

Organoborate Acids as Initiators for Cationic Polymerization of Styrene in an Ionic Liquid Medium

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ABSTRACT: A controlled cationic polymerization of styrene has been achieved using bisoxalatoboric acid (HBOB) as an initiator in a room temperature ionic liquid (IL) under mild reaction conditions to obtain polymers of low molecular weights and narrow polydispersity. HBOB represents a relatively easily handled cationic initiator as compared to those often used in cationic polymerization reactions. The concentration of HBOB was optimized, and it was found that the molecular weights of these polymers increased with decreasing HBOB concentration. Studies were performed with different water contents in the reaction mixture to gauge the water tolerance above which the polymerization is inhibited. Experiments were also carried out with other organoborate acids, and it was found that the trend in yields followed trends in Bronsted acidity. The efficiency of different ILs as reaction solvents is also discussed.

Introduction

Monomers such as styrene that are capable of undergoing carbocationic polymerization^{1–3} usually have the characteristic of being able to form relatively stable carbocations. In the case of styrene this is the result of resonance stabilization of the positive charge over the system of the aromatic ring. Thus, carbocationic polymerization of styrene and its derivatives using different initiator molecules in combination with various Lewis acids such as BCl_3 , SnCl_4 , TiCl_4 , AlCl_3 , etc., in conventional solvents has been well studied.^{4–8} Nonetheless, carbocationic living polymerization is generally considered difficult because of the high reactivities of the carbocations, which tend to enter into irreversible termination and chain transfer reactions via β -proton expulsion. The key to the development of living polymerization has been finding conditions wherein the carbocation is *protected* by reversible temporary deactivation from entering into side reactions.^{6,9} This temporary deactivation reduces the overall rate of polymerization relative to the rate of initiation, which coincidentally allows the bulk of initiation to occur in the early stages of polymerization. This also allows the polymer chains to propagate with the same overall rate leading to polymers of narrow molecular weight distribution.

Pepper¹⁰ first suggested the existence of “long-lived” active species in the polymerization of styrene initiated by perchloric acid. This “living” cationic polymerization of styrene derivatives was obtained¹¹ at $-78\text{ }^\circ\text{C}$ by suppressing the formation of nonliving species, for example by the use of nonpolar solvents, or added salts (e.g., tetra-*n*-butylammonium perchlorate) such that the counterion concentration was high. Recently, there have been reports of SnCl_4 initiation systems, which induce living cationic polymerization with better molecular weight control.¹² Another possibility for living styrene polymerization was reported¹³ in which the adduct of acetic acid and *p*-methylstyrene was coupled with BCl_3 to give polymers with controlled molecular weights but broad molecular weight distributions. There have also been reports on the TiCl_4 initiation systems with added salts, e.g., tetra-*n*-butyl ammonium chloride, to produce living polymers.⁵ It has also been reported that the addition of nitrogen base compounds⁹ including *N,N*-dimethyl-

acetamides on the TiCl_4 initiation systems produced controlled molecular weight polymers. However, the majority of successful reactions rely on an appropriate choice of the Lewis acid, the polarity of the solvent, and the added salt which may stabilize the carbocation.¹⁴ The polymerization is said to be living, according to Matyjaszewski,¹⁵ if it exhibits a linear semilogarithmic kinetic plot, a linear increase in M_n with conversion, and produces high molecular weight polymers with narrow polydispersity values.

The Lewis acid catalysts, such as AlCl_3 , employed in conventional cationic polymerization, require strict precautions in use because these are typically very corrosive in nature. Their separation from the reaction products can also be difficult. Because of this difficulty, the reuse/disposal of the catalyst is a challenge to industry, as large volumes of acidic aluminum waste is created.^{16,17} The chlorinated solvents often used to solubilize the anhydrous aluminum chloride¹⁸ are not considered eco-benign and there is an imperative to replace these. Apart from these process problems, the molecular weight control is also generally poor. In order to overcome these problems attempts have been made to arrest the AlCl_3 by vapor deposition onto an inorganic surface.^{19,20} Similarly, mesoporous silica supported aluminum chloride catalysts have been prepared and used as heterogeneous initiators for cationic polymerization of styrene with improved control over molecular weights compared to homogeneous Lewis acid catalysts.²¹ Even under these conditions, however, there was reduction in molecular weight and the polydispersities remain high.

