

Studies on Synthesis and Characterization of a Novel Acrylic Aromatic Amide Oligomer of Aminolysed Endproducts Generated from Pet Waste with Hydrazine Monohydrate and Its Photocuring with Acrylate Monomers

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ABSTRACT: A novel acrylic aromatic amide oligomer was synthesized by using depolymerized end product of PET waste with hydrazine monohydrate. The end product of aminolysed PET waste was synthesized under ambient conditions and was used in the preparation of novel acrylic oligomer with the reaction of acryloyl chloride prepared from acrylic acid. The acrylic oligomer was characterized by spectroscopic techniques, such as FTIR, $^1\text{H-NMR}$, UV, Mass spectrometry, and by other analytical techniques such as, Iodine value, TGA, and DSC. The proposed structure of the oligomer is supported by its spectral analysis and the same is inferred from other

techniques. The acrylic oligomer mixed with other acrylate monomers such as methylmethacrylate, ethylhexylacrylate, acrylic acid, and photoinitiator, can be cured by UV radiation and can thus be used as an adhesion promoter on metal/glass surface. This article presents the possibility of using a difunctional aromatic amide oligomer with excellent hydrogen bonding capacity as an alternative to urethane acrylates in radiation curable formulations. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 638–645, 2010

Key words: acrylate; PET waste recycling; UV curing

INTRODUCTION

Radiation induced polymerization is an efficient method for fast generation of highly crosslinked polymer networks from liquid resin systems.¹ Various types of radiations, such as UV radiation,² γ radiation,³ and electron beams⁴ are used for initiation of polymerization reaction. Of these, UV radiation curing is a method of choice because of lower cost of equipment and also the safety requirements can easily be met. UV cured coatings have both ecological and economical benefits over other kinds of coatings. It is the most ecoefficient technology when compared with different industrial coating technologies under ecoefficiency analysis.⁵ The UV radiation curable resins are widely used in various industrial sectors, due to their distinct advantages, mainly a great speed of cure, low energy consumption, solvent free formulations, high quality end products, and room temperature operations.^{6–11} This technology has experienced steady growth over the past decade and has found a large variety of applications mainly in coating industry, printing inks, fast drying

varnishes, UV curable adhesives,¹² and as photore-sist for imaging applications.¹³ Glass laminates have been readily obtained by photocuring of acrylic adhesives consisting either of a liquid resin or a solid thermoplastic polymer.¹⁴ A UV curable composition consists usually of multifunctional monomers and oligomers, with small amount of photoinitiator that generates reactive species on UV exposure. Acrylate, methacrylate, and other unsaturated monomers are widely used in coatings, adhesives, sealants and can be crosslinked by UV light radiation or by peroxide initiated free radical cure.¹⁵ Urethane coatings are used wherever applications require abrasion resistance, skin flexibility, good adhesion, and chemical resistance.^{16,17} Urethane acrylate monomers introduce toughness into cured coatings. The increased toughness is attributed in part to the hydrogen bonding capacity of the urethane group. Hydrogen bonds from the urethane groups of the hard segments give rise to the physical network,^{18,19} which account in part for many desired properties, such as tensile strength, elongation, and improved surface or pigment wetting. Their synthesis involves reactions of alcohols and amines with toxic isocyanates and hence has a higher risk factor.²⁰ Oligomers are often not commercially available because of the difficulty or expense required to produce them in large quantities. Now, it is the time to meet the

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future demands of this fast growing market of UV technology, i.e., simplified formulations, increased cost efficiency, and easier environmental compliance.

There are very few synthetic approaches to introduce nitrogen based hydrogen bonding moieties into radiation curable formulations. In our present work, we introduce a novel hydrogen bonding oligomer which is derived from the reaction of aminolysed end products of PET waste with acryloyl chloride. The synthesis of the oligomer involves two steps i.e. degradation of PET waste through aminolysis using hydrazine mono hydrate and then reacting the resulting end products with acryloyl chloride. The synthesized oligomer contains unsaturation which can be crosslinked using UV radiation. The oligomer can be added to other resins used in adhesives or composites and the developed films can be used as protective coatings and for laminating glasses and other substrates.

