

Supercritical Secondary Alcohols as Useful Media To Convert Polyamide into Monomeric Lactams

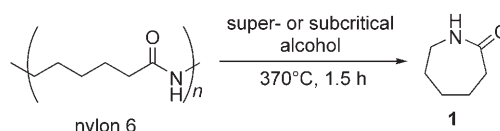
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Adequate treatment of waste plastics and polymers is one of the current environmental problems that need to be solved promptly. From an environmental point of view, monomer recycling is an ideal technique for the treatment of waste plastics as recycled plastics can be produced from waste ones. Therefore, monomer recycling may be a potentially promising waste-management method for creating a zero-emission plastic-recycling process. To establish effective monomer recycling, the following three chemical transformations are regarded as the key steps: 1) depolymerization reactions that convert waste plastics into monomers properly, 2) purification methods that give sufficiently pure monomers from the recovered crude monomers, and 3) repolymerization reactions that form recycled polymers from the recovered monomers.^[1] Of these three steps, depolymerization is regarded as the most important to accomplish successful monomer recycling.^[2] For this purpose, the depolymerization reaction has to go smoothly, giving the corresponding monomer in high yields. It is also highly desirable that the depolymerization reaction should selectively form a monomer which is suitable for the following repolymerization reactions. If the depolymerization reaction affords a complex mixture of monomers and their decomposed products, it becomes totally ineffective for the repolymerization reactions and the whole recycling process fails. Most of the depolymerization reactions that have been developed so far demand high-temperature conditions with the presence of a strong acid or base catalyst, which tends to give a complex mixture of the monomers and decomposition products.

Polyamides such as nylon 6 are one of the most common plastics or fibers and are widely used in our daily life. Since the 1960s, a number of methods for the depolymerization of polyamides have been reported.^[3] For example, Czernik et al.^[3h] and Hornung and co-workers^[3g] reported pyrolytic methods that effectively converted nylon 6 into caprolactam in good yields. Supercritical water offers another medium for this purpose, and several efforts have been reported thus far.^[4] However, supercritical or subcritical water frequently provides very severe conditions that provoke undesirable side reactions and

generate a complex mixture of many decomposed products of caprolactam.^[3b,c,e,f] Recently, we have focused on the use of supercritical alcohols instead of water as depolymerization media and have successfully found a new excellent method for the recycling of monomers of fiber-reinforced plastics (FRP), which are known to be one of the most difficult plastics to recycle.^[5] We also recently reported that ionic liquids are potentially useful media for the depolymerization reactions for zero-emission recycling.^[6] Here, we report the use of supercritical secondary or tertiary alcohols for the depolymerization of nylon 6, with very efficient conversion of nylon 6 observed to afford caprolactam (**1**) in high yields and with sufficient purity.

We examined several alcohols for the decomposition reaction of nylon 6. The reactions were carried out at 370 °C for 1.5 h in an autoclave. Under such conditions, some of the alcohols were in the supercritical phase (Scheme 1). For example,



Scheme 1. Depolymerization of nylon 6 in super- or subcritical alcohols.

when MeOH was employed in the reaction at 370 °C, the pressure in the reaction vessel reached about 22 MPa, which was sufficient to achieve the supercritical phase of MeOH. The results are summarized in Table 1.

Table 1. Conversion of nylon 6 into ϵ -caprolactam (**1**) in various alcohols.

Entry	Solvent	H ₂ O [ppm] ^[a]	Yield [%] ^[b]	T _c [°C] ^[c]	P _c [MPa] ^[d]
1	MeOH	1600	14	239.0	8.10
2	EtOH	545	36	243.0	6.38
3	PrOH	270	35	–	–
4	BuOH	250	47	–	–
5	<i>i</i> BuOH	176	44	–	–
6	C ₅ H ₁₁ OH	340	41	–	–
7	C ₆ H ₁₃ OH	414	46	–	–
8	C ₇ H ₁₅ OH	280	54	–	–
9	C ₈ H ₁₇ OH	70	55	384.8	2.69
10	C ₁₀ H ₂₁ OH	1800	55	–	–
11	C ₁₂ H ₂₅ OH	214	61	–	–
12	<i>i</i> PrOH	225	93 ^[e]	235.2	4.76
13	<i>s</i> BuOH	93	96	262.8	4.19
14	cyclohexanol	504	96	351.9	3.75
15	<i>t</i> BuOH	147	95	233.1	3.97
16	CH ₃ CH ₂ C(Me) ₂ OH	2200	97	272	3.88
17	ethylene glycol	–	trace	–	–
18	triethylene glycol	–	trace	–	–

[a] Water content in solvent. [b] Yield determined by GC. [c] Critical temperature. [d] Critical pressure. [e] Yield of isolated product **1**.

