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Influence of temperature and environment on the thermal decomposition of poly(ethylene terephthalate) fibres with and without the flame retardant tris(2,3-dibromopropyl) phosphate

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INFLUENCE OF TEMPERATURE AND ENVIRONMENT ON THE THERMAL DECOMPOSITION OF POLY(ETHYLENE TEREPHTHALATE) FIBRES WITH AND WITHOUT THE FLAME RETARDANT TRIS(2,3-DIBROMOPROPYL) PHOSPHATE *

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SUMMARY

The thermal degradation of poly(ethylene terephthalate) in the presence as well as in the absence of the flame retardant tris(2,3-dibromopropyl) phosphate was studied by pyrolysis–gas chromatography. The study has employed a range of pyrolysis temperatures between 450 °C and 700 °C in both helium and air. Comparison of the pyrolysis products obtained in oxidative (air) and non-oxidative (helium) environments showed that oxygen does not play a large role in the degradation process under the conditions employed in this study. The technique was capable of differentiating between the products produced from the two samples examined (flame retarded and non-flame retarded) and the chemical reactions leading to their formation. The influence of the flame retardant upon specific reaction schemes was postulated.

INTRODUCTION

The chemical tris(2,3-dibromopropyl)phosphate, known as TRIS, was first recognised as a viable commercial flame retardant in the early 1970's. Because it was a convenient economical treatment for 100% polyester fabrics, its use became widespread and it was soon recognised as the flame retardant of choice. In 1977, however, TRIS was identified as a potential carcinogen and was subsequently banned for the treatment of textile garments. The chemical meanwhile, remains an experimental curiosity as researchers investigate its mode of action in an attempt to design alternative flame retardants. Studies in our laboratories have already investigated the role of dosage on pyrolysis product yield [1], the effectiveness of hydrogen

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bromide release [2], and the combustibility of the pyrolysates [3]. Whilst these investigations gave some valuable information on the pyrolysis and combustion of poly(ethylene terephthalate) (PET) with and without flame retardant, it did leave certain questions unanswered, namely: what influence do pyrolysis temperature and pyrolysis environment have upon the pyrolysate? Earlier studies [4,5] have revealed that temperature does indeed influence the pyrolysis product distribution from PET while oxygen has been shown [6–8] to affect the degradation processes. In order to determine the effect of these variables upon the gaseous pyrolysates produced from a flame retarded PET system, a systematic study was undertaken using a rapid heating system employed previously [9].

EXPERIMENTAL

The untreated PET control fabric used in this present investigation was a 100% spun Dacron Type 54 (127 g/m^2) obtained from Testfabrics, Middlesex, NJ, USA (Style 767). The TRIS-treated PET fabric was a commercial fabric (148 g/m^2) obtained from Velsicol Chemical (formerly Michigan Chemical Co., now part of Great Lakes Chemical Co.) and had a bromine level of 6.6% (w/w) on the fabric.

A Pyroprobe 120 from Chemical Data Systems was employed as the pyrolyser coupled to a Hewlett-Packard Model 5730A gas chromatograph via an interface maintained at 250 °C. The samples (0.2–0.4 mg) contained in a quartz tube were pyrolysed using the coil probe attachment. A variety of nominal pyrolysis heating temperatures between 700 °C and 1000 °C were employed with the ramp setting off and an isothermal hold of 10 s. These nominally set conditions gave the temperature–time profiles (as measured by a fine gauge thermocouple) shown in Fig. 1. It should be noted that the use of the coiled filament probe in conjunction with the quartz tubes causes

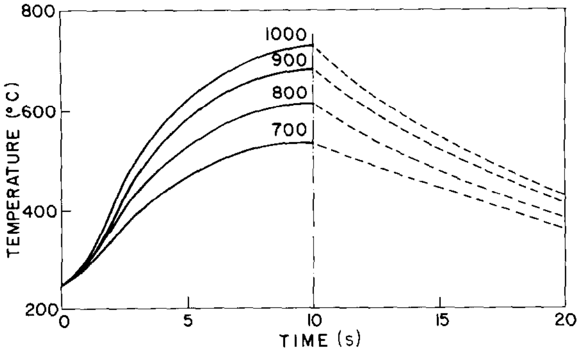


Fig. 1. Sample temperature as measured by thermocouple during pyrolysis at the various nominal temperature settings (700, 800, 900 and 1000 °C) employed in this study.

discrepancies between the set pyrolysis temperatures and actual pyrolysis temperatures. This arises because of the higher thermal mass of this system which results in slower heating rates than those selected. The pyrolysis products were analysed as follows dependent upon their molecular weight. The highly volatile, low molecular weight products were separated using a 3.6 m × 3 mm Chromosorb 102 (80–100 mesh) column, temperature programmed from 60 to 160 °C at 4 °C/min after a 8-min hold at 60 °C. The higher molecular weight products were separated using a 2.4 m × 3 mm, 3% SE-52 on a Chromosorb W (80–100 mesh) column, temperature programmed from 90 to 250 °C at 4 °C/min with a 4-min hold at 90 °C. This technique is the same as that used previously [9] except that a Perkin-Elmer Sigma 15 was used for integration and data reduction.

The air pyrolysis results were obtained using the standard Chemical Data Systems Probe and interface except that the following procedure was adopted. Prior to inserting the probe into the interface the end cap was removed and air was used to flush the helium gas from the interface while the carrier gas was routed directly to the column. The probe was then inserted into the interface, pyrolysed, and the helium gas diverted back through the interface to the column. In this way the pyrolysis was carried out in air rather than helium. Although this technique did result in a large quantity of air being swept into the column, column performance was found to be not seriously affected over the short term. However, it was found necessary to make appropriate corrections for CO_2 yields based upon blank runs in air.

