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Living cationic polymerisation of styrene in an ionic liquid†

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Received (in Cambridge, UK) 21st November 2003, Accepted 20th January 2004
First published as an Advance Article on the web 13th February 2004

For the first time, living cationic polymerisation of styrene has been carried out in room temperature ionic liquids under mild reaction conditions and using mild acid catalysts (*e.g.* organoborate acids) to obtain polymers of narrow polydispersity.

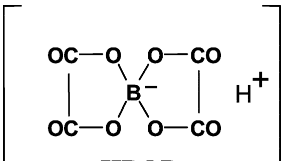
Cationic polymerisation of vinyl monomers using various Lewis acids, such as BF_3, $SnCl_4$, $TiCl_4$, $AlCl_3$, *etc*., in conventional solvents has been well studied.[1–6] Typically, the Lewis acid reacts with small amounts of water in the reaction mixture to generate active hydrogen ions which add to the monomer to form a carbocation. Reaction of the carbocation with further monomer generates the polymer. In some cases, the polymer remains 'living' if its cationic activity is retained after the monomer is completely consumed. Often, the lack of strongly electron-donating groups in the monomer renders the growing carbocation unstable and it suffers from side reactions such as chain transfer accompanied by β-proton elimination. In the case of styrene, Friedel–Crafts alkylation of the phenyl ring is also possible. Thus control of cationic polymerisation of styrene has been considered to be difficult. Recently, there have been reports of $SnCl_4$ initiation systems which induce living cationic polymerisation with better molecular weight control.[7] There have also been reports on $TiCl_4$ initiation systems involving added salts, *e.g.* tetra-n-butylammonium chloride, to produce living polymers.[8] The success of living polymerisation appears to lie in the choice of the Lewis acid, the polarity of the solvent and the salt added to stabilise the carbocation.[9]

The Lewis acid catalysts typically require careful handling, as they are often corrosive in nature. Their separation from the reaction products is also difficult, as is their subsequent recovery for reuse. In the case of $AlCl_3$, a large volume of acidic aluminium waste is created.[10–11] To overcome these problems, recent reports have described attempts to immobilise $AlCl_3$ by vapour deposition onto an inorganic surface.[12–13] In other work, mesoporous silica-supported aluminium chloride catalysts have been prepared and used as heterogeneous initiators for cationic polymerisation of styrene with improved control over molecular weights compared to homogeneous Lewis acid catalysts.[14] Even under these conditions, the polydispersity remains high.

Typically, chlorinated solvents need to be used to solubilise the anhydrous aluminium chloride.[15] In recent years, room temperature ionic liquids (ILs) have been extensively investigated for use as replacement solvents for clean synthesis in a variety of chemical reactions.[16–20] The major advantage of using these ILs is their ability to dissolve a wide range of organic and ionic compounds to an appreciable extent. Their polarity, lack of volatility and their high thermal stability are also important features. The use of ILs as solvents in polymerisation reactions has recently been reported[21–23] for free-radical polymerisation, transition metal-mediated living free-radical polymerisation and charge-transfer polymerisation. Surprisingly however, there are no reports of the application of ILs as solvents in *ionic* polymerisation, despite the fact that they would appear to be ideal solvents for any process that involves a charge separation. The main objective of the present study, therefore, is to replace the traditional ionic polymerisation solvents with ILs and to investigate the potential for the special solvent properties of the IL to enable the use of milder acid catalysts as well as producing polymers with better polydispersities. The IL method may also provide a more green route to the polymers by providing an easy method of recycling the catalyst and the solvent employed in the process. A further objective is to investigate the living nature of ionic polymerisation in the IL; in principle, the IL should provide a long-lived 'living' state by stabilising the carbocation in the polymer backbone.

In this communication, we report the cationic polymerisation of styrene using $AlCl_3$ as catalyst in an IL. The results are compared with the polymers formed in a traditional organic solvent (DCM). The IL chosen for this study is *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide, abbreviated as $[P_{14}][tf_2N]$). We also report the application of a novel acid catalyst, bis(oxalato)boric acid (HBOB), in the cationic polymerisation of styrene in the IL solvent. The use of HBOB as catalyst in Friedel–Crafts reactions and vinyl ether condensations has been previously studied.[24] HBOB is considered to be a strong Brønsted acid but relatively mild compared to the Lewis acids mentioned above. In the present case, this catalyst demonstrates the possibility of the IL solvent enabling the use of a range of other acids in the ionic polymerisation reaction.

Analytical grades of the styrene, boric acid, oxalic acid and $AlCl_3$ were used. The synthesis of the $[P_{14}][tf_2N]$ IL followed the procedures in the literature.[25] The synthesis of HBOB involves[24] dehydrating aqueous solutions of 2 mol of oxalic acid with 1 mol of boric acid under vacuum for 2 h to produce a dry, white solid. Mass spectral analysis of the product indicated that formation of HBOB was substantially complete.



