NEW ASPECTS OF PHOTODEGRADATION AND PHOTO-OXIDATION OF POLYSTYRENE

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Abstract - Polystyrene is degraded, oxidized and discolored when exposed to sun-
light under atmospheric conditions. The chemical effects are ascribed to hydro-
peroxy, hydroxyl and carbonyl group formation. Chemical and spectroscopic data
are not specific enough for identification of these different groups. Therefore,
we have studied the photo-oxidation of the model compound 2-phenyl-butane. The
resulting oxidized compounds have been separated and analyzed using a combined
gas chromatograph-mass spectrometer. Mechanisms for the photo-oxidation of the
model compounds have been proposed. By comparing these results with photo-
oxidation data for polystyrene film, conclusions on the oxidation and degrada-
tion of the polymer have been outlined, including the carbonyl and hydroxyl
group formation. The yellowing of the polymer is largely caused by phenyl ring
opening reactions, for which probable mechanisms are suggested.

INTRODUCTION

When polystyrene is subjected to UV irradiation in the presence of air, it undergoes a
rapid yellowing and a gradual embrittlement. Industrially, the yellow discoloration is an
important adverse effect of the ageing of polystyrene, e.g. during exposure outdoors. The
photo-oxidation of polystyrene has been extensively investigated by many authors (1-15).
The main reactions observed are bond scission, chain crosslinking and oxidative degradation.

The generally accepted theories of oxidation of polymers are based on the free radical
mechanism for thermal oxidation of hydrocarbons, proposed by Bolland and Gee more than
thirty years ago   (16-19). This mechanism involves peroxy group formation and it pro-
ceeds in the following fundamental steps   (5, 20, 21): initiation, propagation, radical
chain branching and termination.

I   Initiation

The initiation of photochemical reactions in polystyrene includes an initial act of ab-
sorption of a quantum of light by a macromolecule or by an impurity present in the polymer,
leading to polymer free radical formation:

$$PH \longrightarrow \overset{\bullet}{P} + \overset{\bullet}{H} \qquad\qquad (1)$$

The amount of energy involved in this process is related to the wavelength of the light
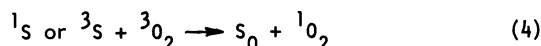absorbed. Therefore, the initiation reaction may occur in different ways.

1.1.   Absorption of Light by Pure Polystyrene Units. Pure polystyrene does not absorb UV
light above 290 nm, e.g. it should be stable in sunlight. When pure polystyrene is irradiat-
ed in the wavelength range well below 280 nm, the absorption of quanta is essentially due to
the phenyl groups of the polystyrene itself. In this initiation process excitation of ben-
zene rings to singlet and triplet states occurs, followed by reactions giving free radical
formation by bond scission.

1.2.   Absorption of Light by Charge-Transfer (CT) Complexes. Complexes resulting from
intra- or intermolecular charge transfer may be formed between electron donating and elec-
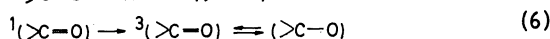tron accepting groups, e.g. molecular oxygen and phenyl groups in polystyrene:

$$(2)$$
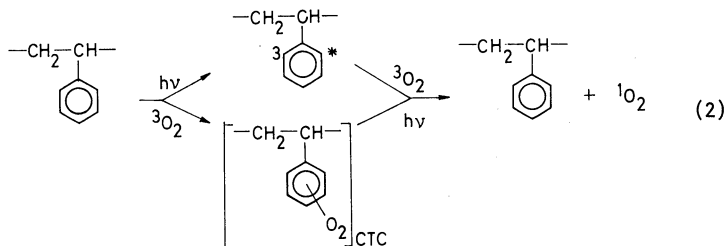
The CTC compound (2) absorbs at wavelengths > 300 nm.

