

Studies on Thermal Degradation of Aromatic Polyesters by Pyrolysis-Gas Chromatography

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Abstract

Thermal degradation of aromatic polyesters ($m=2,3,4,5$, and 6) was studied by pyrolysis/gas Chromatography using a Curie-point pyrolyzer directly attached to a gas Chromatograph with a thermally stable polar separation column (Thermon-1000) to cover a wide range of the degradation products. The characteristic peaks appearing on the pyrograms were identified using a mass spectrometer with a chemical ionization source which was also directly attached to the gas Chromatograph. On the basis of the observed pyrograms, the common degradation mechanisms of the aromatic polyesters were discussed.

Introduction

Among the many aromatic polyesters, polyethyleneterephthalate (PET) and polybutyleneterephthalate (PBT) are most widely used in the fields of fibers and thermoplastics. The thermal behaviors of these polymers are usually investigated by thermogravimetry (TG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC). These thermal methods provide very useful information about the bulk thermal characteristics of materials, such as the glass transition temperature, the heat of crystallization, the melting point, the weight loss during the thermal degradation, etc. These data, however, are usually very difficult to interpret in terms of the molecular structure of the polymers. On the other hand, pyrolysis/gas chromatography (PGC) and pyrolysis/mass spectrometry (PMS) supply very useful information about the structures of the pyrolysis products and the degradation mechanisms.

Recently, Luderwald, et al. (1-3) have reported extensive studies on various polyesters by PMS to elucidate degradation mechanisms. PGC, however, has been applied mostly for the identification of polyesters since they mainly yield relatively small fragments such as carbon monoxide, carbon dioxide, olefins, and some benzene derivatives at elevated temperatures between 500 and 1,000 °C, which are necessary for the mass pyrolysis of the thermally stable polyesters (4,5).

In this work, a series of aromatic polyesters were pyrolyzed between 485 and 765 °C in a Curie-point pyrolyzer which was directly attached to a gas chromatograph with a thermally stable polar separation column. The characteristic peaks appearing on the pyrograms, which cover a fairly wide range of the degradation products were identified using a mass spec-

trometer with a chemical ionization source which was also directly attached to the gas chromatograph. On the basis of the observed pyrograms, the degradation mechanisms of the aromatic polyesters were discussed.

Experimental

Materials. Five kinds of aromatic polyesters such as PET, polypropyleneterephthalate (PPt), PBT, polypenteneterephthalate (PPeT), and polyhexeneterephthalate (PHT) were synthesized by an ordinary method using titanium-n-butoxide as a catalyst, respectively, from dimethylterephthalate and various diols, HO(CH₂)_nOH ($n = 2, 3, 4, 5$, and 6).

Conditions for PGC. A Curie-point pyrolyzer (Japan Analytical Industry, Model JHP-2, Tokyo, Japan) was directly attached to a gas chromatograph with flame ionization detector (FID) (Shimadzu, Model GC-4CM, Kyoto, Japan). About 0.1 mg of the polymer sample was pyrolyzed for 5 sec under a flow of carrier gas (35 ml/min of N₂) using a small piece of ferromagnetic foil, of which the Curie-point was either 485, 590, 690, or 765 °C. A thermally stable and highly polar separation column, 2 m long copper tubing (3 mm i.d.) packed with 5% of Thermon-1000 (Shimadzu, usable up to 270 °C) on 80/100 mesh Chromosorb W (acid washed and DMCS treated) was used. The column temperature was programmed from 50 to 250 °C at a rate of 60 °C/min to separate the fragments with a wide range of boiling points. The peak identification of the pyrograms was carried out using a quadrupole mass spectrometer with a chemical ionization source (JEOLCO, Model JMS-Q10A, Tokyo, Japan), which was also directly attached to the gas chromatograph through a glass jet separator.

