH$_2$).

 Procedures for the synthesis of PTACR homopolymers (styrenic backbone)

Synthesis of PTAC(Al) This procedure was performed open to the atmosphere. PMAS (58.2 mg, 0.40 mmol, 1 equiv) was dissolved in chloroform (4 mL) in a scintillation vial. To polymer solution was added N,N-diisopropylethylamine (153 mg, 1.19 mmol, 3 equiv) and allowed to stir for 10 minutes. The BACAl (169 mg, 0.59 mmol, 1.5 equiv) was dissolved in 3 mL of chloroform and added to the reaction vial. The mixture was allowed to stir at 65 °C for three hours. The resulting solution was concentrated in vacuo, diluted with water, and transferred to a 3.5k MWCO Spectrum Labs dialysis bag, and dialyzed against water and concentrated by rotary evaporation. The polymer was then dissolved in a minimal amount of acetone and precipitated one time into ethyl acetate at -78 °C and again concentrated under vacuum to yield a brown powder (107 mg, 66% yield). $^1$H NMR (400 MHz, CDCl3) $\delta$ 7.38-6.27 (b, 263H, ArH), 5.96-5.60 (b, 260H, NCH$_2$CH=CH$_2$), 5.43-5.04 (b, 560H, NCH$_2$CH=CH$_2$), 4.84-4.42 (b, 130H, ArCH$_2$N), 4.15-3.80 (b, 513H, NCH$_2$CH=CH$_2$), 3.25-2.75 (b, 193H, NCH$_3$), 2.27-1.03 (b, 195H, ArCHCH$_2$).

Synthesis of PTAC(Mo) This procedure was performed open to the atmosphere. PMAS (51.8 mg, 0.39 mmol, 1 equiv) was dissolved in a DMF (3 mL) in a scintillation vial. To the vial was
added \(N,N\)-diisopropylethylamine (130 mg, 1.02 mmol, 3 equiv), followed by a solution of DCM (3 mL) and BACMo (147 mg, 0.51 mmol, 1.5 equiv). **Note:** chloroform is not used here, as the resulting PIL is not soluble. DMF can be used as a co-solvent to soluble resultings PILs. The reaction mixture was allowed to stir at 65 °C for three hours. The resulting solution was diluted with water, and transferred to a 3.5k MWCO Spectrum Labs dialysis bag and dialyzed against water. The resulting solution was concentrated under vacuum to yield a brown powder (126 mg, 91.3% yield). \(^1\)H NMR chemical shifts and integrations have been previously reported for this materials.\(^2\)

**Synthesis of PTAC(Cy)** This procedure was performed open to the atmosphere. PMAS (51.3 mg, 0.345 mmol, 1 equiv) was dissolved in chloroform (4 mL) in a scintillation vial. To the vial \(N,N\)-diisopropylethylamine (135 mg, 1.04 mmol, 3 equiv) was added, followed by a solution of BACCy (180 mg, 0.38 mmol, 1.1 equiv) in 3 mL chloroform. The reaction mixture was allowed to stir at 65 °C for three hours. The resulting solution was concentrated in vacuo and precipitated twice from DCM into dioxane. The resulting powder was dissolved in methanol and transferred to a 3.5k MWCO Spectrum Labs dialysis bag. Dialysis was conducted against a 1:1 H\(_2\)O: methanol solution. The resulting solution was concentrated under vacuum to yield a light-brown powder (161 mg, 80% yield). \(^1\)H NMR chemical shifts and integrations have been previously reported for this materials.\(^2\)

**Synthesis of PTAC(iP)** This procedure was performed open to the atmosphere. PMAS (54 mg, 0.37 mmol, 1 equiv) was dissolved in chloroform (3 mL) in a scintillation vial. To the vial was added \(N,N\)-diisopropylethylamine (141 mg, 1.1 mmol, 3 equiv), and a solution of BACiP (202 mg, 0.40 mmol, 1.1 equiv) in 4 mL chloroform was added. The reaction mixture was allowed to stir at 65 °C for three hours. The resulting solution was concentrated in vacuo and precipitated
twice from acetone into ethyl acetate at -78 °C (if precipitated polymer does not filter nicely, make the polymer/acetone solution more concentrated). The resulting powder was dissolved in water and transferred to a 3.5k MWCO Spectrum Labs dialysis bag and dialyzed against water followed by concentration under vacuum to yield a light-brown powder (110 mg, 65% yield). \(^1\)H NMR chemical shifts and integrations have been previously reported for this materials.\(^2\)

**Synthesis of PTAC(Et)** This procedure was performed open to the atmosphere. PMAS (54 mg, 0.368 mmol, 1 equiv) was dissolved in chloroform (3 mL) in a scintillation vial. To the vial was added \(N,N\)-diisopropylethylamine (142 mg, 1.1 mmol, 3 equiv) followed by a solution of BACEt (140 mg, 0.55 mmol, 1.1 equiv) in 4 mL chloroform. The reaction mixture was allowed to stir at 65 °C for three hours. The resulting solution was concentrated *in vacuo*, diluted with water, and transferred to a 3.5k MWCO Spectrum Labs dialysis bag and dialyzed against water, and subsequently concentrated under vacuum. The polymer was then dissolved in a minimal amount of acetone and precipitated one time into ethyl acetate at -78 °C to yield a brown powder (112 mg, 84% yield). \(^1\)H NMR (400 MHz, CDCl3) \(\delta\) 7.30-6.30 (b, 262H, ArH), 4.83- 4.54 (b, 130H, ArCH\(_2\)N), 3.53-3.31 (b, 502H, NCH\(_2\)CH\(_3\)), 3.26-3.02 (b, 193H, NCH\(_3\)), 1.58-1.08 (b, 1009H, NCH\(_2\)CH\(_3\), ArCHCH\(_2\)).

**Synthesis of PTAC(Pip)** This procedure was performed open to the atmosphere. PMAS (50 mg, 0.339 mmol, 1 equiv) was dissolved in chloroform (2 mL) in a scintillation vial. To the vial was added \(N,N\)-diisopropylethylamine (0.18 mL, 1.02 mmol, 3 equiv) followed by a solution of BACPip (141 mg, 0.509 mmol, 1.5 equiv) in 6 mL chloroform. The reaction mixture was allowed to stir at 65 °C for three hours. The resulting solution was concentrated *in vacuo*, diluted with water, and transferred to a 3.5k MWCO Spectrum Labs dialysis bag and dialyzed against water, and subsequently concentrated under vacuum. The polymer was then dissolved in a
minimal amount of acetone and precipitated one time into ethyl acetate at -78 °C to yield a brown powder (129.7 mg, 97% yield). \(^1\)H NMR (400 MHz, acetone-d\textsubscript{6}) \(\delta\) 7.90-6.30 (b, 609H, ArH), 5.20- 4.60 (b, 274H, ArCH\textsubscript{2}N), 3.85-3.45 (b, 1176H, C\textsubscript{3}(N(CH\textsubscript{2})\textsubscript{2}(CH\textsubscript{2})\textsubscript{2}CH\textsubscript{2})\textsubscript{2}), 3.40-3.13 (b, 382H, NCH\textsubscript{3}), 1.90-1.37 (b, 1895H, ) C\textsubscript{3}(N(CH\textsubscript{2})\textsubscript{2}(CH\textsubscript{2})\textsubscript{2}CH\textsubscript{2})\textsubscript{2}, ArCHCH\textsubscript{2}).

**Procedures for the synthesis of PS-b-PTACR block copolymers**

**Synthesis of PS-b-PBoc** Copper (I) bromide (5.5 mg, 3.87e-2 mmol, 0.5 equiv) was added to a dry Schlenk flask and the material was deoxygenated via five vacuum-argon cycles. Degassed N,N,N',N'-pentamethyldiethylenetriamine (PMDETA) (9.4 mg, 5.4e-2 mmol, 0.7 equiv) was added to the flask and the mixture was stirred for ten minutes, forming a light green mixture. Degassed tert-butyl methyl(4-vinylbenzyl)carbamate (2.6 g, 12 mmol, 150 equiv) was then added to the mixture, and three freeze-pump-thaw cycles were conducted. Lastly, a deoxygenated solution of PS (7k) (535 mg, 0.77 mmol, 1 equiv) in DMF (1 ml) was injected into the Schlenk flask and the mixture was heated to 85 °C and left to react for 24 hours. The resulting solution was concentrated, dissolved in THF, and then precipitated twice into a 3:1 mixture of methanol-water. The resulting powder was further dried under vacuum, yielding the title product (610 mg, 81% recovered yield). SEC and \(^1\)H NMR reveal block copolymer contains ~190 units of styrene and ~127 units Boc-protected monomer. \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.15-6.20 (b, 1494H, ArH), 4.50-4.21 (b, 254H, ArCH\textsubscript{2}N), 2.95-2.56 (b, 370H, NCH\textsubscript{3}), 2.01-1.19 (b, 782H, NC=OtBuH, ArCHCH\textsubscript{2}).
Synthesis of PS-b-PMAS The PS-b-PBoc (500 mg, 1.27 mmol amine-containing monomer, 1 eq amine monomer) was dissolved in a 50/50 DCM:methanol solution (15 mL) in a round bottom flask under argon. The flask was cooled to 0°C and trimethylsilyl chloride (2.47 g, 22.7 mmol, 7 eq) was added. The reaction was allowed to stir at room temperature overnight and concentrated under vacuum to yield a white powder. The powder was then re-dissolved in DMSO and 1M NaOH was added dropwise, with stirring, until the polymer precipitated from solution. The resulting slurry was centrifuged, and the supernatant decanted. The polymer was washed two more times with DI water, and collected by centrifugation. The resulting polymer was dried under vacuum, yielding a fluffy, white powder (235.5 mg, 63% yield).

1H NMR (400 MHz, CDCl3) δ 7.23-6.25 (b, 268H, ArH), 3.77-3.43 (b, 130H, ArCH2N), 2.57-2.23 (b, 197H, NCH3), 1.70-1.19 (b, 205H, ArCHCH2).

Synthesis of PS-b-PTAC(Cy) This procedure was performed open to the atmosphere. PS-b-PMAS (56.8 mg polymer, 0.19 mmol amine unit, 1 equiv amine unit) was dissolved in chloroform (6 mL) in a scintillation vial. To the vial was added N,N-diisopropylethylamine (74 mg, 0.57 mmol, 3 equiv) and the BACCy (98.4 mg, 0.21 mmol, 1.1 equiv). The reaction mixture was allowed to stir at 65 °C for three hours. The resulting solution was concentrated in vacuo, diluted with methanol, and transferred to a 3.5k MWCO Spectrum Labs dialysis bag and dialyzed against methanol. The resulting colloidal solution was concentrated under vacuum to yield a brown powder (130 mg, 91.8% yield). 1H NMR chemical shifts and integrations have been previously reported for this materials.2

Synthesis of PS-b-PTAC(iP) This procedure was performed open to the atmosphere. PS-b-PMAS (88 mg polymer, 0.30 mmol amine unit, 1 equiv amine unit) was dissolved in chloroform (7 mL) in a scintillation vial. To the vial was added N,N-diisopropylethylamine (114 mg, 0.89
mmol, 3 equiv) and the BACiP (163 mg, 0.33 mmol, 1.1 equiv). The reaction mixture was allowed to stir at 65 °C for three hours. The resulting solution was concentrated in vacuo, dissolved in water, and transferred to a 3.5k MWCO Spectrum Labs dialysis bag and dialyzed against a 50/50 mixture of water and methanol. The resulting colloidal solution was concentrated under vacuum to yield a light-brown powder (134 mg, 78.8% yield). ¹H NMR chemical shifts and integrations have been previously reported for this material.²

**Synthesis of PS-b-PTAC(Mo)** This procedure was performed open to the atmosphere. PS-b-PMAS (65.7 mg polymer, 0.33 mmol amine unit, 1 equiv amine unit) was dissolved in a DMF (3 mL) in a scintillation vial. To the vial was added N,N-diisopropylethylamine (130 mg, 1.0 mmol, 3 equiv) and a solution of DCM (3 mL) and BACMo (140 mg, 0.50 mmol, 1.5 equiv). The reaction mixture was allowed to stir at 65 °C for three hours. The resulting solution was diluted with water, and transferred to a 3.5k MWCO Spectrum Labs dialysis bag and dialyzed against a 50/50 mixture of water and methanol. The resulting colloidal solution was concentrated under vacuum to yield a brown powder (157 mg, 93.5% yield). ¹H NMR chemical shifts and integrations have been previously reported for this material.²

**Procedures for the synthesis of PEO-b-PTACR block copolymers**

**Synthesis of PEO-b-PBoc** Copper (I) bromide (4.7 mg, 3.28e-2 mmol, 0.5 equiv) was added to a dry schlenk flask and the material was deoxygenated via five vacuum-argon cycles. Sparged
N,N,N′,N′,N″-pentamethyldiethylenetriamine (PMDTA) (5.7 mg, 3.82e-2 mmol, 0.5) was added to the flask and let stir for ten minutes, forming a light green mixture. Degassed tert-butyl methyl(4-vinylbenzyl)carbamate (2.23 g, 9 mmol, 150 equiv) was then added to the mixture and three freeze-pump-thaw cycles were conducted. Lastly, a solution of poly(ethylene glycol) methyl ether 2-bromoisobutyrate (300 mg, 6e-2 mmol, 1 equiv) in DMF (1 mL) was injected into the Schlenk flask and the mixture was heated to 85 °C and stirred for 20 hours. The resulting solution was diluted with water and transferred to a 3.5k MWCO Spectrum Labs dialysis bag and left to dialyze against a solution of 1:1 water-methanol. The resulting solution was concentrated under vacuum to yield a fine, white powder (350 mg, 20% conversion (30 units Boc monomer per chain), 78.7% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.15-6.20 (b, 117H, ArH), 4.50-4.21 (b, 59H, ArC₂H₂N), 3.72-3.58 (b, 455H, (C₂H₂C₂O)₉₄), 2.95-2.56 (b, 89H, NCH₃), 2.01-1.19 (b, 343H, NC=OtBuH, ArCH₂CH₂).

