BUTTERWORTH
HEINEMANN

polymer papers

Polymer Vol. 36 No. 2, pp. 227–234, 1995

0032-3861/95/\$10.00+0.00

Identification of luminescent species contributing to the yellowing of poly(ethylene terephthalate) on degradation

M. Edge, N. S. Allen* and R. Wiles
Department of Chemistry, The Manchester Metropolitan University, Chester Street, Manchester M1 5GD, UK

and W. McDonald and S. V. Mortlock
ICI Films, Wilton, Middlesborough TS6 8JE, UK
(Received 21 June 1994; revised 15 September 1994)

Changes in the luminescence of poly(ethylene terephthalate) (PET) degraded in the absence and presence of oxygen at melt temperatures has been investigated. On oxidative degradation monomer fluorescence is reduced, with a concurrent increase in dimer fluorescence at long wavelengths. This is consistent with main chain breakdown and aggregation of the terephthalate fragments produced. Longer wavelength fluorescent species have been assigned to hydroxylation of the aromatic rings of PET. Further oxidation of PET degraded in air elicits changes in fluorescence and phosphorescence which have been associated with oxidation of hydroxylated units which exist in equilibrium with quinones by a redox mechanism. Phosphorescence studies on extracts from heavily oxidized PET have indicated the presence of stilbene quinone type impurities. The absence of such changes in the luminescence of PET degraded in nitrogen indicates hydroxylated, quinone and stilbene quinone species arise primarily from oxidation reactions. These species are suggested to contribute to the yellowing of PET on degradation.

(Keywords: luminescence; poly(ethylene terephthalate); degradation)

INTRODUCTION

Although there is a proliferation of data on the degradation of poly(ethylene terephthalate) (PET)[1–8], little effort has been directed to discoloration. The yellowing of PET has significance with respect to melt processing, and reprocessing for recycling operations. An initial insight into species leading to yellowing can be derived from studies on thermal and thermal-oxidative degradation.

Random thermal degradation of PET is considered to proceed via either β-hydrogen atom abstraction, or homolysis followed by hydrogen atom abstraction[5,6] so producing terminal carboxyl and vinyl ester groups. In this process new carboxyl end groups will produce CO_2 as a result of decarboxylation, whereas the vinyl ester end groups may decompose to produce acetaldehyde[5]. A variety of gaseous products have been identified on degradation in an inert atmosphere, in particular CO_2 and acetaldehyde are released in considerable amounts. Degradation in the presence of oxygen is thought to proceed by the formation and decomposition of peroxides. The products of thermal-oxidative degradation are similar to those produced in thermal degradation but are present in much greater quantities[5]. In addition, biphenyl structures have also been identified and associated with crosslinking of the polymer.

Photo-oxidation of PET has been shown to yield similar degradation products as for thermal-oxidation, but in addition hydroxylation reactions have been observed[9–11]. Hydroxyl radicals formed by photolysis of hydroperoxides are believed to undergo substitution reactions to form mono- and dihydroxyterephthalate units. Fluorescence spectroscopy has been used to identify the formation of these species. Attempts have been made to identify the chromophores responsible for both fluorescence and phosphorescence emissions from PET. The luminescence (fluorescence) emanating from the polymer itself has been associated with monomer units at short wavelengths and aggregated ground-state dimers at longer wavelengths[12–15]. In these investigations detailed concentration studies on the fluorescence showed a marked reduction in monomer emission with increasing concentration of polymer. This is associated with the appearance of new red shifted excitation and emission bands which renders the role of any energy transfer processes unlikely.

The present study is a detailed investigation of luminescent species produced on melt degradation of PET in nitrogen and oxygen atmospheres. In this respect the role of luminescent species as agents contributing to the yellowing of PET has been evaluated.

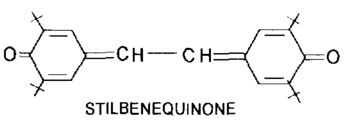
---

*To whom correspondence should be addressed

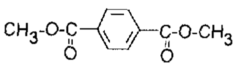
EXPERIMENTAL

Materials and methodologies

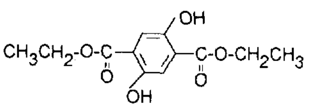
PET in chip form was supplied by ICI Films Division (Wilton, UK) as were the 2,6-ditertiarybutylstilbenequinone, dimethyl terephthalate (DMT) and 4,4-diethyl-2,5-dihydroxyterephthalate (DEDHT). Trifluoroacetic acid (TFA), dichloromethane and lead dioxide were obtained from the Aldrich Chemical Company, UK.



