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Hydrolysis of poly(ethylene terephthalate) and poly(ethylene 2, 6-naphthalene dicarboxylate) using water at high temperature: Effect of proton on low ethylene glycol yield

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Abstract

Depolymerization of poly(ethylene terephthalate) (PET) to terephthalic acid (TPA) and ethylene glycol (EG) and poly(ethylene 2,6-naphthalene dicarboxylate) (PEN) to 2,6-naphthalene dicarboxylic acid (2,6-NPA) and EG in water at high temperature (>523 K) was investigated for the purpose of monomer recycling. In case of the depolymerization of PET in water, the yield of TPA increased to 90% with increasing reaction temperature up to 693 K while the maximum yield of EG achieved was 60% at 573 K. For PEN depolymerization, the yield of 2,6-NPA also increased to 97% with increasing reaction temperature up to 693 K and the maximum yield of EG obtained was 60% at 573 K. The higher yield of 2,6-NPA than that of TPA was ascribed to the higher stability of 2,6-NPA than that of TPA. The lower yields of EG than the corresponding monomers (TPA and 2,6-NPA) in the decomposition of the two kinds of polyesters were caused by the catalytic dehydroxylation of EG by protons derived from dicarboxylic acids.

Keywords: Hydrolysis; Supercritical water; PET; PEN; Monomer recycling; Chemical depolymerization

1. Introduction

Recycling of used chemical products is an issue of great importance for a sustainable society. Environmentally friendly chemical recycling processes involving, decomposition of polymers to corresponding monomers without using any hazardous materials, is an important subject area of research for the chemists. For example, techniques for chemical recycling of poly(ethylene terephthalate) (PET), a semicrystalline polyester composed of terephthalic acid (TPA) and ethylene glycol (EG) and widely used in the manufacture of high strength fibers, photographic films and bottles, involve alcoholysis by methanol [1] or ethylene glycol [2,3] and hydrolysis by an alkaline solution [4]. Supercritical water (critical temperature: 647.3 K and critical pressure: 22.1 MPa) is a dense steam and has received attention as an environmentally friendly reaction solvent [5–7]. Chemical depolymerization of PET without catalysts in supercritical water is a promising environmentally friendly method for monomer recycling [8–10] (Scheme 1). Similar to PET, poly(ethylene naphthalate) (PEN) is also a polyester composed of 2,6-naphthalic acid (2,6-NPA) and EG (Scheme 1); however, its glass transition temperature is high enough to cover a wider range of application temperature than that of PET, e.g. PEN bottles can be sterilized. PET products also can be made more heat resistance by mixing PEN. However, PEN is more expensive than PET, so chemical recycling of PEN is highly desirable.

For successful recycling of used PET and PEN, their chemical depolymerization should ideally give the corresponding dicarboxylic acids and EG with quantitative yields; however, it was reported that the yield of EG was lower than that of TPA for PET depolymerization in subcritical and supercritical water [8]. To understand as to why the lower yields of EG are obtained in this process, the role of proton was studied in this work.

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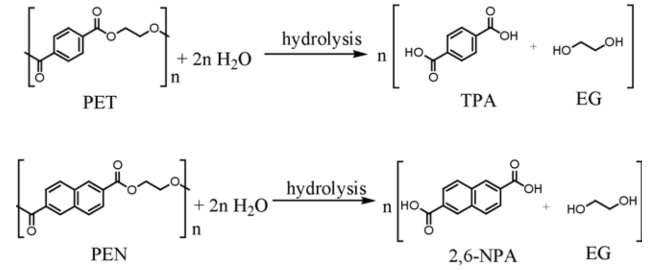

Scheme 1. Chemical depolymerization of poly(ethylene terephthalate) and poly(ethylene 2,6-naphthalate) in water.

