Polymer International SCI

Toward controlled functional sequencing and hierarchical structuring in imidazolium ionenes

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Abstract: This focused mini-review highlights recent advances related to the design and applications of imidazolium ionenes and forward-looking perspectives. Creative strategies which employ established synthetic approaches and utilize the modularity of the imidazole moiety unlock great potential for tailoring both functional and structural features arising from precise spacing of ionic groups within the polymer backbone. As imidazolium ionenes draw more interest, increased sophistication of chemical modifications and material processing is occurring, with a corresponding shift toward more demanding applications. Synthetic routes for placement and sequencing of ionic content will be discussed, in addition to recent approaches to control structure and self-assembly or tune behaviors of imidazolium ionenes and composites.

Classification of Ionenes

Although synthetic ionic polymers have been known for decades, attention has recently intensified as a result of interest in ionic liquid (IL) chemistries and inspiration from advanced high-performance polymers. Ionic polymers are highly tunable through various synthetic approaches that allow for incorporation of versatile structural and functional features, choice of ionic or ionizable moieties and paired counterion, and variation of the spacing and location of charge. Ionic polymers fall into three categories: polyelectrolytes, ionomers, and ionenes. In comparison to polyelectrolytes and ionomers, where ionic groups are pendant from the backbone, *ionenes* are polymers in which the ionic group is directly within the main chain. Nearly all reported ionenes bear a cationic group within the backbone, selected from ammonium [1-14], phosphonium[15, 16], piperidinium[17], pyrrolidinium[18], pyridinium[19-23], triazolium[24, 25], or imidazolium[26-32] moieties, with the majority of ionenes reported based on ammonium cations[1]. However, we postulate that among these choices, imidazolium cations provide the most diversifiable synthetic options. Heterocyclic imidazole rings have two 'N' atoms which can be functionalized independently. Thus, the connectivity of imidazolium ionenes is through the N(1) and N(3) positions while diverse functionalities can be present at the C(2), C(4), and/or C(5) positions (Figure 2). Long's group has previously reviewed the potential of the imidazole- and imidazolium-containing and polymers [32, 33]. The general connectivity of imidazolium ionenes is represented in Figure 1.

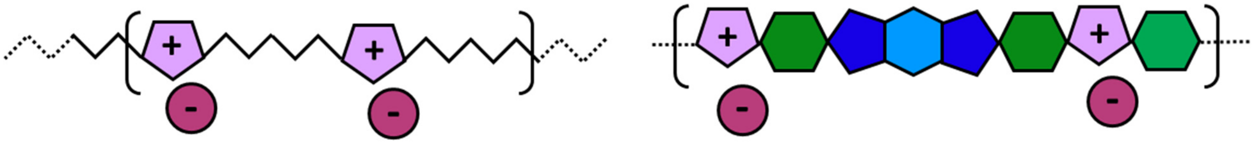


Figure 1: Structural representation of imidazolium groups incorporated within aliphatic and aromatic ionenes.

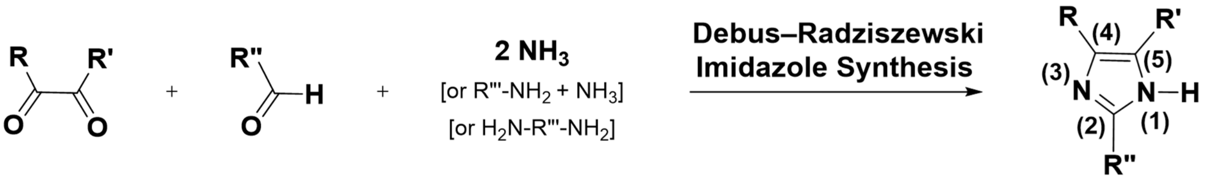
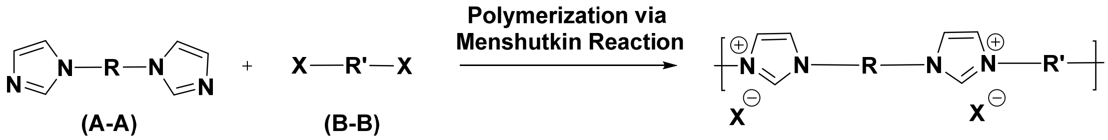


Figure 2: Debus-Radziszewski imidazole synthesis and position numbering convention [N(1), C(2), N(3), C(4), C(5)].

