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THE ROLE OF HYDROPEROXIDES IN PHOTO-OXIDATIVE DEGRADATION OF *cis*-1,4-POLYBUTADIENE

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Abstract—Hydroperoxides undergo various types of homolytic reactions on exposure to u.v. radiation. Free radicals formed from the photodecomposition of the hydroperoxide group (OOH) are oxy (HO.) and peroxy (HOO.) radicals which participate in further reactions. In *cis*-1,4-polybutadiene, they may initiate free radical oxidations. Cleavage of alkoxy (RO.) radicals and crosslinking of polymer radicals through polymer peroxides in the presence of air in solid film nearly balance. Most polymer radicals produced in the absence of oxygen undergo cross-linking but form peroxy radicals (POO.) in its presence. This paper presents results on the photodecomposition of tert-butyl hydroperoxide, cumyl hydroperoxide and 2,5-dimethyl-2,5-dihydroperoxyhexane in *cis*-1,4-polybutadiene in film and in solution.

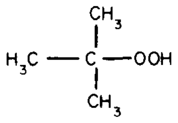
INTRODUCTION

Photo-oxidative degradation of polydienes is generally considered to proceed by reactions of free polymer alkyl-, peroxy-, oxy- and other free-radicals formed by photolysis or photoexcitation of internal (e.g. chromophoric groups such as carbonyl groups) and/or external impurities (e.g. traces of catalysts, initiators and other additives) [1–3].

Some recent publications on the photo-oxidative degradation and photostabilization of polydienes [4–16] have postulated the role of singlet oxygen ($^1O_2$) in the initial step of photo-oxidation in which allylic hydroperoxide groups are formed.

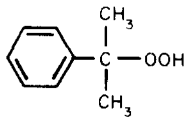
It is important to consider the fact that polymer hydroperoxides formed during photo-oxidation and/or singlet oxygen oxidation are not simple hydroperoxides but are most likely to have neighbouring groups of hydroxy, carbonyl, hydroperoxy and unsaturated bonds. These groups may be important in the photosensitized decomposition of hydroperoxide groups, formation of hydrogen bonds and reaction with free radicals, etc.

This paper contributes to the general problem of photodecomposition of hydroperoxide groups, and is particularly devoted to the study of the role of free radicals formed from photodecomposition of hydroperoxides in the photo-oxidative degradation of *cis*-1,4-polybutadiene.

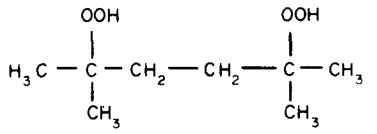


$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OOH$$

I—OOH



II—OOH



$$H_3C-\overset{\displaystyle OOH}{\underset{\displaystyle CH_3}{C}}-CH_2-CH_2-\overset{\displaystyle OOH}{\underset{\displaystyle CH_3}{C}}-CH_3$$

III—OOH

EXPERIMENTAL

tert-Butyl hydroperoxide (I-OOH)(Fluka AG, Germany) and cumyl hydroperoxide (α,α-dimethyl-benzylhydroperoxide)(II-OOH)(Suchard, Germany) were purified by vacuum distillation (b.p. for I-OOH = 33–34°C at 17 mm Hg, and for II-OOH = 52°C at 0.01 mm Hg). 2,5-Dimethyl-2,5-dihydroperoxy-hexane (III-OOH) was prepared by reaction of 2,5-dimethylhexanediol-2,5 (Fluka AG, Germany) with 50% hydrogen peroxide (BDH Chemicals, England) [16]. Recrystalized from benzene, it has 98% purity and m.p. 105 C. Commercial samples of *cis*-1,4-polybutadiene (PB) (Ameripol CB200 from Goodrich Chemical Co.) were purified by dissolving in benzene (analytically pure grade) and precipitating with spectral grade ethanol in N_2 atmosphere. The procedure was repeated.

Spectral, viscometric and gel permeation chromatographic measurements have been described in detail [9–11]. The electron spin resonance (ESR) spectra were determined with an X-band spectrometer (Model JES-ME-1X, Japan Electron Optics Laboratory Co.), operated with 100 kHz field modulation. A cylindrical TE_{011} cavity was used. Some of the spectra were recorded with variable temperature accessories attached to the spectrometer. As u.v. light source, a high pressure mercury lamp SP500 W (Philips, Holland) (280–480 nm) was used.

RESULTS AND DISCUSSION

The absorption spectra of tert-butyl hydroperoxide (I-OOH), cumyl hydroperoxide (II-OOH) and 2,5-dimethyl-2,5-dihydroperoxy-hexane (III-OOH) are shown in Fig. 1.

