EFFICIENT DEPOLYMERIZATION METHODS OF POLYAMIDES IN SUPERCRITICAL ALCOHOLS AND IONIC LIQUIDS

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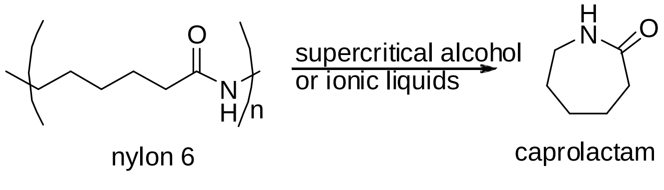
Abstract: Development of a new efficient method for the depolymerization of plastics is of interest for utilizing chemical recycling of waste plastics. In this presentation, we are going to show our recent results for the depolymerization of polyamides, especially for nylon-6, by using supercritical lower alcohols and ionic liquids. Use of supercritical secondary or tertiary alcohols resulted in the clean depolymerization to give caprolactam in good yields. The obtained caprolactam was usually highly pure. Use of ionic liquids provides another successful method for the depolymerization of nylon-6, in which caprolactam are usually isolated in very pure form and the ionic liquids are repeatedly useful for the reaction. This method is the first use of ionic liquids for this purpose and has opened a new perspective in not only plastic recycling chemistry but also ionic liquids chemistry. Both of the new methods provide useful methodologies for the chemical recycling of polyamides.

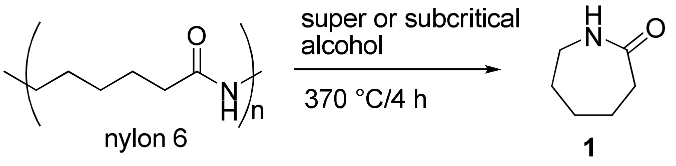


1. Introduction

Development of a new efficient method for the depolymerization of plastics is of interest for utilizing chemical recycling of waste plastics.[1] Polyamides such as nylons are one of the plastics that are used widely in our life. Depolymerization of nylon was explored from 30 years ago and many efforts have been reported so far.[2] Use of supercritical fluids is one of the fascinating methods.[3] Exposure of nylon to supercritical water, however, gave a complex mixture due to the high reactivity of supercritical water. Supercritical alcohols are another candidate for this purpose because its supercritical phase was achieved under much milder conditions than that of water. Additionally, mild properties of supercritical alcohols are another important point for the purpose to achieve selective depolymerization. In this presentation, we will show our recent results for the depolymerization of polyamides, especially for nylon-6, by using supercritical lower alcohols and ionic liquids[4]. Use of supercritical secondary or tertiary alcohols resulted in the clean depolymerization to give caprolactam in good yields.[5] Caprolactam was isolated by direct distillation from the reaction pot when ionic liquids were used as a depolymerization media. Obtained caprolactams by both methods were usually highly pure.

2. Experimental

Treatment of nylon 6 with a variety of supercritical lower alcohols is examined. The results are summarized in Scheme 1.



MeOH, 14%; EtOH; 36%; PrOH, 35%
BuOH, 47%; $C_8H_{17}OH$, 55%; $C_{12}H_{25}OH$, 61%
iPrOH, 91%; *sec*-BuOH, 96%,
c-$C_6H_{11}OH$, 95%; tBuOH. 95%.

Scheme 1

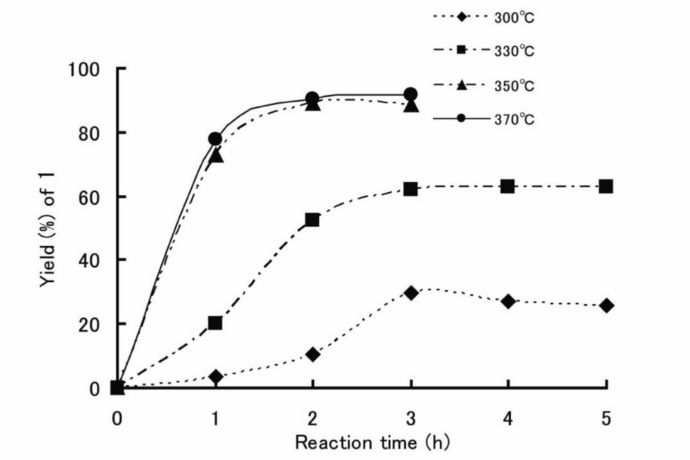


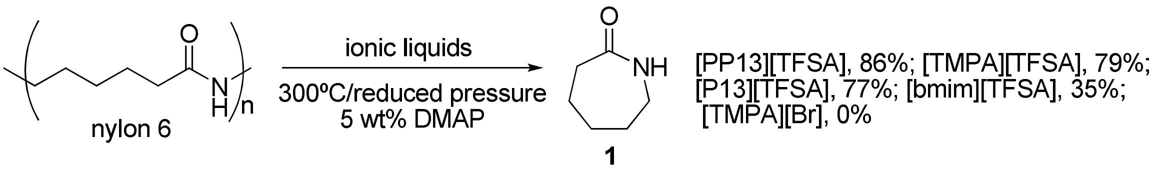
Fig. 1 Depolymerization of nylon 6 in supercritical iPrOH

