



Review article

Glycolysis of poly(ethylene terephthalate) (PET) using basic ionic liquids as catalysts

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ABSTRACT

The glycolysis of poly(ethylene terephthalate) (PET) was studied using several ionic liquids and basic ionic liquids as catalysts. The basic ionic liquid, 1-butyl-3-methylimidazolium hydroxyl ([Bmim]OH), exhibits higher catalytic activity for the glycolysis of PET, compared with 1-butyl-3-methylimidazolium bicarbonate ([Bmim]HCO₃), 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) and 1-butyl-3-methylimidazolium bromide ([Bmim]Br). FT-IR, ¹H NMR and DSC were used to confirm the main product of glycolysis was bis(2-hydroxyethyl) terephthalate (BHET) monomer. The influences of experimental parameters, such as the amount of catalyst, glycolysis time, reaction temperature, and dosages of ethylene glycol on the conversion of PET, yield of BHET were investigated. The results showed a strong influence of the mixture evolution of temperature and reaction time on depolymerization of PET. Under the optimum conditions of m(PET):m(EG): 1:10, dosage of [Bmim]OH at 0.1 g (5 wt%), reaction temperature 190 °C and time 2 h, the conversion of PET and the yield of BHET were 100% and 71.2% respectively. Balance between the polymerization of BHET and depolymerization of PET could be changed when the reaction time was more than 2 h and contents of catalyst and EG were changed.

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1. Introduction

Poly(ethylene terephthalate) (PET) is a thermoplastic polyester widely used in the manufacture of video and audio, X-ray films, food packaging and especially in the manufacture of soft-drink bottles. This polyester, PET, cannot be decomposed rapidly in ecosystem, resulting in growing of waste PET. From the perspectives of preservation of natural resources and protection of environment, the effective recycling of PET waste is a significant subject for researchers. There are two main methods for recycling waste PET, which are physical and chemical ones. Chemical method is preponderant because it can reproduce virgin monomer products.

Several processes for PET depolymerization have been put forward, such as hydrolysis, aminolysis and alcoholysis processes. Alcoholysis reaction was carried out with using ethylene glycol, diethylene glycol, propylene glycol, and dipropylene glycol. The glycolysis of PET, which was one of the most widely studied processes for PET degradation and recycling, can produce the virgin monomer, bis(2-hydroxyethyl)terephthalate (BHET). The glycolysis reaction was very slow with the absent of catalyst [1,2]. In recent years, large quantities of catalyst were developed for the glycolysis

of PET, such as metal acetates, titanium-phosphate, solid superacids, metal oxide, carbonate [3], sulfate [4], and so on. The high conversion of PET and the high selectivity of BHET were obtained in the presence of these catalysts. However, it is difficult to separate the catalysts from the depolymerized products and remaining catalysts disturb analysis of products. Therefore, it is necessary to develop a new catalyst for the glycolysis of PET.

The room temperature ionic liquid, a kind of environmental friendly solvent and catalyst, because of its adjustable physical and chemical properties, got broad attention of scholars from various fields such as synthesis, catalysis, separation, and electrochemistry [5]. Deng et al. first published an article concerning chloroaluminate ionic liquids were used as catalyst for the depolymerization of polycarbonate [6]. Kamimura et al. [7] have employed quaternary ammonium ionic liquids, which were functionalized by a group with strong Brønsted acidity, to depolymerize polyamide plastics, and the 86% yield of caprolactam monomer was obtained. Ionic liquid was easily separated from the solid products when it was used as a catalyst in the glycolysis of PET. Recently, it has been reported that ionic liquids were used as solvent and catalyst in the depolymerization of PET [8]. Zhang et al. used ionic liquid as catalyst for the glycolysis of PET [9,10], and the 100% conversion of PET and the 59.2% selectivity of BHET were obtained in the presence of Fe-containing magnetic ionic liquid [11]. To the best of our knowledge, no article about basic ionic liquid used in glycolysis of

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PET has been published. In our previous study, we have found that basic ionic liquids could catalyze the hydrolysis of propylene carbonate [12] and more than 99% conversion of propylene carbonate and more than 99% selectivity of 1,2-propylene glycol were obtained.

In this paper, several ionic liquids and basic ionic liquids were synthesized and used in the glycolysis of PET. The results showed that using 1-butyl-3-methylimidazolium hydroxyl([Bmim]OH) as catalyst for glycolysis of PET, the high conversion of PET and yield of BHET were obtained. Moreover, influences of the reaction conditions on the conversion of PET and yield of BHET also been investigated in this paper.

2. Experimental

2.1. Materials and instruments

Poly(ethylene terephthalate) (PET) waste bottles were collected, cleared, dried and cut into 1 mm × 1 mm size pieces. Their average molecular weight, measured in 50:50 (w/w) phenol/1,1,2,2-tetrachloroethane solution at 25 °C, was found to be 1.8×10^4 g mol⁻¹. Other chemicals were commercially available and were used without further purification. The products were analyzed by ¹H NMR spectra, which were recorded on a Bruker 400 MHz NMR spectrometer with TMS as the internal standard, and FT-IR spectra, which were determined using a Perkin–Elmer SP100 spectrometer. DSC scans of the main products were obtained using QMS 403 C (Netzsch) by heating from room temperature to 300 °C at a rate of 10 °C/min in an atmosphere of nitrogen.

