

## Photooxidation of styrene–ethylene–butadiene–styrene (SEBS) block copolymer

Norman S. Allen<sup>a,\*</sup>, Cristina Luengo<sup>a</sup>, Michele Edge<sup>a</sup>, Arthur Wilkinson<sup>a</sup>,  
M. Dolores Parellada<sup>b</sup>, Juan A. Barrio<sup>b</sup>, V. Ruiz Santa Quiteria<sup>b</sup>

<sup>a</sup> Chemistry and Materials Department, Faculty of Science and Engineering, The Manchester Metropolitan University Chester Street, Manchester M1 5GD, UK

<sup>b</sup> Centro Tecnológico Repsol-YPF, Carretera Extremadura Km 18, 28931 Móstoles, Madrid, Spain

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### Abstract

The photooxidation of hydrogenated poly[styrene-*b*-butadiene-*b*-styrene] or poly[styrene-*b*-(ethylene-co-butylene)-*b*-styrene] (SEBS), has been studied using a variety of analytical and spectroscopic methods including yellowness, luminescence and FTIR spectroscopy coupled with crosslinking and hydroperoxide analysis in order to understand the nature of the processes involved. FTIR and luminescence analysis show complex oxidation processes with distinct features associated with each phase. Rates of photooxidation measured by carbonyl growth and discolouration show that low molecular weight samples are more photostable than those with high molecular weight. Oxidation primarily due to the aliphatic part occurs with a predominant absorption associated with terminal carboxylic acid groups at 1712 cm<sup>-1</sup>. Anhydrides, ketones, aldehydes, esters and  $\alpha,\beta$ -unsaturated carbonyl species are also formed in this matrix. Unlike thermal oxidation there is no evidence for crosslinking. Thus, end group oxidation is a predominant process at the interphase boundary of the soft aliphatic and hard aromatic segments with the immediate autocatalytic formation of high concentrations of primary hydroperoxides during the early stages of oxidation. These species are unstable and breakdown rapidly leaving a steady-state concentration of more stable hydroperoxides. The luminescence confirms a rapid initial disruption of the polystyrene excimers coupled with the formation of long wavelength emitting polyconjugated chromophores, possibly, stilbene type in nature giving rise to weak colour formation. Phosphorescence analysis also indicated the presence of initial acetophenone chromophores, which are associated with polystyrene end-groups formed by chain breakage at the aliphatic links. These species can act as initial active sensitive sites for further breakdown, possibly via a thermally induced hydrogen atom abstraction process to give benzaldehyde and benzoic acid. These active end-groups show a typical autocatalytic growth and decay process. The end-chain aliphatic radicals then become the sites for initial rapid hydroperoxidation as well as attack of the butene-1 tertiary groups. The presence of phenolic antioxidants and phosphites appear to exhibit a synergistic effect in inhibiting the discolouration and oxidation processes. This is evident through thermal analysis (OIT) and luminescence. In the latter case the consumption of excimer is impaired by the presence of stabilisers while the initial acetophenone end-groups in SEBS are destroyed. This is in complete contrast to the effects observed in control unstabilised SEBS material. Mechanisms are proposed and discussed for each phase oxidation.

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### 1. Introduction

In their unstabilised form, thermoplastic elastomers (TPEs) can undergo degradation and oxidation processes typical of those of conventional thermoplastics. Despite the extensive literature published on the degradation of most thermoplastic and rubber materials, TPEs are relatively newly developed, and consequently research studies on

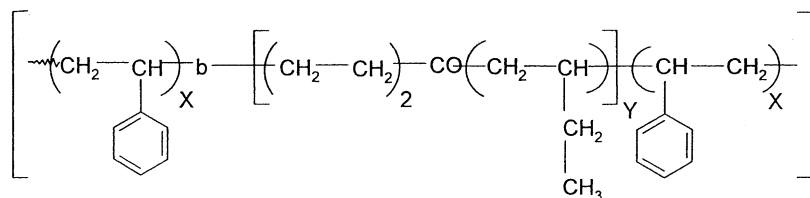
their degradation, is so far limited. Degradation processes in styrene-block copolymers (SBCs) are known, to occur in both the polystyrene and elastomer phases [1]. However, the elastomer phase is considered more liable to degradation because its low T<sub>g</sub> promotes permeability toward oxygen diffusion. The unsaturated SBCs are considered similar to styrene–butadiene rubber and natural rubber, respectively as regards resistance to oxidation, ozone attack and UV irradiation [2]. However, hydrogenated SBCs are claimed to have improved resistance toward degradation processes [3,4], a typical example being styrene–ethylene–butylene–styrene-block copolymer (SEBS). Although there are claims

\* Corresponding author. Tel.: +44-161-247-6357;

fax: +44-161-247-1432.

E-mail address: [n.allen@mmu.ac.uk](mailto:n.allen@mmu.ac.uk) (N.S. Allen).

that this material undergoes degradation and chain scission, there is no experimental evidence to support this statement. The stabilisation of SBCs and composites involves the use of synergistic mixtures of hindered phenolic and phosphite antioxidants [1] while in recent work hydrogen atom donating hydrocarbon solvents have been claimed to inhibit the degradation of SBCs [5]. In an earlier study on the thermal oxidation of SEBS oxidation and chain scission were found to dominate at the boundary of the polystyrene–olefin phases [6]. This was found to give rise to the formation of acetophenone end groups on the styrene units and carboxylic acids on the olefin chain ends. Concurrent and further reactions gave rise to the formation of anhydrides and peresters/acids in the longer term together with vinyl and  $\alpha,\beta$ -unsaturated carbonyl products, predominantly carboxylic acids. The olefin phase was found to exhibit severe oxidation and crosslinking associated with the initial formation of unstable primary hydroperoxide species. The presence of a hindered phenolic antioxidant and phosphite were also highly synergistic in inhibiting oxidation and phase separations at the boundaries by destroying the acetophenone end-groups and preventing excimer disaggregation. Thus, in this work we have extended our previous study here to include a photooxidation study on the behaviour of hydrogenated poly[styrene-*b*-butadiene-*b*-styrene] or poly[styrene-*b*-(ethylene-co-butylene)-*b*-styrene] (Structure 1). This has been studied using a variety of analytical and spectroscopic methods including luminescence and FTIR spectroscopy coupled with yellowing measurements, crosslinking and hydroperoxide analysis in order to understand the nature of the processes involved. As for thermal oxidation the degradation reactions appear to proceed in two distinct phases with the predominant chemistry occurring in the elastomer region but with no evidence for crosslinking. Rate processes and product distributions were also notably different.



