Depolymerization of Poly(ethylene terephthalate) to Terephthalic Acid and Ethylene Glycol in High-temperature Liquid Water

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Poly(ethylene terephthalate) (PET) was depolymerized to ethylene glycol and terephthalic acid in high-temperature liquid water at temperature higher than 493 K and the depolymerization of PET was enhanced by the addition of terephthalic acid in the reaction system.

Efficient use of resources and recycling of products are indispensable for establishing a sustainable society. Thermal recycling involving recovery of energy as heat of burning waste plastics, is one choice but it is possible only once in a whole product's life, and furthermore, it cannot contribute to mitigation of carbon dioxide emission. Plastics are the most widely used synthetic chemical products from petroleum. Hence, material recycling is valuable for efficient utilization of thermoplastics; however, iterative recycling has a problem of degradation of polymers during repeated thermal treatments.[1] Chemical recycling involving decomposition of polymers to their respective monomers and reproduction of the polymers from the monomers, is the most desirable way for sustainable chemistry;[2,3] however, there are several key challenges for its application such as (1) total energy for collecting waste products, separating target plastics, and decomposing the polymers to monomers should be lower than that for the production of virgin monomers from petroleum and (2) safe and easy techniques utilizing nonhazardous chemicals for the decomposition should be used.

Poly(ethylene terephthalate) (PET), used for fibers, films, and bottles,[4] is a polyester of terephthalic acid (TPA) and ethylene glycol (EG). PET bottles are one of the most suitable products for chemical recycling because pure poly(ethylene terephthalate) resin can be obtained from bottles by removing labels and caps made of several kinds of polyolefins. Several chemical recycling processes are commercialized such as methanolysis[5–7] and glycolysis-transesterification[8,9] methods, in which organic solvents and alkali catalysts are used; however, the development of much safer and environmentally benign systems is desired. High-temperature liquid water has attracted much attention as an alternative to a harmful organic solvent because of its high proton concentration, which enhances the rates of acid-catalyzed reactions such as hydrolysis in water without adding any hazardous acid.[10,11] Campanelli et al. reported that high-temperature water at 523 K was effective for depolymerization of PET to TPA and EG; however, more than one hour was needed for complete decomposition.[12] Adschiri et al. reported that supercritical water at 673 K, efficiently decomposed PET to TPA and EG; however, the EG yield was quite low because the dehydration of EG also proceeded in the reactive supercritical water.[13] Fang et al. reported that the phase behavior and reaction rate of PET in high-pressure water.[14] We also reported that subcritical water at 573 K effectively depolymerized PET to TPA and EG in 10 min.[15,16] In this paper we now report the additive effect of terephthalic acid, a starting monomer for the polymer, subcritical water (high-temperature liquid water) system for depolymerization.

Pellets (4 mm × 4 mm × 4 mm) of PET (average molecular weight ca. 18000) purchased from Aldrich were used without further treatment. Hydrolysis of PET in water was conducted in a SUS 316 tube reactor of 10 cm^3 in volume. After PET pellets and water were loaded in the reactor under nitrogen atmosphere, the reactor was submerged into a $\mathrm{KNO_3}$–$\mathrm{NaNO_3}$ bath kept at the desired reaction temperature. It took 40 s for the reactor to reach the desired temperature. In this paper, the reaction starting point was set at the moment when the reactor was submerged into the molten-salt bath, therefore, the reaction time includes the initial heating period. After a given reaction time, the reactor was taken out from the $\mathrm{KNO_3}$–$\mathrm{NaNO_3}$ bath and rapidly quenched in a water bath to cool down to room temperature. After cooling, the products were collected from the reactor and divided into the water-soluble and solid (Solid A) fractions with a membrane filter (pore size: 200 nm). EG was recovered in the water-soluble fraction. Quantitative analysis of EG was done with a GC-FID method (HP-6890). The water-insoluble solid A was treated with 1.5 M sodium hydroxide solution to separate unreacted PET (Solid B) from a NaOH-soluble fraction. TPA was obtained in a solid state from the NaOH-soluble fraction by treating it with 4 M hydrochloric acid. Quantitative analysis of unreacted PET and TPA produced was done by weighing them separately. Product yields of TPA and EG were defined as follows:

$$\text{Yield of EG (\%)} = \text{(moles of EG obtained)/(moles of ethylene terephthalate units in initial PET)} \times 100 \quad (1)$$

$$\text{Yield of TPA (\%)} = \text{(moles of TPA obtained)/(moles of ethylene terephthalate units in initial PET)} \times 100 \quad (2)$$

In the experiment of TPA addition, the yield of TPA:

$$\text{Yield of TPA (\%)} = \text{((moles of TPA obtained)} - \text{(moles of TPA added))/(moles of ethylene terephthalate units in initial PET)} \times 100 \quad (3)$$

The amount of unreacted PET is expressed as a "yield of PET" and determined as follows:

$$\text{Yield of PET (\%)} = \text{(weight of recovered PET as Solid B)/(weight of PET introduced)} \times 100 \quad (4)$$

