1016 Chemistry Letters Vol.38, No.11 (2009)

Preparation of Novel Functionalized Ammonium Salts that Effectively Catalyze Depolymerization of Nylon-6 in Ionic Liquids

Shigehiro Yamamoto and Akio Kamimura*

Department of Applied Molecular Bioscience, Graduate School of Medicine, Yamaguchi University, Ube 755-8611

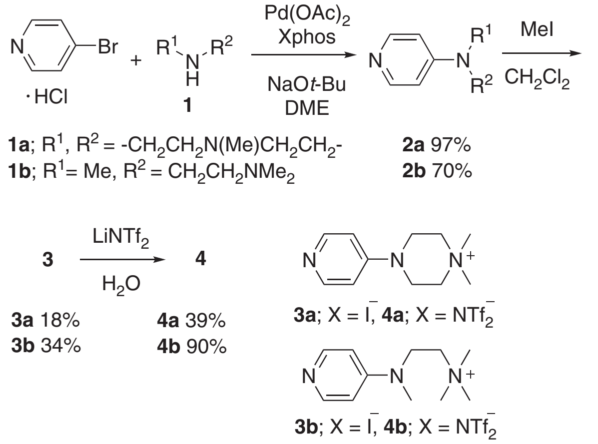
(Received July 24, 2009; CL-090695; E-mail: ak10@yamaguchi-u.ac.jp)

A new type of ammonium salt containing DMAP in the cation was prepared and applied for the depolymerization of nylon-6 giving monomeric caprolactam in high yield through direct distillation. The ionic liquids could be used at least five times.

Development of a new method for plastic recycling is one of an urgent problem to be solved.[1] To achieve efficient recycling of plastics, a convenient and effective depolymerization reaction which selectively gives monomeric materials suitable for further recycling is necessary. During such reaction, monomeric materials should be isolated in high yields as well as in sufficient purity through simple manipulation. On the other hand, depolymerization however usually requires high temperatures which complicate the process. Nylon-6 is a commonly used polymer and depolymerization has been explored for over 30 years, however, efficient isolation of the resulting monomer remains problem.[2] Recently, we developed a new method for depolymerization of nylon-6 in ionic liquids.[3] This is the first example employing ionic liquids for the depolymerization and showed a new methodology for plastic chemical recycling as well as a new use of ionic liquids. Our methodology enabled depolymerization of nylon-6 into caprolactam in a selective manner, and the monomeric material was isolated in pure form by direct distillation from the reaction pot. For efficient progress of the reaction, *N*,*N*-dimethylaminopyridine, (DMAP),[4] was needed as a catalyst, which promoted cleavage of amide linkages in the polymer. Although the ionic liquids could be used several times, addition of fresh DMAP was necessary for each reaction. If a DMAP unit were to be appended to the cation of an ionic liquid, the resulting functionalized solvent could be expected to be widely employed in not only depolymerization but also in organic synthesis.[5] In this paper we report the preparation of new type of ammonium salts **3** and **4** in which DMAP was installed. Prepared salts were examined for the depolymerization reaction of nylon-6.

DMAP-containing ammonium salts **3** and **4** were prepared in the following procedure (Scheme 1). The first step is installation of a 4-amino group by using the Buchwald–Hartwig reaction.[6] Commercially available 4-bromopyridinium was treated with piperazine **1a** in the presence of palladium catalyst resulting in the formation of 4-aminopyridine derivatives **2a**. The results are summarized in Table 1. We examined various reaction conditions for the conversion. Use of BINAP as a ligand only gave **2a** in 27% yield (Entry 1). Prolonged reaction time did not improve the yield (Entry 2). Use of dppp, dppf, and Xphos also provided similar results (Entries 3, 4, and 6). Finally we found that use of DME as the solvent and Xphos for the additional ligand led to successful introduction of amine at the C4 position in pyridine and desired **2a** was isolated in 97% yield (Entry 7).