STILBENEQUINONE



DIMETHYLTEREPHTHALATE



DIETHYLDIHYDROXYTEREPHTHALATE

The PET chip was melt heated in both air and nitrogen glass tubes on thermostatically controlled aluminium heating blocks (Fisons Scientific Equipment Ltd, Loughborough, UK) at times ranging from 1 to 8 h and at temperatures of 280 and 300°C. After heating, the tubes were quenched cooled in water and the polymer freeze ground for solution study in TFA. Solutions of the oxidized PET in TFA (20 cm^3 of 1% w/w) were refluxed in the presence of lead dioxide (1 g) for 1 h followed by subsequent filtration. Samples of oxidized PET were also extracted with boiling dichloromethane for 4 h to remove any soluble products for analysis.

Fluorescence and phosphorescence excitation and emission spectra were recorded on the PET solutions in TFA at a 1% w/w concentration using a Perkin-Elmer model LS-5 luminescence spectrometer. The fluorescence spectra were all obtained at ambient temperature while the phosphorescence spectra were obtained at 77 K using liquid nitrogen as a coolant. The model compounds were used at 10^{-4} molar concentration in TFA.

RESULTS AND DISCUSSION

In this study monomer fluorescence emission was observed at 335 nm (excitation at 250 nm). The fluorescence is matched in *Figure 1* to the short wavelength emission of the compound DMT; used here as a model for the unit structure of the polymer. On melt oxidation of the PET there is a reduction in the monomer fluorescence; this effect being more pronounced with longer degradation times and at higher temperatures (4 h at 280°C, cf. 5 h at 300°C). This observation can be attributed to oxidation and scission of the backbone structure of the polymer. This is confirmed by the data in *Figure 2* which highlights the severity of degradation in an oxygen atmosphere when compared to a nitrogen atmosphere. One interesting feature arising from the spectra in *Figures 1* and *2* is the observation of a long wavelength fluorescence emission. Scission of the backbone structure of the polymer will result in an increase in the concentration of smaller molecular aggregates (mostly in the dimeric state although higher order associates may be present) and the long wavelength fluorescence may be assigned to this. Confirmation of this is given in *Figure 3* which shows an increase in dimer aggregate excitation at 333 nm with increasing degradation.

Excitation at the dimer excitation maximum shows an increase in fluorescence emission with degradation in air at 300°C. In contrast, degradation in nitrogen shows little increase in fluorescence emission (*Figure 4*). The excitation of the oxidized PET at 333 nm generates a fluorescence emission spectrum which has three main bands at 400, 450 and 520 nm. The band at 400 nm is

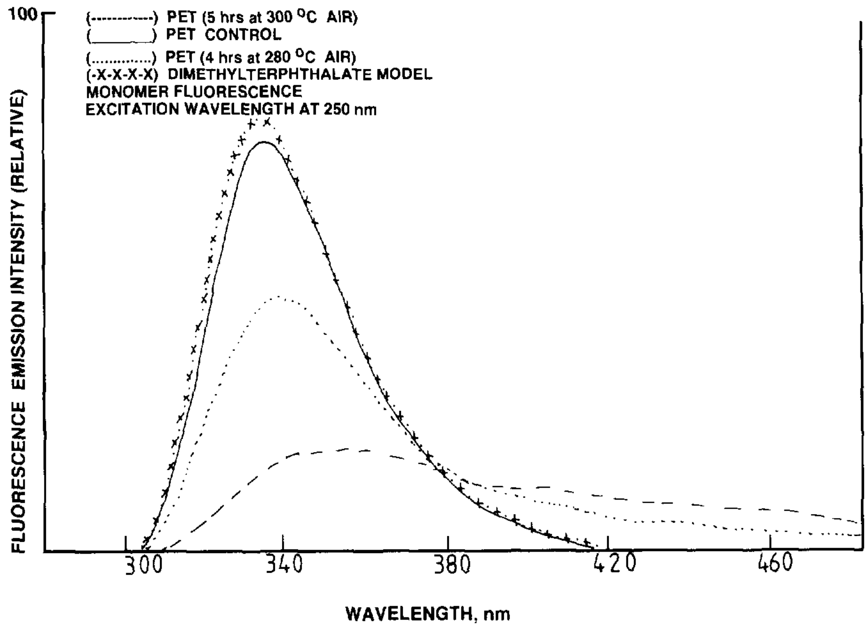


Figure 1 Fluorescence emission spectrum of PET (1% w/w) before and after 4 h of heating in air at 280°C and 5 h heating in air at 300°C compared with that of the model DMT (10^{-4} M) in trifluoroacetic acid. (Excitation wavelength at 250 nm)