Nylon 6 underwent smooth depolymerization on exposure to supercritical alcohol (Scheme 1). For example, heterogeneous mixture in supercritical MeOH turned into homogeneous solution after 1 h of the reaction. However, GC analyses revealed that the content of caprolactam **1** was only 14%. Indeed this was a complex mixture containing many side products. To improve the yield of **1**, we examined various primary alcohols for the reaction. Use of EtOH slightly improved the yield of **1** to 35%. As primary alcohols with longer-alkyl chain was used, the yield of **1** increased. The best yield of **1** reached 61% when C12 alcohol was used for the reaction.

The yield of **1** dramatically improved when secondary and tertiary alcohols were employed for the reaction. To our surprise, exposure of nylon 6 to iPrOH in 370 °C for 1.5 h resulted in clean formation of **1** more than 90% yield. Other secondary alcohols and tertiary alcohols also selectively gave **1** in very high yields. Simple concentration of the reaction mixture afforded **1** in very pure form which showed the melting point at 68.7-71.3 °C (lit.

68-71 °C). It should be noted that tertiary alcohols in the reaction mixture sometimes spurted out during opening the reaction vessel. This is probably due to partial decomposition of tertiary alcohols under the reaction conditions.

The present selective conversion to **1** depended on the reaction temperature (Fig. 1). The depolymerization progressed smoothly when carried out at 350 °C or higher temperature. However, the reaction became sluggish when the mixture was heated at lower temperature. For example, treatment of nylon 6 at 330 °C only gave **1** in 60% yield. It should be noted that the yield of 1 was never improved when the reaction was prolonged to 5 hours.



Scheme 2

We next examined ionic liquids for the depolymerization (Scheme 2).[6] At first we used [emim][BF_4] as the reaction solvent because this ionic liquid was stable at 350 °C or lower. A mixture of nylon 6 chip and [emim][BF_4] was heated at 300 °C for 6 h. After 6 h, heterogeneous mixture became black homogeneous thick oil, so we thought most of nylon 6 had reacted under the present conditions. To our delight we succeeded to isolate **1** in 54% yield after tedious 25 times of extraction with ether. This was somewhat problematic because extraction is a kind of laborious work. Thus, we tried to improve an isolation method from ionic liquid. Fortunately, caprolactam was a small molecule that showed its bp at 136-138 °C/10 mmHg. Ionic liquids were usually non-volatile and showed no boiling points even at high temperature (>300 °C). As a result, ionic liquids would not vaporize even if exposed under reduced pressure conditions. With this idea in hand, we examined direct distillation for the present depolymerization reaction. Finally we found great improvement for the isolation and obtained **1** in 86% yield. In this case, addition of 5 wt% of DMAP promoted the depolymerization effectively.

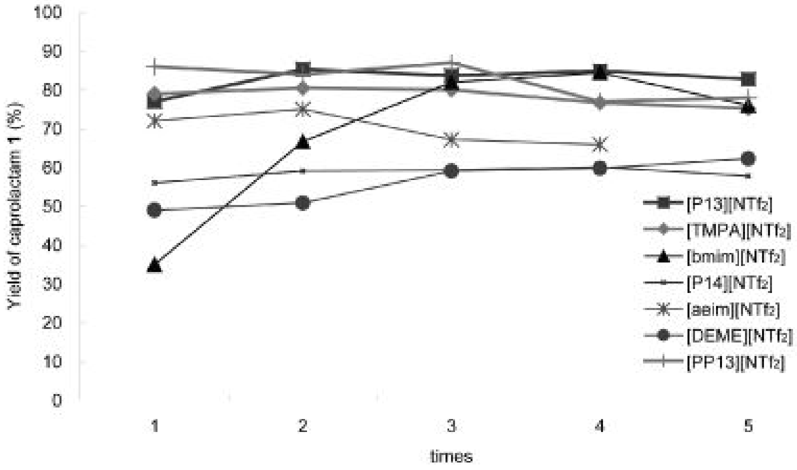


Fig. 2 Depolymerization of nylon 6 in ionic liquids

The depolymerization took place smoothly in various ionic liquids that contains TFSA in counter anion. The reaction rate depended on the cationic part of the ionic liquids; ammonium cations provided the good results. The depolymerization in imidazolium ionic liquid gave only 35% of **1**.