Polystyrene-*b*-poly[ethylene-co-(but-1-ene)]-*b*-Polystyrene Triblock Copolymer

## 2. Experimental

### 2.1. Materials

The SEBS samples used in this study were supplied by Repsol S.A., in Madrid and were all experimental grade products. The sample grades together with their molecular weights and antioxidant concentrations are shown in Table 1.

Ratios of polystyrene to olefin are proprietary. All the samples were specially prepared for this project in order that the control and stabilised products had a similar history. The antioxidants used for this work have the structures shown in A and B and were added to the polymer during the polymerisation step. The SEBS materials were all compression moulded at 205 °C. All the solvents used in this work were of ‘Analar’ purity and obtained from Aldrich, Gillingham, UK.

### 2.2. Crosslinking

Sample of aged SEBS were soxhlet extracted with chloroform for 12 h, the thimble weighed after 2 h drying at 60 °C.

Samples were also extracted with chloroform in glass tubes maintained in a water bath at 60 °C for 24 h followed by separation of the gel, drying at 60 °C for 2 h and then weighing the residue.

### 2.3. FTIR analysis

The samples of SEBS films were placed in a transmission cell fitted to a Nicolet 510 Fourier transform infra-red (FTIR) spectrophotometer (DTGS detector) with air purge. Spectra were made up of 50 scans with a resolution of 2 cm<sup>-1</sup>. Samples were also measured by total internal reflection using an ATR accessory. Carbonyl index errors were small of the order  $\pm 0.01$  units.

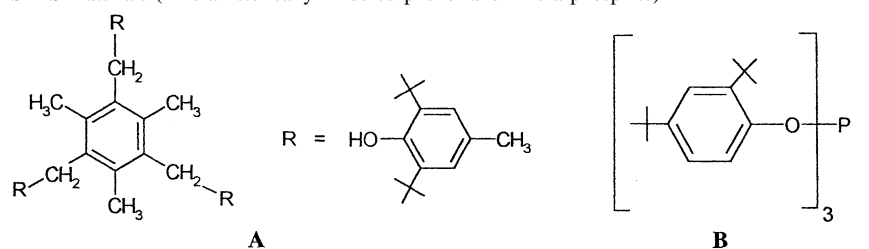
### 2.4. Hydroperoxide analysis

Hydroperoxide concentration in photooxidised SEBS copolymers were measured using the standard iodometric method established previously [7].

### 2.5. Luminescence analysis

Luminescence analysis was undertaken using a Perkin-Elmer Model LS-50B research spectrometer. Fluorescence spectra were obtained at ambient conditions on thin films using a front face accessory, while phosphorescence spectra were obtained at 77 K on thin strips of film placed in quartz tube cells. All measurements taken here were relative to that of the control samples.

Table 1  
SEBS materials (A is a sterically hindered phenol and B is a phosphite)



Sample code	Molecular weight		Additives (% w/w)
	$M_w$	$M_n$	
1	183450	154862	None
2	183450	154862	0.1% A
3	183450	154862	0.1% A + 0.1% B
4	57593	53840	0.1% A
5	57593	53840	0.1% A + 0.2% B

## 2.6. Yellowness index

Colour formation was obtained using yellowness index (ASTM 313) via a Gretag Spectral Eye Colour measurement instrument (Colour data Systems Ltd., Wirral, UK). Only relative measurements are shown here against that for the control samples hence original samples are set at zero. Errors in measurements are of the order  $\pm 0.2$  units.

## 2.7. Photooxidation

Irradiation studies were undertaken in an Atlas Suntest Model CPS+ using a 1.5 kW xenon source and Black Body temperature of 50 °C (available from Alplas Technology, Oxford, UK). Samples have a constant irradiance in this unit of 765 W/m<sup>2</sup>.

## 3. Results and discussion

SEBS block copolymer is a complex system being dependent on the nature of the olefin starting materials, their composition and the manufacturing process [1]. The elastomer block consists of a copolymer of ethylene and butylene, which is derived from a butadiene precursor by hydrogenation. The blocks tend to possess a sharp compositional boundary with pure “polystyrene” and pure “elastomer” giving a phase of immiscible domains of polystyrene in an elastomeric matrix. Usually, at less than 50% polystyrene the domains are well-dispersed. A typical structure of SEBS is shown in Structure 1.

The SEBS samples utilised in this study are shown in Table 1 with their respective molecular weights and additive formulations used. The control used is a high molecular weight grade material. The stabilisers A and B are shown in A and B and are typical commercial hindered phenolic and phosphite antioxidants.

Unlike thermal oxidation [6] photooxidation of SEBS did not give rise to any evident crosslinking indicating chain scission to be the dominant process. Clearly under this condition radical coupling processes via hydroperoxy, oxy or alkyl radicals were minimal.

To determine the chemical changes induced in the SEBS FTIR analysis was undertaken on films of the materials. Table 2 summarises the main functional group frequencies observed in the SEBS material and were consistent for all samples examined. Fig. 1 shows typical FTIR transmission changes observed in the photoaged material in the region 4000–2000 cm<sup>-1</sup>. Here, a strong hydroxyl absorption is observed in the SEBS at the rate of 3450 cm<sup>-1</sup> due to the formation of associated groups together with some

Table 2  
Band positions and assignments of FTIR spectra in irradiated SEBS

Wavenumber (cm <sup>-1</sup> )	Group	Remark
3540	Hydroxyls (alcohols/peroxides/hydroperoxides)	O–H stretch (unassociated)
3450	Hydroxyls	O–H stretch (associated)
1775	Anhydride/γ-lactone/peracids	C=O stretch
1735	Aliphatic esters Carboxylic acids Benzoic acid (monomeric form) δ-Lactone	C=O stretch
1720	Aliphatic aldehydes	C=O stretch
1715	Aliphatic ketones	C=O stretch
1712	Carboxylic acids	C=O stretch
1700	Carboxylic acids Benzoic acid (dimer form) Benzaldehyde	C=O stretch
1690	Aromatic ketones/acetophenone groups	C=O stretch
1680	α,β-Unsaturated carbonyls	C=O stretch
1640	α,β-Unsaturated carbonyls	C=O stretch

