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Abstract

One of the important reactive halogenated dicarboxylic acids used in the synthesis of flame retardant unsaturated polyester resins is 1,4,5,6,7,7-hexachlorobicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid (HET acid). In the present investigation four different oligoesters are synthesized using HET acid as the diacid component and 1,2-ethane diol, 1,2-propane diol, 1,3-propane diol and 1,4-butane diol as the aliphatic diols. Melt condensation technique in vacuum is used for the synthesis of the oligoesters. The number average molecular weights of the oligoesters are determined using end group analysis. The degree of polymerization is estimated

to be 3–5. The structural characterization is done using FTIR and NMR (^{1}H and ^{13}C) techniques. In the present investigation, TGA-FTIR studies for the different oligoesters are carried out in nitrogen atmosphere. The materials are heated from ambient to 600 °C at a heating rate of 20 °C/min. The main volatile products identified are CO, HCl, H_2O, CO_2, hexachlorocyclopentadiene and HET acid/anhydride. The evolution profile of these materials with respect to the structure of the oligoesters is discussed in detail and presented. The importance of β-hydrogens in the diol component and the plausible mechanism for the flame retardant behavior of these oligoesters are presented.

Keywords
Flame retardancy, HET acid, Oligoester, NMR, TGA/FTIR, Kinetics of degradation

1. Introduction

Presently, polymeric materials are widely used for engineering as well as domestic purposes and also to replace conventional materials like wood, metal, glass, paper, etc. because of their light weight nature, excellent mechanical properties and corrosion resistance, but they are not suitable for high temperature applications because of their flammability [1]. Although increased usage of plastics in cars, trains, airplanes [2], [3], [4], [5] offers lower weight and so improved fuel economy, further the usage of plastics in electrical components and building components in various forms like foams, fibers [6], [7], etc. necessitates the use of flame retardants so that the material complies fire safety regulations.

Flame retardants can be incorporated into many different flammable materials both natural and synthetic to delay or prevent the mechanical deterioration in the case of fire by hindering the combustion process [8], [9]. Flame retardants protect modern materials such as technical plastics, building insulation, circuit boards and cables from igniting and from spreading the fire. The release of heat, smoke, toxic gases and spread of flame will be severely hindered by fame retardants allowing more time for the people to escape from the fire. Minerals based on magnesium and aluminium, borax, antimony trioxide, compounds containing halogens (bromine and chlorine), phosphorous, nitrogen, intumescent systems and others [10], [11], [12] are some of the materials having flame retardant character. Among these, halogenated flame retardant materials offer not only excellent flame retardancy but also provide corrosion resistance towards inorganic acids.

1,4,5,6,7,7-Hexachlorobicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid (HET acid) is one of the halogen containing reactive flame retardant materials [13], [14]. It has a very good chemical resistance towards inorganic acids like nitric and hydrochloric acid even at 54 °C [15]. Flame retardant HET acid based polyester resins have found wide applications in the manufacture of plastics, paints, varnishes, textile fibers, etc. having sufficient flame retardancy and self extinguishing characteristics.

Mullens et al. [16] studied the gases released during the thermal degradation of HET acid at a heating rate of 20 °C/min in a dynamic air purge of 50 cm^3/min using on-line coupling technique TG-FTIR and TG–MS and off-line coupling TG–GC–MS. The main products identified were CO_2, H_2O, Cl_2, HCl, maleic anhydride, HET acid/anhydride, chlorinated cyclic hydrocarbons (1,2,3,4-tetrachloro-1,3-cyclo-pentadiene, hexachlorocyclopentadiene, etc.) and chlorinated unsaturated linear hydrocarbons (C_2Cl_4, hexachloropropene, hexachlorobutadiene, etc.).

Vijayakumar et al. [17], [18], [19], [20], [21], [22], [23], [24], [25], [26] synthesized HET acid based polyesters with ethylene glycol, 1,2-propane diol and 1,4-butane diol and studied their thermal degradation behavior using different instrumental techniques and established the degradation mechanism of HET acid based polyesters.

