

## Recycling of PET Waste Using 3-Amino-1-propanol by Conventional or Microwave Irradiation and Synthesis of Bis-oxazin There From

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**ABSTRACT:** There is a growing interest in recycling of post-consumer poly(ethylene terephthalate) (PET) waste for both environmental and economic reasons. PET in the form of disposable soft drink bottle waste was subjected to depolymerization via aminolysis using excess of 3-amino-1-propanol under soxhlet by conventional heating as well as microwave irradiation using catalyst sodium acetate or potassium sulfate. The product obtained was characterized after purification by using melting point, IR spectroscopy, nuclear magnetic resonance, and differential scanning calorimeter and was found to be bis-(3-hydroxy propyl) terephthalamide (BHPTA). The BHPTA thus obtained was subjected to cyclization reaction using thionyl chloride to obtain bis-oxazin under conditions of ambient temperature. Bis-oxazin has applications in polymer synthesis as a chain extender or a cross linking agent. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** PET bottle waste; recycling; Aminolysis; 3-amino-1-propanol; bis-oxazin

Received 2 March 2012; accepted 13 April 2012; published online

DOI: 10.1002/app.37900

### INTRODUCTION

Ever since the first industrial scale production of synthetic polymers took place in the 1940s, the production, consumption, and waste generation rate of the plastic solid waste has increased considerably. Its recycling has been a focus of many researchers in the past few decades. Such research is also driven by the changes in the regulatory issues concerned with the environmental protection.<sup>1</sup>

Poly(ethylene terephthalate) (PET) is one of the versatile engineering plastics showing excellent thermal and mechanical properties. It is a nontoxic, semi-crystalline, thermoplastic polyester with high strength and crystal clear transparency. Although its main application is in the apparel sector, large quantities are also consumed in the manufacture of X-ray films, food packaging, and especially of soft-drink bottles. The post-consumer PET product waste does not create a direct hazard; however, its substantial volume fraction in solid waste streams coupled with its high resistance to the atmospheric and biological degradation is the main threat to the environment.<sup>2</sup> As it is not appropriate to dispose off waste PET on land-fill sites, alternate methods of recycling, including physical and chemical ones, have been developed.

Chemical recycling appears to be the only alternate that is sustainable.<sup>3</sup> PET possesses ester groups, which can be cleaved by some reagents, such as water (hydrolysis),<sup>2–9</sup> alcohols (alcoholysis),<sup>8,9</sup> glycols (glycolysis),<sup>10–15</sup> and amines (aminolysis).<sup>16–24</sup> Great attention has been paid to chemical recycling of PET waste leading to recovery of the monomeric products that can be further used in the synthesis of chemicals or intermediates of interest.<sup>17,19</sup> The aminolysis of PET waste is one such approach with the advantage over other chemical recycling processes since the end products of aminolysis needs less separation stages to purify them.<sup>4</sup> Amines are organic bases and cause polyester depolymerization faster than alcohols.<sup>25</sup> Compared to other methods of depolymerization, the aminolysis is still a little explored method. The solvolytic activity of amines at boil, which cleave the ester bond in the PET chain, is connected with their basicity.

Zahn and Pfeifer<sup>21</sup> carried out aminolysis of PET with solutions of benzyl amine, ethylene diamine, hexamethylene diamine, piperidine, and aniline and obtained different reaction products as the diamides of terephthalic acid, which do not possess any potential for further chemical reactions. During aminolysis of PET with methylamine, the methyl terephthalamide is obtained, which is not enough reactive for its recycling into any useful

product through further reactions.<sup>22</sup> Earlier, in our laboratory, we have carried out aminolysis of PET waste using ethanol amine to get pure bis (2-hydroxy ethylene) terephthalamide<sup>16</sup> which has been utilized in synthesis of polyurethanes,<sup>26,27</sup> unsaturated polyesters,<sup>28</sup> epoxy hardners,<sup>26</sup> and nonionic polymeric surfactants.<sup>29</sup>

In addition to application of conventional heating, a growing interest has been shown in the last few years in the use of microwave irradiation in organic synthesis.<sup>30,31</sup> Our previous work on microwave assisted recycling of post consumer PET waste with ethanolamine and ethylene glycol gave comparable results to conventional heating with advantages of time saving.<sup>13,32</sup>

