

# Ionic Liquids as Environmentally Friendly Solvents in Macromolecules Chemistry and Technology, Part I

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Published online: 2 March 2011  
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**Abstract** With the increasing emphasis on the environment and the need to find environmentally friendly solvent systems, ionic liquids (IL)s have been emerging as promising green solvents to replace conventional solvents in recent years. They possess unique properties such as non-volatility, low toxicity, ease of handling, nonflammability and high ionic conductivity; thus they have received much attention as green media for various chemistry processes. This report provides an extensive overview of use of ILs in polymers chemistry and technology.

**Keywords** Ionic liquids · Green chemistry · Polymers synthesis and modifications

## Abbreviations

[AMIM][Cl]	1-Allyl-3-methylimidazolium chloride
[B <sub>4</sub> P][Cl]	Tetrabutylphosphonium chloride
[BDMIM][PF <sub>6</sub> ]	1-Butyl-2,3-dimethylimidazolium hexafluorophosphate
[BIEMIM][PF <sub>6</sub> ]	1-(2-Bromoisobutyryloxyethyl)-3-methylimidazolium hexafluorophosphate

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[BIM][BF <sub>4</sub> ]	1-Butylimidazolium tetrafluoroborate
[BIM][TSA]	1-Butylimidazolium <i>p</i> -toluenesulfonate
[BIM][NO <sub>3</sub> ]	1-Butylimidazolium nitrate
[BMIM][BF <sub>4</sub> ]	1-Butyl-3-methylimidazolium tetrafluoroborate
[BMIM][Cl]	1-Butyl-3-methylimidazolium chloride
[BMIM][AlCl <sub>4</sub> ]	1-Butyl-3-methylimidazolium tetrachloroaluminate
[BMIM][SnCl <sub>3</sub> ]	1-Butyl-3-methylimidazolium chlorostannate
[BMIM][H <sub>2</sub> PO <sub>4</sub> ]	1-Butyl-3-methylimidazolium dihydrogen phosphate
[BMIM][HSO <sub>4</sub> ]	1-Butyl-1-methylimidazolium hydrogen sulphate
[BMIM]	1-Butyl-3-methylimidazolium
[MDEGSO <sub>4</sub> ]	diethylene glycol monomethyl ether sulfate
[BMIM][N(CN) <sub>2</sub> ]	1-Butyl-3-methylimidazolium dicyanamide
[BMIM][OctSO <sub>4</sub> ]	1-Butyl-3-methylimidazolium octyl sulfate
[BMIM][PF <sub>6</sub> ]	1-Butyl-3-methylimidazolium hexafluorophosphate
[BMIM][Tf <sub>2</sub> N]	1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide
[BMMor <sub>1,4</sub> ][BF <sub>4</sub> ]	<i>N</i> -butyl- <i>N</i> -methyl morpholinium tetrafluoroborate
[BMPyrr][Tf <sub>2</sub> N]	<i>N</i> -butyl- <i>N</i> -methylpyrrolidinium bis(trifluoromethane sulfonyl)amide
[BPyr][Cl]	<i>N</i> -butylpyridinium chloride
[BPyr]	<i>N</i> -butylpyridinium
[AlCl <sub>4</sub> ]	tetrachloroaluminate
[Bu <sub>4</sub> N][Br]	Tetrabutylammonium bromide

[OTf]	Trifluoromethanesulfonate	BA	Butyl acrylate
[C <sub>18</sub> MIM][Cl]	1-Octadecyl-3-methylimidazolium chloride	BLG-NCA	$\gamma$ -Benzyl-L-glutamate- <i>N</i> -carboxyanhydride
[C <sub><i>n</i></sub> MIM][PF <sub>6</sub> ]	1-Alkyl-3-methylimidazolium hexafluorophosphate	BMA	<i>n</i> -butyl methacrylate
[C <sub><i>n</i></sub> Pyr][Tf <sub>2</sub> N]	<i>N</i> -alkylpyridinium bis (trifluoromethanesulfonyl)amide	BPO	Benzoyl peroxide
[DEME][Tf <sub>2</sub> N]	<i>N,N</i> -diethyl- <i>N</i> -(2-methoxyethyl) ammonium bis(trifluoromethane sulfonyl)amide	CAL-B	<i>Candida antarctica</i> lipase B
[C <sub>12</sub> MIM][BF <sub>4</sub> ]	1-Dodecyl-3-methylimidazolium tetrafluoroborate	ChMI	<i>N</i> -cyclohexylmaleimide
[EDMIM][Tf <sub>2</sub> N]	1-Ethyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)amide	CTA	Chain transfer agent
[EIM][TFA]	1-Ethylimidazolium trifluoroacetate	DCM	Dichloromethane
[EMIM]	1-Ethyl-3-methylimidazolium	DPHLi	Diphenylhexyl lithium
[EMIM][AlCl <sub>4</sub> ]	1-Ethyl-3-methylimidazolium tetrachloroaluminate	DSC	Differential scanning calorimetry
[EMIM][OTf]	1-Ethyl-2,3-dimethylimidazolium trifluoromethanesulfonate	DSSC	Dye sensitised solar cells
[EMIM][HexSO <sub>4</sub> ]	1-Ethyl-3-methylimidazolium hexyl sulfate	EC	Ethylene carbonate
[EMIM][I]	1-Ethyl-3-methylimidazolium iodide	EOX	3-Ethyl-3-hydroxymethyloxetane
[EMIM][Tf <sub>2</sub> N]	1-Ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide	EPN-Br	Ethyl-2-bromopropionate
[EMIM][TSA]	1-Ethyl-3-methylimidazolium tosylate	EQCM	Electrochemical quartz-crystal microbalance
[EMIM][EtSO <sub>4</sub> ]	1-Ethyl-3-methylimidazolium ethylsulfate	[Et <sub>4</sub> N][BF <sub>4</sub> ]	Tetraethylammonium tetrafluoroborate
[EtNH <sub>3</sub> ][NO <sub>3</sub> ]	Ethylammonium nitrate	GMA	Glycidyl methacrylate
[HMIM][BF <sub>4</sub> ]	1-Hexyl-3-methylimidazolium tetrafluoroborate	GTP	Group transfer polymerization
[HPyr][Tf <sub>2</sub> N]	<i>N</i> -hexylpyridinium bis (trifluoromethanesulfonyl)amide	HBOB	Bis(oxalato)boric acid
[IM][BF <sub>4</sub> ]	Imidazolium tetrafluoroborate	HexT	3-Hexylthiophene
[Me <sub>3</sub> S][Tf <sub>2</sub> N]	Trimethylsulfonium bis (trifluoromethanesulfonyl)amide	HPMA	2-Hydroxypropyl methacrylate
[MMIM]Me <sub>2</sub> PO <sub>4</sub> ]	1,3-Dimethylimidazolium dimethylphosphate	IA	Isophthalic acid
[OMIM][BF <sub>4</sub> ]	1-Octyl-3-methylimidazolium tetrafluoroborate	ILs	Ionic liquids
[OMIM][PF <sub>6</sub> ]	1-Octyl-3-methylimidazolium hexafluorophosphate	ITO	Indium tin oxide
[PF <sub>6</sub> ]	Hexafluorophosphate	<i>k<sub>p</sub></i>	Rate constant of propagation
[PMIM][PF <sub>6</sub> ]	1-Propyl-3-methylimidazolium hexafluorophosphate	<i>k<sub>t</sub></i>	Rate constant of termination
[Tf <sub>2</sub> N]	Bis(trifluoromethanesulfonyl)amide	MA	Methyl acrylate
AFM	Atom force microscopy	MALDI-TOF	Matrix-assisted laser desorption/ionization time-of-flight
AN	Acrylonitrile	MAN	Methacrylonitrile
ANI	Aniline	MDOB	1,2-Methylenedioxybenzene
ATR-FTIR	Attenuated total reflection Fourier transform infrared spectroscopy	MeT	3-Methylthiophene
ATRP	Atom transfer radical polymerization	MMA	Methyl methacrylate
		M <sub><i>n</i></sub>	Number-average molecular weight
		M <sub><i>r</i></sub>	Relative molecular mass
		MnMA	Menthyl methacrylate
		MITO	Modified indium tin oxide
		MW	Molecular weight
		MWD	Molecular weight distribution
		NBMI	<i>N</i> -butylmaleimide
		NMP	Nitroxide-mediated polymerization
		NPhMI	<i>N</i> -phenylmaleimide
		OcT	3-Octylthiophene
		PAN	Poly(acrylonitrile)
		PANI	Polyaniline
		PBMA	Poly( <i>n</i> -butylmethacrylate)
		PCIT	Poly(3-chlorothiophene)
		PD	Polydispersity
		PDI	Polydispersity index
		PEDOT	Poly(3,4-ethylenedioxythiophene)

PEO	Poly(ethylene oxide)
PET	Poly(ethylene terephthalate)
PFPT	Poly(3-(4-fluorophenyl) thiophene)
PLA	Poly(lactide)
PLP	Pulsed laser polymerization
PMDETA	Pentamethyldiethylenetriamine
P(MEH-PPV)	Poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene)
PPP	Poly( <i>p</i> -phenylene)
PSt	Polystyrene
P(VdF-HFP)	Poly(vinylidene fluoride- <i>co</i> -hexafluoropropylene)
Py	Pyrrrole
PTMC	Poly(trimethylene carbonate)
$r_p$	Rate of propagation
$r_t$	Rate of termination
RAFT	Reversible addition-fragmentation chain transfer
ROGP	Ring-opening graft polymerization
ROMP	Ring-opening metathesis polymerization
RTILs	Room-temperature ILs
SA	Succinic acid
SAXS	Small-angle X-ray scattering
SEM	Scanning electron microscopy
St	Styrene
T	Thiophene
$T_g$	Glass-transition temperature
THF	Tetrahydrofuran
TGA	Thermogravimetric analysis
TEMPO	2,2,6,6-Tetramethyl-1-piperidinyloxy
TMPPAH	2,2,5-Trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane
TT	Terthiophene
VAc	Vinyl acetate
[VBBIM][BF <sub>4</sub> ]	1-(4-vinylbenzyl)-3-butyl imidazolium tetrafluoroborate
$\epsilon$ -CL	$\epsilon$ -Caprolactone
WAXD	Wide angle X-ray scattering

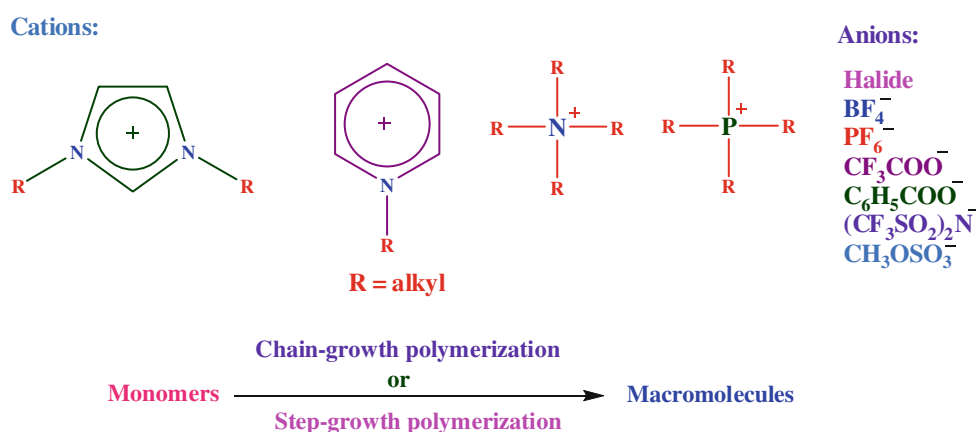
## Introduction

One of the main principles of green chemistry is to develop an alternative reaction medium, which is the basis for the progress of many cleaner chemical technologies. In particular, ionic liquids (IL)s have recently gained recognition as possible environmentally safe in wide variety of organic transformations [1–4]. ILs unlike conventional molten salts (for example, molten sodium chloride) are defined as organic salts that melt being below 100 °C or even at room

temperature and consist only of ionic species [5]. The cations are typically bulky asymmetric, limiting their packing in a crystal and giving the low melting point. In very rough terms, the choice of cation determines the principal physical properties (e.g., melting point, viscosity, density, solubility, etc.), whilst the nature of the anion affects more the chemistry. “The Structure and Properties of Ionic Melts” was the title of a Faraday Society Discussion held in Liverpool in 1961; it dealt exclusively with molten inorganic salts [6]. “Ionic Liquids” was the title of chapter 6 of the textbook *Modern Electrochemistry* by Bockris and Reddy, published in 1970: it discussed liquids ranging from alkali silicates and halides to tetraalkylammonium salts [7]. ILs have received significant interest in both academic and industrial research as environmentally benign alternatives to conventional organic solvents in an extensive range of processes owing to remarkable intrinsic characteristics such as low toxicity, nonflammability, high ion conductivity, excellent thermal and chemical stability and ability to dissolve a wide range of compounds. ILs have negligible vapor pressure, hence they may be employed in high vacuum systems and remove many containment problems. ILs can be recycled, thus making synthetic processes less expensive and potentially more efficient and environmentally friendly. These solvents can offer a new chemical environment that can uniquely influence the course of chemical reactions as compared to those in traditional solvents. Their liquid range can be as large as 300 °C allowing for large reaction kinetic control, which coupled with their good solvent properties, allows small reactor volumes to be utilized. Provoked by these intriguing and fascinating properties, the number of experimental studies on ILs has grown enormously in the last two decades. The most common ILs pair *N,N'*-dialkylimidazolium, alkylammonium, alkylphosphonium, or *N*-alkylpyridinium cations with various anions (Scheme 1). The properties of ILs differ from being completely miscible with water (hydrophilic) to liquids which are immiscible with water (hydrophobic). In general, the hydrophobicity enhances with the length of the alkyl side chain and is higher for larger anions such as hexafluorophosphate (PF<sub>6</sub>) and bis(trifluoromethanesulfonyl)amide ([Tf<sub>2</sub>N]) than for small ones such as halide, acetate and nitrate. ILs with imidazolium tetrafluoroborate ([IM][BF<sub>4</sub>]) salts can be totally miscible or immiscible depending on the substituents on the cation component.

ILs have been recognized for many years, one of the earliest known these liquids, ethylammonium nitrate ([EtNH<sub>3</sub>][NO<sub>3</sub>]) with a melting point of 12 °C was first reported by Paul Walden in 1914 [8], but this did not begin attention in ILs until the development of binary ILs made from the mixtures of aluminum (III) chloride and *N*-alkylpyridinium or 1,3-dialkylimidazolium chloride in the

**Scheme 1** Structure of the most common ILs used for polymerization reactions



mid-1970s. The first preparation of relatively air- and water-stable ILs based on 1-ethyl-3-methylimidazolium ([EMIM]) cation was reported by Wilkes and Zaworotko in 1992 [9]. This preparation involved a metathesis reaction between 1-ethyl-3-methylimidazolium iodide ([EMIM][I]) and a range of silver salts ( $\text{AgNO}_3$ ,  $\text{AgNO}_2$ ,  $\text{AgBF}_4$ ,  $\text{Ag}[\text{CO}_2\text{CH}_3]$ , and  $\text{Ag}_2\text{SO}_4$ ) in methanol or aqueous methanol solution. For literature review about history of ILs refers to Wilkes [10].

Owing to their unique chemical and physical properties, ILs have received recent attention for a wide variety of applications. Research was verified that replacing an organic solvent with an IL can create significant improvements in recognized chemical processes. Thus far, most attempts in ILs has been focused on the exploration of their potential applications such as solvent systems for chemical synthesis [1–5], biocatalysis [11], polymerization reactions [1, 2], nanomaterial technologies [12, 13], in the adaptation of enzymatic reactions to organic media [14] and for hydrogen production through water electrolysis [15]. ILs have also been extensively employed in separation science, such as mobile phases additives [16] and stationary phases in liquid chromatography [17], stationary phases in gas chromatography [18] and capillary electrophoresis [19]. ILs have successfully been utilized for liquid–liquid extraction processes [20], extraction of metal ions [21], in concert with supercritical  $\text{CO}_2$  to modify and enhance the overall extraction capabilities [22] and pre-concentration of metal ions prior to detection by graphite furnace atomic absorption spectrometry [23]. They have also been exploited in diverse electroanalytical applications as electrolytes (or electrolyte components) instead of conventional organic solvent-supporting electrolyte solutions for electrochemical devices including rechargeable lithium batteries [24], fuel cells [25], double-layer capacitors [26], hybrid supercapacitors [27], photoelectrochemical cells [28], electrodeposition of electropositive metals [29] and electrochemical sensors [30]. ILs have also used as media

to store gases [31]. ILs can be used as novel versatile lubricants for many frictional pairs such as steel/steel, steel/aluminum, steel/copper, steel/silicon, steel/sialon ceramics in the macro-scale [32, 33] and exhibited excellent friction-reduction, anti-wear performance and high load-bearing capacity. They have been largely employed as matrices for matrix-assisted laser desorption/ionization (MALDI) mass spectrometry [34]. ILs have been investigated in developing materials of unique properties for biotechnological applications [35]. ILs have been utilized for preparation inorganic oxide nanostructures [36], including titania nanomaterials [37], synthesis of rutile nanoparticles [38], very small anatase nanocrystals [39], ultrafine anatase nanocrystals [40] and rutile hierarchical nanostructure [37]. Recent developments involve their use for biopolymers [41] and molecular self-assemblies [42].

Several excellent books and reviews on the synthesis, properties, and applications of ILs, including ILs in synthesis [1], ILs in polymer systems: solvents, additives, and novel applications [2], ILs as green solvents: progress and prospects [3], ILs: industrial applications to green chemistry [4], electrochemical aspects of ILs [43], green reaction media in organic synthesis [44], electrodeposition from ILs [45], ILs in chemical analysis [46], ILs for clean technology [47], room-temperature ILs (RTILs). solvents for synthesis and catalysis [5], ILs-new solutions for transition metal catalysis [48], RTILs of alkyimidazolium cations and fluoroanions [49], ILs: green solvents for the future [50], new developments in catalysis using ILs [51], IL (molten salt) phase organometallic catalysis [52], ILs: applications in catalysis [53], enzyme catalysis in ILs [54], ILs: perspectives for organic and catalytic reactions [55], biocatalysis in ILs [56, 57], ILs and chirality: opportunities and challenges [58], application of ILs as solvents for polymerization processes [59], chromatographic and spectroscopic methods for the determination of solvent properties of RTILs [60], RTILs and their mixtures-a review [61], ILs for the convenient synthesis of functional

nanoparticles and other inorganic nanostructures [62], ILs: solvent properties and organic reactivity [63], ILs in chemical analysis [64], ILs: green solvents for non-aqueous biocatalysis [65], sonochemistry and sonoluminescence in ILs, molten salts, and concentrated electrolyte solutions [66], metal-containing ILs and ILs crystals based on imidazolium moiety [67], development in the green synthesis of cyclic carbonate from carbon dioxide using ILs [68], chiral ILs: synthesis and applications [69], ILs in the synthesis and modification of polymers [70], IL crystals [71], chemical and biochemical transformations in ILs [11], solubilization of polymers by ionic liquids [72] recent developments in thermodynamics and thermophysics of non-aqueous mixtures containing ILs [73], effect of ions and other compatible solutes on enzyme activity, and its implication for biocatalysis using ILs [74], practical considerations associated with voltammetric studies in RTILs [75], biodegradable ILs [76], chiral ILs, a renewal for the chemistry of chiral solvents? design, synthesis and applications for chiral recognition and asymmetric synthesis [77], analytical applications of RTILs: a review of recent efforts [78], review of ILs with fluorine-containing anions [79], the coordination chemistry of actinides in ILs: a review of experiment and simulation [80], ILs as electrolytes [81], dissolution of cellulose with ILs and its application [82], ILs as a medium for enantioselective catalysis [83], applications of ILs in carbohydrate chemistry: a window of opportunities [84], design of sustainable chemical products—the example of ILs [85], catalysis in ILs [86], lanthanides and actinides in ILs [87], IL Thermo: a free-access web database for thermodynamic properties of ILs [88], ILs towards supercritical fluid applications, chemical and biochemical transformations in ILs [89], reactivity of ILs [90], ionic green solvents from renewable resources [91], applications of ILs in the chemical industry [92], protic ILs: properties and applications [93], predictive molecular thermodynamic models for liquid solvents, solid salts, polymers, and ILs [94], hydroformylation in RTILs: catalyst and process developments [95], ILs in heterocyclic synthesis [96], electrochemical reactivity in RTILs [97], macromolecules in ILs: progress, challenges, and opportunities [98], applications of chiral ILs [99], ILs in microemulsions [100], ILs in separation techniques [101], advances in chiral ILs derived from natural amino acids [102], applications of ILs in electrochemical sensors [103], understanding ILs at the molecular level: facts, problems, and controversies [104], olefin metathesis in ILs [105], ILs as amphiphile self-assembly media [106], metal complexation in ILs [107], research progress on dissolution and functional modification of cellulose in ILs [108], advanced applications of ILs in polymer science [109], biocatalytic reactions in hydrophobic ILs [35], halogenation of organic compounds in ILs [110], RTILs: a new and versatile

platform for cellulose processing and derivatization [111], retention characteristics of organic compounds on molten salt and IL-based gas chromatography stationary phases [112], ILs-based catalysis with solids: state of the art [113], IL lubricants: designed chemistry for engineering applications [114] and ILs as solvents for polymerization processes—progress and challenges [115] have been published.

Among these applications, ILs have attracted growing attention as reaction media for polymerization systems such as reversible addition-fragmentation chain transfer (RAFT) polymerization, atom transfer radical polymerization (ATRP), reverse ATRP, cationic, conventional free radical polymerization (FRP), charge-transfer, olefin polymerization, oxidative polymerization, condensation polymerization, enzymatic polymerization, electrochemical polymerization. Moreover, ILs are used as catalysts or additives in polymerization processes. They can be employed as solvents for different polymers. Recently synthesis of polymeric ILs derived from monomers bearing IL's fragments has attracted increasing interest. ILs also utilized for the synthesis and use of conducting polymers. This review paper focuses on the new developments using ILs in the field of polymer chemistry and technology up to now.