HBOB

In order to make a comparison with the conditions which are conventionally used, the polymerisation of styrene was carried out at 0 °C using either neat styrene, dichloromethane as solvent or the IL as solvent. Typically, 0.028 g of $AlCl_3$ was dissolved in 0.40 g solvent, 0.175 g of styrene was added and the reaction mixture stirred for 2 h. Subsequently, the polymer was precipitated from methanol. Representative reactions are summarised in Table 1. The ionic polymerisation proceeds smoothly to high yields (88%) in the IL (run 4). Traditional reactions in DCM (run 3) and bulk monomer (run 1) produce 95 and 42% yields, respectively, under similar conditions. The results of a study recently reported in the literature[15] are presented (entry 2) for comparison. The slightly higher yield when using DCM is likely a result of the higher fluidity of this solution at 0 °C. The polymers synthesised were characterised (Table 1) for number and weight average molecular weights and polydispersity index, PI ($= M_w/M_n$), using gel permeation chromatography (GPC; using THF as solvent, a refractive index

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† Electronic supplementary information (ESI) available: GPC results for the two-step living polymerisation of styrene by HBOB in the IL. See http://www.rsc.org/suppdata/cc/b3/b315100j/

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DOI: 10.1039/b315100j

detector and polystyrene standards). The IL reaction produces lower molecular weights and polydispersity compared to the reaction in DCM. This may be related to differences in the concentration of the active initiator species in each case and, as shown below, can be varied by altering the initiator concentration.

The cationic polymerisation of styrene was also carried out using HBOB in DCM and in the IL at 0 °C. Polymerisation did not occur in either case, presumably due to the poor ionisation of HBOB at low temperatures. The polymerisation was then carried out at various temperatures between 0 and 60 °C; the reaction was observed to proceed in high yield when carried out in the IL medium at 60 °C (run 6). This is consistent with the acidity of HBOB only producing significant dissociation *via* HBOB $\rightarrow H^+ + BOB^-$ in the IL solvent. The GPC study (Table 1) indicates that lower molecular weights coupled with low polydispersities are obtained when styrene is polymerised using HBOB; nonetheless, the molecular weights are higher than predicted on the basis of full dissociation of the HBOB, as expected if the acid is only partly dissociated. Polystyrene with molecular weights in this range is of interest for coating applications.

Table 1 Comparison of the properties of polystyrene prepared in ionic liquid and conventional solvents[a]

Run	Catalyst	T/°C	Solvent	M_w/kg mol^{-1}	M_n/kg mol^{-1}	PI	Yield (%)
1	$AlCl_3$	0	Bulk	4.5	1.6	2.9	42
2	Silica–$OAlCl_2$[b]	0	Bulk	5.8	2.4	2.4	60
3	$AlCl_3$	0	DCM	15.6	4.4	3.6	95
4	$AlCl_3$	0	IL	5.2	1.7	3.1	88
5	HBOB	60	DCM	4.1	2.3	1.8	15
6	HBOB	60	IL	1.3	1.0	1.3	96
7	HBOB (high sty)	60	IL	1.7	1.1	1.5	93
8	HBOB (low sty)	60	IL	1.3	1.0	1.3	94
9	Me_4N^+	60	IL	—	—	—	—
10	HBOB + MMA	60	IL	—	—	—	—

[a] Reaction time 2 h. [b] Data from ref. 15.

To substantiate that HBOB acts as an acid initiator under these conditions, the hydrogen of HBOB was substituted by a quaternary ammonium cation, Me_4N^+, producing the neutral salt Me_4NBOB. Polymerisation did not occur when this was used as the catalyst (run 9). This verifies that the presence of the proton is important in the action of HBOB. Another reaction was carried out to substantiate that HBOB acts as a *cationic* initiator in the polymerisation; the monomer was replaced by methyl methacrylate (MMA) (run 10). Polymerisation did not occur at all, as expected, since MMA is known not to be polymerised by cationic initiators. This set of experiments proves that HBOB initiates a *cationic* polymerisation and that its action is promoted by the IL solvent. The acidity of HBOB is too weak to provide a substantial concentration of active protons in a solvent such as DCM. It thus appears that the action of the IL in promoting dissociation of the acid is sufficiently strong that a range of other acids may become useful in initiating polymerisation.

Two further reactions were carried out, one using a higher monomer concentration (0.80 g, run 7) and the other a higher IL concentration (0.40 g, run 8) to investigate the effect of monomer concentration on the molecular weight of the polystyrene produced. In both cases, rapid polymerisation took place and almost complete conversion (> 90%) was achieved. The molecular weights of the polystyrene produced are higher in the case of run 7 as a result of the relatively lower initiator concentration. In run 8, the styrene and HBOB were diluted in proportion compared to run 6 and the polystyrene molecular weights are, accordingly, unchanged.

To examine the living nature of these polymerisation reactions, a second (identical) aliquot of styrene was added to the reaction mixture after the initial charge of the monomer had been completely polymerised and the reaction allowed to continue for a further 1 h. Continued polymerisation to higher molecular weights is indicative of a living polymerisation, *i.e*. the polymer cation remains active once the monomer is depleted. An example is summarised in Table 2 and GPC results are presented as ESI†. Continued monomer conversion and an approximate doubling in the number average molecular weight after reaction of the second aliquot indicates that living polymerisation occurs when HBOB is used as a catalyst in the IL solvent. In the case of $AlCl_3$ and HBOB in DCM, there was only partial occurrence of living polymerisation.

Table 2 Living polymerisation of styrene in ionic liquid

Step	Catalyst	T/°C	Solvent	M_w/kg mol^{-1}	M_n/kg mol^{-1}	PI	Yield (%)
1	HBOB	60	IL	1.3	1.0	1.3	96
2	HBOB	60	IL	3.0	1.9	1.6	58

Thus, these studies of cationic polymerisation of styrene in an ionic liquid and using a novel organoborate acid catalyst have produced living polymers with low molecular weights and good polydispersities. The recovery and reuse of the catalyst–ionic liquid mixture can be achieved by removal of the methanol after polymer precipitation. This provides an overall green route for the process. Polymerisation of other vinyl monomers by organoborate acids will be reported elsewhere.

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