

# A Mechanism for Flame Retardation of Poly(ethylene Terephthalate)

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## Synopsis

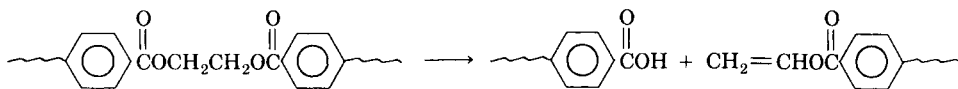
The thermolysis of vinyl methylterephthalate has been studied as a model of poly(ethylene terephthalate) (PET) thermolysis. Based upon this reaction, a potential mechanism for PET flame retardation is proposed. The assumption is made, based upon firm experimental evidence, that the initial step in PET degradation is formation of a vinyl ester and a carboxylic acid. The essentials of the mechanism are that this vinyl ester participates in a vinyl polymerization reaction and produces a linear polymer. This linear polymer then is involved in a chain-stripping reaction with the loss of methylterephthalate and the concomitant formation of a polyene. In the last step, this polyene undergoes a cyclization reaction and yields a crosslinked product. There are two stages at which PET undergoes crosslinking: In the second step the linear vinyl polymer is produced; in the last step ultimate crosslinking with the formation of cyclic structures is observed.

## INTRODUCTION

The thermal degradation of poly(ethylene terephthalate) (PET) has been studied by many workers in the past several years.<sup>1-35</sup> The surface temperature of the burning polymer is reported at 380°C<sup>2</sup>; thus at this temperature volatiles must be generated. In confirmation of this, dynamic thermogravimetric analysis showed substantial weight loss at 400°C. Cooney et al.<sup>3</sup> and Vijayakumar et al.<sup>4</sup> report that the decomposition takes place in at least four distinct steps under low heating rates; at higher heating rates only two stages may be distinguished.

The decomposition of PET has been studied under a variety of conditions, under thermooxidative conditions<sup>20</sup> a radical chain mechanism is initiated by the formation of peroxide and hydroperoxide radicals. Radical processes have also been proposed<sup>11</sup> under conditions in which oxygen is not present; later work has shown that radicals are not important under these conditions.<sup>6</sup>

There is some agreement that the initial step of PET decomposition occurs via a typical ester pyrolysis mechanism, with the formation of a carboxylic acid and a vinyl ester<sup>6,12-16</sup>.



Bednas et al.<sup>33</sup> and Sugimura,<sup>14</sup> with flash pyrolysis coupled with GC-MS, as well as this group,<sup>34,35</sup> by actual analysis of the products of limited pyrolysis, have shown that this is the first step. Subsequent steps in the reaction mechanism, ultimately leading to the formation of gaseous products, have been proposed but there is no agreement in these steps.

Work has been carried out by Yoda et al.<sup>21</sup> and Zimmermann<sup>18,19</sup> that suggests that crosslinking of PET occurs upon pyrolysis. They indicate that the initially formed vinyl ester participates in a vinyl polymerization reaction; this is then followed by a chain-stripping reaction with the elimination of terephthalic acid. The residue is noted to be insoluble and does undergo gelation. Yoda has noted that the infrared spectrum of the product of thermooxidative pyrolysis of PET is quite similar to that of pyrolysis of poly(vinyl methylterephthalate).

Our work is directed towards the discovery of routes that will lead to crosslinking of the initial polymer and thus produce materials that will produce a char under thermal conditions. Van Krevelen<sup>36</sup> has shown that there is a correlation between char residue and the oxygen index of the polymer: The higher the char, the lower is the flammability. Parker et al.<sup>37</sup> have noted that an increase in aromaticity yields high char residues which also correlate with the oxygen index. The product that is desired is a material which will be much more resistant to thermal degradation than the starting polymer. The crucial steps in a polymer decomposition sequence for flame retardance are the early steps; it is in these steps that the material that will produce the fuel for the fire is generated. In this work we present results for the pyrolysis of vinyl methylterephthalate and poly(vinyl methylterephthalate), indicate a scheme for the trapping of the material produced in the initial decomposition step of PET, and show how an understanding of this scheme may be used for flame retardance of PET.

