

# Glycolysis of Polyethylene Terephthalate Waste Fibers

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**ABSTRACT:** Glycolysis of polyethylene terephthalate waste fibers was carried out using excess ethylene glycol in the presence of different simple chemicals, namely, glacial acetic acid, lithium hydroxide, sodium sulfate, and potassium sulfate. Good yields (> 60%) of the monomer bis(2-hydroxyethylene terephthalate) were obtained using these chemicals as depolymerization catalysts. The purified monomer was characterized by elemental analysis, melting point, IR spectroscopy, and nuclear magnetic resonance. The qualitative and quantitative yields of the monomer obtained

using these catalysts are most comparable with the conventionally used heavy metal catalysts such as zinc acetate and lead acetate. The chemicals used, being cheap and comparatively less harmful to the environment, offer further advantages in chemical recycling of polyester waste fibers. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 513–517, 2005

**Key words:** polyester; catalysts; degradation; NMR; infrared spectroscopy

## INTRODUCTION

Nature is full of polymeric materials such as proteins, cellulose, starch, rubber, etc., having highly complex and precise structures. The synthetic polymers, on the other hand, are comparatively crude in quality and molecular architecture. In recent decades, polymers have experienced an overall spectacular growth in terms of variety, quality, and quantity by the way of better understanding of polymer chemistry and technology.

The major difference in the natural and synthetic polymers lies in the fact that the former are biodegradable, making them less durable, whereas the latter last considerably longer, being almost nonbiodegradable. This aspect has caused a major concern to environmentalists from the point of view of polymer waste management.

Polyethylene terephthalate (PET) is one such versatile polymer, which is being used in the preparation of a variety of products differing widely in their physical characteristics and, hence, their end uses. It is a polymer that was first synthesized in Du Pont laboratories in 1929 by W. H. Carothers, and, after about two decades, the first apparel stitched from the PET fiber fabric made its appearance in the market. In India, production of polyester staple fiber and filament yarn started in the 1960s and the annual growth rate was

19.4% from 1980 to 2000. Today, as a textile fiber, it has captured the market next only to cotton and lagging behind only by a small margin. The better properties like high strength and durability, creaseless wearing, and easy laundering of the garments made out of this fiber may soon bridge the gap and surpass cotton. This will also be assisted by a variety of physical and chemical modifications, which the PET fiber is continuously undergoing, to further improve its useful properties. Global demand for PET filament has grown since 1995 onward at the rate of 8.3% per annum.

In the 1980s, another major area of utilization was found for PET, the production of disposable soft drink bottles. Other areas of PET consumption include non-apparel uses through articles in the form of various molds, films, chips, coatings, etc. that are possible due to the thermoplastic nature of this polymer.<sup>1</sup> Being used in more than one hundred separate technical end use products, it is now also finding major use in sportswear, as it is a fast drying fiber.

As for anything on the earth, PET products also become waste after their useful life is over in addition to the waste produced in its manufacture<sup>2</sup> Due to its nonbiodegradable nature, the major concern about this huge PET waste is the development of a recycling process.

The chemical recycling or solvolysis of PET has been the subject of keen interest as a valuable feedstock for different chemical processes. A variety of depolymerization techniques are available leading to various end products. Methanolysis<sup>3</sup> and hydrolysis<sup>4–8</sup> of PET were the first to be invented, whereas glycolysis was claimed in the mid-1960s.<sup>9</sup> PET glycolysates have been

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used in the preparation of various types of unsaturated polyester resins.

The depolymerization processes such as reaction under pressure and heat, methanolysis using methanol,<sup>10,11</sup> and hydrolysis using water, acid, or alkalis, are known to degrade PET to the original reactants dimethyl terephthalate/terephthalic acid and ethylene glycol.

