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Progress in Ionic Liquids as Reaction Media, Monomers and Additives in High-Performance Polymers

Dan He, Zhengping Liu and Liyan Huang

Abstract

In this chapter, we will review the progress in ionic liquids (ILs) widely used as reaction media, monomers and additives in the synthesis, chemical modification and physical processing of high-performance polymers (HPPs). Using ILs as reaction media in the syntheses of HPPs, the high-molecular-weight polymers were obtained in good yields and the shortened dehydration time compared to the conventional methods, the separation efficiency of products was improved. It is particularly noteworthy that the number of novel copolymers of HPPs with polymerisable ILs has steadily increased in recent years. In addition, ILs have been used as various types of additives such as the components of polymer materials, plasticizers and porogenic agents in the physical processing of HPPs, and the materials prepared include membranes, microcapsules, nanocomposites (NCs), electrolytes and grease.

Keywords: ionic liquids (ILs), high-performance polymers (HPPs), reaction media, monomers, additives, polyimides (PIs), polysulphones (PSFs)

1. Introduction

1.1 Ionic liquids (ILs) and their properties

The melting points of ILs, also known as low-melting-point organic salts, are usually below 100°C; ILs are composed of organic cations and inorganic/organic anions, as shown in **Figure 1** [1, 2]. The number of possible cation-anion combination has been estimated to be $>10^6$ [3]. ILs are most commonly abbreviated by writing the abbreviation/formula of the cation and anion in square brackets (without charges); e.g., [bmim][PF₆], [bmim][Tf₂N] and [emim][Cl] are the abbreviations for 1-butyl-3-methyl-imidazolium hexafluorophosphate, 1-butyl-3-methylimidazolium bis(trifluoromethanesulphonyl)imide and 1-ethyl-3-methylimidazolium chloride, respectively. Owing to their high chemical and thermal stability, low volatility, and low toxicity, ILs have attracted much attention for applications in chemistry and industry. In addition, the properties of ILs include high conductivity, wide electrochemical window, low flammability, ability to dissolve organic and inorganic solutes and gases, and recyclability. As far as vapour pressures are concerned, several

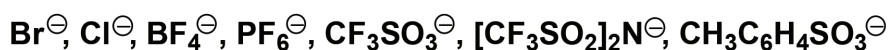
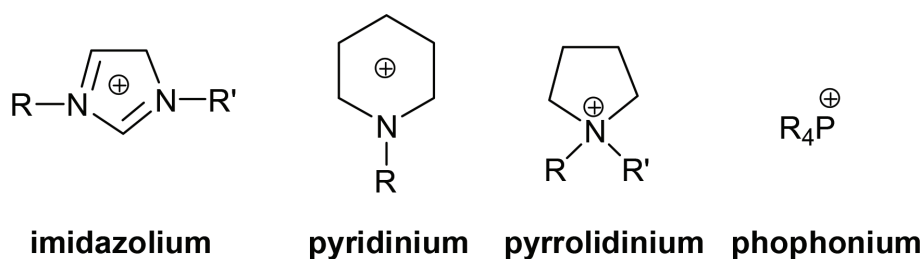


Figure 1.
Typical cationic and anionic components of ILs.

ILs can be vaporised under a high vacuum at 200–300°C and then recondensed [4]; however, ILs indeed have negligible vapour pressures at near ambient conditions. Thus, for general reactivities or processes, they may be considered as low-volatile reaction media. ILs are generally chemically stable reaction media, but this cannot be taken as granted. The proton at the C(2)-position of imidazolium cation is acidic, and under basic conditions, deprotonation leading to carbene is possible [5]. ILs are considered as rational designable solvents that can be easily tuned by using various combinations of cations and anions to achieve ILs exhibiting appropriate properties and achieving practical applications for a desired task (so-called task-specific ILs), making it possible to introduce ILs into specific synthesis processes [6].

Because of these special properties, ILs have emerged as novel and exciting reaction media in their own right. Every year, an increasing number of papers are being published on the applications of ILs for enhancing reactivities or processes in both chemical research and industry. So far, free-radical polymerisation, polycondensation and ionic polymerisation have been successfully carried out using ILs as the reaction media. In the step polymerisation field, there is a huge interest for high-performance polymers (HPPs). Despite improved synthesis methods and commercial availability of various ILs for replacing typical organic reaction media, they are still more expensive than typical organic reaction media. Therefore, the application of ILs as reaction media for enhancing reactivities or processes is limited.

1.2 High-performance polymers (HPPs) and their categories

HPPs are also known as high-temperature polymers, special engineering plastics, advanced engineering materials, and heat-resistant polymers [7]. They are defined as polymers that can retain the desirable properties when exposed to very harsh conditions, including, but not limited to, a high-temperature, a high-pressure, and corrosive environment. They are well known for outstanding thermal stability and service temperatures, good mechanical properties, dimensional and environmental stability, high resistance to most chemicals, gas barrier and electrical properties, etc., under extreme conditions, even at elevated temperatures [8, 9]. To better understand the reason for their strength, one must consider the bond strength that can be quantified by bond dissociation energy. First, the higher the bond dissociation energy, the harder it is to break the polymer chain, and thus the better the resistance of the polymer to harsh environment. The bond energies of C–C and C=C bonds are 83 and 145 kcal mol⁻¹, respectively; thus, it is harder to break a C=C bond than a C–C bond. Most HPPs contain more C=C bonds than C–C bonds. Similarly, the bond energies of C–H and C–F bonds are 99 and 123 kcal mol⁻¹,

respectively; some of the C–H groups are also replaced with C–F groups. The resonance stabilisation is enhanced by adding aromatic components along the backbone, and it is estimated that the incorporation of resonance-stabilised units can add 40–70 kcal mol⁻¹ to the bond strength. Such a molecular structure of HPPs improves their resistance and stability; thus, they can retain the desirable properties under very harsh conditions.

HPPs include polysulphones (PSFs), polyimides (PIs), polyaryletherketones (PAEKs), poly(arylene sulphide)s (PASs), polyarylates (PARs), liquid crystalline polymers (LCPs), fluoroplastics (PVDFs), *p*-hydroxybenzoic acid polymers, poly(naphthalene), poly(oxadiazole), and high-temperature nylon (HTN). HPPs can be divided into amorphous polymers, semi-crystalline polymers, and LCPs; e.g., PSFs are described as amorphous polymers and polyetheretherketones are semi-crystalline polymers. The applications of HPPs span across aerospace, defence, weaponry, energy, electronics, automotive, construction, nuke industry, membrane technologies, etc. In recent years, new HPPs and materials containing HPPs with enhanced application potential in more fields have been reported, including materials obtained by the chemical modification and blending of HPPs containing ILs.

1.3 Overview

The aim of this article is to review the recent progress in the field of ILs as reaction media, monomers and additives in the synthesis, chemical modification and physical processing of HPPs based on recent literatures, with the main emphasis on possible advantages, limitations and importance of the work. The article is structured as follows: section 2 focuses on progress in IL application in HPPs. Section 2.1 focuses on ILs as reaction media in the synthesis of HPPs, including PIs, PSFs, and PAEKs, and synthesis of HPPs in ILs under microwave (MW) irradiation. Section 2.2 focuses on ILs as monomers for the chemical modification of HPPs. The last part of Section 2 focuses on ILs as additives for the physical processing of HPPs, including membranes, microcapsules, electrolytes, nanocomposites (NCs) and grease.