## Ionic Liquids as an Alternative to Conventional Solvents in Polymerization Processes

### Ziegler-Natta Polymerization

The first report of the use of an IL as a solvent in polymerization reaction was Ziegler-Natta polymerization of ethylene reported in 1990 [116, 117]. The polymerization reaction performed by dichlorobis( $\eta^5$ -cyclopentadienyl)titanium (IV) with an alkyl-chloroaluminum (III) co-catalyst in acidic 1-ethyl-3-methylimidazolium tetrachloroaluminate ([EMIM][AlCl<sub>4</sub>]), IL solvent. The polymer with low yields was obtained, but polymerization carried out in this IL has shown that these solvents may be outstanding media for the generation of polymers.

### Ionic Polymerization

#### Cationic

Chauvin et al. [118] used organochloroaluminate molten salts based on aluminum trichloride or ethylaluminum dichloride and 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]), *N*-butylpyridinium chloride ([BPyR][Cl]) or tetrabutylphosphonium chloride ([B<sub>4</sub>P][Cl]) as solvents for the catalytic dimerization of propene to hexenes isomers by nickel complexes. Using the Lewis-acidic chloroaluminate ILs, the catalytic activity of the nickel catalyst enhanced.

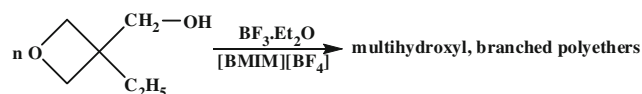
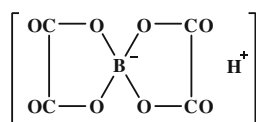
No catalytic activity was observed in basic ILs with molar fraction of aluminum less than 0.5.

Several patents described cationic polymerization of olefins in [EMIM][AlCl<sub>4</sub>] IL as both solvent and catalyst. Minimizing of side-reactions and the possibility of recovery and reuse of IL/catalyst system, were the major advantages of the use of ILs in the cationic polymerization of olefins as compared with the reactions performed under conventional cationic polymerization processes [119–122].

Vijayaraghavan and MacFarlane [123] described for the first time, the living cationic polymerization of styrene (St) using different acid catalysts in IL, *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide ([BMPyrr][Tf<sub>2</sub>N]) under mild reaction conditions at temperatures between 0 and 60 °C. The polymerization reaction was performed in IL, showed living polymers with lower molecular weights (MW)s and polydispersity (PD) compared with the reaction performed in molecular solvent, such as dichloromethane (DCM). The authors believed that this may be related to differences in the concentration of the active initiator species in each case and can be varied by altering the initiator concentration. They claimed that in the presence of bis(oxalato)boric acid (HBOB) as catalyst (Scheme 2), the temperature 60 °C, was essential for polymerization, while at temperature 0 °C the polymerization did not proceed in DCM as well as in the IL, presumably due to the poor ionization of HBOB at low temperatures. The best results were achieved when the reactions were carried out in the IL medium at 60 °C. It found that the reaction was fruitless via substitution a quaternary ammonium cation, Me<sub>4</sub>N<sup>+</sup> by hydrogen of HBOB. This confirms that the presence of the proton is important for the action of HBOB.

Biedron and Kubisa [124] reported the use of a neutral IL, [BMIM][PF<sub>6</sub>], with *sec*-phenethyl chloride [CH<sub>3</sub>CH(C<sub>6</sub>H<sub>5</sub>)Cl] (or its methyl-substituted derivative) in conjunction with TiCl<sub>4</sub> as an initiating system for cationic polymerization of St. The polymerization reactions proceeded at ambient temperatures at reasonable rates to a high conversion, although the MWs did not increase linearly with the conversion and were not related to number-average molecular weight (M<sub>n</sub>) calculated on the basis of the [monomer]<sub>0</sub>/[initiator]<sub>0</sub> ratio. The polymerization mechanism was investigated by the MALDI time-of-flight (MALDI-TOF) spectra of the polymers. The results showed chain transfer reaction that occurs during the polymerization is significant and lead to absence of control over the MW and molecular weight distribution (MWD).

**Scheme 2** Structure of HBOB



**Scheme 3** Polymerization reaction of EOX

The same research group investigated cationic ring-opening polymerization (ROP) of 3-ethyl-3-hydroxymethyloxetane (EOX) in a neutral IL, [BMIM][BF<sub>4</sub>] (Scheme 3) [125]. Polymerization of EOX in this IL proceeded to high conversion even at room temperature and led to formation of multihydroxyl, branched polyether. The M<sub>n</sub> of the resulting polymer was relatively low and did not differ considerably from the M<sub>n</sub> values observed for bulk polymerization or polymerization in organic solvents. The degree of branching, as determined based on <sup>13</sup>C NMR spectra, was not different to that observed for bulk polymerization or polymerization in organic solvents. MALDI-TOF spectra of PEOX obtained in ILs were identical with those observed for bulk polymerization, which indicated that in those systems intermolecular chain transfer also leads to the formation of cyclic macromolecules. The polar nature of ILs seems to limit the extent of intermolecular hydrogen bonding, especially at higher temperatures, but it does affect those factors that limit the MWs, i.e., most probably intramolecular hydrogen bonding.

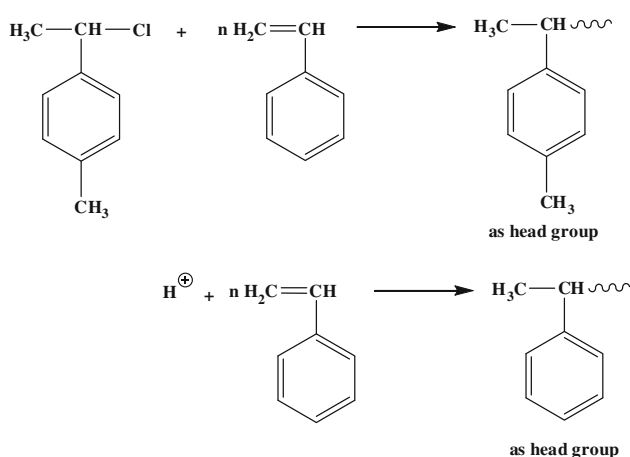
Kubisa et al. [126] also studied cationic polymerization of St with 1-(*p*-methylphenyl)ethyl chloride as initiator in [BMIM][PF<sub>6</sub>] in the absence of coinitiator (Lewis acid) at 90 °C. They ascribed that initiation (ionization of C–Cl bond in 1-phenylethyl chloride) proceeding in the solution in IL even in the absence of coinitiator. Formation of two populations of macromolecules, one containing *p*-methyl substituent in the head-group and the other having head groups devoid of methyl substituent (apparently formed by transfer) were confirmed by MALDI-TOF mass spectrometry of polymers formed in polymerization initiated with 1-(*p*-methylphenyl)ethyl chloride. Based on findings from three experiments, polymerization with no additives, polymerization in the presence of radical inhibitor and polymerization in the presence of proton sponge, and the measurements of the rate of racemization of optically active 1-phenylethyl chloride, authors ascribed that ionization of C–Cl bond, is not sufficiently fast to ensure fast initiation and fast activation of dormant species and therefore polymerization is not controlled.

Vijayaraghavan and MacFarlane [127] reported a controlled cationic polymerization of St by HBOB as an initiator in a conventional solvent, DCM, and in an IL, [BMPyrr][Tf<sub>2</sub>N] at different temperatures (0–60 °C). They optimized concentration of HBOB and it found that the MWs of these polymers increased with decreasing HBOB concentration. The obtained polymers using HBOB had



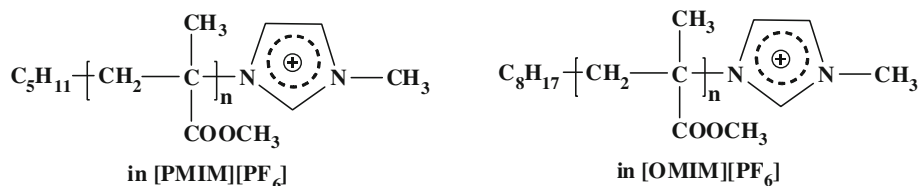
narrow PD and were predominantly syndiotactic. They also studied effect of added water contents in the reaction mixture on the polymer yield to determine the water tolerance in these systems. It found that polymerization to high yields occurs only at 60 °C using [BMPyrr][Tf<sub>2</sub>N] as solvent due to an increased degree of dissociation of the HBOB acid at high temperatures in the IL compared with the molecular solvent. Experiments were also carried out with other organoborate acids such as bisuccinoboric acid and bisglutaroboric acid, and it was found that the trend in yields followed trends in Bronsted acidity. The efficiency of different ILs as reaction solvents was also discussed. The results exhibited that the polymerization takes place using [Tf<sub>2</sub>N] anion independent of the cation, but upon changing from [Tf<sub>2</sub>N] anion, the polymerization did not occur. The IL was recycled and reused without significant effect on yield of polymers.

Kubisa and co-workers [128] studied the cationic polymerization of St initiated by aryl (alkyl) chlorides in the absence of Lewis acid coinitiator in IL/sulfur dioxide mixture as a solvent. The polymerization proceeded to high conversion in 24 h. MALDI-TOF spectra of polymers obtained with *p*-methyl derivative of 1-phenylethyl chloride revealed the presence of two populations of macromolecules with different head-groups (Scheme 4). With increasing ratio of sulfur dioxide to IL, polymerization rate became faster. They found that ionization of the C–Cl bond is facilitated in this reaction medium, and compared to



**Scheme 4** Two populations of macromolecules with different head-groups obtained with *p*-methyl derivative of 1-phenylethyl chloride

**Scheme 5** Structures of PMMA macromolecules



polymerization in IL alone, the contribution of chain transfer reaction can be reduced. The results of experiments performed in the presence of proton sponge demonstrated that the mechanism of polymerization may involve reversible ionization of dormant species in accordance with controlled polymerization scheme. Nevertheless, ionization of the C–Cl bond was too slow to allow truly controlled polymerization.

#### Anionic

The effect of imidazolium salts with [PF<sub>6</sub>] and [BF<sub>4</sub>] anions as reaction media was investigated on the anionic polymerization of methyl methacrylate (MMA) using alkyllithium as an initiator by Biedron and Kubisa [129]. The structures of PMMA macromolecules formed by anionic polymerization of MMA in 1-propyl-3-methylimidazolium ([PMIM])[PF<sub>6</sub>] and 1-octyl-3-methylimidazolium ([OMIM])[PF<sub>6</sub>] using BuLi as initiator are shown in Scheme 5. The resulting products were characterized by MALDI-TOF, and it was found that polymers synthesized had low MW terminated with an imidazolium moiety. Thus, it discovered a chain transfer to ILs occurs, and the imidazolium ILs are not neutral solvents. According to the authors, although imidazolium ILs are not appropriate solvents for controlled polymerization of MMA, owing to significant chain transfer to IL, single series of MMA oligomers terminated with ionic group is formed in high yield which may be of synthetic interest.

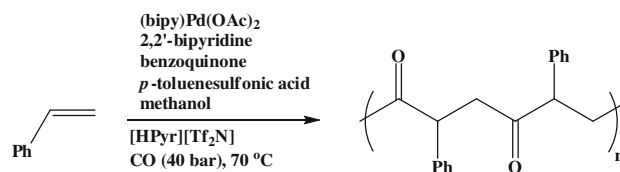
Kokubo and Watanabe [130] employed ILs for the anionic polymerization of MMA using alkyl lithium initiators such as *n*-butyl lithium and diphenylhexyl lithium (DPHLi) at 0 °C. Four ILs were used, [BMIM][PF<sub>6</sub>], [EMIM][Tf<sub>2</sub>N], trimethylsulfonium ([Me<sub>3</sub>S])[Tf<sub>2</sub>N] and *N,N*-diethyl-*N*-(2-methoxyethyl)ammonium ([DEME])[Tf<sub>2</sub>N]. When the polymerization performed in ILs containing [Tf<sub>2</sub>N] anion, polymer did not result, owing to the initiator deactivation by the attacking of the Tf<sub>2</sub>N anion. However, the polymerization proceeded in [BMIM][PF<sub>6</sub>] with low yields compared to those in organic solvent, tetrahydrofuran (THF). This was attributed to the high reaction temperature (0 °C) in comparison to the common anionic polymerization temperature (–78 °C) and the reaction between the initiator and the imidazolium cation. They also found that the tacticity of the PMMA

synthesized in [BMIM][PF<sub>6</sub>] using DPHLi, was rich in isotactic triads.

Vijayaraghavan et al. [131] reported anionic polymerization of St at ambient temperatures in IL, trihexyl(tetradecyl) phosphonium [Tf<sub>2</sub>N]. The reaction conditions were milder in ILs than those in classical methods. When the polymerization was carried out at 60 °C using *s*-butyl lithium as initiator in IL, high MW polymer with a low yield (20%) was obtained after 70 h. Under similar reaction conditions, sodium acetate formed only 10% yield. The addition of the zwitterion compounds bearing a more basic functionality resulted in better dissociation of the metal cation based initiators and the IL based reaction allowed the use of a much milder Lewis base initiator than was usually required. The addition of the zwitterion increased the yield of polymer to 75% in 70 h and 94% in 140 h, in the presence of initiator, *s*-butyl lithium and 65% in the presence of sodium acetate. The polymer had MWs high, up to 4,00,000 gmol<sup>-1</sup> and PDs in the range of 1.4–2.1. This showed that transfer reactions are not significant in this system hence perhaps phosphonium ILs are more appropriate as solvents for anionic polymerization than imidazolium ILs, although zwitterionic compounds had imidazolium cation.

#### Alkenes Copolymerization with Carbon Monoxide (CO)

Hardacre and co-workers [132] prepared polyketone by the alternating carbonylation of St and CO, using [Pd(bipy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> in different ILs. The effects of various ILs, the nature and concentration of palladium catalyst, and the reusability of the catalyst-IL system were investigated. The yield of polymers was found to decrease following the order [Tf<sub>2</sub>N]<sub>2</sub> > [PF<sub>6</sub>]<sub>2</sub> > [BF<sub>4</sub>]<sub>2</sub> for both pyridinium and imidazolium based ILs. Comparison of the activity in pyridinium, imidazolium, quaternary nitrogen- and phosphonium-based [Tf<sub>2</sub>N] ILs showed that the polyketone yield also decreases in the similar order. No appreciable catalyst leaching was observed, however, the type of IL used was found to have effect on the catalyst leaching, so in *N*-alkylpyridinium ([C<sub>*n*</sub>Pyr])[Tf<sub>2</sub>N] ILs, for *n* = 8, 10 and 18, the inclusion of palladium, via the decomposition of the catalyst, in the polymer was exhibited. Furthermore, the higher yields was found with increasing alkyl chain length of the pyridinium ILs [C<sub>*n*</sub>Pyr][Tf<sub>2</sub>N] (*n* = 4 to 10). The higher yields and MWs were observed than polymerization reactions in conventional solvent methanol. Using equal volumes of *N*-hexylpyridinium ([HPyr])[Tf<sub>2</sub>N] and methanol, it was found that polyketone obtained with the lowest MW. The IL containing catalysts was recovered and reused four times with no appreciable decrease in the yield or the quality of the polyketone.



**Scheme 6** The palladium-catalyzed copolymerization of St and CO in [HPyr][Tf<sub>2</sub>N]

Shaughnessy et al. [133] utilized the ILs as solvents for the palladium-catalyzed, alternating copolymerization of St and CO (Scheme 6). The experiments were carried out using a standard catalyst system consisting of LPd(OAc)<sub>2</sub> (L = 2,2'-bipyridine and 1,10-phenanthroline), excess ligand, benzoquinone and *p*-toluenesulfonic acid in [HPyr], [BMIM] and [C<sub>14</sub>H<sub>29</sub>P(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>] based ILs containing [Tf<sub>2</sub>N] anion. The higher MWs and improved catalyst stability were obtained in [HPyr][Tf<sub>2</sub>N] compared with methanol. Copolymerization in [HPyr][Tf<sub>2</sub>N] yielded St homopolymer as the major product, while in the IL/methanol mixture (10:1), high yields of copolymer was formed. This was attributed to the reaction of methanol with L<sub>*n*</sub>Pd<sup>2+</sup> and CO to form [LPdC(O)OCH<sub>3</sub>]<sup>+</sup>, which initiates the copolymerization. The productivity and yields of copolymer were found to be dependent on both [HPyr][Tf<sub>2</sub>N] and methanol volumes. They observed that lower yields were obtained in [BMIM][Tf<sub>2</sub>N], whereas no copolymer was formed in a phosphonium based IL.

Recently, Chan and co-workers [134] applied 1-alkyl-3-methylimidazolium ([C<sub>*n*</sub>MIM])[PF<sub>6</sub>] (*n* = 4, 6, 8) or [BMIM][BF<sub>4</sub>] for Pd-catalyzed stereoselective copolymerization of propene and CO using (2*S*,3*S*)-DIOP and (*R*)-*P*-Phos as chiral ligands (Scheme 7) and produced polyketone with almost complete regioregularity and moderate stereoregularity. Compared with conventional solvent, methanol/CH<sub>2</sub>Cl<sub>2</sub> enhanced productivity, higher MW and lower PD were the main advantages demonstrated by ILs.

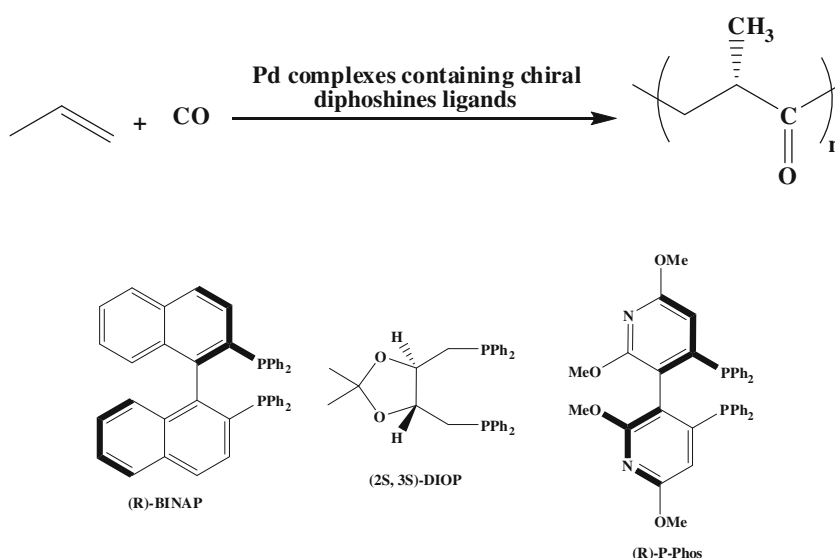
#### Radical Polymerization

[BMIM][PF<sub>6</sub>] was used as solvent for the copper(I) mediated living radical polymerization of MMA by Haddleton et al. [135]. Using this solvent, the rate of reaction was increased and narrow PD polymers were obtained which were easily isolated from the catalyst.

Biedron and Kubisa [136] reported the ATRP of differently substituted acrylates using CuBr/pentamethyldiethylenetriamine (PMDETA) as the catalyst in [BMIM][PF<sub>6</sub>]. They found that the solubility of the acrylates and their polymers depends upon the size of the substituent in the ester group. Methyl acrylate (MA) and its polymer were soluble in IL, butyl acrylate (BA) was only partly soluble



**Scheme 7** Asymmetric alternating copolymerization of propene with CO catalyzed by Pd complexes containing chiral diphosphine ligands



(1 g of [BMIM][PF<sub>6</sub>] dissolves 0.40 g of BA) whereas the corresponding polymer was insoluble in IL. Thus ATRP of BA in [BMIM][PF<sub>6</sub>] proceeded in a two-phase system. The catalyst (CuBr/PMDETA) was dissolved in the IL phase and the monomer was presented partly in IL phase and partly generated a separate organic phase. The resulting polymers were obtained with relatively low MW (in the range of  $2\text{--}3 \times 10^3 \text{ g mol}^{-1}$ ). The semi-liquid polymer separated from IL phase in the course of polymerization. After reaching nearly quantitative conversion, the separation of the polymer from the IL phase containing copper salt occurred spontaneously when the stirring of reaction mixture was stopped.

Haddleton et al. [137] applied pulsed laser polymerization (PLP) technique to determine the rate of propagation ( $r_p$ ) of FRP of MMA in [BMIM][PF<sub>6</sub>] at 25 °C. They found that rate constant of propagation ( $k_p$ ) increased as the concentration of IL was increased, so  $k_p$  enhanced from  $323 \text{ L mol}^{-1} \text{ s}^{-1}$  in bulk to above  $800 \text{ L mol}^{-1} \text{ s}^{-1}$  in 60 vol% IL. The authors mentioned that the reason probably was increased polarity of the medium that favors transition state involving charge.

Davis et al. [138] reported the RAFT polymerization of MA, MMA and St in [C<sub>n</sub>MIM][PF<sub>6</sub>],  $n = 4, 6, 8$  at 60 °C mediated with 2-(2-cyanopropyl) dithiobenzoate. Under these reaction conditions, only MMA and MA exhibited a living character and achieved high conversion with outstanding control of the MWD in the IL. St reached less than 2% conversion due to the insolubility of PSt in the IL. They found that as was frequently observed in FRPs, the RAFT polymerization of MA and MMA showed a faster rate of polymerization in ILs compared with those in toluene.

Xi and coworkers [139] studied the atom transfer radical copolymerization of *N*-hexylmaleimide and St in an IL, [BMIM][PF<sub>6</sub>] at room temperature using dendritic

polyarylether 2-bromoisobutyrate of different generations (G<sub>n</sub>-Br,  $n = 1\text{--}3$ ) as macroinitiators and CuBr/PMDETA as a catalyst at room temperature. The obtained copolymers had well-defined MWs, low PDs ( $1.18 < M_w/M_n < 1.36$ ) and predominantly alternating structures over a wide range of monomer feeds ( $f_1 = 0.3\text{--}0.8$ ). They also found that the tendency to form alternating copolymers for the two monomers was stronger in ILs compared with that in anisole.