Results and Discussion

Previous pyrograms of polyesters have primarily dealt with only relatively small fragments (4,5). In this work, however, relatively large fragments were separated using a thermally stable polyester column, Thermon-1000, whose characteristics are basically the same as those of PEG-20M. Figures 1a and b show the typical pyrograms of PET and PBT at 590 °C. On these pyrograms clearly separated peaks of fairly large fragments can be seen. Although the first cluster of peaks with shorter retention time than that of benzene were not sufficiently separated under the column conditions utilized, it was expected that they were composed of olefins, some aldehydes and alcohols. Of course, considerable amounts of carbon dioxide and carbon monoxide should also have eluted

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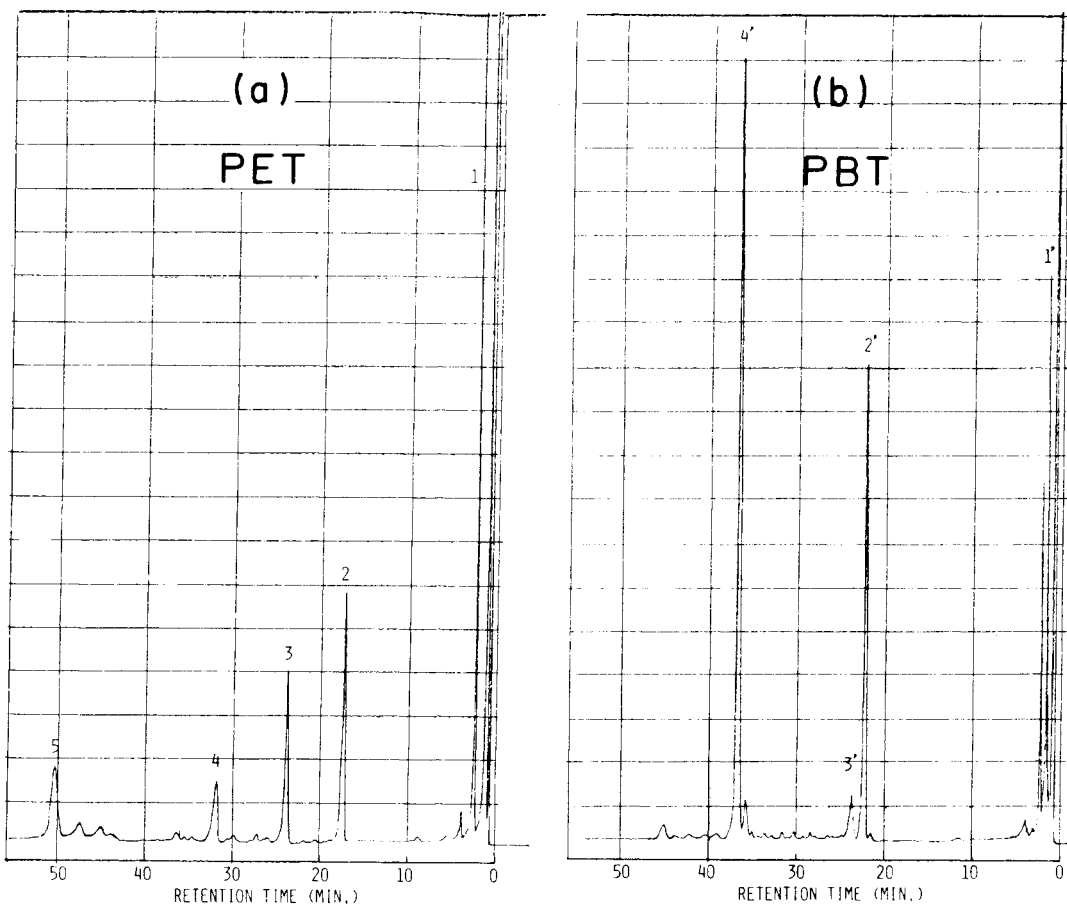


Figure 1. Pyrograms of PET and PBT at 590°C. (a) PET, 1: benzene; 2: vinyl ester of benzoic acid; 3: biphenyl; 4: divinyl ester of terephthalic acid; and 5: dibenzoate of ethyleneglycol. (b) PBT, 1': benzene; 2': allylcarbinol ester of benzoic acid; 3': biphenyl; and 4': diallylcarbinol ester of terephthalic acid.

