Eur. Polym. J. Vol. 29, No. 1, pp. 75–81, 1993
Printed in Great Britain. All rights reserved

0014-3057/93 \$5.00 + 0.00

FLUORESCENCE OF POLYOLEFINS—1. EFFECT OF THERMAL DEGRADATION ON FLUORESCENT EXCITATION AND EMISSION SPECTRA

P. P. L. JACQUES and R. C. POLLER*
Department of Chemistry, King's College, Strand, London WC2R 2LS, England

(Received 21 April 1992)

Abstract—Using computer generated stack-plots, the fluorescent excitation and emission spectra were determined for various specimens of polyethylene and polypropylene and the effects of extraction with hexanes and propan-2-ol recorded. Changes in fluorescence caused the thermal degradation, monitored by two methods, are reported and discussed.

INTRODUCTION

The fluorescence of poly(vinyl chloride) is being used to gain information on the thermal history of the polymer and to estimate effective residual stabilizer levels [1]. It is therefore of interest to see if the technique could also be used for the same purpose with polyolefins. The fluorescent emission of visible light when polyethylene (PE) is subject to u.v. irradiation was reported >25 years ago [2, 3] when it was noted that the luminescence was modified by oxidation of the polymer. In subsequent reports [4–19], there has been disagreement as to the nature of the fluorescence spectrum and to its cause.

The results of previous measurements are summarized in Table 1 from which it can be seen that u.v. excitation in the range 225–340 nm has been used with emissions reported over the range 275–470 nm. In many cases Stokes' shifts cannot be determined as the excitation radiation which gives rise to a given emission band has not been identified. Thus it seems unlikely that all the six emission bands reported for Entry 1 (Table 1), which range from 275–467 nm, have all been excited by irradiation at 254 nm. However Allen's group published excitation and emission spectra for PE (Entry 2) showing that excitation at λ_{max} 230 nm caused emissions at 300, 340, 360, 390, 400 and 430 nm [6]. This result differs from that of Osawa and Kuroda [18] Entry 5 (Table 1) who identify, for HDPE, two bands at λ_{max}EX 232 nm/λ_{max}EM 333 nm and λ_{max}EX 292 nm/λ_{max}EM 340 nm. Ahmad [20] by contrast reports, for HDPE, emission bands at 350–360 and 410 nm excited by a laser operated at 249 nm with the same emissions being excited by irradiation 337 nm.

Allen *et al.* [6] recorded three emission bands for polypropylene (PP) at 295, 330 and 400 nm excited by irradiation at 225 nm (Table 1, Entry 11) but in later papers [7, 10] an emission band at 340 nm is seen by irradiation at either 230 or 290 nm. Carlsson and Wiles [5] found that irradiation of PP at 287 nm gave emissions at 320–330 and 470 nm (Table 1, Entry 12).

The reasons for the discrepancies reported in the positions of the fluorescent bands is not clear though the relatively primitive instrumentation available must have been a factor in the earlier work.

The aim of the present work is to remove uncertainties in the literature by recording the spectra of samples of PE and PP in such a manner that the position of the radiation which is exciting a given emission band is shown clearly. The effect of, mainly, thermal degradation of the polymers on the fluorescence spectra is also investigated. Structural elements which may be responsible for the fluorescence are discussed and this topic is explored in a later paper.

EXPERIMENTAL PROCEDURES

Unstabilized isotactic PP powder (supplied by ICI) was diluent polymerized: $\bar{M}_W \sim 300{,}000$; $\bar{M}_W/\bar{M}_n \sim 8$; MFI 21 (230°C, 2.16 kg); 20 ppm Ti; 20–30 ppm Cl; 150 ppm Al. Atactic PP was supplied by ICI as a sludge containing *ca* 50% pentamethylheptane; before use, the polymer was precipitated by addition of hexanes and the insoluble material dried *in vacuo*. Diluent polymerized PE was supplied by Solvay et Cie; no polymer characteristics were provided. High density PP (British Petroleum) was stabilized by an undisclosed commercial antioxidant package: $\bar{M}_W$ 140,000; $\bar{M}_n$ 18,000. Unstabilized low density PE was prepared by the ICI high pressure process and supplied by British Petroleum: $\bar{M}_W$ 122,000; $\bar{M}_n$ 19,000; long chain branching frequency 1.8/1000C.

Where necessary, additives were incorporated into the polymer powders using a standard dry blending technique and films were generated either by melting and rolling in a RAPRA micromill or by melting in a Metrastat oven. Test pieces of film prepared in the micromill were thermally degraded by heating in a specially modified oven at 190°C. Samples obtained from the Metrastat oven emerged at constant speed from the hot chamber which was set at 190°C and thus progressively thermally degraded along the length of the specimen.

