

Spectral differences in photodegraded polystyrene in various solvents

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During ultra-violet irradiation of polystyrene in solution in cyclohexane, dichloromethane or chloroform, yellowing of the dissolved polymer occurs. Ultra-violet/visible absorption and fluorescence emission spectra show some spectral differences but in general they support the formation of conjugated polyene structures, which are probably formed by the same mechanism independent of type of solvent and/or the presence of oxygen.

(Keywords: photodegradation; photooxidation; polystyrene; excimers; fluorescence spectra)

INTRODUCTION

Photodegradation of polystyrene (PS) in solution (denoted here as PS-S) depends greatly on the type of solvent used, e.g. chloroform¹⁻¹⁰, carbon tetrachloride^{1,6-10}, benzene^{1,11,12}, 1,4-dioxane^{1,4}, cyclohexane¹ and methylene chloride¹⁻¹³.

The highest quantum yields (ϕ_s) for main-chain scission have been reported for CCl_4 ($\phi_s \times 10^4 = 1130$) and CHCl_3 ($\phi_s \times 10^4 = 440$); they are lower for CH_2Cl_2 ($\phi_s \times 10^4 = 44$) and benzene ($\phi_s \times 10^4 = 7$) and lowest for dioxane ($\phi_s \times 10^4 = 7$) and cyclohexane ($\phi_s \times 10^4 = 2$)¹. The rate of photo-oxidative degradation of polystyrene in halogenated solvents increases in the order: methylene chloride < chloroform < carbon tetrachloride, i.e. increases with increasing electron affinity of the solvent¹⁰. Insolubility, indicating crosslinking, was never observed in solutions of polystyrene irradiated in air. These results suggest that the degradation of PS by main-chain scission in chlorinated solvents is caused by solvent radicals such as Cl^\cdot , CCl_3^\cdot or CHCl_2^\cdot ^{3,4,7}. In these investigations¹⁻¹³ very little has been reported on changes of chemical structure of the degraded PS-S molecules during ultra-violet (u.v.) irradiation in various solvents. It is obvious that yellowing of the PS-S samples during u.v. irradiation is a result of chemical changes of the PS structures. This paper presents results from a study of changes of the PS structure upon the u.v. irradiation of PS in cyclohexane, dichloromethane and chloroform.

EXPERIMENTAL

A commercial polystyrene (PS) sample (MW 200 000), supplied by Polysciences Ltd, has been very carefully purified by dissolving in spectral pure dichloromethane (concentration about 1 wt%) and precipitated by slowly adding the solution dropwise to stirred methanol under a nitrogen blanket. The procedure was repeated four times

to ensure that most of the possible impurities were removed¹⁴.

In order to obtain comparable results, solutions of the same concentration of PS (1.35×10^{-3} M) in cyclohexane (for fluorescence spectroscopy, Merck, Germany), dichloromethane (for fluorescence spectroscopy, Merck, Germany) and chloroform (for spectroscopy, Merck, Germany) were used for u.v. irradiation. Solution samples were directly irradiated with 254 nm u.v. irradiation (Philips type HPK 125 W lamp) in spectral quartz cuvettes, which were specially designed for degassing the solutions by the freezing-thawing method.

Ultra-violet/visible (u.v./vis.) absorption spectra and fluorescence emission spectra were recorded using a Perkin-Elmer 575 UV/VIS and a LS-5 Fluorescence Spectrometer respectively.

Infra-red (i.r.) spectra were recorded from thin PS films on NaCl plates using a Perkin-Elmer computerized 580 B Spectrometer.

Elemental analyses for the presence of chlorine in u.v. irradiated PS-S samples in CH_2Cl_2 and CHCl_3 were made by combustion of samples and absorption of chlorine on BaCO_3 . The chlorine content was further determined by titration with 0.05 N AgNO_3 in the presence of uranine as indicator.

RESULTS

Solutions of PS in cyclohexane, dichloromethane or chloroform (degassed or in the presence of air) become yellow coloured upon u.v. irradiation (at 254 nm). This yellowing is accompanied by changes in the u.v./vis. spectra (Figures 1-3), fluorescence spectra (Figures 4-7) and i.r. spectra (Figure 8). The observed changes of PS in solution caused by u.v. irradiation are due to photochemical changes of the polymer structure, e.g. formation of light-absorbing chromophores, chain scission and/or crosslinking reactions. Pure solvents irradiated under the same conditions as the PS-S solutions do not show any change in their absorption or emission spectra.

