

# Studies on the Photo-Oxidative Mechanism of Polymers. VII. The Role of Singlet Oxygen in the Dye-Photosensitized Oxidation of *cis*-1,4- and 1,2-Polybutadienes and Butadiene–Styrene Copolymers\*

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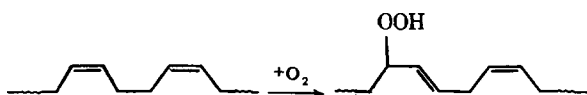
## Synopsis

This paper presents an extensive study on dye-photosensitized singlet oxygen oxidation of *cis*-1,4-polybutadiene, 1,2-polybutadiene, and butadiene–styrene copolymers. The singlet oxygen oxidation occurs by “ene” type mechanism which involves formation of hydroperoxide groups by addition and a shift of the double bond. The oxidation is accompanied by chain scission and crosslinking reactions.

## INTRODUCTION

Photodegradation and photostabilization of polydienes are very important from the industrial point of view. Under normal environmental conditions molecular oxygen, ozone, and atomic oxygen are active agents in the photooxidative degradation of polydienes.<sup>1–8</sup> Recently, a strong interest has arisen in the singlet oxygen oxidation of polydienes.<sup>9–20</sup> For the interpretation of singlet oxygen oxidation of polydienes, several low molecular compounds were oxidized.<sup>11–13,18,21,22</sup>

All available results from studies of singlet oxygen oxidation of polydienes show that singlet oxygen attacks double bonds with formation of allylic hydroperoxide groups and a shift of the double bonds, according to the “ene”-type process



It has been observed that dye-photosensitized oxidation of polydienes in solution causes rapid degradation and, after evaporation of the solvent, also crosslinking of the polymer.<sup>9,10,23,24</sup> The sensitivity of polybutadiene copolymers such as SBR, NBR, etc., to oxidation processes can therefore be explained as due to the presence of double bonds.

Recently, a new class of block copolymers called “thermoplastic elastomers”

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has achieved commercial importance.<sup>25-28</sup> These block copolymers exhibit rubberlike properties similar to vulcanized elastomers after cooling from the melt and without vulcanization. They may be processed into useful products by modern rapid thermoplastic processing techniques. The presence of polybutadiene blocks (chain segments) introduces the same problems regarding oxidation as in the case of pure polybutadiene.

In this paper extensive experimental work on singlet oxygen oxidation of polybutadiene and its block and random copolymers is reported.

## EXPERIMENTAL

The commercial elastomers *cis*-1,4-polybutadiene (Ameripol CB220, Goodrich Chemical Co.) and a styrene-butadiene random copolymer (SBR Ameripol 4506, containing 43.5 wt-% styrene) and a polystyrene-polybutadiene star teleblock copolymer (Solprene No. 414, containing 40.0 wt-% styrene, kindly supplied by Japan Elastomer Co., Oita City, Japan) were purified by dissolving in benzene (pure, analytical grade) and precipitating into spectral-grade ethanol in nitrogen atmosphere. This procedure was repeated once.

A 1,2-polybutadiene (1,2-configuration 100%) ( $\bar{M}_n$  262,000 and  $\bar{M}_w$  650,000) (kindly supplied by Dr. F. Lohr, Jr., Firestone Rubber Co., U.S.A.) was used without further purification.

Dye-photosensitized oxidation (using methylene blue) was performed in 1 wt-% of polymer in methanol-benzene (1:9) using visible light from a Philips tungsten lamp (500 W, PF318E/49). The sensitized generation of singlet oxygen in the polymer solution was carried out directly in a specially constructed viscometer described earlier.<sup>10,29</sup>

Infrared transmission spectra were obtained by using a Perkin-Elmer infrared spectrometer Model 225. For the study of IR spectra the following technique was applied. Films of polymer sample were prepared from irradiated solutions by direct evaporation of 2 ml solution (1 wt-%) on a 5-mm-thick salt plate. This plate with the polymer coated on the surface was then placed in a heating attachment of the IR spectrometer. The programmed heating unit could be set to temperature up to 220°C. The films were heated in nitrogen atmosphere for 1 hr at the required preset temperature.

