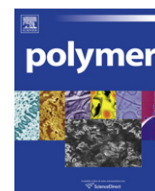




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Feature Article

Poly(ionic liquid)s: Polymers expanding classical property profiles

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ABSTRACT

In recent years, polymeric/polymerized ionic liquids or poly(ionic liquid)s (PILs) were found to take an enabling role in some fields of polymer chemistry and material science. PILs combine the unique properties of ionic liquids with the flexibility and properties of macromolecular architectures and provide novel properties and functions that are of huge potential in a multitude of applications, including solid ionic conductor, powerful dispersant and stabilizer, absorbent, precursor for carbon materials, porous polymers, etc. So far, the preparation of PILs with various forms in cations and anions has mostly focused on the conventional free radical polymerization of IL monomers. Recent progress in the preparation of PILs *via* controlled/"living" radical polymerizations points out an unprecedented opportunity to precisely design and control macromolecular architecture of IL species on a meso-/nanoscale within a polymer matrix. There are also newly emerging polymerization techniques that have appeared for the preparation of PILs which have further pushed the limit of the design of PILs. In this review, we try to summarize the current preparative strategies of PILs, providing a systematic and actual view on the polymer chemistry behind. A discussion of the properties and applications of PILs constitutes the second part of this review.

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1. Introduction

The first publication describing an ionic liquid (IL) is about 100 years ago, in 1914 by Paul Walden, who observed the special physical properties of ethylammonium nitrate ([EtNH₃][NO₃]; mp 13–14 °C) [1]. Although this discovery of a new class of materials did not draw much interest at the time, today it is generally acknowledged as the starting point of the field of ILs. The widely accepted definition of ILs is that these are substances that are composed of cations and anions which melt below 100 °C [2].

Most ILs are monovalent, and their liquid character is derived from a judicious choice of ionic structures which have weak tendencies to coordinate with oppositely charged ions, low intermolecular interaction and asymmetric chemical structures. Despite this simple definition, the family of ILs is very broad, because there are many known and potential cations and anions. Common IL cations include imidazolium, pyridinium, alkylammonium, alkylphosphonium, pyrrolidinium, and guanidinium. Generally, it is believed that the anion influences the properties of an IL substantially. It can be selected from a broad range of inorganic and organic species. Frequently used inorganic anions include halides, mineral acid anions, polyatomic inorganics (PF₆⁻, BF₄⁻), polyoxometallates, etc. Organic anions can be hydrophobic (like bis(trifluoromethylsulfonyl)-

imide (TFSI⁻)) or hydrophilic. Fig. 1 sketches the most commonly used cations and anions. The expanding research interest on ILs stems from the unique properties of ILs, such as high ion conductivity, thermal stability, non-flammability, high heat capacity, negligible volatility at room temperature, and strong polarizability and solubilizing effects.

Polymeric/polymerized ionic liquids or poly(ionic liquid)s (PILs) refer to a special type of polyelectrolytes which carry an IL species in each of the repeating units. Thus, the cationic or anionic centers are constrained to the repeating units in the polymer chain. It is worth noting that although ILs are in a liquid state near room temperature, PILs are in fact solid in most cases, except a couple of exceptions [3]. Nevertheless, as opposed to solid polyelectrolytes, PILs have a reportable glass transition temperature in most cases, being well below usual ionic glasses.

PILs have stirred great interest in the fields of polymer chemistry and materials science, not only because of the combination of the unique properties of ILs with the macromolecular architecture, but also a matter of creating new properties and functions. The major advantages of using a PIL instead of an IL are the enhanced mechanical stability, improved processability, durability, and spatial controllability over the IL species. The initial research of PILs could be dated back to 1970's when the free radical polymerization of cationic vinyl monomers was an area of increased interest [4–6]. Vinylpyridinium and vinylimidazolium salts attracted special attention due to the positive charge being on an aromatic ring and adjacent to the vinyl groups [7–16]. PILs regained considerable

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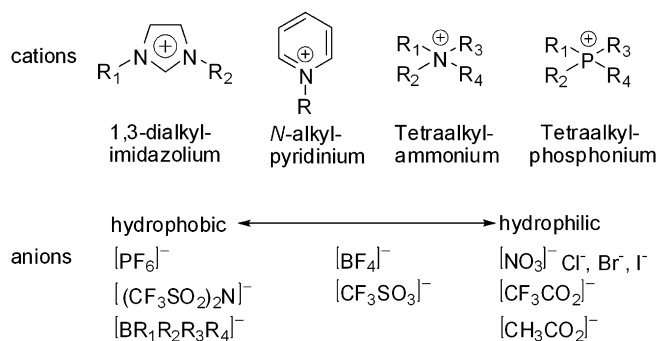


Fig. 1. Most commonly used cations and anions in the formation of ILs.

interest around 2000, following the work performed by Ohno et al. in pursuit of solid electrolytes that could potentially substitute IL for electrochemical applications [17–27]. The intensive studies on PILs in the last five years significantly expanded the research scope of PILs. New structures, properties and applications have been spotted, which in turn provide several valuable branches for researchers [28–36]. Very recently there has been one review on PILs by Firestone et al., which summarized several applications of PILs [37]. Meanwhile, three other reviews by Long and Texter et al., which discussed partially the synthesis of some poly(ionic liquid)s and introduced the application of ILs, especially imidazolium-based ILs in the field of polymer science [38–40]. The rapid progress and explosive development of research activities in this field as reflected by the very large body of recent publications indicates that it is the time to update the status of PILs, especially the state-of-the-art synthetic strategy. In this feature article, we try to catch the field again by presenting a systematic view on the synthesis of PILs, and briefly introduce their properties and applications in various fields.

2. Synthetic strategy

PIL can be synthesized via two basic strategies: (1) direct polymerization of IL monomers, (2) chemical modification of existing polymers. In each strategy, a couple of polymerization techniques are involved, such as conventional and controlled radical polymerizations, ring opening metathesis polymerization, step-growth polymerization, and many more. From a synthetic perspective, each of these strategies as well as the polymerization techniques governs different structural parameters of PILs, and demonstrates distinct advantages as well as limitations with respect to the molecular design. In the following chapters, a comparative view of the synthesis of PILs is presented. We pay special attention to imidazolium-type PILs, whose characters are presumably most widespread and under intense investigation in the field at moment.

2.1. Polymerization of IL monomers

An IL monomer is an IL in which one or more polymerizable units are incorporated. The polymerization of IL monomers is a conceptually simple, intuitive, straightforward, and widely adopted strategy to prepare PILs in many research groups. Fig. 2 illustrates five basic forms of IL monomers. In an IL monomer, a polymerizable unit can locate either on the cation (Fig. 2A) or anion (Fig. 2B), depending on the desired polymeric architecture. The IL monomer with a polymerizable unit on the cation (Fig. 2A) is so far the dominant form. IL monomers with two polymerizable units separated in the cation and anion (Fig. 2C), or located on the cations (Fig. 2D and E) have also been reported to build up PIL networks. The polymerization of an IL monomer results in a homologous

polyelectrolyte possessing the same type of IL moiety in each repeating unit. Copolymerizations of an IL monomer with a common comonomer have been applied to tune the distribution of the IL species along the polymer chain and modify the physical properties of PILs.

2.1.1. Free radical polymerization

Since the 1990s, the group of Ohno has constantly been devoted to the synthesis of PILs via free radical polymerization of various types of IL monomers, aiming at a solid ionic conductor. Their pioneering research work has brought intensive studies of PILs in various directions. To date, conventional free radical polymerization of IL monomers remains the key method to prepare PILs. Its popularity lies in the great tolerance of a radical polymerization toward impurities, moistures, and other active and functional groups. It is well-known in industry and academia that ILs are excellent solvents for many chemicals and material, and especially of higher polarity. Accordingly, ILs may contain hard-to-separate impurities from their synthesis and appear light yellow in spite of the absence of chromophores in their chemical structures. As ILs possess negligible vapor pressure, distillation as a widespread method to purify reagents is unrealistic for IL monomers. This is the main obstacle to polymerize IL monomers via ionic polymerization techniques that are highly sensitive to impurities. This sensitivity holds especially true for hydrophilic IL monomers, in which trace amount of moisture coexists even after careful purification. All these concerns favor a polymerization technique, in which the propagating species are tolerant to impurities and moisture, that is the radical polymerization technique.

2.1.1.1. Homopolymerization. The IL monomers used in free radical polymerizations have overwhelmingly a polymerizable unit in the IL cation in three standard forms—a (meth)acryloyl, styrenic or N-vinylimidazolium group. In the following chapters, these three types of IL monomers are introduced in detail.

2.1.1.1.1. (Meth)acryloyl-based IL monomer. A general approach for the preparation and polymerization of (meth)acryloyl functionalized IL monomers is accomplished in a three-step synthetic protocol, as illustrated in Fig. 3. In the first step, a (meth)acryloyl group is introduced by treatment of a hydroxyl-containing halo-alkane with (meth)acryloyl chloride resulting in the formation of the corresponding ester. In the second step, the halo-alkane bearing the (meth)acryloyl moiety reacts with an N-alkyl imidazole molecule, and the quaternization reaction yields the (meth)acryloyl-based IL monomers with a dialkylimidazolium cation covalently connected to the (meth)acrylate part. In the third step, the formed (meth)acryloyl-based IL monomer is thermally polymerized similar to other common (meth)acrylates in the presence of initiators, such as 2,2'-azo-bis-isobutyronitrile (AIBN). In literature, widespread attention has been drawn to this kind of IL monomers. Their synthesis and polymerization have been often reported [18,24,33]. They differ from each other in the variables of (1) the spacer between the (meth)acryloyl and imidazolium groups, (2) the alkyl chain on the imidazolium ring, and (3) the anions. From a structural point of view, these variables allow one to modulate the chemical and physical properties of IL monomers and PILs. For example, Texter et al. reported a surfactant IL monomer with a rather long alkyl spacer and a methyl group as the choice of dialkyl moieties, which can be used as surfmer in microemulsion of methyl methacrylate (MMA) [41].

