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Accelerated photodegradation of *cis* 1,4-polybutadiene in the presence of hydrogen peroxide

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Summary

Photooxidative degradation of *cis* 1,4-polybutadiene in diluted benzene solution and benzene/hydrogen peroxide emulsion have been examinated using viscosimetry, GPC, FTIR, UV-Vis spectrometry and iodometric titration. Efficient photooxidation and photodegradation of PB in presence of hydrogen peroxide was observed. The acceleration effect of photoprocesses in PB is caused by hydroxy (HO·) and hydroperoxide (HOO·) radicals. The mechanism of PB reactions with free radicals proceeding from hydrogen peroxide and influence of benzene on photodegradation of PB have been discussed.

Introduction

Polybutadiene is one of the most popular elastomeres widely used in the industry because of its unique, physical properties as elasticity, tougness and durability[1]. These properties can be modyfing by controlled crosslinking (vulcanization) or by blending with another polymers. Different type of polydienes or their co- and terpolymers are used as impact modyfing agents for PE, PS and PVC. These elastomeric materials are susceptible to UV-irradiation because PB chains contain unsaturated double bonds weaken neighbouring methylene groups[2-4]. Photooxidative degradation of different PB type was a subject of many, extensive works[5-15]. Recently, the accelerated degradation of polymers has drawn the attention of scientists in aspect of the reduction of environmental pollution by waste plastic[16-21]. The lifetime of a polymeric products is dependent on many factors: structure defects, residual of initiators or catalysts, oxygen, water, impurities, temperature and sunlight. The dominant influence of hydroperoxides incorporated into macromolecules on photoinitiation processes has been pointed out[22-24]. The role of hydroxy and hydroperoxide radicals in acceleration of polymer photodegradation has been lately reported[25,26]. The aim of this work was to investigate the accelerated photodegradation of cis 1,4-polybutadiene (PB) in presence of hydrogen peroxide as a source of hydroxy (HO·) and hydroperoxide (HOO·) radicals.

Experimental

A sample of commercial *cis* 1,4-polybutadiene (Buna CB23, Bayer) has been used in this study. The photodegradation of PB was carried out in 1% benzene solution and well stirred emulsion mixture of benzene with 30% hydrogen peroxide. Molar ratio of polymer to H_2O_2 was 1:1. High pressure mercury lamp (HPK 125W UV, Philips) emitted light from 254 to 578 nm was applied as a light source. The distance between the lamp and surface of polymer solution was 10 cm, the light intensity at this position being 32 mW/cm^2. After irradiation, PB was precipitated by methanol and dried to a constant weight in vacuum. Degradation products were characterized by IR and UV-Vis spectrometry using FTIR 1650 Spectrometer (Perkin Elmer) and Specord M-40 (Carl Zeiss, Jena), respectively. The weight and number average molecular weights as well as polydispersity were determined by gel permeation chromatography (GPC) with Shimadzu C-R4A Chromatograph and Chrompack PL Gel column calibrated with PS standarts. The limiting viscosity number [η] and number of chain scission per molecule

$$S = \left(\frac{[\eta]_o}{[\eta]_t}\right)^{1/a} - 1 \qquad \text{(where "a" is a constant in Mark-Houwink equation)}$$

were calculated from the viscosity measurement in benzene at 25±0.05°C using an Ubbelohde viscometer. The hydroperoxide groups amount was measured by an iodometric method[27].

Results and discussion

Hydrogen peroxide solution undergoes fast photolysis with generation of hydroxy (HO•) and hydroperoxide (HOO•) radicals according to Haber-Willstätter reactions[3,26]. These very reactive radicals may, before their termination, abstract hydrogen atom from methylene group in PB and initiate polymer decomposition.

UV-irradiation of PB solutions causes the main chain scission reactions what was observed as a decrease of the limiting viscosity number (Table 1). The changes of [η] values of photodegradated PB are much higher when the photoprocess is carried out in the presence of hydrogen peroxide. Number of chain scission per macromolecule (S) for PB degradated in emulsion containing H_2O_2 is more than 2-3 times higher than this value for PB photodegradated in pure benzene solution.