2. Progress in IL application in HPPs

2.1 ILs as reaction media for synthesis of HPPs

Most HPPs are synthesised by step polymerisation reactions. Step polymerisation is one of the main polymerisation reactions for preparing polymers, usually requiring elevated temperatures, high-boiling-point reaction solvents, high vacuum and the removal of small molecules to reach the equilibrium. Therefore, it seems to be suitable to introduce ILs into step polymerisation owing to their intrinsic properties as described above. In 2002, high-molecular-weight aromatic PIs and polyamides were synthesised for the first time, obtaining polymers with inherent viscosities from 0.52 to 1.35 dL/g in ILs 1,3-dialkylimidazolium bromides [10]. The use of ILs as novel solvents for the synthesis of other HPPs has been reported, such as PAEK [3, 11] and PSF [12, 13].

2.1.1 Synthesis of PIs in ILs

In 1908, Jones et al. first synthesised PIs, but it was difficult to process and fabricate them [14]. Until the early 1960s, Du Pont, USA, made a substantial progress in the processing of PIs; thus, PIs were developed and widely utilised in various applications [15]. These polymers are known as HPPs and possess outstanding

thermal stability, excellent electrical properties, improved mechanical properties and good resistance to organic solvents. They are widely applied in various modern industries such as gas separation membranes, insulator films for electrical/electronics, semi-conductor devices, coatings and composites, high-temperature adhesives, cell processing, and biochip design [16]. In general, PIs are produced in two steps via the formation of polyamic acids from diamines and dianhydrides. Other reported synthetic routes utilised tetracarboxylic acids, half-esters, a combination of bis(*o*-diiodoaromatics) with carbon monoxide, etc., [17]. Co-PIs with flexible linkages, such as ether and ester linkages between the aromatic rings of the main chain, have been synthesised, such as poly(amide-imide)s (PAIs), poly(ether amide-imide)s (PEAIs), poly(ester-amide-imide)s, poly(ether-imidazole-imide)s, and poly(amine-amide-imide)s [18].

In 2002, Vygodskii et al. first reported a novel one-step strategy for the synthesis of high-molecular-weight aromatic PIs by the polycyclisation reaction of 1,4,5,8-naphthalene tetracarboxylic acid dianhydride (DANTCA) with 3,3-bis(4'-aminophenyl)phthalide (Aph) in 1,3-dialkylimidazolium-based ILs without using catalyst at 180–200°C, as shown in **Figure 2** [10]. These ILs seem to be suitable reaction and activating media for the synthesis of aromatic PIs and polyamides. The polymerisation process and molecular weights of PIs are significantly affected by the structure and nature of ILs. The effects of IL structure include the following: (1) the best results were obtained in ILs with a symmetrical structure, obtaining polymers with a maximum inherent viscosity of 1.35 dL/g. (2) When using ILs with a symmetrical structure bearing alkyl chains of carbon atoms $n = 2-6$ and 12, polycyclisation occurred in a homogeneous solution for ILs with $n \leq 4$, but rapid precipitation of the PI occurred for ILs with $n > 4$. (3) High-molecular-weight polymers could be obtained in ILs with Br^- . (4) PIs insoluble in organic solvents do not precipitate from reaction solutions in ILs with anions SiF_6^- , HSO_4^- , NO_3^- , I^- and CH_3COO^- . (5) As far as cations were concerned, the molecular weights of PIs are lower in ILs based on quinoline and pyridine bearing the same alkyl chains longer than imidazole. In summary, it is possible to tailor ILs as active solvents for the step polymerisation reactions of PIs by varying the structures of the cations and anions of ILs. Studies on using ILs as reaction media for synthesising other step polymerisation polymers are in progress. Later, Vygodskii and co-workers reported studies on using different ILs as reaction media for synthesising other step polymerisation polymers with high molecular weights, such as poly(amide imide)s (PAIs) [19–21]. Although relatively high-molecular-weight PIs have been obtained in the absence of any added catalysts and lower reaction temperatures than the conventional synthetic method [17, 22, 23], the limited solubility of some aromatic substrates in ILs was still the main problem. In 2006, Ohno et al. reported that the solubility of starting materials was improved by adding imidazolium-type zwitterion (ZI), 1-(1-butyl-3-imidazolium)butane-4-sulphonate in ILs, leading to higher molecular weights of the resulting PIs [24]. On the other hand, in some studies of the step polymerisation of PIs, catalytic effect of ILs was observed. A type of PI was synthesised by the step polymerisation reactions of 1,4-bis(3-aminopropyl)

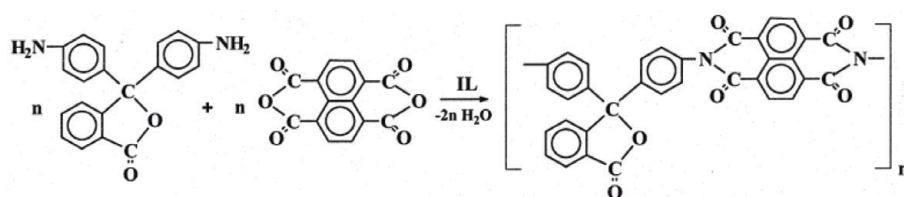


Figure 2.
Synthetic route for PI in IL.

piperazine with 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) in the presence of ILs as the catalyst and N-methylpyrrolidone (NMP) as the solvent. The degrees of polymerisation are not only high, but the IL also exerts a detectable effect on polymer solubility. The PI with a higher degree of polydispersity was obtained in ILs based on imidazole than that obtained with pyridine and alkylamine [25]. PI nanoparticles were obtained in an IL, namely, 1-ethyl-3-methylimidazolium bis(trifluoromethyl-sulphonyl)imide ([emim][Tf₂N]), as a continuous phase without the addition of any further activating or stabilising agents by the hetero-phase step polymerisation of different aromatic tetracarboxylic acids and diamines. These PI particles with a range of 100 nm showed a high thermal stability by TGA and a decomposition temperature of ~520°C [26]. A sulphonated co-PI (SPI) was prepared in an IL, 1-ethyl-3-methyl imidazolium bromide [emim][Br], without any catalyst. These co-PIs prepared showed superior properties compared to those prepared in a common solvent, indicating promising properties for applications in proton-exchange membrane fuel cells [27, 28]. The trifluoromethylated poly(ether-imidazole-imide)s (PEII)s based on an unsymmetrical-diamine-bearing carbazole and imidazole chromophores were obtained with 80–96% yields in imidazolium-based ILs. They were amorphous with good thermal and thermo-oxidative stability, excellent solubility, and ability to form tough and flexible films [29].