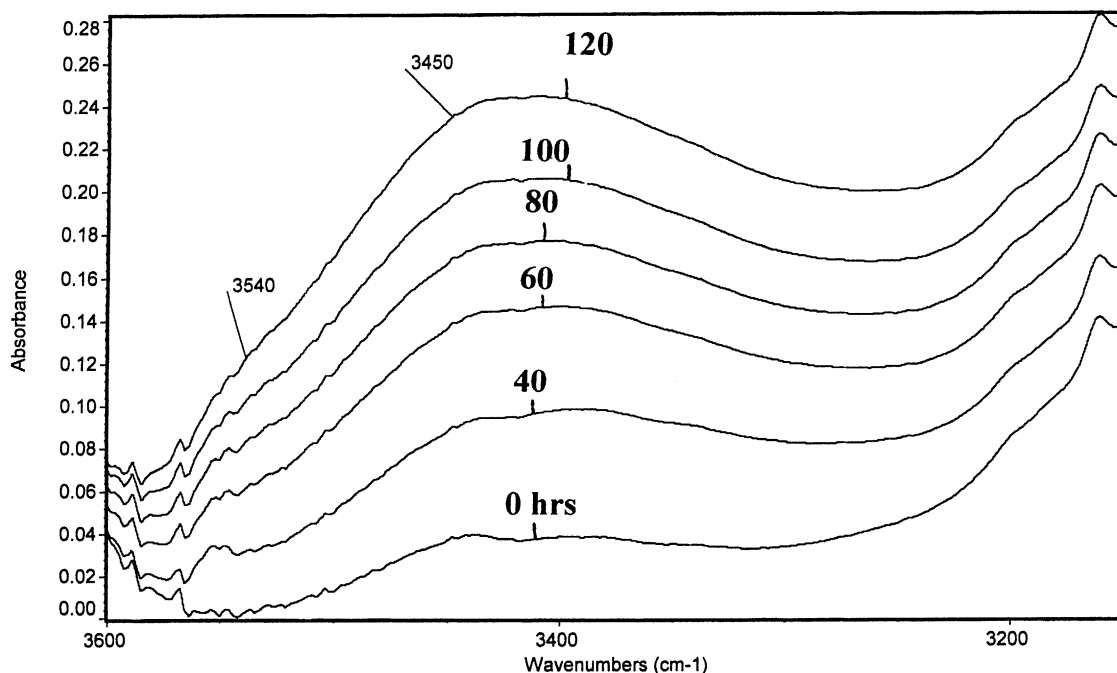


Fig. 1. FTIR spectra using in the range 4000–2000  $\text{cm}^{-1}$  of SEBS copolymer before and after periods of irradiation in the Atlas CPS+ weatherometer.

unassociated hydroxyl species in the region 3540  $\text{cm}^{-1}$  [8,9], possibly hydroperoxides. Thus, oxidation appears to be consistent with rapid hydroperoxidation of the SEBS. Fig. 2 shows changes in the region 2000–1000  $\text{cm}^{-1}$  where strong carbonyl absorptions are observed in the SEBS with a maximum at 1712  $\text{cm}^{-1}$  due to carboxylic acids plus a

weak shoulder at 1715  $\text{cm}^{-1}$  due to ketones and aldehydes at 1720  $\text{cm}^{-1}$ . Derivatisation with sodium hydroxide treatment (2 M) removed the band at 1712  $\text{cm}^{-1}$  confirming the presence of carboxylic acids. Ester absorption is observed at 1735  $\text{cm}^{-1}$  and  $\alpha,\beta$ -unsaturated carbonyl species at 1680 and 1640  $\text{cm}^{-1}$ . Aromatic carbonyls may also be absorbing

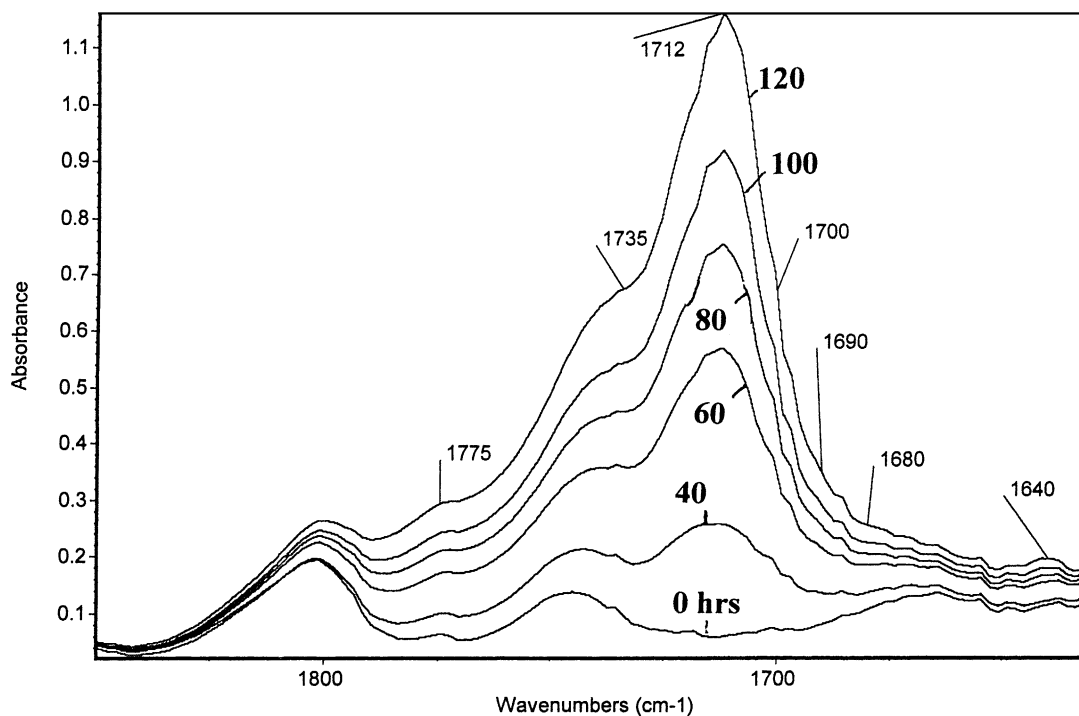


Fig. 2. FTIR spectra using in the range 2000–1000  $\text{cm}^{-1}$  of SEBS copolymer before and after periods of irradiation in the Atlas CPS+ weatherometer.