Alkyl hydroperoxides (I-OOH and III-OOH) absorb at much longer wavelengths than alcohols (ethanol used as solvent). The overlapping lone-pair orbi-

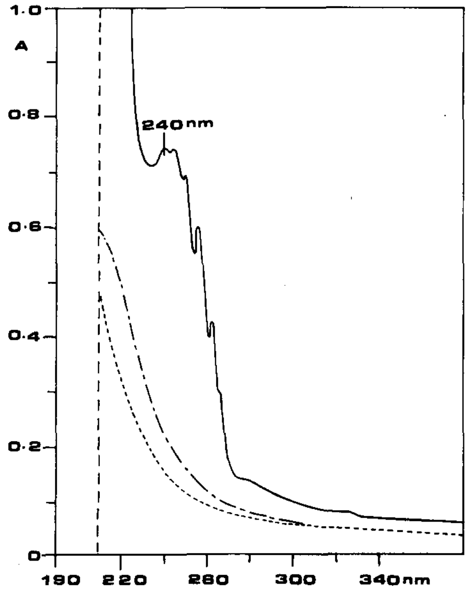


Fig. 1. u.v. Absorption spectra of: (—·—) I-OOH (0.111 M); (——) II-OOH (0.00197 M) and (- - -) III-OOH (0.00281 M) in spectrally pure ethanol in the presence of air.

tals of the two adjacent peroxide oxygen atoms lead to low-energy bonding and high-energy antibonding lone-pair molecular orbitals that are correspondingly filled with electrons [17]. The transitions are assumed to involve two closely adjacent levels $\pi_{p_{x,y}} \rightarrow \sigma_z^*$ that may account for the absorption shift to longer wavelengths.

Aromatic hydroperoxides (II-OOH) show absorption bands typical of benzene and its derivatives [18]. The presence of the phenyl ring may increase absorption up to 300 nm [19]. The molar absorption coefficients calculated for 280 nm in ethanol are: $\epsilon_{\mathrm{I-OOH}} = 8$; $\epsilon_{\mathrm{II-OOH}} = 70$ and $\epsilon_{\mathrm{III-OOH}} = 20\,\mathrm{mol^{-1}\,cm^{-1}}$.

Hydroperoxides probably form hydrogen bonded association with alcohols, although the evidence derives mainly from rate studies on thermal decomposition rather than from direct spectroscopic measurements [20]. It is also possible that hydroperoxides may form charge-transfer complexes (CT) with molecular oxygen. For many alkane–O_2 CT complexes, the u.v. absorption is extended up to 300 nm and further [21]. Free radicals can be formed during the absorption of u.v. light by these CT complexes. Hydroperoxides undergo four general types of homolytic reactions:

1. Unimolecular homolysis (photolysis and/or thermolysis) [22–26]:

$$\mathrm{ROOH} \xrightarrow[\Delta]{+h\nu} \mathrm{RO.} + \mathrm{.OH} \tag{1}$$

The quanta (280–480 nm) used in our experiments have sufficient energy to cleave the RO—OH bond (bond energy 42–43 kcal/mol) [27–29]. The RO—OH bond energy should be relatively independent of R [27, 30]. In concentrated hydroperoxide solutions, second-order processes may also occur [31–33]:

$$2\mathrm{ROOH} \xrightarrow[\Delta]{+h\nu} \mathrm{RO.} + \mathrm{RO_2.} + \mathrm{H_2O}. \tag{2}$$

2. Molecule-induced homolysis, when radicals are formed at high rate from the interaction of nonradical species [34]:

$$\mathrm{ROOH} + \mathrm{A} \rightarrow \mathrm{RO.} + (\mathrm{AOH}).. \tag{3}$$

This reaction occurs, e.g. in the presence of olefin solvents, but it can be considered in the case of other compounds containing double bonds (e.g. polydienes).

3. Radical induced decomposition [28]:

$$\mathrm{ROOH} + \mathrm{R.'} \rightarrow \mathrm{RO_2.} + \mathrm{R'H} \tag{4}$$

$$2\,\mathrm{RO_2.} \rightarrow 2\,\mathrm{RO.} + \mathrm{O_2} \tag{5}$$

$$\mathrm{RO.} + \mathrm{ROOH} \rightarrow \mathrm{ROH} + \mathrm{RO_2.}. \tag{6}$$

A small amount of the oxygen evolved from the sec-butyl peroxy radical coupling reaction has been trapped with 9,10-diphenylanthracene with formation of the transannular peroxide [35]. Since this reaction is usually considered to be a test for singlet oxygen [36, 37], the observation gives additional support for the possibility of singlet oxygen oxidation reactions.

