

Room Temperature Ionic Liquids for Polymer Synthesis

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Chemistry has been dominated by the study of reactions in molecular solvents; however, a new class of solvent has recently been developed- room temperature ionic liquids. In contrast to high melting point ionic compounds like sodium chloride, these ionic compounds are liquid at room temperature. Inefficient packing of the ionic species, caused by the use of bulky, low symmetry organic cations, leads to the depressed melting point.¹ The most commonly encountered ionic liquid cations and anions are shown in Figure 1.



Anions = BF_4^- , PF_6^- , $AlCl_4^-$, NO_3^- , OTf^-

Figure 1

The interest in ionic liquids as a reaction medium has been accelerated by the growing desire for cleaner chemical processes. The emissions of volatile organic compounds and disposal of such solvents during chemical processes are a large source of pollution worldwide.² Ionic liquids, with their negligible vapor pressure, make them attractive, green alternatives to conventional solvents. A wide variety of organic transformations have been demonstrated in ionic liquids, often with increased yields, faster rates of reaction, and greater ease of product isolation.^{3,4}

In the realm of materials chemistry, an obvious extension of this chemistry would be the demonstration of polymerization reactions in ionic liquids. The first polymerization reaction to be demonstrated in an ionic liquid was the Ziegler-Natta polymerization of ethylene.^{5,6} The reaction utilized dichlorobis(η^5 -cyclopentadienyl)titanium(IV) with an alkyl-chloroaluminum(III) co-catalyst in acidic 1-ethyl-3-methylimidazolium tetrachloroaluminate, $[emim][AlCl_4]$, ionic liquid solvent. Yields were low, but importantly, this demonstration of polymerization has prompted subsequent studies of polymer synthesis in ionic liquids.

Cationic polymerization of isobutylene is industrially relevant for the synthesis of poly(isobutylene). For the synthesis of high molecular weight species via cationic polymerization, the propagating cationic species must be stabilized by solvation; however, polar solvents tend to destroy the Lewis acids necessary to initiate polymerization. Additionally, low reaction temperatures are generally needed. As many

ionic liquids display Lewis acidity, they are attractive alternative solvent-catalyst systems. The synthesis of high molecular weight poly(isobutylene) in acidic [emim][AlCl₄] ionic liquid without an additional catalyst has been demonstrated at more convenient reaction temperatures.⁷

Free radical polymerization is the most widely employed polymerization technique in industry due to its insensitivity to monomer type. The free radical polymerization of methyl methacrylate in ionic liquids is the most studied system.^{8,9} Copolymerization of styrene and methyl methacrylate has also been demonstrated in ionic liquids.^{10,11} Considering the homopolymerization of methyl methacrylate in 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF₆], ionic liquid, the resulting polymer achieved higher molecular weights with a faster reaction rate than poly(methyl methacrylate) synthesized in a conventional solvent. The polydispersity of the resultant polymer was unaffected. Additionally, as long as the ionic liquid has been successfully extracted from the synthesized polymer, the materials properties of the polymer are unaffected.⁹ When the ionic liquid is not extracted, the ionic liquid acts as a plasticizer, depressing the glass transition temperature of the polymer.¹²

Condensation polymerization has also been demonstrated in ionic liquids for the synthesis of organic polymers¹³ as well as inorganic polymer networks such as silica aerogels via sol-gel processing.¹⁴ The synthesis of silica aerogels in ionic liquids instead of traditional alcoholic solvent systems allows for longer aging times of the silica network prior to solvent removal. Consequently, supercritical drying is not necessary, eliminating this costly and potentially dangerous procedure from the synthesis. While the synthesis of bulk organic polymers in ionic liquids is motivated by the push for cleaner industrial processes, the synthesis of silica aerogels in ionic liquids is motivated by the prospect of discovering unique advantages to using these new solvents.

This transition has led to the recent synthesis of more advanced inorganic materials in ionic liquids including carbon nanotube-ionic liquid gels,¹⁵ hollow titania microspheres,¹⁶ the MCM-41 zeolite,¹⁷ and nanoparticles.¹⁸ Further research into the unique advantages afforded by ionic liquids is likely to continue for both polymer and advanced materials synthesis.

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