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AN INSIGHT INTO THE DEGRADATION ASPECTS OF 1,4,5,6,7,7-HEXACHLOROBICYCLO[2.2.1]HEPT-5-ENE-2,3-DICARBOXYLIC ACID BASED TWO COMPONENT POLYESTERS

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ABSTRACT

1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid (HET-acid) was melt condensed with 1,2-ethanediol (EG) and 1,4-butanediol (BD). The prepared polyesters were pyrolysed under vacuum. The components of the volatile and cold ring fractions were separated using a gas chromatograph provided with a capillary column and were identified in a mass-selective detector. The occurrence of several secondary reactions during the degradation process due to the release of hydrogen chloride from the chlorinated part of the poly(ester) ester chain are evidenced by the identification of several chlorinated products. Although the presence of HET units in HETBD does not have any radical influence on the degradation of the diol component, it has a tremendous influence on the degradation of the diol component in HETEG polyester.

INTRODUCTION

Pyrolysis studies on poly(ethyleneterephthalate) (PET) and poly(butyleneterephthalate) have been reported [1]. Similarly, the off-line pyrolysis aspects of poly(ethylenephthalate) (P122) and poly(butylenephthalate) (P144) have been detailed by us elsewhere [2]. The effect of substituting *o*-dicarboxylic acid in the place of *p*-dicarboxylic acid on the pyrolysis products in 1,2-ethanediol and 1,4-butanediol based polyesters has been described [3].

The results of detailed studies on the degradation of oligoesters based on 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid (HET-acid)–1,2-ethanediol (HETEG) and HET-acid–1,4-butanediol (HETBD) by flash pyrolysis–gas chromatography have been presented and discussed previously [4]. Since a packed column was used in that study, it was possible for us to identify only the major degradation products. The present work was undertaken to obtain a more detailed comparison between P122 and

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P144 polyesters with HETEG and HETBD polyesters, and the results are discussed herein.

EXPERIMENTAL

Materials

HET-acid and 1,4-butanediol were supplied by Vianova (Austria) as gift samples. 1,2-Ethanediol (Merck) and 1,4-butanediol were purified by vacuum distillation. Methanol was used as the solvent for recrystallizing HET-acid. HETEG and HETBD were synthesized by melt condensation in vacuo (50 Pa) at 150 °C for 24 h from the respective monomers. A Knauer vapour-pressure osmometer was used to determine the molecular weight of these polyesters. The measurements were made at 60 °C in carbon tetrachloride. The number-average molecular weights obtained for HETEG and HETBD were 1590 and 2240, respectively [4].

Methods

Off-line pyrolysis in vacuo

The all-glass apparatus used for the off-line pyrolysis in vacuo has been described previously [1,3]. HETEG and HETBD polyesters (1.0 g) were degraded by linearly raising the temperature of the material from 50 °C to 440 °C at a rate of 10 °C min^{-1}. The volatile products were allowed to condense over a frozen matrix of 0.5 ml 1,2,4-trichlorobenzene, whereas the cold ring fraction was extracted using 2.0 ml acetone.

Gas-chromatographic–mass-spectrometric studies

The separation and identification of the pyrolysis products obtained from HETEG and HETBD were done in a Hewlett Packard HP5890A gas chromatograph containing a 12 m long capillary column (cross-linked methylsilicone gum, HP1) coupled to a Hewlett Packard HP5970B mass-selective detector.

The data acquisition and analyses were done using a Hewlett Packard HP59970A work station.

In all measurements the injector temperature, detector temperature, the masses scanned and the injector volume were 250 °C, 280 °C, 20–550 amu and 1 μl, respectively. Helium was used as the carrier gas. The temperature profile used in the gas chromatograph to achieve the separation of the components of the volatile and cold ring fraction was: initial temperature 40 °C, initial time 5.0 min, heating rate 10 °C min^{-1}, final temperature 240 °C and final time 5.0 min. For the analyses of the volatile fraction, the data acquisition was stopped from 12.5 to 14.0 min owing to the elution of the solvent, 1,2,4-trichlorobenzene. The data acquisition in the mass-selective detector was started only after 2.0 min into the analysis of the cold ring fractions owing to the elution of acetone from the column at 0.71 min.

RESULTS AND DISCUSSION

The quantification of the major degradation products from HETEG and HETBD, viz. hexachlorocyclopentadiene, maleic anhydride and HET-anhydride, by flash pyrolysis–gas chromatography are detailed elsewhere [4]. From this qualitative study on the volatile and cold ring fractions obtained by off-line pyrolysis of HETEG and HETBD, plausible mechanisms for the formation of various products have been proposed and discussed.

