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Synthesis of Piperazine Based Polyimide in the Presence of Ionic Liquids

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Ionic liquids derived from imidazolium, pyridinium, and alkylammonium salts were investigated not only as catalysts but also as solvents in polymerization of 1,4-bis(3-aminopropyl) piperazine. Results were compared with the conventional polymerizations in *N*-methylpyrrolidone (NMP). The catalyst has not only a detectable influence on polymer solubility, but also the degrees of polymerization are notably higher. They are even greater than the values obtained by conventional 2-stage polymerization in organic liquids. Ionic liquids based on imidazolium salts seem preferable over pyridinium and alkylammonium salts due to the higher degree of polydispersity of the polyimides obtained. The glass transition temperatures and thermal stabilities were higher for polyimide synthesized in ionic liquids than conventional polyimides prepared in aprotic solvents.

Key Words: Ionic liquids, polyimide, catalysts, condensation polymers.

Introduction

Room-temperature ionic liquids (RTILs) are compounds consisting of abundant ions that exist in the liquid state at room temperature.[1,2] As novel attractive solvents, they hold unique properties such as appropriate vapor pressure, wide potential windows, high thermal stability, high viscosity, and good conductivity and solubility.[3] In recent years, researchers have started to explore RTILs, especially 1-butyl-3-methyl-imidazolium tetrafluoroborate (bmim·BF_4) and 1-butyl-3-methyl-imidazolium hexafluorophosphate, as alternative media for biocatalysis.[4,5] Another interesting application is to use ionic liquids in polymerization. Conventional polymerizations have usually been carried out in volatile organic solvents or in water. To date, studies have investigated ionic liquids[6−9] and supercritical fluids[10] as new solvents in polymerization. However, the latter requires special equipment and safety measures due to the high pressures involved. Ionic liquids offer the use of standard reactions, and solvent properties may vary broadly with structural changes in the cation and the anion. This structural variability is inherently limited by the stability of the ionic

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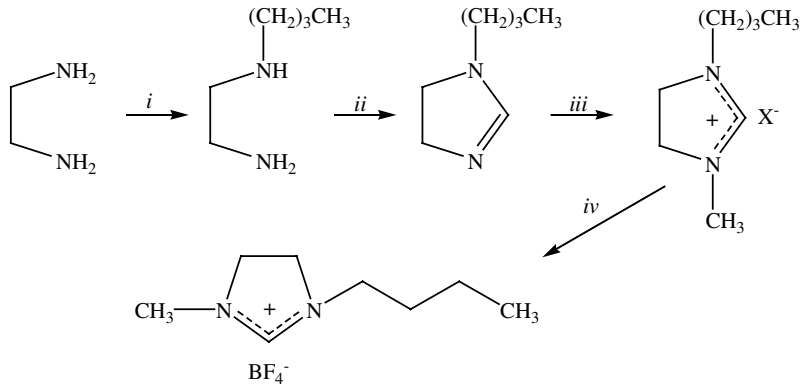
liquids under the reaction conditions. The benefits of using ionic liquids can be seen in their negligible volatility and nonflammability, their ability to dissolve homogeneously in many organic and inorganic compounds, and the possibility to influence the chemical reaction products. Free radical,[10−24] coordination,[25,26] cationic,[27,28]group transfer,[29] or enzymatic[30] reactions were also carried in ionic liquids. In fact, the beneficial effect of ionic liquids on the molar masses of the polymers obtained is not a general feature because, in other examples, small or even negative effects on the molar masses using ionic liquids as solvents of polymerization were reported.[31−39] Moreover, most free radical polymerization studies have focused on the use of 1-butyl-3-methylimidazolium hexafluorophosphate.

In this paper, we report the polymerization of 1,4-bis(3-aminopropyl) piperazine in N-methyl-2-pyrrolidinone (NMP) catalyzed by an ionic liquid (Scheme 1) as a catalyst. The ionic liquid used was only 5 wt% of the organic solvent. The polymerization by the ionic liquid catalyst was well-controlled, producing polymers with controlled molecular weights and low polydispersity. After the polymerization, the ionic liquid catalyst settled on the bottom of the reactor, where it was easily separated from the polymer solution.

