

Novel Synthetic Method for Polyureas from Diamines and CO₂ Using Ionic Liquids or Cesium Salts as Catalysts

Masaru YONEYAMA (米山 賢), Hiroki HASHIZUME (橋詰大器), Yuuto NISHIDA (西田悠人)

*Division of Molecular Science, Faculty of Science and Technology, Gunma University
1-5-1 Tenjin-cho, Kiryu, Gunma 376-8515, Japan*

Abstract: Novel synthetic methods for polyureas from diamines and CO₂ using ionic liquids as both catalysts and solvents or Cesium salts as catalysts in NMP were developed, instead of the conventional methods using toxic monomers such as diisocyanates and phosgene. Among 1-methyl-3-butylimidazolium-type ([bmim]) ionic liquids, [bmim][Cl] was most effective to give polyurea with inherent viscosity of 0.17~0.23 dL/g at 170 °C for 36h from various aliphatic diamines and CO₂ (3MPa). However, aromatic diamine could not be used as monomer in this polymerization. Among various cesium salts, cheaper Cs₂CO₃ with NMP as solvent was more suitable catalytic system to provide polyurea with inherent viscosity of about 0.56 dL/g in high yield at higher temperature (190 °C) for 36h from 1,6-hexamethylenediamine and CO₂ (4MPa). It was found that the use of Cs₂CO₃ (10mol%) could provide desired polyureas with higher molecular weights compared with the use of [bmim][Cl], even though the polymerization condition was severe.

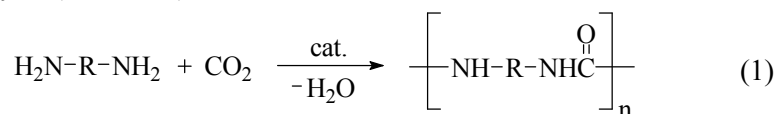
Keywords: Polyureas / Diamines / Carbon Dioxide / Ionic Liquids / Cesium Salts / Phosgene-free

1. Introduction

Polyureas are a class of polymers that have excellent physical and chemical properties, such as good thermal stabilities, flexibilities, abrasive resistances, and age resistances. Corrosion protection is considered as an important application for the polyurea materials. Polyureas were prepared mainly by two synthetic methods¹. One is the polyadditions of high reactive diisocyanates with diamines. Another is the polycondensations of phosgene and diamines. As diisocyanates and phosgene are highly toxic compounds, the developments of safe and environmentally friendly methods for the synthesis of polyureas are desirable.

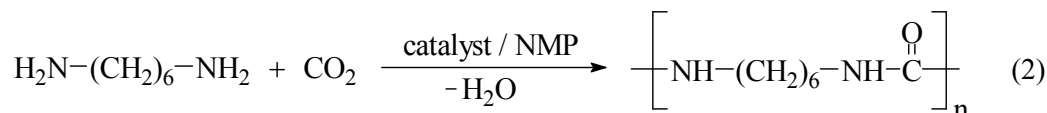
Carbon dioxide (CO₂) is a easily available renewable carbon resource, which has the advantages of being nontoxic, abundant, and economical. CO₂ is also attractive as an environmentally friendly chemical reagent and is especially useful as a phosgene substitute. A lot of research has been conducted on reaction using CO₂ as a raw material to produce methanol, carboxylic acids, organic carbonates, carbamates, and ureas². Among these products, urea, as one of the most important bulk chemicals, was first industrialized in the 1920s from ammonia and CO₂³. As CO₂ is a relatively inert molecule, drastic conditions (200 °C, and CO₂ pressures higher than 10MPa (100 atm) or the presence of stoichiometric amounts of bases, such as DBU⁴, and dehydrating agents such as dicyclohexylcarbodiimide⁵, Me₃NSO₃⁶, or diphenylphosphite⁷. Ureas have also been prepared catalytically in fair yields using ionic liquids (ILs) and cesium salts⁸⁻¹¹.

Herein, we will show a new process for the synthesis of polyureas from diamines and CO₂ with ILs and Cs salts as catalysts (Scheme 1).



2. Results and Discussion

In an initial approach, the polymerizations of 1,6-hexamethylenediamine and CO₂ using catalytic amounts of 1-methyl-3-butylimidazolium-type ILs ([bmim][X]) or Cs salts in N-methylpyrrolidone (NMP) as reaction mediums were carried out (Scheme 2). The results were shown in Table 1.