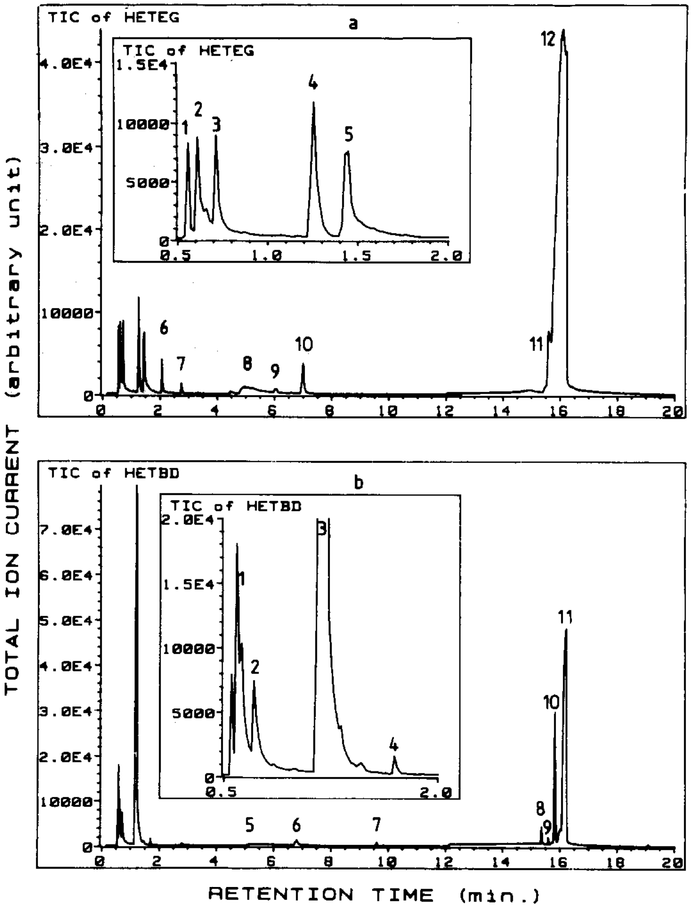

Fig. 1. Total ion chromatograms (TIC) for the volatile fractions obtained from HETEG (a) and HETBD (b) polyesters. Inserts are the zoomed TICs for retention time 0.5–2.0 min. For product identification see Table 1.

The total ion chromatograms (TIC) obtained for the volatile and the cold ring fractions collected during the pyrolysis of HETEG and HETBD are presented in Figs. 1 and 2, respectively. The products identified in the volatile fractions of both HETEG and HETBD are listed in Table 1.

It is interesting to note that acetaldehyde formation from HETEG is not the major degradation route in HETEG in comparison with PET [1] and P122 [2] polyesters. The different products formed from the glycol part of HETEG are vinyl chloride, 1,2-dichloroethane, 2-chloroethanol, 2-chloroethylvinyl ether and di(2-chloroethyl) ether.

TABLE 1

Products identified in the volatile fraction of HETEG and HETBD collected during vacuum pyrolysis

No.	Retention time (min)	Molecular formula	Molecular weight	Suggested structure	Area (%)
HETEG					
1	0.556	CO_2/C_2H_4O	44	Carbondioxide/acetaldehyde	0.78
2	0.608	C_2H_3Cl	62	Vinyl chloride	1.56
3	0.712	C_3H_6O	58	Acetone (?)	1.80
4	1.254	$C_2H_4Cl_2$	98	1,2-Dichloroethane	2.27
5	1.438	C_2H_5ClO	80	2-Chloroethanol	2.67
6	2.066	C_4H_7ClO	106	2-Chloroethylvinylether	0.74
7	2.749	C_7H_8	92	Toluene	0.27
8	4.941	$C_4H_2O_3$	98	Maleic anhydride	2.11
9	6.062		$m/z = 93$	Compound with C_3H_6ClO unit	0.39
10	7.002	$C_4H_8Cl_2O$	142	Di(2-chloroethyl)ether	1.48
11	15.600	C_5HCl_5	236	Pentachlorocyclopentadiene	5.05
12	16.083	C_5Cl_6	270	Hexachlorocyclopentadiene	80.87
Total of the products identified					99.99
HETBD					
1	0.624	C_4H_6	54	1.3-Butadiene	2.46
2	0.713	C_3H_6O	58	Acetone (?)	2.77
3	1.199	C_4H_8O	72	Tetrahydrofuran	39.14
4	1.698	$C_5H_{10}O$	86	2-Methyltetrahydrofuran (?)	0.31
5	5.376	$C_4H_2O_3$	98	Maleic anhydride	2.14
6	6.805	C_4H_7Cl	90	4-Chloro-but-1-ene	0.88
7	9.597		$m/z = 101$	Compound with $C_5H_9O_2$ unit (I)	0.25
8	15.362		$m/z = 101$	Compound with $C_5H_9O_2$ unit (II)	0.94
9	15.593		$m/z = 101$	Compound with $C_5H_9O_2$ unit (III)	0.31
10	15.833	C_5HCl_5	236	Pentachlorocyclopentadiene	8.95
11	16.221	C_5Cl_6	270	Hexachlorocyclopentadiene	41.84
Total of the products identified					99.99

