Effect of Structure on the Thermal Degradation and Flame Retardancy of Hexolic Anhydride Based Polyesters

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Summary: Based on the anhydrides like hexolic (5,6,7,8,10,10-hexachloro - 3a,4,4a,5,8,8a,9,9a-octahydro-5,8-methanonaphtho-[2,3-c]-furan-1,3-dione), maleic and phthalic and diols like 1,4-butanediol, *cis*-2-butene-1,4-diol and 2,3-dichloro-2-butene-1,4-diol, a family of polyesters has been synthesized using azeotropic condensation technique. The structural characterizations of the polyesters have been carried out using infra-red, ^{1}H - and ^{13}C- nuclear magnetic resonance spectroscopic methods. The thermal properties of the polyesters have been studied using thermogravimetric technique. The off-line pyrolysis of these materials was done. The qualitative and semi-quantitative analyses of the volatiles as well as the heavy mass fractions of the degradation products were carried out using a gas chromatograph coupled to a mass selective detector (GC-MSD).

Thermogravimetric data indicate that the thermal stability and the char residue of the polyester resins decrease in the order 1,4-butanediol based > *cis*-2-butene-1,4-diol based > 2,3-dichloro-2-butene-1,4-diol based polyesters. The GC-MSD data indicate that the amount of flame cooling agents (hexa-, isomeric penta-, tetra- and isomeric tri-chlorocyclopentadienes) produced during the pyrolysis of the polyesters increases in the order 2,3-dichloro-2-butene-1,4-diol based < *cis*-2-butene-1,4-diol based < 1,4-butanediol based polyesters. The trends observed in these two parameters which are contributing factors to the flame retardancy of the polyester materials were suitably explained on the basis of the effect of the structural changes in the diol part of the polyesters on the primary degradation mechanism, the β-chain scission process.

Introduction

Hexolic anhydride (5,6,7,8,10,10-hexachloro-3a,4,4a,5,8,8a,9,9a-octahydro-5,8-methanonaphtho-[2,3-c]-furan-1,3-dione) (I), a reactive type flame retardant, is widely used in poly-

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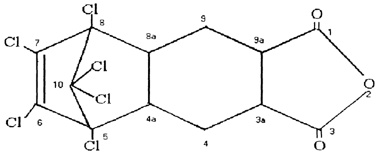
ester industries. The application of this anhydride and its hydrolysis product in the field of polymers are reviewed.[1] Quantitative pyrolysis gas chromatographic study of the thermal degradation of standard unsaturated polyester resin was carried out by Ravey.[2] He considered the rearrangement of the phthalate C-O bond as the primary degradation step during pyrolysis. A detailed degradation study on linear polyesters prepared from phthalic anhydride and 1,4-butanediol / 2-butene-1,4-diol / 2-butyne-1,4-diol clearly showed the important role of β-hydrogens in the diol part (Scheme 1) on the degradation of the polyesters.[3] The effect of introducing halogens in the place of β-hydrogens in the diol part on the degradation of the polyester chains and the effect of loading halogens in the diol part on the flame retardancy of the polyesters are investigated in the present work.



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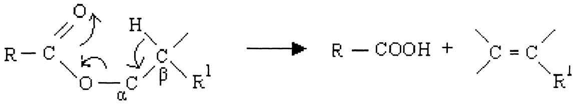

Scheme 1

Experimental

Hexolic anhydride (Hooker Chemical Corporation, Belgium, m.p. 241-242 °C) was used as such without further purification. Phthalic anhydride (Merck, India, m.p. 130-131 °C) and maleic anhydride (British Drug House, India, m.p. 52-53 °C) were purified by sublimation and recrystallization from chloroform respectively. 1,4-Butanediol (b.p. 138-140 °C / 10 mm Hg) and *cis*-2-butene-1,4-diol (Fluka, Swiss, *cis*-92%, b.p. 130-131 °C / 10 mm Hg) were purified by vacuum distillation. 2,3-Dichloro-2-butene-1,4-diol was synthesized according to the method of Kleinert and Furest.[4] The components, feed composition of the monomers and the acid-number of the resulting polyesters are detailed in Table 1. All polyester resins were synthesized by azeotropic condensation technique using toluene for the removal of water. The number average molecular weights of the resin based on acid-number value are also included in Table 1.