Fluorescence was measured on solid samples using a Perkin–Elmer LS5 lumospectrophotometer attached to Perkin–Elmer Atomic Spectroscopy Data System 10 computer running PECLS software at Birkbeck College, University of London. The program allowed generation of stack-plots (e.g. Fig. 1) assembled from a series of spectra each showing the effect on the emission of an incremental

---

*To whom all correspondence should be addressed.

Table 1. Fluorescence spectra of PE and PP

Entry No.	Polymer	λ_{max} EX (nm)	λ_{max} EM (nm)
1	LDPE[a]	254	275, 330, 350, 378, 400, 422, 467
2	PE[b]	230	300, 340, 360, 390, 400, 430
3	LDPE[c]	230, 290	300, 345
4	PE[d]	300	350, 470
5	HDPE[e]	232	333
		292	340
6	PE[f]	240, 290	340
7	HDPE[g]	249	350–360, 410
8	HDPE[h]	230, 290	360 (doublet)
9	photolysed PE[f]	298, 312,	
		327,340	420
10	LDPE[e]	236	333
		292	343
11	PP[b]	230	295, 330, 400
12	PP[i]	287	320–330, 470
13	PP[j]	230, 290	340
14	PP[k]	230, 285	340
15	PP[e]	232	332
		295	342
16	APP[e]	232	330
		290	340

[a] Ref. [3], [b] Ref. [6], [c] Ref. [8], [d] Ref. [17], [e] Ref. [18], [f] Ref. [19], [g] Ref. [20], [h] Ref. [16] [i] Ref. [5], [j] Ref. [7], [k] Ref. [10].

change in the wavelength of the exciting radiation (or vice versa). Individual spectra were then examined to obtain accurate fluorescence maxima. All wavelengths recorded are uncorrected.

Changes in fluorescence of the samples from the Metrastat oven were monitored using a Metrastat Reflectometer (Dr Stapfer GmbH, Düsseldorf) in which the sample passes at constant speed under either a 254 or a 365 nm lamp with emitted fluorescence detected by a photocell at 45° to the irradiating beam. The 254 nm source was filtered through a 254 nm line filter and the resulting emitted radiation, before entering the photocell, passed through a band filter with a maximum at 340 nm, see Fig. 2; this setting is suitable for observing initial fluorescence. Post-oxidation fluorescence can be seen by using the 365 nm source and a band filter before the detector having a maximum at 530 nm (see Fig. 3 for optical characteristics). The reflectometer results were recorded using a Hewlett Packard ColorPro plotter linked to an IBM-PS2 computer running Metrastat software developed by the Centre for Research in Analytical Chemistry and Instrumentation, King's College.

Fluorescence lifetime measurements were carried out by Dr G. Rumbles in the Davy Faraday Research Laboratory of the Royal Institution, London using a laser excitation source set at 282 nm. The lifetimes for virgin PP, nsec (%), were: 4.4 (29.1), 32.7 (52.2), 1.5 (18.7); for thermally degraded PP, 6.0 (37.8), 20.5 (50.5), 1.4 (11.6).

RESULTS

Measurements were made using a Perkin–Elmer LS5 lumospectrophotometer, the output being computer processed so as to give three dimensional stack-plot spectra exemplified in Fig. 1. This presentation