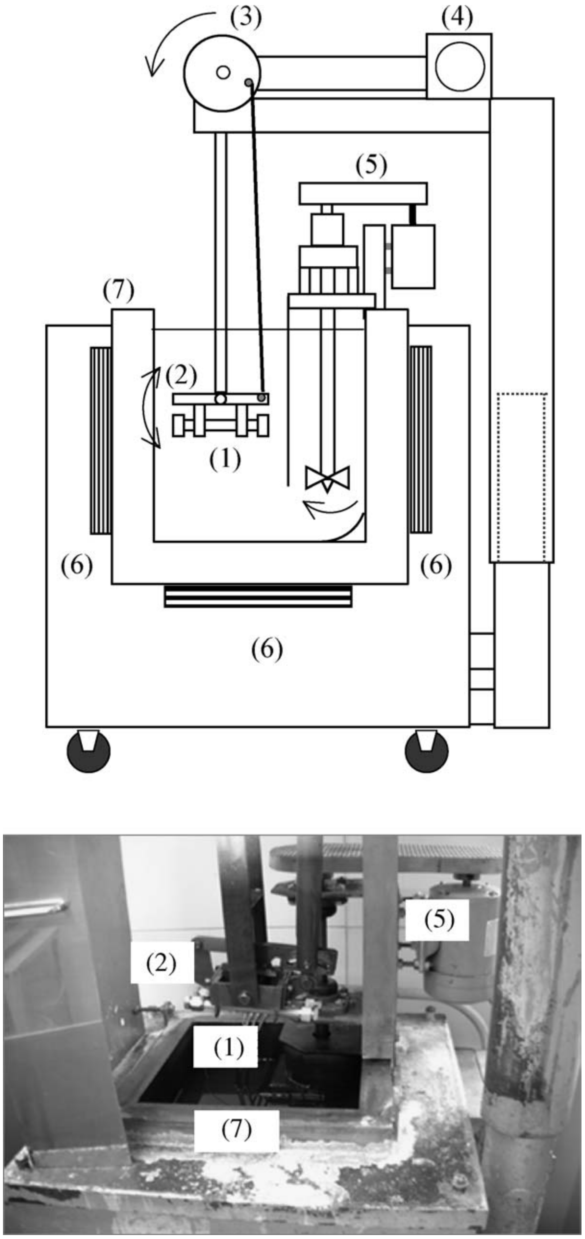

Fig. 1. Apparatus of batch reaction system: (1) SS 316 tube reactor, (2) motor, (3) crank, (4) stirrer, (5) KNO_3–$NaNO_3$ salt, (6) heater and (7) bath.

2. Experimental

2.1. Materials and decomposition procedure

Pellets (4 mm × 4 mm × 4 mm) of PET (average molecular weight ca. 18,000) and PEN (average molecular weight ca. 35,000) purchased from Aldrich were used without further treatment. Hydrolysis of PET and PEN in water was conducted in a 10 cm^3 of stainless steel 316 tube reactor. In a typical experiment, 533 mg of PET or 672 mg of PEN and 5 g of water were introduced into the reactor. This amount of water corresponded to 0.5 g cm^{-3} of water density and up to 48 MPa partial pressure of water at 693 K [11]. After charging the material, the reactor was submerged into a KNO_3–$NaNO_3$ bath that was controlled at the reaction temperature. The batch reaction system used in this study is shown in Fig. 1. Forty seconds were required for the reactor to reach reaction temperatures. In this paper, reaction time includes this heat up time. After a given reaction time, the reactor was taken out from the KNO_3–$NaNO_3$ bath and rapidly quenched in a water bath to cool down to the room temperature. After cooling, the reactor was opened and products from the reactor were recovered with pure water.

2.2. Recovery procedure

Products recovered from the reactor were separated into the water-soluble and solid (Solid A) fractions with a membrane filter (pore size: 200 nm). Ethylene glycol was recovered in the water-soluble fraction. The water-insoluble Solid A was treated with 1.5 M sodium hydroxide solution and separated into NaOH-soluble and solid (Solid B) fractions. Terephthalic acid or 2,6-naphthalic acid was obtained from the NaOH-soluble fraction by treating with 4 M hydrochloric acid. Product yield in this paper was defined as follows: yield of EG (%) = (moles of EG obtained)/(moles of EG in PET (or PEN) used) × 100; yield of TPA (%) = (moles of TPA obtained)/(moles of TPA in PET used) × 100; yield of 2,6-NPA (%) = (moles of 2,6-NPA obtained)/(moles of 2,6-NPA in PEN used) × 100.

3. Results and discussion

3.1. Depolymerization behavior of PET in subcritical and supercritical water

The yields of TPA and EG as a function of residence time at various temperatures in the depolymerization of PET are shown in Fig. 2(a–d). TPA and EG were not obtained by treating PET pellets in water at temperatures less than 500 K. The TPA yield was only 20% and EG was not obtained at 523 K for initial residence time of 10 min (Fig. 2(a)). Oligomers of PET were also observed in the water-soluble fraction for residence time <40 min at 523 K. The TPA yield increased to 80% with increase in reaction time up to 60 minuets while, the yield of EG obtained after 60 min treatment was lower than that of TPA. The yield of oligomers decreased with increasing time and became zero after 40 min of residence time at 523 K.

