Ionic Liquid-Catalyzed Aminolysis of Poly(ethylene terephthalate) Waste

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ABSTRACT: Aminolytic depolymerization of poly(ethylene terephthalate) (PET) bottle waste with ethanolamine and hydrazine hydrate under atmospheric conditions was investigated in the presence of room temperature ionic liquids. 1-Hexyl-3-methylimidazolium trifluoromethanesulfonate (Hmim.TfO) and 1-butyl-3-methylimidazolium hydrogen sulfate (Bmim.HSO$_4$). (Hmim.TfO) was found to be the most efficient catalyst to obtain high yields of the aminolysis products bis(2-hydroxy ethylene) terephthalamide and terephthalic dihydrazide using ethanolamine and hydrazine hydrate, respectively. These products were characterized by IR spectroscopy, ^{1}H NMR, ^{13}C NMR, mass spectroscopy, and differential scanning calorimetry. The influence of experimental parameters, such as the amount of catalyst, reaction time, molar ratio of ethanolamine, and hydrazine hydrate with respect to PET was investigated. This protocol proves to be efficient and environmentally benign in terms of high yields (>84%) and low reaction times (up to 30 min). © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: PET waste; aminolysis; ionic liquid; bis (2-hydroxyethylene) terephthalamide; terephthalic dihydrazide

INTRODUCTION

Synthetic polymers have become versatile and useful materials of modern technology. Most of their applications are based on relatively high resistance to environmental degradation including biodegradation, better strength, and durability, which, however desirable, may be a threat to the environment causing pollution when discarded after use.

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. Such desirable properties have caused wide spread applications coupled with rising volumes of consumption and hence the PET waste disposal poses a serious problem to the efforts to maintain a clean environment. 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 degradation by the atmospheric and biological agents makes it to be seen as a noxious material.[2] Global consumption of PET for packaging is valued at $ 17 billion in 2010 and is forecast to reach $ 24 billion in 2011. Thus, the extensive use of PET in various fields, generating huge solid waste coupled with nonbiodegradability is a matter of serious concern.[3]

Although physical recycling of this thermoplastic material into second grade coarser fibers is widely practiced, the only acceptable technique of recycling according to the principles of sustainable development[4] is the chemical recycling through various routes such as hydrolysis, glycolysis, aminolysis, etc.,[2–6] as it leads to the formation of the breakdown materials from which the polymer itself or some other useful chemicals may be derived.[7] Aminolysis is one of the techniques of chemical degradation of PET, which has been reported way back in 1960s. Depolymerization of the PET waste using different amines such as allylamine,[8] morpholine and hydrazine,[9] and polyamines[10] has been reported.

We have carried out aminolytic depolymerization of PET using ethanolamine to give the pure product bis(2-hydroxy ethylene) terephthalamide (BHETA).[11] The catalysts used were glacial acetic acid, sodium acetate, and potassium sulfate. In this reaction, amine group of ethanolamine attacks the ester linkage of PET. The catalysts form complexes with the carbonyl group and increase its polarity and subsequently increase the rate of PET degradation, leading to pure BHETA.[11] Achilias et al.[12] have reported aminolysis of PET using ethanolamine under microwave in a sealed reactor without use of any catalyst.

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The popularity of room temperature ionic liquids (ILs) has recently resurged as possible environmental alternatives to common organic solvents and catalysts. Scientists have shown great interest in ILs because of their unique features, such as the strong solvent power for organic and inorganic compounds, thermal stability, nonvolatility, electrochemical stability, and low flammability.[13–15] In the last decade, ILs have been widely used in extraction,[16] catalysis,[17,18] electrochemistry,[19] and organic synthesis.[20] Glycolysis and hydrolysis of PET waste have been carried out using IL as catalyst. Glycolysis of PET waste in the presence of basic IL gives highest yield (72%) of monomer bis-2-(hydroxyethyl terephthalate) (BHET),[21] whereas hydrolysis using mixture of ILs gave 88% yield of monomer terephthalic acid.[22] Kamimura and Yamamoto[23] have employed ILs to depolymerize polyamides to obtain caprolactum monomer. No reports are found on the use of ILs in the aminolytic depolymerization of PET waste.