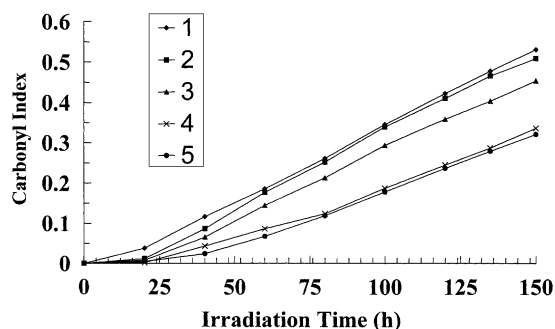


Fig. 3. Carbonyl index vs. irradiation time in the ATLAS CPS+ in hours for SEBS samples 1–5.

at  $1700$  and  $1690\text{ cm}^{-1}$ . A band is also evident at  $1775\text{ cm}^{-1}$  and may be assigned to lactones, peracids/peresters or anhydrides [8,11]. Below  $1000\text{ cm}^{-1}$  no other absorption changes were observed indicating the possible instability and transient nature of any formed vinyl groups except those associated with carbonyl groups albeit weakly. Other potential absorbing species are also given in Table 2 and their mode of formation is discussed below.

Using carbonyl formation as a measure of photooxidative stability differences in relative stability are noted in Fig. 3 by ATR. These are measured via the well-established carbonyl index method [7,8]. Here the control is the most unstable followed by the sample 2 containing the phenolic antioxidant only. Samples with phosphite were somewhat more stable. Generally, however, antioxidants of this type are not expected to impart superior light stability. The low molecular weight samples 4 and 5 are however, more light stable. In terms of yellowness index colour formation is significantly weaker than that found earlier in thermal oxidation (Fig. 4). This is due to the transient nature of any formed colour chromophores under light exposure that would otherwise be stable thermally. The sample with phenolic antioxidant alone gives rise to more yellowing and this is due to quinone formation.

The FTIR changes noted above are also consistent with the hydroperoxide analysis on the irradiated SEBS materials. In unstabilised non-degraded polymer there is little hydroperoxide initially, i.e.  $<6\text{ ppm}$ . During the first 10 h of

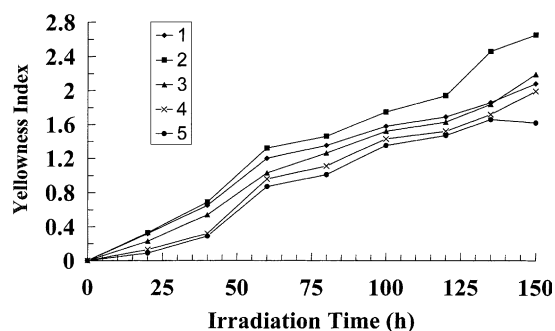


Fig. 4. Yellowness index vs. irradiation time in the ATLAS CPS+ in hours for SEBS samples 1–5.

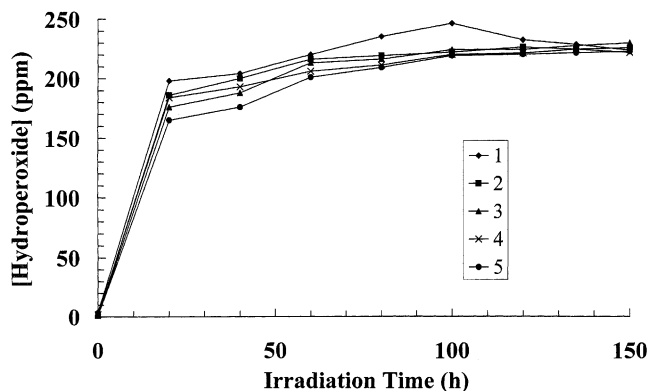


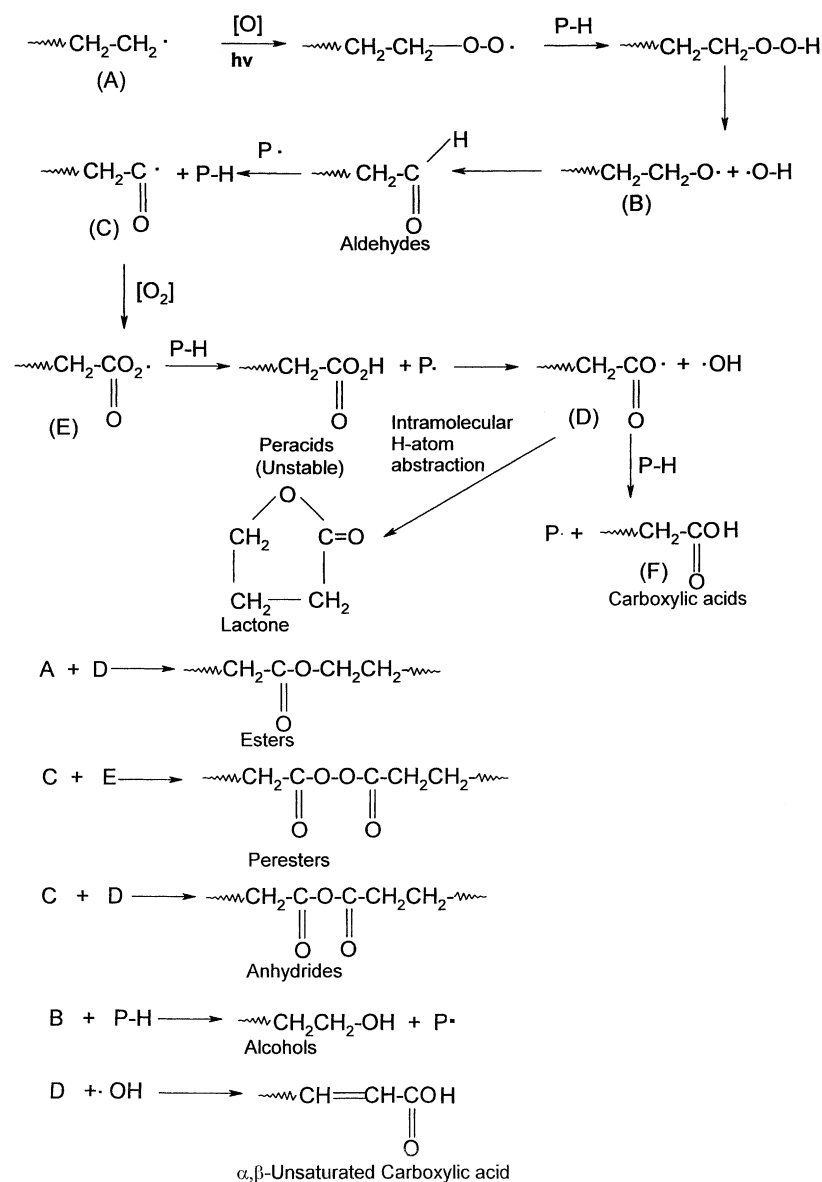
Fig. 5. Hydroperoxide concentration vs. irradiation time in the ATLAS CPS+ in hours for SEBS samples 1–5.

