

# Phosphonium cation-containing polymers: From ionic liquids to polyelectrolytes



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## ARTICLE INFO

### Article history:

Received 6 March 2014

Accepted 9 April 2014

Available online 26 April 2014

### Keywords:

Macromolecules

Ionic liquids

Polyelectrolytes

## ABSTRACT

Phosphonium cation-based ionic liquids (ILs) are a readily available family of ILs that often offer superior properties compared to ammonium cation-based ILs. Recently investigated applications include extraction solvents, electrolytes in batteries and super-capacitors, and corrosion protection. At the same time, the range of cation–anion combinations available commercially has also increased in recent years. Polymerized ionic liquids and polyelectrolytes play major roles in a broad range of biological applications including antimicrobials, non-viral gene delivery, synthetic enzymes, metal chelation, and drug delivery. Ammonium- and phosphonium-containing macromolecules will be reviewed with a focus on structure–property relationships of these polyelectrolytes and ionic liquids. Phosphonium-containing macromolecules often display enhanced performance compared to ammonium analogs.

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## 1. Introduction

Recently, ammonium and phosphonium ion-containing polymers have gained technological importance as potential phase-transfer catalysts, anti-static agents, biocides, humidity sensors, and water filtration membranes [1–3]. A larger commercial phosphine library has facilitated the synthesis of low viscosity, high conductivity phosphonium ILs [4]. Nitrogen and phosphorus atoms have significantly different atomic radii and electronegativity that leads to unique cationic structures. Nitrogen has an atomic weight of 14.01 g/mol as compared to phosphorus with an atomic weight of 30.97 g/mol. Thus, phosphorus has a larger atomic radius than nitrogen [5], and electronegativity differences result in a different charge distribution for the corresponding cation. Colby et al. determined the specific charges on each atom for the ammonium and phosphonium cations using *ab initio* calculations [6]. The nitrogen in ammonium cations exhibited a slightly negative partial charge of  $-0.5$  eV, while the surrounding alpha carbons displayed a slightly positive charge of  $0.3$  eV because nitrogen is more electronegative than carbon. Conversely, phosphonium cations contained a reversed charge density because phosphorus is less electronegative than carbon; therefore, the phosphorus atom displayed a partial positive charge of  $+1.1$  eV and the adjacent carbon atoms exhibited a partial negative charge of  $-0.2$  eV. These

differences are expected to markedly alter properties in emerging applications [7].

Due to the difference in the cationic structures, ammonium and phosphonium cation-based macromolecules exhibit different properties. Ammonium ionic liquids (IL) are often limited by their poor thermal stability [4]. On the other hand, phosphonium cation-based ILs potentially offer superior properties, such as higher thermal stabilities, higher conductivities, and lower viscosities compared with the corresponding ammonium ILs. Ammonium and phosphonium ionic liquids degrade through two different pathways under alkaline conditions. The literature proposed different degradation pathways for ammonium polyelectrolytes, predominantly Hofmann elimination and a reverse Menschutkin degradation [4]. Phosphonium cations generally resist Hofmann elimination and Menschutkin degradation, leading to improved thermal stabilities. Ammonium ILs typically degrade through Hofmann elimination, while phosphonium ILs degrade into tertiary phosphine oxides and alkanes [7]. The overall structure of the ammonium or phosphonium cation largely impacts its overall base stability [8,9]. Therefore, many phosphonium-containing macromolecules with improved thermal stabilities as compared to ammonium analogs are also suitable for alkaline fuel cells and anion exchange membranes [1,8,10].

Apart from the enhanced thermal stability, many researchers have examined high flame retardancy of phosphorus-containing macromolecules, ideal for high temperature aerospace and transportation applications. Also, natural occurrence of phosphorus-containing macromolecules in nucleic acids highlights their

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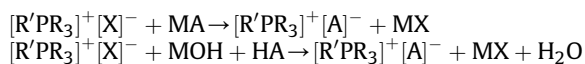
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importance in biological environments. The overall focus of this review is novel phosphonium-containing macromolecules with recent trends as ionic liquids and polyelectrolytes.

## 2. Phosphonium cation-containing polymers as ionic liquids

According to the current convention, ionic liquids (ILs) are salts that exhibit a melting point ( $T_m$ ) below 100 °C; however, this strict definition is often challenged in the literature [11]. These ILs are typically an organic cation (imidazolium, pyridinium, quaternary ammonium, and phosphonium) and an anion such as halide, tetrafluoroborate ( $\text{BF}_4$ ), hexafluorophosphate, triflate, amidotriflate, and bis(trifluorosulfonyl)imide [7,12,13]. The literature has reported significant variation in physical properties among these salts, despite a common cation with different anions e.g. *n*-butylmethylimidazolium with hexafluorophosphate anion [ $\text{C}_4\text{mim}$ ][ $\text{PF}_6$ ] is immiscible with water, whereas the tetrafluoroborate anion [ $\text{C}_4\text{mim}$ ][ $\text{BF}_4$ ] is water-soluble [14]. Seddon described ILs as designer solvents due to variation in physical properties with change in cation or anion [15]. Structural variation enables high thermal stabilities, low vapor pressures, high ionic conductivities, and variable solubility for their applications as potential electrolytes for various electrochemical devices [3,16–26], including rechargeable lithium batteries [27,28], solar cells [29–31], actuators [32–34], and capacitors [35–40] (Fig. 1).

