1

Advanced Applications of Ionic Liquids in Polymer Science

Elaheh Kowsari
Amirkabir University of Technology
Islamic Republic of Iran

1. Introduction

During past few years, ionic liquids have kept attracting much attention as "green and designer" media for chemical reactions. Room-temperature ionic liquids have emerged as a potential replacement for organic solvents in catalytic processes on both laboratory and industrial scales (Holbrey & Seddon, 1999b). Literature reports on a wide range of reactions including advances in alkylation reactions (Earle et al., 1998), Diels-Alder cyclizations (Earle et al., 1999; Jaeger & Tucker, 1989), and the development of commercially competitive processes for dimerization, oligomerization, and polymerization of olefins (Abdul-Sada et al., 1995a; 1995b; Ambler et al., 1996; Chauvin et al., 1988; 1989). Effectively, Ionic liquids, among a unique set of chemical and physical properties (Chauvin, 1996; Chauvin & Mussmann 1995; Seddon, 1997), have no measurable vapor pressure, which lends them as ideal replacements for volatile, conventional organic solvents. The wide and readily accessible range of room-temperature ionic liquids with corresponding variations in physical properties, prepared by simple structural modifications to the cations (Gordon et al., 1998; Holbrey & Seddon, 1999a) or changes in anions (Bonhôte et al., 1996; Wilkes & Zaworotko, 1992), offers the opportunity to design an ionic liquid-solvent system optimized for particular processes. In other words, these ionic liquids can be considered as "designer solvents" (Freemantle, 1998).

Applications of ionic liquids as solvents for polymerization processes have widely been reviewed in literature (Kubisa, 2004; Shen & Ding, 2004; Lua et al., 2009). Ionic liquids have been used in polymer science, mainly as polymerization media in several types of polymerization processes, including conventional free radical polymerization (Sarbu, & Matyjaszewski, 2001), living/controlling radical polymerizations (such as atomtransfer radical polymerizations (ATRP) (Ding et al., 2005; Shen & Ding., 2004; Biedron & Kubisa., 2001; Biedron & Kubisa., 2002; Biedron & Kubisa., 2003), reversible addition-ragmentation transfer (RAFT) (Perrier & Davis, 2002), as well as in ionic and coordination polymerizations (Chiefari et al., 1998; Vijayaraghavan & MacFarlane et al., 2004). When radical polymerizations are conducted in an ionic liquid, a significant increase of kp/kt ratio is normally observed in comparison to those carried out in other polar/coordinating solvents. As solvents for ATRP and RAFT, ionic liquids facilitate separation of the polymer from residual catalyst and reduce the extent of side-reactions.

The use of ionic liquids in polymer science is not limited to their application as solvents. Ionic liquids are also used as additives, including plasticizers, components of polymer electrolytes, and porogenic agents) to polymers. More recently, properties of polymers containing chemically bound ionic liquid moiety (polymeric ionic liquids) are studied and the possibilities of their applications are being explored. Ionic liquids are also investigated as components of the polymeric matrixes (such as polymer gels), templates for porous polymers, and novel electrolytes for electrochemical polymerizations (Przemysław & Kubisa, 2009). This chapter focuses on the recent developments and achievements gained from applications of ionic liquids in the preparation of functional polymers as well as properties modification of polymers caused by ionic liquids.

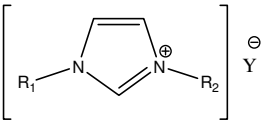## 2. Radical polymerization

2.1 Radical polymerization (ATRP) of acrylates in ionic liquids

It is known, that properties of ILs commonly depend on the structure of the cation (the symmetry and the length of alkyl substituents, the presence of hydrophobic groups, etc.) as well as on the degree of anion charge delocalization. To elucidate the influence of the nature of ILs on the yield and molecular weight of vinyl polymers, the radical polymerization of appropriate monomers (MMA) in different ionic liquids has been studied (Yakov et. al, 2007).For the MMA polymerization, the dependence between polymer η_{inh} and the length of alkyl substitute in asymmetrical 1-methyl-3-alkylimidazolium ILs was examined (Table 1). The results presented in Table 1 (entries 1–9) show, that increase of carbon chain length of imidazolium ILs leads to the reduction of polymer molecular weight, especially in the case of tetrafluoroborate ILs (Table 1, entries 5–9). Table 1 (entries 10, 11) shows, that a polymer having relatively high η_{inh} value was obtained in both tetrafluoroborate IL: [1,3-Bu$_2$Im]BF$_4$ and [1-Bu-3-(*iso*-Bu)Im]BF$_4$, but in the case of 1,3-di-n-butylimidazolium tetrafluoroborate (entry 10) the η_{inh} value of the polymer is higher (3.13 and 2.30 dl g^{-1}, respectively).

The influence of the anion nature on the radical polymerization of MMA can be revealed by comparison of the data, obtained in ILs with ordinary used [1-Me-3-BuIm] cation (Table 1, High values of polymer molar mass and an increase in the rate of free radical polymerization of MMA in ILs can be assigned to the strong effect of ionic media on the chain propagation (activation energy decrease) and chain termination, for the reason of high viscosity of the reaction system, the so-called gel effect. (Yakov et. al, 2007).

2.2 Polymerized ionic liquids: synthesis and applications

Recently, much attention has been paid to polymerized ionic liquids or polymeric ionic liquids, which are macromolecules obtained from polymerizing ionic liquid monomers (Lu et. al, 2009). Their potential applications involve polymeric electrolytes (Galiński et. al, 2006; Ricks-Laskoski& Snow, 2006; Sato et. al, 2007; Susan et. al, 2005), catalytic membranes (Carlin & Fuller 1997), ionic conductive materials (Hirao et. al, 2000; Washiro et. al, 2004; Matsumi et. al, 2006), CO_2 absorbing materials (Tang et. al, 2005a; Tang et. al, 2005b; Tang et. al, 2005c; Tang et. al, 2005d), microwave absorbing materials (Tang et. al, 2008; Amajjahe, & Ritter 2009), and porous materials (Yan & Texter, 2006; Yan et. al, 2007).

Entry[a]	R_1	R_2	Y	PMMA Yield (%)	η_{inh}[b] (dlg^{-1})
1	CH_3	C_2H_5	$(CF_3SO_2)_2N$	98	3.06
2	CH_3	C_4H_9	$(CF_3SO_2)_2N$	98	2.81
3	CH_3	C_2H_5	CF_3SO_3	96	4.09 [c]
4	CH_3	C_4H_9	CF_3SO_3	94	2.97
5	CH_3	C_3H_7	BF_4	93	3.00
6	CH_3	C_4H_9	BF_4	92	2.70
7	CH_3	C_5H_{11}	BF_4	91	2.86
8	CH_3	C_6H_{13}	BF_4	90	1.58
9	CH_3	C_7H_{15}	BF_4	95	1.55
10	C_4H_9	C_4H_9	BF_4	92	3.13
11	C_4H_9	i-C_4H_9	BF_4	96	2.30
12	CH_3	C_4H_9	PF_6	97	3.89
13	CH_3	C_4H_9	SbF_6	98	2.92
14	CH_3	C_6H_{13}	$(CF_3CF_2)_3PF_6$	98	3.29
15		$[P^+(C_6H_{13})C_{14}H_{29}]BF_4^-$			96	3.01
16		$[P^+(C_6H_{13})C_{14}H_{29}]PF_6^-$			98	3.31
17		$[P^+(C_6H_{13})C_{14}H_{29}]C^-$			98	3.48 [d]
18		$[P^+(C_8H_{17})_4]B^-$			95	3.32
19		Benzene [e]			41	0.36

[a] Polymerization parameters: [AIBN]= 0.5 wt%, [MMA] =50 wt%,
reaction time = 4 hr, reaction temperature, T = 60 ºC.
[b]For the solutions of 0.05 g of PMMA in 10.0 ml of CHCl$_3$ at 25.0 ºC.
[c]M_w = 5,770,000 g/mol (determined by static light scattering in acetone).
[d]Mw = 4,100,000 g/mol (determined by static light scattering in acetone).
[e]For comparison. (Reproduced from Vygodskii1, et. al (2007) *Polym. Adv. Technol.* 3, 18, 50–63,
Copyright (2007), with permeation from John Wiely & Sons**)**

Table 1. IL's nature effect upon the radical polymerization of MMA

A variety of polymers having imidazolium moieties in the side chains have been reported, including poly (meth) acrylate (Washiro et. al, 2004; Ding et. al, 2004; Nakashima et. al, 2007; Juger et. al, 2009), polystyrene (Tang et. al, 2005c; Tang et. al, 2005e), and poly(*N*-vinylimidazolium) derivatives (Amajjahe, & Ritter 2009; Leddet et. al, 2001; Marcilla et. al, 2004; Marcilla et. al, 2005), and most of these poly(ionic liquid)s were prepared by conventional radical polymerizations. Free radical polymerizations of various *N*-vinylimidazolium derivatives were reported to proceed in the presence of conventional radical initiator, and various copolymers involving the imidazolium group were also synthesized by this method (Mu, et. al, 2005; Sugimura et. al, 2007).

2.2.1 Microwave-absorbing ionic liquid polymer

Microwave-absorbing materials are applicable to reducing electromagnetic interference from personal computers, stealth aircraft technology, microwave cookware, and microwave darkroom protection (Petrov & Gagulin, 2001; Bregar, 2004; Yoshihiro et. al, 2002; Saib et. al, 2006; Zou et. al, 2006). Microwave absorption is usually achieved by combining dielectric and magnetic loss. Most microwave absorbing materials are polymer composites with conductive fillers, such as graphite, carbon black, and metals, or magnetic fillers, such as ferrites and carbonyl iron powders. These fillers make the microwave-absorbing materials black and hard to fabricate, for example, into precise parts or thin films (Peng et. al, 2005; Bosman et. al, 2003). Conductive polymers such as polyaniline, polypyrrole, polyalkylthiophenes, and poly(4,4'-diphenylene diphenylvinylene) were also reported as microwave-absorbing materials (Truong et. al, 2003; Chandrasekhar & Naishadham, 1999; Olmedo et. al, 1995; Wan, et. al, 2001; Phang, et. al, 2005). The structures of poly(ionic liquid)s studied by Tang and coworker are shown in Fig. 1.