The kinetics of hydroperoxide group (—OOH) formation was measured by a modified iodometric method for the analysis of —OOH concentration.<sup>30</sup> Determination of molecular weight distribution for polymer samples was made by gel permeation chromatography (GPC) with tetrahydrofuran (THF) as solvent with the use of a Waters Associate instrument Model M-6000 A after removing gel from the solutions.

## RESULTS

During the irradiation with visible light of polybutadiene and its copolymers in benzene-methanol solution in the presence of methylene blue ( $10^{-3}M$ ), a rapid decrease in viscosity is observed (Fig. 1). Plots are given as relative viscosity versus time of irradiation, which give a relative measure of the degradation. Such a presentation of data is not particularly helpful in degradation studies. It is better to plot the inverse of the average viscosity molecular weight ( $\bar{M}_v$ ) calculated from

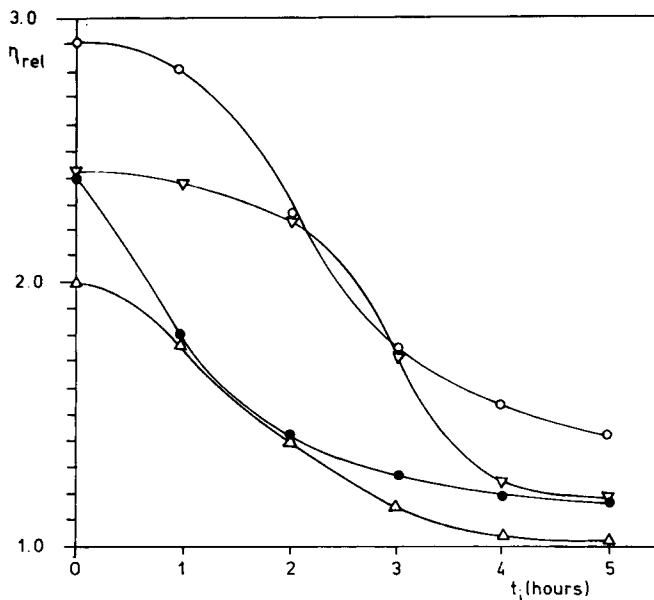
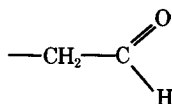


Fig. 1. Change of relative viscosity of methanol-benzene (1:9) solutions of (O) *cis*-1,4-polybutadiene (0.9 wt-%) and (●) 1,2-polybutadiene (1 wt-%); (Δ) SBR copolymer (1 wt-%) and (∇) Solprene copolymer (1 wt-%) vs time during visible light irradiation in the presence of methylene blue ( $10^{-3}M$ ) and air.

the specific viscosity. In our experiments we have used a mixture of methanol-benzene as solvent for which constants  $a$  and  $K$  in the Mark-Houwink-Sakurada equation are unknown. The change in viscosity may be the result of two processes which can occur simultaneously: chain scission and/or change in the hydrodynamic shape of the macromolecules due to crosslinking (from linear to branched structure). No formation of macrogel in solution was observed.

It is very characteristic that after evaporation of solvent from the irradiated solution insoluble gel (40–50 wt-%) is formed (measured as residue after 24 hr of extraction of a 0.2-g polymer sample with THF). The soluble part in the THF extraction gives reproducible GPC chromatograms (Fig. 2) which show changes in molecular weight distribution, indicating chain scission processes. For the gel formation process it should be pointed out that the higher molecular weight fractions of the polymer have a higher probability of forming an infinite network than the low molecular weight fractions. Therefore, extraction of the resultant gel is expected to give a soluble fraction of low molecular weight.