When no catalyst was used, the urea forming reaction did not proceed and polymer was hardly obtained. Ionic liquids and Cs salts except for cesium chloride provided the desired polyureas in moderate to high yields. In particular, [bmim][Cl], cesium hydroxide, and cesium carbonate were effective for this polymerization of diamines and CO₂. In next sections, further studies were accomplished for each catalyst to discuss the optimum polymerization conditions in detail.

Table 1 Effect of ionic liquids or Cs salts on the polymerization of 1,6-hexamethylenediamine and CO₂ in NMP^a

ILs or Cs salts	Yield (%)	η_{inh} (dL/g) ^b
—	3	—
[bmim][Cl]	43	0.22
[bmim][Br]	39	0.20
CsF	35	0.07
CsCl	2	—
CsOH	72	0.29
Cs ₂ CO ₃	63	0.31

a) conditions : 1,6-hexamethylenediamine (6.0mmol), CO₂ (4MPa), ILs or Cs salts (25mg), NMP (2mL) at 70°C for 36h. b) Measured at a concentration of 0.5 g/dL in H₂SO₄ at 30°C.

2-1) Synthesis of Polyureas using Ionic Liquids

The polymerizations of 1,6-hexamethylenediamine and CO₂ were carried out in various mixtures of [bmim][Cl] and NMP (Table 2). Total amount of solvents were kept in about 2mL to prevent the change of the string. The yields of obtained polyureas increased with the increase of amount of [bmim][Cl] in the mixtures. Even in the use of only [bmim][Cl] without NMP, the polymer could be obtained in high yield and its molecular weight was the highest. It was found that [bmim][Cl] could act as both catalysts and medium to provide polyureas.

Other [bmim]-type ionic liquids such as [bmim][Br], [bmim][OH], [bmim][BF₄], and [bmim][PF₆] were used as medium for the polymerization (Table 2). Whereas [bmim][PF₆], [bmim][BF₄], and [bmim][AcO] with low Lewis basicity gave the polyureas in low yields, [bmim][Cl] and [bmim][Br] with high Lewis basicity provided polymers with higher molecular weights in high yields.

Table 2 Effect of amount of [bmim][Cl] on the polymerization of 1,6-hexamethylenediamine and CO₂ in NMP^a

[bmim][Cl] (mL)	NMP (mL)	Yield (%)	η_{inh} (dL/g) ^b
0	2.0	3	—
0.03	2.0	43	0.22
0.5	1.5	67	0.13
1.0	1.0	84	0.22
2.0	0	73	0.25

a) conditions : 1,6-hexamethylenediamine (6.0mmol), CO₂ (4MPa) at 170°C for 36h. b) Measured at a concentration of 0.5 g/dL in H₂SO₄ at 30°C.

Table 3 Effect of ionic liquids on the polymerization of 1,6-hexamethylenediamine and CO₂^a

Ionic liquids	Yield (%)	η_{inh} (dL/g) ^b
[bmim][Cl]	73	0.25
[bmim][Br]	70	0.19
[bmim][OH]	50	0.06
[bmim][AcO]	3	—
[bmim][BF ₄]	28	0.10
[bmim][PF ₆]	4	—

a) conditions : 1,6-hexamethylenediamine (6.0mmol), CO₂ (4MPa), ionic liquids (2mL) at 170°C for 36h. b) Measured at a concentration of 0.5 g/dL in H₂SO₄ at 30°C.

Using [bmim][Cl], the effect of temperature on the polymerization was investigated. As shown in Figure 1, temperature more than 160 °C were at least necessary to provide the polyureas. The polymerization at 170 °C gave the polyurea with the inherent viscosity of 0.14 dL/g in 95%. Therefore, further polymerization were carried out at 170°C.

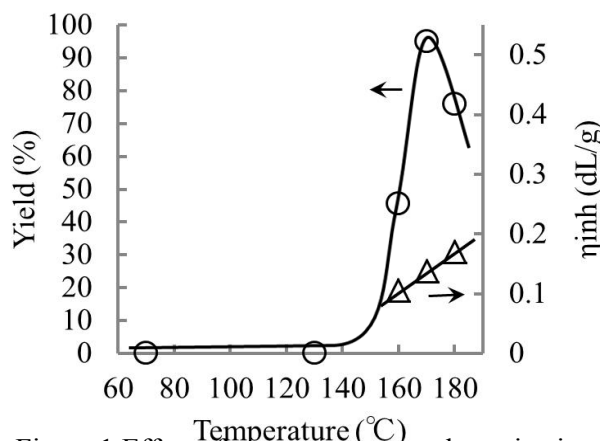


Figure 1 Effect of temperature on polymerization of 1,6-hexamethylenediamine and CO₂ (4MPa) in [bmim][Cl] for 36h.