RESULTS

The production of volatile pyrolysis products involves weight loss which can be measured by weighing the samples before and after pyrolysis. Fig. 2

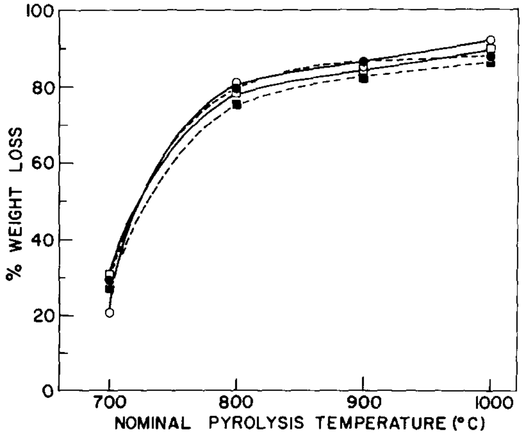
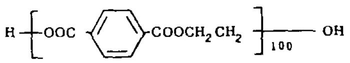


Fig. 2. Percentage weight loss for untreated poly(ethylene terephthalate) (———) and tris(2,3-dibromopropyl) phosphate-treated samples (– – –) pyrolysed in helium (○, ●) and air (□, ■) as a function of nominal pyrolysis temperature.

shows the calculated percentage weight losses based upon the "before" and "after" weights of the sample tubes for all the experimental conditions employed in this study. It should be noted that each point in this and subsequent graphs represent the average value from at least four determinations for each sample at each temperature and environment. The data presented in Fig. 2 clearly indicate that, in terms of weight loss as a function of temperature, the behaviour of the flame-retarded PET closely approximates that of the untreated PET, both in air and in helium. Thus, in terms of the overall volatilisation, no large differences are detectable.

In earlier studies we showed that the pyrolysis of PET and Tris-treated PET leads to the formation of numerous pyrolysis products [1,9]. However, although over 40 such products were isolated and identified, it was shown that the majority of the pyrolysate can be accounted for by ten major pyrolysis products. These products are carbon monoxide, carbon dioxide, methane, acetylene, acetaldehyde, benzene, vinyl benzoate, benzoic acid, divinyl terephthalate and ethylene dibenzoate. The actual evolution of these species as a function of the nominal pyrolysis temperatures is presented in Figs. 3–12. The data are normalised to moles of products species per mole of polymer subjected to the heating process. For the sake of simplicity, the molecular weight has been taken to be 19,200 (a reasonable value based upon solution viscometry). Using this value the empirical formula for PET can then be written as:



The evolution of carbon monoxide as a function of nominal pyrolysis temperature is shown in Fig. 3. It will be noted that its evolution continually

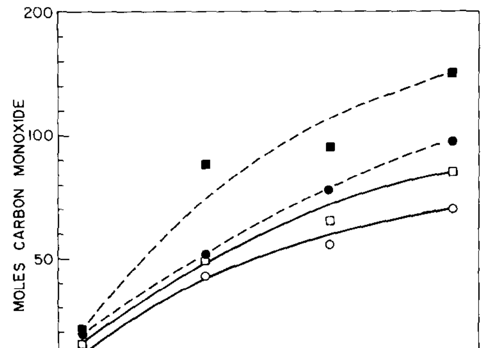


Fig. 3. Evaluation of carbon monoxide from untreated poly(ethylene terephthalate) (———) and tris(2,3-dibromopropyl) phosphate-treated samples (- - -) pyrolysed in helium (○, ●) and air (□, ■) as a function of nominal pyrolysis temperature.

increases with increased pyrolysis temperature, only showing a slight levelling off at the higher temperatures as the starting material is depleted. This figure also indicates that on average 46% more carbon monoxide is produced per mole of polyester with the TRIS-treated PET than per mole of untreated PET not only in air but also in helium. It would also appear that the yield of carbon monoxide is higher in air than in helium, although with an average increase of approximately 29% it is not substantially larger.

Carbon monoxide and carbon dioxide represent the largest molar concentrations of all the species evolved from PET. The evolution of carbon dioxide is given in Fig. 4. It will be noted that both samples give similar responses in both environments, i.e. a sharp initial rise up to about 800 °C followed by a gradual levelling off (or even slight reduction) at the higher temperatures. Although not very conclusive due to the magnitude of the changes, it would appear that the Tris samples show a slight increase between 900 and 1000 °C whilst the untreated PET shows a slight decrease in this temperature range. Interestingly, if the CO_2 is originating from chain scission reactions, its concentration should have continued to increase in a similar manner to that observed for the CO. The fact that this is not observed would suggest that some of the CO_2 formed at the lower temperatures is reacting at the higher temperature to give other species. A possible reaction to explain the reduction of CO_2 at the higher temperatures is the following:

$$CO_2 + C \rightarrow 2CO \tag{1}$$

a reaction known to be favoured at temperatures above 800 °C. Comparison of the results obtained in air with the results obtained in helium suggests that CO_2 formation is slightly enhanced in the oxidative air environment.

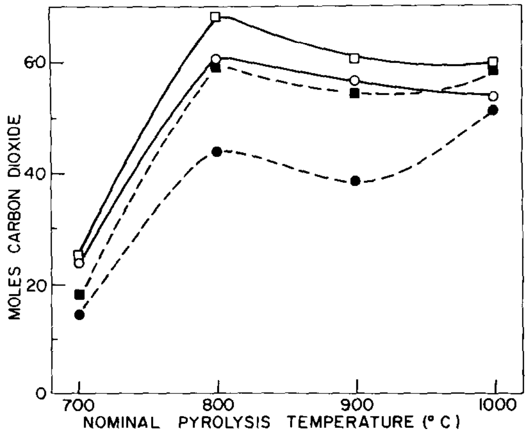


Fig. 4. Evolution of carbon dioxide from untreated poly(ethylene terephthalate) (———) and tris(2,3-dibromopropyl) phosphate-treated samples (– – –) pyrolysed in helium (○, ●) and air (□, ■) as a function of nominal pyrolysis temperature.

