

Polymerizations using Diisocyanates in Ionic Liquids

Masaru Yoneyama*, Hiroko Ueda, Nahoko Ichimura, and Daisuke Ohga

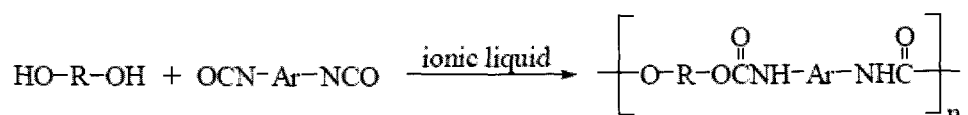
Department of Chemistry and Chemical Biology
Graduate School of Engineering, Gunma University
Tenjin-cho 1-5-1, Kiryu, Gunma 376-8515, Japan

Introduction Ionic liquids (ILs) are low melting salts and consist of organic cations and inorganic anions. Research in the field of ILs has grown exponentially in recent years, because of their unique chemical and physical properties such as low vapor pressure, highly thermal and chemical stability, high polarity, and so on¹⁾. Furthermore, ILs are advanced solvents, which can be designed to fit a particular application. Regarding industrial safety and environmentally friendly use, ILs can serve as effective substitutes for the conventional organic solvents. So far, ILs are employed as media for a wide variety of reactions and polymerizations such as radical polymerizations²⁾, cationic polymerizations³⁾, and polycondensations⁴⁾. However, there are no reports of polyadditions using ILs.

Isocyanates are highly unsaturated organic compounds and react readily with many compounds containing active protons as alcohols, amines, and carboxylic acids to provide urethanes, ureas, and amides. In ILs as a reaction medium, these reactions of isocyanates also proceed smoothly^{5,6)}. In this work, three types of polyadditions of high reactive aromatic diisocyanates with diols, diamines, and dicarboxylic acids were discussed in details using ILs to give polyurethanes, polyureas, and polyamides.

Results and Discussion

<Synthesis of Polyurethanes>



Polyaddition of ethylene glycol and diphenylmethane-4,4'-diisocyanate were carried out in various reaction conditions. During the polymerization in four kinds of imidazolium-type ILs such as 1-butyl-3-methylimidazolium chloride ([bmim][Cl]), [bmim][Br], [bmim][BF₄], and [bmim][PF₆], the precipitations of the polymers were observed. Among these ILs, there is no clear difference for the molecular weights and yields of polyurethanes obtained. Figure 1 shows the yields and inherent viscosities of the polymers prepared in [bmim][BF₄] at various polymerization temperature for 1.5 h. Both yields and inherent viscosities increased with the increase of temperature up to 150°C. Over 160°C, the molecular weights decreased. The addition of isocyanates with alcohols in ILs proceeded rapidly similar to that in the conventional organic solvents, as shown in Figure 2. While the yields over 80% of the polymers were obtained for only 0.25 h, the molecular weight of the polymer

* 群馬大学大学院 応用化学・生物化学専攻 米山 賢

continued to increase and the highest value of inherent viscosities for the polymers was obtained for 1.5h. However, longer polymerization time caused the decrease of the inherent viscosities.

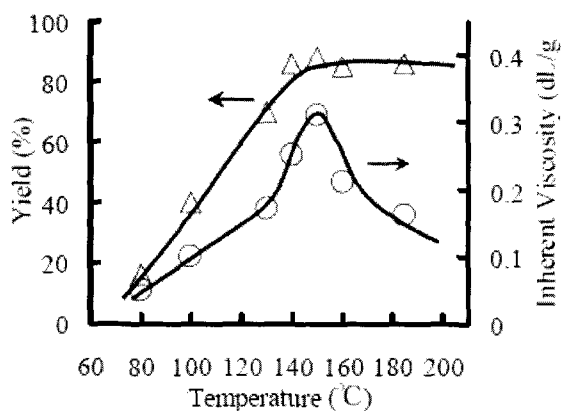


Figure 1. Effect of temperature on polymerization in [bmim][BF₄] for 1.5h

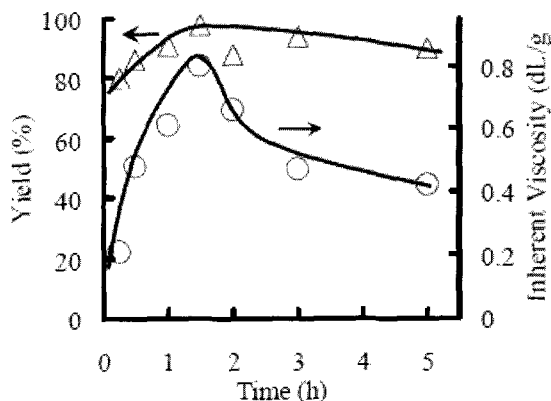


Figure 2. Effect of time on polymerization in [bmim][BF₄] at 150°C

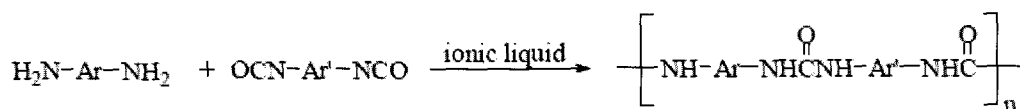
Under the optimum condition obtained above, two diisocyanates (diphenylmethane-4,4'-diisocyanate and tolylene-2,4-diisocyanate) reacted with diols (ethylene glycol and 1,4-butanediol) in [bmim][BF₄] at 150°C (Table 1). All polyurethanes were prepared in high yields. The polymers prepared from diphenylmethane-4,4'-diisocyanate have higher molecular weights than that prepared from tolylene-2,4-diisocyanate, because of the steric hindrance.