In recent years, the design of ionenes has trended toward more high-performance (HP) applications, as researchers draw inspiration from the structural and functional features of classic condensation polymers[34].

Synthetic Routes: Building Blocks and Polymerization Pathways

The dominant route for the synthesis of imidazolium (as well as ammonium, pyridinium, etc.) ionenes is the Menshutkin Reaction, most typically performed with stoichiometric equivalents of a diamine (tertiary or cyclic) and an α,ω-dihaloalkane. The Menshutkin Reaction is usually performed as the polymerization step, which propagates as a step-growth mechanism between these A-A and B-B monomers (Scheme 1). However, Menshutkin polymerization with self-condensing A-B monomers has also been shown [35]. This approach is often followed by anion metathesis from halides to more delocalized molecular anions akin to those commonly used in ILs. An alternative approach (with limited examples) involves direct, or "one-pot", formation of imidazolium and benzimidazolium ionenes which uses the *Debus–Radziszewski* (D-R) imidazole synthesis [36-39] (Figure 2). The D-R method forms the imidazolium moieties through cyclization between a diamine, aldehyde, and diketone in EtOH/CH_3COOH as the polymerization step. A recent mini-review by Saxer, et al. highlights the utility of D-R imidazole synthesis in macromolecular chemistry[39]. Ionenes containing benzimidazolium groups also rely upon these methods, although the benzimidazole may be formed within a monomer which is subsequently reacted in a later polymerization step. Few examples demonstrate incorporation of the imidazole moiety in its ionic form, through preparation of an A-A monomer containing one or two imidazolium units, most commonly within dihalides [40-43]. This is achieved from reaction of sodium imidazolate or an aliphatic bis(imidazole) with an excess of a α,ω-dihalide[44]. Scheme 1 highlights the most common approach for achieving imidazolium ionenes.



Scheme 1: The most common A-A + B-B polymerization method for obtaining imidazolium ionenes.

The ability to design and construct highly tailored monomeric building blocks is a major advantage of the imidazolium ionene platform. Despite the expansive synthetic possibilities for designing bifunctional building blocks, nearly all imidazolium ionenes in the literature rely on symmetric bis(imidazoles) tethered by "simple" linkages, specifically linear alkyl or ether chains, or benzylic (e.g., xylyl) groups[34]. Additionally, nearly all α,ω-dihalides used contain the same types of linkages. However, the complexity and functionality within both the A-A and B-B monomers can be designed, and are certainly not limited to commercially available compounds. Innumerable bis(imidazole) derivatives containing a wide range of structural/functional features are synthetically possible using commercially available starting materials and employing established C-N bond forming reactions. N-alkylation is foundational chemistry for imidazolium ILs and bis(imidazoles), proceeding as an S_N2 reaction between an alkyl halide or α,ω-dihaloalkane with imidazole in the presence of base[44-46]. Ullmann couplings between aryl halides and N-heterocycles expand these options with N-aryl aromatic connectivity within bis(imidazoles). Ullmann coupling has been utilized in the preparation of asymmetric imidazole precursors, subsequently linked (via conventional condensation reactions) to form robust functional elements while retaining reactive imidazole end-groups[47-51]. Other researchers have discussed less conventional routes to obtain asymmetric, bis(imidazole), or fused imidazole molecules with alternative connectivities[53-60]. Yet, the design of imidazole-containing molecules is still not limited to S_N2 and Ullmann coupling reactions, as customization of substitution and connectivity at one or more of the C(2,4,5) positions or even crosslinking is attainable using D-R chemistry, via selection of the aldehyde, diketone, and amine precursors[39, 61, 62]. These methods elucidate the vast opportunities for the customization of intriguing imidazole-containing building blocks which can be utilized in ionene design.