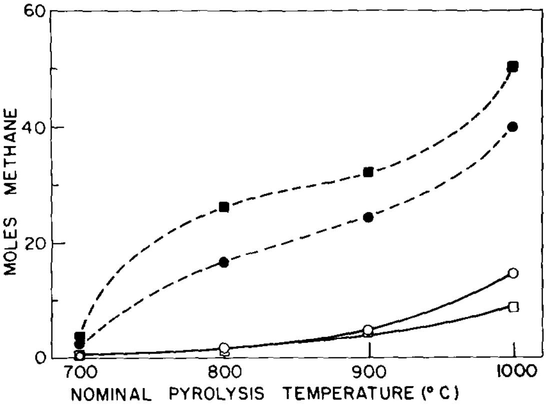


Fig. 5. Evolution of methane from untreated poly(ethylene terephthalate) (———) and tris(2,3-dibromopropyl) phosphate-treated samples (– – –) pyrolysed in helium (○, ●) and air (□, ■) as a function of nominal pyrolysis temperature.

Fig. 5 illustrates that the evolution of methane is significantly greater for the TRIS-treated PET than it is for the untreated PET. The evolution of the large concentrations of methane from the TRIS sample raises concerns over the effectiveness of the chemical as a flame retardant species since methane is well recognised as an efficient high energy fuel. Based on the data presented in Fig. 5 the importance of oxygen in methane production is not entirely clear. Although in the case of the TRIS-treated PET methane production is enhanced in the presence of air, with untreated PET this effect, although only marginal, is reversed. However, because of the large differences between the methane concentrations involved in these two systems, this observation could be a concentration phenomenon.

In the case of acetylene formation (Fig. 6) the concentrations obtained

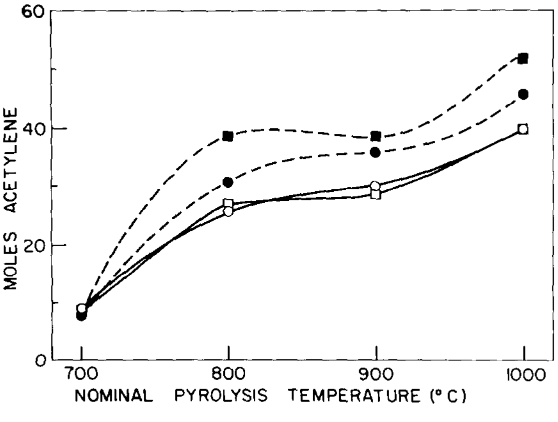


Fig. 6. Evolution of acetylene from untreated poly(ethylene terephthalate) (———) and tris(2,3-dibromopropyl) phosphate-treated samples (– – –) pyrolysed in helium (○, ●) and air (□, ■) as a function of nominal pyrolysis temperature.

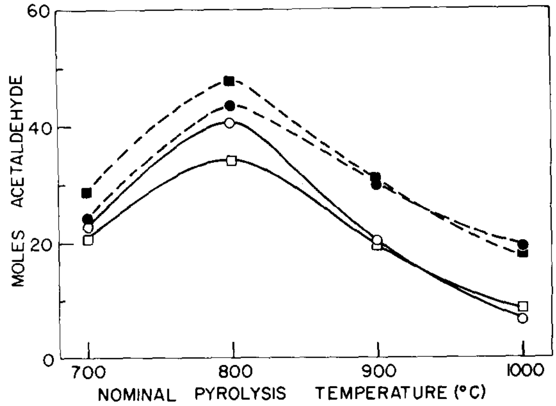


Fig. 7. Evolution of acetaldehyde from untreated poly(ethylene terephthalate) (———) and tris(2,3-dibromopropyl) phosphate-treated sample (– – –) pyrolysed in helium (○, ●) and air (□, ■) as a function of nominal pyrolysis temperature.

from the TRIS-treated samples are again significantly higher than those obtained from the untreated PET, although the difference is of a smaller magnitude than in the case of methane. Once again the presence of air appears to result in the production of more hydrocarbon product from the TRIS-treated PET, whereas the yield for the untreated sample is uneffected. Interestingly, the curves for the production of methane and acetylene from the TRIS-treated PET are very similar in nature, both in air and helium environments. This suggests that very similar reactions are responsible for their formation.

In contrast the yield of acetaldehyde appears to reach a maximum at about 800 °C, above which the yield falls off dramatically with increasing temperature (Fig. 7). Although all samples gave similar shaped curves in both helium and air, the yields from the TRIS-treated samples were always consistently higher than those from the untreated PET. The role of the oxygen on acetaldehyde production, however, appears to be negligible since the results in air and helium are very similar.

Benzene (Fig. 8) is obviously a high temperature pyrolysis product since its yield is only significant at the higher temperatures. The exponential nature of the benzene formation suggests that it is a product of secondary and tertiary pyrolysis reactions rather than a primary pyrolysis product. The close similarity of all four curves also indicates that benzene formation is not influenced by the presence of a flame retardant or an oxidising atmosphere.