Another 4-aminopyridine **2b** was also prepared in 70% yield under the optimized conditions. The next stage was N-methylation of **2**. Treatment of **2a** with MeI in CH_2Cl_2 resulted in the formation of precipitation, the filtration of which readily gave pure N-metyhylated product **3a** in 18% yield. Although the yield was poor, this preparation was quite simple because the precipitate only included **3a** and further methylated compounds were not observed in the precipitate. We proceeded to optimize the reaction conditions, however, use of large excess of MeI provided dimethylated product as a side product. Compound **2b** was also methylated under the same conditions, and compound **3b** was isolated in pure form. It should be noted that use of other alkyl iodide such as propyl iodide did not provide the desired product **3c** but led to N-alkylation of another position as in **2a**.

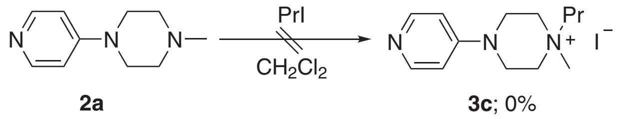


Scheme 1. Preparation of DMAP-containing ammonium salts **3** and **4**.

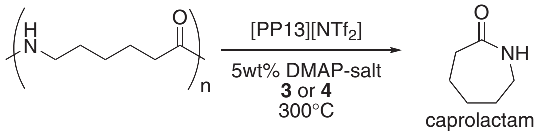
Table 1. Preparation of 4-aminopyridine **2a**

Entry	Catalyst	Solvent	Temp. /°C	Time /h	Yield[a] /%
1	$Pd(OAc)_2$/BINAP 4 mol %	toluene	70	2	27
2	$Pd(OAc)_2$/BINAP 4 mol %	toluene	70	20	18
3	$Pd(OAc)_2$/dppp 4 mol %	toluene	70	3	22
4	$Pd(OAc)_2$/dppf 4 mol %	toluene	70	1	Trace
5	$Pd(OAc)_2$/BINAP 4 mol %	CPME	70	7	30
6	$Pd(OAc)_2$/Xphos 4 mol %	toluene	90	20	26
7	$Pd(OAc)_2$/Xphos 4 mol %	DME	90	44	97

[a]Isolated yield.



Scheme 2. N-propylation of **2a**.



Scheme 3. Depolymerization of nylon-6 in ionic liquids containing **3** and **4**.

Table 2. Depolymerization of nylon-6

Entry	DMAP salt		Yield %[a]				
			1st	2nd	3rd	4th	5th
1	**3a**	I^-	70	67	79	61	42
2	**4a**	Tf_2N^-	64	74	38	67	42
3	**3b**	I^-	61	66	77	72	76
4	**4b**	Tf_2N^-	67	80	75	78	79

[a] Isolated yields.

The last step of the preparation of **4** was anion exchange of **3**, which was performed by simple extraction method to give **4a** and **4b** in good yields. Unfortunately, all of these ammonium salts **3** and **4** were solid at room temperature.

With desired DMAP-containing ammonium salts **3** and **4** in hand, we examined the depolymerization of nylon-6 (Scheme 3). The depolymerization was carried out in [PP13][TFSA] in the presence of catalytic amounts of **3** and **4**. The results are summarized in Table 2.

The ionic liquids containing ammnonium salts **3** and **4** smoothly depolymerized nylon-6 in good yield. A mixture of nylon-6 chips were added to a mixed solvent of [PP13][TFSA] with **4a** and heated at 300 °C. After 1 h, the mixture became homogeneous oil. Depolymerized caprolactam was obtained in 64% yield (Entry 2, 1st) by distillation of the oil using Kugelrohr apparatus for 6 h. All of the ammonium salts prepared here were effective for the depolymerization reaction and caprolactam was isolated in more than 60% yield (Entries 1–4, 1st). The counter anion of the salts did not cause a significant difference in the reaction.