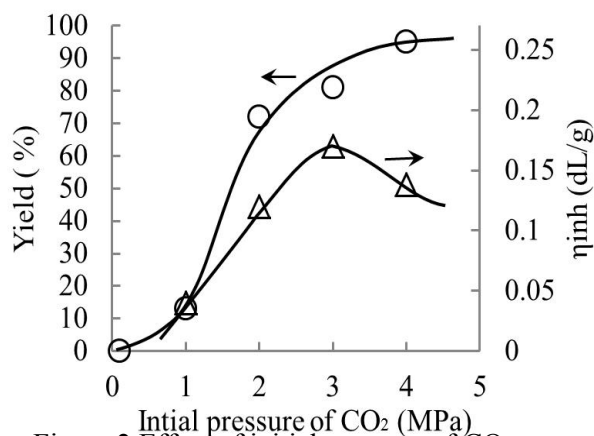


Figure 2 Effect of initial pressure of CO₂ on polymerization of 1,6-hexamethylenediamine and CO₂ in [bmim][Cl] at 170°C for 36h.

All polymerizations were carried with under high pressure of CO₂ in the stemless tube as the polymerization vessel. Lower initial pressure of CO₂ than 1MPa (about 10 atm) gave no polymer. The increase of the initial pressure caused the higher of the inherent viscosities of obtained polyureas as shown in Figure 2. The polymer with the highest molecular weight could be obtained under 3 MPa of CO₂.

Under the optimum condition obtained above, various kinds of diamines reacted with CO₂ in

[bmim][Cl] at 170 °C for 36h (Table 4). Aliphatic diamines such as 1,6-hexamethylenediamine and 1,8-diaminooctane could provide polyureas in high yields. Benzylamine-type diamines such as p-xylylenediamine and m-xylylenediamine gave polymers with lower molecular weights in low yields. Aromatic diamines such as 4,4'-methylenedianiline gave no polymer, because of low nucleophilicity of aromatic amines.

Table 4 Polymerization of various diamines with CO₂ in [bmim][Cl]^a

Diamines	Yield (%)	η_{inh} (dL/g) ^b
1,6-Hexamethylenediamine	81	0.17
1,8-Diaminooctane	75	0.23
p-Xylylenediamine	28	0.13
m-Xylylenediamine	19	0.05
4,4'-Methylenedianiline	0	—

a) conditions : diamines (6.0mmol), CO₂ (3MPa), [bmim][Cl] (2mL) at 170 °C for 36h. b) Measured at a concentration of 0.5 g/dL in H₂SO₄ at 30 °C.

2-2) Synthesis of Polyureas in [bmim][Cl] with Cs Salts

Various Cs salts and potassium hydroxide, which were effective in NMP as solvents, were added to the polymerization solution of 1,6-hexamethylenediamine and CO₂ (4MPa) in [bmim][Cl]. The increase of yields and the inherent viscosities of polyureas prepared with any Cs salts were not observed, as shown in Table 5. On the contrary, large amount of CsOH decreased both the yield and the molecular weight of obtained polymer.

Table 5 Polymerization of 1,6-hexamethylenediamine and CO₂ in [bmim][Cl] with Cs salts^a

Cs salts	Yield (%)	η_{inh} (dL/g) ^b
—	73	0.25
CsF	80	0.25
CsOH	84	0.24
CsOH ^c	71	0.16
Cs ₂ CO ₃	77	0.20
KOH	82	0.10

a) conditions : 1,6-hexamethylenediamine (6.0mmol), CO₂ (4MPa), [bmim][Cl] (2mL), Cs salts (0.17mmol) at 170 °C for 36h. b) Measured at a concentration of 0.5 g/dL in H₂SO₄ at 30 °C. c) Cs salts (1.0mmol)

2-3) Synthesis of Polyureas using Cs Salts

Among four kinds of Cs salt as shown in Table 1, CsOH and Cs₂CO₃ were the effective catalysts for the polymerization of 1,6-hexamethylenediamine and CO₂ to give the polyureas with the moderate inherent viscosities in moderate yields. The difference of catalytic abilities between both CsOH and Cs₂CO₃ are not clear judging from the yields and the inherent viscosities of obtained polyureas. Using various amounts of CsOH and Cs₂CO₃, the polymerizations of 1,6-hexamethylenediamine and CO₂ in NMP were carried out at 170 °C for 36h. Figure 3 shows the effect of amount of CsOH on the polymerization. Even in the use of same amounts of CsOH, constant values could not be obtained, mainly because CsOH absorbed readily water during the measurement of weights. As shown in Figure 4, Cs₂CO₃ shows clear tendency in the yields and molecular weights of obtained polymers.

