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STRUCTURAL CHARACTERIZATION AND THERMAL DEGRADATION OF HEXOLIC-ANHYDRIDE-BASED POLYESTERS

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ABSTRACT

The structural characterization of the polyesters prepared by the melt condensation of hexolic anhydride with ethylene glycol and 1,4-butanediol was carried out using IR and ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopies. From the thermogravimetric curves, the energy of activation for the degradation process was calculated by the method of Coats and Redfern. Flash pyrolysis–gas chromatographic studies were performed at the temperatures 600 and 1000 °C. In contrast with similar polyesters based on 1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic anhydride, the hexolic-anhydride-based materials yielded very low amounts of hexachlorocyclopentadiene during thermal degradation.

INTRODUCTION

Hexolic anhydride (5,6,7,8,10,10-hexachloro-3*a*,4,4*a*,5,8,9,9*a*-octahydro-5,8-methanonaphtho[2,3-*c*]furan-1,3-dione) [1,2] is an attractive reactive comonomer in the field of polyesters. Detailed degradation studies of polyesters based on ethylene glycol (EG), 1,4-butanediol (BD) and 1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic acid (HET acid) have been reported by Vijayakumar and Fink [3].

In order to understand the difference between the degradation behaviour of polyesters based on HET acid (HET) and the degradation behaviour of polyesters based on hexolic anhydride (H), a detailed study was carried out on both HEG and HBD using pyrolysis–mass spectrometric techniques [4].

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The results of the structural characterization of HEG and HBD (IR and ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopies) and the thermal degradation studies (thermogravimetric and flash pyrolysis–gas chromatographic methods) are presented and discussed in this paper.

EXPERIMENTAL

Materials

Ethylene glycol and 1,4-butanediol (Merck) were purified by vacuum distillation before use. Hexolic anhydride was obtained from Hooker Chemical Corporation, Belgium, as a gift sample and was used as received.

Methods

Synthesis of polyesters

The synthesis and purification of the polyesters HEG and HBD have been presented elsewhere [4]. The structures of these materials are shown in Fig. 1.

IR studies

The IR spectra of the polyesters were recorded with a Perkin–Elmer IR spectrophotometer (model 599) using the KBr pellet technique.

NMR studies

Both ^{1}H and ^{13}C NMR spectra were recorded using a varian T60 NMR spectrometer, operating at room temperature. Deuterated chloroform ($CDCl_3$) was used as the solvent and tetramethylsilane (TMS) was taken as the internal standard.

Thermogravimetric analysis

The thermogravimetric curves of HETEG, HETBD, HEG and HBD were recorded using a Stanton Redcroft thermobalance (model TG 750). The

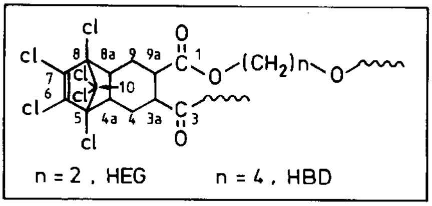


Fig. 1. The structures of the polyesters HEG and HBD.

material (10 mg) was heated at a rate of 10 °C min^{-1} in a static air atmosphere from 50 to 550 °C.

Flash pyrolysis–gas chromatographic studies

Typically 1–5 mg of the sample was deposited on the platinum ribbon of a Hewlett–Packard pyroprobe (model 18580A) from 0.5% polyester solution in acetone. The solvent was evaporated by heating the ribbon several times for 10 s at 200 °C. The ribbon with known amounts of the sample was then pyrolyzed by heating (ramp off) either to 600 or 1000 °C for 10 s. The pyrolysis products were separated in a Hewlett–Packard gas chromatograph (model 5830) with an OV17 column ($\frac{1}{8}$ in × 6 ft). The following temperature profile was used to effect the separation: interface temperature, 200 °C; injector temperature, 250 °C; flame ionization detector (FID) temperature, 320 °C; initial temperature, 35 °C; initial time, 2 min; heating rate, 10 °C min^{-1}; final temperature, 300 °C; final time, 5 min; carrier gas, helium; flow rate, 30 ml min^{-1}.

Product identification was determined both by injecting authentic samples and by recording the mass spectra of the products using a Balzers QMG 511 quadrupole mass spectrometer coupled to the gas chromatograph by means of a jet separator. A quantitative study of hexachlorocyclopentadiene (HEX) evolution from the degradation of HEG and HBD was carried out by the appropriate calibration of the FID response.

RESULTS AND DISCUSSION

The IR spectra of the polyesters HEG and HBD show no absorption at 1815 cm^{-1} but an intense absorption at 1745 cm^{-1} which confirms the presence of an ester group in the materials. The intense peak at 1600 cm^{-1} is attributed to the double bond present in the hexolic unit.