4. Free-radical displacement on O—O bond [38]:

$$\mathrm{ROOH} + \mathrm{R.'} - \!\!<\!\begin{array}{l}\mathrm{ROR'} + \mathrm{.OH}\\ \mathrm{R'OH} + \mathrm{RO.}\end{array} . \tag{7}$$

The structure of the hydroperoxide also influences the course of its decomposition.

After O——O bond scission, several processes compete via radical-radical combination or disproportionation, radical abstraction from, or addition to available substrates, and alkoxy radical scission.

During u.v. (280–480 nm) irradiation (20 min) of pure hydroperoxides I-OOH, II-OOH and III-OOH, almost identical single line asymmetric ESR signals were observed with similar widths and g-values: 2.0134 (I-OOH), 2.0116 (II-OOH) and 2.0119 (III-OOH) without hyperfine structures (Fig. 2). There was no significant change in these ESR spectra when oxygen was carefully removed from samples (Fig. 2c). The ESR signals do not disappear even after warming the samples to room temperatures. Figure 3 shows a change in the ESR spectra of radicals from III-OOH after u.v. irradiation and further warming from 77 K to room temperature. For free radicals from II-OOH, partial averaging of g-anisotropy can be observed during warming. The observed ESR spectra for I-OOH and II-OOH agree with ESR spectra published previously [39, 40].

These asymmetric ESR singlet line spectra can be attributed to the formation of the same type of free radical. There is some difficulty in distinguishing between alkoxy (RO.) and peroxy (RO_2.) radicals, since both have the unpaired electron mainly concentrated on oxygen atoms and neither shows a hyperfine interaction with alkyl protons. Earlier reports of the detection of alkoxy (RO.) radicals by ESR [39] have been later disclaimed [40–42]. The fact that these radicals exist at room temperature shows that the observed ESR signals originate from peroxy radicals

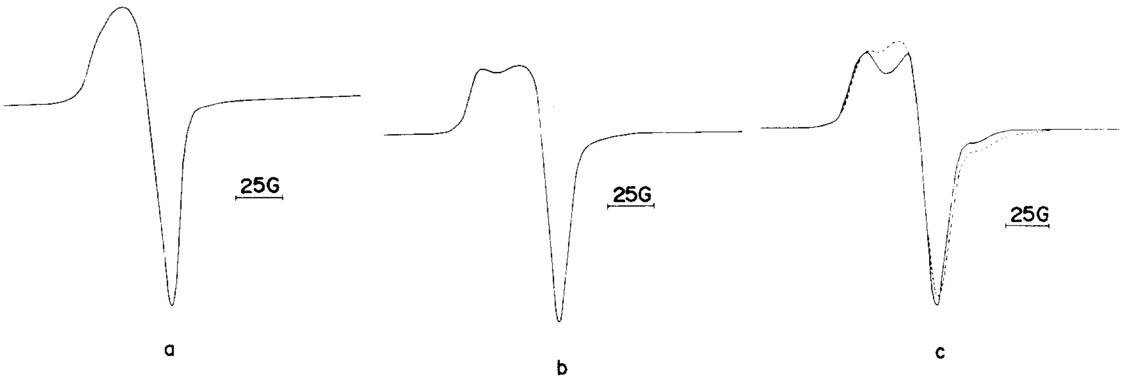


Fig. 2. ESR spectra of: (a) I-OOH; (b) II-OOH and (c) III-OOH in air (——) and in vacuum (· · ·) after u.v. irradiation (20 min) at 77 K.

($RO_2.$) [43]. Peroxy radicals are strongly resonance stabilized, and are relatively selective electrophilic species abstracting tertiary hydrogen in preference to secondary or primary [1]. Alkoxy radicals (RO.) are more reactive than alkylperoxy radicals ($RO_2.$) and they can easily react with other radicals or abstract hydrogen to form alcohols. It is less probable that they can exist even at 77 K and be detected by ESR spectroscopy. The formation of observed peroxy radicals ($RO_2.$) can be described by the following reactions:

$$ROOH \rightarrow RO. + .OH \qquad (8)$$

$$ROOH + HO. \rightarrow ROO. + HOH \qquad (9)$$

$$ROOH + RO. \rightarrow ROO. + ROH. \qquad (10)$$

The nature of the solvent used during photodecomposition is probably important. It has been shown by ESR spectroscopy that photolysis of I-OOH leads to ketyl radicals [44, 45]. The tert-butoxy and hydroxy radicals thus produced may remove the proton from I-OOH to form the tert-butylperoxy radical. Any of the oxy radicals in solution may remove the methine proton of 2-propanol to form the 2-hydroxy-2-propyl radical ($g = 2.00323$) [46]. The validity of the proposed mechanism for alcohol oxidation by photolysis of I-OOH was additionally tested by using CIDNP radical pair theory [47, 48].