Since the poly(ionic liquid)s exhibit no magnetic loss and are insulators (the reported ionic conductivity of a poly(ionic liquid) with a similar structure to the polymers reported here is about 10^{-8}s m^{-1}[34]), their microwave absorptions are solely due to the dielectric loss.
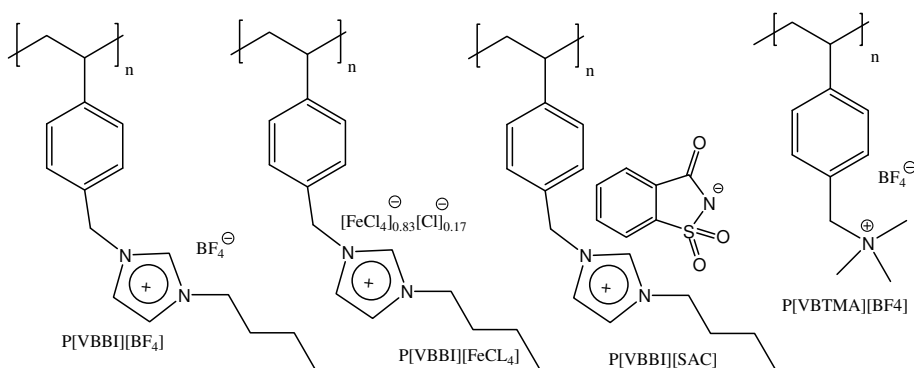

Fig. 1. Structures of poly(ionic liquid)s: poly[1-(*p*-vinylbenzyl)-3-butylimidazolium tetrafluoroborate] (P[VBBI][BF$_4$]), poly[1-(*p*-vinylbenzyl)- 3-butylimidazolium tetrachloroferrate] (P[VBBI][FeCl$_4$]), poly[1-(*p*-vinylbenzyl)-3-butylimidazolium o-benzoicsulphimide] (P[VBBI][Sac]), and poly[*p*-vinylbenzyltrimethylammonium tetrafluoroborate] (P[VBTMA][BF$_4$]).
(Reproduced from Tang et. al, (2008) *Macromolecules*, 41, 2, 493-496, Copyright (2008) with permeation from American Chemical Society)

The dielectric constant $\dot{\varepsilon}$ is shown in Fig. 2 as a function of frequency. At frequencies lower than 1 GHz, the $\dot{\varepsilon}$ decreases with increasing frequency. At higher frequencies, the $\dot{\varepsilon}$ remains essentially constant. The poly(ionic liquid)s with the imidazolium cations have similar dielectric constants ($\dot{\varepsilon} \approx 4$). In contrast, P[VBTMA][BF$_4$] with the ammonium cations has a higher dielectric constant ($\dot{\varepsilon} \approx 5.2$). This is not surprising because this material is more polar than poly(ionic liquid)s with imidazolium cations, which is in line with results of other ionic liquids (Tokuda et. al, 2006).

To probe the effect of anion on the dielectric loss, the dielectric losses of three poly(ionic liquid)s, P[VBBI][Sac], P[VBBI][BF$_4$], and P[VBBI][FeCl$_4$], with the same backbone and cations but different anions are compared. Sac$^-$ is a mostly used organic anion while BF$_4$$^-$ is a widely used inorganic anion in ionic liquids. A poly(ionic liquid) with FeCl$_4$$^-$ anions containing transition metal ions Fe^{3+} is also synthesized to test whether such kinds of anions can further increase the loss factor (Tang et. al, 2008).
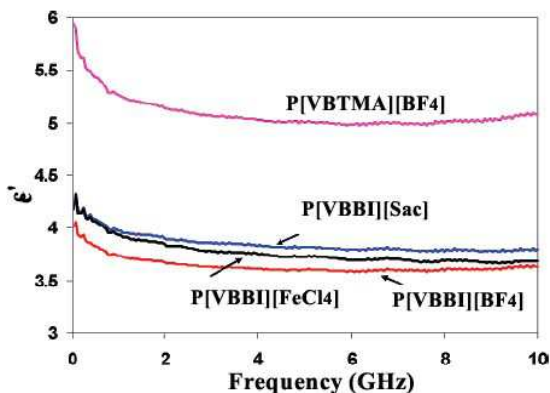
Fig. 2. Dielectric constant έ (the real part of complex permittivity) as a function of frequency (Reproduced from Tang et. al, (2008) *Macromolecules*, 41, 2, 493-496, Copyright (2008), with permeation from American Chemical Society)
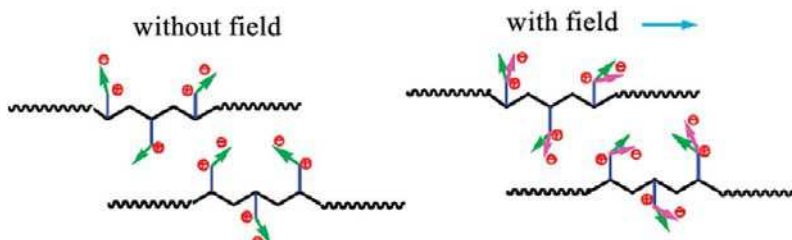

Fig. 3. Orientation of ion-pair dipoles in poly(ionic liquid) without and with an electric field (green vector vs purple vector). (Tang et. al, (2008) *Macromolecules*, 41, 2, 493-496, reprinted with permeation from American Chemical Society)

As sketched in Fig. 3, poly(ionic liquid)s have strong dipole moments created by the permanent ion pairs. In the absence of an external field, these dipoles are randomly oriented (randomly point in different directions) and continually jump from one orientation to another as a result of thermal agitation. In an external field, these dipoles orient themselves in the direction of the applied field (Fig. 3). (Tang et. al, 2008)

2.2.2 Electrowetting of a new ionic liquid monomer and polymer system

Synthesis and electrowetting of a new ionic liquid monomer and polymer system was reported by Holly and coworkers (Holly et. al, 2008). The formation of the monomeric ionic liquid salt and its polymerization is depicted in Fig. 4.
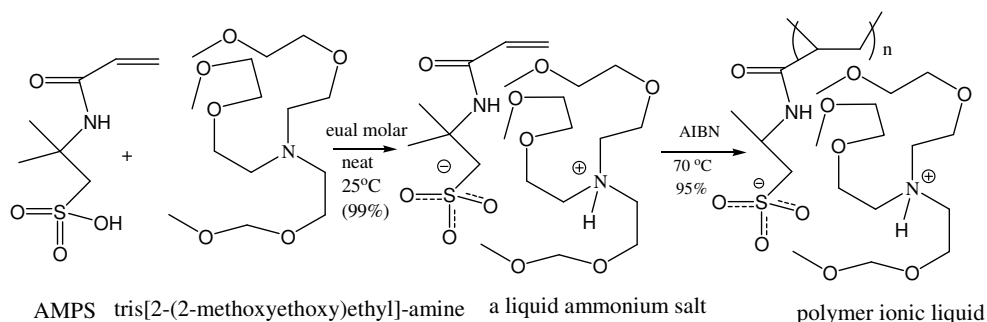

AMPS   tris[2-(2-methoxyethoxy)ethyl]-amine   a liquid ammonium salt   polymer ionic liquid

Fig. 4. Reaction Scheme for AMPS oxyethylene ammonium salt monomer and polymer (Reproduced from Ricks-Laskoski & Snow (2006) *J. Am. Chem. Soc.* 128, 38, 12402-12403, Copyright (2006), with permeation from American Chemical Society)

The uniqueness of the oxyethylene amine in the formation of the ammonium cationic species contributes to both the ionic and liquid nature of the monomer and polymer. Even more remarkable is the ability of this polymer to maintain its liquid nature as a macromolecule and to wet a substrate, showing preference for one polarity based upon the makeup of the ionic backbone of the polymer formed (Ricks-Laskoski & Snow, 2006).

Polymerizable ionic liquids and their actuation in an electric field are a combination of material and properties with unique potential to display structural and fluid dynamics above that found for small molecule ionic liquids.

Electrowetting is an electrostatically driven surface effect where a liquid droplet's spreading on a hydrophobic surface is modulated by application of a voltage to the droplet and an underlying conducting substrate (Quilliet &. Berge 2001). A schematic of this effect is illustrated in Figure 5.
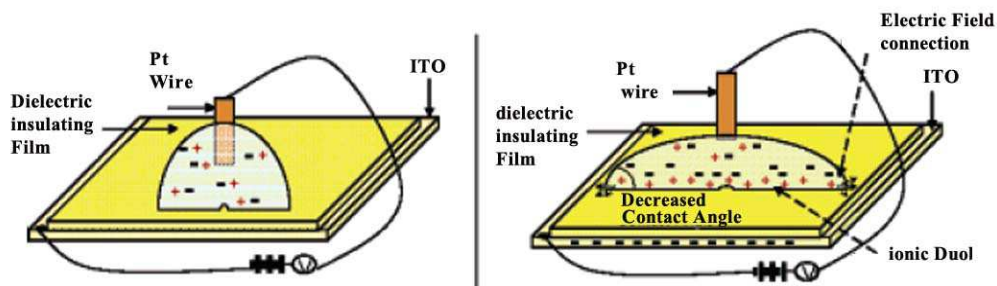

Fig. 5. Depiction of an electrowetting actuation electrode setup with (right) and without (left) an induced electric field (Reproduced from Ricks-Laskoski & Snow (2006) *J. Am. Chem. Soc.* 128, 38, 12402-12403, Copyright (2006), with permeation from American Chemical Society)

The droplet rests on a very thin low-dielectric insulating film (Teflon AF) which is supported on a conducting substrate and is contacted at the top by a very fine wire contact. Application of a voltage builds up a layer of charge on both sides of the interface with the dielectric film and decreases the interfacial energy.

2.2.3 Polymerized ionic liquids: solution properties and electrospinning

The solution properties and electrospinning of a polymerized ionic liquid was explored by Chen and Elabd (Chen & Elabd, 2009) Polymerized ionic liquids are synthesized from polymerizing ionic liquid monomers, where ionic liquids are of great interest due to their unique physiochemical properties. Compared to other polyelectrolyte solutions, this polymerized ionic liquid solution exhibits similar viscosity scaling relationships in the semidilute unentangled and semidilute entangled regimes. However, the electrospraying-electrospinning transition occurs at similar polymer solution concentrations compared to neutral polymers, where electrospinning produced beaded fibers and defect free fibers at ~1.25 and ~2 times the entanglement concentration, respectively. Due to high solution conductivities, electrospinning produces fibers approximately an order of magnitude smaller than neutral polymers at equivalent normalized solution concentrations. In addition, a high ionic conductivity of the solid-state fiber mat was observed under dry conditions and even higher conductivities were observed for polyelectrolyte fiber mats produced from electrospinning polyelectrolyte-ionic liquid solutions, where both anion and cation are mobile species. Structure of polymerized iIonic liquid poly(MEBIm-BF$_4$) is shown in Fig. 6.

Fig. 7 shows the morphology of the fibers at various ionic liquid contents. Instead of reduced fiber sizes, the existence of ionic liquid results in larger fibers with a ribbon structure. This can be attributed to the nonvolatility of ionic liquid that hinders the solidification of fibers to smaller sizes. Moreover, the liquid component in the fiber collapses the fiber into a ribbon structure.

