

# Combustion and Pyrolysis of Poly(ethylene Terephthalate). I. The Role of Flame Retardants on Products of Pyrolysis\*

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## Synopsis

The products of pyrolysis of untreated and flame-retarded poly(ethylene terephthalate) (PET) have been studied at two temperatures using a flash pyrolysis/gas chromatography technique. The pyrolysis products were identified by gas chromatography/mass spectrometry and reaction mechanism for their formation are proposed. A quantitative and qualitative analysis of these products reveals that the phosphorus-only flame retardants have no effect on the solid-phase pyrolysis of PET. The two bromine-containing flame retardants, however, while capable of influencing the pyrolysis, were not capable of producing large changes in the major products. Their main role in the pyrolysis appears to alter slightly the balance of several competing secondary pyrolysis reactions.

## INTRODUCTION

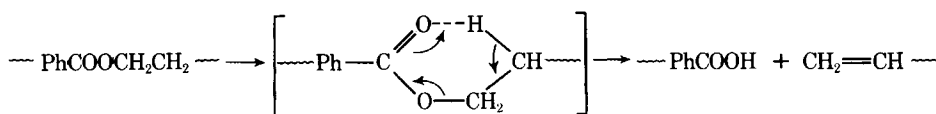
The pyrolysis and combustion of poly(ethylene terephthalate) (PET) is a subject of great concern to a large number of people interested in reducing the number of fire incidents involving textile materials. Polyester fibers, because of their outstanding characteristics of high strength, resistance to shrinkage and stretch, good dyeability, and chemical resistance, are used extensively in carpets, furnishings, and apparel. The flammability characteristics of polyester textiles are usually described as average. When a flame is applied to a polyester fabric, it usually melts and shrinks away from the impinging flame; hence, unless the flame is allowed to follow the shrinking fabric, or the fabric is fed into the flame, the material will not usually ignite and continue burning. However, if the fabric is prevented from moving away from the ignition flame, the polyester may be ignited and burnt. Such is the case when, for example, fibers are used in conjunction with cotton in polyester/cotton blends. This particular combination represents a more flammable situation than that which arises when each fiber type is used separately owing to the well-known "scaffold effect." In this situation, the carbonized cellulose formed when the cotton portion burns provides a supporting framework which allows the molten polyester to burn in much the same way as a candle burns on a wick.

In order to reduce this enhanced burning characteristic associated with these polyester/cotton blends, a substantial amount of research effort has been directed towards identifying economical, effective, and practical flame-retardant chemicals. However, while our understanding of the mechanistic role of flame retardants in the pyrolysis and combustion of cellulose has been increased, our

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comprehension of their interaction with polyesters is still very small despite several studies on the subject.<sup>1-12</sup> This situation has probably arisen since the pyrolysis chemistry of PET is more complex than that of cotton, and as a result, it has not been studied thoroughly.

Most of the earlier work on the pyrolysis of PET was concerned with establishing the thermal stability of the material to the temperatures employed in the melt-spinning process. Although the extent of decomposition is usually small under normal manufacturing and processing conditions, the ramifications, in terms of the quality of the final product, are of immense importance to the producer. Buxbaum<sup>13</sup> reviewed much of this earlier work, comparing the data with that obtained using model esters. Essentially, it was established that PET decomposed by a random scission of the ester links involving a six centered cyclic transition state to give a vinyl ester and carboxylic acid.



These primary products of pyrolysis are then capable of undergoing secondary processes to give a wide variety of products such as CO, CO<sub>2</sub>, acetaldehyde, and aromatic acids and their vinyl esters.

In terms of combustion studies, much of this earlier work is of academic interest only since the temperatures employed were of the order of 300°C and the reaction times were several hours. In the burning process, however, a wide range of temperatures are encountered ranging from a low of about 400°C at the polymers surface to a high of about 1000°C at points in the flame; consequently, reaction times are measured in seconds and milliseconds, not minutes. In changing from these two extremes, the pyrolysis product distribution can change as was demonstrated by Einsele,<sup>14</sup> who studied the pyrolysis of PET between 300 and 1000°C. Thus, in order to study the role of flame-retardant chemicals on the pyrolysis of PET, it is essential to perform the pyrolysis under conditions which reflect the temperature and heating rates encountered during the burning of a textile material. Richard, Vovelle, and Delbourgo<sup>15</sup> studied the pyrolysis of PET at 430 and 480°C, but only reported the very volatile species. The major volatile pyrolysis products produced in TGA analyses at 500 and 700°C have also been analyzed,<sup>9</sup> but once again only the very volatile products were measured. The use of flash pyrolysis, coupled with the gas chromatograph and mass spectrometer, has, however, greatly assisted studies at these higher temperatures and rapid heating rates.<sup>16,17</sup> This study was, therefore, undertaken to elucidate the effect, if any, of various flame-retardant systems upon the pyrolysis of PET using these new, more relevant, techniques.

