Thermochimica Acta, 59 (1982) 51–61
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

PYROLYSIS STUDIES OF AROMATIC POLYESTERS

CHINNASAMY THANGAVEL VIJAYAKUMAR and JOHANNES KARL FINK

Institut für Chemische und Physikalische Technologie der Kunststoffe, Montanuniversität Leoben, A-8700 Leoben (Austria)

(Received 2 April 1982)

ABSTRACT

The products of pyrolysis, at 400°C in vacuo (1 Pa), of poly(ethyleneterephthalate) (PET) and poly(butyleneterephthalate) (PBT) were studied. The products were identified by gas chromatography/mass spectrometry technique. The highly volatile products of PET contained acetaldehyde, benzene, toluene, styrene and ethylbenzene and in the case of PBT, butadiene, tetrahydrofuran, vinylcyclohexene and ethylbenzene were the major products. A qualitative analysis of the products of low volatility revealed that the main components were benzoic acid, terephthalic acid, monovinyl esters of terephthalic acid and higher oligomers in the case of PET, whereas benzoic acid, monobutenyl esters of terephthalic acid and higher oligomers were the main products from PBT. The results obtained were in good agreement with those obtained from pyrolysis experiments, carried out directly in the mass spectrometer. Mechanisms to explain the occurrence of the different products are proposed.

INTRODUCTION

Poly(ethyleneterephthalate) (PET) is extensively used in the production of fibres and films. In particular, PET is starting to be used as container material for soft drinks (e.g., Coca Cola), edible oils, etc. In recent years a new high-performance molding and extrusion grade of thermoplastic polyester, poly(butyleneterephthalate) (PBT), has become increasingly important. The pyrolysis and combustion of PET was studied [1–5] to establish the thermal stability of the material to the temperatures employed in the melt-spinning process. The increasing utilization of PET in textile materials required the development of suitable flame-retardant systems and consequently investigations on their degradation behaviour have been undertaken [6–8]. Some data on highly volatile products formed during the pyrolysis of PET are available [9–11]. But a systematic study of the degradation behaviour of PBT has not yet been attempted. Lüderwald and Urrutia [12,13] studied the products of pyrolysis of both PET and PBT by direct pyrolysis in the mass spectrometer. In the present investigation, PET and PBT were pyrolysed in vacuo at 400°C. A low pyrolysis temperature was chosen to

0040-6031/82/0000–0000/$02.75

identify the primary products of degradation. Apart from the identification of the volatile products formed, the major components constituting the less volatile fraction were identified and compared with the results of direct pyrolysis in the mass spectrometer. The mechanism of formation of the products identified is elucidated in the framework of the general mechanism of polyester degradation.

EXPERIMENTAL

Materials

The PET used in the present investigation was supplied by Indian Organic Chemicals Ltd., Madras, India, and the PBT was from General Electric Company, U.S.A.

Methods

DTA studies

The DTA studies were carried out in an atmosphere of air between 30 and 490°C using a Mettler TA 2000 system at a linear heating rate of 10°C min^{-1} with 2 mg samples in aluminium sample holders. An empty aluminium sample holder was taken as reference.

Pyrolysis studies

A schematic diagram of the glass apparatus used for the pyrolysis is shown in Fig. 1. The sample (200 mg) was loaded in the pyrolysis tube (2) and the entire system was evacuated. When the pressure of the system reached 10 Pa, the stopcock (S3) was closed. The U-shaped tube used to trap the volatile products (4) and the main trap (5) were cooled using liquid nitrogen. The oven (1) heated to 400°C was attached to the pyrolysis vessel. Pyrolysis was carried out for 30 min, and the stopcocks (S1 and S2) were then closed. The products of pyrolysis were condensed into a glass finger (3). The products of low volatility generally condense at the colder inner walls of the pyrolysis tube. This cold ring fraction was extracted with 2 ml of warm

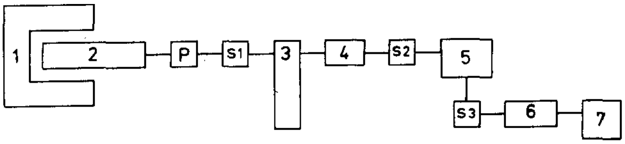


Fig. 1. Schematic layout of the pyrolysis apparatus: (1) oven; (2) pyrolysis tube (glass) with the sample; (3) glass finger suitable for transferring the products to the gas chromatograph; (4) sample collecting U-tube trap; (5) main trap; (6) mercury diffusion pump; (7) oil pump; (P) Pirani gauge; (S1), (S2), (S3) stopcocks.