## EXPERIMENTAL

The silating agent, TRI-SIL, was obtained from the Pierce Chemical Co.; all other materials were obtained from the Aldrich Chemical Co. <sup>1</sup>H-NMR spectra were obtained on a Varian EM-360 spectrometer; <sup>13</sup>C-NMR spectra were obtained on a JEOL FX60Q spectrometer. FT-IR spectra were obtained on an Analect FX-6200 instrument. GC-MS were performed on a Hewlett-Packard Model 5890 instrument equipped with a Model 5970 mass selective detector. Thermogravimetric analysis was performed on a Perkin-Elmer TGA-7 instrument. GPC analysis was performed on a Waters instrument.

**Synthesis of Vinyl Methylterephthalate.** Concentrated sulfuric acid, 0.36 g (0.2 mL), was added dropwise to a stirred mixture of 25.0 g (0.014 mol) of *p*-carbomethoxybenzoic acid, 150 g (1.74 mol) of vinyl acetate, and 0.63 g of mercuric acetate at 60°C. The mixture was then brought to reflux for 1 h. The reaction mixture was maintained at 70°C for 70 h; then 0.25 g sodium acetate was added. The acetic acid and excess vinyl acetate were distilled off at 30°C under reduced pressure. The brownish-yellow residue was extracted with boiling petroleum ether and the extract was cooled to crystallize vinyl methylterephthalate. The crude product was purified by vacuum sublimation at

80–100°C. The yield was 16.3 g (57%), mp = 59.5–60.5°C (lit. = 61.0–61.5°C):

IR (KBr): 1734 (C=O), 1652 (C=C), 956, 873  $\text{cm}^{-1}$ .

$^1\text{H-NMR}$  (acetone- $d_6$ ): 3.9 (3H, s), 4.7–5.2 (2H, d, d), 7.3–7.7 (1H, d, d), 8.2 ppm (4H, m).

$^{13}\text{C-NMR}$  (acetone- $d_6$ ): 52.75, 99.12, 130.41, 133.56, 135.61, 142.26, 163.33, 166.32 ppm.

**Synthesis of Poly(vinyl Methylterephthalate.** PVMT was prepared by a radical polymerization following the procedure of Yoda.<sup>21</sup> A 3.0-g sample of vinyl methylterephthalate and 0.02 g of benzoyl peroxide were combined in 5 mL of benzene in a round bottom flask and thoroughly evacuated. The mixture was heated to 60°C for 1 day; then it was coagulated in petroleum ether and the polymer was collected:

IR (KBr): 1730  $\text{cm}^{-1}$  (C=O), no C=C.

**Thermolysis Reactions.** In general thermolysis reactions were performed in well-evacuated sealed tubes of about 60  $\text{cm}^3$  volume. The tube was thoroughly evacuated on the high vacuum line for at least 2 h; then the desired material, either VMT or PVMT, was added and the vessel was again evacuated for at least 2 h. It was then sealed off from the vacuum line and placed in a muffle furnace regulated at the desired temperature. After 2 h, the oven was turned off and allowed to cool to room temperature; then the tube was removed from the oven, cooled in liquid nitrogen, opened, and analyzed. *Care must be taken in these operations. Tubes have been known to develop excess pressure and explode.* Products were analyzed by infrared spectroscopy, NMR spectroscopy, and GPC.