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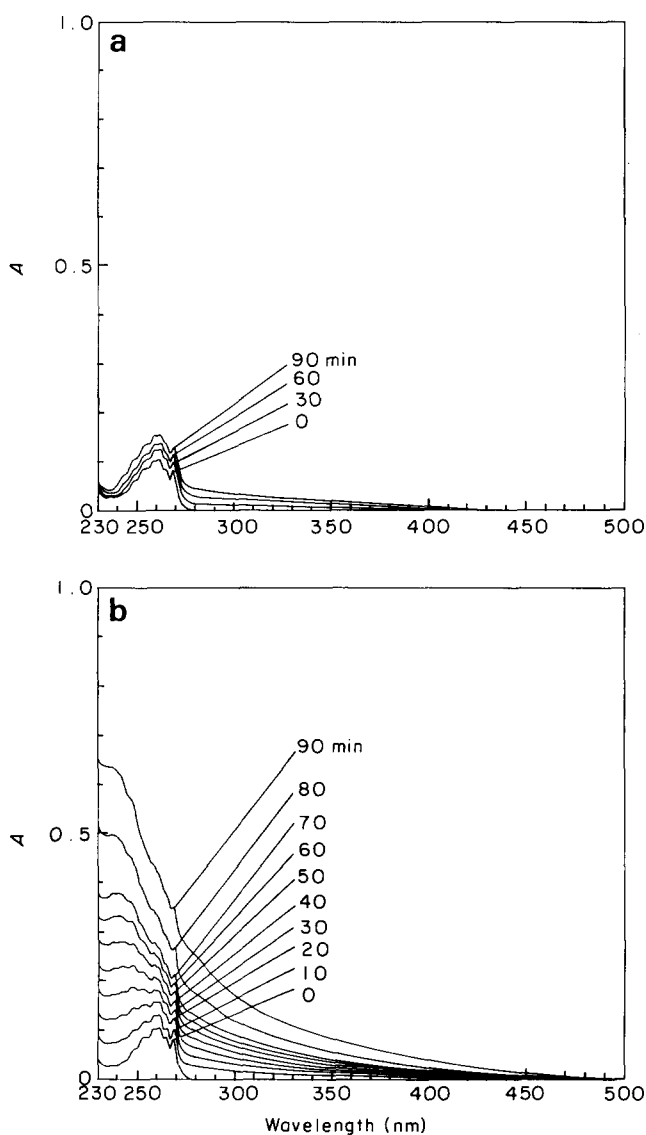


Figure 1 U.v./vis. absorption spectra of PS-S in cyclohexane (1.35×10^{-3} M) after irradiation times (min): (a) degassed and (b) in air

Polystyrene in solution (PS-S) exhibits a characteristic spectrum in the wavelength region of 230–280 nm associated with the $\pi-\pi^*$ transitions of the benzene ring. Polystyrene solid or in some solutions (e.g. in benzene) shows extended absorption up to 350 nm, which is a result of the formation of charge-transfer contact complexes with oxygen^{15,16}. Pure solvents such as benzene¹⁷ and methylcyclohexane¹⁸ show weak absorption of charge-transfer oxygen complexes. It has not yet been reported if cyclohexane, dichloromethane or chloroform participate in such complex formation.

Polystyrene u.v. irradiated in cyclohexane (Figure 1), dichloromethane (Figure 2) and chloroform (Figure 3) shows changes in absorption spectra: a remarkable increase of absorption in the 250–280 nm region and formation of a new tail absorption in the region of 280–450 nm. Presence of oxygen enhances formation of the absorption at 280–450 nm in cyclohexane (Figure 1) and in dichloromethane (Figure 2) but has the opposite effect in chloroform (Figure 3). Results of this effect are collected in Figure 9, where kinetics of the formation of the absorption at 320 nm has been given.

Polystyrene in solution forms intramolecular excimer^{19–22}. The fluorescence of PS-S consists of two bands: at 283 nm and 334 nm (Figures 4–7). The intensity ratio of excimer emission (at 334 nm) to monomer emission (at 283 nm) I_E/I_M is different in various solvents (Table 1).

PS excimer fluorescence in CHCl_3 is quenched similarly to the quenching in CCl_4 (ref. 23). Evidently, oxygen also has a quenching effect on the PS-S excimer fluorescence in the solvents used, in agreement with earlier published data²⁴. The amount of PS-S excimer fluorescence quenched by oxygen in cyclohexane and CH_2Cl_2 was 14.8% and 24% respectively.

The fluorescence spectra of PS-S after u.v. irradiation in cyclohexane (Figures 4 and 5), dichloromethane (Figure 6) and chloroform (Figure 7) oxygen-free and saturated with air differ as follows:

(1) In oxygen-free cyclohexane (Figure 4), formation of emission bands at 353, 370, 390 and 420 nm occurs much slower than in the presence of air (Figure 5). In the latter case a new strong emission band at 310 nm after 90 min u.v. irradiation is formed.

