

AN UPGRADE CHEMICAL RECYCLING OF POLYAMIDES

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Abstract

Polyamides such as nylon 6 and nylon 12 were effectively converted to ω -hydroxyalkanoic acid by treatment with supercritical MeOH. The reaction produced corresponding monomeric ω -aminoaminoalkanoic acid derivatives including lactams as intermediate products, which underwent nucleophilic substitution to give methyl ω -hydroxyalkanoate or elimination reaction to give methyl ω -hydroxyalkenoate. The reaction was sensitive to acid/base catalyst and solvent. Kinetic analysis was performed by simulating products distribution and kinetic parameters were estimated.

Keywords: upgrade recycling, supercritical MeOH, depolymerization, polyamides, ω -hydroxyalkanoic acid.

1. Introduction

Development of effective methods for recycling plastics is desired as a key technology for sustainable development of the world.^[1] Chemical recycling is regarded as a key technology for reserving carbon resources because it provides rebuilt plastics from waste plastics. However, chemical recycling contains economical problems because practical chemical recycling process usually requires huge costs. If the process provides more valuable products than simple rebuilt plastic, this strategy may overcome such problems.

Polyamides are important polymers to support our daily lives and tons of products are produced in every year. We already found that use of supercritical secondary alcohol effectively converted nylon-6 into monomeric caprolactams in more than 90% yields.^[2] Ionic liquids such as [PP13][TfSA] also achieved an interesting depolymerization.^[3] During the course of our investigation to develop a new chemical recycling reaction for plastics, we found that treatment of polyamides with supercritical MeOH resulted in an effective conversion to ω -hydroxyalkanoic acids, which were usually more valuable chemicals than corresponding monomeric compounds.^[4] Thus, the present method will open a new avenue for upgrade chemical recycling technology. In this paper we show details of the conversion and some kinetic analysis.

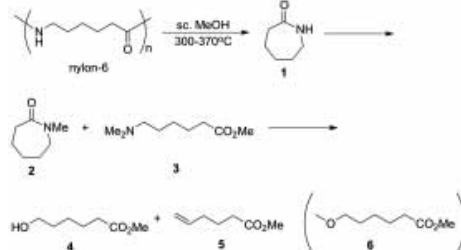
2. Materials and Methods

Procedures for depolymerization of polyamides in MeOH: Polyamide chips (0.3 g, Mw = 22000) and MeOH (4 g) were added to a 10 mL reaction vessel under argon atmosphere. After sealing, the reaction vessel was placed in a hot oven (300 to 370 °C) for an appropriate time. The reaction vessel was immediately cooled by dry-ice/MeOH bath, and an internal standard was added. The

products were analyzed by GC (Shimadzu GC-2014, Intercap 5 (0.25 mm id x 30 m) column) and quantified by the curve fitting method.

3. Results and Discussion

Nylon 6 and MeOH were heated to 330 °C in a sealed tube for several hours. All of solid nylon chip disappeared within 1 h and most of polyamide linkages were cleaved to give monomeric compounds. The products were identified and quantified by GC analyses using the curve fitting method. GC analyses revealed that the following six compounds were formed as major products: caprolactam **1**, *N*-methylcaprolactam **2**, methyl 6-(*N,N*-dimethylamino) capronate **3**, methyl 6-hydroxycapronate **4**, methyl 5-hexenoate **5**, and methyl 6-methoxycapronate **6** (Scheme 1).



Scheme 1. Depolymerization of nylon 6 in supercritical MeOH at 330 °C.

Caprolactam **1** was formed as an initial product and the yield reached about 30% in 80 min. Then the yield of **1** decreased and the compounds **2** and **3** were produced; they reached their peak yields at 120 min. The final reaction products **4** and **5** gradually increased their yields in proportion to the reaction time and reached the maximum yields at 240 min. The yields of **4** and **5** were

unchanged thereafter so that these two products were stable under the reaction conditions. It should be noted that almost no formation of compound **6** was observed. This clearly suggested that no direct substitution of the amino group in compound **3** by MeOH occurred. The sums of the yields of compounds **1** to **6** exceeded 80% so that we supposed that most of products of the reaction were successfully traced. The reaction time course was depicted in Fig. 1.

