Photo-oxidation of polystyrene in dichloromethane solutions

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Photo-oxidation of polystyrene in dichloromethane solution irradiated with light absorbed by the polymer was investigated. The quantum yields of the formation of acetophenone-type carbonyl compounds as well as α, β-enone and dicarbonyl products were calculated based on the analysis of u.v. absorption spectra of irradiated solutions. The relationship between the concentration of these products was found.

Keywords Oxidation; radiation; light; ultra violet; polystyrene; dichloromethane

INTRODUCTION

The oxidative and photo-oxidative degradation of polystyrene has been repeatedly studied using solid samples, mainly in the form of thin films[1]. Several studies were also carried out in the liquid phase[1-8].

In this paper the photo-oxidation of polystyrene in CH_2Cl_2 solution was investigated by means of u.v. spectrophotometry. Photochemical reactions were initiated with light absorbed by the polymer. The aim of this work was to evaluate the quantum yields of carbonyl product formation.

EXPERIMENTAL

Polystyrene was prepared by thermal polymerization of styrene at 80°C for 450 h. The resulting polymer was purified by dissolving in chloroform and precipitating with methanol. This process was repeated three times. The product was Soxhleted with methanol. The weight-average molecular weight of this polymer, determined viscometrically, was 462000. Dichloromethane was an analar reagent.

The polymer solutions were irradiated with the full spectrum of an ASH 400 medium pressure mercury lamp. The radiation density at 254 and 265 nm was of 2.5×10^{-9} mols of photons $cm^{-2}\ s^{-1}$ as determined by ferrioxalate actinometry[9]. The irradiation of solutions was carried out in cylindrical quartz cuvettes 0.5 or 1 cm thick in the presence of air at atmospheric pressure. Additional experiments were made in the presence of argon at the pressure of 1 atm supplied from a bubbler to a flask joined with a quartz cuvette 1 cm thick.

U.v. absorption spectra were recorded with a Zeiss Specord UV VIS spectrophotometer.

RESULTS AND DISCUSSION

The irradiation of PS solutions in the presence of air results in an increase in the u.v. absorption within the 44000–28000 cm^{-1} range. *Figure 1* shows the u.v. absorption spectra of PS solution in CH_2Cl_2 (initial concentration $c^0_{PS} = 3.8 \times 10^{-3}$ mol dm^{-3}) recorded after various times of irradiation with light absorbed by the polymer.

U.v. absorption changes can be connected with the formation of photo-oxidation products, i.e. hydroperoxide (HP) formation followed by the production of carbonyl compounds (CP) and the presence of products of phenyl group photolysis (PhP).

In order to estimate the role of the PS photolysis process some experiments were carried out under identical photochemical conditions but with O_2 excluded. The solutions investigated were bubbled with argon for 15 min, then irradiated in an argon atmosphere. U.v. absorption spectra in the range 44000–28000 cm^{-1} were recorded before and after u.v. exposure.

It was found that for the irradiation times considered, the u.v. absorption increase observed for argon saturated solution could be neglected in comparison with one recorded in the presence of oxygen, e.g. the changes of absorption at 41000 cm^{-1} after 90 min of irradiation were of 0.02 and 0.8 respectively.

Thus it can be assumed that the spectrophotometrically measured changes of absorption of the exposed solution is composed of the decrease of polystyrene absorption ($\Delta A_{PS} < 0$) and the absorption connected with the formation of photo-oxidation products, A_{HP} and A_{CP}. For the initial reaction time $|\Delta A_{PS}| \ll A_{HP} + A_{CP}$ and $A_{HP} \ll A_{CP}$ because of the low values of polystyrene and hydroperoxide extinction coefficients in the u.v. region analysed.

Thus, the rate of absorption changes $dA_{\tilde{\nu}}/dt$ at chosen wavenumber $\tilde{\nu}$ can be taken as a measure of the rate of the formation of carbonyl photo-oxidation products.

The rates of absorption changes observed at 41000, 36000 and 33000 cm^{-1} vary with time. They are summarized in *Table 1*. These two values differ in order of magnitude. That means that besides $R-C(=O)-\Phi$ carbonyl compounds other carbonyl products are formed in the process.

Basing on an analysis of the reactivity of alkoxy polymer radicals and comparing the u.v. spectra of PS solutions and PS films[11], the formation of carbonyl compounds with isolated $>C=O$ group

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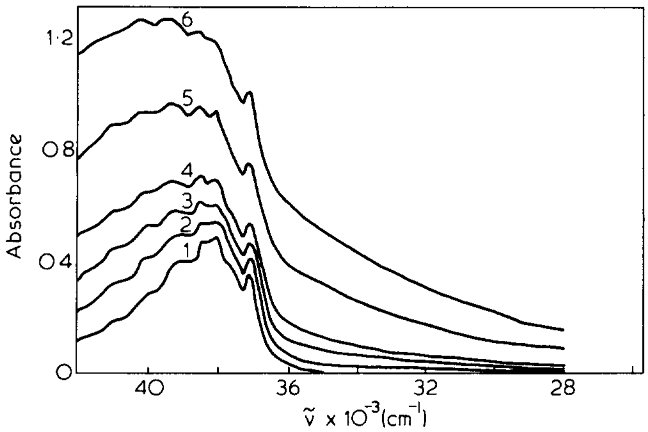
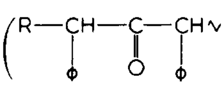
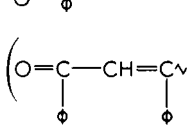
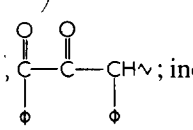


