P-1-04

Polycondensation in Ionic Liquids for Synthesis of Polyamides and Polyimides

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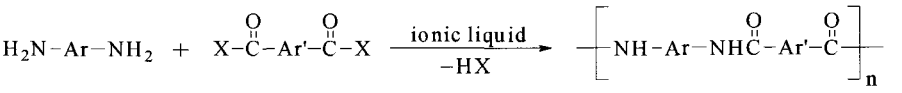
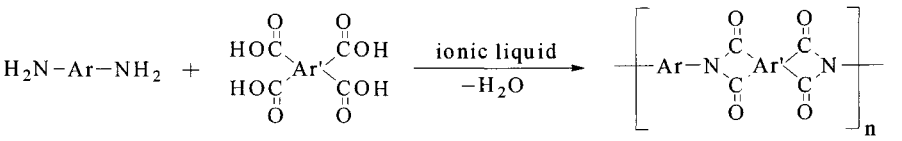
Ionic liquids (ILs) are low melting salts consisted of organic cations and inorganic anions, and have attracted increasing interest for reaction media, because of their unique chemical and physical properties, such as non-volatility, highly thermal stability, chemical stability, chemical inertness, and so on. Furthermore, ILs can be designed to fit a particular application. So far, a number of chemical reactions have been reported to use ILs as reaction media.[1,2] The toxicological studies show also that ILs are rather non- toxic substrates.

For performing the synthesis of polymers, ILs have also received much attentions as new solvents. In the field of chain polymerizations, radical polymerization,[3] living radical polymerization (atom transfer[4] and reversible addition- fragmentation chain transfer[5]), living cation polymerization[6] have been reported. In these polymerizations, high polymerization rate and narrow distribution of molecular weight can be achieved compared with ordinal method using ordinary organic solvents. By the way, only a few polycondensation has been reported.[7,8] In this study, we discuss the synthesis of polyamides (scheme1) and polyimides (scheme2) in ILs.



(1)

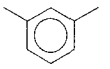
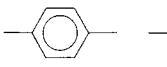
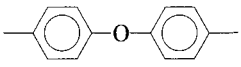
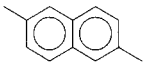
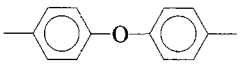
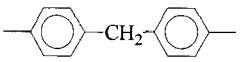
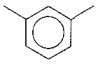
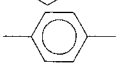


(2)

Generally wholly polyamides were prepared from aromatic diamines and active aromatic diacid chlorides in aprotic polar solvents such as DMAc, DMF, and NMP. First we examined the synthesis of polyamides from diamines and diacids chlorides in ILs (Scheme1, X=Cl) in various reaction condensations. Among many ionic liquids containing 1- butyl- 3- methylimidazolium cation, 1- butyl- 3- methylimidazolium hexafluorophoaphate ([bmim][PF_6]) was most suitable solvents, judging from polymerization proceed rapidly and finished at 155℃ within 1.5h. Acid acceptors such as Na_2CO_3, sodium acetate, and N,N-dimethylaminopyridine were not necessary for this polycondensation, because hydrogen chloride as by-products was released from the reaction solution. Table 1 shows the synthesis of various polyamides in [bmim][PF_6] at 155℃ under nitrogen. All polyamides could be obtained quantitatively and their inherent viscosities were still moderate, because the precipitation of the polymers was observed during the polymerization.

During the use of ILs as reaction solvents, we have found that the amide bonds could be prepared from amines and non- active carboxylic acids in ILs without any activating agents. This novel reaction promises the synthesis of aromatic polyamides from non- active diacids. Then we examined the direct polycondensation of aromatic diamines and aromatic diacids in ILs without condensing agent (Scheme1, X=OH).

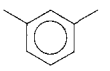
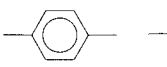
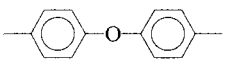
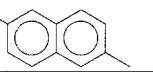
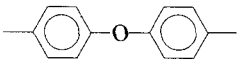
Table 1. Synthesis of Polyamides from Diamines and Diacid Chlorides in [bmim][PF_6] [a)]

diamine \ diacid				
	0.37	0.33	0.69	0.24
	0.24	0.24	0.36	0.36
	0.20	0.23	0.33	0.25
	0.18	0.22	0.23	0.23

a) Polymerization condition: diamine , 1.0 mmol ; diacid chloride , 1.0 mmol ; [bmim][PF_6] , 2.5 mL at 155 °C for 1.5 h under nitrogen.
Inherent viscosity were measured at a concentration of 0.5 g/dL in conc. H_2SO_4 at 30 °C.

While polyamides could not be prepared in aprotic polar solvents such as DMAc without condensating reagents even at high temperature, [bmim][PF_6] gave the polymers in high yields at 155°C, as shown in Table 2. Other ILs such as [bmim][Cl], [bmim][Br], and [bmim][BF_4] could not be used for this polymerization. Compared with active diacid chlorides, reactions proceed slowly and longer reaction time was necessary to give the polyamides with higher molecular weights.

Table 2. Synthesis of Polyamides from Diamines and Diacid in [bmim][PF_6] [a)]

diamine \ diacid				
	0.79	0.21	0.20	0.12

a) Polymerization condition: diamine , 1.0 mmol ; diacid , 1.0 mmol ; [bmim][PF_6] , 5.0 mL at 155 °C for 24 h under nitrogen.
Inherent viscosity were measured at a concentration of 0.5 g/dL in conc. H_2SO_4 at 30 °C.

Based on above results for polyamides, we determined the preparation of polyimides from diamines and tetraacids (Scheme2). In [bmim][Br], [bmim][BF_4], and [bmim][PF_6], except for [bmim][Cl], polycondensation proceeded smoothly at 180°C to give polyimides with inherent viscosities of 0.05 - 0.08 dl/g in high yields.

References

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