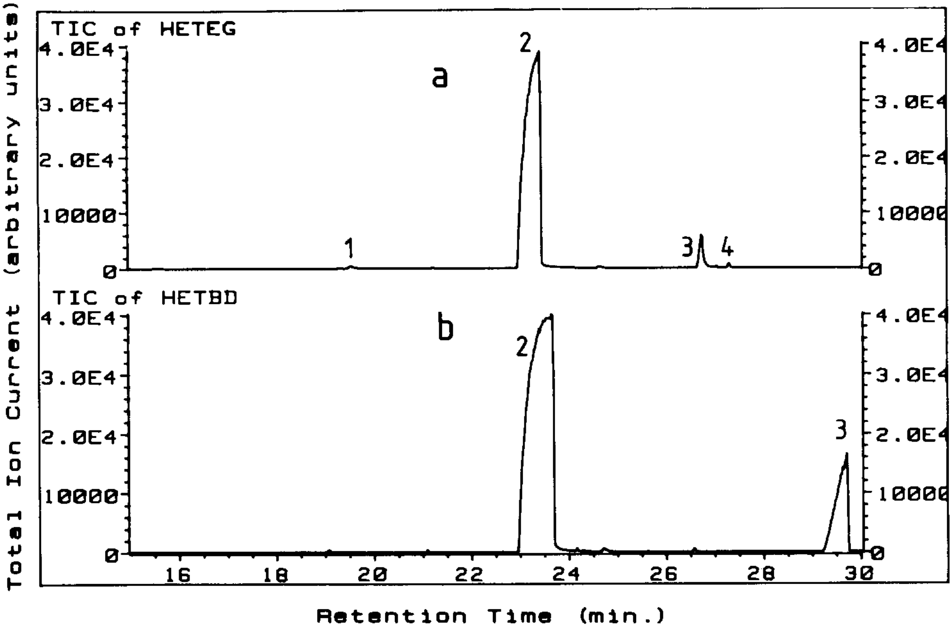

Fig. 2. Total ion chromatograms for the cold ring fractions obtained from HETEG (a) and HETBD (b) polyesters. For product identification see Table 2.

Vinyl chloride and 1,2-dichloroethane may be easily formed by the addition of HCl to acetylene, both products being generated during the pyrolysis of HETEG.

$$HC{\equiv}CH + HCl \rightarrow CH_2{=}CH{-}Cl \qquad (1)$$

$$CH_2{=}CH{-}Cl + HCl \rightarrow Cl{-}CH_2{-}CH_2{-}Cl \qquad (2)$$

The vinyl terminated units initially formed by the β-scission process can add to the HCl liberated to yield the chloroethyl terminated units.

$$\sim\sim CO{-}O{-}CH{=}CH_2 + HCl \rightarrow \sim\sim CO{-}O{-}CH_2{-}CH_2{-}Cl \qquad (3)$$

A successive alkyl–oxygen homolysis followed by either Cl$^\bullet$ addition or H$^\bullet$ elimination is another reasonable route for the generation of these products.

$$\sim\sim CO{-}O{-}CH_2{-}CH_2{-}Cl \xrightarrow{-\sim\sim CO{-}O^\bullet} {}^\bullet CH_2{-}CH_2{-}Cl \qquad (4)$$

$${}^\bullet CH_2{-}CH_2{-}Cl + Cl^\bullet \rightarrow Cl{-}CH_2{-}CH_2{-}Cl \qquad (5)$$

$${}^\bullet CH_2{-}CH_2{-}Cl{-}H^\bullet \rightarrow CH_2{=}CH{-}Cl \qquad (6)$$

