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Ring-closing depolymerization of polytetrahydrofuran to produce tetrahydrofuran using heteropolyacid as catalyst

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ABSTRACT

This paper mainly explores the degradation of polytetrahydrofuran to prepare tetrahydrofuran. Various catalysts including different Lewis' acids and protonic acids are investigated in the degradation process of polytetrahydrofuran. The results show that heteropolyacids exhibit higher catalytic activity and stability than other catalysts. The optimal conditions for the degradation of polytetrahydrofuran using heteropolyacids (eg. phosphotungstic acid) as catalyst are phosphotungstic acid: polytetrahydrofuran = 1: 10 (mass ratio), 130 °C, 15 min, and the yield of tetrahydrofuran is greater than 95%. Heteropolyacid catalysts, especially phosphotungstic acid, could be separated easily and reused up to 10 times, and the yield of tetrahydrofuran reaches up to 90% when the catalyst phosphotungstic acid is reused 10 times. Meanwhile, the degradation mechanism of polytetrahydrofuran using phosphotungstic acid as catalyst is explored via NMR and FT-IR methods, and the ether bonds (C-*O*-C) cleavage mechanism is proposed.

1. Introduction

In recent years, the recycling and reclaiming of various plastics and fiber reinforced plastic composites (FRP) have more and more draw people's attention. The leftover materials and end-of-life products of plastic and FRP have caused serious environmental problems because these materials are stable and hard to degrade in natural environment [1]. The major components of plastics and FRP products are polymeric materials including thermosetting polymers and thermoplastic polymers, for example, unsaturated polyester resin (UP), epoxy resin (EP), polyurethane (PU), polyamide (PA), polyethylene terephthalate (PET), polysiloxane, and so on. In general, the recycling techniques mainly include mechanical recycling, energy recovery and chemical recycling. The mechanical recycling is usually applied to recycle thermosetting resin and FRP, and the thermosetting materials are crushed and ground into fine powder with different size. The recycled powder of low added-value is used as filler during the manufacture process of plastic. The energy recovery ways mainly recover pyrolysis oil or thermal energy via pyrolysis or fluidized bed techniques, respectively. This way will produce plenty of toxic gases, such as NO_x, CO, etc. Overall, chemical recycling is the most promising way to recycle polymeric materials because high added-value chemicals could be obtained in this way [2,3].

The chemical recycling mainly includes supercritical or subcritical water, supercritical alcohols, nitric acid, hydrogen peroxide, ionic liquid, amines (aminolysis), esters of phosphonic or phosphoric acids (phosphorolysis), glycols (glycolysis). However, for different polymers, the recycling methods are not the same. Currently, degradation and recycling of polymer materials are concentrated on epoxy resin (EP), unsaturated polyester resin (UP), polyethylene glycol terephthalate (PET), nylon-66 or nylon-6, polysiloxane and polyurethanes [1–9]. For example, the degradation of EP can be realized by supercritical or subcritical water [10–12], supercritical alcohol [13,14], nitric acid [15,16] and hydrogen peroxide [17,18] methods; the recycling of UP can be obtained through supercritical or subcritical water [19–21], supercritical alcohol [22] or ionic liquid [23]; generally, ionic liquids are used for degradation of PET [24–27]; supercritical alcohols or ionic liquids are also applied to the degradation of nylon including nylon-66 and nylon-6 [28–31]; the recycling of polysiloxane could be achieved via metal salt catalysts methods including iron salts or zinc salts [32–34]. Recovered polyols from polyurethanes waste can be obtained employing different cleavage agents (DEG, crude glycerol and so on) [4–9]. In the above methods, harsh reaction conditions

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and complex degradation products are the biggest hurdles during chemical recycling process of polymer materials. Therefore, above methods cannot be applied to degradation of polyether. Literature about degradation of polyether is relatively rare, but the research of polyether degradation is of great significance to the degradation of polyether type polyurethane.

Polytetrahydrofuran (PTHF), also called polytetramethylene ether glycol (PTMEG), is prepared by cationic ring-opening polymerization of tetrahydrofuran using cationic catalyst. PTHF is a white waxy solid, and it will change into transparent liquid when the temperature exceeds room temperature. Main chain of PTHF is composed of carbon skeleton and ether bond, which exhibits good flexibility, superior mechanical properties and excellent water resistance. Therefore, PTHF has already been widely applied in the manufacturing process of polyurethane elastic fiber and polyurethane elastomer as soft segments. Following the wide application of PTHF and polyurethane (PU), recycling of PTHF scrap and PTHF segments of PU has become an urgent issue that needs to be solved. PTHF segments contained in PU (mainly elastomers) have been successfully recycled by means of glycolysis [4–9]. Because of linear structure and low melting point of PTHF, solvent-free catalytic degradation method is adopted in this work to degrade PTHF. Catalytic effects of various Lewis acids and proton acids are explored for degradation of PTHF, and heteropolyacids are selected as catalysts due to their excellent catalytic effects. The solvent-free catalytic degradation method successfully realizes the degradation of PTHF and this method can obtain monomer tetrahydrofuran (THF) directly via the reaction and separation integrated process. As shown in Scheme 1, monomer THF is prepared via ring-closing depolymerization of PTHF in the presence of Lewis acids or proton acids. The reaction and separation integrated process was realized in one step of reaction and separation equipment (see Fig. S1). The degradation reaction of PTHF was carried out in three-necked round-bottomed flask, and degradation products are collected in round-bottom flask via the condensation of condenser.

