

## Effective Depolymerization of Nylon-6 in Wet Supercritical Hydrocarbons

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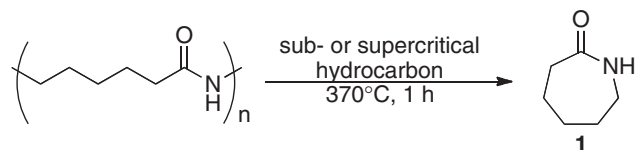
Treatment of nylon-6 with supercritical toluene in the presence of small amounts of water resulted in an effective conversion of polyamide to give  $\epsilon$ -caprolactam in quantitative yield. The presence of a small amount of water is critical for the progress of the reaction; completely anhydrous conditions failed to achieve depolymerization.  $\epsilon$ -Caprolactam was readily isolated after the removal of toluene under reduced pressure. The present method can serve as a useful treatment for the effective chemical recycling of waste plastics. The combined use of hydrocarbon and water is a new technique to control the reactivity of high-temperature water.

Development of an efficient recycling method for waste plastics is an important issue worldwide. Among many strategies for plastic recycling, the most ideal way is monomer recycling, in which waste plastics are converted into corresponding monomers that are converted into new plastics.<sup>1</sup> An advantage of this strategy is the preservation of depleting petroleum resources. To establish a monomer recycling method, an efficient depolymerization method is required. Plastics usually decompose when exposed to high temperatures in the presence of acids or bases. However, these conditions can be harsh enough to destroy polymers as well as monomeric materials during the reaction. To enhance the efficiency of depolymerization, less severe and selective methods are necessary.

Polyamides such as nylon-6 are among the most widely used polymers in our daily lives, and the monomer recycling of nylon is of interest to many chemists.<sup>2</sup> Recently, we have successfully developed a useful depolymerization of nylon-6 in supercritical secondary alcohols.<sup>3</sup> Depolymerization was also achieved in ionic liquids under high-temperature conditions.<sup>4</sup> During the course of our exploration to develop more efficient techniques for depolymerization, we have focused on the use of wet supercritical hydrocarbons because dilution of water with inert hydrocarbon may weaken the excessive reactivity of supercritical water. In this paper, we report high-temperature wet hydrocarbons as novel media for the depolymerization of nylon-6. The presence of a specific amount of water is a key factor for the effective conversion of nylon-6 into  $\epsilon$ -caprolactam in good yield with excellent purity. The combined use of hydrocarbon and water is a new method to control the reactivity of high-temperature water.

The depolymerization reaction of nylon-6 was examined using several types of hydrocarbon solvent. The reactions were carried out at 370 °C for 1 h in an autoclave (Scheme 1). These results are summarized in Table 1.

Treatment of nylon-6 in supercritical water resulted in its smooth consumption; however, the yield of **1** was rather poor (Entry 1). The use of anhydrous supercritical toluene for the



Scheme 1.

Table 1. Depolymerization of nylon-6 in hydrocarbon–water mixture

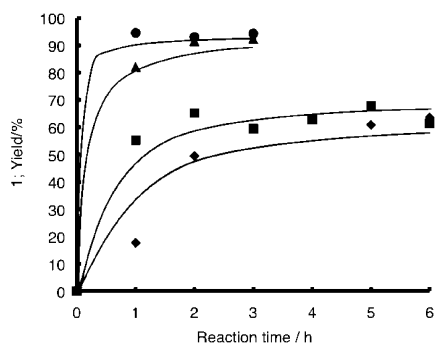
Entry	Solvent	Water /wt %	Time /h	<b>1</b> ; yield /% <sup>b</sup>	$T_c^d$ /°C	$P_c^e$ /MPa
1	Water	100	1 (19.7) <sup>a</sup>	67	374.0	22.1
2	Toluene	0.0001	2 (6.5) <sup>a</sup>	15	318.6	4.1
3	Toluene	10	1 (12.9) <sup>a</sup>	97 (93) <sup>c</sup>		
4	Hexane	0.0001	2	27	234.3	3.0
5	Hexane	10	1	91		
6	Heptane	10	1	92	267.1	2.7
7	Octane	10	1	90	295.6	2.5
8	Cyclooctane	10	1	93	374.1	1.8
9	Dodecane	10	1	96	385.1	1.8
10	Tridecane	10	1	94	402.7	1.7
11	Liq. Paraffin	10	1	74		

<sup>a</sup>Internal pressure (MPa) of the reaction vessel in parentheses.

<sup>b</sup>GC yield. <sup>c</sup>Isolated yield. <sup>d</sup>Critical temperature of the solvent.

