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Polymers and Ionic Liquids

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7.1 Introduction

Ionic liquids (ILs) are inorganic/organic salts possessing elevated ionic conductivity and insignificant vapor pressure, good electrochemical and chemical stability, low flammability, and a melting point less than 100 °C. ILs possess various types of interactions with solutes due to the “dual nature” solvation property [1]. Such interactions include ionic/charge–charge, dispersive, hydrogen bonding, n – π , π – π , and dipolar. In addition, ILs are amenable to dissolving polar and/or nonpolar compounds by tuning their anionic or cationic functions and are miscible with organic

solvents or water. Due to the aforementioned properties, ILs have entirely exhibited their ability in the preparation technique of versatile samples, such as Hollow fiber liquid-phase microextraction (HF-LPME), dispersive liquid-liquid microextraction (DLLME), solid-phase extraction (SPE), single-drop microextraction (SDME), cold-induced aggregation microextraction (CIAME), and in situ solvent formation microextraction (ISFME) [2].

Although ILs were originally used as solvent replacements in green chemistry, they are at the vanguard of confronting emerging global challenges (the production, conversion, and storage of energy, as well as savings in the transportation industry and environmental stewardship). Developing innovative preparation methods for polymerization is essential for the development of novel polymeric materials and subsequently the discovery of solutions for sustainability (future) [3]. Perhaps, researchers seek to advance the platform of materials that contribute to the perception of “function via structural design.” ILs are considered green specialty solvents and functional building blocks in the process of polymerization [4–8], such as polymer additives, biopolymers like cellulose, and enhancer/co-catalysts in polymerization reactions [9] for unprecedented improvements in the physical properties of functional polymers. Because ILs are not only amenable to being incorporated into the macromolecular architecture but also generate a new class of polymeric materials with new functions and properties [10].

Interestingly, multifunctionality of some chemical groups of ILs polymers (with properties impracticable with traditional materials) has shown to be a promising way of synthesizing a novel type of functional materials, which in this document are denoted PILs (polyelectrolytes) [1] and alternatively called poly (ionic liquids) in the scientific literature. These PILs, with an IL moiety in each repeating unit, keep most of the exceptional virtues of ILs, and also possess higher viscosity and thermal stability [11]; as such, compared with ILs, they have demonstrated broader applications in solid-phase microextraction (SPME) [2].

However, there remain some problems in attaining this promise because of the challenges in optimizing the size, distribution, localization, and dispersion of the nanosized components, as well as understanding and tailoring the interfacial role between chemically and structurally disparate phases on bulk properties [12]. ILs were initially used as nanoparticle surfactants and solvents in polymer science [13, 14], and they are now being used as functional additives in polymers. In addition, ILs have been used as compatibilizers or building blocks and proved to have a nanoscale structure with an interesting transition in their properties from the IL into a polymer matrix [11, 12]. Furthermore, the aforementioned properties of ILs open a promising new avenue in the application of ILs in new material production, most especially in industrial applications that use the range of 1–2 wt% of secondary pure ILs, which could also optimize the cost [12]. Therefore, this chapter is aimed at providing a comprehensive overview and detailed discussion of the design, synthesis techniques, characterization, and physicochemical properties of PILs, as well as recent developments and technological implementations. The state-of-the-art approaches and prospects regarding the diverse and unique, properties, true potential, and the utilization of this innovative polymer material are also highlighted.

7.2 Properties of ILs

Diversity is one of the major words that are encountered in IL literature. The term diversity in combinations of anion–cation, purification/preparation mode, diversity mode of use, nature of impurities (quality), diversity of properties, and applications is one of the keywords concerning ILs. The contribution of ILs to the field of polymers as solvent, ligand, stabilizing agent, intermediate/catalyst, and functional compound has more to do with inducing functional groups and improving polymers' functionality, selectivity with new chemistry, and easing the likelihood of separation of catalysts.

