

## A NEW MONOALKYL PHOSPHATE ESTER BASED ON A PRODUCT DERIVED FROM THE RECYCLING OF A POSTCONSUMER POLYETHYLENE TEREPHTHALATE WASTE

Assem K. Merekenova<sup>1</sup>, Galina I. Boiko<sup>1</sup>, Sergey A. Dergunov<sup>2</sup>,  
Raushan G. Sarmurzina<sup>3</sup>, Uzakbay S. Karabalin<sup>3</sup>, Nina P. Lubchenko<sup>1</sup>

<sup>1</sup> Satbayev University, 22 Satbayev str.  
Almaty, Republic of Kazakhstan

<sup>2</sup> University of Connecticut  
55 North Eagleville Road, Mansfield, USA

<sup>3</sup> Association "KAZENERGY"  
19 Kabanbay batyr str., Astana, Republic of Kazakhstan  
E-mail: assem.merekenova@gmail.com

Received 17 May 2017  
Accepted 20 October 2017

### ABSTRACT

A synthesis of new monoalkyl phosphate esters based on chemical recycling products of polyethylene terephthalate bottles is advanced. It refers to glycolysis in excess of ethylene glycol in presence of zinc acetate as a catalyst, followed by phosphorylation of the glycolysis product (bis(hydroxyethyl) terephthalate) with polyphosphoric acid in an aprotic solvent. The structure of the synthesis intermediate and final products is identified by DSC, FT-IR, <sup>1</sup>H<sup>31</sup>P NMR spectroscopy.

**Keywords:** PET bottle, glycolysis, polyphosphoric acid, monoalkyl phosphate.

### INTRODUCTION

Currently, polyethylene terephthalate (PET) is widely used as beverage containers due to its chemical resistance, high mechanical strength, low weight, toughness, and excellent consumer properties [1 - 2]. According to Plastics insight, the global production of PET in 2015 was 27.8 million tons [3]. However, the large amount of packaging inevitably raises the issue of recycling waste. Post-consumer PET products are highly resistant to the atmosphere, they have poor biodegradability and photodegradability, but are highly recyclable [4]. Therefore, chemical recycling is an effective solution to the problem. It affords to convert the plastic bottles into a monomer or low weight oligomers. Further, the monomer, bis(hydroxyethyl)terephthalate (BHET) is a valuable raw material for many useful products. It is used for the synthesis of unsaturated polyester resins [5 - 6], polyurethanes [7 - 8], surface active agents [9], corrosion inhibitors [10], etc. This work describes the synthesis of new monoalkyl phosphate esters on the ground of the

product of PET bottles chemical recycling by glycolysis in excess of ethylene glycol in the presence of a catalyst followed by phosphorylation of bis(hydroxyethyl) terephthalate with polyphosphoric acid in an aprotic solvent.

### EXPERIMENTAL

#### Materials

PET granules from crushed plastic bottles were received from "KazPET polymer" company. The intrinsic viscosity was determined by the viscosimetric method in m-cresol at 25°C, d = 0.73 mm, K = 0.77x10<sup>3</sup> α = 0.95 [11]. Zinc acetate, ethylene glycol (EG), m-cresol, N, N-dimethylformamide (DMF), polyphosphoric acid (115 %), diethyl ether, and hydrochloric acid were supplied by Sigma Aldrich and used without a further purification.

#### Methods

##### Glycolysis of PET bottle

A 250-ml round bottom four-necked flask equipped with a stirrer, a reflux condenser, and a thermometer

was loaded with granulated polyethylene terephthalate and ethylene glycol of a ratio 1:10, respectively, zinc acetate and 1 mass % of PET. The depolymerization reaction was carried out under argon atmosphere at 180°C - 190°C for 5 h. Once the reaction was finished, hot water was added in excess to the reaction products. Then, the mixture was filtrated. The filtrate containing ethylene glycol and BHET was placed in a refrigerator to ensure latter crystallization. A second filtration was performed to separate BHET from EG and the catalyst. BHET was dried at 80°C until a constant weight.