N, *N*-dimethyl formamide. The products were separated in a gas chromatograph and identified using a mass spectrometer. A Hewlett Packard gas chromatograph Model 5830 coupled to a Balzers QMG 511 mass spectrometer by a jet separator was used in the present studies.

RESULTS AND DISCUSSION

The DTA thermograms of both PET and PBT are shown in Fig. 2. PET shows the glass transition temperature at 80°C and the cold crystallization exotherm at 130°C. It melts at 259°C which is followed by the initial exothermic decomposition around 400°C. Under the same experimental conditions PBT does not show any glass transition and cold crystallization. However, its melting point is around 20°C below that of PET, i.e., at 237°C. PBT shows an exothermic decomposition at 337°C which is followed by a severe exothermic decomposition, starting around 400°C.

The main volatile products of PET pyrolyzed in vacuo at 400°C for 30 min are shown in Fig. 3. The mass spectrum of the low molecular weight products agrees very well with the reports in compilation of mass spectral data [14]. The chromatograms of the various products which constitute the cold ring fraction of PET are shown in Fig. 4. Their retention times, mass spectral data and suggested structures are tabulated in Table 1. The following mechanism can explain the occurrence of various products of pyrolysis from PET.

PET decomposes by random chain scission at the ester links. Since PET has β-hydrogen, the first step in the degradation is the classical ester scission reaction resulting in carboxylic acid (A) and olefinic (B) end groups [9] as shown in eqn. (I) (Ph refers to *p*-phenylene units).

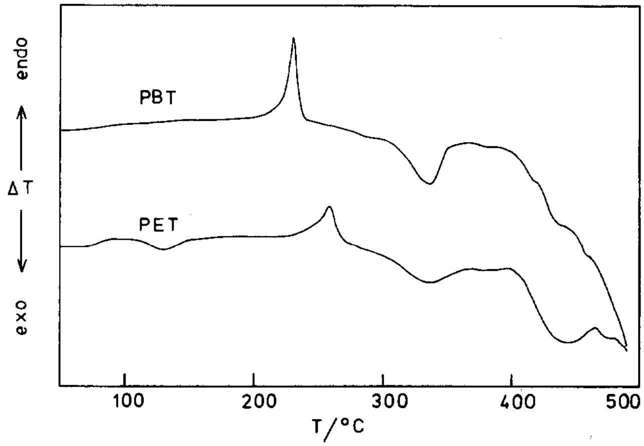


Fig. 2. DTA thermograms of the aromatic polyesters. Heating rate, 10°C min^{-1}.