1.3.   Initiation by Singlet Oxygen.

$$S + h\nu \longrightarrow {}^1S \longrightarrow {}^3S \qquad\qquad (3)$$

$$^1S \text{ or } {}^3S + {}^3O_2 \longrightarrow S_0 + {}^1O_2 \qquad\qquad (4)$$

Singlet oxygen can be formed by energy transfer from the excited triplet state of phenyl groups in polystyrene to molecular oxygen, by energy transfer from a CT complex to molecular oxygen (cf. reaction 2), by energy transfer to molecular oxygen from excited internal impurities (modified groups) or external impurities (added compounds) present in commercial polystyrene.
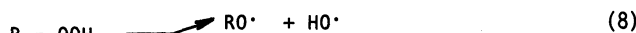
1.4.   Initiation by Free Radicals Formed from Excitation of Carbonyl groups on the Macromolecules. Carbonyl groups absorb in the near ultraviolet, i.e. at 290 to 400 nm:

$$>C=O + h\nu \longrightarrow {}^1(>C-O) \qquad\qquad (5)$$

$$^1(>C-O) \longrightarrow {}^3(>C-O) \rightleftharpoons (>\underset{.}{C}-\underset{.}{O}) \qquad\qquad (6)$$

The carbonyl biradicals may further abstract hydrogen from the same or neighbouring macromolecules (HP):

$$>\underset{.}{C}-\underset{.}{O} + HP \longrightarrow >\underset{.}{C}-OH + P^\bullet \qquad\qquad (7)$$
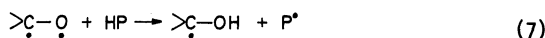
1.5.   Initiation by Photodecomposition of Hydroperoxide Groups on the Polystyrene Chains. Hydroperoxide groups, present on the chains (R) may decompose thermally or photochemically:

$$R - OOH \underset{\searrow}{\overset{\nearrow}{\longrightarrow}} \begin{array}{l} RO^\bullet + HO^\bullet \qquad\qquad (8) \\ R^\bullet + HOO^\bullet \qquad\qquad (9) \end{array}$$

Reaction (8) is the most probable due to the low bond strength of the O-O bond.

2.   Propagation

The propagation reactions of free radicals in the presence of oxygen include formation of peroxy radicals and hydroperoxide groups. Polystyrene alkyl radicals (R·) formed during the initiation can easily react with molecular oxygen (triplet state), producing peroxy radicals by addition:

$$R\bullet + {}^3O_2 \longrightarrow ROO\bullet \qquad\qquad (10)$$

The peroxy radicals abstract hydrogen - preferentially tertiary bonded - from other polystyrene molecules (R'H) to form hydroperoxides and new polystyrene alkyl radicals (R'·):

$$ROO\bullet + R'H \longrightarrow ROOH + R'\bullet \qquad\qquad (11)$$
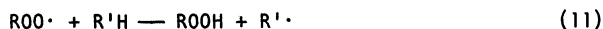
3.   Chain Branching

The chain branching in photo-oxidation of PS includes decomposition of polymer hydroperoxides into free radicals (cf. reactions 8 and 9). The new radicals formed can take part in hydroxyl and carbonyl group formation on polymer chains.
Fig. 1 shows the characteristic IR bands, which appear during UV irradiation of polystyrene in air.
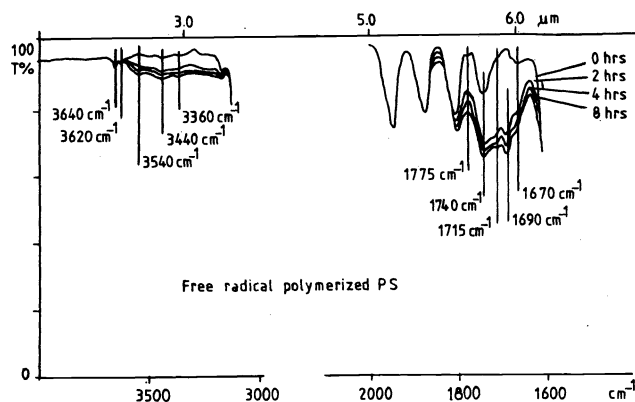

Fig. 1. IR absorption spectra of a thin film of commercial polystyrene sample irradiated at 253.7 nm in the presence of air.

The IR spectra show two complex absorption regions, at 3600-3400 cm^{-1} and 1800-1600 cm^{-1}, which are attributed to hydroxyl (or hydroperoxy) and carbonyl groups, respectively.

The two IR bands contain several absorption peaks indicating formation of several different hydroxyl and carbonyl groups in photo-oxidized polystyrene by different mechanisms simultaneously. The interpretation of the two IR absorption regions by different authors does not agree.

