Photo-oxidation of polystyrene film: 1. Photo-oxidation of polystyrene films with light absorbed by polymer

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The photo-oxidation of polystyrene films irradiated with light absorbed by the polymer has been studied. The overall quantum yield of hydroperoxide as well as the relationship between the concentration of acetophenone-type carbonyl products and α,β-enone and diketone products were found. The spatial distribution of the different types of carbonyl products was investigated.

INTRODUCTION

Several authors[1–4] have assumed that the initiation of the photo-oxidation of polystyrene occurs with the formation of polystyryl radicals followed by the production of hydroperoxides. Wall *et al.*[5] showed that the stationary concentration of hydroperoxides in photo-oxidized PS films is low and that these compounds are very reactive.

Carbonyl compounds, alcohols and polyenes are considered to be the secondary molecular products of the photo-oxidation process[1–7]. Several attempts have been made to evaluate the contribution of the two types of reaction occurring in irradiated PS samples. The first takes place at the ends of polymer chain and gives rise to low molecular weight products. The second, occurring along the polymer chains, leads to the formation of long chain products. Results obtained by various authors[7–10], however, are not consistent.

EXPERIMENTAL

Polystyrene was prepared by thermal polymerization of styrene at 80°C for 450 h. The polymer was purified by dissolving three times in chloroform and precipitating with methanol. The product was Soxhleted with methanol for 85 h. Thin films of polystyrene were prepared of thickness 0.003 mm and mass 2.5×10^{-3} g.

The polymer films were irradiated in air at atmospheric pressure with the full spectrum of an ASH 400 medium pressure mercury lamp. The radiation density at 254 and 265 nm was 2.5×10^{-9} einstein/cm^2 sec.

The modified Carlsson and Wiles[11] iodometric method was used to evaluate the concentration of hydroperoxides. Several films were irradiated, each for the same period of time and then heated in a solution of NaI in isopropyl alcohol and acetic acid[11]. Nitrogen was passed through the reaction apparatus[12]. The concentration of I_3^- ions was measured spectrophotometrically at 360 nm with a Zeiss VSU 2P spectrophotometer.

Low molecular weight products were extracted from the irradiated films with methanol[12].

Ultra-violet spectra of films and ethanol extracts were recorded with a Zeiss Specord UV VIS spectrophotometer.

Samples for i.r. analysis were prepared by irradiation of six films (0.003 mm thick) each for the same length of time. These were then joined together and placed between the two KBr plates. I.r. absorption spectra were recorded with a Zeiss UR 20 spectrophotometer with two KBr plates of the same thickness as the reference.

Preparation of PS films with the addition of model carbonyl compounds has been described in the previous paper[13].

RESULTS AND DISCUSSION

It was found by iodometric analysis that long time irradiation of PS films with light at a frequency absorbed by the polymer results in an increase in the hydroperoxide concentration and that after several hours of irradiation (from 8 to 14 h) reaches a value of about 10^{-2} mol/dm^3. The overall quantum yield of hydroperoxide is of the order of $\sim 10^{-4}$ mol/einstein. The low values of the hydroperoxide extinction coefficients in the u.v. and i.r. regions made precise measurements of the absorption changes due to the presence of these compounds in thin PS films impossible.

U.v. and i.r. spectroscopy, however, allowed us to monitor the formation of carbonyl photo-oxidation products.

I.r. absorption spectra of carbonyl products of PS photo-oxidation, calculated by the comparison method[14] (key band at 1582.5 cm^{-1}) are shown in *Figure 1*. I.r. absorption

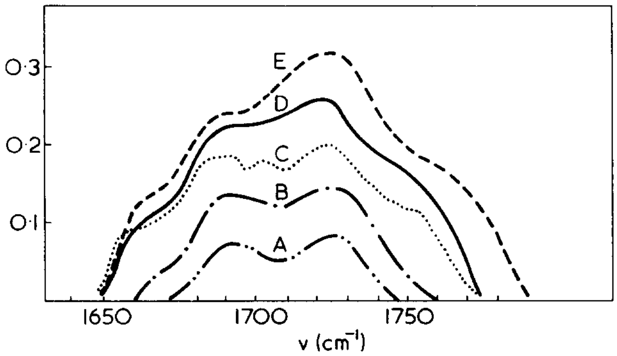

Figure 1 I.r. absorption spectra of PS samples irradiated with light absorbed by polymer for various times. A, 40 min; B, 60 min; C, 120 min; D, 180 min; E, 240 min