The most common technique capable of yielding information about the hydroperoxide (OOH) groups is i.r. spectroscopy. The bonds of interest for distinguishing hydroperoxy groups are [19, 49–53]:

1. O—O stretching vibration at 877 cm^{-1}.
2. O—H stretching vibration at 3560–3530 cm^{-1} (and even 3600 cm^{-1}),
3. Asymmetrical bending of the OH group at 1353 cm^{-1}.

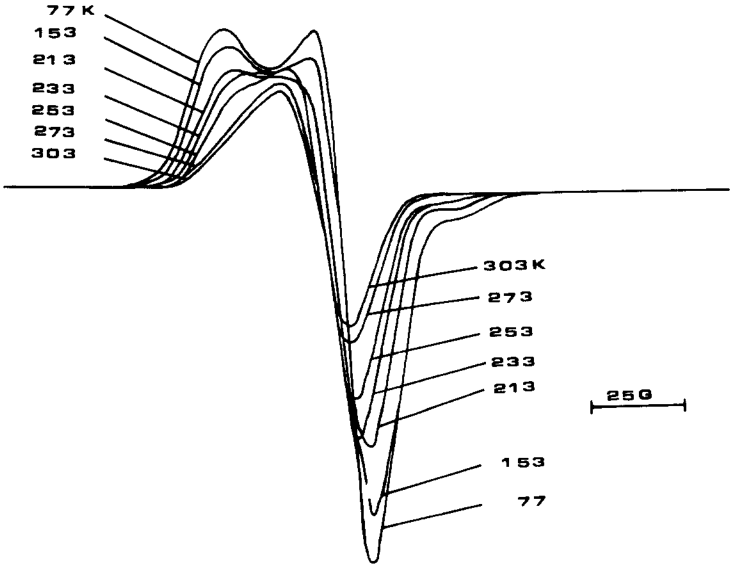


Fig. 3. Change of ESR spectra of III-OOH observed during warming the sample in air.

Fig. 4. i.r. Transmission spectra of: (·····) III-OOH in PB (0.3:1 M:M) before irradiation and (—·—) after u.v. irradiation (3 hr) in vacuum; (——) pure PB and (– – –) after u.v. irradiation (3 hr) in vacuum.

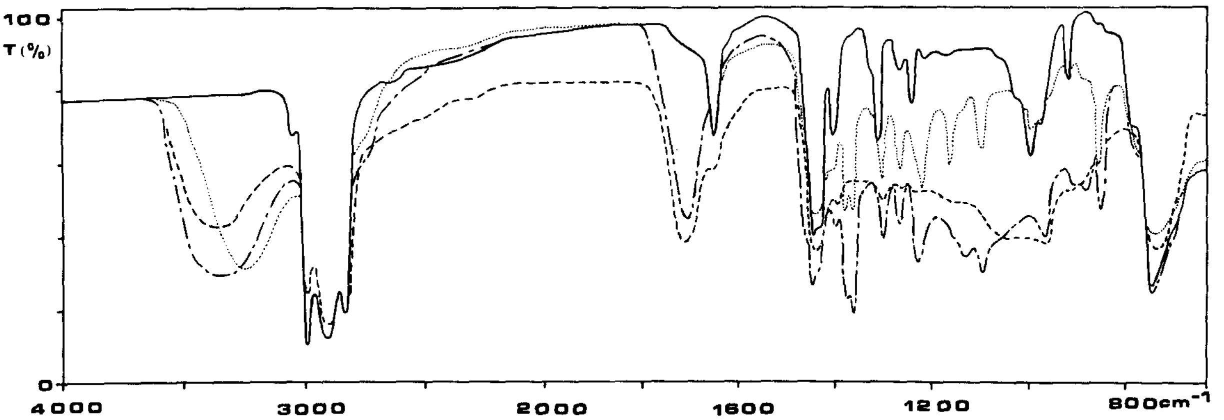


Fig. 5. i.r. Transmission spectra of: (·····) III-OOH in PB (0.3:1 M:M) before irradiation and (—·—) after u.v. irradiation (3 hr) in the presence of air; (——) pure PB and (– – –) after u.v. irradiation (3 hr) in the presence of air.