Synthesis of PEO-b-PMAS The PEO-b-PBoc (350 mg polymer, 0.85 mmol Boc unit, 1 equiv Boc unit) was dissolved in methanol (10 mL) in a dry round bottom flask under argon. The flask was cooled to 0 °C and trimethylsilyl chloride (1.25 g, 12.5 mmol, 14.7 equiv) was added. The reaction was allowed to stir at room temperature overnight and then a 0.5M NaOH solution (5 mL) was added to the system. This mixture was stirred for 1 hour and then transferred to a 3.5k MWCO Spectrum Labs dialysis bag and left to dialyze against water. Finally, the solution was concentrated under vacuum yielding a white powder (191.6 mg, 72% yield). ¹H NMR (400 MHz, MeOD) δ 7.55-6.35 (b, 128H, ArH), 4.35-4.04 (b, 59H, ArCH₂N), 3.72-3.58 (b, 455H, (CH₂CH₂O)₁₁₄), 2.95-2.56 (b, 91H, NCH₃), 2.01-1.19 (b, 93H, ArCHCH₂).

Synthesis of PEO-b-PTAC(Cy) ¹This procedure was performed open to the atmosphere. PEO-b-PMAS (75.9 mg polymer, 0.24 mmol amine unit, 1 equiv amine unit) was dissolved in
chloroform (4 mL) in a scintillation vial. N,N-diisopropylethylamine (150 mg, 1.16 mmol, 4.8 equiv) and a solution of BACCy (199 mg, 0.42 mmol, 1.75 equiv) in 3mL of chloroform were added to the vial. The reaction mixture was allowed to stir at 65 °C for three hours. The resulting solution was concentrated in vacuo and dissolved in methanol before being transferred to a 3.5k MWCO Spectrum Labs dialysis bag and dialyzed against a 50/50 mixture of water and methanol. The resulting solution was concentrated under vacuum to yield a light-brown powder (118 mg, 64.5% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.35-6.15 (b, 116H, ArH), 5.10-4.60 (b, 54H, ArCH₂N), 3.72-3.58 (b, 455H, (CH₂CH₂O)₁₁₄), 3.50-2.56 (b, 188H, NCyH, NCH₃), 1.75- (b, 102H, ArCHCH₂).

Synthesis of PEO-b-PTAC(iP)¹ This procedure was performed open to the atmosphere. PEO-b-PMAS (50 mg polymer, 0.16 mmol amine unit, 1 equiv amine unit) was dissolved in chloroform (4 mL) in a scintillation vial. To the vial was added N,N-diisopropylethylamine (132 mg, 1.0 mmol, 6 equiv) and the BACiP (117 mg, 0.50 mmol, 3 equiv). The reaction mixture was allowed to stir at 65°C for three hours. The resulting solution was diluted with water, and transferred to a 3.5k MWCO Spectrum Labs dialysis bag and dialyzed against water. The resulting solution was concentrated under vacuum to yield a brown powder (71.8 mg, 77% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.40-6.20 (b, 133H, ArH), 5.05-4.50 (b, 60H, ArCH₂N, NCH(CH₃)₂), 4.00-2.90 (b, 630H, NCH(CH₃)₂, (CH₂CH₂O)₁₁₄, NCH₃), 2.00-0.80 (b, 805H, ArCHCH₂, NCH(CH₃)₂).

Synthesis of PEO-b-PTAC(Mo)¹ This procedure was performed open to the atmosphere. PEO-b-PMAS (65.7 mg polymer, 0.21 mmol amine unit, 1 equiv amine unit) was dissolved in DMF (6 mL) in a scintillation vial. To the vial was added N,N-diisopropylethylamine (130 mg, 1.0 mmol, 5 equiv) and the BACMo (140 mg, 0.50 mmol, 2.4 equiv). The reaction mixture was allowed to stir at 65 °C for three hours. The resulting solution was diluted with water, and transferred to a
3.5k MWCO Spectrum Labs dialysis bag and dialyzed against water. The resulting solution was concentrated under vacuum to yield a brown powder (106 mg, 90.4% yield). $^1$H NMR (400 MHz, MeOD) $\delta$ 7.40-6.25 (b, 142H, ArH), 4.85-4.40 (b, 60H, ArCH$_2$N), 3.85-3.35 (b, 805H, N(CH$_2$CH$_2$)$_2$O, (CH$_2$CH$_2$)$_{114}$, N(CH$_2$CH$_2$)$_2$O), 3.25-3.00 (b, 90H, NCH$_3$), 1.70-1.10 (b, 102H, ArCHCH$_2$).

$^1$For this reaction, excess of $N,N$-diisopropylethylamine and the BACCl ClickabIL was used, although stoichiometric quantities as used in other functionalization reactions would also work.

**Procedures for the synthesis of PEI-TACR block copolymers**

![Diagram](image)

**Synthesis of PEI-Cy** This procedure was performed open to the atmosphere. Linear polyethyleneimine (10k) (80 mg, 1.86 mmol, 1 equiv) was dissolved in chloroform (7 mL) in a scintillation vial. To the vial was added $N,N$-diisopropylethylamine (720 mg, 5.57 mmol, 3 equiv) and the BACCy (1.92 g, 4.1 mmol, 2 equiv). The reaction mixture was allowed to stir at 65 °C for 27.5 hours. *Note*: these reaction conditions require longer time and more equivalents of BACCy than other ClickabIL conditions, potentially because of the steric hindrance of cyclohexyl substituents. The resulting solution was concentrated *in vacuo* and precipitated twice into dioxane. The resulting powder was dissolved in methanol and transferred to a 3.5k MWCO Spectrum Labs dialysis bag and dialyzed against methanol. The resulting solution was concentrated under vacuum to yield a yellow-brown powder (220 mg, 25% yield). $^1$H NMR (400 MHz, MeOD) $\delta$ 7.40-6.25 (b, 142H, ArH), 4.85-4.40 (b, 60H, ArCH$_2$N), 3.85-3.35 (b, 805H, N(CH$_2$CH$_2$)$_2$O, (CH$_2$CH$_2$)$_{114}$, N(CH$_2$CH$_2$)$_2$O), 3.25-3.00 (b, 90H, NCH$_3$), 1.70-1.10 (b, 102H, ArCHCH$_2$).
MHz, CDCl$_3$ $\delta$ 4.45-3.15 (b, 1810, (CH$_2$CH$_2$N)$_{233}$, NCyH), 1.90-0.65 (10165H, NCyH).

**Synthesis of PEI-iP** This procedure was performed open to the atmosphere. Linear polyethyleneimine (10k) (91 mg, 23 mmol, 1 equiv) was dissolved in chloroform (10 mL) in a scintillation vial. To the vial was added N,N-diisopropylethylamine (901 mg, 79 mmol, 3 equiv) and the BACiP (1.16 g, 26 mmol, 1.1 equiv). The reaction mixture was allowed to stir at 65 °C for three hours. The resulting solution was concentrated in vacuo and then dissolved in water and transferred to a 3.5k MWCO Spectrum Labs dialysis bag and dialyzed against water. The resulting solution was concentrated under vacuum to yield a yellow-brown powder (394 mg, 60% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.45-3.15 (b, 1860, (CH$_2$CH$_2$N)$_{233}$, NC$_2$H$_3$), 1.90-0.65 (5265H, NCH(CH$_3$)$_2$).

**Synthesis of PEI-Mo** This procedure was performed open to the atmosphere. Linear polyethyleneimine (10k) (26.8 mg, 0.623 mmol, 1 equiv) was dissolved in a DMF (3 mL) in a scintillation vial. To the vial was added N,N-diisopropylethylamine (130 mg, 1.02 mmol, 3 equiv) and a solution of DCM (3 mL) and BACMo (251 mg, 0.93 mmol, 1.5 equiv). The reaction mixture was allowed to stir at 65 °C for three hours. The resulting solution was diluted with water, and transferred to a 3.5k MWCO Spectrum Labs dialysis bag and dialyzed against water. The polymer-water solution was then washed with room temperature chloroform (3 x 50 mL). The polymer was recovered from rotary evaporation of the aqueous layer to yield a yellow-brown powder (155 mg, 87% yield). $^1$H NMR (400 MHz, MeOD) $\delta$ 3.95-3.35 (b, 5581H, (CH$_2$CH$_2$N-C$_3$(N(CH$_2$)$_2$(CH$_2$)$_2$O)$_2$).

**Synthesis of PEI-Pip** This procedure was performed open to the atmosphere. Linear polyethyleneimine (25k) (50 mg, 1.16 mmol, 1 equiv) was dissolved in chloroform (4 mL) in a
scintillation vial. To the vial was added \(N,N\)-diisopropylethylamine (0.61 mL, 3.49 mmol, 3 equiv) and a solution of BAC Pip (480 mg, 1.74 mmol, 1.5 equiv) in 4 mL chloroform. The reaction mixture was allowed to stir at 65 °C for three hours. The resulting solution was diluted with water, and transferred to a 3.5k MWCO Spectrum Labs dialysis bag and dialyzed against water. The resulting solution was concentrated under vacuum, and precipitated from acetone into ethyl acetate (-78 °C) and recovered by centrifugation to yield a brown powder (68 mg, 20% recovered yield). \(^1\)H NMR (400 MHz, MeOD) \(\delta\) 3.95-3.40 (b, 6,972H, ((CH\(_2\)CH\(_2\)N)-C\(_3\)(N(CH\(_2\)_2(CH\(_2\)_2CH\(_2\))\(_{581}\)) \(\delta\) 1.90-1.60 (b, 6,972H, ((CH\(_2\)CH\(_2\)N)-C\(_3\)(N(CH\(_2\)_2(CH\(_2\)_2CH\(_2\))\(_2\))\(_{581}\).}
Chapter Two

Biomedical applications of cyclopropenium-based polyelectrolytes

Gene delivery is the process by which exogenous DNA is carried into cells by a delivery agent to impart a therapeutic effect with incredible potential to address hereditary diseases and cancer. One of the main challenges in the realization of this therapeutic class is the development of delivery agents to safely and reliably bring genetic material into the cell of interest. Cationic polymers are commonly used as non-viral transfection agents because they pose less safety risk than viral alternatives and offer the opportunity to reliably tune macromolecular structure. They are able to complex with the negatively charged phosphate backbone of DNA or RNA and form polypelexes that prevent degradation of genetic material and encourage cellular uptake.\textsuperscript{1-4} However, cationic polymers are much less effective delivery vehicles than viruses, as they have not evolved over many years to perform this function. Thus, materials chemists and biologists must collaborate to design polymers capable of overcoming a broad array of obstacles and barriers both outside and inside the cell to execute effective gene delivery, which have been described in detail.\textsuperscript{5} Ideal gene delivery vectors must be engineered to localize at the cells of interest, permeate cell membranes, and subsequently escape an endosome all while shielding their nucleic acid cargo from degradation and not provoking an immunogenic response (Figure 1). These hierarchical complexities of biological systems make distillation of accurate design principles for synthetic delivery agents extremely challenging. In spite of the steep challenges, the potential of effective gene therapy propels efforts towards the development of safe and efficient gene delivery vehicles. Manipulations of cationic polyelectrolytes at the building block level to balance hydrophobicity and charge density and the resulting insight towards optimized non-viral vectors are described to contextualize our additions to this field.
Figure 1. The intracellular journey of gene delivery vectors. Polyplexes comprising genetic material (e.g. DNA) and a polyelectrolyte vector must enter the cell (typically through endocytosis), escape the endosome via either the proton sponge effect or lysing of the endosomal membrane, and finally the delivery vehicle must release its genetic cargo for nuclear uptake.