Bansal and Ghogare [27] investigated the thermal degradation of polyesters synthesized from HET acid, maleic anhydride and ethylene and/or propylene glycol and their cured products with methyl methacrylate and styrene using thermogravimetric analysis and found that the polyester resin prepared from propylene glycol is thermally more stable. They also prepared HET anhydride based polyester resins and studied their chemical resistance [28] and moisture sensitivity in various reagents like acids, alkalis and water at 25 and 65 °C.

Gupta and Thampy studied the thermal degradation, fire retardant efficiency [29] and the γ-ray resistance [30] of polyester resins from HET acid, isophthalic acid, maleic anhydride and propylene glycol and correlated the polyester resin structure to their flame resistance behaviour.

Roberts et al. [31] incorporated a Diels–Alder adduct of *cis*-4-cyclohexene-1,2-dicarboxylic anhydride with hexachlorocyclopentadiene, 2,3-dicarboxy-5,8-endomethylene-5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydronap-hthalene anhydride as a dicarboxylic acid component for the synthesis of fire retardant polyester compositions and compared their thermal and light stability with HET acid based polyesters.

The off-line pyrolysis, the separation and the identification of the degradation products from HET acid based polyesters [21], [25] paved a way to understand the degradation mechanism. These studies do not provide any information regarding the profile of the degradation products during thermal degradation. In order to establish the effect of the diol structure on the degradation temperature and the profile of the different degradation products evolved during dynamic heating of HET acid based oligoesters, in the present investigation, TGA-FTIR technique is used and the results are discussed. Based on the results obtained, it is intended to use these oligoesters as flame retardant additives for vinyl polymers.

2. Experimental

2.1. Materials

Analytical grades of ethylene glycol (EG), 1,2-propane diol (1,2-PD), and 1,4-butane diol (1,4-BD) from Merck and 1,3-propane diol (1,3-PD) from Alfa Aesar were used after purification by distillation under reduced pressure. HET acid obtained as a gift sample was used as such.

2.2. Synthesis of oligoesters

HET acid based oligosters, HET EG, HET 1,2-PD, HET 1,3-PD and HET 1,4-BD were synthesized by melt condensation technique using p-toluene sulphonic acid as a catalyst [25]. Stoichiometric quantities of the monomers were heated together (Table 1) to effect the polycondensation. Gradual increase of the condensation temperature with the application of vacuum facilitates the removal of water formed during condensation and also restricts the discoloration of the material due to oxidation.

Table 1. Stoichiometric proportion of monomers used for the synthesis of the oligoesters and the number average molecular weight of the oligoesters

Oligoester	Stoichiometric ratio (mol)					M_n
	HET acid	EG	1,2-PD	1,3-PD	1,4-BD	
HET EG	1.0	1.1	–	–	–	1,361
HET 1,2-PD	1.0	–	1.1	–	–	1,917
HET 1,3-PD	1.0	–	–	1.1	–	2,918
HET 1,4-BD	1.0	–	–	–	1.1	1,978

2.3. Determination of molecular weight

Exactly 1.0 g of synthesized polyester was dissolved in a mixture of toluene and 30 ml of ethanol. This solution was titrated against standardized alcoholic potassium hydroxide solution using methyl orange as indicator. The number average molecular weight determined by this end group analysis for the oligoesters are presented in Table 1.

2.4. Analytical methods

2.4.1. Spectral studies

The Fourier transform infrared (FTIR) spectra of the oligoesters were recorded on a JASCO, FTIR-460 PLUS Fourier transform infrared spectrometer using the potassium bromide pellet technique.
The proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on AV-300 instrument with tetramethylsilane as the internal standard.