The present communication reports the catalytic activities of imidazolium ILs for depolymerization of PET waste through aminolysis using ethanolamine to obtain BHETA and hydrazine hydrate to obtain TH (Scheme 1).

EXPERIMENTAL

Materials

Discarded PET bottles were obtained from 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. The pieces were cleaned by boiling in a weak detergent solution followed by washing and drying.

Chemicals

Hydrazine hydrate and ethanol amine were of Laboratory grade reagent obtained from Merck Chemicals, India, and used without any further purification. 1-Methylimidazole, n-butyl chloride, acetone, sodium fluroborate, chloro hexane, trifluro acetic acid, sulfuric acid, and methylene chloride were of analytical grade.

Synthesis of ILs

Synthesis of 1-butyl-3-methylimidazolium chloride

A mixture of 1-methylimidazole and n-butyl chloride in a 1 : 1.2 molar ratio was reacted with stirring at 70°C for 72 h until two phases formed. The upper phase, containing unreacted starting material, was decanted and acetone was added with thorough mixing. It was decanted followed by the addition of fresh acetone. This step was repeated twice. After
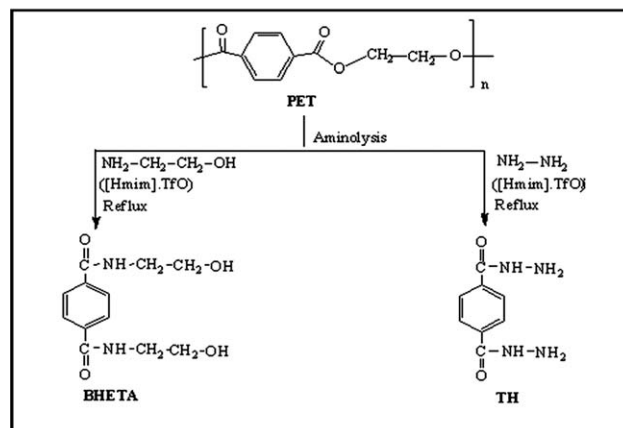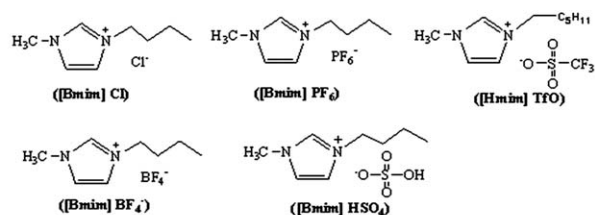
Scheme 1 Schematic representation of IL catalyzed aminolysis of PET.

the third decanting of acetone, any remaining acetone was evaporated using rotary evaporator. The product, 1-butyl-3-methylimidazolium chloride [(Bmim).Cl], was obtained and dried in a vacuum oven at 70°C for 48 h (yield, 95%). Synthesis of 1-butyl-3-methylimidazolium hexafluorophosphorate [(Bmim).PF$_6$] and 1-butyl-3-methylimidazolium tetrafluoroborate [(Bmim).BF$_4$] was carried out in a similar way.[24–27]

Synthesis of 1-hexyl-3-methylimidazolium trifluoromethanesulfonate

The same procedure was used as indicated for [(Bmim).Cl] with the exception of the use of chlorohexane instead of n-butyl chloride. Trifluoromethanesulfonic acid was used to form light yellow viscous liquid.

