

# Pyrolysis of Poly(ethylene Terephthalate) Fibers: Characterization of Involatile Residues\*

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## Synopsis

Poly(ethylene terephthalate) fabric was degraded under rapid heating conditions and the solid residue characterized by diffuse reflectance infrared spectroscopy. Fabric samples with and without flame retardant were pyrolyzed in air or nitrogen and spectra recorded after various percentage weight changes. Dominant species included carboxylic acid end groups and linear anhydrides, based on infrared absorbances before and after chemical treatments of the residues. Vinyl benzoate end groups were clearly precluded, as were cyclic anhydrides. Diffuse reflectance spectra were also compared with spectra obtained by transmission infrared on conventional KBr discs prepared from the same residue. The former technique was shown to be superior to the pressed disc method for the tough residues obtained by thermolysis.

## INTRODUCTION

The thermal degradation of poly(ethylene terephthalate) (PET) has been extensively studied both in the presence and absence of oxygen.<sup>1-6</sup> Many investigators have concentrated on thermal analysis methods, some have identified gaseous products, and a few have attempted analysis of involatile residues. Obviously all three approaches are essential to give a comprehensive picture of the thermal degradation and to aid in the investigation of PET combustion processes. However, the residue analysis in particular presents many problems and has produced a contradictory literature. Complications result from the crosslinked, black nature of the solid PET residue, which severely limits analytical techniques. Infrared analysis (IR) by the KBr disc technique has been used,<sup>1,4-6</sup> but (when published) spectra are frequently of very poor quality with poorly resolved bands, presumably because of the optical problems which result from inability to finely disperse these tough residues and from their low transmission. IR investigations have led to the postulation of various products including aromatic anhydrides (both linear and cyclic),<sup>2,6</sup> carboxylic acids, terminal vinyl benzoates,<sup>5</sup> and polyenes,<sup>6</sup> in some cases from the same absorptions and in some cases from band assignments differing by only a few wavenumbers. IR band assignment from model compound values can be useful, but is seldom unambiguous because of the dependence of band locations on the nature of the dispersing matrix and even from pressing into KBr pellets.<sup>7</sup> Well-chosen derivatization reactions on the polymer residue, followed by further IR characterization as well as comparison with IR spectra of model compounds dispersed in PET itself, can, however, give quite reliable identification of product groups.

The technique of diffuse reflection in the IR has been suggested to be partic-

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ularly suitable for the characterization of intractable materials such as coals when these materials are powdered and dispersed in KCl powder.<sup>8</sup> Fourier transform IR (FTIR) spectroscopy allows the treatment of even weak IR signals and the manipulation of the stored digitized spectra, especially by the use of spectral subtraction.<sup>9</sup> The quantitative use of diffuse reflection by FTIR (known by the acronym DRIFT) and the reliability of the subtraction of DRIFT spectra have been frequently discussed in the literature.<sup>8,10</sup>

As part of a comprehensive study of the pyrolysis and combustion of PET (including thermal analysis and gaseous analysis),<sup>11,12</sup> we have applied the DRIFT technique to the investigation of involatile products, produced both in the presence and absence of oxygen and/or flame retardants. Comparisons have also been made with samples examined by the KBr disc technique, and product identification has been assisted by specific chemical reactions to give other distinctive IR absorptions.