EXPERIMENTAL

Synthesis of aminolysed end product with hydrazine mono hydrate

PET waste used in this study was of blow molded grade and was procured from M/S NMC Ltd. Kolkata having a softening temperature of 260°C. The postconsumer PET bottles were chopped into small flakes and cleaned thoroughly by washing with soapy water and then with distilled water. The cleaned PET waste flakes were dried at 80°C for 5 h and then subjected to degradation with hydrazine monohydrate. Hydrazine monohydrate (99–100%) was procured from M/S Qualigens fine chemicals and used as received without further purification and was of LR grade.

The aminolysis of PET waste flakes was carried out with hydrazine monohydrate in a properly sealed reaction vessel with continuous constant stirring at ambient temperature and pressure. The reaction was started by mixing PET waste (10 g) with hydrazine monohydrate (20 mL) in a round bottom flask equipped with a mechanical stirrer. The reaction mixture is heterogeneous and to make a homogeneous suspension, it was stirred at a constant rate. After 12 h, the reaction was stopped and light yellow precipitate was separated and washed with plenty of water and then recrystallized with DMSO and dried at 70°C under vacuum. The synthesized aminolysed end product was characterized for FTIR, ¹H-NMR, UV, DSC as per procedure described in our earlier publication.²¹

Synthesis of novel acrylic aromatic amide oligomer of aminolysed end product

The aminolysed end products have been used to synthesize a UV curable acrylic aromatic amide

oligomer by reacting it with excess of acryloyl chloride.

Materials and characterization

The aminolysed end products used in the synthesis of novel oligomer were synthesized and characterized as per procedure given in the previous section. The recrystallized aminolysed end products were dried at 70°C under vacuum for 4 h to constant weight and used in the synthesis of TPDAC without further purification. Acryloyl chloride was synthesized by the reaction of acrylic acid with thionyl chloride. It was stabilized with 1% hydroquinone to avoid light induced polymerization. Nitrogen gas was passed through it at 40–50°C till it was free from HCl.

Procedure

Acryloyl chloride (100 mL) was measured into a 500 mL round bottom flask equipped with a mechanical stirrer, a water condenser and addition funnel. Aminolysed end products (10 g) was weighed and added in small portions to the flask through the addition funnel. The reaction was carried out for 48 h at a temperature of 70°C. Nitrogen gas was flushed continuously through the reaction mixture. The reaction was completed when a viscous yellow liquid was obtained, which solidify on cooling. The resulting reaction product was washed with water to make it free from excess of acryloyl chloride and then dried under vacuum dessicator at room temperature.

Characterization of oligomer obtained by reaction of aminolysed end products with acryloyl chloride

The iodine value of the oligomer was determined by dissolving 0.2 g of the oligomer in CHCl₃ by treating with iodine monochloride solution (N/10) in glacial acetic acid, the unused iodine is determined by titrating against standard sodium thiosulphate solution (N/10).

The iodine value was determined with the following formula-

$$\text{Iodine number} = \frac{(X - Y) \times 12.7 \times 100}{1000 \times \text{wt. of sample (g)}}$$

where *X* is the amount of sodium thiosulphate solution used (mL) for blank solution and *Y* is the amount of sodium thiosulphate solution (mL) used for sample solution.

The solubility of oligomer was determined in different solvents and was found soluble in dimethyl formamide and dimethyl sulphoxide. The synthesized oligomer was analyzed for the elements C, H, and N with the help of Varion EL III.

TABLE I
Composition of the Formulations Developed by Using Synthesized Oligomer (TPDAC), that has been Used for Preparing Glass laminates

Formulation no.	1	2	3	4	5	6	7
VER (g)	100	100	100	100	100	100	100
MMA (g)	12	12	12	12	12	12	12
EHA (g)	12	12	12	12	12	12	12
AA (g)	12	12	12	12	12	12	12
Photoinitiator (wt %)	3	3	3	3	3	3	3
TPDAC (g)	–	10	12	14	16	18	20

VER, divinylester resin; MMA, methylmethacrylate; EHA, 2-ethyl hexyl acrylate; AA, acrylic acid.