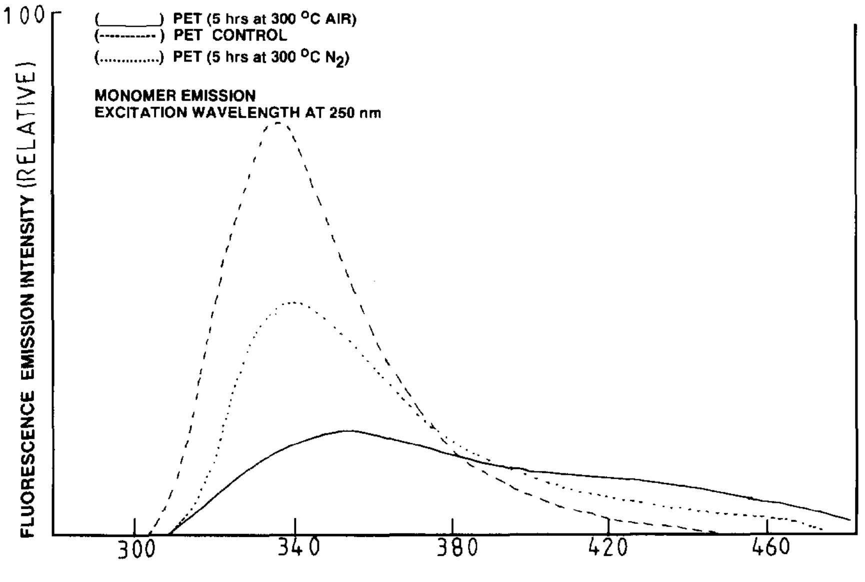


Figure 2 Fluorescence emission spectrum of PET before and after 5 h of heating in air at 300°C and 5 h heating in nitrogen at 300°C in trifluoroacetic acid at 1% w/w concentration. (Excitation wavelength at 250 nm)

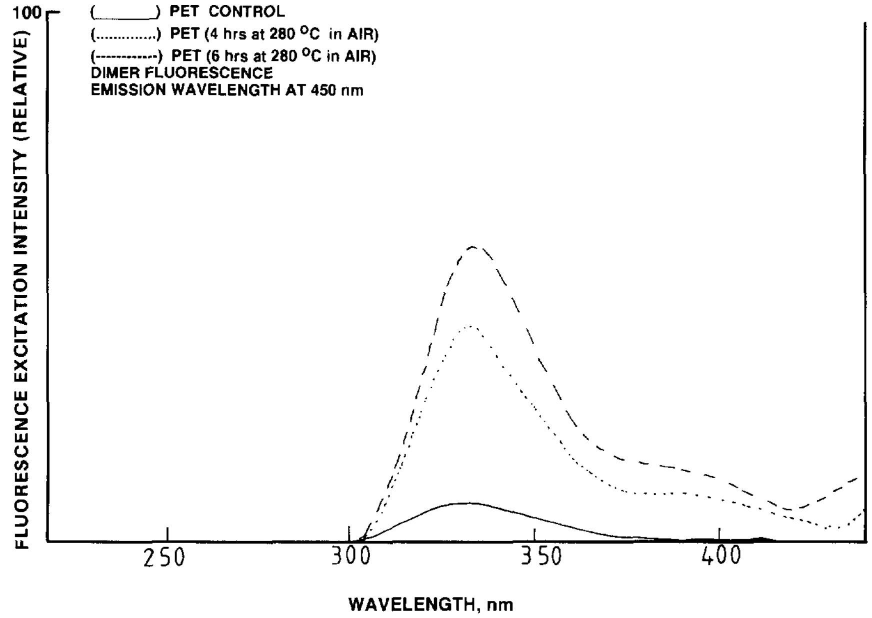


Figure 3 Fluorescence excitation spectrum of PET before and after 4 h of heating in air at 280°C and 6 h heating in air at 280°C in trifluoroacetic acid at 1% w/w concentration. (Emission wavelength at 450 nm)

representative of dimer emission[12–15]. *Figure 5* shows the fluorescence emission spectrum of a model hydroxylated terephthalate compound (DEDHT) compared to that of the oxidized PET. From this it can be seen that the band at 520 nm arising in degraded PET matches that of hydroxylated species, while that at 450 nm is a mixture of dimer and hydroxylated PET. Undegraded PET gives only a weak dimer emission at 400 nm.

In an attempt to confirm the presence of hydroxylated species the oxidized PET was extracted with dichloromethane. Fluorescence analysis of the extract indicated that these species were indeed present. Excitation spectra (for emission at 450 nm) of the extract showed a peak at 385 nm (absorptions of the dimer which is not extracted so being eliminated) (*Figure 6*). In comparison the hydroxylated terephthalate model exhibited emission maxima at 335 and 385 nm (*Figure 7*). This further suggests the hydroxylation of terephthalate units in the polymer on thermal oxidation.