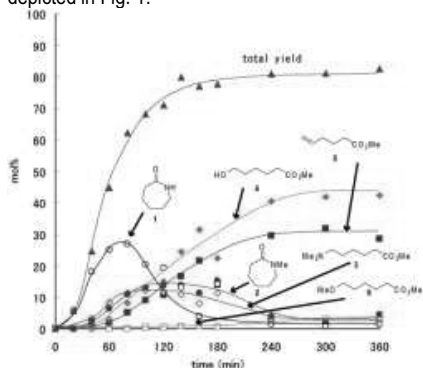
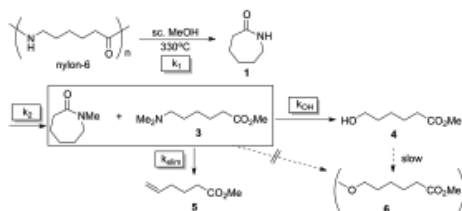


Fig. 1. The time course of the reaction of nylon 6 in supercritical MeOH at 330 °C.

The reaction performed under much higher temperature conditions progressed faster than the reaction at 330 °C, while decrease of the final products **4** and **5** was observed. This suggests that compounds **4** and **5** decomposed under the reaction conditions at 350 °C or higher. Products ratio between **4** and **5** was usually 1.5:1 and the ratio did not change during the reaction. We supposed that the chemoselectivity between **4** and **5** was determined kinetically. To improve the chemoselectivity of compound **4**, we examined various additives for the reaction. To our surprise, the ratio was enhanced to 6.7:1 when excess amounts of glycolic acid were added in the reaction. Finally compound **4** was successfully obtained in 69% yield in a highly chemoselective manner. The present methodology was useful for the treatment of other polyamide. For example, use of nylon 12 and nylon 66 gave methyl ω -hydroxydodecanoate and 1,6-hexanediol in good yields, respectively.

To analyze kinetics of the reaction, we performed a simulation of products distribution. Numerical integrations and optimizations using the Runge-Kutta method and Simplex algorithm were performed to estimate the kinetic parameters and to simulate the reactions, respectively. We hypothesized that the reaction took place through the pathway shown in Scheme 2, and that each step progressed as a first-order reaction. To simplify the simulation, the sum of the yields of compounds **2** and **3** was treated as a single intermediate. To fit the simulation with actual data, we introduced an induction period of the reaction. This is reasonable because 10 to 30 min were required until heating up the reaction vessel to the desired temperature. The kinetic parameters obtained by the simulation were summarized in Table 1.



Scheme 2. Kinetic simulation of the depolymerization of nylon 6 in supercritical MeOH at 330 °C.

Table 1. Kinetic parameters of the depolymerization at 330 °C.

First order rate k (10 ⁻³ min ⁻¹)	k ₁	k ₂	k _{OH}	k _{elim}
	14.7	29.1	11.9	8.2

The simulation was also successfully achieved for the reaction at 300 °C, 350 °C, and 370 °C. Based on these first order rate constants, the activation energies for each step were estimated using the Arrhenius plots. The estimated activation energies were 94.2 kJ/mol for the first step, nylon-6 to compound **1**, 100.1 kJ/mol for the second step, N-alkylation from compound **1**, 84.8 kJ/mol for the formation of compound **4**, and 94.4 kJ/mol for the formation of compound **5**.

4. Conclusions

We have successfully developed a new chemical conversion of polyamide. Treatment of polyamides with supercritical MeOH as a reaction solvent resulted in the direct conversion of amino group into hydroxyl group to give ω -hydroxycarboxylic acids or diols, which are more valuable compounds than simple monomeric materials of the polyamides. The hydroxyl/alkene selectivity is greatly improved by the presence of extra amounts of carboxylic acids. This methodology will open a new concept for upgrade chemical recycle which will be expected as a key technology to overcome the economical problems in the plastic chemical recycling.

References

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