

# Synthesis and Characterization of Terephthalamides from Poly(ethylene terephthalate) Waste

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**ABSTRACT:** Poly(ethylene terephthalate) (PET) waste flakes (blow-molded-grade industrial waste) were degraded with aqueous methylamine and ammonia at room temperature in the presence and absence of quaternary ammonium salt as a catalyst for various times. The catalyst reduced the time required for the degradation of the PET waste. The degraded products were analyzed with IR, nuclear magnetic resonance, mass spectrometry, and differential thermal anal-

ysis and were characterized as *N,N'*-dimethylterephthalamide and terephthalamide in the case of methylamine and ammonia, respectively. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1515–1528, 2005

**Key words:** degradation; infrared spectroscopy; NMR; polyesters; recycling

## INTRODUCTION

Poly(ethylene terephthalate) (PET) has excellent mechanical properties in comparison with other commodity polymers, especially when it is used as a film or fiber.<sup>1,2</sup> Extensive studies<sup>3</sup> on the thermal, chemical, and catalytic photolytic degradation of PET waste have developed many processes of commercial importance<sup>4</sup> for saving the environment.<sup>5</sup> Various processes, such as hydrolysis,<sup>6</sup> methanolysis,<sup>7</sup> and glycolysis,<sup>8,9</sup> have been employed to study the degradation of the main chain of PET by chain scission. However, a disadvantage associated with these processes is that PET flakes are subjected to higher temperatures and higher pressures, which change the morphological structure. The hydrolysis of PET<sup>10</sup> with water at 150–250°C under pressure<sup>11</sup> in the presence of a catalyst results in the reclamation of terephthalic acid and ethylene glycol monomer. The methanolysis of PET<sup>12</sup> occurs at 160–240°C under a pressure of 20–70 atm and provides an excellent yield of monomers.<sup>13</sup> The glycolysis of PET<sup>14</sup> involves the treatment of high-molecular-weight PET with an excess of glycol<sup>15</sup> at 180°C in the presence of a catalyst<sup>16</sup> and produces hydroxyl-terminated short-chain fragments. These reactions are carried out at high temperatures and high pressures and thus consume a lot of energy. The degradation of PET

waste at lower temperatures would convert this reaction into a green reaction.

Overtone and Murayama<sup>17</sup> used methylamine ( $\text{CH}_3\text{NH}_2$ ) to selectively separate amorphous and crystalline regions and characterize the morphology of PET. Mehta and Bell<sup>18</sup> concluded, on the basis of the weight loss, crystallinity, and molecular weight of aminolyzed PET, that aminolysis was effective in removing the amorphous phase selectively.

In this study, an attempt was made to synthesize terephthalamides<sup>19</sup> through the reaction of PET waste<sup>20</sup> with 40% aqueous  $\text{CH}_3\text{NH}_2$  and ammonia ( $\text{NH}_3$ ) at room temperature; the tedious conditions of a high temperature and a high pressure were avoided with a catalyst. The products were characterized with different spectroscopic techniques [IR, proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ), and mass spectrometry (MS)], differential thermal analysis (DTA), chromatography, and chemical tests.

## EXPERIMENTAL

PET waste flakes, obtained from industry, were placed in a hot water bath maintained at 70–100°C to ensure the effective separation of the PET flakes from other impurities. The basis of separation was that PET under such conditions underwent shrinkage, whereas other impurities, such as labels, high-density polyethylene cups, and polypropylene cups, did not. The separated PET flakes were washed thoroughly with water.

The PET waste (10 g) was reacted with aqueous  $\text{CH}_3\text{NH}_2$  (40% w/v, 100 mL) in a properly sealed round-bottom flask. A quaternary ammonium salt (cetyl ammonium bromide; 0.15 g) was used as a

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TABLE I  
Amount of  $\text{CH}_3\text{NH}_2$ , PET Waste,  $\text{NH}_3$ , and Catalyst  
Taken for Aminolysis and Ammonolysis

Ingredient	Aminolysis		Ammonolysis	
	With catalyst	Without catalyst	With catalyst	Without catalyst
PET waste (g)	10	10	10	10
$\text{CH}_3\text{NH}_2$ (mL)	100	100	—	—
$\text{NH}_3$ (mL)	—	—	100	100
Quaternary salt (g; catalyst)	0.15	—	0.15	—

catalyst. The reaction was carried out under continuous and constant stirring at  $40^\circ\text{C}$ .  $\text{CH}_3\text{NH}_2$  was used in excess in comparison with PET waste in a 10:1 weight ratio. The white precipitates of terephthalamide started appearing within a few hours of the start of the reaction. However, all the PET reacted completely in 45 days. After 3 days, fine white precipitates were separated from unreacted PET waste by dissolution in warm ethanol, and the precipitates were regenerated by the addition of distilled water. The white precipitates so obtained were dried *in vacuo* at  $60^\circ\text{C}$  until a constant weight was obtained. Table I summarizes the amounts of PET waste,  $\text{CH}_3\text{NH}_2$ ,  $\text{NH}_3$ , and catalyst taken for the aminolysis and ammonolysis of PET waste.

The degradation of PET waste was studied under similar conditions for various times (7, 15, 21, 25, 30, and 45 days). Every time, white precipitates were separated from unreacted PET waste flakes and purified. The weight of unreacted PET waste flakes during the course of degradation was determined after they were thoroughly washed and dried *in vacuo* for 2 h at  $60^\circ\text{C}$  (until a constant weight was obtained).

The same experiment was performed under similar conditions in the absence of a catalyst, and so comparative studies of PET waste degradation were made in the presence and absence of a catalyst. The fine white precipitates were characterized with chemical tests, spectroscopic techniques [IR, nuclear magnetic resonance (NMR), and MS], DTA, and chromatographic techniques.

The ammonolysis of PET waste flakes was studied in a similar manner, except that degradation experiments were carried out with aqueous  $\text{NH}_3$  solutions. Dried PET waste flakes (10 g) were reacted with an excess of aqueous  $\text{NH}_3$  (100 mL) in a weight ratio of 1:10 at room temperature ( $40^\circ\text{C}$ ) with continuous and constant stirring. The same reaction was carried out under two different conditions—in the presence of a quaternary ammonium salt (0.15 mg) and without a quaternary salt—for various times (3, 7, 15, 21, 25, 30, and 45 days). The products were separated from degraded PET flakes every time, purified, and character-

ized with chemical tests, spectroscopic techniques (IR, NMR, and MS), DTA, and chromatographic techniques.

The reference terephthalamide and *N,N'*-dimethylterephthalamide were prepared through the reaction of terephthaloyl chloride with  $\text{NH}_3$  and  $\text{CH}_3\text{NH}_2$ , respectively. The terephthaloyl chloride with  $\text{NH}_3$  was prepared through the reaction of dry terephthalic acid (3 g, 0.018 mol) and thionyl chloride (7 mL, excess) with continuous stirring for 24 h and purified with vacuum distillation. To the freshly prepared terephthaloyl chloride (5 mL), aqueous  $\text{CH}_3\text{NH}_2$  was added dropwise at room temperature. Solid white precipitates were filtered and washed with distilled water and recrystallized with ethanol. The recrystallized products were then weighed for the yield and characterized with sodium bicarbonate tests, spectroscopic techniques (IR,  $^1\text{H-NMR}$ , and MS), and DTA. Similarly, terephthalamide was prepared through the reaction of terephthaloyl chloride and  $\text{NH}_3$  and was purified and characterized as previously discussed.

IR spectra were recorded on a Nicolet 5DX IR spectrophotometer (Madison, WI) with KBr discs for the ultimate degraded products obtained from the aminolysis and ammonolysis of PET waste at different times (3, 7, 15, 21, 25, 30, and 45 days) and were interpreted for various bonds through the identification of their characteristic frequencies as absorption bands.

All the  $^1\text{H-NMR}$  spectroscopy simulations in this work were recorded on a JEOL JNM-FS-100 FT-NMR instrument at 100 or 300 MHz for all the ultimate degraded products. All the MS spectra were recorded on a JEOL JMS-DX 303 mass spectrometer for the ultimate degraded products resulting from the aminolysis and ammonolysis of PET waste. DTA thermograms of the ultimate degraded products obtained from the degradation of PET waste flakes with 40% aqueous  $\text{CH}_3\text{NH}_2$  (aminolysis) and  $\text{NH}_3$  (ammonolysis) were recorded on a Rigaku thermoflex (Tokyo, Japan). The solubility of *N,N'*-dimethylterephthalamide and terephthalamide was determined in different solvents, such as water, ethanol, dimethylformamide, and dimethyl sulfoxide (DMSO).

The amine contents of *N,N'*-dimethylterephthalamide and terephthalamide were determined through the boiling *N,N'*-dimethylterephthalamide (2 g, 0.01 mol) or terephthalamide (1.98 g, 0.01 mol) in 250 or 300 mL of a standard NaOH solution (0.15 or 0.17N), respectively. The unreacted NaOH was titrated back with oxalic acid (0.09N).