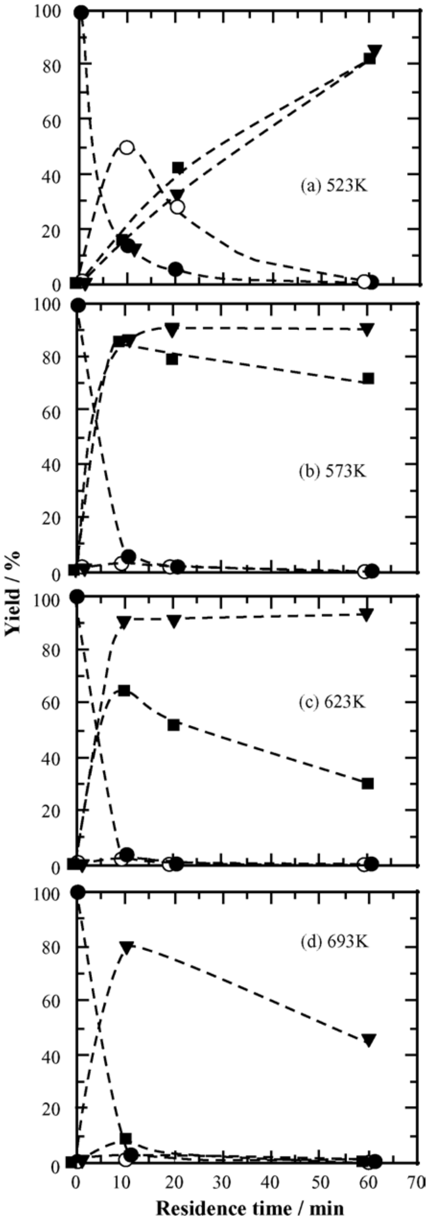

Fig. 2. Depolymerization of PET in water at: 523 K (a), 573 K (b), 623 K (c) and 693 K (d) ((●) PET; (○) oligomer; (▼) TPA; (■) EG).

The yields of TPA and EG increased to 90 and 70%, respectively, at 573 K after 10 min of residence time (Fig. 2(b)). Small amount of oligomers were also obtained under these treatment conditions. The higher yield of TPA than that of EG was maintained by the treatment in water at 573 K for 60 min of residence time. Fang et al. reported that the complete dissolution of PET in water occurred between 570 and 591 K with a hydrothermal anvil cell [12]. At 523 K, only part of PET dissolved in water resulted in the lower yields of TPA and EG while, at 573 K all PET dissolved in water, gave higher yields of TPA (90%) and EG (70%).

As high as 90% TPA yield was obtained; however, EG yield decreased further with increasing time of treatment at 623 K (Fig. 2(c)). With further increase in temperature to 693 K, the TPA yield deceased to 80% and that of EG dramatically decreased to 10% for 10 min of residence time (Fig. 2(d)). Formation of acetaldehyde, diethylene glycol and triethylene glycol was also observed in the water-soluble fraction, indicating that dehydroxylation and dimerization of EG would have occurred during the treatment under these conditions.

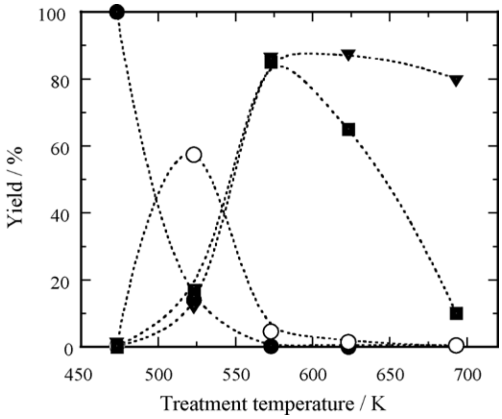

Fig. 3. Yields of: PET (●), oligomer (○), TPA (▼) and EG (■) in water for 10 min residence time.

The monomer yields as a function of temperature in the depolymerization of PET in water at 10 min residence time are summarized in Fig. 3. Higher TPA yields (>80%) were obtained for treatment at temperatures more than 573 K. EG was also obtained; however, the maximum yield was only 60% by the treatment of water in the temperature range of 573–623 K.