**Design principles for cationic polymer delivery agents**

Hydrophobic modification of cationic polymers is one of the most common strategies to enhance transfection efficiency.\(^6\)\(^7\) Hydrophobic groups on a delivery agent have been reported to aid in polyplex formation through non-covalent interactions with the grooves of double-stranded DNA. For example, Vijayakrishna and co-workers characterized the biophysical relationship between DNA and a series of alkyl-imidazolium-based polyelectrolytes with ethyl, butyl, and hexyl substituents to assess how increasing hydrophobicity impacted DNA binding.\(^8\) Through a variety of experimental approaches and molecular docking studies, the authors confirmed that polymers bearing hexyl substituents showed the most efficient binding to DNA, with binding
efficiency clearly trending with increasing hydrophobicity. However, binding efficiency alone is not a clear indicator of delivery efficiency. In fact, too favorable an interaction between the vector and DNA is detrimental to transfection, as the vector must eventually release the genetic material inside the cell.\textsuperscript{9} Thus, more relevant studies relate chemical structure and resulting binding interactions directly to transfection efficiency and cell viability. One such study by Long and coworkers compared triethyl and tributyl quaternized phosphonium polymers for their DNA binding efficiency, cell viability, and transfection efficiency.\textsuperscript{10} DNA gel shift assays indicated that less sterically hindered triethyl-containing polymers bound DNA more tightly and efficiently, but interestingly this did not translate to a more effective transfection reagent. Instead, the more hydrophobic tributyl phosphonium polymers displayed significantly improved transfection efficacy. Fluorescence microscopy studies of labeled DNA showed that both phosphonium polymers successfully entered cells, which led the authors to conclude that the tributyl polymer’s superior transfection efficiency resulted from enhanced endosomal escape. However, hydrophobicity must be rationally installed to avoid critical destabilization of the cellular membrane, which results in high cytotoxicity.\textsuperscript{11-12} Thus subtle changes in hydrophobicity via modulation of alkyl substituent chain length can have potent effects on DNA binding and a delivery vector’s capacity to overcome the various barriers to gene delivery.
Figure 2. Minor hydrophobic modifications have a large impact on transfection efficiency and cytotoxicity. A) Polycyclopropenium polymers bearing diisopropyl groups (left) are less viable transfection agents than those with piperidine substituents (right).\(^{13}\) B) Modification of 25 kDa branched PEI with leucine (left) yields a significantly inferior transfection agent than modification with alanine (right).\(^{14}\) Common design principles for gene delivery vectors are highlighted.

Perhaps the key barrier, endosomal escape of the delivery vector, is mediated either by disruption of the endosomal membrane, as described above, or the proton sponge effect.\(^ {15}\) Engineering a buffering capability into cationic polyelectrolyte structure typically involves incorporation of a Brønsted base with a pKa in the range of the pH of an endosome (~6), which makes them effective proton sponges. For example, Klibanov and coworkers modified branched polyethyleneimine (PEI), a highly effective albeit toxic transfection reagent, with a variety of
alkyl amino acids.\textsuperscript{14} Grafting alanine onto the parent PEI resulted in a transfection reagent that was twice as effective as the parent PEI while functionalization with the more hydrophobic leucine yielded no gene expression (Figure 2B). The drastic difference in transfection efficiency affected by these minor structural variations showcases the need for synthetic strategies to modularly access a wide variety of structures. Furthermore, this derivatization of PEI significantly benefitted from incorporating both hydrophobic moieties and protonatable amines that can participate in the proton sponge effect, which represents an effective route to promote endosomal escape while minimizing the toxicity associated with high charge densities.

\textit{Cyclopropenium polymers as transfection agents}

If the electrostatic cohesion between polymer and DNA is too strong for adequate release of DNA into the cell, transfection efficiency can be dramatically suppressed.\textsuperscript{16-17} In fact, Schmuck and co-workers have shown that the specific nature of the association between the cationic building block and the DNA, and the ability to manipulate these Coulombic interactions is instrumental for optimization of transfection efficiency.\textsuperscript{18} It is therefore important to study how various types of building blocks affect transfection.\textsuperscript{19-21} Considering that trisaminocyclopropenium ions are remarkably stable cations that have been observed to only weakly associate with their counterions,\textsuperscript{22-23} we sought to investigate how these moieties would behave as transfection agents. Furthermore, because the cyclopropenium cation is stable across a broad pH range,\textsuperscript{24-25} we postulated resulting polypelexes would be particularly robust. For these reasons, coupled with the acute control of macromolecular architecture and molecular structure this system permits, we anticipated that the employment of materials made via post polymerization would serve as an effective platform for analyzing transfection agents.
For the study of cationic polymer families, precise and modular syntheses are necessary to reliably access a variety of derivatives. Our group demonstrated the importance of such a modular platform in a report describing the first example of cyclopropenium-based non-viral vectors comprising alkyl substituents of varying hydrophobicity of an electron-rich cation (Figure 2A).\textsuperscript{13, 26} As cyclopropenium is a permanent positive charge and contains no basic amines to protonate, polyplexes likely escape the endosome via membrane lysing rather than a proton sponge mechanism. We found that cyclopropenium polymers derivatized with piperidine were far less cytotoxic and displayed significantly increased gene expression compared to their diisopropyl counterparts, illustrating how subtle changes in hydrophobicity can have an enormous impact on the viability of a transfection agent.

*Cell viability, transfection efficacy, and characterization of TAC delivery systems*

While we synthesized many polymers, for our transfection studies we focused on homopolymers that are highly water-soluble. Furthermore, to simplify comparisons between materials, we elected to change only subtle elements of TAC structure on a styrenic (PMAS) and polyethyleneimine (PEI) polymer backbones. Cytotoxicity assays and luciferase transfections in HEK-293T cells revealed a significant dependence on the chemical structure of the pendent TAC ion, namely its amino substituents, and on the identity of polymer backbones: PEI and PMAS. All four TAC polymers showed a similar toxicity profile to linear PEI (25 kg mol\textsuperscript{-1}) at low dosages. However, at high loadings polyTACs were found to be more biocompatible, especially those bearing a styrene backbone (Figure 3). Functionalizing PEI with TAC(Mo) endowed the polymer with a cell viability of \textasciitilde50\% at both 50 and 100 µg mL\textsuperscript{-1} loadings.
While the structural modification of PEI with the TAC ions led to a lower transfection efficacy as compared to the parent polymer (Figure 4), comparing the two modified PEI materials bearing TAC(Pep) and TAC(Mo) led to notable differences in transfection efficiency. These two materials differ in the chemistry at the 4-position of the six-membered ring – a simple variation between a methylene group and an ether oxygen. Here, PEI(Pep) polyplexes transfected cells almost as well as the PEI parent polymer, but polyplexes of PEI(Mo) exhibited poor transfection efficiency (Figure 4). Potentially, this difference may be attributed to the increased hydrophobic nature of PEI(Pep) over PEI(Mo), which has been shown to play a key role in non-viral transfection agents, as described above.\textsuperscript{7, 27-28} Polyplexes of PEI and TAC polymers with plasmid DNA (pDNA), at the loadings noted in Figure 4, were further characterized by dynamic light scattering for their hydrodynamic diameter ($D_H$) and zeta ($\zeta$) potential (Table 1). As the $D_H$
and surface charge of PEI(Pep), PEI(Mo), and unfunctionalized PEI polyplexes are similar (Table 1), the observed discrepancy in transfection efficacy may be due to fine structural variations between each agent. However, it was challenging to draw conclusions at this stage, and further investigation of the complex relationships between transfection efficiency, TAC structure, and polymer molecular mass are still ongoing. Changing the backbone from PEI to PMAS resulted in smaller polyplexes that were also viable transfection agents [Figure 4, PMAS(Pep) and PMAS(Mo)]. All of our most effective formulations (Table 1 and Figure 4) are within the size regime that Zhou and coworkers outlined for highest efficiency transfection reagents, i.e. sub 500nm. Furthermore, PMAS-based materials exhibited optimal pDNA transfection at lower charge ratios than PEI and PEI(R) polymers (Table 1). Within the range of the error bars, both the more hydrophobic PMAS(Pep) and the PMAS(Mo) derivatives are similar, unlike in the PEI systems. These results portend ClickabIL chemistry as a platform to tune the chemical composition of TAC-based polyelectrolytes, build detailed structure-property relationships, and inform design principles for optimization of transfection agents.

Table 1. Characterization of transfection agents and polyplexes corresponding to optimal transfection efficacy.

<table>
<thead>
<tr>
<th>Transfection Agent[a]</th>
<th>MM[b] [kDa]</th>
<th>Charge ratio[c]</th>
<th>Dₜ [nm]</th>
<th>ζ potential [mV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI</td>
<td>25</td>
<td>50 : 1</td>
<td>490 ± 60</td>
<td>40 ± 10</td>
</tr>
<tr>
<td>PEI(Pep)</td>
<td>166</td>
<td>8 : 1</td>
<td>425 ± 100</td>
<td>65 ± 5</td>
</tr>
<tr>
<td>PEI(Mo)</td>
<td>164</td>
<td>20 : 1</td>
<td>400 ± 110</td>
<td>60 ± 6</td>
</tr>
<tr>
<td>PMAS(Pep)</td>
<td>53</td>
<td>5.5 : 1</td>
<td>140 ± 60</td>
<td>27 ± 8</td>
</tr>
<tr>
<td>PMAS(Mo)</td>
<td>53</td>
<td>5.5 : 1</td>
<td>215 ± 25</td>
<td>43 ± 6</td>
</tr>
</tbody>
</table>

[a] Polyplexes of polymers tested at loadings noted in Figure 4. [b] Molecular mass of transfection agent, calculated based on commercial linear PEI; for PMAS(R) materials, PMAS
was measured by SEC using PS standards of narrow dispersity, then calculated for corresponding TAC group. [c] Ratio of either N to phosphate anion (PEI) or TAC to phosphate anion.

Figure 4. Luciferase expression of transfected HEK-293T cells using TAC polymers and 25 kg mol\(^{-1}\) linear PEI. Polymer backbones are noted in white boxes and amino substituents pictured above respective bars. Luciferase expression of cells is measured after 48 h incubation with specified polymer loadings (all with pDNA loading of 3 µg mL\(^{-1}\)) and normalized by cell count. Error bars are standard deviation of triplicate measurement.

Despite these advancements, and the seemingly limitless attempts by material chemists to engineer effective synthetic vectors, cationic polyelectrolytes have not yet made a significant impact on gene therapy. Iterative approaches designing delivery vectors by building on previous reports are often unproductive because of the lack of standardization in protocols. For example, many different cell lines are used and, generally, studies only report in vitro transfection efficiency, which is a poor metric of efficacy in vivo. Only through understanding how chemical manipulations at the building block level and variations of macromolecular architecture affect a
material’s viability as a gene delivery agent can we uncover design principles and areas in need of further exploration. 30-32
References


Chapter Two: Biological Applications of Cyclopropenium Polymers

Supplementary Information

I. General

Polyplex size and zeta potential were measured on a Malvern Zetasizer Nano ZS (Malvern, United Kingdom). For all measurements, polyplexes were diluted 1:100 in Milli-Q water at neutral pH. The reported diameters are the average of three measurements, where each measurement comprises at least 10 acquisitions, and the zeta potential was calculated according to the Smoluchowski approximation.

II. Figures

![Graph showing luciferase expression of transfected 293T cells with all tested polymers across loading series.](image)

**Figure S1.** Luciferase expression of transfected 293T cells with all tested polymers across loading series. Error bars represent standard deviation of four measurements.
III. Methods

**Cell Culture:** HEK 293T cells (American Type Culture Collection) were grown in Dulbecco’s Modified Eagle Medium with L-glutamine (Gibco) supplemented with 10% FBS (Atlanta Biologicals) and 1% penicillin/streptomycin (Gibco). Cultures were incubated in humidified tissue incubators (Thermo Scientific) at 37°C and 5% CO₂.

**Cell Viability Measurements:** Trypan blue dye exclusion counting was performed in triplicate with an automated cell counter (ViCell, Beckman-Coulter). Cell viability under experimental conditions is reported as a percentage relative to untreated cells.

**Polymer-DNA Complexation:** Solutions of polymer in RNase-free water were added to 3 µg of pDNA (gWiz-Luciferase, Aldevron, Fargo, ND) at specified loadings. The solutions were then vortexed at 1500 rpm for 3 min at room temperature.