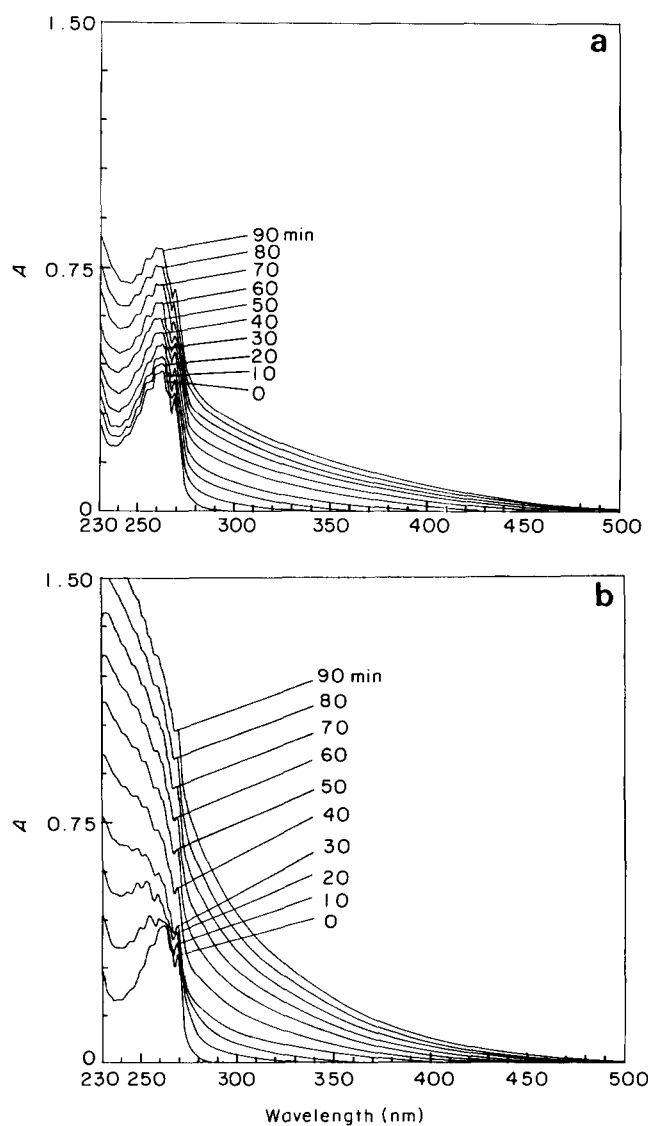


Figure 2 U.v./vis. absorption spectra of PS-S in dichloromethane (1.35×10^{-3} M) after different irradiation times (min): (a) degassed and (b) in air

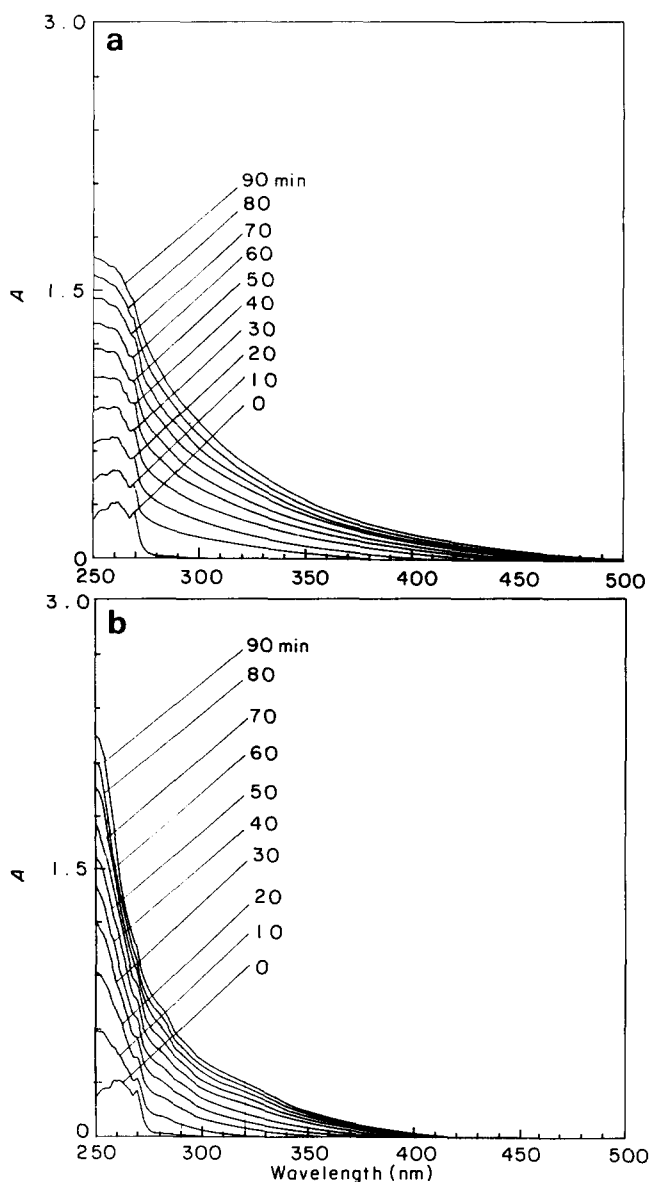


Figure 3 U.v./vis. absorption spectra of PS-S in chloroform (1.35×10^{-3} M) after different irradiation times (min): (a) degassed and (b) in air

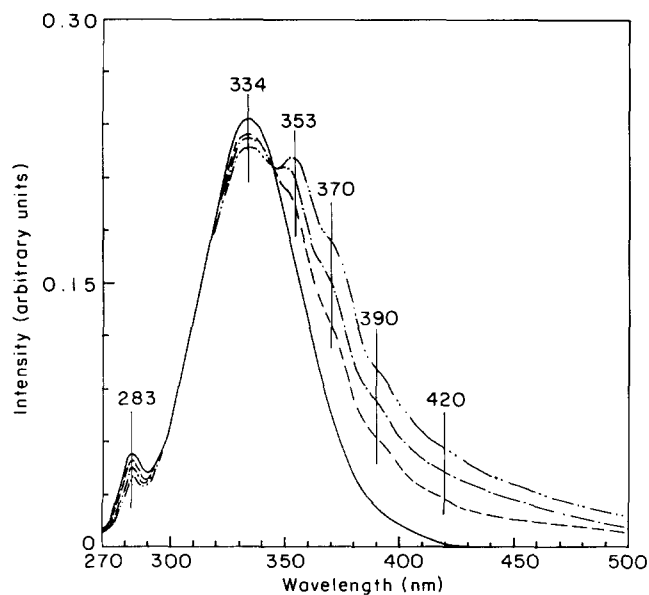


Figure 4 Fluorescence emission spectra of PS-S in cyclohexane (1.35×10^{-3} M) degassed after different radiation times: —, 0 min; ---, 30 min; - - - -, 60 min; · · · ·, 90 min. $\lambda_{exc} = 260$ nm