Synthesis of 1-butyl-3-methylimidazolium hydrogen sulfate

1-Butyl-3-methylimidazolium hydrogen sulfate [(Bmim).HSO$_4$] was obtained by dropwise addition of one equivalent of concentrated sulfuric acid (85%) to a cooled solution of [(Bmim).Cl] (one equivalent) in anhydrous methylene chloride. The mixture was refluxed for 48 h with stirring; the HCl by-product formed in the reaction was distilled out of the

TABLE I
Effect of Different ILs on Aminolysis of PET[a]

No.	ILs	Yield of BHETA (%)	Yield of TH (%)
1	No catalyst	No reaction	Trace
2	[Bmim]PF$_6$	60	44
3	[Bmim]HSO$_4$	84	79
4	**[Hmim]TfO**	**89**	**84**
5	[Bmim]Cl	66	54
6	[Bmim]BF$_4$	53	46

[a] Reaction conditions: PET : ethanolamine =1 : 6; PET : hydrazine hydrate = 1 : 6; IL: 0.2 g; and time: 60 min.

condenser under a stream of dry nitrogen and was dissolved in deionized water at 0°C. When the HCl formed was completely removed, CH_2Cl_2 was evaporated using rotary evaporator. The IL thus obtained was dried in a vacuum oven at 70°C for 48 h.

Synthesis of BHETA from polyester waste

The PET bottle waste chips were treated with ethanolamine under reflux at 196°C in the presence of certain amount of ILs for varying time periods up to 120 min. The ILs, namely, [(Bmim).Cl], [(Bmim).HSO$_4$], [(Bmim).BF$_4$], [(Bmim).PF$_6$], and 1-hexyl-3-methylimidazolium trifluoromethanesulfonate [(Hmim).TfO] were screened in various concentrations. At the end of the reaction, distilled water was added in excess to the reaction mixture with vigorous agitation to precipitate out the product, BHETA. The filtrate contained mainly unreacted ethanolamine and little quantities of a few water soluble PET degradation products. The precipitate obtained was filtered and dissolved in distilled water by boiling for about 30 min. White crystalline powder of BHETA was obtained by first concentrating the filtrate by boiling and then chilling it. It was further purified by recrystallization in water. It was then dried in an oven at 70°C and weighed for estimating the yield. Different techniques of analysis were used for its characterization.

Synthesis of TH from polyester waste

In a similar manner, the PET bottle waste was treated with hydrazine hydrate under reflux at 110°C in the presence of ILs and at the end of reaction, TH was precipitated out by adding excess of distilled water. It was then filtered and dissolved in distilled water by boiling for about 30 min. White crystalline powder of TH was obtained by first concentrating the filtrate by boiling and then chilling it. It was further purified by recrystallization in water. It was then dried in an oven at 70°C and weighed for estimating the yield. Different techniques of analysis were used for its characterization.

Characterization of the product

Melting points of the purified BHETA and TH were determined in an open capillary. Fourier transform infrared (FTIR) spectra were recorded on Shimadzu FTIR-470 spectrophotometer and reported in wave numbers (cm^{-1}). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-300 spectrometer at 300 and 75 MHz, respectively. NMR spectra were obtained in deuterated chloroform CDCl$_3$ and deuterated dimethylsulfoxide. Chemical shifts are expressed in δ units (ppm) using tetramethyl silane as an internal reference. Mass spectra were measured on Thermo mass spectrometer by electron ionization. The melting characteristic was determined by differential scanning calorimeter (DSC) (Shimadzu 60) at the heating rate of 10°C/min from 25 to 350°C in nitrogen atmosphere. Analytical TLC of all reactions was performed on Merck-prepared plates.

RESULTS AND DISCUSSION

The depolymerization of PET waste by aminolysis with excess ethanolamine and hydrazine hydrate with conventional heating and under microwave irradiation in the presence of various catalysts such as lead acetate, sodium acetate, sodium bicarbonate, and sodium sulfate has also been reported.[28,29] As the depolymerization products possess terminal reactive groups, they were further subjected to the synthesis of useful compounds such as unsaturated polyester resins, polyurethanes, and heterocyclic moieties possessing biological activities.[30–32] As no reports are found on the use of ILs in the aminolysis of PET, the same has been attempted in the present study.