The amides prepared by the aminolysis and ammonolysis of PET waste flakes were subjected to thin-layer chromatography (TLC) and compared with reference samples to determine the purity of the prepared compounds. The retention factor ( $R_f$ ) values were determined and compared with those of the reference samples.

## RESULTS AND DISCUSSION

Two different series of reactions (aminolysis and ammonolysis) of PET waste flakes were studied at room temperature in the presence and absence of a quaternary ammonium salt as a catalyst. The PET waste flakes aminolyzed and ammonolyzed more quickly with much greater yields in the presence of a catalyst, as expected, and white precipitates of amides were obtained within a few hours after the start of the reaction. With the passage of time during both aminolysis and ammonolysis, the concentration of precipitation increased, and after 45 days, all PET flakes completely disintegrated into fine white precipitates. No PET flakes were left unreacted. The reactions were carried out in excesses of  $\text{CH}_3\text{NH}_2$  and  $\text{NH}_3$ . If an excess of the solvent was not used, the rate of degradation of PET waste was very slow. Higher concentrations of  $\text{CH}_3\text{NH}_2$  and  $\text{NH}_3$  resulted in the cleavage of all folds within the experimental

timescale, whereas lower concentrations could leave some of the less accessible ones intact. In the absence of a catalyst, the degradation proceeded very slowly, as shown by the fact that a smaller amount of white precipitates were obtained in a longer time. However, precipitation increased with time, but even after 45 days, some PET waste flakes were unreacted. This was attributed to the fact that aminolysis and ammonolysis rapidly degraded the amorphous regions initially, and then highly crystalline PET was degraded. The weights of unreacted PET waste flakes during the course of degradation in the presence and absence of a catalyst were determined. The aminolysis and ammonolysis of PET waste at the ambient temperature were green reactions.

The amine values of *N,N'*-dimethylterephthalamide and terephthalamide were determined with the following formula:

Amine value of terephthalamides (%) =

$$\frac{\text{Molecular weight of NH}_3 \times \text{Normality of NaOH taken}(\text{Volume of NaOH taken} - \text{Volume of NaOH consumed}) \times 100}{1000 \times \text{Weight of } N, N'\text{-dimethylterephthalamide or terephthalamide taken}}$$

The calculated values were 17.00 and 20.14%, respectively, and were in good agreement with the theoretical values of 17.70 and 20.73%, respectively.

### Characterization of the aminolyzed and ammonolyzed products

The white precipitates obtained from the degradation reactions of PET waste with  $\text{CH}_3\text{NH}_2$  and  $\text{NH}_3$  were characterized with different spectroscopic techniques (IR,  $^1\text{H-NMR}$ , and MS), DTA, TLC, and chemical tests, which are discussed next.

### Spectroscopy and DTA of the white precipitates obtained by the reaction with $\text{CH}_3\text{NH}_2$

Figure 1 shows the  $^1\text{H-NMR}$  spectrum of the products obtained by the aminolysis of PET waste flakes in the presence of a catalyst. The spectrum shows three absorption peaks. The peak at  $8.4\delta$ , a broad, low hump, was attributed to  $\text{CO-NH}$  protons. A doublet at  $2.9\delta$  accounted for  $\text{N-CH}_3$  protons, and a sharp singlet at  $7.9\delta$  was associated with four  $\text{Ar-H}$  protons. When the  $^1\text{H-NMR}$  spectra of the products separated by the aminolysis of PET waste flakes in the presence and absence of a catalyst were recorded after 3, 7, 15, 21, 25, 30, and 45 days of the reaction, the peak positions were found to be exactly same as those mentioned previously. This NMR spectrum matched that of the reference sample synthe-

sized by the reaction of terephthaloyl chloride with  $\text{CH}_3\text{NH}_2$ , as shown in Figure 2.

Figure 3 shows the mass spectrum for the white precipitates obtained from the aminolysis of PET waste in the presence of a catalyst. An electron impact yielded a molecular ion peak at  $m/z = 192$  ( $\text{M}^+$ ) and a base peak at  $m/z = 162$  (100%). Subsequent fragment peaks at  $m/z$  values of 163, 134, 135, 106, 77, 78, 57, and 58 were attributed to *N,N'*-dimethylterephthalamide. The mass spectra of products separated after 3, 7, 15, 21, 25, 30, and 45 days of the reaction, in the presence and absence of a catalyst, exactly matched one another and the mass spectra of the reference sample, as shown in Figure 4.

Figure 5 shows the DTA thermograms recorded for the white precipitates obtained as the result of aminolysis in the presence of a catalyst from room temperature to  $400^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ . They confirmed that the white solids obtained after different times were *N,N'*-dimethylterephthalamide only. The thermograms showed a single endothermic peak at  $318^\circ\text{C}$  that was indicative of their melting point and the formation of a single compound. The same endothermic peak at  $318^\circ\text{C}$  was recorded in the DTA thermogram of the white precipitates obtained after aminolysis in the absence of a catalyst and in the DTA thermogram of the reference sample, as shown in Figure 6.

Figures 7 and 8 show the IR spectra of the white precipitates obtained in the presence of a catalyst dur-

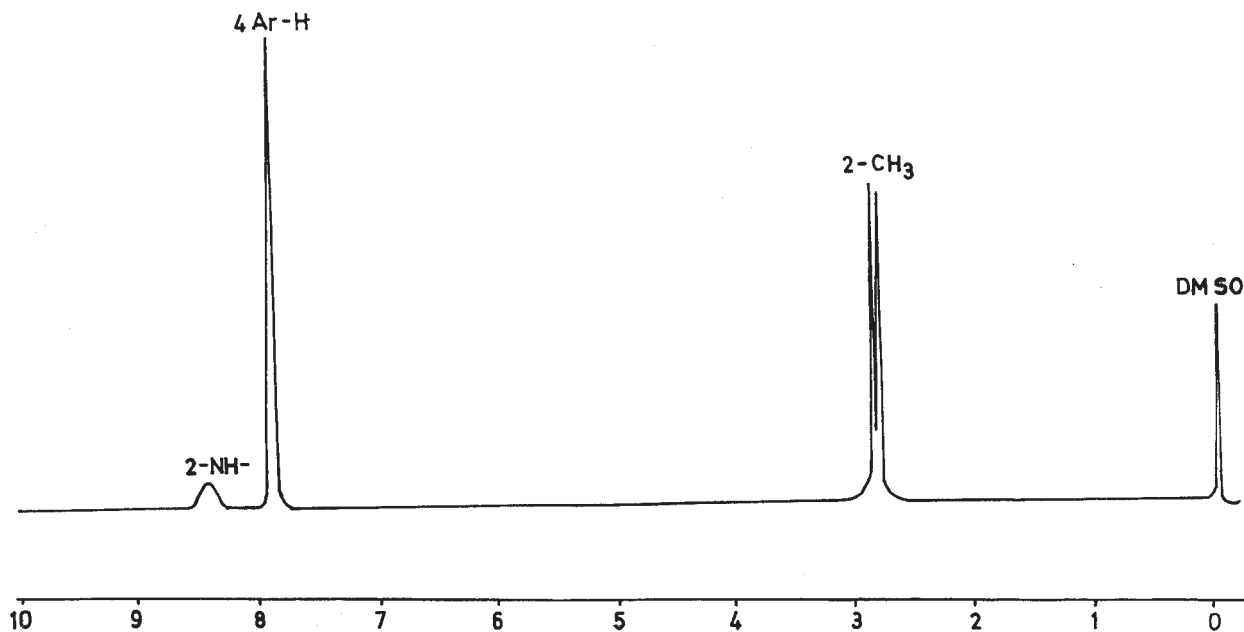


Figure 1  $^1\text{H-NMR}$  spectrum of  $N,N'$ -dimethylterephthalamide synthesized by the aminolysis of PET waste in the presence of a catalyst.

ing aminolysis and  $N,N'$ -dimethylterephthalamide synthesized by the reaction of terephthaloyl chloride with  $\text{CH}_3\text{NH}_2$ . The IR spectra clearly show the same characteristic absorption bands for  $N,N'$ -dimethylterephthalamide and the reference sample. The absorption bands at  $3310$  and  $1670\text{ cm}^{-1}$  were attributed to  $\text{N-H}$  stretching and  $\text{C=O}$  stretching, respectively, and these bands were characteristic of a secondary amide. The  $\text{C=O}$  absorption of amides occurred at

longer wavelengths than the normal carbonyl absorption because of mesomerism. Absorption bands characteristic of a benzenoid compound were also observed at  $1660\text{--}2000\text{ cm}^{-1}$ . Furthermore, the fingerprint region ( $990\text{--}1400\text{ cm}^{-1}$ ) and the large number of unassigned vibrations in this region were the same in all the IR spectra. This proof of identity of the white precipitates with the reference sample of  $N,N'$ -dimethylterephthalamide was far more characteristic than a

