

Supercritical Lower Alcohols as a Useful Media for Depolymerization of Plastics

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INTRODUCTION

Development of proper method for treating waste plastics is desired in these days. Plastics are made from petroleum which is recognized as useful natural resources. Most of plastics were consumed in a just one-time use and then disposed as a waste. This is enormous loss of our precious resources. Moreover, the process of plastic disposal usually induces additional waste of energies and significant emission of carbon dioxide, which is currently recognized as a problematic chemical species. If recycled plastics are possible to be made from the waste plastics, such method contributes very much to the progress of sustainable social system. With these backgrounds of global demand, monomer recycles of waste plastic is desired [1].

To achieve efficient monomeric recycle of plastic, the following three steps are required. These are depolymerization, purification, and repolymerization steps. Among these steps, the depolymerization, the first step, is the most important and decides how successfully the whole monomeric recycling works. Depolymerization is the back reaction of the polymerization and usually takes place when polymers are treated under high temperature conditions. But the thermal treatments often resulted in just a decomposition of the plastics and after the treatment the reaction afforded rather complex mixture which is useless for the further recycling process. As a result, selective monomerization are really required to realized the efficient monomer recycle.

Supercritical water is an interesting reaction media that have high reactivity as well as solubility. Although there are several known examples that employ supercritical water for the depolymerization reaction of plastics, this reaction media is too much reactive to accomplish selective depolymerization of waste plastics in most of cases [2]. On the other hand, lower alcohols such as methanol have their critical points at much lower temperature than that of water. It is expected that the reactivity of supercritical alcohol is much milder than supercritical water. These mild properties of supercritical alcohols should be a useful media to

achieve the selective depolymerization of waste plastics for monomer recycling. In this paper, we report our recent results for the examination of supercritical alcohols for the selective depolymerization of waste unsaturated polyesters [3] and polyamides [4]. Successful depolymerization that gives suitable monomers for chemical recycling has been achieved.

MATERIALS AND METHODS

Waste FRP was gifted from Nakamura Tsusan Co. Ltd. Nylon-6 chips (0.3 g, Mw = 22000) was gifted from Ube Industries Co., Ltd. All depolymerizations were performed in a stainless-steel autoclave (10 mL or 100 mL) under a nitrogen atmosphere. Reagent-grade alcohol and DMAP were used for the reaction. The GC-MS analyses were performed using Shimadzu QP-2000 GC-MS or QP-2010 GC-MS spectrometer with SE-30 or InertCap 5 column and helium as a carrier gas. Quantitative analyses by GC were performed with calibration curve method.

RESULTS

To depolymerize waste FRP, we employed supercritical methanol for the reaction media. A suspension of flaked FRP (abt 5g) in MeOH was put in an autoclave and heated to 275 °C for 6 hours. The pressure in the reaction vessel reached about 10 MPa which is sufficient pressure to achieve supercritical phase of MeOH. Partial melting of FRP was observed but much amounts of resins was sticking on the inorganic ingredients. The present conditions seemed not enough to solubilized whole parts of FRP. FRP was made from unsaturated polyester which was built by ester linkage. Depolymerization of polyester should be achieved by hydrolysis or solvolysis of the ester groups. We supposed that any catalysts that promoted the ester formation should enhance the reaction rate of the present depolymerization. However, classical acid and base catalysts might damage the high pressure apparatus. We chose DMAP, *N,N*-dimethylaminopyridine, which was a well-known catalyst that dramatically enhanced the reaction rate of the esterification and amidation [5]. This was an organocatalyst and a neutral compound so that we needed not worry about damaging the apparatus.

The depolymerization of FRP in the presence of 3 wt% of DMAP was examined. During the reaction, melting down of FRP was observed and whole solubilization of FRP was achieved. After cooling, the following three components were obtained; MeOH-soluble oil,

