

**Recent Advances in the Design of Ionenenes: Toward Convergence with High-Performance Polymers**

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Ionenenes, condensation polymers wherein the charge (typically cationic) lies directly within the polymer backbone have been known for over 85 years. Historically, ionenes have been synthesized from 3° diamines and  $\alpha,\omega$ -dihaloalkanes, forming chains of ammonium cations tethered by flexible hydrocarbon linkages with “free” halide anions. However, the requisite building blocks of ionenes are by no means limited only to such molecules. In recent years, ionenes with more sophisticated backbone chemistries have been produced, with a trend toward the use of functionalities associated with classical “high-performance” condensation polymers such as polyimides and polyarylamides. The expansion of ionenes is also catalyzed by the rapid growth of research in imidazolium-based ionic liquids (ILs), wherein the combination of ionenes with ILs can yield unexpected behaviors. Furthermore, when considering the largely unexplored experimental space in anionic ionenes, the opportunities for new materials are virtually endless. This review primarily focuses on developments in ionenes published in the scientific literature since 2010, but also includes some older examples that may not have received sufficient attention at the time of their original publication yet can provide some key lessons for the future of ionene design.

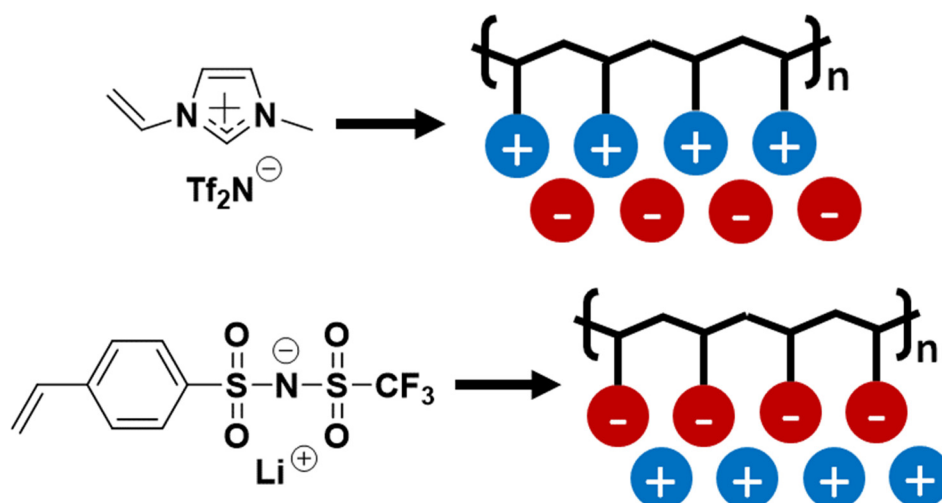
## 1. Comparison of Polyelectrolytes and Ionenes

Research interest in charged polymers that are based upon, derived from and/or able to strongly interact with ionic liquids (ILs) has significantly accelerated in recent years.<sup>[1-3]</sup> The majority of these charged polymers take the form of **polyelectrolytes**, wherein the cation and/or anion is pendant from the polymer backbone. IL-derived **polyelectrolytes**, commonly referred to as “poly(ILs)”, are typically formed via free-radical (i.e., chain-addition) polymerization of an IL monomer(s) where a cation or anion is functionalized with styrene, acrylate or vinyl groups. Zwitterionic (betaine) monomers formed from 1-vinylimidazole and 1,3-propanesultone (or similar compounds) are also known.<sup>[4-7]</sup> Reviews by Mecerreyes,<sup>[2, 3]</sup> Long<sup>[8, 9]</sup> Shaplov,<sup>[10]</sup> Firestone<sup>[11]</sup> and Qian<sup>[12]</sup> provide excellent and detailed discussions focused on the development and applications of poly(IL) materials.

In the context of conventional polymers, the earliest studied uses of ILs were as plasticizers<sup>[13, 14]</sup> and as solvents for polymers and polymerization reactions, whether free-radical or condensation processes.<sup>[15-20]</sup> Work by Ohno’s group in the area of ion-conducting materials illustrated the various ways in which ILs themselves could be directly polymerized, forming poly(ILs).<sup>[21-24]</sup> This concept was subsequently applied to the design of gas separation membranes and sorbents based on poly(ILs),<sup>[25-31]</sup> including a number of reports by Bara and co-workers in this area.<sup>[32-40]</sup> Lodge identified the significant role that ILs could play in the design of polymers with controlled structures.<sup>[1]</sup> Furthermore, poly(ILs) are also able to incorporate and hold “free” ILs into their structures due to non-covalent, Coulombic interactions,<sup>[1]</sup> which can result in enhanced transport properties<sup>[33, 35, 36, 41]</sup> and self-assembly/nanostructuring.<sup>[1, 42-44]</sup>

**Figure 1** provides examples of poly(ILs) produced from cationic vinylimidazolium and anionic styrenic sulfonimide monomers. Unlike conventional **polyelectrolytes** such as alkali

metal salts of poly(acrylic acid) (PAA) and poly(styrene) sulfonic acid (PSSA) which bear a negative charges attached to the backbone, cationic poly(ILs) are far more commonly reported in the literature than anionic poly(ILs), likely due to the relative ease with which cationic monomers can be synthesized (and the relative difficulty of synthesizing anionic monomers).

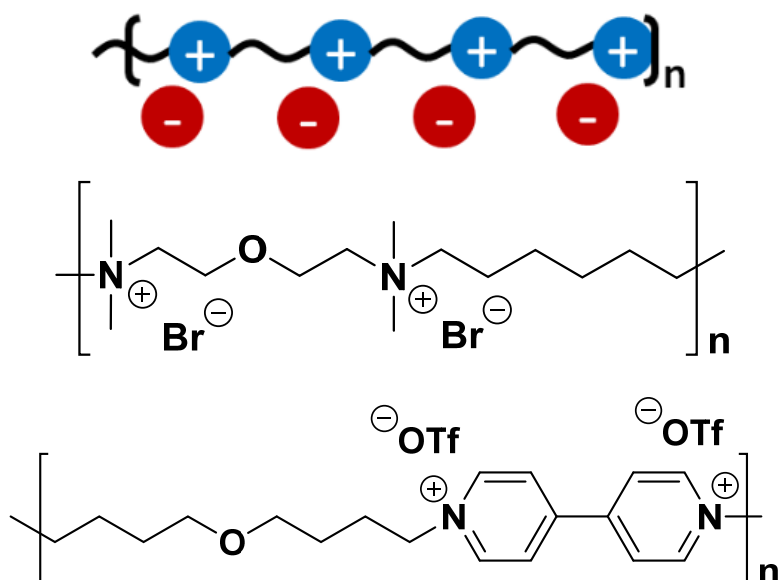


**Figure 1:** Examples of IL monomers and representations of typical cationic imidazolium poly(IL) structure with free bistriflimide ( $\text{Tf}_2\text{N}^-$ ) anions (top) and sulfonimide anionic poly(IL) with “free”  $\text{Li}^+$  cations (bottom).

Ionenes\* are an analogous, yet far less common, class of ionic polymers wherein the charged moiety (typically cation) resides directly within the polymer backbone rather than as pendants.<sup>[45-47]</sup> In the literature, ionenes are also sometimes referred to in a seemingly redundant manner as “polyionenes” or less elegantly as “main-chain polycations”. As evidenced by a search of the patent literature, ionenes are used several commercial applications including cosmetics, oil drilling and printing. Applications of ionenes in the scientific literature corresponding to specific structural motifs will be discussed throughout this review.

To our knowledge, the only dedicated review of ionenes was published by Williams and Long in 2009.<sup>[45]</sup> A discussion of ionenes was also featured in a broader review of polymers containing quaternary ( $4^\circ$ ) nitrogen atoms by Laschewsky and co-workers in 2010.<sup>[48]</sup> At that

time, nearly all reported ionenes were based on ammonium or *N*-heterocyclic cations tethered by alkyl, xylyl or ether linkages. The associated anions can either be halide (i.e., Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) or molecular species such as Tf<sub>2</sub>N<sup>-</sup>, triflate (OTf<sup>-</sup>), hexafluorophosphate (PF<sub>6</sub><sup>-</sup>), tetrafluoroborate (BF<sub>4</sub><sup>-</sup>) and numerous others. **Figure 2** provides a general representation of cationic ionenes and two specific structures.



**Figure 2:** Representation of cationic ionene archetype (top) with ammonium- and pyridinium-based examples (middle and bottom). Top image reprinted with permission<sup>[49]</sup> from Industrial & Engineering Chemistry Research, 56, Mittenthal, M. S.; Flowers, B. S.; Bara, J. E.; Whitley, J. W.; Spear, S. K.; Roveda, J. D.; Wallace, D. A.; Shannon, M. S.; Holler, R.; Martens, R.; Daly, D. T. Ionic Polyimides: Hybrid Polymer Architectures and Composites with Ionic Liquids for Advanced Gas Separation Membranes, 5055-5069. Copyright 2017 American Chemical Society.

[\*Interestingly, a common name for 1,2,3,4-tetrahydro-1,1,6-trimethylnaphthalene (CAS: 475-03-6) is ‘ionene’ (or ‘ $\alpha$ -ionene’), which is derived from the dehydration of  $\alpha$ -ionone (CAS: 127-41-3),<sup>[50, 51]</sup> a naturally occurring aroma compound which itself is a degradation product of carotenoids.]

Cationic ionenes are typically synthesized via the Menshutkin reaction where “A-A + B-B” condensation polymerizations occur between 3° diamines and dihalides (or other electrophiles with similar reactivity),<sup>[52, 53]</sup> resulting in covalently-tethered chains of cations.<sup>[45, 54, 55]</sup> Pyridine,<sup>[56]</sup> phosphine,<sup>[57]</sup> imidazole<sup>[8, 9, 45, 58-62]</sup> and triazole<sup>[63, 64]</sup> compounds have also been used in place of diamines to respectively form pyridinium, phosphonium, imidazolium and triazolium ionenes.

Long points out that ammonium-based ionenes are subject to several degradation mechanisms, such as Hofmann eliminations, at 200°C via anion attack on the ammonium cation, resulting in the elimination of small molecules and truncated polymer MW.<sup>[45]</sup> Imidazolium- and phosphonium-based ionenes have been identified as likely to exhibit much better thermal stability.<sup>[45]</sup> Segalman’s group has directly compared poly(IL) and ionene architectures in terms of their ion conductivity and nanostructure, noting that the ionene configuration enhances ion mobility and was much more ordered.<sup>[62]</sup>

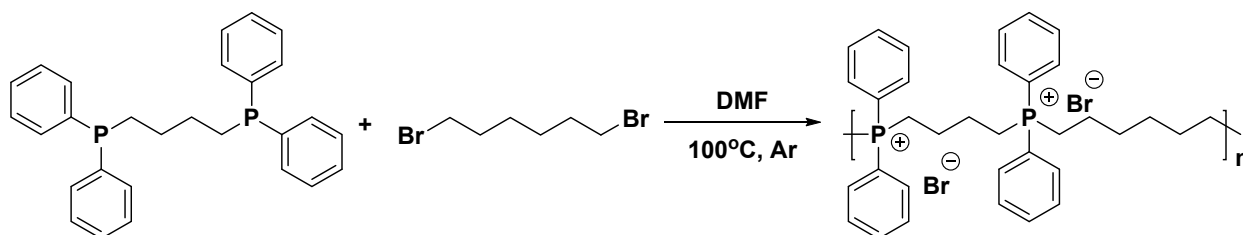
It is easy to recognize that there are a number of shared commonalities between ILs, polyelectrolytes/poly(ILs), and ionenes. However, in most cases, describing ionenes in terms such as “polymeric ILs”, “poly(ILs)” or similar terms is incorrect and potentially misleading. We are concerned with by our observation of a trend in the scientific literature toward classifying any and all charged organic species (especially those based on imidazolium cations) as ‘ILs’ without much thought as to whether such a label is accurate or appropriate. Perhaps this is due the attention that ILs have received in recent years, although ammonium, pyridinium and imidazolium salts were well-known long before the modern concept of an ‘IL’. With limited exceptions, ionenes are the polycondensation product of two neutral monomers and there is no discrete IL present or formed at any point during the synthesis.