## EXPERIMENTAL

The five types of commercial PET investigated are given in Table I along with their limiting oxygen indices (LOI) values as determined previously.<sup>18</sup> Although not all of these materials are currently in production for a variety of reasons, they do represent commercially viable materials.

The pyrolysis experiments were performed using a Chemical Data Systems

TABLE I  
 Polyester Fabrics Investigated

| Fabric designation | Source                         | Nature of flame retardant  | % Chemical w/w on fabric |      | LOI  |
|--------------------|--------------------------------|--|--------------------------|------|------|
|                    |                                |  | %Br                      | %P   |      |
| Std.               | Testfabrics                    | none   | —                        | —    | 18.9 |
| AB19               | Mobil Chemical                 | mixture of cyclic phosphonate esters   | —                        | 0.28 | 21.8 |
| T271               | Hoechst Fibers Industries      | phosphinic comonomer-modified PET  | —                        | 0.20 | 20.5 |
| Tris 900F          | Velsicol Chemical E.I. du Pont | Tris(2,3-dibromo-propyl) phosphate ethoxylated tetrabromo bisphenol A-comonomer with PET | 6.6                      | 0.33 | 23.9 |
|                    |                                |  | 4.3                      | —    | 21.8 |

(CDS) Pyroprobe 120 with a coil-probe attachment with the sample contained in a quartz tube. Two pyrolysis conditions were used during this investigation: (1) heater setting at 700°C with the ramp off and the final temperature being held for 10 sec, and (2) heater setting of 900°C with the ramp off and the final temperature being held for 10 sec.

Using these conditions with the ramp off was supposed to give instantaneous heating to 700 and 900°C, respectively, which is maintained for 10 sec. The actual temperature profile was measured with a 50-gauge low-thermal mass thermocouple and found to be as shown in Figure 1. This discrepancy from the ideal heating rate can be accounted for by the heat transfer delay and thermal mass of the quartz tube. In all cases, the amount of material pyrolyzed was of the order of 0.2–0.4 mg, which was weighed accurately into the quartz tube using a Cahn Electrobalance. This quartz tube was reweighed after all pyrolyses in order to determine the percentage weight loss due to pyrolysis.

The standard pyrolysis/gas chromatography measurements were performed using a temperature programmed Hewlett-Packard 5730A linked to the CDS

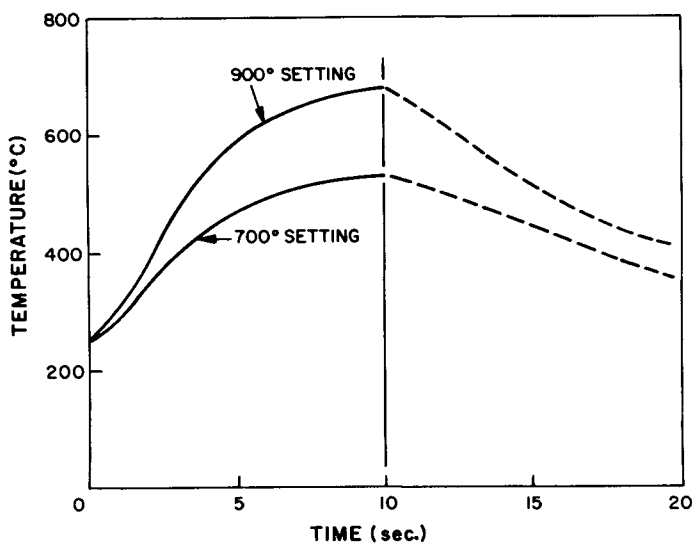


Fig. 1. Temperature-time profile in center of quartz tube with heater settings of 700 and 900°C, ramp off, and 10-sec heating time (interface temperature 250°C).

Pyroprobe 120 by an interface maintained at 250°C (explaining why the temperature profiles in Fig. 1 start at 250°C). The highly volatile products were separated using a 12 ft  $\times$   $\frac{1}{8}$  in. Chromosorb 102 (80/100 mesh) column, temperature programmed from 60 to 160°C at 4°/min after a hold of 8 min at 60°C. Helium at a flow rate of 26 ml/min was used as a carried gas, and both flame ionization and thermal conductivity detectors were employed. The higher-molecular-weight products were separated using a 8 ft  $\times$   $\frac{1}{8}$  in. 3% SE52 on a Chromosorb W (80/100 mesh) column, temperature programmed from 90 to 250°C at 4°/min with a 4-min delay at 90°C. Helium at a flow rate of 26 ml/min was once again used as the carrier gas with a flame ionization detector. In all cases the pyrolyses were carried out in helium with the products being swept directly into the column.