Bis-oxazolines and bis-oxazines have been used as chain extenders and crosslinkers in polymers<sup>33–35</sup> and are reported to be prepared from nitriles and amines using zinc-2-ethyl hexanoate as catalyst<sup>36</sup> or halo amides using strong base such as potassium fluoride on solid support.<sup>37</sup>

The present communication deals with the results on the use of 3-amino-1-propanol for the aminolytic depolymerization of PET bottle waste in the presence of simple chemicals such as sodium acetate or potassium sulfate as catalysts under conventional and microwave source of heating. The depolymerization product after purification was found to be bis-(3-hydroxy propyl) terephthalamide (BHPTA) as characterized by melting point, IR spectroscopy, nuclear magnetic resonance (NMR) and differential scanning calorimeter (DSC). It was further used for synthesis of 1,4-bis (5,6-dihydro-4H-1,3-oxazin-2-yl) benzene which is used as chain extender and crosslinker.

## EXPERIMENTAL

### Materials

Waste PET bottles were obtained from a local market. These bottles were cut into small pieces of approximate size 5 × 5 mm after separating from the non-PET components such as labels and caps.

### Chemicals

Sodium acetate, potassium sulfate, thionyl chloride, sodium bicarbonate, methylene chloride were of Laboratory Reagent grade and 3-amino-1-propanol was of Guaranteed Reagent grade procured from SD fine chemicals, India.

### Cleaning of PET Waste Material

PET bottle pieces were boiled with a solution containing 2 g/L of nonionic detergent for 1 h to remove any dirt present. It was then washed thoroughly with water and dried in an oven at 80°C.

### Aminolysis of PET Waste Material

**Aminolysis by Conventional Method.** 3-amino-1-propanol was used for the aminolysis of PET waste material in the molar ratio 1:5 (PET: 3-amino-1-propanol) under reflux in the presence of different catalysts such as potassium sulfate and sodium acetate in concentration ranging from 0.3 to 1% by weight of polymer for time periods varying up to 6 h. At the end of the reaction, distilled water was added in excess to the reaction mixture with vigorous agitation to precipitate out the product. The filtrate

contained mainly unreacted 3-amino-1-propanol and little quantities of a few water soluble PET depolymerization products. The precipitate obtained was dissolved in distilled water by boiling for about 30 min. White crystalline powder of BHPTA was obtained by first concentrating the filtrate by boiling and then chilling it. It was further purified by recrystallization in water, dried in an oven at 80°C and weighed for estimating the yield. Different techniques of analysis used for its characterization were thin layer chromatography (TLC), FTIR, NMR and DSC.

### Aminolysis by Nonconventional (Microwave Irradiation)

**Method.** As a nonconventional method, a 700W Electrolux (17 L) domestic microwave oven was used for the aminolysis reaction. It was modified to allow fitting of a condenser as described in the previous communication.<sup>13</sup> The PET waste was treated with the amine under reflux in the presence of catalysts for time period up to 9 min using microwave oven. The catalyst and work up process was similar to that as given in conventional method.

### Synthesis of Bis-Oxazin from BHPTA

To a solution of BHPTA (2 g) in 20 mL of methylene chloride, thionyl chloride (2.5 mL) was added drop wise at 0°C. After 16 h of stirring at room temperature (30°C), the product was filtered, washed with water and 5% aqueous solution of NaHCO<sub>3</sub> was added under vigorous stirring. The precipitate was repeatedly washed with water, recrystallized from water and dried in a vacuum to give white crystalline powder which was characterized by TLC, FTIR, NMR, and DSC and found to be 1, 4-bis (5, 6-dihydro-4H-1, 3-oxazin-2-yl) benzene (PBOXA). Yield: 56%.

### Characterization of Products

Melting points of the products, BHPTA and PBOXA were determined in an open capillary. For NMR, the products were dissolved in solvent d<sup>6</sup>-DMSO. Tetramethyl silane was used as an internal standard and the spectrogram was recorded on BRUKER DRX (300 MHz). Infrared spectrum was recorded on Shimadzu FTIR-470 spectrophotometer. The thermal characteristics were determined by DSC (Shimadzu 60). All runs were carried out with sample consisting of ≈2–6 mg of compound. They were carefully put into an aluminum pan while another empty aluminum pan was used as a reference. Scans were performed at the heating rate of 10°C/min from 30 to 300°C in nitrogen atmosphere. The aminolytic product obtained was subjected to TLC analysis with ethanol: chloroform (2:8) mixture as an eluent.