Several notable advancements in ionene design has focused on using highly substituted benzimidazolium cations,<sup>[65]</sup> localizing the ammonium cation within sterically-protected spiro groups,<sup>[66]</sup> and using diphosphine monomers rather than diamines. Furthermore, the linking groups between cations are becoming more sophisticated with ionenes. Historically, most ionenes resembled polyethylene (PE) or polyethylene glycol (PEG), but in recent years there is more interest in the inclusion of functional groups associated classical condensation polymers such as polyesters, polyamides and polyimides. Additionally, a few examples of anionic ionenes have also been recently reported, although the first concept of an anionic ionene was nearly 45 years ago. This review will summarize progress in ionene design since 2009-2010, **with an emphasis on application-driven design**, and discuss future opportunities in the field.

## 2. Phosphonium Ionenes

Long's group has reported on phosphonium ionenes which were synthesized with the goal of improved known issues of ammonium ionenes associated with thermal and chemical stability.<sup>[57]</sup> **Scheme 1** illustrates one example phosphonium ionene formed from 1,4-bis(diphenylphosphino)butane and 1,6-dibromohexane, denoted as *4P,6* in the original manuscript.

**Scheme 1:** Phosphonium ionene synthesized by Hemp.<sup>[57]</sup>



The authors synthesized nine ionenes using combinations of four bis(diphenyl)alkylphosphine monomers (2, 4, 6 and 12 carbon linkers) with  $\alpha,\omega$ -dibromoalkanes

of the same length. The *2P,2* ionene was reported to only form cyclic structures. All other combinations produced linear polymers, but several of these (*4P,4*, *4P,6*, and *6P,4*) also produced cyclic structures. Number average molecular weights ( $M_N$ ) for the linear ionenes measured using size exclusion chromatography with multiple angle laser light scattering (SEC MALLS) were typically in the range of 15 – 18 kDa, although values as high as 23.6 kDa (*4P,12*) and as low as 10.7 kDa (*2P,12*) were observed.

Furthermore, the thermal stability of phosphonium ionenes (as measured using TGA) was markedly improved for the *6P,12* ionene (degradation onset  $\sim 300$  °C) compared to an analogous “*6N,12*” ammonium ionene (onset  $\sim 225$  °C).

These phosphonium ionenes were reported to have better alkaline stability compared to corresponding ammonium-based ionenes, with only a small decrease in  $M_N$  observed for the *4P,4* ionene after 24 h exposure to a methanolic 2 M NaOH solution for 24 h at 23°C. The authors also successfully used the phosphonium ionenes for DNA binding which demonstrated their potential for nucleic acid delivery.

Long’s group also published a follow-up paper exploring the effect of different anions on the properties of the *4P,12* ionene, where  $\text{Br}^-$  was exchanged with tetrafluoroborate ( $\text{BF}_4^-$ ), triflate (OTf) or  $\text{Tf}_2\text{N}^-$ .<sup>[67]</sup> Abdulahad, et al. reported that the thermal stability of the *4P,12* ionene was improved to  $\sim 450$  °C when these anions were present instead of  $\text{Br}^-$ . The ion conductivity of the *4P,12* ionene increased in the order  $\text{Br}^- < \text{BF}_4^- < \text{OTf}^- < \text{Tf}_2\text{N}^-$ .

However, these two manuscript appear to be the only examples of phosphonium ionenes in the literature. Of course, the inherent challenge with phosphonium ionene synthesis is the sensitivity of the bis(phosphine) monomers to air and water, which is likely even more of a concern with species such as 1,2-bis(dimethylphosphino)hexane and similar alkyl-bridged

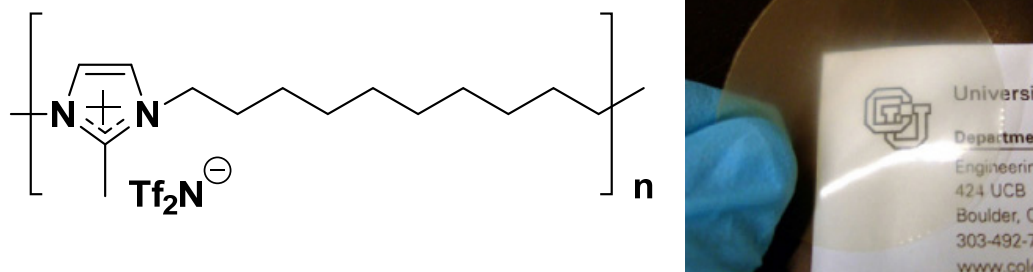
monomers which would yield phosphonium ionenes which were exact analogues to the simplest of ammonium-based ionenes. In this respect, there appears to have been no further progress reported in the literature with respect to linear phosphonium ionenes since the works of Hemp<sup>[57]</sup> and Abdulahad.<sup>[67]</sup> Very recently, Yang and Smith have incorporated tetrarylphosphonium linkages in high surface area networks which show high thermal and alkaline (OH<sup>-</sup>) stability.<sup>[68]</sup>

### 3. Imidazolium Ionenenes

Imidazolium ionenes offer a much more tailorable platform than many other viable ionene linkages due to the many types of imidazole starting materials that are commercially available and bis(imidazole) compounds that can be readily synthesized.<sup>[58, 69, 70]</sup> Imidazoles are also typically more convenient to work and more synthetically versatile than amines, pyridines and especially phosphines.<sup>[71]</sup> Furthermore, in addition to the Menshutkin reaction, modified Debus-Radziszewski reactions can also be employed to form imidazolium-based ionenes.<sup>[72, 73]</sup> Yet, despite these promising characteristics, there has been scant fundamental or applied studies with even simple imidazolium ionenes and what knowledge does exist is relatively disparate compared to ammonium ionenes.

**Figure 3** shows the repeat unit of an imidazolium-based ionene synthesized by Carlisle, et al. from 1,10-dibromodecane and 1,1'-(1,10-decanediyl)bis(imidazole) followed by anion metathesis with LiTf<sub>2</sub>N.<sup>[58]</sup> Figure 3 also shows a picture of a 47 mm diameter, ~120 μm thick film of this material formed via melt-pressing at 75°C.<sup>[58]</sup> A *n*-decyl (i.e., -(CH<sub>2</sub>)<sub>10</sub>-) spacer was chosen because it resulted in a processable and flexible polymer material when melt-pressed, while polymers with shorter linkers (e.g. *n*-hexyl, *n*-octyl) were not amenable to film formation or were simply too brittle to form films that could be tested as gas separation membranes.<sup>[58]</sup>





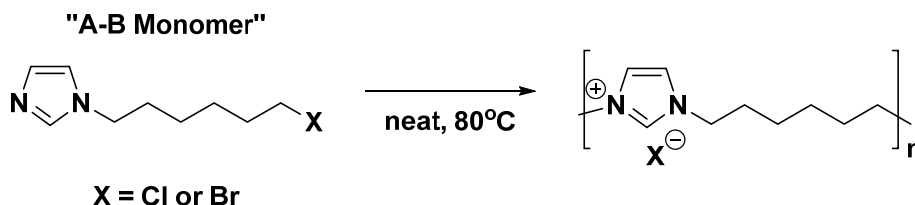
**Figure 3:** Repeat unit of imidazolium-based ionene (left) and picture of melt-pressed film (right). Photograph reprinted<sup>[58]</sup> from Journal of Membrane Science, 359, Carlisle, T. K.; Bara, J. E.; Lafrate, A. L.; Gin, D. L.; Noble, R. D., Main-chain imidazolium polymer membranes for CO<sub>2</sub> separations: An initial study of a new ionic liquid-inspired platform, 37-43, Copyright 2010, with permission from Elsevier.

Carlisle's work also demonstrated that imidazolium ionenes with  $\text{Tf}_2\text{N}^-$  anions were capable of stabilizing a “free” IL, 1-hexyl-3-methylimidazolium bistriflimide ( $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ ), within their structures and that the IL could not be squeezed from the matrix under applied pressure. Previously, this desirable behavior had only been demonstrated for imidazolium-based **polyelectrolytes** and block copolymers.<sup>[1, 36]</sup>

Imidazolium ionenes with short *n*-alkyl spacers (e.g., pentyl, hexyl) and  $\text{I}^-$  anions were studied as polymer electrolytes for dye-sensitized solar cells.<sup>[60]</sup> Similar imidazolium ionenes with *n*-hexyl spacers and  $\text{Br}^-$  anions have been reported to exhibit better antibacterial properties than corresponding imidazolium-based **polyelectrolytes**.<sup>[74]</sup>

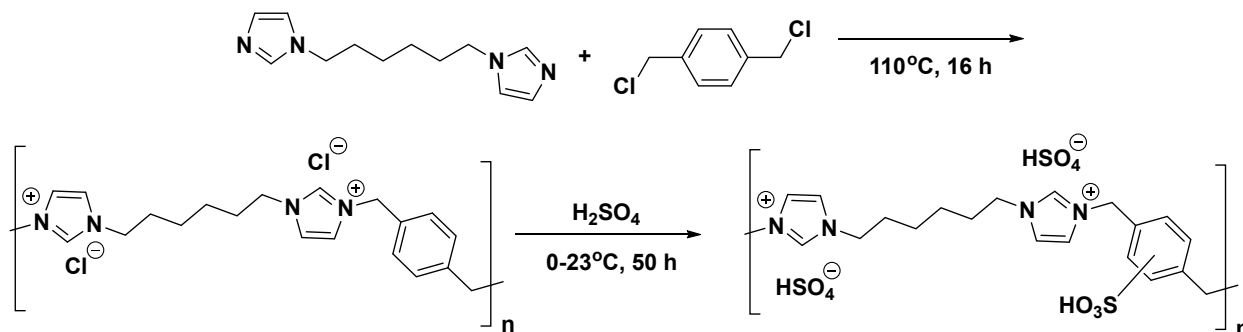
Suckow, et al. explored the synthesis of imidazolium ionenes from “A-B” monomers such as 1-(6-chlorohexyl)imidazole (**Scheme 2**).<sup>[75]</sup>

**Scheme 2:** Polymerization of an imidazole-alkyl halide “A-B” monomer to form an imidazolium ionene.



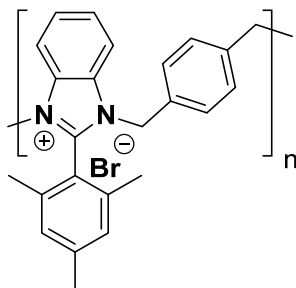
A-B monomers are theoretically “ideal” for condensation polymerization reactions as they are already in precise stoichiometry unlike “A-A + B-B” type condensation reactions, wherein stoichiometry is subject to precise measurements of starting materials by the synthetic chemist. However, A-B monomers have a tendency to polymerize spontaneously unless inhibited in some manner or if the end groups are too reactive. Such challenges were encountered by Suckow who noted that 1-(6-bromohexyl)imidazole was too reactive to store at ambient conditions, while 1-(6-chlorohexyl)imidazole was much slower to react spontaneously and as such the start of polymerization could be controlled. In order to limit the degree of polymerization to about 20 repeat units for characterization purposes, 1-butylimidazole was included as a monofunctional endcap.<sup>[75]</sup>

An “acidic” imidazolium-based ionene was synthesized from 1,1'-(1,6-hexanediyl)bis(imidazole) and *p*-dichloroethylene and subsequent modification through exposure to conc. H<sub>2</sub>SO<sub>4</sub>, sulfonating the benzene ring and replacing the Cl<sup>-</sup> anions with bisulfate (HSO<sub>4</sub><sup>-</sup>) anions (**Scheme 3**).<sup>[76]</sup> The authors reported an M<sub>N</sub> = 16.9 kDa (X<sub>N</sub> ~ 28) for final sulfonated product. The H<sup>+</sup> catalytic activity of this ionene was demonstrated through the condensation of naphthol, benzaldehyde, and either acetamide or urea. The yields of the resulting 1-amido-2-naphthols were superior for the acidic ionene than when conc. H<sub>2</sub>SO<sub>4</sub> was used directly.

**Scheme 3:** Synthesis of “acidic” imidazolium ionene reported by Amarasekara, et al.<sup>[76]</sup>

The concept of imidazolium ionenes can also be extended to benzimidazolium ionenes. However, we are not aware of any reports of benzimidazolium ionenes formed from species such as 1,1'-(1,6-hexanediyl)bisbenzimidazole – the benzimidazole analog to the imidazole compound in Scheme 3. While bisbenzimidazole should certainly be viable for ionene formation, instead it seems that compounds have been of interest to coordination polymers and metal-organic frameworks (MOFs),<sup>[77-79]</sup> as well as for carbene precursors<sup>[80]</sup> and for formation of various macrocycles..<sup>[81, 82]</sup>

One report from Henkensmeier and co-workers (**Figure 4**) synthesized a relatively rigid benzimidazolium ionene from 2-mesitylene-benzimidazole and *p*-dibromoxylene and studied as a potential membranes in a vanadium redox flow battery.<sup>[83]</sup> However, the authors reported generally low values of  $M_N$  (1.0 - 6.8 kDa) corresponding to a maximum  $X_N = 16$ . It was noted that the ionene was too brittle to form membranes on its own, although blends of this benzimidazolium ionene with a polybenzimidazole material did result in stable membranes.