In addition to diversity, prediction on rational design or ionic combination of ILs is the other keyword for the end user to estimate a given set of properties; although most previous works certainly relied on the most popular cation (imidazolium cations), it is not the only type. Last decade, ILs of the new class having innumerable other cations have been synthesized. ILs are generally known for having different shaped and sized flexible and asymmetric ions, possessing various dominant types of interactions and are not trivial. Although there remained complicated hypothetical interpretations and treatments, a better understanding of interactions with other species and the properties of ILs is very important to better comprehend their role in the field of polymers [15].

Bearing in mind the versatility and applications of ILs, it is not easy to report their general propensities and conclude their properties. In some cases, emphasis on their variation in the literature could be a source of good data. In this chapter, only a list of critical annotations is discussed (Table 7.1).

PILs, i.e. introduction of anionic (hexafluorophosphate, tetrafluoroborate, and triflates) and cationic functional groups (pyrrolidonium, imidazolium, and pyridinium) into IL functional polymers, lead to the production of a new class of materials with certain properties and fascinating applications (Figure 7.1). Although the definition of PILs is not clear, PILs are polymers synthesized from IL monomers, despite those polymers synthesized from monomers of solid salt (polyelectrolytes). However, PILs are seemed to be polyelectrolytes, i.e. polymers bearing a cationic or anionic (electrolyte) group (Figure 7.2). In addition to intrinsic polymer properties, PILs present some properties reflected by ILs such as chemical stability, ionic conductivity, thermal stability, and tunable solution characteristics.

Classical polyelectrolytes are hydrophilic (aqua-soluble), which makes them dissociate into charged species (polysalts), where the halide anions (Cl^- , Br^- , or I^-) are the most common counteranions. In contrast, due to the reduced columbic interactions and the lipophilic character of counterions (tetrafluoroborate (BF_4^-), fluorinated amides ($(\text{CF}_3\text{SO}_2)_2\text{N}^-$ and $(\text{CF}_3\text{CF}_2\text{SO}_2)_2\text{N}^-$), or hexafluorophosphate (PF_6^-), PILs are soluble in polar organic solvents but not in water. In addition, contrary to metallic counteranions of conventional anionic polyelectrolytes (Li^+ , Na^+ , or K^+), PILs possess organic cationic counterions (alkylpyrrolidonium, alkylpyridinium, dialkyl imidazolium, and tetraalkylammonium). Therefore, PILs are a type of polyelectrolytes resulting in monomers of ILs that are miscible with organic solvents, but not with water. In general, PILs are classified as polycations

Table 7.1 Basic properties of ILs.

Properties	Critical comments	Reason	References
Melting point	Care must be given to the data	The potential presence of impurities and super cooling nature of ILs lead to uncertainty in their melting point	[15]
Volatility	The normal boiling temperatures correlated with 1 atmospheric vapor pressure are difficult to determine experimentally. Nevertheless, at a very low distillation rate ($<0.01 \text{ g h}^{-1}$) and significantly reduced pressure, it is possible to distil ILs at 200–300 °C	Due to the decomposition of ILs at a lower temperature	[16]
Thermal and chemical stability	Although high thermal stability ($>35 \text{ °C}$) of many ILs was determined by previous thermogravimetric analysis, lower values have been reported for long-term stability e.g. ILs based on phosphonium with $[\text{N}(\text{CN})_2]$ or $[\text{NTf}_2]$ anions. However, nitrogen cation-based ILs generate residues as they do not decompose completely	Because of the propensity of the cyano groups in the nitrogen cation to polymerization	[17]
Viscosity	In many applications, the less viscous ILs' design remains a challenging task	Compared to conventional solvents, many ILs demonstrate relatively high (1–3 order of magnitude higher) viscosity	[18]
Nonflammability	As a result of nonvolatility and consequently nonflammability at high as well as ambient temperatures, ILs have been reported as a possible “green” alternative to volatile organic solvents. However, they can replace hydrazine and its derivatives to be used for energetic content (fine-tuned)	ILs are combustible	[11, 19, 20]