## RESULTS AND DISCUSSION

### Aminolytic Depolymerization Process

The amine, 3-amino-1-propanol, was studied for the optimization of aminolysis parameters to get the maximum yield of the product. These results are given in Tables I–III. Initially, the reaction mixture is biphasic, a solid phase (PET) and a liquid phase (amine), which becomes single phase reaction mass after some time under reflux. The said amine has two nucleophilic centres, wherein nitrogen is less electronegative than oxygen.

**Table I.** Effect of Amine on BHPTA Yield

PET: amine (molar ratio)	BHPTA yield (%)			
	Conventional heating		Microwave irradiation	
	Sodium acetate	Potassium sulphate	Sodium acetate	Potassium sulfate
1:3	58	50	65	62
1:5	80	74	82	79
1:7	69	68	74	69
1.9	71	68	72	70

Time was selected on the basis of optimum yield as indicated in Table III. Catalyst concentration: 0.5% (w/w).

The amine group of 3-amino-1-propanol attacks the ester linkage of PET.

The results on optimization of the reaction parameters, viz., PET: amine ratio (Table I), catalyst concentration (Table II) and time of reaction under conventional and nonconventional microwave heating methods (Table III) indicate that the maximum yield of the purified product was obtained with PET: amine ratio as 1:5 and catalyst concentration for both sodium acetate and potassium sulfate as 0.5% (w/w).

The time required for completion of the aminolysis reaction was 5 h for conventional heating with 80% yield of purified BHPTA for sodium acetate and 74% for potassium sulfate catalysts, whereas, time required for nonconventional (microwave irradiation) method was only 7 min with yields comparable to the conventional method. Thus, a drastic decrease in the time of reaction from 5 h to 7 min was achieved on using microwave irradiation as a heating source for refluxing the reaction mixture.

Sodium acetate gave better yields than potassium sulfate which agrees with literature reported for aminolysis of PET.<sup>16</sup> Mechanism shows that when the salts of Na or K are used they are ionized forming complex with carbonyl group of ester to facilitate the attack of an amine and subsequently losing the proton

**Table II.** Effect of Catalyst Concentration on BHPTA Yield

Catalyst concentration (w/w)	BHPTA yield (%)			
	Conventional heating		Microwave irradiation	
	Sodium acetate	Potassium sulfate	Sodium acetate	Potassium sulfate
0.3	70	66	78	73
0.5	80	74	82	79
0.7	76	72	79	77
1.0	75	72	76	70

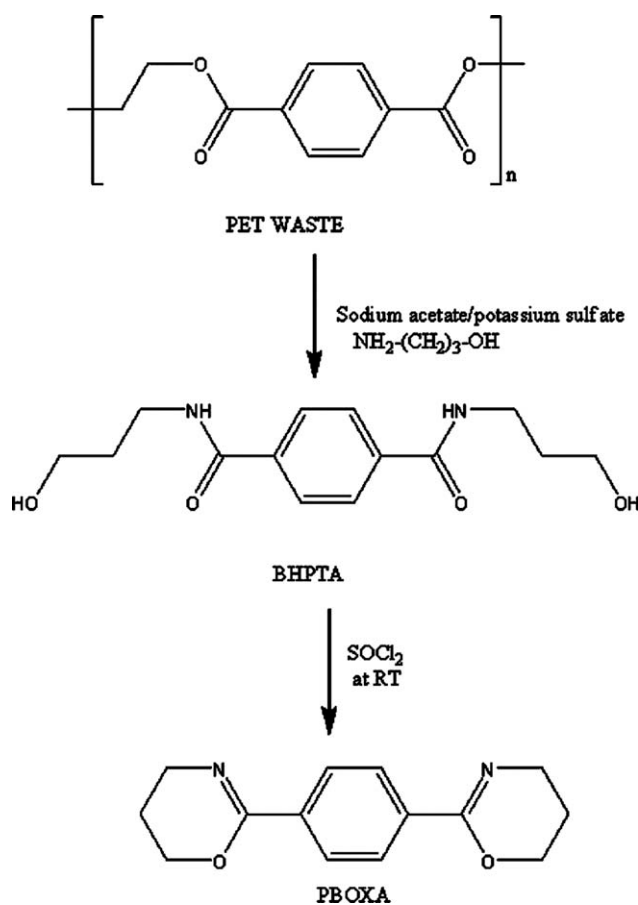
Time was selected on the basis of optimum yield as indicated in Table III. PET: amine: 1:5