The synthesis and characterization of block copolymer of BA with MA prepared by ATRP using CuBr/CuBr<sub>2</sub>/amine as the catalyst in IL, [BMIM][PF<sub>6</sub>] reported by Biedron and Kubisa [140]. The M<sub>n</sub> of the copolymer was slightly higher than calculated, but the MWD was low ( $M_w/M_n = 1.12$ ). Block copolymer free of homopolymer of the first block with PD, 1.13 may be obtained only if the conversion of MA at the stage when second monomer was added was not higher than 70%. The irreversible deactivation of growing macromolecules was significant for MA polymerization at a monomer conversion above 70%, while it was still not important for BA even at practically quantitative conversion, which was confirmed by MALDI-TOF analysis. These results exhibited that ATRP of BA in IL followed by addition of a second acrylate monomer permitted the clean synthesis of block copolymers by one-pot sequential polymerization even if the first stage was carried out to complete conversion of BA.

Mays et al. [141] demonstrated FRP of MMA and St using conventional organic initiators 2,2-azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) in the RTIL, [BMIM][PF<sub>6</sub>] without the need for any organic solvent. It found that ILs were superior to benzene as solvent, in view of the higher polymerization rates and MWs.

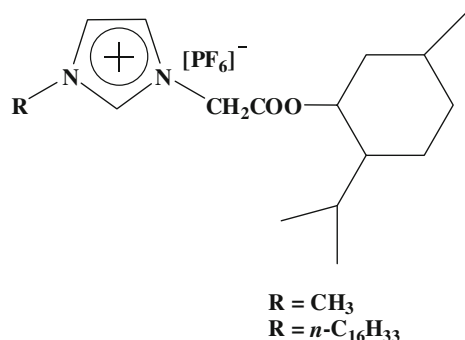
The same research group also developed conventional FRP of MMA and St by sequential addition of the

monomers in the RTIL, [BMIM][PF<sub>6</sub>] using BPO as the initiator [142]. They took benefit of the poor solubility of PSt in IL, where precipitation of PSt from the medium hindered diffusion of the propagating radical centers, which must find one another to terminate, and hence increased their lifetimes. When MMA that is miscible with the polymer dispersion was added, it diffused to radical sites, polymerization continued, resulting in production of block copolymers.

Wan and his group described a well-controlled reverse ATRP of MMA in the presence of AIBN/CuCl<sub>2</sub>/bipyridine as the initiating system using [BMIM][PF<sub>6</sub>] or 1-dodecyl-3-methylimidazolium ([C<sub>12</sub>MIM][BF<sub>4</sub>]) as the solvent [143]. The polymerization proceeded in a well-controlled manner in [C<sub>12</sub>MIM][BF<sub>4</sub>], while, the use of other IL [BMIM][PF<sub>6</sub>] failed to do the polymerization. This was attributed to poor solubility of PMMA in this IL. In addition, [C<sub>12</sub>MIM][BF<sub>4</sub>] was recovered and reused after simple purification without affecting the living nature of polymerization.

The same group prepared two chiral ILs, 1-[-(-)-menthoxy-carbonylmethylene]-3-methylimidazolium [PF<sub>6</sub>] and 1-[-(-)-menthoxy-carbonylmethylene]-3-hexadecylimidazolium [PF<sub>6</sub>] (Scheme 8) [144]. Reverse ATRP of MMA was carried out using CuCl<sub>2</sub>/bipyridine as the catalyst and AIBN initiator at 80 °C in these two chiral ILs. Subsequently, the resultant well-defined PMMA was employed as a macroinitiator to induce the ATRP of menthyl methacrylate (MnMA) in chlorobenzene and PMMA-*b*-PMnMA copolymer was produced with narrow PD.

Biedron and Kubisa [145] reported ATRP of MA in a chiral IL 1-(*R*(+)-2'-methylbutyl)-3-methylimidazolium [PF<sub>6</sub>] an analogue of [BMIM][PF<sub>6</sub>] with a chiral substituent at the imidazolium ring. The authors observed that the use of ILs decreases the extent of side reactions. It also found that radical polymerization of MA produces atactic polymers in an achiral environment, while, the isotactic fraction enhanced using the chiral IL. The results showed that the fraction of isotactic sequences increases with growing ratio of chiral IL to monomer.



**Scheme 8** Structure of two chiral ILs

The dendritic polyarylether 2-bromoisobutyrate used to initiate the copolymerization of *N*-substituted maleimides such as *N*-phenylmaleimide (PhMI), *N*-cyclohexylmaleimide (ChMI), and *N*-butylmaleimide (NBMI) with St via ATRP in [BMIM][PF<sub>6</sub>] and anisole, at room temperature by Xi et al. [146]. The resulting dendritic-linear block copolymers with well-defined MWs and low PDs ( $1.05 < M_w/M_n < 1.32$ ) were subsequently used as a macroinitiator for the chain-extension polymerization. The recycled IL solution of catalyst had catalytic activity relatively similar to that of the fresh catalyst. The reaction performed in ILs showed a stronger tendency for alternation compared with the reaction performed in anisole. The tendency for alternation decreased in the order PhMI > NBMI > ChMI in [BMIM][PF<sub>6</sub>] and PhMI > ChMI > NBMI in anisole.

Wan et al. [147] studied the well-controlled reverse ATRP of MMA in [BMIM][PF<sub>6</sub>] with AIBN/CuCl<sub>2</sub>/bipyridine as the initiating system at different temperatures. They reported that a much smaller amount of the catalyst was used in comparison to that observed in bulk or conventional solvents and IL and catalytic system recovered and reused without further treatment.

Mays et al. [148] studied statistical copolymerization of St and MMA via conventional FRP using AIBN or BPO as initiator in [BMIM][PF<sub>6</sub>]. It found that monomer reactivity ratios were considerably different from those in conventional organic solvents or in bulk, which might have a significant effect on monomer sequences of copolymer.

Perrier et al. [149] reported the RAFT polymerization of MMA, MA and St in [C<sub>*n*</sub>MIM][PF<sub>6</sub>], where *n* = 4, 6–8 at 60 °C. When polymerizing St, precipitation in the ILs was observed at an early stage of the polymerization due to the insolubility of PSt in ILs. In this process, the polymerization reactions of methacrylate and acrylate were living radical polymerization and resulted in polymers formation with high conversions and polydispersity indexes (PDI)s lower than 1.3 at higher rate than those observed in toluene.

Wang et al. [150] reported FRP of acrylonitrile (AN) using AIBN as initiator in [BMIM][BF<sub>4</sub>]. The improved thermal stability for the synthesis of the PAN in IL, was attributed by the authors to the breaking of crosslinking points in the polymer. They also found that polymerization of AN in IL leads to rapid reaction rates and production of polymer with higher MWs than that in organic solvents.

Benton and Brazel [151] demonstrated free radical solution polymerization of MMA in [BMIM][PF<sub>6</sub>] or benzene at 70 °C. They found that degree of polymerization was five times higher in [BMIM][PF<sub>6</sub>] than that in benzene and the rate of reaction was approximately four times faster in [BMIM][PF<sub>6</sub>].

Nitroxide-mediated polymerization (NMP) of St and MMA using a bimolecular initiation system, BPO along with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and

a unimolecular initiation system, 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane ( $\alpha$ -hydrido alkoxyamine, TMPPAH) in [BMIM][PF<sub>6</sub>] investigated by Mays et al. [152]. They polymerized St in bulk, dichlorobenzene and [BMIM][PF<sub>6</sub>] mediated by BPO/TEMPO and it found that polymers prepared in IL had lower conversions, lower MWs and higher PDs than those prepared by bulk polymerization. The authors claimed that this was probably due to interference of [BMIM][PF<sub>6</sub>] with the TEMPO mediated radical equilibrium. They also found that ratio of capping agent moiety (TEMPO) to initiator moiety (benzoyl) was higher in IL than that in bulk polymerization. Furthermore, when the polymerization was carried out in TMPPAH as an initiator, the yields were higher in comparison to those from the BPO/TEMPO system.

Vygodskii and coworkers [153] used ILs based on 1,3-dialkyl-substituted imidazole for the FRP of MMA. They showed that ILs are effective solvents, reaching high MW of PMMA with a high yield compared with reactions performed in organic solvents.

Aldabbagh et al. [154] reported the NMP of MA using alkoxyamine as an initiator in 50%v/v of [HMIM][PF<sub>6</sub>] at 140–155 °C. It found that the  $M_n$ s increased linearly with conversion, although there has been significantly higher than the theoretical values. A decrease in  $M_n$  by a factor of two was observed on increasing in the AIBN and 4-oxo-TEMPO concentrations by a factor of two (i.e., constant [4-oxo-TEMPO]/[AIBN]), but there was no important effect on the rate of polymerization. They also found that the rates of polymerization were greater in IL compared with those in organic solvent, anisole and MWs close to the calculated values were obtained.

Strehmel et al. [155] employed imidazolium salts as solvents for polymerization of hydrophobic and hydrophilic monomers. Thermal properties and viscosity of the imidazolium salts played an important role in polymerization processes. Poly(*n*-butylmethacrylate) (PBMA) with higher MW was obtained in the ILs compared to molecular solvent. They also synthesized copolymers based on hydrophobic and hydrophilic monomers using imidazolium salt as solvent. The structure of the polymer and the properties of the imidazolium salt were affected the amount of the IL recycled after polymerization in the absence of any solvent or using a traditional solvent. In case of polymeric sulfobetaines, approximately equimolar amounts of imidazolium salt are bound ionically by the sulfobetaine moiety incorporated in the polyzwitterion.

Vygodskii and co-workers [156] investigated the FRP of AN and its copolymerization with MMA in ILs based on 1,3-dialkyl-substituted imidazole. High MW, PAN with higher onset temperature of degradation and copolymers with high yields were produced in liquid organic salts than in molecular solvents.

Watanabe et al. [157] reported in situ polymerization of compatible vinyl monomers (such as MMA, AN, vinyl acetate (VAc), St, 2-hydroxyethyl methacrylate, MA and acrylamide) in [EMIM][Tf<sub>2</sub>N] to present a new methodology affording highly conductive polymer electrolytes. The polymerization of MMA in IL in the presence of a small amount of a cross-linker led to self-standing, flexible, and transparent films known as ion gels. With increasing mole fraction of [EMIM][Tf<sub>2</sub>N], the glass-transition temperatures ( $T_g$ )s of the gels was decreased and behaved as a simple binary system of polymer and IL and ionic conductivity reached a very large value close to  $10^{-2}$  Scm<sup>-1</sup> at ambient temperature.

Percec et al. [158] studied the effect of [BMIM][PF<sub>6</sub>] salt on the living radical polymerization of MMA using arenesulfonyl chlorides as initiator and Cu<sub>2</sub>O/2,2'-bipyridine as catalyst. They observed a remarkable acceleration in the living radical polymerization of MMA, that may lead to an initiation efficiency of 100%, elimination the induction period of this catalyst, and formation of polymer with MWD of 1.1 and perfect bifunctional chain-ends. Results from kinetic studies indicated that the  $k_p$  is almost first order with respect to IL concentration. It also found that the catalytic effect of the IL facilitates the reduction of the catalyst concentration from stoichiometric to catalytic and allows the decrease of the polymerization temperature from 80 to 22 °C.

Biedron and Kubisa [159] utilized a chiral IL with a chiral substituent on the imidazolium ring as a solvent for ATRP of MA and ethyl acrylate. They found that using this chiral IL, more isotactic polymer produced than that in achiral [BMIM][PF<sub>6</sub>] salt and the formation of isotactic polymer increased with a rising molar ratio of the chiral IL to the monomer.

Shen et al. [160] synthesized two IL monomers, 1-(4-vinylbenzyl)-3-butyl imidazolium ([VBzBIM])[BF<sub>4</sub>] and [VBzBIM][PF<sub>6</sub>] and used them in copper-mediated ATRP. The effects of various initiator/catalyst systems, monomer concentrations, solvent polarities, and reaction temperatures on the polymerization reaction were examined. Using CuBr/1,1,4,7,10,10-hexamethyltriethylenetetramine or CuBr/2,2'-bipyridine as the catalyst and ethyl 2-bromoisobutyrate as the initiator, the polymerization was well controlled and exhibited living characteristics. The obtained P([VBzBIM][BF<sub>4</sub>]) was amorphous and had excellent thermal stability, with a  $T_g$  of 84 °C. The CO<sub>2</sub> absorption ability of P([VBzBIM][BF<sub>4</sub>]) was 0.305% (w/w) at room temperature and 0.78 atm.

Shen and co-workers [161] reported the biphasic polymerization of MMA catalyzed by an IL. They found that tethering the catalyst to an IL moiety to form IL catalyst, afforded an efficient and economical way to remove/reuse the catalyst of ATRP. The used IL was only 5 wt % of the

organic solvent. The polymerization by the IL catalyst was well-controlled, generating polymers with controlled MWs and low PD. After the polymerization, the IL catalyst settled on the bottom of the reactor and easily separated from the polymer solution. The recycled catalyst could be reused for second run polymerization with same or even higher catalytic activity and similar or even better control over the polymerization.

Wan et al. [162] employed, [1-(2-bromoisobutyryloxyethyl)-3-methylimidazolium] ([BIEMIM])[PF<sub>6</sub>] salt, as an initiator to polymerize MMA via ATRP with controlled MW and narrow MWDs. End-group analysis by <sup>1</sup>H NMR indicated the presence of the initiator fragments at the ends of the polymer main chain. An increase in the content of syndiotactic triads was observed with lowering the reaction temperature. PMMA obtained at lower temperature had higher T<sub>g</sub> compared with that at higher temperature. The incorporation of imidazolium groups in the polymer led to increase of the solubility of the PMMA in methanol.

Strehmel et al. [163] reported free radical homo- and copolymerization of the nonpolar BMA and highly polar zwitterionic 3-(*N*-[2-methacryloyloxyethyl]-*N,N*-dimethylammonio)propane sulfonate in two ILs, based on [BMIM] cation and [BF<sub>4</sub>] or [PF<sub>6</sub>] anions. Compared with the classical reaction in water, the polymerization in an IL led to zwitterionic homopolymer with higher MWs. They found that, although phase separation occurs during the homopolymerization process of sulfobetain or of BMA, transparent gels are formed by copolymerization of a stoichiometric ratio of the two monomers in the ILs. Using ILs as solvents, the content of BMA units relative to sulfobetaine substituted units enhanced whereas use of acetonitrile, incorporated only minor amounts of BMA in the copolymer.

The same research group also investigated the polymerization of *n*-butyl methacrylate (BMA) in ILs based on imidazolium, pyridinium, and alkylammonium salts with a systematic variation of the length of the alkyl substituents on the cations, and utilizing different anions such as [BF<sub>4</sub>], [PF<sub>6</sub>], [TSA], [OTf], alkyl sulfates and dimethyl phosphate [164]. It found that polymer tacticity was not obviously affected by ILs, whereas polymer were obtained using ILs with drastically higher degrees of polymerization compared to that in toluene or by bulk polymerization. Furthermore, by replacing the C(2) proton with a methyl group in 1,3-dialkylimidazolium-based ILs, an enhance in the degree of polymerization with increasing viscosity resulted in a viscosity independent degree of polymerization. It seemed that ILs based on imidazolium salts preferable over pyridinium and alkylammonium salts due to the higher degree of polymerization. The authors mentioned that PBMA synthesized in the ILs had many obvious advantages compared with those synthesized in the toluene,

including markedly higher degrees of polymerization, higher T<sub>g</sub>s, and higher thermal stabilities.

Zhang et al. [165] studied the free radical copolymerization kinetics of AN and MA in [BMIM][BF<sub>4</sub>] using AIBN as an initiator. The effects of initiator concentration, monomer concentration, monomer ratio, and temperature on the copolymerization process reactions were also investigated. They authors found that in the steady state, the copolymerization rate R<sub>p</sub> can be noted as  $R_p = KC_{AIBN}^{0.74}C_{MA}^{0.61}C_{AN}^{0.44}$  (C<sub>AIBN</sub>, C<sub>AN</sub>, and C<sub>MA</sub> are the concentration of the AIBN, AN, and MA). The apparent activation energy in IL (87.94 kJ mol<sup>-1</sup>) was higher than that found in molecular solvents such as DMF (~81 kJ mol<sup>-1</sup>) and the reactivity ratios were r<sub>AN</sub> = 0.36 and r<sub>MA</sub> = 0.68.

The same research group also exploited the applicability of ILs in FRP of MMA using AIBN as an initiator [166]. The authors performed the polymerization reactions in polar organic solvent acetonitrile to compare the efficiency of ILs. The advantages of ILs over conventional solvent were superior MWs and lower PDs presumably due to the higher viscosity of ILs compared with acetonitrile, thereby diminishing chain terminations and/or chain transfers. Furthermore, it found that the structure of IL has little effect on the PDs while it influences the MW considerably. The stereostructure of the polymers produced in ILs was not consistent with that observed in acetonitrile, and the fraction of syndiotactic triads was decreased as the viscosity and polarity increased.

Liu et al. [167] investigated the copolymerization of AN with St by conventional free radical copolymerization in RTILs, [BMIM][BF<sub>4</sub>] and [BMIM][PF<sub>6</sub>], under mild conditions. The resulting P(St-co-AN) (PSAN) could be formed with a bimodal MWD due to poor compatibility of the reaction systems, which is caused by the immiscibility of the product with RTILs and the enhance of viscosity of the reaction system as the reactions proceeding. Moreover, the copolymerization was more rapid and MW was higher in RTILs compared with those in DMF or by bulk copolymerization.

Li et al. [168] prepared a kind of gel polymer electrolyte by in situ polymerization of MMA monomer in [BMIM][PF<sub>6</sub>]. These gel polymer films showed excellent thermal stability over 260 °C in comparison with other gel polymer electrolytes. T<sub>g</sub> value of the resulting gel polymer electrolyte decreased with an increase in the ratio of IL to polymer matrix. The ionic conductivity of this polymer electrolyte was 0.15 × 10<sup>-3</sup> Scm<sup>-1</sup> at 25 °C, with the mass ratio of [BMIM][PF<sub>6</sub>] to MMA monomer of 1. Analysis of FT-IR spectra suggested that there exists a hydrogen-bonded interaction between [BMIM][PF<sub>6</sub>] and PMMA matrix in the polymer electrolyte.

Woecht and Schmidt-Naake [169] used [BMIM][PF<sub>6</sub>], 1,3-dimethylimidazolium dimethylphosphate ([DMIM]



[Me<sub>2</sub>PO<sub>4</sub>]) and [EMIM] ethylsulfate ([EtSO<sub>4</sub>]) ILs as reaction media for free radical copolymerization of St and AN and examined the influence of ILs on the copolymerization of these two monomers. The results showed that, two ILs [BMIM][PF<sub>6</sub>] and [EMIM][EtSO<sub>4</sub>] had a greater influence on conversion and MWs than [MMIM][Me<sub>2</sub>PO<sub>4</sub>]. The copolymerizations rate was faster in [BMIM][PF<sub>6</sub>] and [EMIM][EtSO<sub>4</sub>] than that in [MMIM][Me<sub>2</sub>PO<sub>4</sub>] despite higher viscosity of the latter IL. However, this was probably due to deviation of pH values of [EMIM][EtSO<sub>4</sub>] and [MMIM][Me<sub>2</sub>PO<sub>4</sub>] from each other. They also found that, the PDs and MWs of the polymers synthesized in ILs were higher than those in the conventional organic solvents such as DMF and methanol. This was attributed to the increased  $k_p/k_t$  ratio due to the high viscosities and relatively high polarity of the ILs. The results revealed that the influence of the [EMIM][EtSO<sub>4</sub>] on  $k_t$  decreases with increasing temperature and decreasing viscosity, respectively, whereas the influence on  $k_p$  is increased.

The same research group also utilized [EMIM][EtSO<sub>4</sub>] as a solvent for the homo- and copolymerization of St and MMA, glycidyl methacrylate (GMA) and 2-hydroxypropyl methacrylate (HPMA) with AN [170]. It found that the polymerization rate and the  $M_n$  values increase with rising content of AN in the monomer feed, while in the case of the methacrylate/AN copolymers, the influence of the IL on the conversion decreases with increasing AN content in the monomer feed. The MWs of the polymer samples synthesized in [EMIM][EtSO<sub>4</sub>] were at least 1 to 2 orders of magnitude higher than those in methanol. They also showed that there is a stronger influence of the IL for the methacrylate polymerizations which lead to higher polymerization rates.

The effects a series of imidazolium and ammonium based ILs on FRP processes investigated by Strehmel [171]. They found that liquidus range, viscosity and polarity of ILs strongly affected FRP processes. Degree of polymerization was higher in ILs with higher viscosity. Additionally, the micropolarity of ILs influenced the composition of copolymers synthesized in ILs.

Kubisa et al. [172] reported the ATRP of methyl acrylate (MA) in [BMIM][PF<sub>6</sub>] with a molybdenum halide catalytic system. Using ethyl-2-bromopropionate as an initiator and [MoCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>/MoCl<sub>4</sub>(PMe<sub>3</sub>)<sub>3</sub>] as catalyst, the polymerization proceeded in a controlled manner, and MALDI-TOF analysis of the polymers showed that the reversibly deactivated macromolecules contained both bromine and chloride end groups.

Lu et al. [173] studied reverse ATRP of MMA in [OMIM][PF<sub>6</sub>], [HMIM][BF<sub>4</sub>], [OMIM][BF<sub>4</sub>] and [C<sub>12</sub>MIM][BF<sub>4</sub>] using the immobilized catalyst system at relatively low temperature. The best results were obtained in the presence of [OMIM][PF<sub>6</sub>]. In addition, the resulting polymer and the

immobilized catalyst were easily separated from IL and recycled and reused after simple purification without affecting the living nature of polymerization.