**Cell Transfection and Luciferase Expression:** 293T cells were seeded on 12-well plates at a density of 50,000 cells per well 24 hours prior to transfection. The media was then evacuated, replaced with fresh media, and supplemented with the polymer-pDNA complex. After 48 hours of incubation, cell viability was measured, and cells were re-plated on 96-well plates and analyzed for luciferase activity according to manufacturer’s protocol. Briefly, cells were rinsed with PBS and lysed with 20 µL/well 1X Cell Lysis Buffer (Promega, Madison, WI). To the cell lysates was added 100 µL/well of Luciferase Assay Reagent (Promega) and the light produced was measured on a plate reader (PerkinElmer, Waltham, MA). Results were expressed as relative light units (RLU) normalized to cell counts, with error bars representing the standard deviation from the triplicate measurement.

**Charge Ratio Calculation:**

\[
\frac{(3 \, \mu g \, pDNA) \times (MW \, per \, polymer \, repeat \, unit)}{330 \, g \, per \, pDNA \, nucleotide}
\]
= Mass of polymer required for 1:1 charge ratio with pDNA
Chapter Three

Nanoscale morphology and ion transport properties of cyclopropenium materials

The polymerization of ionic liquid monomers (mono-ILs) into mechanically robust and processable materials has promoted their use in a variety of modern technologies, ranging from electrolyte materials in batteries and fuel cells to transfection agents in biological applications.\(^1\)-\(^5\) The potential for polymerized ionic liquids (poly-ILs) to provide a materials platform in which efficient, liquid-like ionic conductivity may occur through a mechanically robust polymer network has notably sparked significant effort toward developing poly-ILs for energy storage and conversion applications.\(^6\)-\(^14\) However, the fundamental mechanisms by which ion transport occurs in poly-ILs remain incompletely understood. According to the Nernst-Einstein relation (equation 1), ionic conductivity is coupled to mass transport via segmental or molecular diffusion\(^15\)-\(^16\)

\[
\sigma_{DC} = \frac{1}{kT} (n_+ D_+ q_+^2 + n_- D_- q_-^2) \tag{1}
\]

where \(\sigma_{DC}\) is the dc conductivity, \(k\) is the Boltzmann constant, \(n\) the number density of free ions, \(q\) the ionic charge, and \(D\) the translational diffusion coefficient for the cations (+) and anions (-). Indeed, this is the case for many molecular ionic liquids\(^17\)-\(^19\) and polymer/salt blends.\(^15\), \(^20\)-\(^21\) Attempts to translate this concept to highly conductive poly-ILs have emphasized lowering the glass transition temperature \((T_g)\), thus widening the temperature window in which poly-ILs are meaningfully conductive.\(^22\) Despite this effort, the ionic conductivity in poly-ILs remains too low to be viable as ion exchange membranes in energy storage and conversion applications.

It has come to light in recent years that the mechanisms underlying ion transport in poly-ILs may be fundamentally different from those in mono-ILs.\(^23\)-\(^28\) While molecular diffusion is found to directly correlate to the conductivity in most mono-ILs from above the melting point.
through the glass transition, segmental diffusion (structural relaxation) and ionic conductivity in poly-ILs can exhibit strongly divergent temperature dependences, indicating a fundamentally different transport mechanism. The effect is stark and somewhat counterintuitive: the conductivity of glassy poly-ILs can be orders of magnitude higher than that found in glassy mono-ILs at their respective $T_g$.\textsuperscript{18,24} In these cases, conductivity is said to be “superionic” and “decoupled” from segmental motion.\textsuperscript{14,29-31} Thus, focusing exclusively on lowering $T_g$ may not be the only way to enhance conductivity in ion-containing polymeric materials.

The physical mechanism for the high ionic conductivity below $T_g$ in poly-ILs is qualitatively attributed to an efficient activated hopping process of counter ions in an amorphous and immobilized network of polymeric ionic sites. Results of recent simulations suggest that ion mobility in poly-ILs is correlated to ion association lifetimes rather than structural dynamics,\textsuperscript{32} thus supporting the experimentally developed hypothesis that ion transport in mono-ILs and poly-ILs occurs via different mechanisms. It is critical to explore the implications of these results by studying poly-ILs comprising ion pairs with dramatically different Coulombic and/or steric interactions to probe how tuning the chemical structure, electrostatics, and nanoscale morphology lead to “superionic” behavior in poly-ILs.

The most common cationic poly-ILs contain units with the formal charge on heteroatoms, such as ammonium-, phosphonium-, and imidazolium-based polymers.\textsuperscript{1-2} Yet while there are recent examples of poly-ILs that exhibit superionic conductivity,\textsuperscript{18} only hints of how the chemical and electronic structures mediate the interaction between the ion pairs have been reported.\textsuperscript{33} For example, the delocalized charge on imidazolium (and other species) has been found to improve ion mobility,\textsuperscript{34-35} and the tetrahedral geometry of ammonium and phosphonium ions purportedly dampens the association with its counter ion due to steric hinderence.\textsuperscript{33,36} Using
these types of chemical and physical insights to engineer short-lived ion pairs that promote ion hopping is likely critical to enhancing the performance of poly-ILs in energy applications.

Figure 1. The chemical structure of PS-TAC and its various counterions. Structures were optimized by Gaussian 09 Rev D.01, and the electrostatic potentials highlight TAC’s delocalized charge and the various degrees of charge distribution of the anions.

Homopolymers and monomeric ionic liquids

As previously outlined, we recently developed a straightforward chemical pathway to access poly-ILs comprising the aromatic cyclopropenium cation.37 The trisaminocyclopropenium ion (TAC) is an electron-rich cation with a highly delocalized charge (Figure 1) formally on carbon, and represents a unique scaffold in the poly-IL chemistry toolbox. TAC has an exceptionally high highest occupied molecular orbital (HOMO) and has been observed to repel halides38-39 and even form facially stacked dimers, as Wallace et al. elegantly demonstrated.40 On the other hand, TAC’s electron-rich properties have been leveraged to form inverse charge transfer salts with electron-deficient anions, and can be readily oxidized to an isolatable radical dication.41-44 We therefore hypothesize that the Coulombic interaction between ion pairs in these
systems will be uniquely modular, and that the physical properties of the counter ion could be used to tune the dominant mechanism of ion transport.\textsuperscript{32}

We characterize and report the thermal properties, local morphology, and dielectric response of a series of monomeric and polymeric TAC ionic liquids with different counter ions—from chloride (Cl), to bis(trifluoromethane)sulfonamide (TFSI), to pentacarboxycyclopentadienyl (CPDE) (Figure 1). Indeed, the TAC-based polymers and monomers in this study do not follow trends typically observed in cationic poly-ILs, namely that the glass transition temperature of the material ($T_g$) does not solely predict the magnitude of ionic conductivity. A dramatic decoupling behavior is observed in the Cl- and TFSI-based poly-ILs, with dc conductivity approximately 4-6 orders of magnitude higher in the poly-IL than the mono-IL at their respective calorimetric $T_g$. Furthermore, we report the first observation of an aprotic polymerized ionic liquid having higher absolute ambient temperature dc conductivity than its monomeric counterpart, and attribute this result to the efficiency of chloride hopping in the TAC-based polymer network below $T_g$. These results underscore the significant impact that electrostatic properties can have on the mechanism of ion transport in poly-ILs and further demonstrate how decoupling of ion mobility from polymer segmental dynamics represents a promising design paradigm for enhancing the performance of polymer electrolytes.

The series of six TAC-based mono- and poly- ILs were characterized using differential scanning calorimetry to understand the thermal properties and structural (segmental) dynamics of the materials (Figure 2). The calorimetric $T_g$ increase by \textasciitilde60–90 K upon polymerization, reflecting the expected dramatic reduction in segmental mobility (Table 1). The calorimetric $T_g$ is also notably impacted by the counter ion chemical structure. The CPDE and TFSI-based mono-ILs exhibit nominally similar $T_g$’s that are significantly lower than that of the Cl-based mono-IL.
For the poly-ILs, $T_g$ increases considerably from CPDE to TFSI to Cl. These trends agree well with previously reported correlations between the van der Waals volume of the monomeric species (estimated according to Zhao and coworkers,\textsuperscript{45} Table 1) and $T_g$, although the absolute values of $T_g$ in these TAC-based materials appear systematically higher than the values shown by Colby \textit{et al.}\textsuperscript{22} We speculate that the polystyrene backbone functionalized with a pendent aromatic unit may strongly suppress segmental dynamics of similarly sized monomers due to an increase in chain rigidity.

![Figure 2. Reversing part of the heat flow as measured by temperature modulated differential scanning calorimetry upon cooling. The midpoint in the step of the heat flow corresponds to the calorimetric glass transition. Dashed and solid lines represent data for monomeric and polymeric ionic liquids, respectively.](image)

Figure 2. Reversing part of the heat flow as measured by temperature modulated differential scanning calorimetry upon cooling. The midpoint in the step of the heat flow corresponds to the calorimetric glass transition. Dashed and solid lines represent data for monomeric and polymeric ionic liquids, respectively.

Just as $T_g$ increases substantially upon polymerization, the observed temperature-dependent dc conductivities of the poly-ILs are also significantly different than the values measured for the mono-ILs, Fig. 3. The dc conductivity of the mono-ILs at all measured temperatures is surprisingly similar despite the fact that the calorimetric $T_g$ of the Cl-based mono-IL is nearly 40 K above that of the TFSI and CPDE materials. Furthermore, the dc conductivities of the poly-IL samples follow an unusual trend with counter ion chemical structure that deviates from the
Table 1. Estimated van der Waals volumes and diameters (assuming spherical geometry) of the cyclopropenium cation and the three studied counterions, as well as the calorimetric glass transition temperature of the mono- and poly-ILs.

<table>
<thead>
<tr>
<th>cation or anion</th>
<th>van der Waals volume (nm$^3$)</th>
<th>van der Waals diameter (nm)</th>
<th>$T_g$ (C) of mono-IL</th>
<th>$T_g$ (C) of poly-IL</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{TAC}]^+$</td>
<td>0.326</td>
<td>0.85</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$[\text{CPDE}]^-$</td>
<td>0.313</td>
<td>0.84</td>
<td>-18.4</td>
<td>41.0</td>
</tr>
<tr>
<td>$[\text{TFSI}]^-$</td>
<td>0.141</td>
<td>0.64</td>
<td>-26.6</td>
<td>62.4</td>
</tr>
<tr>
<td>$[\text{Cl}]^-$</td>
<td>0.022</td>
<td>0.35</td>
<td>28.4</td>
<td>82.9</td>
</tr>
</tbody>
</table>

expected trends based on $T_g$ measured via calorimetry. The CPDE-based poly-IL exhibits dc conductivities that are many orders of magnitude below those measured in the TFSI and Cl-based polymers at all measured temperatures, even though the calorimetric $T_g$ of this material is ~20 K and ~40 K below that of $[\text{PS-TAC}][\text{TFSI}]$ and $[\text{PS-TAC}][\text{Cl}]$, respectively. This unusual finding clearly demonstrates that the logic that has made $T_g$ a proxy for dc conductivity in amorphous ionic materials does not generally hold.

Figure 3. dc ionic conductivity plotted as a function of inverse temperature for the studied monomeric (open symbols) and polymeric (solid symbols) ionic liquids.
A comparison between the dc conductivity of the Cl-based mono and poly-ILs (open and closed black symbols in Figure 3) reveals a truly surprising departure from typical conductivity behavior of ionic liquid materials. It can be seen in Figure 3 that the Cl-based poly-IL exhibits measurably higher conductivities than the corresponding mono-IL at ambient temperature. This stands in contrast to the expectation that a polymeric ionic liquid should exhibit dc conductivities decades lower than that of a monomeric ionic liquid, especially considering the poly-IL $T_g$ is nearly 60 K higher than the mono-IL. This result, to our knowledge, has not been observed in any class of ion-containing polymers, and testifies to the unique structural and electronic factors at play in these TAC-based materials.

