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# QUANTITATIVE PHOSPHORESCENCE SPECTROSCOPY OF POLYSTYRENE DURING PHOTO-DEGRADATION AND THE SIGNIFICANCE OF IN-CHAIN PEROXIDES

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**Abstract**—Phenyl alkyl ketone end-groups in polystyrene have been determined by quantitative phosphorescence spectroscopy. A typical commercial sample of polymer has a concentration of 0.14 carbonyl groups per number average chain. The photochemistry and emission properties of a series of samples prepared under differing oxygen partial pressures suggest that these carbonyl groups originate from in-chain peroxides. On photo-oxidation, the carbonyl concentration increases rapidly and is quantitatively related to the number of chain scissions. The mechanistic significance of these results and the temperature dependence of the formation of carbonyl groups after the low temperature photolysis of peroxides in polystyrene, are discussed.

Luminescence spectroscopy, especially at low temperatures, provides a sensitive probe for determining the nature of some impurities present in polymers and for investigating their photophysical and photochemical behaviour. Recent studies have reported on the phosphorescence of polystyrene [1,2], polybutadiene [3], polypropylene [4], and nylon [5]. Of particular interest is the significance of these impurities in the photodegradation of the polymer, both in initiation and in subsequent reactions leading to oxidation of the polymer.

The low temperature phosphorescence of polystyrene has been clearly assigned to emission from phenyl alkyl ketone end-groups [1,2]. It has been suggested [2,6] that these end-groups arise from disproportionation reactions of in-chain peroxide linkages formed during the synthesis of the polystyrene as a result of residual oxygen reacting with the growing polystyrenyl radical. At the high temperatures (up to 200°C) involved in commercial polymerizations, the residual peroxide concentration would be expected to be low but, in lower temperature laboratory polymerizations, thermal peroxide scission may be incomplete, leading to a significant concentration of in-chain peroxide linkages in the polymer.

Lawrence and Weir [7] have suggested that these peroxide linkages are important in the initiation of photo-oxidation of polystyrene by photolysis to alkoxy radicals which may abstract hydrogen atoms producing alkyl radicals, and ultimately, in the presence of oxygen, hydroperoxides. During auto-oxidation, the fragmentation of alkoxy radicals formed by scission of these hydroperoxides produces an end-of-chain phenyl alkyl ketone. Klöpffer [1] suggested that this latter step is the most likely route to carbonyl impurities in commercial and laboratory prepared polystyrene but considered that the process is initiated by mild oxidation during polymerization and processing rather than by fragmentation of in-chain peroxides.

Most studies of the emission from polymers have so far been limited to qualitative and semiquantitative observations and no indication has been given of the concentration of the emitting groups. This study has aimed at using phosphorescence spectroscopy for (i) a quantitative determination of carbonyl group concentrations in commercial and laboratory prepared polystyrene, especially during photodegradation, and a correlation with changes in polymer molecular weight; (ii) a study of the emission properties of polystyrene polymerized under controlled concentrations of oxygen to ascertain the role of in-chain peroxides in the formation of carbonyl end-groups. The behaviour of polystyrene synthesized in the presence of oxygen has been further studied by photolysis in solution.

## EXPERIMENTAL

### *Materials*

(1) Commercial polystyrene (Dow Chemical Co: Styron 685) was extracted for 72 hr with methanol to remove antioxidants. The number average molecular weight, $\overline{M}_n$, determined using a Melabs membrane osmometer, was $1.52 \times 10^5$.

(2) Hydroperoxidized polystyrene was prepared by dissolving 1 g of extracted Styron and 0.06 g of azobisisobutyronitrile (AIBN) in benzene and maintaining the solution at 70° while bubbling with oxygen. After oxidation for 45 min the polymer was twice precipitated and stored at $-20°$. Iodometric determination [8] gave a hydroperoxide concentration of $8.4 \times 10^{-3}$ mol/l., or, since $\overline{M}_n = 9.8 \times 10^4$, about 0.8 hydroperoxide groups per number average chain.

(3) Styrene–oxygen copolymers were prepared by polymerization of styrene under controlled concentrations of oxygen. Styrene, purified by washing with dilute alkali and vacuum distillation, was degassed and distilled into break-seal tubes on a vacuum line. The styrene was introduced into the evacuated reaction vessel and the AIBN initiated polymerization carried out at 60° to approximately 10%

conversion whilst stirring vigorously and bubbling continuously with oxygen–nitrogen mixtures of known oxygen content. The pressure above the polymerizing styrene was kept constant so that, allowing for the vapour pressure of styrene, the sum of the oxygen and nitrogen partial pressures remained at 10 mmHg throughout the reaction. Oxygen partial pressures in the range $10^{-4}$–$10^{-1}$ mmHg were used. The polymers were purified by repeated precipitation of toluene solutions from methanol and stored in the dark at $-20°$. These conditions ensured minimum decomposition of in-chain peroxide linkages.

(4) 1,3-Diphenylpropan-1-one (DPP) was the central zone refined fraction from a previous synthesis [2]. Films doped with DPP were obtained by evaporation of a toluene solution of polystyrene and DPP; the actual DPP concentration was measured by absorption spectrophotometry.

*Photo-oxidation*

Films of 15 $\mu$m thickness were cast from a 16 g/l. solution of the appropriate polymer in benzene and residual solvent removed under vacuum. These films were positioned at 200 mm from a 300 W Philips G74 mercury–tungsten–phosphor (MBTF) lamp and, after exposure, were dissolved in toluene and the viscosity average molecular weight ($\bar{M}_v$) determined by dilution viscometry at 30° using the values [9a] of $K = 1.10 \times 10^{-2}\,\mathrm{cm^3\,g^{-1}}$ and $a = 0.725$ in the Mark–Houwink equation.