Vinyl benzoate formation (Fig. 9) has a rather interesting characteristic. The concentration shows a steady, almost linear, increase from 700 °C to 900 °C at which temperature its yield reaches a maximum. Above 900 °C the yield falls off, presumably due to subsequent decomposition of vinyl benzoate to secondary reaction products. In a helium atmosphere the difference in yield of vinyl benzoate is almost the same for the TRIS-treated PET as it is

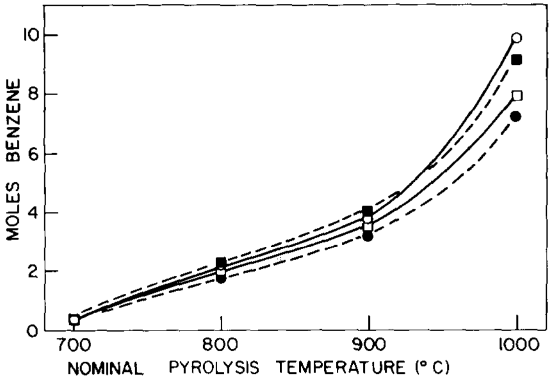


Fig. 8. Evolution of benzene from untreated poly(ethylene terephthalate) (———) and tris(2,3-dibromopropyl) phosphate-treated sample (– – –) pyrolysed in helium (○, ●) and air (□, ■) as a function of nominal pyrolysis temperature.

for the untreated PET. However, when the thermal decomposition is carried out in an oxidative environment, the yield is increased slightly for the untreated PET, while the TRIS-treated PET shows a significant reduction in yield. Thus the flame retardant's influence on vinyl benzoate formation is only detectable when air is present.

Fig. 10 illustrates the formation of benzoic acid, which like vinyl benzoate peaks at 900 °C. Presumably, above this temperature decarboxylation occurs resulting in a reduction in benzoic acid and the production of benzene. Interestingly, the production of benzoic acid was found to be less in air than it was in helium, an observation consistent for both samples. This suggests the production of this species is not an oxidative process but the product of

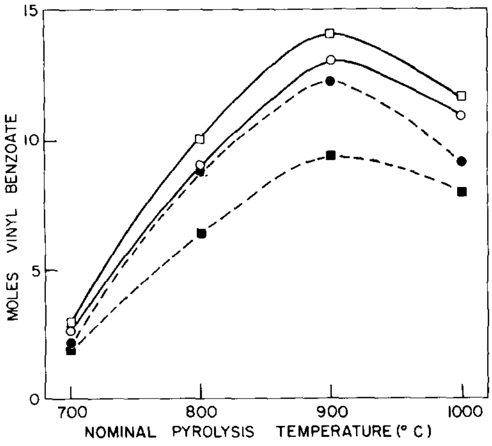


Fig. 9. Evolution of vinyl benzoate from untreated poly(ethylene terephthalate) (———) and tris(2,3-dibromopropyl) phosphate-treated sample (– – –) pyrolysed in helium (○, ●) and air (□, ■) as a function of nominal pyrolysis temperature.

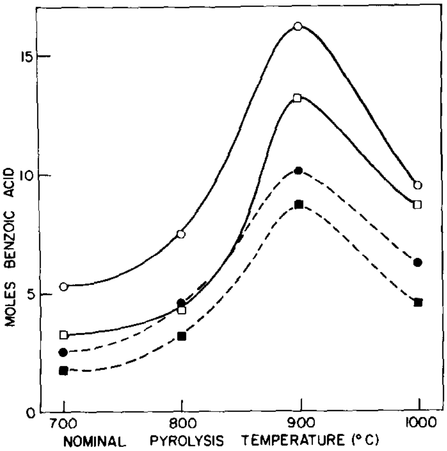


Fig. 10. Evolution of benzoic acid from untreated poly(ethylene terephthalate) (———) and tris(2,3-dibromopropyl) phosphate-treated sample (– – –) pyrolysed in helium (○, ●) and air (□, ■) as a function of nominal pyrolysis temperature.

a chain scission reaction. The presence of the TRIS treatment is noted to have a significant effect on benzoic acid formation in that treated samples produce only about 70% of the benzoic acid yield obtained from the untreated sample.

The production profile of divinyl terephthalate, shown in Fig. 11, resembles very closely that observed for vinyl benzoate. i.e., there is a maximum in its concentration at about 900 °C above which there is a noticeable decrease in molecular concentration. The formation of divinyl terephthalate is also

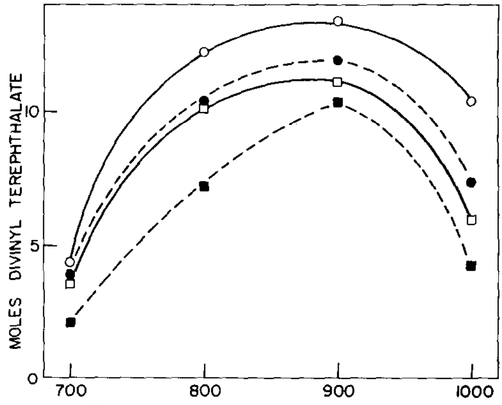


Fig. 11. Evolution of divinyl terephthalate from untreated poly(ethylene terephthalate) (———) and tris(2,3-dibromopropyl) phosphate-treated sample (– – –) pyrolysed in helium (○, ●) and air (□, ■) as a function of nominal pyrolysis temperature.

