

Effect of dicumyl peroxide on photo-oxidation of polystyrene films:1

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The effect of dicumyl peroxide on polystyrene film photo-oxidation was studied. Comparison of the rate and quantum yield of long-chain PS photo-oxidation product formation was made between pure PS films and PS films containing dicumyl peroxide.

INTRODUCTION

It is known that hydroperoxides and peroxides are the primary molecular products of polystyrene film photo-oxidation processes initiated with 254 and 265 nm radiation¹. Achhammer², Zapolskij³ and Kariakin observed the increase of i.r. absorption at 3450, 3400 and 3480 cm^{-1} , respectively, due to the accumulation of -OH groups in irradiated PS films.

Wall *et al.*⁵ investigated the kinetics of thermal decomposition of polystyrene hydroperoxides previously formed during the photo-oxidation process. They showed that the stationary concentration of hydroperoxides in photo-oxidized PS films is low and these compounds are very reactive.

It was found in the previous work⁶ that the long-time irradiation of PS films with light absorbed by the polymer results in increasing hydroperoxide and peroxide concentration. The overall quantum yield for the formation of these compounds is of the order of 10^{-4} mol/einstein.

The presence of hydroperoxides and peroxides in PS films leads to branching of the kinetic chain of photo-oxidation, especially as they can be considered as the source of alkoxy radicals which are formed in the hydroperoxide photolysis process⁷. Alkoxy radicals are known as efficient hydrogen acceptors and are able to decompose by β -scission reactions giving carbonyl compounds - secondary molecular products of PS photo-oxidation.

Based on an analysis of u.v. and i.r. absorption spectra of irradiated pure PS films and ethanol extracts from exposed samples, three main groups of carbonyl products from the photo-oxidation process were distinguished⁸: (1) acetophenone type compounds (2), α , β -enones and diketones and (3) compounds with an isolated carbonyl group. They can also be divided into two different groups: low-molecular-weight products (extractable with ethanol) and long-chain (polymeric) products.

An attempt to evaluate the effect of peroxides on PS photo-oxidation, especially on the formation of long-chain photo-oxidation products, was the aim of this work.

Investigations were based on using di(α , α -dimethylbenzyl) peroxide (dicumyl peroxide) (DCP). Photolysis of DCP leads to the formation of alkoxy radicals, low-molecular-weight models of alkoxy radicals formed in irradiated PS.

EXPERIMENTAL

Polystyrene was prepared by thermal polymerization of styrene at 80°C for 450 h. The polymer was isolated by precipitating three times from chloroform solution with methanol.

DCP was Analar quality.

Samples of PS and PS containing DCP were prepared in the form of thin films of thickness 0.003 mm as described in the previous paper⁹.

The polymer films were irradiated in air with the full spectrum of an ASH 400 medium pressure mercury lamp. The incident radiation intensity at 254 and 265 nm was 2.5×10^{-9} moles of photons $\text{cm}^{-1} \text{s}^{-1}$ as determined by ferrioxalate actinometry¹⁰.

Low-molecular-weight compounds were extracted from unexposed and exposed films 0.003 mm thick with ethanol pure for spectral analysis.

U.v. absorption spectra were recorded with a Zeiss VSU 2P and Specord UV-VIS spectrophotometers.

RESULTS AND DISCUSSION

In order to investigate the effect of DCP on photo-oxidation of PS the following experiments were made.

Four thin pure PS films of thickness 3×10^{-4} cm and surface 7 cm^2 were extracted with 2 cm^3 of ethanol for 0.5 h to obtain a blank test value of absorption due to low-molecular-weight impurities of the polymer (*Figure 1*, curve A).

PS films containing DCP (initial concentration: 0.4 mol/dm^3) were prepared. A u.v. absorption spectrum of the sample of thickness 0.003 mm is shown in *Figure 1*, curve B.

These films were then extracted with methanol. The u.v. absorption of the extract was measured in the range 44 000–28 000 cm^{-1} (see *Figure 1*, curve C) and the blank values at various $\tilde{\nu}$ were subtracted from it giving the values of $A_{\text{extr}}^{t=0}$.