## EXPERIMENTAL

PET fabric (100% spun Dacron type 54 woven fabric 127 g/m<sup>2</sup>, ~0.3 mm thick) was cut into discs (1 cm diameter, ~10 mg) and single discs were pyrolyzed by heating in N<sub>2</sub> or air with an IR spot heater (Research Inc. Model 4085 operated at 40 V to give a nominal radiative flux at the sample of ~20 W·cm<sup>-2</sup>). The fabric discs were mounted on annealed Pyrex discs in a Cahn RG Microbalance, so that weight changes could be continually monitored during pyrolysis. The spot heater gave a rapid initial heating rate of ~30°C s<sup>-1</sup>, up to ~400°C followed by a slower rate (~25°C min<sup>-1</sup>) up to 500°C,<sup>12</sup> comparable to the heating rate which can be experienced near a flame front during the burning of PET. Representative heating times were 2.0 min to ~50% weight loss and 3.0 min to ~80% weight loss. PET fabric containing 20.1 wt% *tris*-(2,3-dibromopropyl) phosphate, (TRIS, ICN Pharmaceuticals) was prepared by solution application from methylene chloride followed by air drying. These TRIS-containing samples were also pyrolyzed as described above. Starting materials, standards, and pyrolyzed residues were powdered cryogenically (under liquid nitrogen in a miniature ball mill). These powdered materials were then briefly (~10 s) milled with a predetermined quantity of powdered KCl to give a uniform dispersion. This procedure gave KCl particles averaging 20 μm in diameter (95% in the 10–30 μm range) and PET particles averaging 25 μm in diameter (95% in the 5–40 μm range) as measured by optical microscopy.

Samples were analyzed by FTIR on a Nicolet 7199 System, equipped with a mercury cadmium telluride detector. Normally 100 scans of each sample were averaged. Powders were studied either by transmission IR as pressed KBr discs or by DRIFT after mixing with KCl powder, using a Harrick Diffuse Reflectance Attachment (elliptical optics, collecting ~10% of the 2π solid angle of the scattering hemisphere). For DRIFT, powder samples were lightly tamped into 4.5 mm diameter by 2.5 mm deep wells, designed to use the minimum of powder yet prevent the incident beam reflecting from the aluminum surfaces of the holder. Undiluted, the black, pyrolyzed samples gave signals too weak for practical use; dilution with KCl powder (a close to perfect diffuse reflector) at 2.0 wt% PET residue (0.4 mg in 20 mg KCl) was found to give the best compromise of signal intensity and quality of the absorption spectrum. Diffuse reflections ( $R_{\lambda}$ ) were

ratioed to pure KCl reflections ( $R_{\lambda}^{\circ}$ ). The resultant diffuse reflectance spectrum ( $R_{\lambda}/R_{\lambda}^{\circ} = R_{\infty}$ ) does not obey the Lambert-Beer Law, but can be linearly related to concentration through the Kubelka-Munk expression.<sup>13</sup> All DRIFT spectra shown are expressed in terms of the Kubelka-Munk factor,  $f(R_{\infty}) = (1 - R_{\infty})^2/2R_{\infty}$ . To obtain comparable DRIFT spectra, samples must be reproducibly milled; poorly milled samples (large particles visible) gave weak, distorted spectra as a result of specular reflection and nonhomogeneous dispersion in KCl. In order to minimize interference from absorbed water in the KCl diluted powders, all samples were rigorously vacuum-dried and loaded into the sample wells under dry  $N_2$  before installation in the  $N_2$ -purged optical bench of the FTIR spectrometer. KBr pellets were also vacuum dried before analysis.

Vinyl benzoate (K and K Division, ICN Pharmaceuticals), benzoic acid, and benzoic anhydride (Aldrich) were used as supplied.

## RESULTS

Preliminary experiments with various heating methods showed that it was not possible to achieve uniform heating of large samples ( $\sim 0.2$  g) at high heating rates. Large samples yielded residue which was obviously inhomogeneous to