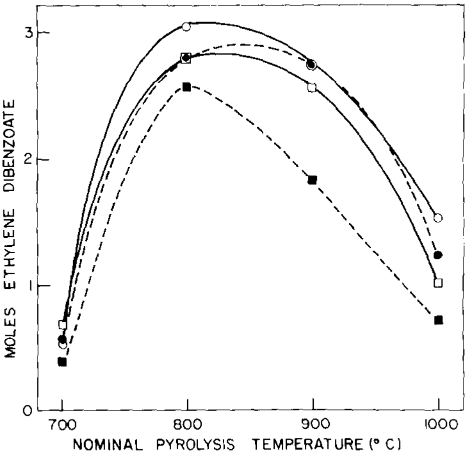


Fig. 12. Evolution of ethylene dibenzoate from untreated poly(ethylene terephthalate) (———) and tris(2,3-dibromopropyl) phosphate-treated sample (– – –) pyrolysed in helium (○, ●) and air (□, ■) as a function of nominal pyrolysis temperature.

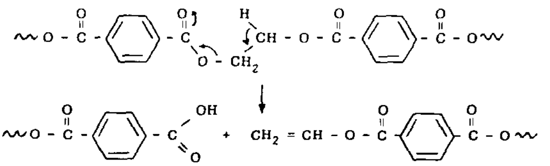
observed to be slightly more pronounced in helium and in the absence of the flame retardant TRIS.

The evolution of ethylene dibenzoate, although not very large in terms of molar concentrations, does represent a reasonably large contribution in weight. Examination of its production as a function of pyrolysis temperature (Fig. 12) reveals that once again it shows an initial increase in concentration at lower pyrolysis temperatures, while at higher temperatures its concentration decreases, presumably due to subsequent thermal degradation to secondary pyrolysis products. Like vinyl benzoate and divinyl terephthalate, its formation appears to be more pronounced in the absence of air and the flame retardant TRIS.

DISCUSSION

The flamming combustion of polymeric materials results in flame temperatures in the range of 500–1000 °C and surface temperatures between 300 and 600 °C dependent upon the polymer and the burning configuration [10]. In addition, surface heating rates of about 300 °C/min and higher are encountered. For this reason the utilization of rapid pyrolysis conditions obtained with the use of the Pyroprobe with coil attachment and quartz tube provides conditions representative of those encountered in the burning process. Unfortunately, under these high pyrolysis temperature conditions, a clear understanding of the primary pyrolysis reactions becomes difficult because of added complexities associated with secondary reactions. This means that many of the reaction mechanisms proposed in a study such as this have to be speculative in nature, and rely upon the assumption that many of the volatile primary pyrolysis products are capable of escaping the pyrolysis zone prior to excessive secondary reaction processes. However, despite this limitation, the technique is capable of giving important information relevant to an understanding of the combustibility of pyrolysis products which represent the fuel for the flame. The technique is also capable of providing much needed information on the role of the flame retardant TRIS on the thermal pyrolysis of PET under combustion type conditions.

The predominant mechanism invoked [4] to explain the thermal decomposition of PET involves a cyclic transition state:



(2)

Further random scission of the ester links will yield a mixture of monomeric terephthalic acid and vinyl ester oligomers according to the following equations:

$$\begin{aligned}&\sim\sim C_6H_4COOCH_2CH_2OCOC_6H_4COOH\\&\quad\rightarrow \sim\sim C_6H_4COOH + CH_2{=}CHOCOC_6H_4COOH\end{aligned} \tag{3}$$

$$\begin{aligned}&\sim\sim C_6H_4COOCH_2CH_2OCOC_6H_4COOH\\&\quad\rightarrow \sim\sim C_6H_4COOCH{=}CH_2 + HOOCC_6H_4COOH\end{aligned} \tag{4}$$

$$\begin{aligned}&\sim\sim C_6H_4COOCH_2CH_2OCOC_6H_4COOCH{=}CH_2\\&\quad\rightarrow \sim\sim C_6H_4COOH + CH_2{=}CHOCOC_6H_4COOCH{=}CH_2\end{aligned} \tag{5}$$

$$\begin{aligned}&\sim\sim C_6H_4COOCH_2CH_2OCOC_6H_4COOCH{=}CH_2\\&\quad\rightarrow \sim\sim C_6H_4COOCH{=}CH_2 + HOOC_6H_4OCOC_6H_4CH{=}CH_2\end{aligned} \tag{6}$$

The above equations show the production of some primary acids and vinyl esters due to chain scissions in close proximity to the chain ends. However, several chain scission processes will generally be required to produce these species. Although of the compounds produced by eqns. 3–6 only divinyl terephthalate has been listed in this report, vinyl benzoate, benzoic acid and benzene are readily obtained by decarboxylation reactions:

$$CH_2{=}CHOCOC_6H_4COOH \rightarrow CH_2{=}CHOCOC_6H_5 + CO_2 \tag{7}$$

$$HOOCC_6H_4COOH \rightarrow C_6H_5COOH + CO_2 \tag{8}$$

$$C_6H_5COOH \rightarrow C_6H_6 + CO_2 \tag{9}$$

According to eqns. 2–9 it would be anticipated that the production of CO_2 should be related to the production of divinyl terephthalate, vinyl

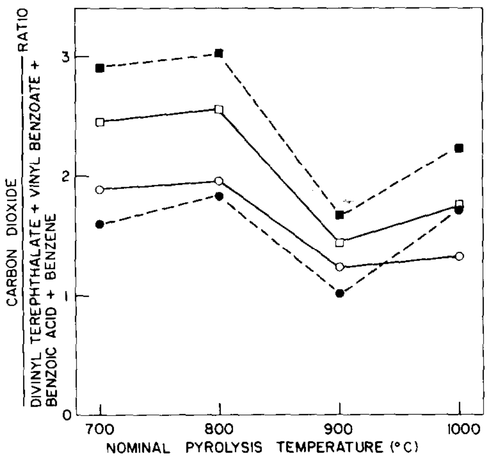


Fig. 13. Ratio of the formation of (carbon dioxide) to (divinyl terephthalate + vinyl benzoate + benzoic acid + benzene) for untreated poly(ethylene terephthalate) (———) and tris(2,3-dibromopropyl) phosphate-treated sample (– – –) pyrolysed in helium (○, ●) and air (□, ■) as a function of nominal pyrolysis temperature.