3.2. Depolymerization behavior of PEN in subcritical and supercritical water

The yields of 2,6-NPA and EG as a function of residence time at various temperatures in the depolymerization of PEN are shown in Fig. 4(a–d). Similar to PET decomposition, 2,6-NPA and EG were also not obtained by treating PEN in water below 500 K. The 2,6-NPA yield was only 64% for initial residence time of 10 min and increased with increasing residence time at 523 K (Fig. 4(a)). EG was obtained after 20 min; however, the yield was less than that of 2,6-NPA at 523 K. The yields of 2,6-NPA and EG were increased to 94 and 70%, respectively, at 573 K (Fig. 4(b)). The yields of both 2,6-NPA and EG were improved to 98 and 86%, respectively, by increasing the time of treatment at the same temperature. The yield of 2,6-NPA yield was higher at 623 K for 10 min; however, EG yield was still lower than that of 2,6-NPA and decreased with increasing time of treatment (Fig. 4(c)). Treatment at 693 K gave 80% of 2,6-NPA; however, the EG yield was very low (<20%). Acetaldehyde, diethylene glycol and triethylene glycol were also obtained in the water-soluble fraction at 693 K. The depolymerization behavior of PEN in water at high temperature was similar to that of PET (Fig. 5). Higher 2,6-NPA yields (>90%) were obtained for treatment at temperatures more than 573 K. EG was also obtained; however, the maximum yield was only 60–70% by the treatment of water in the temperature range of 573–623 K.

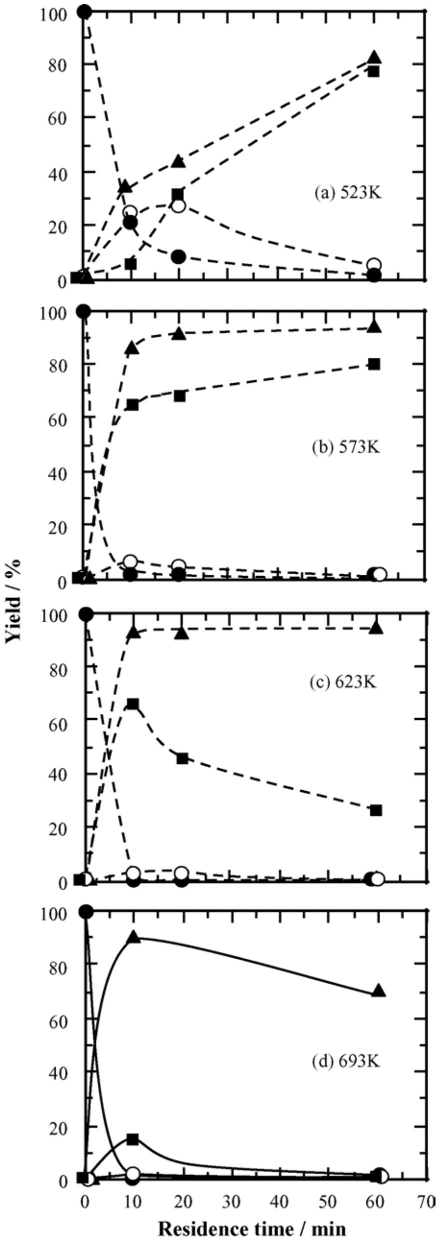

Fig. 4. Depolymerization of PEN in water at: 523 K (a), 573 K (b), 623 K (c) and 693 K (d) ((●) PEN; (○) oligomer; (▲) 2,6-NPA; (■) EG).

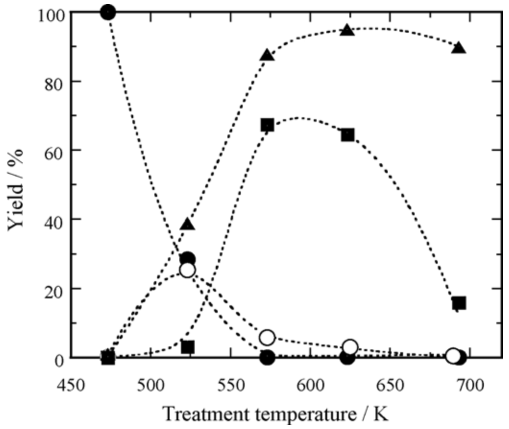

Fig. 5. Yields of: PEN (●), oligomer (○), 2,6-NPA (▲) and EG (■) in water for 10 min residence time.