**Table III.** Effect of Time on BHPTA Yield

Time	BHPTA yield (%)			
	Conventional heating		Microwave irradiation	
	Sodium acetate	Potassium sulfate	Sodium acetate	Potassium sulfate
1 h	45	37	-	-
2 h	58	49	-	-
3 h	69	55	-	-
4 h	76	69	-	-
5 h	80	74	-	-
6 h	78	73	-	-
1 min	-	-	45	38
3 min	-	-	62	54
5 min	-	-	76	68
7 min	-	-	82	79
9 min	-	-	78	76

Catalyst concentration: 0.5% (w/w).  
PET: amine: 1:5.

to give corresponding amide.<sup>16</sup> According to conjugate acid-base theory, acetate ion is stronger base than sulfate ion. Therefore, the former may give deprotonation step faster than latter



**Figure 1.** Synthesis of PBOXA from BHPTA through PET waste.

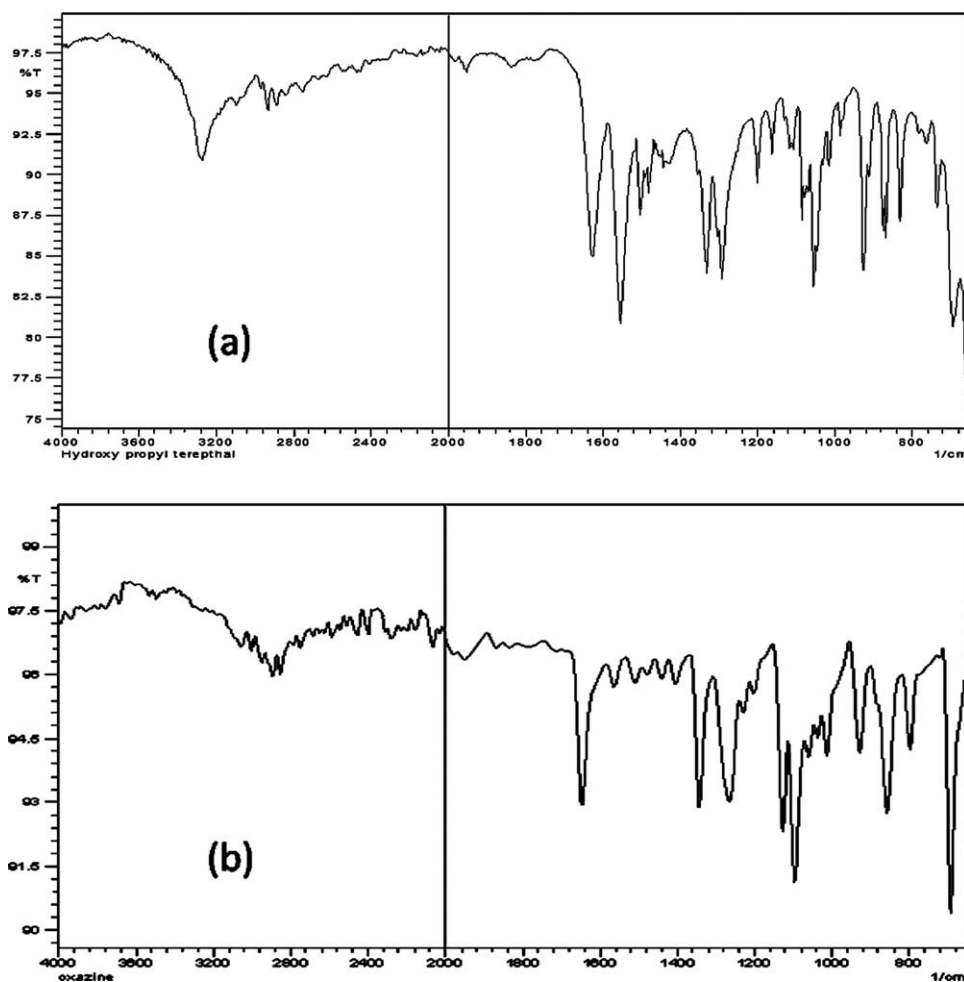


Figure 2. FTIR Spectra of (a) BHPTA and (b) PBOXA.

one. However, conclusive mechanism of the catalytic activity can only be determined by studying chemical kinetics, which is not the scope of present communication.