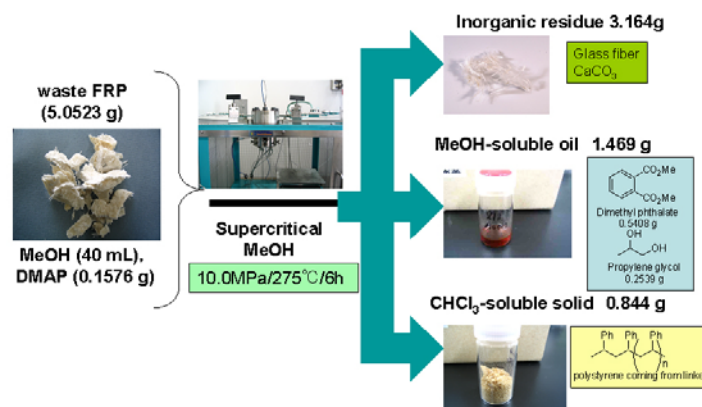
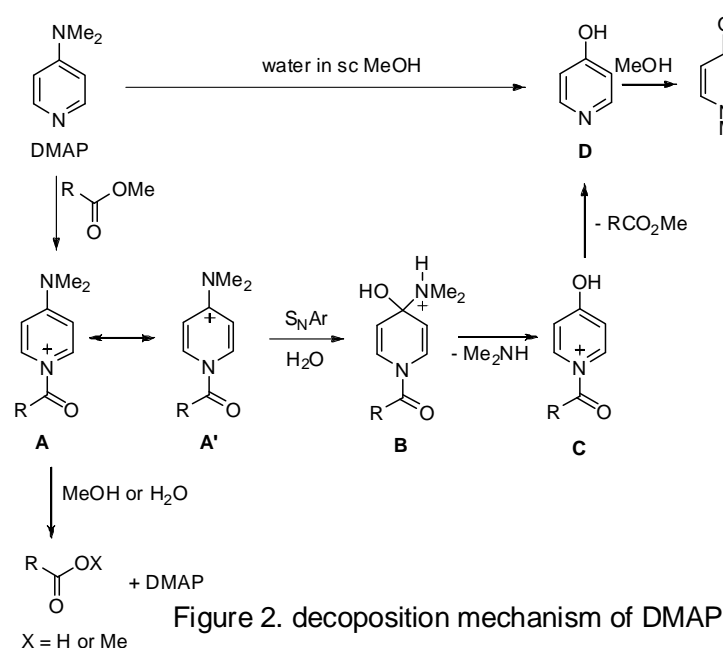


Figure 1. Depolymerization of FRP

CHCl₃-soluble solid, and inorganic residue (Figure 1). The first component mainly contained dimethylphthalate (DMP) and propylene glycol, which were the key monomeric parts of the unsaturated polyesters. The second part was a solid compound and consisted with polystyrene which was used as a linker unit for unsaturated polyesters. The last residue was a mixture of glass fiber and CaCO₃ that was used as a filler of the plastic. Recovered glass fiber was collected in pure form by treatment with water. The glass fiber still maintained almost the same strength as the new glass fiber had. Thus, the present method provided useful recovery of the glass fibers as ready-to-use form.



The first part of monomeric unit was examined for building recycled plastic. Standard treatment of the monomeric units for the preparation of unsaturated polyester failed the formation of resins. This was due to the contamination of the compounds derived from DMAP, which was decomposed during the reaction. The assumed decomposition route was depicted in Figure 2. DMAP reacted with phthalic esters to give reactive intermediate **A** in the transesterification reaction. However, its resonance form **A'** activated the pyridine ring toward S_NAr reaction that passed through the formation **B** to give **C**. Once intermediate **C** was formed, it provided **D**. Then the nitrogen atom in the ring was methylated by methanol under supercritical conditions [6] to give **E**, the contaminant of the monomeric unit.

Fortunately the present contaminants and other unknown materials in the MeOH-soluble components were readily removed by simple washing purification and very pure form of DMP was obtained by this procedure. It should be noted that more than 90% of DMP formed through the depolymerization reaction was recovered in the purified DMP unit. As we expected, the purified DMP smoothly gave unsaturated polyesters [7]. Hardness test for the

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Figure 3. Chemical recycling of FRP

recycled resin indicated almost the same values as the virgin polymers showed. Thus the present procedures realized a practical recycling for FRP, in which an ideal recycle, from waste plastic to new plastic, was achieved (Figure 3).

We next applied the present supercritical alcoholic conditions to depolymerize other plastics. Among many plastics we examined, nylon-6 showed remarkable results. Treatment of nylon-6 with supercritical MeOH resulted in the formation of a complex mixture of depolymerized products. Contents of caprolactam were estimated to be only 14% of the recovered material (Table 1, entry 1). Most of the recovered material contained further decomposed product of caprolactam. We were very disappointed to the result. Use of DMAP did not improve the result in this time. We assumed that the present reaction conditions were too strong that provoked undesirable decomposition of caprolactam. To reduce the reactivity of the supercritical alcohol, we examined several alcohols for the reaction. The results are summarized in Table 1.