### Esterification of BHET

A 50-ml round bottom four-necked flask equipped with a stirrer, a reflux condenser, a thermometer and an argon inlet was loaded with 1mmol BHET, 2 mmol N,N-dimethylformamide and was heated to 70°C until complete dissolution. 1mmol polyphosphoric acid (115 %) was added under constant stirring and the temperature was raised to 140 °C. The reaction was completed within 12 h. Then distilled water was poured to neutralize the polyphosphoric acid. This step proceeded 3 h at 80°C.

### Products analysis

#### Viscosimetry

The intrinsic viscosity  $[\eta]$  was measured in m-cresol at 25°C. Ubbelohde viscometer was used. The granulated PET was dissolved in m-cresol at 130°C (approximately 15 - 20 min) and solutions of 1 mass % were prepared.

They were then cooled to room temperature and filtered through a disposable Schott glass filter. The intrinsic viscosity was calculated using the Solomon–Ciuta equation [12]:

$$[\eta] = \frac{(2 \left( \frac{t}{t_0} - \ln \frac{t}{t_0} - 1 \right))^{1/2}}{c}$$

where  $c$  was the concentration of the solution,  $t$  was the flow time of the solution, while  $t_0$  was the flow time of the pure solvent. The number-average molecular weight ( $M_n$ ) of PET was calculated from the intrinsic viscosity  $[\eta]$  values using the Mark-Houwink equation [13]:

$$M_n = \sqrt{\frac{[\eta]}{K}}$$

where  $\alpha$  and  $K$  were constants for a particular polymer solvent system.

#### Differential scanning calorimetry (DSC)

DSC analysis was performed with DSC 131 evo Setaram instrumentation. The experiments were carried out under nitrogen atmosphere. The temperature range was between 40°C and 310°C, while the heating rate was 10°C/min.

#### FT-IR Spectroscopy

FT-IR Spectroscopy (a spectrometer model Agilent Cary 660) was applied to identify the chemical structure of BHET and the mono alkyl phosphate ester.

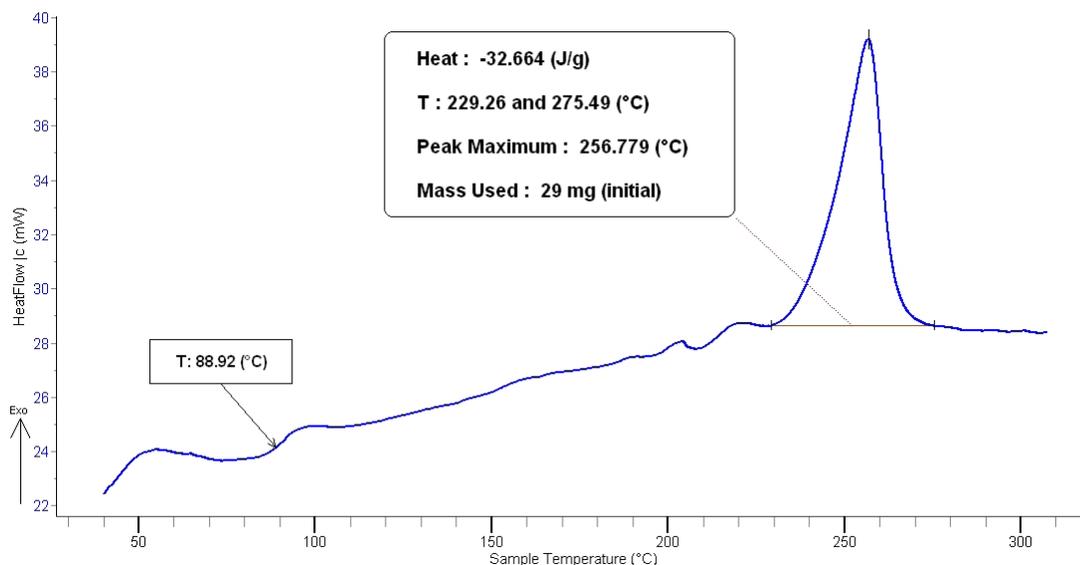


Fig. 1. DSC Curve for granulated PET.