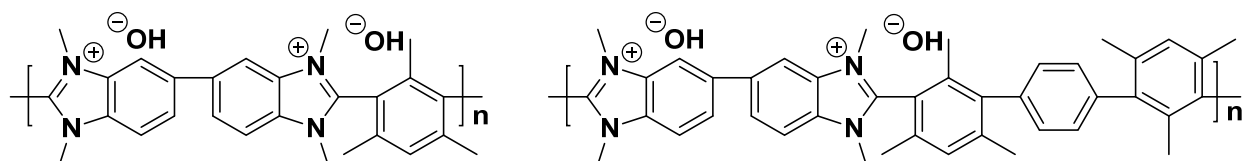
**Figure 4:** Benzimidazolium ionene synthesized by Henkensmeier and co-workers.<sup>[83]</sup>

There have also been recent reports of imidazolium-containing cross-linked networks with ionene character. The groups of Noble and Gin have used ILs with diol and triol pendant groups in combination toluene diisocyanate with to form cross-linked ionene polyurethanes which were used for decontamination of chemically-contaminated surfaces.<sup>[84]</sup> Additionally, these groups also used imidazolium ILs functionalized with epoxides in combination with 2,2',2''-triaminotriethylamine to form epoxy networks which were studied as fixed-site carrier membranes for the facilitated transport of CO<sub>2</sub>.<sup>[85]</sup> Miller and co-workers have demonstrated that cross-linked imidazolium networks with a combination of ionene and **polyelectrolyte** character can be formed from divinyl-functionalized ILs and thiols through thiol-ene chemistry.<sup>[86]</sup> Hypercrosslinked imidazolium ionenes have been synthesized from species such as 1,1',1''-(1,3,5-benzenetriyl)trisimidazole and 2,4,6-tris[4-(bromomethyl)phenyl]-1,3,5-triazine.<sup>[87, 88]</sup>

#### 4. Hydroxide Stable Ionenes

The sensitivity of the ammonium and imidazolium cations to strong base (e.g., 6 M NaOH) precludes the use of many cationic ionenes in alkaline media,<sup>[89]</sup> although ionenes with hydroxide (OH<sup>-</sup>) counterions would be of interest for fuel cells and catalysts. Arges and Zhang have published a recent review fully detailing the progress in anion exchange membranes toward high OH<sup>-</sup> conductivity and alkaline resiliency.<sup>[90]</sup>

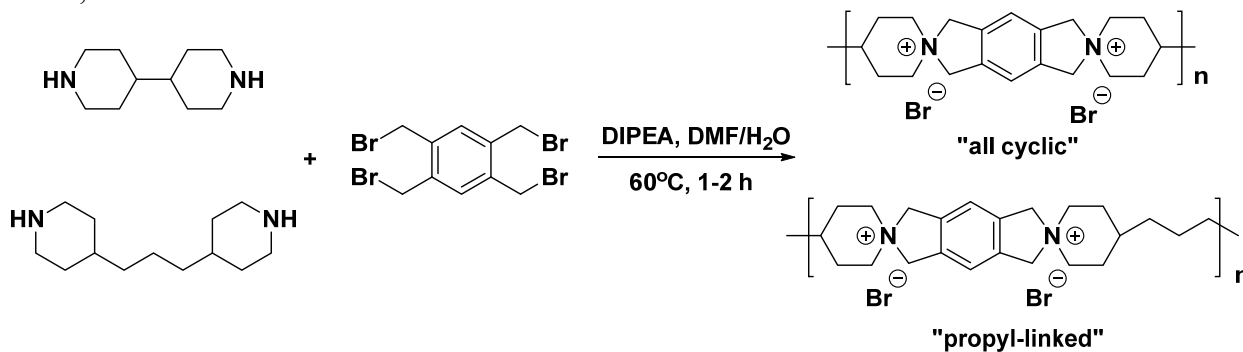
Holdcroft and co-workers have developed highly substituted benzimidazolium ionenes (derived from parent, uncharged polybenzimidazoles). The water solubility of these ionenes was dependent on the repeat unit structure and whether or not the benzimidazole moieties were fully converted to benzimidazolium cations. However, unlike the benzimidazolium ionenes in Figure 4, in which the polymer backbone is connected through the N(1) and N(3) atoms of the imidazolium ring, those synthesized by Holdcroft and co-workers are connected through the C(2) and C(6) atoms of the fused benzimidazolium ring system. Examples of these polymers are shown in **Figure 5**, where the polymer on the left was fully water soluble while the example on the right was insoluble if all N atoms were not fully methylated.



**Figure 5:** OH<sup>-</sup> stable ionenes with polybenzimidazolium backbones synthesized by Thomas<sup>[91]</sup> (left) and Wright<sup>[65]</sup> (right).

4<sup>o</sup> ammonium ionenes can also be made to be much more stable toward OH<sup>-</sup> when starting from 4,4'-bipiperidine derivatives followed by alkylation with tetrabromodurene. The synthesis of these ionenes is depicted in **Scheme 4**.

**Scheme 4:** Synthesis of OH<sup>-</sup> stable ionenes containing *N*-spirocyclic 4<sup>o</sup> ammonium salts by Pham, et al.<sup>[66]</sup>



The all-cyclic and propyl-linked ionenes in Scheme 4 had  $M_N = 67$  kDa and 80 kDa, respectively. The highly sterically hindered *N*-spirocyclic 4° ammonium centers were fully resistant to OH<sup>-</sup> attack up to ~80 °C. However, when these ionenes were held at 120 °C for 336 h (2 wk), degradation was observed with spectroscopic evidence pointing to a ring-opening mechanism in the case of the propyl-linked ionene (which experienced only 10% cation loss) and a combination of ring opening and elimination reactions for the all-cyclic ionene (which experienced about 25% cation loss). The authors hypothesized that the flexible propyl chain facilitates ring strain relaxation which increased the stability of this ionene relative to the all-cyclic analogue.

## 5. Cationic Ionenenes Containing Elements of Classic Condensation Polymers

Regardless of how ionenes have been assembled, nearly all examples featured in Williamson and Long's 2009 review of ammonium-based ionenes relied on the use of hydrocarbon, ether or xylyl spacers. There has been limited work to date in extending the ionene concept to polyarylestere, polyamide, polyarylamide, polyimides, polyamide-imide or other types of (ultra) high-performance (UHP/HP) polymer materials.

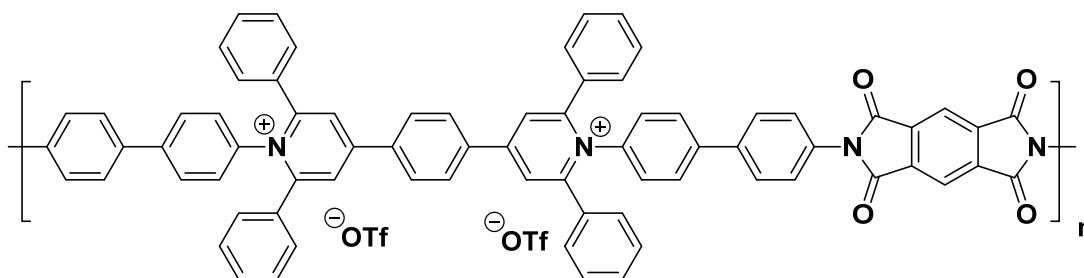
There is potentially great value to be unlocked through the realization of UHP and HP ionenes as they may have unexpected combinations of properties, especially when in the presence of ILs. However, to create such materials, the methodologies by which cationic ionenes are constructed must be reconsidered and new building blocks designed.

### 5.1 Polyimide-Ionenenes

Polyimides are among a small group UHP polymers based on their outstanding chemical, thermal and mechanical properties, placing them atop the “polymer performance pyramid”.<sup>[92]</sup>

Polyimides are conventionally synthesized from an aromatic dianhydride and aromatic diamine in a two-step process. First, a poly(amic acid) is formed via ring opening of anhydride by the amine at low temperature, followed by thermal or chemical imidization (i.e., ring closing). Kapton™ is perhaps the most well-known polyimide and is synthesized from pyromellitic dianhydride (PMDA) and 4,4'-oxydiphenylamine (ODPA). The use of Kapton™ film as thermal and electrical insulation is ubiquitous in electronic devices.

Assuming the use of a conventional dianhydride, then any molecule containing both a 1° amine and 3° amine (or *N*-heterocycle) would be a candidate to form a polyimide-ionene. Yang and co-workers produced several polyimide-ionenes based on pyridinium cations over 20 years ago with a representative structure shown in **Figure 6**.<sup>[93-95]</sup>

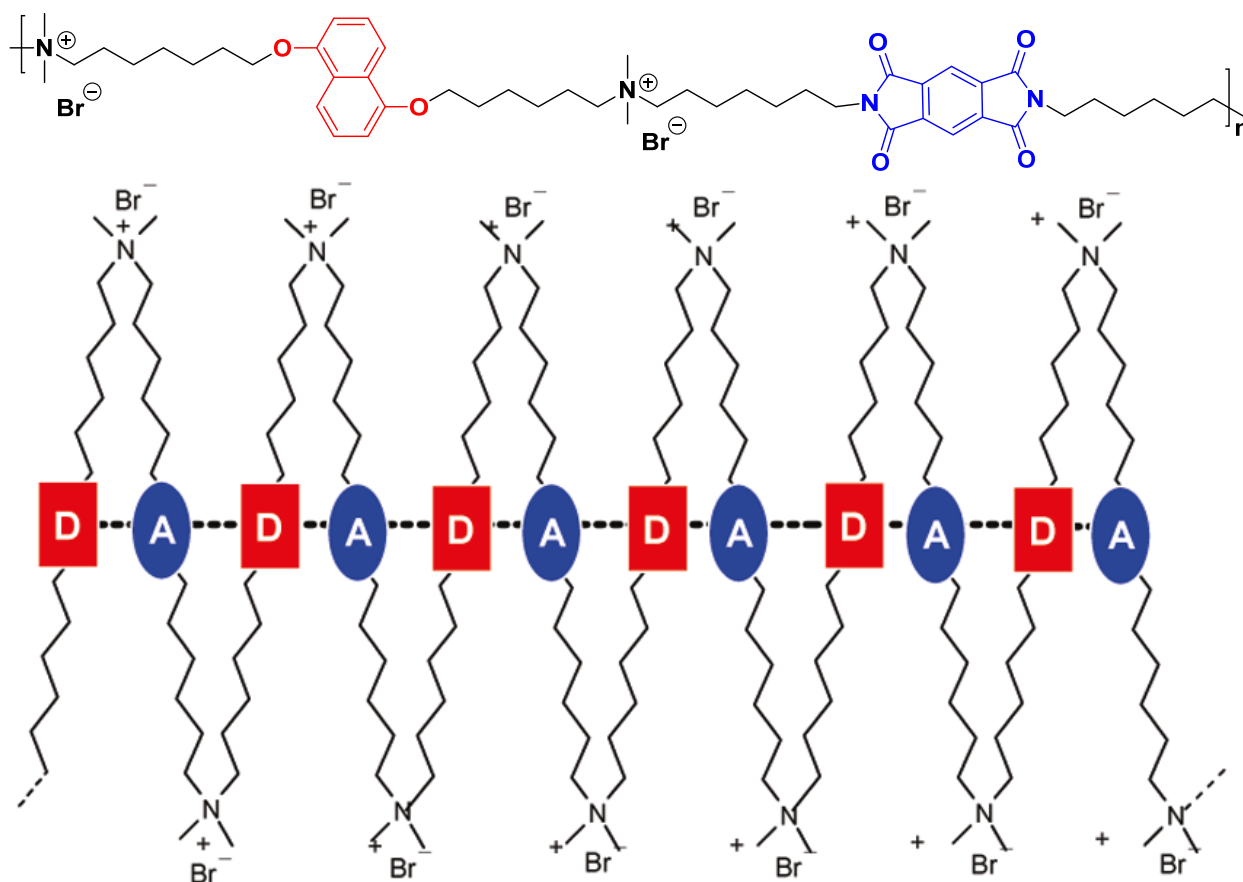


**Figure 6:** One example of a rigid rod polyimide ionene based on bipyridinium cations and PMDA synthesized by Sun, et al.<sup>[93]</sup>

Specifically, the polyimide-ionene in Figure 6 contains a bipyridinium moiety which would be classified as a viologen, meaning that the polymer can undergo reversible color changes through redox reactions.