Schubert et al. [174] reported microwave-assisted homogeneous polymerizations of hydrophobic monomers in the presence of water-soluble ILs as reaction media. In this case, they studied the FRP of MMA and the cationic ROPs of 2-phenyl-2-oxazoline and 2-(*m*-difluorophenyl)-2-oxazoline. Compared with the polymerization in bulk, the polymerization reactions using of ILs exhibited a more efficient heating profile of the reaction mixtures.

Vygodskii and co-workers [175] investigated influence of the nature of ILs based on cations 1,3-dialkylimidazolium and tetraalkylphosphonium upon the free radical addition polymerization of MMA, AN and 1-vinyl-3-ethylimidazolium ([VEIM]) salts. They found that using ILs are resulted the polymers with high MWs and high yields and are also able to control the polymerization rate and MWs. The authors also showed that elongation, tensile modulus and strength of PAN synthesized in IL were higher than those in conventional media. Furthermore, the polymerization of [VEIM] salts in ILs led to flexible, transparent polymer films with high ionic conductivity.

Tsubokawa and his group [176] investigated radical graft polymerization of vinyl monomers, such as St and MMA, initiated by azo groups introduced onto silica nanoparticle and carbon black surfaces in [BMIM][PF<sub>6</sub>], whose the percentage of grafting increased with increasing reaction time. Compared with polymerization in 1,4-dioxane, the percentage of grafting in IL was much larger. The MW of PSt grafted onto the silica surface in IL was almost equal to that in 1,4-dioxane. The results showed that the amount of grafted PSt in IL is five times that in 1,4-dioxane. The authors attributed this finding to the fact that lifetime of the surface radical formed by the group of azo is prolonged because of high viscosity of IL. Furthermore, the reduction of waste solvent was attained using IL as reaction solvent, because unreacted monomer could be removed and the IL reused.

Wang et al. [177] examined the kinetics of ATRP of MMA initiated by ethyl-2-bromopropionate (EPN-Br) in the presence of CuBr as catalyst, and PMDETA as ligand in three ILs, [BMIM][Br], [EMIM][BF<sub>4</sub>], and [BMIM][BF<sub>4</sub>]. They investigated the effects of solvents, temperature, and reaction ingredients ratios on the polymerization kinetics. The apparent activation energy for the ATRP of MMA in [BMIM][BF<sub>4</sub>] was 6.95 KJmol<sup>-1</sup> which was much lower than ATRP of MMA in diphenyl ether (62.7 KJmol<sup>-1</sup>). The  $M_n$ s increased linearly with conversion but were much higher than the theoretical values probably owing to the low concentration of deactivator at the early stage of polymerization and the lower bond energy of C–Br in PMMA-Br compared with that in EPN-



Br. The catalyst was easily separated from the polymer and reused more than three times.

Strehmel et al. [178] studied the influence of imidazolium-based ILs as solvents on the synthesis of amphiphilic copolymers based on BMA and 3-(*N*-2-[methacryloyloxyethyl]-*N,N*-dimethyl-3-ammonio)propane sulfonate. They found that the relative reactivity of the monomers and therefore the copolymer composition is influenced by the IL used. The polymers synthesized in acetonitrile mainly contained monomer segments with the zwitterionic structure independent of the monomer ratio selected for copolymer synthesis, while, true copolymers were obtained when the ILs [BMIM][BF<sub>4</sub>] and [BMIM][PF<sub>6</sub>] were employed as solvents, though, upon copolymerization in these two ILs, the monomer bearing the zwitterionic structure was preferred. Using [EMIM][TSA] and with the same molar ratio, the copolymer synthesized under otherwise identical conditions contained a significantly higher content of BMA segments compared to that in [BMIM][BF<sub>4</sub>] or [BMIM][PF<sub>6</sub>]. The ratio of monomer segments in the copolymer can be influenced by the selection of the IL used for polymer synthesis and by the variation of the monomer ratio selected for copolymerization.

Hong et al. [179] reported copper-mediated ATRP of MMA in the presence of limited amounts 2,2'-bipyridine as the ligand and methyl-2-bromopropionate (MPN-Br) as the initiator, in IL, *N*-butyl-*N*-methyl morpholinium ([BMMor<sub>1,4</sub>])[BF<sub>4</sub>]. They found that the dosage of catalyst for well-controlled polymerization could be reduced obviously in [BMMor<sub>1,4</sub>][BF<sub>4</sub>] than that in organic solvent. The bromine-atom-ended PMMA can serve as macroinitiator in the ATRP of *t*-BMA. The resultant polymers were easily isolated, and the IL/catalyst system could be recovered and reused with a simple treatment.

Hou and his group [180] described AIBN-initiated reverse ATRP of AN in the presence of FeCl<sub>3</sub>/succinic acid (SA) with a well-controlled manner in [BMIM][BF<sub>4</sub>]. The rate of polymerization was found to be faster than a comparative polymerization carried out in bulk with higher control MW and its distribution. It also found that the polymerization apparent activation energy decreased from 55.7 kJ mol<sup>-1</sup> in bulk to 48.2 kJ mol<sup>-1</sup> in IL. The resulting polymer used as a macroinitiator for the chain extension polymerization in [BMIM][BF<sub>4</sub>] by conventional ATRP process. The catalyst system dissolved in the IL were recycled and reused after simple purification without effect on the living nature of polymerization.

Tsubokawa et al. [181] investigated the radical polymerization of vinyl monomers such as St, MMA and VAc, initiated by BPO and AIBN in the presence of carbon black in [BMIM][PF<sub>6</sub>]. They found that the polymerization of St initiated with BPO was outstandingly retarded in the presence of carbon black, and during the polymerization, a

part of polymer was grafted onto the surface based on the termination of growing polymer radical by carbon black. In toluene using carbon black the polymerization was remarkably retarded. Interestingly, the use of IL led to no the retardation of polymerization in the initial stage of the polymerization. The grafting of PSt onto the carbon black surface was less than 1% in toluene. The percentage of grafting increased with rising reaction time using IL.

Garcia et al. [182] studied  $k_p$  of MMA and glycidyl methacrylate (GMA) homopolymerizations in four different ILs, including [EMIM][EtSO<sub>4</sub>], [EMIM] hexyl sulfate ([HexSO<sub>4</sub>]), [BMIM][PF<sub>6</sub>] and [BMIM][BF<sub>4</sub>] at ambient pressure using the PLP size-exclusion chromatography technique. Compared with bulk polymerization,  $k_p$  was enhanced by up to a factor of 4 with MMA and by a factor of 2 with GMA in IL solution containing 20 vol % monomer at 40 °C, because of lowering of the activation energy for propagation upon gradually replacing monomer molecules by IL species.

Zhang et al. [183] reported the ATRP and FRP of AN in [BMIM][Cl]. The experimental MW of polymer found to be in well agreement with theoretical value. The higher conversion and lower MW dispersion were obtained in IL than those in DMF. They also showed that polymer with higher percentage of isotactic diads was produced in IL compared with that in DMF.

Irvine et al. [184] studied the reaction kinetics of MMA polymerization in both ILs and organic solvents in more detail. With addition of chain transfer agent (CTA), the extent of MW reduction for a set of the CTA concentration was much less than the analogous reaction in an organic medium while the observed reduction of PD as CTA concentration was increased was more pronounced in ILs. Almost quantitative yield can be obtained for polymerization at temperatures up to 120 °C in [EMIM][EtSO<sub>4</sub>], whereas almost no polymer was formed in an organic solvent due to rapid initiator burnout. It has been proposed that a protected radical mechanism is in operation; but, explanation of the exact nature of this protection remains elusive. Furthermore, the formation of protected macro-radical in an IL medium suggested the possibility to synthesize catalyst-free high MW block copolymers.

Hou et al. [185] studied ATRP of AN with ethyl 2-bromoisobutyrate as the initiator in the absence of any ligand in three novel ILs, [MIM] acetate ([Ac]), [MIM] valerate ([VT]) and [MIM] caproate ([CT]), respectively. All the polymerizations proceeded in a well-controlled manner in the ILs. The polymerization in [MIM][Ac] not only exhibited the best control of MW and its distribution but also afforded a rather rapid reaction rate. The obtained PAN was successfully employed as the macroinitiator to proceed the chain extension polymerization in [MIM][Ac]. After simple purification, the ILs and FeBr<sub>2</sub> could be

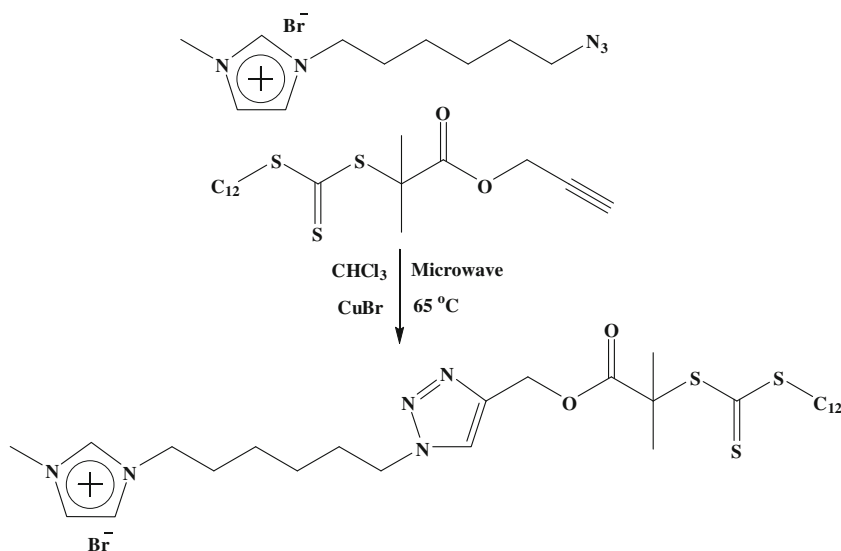
recycled and reused without effect on the living nature of polymerization.

Licence and co-workers [186] described RAFT polymerization of MMA using two different RAFT agents 2-cyanoprop-2-yl dithiobenzoate (CTA1) and 2-dodecylsulfanyl thiocarbonyl sulfanyl-2-methyl propionic acid (CTA2) in imidazole based RTILs [BMIM] and [EMIM] containing [PF<sub>6</sub>], [EtSO<sub>4</sub>], [Tf<sub>2</sub>N] and [BF<sub>4</sub>] as counter anions. They showed that the nature of the anion is important in the success of RAFT control in RTILs and this was attributed to three phenomena including the solubility of the monomer and polymer in the RTIL, the affinity of the RAFT agent for the ionic domains of the RTIL and partitioning of the radical species in the ionic domains of the RTIL. When [EMIM][EtSO<sub>4</sub>] and [EMIM][BF<sub>4</sub>] was used as solvent, there was poor MW control for both RAFT

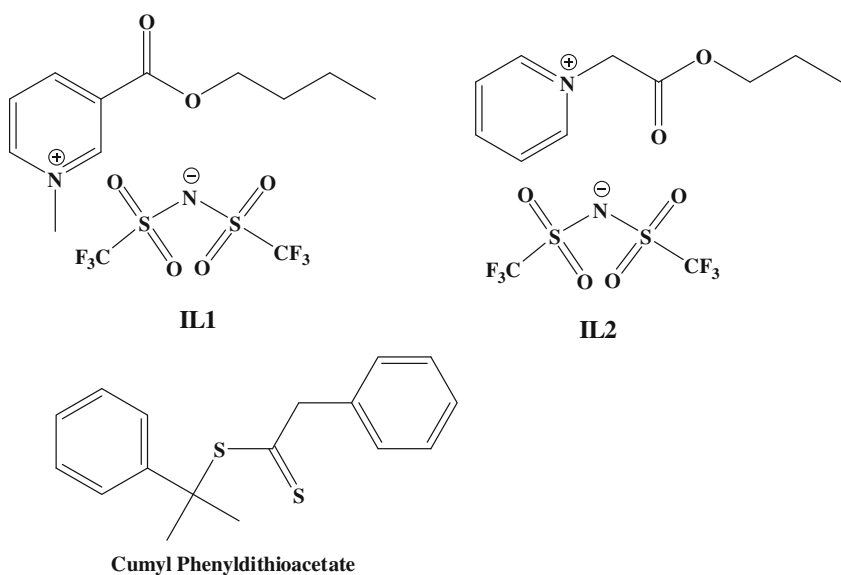
agents. The reactions carried out in [BMIM][PF<sub>6</sub>] and [BMIM][Tf<sub>2</sub>N] exhibited a much greater degree of control and production of polymer with very low PD compared to those in toluene even with the large amount of AIBN required to yield polymer. They also synthesized a novel RAFT-tethered IL by click type chemistry (Scheme 9) to act as a compatibilizer that overcomes many of the observed phase partitioning effects observed in free RAFT and resulted in high levels of control never before achieved using RAFT in such a broad range of RTILs.

Recently, Monteiro et al. [187] synthesized two readily biodegradable ILs based on pyridinium (Scheme 10) and used these ILs as solvents in the RAFT-mediated radical polymerization of St initiated with 1,1-azobis(cyclohexanecarbonitrile) at 90 °C. No considerable difference in the rate of polymerization was found in ILs and molecular

**Scheme 9** Synthetic approach for synthesis of RAFT-functional RTIL using click chemistry



**Scheme 10** ILs 3-(butoxycarbonyl)-1-methylpyridinium [Tf<sub>2</sub>N] (IL1) and 1-(2-ethoxycarbonyl)-methylpyridinium [Tf<sub>2</sub>N] (IL2) and RAFT agent cumyl phenyldithioacetate



solvent toluene. Ideal living radical behavior of the polymerization was confirmed by the linear increase in  $M_n$  with conversion and PDIs below 1.2. The authors noted that in the absence of RAFT agent, rates conventional FRPs in ILs were slightly lower as compared with those in toluene and after a few minutes the cloudy solution was observed, resulting, the start of a precipitation polymerization or an occlusion polymerization. It also found that the change in initiator efficiency factor with conversion remained relatively constant at close to 0.6 for the polymerization in toluene, but for ILs decreased down to 0.2 at high conversions. Interestingly, based on a detailed kinetic analysis they found that the ratio of termination to  $k_p$ s remained relatively constant over the conversion range, suggesting that trapped or protected radicals were not present in systems.

Schmidt-Naake and co-workers [188] studied effect of ILs upon  $k_p$  and  $k_t$  in radical polymerization. They observed a considerable increase in the rate of polymerization in these liquids. It found the increase in  $k_p$  and the reduction of activation energy which can be explained by hydrogen bonds of the monomer and growing radical chain with the cations and anions of the IL. The authors claimed that the high viscosity of the IL and the increased viscosity in the course of the reaction are responsible for the high MWs and PDs generally important.

Woecht and Schmidt-Naake [189] investigated the influence of [BMIM][BF<sub>4</sub>] on the polymerization rate, the MWs, the MWDs, the  $T_g$ , the copolymer composition and the rheological behavior for free radical copolymerization of MMA and *N*-phenyl maleimide (NPhMI). With increasing initial concentration of NPhMI,  $r_p$  strongly decreased in IL and became even lower than in DMF for 70 to 90 mol% NPhMI in the monomer feed. The  $M_n$  of the copolymers formed in the IL strongly decreased but was always higher than that in DMF. Comparing the copolymer composition and the  $T_g$ s in organic solvent and IL showed little difference.

Schmidt-Naake and his group [190] compared microwave-assisted homopolymerization of MMA in [EMIM][EtSO<sub>4</sub>] and DMF using AIBN or BPO as initiator at 60 and 80 °C with the polymerization reactions presented under conventional heating. They also investigated the homopolymerization of St and the copolymerizations of it with AN and MMA with NPhMI in [EMIM][EtSO<sub>4</sub>] or [BMIM][BF<sub>4</sub>] and in DMF or methanol under microwave irradiation or conventional heating. The rate of conversion in ILs was higher than that in methanol and DMF under conventional heating. The overall polymerization rate  $r_p$  using microwave was lower than that using conventional heating in ILs. In the case the homopolymerization of MMA and the copolymerization of St/AN (50/50 mol%)  $r_p$  of the reactions performed in the microwave was higher

using [EMIM][EtSO<sub>4</sub>] than a conventional solvent.  $r_p$  of the homopolymerization of St and the MMA/NPhMI (50/50 mol%) copolymerization performed in the microwave was nearly the same using either IL or conventional organic solvents. They also found that there are no outstanding differences in the MWs between both heating methods, neither in the case of using the conventional organic solvents DMF and methanol nor in the case when the ILs used.

Liang et al. [191] described reverse ATRP of methacrylonitrile (MAN) initiated with AIBN using FeCl<sub>3</sub> and isophthalic acid (IA) as catalyst and ligand in an IL, [BMIM][PF<sub>6</sub>] at 75 °C. The controlled manner of the polymerization was confirmed by kinetic studies. The control of MW and narrower MWD using IL were better than those in DMF. Rate of polymerization was also much more rapid, relative to polymerization in common organic solvent. They also synthesized the block copolymer PMAN-*b*-PSt using PMAN as macroinitiator via a conventional ATRP process in [BMIM][PF<sub>6</sub>]. The IL and catalytic system could be reused without effect on the living nature of polymerization.

Huai-yu et al. [192] prepared cellulose graft PMMA copolymers by ATRP in an IL. Cellulose chloroacetate, as a macroinitiator, was first synthesized by direct acylation of cellulose with chloroacetyl chloride without any catalysts under mild conditions in an IL, [AMIM][Cl]. Then, the macroinitiator was used for the ATRP of MMA mediated by the CuBr and 2,2'-bipyridine catalysis system. The copolymerization was carried out in [AMIM][Cl] without homopolymer byproduct. The polymers were easily separated from the catalyst when the IL was used as reaction medium. The results showed that the obtained copolymers had grafted polymer chains with well-controlled MW and PD, and the polymerization was a living/controlled system. Further, through atom force microscopy (AFM) observation, it was found that the cellulose graft copolymer in solution could aggregate and self-assembly into sphere-like polymeric structure.

Chen et al. [193] used ILs, [C<sub>12</sub>MIM][BF<sub>4</sub>], [OMIM][BF<sub>4</sub>] and [BMIM][BF<sub>4</sub>] as the reaction media for reverse ATRP of ethyl acrylate (EA) initiated by AIBN with CuBr<sub>2</sub> and PMDETA as catalyst and ligand. Compared with the polymerization in [OMIM][BF<sub>4</sub>] and [BMIM][BF<sub>4</sub>], the polymerization in [C<sub>12</sub>MIM][BF<sub>4</sub>] not only showed better control of MW and narrower MWD but also provided more rapid reaction rate with the ratio of [EA]:[AIBN]:[CuBr<sub>2</sub>]:[PMDETA] at 400:1:3:4. Block copolymer PEA-*b*-PSt was obtained via a conventional ATRP process in [C<sub>12</sub>MIM][BF<sub>4</sub>] using the resulting PEA as macroinitiator. [C<sub>12</sub>MIM][BF<sub>4</sub>] and CuBr<sub>2</sub>/PMDETA could be easily recycled and reused and had no effect on the living nature of reverse ATRP of EA.

Buback et al. [194] measured  $k_t$  for FRP of 15 vol.-% MMA dissolved in [EMIM][Tf<sub>2</sub>N] and [BMIM][BF<sub>4</sub>] at 10 °C via the single pulse-pulsed laser polymerization electron paramagnetic resonance (SP-PLP-EPR) technique. While absolute  $k_t$  in IL solution was by about one order of magnitude below the associated bulk MMA value, the chain-length dependence of  $k_t$  was very similar in both liquid environments.

Sun et al. [195] prepared copolymer hydrogel, poly (acrylamide-co-diallyl dimethyl ammonium chloride) by the radical copolymerization of acrylamide and diallyl dimethyl ammonium chloride in an IL-water binary system in the presence of the crosslinker *N,N'*-methylene bisacrylamide. The equilibrium swelling ratios of the hydrogels synthesized in the IL-water binary system increased with the content of IL and were remarkably higher than that of the gel synthesized in water. DSC measurements showed that the  $T_g$ s of the dry hydrogels that were synthesized in the IL-water binary system were remarkably lower than that of the gel synthesized in pure water. The mechanical properties of the gels synthesized in both water and the IL-water binary system were characterized with a universal material-testing machine. The results showed that fracture toughness of the hydrogels was improved when they were synthesized in the IL-water binary system. The response rates of the gels that were synthesized with the IL-water binary system were faster than that of the gel synthesized in water.

### Charge Transfer Polymerization (CTP)

Vijayaraghavan and MacFarlane [196] investigated CTP of MMA using *n*-butyl amine and CCl<sub>4</sub> as CT initiators and hydroquinone as promoter in several RTILs. Compared with the same procedure using molecular solvents, the IL solvent showed improved reaction rate and polymer yields at short reaction times. They found that the yield of polymer to be dependent on addition of a free-radical quencher such as hydroquinone and the concentration of the amine additive in the IL.

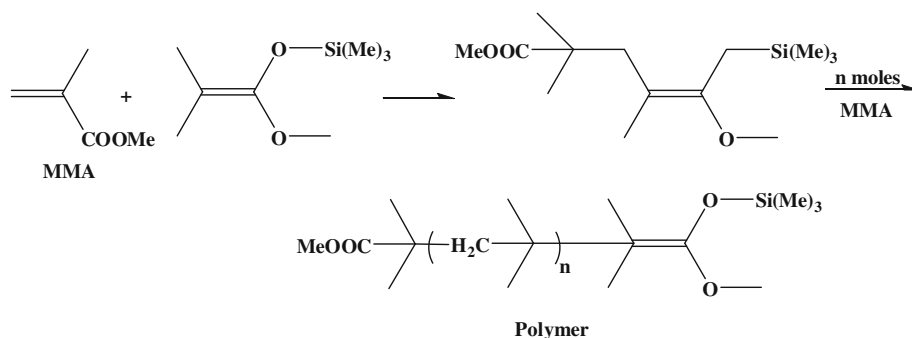
### Group Transfer Polymerization (GTP)

The same group also demonstrated for the first time the possibility of obtaining living polymers via GTP of MMA at ambient temperatures in an IL with and without the addition of tetrabutylammonium bromide ([Bu<sub>4</sub>N][Br]) as catalyst (Scheme 11) [197]. Compared with conventional solvent such as THF, high MWs and improved PDs were the main advantages using ILs.