Glycolysis of polyester is carried out conventionally in boiling ethylene glycol solution under atmospheric pressure using different types of metal catalysts, with zinc acetate being more common.<sup>12</sup>

In earlier studies, we have used simple alkalis such as sodium carbonate and sodium bicarbonate for the glycolysis reaction of PET waste and observed that the yields of the degradation product bis-2-hydroxyethylene terephthalate (BHET) are comparable to those obtained by the heavy metal catalysts, zinc acetate or lead acetate.<sup>13</sup>

Zinc and lead both belong to the category of heavy metal cations, which cause pollution due to their non-biodegradable and toxic nature. They possess a tendency to accumulate in living organisms over a period of time. The toxicity caused by the heavy metal cations is slow and long lasting. High exposure levels to lead induce anemia. It also affects the central nervous system. Although zinc is an essential element in living organisms at trace levels, its large doses cause gastrointestinal problems. The permissible limits of Pb and Zn cations in the effluent discharged to the surface water are 5 and 0.1 ppm, respectively.<sup>14</sup>

The present article deals with the use of different simple chemicals as catalysts for the glycolysis of PET waste and characterization of the degradation product. The catalysts selected were acetic acid, sodium sulfate, potassium sulfate, and lithium hydroxide. The mechanism of depolymerization has also been discussed.

## EXPERIMENTAL

### Materials

PET waste was a mixture of varied staple length fibers of 1.44 d, obtained from Reliance Industry (Mumbai, India).

**TABLE I**  
Effect of Glycolysis Time on Yield of BHET in the Presence of Different Catalysts

Time (h)	BHET yield in the presence of			
	Acetic acid	Lithium hydroxide	Sodium sulfate	Potassium sulfate
5	53.00	53.50	37.82	54.50
6	58.00	57.20	52.54	57.30
7	61.57	61.02	63.54	62.32
8	62.42	63.50	65.72	64.42
9	61.09	60.07	65.07	63.00

**TABLE II**  
Effect of Concentration of Different Catalysts on Yield of BHET

Catalyst concentration	BHET yield in the presence of			
	Acetic acid	Lithium hydroxide	Sodium sulfate	Potassium sulfate
0.3	52.00	55.07	57.00	52.00
0.4	57.00	57.09	61.00	54.00
0.5	62.42	63.50	65.72	64.42
0.6	59.00	60.05	63.00	63.00
1.0	57.00	54.07	60.00	60.00

### Chemicals

All the chemicals were of analytical reagent grade. The nonionic detergent used was Lentol FBOL of ICI Uniqema (Mumbai, India).

### Cleaning of polyester waste

The PET fiber waste was boiled in a 2 g/L nonionic detergent solution for about 1 h to remove any surface impurities and finishes followed by thorough washing with water and drying in an oven at 80°C.

### Glycolysis of polyester waste

The PET fiber waste was treated with ethylene glycol at a molar ratio of 1 : 6 (PET : glycol) under reflux in the presence of different catalysts for time periods up to 8 h. The catalysts, namely lithium hydroxide, sodium sulfate, potassium sulfate, and glacial acetic acid were used in concentrations ranging between 0.3 and 1% (w/w). At the end of the reaction, distilled water was added in excess to the reaction mixture with vigorous agitation. The glycolized product was obtained as a residue after filtration. The filtrate contained unreacted ethylene glycol, bis-2-hydroxyethylene terephthalate (BHET), and small quantities of a few water-soluble oligomers. White crystals of BHET were obtained by first concentrating the filtrate by boiling and then chilling it. The glycolized residue was then boiled with water to extract any remaining BHET. White crystalline powder of BHET was purified by repeated crystallization from water, dried in an

**TABLE III**  
Characterization of BHET Obtained

Formula	$C_{12}H_{14}O_6$
Mol wt	254
Melting point	109–112°C
Elemental analysis (%)	
C	55.9
H	5.4
O	38.7