Selection of the catalysts

The catalytic effect of the synthesized ILs on the aminolysis of PET was investigated. According to the results summarized in Table I, the acidic ILs [(Bmim).HSO$_4$] and [(Hmim).TfO] accelerate aminolysis process both for ethanolamine and hydrazine

TABLE II
Effect of [Hmim]TfO Concentration on the Yield of Aminolysis Products[a]

No.	Catalyst concentration (g)	Yield of BHETA (%)	Yield of TH (%)
1	0.10	71	68
2	0.15	82	73
3	**0.20**	**89**	**84**
4	0.25	90	86
5	0.30	91	87

[a] Reaction conditions: PET : ethanolamine =1 : 6; PET : hydrazine hydrate = 1 : 6; and time: 60 min.

TABLE III
Effect of Reaction Time on the Yield of Aminolysis Products[a]

No.	Time (min)	Yield of BHETA (%)	Yield of TH (%)
1	**15**	**84**	64
2	25	86	72
3	30	87	77
4	**40**	89	**82**
5	60	89	84
6	90	90	86
7	120	91	87

[a] Reaction conditions: PET : ethanolamine = 1 : 6; PET : hydrazine hydrate = 1 : 6; and [Hmim]TfO: 0.2 g.

TABLE IV
Effect of PET : Ethanol Amine and PET : Hydrazine Hydrate Ratio on the Yield of Aminolysis Products[a]

No.	PET: ethanolamine ratio	Yield of BHETA (%)	PET: hydrazine hydrate ratio	Yield of TH (%)
1	1 : 3	79	1 : 3	52
2	1 : 4	84	1 : 4	63
3	1 : 5	87	1 : 5	75
4	**1 : 6**	**89**	**1 : 6**	**84**
5	1 : 8	91	1 : 8	88
6	1 : 10	92	1 : 10	89
7	1 : 12	93	1 : 12	91

[a] Reaction conditions: [Hmim]TfO: 0.2 g; time: 60 min.

hydrate (entries 3 and 4). The basic ILs were not found much efficient. The use of ILs as a catalyst was found to rapidly enhance the solubility of PET in the reaction system although suppressed in the presence of moisture. The cations and anions of ILs were found to have significant effect on the results of aminolysis. When the anions of IL are [TfO] or [HSO$_4$], the conversion and yield are much better than when the anions are [PF$_6$] (entry 2) or [BF$_4$] (entry 6). The results showed that [(Hmim).TfO] was an excellent catalyst for aminolysis of PET, giving good yield of TH (up to 84%) and BHETA (up to 89%) in <1 h.

Effect of catalyst concentration

Table II summarizing data on the optimization [(Hmim).TfO] catalyst concentration indicate that 10% by weight of catalyst (w.r.t. PET = 0.2 g) produces maximum yield of both BHETA and TH with 1 : 6

molar ratio (PET : ethanolamine/hydrazine hydrate) and reaction time of 60 min. The product yield increased rapidly with the amount of catalyst up to 0.2 g and thereafter it increased only marginally.