Table 1 Synthesis of various polyurethanes in [bmim][BF₄] at 150°C^{a)}

diisocyanate	diol	
	HO-(CH ₂) ₂ -OH	HO-(CH ₂) ₄ -OH
	0.77	0.63
	0.23	0.46

a) Polymerization condition. diols : 4mmol, diisocyanates : 4mmol, [bmim][BF₄] : 5mL, under N₂ at 150°C for 1.5h. Inherent viscosities were measured at a concentration of 0.5 g/dL in DMF at 30°C.

<Synthesis of Polyureas>



Polyaddition of 4,4'-diaminodiphenyl ether and diphenylmethane-4,4'-diisocyanate were carried out in various conditions (Table 2). While the polyadditions proceeded homogenously in [bmim][Cl], the inherent viscosities of the polymer obtained were still low even for longer polymerization time. In other three ionic liquids, the precipitations of the polyureas were observed at early stage of the

polymerization and the polyaddition proceeded heterogeneously. The highest yield and molecular weight of the polymers was obtained using [bmim][BF₄].

Table 2 Synthesis of polyureas in various ionic liquids at 150°C^{a)}

Ionic liquids	Time (h)	Yield (%)	η inh (dL/g) ^{b)}
[bmim][Cl]	1.5	75	0.17
	3	89	0.18
	24	84	0.17
[bmim][Br]	1.5	90	0.19
[bmim]PF ₆	1.5	81	0.19
[bmim][BF ₄]	1.5	97	0.40

a) Polymerization conditions. diamines 2mmol, diisocyanate : 2mmol, ionic liquids : 5mL under N₂ at 150°C.

b) Measured at a concentration of 0.5 g/dL in H₂SO₄ at 30°C.

Figure 3 shows the effect of temperature on the polymerization in [bmim][BF₄] for 1.5h. Even at 100°C, the polyureas were obtained in high yields. However, their molecular weights were still low. Between 130°C to 180°C, the inherent viscosities of the polymers were high values (about 0.4 dL/g). It was found that the reaction temperature exerted less effect on the polyadditions. The reaction of isocyanates with amines proceeded very fast to complete within 15min, judging from no change of the inherent viscosities of the polymers prepared for longer polymerization time.

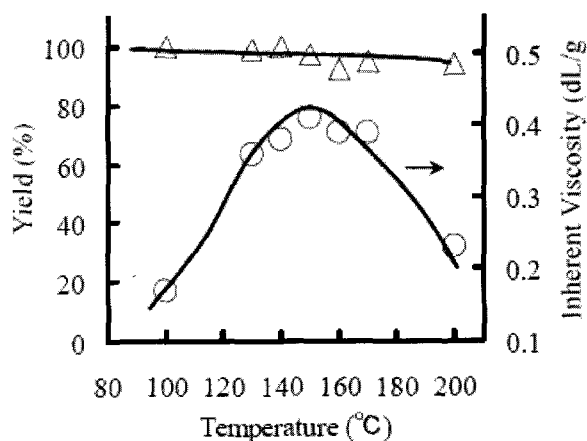


Figure 3. Effect of temperature on polymerization in [bmim][BF₄] for 1.5h

Table 3 Synthesis of various polyureas in [bmim][BF₄] at 150°C^{a)}

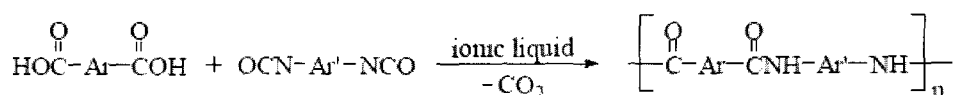
diisocyanate	diamines	
	<chem>H2N-C6H4-O-C6H4-NH2</chem>	<chem>H2N-C6H4-CH2-C6H4-NH2</chem>
<chem>NCO-C6H4-CH2-C6H4-OCN</chem>	0.39	0.28
<chem>NCO-C6H2(CH3)-NCO</chem>	0.30	0.23

a) Polymerization condition. diamines : 1mmol, diisocyanates : 1mmol, [bmim][BF₄] : 5mL, under N₂ at 150°C for 2h. Inherent viscosities were measured at a concentration of 0.5 g/dL in H₂SO₄ at 30°C.

After 2h 10 mol% of diisocyanates based on starting monomers (1mmol) was added to the reaction solution and further polymerization was carried out at 150°C for 2h. The polymers obtained are soluble in H₂SO₄ and their inherent viscosities increased.