benzoate, benzoic acid and benzene since they are all produced by the same reaction schemes involving a random chain scission process (2) and decarboxylation reactions (7–9). The relationship between these species and CO_2 has been plotted in Fig. 13. The first thing to note regarding this graph is that it can be divided into two zones, the lower temperature zone (700–800 °C) and the high temperature zone (900–1000 °C). In each zone it is first apparent that the ratio of CO_2 to the four aromatics is always consistently higher for the samples pyrolysed in air than in helium. An assessment of the magnitude of this difference would suggest that about one in every three moles of CO_2 produced in air is attributable to an oxidation process. Meanwhile the remaining moles of CO_2 in air and the CO_2 moles in helium are produced by a decarboxylation process. Based upon the decarboxylation reaction (7–9) it would appear that for each CO_2 mole produced there should be one mole of the above aromatic species produced, provided that chain scissions were taking place in close proximity to the chain ends, as outlined in eqns. 3–6. The fact that the ratio of CO_2 to these species is greater than unity confirms that the chain scission processes are indeed random. The random scheme outlined in Fig. 14 therefore realistically reflects this situation in that several moles of CO_2 are produced before the low molecular weight vinyl esters, acids and benzene are produced. The scheme outlined in Fig. 14 was actually generated by random number selection and can be seen to produce two aromatic species: divinyl terephthalate and benzoic acid whilst at the same time liberating four moles of CO_2 to give a ratio of 2, similar to that observed in Fig. 13 at the lower temperatures. The reduction of this ratio at higher temperatures is obviously due to the greater fragmentation of the lower molecular weight fragments

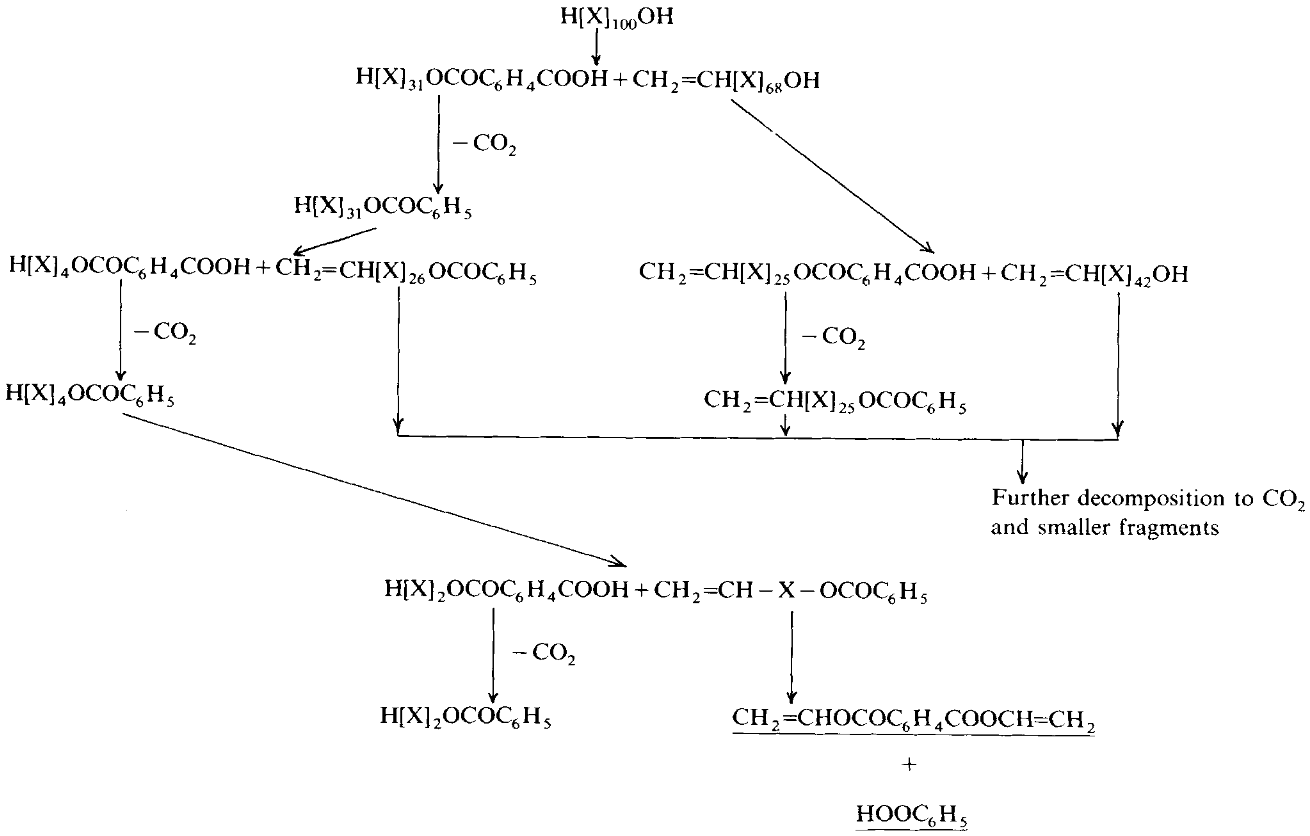


Fig. 14. Proposed randomly generated chain scission process for the thermal decomposition of poly(ethylene terephthalate). $X = -OCOC_6H_4COOCH_2CH_2-$.

which are now capable of producing the aromatic species with less chain scissions than required at the lower temperature. An alternative process which also cannot be overlooked at the higher temperatures is the reduction in CO_2 yield according to eqn. 1 already mentioned.