With the increase of ionic liquid content, more ribbons were observed in the fiber mat (Fig 7).
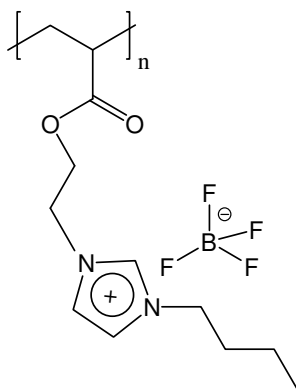

Fig. 6. Structure of polymerized ionic liquid poly(MEBIm-BF$_4$) (Reproduced from Chen et al., (2009) *Macromolecules* 42, 3368-3373, Copyright (2009), with permeation from American Chemical Society)
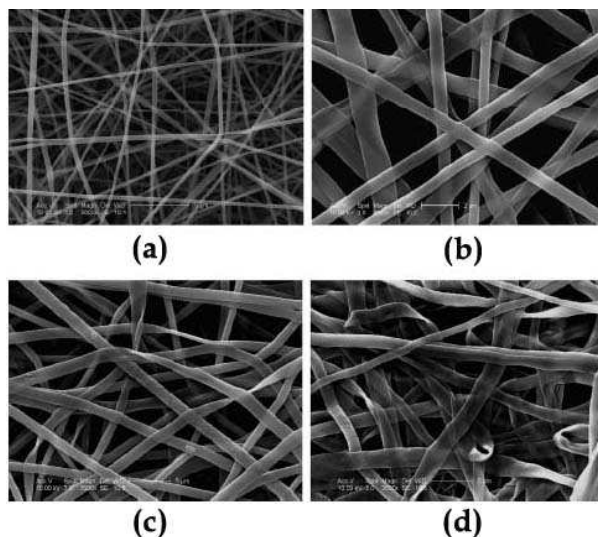
Fig. 7. Field emission scanning electron microscope images of electrospun Nafion-PAA-BMIm-BF4 blend at ionic liquid weight fraction of (a) 0%, (b) 10%, (c) 20%, (d) 30%. The weight ratio of Nafion:PAA is 3:2 at a 10 wt % total polymer concentration (Reproduced from Chen et al., (2009) *Macromolecules* 42, 3368-3373, Copyright (2009), with permeation from American Chemical Society)

2.3 Ultrasound and ionic-liquid-assisted synthesis method

Currently, the study of physical and chemical effects of ultrasound irradiation is a rapidly growing research area. When liquids are irradiated with high-intensity ultrasound irradiation, acoustic cavitations (the formation, growth, and implosive collapse of bubbles) provide the primary mechanism for sonochemical effects. During cavitation, bubble collapse produces intense local heating, high pressures, and extremely rapid cooling rates (Suslick et.al 1991, Suslick 1988). These transient, localized hot spots can drive many chemical reactions, such as oxidation, reduction, dissolution, decomposition, and promotion of polymerization (Suslick 1988). One of the most important recent aspects of sonochemistry has been its application in the synthesis of nanodimensional materials (Suslick & Price, 1999). Ultrasound irradiation offers a very attractive method for the preparation of novel materials with unusual properties and has shown very rapid growth in its application in materials science due to its unique reaction effects and ability to induce the formation of particles of much smaller sizes (Suslick 1988, Suslick & Price, 1999). The advantages of the sonochemical method include a rapid reaction rate, controllable reaction conditions, and the ability to form nanoparticles with uniform shapes, narrow size distributions, and high purity.

2.3.1 Ultrasound and ionic-liquid-assisted synthesis and characterization of polyaniline/Y$_2$O$_3$ nanocomposite with controlled conductivity

A sonochemical method has been employed to prepare polyaniline-Y$_2$O$_3$ (PANI/Y$_2$O$_3$) nanocomposite with controlled conductivity with the assistance of an ionic liquid by

Kowsari and Faraghi (Kowsari & Faraghi, 2010) Ultrasound energy and the ionic liquid replace conventional oxidants and metal complexes in promoting the polymerization of aniline monomer. Ionic liquids (with unique properties) can act as morphology templates for the synthesis of PANI/ Y_2O_3 nanocomposite with novel or improved properties. Here task specific acidic ionic liquids with different counter ions induce different template and different PANI morphology. The structures of ionic liquids studied by Kowsari Faraghi are shown in Fig. 8.
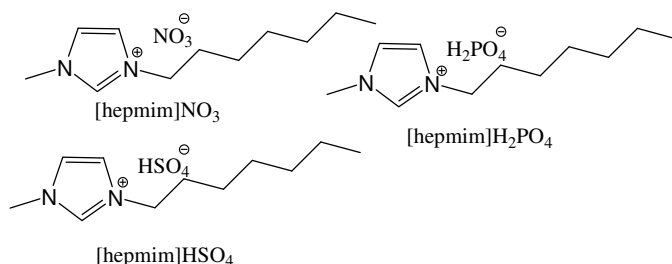

[hepmim]NO₃

[hepmim]H₂PO₄

[hepmim]HSO₄

Fig. 8. The structures of ionic liquids in this study

Fig. 9a–d exhibits the morphology of PANI/Y_2O_3 nanocomposite in the presence of different type of ionic liquid. Interesting morphologies were obtained for PANI/Y_2O_3 nanocomposites. To compare the effects of ionic liquid additives on the properties of the resulting PANI/ Y_2O_3 nanocomposite, the monomer concentration ratio was kept constant. The differences in the structure of PANI/ Y_2O_3 nanocomposite prepared, in the presence of ionic liquids are clearly visible. At the same magnification PANI/ Y_2O_3 nanocomposite (with [hepmim]. H_2PO_4 ionic liquid) reveals an interesting ribbon structure (Fig. 9a). The nanosheet structure of PANI/ Y_2O_3 in the presence of [hepmim] HSO_4, ionic liquid is shown in Fig. 9b. In Fig. 9b the smooth surface of PANI/ Y_2O_3 is visible. Smooth surfaces of it can be a reason for the better conductivities of these samples compared to Y_2O_3-free PANI. The SEM study shows that the presence of ionic liquid additives in polymerization strongly affects the morphology of PANI/ Y_2O_3. ionic liquids play a key role in tailoring the resultant conducting PANI/ Y_2O_3 structures. It was found that in the presence of [hepmim] NO_3, the products were regular solid microspheres covered with some nanoparticles.(Fig 9c) .TEM image of Y_2O_3 is shown in Fig 9d.

The influence of three different ionic liquid counter anions, namely HSO_4^-, $H_2PO_4^-$ and NO_3^- on conductivity was investigated by preparing composites in the presence of these anions. It was observed that the conductivity was strongly influenced by the type of anion, although the yields of the respective composites were subject to variation. Since the PANI in the composite is in its emeraldine salt form irrespective of the acid used, the variation in conductivity most probably stems from the differences in the size and nature of the dopant anions.

As can be seen in Fig. 10, the conductivities may be classified in the decreasing order NO_3^- < HSO_4^- < $H_2PO_4^-$

The effect of the concentration of ionic liquid = [hepmim]HSO_4) on PANI-Y_2O_3 morphology is shown is Fig 11. As is vivid, at 0.2 M concentration morphology is a mixture of fibers and plates. When the concentration increases to 0.4, fibers gradually disappear and change into plates. Also, when the concentration reaches 0.6, the plates become thin in terms of
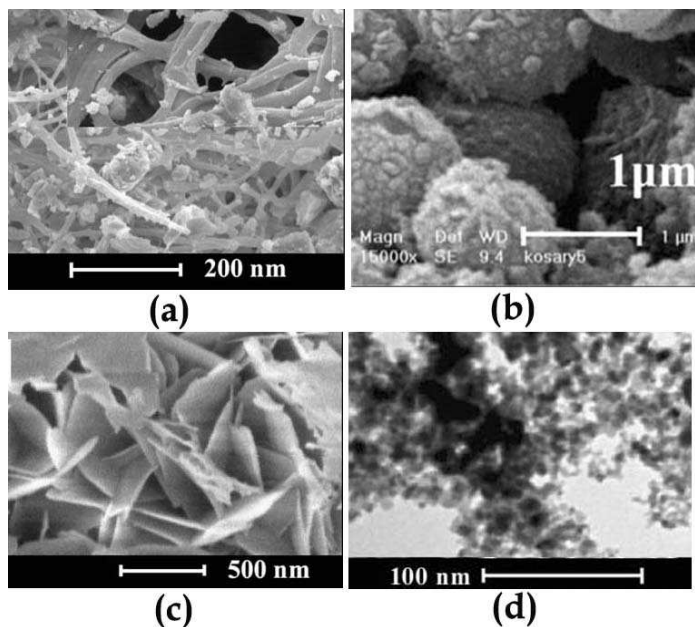
Fig. 9. SEM images of PANI/Y$_2$O$_3$ composite at different type of IL: (a) PANI/ Y$_2$O$_3$ composite (Y2O3 = 30%, aniline = 0.2 M, and IL = [hepmim]•H$_2$PO$_4$ = 0.6 M), (b) PANI/ Y$_2$O$_3$ composite (Y$_2$O$_3$ = 30%, aniline = 0.2 M, and IL = [hepmim]•HSO$_4$ = 0.6 M), (c) PANI/ Y$_2$O$_3$ composite (Y$_2$O$_3$= 30%, aniline = 0.2 M, and IL = [hepmim]•NO$_3$ = 0.6 M). (d) TEM image of Y$_2$O$_3$ (Reproduced from Kowsari & Faraghi (2010) *Ultrason. Sonochem.* 17, 4, 718-725, Copyright (2010), with permeation from Elsevier)
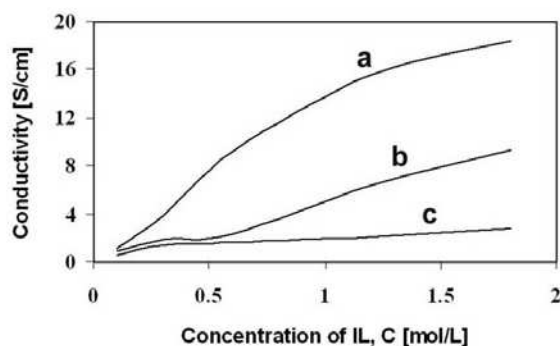

Fig. 10. The conductivities of PANI/Y$_2$O$_3$ composites at different concentrations of ILs: (a) PANI/Y$_2$O$_3$ composite (Y$_2$O$_3$ = 30%, aniline = 0.2 M, and IL = [hepmim] ·H$_2$PO$_4$ = 0.6 M), (b) PANI/Y$_2$O$_3$ composite (Y$_2$O$_3$ = 30%, aniline = 0.2 M, and IL = [hepmim] ·HSO$_4$ = 0.6 M), (c) PANI/Y$_2$O$_3$ composite (Y$_2$O$_3$ = 30%, aniline = 0.2 M, and IL = [hepmim] · NO$_3$ = 0.6 M). (Reproduced from Kowsari & Faraghi (2010) *Ultrason. Sonochem.* 17, 4, 718-725, Copyright 2010), with permeation from Elsevier)

thickness. As for both mentioned ionic liquids, increase in concentration brings about higher conductivity and yield, as well.

In the present study, when there is an increase in a frequency from 20 to 40 kHz, the morphology evolves as sphere shapes. In additions, the yield would be 55 wt %, 76 wt %, and 80 wt % at 20, 30, and 40 kHz for frequency.

Ultrasonic irradiation at 40 kHz, yields constantly higher degradation efficiencies compared with that at 20 kHz for all ionic liquids. Since, in the present study, the ionic liquid replaces conventional oxidant and metal complexes for polymerization, the increase of ionic liquids degradation leads to the increase of the concentration of alkyl radicals and the increase of aniline polymerization and, therefore, the increase of yield of product.