Solution photo-oxidation and vacuum photolysis of the styrene–oxygen copolymers were carried out in a combined photolysis cell and viscometer. The apparatus was similar for each experiment except that for photo-oxidation the cell was connected to a supply of oxygen and the solution stirred vigorously with a magnetic stirrer; for vacuum photolysis the apparatus incorporated a side-arm for degassing the solution by the freeze–thaw method. A collimated beam from a 150 W xenon arc (dose rate approximately $5 \times 10^{15}$ quanta sec$^{-1}$ at 330 nm) was used for photolysis of a 10 g/l. solution of the polymer in benzene. The change in $\bar{M}_v$ of the polymer during photo-oxidation or vacuum photolysis was determined from single point viscosity measurements at 25°C using the Huggins equation, $\eta_{sp}/c = [\eta] + [\eta]^2 kc$, and the values [9b] of $K = 1.13 \times 10^{-2}\,\mathrm{cm^3\,g^{-1}}$ and $a = 0.73$ in the Mark–Houwink equation. The Huggins constant, $k$, was determined by dilution viscometry. Chain scissions were approximated by $(\bar{M}_v^0/\bar{M}_v) - 1$, where $\bar{M}_v^0$ refers to the unexposed sample. Using the combined photolysis cell and viscometer, the chain scissions occurring during photolysis were determined using only a small sample of polymer.

Solution photo-oxidation was also performed using a large photo-chemical reactor with a central medium pressure mercury arc (Osram 125 W) separated from a 10 g/l toluene solution of the polystyrene by a Pyrex water jacket. The solution was vigorously stirred and oxygen bubbled in prior to and during exposure. At intervals, 10 ml of solution was withdrawn and diluted; the concentration of the solution was checked by differential refractometry using a Zeiss interferometer. The number average molecular weight of the sample was determined by membrane osmometry and chain scissions were calculated as $(\bar{M}_n^0/\bar{M}_n) - 1$, where $\bar{M}_v^0$ refers to the unexposed polymer. Due to the large polymer sample required, this method was only used for the commercial polystyrene.

*Emission spectroscopy*

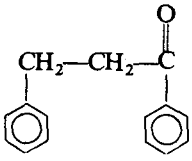
Quantitative phosphorescence spectra were obtained at 77°K using apparatus previously described [2]. A small cryostat was used for vacuum photolysis of films at controlled temperatures with subsequent emission measurement. In this case the emission was gathered at an angle of 45° from the excitation beam and separated by a single blade chopper rotating at from 10 to 80 Hz. The sample was held in contact with a copper cooling block, the temperature of which could be varied from 77°K to 400°K by heating with embedded resistors. For experiments in which the polymer sample was photolysed at 77°K and then warmed prior to emission measurement, the sample was held at the required temperature for 10 minutes before recooling to 77°K.

For estimation of the absolute carbonyl group concentration, the total immersion system with back-face observation was used.

## RESULTS AND DISCUSSION

### 1. *Emission from polystyrene*

A typical emission spectrum of polystyrene and the changes occurring on photo-oxidation are shown in Fig. 1. During photo-oxidation by the MBTF lamp, there is a marked growth in the structured emission attributed to the end-of-chain aromatic carbonyl group. The total emission observed consists of a broad underlying band ($\lambda_{max} \simeq 460$ nm) previously tentatively assigned to the triplet excimer [2] upon which is built the structured carbonyl emission. On photo-oxidation, the growth in carbonyl group concentration results only in a change in the spectral intensity distribution of the vibronic bands of the carbonyl emission. The underlying phenyl excimer emission remains unchanged. After extensive oxidation, the phosphorescence spectral intensity distribution (Fig. 1) approaches that of the model compound 1,3-diphenylpropan-1-one (DPP).



DPP

Using DPP as a phosphorescence standard, the concentration of end-of-chain aromatic carbonyl groups can be obtained quantitatively. In order to correlate the emission intensity of polystyrene with concentration, several experimental requirements must be met.

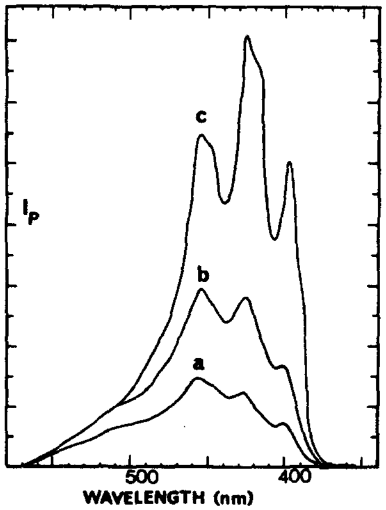
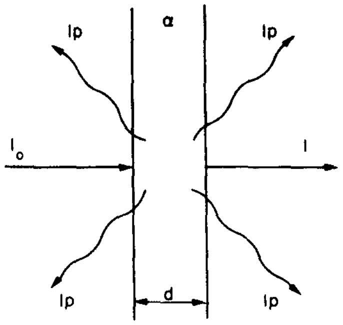


Fig. 1. The phosphorescence spectrum of polystyrene. (a) commercial, extracted with MeOH; (b) photo-oxidized 144 h; (c) doped with $10^{-2}$ mol/l. 1,3-diphenylpropan-1-one (DPP).