Optically active PAIs were successfully synthesised in an IL, namely, 1,3-dipropylimidazolium bromide ([dpim][Br]), using triphenyl phosphite (TPP) (a condensing agent) without any additional extra components such as LiCl and pyridine. Therefore, it was concluded that ILs not only act as solvents, but also act as catalysts in this step polymerisation [30]. At the same time, various types of ILs were investigated as solvents and catalysts for the polymerisation of PAIs [31]. A PAI based on 2-[5-(3,5-dinitrophenyl)-1,3,4-oxadiazole-2-yl]pyridine was synthesised in [bmim][Br]. Heterocyclic and optically active PAIs incorporating L-amino acids were synthesised in [pmim][Br] [18, 32]. Shadpour et al. later reported several relative articles in succession. For example, organosoluble and optically active PAIs bearing an S-valine moiety were synthesised by the step polymerisation of different aliphatic and aromatic diisocyanates with a chiral diacid monomer in tetrabutylammonium bromide (TBAB) IL. These polymers exhibited good thermal properties and were soluble in amide-type solvents [33]. The poly(amide-ether-imide-urea)s (PAEIUs) were synthesised by the step polymerisation of a chiral diamine with several diisocyanates in [dpim][Br] IL [34]. Heat-stable and optically active processable PAI nanostructures bearing a hydroxyl pendant group were synthesised by step polymerisation in the presence of IL and TPP [35]. In recent years, using TBAB IL/TPP and ultrasonic irradiation, optically active PAI/TiO₂ bio-NCs containing N-trimellitylimido-L-isoleucine linkages, poly(vinyl alcohol) (PVA) with chiral PI nanoparticles containing S-valine, and optically active PAI/zinc oxide bio-NCs (PAI/ZnO BNCs) containing L-valine were obtained one after the other [36–38].

2.1.2 Synthesis of PSFs in ILs

In 1965, PSF was first successfully developed and commercialised by Union Carbide, USA, currently known as Udel PSF. Usually, the number-average molecular weights of commercial products are in the range of 16,000–35,000, and the weight-average molecular weights are in the range of 35,000–80,000 [6]. They are well known for their outstanding thermal stability, good mechanical properties, electrical properties, transparency and resistance to most chemicals. They are widely used in various modern industries such as electrical/electronics, machineries, medical equipment, transportation and aerospace, and membrane separation technologies [39–42]. In recent studies, PSFs were mainly studied in

the development of membrane technologies such as hemodialysis, micro-/ultra-filtration membrane and gas separation. PSFs are usually synthesised via nucleophilic aromatic substitution polymerisation (S_NAR) reactions [43]. For example, bisphenol-A PSF is synthesised from 2,2-bis(4-hydroxyphenyl) propane (bisphenol A) and 4,4'-dichlorodiphenylsulphone (DCDPS) or 4,4'-difluorodiphenylsulphone (DFDPS). Poly(ether sulphone)s (PESs) are usually synthesised from 4,4'-dihydroxydiphenylsulphone (bisphenol-S) and DCDPS/DFDPS [13].

Liu's research group is one of the most active research groups in this field. In 2012, high-molecular-weight PSFs were synthesised in high yields by step polymerisation of bisphenol A with DFDPS for the first time in various ILs/zwitterions (ZIs) as the reaction media in the presence of potassium carbonate (K_2CO_3) using a one-pot green protocol shown in **Figure 3**. In this work, the dehydration time was shortened to 80% (2.5–8 to 0.5 h) compared to the conventional methods, and the weight-average molecular weights ranged from 30,000 to 130,000, with great potential for commercial applications. The polarity of ILs strongly affected the molecular weight of PSF, and ILs containing PF_6^- were better [6]. Recently, PESs were also successfully synthesised by the step polymerisation of bisphenol S with DFDPS in ILs/ZIs as the reaction media in the presence of K_2CO_3 using a one-pot green protocol. The dehydration time was shortened to 0.5 h compared to the conventional methods, and a high solubility of bisphenol-s dipotassium salt in IL/ZI significantly lowered the reaction temperature ($150^\circ C$) than the conventional temperature ($220 - 300^\circ C$). The proposed method has clear advantages for synthesising PSF and PES compared to volatile organic solvents and, in principle, can be applied to the synthesis of other HPPs via nucleophilic aromatic substitution polymerisation reactions [13]. In 2017, the synthesis of poly(phenylene sulphide sulphone) (PPSS) in ILs was presented [44].

2.1.3 Synthesis of PAEKs in ILs

PAEK was reported by Bonner of Du Pont, USA, in 1962 and Goodman of Imperial Chemical Industries (ICI), UK, but the molecular weight of products synthesised was the lower. Until 1979, Rose et al. of ICI reported that PEK with a high molecular weight was synthesised, laying the foundation for the synthesis of PAEK. Commercially available as VICTREX® PEEK™, it was introduced into the market by ICI. Poly(ether ether ketone) (PEEK) is one of the most recently developed materials. PAEKs exhibit many outstanding characteristics including high thermal stability, excellent mechanical, thermo-oxidative, and chemical resistance

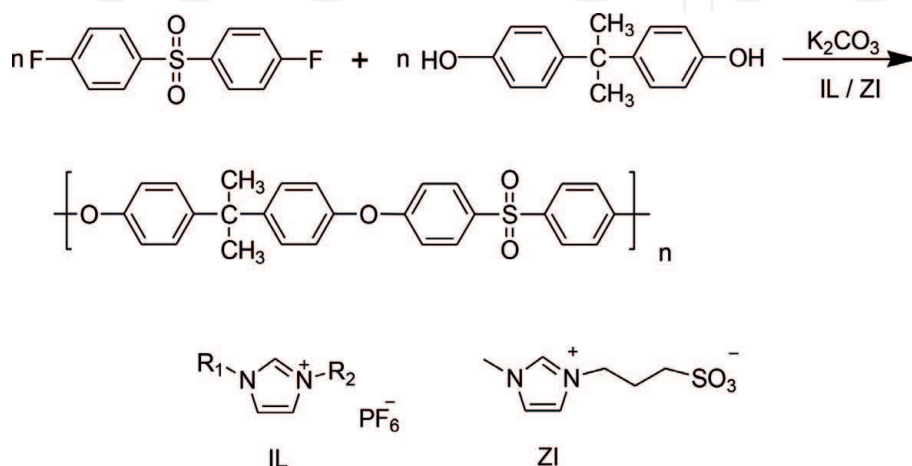


Figure 3. Synthetic route for PSF in IL/ZI and structures of ILs and ZI.

properties under diverse conditions, and good electrical insulation [45, 46]. The PAEK applications span across automotive, aerospace or chemical industries, orthopaedics and surgery, cable insulation, and membrane technologies. In addition, high temperatures, intense mechanical stress, and/or exposure to harsh chemical environments are required; thus, PAEK can be a lightweight replacement for metals.

In 2013, PAEKs were successfully synthesised via S_NAR mechanism using ILs [*i*-pmim][PF₆] as the green reaction media. The optimised step polymerisation conditions were 50 wt% monomer concentration, dehydration at 150°C for 0.5 h and polymerisation at 180°C for further 1.5 h. The number-average molecular weights of PAEKs ranged from 10,000 to 18,000 g mol⁻¹ with high yields. In addition, the interactions of bisphenol A with ILs were investigated, exhibiting a strong influence on the PAEK synthesis [11]. In the same year, PEEKs were also synthesised in IL [bmim][Tf₂N], by polycondensation reactions of hydroquinone with 4,4'-dihalo-benzophenones in the presence of K₂CO₃ at 320°C. The materials produced in IL were similar to those produced in the industrial solvent of choice, but the molecular weights were lower, possibly due to the lower solubility of the polymer. The advantage of using IL [bmim][Tf₂N] over diphenyl sulphone as the solvent is that the separation efficiency significantly improved [3]. It is expected that more custom-designed ILs would be used for PAEK production, potentially widening the scope of the choice of solvents currently used.