The reaction temperature was important for the efficient depolymerization. 300 °C was the best temperature. When treated at 270 °C, most of nylon was still remaining in the reaction mixture and the yield of **1** decreased. Higher temperature caused another problem. Treatment of nylon 6 at 330 °C provided caprolactam **1** along with *N*-alkylated side produces. This clearly showed that cationic part of ionic liquids reacted with caprolactam as an alkylating agent. Indeed, NMR spectra of used ionic liquids indicated some decomposition happened when the reaction temperature was higher than 330 °C.

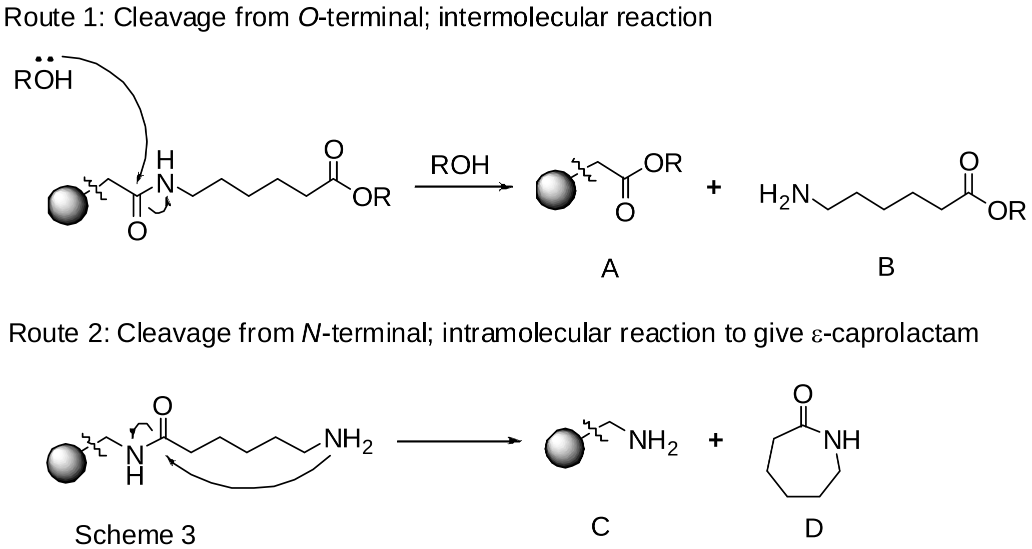
These ionic liquids were repeatedly useful at least five times for the reaction (Fig. 2). For example, treatment with nylon 6 in [PP13][TFSA] gave **1** in 86% for the first time, and 78% in the fifth time, although DMAP should be added at each times for the reaction. Thus, the ionic liquids were possible for recycling use

With these results in hand, we supposed the reaction mechanism as the following way (Scheme 3). The depolymerization progresses through addition-elimination reaction at the carbonyl carbon. When an external nucleophile such as methanolic oxygen atom attacks the carbonyl carbon, a methyl ester at the C-terminal of nylon A and 6-aminocapronic ester B should be formed (route 1). Caprolactam contained 7-membered ring which is not readily formed from the open-chain precursor such as B. Additionally the amino group in B should be methylated by methanol under the present reaction conditions.[8] On the other hand, the oxygen atom in secondary and tertiary alcohols is less nucleophilic than methanol. Thus, the reaction rate for route 1 should be much suppressed for the reaction employed with these alcohols. As a result, the most nucleophilic species in the reaction mixture should be the terminal amino group of nylon-6, which internally attacks the carbonyl carbon to give caprolactam D and next terminal amino group of the polymer C (route 2).[8]Thus, use of secondary and tertiary alcohols affords efficient depolymerization to caprolactam.

The reaction in ionic liquids should be assumed in a similar manner. There are virtually no nucleophiles because the counter anion of ionic liquids is almost non-nucleophilic. The route 2 in Scheme 3 is the only way to progress the depolymerization in ionic liquids. Thus, selective formation of caprolactam **1** was achieved by the back-bite mechanism

3. Conclusion

In conclusion, we have successfully depolymerized nylon 6 to its monomer caprolactam in good yield. As iPrOH can be reused after distillation from the reaction mixture, almost no waste comes out from the process. Ionic liquids can be used directly after the reaction and it can be used at least 5 times repeatedly although the costs of ionic liquids are not very cheap now. These new methodologies will open a new efficient strategy toward chemical recycling for waste plastics.


Route 1: Cleavage from *O*-terminal; intermolecular reaction

Route 2: Cleavage from *N*-terminal; intramolecular reaction to give ε-caprolactam

Scheme 3

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