Table1. Changes of the limiting viscosity number and the number of chain scission per molecule in photodegradated PB

Time of irradiation, min	Degradation in benzene		Degradation in benzene/H_2O_2	
	[η], dl/g	S	[η], dl/g	S
0	2.76		2.76	
30	2.69	0.03	2.59	0.08
60	2.44	0.17	2.12	0.40
90	2.32	0.25	1.90	0.61
120	2.27	0.28	1.61	0.99
150	2.05	0.46	1.43	1.32

GPC analysis shows rapid decrease of number average molecular weight ($\overline{M}_n$) of PB during 1 and 2h of UV irradiation in benzene and in benzene/ hydrogen peroxide mixture what is the evidence of efficient chain scission reaction (Table 2). However, irregular changes in weight average molecular weight ($\overline{M}_w$) as well as long tail on the molecular weight distribution curve can indicate that reaction of macroradicals recombination leading to higher molecular weights occurs simultaneously. Insoluble gel is not formed in these conditions, in the contrary to solid PB films irradiated upon UV light[4,5]. Changes of polydispersity ($\overline{M}_w/\overline{M}_n$) of PB irradiated in benzene/H_2O_2 are higher than those in pure benzene solution. It means, that photoprocesses in PB are much efficient in presence of hydrogen peroxide.

Table 2. Changes in the average molecular weights and polydispersity of PB photodegradated in benzene solution and benzene/H_2O_2 mixture

Time of irradiation, h	Solvent	$\overline{M}_n 10^{-3}$	$\overline{M}_w 10^{-3}$	$\overline{M}_w/\overline{M}_n$
0		121	467	3.85
1	benzene	86	284	3.30
2	benzene	75	349	4.65
1	benzene/H_2O_2	107	472	4.41
2	benzene/H_2O_2	66	343	5.20

The observed gradual changes of absorption spectra of PB irradiated in presence of hydrogen peroxide are caused by chromophores formation (Fig.1). The absorption increase is significant in 220-300 nm and negligible in 300-400 nm range. The band at 270 nm is assigned to end carbonyl groups and broad band at 300-400 nm is due to the conjugated carbonyl structures or conjugated double bond sequences[3,11,28].

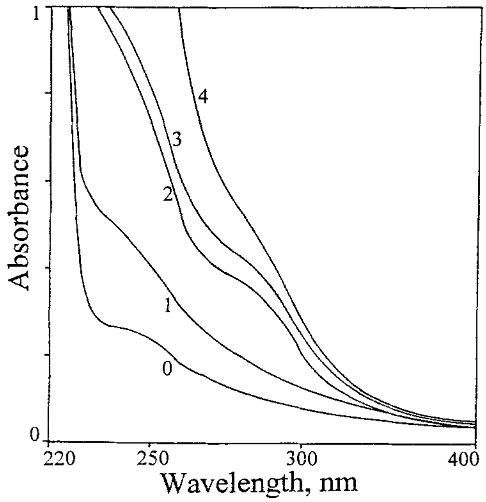


Fig. 1. Absorption spectra of PB photoirradiated in benzene/H_2O_2 mixtures during 0, 1, 2, 3, 4 h.

Photodegradated PB samples show the great differences in the IR spectra (Fig.2). The broad, rich carbonyl band is formed in PB in earliest stages of photooxidation (after 1h). In PB irradiated in pure benzene solution the band centered at 1733 cm^{-1} with smaller branches at 1693, 1711 and 1778 cm^{-1} appears and may be ascribed to esters, α,β-unsaturated ketones, saturated ketones/aldehydes and peroxyesters/ peroxyacids, respectively[5,6,11,19]. The similar but more efficient changes of carbonyl bands were observed when PB was irradiated in the presence of H_2O_2. An increase of the IR absorption upon light exposure was also observed around 1100-1200 cm^{-1}. Bands in this region have been assigned to C-O vibration in carbonyl compounds.

Simultaneously, the bands at 1654 and 738 cm^{-1} assigned to *cis* C=C unsaturated bonds gradualy decrease but do not disappear completly even after 4h of PB irradiation in benzene solution as well as in mixture containing H_2O_2. It means that reaction of addition to double bonds occurs with relatively small efficiency. It is necessary to mention that new, weak absorption appears at 1611, 704 cm^{-1} in case of PB irradiated in benzene and 1611, 710, 680 cm^{-1} when PB was irradiated in presence of H_2O_2. These bands can be assigned to new type of unsaturated C=C bonds what was previously suggested on the base of UV-Vis spectra.

Moreover weak band at 892 cm^{-1} due to epoxide groups in PB oxidized in benzene solution appears but is absent during PB degradation in benzene/H_2O_2.

