

Analysis of Thermal Degradation of Terephthalate Polyesters by High-Resolution Pyrolysis-Gas Chromatography

Hajime OHTANI, Tadashi KIMURA and Shin TSUGE

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Nagoya 464

Thermal degradation of a series of terephthalate polyesters has been studied by high-resolution pyrolysis-gas chromatography. A wide range of the degradation products can be separated by using a fused silica capillary column. Sharp peaks of the polar compounds which are characteristic of the polymer structures are observed even in the fragments of the degradation products which carry acid end groups. The degradation mechanisms of the terephthalate polyesters are discussed on the basis of the observed pyrograms.

Keywords Pyrolysis-gas chromatography (PyGC), fused-silica capillary column (FSCC), terephthalate polyesters

Pyrolysis-gas chromatography (PyGC) is one of the most powerful techniques to study the chemical structures and the thermal degradation mechanisms of polymers. However, the ordinary packed columns are difficult to apply to the polymers containing polar groups such as polyesters. Since such polymers yield a number of complex polar degradation compounds, it is necessary to use thermally unstable polar separation columns in most cases and, therefore, only the low-boiling point fragments can undergo the subsequent separation.

With the use of a thermally stable column packed with a polar polyester (Thermon-1000), which is able to cover a wider range of the polar degradation products, Sugimura *et al.*¹ studied the thermal degradation of a series of terephthalate polyesters (including polyethyleneterephthalate (PET) and polybutyleneterephthalate (PBT)) at 485, 590, 690 and 765°C by PyGC with a Curie-point pyrolyzer. According to their results, homologous series of the polyesters have shown analogous pyrograms, in which relatively high-boiling point fragments with vinyl- and/or phenyl-end groups are observed. The fragments with acid end groups, however, are not observed. Accordingly, they have assumed that the acid-form terminals are reduced rapidly to the more stable phenyl terminals by elimination of carbon dioxide at the pyrolysis temperatures.

On the other hand, it has been reported that several thermal fragments with acid end groups are observed by *in vacuo* pyrolysis-mass spectrometry (PyMS) of terephthalate polyesters.²⁻⁵ Furthermore, Day *et al.*^{6,7} have shown that benzoic acid clearly appears in the pyrograms of PET by flush pyrolysis-GC at 700 and 900°C. Vijayakumar *et al.*⁸ also pyrolyzed PET and PBT at 400°C *in vacuo* and identified the condensed pyrolysis products by gas chromatography/mass spec-

trometry technique. They showed that the main components in the low-volatile fraction contained several kinds of species with acid end groups.

In this work, the thermal degradation of a series of terephthalate polyesters was studied by high-resolution pyrolysis-gas chromatography (PyGC). Samples were pyrolyzed at 590°C in a microfurnace pyrolyzer directly attached to a gas chromatograph. A wider range of degradation products, including the species with acid end groups, was separated by a highly effective, thermally stable and chemically inert fused silica capillary column (FSCC). On the basis of the characteristic peaks appearing on the pyrograms, the modified degradation mechanisms of the terephthalate polyesters are presented.

Experimental

Samples

Five kinds of terephthalate polyesters: PET, polypropyleneterephthalate (PPrT), PBT, polypropyleneterephthalate (PPeT), and polyhexyleneterephthalate (PHT), were subjected to the analysis. All are the same materials as those studied in the previous work.¹

Conditions for PyGC

Figure 1 illustrates the flow diagram for the high-resolution PyGC system utilized. A vertical microfurnace-type pyrolyzer (Yanagimoto GP-1018) was directly attached to a gas chromatograph with a flame ionization detector (FID) (Shimadzu GC-9A). About 0.1 mg of the polymer sample was pyrolyzed at 590°C under a flow of nitrogen carrier gas. The glass insert tube in the injection port, maintained at 320°C, was packed with 5% of OV-101 on Diasolid-H (80-100