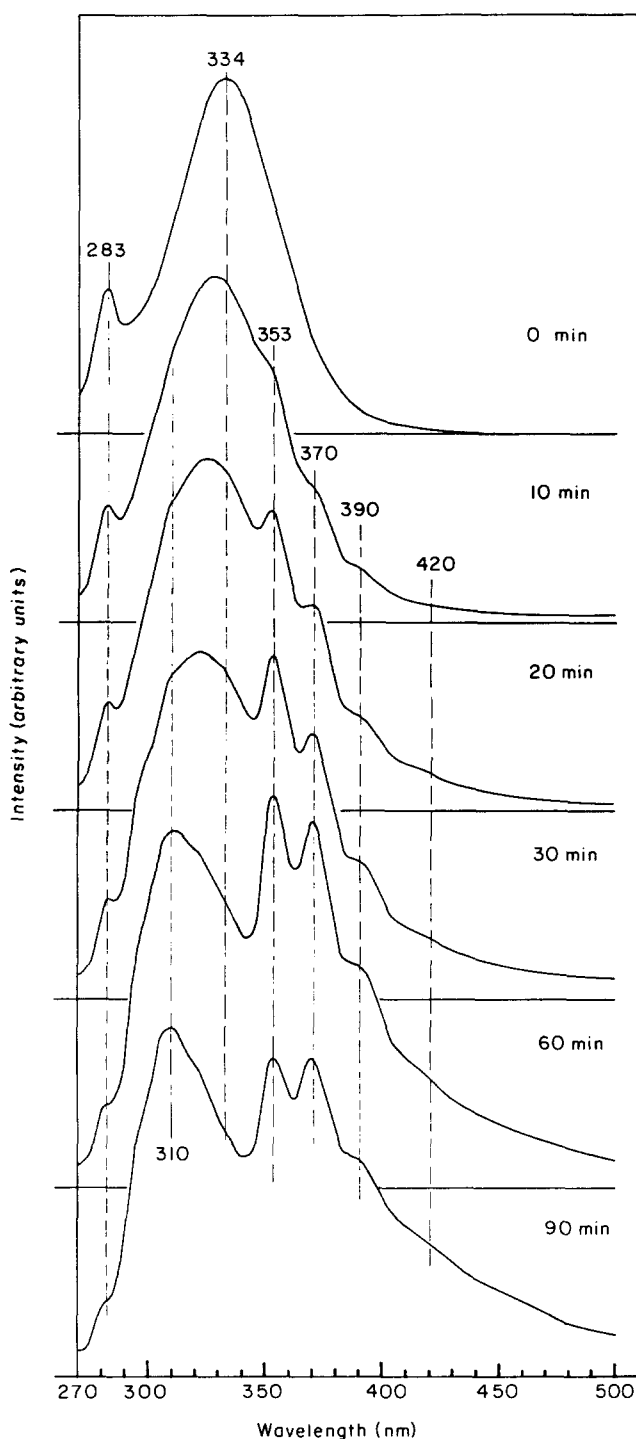


Figure 5 Fluorescence emission spectra of PS-S in cyclohexane (1.35×10^{-3} M) in air after different irradiation times. $\lambda_{exc} = 260$ nm

(2) In dichloromethane (Figure 6) and chloroform (Figure 7), formation of emission bands at 353 (351), 370, 390 and 420 nm, similar to those in cyclohexane, occurs. The intensity of the bands at 353, 370 and 390 nm in chlorinated solvents is much higher in the presence of air than in oxygen-free samples. In the case of fluorescence emission at longer wavelength (420 nm), this effect is the opposite. After 60 min u.v. irradiation in oxygen-free chloroform, the fluorescence maximum at longer wavelengths is shifted to 450 nm (Figure 7).

(3) The intensity of the emission bands in the region of 420–450 nm after u.v. irradiation in dichloromethane and chloroform, oxygen-free or saturated with air, is higher

than those of similar samples in cyclohexane (Figures 4-7).

(4) Monomer (at 283 nm) and excimer (at 334 nm) emissions of PS in all u.v. irradiated solutions decrease progressively during the time of irradiation and disappear almost completely in dichloroemethane after 90 min (Figure 6) and in chloroform after 30 min (Figure 7).

I.r. spectra of u.v. irradiated PS-S samples (after 90 min) (Figure 8) show differences only in the region of absorption for carbonyl groups ($1600-1800\text{ cm}^{-1}$). In the