The possibility then arises that the hydroxylated units themselves may be further oxidized and as such would produce quinonoid analogues. To enable identification of any such species the degraded PET was oxidized with lead dioxide for 1 h, to convert any phenolic structures to quinones. The presence of these species would result in a reduction in fluorescence; a consequence of their low

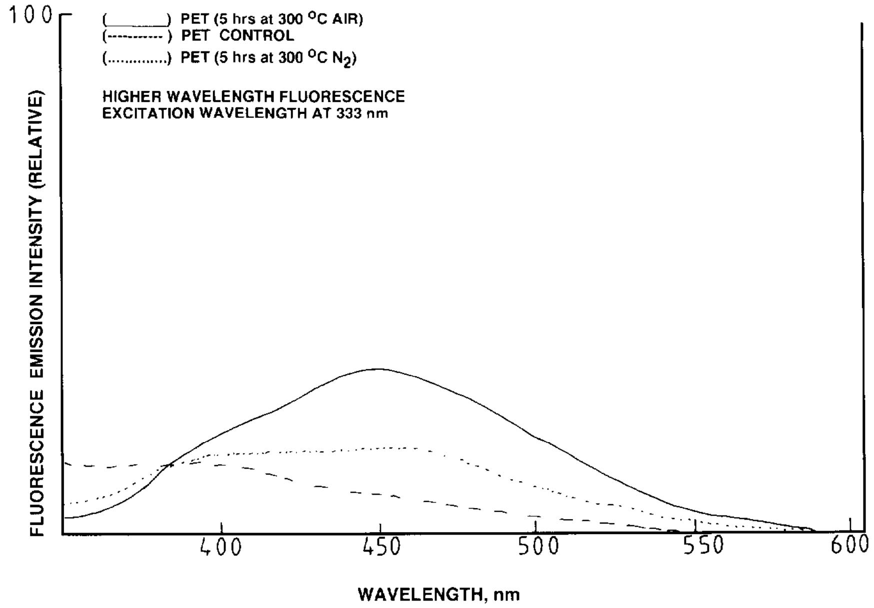


Figure 4 Fluorescence emission spectrum of PET before and after 5 h of heating in nitrogen at 300°C and 5 h heating in air at 300°C in trifluoroacetic acid at 1% w/w concentration. (Excitation wavelength at 333 nm)

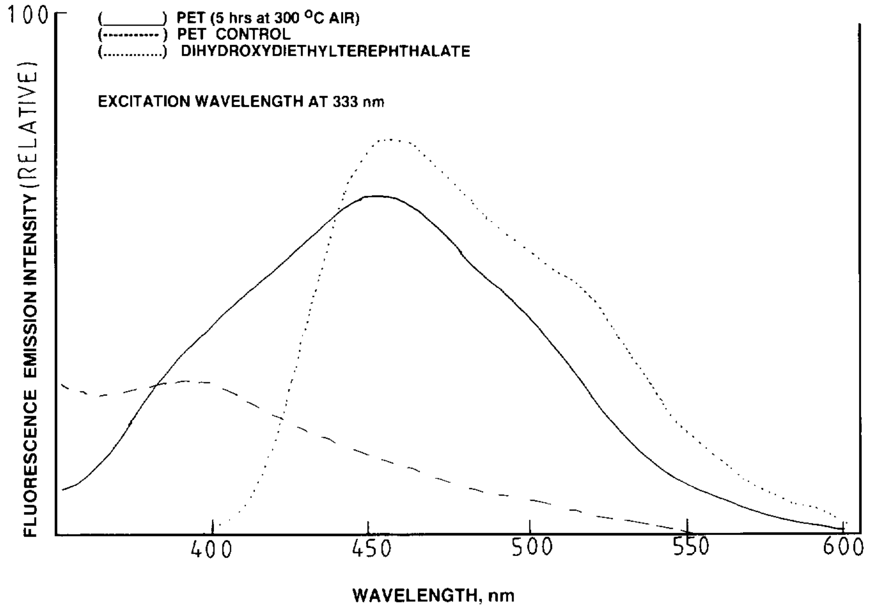


Figure 5 Fluorescence emission spectrum of PET before and after 5 h of heating in air at 300°C (1% w/w in TFA) and dihydroxydiethylterephthalate model (10^{-4} M in TFA). (Excitation wavelength at 333 nm)

lying singlet nπ^* character. *Figure 8* is an emission spectrum (excitation at 333 nm) for degraded PET which has been further oxidized by lead dioxide. A reduction in both bands at 450 and 520 nm is seen, leaving only a maximum at 400 nm arising from the dimer.

The high extinction coefficients associated with the absorption of visible light by quinones suggest that their presence in degraded PET will undoubtedly contribute to yellowing. More direct identification of these species is possible by low temperature phosphorescence; though account must be taken that this technique will detect any emitting carbonyl species and as such the spectra will be more complex.