In recent years, room temperature ILs have been extensively employed as replacement solvents for clean synthesis in a variety of chemical reactions.^{22–26} The major advantage in using these ILs is their ability to dissolve a wide range of organic and ionic compounds to an appreciable extent. Although there is no generic set of properties exhibited by ILs, some examples exhibit a favorable combination of properties including polarity, lack of volatility, hydrophobicity, and high thermal stability. The use of ILs as solvents in polymerization reactions has therefore, not surprisingly, been reported recently.^{27–29} In our earlier communication³⁰ we reported the use of bisoxalatoboric acid (HBOB) in the cationic polymerization of styrene in an IL medium. The experiments indicated that HBOB acts as a strong

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proton donor in this reaction and that it can thereby initiate a cationic polymerization. The significance of these observations was that HBOB is a relatively easily handled solid and that the reaction only takes place with appreciable rate at moderately elevated temperatures, both of these facts making the reaction very straightforward to carry out.

The main objective of the present study was to investigate the other organoborate acids such as bisuccinoboric acid (HBSB) and bisglutaroboric acid (HBGB) as initiators in the cationic polymerization of styrene as well as further investigating the HBOB initiated reaction. Since water is a key issue in cationic polymerizations, (water can inhibit the polymerization by quenching the carbocation), the effect of added water on the polymer yield was also studied to determine the water tolerance in these systems. Yet another objective was to study the effect of IL recycling on the polymer yield and on the molecular weights since the IL solvent would need to be reusable in larger scale applications. The effect of the cations and anions of different ILs was also studied with respect to polymer yield.

Experimental Section

Materials. Analytical grades of styrene (99.5%) (MERK), oxalic acid (99%) (MERK), boric acid (99%) (BDH), succinic acid (99.5%) (Aldrich), and glutaric acid (99%) (MERK) were used. Styrene was washed with 10% aqueous sodium hydroxide and then with distilled water and distilled under reduced pressure prior to use. The synthesis of *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide, abbreviated as ([C₄mpyr][NTf₂]), methylethyl imidazolium bis(trifluoromethanesulfonyl)amide, abbreviated as ([C₂mim][NTf₂]), trihexyltetradecylphosphonium bis(trifluoromethanesulfonyl)amide, abbreviated as ([P_{6,6,6,14}][NTf₂]), and trihexyltetradecylphosphonium xylene sulfonate, abbreviated as ILs ([P_{6,6,6,14}][XS]) followed the procedures in the literature.^{31–34}

Measurements. ¹H NMR (300 MHz) spectra of polystyrene samples were recorded using a Bruker 300 FT-NMR instrument with CDCl₃ as solvent and TMS as internal standard. ¹³C NMR (400 MHz) spectra of polystyrene samples were recorded at room temperature using Bruker 400 FT-NMR instrument. The protons were decoupled by broadband irradiation. The molecular weights and their distributions were determined by means of gel permeation chromatography (GPC) at room temperature in a setup comprising a Waters pump equipped with a PLGEL mixed column (particle size 10 μm, dimension 7.5 mm × 600.00 mm with porosity ranging from 50 to 10⁶ Å) calibrated with different polystyrene standards and a differential refractometer detector using tetrahydrofuran as eluent with a flow rate of 1.0 mL/min. The glass transition temperature (*T*_g) was determined by the slope measurement at the onset temperature using Thermal Analysis (TA) software of differential scanning calorimetry (DSC). A standard sample of indium was used to calibrate temperature and power measurements in the DSC over the temperature range from 30 to 170 °C. Typically 5–10 mg of the sample was taken in DSC aluminum pan, and a heating rate of 10 °C/min was used. The carrier gas was helium, and a flow rate of 40 mL/min was maintained during the analysis. Thermal stability was determined by thermogravimetric analysis (TGA). Polymer samples of 4–10 mg were analyzed at a heating rate of 10 °C/min under nitrogen purge at a flow rate of 50 mL/min. The organoborate acids were characterized by electrospray ionization mass spectroscopy which we found to be a useful method of characterizing the anion of the acid (dissociation of the proton takes place in the electrospray process).