In our laboratory (12-15) we tried to resolve the complex hydroxyl and carbonyl IR bands in polystyrene using photo-oxidation of 2-phenyl-butane as model compound. The UV irradiation was carried out in methanol solution in the presence of oxygen, using light of 253.7 nm. During the photo-oxidation of 2-phenyl-butane several different compounds are formed from which the following were separated by thin layer chromatography and identified by combined gaschromatography/mass spectrometry and common analytical methods:
1) acetophenone,2) propiophenone,3) 2-phenyl-2-butanol,4) 2-phenyl-2-hydroxy- (3,4)buten, 5) 2-hydroxy-acetophenone, 6) 2-hydroxy-propiophenone, 7) o-methyl(methyl-benzoate), 8) 1-keto-1(2)hydroxy butyl-(2,4)hexadienoic acid methyl ester, and 9) 1-(2)hydroxy butyl-2-keto-butyrolactone. The probable formation mechanisms of these compounds are shown in the scheme 1,2 and 3 (12,14). Analyzing the data from the Scheme 1,2 and 3 conclusions about formation of modified groups in photo-oxidized polystyrene can be drawn.

3.1.   Formation of Hydroxyl Groups. Hydroxyl groups in photo-oxidized polystyrene are formed in the reaction between alkoxy polystyrene radicals and other polystyrene molecules:
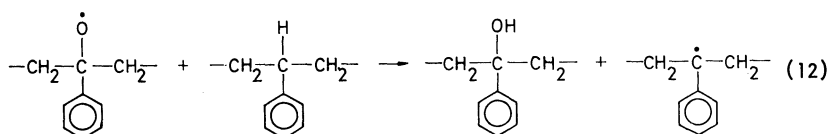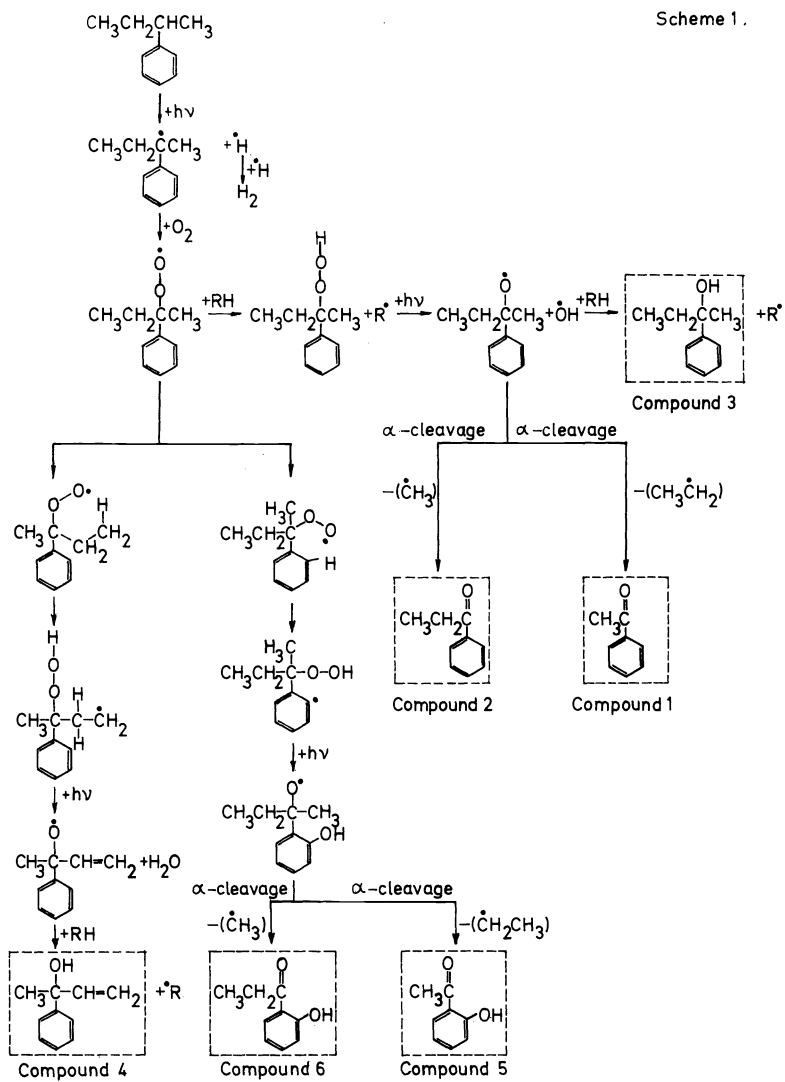