3.3. Stability of EG in subcritical and supercritical water

Lower EG yields were obtained in comparison with high TPA and 2,6-NPA yields in PET or PEN decomposition studied in this work. Especially, EG yields rapidly decreased with increase in temperature and time of treatment (Figs. 2 and 4). To elucidate of the lower EG yields, we also investigated separately the depolymerization behavior of EG in water with and without TPA, 2,6-NPA and sulfuric acid at high temperature. Fig. 6 shows the recovery of EG after the treatment in water at 623 K. More than 80% of EG was recovered after its treatment without any acid in water at 623 K for 60 min of residence time. On the other hand, the EG recovery decreased with increasing time of treatment in presence of the molar equivalent amounts of TPA or 2,6-NPA at 623 K. We also checked the EG recovery in presence of sulfuric acid with varying concentrations. The EG recovery was hardly affected by 5×10^{-5} M of sulfuric acid; however, the EG yield decreased to 70 and 50% after the treatment with water in presence of 5×10^{-4} or 5×10^{-3} M of sulfuric acid, respectively. Also, the EG recovery decreased with increasing time of treatment in the presence of sulfuric acid. Acetaldehyde, diethylene glycol and triethylene glycol were also shown in presence of dicarboxylic acids or sulfuric acid; however, the yields of diethylene glycol and triethylene glycol were only few percents of initial amount of EG. Also, we could not determine the amounts of acetaldehyde quantitatively. Oligomers such as tetra- and pentaglycol would be formed; however, we could not determine them by GC analysis. The EG yield profiles in PET and PEN decomposition at 623 K are also shown in Fig. 6. The EG yields in the PEN and PET depolymerization processes decreased with increasing time of treatment and the behaviors are similar to those in the presence of molar equivalent amounts of TPA and 2,6-NPA. Antal et al. have reported that dehydroxylation of alcohol to ether

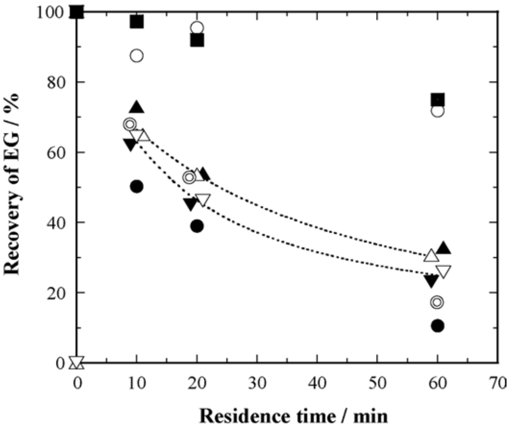

Fig. 6. Recovery of: 2.74 mmol of EG (■) in water at 623 K; in presence of 2.74 mmol of TPA (▼); 2.74 mol of 2,6-NPA (▲); 5×10^{-5} M of H_2SO_4 (○); 5×10^{-4} M of H_2SO_4 (◎); 5×10^{-3} M of H_2SO_4 (●). The yield of EG (▽) in the decomposition of PET and in the decomposition of PEN (△).

proceeded in supercritical water in the presence of $5 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ sulfuric acid [13]. Ethylene glycol molecules are converted to acetaldehyde and diethylene glycol molecules by protons. One possible explanation for the low EG yields in PET and PEN hydrolysis is that protons from TPA and 2,6-NPA catalyze the intra- and intermolecular dehydration of EG in water at high temperatures.

4. Summary

Decomposition behavior of PET and PEN to their corresponding monomers (terephthalic acid, 2,6-naphthalene dicarboxylic acid and ethylene glycol) in water at high temperature was investigated. The yields of terephthalic acid and 2,6-naphthalene dicarboxylic acid increased up to 80% with increasing temperature from 523 to 623 K, while ethylene glycol yields for PET and PET depolymerization was lower than that of TPA/2,6-NPA at 573–623 K. The stability studies of EG conducted separately with and without acids showed that the lower yield of ethylene glycol in the depolymerization process was due to its dehydroxylation to aldehyde and polymerization to diethylene glycols catalyzed by the protons of corresponding dicarboxylic acids (terephthalic and 2,6-naphthalene dicarboxylic acid).

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