The peak identifications of the pyrograms were carried out using a Finnigan 4000 automated gas chromatography/EI-CI quadrapole mass spectrometer coupled directly to the CDS Pyroprobe interface. The mass fragmentation patterns of the separated peaks were analyzed using a 70 eV excitation voltage, while the parent peaks were determined using methane chemical ionization with a methane pressure of 0.23 torr and excitation energy of 41 eV. In addition to using the gas chromatograph/mass spectrometer for product identification, the retention times of certain products were compared with authentic samples.

## RESULTS AND DISCUSSION

The results of the pyrolysis/GC conducted on the untreated PET (Std) performed at the 900°C setting are given in Figures 2 and 3. The pyrogram shown in Figure 2 corresponds to that obtained with the highly volatile species using the Chromosorb 102 column, while Figure 3 is the pyrogram of the higher-molecular-weight species separated on the 3% SE52 column. It should be noted that these pyrograms do not take into consideration changes in attenuation and, therefore, should not be taken as directly representing actual concentration of

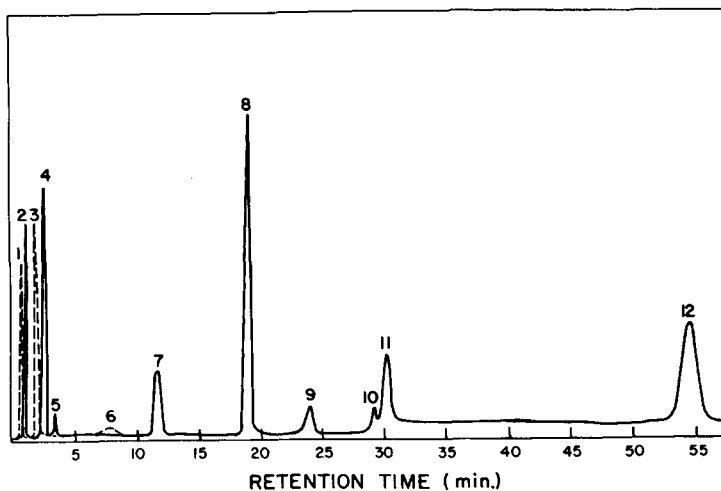


Fig. 2. Pyrogram of low-molecular-weight species obtained from pyrolysis of untreated PET heated at 900°C, using Chromosorb 102 column. (—) Peaks identified using flame ionization detector; (---) peaks identified with thermal conductivity detector.

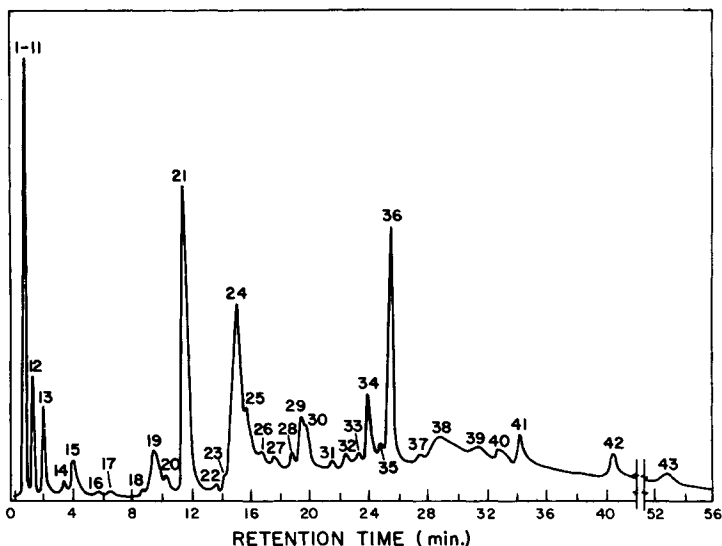


Fig. 3. Pyrogram of higher molecular-weight species obtained from pyrolysis of untreated PET heated at 900°C using SE52 column.

individual species. The mass fragmentation patterns, determined by the electron ionization technique, and the parent ion, as determined by chemical ionization, are listed in Table II for each of the resolved peaks identified in Figures 2 and 3. Where a peak has not been assigned because of lack of positive identification, the peak has simply been designated as  $X_1$ ,  $X_2$ , etc. The peaks whose retention times have been compared with authentic samples have also been identified in this table.

The average percentage weight losses observed for each polyester examined in this study using the pyroprobe technique are listed in Table III for both the 700 and 900°C temperature settings. Although some scatter in the individual values was observed from run to run, it is rather interesting to note that generally speaking, the presence of the flame-retardant chemicals appears to have only a slight effect on the observed percentage weight losses under these pyrolysis conditions. The slight reduction in the percentage weight loss associated with the bromine-containing compounds Tris and 900F when compared with the untreated and phosphorus-only-containing polyesters, while being statistically significant, is very close to the experimental variation from sample to sample.