PS + DCP films were then irradiated for various times in following experiments. Curve D in *Figure 1* represents the u.v. absorption spectrum recorded for a PS + DCP film irradiated for 5 min.

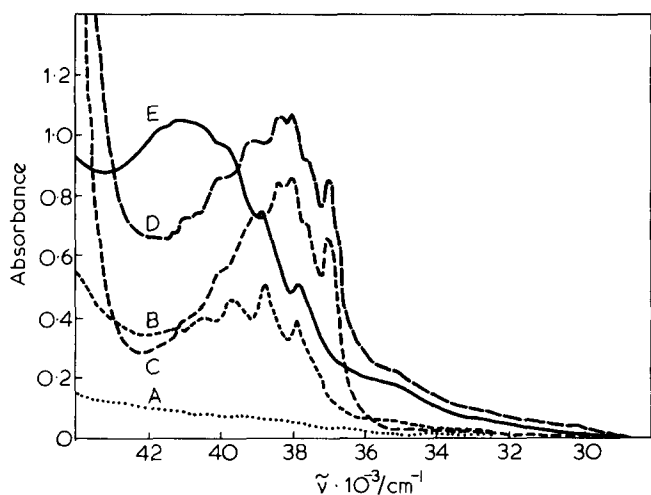


Figure 1 U. v. absorption spectra of PS film containing DCP/conc.: 0.4 mol/dm³, film thickness: 0.003 mm/irradiated with the full spectrum of the Hg-lamp for (C): 0 min, (D): 5 min. U.v. absorption spectra of low-molecular-weight compounds extracted with ethanol from (A): (D) pure not exposed PS films and two PS + DCP films irradiated for (B): 0 min, (E): 5 min

The measured absorption of the film after irradiation time t ,

$$A_f^t = A_{PS}^t + A_{PP}^t + A_{LC}^t \quad (2)$$

consists of absorption due to polystyrene (PS), long-chain (polymer) PS photo-oxidation products (PP) and absorption connected with the presence of low-molecular-weight compounds (LC) i.e., DCP, DCP photolysis products and low-molecular-weight products of PS photo-oxidation.

Irradiated for a given time t , PS + DCP films were extracted with ethanol and extract absorption was recorded (see Figure 1, curve E). Taking into account the blank value of absorption of extract, the value of A_{extr}^t was obtained and A_{LC}^t (equation 2) could be evaluated at a given $\tilde{\nu}$.

Absorption changes at 41 000 and 33 000 cm⁻¹ i.e., at u.v. absorption maxima of carbonyl photo-oxidation products (1) and (2), were analysed. The following mean molar extinction coefficients in dm³ mol⁻¹ cm⁻¹ of PS and carbonyl products (1), (2) and (3) were considered:

$\tilde{\nu}/\text{cm}^{-1}$	ϵ_{PS}	ϵ_1	ϵ_2	ϵ_3
41 000	$\ll \epsilon_1, \epsilon_2$	1.5×10^4	1.5×10^4	$\ll \epsilon_1, \epsilon_2$
33 000	0	10^2	2.5×10^4	$\ll \epsilon_1, \epsilon_2$

Assuming that the measured change of absorption of the film, ΔA_f^t at $\tilde{\nu} = 41\ 000\ \text{cm}^{-1}$ and $33\ 000\ \text{cm}^{-1}$ after the time of irradiation t is much greater than the absorption decrease caused by polystyrene consumption during the same time period, the relation

$$A_{PP}^t = \Delta A_f^t - 0.4 A_{extr}^t + A_{extr}^{t=0} \quad (3)$$

was derived.

The dependences of absorption at 41 000 and 33 000 cm⁻¹ due to the presence of long-chain PS photo-oxidation products in the pure PS film⁸ and PS film containing DCP on irradiation time are shown in Figure 2.