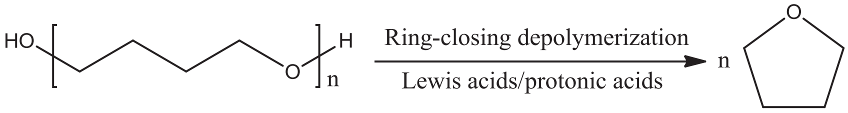
2. Material and methods

2.1. Experimental materials

Polytetrahydrofuran (hydroxyl as end group, PTHF, 2000 g/mol, 1000 g/mol) was purchased from Aladdin (Shanghai, China); PTHF (acetyl as end group, 2000 g/mol) was provided by Shanxi Sanwei Group Co., LTD; Polyethylene glycol (PEG, 2000 g/mol), Polypropylene glycol (PPG, 2000 g/mol) were provided by Junwei Wang' group which mainly engaged in synthesis and modification of PU; $FeCl_3$, $AlCl_3$, $Zn(OTf)_2$, $ZnCl_2$, $CuCl_2$, $MgCl_2$, $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$, $CrCl_3$, $Fe_2(SO_3)_3$, $Al(CH_3COO)_3$, $Al_2(SO_4)_3$, H_2SO_4 (98%) and H_3PO_4 (85%) etc. were purchased from J&K scientific LTD (Beijing, China) etc.; Phosphotungstic acid, Phosphomolybdic acid, Silicotungstic acid and Silicomolybdic acid were purchased from Aladdin (Shanghai, China).

2.2. Experimental section

General procedure for the degradation of PTHF is as followed. The experimental device is shown in Figure S1, 2.0 g PTHF and 0.2 g catalysts were mixed in the three-necked round-bottomed flask. The mixture was stirred and heated to the corresponding temperature by using an oil bath. When the oil temperature rose up to about 130 °C, the PTHF began to degrade and many bubbles formed. Finally, the vapor of THF was collected through the condenser pipe in round-bottom flask. After the reaction was completed, the yield was determined and the purity of the THF was analyzed by using



Scheme 1. Degradation of PTHF to produce monomer THF.

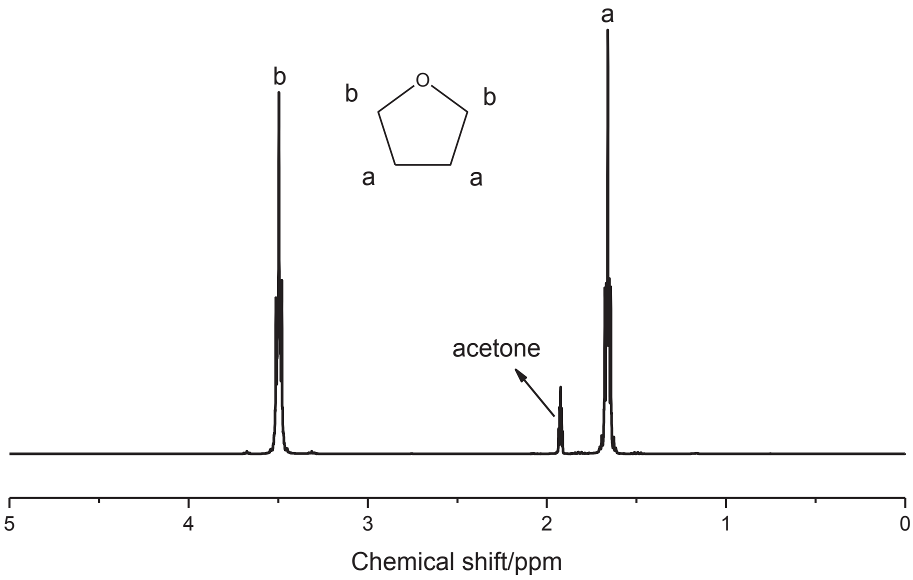


Fig. 1. ^{1}H-NMR spectra of recycled degradation products.