From the recorded ^{1}H NMR spectrum of HEG the following peak assignments can be made: the broad peak at 2.24 ppm is due to the hydrogens at C-4 and C-9; the broad singlet at 3.00 ppm is attributed to the hydrogens at C-3*a* and C-9*a*; a similar singlet observed at 3.38 ppm is due to the hydrogens at C-4*a* and C-8*a* and the broad signal at 4.32 ppm is due to the $-CH_2-$ protons of the ethylene glycol unit. The ratio of hexolic unit to ethylene glycol unit present in HEG, calculated from the integrated peak intensities, is 1: > 1.0 (but 1: < 1.3), indicating the presence of one glycol unit per unit of the anhydride.

In HBD, the signals arising from the protons at the various sites of the hexolic unit are the same as explained above for HEG. In addition to these peaks, there are two other signals at 1.69 and 4.12 ppm arising from the protons present in the 1,4-butanediol unit. The ratio of H unit to BD unit in HBD is 1 : 1.

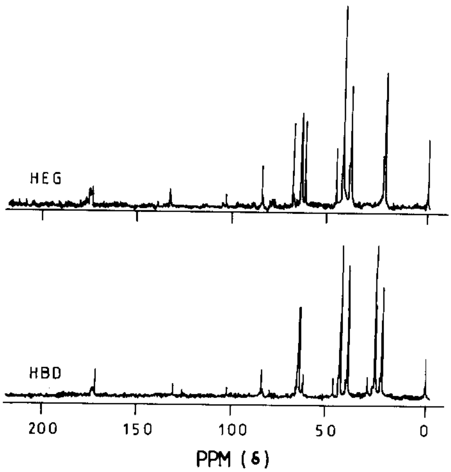


Fig. 2. ^{13}C NMR spectra of HEG and HBD (refer to Fig. 1 for the structures and to Table 1 for the chemical shifts).

The ^{13}C NMR spectra recorded for HEG and HBD are shown in Fig. 2. The chemical shifts arising from the different carbons present in HEG and HBD are given in Table 1.

The thermogravimetric curves obtained for the four polyesters are presented in Fig. 3(a). These polyesters start to degrade slowly in the temperature range 200–250 ° C. At 500 ° C HEG and HBD show residues of 11% and

TABLE 1

Observed ^{13}C chemical shifts for HEG and HBD (all shifts are in ppm from TMS; see Figs. 1 and 2)

^{13}C no.	HEG	HBD
1	173.90	172.87
3	172.54	172.87
3*a*	45.83	45.83
4	39.49	39.92
4*a*	40.09	40.09
5	66.79	65.12
6	131.91	132.02
7	131.91	132.02
8	62.95	62.95
8*a*	42.63	42.85
9	39.28	39.43
9*a*	43.17	43.39
10	82.88	82.94
$-O\underline{C}H_2-$	60.78	60.78
$-OCH_2\underline{C}H_2-$	–	29.15 25.41

