

Effective Aminolytic Depolymerization of Poly(ethylene terephthalate) Waste and Synthesis of Bisoxazoline Therefrom

Rikhil V. Shah, Sanjeev R. Shukla

Department of Fibres and Textile Processing Technology, Institute of Chemical Technology, Mumbai 400019, Maharashtra, India

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ABSTRACT: Aminolytic depolymerization of postconsumer poly(ethylene terephthalate) (PET) bottle waste with 2-amino-2-methyl-1-propanol and 1-amino-2-propanol under atmospheric condition was investigated in the presence of catalysts zinc acetate or sodium acetate. The virtual products obtained in pure form were, respectively, bis(1-hydroxy-2-methylpropan-2-yl)terephthalamide and bis(2-hydroxypropyl)terephthalamide. The latter was taken for further studies because of its higher yield and subjected to cyclization using thionyl chloride under low-temperature conditions to get 1,4-bis(5-methyl-4,5-dihydrooxazol-2-yl)benzene, which is

used as chain extender in polyester and nylon compositions and as a crosslinking agent in powder paint compositions. The products obtained from depolymerization were characterized by TLC, melting point, IR spectroscopy, ¹H-NMR, ¹³C-NMR, and DSC. We have shown that it is possible to synthesize new utility products by recycling of PET waste. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: PET bottle waste; recycling; 1-amino-2-propanol; 2-amino-2-methyl-1-propanol; bis-oxazoline

INTRODUCTION

Waste is an unavoidable by-product of any natural process on earth, but nature reuses all of its by-products. However, human interventions have disturbed this balance, by producing toxic and nonbiodegradable wastes. The quantity of solid waste is ever increasing due to increase in population, developmental activities, changes in life style, and socioeconomic conditions. Plastics waste is a significant portion of the total solid waste, and therefore it deserves special attention.

Poly(ethylene terephthalate) (PET) is formed through polycondensation of terephthalic acid and ethylene glycol, which are both derived from oil feedstock.¹ Primarily developed as a textile filament, its high durability, crystal clear appearance, and nontoxicity have led to rapid exploitation as lightweight, tough, and unbreakable bottles. The growing bottle industry has been an active contributor to the increasing quantity of solid waste. Although PET does not create a direct hazard to the environment,

its substantial fraction by volume in the waste stream and its high resistance to the atmospheric and biological agents, makes it to be seen as a main threat to the environment.²

Chemical recycling is the only sustainable process leading to the formation of the breakdown materials from which the polymer itself or some other useful chemicals may be derived.³ PET possesses ester groups that can be cleaved by some reagents, such as water (hydrolysis),^{2–8} alcohols (alcoholysis),^{7,8} glycols (glycolysis),^{9–14} and amines (aminolysis).^{15–23} Aminolysis has advantages over other chemical recycling processes as it gives very high yields of purified products with less severe reaction conditions. In our laboratory, the product (terephthalic dihydrazide) obtained from aminolytic depolymerization of PET using hydrazine hydrate has been converted into various useful chemicals such as textile dyes and some of them were found to possess even antibacterial activity.^{16,18}

Microwave-assisted organic synthesis has become an important tool to chemists for rapid organic synthesis. A huge number of research articles have appeared over the last decades on the application of microwave technology in organic synthesis.^{24,25} Some of the major advantages include decrease in reaction time, improved conversions, clean product formation, and wide scope for the development of new reaction conditions. In our previous work on microwave-assisted recycling of postconsumer PET

Correspondence to: S. R. Shukla (sanjeevrshukla@rediffmail.com).

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waste with amine and glycol gave comparable results to conventional heating with advantages of time saving.^{12,26}

Bis-oxazolines and bis-oxazines have been reported to be prepared from nitriles and amines using highly sulfonated carbon acids as catalyst^{27,28} or from halo amides using strong base such as potassium fluoride on solid support²⁹ and have been used as chain extenders in polyester and nylon compositions and crosslinking agents in powder paint compositions.^{30–33}

Present communication reports the results on aminolytic depolymerization of PET bottle waste using 2-amino-2-methyl-1-propanol and 1-amino-2-propanol, in the presence of zinc acetate or sodium acetate as catalysts under conventional and microwave source of heating. The depolymerization products after purification were found to be bis(1-hydroxy-2-methylpropan-2-yl)terephthalamide (BHMPPTA) and bis(2-hydroxypropyl)terephthalamide (BHIPTA), respectively. BHIPTA was subjected to cyclization at ambient temperature condition to get 1,4-bis(5-methyl-4,5-dihydrooxazol-2-yl)benzene (PBIOXA). The products were characterized by melting point, IR spectroscopy, ¹H-NMR, ¹³C-NMR, and DSC.

EXPERIMENTAL

Materials

Waste PET bottles were obtained from a local market and cut into small pieces of approximate size 5 × 5 mm² after separating from the non-PET components such as labels and caps. These were boiled in 2 g/L of nonionic detergent solution for 1 h to remove any dirt present, washed thoroughly with water, and then dried in an oven at 80°C.

Chemicals

Sodium acetate, zinc acetate, thionyl chloride, sodium bicarbonate, and methylene chloride were of laboratory reagent (LR) grade, whereas 2-amino-2-methyl-1-propanol and 1-amino-2-propanol were of guaranteed reagent (GR) grade, all procured from SD Fine Chemicals, India.

Aminolysis of PET waste material

Aminolysis using 2-amino-2-methyl-1-propanol

PET bottle waste flakes were refluxed under conventional heating with 2-amino-2-methyl-1-propanol in the molar ratio 1 : 5 in the presence of catalysts zinc acetate or sodium acetate (0.5% w/w) for time periods varying up to 6 h. At the end of the reaction, diethyl ether was added in excess to the reaction mixture with vigorous agitation to dissolve the

excess amine present in the reaction mass. It was decanted and then a little quantity of methanol was added to the sticky white reaction mass to get free flowing solid of BHMPPTA. It was further purified by recrystallization in water, dried in an oven at 80°C, and weighed for estimating the yield. It was then subjected to characterization.