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spectra of PS films containing low molecular weight carbonyl compounds, chosen to model the most likely carbonyl products of PS photo-oxidation[13], were recorded. The absorption maxima of these compounds are indicated in *Figure 2*.

U.v. absorption spectra of irradiated PS film and ethanol extracts from exposed films, recorded after various times of irradiation, are shown in *Figures 3* and *4*[15].

Based on an analysis of the u.v. and i.r. absorption spectra three groups of carbonyl products of PS photo-oxidation were distinguished: (1) acetophenone-type compounds with the $>C=O$ group conjugated with a benzene ring (aph); (2) α,β-enones and diketones (E,α) and (3) compounds with an isolated carbonyl group.

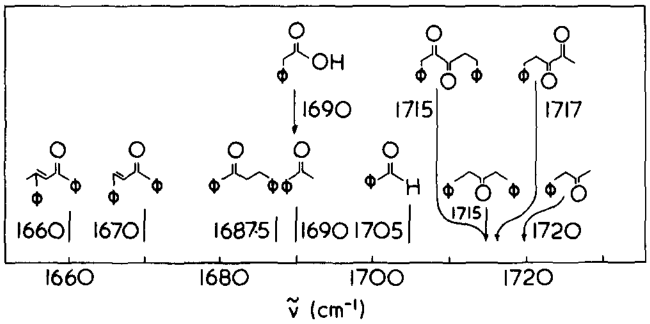

Figure 2 I.r. absorption band maxima for model low molecular weight carbonyl compounds included in PS film

The u.v. absorption spectra were then subjected to a closer examination. Compounds of type (3) are characterized by low extinction coefficients of about 10^2 dm/mol cm in the u.v. region analysed, and therefore their contribution to the measured absorption changes is negligible. The following extinction coefficients (in dm^3/mol cm) were assumed for the first two groups of carbonyl product.

	$\tilde{\nu}=41\,000$ cm^{-1}	$\tilde{\nu}=36\,000$ cm^{-1}	$\tilde{\nu}=33\,000$ cm^{-1}
$\bar{\varepsilon}^{aph}_{\nu}$	1.5×10^4	1.2×10^3	10^2
$\bar{\varepsilon}^{E,\alpha}_{\nu}$	1.5×10^4	1.5×10^4	2.5×10^4

Figure 5 shows the dependence of ratio of the absorptions at 41 000, 36 000 and 33 000 cm^{-1} on u.v. irradiation time. The values of these ratios decrease with time in different ways and become constant after about 2 h. Results obtained confirm the fact that various types of carbonyl products are formed at different photo-oxidation stages. Thus, for the times of irradiation when the ratio $A_{41\,000}/A_{33\,000}$ can be expressed as:

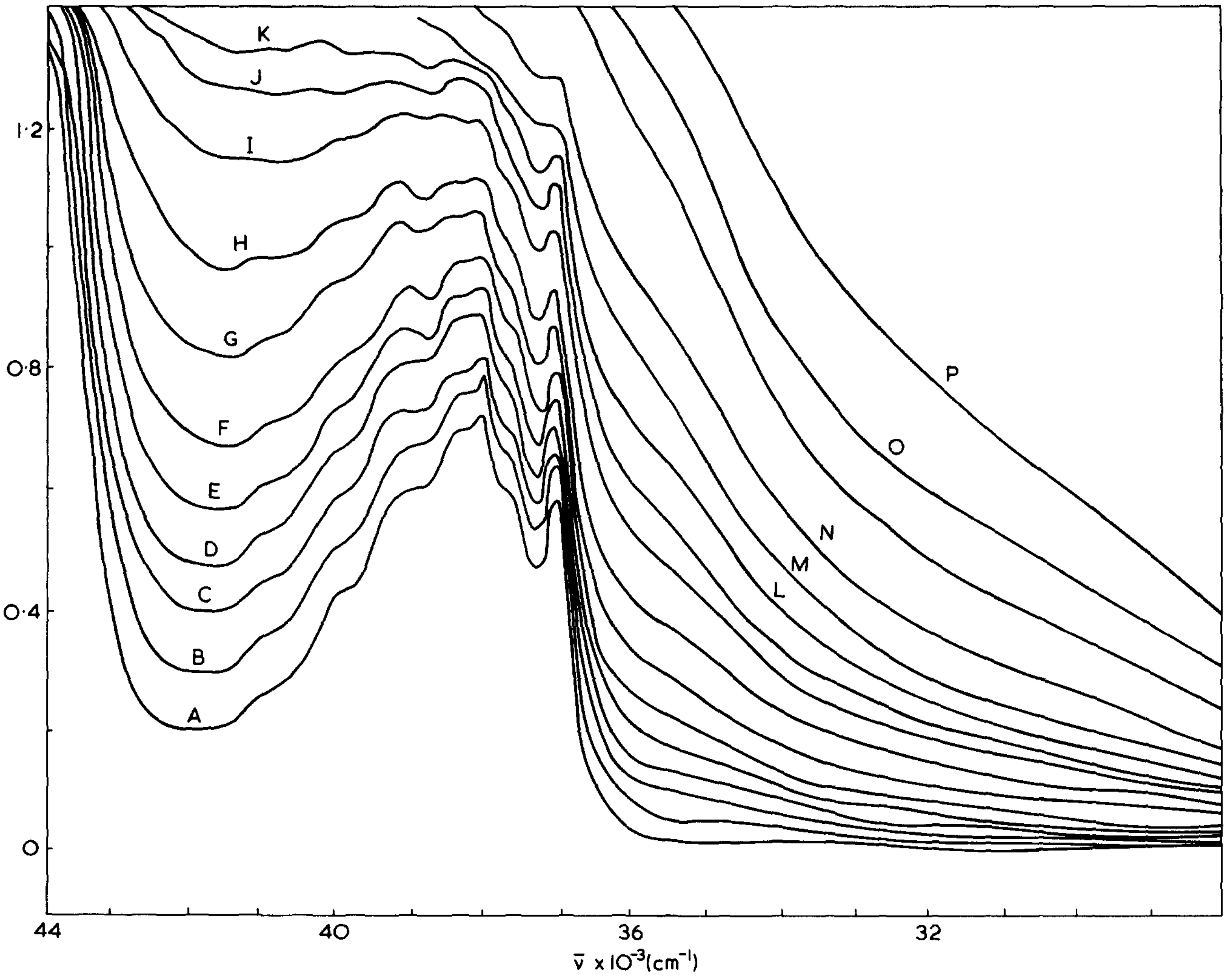

Figure 3 U.v. absorption spectra of PS film, recorded after different irradiation times, with air as reference. A, 0 min; B, 15 min; C, 3.5 min; D, 5 min; E, 8.5 min; F, 14 min; G, 23 min; H, 36 min; I, 54 min; J, 65 min; K, 89 min; L, 122 min; M, 195 min; N, 350 min; O, 755 min; P, 2300 min