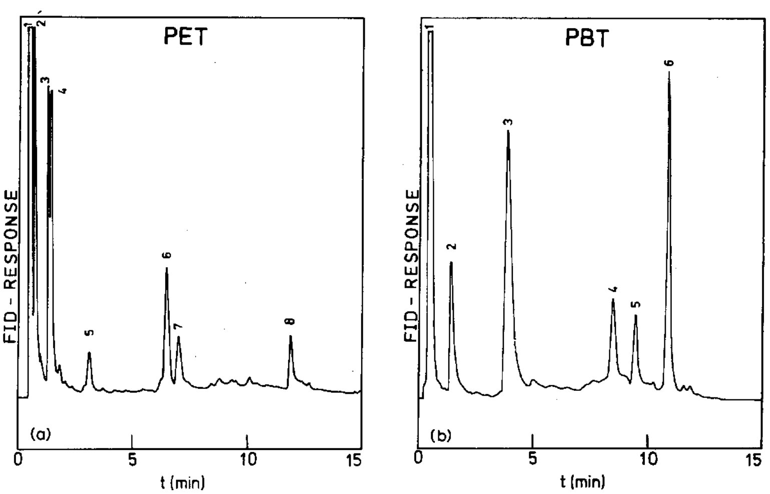


Fig. 3. Gas chromatograms of the volatile products of pyrolysis of aromatic polyesters (isothermal pyrolysis in vacuo at 400°C for 30 min). (a) PET; column, SE-30; 5 min, 50°C; 10°C min^{-1} to 150°C; 23 ml min^{-1} helium. (1) Acetaldehyde; (2) acetone; (3) 2-methyl-1,3-dioxolane; (4) benzene; (5) toluene; (6) ethylbenzene; (7) styrene; (8) not identified. (b) PBT: column OV-17; 5 min, 35°C; 10°C min^{-1} to 130°C; 32 ml min^{-1} helium. (1) 1,3-Butadiene; (2) acetone; (3) tetrahydrofuran; (4) 3,4-dimethyl-1-pentanol or 5-methyl hexanol; (5) 4-vinyl-1-cyclohexene; (6) ethylbenzene.

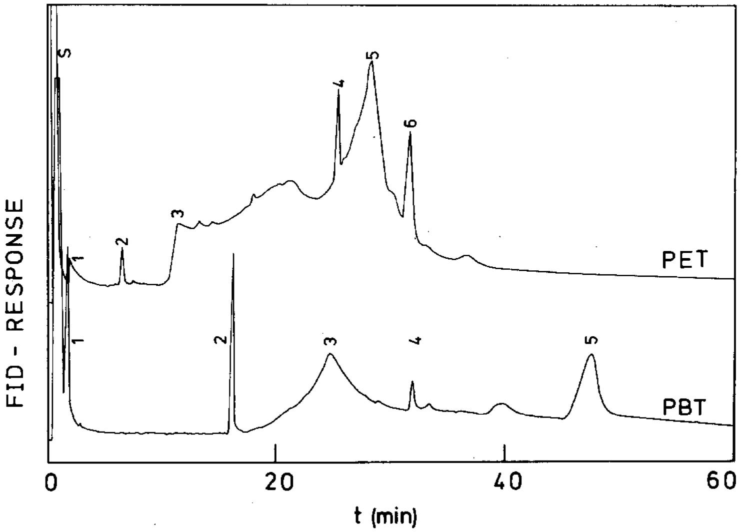
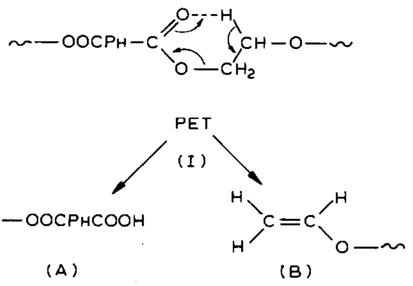


Fig. 4. Gas chromatograms of the products of the cold ring fraction from aromatic polyesters (isothermal pyrolysis in vacuo at 400°C for 30 min). PET and PBT: column SE-30; 5 min, 150°C; 5°C min^{-1} to 290°C; 23 ml min^{-1} helium. (Refer to Tables 1 and 2 for the product identification of PET and PBT, respectively.)

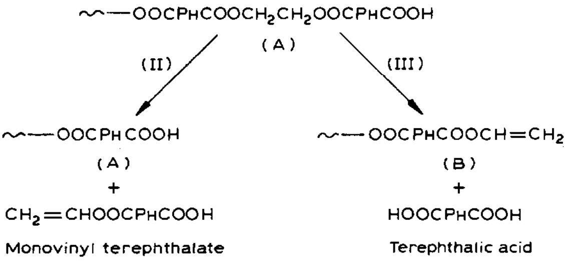
TABLE 1

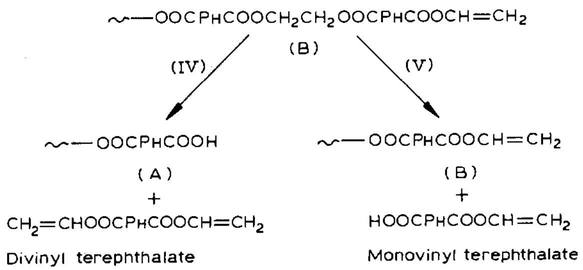
Gas chromatography–mass spectrometry analysis of the products of the "cold ring fraction" obtained from PET