The iodometric analysis of hydroperoxide group ( $-OOH$ ) formation in polymer samples is shown in Figure 3. The presence of hydroperoxy groups in dye-oxidized polymers is also visible from IR spectra in the range of  $3600$  to  $3100\text{ cm}^{-1}$ , Figure 4(a). During heating of the oxidized sample to  $100^\circ\text{C}$  and then to  $180^\circ\text{C}$ , a decrease of this absorption band can be observed with simultaneous formation of a new absorption band at  $1720\text{ cm}^{-1}$  (Fig. 4) assigned to carbonyl groups of the type



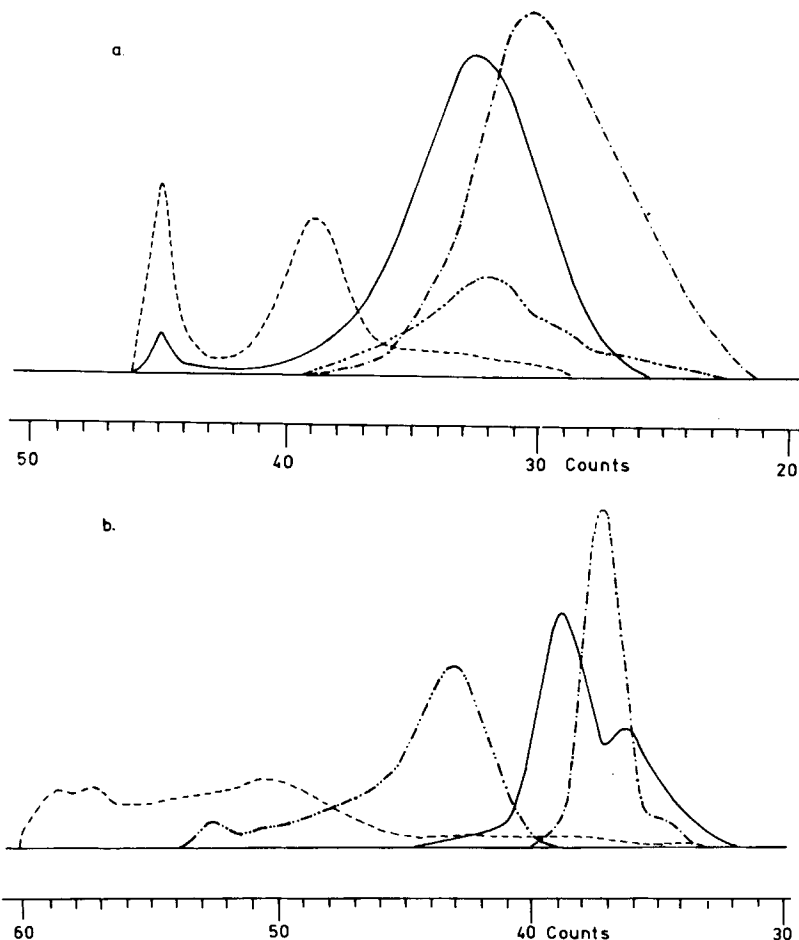


Fig. 2. Gel permeation chromatograms of (a) *cis*-1,4-polybutadiene before (—) and after (---) light irradiation; 1,2-polybutadiene before (- - -) and after (- · - ·) light irradiation; (b) SBR copolymer before (—) and after (---) light irradiation; Solprene copolymer before (- - -) and after (- · - ·) light irradiation. All polymers were irradiated in methanol-benzene solution (1:9) (1 wt-%) in the presence of methylene blue ( $10^{-3}M$ ) and air.

It is characteristic that even after prolonged heating of an oxidized sample at  $180^{\circ}C$  (3 hr) the absorption band at  $3440\text{ cm}^{-1}$  which is attributed to hydroxyl groups ( $-\text{OH}$ ) is retained. The hydroxyl groups are formed rather from the decomposition of hydroperoxy groups at elevated temperatures than from direct oxidation of the polymer sample, e.g., via endoperoxide from singlet oxygen addition. The absorption band of the hydroxyl groups ( $-\text{OH}$ ) at about  $3440\text{ cm}^{-1}$  is partially overlapping the absorption band of the hydroperoxy groups ( $-\text{OOH}$ ) at  $3380\text{--}3400\text{ cm}^{-1}$ , due to band broadening. Since the heating of the sample was done in an oxygen-free atmosphere, we can exclude the possibility of thermal oxidation of the polybutadiene sample.