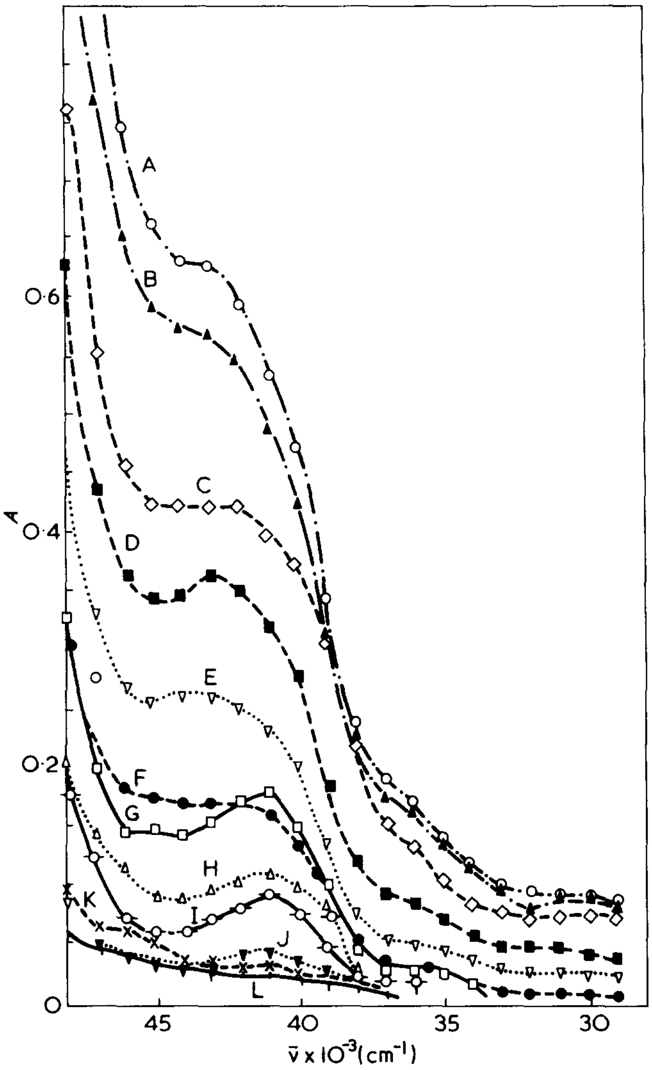

Figure 4 U.v. absorption spectra of low molecular weight photo-oxidation products extracted from PS films after various irradiation times. A, 240 min; B, 210 min; C, 180 min; D, 150 min; E, 120 min; F, 90 min; G, 60 min; H, 45 min; I, 30 min; J (▲), 15 min; K (x), 10 min; I (i), 5 min

$$\frac{A_{41\,000}}{A_{33\,000}} \approx \frac{1.5 \times 10^4\, c_{\mathrm{aph}} + 1.5 \times 10^4\, c_{\mathrm{E},\alpha}}{10^2\, c_{\mathrm{aph}} + 2.5 \times 10^4\, c_{\mathrm{E},\alpha}} \approx 6$$

the following relation is valid:

$$c_{\mathrm{aph}} \approx 9 c_{\mathrm{E},\alpha}$$

This means that after long times of irradiation of PS films the concentration of acetophenone-type products is about ten-fold greater than that of α,β-enone and dicarbonyl products. The effect of acetophenone-type compounds on the secondary reactions in irradiated PS samples has been studied in the previous paper[13].

In order to evaluate the distribution of the various types of carbonyl product inside, the photo-oxidized PS samples the following experiment was carried out. PS samples, consisting of 6 thin films (each of thickness 0.003 mm) coupled together, were irradiated for various times from 20 to 240 min. U.v. absorption spectra of each thin film were recorded before and after a given time of irradiation of the sample. Values of $\Delta A_{\tilde{\nu}}$ at $\tilde{\nu}$ = 41 000, 36 000 and 33 000 for thin films forming the sample irradiated for 1 h, dependent on their relative distances from the light source (expressed as consecutive film numbers) are indicated in *Figure 6*. The curves obtained describe the carbonyl product distribution in the PS sample, analysed along the direction of incident radiation. It is evident that the photo-oxidation process occurs mainly in the surface layer of the polystyrene sample if it is irradiated with light at a frequency absorbed by the polymer.