Although the classical ester scission reaction (2) giving carboxylic acid and vinyl ester end groups followed by decarboxylation is capable of accounting for the formation of CO_2, divinyl terephthalate, vinyl benzoate, benzoic acid and benzene, this reaction fails to account for the formation of carbon monoxide in high yields in the lower temperatures pyrolysis regions. An alternative primary scission process involving α-cleavage has been proposed by Marshall and Todd [12] and, based upon an ester bond dissociation energy of 368 kJ mol^{-1}, seems a likely route for carbon monoxide production:

$$\sim\sim C_6H_4COOCH_2CH_2\sim\sim \rightarrow \sim\sim C_6H_4CO\cdot + \cdot OCH_2CH_2\sim\sim \rightarrow$$

$$\sim\sim C_6H_4\cdot + CO + \cdot OCH_2CH_2\sim\sim \qquad (10)$$

Energetically, this scission process is less favourable than that involving the cyclic transition state already discussed for CO_2 production; hence a plot of CO/CO_2 production as a function of pyrolysis temperature should prove informative. These data have been plotted in Fig. 15, which does indeed reveal that CO_2 formation is more favoured at lower temperatures that at high temperatures. In the case of the standard PET, it is readily apparent that CO_2 formation at the lower pyrolysis temperatures is favoured by about 2 : 1, indicative of the favourable energetics of the cyclic process compared to the α-scission process. At the higher pyrolysis temperatures, however, the CO

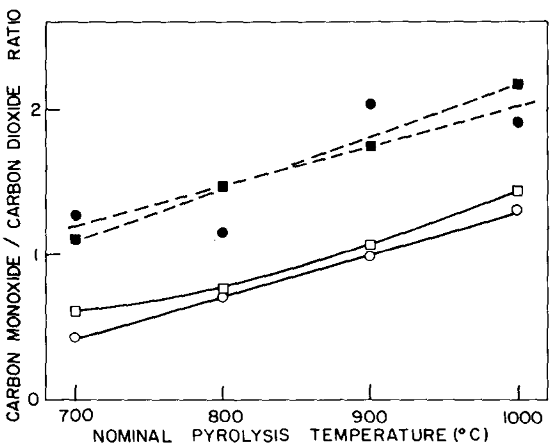
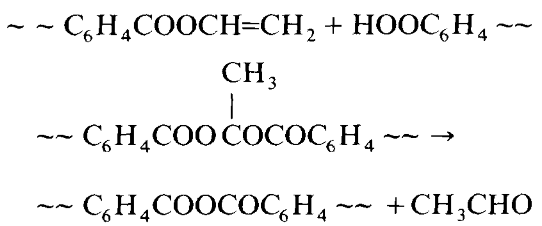


Fig. 15. Ratio of the formation of carbon monoxide to carbon dioxide for untreated poly(ethylene tetraphthalate) (———) and tris(2,3-dibromopropyl) phosphate-treated sample (– – –) pyrolysed in helium (○, ●) and air (□, ■) as a function of nominal pyrolysis temperature.

and CO_2 production are comparable as would be expected. In addition reaction 1, converting CO_2 to CO, becomes important at these higher pyrolysis temperatures thus contributing to an increase in the CO/CO_2 ratio. Interestingly, whilst the slopes for the TRIS and standard PET samples are similar, the CO/CO_2 ratio is significantly higher for the TRIS-treated sample than for the untreated PET. This would suggest that TRIS is capable of reducing the strength of the C–O ester bond sufficiently to favour the α-chain scission process which leads to the formation of carbon monoxide.

Thus it can be seen that the α-scission process and the cyclic scission process enable many of the pyrolysis products to be accounted for. However, explanations are still required for the formation of acetaldehyde, acetylene and methane. In our previous study [9] the formation of acetaldehyde was explained utilising the following equations originally proposed by Ritchie [11] for the model compound ethylene dibenzoate:



$$\sim\sim C_6H_4COOCH{=}CH_2 + HOOC_6H_4 \sim\sim \rightarrow$$

$$\sim\sim C_6H_4COO\overset{\overset{\textstyle CH_3}{|}}{C}OCOC_6H_4 \sim\sim \rightarrow$$

$$\sim\sim C_6H_4COOCOC_6H_4 \sim\sim + CH_3CHO \qquad (11)$$

This scheme is not only consistent with acetaldehyde formation observed in this and previous studies [9] but has been substantiated by the detection of the anhydride species in the involatile char residues [14]. Whilst the above reaction is a favourable scheme at relatively low pyrolysis temperatures, competing reactions become important at higher pyrolysis temperatures as is evident by the data presented in Fig. 7.

The competing reactions however, are capable of producing acetylene and a precursor to methane production as follows:

$$\sim\sim C_6H_4COOCH{=}CH_2 \rightarrow \sim\sim C_6H_4COOH + CH{\equiv}CH \qquad (12)$$

$$\sim\sim C_6H_4COOCH{=}CH_2 \rightarrow \sim\sim C_6H_4CH = CH_2 + CO_2 \qquad (13)$$

$$\sim\sim C_6H_4COOCH{=}CH_2 \rightarrow \sim\sim [C_6H_4COCH_2CHO] \rightarrow$$

$$\sim\sim C_6H_4COCH_3 + CO \qquad (14)$$

Because eqns. 13 and 14 represent alternative routes to the formation of CO_2 and CO respectively, in addition to their production via the cyclic scission and α-scission processes, it becomes difficult to get a clear indication of the relative importance of eqns. 11–14. Eqn. 12, however, represents the sole source of acetylene that has been considered so far. It therefore becomes of interest to compare the production of acetylene and acetaldehyde in order to get some insight into the potential competitiveness of eqns. 11 and 12. Fig. 16 illustrates the curves obtained by plotting the ratio of acetylene to acetaldehyde as a function of pyrolysis temperature. This graph clearly