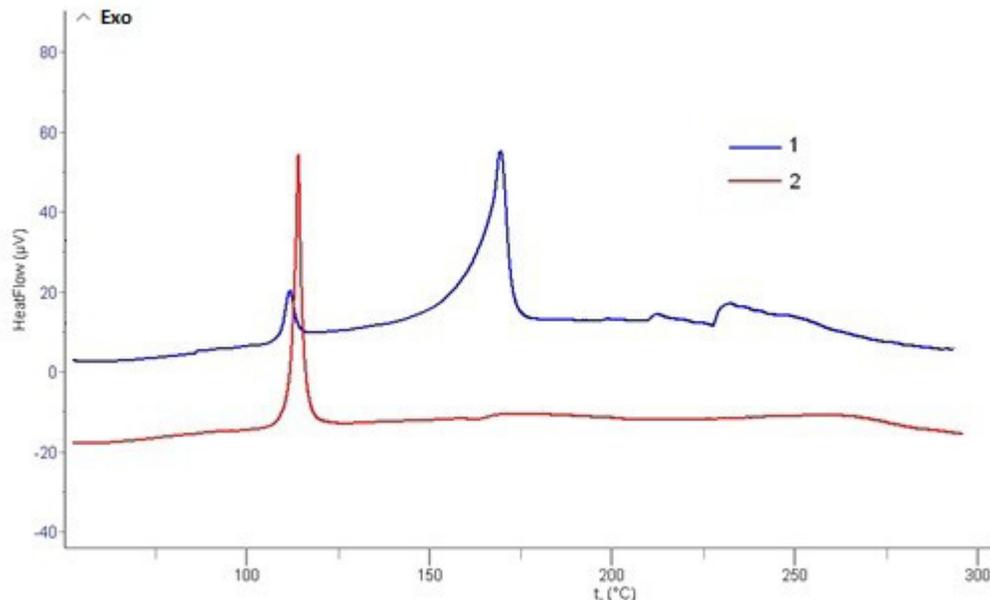


Fig. 2. DSC curves of glycolysed PET: Curve 1 - dimers, PET oligomers and a residue containing unseparated BHET; Curve 2 - separated BHET.

### **<sup>1</sup>H <sup>31</sup>P NMR spectroscopy**

<sup>1</sup>H <sup>31</sup>P NMR spectra were recorded on a Bruker AVANCE 400 Mhz spectrometer in deuterium oxide and dimethyl sulfoxide solutions.

## **RESULTS AND DISCUSSION**

PET granules from crushed plastic bottles with a molecular weight of 46,700 Da and a melting point of 256°C according to the DSC curve (Fig. 1) are subjected to a depolymerization reaction in the presence of an excess of ethylene glycol and a catalyst for 5 h at 180°C - 190°C. Upon reaction completion, hot water is added to the reaction mixture containing ethylene glycol, a catalyst and dissolved monomer. It is filtered off. Dimers, PET oligomers and a residue of unseparated monomers (Fig. 2, Curve 1) of melting points of 168°C, 227°C and 113°C, respectively, remain on the filter, while the filtrate is placed in a refrigerator for 48 h. The precipitated crystals are filtered off and washed with cold water. BHET obtained is a white crystalline powder. The DSC curve (Fig. 2, Curve 2) shows a single endothermic peak with a melting point at 113°C. This indicates that the glycolysed product is of a high purity.