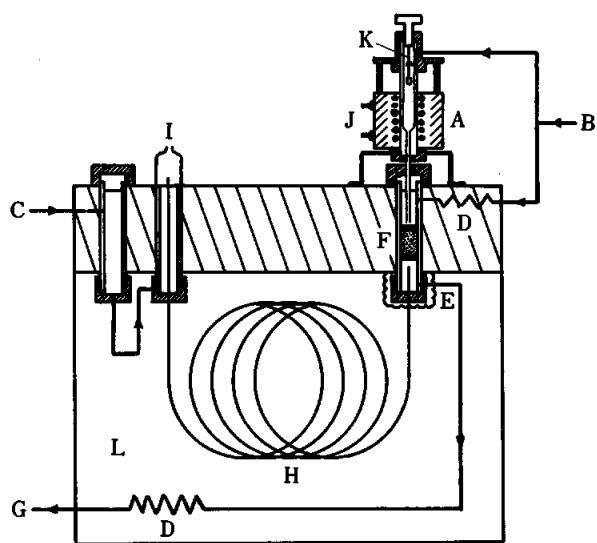


Fig. 1 Schematic flow diagram for high resolution PyGC. A, microfurnace pyrolyzer; B, carrier gas inlet (N_2); C, scavenger gas inlet (N_2); D, resistance tube; E, splitter (covered with heat insulation); F, glass insert tube packed with 5% of OV-101 on Diasolid-H (80-100 mesh); G, vent; H, FSCC; I, FID; J, power supply; K, sample holder; L, column oven.

mesh) to protect the separation column from less volatile tarry products. A fused silica capillary column (0.32 mm o.d. \times 0.2 mm i.d. \times 30 m long) coated with polydimethylsiloxane immobilized through chemical cross-linking was used. The 50 ml/min carrier gas flow at the pyrolyzer was reduced to 0.7 ml/min at the capillary column by a splitter. The column temperature was programmed from 50 to 320°C at a rate of 6°C/min. The peak identification of the pyrograms was carried out using a directly coupled gas-chromatograph/mass spectrometer (JEOL JMS-DX300) to which the pyrolyzer was also directly attached.

Results and Discussion

Figure 2 (a)–(e) illustrates the high-resolution pyrograms of PET, PPrT, PBT, PPeT and PHT, respectively. The pyrograms show analogous patterns reflecting the polymer structures. The peaks identified by PyGC-MS and their relative yields are listed in Table I.

The first cluster peaks, with shorter retention times than b peak, are mainly composed of unsaturated hydrocarbons derived from the methylene sequences in the polymer chains.¹ In particular, α,ω -dienes are most likely formed through the predominant pyrolysis mechanism involving a cyclic transition state^{1-6,8} at two neighboring ester linkages for PBT, PPeT and PHT as follows:

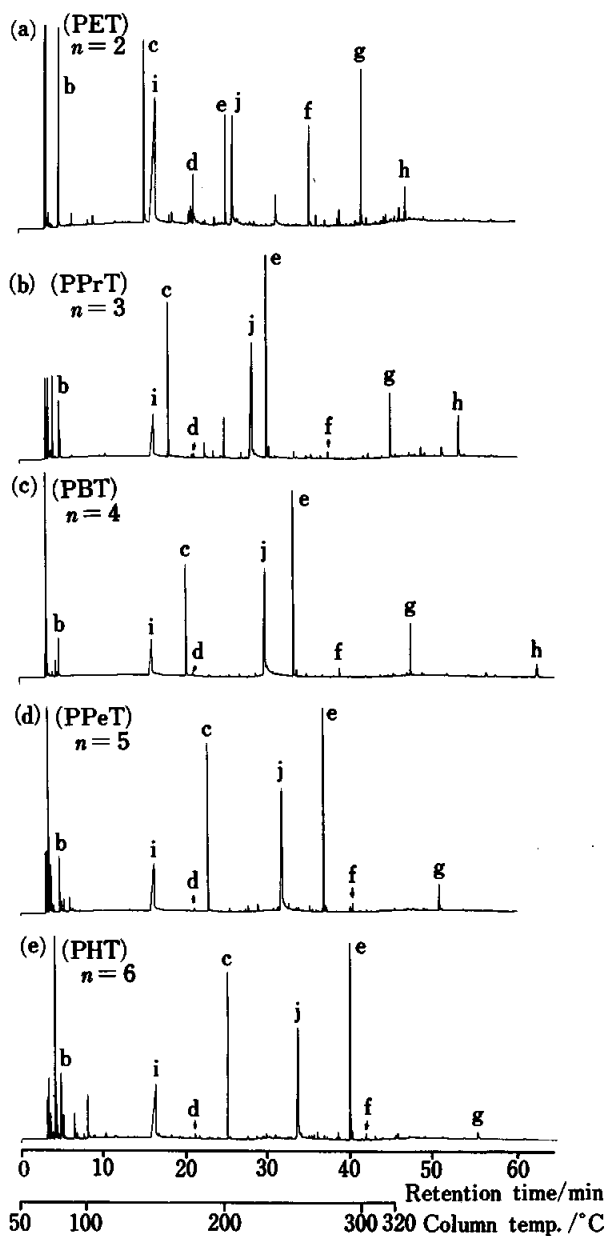
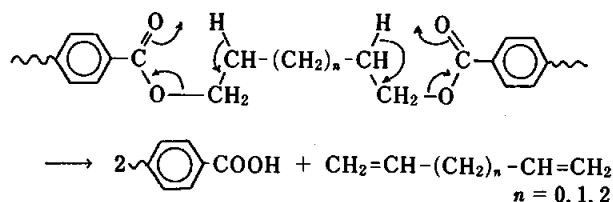



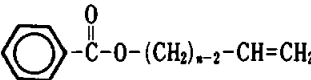
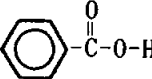

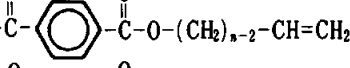
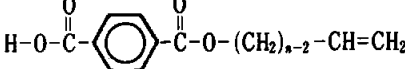
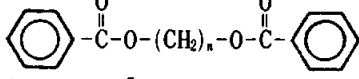
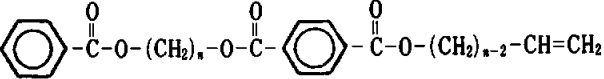
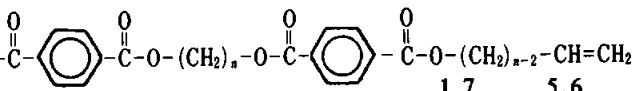
Fig. 2 Pyrograms of (a)PET, (b)PPrT, (c)PBT, (d)PPeT and (e)PHT at 590°C. Peak notations correspond to those in Table I.



whereas the methylene sequences are too short for PET and for PPrT to yield the associated dienes. As shown in Table I, therefore, the relative yields of the small fragments were much higher for PBT, PPeT and PHT than those for PET and PPrT.

The b, c, d and e peaks correspond to benzene, alkenyl esters of benzoic acid, biphenyl, and dialkenyl

Table 1 Assignment and relative intensities of the characteristic peaks on the pyrograms of terephthalate polyesters

Peak notations	Structure ^a	Relative peak intensity, ^b %				
		PET	PPrT	PBT	PPeT	PHT
Small products ^c		19.0	9.6	37.6	34.8	38.6
b		5.1	2.3	1.5	1.7	2.7
c		5.9	8.5	6.7	7.5	7.0
i		32.0	14.2	10.4	13.3	15.1
d		1.8	>0.3	>0.3	>0.3	>0.3
e		3.7	21.7	13.2	17.6	11.3
j		9.2	26.0	21.7	21.0	14.2
f		3.4	0.6	0.7	0.6	>0.5
g		5.7	4.5	4.1	2.2	0.9
h		1.7	5.6	3.1	—	—

a. $n=2$ (PET), 3 (PPrT), 4 (PBT), 5 (PPeT) and 6 (PHT).

b. Relative peak area (%) among all peaks appearing on the pyrograms.

c. Total intensities of the peaks with shorter retention times than that of benzene.

esters of terephthalic acid, respectively, which were also the main peaks on the pyrograms of the polyesters obtained by a conventional packed column.¹ However, the relative intensities of d peak (biphenyl) were smaller than those reported in the previous work using a Curie-point pyrolyzer.¹ Since biphenyl is presumed to arise from the recombination of two phenyl groups, this result suggests that some undesirable bimolecular reactions are taking place to a lesser extent in the microfurnace pyrolyzer used in this work than in the Curie-point pyrolyzer.