Experimental

Chemicals. 1-Ethyl-3-methylimidazolium tetrafluoroborate (**1**) (purity ≥98%), 1-ethyl-3-methylimidazolium hexafluorophosphate (**2**) (purity ≥97%), 1-ethyl-3-methylimidazolium tosylate (**3**) (purity ≥98%), 1-ethyl-3-methylimidazolium ethyl sulfate (**4**) (purity ≥98%)1-butyl-3-methylimidazolium octyl sulfate (**5**) (purity ≥98%), 1,3-dimethylimidazolium dimethyl phosphate (**6**) (purity ≥98%), 1-butyl-4-methylpyridinium tetrafluoroborate (**7**) (purity ≥97%), and 1-butyl-4-methylpyridinium hexafluorophosphate (**8**) (purity ≥97%) were purchased from Fluka, and reagent grade aromatic dianhydride was used as received.



Scheme 1. Synthetic route for RT-ILs (room temperature ionic liquids) *i*: Li, 110 °C, BuCl 24 h, *ii*: $(CH_3)_2NCH(OCH_3)_2$, 110°C, *iii*: DMF CH_3I; *iv*: Cl_2CH_2, NH_4BF_4.

Characterization. Infrared spectra were recorded as KBr pellets in the range of 4000-400 cm^{-1} on an ATI UNICAM systems 2000 Fourier Transform spectrometer. Differential scanning calorimetry (DSC), differential thermal analysis (DTA), and thermogravimetry (TGA) were performed on Shimadzu DSC-60, DTA-50, and TGA-50 thermal analyzers, respectively.

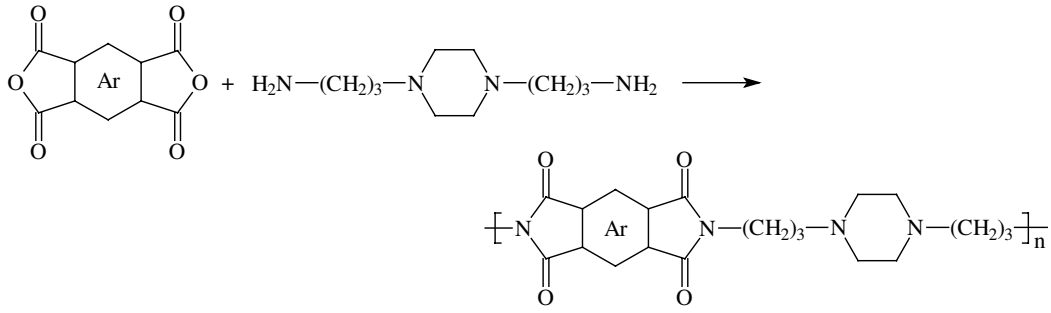
GPC analyses were performed at 30 °C using NMP as eluent at a flow rate of 0.5 mL/min. A differential refractometer was used as a detector. The instrument (Agilent 1100 series GPC-SEC system)

was calibrated with polystyrene standards (polysciences; molecular masses between 200 and 1,200,000 Da) using GPC software for the determination of the average molecular masses and the polydispersity of the polymer samples.

Electrochemical measurements were performed at room temperature using a CHI 830 workstation (CH Instruments, Inc.). Electrochemical measurements were carried out in a conventional 3-electrode system with a free standing film electrode as the working electrode, a platinum wire as the auxiliary electrode, and a Ag/AgCl (saturated KCl) electrode as the reference electrode. A 50 mM phosphate buffer solution or 50 mM glycine-hydrochloric acid (GHA, pH 3.0) buffer solution was used as the electrolyte in all experiments. The buffer solutions were purged with highly purified nitrogen for at least 30 min by continuously bubbling nitrogen before measurements, and a nitrogen blanket was kept on the cell.

Synthesis of polyimides

The polymer synthesis is shown in Scheme 2. A typical polyimide synthesis was performed as follows: monomer 1,4-bis(3-aminopropyl) piperazine (4.15 mmol) and ionic liquid 1-8 5% of the solvent were dissolved in 15 mL of NMP in a 100 mL Schlenk tube equipped with a nitrogen line, overhead stirrer, and a condenser. BTDA (4.15 mmol) was added to the amine solution which was stirred to 30 °C for 0.5 h to give a viscous solution. The ionic liquid was only 5 wt% of the organic solvent. The polymerization by the ionic liquid catalyst was well-controlled, producing polymers with controlled molecular weights and low polydispersity. The mixture was refluxed to 200 °C for 18-20 h. Following the reaction, the mixture was cooled to room temperature and precipitated in excess methanol. The dark amber product was isolated and dried at 100 °C under vacuum and then heated to 200-230 °C under nitrogen for 2 h.



