Effect of dicumyl peroxide on photo-oxidation of polystyrene films: 2.

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The effect of dicumyl peroxide on the photo-oxidation of polystyrene film has been studied using light of a wavelength absorbed by the polystyrene–oxygen complex. Energy transfer from the excited polystyrene–oxygen complex to the peroxide present in polystyrene film was considered to be the process of most importance in the initiation of polystyrene long-wave photo-oxidation.

INTRODUCTION

The mechanism of the long-wave u.v. ($\lambda > 300$ nm) photo-oxidation of polystyrene has been studied repeatedly[1–10], but the initial step of this process has not been well-defined.

Carbonyl compounds, formed during the thermal auto-oxidation of the polymer, were considered to be of crucial importance in the initiation of near u.v. photo-oxidation[7,10]. Lawrence and Weir[11] suggested that peroxides are important in this process because active alkoxy radicals are formed during their photolysis. In the opinion of George and Hodgeman[12] a significant peroxide concentration would be expected to arise in samples obtained by low temperature polymerization processes.

Bateman and Gee[13] found that hydroperoxides are the most important photoinitiators in the photo-oxidation of pure hydrocarbons in the early stage of the process. Hydroperoxide decomposition is considered to be responsible for the deterioration of polyethylene and polypropylene in natural weathering conditions[14].

The possibility of the participation of singlet oxygen in the initiating step of polystyrene long-wave photo-oxidation was recently proposed[5,15].

In previous papers[16,17] irradiation of polystyrene film with light absorbed by the polystyrene-oxygen complex ($\lambda >$ 300 nm) was found to be followed by polymer photo-oxidation. This was explained as a result of reaction between polystyrene and singlet oxygen generated by intramolecular energy transfer in a polystyrene–oxygen ($PS \cdot O_2$) collision complex.

The effect of di(α,α-dimethylbenzyl) peroxide (dicumyl peroxide) (DCP) on the course of PS film photo-oxidation using light absorbed by the polystyrene–oxygen complex is investigated in this work.

EXPERIMENTAL

Polystyrene, prepared and purified as described in the previous paper[16], was investigated in the form of films of thickness 0.15 mm. Dicumyl peroxide was an Analar reagent. Samples were irradiated with an HBO-200 high pressure mercury lamp. A pyrex-glass filter was employed to obtain radiation at $\lambda > 300$ nm. The incident radiation intensity at $\lambda = 313$ nm was 1.3×10^{-7} einstein cm^{-2} s^{-1}.

The polymer films were put into a pressure cell containing two quartz optical windows 6 mm thick, and irradiated in the presence of oxygen under pressures of 0.2 and 20 atm.

U.v. and i.r. absorption spectra of the films after various irradiation times were recorded with a Zeiss Specord UV VIS and UR 20, respectively.

RESULTS AND DISCUSSION

The following experiments were carried out. A pure PS film (without any DCP) was irradiated in the presence of oxygen at a pressure of 20 atm with light of wavelength absorbed by the ($PS \cdot O_2$) complex ($\lambda > 300$ nm).

From the i.r. and u.v. absorption spectra it has been found that carbonyl compounds, especially of the acetophenone-type, are formed in such a system[9,16]. Taking into account the results obtained and the literature data[15] the following course of reactions can be proposed:

Process		Rate
I $(PS \cdot O_2)_{complex} + h\nu$	$\rightarrow (PS \cdot O_2)^*_{complex}$	I^C_a
II $(PS \cdot O_2)^*_{complex}$	$\rightarrow PS + {}^1O_2{}^*$	$k_1[(PS \cdot O_2)^*]$
III $(PS \cdot O_2)^*_{complex}$	$\rightarrow (PS \cdot O_2)_{complex}$	$k_{nr}[(PS \cdot O_2)^*]$
IV $PS + {}^1O_2{}^*$	$\rightarrow Af + P$	$k'_3\ [{}^1O_2{}^*]$
V ${}^1O_2{}^*$	$\rightarrow {}^3O_2$	$k_i[{}^1O_2{}^*]$