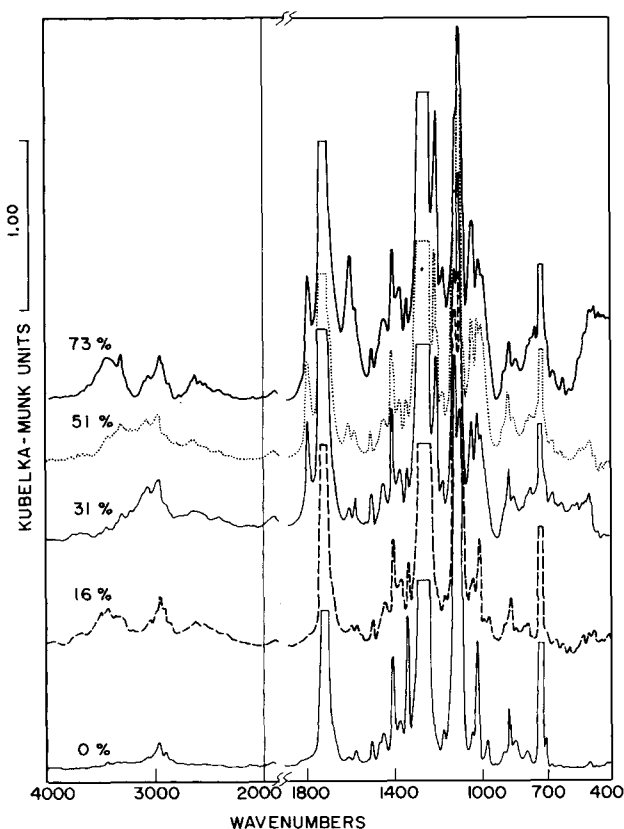


Fig. 1. DRIFT spectra of PET with 20% TRIS. After various degrees of weight loss on pyrolysis in air. Bands at 1725, 1260, and 725  $cm^{-1}$  truncated for clarity.

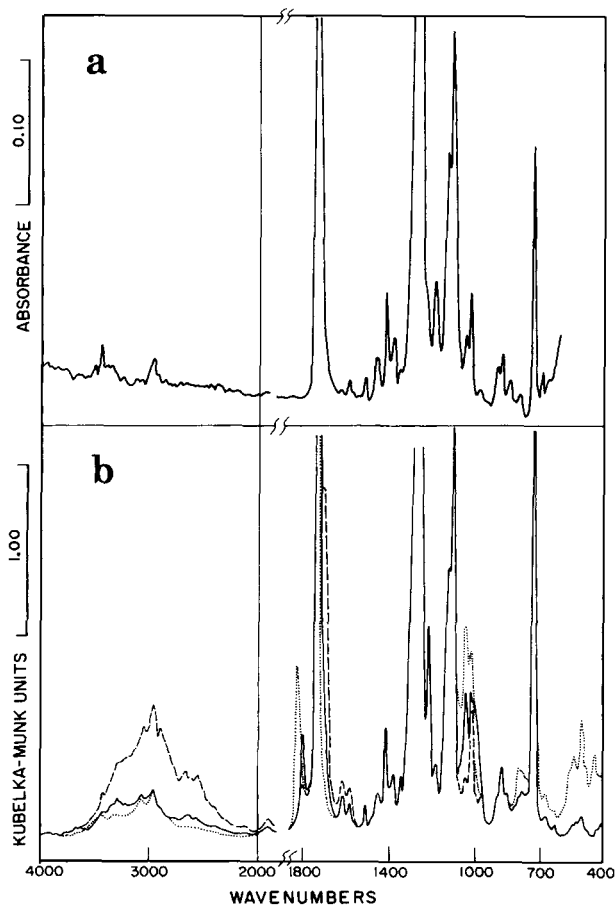


Fig. 2. Spectra of PET with 20% TRIS. After 51% weight loss on pyrolysis: (a) Transmission IR spectrum of a thin PET film, solution cast on NaCl window from hexafluoropropanol; (b) DRIFT spectra: (—) as pyrolyzed; (---) H<sub>2</sub>O hydrolysis after pyrolysis; (.....) SF<sub>4</sub> exposure after pyrolysis. Spectra identical to "as pyrolyzed" except where shown.

the eye because of uneven heating and shrinkage from the heated zone. This necessitated the use of fabric samples (~10 mg) smaller than the focused beam diameter of the spot heater. At high degrees of pyrolysis, only 1–2 mg of usable residue was recovered after milling. However, the DRIFT technique was found to produce adequate spectra from 0.03 mg of residue or less.