Scheme 2. Synthesis of polyimides.

Results and Discussion

The synthesis 1-(methyl)-3-butylimidazolium tetrafluoroborate is shown in Scheme 1. To fulfill the requirements as a polymerization solvent, ionic liquids should preferentially exhibit good thermal and chemical stability, a broad temperature window for the liquid state, and low melt viscosity. These properties depend sensitively on the nature and the substitution pattern of the organic cation and the nature of the anion. They are also markedly influenced by the water content. The ionic liquids distinguished by the substitution pattern of the cation and by the nature of the anion. The anions comprise either classical examples, such as tetrafluoroborate and hexafluorophosphate, or oxyanions with low nucleophilicity, such as tosylate, ethyl sulfate, octyl sulfate, trifluoro methane sulfonate, and dimethyl phosphate.

Table 1. Water content and physical properties of the ionic liquids investigated.[a]

Ionic liquid	water (wt%)	T_g (°C)	$T_{recryst}$ (°C)	T_m (°C)	pKa
1	0.8	-97	-67	16	4.67
2	0.2	-78		-12	5.92
3	1.5	-46	12	53	5.67
4	0.7	-92			5.90
5	1.8			-33	5.76
6	0.1	-64			4.48
7	0.1	-74			5.54
8	0.08	-55	1	20	5.45
NMP					4.75

[a] T_g = glass transition temperature, $T_{recryst}$ = temperature of recrystallization, T_m = melting temperature, all values derived from DSC heating scans.

The latter anions are chemically more inert and less toxic. The physical properties of the ionic liquids vary broadly because of their molecular structure (Table 1).

DSC studies (Table 1) show that ionic liquids can be glass forming materials (**4**, **6**, and **7**), semicrystalline materials (**1**, **2**, **3**, and **8**), or crystallizing substances (**5)**.

The nature of ionic liquids has a well-defined influence on the behavior of the monomer. The polymer conversion is strongly influenced by the acidity and the basicity of the monomers; hence, molecular weight is affected. The polymer yields varied markedly with the specific solvent used for polymer synthesis although the conditions were the same in all cases (Table 2). Mostly, yields are higher for the polymers prepared in ionic liquids than for the polymers produced in NMP as shown in Table 2.

Table 2. Gravimetric yield, number of average molar mass (M_n), weight average molar weight (M_w), and polydispersity (PDI) of polyimide synthesized from PMDA in ionic liquids as catalyst (5% of the solvent), and the total amount of recovered ionic liquid (IL_{total})^{b,a} measured at a concentration of 0.5 g/dL in NMP at 30 °C using an Ubbelohde viscometer.

Solvent	Polymer Yield (%)	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$	*PDI*	η (dL/g)^a	IL_{total} (%)^b
1	91	3.84	5.17	1.34	2.09	97
2	94	2.09	3.55	1.69	1.99	95
3	92	3.89	5.81	1.49	1.89	92
4	95	3.85	5.18	1.34	2.23	89
5	89	2.88	4.22	1.46	1.98	99
6	87	3.91	5.81	1.49	2.32	98
7	85	2.59	5.15	1.98	2.65	93
8	88	3.09	5.21	1.68	2.37	97
NMP	78	0.89	3.28	3.68	1.15	-

Table 3. Solubility of polyimides.

Polymer	P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8	PI
Solvent	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**NMP**
Solubility[a]									
NMP	+	+	+	+	+	+	+	+	-
DMF	+	+	±	+	+	+	±	+	±
DMAc	+	+	+	+	+	+	+	+	-
THF	±	-	-	-	±	±	±	±	-
Hexane	-	-	-	-	-	-	-	-	-
DMSO	±	+	+	±	+	+	+	+	-

[a](Solubility tested at 2% solid concentration; + soluble at room temperature (25 °C); ± soluble upon heating; - insoluble at room temperature)