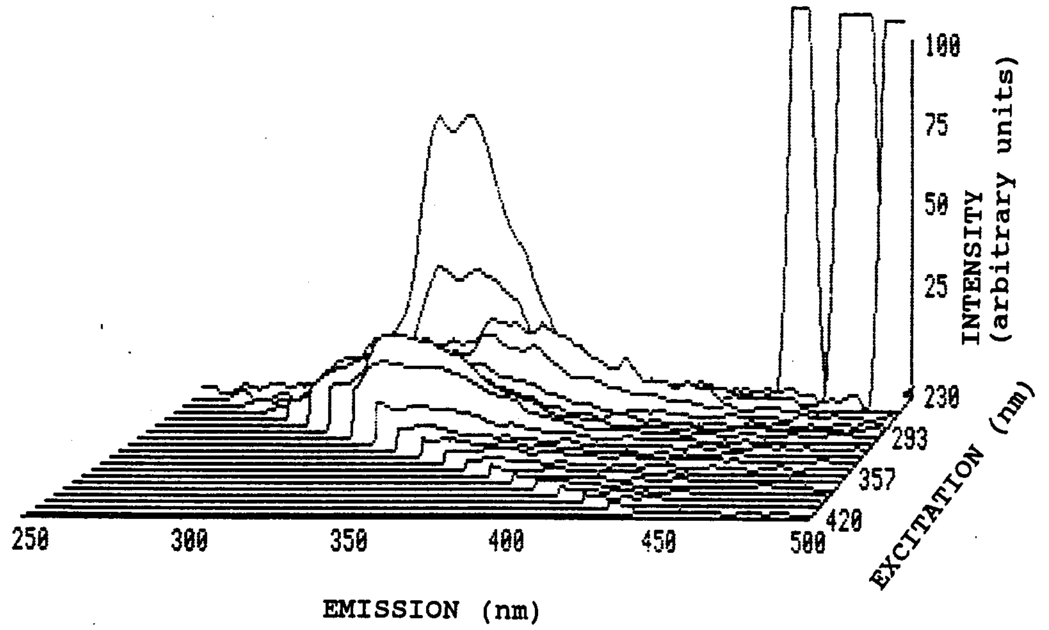


Fig. 1. Fluorescence stack plot spectrum of PE (Solvay et Cie).

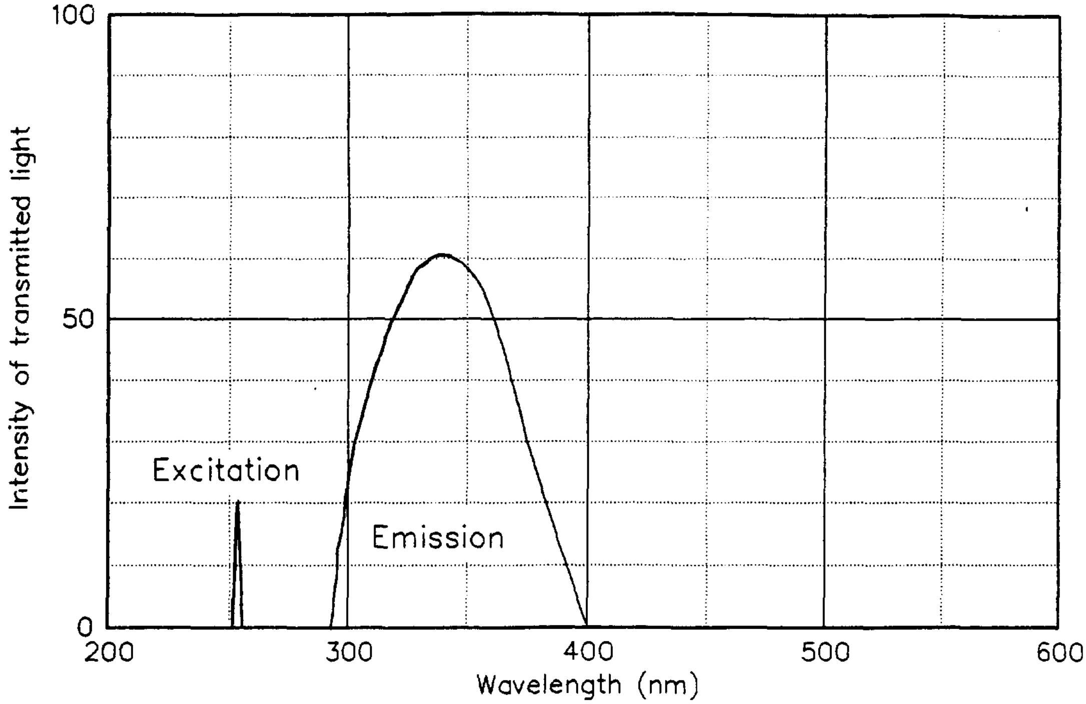


Fig. 2. Optical characteristics of filters used in Metrastat Reflectometer set up to monitor pre-oxidation fluorescence.

enables clear correlation between exciting and emitting radiation. The results for virgin polyolefin films are shown in Table 2. The PP and one sample of PE exhibited three distinct fluorescent signals at λ_{max}EX 230/λ_{max}EM 330–340, λ_{max}EX 260/λ_{max}EM 345–350 and λ_{max}EX 290/λ_{max}EM 330–340 nm. The other two samples of PE did not exhibit the λ_{max}EX 260/λ_{max}EM 345–350 nm band. This band does