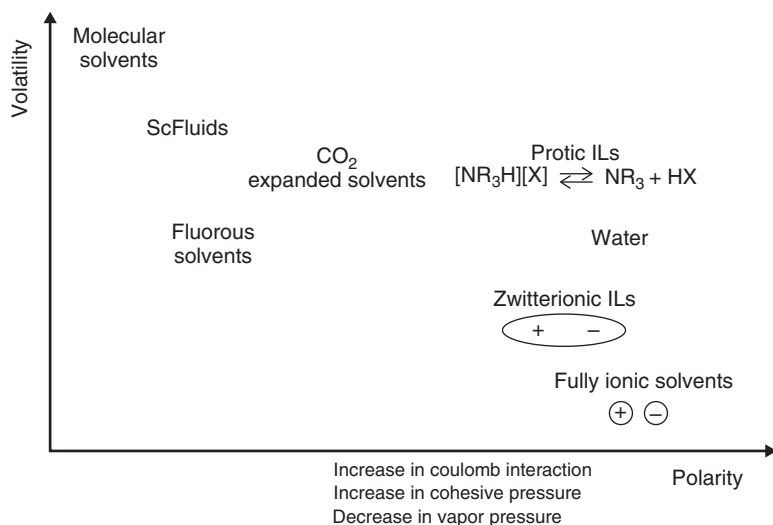


Figure 7.1 Qualitative description for typical volatility and polarity characteristics of alternative solvents. ScFluid, Super critical fluid. Source: Olivier-Bourbigou et al. [15] / with permission of Elsevier.

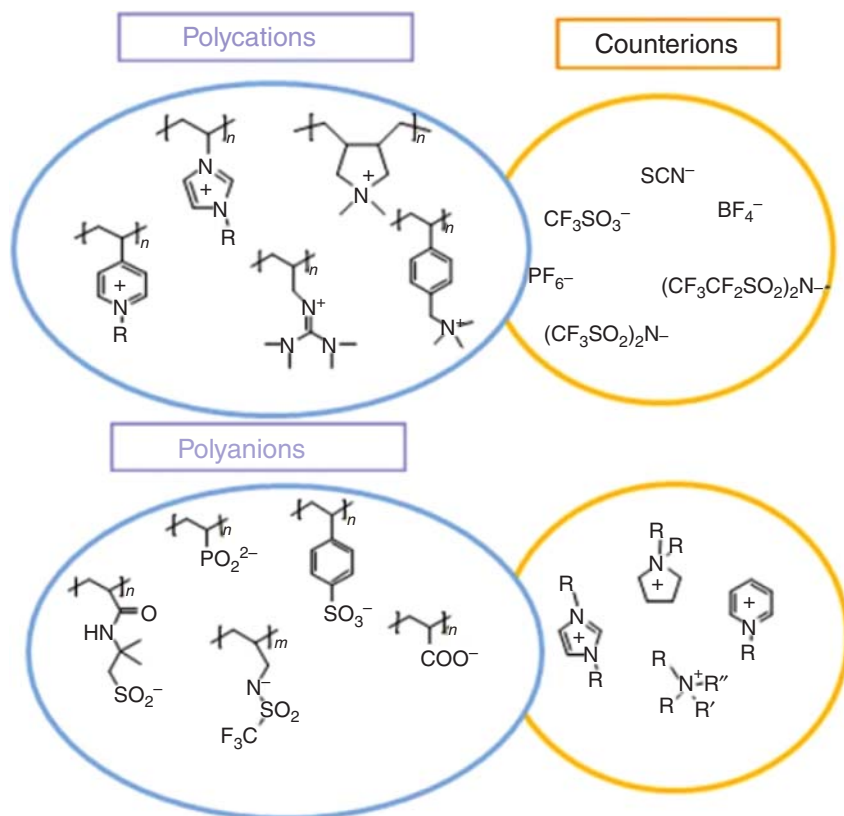


Figure 7.2 Characteristic chemical structures of PILs.

containing the monomer unit with a cationic backbone and polyanions consisting of either a polyzwitterion (both cation and anion) or an anion alone. Besides, PILs can potentially possess diverse types of large molecular architectures (dendritic, branched, or ramified) or copolymers (alternating, random, or block), making the number of synthesized PILs enormously high.