In the stretching vibration region, broad absorption band within the range of 3200-3600 cm^{-1} with maximum at 3440 cm^{-1} due to asocciated hydroxy and hydroperoxide groups appeared immediately. The intensity of this band is higher if PB is photodegradated in benzene/H_2O_2 mixture. After loger duration of exposure, absorption of this band does not increase significantly.

The hydroxy and hydroperoxide groups cannot be distinguished from IR spectra therefore iodometric titration was used to estimate the amount of formed OOH groups. Table 3 shows that overall amount of OOH groups is above 10 times higher in case of PB photooxidation in presence of H_2O_2. During first hour of UV irradiation of PB in benzene/H_2O_2 mixture fast formation of hydroperoxide groups occurs but in second hour slight decrease of OOH concentration is observed what indicates on their decomposition. These data are in agreement with findings from IR measurements.

Table 3. Overall amount of hydroperoxide groups in photodegradated PB

Time of irradiation, h	Solvent	[ROOH] 10^4, mol/l
0		0.00
1	benzene	0.12
2	benzene	0.25
1	benzene/H_2O_2	2.95
2	benzene/H_2O_2	2.25

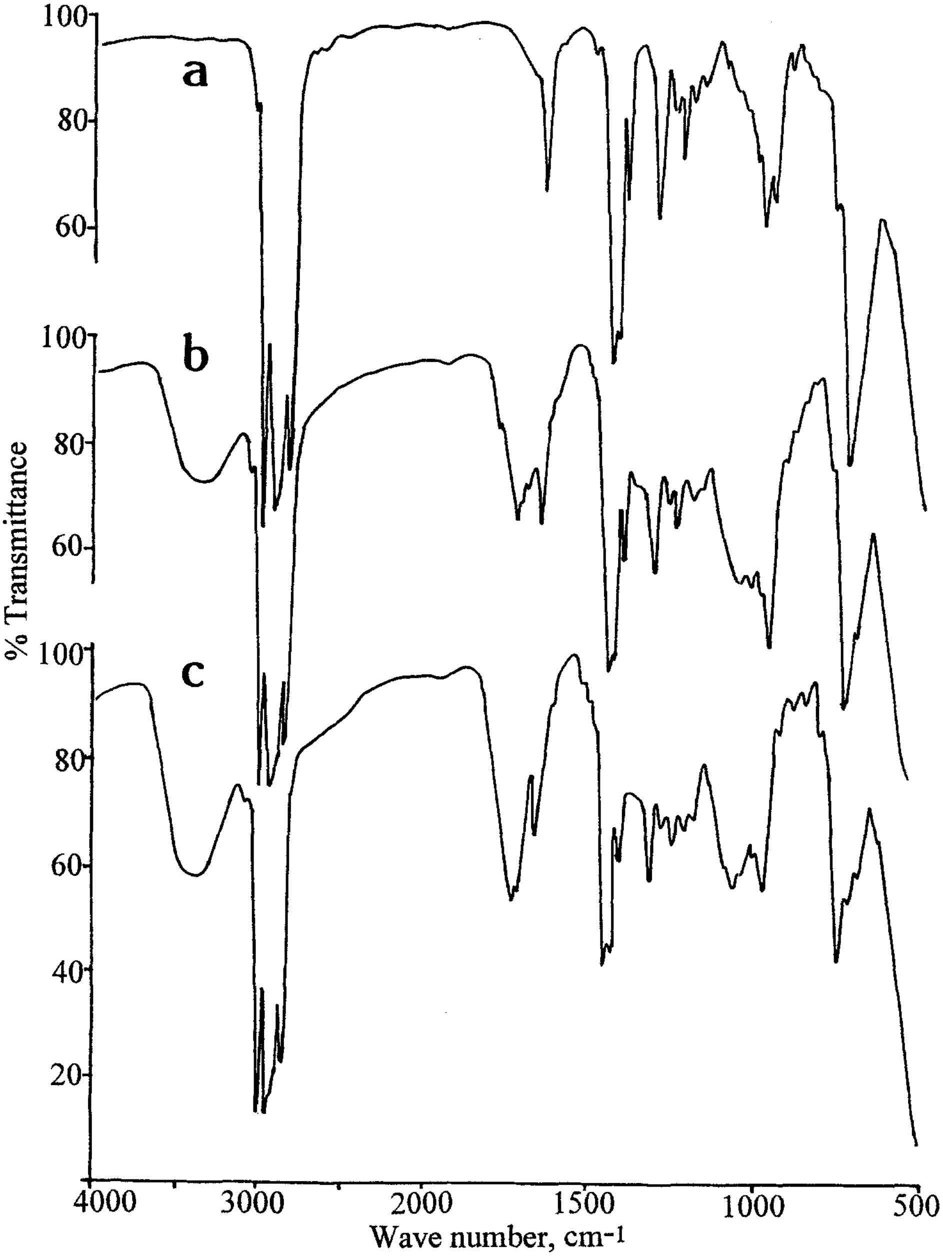