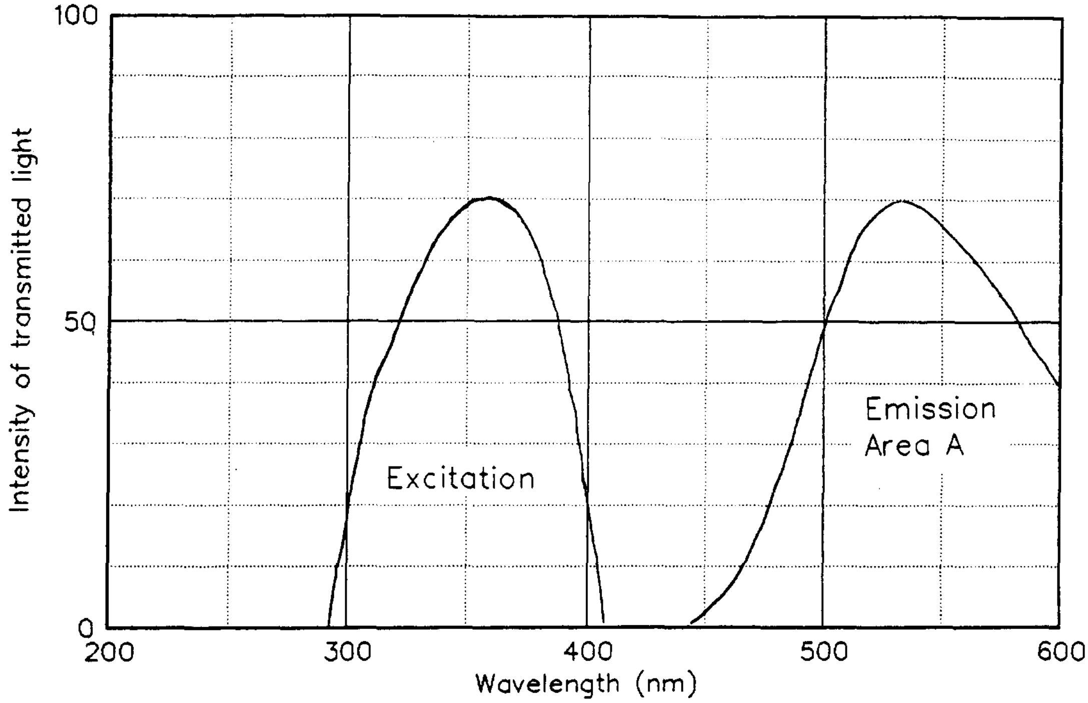


Fig. 3. Optical characteristics of filters used in Metrastat Reflectometer set up to monitor post-oxidation fluorescence.

Table 2. Fluorescence signals of PE and PP films determined from three-dimensional stack plot spectra

Polymer	λ_{max} EX (nm)	λ_{max} EM (nm)
PE (Solvay et Cie)	230	330–340
	260	350
	290	340
LDPE unstabilized	230	330–340
	290	330
HDPE stabilized	230	330–340
	290	340
PP unstabilized	230	330–340
	260	345
	290	330–340

not appear to have been reported previously but otherwise our results are similar to those in the literature (Table 1).

Solvent extraction

Pioneer workers [3] showed that the luminescent species in PE could be partially extracted with hydrocarbon solvents. Osawa and Kuroda [18] found that all the fluorescence of HDPE was extracted into the solvent when the polymer was treated with hot hexane.

We found that extraction of PP film with cold hexane did not apparently alter its fluorescence and no fluorescence was detected in the extract (Table 3). The fluorescence of unstabilized PE also appeared to be unaffected by treatment with cold hexane but, in this case, the extract showed the same fluorescence spectrum as the polymer. The effects of hot hexanes and of cold propan-2-ol (Table 3) indicate that hot hexanes completely dissolve out the fluorescent species from both PE and PP whereas the more polar propanol extracts it fully from PP but only partially from PE. A reasonable conclusion is that the fluorescent species is not an uncombined foreign compound but is specifically bound to the lower molecular weight fractions in PE and to the atactic and lower MW fractions of PP.

Thermal degradation

Initially, samples of film which had been heated for various periods in an oven at 190°C were examined in the lumospectrophotometer. The initial fluorescence spectrum of unstabilized PP disappeared after heating for *ca* 10 min to be replaced by a single band at λ_{max}EX 390/λ_{max}EM 460 nm. Altering the time of heating in an attempt to obtain specimens with an intermediate fluorescence was unsuccessful and it seems that the transformation of initial spectrum to post-oxidation spectrum occurred over a very short time interval.

The experiment was repeated with a PP sample containing 0.1% of the commercial radical scavenger Irganox 1010 and 0.1% of the peroxide decomposer Hostanox SE2. The initial fluorescence was identical to that observed previously except that there was an extra, weak intensity, band at λ_{max}EX 230/λ_{max}EM 310 nm which was shown to be caused by the Irganox 1010. The fluorescent behaviour of stabilized PP was the same as that of the virgin polymer except that the post-oxidation spectrum did not appear until the sample had been heated at 190°C for 120 min.