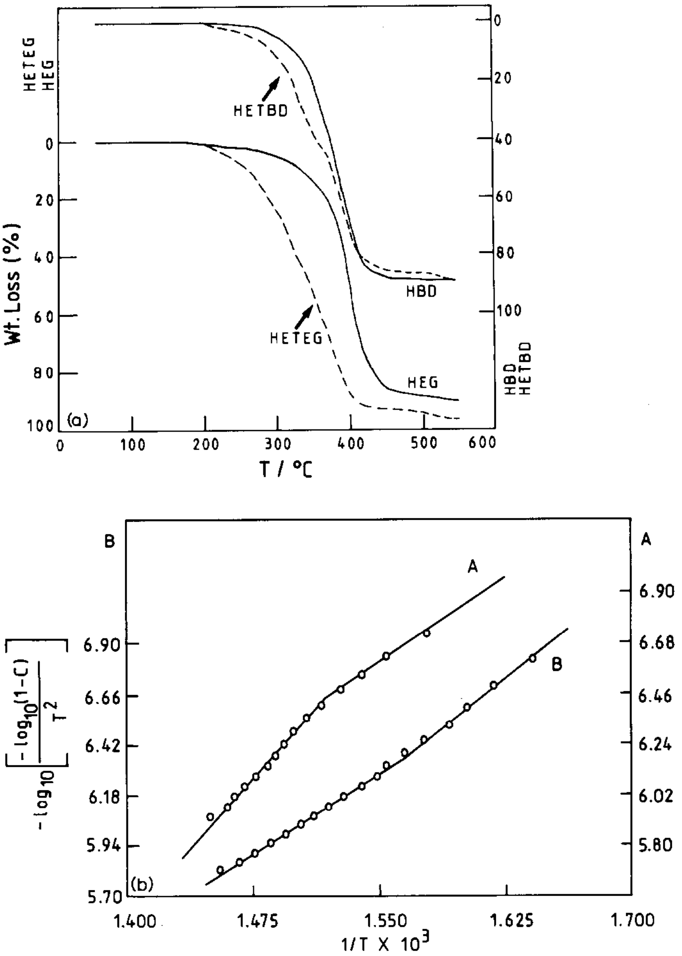


Fig. 3. (a) TG curves of HETEG, HETBD, HEG and HBD recorded in a static air atmosphere (heating rate, 10 °C min^{-1}). (b) Coats and Redfern plots for the calculation of activation energies of the degradation processes (T (K); C, fraction decomposed at time t): (A) HEG; (B) HBD.

9%, respectively. This result is in accordance with the finding that the amount of char increases with increasing halogen content of the material [5]. The thermogravimetric curves can be evaluated using the method of Coats and Redfern [6]. The reaction order n is assumed to be unity, and a plot of $-\log_{10}[-\log_{10}(1-C)/T^2]$ vs. $1/T$ is drawn (Fig. 3(b)), where C is the fraction decomposed at time t. It can be seen from the Coats and Redfern plot that both the polyesters show two distinct stages of degradation. From the slopes of the lines, the energy of activation E can be calculated, since the slope equals $E/2.303R$.

Changes in slope occur at 386 and 366 °C for HEG and HBD, respectively. For HEG the energy of activation for degradation is estimated as

TABLE 2

Calculated first-order activation energies for the different stages of degradation of HETEG and HETBD (Coats and Redfern method)

Sample	T (°C)	Region	Fractional weight loss (C)	Activation energy (kJ mol^{-1})
HETEG	264–332	Stage I	0.12–0.44	49.79
	341–364	Stage II	0.48–0.64	50.37
	370–392	Stage III	0.68–0.84	90.96
HETBD	300–338	Stage I	0.12–0.32	70.92
	345–370	Stage II	0.36–0.48	43.97
	375–403	Stage III	0.52–0.76	75.56

93.64 kJ mol^{-1} for the initial stage of degradation and increases to 157.19 kJ mol^{-1} after 386 °C. In contrast with HEG, HBD shows a slight decrease in energy of activation in the latter degradation step, i.e. from a value of 122.55 kJ mol^{-1} to 96.32 kJ mol^{-1}.

A similar data analysis for the TG curves of HETEG and HETBD shows three distinct stages of degradation. The results are summarized in Table 2. In both the polyesters, the second and third stages of degradation start in the temperature ranges 335–345 °C and 365–375 °C, respectively. In HETEG, the energies of activation progressively increase from the first to

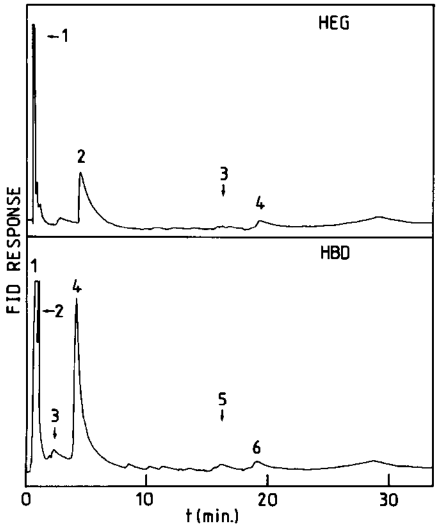


Fig. 4. Gas chromatograms of the volatile products formed during the flash pyrolysis of HEG and HBD at 1000 °C for 10 s. HEG: 1, high volatiles (molecular weight ≤ 44); 2, benzene; 3, halo compounds; 4, phthalic anhydride. HBD: 1, high volatiles (molecular weight ≤ 44); 2, 1,3-butadiene; 3, tetrahydrofuran; 4, benzene; 5, halo compounds; 6, phthalic anhydride.

TABLE 3

Yields of the major degradation products from HEG and HBD during flash pyrolysis studies

Sample	Pyrolysis temperature (T) (°C)	Product and yield ((area count mg^{-1})$\times 10^{-5}$)				
		High volatiles [a]	Benzene	THF	Halogenated compounds [b]	Phthalic anhydride
HEG	600	18	–	–	1.2	27
HEG	1000	32	21	–	2.2	11
HBD	600	17	–	120	6.0	25
HBD	1000	110	52	–	2.2	2

[a] Products eluting in the retention time region 0.0–1.1 min. [b] Products eluting in the retention time region 15.5–16.5 min (tetrachlorocyclopentadiene, pentachlorocyclopentadiene and hexachlorocyclopentadiene).

the third stage of degradation, whereas HETBD shows a different trend. A comparison of the energies of activation for the degradation of HET-acid-based and hexolic-anhydride-based polyesters clearly indicates that the latter system requires a higher energy of activation for the degradation process. Since the degradation of polyesters involves several different chain scission reactions, it is not possible to assign these values for a specific degradation process.