2.4.2. Thermal studies

TGA/FTIR studies were performed under nitrogen flow (40 ml/min) on Cahn TG 131 instrument that was connected to Mattson Research grade FTIR through heated stainless steel tubing. The rate of heating was maintained at 20 °C/min for all the oligoesters and the final temperature was 600 °C. The volatile degradation products were sampled using a sniffer tube that extends into the sample cup to remove the evolved gases at a rate of 40 ml/min. The evolved volatile products were introduced to the IR chamber through the heated stainless steel tubing and analysed by in situ vapour phase FTIR. The sample size was 35–50 mg.

The amount of energy required to activate the degradation of the synthesized oligoesters was determined using Dharwadkar and Kharkhanavala equation [32], [33], [34], [35]. The equation is

$$\ln\{\ln[1/1-\alpha]\} = \left(E_a/\mathrm{RT}_i^2\right)\left[100\theta/T_f - T_i\right] + C$$

where α = fraction reacted/degraded, E_a = activation energy, R = gas constant, T_i = temperature of inflection of the reaction, T_f = temperature of completion of the reaction, $\vartheta = (T - T_s)$, difference between T_s and temperature under consideration, T_s = Temperature at the point of inflection in TG curve and C = Constant. A plot of $\ln\{\ln[1/(1 - \alpha)]\}$ against ϑ, the difference between inflection temperature and temperature under consideration results in a straight line with a slope of $(E_a/RT_i^2)[100/(T_f - T_i)]$ from which E_a can be computed.

3. Results and discussion

3.1. Spectral studies

The FTIR spectra of the oligoesters are presented in Fig. 1. The shifting of carbonyl absorption band from 1725 cm^{-1} (for HET acid) to 1750–1735 cm^{-1} (for saturated ester) and characteristic absorption bands at 1680–1620 cm^{-1} (for strained and substituted C$=$C) and at 1195–1185 cm^{-1} and 1070–1060 cm^{-1} (for C–O–C asymmetric and symmetric stretching) confirm the melt condensed product as oligoesters. The broad absorption band in the range 3600–3200 cm^{-1} (for hydrogen bonded O–H) may be attributed to the hydroxyl and carboxylic acid end groups in the oligoesters.
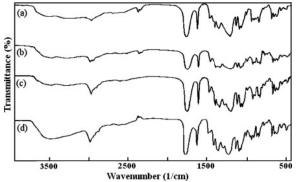

Fig. 1. FTIR spectra of the HET acid based oligoesters: (a) HET EG, (b) HET 1,2-PD, (c) HET 1,3-PD and (d) HET 1,4-BD.

The ^{1}H and ^{13}C NMR spectra of the synthesized oligoesters are presented in Fig. 2, Fig. 3, respectively. The repeat unit structures with the proton labeling are shown in Scheme 1. The ratio of integrated peak intensities of HET acid and diol protons is 1:0.97 for HET EG, 1:1.25 for HET 1,2-PD, 1:1.03 for HET 1,3-PD and 1:1.13 for HET 1,4-BD, indicating the presence of one diol unit per one HET acid unit. All the NMR spectroscopic data are consistent with the molecular structure.
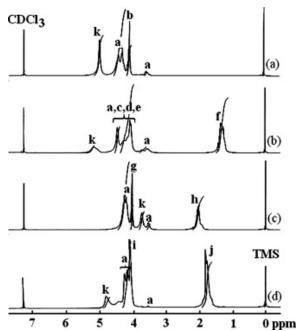
Fig. 2. ^1H NMR spectra of HET acid based oligoesters: (a) HET EG, (b) HET 1,2-PD, (c) HET 1,3-PD and (d) HET 1,4-BD.
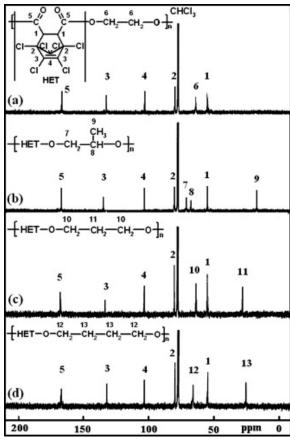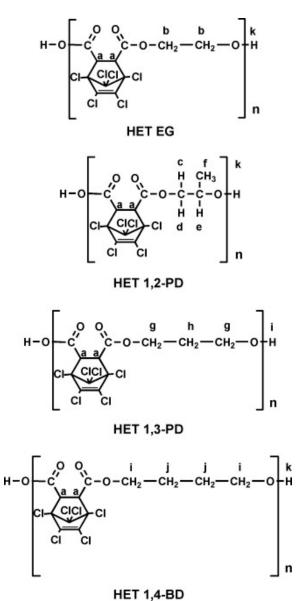