Functionality, Properties, and Applications of Imidazolium Ionenes in Literature

An array of compatible functional and structural features, incorporated between and pendant from the imidazolium cations, dictate the diverse and tunable behavior by altering the intermolecular forces within the ionene matrix. Modification of the cation structure, paired anion, linking group, and charge density are just a selection of the "knobs" which can be turned in ionene design. The following sections summarize imidazolium ionenes reported in the scientific literature thus far, reflecting the aforementioned scope of monomers utilized and highlighting the uses for these polymers. Imidazolium ionenes also frequently appear in the patent literature particularly in applications related to cosmetic, personal care, and antimicrobial products.

While solution behavior, counterion effects, conductivity, and charge spacing have been explored for ammonium ionenes, the structure-property relationships in simple imidazolium ionenes with these variations is essentially uncharted territory [63-66]. A few groups have compared effects of charge location in imidazolium-based polymers with pendant versus backbone incorporation of charged features [35, 67].

Simple Imidazolium Ionenes

"Simple" imidazolium ionenes, those with only alkyl or xylyl linkages, are the most prevalent. Carlisle, Bara and co-workers introduced a set of imidazolium ionenes tethered by *n*-decyl groups, which were melt pressed into membranes both in their neat forms and as composites with an imidazolium IL for pure gas permeation studies[31]. Erdmenger and coworkers demonstrated an interesting microwave assisted preparation of *n*-butyl-spaced imidazolium ionenes, which (with halide counterions) showed excellent water uptake as humidity absorbers.[68] Grygiel, et al. showed a "one pot" D-R synthesis of simple imidazolium ionenes as potential N-doped carbon materials, which were studied as the dicyanamide salt to probe the crosslinking and dehydrogenation behavior from high-yielding carbonization experiments[38]. Guo, et al. revealed the superior antibacterial efficacy of main chain cationic polymers relative to similar cationic ILs or side-chain cationic polyelectrolytes, for imidazolium and ammonium systems[67]. Liu, et al. also reported xylyl-linked imidazolium ionene oligomers as antimicrobial compounds[43].

Polyester Imidazolium Ionenes

Long's group has published multiple works related to the synthesis of aliphatic imidazolium ionenes with poly(tetramethylene oxide) (PTMO) soft segments, investigating the structure-property relationships corresponding to variation of hard segment content and later reporting rheological properties and processing via electrospinning techiques[27, 28, 32]. Lee, et al. reported the synthesis of polyester (PE) imidazolium ionenes, detailing thermal and conductive properties [40]. Li, et al. relied on an asymmetric imidazolium monomer with hydroxyl and ester end groups to form PE ionenes [69]. Thankamony, et. al. introduced a ternary gel electrolyte for Li-ion battery applications, formed from a poly(ethylene oxide)-based (PEO) imidazolium PE-ionene on a PVDF support doped with lithium bistriflimide ($LiTf_2N$)[70]. Kammakakam also showed a PEO-imidazolium PE-ionene blend applied as CO_2-selective gas separation membranes[71]. These studies demonstrate the diversity in both synthetic approaches and targeted applications for polyester imidazolium ionenes.

Polyimide Imidazolium Ionenes

Polyimide (PI) imidazolium ionenes have primarily been studied as candidates for membrane-based gas separations, given the history of conventional polyimides in this application. Mittenthal, et al. produced a high-performance PI-ionene, formed from the condensation of pyromellitic dianhydride (PMDA) and 1-(3-aminopropyl)imidazole (API) to form a diimide-containing bis(imidazole), which was subsequently polymerized with a xylyl linkage. The structural and thermal properties of the neat imidazolium PI-ionene and IL soaked composite were analyzed, and the IL-ionene composite showed improved gas separation performance[72]. This work was expanded upon by O'Harra, et al. reporting the synthesis and characterization of high molecular weight (number average molecular weight, M_n ~ 60-110 kDa), 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) containing PI ionenes, investigating both aliphatic and aromatic derivatives and IL-ionene composites as gas separation membranes. The effects of modifying and alternating aromatic regiochemistry (i.e., *p*-, *m*-, *o*-) and variation of the associated anion on thermal and mechanical properties were investigated [29, 30].