For quantitation of the reaction products the reactions were carried out in 5-mL vials. These were weighed in air, then loaded with sample, reweighed, evacuated, sealed, and placed in the oven. Upon removal from the oven, the tubes were cooled in liquid nitrogen then opened. A 2.0-mL aliquot of silylating mixture and internal standard, hexadecene, was added to each vial, and they were then stirred for 1 or 2 h. An aliquot was then injected into the GC-MS and analyzed. Calibration curves were prepared for each compound, methyl terephthalate, dimethylterephthalate, and terephthalic acid, these were used to ascertain the amount of each material present in the sample. The results reported are an average of three determinations, two used a 1-h silylation time while the third was allowed to proceed for 2 h. The silylation time does not appear to have an effect upon the results.

## RESULTS

Authentic vinyl polymer, poly(vinyl methylterephthalate) (PVMT) has been produced by the free radical polymerization of vinyl methylterephthalate (VMT) following a literature procedure,<sup>21</sup> and it has been characterized by NMR and IR spectroscopy. The thermolysis of VMT at temperatures from 200° to 400°C produces a material which has an identical IR spectrum to that of the polymer produced under free radical conditions. As the temperature is raised, additional products appear in the reaction system; these have been identified as dimethylterephthalate (DMT) methylterephthalate (MA), and terephthalic acid (TPA). The thermolysis of the polymer, PVMT, under

TABLE I  
Products from the Thermolysis of Vinyl Methylterephthalate and  
Poly(Vinyl Methylterephthalate) as a Function of Temperature

Starting material (mg)	T (°C)	DMT (mg)	MA (mg)	TPA (mg)	Residue
VMT, 50.0	200	2.8	8.6	0.8	39.5
VMT, 50.3	250	3.5	15.7	2.9	24.1
VMT, 50.0	300	8.7	8.7	7.8	25.8
VMT, 50.8	350	13.1	12.0	9.7	6.0
VMT, 50.8	400	10.5	12.0	7.1	13.5
PVMT, 51.0	200	2.2	7.1	1.5	40.5
PVMT, 50.1	250	3.6	18.4	4.4	23.2
PVMT, 50.5	300	10.7	11.3	9.8	22.3
PVMT, 50.0	350	12.4	14.0	10.7	12.3
PVMT, 50.3	400	6.9	9.9	6.1	11.6