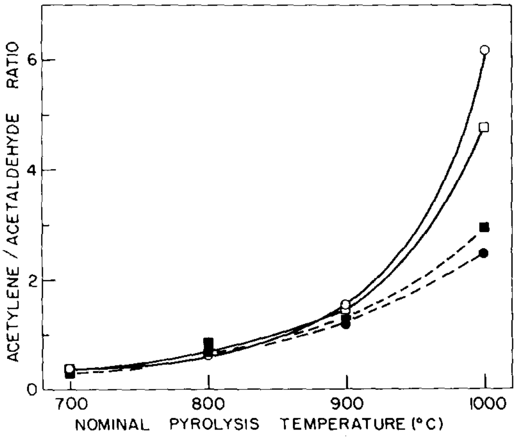


Fig. 16. Ratio of the formation of acetylene to acetaldehyde for untreated poly(ethylene terephthalate (———) and tris(2,3-dibromopropyl) phosphate-treated sample (– – –) pyrolysed in helium (○, ●) and air (□, ■) as a function of nominal pyrolysis temperature.

indicates the temperature dependence of these two reactions and the relative importance of eqn. 11 at the lower pyrolysis temperatures and eqn. 12 at the higher pyrolysis temperatures.

Model compound studies with vinyl benzoate [11] have indicated that at 520°C the above three reactions (12, 13 and 14) occur at rates of 1 : 3 : 15 respectively. This immediately suggests that based upon eqns. 13 and 14, the yield of CO would be expected to be higher than that of CO_2. However, as mentioned previously, competing reactions leading to CO and CO_2 have been identified making it difficult to verify the above relative rates in our polymer system. Eqn. 14, meanwhile, produces a species which is a likely precursor to methane formation:

$$\sim\sim C_6H_4COCH_3 \rightarrow \sim\sim C_6H_4CO\cdot + CH_3\cdot \xrightarrow{\text{H-R}} CH_4 + R\cdot \qquad (15)$$

In an earlier publication [9] we speculated that eqn. 14 was sufficient to account for CO formation without invoking the α-scission process. If that was the case there should be a reasonable agreement between CO and CH_4 production. In Fig. 17, this ratio of CH_4 to CO as a function of pyrolysis temperature has been plotted. This graph clearly indicates that the ratio between the two species is far from constant, suggesting that eqn. 14 alone is insufficient to account for CO production and suggesting that several processes such as eqns. 1, 10 and 14 all contribute their share to its production. If it is assumed that eqn. 14 followed by eqn. 15 is the major source of methane and the species $\sim\sim C_6H_4COOCH{=}CH_2$ is the common precursor to both methane and acetylene, it would be anticipated that there would be a link between their rates of formation. The nature of the relationship between these two species is plotted in Fig. 18. Based upon

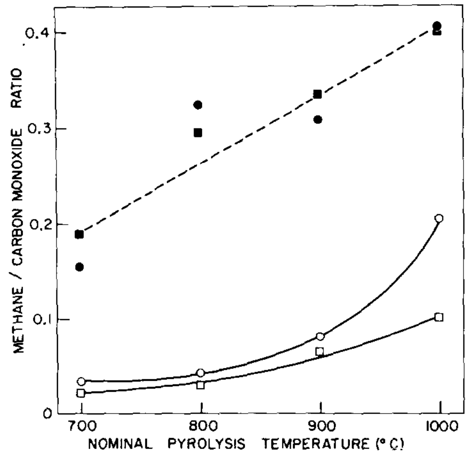


Fig. 17. Ratio of the formation of methane to carbon monoxide for untreated poly(ethylene terephthalate) (———) and tris(2,3-dibromopropyl) phosphate-treated sample (– – –) pyrolysed in helium (○, ●) and air (□, ■) as a function of nominal pyrolysis temperature.

Ritchie's work [11] with the model compound vinyl benzoate, which indicated that eqn. 14 is favoured over eqn. 12 by a ratio of 15 : 1, a higher yield of methane than of acetylene would have been anticipated provided that eqn. 15 was not rate controlling. The fact that this is not the case suggests that indeed eqn. 15 is rate controlling in the case of methane production from the species ~~ $C_6H_4COOCH{=}CH_2$ via eqns. 14 and 15. Furthermore, because of the large differences in the behaviour of the Tris-treated sample in comparison to the standard PET, it would appear that TRIS is capable of promoting eqn. 15, thereby enhancing methane production.

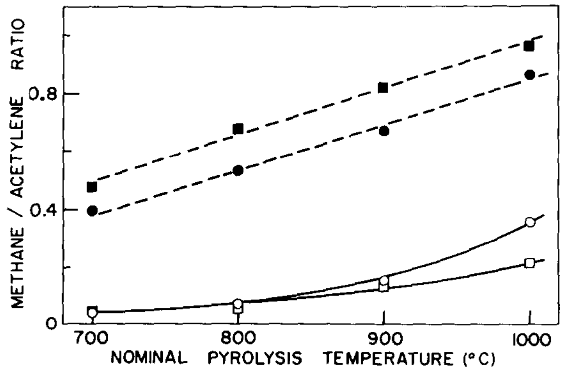


Fig. 18. Ratio of the formation of methane to acetylene for untreated poly(ethylene terephthalate) (———) and tris(2,3-dibromopropyl) phosphate-treated sample (– – –) pyrolysed in helium (○, ●) and air (□, ■) as a function of nominal pyrolysis temperature.

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