Synthesis of Organoborate Salts. Bisoxaloboric Acid (HBOB). The synthesis involves dehydrating 2 mol of aqueous solutions of oxalic acid (9.6 g) with 1 mol of boric acid (3.3 g) under vacuum for 2 h to produce dry white solids (9.8 g) with 98% yields. The electrospray ionization mass spectroscopy was carried out to confirm the purity (HBOB, *m/e* = 186.8 for BOB anion).

Bissuccinoboric Acid (HBSB). This involves dehydrating 2 mol of aqueous solutions of succinic acid (9.7 g) with 1 mol of boric acid (2.5 g) under vacuum for 2 h to produce dry white solids (9.6 g) with 96% yields. The electron spray ionization analysis was carried out to confirm the purity (HBSB, *m/e* = 242.8 for BSB anion).

Bisglutaroboric Acid (HBGB). This involves dehydrating 2 mol of aqueous solutions of glutaric acid (9.7 g) with 1 mol of boric acid (2.3 g) under vacuum for 2 h to produce dry white solids (9.5 g) with 95% yields. The electron spray ionization analysis was carried out to confirm the purity (HBGB, *m/e* = 270.8 for BSB anion).

A single peak obtained for the anions of these salts reveal that the samples prepared were pure and free from impurities.

Synthesis of [C₄mpyr][NTf₂] IL. The synthesis of IL³⁴ was made by stirring equimolar aqueous solutions of *N*-butyl-*N*-methylpyrrolidinium bromide ([C₄mpyr] Br[−] (5.3 g) and lithium bis(trifluoromethanesulfonyl)amide (6.8 g) at room temperature for 3 h. The product (organic phase) was separated from the aqueous phase by a separating funnel and washed with distilled water twice to remove water-soluble impurities. The final product was dried under vacuum at room temperature, and 8.6 g (yield 86%) was obtained. The cation (*m/e* = 142.2) and anion (*m/e* = 280.2) present and the absence of any other ionic impurities were confirmed by ESI mass spectrometry. ¹H NMR (300 MHz, DMSO-*d*₆, δ/ppm relative to TMS) of [C₄mpyr][NTf₂] IL 3.52–3.39 (4H, 2 × CH₂); 3.33–3.27 (2H, NCH₂); 2.98 (3H, NCH₃); 2.15–2.04 (4H, 2 × CH₂); 1.74–1.64 (2H, CH₂); 1.32 (2H, CH₂ *J* = 7.4 Hz); 0.94 (3H, CH₃ *J* = 7.4 Hz).

Synthesis of [P_{6,6,6,14}][BOB] IL. The synthesis involves dehydrating 1 mol of aqueous solutions of trihexyltetradecylphosphonium hydroxide (7.5 g) (abbreviated as [P_{6,6,6,14}][OH]), 2 mol of oxalic acid (2.7 g), and 1 mol of boric acid (0.9 g) under vacuum for 2 h to produce (8.5 g) the product (yield 85%) as a liquid at room temperature. The synthesis of [P_{6,6,6,14}][OH] from [P_{6,6,6,14}][Cl] followed the literature procedure.³¹ The product was confirmed by mass spectrometry for the cations and anions (*m/e* = 484.5 for [P_{6,6,6,14}] cation and *m/e* = 186.8 for BOB anion).

Synthesis of Polystyrene Using HBOB. The polymerization was carried out by dissolving HBOB (0.04 g, 0.21 mmol) in IL medium (0.40 g, 0.94 mmol), and to the homogeneous reaction mixture, 0.18 g (1.7 mmol) of styrene was added and kept at 60 °C for 2 h. Then the reaction mixture was quenched with excess methanol. The IL and initiator dissolved in the methanol, and the polymer was precipitated. The polymer was then washed several times with fresh methanol and dried in a vacuum oven at room temperature. The yield was calculated to be 99%. GPC (THF); *M*_n = 1000 g/mol, *M*_w = 1300 g/mol, *M*_w/*M*_n = 1.3. ¹H NMR (300 MHz, CDCl₃, δ/ppm relative to TMS) of polystyrene: 7.26–6.59 (5H, C₆H₅); 1.83–1.87 (1H, CH); 1.56–1.27 (2H, CH₂). Thus, ¹H NMR spectra of polystyrene samples reveal the absence of [C₄mpyr][NTf₂] IL, suggesting that the polymer obtained was pure.