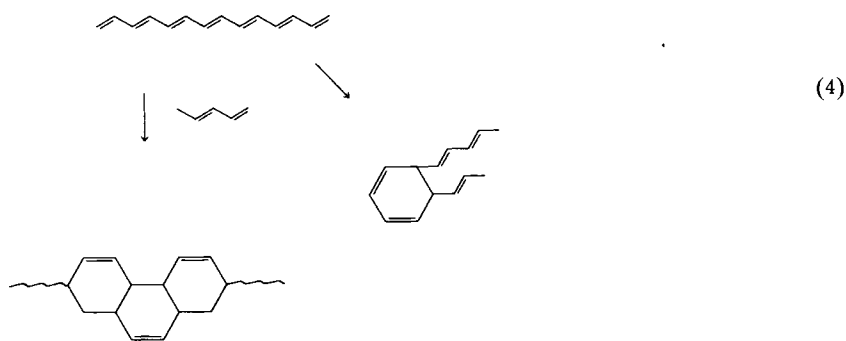
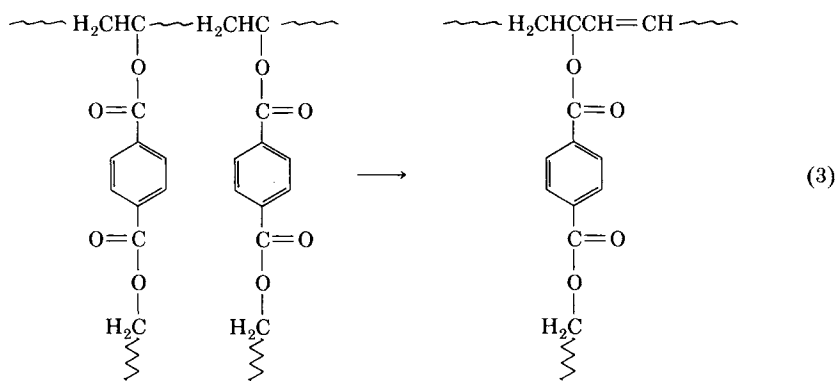
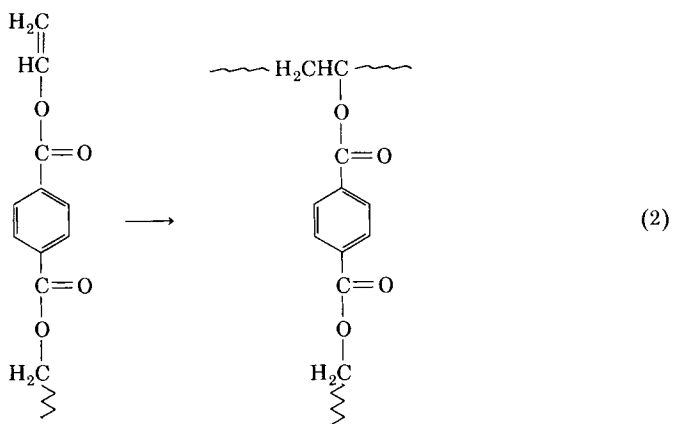
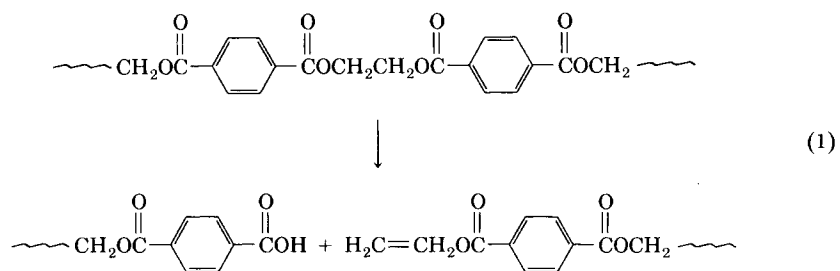
identical conditions produces similar products. The results of the thermolyses are shown in Table I. In all cases some quantity of gas is produced, since the results are an average of three determinations, the numbers do not add up to give the total charge to the vessel. We estimate that all results are about  $\pm 10\%$ . Yoda et al.<sup>21</sup> have noted the formation of only MA from a similar reaction, since their work was conducted in air the MA may sublime before disproportionation may occur.

## DISCUSSION

Flame retardation of PET requires that the decomposition of the polymer to produce small molecules be prevented and, instead, that some other route become the dominant decomposition pathway for the polymer. This new mode must be one in which small molecules are not produced, rather a route in which crosslinking of the polymer strands occurs would be preferred. The discovery of such a route requires a clear understanding of the mode to be repressed as well as that to be promoted. The process of combustion actually consists of two steps, the generation of the fuel and the actual combustion. The fuel generation step probably does not involve oxygen, sealed tube reactions will permit one to study this step. Scheme 1 delineates the pathway that we propose for PET decomposition.

It is virtually impossible to study only the first step of the mechanism, since upon the formation of the vinyl ester and carboxylic acid there seems to be an immediate reaction, or series of reactions, that occur and lead to the final product. Decomposition of PET<sup>34</sup> alone does not commence until about 350°C; at 400°C an aromatic char is obtained. In the presence of red phosphorus,<sup>34</sup> the char-producing reactions are accelerated and the aromatic char is obtained at 325°C. With ZnCl<sub>2</sub> as the additive,<sup>35</sup> this char-forming reaction is important at 300°C. We have chosen to begin our study with the active product of the first reaction, the vinyl ester, and investigate its subsequent reactions.