Although it is prevalent to confine the (meth)acryloyl group on the cation, there are several examples in which it is separated from the cation. Firestone et al. reported the synthesis of an IL monomer consisting of an acrylate-type anion and a 1-decyl-3-methyl-imidazolium cation. The monomer was synthesized by a metathesis

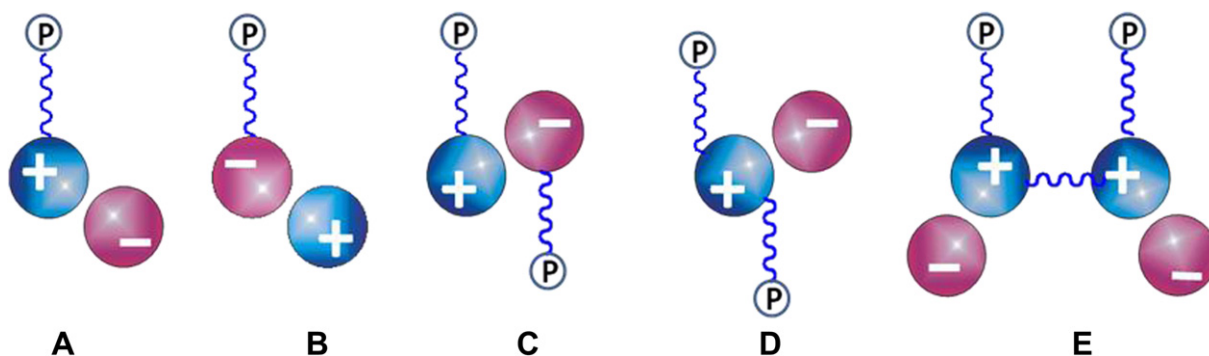


Fig. 2. Basic IL monomers. “p” represents a polymerizing unit in an IL monomer.

reaction involving the treatment of an aqueous solution of 1-decyl-3-methylimidazolium bromide with silver acrylate [42]. Snow et al. reported the preparation of a viscous liquid-like PIL from an IL monomer in which the methacryloyl group was localized in the anion [3]. The formation and polymerization of this IL monomer is depicted in Fig. 4. The polymerizable component is a 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) monomer which is a crystalline compound with a melting point of 192 °C. It is converted to a liquid ammonium salt by addition of an equimolar quantity of tris[2-(2-methoxyethoxy)ethyl]amine. This tertiary amine was selected since (1) it solvates the AMPS monomer without the need of a solvent; (2) the oxyethylene substituent could shield the protonated ionic center from coordinating with the sulfonated anion, thereby depressing the glass transition temperature to -57 °C. Following the formation of the liquid ammonium sulfonate monomer, AIBN was directly added and initiated the polymerization at 70 °C, resulting in a PIL that is a clear acetone-soluble viscous liquid. It is worth noting that this PIL is the first reported example of a PIL that is also an IL.

2.1.1.2. N-vinylimidazolium-based IL monomer. N-vinylimidazolium-based IL monomers are prepared via a simple one-step quaternization reaction of N-vinyl imidazole with a halo-alkane compound. In these monomers, the positively charged imidazolium ring is directly connected to a vinyl group. Free radical polymerization of the N-vinylimidazolium-based IL monomers runs straightforward in the presence of a thermal initiator (Fig. 5). A unique feature of PILs derived from N-vinylimidazolium-based IL monomers is the availability of a high content of imidazolium moieties by selecting a short alkyl chain like a methyl or ethyl group. This is of huge interest when the function or performance of PILs is directly related to the content of imidazolium moieties.

The structural variables in this monomer family are the alkyl chain and the anion. Salamone et al. have studied the polymerization of 1-vinyl-3-alkylimidazolium iodide with different length scale of the

alkyl chains in aqueous solution [11]. The solubility of the resulting polymeric solutions was found to be related to the length of the alkyl chain. For the homologous alkyl iodide series, the short alkyl-chain PILs of poly(3-methyl-1-vinylimidazolium iodide) and poly(3-*n*-propyl-1-vinylimidazolium iodide) were readily soluble in water. The intermediate alkyl-chain PILs of poly(3-*n*-hexyl-1-vinylimidazolium iodide) and poly(3-*n*-heptyl-1-vinylimidazolium iodide) were on the contrary completely insoluble in water. On the other hand, the long alkyl-chain PILs of poly(3-*n*-dodecyl-1-vinylimidazolium iodide) and poly(3-*n*-hexadecyl-1-vinylimidazolium iodide) gave opaque solutions which frothed easily. From these solutions, it was indicated that the short alkyl-chain PILs were hydrophilic whereas the long alkyl-chain PILs were sufficiently amphiphilic to enable micellization of the macromolecules in aqueous solution such as polysoaps. The intermediate alkyl-chain PILs were apparently not sufficiently flexible to allow the formation of polymeric micelles through the hydrophobic intramolecular or intermolecular interactions of the pendent alkyl chains.

Anion exchange is another efficient method to modify the N-vinylimidazolium-based IL monomers. By replacing halide with TFSI^- or PF_6^- , IL monomers may become hydrophobic enough to precipitate out of water. Related to this, Mecerreyes and co-workers examined the synthesis of 1-vinyl-3-ethylimidazolium and 1-vinyl-3-butylimidazolium halide monomers and carried out their bulk polymerization in chloroform [43]. The solubility characteristics of the polymers were tuned by anion exchange in the presence of excesses of salts (BF_4^- , PF_6^- , CF_3SO_3^- , $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, $(\text{CF}_3\text{CF}_2\text{SO}_2)_2\text{N}^-$, ClO_4^-) producing polymers that ranged from hydrophilic to hydrophobic. In another interesting study, Ritter et al. showed that a hydrophobic N-vinylimidazolium-based IL monomer with bis(trifluoromethylsulfonyl)imide (TFSI) as anion could be easily transferred into aqueous solution in the presence of β -cyclodextrin due to the formation of host-guest complexation between the hydrophobic anion and β -cyclodextrin. It was found that the uncomplexed IL

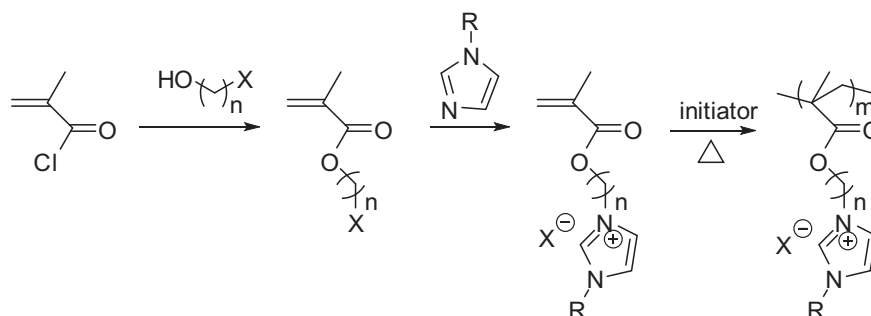


Fig. 3. General synthetic route to PILs from methacryloyl IL monomers bearing an imidazolium species. (R: alkyl chain; X: halide).

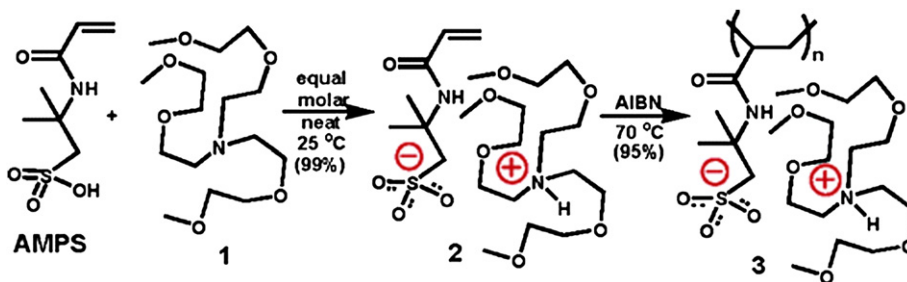


Fig. 4. Reaction scheme for AMPS oxyethylene ammonium salt monomer and polymer [3]. Reprinted with the permission of ACS.

monomer was easily polymerized in organic solvents like tert-butanol, however the complexed IL monomer could not be polymerized due to the spatial ion pair separation which led to quasi “naked vinylimidazolium cations” caused by the complex formation. Only after the addition of a foreign salt did a polymerization take place [44].

For some anions such as nitrate and dicyanamide that less impact the hydrophobicity of IL monomers, the anion exchange process can be assisted by silver salts. However, the type of starting silver salts is limited and as such expensive; sometimes the complete removal of the by-product (silver halide) becomes problematic. In pursuit of a direct synthesis of halide-free N-vinylimidazolium-based IL monomers, several attempts have been performed. In an example demonstrated by Ohno et al., a neutralization reaction of N-vinylimidazole with a corresponding acid was carried out to synthesize IL monomers in a single step (Fig. 6) [21]. An IL monomer with tetrafluoroborate anion was prepared by reacting N-vinylimidazole with tetrafluoroboric acid in a mixture of water and ethanol. The preparation process is quite easy, generating no by-product and can be extended to other acids, such as hexafluorophosphoric acid. In this case, a non-halide anion is incorporated in the N-vinylimidazolium-based IL monomer simultaneously with the formation of an IL monomer without the aid of silver salts.