To determine the efficiency of an ionic liquid as a catalytic medium in polyimide synthesis, a piperazine based monomer was chosen as a model compound. We do know that piperazine based monomers exhibit low reactivity toward dianhydrides and do not form high molecular weight polyimides via common 2-stage polycondensation procedure in organic solvents (e.g., NMP and m-cresol) in the absence of a catalyst. The results demonstrate that high molecular weight polyimides are formed in such a novel reaction medium with ionic liquids acting as a catalyst. Properties of polyimides greatly depend on the nature of the ionic liquids as well as pKa values of the monomer. The polyimide samples obtained by polymerization in various ionic liquids were analyzed by size exclusion chromatography (SEC). In comparison with the polymer made in NMP, the samples synthesized in ionic liquids show higher molar masses and polydispersity on one hand, and higher solubility in dipolar aprotic media on the other hand (Tables 2 and 3). As depicted in Figure 1, the molar mass of the polymer synthesized in **3** is significantly higher than that of the one synthesized in NMP. Furthermore, the molar masses of the polymers exceed even the value of the polymer obtained by classical polymerization.

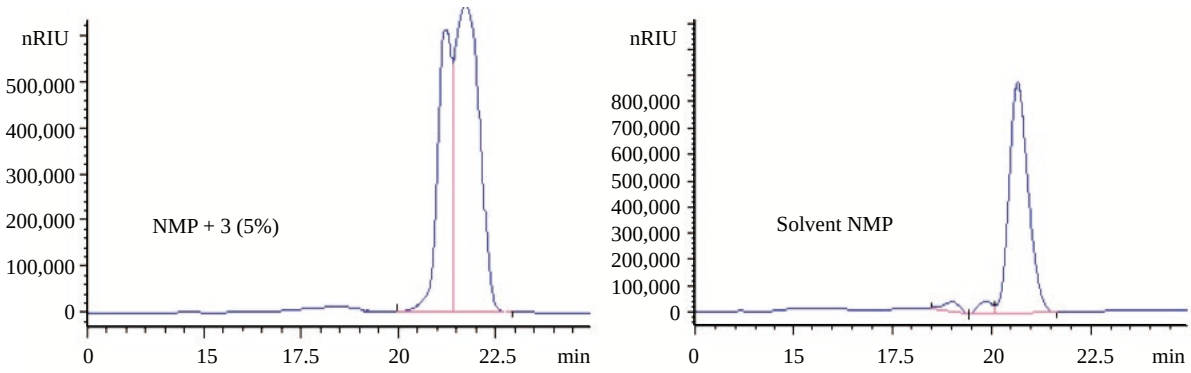


Figure 1. GPC chromatograms of polyimide polymerized in **3** and NMP.

However, when the data were analyzed, a general increase in the molar mass with the viscosity was not found for all ionic liquids investigated in polymerization. On the other hand, the viscosity of the ionic liquids seems to exert a beneficial influence on polymerization. The degrees of polymerization (X_n) obtained when

polymerizing in 1-alkyl-3-methylimidazoliumtetrafluoroborate, **1**, in 1-alkyl-3-methylimidazolium hexafluorophosphates, **2**, and in the 1-alkyl-3-methylimidazolium salts **4**, **6**, and **7** tend to increase approximately with the increase in viscosity. All X_n obtained, when ionic liquids with 1-alkyl-2,3-dimethylimidazolium cations are used, are analogous even though the solvent viscosities change considerably. Nonetheless, the higher viscosity of 1-alkyl-2,3-dimethylimidazolium salts is reflected by higher X_n values for the polymers obtained as compared with the one using their 1-alkyl-3-methylimidazolium analogues. Moreover, the hexafluorophosphate **2**, the tosylate **3** (X_n is about 2900), and the octyl sulfate **5** (X_n is about 1100) do not fit into the trend of an increase in X_n of the polymer with ever-increasing viscosity of the ionic liquid used for polymerization. The polymers synthesized in **2** and **3** show a high degree of polymerization although the viscosity of these ionic liquids is not quite as high. High melting points of **2** and **3** and locally ordered structures may favor the polymerization in these solvents. Differing from the other imidazolium salts with only small substituents at the anion, the relatively high viscosity of the polymer using octyl sulfate **5** is caused by the long alkyl chain at the anion. The ionic liquids **7** and **8** were used as a reference in order to have an idea on the role of the chemical nature of the cation on polymerization. The use of the *N*-alkyl-4-methylpyridinium salts tends to result in moderately low degrees of polymerization and very high polydispersities compared to the ones in which analogously substituted 1-alkyl-3-methyl imidazolium tetrafluoroborate and hexafluorophosphate were used, although the viscosities of **7** and **8** are higher. Possibly, the benzylic methyl group gives rise to chain transfer side reactions, which needs to be explored further in future studies. As shown, the glass transition temperatures of the polymers increase significantly with the increasing degree of polymerization for values of X_n below 400. Above this value, the glass transition temperature levels off. The lowest glass transition temperature is observed for the polymer produced in NMP, which is in agreement with the lowest value of X_n. The majority of the polymers synthesized in ionic liquids show a glass transition temperature similar to the ones obtained by bulk polymerization.