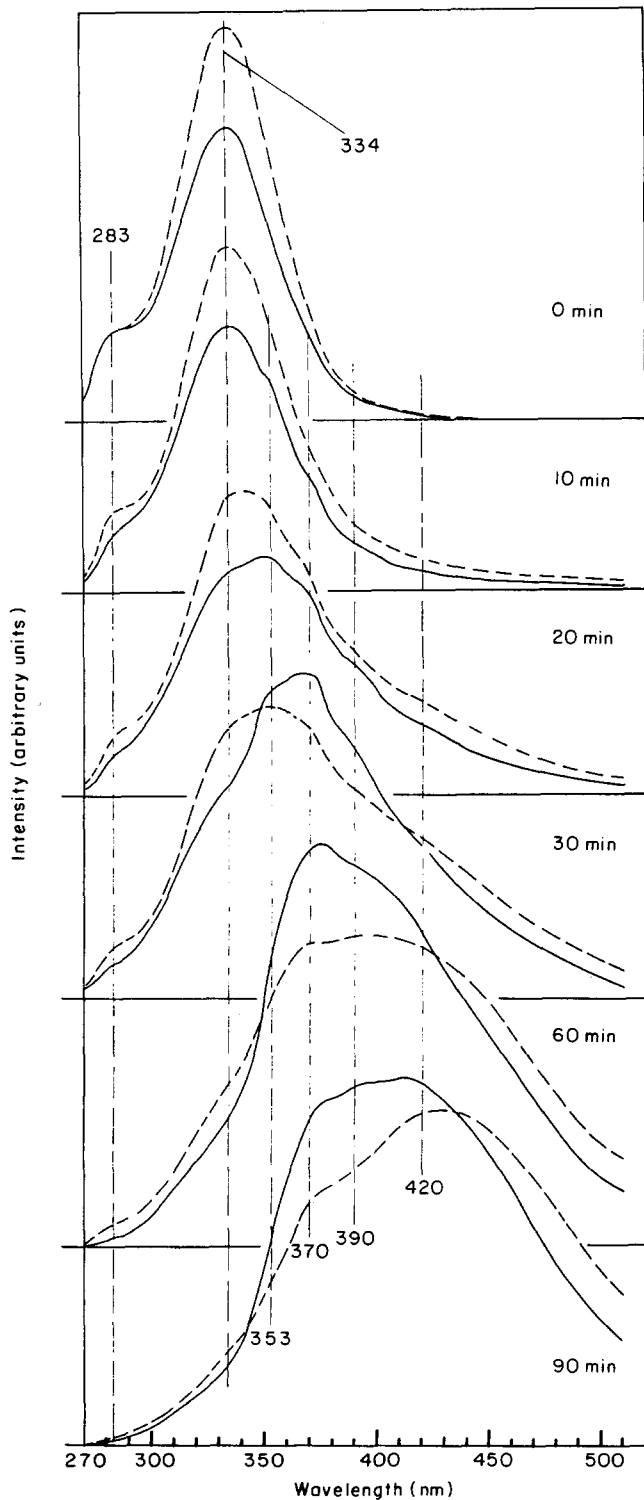


Figure 6 Fluorescence emission spectra of PS-S in dichloromethane ($1.35 \times 10^{-3}\text{ M}$) after different irradiation times (min): ---, degassed; —, in air. $\lambda_{\text{exc}} = 260\text{ nm}$

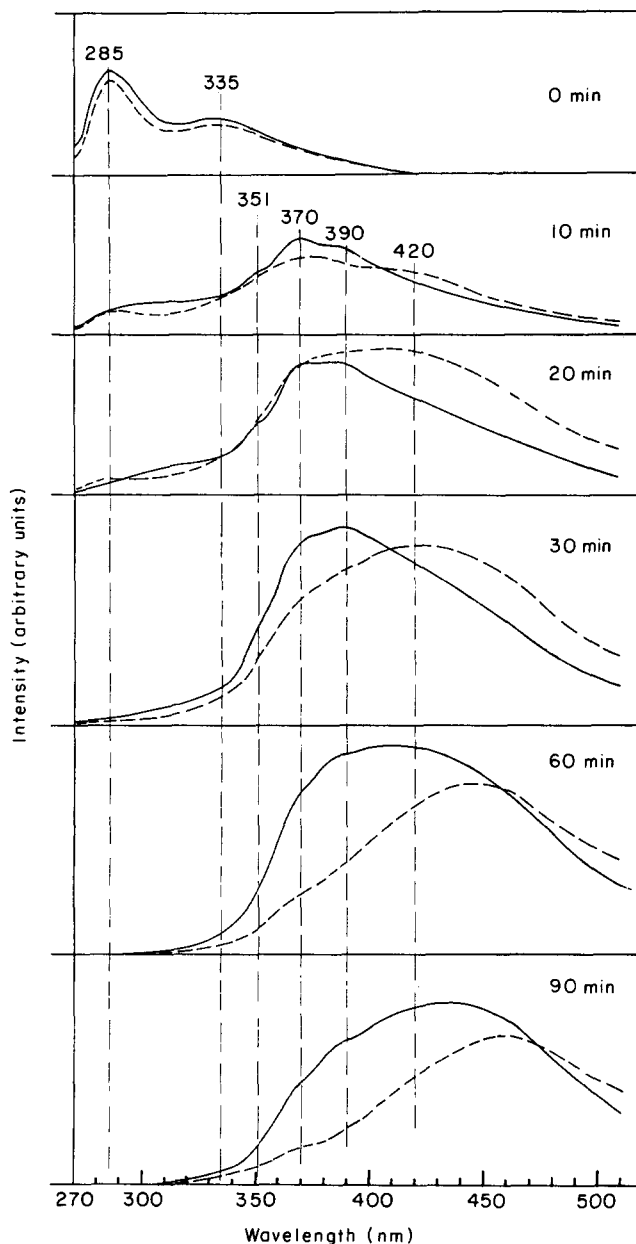


Figure 7 Fluorescence emission spectra of PS-S in chloroform ($1.35 \times 10^{-3}\text{ M}$) after different irradiation times (min): ---, degassed; —, in air. $\lambda_{\text{exc}} = 260\text{ nm}$

PS-S sample irradiated in CHCl_3 the intensity at 1685 cm^{-1} is predominant in comparison with the absorption bands at 1720 cm^{-1} and 1745 cm^{-1} . The intensity of the band at 1685 cm^{-1} in PS-S sample irradiated in chloroform is higher than that in dichloromethane or cyclohexane. The interpretation of these bands by different authors is still conflicting (see Table 2).