2.1.1.1.3. Styrenic IL monomer. Styrene or styrenic monomers are archetypes in polymer chemistry and industrial production. IL monomers with a styryl group have been intensively studied by Gin, Noble, and Shen et al. [45–47]. The monomers can be easily obtained by reacting 4-chloromethyl styrene with imidazole through a simple quaternization reaction (Fig. 7). This reaction is favorable as 4-chloromethyl styrene is a commercially available product. Polymerization of the styrenic IL monomers resembles that of styrene, ending up with a PIL with imidazolium cations covalently attached onto the repeating units of the polystyrene backbone. For styrenic IL monomers, the structural variables are the alkyl group and the anion. So far, most of studies of styrenic PILs dealt with different of anions. Tetraalkylammonium and phosphonium cations have also been integrated into the IL monomers instead of the imidazolium cation [48,49].

2.1.1.1.4. Crosslinkable IL monomers. Some IL monomers have two polymerizable groups. From a structure point of view, they can act as crosslinkers to prepare PIL networks, which are expected to be more stable than non-crosslinked PIL against moisture and solvents.

Fig. 8 depicts three common types of crosslinkable IL monomers. Ohno et al. reported the introduction of two types of vinyl groups separated on the IL cation and anion *via* a simple protocol [19]. In the first step, alkali metal cations of sodium vinylsulfonate and 3-sulfo-propyl acrylate potassium salt were exchanged by protons by means of cation exchange resin to afford the corresponding acids. In the second step, aqueous solutions of these acids were slowly mixed with equimolar amount of N-vinylimidazole cooled by an ice bath. The formed IL monomers (Fig. 8A) possessing an N-vinylimidazolium cation and a vinylsulfonate anion were thermally polymerized in the presence of a radical initiator (AIBN) in ethanol to yield a PIL network. Another example reported by Texter et al. dealt with a unique IL monomer, 1-(2-acryloyloxyundecyl)-3-methylimidazolium 2-acrylamido-2-methylpropyl-sulfonate, which contained an acryloyl-type imidazolium cation and a sulfonyl-terminated acryamide anion [50]. Kadokawa et al. prepared a special type of crosslinkable IL monomers with two types of polymerizable groups connected to a single imidazolium ring (Fig. 8B) [51]. For example, the IL monomer N-vinyl-4-vinylbenzylimidazolium chloride in which styryl and N-vinylimidazolium moieties were united was synthesized by reacting N-vinylimidazole with 4-chloromethyl styrene. Fig. 8C sketches the third type of frequently reported crosslinkable IL monomers, in which two monovalent IL monomers of the same type are covalently bridged through an alkyl chain. They are commonly (meth)acryloyl-, styrenic or N-vinylimidazolium-based ILs. For example, an acryloyl-based monomer, 1,4-bis[3-[2-(acryloyloxy)ethyl]imidazolium-1-yl] butane bis[bis(trifluoromethylsulfonyl)imide], was prepared *via* an ester formation between methacrylic acid and 1,4-bis[3-hydroxyethylimidazolium-1-yl] butane bis[bis(trifluoromethylsulfonyl)imide] [25]; a styrenic monomer with a hexyl bridge, 1,6-bis[3-(vinylbenzyl)imidazolium-1-yl]hexane chloride, was prepared in a single step *via* the reaction of 4-chloromethyl styrene and 1,6-bis(imidazole-1-yl)hexane in a molar ratio of 2:1 [25]. The preparation of N-vinylimidazolium-based crosslinkable monomer was accomplished in one step by reacting N-vinylimidazole with dibromoalkane in a molar ratio of 2:1, as reported by Armstrong et al. [52,53].

2.1.1.1.5. Other IL monomers. In the area of polymer chemistry there are a good many of vinyl groups that can undergo free radical polymerizations. Apart from the IL monomers mentioned above, several other types of IL monomers have been polymerized for the preparation of PILs *via* free radical polymerization. Most examples deal with a neutralization reaction of vinyl acid with N-alkyl

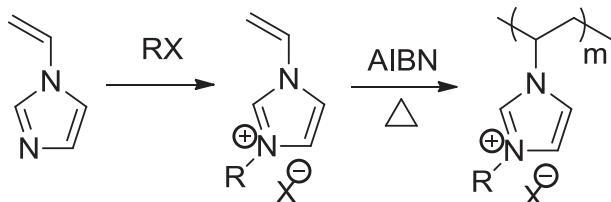


Fig. 5. General synthetic route to PILs from N-vinylimidazolium-based IL monomers.

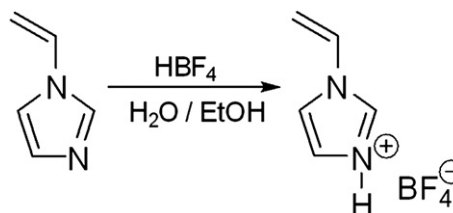


Fig. 6. Preparation of halide-free N-vinylimidazolium-based IL monomers in the absence of silver salts.

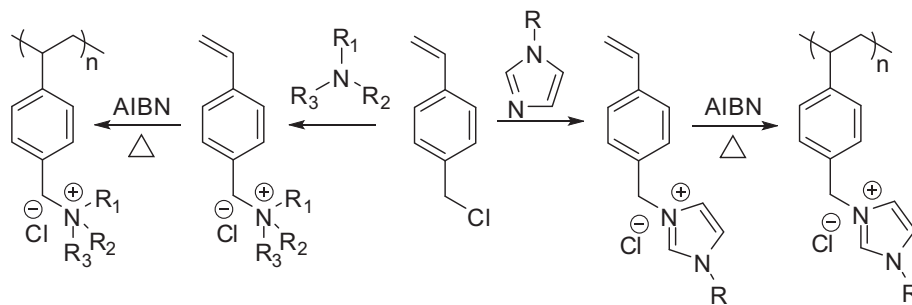


Fig. 7. Polymerization of styrenic IL monomers prepared from 4-chloromethyl styrene.

imidazole (Fig. 9). Polymerization through the vinyl anion leads to polyanion PILs. For example, Ohno et al. reported the synthesis of N-ethylimidazolium vinylsulfonate and N-ethylimidazolium vinylphosphate by neutralizing N-ethyl imidazole with vinyl sulfonic acid and vinyl phosphoric acid, respectively [17,54]. Jin et al. reported the synthesis of 1-methylimidazolium sorbate IL monomer by the neutralization of sorbic acid with N-methyl imidazole [55]. The use of polymerizable anion is considered to be effective to maintain high flexibility of imidazolium cation to obtain higher ionic conductivity for PILs.

2.1.1.2. Copolymerization. In a homopolymer of PILs, each repeating unit carries an IL species. Extending that, copolymers of PILs present the possibility to deposit IL species randomly or selectively into the polymer architectures [56,57]. Kou et al. copolymerized 1-vinyl-3-butylimidazolium halide and N-vinyl-2-pyrrolidone radically using AIBN as the initiator in methanol at 60 °C (Fig. 10) [58]. The random distribution of the 1-vinyl-3-butylimidazolium halide in the polymer chain renders the copolymers favorably soluble in an IL of 1-butyl-3-methylimidazolium tetraborate. The synthesized copolymers are capable of acting as soluble bifunctional stabilizers for IL media. They for instance enabled to synthesize highly stable and active metal nanoparticles in 1-butyl-3-methylimidazolium tetrafluoroborate. (Meth)acryloyl-based and styrenic IL monomers have also been used to copolymerize with their analog comonomers [59,60]. Endo et al. reported that AIBN-initiated radical copolymerization of a methacryloyl-based IL monomer, 1-(2-methacryloxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (Met-IL) with MMA in both DMF and an IL of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMImTFSI) [61]. Analysis of copolymer composition revealed that the reactivity of Met-IL was lower than that of MMA in both DMF and EMImTFSI

solutions. Elabd et al. reported the synthesis of random copolymers of hexyl methacrylate (HMA) and a methacryloyl-based imidazolium IL monomer 1-[2-(methacryloyloxy)ethyl]-3-butylimidazolium tetrafluoroborate (MEBIm-BF₄) [61]. It was found that a high content of HMA in the copolymer significantly lowered the glass transition temperature so that the ionic conductivity increased by over an order of magnitude with increasing HMA composition, even though the overall charge content decreased. They also presented that the ionic–ionic copolymers derived from two IL monomers with the same cation in the polymer chain were prepared simply by a partial anion exchange of a poly(MEBIm-BF₄) homopolymer with LiTFSI.

2.1.2. Controlled/living radical polymerization

The fast development of controlled/living radical polymerization techniques in the last two decades has made a strong impact on polymer science in general, as well as on PILs. The recent success in preparing PILs *via* controlled/living radical polymerizations points out an unprecedented opportunity to precisely design and control macromolecular architecture of IL species on a meso-/nanoscale in a polymer matrix. So far, atom transfer radical polymerization (ATRP) and reversible addition–fragmentation chain transfer (RAFT) polymerization have been successfully employed to prepare homopolymers and block copolymers of PILs. In the following two sessions, these efforts will be introduced in detail to provide an initial view of this new trend.