The formation of 2-chloroethanol may be explained by the acyl–oxygen homolysis of the chloroethyl terminated units followed by the addition of the hydrogen radical to the liberated 2-chloroethoxy radical as shown below.

$$\sim\!\sim\!\sim\mathrm{CO{-}O{-}CH_2{-}CH_2{-}Cl} \xrightarrow{-\sim\sim\sim\mathrm{CO}^{\bullet}} {}^{\bullet}\mathrm{O{-}CH_2{-}CH_2{-}Cl} \tag{7}$$

$${}^{\bullet}\mathrm{O{-}CH_2{-}CH_2{-}Cl} + \mathrm{H}^{\bullet} \rightarrow \mathrm{HO{-}CH_2{-}CH_2{-}Cl} \tag{8}$$

The other possibilities for the formation of 2-chloroethanol are either hydrolysis or transesterification of the chloroethylterminated units. Thus the 2-chloroethanol formed can condense in the presence of strong acids to yield di(2-chloroethyl)ether.

$$2\ \mathrm{HO{-}CH_2{-}CH_2{-}Cl} \xrightarrow{-\mathrm{H_2O}} \mathrm{Cl{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}Cl} \tag{9}$$

Maleic anhydride may be formed from the retro-Diels–Alder reaction of the HET-acid or anhydride, liberated during the degradation of HETEG. The mechanism of formation of hexachlorocyclopentadiene and pentachlorocyclopentadiene from HET-acid based polyesters has been discussed briefly in our earlier papers [5,6].

From these results it is clear that, even though the pyrolysis products of PET and P122 are not very different with respect to the products formed from the glycol unit, incorporation of HET-acid units in the 1,2-ethanediol based polyesters has a tremendous effect on the degradation path of the 1,2-ethanediol unit. Furthermore, the absence of 2-methyl-1,3-dioxolane from the pyrolysis products of HETEG also strongly supports the foregoing conclusion.

In HETBD polyester, the major volatile compound formed from the diol component during thermal degradation was tetrahydrofuran (Fig. 1 and Table 1), a result very similar to that obtained for the degradation of PBT and P144 polyesters. Detailed mechanistic aspects for the formation of 1,3-butadiene and tetrahydrofuran from 1,4-butanediol based polyesters have been described previously [1,2]. A minor amount (0.88%) of 4-chlorobut-1-ene was detected in the volatile fraction obtained from HETBD polyester. Its formation can be easily explained by the addition of HCl to the 1,3-butadiene formed:

$$\mathrm{CH_2{=}CH{-}CH{=}CH_2} + \mathrm{HCl} \rightarrow \mathrm{CH_2{=}CH{-}CH_2{-}CH_2{-}Cl} \tag{10}$$

The major product identified in the cold ring fractions obtained from HETEG and HETBD was HET-anhydride (Fig. 2 and Table 2). The identification of butenyl ester of HET-acid in the cold ring fraction of HETBD in appreciable quantities (16.17%) provides proof for the occurrence of a β-scission process in this polyester. In the cold ring fraction of HETEG and HETBD, compounds containing maleic acid units were not registered. This finding strongly supports the idea that the in-chain retro-Diels–Alder reaction of the HET units yielding hexachlorocyclopentadiene and maleic acid–diol polyester chain is less favoured. It is explicit from this study that the presence of HET units in HETBD does not have a radical

TABLE 2

Products identified in the cold ring fraction of HETEG and HETBD collected during vacuum pyrolysis

No.	Retention time (min)	Molecular formula	Molecular weight	Suggested structure	Area (%)
HETEG					
1	19.535		$m/z = 177$	Unknown	0.39
2	23.414	$C_9H_2Cl_6O_3$	368	HET-anhydride	95.48
3	26.738		$m/z = 379$	Compound with $C_9H_2Cl_6O_3$ unit	3.83
4	27.198		$m/z = 274$	Ester having HET-unit	0.30
Total of the identified products					100.00
HETBD					
1	6.336		$m/z = 115$	Unknown	0.26
2	23.652	$C_9H_2Cl_6O_3$	368	HET-anhydride	83.56
3	29.715	$C_{13}H_{10}Cl_6O_4$	440	$HOOC-C_7H_2Cl_6-COO(CH_2)_2CH{=}CH_2$	16.17
Total of the identified products					99.99

influence on the degradation of the diol component, a result completely contrary to that obtained for HETEG polyester.

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