2.2. Synthesis of ionic liquids

The ionic liquids used in this article were synthesized according to previous literature [13].

2.2.1. Synthesis of 1-*n*-butyl-3-methylimidazolium chloride ([Bmim]Cl)

Equal molar amounts of chlorobutane and 1-methylimidazole were added to a round-bottom flask fitted with a reflux condenser. The mixture was refluxed for 48–72 h at 70 °C with stirring until two phases formed. The top phase, containing unreacted starting material, was decanted and acetone was added and mixed thoroughly. Then the flask was frozen in the refrigerator for 24 h. Crystals of [Bmim]Cl were formed. The liquid phase, containing unreacted material and acetone, was decanted followed by the addition of fresh acetone and this step was repeated twice. After the third decanting of acetone, any remaining acetone was evaporated with a rotary evaporator. The product, [Bmim]Cl, was obtained and dried in the vacuum oven at 70 °C for 48 h.

1-*n*-butyl-3-methylimidazolium bromide ([Bmim]Br) was prepared with a similar procedure.

2.2.2. Synthesis of basic ionic liquids

The basic ionic liquid [Bmim]OH was prepared by anion change of [Bmim]Cl using 1 mol equivalent NaOH. The ionic liquid was dried under vacuum for 24 h and stored in a desiccator.

[Bmim]HCO₃ was prepared with a similar procedure.

2.3. Glycolysis of PET waste bottles in the presence of the basic ionic liquid

A 50 ml round-bottom three-necked flask equipped with a thermometer and a reflux condenser was loaded with 2.0 g of PET, certain amount of ethylene glycol, and certain amount of ionic liquids. The glycolysis reactions were carried out under atmospheric

pressure at reaction temperatures ranging from 150 °C to 190 °C for glycolysis times of 0.5–8 h. The flask was immersed in an oil bath at a specific temperature for the required time. When each glycolysis reaction finished, the undepolymerized PET pellets were quickly separated from the liquid phase before the products precipitated. Then an excess amount of cold distilled water was used to wash the undepolymerized PET pellets, and the water was then mixed with the product fraction. The undepolymerized PET was collected, dried, and weighed. The conversion of PET is defined by Eq. (1):

$$\text{Conversion percentage of PET} = \frac{w_0 - w_1}{w_0} \times 100\% \quad (1)$$

where w_0 represents the initial weight of PET and w_1 represents the weight of undepolymerized PET. Meanwhile, the glycolysis product mixture was vigorously agitated (cold distilled water would dissolve the remaining ethylene glycol, ionic liquids, and the monomer) and then filtered. The fraction insoluble in cold water was a mixture of the oligomers. It was collected and dried, not been studied further in this paper. The collected filtrate was concentrated to about 40 ml at the water boiling point. The concentrated filtrate was stored in a refrigerator at 0 °C for 24 h. White crystalline flakes were formed in the filtrate, then separated and dried. This white crystalline was the main product of glycolysis. The yield of main product is defined by Eq. (2):

$$\text{Yield (\%)} = \frac{\text{actual production}}{\text{theoretical production}} \times 100\% \quad (2)$$

2.4. Qualitative analysis of the main product

In order to confirm that main product of glycolysis is BHET, FT-IR, ¹H NMR and DSC of main product were performed. FT-IR spectra of this fraction are shown in Fig. 1. It can be clearly seen that the spectrograph contains a –OH band at 3347 cm⁻¹ and 1135 cm⁻¹, a C=O stretching at 1716 cm⁻¹, an alkyl C–H at 2873 cm⁻¹ and 2954 cm⁻¹, and an aromatic C–H at 1456–1504 cm⁻¹.

¹H NMR spectra of this fraction are reproduced in Fig. 2 for illustration. The signal at δ 8.00 ppm indicates the presence of the four aromatic protons of the benzene ring. Signals at δ 4.47 ppm and 3.96 ppm are characteristic of the methylene protons of COO–CH₂

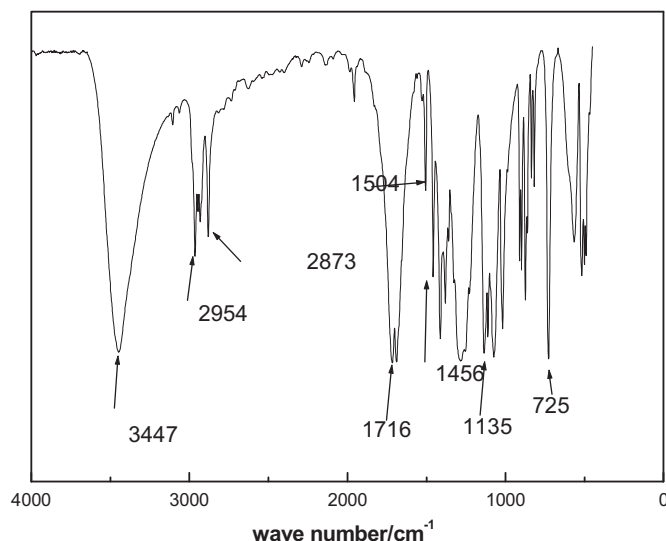


Fig. 1. FT-IR spectra of glycolysis main product.

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