Assuming monochromatic light, intensity $I_0$, incident normally on a film of thickness $d$ and absorption coefficient $\alpha$ at the incident wavelength, the light absorbed, $I_a$, is given by

$$I_a = I_0[1 - \exp(-\alpha d)].$$

If a constant fraction, $k$, of the emitted light is detected by the emission apparatus as $I_p$, then

$$I_p = k\,\phi_p\,I_a$$

where $\phi_p$ is the emission quantum yield.

i.e. $I_p = k\,\phi_p I_0[1 - (1 - \alpha d + \alpha^2 d^2 - \ldots)]$

$$\simeq k\,\phi_p\,I_0\,\alpha d$$

since $\alpha d \ll 1$ for the thin films used in these experiments.

Since $\alpha = 2.303\,\epsilon\,c$, where $\epsilon$ is the molar extinction coefficient, the carbonyl concentration, $c$, is given by

$$c = \frac{I_p}{2.303\,k\phi_p I_0 \epsilon d}. \qquad (1)$$

The constants in Eqn. 1 may be evaluated using polystyrene doped with known amounts of DPP as a standard. $I_p$ was measured as the intensity of the first vibronic band at 398 nm after subtraction of the initial emission.

The experimental arrangement was chosen so that normal incidence was used for the excitation beam and the delayed emission gathered from the back face of the sample mounted in a holder with a fixed aperture. All samples were measured under the same conditions as the standards containing DPP so that

$$c = k'\,I_p/d$$

where $k'$ represents the accumulated constants from Eqn. 1. The assumption was made from spectroscopic evidence that $\phi_p$ and $\epsilon$ are identical for the polystyrene aromatic carbonyl and the DPP-doped polystyrene. The calibration curve for polystyrene containing DPP over the concentration range $10^{-3}$–$10^{-2}$ mol/l. (for which $\alpha d \ll 1$) is shown in Fig. 2. The relationship is linear throughout this range. This calibration was used to express the phosphorescence spectra of the photo-oxidized polystyrene in terms of the increase in carbonyl group concentration (Fig. 3).

Due to the underlying excimer emission, the concentration of carbonyl groups in the polystyrene prior to photo-oxidation was more difficult to obtain quantitatively. However, it was determined using the known intensity distribution of the excimer emission [2] and the DPP emission (Fig. 1). At 398 nm the carbonyl emission accounted for 80% of the total measured intensity, corresponding to $I_p/d = 0.04$. From Fig. 2 this is equivalent to a concentration of $1.05 \times 10^{-3}$ mol/l. of DPP in polystyrene or 0.14 carbonyl groups per number average chain prior to photo-oxidation, the origin of which is discussed in Section 3.

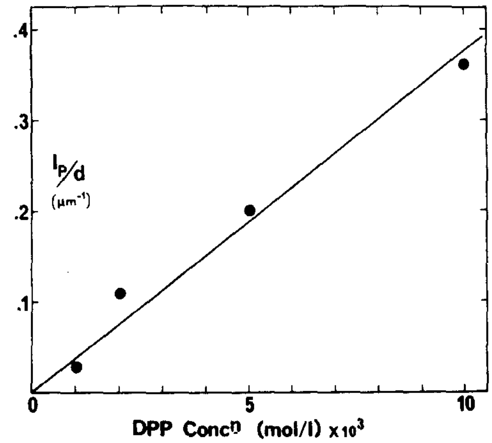


Fig. 2. Dependence of phosphorescence intensity corrected for thickness ($I_p/d$) on DPP concentration.

### 2. *Polymer molecular weight and carbonyl concentration changes on photo-oxidation*

The change in $\overline{M}_v$ of the polystyrene during photo-oxidation by the MBTF lamp was used to calculate the number of polymer chain scissions per molecule, $S$, (Table 1), using the expression $(\overline{M}_v^0/\overline{M}_v) - 1$. This expression will be equivalent to $S$ as measured by $\overline{M}_n$ provided the ratio $\overline{M}_v/\overline{M}_n$ is unaltered during the degradation. Also shown in Table 1 are the changes in carbonyl concentration for various oxidation times as taken from Fig. 3. A plot of the data in Table 1 for polymer chain scissions vs carbonyl concentration produced a straight line passing through the origin giving the empirical relation, $S = 110$ [$>$C=O].

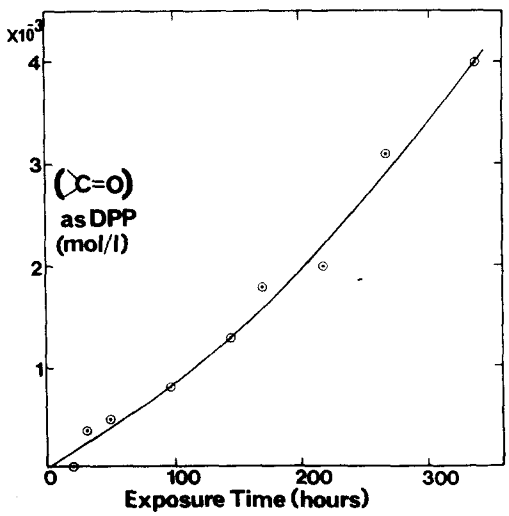


Fig. 3. Growth in carbonyl group concentration in 15 μm polystyrene film as determined by phosphorimetry with time of photo-oxidation (MBTF lamp exposure).