Effect of aminolysis time

Time study was carried out from 15 to 120 min and it was observed that the yield of BHETA and TH increases with time. As summarized in Table III, it is clear that the optimum reaction time with ethanol amine was as low as only 15 min for nearly 84% yield of BHETA in the present study, whereas 8 h was required to get similar yield of BHETA in the earlier studies conducted by using sodium acetate or glacial acetic acid as catalysts.[11] In the case of reaction with hydrazine hydrate, the optimum reaction time was 40 min with 82% yield of TH, whereas 4 h was required in the earlier studies to get similar yield of TH using sodium acetate as catalyst.[33] This
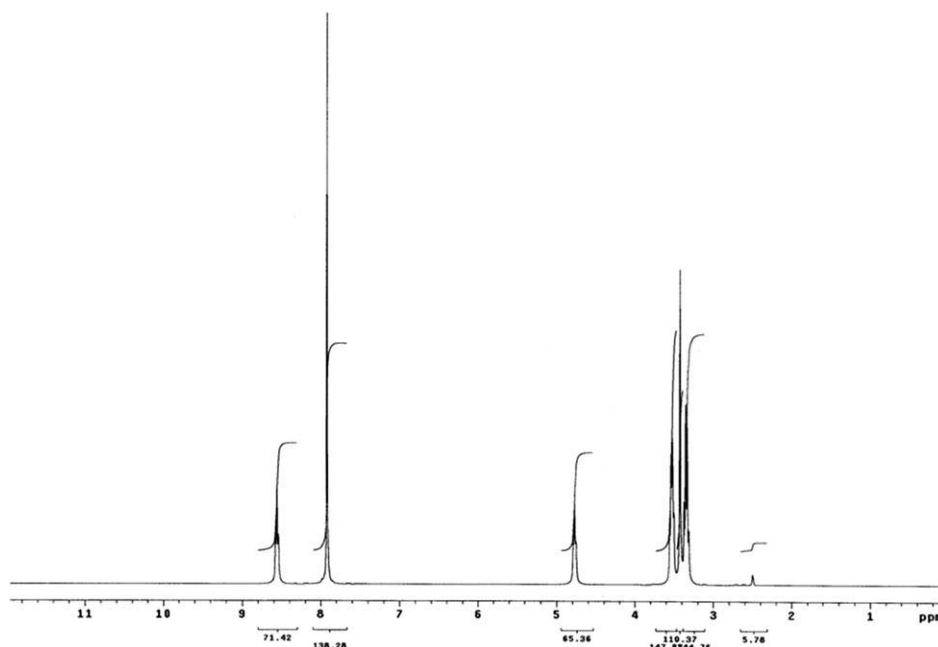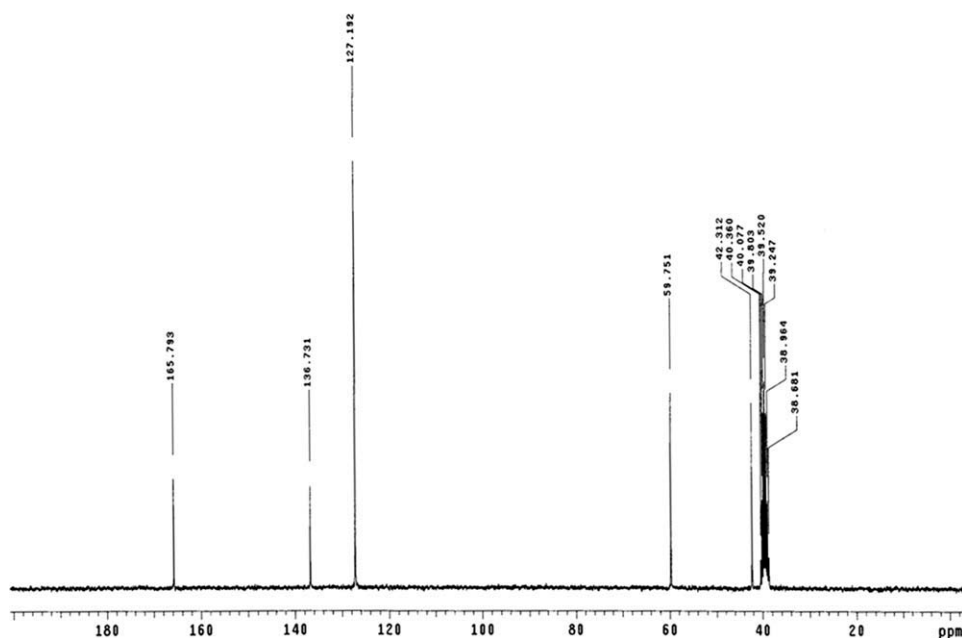

Figure 1 ^{1}H NMR spectra of BHETA.

Figure 2 ^{13}C NMR spectra of BHETA.

is attributed to the use of ILs, which have the action of faster dissolution of PET. In case of hydrazine hydrate, the presence of moisture decreases the initial degradation of PET and hence increases the reaction time. The faster degradation of PET is owing to the presence of ILs containing imidazolium salt.