Representing the dc conductivities on a $T_g/T$-normalized plot helps shed light on the mechanism responsible for these unusual and unexpected trends in the dc conductivity of TAC-based mono- and poly-ILs, Figure 4. For prototypical room temperature ionic liquids (such as [BMIM][TFSI]) or polymer/salt blends, the ionic conductivity generally follows a Vogel-Fulcher-Tammann (VFT) type of temperature dependence above and down to $T_g$, at which point the conductivity reaches values of $10^{-14}$–$10^{-15}$ S/cm and the characteristic timescales of ion transport reach ~100 s. In these cases, the process of ion transport is directly “coupled” to the mass transport and structural-relaxation process (i.e. segmental mobility). As is seen in Figure 4, TFSI and CPDE-based mono-ILS, as well as [PS-TAC][CPDE], appear to follow this trend following an extrapolation of their respective temperature dependent dc conductivities to $T_g$. Unfortunately, instrument limitations prevent measurement of these materials in the near vicinity of $T_g$ due to very high impedances and slow ionic relaxation times. Additionally, their values of conductivity are significantly lower than that observed in [BMIM][TFSI] over the measured temperature range, which may be attributed to a reduced dynamic fragility $m$ (the curvature of
the temperature dependence of conductivity) and/or a lower concentration of simultaneously conducting ions.\textsuperscript{48}

Figure 4. dc ionic conductivity plotted as a function of $T_g$-normalized inverse temperature for the studied monomeric (open symbols) and polymeric (solid symbols) ionic liquids. Data for the prototypical room temperature ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BMIM][TFSI] are plotted for reference.\textsuperscript{46}

It is clear from the VFT temperature dependence of the dc conductivity that ion transport is coupled to segmental motion/structural relaxation in [TAC][TFSI], [TAC][CPDE], and [PS-TAC][CPDE]. In contrast, Figure 4 illustrates that conductivity is strongly decoupled from segmental dynamics in the TFSI and even more significantly in the Cl-based poly-ILs. Ionic conductivity in these polymers is less sensitive to temperature than the segmental relaxation process, as evidenced by the high values of the dc conductivity at the calorimetric glass transition temperature ($\sigma_{dc}(T_g) \sim 10^{-6}$ S/cm and $10^{-8}$ S/cm for [PS-TAC][Cl] and [PS-TAC][TFSI], respectively). The transition from a high temperature VFT to a low temperature Arrhenius type of temperature dependence at $T_g$ clearly indicates “decoupled” or “superionic” ion transport, which has been observed in several recent studies of poly-ILs.\textsuperscript{23-26, 28} In this case, the cationic sites may facilitate ion motion, as the TAC charge is spread over a very large area and easily polarized to accommodate changes in local dielectric environment caused by anion motion.
Interestingly, the ion transport process also appears to be decoupled from structural relaxation in [TAC][Cl], where a VFT-to-Arrhenius transition is observed and the conductivity at $T_g$ is high $\sigma_{dc}(T_g) \sim 10^{-10}$ S/cm. This observation indicates that the superionic transport mechanism is not a direct result of the polymeric nature of the material, although polymerization clearly enhances its efficacy. To our knowledge, superionic conductivity is seldom realized in aprotic small molecule ILs, although it has been reported for a variety of protic molecular ILs.\textsuperscript{49-50}

While the ion transport properties of these TAC-based materials exhibit dramatic changes with chemical structure, measurements of the local morphology of the glassy polymer films by multi-angle X-ray scattering reveal only modest structural changes, Figure 5. As is ubiquitously observed in small molecule and polymeric ionic liquids, three main correlation peaks are observed in these TAC-based poly-ILs.\textsuperscript{51-52} At low momentum transfer $q$ centered near 3 nm$^{-1}$, a small and rather narrow peak is present in the structure factor of the Cl and CPDE-based poly-ILs. This peak $q_b$ is typically assigned to polarity alternation between nanophases rich in the non-polar backbone/side-groups or the polar ionic moieties. It is somewhat striking that this peak is so narrow in the Cl and CPDE-based amorphous poly-ILs, and we speculate this could result from more efficient packing of Cl and CPDE anions in the interstitial volume of the polymer matrix. While such narrow structural features are rarely seen in amorphous polymers, they are reminiscent of the remarkably well-defined amorphous structures recently reported for the class of precise polyethylene-based ionomers.\textsuperscript{53-56} It should be noted that the narrow $q_b$ peak is not present for the TFSI-based poly-IL, which may result from TFSI’s flexible nature that inhibits polar-apolar structural organization in these TAC-based poly-ILs.

Examination of the peaks in the smaller size regime further reveals that changes in polymer morphology are subtle despite the drastically different anion chemistries. The peak $q_i$
observed at intermediate $q$ is associated with charge alternation and reflects the average anion-anion (and cation-cation) correlation distance in these films. This peak changes most systematically with anion chemistry, moving as expected to lower $q$ (from 9 to 7 nm$^{-1}$) and larger distances with increasing anion van der Waals volume. The final feature revealed by X-ray scattering is a high-$q$ peak $q_a$ centered near 13 nm$^{-1}$ and corresponds to adjacency correlations between monomers and cation-anion pairs. This feature is seemingly unaffected by counterion chemical structure. Given that the $q_a$ peak position is essentially identical to that observed in neat polystyrene glasses and that these structural features are exceedingly tolerant to changes in anion chemistry, it appears that the rigid aromatic backbone has a defining impact on the local polymer morphology.

Comparing the X-ray scattering data to the ion transport measurements reveals that there are no obvious changes in morphology that can be invoked to account for the observed changes in conductivity. Indeed, the poly-IL [PS-TAC][TFSI] shows a superionic transport mechanism but no nanostructural organization, while [PS-TAC][CPDE] exhibits a liquid-like ion transport mechanism over the measured temperature range and a clear morphological signature of polar-apolar nanostructural organization. Instead, we speculate that the strong decoupling of ionic conductivity from mass transport in [PS-TAC][Cl] and [PS-TAC][TFSI] (and the corresponding lack of decoupled conductivity in [PS-TAC][CPDE]) arises from some combination of structural and electronic effects. As is seen in Table 1, the TAC monomer is more than ten times larger than Cl, while it is nearly equivalent in size to CPDE. The size mismatch between the cationic and anionic species, in conjunction with TAC’s electron-rich and delocalized charge seem to work together to achieve high conductivity below $T_g$. The different extents of electrostatic
attraction between ion pairs may also impact the dominant mechanism of ion transport, which is a subject of continued investigation.

![Figure 5](image)

Figure 5. X-ray scattering measurements of TAC poly-IL films at ambient temperature in the glassy state. The symbols correspond to measured data, while the solid line depicts the best-fit of the [PS-TAC][Cl] data with a superposition of three Lorentzians (dashed lines). The three peaks arise due to polarity alternation ($q_b$), charge alternation ($q_i$), and adjacency correlations ($q_a$).

As a polymer with large pendent cations cools through the glass transition, the polymeric chains vitrify and inevitably leave behind pockets of free volume due to packing constraints. These free volume pockets may be substantial in these TAC-based materials because of the rigid aromatic groups and bulky isopropyl substituents. If the anions are smaller than these void spaces in the vitreous state, it is feasible that anions can continue to diffuse via an activated hopping mechanism, mediated by TAC’s diffuse and polarizable charge, which does not require the cooperative rearrangement of monomers. This type of physical picture may also apply to monomeric ionic liquids, especially when the anionic and cationic volumes are vastly
imbalanced, as they are for [TAC][Cl]. In contrast, large anions such as CPDE require the cooperative rearrangement of polymer segments to execute long-ranged diffusion as is evidenced by the coupled, VFT-like conductivity mechanism for [PS-TAC][CPDE]. It is worth noting that the van der Waals diameters of Cl and TFSI are smaller than the characteristic distance between like charges (~q\textsuperscript{-1}) as determined by X-ray scattering in the glassy state (Figure 2 and Table 1), although it is measurably larger in the case of [PS-TAC][CPDE]. In vitrified materials, the difference in size between counter ions represents a possible design principle for enhancing the degree of decoupling and the glassy conductivity in polymeric ionic liquids.

The ion transport properties and local morphologies of a series of monomeric and polymeric ionic liquids based on the trisaminocyclopropenium cation with three different counter ions were measured using calorimetry, dielectric relaxation spectroscopy, and multi-angle X-ray scattering. The glass transition temperatures of the poly-ILs are significantly higher (~60–90 K) than their monomeric counter parts and increase significantly with decreasing molecular volume of the anion by a factor of ten from CPDE to TFSI to Cl. Clear evidence of a “superionic” transport mechanism is found in the [PS-TAC][Cl] and [PS-TAC][TFSI] poly-ILs, resulting in anomalously high conductivity at the calorimetric T\textsubscript{g} (σ\textsubscript{DC}(T\textsubscript{g}) ~ 10\textsuperscript{-6} and 10\textsuperscript{-8} S/cm, respectively) accompanied by an abrupt VFT-to-Arrhenius type of temperature dependence at T\textsubscript{g} in these materials. The result of this “superionic” transport is striking in the Cl-based materials: the solid polymerized ionic liquid exhibits measurably higher dc ionic conductivity than the supercooled monomeric analog at ambient temperature. Both structural and electronic factors may play a role in the surprisingly efficient conductivity in chloride materials, with structural rigidity leading to significant free volume and diffuse charge mediating anion hopping below T\textsubscript{g}. With increasing anionic molecular volume, the degree of decoupling (as indicated by the value of the
conductivity at $T_g$) and the efficacy of the superionic transport mechanism decreases precipitously, and it is found that the ion transport mechanism in the CPDE-based poly-IL is completely coupled to that of segmental relaxation. Despite having observed these dramatic changes in the mechanism of ion transport upon changing the anion chemical structure, we find only subtle and seemingly uncorrelated changes in the local morphology of these poly-ILs. These results suggest that the molecular volumes of the cationic and anionic species are crucial parameters that control ion transport in poly-ILs and can importantly be tuned to achieve favorable ion transport properties in otherwise solid polymeric materials. The extent to which the delocalized charge of TAC and Coulombic interactions between ion pairs enable ion hopping through the glassy polymer below $T_g$ is the subject of continuing investigation.

*Hydrated block copolymer systems*

Block copolymer architectures can give rise to discrete nanostructured morphologies that have a dramatic impact on ionic conductivity, predominantly when materials are hydrated. Controlling phase segregation of block copolymers into one-dimensional (i.e. cylinders) or two-dimensional (i.e. lamellae) cationic domains stymies ionic transport as compared to when ions are free to move in three dimensions as in gyroidal or network structures, or homopolymer films. Fewer translational degrees of freedom result in dead ends for mobile ions, and this problem is exacerbated by film grain boundaries.\(^{58}\) Hydrating cationic polyelectrolyte films also plays an essential role in facilitating conductivity as water molecules mediate ion transport.\(^{59-60}\) This is the case for Nafion, a gold standard material for proton transport in hydrated systems based on a copolymer containing anionic sulfonic acid groups.\(^{61-63}\) In a study on ammonium-containing polyelectrolytes for alkaline fuel cells, the authors found that comb-shaped polymers incorporating long alkyl sides chains – up to 16 carbons – induced phase separation to yield
uniform ionic domains with high local concentrations of water.\textsuperscript{7} Hydroxide ion transport was significantly increased compared to analogous polymers lacking the long alkyl chains, suggesting that water and ions confined within channels facilitate ion transport. In another study, ion mobility was suppressed by an order of magnitude in random copolymers compared to phase-segregated block copolymers at that same degree of hydration and incorporation of charged monomers.\textsuperscript{64} Significant clustering of water was observed within the block copolymer samples, while random copolymer films displayed an even distribution of water. Thus, the increased conductivity in phase-segregated films is attributed to the confinement of water within the block copolymer’s ionic nano-channels. Furthermore, diblock copolymers displayed even higher conductivity than corresponding homopolymers, though only at the highest humidity tested (i.e. 90% relative humidity), which demonstrates that morphology effects in highly hydrated systems can dominate performance. These data illustrate how ion transport appears to occur via a more efficient mechanism when high concentrations of water molecules exist within organized ionic domains.

While hydrating films boosts ion transport it also limits operating temperatures, so many studies examine anhydrous conductivity to glean more fundamental structure-property relationships.\textsuperscript{65} However, without water molecules concentrated within ionic nano-channels to mediate ion transport, the advantage afforded by block copolymer phase segregation all but disappears. Furthermore, the composition and volume fraction of the neutral block overwhelm the subtler impact of alkyl substituents on macromolecular properties. Elabd and Mahanthappa examined a series of anhydrous alkyl-imidazolium block copolyelectrolytes with various alkyl side chains and volume fractions of the two blocks.\textsuperscript{66} They found that the ionic conductivity and nanoscale morphology were independent of the alkyl substituent and solely determined by the
volume fraction of each block. Transitioning from 1D cylinders to 2D lamellae increased the conductivity by an order of magnitude, however this represents still inferior conductivity compared to corresponding homopolymers. In a similar vein, Winey and Elabd observed that ionic conductivity increased as the imidazolium block copolymer film morphology moved from cylinders (1D path) to lamellae (2D) to a network or gyroid structure (3D) (Figure 6).67 The connectivity and dimensionality of ionic domains is evidently an essential property for ionic transport, and phase segregation is an effective strategy towards high ion transport in polyelectrolyte films in so far as it can increase local concentrations of moieties that mediate ion hopping, whether they are water, ionic liquids, or covalently tethered polar species.8

Figure 6. A) Schematic of self-assembled block polyelectrolytes with 1D hexagonally packed cylinders (top) and 3D gyroid/network (bottom) ion conducting channels within a neutral matrix reproduced from ref. 1. B) TEM images of phase segregated block polyelectrolytes denoted with corresponding morphology and dimensionality of ion conducting phase reproduced from ref. 2.