2.1.2.1. Atom transfer radical polymerization. Shen et al. firstly reported a living/controlled radical polymerization of a methacryloyl-based IL monomer, 2-(1-butylimidazolium-3-yl)ethyl methacrylate tetrafluoroborate (BIMT) *via* ATRP [62]. It was found in their study that when a copper(I) bromide/2,2'-bipyridine based catalyst system

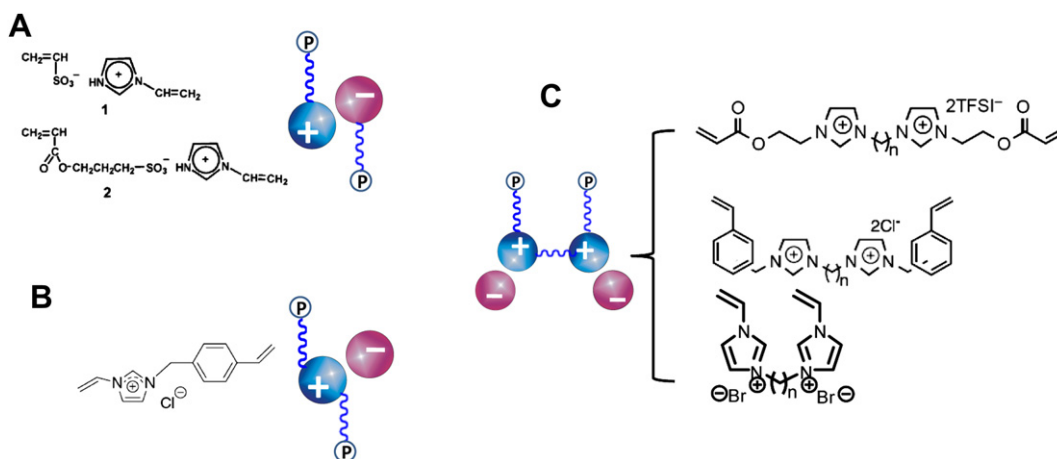


Fig. 8. Sketches and chemical structures of three types of crosslinkable IL monomers.

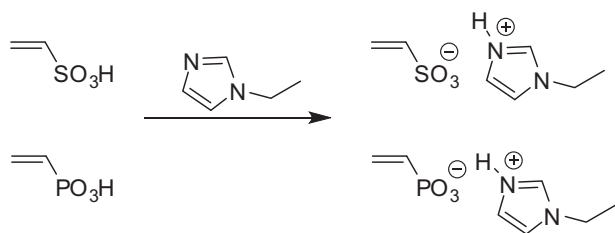


Fig. 9. Synthesis of protic IL monomers via a neutralization reaction of N-ethyl imidazole with vinyl acids.

was applied to polymerize BIMT, the polymerization proceeded very quickly, however with little control of the molecular weight because of the fast activation and slow deactivation. With copper(I) chloride/2,2'-bipyridine as the catalyst system and trichloroacetate, CCl_4 , or ethylchlorophenylacetate as initiator, BIMT was polymerized at 60°C in acetonitrile with first-order kinetics with respect to the monomer concentration. The molecular weight was linearly dependent on the conversion. Another important factor that affected the polymerization was the concentration of IL monomers. A low monomer concentration caused the polymerization to be incomplete.

Later, this group further extended this polymerization technique to styrenic IL monomers of 1-(4-vinylbenzyl)-3-butyl imidazolium tetrafluoroborate (VBIT) and 1-(4-vinylbenzyl)-3-butyl imidazolium hexafluorophosphate (VBIH) (Fig. 11) [62]. The monomers were synthesized through the quaternization of N-butyl imidazole with 4-vinylbenzylchloride and a subsequent anion exchange procedure with sodium tetrafluoroborate or potassium hexafluorophosphate. The polymerization was well controlled and exhibited living characteristics when $\text{Cu}(\text{I})\text{Br}/1,1,4,7,10,10$ -hexamethyltriethylenetetramine or $\text{Cu}(\text{I})\text{Br}/2,2'$ -bipyridine was used as the catalyst system and ethyl 2-bromoisobutyrate as initiator.

2.1.2.2. RAFT. Compared to ATRP, RAFT polymerization of IL monomers comes with a short delay. An apparent disadvantage of applying ATRP for the synthesis of PILs is the unavoidable complex of PIL with the catalytic copper ions. RAFT polymerization is free of this problem, as no metal source is involved. Taking advantage of the living character of the RAFT process, block copolymers with a PIL segment are accessible. This is, according to our opinion, a significant progress in the synthesis of PIL block copolymers. Block copolymers in general have been heavily studied from various aspects, including their self-organization in solution, bulk and thin film. The inclusion of PILs into block copolymers opens a new avenue to process PIL polymers, including ordering, spatial control, and manipulation of the IL species in a polymer matrix.

In 2008, two publications from the groups of Gnanou and Shen independently reported the controlled synthesis of PILs via RAFT process. Gnanou et al. demonstrated the synthesis of a series of PIL-based double hydrophilic block copolymers by sequential RAFT polymerizations of a methacryloyl-based IL monomer and acrylamide or methacrylic acid [63]. As shown in Fig. 12, RAFT-mediated

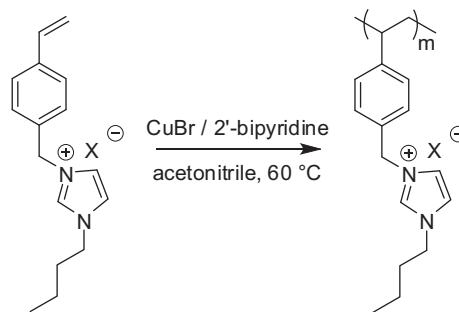


Fig. 11. ATRP of 1-butyl-3-(4-vinylbenzyl)imidazolium tetrafluoroborate or hexafluorophosphate in acetonitrile at 60°C using $\text{Cu}(\text{I})\text{Br}/2,2'$ -bipyridine as the catalyst system (X : BF_4^- or PF_6^- anion) [62].

polymerization of methacryloyl-based IL monomers in methanolic solutions led to well-defined PILs with chain transfer agent (CTA) at the chain end. These were in turn used as a macro-chain transfer agent (macro-CTA) in the chain extension experiments performed in aqueous solutions to afford the targeted water-soluble double hydrophilic block copolymers. These novel block copolymers combine the anionic sensitivity of PILs with the self-assembly properties of block copolymers in water used as a selective solvent for one of the two blocks. The IL hydrophilicity was reversibly adjustable, depending on the counteranion, and shown to alter the water solubility of the block copolymers, thus varying the aggregation states of the polymers from unimers to micelles. Shen et al. described in the same time the preparation of diblock copolymers by sequential RAFT polymerizations of N-2-thiazolylmethacrylamide and 2-(1-butylimidazolium-3-yl) ethyl methacrylate tetrafluoroborate [64].

In the RAFT polymerization of methacryloyl-based IL monomers as introduced by Gnanou and Shen et al., the imidazolium cation is well-separated from the polymerizing unit by an alkyl spacer in the monomers. The radical polymerization proceeded without or with fewer disturbances by the imidazolium ring. Controlled radical polymerization of N-vinylimidazolium-based IL monomers is more challenging, since the generated radical species are highly reactive due to their nonconjugated nature. Recent progress of RAFT/MADIX (macromolecular design via the interchange of xanthates) process allows for the synthesis of well-defined polymers by radical polymerization of nonconjugated monomers. In particular, xanthate-type CTAs are useful for controlling the radical polymerization of N-vinyl monomers, because xanthate-type CTAs increase the electron density at the radical center, which increase the fragmentation rate. The electron-donating O-alkyl substituent may lead to stabilization of the polymeric thiocarbonylthio product through their conjugation with the $\text{C}=\text{S}$ double bond, which lowers the rate of addition of the propagating radicals to the sulfur atom. Consequently, a delicate balance of the forward and reverse rates of addition and fragmentation can be obtained to afford controlled radical polymerization of N-vinylimidazolium salt using the

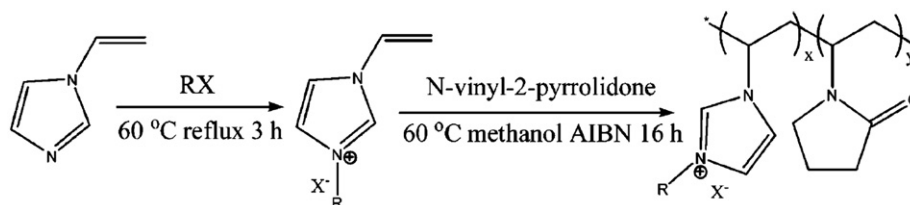


Fig. 10. Preparation of poly[(N-vinyl-2-pyrrolidone)-co-(1-vinyl-3-alkylimidazolium halide)] copolymers [58]. Reprinted with the permission of ACS.

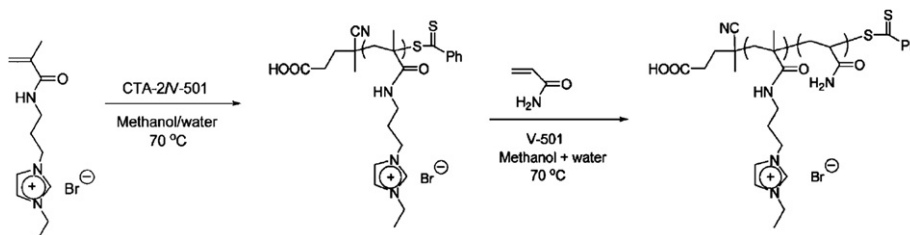


Fig. 12. Synthesis of double-hydrophilic diblock copolymers containing a segment of PIL by RAFT polymerization [63]. Reprinted with the permission of ACS.

xanthate-type CTA. Mori et al. first demonstrated the synthesis of N-vinylimidazolium PILs with controlled molecular weights and narrow polydispersity by RAFT/MADIX polymerization of three N-vinylimidazolium-based IL monomers [65]. By employing a macro-CTA of poly(N, N-isopropylacrylamide) (PNIPAAm), the polymerization of IL monomers resulted in a double stimuli-responsive block copolymer that contained one block of PIL (Fig. 13). The copolymer formed micelles in aqueous solution triggered by either temperature or ionic strength.