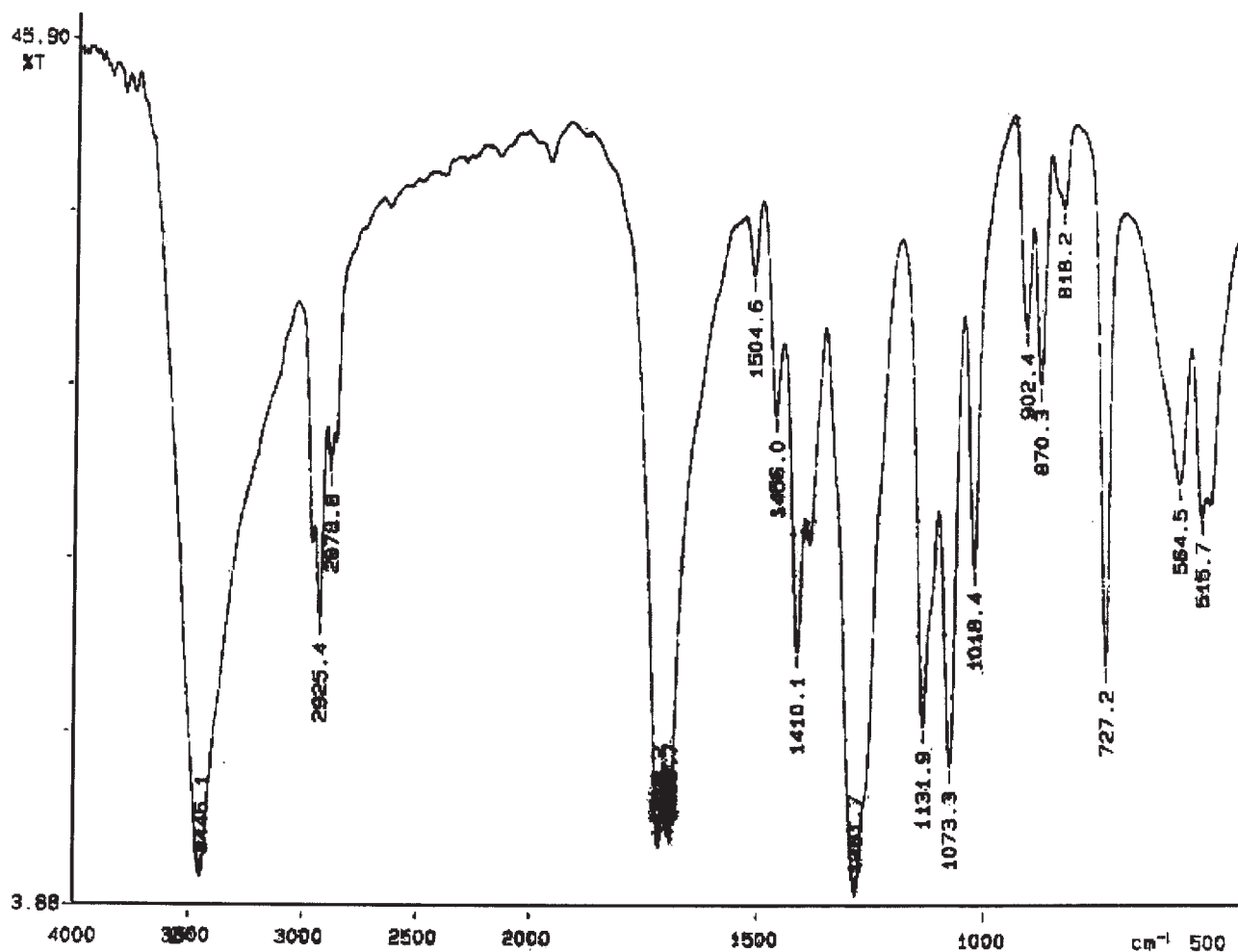


Figure 1 IR Spectrum of BHET.

oven at 80°C, and weighed to estimate the yield. It then was subjected to different characterization techniques.

### Characterization

Melting point of the purified monomer BHET was determined in an open capillary.

Elemental analysis was carried out by using the Heraeus Combustion Apparatus.