Results and Discussion

Cationic Polymerization of Styrene with HBOB. Our preliminary experiments³⁰ on cationic polymerization of styrene were carried out using HBOB in a conventional solvent, dichloromethane (DCM), and also in an IL at different temperatures (0–60 °C). Polymerization to high yields occurs only at 60 °C when an IL ([C₄mpyr][NTf₂]) was employed as solvent. This was attributed to an increased degree of dissociation of the HBOB acid at high temperatures in the IL as compared to the molecular solvent. A reaction temperature of 60 °C was therefore employed throughout the present work. Attention was first focused on the HBOB concentration dependence of the cationic polymerization (at fixed reaction time). The results are summarized in Figure 1, where it is seen that the polymer yield increases with concentration and goes effectively to completion when the concentration of HBOB in the mixture was 0.34 mol/

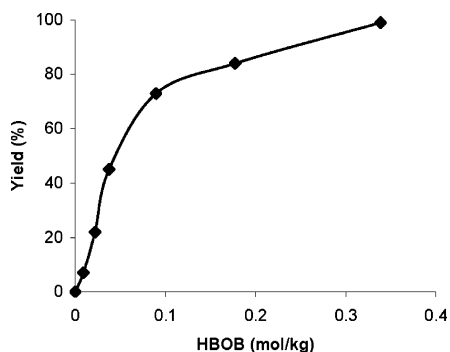


Figure 1. Effect of bisoxalatoboric acid concentration on polymer yield: styrene used = 2.78 mol/kg; $T = 60\text{ }^{\circ}\text{C}$, reaction time = 120 min.

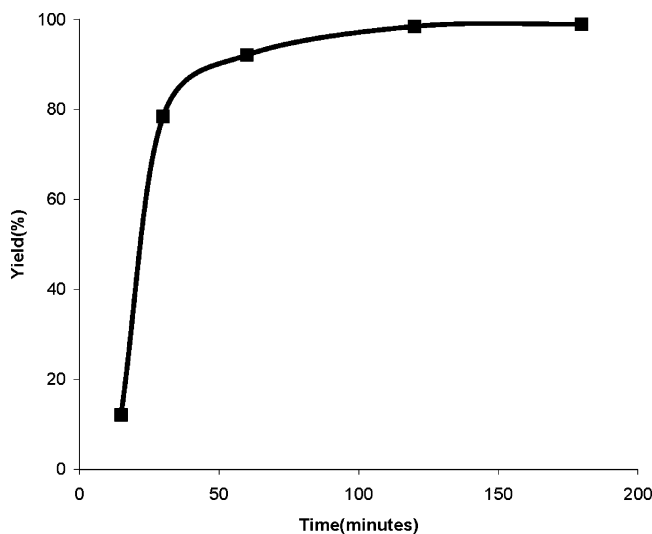


Figure 2. Effect of time (t) on polymer yield: styrene used = 2.78 mol/kg; bisoxalatoboric acid = 0.34 mol/kg; $T = 60\text{ }^{\circ}\text{C}$.

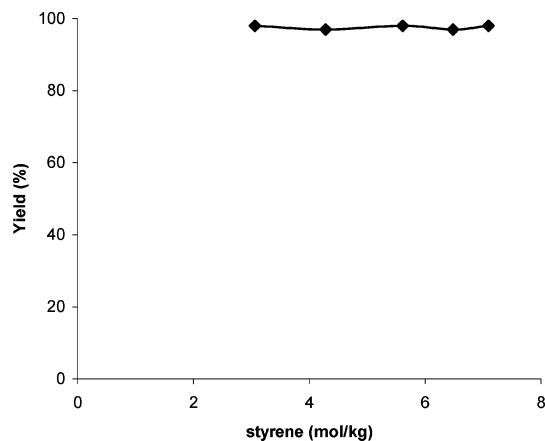


Figure 3. Effect of monomer concentration on polymer yield: bisoxalatoboric acid used = 0.34 mol/kg; $T = 60\text{ }^{\circ}\text{C}$; $t = 120$ min.

kg. The effect of reaction time on the reaction is shown in Figure 2. The results indicate that polymer yields increased with reaction time and reached $\sim 100\%$ at 120 min.