Polyamide Imidazolium Ionenes

Polyamide (PA) imidazolium ionenes integrate regularly spaced H-bonding donor/acceptor sites along the main chain, which in conjunction with Coulombic forces affect intermolecular interactions. Our group has introduced a series of PA-ionenes formed from the condensation of terephthaloyl chloride (TC) and API to form a diamide-containing bis(imidazole) which was subsequently polymerized with a xylyl linkage[73]. These materials are fully water soluble as the Cl^- salt, yet upon anion metathesis to the Tf_2N^- form, they become hydrophobic and possess remarkably rapid and robust self-healing and shape memory behaviors. These PA-ionenes showed good thermal stability and achieved high molecular weights (M_n~50-75 kDa), and processing revealed potential as fibers or films; and their performance as gas separation membranes was quantified[26, 74]. O'Harra, et al. also introduced a corresponding series of aromatic PA-ionenes, which were suitable for forming very thin films and showed moderately high CO_2/CH_4 and CO_2/N_2 selectivities as gas separation membranes[75]. A series of imidazolium poly(amide-amide) and poly(imide-amide) ionenes were designed by O'Harra, et al., constructed from imide or amide-containing bis(imidazoles) linked by an aromatic diamide dichloride linkage[76]. The structure-property relationships and self-assembly behaviors were studied for the neat materials and for composites with mono- and tris(imidazolium) ILs[76]. Tan, et al. also demonstrated antimicrobial properties of PA imidazolium and ammonium-functionalized ionenes, as the Cl^- salts[77].

Polyurea and Polycarbonate Imidazolium Ionenes

Demarteau, O'Harra, and co-workers recently reported a series of self-healing and elastomeric PA- and polyurea-ionenes, synthesized from the "upcycling" of polyethylene terephthalate (PET) and bisphenol A polycarbonate (BPA PC) plastic wastes[26]. These ionenes contain alternating ionic segments and H-bonding segments, which suggest a synergistic effect impacts the observed elastomeric, self-healing qualities. Yuan, et al. synthesized a series of symmetric or asymmetric carbonate, hemiaminal, urea, or ester-containing bis(imidazoles), which were used to form ionene oligomer end groups for pH-degradable antimicrobials[78].

Benzimidazolium Ionenes

Mokhtari, et. al. computationally studied electronic structures and conformations of polybenzimidazole (PBI) based ionenes, proposing materials for anion-exchange membranes[79]. Wright and Holdcroft produced several articles highlighting PBI ionenes which were hydroxide-stable due to sterically protective, substituted ring systems[80]. These benzimidazolium ionenes were polymerized via D-R synthesis, exhibiting good mechanical properties as well as high ionic conductivity and ion-exchange capacity[80-82]. Pham and coworkers introduced anion exchange membranes comprised by blending a partially deprotonated PBI with a spiro-ionene, formed from condensation of dipiperidines and 1,2,4,5-tetrakis(bromomethyl)benzene[17].

Other Imidazolium Ionenes

Matsumi and coworkers introduced a borane-containing imidazolium ionene of low molecular weight (4-9 kDa), formed via hydroboration polymerization between 1,3-diallylimidazolium bromide and a borane comonomer[83]. Amarasekara, et al. introduced a Brønsted acidic imidazolium ionene by sulfonating the xylene linkage in H_2SO_4, causing anion metathesis to the HSO_4^- form.[84] Xu and coworkers recently introduced benzimidazole-based PIs containing 6FDA and Tröger's base (TB) structural features, comparing ionene and ionomer-like systems. However, these were not alkylated and quaternized, but rather were protonated with an excess of fluoroboric acid [85]. Our group has demonstrated the formation of TB-containing bis(imidazole) monomers which were subsequently polymerized with hydrocarbon or xylyl linkages to form high molecular weight (50-170 kDa) ionenes which performed well as CO_2-selective gas separation membranes[86]. Strużyńska-Piron, et al. investigated blends of a diphenyl-ether bridged poly(benzimidazole) and a benzimidazolium ionene as membranes for vanadium redox flow batteries. This ionene was formed via the Menshutkin reaction of 2-(2,4,6-trimethylphenyl)benzimidazole and dibromo-xylene, achieving M_n ~ 40 kDa. Toba and coworkers introduced phenyleneethynylene- and thienyleneethynylene-based conjugated polymers containing imidazolium groups along the main chain through the 2,5-positions of the imidazole ring[87].