Fig. 3. ^{13}C NMR spectra of HET acid based oligoesters: (a) HET EG, (b) HET 1,2-PD, (c) HET 1,3-PD and (d) HET 1,4-BD.

HET EG

HET 1,2-PD

HET 1,3-PD

HET 1,4-BD

Scheme 1.

3.2. Thermal studies

Thermal analysis is the most informative in assessing the thermal stability and identifying the various stages of degradation. The TG curves and their first derivative (DTG) curves recorded in nitrogen environment of the synthesized oligoesters are given in Fig. 4, Fig. 5, respectively. The thermogram of all the oligoesters shows a single stage thermal decomposition. The effect of the diol component on the various thermal properties of the oligoesters is presented in Table 2.
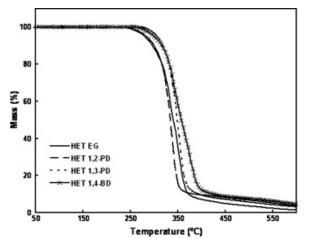
Fig. 4. TG thermograms of HET acid based oligoesters (Nitrogen atmosphere; heating rate 20 °C/min).
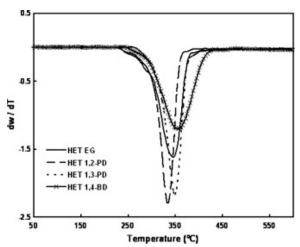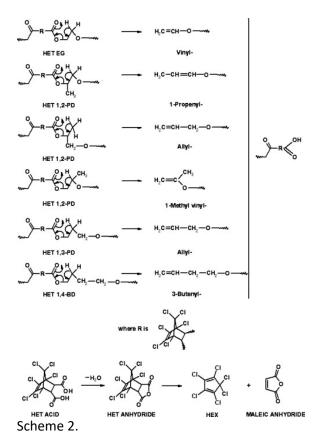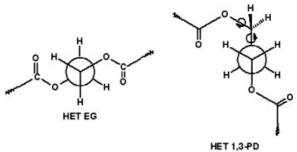

Fig. 5. DTG curves of HET acid based oligoesters (Nitrogen atmosphere; heating rate 20 °C/min).

Table 2. Parameters derived form the TGA data obtained for the oligoesters in nitrogen environment

Oligoesters	Temperature (°C)		E_a (kJ mol^{-1})	Char residue (%) at 500 °C
	Onset	T_{max}		
HET EG	241	345	84	3.6
HET 1,2-PD	239	337	74	6.8
HET 1,3-PD	277	348	104	5.8
HET 1,4-BD	261	357	91	7.5