The effect of different monomer concentrations on polymer yield was studied by keeping the HBOB concentration constant. The reaction conditions were maintained at $60\text{ }^{\circ}\text{C}$, and the polymerization time was maintained at 2 h as determined from Figure 2; however, the monomer concentration was progressively increased from that of Figure 2. The experimental observations are presented in Figure 3. It can be seen that the yield of the polymer remains close to 100% with increase in

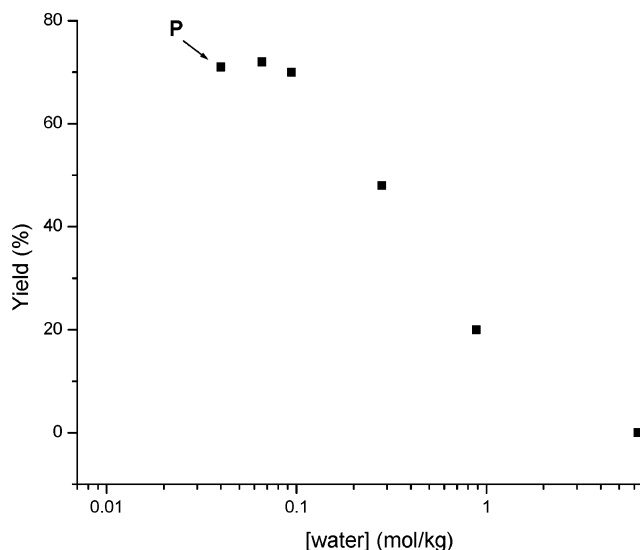


Figure 4. Effect of addition of water on polymer yield: $T = 60\text{ }^{\circ}\text{C}$; $t = 120$ min; bisoxalatoboric acid = 0.09 mol/kg.

monomer concentration. This indicates that the propagating species are active during the entire polymerization, consistent with our earlier observation.

Effect of Water on Cationic Polymerization. The conventional cationic polymerization is carried out under anhydrous conditions,^{14,35} and it can be difficult to achieve these stringent reaction conditions; on the other hand, no real precautions to maintain anhydrous conditions are required for the polymerization carried out here. In order to understand the maximum content of water the process can sustain before which it is inhibited completely, a known amount of water has been added to the reaction mixture to investigate its effect on polymer yield. Before the addition of water, the water contents of monomer, catalyst, and the IL were determined by Karl Fischer (KF) (styrene = 0.02%, IL = 0.04%, and HBOB = 1.2%). Then polymerizations were carried out as a function of water content (3.8×10^{-2} , 5.5×10^{-2} , 1.7×10^{-1} , and 4.2 mmol). The results (Figure 4) show that the polymer yields did not vary much when the water added was 3.8×10^{-2} and 5.5×10^{-2} mmol. But with further increase in water the polymer yield dropped. The polymerization did not occur at all when the water added was 4.2 mmol. The point "P" in Figure 4 shows the water naturally present in the mixture before any addition of water is made. The point at which the water sensitivity appears is approximately the point at which it equals to the initiator concentration, therefore suggesting that the water provides a chain stopping mechanism via production of an OH^- ion to react with the growing carbocation. This would effectively regenerate the original initiator proton, such that water would appear to act as a chain transfer agent. Since the water is very active in the acid/base sense, these transfer events are likely to take place early in the reaction, producing a small amount of terminated oligomeric species which are ultimately washed out of the product. This stage of the reaction would give rise to the induction period observed in Figure 1. Nonetheless, these experiments indicate that the hydrophobic IL environment enables appropriately low water contents to be achieved and maintained such that cationic polymerization can be readily carried out.