In a very recent report, Yuan et al. demonstrated a similar procedure to synthesize double hydrophilic block copolymers comprising a PIL segment [66]. The non-ionic segment was made up from either PNIPAAm or poly(N,N-dimethylacrylamide) due to their favorable controllable solubility in water at room temperature. They were employed as macro-CTAs for the RAFT polymerization of four 1-vinylimidazolium IL monomers possessing different alkyl substituents and anions. It was found that in the chain extension reaction the reactivity of an IL monomer bearing a dicyanamide anion was significantly lower than that of monomers with halides, due to the large anion size. This caused difficulty in preparing block copolymers containing a long PIL with dicyanamide anion. A solution to this problem is to take advantage of the dual stimuli-responsiveness of the block copolymers to temperature and ionic strength in aqueous solution, from which an anion exchange of the halide-containing PIL segment with dicyanamide anions could be readily performed to form a long PIL segment with dicyanamide anions.

2.1.3. Other polymerizations

Polymerization techniques other than radical ones have been employed for the synthesis of PILs as well. Ohno et al. have synthesized novel PILs that had an organoboron unit in the repeating unit along the main chain for the purpose of selective lithium cation transport [67]. As shown in Fig. 14, an IL monomer of 1,3-diallylimidazolium bromide was first prepared from the quaternization of N-allyl imidazole with allyl bromide. In the second step, hydroboration polymerization of this difunctional IL monomer with several boron containing molecules and subsequent anion exchange reaction with TFSI⁻ anion afforded the corresponding organoboron PIL in 89–81% yield. The lithium transference number for these systems was 0.87–0.45 at 30 °C. This demonstrates that anion trapping of the organoboron unit worked very effectively in PIL-based matrices, as compared to polyether-type matrices.

Buchmeiser et al. described the synthesis of poly(norbornene) PILs with pendent imidazolium moieties and the three different

counter anions of TFSI⁻, BF₄⁻ and hexfluorophosphate, *via* ring opening metathesis polymerization of norbornyl-based IL monomers in IL as a reaction medium [68]. The limited solubility of the formed poly(norbornene) PILs in common organic solvents provided high yields during the polymerization. Measurements of ionic conductivity and thermal stability suggested that the properties of the new PILs were found to be mainly dependent on the nature of anions chosen.

Firestone et al. have made further efforts to incorporate a thiophene unit into an IL so that the IL can be polymerized by oxidative polymerization. In their first attempt, they polymerized an N-methylimidazolium-based IL monomer with a thiophene moiety at the terminus of a C₁₀ alkyl chain (Fig. 15) [69]. The chemically-induced oxidative polymerization of the monomer 1-(10-thien-3-yl) decyl-3-methylimidazolium nitrate yielded a highly water-soluble cationic polythiophene that was regio-irregular, as judged from both optical spectroscopy and small-angle X-ray scattering (SAXS). The structural disorder in the polymer was believed to arise from anion exchange with a divalent anion (sulfate and sulfite) during bulk chemical oxidative polymerization that employed a combination of FeCl₃ and (NH₄)₂S₂O₈ (as chemical oxidants). Electrochemical studies showed that the polymer possessed a high oxidation potential (1.95 V) and thus, was resistant to chemical doping. Later, this group improved the synthetic approach by using electropolymerization of a bifunctional monomer possessing both vinyl and thienyl groups appended to an alkylimidazolium-based IL. The preparation of PILs *via* electropolymerization offers several advantages over chemical polymerization, including facile generation of thin polymer films on a variety of surfaces and the ability to modify and/or engineer surfaces with redox active molecules. The resulting polymer film strongly adhered to the electrode surface and was optically birefringent when examined under polarized light. The liquid-crystalline textures correlated well with the fibril morphology observed by topographic atomic force microscopy. The meso- to nanoscale structural characterization using a combination of grazing-incidence small-angle X-ray scattering (GISAXS) and wide angle X-ray diffraction (WAXD) revealed a lamellar structure, a common architecture found for many polyalkylthiophenes. The diffraction data suggested that the polythiophene component was organized orthogonally to the polyvinylimidazolium backbone.

PILs can be incorporated into an organic-inorganic hybrid nanocomposite, which combines the unique features of inorganics with that of a PIL. For example, a polysilsesquioxane structured organic-inorganic composite was prepared from a precursor-containing IL

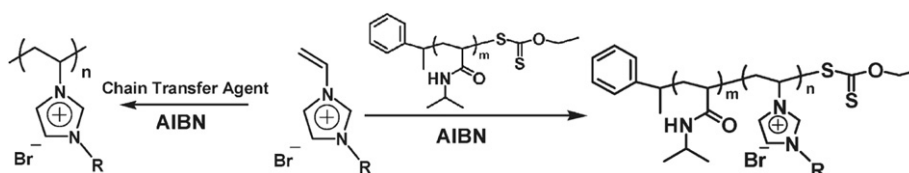


Fig. 13. Synthesis of PIL homopolymers and double-hydrophilic diblock copolymers containing a segment of N-vinylimidazolium PIL by RAFT/MADIX polymerization [65]. Reprinted with the permission of ACS.

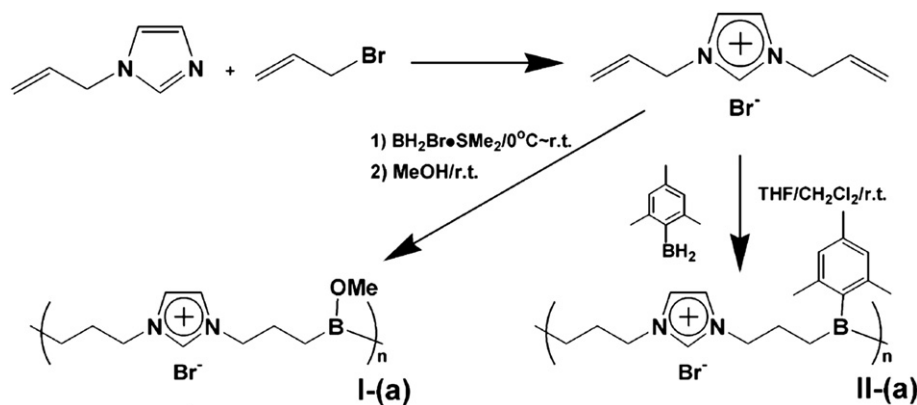


Fig. 14. Preparation of novel PILs with organoboron unit in the main chain via hydroboration polymerization [67]. Reprinted with the permission of ACS.

monomer, 1-methyl-3-[3-(trimethoxy- λ^4 -silyl)propyl]-1H-imidazolium iodide [71]. In its chemical structure, an imidazolium cation was functionalized with a trimethoxysilane group. The monomer was prepared by refluxing the mixture of 3-iodopropyltrimethoxysilane and 1-methylimidazole in 1,1,1-trichloroethane (Fig. 16). The IL precursor monomer yielded a polysilsesquioxane-type structure through a formic acid initiated polycondensation reaction. The hybrid organic-inorganic material has shown potential as an electrolyte for use in quasi-solid state dye-sensitized solar cells.

2.2. Polymer reactions

PILs can be accessed via chemical modification of currently existing polymers, i.e., using existing polymer and its predefined architecture to generate the PIL through chemical reactions afterward. The modified polymers can have the same chemical structure as those of PILs prepared by direct polymerization of IL monomers. The attractiveness of this strategy is that the formed PIL will naturally adopt the degree of polymerization, architecture and monomer composition that present in the original polymer or copolymer chains. Thus way, PILs with unique architectures and composition that are inaccessible by direct polymerization of IL monomers can be prepared by modifying a carefully chosen precursor polymer of well-defined structure, mass, and architecture.

In the case of imidazolium-based PILs, there are two main paths to perform the modification: (1) grafting N-alkyl imidazole or its derivatives onto the halo-alkyl function present in each repeating unit of polymers; (2) reacting halo-alkane with polymers containing imidazole. Shen et al. reported the preparation of poly(1-butyl-3-vinylbenzylimidazolium chloride) by postpolymerization modification of poly(*p*-chloromethylstyrene) (PCMS) with 1-

butylimidazole (Fig. 17) [62]. The precursor polymer, PCMS with controlled molecular weight and narrow molecular weight distribution was prepared by RAFT polymerization of *p*-chloromethylstyrene. The quaternization of the chloromethyl units with 1-butylimidazole was proven to be a very quantitative reaction and proceeded to 100% at 80 °C in DMF, as confirmed by the vanishing of chloromethyl signals in the ^1H NMR spectrum. The molecular weight of the PIL was calculated from that of its precursor polymer PCMS. The modified PIL would be similar to a PIL that could be prepared by the RAFT polymerization of the IL monomer 1-butyl-3-vinylbenzylimidazolium chloride, although this polymerization has not been reported yet.

Although RAFT polymerization technique affords the preparation of block-type PIL copolymers, in fact the first examined block copolymer containing a PIL segment was prepared by post-polymerization modification of a preformed diblock copolymer [72]. The synthetic route is shown in Fig. 18. A controlled radical polymerization technique, nitroxide-mediated polymerization (NMP) was employed to prepare a diblock copolymer of PS-*b*-PCMS via sequential NMP of styrene and *p*-chloromethylstyrene. As the PS segment was free of potential reactions with N-methyl imidazole, only the PCMS segment was converted to poly(1-methyl-3-vinylbenzylimidazolium chloride) (PMVBI) by reacting the block copolymer with N-methyl imidazole. The self-assembly of the formed nonionic–ionic diblock copolymer in toluene was then examined by neutron and dynamic light scattering, indicating that the PIL block strongly influenced the dimensions of the micelle formed. The copolymers assembled into elongated micelles where the IL block formed the micelle core. The elongated micelle core cross-sectional radius and length depended linearly on the length of the PIL block.