As ammonium ionenes with long alkyl spaces (> 12 carbons) were shown to adopt folded, “accordion-like” conformations in aqueous solutions,<sup>[96]</sup> De and Ramakrishnan sought to reinforce these folded ionenes by incorporating a diimide component which experienced charge-transfer complexation between two aromatic components which were brought into close

proximity upon folding. Their ammonium polyimide-ionene structure is shown in **Figure 7** (top) with the accordion-like folding reinforced from the interactions between naphthalene (donor, D) and diimide (acceptor, A) segments (**Figure 7**, bottom).<sup>[97]</sup>



**Figure 7:** Ammonium polyimide-ionene synthesized by De and Ramakrishnan (top) and representation of accordion folding (bottom). Reprinted with permission<sup>[97]</sup> from *Macromolecules*, 42, De, S.; Ramakrishnan, S. Charge-Transfer Reinforced Folding of Novel Ionenes, 8599–8603. Copyright 2009 American Chemical Society.

Perylene diimide species have garnered interest as building blocks for polymers due to their intrinsic colors (several are used as commercial dyes and pigments) as well as for their promise in organic electronics<sup>[98]</sup> among other applications. Thus the extension of the perylene moiety to ionenes is a logical progression in that ionic components may impart greater solubility and processability to perylene-containing polymers. Hu, et. al<sup>[99]</sup> and Cole, et. al<sup>[100]</sup> have

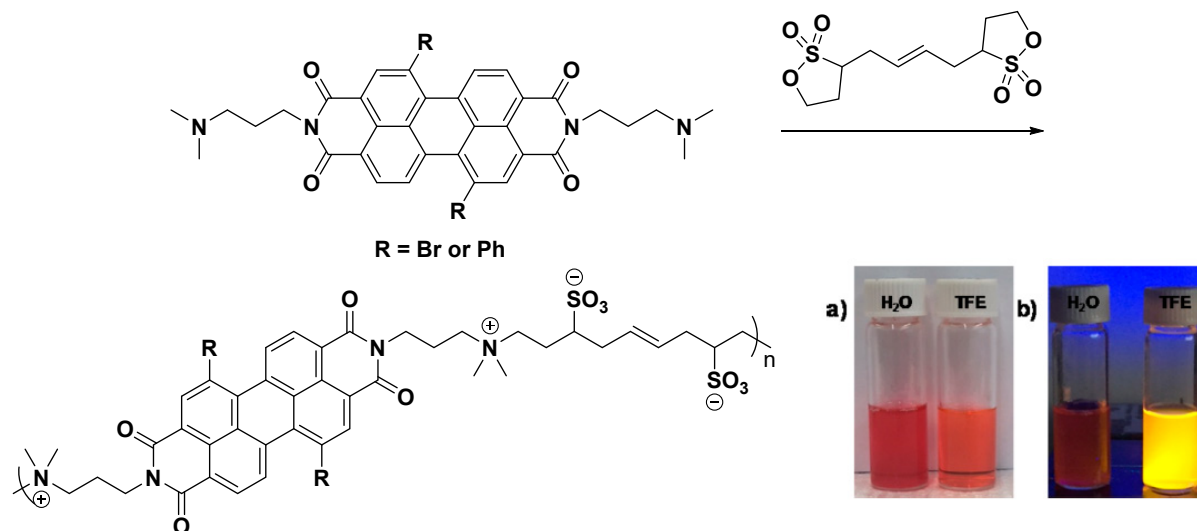


synthesized ionenes from a 3° diamine-terminated derivative of perylene diimide, followed by reaction with an  $\alpha,\omega$ -dibromoalkane.

Cole also demonstrated ionene formation via reaction with a unique disulfone species, resulting in a zwitterionic polyimide-ionene wherein the negatively charged counterions are covalently bound to the backbone as pendant sulfonate ( $\text{RSO}_3^-$ ) groups (**Figure 8**).<sup>[100]</sup>

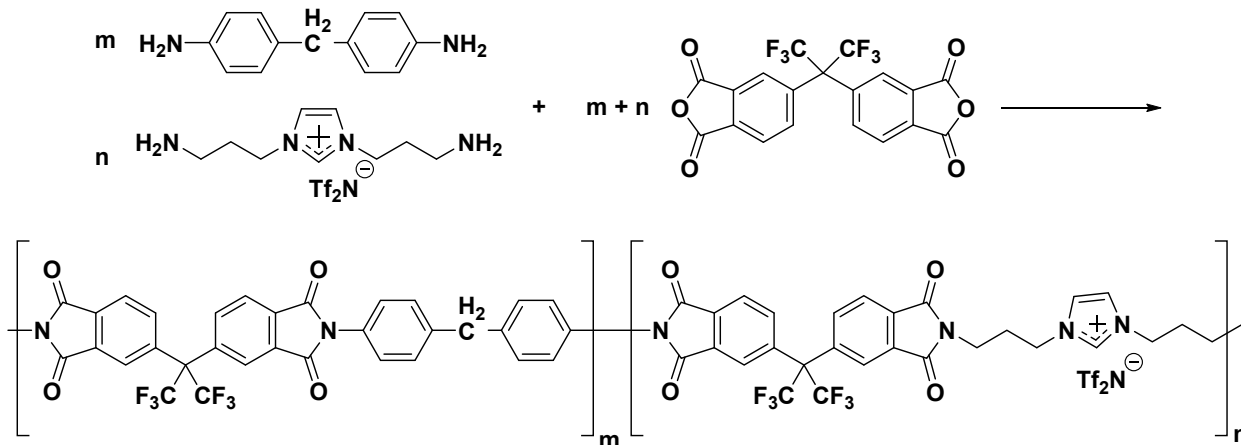
Significantly larger  $M_N$  values (e.g., 18.5 kDa vs. 4.5 kDa) were achieved for the conventional polyimide-ionene (i.e., “free”  $\text{Br}^-$  anions) than for the zwitterionic polyimide-ionene.

Copolymerization with 10 or 50 mol% *N,N,N',N'*-tetramethyl-1,6-hexanediamine (TMHDA) improved  $M_N$  for all examples as it helped the growing polymer remain in solution, although the perylene moiety was still incorporated into the polymer backbone in the expected amount. The solution-based photophysical properties of the conventional and zwitterionic polyimide-ionenes were characterized through UV-vis and photoluminescence spectroscopy, observing that the properties were tunable based on the polymer structure. Figure 8 also contains an inset depicting the ionene-zwitterion in both aqueous and 2,2,2-trifluoroethanol (TFE) solutions under visible and UV light.



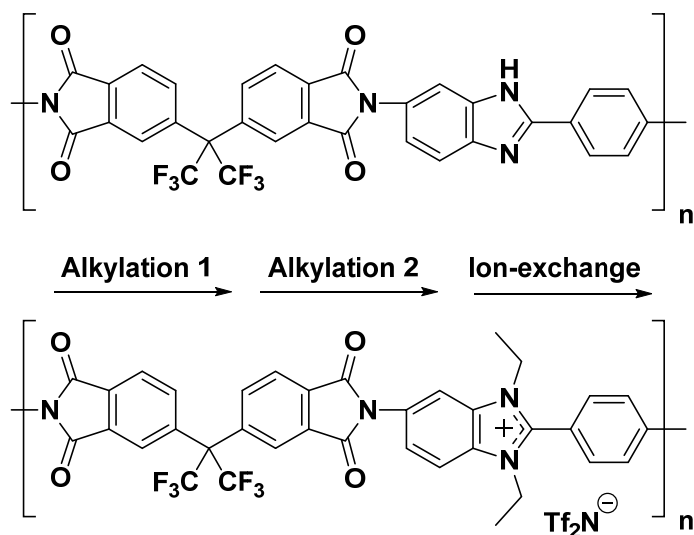
**Figure 8:** Synthesis of perylene-containing ammonium polyimide ionene-zwitterion with pendant sulfonate anions with inset photograph of 0.1 mg/mL of ionenes (R = Br, 50 mol% copolymer with TMHDA) in water and TFE under (a) ambient light and (b) 365 nm UV light. Photographs reprinted with permission<sup>[100]</sup> from *Macromolecules*, 50, Cole, M. D.; Madhu, S.; Bielicki, C.; Emrick, T. Perylene Diimide-Based Ionene and Zwitterionic Polymers: Synthesis and Solution Photophysical Properties, 7535-7542. Copyright 2017 American Chemical Society.

There is currently a small, but growing, research effort in the development of polyimide-ionenes for use as gas separation membranes. Coleman and co-workers have used an imidazolium-based diamine in combination with 4,4'-methylenedianiline (MDA) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6-FDA) to form random and block copolymers that contain imidazolium cations within the polymer backbone (**Scheme 5**).<sup>[101-103]</sup>

**Scheme 5:** Synthesis of random polyimide copolymer with an ionene component.

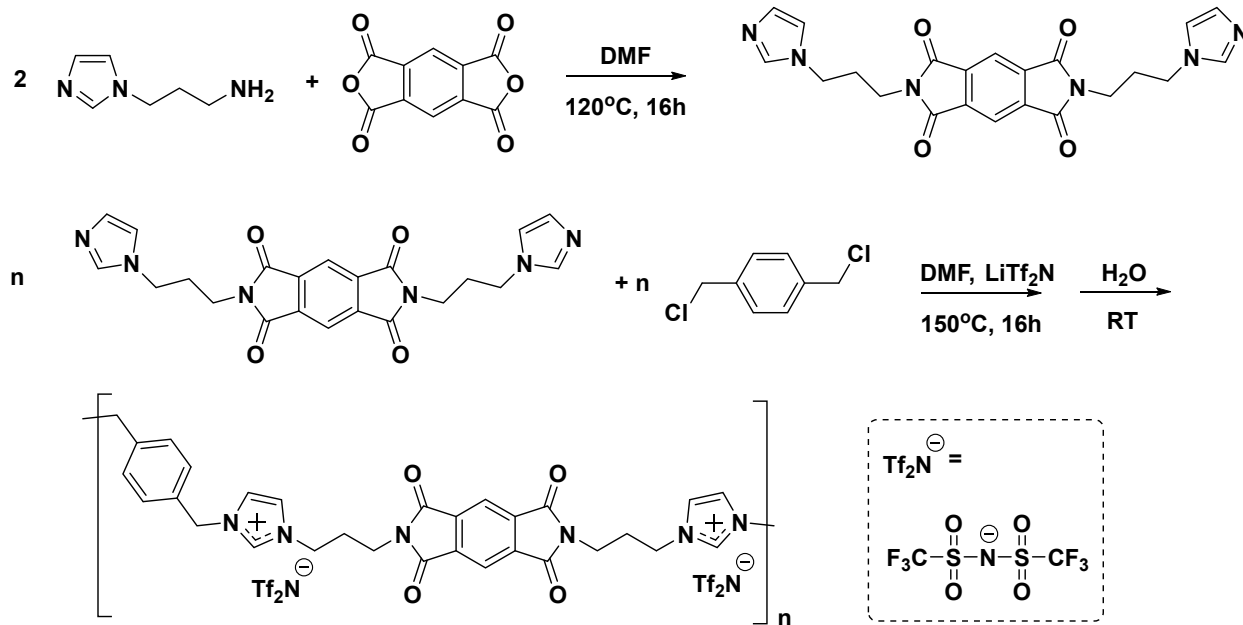
Conventional polyimides built from 6-FDA have shown favorable performances as gas separation membranes due to increased CO<sub>2</sub> permeability associated with increased fractional free volume (FFV) which is created from the bulky, bent nature of the 6-FDA linkage which prevents interchain associations.<sup>[104, 105]</sup> Coleman and co-workers did not have particularly good success with forming high MW ionic polyimides using just the imidazolium-based diamine and 6-FDA. This is likely due to the fact that imidazolium-based amine compounds are relatively difficult to synthesize/purify<sup>[106]</sup> and may have a tendency to degrade prior to the polymerization via intra- and intermolecular reactions such as a Stevens Rearrangement.<sup>[107]</sup> Here, the Menshutkin Reaction does not factor into the polymerization reaction, but is used to form the IL diamine monomer.

Shaplov and co-workers<sup>[108]</sup> formed a polyimide-ionene through post-polymerization modification of conventional (i.e., non-ionic) 6-FDA/benzimidazole polyimide. Although the Menshutkin Reaction still factors into the synthesis of this polyimide-ionene, it was not used as the polymerization reaction. Instead, this ionene is formed through two alkylations of the benzimidazole ring followed by ion-exchange, converting the conventional polyimide to a polyimide-ionene (**Scheme 6**).