Fig. 2. IR spectra of PB undegradated (a), photodegradated 1h in benzene solution (b) and irradiated 1h in benzene/hydrogen peroxide emulsion (c).

According to present knowledge about the photooxidative degradation of PB[5-15] the following mechanism of the reactions occuring in PB solution in the presence of hydrogen peroxide can be proposed (only most important steps are presented):

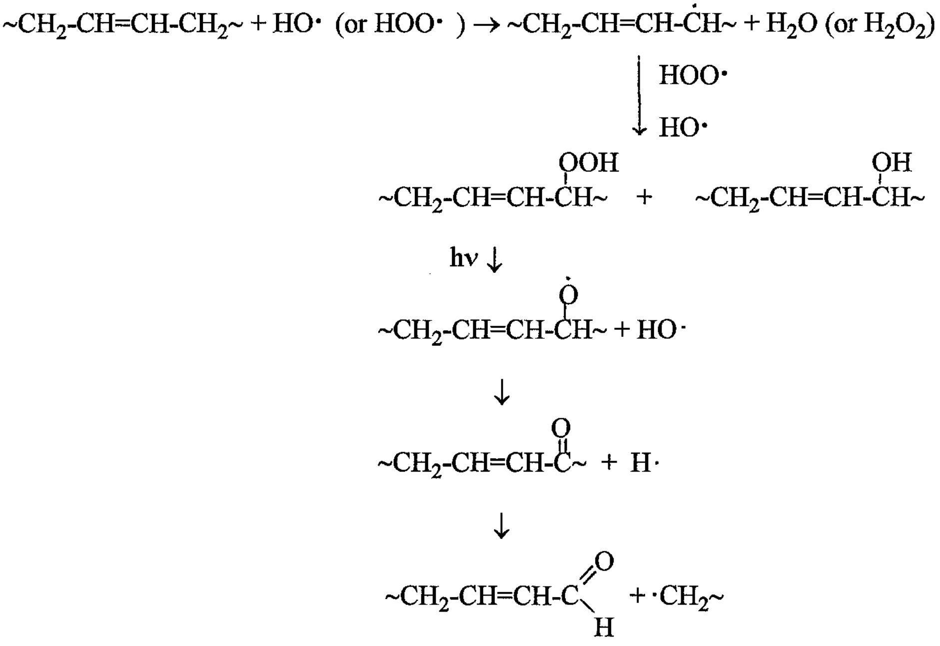
$$H_2O_2 \xrightarrow{h\nu} 2\,HO^{\bullet}$$

$$H_2O_2 + HO^{\bullet} \rightarrow HOO^{\bullet} + H_2O$$

$$2\,HO^{\bullet} \rightarrow H_2O + 1/2\,O_2$$

$$HO^{\bullet} + HOO^{\bullet} \rightarrow H_2O + O_2$$

$$2HOO^{\bullet} \rightarrow H_2O_2 + O_2$$



$$\sim CH_2\text{-}CH\text{=}CH\text{-}CH_2\sim + HO^{\bullet}\ (\text{or } HOO^{\bullet}) \rightarrow \sim CH_2\text{-}CH\text{=}CH\text{-}\dot{C}H\sim + H_2O\ (\text{or } H_2O_2)$$

$$\Big\downarrow\ \begin{matrix} HOO^{\bullet} \\ HO^{\bullet} \end{matrix}$$

$$\sim CH_2\text{-}CH\text{=}CH\text{-}\overset{OOH}{\overset{|}{C}H}\sim \quad + \quad \sim CH_2\text{-}CH\text{=}CH\text{-}\overset{OH}{\overset{|}{C}H}\sim$$

$$h\nu \downarrow$$

$$\sim CH_2\text{-}CH\text{=}CH\text{-}\overset{\dot{O}}{\overset{|}{C}H}\sim + HO^{\cdot}$$