To probe the impact of these design principles on TAC systems, we synthesized block copolymers of various compositions and characterized the morphology of bulk films comprising various TAC building blocks. As discussed above, nanostructured block polyelectrolytes (BCPE) have broad implications in materials chemistry, specifically for fuel cells and batteries,
if they undergo microphase segregation. Experimental results from Winey and Elabd report that water and ions confined within nanochannels may accelerate transport, and computational studies from Olvera de la Cruz and co-workers suggest this effect may be enhanced if the conducting path is a continuous, percolating structure. With this in mind, we characterized block copolymer samples by SAXS and TEM to understand microphase segregation in TAC-containing BCPEs.

In Figure 7, we show X-ray scattering (SAXS) profiles of three representative diblock copolymers. The primary scattering peaks seen in each sample (indicated by filled triangles) is attributed to microphase separation. The scattering profile of PS-\(b\)-PTAC(Mo)(35) contains a higher order peak at \(q = 3q^*\). This suggests the presence of a symmetric lamellar phase. The scattering profiles of the other polymers contain only one peak, which indicates a lack of long-range order. The domain spacing, \(d\), of the microphase separated diblock copolymers is calculated by the equation \(d = 2\pi/q^*\). The domain spacing values corresponding to each diblock copolymer are given in Table 1. As expected, \(d\)-spacing increases with molecular mass and molar fraction of styrene. We next sought to probe the potential application of TAC-based polyelectrolytes in electrochemical devices.

Table 2. Characterization of PS-\(b\)-PTAC(R)(TAC mol\%) block copolymers. Block copolymers were synthesized by addition of styrene to the three homopolymers, and domain spacing was calculated by SAXS (Figure S3). Molecular mass (MM) was determined by \(^1\)H-NMR spectroscopy. DP is degree of polymerization.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>MM/kg mol(^1)</th>
<th>TAC% by DP</th>
<th>TAC% by MM</th>
<th>SAXS domain spacing (nm)</th>
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</thead>
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<tr>
<td>PS-(b)-PTAC(Cy)(45)</td>
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<td>15</td>
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<td>18</td>
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<tr>
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<td>50%</td>
<td>80%</td>
<td>18</td>
</tr>
<tr>
<td>PS-(b)-PTAC(iP)(50)</td>
<td>27</td>
<td>30%</td>
<td>60%</td>
<td>24</td>
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</tbody>
</table>
Figure 7. SAXS profiles of microphase separated diblock copolymers collected at 25 °C. Scattering intensity is plotted as a function of the magnitude of the scattering vector, $q$. Filled triangles represent the primary scattering peaks and the open triangles represent the higher order scattering peaks.

Ion conductivity experiments were performed on block copolymers comprising 20% TAC functionality using electrochemical impedance spectroscopy. Since conductivity is closely related to morphology, we complemented our SAXS experiments with transmission electron
microscopy (TEM). A sample of this block copolymer (drop cast, no annealing) was micromted and imaged by TEM (Figure 8A and B). Even without staining, we clearly observe microphase segregation (cylindrical morphology) (Figure S4). Staining with RuO$_4$ vapor for two minutes preferentially stains the cationic block and helps to visualize the internal structure. The electron micrographs obtained (Figures 8A and 8B) show hexagonally packed cylinders in different orientations. The domain spacing by TEM was 29 nm, which is consistent with the domain spacing determined by SAXS (31 nm; see Table 2). The lighter color of the cylinders with respect to the matrix in Figure 8A and B indicates that PS cylinders are embedded in a TAC matrix. The stained TAC block scatters more electrons, and therefore appears darker by TEM. The non-functionalized PS cylinders in Figures 8A and B occupy a very large fraction of the image because the mole fraction of the functional block in this polymer is only 20%. The continuous nature of the conducting phase matrix, as reported above, is expected to facilitate ion transport.$^{68-69}$
Figure 8. Morphology and ionic conductivity of bulk PS-\textit{b}-PTAC(iP)(2) films. A) and B) Two representative TEM images of PS-\textit{b}-PTAC(iP)(20) reveal a morphology of hexagonally packed cylinders (d-spacing = 29 nm; the light color corresponds to PS). C) Ionic conductivity as a function of inverse temperature, from 25 to 65 °C, for PS-\textit{b}-PTAC(iP)(20) (ion exchange capacity, IEC = 1.3, at 90% relative humidity).

The in-plane conductivity, $\sigma$, of PS-\textit{b}-PTAC(iP)(20) equilibrated in humid air with 90% relative humidity (RH) was measured as a function of increasing temperature from 25 to 65 °C (Fig. 5C). To ensure equilibration, samples were initially annealed for one week at 90% RH at 25 °C and for 48 hours at each subsequent temperature of interest. The straight line in Figure 8C is the least-squares fit through the equilibrated conductivity data at each temperature value. In principle, the change in conductivity with temperature, shown in Figure 8, could either be due to changes in the mobility of chloride ions, or to a change in ion concentration in the membrane. The fact that ion concentration in the membranes is constant indicates that the slope of the line provides an estimate of the activation energy for transport of chloride ions through the membrane.
(Arrhenius law). The estimated activation energy for this system is 25 kJ mol\(^{-1}\). This value is comparable to that reported previously for the imidazolium-containing diblock copolymer analog in water, poly(styrene-b-4-vinylbenzyltrimethylimidazolium chloride) (PS-b-PIm(35)), 27 kJ mol\(^{-1}\). However, at room temperature, the conductivity of the PS-b-PTAC(iP)(20) polymer (ion exchange capacity, IEC= 1.3 meq g\(^{-1}\)) is rather high, 0.004 S cm\(^{-1}\), considering the low water uptake, \(\lambda_w = 7\), of this membrane (\(\lambda_w\) is the number of water molecules per chloride ion in the membrane). This value of \(\lambda_w\) is four times lower than the value obtained for PS-b-PIm(35) immersed in water, for the same conductivity (\(\lambda_w = 30\), \(\sigma = 0.004\) S cm\(^{-1}\)), and higher ion exchange capacity (IEC = 2.1 meq g\(^{-1}\)). These results indicate that the TAC-based polyelectrolytes conduct ions more effectively than the optimized membranes from imidazolium-containing polymers, with a minimum amount of water present. Further tuning of the functional groups, backbone structure, and morphology is expected to result in polyelectrolytes with exceptionally high ion conductivities.\(^{62, 67, 73-74}\)
References


Chapter Three: Nanoscale morphology and ion transport of membranes comprised of polymeric cyclopropenium

Supplementary Information

I. General Information

All materials were purchased from Sigma Aldrich and were used without further purification except as noted below. Deuterated solvents used for NMR spectroscopy were purchased from Cambridge Isotope Laboratories, Inc. Eluents for column chromatography were HPLC grade and purchased from Fisher Scientific. Organic solutions were concentrated by use of a Buchi rotary evaporator. All polymerizations were carried out with temperature control via an oil bath under an argon atmosphere in Schlenk flasks.

\(^1\)H and \(^{13}\)C NMR spectra were recorded in CDCl\(_3\) (except where noted in Experimental Methods) on a Bruker AMX-300, AMX-400, or AMX-500 spectrometer. Data for \(^1\)H NMR are reported as follows: chemical shift in reference to residual CHCl\(_3\) at 7.26 ppm (\(\delta\) ppm), multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, m = multiplet), coupling constant (Hz), and integration. Data for \(^{13}\)C NMR are reported in terms of chemical shift in reference to the CDCl\(_3\) solvent signal (77.16 ppm).

Thin layer chromatography (TLC) was performed using Teledyne Silica gel 60 F254 plates and viewed under UV light. Flash column chromatography was performed using Teledyne Ultra Pure Silica Gel (230 – 400 mesh) on a Teledyne Isco Combiflash Rf.
II. Figures

Figure S1. Dielectric relaxation spectra showing (a) the real conductivity and (b) imaginary electric modulus for [PS-TAC][CPDE] measured on cooling from 450 down to 335 K. Arrows indicate the direction of decreasing temperature.

Figure S2. BNN plot comparing the characteristic timescale of charge transport and DC conductivity for the studied monomeric (open symbols) and polymeric (solid symbols) ionic liquids.
Figure S3. Small angle X-ray scattering (SAXS) profiles of microphase segregated diblock copolymers collected at 25 °C. Scattering intensity is plotted as a function of the magnitude of the scattering vector, $q$. Filled triangles represent the primary scattering peaks, and the open triangles represent the higher order scattering peaks.
Figure S4. Transmission electron microscopy (TEM) images of PS-\textit{b-PTAC(iP)}(20) without exposure to RuO$_4$ vapor. \textbf{a.} Cross-section of the cylinders. \textbf{b.} Hexagonally packed cylinders orientated orthogonal to the section.
Figure S5. $^1$H NMR of [TAC][TFSI] in CDCl$_3$. 
Figure S6. $^1$H NMR of [TAC][CPDE] in MeOD.
Figure S7. $^1$H NMR of [PS-TAC][TFSI] in CD$_2$Cl$_2$. 
**Figure S8.** $^1$H NMR of [PS-TAC][CPDE] in CD$_2$Cl$_2$.

**III. Tables**

Table S1. Correlation distances and corresponding coherence lengths present in cyclopropenium-based polymeric ionic liquids as determined by peak fitting of X-ray scattering data.

<table>
<thead>
<tr>
<th></th>
<th>$d_b$ (nm)</th>
<th>$\Delta d_b$ (nm)</th>
<th>$d_i$ (nm)</th>
<th>$\Delta d_i$ (nm)</th>
<th>$d_a$ (nm)</th>
<th>$\Delta d_a$ (nm)</th>
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<td>[PS-TAC][CPDE]</td>
<td>2.42</td>
<td>8.65</td>
<td>0.82</td>
<td>1.74</td>
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<td>0.95</td>
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<td>[PS-TAC][TFSI]</td>
<td>--</td>
<td>--</td>
<td>0.75</td>
<td>1.65</td>
<td>0.47</td>
<td>1.28</td>
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<td>[PS-TAC][Cl]</td>
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<td>4.52</td>
<td>0.70</td>
<td>2.03</td>
<td>0.49</td>
<td>0.92</td>
</tr>
</tbody>
</table>
IV. Materials

*TAC mono-IL synthesis*

TAC monomers with chloride counter ion were synthesized according to a previously published procedure.¹

*TAC poly-IL synthesis*

All cyclopropenium containing polymers were synthesized from the same neutral parent polymer to keep effects of molecular weigh and dispersity constant, according to a previously reported procedure.² The degree of polymerization was calculated to be 137 units based on GPC calibrated with polystyrene standards and a dispersity of 1.29. The molecular weigh of [PS-TAC][Cl] is 60 kDa. Molecular weights of polymers with different anions are noted below.

*Anion metathesis*

Chloride mono- and poly-ILs underwent ion exchange to achieve the corresponding [TFSI] and [CPDE].

[TAC][TFSI] was prepared by dissolving (293 mg, 0.697 mmol, 1 eq) in 15 mL of methanol. Bis(trifluoromethane)sulfonimide lithium salt (2.23 g, 8.36 mmol, 11 eq) was dissolved in 15 mL of methanol and added to the [TAC][Cl]/ methanol solution and was allowed to stir for 24 hours. The solution was dried under reduced pressure, redissolved in 100 mL of DCM and washed with DI water (3 x 100mL) in a separatory funnel. The DCM layer was then dried with magnesium sulfate and solvent was removed via rotary evaporation to yield a pale yellow solid (290 mg, 63% yield). 1H NMR (400 MHz, CDCl3) δ 7.45 (m, 2H, ArH), 7.21 (m, 2H, ArH), 6.72 (dd, 1H, H2C=CHAr), 5.77 (dd, 1H, H2C=CHAr), 5.29 (dd, 1H H2C=CHAr), 4.66 (s, 2H, ArCH2N), 3.87 (hept, 4H, C3NCH(Me)2), 3.13 (s, 3H, NCH3), 1.35(d, 24H, NCH(CH3)2). Spectrum shown in Figure S3.
[TAC][CPDE] was prepared by dissolving [TAC][Cl] (307 mg, 0.731 mmol, 1 eq) in 10 mL of acetone. Pentakis(methoxycarbonyl)cyclopentadiene [CPDE] potassium salt (584 mg, 1.46 mmol, 2 eq) was prepared according to a previously published procedure,\(^3\) and was dissolved in 20 mL of acetone, and added to the [TAC][Cl]/acetone mixture. The solution was allowed to stir for 24, over the course of which KCl precipitated from the solution. The solution was filters and dried under reduced pressure. The reaction mixture was redissolved in 100 mL DCM, and washed with DI water (3 x 100 mL), dried over magnesium sulfate, and rotary evaporated. 1H NMR (400 MHz, MeOD) \(\delta\) 7.50 (m, 2H, ArH), 7.27 (m, 2H, ArH), 6.75 (dd, 1H, H2C=CHAr), 5.81 (dd, 1H, H2C=CHAr), 5.27 (dd, 1H H2C=CHAr), 4.69 (s, 2H, ArCH2N), 3.94 (hept, 4H, C3NCH(Me)2), 3.70 (s, 15H, C5CO2CH3), 3.19 (s, 3H, NCH3), 1.36 (d, 24H, NCH(CH3)2). ). Spectrum shown in Figure S4.