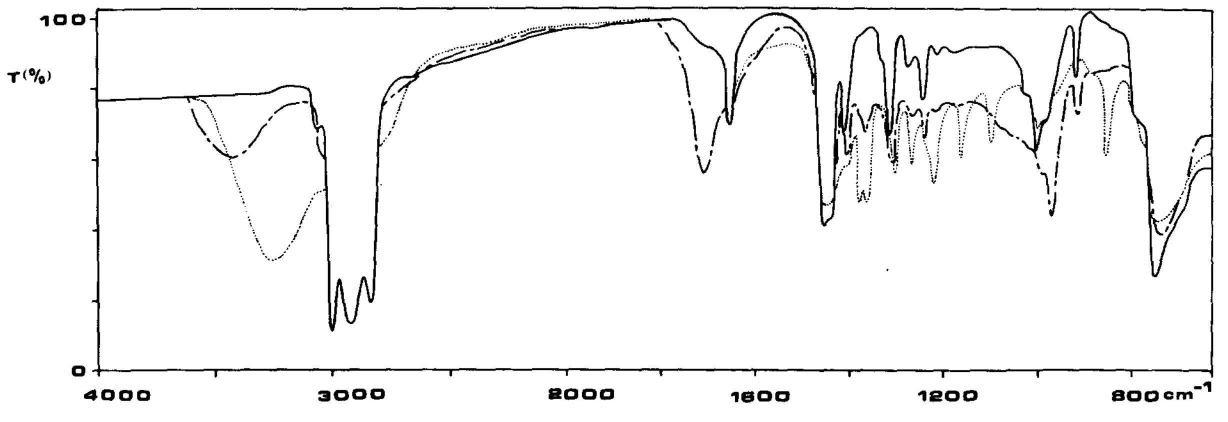


Fig. 6. i.r. Transmission spectra of: (·····) III-OOH in PB (0.3:1 M:M) before heating and (—·—) after heating at 180°C (3 hr) in vacuum: (——) pure PB and (– – –) after heating at 180°C (3 hr) in vacuum.

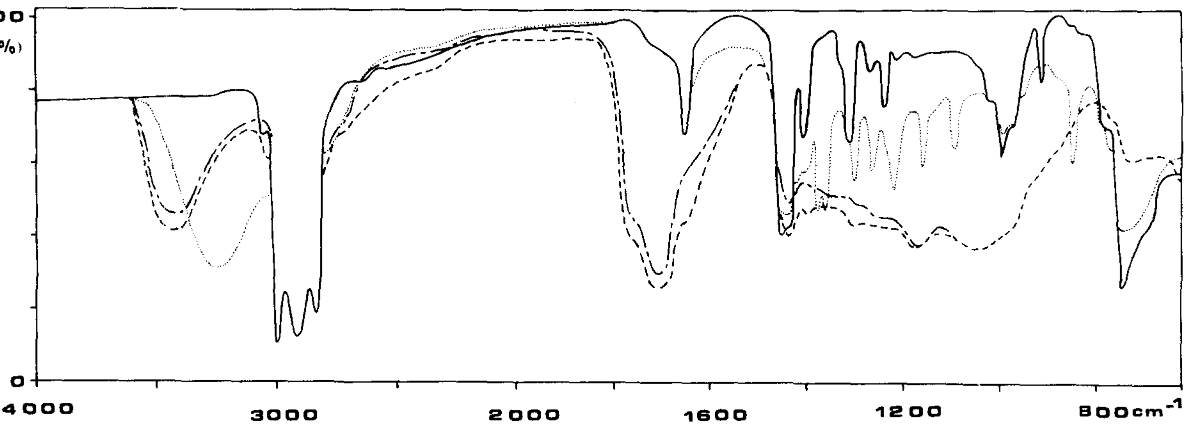


Fig. 7. i.r. Transmission spectra of: (· · · · ·) III-OOH in PB (0.3:1 M:M) before heating and (– · –) after heating at 180°C (3 hr) in the presence of air: (——) pure PB and (– – –) after heating at 180°C (3 hr) in the presence of air.

4. Symmetrical bending vibration of the OH group at 1380 cm^{-1}.

The frequencies of these vibrations depend not only on the nature of the particular bonds themselves but also on the entire molecule and its environment. In other regions of the i.r. spectrum, hydroperoxides do not exhibit specific O—H vibrations distinguishing them from other OH containing compounds [52].