The variations of the products of pyrolysis obtained in this study for the five polyesters examined are given in Tables IV and V for the 700 and 900°C temperature settings, respectively. The data were calculated from the average of several experiments and have been corrected to a standard percent weight loss of 28% for the 700°C data and 86% for the 900°C data. In order to obtain quantitative data from the gas chromatography traces, it was necessary to use known response factors ( $\Delta$ ), which correct for the variation of the response of the detecting device to different chemical compounds. This means that the measured areas under the GC curve for a particular peak had to be divided by these relative response factors ( $\Delta$ ) for each compound in order to get a true area

TABLE II  
Pyrolysis Products Formed by Pyrolysis of Untreated PET at 900°C for 10 sec

| Peak No. | Compound                             | Molecular ion determined by chemical ionization | Mass fragmentation pattern using 70 eV electron excitation | RT <sup>a</sup> checked |
|----------|--------------------------------------|---|--|-------------------------|
| 1        | carbon monoxide                      | —   | 28, 12, 16, 29, 14   | ✓                       |
| 2        | methane                              | —   |  | ✓                       |
| 3        | carbon dioxide                       | —   | 44, 16, 12, 28, 45, 22                                     | ✓                       |
| 4        | ethylene + acetylene                 | —   | 26, 28, 27, 25, 14   | ✓                       |
| 5        | ethane                               | —   |  | ✓                       |
| 6        | water                                | —   | 18, 15, 14   |                         |
| 7        | propylene                            | —   | 41, 39, 42, 27, 40, 38                                     | ✓                       |
| 8        | acetaldehyde                         | —   | 29, 15, 44, 43, 14, 26                                     | ✓                       |
| 9        | acetone                              | —   |  | ✓                       |
| 10       | propenal                             | —   | 27, 26, 29, 28, 56, 55                                     | ✓                       |
| 11       | ethanol                              | —   |  | ✓                       |
| 12       | benzene                              | 78  | 78, 52, 51, 77, 50, 39                                     | ✓                       |
| 13       | toluene                              | 92  | 91, 92, 39, 65, 51, 63                                     | ✓                       |
| 14       | ethyl benzene                        | 106   | 91, 106, 39, 51, 65, 77                                    | ✓                       |
| 15       | styrene                              | 104   | 104, 103, 78, 51, 77, 50                                   | ✓                       |
| 16       | <i>p</i> -vinyl toluene              | 118   | 117, 118, 39, 115, 91, 58                                  |                         |
| 17       | benzaldehyde                         | 106   | 77, 105, 106, 51, 50, 39                                   | ✓                       |
| 18       | <i>p</i> -ethyl toluene              | 120   | 91, 65, 92, 39, 120, 51                                    |                         |
| 19       | acetophenone                         | 120   | 105, 77, 51, 120, 43, 50                                   | ✓                       |
| 20       | methyl benzoate                      | 136   | 117, 105, 77, 51, 39, 43                                   |                         |
| 21       | vinyl benzoate                       | 148   | 105, 77, 51, 106, 50, 78                                   | ✓                       |
| 22       | ethyl benzoate                       | 150   | 105, 77, 130, 131, 51, 122                                 | ✓                       |
| 23       | <i>p</i> -methyl acetophenone        | 134   | 119, 91, 39, 134, 65, 51                                   |                         |
| 24       | benzoic acid                         | 122   | 105, 77, 122, 51, 50, 39                                   | ✓                       |
| 25       | <i>p</i> -methyl vinyl benzoate      | 162   | 119, 91, 65, 39, 120, 63                                   |                         |
| 26       | <i>p</i> -vinyl acetophenone         | 146   | 131, 103, 77, 146, 51, 43                                  |                         |
| 27       | propyl benzoate                      | 164   | 105, 77, 51, 50, 106, 73                                   |                         |
| 28       | <i>p</i> -ethyl vinyl benzoate       | 176   | 133, 79, 77, 105, 103, 134                                 |                         |
| 29       | <i>p</i> -vinyl vinyl benzoate       | 174   | 131, 103, 77, 51, 132, 102                                 |                         |
| 30       | biphenyl                             | 154   | 154, 153, 76, 152, 51, 77                                  | ✓                       |
| 31       | 1-hydroxy ethyl benzoate             | 166   | 105, 77, 123, 51, 106, 50                                  |                         |
| 32       | diacetyl benzene                     | 162   | 147, 43, 145, 91, 119, 115                                 |                         |
| 33       | X <sub>1</sub>                       | 188   | 147, 105, 77, 91, 43, 51                                   |                         |
| 34       | <i>p</i> -acetyl vinyl benzoate      | 190   | 147, 43, 91, 76, 119, 50                                   |                         |
| 35       | X <sub>2</sub>                       | 190   | 147, 91, 90, 84, 145, 65                                   |                         |
| 36       | divinyl terephthalate                | 218   | 175, 104, 76, 50, 133, 66                                  |                         |
| 37       | ethyl vinyl terephthalate            | 220   | 177, 149, 65, 76, 50, 104                                  |                         |
| 38       | <i>p</i> -acetyl benzoic acid        | 164   | 149, 65, 43, 161, 51, 77                                   |                         |
| 39       | X <sub>3</sub>                       | 234   | 181, 152, 196, 153, 76, 43                                 |                         |
| 40       | X <sub>4</sub>                       | 196   | 181, 152, 73, 153, 76, 182                                 |                         |
| 41       | methyl 1-hydroxy ethyl terephthalate | 224   | 149, 41, 195, 57, 56, 76                                   |                         |
| 42       | ethylene dibenzoate                  | 270   | 105, 77, 51, 106, 50, 76                                   |                         |
| 43       | X <sub>5</sub>                       | 278   | 149, 57, 43, 41, 71, 167                                   |                         |