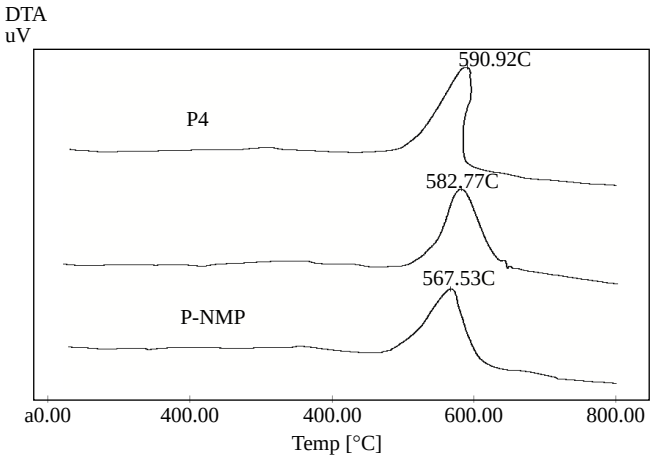


Figure 2. DTA thermograms of typical polyimides P4, P6, and P-NMP.

DTA and thermogravimetric analyses (Figures 2 and 3) indicated that thermal stability is lower for the polymer produced in NMP compared to the ones produced in ionic liquids. No significant differences were found between the samples. The higher thermal stability of the polymers synthesized in ionic liquids may be explained by the higher degree of polymerization for these polymers, leading to less volatile thermolysis fragments. Alternatively, a different ratio of termination by recombination and disproportionation might be discussed. The use of ionic liquids as solvents in polymerization instead of classical solvents such as NMP

offers attractive advantages, such as markedly higher degrees of polymerization, higher glass transition temperatures, and higher thermal stabilities. However, additional efforts are necessary for purification of the polymers and recovery of the precious ionic liquids after polymerization. The FT-IR spectra of polyimide (Figure 4) showed aliphatic C-H stretching frequencies between 2850 and 2930 cm^{-1}, symmetrical imide stretching ν (C=O) between 1725 and 1727 cm^{-1}, asymmetrical imide ν (C=O) stretching between 1783 and 1785 cm^{-1}, and C-N imide ring stretching between 1382 and 1396 cm^{-1}. Imide ring deformation appeared at near 1070 cm^{-1} and C-N bending at 723-759 $cm^{-1}$and the C=N peak at 1641 cm^{-1}. The formation of polyimides was confirmed by the appearance of absorption bands at around 1770 cm^{-1} and 1720 cm^{-1} (C=O) and at about 1360 cm^{-1} (C–N), which are characteristic of imide group.

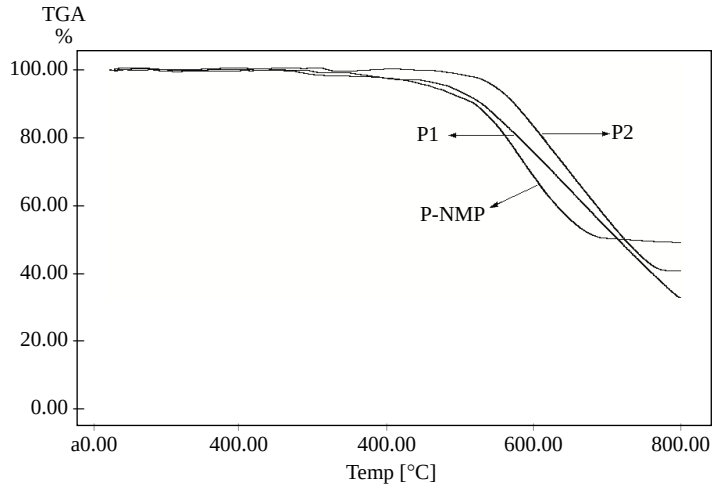


Figure 3. Weight loss of polyimide manufactured in selected solvents upon heating under nitrogen.

