



Depolymerization of poly(trimethylene terephthalate) in hot compressed water at 240–320 °C

Jing Gao, Zangfang Jin, Zhiyan Pan*

Department of Environmental Engineering, Zhejiang University of Technology, Chaowang Road, Hangzhou 310032, PR China

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ABSTRACT

Poly(trimethylene terephthalate) (PTT) was depolymerized in hot compressed water (HCW) using a fused-silica capillary reactor (FSCR) and a batch-type autoclave reactor. The phase behavior of PTT in water during the heating, reaction, and cooling processes was observed in an FSCR with a microscope and recorded by a digital camera. It was found that PTT can dissolve in water in a temperature range of 240–320 °C and form a homogeneous aqueous solution. The effects of the reaction temperature (240–320 °C) and reaction time (5–60 min) were evaluated in a batch-type autoclave reactor. The main depolymerization products of PTT were terephthalic acid (TPA) and 1,3-propanediol (1,3-PDO), which were identified by liquid chromatography mass spectrometry, Fourier-transform infrared spectroscopy, gas chromatography mass spectrometry, Raman spectroscopy, and quantified by high-performance liquid chromatography as well as gas chromatography. Additionally, it was found that 1,3-PDO was converted to 1,5-dioxocane partly in the presence of TPA. Under optimal reaction conditions, i.e. 300 °C, 15 min, with a water/PTT ratio of 8:1 (w/w), complete depolymerization was achieved, and the yields of TPA and 1,3-PDO reached 90.5% and 69.03%, respectively. Based on the results, a reaction mechanism for PTT depolymerization in HCW was proposed.

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1. Introduction

Poly(trimethylene terephthalate) (PTT) is a thermoplastic aromatic polyester, which was first synthesized by Whinfield and Dickson in 1941 [1]. However, it was not commercialized until significant developments were established in the synthesis technology of 1,3-propanediol (1,3-PDO) monomer. PTT is an attractive material for use in carpet, textile, film, packing, and engineering thermoplastics applications with various desirable characteristics as good chemical resistance, high strength, thermal stability, excellent softness, outstanding elastic recovery, and good dyeability [2–6]. The recycling of PTT has become increasingly important due to the rise in PTT consumption.

The recycling of waste polymers can be classified into three main processes as materials recycling, thermal recycling and chemical recycling [7,8]. Among these methods, chemical recycling is the only acceptable process according to the principles of sustainable development as polymers can be converted into their corresponding monomers using this method, which can then be re-used as raw materials for virgin polymers [8,9].

Currently, the depolymerization of PTT by glycolysis and methanolysis have been investigated as a method for chemical recycling of PTT to recover monomers. Kim et al. [10] investigated the depolymerization of PTT in different alcohols in the presence of NaOH at 160–190 °C, and it was found that PTT was depolymerized completely at 190 °C for 60 min and the products of disodium terephthalate and 1,3-PDO were obtained. Disodium terephthalate was acidified with hydrochloric acid to obtain terephthalic acid (TPA). Zhang et al. [11–13] studied the methanolysis of PTT under supercritical conditions. The yield of the main products, dimethyl terephthalate and 1,3-PDO, increased significantly as the temperature increased and reached 98.2% at 320 °C/10.0 Mpa. However, water is an attractive alternative to alcohols since it is readily available, non-toxic, cheap, and environmental friendly. Hot compressed water (HCW, here sub-critical and supercritical water above 200 °C at sufficiently high pressure) shows extraordinary physical and chemical properties that can vary between gas-like and liquid-like extremes, thus offering an opportunity for chemical reactions [14–18]. Several recent papers indicate that polymers with an ether bond (such as polycarbonate and polyethylene terephthalate) are converted into their monomers easily and efficiently in HCW [19–24]. Ikeda et al. [22] investigated the decomposition of polycarbonate in water in a temperature range of 130–300 °C and the main products recovered were phenol

* Corresponding author. Tel./fax: +86 571 88320061.

E-mail address: panzhiyan@zjut.edu.cn (Z. Pan).

bisphenol A and *p*-isopropenylphenol. Sato et al. [23] reported the hydrolysis of polyethylene terephthalate in water at high temperature and the monomers TPA and ethylene glycol were obtained. In the present work, water was applied as a reaction medium for the depolymerization of PTT. The phase behavior during the PTT depolymerization process in HCW was observed in a fused-silica capillary reactor (FSCR) [25,26] under a microscope and images were recorded continuously with a computer using a digital camera. The effects of temperature and time on the depolymerization of PTT in HCW were examined in a batch autoclave reactor. Based on the experimental results, a reaction mechanism for the depolymerization of PTT in HCW was proposed.

2. Experimental

2.1. Materials

The PTT resins (weight average molecular weights 46,000–50,000) used in this study were commercial slices obtained from Shanghai Dong Hua Haitian Textile Technology Development Co., Ltd. (Shanghai, China). TPA (purity 99% minimum) and 1,3-PDO (purity 99.5%) were supplied by Acros Organics (Geel, Belgium) and Aladdin Chemistry Co., Ltd. (Shanghai, China), respectively. These materials were used as received without further purification. The silica capillary (665 μm O.D. and 300 μm I.D., with polyimide coating) used in this study was purchased from Polymicro Technologies LLC (Phoenix, AZ, USA).