Aminolysis using 1-amino-2-propanol

By conventional heating. PET bottle waste flakes were refluxed with 1-amino-2-propanol with the molar ratio 1 : 5 in the presence of catalysts zinc acetate or sodium acetate (0.3–1% 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. It was filtered and the filtrate was cooled to 10–15°C overnight to precipitate out the remaining product. The precipitates were dissolved in distilled water by boiling for about 30 min and white crystalline powder of BHIPTA 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. It was then subjected to characterization.

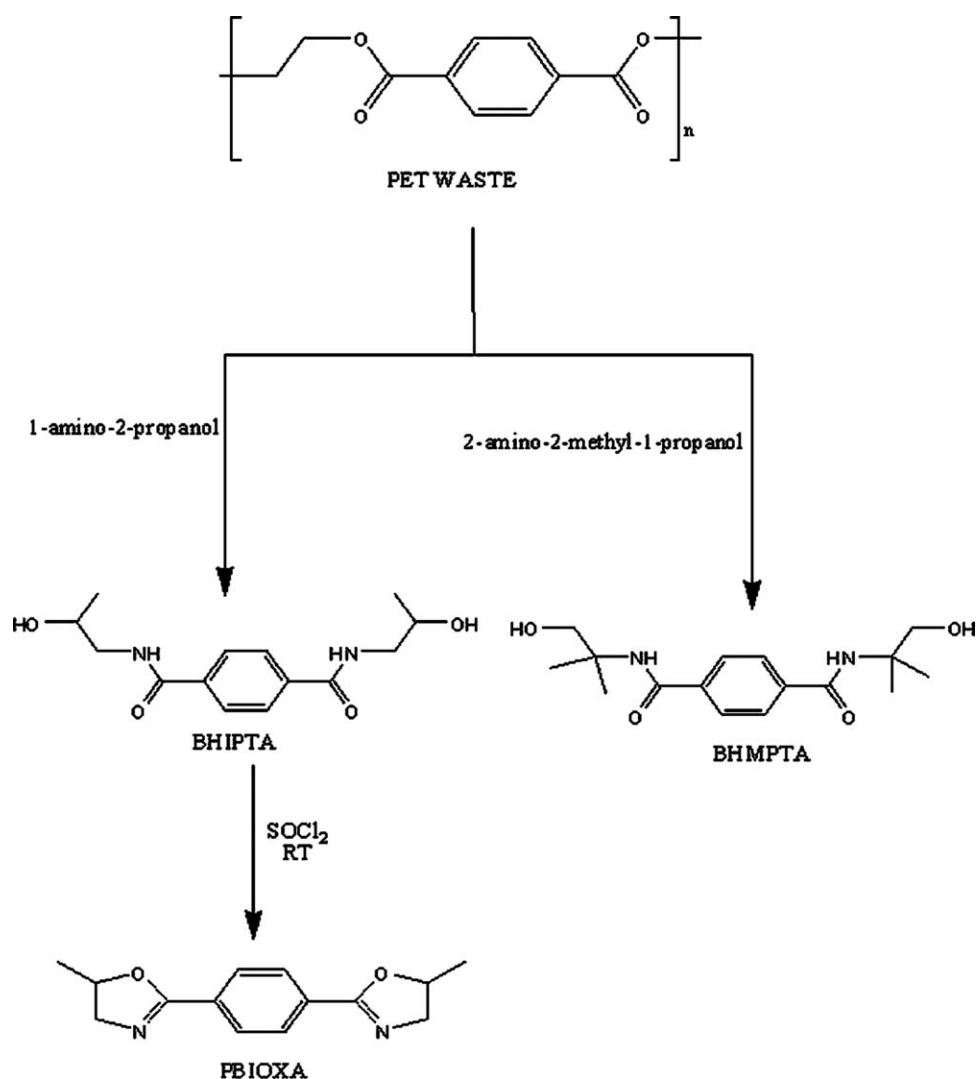
By microwave irradiation. As a nonconventional heating source, a 700W Electrolux (17 L) domestic microwave oven was used. It was modified to allow fitting of a condenser as described in the previous communication.¹² The PET waste was treated with the 1-amino-2-propanol under reflux in exactly the same manner as that using the conventional heating process except that the time period was varied up to 9 min.

Synthesis of bis-oxazoline from BHIPTA

To a solution of BHIPTA (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 NaHCO₃ was added under vigorous stirring. The precipitate was repeatedly washed with water, recrystallized from water, and dried in vacuum to get white crystalline powder, which was characterized by thin layer chromatography (TLC), FTIR, ¹H-NMR, ¹³C-NMR, and DSC and found to be PBIOXA with 72% yield.

Characterization of products

All the three products, BHMPPTA, BHIPTA, and PBIOXA were characterized. Melting points of the products were determined in an open capillary. For NMR, the products were dissolved in solvent *d*₆-DMSO. Tetramethyl silane (TMS) was used as an



Scheme 1 Aminolysis of PET waste and preparation of PBIOXA.

internal standard and the spectrogram was recorded on BRUKER DRX (300 MHz). Infrared spectra were 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 $10^\circ\text{C}/\text{min}$ from 30 to 300°C in nitrogen atmosphere. The aminolytic products obtained were subjected to TLC analysis with ethanol : chloroform (1 : 9) mixture as an eluent.

RESULTS AND DISCUSSION

Zahn and Pfeifer²⁰ 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.²¹

Scheme 1 represents aminolytic depolymerization of PET waste using propanol amines to get respective terphthalamides, which have free hydroxyl groups and can be converted into different useful products. We have studied the reaction with BHIPTA, the aminolysis product of PET using 1-amino-2-propanol, to obtain PBIOXA, which has been useful in polymer and paint industry as chain extender and crosslinking agent.

