

# Photo-oxidation of polystyrene film:

## 2. Photo-oxidation of polystyrene film with light absorbed by the polystyrene—oxygen complex

Maria Nowakowska, Joanna Kowal and Boleslaw Waligora

Department of Physical Chemistry and Electrochemistry, Institute of Chemistry, Jagiellonian University, 30-060 Kraków, Krupnicza 41, Poland  
(Received 28 April 1978)

Photo-oxidation of polystyrene films prepared from carefully purified polymer, irradiated with light absorbed only by a polystyrene—oxygen complex has been studied. It was found that photo-oxidation of polystyrene under such conditions results in carbonyl compound and hydroperoxide formation. Photo-oxidation of polystyrene with light of a frequency absorbed by the polystyrene—oxygen complex occurs throughout the whole volume of sample.

### INTRODUCTION

Pure polystyrene does not absorb long wave u.v. radiation ( $\lambda > 300$  nm) but nevertheless undergoes atmospheric deterioration. In order to describe the long wave u.v. photo-oxidation of commercial polystyrene we used a theory of the initiation of photo-oxidation by hydroperoxides and carbonyl compounds. Carbonyl compounds exhibiting  $n \rightarrow \pi^*$  type absorption bands in the range 300–360 nm can be responsible for the absorption of radiation from the spectral region in which the polymer itself does not absorb ( $\lambda > 300$  nm)<sup>1–6</sup>.

According to Rabek and Ranby singlet oxygen takes place in the initiation of pure polystyrene long wave photo-oxidation ( $\lambda > 280$  nm)<sup>7,8</sup>.

As shown in previous papers<sup>9,10</sup> the collision complex PS.O<sub>2</sub> is formed by polystyrene with oxygen. The absorption band induced in polystyrene by oxygen begins at  $\tilde{\nu} \approx 28\,000$  cm<sup>-1</sup> ( $\lambda = 357$  nm) and extends towards higher wavelengths. Thus the polystyrene—oxygen complex can absorb long wave radiation at  $\lambda > 300$  nm. Photo-oxidation of carefully purified polystyrene in the form of thin films irradiated with light absorbed only by the PS.O<sub>2</sub> complex has been studied in this paper.

### EXPERIMENTAL

Polystyrene, prepared as described in the first part of this paper, was investigated in the form of films varying in thickness from  $3 \times 10^{-4}$  to  $300 \times 10^{-4}$  cm. The samples were irradiated with a HBO-200 high pressure mercury lamp at  $\lambda > 300$  nm or  $\lambda = 313$  nm when Zeiss glass filters UG 10 and GG 10 were applied.

The films were placed in a pressure cell with two quartz optical windows 6 mm thick. U. v. and i.r. absorption spectra of the films were recorded after various irradiation times with Zeiss Specord UV VIS and UR 20 spectrophotometers, respectively. The fluorescence equipment used was described in the previous paper<sup>9</sup>.

### RESULTS AND DISCUSSION

Polystyrene films saturated with oxygen at high pressures were irradiated with light of a frequency absorbed only by polystyrene—oxygen complex ( $\lambda = 313$  nm or  $\lambda > 300$  nm). An increase of the absorption at  $\tilde{\nu} > 28\,000$  cm<sup>-1</sup> was observed under these experimental conditions. *Figure 1a* shows the absorption spectra of a polystyrene film recorded after various times of irradiation at  $\lambda > 300$  nm in the presence of oxygen at a pressure of 20 atm.

The aryl carbonyl compounds show strong absorption bands within the range 35 000–38 000 cm<sup>-1</sup> with a maximum at about 36 000 cm<sup>-1</sup> and a molar extinction coefficient of about 10<sup>3</sup> dm<sup>3</sup>/mol cm. The considerable absorption increase observed for  $\tilde{\nu} > 34\,000$  cm<sup>-1</sup> (see *Figure 1b*) can be explained by the formation of carbonyl compounds in the irradiated films.

I.r. spectra of a polystyrene film recorded after various times of irradiation under the same conditions are presented in *Figure 2*. The absorption changes within the range 1620–1800 cm<sup>-1</sup> confirms the formation of carbonyl products. A small increase in absorption at about 3400 cm<sup>-1</sup> connected with the presence of hydroperoxides was observed. The stability of hydroperoxides and the long times required for penetration of reagents made the iodometric method useless in the case of thick films.

It was found that the intensity of polystyrene excimer fluorescence decreases even after short periods of PS film irradiation. *Figure 3* shows the excimer fluorescence spectra of PS film irradiated with light at  $\lambda > 300$  nm in the presence of oxygen at a pressure of 20 atm for 0, 20, 40 and 60 min.

