

Hydrolysis of Polyurea under High Pressure of Carbon Dioxide

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Abstract

A chemical decomposition of polyurea (PUA) by hydrolysis under high pressure of carbon dioxide (CO₂) was proposed. The hydrolysis of PUA was carried out at 190 °C for 2 h under 7.0 MPa of CO₂ in the presence of water. The hydrolysis reaction gave white residual solid and water soluble compound. The white residual solid was characterized to be degraded PUA by FT-IR spectrum and elemental analysis. ¹H-NMR spectra of the water soluble compound revealed that the hydrolysis of PUA produced diamine only from repeating unit of PUA, which was a component of PUA. This hydrolysis gave the corresponding diamine for quantitative yields.

Key words

Hydrolysis reaction, Carbonic acid, Carbon dioxide, Sustainable chemistry

INTRODUCTION

Efficient use of resources and recycling of products are indispensable for establishing a sustainable society. Chemical recycling involving decomposition of polymers to their respective monomers and reproduction of the polymers from the obtained monomers is the most desirable way for sustainable chemistry.[1-3] Although there are several key challenges for its application such as decomposing the polymers to monomers, they should require high selectivity of conversion to desired monomers and easy techniques utilizing nonhazardous chemicals for the decomposition. Several chemical recycling processes are commercialized, i.e., solvolysis methods,[4-9] in which organic solvents and alkali catalysts are used; however, the development of much safer and environmentally benign systems is desired. High-temperature liquid or supercritical water has attracted much attention as an alternative to a harmful organic solvent because of its high proton concentration, which enhances the rates of acid-catalyzed reactions such as hydrolysis in water without adding any hazardous acids.[10-12]

Campanelli et al. reported that high-temperature water at 250 °C was effective for hydrolysis of Poly(ethylene terephthalate) (PET) to terephthalic acid (TPA) and ethylene glycol (EG).[13] Sato et. al. reported that PET was depolymerized to TPA and EG in water at higher than 220 °C and the hydrolysis of PET was enhanced by the addition of TPA in the reaction system.[14] They described that protons effectively catalyzed hydrolysis of PET by the addition of TPA. The addition of TPA serves protons for the hydrolysis of PET. However, for the polymer which consists of the monomer of non-acidity, such as polyurea (PUA), the degradation of polymer cannot be enhanced by a monomer addition. PUA is produced as by-product, when an

isocyanate was produced from the reaction of diamine with phosgene in industrially. Generally, the produced **PUA** is incinerated and produce CO₂ and NO_x. These gases are environmentally harmful chemicals. From the point of protection of our environment, the development of hydrolysis reaction of **PUA** is important.[9, 15] Here we investigate the hydrolysis of **PUA** by the using water under high pressure of CO₂. It is well-known that the reversible reaction of CO₂ with H₂O forms carbonic acid, leading to a temporary generated proton specie *in situ* with pK_a value as low as 3.6.[16,17] The pK_a of carbonic acid is similar pK_a of TPA. The formed carbonic acid,[17] which is *in situ* Brønsted acid, could serve as an acid catalyst. We have already patented the hydrolysis of **PUAs**.[15] However, details of the hydrolysis condition and reaction mechanism were unclear, and studied in this literature.

EXPERIMENTAL

Materials. 1,6-Hexamethylene diisocyanate (HDI, Nippon Polyurethane Industry Co. Ltd., Yamaguchi, Japan), toluene diisocyanate (TDI, WAKO Chemicals Co., Ltd., Osaka, Japan) and *N,N*-dimethyl formamide (DMF, WAKO Chemicals Co., Ltd., Osaka, Japan) were used after distillation under reduced pressure. 4,4'-Diphenylmethane diisocyanate (MDI, Nippon Polyurethane Industry Co. Ltd., Yamaguchi, Japan) was used as received.

Characterization. IR spectrum was recorded with Bio-Rad Laboratories FTS 3000MXN, and the values are given in cm⁻¹. ¹H-nuclear magnetic resonance (¹H-NMR) spectra of products were recorded on a JNM-GX400 at 400 MHz. Elemental analyses of samples were analyzed on PerkinElmer PE2400II.