10mol% of Cs₂CO₃ based to diamines gave the highest yield of 79% and the inherent viscosity of 0.3 dL/g. It has been thought that Cs₂CO₃ is the suitable catalyst than CsOH for this polymerization.

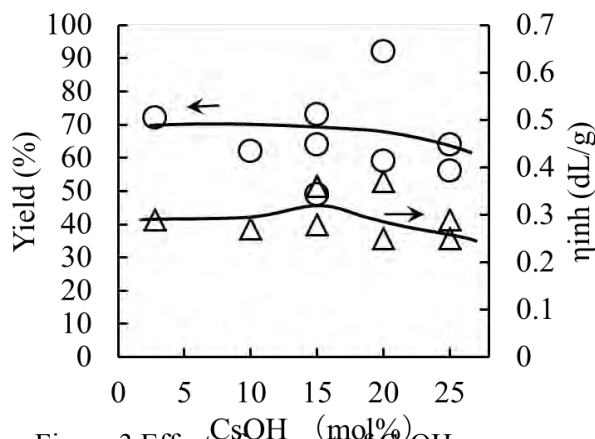


Figure 3 Effect of amount of CsOH on polymerization of 1,6-hexamethylenediamine and CO₂ (4MPa) in NMP at 170°C for 36h.

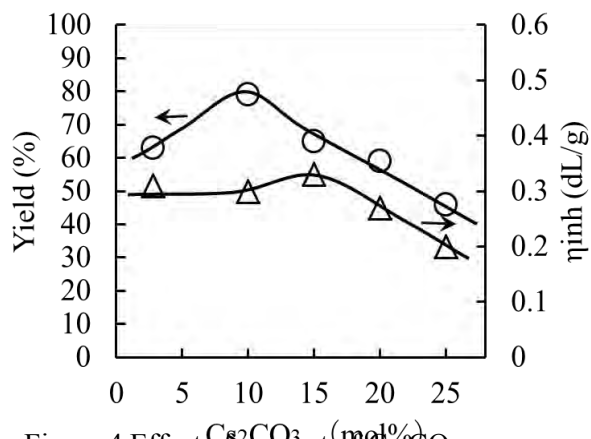


Figure 4 Effect of amount of Cs₂CO₃ on polymerization of 1,6-hexamethylenediamine and CO₂ (4MPa) in NMP at 170°C for 36h.

The effect of temperature on the polymerization with 10mol% of Cs₂CO₃ in NMP was investigated. As shown in Figure 5, the increase of temperature from 160°C increased both yields and the inherent viscosities of obtained polyureas. According to the ability of heating system to keep temperature constant, further polymerization were carried out at 190°C.

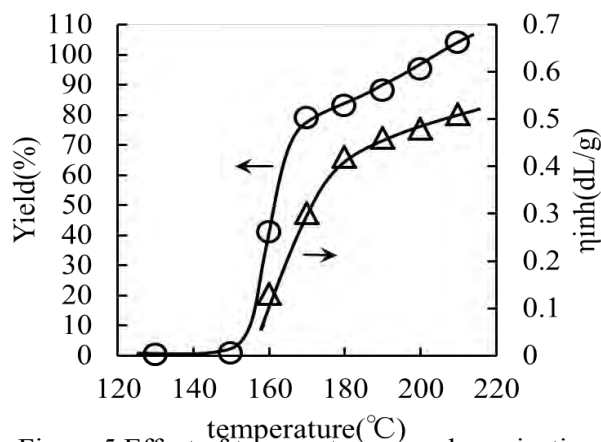


Figure 5 Effect of temperature on polymerization of 1,6-hexamethylenediamine and CO₂ (4MPa) with Cs₂CO₃ (10mol%) in NMP for 36h.

Using eight solvents, which could absorb CO₂, the polymerization of 1,6-hexamethylenediamine and CO₂ were carried out at 190°C for 36h (Table 6). The solvent with higher boiling temperature such as hexamethylphosphoric triamide and NMP gave the polyureas with higher molecular weight.