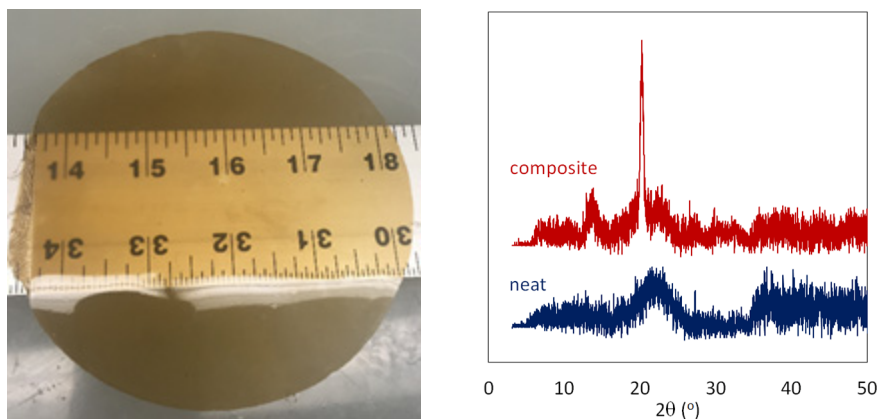
**Scheme 6** Synthesis of a polyimide-ionene from a conventional polyimide-benzimidazole.

The polyimide-ionene in Scheme 6 had  $M_N = 97$  kDa and through solvent casting techniques, was able to form mechanically robust films which were suitable for membrane permeability testing. Furthermore, the authors demonstrated that this polyimide-ionene was able to “hold” one equivalent of an IL, 1-ethyl-3-methylimidazolium bistriflimide ( $[\text{C}_2\text{mim}][\text{Tf}_2\text{N}]$ ) per polymer repeat unit within the polymer matrix. The polyimide-ionene + IL experienced improved  $\text{CO}_2$  flux and selectivity.

Our group has also recently reported on the synthesis of a polyimide-ionene built around a bis(imidazole) diimide monomer synthesized from 1-(3-aminopropyl)imidazole (API) and PMDA, both of which are commercially available in large quantities. This monomer was then reacted with a stoichiometric equivalent of *p*-dichloroxylylene in the presence of  $\text{LiTf}_2\text{N}$  and thoroughly washed with water to remove the  $\text{LiCl}$  by-product. The overall synthesis is detailed in **Scheme 7**.<sup>[49]</sup>

**Scheme 7:** Synthesis of polyimide-ionene via Menshutkin reaction as described in Mittenthal, et al.<sup>[49]</sup>

Although this polyimide-ionene largely precipitated from DMF solution during the course of the reaction,  $M_N = 50$  KDa ( $X_N = 50$ ) was achieved as confirmed by both  $^1\text{H}$  NMR endgroup analysis and MALDI-TOF MS. This polyimide-ionene exhibited excellent film formation through melt-pressing at  $220^\circ\text{C}$  and 1600 psi between two sheets of Kapton®. Films of  $\sim 12$  cm diameter and  $90\ \mu\text{m}$  thickness were formed in this manner (**Figure 9**, left). Upon soaking these films in an IL, 1-butyl-3-methylimidazolium bistriflimide ( $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ ), this polyimide-ionene also absorbed one equivalent of  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  within its structure at equilibrium. Furthermore, analysis of the x-ray diffractometry (XRD) profiles of the neat polyimide-ionene and polyimide-ionene + IL (**Figure 9**, right) revealed that the presence of IL had clearly resulted in a more ordered material, which also exhibited greatly improved  $\text{CO}_2$  permeability. A number of additional ionene-polyimide materials have been synthesized by our group and are currently under investigation for their performances as gas separation membranes.



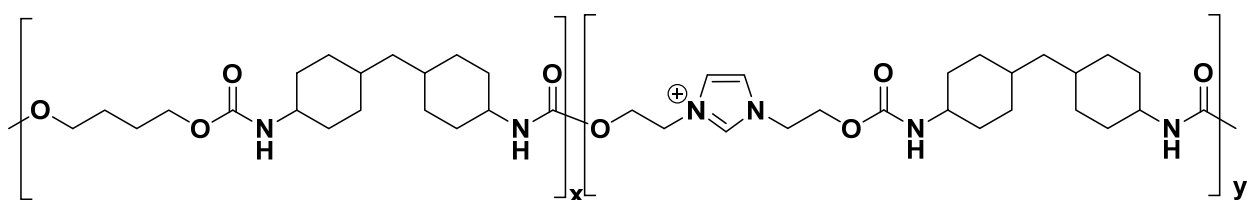
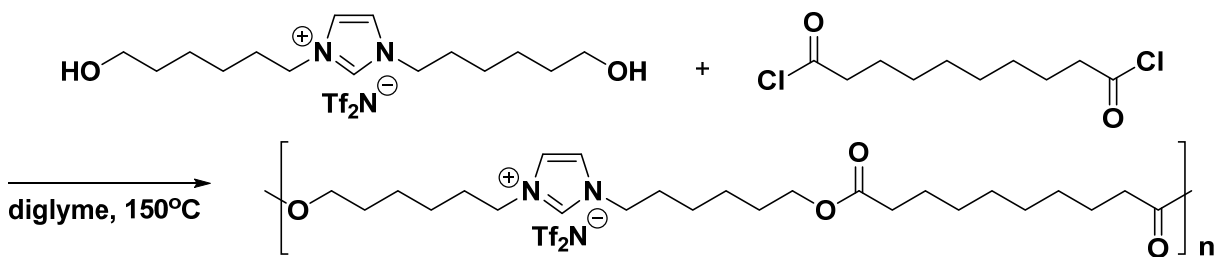
**Figure 9:** Polyimide-ionene film (left) and XRD profiles (right) without (“neat”, lower, blue) and with (“composite”, upper, red)  $[C_4mim][Tf_2N]$  present. Although the XRD profiles are offset, both data sets have been scaled to the same relative intensity. Reprinted with permission<sup>[49]</sup> from Industrial & Engineering Chemistry Research, 56, Mittenthal, M. S.; Flowers, B. S.; Bara, J. E.; Whitley, J. W.; Spear, S. K.; Roveda, J. D.; Wallace, D. A.; Shannon, M. S.; Holler, R.; Martens, R.; Daly, D. T. Ionic Polyimides: Hybrid Polymer Architectures and Composites with Ionic Liquids for Advanced Gas Separation Membranes, 5055-5069. Copyright 2017 American Chemical Society.

## 5.2 Polyester- and Polyurethane-Ionenes

It appears that in most of the examples of polyester- and polyurethane-ionenes that exist in the literature, the Menshutkin Reaction has not been the preferred mechanism for ionene formation. In these materials, one of the monomers is already an IL or the cationic charge is introduced post-polymerization.

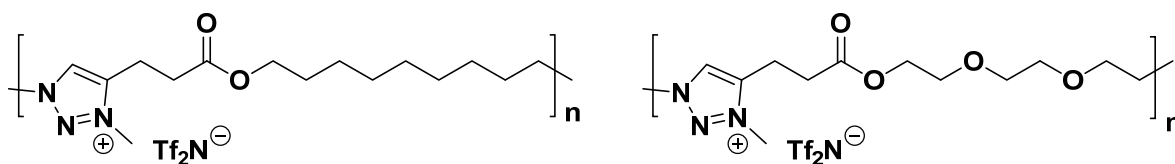
Condensation of an imidazolium-based diol with a di(acid chloride) was successfully applied by Lee, et al. to produce polyester-ionenes (**Scheme 8**),<sup>[109]</sup> and a similar imidazolium-based diol was used by Gao, et al. to form polyurethane copolymers with ionene content (**Figure 10**).<sup>[110]</sup> Choi, et al. synthesized co-polyesters with partial ionene character in a manner similar to that in Scheme 8 from imidazolium-based diols and conventional di(acid chloride), but also included long PEG diols (i.e.,  $HO-(CH_2CH_2O)_n-OH$ ;  $n = 6$  or  $11$ ) as co-monomers.<sup>[111]</sup>

**Scheme 8:** Example of ionic polyester produced from symmetric imidazolium diol and diacid chloride.



**Figure 10:** Example of polyurethane copolymer with ionene component.

Obadia and Drockenmoller utilized “click” chemistry to synthesize triazole-based polymers which were then alkylated and ion-exchanged to form triazolium-based polyester-ionenes.<sup>[63, 64]</sup> In addition to the polyester-ionenes shown in **Figure 11**, a variety of other alkyl- and ether-linked triazolium ionenes were also synthesized.

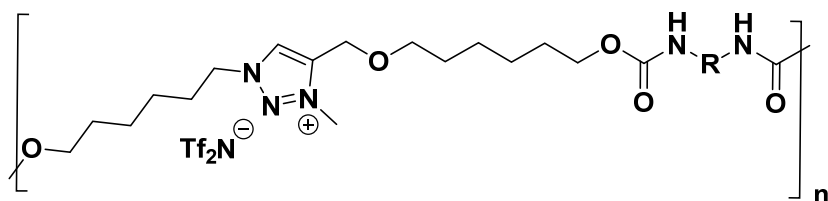


**Figure 11:** Examples of 1,2,3-triazolium polyester-ionenes synthesized by “click” chemistry.

Jourdain, et. al also used “click” chemistry to synthesize 1,2,3-triazolium-based diols which were reacted with conventional alkyl, cycloalkyl and aromatic diisocyanate monomers to form polyurethane-ionenes (**Figure 12**). The resulting materials formed mechanically stable

films and were tested as gas separation membranes in CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> separations.

Puguan, et al. also utilized a similar strategy with “click” chemistry to for triazolium ionenes with PEG backbones that were used within electrochromic devices that could switch from relatively transparent and colorless “bleached” states to translucent blue-colored states within a few seconds.<sup>[112]</sup>

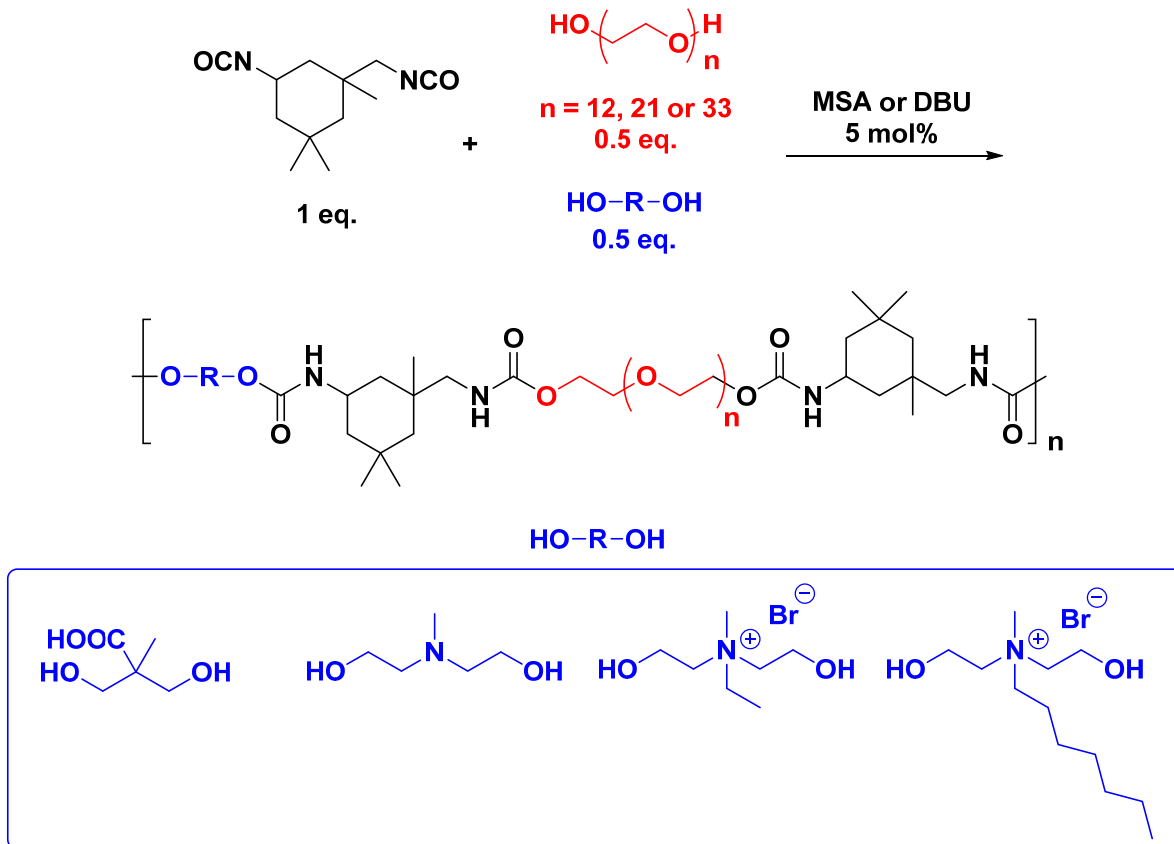


**Figure 12:** 1,2,3-triazolium-based polyurethane-ionenes synthesized from 1,2,3-triazolium diol and conventional diisocyanates.