Microwave effects result from material-wave interactions and, due to the dipolar polarization phenomenon, the greater the polarity of a molecule (such as the solvent) the more pronounced will be the microwave effect as far as the rise in temperature is considered. In terms of reactivity and kinetics, the specific effect has therefore to be considered in relation to the reaction mechanism, and particularly with regard as to how the polarity of the system is altered during the progress of the reaction.<sup>38</sup> Similar mechanism is likely to apply in the present case of domestic microwave oven, wherein the polar solvent is amine instead of water. Conclusive mechanism can however be determined only if studies are conducted with microwave frequency changes, which has not been attempted.

#### Spectroscopic and Thermal Analysis

Figure 1 gives the reaction scheme for the aminolytic depolymerization of PET bottle waste to BHPTA followed by synthesis of 1, 4-bis (5, 6-dihydro-4H-1, 3-oxazin-2-yl) benzene (PBOXA). The BHPTA was first characterized and then subjected to the synthesis of PBOXA.

The FTIR spectrogram for the BHPTA indicates the peaks at 1054 and 3289  $\text{cm}^{-1}$  due to the presence of primary alcohol and the peaks at 1330 and 1553  $\text{cm}^{-1}$  due to secondary amide (Figure 2). Figure 3 shows  $^1\text{H}$  NMR for the BHPTA wherein it may be observed that the peak at  $\delta$  8.57 corresponds to  $-\text{NHCO}$  groups,  $\delta$  3.38 corresponds to aliphatic  $\text{CH}_2$  proton attached to  $-\text{NH}$  group,  $\delta$  3.48 corresponds to  $\text{CH}_2$  proton attached to  $-\text{OH}$  group,  $\delta$  1.65 corresponds to middle  $-\text{CH}_2$  group,  $\delta$  7.98 corresponds to aromatic ring protons and  $\delta$  4.50 corresponds to  $-\text{OH}$  group. Figure 4 shows DSC scan of BHPTA, which indicates that the range of melting point of the compound is 206–210 $^\circ\text{C}$ ; which agrees with melting point of BHPTA reported by Thinius et al.<sup>39</sup>

In the FTIR spectrogram for PBOXA, the peak at 1646  $\text{cm}^{-1}$  indicates the presence of  $-\text{C}=\text{N}$  stretching (Figure 2) and disappearance of peaks of alcoholic groups of BHPTA. The  $^1\text{H}$  NMR for the PBOXA (Figure 3) shows the peak of  $\delta$  1.9 corresponding to middle  $-\text{CH}_2$  group protons,  $\delta$  3.52 corresponding to  $-\text{CH}_2$  group attached to oxygen,  $\delta$  4.3 corresponds to other  $-\text{CH}_2$  group protons and  $\delta$  7.88 corresponding to aromatic ring protons. The values of  $\delta$  8.57 and  $\delta$  4.50, which correspond to  $-\text{NHCO}$  and  $-\text{OH}$  group protons respectively in BHPTA were not observed in PBOXA due to cyclization and dehydration.