Table 1. Exposure of 15 μm polystyrene films to the MBTF lamp (dose rate 0.65 kW/m² total; u.v. 300–400 nm 0.04 kW/m²). Change in molecular weight and concentration of end-of-chain carbonyl (by phosphorimetry—Fig. 3)

| Exposure time (hr) | $[\eta]_0$ | $\overline{M}_v \times 10^{-5}$ | $S = (\overline{M}_v^0/\overline{M}_v) - 1$ | $\Delta[>C{=}O]$ as DPP × $10^3$ mol/l. |
|---|---|---|---|---|
| 0 | 88.30 | 2.427 | 0 | 0 |
| 65 | 85.27 | 2.316 | 0.048 | 0.6 |
| 112 | 82.03 | 2.196 | 0.105 | 0.98 |
| 163 | 77.84 | 2.042 | 0.188 | 1.54 |
| 210 | 76.49 | 1.991 | 0.219 | 2.08 |
| 322 | 66.87 | 1.67 | 0.45 | 3.8 |

Using this relationship, it is possible to calculate the number of aromatic carbonyl groups produced per chain scission on photolysis. With $\overline{M}_n = 1.52 \times 10^5$ and $1.05\,\mathrm{g\,cm^{-3}}$ as the density of polystyrene, the concentration of carbonyl groups in molecules per number average chain, $C$, is given by

$$C = [>\mathrm{C{=}O}] \Big/ \frac{1.05 \times 10^3}{1.52 \times 10^5}$$

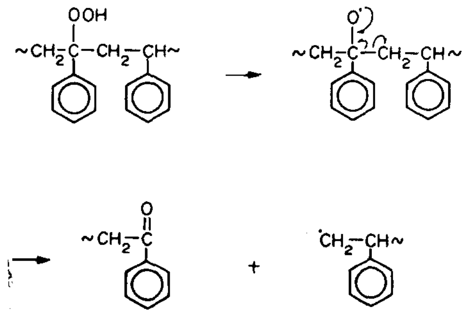
so that the number of carbonyl groups produced for each chain scission is

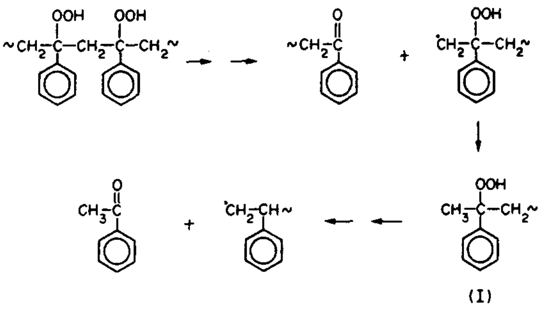
$$C/S = 1.31.$$

Since each chain scission forms two new end-groups, this corresponds to 0.65 carbonyl groups for each new end-group. When the errors inherent in this analysis are considered (both in the precision of measuring phosphorescence intensities and polymer chain scissions), this result is in reasonable agreement with the value of 0.5 expected from the reaction scheme for polymer chain scission by alkoxy radical fragmentation after hydroperoxide thermolysis or photolysis (Scheme 1).

There is evidence that intramolecular propagation can occur in the thermal and photochemical oxidation of polystyrene solutions[10,11] leading to the formation of sequences of hydroperoxides on adjacent tertiary carbon atoms. In this case, after the reaction of Scheme 1 above, the alkyl radical may abstract hydrogen[10] from the hydroperoxide, or some other suitable hydrogen donor leading ultimately to the hydroperoxide (I) (Scheme 2). Fragmentation of the alkoxy radical from this hydroperoxide results in the formation of acetophenone.

Elimination of acetophenone will not alter the molecular weight compared with the simple reaction in Scheme 1 but it will be detected by the phosphorescence technique since the phenyl alkyl ketone end-group and acetophenone have identical spectra. This could explain a value of greater than 0.5 carbonyl groups per new end-group on chain scission. The volatility of the acetophenone produced makes the analysis uncertain and no definite conclusions can be drawn as to the extent of intramolecular propagation and formation of adjacent hydroperoxides by this technique.


Scheme 1.



Scheme 2.

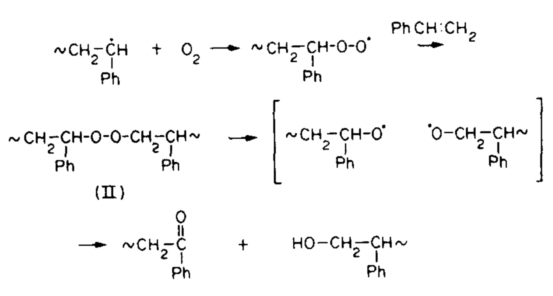
In addition, photolysis of terminal aromatic carbonyl groups by Norrish I and II processes, reactions which are highly probable at the wavelengths used, could lead after further reaction with oxygen to the formation of additional aromatic carbonyl groups without a detectable chain scission.

The significant conclusion to be drawn from the relation between carbonyl concentration and the change in molecular weight on photo-oxidation is that the alkoxy radical fragmentation is the predominant route for chain scission.

### 3. *The origin of carbonyl groups in undegraded polystyrene*

In section 1 the concentration of carbonyl end-groups in polystyrene prior to photo-oxidation was measured. As mentioned in the Introduction, two distinct routes have been proposed for the origin of these carbonyl groups; the decomposition of in-chain peroxides and the decomposition of polymer hydroperoxides.