Under the optimum condition obtained above, two diisocyanates (diphenylmethane-4,4'-diisocyanate and tolylene-2,4-diisocyanate) reacted with aromatic diamines (4,4'-diaminodiphenyl ether and 4,4'-diaminodiphenylmethane) in [bmim][BF₄] at 150°C for 2h (Table 3). All polyurethanes were prepared in high yields and the inherent viscosities of the polymers were 0.23 ~ 0.39 dL/g, measured at a concentration of 0.5 g/dL in H₂SO₄ at 30°C.

<Synthesis of Polyamides>



Generally aromatic polyamides are synthesized by the polycondensation of diamines with dicarbonyl dichlorides in aprotic polar solvents such DMAc and NMP. In these polycondensations, ionic liquids could be used as reaction medium instead of the conventional organic solvents. Polyamides can be also prepared from dicarboxylic acids and diisocyanates with the elimination of carbon dioxide. In this study, polyaddition of 4,4'-oxydi(benzoic acid) with diphenylmethane-4,4'-diisocyanate were carried out in various ionic liquids (Table 4). 4,4'-Oxydi(benzoic acid) could not be soluble in [bmim][PF₆] and [bmim][BF₄] even on heating and the reaction proceeded heterogeneously. The yields of the polymers were very low, as shown in Table 4. On the other hand, diacids were soluble in [bmim][Cl] and [bmim][Br] and the reaction solution kept homogenous during the polymerization. The polyamides could be obtained quantitatively in [bmim][Cl] and [bmim][Br].

Table 4 Synthesis of Polyamides in Various Ionic Liquids ^{a)}.

Ionic Liquids	Temperature (°C)	Yield (%)	η inh (dL/g) ^{b)}
[bmim][Cl]	100	61	0.14
[bmim][Br]	100	78	0.10
[bmim][PF ₆]	100	19	0.14
[bmim][BF ₄]	100	11	0.07

a) Polymerization condition. diacids : 1mmol, diisocyanates : 1mmol, ionic liquids : 5mL for 6h under N₂.

b) Measured at a concentration of 0.5 g/dL in H₂SO₄ at 30°C.

Figure 4 shows the effect of temperature on the polymerization of dicarboxylic acids with diisocyanates in [bmim][Cl] and [bmim][Br] for 6h. Higher temperature caused to increase the yield and molecular weights of the polyamide. In the use of [bmim][Br], polymerization temperature gave large influence on the molecular weight of the polyamides.

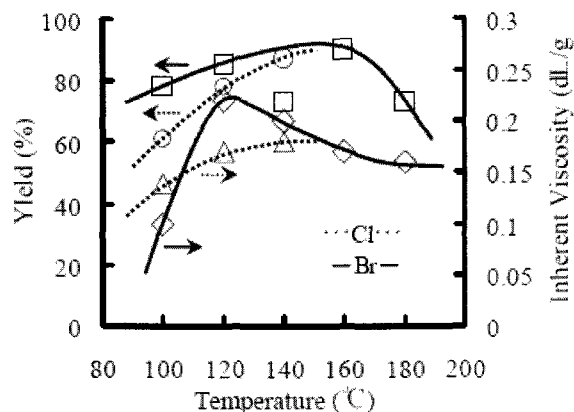


Figure 4. Effect of temperature on polymerization in [bmim][Cl] and [bmim][Br] for 6.0h.

Conclusions

Polymerizations using aromatic diisocyanates with various nucleophilic bi-functional compounds such as diols, diamines, and dicarboxylic acids proceeded smoothly in imidazolium-type ionic liquids and provided corresponding polymers such as polyurethanes, polyureas, and polyamides in high yields. Suitable ionic liquid are different for each polyadditions. For the use of diols and diamines as nucleophiles, [bmim][BF₄] is suitable medium. For the use of dicarboxylic acids as nucleophiles, [bmim][Cl] is effective.

Reference

- 1) P.Wasserscheid and T. Welton Eds, "Ionic Liquids in Synthesis", Wiley-VSH, Weinheim (2003).
- 2)a) R.T. Carlin and J.S. Wilkes, *J. Mol. Catal.*, **63**, 125 (1990). b) A.J. Carmichael, D.M. Haddleton, S.A.F. Bon, and K.R. Seddon, *Chem. Commun.*, 1237 (2000).
- 3) T. Biedron and P. Kubisa, *J. Polym. Sci., Part A, Polym. Chem.*, **42**, 3230 (2004).
- 4)a)M. Yoneyama and Y. Matsui, *High Perform. Polym.*, **18**, 817-823 (2006). b)Y.S. Vygodskii, E.I. Lozinskaya, and A.S Shaplov, *Macromol Rapid Commun.*, **23**, 676 (2002). c)E.I. Lozinskaya, A.S. Shaplov, and Y.S. Vygodskii, *Eur Polym J.*, **40**, 2065 (2004).
- 5) W.X. Qian, F.Y. Ju, Y.M. Zhang, and W.L. Bao, *Chinese Chem. Lett.*, **15**, 1269 (2004).
- 6) S. Mallakpour and F. Yousefian, *J. Braz. Chem. Soc.*, **18**, 1220 (2007).