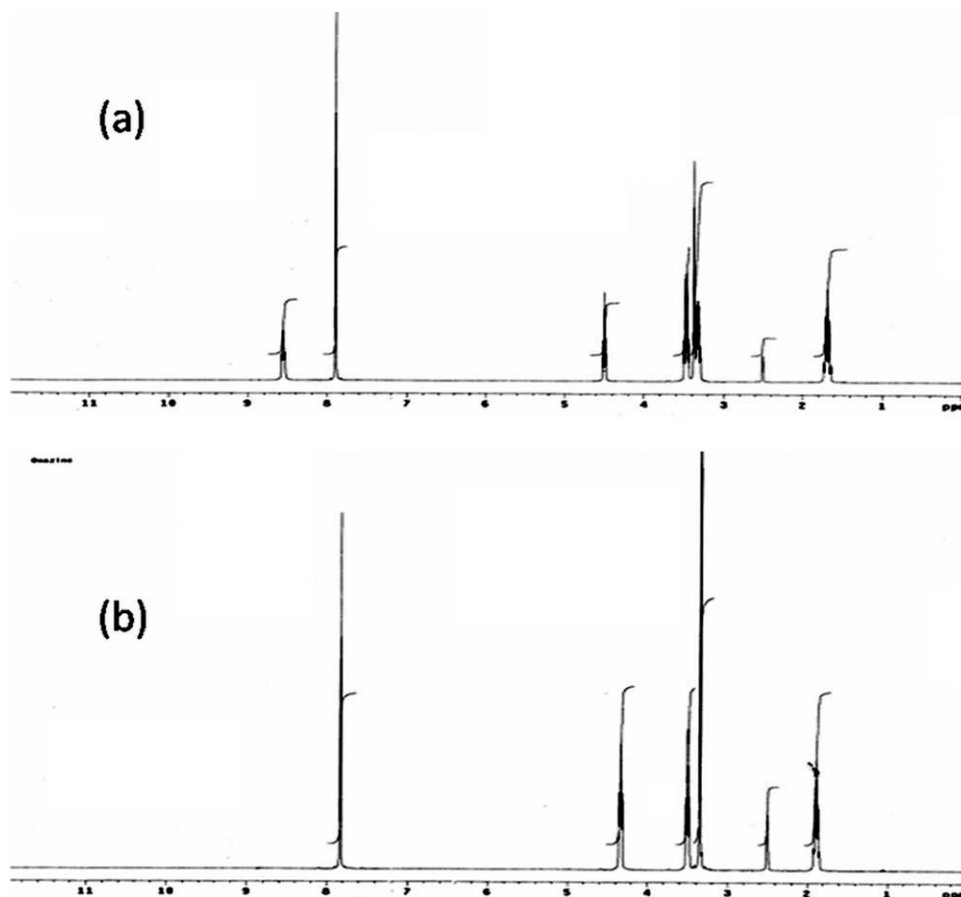


Figure 3. NMR Spectra of (a) BHPTA and (b) PBOXA.

Figure 4 shows DSC scan of PBOXA, which indicates that the melting point of the compound is 219–223°C. This agrees with melting point of PBOXA reported by Kubelbaeck et al.<sup>36</sup>

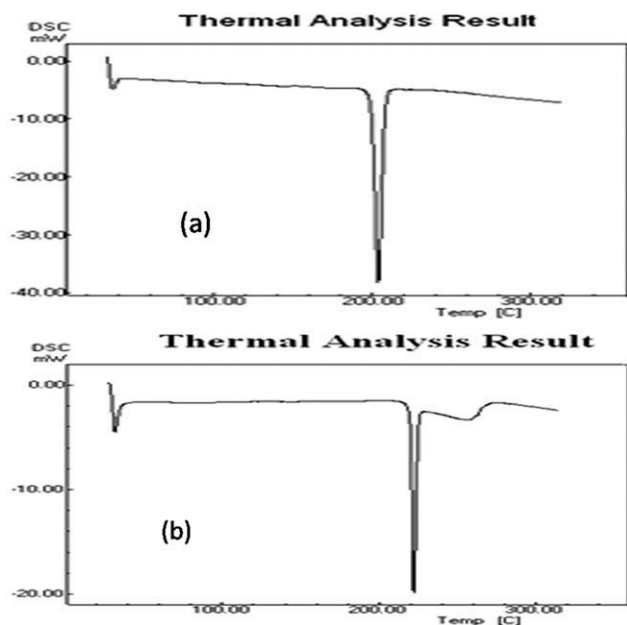


Figure 4. DSC scans of (a) BHPTA and (b) PBOXA.

