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Aminolysis of poly(ethylene terephthalate) waste with ethylenediamine and characterization of α,ω-diamine products

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ABSTRACT

Bis(2-aminoethyl) terephthalamide (BAET, or trimer) and α,ω-aminoligo(ethylene terephthalamide) (AOET, or oligomers) were obtained from the reaction of poly(ethylene terephthalate) (PET) waste with excess amount of ethylenediamine (EDA). The structures of trimer BAET and oligomers AOET were confirmed by FTIR, NMR, HPLC-MS analysis. The influence of input molar ratio of reactants on oligomer yield was also investigated. The formation of oligomers competed with the formation of trimer even though EDA was used in excess amount. The melting points, thermal properties of BAET and AOET were determined by DSC, TGA techniques. The physical melting process and chemical transamidation of amino end capped BAET/AOET occurred concurrently before thermal decomposition.

1. Introduction

Poly(ethylene terephthalate) (PET) is a thermoplastic polymer, which is used as fibres, sheets and soft drink bottles. With increasing of production, application and therefore waste materials, then pressure of keeping the environment clean, recycling PET waste is the only solution.

Two major conventional methods of recycling postconsumer PET exist: mechanical recycling and chemical recycling [1,2]. Because of the degradation reaction occurring during mechanical recycling, then recycled PET generally ends up in low grade products such as fibre. Mechanical recycled PET can be used in the blends with other polymers, such as high and low density polyethylene, polycarbonates [3,4], etc.

Depolymerization processes for chemical recycling mainly include hydrolysis, methanolysis, and glycolysis [5–8]. The organocatalytic depolymerization of PET with excess amount of ethylene glycol, using a commercially available guanidine catalyst, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) has been reported [9].

Aminolysis is another method of chemical degradation of PET, which has been little investigated as compared to other techniques. The degradation of PET by aqueous methylamine and ammonia at room temperature in the presence and absence of quaternary ammonium salt as a catalyst has been reported by Soni and Singh [10]. Terephthalic diamides were obtained from PET waste in the reaction with excess aliphatic amines such as: n-butylamine, n-hexylamine, n-octylamine and n-dodecylamine [11]. The terephthalic diamides have been used as stabilizers for LDPE [12].

PET in the form of waste fibres and disposable soft drink bottles was subjected to depolymerisation through aminolysis using excess of ethanolamine in the presence of different simple chemicals, namely glacial acetic acid, sodium acetate and potassium sulphate, as catalysts [13]. The obtained product from reaction with ethanolamine, bis(2-hydroxyethyl) terephthalamide (BHETA), was used to prepare polyurethane [14].

Magda E. Tawfik and Samir B. Eskander [15] have investigated the aminolysis degradation of PET waste by ethanolamine (EA) in the presence of dibutyl tin oxide (DBTO) as a catalyst.

The chemical degradation of waste PET with polyamines, such as diethylenetriamine, triethylenetetramine, and their mixtures, as well as mixtures of triethylenetetramine and *p*-phenylenediamine or triethanolamine, and the characteristics of the products were described by Spychaj et al. [16].

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Loic Bech et al. [17] have also carried out the aminolysis of PET fibres with diamines, such as 1,2-diaminoethane, 1,6-diaminohexane, 3,6-dioxa-1,8-diaminooctane, and 4,9-dioxa-1,12-diaminododecane, to give amino functional groups on the surface.

Following Lecuyer's Master Thesis [18], the degradation of PET was carried out in a diverse set of amines, such as primary amines (aliphatic, aromatic, click functionalized, tertiary functionalized), secondary amines, and asymmetric amines, using the organocatalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). After heating at 100 °C under vacuum for 17 h, the reaction mixture was treated with ethyl acetate. However this solvent may react with the excess amount of ethylenediamine or even with the diamine product. Therefore the procedure to obtain bis(2-aminoethyl)terephthalamide seems to be not feasible.

The reaction of 1 mol poly(ethylene terephathalate) with 0.05–0.5 mol ethylenediamine in solvent, followed by solid-phase polycondensation or melt polycondensation to produce copoly(ethylene terephthalate/ethylene terephthalamide) has been reported by Nakano, Masayoshi [19].

The purpose of this research is to study the aminolysis of PET with ethylenediamine without catalysis and propose a procedure to isolate trimer and α,ω-diamine oligomer products and their characterization. The influence of excess amount of ethylenediamine on the trimer and oligomer yields was also studied.

2. Experimental

2.1. Materials

PET was used in the form of post-consumed plastic bottles. It was cut into squares (flakes) no larger than 0.5 cm × 1 cm, rinsed with water, acetone, and then dried in an oven at 70–80 °C for 3 days. EDA, methanol, acetone were purchased from Chemsol-VN.