Depolymerization of PET waste using 2-amino-2-methyl-1-propanol

Table I gives the optimization of depolymerization time in the presence of zinc acetate or sodium

TABLE I
Effect of Time on Aminolysis Product of PET

| Time (h) | Yield (%) | | | |
|----------|--------------------|----------------|-----------------------------|----------------|
| | 1-Amino-2-propanol | | 2-Amino-2-methyl-1-propanol | |
| | Zinc acetate | Sodium acetate | Zinc acetate | Sodium acetate |
| 1 | 52 | 39 | 34 | 18 |
| 2 | 75 | 52 | 42 | 26 |
| 3 | 84 | 69 | 60 | 42 |
| 4 | 83 | 76 | 64 | 55 |
| 5 | 85 | 82 | 67 | 58 |
| 6 | 85 | 81 | 63 | 59 |

Heating: conventional; catalyst concentration: 0.5% (w/w); PET : amine = 1 : 5.

acetate as catalyst. Four hours of depolymerization with zinc acetate as catalyst gave 64% yield of BHMPTA, whereas with sodium acetate, 5 h were needed to get 58% yield. 2-Amino-2-methyl-1-propanol has two methyl groups attached to carbon atom adjacent to nitrogen, which may cause steric hindrance to its attack on carbonyl carbon atom of PET.²²

Analysis of BHMPTA

The FTIR spectrogram for the BHMPTA indicates the peaks at 1053 and 3333 cm^{-1} due to the presence of primary alcohol and the peaks at 1319 and 1542 cm^{-1} due to the secondary amide (Fig. 1). The $^1\text{H-NMR}$ spectrum (Fig. 2) gave the peak at δ 7.7 corresponding to $-\text{NHCO}$ groups, at δ 3.5 corresponding to aliphatic CH_2 proton, at δ 1.3 corresponding to $-\text{CH}_3$ protons, at δ 7.9 corresponding to aromatic ring protons and at δ 4.9 corresponding to $-\text{OH}$ groups. $^{13}\text{C-NMR}$ spectrum (Fig. 3) of BHMPTA shows peak at δ 165.8 due to carbonyl carbon attached to aromatic ring and the peaks at δ 137.5 and 127.1 corresponding to aromatic carbons. The peak at δ 67.2 relates to aliphatic carbon attached to the $-\text{OH}$ group, peak at δ 55.1 is due to carbon attached to amide group and peak at δ 23.6 is due to $-\text{CH}_3$ protons. BHMPTA melts at 230–234°C. The DSC scan also shows reasonably sharp endothermic peak at 236°C.

Depolymerization of PET waste using 1-amino-2-propanol

By conventional method

The amine, 1-amino-2-propanol, was studied for the optimization of aminolysis parameters to get the maximum yield of the product. These results are given in Tables I and II. 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.

Table I gives the effect of time of reaction on the product yield. The depolymerization with zinc acetate as catalyst, time of 3 h gave 84% yield of BHIPTA, whereas using sodium acetate 82% yield was obtained in 5 h.

Table II giving data on the optimization of catalyst concentration indicates that 0.5% by weight of catalyst (w.r.t. PET) produces maximum yield of the monomer with 1 : 5 molar ratio of PET : amine and reaction time of 3 h for zinc acetate and 5 h for sodium acetate. Zinc acetate has characteristics as a catalyst³⁴ and complexation ability.³⁵ Our results indicate that zinc acetate is a better catalyst than sodium acetate in depolymerization of PET. Kao et al. have proposed during their studies on glycolysis of PET that zinc acetate might facilitate the bond scission of polymer chains and subsequently enhance the depolymerization rate.³⁶ Table II gives data on the optimization of PET : 1-amino-2-propanol ratio. The ratio of 1 : 5 provides maximum yields with both the catalysts. With increase in the amine ratio further, the yield decreased due to difficulty in isolation of the product.

1-Amino-2-propanol has two nucleophilic centers. Oxygen being more electronegative than nitrogen, the amine group attacks the ester linkage of PET. The methyl group attached to carbon atom adjacent

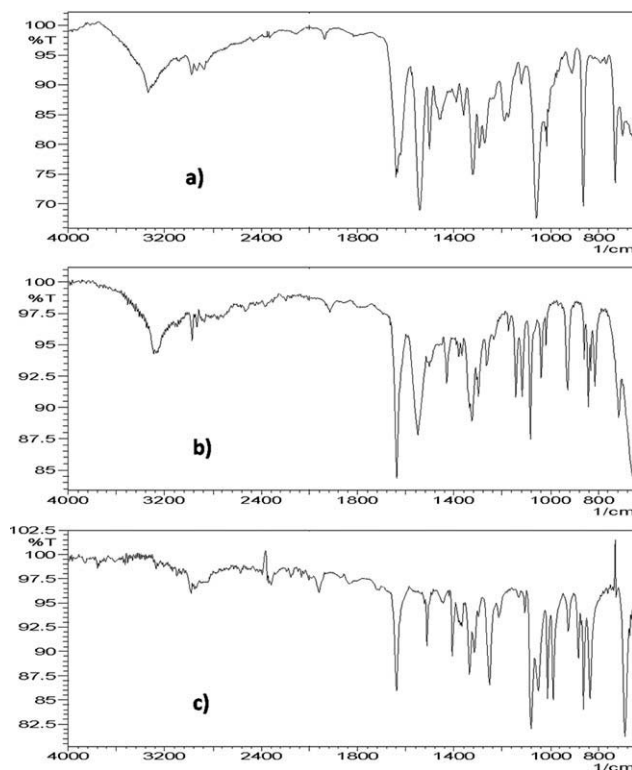


Figure 1 FTIR spectra of (a) BHMPTA, (b) BHIPTA, and (c) PBIOXA.