(i) In-chain peroxide linkages may be formed during the synthesis of polystyrene by reaction of residual oxygen with the growing polystyrenyl radical (Scheme 3). Thermal decomposition of the in-chain peroxide (II) during polymerization and processing produces an alkoxy radical pair which, on disproportionation, gives the end-of-chain aromatic carbonyl group [2]. The above carbonyl concentration would suggest an



Scheme 3.

initial oxygen mole fraction of less than $10^{-4}$ in the styrene monomer.

(ii) Polymer hydroperoxides may form as a result of mild oxidation during polymerization and processing of polystyrene. Thermal decomposition of these hydroperoxides can lead to the end-of-chain aromatic carbonyl group by fragmentation of the alkoxy radical according to Scheme 1.

To show that the measured concentration of carbonyl groups present in polystyrene which has not apparently undergone photo-oxidation could arise via the first mechanism, polymerizations were carried out under various partial pressures of oxygen and the behaviour of the polymers on photolysis examined. The AIBN initiated polymerizations were performed in the presence of low partial pressures of oxygen ($10^{-4}$–$10^{-1}$ mmHg) and the synthesis, purification and storage of the products carried out under conditions which would lead to a minimum decomposition of in-chain peroxide linkages. The formation of styrene–oxygen copolymers in free radical polymerizations in the presence of oxygen has been well established and the copolymers have been characterized by degradation product analysis, DTA and dielectric measurements [12,13]. Previous studies have utilized relatively high oxygen partial pressures ($>0.5$ mmHg) for preparation of the copolymers. In the present study, much lower oxygen partial pressures were used, which would lead to the incorporation of very low amounts of oxygen and would better simulate the commercial synthesis. For comparison hydroperoxidized polystyrene prepared as described before was also studied.

Examination of the emission properties of these two types of polystyrene showed that it was possible to distinguish between the presence of in-chain peroxide linkages and hydroperoxide groups. The polystyrene samples synthesized in the presence of oxygen showed very low emission intensities in the carbonyl region and it was concluded that the carbonyl concentration in these polymers was $\ll 10^{-3}$ mol/l. Photolysis at 77°K in liquid nitrogen produced no change in the emission intensity. However, when the photolysed samples were warmed to room temperature without further irradiation, recooled, and the emission measured again, a rapid increase in the intensity was observed. These results are shown in Fig. 4 for the samples prepared under $10^{-1}$ and $10^{-3}$ mmHg of oxygen. Long term photolysis and subsequent warming produced only a slight increase in the emission intensity. The final concentrations of carbonyl groups, measured as DPP, obtained from this experiment were $2.2 \times 10^{-3}$ and $1.8 \times 10^{-3}$ mol/l. for the two samples respectively.

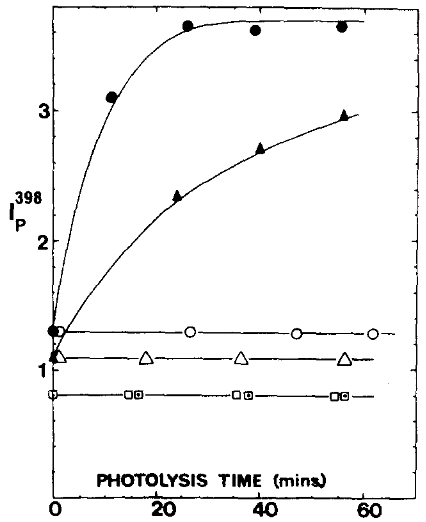


Fig. 4. Phosphorescence intensity from styrene–oxygen copolymers and hydroperoxidized polystyrene measured at 398 nm. (i) Photolysed at 77°K without warming, □ hydroperoxidized polystyrene; ○ polystyrene prepared under $10^{-1}$ mmHg $O_2$; △ polystyrene prepared under $10^{-3}$ mmHg $O_2$. (ii) Photolysed at 77°K, warmed to 290°K and recooled to 77°K, ▣ hydroperoxidized polystyrene; ● polystyrene prepared under $10^{-1}$ mmHg $O_2$; ▲ polystyrene prepared under $10^{-3}$ mmHg $O_2$.

These observations indicate the presence of a photolabile group which, on warming, leads to the formation of aromatic carbonyl groups. This phenomenon of carbonyl growth on warming will be discussed in the next Section. Assuming that one carbonyl group is produced for each chain scission (Scheme 3), this corresponds to approximately 0.2 chain scissions per molecule. It is interesting that the two polymer samples prepared under such different oxygen pressures produced similar results.

To test if these results could be explained by hydroperoxide formation during synthesis rather than by in-chain peroxides, the phosphorescence behaviour of hydroperoxidized polystyrene after photolysis was examined under conditions equivalent to those used above. The results were found to differ from those for the polystyrene samples prepared in the presence of oxygen and are shown in Fig. 4. The hydroperoxidized polystyrene was found to have a higher initial carbonyl concentration which is consistent with it having been prepared from commercial polystyrene and also indicates some thermal decomposition of the hydroperoxides occurred in the oxidation reaction. An increase in carbonyl group concentration was detected by phosphorescence only after vacuum photolysis of the hydroperoxidized polystyrene at temperatures greater than 273°K.

The difference in phosphorescence behaviour of the two types of polystyrene on photolysis indicates the presence of different photolabile groups in the polymer samples. The carbonyl groups obtained on photolysis of the polystyrene prepared in the presence of oxygen do not arise from photolysis of hydroperoxides and the results are consistent with the disproportionation of in-chain peroxides.