No.	Retention time (min)	Mass/charge Relative intensity Suggested structure							
		105	77	122	51	50	39	38	74
1	1.94	1000	850	735	590	391	147	130	121
		HOOCPhH							
		175	104	76	147	50	132	91	64
2	6.47	1000	950	650	410	400	350	210	200
		$HOOCPhCOOCH=CH_2$							
		149	121	65	166	50	51	45	74
3	11.57	1000	333	120	90	85	80	77	73
		HOOCPhCOOH							
		149	297	105	65	77	104	121	76
4	25.36	1000	470	432	364	303	242	220	205
		$HOOCPhCOOCH_2CH_2OOCPhH$							
		149	65	121	166	50	39	105	75
5	28.39	1000	632	396	340	245	217	179	170
		Unidentified product							
		367	104	324	147	76	149	73	65
6	31.79	1000	954	939	833	561	424	379	303
		$HOOCPhCOOCH_2CH_2OOCPhCOOCH=CH_2$							

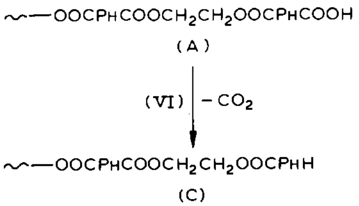


Similar ester scission of the adjacent ester groups of (A) and (B) can then lead to the formation of the following products.

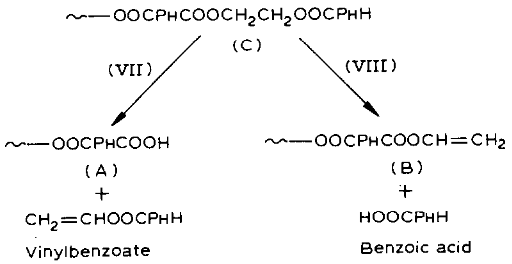




Apart from the above reactions, the carboxylic acid end group products (A) can undergo decarboxylation to yield phenyl end group compounds as shown below.

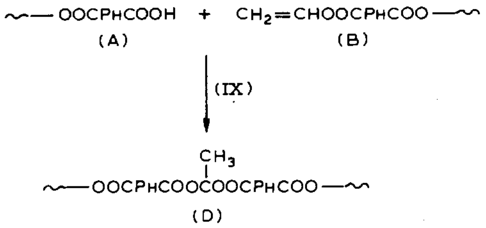


Products having the structure (C) can also undergo an ester cleavage on the adjacent ester linkages yielding the following products.

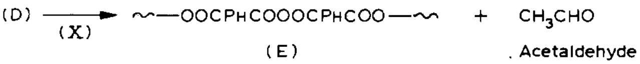


Since the polymer suffers random chain scission, oligomers with end groups of the type (A), (B) and (C) can also be formed.

The formation of acetaldehyde in the pyrolysis of PET has been explained by a reaction [5] between carboxylic acid (A) and olefinic (B) end groups as shown below.



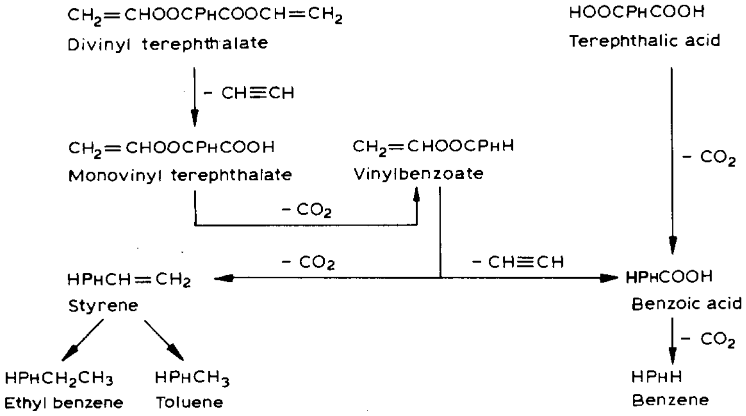
From (D), acetaldehyde may be ejected to form the corresponding anhydride (E).



$$(D) \xrightarrow[(X)]{} \sim\!\!\sim\text{OOCPhCOOOCPhCOO}\sim\!\!\sim \; + \; CH_3CHO$$

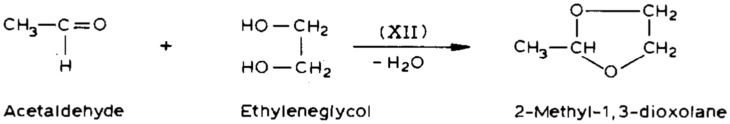
The other volatile products (Fig. 3) formed from PET are benzene, toluene, styrene and ethylbenzene. The formation of these compounds can be explained through the secondary reactions which are taking place on the primary degradation products.