2.1.4 Synthesis of HPPs in ILs under microwave irradiation

Microwave (MW) is a type of electromagnetic wave with frequency ranging from 300 MHz to 300 GHz, usually 2450 MHz for radiation chemical reaction; the temperature of the system depends on the power of MW and electrical properties of the medium. MW radiation can accelerate the reaction rate for a specific system and complete these reactions within a short period. Thus, as a non-conventional energy source, MW radiation has become an increasingly more practical and popular technology in organic chemistry, including polymerisation. Owing to their high ionic conductivity and polarisability, ILs act as excellent MW-absorbing agents and are, therefore, used in polymerisation. Mallakpour's research group is one of the most active research groups in this field. In 2007, poly(urea-urethane)s (PUU)s were prepared using IL 1,3-diallylimidazolium bromide and tetrabutyl-ammonium bromide (TBAB) under MW irradiation as well as conventional heating. The polymerisation reactions occurred rapidly, producing a series of PUUs in good yields and with moderate inherent viscosities of 0.21–0.46 dL/g. These PUUs showed a good solubility and could be readily dissolved in traditional organic solvents [47].

MW-assisted synthesis can provide higher yields and purer products than traditional heating; therefore, recently, MW radiation has been used for the synthesis of HPPs, especially PAIs. In 2010, poly(urethane-imide)s (PUIs) were prepared in the presence of IL TBAB under MW irradiation conditions. All the PUIs showed thermal stability and good solubility in various organic solvents. In *in vitro* toxicity studies, the prepared materials showed biological activity and non-toxicity to microbial growth and were classified as bioactive and biodegradable compounds [48]. In 2012, chiral-nanostructured PAIs were synthesised in TBAB IL under MW irradiation by the polymerisation reactions of several amino-acid-based chiral diacids with an aromatic diamine, 2-(3,5-diaminophenyl)-benzimidazole. The PAIs obtained were organo soluble, and the HPPs were obtained in high yields and with inherent viscosities in the range 0.40–0.52 dL/g. The materials synthesised were amorphous polymers with nanostructures containing nanosized particles in the range from 40 to 80 nm [49]. Chiral-PAI-nanostructures-bearing hydroxyphenyl pendant units in the side chain were also prepared using TBAB IL and TPP as the

condensing agent under MW irradiation. The obtained PAIs had inherent viscosities in the range 0.32–0.49 dL/g; they were amorphous polymers with nanostructures in which the nanosized particles are in the range from 66 to 78 nm [50]. Soluble, thermally stable PAIs modified with siloxane linkages with a reduced dielectric constant were synthesised via the isocyanate method in TBAB, tetrabutyl-phosphonium bromide (TBPB), and 1-butyl-3-methyl imidazolium chloride ([bmim][Cl]) under MW irradiation [51].

2.2 ILs as monomers for chemical modification of HPPs

In 2010, Li et al. reported that block co-PIs based on aromatic dianhydrides and diamines copolymerised with diamino IL monomers, specifically 1,3-di(3-aminopropyl) imidazolium bis[(trifluoromethyl)sulphonyl]imide ([DAPIM]-[Tf₂N]) and 1,12-di[3-(3-aminopropyl)imidazolium]dodecane bis[(trifluoromethyl)sulphonyl]imide ([C₁₂(DAPIM)₂][Tf₂N]₂), as shown in **Figure 4**, were synthesised by the Boc protection method and using diverse compositions. These two ILs were first reacted with 2,2-bis(3,4-carboxylphenyl)hexafluoropropane dianhydride (6FDA) to produce 6FDA-IL oligomers as the IL component for block co-PIs. Later, the oligomers were reacted with 6FDA and *m*-phenylenediamine (MDA) at an oligomer concentration from 6.5 to 25.8 mol% to form block co-PIs. As the concentration of 6FDA-IL oligomer increased in the block co-PIs, the thermal degradation temperature and glass transition temperature of the produced co-PIs decreased, but their density increased. Compared to pure 6FDA-MDA, the gas permeability of the IL-based block co-PI decreased, but the ideal permeability selectivity for CO₂/CH₄ gas pair increased [52]. The co-PIs were mainly used in the separation of gases such as O₂, N₂, CH₄ and CO₂ [53, 54].

Later, a series of poly(arylene ether sulphone)s containing bulky imidazole groups (PSf-Im-*x*) based on a monomer 2,2'-bis-(2-ethyl-4-methylimidazole-1-ylmethyl)-biphenyl-4,4'-diol (EMIPO) were successfully synthesised. After the quaternisation by *n*-bromobutane, these polymers were evaluated as alkaline anion exchange membranes (AEMs) as shown in **Figure 5**. 2-Ethyl-3-butyl-4-methylimidazolium was introduced as the functional group in these polymers; the bulky groups present around the imidazolium ring reduced the access of OH⁻ to imidazolium, thus increasing the alkaline stability of the membranes. The membrane showed an IEC value of 2.07 and ionic (OH⁻) conductivity of 0.014 S cm⁻¹ at 30°C, in which 80% of the ionic conductivity was maintained even for the treatment in 1 M KOH at 60°C for 144 h [12].

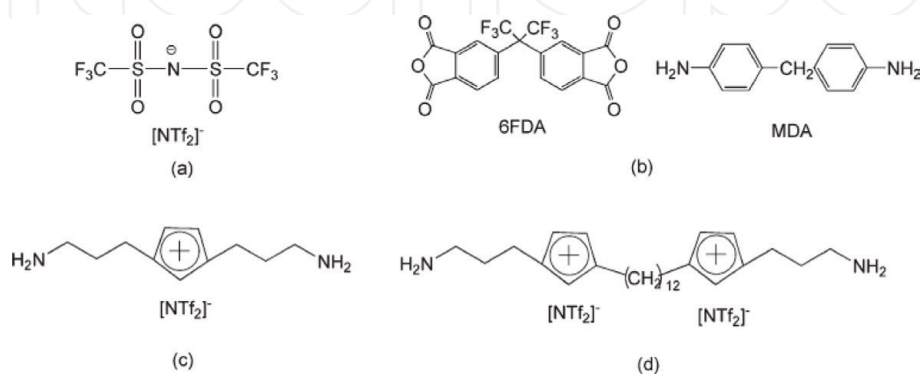


Figure 4.

Structures of monomers used in polyimide synthesis: (a) bis[(trifluoromethyl)sulphonyl]imide ([Tf₂N]), (b) 2,2-bis(3,4-carboxylphenyl)hexafluoropropane dianhydride (6FDA), *m*-phenylenediamine (MDA), (c) 1,3-di(3-aminopropyl)imidazolium bis[(trifluoromethyl)sulphonyl]imide ([DAPIM][Tf₂N]), and (d) 1,12-di[3-(3-aminopropyl)imidazolium]dodecane bis[(trifluoromethyl)sulphonyl]imide ([C₁₂(DAPIM)₂][Tf₂N]₂).