Effect of PET: Amine ratio

In the aminolytic depolymerization reaction, ethanolamine has two nucleophilic centers. Nitrogen being more electronegative than oxygen, the amine group of ethanolamine or hydrazine hydrate attacks the ester linkage of PET. Initially, the reaction mixture is biphasic, a solid phase (PET), and a liquid phase (amine). When the chemical structure of polyester (molecular weight and compositions) allows its degradation, it passes into solution, more quickly in the presence of IL. The effect of weight ratio of PET to ethanolamine on the depolymerization reaction, summarized in Table IV, indicates that the increase in PET: ethanolamine ratio from 1 : 3 to 1 : 12 causes increase in the yield of the product BHETA from 81 to 93% when the reaction was carried out for 60 min using (Hmim.TfO). In the case of PET : hydrazine hydrate, the ratio of 1 : 6 is sufficient to give high yield (up to 84%) of TH.
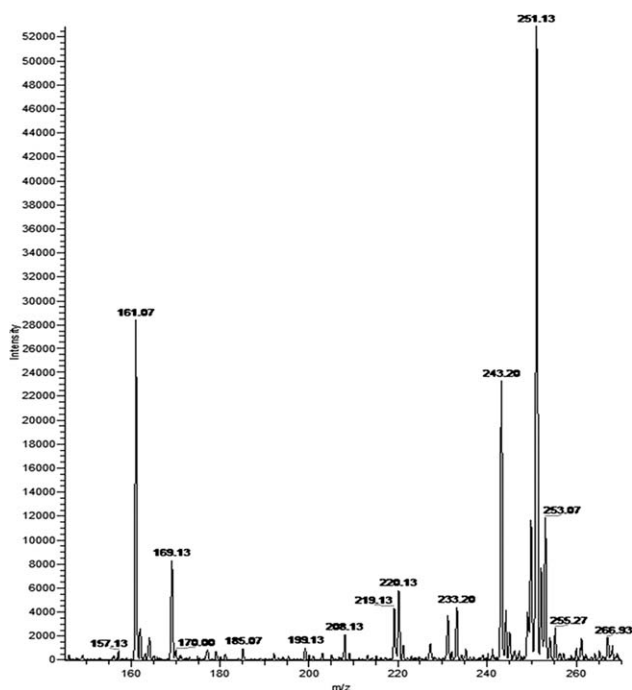
Mechanism and characterization

The mechanism of depolymerization of PET through aminolysis has been explained earlier.[11] The catalyst
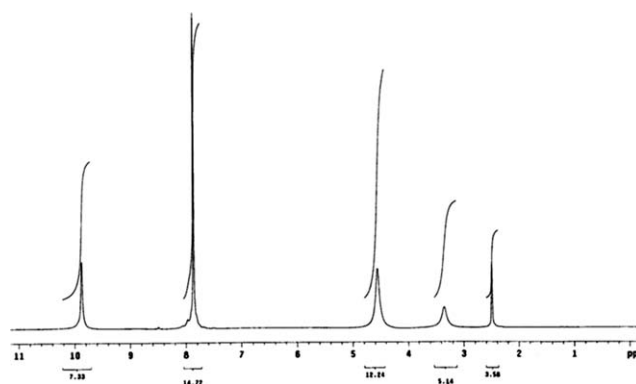