The yields of TPA and EG obtained by the treatment of PET in water for 10 min as a function of treatment temperature are shown in Figure 1a. TPA and EG were not obtained by the treatment at temperature lower than 473 K. A small amount of TPA (3%) and EG (2%) were obtained at 523 K and both the yields

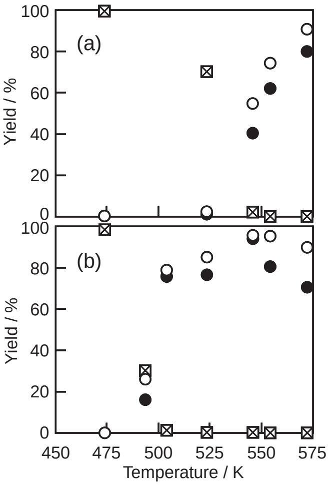

Figure 1. Yield of PET (☒), TPA (○), and EG (●) in water for 10 (a) and 60 (b) min. The amount of PET and water introduced are 0.530 and 5.0 g, respectively.

increased to 92 and 80% respectively with increase in temperature to 573 K. The yields of TPA and EG were very close regardless of the conditions.

The yields of TPA and EG for 60 min as a function of treatment temperature are also shown in Figure 1b. TPA and EG were not produced even after 60 min, when PET pellets were treated in water at 473 K. The yields of TPA, EG, and unreacted PET at 493 K were 25, 16, and 30%, respectively. Thus, some of oligomers, such as bis(2-hydroxyethyl) terephthalate would be formed. Both TPA and EG yields increased with increase in temperature. The highest yields for TPA and EG (both 95%) were obtained at 543 K. At temperature higher than 543 K, the TPA yield dropped marginally but still was 90%, whereas the EG yield decreased drastically (70%) at 573 K.[17] This could be due to fact that dehydration of EG to diethylene glycol proceeded in the presence of protonic acid such as TPA at higher temperature.[6] These results also suggest that TPA could be the proton source which catalyzes the depolymerization of PET. Hence, addition of TPA to the reaction system would increase the concentration of protons and this was actually observed in the following experiments.

Figure 2a shows the yield of EG by the depolymerization of 0.530 g of PET in the presence of 0.460 g of TPA in water for 10 min. Production of EG was not observed at 473 K, indicating that at low-temperature addition of TPA did not have a noticeable effect on PET depolymerization. On the other hand, the EG yield increased to 15% (only 2% in the absence of TPA (Figure 1)) by the addition of TPA at 523 K for 10 min. The yield of EG increased with an increase in temperature and 80% yield was obtained at 573 K. The yield of EG for 60 min as a function of treatment temperature is also shown in Figure 2b. Even after 60 min, EG was not observed at 473 K, indicating that prolonged reaction time had no effect on PET depolymerization at 473 K. The yield of EG at 493 K was 48% [16% in the absence of TPA (Figure 1b)] and increased to 87% at 523 K for 60 min. At temperature higher than 543 K, the EG yield decreased with temperature. It is concluded that protons effectively catalyzed depolymerization of PET; however, high concentration, higher treatment temperature, and longer contact time cause a decrease of EG yield because the protons promote subsequent dehydration of EG to diethylene glycol.

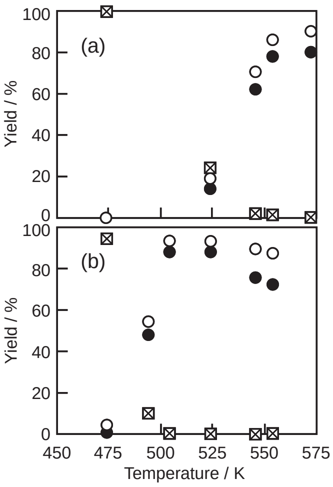

Figure 2. Yield of PET (☒), TPA (○), and EG (●) in water for 10 (a) and 60 (b) min. The amount of PET, TPA, and water introduced are 0.530, 0.460, and 5.0 g, respectively.

We also investigated the depolymerization of 0.670 g of poly(ethylene 2,6-naphthalenedicarboxylate) (PEN) in 5 g of water in the 10 cm^3 SUS 316 tube reactor. Poly(ethylene 2,6-naphthalenedicarboxylate) was depolymerized to EG and 2,6-naphthalenedicarboxylic acid (NDA), and the yields of NDA and EG for 10 min at 548 K were 38 and 31%, respectively. The effect of addition monomer dicarboxylic acid was also investigated. EG yield increased substantially to 62% by addition of 0.300 g of NDA for 10 min at 548 K.

Thus, we have successfully demonstrated the efficient promotion of hydrolysis of polyesters in high-temperature water by addition of starting monomer dicarboxylic acids which are non hazardous in nature. Yet another important advantage of this process is that it does not require any inorganic catalyst, hence the separation process of the later is completely eliminated.

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17 The internal steam pressure in the reactor from 473 to 573 K is estimated from 1.55 to 8.57 MPa.

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