IONIC LIQUIDS AS GREEN SOLVENTS-POLYMERIC AND CATALYTIC APPLICATIONS- A REVIEW

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ABSTRACT

Ionic liquids are usually defined as organic/inorganic salts with a melting point lower than 100^0C. The introduction of novel ionic moieties, cations and anions, is extending the properties and traditional applications of polyelectrolytes. This is giving rise to a latest family of functional polymers with particular properties and new applications. The first part of this review will focus on the applications of these polymers such as polymer electrolytes in electrochemical devices. This second part gives a survey on the latest representative developments and development concerning ionic liquids, from their fundamental properties to their applications in catalytic processes.

Key Words: Ionic liquids, polyelectrolytes, Catalytic Processes.

INTRODUCTION

Ionic Liquids (ILs) have fascinated rising interest in the last decades with a diversified range of applications. The types of ionic liquid available have also been extended to include new families and generations of ionic liquids with more specific and targeted properties. This mounting interest has led to a number of reviews on their physico-chemical properties, the design of new families of ionic liquids, the chemical engineering and the wide range of arrangements in which ILs have been utilized and pilot or industrial developments[1]. Although originally, most of the research and industrial activities related to ILs were associated to their applications in green chemistry[2]as substitutes of volatile organic solvents, ILs have been finding an increasing number of applications in other technological fields such as catalysis[3], organic and polymer chemistry, electrochemistry[4,5], analytical chemistry[6], energy[7], nanotechnology[8] and biotechnology[9], among others. In the case of polymer science[10], ILs are being investigated as green solvents in polymerization processes[11], as specialty solvents of biopolymers like cellulose[12], as co-catalysts/initiators in polymerization reactions[13,14], as area of expertise polymer additives and in the development of functional polymers[15–17]. fascinatingly, functionalization of polymers having some of the chemical groups of ILs has been pursued as a way of developing a new class of polyelectrolytes which here we will name polymeric ionic liquids (PILs) also named in the scientific literature as poly(ionic liquid)s. It is the aim of this review to get a close and absolute view to the synthetic methods, physico-chemical properties and technological applications of these new polymers. During the last few years, the introduction of the functional groups associated to ILs (i.e. cations such as imidazolium, pyrrolidonium, pyridinium and anions such as tetrafluoroborate, hexafluorophosphate, triflates) into functional polymers is giving rise to a new family of materials with particular properties and interesting applications. By looking at their chemical structure, PILs are polyelectrolytes, polymers whose repeating unit bear an electrolyte group (cation or anion). Although there is not a clear definition for PILs, we will consider those polymers synthesized from IL monomers in opposition to polyelectrolytes which are synthesized from solid salt monomers. PILs present some of the unique properties of ILs (ionic conductivity, thermal stability, tunable solution properties and chemical stability) together with the intrinsic polymer properties. Contrary to classic polyelectrolytes which are water soluble and dissociate in aqueous solutions making the polymers charged (polysalts), most PILs are not soluble in water but in polar organic solvents. This is mainly due to the hydrophobic character of the counter-ion and the reduced columbic interactions. As illustrative examples, in the case of classic cationic polyelectrolytes the common counter- anions are halide anions such as Cl^-, Br^- or I^-. As in the case of polyelectrolytes, PILs can be classified as polycations bearing a cation in the backbone’s part of the monomer unit, polyanions bearing an anion or polyzwitterions having both anion and cation. Further- more, different types of copolymers (random, alternating, block) and macromolecular architectures such as branched, dendritic or ramified structures are potentially possible. This makes the number of PILs that can be synthesized extremely high due to all of the potential combinations between cations, anions and different polymer backbones and architectures. Thus, this review will only present the actual reported PILs and its applications which will be further developed in the future depending on the scientific curiosity of the scientists and the future technological interest on these functional polymers.

2. Applications of polymeric ionic liquids: In analogy to the case of ILs, PILs are finding applications in many different technological fields such as energy and environmental applications, analytical chemistry, materials science, biotechnology, catalysts or surface science among others. In the next section the main reported applications of PILs will be described.