BHET structure is verified by FT-IR spectroscopy (Fig. 3). The spectrum obtained shows peaks of a high

intensity at ca 3440 cm<sup>-1</sup>. They refer to OH groups vibrations. The bands at ca 1715 cm<sup>-1</sup> correspond to the stretching vibrations of the carbonyl group (C=O) of the ester. The bands at 2966 cm<sup>-1</sup> and 2881 cm<sup>-1</sup> are attributed to the vibrations of CH bonds in the CH<sub>2</sub> groups. The stretching of the aromatic ring (-C=C-) is outlined at 1504 cm<sup>-1</sup>.

The <sup>1</sup>H NMR spectrum of BHET is shown in Fig. 4. It exhibits the appearance of O-H δ (ppm) = 4.89, COO-CH<sub>2</sub> δ (ppm) = 4.31, CH<sub>2</sub>-OH δ (ppm) = 3.72 and benzene ring δ (ppm) = 8.11. The FT-IR and <sup>1</sup>H NMR spectrums of BHET obtained correlate well with those reported in the literature [14 - 15].

### **Phosphorylation of BHET with polyphosphoric acid**

It is known that phosphoric acid monoesters are produced by phosphorylation of alcohols with polyphosphoric acid, phosphorus anhydride and phosphoric acids [16]. The phosphorylation of BHET with polyphosphoric acid (115 %) is carried out in an aprotic solvent (DMF) medium. At the end of the reaction, DMF is distilled off, water is added and a hydrolysis reaction of polyphosphoric acid in orthophosphoric acid is carried out for 3 h at 80°C. The resulting phosphoric acid ester is dissolved in methanol, then monoalkyl phosphate is extracted with diethyl ether; it is washed with 0.1 N hydrochloric acid

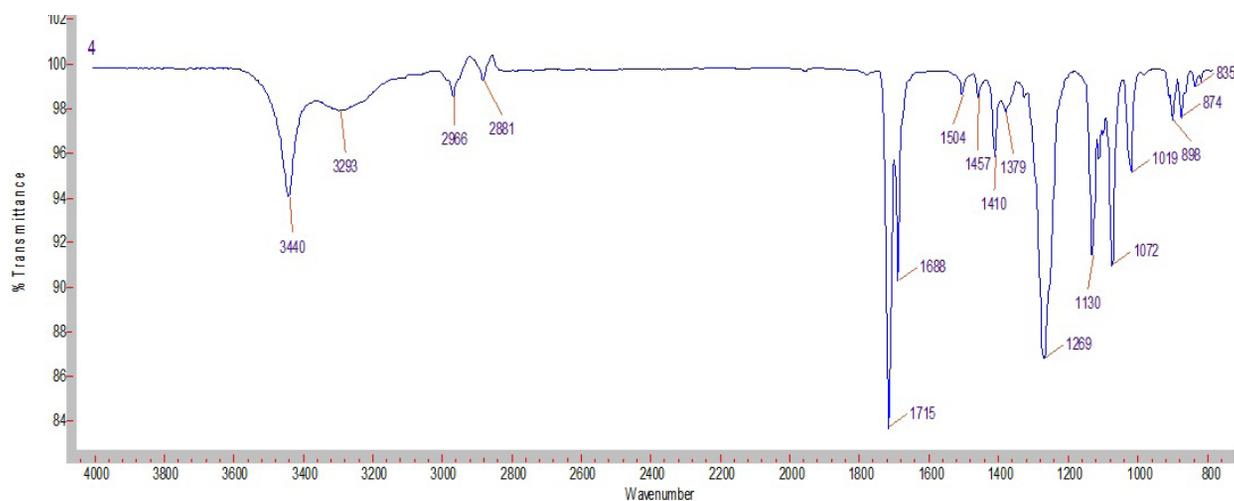
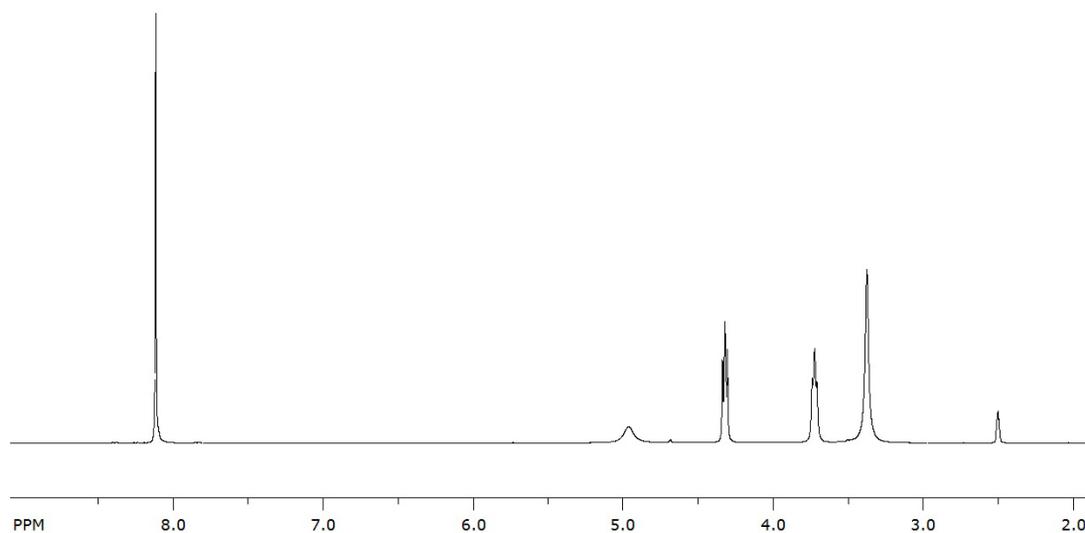