It was characterized with the help of UV, FTIR, ¹H-NMR, and Differential Scanning Calorimeter, Thermal Gravimetric analysis and Mass spectrometry. The ¹H-NMR Spectrum of the oligomer was recorded by using bruker spectrometer. The UV-Visible spectrum was recorded by dissolving the sample in DMSO using Double beam UV-Visible spectrophotometer, (Systronic 2201) at the scan rate of 2 nm/s. The FTIR spectrum was recorded on a Shimadzu IR spectrophotometer using KBr discs at scan rate of 4 cm⁻¹/s. The sample was also analyzed with the help of DSC, Mettler Star SW 9.01 at heating rate of 5°C/min from 50 to 300°C. Thermal gravimetric analysis was carried out at a heating rate of 20°C/min from 50 to 850°C with the help of thermal analyzer DuPont 2100 with module 951. Mass spectrum was recorded on a JEOL JMS-DX 303 mass spectrometer.

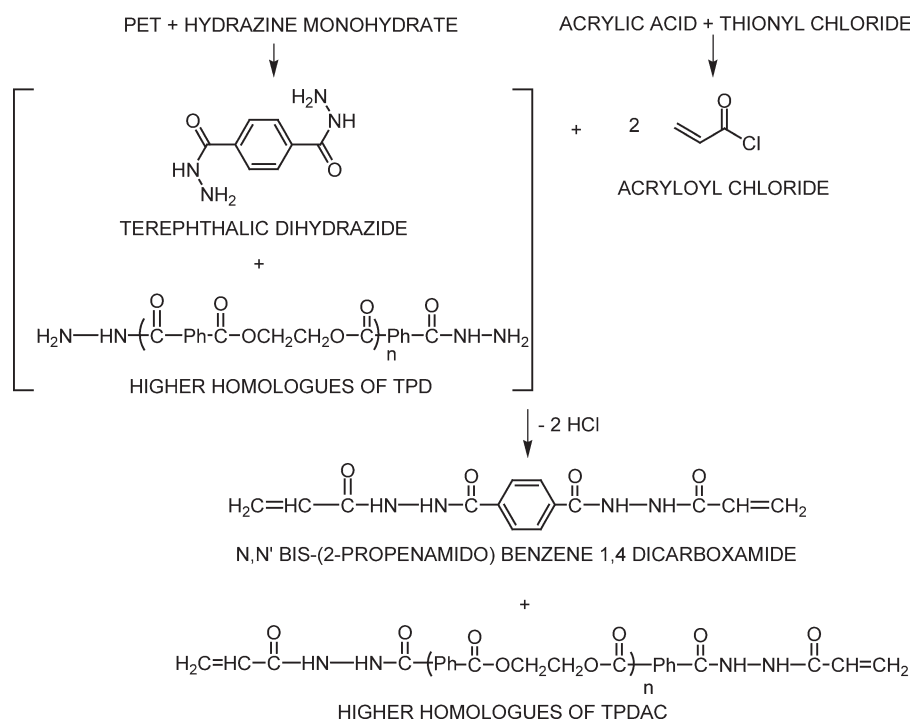
UV curing of oligomer with other acrylate monomers

The different UV curable formulations prepared from the synthesized oligomer (TPDAC) by mixing it with other acrylate monomers in different proportions are presented in Table I. The table also includes a formulation without TPDAC. These formulations include divinylester resin of DGEBA (diglycidal ether of bisphenol A), which was used as a base, monomers i.e. methylmethacrylate, 2-ethylhexylacrylate, acrylic acid, and TPDAC and Irgacure as a photoinitiator. These photo curable formulations were prepared from 100 g of Divinylester resin, 12 g of Acrylic acid, 12 g of EHA, 12 g of MMA, 3% by weight Irgacure, and a

