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Conventional free radical polymerization in room temperature ionic liquids: a green approach to commodity polymers with practical advantages

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Free-radical polymerization of methyl methacrylate and styrene using conventional organic initiators in the room temperature ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$) is rapid and produces polymers with molecular weights up to 10× higher than from benzene; both polymerization and isolation of products were achieved without using VOCs, offering economic as well as environmental advantages.

Free radical polymerization is one of the most important means of producing polymers, accounting for about 50% of all mass-produced polymers.[1] One of the major virtues of radical polymerization is the relative insensitivity to monomer and media impurities, as compared to ionic polymerization. Thus radical polymerization can be carried out under less rigorous conditions, resulting in reduced cost. Another advantage of this process is that it can be applied to a broad range of monomers. Many free radical polymerizations are carried out in volatile organic compound (VOC) solvents, which have been blamed for increasing air pollution.[2]

Room temperature ionic liquids (ILs) have been investigated for electrochemical[3] and separations processes,[4,5] and as media for chemical and biochemical synthesis.[6] Of principal interest is the potential to use ILs as substitutes for VOCs: ILs exhibit negligible vapor pressure. The combination of properties exhibited by ILs (ionic, non-coordinating *etc.*) are different to those of molecular solvents, and can lead to differing solvent behavior, and differing chemical reaction outcomes characteristics of interest. In addition, studies are starting to address toxicity concerns about ILs.[7]

Chloroaluminate-based ILs have been investigated as solvents for ethylene polymerization.[8,9] Electrochemical polymerization of benzene in ionic liquids to prepare poly(*p*-phenylene) has also been reported.[10]

Haddleton *et al.*[11] reported the first example of transition-metal mediated living-radical polymerization of methyl methacrylate (MMA) in an IL. Rate of polymerization was enhanced compared to other polar/coordinating solvents, but only low molecular weight polymer products were obtained. Polymerizations employing copper-catalysts and ILs containing cuprous and ferrous anions have recently been reported.[12] Noda and Watanabe[13] have described the formation of polymer-in-salt electrodes, formed by *in-situ* polymerization of vinyl-monomers in ILs. However, to our knowledge, ILs have not been used as solvents for the synthesis and isolation of polymers formed by conventional free-radical polymerization. In this study, free-radical polymerization of the two monomers MMA and styrene, in the IL $[C_4mim][PF_6]$, was investigated using the conventional radical initiators, AIBN and benzoyl peroxide (BPO). Resulting polymers were purified from the reaction mixture using ethanol–water mixtures and the IL solvents recovered.†

In Table 1, results from polymerization of MMA and styrene in $[C_4mim][PF_6]$, initiated by AIBN and BPO respectively, are shown and are compared with data obtained under comparable conditions using benzene as solvent. Both polymers, polymethyl methacrylate (PMMA) and polystyrene (PS), had up to 10× higher molecular masses than when synthesized in benzene, at the same monomer to initiator molar ratio. In both the IL and organic solvents, the polymers exhibit polydispersities typical of homogeneous free radical polymerization products, despite the fact that in the IL case, the polymers formed are insoluble in the reaction medium. Also, it was noted that the polymerizations in the IL were very rapid; complete conversion of monomer to polymer was achieved after only eight hours polymerization time. In contrast, in conventional solvents the polymerization would require several times this period to generate complete conversion. Fig. 1 shows the SEC traces of PMMA obtained using AIBN in $[C_4mim][PF_6]$ and in benzene. The molecular weight of PMMA obtained in $[C_4mim][PF_6]$ is much higher than that obtained in benzene.

The reactions were terminated by quenching the reaction mixtures into methanol, or aqueous ethanol. The IL is completely miscible with methanol, and although regarded as ‘hydrophobic’, is miscible with aqueous ethanol over a large composition range.[14] The polymer products formed are insoluble in these solvents and were isolated by filtration, the IL was recovered by evaporation of the filtrates. Alternatively, since the polymer phase separates from the IL a simple gravimetric separation of polymer from most of the IL is possible. Entrainment of IL in the bulk polymers was an issue of concern; the ability for relatively high IL concentrations to act as plasticizers for PMMA has been investigated in a parallel study.[15] Initial precipitation and isolation of polymer yields materials containing low concentrations of entrained IL, identified by DSC.