Controlled Polymerization of Styrene in HBOB. To examine the nature of this polymerization reaction, a fresh aliquot of monomer (1.72 mmol) was charged to the reaction mixture immediately after the initial charge of the monomer

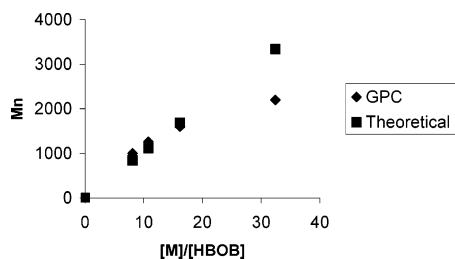
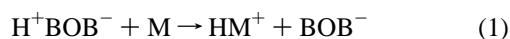


Figure 5. Effect of ratio of styrene to bisoxalatoboric acid ($[M]/[HBOB]$) on number-average molecular weight (M_n).

was completely polymerized (120 min). The reaction was allowed to proceed for another 1 h. The yield was computed and the resulting polymer characterized for molecular weight. As described in our earlier report,³⁰ it was found that the polymer yield increased and the number-average molecular weight (M_n) shows an increase compared to the original value. This shows that the carbocation remains active for further polymerization to take place.

In order to show that all of the carbocations produced during the polymerization were active for different concentrations of initiators, which is necessary for a true *living* polymerization, experiments with increase in molar ratio of monomer to HBOB were performed and are shown in Figure 5. The dependence is linear and the molecular weight close to that predicted from stoichiometry up to around 2250 g/mol. Above this the dependence deviates from the linear behavior, probably as a result of chain transfer (transfer to monomer and initiator) reactions beginning to have an effect, thus lowering the average molecular weight. This would not be the case in a true living polymerization. Thus, in the present system a *controlled* cationic polymerization is taking place.

Mechanism. In order to provide direct evidence for a cationic mechanism, we have carried out experiments in which we substituted the proton of the initiator (HBOB) with Me_4N^+ ; no polymerization was observed, suggesting that the proton is necessary for the polymerization reaction. We have also carried out polymerization experiments using methyl methacrylate, a monomer not susceptible for cationic polymerization, employing HBOB as initiator. The results were, again, no polymerization. These tests prove that HBOB initiates via a cationic mechanism. Therefore, a probable mechanism of HBOB initiated cationic polymerization of styrene in an IL is represented as follows. The initiator HBOB (existing as ion pairs of H^+ and BOB^-) interacts with the monomer to generate the initiation:



Here M represents styrene monomer. It then propagates to form



and the BOB^- anion becomes progressively “lost” within the IL medium of other cations and anions. The ionic atmosphere of the carbocation will be predominantly the anion of the IL. The action of the IL in this process is unlikely to involve direct deprotonation of the HBOB since this particular IL is known to be a member of the exceedingly weak base category of ILs.³⁶ Also, as a consequence of the IL anion being a very weakly basic species, the proton in HBOB is largely unsolvated. Thus, interaction between an HBOB molecule and the monomer, which by comparison is a distinctly nucleophilic species, produces a proton-transfer reaction and thus initiates the reaction. Thus, we propose that the proton transfer must take place directly from the HBOB to the monomer as shown in reaction

Table 1. Effect of Other Organoborate Acids on the Cationic Polymerization of Styrene in IL^a

S no.	initiator	initiator (mol/kg)	yield (%)
1	bisoxalatoboric acid	0.34	96
2	bisoxalatoboric acid	0.17	80
3	bisoxalatoboric acid	0.57	73
4	bissuccinatoboric acid	0.26	27
5	bissuccinatoboric acid	0.13	18
6	bissuccinatoboric acid	0.44	23
7	bisglutaratoboric acid	0.23	23
8	bisglutaratoboric acid	0.12	24
9	bisglutaratoboric acid	0.39	26

^a Styrene = 2.78 mol/kg, reaction time = 120 min, and temperature = 60 °C.