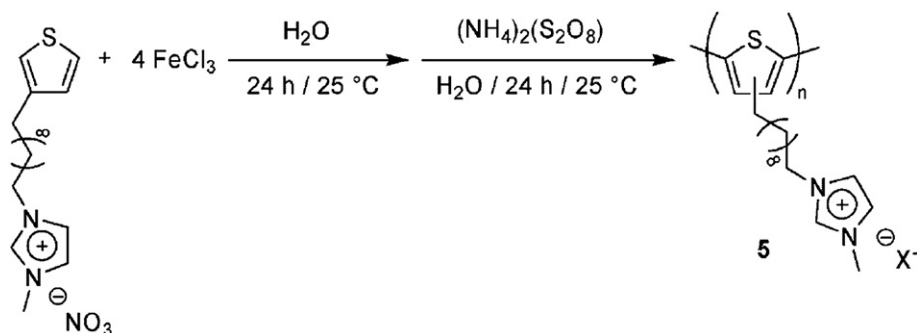


Fig. 15. Oxidative polymerization of 1-(10-thien-3-yl)decyl-3-methylimidazolium nitrate [70]. Reprinted with the permission of Wiley.

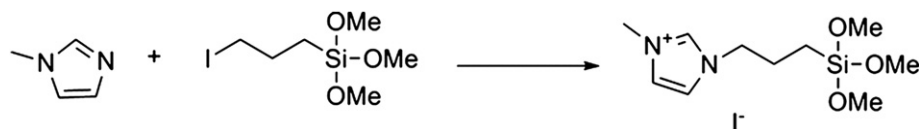


Fig. 16. Synthesis of 1-methyl-3-[3-(trimethoxy- λ^4 -silyl)propyl]-1H-imidazolium iodide ($[\text{Si}(\text{OMe})_3\text{C}_3\text{MIm}^+][\text{I}^-]$), which is a precursor IL monomer of polysilsesquioxane structured organic-inorganic nanocomposite [71]. Reprinted with the permission of ACS.

3. Properties and applications

3.1. Ionic conductors

Ion conductivity is a fundamental physical property of PILs. PILs as solid-state polymeric electrolytes are of significant interest in the field of electrochemistry because they may avoid some disadvantages of liquid electrolytes, such as leakage and flammability, in the application areas of batteries and fuel cells. In addition, the polymer nature of PIL potentially permits production of ion-conductive materials with defined size, shape and geometry, such as thin films, fibers, coatings and even complete circuits. Ohno et al. have systematically studied the structure-related ionic conductivity of (meth)acryloyl- and N-vinylimidazolium-based PILs. They found that polymerization of IL monomers in general causes lower ionic conductivity compared to the IL monomers due to both considerable elevation of glass transition temperature and reduced number of mobile ions after covalent bonding of the polymerizable ions. The structural parameters of PILs that influence the ion conductivity include types of IL monomers, cations [24], anions, the spacer between the polymerizable group and the cation (for methacryloyl-based IL monomers) [22,54], the alkyl chain on the imidazolium ring (for N-vinylimidazolium-based IL monomers), the presence of networks, etc. For instance, a poly(ethylene oxide) (PEO) macro-monomer in which a N-ethylimidazolium cation and a methacryloyl moiety are located on two ends of the PEO chain was polymerized. The length of the PEO chain, i.e. the spacer between the methacryloyl group and imidazolium cation was systematically varied, and it showed the longer the space, the higher the ion conductivity. In addition, the effects of different anions on the polymer T_g and ion conductivity was examined. A maximum ion conductivity was attained for the TFSI⁻ anion containing polymer, since the large sized TFSI⁻ anion significantly lowered the glass transition temperature of the polymer. Compared to anion, modifications of the cation structure contributed less in determining the T_g and hence ion conductivity of the PIL. PIL networks or gels prepared from the polymerization of crosslinkable IL monomers often showed poor ion conductivity due to its lack of both mobile cations and anions. Nevertheless, crosslinked PIL matrix in the presence of doping with a small amount of salts has been reported

to show high proton and silver ion conductivity in the temperature range from 25 to 125 °C [50].

3.2. Dispersants

Imidazolium-based PILs were recently used as dispersants to stabilize nanomaterials in aqueous and organic solution, especially carbon nanotubes. Several reports have confirmed that single-wall carbon nanotubes (SWCTs), multi-wall carbon nanotubes (MWCTs) and graphene sheets can be successfully dispersed in aqueous solution of imidazolium-based PILs. The strong solubilizing effect of PILs stems from a π -cation interaction between the nanotube and the imidazolium ring, as evidenced in the FTIR spectrum of the 1:1 imidazolium IL-treated MWCTs [73]. Mecerreyes et al. employed poly(1-vinyl-3-ethylimidazolium bromide) as dispersants to stabilize nanomaterials, such as SWCT, gold nanorods and silver nanoparticles in aqueous solutions [74]. Upon addition of excessive bispentafluoromethanesulfonimide lithium salt, the dispersed nanomaterials formed a precipitate which was separated and dissolved in acetone. The stable dispersion of the nanomaterials in acetone, when added dropwise into an aqueous solution of tetrabutylammonium bromide, formed a precipitation that could be separated and dissolved in water. Thus, the nanomaterials could be reversibly transferred between the aqueous and organic phases by simple anion exchange of the attached PILs. In a similar approach, Suh et al. used PILs to stabilize the isolated graphene sheets and they provided a functionality for transferring graphene sheets between the aqueous and organic phases [75].

Fukushima et al. demonstrated the preparation of SWCT bucky gels with imidazolium-based ILs, in which ILs formed a soft organic layer on the SWCT surface and made nanotubes dispersed in organic media [76]. Later, they extended this research by using IL monomers instead of normal ILs to disperse SWCTs and similarly formed the bucky gels. *In situ* free radical polymerization of IL monomers generated a polymeric bucky gels or bucky plastics [77]. Preliminary studies have shown that a bucky plastic film containing 3.8 wt% of SWCTs exhibited an enhancement of dynamic hardness by a factor of four and also developed an electrical conductivity of 0.56 S cm^{-1} , much higher than those of SWNT-modified polymers at comparable loading levels of SWCTs.

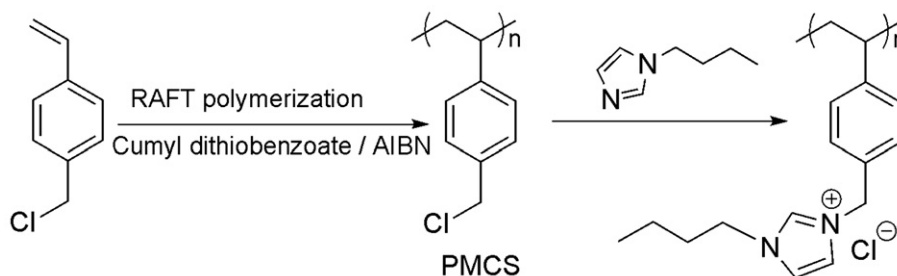


Fig. 17. Synthesis of poly(1-butyl-3-vinylbenzylimidazolium chloride) by postpolymerization modification of poly(*p*-chloromethylstyrene) [62]. Reprinted with the permission of Wiley-VCH.

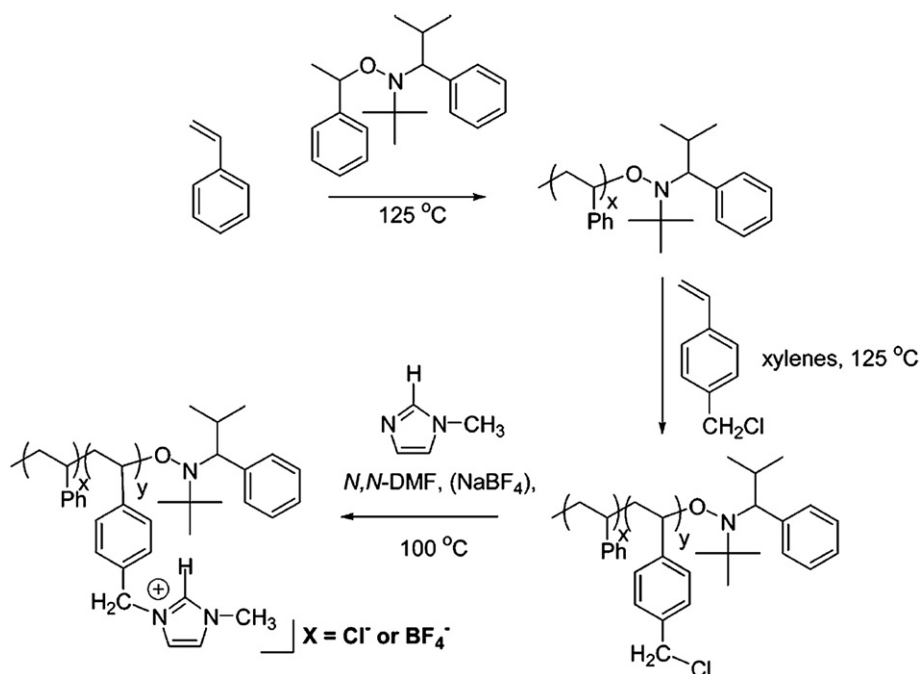


Fig. 18. Synthetic route to PS-*b*-PMVBI block copolymers via postpolymerization modification of a preformed diblock copolymer [72]. Reprinted with the permission of ACS.

A recent study described the surface-functionalization of MWCTs with PILs as a metal nanoparticle catalyst support for fuel cell application [78]. In this work, PILs were prepared by thermally-initiated free radical polymerization of 1-vinyl-3-ethylimidazolium tetrafluoroborate in the presence of MWCTs. This formed a uniform and dense thin PIL film on the surface of MWCTs and introduced a large number of functional groups for the further growth of metal (Pt/Ru and Pt) nanoparticles. The as-synthesized nanoparticle/PIL/CNT hybrid showed good electrocatalytic behavior toward the electrooxidation of methanol. The improved performance was attributed both to the enhanced structural integrity of the MWCTs and the smaller size and more uniform distribution of the nanoparticles generated within the PILs on the surface of MWCTs.