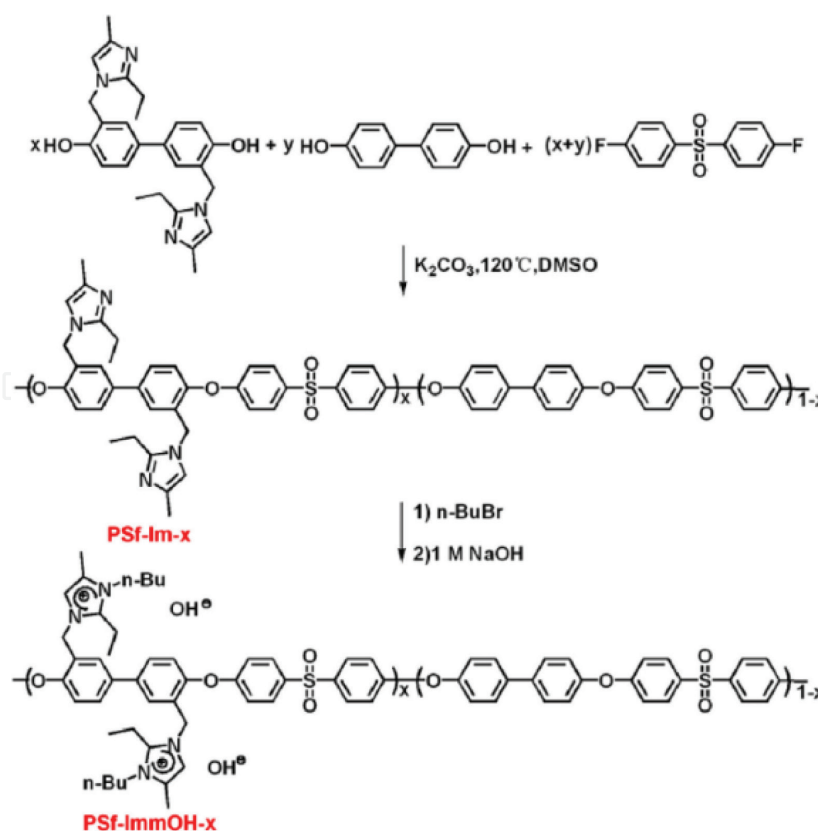


Figure 5.
Synthetic routes of PSf-Im-x and PSf-ImmOm-x.

Recently, a new synthetic method was reported for the modification of PIs; the PIs were first transformed to their ionic forms via the subsequent *N*-alkylation and quaternisation of benzimidazole or quinuclidine moieties; then, an ion exchange reaction was carried out to prepare polymers bearing the bis(trifluoro-methylsulphonyl)imide anion. High-molecular-weight ($M_n = 22,000\text{--}97,000$) cationic polyelectrolytes with the degree of quaternisation as high as 96% were obtained under the optimal conditions. These new materials showed excellent mechanical and thermal properties, adjustable surface wettability, and improved gas transport properties [55]. Several recent articles reported that the incorporation of IL moieties into HPP by copolymerisation is a promising strategy to prepare novel copolymers of ILs with HPPs with improved properties. It is presumed that further related work will be reported in the future.

2.3 ILs as additives for physical processing of HPPs

The application of ILs for HPPs is not limited to their use as reaction media in polymerisations for preparing HPPs, and ILs are miscible with some HPPs and used as additives in the materials such as the components of polymer materials, plasticizers, and porogenic agents. By blending ILs with HPPs, the properties of the obtained mixtures can be considerably affected [56]. Thus, applications of ILs are being explored in the fields of membranes, microcapsules, electrolytes, NCs and grease.

2.3.1 Membrane

Supported IL materials have two main processes. First, ILs are covalently linked to polymers, inorganic surfaces or particles, thereby supporting the IL materials. In such systems, the properties of the ILs are modified to some extent, but generally,

the main features are retained. Second, ILs are dissolved and imbibed in a polymeric membrane, porous matrix, particle or bulk material as the components of the mixture, and the properties of the IL are retained [57]. In recent years, supported IL membranes (SILMs) have received considerable attention for their applications in gas separation, electrolyte, proton exchange, etc.

Early on, it was reported that ILs based on 1-*n*-alkyl-3-methylimidazolium cation (*n*-butyl, *n*-octyl, and *n*-decyl) can be used together with the anions PF₆⁻ or BF₄⁻. Immobilisation of these ILs on a polyvinylidene fluoride (PVDF) membrane provides an extremely highly selective transport for secondary amines over tertiary amines [58]. Later, the PVDF/ILs composite membranes were prepared. A membrane using [emim][Tf₂N] and PVDF hollow fibre was prepared as a support for CO₂/N₂ separation [59].

A quasi-solid-state dye-sensitised solar cell based on poly(vinylidene fluoride-co-hexafluoro-propylene) P(VDF-HFP)/SBA-15 nanocomposite membranes was obtained using dimethyl-propylimidazolium iodide (DMPII) IL [60]. The SILM was prepared using a hydrophilic PVDF support immobilised in the IL 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ([*bdmim*][PF₆]) [61]. The preparation of PVDF-blended membranes with dominating β-phase crystals was studied in ILs 1-butyl-3-methylimidazolium tetrafluoroborate ([*bmim*][BF₄]), [*bmim*][PF₆] and 1-methylimidazolium trifluoromethanesulphonic ([*mim*][CF₃SO₃]) as the co-solvents for zwitterionic copolymers [62]. A PVDF membrane with piezoelectric β-form was prepared by immersion precipitation in mixed solvents containing an IL [*bmim*][BF₄] [63]. Composite membranes were prepared as electroactive actuators using PVDF and [emim][Tf₂N] as the plasticiser [64]. A 1-butyl-3-methylimidazolium triflate ([*bmim*][OTf])/PVDF composite membrane was prepared by the impregnation method and used for the separation of C₆H₆/H₂ and C₆H₁₂/H₂, as shown in **Figure 6** [65]. Thin films containing 1-ethyl-3-methylimidazolium nitrate ([emim][NO₃]) IL and PVDF were investigated [66]. Another HFP-containing fluorine, polytetrafluoroethylene (PTFE), was often prepared using an SILM. For example, gelled SILMs were synthesised by the gelation of [*bmim*][PF₆] in the pores of PTFE hollow fibres and used in the separation of butanol from acetone-butanol-ethanol mixtures (ABE) by sweep gas pervaporation [67]. Amino-acid-IL-based-facilitated transport membranes containing PTFE were prepared via impregnation [68].

The SILMs prepared with PSF supports are often used for CO₂ separation such as CO₂/He, CO₂/CH₄ and CO₂/N₂ separation, even at elevated temperatures [69–71]. In addition, ion-conductive membranes were prepared by casting a solution of Udel-type PSF and IL 1-butyl-3-methylimidazolium trifluoromethane-sulphonate ([*bmim*][TfO]) or 1-ethylimidazolium trifluoromethanesulphonate ([emim][TfO]) [72]. The SILMs prepared with PES supports are frequently used in the separation of gases, especially SO₂ [73, 74] and CO₂ [75–78]. In addition, PES membranes with ion exchange and anti-biofouling properties were prepared by the surface immobilisation of Brønsted acidic ILs via double-click reactions [79]. A sulphonated PES (SPES) film containing ILs was obtained by solution casting and prepared using double-side, self-cleaning polymeric materials, as shown in **Figure 7** [80]. Hydrophilic porous PES membranes and microcapsules were prepared via non-solvent-induced phase separation (NIPS) using IL [*bmim*][PF₆] as the structure control agent [81].