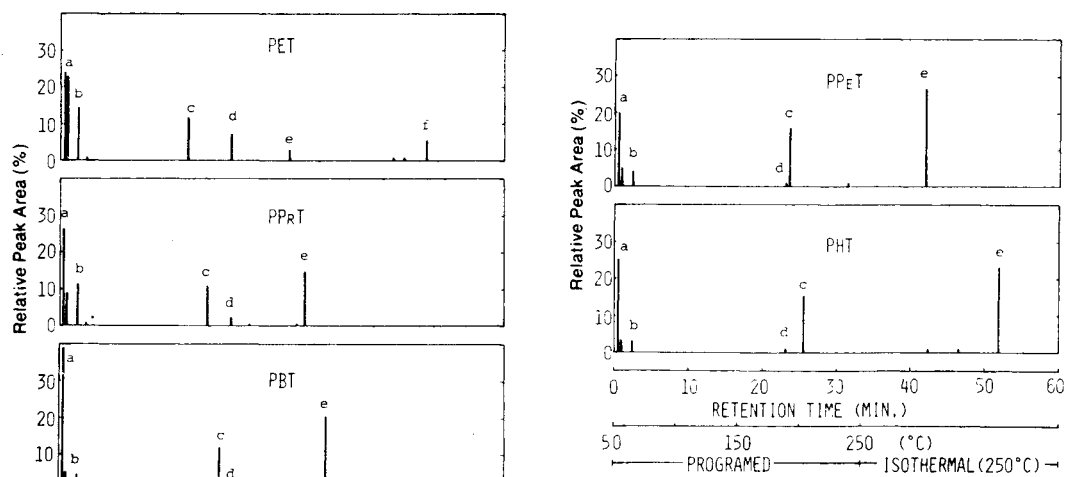
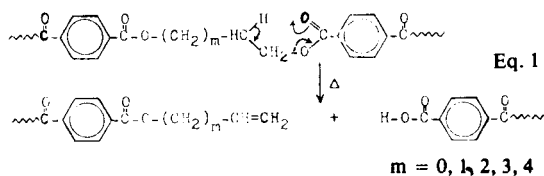


Figure 2. Bar-pyrograms of aromatic polyesters at 590°C. Peaks a, b, c, d, e, and f correspond to the compounds in Figure 3.

here. However, these components were not detected by FID. The identified main peaks above benzene (peak 1) on the pyrogram of PET were vinyl ester of benzoic acid (peak 2), biphenyl (peak 3), divinylester of terephthalic acid (peak 4), and dibenzoate of ethyleneglycol (peak 5). On the pyrogram of PBT, the peaks of the homologous esters can be seen.

Figure 2 illustrates comparative bar-pyrograms of the five polyesters at 590 °C where minor peaks whose intensity was less than 1% among the total were neglected. It is worth noting that the homologous series of the polyesters shows the analogous pyrograms corresponding to the chemical structures of the polymer chain. From these data it was possible to deduce the following common degradation mechanisms for these homologous polyesters.

Among the thermally weak linkages, i.e., the C-O bonds along the polymer chain (6), those located at β -position from C=O bonds were most likely subject to the following thermal cleavage (1, 3, 7):



However, at elevated temperatures used for mash pyrolysis, the acid-form terminals were rapidly reduced into the more

stable phenyl terminals by elimination of carbon dioxide. Therefore, the final degradation products appearing on the pyrograms were supposedly formed by taking either pathway shown in Figure 3. Although the corresponding esters of benzoic acid (c) and terephthalic acid (e) can be seen on every pyrogram, the peak of dibenzoate (f) was observed only on the pyrogram of PET under the column conditions utilized.

Among the degradation products, biphenyl (peak d) was most likely formed through the bimolecular reaction of the formed terephthalic acid. This mechanism was supported by the fact that terephthalic acid yields biphenyl as well as benzene at elevated temperatures above 500 °C. It is interesting to notice that the formation of both benzene and biphenyl decreased as the number of methylene groups in the polymer chain rose.

Figure 4 shows a series of the bar-pyrograms of PET at various pyrolysis temperatures, 485, 590, 690, and 764 °C. The main degradation products were basically the same regardless of the pyrolysis temperatures utilized. However, at the pyrolysis temperature of 485 °C, the formation of biphenyl became negligibly small, while the relative yield of benzene increased with the rise of the pyrolysis temperature. Basically, the same tendency was observed for the other polyesters.

Since the peaks (c), (e), and (f) were quite characteristic of the chemical structures of the original polymers, the identification of the polyesters and the quantitative estimation of the components in a given mixture system of the polyesters can easily be done using the pyrograms observed under the same pyrolysis conditions.