Significant changes are observed in the IR region of  $750\text{--}1450\text{ cm}^{-1}$  with a developing band at  $975\text{ cm}^{-1}$  assigned to  $\text{trans } -\text{CH}=\text{CH}-$  units. The  $1080\text{--}1110\text{ cm}^{-1}$  region is characteristic of C-O groups. The  $1775\text{ cm}^{-1}$  shoulder is probably due to a five-membered lactone structure. During heating of the ox-

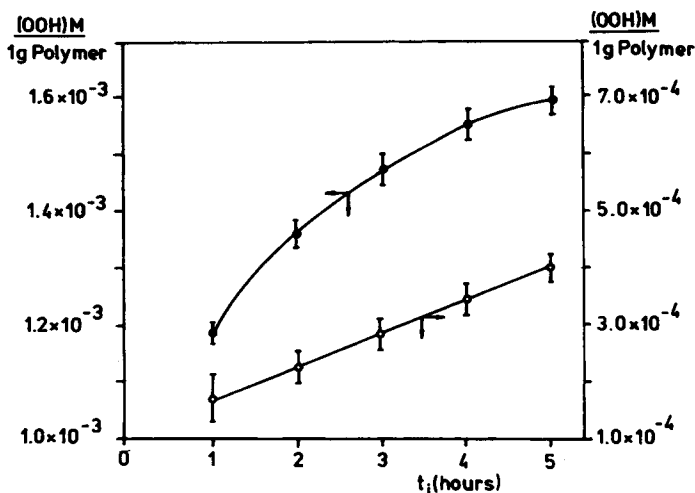
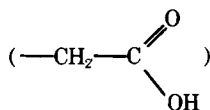


Fig. 3. Kinetics of hydroperoxy group formation in (●) *cis*-1,4-polybutadiene and (○) 1,2-polybutadiene during visible light irradiation in methanol-benzene (1:9) solution (~1 wt-%) in the presence of methylene blue ( $10^{-3}M$ ) and air.

idized samples, different types of carboxylic acids may be formed. These various acids broaden the carbonyl absorbance in the region of  $1760\text{--}1680\text{ cm}^{-1}$ . Saturated acids



absorb at  $1760\text{ cm}^{-1}$ , associated acid species (hydrogen-bonded) at  $1724\text{--}1700\text{ cm}^{-1}$ , and  $\alpha,\beta$ -unsaturated carbonyls at  $1694\text{--}1689\text{ cm}^{-1}$ . A broadening of the C=O region appears during formation of hydroxyl groups from the decomposition of hydroperoxy groups.

In the case of styrene-butadiene random copolymer, shown in Figure 5(a), and polystyrene-polybutadiene block copolymer, Figure 5(b), the changes in IR spectra during dye-photosensitized oxidation occur in similar ranges as those observed for polybutadiene homopolymer, Figure 4(a).

From comparison of the GPC chromatogram (Fig. 2) it appears that the random copolymer (SBR) undergoes more extensive chain degradation in the soluble fraction than the Solprene block copolymer.

The dye-photosensitized singlet oxygen oxidation of 1,2-polybutadiene occurs much less efficiently than of *cis*-1,4-polybutadiene, Figure 1(b). The amounts of hydroperoxy groups formed, determined from iodometric analysis (Fig. 3) and IR spectra (Fig. 4(b)), are smaller and do not exceed ca.  $4.0 \times 10^{-4}$  mole (OOH)/g polymer after 5 hr of visible irradiation, in comparison with  $1.6 \times 10^{-3}$  mole (OOH)/g polymer for *cis*-1,4-polybutadiene. Moreover, the molecular weight distribution curve obtained from GPC chromatogram (Fig. 2(a)) shows that the chain scission process is also less efficient for 1,2-polybutadiene.