Typical DRIFT spectra are shown in Figure 1 for various degrees of pyrolysis. For clarity, intense overlaid peaks at ~1725, 1260, and 725 cm<sup>-1</sup> (which do not change on pyrolysis) have been truncated in Figure 1. To aid in the characterization of the new absorption bands, controlled chemical changes were employed. Hydrolytically sensitive species in the residue were detected by heating a few milligrams of residue with water at 70°C for 4 h. After complete evaporation of the water, the whole sample was studied by DRIFT. In addition, —OH groups were separately identified by exposure of the residue to SF<sub>4</sub> gas for 48 h. This treatment is known to cleanly fluorinate all —OH groups.<sup>14</sup> Typical spectra

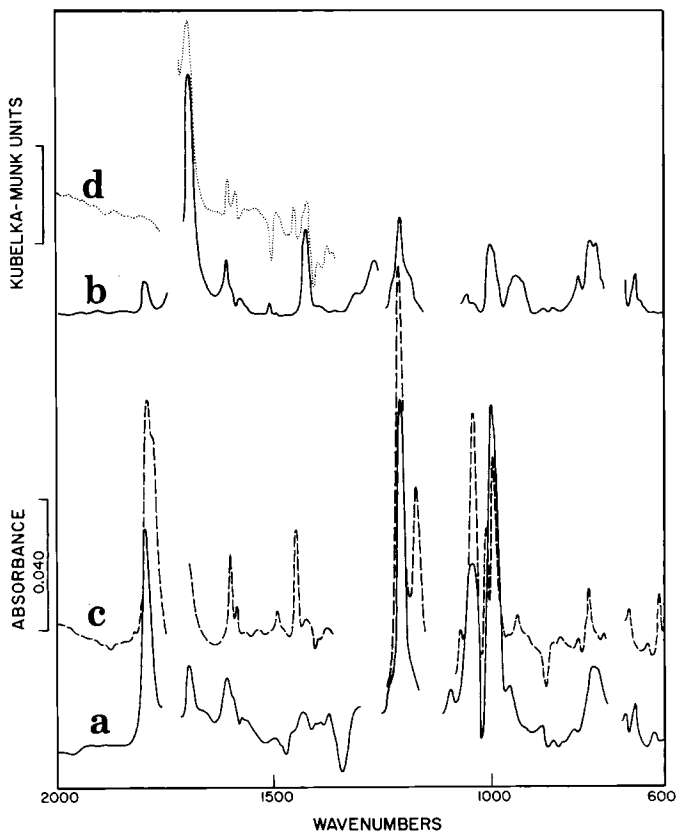


Fig. 3. Difference spectra of PET with 20% TRIS. DRIFT spectra: (a) (51% weight loss on pyrolysis) minus (nonpyrolyzed); Kubelka-Munk bar = 0.20; (b) As for (a), but pyrolyzed sample hydrolyzed; Kubelka-Munk bar = 0.60. Transmission spectra: (c) (PET film + benzoic anhydride diffused in) minus (PET film); (d) (PET film + benzoic acid diffused in) minus (PET film).

of hydrolyzed and fluorinated residues are shown in Figure 2, together with the transmission spectrum of a thin PET film cast on a NaCl window, for comparison with DRIFT spectra.

The spectral subtraction ability of the FTIR system allows small spectral changes to be emphasized once the scaled background spectrum of the original polymer is subtracted. Spectral subtract data are shown in Figure 3 for a series of samples pyrolyzed to  $\sim 50\%$  weight loss. These changes were compared with the spectra of two model compounds, benzoic acid and benzoic anhydride, both individually dispersed in KCl (by DRIFT) and also after diffusion into PET film ( $10\ \mu\text{m}$ ) from  $\text{CH}_2\text{Cl}_2$  solution (by transmission IR). Only these latter transmission spectra are shown in Figure 3. Spectral subtraction of the more intense PET bands cannot be done reliably, and this accounts for the gaps in the spectra shown in Figure 3.

For comparison with the DRIFT technique, some pyrolysis residues were pressed into the usual KBr discs, and transmission spectra of these discs recorded by FTIR. Examples of these spectra (using slightly higher weights of residues than employed for each DRIFT measurement) are shown in Figure 4.