The decrease of polystyrene excimer fluorescence intensity can be explained by an energy transfer process from phenyl groups having a configuration suitable for excimer formation to molecules formed by PS photo-oxidation. There were no new fluorescence or phosphorescence bands which could indicate the presence of carbonyl compounds in irradiated PS films. Therefore the decrease of polystyrene

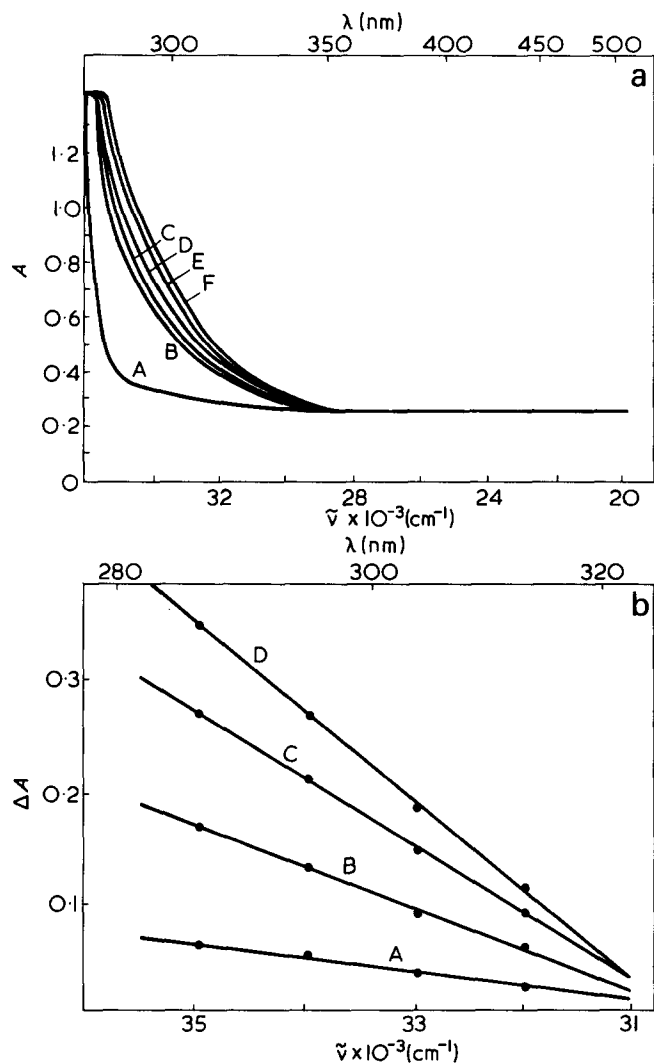


Figure 1 (a) U.v. absorption spectra of PS film. A, In the presence of oxygen under atmospheric pressure; B, in the presence of oxygen under a pressure of 20 atm and after irradiation for: C, 15 min, D, 30 min, E, 45 min, F, 60 min in the presence of oxygen under a pressure of 20 atm with light at  $\lambda > 300$  nm. (b) The absorption changes  $\Delta A$  vs. wavenumber,  $\tilde{\nu}$ , observed after various times of the PS film irradiation: A, 15 min; B, 30 min; C, 45 min; D, 60 min

excimer fluorescence intensity observed in the initial period of irradiation of PS films may be caused by the presence of hydroperoxides. One can conclude that hydroperoxides are the primary molecular products of polystyrene photo-oxidation with light absorbed by the  $PS.O_2$  complex.

Polystyrene films of various thickness (from 3 to  $300 \times 10^{-4}$  cm) in the presence of oxygen under a fixed pressure of 20 atm were irradiated with light at  $\lambda = 313$  nm. The dependence of the rate of change of absorption on the PS film thickness in the initial period of photo-oxidation,  $dA/dr$ , at  $\tilde{\nu} = 32\,000$   $cm^{-1}$  is shown in Figure 4 as an example.

The increase of rate of polystyrene photo-oxidation under such conditions due to an increase in the thickness of the polystyrene films suggests that polystyrene photo-oxidation with light absorbed only by the  $PS.O_2$  complex occurs throughout the whole volume of the polymer sample. This explains the failure to find the low molecular weight PS photo-oxidation products in thick films by the extraction method, used successfully in the case of thin PS samples.

CONCLUSIONS

From the results described in the two parts of this paper the following conclusions can be drawn.