The phosphorescence emission from air oxidized PET is shown in *Figure 9*, and compared with that of the model hydroxylated terephthalate (DEDHT) before and after oxidation. A broad emission spectrum (390–600 nm) results for the oxidized PET with a maximum at 450 nm and shoulders appearing at 420, 480 and 520 nm. These features can be resolved by comparison with a spectrum of air oxidized PET which has been further oxidized with lead dioxide. It is seen that on further oxidation the emission is red-shifted (maximum now at 500 nm) and exhibits strong shoulders at 420, 460 and 520 nm. Comparing these spectra with those of the model compound and its oxidized analogue the formation of

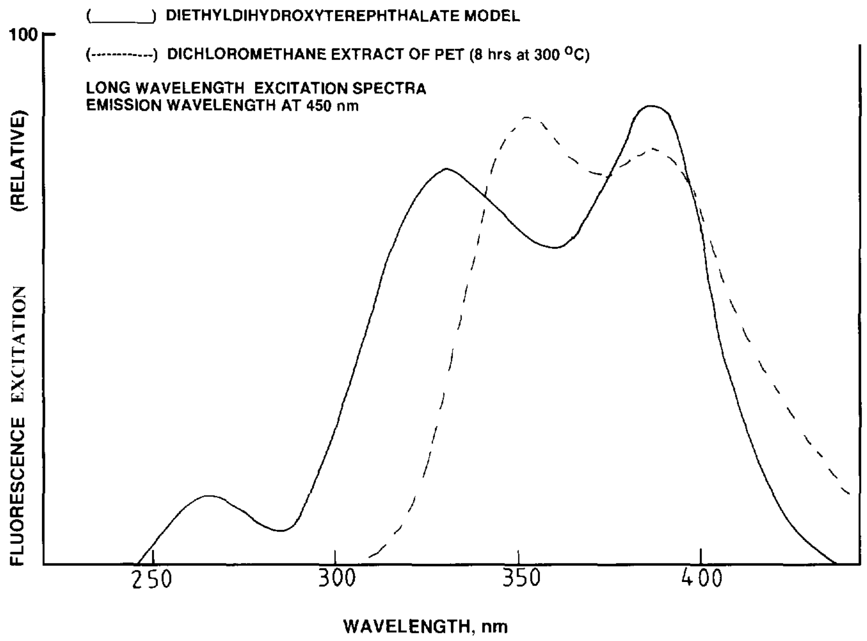


Figure 6 Fluorescence excitation spectra of a dichloromethane extract of PET after 8 h of heating in air at 300°C and dihydroxydiethylterephthalate model (10^{-4} M in TFA). (Emission wavelength at 450 nm)

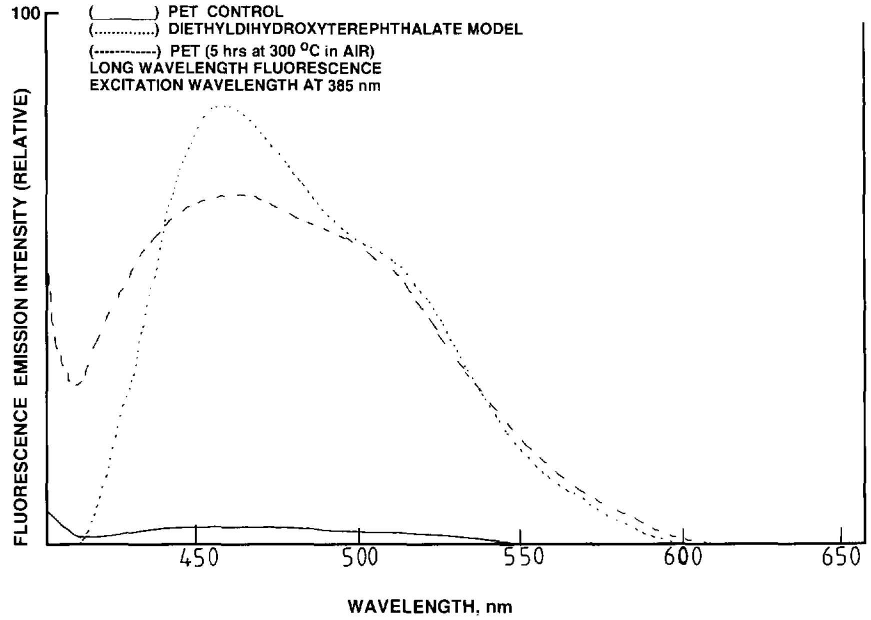


Figure 7 Fluorescence emission spectrum of PET before and after 5 h of heating in air at 300°C (1% w/w in TFA) and dihydroxydiethylterephthalate model (10^{-4} M in TFA). (Excitation wavelength at 385 nm)

quinone structures is suggested. The DEDHT itself exhibits a very weak phosphorescence with a maximum at 425 nm. On oxidation with lead dioxide the maximum emission from the DEDHT is not only enhanced but considerably red-shifted to 520 nm matching that of the oxidized polymer (via lead dioxide). Because of the complex structural changes in the oxidized polymer several other emitting components will undoubtedly be present, giving rise to a broad spectrum. There is however, sufficient detail to allow some of the bands to be matched to the spectral shifts associated with the model compounds.