From the experimental point of view, the most useful is the study of O—H stretching vibration in the range 3560–3530 cm^{-1}, e.g. for I-OOH at 3559 cm^{-1} [54, 55] and for II-OOH at 3530 cm^{-1} [56]. Intermolecular H-bond OH stretching frequency lies between 3450–3400 cm^{-1} [56–58]. The frequency and intensity of intramolecular H-bonded O—H bond change with dilution [59]. Hydrogen bonded OOH groups in pure hydroperoxides show remarkable changes in their i.r. spectra, where shifting of the OH stretching frequency up to 3200 cm^{-1} may occur. Such strong effects of the intramolecular hydrogen bond on OH stretching frequency were observed for III-OOH, where a band is formed at 3260 cm^{-1} (Figs 4–7).

In polypropylene hydroperoxide, the content of intramolecular H-bonded hydroperoxide is about 87% and an absorption band at 3378 cm^{-1} was observed [60].

During photo-oxidation of polydienes a strong absorption i.r. band in the range 3300–3600 cm^{-1} (Fig. 5) is formed [9]. The maximum of this band lies at 3360 cm^{-1} and the content of intermolecular H-bonded hydroperoxides is about 100%. Isolated hydroperoxides are not formed, because all hydrogens in methylene groups in polybutadiene are in a favoured location for intramolecular reactions.

i.r. Spectra for the system III-OOH in PB film (0.3:1 M/M) photo-irradiated (3 hr) or thermally treated (180°C, 3 hr) in vacuum or in air show that:

(i) Photodecomposition of III-OOH in PB film in vacuum (Fig. 4) and in air (Fig. 5) occur to different extents. In the latest case almost complete photodecomposition of III-OOH is observed.

(ii) Thermal decomposition of III-OOH at 180°C in vacuum (Fig. 6) and in air (Fig. 7) is complete. Formation of a new band with a maximum at 3440 cm^{-1} was attributed to the formation of OH groups.

(iii) Products of photolysis and thermal decomposition of III-OOH do not significantly influence a change in the i.r. spectra of photo (Figs 4 and 5) and thermally (Figs 6 and 7) oxidized PB.

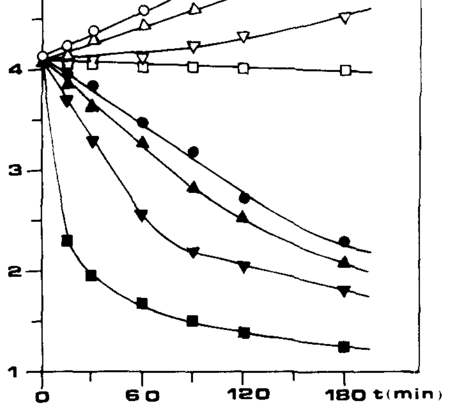


Fig. 8. Change of relative viscosity of PB in benzene solution (0.9 wt%) during u.v. irradiation: (□) pure PB; (△) with I-OOH (10^{-2} M); (▽) with II-OOH (10^{-2} M) and (○) with III-OOH (10^{-2} M) in oxygen free atmosphere; (■) pure PB; (▲) with I-OOH (10^{-2} M); (▼) with II-OOH (10^{-2} M) and (●) with III-OOH (10^{-2}) in the presence of air.

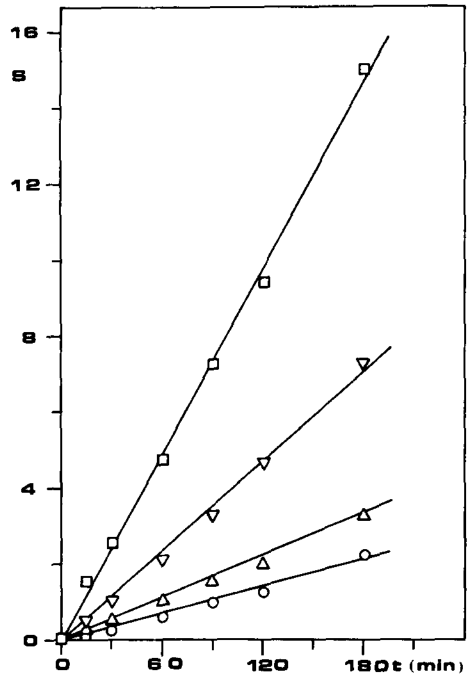


Fig. 9. Change of chain scission parameter (S) of PB after u.v. irradiation of PB in benzene solution (0.9 wt%) in the presence of I-OOH and in air: (○) 10^{-2} M; (△) 10^{-3} M and (▽) 10^{-4} M and (□) pure PB.