irradiation there is a very rapid autooxidation of the polymer resulting in a sharp rise in the formation of hydroperoxide species (Fig. 5) [7,8]. This effect can be associated with chain scission at the styrene–aliphatic links giving primary alkyl and benzyl radicals, which are then oxidised to form hydroperoxides. These primary hydroperoxides will grow rapidly during the early stages of photooxidation but quickly decompose to give carboxylic acids and this is borne out by the rapid subsequent decline and observed plateau effect in hydroperoxide concentration to a steady-state concentration. Although there is little difference in the hydroperoxide levels the control unstabilised sample achieves a higher initial hydroperoxide concentration than the other SEBS stabilised samples.

Scheme 1 depicts the various functional group changes consistent with those seen in the FTIR spectra and listed in Table 1. The dominant formation of primary carboxylic acids throughout the oxidation suggests the predominance of an end-chain oxidation step and this is consistent with the phosphorescence analysis data below. The only evident vinyl group formation in FTIR analysis was associated with carbonyl groups.

Luminescence (fluorescence and phosphorescence) analysis provides more specific information on photoactive chromophores in the polymer either present initially or formed during the oxidation/degradation processes. Such species may also be consumed by the ensuing degradation reactions/products. These species are normally carbonylic in nature or vinyl groups or aromatic species. In the case of aliphatic species these can be ketonic or aldehydic in nature either alone or coupled with vinyl groups. Carboxylic acids and ester groups, hydroperoxides and peresters/acids are non-luminescent following excitation by light energy. Such species have higher energy excitation bands (below  $250\text{ nm}$ ) and tend to dissipate their absorbed energy through chain scission reactions rather than emit light.

Fluorescence analysis of the SEBS material as film using the reflective mode shows a strong emission band centred at  $335\text{--}340\text{ nm}$ , which is associated primarily with the pres-



Scheme 1. End-chain olefin oxidation via hydroperoxides.

ence of excimer sites in the polystyrene phase. This is due to the association of a ground-state styrene unit with an excited unit and emits to the red of the styrene monomer emission [8]. The distinct observation of excimer emission is supportive of the presence of discrete polystyrene phases and is unaffected by the olefin phase. Upon degradation however, there is a rapid loss and reduction in the excimer sites due to chain scission and disaggregation of the styrene units (Fig. 6). This process occurs rapidly during the early stages of the degradation process. The reduction process is related on a semi-quantitative basis in Fig. 7 for all the SEBS samples. The interesting feature of this data is that the presence of the mixture of stabilisers in the low molecular weight sample appears to impair the reduction in the excimer emission sites. Here, the presence of antioxidants will destroy free radicals and/or scavenge active oxidation

products likely to cause chain scission. The higher concentration of phosphite antioxidant appears to be very effective in this regard (sample 5). Magnification of the fluorescence spectra with degradation also showed the initial formation of a longer wavelength emitting species, i.e. a broad spectral shift to 350–380 nm. Under light exposure the instability of such chromophores will not give rise to such an apparent spectrum as was observed thermally [6]. It is known that in the degradation of polystyrene, phenyl–vinyl units are formed similar to that of stilbene and that these can contribute to yellowing [8–10]. The fluorescence of a model stilbene compound is shown for comparison (Fig. 8). The absence of other stronger emitting chromophores, such as  $\alpha,\beta$ -unsaturated carbonyls, suggests that if indeed they are formed then they must be non-emissive (as in carboxylic acids).

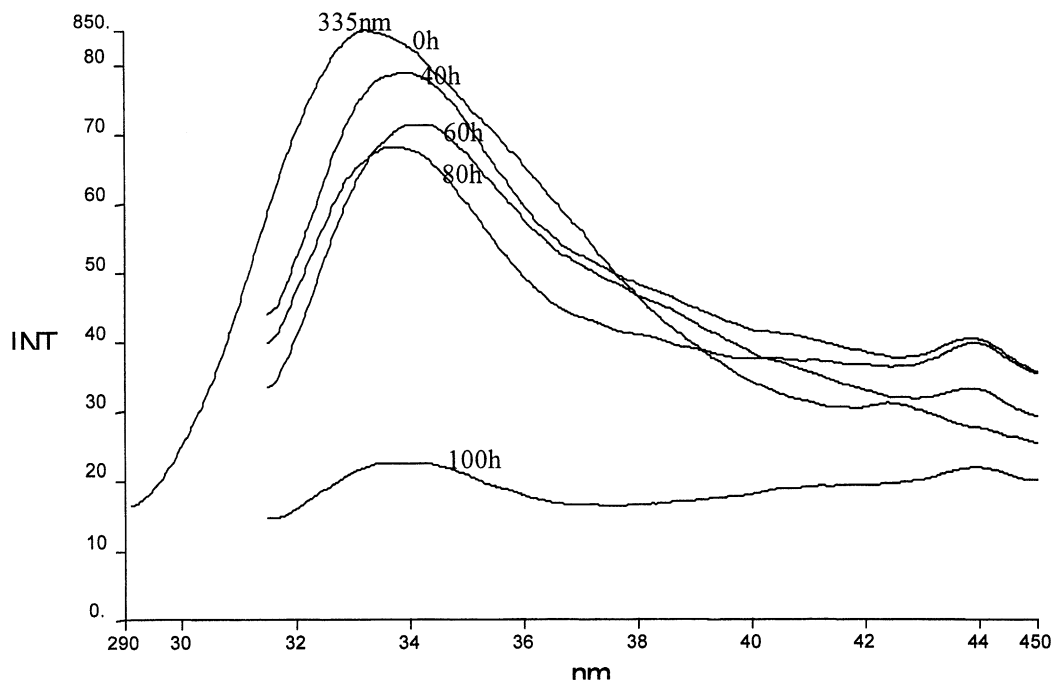


Fig. 6. Relative excimer emission spectral changes with irradiation time in the ATLAS CPS+ in hours for SEBS control sample 1 (excitation wavelength 280 nm).