A rapid absorption increase at 41 000 cm⁻¹ and 33 000 cm⁻¹ is observed in the initial period of PS + DCP sample photo-oxidation compared with a slow, nearly linear one for pure

PS films. The maximum values of the slopes dA_{PP}/dt in s⁻¹ at $t = 180\ \text{s}$ are as follows:

$\tilde{\nu}/\text{cm}^{-1}$	PS + DCP	PS
41 000	9.1×10^{-4}	1.05×10^{-4}
33 000	2.6×10^{-4}	2.7×10^{-5}

It can be seen that DCP accelerates the process of formation of long-chain photo-oxidation products (1) and (2) in PS films.

In order to estimate the quantum yields of their formation the following expression was used:

$$\phi = \frac{dA_{PP, \tilde{\nu}}}{dt} / 10^3 J_A \epsilon_{\tilde{\nu}} \quad (4)$$

where

$$v_{\tilde{\nu}} = \frac{dA_{PP, \tilde{\nu}}}{dt} = \frac{\epsilon_{\tilde{\nu}}}{s_f} \frac{dn_{PP}}{dt}$$

= rate of long-chain carbonyl product absorption changes at wavenumber $\tilde{\nu}$;

$\epsilon_{\tilde{\nu}}$ = mean molar extinction coefficient of carbonyl products at $\tilde{\nu}$;

s_f = surface of exposed film in cm²;

n_{PP} = number of moles of products;

$$J_A = \frac{1}{s_f} \frac{dN_A}{dt} = \text{intensity of absorbed radiation}$$

N_A = number of moles of photons

Under experimental conditions in the initiation stage of the process J_A^{PS} and J_A^{PS+DCP} were close to each other, therefore

$$\phi^{PS+DCP} / \phi^{PS} \cong v_{\tilde{\nu}}^{PS+DCP} / v_{\tilde{\nu}}^{PS} \quad (5)$$

When $v_{\tilde{\nu}}$ at $\tilde{\nu} = 33\ 000\ \text{cm}^{-1}$ and $\tilde{\nu} = 41\ 000\ \text{cm}^{-1}$ are considered, the quantum yield of formation of second type long-chain products (ϕ_2) and the overall quantum yield of formation of long-chain products of type (1) and (2) ($\phi_{(1)+(2)}$), respectively, can be compared for PS + DCP and PS films.

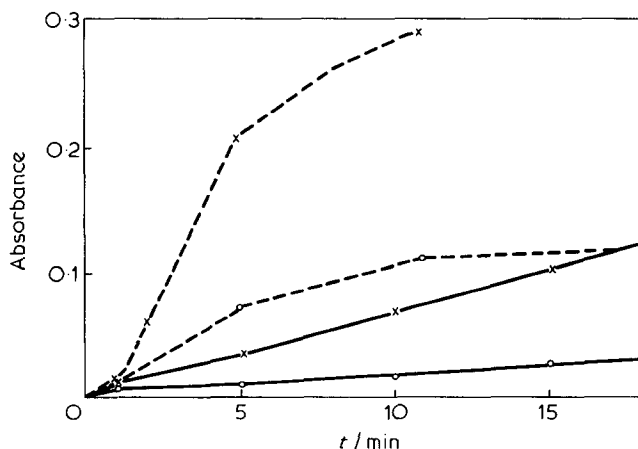


Figure 2 Dependence of the absorption of long-chain PS photo-oxidation products (1) and (2) at 41 000 cm⁻¹ (x) and 33 000 cm⁻¹ (o) on the time of irradiation with the full spectrum of the Hg lamp. (—): products formed in pure PS films, (---): products formed in PS + DCP films

Taking into account the maximum $v_{\tilde{\nu}}$ found, we obtain:

$$\phi_{(2)}^{\text{PS+DCP}} / \phi_{(2)}^{\text{PS}} = 9.6$$

$$\phi_{(1)+(2)}^{\text{PS+DCP}} / \phi_{(1)+(2)}^{\text{PS}} = 8.7$$

The results obtained here suggest that DCP added to PS films determines the kinetics of the formation of long-chain PS photo-oxidation products (1) and (2) in the early stage of the process.

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