[PS-TAC][TFSI] was prepared by dissolving [PS-TAC][Cl] (501 mg, 1.19 mmol repeat unit, 1 eq) in 20 mL of acetone. Bis(trifluoromethane)sulfonimide lithium salt (2.55g, 8.89 mmol, 7.5 eq) was dissolved in 15 mL of acetone and added to the polymer/ acetone solution and allowed to stir for 24 hours. The reaction mixture was concentrated to 15 mL of solvent, and water was added dropwise with vigorous stirring until the polymer precipitated to form a pale beige slurry. The solid precipitate was collected, and this process was completed 3 more times. Finally, the polymer was collected, dried, and precipitated from DCM into ethyl acetate at \(-78\) °C. The precipitate was collected and dried to yield a pale beige solid (580 mg, 74% yield). The degree of polymerization is \(~137\) with a dispersity of 1.29 and a molecular weigh of 91kDa. 1H NMR (400 MHz, CD2Cl2) \(\delta\) 7.20-6.30 (b, 590H, ArH), 4.80-4.35 (b, 274H, ArCH2N), 4.00-3.74 (b, 561H, C3NCH(iPr)2), 3.20-2.83 (s, 416H, OCH3), 1.50-1.00 (b, 3780H, iPrH, ArCHCH2). ). Spectrum shown in Figure S5.
[PS-TAC][CPDE] was prepared by dissolving [PS-TAC][Cl] (436 mg, 1.04 mmol repeat unit, 1 eq) in 20 mL of acetone. Pentakis(methoxycarbonyl)cyclopentadiene [CPDE] potassium salt (1.65g, 4.15 mmol, 4 eq) was dissolved in 20 mL of acetone and added to the polymer/acetone mixture. A small amount of methanol was added to homogenize the mixture, which was then heated to 40 °C to facilitate dissolution. The mixture was stirred for 24 hours at 40 °C, and then allowed to cool to RT. The KCl precipitate was filtered off, and the resulting polymer was dried under reduced pressure, redissolved in methanol, and dialyzed against methanol until pure. A tan solid was recovered (540 mg, 70% yield). As the material was prepared from the same parent polymer, the degree of polymerization is ~137 with a dispersity of 1.29 and a molecular weigh of 101kDa. 1H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.15-6.30 (b, 630H, ArH), 4.65-4.35 (b, 274H, ArCH2N), 3.92-3.72 (b, 570H, C3NCH(iPr)2), 3.65-3.50 (b, 2030H, C5COOMe), 3.10-2.70 (s, 450H, OCH3), 1.50-1.00 (b, 3980H, iPrH, ArCHCH2). Spectrum shown in Figure S6.

V. Methods

**Differential Scanning Calorimetry (DSC)**

Polymeric (poly-IL) and monomeric (mono-IL) ionic liquid samples were dissolved in acetone, filtered through 0.22 µm Teflon filters, cast in Teflon molds, and dried under vacuum at 100°C for 24 h to remove solvent and any absorbed water. The necessary amount of the as-dried material (around 5 mg per sample) was then placed in aluminum hermetic DSC pans and quickly sealed under ambient conditions. DSC measurements were performed on cooling using the TA instruments Q2000 differential scanning calorimeter in temperature modulated mode with a modulation of ±1°C/min at a cooling rate of 5°C/min. The poly-IL samples were equilibrated at 150°C (CPDE and TFSI) or 175°C (Cl) for 10 minutes and cooled to 10°C, while the mono-IL
samples were equilibrated at 100°C (CPDE and TFSI) or 150°C (Cl) for 10 minutes and cooled to -75°C.

Multi-angle X-ray Scattering (MAXS)

Measurements were performed using the multi-angle X-ray scattering (MAXS) diffractometer system at the University of Pennsylvania. As-cast, dried poly-IL films were processed into uniformly thick (~100 µm) films by hot-pressing the samples in a Teflon mold at 150°C under 0.5 ton for ~60 s using a Carver press. The as-pressed poly-IL films were taped to aluminum mounts, placed into the X-ray beam line, and measured under vacuum at room temperature (~25°C) in the transmission geometry. Copper Kα X-rays (λ = 1.54 Å) were generated by a Nonius FR591 rotating anode source operated at 40 kV and 85 mA and focused using Osmic Max-Flux optics and pinhole collimation. 2-dimensional scattering patterns were collected with a Bruker Hi-Star multi-wire area detector at a sample to detector distance of 11 cm (corresponding to a wave vector range \( q = 1–16 \text{ nm}^{-1} \)). 2D raw data were accumulated for ~30 minutes per sample, then reduced and azimuthally integrated to yield the final 1D scattering data using the Datasqueeze software package. The scattering data were fit to a superposition of three Lorentzian functions to determine the characteristic peak position and full-width at half-maximum for the three characteristic structural features observed in these cyclopropenium-based poly-ILs, and the results are compiled in Table S1. The corresponding real space correlation distances associated with the peak maxima were calculated per the relation \( d = 2\pi/q \), and the corresponding coherence lengths associated with the peak width were estimated via the Scherrer equation \( \Delta d \approx 2\pi/\Delta q \).

Dielectric Relaxation Spectroscopy (DRS)
DRS was used to characterize the ionic conductivity and timescales of charge transport in the poly-IL and mono-IL samples over a wide range of temperatures from well above to well below the calorimetric glass transition temperatures ($T \approx 270–450$ K). The measurements were performed using a Solartron Modulab XM materials test system in the frequency window $10^{-1}–10^6$ Hz under an applied 0.5 V (tests were performed to ensure the measurements were in the linear response regime). The poly-IL films and mono-IL viscous liquid samples were mounted between parallel plates with upper electrode diameter = 10 mm, separated by 50 µm glass spacers to maintain a constant sample thickness. The sample was measured under vacuum in a Janis VPF-100 cryostat to maintain sample temperature to within ±0.1 K. The samples were first equilibrated at the highest measurement temperature (typically 450 K) for ~12 h, then isothermal frequency sweeps were performed on cooling after equilibrating for 10 min at each measurement temperature. See the Supplementary Information for further discussion of the dielectric relaxation spectroscopy measurements and analysis. For reference, $M^*(f) = 1/\varepsilon^*(f) = i\omega\varepsilon_0/\sigma^*(f)$, where $M^*(f)$ is the complex electric modulus, $\varepsilon^*(f)$ is the complex relative permittivity, $\sigma^*(f)$ is the complex conductivity, and $\varepsilon_0$ is the vacuum permittivity. Figure S1(a) depicts the real part of the conductivity spectra $\sigma'(f)$ of [PS-TAC][CPDE] measured on cooling from 450 K to 335 K (measured spectra for other samples are similar and not shown for brevity). These conductivity spectra exhibit three main features that are generally observed in mono- and poly-ILs. On the low frequency side of the high temperature spectra, electrode polarization is observed as a frequency dependent increase in the conductivity (with increasing frequency). A frequency-independent plateau is observed at intermediate frequencies in all spectra, and this feature corresponds to the DC conductivity in the material. On the high frequency side of the DC plateau, a transition to localized, frequency-dependent
conductivity is observed. Figure S1(b) shows the corresponding data for the imaginary part of the electric modulus $M''(f)$, the peak of which corresponds to the onset frequency of long-ranged ionic diffusion and provides the characteristic timescales of ionic relaxation in these materials. As is seen in Figure S1, large reductions in both the DC conductivity and ion transport relaxation frequencies (longer relaxations times) occur upon decreasing temperature. A BNN plot is also shown in Figure S2.

Quantification of water uptake

Water uptake of the polymer membrane was measured in a humidity-controlled environmental chamber (Espec). A small piece of water-equilibrated membrane was placed in a quartz pan which was hooked on the end of a quartz spring (Deerslayer) in the humidity chamber. The membrane was equilibrated at room temperature at 90% relative humidity for 48 hr. The mass of the hydrated film was obtained by measuring spring length through a port on the wall of the humidity chamber by a cathetometer equipped with an optical zoom telescope located outside the chamber. Care was taken to minimize the time when the port was opened (typically 10 s). The spring was calibrated with standard masses at experimental temperature and relative humidity in the chamber before use (spring constant was about 0.5 mN mm$^{-1}$). Dry mass of humid air-equilibrated membrane was measured following the same procedure as described above. The degree of hydration, $\lambda_w$, defined as the moles of water per mole of cationic groups in the membrane, is calculated using:

$$\lambda_w = \frac{[\text{H}_2\text{O}]}{[\text{TAC}]} = \frac{\text{hydrated film weight} - \text{dry film weight}}{\text{dry film weight}} \times \frac{M_{\text{TAC}}}{M_w} \times \left(\frac{1}{x_{\text{TAC}}} - 1\right) M_S$$

(1)

where the molar mass of water and of the styrene (S) and cyclopropenium (TAC) monomers are $M_w = 18.02$ g mol$^{-1}$, $M_S = 104.15$ g mol$^{-1}$ and $M_{\text{TAC}} = 419$ g mol$^{-1}$.
Small Angle X-ray Scattering (SAXS) (BCPE samples)

1 mm thick polymer samples were prepared by pressing the powder into a teflon washer. Synchrotron small-angle X-ray scattering (SAXS) measurements were performed using the 7.3.3 beamline at the Advanced Light Source (ALS, Lawrence Berkeley National Laboratory). The wavelength $\lambda$ of the incident X-ray beam was 0.124 nm ($\Delta\lambda/\lambda = 10^{-4}$), and a sample-to-detector distance of 4 m. The resulting two-dimensional scattering data were averaged azimuthally to obtain intensity versus magnitude of the scattering wave vector $q$ ($q = 4\pi \sin(\theta/2)/\lambda$, where $\theta$ is the scattering angle). All of the scattering profiles were azimuthally symmetric. The scattering data were corrected for the detector dark current and the scattering from air and Kapton windows. In-plane chloride conductivity of hydrated membranes with dimensions $2 \text{ cm} \times 1 \text{ cm} \times 450 \text{ µm}$ was measured by AC impedance spectroscopy using platinum electrodes in the standard four probe configuration using a BekkTech sample clamp.

Electrochemical Impedance Spectroscopy (BCPE films)

Polymer films of PS-$b$-PS-TACiP(20) were prepared by drop casting a 100 mg mL$^{-1}$ solution of polymer onto a clean Teflon substrate. In-plane chloride conductivity of a hydrated membrane composed of PS-$b$-PS-TACiP(20) (calculated molecular mass = 31KDa, DP = 174) with dimensions $2 \text{ cm} \times 1 \text{ cm} \times 450 \text{ µm}$ was measured by AC impedance spectroscopy using platinum electrodes in the standard four probe configuration using a BekkTech sample clamp. Conductivities were collected under humidified conditions, and temperature and relative humidity were controlled by an environmental chamber (Qualitest). Data were collected using 10mV amplitude over a frequency range of 1 Hz – 10 MHz. Separate experiments were conducted to ensure that the response of the sample was linear in this window. Samples were
annealed at the temperature of interest for 24 to 48 hours until the measured impedance did not change. Conductivity, $\sigma$, is given by equation (2):

$$\sigma = \frac{w}{rS}$$  \hspace{1cm} (2)

where $S$ is the cross-sectional area of sample film, $r$ is the intercept of the Nyquist semi-circle on the real axis (Ω), and $w$ is the distance between the inner platinum electrodes.