Fig. 3. FT-IR spectrum of BHET.

Fig. 4. <sup>1</sup>H NMR spectrum BHET in d<sub>6</sub>-DMSO.

and distilled water several times [17].

The phosphorylation products are a mixture of phosphate mono- and diester, polyphosphate mono- and diester, and a small amount of phosphoric acid [18]. A scheme of the reaction and the expected chemical structure of the obtained phosphate ester of BHET is suggested (Fig. 5). PET is converted to BHET via reaction of glycolysis during the first stage. Then polyphosphate monoester is obtained by a reaction of phosphorylation of BHET with polyphosphoric acid in an aprotic solvent. During the third stage a small amount of water is added

to hydrolyze the residual polyphosphate intermediates.

The structure of obtained phosphate ester of BHET is verified by FT-IR spectroscopy (Fig. 6). The spectrum recorded in the range of 835 nm - 4000 nm shows the presence of a carbonyl group (C = O) in the ester at 1719 cm<sup>-1</sup>. Noticeable band changes are observed in CH vibrations in the CH<sub>2</sub> groups at 2984 cm<sup>-1</sup> and 2886 cm<sup>-1</sup>. P-OH vibrations are outlined at 2800 cm<sup>-1</sup>. Vibration at 985 cm<sup>-1</sup> is attributed to P-OC oscillations, while P = O stretching is recorded at 1106 cm<sup>-1</sup>.

