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An Efficient Method To Depolymerize Polyamide Plastics: A New Use of Ionic Liquids

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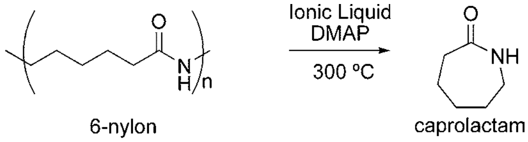
ABSTRACT



Treatment of polyamides in an ionic liquid at 300 °C resulted in the efficient depolymerization of polyamides to give corresponding monomeric lactam in good yields. The recovered monomer was collected by direct distillation of the reaction mixture. PP13 TFSI furnished the best results for the depolymerization. The ionic liquid could be recycled five times in the present reaction.

Development of an effective method for treating waste plastics is one of the important problems in recent environmental issues. Among several treatments developed thus far, the ideal one is undoubtedly chemical recycling, in which waste plastics are converted into corresponding monomers suitable for repolymerization reactions that reform recycled plastic.[1] To accomplish optimal recycling, an easy and efficient method to depolymerize polymers into corresponding monomers must be developed. Depolymerization methods developed thus far are usually performed under high-temperature conditions, and therefore, high-boiling-point solvents or high-pressure apparatus is necessary. For these purposes, supercritical water[2] or other solvent systems[3] frequently have been employed, and pyrolysis of polymers has been used in some cases.[4] These methods have sometimes taken advantage of depolymerization; however, due to the high temperature of the reaction, special care is required to prevent the possibility of fire. In addition, special apparatus that tolerates the high-pressure conditions is essential to perform the reaction. Recently, ionic liquids have been of interest in many fields of chemistry because of their unique properties such as solubility, nonvolatility, high-reactivity, low-flammability, etc.[5] Nonvolatility and stability at high temperature make the ionic liquids suitable for this purpose. Moreover, the possibility of recycling is important for achieving a zero-emission recycling system. To the best of our knowledge, thus far, there have been no practical reports on such use of ionic liquids.[6] In this paper, we discuss

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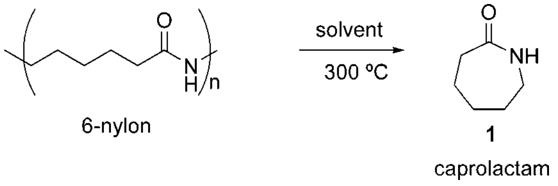
a new use of ionic liquids, i.e., depolymerization of polyamides. With our method, effective depolymerization is accomplished under normal or reduced pressure, and therefore, easy manipulation can be achieved even with ordinary glassware and the usual organic laboratory equipment. Also, ionic liquids can be reused five times without loss of depolymerization efficiency.

We first examined several ionic and non-ionic solvents for depolymerization of 6-nylon. The results are summarized in Table 1.

Table 1. Depolymerization of 6-Nylon in Various Solvents and Conditions



entry	solvent[d]	catalyst	wt %	time (h)	**1**; yield (%)[a]
1	ethylene glycol	none	0	4	0.2
2	triethylene glycol	none	0	4	0.8
3	emim BF_4	none	0	5	43
4	PP13 TFSI	none	0	6	55
5	PP13 TFSI	DMAP[b]	5	6	86
6	PP13 TFSI	NMI[c]	5	6	55
7	P13 TFSI	DMAP	5	6	77
8	TMPA TFSI	DMAP	5	6	79
9	bmim TFSI	DMAP	5	6	35
10	TMPA Br	DMAP	5	6	0
11	TMPA BF_4	DMAP	5	6	0

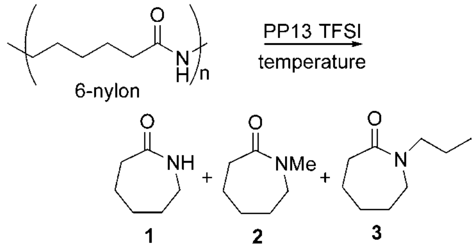
[a] Isolated yield. [b] *N*,*N*-Dimethylaminopyridine. [c] *N*-Methylimidazole. [d] emim: 1-ethyl-3-methylimidazolium. PP13: *N*-methyl-*N*-propylpiperidinium. P13: *N*-methyl-*N*-propylpyrrolidinium. TMPA: *N*,*N*,*N*-trimethyl-*N*-propylammonium. bmim: 1-butyl-3-methylimidazolium.

The experimental procedure was quite simple. A 6-nylon chip, with a mean molecular weight of 22 000, was added to the reaction solvent in the presence or absence of a catalyst and then heated at 300 °C and stirred under a nitrogen atmosphere for 1 h until the reaction mixture became homogeneous. Then, the reaction vessel was attached to a Kugelrohr apparatus and heated at 300 °C under reduced pressure to collect the monomerized material, whose purity was then checked by GC-MS analyses.

No depolymerization took place from 6-nylon by simply heating in glycolic solvent (Table 1, entries 1 and 2). Ionic liquid showed some preference for depolymerization, and the treatment of 6-nylon in emim BF_4 afforded caprolactam **1** in 43% yield (entry 3). To enhance the efficiency of depolymerization, we added DMAP as a catalyst,[7] and the yield increased significantly (compare entries 4 and 5).[8] NMI, another useful acylating catalyst,[9] did not catalyze the reaction effectively (entry 6). This may be because of the volatility of NMI at 300 °C. The counteranion of the ionic liquid was important for efficient depolymerization. TFSI was the best choice for the reaction (entries 8, 10, and 11). Employing quaternary ammonium salt furnished better results than imidazolium salts.

We next examined the optimum reaction temperature. The results are summarized in Table 2.