It is desirable to measure the relative intensities of fluorescence in different polymer samples; this was done for PVC by using solutions of the polymer in THF. Considerable efforts were made to find a suitable, non-fluorescent solvent for PP and the most promising was decalin which, however, was fluorescent due to the presence of traces of tetralin. Removal of the tetralin by distillation was not possible but was effected by treatment with sodium hypochlorite in the presence of catalytic amounts of ruthenium chloride [21]. However, the PP was then found to be insoluble in the purified decalin. Since atactic PP is soluble, a study was made of its fluorescence as a solution in hexanes and of the effect of thermal degradation. In the undegraded polymer, two bands were observed at λ_{max}EX 260/λ_{max}EM 335 and λ_{max}EX 290/λ_{max}EM 345 nm. This result is identical with the spectrum of isotactic PP except that the λ_{max}EX 230/λ_{max}EM 330–340 nm band is missing (*cf* Osawa and Kuroda [18] who reported fluorescence at λ_{max}EX 232/λ_{max}EM 330 and λ_{max}EX 290/λ_{max}EM 340 nm for APP). When we degraded the polymer at 190°C and measured the fluorescence spectrum using solutions in hexanes, we found that the intensity of the 290/345 band was reduced by more than a half after heating for 120 min and was eventually reduced to zero. Unlike isotactic PP, the polymer did not exhibit the post-oxidation emission at 460 nm (or any other bands) after the initial fluorescence decayed to zero. A plot of the change in intensity of the 345 nm emission with time of heating is shown in Fig. 4.

Although we had succeeded in obtaining relative intensity measurements of fluorescence in APP the problem remained of how to compare the fluorescence of two pieces of the same polymer film which had been degraded for different periods. The difficulty is that, when a solid specimen is placed in the sample cell of the lumospectrophotometer, the intensity of the spectrum is extremely sensitive to the position and orientation of the film and it is not possible to obtain repeatable intensity measurements on a given sample. We therefore began generating specimens by placing polymer powder in the 260 mm

Table 3. Effect of solvent extraction on the fluorescence of polyolefins

		Fluorescence of:	
Polymer	Solvent	Extracted polymer	Extract
PP	Cold hexanes	Unchanged	Absent
PP	Hot hexanes[a]	Absent	Same as unextracted PP
PP	Cold propan-2-ol	Absent	230 EX/340 EM 260 EX/320 EM
PE	Cold hexanes	Unchanged	Same as unextracted PE
PE	Hot hexanes[a]	Absent	Same as unextracted PE
PE	Cold propan-2-ol	Unchanged	Same as unextracted PE

[a]Extracted for 6–10 hr in a Soxhlet flask.

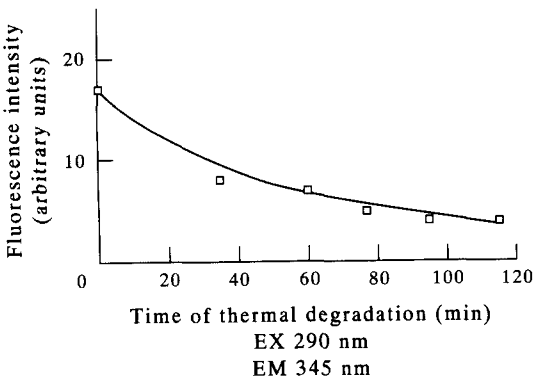


Fig. 4. Intensity of fluorescence emission at 345 nm (excitation at 290 nm) plotted against time of heating at 190°C for atactic PP in hexanes.

by 26 mm trays of a Metrastat oven which were then fed at a constant speed out of the oven (set at 190°C) producing polymer strips which were progressively degraded along the length of the specimen. The specimen was then scanned in a Metrastat Reflectometer where it passed, at a fixed speed, under either a 254 or a 365 nm light source. The resulting fluorescent radiation was then collected using a photocell which could be adjusted to receive a band centred at 340 nm (suitable for monitoring the initial EX 260/EM 340 nm band) or at 550 nm (suitable for the EX 390/EM 460 nm post-oxidation band). The 245 nm radiation passed through a line filter and was, consequently, a low intensity source giving a weak fluorescent emission but light from the 365 nm source emerged from a band filter giving a much stronger fluorescent signal. The advantage of the method is that the variation in intensity of an initial or a post-oxidation fluorescent band can be monitored for a sample which has been progressively degraded. Comparison with the previous technique is possible by cutting up the progressively degraded strip into pieces and examining these in the lumospectrophotometer.