The phosphonium-based ILs are typically produced using two approaches of ion exchange reactions.



where R, R' = alkyl; X = halogen; M = alkali metal; and A = an anion such as phosphinate, carboxylate, tetrafluoroborate, and hexafluorophosphate [4]. Parshall published phosphonium ILs in 1970s using stannate and germanate salts [41–43], and in the 1980s, Knifton et al. used molten tetrabutylphosphonium bromide as an ionic solvent [44–46].

ILs containing a polymerizable functionality enable the polymerization of ionic liquids [38]. Polymerization of IL monomers typically results in reduced ionic conductivities due to immobilization of the cation and a higher  $T_g$  [47], but PILs result in single-ion conductors suitable for electromechanical actuators [48], gas separation membranes [49], and ion exchange membranes [50]. Common ammonium PILs include quaternized poly(2-dimethylaminoethyl methacrylate) [51], poly(vinylbenzyl ammonium)s [52], and poly(diallyldimethylammonium chloride) [53]. Fig. 2 depicts broad potential applications of ILs. Imidazolium ionic liquids are the most common ionic liquids with a broad range of structural diversity through substituent control and counterion structure [54]. Phosphonium cation-based ILs offer a broad range of useful properties and recently received attention in the recent literature [7]. Typically, researchers examine structure–property relationships of ammonium- and phosphonium-containing polymerized ionic liquids to examine the impact of cation structure on macromolecular properties.

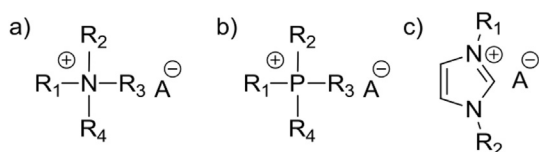


Fig. 1. Example structures of ionic liquids (a) ammonium, (b) phosphonium, (c) imidazolium.

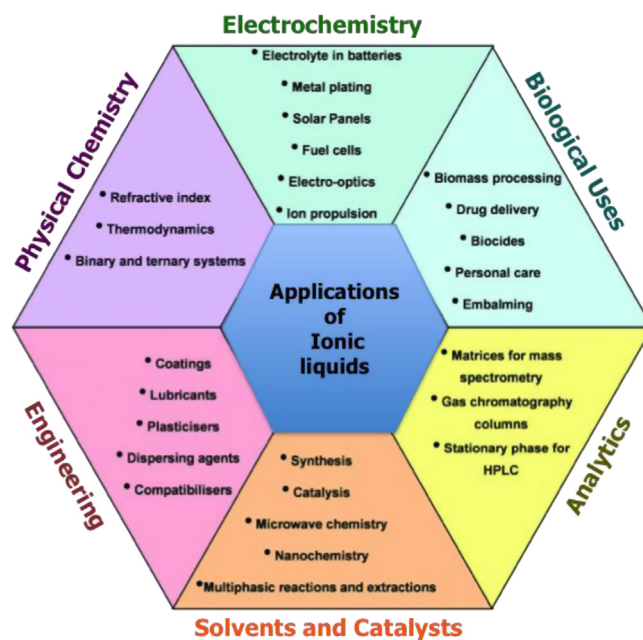


Fig. 2. Applications of ionic liquids [11].

MacFarlane et al. summarized the history, commercial synthesis, and several of the enhanced physical properties of phosphonium ILs as compared to ammonium and imidazolium ILs. MacFarlane also described their superior stability in basic environments, i.e., higher chemical, electrochemical, and thermal stabilities with typical densities less than water. The structural studies concluded that the length and symmetry of the alkyl substituents on the phosphonium cation significantly influenced the physical state, and anion selection favored smaller charge-diffuse ions. Clyburne et al. studied the use of phosphonium ILs as reaction media for strong bases [55,56]. Phosphonium ILs are also under consideration for their application as extraction agents [57,58], where Chen et al. studied the adsorption of Cr(III) and Cr(IV) onto silica-based systems embedded with phosphonium ILs. Their work displayed improved thermal stability, higher metal extraction, and quantitative desorption of chromium ions relative to ammonium IL counterparts. Frackowiak et al. investigated phosphonium ILs for their potential applications as super-capacitors [3]. Their findings suggested that phosphonium ILs provided an enhanced electrochemical window relative to currently available ammonium ILs, while providing suitable capacitance values at reasonable applied voltages and scan rates. Tsunashima et al. also studied the potential of phosphonium ILs as battery electrolytes; their studies revealed that through chemical tuning, the phosphonium IL viscosity reduced to values that provided high discharge capacities relative to ammonium IL counterparts [3,59,60].

Downard et al. discussed the potential for commercialization of phosphonium ILs, citing synthetic procedures, structural tuning through phosphonium-substituent and anion choice, physical properties, and the potential for application-specific materials [4,61,62]. Janus and Stefaniak utilized tri(hexyl) tetradecylphosphonium TFSI as a solvent for the Diels–Alder reaction, and the product was easily distilled from the IL reaction media due to the thermal stability and negligible volatility of the phosphonium IL [63]. Pawar et al. also analyzed tri(hexyl) tetradecylphosphonium chloride as a phosphonium IL reaction media for Michael additions. They also noted the lower potential for chemical side reactions and intermolecular interactions among phosphonium ILs [61].

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