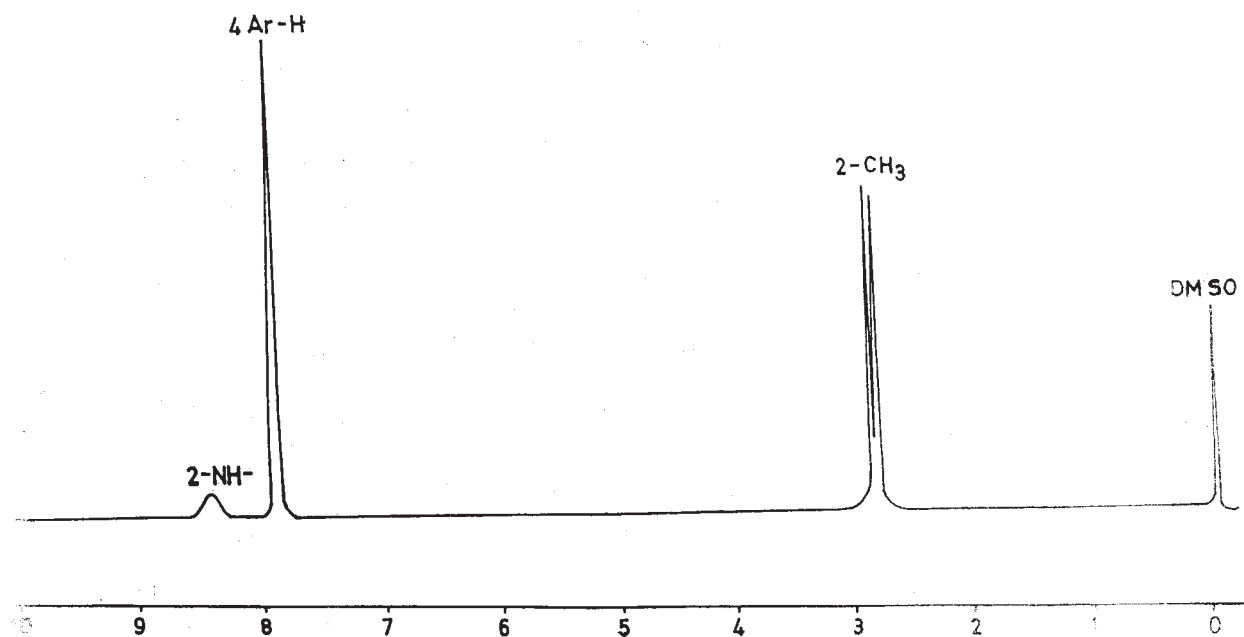
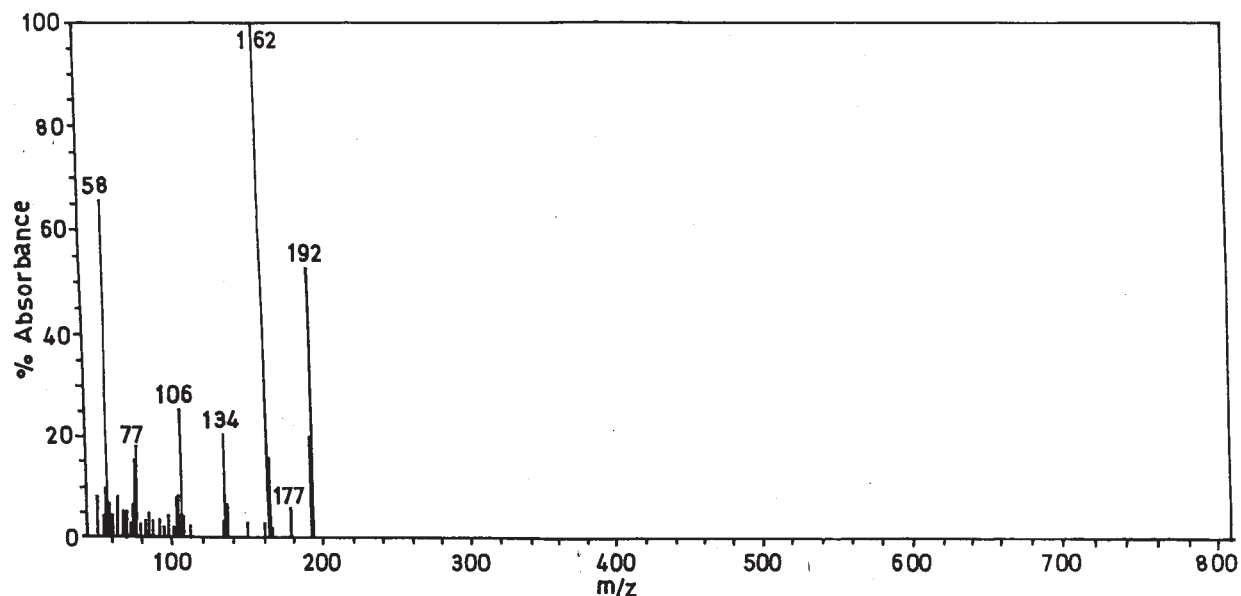


Figure 2  $^1\text{H-NMR}$  spectrum of reference  $N,N'$ -dimethylterephthalamide.



**Figure 3** MS spectrum of *N,N'*-dimethylterephthalamide synthesized by the aminolysis of PET waste in the presence of a catalyst.

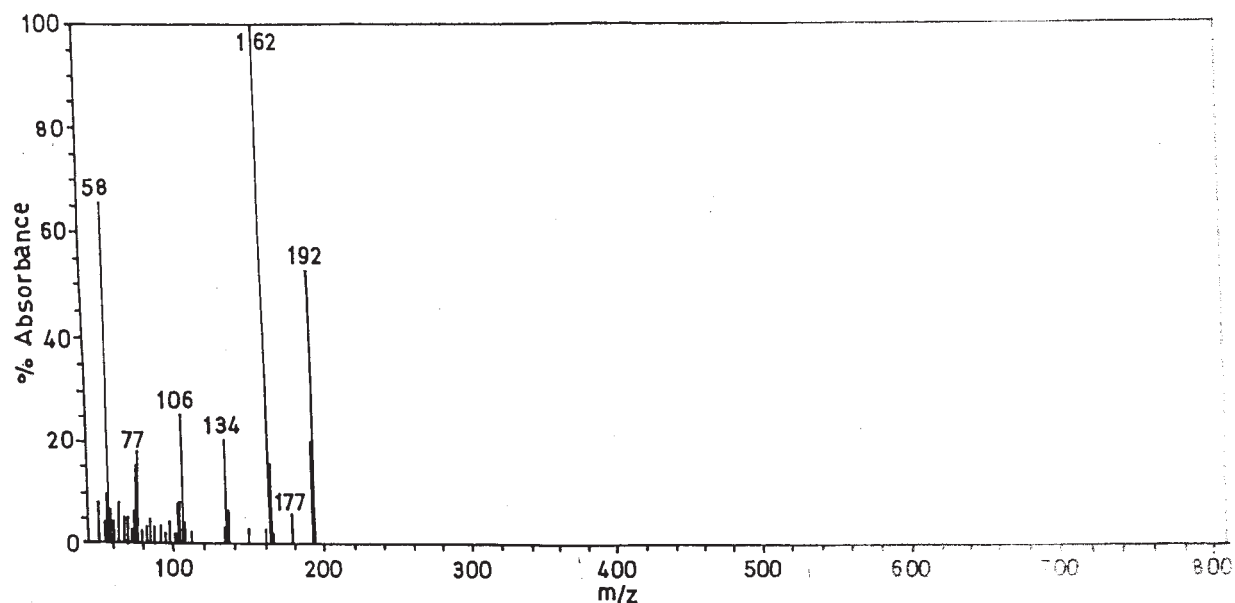
comparison of any other physical property. The IR spectra of all the white precipitates obtained during the course of degradation through aminolysis for various times were also the same.

Only one product as *N,N'*-dimethylterephthalamide was obtained throughout the aminolysis of PET waste carried out for various times (3, 7, 15, 21, 25, 30, and 45 days). Table II summarizes the weight of unreacted PET waste and degraded products so formed in the presence and absence of a catalyst after different periods. This revealed that in the absence of a catalyst,

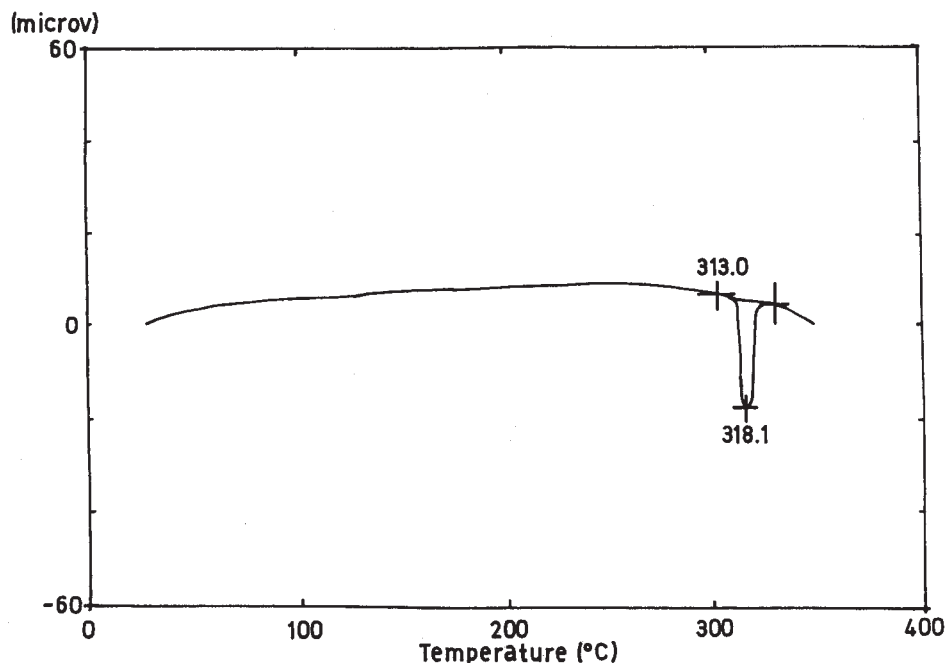
even after 45 days of reaction, 13 wt % of the PET waste was unreacted, whereas in the presence of a catalyst, the reaction was completed after 30 days, and after 45 days, no PET waste flakes were unreacted.

