A kinetic study on the conversion of nylon 12 to methyl 12-hydroxydodecanoate in supercritical MeOH in the presence of carboxylic acid

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ABSTRACT

Polyamides were effectively converted into hydroxyl esters by treatment with supercritical MeOH in the presence of glycolic acid. This transformation progressed smoothly over a period of 240 min, and the presence of glycolic acid accelerated the reaction. Kinetic analyses of the depolymerization of nylon 12 were performed by measuring the product distribution in the reaction mixture. The chemoselectivity of hydroxyl ester formation was linearly dependent on the amount of glycolic acid used. The product distribution of the reaction using pivalic acid was also measured. Simulations based on the actual time-course data enabled the estimation of kinetic parameters. The obtained kinetic parameters revealed that the rate constant for the formation of the hydroxyl ester was significantly enhanced by the presence of glycolic acid. These results clearly indicate that the monomeric unit, an amino ester, underwent a bimolecular substitution reaction with glycolic acid. Based on these results, we proposed a reaction mechanism for the formation of hydroxyl esters. Arrhenius plots of the reaction rates were used to effectively estimate the activation energy for each step.

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1. Introduction

Plastics are important materials in modern daily life. Various types of plastics in large amounts are produced and discarded each year. From the viewpoint of the conservation of carbon resources, plastics should be recycled and reused in a similar manner to iron or other metals. The plastic recycling is classified into three categories: material recycling, energy recycling, and chemical recycling. Among these, chemical recycling, especially monomer recycling, is preferable because this method enables the conversion of waste plastics into new plastics [1]. However, plastic recycling is challenging owing to a range of issues; a chemical issue and an economical issue. The former problem depends on the properties of the plastic. It should be solved by invention of new reaction to convert waste plastics into monomeric materials efficiently. On the other hand, the latter problem is much more serious, because the recycled plastic is usually low-valued products in market and

difficult to compensate the cost required during the recycling processes. As a result, chemical recycling is still on the way of developing. Thus, the innovation on a concept and a method for a practical chemical recycling are highly desired.

Recently, we developed a novel and effective method for the depolymerization of polyamides [2–8] to a monomeric material using supercritical alcohols [9]. Polyamides are typical plastics, the depolymerization of which has been examined by several methods that employ supercritical or subcritical fluids [10–13], thermolysis [14–17], or acid hydrolysis [18,19]. The treatment of polyamides in supercritical MeOH converted monomeric amino carboxylic acids to hydroxyl carboxylic acids [20]. This conversion was enhanced by the presence of additional carboxylic acids such as glycolic acid, and the yield of the hydroxyl carboxylic acid ester reached over 70% [21]. The method addresses both way the chemical and economic issues associated with the plastic recycling. The important point of the reaction is the product, hydroxyl carboxylic acid ester, is much valuable product in market than simple monomer, lactams, and provides high-value in product that opens a new possibility to solve the economical issue. This is the breakthrough in the concept for

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the chemical recycling of plastics. However, the reaction mechanism has remained unclear. A major question exists regarding why and how hydroxyl carboxylic acids are formed in the presence of additional carboxylic acids. The substitution reaction of an amino group with a hydroxyl group is recognized as a difficult transformation in organic chemistry, and to our best of knowledge, there has been no reports that shows a simple amino group is efficiently substituted to a hydroxyl group in one-step [22–25]. Our preliminary experiments using ^{18}O-enriched acetic acid suggest that the oxygen atom in the hydroxyl group originates from the additional carboxylic acid, not from supercritical MeOH or water produced under these conditions. To discuss and clarify the reaction mechanism, we measured the product distribution of the reaction. On the basis of these data, we performed simulations of the reaction, which allowed us to estimate the kinetic parameters. In this study, we report kinetic analyses of our reaction and discuss the reaction mechanism.

2. Experimental

2.1. Materials

A nylon 12 chip ($Mw = 22000$) was supplied by Ube Industries. Reagent-grade MeOH was purchased from Katayama Chemical Inc., Osaka, Japan, while all other chemicals, such as 12-aminododecanoic acid **4b** (see Scheme 2), were purchased from Aldrich or Tokyo Chemical Industry (TCI). The products, including compounds **1**, **2**, **3** (see Scheme 1), **5a**, and **5b** (see Scheme 3), were prepared separately. Details of the preparation have already been reported [21]. The amounts of extra acid (in equivalents) were calculated on the basis of the amounts of monomeric unit in nylon 12 (in mmol).