Table 2. Optimization of Reaction Temperature for the Depolymerization of 6-Nylon



entry	temp (°C)	**1**; yield[a] (%)	**2**; yield[a] (%)	**3**; yield[a] (%)
1	270	7	0	0
2	300	86	0	0
3	330	55	0	8
4	350	6	2	7

[a] Isolated yields based on GC-MS analyses.

The reaction at 270 °C did not provide sufficient depolymerization and the yield of the desired lactam was only 7% (entry 1). After cooling, the reaction mixture solidified so that oligomeric polyamides still remained in the reaction mixture. The reaction took place smoothly at 300 °C and caprolactam was isolated in good yield (entry 2). 6-Nylon underwent good depolymerization in the reaction performed at 330 °C, but small amounts of *N*-propylcaprolactam (**3**) were formed as a byproduct (entry 3). This propyl group may be derived from the propyl group in PP13; therefore, a certain amount of decomposition of PP13 may have occurred at this temperature. When the reaction was carried out at 350 °C, very small amounts of the desired monomer **1** were obtained as a mixture that contained *N*-methyl and *N*-propyl lactams **2** and **3** (entry 4). Thus, we concluded that 300 °C is the optimum temperature for the depolymerization reaction, while some decomposition takes place when the ionic liquid is exposed at a temperature of 330 °C or higher.

Finally, we examined the recycling use of ionic liquids. The results are summarized in Table 3.

For example, PP13 TFSI converted 6-nylon in 86% yield for first time use, and in 84% yield for fifth time use. Other ionic liquids such as TMPA TFSI also worked efficiently

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(6) Earle, M.; Seddon, K. R.; Forsyth, S.; Frohlich, S.; Gunaratne, N.; Katdare, S. WO2006/072775. Earle, M.; Frohlich, U.; Huq, S.; Katdare, S.; Lukasik, R. M.; Bogel, W.; Plechkova, N. V.; Seddon, K. R. WO2006/072785. They have commented on the possibility of using ionic liquids for depolymerization, but no practical examples have been provided.

(7) Recent review: Spivey, A. C.; Arseniyadis, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 5436.

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Table 3. Yield of ϵ-Caprolactam **1** in the Reaction Employing Recycled Ionic Liquid for the Depolymerization Reaction of 6-Nylon.

times	TMPA TFSI	PP13 TFSI	P13 TFSI	P14 TFSI
1	79	86	77	56
2	80	84	85	59
3	80	87	84	59
4	77	77	85	60
5	75	78	83	58

after being reused five times and the desired caprolactam **1** was isolated in good yields. We confirmed that no trace amounts of **1** or materials derived from 6-nylon remained in the ionic liquid after being reused five times. Therefore, the present depolymerization occurred as a clean reaction.

We also analyzed the ionic liquid by NMR after use in the present reaction. Figure 1 shows the combined NMR spectra for PP13 TFSI. NMR spectra for PP13 TFSI after being used for depolymerization at 300 (third spectrum from the bottom) and 270 °C (second bottom spectrum) looked similar to that of the original PP13 TFST (bottom spectrum). These results reflect the fact that PP13 TFSI underwent virtually no decomposition throughout the reaction (Figure 1).

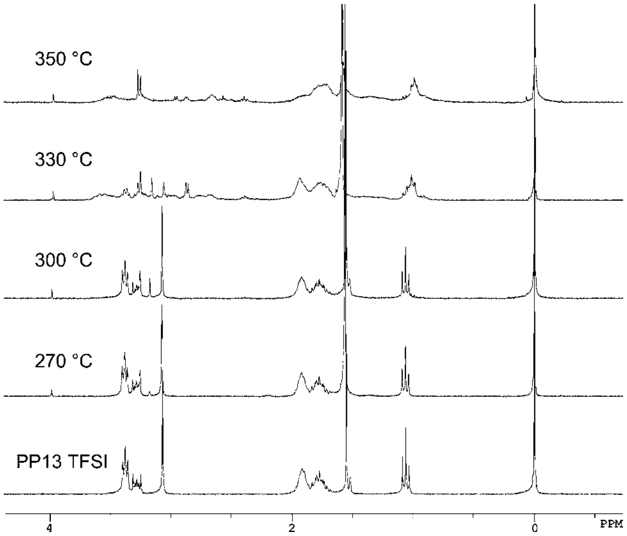

Figure 1. Comparison of NMR spectra of PP13 TFSI after being reused five times for the depolymerization reaction at various temperatures.

On the other hand, NMR spectra for the top two reactions looked very different from the original profile (bottom spectrum) and the ionic liquid had experienced significant decomposition during the reaction. This means that the temperatures of 330 °C or higher were too high for PP13 TFSI. Indeed, some *N*-alkylated products such as **2** and **3** were detected by GC-MS analyses (Table 2, entries 3 and 4). Therefore, we concluded that 300 °C was the optimum temperature for depolymerization to proceed smoothly and also to prevent decomposition of the ionic liquid.

Thus, we have succeeded in developing a novel depolymerization reaction for 6-nylon. Through the present reaction, 6-nylon was readily converted into ϵ-caprolactam **1** in good yield. The most effective ionic liquids were quaternary ammonium salts such as PP13 and TMPA. The ionic liquid was used repeatedly at least five times without significant decomposition. It should be mentioned again that the present method requires only ordinary glassware, and there is no need to use special high-pressure apparatus. This is the first example of the use of ionic liquids for effective depolymerization of polymeric materials and will open a new field in ionic liquid chemistry as well as plastic recycling. Further investigations on this issue are now underway in our laboratory.

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Supporting Information Available: Experimental procedures and NMR spectra for depolymerized products. This material is available free of charge via the Internet at http://pubs.acs.org.

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