Figure 3 Mass spectra of BHETA.
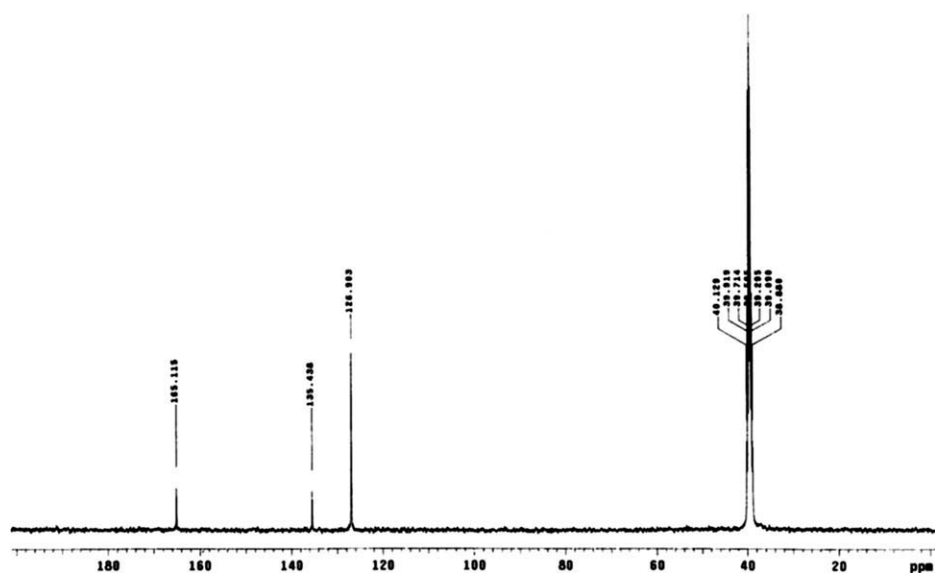

Figure 4 ^{1}H NMR spectra of TH.

Figure 5 ^{13}C NMR spectra of TH.

forms complex with carbonyl carbon of PET to facilitate the attack of nitrogen of the amine. According to Popoola,[34] the basicity of an amine relative to water as well as its steric hindrance owing to size decides the rate of PET degradation.

In the literature, imidazolium-based acidic ILs have been used by Fusheng et al.[22] for hydrolysis of PET showing good results with decrease in time. They have shown that imidazolium-based ILs possess strong solvent power which can improve solubility of PET in reaction system, making it homogeneous reaction mixture susceptible to better reaction. Also, these ILs possess high thermal stability, often beginning to decompose around 400°C with minimal vapor pressure below their decomposition temperatures.[24] The acidic ILs have shown good catalytic activity, it may act as an acid and enhance nucleophilic attack of amine on the carbonyl ester of PET, resulting in chain scissoring of polyester into the product.

Ethanolamine has two nucleophilic centers. The amine group, being less electronegative than hydroxyl group of ethanolamine, attacks the ester linkage of PET easily to form BHETA. Hydrazine hydrate being symmetrical, the amine group attacks the carbonyl ester with chain cleavage of PET occurring in the presence of ILs in a similar way.

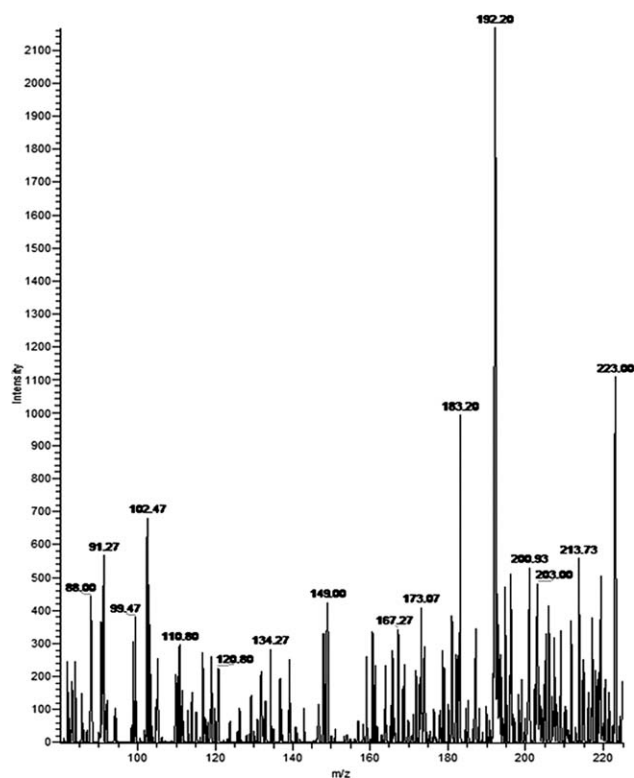The FTIR spectrograph of the purified BHETA clearly shows the peaks at 1049 and 3282 cm^{-1},
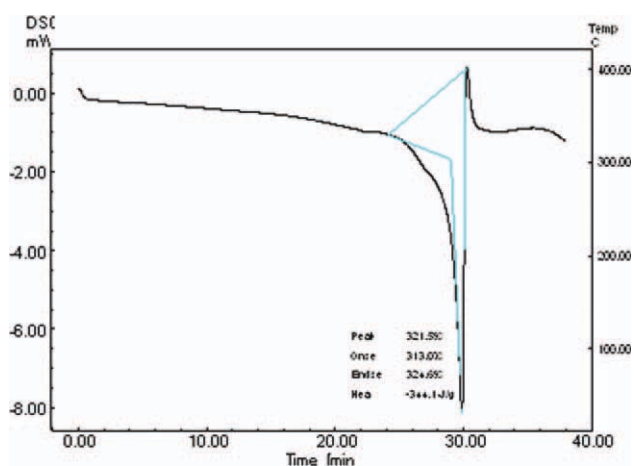