In *Figure 10* the phosphorescence emission spectrum of an extract from severely degraded PET (8 h in air at 300°C) is shown together with that of less degraded material (5 h in air at 300°C) and undegraded PET (control). The emission from the extract was found to be a good match to that of a 2,6-di-tertbutyl stilbene quinone model. Evidence that the formation of these quinone impurities arise principally from oxidation is given by comparison to a phosphorescence emission spectrum for PET degraded in a nitrogen atmosphere. Here no significant change in the spectrum is seen compared to that of the PET control.

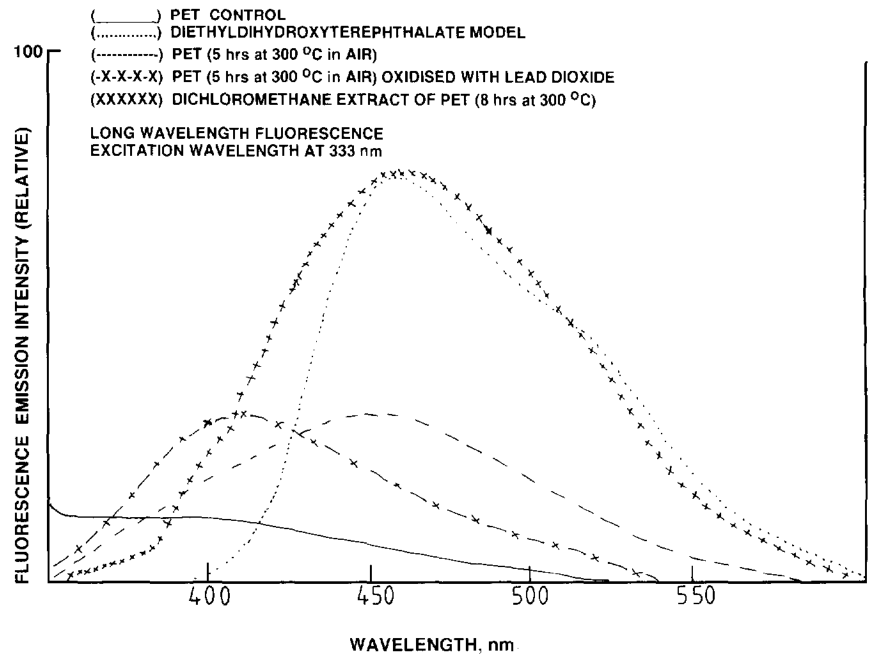


Figure 8 Fluorescence emission spectra of PET before and after 5 h of heating in air at 300°C and then oxidation with lead dioxide (1% w/w in TFA), dihydroxydiethylterephthalate model (10^{-4} M in TFA) and dichloromethane extract of PET (8 h at 300°C in air). (Excitation wavelength at 333 nm)

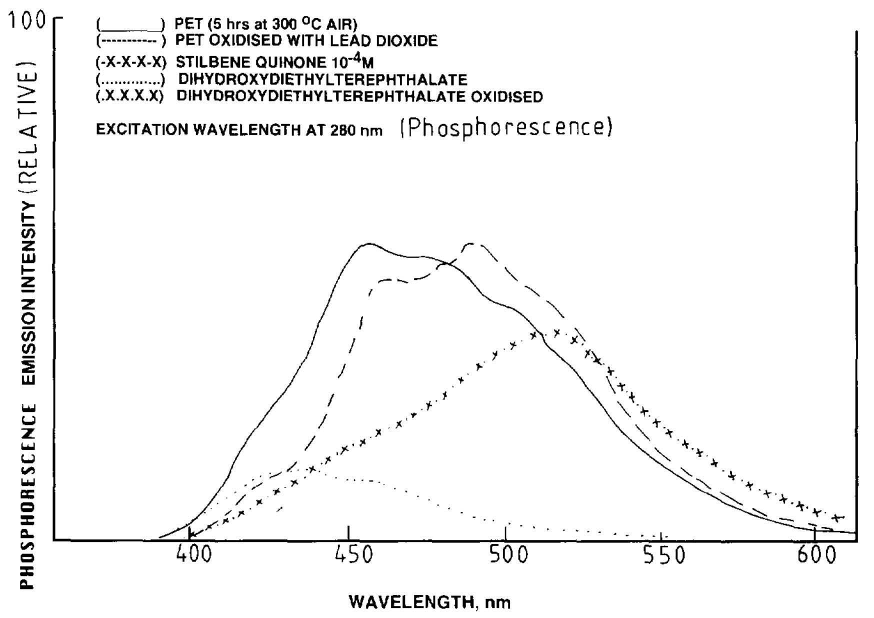


Figure 9 Phosphorescence emission spectra of PET after 5 h of heating in air at 300°C and then oxidation with lead dioxide (1% w/w in TFA), dihydroxydiethylterephthalate model (10^{-4} M in TFA) before and after oxidation with lead dioxide. (Excitation wavelength at 280 nm)

CONCLUSIONS AND MECHANISMS

Degradation mechanisms proposed in the existing literature can now be considered in the light of the information arising from the luminescence data which have been obtained in this study. *Scheme 1* shows three primary degradation processes which are given in the literature as follows[1–6]:

1. Main chain scission at the ethoxy link resulting in a terminal carboxyl radical (A) and terminal alkyl radical (B).
2. Hydrogen atom abstraction by an adventitious species (X) to produce an in-chain alkyl radical (C).
3. Direct decarboxylation followed by radical recombination to give a 1,2- (substituted diphenyl) ethane link and dehydrogenation of this to produce a stilbene.