The <sup>1</sup>H NMR spectrum of BHET phosphate ester

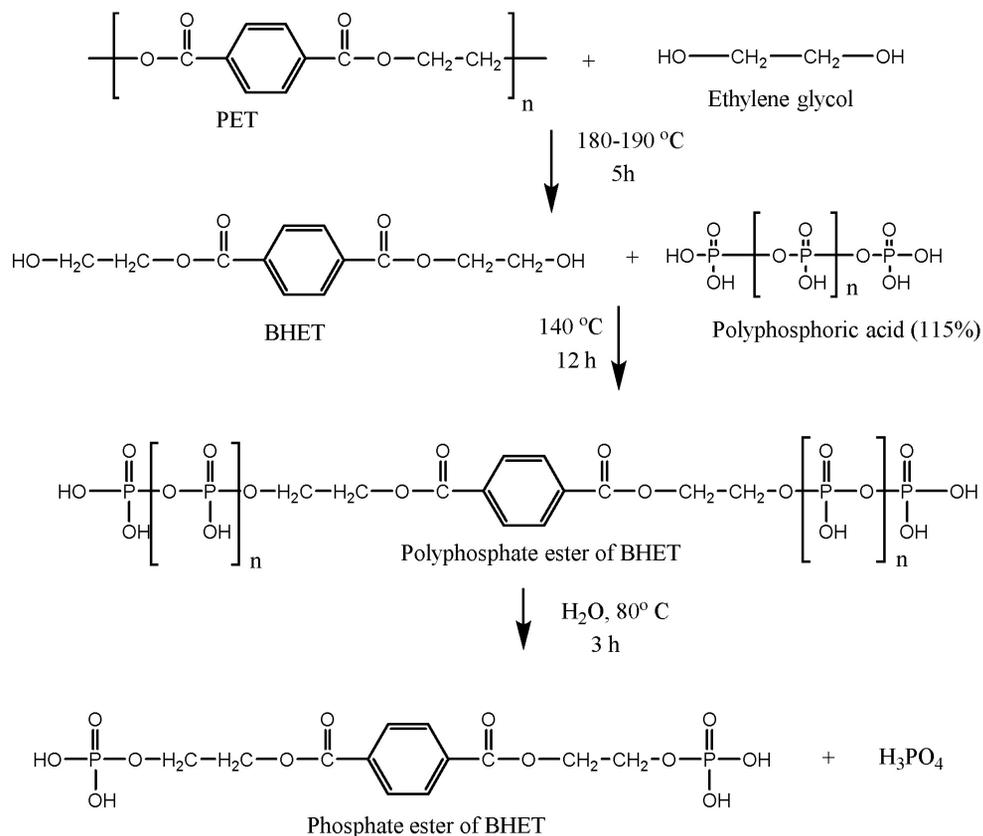


Fig. 5. Synthesis of phosphate ester of BHET based on glycolysis of PET.

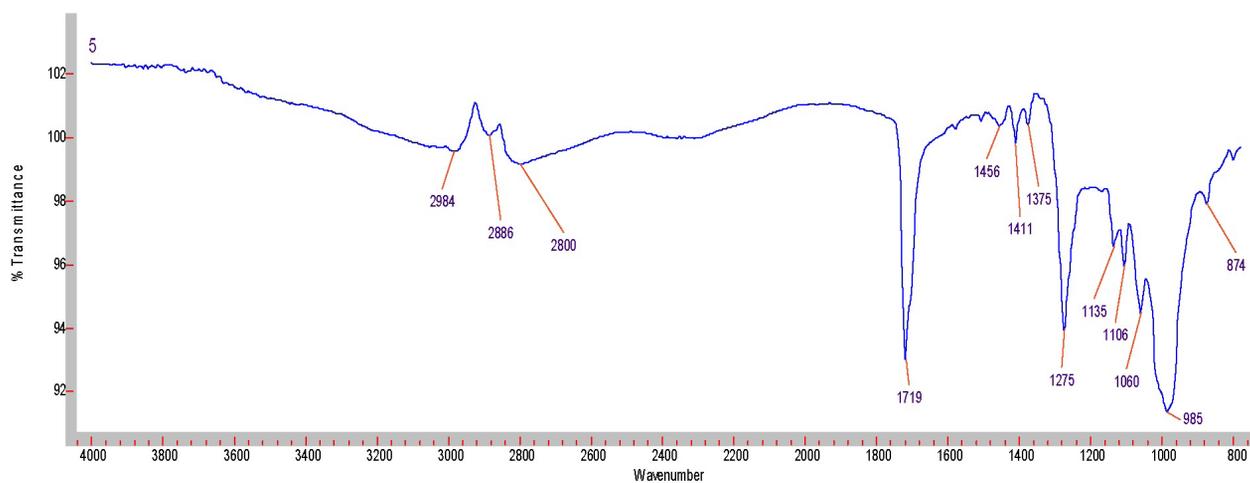


Fig. 6. FT-IR spectrum of the phosphate ester of BHET.