Infra-red spectra of the resins were recorded in a Perkin Elmer 283 Infra-red Spectrophotometer. Both ^{1}H (300 MHz) and ^{13}C (75.2 MHz) NMR spectra of the resins were recorded in a Varian XL 300 NMR spectrometer using $CDCl_3$ as solvent.

Table 1. The components, feed composition, acid-number and the number average molecular weight of the polyester resins synthesized.

Code	Feed Compositions of the monomers (mol)*				Acid-number (mg KOH / g polyester)	Molecular weight
	M	P	H	Diol		
MPH2	1.0	0.4	0.6	(diol 2)	46.0	2439
MPH1	1.0	0.5	0.5	(diol 1)	35.2	3188
MPH0	1.0	0.5	0.5	(diol 0)	28.7	3909

* M – Maleic anhydride, P – Phthalic anhydride, H – Hexolic anhydride. The numbers 2, 1 and 0 in the sample code represent the diols, 1,4–butanediol, 2-butene–1,4–diol and 2,3–dichloro–2– butene–1,4–diol respectively

Thermogravimetry studies were performed in a Mettler TA 3000 analyzer with a sample size of 5-10 mg in static air atmosphere at a heating rate 10 °C min^{-1}. The off - line pyrolysis of the resins was carried out in an all-glass apparatus detailed elsewhere.[5,6] The pyrolysis products were separated in a Hewlett Packard HP 5890 Gas Chromatograph containing a 12 m capillary column coated with cross-linked methyl silicone gum HP-1. The identification of the separated degradation products was done using a Hewlett Packard Mass Selective Detector HP 5970 which was interfaced with the gas chromatograph using a jet-separator. The data analysis was performed using a HP 59970 work station.

Results and Discussion

Spectral Characterization.

The doublet feature of carbonyl frequencies (1850-1835 and 1770-1600 cm^{-1}) observed in the monomeric anhydrides is completely lost and a single peak is observed in the region 1740-1725 cm^{-1} in the infra-red spectra of the polyester resins. This indicates the formation of ester linkages. Another evidence for the formation of ester linkages comes from the unique broad and intense O-H stretching band. This band is observed in monomeric diols but almost absent in the infra-red spectra of the resins.

The detailed ^1H and ^{13}C NMR studies on MPH1 and MPH0 have been presented elsewhere.[7] The major conclusions derived from these studies are: i) all the monomers employed for the polymer syntheses are incorporated in the polyester backbone, ii) the molar concentrations of the monomers present in the polyester chains calculated using the intensities of the appropriate ^1H and ^{13}C signals agree well with the feed composition values, iii) the isomerization of the maleate to fumarate units during the polymerization takes place to an extent of 16% in MPH1 and 31 % in MPH0 and iv) a random distribution of the monomers is noted in the resins .

Thermal Characterization.

Thermogravimetric traces recorded for the three polyester resins at a heating rate of 10 °C min^{-1} in static air are used to assess the thermal stability of the polyester resins by the qualitative methods due to Marvel[8] and Jeffreys[9] and semi-quantitative method employed by Doyle.[10,11] The indices of the thermal stability and char residue above 600 °C for the polyester resins are presented in Table 2. From the Table, it is obvious that the thermal stability and char residue of the polyesters decrease in the order 1,4-butanediol based > *cis*-2-butene-1,4-diol based > 2,3-dichloro-2-butene-1,4-diol based polyesters. The order of stability of the polyesters corresponds to the order of C-H and C-Cl bond dissociation energies (C –H 364 - 393 kJ mol^{-1} and C - Cl 280 kJ mol^{-1}).[12]

Table 2. The indices of thermal stability of the polyester resins and char value.