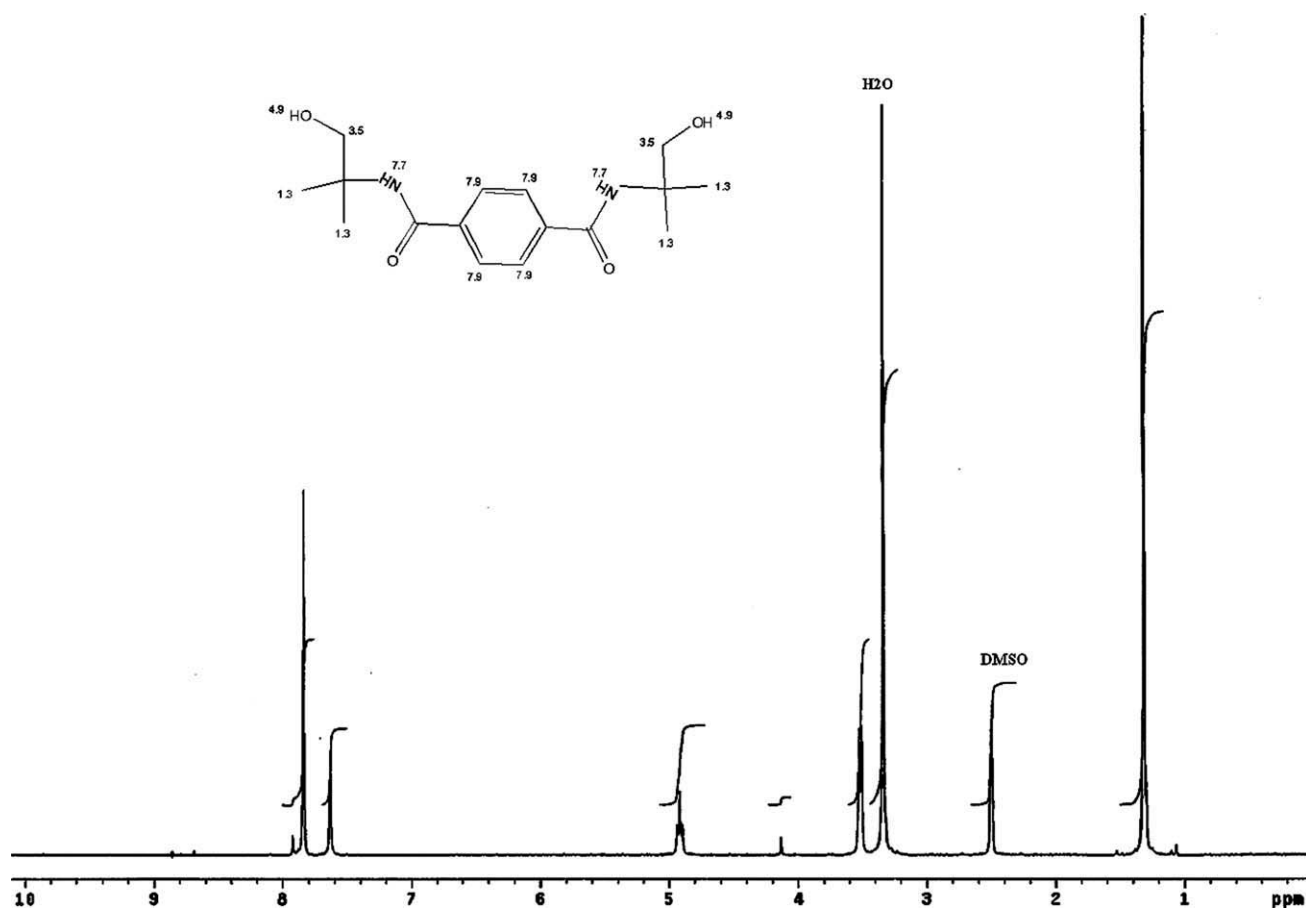
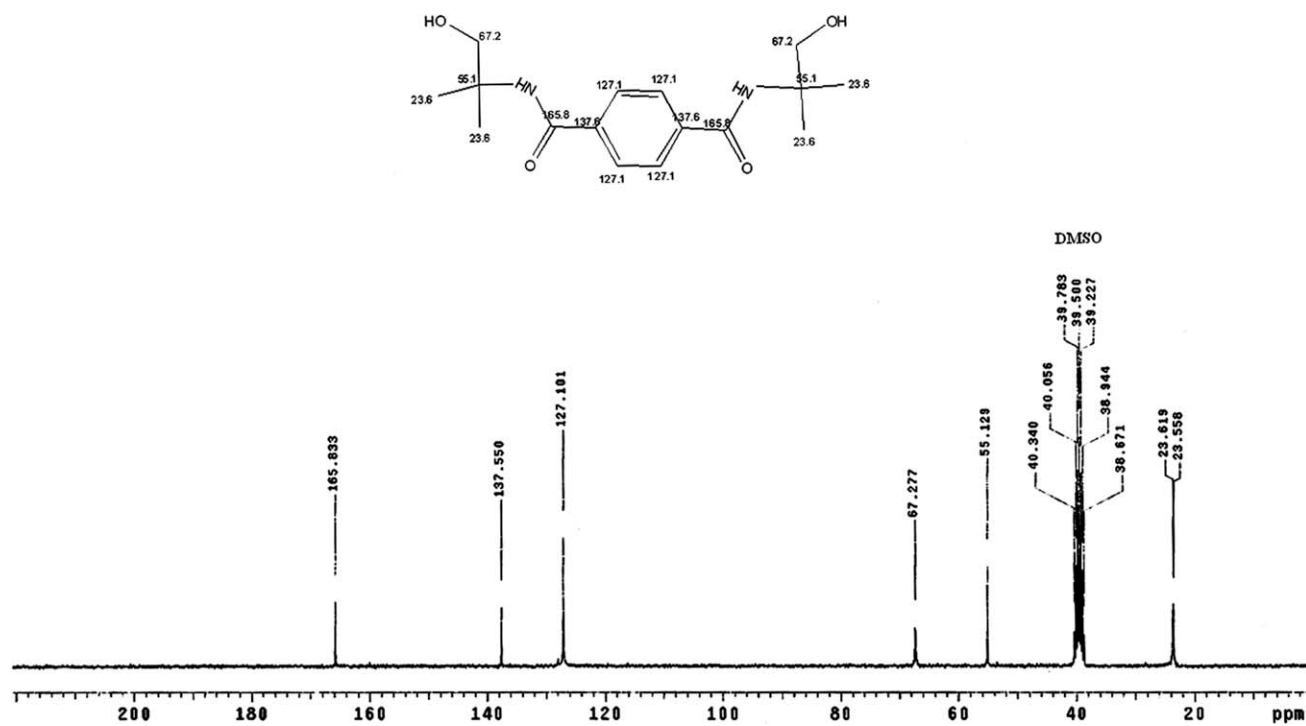
Figure 2 $^1\text{H-NMR}$ spectra of BHMPA.Figure 3 $^{13}\text{C-NMR}$ spectra of BHMPA.