The f peaks, which are the dibenzoates of the corresponding diols, were observed only for PET by the packed column with Thermon-1000.¹ In this work, however, the f peaks are observed on the pyrograms of all polyesters. The data in Table 1 indicate that the dibenzoates are minor degradation products from the polyesters, except for PET.

Furthermore, the g and h peaks are assigned to the mono- and dialkenyl esters concerning with two terephthalic acid units. Neither of them was observed on the previous pyrograms, mainly because of the lower column temperature (max. 250°C).¹ In this work,

however, since the column temperature could be raised to 320°C by use of the thermally stable FSCC, these high-molecular weight (up to 494) fragments became observable for the first time. The h peaks, however, were no longer observable on the pyrograms of PPeT and PHT under the given experimental conditions.

The broader i and j peaks were also newly identified as benzoic acid and the monoalkenyl esters of terephthalic acid. In the previous work¹, these fragments with acid end groups were not observed at all, and therefore it was concluded that the acid-form terminals might be reduced into the more stable phenyl terminals by the elimination of carbon dioxide at elevated temperatures. Nevertheless, the fact that these compounds with acid end groups are actually detected as major degradation products (about 30–40% among all peaks on the pyrograms, as shown in Table 1) suggests that such polar fragments might be adsorbed irreversibly in the copper packed column. However, the dibasic acids such as terephthalic acid, which are also expected to form during the pyrolysis of the polyesters, were not detected even under the experimental conditions with use of FSCC.