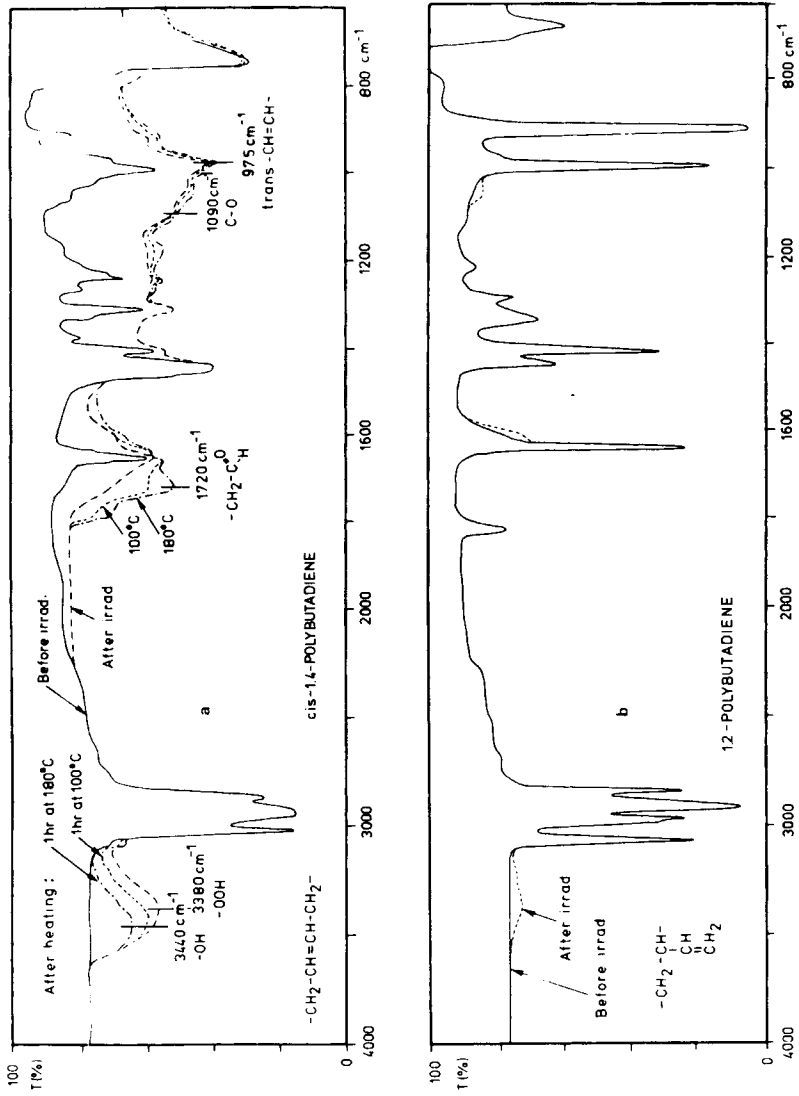


Fig. 4. IR transmission spectra of (a) *cis*-1,4-polybutadiene and (b) 1,2-polybutadiene after visible light irradiation in methanol-benzene (1:9) solution (~1 wt-%) in the presence of methylene blue ( $10^{-3}M$ ) and air. Figure 5(a) also gives IR transmission spectra obtained after 1 hr of heating of the oxidized sample at 100°C (---) and 180°C (- - -).