Ronco, et al. synthesized a series of polyurethane materials, some of which were ionenes, from 1 eq. of isophorone diisocyanate, 0.5 eq. of a PEG diol (i.e., HO-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>-H, n = 12, 21, 33), and 0.5 eq. of a second diol, two of which were 4<sup>o</sup> ammonium salts.<sup>[113]</sup> The synthesis of these polyurethanes and polyurethane-ionenes is depicted in **Scheme 9**.

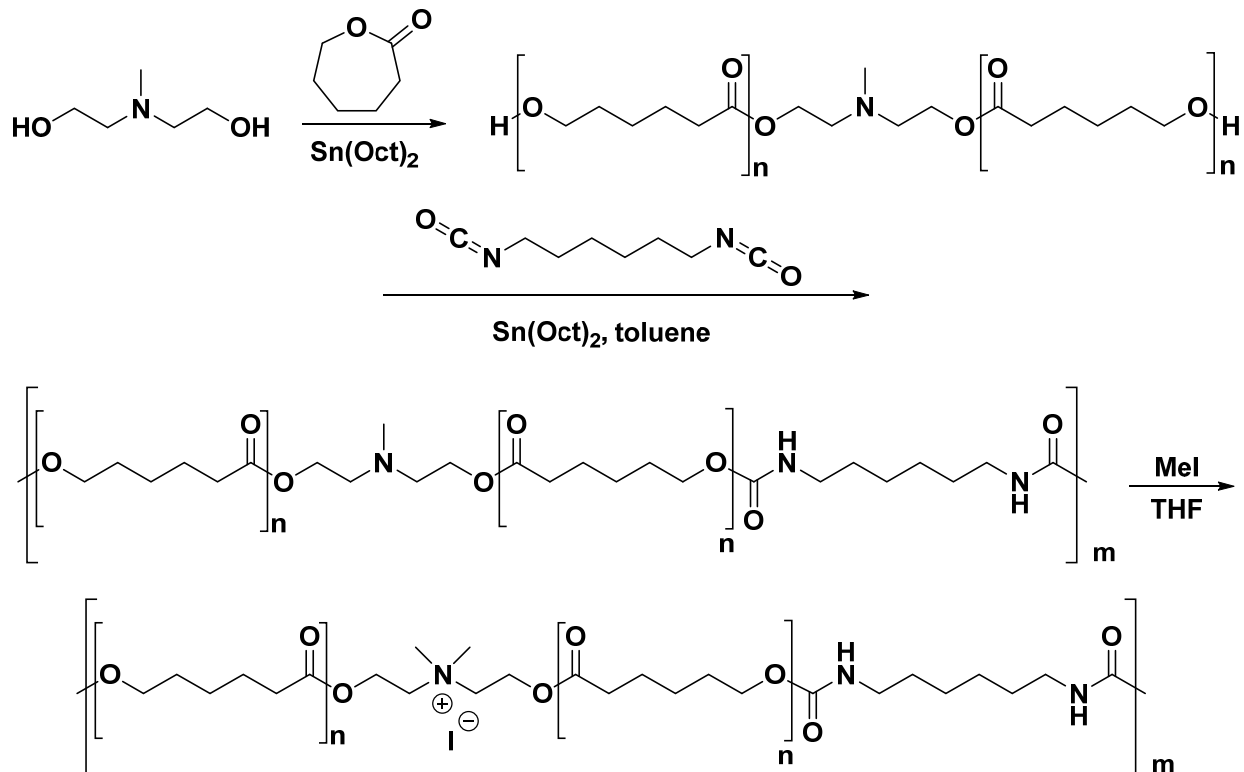


**Scheme 9:** Synthetic scheme for polyurethanes and polyurethane-ionenes used in Ronco, et al.<sup>[113]</sup>



These materials were synthesized for temperature-responsive properties and their biocompatibility. Although a number of variables influenced the properties of these polymers, it was clear that the ionene-polyurethane with the ethyl side chain had the highest cloud point temperature

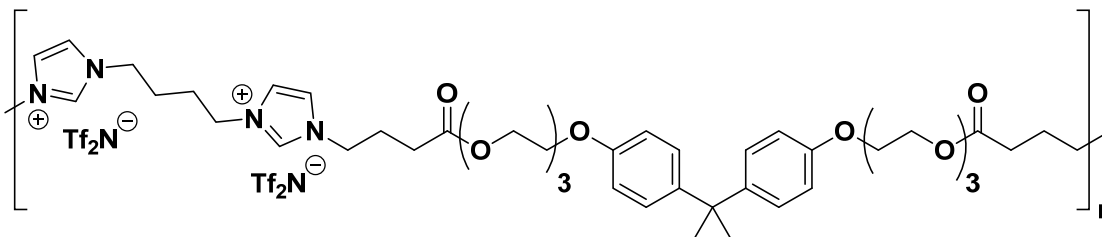
The synthesis of a polyester-urethane-ionene was reported by Nakayama, et al. where alcohol-terminated oligomeric esters derived from  $\epsilon$ -caprolactone and *N*-methyldiethanolamine (MDEA) were reacted with a stoichiometric equivalent of 1,6-diisocyanatohexane.<sup>[114]</sup> The polymer, which contains 3<sup>o</sup> amine sites was subsequently treated with iodomethane to yield 4<sup>o</sup> ammonium groups in the backbone (**Scheme 10**).

**Scheme 10:** Synthesis of polyester-urethane-ionene by Nakayama, et al.<sup>[114]</sup>

Buruiana and Buruiana also demonstrated the formation of a polyurethane-ionene via a multi-step process. First, a 3° diamine monomer was synthesized starting from hydroquinone, diethylamine and formaldehyde. Separately, a large cationic monomer was synthesized containing urethane linkages and 4° ammonium groups terminated with alkyl bromide endgroups. These two monomers were then polymerized via the Menshutkin Reaction.<sup>[115]</sup> The authors demonstrated that the hydroquinone moieties could be oxidized to benzoquinone species in the presence of  $\text{Fe}^{3+}$ .

The Menshutkin Reaction was directly to form a polyester-ionene as shown by Kammakam, et. al. Here, a polyester-ionene was produced from 1,1'-(1,4-butanediyl)bis(imidazole) and a bisphenol A (BPA)-derived diester dibromide followed by ion-exchange with  $\text{LiTf}_2\text{N}$ .<sup>[116]</sup> The resultant polyester-ionene is shown in **Figure 13**, and this

material, in combination with cross-linked polyethylene oxide (PEO), was studied as gas a separation membrane.

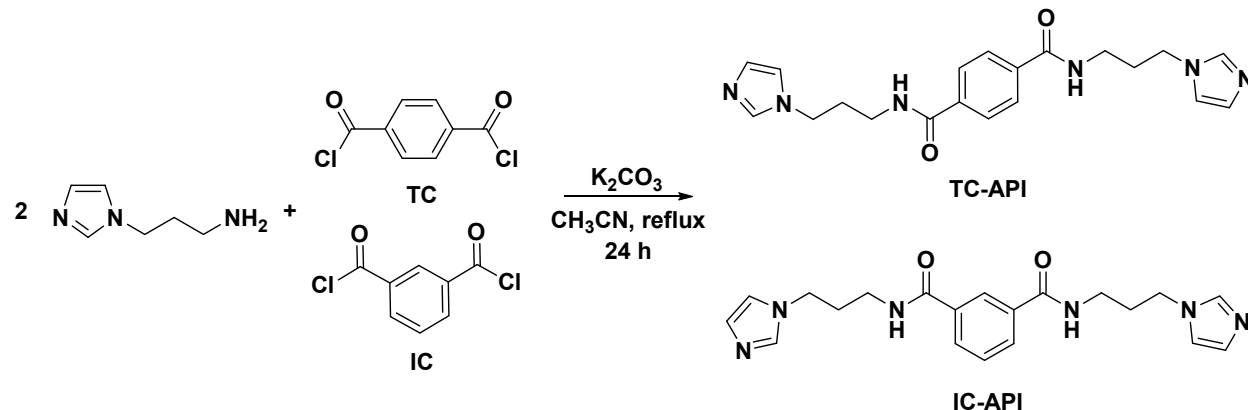


**Figure 13:** Polyester-ionene synthesized directly from the Menshutkin Reaction.

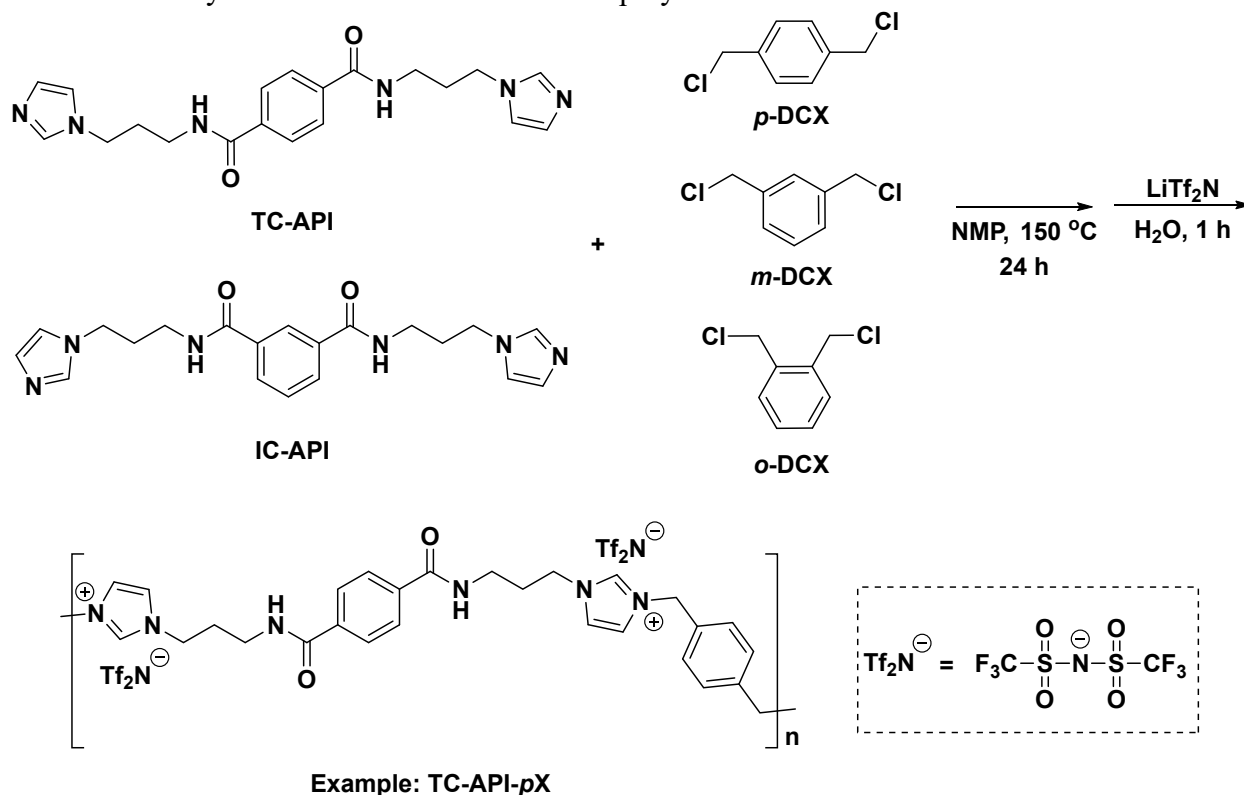
Schreiner, et al. also used the Menshutkin reaction to form a non-aromatic polyester-ionene (similar to that in Figure 13) which was then processed via electrospinning.<sup>[117]</sup>

### 5.3 Polyamide-Ionenes

Our research group has also recently demonstrated the synthesis of imidazolium polyamide-ionenes analogous to the polyimide-ionene in **Scheme 11a**. Using API and either terephthaloyl chloride (TC) or isophthaloyl chloride (IC), a bis(imidazole) diamide monomer is formed first (Scheme 11a).<sup>[118]</sup>

**Scheme 11a:** Synthesis of bisimidazole diamides from API and TC or IC.

Of course, TC and IC are key starting materials to the HP polyaramids Kevlar® and Nomex®. The TC-API and IC-API monomers were then reacted with either para-, meta- or ortho-dichloroxylylene (i.e., *p*-DCX, *m*-DCX and *o*-DCX), with the polyamide-ionene precipitating from NMP during the course of the reaction. The Cl<sup>-</sup> forms of these polyamide-ionenes were water soluble, but ion-exchange with LiTf<sub>2</sub>N resulted in a hydrophobic precipitate. MALDI-TOF MS revealed that these ionene-polyamides all had M<sub>N</sub> values of ~50 kDa with relatively broad dispersity. Six imidazolium polyamide-ionene isomers with differing regiochemistry were synthesized in this manner entirely from commercially available starting materials as shown in **Scheme 11b**.