2.4 Ziegler-Natta polymerisation of ethylene

Ziegler-Natta polymerisation is used extensively for the polymerisation of simple olefins (e.g. ethylene, propene and 1-butene) and is the focus of much academic attention, as even small improvements to a commercial process operated on this scale can be important. Ziegler-Natta catalyst systems, which in general are early transition metal compounds used in conjunction with alkylaluminium compounds, lend themselves to study in the chloroaluminate(III) ionic liquids, especially the ones with an acidic composition.

During studies into the behaviour of titanium(IV) chloride in chloroaluminate(III) ionic liquids Carlin *et al* carried out a brief study to investigate if Ziegler-Natta polymerisation was possible in an ionic liquid (Carlin et. al 1990)
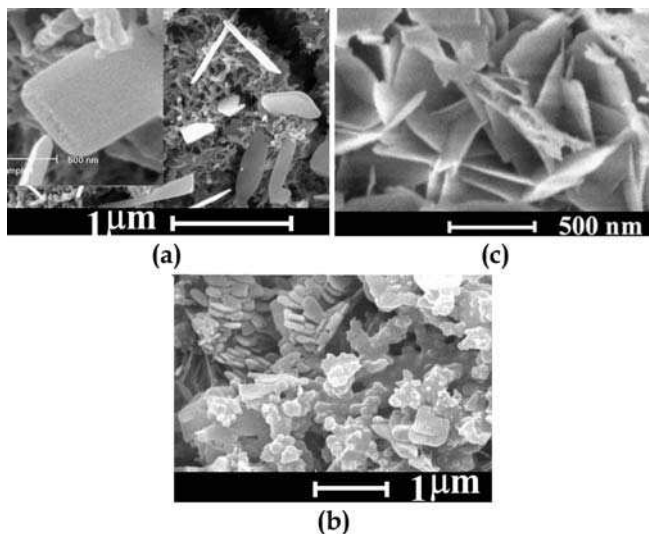

Fig. 11. SEM images of PANI/Y_2O_3 composite (Y_2O_3 = 30%, aniline = 0.2 M, and IL = [hepmim] $\cdot$HSO$_4$) at different concentrations of ILs (a) [IL] = 0.2 M, (b) [IL] = 0.4 M, (c) [IL] = 0.6 M (Reproduced from Kowsari & Faraghi (2010) *Ultrason. Sonochem.* 17, 4, 718-725, Copyright (2010), with permeation from Elsevier)

2.5 Microemulsion polymerization by ionic liquids

Microemulsions are thermodynamically stable dispersions containing two immiscible liquids stabilized by surfactants at the liquid-liquid interface. Compared with "classic" water-inoil microemulsions, ionic liquid-in-oil microemulsions, in which an ionic liquid dispersed in an oil-continuous phase by suitable surfactants, are of great interest due to the unique features of both ionic liquid and microemulsion system (Eastoe et al., 2005; Binks et al., 2003; He et al., 2006; Atkin et al., 2007; Gao et al., 2004; Li et al., 2007). Microemulsions composed of a room temperature ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF$_4$]), cyclohexane, and a surfactant, Triton X-100, have been recently studied by Han (Gao et al., 2004) and Eastoe (Eastoe et al., 2005). Small angle neutron scattering data clearly demonstrated the formation of ionic liquid nanodroplets dispersed in cyclohexane (Eastoe et al., 2005). More recently, microemulsions composed of an ionic liquid dispersed in a variety of organic oils, such as toluene, (Li et al., 2007; Gao et al., 2006) xylene (Gao et al., 2006b) and benzene, (Gao et al., 2007) have been investigated by several groups. These microemulsions behaviors are consistent with water-in-oil microemulsions and provide nanosized ionic liquid domains as reaction or extraction media which should avoid contacting with water. However, potential uses of these ionic liquid - based microemulsions have not been intensively studied so far.

2.5.1 Microemulsions with an ionic liquid surfactant

The formation of amphiphilic association structures in and with ionic liquids, such as micelles, vesicles, microemulsions and liquid crystalline phases has been reviewed recently (Hao & Zemb, 2007, Qiu, & Texter, 2008). The formation of micelles formed by common surfactants in EAN was first documented in 1982 by Evans and coworkers (Evans et al, 1982, 1983), whereas the formation of liquid crystals of lipids in ethyl ammonium nitrate (EAN) (Evans, & Kaler, 1983) as well as lyotropic liquid crystals of non-ionic surfactants were observed in the same room temperature ionic liquid (Araos & Warr, 2005). The formation of liquid crystalline phases of binary mixtures of [C$_{16}$mim][Cl] and EAN has also been described lately (Zhao et al, 2009). The self-aggregation of common ionic and non-ionic surfactants in imidazolium based RTIL was also reported. (Anderson et al, 2003; Patrascu et al, 2006; Hao et al, 2005)

As imidazolium based ionic liquids (ILs) with long-chain hydrocarbon residues exhibit surfactant properties in water (Thomaier& Kunz, 2007; (Bowers et al, 2004; Miskolczy et al, 2004; Sirieix-Plenet et al, 2004; Kaper & Smarsly, 2006; Seoud et al, 2007), Thomaier and coworkers could recently demonstrate that the surfactant like ionic liquid (SLIL) 1-hexadecyl-3-methylimidazolium chloride ([C$_{16}$mim][Cl]) forms colloidal structures in EAN as well. They found a critical aggregation concentration (cac) approximately ten times higher than the critical micelle concentration (cmc) in the corresponding aqueous system. (Thomaier & Kunz, 2007) This gap is in accordance with the results of Evans *et al.*, who found that the cacs of classical surfactants in EAN are between 5 and 10 times higher than in water. (Evans et al, 1982)

2.5.2 Polymerization of ionic liquid-based microemulsions: The synthesis of polymer electrolytes

S. Yu and coworkers (Yu et al, 2008) reported the first example of polymerization of microemulsions comprising surfactant stabilized ionic liquid nanodomains. Polymerization of these ionic liquid-based microemulsions yielded free-standing, flexible, and transparent

polymer electrolytes even though the resulting vinyl polymers are incompatible with ionic liquid cores. The obtained ionic liquid/ polymer composites show high conductivity at both room temperature and elevated temperature. This facile yet and effective method provides a versatile platform for the preparation of semisolid polymer electrolytes containing ionic liquids. Although They only demonstrated this method with vinyl monomers of styrene, methyl methacrylate, vinyl acetate, and *N,N*-dimethylacrylamide and only one surfactant as examples, they believe that this method should be extendable to other liquid monomers with similar polarity and ionic liquids with desirable properties. The elucidation of interaction between the polymeric matrix and ionic liquids need to be further explored in future work.

2.6 Aqueous/ionic liquid interfacial polymerization

Interfacial polymerization (IP) involves step polymerization of two reactive monomers or agents, which are dissolved respectively in two immiscible phases and the reaction takes place at the interface of the two liquids. IP has been used to prepare various polymers, such as poly(urea), poly(amide), and poly(ester) capsules.

It allows the synthesis of polymers at low temperature with limited side reactions, and can avoid the use of catalysts or phase transfer agents. The relative ease of IP has made it the preferred technique in many fields, ranging from microencapsulation of pharmaceutical products to preparing conducting polymers. IP is commonly done with volatile organic solvents as the organic phase, such as benzene (Chu et al, 2002), chloroform (Ashgarian et al, 1999), and toluene (Lu et al, 2002). The nonvolatile nature of ionic liquids gives them significant advantage in minimizing solvent consumption. They are good solvents for organic, inorganic, and polymeric compounds, and have been used as media for chemical reactions (Dupont et al, 2002), including polymerization (Harrisson et al, 2003) and ionic liquid/CO_2 biphasic reactions. Poly aniline (PANI) has been synthesized with water/ionic liquid IP by Kowsari and Yavari (Kowsari & Yavari, 2009). This method has some obvious advantages, such as PANI nanofiber can be fabricated and both solvents used are environmentally benign.

3. Polycondensation processes in ionic liquids

Polycondensation is typically conducted at relatively high temperature thus non-volatile and thermally stable ionic liquids seem to be suitable solvents for polycondensation processes. Research in this area has mainly been directed towards synthesis of polyamides, polyimides and polyesters. On the other hand, in some studies of polycondesation catalytic effect of ionic liquids was observed. More recently, two step procedures (involving post polycondensation in ionic liquid) was applied to polycondensation of sebacic, adipic, and succinic acid with aliphatic diols. Aliphatic polyesters with Mw up to $6{\times}10^4$ were obtained and once more it was noted that solubility of polyesters in ionic liquid was a limiting factor. Solubility depends on structure of IL (nature of cation and anion) and correlation was found between the miscibility of aliphatic polyester/ionic liquid system and the extent to which their solubility parameters matched (Kubisa, 2009).

3.1 Ionic liquids as novel solvents and catalysts for the direct polycondensation

The direct polycondensation of *N,N'*-(4,4'-oxydiphthaloyl)- bis-L-phenylalanine diacid with various aromatic diamines was performed in ionic liquid media by Mallakpour and Kowsari

(Mallakpour & Kowsari, 2005). The influence of various reaction parameters, including the nature of the ionic liquid cations and anions, the monomer structures, the reaction temperature, and the reaction time, on the yields and inherent viscosities of the resulting optically active poly(amide imide)s (PAIs) were investigated. Direct polycondensation preceded in ionic liquids and triphenyl phosphite (a condensing agent) without any additional extra components, such as LiCl and pyridine, which are used in similar reactions in ordinary molecular solvents. Therefore, ionic liquids can act as both solvents and catalysts. Various high-molecular weights, optically active PAIs were obtained in high yields with inherent viscosities ranging from 0.54 to 0.88 dL/g. This method was also compared with three other classical methods for the polycondensation of the aforementioned monomers.

3.2 Polycondensation processes in ionic liquid under microwave irradiation

Application of ionic liquids as media to microwave-assisted reactions offers several advantages. Typical organic solvents are frequently flammable and volatile, which is a safety hazard for high-temperature and closed-vessel applications using microwaves. In contrast, ionic liquids have high boiling-points, low vapor pressures, and high thermal stabilities. In addition, typical ionic liquids have moderately high dielectric constants (in the range of 10–15), and relatively low heat capacities (in the range of 1–2 J/g K). This combination allows ionic liquids to absorb microwaves efficiently. Owing to these advantages, ionic liquids have been investigated as solvents in a number of microwave-mediated reactions. Microwave heating in ionic liquids was used also for polycondensation reactions leading to polyamides (Mallakpour& Kowsari, 2006). Certain advantages have been indicated, but until now only slight improvement of reactions conditions (more efficient heating, higher rates) has been achieved.

4. Ionic polymerization

4.1 Cationic polymerization

Ability of ionic liquids to dissolve wide range of inorganic compounds was exploited in the study in which organoborate acids (HBOB) (bisoxalatoboric acid, bissuccinatoboric and bisglutaratoboric acids) were used as initiators of the cationic polymerization of styrene in pyrollidonium, imidazolium and phosphonium bis (trifluromethanesulfonyl) amide ionic liquids. In another study, cationic polymerization of styrene initiated with $AlCl_3$ in ionic liquid ([bmim][PF6]), supercritical CO_2 and organic solvent (CH_2Cl_2) was investigated. The only conclusion was that in ionic liquids rates and molecular weights are higher than in organic solvent (Kubisa, 2009).