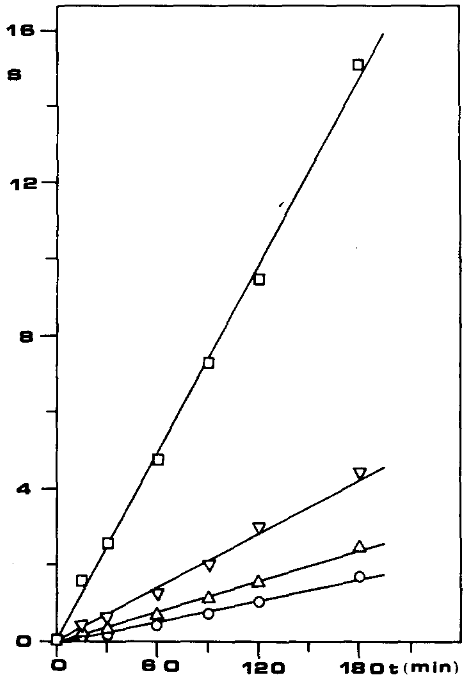


Fig. 11. Change of chain scission parameter (S) of PB after u.v. irradiation of PB in benzene solution (0.9 wt%) in the presence of III-OOH and in air: (○) 10^{-2} M; (△) 10^{-3} M and (▽) 10^{-4} M and (□) pure PB.

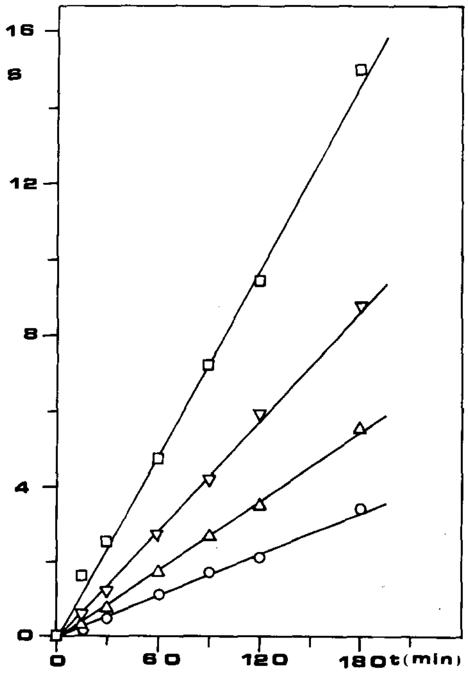


Fig. 10. Change of chain scission parameter (S) of PB after u.v. irradiation of PB in benzene solution (0.9 wt%) in the presence of II-OOH and in air: (○) 10^{-2} M; (△) 10^{-3} M and (▽) 10^{-4} M and (□) pure PB.

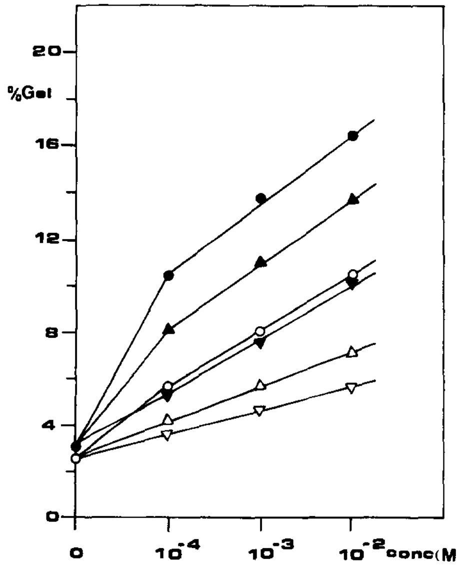


Fig. 12. Change of gel content (%) formed during u.v. irradiation of PB in benzene solution (0.9 wt%) in air and in the presence of: (△) I-OOH; (▽) II-OOH and (○) III-OOH: and in film in the presence of (▲) I-OOH; (▼) II-OOH and (●) III-OOH.

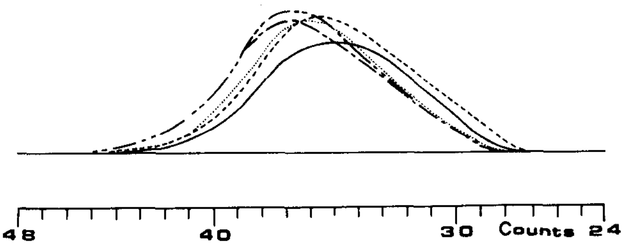


Fig. 13. Gel permeation chromatograms of PB: (——) before irradiation and (- - -) after u.v. irradiation (1 hr); (· · · · ·) with I-OOH; (—·—) with II-OOH and (-----) III-OOH in the presence of air. Concentration of added hydroperoxides was in all samples 10^{-3} M.