varying amount of TPDAC in the range about 10 to 20 g. The formulations were flushed with nitrogen (4 h) and used in the preparation of glass laminates of dimensions 4 × 4 inch. 20 mg of each formulation was dispensed on a glass sheet of 3.5 mm thickness and another sheet of glass was placed carefully over this sheet in such a manner that no air bubble entrapped between the sheets and then exposed to UV radiation. The samples were cured under UV radiation by using four Philips TL-D 18W BLB UV tubes (made in Holland) arranged horizontally, two on each side in a UV chamber of dimensions 25 × 15.5 × 21 inch. The prepared glass laminates were tested for curing time and adhesion (boiling water test, hammer test). Each laminate was checked after 15 s while curing and the interlayer was tacky or sticky hence not completely cured (tacky time). The tack free time i.e. completely cured interlayer was noted for each laminate and reported in Table II. In the boil test, the prepared glass laminates were immersed in boiling water. The samples were kept in boiling water for 72 h and then removed. The pummel test was used to measure interlayer adhesion to glass. For hammer test (pummel test) twelve inch square glass laminates with 1.5 mm thick interlayer were prepared. The glass laminates were placed in a –18°C refrigerator for at least 2 h. After removal from the refrigerator, the laminates were placed on a metal substrate and hit repeatedly with a 16 oz hammer to break the glass. All broken glass unadhered to the interlayer was then removed. The amount of glass left adhered to the interlayer was visually compared with a set of standards of known

TABLE II
Shows Adhesion of Interlayer with Glass Through Boiling Water Test and Pummel Test

Formulation no.	Tacky time (s)	Tack free time (s)	Boiling water test (72 h)	Pummel value
1	15	>30	Delamination after 58 h	4
2	15	30	No delamination	6
3	15	<30	No delamination	7
4	15	28	No delamination	7
5	15	25	No delamination	8
6	15	25	No delamination	9
7	15	23	No delamination	9



Scheme 1 Synthesis of TPDAC from PET Waste.

pummel scale and a pummel value for each sample was assigned, ranging from a pummel value of 0 (no adhesion, no glass adhered) to 10 (high adhesion, 100% of the glass adhered).

RESULTS AND DISCUSSION

Synthesis of novel acrylic aromatic amide oligomer of aminolysed end product

The rate of depolymerization of PET waste is different with different amines, such as methyl amine, ethyl amine, *n*-butyl amine,²² etc. The degradation period of PET waste was found to be reduced in the presence of catalyst.²³ In case of hydrazine monohydrate complete degradation of PET waste was achieved in 24 h.²¹ In the present reaction, the yellow precipitate was separated after 12 h and an oligomeric mixture is obtained, which contains terephthalic dihydrazide with its higher homologues having molecular weights in the range 194–962.

The reaction of aminolysed end product with acryloyl chloride is an example of nucleophilic addition elimination reaction. Here NH_2 group present in aminolysed end product acts as a nucleophile and attacks the carbonyl carbon of acid chloride and then HCl molecule is eliminated. HCl is the side product in this reaction. Nitrogen gas is flushed continuously in order to avoid polymerization and flush out the HCl.

Characterization of novel acrylic aromatic amide oligomer of aminolysed end products

The synthesized aromatic amide oligomer i.e. TPDAC was characterized by spectroscopic techniques and other analytical techniques. Scheme 1 presents the synthesis of TPDAC from PET waste.

Iodine value

The iodine value of aromatic amide oligomer was determined as per procedure given in experimental section and it was found to be 74.10. Iodine value is the number of grams of iodine that combine with 100 g of the sample. Molecular weight (number average) of the synthesized oligomer was calculated on the basis of iodine value and was determined as 684.21 g. The experimental iodine value is less than the theoretical iodine value (168.07) of the monomer. The results of elemental analysis of TPDAC were C 59.6%, H 4.9%, and N 8.1%. The results indicate the presence of higher homologues in the aminolysed product of PET waste.

The oligomer is sparingly soluble in chloroform, carbon tetra chloride and ethanol, and completely soluble in dimethyl formamide and dimethyl sulphoxide.