Studies on the dimerisation and hydrogenation of olefins with transition metal catalysts in acidic chloroaluminate(III) ionic liquids report the formation of higher molecular weight fractions consistent with cationic initiation (Chauvin et. al 1990; Ellis et. al 1999). These studies ascribe the occurrence of the undesired side reaction to both the Lewis acid and the proton catalysed routes. Their attempts to avoid these side reactions led to the preparation of alkylchloroaluminate(III) ionic liquids and buffered chloroaluminate(III) ionic liquids (Chauvin et. al 1990; Ellis et. al 1999).

Attempts to bring the benefits of ionic liquid technology by drawing on the inherent ability of the chloroaluminate(III) ionic liquids to catalyse cationic polymerisation reactions, as

opposed to minimising them, were patented by Ambler et al of BP Chemicals Ltd in 1993 (Ambler, 1993). They used acidic [EMIM][Cl-AlCl$_3$] (X(AlCl$_3$) = 0.67) for the polymerisation of butene to give products that find application as lubricants. The polymerisation can be carried out by bubbling butene through the ionic liquid. The product formed a separate layer that floats upon the ionic liquid and was isolated by a simple process. Alternatively, the polymerisation was carried out by injecting the ionic liquid into a vessel charged with butene. After a suitable settling period the poly(butene) was isolated in a similar fashion. The products from these reactions must be best described as oligomers as opposed to polymers as the product is still in the liquid form. Chain transfer to impurities, ionic liquid, monomer and polymer will terminate the propagation reaction resulting in the low-mass products.

4.1.1 Cationic polymerization of styrene in scCO$_2$ and [bmim][PF$_6$]

Bueno and coworkers (Bueno. et. al 2009) presented a study on the cationic polymerization of styrene in different reaction media, supercritical CO$_2$ (scCO$_2$), [bmim][PF$_6$], dichloromethane, and scCO$_2$ plus [bmim][PF$_6$] using AlCl$_3$ as initiator at temperatures from 273 to 333 K. The reactions were analyzed in relation to the monomer conversion rate, polymer structures, average molecular weights and molecular weight distribution. In all cases, the styrene polymerization produced oligomers. Reactions using ionic liquid as a solvent led to higher molecular weight and monomer conversion rate. Monomer conversion rates of about 100% and weight average molecular weight (Mw) of 2400 at 298 K were obtained. Reactions with scCO$_2$ as a solvent yielded low monomer conversion rates (around 50%) and a Mw = 2000 at 298 K. The oligolystyrenes presented rr syndiotactic-rich sequences in the microstructure in all reaction conditions. The use of ionic liquid and scCO$_2$ results in better yields than the use of the other organic solvents.

4.2 Anionic polymerization
4.2.1 Anionic polymerization of methyl methacrylate in an ionic liquid

Anionic polymerization reactions of methyl methacrylate (MMA) in ionic liquids were carried out by utilizing alkyl lithium initiators such as n-butyl lithium (n-BuLi) and diphenylhexyl lithium (DPHLi) by H. Kokubo and Watanabe (Kokubo & Watanabe, 2008). The polymerization in ionic liquids having bis(trifluoromethyl sulfonyl)amide ([NTf$_2$]) anion did not yield poly(MMA) (PMMA), because of the deactivation of the initiator due to an attack on the trifluoromethyl group. By using 1-butyl-3-methylimidazolium hexafluorophosphate ([C$_4$mim][PF$_6$]), the polymerization reactions proceeded. The PMMA prepared in [C$_4$mim][PF$_6$] gave low yields (5–9%), as compared with those (15–62%) obtained forPMMAprepared in tetrahydrofuran (THF), and the prepared PMMA had large polydispersity indices (≈ 2.0). The results obtained can be attributed to the high reaction temperature (0 °C), in comparison to the common anionic polymerization temperature of MMA, -78 °C, and the reaction between the initiator and the imidazolium cation. The initiator was considered to be deactivated because the hydrogen atom at the 2-position of the imidazolium ring was withdrawn by the alkyl lithium initiator. The tacticity of the obtained PMMA, prepared in [C$_4$mim][PF$_6$] by utilizing DPHLi, was rich in *mm* triads, similar to that polymerized in toluene

5. Miscellaneous application of ionic liquids in polymer chemistry

5.1 Polymer electrolytes: Compatible system between polymers and ionic liquids (Ion gels)

Polymer electrolytes containing room temperature ionic liquids were first reported on such a system by Noda & Watanabe (Noda & Watanabe, 2000). Successively, the study was expanded to polymer electrolytes containing chemically stable ionic liquids (Noda & Watanabe, 2000; Watanabe et. al 1993; Watanabe et. al 1995; Watanabe & Mizumura 1996; Ogata et. al 1995; Susan et. al 2005). Watanabe and coworkers found that common vinyl monomers were widely soluble in common ionic liquids and that they could be polymerized by free radical polymerization (Noda & Watanabe 2000; Susan et. al 2005). In certain cases, surprisingly good compatibility of the resulting polymers with the ionic liquids could be achieved irrespective of the polymer concentration and temperature (Fig. 12).

Typically, the polymerization of methyl methacrylate (MMA) in a common ionic liquid, 1-ethyl-3-methyl imidazolium bis(trifluoromethane sulfone)imide ($[C_2mim][NTf_2]$) in the presence of a small amount of a cross-linker gives self standing, flexible, and transparent polymer gels. The polymer and ionic liquid composite gels, which they term "ion gels", show a single T_g for a given range of $[C_2mim][NTf_2]$ composition, and the T_g decreases with an increase in the mole fraction of $[C_2mim][NTf_2]$ (Fig 13) (Susan et. al 2005; Ueki &.Watanabe 2008).
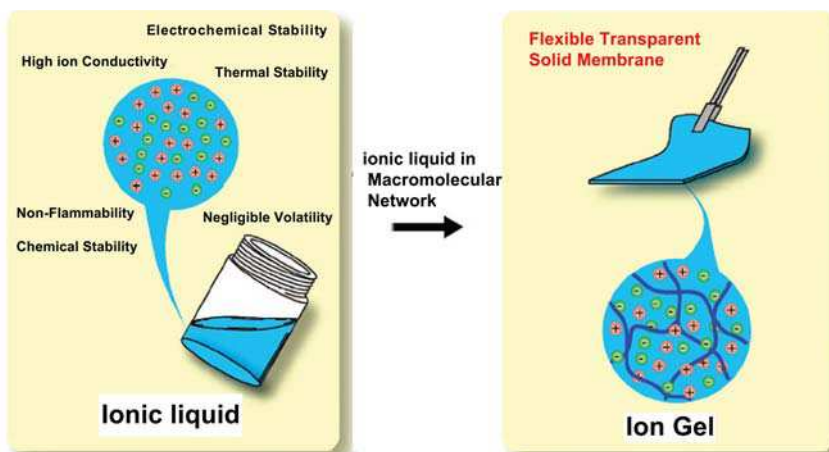

Fig. 12. Preparation of ion gels (compatible binary systems between polymer networks and ionic liquids) by a variety of methods such as in situ radical polymerization of vinyl monomers in ionic liquids and sol–gel transition of macromolecules in ILs. The flexibility of molecular design of ionic liquids can facilitate various interesting applications of ion gels, particularly as ion-conducting polymer electrolytes (Reproduced from Ueki & Watanabe (2008) *Macromolecules*, 41, 11, 3739-3748, Copyright (2008) ,with permeation from American Chemical Society)

5.2 Ion gel gated polymer thin-film transistors

Lee and coworkers (Lee et. al 2007) demonstrate that a gel electrolyte (a so-called "ion gel") based on a mixture of an ionic liquid and a block copolymer can provide both large specific

capacitance (>10 µF/cm2) and greatly improved polarization response times (1 ms) when used as the gate dielectric in a polymer TFT (thin-film transistor). The improved properties allow transistor operation at frequencies greater than 100 Hz, significantly faster than what has been demonstrated previously and opening the door to a broader range of applications. Furthermore, the ion gel material is solution processible, making it potentially compatible with high throughput patterning methods (e.g., ink jet printing). Unlike traditional solid polymer electrolytes, which are obtained by the dissolution of salts by ion-coordinating polymers, the ion gel electrolyte is formed by gelation of poly(styrene-block-ethylene oxide-block-styrene) (SOS) triblock copolymer in 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF$_6$]), a room temperature ionic liquid; the structures of these materials are shown in Fig. 14.

6. Conclusions

Further progress in the area of ionic liquids and specifically polymerization mechanisms is inevitable. Due to distinctive features and "green" applications of ionic liquids in industry, researchers have found this research topic an interesting and promising one. Very attractive initial applications for the incorporation of ionic liquids monomers into polymers have been reported, but the range of possible ionic liquid structures is much larger than has so far been explored. What seems to be necessary and needed is careful selection of the systems studied where real synthetic advantages of applying ionic liquids are offered or new insights into polymerization mechanisms are provided. These research requirements are opposed to mere mentioning, although new, examples of processes that can be carried out with regard to ionic liquids. This way, achievements in the field can be foreseen.
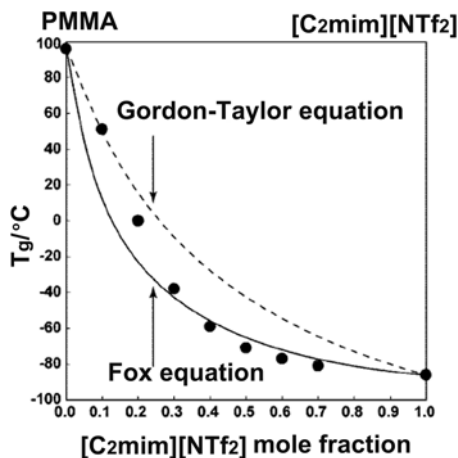

Fig. 13. Glass transition temperatures (Tg) of PMMA network polymers with dissolved [C$_2$mim][NTf$_2$] as a function of [C$_2$mim][NTf$_2$] mole fraction. The points denote experimental Tg results, the broken lines denote the fitted profiles by the Gordon-Taylor equation, and the solid lines denote those by the Fox equation. (Reproduced from Susan et. al (2005) *J Am. Chem. Soc.* 2005, 127, 4976, Copyright (2005), with permeation from American Chemical Society)
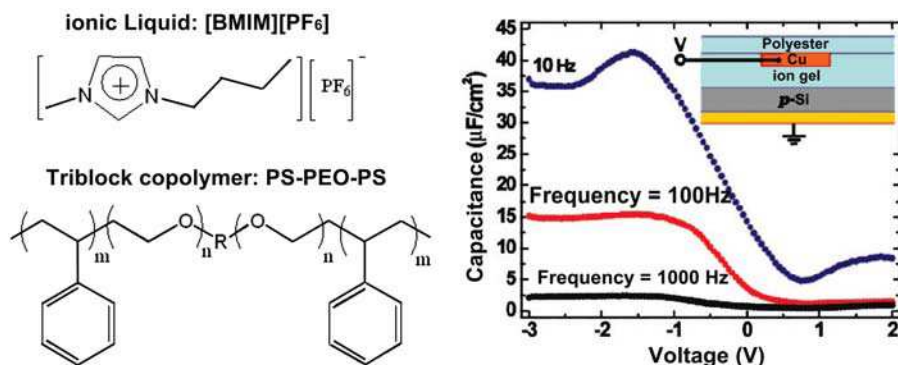
Fig. 14. Structure of the ionic liquid and triblock copolymer ion gel components (left) and C-V characteristics of a p-Si/ion gel/Cu test structure (see inset) at three frequencies (right). The C-V curves indicate large frequency-dependent hole accumulation in the Si at negative bias on the top contact (Reproduced from Lee et. al (2007) *J. Am. Chem. Soc.* 129, 4532-4533, Copyright (2007), with permeation from American Chemical Society)

7. Acknowlegment

8. Reference

Abdul-Sada, A. K.; Ambler, P.W.; Hodgson, P. K. G., Seddon, K. R. & Stewart N. J. (1995a). Ionic liquids. *World patent*, WO95/21871.