TABLE II
Effect of Catalyst Concentration and 1-Amino-2-propanol Concentration on BHIPTA Yield

| Parameters | Yield (%) | |
|---------------------------------------|--------------|----------------|
| | Zinc acetate | Sodium acetate |
| Catalyst conc. ^a (w/w) | | |
| 0.3 | 72 | 60 |
| 0.5 | 84 | 82 |
| 0.7 | 86 | 83 |
| 1.0 | 84 | 79 |
| PET : amine ^b (mole ratio) | | |
| 1 : 3 | 58 | 38 |
| 1 : 5 | 84 | 82 |
| 1 : 7 | 72 | 69 |
| 1 : 9 | 64 | 63 |

Heating: conventional; time: 5 h for sodium acetate and 3 h for zinc acetate.

^a Catalyst conc. varied by keeping PET : amine ratio to 1 : 5.

^b PET : amine ratio varied by keeping catalyst conc. 0.5% (w/w).

to the hydroxyl group of the amine can enhance the electron density of nitrogen and therefore can increase the reaction rate providing better yields.²² Since 1-amino-2-propanol has shown better result for depolymerization of PET than 2-amino-2-methyl-1-propanol, the studies were continued with former.

TABLE III
Effect of Time on BHIPTA Yield

| Time (min) | Yield (%) | |
|------------|--------------|----------------|
| | Zinc acetate | Sodium acetate |
| 1 | 39 | 29 |
| 3 | 70 | 42 |
| 5 | 87 | 62 |
| 7 | 83 | 78 |
| 9 | 86 | 84 |

Heating: microwave irradiation; catalyst concentration: 0.5% (w/w); PET : amine = 1 : 5.

By microwave irradiation

Microwave heating was studied for aminolytic depolymerization of PET waste using 1-amino-2-propanol. The same optimized reaction parameters of conventional heating, viz; 0.5% w/w zinc acetate and 1 : 5 molar ratio of PET : amine were used by varying time of reaction up to 9 min. The data in Table III indicate that only 5 min are required to obtain the maximum yield of 87% of BHIPTA for zinc acetate whereas, for sodium acetate catalyst 9 min were required to get 84% yield. The yields were comparable with those obtained by conventional heating. Thus, a significant decrease in the time of aminolytic depolymerization reaction from 3