**Scheme 11b:** Synthesis of imidazolium ionene-polyamides.

The polyamide-ionenes in Scheme 11b are all mechanically robust and generally behave as tough rubbers. Furthermore, all appear to behave as thermoplastic elastomers and exhibited self-healing and shape memory qualities.

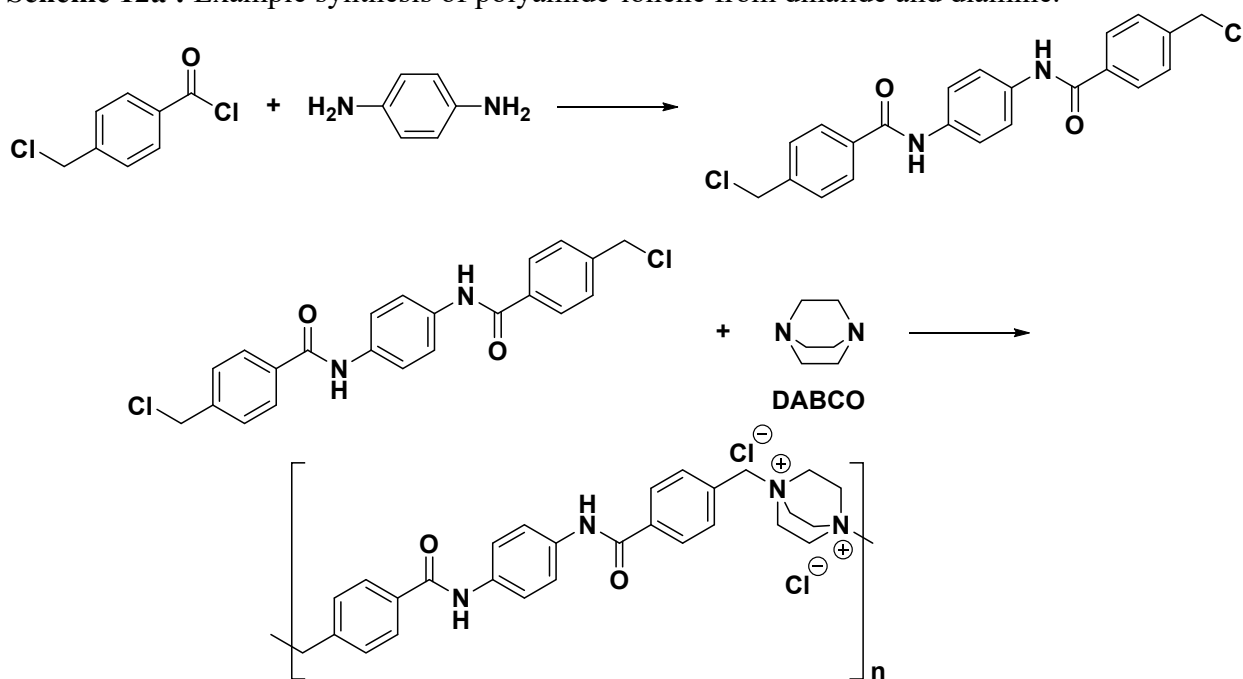
One of the primary applications reported for polyamide-ionenes in the literature has been as gelators for both water (i.e., hydrogels) and ILs (i.e., ionogels). Yoshida and coworkers have formed ammonium polyamide-ionenes for these purposes via controlled A-A + B-B reactions (**Scheme 12a**)<sup>[119]</sup> wherein the 3° diamine is 1,4-diazabicyclo[2.2.2]octane (DABCO).

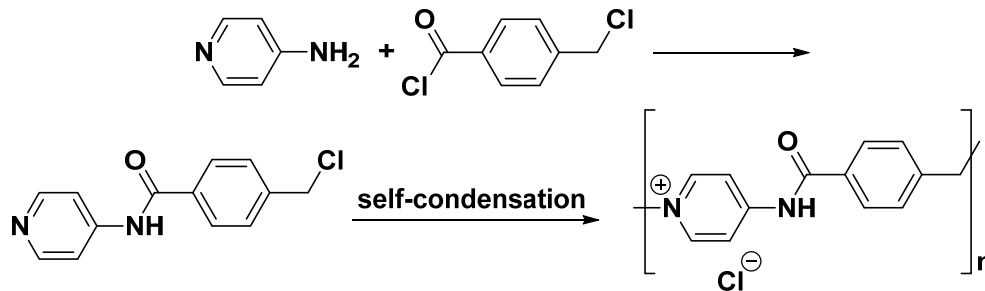
Alternatively, pyridinium polyamide-ionenes were formed via uncontrolled reactions wherein the synthesis of an A-B monomer from 4-aminopyridine and 4-chloromethylbenzoyl chloride immediately resulted in self-condensation (**Scheme 12b**).<sup>[120, 121]</sup> When Cl<sup>⊖</sup> was present as the counterion, the polyamide-ionenes were soluble in hot water, but when exchanged to Tf<sub>2</sub>N<sup>⊖</sup> they

were no longer water soluble. The controlled synthesis with diamine and di(benzyl chloride) species yields  $M_N$  of  $\sim 6.2 - 17.4$  kDa as  $\text{Tf}_2\text{N}^-$  salts. However, for the polyamide-ionene produced from the self-condensing A-B monomer, very low molecular weight (2.8 kDa) was reported.<sup>[121]</sup> It was observed that the  $\text{Cl}^-$  forms of these polyamide ionenes form hydrogels upon cooling from a heated aqueous solution<sup>[119]</sup> while the  $\text{Tf}_2\text{N}^-$  forms (as well as those with anions such as  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ , etc.) can form ionogels with imidazolium ILs such as  $[\text{C}_2\text{mim}][\text{BF}_4]$ ,  $[\text{C}_2\text{mim}][\text{Tf}_2\text{N}]$  and  $[\text{C}_4\text{mim}][\text{PF}_6]$ .<sup>[120, 121]</sup>

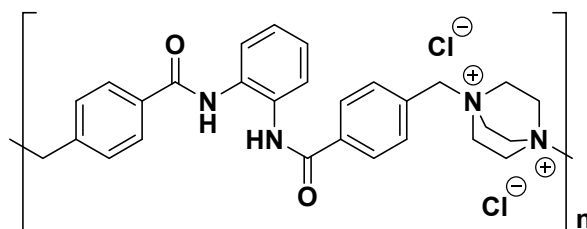
The gelation behaviors of the ionene-polyamides in Scheme 12b were computationally modeled and visualized in Kovalenko, et al. wherein  $\text{H}_2\text{O}/\text{Cl}^-/\text{amide}$  H-bonds were observed to be responsible for the non-covalent crosslinks which stabilized the hydrogel.<sup>[122]</sup>

**Scheme 12a** : Example synthesis of polyamide-ionene from dihalide and diamine.<sup>[119]</sup>



**Scheme 12b:** Synthesis of self-condensing polyamide-ionene.<sup>[120-122]</sup>

Diaz-Diaz and co-workers have also studied the gelation/hydrogel behaviors of polyamide-ionenes from both experimental and computational approaches looking at the effects of regiochemistry of the amide linkages formed with *p*-, *m*- and *o*-phenylenediamine in the monomer synthesis (cf. Scheme 12a).<sup>[123, 124]</sup> Their work concluded that when the diamide link was in the ortho configuration (**Figure 14**) the polyamide ionenes exhibited the best hydration characteristics and lowest critical gelation concentration.

**Figure 14:** Structure of polyamide-ionene where amide linkages are present at ortho position.

Saborio, et. al synthesized an isomer of the ionene shown in Scheme 12a by replacing *p*-phenylenediamine with *m*-phenylenediamine in the monomer synthesis.<sup>[125]</sup> In this work, the premise was to produce n-doped poly(3,4-ethylenedioxythiophene) (PEDOT) with a ionene dopant in place of conventionally employed tetramethylammonium (TMA) salts. The use of the polyamide-ionene with PEDOT provided improved thermal stability at comparable levels of doping compared to TMA salts.

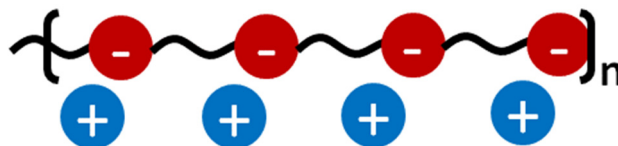
Lou et. al, also utilized an approach similar to that in Scheme 12a to synthesize polyamide-ionenes, replacing *p*-phenylenediamine with ethylenediamine or *m*-diaminoxylene in the monomer synthesis followed by reaction with *N,N,N',N'*-tetramethyl-1,3-propanediamine (TMPDA) in the ionene formation step.<sup>[126]</sup> The interest in polyamide-ionenes for this application stemmed from prior results from this group, wherein it was discovered that conventional ammonium ionenes were potent for this purpose,<sup>[127]</sup> although it was hypothesized that increased backbone rigidity<sup>[128, 129]</sup> and amide linkages<sup>[130, 131]</sup> might be even more effective antimicrobials.

The resultant polyamide-ionenes were demonstrated to be potent against a broad-spectrum of microbes in vitro, including the multidrug-resistant (MDR) *K. pneumoniae* lung infection. The antimicrobial activity of these polyamide-ionenes were effective against 20 strains of *K. pneumoniae* with more rapid killing kinetics than commonly used antibiotics such as imipenem. Repeated use of the polyamide-ionenes did not lead to resistance development in *K. pneumoniae* due to the mechanism of action (membrane disruption). It was concluded that these polyamide-ionenes might be effective treatments for lung infections caused by MDR *K. pneumoniae*, and neither acute toxicity nor interference with blood electrolyte balance were observed.

## 6. Anionic Ionenes

There have been very limited examples of anionic ionenes reported in the literature, which are corollaries to cationic ionenes and can be represented according to the illustration in **Figure 15**.





**Figure 15:** Representation of anionic ionene archetype.

Unlike cationic ionenes which can be formed from a variety of amines, phosphines and *N*-heterocycles, there are perhaps but a few viable linkages from which to create anionic ionenes. However, anionic ionenes may be a worthwhile pursuit as they will most likely offer further improved thermal stability as well as unique capabilities that are unavailable with cationic ionenes, such as the inclusion of reactive/catalytic cations including  $H^+$  and transition metals ( $M^{n+}$ ), as well as act as  $H^+$  or  $Li^+$  conductors.

It appears that all reported anionic ionenes have been based on (aryl)sulfonimide linkages, the earliest report of which was in 1974 by Daly and Hölle<sup>[132]</sup> using a self-condensing “A-B” sulfonyl chloride – sulfonamide monomer (**Scheme 13**).