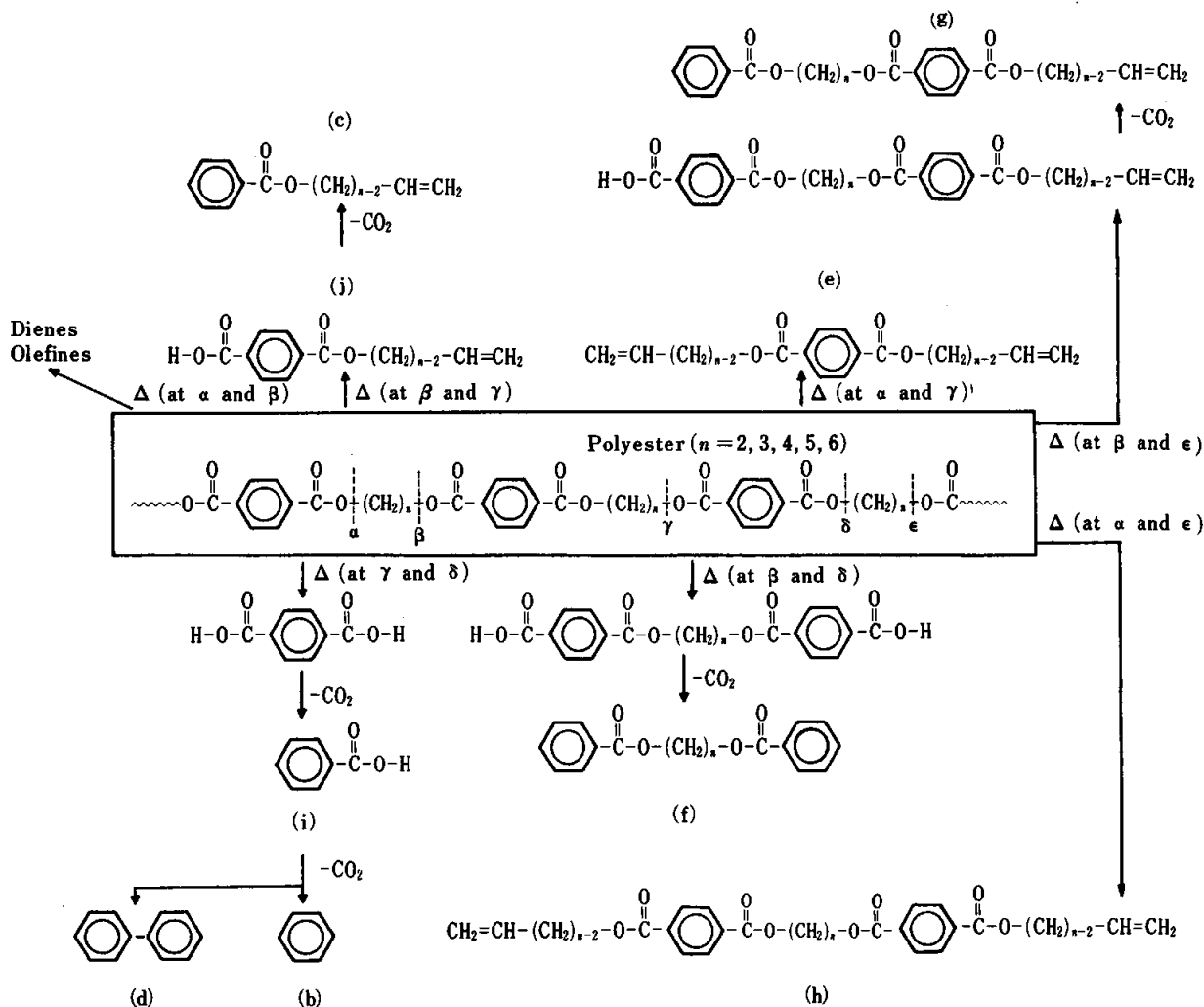


Fig. 3 Thermal degradation mechanisms of the terephthalate polyesters on the basis of the pyrograms at 590°C obtained with FSCC. Δ : thermal cleavage. b-j correspond to the peaks in Fig. 2.

On the basis of the results obtained, the common degradation pathways of the terephthalate polyesters are summarized in Fig. 3. In conclusion, (1) the fragments with an acid end group were observed as clearly separated peaks (i and j peaks), and (2) the fragments containing two terephthalic acid units (g and h peaks), which provide the information about relatively long sequences in the polymer chain, were also observed on the pyrograms of the polyesters obtained by PyGC with use of the thermally stable and chemically inert FSCC. Although the fragmentation of such large and polar fragments were also reported by direct PyMS²⁻⁵, it is often difficult to discriminate whether the degradation products of interest are formed through the thermal fragmentation or the mass spectral fragmentation during the ionization processes. On the other hand, all the fragments observed by PyGC are formed only through the thermal degradation processes. Thus the high-resolution PyGC is a very effective method even for the study of the thermal degradation mechanisms of the polymers such as polyesters which yield a wide range of polar degrada-

tion products.

References

1. Y. Sugimura and S. Tsuge, *J. Chromatogr. Sci.*, **17**, 269 (1979).
2. I. Lüderwald and H. Urrutia, *Makromol. Chem.*, **177**, 2079 (1976).
3. R. M. Lum, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 203 (1979).
4. R. E. Adams, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 119 (1982).
5. S. Foti, M. Giuffrida, P. Maravigna and G. Montaudo, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 1217 (1984).
6. M. E. Bednas, M. Day, K. Ho, R. Sander and D. M. Wiles, *J. Appl. Polym. Sci.*, **26**, 277 (1981).
7. M. Day, V. Parfenov and D. M. Wiles, *J. Appl. Polym. Sci.*, **27**, 575 (1982).
8. C. T. Vijayakumar and J. K. Fink, *Thermochim. Acta*, **59**, 51 (1982).

(Received February 21, 1986)

(Accepted February 28, 1986)