$$\downarrow$$

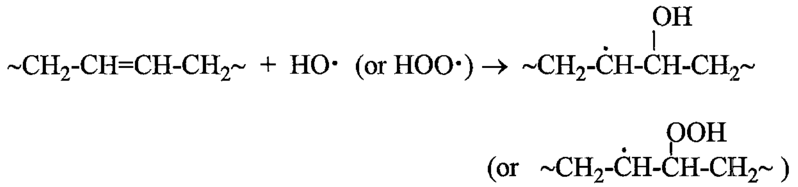
$$\sim CH_2\text{-}CH\text{=}CH\text{-}\overset{O}{\overset{\|}{C}}\sim \ + H^{\cdot}$$

$$\downarrow$$

$$\sim CH_2\text{-}CH\text{=}CH\text{-}C\begin{matrix} {}^{\nearrow O} \\ {}_{\searrow H} \end{matrix} \quad + {}^{\cdot}CH_2\sim$$

Photooxidation of PB starts with HO· and HOO· radicals attack on the hydrogen atom in the allylic position. The formed photounstable hydroperoxides and internal peroxides (ROOH and ROOR) can initiate the further decomposition of PB macromolecules leading to the creation of different kind of carbonyl groups and new type of unsaturation. Detailed mechanism of photodecomposition of macromolecular hydroperoxides was described elsewhere[2,3,22-24].Simultaneously very efficient chain scission reaction takes place resulting of β-scission of alkoxy radicals and Norrish Type I and II reaction of carbonyl groups. Because of the efficient chain cleavage the great amount of aldehyde groups on the end of PB chains are created. The terminal carbonyls can be further oxidized to carboxylic acids. All macroradicals generated in PB during UV irradiation are able to react with atmospheric oxygen and oxygen generated during H_2O_2 photolysis what additionaly increases the concentration of photoproducts. The reaction of PB with oxygen leads to formation of the different type of carbonyls as ketone, aldehyde, ester, carboxylic, peroxyester and peroxyacid groups[4,5,11]. It has been found that carbonyl groups in PB act as weak photostabilizing groups rather than initiation sites in contrary to hydroperoxides.

The hydrogen abstraction usually competes with the addition of radicals to the double bonds:



$$\sim CH_2\text{-}CH{=}CH\text{-}CH_2\sim \; + \; HO^{\bullet} \; (\text{or } HOO^{\bullet}) \rightarrow \sim CH_2\text{-}\dot{C}H\text{-}\overset{OH}{C}H\text{-}CH_2\sim$$

$$(\text{or } \sim CH_2\text{-}\dot{C}H\text{-}\overset{OOH}{C}H\text{-}CH_2\sim)$$

Main chain scission reaction of photoirradiated PB is accompanied by a shift of a double bonds to the terminal position:

$$\sim CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\sim \; \xrightarrow{h\nu} \; 2 \sim CH_2\text{-}CH{=}CH\text{-}CH_2^{\bullet}$$

$$\sim CH_2\text{-}CH{=}CH\text{-}CH_2^{\bullet} \rightarrow \sim CH_2\text{-}\dot{C}H\text{-}CH{=}CH_2$$

The influence of photochemical reactions of solvent cannot be neglected. UV irradiated benzene undergoes photooxidation leading to phenol and o-quinone formation and ring opening reactions causing long-chain conjugated dialdehydes[3]. It is known that hydroxy radicals from photolysis of hydrogen peroxide can also react with benzene rings giving photooxidized products. Moreover, in the presence of molecular oxygen a charge transfer complexes (benzene-O_2) expending the absorption spectrum up to 340 nm, are formed. The quinones and endoperoxides can efficiently sensitize the photooxidation processes of PB.

Conclusions

Cis 1,4-polybutadiene UV-irradiated in diluted benzene and in benzene/ hydrogen peroxide solution undergoes mainly chain scission reaction and oxidation. Insoluble gel is not formed in these conditions and only small extent of addition reaction to double bonds occurs. Presence of hydrogen peroxide in PB solution accelerate significantly process of photooxidative degradation of PB because of efficient reaction of hydroxy (HO·) and hydroperoxy (HOO·) with PB macromolecules. Specially fast and efficient reaction of hydroperoxide formation was observed in earliest stages of photooxidation. The longer time of light exposure leads to their decomposition and secondary reactions in degradated PB. The photooxidation products of solvent can also accelerate the PB photodegradation.

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