Initial experiments with the Metrastat oven showed that unstabilized PP which had only been heated at 190°C long enough to solidify and then immediately ejected from the oven had yellowed and the lumospectrophotometer showed that the initial fluorescence had been completely replaced by the 390/460 nm post-oxidation band. These results were confirmed by the Reflectometer which showed no fluorescence using the 254 nm lamp but a strong signal with increasing intensity along the strip excited by the 365 nm source (Fig. 5). Maximum intensity was achieved where the specimen had been heated for about 100 min. When the experiment was repeated with a N_2 atmosphere maintained in the oven, 133 min heating was needed to obtain maximum intensity for the same band. Using samples of PP stabilized with Irganox 1010 and Hostanox SE2, the onset of yellowing was delayed and coincided with the appearance of the post-oxidation fluorescence signal. However, the Reflectometer trace now showed a weak initial fluorescence using the 254 nm source which reached a maximum at *ca* 30 min and decayed to zero after 100 min (if a N_2 atmosphere was used the signal persisted for more than 3 hr). Repeating the scan using the 365 nm source showed that the air-degraded sample did not produce the post-oxidation signal until it had been heated for *ca* 130 min (extended to 170 min if the sample was heated in N_2).

Strips of unstabilized PE were colourless when they first emerged from the oven and did not begin to yellow until they had received about 60 min heating at 190°C. Use of the Reflectometer showed that the initial fluorescence (254 nm source) persisted for about 45 min. When the same strip was scanned using the 365 nm source, the post-oxidation fluorescence appeared after about 45 min i.e. at the point where the initial fluorescence disappeared.

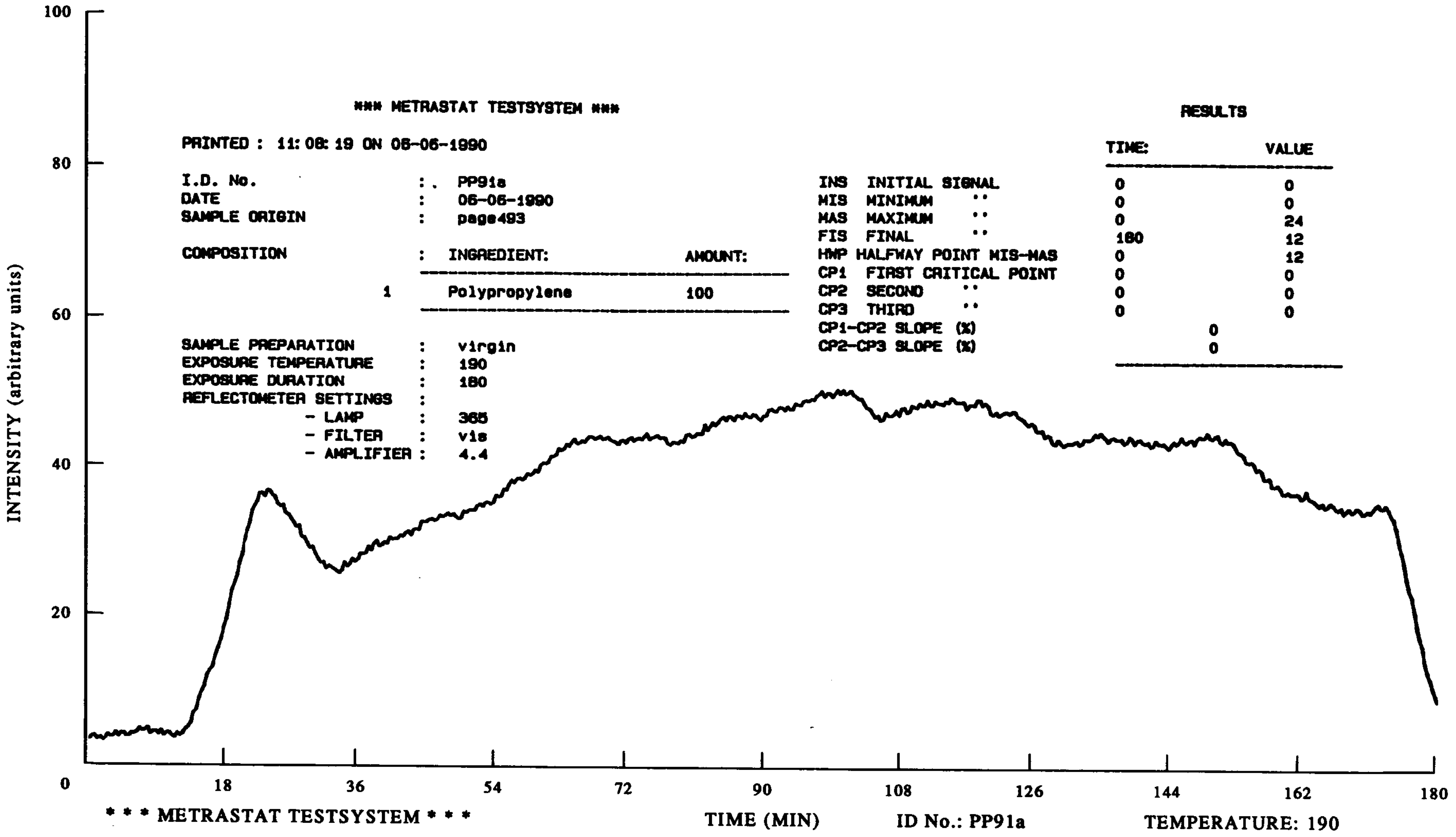
Thus the generation of polymer specimens, which had been thermally degraded progressively along their length, did allow measurement of changes in intensity of fluorescence within a single specimen. In general the initial fluorescence decayed rapidly (sometimes before the sample emerged from the oven) and this was followed by a build-up of post-oxidation fluorescence. The point where yellowing occurred was roughly coincident with the point where post-oxidation fluorescence began.