The presence of in-chain peroxides in polystyrene and the extent to which they are produced was further

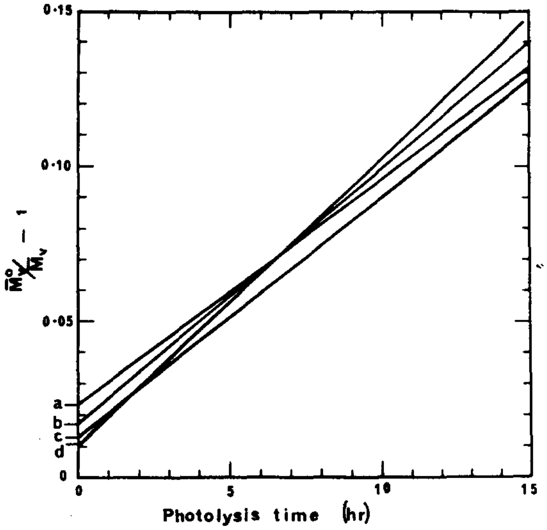


Fig. 5. Photo-oxidation of polystyrene in solution. Chain scission vs photolysis time for polystyrene prepared in the presence of oxygen. (a) Prepared under $10^{-1}$ mmHg $O_2$; (b) prepared under $10^{-2}$ mmHg $O_2$; (c) prepared under $10^{-3}$ mmHg $O_2$; (d) prepared under $10^{-4}$ mmHg $O_2$.

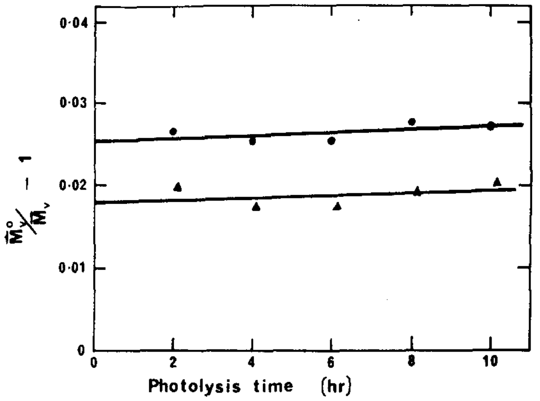


Fig. 7. Vacuum photolysis of polystyrene in solution. Chain scissions vs photolysis time for polystyrene prepared in the presence of oxygen. ● polystyrene prepared under $10^{-1}$ mmHg $O_2$; ▲ polystyrene prepared under $10^{-2}$ mmHg $O_2$.

investigated by photolysis in solution. In these experiments photo-oxidation and vacuum photolysis of the polymer in benzene solution was carried out in a combined photolysis cell and viscometer. The molecular chain scissions (expressed as $(\overline{M}_v^0/\overline{M}_v) - 1$) were measured as a function of photolysis time.

The solution photo-oxidation of the series of polystyrene samples prepared under differing concentrations of oxygen is shown in Fig. 5. Each produced a non-zero intercept on the chain scission axis and, although the rates of chain scission vary, it can be seen that the height of the intercept increases with increasing amount of oxygen present in the synthesis. Lawrence and Weir [7] have suggested that this non-zero intercept is due to the rapid photolysis of in-chain peroxides followed by slower photo-oxidation of the polymer. Examination of the early stages of photo-oxidation for one of the polymer samples confirms that the chain scission plot rises steeply in the initial stages of photolysis and then flattens out to the photo-oxidation line (Fig. 6). On photolysis *in vacuo*, the same intercepts were observed for two of the polymer samples and very little increase in chain scissions was observed on extended photolysis (Fig. 7). These two sets of observations are consistent with the explanation of Lawrence and Weir for the non-zero intercepts. Further examination of the intercepts of Fig. 5 shows that, as the partial pressure of oxygen present in the synthesis decreases, the intercept tends to a value in the vicinity of 0.005 rather than zero. This might indicate that some other photolabile group is produced, the amount of which is independent of the oxygen pressure.

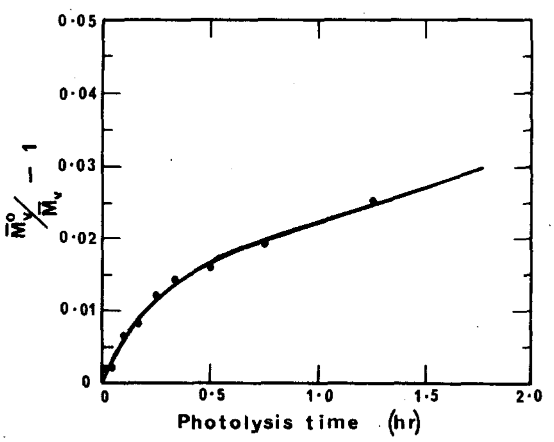
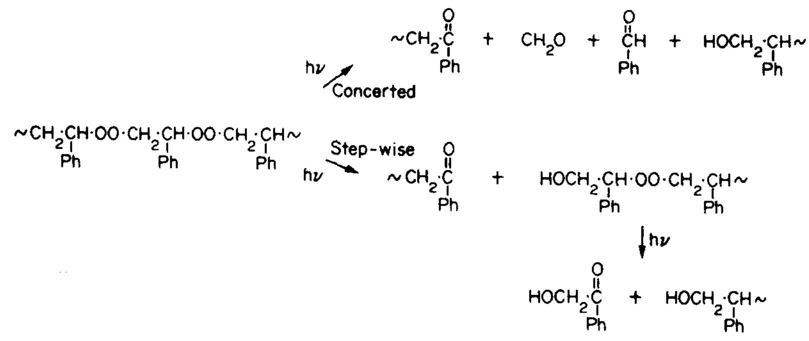