Sample	Indices of thermal stability (°C)			Char residue above 600 °C (%)
	ipdt [a]	10% DT [b]	50% DT [b]	
MPH 2	372	279	400	17.8
MPH 1	309	219	329	5.0
MPH 0	276	167	309	2.5

a - Doyle method b - Marvel and Jeffreys method DT - decomposition temperature

Pyrolysis and Analysis of the Products of Degradation.

As a representation, the total ion chromatogram [TIC] recorded for the volatile pyrolusates of 2-butene-1,4-diol based polyester resin [MPH1] is only given in Figure 1. The products of degradation identified in the volatile fractions of the three polyesters investigated are summarized in Table 3. Out of the 43 volatile compounds identified, one third of the components has been identified by injecting authentic samples and the structures of remaining compounds are proposed from the mass spectral fragmentation pattern. The ratio of the amount of polychlorocyclopentadienes (tri-, tetra-, penta- and hexa-) obtained during thermal degradation of the polyesters MPH2: MPH1: MPH0 equals to 1: 0.52 : 0.17 (percentage ratio 17.46 : 9.33 : 3.02). The discussion is focused mainly on the volatile polychlorocyclopentadienes because they act as the best flame cooling agents in real fire situation. The possible pathways for the formation of these compounds are i) in-chain retro-Diels-Alder reaction of hexolic anhydride moiety in the polyester backbone and ii) retro-Diels-Alder reaction of the hexolic anhydride set freed during degradation.

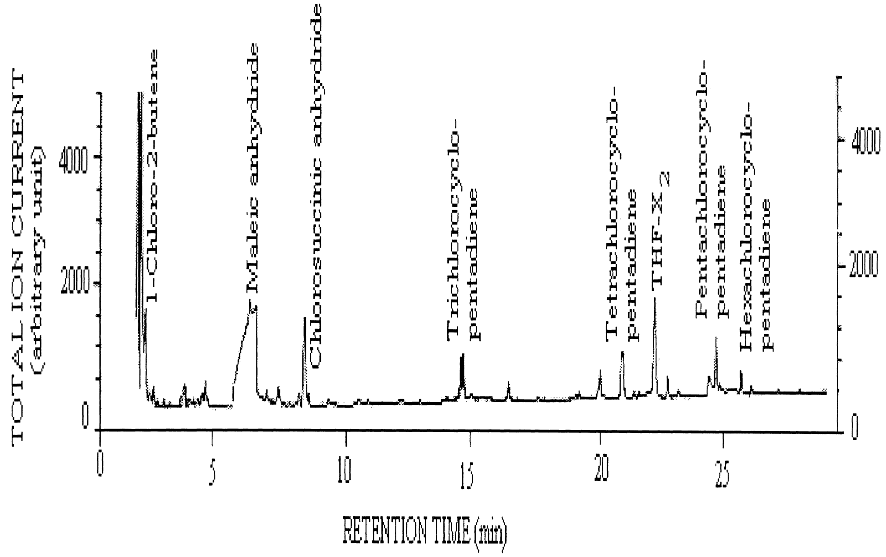

Figure 1. The total ion chromatogram for the volatile pyrolusate of 2-butene-1,4-diol based polyester resin [MPH1].

In a detailed study of a family of butanediol based polyester containing varying amount of hexolic anhydride, it is observed that in-chain retro-Diels-Alder reaction of hexolic anhydride moiety takes place to very little extent as evidenced by the formation of very low quantities of 4-cyclohexene-1,2-dicarboxylic anhydride.[13] Hence, it is concluded that majority of the hexachlorocyclopentadiene and its other catabolic polychloro-

Table 3. Products identified in the volatile fraction obtained during programmed pyrolysis of the polyesters MPH2, MPH1 and MPH0.