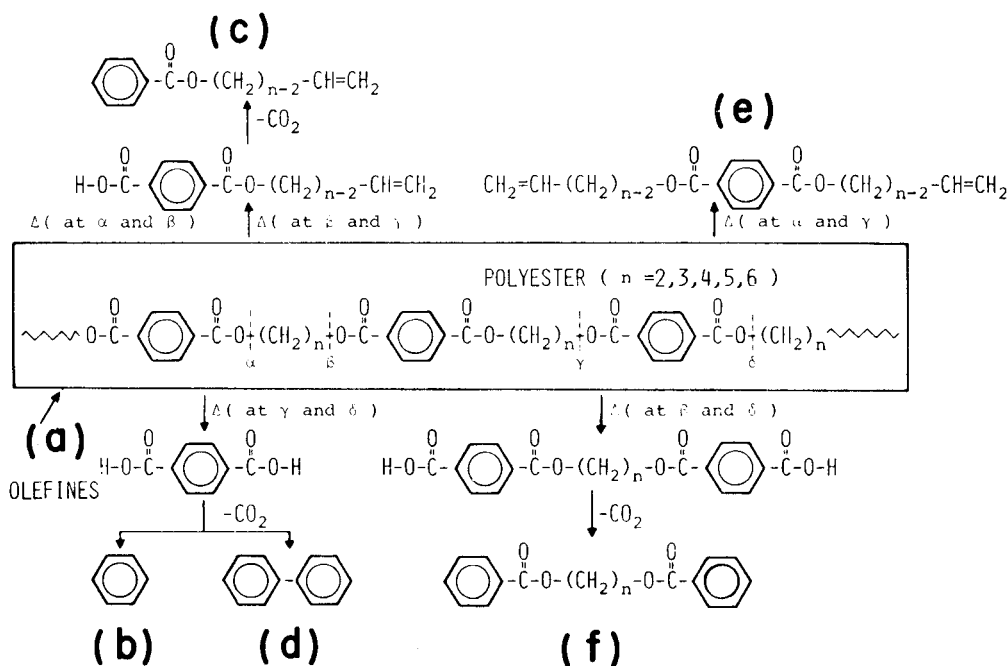


Figure 3. Typical thermal degradation mechanisms of aromatic polyesters at relatively high temperatures. Δ : thermal cleavage, peaks a, b, c, d, e, and f correspond to the peaks in Figures 2 and 4.

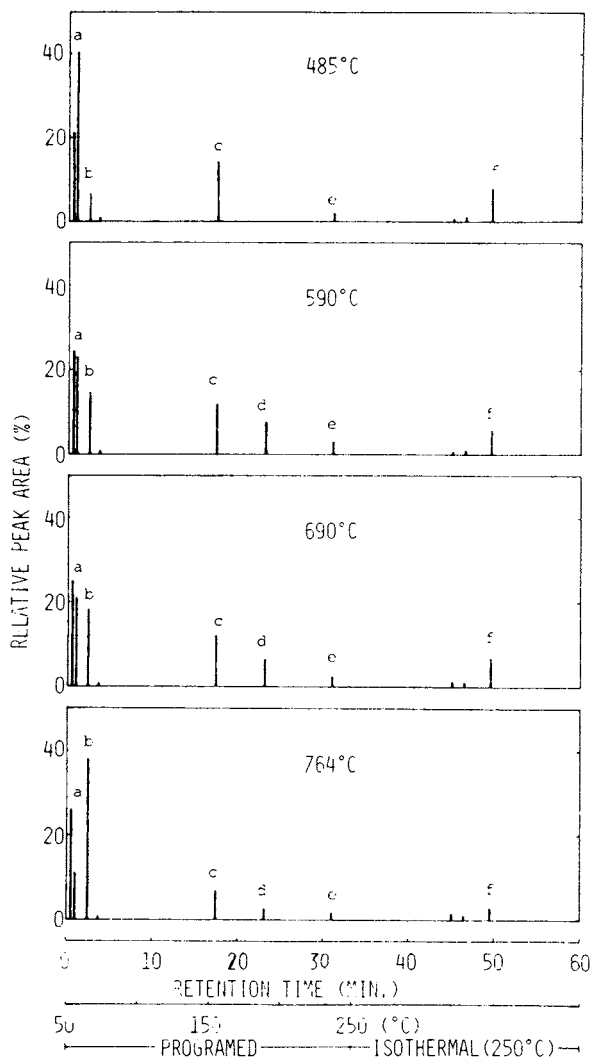


Figure 4. Bar-pyromograms of PET at various pyrolysis temperatures. Peaks a, b, c, d, e, and f correspond to the compounds in Figure 3.

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