For nuclear magnetic resonance (NMR), the glycolized residue was dissolved in solvent  $\text{CDCl}_3$ ; trimethyl silane (TMS) was used as an internal standard and the spectrograph was recorded on a JEOL, FT-NMR (60 MHz).

The infrared spectrum was recorded using the KBr disc technique on a Perkin-Elmer IR Spectrophotometer (Buck Scientific Model 500).

## RESULTS AND DISCUSSION

Although PET does not create a direct hazard to the environment, its substantial proportion in the poly-

meric waste volume and its high inertness to the atmospheric and biologic agents causes it to be seen as a noxious material. Chemical recycling of PET has been made feasible due to the availability of a number of depolymerizing agents and a variety of low molecular weight products useful for recycling into raw materials for synthesis of saturated and unsaturated polyesters, coatings, additives, etc.

During the production of PET, the direct esterification or the transesterification reaction leads to BHET, which is then polycondensed to obtain PET. The polycondensation step is reversible and, in the presence of the excess of ethylene glycol, glycolysis of PET occurs to promote the reverse reaction to give BHET, which is supposed to be a true monomer of PET.

The present work attempts the use of glacial acetic acid, sodium sulfate, potassium sulfate, and lithium hydroxide as catalysts for depolymerization of PET.

Table I give the results on the effect of time of glycolysis on the yield of BHET in the presence of different catalysts. For all the catalysts, it was observed that the % yield of BHET increases with time up to 8 h and thereafter it decreases. Similarly, the