#### Spectroscopy and DTA of the white precipitates obtained by the reaction with $\text{NH}_3$

Figure 9 shows the  $^1\text{H-NMR}$  spectra of the products obtained through the ammonolysis of PET waste flakes in the presence of a catalyst; they show absorp-



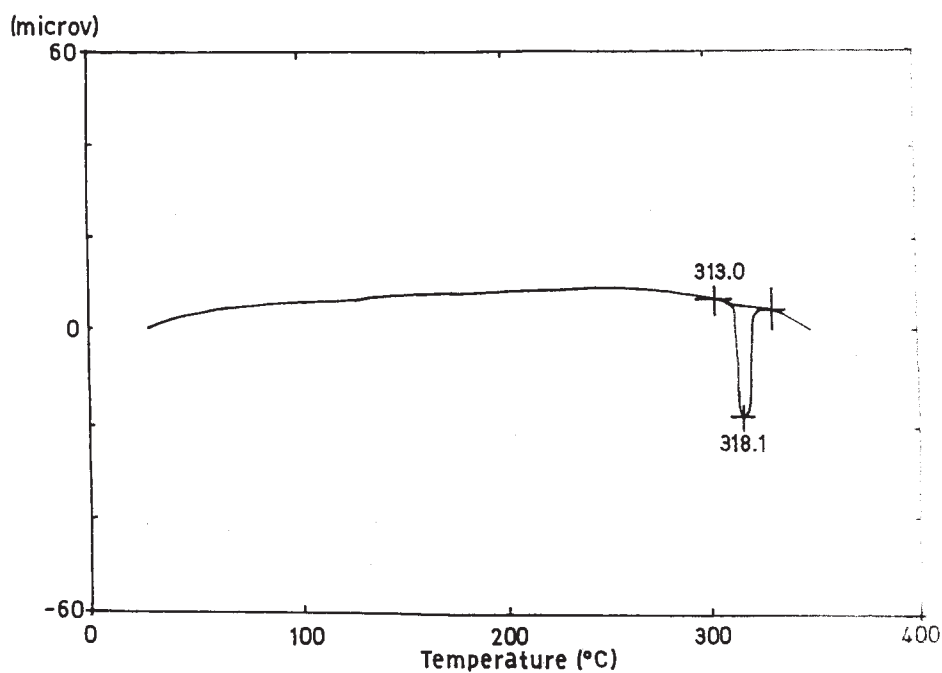
**Figure 4** MS spectrum of reference *N,N'*-dimethylterephthalamide.



**Figure 5** DTA thermogram of *N,N'*-dimethylterephthalamide synthesized by the aminolysis of PET waste in the presence of a catalyst.

tion by CO—NH protons at  $7.3\delta$  as a low hump. A sharp singlet at  $8.02\delta$  was attributed to four Ar—H protons. The same  $^1\text{H-NMR}$  spectra were obtained for the products obtained in the absence of a catalyst and for the reference sample prepared through the reaction of terephthaloyl chloride with  $\text{NH}_3$ , as shown in Figure 10.

Figure 11 shows the mass spectrum of the white precipitates obtained from the ammonolysis of PET waste in the presence of a catalyst. These precipitates upon an electron impact yielded a molecular ion peak at  $m/z = 164$  ( $\text{M}^+$ ) and a base peak at  $m/z = 148$  (100%). Subsequent fragment peaks were found at  $m/z$  values of 120, 103, 92, 57, and so forth and could



**Figure 6** DTA thermogram of reference *N,N'*-dimethylterephthalamide.



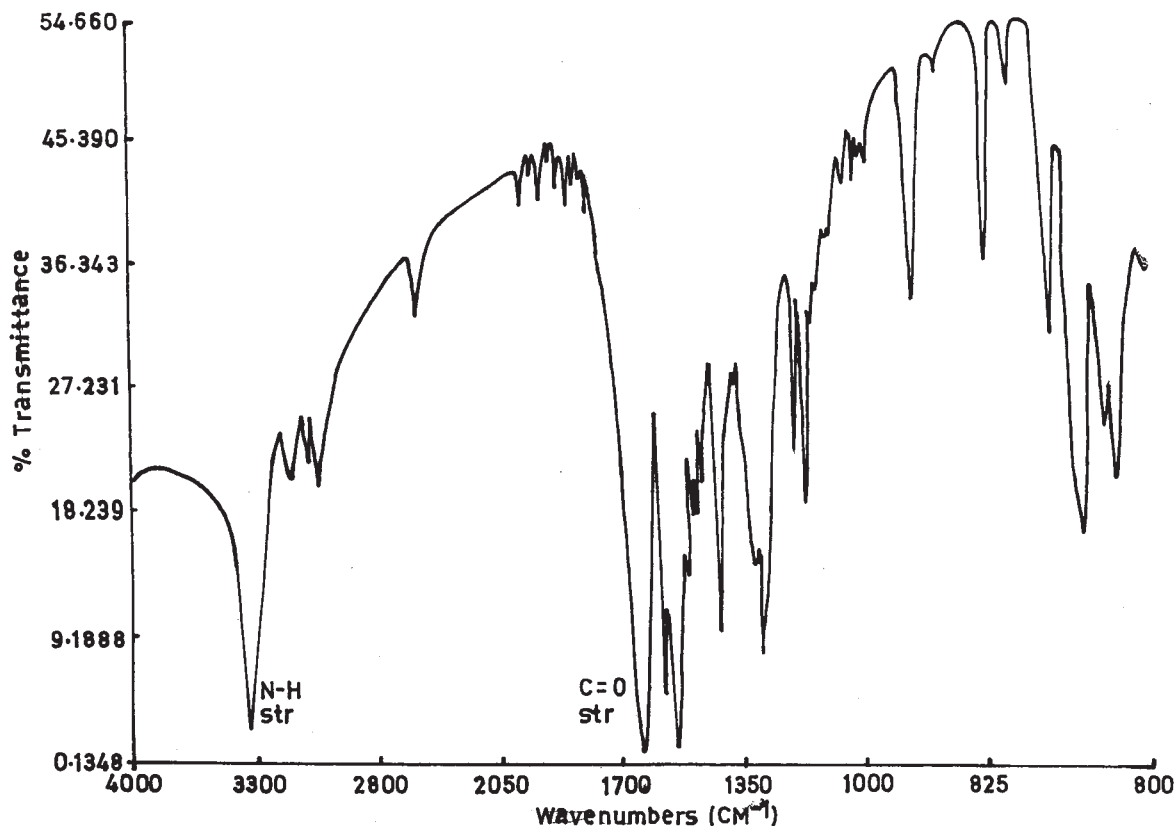


Figure 7 IR spectrum of *N,N'*-dimethylterephthalamide synthesized by the aminolysis of PET waste in the presence of a catalyst.

only result from terephthalamide. Exactly the same results were recorded in the mass spectrum of the white precipitates obtained by ammonolysis in the absence of a catalyst and for the reference sample prepared through the reaction of terephthaloyl chloride with  $\text{NH}_3$ , as shown in Figure 12.

Figures 13 and 14 show the DTA thermograms recorded for the white solids obtained by ammonolysis in the presence of a catalyst and for the reference sample of terephthalamide from room temperature to  $400^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ . They confirmed that the two white solids prepared from PET waste flakes under different conditions were the same. The thermograms showed a single endothermic peak at  $333\text{--}334^\circ\text{C}$  that was indicative of their melting point and the formation of a single compound.