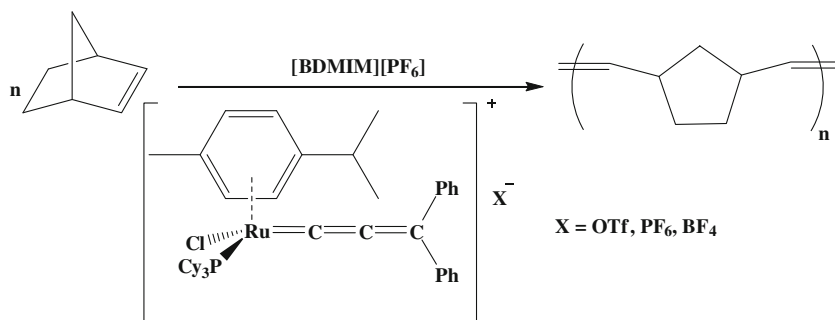
### Ring Opening Polymerization (ROP)

Dixneuf et al. [198] reported the biphasic ring-opening metathesis polymerization (ROMP) of norbornene in 1-butyl-2,3-dimethylimidazolium ([BDMIM]) [PF<sub>6</sub>]/toluene mixture using a cationic ruthenium allenylidene pre-catalyst (Scheme 12). It found that the cationic ruthenium

**Scheme 11** The initiation of MMA by the GTP initiator



**Scheme 12** ROMP of norbornene



allenylidene precatalyst  $[(p\text{-cymene})(\text{PCy}_3)\text{RuCl}(\text{=C=C=CPh}_2)][\text{OTf}]$  leads to a recyclable catalyst for this polymerization. The catalyst and IL were recycled and reused several times.

Kadokawa et al. [199] studied the ROP of ethylene carbonate (EC) with acidic ILs,  $[\text{BMIM}][\text{Cl-AlCl}_3]$  and  $[\text{BMIM}]$  chlorostannate ( $[\text{Cl-SnCl}_2]$ ) melts, as polymerization catalysts. It found that polymerization proceeded with decarboxylation even at reaction temperatures below 100 °C, such as 60–80 °C and polymers with low content of EC units were produced. Furthermore, polymerization in the presence of  $[\text{BMIM}][\text{Cl-SnCl}_2]$  IL did not proceed at temperatures below 100 °C due to lower activity of this IL as compared with  $[\text{BMIM}][\text{Cl-AlCl}_3]$ . An increase in contents of carbonate units and  $M_n$  values of the polymers was observed using  $[\text{BMIM}][\text{Cl-SnCl}_2]$  compared with  $[\text{BMIM}][\text{Cl-AlCl}_3]$  at 100 °C. The authors also showed that the carbonate content significantly decreased when the polymerization was carried out at 100 °C, indicating the occurrence of frequent decarboxylation.

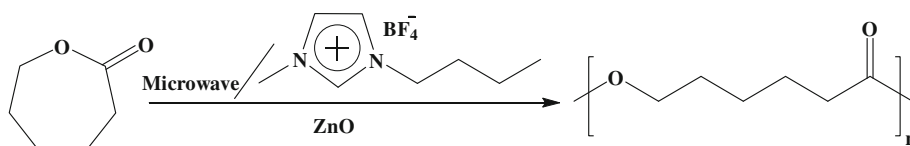
More recently, Liao et al. [200, 201] examined the microwave-assisted ROP of  $\epsilon$ -caprolactone ( $\epsilon$ -CL) in the presence of  $[\text{BMIM}][\text{BF}_4]$  using zinc oxide as the catalyst (Scheme 13). Polymer with higher yield was synthesized rapidly using this microwave-assisted polymerization method in comparison with conventional heating method in the presence of IL (30 wt%). The temperatures of the reaction mixtures increased with rising IL concentrations owing to the strong microwave absorption capability of IL, the MW of the resulting polymer also improved with increasing concentrations of  $[\text{BMIM}][\text{BF}_4]$ . PCL with a

MW of 28,500  $\text{g mol}^{-1}$  was obtained during 30 min in a domestic microwave oven at power of 85 W by adding 30 wt% IL to the reaction mixture.

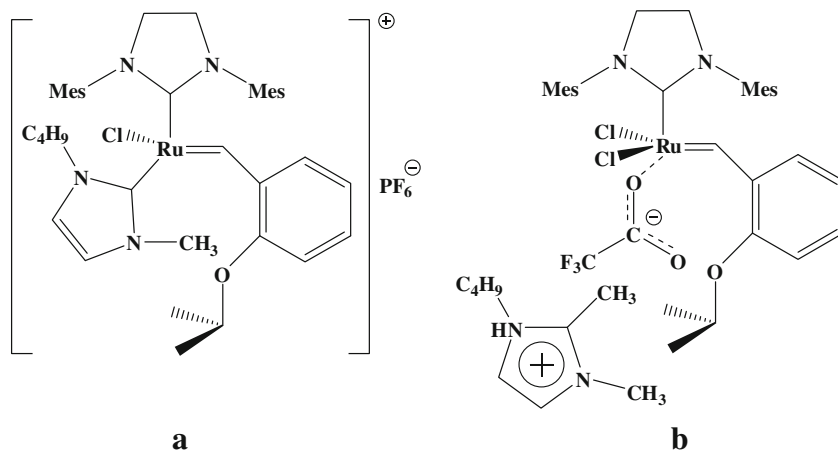
Buchmeiser et al. [202] investigated the ROMP of many functional norbornenes in a variety of pure ILs with a series of ruthenium-based catalysts. The influence of temperature, concentration of both the initiator and the monomer and nature of the IL on ROMP was discussed. It found that the use of  $[\text{Br}]^-$ ,  $[\text{Cl}]^-$ , or  $[\text{NO}_3]^-$ -based ILs does not produced the desired polymers, while using ILs consisting of low coordinating anions such as  $[\text{BF}_4]^-$  and  $[\text{PF}_6]^-$  leads to polymers with high MWs and high yields. They also found that for the attainment of high MW polymers via ROMP only ILs based on weakly coordinating anions and cations without the ability to form carbene species should be used. ROMP of norbornene derivatives in ionic solvents proceeded with a high rate of polymerization and offered access to high MW polymers (MW up to 15,00,000  $\text{g mol}^{-1}$ ) in high yields. Proposed interaction of catalyst with two ILs,  $[\text{DMBIM}][\text{PF}_6]$  (a) and  $[\text{MBIM}][\text{CF}_3\text{COO}]$  (b) is shown in Scheme 14.

Schubert et al. [203] reported microwave-assisted cationic ROP of 2-ethyl-2-oxazoline using ILs as solvent. Reaction mechanism of the cationic ROP of 2-ethyl-2-oxazoline is shown in Scheme 15. In comparison with organic solvents, the IL showed higher polymerization rate. The resulting polymer can be isolated simply by water extraction and the used IL can be efficiently recovered and reused in new reaction cycles. This observation was attributed to the solubility difference between the polymer and the hydrophobic ILs in water.

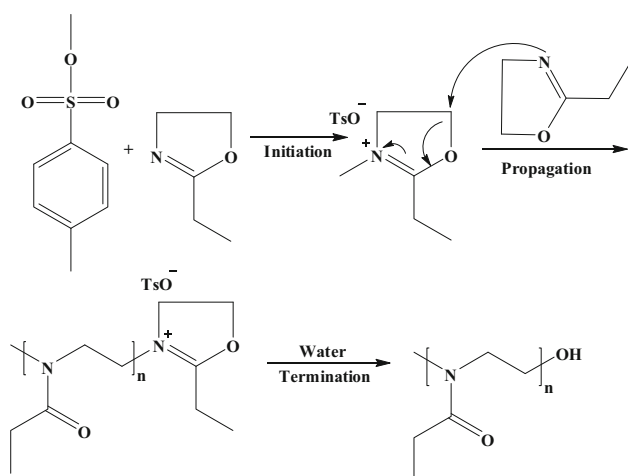
**Scheme 13** Zinc oxide-catalyzed MROP of  $\epsilon$ -CL in the presence of  $[\text{BMIM}][\text{BF}_4]$



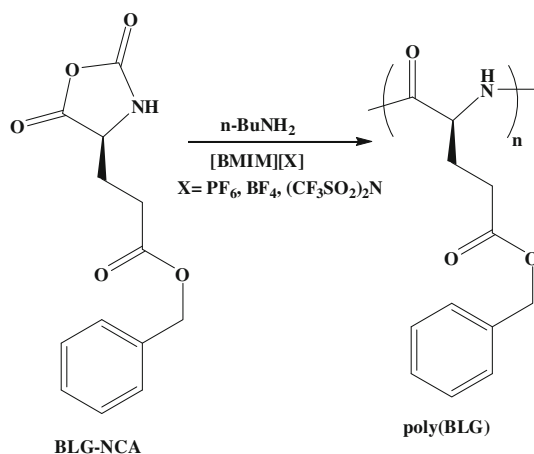
**Scheme 14** Proposed interaction of catalyst with different ILs:  $[\text{DMBIM}][\text{PF}_6]$  (a) and  $[\text{MBIM}][\text{CF}_3\text{COO}]$  (b)







**Scheme 15** Reaction mechanism of the cationic ROP of 2-ethyl-2-oxazoline



**Scheme 16** ROP of BLG-NCA in IL

Mori et al. [204] utilized room-temperature imidazolium ILs as a reaction medium for ROP of  $\gamma$ -benzyl-L-glutamate-*N*-carboxyanhydride (BLG-NCA) (Scheme 16). Using [BMIM][PF<sub>6</sub>] and *n*-butylamine as an initiator, poly(amino acid)s with low PD, MWs close to the theoretical values and helical secondary structure afforded [204]. They showed that the polymerization rate is slightly affected by the nature of the anion and hydrophobicity of the ILs, while poly(BLG)s with low PDs can be obtained regardless of the kind of the ILs. It found that the polymerization rate is slower in the IL compared with that in the organic solvent, while the polymerization in the IL exhibited shorter induction period than that in the organic solvent.

Gong et al. [205] reported microwave-assisted ROP of trimethylene carbonate (TMC) in the presence of 5 wt % [BMIM][BF<sub>4</sub>] in a single-mode microwave oven using stannous octoate (Sn(Oct)<sub>2</sub>) as catalyst. Poly(trimethylene carbonate) (PTMC) with  $M_n$  of 36,400 gmol<sup>-1</sup> was

obtained at 5 W for 60 min. The  $M_n$  of PTMC synthesized in the presence of [BMIM][BF<sub>4</sub>] was much higher than that formed in bulk at the same reaction time. In addition, the  $M_n$  of PTMC and monomer conversion by MROP with or without [BMIM][BF<sub>4</sub>] were both higher compared with those under conventional heating. Degradation of the polymer chain was took place with higher IL concentrations (10–30 wt%) due to creation of the high polymerization temperature at high [BMIM][BF<sub>4</sub>] concentrations after the initial stage of rapid polymerization.

Xie et al. [206] synthesized a monomer of 5-substituted cyclooctene with the pendant of imidazolium salt and then described the ROMP of the functionalized cyclooctenes in CH<sub>2</sub>Cl<sub>2</sub> and [BMIM][PF<sub>6</sub>] in the presence of ruthenium-based catalyst RuCl<sub>2</sub>(PCy<sub>3</sub>)(SIMes)(CHPh). The polymerization efficiency was strongly dependent on the solubility of the resulting polymer. The polymerization in IL was progressed rapidly, and the reaction mixture became very viscous in several minutes but still kept a homogeneous system. The polymers were obtained with higher MWs, lower PD and better control over the polymerization in [BMIM][PF<sub>6</sub>] than those in organic solvent, CH<sub>2</sub>Cl<sub>2</sub>.

Liu et al. [207] studied the ring-opening graft polymerization (ROGP) of L-lactide (L-LA) onto starch chains in 1-allyl-3-methylimidazolium chloride ([AMIM][Cl]) as reaction media. The highest grafting efficiency (30.3%) was obtained when the ROGP proceeded at 100 °C for 10 h with L-LA/starch 0.5:1 (wt/wt) in the presence of Sn(Oct)<sub>2</sub> as a catalyst, which was calculated according to a standard curve newly created by FTIR method. The main competition reactions were the homopolymerization of L-LA and the disconnection of grafted PLLA from starch-g-PLLA.

Liu et al. [208] employed [AMIM][Cl], for the dissolution of starch and the homogeneous ROGP of  $\epsilon$ -CL onto starch granules. The polymerization occurred smoothly in this system with the grafting efficiency of PCL, 24.42%.

Xie et al. [209] synthesized a new amphiphilic ABA triblock copolymer by ROMP and ATRP in [BMIM][BF<sub>4</sub>]. The bromo-terminated macroinitiator was prepared via ROMP of norbornene derivative, which was compatible with IL, in conjunction with a chain transfer agent (CTA) in [BMIM][BF<sub>4</sub>]. ROMP with CTA in [BMIM][BF<sub>4</sub>] exhibited a different performance by changing the reaction conditions, and importantly there has been a good control over polymerization process and relatively low PDI of polymer in [BMIM][BF<sub>4</sub>]. Based on the telechelic macroinitiator, the amphiphilic ABA triblock copolymer was synthesized by ATRP in [BMIM][BF<sub>4</sub>].

Wang et al. [210] synthesized a cellulose graft copolymer in [BMIM][Cl] by the ROGP of *p*-dioxanone onto cellulose. Cellulose graft copolymers with a molar substitution (MS) in the range of 2.08–4.60 were obtained with

24 h at 80 °C in a completely homogeneous procedure. The obtained copolymers exhibited the clear  $T_g$  indicating the inter-molecular and intra-molecular hydrogen bonds in cellulose molecules had been destroyed. The reaction media applied can be easily recycled and reused.

Rooney et al. [211] studied ROMP a number of cyclic olefins using  $\text{Cl}_2(\text{PCy}_3)_2\text{Ru}[\text{CH}(\text{Ph})]$  and  $[(6\text{-}p\text{-cymene})(\text{PCy}_3)\text{RuCl}(\text{CCCPH}_2)]\text{OTf}$  in dichloromethane and a range of ILs. The findings indicated that an increase in activity of both catalysts can occur in certain ILs systems. It was also observed that the activity of  $[(6\text{-}p\text{-cymene})(\text{PCy}_3)\text{RuCl}(\text{CCCPH}_2)]\text{[OTf]}$  increases upon addition of an excess of phenol.

Wu et al. [212] presented an effective method for grafting L-lactide (LA) from unmodified cellulose by ROP in homogeneous mild conditions. Using 4-dimethylaminopyridine (DMAP) as an organic catalyst, cellulose-graft-poly(L-lactide) (cellulose-g-PLLA) copolymers with a molar substitution ( $\text{MS}_{\text{PLLA}}$ ) of PLLA in a range of 0.99–12.28 were successfully synthesized in  $[\text{AMIM}][\text{Cl}]$  at 80 °C. By adjusting the molar ratios of LA monomer to cellulose, the amount and length of grafted PLLA in cellulose-g-PLLA copolymers were controlled. The copolymers exhibited a single glass transition temperature,  $T_g$ , which sharply decreased with the increase of  $\text{MS}_{\text{PLLA}}$  up to  $\text{MS}_{\text{PLLA}} = 8.28$  and increased a little with a further enhance of the lactyl content. When  $\text{MS}_{\text{PLLA}}$  was above 4.40, the graft copolymers showed thermoplastic behavior, indicating the inter-molecular and intramolecular hydrogen bonds in cellulose molecules had been effectively destroyed. Using a conventional thermal processing method, fibers and disks of cellulose-g-PLLA copolymers were prepared.

Martinez-Richa et al. [213] reported the enzymatic ROP of  $\epsilon\text{-CL}$  by *Yarrowia lipolytica* (YLL), *Candida rugosa* (CRL), and porcine pancreatic lipase (PPL) as catalysts in the presence of ILs,  $[\text{EMIM}][\text{BF}_4]$ ,  $[\text{BMIM}][\text{BF}_4]$ ,  $[\text{BPyR}][\text{BF}_4]$ ,  $[\text{BPyR}][\text{CF}_3\text{COO}]$ ,  $[\text{EMIM}][\text{NO}_3]$ . The anion species of the used ILs showed considerable effects on conversion and MW of polymer. The best IL for polyester synthesis by YLL and CRL was  $[\text{BPyR}][\text{BF}_4]$  which led to short polymerization times and narrower PDs. Under these conditions PCLs with

MW in the range of 300–9,000  $\text{gmol}^{-1}$  were obtained. The obtained polyesters via ROP using ILs proceed significantly faster than those obtained in the presence of organic solvents.

### Oxidative Polymerization

Kobryanskii and Arnautov [214, 215] reported the oxidative dehydropolycondensation of benzene in the acidic IL  $[\text{BPyR}][\text{Cl-AlCl}_3]$  ( $X(\text{AlCl}_3) = 0.67$ ) using  $\text{CuCl}_2$  as the catalyst and poly(*p*-phenylene) (PPP) with relative molecular masses ( $M_r$ )s significantly higher compared with those in conventional solvents. The  $M_r$  can be tuned by varying the benzene concentration. The high  $M_r$  values obtained in IL were attributed to a greater solubility of PPP in the IL which allows the greater degree of polymerization before the occurrence of phase separation.

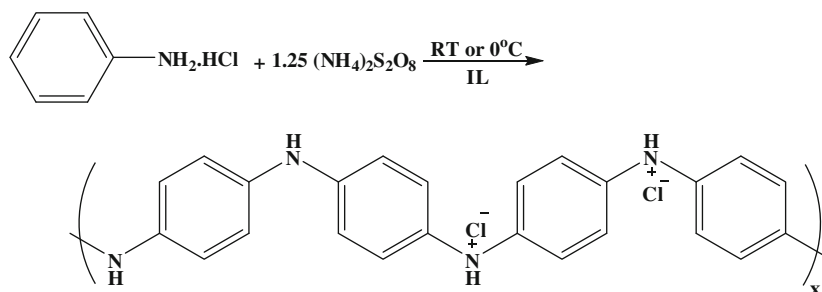
The same research group also investigated oxidative polymerization of benzene in chloroaluminate ILs based on  $[\text{BPyR}][\text{Cl}]$  using  $\text{CuCl}_2$  as a catalyst [216]. Therein, PPP was obtained with degree of polymerization higher than 35. In this case, the benzene molecules react with catalyst, therefore, polymerization only proceeded when the number of moles of benzene was greater than the oxidative agent.

Arnaudov described the synthesis of PPP in a IL based on  $[\text{BPyR}][\text{Cl}]$  in the presence of alkoxy aluminum chloride  $\text{AlCl}_2(\text{OC}_2\text{H}_5)$  [217]. It observed that the quality and the degree of polycondensation of the PPP approximately agree with those obtained by the Kovacic method.

The same authors studied the electrochemical polymerization of benzene to PPP in the acidic IL  $[\text{BPyR}][\text{Cl-AlCl}_3]$  ( $X(\text{AlCl}_3) = 0.67$ ) as a solvent [215, 218]. The polymerization led to formation of flexible and transparent conductive films with very high  $M_r$ s and degrees of polymerization up to 200.

Bicak et al. [219] synthesized organo-soluble polyaniline (PANI) with MWs, 86,400  $\text{gmol}^{-1}$  by oxidative coupling polymerization of anilinium chloride with ammonium persulfate in an IL, 2-hydroxyethyl ammonium formate (Scheme 17). The conductivities of up to 37.0  $\text{Scm}^{-1}$  were observed for thin films of PANI prepared by solvent casting at 0 °C, when doped with *p*-toluene sulfonic acid.

**Scheme 17** Oxidation of anilinium chloride with ammonium persulfate in the IL



## Enzymatic Polymerization

Uyama et al. [220] studied lipase-catalyzed ROP of  $\epsilon$ -CL and the polycondensation of diethyl adipate and diethyl sebacate, respectively, with 1,4-butanediol in [BMIM][BF<sub>4</sub>] and [BMIM][PF<sub>6</sub>]. Low MW oligomers ( $M_n < 850 \text{ gmol}^{-1}$ ) were obtained by means of ROP in [BMIM][PF<sub>6</sub>] for less than 3 days, while  $M_n = 4,200 \text{ gmol}^{-1}$  resulted within a week. In both [BMIM][PF<sub>6</sub>] or [BMIM][BF<sub>4</sub>] the MWs of the polycondensates were less than  $1,500 \text{ gmol}^{-1}$ .

Salunkhe et al. [221] employed [BMIM][PF<sub>6</sub>] as a reaction medium for lipase-catalysed polycondensation of diethylene octane-1,8-dicarboxylate and 1,4-butanediol at room temperature and at 60 °C. The MW of oligomers was low (around  $2,000 \text{ gmol}^{-1}$ ) at room temperature after 7 days, whereas polymer with a relatively high MW ( $4,500 \text{ gmol}^{-1}$ ) was obtained at 60 °C. The PD values; were found to be low and below 1.26, due to the insolubility of the polymer in the IL after it exceeds a certain MW.

Heise et al. [222] reported the enzymatic synthesis of polyesters via ROP of  $\epsilon$ -CL and the polycondensation of diesters with glycols in [BMIM][Tf<sub>2</sub>N], [BMIM][PF<sub>6</sub>] and [BMIM][BF<sub>4</sub>]. An inhomogeneous reaction mixture upon enzymatic ROP of  $\epsilon$ -CL in [BMIM][PF<sub>6</sub>] and [BMIM][BF<sub>4</sub>] was observed, whereby the polymerization under this conditions showed characteristics similar to bulk polymerization and using [BMIM][Tf<sub>2</sub>N] polymerization characteristics were similar to polymerization in toluene. PCL was synthesized in ILs with MW ranging from 7,000 to  $9,500 \text{ gmol}^{-1}$  and PD below 2.5 in 24 h. The polycondensation of dimethyl adipate and dimethyl sebacate with 1,4-butanediol in the low volatility of the ILs allowed the reactions to proceed in an open vessel at temperatures close to the boiling point of the condensation by-product (methanol), resulting in formation of polymers with MWs up to  $5,400 \text{ gmol}^{-1}$ . This, in combination with the tunable solvent hydrophilicity of ILs, might offer an advantage in the polymerization of highly polar monomers with low solubility in organic solvents such as sorbitol.