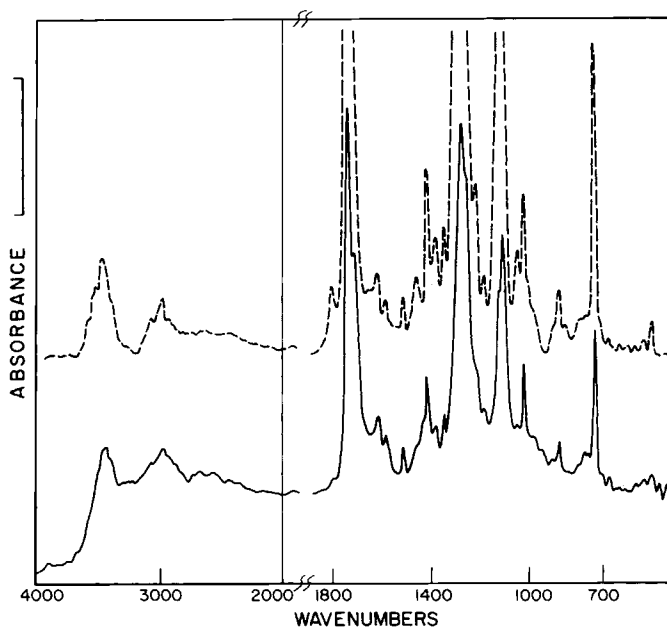


Fig. 4. Pyrolyzed PET with 20% TRIS dispersed in KBr discs: (—) 73% weight loss by pyrolysis, 0.75 mg residue in 500 mg KBr; absorbance bar = 0.20; (---) 51% weight loss by pyrolysis, 0.55 mg residue in 500 mg KBr; absorbance bar = 0.16.

## DISCUSSION

Although the DRIFT technique is not without its problems, it is less dependent on producing powders of very small particle size than is the KBr disc method. In fact, strong diffuse scatter (which degrades KBr disc transmission spectra) is an essential factor for good quality DRIFT spectra. In addition, dispersion in a KCl powder for DRIFT does not lead to the marked spectral shifts in bands caused by polar interactions, as are found in pressed KBr discs.<sup>7</sup> A comparison of samples studied by both techniques and by film transmission (cf. Figs. 1, 2, and 4) shows that the KBr disc spectra are frequently poorer in quality than DRIFT spectra, [cf. spectrum of the 73% pyrolyzed sample in Fig. 4, with weak bands enhanced and strong bands deemphasized, implying IR spectral leakage, relative to the film spectrum, Fig. 2(a)], presumably because of poor dispersion of relatively large particles, even after grinding at  $-180^{\circ}\text{C}$ , and because of refractive index mismatching.<sup>7</sup> Absorbed water contributes to the band observed at  $3400\text{ cm}^{-1}$  and possibly also  $\sim 1600\text{ cm}^{-1}$ . Similar problems of dispersion and water absorption are shown in the KBr disc spectra of pyrolyzed aramids reported recently.<sup>15</sup> This does not imply that DRIFT is a replacement for the KBr disc technique, except where particularly intractable samples are concerned. In addition, more severe sample preparation might well finally give KBr disc spectra of comparable quality, particularly if a microdisc approach is used for the very low weights of residue. Overgrinding of samples can lead to problems; DRIFT spectra become distorted by a wavelength-dependent scattering factor as the particle size drops below the size of the larger wavelengths employed.<sup>13</sup> Conversely, particles which are too large or in too high a concentration can add an

intense specular reflection to the diffuse reflection, giving a strong signal at the detector, but little spectral information and can cause deviation from the Kubelka–Munk relationship.

DRIFT of PET powder and transmission spectra of thin PET film are very similar (cf. Fig. 1 and 2), bearing in mind differences which occur in trans/gauche isomer ratios as a result of different sample histories.<sup>16</sup> Consequently, DRIFT and transmission spectra can be directly compared. Variations in trans/gauche ratios with thermal history make difficult the choice of the zero time (pre-thermolysis) spectrum for comparison with degraded samples. The PET fabric could be milled to give good quality DRIFT spectra, but the filaments are highly oriented, and with a high trans content, both of which are changed upon melting and quenching. The zero time spectrum in Figure 1 was taken from a sample briefly fused in nitrogen and then powdered as usual, that is, after a similar fussion/quench cycle as the degraded samples, but without degradation.