The surface wettability of negatively charged PI films was tuned by the electrostatic self-assembly of ILs and formation of spherical nanoparticles, indicating the assembly of longer-substituent cations [82]. The membranes containing ILs prepared with PI supports were often used in gas separation [83–86] and fuel cells [87–89]. In addition, available PAIs [90], copolymers of poly(ethylene glycol) (PEG) and aromatic PI [91, 92], and SPI [93–95] were also used in the preparation

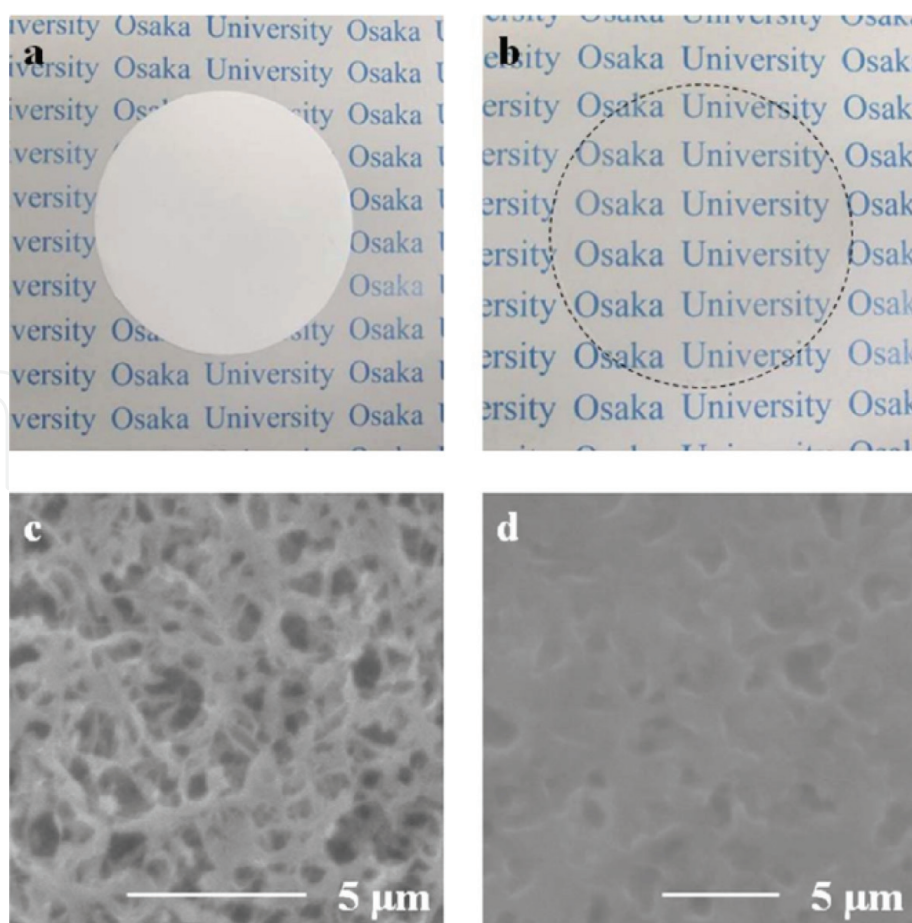


Figure 6.
Photographs (a and b) and SEM images (c and d) of the PVDF membrane before (a and c) and after impregnation (b and d) with [bmim] OTf.

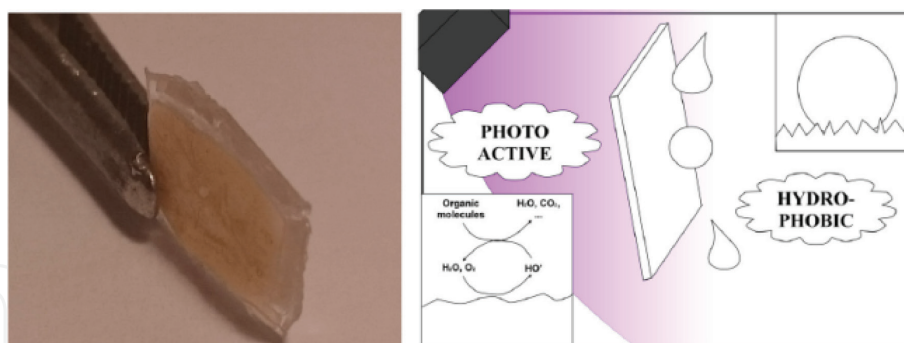


Figure 7.
Picture and schematic of the final material.

of membranes containing ILs. For example, SPI/IL composite membranes as proton-exchange membranes have been reported in recent years [96, 97].

Composite membranes based on sulphonated poly(ether ether)ketone (SPEEK) with ILs [CH₃CH₂CH₂NH₃][CF₃COO] (TFAPA), [bmim][Cl] and [bmim][PF₆] have been prepared [98, 99]. Composite membranes have been prepared using SPEEK ILs in the presence of Y₂O₃ [100].

2.3.2 Microcapsule

In 2007, monodispersed microcapsules enclosing [bmim][PF₆] were prepared via a two-stage microfluidic approach, as shown in **Figure 8**; the hollow PSF microcapsules showed an encapsulation capacity of 30.8% [101]. PSF microcapsules containing

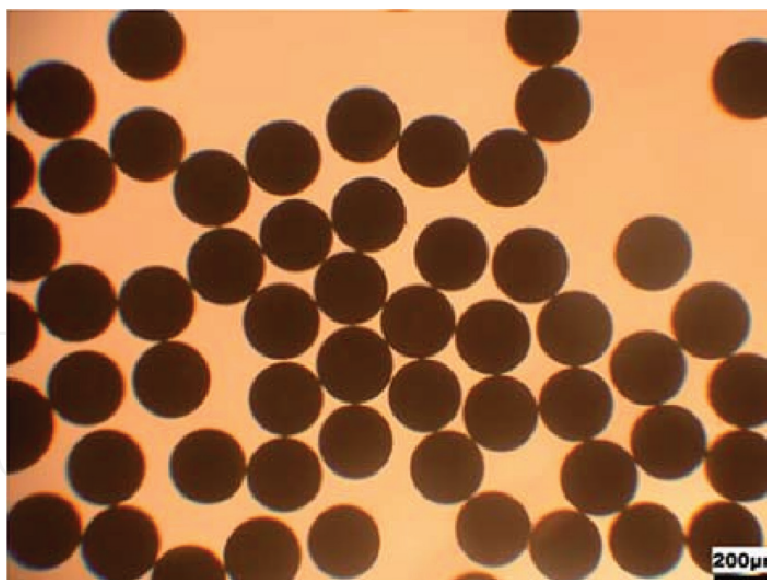


Figure 8.

Optical microscopic images and composition of organic phase is PSF: dichloromethane (DCM): [bmim] PF₆ = 5 g; 80 ml; 3 g; continuous phase is 0.1 wt% gelatin solution; inner size of nozzle: 0.6 mm, IL microcapsules, flow rate of continuous phases (CP): 30 ml/min; and flow rate of droplet phases (DP): 125 μl/min.

[bmim][PF₆] were also obtained by spraying a suspension dispersion with an encapsulation capacity of 29% [102]. PSF microcapsules have practical use such as the removal of caprolactam from water [103]. PEEK microcapsules containing trihexyl(tetradecyl) phosphonium chloride IL was obtained in *N,N*-dimethylformamide (DMF) as the dispersing phase and dodecane [104]. PTFE microcapsules containing [hmim][Tf₂N] IL lubricant with small sizes (below 10 μm) have been reported [105].