Literature reports the aminolysis of PET using alkyl amines<sup>21,22</sup> to get corresponding diamides of terephthalic acid, which do not possess any potential for further chemical reaction. Alkanol amines such as ethanol amine, diethanol amine, 2-amino-2-methyl-1-propanol and 1-amino-2-propanol have been reported for aminolysis of PET.<sup>16,24,40</sup> With diethanol amine, a mixture of amide and ester with the formation of substantial amounts of piperazine and terephthalic acid as side products were obtained; while 2-amino-2-methyl-1-propanol gave after 6 h, a low yield (59%) of corresponding diamide (bis(1-hydroxy-2-methylpropan-2-yl)terephthalamide) due to the steric hindrance. Ethanol amine has been reported to give close to 83% of pure bis (2-hydroxy ethylene) terephthalamide from PET bottle waste in presence of sodium acetate catalyst in 8 h with 1:8 PET: amine ratio while 1-amino-2-propanol gave 82% of pure bis (2-hydroxy propyl) terephthalamide in 5 h with 1:5 PET: amine ratio. These results are comparable to those reported in the present study using 3-amino-1-propanol. When compared to ethanol amine, the 3-amino-1-propanol has an extra methylene group, which can enhance electron density on nitrogen and therefore can increase the reaction rate.<sup>23</sup>

Further, the cyclization reaction of BHPTA to get PBOXA as a useful product was successful at ambient temperature using thionyl chloride as catalyst. Literature reports the synthesis of PBOXA from terephthalonitrile obtained using 3-amino-1-



propanol in the presence of a heavy metal catalyst such as zinc-2-ethyl hexanoate at high temperature 140–150°C.<sup>36</sup> 3-amino-1-propanol gave pure bis-oxazin which is a less strained six-membered ring with high melting point in the range of 219–223°C. Bis-oxazoline obtained from 1-amino-2-propanol is a more strained five-membered ring with low melting point in the range of 85–89°C and with a chiral centre that increases the chances of presence of different isomers simultaneously. BHPTA can undergo further reactions with its free hydroxyl groups and can be converted into polyurethanes by reacting with different di-isocyanates.

## CONCLUSION

The aminolysis of PET bottle waste using 3-amino-1-propanol under atmospheric pressure and in the presence of sodium acetate or potassium sulfate as catalysts gave good yield of the pure product BHPTA under both conventional and nonconventional microwave heating methods. Heating under microwave reduced the time of depolymerization from 5 h to 7 min affording great saving in time and energy for the reaction. BHPTA was converted into PBOXA by cyclization, which is a useful product in polymer chemistry as chain extender and crosslinker. BHPTA has the potential of recycling it into useful products through various chemical reactions of its primary alcoholic groups.

## ACKNOWLEDGMENTS

Authors are grateful to Council of Scientific and Industrial Research, New Delhi, Govt. of India for funding this project and to University Grants Commission, New Delhi for fellowship to RVS.