Low temperature phosphorescence analysis is also valuable for probing the formation or presence of carbonylic species either of an aromatic or aliphatic nature. The interesting feature of this analysis was the observation of the initial presence of acetophenone chromophores in the polymer (Fig. 9). It is to be noted that although such chromophores are easily observed by phosphorescence they may not necessarily be observed by the much less sensitive FTIR technique. However, in this case weak FTIR absorption was evident. On photooxidation acetophenone chromophores were formed rapidly after an initial 60 h period and varied with the sam-

ple type (Fig. 10). Thus, acetophenone groups are rapidly formed during oxidation in the polystyrene phase due to end-chain oxidation and scission. Plots of phosphorescence emission intensity versus irradiation for the different SEBS samples are given in Fig. 11. Consistent with the other data analysis on stability the control SEBS sample 1 exhibited the highest levels of acetophenone chromophores after 60 min of irradiation. Their concentration then declined rapidly on further irradiation due their transient nature and subsequent photoreactivity in the polymer. The lower molecular weight sample 5 was again found to be the more stable in this regard.

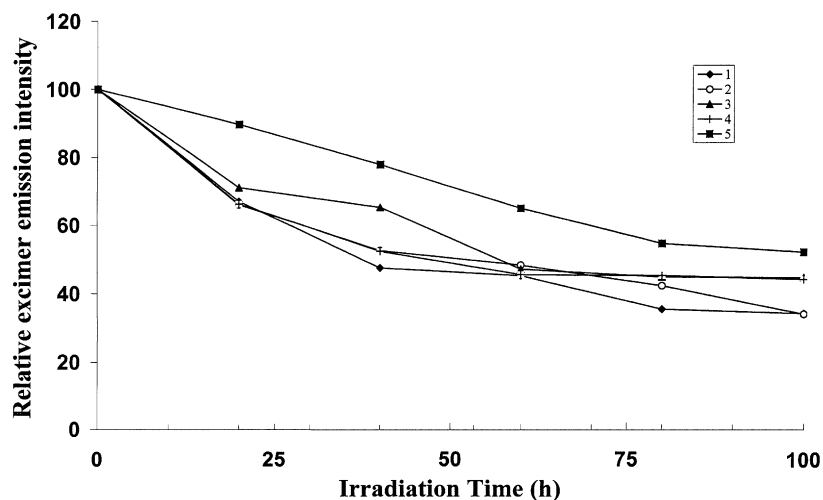


Fig. 7. Relative excimer emission intensity changes at the rate of 335 nm with irradiation time in the Atlas CPS+ in hours for SEBS samples (excitation wavelength 280 nm).

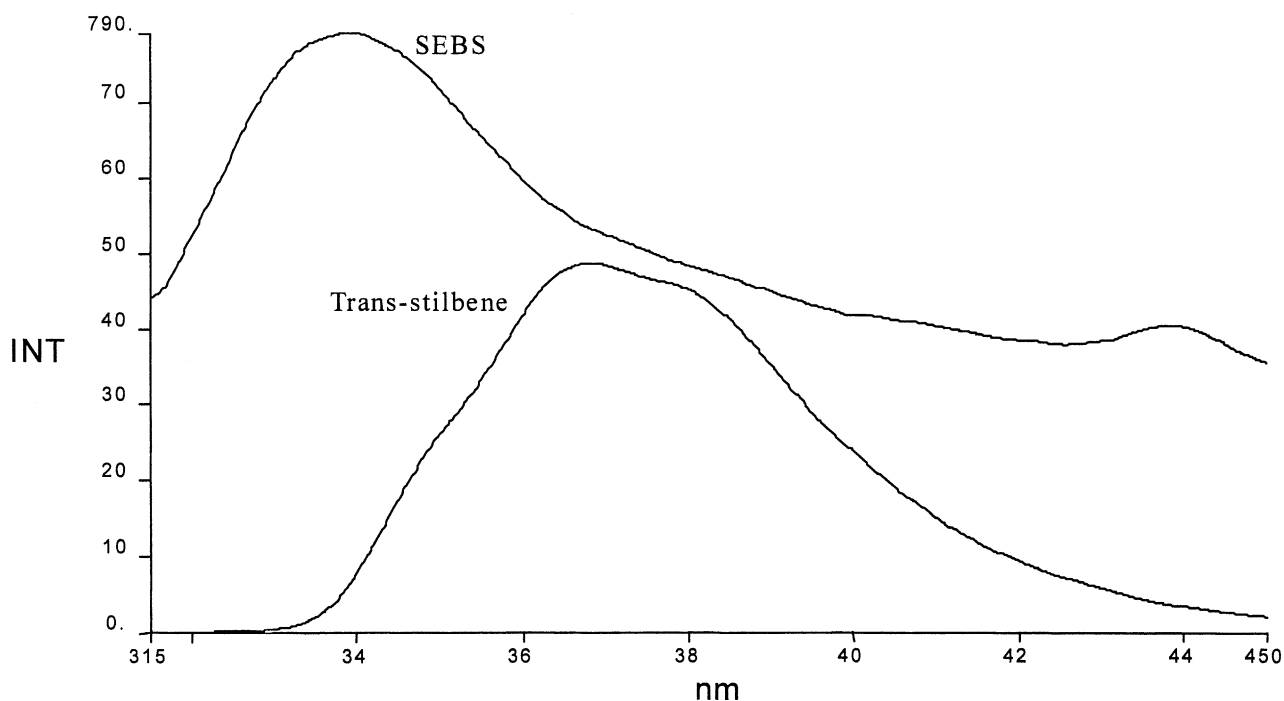


Fig. 8. Fluorescence emission spectra (EX = 280 nm, EM = 335 nm) of control SEBS sample irradiated for 40 h in the ATLAS CPS+ compared to that of the emission spectrum of trans-stilbene in ethanol ( $10^{-4}$  M).