FTIR spectral analysis

Figure 1 compares the FTIR spectrum of novel acrylic amide oligomer with that of aminolysed end

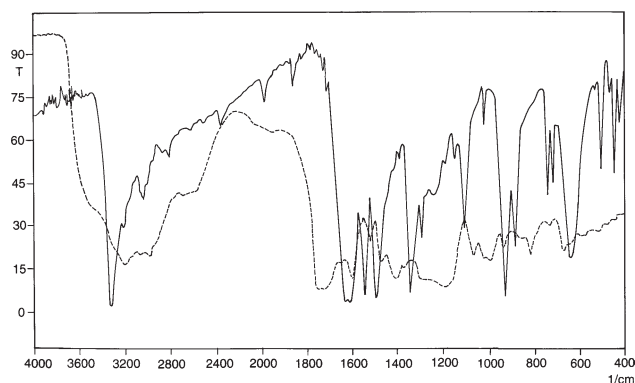


Figure 1 Comparative FTIR spectra of novel aromatic amide oligomer synthesized from PET waste (--) and aminolysed end products of PET waste with hydrazine monohydrate (—).

product obtained from PET waste. The FTIR spectrum of yellow precipitate (TPDAC) shows a single band at 3188 cm^{-1} that is attributed to N—H stretch, which is a characteristic of secondary amides in the solid samples. The bands at 1625 and 1517 cm^{-1} are amide I band and amide II band, respectively. These bands arise due to coupled vibrations of C=O stretch and N—H bending. The higher frequency band is predominantly C=O stretch and the lower is predominantly N—H bending. These are characteristic bands of secondary acyclic amides. The bands at 1598 and 1467 cm^{-1} suggest the presence of aromatic ring. The peak with an absorption band at 1361 cm^{-1} may be attributed to C—N stretch. A band at 812 cm^{-1} confirms Para substitution of aromatic ring. Two bands at 3028 and 2972 cm^{-1} are due to C—H stretch of sp^2 and sp^3 hybridized protons respectively. A band at 1728 cm^{-1} is due to C=O stretch of polymerized acryloyl chloride which is present as an impurity.

On examining the N—H stretch region it was found that a pair of absorption bands present at 3315 cm^{-1} in the FTIR spectrum of Aminolysed end products is absent in the FTIR spectrum of oligomer (Fig. 1) and instead a single band at 3188 cm^{-1} is present. The absence of doublet in the N—H stretch region indicates that acrylic moiety has been attached to both ends of terephthalic dihydrazide and its higher homologues. This N—H stretch band is broad and is at lower wavenumber, which may be due to intermolecular hydrogen bonding. One new C=O stretch has been introduced in the oligomer but both the C=O stretches are not so different to give absorptions at different wave numbers as both are accompanied by +R & -I effect of nitrogen on one side and +R & -I effect of aromatic ring and vinyl group on another side so the amide I band at 1625 cm^{-1} is overlapped with the C=O stretch of aminolysed product.

$^1\text{H-NMR}$ spectral analysis

Figure 2(A) shows the Proton NMR spectrum of Aminolysed end products of PET waste with hydrazine monohydrate and Figure 2(B) shows the $^1\text{H-NMR}$ spectrum of novel acrylic aromatic amide oligomer of Aminolysed end products. The $^1\text{H-NMR}$ spectrum of TPDAC [Fig. 2(B)] gives symmetrical singlet in the aromatic region due to four equivalent protons in the ring at δ value 7.9. Two signals at δ values 10.10 and 10.53 are due to secondary amide protons. Signals at δ values 6.30, 6.14, and 5.93 in the alkenes region are attributed to vinyl protons. The δ value 3.7 is attributed to DMSO signal which is used as solvent. The signals in the region from δ value 4.3 to 2.5 shows the presence of polymerized acryloyl chloride, which is present as an impurity in the sample and it also overlaps the signal due to $-\text{CH}_2\text{CH}_2\text{O}-$ moiety at δ value 2.5.

On comparing the $^1\text{H-NMR}$ spectra it was found that the acrylic moiety has been introduced in terephthalic dihydrazide and its higher homologues. There is no signal in the alkenes region in $^1\text{H-NMR}$ spectrum of Aminolysed end products [Fig. 2(A)]. However, the three splitted signals are present in the NMR spectrum of synthesized oligomer. The NMR spectrum of oligomer does not show a signal at δ value 4.5, which is attributed to NH_2 protons in TPD and its higher homologues hence it confirms that acrylic moiety has been attached to both ends. The signal at δ value 2.5 is attributed to the presence of higher homologues in the aminolysed end products.