7.3 Synthesis of PILs

As shown in Figure 7.3, for the vinyl imidazolium-based polymers, PILs are synthesized by two main approaches, independent of their natures. In the synthesis of ILs, an aqueous halide anion exchange or metathesis reaction driven by the liquid/liquid phase separation of the formed hydrophobic ILs has been known as the most typical chemical reaction. Perhaps, Ito et al. [21] pioneered the natural approach to synthesizing different types of IL monomers by monomeric cationic 1-vinyl-3-alkylimidazolium-based halide form of anion exchange reaction with different counteranions. Thus, the upper route (direct polymerization of each different IL monomer) has become the main preparation method for the copolymeric or homopolymeric PILs [22]. However, the necessity of monitoring each individual monomer's polymerization conditions as well as the amount of monomer-level organic synthesis and refining stages are the main issues.

Alternatively, a lower route, where the imidazolium monomer polymerization is followed by direct ion exchange into a poly(1-vinyl-3-alkyl imidazolium) chloride-based polyelectrolyte precursor, is the other strategy for the synthesis of PILs. Whereas, the solid PIL precipitation in water obtained after the halide anion exchange by a more hydrophobic counteranion resulted in PILs [23]. Contrary to the first approach, it is easier to synthesize following the second method using monomer polymerization and purification. However, it may show some limitations

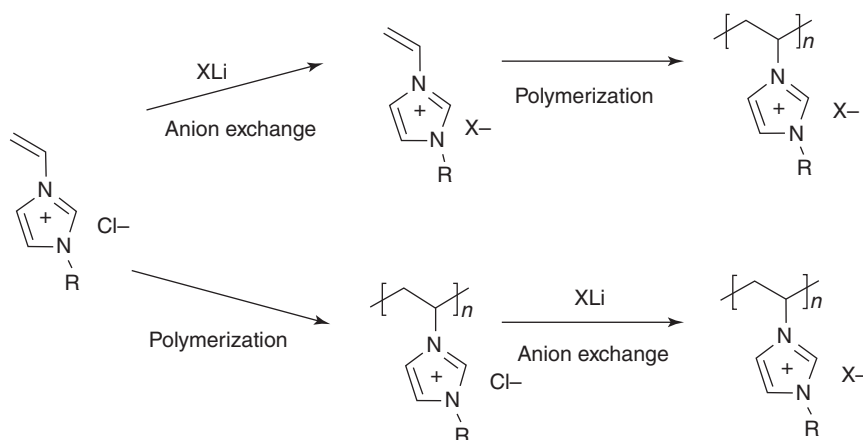


Figure 7.3 Common route of polymeric ionic liquids.

when more complex polymer structures or random copolymers are searched, and the anion exchange reaction is not quantitative [22]. Some common synthetic approaches are described in Table 7.2.

7.4 Types and Application of Common PILs

In recent years, there has been an exponential increment in the number of ILs. A design of such new class ILs with many cations and anions moieties could be explained by diverse motivations. Only some of the most common are given a great deal of attention (Tables 7.3 and 7.4) based on the following remarks:

- Access to ILs having targeted properties resulting from the tunability of anions and cations combinations as well as their modification [79].
- A great deal of consideration has increasingly been devoted to using their chemical properties' synergy due to the task specificity and multifunctionality of ILs [80].
- ILs resulting from starting materials of renewable origin (biodegradable) and low cost have also been the main concern [81].
- There has been a need to develop unique materials from backbone monomers (e.g. imidazolium) of carbon nanotubes or functional silica gels with flexible properties.
- When process developments are proposed, the recyclability of ILs becomes one of the core issues. Besides, designing ILs with low thermal stability or those that are distillable under relatively normal conditions of temperature and pressure has to be considered [82].