Repeated use of the ionic liquid system was also examined. Nylon-6 chips were added to the recovered mixed ionic liquid and the resulting mixture was heated at 300 °C under reduced pressure for 6 h. Caprolactam was collected in a similar manner. The yield of caprolactam was usually about 70–80%, so effective depolymerization was accomplished by using these ionic liquids several times. It should be mentioned that no addition of DMAP was needed for the effective depolymerization with the present mixed ionic liquids system. Thus, DMAP installed in the cationic part of ammonium salt survived under the high temperature conditions and catalysed the reaction several times effectively. Use of **3a** and **4a** tended to lower the yield of the depolymerization the 5th time; this is probably due to the partial decomposition of the ammonium portion of **3a** and **4a** (Entries 1 and 2). On the other hand, compound **4b** endowed with both DMAP and [TMPA] structures, showed the best results for the repeated depolymerization. The yields over 5 reaction cycles constantly exceeded 70% except for the 1st time (Entry 4). Comparing the counter anion, TFSA seemed to provide better results than iodide (Entries 3 and 4). These results suggest that the ammonium salts **3b** and **4b** were stable and survived through the treatment at 300 °C for several times. Thus, the installation of DMAP led to effectictively catalyzed depolymerization of nylon-6 in ionic liquid.

In conclusion we have successfully prepared a new type of ammonium salt containing DMAP in the counter cation. This salt well catalyzed the depolymerization of nylon-6, and was useful for several reaction cycles. With the expectation that the novel ammonium salts could catalyze not only high-temperature reactions but also other organic transformations, we are now investigating the use of the ammonium salt in organic synthesis.

This work was partially supported by Grant-in-Aid for Scientific Research on Priority Areas (Science of Ionic Liquids, 2005–2009) from The Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

1 *Technology for Feedstock Recycling of Plastic Wastes*, ed. by Research Association of Feedstock Recycling of Plastics, Japan, CMC Books, Tokyo, Japan, **2005**.

2 a) A. Kamimura, Y. Oishi, K. Kaiso, T. Sugimoto, K. Kashiwagi, *ChemSusChem* **2008**, *1*, 82. b) S. R. Shukla, A. M. Harad, D. Mahato, *J. Appl. Polym. Sci.* **2006**, *100*, 186. c) M. Goto, M. Sasaki, T. Hirose, *J. Mater. Sci.* **2006**, *41*, 1509. d) T. Iwaya, M. Sasaki, M. Goto, *Polym. Degrad. Stab.* **2006**, *91*, 1989. e) L. Meng, Y. Zhang, Y. Huang, M. Shibata, R. Yosomiya, *Polym. Degrad. Stab.* **2004**, *83*, 389. f) O. Sato, Y. Ikushima, *Kobunshi Ronbunshu* **2001**, *58*, 533. g) M. Goto, M. Umeda, A. Kodama, T. Hirose, S. Nagaoka, *Kobunshi Ronbunshu* **2001**, *58*, 548. h) H. Bockhorn, A. Hornung, U. Hornung, J. Weichmann, *Thermochim. Acta* **1999**, *337*, 97. i) S. Czernik, C. C. Elam, R. J. Evans, R. R. Meglen, L. Moens, K. Tatsumoto, *J. Anal. Appl. Pyrolysis* **1998**, *46*, 51. j) A. Ballistreri, D. Garozzo, M. Giuffrida, G. Impallomeni, G. Montaudo, *Polym. Degrad. Stab.* **1989**, *23*, 25. k) H. Ohtani, T. Nagaya, Y. Sugimura, S. Tsuge, *J. Anal. Appl. Pyrolysis* **1982**, *4*, 117. l) I. Lüderwald, F. Merz, M. Rothe, *Angew. Makromol. Chem.* **1978**, *67*, 193. m) N. Ogata, *Bull. Chem. Soc. Jpn.* **1961**, *34*, 1201.

3 a) A. Kamimura, S. Yamamoto, *Org. Lett.* **2007**, *9*, 2533. b) A. Kamimura, S. Yamamoto, *Polym. Adv. Technol.* **2008**, *19*, 1391.

4 Recent review: A. C. Spivey, S. Arseniyadis, *Angew. Chem., Int. Ed.* **2004**, *43*, 5436.

5 A. R. Katritzky, B. L. Duell, R. P. Seiders, H. D. Durst, *Langmuir* **1987**, *3*, 976.

6 a) S. Wagaw, S. L. Buchwald, *J. Org. Chem.* **1996**, *61*, 7240. b) Q. Shen, T. Ogata, J. F. Hartwig, *J. Am. Chem. Soc.* **2008**, *130*, 6586.