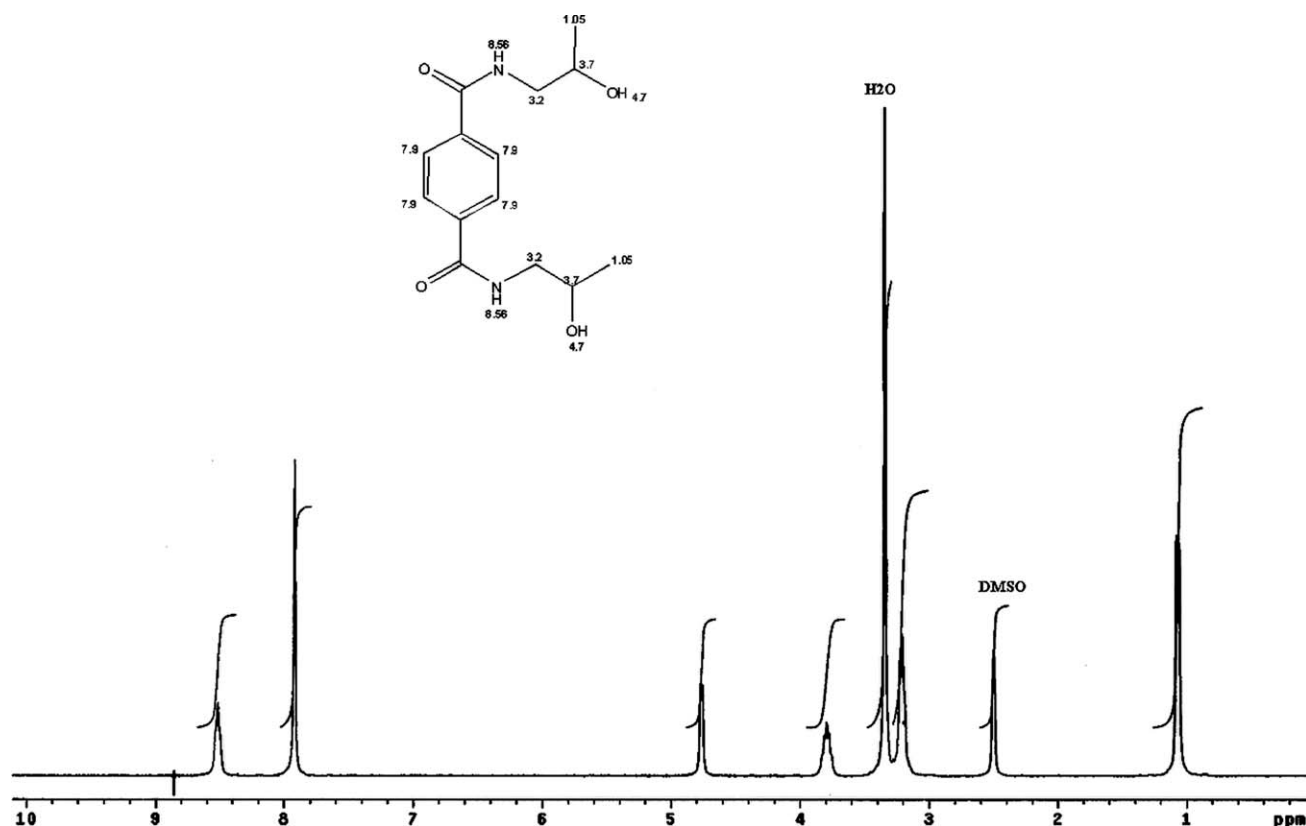


Figure 4 ¹H-NMR spectra of BHIPTA.

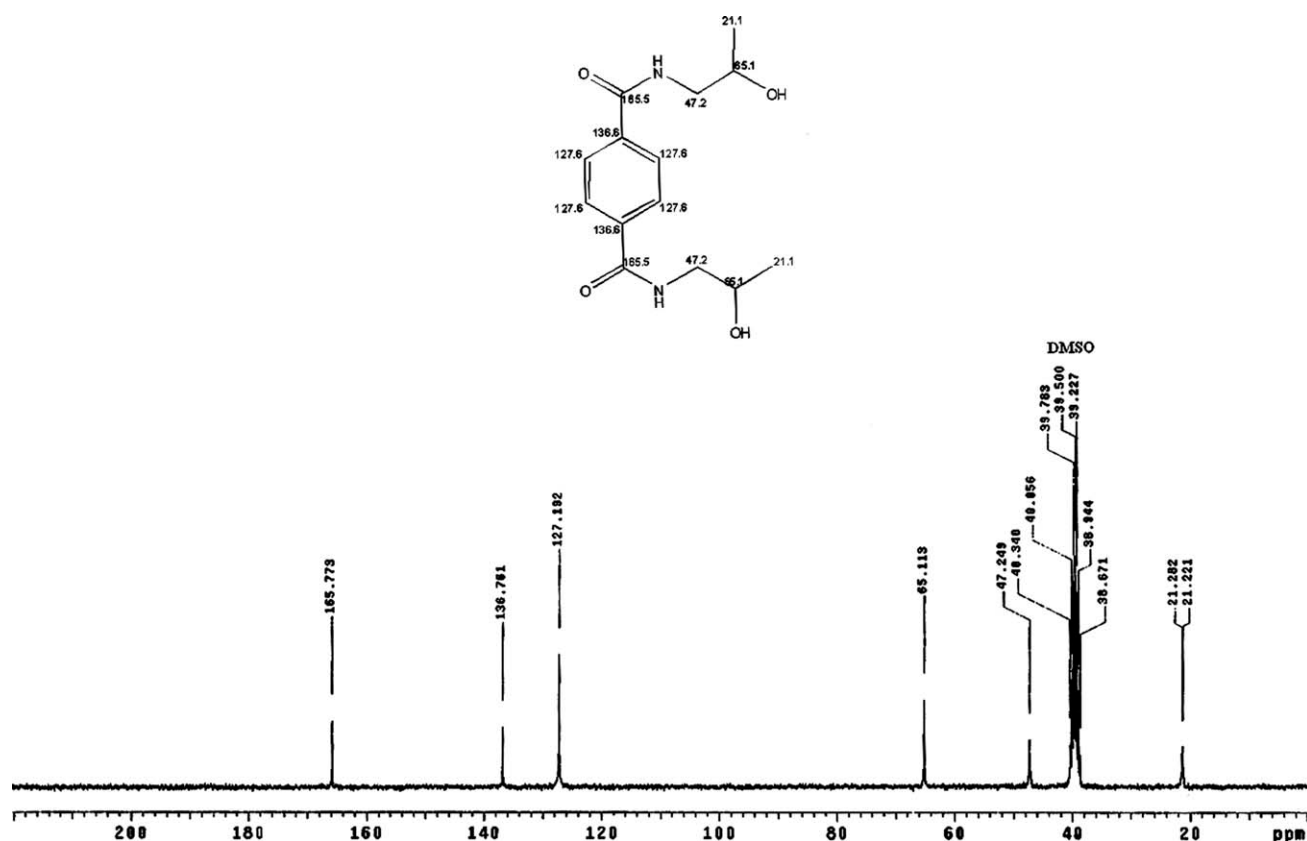


Figure 5 ^{13}C -NMR spectra of BHIPTA.

h to 5 min was achieved on using microwave irradiation as a heating source for refluxing the reaction mixture.

This may be attributed to the fact that 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 is the microwave effect when the temperature rise is considered.³⁷

The microwaves are known to couple directly with the molecules present in a reaction mixture and lead to rapid but controllable rise in the temperature. Dipole rotation is an interaction between the polar molecules that try to align themselves with the rapidly changing electric field of the microwaves, resulting in transfer of energy. Ionic conduction results if there are free ions or ionic species present in the substance, which try to orient themselves to the rapidly changing electric field, generating ionic motion.²⁴ 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. Similar mechanism is likely to apply in the present case, 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 is beyond the scope of this study.