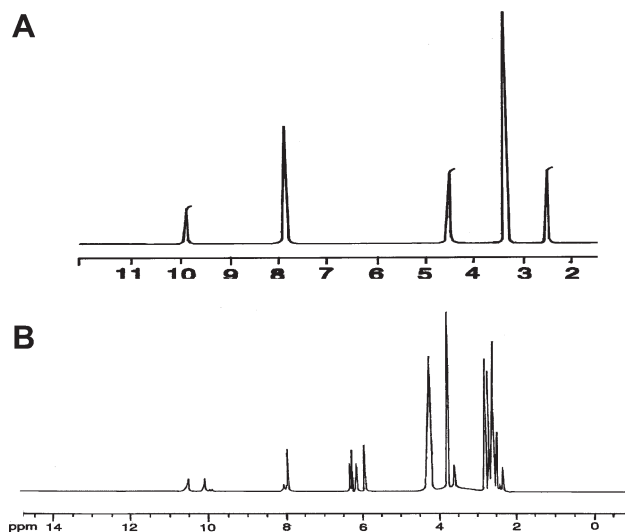


Figure 2 (A) $^1\text{H-NMR}$ spectrum of aminolysed end products of PET waste with hydrazine monohydrate (B) $^1\text{H-NMR}$ spectrum of novel aromatic amide oligomer synthesized from PET waste.

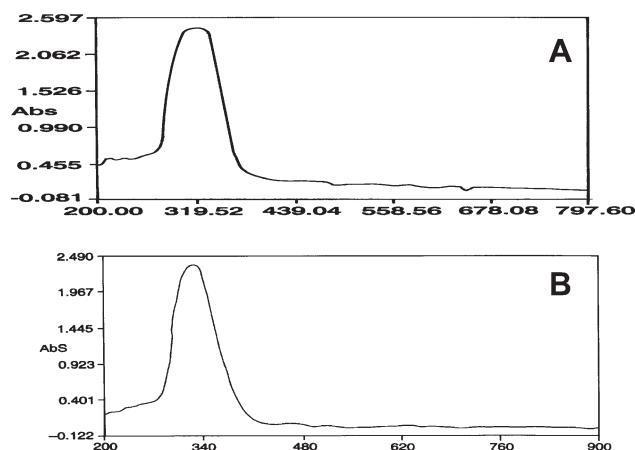


Figure 3 (A) UV-visible spectrum of aminolysed end products with hydrazine monohydrate (B) UV-visible spectrum of novel aromatic amide oligomer.

UV-visible spectral analysis

Figure 3(A) Shows the UV-visible spectrum of the products obtained by the aminolysis of PET waste with hydrazine monohydrate. The figure shows strong absorption in the region about 200–400 nm with maximum absorption at 320 nm. Figure 3(B) shows UV-visible spectrum of the novel acrylic aromatic amide oligomer of TPD and higher homologues. There is a strong absorption in the region 280 to 400 nm, which confirms the presence of carbonyl group and aromatic ring. The synthesized oligomer has two chromophoric groups, one is Para substituted benzene ring and other is acrylic moiety introduced through acryloyl chloride. The absorption band with maximum absorption at 326 nm may be due to the combination of π - π^* and n - π^* transitions of the two chromophoric groups, respectively.

Thermal analysis

Figure 4 shows a DSC thermogram of novel acrylic aromatic amide oligomer of Aminolysed end products synthesized from PET waste recorded with the help of Differential Scanning Calorimeter, Mettler Star SW 9.01 keeping a constant heating rate of 5°C/

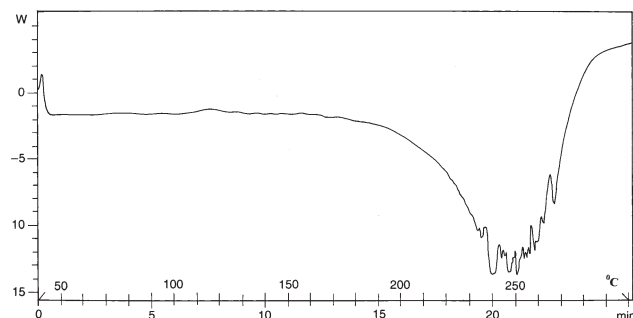


Figure 4 DSC of novel aromatic amide oligomer synthesized from PET waste.