The above analysis indicates that chain degradation, scission and oxidation are occurring primarily at the styrene-olefin phase boundary. This is confirmed by the rapid formation of end-chain carboxylic acids (FTIR at the rate of  $1712\text{ cm}^{-1}$ ) and concurrent formation of acetophenone

end-groups as measured by phosphorescence analysis. The latter may be observed in the FTIR but are certainly masked by the formation of other abundant species. However, it may be argued that the species at  $1690\text{ cm}^{-1}$  in the irradiated SEBS could also be acetophenone groups. [Scheme 1](#)

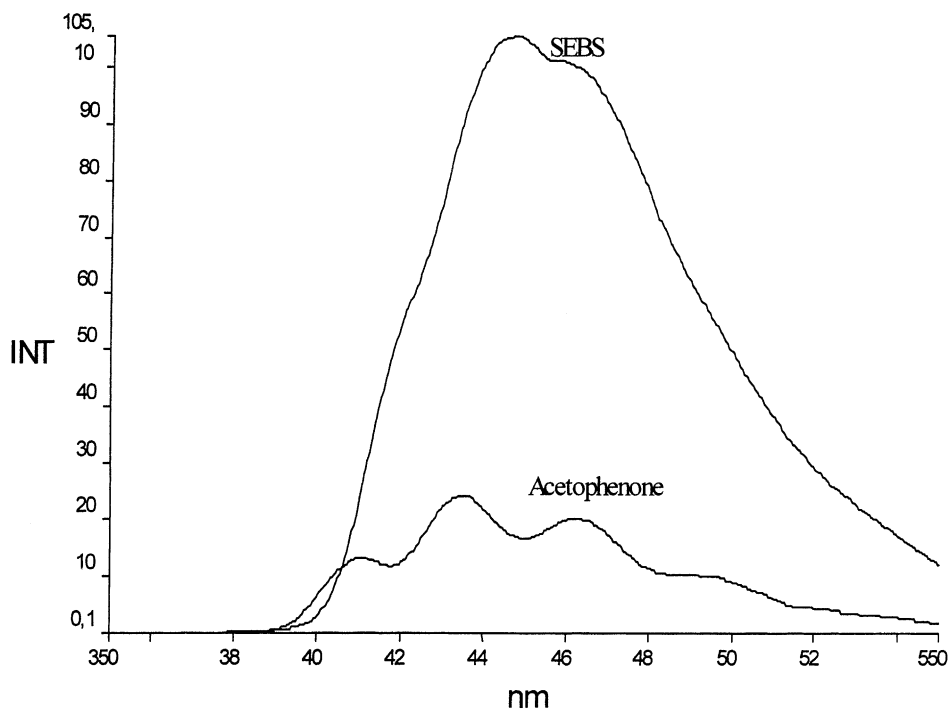


Fig. 9. Phosphorescence emission spectra (EX = 250 nm) of unstabilised SEBS sample 1 after irradiation for 40 h in the ATLAS CPS+ compared to that of the emission spectrum of acetophenone in ethanol ( $10^{-4}$  M) at 77 K.



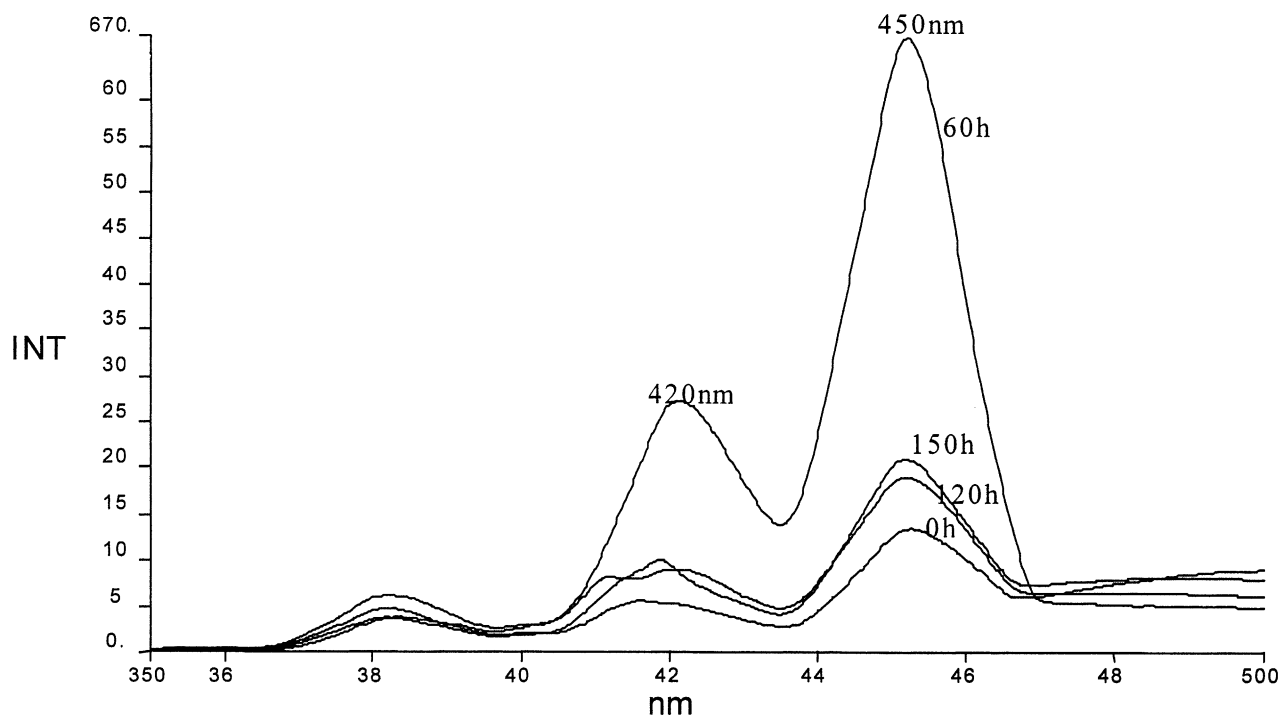


Fig. 10. Phosphorescence emission spectra at 77 K (EX = 250 nm) of unstabilised SEBS sample 1 during irradiation in the ATLAS CPS+.

depicts end-chain oxidation to form carboxylic acids via aldehydes and then peracids ( $1720$  and  $1775\text{ cm}^{-1}$ ). Other labile sites in the SEBS such as the butene-1 groups are also expected to be sites of attack but from our data here lability at the phase boundary is evident. Lactones, are known to be formed in polyolefin oxidation by an intra-molecular backbiting reaction (H-atom abstraction) by a carboxyl radical. The esters, peresters and anhydrides are formed through appropriate radical recombination reactions and alcohols through hydrogen atom abstraction. Unsaturated carbonyl products (carboxylic acids) can be formed by further hydrogen atom abstraction reactions down the chain. Hydroperoxide build-up in the olefin phase is predominant as shown

by the FTIR and iodometric analysis and will be representative of the total amount of hydroperoxidation in the SEBS and not just end-group oxidation. Breakage of the olefin–styrene chain will result in the formation of benzyl radicals which can then be oxidised to form hydroperoxides (Scheme 2). These species, breakdown easily to give acetophenone end-groups as shown by the phosphorescence emission. Phenyl–propene or stilbene groups can also be formed by further hydrogen atom transfer reactions resulting in the release of acetophenone as a product (Scheme 2). Subsequent photoreactions of the acetophenone end-groups can give rise to the formation of benzaldehyde and benzoic acid products.