Figure 15 shows the IR spectra recorded for the resulting terephthalamide obtained in the presence of a catalyst and similar results in the absence of a catalyst. The spectra show a pair of absorption bands at  $3200\text{--}3350\text{ cm}^{-1}$  that were attributed to N—H stretching and were characteristic of a primary amide (the separation between the two bands was  $150\text{ cm}^{-1}$ ). These bands were not associated simply with symmetrical and asymmetrical N—H stretching but arose from different degrees of asso-

ciation in amides. Two absorption bands observed at  $1640\text{--}1690\text{ cm}^{-1}$  were attributed to C=O stretching. C=O absorption was observed at longer wavelengths than normal C=O absorption because of mesomerism. C=O stretching and N—H deformation, being coupled vibrations, led to a pair of bands; the higher frequency band was predominantly C=O stretching, and the lower was predominantly N—H deformation. C—C multiple-bond stretching absorptions in aromatics, characteristic of a benzenoid compound, were observed at  $1660\text{--}2000\text{ cm}^{-1}$ . The IR spectra of the reference sample of terephthalamide, as shown in Figure 16, clearly shows the same absorption bands and the same unassigned vibrations in the fingerprint region ( $990\text{--}1400\text{ cm}^{-1}$ ) observed in the IR spectra of the two white precipitates. IR spectra of all the white precipitates obtained during the course of degradation through ammonolysis for various times were the same, and so only one spectrum is presented for each condition.

TLC of terephthalamide synthesized by aminolysis and ammonolysis and a comparison with a reference terephthalamide confirmed the purity of the compounds so synthesized. The  $R_f$  values for all the compounds were found to be the same (i.e., 0.8).

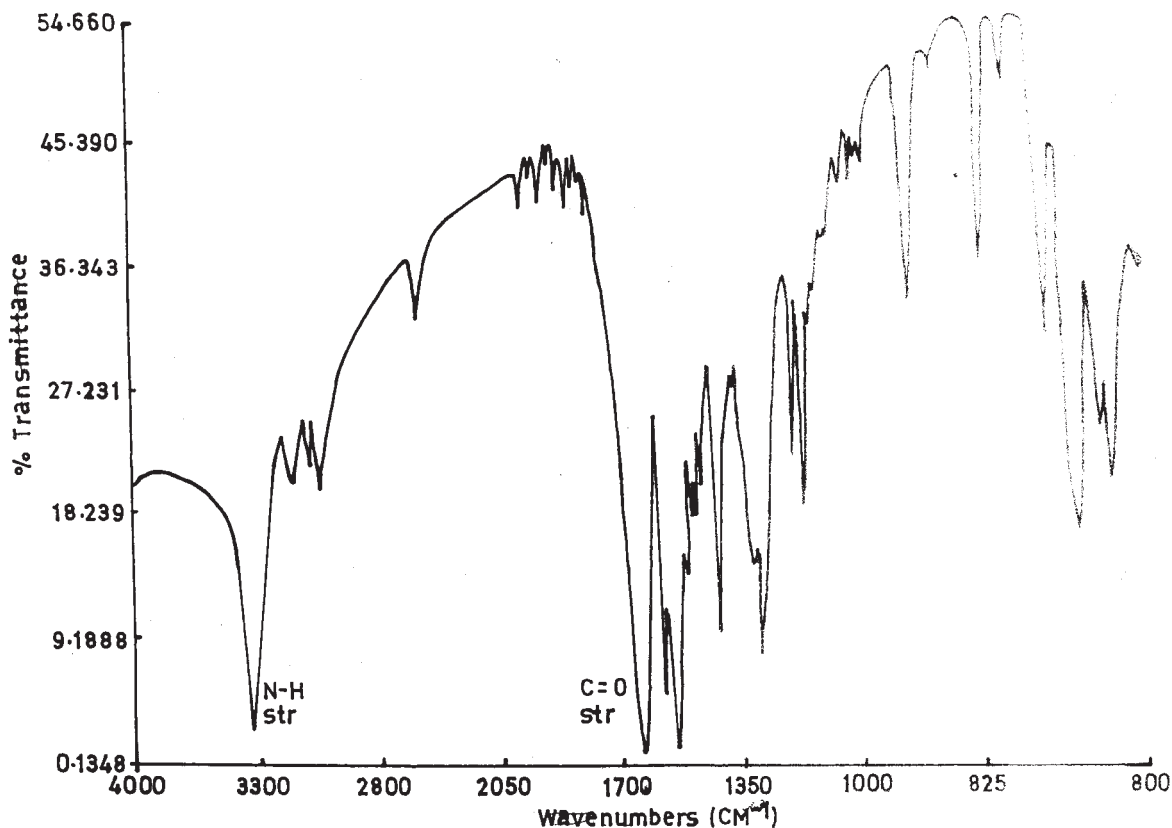
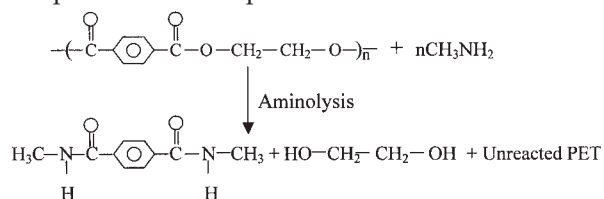


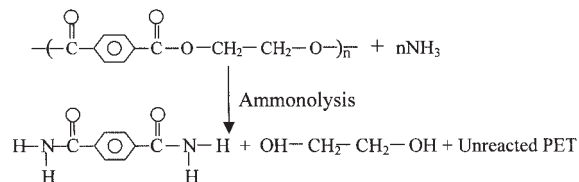
Figure 8 IR spectrum of reference *N,N'*-dimethylterephthalamide.

**Chemical structure of the white precipitates obtained by aminolysis and ammonolysis**

The aminolysis of PET waste produced *N,N'*-dimethylterephthalamide as per follows:



The ammonolysis of PET waste produced terephthalamide as follows:



**TABLE II**  
Weight of Unreacted PET and Degraded Product During Aminolysis and Ammonolysis in the Presence and Absence of a Catalyst

Days	Unreacted PET waste (g)				Product (g)			
	Aminolysis		Ammonolysis		Aminolysis		Ammonolysis	
	Catalyst	No catalyst	Catalyst	No catalyst	Catalyst	No catalyst	Catalyst	No catalyst
0	10.0	10.0	10.0	10.0	0	0	0	0
3	6.7	8.3	9.0	9.4	3.1	1.5	0.7	0.6
7	5.3	7.2	8.1	8.6	4.5	2.6	1.7	1.4
15	4.1	5.6	6.9	7.3	5.6	4.2	3.0	2.7
21	3.2	4.0	6.2	7.1	6.3	5.7	3.6	2.9
25	2.7	3.5	6.0	6.9	7.0	6.2	3.8	3.1
30	1.9	2.9	PET becomes Brittle		7.9	6.8	PET becomes Brittle	
45	0.0	1.3			9.4	8.4		



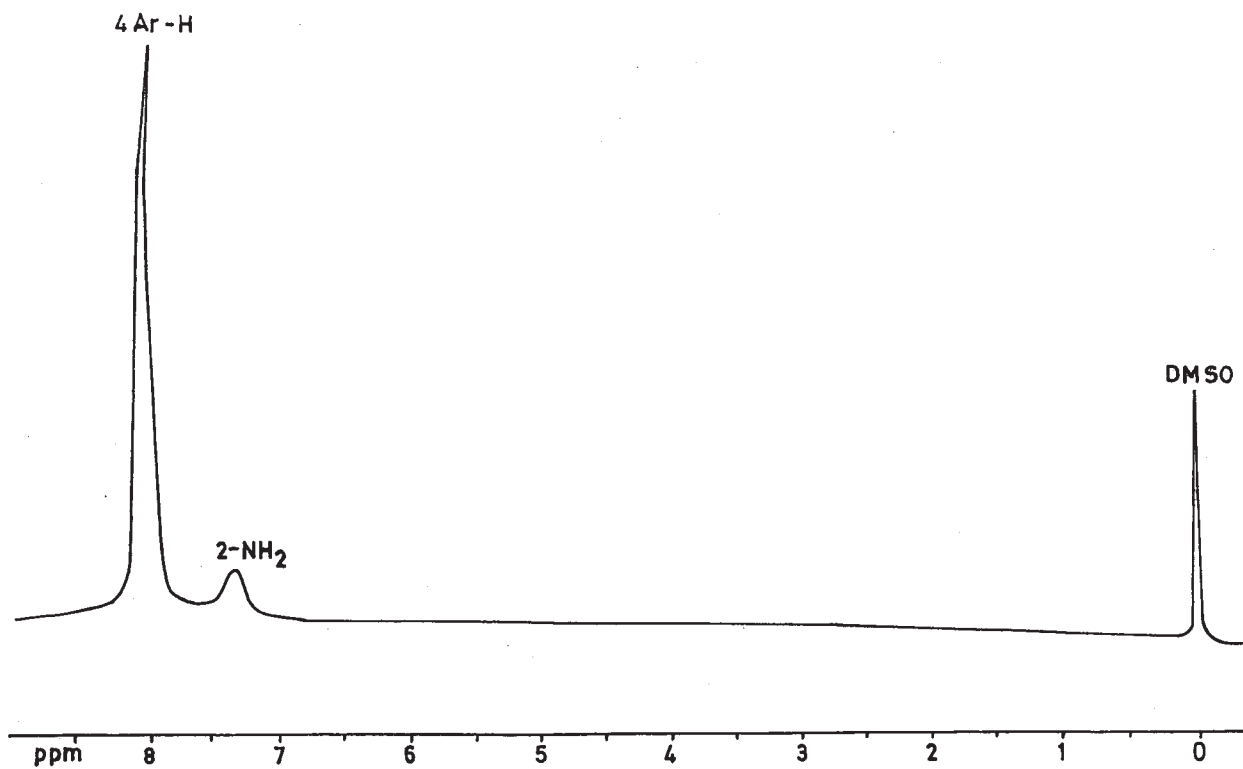


Figure 9 <sup>1</sup>H-NMR spectrum of terephthalamide synthesized by the ammonolysis of PET waste in the presence of a catalyst.