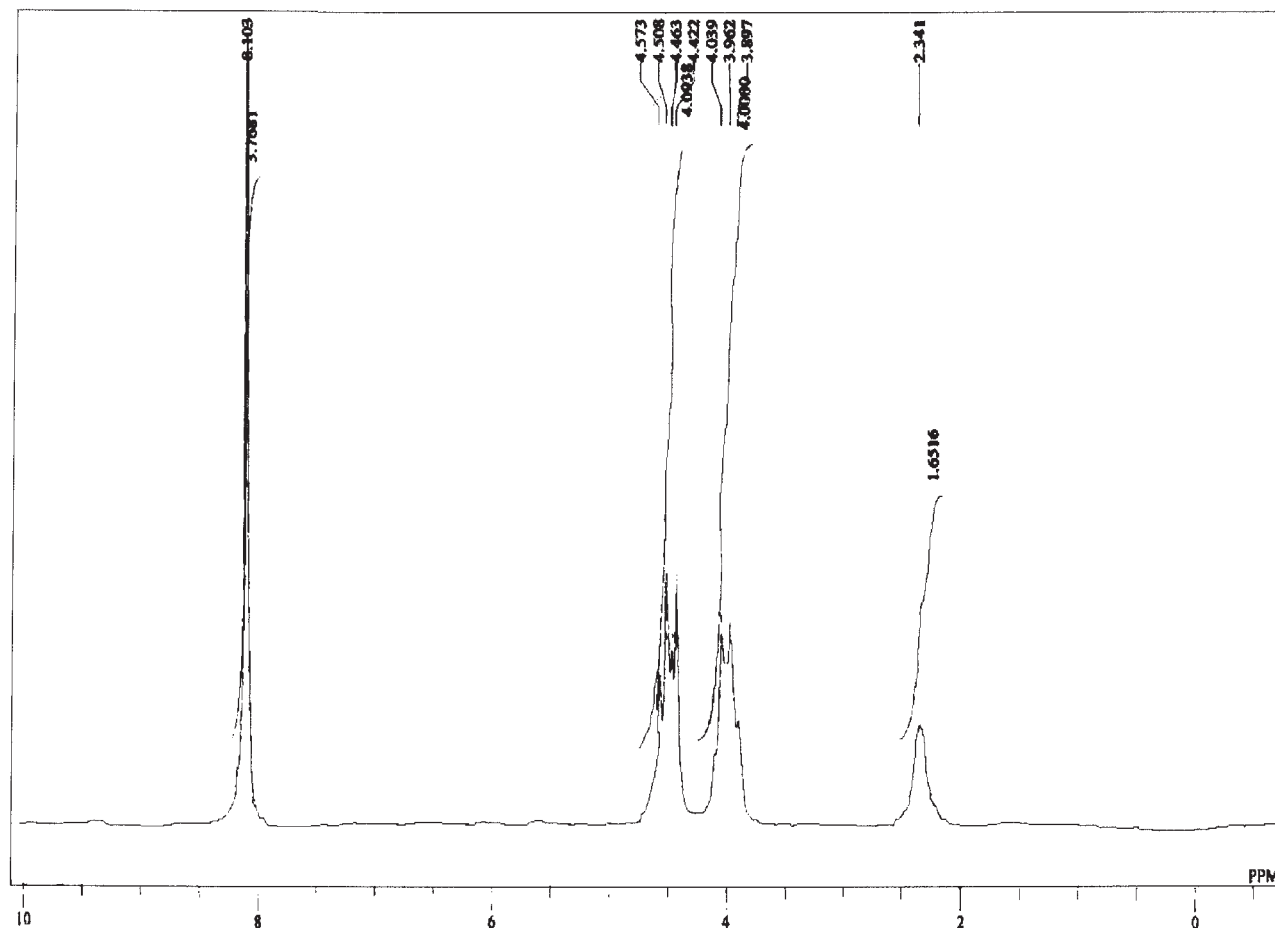


Figure 2 NMR Spectrum of BHET.

data in Table II show that 0.5% (w/w) was the optimum concentration of any catalyst to give the maximum BHET yield. With further increase in the amount of a catalyst, the yield of BHET decreased. Ethylene glycol used in the present study was in the proportion 1 : 6 with the PET waste fibers, i.e., in excess of that required for the depolymerization reaction.

Choi<sup>15</sup> reported that, in the presence of excess glycol, the oligomers produced at high conversion of methyl ester end groups are mostly dimers and the BHET concentration reaches a steady state. Baliga and Wang<sup>16</sup> made a similar observation. They found that, after a long time of reaction (up to and above 8 h), equilibrium is attained between the dimer and BHET.

The BHET yield varied between a small margin on optimization of the reaction time and the catalyst concentration. Thus, among the four catalysts used, the lower yield of BHET was obtained using acetic acid as a catalyst for depolymerization (62.42%) whereas the maximum was achieved using sodium sulfate catalyst (65.72%) with 0.5% (w/w) concentration and an 8 h reaction time.

In our earlier work, we had made a comparison of the efficiencies of different catalysts such as zinc

acetate, lead acetate, sodium carbonate, and sodium bicarbonate used for depolymerization of PET waste into BHET.<sup>13</sup> It was reported that the yield of BHET using the conventional catalyst zinc acetate was the highest viz., 67.63%. The yields obtained in the present work were a little lower than this value, although sodium sulfate as a catalyst gave a close value of 65.72% yield of BHET.

The purified BHET was characterized by elemental analysis and melting point. These results are given in Table III, which confirm that the product of depolymerization of PET was BHET.

The IR spectrograph of the purified monomer is shown in Figure 1. It can be clearly seen that the spectrograph contains a  $\text{-OH}$  band at 3448 and 1131  $\text{cm}^{-1}$ , a  $\text{C=O}$  stretching at 1715  $\text{cm}^{-1}$ , an alkyl  $\text{C-H}$  at 2878 and 2925  $\text{cm}^{-1}$ , and an aromatic  $\text{C-H}$  at 1455–1504  $\text{cm}^{-1}$ .

Figure 2 gives  $^1\text{H-NMR}$  for the same compound wherein it may be observed that the peak at  $\delta$  2.3 corresponds to  $\text{-OH}$  groups,  $\delta$  3.99 corresponds to aliphatic  $(\text{-CH}_2)_a$  proton,  $\delta$  4.51 to aliphatic  $(\text{-CH}_2)_b$  proton, and  $\delta$  8.12 to aromatic ring protons.