<sup>a</sup> Compounds verified by comparison of retention times (RT) with authentic samples.

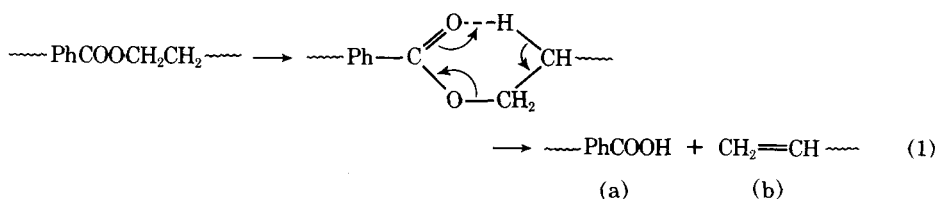
for that compound. When this true area was normalized, the mole concentrations shown in Tables IV and V were obtained. The relative response factors used were those given by Dietz<sup>19</sup> for the flame ionization detector and Messner, Rosie, and Argalbright<sup>20</sup> for the thermal-conductivity detector. In cases where

TABLE III  
% Weight Loss of PET Fabrics during Pyroprobe GC Determinations

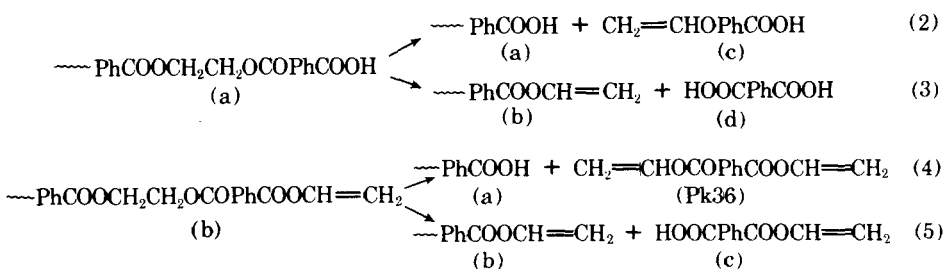
| Pyrolysis temp., °C | Sample |        |         |        |        | Mean of samples |
|---------------------|--------|--------|---------|--------|--------|-----------------|
|                     | Std.   | AB19   | T271    | Tris   | 900F   |                 |
| 700                 | 32 ± 2 | 29 ± 6 | 30 ± 12 | 26 ± 7 | 25 ± 2 | 28 ± 3          |
| 900                 | 85 ± 5 | 87 ± 3 | 91 ± 2  | 86 ± 1 | 84 ± 1 | 86 ± 3          |

no response factors have been reported, the value of a similar compound was chosen. In the case of the unidentified compounds,  $X_1$ - $X_5$ , a value of 0.8 was used.

Based upon the data contained in Tables IV and V, it can be seen that the major products in the pyrolysis of untreated PET are carbon monoxide, carbon dioxide, ethylene-acetylene, acetaldehyde, benzene, benzoic acid, vinyl benzoate, divinyl terephthalate, acetophenone, and *p*-acetyl vinyl benzoate. The proposed mechanism for the pyrolysis of PET should, therefore, be able to account for all these major products plus others found in smaller amounts. Since PET has a  $\beta$  hydrogen, the first step in the degradation is most probably the classical ester scission reaction to give a carboxylic acid and olefinic end groups.<sup>13</sup>



Further ester scission on the adjacent ester groups of (a) and (b) can then lead to the following product formation:



Divinyl terephthalate (Pk36) can be considered to be a primary scission product. The two acid products, (c) and (d), while not detected by our analysis systems, cannot be ruled out since the products of decarboxylation of these two species were detected, namely vinyl benzoate, benzoic acid, and benzene.