Analysis of BHIPTA

Single spot of BHIPTA was obtained through TLC analysis using eluent ethanol : chloroform (1 : 9) at retardation factor (R_f) value 0.7 indicating purity of product. The FTIR spectrogram for the BHIPTA indicates the peaks at 1061 and 3278 cm^{-1} due to the presence of primary alcohol, peak at 1636 cm^{-1} indicates presence of carbonyl group and the peaks at 1323 and 1548 cm^{-1} are due to secondary amide (Fig. 1). The ^1H -NMR spectrum (Fig. 4) gave peak at δ 8.5 corresponding to $-\text{NHCO}$ groups, at δ 3.2 corresponding to aliphatic CH_2 proton, at δ 3.7 corresponding to aliphatic $-\text{CH}$ protons, at δ 1.0 corresponding to $-\text{CH}_3$ protons, at δ 7.9 corresponding to aromatic ring protons and at δ 4.7 corresponding to $-\text{OH}$ groups. ^{13}C -NMR spectrum (Fig. 5) of BHIPTA shows peak at δ 165.7 due to carbonyl carbon attached to aromatic ring and the peaks at δ 136.7 and δ 127.1 corresponding to aromatic carbons. The peak at δ 65.1 relates to aliphatic carbon

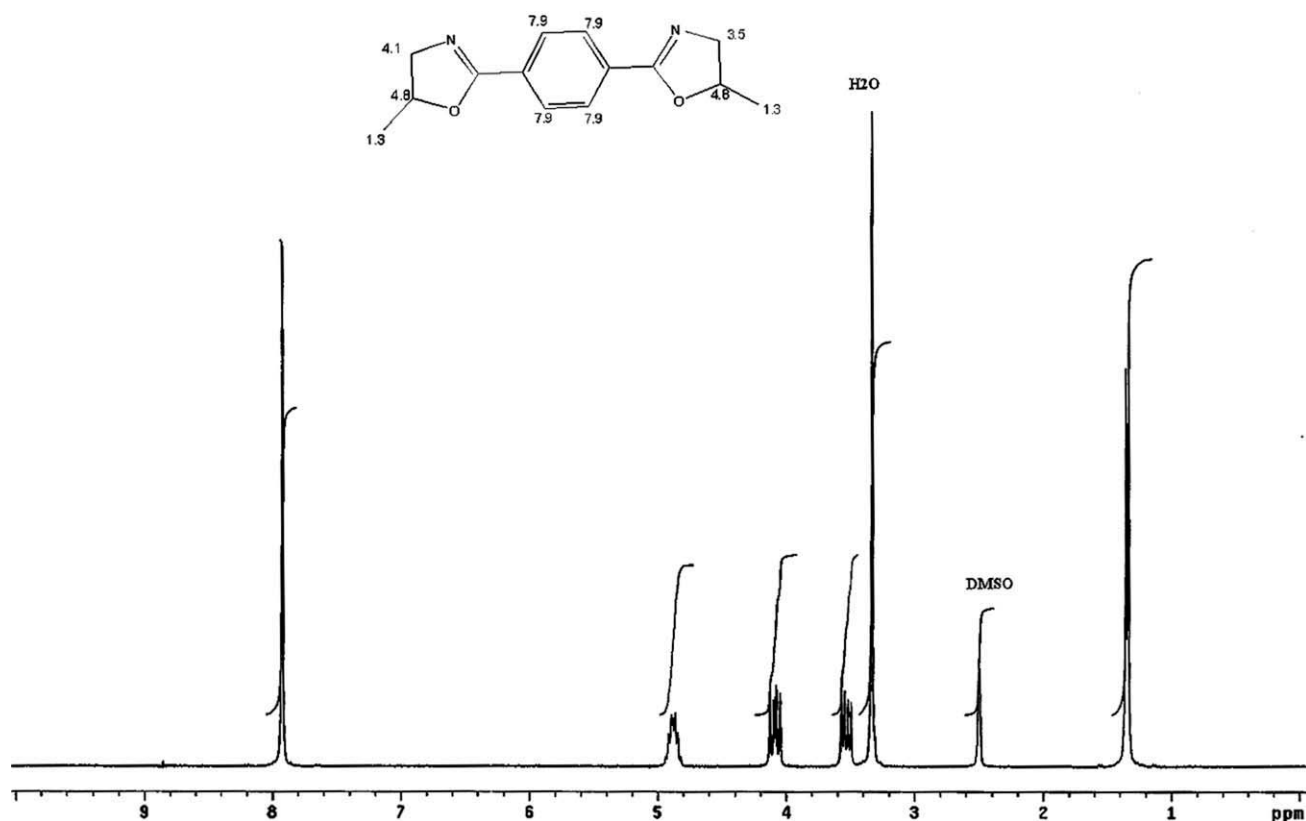


Figure 6 ^1H -NMR spectra of PBIOXA.

attached to the $-\text{OH}$ group, peak at δ 47.2 is due to carbon attached to amide group and peak at δ 21.2 is due to $-\text{CH}_3$ carbon. Melting point range

observed for BHIPTA is 206 – 210°C . The DSC scan also shows reasonably sharp endothermic peak at 208°C .