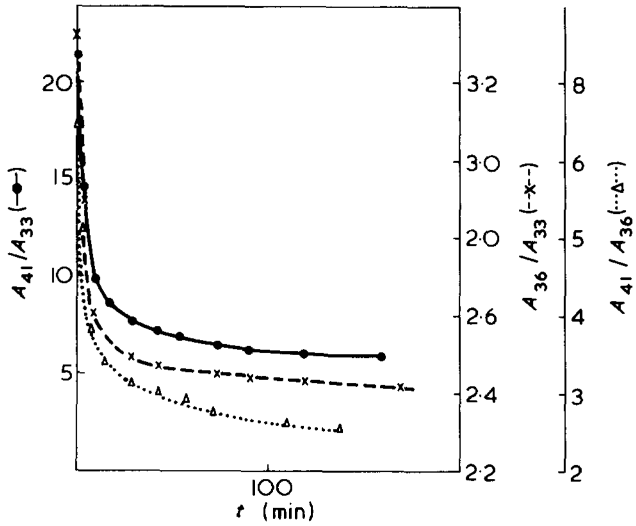

Figure 5 Dependence of ratios of absorptions at 41 000, 46 000 and 33 000 cm^{-1} on irradiation time for PS film.

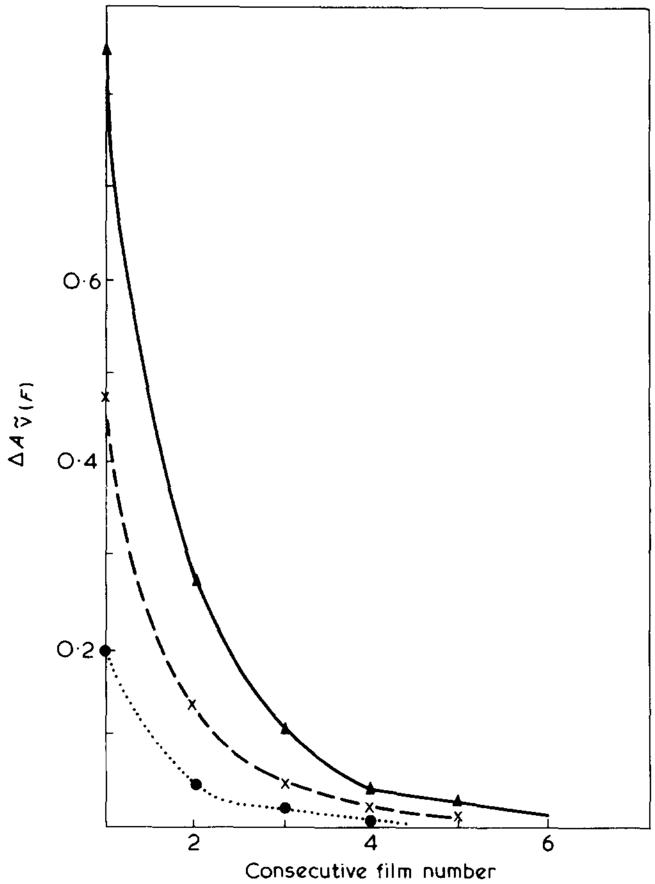

Figure 6 Dependence of the absorption of PS films at 41 000, 36 000 and 33 000 cm^{-1} on their relative distance from the light source for PS sample irradiated for 1 h. $\Delta A_{\tilde{\nu}}$ is the difference between the absorption before and after irradiation. ▲, 41 000; x, 36 000; ●, 33 000

Table 1

PS thin film number	Time of irradiation of PS samples (min)		
	20	60	100
	$c_{\text{aph}}/c_{\text{E},\alpha}$		
1	12.6	10.5	–
2	7.4	10.0	9.6
3	5.6	8.4	8.0
4	3.7	6.1	6.3
5	1.5	2.5	5.1

The ratios $A_{41\,000}/A_{33\,000}$ were found for each thin film forming the PS samples after given irradiation times. Taking into account the mean extinction coefficients of carbonyl products, the values of $c_{\text{aph}}/c_{\text{E},\alpha}$ were calculated. Sample data are summarized in *Table 1*.

It may be concluded that acetophenone-type products are formed in greater quantity in the surface layer than inside PS samples where the concentrations of dicarbonyl and enone products are comparatively higher.

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