The hydroxyl groups are assumed to be formed along the polystyrene main chains. The oxidation of phenyl groups in polystyrene with formation of hydroxyl groups in ortho position may occur by a similar mechanism as proposed for photo-oxidation of the model compound which gives ortho-hydroxy compounds (cf. Scheme 1, Compounds 6,5).
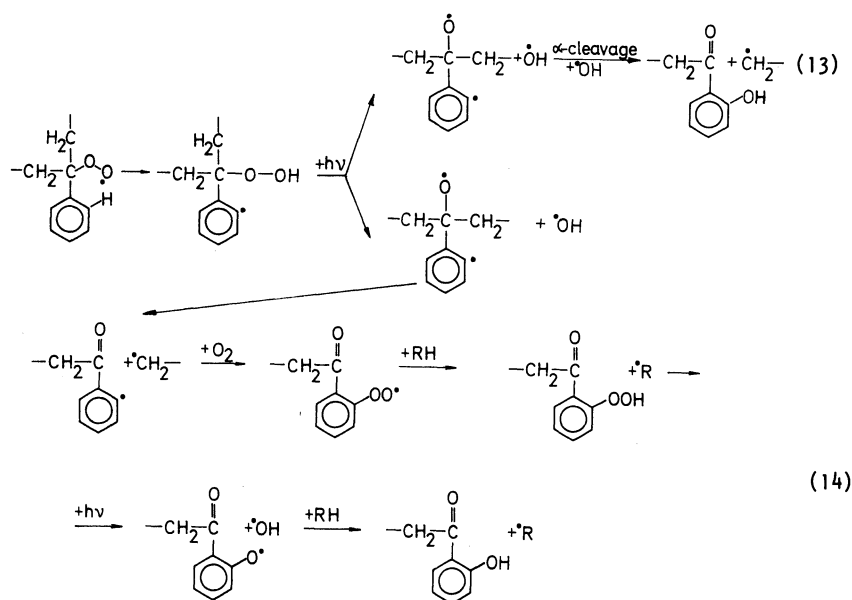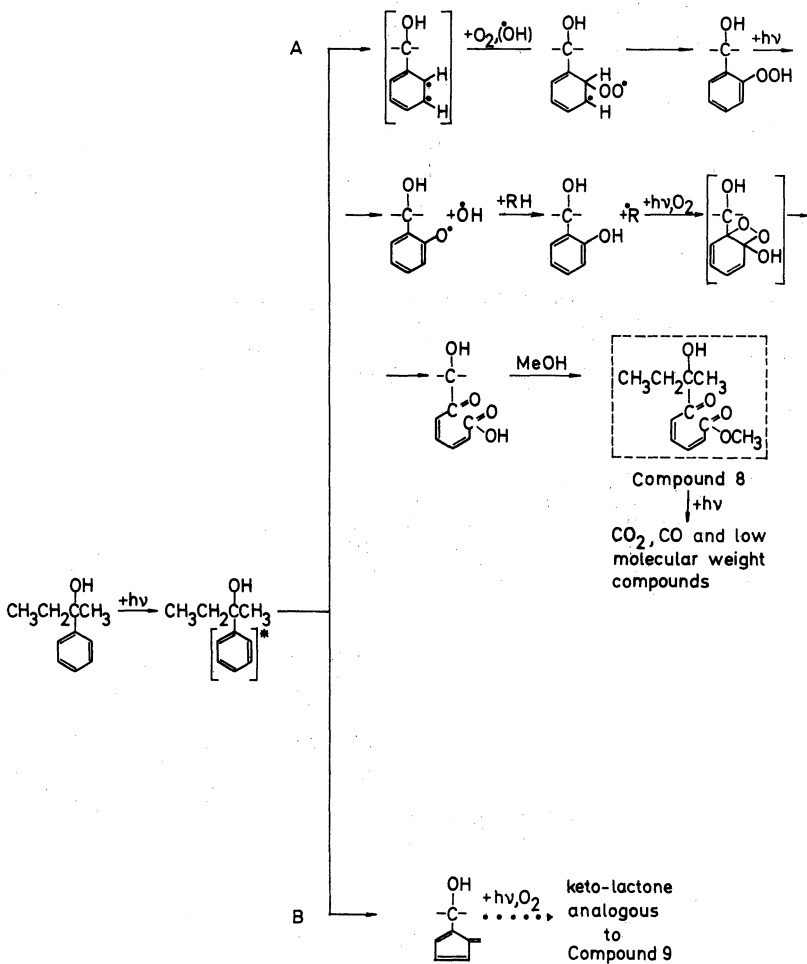