The combination of high molecular weight products and fast reaction rates in the IL system can be explained by influences on chain-termination processes in the IL. A combination of relatively high viscosity and precipitation of the polymeric radicals as the polymerization proceeds leads to ‘diffusion-controlled termination’ throughout the polymerization. A diminished rate of termination would explain both the higher than expected molecular weights and rapid polymerization rates. As the polymerization proceeds, polymer chains form a monomer swollen polymer phase limiting polymer termination (radicals in this entangled polymer phase have difficulty diffusing together). These results are similar to those obtained for polymerization in the glassy state.[16]

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Table 1 Homopolymerization in $[C_4mim][PF_6]$, of styrene using BPO as initiator and MMA using AIBN as initiator.

Run	Solvent (cm^3)	Monomer (cm^3)	Initiator ($\times 10^3$ mmol)	Time (h)	Yield (%)	$M_n \times 10^{-53}$	M_w/M_n
Styrene polymerization using BPO as initiator (75 °C)							
1	$[C_4mim][PF_6]$ 10	1	4.1	8	96	1.18	3.63
2	10	1	20.7	8	99	0.86	2.70
3	10	1	41.3	8	97	0.45	2.46
4	10	1	20.7	1	27	0.41	2.04
5	Benzene 10	1	20.7	8	9	0.091	1.98
6	10	1	4.1	1	No polymer formed		
MMA polymerization using AIBN as initiator (65 °C)							
7	$[C_4mim][PF_6]$ 10	1	6.1	8	100	9.91	2.05
8	10	1	30.4	8	98	8.40	1.91
9	10	1	60.9	8	99	7.57	1.72
10	10	1	30.4	1	33	4.04	2.02
11	Benzene 10	1	30.4	8	17	1.32	1.89
12	10	1	30.4	1	3	0.89	1.84

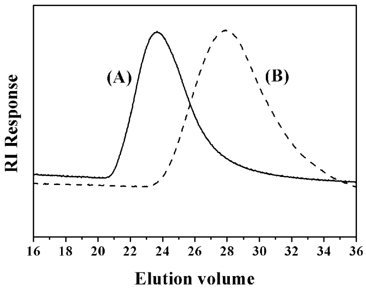

Fig. 1 SEC Traces of PMMA (A) polymerized using AIBN in $[C_4mim][PF_6]$ at 65 °C for 1 h, (B) polymerized using AIBN in benzene at 65 °C for 1 h.

In summary, $[C_4mim][PF_6]$ was used as solvent for conventional free radical homopolymerization of MMA and styrene. For both polymers, the degree of polymerization obtained using ILs was much higher than that obtained *via* conventional radical polymerization in benzene under the same conditions. Rates of polymerization were also much more rapid, relative to polymerization in common organic solvents. We believe that the simultaneous rapid polymerization rates and high molecular weights are due to diffusion-controlled termination, reflecting both the high viscosity of the ILs and phase separation of macroradicals. Furthermore, the polymers could be purified by washing with water and ethanol mixtures, making this polymerization process attractive for 'green' polymer synthesis. The polymerization process reported herein shows enormous commercial potential, given the great importance of conventional radical polymerization, the rapid rates of polymerization, high molecular weights, and Green synthesis and isolation. Work to extend this methodology to other polymer systems is presently underway.

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Notes and references

† *Materials.* MMA and styrene (Aldrich, 99%) were distilled to remove inhibitor and stored in calibrated ampoules. $[C_4mim][PF_6]$ (provided by Sachem Inc. or synthesized as reported elsewhere[4]) was washed with pure water five times. Benzene (Fisher, ≥99%) and toluene (Fisher, ≥99.8%) were distilled from freshly crushed calcium hydride. BPO (Aldrich, 97%) and AIBN (Aldrich, 98%) were recrystallized from methanol. *Instrumentation.* Size exclusion chromatography (SEC) was used to measure number-average (M_n) and weight-average (M_w) molecular weights and polydispersities, M_w/M_n, of the polymers with respect to PMMA and PS standards (Pressure Chemical Co.). The SEC experiments were carried out at 30 °C in tetrahydrofuran using a Waters 510 pump and Waters 410 differential refractometer detector (flow rate: 1 cm^3 min^{-1}, columns: Waters 500 Å, 10^3 Å, 10^4 Å, 10^5 Å, 10^6 Å pore sizes). *Polymerization.* All polymerizations were performed under high vacuum to ensure that the systems were oxygen free. The initiator (BPO or AIBN) and solvent ($[C_4mim][PF_6]$) were charged into a round bottom flask with a constriction, and degassed for 2 h. A predetermined quantity of monomer was then distilled into the reactor. The flask was removed from the vacuum line by heat-sealing at the constriction and placed in a pre-heated water bath. The polymerization was allowed to continue for 18 h and was stopped by precipitation into methanol or ethanol–water mixture. Although these monomers and initiators are soluble in this IL, in all polymerizations the polymer began to phase-separate shortly after polymerization began.

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