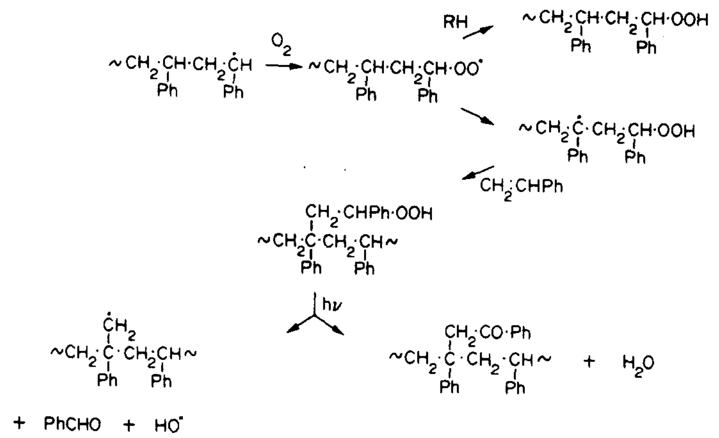
Fig. 6. Early stages of the relationship between chain scissions and photolysis time for the solution photo-oxidation of polystyrene prepared under $10^{-1}$ mmHg $O_2$.

For the polystyrene prepared under $10^{-1}$ mmHg of oxygen, the number of chain scissions per molecule due to the photolysis of peroxide linkages was found during photo-oxidation in solution to be approximately 0.02 whilst that found from carbonyl concentration by phosphorescence on photolysis *in vacuo* was approximately 0.2. Several factors could contribute to this discrepancy between the two methods. One is the use of viscosity data for the measurement of chain scissions. (If the molecular weight distribution broadens on photolysis, use of $\overline{M}_v$ instead of $\overline{M}_n$ will lead to a low value of *S*.) A more likely explanation is that in the phosphorescence method it was assumed that each carbonyl group arises from a chain scission. This is not necessarily the case. If blocks of peroxide linkages are formed, one chain scission may lead to the formation of several carbonyl groups (Scheme 4). Also, terminal hydroperoxide groups may be produced by hydrogen abstraction (either inter- or intramolecularly) which, on photolysis, produce an aromatic carbonyl group without a chain scission (Scheme 5).

Photo-oxidation of a commercial sample of polystyrene was also investigated in solution and the concentration of residual peroxides found to be very low. A plot of chain scissions (measured as $(\overline{M}_n^0/\overline{M}_n) - 1$) against photolysis time (Fig. 8) passed through the origin. This is consistent with the observation of Rabek and Ranby [14] who reported no zero intercept chain scissions for the vacuum photolysis of a commercial polystyrene sample, and suggests that rapid thermolysis of any peroxide linkages occurs at



Scheme 4.



Scheme 5.

the high temperature of the commercial synthesis. This was confirmed by heating under vacuum at 135° a sample of the polystyrene prepared under $10^{-1}$ mmHg of oxygen. After heating for 6 hr at this temperature, the photo-oxidation plot now passed very nearly through the origin (Fig. 9). Thermolysis of the in-chain peroxides will lead to the same aromatic ketones produced on their photolysis (Scheme 3) and since photolysis of these peroxides occurs rapidly in the early stages of photo-oxidation (see Fig. 6) both the heated and unheated samples of polystyrene show the same rates of photo-oxidation as seen from the approximately parallel plots in Fig. 9. Using the values of $\bar{M}_v$ obtained for the heated and

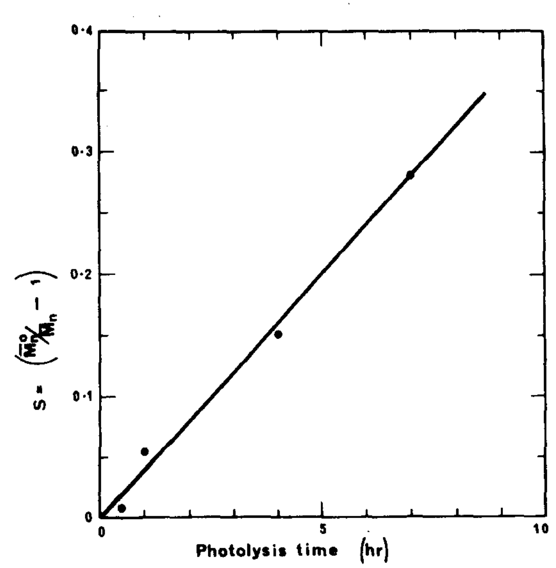


Fig. 8. The relationship between chain scissions and photolysis time for the photo-oxidation of commercial polystyrene in solution.