(XI)



Thus the styrene formed undergoes fragmentation and hydrogen abstraction, leading to the formation of toluene and ethylbenzene.

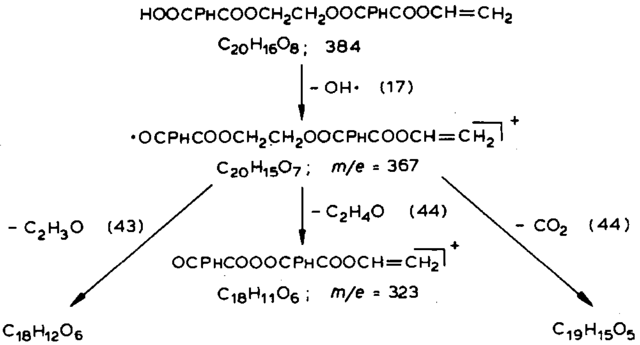
The formation of 2-methyl-1,3-dioxolane can be explained by the reaction of acetaldehyde with ethylene glycol as shown [15] by



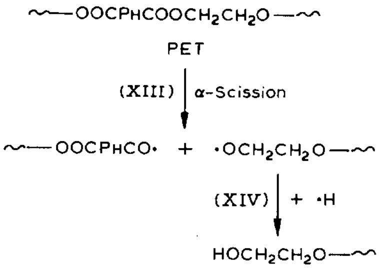
Analysis of the cold ring fraction of PET (Fig. 4 and Table 1) showed the presence of benzoic acid, monovinyl terephthalate, terephthalic acid and higher fragmentation products with both phenyl-, vinyl- and acid end groups. Though acetaldehyde is the major product of pyrolysis of PET, identification of compounds with anhydride linkages has not yet been done.

Lüderwald and Urrutia [12,13], however, were able to identify some ions with this particular structure in their studies on direct pyrolysis of PET in the mass spectrometer. Similarly, from the fragmentation pattern of compound 6 (Fig. 4; Table 1), there is a possibility of –COOOC– linkage being formed because of a broad peak covering three mass numbers being centered between *m/e* 324 and 325.

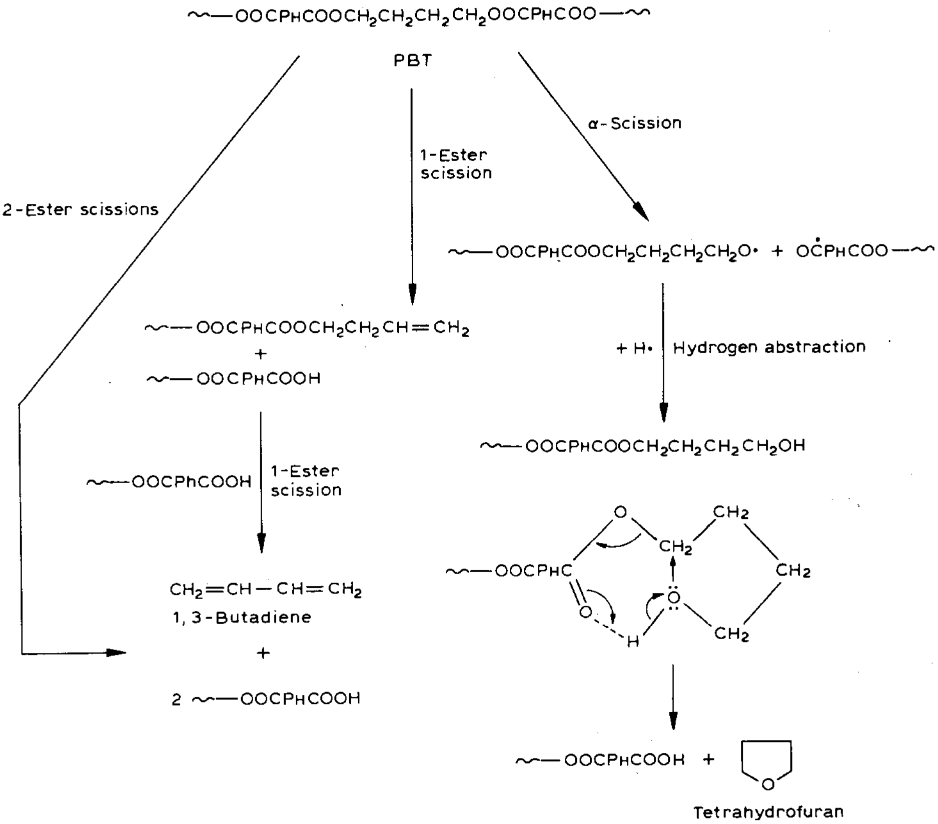
Marshall and Todd [16] proposed α-cleavage of the ester bond as the primary scission to account for the pyrolysis products of PET. Similarly in the pyrolysis of PET in the mass spectrometer [12,13] the glycol end group