Figure 1 **U.v. absorption spectra of polystyrene solution in CH_2Cl_2 (initial conc. 0.0038 mol dm^{-3}), recorded after various times of irradiation with an ASH-400 mercury lamp, 1, 0 min; 2, 15 min; 3, 30 min; 4, 45 min; 5, 90 min; 6, 150 min**

Table 1 Rates of absorption changes at various wavenumbers

Time period (min)	$dA_{\tilde{\nu}}/dt$ (s^{-1})		
	$\tilde{\nu}$ = 41 000 cm^{-1}	$\tilde{\nu}$ = 36 000 cm^{-1}	$\tilde{\nu}$ = 33 000 cm^{-1}
0–45	1.3×10^{-4}	6.3×10^{-5}	2.6×10^{-5}
45–90	1.2×10^{-4}	7.7×10^{-5}	5.2×10^{-5}
90–150	9.4×10^{-5}	6.1×10^{-5}	3.6×10^{-5}

( ; index A), α,β-enones as well as diketones (, ; index E,α) can be also expected in irradiated polystyrene solutions.

Compounds of type (A) are characterized by low extinction coefficients of about 10^2 dm^3 mol^{-1} cm^{-1} in the region analysed, and therefore their contribution to the measured absorption changes is negligible.

Because of the fact that $\bar{\varepsilon}^{aph}_{41\,000}$ and $\bar{\varepsilon}^{E,\alpha}_{41\,000}$ at $\tilde{\nu} = 41\,000$ cm^{-1} are close to each other, the quantum yield calculated according to equation (1) for $\tilde{\nu} = 41\,000$ cm^{-1} can be considered as the overall quantum yield of the formation of acetophenone type compounds, enones and dicarbonyl products. Thus we obtain

$$\varphi^{aph+E\alpha} = 4.8 \times 10^{-3} \text{ mols of products/mol of quanta.}$$

However, one can conclude that $dA_{\tilde{\nu}}/dt$ at $\tilde{\nu} = 33\,000$ cm^{-1}, where the absorption changes are connected mainly with the presence of enones and diketones, is the base for calculating the quantum yield of the formation of E,α products of photo-oxidation

$$\varphi^{aph+E,\alpha} = 4.8 \times 10^{-3} \text{ mols of products/mol of quanta.}$$

The ratios of the absorption changes at 41 000, 36 000 and 33 000 cm^{-1} decrease with u.v. irradiation time in different ways and become constant after about 2 h. This result confirms the fact that various types of carbonyl

Table 2 **Mean extinction coefficients used for (aph) and (E, α) compounds**

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

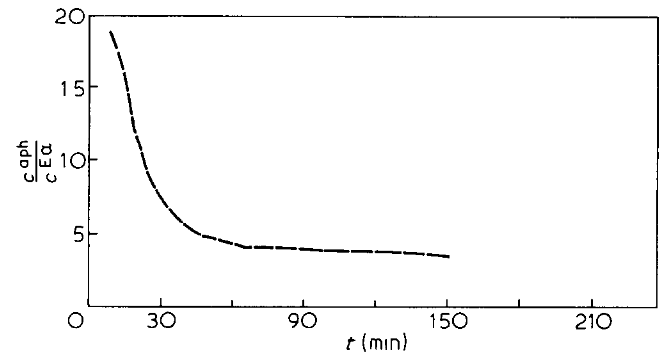


Figure 2 **Dependence of the ratio of concentrations acetophenone type products and enones as well as diketones on the time of irradiation of PS solution in CH_2Cl_2**

products are formed at different photo-oxidation stages. Especially, taking into account the mean extinction coefficients given above, the ratio $\Delta A_{41\,000}/\Delta A_{33\,000}$ can be expressed as

$$\frac{\Delta A_{4100}}{\Delta A_{33000}} = 0.7\left(\frac{c^{aph}}{c^{E,\alpha}} + 1\right) \qquad (2)$$

where $\Delta A_{\tilde{\nu}}$ denotes absorption changes observed after irradiation time t and c^{aph}, $c^{E,\alpha}$ are the concentrations of carbonyl products of photo-oxidation.

Figure 2 shows the dependence of the ratio $c^{aph}/c^{E,\alpha}$ on the irradiation time.

One can conclude that the formation of acetophenone type carbonyl compounds is more efficient in the initial period of the process in comparison with E,α products. After long times (above 2 h) of irradiation of polystyrene solutions the concentration of (aph) photo-oxidation products is about five times greater than that of α,β-enone and dicarbonyl compound.

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