Thus the rate of formation of acetophenone-type products (Af) is given by:

$$V^{Af} = k'_3\ [{}^1O_2{}^*] \tag{1}$$

Substitution of the expression for $[{}^1O_2{}^*]$ calculated from equations (I)–(V) gives:

$$V^{Af} = I^C_a\, \phi_1 \phi'_3 \tag{2}$$

where

$$\phi_1 = \frac{k_1}{k_1 + k_{nr}} \tag{3}$$

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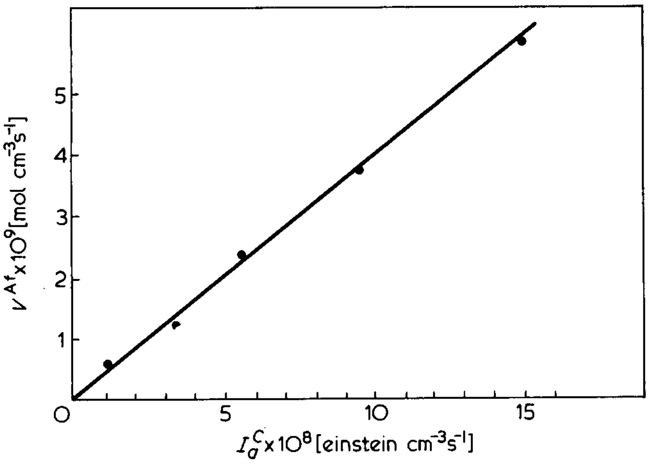

Figure 1 Dependence of the rate of acetophenone-type product formation (V^{Af}) on intensity of light absorbed by PS•O$_2$ complex (I_a^C)

$$\phi'_3 = \frac{k'_3}{k'_3 + k_i} \tag{4}$$

Figure 1 shows a graph of V^{Af} vs. I_a^C*. The slope of the line in *Figure 1* gives the quantum yield of acetophenone-type for product formation in the PS•O$_2$ system, irradiated at $\lambda >$ 300 nm:

$$\gamma^{Af} = \phi_1 \cdot \phi'_3 = 3.9 \times 10^{-2} \tag{5}$$

Films containing DCP (PS + DCP) were irradiated at $\lambda >$ 300 nm in the presence of oxygen at a pressure of 20 atm. It was found that DCP accelerates the photo-oxidation of polystyrene films under such conditions. The dependence of $\Delta A_{\tilde{\nu}}$ at a few chosen wavenumbers (30 000–35 000 cm^{-1}) on the irradiation time in the presence of oxygen at 20 atm, for pure PS and PS + DCP films (initial concentration of DCP 0.5 mol dm^{-3}) is shown in *Figures 2a* and *2b*. These figures show considerably greater changes of absorption at $\tilde{\nu} > 33\,000$ cm^{-1} for PS + DCP than for pure polystyrene. This can be explained by the assumption that photolysis of DCP accelerates the formation of carbonyl compounds in irradiated PS film. This explanation is in accordance with the i.r. spectra of PS and PS + DCP films irradiated under the same conditions (*Figure 3*). It was also found that relatively small amounts of DCP present in PS films (c_{DCP} $\sim 5 \times 10^{-2}$ mol dm^{-3}) are sufficient to increase the rate of polystyrene photo-oxidation.

Because of the low value of the DCP extinction coefficient at $\lambda > 300$ nm ($\epsilon_{313}^{DCP} \cong 0.25$ dm^3 mol^{-1} cm^{-1}) we suggest that energy transfer from the polystyrene–oxygen complex to DCP molecules ought to be taken into consideration.

Further experiments were carried out with oxygen at *atmospheric pressure*. It was found that the rate of PS + DCP system photo-oxidation with light at $\lambda > 300$ nm is much slower in the early stages of the process than in the case of oxygen at 20 atm (*Figure 4*).

It can be seen in this figure that after longer times of irradiation the photo-oxidation rate is higher when oxygen is present at lower pressures. The role of carbonyl compounds previously formed in irradiated PS + DCP samples seems to be important at this stage: participitation in the propagation step may occur, but oxygen quenching by their excited electronic states competes with other photochemical process. The quenching process is more efficient in the high pressure system. Thus after long irradiation times the overall photo-oxidation rate is lower when the oxygen pressure is increased.