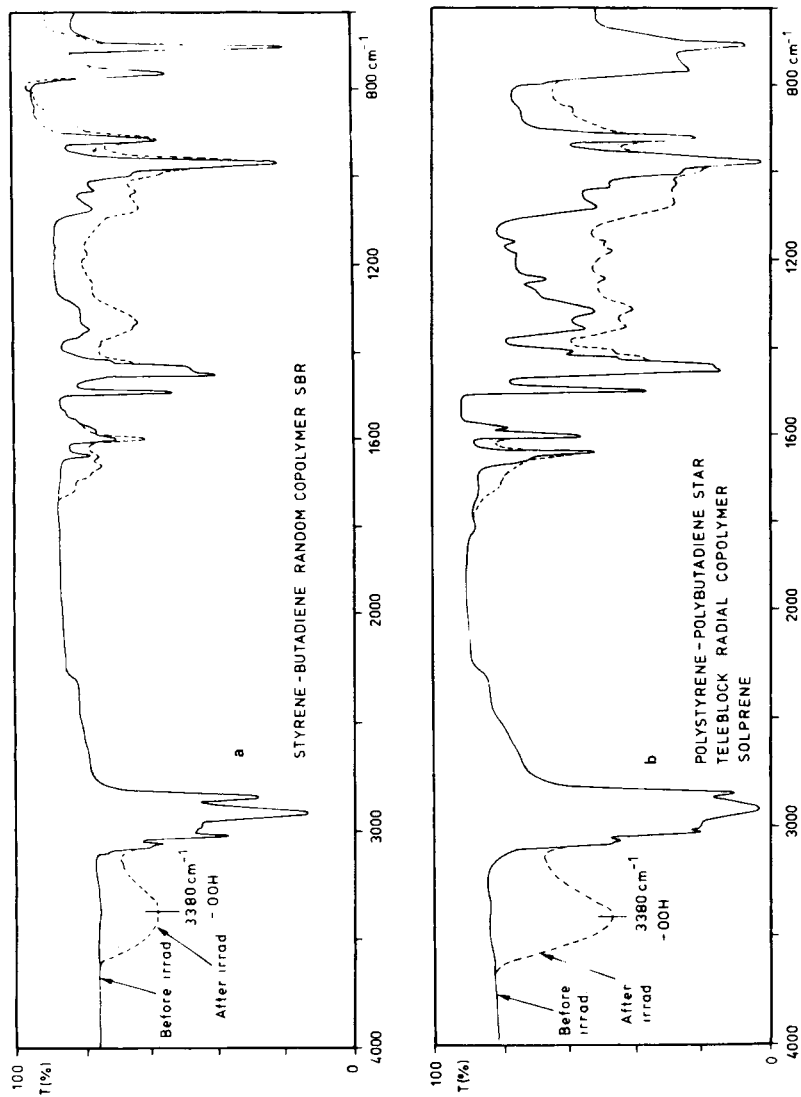


Fig. 5. IR transmission spectra of (a) SBR copolymer and (b) Solprene copolymer before (—) and after (---) visible light irradiation in methanol-benzene (1:9) solution (~1 wt-%) in the presence of methylene blue ( $10^{-3}M$ ) in air.

## DISCUSSION

The results of this study are well interpreted as effects of "ene" type reactions of singlet oxygen with formation of hydroperoxy groups and a simultaneous shift of the double bonds in position and type from the *cis* to the *trans* form.

Singlet oxygen oxidation is accompanied by chain scission and crosslinking reactions of the diene chains. During light irradiation of polymer solutions in the presence of methylene blue ( $10^{-3}M$ ) and air, a rapid change in viscosity without formation of macrogel can be observed. When the oxidized polymer is kept at room temperature, no further change in viscosity is observed. When the polymer is isolated by evaporation of solvent, it is gradually gelled. The gel formation is not reversible and the amount of gel can vary from 40% to 60% depending on the polymer sample, its pretreatment, and the evaporation conditions, e.g., low or fast removal of solvent. The crosslinking reaction may occur through formation of peroxide bridges or carbon-carbon bonds, depending on the mode of hydroperoxide decomposition.

The rapid change in solution viscosity may also be a result of macromolecular entanglements or introduction of hydroperoxide groups which affect the hydrodynamical properties of the macromolecules in solution. During evaporation of solvent, the number of crosslinks increases as a result of a partial decomposition of hydroperoxide groups. Entangled macromolecules which are partially crosslinked cannot return to solution as free chains.

The chains scission is initiated by free radicals which are formed during photoirradiation of the dye rather than a result of singlet oxygen oxidation mechanism. The reaction mechanism of photochemical fading of dyes is very complex, with unstable intermediates playing a significant role. Such intermediates are biradicals, radicals, peroxides, etc.<sup>31-33</sup> The addition of polybutadiene accelerates photobleaching of a dye. The separation of decomposition products from the dye (green colored) from the oxidized polymer sample is difficult and not completely possible. This indicates that dye molecules may be partially bound to polymer chains. A more detailed study of this mechanism will be presented separately in a later publication.<sup>34</sup>