Preparation of PUA. To a solution of HDI (8.40 g, 500 mmol) in DMF (150 mL), water (0.90g, 500 mmol) was added at room temperature, and the reaction temperature was raised up to 80 °C. Then the white solid was precipitated in the reaction mixture, and the mixture was stirred for 24 h. The resulting precipitate was collected by filtration and dried *in vacuo* to give a white solid of **PUA-HDI** (6.95 g, 98%). **PUA-HDI** was insoluble in several solvents, such as DMF, dimethyl sulfoxide (DMSO), methanol, ethanol, toluene, chloroform, hexane, ethyl acetate and water.

IR (KBr) 3330(ν (NH)), 2935, 2857(ν (C-H)), 1618(ν (C=O)) and 1575(δ (N-H)) cm^{-1} ;
Elemental Analysis, Calcd. for $\text{C}_7\text{H}_{14}\text{N}_2\text{O}$: C, 59.12%; H, 9.92%; N, 19.70%. Found: C, 59.09%; H, 10.11%; N, 19.80%.

Preparation of PUA-MDI and PUA-TDI: The preparation of **PUA-MDI** and **PUA-TDI** were follow a similar procedure as described above. The yields of **PUA-MDI** and **PUA-TDI** were 99% and 98%, respectively. These **PUAs** were white solid and insoluble in several solvents, such as DMF, DMSO, methanol, ethanol, toluene, chloroform, hexane, ethyl acetate and water.

PUA-MDI: IR (KBr) 3306(ν (NH)), 3033(ν (C-H)), 2899(ν (C-H)), 1643(ν (C=O)) and 1595(ν (C=C)aromatic ring), 1304(δ (C-N)) cm^{-1} ; Elemental Analysis, Calcd. for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}$: C, 74.98%; H, 5.39%; N, 12.49%. Found: C, 75.12%; H, 5.21%; N, 13.80%.

PUA-TDI: IR (KBr) 3301(ν (NH)), 2924, 2861(ν (C-H)), 1645(ν (C=O)), 1542(δ (N-H)) and 1228 cm^{-1} ; Elemental Analysis, Calcd. for $\text{C}_8\text{H}_8\text{N}_2\text{O}$: C, 64.85%; H, 5.44%; N, 18.91%. Found: C, 64.71%; H, 5.56%; N, 19.04%.

General procedure of hydrolysis of PUA. 0.5 g of **PUA-HDI** and 20 mL of water were placed into a 200 mL stainless autoclave equipped with a pressure gauge followed by the introduction of appropriate amount of liquid CO₂. Then, the autoclave was heated using a band heater under high pressure of CO₂ (7.0 MPa). After a given reaction time, the reactor was rapidly immersed into an ice bath to cool down to room temperature. Finally, the reaction mixture was collected from the reactor and separated to the filtrate and residual solid fractions with a filter paper. The obtained solid was dried under vacuum and weighed. The solid was analyzed by FT-IR spectroscopy and elemental analysis. The filtrate was concentrated by the rotary evaporator and gave the non-volatile residue. The non-volatile residue was weighed after drying. The residue was analyzed by ¹H-NMR spectroscopy and elemental analysis. The residue was purified by silica-gel column chromatography (eluent with CHCl₃).

RESULTS and DISCUSSION

Preparation of PUAs

Three **PUAs** were easily obtained by the addition reaction of several diisocyanates with water. The equal molar reaction completed within 24 h at 80 °C. All **PUAs** did not dissolve in the water and various organic solvents, such as DMF, DMSO, methanol, ethanol, toluene, chloroform, hexane and ethyl acetate. The **PUAs** were characterized by Fourier transform infrared (FT-IR) spectroscopy and elemental analysis.

Hydrolysis Reaction of PUA-HDI and Identification of Reaction Mixture

The hydrolysis of **PUA-HDI** (0.50 g) was carried out under high pressure CO₂ of 7.0 MPa at 190 °C for 0.5 h. The reaction mixture was filtrated and gave residual solid and filtrate. At the first, the residual solid was washed with diluted water and methanol and dried *in vacuo* at room temperature for 24 h. 0.23 g of the white solid was obtained at this reaction condition. The absorption bands of FT-IR spectrum of residue were observed identical to **PUA-HDI**'s ones. This result suggested that the terminal amino group affected the nitrogen content. These experimental data suggested that the residue have same repeating structure of **PUA-HDI** and was converted to low molecular weight of **PUA-HDI** *via* the hydrolysis reaction.