Abdul-Sada, A. K.; Atkins, M. P.; Ellis, B.; Hodgson, P. K. G.; Morgan, M. L. M.& Seddon K. R. (1995b). Alkylation process. *World patent*, WO95/21806.

Amajjahe, S. & Ritter, H. (2009). Microwave-Sensitive foamable poly(ionic liquids) bearing tert-butyl ester groups: Influence of counterions on the ester pyrolysis. *Macromol. Rapid Commun*, 30, 2, 94–98, 1521-3927

Ambler, P. W.; Hodgson, P.K G & Stewart, N.J. (1993) *European Patent*, EP, 0558187.

Ambler, P. W.; Hodgson, P. K. G. & Stewart, N. J. (1996). Butene polymers. *European patent application, EP*/0558187A0558181.

Anderson, J. L.; Pino, V.; Hagberg, E. C.; Sheares, V. V. & Armstrong, D. W. (2003). Surfactant solvation effects and micelle formation in ionic liquids. *Chem. Commun,* 19 2444-2445, 1359-7345

Araos, M. U. & Warr, G. G. (2005). Self-assembly of nonionic surfactants into lyotropic liquid crystals in ethylammonium nitrate, a room-temperature ionic liquid. *J. Phys. Chem. B*, 109, 30, 14275-14277, 1520-6106

Ashgarian, B.; Cadenhead, D. A. (1999). nterfacial Compression and Polymerization of 4- and 9-((Butoxycarbonyl)methyl)urethane−Diacetylene Monomolecular Films: A Fluorescence Microscopy Study. *Macromolecules*, 32, 17, 5575-5580, 0024-9297

Atkin, R.; Warr, G. G. (2007). Phase behavior and microstructure of microemulsions with a room-temperature ionic liquid as the polar phase. *J. Phys. Chem. B,* 111, 31, 9309–9316, 1520-6106

Biedron, T. & Kubisa, P. (2001). Atom-transfer radical polymerization of acrylates in an ionic liquid. *Macromol Rap Commun*, 22, 15, 1237–1242, 1521-3927

Biedron, T. & Kubisa P. (2002). P. Atom transfer radical polymerization of acrylates in an ionic liquid: synthesis of block copolymers. *J Polym Sci Part A Polym Chem,* 40, 16, 2799–809, 1099-0518

Biedron, T. & Kubisa, P. (2003) Ionic liquids as reaction media for polymerization processes: atom transfer radical polymerization (ATRP) of acrylates in ionic liquids. *Polym Int*, 52, 10, 1584–8, 1097-0126

Binks, B. P.; Dyab, A. K. F.; Fletcher, P. D. I. (2003) Novel emulsions of ionic liquids stabilised solely by silica nanoparticles. *Chem. Commun.*, 20, 2540–2541, 1359-7345

Bosman, Y.; Lau, Y.; Gilgenbach, R. M. (2003) Microwave absorption on a thin film. *Appl. Phys. Lett.*, *82*, 9, 1353-1355, 0003-6951

Bowers, J.; Butts, C. P.; Martin, P. J.; Vergara-Gutierrez, M. C. & Heenan, R. K. (2004). Aggregation behavior of aqueous solutions of ionic liquids. *Langmuir,* 20, 6, 2191-2198, 0743-7463

Bregar, V. B. (2004). Advantages of ferromagnetic nanoparticle composites in microwave absorbers. *IEEE Trans. Magn.,* 40, 3, 1679-1684, 0018-9464

Bueno, C.; Cabral,V. F.; Cardozo-Filho, L.; Dias, M.L. & Antunes.O. A. C. (2009). Cationic polymerization of styrene in scCO$_2$ and [bmim][PF$_6$], *J. of Supercritical Fluids,* 48, 2, 183–187, 0896-8446

Carlin, R. T.; Osteryoung, R. A.; Wilkes, J. S. & Rovang, J. (1990). Studies of titanium(IV) chloride in a strongly Lewis acidic molten salt: electrochemistry and titanium NMR and electronic spectroscopy. *Inorg. Chem,* 29, 16, 3003-3009, 0020-1669

Carlin, R. T. & Fuller, J. (1997) Ionic liquid–polymer gel catalytic membrane. *Chem. Commun.*, 15, 1345–1346, 1359-7345

Chandrasekhar, P.; Naishadham, K. (1999). Broadband microwave absorption and shielding properties of a poly(aniline). *Synth. Met,* 105, 2, 115- 120, 0379-6779

Chauvin, Y. (1996). Two-phase catalysis in nonaqueous ionic liquids. *Actualite chimique* v, 44–46, 0151-9093

Chauvin, Y.; Commereuc, D.; Hirschauer, A.; Hugues, F. & Saussine, L. (1988). Process and catalyst for the dimeriation or codimerization of olefins. *French Patent, FR* 2,611,700.

Chauvin, Y.; Commereuc, D.; Hirschauer, A.; Hughes, F. & Saussine, L. (1989). Process and catalyst for the alkylation of isoparaffins with alkenes. *French Patent, FR* 2,611,572.

Chauvin, Y.; Gilbert, B. & Guibard, I. (1990) Catalytic dimerization of alkenes by nickel complexes in organochloroaluminate molten salts. *J. Chem. Soc., Chem. Commun,* 23, 1715-1716, 0022-4936

Chauvin, Y.; Mussmann, L.& Olivier, H. (1995). A novel class of versatile solvents for two-phase catalysts: Hydrogenation, isomerization, and hydroformylation of alkenes catalyzed by rhodium complexes in liquid 1,3-dialkylimidazolium salts. *Angew Chem Int Ed Engl*, 34, 23-24, 2698–2700, 1521-3773

Chen, H.; Yossef A. Elabd,Y. A.(2009). Polymerized ionic liquids: solution properties and electrospinning. *Macromolecules, 42*,9, 3368-3373, 0024-9297

Chiefari, J.; Chong, Y. K.; Ercole, F., Krstina, J.; Jeffery, L.; Mayadunne, R. T. A. (1998). Living free-radical polymerization by reversible additionfragmentation chain transfer: the RAFT process. *Macromolecules*, 31, 16, 5559–5562, 0024-9297

Chu, L. Y.; Park, S. H.; Yamaguchi, T.; Nakao, S. I. (2002). Preparation of micron-sized monodispersed thermoresponsive core−shell microcapsules. *Langmuir,* 18, 5, 1856-1864, 0743-7463

Ding, S.; Tang, H.; Radosz, M. & Shen, Y. (2004). Atom transfer radical polymerization of ionic liquid 2-(1- butylimidazolium-3-yl) ethyl methacrylate tetrafluoroborate. *J. Polym. Sci., Part A: Polym. Chem,.* 42, 22, 5794–5801, 1099-0518

Ding, S.; Radosz, M. & Shen, Y. (2005). Ionic liquid catalyst for biphasic atom transfer radical polymerization of methyl methacrylate. *Macromolecules,* 38, 14, 5921–5928, 0024-9297

Dupont, J.; de Souza, R. F.; Suarez P. A. Z. (2002). Review ionic liquid (Molten Salt) phase organometallic catalysis. *Chem Rev*, 102, 10, 3667-3692, 0009-2665

Earle, M. J.; McCormac, P. B. & Seddon, K. R. (1999). Diels-Alder reactions in ionic liquids. *Green Chem*, 1, 23–25, 1463-9262

Eastoe, S.; Gold, S. E.; Rogers, A.; Paul, T.; Welton, R. K.; Heenan, I. G.(2005). Ionic liquid-in-oil microemulsions. *J. Am. Chem. Soc,* 127, 20, 7302–7303, 0002-7863

Ellis,B.; Keim,W. & Wasserscheid, P.(1999). Linear dimerisation of but-1-ene in biphasic mode using buffered chloroaluminate ionic liquid solvents. *J. Chem. Soc., Chem. Commun,* 4, 337-338, 0022-4936

Elseoud, O. A.; Pires, P. A. R.; Abdel-Moghny, T.; Bastos E. L. (2007). Synthesis and micellar properties of surface-active ionic liquids: 1-alkyl-3- methylimidazolium chlorides. *J. Colloid Interface Sci*., 313, 1, 296-304, 0021-9797

Evans, D. F.; Yamauchi, A.; Roman R.& Casassa E. Z. (1982). Micelle formation in ethylammonium nitrate, a low-melting fused salt. *J. Colloid Interface Sci*., 88, 1, 89-96, 0021-9797

Evans,D. F.; Kaler, E. W. & Benton; W. J. (1983). Liquid crystals in a fused salt: distearoylphosphatidylcholine in *N*-ethylammonium nitrate *J. Phys Chem*, 87, 18, 533-535

Evans, D. F.; A. Yamauchi, A.; Wei, G. J.; Bloomfield, V. A. (1983). Micelle size in ethylammonium nitrate as determined by classical and quasi-elastic light scattering. A, *J. Phys. Chem. 87*, 18, 3537-3541

Flannigan, J. D; Hopkins, D. S. D.; Suslick, K. S. (2005). Sonochemistry and sonoluminescence in ionic liquids, molten salts, and concentrated electrolyte solutions. *J. Organomet. Chem,* 690,15, 3513–3517, 0022-328X

Freemantle, M. (1998). Designer solvents—Ionic liquids may boost clean technology development. *Chem Eng News*, 76, 32–37, 0009-2347

Galiński, M.; Lewandowski, A. & Ste-pniak, I. (2006) Ionic liquids as electrolytes. *Electrochim. Acta*, 51, 26, 5567–5580, 0013-4686

Gao, H. X.; Li, J. C.; Han, B. X.; Chen, W. N.; Zhang, J. L.; Zhang, R.; Yan, D. D. (2004) Microemulsions with ionic liquid polar domains. *Phys. Chem. Chem. Phys.* 6, 2914–2916, 1463-9076

Gao, Y. A.; Wang, S. Q.; Zheng, L. Q.; Han, S. B.; Zhang, X.; Lu, D. M.; Yu, L.; Ji, Y. Q.; Zhang, G. Y. (2006) Microregion detection of ionic liquid microemulsions. *J. Colloid Interface Sci.*, 301, 2, 612–616, 0021-9797