2.1 Polymer electrolytes for electrochemical devices: Without doubts, one of the main applications of monomeric ILs is found as electrolytes in electrochemical devices. Thus MacFarlane et al. demonstrated that IL based electrolytes radically improved the performance, speed, cyclability and long-term stability of electro chromic devices and actuators[18]. Further works extended the application of ILs to other electrochemical devices such as lithium batteries, dye sensitized solar cells, fuel cells, super capacitors, light-emitting electrochemical cells and field effect transistors. However, liquid electrolytes do present some drawbacks hard to overcome, such as need of encapsulation due to leakage of the electrolyte. On the other hand, an all-solid state polymer electrolyte has important advantages including mechanical stability, safety and simple processing, but their conductivity is still insufficient for practical use. For these reasons, there is an increasing interest in designing polymer electrolytes composed of polymer matrices and ILs, so-called gel electrolytes or ion gels. Thus several commercial polymers have been used for mixing them with ILs such as poly (ethylene oxide), poly (methyl methacrylate) or poly (vinylidene fluoride) copolymers. However, depending on the type of IL and their relative amount different problems such as leakage, phase separations, electrode delamination or bad mechanical properties are found. At this respect, PILs are ideally suited to develop tailor-made polymer electrolytes due their similar chemical structure than ILs.

2.2. Polymeric surfactants in the synthesis of conductive polymer organic dispersions: Polypyrrole (PPy), polyaniline (PANI) and poly (3, 4- ethylenedioxythiophene) (PEDOT) organic dispersions have been prepared using PILs as stabilizers. The synthetic method takes advantage of the solubility change of the cationic PIL which occurred after anion exchange. As illustrated in Fig. 15 for PEDOT, in a first step an aqueous dispersion is prepared by polymerizing the corresponding monomer in the presence of a PIL such as poly (1-vinyl-3-ethylimidazolium bromide). By addition of bispentafluoroethanesulfonimide lithium salt, the PIL stabilizer becomes insoluble and precipitates in water trapping the conducting polymer micro particles. The recovered powders can be dispersed in a variety of organic solvents where the PIL becomes soluble such as ace- tone, acetonitrile, butyrolactone, methylene carbonate, dimethylformamide or dimethylacetamide. As a result PPy, PANI or PEDOT dispersions in organic solvents were originally obtained[19]. The properties of the PEDOT/PIL layers can be tuned depending on the final applications by changing the reaction conditions, the relative amount of PEDOT or PIL stabilizers and the molecular mass of both polymers[20–23].

3. Overview of Catalytic applications: Since the early days of ionic liquids in electrochemistry, the scope of their applications has been extended to many domains and is now much broader than assumed. Following this tremendous development associated with the commercial avail- ability of ILs, the industrial applicability of ILs rapidly appeared as an important aspect as demonstrated by the accelerating number of patents associated with the keyword IL. The patents (and publications) often describe numerous applications such as catalysis with increased rates and yields, recovery of catalytic systems, use of ILs as solvents that can reduce environmental impacts and that lead to more energy-efficient separation. ILs appeared as novel solutions to the chemical industry. However, despite these significant benefits, their translation into viable industrial processes is far from being obvious and the industrialization of IL technologies is rather slow, particularly in the field of catalysis. For the industrial use of ILs, some major issues must be addressed such as IL synthesis scale-up, purity, stability, toxicity, recycling, disposal and price and may constitute barriers to IL process commercialization. Several pilots or industrial processes using ILs were nevertheless publicly announced. It is probable that some other processes have been developed but the information has not been made public. In recent literature, good reviews describe these examples in a fully detailed manner[24, 25]. Some of other catalytic applications are dimerization and oligomerization of olefins, IL as solvent and Ni-co-catalyst[26,27], Oligomerization of olefins for synthetic lubricants production[28], Friedel-Crafts alkylation and acylation of aromatic hydrocarbons, IL as solvent and catalyst Friedel-Crafts acylation of aromatic hydrocarbons[29],Alkylation of olefins with isobutane: IL as solvent and acid catalyst[30,31], Chlorination and fluorination reactions[32] and Ether cleavage[33].

3. CONCLUSIONS

In the last years, polymeric ionic liquids are broadening the chemistry, physico-chemical properties and applications of conventional polyelectrolytes. The introduction of new cations and anions is producing the renaissance of the field of ionic polymers. Although an important number of new polymers have been already synthesized as summarized in this review, the potential for innovative polyelectrolytes is extremely high due to the new types of ions which are being developed coming from the ionic liquid area and the recent advances in precise/controlled polymer chemistry. Developments of new copolymers, dendritic or supramolecular may be around the corner. However, a better understanding of their physico-chemical properties is still necessary. As point out here, they are still a lot of open questions related to the effect of the different ions in the polymer properties. In case of catalytic applications, we try to give a general overview of what can be done. In this context, many topics have not been broached while being the object of much interest.

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