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Studies on the oxidative degradation of nylons by nitrogen dioxide in supercritical carbon dioxide

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ABSTRACT

Oxidative degradation of nylons was carried out using nitrogen dioxide (NO_2) as the oxidizing agent and supercritical carbon dioxide ($scCO_2$) as the reaction medium. Seven typical nylons were studied: three ring opening polymerization type nylons (nylon-6, -11 and -12) and four condensation co-polymerization type nylons (nylon-4/6; -6/6; -6/9 and -6/12). All the nylons decomposed in the NO_2/$scCO_2$ system under relatively mild conditions (140 °C, 1 h, and 10 MPa) and provided aliphatic α, ω-diacids such as succinic, glutaric and adipic acids in good yields. The product distribution of these α, ω-diacids strongly depended on the reaction conditions such as temperature, time and amount of NO_2, but not on the total pressure. Furthermore, the proportions of the products were affected by the type of nylon. A mechanism is proposed and a detailed discussion regarding the degradation of nylon in the NO_2/$scCO_2$ system is provided.

1. Introduction

Synthetic polymers are made from limited resources such as petroleum and natural gas. These polymers are now truly indispensable and are used extensively in clothing, buildings, vehicles and communications equipment [1]. With the increase in polymer consumption, recycling has become increasingly important to preserve resources and protect the environment.

It has been reported [2] that approximately 11 million tons of plastic materials were produced in Japan in 2011, resulting in 9.5 million tons of waste plastic, of which 7.2 million tons were effectively recycled. Consequently, the effective rate of utilization was 77%. As percentages of this recycled plastic, 64.2% was thermally recycled (known as *energy recovery recycling* in Europe), 30.0% was material recycled (*mechanical recycling*) and 5.8% was chemically recycled (*feedstock recycling*). Chemical recycling involves the breakdown of polymeric waste into materials reusable as fuel or chemicals, but it makes up a small proportion of all recycled plastic both in Japan and worldwide.

The most common plastics are polyethylene (PE), polypropylene (PP) and polyvinylchloride (PVC). By comparison, the consumption of nylons is small. However, nylons have a high melting point and low solubility, providing nylon with advantageous properties such as thermal, mechanical and chemical resistance. Thus, nylons are used in an extremely broad range of applications, and their production and consumption has recently increased [2]. However, the positive attributes of nylons makes their recycling technically challenging and requires high temperature and/or high pressure.

Nylon recycling has mainly focused on non-catalytic or catalytic hydrolysis, ammonolysis, and pyrolysis. For example, high molecular weight nylon 4/6 and 6/6 fibers were depolymerized in the presence of benzyltrimethylammonium bromide in 5% sodium hydroxide, and the corresponding oligomers and monomers were isolated [3]. Glycolysis of nylon-6 in the presence of phosphoric acid at 250 °C provided a mixture of ethylene glycol derivatives of ε-caprolactam and linear oligomers [4]. Duch et al. [5] reported that nylon-6 and/or nylon-6/6 can be recycled via a combination of ammonolysis, dehydration, and nitrile hydrogenation in the presence of a Raney catalyst to produce predominantly hexamethylenediamine. On the other hand, thermal decomposition of nylon-12 and poly(1,4-phenylene terephthalamide) (Kevlar) in the presence of PVC at 700 °C produced alkenenitriles and benzenediamine, as well as hydrogen cyanide [6]. ε-Caprolactam was recovered from the catalytic pyrolysis of nylon-6 in the presence of phosphoric acid [7] and α-alumina supported KOH [8].

Recently, new approaches using supercritical fluids (SCFs) have been shown to be effective and are replacing traditional organic liquid solvents for the degradation of some nylons. SCFs show

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properties of both liquid and gas phases and have a density similar to liquids. Thus, the physicochemical characteristics of SCFs, such as high mixing rates, high diffusivity and low viscosity, as well as relatively weak molecular association, make them unusual media for chemical reactions [9]. Nylon-6 has been frequently used as a typical nylon for depolymerization in various SCFs and was effectively converted into its monomer or derivatives in several SCFs: SC toluene in the presence of small amounts of water [10], SC water [11], and SC alcohol [12]. The mechanism underlying nylon-6 depolymerization in SC methanol and isopropanol has been experimentally and theoretically studied using the quantum mechanical (QM)/Monte Carlo (MC)/free-energy perturbation (FEP) method [13].

Although SCFs appear promising for the depolymerization of nylons, to date only nylon-6 and a few SCFs have been studied. The present study focuses on supercritical CO_2 ($scCO_2$) because of its low cost, low critical temperature (31 °C) and pressure (7.4 MPa), and its non-toxic and non-flammable nature [14]. In addition, CO_2 separation from the reaction mixture is energy-efficient, so the product is directly obtained by simple pressure reduction. As the oxidant, we selected NO_2 because it is a gas and should be easily miscible with $scCO_2$. We expected the oxidation properties of NO_2 to be at least equal to HNO_3, a traditional oxidizing agent for organic compounds [15]. In this follow-on study to an earlier report [16], we describe the use of $scCO_2$ as a solvent and NO_2 as an oxidant for the oxidative degradation of several nylons.