From these observations it was concluded that the purified monomer is BHET. Also, when the product

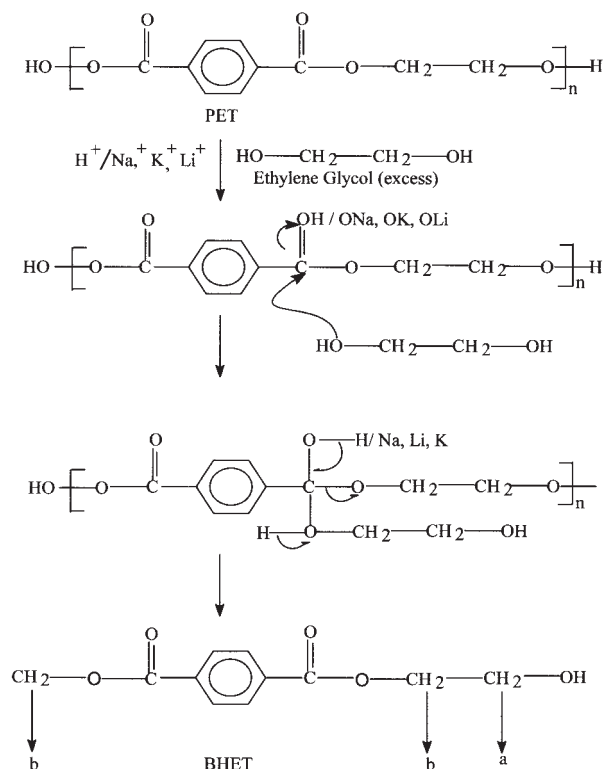


Figure 3 Mechanism of depolymerization of BHET.

was subjected to thin layer chromatographic analysis using the eluent ethyl acetate : hexane (7 : 3), a single spot was obtained, indicating the purity of the glycolized product, BHET.

Thus, the present work indicates that simple chemicals such as acetic acid as well as salts of lithium, sodium, and potassium are equally useful in depolymerizing the PET waste, although the BHET yields vary a little in their amounts. The conventional catalysts, namely zinc acetate and lead acetate, are not ecofriendly since their cations belong to the category of noncofriendly heavy metals. In comparison, the catalysts used in the present study are an organic acid and the salts of metals lithium, sodium, and potassium, which are not harmful to the environment, other than the fact that, in large quantities, these metal salts substantially add to the dissolved solid content of the effluent and acetic acid contributes to large BOD. It is worth mentioning here that we have also attempted to remove toxic heavy metals efficiently by making use of dye-loaded cellulosic materials as adsorbents, with nearly complete recovery.<sup>17-20</sup>

The depolymerization of PET can take place in acidic medium. The ester group present in a polyester

macromolecule gets protonated in the presence of glacial acetic acid as shown in Figure 3. This increases the polarity of the carbonyl group. In the glycolysis reaction, excess of ethylene glycol is used as a solvent. The nucleophile ethylene glycol attacks the protonated carbonyl group of polyester and causes cleavage of the polymeric chain to get the monomer, BHET, as shown.

When the salts of Li, Na, or K are used in the place of glacial acetic acid, they are ionized, forming a complex with the carbonyl group of ester in PET.<sup>21</sup> This complex facilitates the attack of ethylene glycol on PET, which in turn leads to the formation of BHET.

## CONCLUSIONS

The simple chemicals such as glacial acetic acid or salts of simple metal cations lithium, sodium, and potassium are found to be capable of depolymerizing PET fiber waste through glycolysis. Although the BHET yields are little less compared to the conventional catalysts such as zinc acetate, considering the environmental safety factors, the chemicals used in the present work stand better acceptance for the depolymerization reaction. Thus, glycolysis has been made possible with cheap, ecofriendly, and almost equally effective catalysts without the requirement of a pressure reaction.

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