is shown in Fig. 7. The disappearance of the OH peak and the appearance of one new peak at 8.34 ppm (P-OH) indicate the formation of a phosphate monoester.

The <sup>31</sup>P-NMR spectrum of the phosphorylation

products is shown in Fig 8. A phosphate ester of BHET is the product of phosphorylation reaction after extraction of phosphoric acid with a small amount of polyphosphate ester of BHET as a residue. The

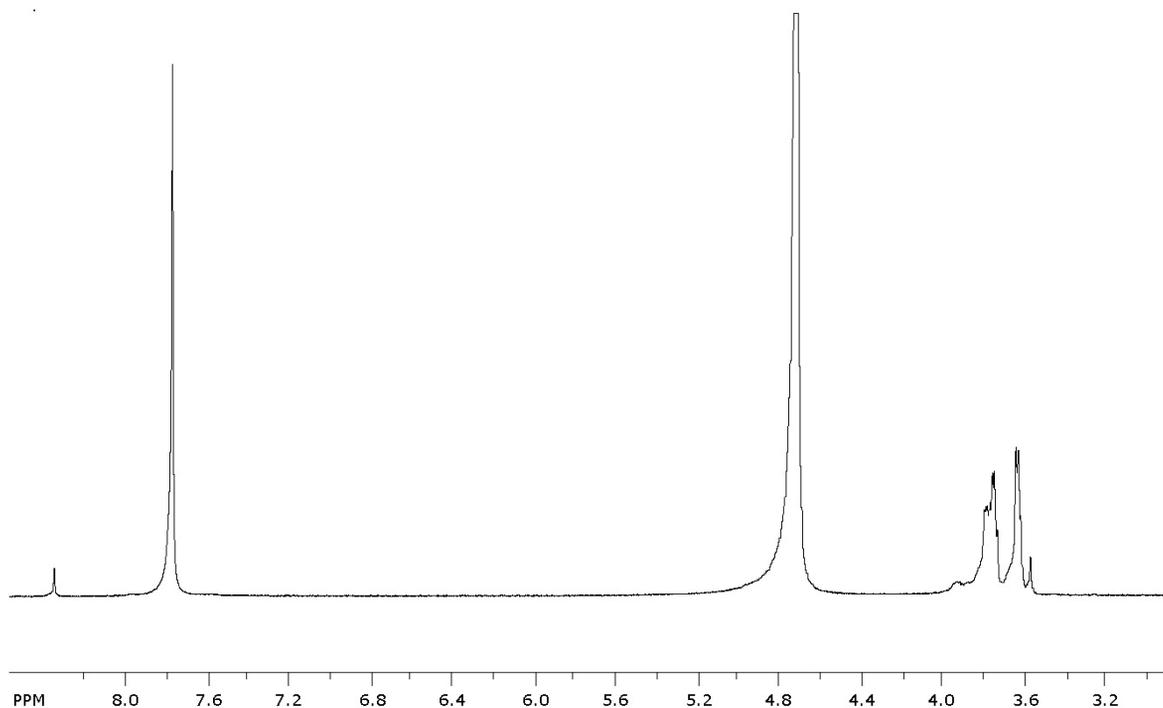


Fig. 7. <sup>1</sup>H NMR spectrum of the phosphate ester of BHET in deuterium oxide.