S.No.	Identified product	Area per cent		
		MPH2	MPH1	MPH0
1	HCl	..	..	65.20
2	THF	10.33	..	..
3	1-Butanol	2.71	..	..
4	2-Butenal	..	20.54	..
5	1-Chloro-2-butene	..	4.90	..
6	CH_3-CH=CH-CH_2-O-CH_3	2.14	..	..
7	1,2-Dichlorocyclo-1-butene	..	..	0.95
8	THF-X_1	0.21	..	..
9	CH_3-CH=CH-CH_2-O-CH=CH_2	1.50	..	..
10	Compound containing dihydrodioxepin unit	..	1.64	..
11	2,3-Dichloro-1-propenal	..	..	0.59
12	Maleic anhydride	20.30	42.84	11.63
13	Isomer of 9	5.41	..	..
14	Ethylbenzene	..	1.01	..
15	Chlorosuccinic anhydride	5.06	6.36	..
16	Unknown	..	..	0.90
17	Cl-CH=CH-O-CH_2-CH_2-CH_3	2.49	..	..
18	Cyclooctatetraene	..	0.49	..
19	Unknown	..	..	0.37
20	Dichloro-2-butenal	..	..	3.25
21	Isomer of 15	5.91	..	..
22	Isomer of 20	..	..	3.09
23	1,2,3, -Trichloro-2-butene	..	..	0.67
24	Hydroxypyran	0.43	..	..
25	Allylpyran	1.00	..	..
26	Trichlorocyclopentadiene	2.78	1.80	..
27	Isomer 26	1.71	0.92	..
28	Compound containing dihydromethyldioxepin unit	..	0.36	..
29	$C_4H_4Cl_4$	..	..	0.35
30	Tetrachlorocyclopentadiene	10.83	4.24	0.50
31	May be dimethylindene	..	1.89	..
32	Pentachlorocyclopentadiene	0.71	2.56	1.60
33	Isomer of 32	0.36	..	..
34	$C_4H_5Cl_3O$	..	..	3.05
35	THF-X_2	1.14	6.77	..
36	Isomer of 31	..	0.89	..
37	THF-X_3	3.63	..	..
38	THF-X_4	2.71	..	..
39	Isomer of 31	..	0.31	..
40	Phthalic anhydride	2.99	1.74	6.93
41	Isomer of 32	11.61	..	..
42	Hexachlorocyclopentadiene	2.78	0.73	0.92
43	1,4-Butanedioldibenzoate	1.28	..	..

cyclopentadienes are derived from the retro-Diels-Alder reaction of the set freed hexolic anhydride in the degradation.

β-Scission in the polyester backbone leading to the formation of the dicarboxylic acid with concomittant dehydration, cyclisation of the $\sim\!\sim CO^{\bullet}$ terminated radicals produced via acyl-oxygen bond homolysis and in-chain ejection of the anhydride leading to the polyether formation are the important mechanisms contributing to the formation of anhydride during thermal degradation of polyesters.[3,14] From detailed studies with polybutylene phthalates,[3] it has been proved that 58 per cent of the anhydride is formed through β-scission process owing to the availability of four β-hydrogens. It has also been proved that as the number of β-hydrogen decreases, the per cent formation of anhydride is also decreased.

In the present investigation also, it is observed that as the β-hydrogen in the diol part decreases, the amount of anhydride released from the system considerably decreases. This is reflected in the decrease in the total amount of polychlorocyclopentadienes formed during the thermal degradation. Hence, the presence of β-hydrogen is vital for imparting flame retardancy in the family of polyesters investigated.

One of the ideas to use 2,3-dichloro-2-butene-1,4-diol is to load the polyester with higher amounts of chlorine (apart from hexolic anhydride part) at the expense of β-hydrogens. Incorporation of higher amounts of halogen impulses one to come to the conclusion that the polyesters may have higher flame retardancy and char value. In contradiction, both parameters are found to be less in chlorinated diol based polyester.

Conclusion

In hexolic anhydride based polyesters, it is essential to have β-hydrogens in the diol component to release hexolic anhydride, the precursor for the evolution of hexachloro-cyclopentadiene (HEX) by a retro-Diels-Alder reaction and other flame cooling agents, the isomeric polychlorocyclopentadienes from HEX. Incorporation of chlorine in the place of β-hydrogens in the diol part does not improve the liberation of hexolic anhydride and other subsequent flame cooling products.

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