2.2. General procedures for depolymerization of nylon 12 in MeOH

Polyamide chips (0.10 g or 0.07 g, $Mw = 22000$), glycolic acid (0–0.0269 g), and MeOH (3 g) were added to a 10 mL reaction vessel (stainless steel tube, internal diameter 7.35 mm × 23 cm, capped at both ends with Swagelok nuts) under an argon atmosphere. After sealing, the reaction vessel was placed in a hot oven (330–360 °C) for the appropriate time. The reaction vessel was cooled in a dry-ice/MeOH bath, and the internal standard (1-decanol) was added. The products were analyzed by GC (Shimadzu GC-2014, Intercap 5 column (internal diameter 0.25 mm × 30 m)) and quantified using curve fitting methods. The sum of the yields for all major products exceeded 80% in each case.

### 2.3. Decomposition reaction of 12-aminododecanoic acid **4b** in MeOH

Compound **4b** (0.10 g, 0.46 mmol), glycolic acid (0–0.0353 g, 0–0.46 mmol, 0 to 1 equivalent), and MeOH (3 g) were added to a 10 mL reaction vessel (stainless steel tube, internal diameter 7.35 mm × 23 cm, capped at both ends by Swagelok nuts) under an argon atmosphere. After sealing, the reaction vessel was placed in a hot oven (300 °C) for the appropriate time. The reaction vessel was cooled in a dry-ice/MeOH bath, and the internal standard (1-decanol) was added. The products were analyzed by GC (Shimadzu GC-2014, Intercap 5 column (internal diameter 0.25 mm × 30 m)) and similarly quantified using curve fitting methods. The sum of the yields for all major products exceeded 80% in each case.

2.4. Decomposition reaction of 12-pivaloxydodecanoic acid methyl ester **5a** in MeOH

Compound **5a** (0.1000 g, 0.32 mmol), pivalic acid (0.2265 g, 2.22 mmol, 7 equivalents) and MeOH (3 g) were added to a 10 mL reaction vessel (stainless steel tube, internal diameter 7.35 mm × 23 cm, capped at both ends with Swagelok nuts) under an argon atmosphere. After sealing, the reaction vessel was placed in a hot oven (300 °C) for 1 h. The reaction vessel was cooled with a dry-ice/MeOH bath, and the internal standard (1-decanol) was added. The products were analyzed by GC (Shimadzu GC-2014, Intercap 5 column (internal diameter 0.25 mm × 30 m)) and similarly quantified using curve fitting methods to give **2** in 15% yield, **3** in 14% yield, and recovery of **5a** in 60%.

2.5. Decomposition reaction of 12-(methoxyacetoxy)dodecanoic acid methyl ester **5b** in MeOH

Compound **5b** (0.1525 g, 0.505 mmol), methoxyacetic acid (0.0466 g, 0.52 mmol, 1 equivalent) and MeOH (3 g) were added to a 10 mL reaction vessel (stainless steel tube, internal diameter 7.35 mm × 23 cm, capped at both ends with Swagelok nuts) under an argon atmosphere. After sealing, the reaction vessel was placed in a hot oven (300 °C) for 1 h. The reaction vessel was cooled in dry-ice/MeOH bath, and the internal standard (1-decanol) was added. The products were analyzed by GC (Shimadzu GC-2014, Intercap 5 column (internal diameter 0.25 mm × 30 m)) and quantified using curve fitting methods to give **2** in 78% yield and **3** in 0.6% yield.
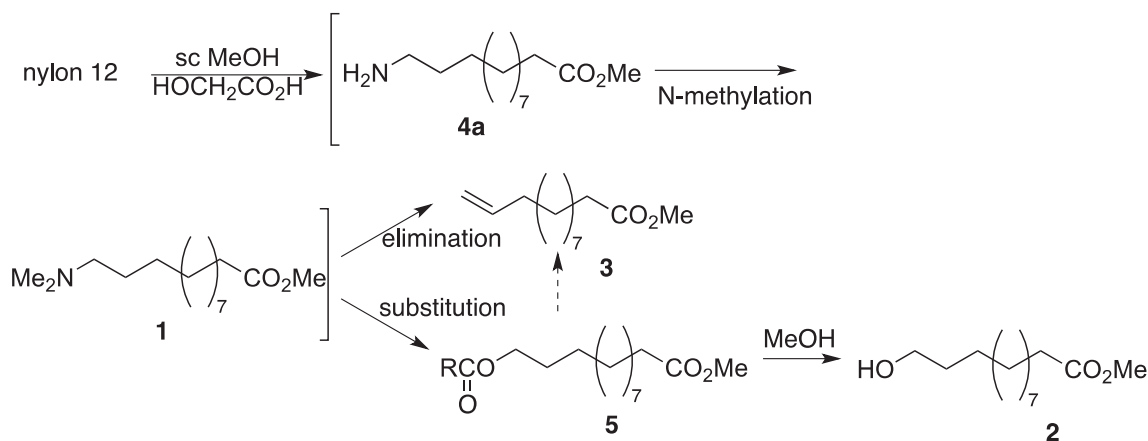
Scheme 1. Reaction mechanism of depolymerization of nylon 12.