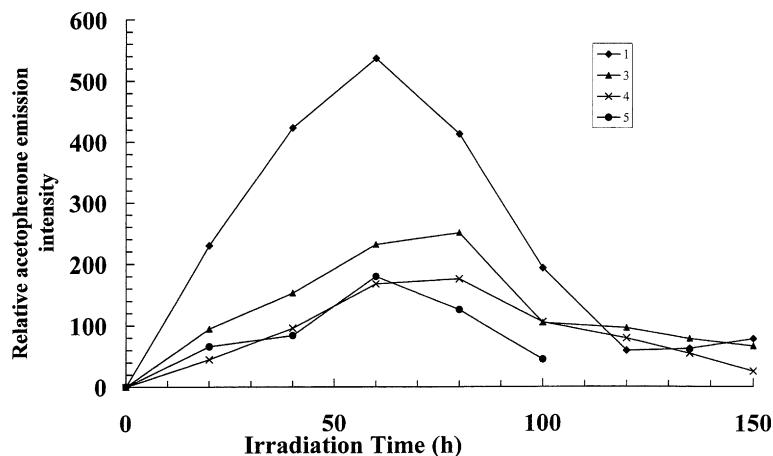
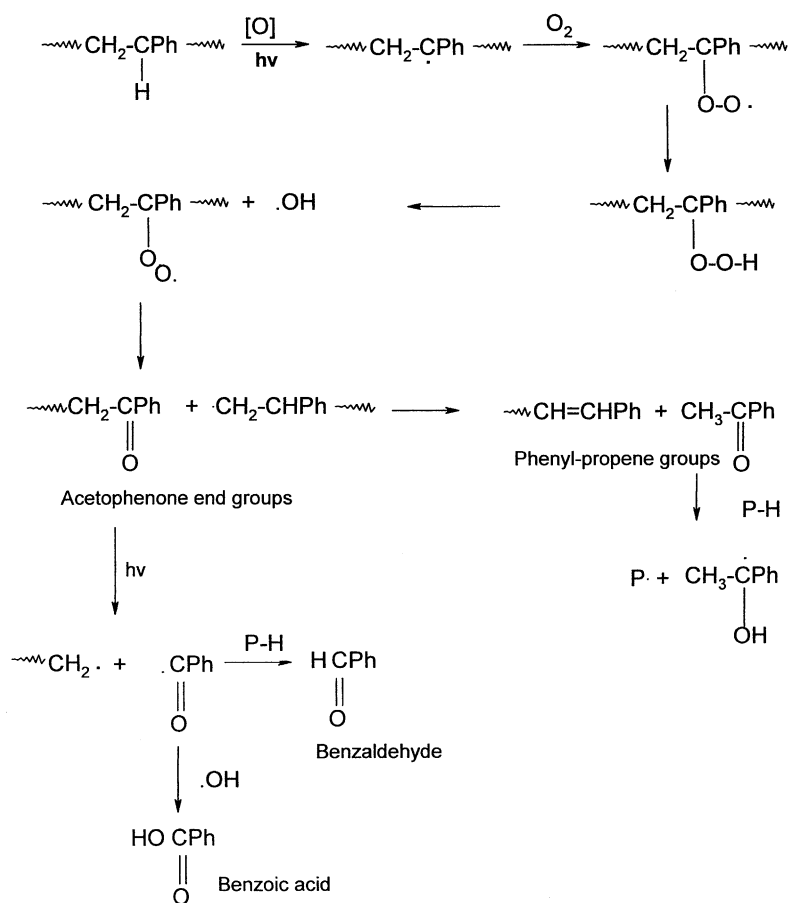


Fig. 11. Phosphorescence emission intensities at 77 K (EX = 250 nm) vs. irradiation time in the ATLAS CPS+ of SEBS samples 1–4.



Scheme 2. Polystyrene oxidation via hydroperoxides.

The major observation in this work is the observed significance of inhibition by the antioxidants in the consumption of the excimer styrene units and the direct consumption of the acetophenone units initially present and/or formed in the SEBS. The latter species can be reactive as has already been shown in earlier work for aromatic ketones [12]. These chromophores can react through a photochemically generated hydrogen atom abstraction process to give ketyl radicals (see Scheme 2 at end) and alkyl radicals. In this case, the presence of the antioxidant is acting as a sacrificial H-atom donor to the acetophenone groups thus protecting the polymer from further oxidation. It is to be understood that the presence of the antioxidants in this work are used purely for thermal stabilisation but that their significance in terms of photochemical activity is noteworthy. In future analysis light stabiliser interactions will be of interest.

#### 4. Conclusions

This work shows a number of interesting features associated with SEBS photooxidation. Photooxidation gives rise to oxidation and chain scission at the boundary of the polystyrene–olefin phases in terms of the analysis of data presented here. This gives rise to the formation of acetophe-

none ends groups on the styrene units and carboxylic acids on the olefin chain ends. Concurrent and further reactions give rise to the formation of anhydrides and peresters/acids in the longer term together with  $\alpha,\beta$ -unsaturated carbonyl products, predominantly carboxylic acids. It is understood in the context of the structure of SEBS that any tertiary groups in the butene-1 units would also be labile centres for hydroperoxidation. There is no evidence for crosslinking in the SEBS unlike that for thermal oxidation. The olefin phase exhibits severe oxidation associated with the initial formation of unstable primary hydroperoxide species while the polystyrene phase exhibits oxidation to form acetophenone end-groups. The latter are transient and photounstable in the longer term causing further photoreactions. The presence of a hindered phenolic antioxidant and phosphite are highly synergistic in inhibiting oxidation and phase separations at the boundaries by destroying the acetophenone end-groups and preventing excimer disaggregation. Future work will centre on HALS behaviour.

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