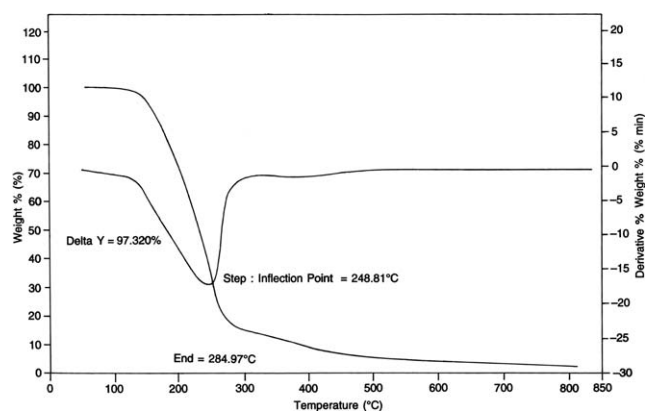


Figure 5 TGA thermogram of novel aromatic amide oligomer synthesized from PET waste.

min from 50–300°C. The yellow colored waxy solid compound shows a very broad endothermic peak in the range 230–270°C, which suggests melting of the oligomer with decomposition as a black residue was left behind in the crucible, which is further supported by the TGA thermogram of decomposed oligomer (Fig. 5). The peak decomposition temperature for the oligomer was found to be around 250°C. The decomposition shows complete degradation leaving no residue. Figure 6 shows DSC thermogram of aminolysed end products obtained by aminolysis of PET waste with hydrazine monohydrate. It shows a single endothermic peak with peak temperature of 340°C. The sharp melting point shows that the material is crystalline in nature. The melting peak is immediately followed by an exothermic peak at 346°C suggesting the decomposition of the material.

Mass spectral analysis

The mass spectrum of the synthesized oligomer of aminolysed end products generated from PET waste with hydrazine monohydrate is shown in Figure 7. The spectrum shows large number of peaks corresponding to the presence of different oligomers and

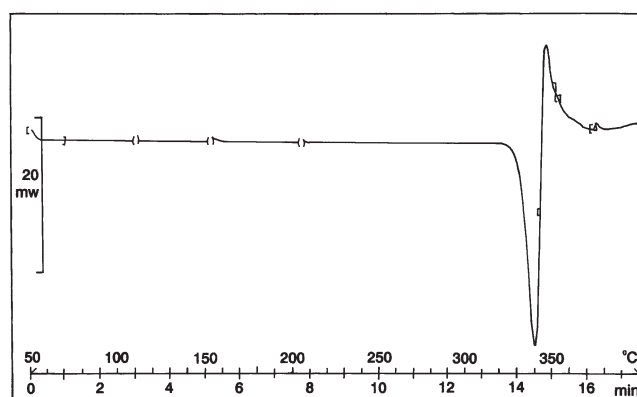


Figure 6 DSC of aminolysed end products with hydrazine monohydrate.

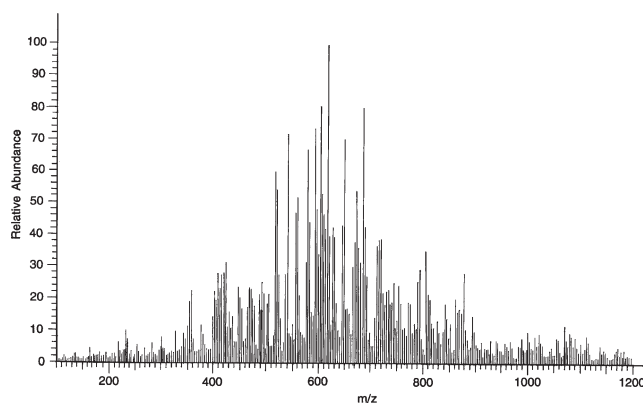


Figure 7 Mass spectrum of Novel Aromatic Amide Oligomer synthesized from PET waste.