2. Experimental

2.1. Materials

All nylons (3–5 mm pellets) were purchased from Aldrich Chemical Co. and used as received. Their chemical structures and some physical properties are listed in Scheme 1. All other chemical reagents were obtained from Wako Pure Chemical Industries Ltd. Japan and were used without further purification. Liquid CO_2 (99.9% purity) was obtained from Hikari Sanso Industries Inc. Japan and 99% purity liquid NO_2 was bought from Seitetsu Kagaku Industries Inc. Japan; these were used directly from their high-pressure cylinder containers.

2.2. Oxidative degradation

All reactions were conducted in a 50 cm^3 batch-type autoclave (TVS-N2, Taiatsu Techno Corp. Japan) made of stainless steel (SS-316) and equipped with an electromagnetic stirrer, thermometer, inlet and outlet high pressure Swagelock® valves purchased from Taiatsu Techno Corp. Japan, and a Bourdon tube pressure gauge (Takashima Keiki Co. Ltd. Japan). The temperature of the system was measured using a K-type thermocouple (Custom Corp. Co. Ltd. Japan); the temperature in the reactor was controlled to an accuracy of ±1.0 K. The accuracy of the pressure gauge was ±0.05 MPa.

For the reaction, 0.5 g of polymer sample was placed into the reactor, then the reactor was purged with a small amount of liquid CO_2 to prevent direct contact of the sample with neat NO_2. Then, a measured amount of liquid NO_2 was added, and liquid CO_2 was introduced into the reactor for a second time. Each introduction of NO_2 and CO_2 required weighing the whole reactor to determine how much NO_2 and CO_2 was added. This allowed the reaction pressure to be controlled, since the final total pressure of the reactor at a given temperature can be predicted based on the starting conditions (pressure was determined by the amount of CO_2 and the temperature).

Using an oil bath, the reactor was heated as quickly as possible (typically 10–20 min) to the temperature specified for the degradation reaction. After the degradation reaction had proceeded for the designated time, the reactor was removed from the oil bath and immediately put in an ice-water bath, cooling it to room temperature. It was then depressurized. The reaction products were removed using acetone and analyzed by nuclear magnetic resonance (NMR) and gas–liquid chromatography (GLC).

2.3. Analysis

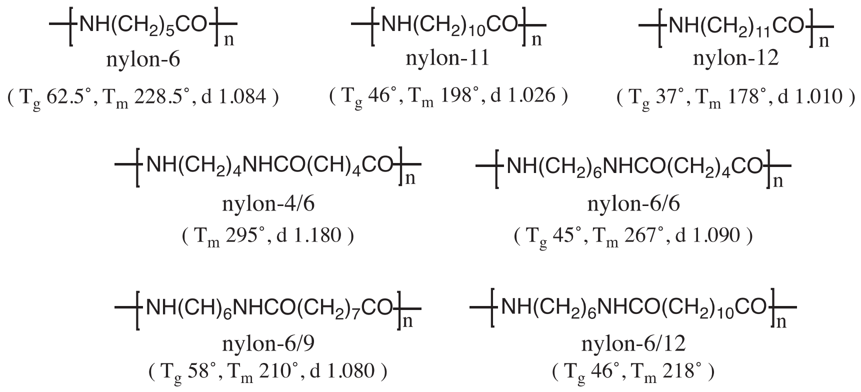
^1H NMR spectra of the reaction products as recovered were recorded on a Varian Unity INOVA-400 (400 MHz) spectrometer; chemical shifts were determined with respect to $(CD_3)_2SO$ ($\delta = 2.50$). All products were well known compounds and identified by comparison to commercially available authentic samples.

The obtained degradation products were esterified using Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) and analyzed on a Shimadzu GC-16A equipped with a flame ionization detector (FID). GLC separation and quantitative analysis of a mixture of dimethyl ester derivatives of the products were carried out at 90 °C using a 6-ft column of silylated diatomaceous earth (NEOSRB-NCS) containing 5% (w/w) SE-30 with helium as a carrier gas. The temperatures of the column, detector and injector port were 393, 513 and 513 K, respectively. The results of GLC analysis using chlorobenzene as an internal standard were also used to evaluate the concentrations of the components in the product mixture.

3. Results and discussion

3.1. Identification and quantification of products

The seven nylons studied can be grouped into two classes based on the type of polymerization used in their synthesis: three nylons



Scheme 1. Chemical structures and physical properties of nylons used in this study.