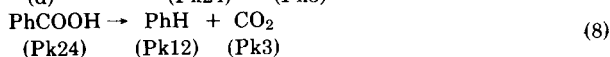
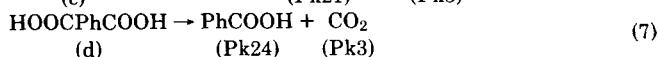
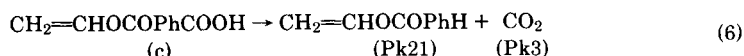




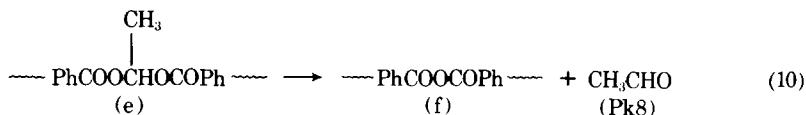


TABLE V  
Product Distribution for Pyrolyzed PET Samples at 900°C for 10 sec.<sup>a</sup>

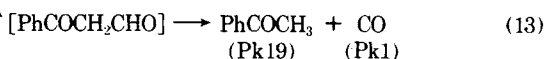
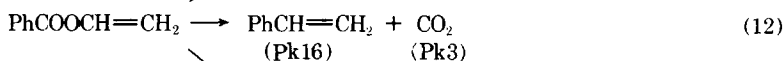
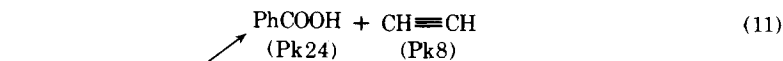
| Peak No.<br>(Pk) | Sample |       |       |       |       |
|------------------|--------|-------|-------|-------|-------|
|                  | Std.   | AB19  | T271  | Tris  | 900F  |
| 1                | 0.470  | 0.554 | 0.471 | 0.780 | 0.752 |
| 2                | 0.023  | 0.023 | 0.035 | 0.119 | 0.049 |
| 3                | 0.178  | 0.180 | 0.195 | 0.270 | 0.265 |
| 4                | 0.070  | 0.072 | 0.083 | 0.106 | 0.139 |
| 5                | trace  | trace | trace | 0.006 | 0.013 |
| 6                | trace  | trace | trace | trace | trace |
| 7                | 0.005  | 0.005 | 0.005 | 0.009 | 0.009 |
| 8                | 0.048  | 0.044 | 0.064 | 0.065 | 0.009 |
| 9                | 0.004  | 0.004 | 0.009 | 0.004 | 0.004 |
| 10               | trace  | trace | trace | 0.003 | trace |
| 11               | 0.008  | 0.013 | 0.012 | 0.017 | 0.004 |
| 12               | 0.121  | 0.082 | 0.062 | 0.077 | 0.078 |
| 13               | 0.023  | 0.017 | 0.014 | 0.021 | 0.036 |
| 14               | 0.008  | 0.004 | 0.004 | 0.008 | 0.009 |
| 15               | 0.023  | 0.016 | 0.016 | 0.018 | 0.016 |
| 16               | 0.001  | 0.001 | 0.001 | 0.004 | 0.001 |
| 17               | 0.001  | 0.001 | 0.001 | 0.004 | 0.001 |
| 18               | 0.002  | 0.001 | 0.004 | 0.002 | 0.001 |
| 19               | 0.061  | 0.027 | 0.045 | 0.022 | 0.030 |
| 20               | trace  | —     | trace | trace | trace |
| 21               | 0.192  | 0.218 | 0.226 | 0.147 | 0.192 |
| 22               | 0.005  | 0.004 | 0.001 | 0.003 | 0.001 |
| 23               | trace  | trace | trace | trace | trace |
| 24               | 0.344  | 0.196 | 0.302 | 0.234 | 0.341 |
| 25               | 0.009  | 0.019 | 0.009 | 0.019 | 0.025 |
| 26               | 0.008  | 0.005 | 0.004 | 0.004 | 0.004 |
| 27               | 0.005  | 0.001 | 0.006 | 0.002 | 0.002 |
| 28               | 0.005  | 0.008 | 0.009 | 0.007 | 0.002 |
| 29               | 0.022  | 0.030 | 0.027 | 0.019 | 0.022 |
| 30               | 0.014  | 0.010 | 0.006 | 0.008 | 0.016 |
| 31               | 0.005  | 0.006 | 0.008 | 0.007 | 0.006 |
| 32               | 0.006  | 0.006 | 0.009 | 0.006 | 0.005 |
| 33               | 0.003  | 0.003 | 0.002 | 0.030 | 0.034 |
| 34               | 0.033  | 0.037 | 0.037 | 0.031 | 0.024 |
| 35               | 0.004  | 0.008 | 0.006 | 0.001 | —     |
| 36               | 0.093  | 0.147 | 0.104 | 0.083 | 0.051 |
| 37               | 0.004  | 0.003 | 0.001 | 0.003 | 0.004 |
| 38               | 0.023  | 0.043 | 0.041 | 0.040 | 0.026 |
| 39               | 0.002  | 0.006 | 0.002 | 0.001 | 0.001 |
| 40               | 0.003  | 0.003 | 0.003 | 0.006 | 0.003 |
| 41               | 0.014  | 0.015 | 0.011 | 0.008 | 0.009 |
| 42               | 0.009  | 0.012 | 0.011 | 0.007 | 0.014 |
| 43               | 0.002  | 0.004 | 0.003 | 0.012 | 0.008 |