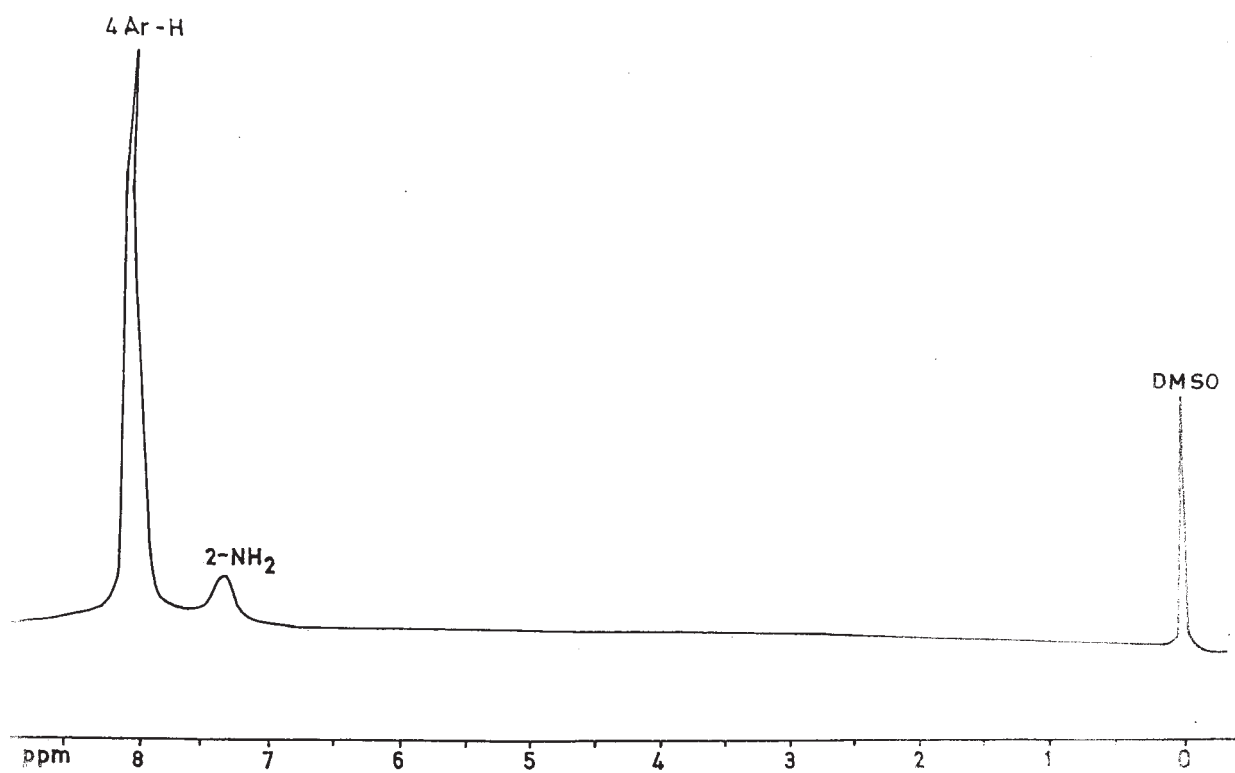


Figure 10 <sup>1</sup>H-NMR spectrum of reference terephthalamide.

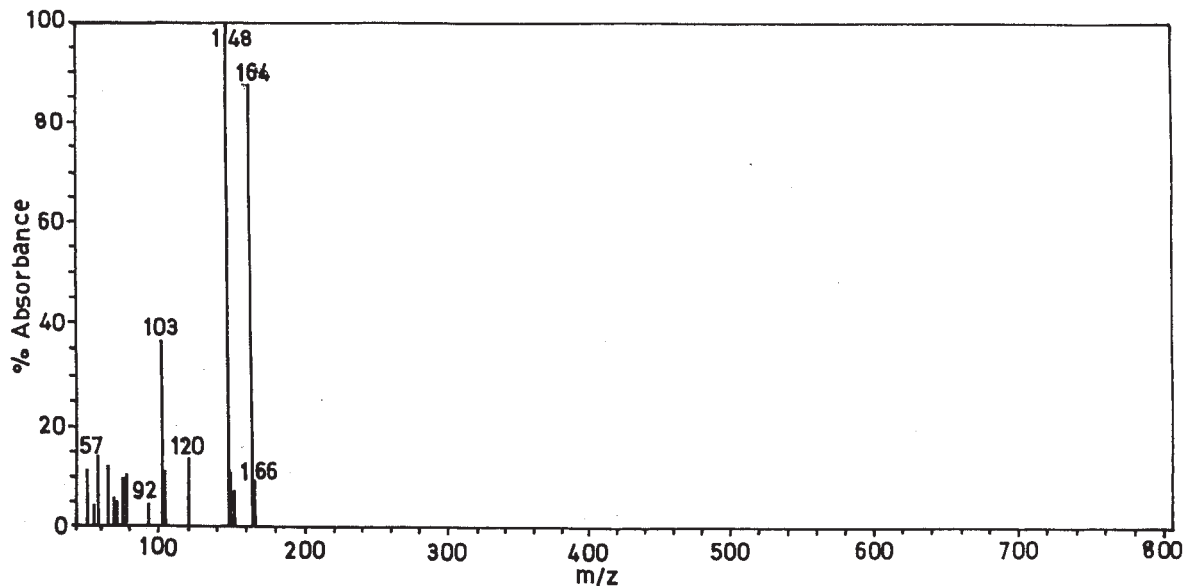


Figure 11 MS spectrum of terephthalamide synthesized by the ammonolysis of PET waste in the presence of a catalyst.

The ammonolysis of PET waste led to the formation of the same terephthalamide as the sole product throughout the reaction carried out for various times (3, 7, 15, 21, 25, 30, and 45 days). Furthermore, Table II shows the weights of unreacted PET under both conditions and indicates that degradation in the presence of a catalyst occurred at a faster rate than in the absence of a catalyst. Reference terephthalamides were prepared successfully in the laboratory via terephthaloyl chloride (bp = 263°C) and were characterized. Comparative studies of aminolyzed and ammonolyzed products were performed

with the reference terephthalamides with spectroscopic techniques (IR,  $^1\text{H-NMR}$ , and MS), DTA, and chromatographic studies. On the basis of these studies, the products so prepared were characterized and elucidated for their structures.

Thus, on the basis of spectral analysis, DTA, and a comparison with reference samples, the white precipitates obtained from the aminolysis and ammonolysis of PET waste flakes were confirmed to be *N,N'*-dimethylterephthalamide and terephthalamide, respectively:

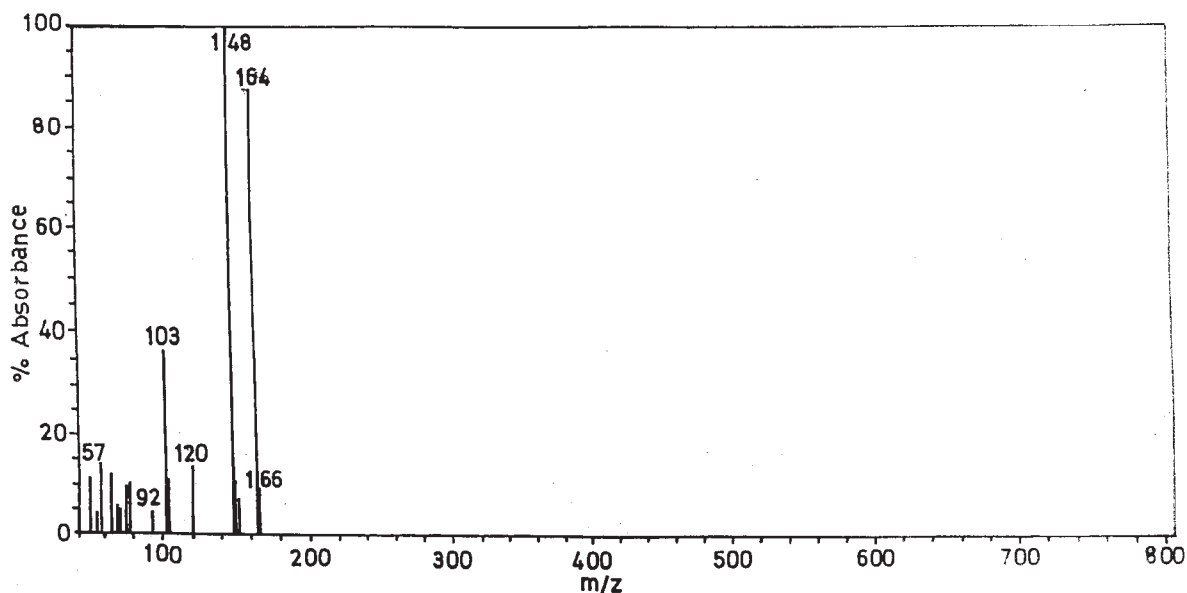


Figure 12 MS spectrum of reference terephthalamide.