Figure 6 Mass spectra of TH.

Figure 7 DSC scan of TH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

indicating the presence of primary alcohol. The peaks for secondary amide stretching are observed at 1315, 1550, and 3358 cm^{-1}. The ^{1}H NMR (Fig. 1) gave peak at $\delta = 8.59$ corresponding to ─NHCO groups, the peak at $\delta = 3.25–3.65$ corresponding to aliphatic CH$_2$═CH$_2$ proton, at $\delta = 7.98$ corresponding to aromatic ring protons and at $\delta = 4.70$ corresponding to ─OH groups. ^{13}C NMR spectra of BHETA (Fig. 2) shows peak at $\delta = 167.7$ owing to carbonyl carbon attached to aromatic ring and the peaks at $\delta = 137.2$ and 127.3 corresponding to aromatic carbons. The peak at $\delta = 61.0$ relates to aliphatic carbon attached to the ─OH group and peak at $\delta = 42.2$ is owing to ═CH$_2$ attached to amide group. The mass spectra show peak at $m/e = 251.13$ with intensity almost 100% relating to molecular weight of BHETA (Fig. 3). The DSC scan also shows reasonably sharp endothermic peak at 222°C in agreement with the known melting point.[29,35]

The FTIR spectrum of TH shows absorption peak at 1630 cm^{-1} owing to amide group and broad peak at 3254 cm^{-1} owing to NH. Its ^{1}H spectrum reveals a singlet at $\delta = 7.86$ for aromatic protons; broad peaks at $\delta = 9.87$ and 4.55 owing to the amide and NH protons (Fig. 4), rest of the peaks are owing to the deuterated DMSO and moisture content in the solvent. ^{13}C spectrum shows peaks at $\delta = 126.9$, 135.4, and 165.1 for aromatic CH, Ar─C─CO, and CO groups, respectively. These spectral values of synthesized TH are in good agreement with those reported in the literature (Fig. 5).[28] The mass spectrum of pure TH in Figure 6 shows the peak at $m/e = 194$ with almost 100% intensity. This peak is related to molecular weight of TH that is 194 g/mol. The DSC scan (Fig. 7) also shows reasonably sharp endothermic peak at 332°C, which is the melting point of TH.

During aminolytic depolymerization of PET, the products in pure forms are obtained in higher yield (>80%) along with negligible amount of oligomeric mixture. This is not the case with other chemical recycling processes for PET. For example, the glycolytic depolymerization gave the yield of pure product BHET only about 62.5%.[36] Thus, aminolysis appears to be advantageous from the point of view of the depolymerization products which are obtained in higher yield with highly reactive end groups and possessing higher thermal stability.

Thus, the pure aminolysis products BHETA and TH were obtained after aminolysis of PET waste catalyzed by IL with the advantages of comparable yield and lower reaction time. These are well characterized and their structures are confirmed.

CONCLUSIONS

The aminolysis of PET waste was catalyzed by different kinds of ILs at atmospheric pressure.

[Bmim]TfO was chosen as the aminolysis catalyst for our investigation. Optimization of the parameters of aminolysis gives the yield of BHETA and TH products >84%. The yield and purity of these reactive products are of high order with much less reaction time. Furthermore, the products of depolymerization have the potential of recycling it into useful compounds through various chemical reactions with varied applications, which is being explored.

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