Texter et al. reported a nanolatex copolymer (25–30 nm) of an imidazolium bromide acrylate the simple mixing of which with SWCTs provided stable waterborne dispersions of SWCTs (Fig. 19), and thermally and electrically conducting coatings that adhered to plastics [79]. This approach to dispersing SWCNT leapt previous reports by providing stabilization and binder functions simultaneously. Resulting films exhibited 10-fold anisotropy in both thermal and electrical conductivity and appeared free of interfacial phonon scattering problems. The electrically conducting networks assembled upon film formation provided a new route to priming plastics for electrodeposition in addition to providing simple anti-static layer formulations. The efficacy of these nanolatexes was assigned to the imidazolium and bromide components that both had an affinity for graphene surfaces. Such kind of PIL nanolatexes have also been employed to stabilize tungsten carbide nanoparticles in aqueous solution, assisted by ultrasonic tip [80].

In parallel with attempts to use PIL as CNT stabilizers, the use of poly(1-vinyl-3-ethylimidazolium bromide) as a non-aqueous dispersion media for intrinsically electrically conducting polymers, such as polypyrrole, polyaniline and poly(3,4-ethylenedioxythiophene) have been reported [81,82]. By combining the stabilizing effect of PILs to SWCTs as well as conducting polymers, Suh et al. demonstrated a practical approach for the hybridization of SWNTs with conducting polymers through a PIL as binder [83]. The PIL formed a close contact

and interaction with SWNTs and acted as a functional layer to provide a good solubility and effective template for hybridizing conducting polymer chains.

3.3. Ordered nano- and mesostructures

Spatial organization and ordering of IL species in nano- and mesoscale, originally derived from the research activities of producing anisotropic, ion-conductive thin films, not only represents interesting basic research, but also broadens the application spectrum of PILs in the fields of nanoelectronics, nanolithography, optoelectronics, nanophotonics, etc. Current efforts focus on the prepolymerization ordering of bulk IL monomers by making use of the basic concepts of molecular self-assembly, followed by photopolymerization to lock *in situ* the ordering. Several groups have reported that IL monomers with mesogen character self-assemble into various liquid-crystalline phases with different orderings [18,84–91]. Ritter et al. synthesized two types of vinylimidazolium-based IL containing mesogenic coumarin and biphenyl unites; the attached mesogenic units induced the self-assembly of IL

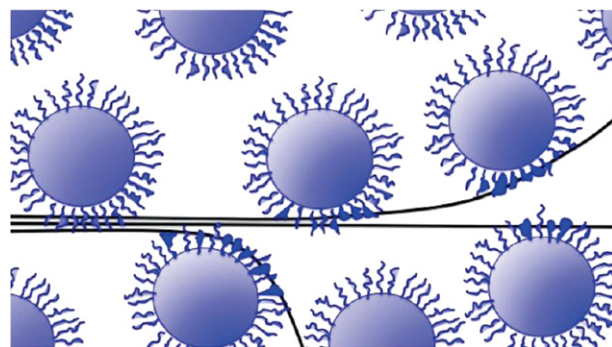


Fig. 19. Two-dimensional model illustrating possible mechanism of nanolatex stabilization of SWCNT during bundle exfoliation [79]. Reprinted with permission of ACS.

monomers and the occurrence of liquid-crystalline phase [91]. Ohno and co-workers reported the synthesis of a methacryloyl-based IL monomer that contained a rod-shaped mesogen (biphenyl) and a terminal *N*-alkylmethylimidazolium functionality [18]. The photopolymerized free-standing PIL film was found to exhibit enhanced ion conductivity parallel to the direction of the smectic A layers. In the continuing efforts of the same group [87,92], an alternative mesogen, tris-(alkoxy)phenyl groups appended to the acryloyl groups, was synthesized as a mean to improve the liquid-crystalline order. The changes in the structure of the IL monomer resulted in the formation of columnar phases that produced 1-D ion-conductive channels which could be oriented both perpendicular and parallel to the polymer film surface. Photopolymerization was carried out for producing well-ordered liquid-crystalline PILs.

A different approach reported by Firestone and co-workers exploited the noted amphiphilic characteristic of *N*-alkylmethylimidazolium halides to self-assemble when dispersed in water [93]. In their initial research on ILs, they found that the feature sizes and mesophase morphology could be controlled by the water content and choice of anions of ILs [94]. By using a polymerizable IL monomer, 1-decyl-3-vinylimidazolium monomer, a 2-D hexagonal structured physical gel was prepared in the presence of 15 wt% water. Upon UV radiation, the IL monomers were *in situ* polymerized into a durable, self-supporting chemical gel that adopted a hexagonal perforated lamellar structure. This ordered structure with well-defined hydrophilic (pores) and hydrophobic regions have been used as a soft template and scaffold for the *in situ* nucleation and growth of metal and semiconductor nanoparticles [95]. In another contribution from the same group, the synthesis, self-assembly, and polymerization of an acrylate-IL monomer, 1-(8-(acryloyloxy)octyl)-3-methylimidazolium chloride, $[\text{AcrC}_8\text{MIm}^+][\text{Cl}^-]$ with 22 wt% water content was carried out, yielding a lamellar structured hydrogel that reversibly swelled in water (to 200 times its original volume with retention of structure) [96]. Additionally, they have investigated the effect of cation structure on the mesophase architecture of self-assembled and polymerized imidazolium-based IL monomers [97].

Although most nanostructured PIL matrix are prepared by poly-cations, a polymerizable acrylate anion pairing with a 1-decyl-3-methylimidazolium cation ($[\text{C}_{10}\text{MIm}^+][\text{Acr}^-]$) has been investigated by Firestone et al. The IL monomer self-assembled in water at a variety of weight percents, and was photopolymerized with the addition of a water-soluble crosslinker comonomer, poly(ethylene glycol) diacrylate (PEGDA). In the obtained polymer matrix, full access to the alkyl chain region of the self-assembled IL cation was possible. Characterizations confirmed that the formed hierarchical copolymer was comprised of IL cation bilayers containing hydrophilic pores with hexagonal symmetry and a cytoskeleton-mimicking network containing the IL anion and comonomer (Fig. 20)

[98]. Furthermore, the same group took the advantage of electro-polymerization to introduce ordered structures in a polymer thin film on the electrode [69].

3.4. Sorbents and separation

PILs have been proven as promising sorbents of CO_2 since they exhibit high CO_2 absorption capacity. Shen et al. first reported the study of CO_2 absorption by imidazolium-based PILs including poly[1-(4-vinylbenzyl)-3-butylimidazolium tetrafluoroborate] (poly[VBBIm⁺][BF₄⁻]) and the corresponding hexafluorophosphate (poly[VBBIm⁺][PF₆⁻]) derivative. Later, this group extended their research to tetraalkylammonium-based PILs, such as poly[*p*-vinylbenzyltrimethylammonium tetrafluoroborate], and poly[2-(methacryloyloxy)ethyl]trimethylammonium tetrafluoroborate. The tetraalkylammonium-based PILs showed higher CO_2 sorption capacities than the imidazolium ones, although the underlying mechanism of gas adsorption remained unclear. Noble et al. showed that increasing the length of the *N*-alkyl substituent on the imidazolium cation could improve CO_2 permeability [45]. In addition, a crosslinkable IL monomer has been photopolymerized into a thin film, which is significantly less permeable to gases than other types of PILs due to the higher crosslinking density [99].

In the field of separations science, PILs have been examined for use in solid phase extraction and chromatography [100–102]. Hsieh and co-workers have recently constructed stationary phases based upon imidazolium-derived PILs for use in gas chromatography, showing good reliability and structural selectivity [102]. These properties were attributed to the ordered arrangement of the octylimidazolium side chains. PIL-based stationary coatings for solid-phase microextraction have also been prepared by free radical polymerization of vinyl-substituted imidazolium monomers and showed good reproducibility, sensitivity, and yielded good detection limits.

3.5. Porous polymers

Porous polymers have found numerous uses in a wide range of commercial products including ion-exchange applications, supports for liquid chromatography, metal recovery, cosmetics, etc. Combining the advantages of microemulsions and the properties of imidazolium-based ILs, Texter et al. produced PIL nanoparticles, gels, and open-cell porous materials. The IL monomer 1-(2-acryloyloxyundecyl)-3-methylimidazolium bromide $[\text{C}_{11}\text{MIm}^+][\text{Br}^-]$, that consists of an imidazolium cation polar group and a hydrophobic tail, can efficiently stabilize microemulsions of MMA in aqueous solution. PIL latexes as small as 30 nm were obtained during the bulk microemulsion polymerization in the $[\text{C}_{11}\text{-MIm}^+][\text{Br}^-]/\text{MMA}/\text{H}_2\text{O}$ (0.04/0.04/0.92) system by AIBN at 60 °C. Transparent gels were produced when the surfactant IL monomer and MMA

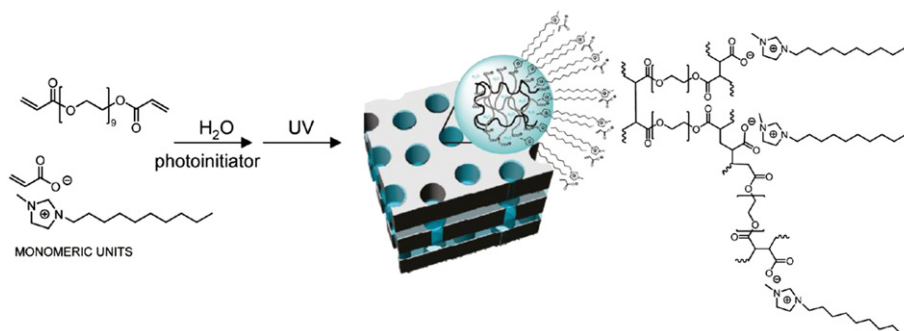


Fig. 20. Schematic illustrations of proposed structure for the *net*-poly($[\text{C}_{10}\text{mim}^+][\text{Acr}^-]$ -co-PEGDA). Reprinted with permission of ACS.

concentrations were higher ($[\text{C}_{11}\text{-MIm}^+][\text{Br}^-]/\text{MMA}/\text{H}_2\text{O} \sim 0.15/0.10/0.75$). Such a transparent polymer gel shrank and became opaque after being immersed in aqueous KPF_6 . This opaque material could be converted back to a semitransparent gel by further treatment with aqueous NaBr . Scanning electron microscopy (SEM) characterization of the transparent gel (Fig. 21A) showed the absence of the pore structures. However, pores with diameters of 3–8 μm were observed in the opaque gel (Fig. 21B). Most of these pores connected to others through small circular “windows”, with diameters of 1–3 μm . The pores formed due to the shrinkage of the copolymer at the interfaces between aqueous and polymer domains. The IL monomer molecules were situated along the interfaces between aqueous and MMA domains prior to polymerization. Once the vinyl groups of IL monomer and MMA were copolymerized, the hydrophilic portions of IL monomer protruded into the aqueous channels in the gel. The anion exchange from Br^- to PF_6^- changed the copolymer from being hydrophilic to being hydrophobic at these interfaces, and thus caused shrinkage at the interface to make pores. These pores were partially closed (self-healed) by further immersion in NaBr solution (Fig. 21C), because the shrunken polymer domains at the interface were converted back to hydrophilic and swollen by imbibing water.