DISCUSSION

The yellowing of PS samples irradiated in solid or in solution (in absence or presence of air) has been the subject of many earlier publications directed to interpretation and formulation of yellowing mechanisms. It is obvious that formation of strongly absorbing chromophoric groups must be responsible for yellowing or irradiated samples. Several different chromophoric

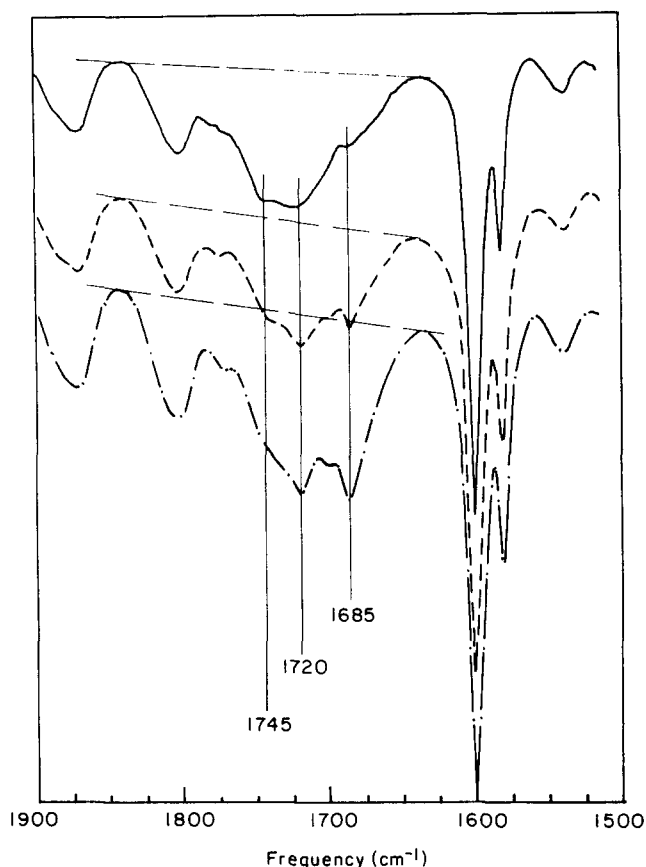
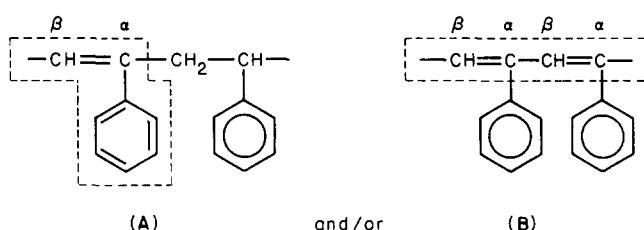


Figure 8 I.r. absorption spectra of PS-S after irradiation (90 min) in air in different solvents: —, cyclohexane; ---, dichloromethane; - · - ·, chloroform

groups that can absorb in the region 280–450 nm have been proposed (Table 2), but interpretation of the experimental data is still conflicting^{11,25,26,30,41,42}. The yellow colour of PS-S samples, which is a consequence of absorption in the range 280–450 nm, can be interpreted by formation of conjugated polyene structures of the types^{26,27}:



Formation of such structures requires abstraction of two hydrogen atoms at the alpha and beta carbons of a PS molecule and H₂ evolution^{25,43}. Such a process has been observed upon u.v. irradiation of alkyl-substituted benzenes⁴⁴.

Conjugated polyene structures exhibit absorption in the range 280–500 nm and u.v./vis. spectra of u.v. irradiated PS-S (Figures 1–3) support suggestions that this type of chromophore can be formed both in oxygen-free solution and in the presence of air.

Formation of polyene sequences of type $(-\text{CH}=\text{CH}-)_n$ in PS-S is less probable, because this requires photocleavage of $-\text{HC}-\text{phenyl}$ bonds and evolution of benzene. Such a process has not yet been reported.

On the other hand, polyenes such as tetraenes $(-\text{CH}=\text{CH}-)_4$ have a strong absorption maximum at

321 nm, with high extinction coefficient⁴⁵, $\epsilon = 73\,000\text{ l mol}^{-1}\text{ cm}^{-1}$. Formation of this structure in u.v. irradiated PS-S should give an increase of absorption at 312 nm in the form of a well developed peak.