Gao, Y. A.; Zhang, J.; Xu, H. Y.; Zhao, X. Y.; Zheng, L. Q.; Li, X. W.; Yu, L. (2006). Structural Studies of 1-Butyl-3-methylimidazolium Tetrafluoroborate/TX-100/ *p*-Xylene Ionic Liquid Microemulsions. *Chem Phys Chem* , 7, 7, 1554–1561, 1439-7641

Gao, Y.; Li, N.; Zheng, L.; Bai, X.; Yu, L.; Zhao, X.; Zhang, J.; Zhao, M.; Li, Z. (2007). Role of solubilized water in the reverse ionic liquid microemulsion of 1-Butyl-3-methylimidazolium Tetrafluoroborate/TX-100/Benzene. *J. Phys. Chem. B,* 111, 10, 2506–2513, 1520-6106

Gordon, C. M., Holbrey, J. D.; Kennedy, A. & Seddon, K. R. (1998). Ionic liquid crystals: Hexafluorophosphate salts. J Mater Chem, 8, 2627–2636, 0959-9428

Hansen, F. K. & Rødsrud, G. (1991). Surface tension by pendant drop: I. A fast standard instrument using computer image analysis. *J. Colloid Interface Sci.*, 141,1, 1-9, 0021-9797

Hao, J.; Song, A.; Wang, J.; Chen, X.; Zhuang, W.; Shi, F.; Zhou, F. & Liu, W. (2005). Self-assembled structures in room-temperature ionic liquids, *Chem. Eur. J.,* 11,13, 3936-3940, 1521-3765

Hao, J.; Zemb,T. (2007). Self-assembled structures and chemical reactions in room-temperature ionic liquids, *Curr. Opin. Colloid Interface Sci.*, 12, 3, 129-137, 1359-0294

Harrisson, S., Mackenzie, S. R.; Haddleton, D. M. (2003). Pulsed laser polymerization in an ionic liquid: Strong solvent effects on propagation and termination of methyl methacrylate. *Macromolecules*, 36, 14, 5072-5075, 0024-9297

He, Y.; Li, Z.; Simone, P.; Lodge, T. P. (2006). Self-assembly of block copolymer micelles in an ionic liquid. *J. Am. Chem. Soc.*, 128, 8, 2745–2750, 0002-7863

Hirao, M.; Ito, K. &; Ohno, H. (2000). Preparation and polymerization of new organic molten salts; *N*-alkylimidazolium salt derivatives. *Electrochim. Acta*, 45, 8-9, 1291– 1294. 0013-4686

Jaeger, D. A. & Tucker, C. E. (1989). Diels-Alder reactions in ethylammonium nitrate, a low-melting fused salt. *Tetrahedron Lett*, 30, 1785–1788, 0040-4039

Holbrey, J. D. & Seddon, K. R. (1999a). The phase behaviour of 1-alkyl-3-methylimidazolium tetrafluoroborates: ionic liquid and ionic liquid crystals. *J Chem Soc Dalton Trans*, 13, 2133–2139, 1472-7773

Holbrey, J. D. & Seddon, K. R. (1999b). Ionic liquids. *Clean Prod Proc*, 1, 223–237, 1435-2974

Bonhoˆte, P., Dias, A. P.; Papageorgiou, N., Kalyanasundaram, K. & Graˆtzel, M. (1996). Hydrophobic, highly conductive ambient-temperature moltensalts. *Inorg Chem*, 35, 5, 1168–1178, 0020-1669

Holly L. Ricks-Laskoski, and Arthur W. Snow (2006). Synthesis and electric field actuation of an ionic liquid polymer. *J. Am. Chem. Soc.*, 128, 38, 12402-12403, 0002-7863

Juger, J.; Meyer, F.; Vidal, F.; Chevrot, C. & Teyssie, D. (2009). Synthesis, polymerization and conducting properties of an ionic liquid-type anionic monomer. *Tetrahedron Lett.*, 50, 1, 128–131, 0040-4039

Kaper, H. & SmarslyB. (2006). Templating and phase behavior of the long chain ionic liquid C_{16}mimCl,. *Phys. Chem, 220*, 10, 1455-1471, 0942-9352

Kato, Y.; Satoshi, S.; Sugimoto, S.; Shinohara, K., Tezuka, N., Kagotani, T. & Inomata, K. (2002). Magnetic Properties and Microwave Absorption Properties of Polymer-Protected Cobalt Nanoparticles. *Mater. Trans,* 43, 3, 406-409, 1345-9678

Kokubo, H. & Watanabe M. (2008). Anionic polymerization of methyl methacrylate in an ionic liquid. *Polym. Adv. Technol*, 19,10, 1441– 1444, 1099-1581

Ku, C. C.; Liepins, R. (1987). *Electrical Properties of Polymers: Chemical Principles*, Hanser Publishers, 978-3446142800, New York

Kubisa, P. (2004). Application of ionic liquids as solvents for polymerization processes. *Prog Polym Sci,* 29, 1, 3–12, 0079-6700

Kubisa, P. (2009) Ionic liquids as solvents for polymerization processes—progress and challenges. *Prog Polym Sci ,* 34, 12, 1333–1347, 0079-6700

Kowsari, E.; Yavari, I. (2009) Proceedings of the Polymer Processing Society Europe/Africa Regional Meeting ~ PPS-2009 ~ October 18-21, 2009 Larnaca (Cyprus)

Kowsari, E.; Faraghi, G. (2010). Ultrasound and ionic-liquid-assisted synthesis and characterization of polyaniline/Y_2O_3 nanocomposite with controlled conductivity. *Ultrason. Sonochem*, 17, 4, 718-725, 1350-4177

Leddet, C. & Fischer, A.; Brembilla, A.; Lochon, P. (2001). Influence of the alkyl-chain size on the amphiphilic behaviour of poly(3-alkyl-1-vinylimidazolium) bromide in aqueous medium . *Polym. Bull.*, 46, 1 , 75–82, 0170-0839

Lee, J; Panzer, M. J.; He, Y.; Lodge, T. P & Daniel Frisbie, C. (2007) Ion gel gated polymer thin-film transistors, *J. Am. Chem. Soc. ,* 129, 4532-4533, 0002-7863

Li, N.; Gao, Y.; Zheng, L.; Zhang, J.; Yu, L.; Li, X. (2007) Studies on the micropolarities of bmimBF_4/TX-100/Toluene ionic liquid microemulsions and their behaviors characterized by UV−Visible spectroscopy. *Langmuir*, 23, 3, 1091–1097, 0743-7463

Lu, X. F.; Bian, X. K., Shi, L. Q. (2002) Preparation and characterization of NF composite membrane. *J. Membr Sci* 210, 1, 3-11, 0376-7388

Lu, J.; Yan, F. & Texter, J. (2009) Advanced applications of ionic liquids in polymer science *Prog. Polym. Sci.*, 34, 5, 431–448, 0079-6700

Mallakpour, S., Kowsari, E. (2005). Ionic liquids as novel solvents and catalysts for the direct polycondensation of *N,N*′-(4,4′-oxydiphthaloyl)-bis-L-phenylalanine diacid with various aromatic diamines. *J. Polym. Sci. Part A: Polym. Chem*, 43, 24, 6545-6553, 1099-0518

Mallakpour, S; Kowsari, E. (2006). Microwave heating in conjunction with ionic liquid as a novel method for the fast synthesis of optically active poly(amide-imide)s derived from *N,N*′-(4,4′-hexafluoroisopropylidenediphthaloyl-(bis-*L*methionine and various aromatic diamines. *Iranian Polym., J.* 15, 3, 239-247, 1026-1265

Marcilla, R.; Blazquez, J. A.; Rodriguez, J.; Pomposo, J. A. & Mecerreyes, D. *J.* (2004). Tuning the solubility of polymerized ionic liquids by simple anion-exchange reactions. *Polym. Sci., Part A: Polym. Chem.*, 42, 1, 208–212, 1099-0518

Marcilla, R.; Blazquez, J. A.; Fernandez, R.; Grande, H.; Rodriguez, J.; Pomposo, J. A. & Mecerreyes, D. (2005) Synthesis of novel polycations using the chemistry of ionic liquids. *Macromol. Chem. Phys.*, 206, 2, 299–304, 1521-3935

Matsumi, N.; Sugai, K.; Miyake, M. & Ohno, H. (2006). Polymerized ionic liquids via hydroboration polymerization as single ion conductive polymer electrolytes. *Macromolecules*, 39, 20, 6924–6927, 0024-9297

Miskolczy, Z.; Sebok-Nagy, K.; Biczok, L. & Goektuerk, S. (2004). Aggregation and micelle formation of ionic liquids in aqueous solution. *Chem. Phys. Lett,.* 400, 4-6, 296-300, 0009-2614

Mu, X. d.; Meng, J. q.; Li, Z. C.; Kou, Y. (2005). Rhodium nanoparticles stabilized by ionic copolymers in ionic liquids: long lifetime nanocluster catalysts for benzene hydrogenation. *J. Am. Chem. Soc,.* 127, 27, 9694–9695, 0002-7863

Nakashima, T.; Sakashita, M.; Nonoguchi, Y. & Kawai, T. (2007). Sensitized photopolymerization of an ionic liquid-based monomer by using CdTe nanocrystals. *Macromolecules,* 40, 18, 6540–6544, 0024-9297

Noda, A. & Watanabe, M. (2000). Highly conductive polymer electrolytes prepared by in situ polymerization of vinyl monomers in room temperature molten salts. *Electrochim. Acta,,* 45, 8-9, 1265-1270, 0013-4686

Ogata, N.; Sanui, K.; Rikukawa, M.; Yamada, S.;Watanabe, M.; Mizumura, T. (1996). *Solid State Ionics* 353, 86.

Olmedo, L.; Hourquebie, P.; Jousse, F. (1995). Microwave properties of conductive polymers. *Synth. Met.*, 69, 1-3, 205- 208, 0379-6779

Patrascu, C.; Gauffre, F.; Nallet, F.; Bordes, R.; Oberdisse, J.; de Lauth-Viguerie, N. & Mingotaud, C. (2006). Micelles in ionic liquids: aggregation behavior of alkyl poly(ethyleneglycol)- ethers in 1-butyl-3-methyl-imidazolium type ionic liquids, *Chem. Phys. Chem,. 7,* 99- 101, 1439-7641, 1439-7641

Peng, C. H.; Hwang, C. C.; Wan, J.; Tsai, J. S.; Chen, S. Y. (2005). Microwave-absorbing characteristics for the composites of thermal-plastic polyurethane (TPU)-bonded NiZn-ferrites prepared by combustion synthesis method. *Mater. Sci. Eng., B* , 117,1, 27-36, 0921-5107

Perrier, S.; Davis, T. P.; Carmichael, A. J.; Haddleton, D. M. (2002). First report of reversible addition-fragmentation chain transfer (RAFT) polymerization in room temperature ionic liquids. *Chem Commun,* 19, 2226–2227, 1359-7345

Petrov, V. M. & Gagulin, V. V. (2001). Microwave absorbing materials. *Inorg. Mater.,* 37,2, *93-98*, 0020-1685

Phang, S.W.; Daik, R; Abdullah, M. H. (2005). Poly(4,4′-diphenylene diphenylvinylene) as a non-magnetic microwave absorbing conjugated polymer. *Thin Solid Films*, 477, 1-2, 125- 130, 0040-6090

Qiu, Z. & Texter, J. (2008). Ionic liquids in microemulsions, *Curr. Opin. Colloid Interface Sci,* 13, 4, 252-262, 1359-0294

Quilliet, C. & Berge, B. (2001). Electrowetting: a recent outbreak. *Curr. Opin. Colloid Interface Sci.*, 6, 1, 34-39, 1359-0294

Ricks-Laskoski, H. L. & Snow, A. W. (2006). Synthesis and electric field actuation of an ionic liquid polymer. *J. Am. Chem. Soc.*, 128, 38, 12402–12403, 0002-7863.