The reactions (13) and (14) are two alternatives of peroxy radical reactions by intermediate sex-membered ring mechanisms. Both these reactions lead to chain scission and formation of the same ortho-substituted acetophenone end group and a free radical. The intermediate steps are known and accepted in photo-initiated oxidation of hydrocarbons.

3.2.   Formation of Acetophenone Type Carbonyl Groups. Four of the compounds formed during photo-oxidation of 2-phenyl-butane have carbonyl groups (>C=O) attached directly to phenyl groups. These CO groups are derived from hydroperoxy groups either by thermally or by photo-decomposition of alkoxy radicals as intermediates. α-Cleavage of alkoxy radicals lead to acetophenone and propiophenone formation (Cf. Scheme 1, compounds 1 and 2). These reactions appear to occur also in polystyrene for which the formation of acetophenone type end-groups during photo-oxidation is well established (1-10).
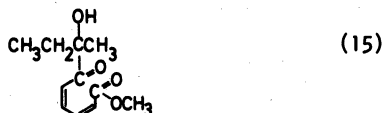
3.3.   Ring Opening Reactions. UV irradiation at 253.7 nm of 2-phenyl-butane in methanol solution and oxygen atmosphere gives 1-keto-1(2)hydroxy butyl-(2,4)hexadienoic acid methyl ester:

Scheme 1.

Scheme 2

Scheme 3

$$CH_3CH_2\overset{\underset{\textstyle |}{OH}}{\underset{\underset{\textstyle OCH_3}{\overset{\textstyle |}{\underset{}{}}}}{C}}CH_3 \qquad (15)$$
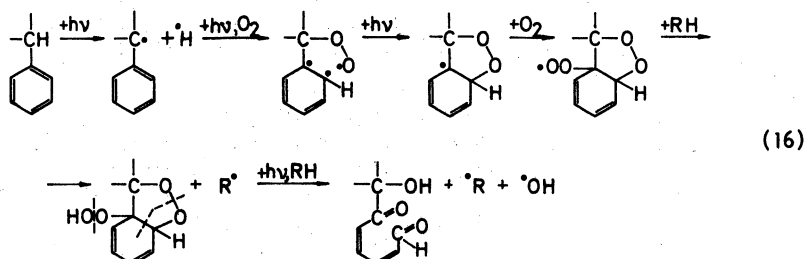
The probable mechanism for the formation of this compound is given in Scheme 2 (Compound 8). The presence of such structures in polystyrene, photo-oxidized in the solid state, is rather improbable, however. The model compound is photo-oxidized in methanol solution, which is interpreted to give methyl ester formation.

Analogous with the ring opening mechanism in 1,2-position during the photo-oxidation of 2-phenyl-butane, we suggest another ring opening reaction in polystyrene (14), occurring by a five-membered ring mechanism between an alkyl peroxy radical and an adjacent excited phenyl group:

$$-\overset{|}{\underset{|}{C}}H \xrightarrow{+h\nu} -\overset{|}{\underset{|}{C}}\cdot \; +\cdot H \xrightarrow{+h\nu, O_2} \cdots \xrightarrow{+h\nu} \cdots \xrightarrow{+O_2} \cdots \xrightarrow{+RH}$$

$$(16)$$

$$\longrightarrow -\overset{|}{\underset{|}{C}}-O + R\cdot \xrightarrow{+h\nu, RH} -\overset{|}{\underset{|}{C}}-OH + \cdot R + \cdot OH$$