<sup>e</sup>Critical pressure of the solvent.

reaction also offered unsatisfactory results (Entry 2). Conversely, the presence of 10 wt % of water dramatically improved the conversion of nylon and the yield of  $\epsilon$ -caprolactam (**1**) increased to 97% (Entry 3). The isolation of **1** was quite simple. Removal of the solvents under reduced pressure resulted in nearly pure  $\epsilon$ -caprolactam (**1**) in 93% yield.<sup>5</sup> Isolated **1**, for example, displayed a sharp melting point at 67.8–69.2 °C, which was sufficiently close to the literature data.<sup>6</sup> As long as we checked, there seemed to be no side products derived from toluene. A similar improvement was also observed when hexane was employed for the reaction (Entries 4 and 5). Thus, the addition of water to hydrocarbon was very effective in enhancing the reaction rate of the depolymerization reaction. The same improvement was also observed with the use of other hydrocarbon solvents (Entries 6–10). It should be noted that the supercritical phase seemed unnecessary for the depolymerization of the polyamide (Entries 8–10). However, liquid paraffin did not affect the depolymerization reaction (Entry 11). Thus, the present modification provides a useful and selective method for the depolymerization of nylon-6 into a sufficiently pure monomer. No further reaction for **1** progressed under the present conditions.



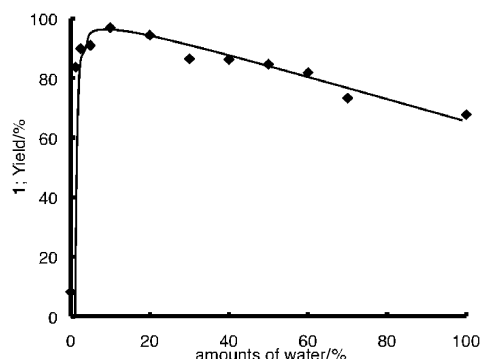
**Figure 1.** Depolymerization in toluene–water (9:1) mixture.  $T = 250$  (◆),  $280$  (■),  $300$  (▲), and  $350$  °C (●).

To clarify the reaction profiles, we next examined temperature dependence of the reactions. We chose a 90:10 toluene–water system as a model and examined the reactions at several temperatures for 1 h. The results are summarized in Figure 1.

The reaction performed at  $350$  °C for 1 h produced a liquid–liquid two-phase mixture with no observed precipitates of oligomeric polyamides. It should be noted that the yield of **1** did not change when the reaction time was prolonged to 3 h. This indicated that compound **1** remained under these reaction conditions for several hours. Conversely, the reaction rate became much slower when the temperature was set to  $280$  °C or below; the yield of **1** only reached around 60% after 3 h. Under these conditions, the reaction mixture was a heterogeneous mixture that contained solid material. This observation clearly indicates that oligomeric polyamides remained in the reaction mixture. The oligomer was isolated by filtration. The mean molecular weight of the oligomer was estimated to be about  $1300 \text{ g mol}^{-1}$  based on GPC analysis. It should be noted that the oligomer gave  $\epsilon$ -caprolactam (**1**) when treated at  $350$  °C under the same reaction conditions.

We next investigated the effects of water content. The results are illustrated in Figure 2. When the reaction was carried out in anhydrous toluene, the depolymerization did not progress well, and insoluble solids remained in the reaction mixture. GC analysis determined the yield of **1** to be only 8%. The results changed completely when 1.25 wt % of water was added to the reaction mixture, increasing the yield of **1** to 83%. The yield of **1** rose as the amount of water increased, and the maximum yield was observed when 10 wt % of water was added to the reaction mixture. Although depolymerization occurred smoothly, the yield of  $\epsilon$ -caprolactam gradually decreased when more than 10% water was present in the reaction mixture. Thus, 10 wt % water was determined to be the optimum reaction condition for the present depolymerization.

It is not easy to explain the role of water in the reaction; however, we hypothesized the following. The presence of water enhanced the hydrolysis rate of nylon-6. This reaction forms monomeric 6-aminocaproic acid, which readily cyclizes to yield  $\epsilon$ -caprolactam. Water may also react with these monomers to give undesirable side products.<sup>2b</sup> However, the limited water content under the present conditions likely suppresses the side reaction efficiently. As a result,  $\epsilon$ -caprolactam became the sole product of the reaction and the yield of **1** increased to more than 90%.



**Figure 2.** Effect of the amounts of water.

We have successfully demonstrated that the use of supercritical hydrocarbon containing water dramatically improves the depolymerization of nylon-6. It should be noted that the combined use of water and hydrocarbon effectively controlled reactivity and provided selective depolymerization. The present method, which consisted of a simple manipulation to produce a high yield of **1** with excellent purity, will prove viable for plastic recycling chemistry. Further investigation and application of the present method is now underway in our laboratory.

#### References and Notes

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- 5 **General procedure for the depolymerization of nylon-6:** Nylon chip (1.2 g,  $M_w = 22000 \text{ g mol}^{-1}$ ) was put in a mixture of toluene–water (16 g, 90:10). The reaction vessel was sealed and heated at  $370$  °C for 1 h. The reaction vessel was cooled by water. Toluene and water were removed under reduced pressure to give  $\epsilon$ -caprolactam (**1**) in 93% yield (1.099 g); mp  $67.8$ – $69.2$  °C;  $^1\text{H NMR}$  (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.73 (m, 6H), 2.47 (t,  $J = 5.5$  Hz, 2H), 3.21 (dd,  $J = 5.9, 9.9$  Hz, 2H), 6.2–6.5 (br, 1H);  $^{13}\text{C NMR}$  (67.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  23.1, 29.6, 30.5, 36.7, 42.7, 179.4.
- 6 For example: *Aldrich Handbook of Fine Chemicals*, **2009**, p. 600.