This synthetic concept was extended by the same group for the preparation of reversible solvent-induced porous polymers by emulsion copolymerization of a surfactant IL monomer 1-(2-acryloyloxyundecyl)-3-methylimidazolium tetrafluoroborate and MMA in a mixture of water and 1-propanol [103]. The resulting copolymer structure were reversibly tuned between a hydrogel and a porous structure by changing the anions in the IL moiety of the copolymer. This new class of porous polymers are expected suitable for diverse applications, including controlled-release chemical- and drug-

delivery, tissue scaffolding, bicontinuous materials templating, antimicrobial filtration, and fire-resistant foams.

Li et al. [33] reported the preparation of three-dimensional (3D) ordered macroporous PILs from a colloidal crystal templating method in three steps: (1) fabrication of a face centered cubic SiO_2 opal template; (2) infiltration of the template by a solution of IL monomer, crosslinker and initiator followed by polymerization; and (3) selective dissolution of SiO_2 template to produce an inverse opal structure. By association of three-dimensional ordered macroporous structure with PILs in this work, it was found that the prepared 3D ordered macroporous PILs could not only serve as tunable photonic crystals, electro-optic switches, molecular gating systems and functional surface with enhanced tunable wettability, but also provide a unique platform for the design of further functional materials.

3.6. Carbon precursors

Recently, N-vinylimidazolium-based IL monomers and PILs have also been employed as carbon precursors. In the absence of metal salt, the IL monomers provide a favorable carbonization yield that however was related to the choice of anions and the alkyl chain on the imidazolium ring. Here, the process took advantage of the negligible vapor pressure of ionic compounds. IL monomers with a dicyanamide anion showed a carbonization yield of 28.6 wt%, dramatically higher than 6.5 wt% obtained from that with a bromide anion; the alkyl chain bearing a cyano-group enhanced the carbonization yield as well. In the presence of metal salts, IL monomers and PIL could efficiently act as precursor of mesoporous graphitic and highly conductive carbon nanostructures in a template-free approach [35]. The carbonization was performed in the presence of FeCl_2 at temperatures between 900

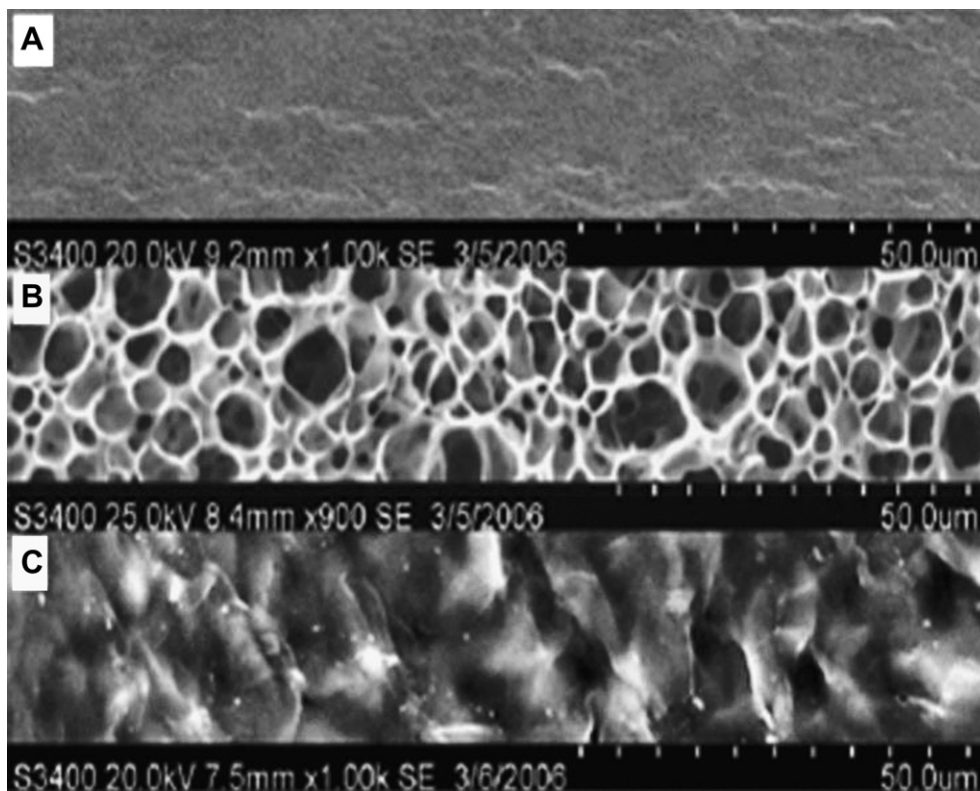


Fig. 21. Anion characteristics affect 1-(2-acryloyloxyundecyl)-3-methylimidazolium bromide ($[\text{AcrC}_{10}\text{MIm}^+][\text{Br}^-]/\text{MMA}/\text{H}_2\text{O}$ ternary system morphology. The morphology of (a) the material containing the bromide (Br^-) anion is changed upon its replacement with the (b) hexafluorophosphate (PF_6^-) anion resulting in the formation of pores in the polymer gel. (c) Replacing the PF_6^- anion with Br^- leads to collapse of the pores, demonstrating the role of the anion in the structure of the polymeric IL material [41]. Reprinted with permission of RSC.

and 1000 °C. It was found that FeCl₂ plays a key role in controlling both the chemical structure and the texture morphology of the graphitization process. A detailed investigation on the carbonization process demonstrated that 900 °C was a threshold temperature where a synergistic formation process enabled the development of superior physical properties of the as-formed carbon, such as large surface area and low resistance. *Via* an acid etching process, iron and iron carbide nanoparticles, the remainder of the primary catalyst, could be removed, leaving pure mesoporous carbon nanomaterials with a comparably well developed graphitic structure. Without demand for any template, this method is facile and easy to scale up. In addition, a block copolymer with a PIL segment has also been successfully used to prepare mesoporous graphitic nanostructures in the presence of FeCl₂ or CrCl₃ [66].

3.7. Other applications

Apart from those applications mentioned above, a colorful variety of additional applications have also been demonstrated by different groups. PILs contain anion–cation pairs and therefore have a relatively high density of strong dipoles, which are interesting candidates of microwave absorbing materials [48]. Shen et al. have investigated the microwave absorption properties of several model PILs containing either imidazolium or ammonium cations. These PILs were proven to have higher dielectric constants and dielectric loss factors compared with most ordinary polymers. In the same area, PILs were reported to serve as actuators in electric fields [3]. The electrowetting behaviors of an AMPS-ammonium polymer have been investigated, which exhibited a large contact angle of ~90° (non-wetting) in the absence of voltage and a significantly reduced contact angle of ~47° upon voltage application. Optical active hybrid materials of PILs and inorganic nanoparticles were characterized in several reports. For instance, gold nanoparticles organized within a solvent responsive PIL produced a plasmonic material [95]; semiconductor CdTe nanoparticles confined in PILs have been found to be highly luminescent [104]. In addition, the integration of photoactive organic molecules in a PIL has been carried out as an alternative to prepare optical materials from PILs [105,106].

4. Conclusions

We have presented a general review of recent work on PILs, including the state-of-the-art synthetic strategies and their properties and applications in a variety of branches of materials and polymer science. In spite of the intensive research activity performed in the last decade, the field of PILs, according to our opinion, is still in its infancy. Many novel properties and functions have just recently been reported and clearly indicate the rapid progress in this field. At present the research scope of PILs is under significant expansion from the traditional design of conductive polymeric solid electrolytes and sorbents to electrical, optical and bio-related functional materials with high structure order on the meso-/nanoscale. Although conventional free radical polymerizations of IL monomers remain a major synthetic strategy, the newly emerging polymerization techniques, such as controlled/living radical polymerization and electropolymerization provide a promising means to design and control the macromolecular architecture of IL species on a meso-/nanoscale. We expect that all these efforts will help to realize the full potential of PILs soon and make them even more important within polymer materials in the future.

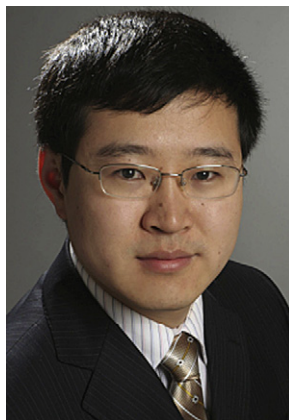
Acknowledgments

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