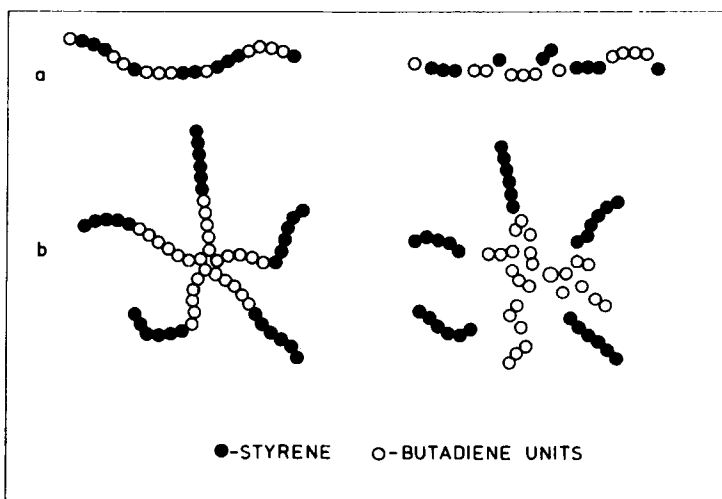


Fig. 6. Mechanism of oxidative degradation (chain scission) of (a) styrene-butadiene random copolymer SBR, (b) polystyrene-polybutadiene star teleblock copolymer Solprene.

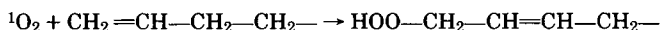


Our results show that singlet oxygen oxidation of butadiene–styrene copolymers may well be limited to the diene units but rather not be affected by styrene segments. Singlet oxygen oxidation of polystyrene is still a controversial problem.

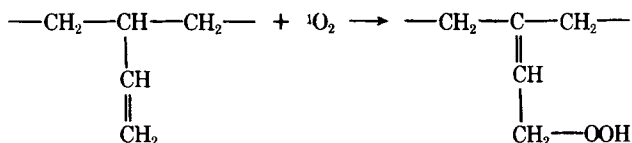
Several hours of exposure of polystyrene film to singlet oxygen generated by microwave discharge produce no visible changes in the polymer.<sup>35,36</sup> On the other hand, photoirradiation of polystyrene in solution or in solid state in the presence of sensitizers such as anthracene<sup>37,38</sup> and quinones<sup>39,40</sup> and air induces oxidative degradation of the polymer. Irradiation of polystyrene by visible light in methanol–benzene solution (1:9) for 5 hr in the presence of methylene blue ( $10^{-3}M$ ) gives no visible changes in molecular weight distribution curves (GPC chromatograms) and IR absorption spectra. The reaction of singlet oxygen with polystyrene occurs probably with double bonds that may be present in a polymer sample as residues from the polymerization process.

The molecular decomposition of a styrene–butadiene random copolymer is much more deep than the decomposition of polystyrene–polybutadiene star teleblock copolymer (Solprene) (Fig. 6). In the last case the polystyrene blocks do not seem to be degraded, because GPC chromatograms are obtained with well-defined peaks. The IR spectrum of a polymer sample obtained from eluents responsible for that peak shows mostly absorption bands characteristic for polystyrene.

Results obtained from dye-photosensitized oxidation of 1,2-polybutadiene show that there is a low efficiency in the singlet oxygen oxidation of vinyl groups ( $\text{CH}_2=\text{CH}-$ ) in this polymer. Trozollo and Winslow<sup>41</sup> suggested that singlet oxygen reacts efficiently with every type of vinyl group available in polyolefins, e.g., also terminal groups:



The relative rates for singlet oxidation of various simple olefins show the order of reactivity of olefins with  ${}^1\text{O}_2$  as tetra- > tri- > disubstituted, while monosubstituted double bonds are essentially unreactive.<sup>42,43</sup> The “ene” reaction with singlet oxygen is less likely to occur for a 1,2-diene chain (I) than for a 1,4-diene chain:



Kagiya and Takemoto<sup>8,44</sup> reported that even 100% 1,2-polybutadiene may contain a small amount (3% of total double bonds) of *trans*-vinylene structures formed by 1,4-addition of butadiene. The probable presence of this structure could be responsible for the observed effect of singlet oxygen oxidation of 1,2-polybutadiene.

## CONCLUSIONS

The collected results indicate that singlet oxygen reacts predominantly with double bonds present in polybutadiene by “ene” mechanism with formation of hydroperoxide groups and a shift of the double bonds. The presence of double bonds is responsible for the vulnerability of butadiene copolymers toward singlet

oxidation. Accumulation of hydroperoxide groups during the singlet oxygen oxidation process is responsible for secondary processes which may include chain scission and crosslinking processes. The dye-photosensitized oxidation of polymer samples is accompanied by other more complex reactions which may occur by free radical mechanism.

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