2.1.1. Reaction of PET with EDA

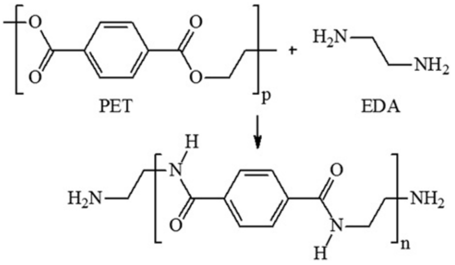
A mixture of 3.00 g (0.0156 mol) of PET flake and 15.0 g (0.250 mol) of EDA was heated in a 100 mL round bottom flask at 100 °C for 17 h. After adding 50.0 mL of methanol to the reaction mixture, it was refluxed for further 3 h. The reaction mixture was then cooled to room temperature, and filtered. The insoluble material (called as part A) was rinsed carefully with methanol and acetone, dried at 60 °C for 24 h in a vacuum oven, and its mass was recorded.

The volatile materials in the combined filtrate were removed by rotary evoporator. The obtained viscous material was left at room temperature until it recrystallized completely. The solid material was filtered, rinsed carefully with cool methanol, acetone, dried at 60 °C for 24 h in a vacuum oven, and then its mass was recorded. This solid material (called as part B) became insoluble in pure methanol or acetone. After recrystallization from DMSO, part B was subjected to FTIR, NMR, HPLC-MS analysis.

2.2. Characterisation of the product

High performance liquid chromatography analysis of the aminolysis products was performed using an Agilent Technologies 1200 series HPLC instrument equipped with a ACE 3– C18 column (150 mm long, 4.6 mm diameter, 3 µm particle size, 100 Å pore size). Elution was performed at room temperature by using solvent A (0.1% aqueous formic acid) and solvent B (0.1% formic acid in methanol), at a flow rate of 0.40 mL/min and a linear gradient of A/B from 90/10 to 0/100 in 20 min. The solution for HPLC analysis was prepared by dissolving about 4 mg solid materials in 50 mL of acetic acid. The injection volume was 10 µL.

The HPLC instrument was connected to a Bruker Daltonics MicrOTOF QII time-of-flight mass spectrometer, equipped with an orthogonal ESI source and a 6-port divert valve. The instrument was operated in positive ion mode using a range of 50–3000 m/z. External calibration was performed prior to each run using cluster ions from an Agilent tune mix solution.



Scheme 1. The reaction of PET with EDA. $n = 1$: bis(2-aminoethyl) terephthalamide (BAET); $n \geq 2$: α,ω-aminoligo(ethylene terephthalamide) (AOET).

An FTIR EQUINOX 55 – Brucker spectrometer was used in transmission mode to record spectra from KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Brucker ARX-500 Advance Spectrometer operating at 500 MHz in d4-acetic acid solution.

Differential scanning calorimetry was performed with a METTLER STARe SW 11.00 instrument. Samples were heated from room temperature to 400 °C/450 °C, with heating rate of 10 °C/min in nitrogen atmosphere. Thermogravimetric analysis was carried out on a Q500 Universal V4.5A TA Instrument, heating from room temperature to 800 °C with heating rate of 10 °C/min in nitrogen atmosphere.

3. Results and discussion

The aminolysis reaction of PET with excess amount of ethylenediamine can be proposed as the chemical reaction in Scheme 1.

The names, formula and masses of trimer/oligomers are given in the Table 1.

3.1. Characterization of bis(2-aminoethyl) terephthalamide (BAET or trimer) and α,ω-aminoligo(ethylene terephthalamide) (AOET)

The obtained part B could contain trimer (BAET) and part A could contain higher molecular weight oligomers of α,ω-aminoligo(ethylene terephthalamide) (AOET), as confirmed by the following analytical methods.

3.1.1. Characterization by FTIR

The FTIR spectrum of part B was shown in Fig. 1.

The main features of the infrared spectrum of part B are the N–H stretching band of secondary amide at 3286 cm^{-1}, the stretching vibration of C=O (amide-I band) at 1632 cm^{-1}, and the N–H deformation at 1549 cm^{-1} (amide-II band). Primary aliphatic amines with RCH_2NH_2 structure exhibit $\nu_{sym.}NH_2$ in the region 3340–3361 cm^{-1}, and $\nu_{asym.}NH_2$ when observed in the region 3404–3422 cm^{-1} [20]. Both IR bands are weak. However, the

Table 1
The names, formula and masses of trimer/oligomers.

n	n-mer[a]	Symbol	Molecular formula	Exact molecular mass	Average molecular mass
1	Trimer	M3	$C_{12}H_{18}N_4O_2$	250.1430	250.30
2	Pentamer	M5	$C_{22}H_{28}N_6O_4$	440.2172	440.50
3	Heptamer	M7	$C_{32}H_{38}N_8O_6$	630.2914	630.70
4	Nonamer	M9	$C_{42}H_{48}N_{10}O_8$	820.3657	820.91

[a] n-mer: assuming that n-mer was prepared from x molecules of terephthalic acid and $(n - x)$ molecules of ethylenediamine.