The temperature of onset of degradation is one of the measures of the thermal stability of the material. All the oligoesters start to degrade in the temperature range 239–277 °C. The order of increasing stability of the synthesized oligoesters is observed as HET 1,2-PD < HET EG < HET 1,4-BD < HET 1,3-PD (Table 2). It has been well established that in polyesters containing β-hydrogen either in the acid or in the diol component, thermal degradation will proceed via a cyclic six membered transition state [36] and produce olefinic and carboxylic acid end capped degradation products, which is the primary degradation (Scheme 2). All other routes like acyl-oxygen, alkyl-oxygen and carbon–carbon homolytic scissions require higher energy compared to β-scission process which involves simple electronic reorganization. The oligoester, HET 1,3-PD is thermally more stable compared to other oligoesters since the total number of available β-hydrogens is less (2 β-hydrogens). On the other hand all the available hydrogens in the diol component of HET 1,2-PD can participate in β-scission reaction. So in HET 1,2-PD there are six available β-hydrogens and so conformationally several possibilities exist and this statistical probability leads to its lowest thermal stability. In the case of HET 1,4-BD, 4 β-hydrogens are

present as in the case of HET EG but the former is comparatively thermally less stable than the later. A plausible explanation for this is the chain flexibility of the 1,4-butane diol (4 methylene groups) unit compared to ethylene glycol (2 methylene groups) unit. Comparing the thermal stability of the oligoesters, HET 1,2-PD (6 β-hydrogens) and HET 1,3-PD (2 β-hydrogens), the former starts to degrade at a lower temperature than the later. Thus the presence of more number of β-hydrogens in the oligoester backbone decreases the thermal stability.

Scheme 2.

A pronounced mass loss was observed in the range of 300–395 °C for all the oligoesters. This range was selected for kinetic studies using Dharwadkar and Kharkhanavala equation. Energy of activation (E_a) calculated for the degradation from the slope values of a plot of $\ln\{\ln[1/(1 − \alpha)]\}$ vs ϑ are given in Table 2. Comparison of the energy of activation (E_a) values for the different oligoesters investigated showed that HET 1,2-PD oligoester requires less amount of energy for its degradation than other oligoesters, which may be ascribed to the total number of available β-hydrogens. The order of increasing stability of the synthesized oligoesters is observed as HET 1,2-PD < HET EG < HET 1,3-PD < HET 1,4-BD (Table 2) if T_{max} is taken as the criterion for the thermal stability. The oligoester, HET 1,2-PD is found to be the least stable material. A discrepancy is noted in the order of stability of HET 1,3-PD and HET 1,4-BD. Of the three parameters investigated, the thermal onset degradation temperature and the E_a values calculated for the degradation provide nearly the same order of stability of the oligoesters. In Scheme 3, the conformational aspects of HET EG and HET 1,3-PD are shown. From the conformation of HET EG, it is evident that C–C bond rotation will not hamper the β-scission process whereas owing to the presence of one more methylene group in HET 1,3-PD, the availability of β-hydrogens is restricted, which is reflected in its enhanced thermal stability. The char residue obtained for the synthesized oligoesters in nitrogen environment at 500 °C is also presented in Table 2.

HET EG

HET 1,3-PD

Scheme 3.

In TG analysis, major weight loss was observed between 302 and 373 °C for HET EG, 311–353 °C for HET 1,2-PD, 310–373 °C for HET 1,3-PD and 312–395 °C for HET 1,4 BD. The FTIR spectra of the degradation products of all the synthesized oligoesters are shown in Fig. 6, Fig. 7, Fig. 8, Fig. 9. The IR spectra of evolved gases in the above mentioned temperature range shows the degradation products contain CO (2100–2300 cm^{-1}), HCl (2700–2900 cm^{-1}), CO_2 (600–700 and 2300–2400 cm^{-1}), H_2O (1500–1600 cm^{-1}) and HET acid/anhydride (800–1300 and 1750–1900 cm^{-1}).
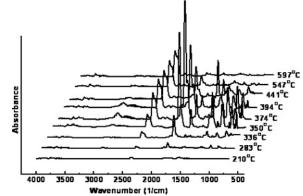

Fig. 6. FTIR spectra of the gases evolved during pyrolysis of HET EG oligoester.
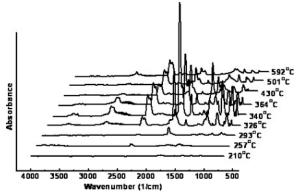