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Although the use of primary alcohols led to decomposition of the polyamide, the yield of **1** remained at medium to low levels (Table 1, entries 1–11). For example, the treatment of polyamides in MeOH produced a homogeneous solution of a mixture of decomposed products that were inseparable. The yield of caprolactam (**1**) was estimated as to be only 14% by GC analysis (Table 1, entry 1). As the length of the alkyl chain of the primary alcohols increased the yield of **1** was improved, and the use of a C12 alcohol afforded **1** in 61% yield; however, many side products were still observed in the crude products (Table 1, entry 11). Note that the supercritical phase seemed unnecessary for the present decomposition of the polyamide. For example, sufficient decomposition of polyamide was achieved under these conditions although the reaction temperature (370 °C) was not high enough to reach the supercritical phase of *n*-octanol (Table 1, entry 9).

The reaction profile of the depolymerization completely changed when secondary and tertiary alcohols were employed. To our surprise, nylon 6 underwent almost quantitative conversion into caprolactam (**1**). For example, the treatment of nylon 6 in *i*PrOH resulted in the formation of a homogeneous solution. Removal of *i*PrOH by using a conventional evaporator gave caprolactam (**1**) in 93% yield in a white solid form. Remarkably, this crude product showed a sharp melting point at 67.8–69.2 °C (lit. 68–71 °C),^[7] which clearly indicated that solid **1** was as pure as reagent-grade caprolactam. ¹H and ¹³C NMR spectra also supported its high purity. Thus, the above modification provides a useful and selective method for depolymerization of nylon 6 that offers a sufficiently pure monomer for repolymerization. The use of other secondary alcohols also resulted in clean conversion to **1** with yields greater than 95% (Table 1, entries 13 and 14). Tertiary alcohols also served as good media for the depolymerization and gave caprolactam (**1**) in almost quantitative yields (Table 1, entries 15 and 16); however, occasional blowouts happened during opening of the reaction vessel. This was probably due to the partial dehydration of the tertiary alcohols to corresponding alkenes, which caused extra pressure in the reaction vessel. Reactions in glycol failed to achieve the depolymerization; with most of the starting nylon 6 remaining in a heterogeneous oligomeric mixture after the treatment (Table 1, entries 17 and 18).

The progress of the current depolymerization reaction in *i*PrOH depended on the reaction temperature. The results are summarized in Figure 1. Depolymerization occurred smoothly when the reaction was performed at or above 350 °C. For example, the reaction performed at 350 °C for 1 h produced a homogeneous solution and no precipitates of oligomeric polyamides were observed. Note that the yield of **1** did not change in the reaction for 3 h, which indicated that caprolactam (**1**) survived under these reaction conditions for a couple of hours. On the other hand, the progress of the reaction became sluggish when the polyamide was treated at 330 °C, and the yield of **1** only reached 62% after 3 h of reaction.

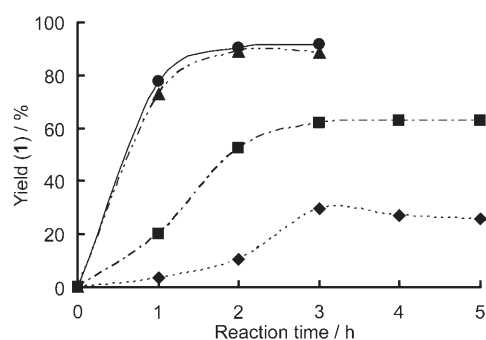
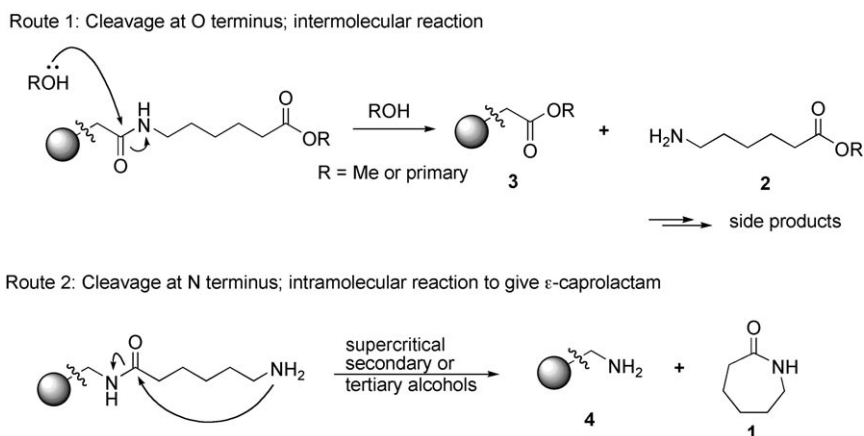


Figure 1. Temperature dependence of the depolymerization reaction in *i*PrOH. *T* = 300 (♦), 330 (■), 350 (▲), and 370 °C (●).