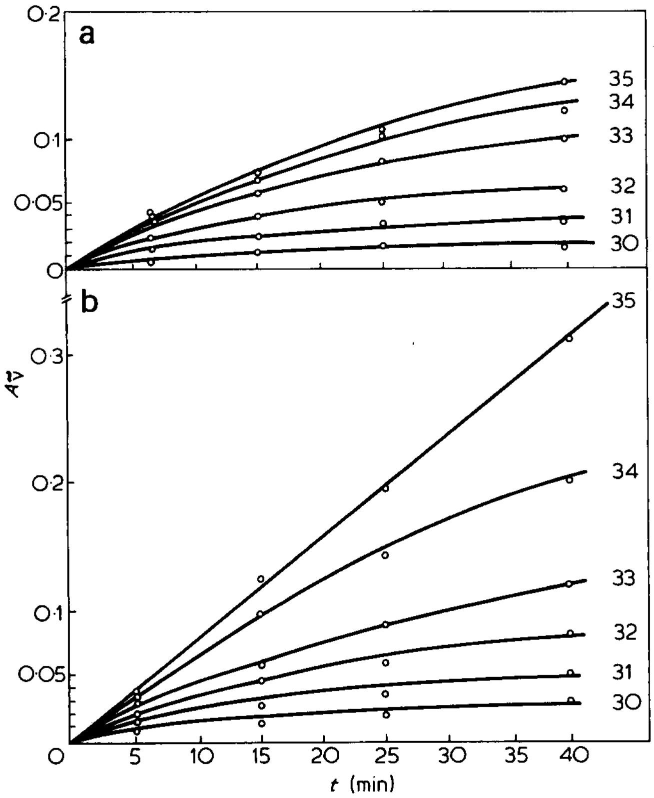

Figure 2 (a) Dependence of the change in absorption ($\Delta A_{\tilde{\nu}}$) on time at a few chosen wavenumbers (30–35 kK) for polystyrene film irradiation with light at $\lambda > 300$ nm in the presence of oxygen under a pressure of 20 atm; (b) Dependence of the change in absorption ($\Delta A_{\tilde{\nu}}$) on time at wavenumbers 30, 31, 32, 33, 34, 35 kK, for PS + DCP film (initial concentration of DCP, 0.5 mol dm^{-3}). Irradiation with light at $\lambda > 300$ nm in the presence of oxygen under a pressure of 20 atm

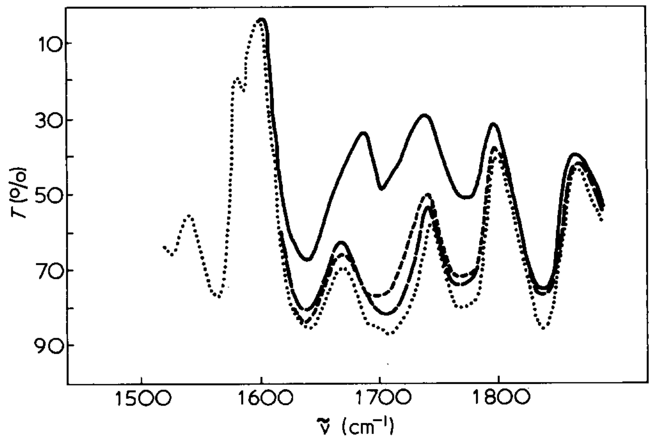

Figure 3 I.r. absorption spectra of PS film: — — —, before irradiation; and ———, after 7 h of irradiation with light at $\lambda > 300$ nm in the presence of oxygen under a pressure of 20 atm and of polystyrene film containing DCP (concentration = 0.5 mol dm^{-3}). . . . ., Before irradiation; and - - - - - - -, after 7 h of irradiation with light at $\lambda > 300$ nm in the presence of oxygen under a pressure of 20 atm

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* Values of V^{Af} were calculated from the increase in absorption at $\tilde{\nu} = 35\,000$ cm^{-1}. It was assumed that the changes in absorption were due to the formation of acetophenone-type products. The mean extinction coefficient $\epsilon_{35000}^{Af} = 7 \times 10^2$ dm^3 mol^{-1} cm^{-1}

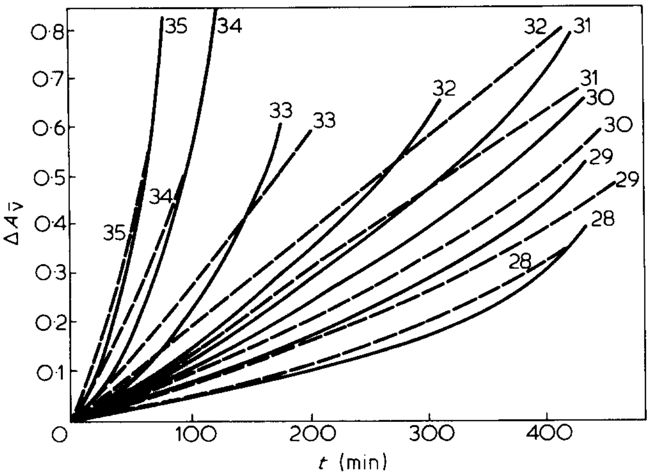

Figure 4 Dependence of absorption changes ($\Delta A_{\tilde{\nu}}$) at a few chosen wavenumbers (28–35 kK) on time of irradiation of PS film containing DCP (concentration, 0.5 mol dm^{-3}) on time of irradiation with light at $\lambda > 300$ nm in the presence of oxygen under a pressure of: ——, 0.2 atm; and – – – –, 20 atm