Fig. 7. FTIR spectra of the gases evolved during pyrolysis of HET 1,2-PD oligoester.
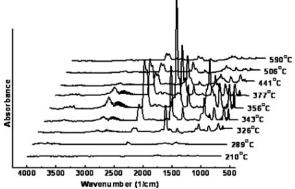
Fig. 8. FTIR spectra of the gases evolved during pyrolysis of HET 1,3-PD oligoester.
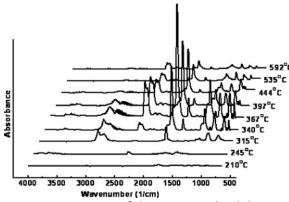

Fig. 9. FTIR spectra of the gases evolved during pyrolysis of HET 1,4-BD oligoester.

The profile of the amount of various gases released during thermal degradation of the oligoesters in nitrogen atmosphere is shown in Fig. 10. The maximum production of all the gases identified occurs in the same temperature region for all the oligoesters but the profile of evolution of the major degradation product HET anhydride/acid varies depending on the diol component. The formation of HET anhydride/acid starts at least 50 °C earlier than the formation of other degradation products like CO, HCl, CO_2 and H_2O. The retro Diels–Alder product from HET anhydride is hexachlorocyclopentadiene (HEX), the potent donor of chlorine free radical, is formed around 50 °C later. The profile of evolution of both HET anhydride/acid and HEX indicates these materials can work as flame retardant materials for materials having degradation temperature in the range of 350–450 °C. The continuous evolution of HET anhydride/acid from these materials proves that these oligoesters can act in a wide temperature region as flame retardants.
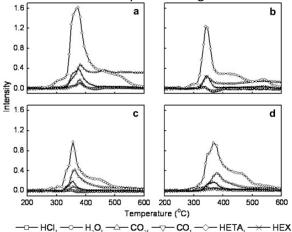

Fig. 10. The evolved gases profile of HET acid based oligoesters on pyrolysis: (a) HET EG, (b) HET 1,2-PD, (c) HET 1,3-PD and (d) HET 1,4-BD.

Evolution of CO_2 persists even after the cease of the evolution of other degradation products like CO, HCl, H_2O, HEX, HET anhydride/acid, etc. Comparison of Fig. 5, Fig. 10 clearly indicate that the temperature region at which different degradation products evolved as evidenced by TGA/FTIR studies and the temperature region at which the maximum is appearing for the various oligoesters as evidenced by DTG curves are very similar. From this it can be reasonably concluded that the temperature region at which the maximum weight loss that is taking place is due to several competitive degradation reactions.

4. Conclusions

HET acid based oligoesters containing different aliphatic diol unit were synthesized and their structural characterization was done by FTIR and ^{1}H NMR studies. The evolved gas profile was derived from TGA/FTIR studies. From the TGA curve the thermal stability was assessed and the energy of activation for the major degradation stage was calculated using Dharwadkar and Kharkhanavala method. The variation in the onset of degradation and the energy of activation for the degradation can be explained by considering the total number of available β-hydrogens in the diol component of the oligoesters. The various degradation products identified in the temperature range 300–395 °C are CO, HCl, CO_2, H_2O, HEX and HET acid/ anhydride. HET acid/anhydride formation is continuously seen from 300 °C till 600 °C. The formation of HEX is noted around 350 °C in all the oligoesters. Formation of HET acid from the oligoesters followed by its conversion to HET anhydride (dehydration reaction) followed by the formation of HEX through retro Diels–Alder reaction of HET anhydride, further catabolism of HEX to pentachloro-, tetrachloro- and trichlorocyclopentadienes with the concomitant play of chlorine free radicals may be the sequence of degradation which is responsible for the flame retardant action of HET acid based oligoesters.

Acknowledgements

Recommended articlesCiting articles (9)

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