2.2. Apparatus and procedure

The phase behavior of PTT depolymerization in HCW was conducted in an FSCR. To prepare an FSCR, a section of silica capillary (2–3 cm long) was cut, then one open end of the tube was sealed with an oxyhydrogen flame. PTT and deionized water were loaded into the capillary, and subsequently, the other open end of the tube was sealed with an oxyhydrogen flame to form an FSCR. The FSCR was placed in a heating/cooling stage (Instec INS0908051, USA), the temperature of which was adjusted via a digital temperature controller (Instec STC200, accurate to ± 0.1 °C). The heating and cooling rates were 10 °C/min. The phase behavior of PTT in water during heating, reaction, and cooling was observed with a microscope (Leica DM2500P, Germany) and recorded continuously on a computer through a digital camera.

The depolymerization of PTT in HCW was carried out in a stainless steel batch-type autoclave (50 mL). The autoclave reactor was heated by a heating collar with an XMT-type controller. The pressure and temperature of the reactor were measured by a pressure gauge and a K-type thermocouple, respectively. In each experiment, PTT (3.0 g) and deionized water (24 mL) were added into the batch reactor. After sealing, the reactor was placed in the heating collar and heated with a ramp rate of 10 °C/min to the specified reaction temperature maintained within ± 1.0 °C. The reactor was immediately removed from the heating collar after the required reaction time interval and rapidly cooled to ambient temperature in a water bath. The reactor contents were subsequently collected and separated into solid and liquid phases by filtration. The liquid phase was transferred to a volumetric flask and diluted to the required volume with ethanol. The liquid products were identified by an Agilent 6890 gas chromatograph (GC) (Agilent Technologies, Santa Clara, CA, USA) equipped with a mass spectrometer (MS), with a 30 m \times 0.25 mm \times 0.25 μm DB-5 capillary column. An Agilent 6890 GC with a flame ionization detection (FID) and a 30 m \times 0.32 mm \times 0.25 μm Agilent 19091J-413 capillary column was used to quantify the products in liquid phase. The oven temperature program was isothermal at 60 °C for

3 min, and raised to 250 °C with a heating rate of 15 °C/min. The solid phase were dissolved in ammonium hydroxide; the pH was adjusted to 7.0 with phosphoric acid, then filtrated again. The insoluble solid was identified by a Nicolet 6700 Fourier-transform infrared (FT-IR) spectrometer (Thermo Nicolet, Waltham, MA, USA). The solution was identified by an Agilent 1200 series liquid chromatography (LC) system coupled with an Agilent 6210 time-of-flight (TOF) mass spectrometer (Agilent Technologies, Santa Clara, CA, USA) and quantified by a Jasco LC-2000 series high-performance liquid chromatography (HPLC) system (Jasco, Tokyo, Japan) with a JASCO PU-2089 quaternary gradient pump and a UV-2075 UV/Vis detector. A Yilite BDS C8 column (4.6 mm \times 250 mm \times 5 μm) was used for both LC/MS and HPLC analysis. The mobile phase used was methanol/water (6/4 vol%) flowing at a rate of 0.7 mL/min.

The depolymerization yield of PTT is defined as:

$$\text{Depolymerization yield of PTT (\%)} = \frac{\text{Weight of PTT feed} - \text{Weight of unreacted PTT}}{\text{Weight of PTT feed}} \times 100\%$$

The yield of TPA is defined as:

$$\text{Yield of TPA (\%)} = \frac{\text{Weight of TPA recovered after reaction}}{\text{Theoretical content of TPA in PTT feed}} \times 100\%$$

The yield of 1,3-PDO is defined as:

$$\text{Yield of 1,3-PDO (\%)} = \frac{\text{Weight of 1,3-PDO recovered after reaction}}{\text{Theoretical content of 1,3-PDO in PTT feed}} \times 100\%$$

3. Results and discussion

3.1. Phase behavior of PTT in HCW in the FSCR

The phase behavior of PTT in water during heating, reaction, and cooling was observed in the FSCR under a microscope and images were recorded continuously in a computer by making use of a digital camera (Fig. 1). During the heating process (as shown in Fig. 1(a)), PTT softened and started to shrink at 207.5 °C, and remained in solid form below this temperature. Three phases (PTT in solid form, aqueous fluid, and vapor phase) were present in the FSCR below 207.5 °C. PTT melted gradually as temperature increased and formed a liquid spherule at 215 °C, which coexisted with the aqueous fluid and vapor phase. The liquid spherule of PTT gradually dissolved in water and became smaller with prolonged time at 240 °C, 280 °C, and 320 °C, ultimately becoming a homogeneous solution as shown in Fig. 1(b)–(d). As the reaction temperature increased, the dissolution of the liquid PTT spherule was accelerated, leading to the decrease of the required reaction time for PTT to dissolve in water to form a homogeneous aqueous solution. Nevertheless, a small particle remained in the FSCR, which did not disappear with further increase in reaction time or temperature; hence, it may be attributed to the presence of additives in the industrial grade PTT. As shown in Fig. 1(e), after the reaction took place at 320 °C for 10 min, the TPA crystals began to separate out from the water at 186.5 °C during cooling. Subsequently, the size and number of TPA crystals increased gradually in the FSCR.

In summary, PTT gradually dissolved in water and formed a homogeneous aqueous solution in a temperature range of

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