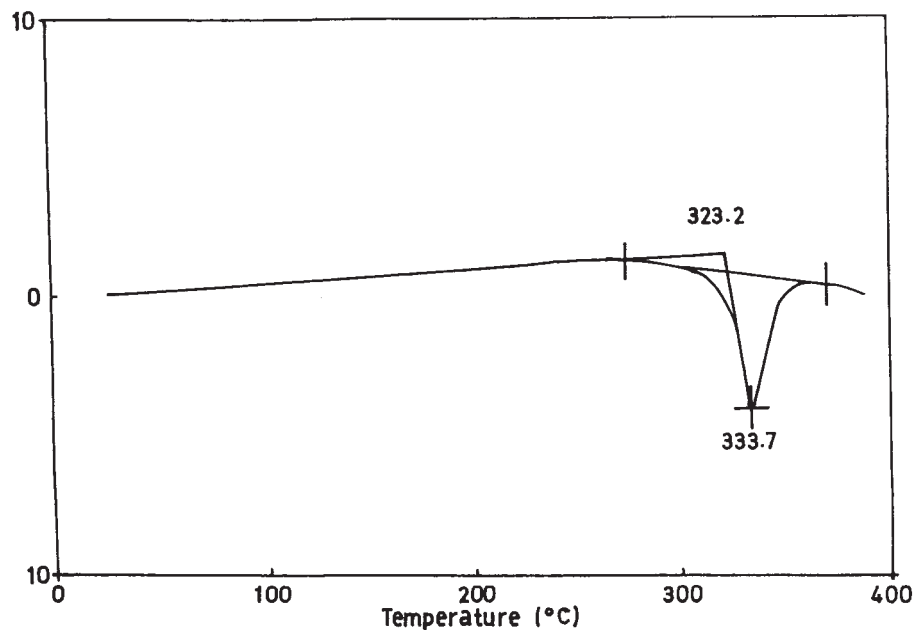
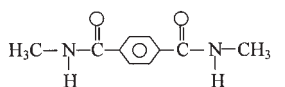
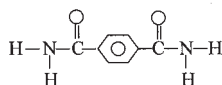


Figure 13 DTA thermogram of terephthalamide synthesized by the ammonolysis of PET waste in the presence of a catalyst.



*N,N'*-Dimethylterephthalamide



Terephthalamide

Scheme 1 provides a clear summary of the preparation of *N,N'*-dimethylterephthalamide and terephthalamide via different routes.

Both *N,N'*-dimethylterephthalamide and terephthalamide were soluble in solvents such as ethanol, dimethylformamide, and DMSO and insoluble in acetone, dichloromethane, carbon tetrachloride, and xylene. TLC of the terephthalamides synthesized by the aminolysis and ammonolysis of PET waste

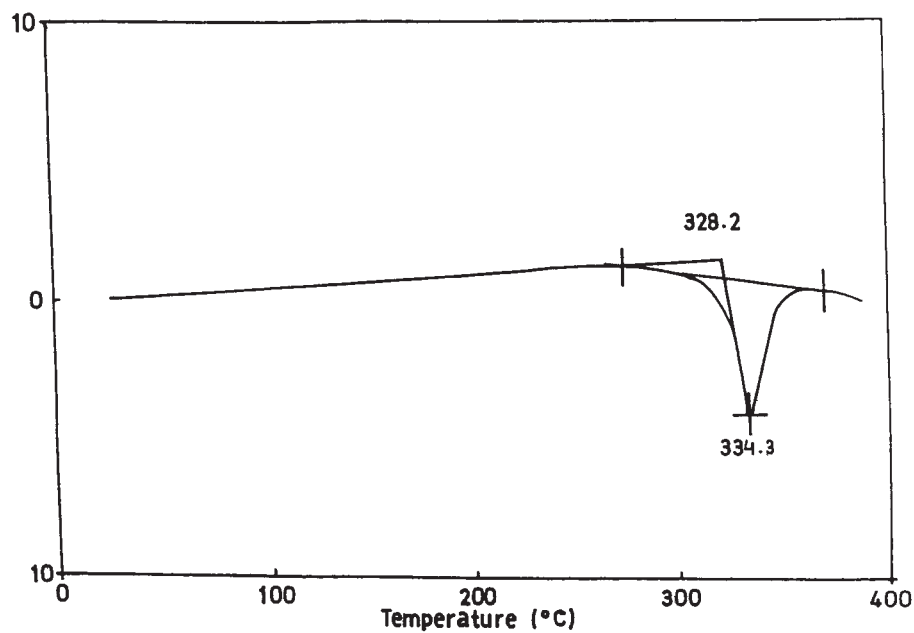


Figure 14 DTA thermogram of reference terephthalamide.

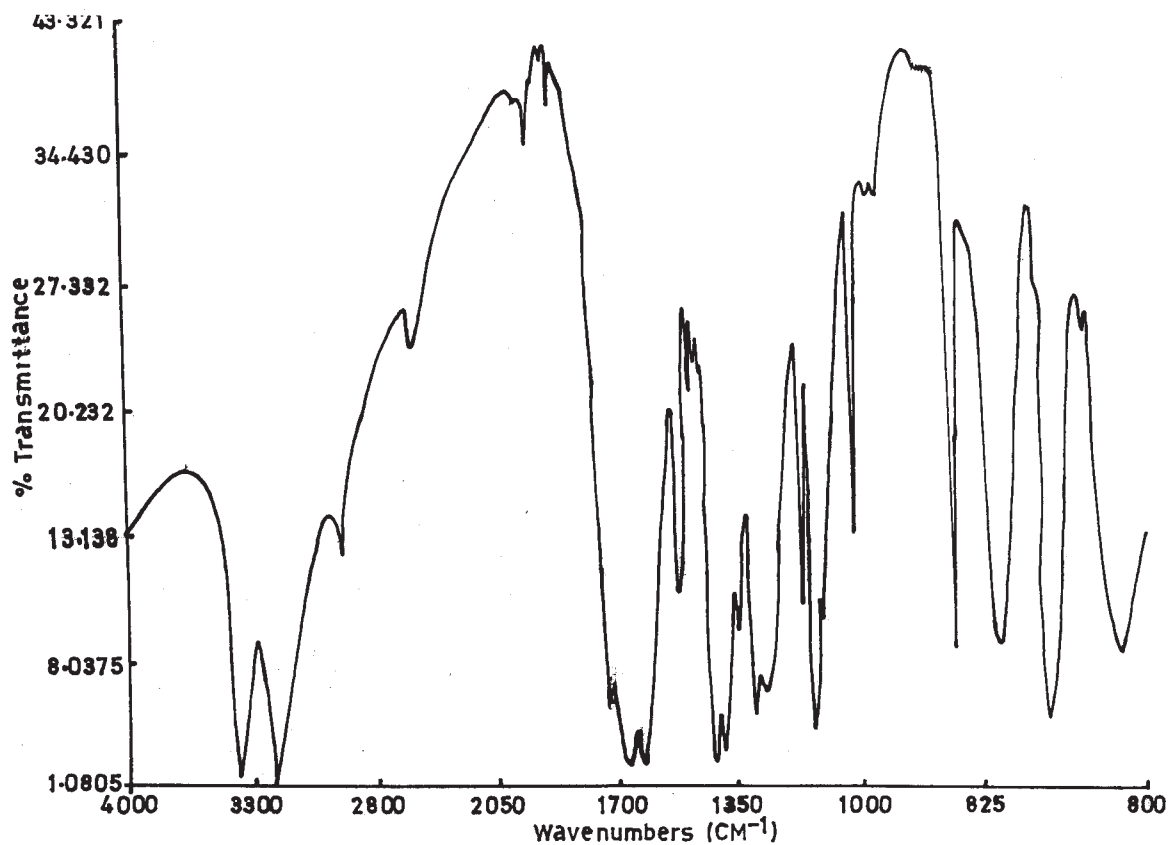


Figure 15 IR spectrum of terephthalamide synthesized by the ammonolysis of PET waste in the presence of a catalyst.