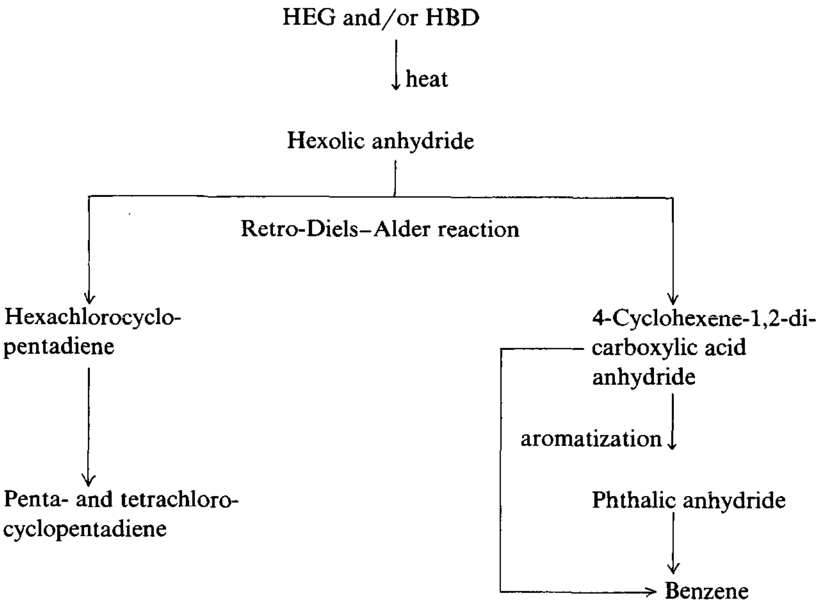
The gas chromatograms obtained for HEG and HBD during flash pyrolysis at 1000 °C for 10 s are presented in Fig. 4. The identified products and their yields are shown in Table 3. The mass spectra recorded at a low retention time (< 1.1 min) show peaks at $m/z = 28$, 44, 35, 36, 37 and 38, characteristic of CO, CO_2 and HCl. For HBD, peaks pertaining to 1,3-butadiene are also observed. Similarly the peaks pertaining to CH_3CHO are observed for HEG. The formation of tetrahydrofuran (THF) from HBD at

TABLE 4

Yield of hexachlorocyclopentadiene during the flash pyrolysis of the polyesters HETEG, HETBD, HEG and HBD

Sample	Pyrolysis temperature (°C)	Yield of HEX (mg g^{-1} sample)	Available HEX (mg g^{-1} sample)
HEG	600	5	580
HEG	1000	5	580
HBD	600	11	550
HBD	1000	9	550
HETEG [a]	600	320	660
HETBD [a]	600	350	620

[a] Results taken from ref. 3.



Scheme 1.

low pyrolysis temperature (600 ° C), and the decrease in THF formation with the subsequent increase in high volatile products at 1000 ° C, clearly demonstrates the breakdown of THF to low molecular weight compounds.

In all cases phthalic anhydride is found as a major decomposition product. This can easily be explained by the degradation of the hexolic unit present in the polyester chain (Scheme 1).

At higher pyrolysis temperatures the amount of phthalic anhydride formed decreases drastically, whereas the formation of benzene increases. This indicates the enhanced decarboxylation and decarbonylation of 4-cyclohexene-1,2-dicarboxylic acid anhydride and phthalic anhydride.

In comparison with HETEG and HETBD polyesters [3], hexolic-anhydride-based polyesters, HEG and HBD, show remarkably low yields of hexachlorocyclopentadiene (HEX). Table 4 shows the yields (mg g^{-1}) of HEX from HEG and HBD during pyrolysis. Only 2%–5% of the theoretically available HEX is released during the pyrolysis, whereas similar polyesters made from HET acid yield approximately 50% of the HEX that is available. A detailed degradation study of polyesters based on hexolic anhydride, phthalic anhydride, maleic anhydride and 1,4-butanediol [7] has shown similar results. From this it can be concluded that the hexolic unit present in the polyester backbone is able to participate more easily in transfer reactions either in the condensed phase and/or in the gas phase than the HET unit incorporated in the polyester chain.

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