Structures and Composites

Imidazolium-containing polymeric materials may extend into new architectures, as alternative geometries, phases, and composites are explored. It is clear that the imidazolium ionene framework is compatible with several functional linkages, yet there are still many opportunities for designing monomeric building blocks and interfacing with additives.

Over the last decade, our group has investigated ionene + IL composites as a means of organizing the ionene matrix through enhancement of the intermolecular forces, resulting in altered gas permeation behavior and structural regularity, as the "free" IL serves as a non-covalent crosslink affecting interchain spacing and mechanical stability [30, 31, 72, 75]. Recently, we have progressed into ionene + IL composites with the design of novel mono- and multivalent ionic fillers, inspired by small molecules which exhibit supramolecular assembly[30, 76]. In 2008, Lodge commented on the unique aspects of ILs + polymers for materials design, and it is clear that despite all of the work in this area, the surface has barely been scratched [88]. Conceptualization of ionene + IL composites (Figure 3) points toward the possibilities of further tuning the ionic matrix via mixed anion compositions, varying cationic structures and ratios, or adding protruding side chains to alter entanglement or chain spacing.

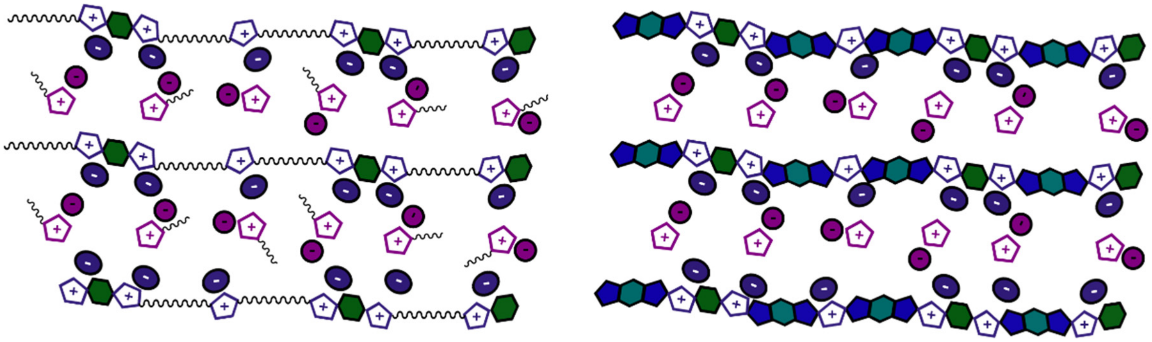


Figure 3: Conceptualization of interaction and coordination of "free" ILs within the ionene matrix.

Examples of branched, ionene-type polymers are sparse in literature. Amarasekara, et al. synthesized branched ether-functionalized imidazolium networks, which contained ionene segments tethered to a 1,3,5-trihydroxybenzene core[89]. Cheng and coworkers explored branched imidazolium-containing networks which demonstrated electrostatic attraction to polysulfides, for use in high-energy-density lithium-sulfur batteries[90]. Methylene- or xylene-bridged bis(imidazole) segments have been incorporated within metal-organic frameworks, coordination polymers, and ligands[91-93].

Functions and Applications of Imidazolium Ionenes

While a portion of the aforementioned literature focuses on the fundamental chemistry and behaviors of imidazolium ionenes, several applied materials are united by their function and performance. Certainly, the functional and structural segments beyond the imidazolium groups are influential, and are often inspired by features utilized in leading materials for the targeted applications. But overall, imidazolium ionenes have been designed for CO_2-selective gas separation processes, use in batteries, as ion conductive materials or anion exchange membranes, within coordination polymers or ligands, or as antimicrobials. Imidazole-containing compounds are known for their ability to interact with CO_2 and prevalent in certain pharmaceuticals (i.e., antifungal, antimicrobial, antiprotozoal); whereas imidazolium cations are noted for their ability to form stable carbenes, while also possessing good electrochemical stability and ion conductivity. The key functions and properties of the imidazolium moiety directly correlate and even dictate the usefulness of imidazolium ionenes in these applications.