7.5 Conclusion

ILs have been known to play an imperative role in the field of polymer science. In this chapter, we have shown that physicochemical properties, chemistry, and application of ILs and polyelectrolytes are broadened by the invention of PILs (ionic polymers) due to the incorporation of new cations and anions in the IL backbone. Indeed, their use as multifunctional agents, ranging from additives or building blocks in material science, electrolytes in electrochemical devices, surfactants or emulsifiers, nanocomposite, plasticizers, gas membranes, processing aids, and smart surfaces act as a new means to the blueprint of high-performance materials. Although this chapter presents “magic” properties of PILs in delivering outstanding ultimate properties for the polymeric materials, there remain several limitations to be conquered, for example: (i) an improved understanding of the physicochemical properties; (ii) reaction between matrix polymers and ILs; (iii) outcome of different ions in the polymer properties; (iv) the expenditure and the ease of access of the original IL structure; and (v) the curiosity of work on combinations of multifunctional PILs.

Table 7.2 Synthesis of PILs with different moieties in their polymer backbone.

Polymer backbone	Moieties	Synthetic approach	Counterion	Cation/anion monomer	References
Vinyl, styrene, ethylene glycol, (meth)acrylic, vinyl ether, (meth)acrylamide, norbornene	Cationic	Chain growth polymerization	Tetrafluoroborate, hexafluorophosphate, triflate, nitrate, alkylsulfonates, bis(trifluoromethane) sulfonimide	Imidazolium	[23–28]
Vinyl, styrene or methacrylic	Cationic	Radical polymerization	Dicyanamide, iron tetrachloride and perchlorate	Tetraalkyl ammonium, pyridinium, pyrrolidonium, guanidinium, or piperidinium	[29–40]
Cross-linked (acryl, styrene [bi- or trifunctional])	Cationic	Radical polymerization with thermal or UV radical curing	Halide and bis(trifluoromethane) sulfonimide	Imidazoliumdiacrylate and distyrenic and vinyl, tetraalkylammonium difunctional styrenic	[40–43]
Poly(pyrrole) poly(alkyl-thiophene), and poly(ethylene dioxathiophene)	Cationic	Chemical (electrochemical)oxidative polymerization	Tetra fluoroborate, chloride, hexafluorophosphatebromide, and bis(trifluoromethane) sulfonimide	Pyrrole, thiophene	[44–49]
Poly(vinyl sulfonate), poly(acrylic acid), poly(styrene sulfonate), poly(phosphonic acid, and poly(acrylamido)-2-methylpropane sulfonate	Anionic	Conventional radical polymerization	Long tetraalkylammonium, ialkylimidazolium, tetraalkylammonium, or alkyl-imidazolium	Styrenic or vinyl (meth) acrylate	[49–51]
Poly(acrylic acid), poly(styrene sulfonate)s, poly(phosphonic acid	Zwitterionic	Radical polymerization	—	Sulfonate, or alkoxydicyanoethenolates, or trifluoromethanesulfonamide anions together with tetraalkylammonium or imidazolium cations	[52–57]
Polyacrylamide, poly(isopropylacrylamide), poly(acrylic acid) or poly(methyl methacrylate)	Random and block copolymers	Random copolymerization	—	Imidazolium	[58, 59]

Table 7.3 Types, properties, and advantages of PILs.