Srienc et al. [223] synthesized poly(hydroxyalkanoate)s with moderate MWs up to  $13,000 \text{ gmol}^{-1}$  in vitro from 4-, 5-, 6- and 7-membered lactones catalyzed by *Candida antarctica* lipase B (CAL-B) via ROP in ILs. They investigated the effects of water content in enzyme and of reaction time on the  $M_n$  of the polyester. The highest  $M_n$  ( $8,100 \text{ gmol}^{-1}$ ) was obtained by the polymerization of  $\epsilon$ -CL in [BMIM][Tf<sub>2</sub>N] after 24 h at 90 °C with a yield of 85%. Although the  $M_n$  did not increase with longer reaction time ( $M_n = 8,000 \text{ gmol}^{-1}$  at 72 h), drying Novozym 435 before polymerization increased the MW of the polymer from 6,300 to  $9,700 \text{ gmol}^{-1}$ .

Yoshizawa-Fujita and his group [224] investigated the effect of ILs on the conversion, MW, and yield of the prepared P(L-LA) by lipase-catalyzed polymerizations of L-LA. The authors claimed that the polymerization reactions carried out in three ILs [BMIM][BF<sub>4</sub>], [BMIM][PF<sub>6</sub>], and [BMIM][Tf<sub>2</sub>N], while the polymerizations did not proceed in IL [BMIM][N(CN)<sub>2</sub>], at 110 and 120 °C. While, P(L-LA) with  $M_n$  of below  $4,000 \text{ gmol}^{-1}$  and the yield of below 10% was prepared in [BMIM][PF<sub>6</sub>], P(L-LA) with  $M_n$  of  $55,000 \text{ gmol}^{-1}$  and the yield of 35% was synthesized in [BMIM][BF<sub>4</sub>]. In comparison with the polymerization reactions conducted in bulk and in toluene, polymerization reactions in the ILs led to polymers with the higher  $M_n$  values at lower temperatures. It also found that the effect of lipase content strongly depended on the anion species of the ILs. When the CAL-B content was 10 wt%, the  $M_n$  value of P(L-LA) prepared in [BMIM][BF<sub>4</sub>] was the highest at both temperatures. Using [BMIM][Tf<sub>2</sub>N] as the solvent, the effect of CAL-B content on the  $M_n$  of P(L-LA)s depended on the polymerization temperature.

Dordick et al. [225] used Soybean peroxidase (SBP) as catalyst for the polymerization of phenols in RTILs. Phenolic polymers with  $M_n$  ranging from 1,200 to  $4,100 \text{ gmol}^{-1}$  were obtained depending on the composition of the reaction medium and the nature of the phenol. Specifically, SBP was highly active in [MIM]-containing RTILs, including [BMIM][BF<sub>4</sub>] and [BMPyr][BF<sub>4</sub>] with the IL content as high as 90% (v/v); the balance being aqueous buffer. Gel permeation chromatography and MALDI-TOF analysis indicated that higher MW polymers can be synthesized in the presence of higher RTIL concentrations, with selective control over polymer size achieved by varying the RTIL concentration. The resulting polyphenols exhibited high thermostability and possessed thermosetting properties.

Gimeno et al. [226] reported the syntheses of P(L-LA) and poly-L-LA-co-glycolide (PLLGA) in [HMIM][PF<sub>6</sub>] mediated by the enzyme lipase B from *Candida antarctica* (Novozyme 435). The highest P(L-LA) yield (63%) was obtained at 90 °C with  $M_n$  of  $37.8 \times 10^3 \text{ gmol}^{-1}$  determined by size exclusion chromatography. This procedure produced relatively high crystalline polymers (up to 85% PL-LA) as determined by DSC. At 90 °C product synthesis also happened without biocatalyst, however, synthesis of P(L-LA) in [HMIM][PF<sub>6</sub>] at 65 °C followed only the enzymatic mechanism as ring opening was not observed without the enzyme.

## Electropolymerization

Osteryoung et al. [227] investigated simultaneous electron paramagnetic resonance (EPR) electrochemical measurements on PPy in RTILs. EPR, current and charge measurements have been made simultaneously *versus* potential

during linear scan experiments and *versus* time during chronoamperometric experiments on a PPy film in an ambient temperature molten salt consisting of [MEIM][Cl]/aluminium chloride. The linear scan experiments revealed an EPR absorption over a very narrow potential region, about 200 mV, and a strong correlation between the maximum EPR absorption and the peak current. Chronoamperometric experiments exhibited that equilibrium is attained after 10–15 s, and that the paramagnetic species was necessarily an intermediate in the process of switching the film from its neutral to fully oxidized state, or the reverse.

Lere-Porte et al. [228] synthesized films of PPP via electrochemical oxidation of benzene dissolved in ketyl pyridinium chloride-AlCl<sub>3</sub> (1:2) melting salt. The obtained films characterized by X-ray photoelectron, Raman, photoluminescence and FT-IR spectroscopies. A small amount of residual chlorine was detected from X-ray photoelectron spectroscopy experiments. The shape and strong intensity of the extrinsic part of the photoluminescence (2.0 eV) related to a large amount of structural defects in the films; however, the distribution of these defects was relatively homogeneous. Raman spectra clearly showed the presence of segments with small conjugation lengths in the films under consideration. The degree of polymerization was smaller ( $N_{dp} = 15$ ) than those reported ( $N_{dp} = 30$ ) for electrochemical oxidation of benzene in SO<sub>2</sub> at low temperature based on findings from FT-IR spectra. These results suggested that the films obtained by this method present some similarities with Kovacic compounds.

Goldenberg and Osteryoung [229] prepared PPP films by the electropolymerization of benzene in an ambient-temperature molten salt, or IL, consisting of [EMIM][Cl]-aluminum chloride. Polymerization was carried out in melts of varying acidity in neutral buffered melts. The films were then examined in [EMIM][Cl]-aluminum chloride-aluminum chloride melts of varying acidity. The polymerization and electrochemical behavior of the films were independent of melt acidity; the films exhibited reasonably facile electrochemical behavior.

Breau et al. [230] investigated the electrochemical synthesis of poly(3-(4-fluorophenyl) thiophene) (PFPT) by imidazolium-based ILs, 1-ethyl-2,3-dimethylimidazolium ([EDMIM]) [Tf<sub>2</sub>N], and [DEMIM][Tf<sub>2</sub>N]. Comparing the oxidation potential of the monomer in these ILs (1.16 and 1.22 V, respectively, for galvanostatic growth at 12.7 mAcm<sup>-2</sup>) and growth of this polymer in propylene carbonate or acetonitrile (0.98 and 1.1 V, respectively) showed that due to the lower stability of the monomer cation radical in the ILs, oxidation potential of the monomer was higher. Voltammetric cyclic data for PFPT and PFPT in pure ILs and an electrolyte such as 1 M tetraethylammonium tetrafluoroborate (Et<sub>4</sub>NBF<sub>4</sub>)/acetonitrile showed that the kinetics of the redox processes for a PFPT film electrode grown from a pure

IL solution were slower in an IL relative to Et<sub>4</sub>NBF<sub>4</sub>/acetonitrile. This was confirmed by the larger anodic and cathodic peak potential separation for the p-doping and p-dedoping waves of 0.41 V in [EDMIM][Tf<sub>2</sub>N] compared to 0.09 V in Et<sub>4</sub>NBF<sub>4</sub>/acetonitrile. This peak separation was partly attributed to the lower ionic conductivity of the ILs (3.2 and 6.6 mScm<sup>-1</sup>, respectively) compared to the acetonitrile solution (43 mScm<sup>-1</sup>) and also reflects differences in the polymer films. The authors found that due to overlapping the n-doping wave with the onset of irreversible degradation of the IL, a negative limit of -2.1 V should not be exceeded, otherwise no n-dedoping wave is observed. They observed a rapid loss of electroactivity of the polymer upon cycling in pure IL, which was attributed to gradual deswelling of the polymer film. The authors also found that the decrease of electroactivity could be owing to ion trapping in the polymer during the dedoping process, as demonstrated by a considerable charge imbalance between the n-doping and n-dedoping charges in the cyclic voltammogram (CV). These groups note that a polymer film cycled in the n-doping region in pure IL could be reactivated by cycling in the p-doping region in the same IL, or by transferal of electrode to the 1 M Et<sub>4</sub>NBF<sub>4</sub>/acetonitrile solution to re-swell the polymer.

Fuchigami et al. [231] reported the electrooxidative polymerization of pyrrole (Py) in different air and moisture stable [EMIM]-based ILs with anions containing [OTf], [BF<sub>4</sub>] and [PF<sub>6</sub>] as an electrolyte. The anion component of the IL influenced the polymerization, with [OTf] showing the highest polymer oxidation and reduction currents, while with [PF<sub>6</sub>] exhibiting lowest. The authors proposed that the radical-radical coupling, further oxidation of oligomers and polymer deposition in the electrooxidative polymerization were favorably affected as the reaction products were accumulated in the vicinity of the electrode surface under slow diffusion condition, and therefore the polymerization rate was increased. Therefore, due to the higher viscosity of [EMIM][OTf] compared with [EMIM][BF<sub>4</sub>] and [EMIM][PF<sub>6</sub>], the polymerization rate in [EMIM][OTf] was higher than [EMIM][BF<sub>4</sub>] and [EMIM][PF<sub>6</sub>]. In comparison with the polymerizations conducted in solutions of the IL in water or acetonitrile, neat IL showed greater polymer redox peak currents and smaller redox peak separation. Furthermore, authors found that the film polymerized in [EMIM][OTf] was thinner than that in conventional electrolytic solutions, H<sub>2</sub>O and acetonitrile, nevertheless in the case of the former film electrochemical capacity and the doping level were higher. They also observed that the films polymerized in the aqueous and acetonitrile solutions showed grains with sizes quite different from each other while surface of the film prepared in IL was very smooth. More than 90% of [EMIM][OTf] was recovered simply by extracting the remaining Py monomer with chloroform and reused five times without significant changes in the reactivity.



The same research group also reported electrooxidative polymerization of Py, thiophene (T) and ANI in air- and moisture-stable IL, [EMIM][OTf] [232]. In the case of Py and T, the polymerization rate in [EMIM][OTf] was higher than that in conventional media because of the higher viscosity of [EMIM][OTf] than the others. The polypyrrole (PPy) films were used as a matrix for hosting catalyst particles, so that submicron palladium clusters were highly dispersed on the whole surface of PPy matrix prepared in [EMIM][OTf] than those in aqueous solutions. PPy was obtained with a higher growth rate, smoother films and enhanced electrochemical capacity in IL than that in conventional media. The polymerization rate of ANI was affected by the mass transport of ANI monomer to the anode surface from the bulk electrolyte and decelerated in [EMIM][OTf] compared with that in conventional media.

Randriamahazaka et al. [233] studied the electrochemical behavior and the redox switching dynamics of poly(3,4-ethylenedioxythiophene) (PEDOT) in [EMIM][Tf<sub>2</sub>N]. The shape of the CVs showed two anodic and two cathodic peaks. These peak currents varied linearly with the scan rate, indicating thin-layer behavior. They found that no memory effects during the cycling of the films in this IL were observed. The analysis of chronocoulograms in terms of RC-circuits indicated that the time dependence of the charge transferred during the potential step showed two time constants. These results were consistent with the postulated structure or morphology of the PEDOT film, which contained two types of coexisting zones. The first type of zone includes compact and rigid polymer with long and highly conjugated chains, while the second type of zone contains a more open polymer configuration with chains of short conjugation.

The same research group also reported the electrochemical responses of PEDOT electrodeposited on a platinum electrode surface in [EMIM][Tf<sub>2</sub>N] [234]. They observed a continuous change in the shape of the CV and increases in the redox current (up to 20 cycles), when the PEDOT film from acetonitrile was cycled in the IL, due to the uptake of [EMIM][Tf<sub>2</sub>N] in the polymer film. The PEDOT-modified electrode prepared in acetonitrile (PEDOT-CAN), transferred in [EMIM][Tf<sub>2</sub>N] displayed two anodic and two cathodic peak currents. It was found that by increasing the concentration of Li[Tf<sub>2</sub>N], the first anodic current increased. In contrast, PEDOT-modified electrodes prepared in [EMIM][Tf<sub>2</sub>N] showed one anodic and one cathodic peak at the same location of the second anodic peak potential obtained for PEDOT-CAN and the presence of Li[Tf<sub>2</sub>N] in the IL did not have a notable effect on the electrochemical behavior of the film.

Endres et al. [235] studied electropolymerization of benzene in an air- and water-stable IL, [HMIM]tris(pentafluoroethyl)trifluorophosphate. It was found that this IL can be dried to water contents below 3 ppm, and is remarkably

stable, especially in the anodic regime. PPP was deposited onto platinum as a coherent, electroactive film using this IL. The authors reported that in comparison with solvents such as 18 M sulfuric acid or liquid SO<sub>2</sub>, ILs are chemically not at all aggressive.

Pringle et al. [236] reported the electrochemical synthesis and electrochemical cycling of the polymer films in three different ILs, namely [BMIM][PF<sub>6</sub>], [EMIM][Tf<sub>2</sub>N] and [BMPyr][Tf<sub>2</sub>N] as the growth medium and as an electrolyte. Considerably smoother film morphologies were observed for polymer grown from the ILs compared to those grown under the same experimental conditions from conventional solvents, which may also result in improved conductivities.

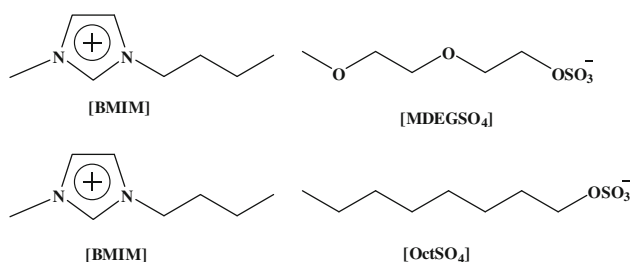
Damlin et al. [237] described the electrochemical synthesis and p-doping and n-doping of PEDOT in two RTILs, [BMIM][BF<sub>4</sub>] and [BMIM][PF<sub>6</sub>]. The resulting polymer films were characterized by CV, in situ attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and in situ UV-Vis spectroelectrochemistry. The authors observed two oxidation peaks (−0.05 and +0.32 V) in the first few growth cycles in the [BMIM][BF<sub>4</sub>] using a 50 mVs<sup>−1</sup> scan rate, which merged into one as the film became thicker, and in the reduction half-cycle two reduction peaks (−0.64 and +0.13 V) were seen. In the [BMIM][PF<sub>6</sub>] three oxidation peaks (+0.04, +0.28 and +0.64 V) were seen during the first polymerization cycles, when the film has grown thicker the three oxidation peaks merge into one peak at +0.39 V. In the reverse scan two reduction peaks (−0.54 and −0.17 V) were observed during the first scans but the latter is quickly overlapped by a new reduction peak first seen at +0.2 V. Additionally, they presented that the shapes of the CVs, and the oxidation potential of the monomer, were the same in the ILs in comparison to those observed in organic solvents using tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) or Et<sub>4</sub>NBF<sub>4</sub> electrolytes. A small UV-Vis spectral change was observed upon n-doping of a PEDOT film in ILs and in organic solvents because of the formation of only the polaron type of charge carrier, while a large difference in p-doping for PEDOT films was observed, which was attributed to the formation of different charge carriers in the two doping regimes (polarons *versus* bipolarons). The n-doping of PEDOT in organic solvents has been much less examined. This is mainly due to the instability of the reduced form of PEDOT in organic electrolytes under atmospheric conditions. However, the PEDOT films were successfully n-doped in the potential range −0.9 to −1.95 V and p-doped between −0.9 to +0.8 V in the ILs. The current response of the n-doping cycles decreased during the five scans and the peak intensity showed no degradation for the next nine cycles in the [BF<sub>4</sub>]-based IL. At a low degree of doping, i.e. potentials lower than 0.1 V, the changes in the doping-induced infrared active vibrations of the polymers



were the same in ILs and organic solvents, whereas during p-doping at higher potentials the polymers in the ILs showed further increases in the intensities of infrared active vibrations bands that were not observed in the polymer in organic media. The main bands in the in situ FTIR-ATR spectra of the polymer were similar in the ILs and in 0.1 M  $\text{Bu}_4\text{NClO}_4$  + acetonitrile, with only slight shifts in peak position. The relative intensities of the bands upon n-doping in acetonitrile and  $[\text{BMIM}][\text{PF}_6]$  are the same whereas; in  $[\text{BMIM}][\text{BF}_4]$  higher intensities are observed. A lower intensity of the induced infrared active vibrations bands and a shift of the maximum of the electronic absorption to higher energies is also observed upon p-doping of PEDOT, in  $[\text{BMIM}][\text{PF}_6]$  compared to  $[\text{BMIM}][\text{BF}_4]$ . The higher intensity of the infrared active vibrations bands and of the broad absorbance band indicated that it is easier to create charge carriers in a PEDOT film prepared in  $[\text{BMIM}][\text{BF}_4]$  than in  $[\text{BMIM}][\text{PF}_6]$  or the acetonitrile solution.

Bobacka et al. [238] studied the electropolymerization of EDOT in two ILs consisting bulky organic anions namely  $[\text{BMIM}]$  diethylene glycol monomethyl ether sulfate ( $[\text{MDEGSO}_4]$ ) and  $[\text{BMIM}]$  octyl sulfate ( $[\text{OctSO}_4]$ ) (Scheme 18).  $[\text{BMIM}][\text{OctSO}_4]$  is in solid form at room temperature, so needs the addition of either monomer or solvent to form a liquid. The polymerization in a water-free IL solution was only successful in a  $[\text{BMIM}][\text{OctSO}_4]/\text{EDOT}$  1/1 solution, while the polymerization of EDOT was successful in 1.5 M aqueous solutions of the ILs containing 0.1 M EDOT. The PEDOT electrodes showed linear anionic potentiometric response in  $10^{-5}$  to  $10^{-1}$  M KCl aqueous solutions, indicating that the IL anions are mobile inside the polymer and are able to be exchanged by the chloride ions at the polymer-solution interface, however, in aqueous solutions of the ILs, the imidazolium cation suppresses the anionic response at higher concentrations of the ILs in water (0.01–0.1 M). They also found that the ion transport properties of the polymer film were strongly increased by the addition of water of the IL.

Endres et al. [239] applied the electrochemical quartz-crystal microbalance (EQCM) technique for studying the electropolymerization of benzene in  $[\text{HMIM}]\text{tris}(\text{penta-}$



**Scheme 18** Chemical structure of  $[\text{BMIM}][\text{MDEGSO}_4]$  and  $[\text{BMIM}][\text{OctSO}_4]$

fluoroethyl)trifluorophosphate. The authors explained that the damping effect which the IL has on the frequency of the crystal must be considered. It observed that the changes in the damping during the growth and cycling of the polymer are much smaller than the changes in the resonance frequency, so under these conditions it is applicable to convert the frequency change to changes in the mass of the polymer using the Sauerbrey equation. It found that outside the cathodic peak region, anion and cation exchange contributed almost equally to the overall cathodic current and also in the anodic peak region, anion exchange dominated. They also found that at elevated scan rates, cation exchange became the dominant process over the entire potential range, and the shapes of the partial- or ion-specific voltammograms became very similar due to the large size of the anion. While at slow scan rates, there was sufficient time for removal or insertion of the anion into the polymer film and as the scan rate became larger this movement became more difficult. Outside the cathodic peak region, at low scan rates anion and cation movement are approximately equal but, as the scan rate is increased, movement of the IL cation becomes the dominant process over the whole potential range. The films obtained on the quartz crystals after polymerization showed a porous, rough morphology with threadlike polymer strands.

Li et al. [240] investigated the electropolymerization of ANI in a Bronsted acidic IL,  $[\text{EIM}][\text{TFA}]$ . It found that in the presence of IL, the oxidation potential of ANI is lower 0.58 V compared to 0.83 V in 0.5 M  $\text{H}_2\text{SO}_4$ , so PANI is easier to be formed and polymerization rate of ANI is higher than that in  $\text{H}_2\text{SO}_4$  solutions. The resulting polymers were characterized by scanning electron microscopy (SEM), and it was found that polymeric films synthesized in IL medium were smooth, homogeneous and strongly adhered to the Pt working electrode with very electrochemically stable.

Pringle et al. [241] reported the electropolymerization of T, bithiophene (BT) and terthiophene (TT) using the ILs  $[\text{EMIM}][\text{Tf}_2\text{N}]$  and  $[\text{BMPyr}][\text{Tf}_2\text{N}]$  as the growth medium and supporting electrolyte. The oxidation potential of these monomers decreased as the monomer chain length increased, consistent with conventional electrolyte/solvent systems. This was the main advantage of using ILs, the high potential required to oxidise T can result in side-reactions and overoxidation of the PT film. BT was found to be adequately soluble in both IL, under the same conditions the growth CVs propose a stronger influence of the nature of the IL than for the T monomer. In the case, the polymerization of BT, film growth appeared to be more than four times faster in  $[\text{EMIM}][\text{Tf}_2\text{N}]$  than in  $[\text{BMPyr}][\text{Tf}_2\text{N}]$ , and the redox currents in the post-polymerization CVs was also proportionally larger. The second notable difference was that there is only one broad distinct

reduction peak evident during growth and cycling of the film in the imidazolium IL, while there are two distinct peaks evident during growth in the pyrrolidinium species, although in the post-polymerization cycles these are considerably broadened.