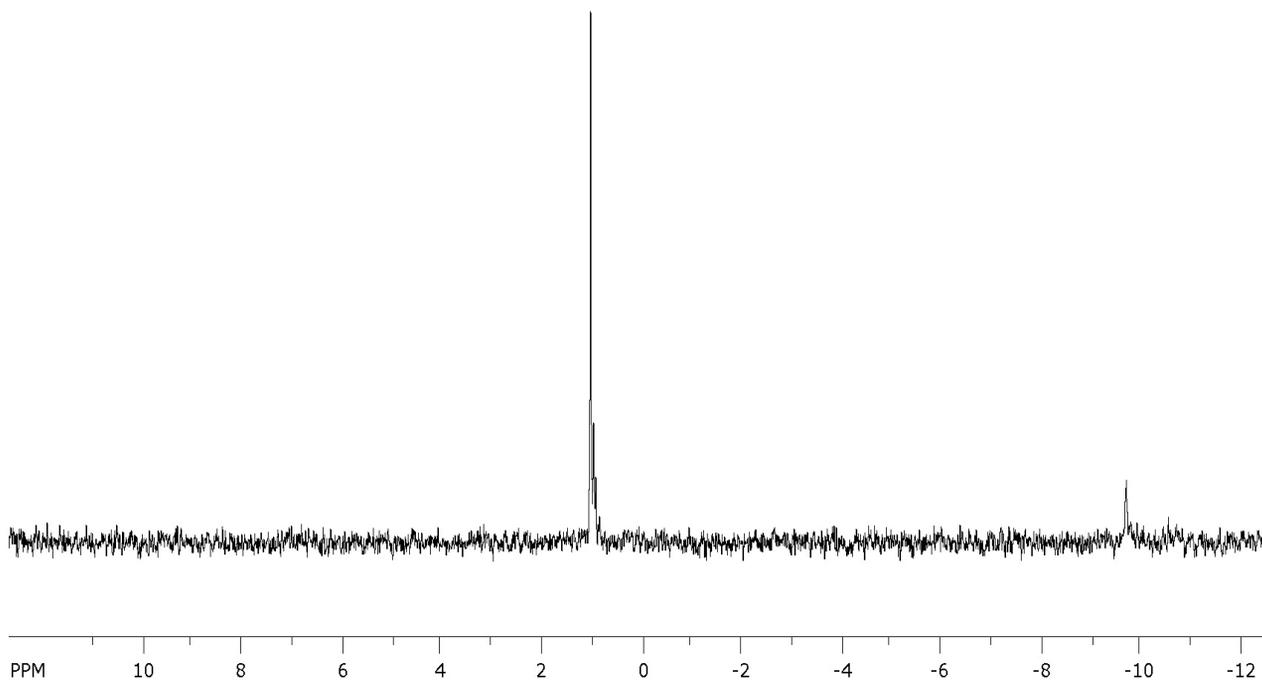


Fig. 8. <sup>31</sup>P MR spectrum of the phosphate ester of BHET in deuterium oxide.

signals of the phosphate ester of bis(hydroxyethyl) terephthalate (0.95 ppm) and the polyphosphate ester of bis(hydroxyethyl) terephthalate (-9.75 ppm) are well outlined in the NMR spectrum.

Thus, the results obtained by FT-IR, <sup>31</sup>P-NMR and <sup>1</sup>H-NMR verify that the synthesized product refers to the phosphate ester of bis(hydroxyethyl) terephthalate.

## CONCLUSIONS

Postconsumer PET bottles were depolymerized by glycolysis in excess of ethylene glycol and zinc acetate presence. The glycolysed products obtained were characterized by DSC, FT-IR, and <sup>1</sup>H NMR spectroscopy. The phosphorylation of bis(hydroxyethyl) terephthalate with polyphosphoric acid in an aprotic solvent provided the formation of the phosphate ester of bis(hydroxyethyl) terephthalate. The structure of the latter was verified by FT-IR, <sup>31</sup>P NMR and <sup>1</sup>H NMR.

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