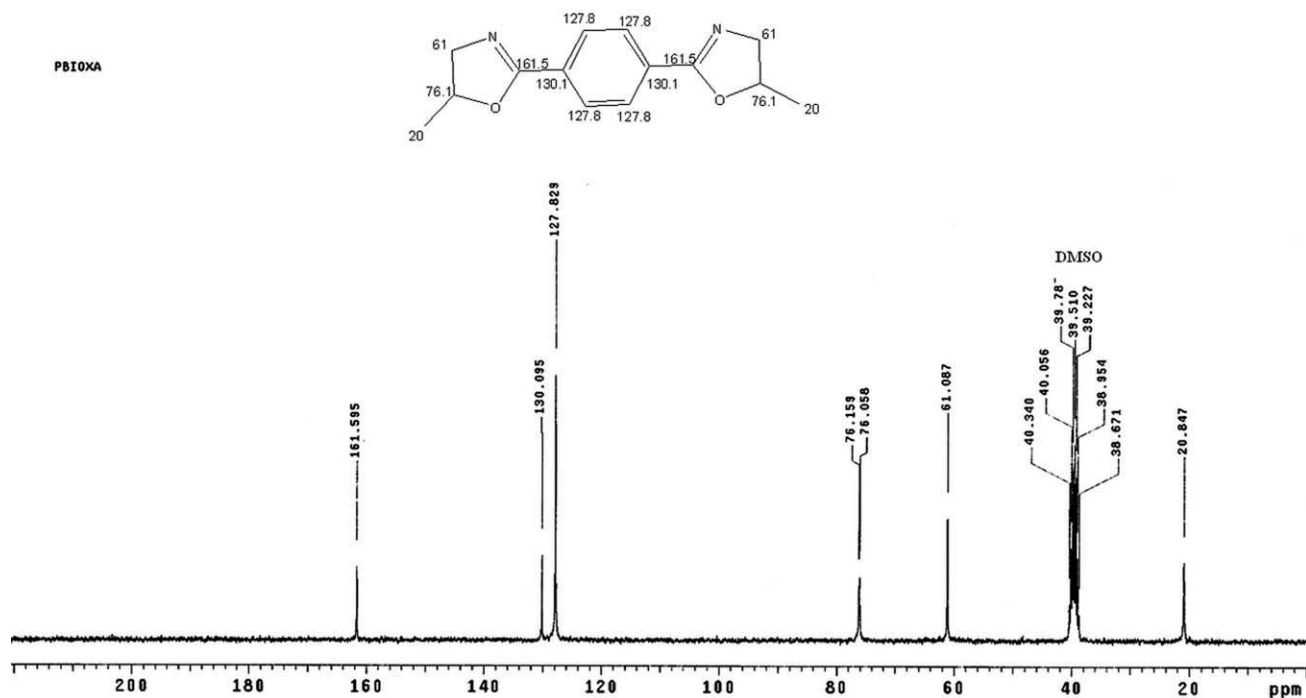


Figure 7 ^{13}C -NMR spectra of PBIOXA.

Synthesis and analysis of PBIOXA

A popular approach to prepare oxazolines involves intermolecular cyclization of β -hydroxy amide through activation of hydroxyl group as leaving group. Thionyl chloride has often been used as dehydrating agent. In the cold with excess of thionyl chloride, complex salts are formed which decomposed by using NaHCO_3 to get oxazoline.³⁸ The BHIPTA obtained from depolymerization of PET waste was subjected to cyclization reaction under low temperature and without any harsh conditions to get PBIOXA, which is a useful product in polymer and paint industry.

Analysis of PBIOXA

Single spot of PBIOXA was obtained through TLC analysis using eluent ethyl acetate : hexane (4 : 6) at R_f value 0.3 indicating purity of product. In the FTIR spectrogram for PBIOXA, the peak at 1637 cm^{-1} indicates the presence of —C=N stretching (Fig. 1) and disappearance of peaks of alcoholic groups of BHIPTA. The $^1\text{H-NMR}$ for the PBIOXA (Fig. 6) shows the peak of δ 1.3 corresponding to —CH_3 group protons, δ 3.5 corresponding to —CH_2 group attached to nitrogen on one side of phenyl group, and δ 4.1 corresponding to —CH_2 group attached to nitrogen on the other side of phenyl group. PBIOXA has two asymmetric carbon atoms; therefore, the protons show different coupling values owing to different chemical and magnetic environment. The peak at δ 4.8 corresponds to —CH group protons and δ 7.9 corresponding to aromatic ring protons. The values of δ 8.5 and δ 4.7, which correspond to —NHCO and —OH group protons, respectively, in BHIPTA were not observed in PBIOXA due to cyclization and dehydration. $^{13}\text{C-NMR}$ spectrum (Fig. 7) of PBIOXA shows peak at δ 161.5 due to carbon atom of imine attached to aromatic ring and the peaks at δ 130.1 and δ 127.8 corresponding to aromatic carbons. The peak at δ 76.1 relates to carbon attached to the methyl group, the peak at δ 61.0 is due to carbon attached to nitrogen other than imine, and the peak at δ 20.0 is due to —CH_3 carbon. Melting point range observed for PBIOXA is $85\text{--}89^\circ\text{C}$. The DSC scan also shows reasonably sharp endothermic peak at 89°C . This is in close agreement with melting point of PBIOXA reported by Deiter et al.³⁹

Aminolysis with PET with alkanol amines has been very useful as the products possess reactive hydroxyl groups. In literature, aminolysis using ethanol amine and diethanol amine has been reported.^{15,23} Ethanol amine has been reported to give close to 83% of pure bis(2-hydroxy ethylene)terephthalamide from PET bottle waste in 8 h with 1 : 8 PET : amine ratio; while DEA gives mixture of

amide and ester with side reaction occurring formation of piperazine and terephthalic acid. In our study, 1-amino-2-propanol has given better results than ethanol amine in terms of pure product yield (82% of BHIPTA) with reduced time (5 h) and PET : amine ratio (1 : 5) using sodium acetate as catalyst. Further, use of 0.5% w/w zinc acetate as catalyst and 1 : 5 PET : amine ratio reduced the time of reaction to only 3 h to get similar BHIPTA yield.

BHIPTA can undergo further reactions with its free hydroxyl groups and can be converted into polyurethanes by reacting with different di-isocyanates. Cyclization reaction of BHIPTA to get PBIOXA as a useful product was successful, which has been reported to be synthesized by reaction of terephthalonitrile with 1-amino-2-propanol using metal salts at high temperature $190\text{--}230^\circ\text{C}$.⁴⁰

CONCLUSION

Aminolysis of PET waste using 2-amino-2-methyl-1-propanol and 1-amino-2-propanol was carried out successfully using zinc acetate or sodium acetate as catalyst. The products BHMPA and BHIPTA were obtained in pure forms with good yields. Optimization of the parameters for aminolysis gave >84% yield of BHIPTA. Microwave heating drastically reduced the reaction time from 3 h to 5 min with the same yield and purity of the reactive monomers. These have the potential of recycling into useful products with wide applications through further chemical reactions. BHIPTA obtained was subjected to further reaction to get PBIOXA as a useful product for polymer and paint industry.

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