Type	Example	Counterion	Properties	Advantage	Application	References
Protic ionic liquids (PILs)	[EtNH ₃][NO ₃]	Thermal instability	Consist very strong acids (HNTf ₂). As a result, the equilibrium moves right. Hence, ILs of entirely ionic salts are produced	Cost-effective Ease of preparation and with no residual byproducts	Particularly applied in catalysis due to their inertness relative to organometallic compounds, chromatography	[60, 61]
PILs	Polyamidoamine (hyperbranched dendrimer polymers) and hydrophilic monodispersed based ILs	Decomposition of some protonated salts (imidazolim) at low temperatures	Hydrophobic IL with low T_m of which results from the flexible nature of the dendritic backbone ($T_m = 2.58^\circ\text{C}$)	Thermal degradation (near 350°C) Conductivity	Use as proton-conductive electrolytes, suitable for particles encapsulation	[62]
(Multi)-functional (solvent, acid, or base function)	ILs with chloroaluminates, or chlorozincate, chloroferrate anion	In the presence of an organic phase, some acid leaching is expected	In the presence of protons, they exhibit potential super acidity and Lewis acidity	Anion (e.g. chloroferrate) associated with [NEt ₃ H] ⁺ generates easily and cheap promoting acidic catalysts It is possible to induce Brønsted acidity by adding HF or HCl (Brønsted acids) into halide-based ILs	Catalysis and or solvent	[63, 64]

Table 7.3 (Continued)

Type	Example	Counterion	Properties	Advantage	Application	References
Chiral ILs (CILs)	Ammonium, guanidinium, imidazolium and phosphonium	Loss of enantioselectivity when supported on inorganic materials	CILs tentatively been supported on inorganic material are amenable to synthesizing chiral camphor sulfonamide-incorporated highly ordered mesoporous functional organosilicas	The cationic hydroxy functionality demonstrates an imperative role in the enantioselectivity	Chromatographic and spectroscopic applications Asymmetric catalysis as sole chirality inducer and as chiral solvents	[65–67]
Switchable-polarity solvents (SPS)	Carbamate	Reactivity of the base	SPS can be considered as neutral liquids that convert to polar ionic liquids in the presence of CO ₂ and reverse to neutral liquids when exposed to N ₂ , heat, or argon gas	Recyclable	Post-reaction separation of the homogeneous catalyst from the product	[68–70]

Table 7.4 Application of ionic liquids.

Application	Example	Use	Challenge	References
Ionic conducting agents for polymer electrolytes	Poly(ethylene oxide) (PEO), poly(vinylidene fluoride) (PVDF) including its copolymers, poly(acrylonitrile) (PAN), and poly(methyl methacrylate) (PMMA)	Exhibit flexibility essential for polymeric electrolytes, high mechanical strength, room-temperature ionic conductivities, and transparency of electrolyte	There remains a real challenge on the development of membranes with excellent ionic conductivities and good mechanical properties	[60, 71, 72]
	Imidazolium- and pyridinium-based ILs	Enhance dynamic mechanical properties and curing behavior of epoxy prepolymers cured with 4,4'-methylene-bis-3-chloro-2,6-diethylaniline (MCDEA). Their degradation products could also represent an extra curing agent for epoxy systems	»	[73, 74]
Structuration agents of polymer matrices	ILs based on pyridinium and imidazolium, and ILs of phosphonium in fluorinated matrices	Functional building blocks incorporated to design a nanostructured phase (originated matrices) with excellent mechanical properties	More studies have to be conducted to find the proper association between the particular IL and the choice of the matrix	[75–78]
	Tetraalkylphosphonium cation-based ILs combined with bistriflimide (IL–TFSI), chloride (IL–Cl), and bis-2,4,4-(trimethylpentyl)phosphinate (IL–TMP) anions	Formation of ionic clusters in poly(butylenes adipate-co-terephthalate) matrix. The hydrophobic nature led to significant improvement in the vapor–water permeability due to the long alkyl chains on the phosphonium cation	»	

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