Although PET samples were studied with and without flame retardant and in air and N<sub>2</sub>, for a given degree of pyrolysis as measured by weight loss, DRIFT spectra were quite similar for all four cases. Dominant features were identical, and only subtle kinetic differences were observed. This apparent similarity of pyrolysis behavior could indicate that even in air, pyrolysis occurs in an O<sub>2</sub>-deficient, local environment. Furthermore, the P-containing flame retardant may have little influence on the melt pyrolysis process, and so must operate primarily in the vapor phase. This latter suggestion is consistent with our own and other studies of gaseous products (Refs. 17 and 18 and references cited therein). However, it must be appreciated that the IR technique is quite insensitive to some changes and cannot even detect the 20% of flame retardant because of overlap with the intense PET spectrum. Detailed pyrolysis differences will be discussed in a later, comprehensive publication dealing with gaseous as well as solid products.

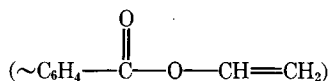
From Figure 1, new absorptions progressively develop at 1796, ~1693 (shoulder), 1602, 1202, 1040, 1000, 775, and 720 cm<sup>-1</sup> whereas a progressive decrease is observed at ~1340 cm<sup>-1</sup>. The 1796 cm<sup>-1</sup> absorption clearly originates from a hydrolysis sensitive species (decreasing upon heating with water) while at the same time a strong 1693 absorption is generated (Fig. 2). The 1796 cm<sup>-1</sup> absorbing species is also destroyed by SF<sub>4</sub>. The new absorption at 1818 cm<sup>-1</sup> after SF<sub>4</sub> treatment is consistent with the formation of —C(=O)—F, and is indicative of reacted carboxylic acid groups in PET<sup>14</sup> as is the loss of the ~1693 cm<sup>-1</sup> shoulder, with a marked narrowing of the ester band. In addition, the difference spectrum obtained by subtracting the scaled initial PET spectrum from the residue spectra show strong similarities to the spectrum of benzoic anhydride dispersed in PET film (Fig. 3; cf. curves a and c). For the hydrolyzed samples, spectral subtraction clearly resolves the carboxylic acid absorption at 1693 cm<sup>-1</sup>, which is very similar to that of benzoic acid, when this model is dissolved in PET film.

It must be noted that carbonyl absorptions are quite sensitive to their immediate environment so that precise agreement between spectra of polymeric products and model compounds is often difficult to achieve. For example, the carboxylic acid group absorption is found at 1693 cm<sup>-1</sup> in pyrolyzed PET, at 1693 cm<sup>-1</sup> for benzoic acid dissolved in PET film (Fig. 3), but at 1704 cm<sup>-1</sup> for powdered benzoic acid (dispersed in KCl, by DRIFT). Anhydride groups in pyro-

lyzed PET appear to absorb at  $1796\text{ cm}^{-1}$ , whereas benzoic anhydride dissolved in PET film absorbs at  $1790\text{ cm}^{-1}$  with a shoulder at  $1775\text{ cm}^{-1}$ . Powdered benzoic anhydride absorbs at  $1775\text{ cm}^{-1}$ , implying that some separation of pure anhydride domains has occurred in our benzoic anhydride-PET sample (Fig. 3, curve c). Bearing in mind the possibility of differences resulting from the comparison of small models with macrogroups, our data clearly show anhydride and carboxylic acid species to be the dominant products in the residue from pyrolyzed PET.

Although KBr disc spectra comparable to the DRIFT spectra could be obtained if a prolonged grinding procedure was used, the PET-residue spectra from discs indicated that carboxylic acid groups dominated, whereas anhydride was only present in small amounts (cf. Fig. 4). These results are consistent with reaction of the anhydride groups with moisture in the KBr during the prolonged grinding/pressing procedure. Presumably, hydrolysis could be avoided if greater care was taken to preclude moisture and to start with absolutely anhydrous KBr.