Emission of conjugated polyene structures (type B) is expected around 350, 400, 450 and 500 nm for dienes, trienes, tetraenes and pentaenes, respectively²⁶. Fluorescence spectra of PS-S (Figures 4–7) show the formation of emission bands at 353, 370, 390, 420 and 450 nm, which supports formation of conjugated polyene structures (type B) in u.v. irradiated PS-S samples independently of whether oxygen is present or not. The acetophenone group does not give fluorescence, since intersystem crossing from the first excited singlet state of

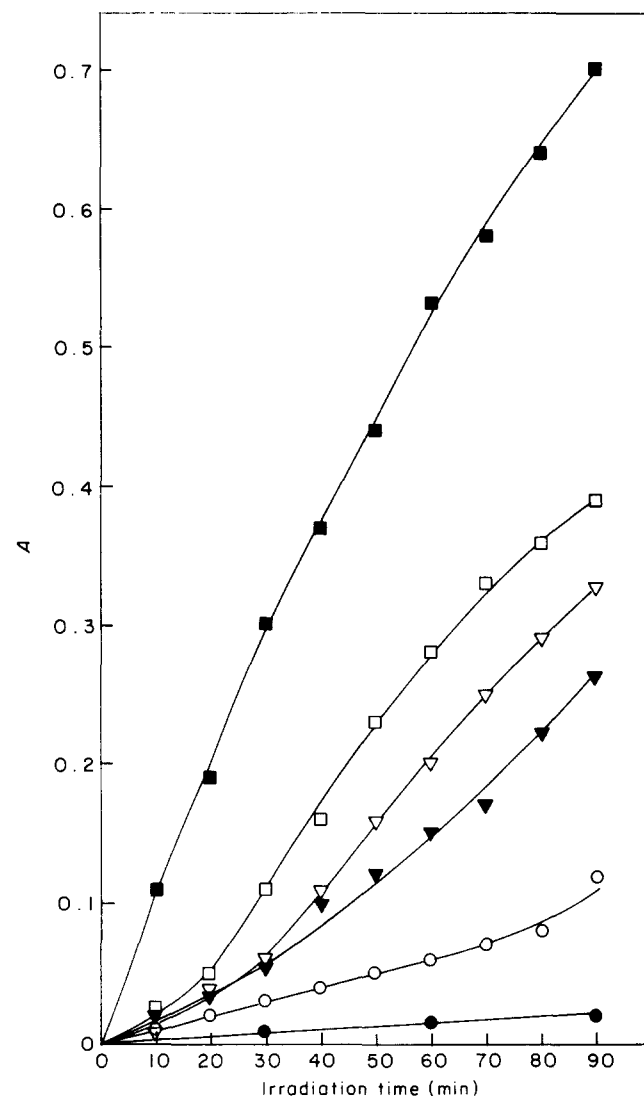
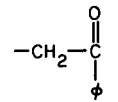
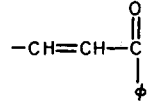
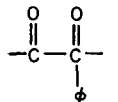
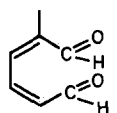
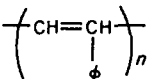
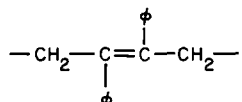
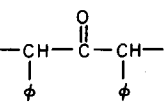
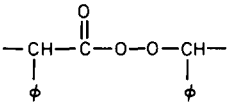
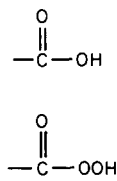
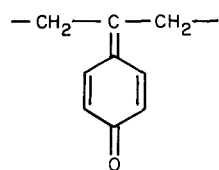


Figure 9 Kinetics of u.v./vis. absorption band at 320 nm formation in PS-S during irradiation in different solvents ($1.35 \times 10^{-3}\text{ M}$): ●, degassed cyclohexane; ○, cyclohexane in air; ▼, degassed dichloromethane; ▽, dichloromethane in air; ■, degassed chloroform; □, chloroform in air

Table 1 Intensity ratio of excimer to monomer emission (I_E/I_M) for polystyrene in various solvents

Solvent	Oxygen-free	In the presence of air
Cyclohexane	4.66 (Figure 4)	2.45 (Figure 5)
CH ₂ Cl	4.46 (Figure 6)	3.3 (Figure 6)
CHCl ₃	0.5 (Figure 7)	0.5 (Figure 7)

Table 2 Assignment of different chromophoric groups considered to be formed during u.v. irradiation of polystyrene samples (based on available literature)

Chromophore group		U.v. assignment		I.r. assignment		Fluorescence/ phosphorescence* assignment	
Name	Structure	nm	ref.	cm ⁻¹	ref.	nm	ref.
Acetophenone		240	25,26	1685	2, 25 27-30	*396/423/454 and 487	14, 36
Benzal- acetophenone		240-350	31-34	-	-	-	-
α,β-Diketone		280-450	35	1660	35	-	-
Muconic aldehyde		-	-	1740	11, 30	-	-
Polyene structure		280 (n=1) 310 (n=2) 340 (n=3)	26	-	-	350-500	26
trans-Stilbene		-	-	-	-	338/355 and 372	14
Carbonyl group in chain		340-390	26	1715-1720	26	-	-
Peroxy ester		-	-	1760-1770	26	-	-
Carboxylic or peroxy acid		-	-	1730	37-39	-	-
Quinomethane structure		-	-	-	40	-	-

this group to the triplet state is fast¹⁴. On the other hand, emission spectra of PS-S samples u.v. irradiated in the presence of air (Figures 5-7) show similarities to those measured in oxygen-free solutions (Figures 4-7). These results do not indicate a special role of oxygen in the formation of conjugated polyene structures.