<sup>a</sup> Values in mol/192 g PET (i.e., per mole unit) normalized to 86% wt loss.

(e) would correspond to ethylene dibenzoate (Pk42) if (a) was benzoic acid and (b) vinyl benzoate, thus tending to confirm reaction (9). The substituted ethylene dibenzoate (e) is now capable of disproportionation to give the acid anhydride (f) plus acetaldehyde (Pk8):

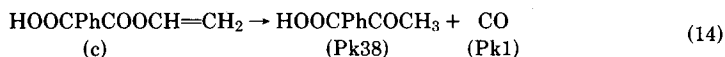


In the case of studies with the model compound ethylene dibenzoate, Richie<sup>21</sup> observed that, while reactions (9) and (10) are favored at low temperatures, the reactions of vinyl benzoate favored at higher temperatures were the following:

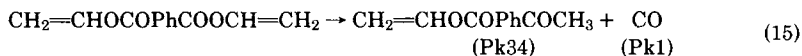


with reaction (13) a two-stage rearrangement cum decarbonylation being the predominant one [molar ratios of reactions (11):(12):(13)  $\approx$  1:3:15 at 520°C].

These three reactions, (11), (12), and (13), are therefore able to account for the formation of acetylene, styrene, acetophenone, and CO—all products of the pyrolysis of PET. The fact that at the higher temperature the acetaldehyde concentration is less than that at the lower temperature would seem to confirm that reactions (11)–(13) are occurring in the case of PET. These same reactions, also help to account for the higher CO and *p*-acetyl compound yields observed at the higher pyrolysis temperatures, i.e., the product from reactions (2) and (5) react as follows:



while divinyl terephthalate (Pk36), the product of reaction (4), reacts to give *p*-acetyl vinyl benzoate (Pk34)



Reactions (1)–(15) are thus capable of describing the pyrolysis of PET since they account for the formation of the majority of products formed without proposing  $\alpha$  cleavage of the ester bond, the primary scission reaction suggested by Marshall and Todd<sup>22</sup>:



However, no other investigators have found evidence to support this free-radical mechanism, and work in our laboratories<sup>23</sup> with a model ester pyrolyzed using the same pyrolysis system as we have used in this investigation suggests that reaction (1), not reaction (16), is the dominant primary scission process.

So far we have only considered the major products of pyrolysis of PET and proposed mechanisms to explain their formation. The major intention of this study was to establish the influence of several flame-retardant systems on these pyrolysis products and on the reactions leading to their formation. For this reason it is necessary to examine in some detail the data presented in Tables IV and V in order to determine the major differences in the pyrolysis product distribution. Although all three pyrograms were examined for new peaks that could

be attributed to the presence of the flame retardant or their products, none were detected.

The data obtained using the 700°C pyroprobe temperature setting will be considered first (Table IV). All the polyesters gave CO<sub>2</sub> as the major product with CO as the second most abundant material. The concentrations of CO<sub>2</sub> and CO were approximately the same for all the polyesters with the exception of the Tris-treated material, which gave about twice the amount of these two materials in comparison to the other polyesters. The Tris-treated material, in addition, gave consistently higher concentrations for all the volatile products analyzed (e.g., ethylene-acetylene, acetaldehyde, acetone, propenal, ethanol). Acetaldehyde was the third most abundant in all cases with the exception of the 900F material, in which its concentration in the pyrolysis products was surprisingly low (about a factor of 10 less than found in the Tris material and 1/5 of that observed with the standard polyester). This would suggest that reactions (9) and (10), a sequence supposedly favored at low temperatures, are being retarded by the presence of the bromine atoms in the 900F polyester. After CO<sub>2</sub>, CO, and acetaldehyde, the esters vinyl benzoate and divinyl terephthalate along with benzoic acid were the most abundant species in all cases, with the exception once again of the Tris-treated material. With the latter, these three products were less abundant than with the other polyesters. When this observation is coupled with the increased concentration of volatile pyrolysis products, it may be concluded that, following the primary scission reactions to give the primary products of pyrolysis, the Tris flame retardant promotes their further pyrolysis to enhance the formation of the smaller, secondary-fragmentation products of pyrolysis.