Officer et al. [242] successfully synthesized PEDOT in ILs having [EMIM] and [BMPyr] cations and [Tf<sub>2</sub>N] anion as both the growth medium and the electrolyte. They also examined the influences of the nature of IL on the morphology and electrochemical activity of the resulting polymers. Using [BMPyr] as the cation resulted in slower polymerization rate than the corresponding IL based on [EMIM] due to the higher viscosity and lower conductivity of [BMPyr] that limits ion/molecule transport kinetics. Post-polymerization CVs of PEDOT films in both acetonitrile/Bu<sub>4</sub>NClO<sub>4</sub> and the IL compared to those of polymer grown in an acetonitrile solution. It found that both films grown from IL showed an increase in the electrochemical activity upon cycling in the acetonitrile solution. In the case better swelling of the polymer and faster transport of ionic species into and out of the polymer during cycling were observed. Thus, the observed activity reflected the electrochemical accessibility of the polymer to the electrolyte, which may suggest that the electrochemistry of the polymer is a surface-dominated phenomenon. In the case IL based on [BMPyr] cation a rapid return to the lower charge capacity regime was observed, which this effect was ascribed to structural changes. The authors compared the chronoamperograms recorded during EDOT electropolymerization in the two ILs and two conventional acetonitrile-based electrolytes. The current transients suggested that the process is initially much slower in the solution containing Bu<sub>4</sub>NClO<sub>4</sub> as the electrolyte than in the other cases. Moreover, the different shape of the curve proposed a different mechanism of deposition. The current transient in acetonitrile/Bu<sub>4</sub>NClO<sub>4</sub> was indicative of progressive nucleation, with a slower growth rate and thus lower currents, whereas the current transients in the ILs and the acetonitrile/Li[Tf<sub>2</sub>N] solution suggested instantaneous nucleation, indicating a strong influence of the anion on polymer growth.

Liu et al. [243] successfully exploited several Bronsted acid ILs such as [HEIM][TFA], [HBIM][BF<sub>4</sub>], [BIM][NO<sub>3</sub>], [BIM][TSA], [BMIM][H<sub>2</sub>PO<sub>4</sub>] and [BMIM][HSO<sub>4</sub>], for the electrochemical synthesis of PANI films on platinum electrode surfaces using CV. The best results were achieved in the presence of [HEIM][TFA] and then [HBIM][BF<sub>4</sub>], while the other four ILs gave unsatisfied results, which could be related to the different acidity of these Bronsted acid ILs. Compared with film prepared in 0.5 mol L<sup>-1</sup> HCl, film prepared in [HEIM][TFA] showed quite dense packing and uniform surface.

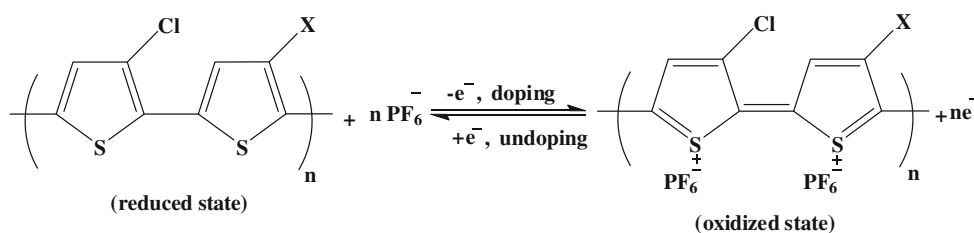
Xiao-gang et al. [244] studied electropolymerization of PANI film in organic acidic media (CF<sub>3</sub>COOH) and then investigated it by CV, AC impedance, and galvanostatic charging and discharging tests in [BMIM][PF<sub>6</sub>] and the mixture electrolytes of [BMIM][PF<sub>6</sub>] and acetonitrile with different ratios. The results showed that the polymer in mixture of [BMIM][PF<sub>6</sub>] and acetonitrile have lower solution resistance, higher cycle life, and higher electrochemical capacitance.

Wallace et al. [245] used an IL as a solvent to prepare films composed of poly(TTh) doped with an anionic dye. They found that potentiodynamic polymerization of [BMIM][Tf<sub>2</sub>N] solutions containing TTh and saturated with anionic dye erioglaucine (Erio) lead to creation thick, mechanically stable films of poly(TTh) doped with Erio (PTTh/Erio) on the surface of indium tin oxide (ITO) coated glass working electrode. The obtained films were more robust than those obtained using DMF as a solvent. The authors reported that the preparation of films with comparable properties failed in molecular solvents such as DMF, propylene carbonate and acetonitrile, showing the crucial role of the IL in facilitating the formation of robust PTTh/Erio films.

Ivaska et al. [246] synthesized PANI nanotubes via electrochemical polymerization on a modified ITO glass electrode in [BMIM][PF<sub>6</sub>] containing 1 M trifluoroacetic acid. Tubular structures of PANI were obtained with the diameter of ~120 nm as shown by SEM. The reaction products accumulated near the surface of the modified ITO glass (MITO) electrode, due to high viscosity of ILs which facilitated the electropolymerization rate of ANI and finally a green film on the MITO substrate was produced. The resulting PANI was in its conducting form, which were confirmed Raman and FTIR spectra. This provides a possible IL media to functionalize conducting PANI with, for example, single wall carbon nanotubes for the application of organic photovoltaics and light emitting diodes.

Jin et al. [247] developed the use of IL, [BMIM][PF<sub>6</sub>] as the growth medium and the supporting electrolyte to electrosynthesize poly(3-chlorothiophene) (PCIT) and copolymerization CIT with 3-methylthiophene (MeT) via potentiodynamic and galvanostat methods. Homopolymer revealed color changes between deep red and deep blue, whereas copolymer showed the most vivid change of color between bright red and greenish blue in fully reduced and oxidized states. Scheme 19 is shown the electrochromic phenomenon of PCIT and its copolymeric system. For PCIT film, the maximum optical contrast % DT and the switching time values were 17% and 2.4 s and for P(CIT-co-MeT) film these values were 26% and 0.9 s. They also found that the copolymer could be cycled up to 2300 times between +0.0 and +1.6 V with a scan rate of 200 mVs<sup>-1</sup>

**Scheme 19** Electrochromism for PCIT(x = Cl) and P(CIT-co-MeT)(x = CH<sub>3</sub>)



before it loses its ability to switch, while PCIT can be cycled for 580 times under the same conditions.

Lu et al. [248] reported electrochemical polymerization of MeT in the RTIL [BMIM][PF<sub>6</sub>]. The undoped and doped PMeT film in the IL was reversible and stable. According to the authors, PMeT film has strong characteristics of electrocatalytic oxidation of ascorbic acid and can separate the oxidation peaks of ascorbic acid and dopamine.

Pringle et al. [249] reported an unusual mechanism of growth during the synthesis of PPy in [EMIM][Tf<sub>2</sub>N], with the polymer growing along the surface of the solution. If the electrochemical polymerization of Py in the IL is performed using a platinum wire as the working electrode, the polymer forms an initial layer on the section of working electrode that is submerged into the monomer/IL solution, but then grows along the surface of the IL. They found that solution-surface polymerization phenomenon only occurs in ILs when the growth solutions are deaerated, but the polymerizations are performed in air rather than under nitrogen. The authors believed that the presence of some water is necessary for the surface polymerization, to react with the H<sup>+</sup> produced in the reaction (water being a stronger base than the [Tf<sub>2</sub>N] anion), and when a dry IL is used this is provided by absorption from the atmosphere.

Zheng et al. [250] reported the electrochemical polymerization of 1,2-methylenedioxybenzene (MDOB) in the hydrophobic IL [BMIM][PF<sub>6</sub>]. The resulting PMDOB films cycled repeatedly between the conducting and the insulating states without decomposition even in concentrated sulfuric acid, implying the good redox activity and high structure stability of the polymer. The polymerization occurred at the C<sub>4</sub> and C<sub>5</sub> positions on the benzene ring of MDOB, resulting in the main backbone of PMDOB similar to polyacetylene, which were confirmed by IR and <sup>1</sup>H NMR spectra. They reported that in contrast to 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> in acetonitrile, IL serves as both the growth medium and an electrolyte and delivers much milder chemical conditions. Smooth and compact PMDOB films with ordered nanostructures were obtained and showed good electrochromic properties between the doped and the dedoped states, from green grass to opalescent.

Passerini et al. [251] studied electrosynthesis of poly-o-phenylenediamine thin films on platinum electrodes in the

RTIL [BMPyr](nonafluorobutanesulfonyl)-(trifluoromethanesulfonyl)imide. They found that polymer films with much higher permeability, good adherence on Pt and more efficient in blocking the interferents in the IL-based electrolyte resulted compared with aqueous H<sub>2</sub>SO<sub>4</sub>.

Jin et al. [252] demonstrated electropolymerization of MeT, 3-hexylthiophene (HexT) and 3-octylthiophene (OcT) in [BMIM][PF<sub>6</sub>] via potentiodynamic and galvanostat methods. The resulting polymers showed slightly different color changes during reversible redox switching. The color changes during oxidation these undoped polymers were bright red to bright blue (PMeT), orange red to blue (PHexT) and orange yellow to black blue (POcT). The polymer films exhibit high chromatic contrast, comparative switching time, great electrochromic efficiency and long-term switching stability.

Ahmad et al. [253] reported a facile method to synthesize poly(3,4-ethylenedioxythiophene) (PEDOT) films at room temperature in a waterproof IL, [EMIM][[(CF<sub>3</sub>CF<sub>2</sub>SO<sub>2</sub>)<sub>2</sub>N] by electropolymerization. The IL led to the formation of randomly oriented nanofibers and particles confined to submicrometer-sized domains in the film microstructure. X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray (EDX) studies provided information about the intercalation of the cation apart from the reported anion in the polymer film, and on how the imidazolium ion controls the growth of PEDOT nanostructures.

Recently, Endres et al. [254] reported the electropolymerization of benzene to PPP in the air and water-stable IL [HMIM]tris(pentafluoroethyl)trifluorophosphate. Analysis using IR showed the average chain lengths 19–21 phenyl rings for polymer films. The authors exhibited that the electropolymerization of benzene in this IL can be probed on the nanoscale with in situ scanning tunneling microscope and that the band gap of the prepared polymer can be determined using in situ tunnelling spectroscopy. The band gap of the electrodeposited polymer film obtained at a constant potential of 1.0 V *versus* PPP was 2.9 ± 0.2 eV.

Zhang et al. [255] synthesized poly(3,4-ethylenedioxythiophene) (PEDOT) using purified [BMIM][BF<sub>4</sub>] as both the growth medium and the supporting electrolyte. The electrochemical performance of the PEDOT thin film was investigated in 1 M, H<sub>2</sub>SO<sub>4</sub> solution. It had nearly ideal

capacitive property, and its specific capacitance was about  $130 \text{ Fg}^{-1}$ . Compared with other conducting polymers, enhanced cycling lifetime (up to 70,000 cycles), which is close to that of active carbon materials, was observed on repetitive redox cycling.

Mastragostino et al. [256] employed the ILs *N*-butyl-*N*-methyl-pyrrolidinium trifluoromethanesulfonate ([BMPyrr][TF]) and *N*-methyl-*N*-propyl-pyrrolidinium bis(fluorosulfonyl)imide ([MPPyrr][FSI]) as electropolymerization media for poly(3-methylthiophene) (PMeT) considering their application in carbon/IL/PMeT hybrid supercapacitors. Data on the viscosity, solvent polarity, conductivity and electrochemical stability of [BMPyrr][TF] and [MPPyrr][FSI] as well as the effect of their properties on the electropolymerization and electrochemical performance of PMeT, which features  $>200 \text{ Fg}^{-1}$  at  $60 \text{ }^\circ\text{C}$  when prepared and tested in such ILs, were reported and discussed.

Xu et al. [257] studied the electrochemical polymerization of selenophene in [BMIM][PF<sub>6</sub>] which led to the formation of free-standing and highly conducting polyselephenene (PSe) films with an electrical conductivity as high as  $2.3 \text{ Scm}^{-1}$ , higher than PSe electrodeposited in conventional media. The polymerization rate was significantly improved as [BMIM][PF<sub>6</sub>] served as both the growth medium and an electrolyte. PSe obtained with good electroactivity and stability even in concentrated sulfuric acid. IR spectra confirmed the polymerization principally through coupling. SEM results indicated the formation of smooth and compact PSe films.

Zheng et al. [258] investigated for the first time the direct anodic oxidation electropolymerization of 3,4-ethylenedioxythiophene (EDOT) in IL microemulsions, [BMIM][PF<sub>6</sub>]/Tween 20/H<sub>2</sub>O. Electrochemical measurements indicated that among water-in-[BMIM][PF<sub>6</sub>] (W/IL), bicontinuous, and [BMIM][PF<sub>6</sub>]-in-water (IL/W) subregions in [BMIM][PF<sub>6</sub>]/Tween 20/H<sub>2</sub>O system, IL/W was the most suitable for the electropolymerization of EDOT, while the electropolymerization did not happen in W/IL. The use of IL microemulsions remarkably decreased the amount of IL, especially for IL/W. UV-vis spectra confirmed the formation of PEDOT. SEM results demonstrated that nanostructures of compact PEDOT films were still obtained as in pure IL, implying their possible utilization in ion-selective electrodes, ion-sieving films, and matrices for hosting catalyst particles

Chen et al. [259] electropolymerized carbazole on ITO electrodes in two air- and water-stable RTILs, [BMIM][PF<sub>6</sub>] and [BMPyr][Tf<sub>2</sub>N], respectively, using three potentiostatic methods (i.e., cyclic voltammetry, potentiostatic electrolysis, and potentiostatic pulse electrolysis). The polymer films obtained in both ILs adhered on the electrode surface well; however, the polycarbazole (PCz)

films obtained in the more viscous, [BMIM][PF<sub>6</sub>] exhibited a denser structure. The PCz films showed electrochromic behavior; deep green was observed in the oxidative state and pale green in the reductive state. Anions or viscosities of the ILs seem to influence the depth of color change.

Lu et al. [260] prepared PPy film modified glassy carbon electrode by electrochemical polymerization in [BMIM][PF<sub>6</sub>]. The PPy film obtained in IL adhered on the electrode surface well and the properties of the PPy film have been characterized via UV-vis spectra and SEM. The electrochemical response of the PPy modified electrodes toward ascorbic acid and dopamine was investigated by differential pulse voltammetry (DPV). Well separated anodic peaks were observed at PPy electrode with peak separation of 200 mV at pH 6.2. Compared with PPy electrode prepared in aqueous solution, dopamine had a higher oxidation currents at the modified electrode prepared in IL. The oxidation peak potentials and currents were affected by the pH valuation and the film thicknesses.

Zheng et al. [261] utilized an air and moisture stable IL, [BMIM][PF<sub>6</sub>] as an electrolyte for the direct anodic oxidation electropolymerization of fluorine. The corresponding electroactive polyfluorene films showed good redox activity and structural stability. <sup>1</sup>H NMR and FTIR spectra together with density functional theory calculations indicated that the polymerization of fluorene occurred at the C2 and C7 positions. SEM results demonstrated that smooth and compact polyfluorene films were obtained, due to the use of [BMIM][PF<sub>6</sub>] as both the growth medium and the electrolyte. Doped polyfluorene films were examined to oxidize formic acid in 0.5 M sulfuric acid by CV and demonstrated stable electrocatalytic activity, showing their potential use in fuel oxidation.

#### Galvanostatic Polymerization

Mastragostino et al. [262] reported for the first time galvanostatic polymerization of PMeT in the [EMIM][Tf<sub>2</sub>N]. They have demonstrated that the addition of the acid trifluoromethanesulfonimide provides a clean electrosynthesis procedure in which the IL is not wasted by counterelectrode reaction nor consumed to balance the PMeT p-doping charge, with advantage in terms of costs. This procedure gave a PMeT electrode featuring  $250 \text{ Fg}^{-1}$  in [EMIM][Tf<sub>2</sub>N] at  $60 \text{ }^\circ\text{C}$ , a very fascinating result in view of application in IL-based hybrid supercapacitors.

#### Radiation Induced Polymerization

Wu et al. [263] investigated radiation induced polymerization of St, MMA and BMA in the presence of RTIL, [Me<sub>3</sub>NC<sub>2</sub>H<sub>4</sub>OH][ZnCl<sub>3</sub>], and the RTIL/THF mixed solutions. The considerable enhance in monomer conversion



and polymer's MW were observed using IL. In the case PSt and PBMA, single-modal MWD was examined at IL < 40 vol.% and multi-modal MWD at IL > 50 vol.%, whereas, PMMA had a nearly single-modal MWD at THF > 20 v%. The results showed that the miscibility of polymer with RTIL/THF solvent is in the order: PMMA > PBMA > PSt. This is consistent with the difference in MWD observed for the same polymer at various RTIL/THF ratios. This difference in MWD was attributed to the inhomogeneous nature of the IL in micro-region and the immiscibility of polymer with medium.

The same research group reported  $\gamma$ -radiation initiated polymerization of MMA and BMA in  $[\text{Me}_3\text{NC}_2\text{H}_4\text{OH}][\text{ZnCl}_3]$  and its mixture with THF and methanol [264]. They observed that for both PMMA and PBMA the MW increases rapidly with raising the RTIL fraction in RTIL/THF mixture. However, the change of MWD with RTIL/THF ratio was clearly different for PMMA and PBMA. PMMA tends to remain a relatively narrow single-modal distribution by changing the RTIL fraction from 20 vol.% to 100 vol.%, while PBMA always has a broad multi-modal MWD and the polymer comprises of several components with obviously different MW and MWD at RTIL content of 40–60 vol.%.

Wu et al. [265] also investigated the effects of a quaternary ammonium IL,  $[\text{Me}_3\text{NC}_2\text{H}_4\text{OH}][\text{ZnCl}_3]$  on radiation polymerization of MMA in ethanol and DMF. They found a substantial increase in monomer conversion and MW at RTIL > 60 vol.%, and the resulting PMMA had a broad multimodal MWD. The authors observed a clear difference in the MWD pattern between EtOH/RTIL and DMF/RTIL systems, probably due to the complicated interactions between the solvent and IL.

Wu and his group studied radiation polymerization of MMA in two typical imidazolium based ILs, hydrophobic [BMIM][PF<sub>6</sub>] and hydrophilic [BMIM][BF<sub>4</sub>], as well as in RTIL/organic (DMF or THF) mixed solutions [266]. PMMA with high monomer conversion, high MW and multi-modal MWD was obtained in the presence of IL, in particular in neat ILs.  $T_g$  of PMMA increased with the increase of IL fraction in the mixed solutions.

#### Pulsed Laser Polymerization

Haddleton et al. [267] measured the  $k_p$  and rate constant of termination ( $k_t$ ) for polymerization of MMA using a pulsed laser polymerization technique in [BMIM][PF<sub>6</sub>] over a range of temperature. They found that with an increase in the RTIL/MMA ratio, the  $r_p$  increased and the rate of termination ( $r_t$ ) decreased. The reason for the observed effect was assigned to increase in the polarity of the medium and viscosity, respectively. The observed high  $k_p/k_t$  ratio gives a good explanation for the fast overall conversion.

#### Polycondensation

Vygodskii et al. [268–270] reported successful application of 1,3-dialkylimidazolium based ILs in aromatic polyimides and polyamides (PA)s synthesis via the polycondensation of diamines and tetracarboxylic acid dianhydrides and dicarboxylic acid chlorides, respectively. The results showed that, ILs allow obtaining high MW polyimides and PAs in the absence of any additional catalyst. The influences of various reaction parameters on such polycyclization reaction in [BBIM][Br] as the reaction medium were also studied, enabling the determination of optimum monomer concentrations, reaction temperatures and duration. The influence of IL structure on the inherent viscosity of the polyimide was studied. Inherent viscosities of the polyimides ranged from 0.52 to 1.09 dLg<sup>-1</sup>. The polycondensation of diamines such as 5(6)-amino-2-(4'-aminophenyl)benzimidazole (ABIZ), 3,3-bis(4'-aminophenyl)phthalide and 1,4-phenylenediamine with terephthaloyl chloride in various ILs was studied at different reaction temperatures (0 to 60 °C). PAs with the highest MW were obtained when ABIZ, containing an imidazole group similar to the IL structure, was used. It found that best results were obtained in ILs of symmetrical structure. When the reactions were performed in recycled IL, high MW PAs were obtained as well.

These groups also investigated the application of ILs in direct polycondensation, which is widely used for different condensation polymers synthesis [271]. They investigated influence of IL's nature and reaction parameters upon the polymer formulation. It is shown that direct polycondensation is successfully proceeded in ILs and TPP (condensing agent) without any additional extra components, such as LiCl and pyridine, using in similar reactions in ordinary molecular solvents. Various PAs ( $\eta_{inh} = 0.11\text{--}1.10\text{ dLg}^{-1}$ ), poly(amide-imide)s ( $\eta_{inh} = 0.48\text{--}1.41\text{ dLg}^{-1}$ ), hydrazides ( $\eta_{inh} = 0.56\text{--}0.60\text{ dLg}^{-1}$ ) and polyhydrazides ( $\eta_{inh} = 0.71\text{--}1.32\text{ dLg}^{-1}$ ) obtained in quantitative yield and high MW. When aliphatic dicarboxylic acids (adipic acid and SiDCA) and aromatic diamines are used as initial compounds, high MWs PAs ( $\eta_{inh}$  up to 0.91 dLg<sup>-1</sup>) are formed. The following three synthetic approaches were tested for poly(amide-imide)s synthesis, so different high MW ( $\eta_{inh} = 0.50\text{--}1.41\text{ dLg}^{-1}$ ) PAI were derived by all these methods.

Kricheldorf et al. [272] prepared polyimides soluble in chloroform and dichloromethane. Two different aliphatic anhydrides and three aromatic diamines were selected. Five synthetic methods were compared: polycondensation with TPP (Higashi method), polycondensation in hot m-cresol and in hot 1,2-dichlorobenzene, polycondensation in bulk or in solution in the presence of acetic anhydride and polycondensation in ILs. The highest MWs were obtained



in *m*-cresol and in [PPIM][Br]. The MALDI-TOF mass spectra revealed that the fraction of cyclic polyimides increased with the MW of the entire sample. The identification of high molar mass cycles (detected up to 12,000  $\text{g mol}^{-1}$ ) was limited by the mass spectrometry, not by the chemical course of the polycondensations.