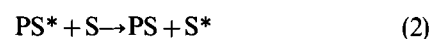
On the other hand, solvent molecules may participate in the formation of these chromophores according to the general mechanism formulated:

(1) Polystyrene (PS) molecules absorb light and are

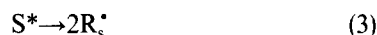
excited to an excited form (PS*):



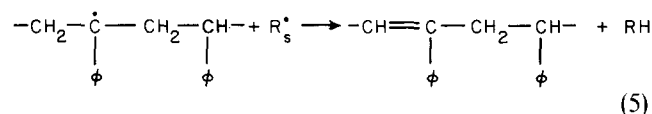
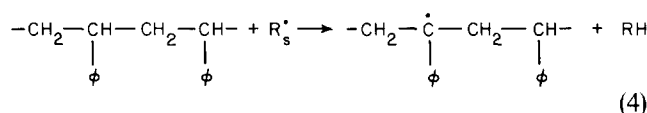
(2) The reactive solvent molecules (S*) are essentially formed by energy transfer from the excited polymer molecule (PS*) to solvent (S):



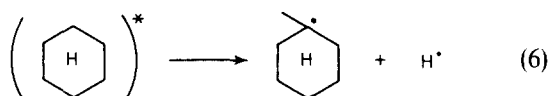
(3) Solvent radicals (R_s^*) are formed from S^* :



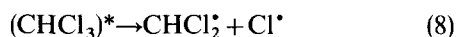
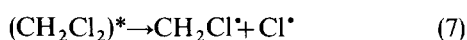
(4) Conjugated polyene structures can be formed in two successive hydrogen abstractions from alpha and beta carbons of PS by solvent radicals R_s^* :



From cyclohexane only cyclohexyl radical and hydrogen radical can be formed:

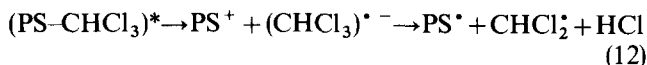
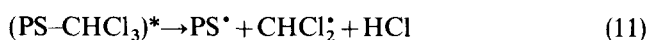
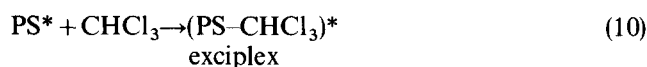


whereas CH_2Cl_2 or CHCl_3 produce very reactive chlorine and halogenated radicals^{6,8,9}:



The role of oxygen in the deactivation of excited states of these solvents and reactions with solvents is not well known. Results shown in *Figure 9* indicate that oxygen has a different effect on the formation of the band at 320 nm, attributed to the conjugated polyene structures. In cyclohexane and CH_2Cl_2 , oxygen enhances formation of the band at 320 nm, whereas in chloroform it has the opposite effect.

Schnabel³⁻⁵ and Easton⁷ have proposed that chlorinated solvents are involved in the formation of macroradicals via an exciplex of charge-transfer character:



It has been reported that photodegradation of PS occurs only in solution of CHCl_3 and CCl_4 in the presence of oxygen, whereas in CH_2Cl_2 degradation could not be detected in the presence nor in the absence of oxygen^{3,5}. The main-chain degradation of PS in CHCl_3 is caused by solvent radicals such as Cl^{\cdot} and $\text{CH}_2\text{Cl}_2^{\cdot}$ attacking the polystyrene macromolecules^{3,5,7}.

I.r. spectra (*Figure 8*) show that the formation of the peak at 1685 cm^{-1} , attributed to acetophenone groups (cf. *Table 2*) in PS-S samples after 90 min u.v. irradiation in air, differs depending on the solvent used, in the following order: $\text{CHCl}_3 > \text{CH}_2\text{Cl}_2 > \text{C}_6\text{H}_{12}$. Polymer alkyl radicals

(PS^{\cdot}) formed in the presence of solvent free radicals (R_s^*) (reactions (4) and (5)) produce peroxy radicals (PSOO^{\cdot}) in the presence of air, hydroperoxide groups (PSOOH) and finally alkoxy free radicals (PSO^{\cdot}). Alpha cleavage of these alkoxy radicals (PSO^{\cdot}) results in the formation of acetophenone groups as new end groups of polymer chains. This main-chain scission reaction is faster in CHCl_3 than in CH_2Cl_2 . I.r. spectra (*Figure 8*) show two other peaks at 1720 cm^{-1} and 1745 cm^{-1} which can be assigned to the formation of other carbonyl groups (cf. *Table 2*).

Results obtained during photochlorination of polystyrene by Cl_2 in chlorinated solvents show that chlorine radicals abstract initially alpha and beta hydrogen atoms from polystyrene and further replace them⁴⁶⁻⁴⁸. In the later stages of photochlorination, even chlorination of phenyl rings may occur. I.r. spectra of PS irradiated in CH_2Cl_2 or CHCl_3 do not show significant reduction in the intensities of bands at 1376 cm^{-1} (associated with CH bending mode) and 2850 and 2920 cm^{-1} (associated with C-H stretching in CH_2 groups), which would be proof for the chlorination of PS. Elemental analysis for chlorine in the samples shows only traces, less than 0.1 wt% of chlorine.

The most important conclusion from this research is that the formation of conjugated polyene structures in PS-S in various solvents probably occurs by the same mechanism (equations (1)-(5)) independent of the presence or absence of oxygen. If the u.v. irradiation is carried out in the presence of oxygen, this process is accompanied by a reaction in which carbonyl groups of different types are formed. It has not been found that chlorine radicals (Cl^{\cdot} , $\text{CH}_2\text{Cl}^{\cdot}$ or CHCl_2^{\cdot}) formed from chlorinated solvents during u.v. irradiation can terminate PS macroradicals.

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