2.3.3 Electrolyte

ILs have also been used as solvents in extraction processes or as electrolytes. Polymer electrolytes comprising IL [emim][Tf₂N] and soluble SPI showed a high ionic conductivity and reliable mechanical strength, suitable for HPP actuators [106]. Gel polymer electrolytes (GPEs) [107–109] and solid polymer electrolytes [110–114] have been widely reported. A series of GPEs were prepared using the electrospun membranes of poly(vinylidene fluoride-co-hexafluoropropylene) [P(VdF-co-HFP)] incorporating ILs, 1-alkyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide in the presence of lithium bis(trifluoromethylsulphonyl)imide (LiTf₂N) [115]. An IL-GPE containing semi-crystal PVDF, amorphous polyvinyl acetate (PVAc) and ionic conductive [bmim][BF₄] was prepared via the solution-casting method for solid supercapacitors [116]. A PVDF-HFP/PMMA-blended microporous gel polymer electrolyte incorporating [bmim][BF₄] was fabricated for lithium-ion batteries [117]. Solid polymer electrolytes using poly(vinylidene-fluoridetrifluoroethylene) and *N,N,N*-trimethyl-*N*-(2-hydroxyethyl) ammonium bis(trifluoromethylsulphonyl)imide ([N_{1112(OH)}][Tf₂N]) IL were fabricated for energy storage applications [118]. PI/IL composite membranes for fuel cells operating at high temperatures were prepared by impregnating a porous Matrimid® membrane with protic ILs: 1-*n*-methyl-imidazolium dibutylphosphate ([C₁im][DBP]), 1-*n*-butylimidazolium dibutyl-phosphate ([C₄im][DBP]) and 1-*n*-butylimidazolium bis(2-ethylhexyl)phosphate ([C₄im][BEHP]). The electrolyte membranes were used as a proton-exchange membrane fuel cell (PEMFC) [119]. An IL-polymer electrolyte film based on a low-viscosity IL (1-ethyl-3-methylimidazolium dicyanamide) incorporated into a polymer matrix

(PVDF-HFP) was prepared, exhibiting liquid-like conductivity, and the maximum conductivity of PVDF-HFP + 25 wt% IL was as high as 10^{-3} S/cm, as shown in **Figure 9** [120]. Quasi-solid-state electrolytes (QSEs) consisting of IL-LiTf₂N-fumed silica nanoparticles were prepared for use in bulk-type all-solid-state cell configuration lithium-sulphur rechargeable batteries [121].

2.3.4 Nanocomposite

Carbon nanotubes (CNTs) consist of rolled-up graphene sheets and can be used as electronic, conductive and reinforcing fillers for polymer composites. MWCNTs possess a nanoscale diameter, a high aspect ratio, excellent mechanical properties, and good electrical conductivity. In recent years, MWCNTs have gained considerable interests of scientists and engineers, especially in polymer composites containing HPPs and ILs. A PI composite film comprising finely IL-dispersed MWCNTs in IL was obtained with a high shielding effectiveness (SE) for use in the packaging of a 2.5-Gbps plastic transceiver module with numerous applications in fibre to the home lightwave transmission systems [122]. PEI NCs consisting of bucky gels of industrial-grade MWCNTs and [bmim][PF₆] were prepared; they are suitable for the aerospace and electronics industries, as shown in **Figure 10** [123]. Some PI and PEI NCs consisting of MWCNTs and polymerised ILs (PILs) were prepared, exhibiting differential function [124, 125].

The crystal structure of PVDF was modified by utilising the long alkyl chains of [C₁₆mim][Br] and IL-modified MWCNTs, and the crystallisation kinetics of the composites was investigated [126, 127]. A series of PVDF composites with 'bucky gels' of MWNTs and ILs were obtained by simple melt compounding. According to the DSC and XRD results, the addition of ILs in the composites changed the crystallinity and crystal form of the PVDF [128]. PTFT and PVDF as the components of NCs containing HPP and ILs have received increasingly more attention. The nanomaterials with a nanoscale structure were prepared using pyridinium, imidazolium and phosphonium ILs as new synthetic building blocks in a PTFT. The cation-anion combination and functionalisation of ILs affect the ionic networks and nanostructures of materials [129, 130]. These nanomaterials show optimised thermal and mechanical properties and have numerous potential applications such as supercritical CO₂ [131]. PVDF/IL/GraNCs were fabricated via the solution casting of PVDF with graphene (Gra) modified with a long alkyl chain IL [C₁₆mim][Br], exhibiting a low loss tangent and low conductivity in the PVDF/ionic liquid-modified graphene

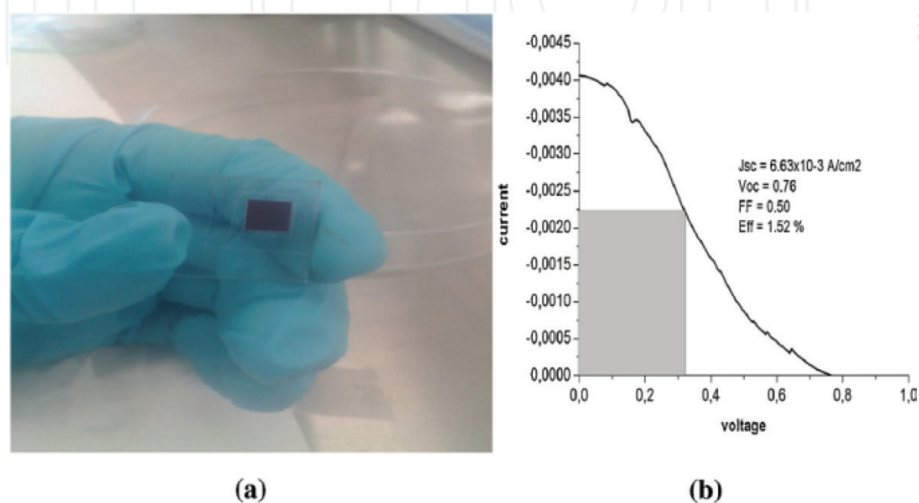


Figure 9. Photograph of (a) assemble DSSC and (b) I-V characteristics of DSSC comprising IL-incorporated PVDF-HFP polymer electrolyte film (maximum conductivity).