Mallakpour et al. [273] studied direct polycondensation of *N,N'*-(4,4'-oxydiphthaloyl)-bis-*L*-phenylalanine diacid with various aromatic diamines in IL media (Scheme 20). They also investigated influence of various reaction parameters, including the nature of the IL 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. Various high MW, optically active poly(amide-imide)s were obtained in high yields with inherent viscosities ranging from 0.54 to 0.88  $\text{dL g}^{-1}$ . The authors compared this method with three other classical methods. The yields and inherent viscosities of the polymers were higher using ILs as the reaction media.

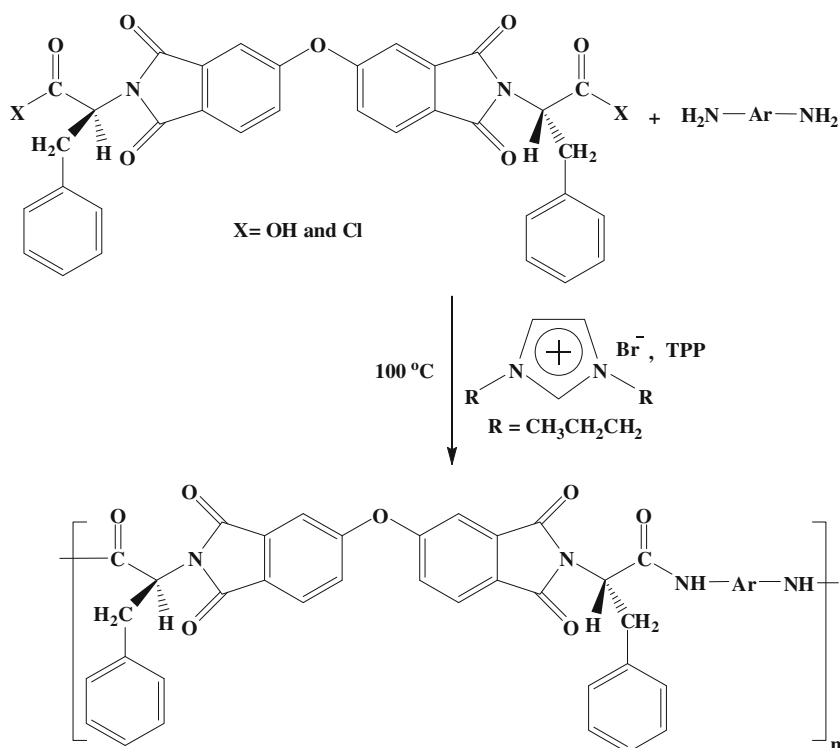
Vygodskii et al. [274] reported the synthesis of high MW aromatic poly(1,3,4-oxadiazole)s (PODs) by one-pot procedure from dicarboxylic acid and hydrazine's salt (sulfate, phosphate) or dicarboxylic acid dihydrazides. The mixture of IL and TPP was used both as a solvent and condensing agent. The polycyclization occurred at a sufficiently low temperature of 210 °C for 2–5 h and resulted

in obtaining film-forming PODs having inherent viscosities up to 0.9  $\text{dL g}^{-1}$  and good thermal stability.

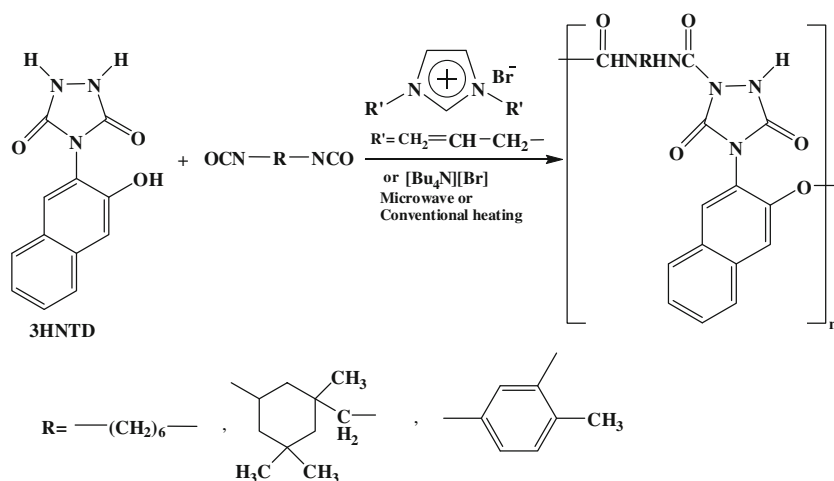
Fradet et al. [275] reported the synthesis of poly(glycolic acid) (PGA) by polyesterification of glycolic acid using ILs, mainly 1,3-dialkylimidazolium salts, as reaction media. The direct polyesterification of glycolic acid at 200–240 °C led to low PGA yields, because of monomer evaporation during the reaction. On the other hand, PGAs of  $\text{DP}_n$  up to 45 were obtained by the postpolycondensation of a preformed oligomer in [BMIM][Tf<sub>2</sub>N]. The precipitation of PGA in reaction medium at long reaction times limited the achievable molar mass. The efficiency of esterification catalysts such as  $\text{Zn}(\text{OAc})_2$  was low in these media, as only about twofold increases in reaction rate were observed. This was assigned to the preferential interaction of  $\text{Zn}^{2+}$  with IL anion instead of the polymer carboxylic acid end-groups.

To combine the advantages of microwave irradiation and ILs, recently, several polymerization reactions for synthesis of optically active poly(amide-imide)s, PAs containing bulky pendent groups and polymers having heterocyclic moieties for the first time have been investigated in IL under microwave heating by Mallakpour et al. (Scheme 21) [276–286]. Since ILs contain organic cations and suitable anions, from the perspective of microwave chemistry the most important properties of ILs that can be utilized are their polarity and their stability at high

**Scheme 20** Direct polycondensation of *N,N'*-(4,4'-oxydiphthaloyl)-bis-*L*-phenylalanine diacid with various aromatic diamines in IL media



**Scheme 21** Polycondensation reaction of 3HNTD with diisocyanates in RTILs and molten  $[\text{Bu}_4\text{N}][\text{Br}]$  under microwave irradiation and conventional heating



temperatures. The combination of IL and microwave irradiation led to large reductions in reaction times, very high heating rate with many benefits of the eco-friendly approach, named green chemistry. ILs absorb microwave emission in a very efficient way because of their high polarity and furthermore, they display a very low vapor pressure, thereby enhancing their fitness even further for microwave heating.

Mallakpour et al. [287–290] also reported synthesis of heterocyclic PAs, polyureas and poly(amide-ester)s containing urazole ring in the presence of RTILs and molten  $[\text{Bu}_4\text{N}][\text{Br}]$ . The effect of various reaction parameters, including the nature of the ILs, the amount of IL, the reaction temperature, and the reaction time were investigated to optimize the conditions for the preparation of heterocyclic polymers. The polymerization proceeded well in ILs without any catalyst and polymers were obtained with high yields and moderate inherent viscosities.

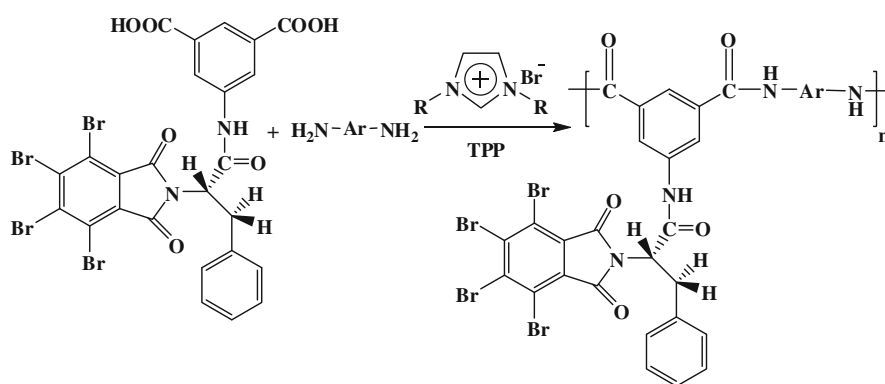
Mallakpour et al. [291] studied application of molten IL,  $[\text{Bu}_4\text{N}][\text{Br}]$  for the synthesis of PAs from the reaction of terephthalic acid with various commercially available diisocyanates with or without dibutyltin dilaurate (DBTDL) as a catalyst. The polymerization reaction gave similar results in the presence or absence of DBTDL, indicating that, the catalyst was not needed in this process. Various PAs were obtained with high yields, moderate inherent viscosities ranging from 0.36 to 0.71  $\text{dLg}^{-1}$  and good thermal stability. This method was also compared with the polymerization reaction in conventional solvent and in the presence of DBTDL as a catalyst. This methodology offered significant improvements with regard to yield of products, inherent viscosities, thermal stability, cost efficiency and green aspects avoiding toxic catalysts and solvents.

A series of optically active and highly organosoluble PAs having phthalimide or tetrabromophthalimide and

$\alpha$ -amino acid pendent groups were synthesized via direct polycondensation chiral dicarboxylic acid with aromatic diamines using several RTILs and triphenyl phosphite (TPP) (a condensing agent) in place of NMP/TPP/ $\text{CaCl}_2$ /Py with reduction in time by Mallakpour et al. [292–295] (Scheme 22). The optimization of the polymerization reactions by varying different type of ILs, the amount of IL, amount of TPP, reaction temperature, and reaction time was carried out to achieve polymers with high yields and inherent viscosities. The polycondensation reactions were carried out in different RTILs bearing different alkyl groups, such as [PPIM], [(i-P) $_2$ IM], [BBIM], [Pent $_2$ IM], [HHIM], [Hep $_2$ IM], [AAIM], [Bz $_2$ IM] with [Br] anion and molten  $[\text{Bu}_4\text{N}][\text{Br}]$ . The significant advantages of using ILs in the preparation of PAs over conventional method were to avoid the use of toxic and volatile pyridine and NMP and  $\text{CaCl}_2$  and reduction in reaction time. Furthermore, in ILs as reaction media yield, inherent viscosity, optical rotation and thermal stability of polymers improved. They reported that ILs not only acts as a solvating medium but also as a promoter for this polycondensation reaction. The inherent viscosities of the resulting polymers were in the range of 0.31–0.75  $\text{dLg}^{-1}$  and the yields were 80–95%. This method of polymerization was also compared with direct polyamidation using conventional phosphorylation reaction. A comparison between presented data two method proves that the PAs synthesized via IL method encompass higher inherent viscosities and yields respect to whom that prepared under conventional method. Furthermore, the use of IL has led to reduce the overall cost of synthesis and cleaner reaction conditions by the removal of some chemicals which are indispensable in conventional methods.

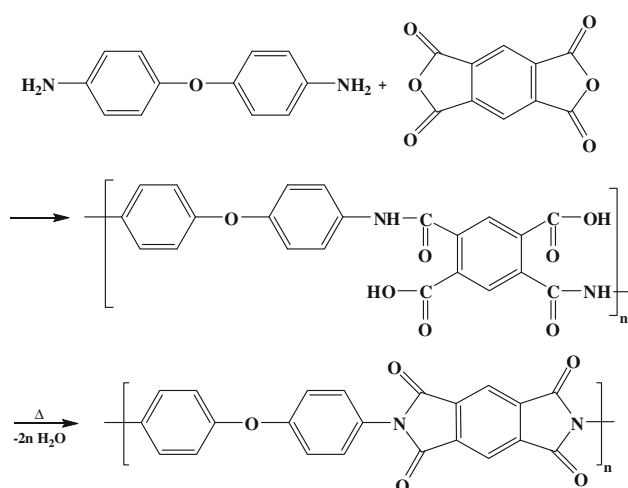
Ohno et al. [296] prepared three different ILs and employed as solvents for polyimide synthesis from reaction of 4,4'-oxydianiline and pyromellitic dianhydride as

**Scheme 22** Synthesis of optically active PAs having tetrabromophthalimide units. *Ar* aromatic groups, *R* Alkyl groups



Ar = Aromatic groups

R = Alkyl groups



**Scheme 23** Synthesis of polyimide

starting materials (Scheme 23). Although IL, [BzMIM][Tf<sub>2</sub>N], was difficult to dissolve starting materials, their solubility was significantly improved by the addition of imidazolium type zwitterion, 1-(1-butyl-3-imidazolium)butane-4-sulfonate (ZI), because of increasing hydrogen-bond accepting ability. When polycondensation was carried out in [BzMIM][Tf<sub>2</sub>N] containing 40 mol % of ZI, high average MW of the polyimide was obtained because poly(amic acid) was prepared without heating.

Abdolmaleki and co-workers [297, 298] synthesized a series of high MW polyhydrazides via direct polycondensation of 4,4'-diphenyl sulphone dicarboxylic acid or benzofuro[2,3-b]benzofuran-2,9-dicarboxylic acid and dihydrazides in imidazolium-based ILs at 140 °C. Direct polycondensation was successfully preceded in IL and TPP as activating agent, without any additional components, such as LiCl and pyridine. Therefore, IL can act as both solvent and catalyst. The polyhydrazides were obtained in quantitative yield and inherent viscosities in the range of 0.21–0.73 dLg<sup>-1</sup>. The polyhydrazides had T<sub>g</sub>s between

165–210 °C. They could be thermally converted into the corresponding PODs approximately in the region of 210–330 °C, as evidenced by the thermogravimetric analysis. As a result, the ILs were excellent media with a high solubilizing power for the polymerization reactions that increased chemical reactivity and, therefore, led to a decrease in reaction time and better results in comparison with conventional solvents.

Seckin et al. [299] studied effect of imidazolium, pyridinium, and alkylammonium salts as catalyst and solvent upon polymerization of 1,4-bis(3-aminopropyl) piperazine. The use of ILs resulted in formation of the polymers with higher MW compared with those obtained from bulk polymerization. It also found that T<sub>g</sub> of the polymers was increased and their thermal degradation was reduced than the polymer obtained via solution polymerization in NMP. The use of imidazolium based ILs was found to be preferred over *n*-alkyl-4-methylpyridinium and aliphatic ammonium salts.

Liu et al. [300] reported for the first time synthesis of high MW aliphatic polyesters, in [C<sub>n</sub>MIM] ILs using catalyst, SnCl<sub>2</sub>·2H<sub>2</sub>O via two-step polycondensation. They found that the MW of the resulting polyesters depended on the activity of the catalyst in the ILs and the miscibility of aliphatic polyester/IL. The former factor was dominated by the anion of the ILs, while the latter factor could readily be tuned by varying the anion and/or the cation of the ILs.

Vygodskii et al. [301] reported synthesis of PODs with pendant phosphonic acid groups via direct polycondensation of dicarboxylic acids and their dihydrazides using [MPIM][Br] in the presence TPP as a reaction activator (Scheme 24). The polymers were obtained with inherent viscosities in the range of 0.46–0.58 dLg<sup>-1</sup> in two steps starting from polyhydrazides formation followed by thermal polycyclization under high vacuum. Membranes having pendant phosphonic acid moieties were thermally and chemically stable and possessed proton conductivities in the range of 4 × 10<sup>-7</sup> to 5 × 10<sup>-6</sup> Scm<sup>-1</sup> at 100% relative



and phase separated. The compatibility of HEMA with the ILs led to its use for the preparation of polymer electrolyte films, which are highly conductive. The resulting HEMA network polymers exhibited an ionic conductivity of  $10^{-3} \text{ Scm}^{-1}$  at  $30^\circ\text{C}$ .

Wallace et al. [306] studied electrochemistry of PPy in [BMIM][PF<sub>6</sub>]. They found that nitrogen purging led to more defined redox responses of PPy in ILs. They also observed an enhanced redox cycling stability protection in IL than cycling in propylene carbonate electrolyte with [Bu<sub>4</sub>N][PF<sub>6</sub>] electrolyte.

Pringle et al. [307] utilized [EMIM][Tf<sub>2</sub>N] for synthesis of nanoparticles of PPy, PT and P(TTh) using a range of oxidants via simple combination of the oxidant and the monomer in one phase. In all cases, the polymerization led to formation of conducting polymer particles, which can be simply removed from the IL by centrifuge and repeated washing with ethanol, then either dried under vacuum to give a powder or dispersed in a molecular solvent for further processing/analysis. For preparing nanoparticles of poly(T), auric chloride and ferric chloride as oxidizing agents were employed. They also used oxidants, auric chloride, silver nitrate, ferric tosylate, and ferric perchlorate for the chemical synthesis of poly(TTh) and PPy. The individual particles of poly(T) synthesized with sizes less than 100 nm using gold chloride.

#### Polymers Processing

Zhang et al. [308] synthesized the AN homopolymer and copolymers using AIBN initiator in [BMIM][Cl] as the solvent. Polyacrylonitrile (PAN) fiber was directly obtained for the first time by spinning of polymer solution. The polymers had high content of AN, large MW and low PDI. The PAN fiber with round profile and good mechanical properties was successfully spun from the PAN/[BMIM][Cl] solution using dry-jet wet spinning technology.

#### Depolymerization

Kamimura and Yamamoto [309, 310] utilized quaternary ammonium ILs to depolymerize PAs via different methods at  $300^\circ\text{C}$  and the caprolactam monomer was obtained. Under these conditions, 6-nylon was readily converted into  $\epsilon$ -caprolactam in good yield. The monomer recovered and then collected by direct distillation of the reaction mixture. It found that *N*-methyl-*N*-propylpiperidinium [Tf<sub>2</sub>N] offered the best results for the depolymerization of nylon 6. The IL was recycled five times without significant decomposition. Interestingly, the current method required only ordinary glassware, and there was no need to use special high-pressure apparatus.

#### Hydrogenation of Polymers in Ionic Liquids

MacLeod and Rosso [311] studied the rhodium catalyzed hydrogenation of polybutadiene (PBD), nitrile-butadiene rubber (NBR) and St-butadiene rubber (SBR) in a [BMIM][BF<sub>4</sub>]/toluene and a[BMIM][BF<sub>4</sub>]/toluene/water system. Even with the addition of water to the catalytic medium the activity of the catalyst followed the trend PBD > NBR > SBR, which corresponds to the order of polymer solubility in the IL. The degree of hydrogenation (as a percent of total hydrogenation) was 94% for PBD (4 h reaction time), 43% for NBR (4 h reaction time), and 19% for SBR (3 h reaction time).

#### Polymerization of Phenylacetylene

Nobile and his group [312] employed [BPyrr][BF<sub>4</sub>] and [BMIM][BF<sub>4</sub>] as solvent for the Rh(I) catalyzed phenylacetylene polymerization using triethylamine as co-catalyst. It found that the catalysts in both ILs could be recycled without significant loss in activity. The obtained polyphenylacetylene had high yield and MWs in the range between 55,000 and 2,00,000  $\text{gmol}^{-1}$ .

Ziolkowski et al. [313] prepared polyphenylacetylene in [BMIM][Cl], [BMIM][BF<sub>4</sub>], 1-methyl-3-oktylimidazolium ([MOktIM][BF<sub>4</sub>] and [BMPyr][BF<sub>4</sub>] using rhodium(I) catalysts. It found that the yield and MW of the polymer depend on the IL used. The highest yields of polyphenylacetylene were obtained in [BMIM][Cl] at  $65^\circ\text{C}$  and in [MOktIM][BF<sub>4</sub>] at  $20^\circ\text{C}$ . Using IL/CH<sub>3</sub>OH as the reaction medium, the polymer yield was like the yield attained in an IL only, but the MW enhanced extremely.

#### Photopolymerization in Ionic Liquids

Andrzejewska et al. [314] studied the kinetics of photopolymerization in ILs. They selected two analogous monomers, tetrafunctional poly(ethylene glycol) dimethacrylate (PEGDM) and difunctional poly(ethylene glycol) monomethacrylate (PEGMM) and four ILs [EMIM][BF<sub>4</sub>], [BMIM][BF<sub>4</sub>], [EMIM][OTf] and [BMIM][OTf] contained the same cation or the same anion in pairs. Analogous polymerizations in bulk and in a molecular diluent of medium polarity, tricresyl phosphate (TCP) served as references. It found that  $k_p$  increases in IL whereas in TCP decreases in comparing to bulk polymerization. The order of decreasing  $k_p$  values corresponds to the order of decreasing values of the polymerization rates for the both monomers. This proposes that the  $k_p$  values influence mainly by the anion structure, which in turn is mainly responsible for IL polarity. They also observed that the polymerization rates in ILs at 10% of conversion are higher than in TCP about 1.3–1.9 times and this increase is fairly



higher than the increase in  $k_p$  (about 1.1–1.6 times). On the other hand, the bimolecular termination rate coefficients in ILs were lower than in TCP by a factor of 1.25–1.68, which increased the polymerization rate by a factor of 1.1–1.3, i.e. to similar or rather lesser degree than the acceleration resulting from the increase in  $k_p$ . They also found that the termination rate coefficients affected by viscosity of the initial monomer/IL mixture.

## Conclusion

As shown in this review, significant progress has been made during recent years towards use of ILs in polymers chemistry and technology. Therefore, it would be most fascinating to be able to bring a number of the benefits of using ILs in polymer science. The benefits of using ILs as reaction media for the synthesis of a wide range of polymers have been obviously demonstrated and the main reason related to the potential to decrease problems such as solvent evaporation that are associated with the application of organic solvents in these reactions. For example, when the ILs were employed as the solvent and catalyst for radical polymerization, higher rate of reaction, enhanced MW, narrower PD, formation of cleaner polymers, increased yield, ease of product separation, and recyclability of the IL-catalyst system in comparison to organic solvents were observed. Recently, the mechanism and kinetics of polymerization in these media studied, by a number of researchers. However more studies in this challenging field are required to further understand.

**Acknowledgments** We wish to express our gratitude to the Research Affairs Division Isfahan University of Technology (IUT), for financial support. Further financial support from National Elite Foundation (NEF) and Center of Excellency in Sensors and Green Research (IUT) are also gratefully acknowledged.

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