Table 6 Effect of polymerization solvents on the polymerization of 1,6-hexamethylenediamine and CO₂ with Cs₂CO₃^a

Solvents	b.p. (°C)	Yield (%)	η_{inh} (dL/g) ^b
Hexamethylphosphoric triamide	235	90	0.53
1,3-Dimethyl-2-imidazolidinone	225.5	35	0.30
N-Methylpyrrolidone	202	90	0.56
N,N-Dimethylformamide	189	52	— ^c
N,N-Dimethylacetamide	166	trace	—

Dimethyl sulfoxide	153	55	0.11
pyridine	115	6	0.08
acetonitrile	82.1	53	0.09

a) conditions : 1,6-hexamethylenediamine (6.0mmol), CO₂ (4MPa), solvent (2mL), Cs₂CO₃ (10mol%) at 190°C for 36h. b) Measured at a concentration of 0.5 g/dL in H₂SO₄ at 30°C. c) partially soluble in H₂SO₄.

3. Conclusions

Due to both environmental and safety concerns, novel synthetic methods for polyureas without the use of irritant diisocyanate or toxic phosgene are necessary. It has been known that urea bonds could be prepared from aliphatic amines and CO₂, which is cheap and stable material, by the use of ionic liquids and/or Cs salts as catalysts. In this study, the synthesis of polyureas from diamines and CO₂ with ionic liquids as both catalysts and solvents or Cs salts as catalysts in NMP was investigated in detail. Among 1-methyl-3-butylimidazolium-type ([bmim]) ionic liquids, [bmim][Cl] was most effective to give polyurea with inherent viscosity of 0.17~0.23 dL/g at 170 °C for 36h from various aliphatic diamines and CO₂ (3MPa). Among various cesium salts, cheaper Cs₂CO₃ with NMP as solvent are most suitable catalytic system to obtain polyureas with inherent viscosities of about 0.56 dL/g in high yields at higher temperature (190 °C) for 36h from 1,6-hexamethylenediamine and CO₂ (4MPa). It was found that the use of Cs₂CO₃ (10mol%) could provide desired polyureas with higher molecular weights compared with the use of [bmim][Cl], even though the polymerization condition was severe.

References

- [1] P.W. Morgan, "Condensation Polymers: by Interfacial and Solution Methods", Wiley-Interscience, New York, Chapter 5.
- [2] T. Sakura, J.-C. Choi, and H. Yasuda, *Chem. Rev.*, 107, 2365 (2007).
- [3] C. Bosch and W. Meiser, US Patent, 1 429 483, 1922.
- [4] P. Munshi, D.V. Heldebrant, E.P. McKoon, P.A. Kelly, C.-C. Tai, P.G. Jessop, *Tetrahedron Lett.*, 44, 2725 (2003).
- [5] H. Ogura, K. Takeda, R. Tokue, and T. Kobayashi, *Synthesis*, 394 (1978).
- [6] C.F. Cooper and S.J. Falcone, *Synth. Commun.*, 25, 2467 (1995).
- [7] N. Yamazaki, F. Higashi, and T. Iguchi, *Tetrahedron Lett.*, 13, 1191 (1974).
- [8] F. Shi, Y. Deng, T. SiMa, J. Peng, Y. Gu, and B. Qiao, *Angew. Chem., Int. Ed.*, 42, 3257 (2003).
- [9] T. Jiang, X. Ma, Y. Zhou, S. Liang, J. Zhang, and B. Han, *Green Chem.*, 10, 465-469 (2008)
- [10] Y.N. Shim, J.K. Lee, J.K. Im, D. K. Mukherjee, D.Q. Nguyen, M. Cheong, and H.S. Kim, *Phys. Chem. Chem. Phys.*, 13, 6197-6204 (2011).
- [11] A. Ion, V. Parvulescu, P. Jacobs, and D.D. Vos, *Green Chem.*, 9, 158-161 (2007).

(continued from p47)

References

- [1] (a) Miller, R. D. *Science* 1999, 286, 421-422; (b) Maier, G. *Prog. Polym. Sci.* 2001, 26, 3-65; (c) Volksen, W., Miller, R. D., Dubois, G. *Chem. Rev.* 2010, 110, 56-110.
- [2] N. M. Smith, C. B. Smith, C. L. Raston and A. N. Sobolev, *Green Chem.*, 2007, 9, 1185-1190.