**Transmission Electron Microscopy**

Films of PS-$b$-PS-TACiP(20) (calculated molecular mass = 33.4KDa, DP = 200) were prepared by drop casting a 100 mg mL$^{-1}$ solution of polymer onto a clean Teflon substrate. After allowing to dry for 24 hours, the film was sectioned with Leica UltraCut 6 ultramicrotome at –40 °C, nominal thickness 70nm using a Diatome Cryo 35° diamond knife. Sections were placed on 300 mesh copper grids with homemade lacy carbon film on top. The sections were stained with RuO4 vapor for 2 minutes, which preferentially stained the TACiP block. Sections were imaged with FEI Tecnai F20 TEM operated at 200kV. Images were analyzed using ImageJ 1.48v software.
References


3. Bruce, M. I.; Walton, J. K.; Williams, M. L.; Hall, S. R.; Skelton, B. W.; White, A. H., Pentakis(methoxycarbonyl)cyclopentadiene chemistry. Part 1. Preparation and properties of the diene, and of derivatives containing the alkali metals or thallium(I): crystal and molecular structures of H[C_5(CO_2Me)_5], Li[C_5(CO_2Me)_5][H_2O], K[C_5(CO_2Me)_5][MeOH], and Tl[C_5(CO_2Me)_5]. *Journal of the Chemical Society, Dalton Transactions* **1982**, *11*, 2209-2220.
Addendum: Polyelectrolytes based on aromatic anions

Having successfully incorporated the trisaminocyclopropenium (TAC) ion into macromolecular topologies and explored these materials for numerous applications, we were inspired to expand the repertoire of aromatic ion-based polyelectrolytes. We sought to establish a material platform analogous to the cationic TAC-polymers, however this time with an aromatic anion. The cyclopentadienyl (Cp) group is a carbon-centered anion, whose charge is stabilized by aromaticity. Lambert and coworkers recently reported on the use of this moiety as a Brønsted acid catalyst and described synthetic access and chemical modifications to functionalize the ring. The Cp scaffold includes methyl ester substituents, whose electron withdrawing nature further stabilizes the anion and also provide chemical handles to install functionality. In a similar vein to TAC, we were interested to probe whether Cp’s highly delocalized π and σ system endowed the resulting materials with unique properties, particularly for ion conduction in the context of polymer electrolyte membranes for lithium ion batteries. We aimed to explore the nature of electrostatic cohesion between Cp and Li⁺, and if weak Coulombic interactions would potentially endow polymer membranes made using this material with high lithium transport. Furthermore, classical liquid electrolyte systems are flammable and prone to safety issues, which were recently observed for Samsung Note 7 smartphone batteries. Developing a new class of highly tunable and synthetically robust solid polymer electrolytes has the potential to transform the energy storage industry by increasing energy density, stability, and by suppressing lithium dendrite growth.

Monomer synthesis

Before investigating the potential applications of Cp-based polyelectrolytes, we had to develop a viable synthesis of both monomers and polymers. Generally, the neutral
pentacarboxycyclopentadiene quickly undergoes amidation by a primary amine with a primary alpha carbon in toluene at vigorous reflux. We sought to exploit this reactivity to install a polymerizable handle to access macromolecular Cp’s, and the polymerization method of interest will inform selection of the polymerizable handle. For example, installation of a vinyl group (e.g. styrene or acrylate) would render this system suitable for controlled radical polymerization techniques such as RAFT or ATRP. Due to the successful employment of styrene with polyTAC, we initially attempted to add a styrenic amine. However, this route proved problematic because the starting amine was expensive (ca. $125 per gram, Sigma and Fisher) and reaction yields were low (25-50%), especially at a larger scale (i.e. 50% at 200mg scale, 25% at 1 gram scale). Low yielding monomer reactions are particularly problematic for RAFT and ATRP, because these polymerizations work best with neat or highly concentrated monomer solutions. Thus, accumulating enough of a styrenic Cp monomer to perform a controlled radical polymerization at a viable concentration would be difficult.

*Polymerization by ROMP*

![Scheme 1. Synthesis of Cp monomer, polymerization by ROMP, and deprotonation. See Supporting information for details.](image)

We next considered a ring opening metathesis polymerization (ROMP) scheme (Scheme 1). In ROMP, a transition metal complex catalyzes the chain growth of strained cyclic olefins, such as norbornene. ROMP has many advantages for this system. First, the norbornene methylamine starting material is significantly less expensive than styrene analogue. In addition, ROMP polymerizations are typically done at low concentrations (0.05-0.1M), such that even
small quantities of material (i.e. < 100mg) can be polymerized with ease. We found that the polymerization of norbornene functionalized Cp monomers was successful in both the acid and the anionic forms (Figure 1, left and right, respectively), though polymerizations were typically performed with the acid monomer due to its superior solubility in organic solvents. Monitoring reaction progress by TLC confirmed that all the monomer was consumed in less than five minutes at room temperature. Polymers were then purified by precipitation in cold diethyl ether. To obtain the anionic polymer with lithium counter ion, the polymer was deprotonated with TEA and subsequently mixed in a concentrated aqueous solution of lithium bromide. Dialysis against water yielded the pure poly-Cp.

Figure 1. Both the acid and ionic form of Cp monomer undergo ROMP.

Qiang Ma et al. recently demonstrated that polymer membranes incorporating a blend of polyethylene glycol (PEG) and anionic polyelectrolytes with a highly delocalized charge results in high dissociation of Li$^+$ ions and thus high Li$^+$ ion transport. This work supports our hypothesis that the delocalized charge on Cp could enhance lithium transport in membranes, and inspired us to incorporate other types of functionality into polymers, such as PEG. To investigate material properties of a PEG-Cp system, we synthesized an additional norbornene-based monomer with a pendant PEG chain of variable molecular weight. We were then able to easily create a variety of macromolecular architectures with this approach, such as random copolymers and block copolymers. Polymerizing a mixture of monomers in solution easily yielded random copolymers and block copolymers were obtained by serial additions of monomer solutions,
adding the second monomer solution once the first was observed to be completely consumed by TLC.

Figure 2. Structure of a PEG-polyCp copolymer synthesized by ROMP.

Despite the successful synthesis of these polymers, the initial characterization of lithium ion transport proved difficult. While there is literature precedent for charge delocalization corresponding to improved ion transport,\textsuperscript{5} that does not take into account the rigidity of the ion itself. Additionally, the alkenes in the polymer backbone compound the material’s poor mechanical properties. Polymer films were extremely brittle and membranes were difficult to process, which resulted in poor contacts with dielectric spectroscopy equipment. Furthermore, the material appeared to decompose gradually as evidenced by a color change from beige to black, and changes in solubility. This decomposition was notably more severe when there were fewer precipitation steps after polymerization: any remaining ruthenium in the system likely caused side reactions. In addition, this pentacarboxy-Cp group has been observed to undergo slow decarboxylation towards highly colored decomposition products, which may also account for the dark coloring of this material over time. Due to these challenges, these materials weren’t investigated further for application in battery technologies. However, with prompt and careful purification after polymerization, careful storage, and optimization of synthetic protocol, this
system has potential to be employed in numerous materials applications and improve understanding of fundamental polyelectrolyte behavior.
References


Addendum: Polyelectrolytes based on aromatic anions

Supplementary Information

I. General Information: All materials were purchased from Sigma Aldrich and were used without further purification except as noted below. Deuterated solvents used for NMR spectroscopy were purchased from Cambridge Isotope Laboratories, Inc. Eluents for column chromatography were HPLC grade and purchased from Fisher Scientific. Organic solutions were concentrated by use of a Buchi rotary evaporator. All polymerizations were carried out with temperature control via an oil bath under an argon atmosphere in Schlenk flasks.

$^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ (except where noted in Experimental Methods) on a Bruker AMX-300, AMX-400, or AMX-500 spectrometer. Data for $^1$H NMR are reported as follows: chemical shift in reference to residual CHCl$_3$ at 7.26 ppm (δ ppm), multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, m = multiplet), coupling constant (Hz), and integration. Data for $^{13}$C NMR are reported in terms of chemical shift in reference to the CDCl$_3$ solvent signal (77.16 ppm).

Thin layer chromatography (TLC) was performed using Teledyne Silica gel 60 F254 plates and viewed under UV light. Flash column chromatography was performed using Teledyne Ultra Pure Silica Gel (230 – 400 mesh) on a Teledyne Isco Combiflash Rf.
II. Figures

Figure S1. $^1$H NMR spectrum norbornene-Cp monomer in CDCl3.
Figure S2. \(^1\)H NMR spectrum polyCpH in CDCl\(_3\).
Figure S3. $^1$H NMR spectrum polyCpLi$^+$ in MeOD.
Figure S4. $^1$H NMR spectrum polyCp$^+$ in DMSO-d$_6$.

III. Materials

*Synthesis of norbornene-Cp monomers.*

Pentacarboxycyclopentadiene (1.97g, 5.50 mmol, 1.1 eq) was added to a clean and dry 250 mL round bottom flask equipped with a stir bar, and argon was added to keep the powder dry. To the round bottom, 50 mL of dry toluene was added, and this solution was gently warmed and stirred until the Cp was dissolved. The norbornene methyl amine (613.9 mg, 4.98 mmol, 1 eq) was then
added to the reaction mixture, which was placed in a 130 °C oil bath and equipped with a reflux condenser and argon balloon. Upon addition of the amine, the reaction mixture became cloudy and an oil phase separated from the reaction mixture on the bottom of the flask. The reaction is complete when that oil fully goes into solution, around 20-30 minutes. At this point, the flask was removed from the heat bath, allowed to cool, and excess toluene was removed by rotary evaporation. The residual crude material was dissolved in DCM and loaded on a silica cartridge for purification by column chromatography on the ISCO. The solvent mixture started at 98% DCM 2% methanol and was slowly ramped to 95% DCM 5% methanol. Pure product was collected and washed with HCl (3 x 100 mL) to collect the protonated product as a beige sticky solid (1.22g, 2.7 mmol, 54% yield).

Polymerization of norbornene-Cp monomers.

The norbornene-Cp monomer (884 mg, 1.95 mmol, 50 eq) was added to a dry 50 mL round bottom flask equipped with a stir bar and septum. 20 mL of dry DMF was added to the monomer, which was stirred and sparged for 15 minutes with argon. Third generation Grubbs catalyst (28 mg, 0.032 mmol, 1 eq) was added to a dry one-dram vial with a septa-cap, and 3 mL of dry DMF was added, and this solution was sparged for 15 minutes with argon. After sparging was complete, the Grubbs 3/ DMF solution was quickly added to the monomer solution. After 5 minutes, an aliquot of reaction mixture was extracted and diluted with DCM and TLC’d to
monitor progress of monomer consumption (eluent: 90% DCM 10% MeOH). Once TLC revealed that all the monomer had been consumed, a few drops of ethyl vinyl ether (0.1 mL, large excess) dissolved in DMF were added to the polymerization mixture to quench the reaction, and this was allowed to stir for ca. 3 minutes. Once the polymerization was quenched, the reaction mixture was concentrated by rotary evaporation until it precipitated nicely in diethyl ether at -78 °C. Upon precipitation into cold diethyl ether, the mixture was filtered to collect the polymer, which was re-dissolved in DCM and the precipitation was repeated two additional times. To accomplish ion exchange, the polymer was dissolved in methanol and triethylamine (592 mg, 5.9 mmol, 3 eq per monomer) and stirred to deprotonate the acidic monomer (solubility of the polymer in methanol improved upon deprotonation. The polymer / TEA mixture was then diluted with a concentrated solution of aqueous lithium bromide and dialyzed initially against a dilute solution of lithium bromide, followed by DI water to remove excess salt. The polymer was collected from the dialysis bag and dried by rotary evaporation to yield a brown solid (600 mg, 67% recovered yield).

Polymerization of Cp-PEG block copolymers.

The norbornene-Cp monomer (400 mg, 0.88 mmol, 35 eq) was added to a dry 50 mL round bottom flask equipped with a stir bar and septum. 10 mL of dry DMF was added to the monomer,
which was stirred and sparged for 15 minutes with argon. Third generation Grubbs catalyst (18 mg, 0.025 mmol, 1 eq) was added to a dry one-dram vial with a septa-cap, and 2 mL of dry DMF was added, and this solution was sparged for 15 minutes with argon. After sparging was complete, the Grubbs 3/ DMF solution was quickly added to the monomer solution. After 5 minutes, an aliquot of reaction mixture was extracted and diluted with DCM and TLC’d to monitor progress of monomer consumption (eluent: 90% DCM 10% MeOH). Once TLC revealed that all the monomer had been consumed, another degassed solution of the PEG monomer (302 mg, 0.38 mmol, 15 equivalent; synthesis was previously reported$^1$) in 7 mL of DMF was added to the polymerization reaction mixture. This again was monitored by TLC until no monomer remained. Purification and ion exchanged was accomplished according to the same procedure as for the homopolymer. Recovered a beige solid (440 mg, 63% yield).
References