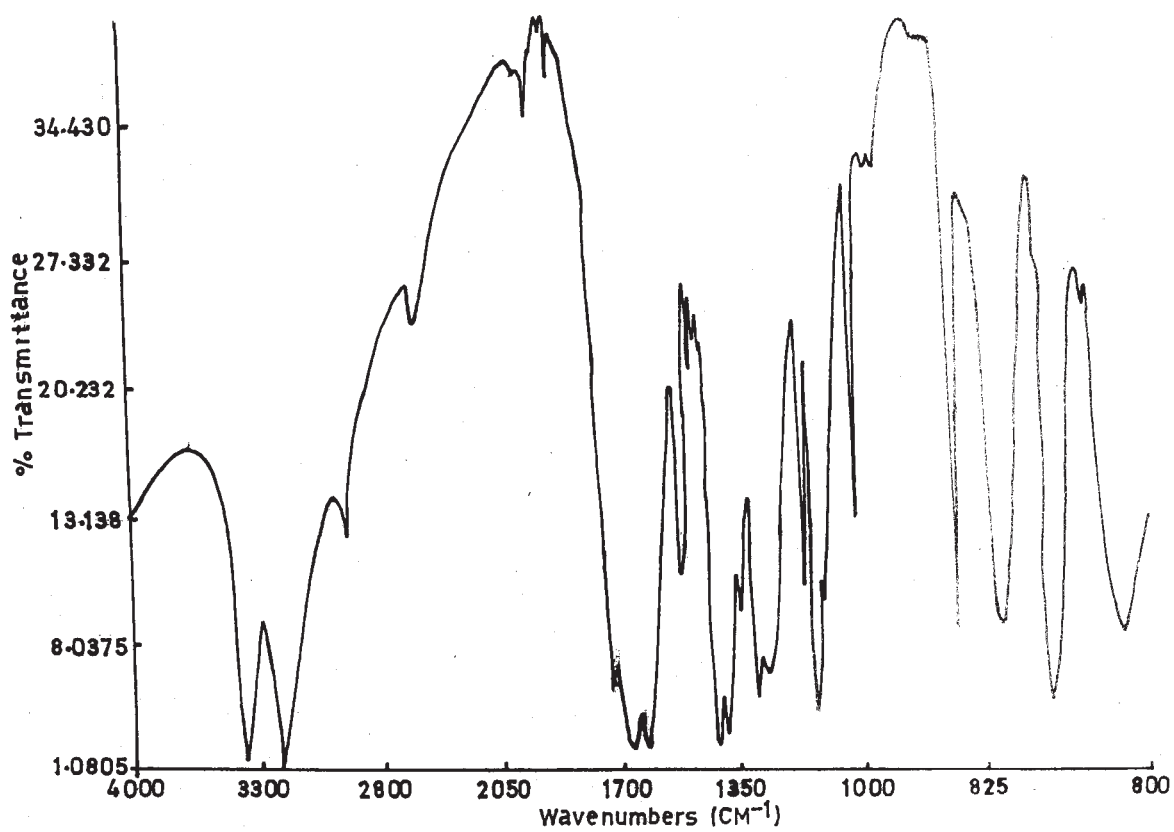
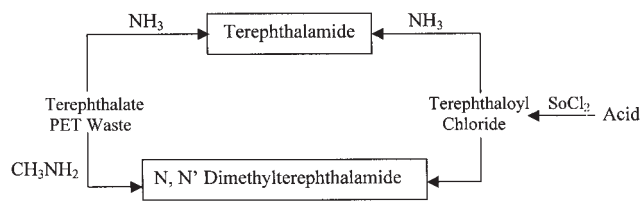


Figure 16 IR spectrum of reference terephthalamide.

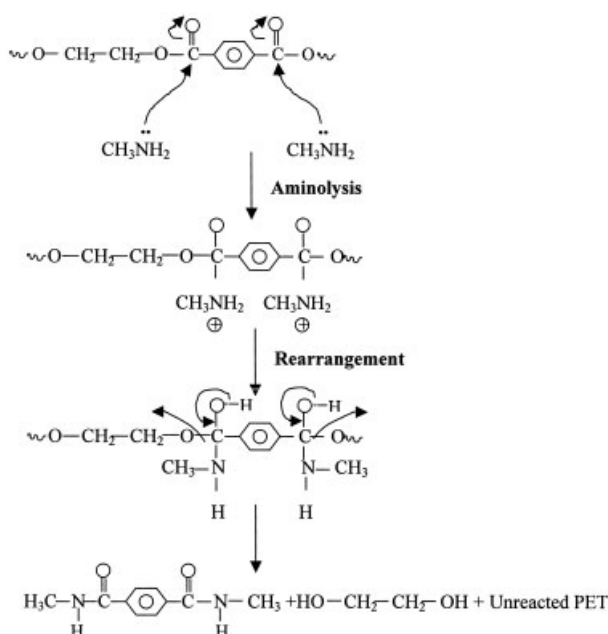


**Scheme 1** Preparation of terephthalamides.

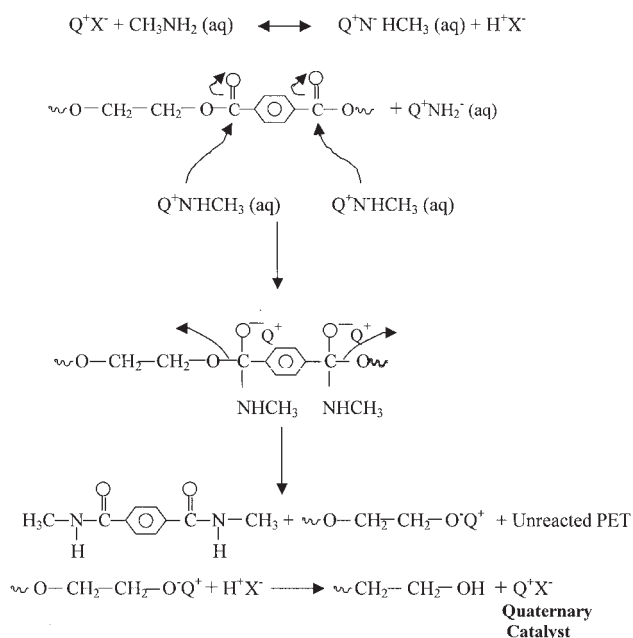
flakes and a comparison with reference terephthalamides confirmed the purity of the synthesized compounds.

The presence of a catalyst increased the rate of degradation for both  $\text{CH}_3\text{NH}_2$  and  $\text{NH}_3$ . In aminolysis, the catalyst increased the rate of degradation throughout the reaction, and the effect was more pronounced for the first few days than toward the completion of the reaction. The reaction was completed after 30 or after 45 days, and no PET waste flakes were unreacted. Although in the ammonolysis of PET waste there was an increase in degradation with the passage of time, ammonolysis proceeded at a slow rate in comparison with aminolysis. Toward the completion of the reaction, the rate of degradation became constant, and all the residual PET flakes became brittle.

There are two different phases involved in both aminolysis and ammonolysis: aqueous ( $\text{CH}_3\text{NH}_2/\text{NH}_3$ ) and solid (polymer). The aqueous phase is expected to carry a nucleophile.  $\text{CH}_3\text{NH}_2$  and  $\text{NH}_3$  are much weaker acids than water. Because acids can hardly catalyze the reaction, this reaction occurs not by an electrophilic mecha-



**Scheme 2** Proposed mechanism of PET degradation by aminolysis (in the absence of a catalyst).



**Scheme 3** Proposed mechanism of PET degradation by aminolysis (in the presence of a catalyst).

nism but by a nucleophilic mechanism, and so the rate of degradation is slow. However, it cannot be concluded whether the reaction occurs by random scission or by unzipping. If degradation occurs by random scission, the same product should not be obtained at different times, and the possibility of the formation of other terephthalamides cannot be ruled out. Because we obtained the same white solid and 100% pure terephthalamides, it cannot be concluded that the reaction occurs by random scission. If degradation occurs by unzipping, degradation should start at one end and finish at the other end. However, because the amorphous region of PET undergoes degradation more rapidly than the crystalline region, unzipping also seems to be unreasonable.  $\text{CH}_3\text{NH}_2$  acts as a nucleophile and attacks PET at the electron-deficient center ( $\text{C}=\text{O}$ ). This is followed by rearrangement resulting in product formation. Scheme 2 presents a proposed picture of PET degradation by aminolysis in the absence of a catalyst.

Ammonolysis is supposed to take place in a similar fashion.

When a quaternary salt ( $\text{Q}^+\text{X}^-$ ) is added to the mixture, it is expected to exchange its anion with the excess of the nucleophile in the aqueous phase. Scheme 3 presents the proposed mechanism for PET degradation by aminolysis in the presence of a catalyst.  $\text{Q}^+\text{NH}_2^-$  attacks the polymer, and displacement occurs with the product formation. The regeneration of the catalyst occurs as shown in Scheme 3.

## CONCLUSIONS

This work involved the formation of amides (*N,N'*-dimethylterephthalamide and terephthalamide) through the

degradation of molded-grade PET waste flakes with 40% aqueous  $\text{CH}_3\text{NH}_2$  (aminolysis) and  $\text{NH}_3$  (ammonolysis), respectively, at room temperature under two different conditions (in the presence of a quaternary ammonium salt and in its absence) for various times. The ultimate degraded products were analyzed and characterized with chemical reactions, spectral data (IR,  $^1\text{H-NMR}$ , and MS), DTA, TLC, and comparisons with the reference samples prepared separately in the laboratory.

Thus, technology has been developed for the reutilization of industrial PET waste. The prepared  $N,N'$ -dimethylterephthalamide and terephthalamide can be used as amide hardeners in epoxies for various applications, such as adhesives and polyurethane foams.

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