ions are detected, which can be formed by the α-cleavage of the ester bond followed by a hydrogen abstraction as shown in eqns. (XIII) and (XIV).



(XV)



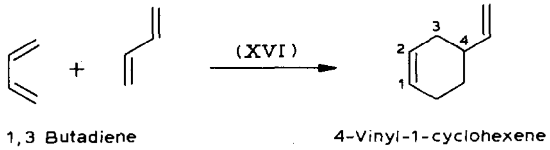
Such type of hydroxyl end group compounds are not detected in the present investigation. It is evident that even if they are formed during the pyrolysis at 400°C in vacuo, they would easily eliminate water resulting in a compound with an olefinic end group, which is detected in the present studies. From the results presented here, it is not possible to decide if α-scission occurs in the course of pyrolysis or only during the fragmentation in the mass spectrometer.

From Fig. 4 it is clear that compound 5 in the case of PET is not well separated, so the identification of this product by its mass spectrum is not possible.

The major volatile products formed from PBT are shown in Fig. 3. The two major products, 1,3-butadiene and tetrahydrofuran, are formed as shown in the reaction scheme (XV).

Thus in any case the major products of pyrolysis of PBT are the diene and tetrahydrofuran, in contrast to PET where acetaldehyde is the major pyrolysis product.

The formation of 4-vinyl-1-cyclohexene can be explained by the secondary reaction (cyclo addition) of the 1,3-butadiene as given below.



Such a type of reaction had already been reported [17] in the case of the pyrolysis of styrene–butadiene polymers.

Ethylbenzene may be formed by scission of a C–C bond of the diol in a similar reaction as pointed out in the case of PET. Likewise there should also occur butylbenzene, propylbenzene and the respective vinyl compounds. In the PBT system styrene, toluene and the compounds mentioned above are totally absent. This finding makes the formation of ethylbenzene by rearrangement and dehydrogenation of vinyl cyclohexene much more suggestive. Following the mechanism of formation of acetaldehyde and the corresponding anhydride given in the PET case, the expected product from PBT is methyl vinylketone. The absence of this product in the volatile fraction of the decomposition products indicates that these reaction steps do not occur in PBT. Even in the fragmentation pattern of compound 5 of Table 2, no $m/e = 351$ peak appears, which would correspond to the respective anhydride ion as indicated in the fragmentation scheme for compound 6 in Table 1.