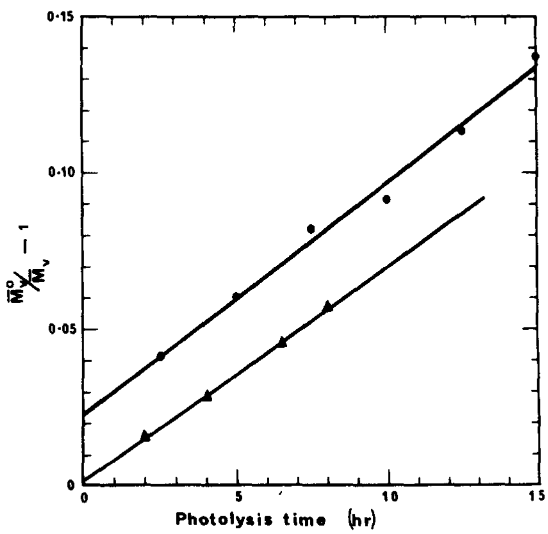


Fig. 9. Photo-oxidation of polystyrene prepared in the presence of oxygen. Effect of prior heating of the sample on the intercept in the chain scission vs photolysis time plot. ● Polystyrene prepared under $10^{-1}$ mmHg $O_2$, before heating; ▲ after heating *in vacuo* at 135° for 6 hr.

unheated samples of polystyrene, the number of chain scissions occurring on heating was found to be 0.058. Considering the large effect small errors in $\overline{M}_v$ will have on the value of $S$ (an error which does not occur in individual photo-oxidation runs), this is in reasonable agreement with the value of 0.023 obtained from the intercept of Fig. 9.

After initial photolysis or thermolysis of the in-chain peroxides, the photo-oxidation reaction is propagated by the photolysis of the aromatic ketones and subsequently formed hydroperoxides.

### 4. *Interpretation of the low temperature photolysis of styrene–oxygen copolymers*

The temperature required to form phenyl alkyl ketone groups after low temperature photolysis of the polystyrene samples prepared under $10^{-1}$ and $10^{-3}$ mmHg of oxygen was studied using a variable temperature cryostat. The results are shown in Fig. 10. A temperature of approximately 170°K was reached before there was significant change in the emission intensity.

Polystyrene shows a relaxation process by dielectric and mechanical methods (the $\gamma$ transition) in this temperature region [15]. This has been interpreted as due to the onset of phenyl group rotation but the interpretation is complicated by the enhancement of this peak in samples containing peroxides or low molecular weight impurities [13]. Guillet and coworkers [16] have observed that this temperature region corresponds to the onset of rapid decrease in phosphorescence intensity due to the enhanced mobility of small quenching molecules, such as oxygen, accompanying the relaxation process of polystyrene. Clearly, at temperatures below the $\gamma$-transition the formation or observation of carbonyl groups from the photolytic disproportionation of a peroxide linkage is inhibited. This could result from trapping of the caged alkoxy radicals before further reaction or re-combination. However, alkoxy radicals are extremely reactive at 77°K in glassy matrices and it could be expected that the disproportionation would occur rapidly at the temperature of photolysis.

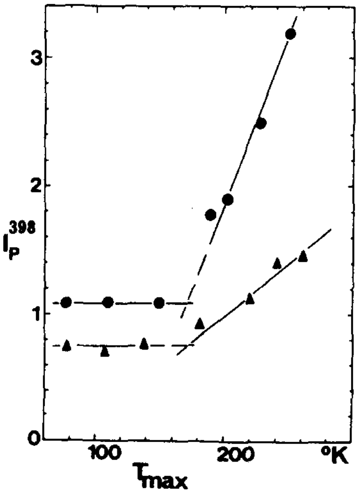
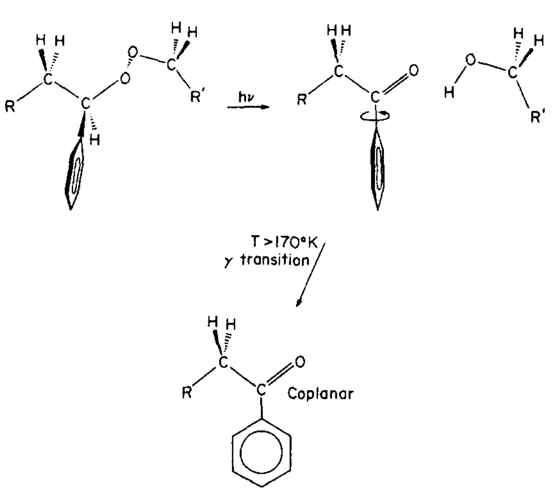


Fig. 10. Vacuum photolysis of polystyrene peroxides at 77°K. Phosphorescence intensity at 398 nm measured after warming to the indicated temperature and recooling to 77°K. ● Polystyrene prepared under $10^{-1}$ mmHg $O_2$; ▲ polystyrene prepared under $10^{-3}$ mmHg $O_2$.



Alternatively, the phenyl alkyl ketone end-groups are formed by disproportionation of the alkoxy radicals at 77°K but are formed in a constrained conformation such that the carbonyl group is not conjugated with the benzene ring. On warming to 170°K, rotation of the phenyl group allows formal conjugation to occur and characteristic aromatic carbonyl emission is observed.

Studies of paracyclophanes with 1-keto substituents have shown that, when the carbonyl group is constrained out of the plane of the benzene ring as in 1-keto [2,2]paracyclophane, the carbonyl group conjugation is destroyed [17]. The emission properties of phenyl alkyl ketones appear to be sensitive to the conformation of the substituent on the $\alpha$ carbon atom [18] although it has been noted that conjugation is retained when there is a small amount of non-planarity of carbonyl and phenyl groups.

If this interpretation is correct, it might be expected that a small proportion of carbonyl groups would have been formed coplanar with the benzene ring as the phenyl group would be expected to adopt no particular conformation with respect to the peroxide linkage. This would produce a small growth in carbonyl emission on photolysis at 77°K. There are, however, considerations of the steric interaction of adjacent phenyl groups, and in isotactic sequences at least the steric interactions between phenyl groups will result in an out-of-plane carbonyl group.

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