For comparison, samples of PE and PP were photo-degraded by rotating a small plaque suspended in a Rayonet Photochemical Reactor, equipped with 16 360 nm sources, for various periods. Examination of unstabilized PP specimens in a lumospectrophotometer showed that the initial fluorescence disappeared after irradiation for about 40 hr and the specimen remained non-fluorescent even after a further 60 hr exposure. These results are in general agreement with those obtained by Allen *et al.* [10] who reported a fall in the intensity of the two excitation bands at 225 and 290 nm when PP was irradiated though this result relied on relative intensity measurements made on different solid samples. However, when we examined stack plot spectra of LLDPE films, we found no change in fluorescence even after 100 hr of irradiation. By contrast Osawa and Kuroda [18] who irradiated HDPE with a high pressure Hg lamp (main emissions 254, 290 and 365 nm) found that the fluorescence signals disappeared after 10 min irradiation. If the irradiation was continued, a new emission band at 420 nm was observed [19]. This discrepancy is presumably due to differences in intensity and wavelength in the sources used for the photodegradation experiments.

Fluorescence lifetimes for samples of unstabilized PP film before and after thermal degradation were determined by excitation with a pulsed laser at 282 nm and photon counting at the maximum intensity (340 nm) of the resulting emission. Computer iterations of the resulting decays were complex and shown to consist of three exponentials corresponding to lifetimes of 1.5 nsec, 4–6 nsec and 20–33 nsec with substantial proportions of each (see Experimental Procedures).

Species responsible for fluorescence

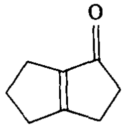
Partridge [4] reported that fluorescence was due to free aromatic compounds which had arisen from oxidation reactions in the polymer. Subsequently it was specifically stated [3] that the fluorescence of



```
                   *** METRASTAT TESTSYSTEM ***                                                      RESULTS

PRINTED : 11:08:19 ON 06-06-1990                                                             TIME:          VALUE
                                                                                             ------------------------
I.D. No.                 : .  PP91a                             INS  INITIAL SIGNAL           0               0
DATE                     :   06-06-1990                         MIS  MINIMUM     ''           0               0
SAMPLE ORIGIN            :   page493                            MAS  MAXIMUM     ''           0               24
                                                                FIS  FINAL       ''           180             12
COMPOSITION              :  INGREDIENT:             AMOUNT:     HMP HALFWAY POINT MIS-MAS     0               12
                            -------------------------------     CP1  FIRST CRITICAL POINT     0               0
                         1  Polypropylene           100         CP2  SECOND      ''           0               0
                            -------------------------------     CP3  THIRD       ''           0               0
SAMPLE PREPARATION       :   virgin                             CP1-CP2 SLOPE (%)                   0
EXPOSURE TEMPERATURE     :   190                                CP2-CP3 SLOPE (%)                   0
EXPOSURE DURATION        :   180                                                              ------------------------
REFLECTOMETER SETTINGS   :
              - LAMP     :   365
              - FILTER   :   vis
              - AMPLIFIER :  4.4
```

Fig. 5. Intensity of post-oxidation fluorescence recorded against time of heating at 190°C for unstabilized PP.