Next, the filtrate was concentrated by the rotary evaporator and gave 0.30 g of residual white solid compound as a water soluble compound. Its IR absorption at 3340, 2930, 2860, 1640 and 1611 cm⁻¹ and result of elemental analysis suggested the preparation of carbamic acid salt of 1,6-hexamethylene diamine (**HDA**) from the hydrolysis reaction of **PUA-HDI**. The water soluble compound was also analyzed with the ¹H-NMR spectroscopy in D₂O. Figure 1 shows ¹H-NMR spectrum of water soluble compound. Observation of resonance peaks at 1.34 (m, 4H), 1.58 (m, 4H) and 2.85-2.92 (m, 4H), assignable to protons of methylene groups of 1,6-, 2,5-, 3,4-positions, respectively, on ¹H-NMR spectrum indicated formation of **HDA**, which was from corresponding carbamic acid salt aforementioned.

The yield of **HDA** was estimated from following equation:

Weight of water soluble compound from filtrate (g) =A

Molecular weight of carbamic acid of **HDA** = 160.21

Weight of obtained residual solid after hydrolysis reaction (g) = **B**

Molecular weight of repeating unit of **PUA-HDI** = 142.20

$$\text{Yield of HDA} = \frac{A/160.21}{[0.50 \text{ (g)} - B] / 142.20} \times 100$$

Effect of the Reaction Conditions for Hydrolysis Reaction of PUAs

Reaction Time and CO₂

The hydrolysis reaction of **PUA-HDI** was carried out at 190 °C under 7.0 MPa of N₂ or 7.0 MPa of CO₂ as shown in Figure 2. At 7.0 MPa of N₂, yield of **HDA** did not reach 20% even after 2 h. Under high pressure of N₂, the hydrothermal decomposition of **PUA** occurred. On the other hand, under 7.0 MPa of CO₂, when the reaction time was elongated from 0.5 to 2.0 h, the yield of **HDA** was smoothly increased from 52% to quantitative yield. It was concluded that the hydrolysis of **PUA-HDI** was accelerated under high pressure of CO₂.

Temperature and other PUA

This hydrolysis reaction was applied to each temperature to investigate the effect of the reaction temperature on this hydrolysis reaction. Figure 3 shows the relationship between temperature and yield of **HDA** for 2 h under 7.0 MPa of CO₂. At 120 °C, the yield of **HDA** was 6.1%. The yield of **HDA** was increased with increasing temperature. We confirmed that the hydrolysis reaction of **PUA** was occurred over 120 °C, and accelerated under high pressure CO₂. Then, **MDI-PUA** and **TDI-PUA** as aromatic **PUAs** were submitted for the hydrolysis reaction under high pressure CO₂. **MDI-PUA** and **TDI-PUA** were hydrolyzed to the corresponding diamines (**DAs**),

4,4'-diaminodiphenyl methane and diamino toluene, in excellent yields, respectively. These indicate that this hydrolysis reaction can be applied to various polyurea.

Pressure of CO₂

Figure 4 shows the relationship between pressure of CO₂ (2.0 – 14.0 MPa) and yield of corresponding **DAs** at 160 and 190 °C for 2 h. At 190 °C, all hydrolyses of **PUAs** were shown in similar trends. The yield of **DA** was increased with increasing pressure. It reached quantitative one at 190 °C. Therefore, the effect of CO₂ pressure was not clear at 190 °C. On the other hand, at 160 °C, it reached maximum yield at 7.0 MPa, which was below critical pressure of CO₂ at the reaction temperature. Especially, **TDA** from **TDI-PUA** was produced with high yields at the 160 °C. This result might suggest that the crystallinity or hydrogen-bonding ability of **PUA** affect hydrolysis reaction. This speculation was suggested from the compared with **MDI-PUA**. The increasing of yield of **DA** until *ca.* 7 MPa might be from the increased formation of carbonic acid due to the dependent on CO₂ pressure. On the other hand, the opposing behavior over *ca.* 7 MPa might come from the decreased dissociation and/or transfer of protons from carbonic acid due to the decreased polarity of the solvent.[18, 19]

In order to confirm effect of carbonic acid, we investigated the effect of the amount of water on yield of **HDA**. This reaction reached quantitative yield of **HDA** at relatively higher temperature of 190 °C, meaning that the effect of the water is not obvious at 190°C. Therefore we carried out the reaction at not 190 °C but 160°C. Figure 5 shows that the relationship between amount of water and yield of **HDA** at 160 °C for 2 h under 7.0 MPa of CO₂ pressure. The yields of **HDA** increased slightly

from 10 to 40 mL of water. Over 40 mL of water, the yield of **HDA** decreased with increasing amount of water. It is assumed that the dissociation of protons from carbonic acid increased due to increasing the polarity of solution by addition of 10 ~ 40 mL water. It is also assumed that the concentration of carbonic acid was diluted by addition of excess amount of 40 ~ 80 mL water. This result means concentration of carbonic acid and dissociation of protons from the acid are important factors for the hydrolysis reaction of **PUA**. Indeed, this assumption was well consistent with that from the relationship between CO₂ pressure and yields of **DAs** in Figure 4.