**Scheme 13:** Synthesis of an anionic polyarylsulfonimide, the first reported anionic ionene.

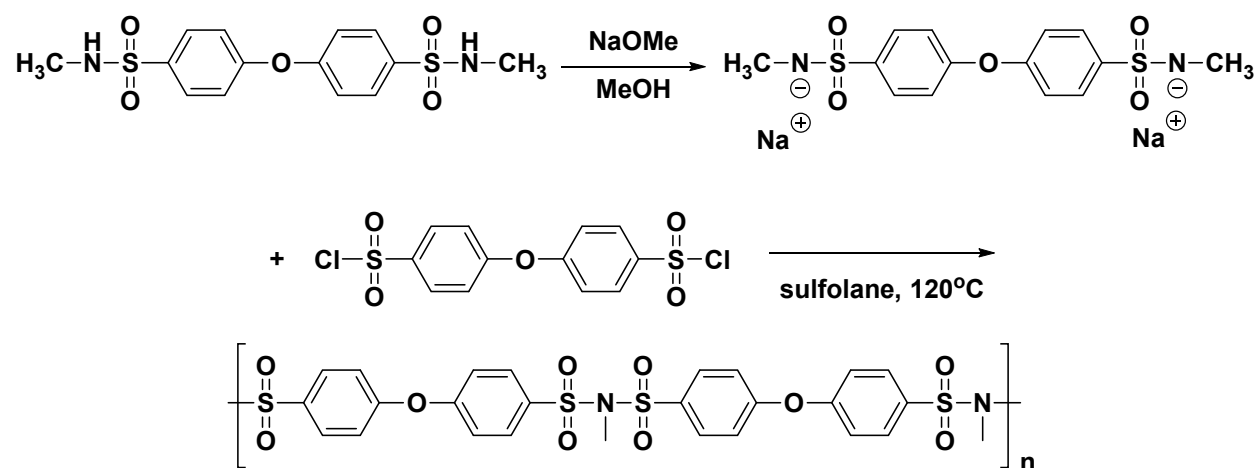


(or  $H^+$  form if dissolved in DMF and treated with  $HCl_{(g)}$ )

The anionic polyarylsulfonimide ionene exhibited poor solubility in most organic solvents and water, but was soluble (upon heating) in DMF and DMSO/LiCl (5 wt%). It was also soluble in  $H_2SO_4$ , although degradation followed dissolution. Viscosity measurements of the polymer in the DMSO/LiCl solution indicated low MW, likely a consequence of precipitation during synthesis. However, the material had very good thermal stability, with the onset of decomposition

under N<sub>2</sub> not beginning 410°C for the H<sup>+</sup> form and 485°C for the K<sup>+</sup> form. It was noted that improvements in product MW and solubility could be achieved by coupling a 2° disulfonamide to a di(sulfonyl chloride), however the resulting polymer no longer had a sulfonimide anion in the backbone (**Scheme 14**).

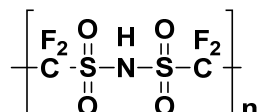
**Scheme 14:** Synthesis of neutral polyarylsulfonimides, yielding an uncharged polymer.



The neutral polyarylsulfonimide in Scheme 14 was more readily soluble in organic solvents, including *m*-cresol, DMSO and diphenylether between 80-100°C, than the anionic form (Scheme 13). However, thermal stability for the neutral polymer was greatly reduced with degradation occurring rapidly between 350-375°C. Daly and Hölle concluded that the difficulties they encountered in working with this system would make the practical use of polyarylsulfonimides as high-temperature polymers a very challenging endeavor. Thus, although there seems to have been no progress in such polymers, Lukin, et al. have reported the synthesis of dendrimers with triarylsulfonimide connectivity.<sup>[133]</sup>

In 1993, Appleby, et al. reported on the synthesis of the acid (H<sup>+</sup>) form of a simple perfluorosulfonimide<sup>[134]</sup> polymer (**Figure 16**) as a potential fuel cell electrolyte. While the

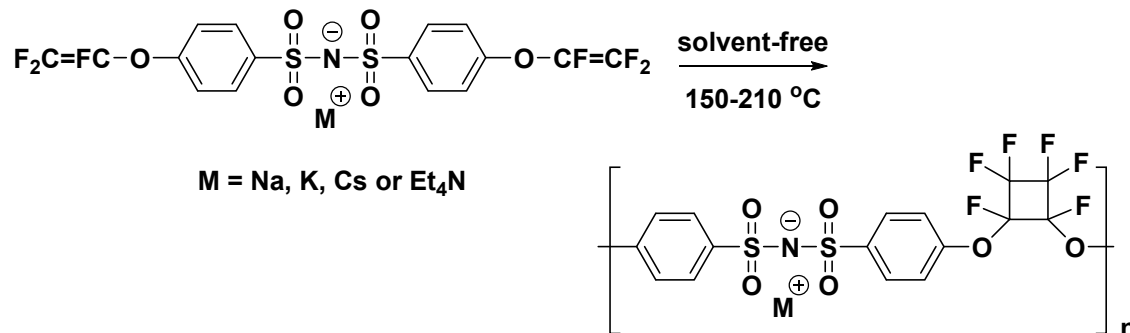
perfluorosulfonimide groups in the polymer backbone impart a strongly acidic character to the material, it was noted that the mechanism of  $H^+$  conduction was through hydronium ions (i.e.,  $H_3O^+$ ) meaning that water was required if any significant ionic conductivity was to be achieved. Furthermore, this would limit the maximum operation temperature to about 100 °C.



**Figure 16:**  $H^+$  form of perfluorosulfonimide polymer.

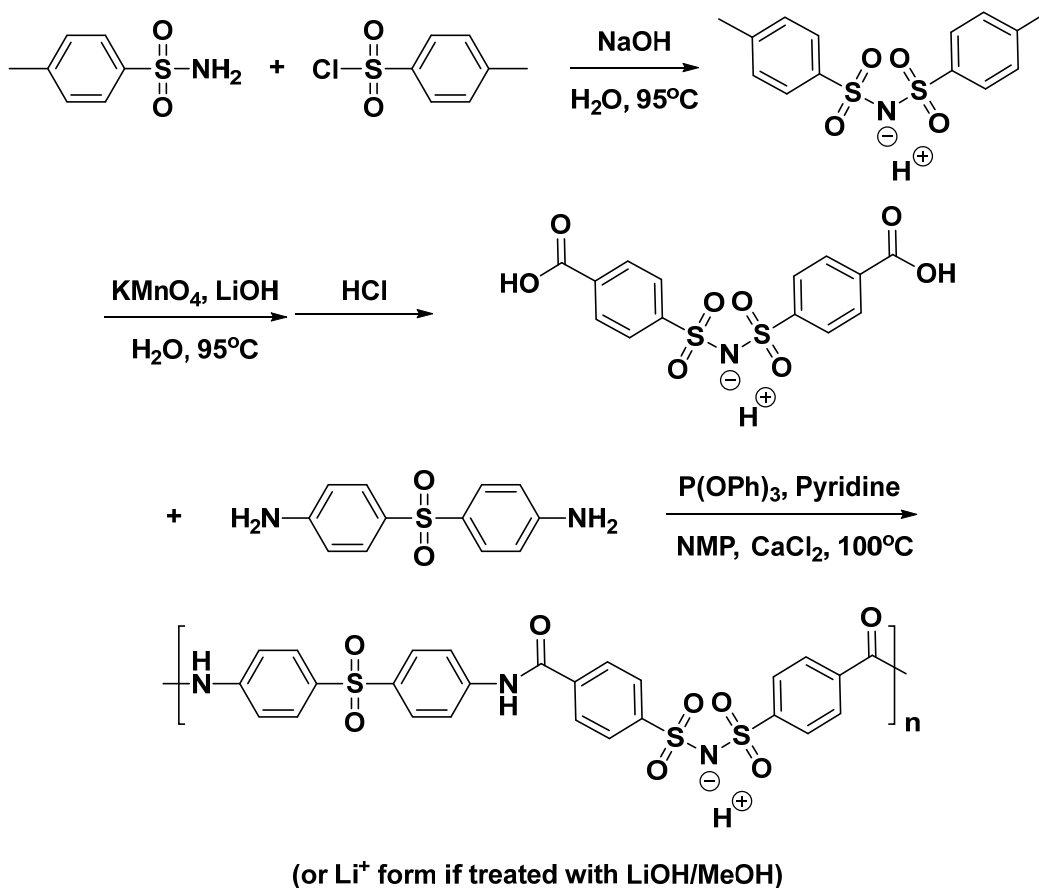
While the synthesis of such perfluorosulfonimide polymers is not trivial, the anionic linkage in the backbone should be of great interest to ionenes as it is essentially the polymeric form of the  $Tf_2N^-$  anion, and the  $H^+$  form could easily be neutralized to variety of  $M^{n+}$  or organic cations.

Desmarteau and co-workers later utilized a strategy to form perfluorocyclobutyl (PFCB) anionic ionenes with fluorosulfonimide linkages via a multi-step synthesis starting from 4-bromophenol. **Scheme 15** details only the polymerization step wherein the trifluorovinyl ether moieties undergo thermally-induced cyclization.<sup>[135]</sup> The authors noted that these polymers were able to be cast into transparent, flexible thin films from THF with  $M_N$  values of at least 20 kDa were assumed based on prior unpublished results from a student thesis.

**Scheme 15:** Formation of anionic ionene via thermally-induced cyclization.

More recently, several works by Cheng and co-workers have reported the synthesis of anionic ionenes via condensation polymerization through amide linkages.<sup>[136-141]</sup> These materials are of interest as  $\text{H}^+$  exchange membranes and as single-ion conductors for  $\text{Li}^+$  batteries. **Scheme 16** details the synthetic approach wherein a symmetric sulfonimide is formed from the coupling of *p*-toluenesulfonylchloride and *p*-toluenesulfonamide, followed by oxidation to a di(carboxylic acid). This sulfonimide monomer is then coupled with diaminodiphenylsulfone to form the anionic polyamide-ionene.

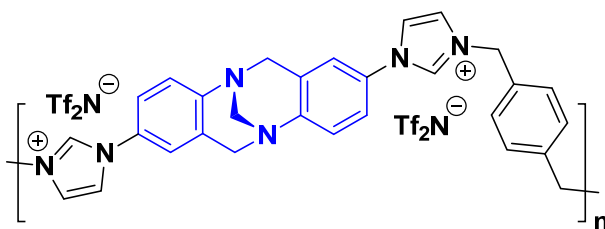
**Scheme 16:** Synthesis of anionic ionene from anionic sulfonimide di(carboxylic acid) monomer and diaminodiphenylsulfone.



## 7. Outlook

Ionenes have certainly become much more complex and robust compared to their in the past 10 years, with a number of new chemistries developed. We foresee great possibilities in ionenes containing functionalities associated with HP and UHP polymers. Some of these opportunities are immediately accessible through the direct use of commercially available reagents, while many more long-term opportunities require synthetic organic chemistry to yield radically new “A-A” and “B-B” building blocks for ionene synthesis. There may also be merit in further exploring “A-B” monomers that allow for better control over the polymerization.

The recent examples published by our group wherein new bisimidazole-functionalized diimide<sup>[49]</sup> and diamide<sup>[118]</sup> monomers are achieved by reacting API with common dianhydrides or di(acid chlorides) underscore how the components needed to synthesize cationic ionenes with new and robust linkages may already be on laboratory shelves. Furthermore, as emphasized throughout this review, when synthetic organic chemistry is employed, even more complex and interesting monomers become available. One example is the recent work from our group with imidazolium ionenes synthesized around Tröger's base (Figure 17) and studied as gas separation membranes.<sup>[142]</sup> Although the Tröger's base (diazocine) linkage contains two 3° amines, these are generally not susceptible to alkylation under mild conditions<sup>[143]</sup> and the ionene synthesis proceeded smoothly via the Menshutkin reaction at the imidazole sites only.



**Figure 17:** Example of a new type of imidazolium ionene synthesized around Troger's base (blue).

In 2012, Agarwal and co-workers published a manuscript entitled, “Closing One of the Last Gaps in Polyionene Compositions”.<sup>[144]</sup> While this may have been true for simple ammonium ionenes (cf. Figure 2) that were based on commercially available diamine and dihalide monomers, it is readily apparent that a veritable “universe” exists wherein the number of possible cationic ionenes is far greater than previously considered. Much of this exploration will be made possible through the design and synthesis of new monomers from small molecules which are not typically associated with ionenes, especially those containing functionalities typically associated with classical condensation polymers, including HP and UHP polymers.

When also considering the “parallel universe” of anionic ionenes and how cationic and anionic ionenes might then be combined, the possibilities become endless.

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**Kathryn E. O’Harra** received a B.S. in Chemical & Biological Engineering and a B.A. in Dance from the University of Alabama in 2017, followed by an M.S. in Chemical Engineering in 2018. Inspired by her experience as an undergraduate research assistant in Bara’s research group, she began her graduate study at the University of Alabama in Fall 2017. She is currently pursuing her PhD in Chemical Engineering, focusing on the design, synthesis, characterization, and application of advanced ionenes.



Ionenes are condensation polymers which contain ionic moieties directly in the polymer backbone, rather than as pendants. Although ionenes have been known for many decades, recent interest in charged polymers for a variety of applications has sparked the evolution of ionenes from ammonium cations tethered by relatively simple functional groups to much more robust architectures found in high-performance polymers.

**Keyword:** ionene

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### Recent Advances in the Design of Ionenes: Toward Convergence with High-Performance Polymers



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