Previous investigations of PET pyrolysis residues have led to the assignment of peaks at  $\sim 1796\text{ cm}^{-1}$  both to linear anhydrides<sup>4</sup> and to terminal vinyl benzoate groups<sup>5</sup>



After pyrolysis, Inagaki et al.<sup>5</sup> observed new bands at  $1200$ ,  $1030$ , and  $990\text{ cm}^{-1}$  as well as  $\sim 1790\text{ cm}^{-1}$ ; all of these bands are clearly visible in our spectra [cf. Fig. 3(a)] but are completely consistent with a linear aromatic anhydride [Fig. 3(c)] rather than the suggested vinyl benzoate groups. In fact, vinyl benzoate has more recently been shown to have medium to strong absorptions at  $1740$ ,  $1647$ ,  $1250$ ,  $1140$ ,  $946$ , and  $870\text{ cm}^{-1}$ ,<sup>19-21</sup> and we have confirmed this with our own sample. These assignments are quite inconsistent with both our new absorptions and those reported by Inagaki et al.<sup>5</sup> Smets et al.<sup>19</sup> have reported that vinyl benzoate frequently contains a persistent impurity (1,1-diacetoxyethane) which absorbs at  $\sim 1762\text{ cm}^{-1}$ , and it may be this latter impurity which lead to the erroneous identification of vinyl benzoate end groups by Inagaki et al. Because of overlap with the background PET spectrum and anhydride bands, identification of the vinyl species (which are predicted from the pyrolysis of model liquid esters) will be quite difficult. We have observed a small band at  $\sim 940\text{ cm}^{-1}$  (consistent with vinyl benzoate ends) in spectra of PET samples after slow, low-temperature ( $\sim 315^\circ\text{C}$ ) pyrolysis reaction, but anhydride and carboxylic acid were still the dominant products detected.

Rohringer et al.<sup>6</sup> have detected bands at  $1608$ ,  $1786$ ,  $1795$ , and  $1852\text{ cm}^{-1}$  from the low temperature pyrolysis of PET. They attributed these bands to polyenes ( $1608\text{ cm}^{-1}$ ), linear anhydride ( $1795\text{ cm}^{-1}$ ), and cyclic anhydride ( $1786$ ,  $1852\text{ cm}^{-1}$ ). However, an  $\sim 1600\text{-cm}^{-1}$  band can also originate from the linear anhydride (cf. Fig. 3). Nevertheless, this band does continue to increase even after the  $1795\text{-cm}^{-1}$  absorption has plateaued (Fig. 1), indicating that, under our conditions, a new species is formed at high conversion. As well as the polyene ( $-\text{HC}=\text{CH}-\text{CH}=\text{CH}-$ ) structure suggested by Rohringer et al.<sup>6</sup> an equally