Mechanism of Hydrolysis Reaction

Figure 6 illustrates a plausible mechanism for this hydrolysis of **PUA**. First, carbonic acid was formed by the reaction of CO₂ with H₂O. The acid could release protons by the dissociation of *in situ* reaction. Then the protons activated to carbonyl group of urea one. And the activated urea group reacted with H₂O to form oxonium cationic intermediate. The intermediate released proton and gave hemiacetal groups. Immediately, the hemiacetal groups gave carbamic acid group and amino ones.[20] The carbamic acid group gave amino group with releasing CO₂.

CONCLUSION

We have successfully demonstrated the efficient promotion of hydrolysis of **PUAs** in high-temperature water under high pressure of CO₂ which are nonhazardous in nature. Moreover another important advantage of this process is that it does not require neutralization and further purification of the corresponding **DA** obtained from **PUA**. The advantageous feature is not attained by various acids.

Although further investigation is needed to precisely settle the mechanism, we have provided a green and general method for the hydrolysis of urea linkage *via* carbonic acid from the reaction of CO₂ with H₂O.

Acknowledgments

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Figure 1

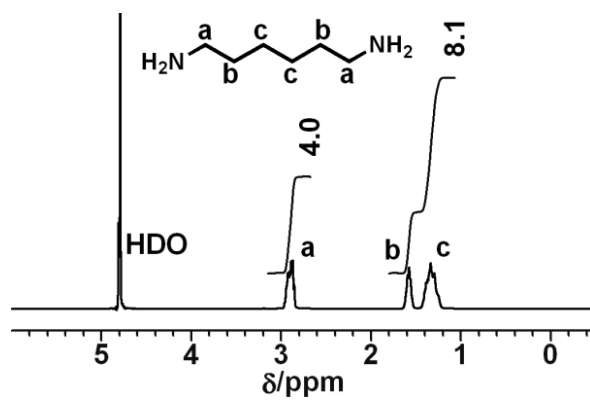


Figure 2

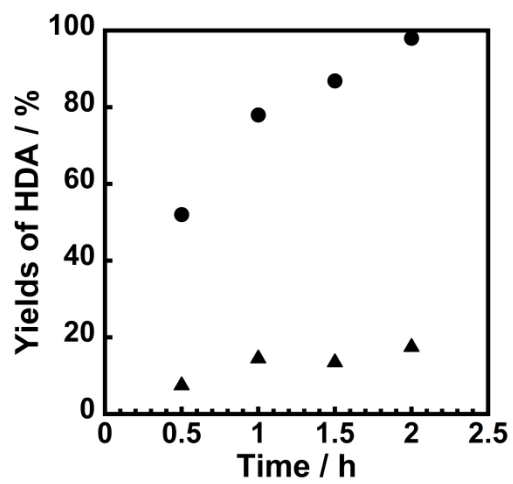


Figure 3

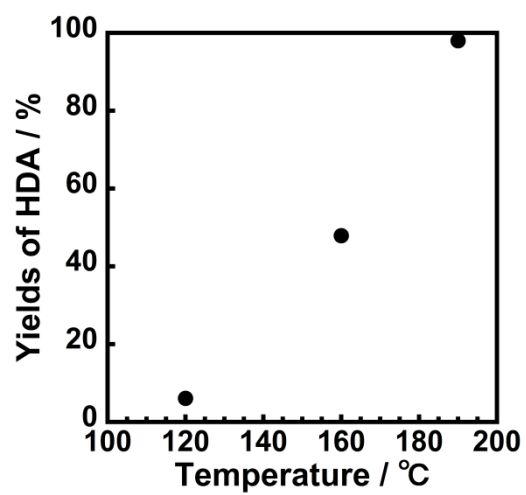


Figure 4

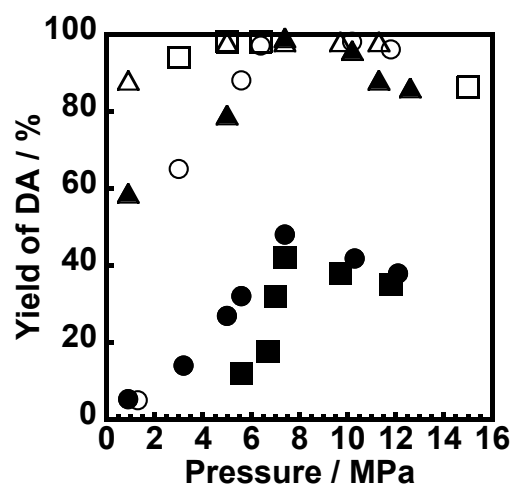


Figure 5

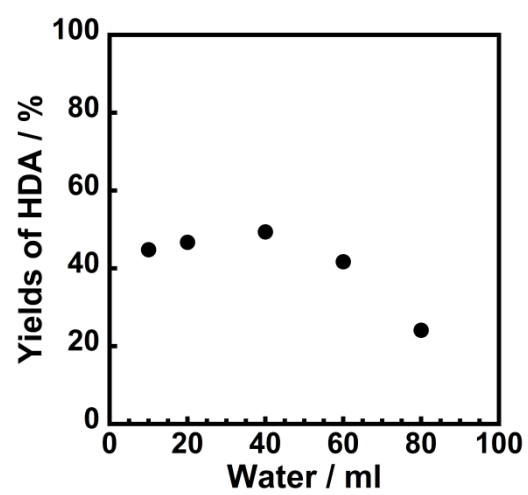
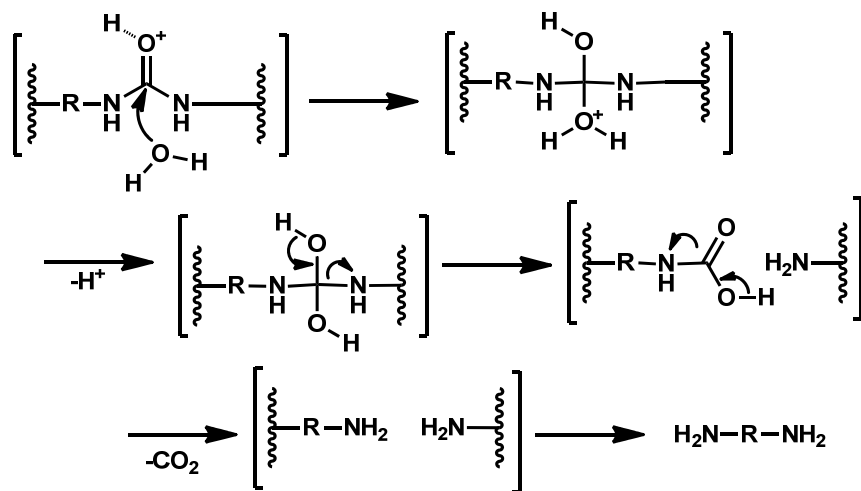
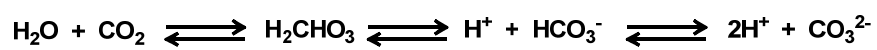


Figure 6



Captions

Figure 1. $^1\text{H-NMR}$ spectrum of residue of filtrate (in D_2O).

Figure 2. The relationships between yield of **HDA** and reaction time at $190\text{ }^\circ\text{C}$ under 7.0 MPa of CO_2 (●) and 7.0 MPa of N_2 (▲).

Figure 3. The relationships between yield of **HDA** and reaction temperature under 7.0 MPa of CO_2 , for 2 h.

Figure 4. The relationships between yields of **DAs** and pressure of CO_2 at $160\text{ }^\circ\text{C}$ (filled symbols: ●;**HDA**, ▲;**TDA** and ■;**MDA**) and $190\text{ }^\circ\text{C}$ (open symbols: ○;**HDA**, △;**TDA** and □;**MDA**) under high pressure of CO_2 .

Figure 5. The relationships between yield of solid and amount of water at $160\text{ }^\circ\text{C}$, for 2 h, under 7.0 MPa of CO_2 .

Figure 6. Mechanism of hydrolysis reaction of **PUA**.