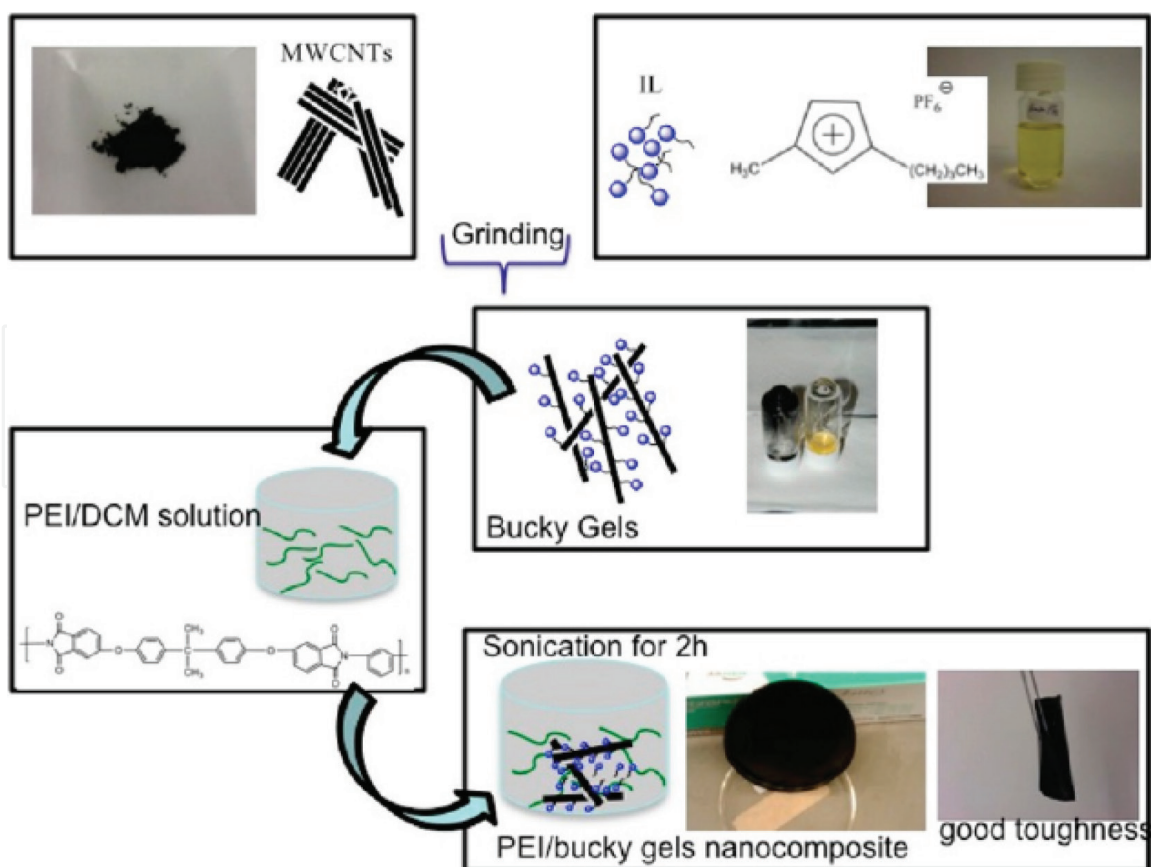


Figure 10.

Processing of PEI/bucky gel nanocomposites; the obtained composites had good toughness as the film could be curved adequately without any damage.

(GIL) composites [132, 133]. NCs, based on a homopolymer PVDF and IL, were fabricated, and the preparation process opens up a new synthesis route for nanostructured polymer composites. Dielectric NCs based on PVDF, conductive carbon black (CB) and IL 1-vinyl-3-ethylimidazolium tetrafluoroborate [VEIM][BF₄] were prepared via melt blending and electron beam irradiation (EBI) methods [134].

A nanostructured PAI was prepared in TBAB as a green medium by the step polymerisation reaction of 4,4'-methylenebis(3-chloro-2,6-diethyl trimellitimidobenzene) with 3,5-diamino-*N*-(4-hydroxy-phenyl)benzamide. Then, amino acid-functionalised multiwalled carbon nanotubes (f-MWCNTs)/PAI NCs were prepared by a solution mixing method [30].

2.3.5 Grease

In 2012, two types of conductive lubricating greases consisting of ILs (abbreviated as 'ILs lubricating greases') and HPPs were synthesised using 1-octyl-3-methylimidazolium hexafluorophosphate ([omim][PF₆]) (L-P108) and 1-octyl-3-methylimidazolium tetrafluoroborate ([omim][BF₄]) (LB108) as the base oil and PTFE as the thickener, exhibiting higher conductivities than the traditional conductive lubricating greases containing conductive stuffing, as shown in **Figure 11** [135]. The conductive lubricating greases using 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim][BF₄]) and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulphonyl)amide ([hmim][Tf₂N]) were prepared, and the conductivity and tribological performance of these greases were studied [136, 137]. By changing the type of ILs, different types of conductive lubricating greases were obtained [138].

In addition, the materials obtained by the blending of ILs with HPPs also include IL marbles containing PTFE and IL [139], PAI hollow fibre containing [bmim]

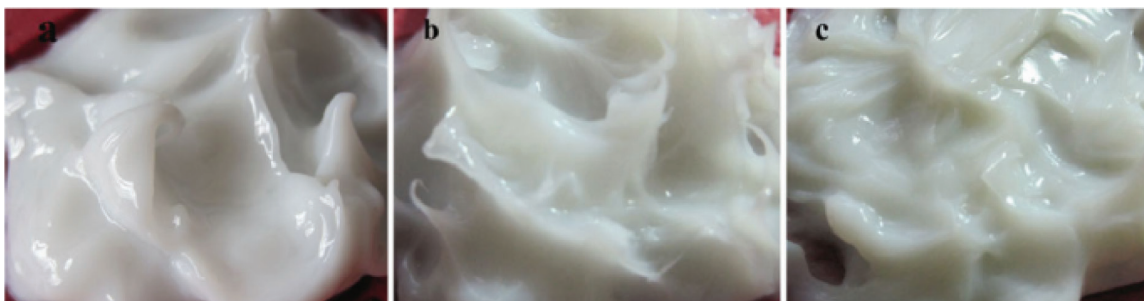


Figure 11.

The photo images of the IL lubricating greases and poly- α -olefin (PAO) grease: PAO10 (abbreviate as 'PAO lubricating grease') (a) L-P108 (b) and LB108 (c).

[Tf₂N] [140], IL-coated PTFE tube [141], PVDF/IL functionalised graphene oxide (GO-IL) composite (PGL) films [142] and electro-active electrospun fibre containing PVDF and [bmim][Tf₂N] [143]. For the materials obtained by the blending of ILs with HPPs, ILs based on imidazole and PF₆⁻ and Tf₂N⁻ are most often used [144, 145]. PVDF, PSF and PI are the most popular [44, 146–148].

3. Conclusions

Studies on ILs as the reaction media, monomers and additives in the synthesis, chemical modification and physical processing of HPPs are in progress. In 2017, the synthesis of poly(phenylene sulphide sulphone) (PPSS) in ILs was also presented. ILs are not only interesting as a replacement for traditional volatile and flammable organic solvents, but also have the potential to reduce energy consumption and increase chemical reactivity, thus leading to more efficient processes for the synthesis of HPPs. Using ILs in the synthesis of HPPs, promising and novel established approaches have been developed under mild conditions. Owing to their high ionic conductivity and polarisability, ILs, as excellent MW-absorbing agents, were introduced to polymerisation reactions to achieve higher yields and purer products than the traditional heating method. Notably, the number of novel copolymers of HPPs with polymerisable ILs has steadily increased in recent years, and they were mainly used in separating gases such as O₂, N₂, CH₄ and CO₂. ILs are not only used as reaction media in polymerisations for preparing HPPs and as monomers in the chemical modifications of HPPs, but also ILs are miscible with some HPPs and used as various types of additives (such as the components of polymer materials, plasticizers and porogenic agents) in the physical processing of HPPs. The materials prepared include membranes, microcapsules, electrolytes, NCs and grease. HPPs and inorganic substrates have been used to support IL materials by the covalent bonding of ILs, where the properties of ILs may be changed to some extent, and HPP membranes and NC-absorbed ILs exhibit concomitant changes in ionic conductivity and mobility. These novel green chemical approaches provide diverse possible new materials, and it is expected that more modified materials of HPPs and ILs with special properties and applications would be obtained. It is believed that more studies on ILs containing HPPs will be reported in the future.

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