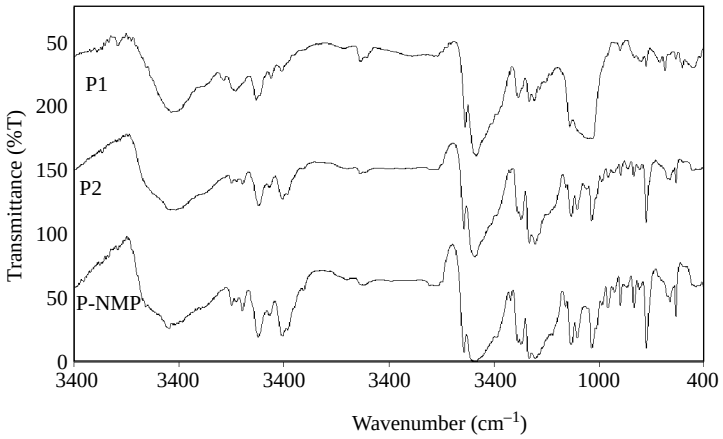


Figure 4. FTIR spectra of the polyimides (P1, P2, and P-NMP).

Cyclic voltammogram (CV) of the typical ionic liquids prepared, **2**, is given in Figure 5, which, in the presence of oxygen, showed a reduction peak at approximately $>$ 1.0 V and an oxidation peak at $<$ 1.0 V vs. Ag/AgCl. The background currents in the 2 reaction medium are comparable, indicating that the ionic liquid is also electrochemically stable.

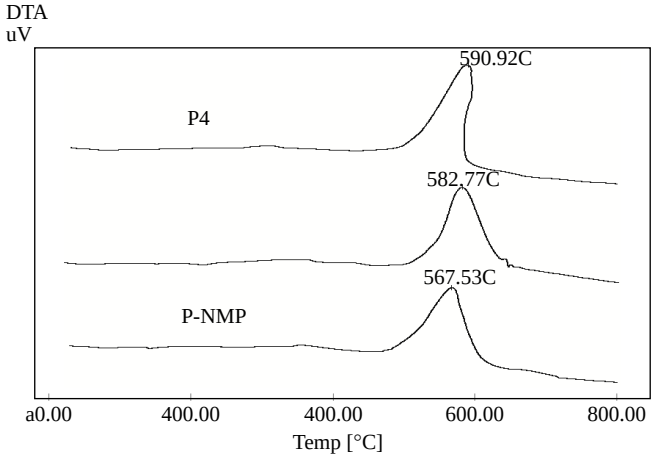


Figure 2. CVs for various scan rates ∼mV/s in oxygen. The working electrode was glassy carbon and the reference electrode was Ag/AgCl.

Conclusions

Ionic liquids do not only offer some general advantages as new solvents, such as low volatility and non-flammability, they also have a beneficial effect on polymerization. The use of ionic liquids results in higher molar masses of the polymers, which can exceed even the molar masses obtained from bulk polymerization. Consequently, the glass transition temperature of the polymers is increased and their thermal degradation is reduced in comparison to the polymer produced via solution polymerization in NMP. Such effects are prevalent for ionic liquids having different cation and anion structures. Nevertheless, significant differences in the molar mass and the polydispersity were found between the polymers synthesized in various ionic liquids; hence the optimization of polymerization requires a careful selection of the ionic liquid. Imidazolium based ionic liquids are preferable over *n*-alkyl-4-methylpyridinium and aliphatic ammonium salts since they exert a more advantageous effect on polymerization. High molar masses of polymers are favored by high viscosities of the imidazolium salts or by conducting polymerizations close to the melting temperature of the ionic liquids. One may speculate that this behavior is due to locally ordered structures that favor the polymerization reaction under these conditions. Importantly, efficient recycling of the ionic liquids after polymerization, as needed for practical applications, is feasible by simple decantation and extraction procedures.

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