Table 2. Effect of Other ILs on the Cationic Polymerization of Styrene^a

S no.	IL used	M_w , GPC (g mol ⁻¹)	M_n , GPC (g mol ⁻¹)	PDI	yield (%)
1	[C ₄ mpyr][NTf ₂]	1300	1000	1.3	99
2	[C ₂ mim][NTf ₂]	1380	1080	1.3	90
3	[P _{6,6,6,14}][NTf ₂]	1470	1100	1.3	75
4	[EmIm][CH ₃ COO]				trace
5	[P _{6,6,6,14}][XS]				trace
6	[P _{6,6,6,14}][BOB]				trace

^a Styrene = 2.78 mol/kg, HBOB = 0.34 mol/kg, T = 60 °C, and t = 120 min.

1. The role of the IL in this respect then is to present an extremely weak basic environment in which direct interaction between the monomer and the acid molecule can take place.

The IL may also have an independent effect on the reactivity of the monomer species. There have been reports that aromatic compounds in ILs have higher electrostatic multipole moments compared to aliphatic compounds and hence are more polarizable.³⁷ The importance of electrostatic interactions in determining the properties of mixtures of aromatic compounds and ILs has also been studied.³⁸ In that work the use of aromatic compounds with differing quadrupole moments showed an interaction of the local molecular electrostatic field and the surrounding ionic atmosphere. The IL thus may reinforce the natural polarization of the vinyl double bond of styrene, thus increasing its reactivity. Ab initio calculations of the polarizability are underway to simulate this effect.

Effect of Other Organoborate Acids. Other organoborate acids (viz., HBSB and HBGB) were prepared and employed as initiators in the cationic polymerization of styrene. The reaction was allowed to proceed for 2 h at 60 °C. As expected, with the increase in alkyl chain length of the organoborate acids, both the acidity and also the polymer yields decreased at a given reaction time. The results are summarized in Table 1. Experiments with different concentrations of the salts were also carried out, and in the case of HBSB and HBGB, the polymer yields did not vary appreciably. The aqueous pH of these acid salts (0.1 M) were measured, and it was found that HBOB has the maximum pH (1.4) compared to HBSB with pH (2.5) and HBGB with pH (4.5). This indicates that the acidity of the initiator is an important factor in the initiation step (reaction 1).

Effect of Other ILs on Polymer Yield. Studies were undertaken to investigate the effect of other ILs in the cationic polymerization of styrene using HBOB as initiator. The results are summarized in Table 2. These show that the polymerization takes place if the anion is $[NTf_2]^-$ independent of the cation, but when the anion is changed from $[NTf_2]^-$, the polymerization did not occur. This observation provides further evidence of

Table 3. Effect of Recycled IL on the Cationic Polymerization of Styrene^a

S no.	HBOB (mol/kg)	IL	M_w , GPC (g mol ⁻¹)	M_n , GPC (g mol ⁻¹)	PDI	yield (%)
1	0.34	1st recycle	2918	2000	1.45	86
2	0.34	2nd recycle	2967	2028	1.46	80
3	0	1st recycle	—	—	—	0

^a Styrene = 2.78 mol/kg, IL used = [C₄mpyr][NTf₂], and t = 120 min.

Table 4. Effect of HBOB Concentration on Polymer Molecular Weights^a

S no.	[M]/[HBOB]	M_w , GPC (g mol ⁻¹)	M_n , GPC (g mol ⁻¹)	PDI
1	32.4	2684	2089	1.28
2	16.2	1707	1332	1.28
3	10.8	1675	1260	1.32
4	8.1	1300	1000	1.30

^a Styrene = 2.78 mol/kg, reaction time = 120 min, and temperature = 60 °C.

the importance of the extremely weak basicity of the [NTf₂]⁻ anion.³⁶ The other anions are distinctly more basic than the [NTf₂]⁻ and are sufficiently so to completely deprotonate the HBOB and effectively “absorb” the proton onto a lower energy site from which it is unable to protonate the monomer. In the case of the acetate and xylene sulfonate anions, a side reaction involving the ester formation with the growing carbocation can be expected to dominate the reaction. In the case of BOB salt the high concentration of the BOB anion will tend to displace reaction 1 toward the left, thus slowing the rate of the reaction.

