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Ionic Interactions

From Ionic Liquids to Supramolecular Polymers**

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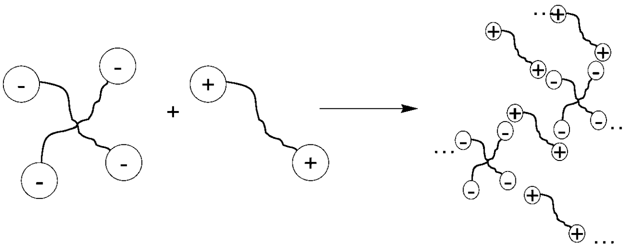
Coulombic interactions · ionic liquids · mechanical properties · polymers · supramolecular chemistry

The facile construction of polymeric materials continues to drive a wide range of fundamental and applied fields of science and engineering. New and improved methods for the synthesis of bulk material, therefore, remain highly desirable. While the efficiency and robustness of covalent polymerizations continue to increase, supramolecular polymerizations have emerged as an attractive and increasingly viable option for the synthesis of materials.[1,2]

Along with hydrogen bonds,[3] metal–ligand coordination,[4] and host–guest interactions,[5,6] pairwise ionic interactions provide an attractive design element for the molecular engineering of supramolecular structures.[7] Most often, ionic interactions are exploited in the context of polyelectrolytes (for example, layer-by-layer assembly[8–11]) and/or the phase segregation of macromolecules.[12–18] The challenges associated with using ionic interactions between small molecules for the rational engineering of supramolecular structures include: a) the relative lack of specificity between partners[7] and b) the isotropy of Coulombic potentials between discrete charges, which compromises even the validity of assuming 1:1 pairwise interactions between oppositely charged partners—consider, for example, the crystal structure of sodium chloride.

Given both the history and underlying physics of ionic approaches to supramolecular design based on small molecules, a recent report by Wathier and Grinstaff[19] is quite noteworthy. The authors combine a dication, comprising two covalently linked tetraalkyl phosphonium moieties, and the tetraanion ethylenediaminetetraacetate (EDTA^{4-}) to form an ionic liquid. Under conditions in which the Coulombic interactions are dominated by pairwise interactions between individual cationic and anionic groups, the extended structure of the ionic liquid would be expected to form what is effectively a supramolecular ionic network (Scheme 1). The dynamic viscosity of the diphosphonium/EDTA ionic liquid (12 kPa s at 1 Hz) is consistent with this expectation. The value is higher than that of either the diphosphonium chloride or a diphosphonium dicarboxylate (each < 2 kPa s), neither of which possesses the multivalency necessary to create an extended network through pairwise interactions. Analogous ionic liquids formed from monocationic phosphonium and EDTA or other anions have viscosities that are lower than that of the new, putative "network" ionic liquid, further supporting the importance of an extended network connectivity.



Scheme 1. Schematic diagram of a supramolecular ionic network.

Such interpretations are necessarily speculative, however, as the structure–activity relationships of ionic liquids formed from multimeric ion building blocks are not clear. They do, in fact, constitute an ongoing area of research, in which progress is currently being made. Recent studies by Armstrong and coworkers,[20,21] for example, reveal differences in the viscosities among dicationic ionic liquids as a function of the ion structure and approach the magnitude of the variations observed by Wathier and Grinstaff. However, the differences in viscosity occur without the presence of structures that are topologically able to form extended ionic networks based on pairwise interactions. Thus, it is impossible to rule out the possibility that some fraction of the relatively high viscosity in the diphosphonium/EDTA ionic liquids is due to effects beyond that of network formation.

Nevertheless, the potential utility of the ionic-liquid approach can still be exploited, even as the mechanism of the effect continues to be investigated. Wathier and Grinstaff recognize that the lack of specificity inherent in the ionic approach provides an opportunity for generality:[7] a wide variety of ionic species might be readily incorporated into the materials. For example, the authors combined the same diphosphonium ion with a porphyrin tetracarboxylate. The viscosity of the resulting ionic material is about 10^6 Pa s at 25 °C, nearly three orders of magnitude greater than the viscosity of the network formed with EDTA. In fact, the new

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ionic material is more of a solid than a liquid, as evident from the relative values of the storage and loss moduli that are observed. The mechanical properties are such that the porphyrin-based materials can be pulled into fibers from hot melts and molded into shape-persistent structures. Despite their solidlike characteristics, however, it is important to note that these materials appear to retain at least some of the character of the tetraalkylphosphonium ionic liquids upon which they are based.[20] For example, the materials are not brittle like the majority of traditional salts; rather, they are reported to be polymer-like in that they are pliable and sufficiently tough to withstand mechanical manipulation with tweezers. The porphyrins are also reported to retain their fluorescence properties within the fibers, thus suggesting potential utility in, for example, sensor fabrication.

Ionic interactions have been used extensively to generate physical and/or chemical cross-links in polymer networks: calcium-mediated cross-linking of alginates,[22] halatopolymers,[23] and a wide range of ionomers,[24] for example, have all found extensive utility for a variety of fundamental and practical applications. The work by Wathier and Grinstaff suggests that ionic networks formed from effectively non-coordinating ionic pairs, in particular those found in ionic liquids, might provide an interesting, and useful, complementary strategy for the formation of networks. The branching of multivalent ions would lead to networks, while the loose coordination of "fatty" ions would allow mobility that facilitates processing and enhances the toughness of the resulting solids. Eventual optimization might therefore lead to an array of materials that combine the mechanical properties found in ionomers with the homogeneity and high charge densities that are typical of ionic liquids.

Several interesting questions remain for future work, for example: what is the extent of network formation? What are the contributions of connectivity/topology versus those arising from variations in the structure of the core ion pairs? To what extent is it appropriate to think of these networks in terms of pairwise but transient interactions? The ability to readily "mix and match" different ions and test the properties of a large range of combinations should provide a large set of data to answer these questions. Helpful, too, will be the significant effort devoted to characterizing and understanding the properties of ionic liquids that do not form networks, and it will be interesting to see under what circumstances the properties of ionic liquid networks, such as those described by Wathier and Grinstaff, reflect the properties of model ionic liquids based on the core ion pairs. Such relationships have been extremely productive in other supramolecular polymer systems,[25] but ionic systems are often prone to phase separation, long-range interactions, and multibody effects that could significantly complicate the structure–activity relationships.

Extending further: what are the thermal properties of the materials (for example, glass and melting transitions), and how do they compare to those of traditional polymers, ionic liquids, and supramolecular polymers? The answers to such questions will address directly the potential advantages in processing and the range of applications for which these materials might ultimately be used. Furthermore, can robust material platforms be developed, into which various functional ionic components could be introduced in small quantities without significantly changing the properties of the platform?

Taken in combination, the recent reports by Armstrong and co-workers[20,21] and Wathier and Grinstaff[19] show that molecular design can have a dramatic impact on the ways that ionic interactions are manifested in bulk properties. The ease of synthesis of the initial systems, the range of properties they exhibit, and the future promise of even greater variety in structure and properties motivate further structure–activity studies and together make a case for increased attention to ionic interactions as a programmable motif in supramolecular synthesis.

[1] For recent books reviewing the field, see *Supramolecular polymers*, 2nd ed. (Ed.: A. Ciferri), CRC, Boca Raton, FL, **2005** and Ref. [2].

[2] *Molecular Recognition and Polymers: Control of Polymer Structure and Self-Assembly* (Eds.: V. Rotello, S. Thayumanavan), Wiley, Hoboken, NJ, **2008**.

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