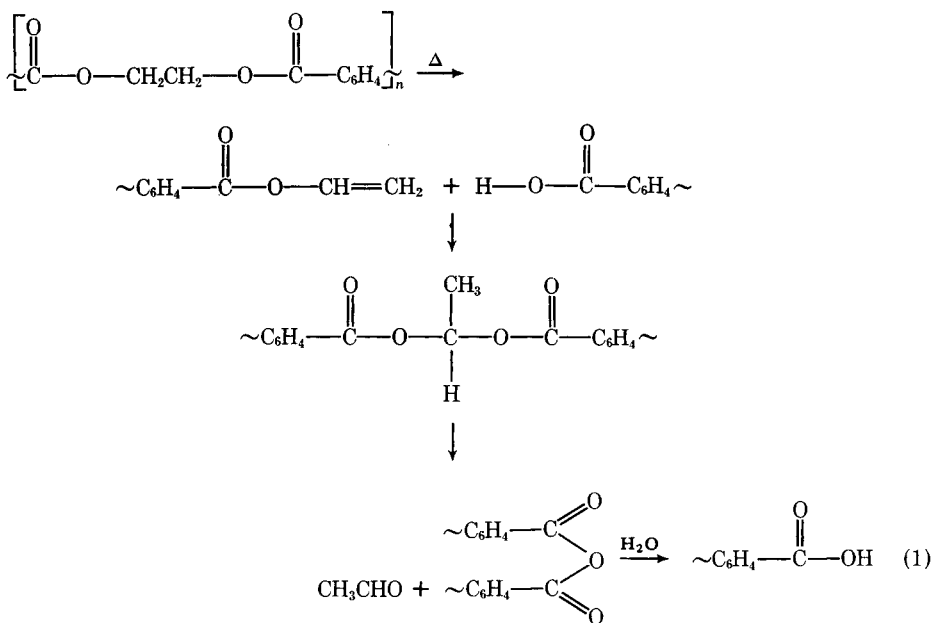


likely candidate is the formation of interphenyl links, a precursor to complete carbonization. Bands at  $\sim 1600\text{ cm}^{-1}$  are present in spectra of 1,2- and 1,3-substituted polyphenylenes and also in the spectra of some fused ring aromatics such as coronene and 1,2-benzopyrene.<sup>22</sup> We detect no new bands at  $1852\text{ cm}^{-1}$  under any of our pyrolysis conditions, and preclude Rohringer's cyclic anhydrides. In addition, although model, ring-strained cyclic anhydrides (e.g. 1,2-anhydrides such as phthalic anhydride) do absorb at  $1852\text{ cm}^{-1}$ , larger ring, cyclic anhydrides (which might reasonably be expected to result from pyrolysis) have IR spectra indistinguishable from linear anhydrides.<sup>22</sup>

The ready hydrolysis of the anhydride product from PET pyrolysis implies that previous attempts to quantify carboxylic acid groups in PET residues by, for example, titration<sup>3,23</sup> could be in serious error unless care was taken in sample handling. In fact, we observed the progressive loss of the  $1795\text{ cm}^{-1}$  absorption and formation of the  $\sim 1695\text{ cm}^{-1}$  during several weeks of storage of our PET residues.

The loss of the  $1340\text{ cm}^{-1}$  absorption (cf. curves in Fig. 1, and the negative band in the difference spectrum in Fig. 3) can be interpreted as the destruction of the glycol- $\text{CH}_2$ -linkage from PET band assignments.<sup>16</sup> In addition, the progressive decrease in the  $1105\text{ cm}^{-1}$  band at the expense of the  $1095\text{ cm}^{-1}$  absorption can be interpreted as progressive loss of the O-C vibration attributed to "crystalline" PET (*trans*-glycol conformer which *can* eventually crystallize) and increase in the O-C vibration from amorphous (*gauche* conformer, noncrystallizable) PET.<sup>16</sup> This change could result from the expected increase in crosslinking and backbone defects with increased pyrolysis levels.

The spectra shown in Figure 1 indicate superficially that carboxylic acid ends are formed at low levels of pyrolysis, but anhydride groups dominate at higher levels ( $\geq 31\%$  weight loss). These products are consistent with the reaction mechanisms



already proposed from our earlier work concerned with gaseous pyrolysis products (reaction 1).<sup>11,12</sup> In this latter study, the formation of acetaldehyde as a gaseous product is consistent with the reaction between carboxylic acid and vinyl ester end groups to give a species capable of disproportionating to backbone anhydride and acetaldehyde (reaction 1). Although vinyl and acid end groups were proposed as products in our earlier reaction mechanisms, these groups will be present at the polymer chain ends. Consequently, secondary fragmentation at an ester link in close proximity to a chain end will yield products such as vinyl benzoate, divinyl terephthalate, and benzoic acid, all species which have been detected in significant amounts as gaseous products. The dominance of anhydride and the absence of vinyl benzoate end groups in the DRIFT spectra of the PET residues implies the rapid reaction of the vinyl benzoate ends (chain scission near an end, or combination with a neighboring carboxylic acid).

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