In addition, from the results presented in this study it is highly likely that the stilbene implied in the literature is then oxidized to a stilbene quinone (SQ) via hydroperoxidation. Subsequent to these primary degradation processes further reactions are possible, as follows[1–6]:

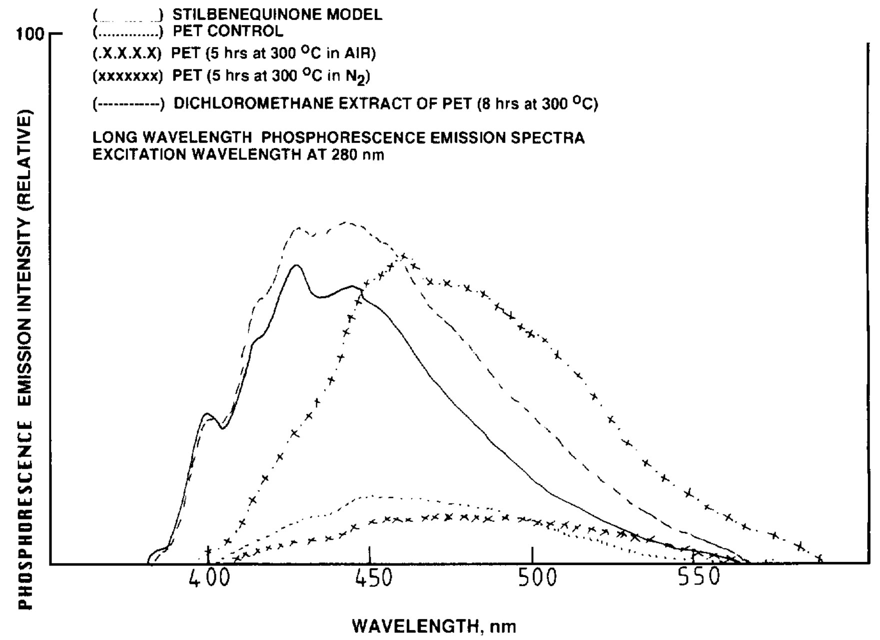
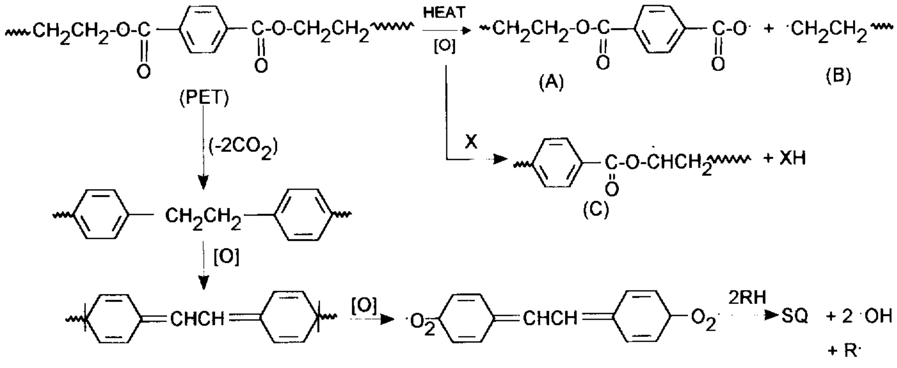
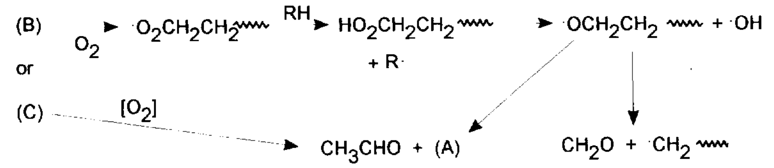


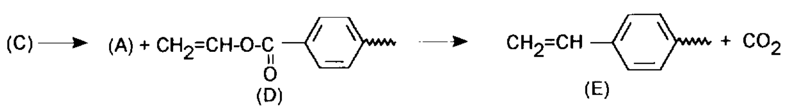
Figure 10 Phosphorescence emission spectra of PET before and after 5 h of heating in air and nitrogen at 300°C, dichloromethane extract of PET after 8 h heating in air at 300°C and 2,6-ditertiarybutylstilbenequinone model (10^{-4} M in TFA). (Excitation wavelength at 280 nm)