The vinyl polymerization reaction (reaction 2) occurs as evidenced by the loss of the double bond frequency in the infrared spectrum and the solubility change, in agreement with the results of Yoda et al.<sup>21</sup>



Scheme 1

The chain-stripping reaction (reaction 3) occurs with the loss of methylterephthalate (MA) and the concomitant formation of double bonds in the polymer. The data that are reported above indicate that, at all temperatures at which the reaction has been performed, some amount of acid is produced. The presence of DMT and TPA may be explained by the disproportionation of MA. We have investigated the thermolysis of MA alone and find that disproportionation does indeed occur within the temperature range of this study. One would expect that this disproportionation would become more favorable the higher the temperature; the equilibrium constant from the data reported above shows a somewhat smooth increase from 200 to 350°C, with an apparent decrease at 400°C. The agreement between the results for DMT and TPA, which should be produced in equal amounts by the disproportionation reaction, is quite good in most cases. We believe that any discrepancies are the result of the analytical procedure utilized for the determination. Yoda et al.<sup>21</sup> report that VMT undergoes polymerization and sublimation, not decomposition, at 280°C in air. Even at 200°C, we see evidence for chain stripping; this is probably a consequence of the difference between reactions in air and vacuum.

The results for PVMT and its precursor, VMT, are identical within experimental error and indicate that the amount of acid that is produced increases from 200 to 350°C but is lower at 400°C. The probable explanation for this is that at 400°C cyclization (reaction 4) may proceed very easily while it does not proceed so easily at lower temperatures. Thus at 400°C some amount of polyene is formed, and it at once cyclizes and produces a crosslinked material. Chain stripping from that cyclized product is less favorable than from the linear polymer leading to a decreased yield of MA.

One might expect a solubility difference between the linear polymer, produced at lower temperature, and the cyclic, crosslinked, material that is produced at 400°C. The solubility of even the linear polymer is not very high and one cannot use this to differentiate these materials. The infrared spectra of the residue at all temperatures is very similar. At 250 and 300°C the presence of double bonds is evident from the frequency near 1600  $\text{cm}^{-1}$ . At higher temperatures this frequency is lost in the many bands that are observed in this region. The material pyrolyzed at 400°C retains solvent to the extent of about 10%, thus indicating that crosslinking does occur under these conditions. Thermogravimetric analysis also allows one to differentiate these materials. The TGA curves of the material formed at low temperatures (200–300°C) show substantial weight loss at low temperatures, while the curves for materials prepared at 350 and 400°C are significantly more stable. Thus at higher temperature cyclization of the polyene does occur and this does lead to increased thermal stability.

The evidence presented above very clearly indicates that the vinyl ester that is initially produced by the thermolysis of PET undergoes vinyl polymerization and that vinyl polymer then undergoes a chain-stripping reaction to produce monomethylterephthalate and a polyene. At 400°C there is clear evidence for crosslinking from the gelation experiment as well as evidence from TGA that the polymer is more thermally stable than that produced at lower temperatures. This result is in accord with the proposed polyene

cyclization reaction which is the last step in the reaction sequence herein proposed.

The application of this scheme to PET flame retardation leads to an anomaly; in order to effectively flame retard PET, it is necessary to cause decomposition to occur at lower temperature. As noted by Yoda, polymerization of vinyl methylterephthalate proceeds at 280°C, before degradation may occur. Thus an additive is required that will assist in the initial chain scission reaction of PET and produce the vinyl ester and carboxylic acid in the temperature range of 280 to 300°C. If this material may be produced at a temperature below its decomposition temperature, then polymerization will surely follow. It seems likely that the latter two reactions, chain stripping and polyene cyclization, will also occur thermally without the requirement of additional additives. This provides a very narrow temperature region since reaction must not occur upon processing but must commence at a temperature only a little higher.

### CONCLUSION

This pathway describes a potential route to increase the thermal stability of PET. The key step in this route is that at all stages the intermediates that are formed have at least two reaction pathways available; they may be subject to degradation or they may participate in the polymerization, chain stripping, or polyene cyclization reactions. The challenge that is faced as a result of this work is to discover a means of promoting these desirable reactions and minimizing the undesirable degradation reactions. Work is actively underway in this laboratory to discover additives that will promote these desired reactions.

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