I

Scheme 1

LDPE was caused by free anthracene, free phenanthrene and polymer-bound naphthalene together with a substituted benzene compound. Carlsson and Wiles [5] discussed the possibility that polynuclear aromatic hydrocarbons, absorbed from the atmosphere rather than produced by oxidation of the polymer, were not only responsible for fluorescence but might also play a role in generating singlet oxygen thereby accelerating oxidative degradation. Support for this view came from the demonstration that, when PP was extracted with hexane, the initial fluorescence disappeared but was restored when the film was exposed for several days to urban air. However, Allen [14] showed that fluorescence returned to the extracted polymer if it was exposed to pure oxygen but did not return in a N_2 atmosphere.

The other favoured candidate species for fluorescence are carbonyl compounds also suggested by Charlesby and co-workers [2, 3] though they noted that simple model carbonyl compounds did not fluoresce at room temperature. Allen [7–14] has proposed that α, β-unsaturated carbonyls are responsible for the initial fluorescence in polyolefins. The principal piece of evidence for this hypothesis is the near-coincidence of the fluorescence excitation spectra of PP with absorption spectrum of the model compound pent-3-en-2-one whereas the similarity with the absorption spectrum of naphthalene is less good. The weakness of this argument is that, in general, absorption of u.v. light does not lead to fluorescence and therefore an absorption spectrum would be expected to contain the requisite fluorescence excitation bands but also to contain other absorption bands. On this basis, naphthalene is as good a candidate for the fluorescent species as the α, β-ketone. Further it is known that, in contrast to the polynuclear aromatics, the α, β-unsaturated carbonyl compounds are generally non-fluorescent. An exception is the bicyclic enone bicyclo[3.3.0.]oct-1-en-2-one (I) which fluoresces in solution in acetonitrile EX 300/EM 345 nm [22]. In a later paper we will describe the use of various model compounds as candidate structures for the initial and post-oxidation fluorescence in polyolefins.

Acknowledgements—We are grateful to Dr Stapfer GmbH, Düsseldorf for a grant which made this work possible. We thank Professor D. Phillips and Dr G. Rumbles of the Royal Institution for the lifetime measurements.

REFERENCES

1. C. E. James and R. C. Poller. *Eur. Polym. J.* **22**, 767 (1986).
2. A. Charlesby and R. H. Partridge. *Proc. Roy. Soc. A* **283**, 312, 329 (1965).
3. I. Boustead and A. Charlesby. *Eur. Polym. J.* **3**, 459 (1967).
4. R. H. Partridge. *J. Chem. Phys.* **45**, 1679 (1966).
5. D. J. Carlsson and D. M. Wiles. *J. Polym. Sci.; Polym. Letts. Edn* **11**, 759 (1973).
6. N. S. Allen, R. B. Cundall, M. W. Jones and J. F. McKellar. *Chem. Ind.* 110 (1976).
7. N. S. Allen, J. Homer and J. F. McKellar. *Chem. Ind.* 692 (1976).
8. N. S. Allen, J. Homer, J. F. McKellar and D. G. M. Wood. *J. appl. Polym. Sci.* **21**, 3147 (1977).
9. N. S. Allen and J. F. McKellar. *J. appl. Polym. Sci.* **22**, 625 (1978).
10. N. S. Allen, J. F. McKellar and G. O. Phillips. *Stabilisation and Degradation of Polymers*, ACS Symposium No. 169, Chap. 6, p. 68 (1978).
11. N. S. Allen and J. F. McKellar. *Polym. Degrad. Stab.* **1**, 47 (1979).
12. N. S. Allen, J. F. McKellar and D. Wilson. *Polym. Degrad. Stab.* **1**, 205 (1979).
13. N. S. Allen. *Polym. Degrad. Stab.* **2**, 155 (1980).
14. N. S. Allen. *Polym. Degrad. Stab.* **6**, 193 (1984).
15. Z. Osawa and K. Nakano. *J. Polym. Sci.* Symposium No. 57, 267 (1976).
16. Z. Osawa. *Degradation and Stabilisation of Polymers* (edited by H. H. G. Jellinek), Chap. 3, p. 162. Elsevier, Amsterdam (1983).
17. Z. Osawa, N. Kurishu and H. Kuroda. *Polym. Degrad. Stab.* **3**, 265 (1980).
18. Z. Osawa and H. Kuroda. *J. Polym. Sci.; Polym. Lett. Edn* **20**, 577 (1982).
19. Z. Osawa and H. Kuroda. *Polym. Photochem.* **7**, 231 (1986).
20. S. R. Ahmad. *J. Phys., Appl. Phys.* **16**, L137 (1983).
21. S. Wolfe, S. K. Hasan and J. R. Campbell. *Chem. Commun.* 1420 (1970).
22. R. O. Loutfy and J. M. Morris. *Chem. Phys. Lett.* **19**, 377 (1973).