This reaction leads to formation of an aldehyde and a ketone group and occurs without polymer chain scission. The new side groups formed are yellow coloured because of the conjugated double bonds.
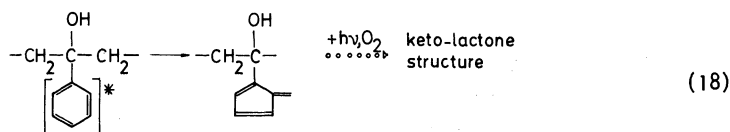
Ring opening reactions during photo-oxidation of polystyrene by singlet oxygen mechanism have been suggested by Rabek and Rånby (3,5). Also Weir has reported (11) reactions of hydroxyl radicals with phenyl rings in polystyrene with formation of phenols (oxidation) and hydroxymucondialdehydes (ring opening).

Also other ring opening reactions with formation of ketolactone groups may be considered for polystyrene, based on model compound studies (14). This mechanism is outlined for 2-phenyl-butane which is photo-oxidized to 1-(2)hydroxy butyl-2-keto-butyrolactone in Scheme 3. For polystyrene we propose the reactions:

$$(17)$$
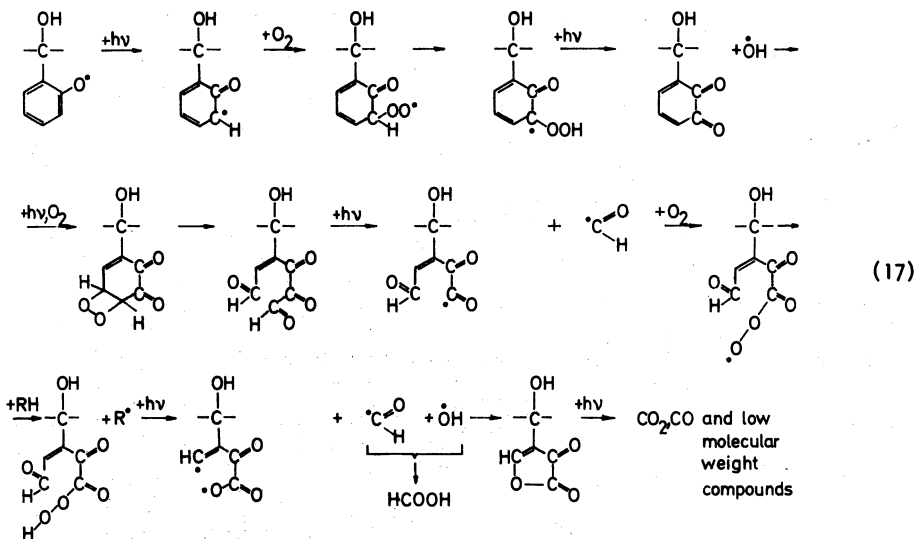
This mechanism involves photo-rearrangement of a phenoxy radical and subsequent formation of a 1,2-diquinone. Photo-oxidation of the 1,2-diquinone may occur by a ring opening mechanism and formation of aldehyde end groups. Photolysis of this compound may give several different radicals which in the end form a keto-butyrolactone structure like in the model compound.

Another possibility is that a keto-lactone type structure in photo-oxidized polystyrene may be formed by isomerization of the excited phenyl ring to a fulvene group (yellow colored) which is photo-oxidized further:

$$\begin{array}{c} OH \\ -CH_2-C-CH_2- \\ [\bigcirc]^* \end{array} \longrightarrow \begin{array}{c} OH \\ -CH_2-C- \end{array} \xrightarrow[\circ\circ\circ\circ\circ]{+h\nu,O_2} \begin{array}{c} \text{keto-lactone} \\ \text{structure} \end{array} \hspace{2cm} (18)$$