Saib, A.; Bednarz, L.; Daussin, R.; Bailly, C.; Lou, X.; Thomassin, J. M.; Pagnoulle, C.; Detrembleur, C.; Jerome, R. & Huynen, I. (2006). Carbon nanotube composites for broadband microwave absorbing materials. *IEEE Trans. Microwave Theor. Tech,* 54, 6, 2745-2754, 0018-9480

Sarbu, T. & Matyjaszewski, K. (2001). ATRP of methyl methacrylate in the presence of ionic liquids with ferrous and cuprous anions. *Macromol Chem Phys*; 202, 17, 3379–91, 1022-1352

Sato, T.; Marukane, S.; Narutomi, T. & Akao, T. (2007). High rate performance of a lithium polymer battery using a novel ionic liquid polymer composite. *J. Power Sources*, 164,1, 390–396. 0378-7753

Seddon, K. R. (1997). Ionic liquids for clean technology. *J Chemical Tech Biotech* 68, 351–356, 0268-2575

Shen, Y. & Ding, S. (2004). Catalyst separation in atom transfer radical polymerization. *Prog Polym Sci,* 29, 10, 1053–1078, 0079-6700

Sirieix-Plenet, J.; Gaillon, L. & Letellier, P. (2004). Behavior of a binary solvent mixture constituted by an amphiphilic ionic liquid, 1-decyl-3-methylimidazolium bromide and water. Potentiometric and conductimetric studies, *Talanta, 63,* 4, 979-986, 0039-9140

Sugimura, R.; Qiao, K.; Tomida, D.; Kume, Y. & Yokoyama, C. (2007) immobilization of palladium acetate on ionic liquid copolymerized polystyrene: A way to eliminate inhibiting effect of imidazolium chloride and enhance catalytic performance. *Chem. Lett,.* 36, 7, 874–875, 0366-7022

Susan, M. A. B. H.; Kaneko, T.; Noda, A.; Watanabe, M. (2005) Ion gels prepared by in situ radical polymerization of vinyl monomers in an ionic liquid and their characterization as polymer electrolytes. *J. Am. Chem. Soc.* 127, 13, 4976-4983, 0002-7863

Suslick, K. S. (1988). *Ultrasound*, VCH, Weinhein, 0-89573-328-5, Germany

Suslick, K. S.; Choe, S. B.; Cichowlas, A. A.; Grinstaff, M. W. (1991). Sonochemical synthesis of amorphous iron. *Nature*, 353, 6343, 414-416, 0028-0836

Suslick, K. S.; Price G. J. (1999) Application of ultrasound to materials chemistry. *Ann. Rev. Mater. Sci,.* 29, 295-326, 0084-6600

Tang, J.; Tang, H.; Sun, W.; Plancher, H.; Radosz, M.; Shen, Y. (2005). Poly(ionic liquid)s: a new material with enhanced and fast CO_2 absorption. *Chem. Commun*, 26, 3325–3327. 1359-7345

Tang, H.; Tang, J.; Ding, S.; Radosz, M. & Shen, Y. (2005). Atom transfer radical polymerization of styrenic ionic liquid monomers and carbon dioxide absorption of the polymerized iIonic liquids. *J. Polym. Sci., Part A: Polym. Chem,.* 43, 7, 1432–1443, 1099-0518

Tang, J.; Sun, W.; Tang, H.; Radosz, M.; Shen, Y. (2005). Enhanced CO_2 absorption of poly(ionic liquid)s. *Macromolecules*, 38,6, 2037–2039, 0024-9297

Tang, J.; Tang, H.; Sun, W.; Radosz, M. & Shen, Y. (2005) Low-pressure CO_2 sorption in ammonium-based poly(ionic liquid)s .*Polymer*, 46, 26, 12460–12467, 0032-3861, 0024-9297

Tang, J.; Tang, H.; Sun, W.; Radosz, M. & Shen, Y. (2005). Poly(ionic liquid)s as new materials for CO$_2$ Absorption. *J. Polym. Sci., Part A: Polym. Chem,*. 43, 22, 5477–5489, 1099-0518

Tang, J.; Radosz, M.; Shen, Y. (2008) Poly(ionic liquid)s as optically transparent microwave-absorbing materials. *Macromolecules*, 41, 2, 493– 496, 0024-9297

Thomaier, S. & Kunz, W. (2007) Aggregates in mixtures of ionic liquids, *J. Mol. Liq,* 130, 1-3, 104-107, 0167-7322

Tokuda, H.; Tsuzuki, S.; Hayamizu, M. K.; Watanabe, M. (2006). How ionic are room-temperature ionic liquids? An indicator of the physicochemical properties. J. Phys. Chem. B, 110, 39, 19593-19600, 1520-6106

Truong, V. T.; Riddell, S. Z.; Muscat, R. F. (1998*).* Polypyrrole based microwave absorbers. *J. Mater. Sci,* 33, 20, 4971-4976, 0022-2461

Ueki, T. & Watanabe, M. (2008). Macromolecules in ionic liquids: progress, challenges, and opportunities. *Macromolecules* , 41, 11, 3739-3748, 0024-9297

Vijayaraghavan, R. & MacFarlane, D. R. (2004) Living cationic polymerisation of styrene in an ionic liquid. *Chem. Commun,*6,700-701

Vijayaraghavan, R.; Pringle, J. M. & MacFarlane D. R. (2008). Anionic polymerization of styrene in ionic liquids. *European Polymer Journal*, 44 , 6,1758–1762, 0014-3057

Vygodskii1,Y. S.; Mel'nik1,O. A.; Lozinskaya1, E. I.; Shaplov1, A. S.; I. A. Malyshkina, I. A.; Gavrilova,n. D.; Lyssenko1,k. A.; Antipin1,M. Y. Golovanov, D. G.; G.; Korlyukov1, A. A.; Ignat'ev, N .& Welz-Biermann, U. (2007). The influence of ionic liquid's nature on free radical polymerization of vinyl monomers and ionic conductivity of the obtained polymeric materials. *Polym. Adv. Technol*, 3, 18, 50–63, 1099-1581

Wan, M. X.; Li, J. C.; Li, S. Z. (2001). Microtubules of polyaniline as new microwave absorbent materials. *Polym. Adv. Technol.*, 12, 11-12, 651- 657, 1099-1581

Wang, Y. Y.; Li,W. & Dai, L. Y. (2007). Cationic ring-opening polymerization of 3,3-bis(chloromethyl)oxacyclobutane in ionic liquids, *Chinese Chemical Letters*, 18, 10, 1187–1190, 1001-8417

Washiro, S.; Yoshizawa, M.; Nakajima, H. & Ohno, H. (2004). Highly ion conductive flexible films composed of network polymers based on polymerizable ionic liquids. *Polymer,* 45, 5 1577–1582, 0032-3861

Watanabe, M.; Yamada, S.; Sanui, K.; Ogata, N. J. (1993). High ionic conductivity of new polymer electrolytes consisting of polypyridinium, pyridinium and aluminium chloride. *J Chem. Soc Chem. Commun.* , 11, 929-931, 0022-4936

Watanabe, M.; Yamada, S. & Ogata, N. (1995) Ionic conductivity of polymer electrolytes containing room temperature molten salts based on pyridinium halide and aluminium chloride. *Electrochim. Acta* , 40,13-14, 2285-2288, *0013-4686*

Wilkes, J. S. & Zaworotko, M. J. (1992). Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids. *J Chem Soc Chem Commun,* 13, 965–967, 0022-4936

Yan, F. & Texter, J. (2006). Surfactant ionic liquid based microemulsions for polymerizatiom. *Chem. Commun*, 2696–2698. 1359-7345

Yan, F. & Texte J. (2007) Solvent-reversible poration in ionic liquid copolymers. *Angew. Chem., Int. Ed,* 46, 14, 2440–2443, 1521-3773

Yu, S.; Yan, F.; Zhang, X.; You, J.; Wu,P.; Lu, J.; Xu, Q.; Xia, X. & Ma, G. (2008). Polymerization of ionic liquid-based microemulsions: A versatile method for the synthesis of polymer electrolytes. *Macromolecules,* 41, 10, 3389-3392, 0024-9297

Zhao, Y.; Chen, X.; WengX. (2009). Liquid crystalline phases self-organized from a surfactant-like ionic liquid C_{16}mimCl in ethylammonium nitrate, *J. Phys. Chem B*, 113,7, 2024-2030, 1520-6106

Zou, Y. H.; Liu, H. B.; Yang, L.; Chen, Z. Z. (2006). The influence of temperature on magnetic and microwave absorption properties of Fe/graphite oxide nanocomposites. *J. Magn. Magn. Mater, 302*, 2, 343-347, 0304-8853
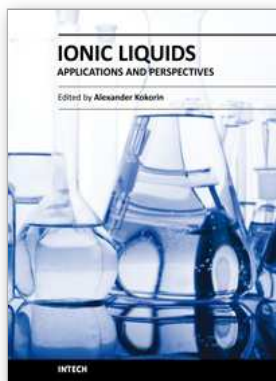
Ionic Liquids: Applications and Perspectives

Edited by Prof. Alexander Kokorin

This book is the second in the series of publications in this field by this publisher, and contains a number of latest research developments on ionic liquids (ILs). This promising new area has received a lot of attention during the last 20 years. Readers will find 30 chapters collected in 6 sections on recent applications of ILs in polymer sciences, material chemistry, catalysis, nanotechnology, biotechnology and electrochemical applications. The authors of each chapter are scientists and technologists from different countries with strong expertise in their respective fields. You will be able to perceive a trend analysis and examine recent developments in different areas of ILs chemistry and technologies. The book should help in systematization of knowledges in ILs science, creation of new approaches in this field and further promotion of ILs technologies for the future.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Elaheh Kowsari (2011). Advanced Applications of Ionic Liquids in Polymer Science, Ionic Liquids: Applications and Perspectives, Prof. Alexander Kokorin (Ed.), ISBN: 978-953-307-248-7, InTech, Available from: http://www.intechopen.com/books/ionic-liquids-applications-and-perspectives/advanced-applications-of-ionic-liquids-in-polymer-science

INTECH

open science | open minds