- (a) Photo-oxidation of polystyrene films with light of a frequency absorbed by polymer and by the polystyrene-oxygen complex results in formation of the same type of products, hydroperoxides and carbonyl compounds.
- (b) The photo-oxidation process in PS films irradiated

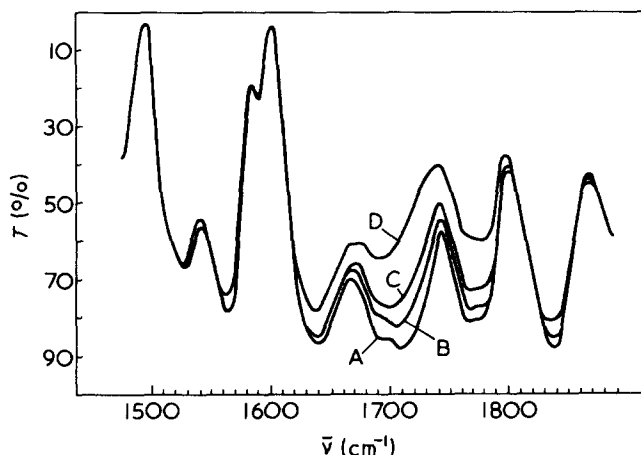


Figure 2 I.r. absorption spectra of PS film, recorded after various times of irradiation in the presence of oxygen under a pressure of 20 atm with light at  $\lambda > 300$  nm. A, before irradiation; B, 1 h; C, 8.5 h; D, 15 h of irradiation

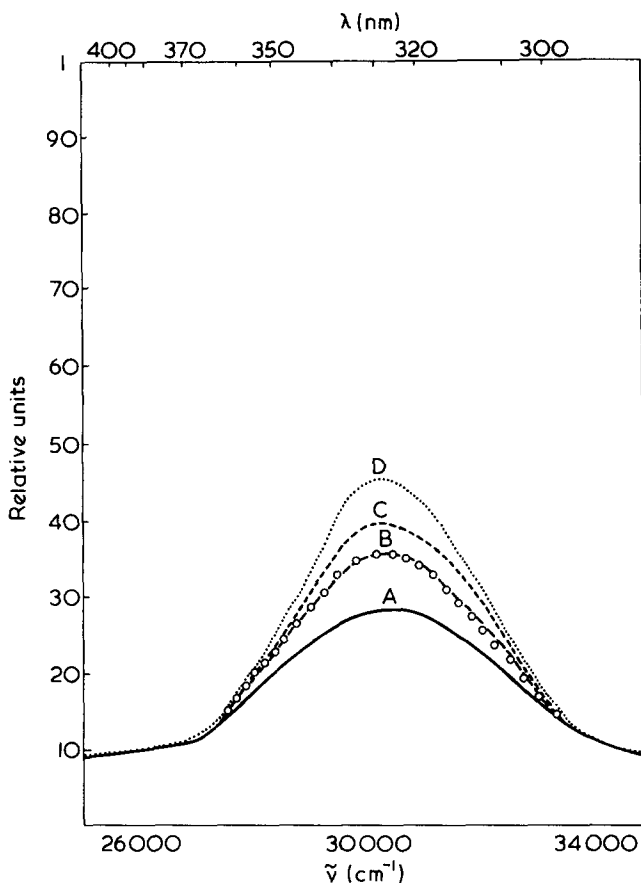


Figure 3 Excimer fluorescence spectra of PS film measured after various times of PS film irradiation in the presence of oxygen at a pressure of 20 atm with light at  $\lambda > 300$  nm: A, before irradiation; B, 20 min; C, 40 mins; D, 60 min of irradiation

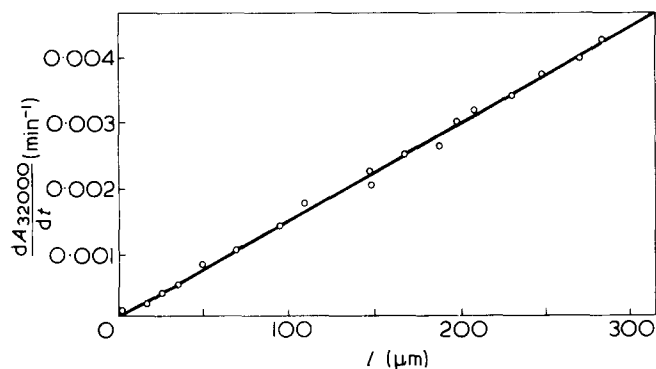


Figure 4 Dependence of the rate of change of absorption for  $\tilde{\nu} = 32\,000\text{ cm}^{-1}$  on the PS film thickness in the initial period of long wave u.v. PS film photo-oxidation.  $P_{O_2} = 20\text{ kg/cm}^2$

with light absorbed by the polymer occurs mainly in the surface layer of the sample whereas photo-oxidation with light not absorbed by PS undergoes in the whole volume of the film.

(c) While the mechanism of initiation of polystyrene photo-oxidation with light absorbed by the polymer is well known, the mechanism of initiation of long wave u.v. PS photo-oxidation is still controversial. The experimental

results indicate that the formation of a polystyrene–oxygen collision complex which can absorb light at  $\lambda > 300\text{ nm}$  is of great importance in the initiation of long wave u.v. photo-oxidation of pure polystyrene.

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