3.4. <u>Olefinic Double Bonds</u>. The formation of double bonds in the backbone of a polystyrene chain seems possible. The double bonds are probably formed as a result of a peroxy radical reaction via an intermediate six-membered ring mechanism (14):

$$\begin{array}{c} H \cdot O^{\diagdown O} \\ -C-C- \\ CH_2 \\ \bigcirc\bigcirc \end{array} \longrightarrow \begin{array}{c} H O^H \\ O \\ -C-CH-C- \\ \bigcirc\bigcirc \end{array} \longrightarrow \begin{array}{c} O \\ -C=CH-C- \\ \bigcirc\bigcirc \end{array} + H_2O \xrightarrow{+RH} \begin{array}{c} OH \\ -C=CH-C-+R^{\bullet} \\ \bigcirc\bigcirc \end{array} \hspace{0.5cm} (19)$$
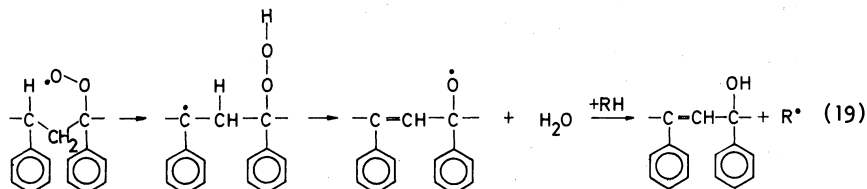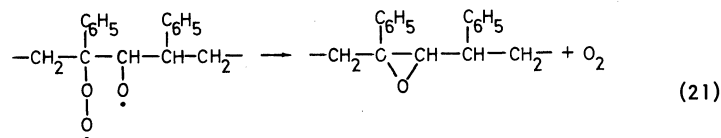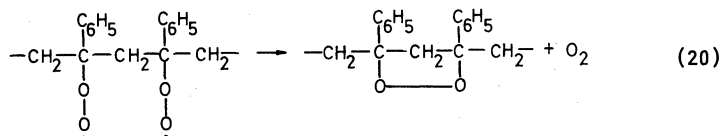
This intermediate ring mechanism has been proposed by Grassie and Weir (1) for hydroperoxide decomposition, leading to an acetophenone end group. Further support for the ring mechanism according to reaction (19) during the photo-oxidation of polystyrene is given by our model compound 2-phenyl-butane which forms 2-phenyl-2-hydroxy-(3,4)buten during photo-oxidation (cf. Scheme 1, Compound 4).

4.   Termination

The termination of polystyrene chain radicals is due to mutual combination, in which cross-linked inactive products are formed. The new bonds are peroxides at high oxygen pressure, e.g. in air, and ether or C-C bonds at low oxygen pressure, e.g. in vacuum or inert atmosphere. All these reactions lead to crosslinking of polymer chains.

If the polymer peroxy radicals are in neighbouring positions on a chain, they can probably also recombine to form stable cyclic peroxides or epoxides as reported by Jellinek (22):

$$\begin{array}{c} C_6H_5 C_6H_5 \\ -CH_2-C-CH_2-C-CH_2- \\ OO \\ OO \\ \bullet\bullet \end{array} \longrightarrow \begin{array}{c} C_6H_5 C_6H_5 \\ -CH_2-C-CH_2-C-CH_2- \\ O\text{------}O \end{array} + O_2 \hspace{1cm} (20)$$

$$\begin{array}{c} C_6H_5 C_6H_5 \\ -CH_2-C-CH-CH-CH_2- \\ OO \\ O\bullet \\ \bullet \end{array} \longrightarrow \begin{array}{c} C_6H_5 C_6H_5 \\ -CH_2-C-CH-CH-CH_2- \\ \diagdown O \diagup \end{array} + O_2 \hspace{1cm} (21)$$

Scission and crosslinking may occur simultaneously in the same polymer sample. Scission may degrade a solid polymer into a thin liquid and crosslinking may create a brittle polymer network.

CONCLUDING REMARKS

Polystyrene of commercial grades without stabilizers has poor weathering properties, mainly because it is easily photo-oxidized. Detailed studies of the photo-oxidation reactions are the basis for new methods for photo-stabilization. Degradation can also be accelerated at will by additions and modifications, and polystyrene samples of controlled life-time can be produced for particular purposes. Stabilization and accelerated degradation of polystyrene are obviously related phenomena. Better understanding of the mechanisms of photo-oxidation supplies background knowledge for treating both processes successfully.

ACKNOWLEDGEMENTS

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