In the cold ring fraction obtained from PBT, the major products are benzoic acid, buten-3-yl terminated and phenyl terminated carboxy compounds. These products correspond to the products of pyrolysis obtained from PET and their formation can be explained using similar arguments. The striking difference in the cold ring fraction of PBT in comparison to that of PET is the absence of terephthalic acid in the PBT cold ring fraction. This

TABLE 2

Gas chromatography–mass spectrometry analysis of the products of the "cold ring fraction" obtained from PBT

No.	Retention time (min)	Mass/charge Relative intensity Suggested structure							
1	1.61	105	77	122	51	50	39	38	74
		1000	851	734	590	391	147	130	121
		$\mathrm{HOOCPhH}$							
2	16.17	54	203	149	65	121	49	76	104
		1000	686	650	257	221	200	186	178
		$\mathrm{HOOCPhCOOCH_2CH_2CH{=}CH_2}$							
3	24.67	149	65	54	121	166	39	50	76
		1000	500	423	365	269	258	231	173
		unidentified product							
4	31.98	54	105	147	149	73	325	77	104
		1000	944	778	750	583	444	417	389
		$\mathrm{HOOCPhCOOCH_2CH_2CH_2CH_2OOCPhH}$							
5	47.61	54	369	149	55	147	104	121	203
		1000	681	648	417	267	264	242	198
		$\mathrm{HOOCPhCOOCH_2CH_2CH_2CH_2OOCPhCOOCH_2CH_2CH{=}CH_2}$							

can be attributed to a backbiting reaction due the length of the butylene units, which is not possible in the case of PET. On examination of this hypothesis by means of molecular models, it turned out that at least carbon atom-4 of the butanediol unit can be involved in such a backbiting reaction. However, no additional experimental proof for the suggested mechanism is available from the results of the present investigation.

Finally it should be stated that the proposed mechanisms to explain the occurrence of the products found do not take place in the gas phase since the primary volatile products will easily diffuse out of the polymer owing to the high vacuum conditions employed during the pyrolysis. The products which are formed by the secondary reactions are formed rather in the molten degrading polymeric matrix.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the Österreichische Nationalbank for financial support for the mass spectrometer. One of the authors (C.T.V.) thanks the Ministry of Education, Government of India, for the travel grant and the Austrian Government for the award of the Austrian Government Fellowship.

REFERENCES

1 H. Herlinger, Textilveredelung, 12 (1977) 13.
2 A. Püntner, H. Herlinger and U. Einsele, Melliand Textilber., 59 (1978) 412.
3 W.C. McNeill, M.J. Drews and R.H. Barker, J. Fire Retard. Chem., 4 (1977) 222.
4 A. Granzow, R.G. Ferillo and A. Wilson, J. Appl. Polym. Sci., 21 (1977) 1687.
5 H. Herlinger, U. Einsele, A. Püntner, P. Meyer, W. Metzger, A. Gröbe and G. Veeser, Lenzinger Ber., 48 (1980) 65.
6 M. Day and D.M. Wiles, Text. Res. J., 48 (1978) 32.
7 M. Day, K. Ho and D.M. Wiles, J. Appl. Polym. Sci., 25 (1980) 2943.
8 M.E. Bednas, M. Day, K. Ho, R. Sander and D.M. Wiles, J. Appl. Polym. Sci., 26 (1981) 277.
9 L.H. Buxbaum, Angew. Chem., Int. Edn. Engl., 7 (1968) 182.
10 J.R. Richard, C. Vovelle and R. Delbourgo, in F.J. Weinberg (Ed.), Comb. Inst. Eur. Symp., Univ. of Sheffield, Academic Press, London, 1973, p. 131.
11 G. Avondo, C. Vovelle and R. Delbourgo, Combust. Flame, 31 (1978) 7.
12 I. Lüderwald and H. Urrutia, Makromol. Chem., 177 (1976) 2079.
13 I. Lüderwald and H. Urrutia, in C.E. Jones and C.A. Cramers (Eds.), Analytical Pyrolysis, Elsevier, Amsterdam, 1977, p. 139.
14 A. Cornu and R. Massot, Compilation of Mass Spectral Data, Vols. 1 and 2, Heyden, London, 1975.
15 R.H. Barker, G.L. Drake, Jr., J.E. Hendrix and J.E. Bostic, Jr., in W.C. Kuryla and A.J. Papa (Eds.), Flame Retardancy of Polymeric Materials, Vol. 5, Marcel Dekker, New York, 1979, p. 92.
16 I. Marshall and A. Todd, Trans. Faraday Soc., 49 (1953) 67.
17 R.W. May, E.F. Pearson and D. Scothern, Pyrolysis–Gas Chromatography, The Chemical Society, London, 1977, p. 92.