(iv) There is a distinct difference between the observed frequency of the H bonded OH group in OOH group (3360 cm^{-1}) in photo-oxidized PB (Fig. 5) and the isolated OH group (3420 cm^{-1}) in thermally oxidized PB (Fig. 7).

The detailed interpretation of particular absorption bands in oxidized PB was given previously [9] and is not discussed here. It was not possible to make similar measurements of the i.r. spectra of I-OOH and II-OOH in PB film, because these hydroperoxides are liquids and easily evaporate from the polymer matrix during the preparation, evacuation and heating.

The formation of hydroperoxide groups in PB as the primary product of photo-oxidation (and/or singlet oxygen oxidation) would not be expected to result in significant changes in the properties of a polymer at low levels of oxidation. The changes therefore must be attributed to reactions which also occur as a result of oxidation. These reactions may be competing processes involving the free radicals formed during the direct oxidation, or they may be subsequent reactions resulting from decomposition of the hydroperoxide formed as the initial product.

There are remarkable results showing the influence of added I-OOH, II-OOH or III-OOH on change of relative viscosity (Fig. 8), chain scission (Figs 9, 10 and 11) and gel content (Fig. 12) during u.v. irradiation. The following information can be deduced from these measurements:

(i) Addition of I-OOH, II-OOH or III-OOH to PB solution (0.9 wt% in benzene) in the presence of air decreases the change of relative viscosity (Fig. 8) and chain scission parameter (S)(Figs 9, 10 and 11). Parallel to chain scission processes (Fig. 13) is the formation of microgel (Fig. 12). These results show that the following reactions can be considered:

1. Formation of polymer (P.)(alkyl and/or alkenyl radicals). Free radicals (RO. and/or RO_2.) formed from the photodecomposition of hydroperoxide groups in added I-OOH, II-OOH or III-OOH may abstract hydrogen atoms from polymer molecules (PH):

$$\mathrm{PH} + \mathrm{RO.}\ (\text{and/or } \mathrm{RO_2.}) \rightarrow \mathrm{P.} + \mathrm{ROH}\ (\text{and/or } \mathrm{ROOH}). \quad (11)$$

In the presence of air it is possible that chain scission reactions occur via the formation of polymer oxy (PO.) and further disproportionations:

$$\mathrm{PO.} \rightarrow \text{degraded products.} \quad (12)$$

2. Termination of polymer radicals (P.) by free radicals RO. and/or RO_2.:

$$\mathrm{P.} + \mathrm{RO.}\ (\text{or } \mathrm{RO_2.}) \rightarrow \mathrm{POR}\ (\text{or } \mathrm{POOR}).$$

The primary oxy radicals account for the rest of the chain termination.

3. Cross-linking reactions of polymeric radicals (P., PO. and/or POO.):

$$\mathrm{P.}\ (\text{or } \mathrm{PO.}, \text{ or } \mathrm{POO.}) + \mathrm{P.}(\text{ or } \mathrm{PO.} \text{ or } \mathrm{POO.}) \rightarrow \text{cross-linked products.} \quad (14)$$

(ii) Addition of I-OOH, II-OOH or III-OOH to PB O_2-free solution (1 wt% in benzene) increases the relative viscosity (Fig. 8). In this reaction there was prominent formation of polymeric radicals (P.) which then undergo further crosslining with each other. No chain scission reactions were observed.

In contrast to the alkoxy (RO.) and peroxy (RO_2.) radicals which preferentially abstract hydrogen or contribute to scission reactions, alkyl and alkenyl radicals preferentially either couple or add to reactive double bonds [26].

(iii) Photolysis of I-OOH, II-OOH or III-OOH in solid PB film increase the insoluble gel (Fig. 12) as a result of cross-linking reactions. Most of the polymer radicals in solid PB cross-link when produced in the absence of O_2, but they form peroxy radicals in its presence.

(iv) The polymeric environment may enhance the recombination of the primary radical pairs. This effect would reduce the chain scission and explain the effect of added hydroperoxides on decreasing chain scission parameter (S).

These results show that several types of free radicals formed from the direct photodecomposition of I-OOH, II-OOH or III-OOH may cause appreciable chain scission and/or cross-linking and indicate that hydroperoxide groups are essential in the initiation of the photodeterioration of polydienes.

Photodecomposition of hydroperoxide groups may also occur by energy transfer reactions from excited carbonyl groups to hydroperoxide groups [15, 61–63]. In view of the above results, the formations of hydroperoxy (OOH), hydroxy (OH) and keto (C=O) groups appear to play a significant role in photooxidation and singlet oxidation of polybutadiene and other polydienes.

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