decomposed products of these oligomers. It can be shown that the expected oligomers formed by the reaction of acryloyl chloride with aminolysed end products of PET waste with hydrazine monohydrate must include oligomers having molecular weights as 302, 494, 686, 878, and 1070 on the basis of value of n corresponding to reaction scheme 1. The relative abundances of these oligomers were noted from MS spectrum (Fig. 7) and a plot of molecular weight distribution was created, which have been shown in Figure 8. Table III gives the value of n for each oligomer and their molecular weights along with their respective relative abundances in the MS spectrum. We also determined the number average molecular weight of the oligomers by measuring iodine value and it was found that the maximum abundance of the oligomers matches with the value obtained by iodine value. It can thus be concluded that a modified acrylic aromatic amide monomer consists of mixture of oligomers with maxima and average molecular weight as 686.

UV curing of TPDAC with other acrylate monomers

The prepared glass laminates were checked for curing time and adhesion. The data shown in Table II

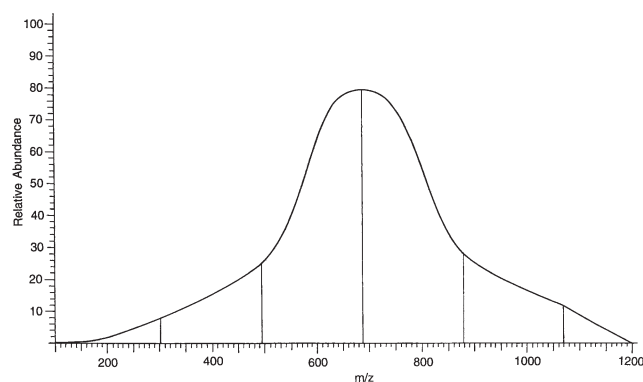


Figure 8 Molecular weight distribution curve of TPDAC synthesized from PET waste.

TABLE III
Shows Molecular Weights and Relative Abundances of Oligomers (TPDAC), Obtained by the Reaction of Acryloyl Chloride with Aminolysed End Products of PET Waste, as Depicted from its MS Spectrum

S. no.	Value of n	Molecular weight	Relative abundance
1	0	302	8
2	1	494	25.5
3	2	686	80
4	3	878	28
5	4	1070	12

provides information on formulations No. 1–7 regarding their ability to cure when exposed to UV radiation. It was found that a curing time of 23–30 s is sufficient to cure the formulation completely. Furthermore the photoinitiator concentration i.e. 3% by weight was found to be suitable to get fully cured laminates. Under boiling water test when the laminated sheets were placed in boiling water for 72 h. The laminated sheet prepared from formulation No. 1 was delaminated after 58 h but no delamination was found for the sheets prepared from the formulations No. 2–7. The glass laminates for formulation No. 2–7 found good adhesion as the fragmented pieces of glass laminates does not get separated under hammer test (Pummel test). When glass laminate was struck with a hammer it showed load distribution and the glass shows fragmentation behavior like safety glass. When the glass was hammered many times small fragments were formed but two different glasses were not delaminated. Table II also includes the results of hammer test (pummel value), which shows that the formulations containing TPDAC have a higher pummel value and it increases with increase in the concentration of TPDAC. These results indicate that TPDAC is working as an adhesion promoter. Such formulations thus can be used in application of laminated glasses.

CONCLUSION

This work involves the formation of a novel acrylic aromatic amide oligomer i.e. *N,N'*-bis-(2-propenamido)benzene-1,4-dicarboxamide with its higher homologues from PET waste. The oligomer is of low cost and can be used as an adhesion promoter on metal/glass surface with other acrylate monomers in UV curable formulations. The synthesized oligomer was characterized and compared with Aminolysed end products generated from PET waste on the basis of spectroscopic techniques. A new synthetic

approach has been developed to introduce nitrogen based hydrogen bonding moieties, which can be used as an alternative to urethane groups in radiation curable formulations.

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