These reaction products were usually heterogeneous; some insoluble white precipitates with mean molecular weights of about 1300 g mol⁻¹ (obtained by gel permeation chromatography (GPC) analysis) were formed in the reaction mixture. A prolonged reaction time did not improve the yield of **1**, which was 63% after the polyamide was treated for 5 h. As the reaction temperature was lowered, the yield of **1** decreased and only 30% of **1** was formed at 300 °C. Thus, efficient depolymerization was achieved only when the reaction was performed at 350 °C or above. Note that the remaining oligomers were readily depolymerized to form caprolactam (**1**) when the reaction temperature was raised. For example, when depolymerized at 330 °C for 4 h, nylon 6 produced a heterogeneous mixture that contained compound **1** in 66% yield and a non-depolymerized oligomer as a white precipitate. Treatment of the mixture at 370 °C for an additional 1 h gave a homogeneous solution, and the yield of compound **1** increased to 79%. Thus, nylon 6 treated at or below 330 °C underwent partial depolymerization; the reaction stopped before the depolymerization was complete, and unreactive oligomers were formed. The oligomers were readily depolymerized when the reaction temperature was raised to 370 °C.

The mechanism of the selective depolymerization reaction is still under investigation; however, we propose the following reaction mechanism (Scheme 2). The oxygen atom of MeOH or primary alcohols is not hindered; therefore, it displays suffi-



Scheme 2. Plausible reaction pathways for depolymerization of nylon 6.

cient nucleophilicity to attack the carbonyl groups randomly in a polyamide chain. This process creates two fragmentation products: the ester-terminated polymer **3** and 6-aminocaproic ester **2** (route 1, Scheme 2). Under supercritical alcoholic conditions, the amino group in compound **2** may be alkylated by MeOH or a primary alcohol to give N-alkylated and further decomposed products.^[8] This reaction is much faster than the intramolecular cyclization that gives caprolactam (**1**). Indeed, we never detected any trace amounts of **1** in GC analyses when 6-aminocaproic acid methyl ester (**2**, R=Me) was treated under supercritical MeOH conditions. As a result, compound **2** should not be a precursor of compound **1**. Thus, the treatment of polyamide with a primary alcohol resulted in the formation of **1** in poor to medium yields.

In contrast to these alcohols, secondary or tertiary alcohols contain an oxygen atom that is sufficiently hindered by the alkyl group. It should be inactive toward nucleophilic attack to the carbonyl carbon atoms in the polyamide chain. Thus, the reaction rate for route 1 decreased. On the other hand, the N terminus of the polyamide chain is occupied by a primary amino group (NH₂), which is inherently nucleophilic. If this amino group attacks the adjacent carbonyl group, the reaction will automatically produce caprolactam (**1**) and NH₂-terminated polyamide chain **4**. Compound **4** again contains an N-terminal primary amino group, which successively reacts in a similar manner to give caprolactam (**1**; route 2, Scheme 2).^[9] The reaction rate of route 2 may be much faster than that of route 1 when secondary and tertiary alcohols are employed in the reaction. In other words, the use of these bulky alcohols not only suppresses route 1 but also makes the depolymerization through route 2 the dominant process. It is also important for the present clean depolymerization that compound **1** was a seven-membered lactam whose formation was slow but not very difficult. This is a key factor for the feasibility of route 2. For example, when nylon 12 was exposed to supercritical *i*PrOH in a similar manner, the reaction became sluggish and almost no formation of laurolactam was observed. This is because a macrocyclic compound such as laurolactam, a 13-membered-ring lactam, is usually very difficult to form even through reaction pathway route 2. Caprolactam (**1**) should be quite stable in the presence of supercritical bulky alcohols because no decrease in the yield of **1** was observed under the reaction conditions during the course of the reaction being examined.

In conclusion, we have successfully demonstrated that the use of supercritical secondary and tertiary alcohols dramatically improved the depolymerization of nylon 6. The present method, which consists of a simple manipulation to produce a high yield of monomeric lactam with excellent purity, will open a new avenue for plastic recycling chemistry. Further investigation and application of the present method is now underway in our laboratory.

Experimental Section

General procedure for depolymerization of nylon 6: in *i*PrOH (Table 1, entry 12): Nylon chips (0.3 g, *M*_n = 22 000 g mol⁻¹) and

*i*PrOH (4 g) were added under argon atmosphere to a 10-mL reaction vessel. After sealing the reaction vessel, it was placed in a hot oven (370 °C) for 1.5 h. After that time, the reaction vessel was cooled with water. For the isolation of caprolactam (**1**), this reaction was performed four times, all of the reaction mixtures were combined, and the combined mixture was concentrated to give caprolactam (**1**) as a white solid in 93% yield (1.099 g); m.p.: 67.8–69.2 °C (lit. 68–71 °C)^[7]; ¹H NMR (270 MHz, CDCl₃, TMS): δ = 1.73 (m, 6H), 2.47 (t, ³J(H,H) = 5.5 Hz, 2H), 3.21 (dd, ³J(H,H) = 5.9, 9.9 Hz, 2H), 6.2–6.5 ppm (br, 1H); ¹³C NMR (67.5 MHz, CDCl₃): δ = 23.1, 29.6, 30.5, 36.7, 42.7, 179.4 ppm; MS (70 eV, EI): *m/z* = 113 [*M*⁺]. The GC analysis was identical to that of an authentic sample.

Keywords: high-pressure chemistry • high-temperature chemistry • polymers • solvolysis • supercritical fluids

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