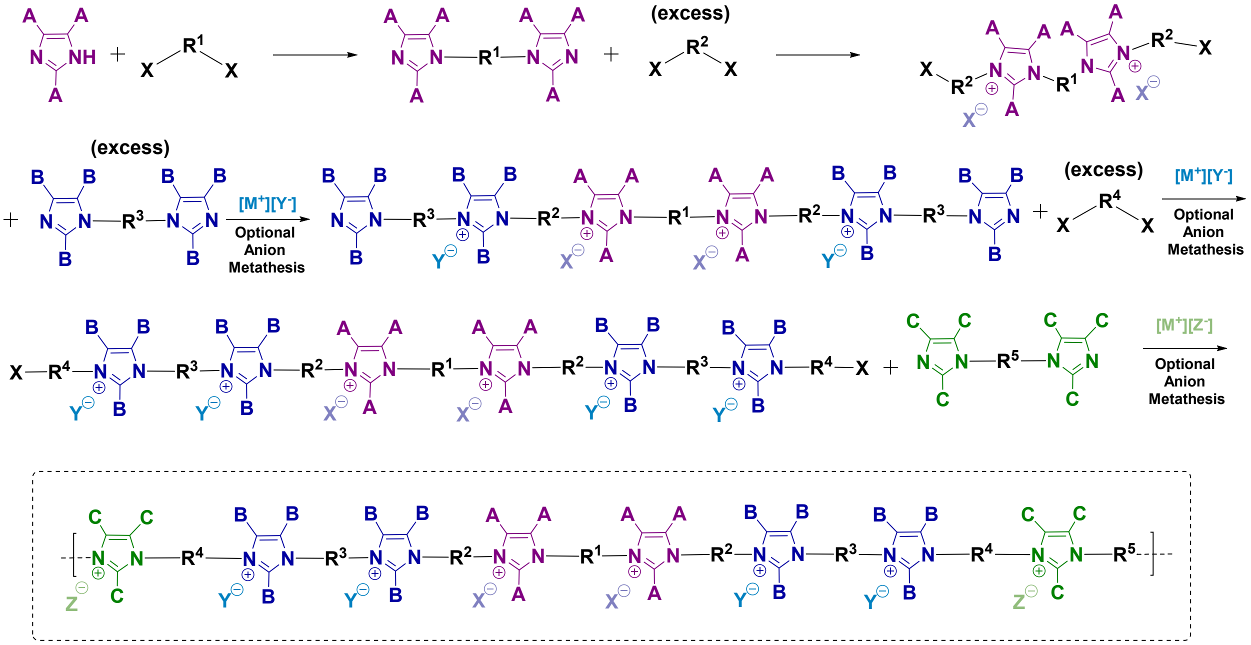
Sequencing in Ionenes: Perspective on Recent Developments and New Directions

Synthetic developments and design strategies drive the potential for imidazolium ionenes toward more ambitious structural and functional possibilities. Many concepts related to "sequencing", or the ordering of ionic and functional elements along each chain, have been explored in ionenes thus far. Yet, certain advances in the chemistry of multivalent imidazolium-based ILs and ionene oligomers can be employed in the design of more sophisticated ionenes, allowing for tuning of an ionic "segment" and direct variation of Im^+X^- units per repeat unit (RU). For example, all of the aforementioned ionenes in literature possess 1 or 2 imidazolium cations per RU. A few groups have demonstrated the power of stoichiometric excesses, to alter end groups and control the synthesis of imidazolium ILs and oligomers [18, 41-43] The building blocks in Scheme 2 demonstrate how an excess of a dihalide (X-X) with a bis(imidazole) (Im-Im) can form a larger α,ω-dihalide species containing two imidazolium cations [X-(Im^+X^-)-(Im^+X^-)-X].