The reaction scheme (I)–(V) may now be completed:

	Process				Rate
VI	$^1DCP_0$	$+ h\nu$	$\rightarrow$	$^1DCP^*$	I_a^{DCP}
VII	$(PS{\cdot}O_2)^*$	$+ {}^1DCP_0$	$\rightarrow$	$^1DCP^* +$ $(PS{\cdot}O_2)$	$k_{ET}[(PS{\cdot}O_2)^*][^1DCP_0]$
VIII	$^1DCP^*$		$\rightarrow$	$2R{\cdot}$	$k_r[^1DCP^*]$
IX	$^1DCP^*$		$\rightarrow$	$^1DCP_0$	$k_{nr}^{DCP}[^1DCP^*]$
X	$R^{\cdot}$	$+ RH/PS/$	$\rightarrow$	$ROH + R^{\cdot\prime}$	$k'_{ab}[R^{\cdot}]$
XI	$R^{\cdot}$		$\xrightarrow{\beta - sc}$	$Af + R^{\cdot\prime\prime}$	$k_{\beta\text{-}sc}[R^{\cdot}]$

The rate formation of acetophenone-type products V'^{Af} in the PS + DCP + O_2 system, irradiated at $\lambda > 300$ nm is given by:

$$V'^{Af} = k_{\beta-sc}[R^{\cdot}] + k'_3[^1O_2^*] \tag{6}$$

Substituting the values of $[R^{\cdot}]$ and $[^1O_2^*]$ from equations (I)–(XI) we obtain

$$V'^{Af} = \phi_r\phi_{\beta-sc}I_a^{DCP} + I_a^C(\phi_r\phi_{\beta-sc}\phi_{ET} + \phi_1\phi'_3) \tag{7}$$

where

$$\phi_r = \frac{k_r}{k_r + k_{nr}^{DCP}} \tag{8}$$

$$\phi_{\beta-sc} = \frac{k_{\beta-sc}}{k_{\beta-sc} + k'_{ab}} \tag{9}$$

$$\phi_{ET} = \frac{k_{ET}[DCP]}{k_{ET}[DCP] + k_1 + k_{nr}} \tag{10}$$

and ϕ_1, ϕ'_3 are as defined before [equations (3) and (4)]. The linear plot of V'^{Af} vs. I_a^{DCP} (*Figure 5*) gives:

$$\phi_r\phi_{\beta-sc} = 8.5 \times 10^{-2} \tag{11}$$

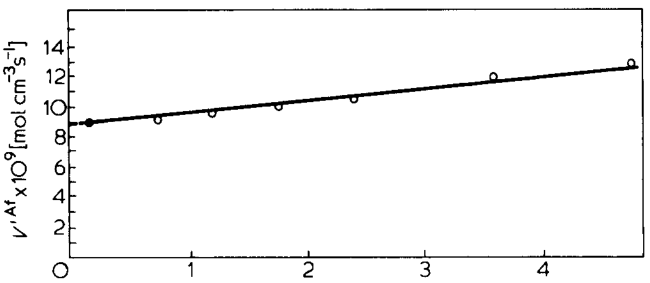

Figure 5 Plot of rate of acetophenone-type product formation (V'^{Af}) in the PS$\cdot$O$_2$ + DCP system *versus* intensity of light absorbed by DCP (I_a^{DCP})

and

$$I_a^C(\phi_r\phi_{\beta-sc}\phi_{ET} + \phi_1\phi'_3) = 8.7 \times 10^{-9} \text{mol cm}^{-3}\text{s}^{-1} \tag{12}$$

Substituting $I_a^C = 1.3 \times 10^{-7}$ einstein cm^{-3} s^{-1}, $\phi_r\phi_{\beta-sc} = 8.2 \times 10^{-2}$ and $\phi_1\phi_3 = 3.9 \times 10^{-2}$ into equation (12), gives:

$$\phi_{ET} = 0.32 \tag{13}$$

Geuskens and David found[18] that transfer of energy to hydroperoxides plays a major role in the long-wave photo-oxidation of polystyrene. They suggested that such a transfer occurs between carbonyl compounds and hydroperoxides. It seems that the energy transfer process from the PS$\cdot$O$_2$ complex to peroxide or hydroperoxide molecules ought to be taken into account. PS$\cdot$O$_2$ can stimulate peroxide decomposition even if the concentration and absorption is small.

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