Recovery and Reuse of IL. The IL ([C₄mpyr][NTf₂]) along with the acid residues were recovered as described in our earlier work.³⁹ This recovered IL was reused in further polymerization reactions (with a fresh quantity of HBOB), and it was found (Table 3) that high, though decreasing, yields were obtained. The decrease in yield could be due to the presence of slightly higher contents of water in the recycled IL as against pure IL. When fresh HBOB was not added, no reaction was observed, confirming the consumption of the HBOB during the reaction.

Molecular Weight Determination. The polymers were characterized for molecular weights by employing gel permeation chromatography (GPC) for different initiator concentrations in Table 4. The results indicate that molecular weights decrease, as expected, with increase in initiator concentration. In all these cases the polydispersity values remained very narrow. The polymers prepared from recycled IL were also characterized for molecular weights, and the results are given in Table 3. Here the molecular weights slightly increased compared to the fresh IL experiment, but the dispersity values were found to be narrow. Thus, the IL solvent can be recycled and used in the cationic polymerization process of styrene without much alteration of the molecular weight properties. In a similar manner the polymers prepared using different ILs were also characterized. The results show (Table 2) that molecular weights were not significantly altered when different ILs were used.

Thermal Properties. A typical thermogram of the polystyrene obtained by cationic mechanism initiated by HBOB is provided as Supporting Information (ESI-1). The T_g in these low molecular weight samples (61 °C) is lower than conventional polystyrene (~100 °C), as expected.^{40,41} Tacticity⁴⁰ and solvents⁴² are also known to have an effect on T_g in polystyrene. There could be a plasticizing effect of residual IL,⁴³ however, ¹H NMR studies reveal that the polymer obtained was substantially free of IL.

The polystyrene produced by the initiation of HBOB was also characterized for thermal stability by thermogravimetric analysis; a typical trace is provided in the Supporting Information (ESI-2). The results reveal high thermal stability for these polymers similar to standard polystyrenes. The polymers were fairly stable up to 300 °C, and the complete decomposition occurred at around 430 °C.

Tacticity. The triplet obtained for the two methylene protons in the ¹H NMR of polystyrene suggests that they are equivalent and that the polymer obtained could have some syndiotactic behavior as compared to the nonequivalent protons expected for isotactic polystyrene.⁴⁴ The expanded ¹³C NMR spectrum (provided as Supporting Information, ESI-3) indicates a mixture of polymer triad sequences (syndiotactic, isotactic, and atactic); however, a predominance (43%) of syndiotactic sequences was noticed. The determination of sequences followed the literature procedure.⁴⁵ The isotactic triad sequences (mm), syndiotactic sequences (rr), and atactic sequences (mr) are observed between 145.5 and 147 ppm on the quaternary carbon signal of polystyrene. A similar trend was also observed in the FTIR spectrum recorded for this polymer. The spectra for pure syndiotactic polystyrene generally contains sharp bands, as opposed to relatively broad bands obtained for atactic and isotactic polystyrene samples.⁴⁶ It has been reported that for pure syndiotactic⁴⁷ polystyrene the bands occur at 543, 739, 895, 1027, and 1200 cm⁻¹. In the present study the polystyrene sample showed sharp bands respectively at 546, 703, 766, 903, 1030, and 1177 cm⁻¹, indicating a component of syndiotactic behavior. Future studies will seek to optimize the tacticity control in this reaction.

Conclusions

We have successfully demonstrated that the cationic polymerization of styrene can be carried out in room temperature ILs employing novel organoborate acids as initiators. The Bronsted acidity of the initiator is one of the factors for the polymerization to take place as is the very weak basicity of the IL. The polymers obtained by using bisoxalatoboric acid produced controlled polymers with narrow polydispersity and are predominantly syndiotactic. The hydrophobic nature of the IL allows relatively easy to achieve polymerization and maintain the low water contents required to avoid water interference in the reaction. Thus, overall, the method described is one that can be carried out under more mild conditions than is typically the case for cationic polymerization.

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Supporting Information Available: Typical thermogram of the polystyrene obtained by the cationic mechanism initiated by HBOB, TGA curve of polystyrene prepared by cationic polymerization, and expanded ¹³C NMR spectrum of quaternary signal of polystyrene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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