While these could subsequently be capped with monofunctional monomers or reacted for form a functional linkage, these X-(Im^+X^-)-(Im^+X^-)-X monomers could be reacted with a bifunctional monomer *including* another bis(imidazole) monomer. If added in a stoichiometric ratio, the Menshutkin reaction could proceed, and each RU would contain 4 Im^+X^- pairs. If an excess of a bifunctional monomer is added, 4 Im^+X^- nested groups within a bifunctional monomer may be possible. This process could propagate or be subsequently be polymerized to incorporate longer segments of charge per RU.

While the concept of adding a sequence of charged moieties along the ionene backbone is intriguing, the true potential lies in the variation of spacing and functionality amongst the ionic backbone. The vast majority of imidazolium ionenes are built by construction and tailoring of a structural or functional element within either a bis(imidazole) or dihalide, which can then be polymerized with the corresponding monomeric counterpart, which is often a simpler or commercially available bifunctional monomer. If Im-R-Im or X-R'-X monomers containing functional linkages can be designed and combined to sequence these nested features, innumerable potential complex ionene structures become accessible. With clever design of monomeric units and the mechanistic options surrounding imidazole synthesis, one could imagine a series of consecutive imidazolium groups, spaced by distinct functional groups or varied linkages using only readily available reagents. The significance and applicability of these ionene sequencing methods provide the opportunity for integration of dissimilar yet sophisticated features precisely spaced and sequenced along the main chain. Analogous to block copolymers, these sequenced ionenes may control phase behavior and promote self-assembly. Additionally, the tuning of the intermolecular interactions within various segments could be used in the control of stimuli responsive materials or selective post-polymerization modifications (i.e. self-healing, thermal rearrangement). Lastly, these sequencing concepts more broadly make the design of ionic "macro-monomers" possible, which can subsequently be polymerized via the Menshutkin reaction to form ionenes with massive, complex repeating units or combined with more conventional (neutral) comonomers to add regular ionic domains along the backbone.

Another less-appreciated benefit of imidazole platform is the accessibility of scalable synthetic routes to achieve diverse substitution[94]. The planarity, entanglement, and chain or counterion interactions could be probed through manipulation of substitution directly on the imidazolium ring. Few of the reported ionenes contain substituents directly on the cationic ring, and nearly all connectivity builds through N(1) and N(3) rather than also utilizing the C(2,4,5) positions. Yet, the addition of electronwithdrawing or electron-donating groups at the C(4) and/or C(5) positions of the imidazolium ring would impact the "acidity" of the C(2) position proton and the strength of cation-anion interactions (as evidenced by ^{1}H NMR chemical shifts). Work by He and Chen demonstrated a finely controlled process toward achieving imidazolium ionene oligomers with defined yet distinct anion pairings[95]. This approach, analogous to peptide synthesis, shows promise for alternative chemistries (other than "excess" approaches) for sequencing a series of tailored imidazolium moieties within ionenes, which theoretically could even allow for the "sorting" or retention of distinct associated anions. These strategies are generally represented in Scheme 2.



Scheme 2: Theoretical pathways sequenced for incorporation of >2 imidazolium cations per repeat unit, with the potential to control counterion, substitution, and "R" linkages spacing ionic groups.

This perspective demonstrates new trends and methodologies we envision leading the design of imidazolium ionenes, with greater control over the sequencing of specifically substituted cations, spacing and alternation of distinct functional and structural features, and the density and length of consecutive ionic segments. The synthetic opportunities for designing complex A-A and B-B monomer building blocks, in combination with these sequencing and sorting strategies, illustrate the seemingly limitless possibilities of the imidazolium ionene platform. There is vast promise for ionenes as a high-performance and tailorable class of materials, as synthetic methodologies and applications continues to expand.

Funding

The authors would like to acknowledge funding from the U.S. Department of Energy, Basic Energy Sciences (DE-SC0018181) and the National Science Foundation (1605411). K. E. O'Harra is supported by the U.S. Department of Education as a GAANN Teaching Fellow (P200A180056).

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