Scheme 1



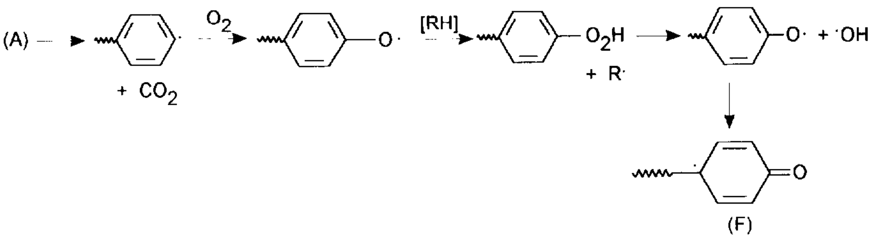
Scheme 2



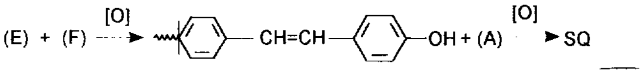
Scheme 3

4. Oxidation of (C) and (B) (*Scheme 2*) giving rise to acetaldehyde and formaldehyde.
5. Decomposition of (C) to give vinyl benzoate (D) which in turn will decarboxylate to produce vinyl benzene end groups (E) (*Scheme 3*).
6. Decarboxylation of (A) to give a phenyl radical which will undergo hydroperoxidation and subsequent breakdown to give a quinone (F) (*Scheme 4*).
7. Combination of (E) and (F) producing stilbene quinones (*Scheme 5*).
8. Scission of hydroperoxides to produce hydroxyl radicals which then substitute on the aromatic rings of PET (*Scheme 6*).

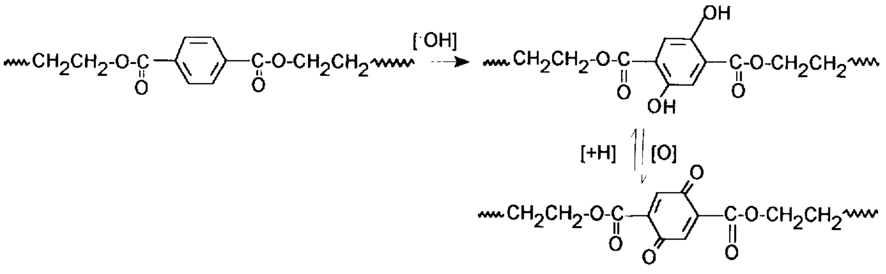
Our studies extend the mechanisms given in the literature to suggest there is an equilibrium between the



Scheme 4



Scheme 5



Scheme 6

hydroxylated species (phenols) and their corresponding quinones via a redox mechanism. Experiments in our laboratory have also shown this process to be reversible and this will be the subject of future work. Studies are currently underway to consolidate these data using preparative chromatographic and spectroscopic methods for the analysis of the extractable impurities and the extracted polymer.

REFERENCES

1 Zimmerman, H. *Polym. Eng. Sci.* 1980, **20**, 680

2 McMahon, W. *J. Chem. Eng. Data* 1959, **4**, 57

3 Ellison, M. S., Miyagi, A. and Wunderlich, B. *J. Polym. Sci., Polym. Chem. Edn* 1972, **10**, 2073

4 Ballara, A. and Verdu, J. *Polym. Degrad. Stabil.* 1989, **26**, 361

5 McNeil, I. C. and Baunekhel, M. *Polym. Degrad. Stabil.* 1991, **34**, 187

6 Sivasany, P., Palaniandavar, M., Viyajakumar, C. T. and Lederer, K. *Polym. Degrad. Stabil.* 1992, **38**, 15

7 Allen, N. S., Edge, M., Mohammadian, M. and Jones, K. *Eur. Polym. J.* 1991, **27**, 1373

8 Allen, N. S., Edge, M., Mohammadian, M. and Jones, K. *Polym. Degrad. Stabil.* 1993, **41**, 191

9 Day, M. and Wiles, D. M. *J. Appl. Polym. Sci.* 1972, **16**, 191

10 Wiles, D. M. *Polym. Eng. Sci.* 1973, **13**, 74

11 Marcotte, F. B., Campbel, D., Cleveland, J. A. and Turner, D. T. *J. Polym. Sci., Polym. Chem. Edn* 1976, **5**, 481

12 Allen, N. S. and McKellar, J. F. *Makromol. Chem.* 1978, **179**, 523

13 Sonnenschein, M. M. and Roland, C. M. *Polymer* 1990, **31**, 2023

14 Heniker, D. J., Frank, C. W. and Thomas, J. W. *Polymer* 1988, **29**, 437

15 Fukazawa, N., Yoshioka, K., Kukumura, H. and Masuhara, H. *J. Phys. Chem.* 1993, **97**, 6753