In the case of the remainder of the pyrolysis products identified, all the polyester systems examined behaved very similarly giving the same products in almost the same relative concentrations (i.e., no peaks specific to one system were identified). Both bromine-containing systems (Tris and 900F) did, however, produce significantly higher concentrations of *p*-acetyl vinyl benzoate, *p*-acetyl benzoic acid, and *p*-acetyl-1-hydroxyethyl benzoate. This suggests that reactions (14) and (15) are enhanced in the thermal degradation of these two polyesters. In the case of the 900F material, this observation further supports the fact that there is competition between reactions (9) and (10) and reactions (13), (14), or (15), and that these latter reactions are being favored by this polyester.

The data obtained using the 900°C pyroprobe temperature setting (Table V) show some surprising differences from those observed with the 700°C pyrolysis conditions. The most striking observation is that CO<sub>2</sub> is no longer the primary product of pyrolysis, being replaced by CO at levels which exceed CO<sub>2</sub> by almost 2:1. This would suggest that, at this higher pyrolysis temperature, the secondary reactions (13), (14), or (15) leading to the formation of CO and the *p*-acetyl compounds are becoming dominant. Meanwhile, a large amount of the potential CO<sub>2</sub> is still tied up in such products as benzoic acid, vinyl benzoate, and divinyl terephthalate, all major products of the pyrolysis of the various polyester systems examined. One of the surprising observations is the sharp reduction in the observed concentration of acetaldehyde at 900°C, when compared to its concentration at 700°C. This observation once again appears to reflect the temperature dependence of reactions (9) and (10), leading to acetaldehyde and reactions (13), (14), or (15) which give rise to CO and the *p*-acetyl species. However, another

possibility is that acetaldehyde being formed as a result of reaction (9) and (10) is decarbonylated to give methane and CO by the well-documented reaction<sup>24</sup>



This reaction could also account for the appreciable concentrations of methane produced at this higher temperature and not observed at 700°C.

When considering the role of the flame-retardant systems on the pyrolysis data obtained at 900°C, it is obvious that both the phosphorus-only polyesters (AB19 and T271) behave very similarly to the standard untreated polyester in terms of the products formed and their concentrations.

The Tris material at 900°C gives higher concentrations of the more volatile products of pyrolysis, especially methane whose concentration is almost a factor of 10 larger than obtained with the untreated material. This suggests that methane is produced by an alternative reaction to (17) mentioned previously, since reaction (17) would require that the precursor to the methane, acetaldehyde found by reactions (9) and (10) to compete strongly with reactions (13), (14), or (15) (unlikely at these high temperatures). A more probable source of methane is the *p*-acetyl compounds produced by reactions (13), (14), or (15) which are capable of undergoing acetyl cleavage to give methyl radicals



These radicals so produced are capable of numerous reactions, including hydrogen abstraction to give methane. The formation of radicals such as these also helps to explain such minor products of pyrolysis as ethane, propylene, acetone, ethanol, toluene, benzaldehyde, methyl benzoate, *p*-methyl acetophenone, *p*-methyl vinyl benzoate, biphenyl and diphenyl methane.

The 900F polyesters system like the other bromine-containing system (Tris) also produces higher concentrations of the more volatile species than obtained with the standard polyester. This suggests that the 900F material is capable of generating species which can activate the secondary-fragmentation process occurring at these higher temperatures.

## CONCLUSIONS

From a comparison of the pyrograms of the untreated polyester fabrics with those containing phosphorus and bromine flame retardants, it can be concluded that there are no large differences in the products of pyrolysis. This, of course, suggests that for the most part the flame retardants studied in this investigation do not greatly influence the mechanisms of pyrolysis, especially the phosphorus-only systems. In the case of the bromine containing polyesters, however, some significant but small changes in the pyrolysis product distribution are observed, suggesting that these species are capable of promoting secondary reactions which lead to the formation of more volatile species. In terms of influencing the mechanisms of pyrolysis, there appears to be some suggestion that the 900F retarding system is capable of influencing the competition between the two reactions (9) and (10) and (13), (14), or (15). However, in view of the generally minor changes in product distribution obtained with the bromine compounds, Tris and 900F, and the negligible changes observed with the phosphorus containing polyesters, AB19 and T271, the major role of these systems in reducing the flammability of the polymer must be ascribed to their action in the gas phase.

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