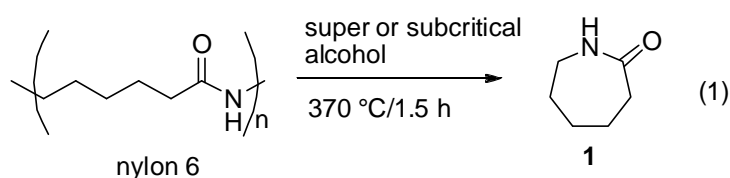


Table 1. Conversion of nylon 6 to ϵ -caprolactam 1 in various alcohols.

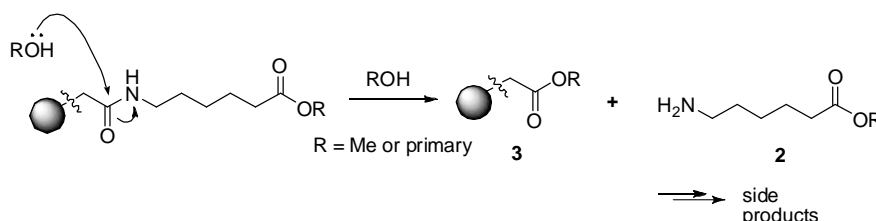
Entry	Solvent	Water contents (ppm)	1; Yield (%) ^[a]	T_c (°C)	P_c (MPa)
1	MeOH	1600	14	239.0	8.10
2	EtOH	545	36	243.0	6.38
3	BuOH	250	47		
4	C ₆ H ₁₃ OH	414	46		
5	C ₈ H ₁₇ OH	70	55	384.8	2.69
6	C ₁₂ H ₂₅ OH	214	61		
7	ⁱ PrOH	225	93	235.2	4.76
8	^{sec} BuOH	93	96	262.8	4.19
9	^t BuOH	147	95	233.1	3.97

The yield of caprolactam was improved as the carbon length of the primary alcohols increased (entry 2-6). Although the yield reached about 61% when C12 alcohol was used as the reaction media, it still remained in unsatisfactory level (entry 6). The yield of the caprolactam was

dramatically enhanced when ⁱPrOH was used as the reaction media. Treatment of nylon-6 with supercritical ⁱPrOH resulted in the formation of caprolactam in 93% yield (entry 7). Other secondary and tertiary alcohols also gave caprolactam in good yields (entry 8 and 9). Obtained caprolactam was pure enough because the product showed a good melting point range that was close to the literature data. Use of tertiary alcohol for the reaction might caused blowout when the reaction vessel was opened because of partial decomposition of tertiary alcohol under the reaction conditions.

The reaction mechanism of the present selective depolymerization of nylon-6 was assumed in Figure 4. The depolymerization progresses through addition-elimination reaction at the carbonyl carbon. When an external nucleophile such as methanolic oxygen atom attacks the carbonyl carbon, a methyl ester at the C-terminal of nylon and 6-aminocapronic ester **2** should be formed (route 1). Caprolactam contained 7-membered ring which is not readily formed from the open-chain precursor such as **2**. Additionally the amino group in **2** should be methylated by methanol under the present reaction conditions [6]. As a result, there seems no chance to give caprolactam from 6-aminocapronic ester **2**. On the other hand, the oxygen atom in secondary and tertiary alcohols are far less nucleophilic than methanol. Thus, the reaction rate for route 1 should be much suppressed for the reaction employed with these alcohols. As a result, the most nucleophilic species in the reaction mixture should be the terminal amino group of nylon-6, which internally attacks the carbonyl carbon to give caprolactam and next terminal amino group of the polymer (route 2) [8]. Thus use of secondary and tertiary alcohols affords efficient depolymerization to caprolactam.

Route 1: Cleavage at O-terminal; intermolecular reaction



Route 2: Cleavage at N-terminal; intramolecular reaction to give ϵ -caprolactam

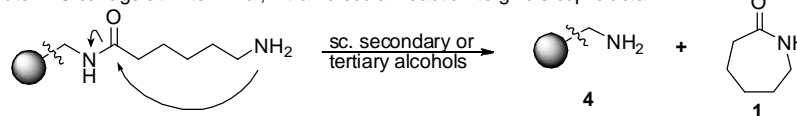


Figure 4. depolymerization mechanism for nylon-6

CONCLUSION

We have successfully depolymerized unsaturated polyesters and polyamides by treatment with supercritical alcohols. Since the present reaction media is less reactive than supercritical water and controllable for their reactivity, this provides useful methods for selective depolymerization of polymers, which is essential reaction for achieving efficient monomer recycling of waste plastics. We have also succeeded for the formation of recycled plastic by using recovered monomeric materials of the reaction. Supercritical lower alcohols should be one of the most preferable media for this purpose.

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