## REFERENCES

- Al-Salem, S.; Lettieri, P.; Baeyens, J. *Waste Manage.* **2009**, *29*, 2625.
- Karayannidis, G. P.; Achilias, D. S. *Macromol. Mater. Eng.* **2007**, *292*, 128.
- Karayannidis, G. P.; Achilias, D. S. *Water Air Soil Poll: Focus* **2004**, *4*, 385.
- Paszun, D.; Spychaj, T. *Ind. Eng. Chem. Res.* **1997**, *36*, 1373.
- Scheirs, J. *Recycling of PET in Polymer Recycling: Science, Technology and Applications*; Wiley: Chichester UK, **1998**.
- Karayannidis, G. P.; Chatziavgoustis, G. P.; Achilias, D. S. *Adv. Polym. Tech.* **2002**, *21*, 250.
- Sato, O.; Mine, E.; Osada, M.; Hiyoshi, N.; Yamaguchi, A.; Bando, K.; Masuda, Y.; Shirai, M. *Chem. Lett.* **2009**, *38*, 268.
- Kosmidis, V. A.; Achilias, D. S.; Karayannidis, G. P. *Macromol. Mater. Eng.* **2001**, *286*, 640.
- Siddiqui, N. M.; Achilias, D. S.; Redhwi, H. H.; Bikaris, N. D.; Kastogiannis, G. A.; Karayannidis, G. P. *Macromol. Mater. Eng.* **2010**, *295*, 575.
- Shukla, S. R.; Kulkarni, K. S. *J. Appl. Polym. Sci.* **2002**, *85*, 1765.
- Shukla, S. R.; Harad, A. M. *J. Appl. Polym. Sci.* **2005**, *97*, 513.
- Shukla, S. R.; Palekar, V. P.; Pingale, N. D. *J. Appl. Polym. Sci.* **2008**, *110*, 501.
- Shukla, S. R.; Pingale, N. D. *Eur. Polym. J.* **2008**, *44*, 4151.
- Shukla, S. R.; Pingale, N. D.; Palekar, V. P. *J. Appl. Polym. Sci.* **2010**, *115*, 249.
- Achilias, D. S.; Siddiqui, N. M.; Redhwi, H. H.; Bikaris, N. D.; Nikolaidis, K. A.; Karayannidis, G. P. *J. Appl. Polym. Sci.* **2010**, *118*, 3066.
- Shukla, S. R.; Harad, A. M. *Polym. Degrad. Stab.* **2006**, *91*, 1850.
- Palekar, V. P.; Damle, A. J.; Shukla, S. R. *Eur. J. Med. Chem.* **2009**, *44*, 5112.
- Soni, R. K.; Dutt, K.; Jain, A.; Soam, S.; Singh, S. *J. Appl. Polym. Sci.* **2009**, *113*, 1090.
- Palekar, V. P.; Pingale, N. D.; Shukla, S. R. *Color. Tech.* **2010**, *126*, 55.
- Achilias, D. S.; Tsnitzou, P. G.; Nikolaidis, K. A.; Bikaris, N. D.; Karayannidis, G. P. *Polym. Int.* **2011**, *60*, 500.
- Zahn, H.; Pfeifer, H. *Polymer* **1963**, *4*, 429.
- Awoodi, Y.; Johnsson, A.; Peters, R. *J. Appl. Polym. Sci.* **1987**, *33*, 2503.
- Popoola, V. A. *J. Appl. Polym. Sci.* **1988**, *36*, 1677.
- Acar, I.; Orbay, M. *Polym. Eng. Sci.* **2011**, *51*, 746.
- Spychaj, T.; Fabrycy, E.; Spychaj, S.; Kacperski, M. *J. Mater. Cycles. Waste. Manag.* **2001**, *3*, 24.
- Spychaj, T.; Pilawka, R.; Spychaj, S.; Bartkowiak, A. *Ind. Eng. Chem. Res.* **2004**, *43*, 862.
- Shamsi, R.; Abdouss, M.; Sadeghi, G. M. M.; Taromi, F. A. *Polym. Int.* **2009**, *58*, 22.
- Elsaeed, S. M. and Farag, R. K. *J. Appl. Polym. Sci.* **2009**, *112*, 3327.
- Elsaeed, S. M. *Int. J. Polym. Mater.* **2008**, *57*, 615.
- Hayes, B. *Microwave Synthesis: Chemistry at the Speed of Light*; CEM Publishing: North Carolina: Weinheim, **2002**.
- Loupy, A. *Microwaves in Organic Synthesis*; Wiley VCH: Weinheim, **2006**.
- Shukla, S. R.; Pingale, N. D. *Eur. Polym. J.* **2009**, *45*, 2695.
- Culbertson, B.; Tiba, O. *U.S. Pat. 4,806,267*, February 21, **1989**.
- Culbertson, B. M. *Prog. Polym. Sci.* **2002**, *27*, 579.
- Van Benthem, R. A. T. M.; Loontjens, J. A.; Hendriks, P. H. M.; Plum, B. J. M. *U.S. Pat. 0,091,203*, **2002**.
- Kubelbaeck, T.; Neumann, M.; Omels, M. *U.S. Pat. 076,186*, July 11, **2010**.
- Benicewicz, B.; Mitchell, M.; Mex, N. *U.S. Pat. 5,382,665*, March 25, **1995**.
- Laurence, P.; Andre, L.; Michael, D. *Tetrahedron* **2003**, *59*, 2185.
- Thinius, K.; Broy, W.; Wingerter, K. *Plaste and Kautschuk.* **1959**, *6*, 372.
- Shah, R. V.; Shukla, S. R. *J. Appl. Polym. Sci.* **2012**, DOI: 10.1002/app.36649.