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Crosslinking and Oxidation of 1,2-Polybutadiene by UV Irradiation

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ABSTRACT

Photoinduced crosslinking and oxidation of 1,2-polybutadiene film were carried out with UV irradiation in vacuo and in air. A small amount of the structures of trans-vinylene, diene, and triene were observed in the infrared spectrum of the nonirradiated film, and bands attributable to conjugated double bond (230, 280 nm) were also observed in ultraviolet spectrum. In the film irradiated in vacuo, intensities of the bands assigned to trans-vinylene, methylene, and methyl groups increased with the increase in irradiation time, but the intensity of the band of pendent vinyl group decreased. With irradiation in air, the formation of carbonyl and hydroxyl groups and ether linkages was observed. Formation of H_2 with the irradiation in vacuo and of H_2O with the irradiation in air was observed. The gel fraction increased with an increase in irradiation time in the absence and presence of oxygen. The gel fraction and the formation of carbonyl groups were markedly accelerated by irradiation with UV rays of wavelength near 280 nm and

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increased with decreasing concentration of pendent vinyl groups. Postreaction of the irradiated film took place in the dark. The gel fraction and the intensity of the carbonyl group increased by radical reaction with α,α'-azobisisobutyronitrile. On the basis of these results, mechanisms of photoinduced crosslinking and oxidation of 1,2-polybutadiene were discussed.

INTRODUCTION

It is well known that 1,2-polybutadiene (1,2-PBD), having a branched vinyl group and a hydrogen atom bonded on allyl position as a reactive unit, is a photosensitive polymer [1]. It has also been reported [1] that 1,2-PBD film becomes embrittled owing to crosslinking by exposure under UV light in air. On the other hand, as previously discussed by us [2], various kinds of high polymers, such as polyethylene and poly(vinyl chloride), are much more subject to photooxidation by graft polymerization with unsaturated compounds.

The purpose of this paper is to report on structural changes and gel formation of 1,2-PBD irradiated by UV light in the absence and presence of oxygen. On the basis of these results, mechanisms of crosslinking and oxidation are discussed.

EXPERIMENTAL

1,2-PBD has a syndiotactic structure containing more than 90% 1, 2 units, and has 25% crystallinity and an intrinsic viscosity measured in toluene at 30° C of 1.30. The film samples used in this investigation (manufactured by Japan Synthetic Rubber Co. Ltd.) were 50 μm in thickness.

The photochemical reaction was carried out as follows. The film was irradiated at a distance of 50 cm with a 1.2-kW high-pressure mercury lamp at 800 Torr. The surface temperature of the film was kept constant at 47 ± 3° C. The film in the presence of oxygen-nitrogen mixture was irradiated from outside a quartz test tube. The monochromatic light source was a 2-kW xenon lamp in an irradiator (CRM-FA Spectro Irradiator, Nippon Bunko Co. Ltd.).

The infrared spectrum of the film was measured with a Nippon Bunko Model DS-403G infrared spectrophotometer with NaCl optics, and the ultraviolet spectrum was obtained with a Hitachi model ESP-3T spectrophotometer.

The sample in a 200-mesh stainless steel basket was placed in a Soxhlet extractor and extracted with refluxing benzene for more than

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50 hr, then dried under reduced pressure at room temperature for 48 hr and weighed. The gel fraction of the polymer was determined from the weight of the insoluble portion.

The mass spectra of gas formed during irradiation under a reduced pressure of less than 10^{-5} Torr and in oxygen at a pressure of 1 Torr were measured by a Nippon Denshi Model 01-SG instrument.

The postreaction of the irradiated film was carried out in an aluminum foil case placed in the dark. After a given time, the structural change and gel fraction of the film were measured. In order to make clear the mechanism of this reaction, the radical reaction in the dark was also performed as follows: 80 mg of *α,α'*-azobisisobutyronitrile (AIBN) was placed in an ampoule containing 300 mg of the film in the absence of oxygen, and the ampoule was kept at 80° C for 90 hr.

RESULTS AND DISCUSSION

Chemical Structure of Nonirradiated Film from IR and UV Spectra

Infrared spectra of the original (nonirradiated) and irradiated 1,2-PBD film are shown in Fig. 1. In the nonirradiated film, strong

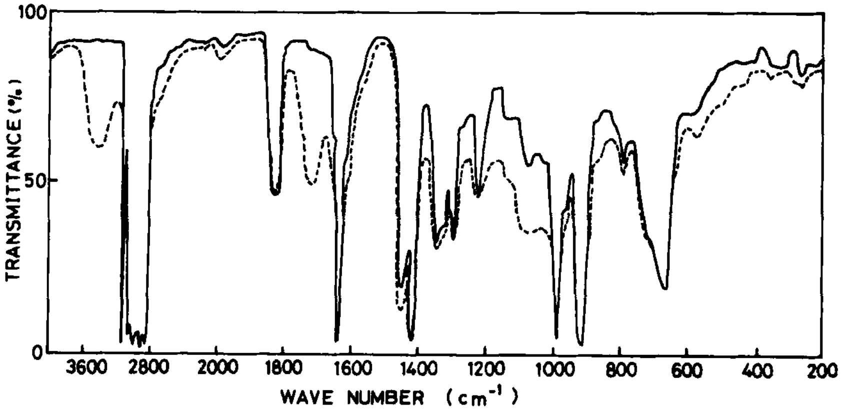

FIG. 1. Infrared spectra of the photooxidized 1,2-polybutadiene film (50 μm in thickness): (——) not photooxidized, (---) 24 hr irradiation by 1.2-kW high-pressure mercury lamp.

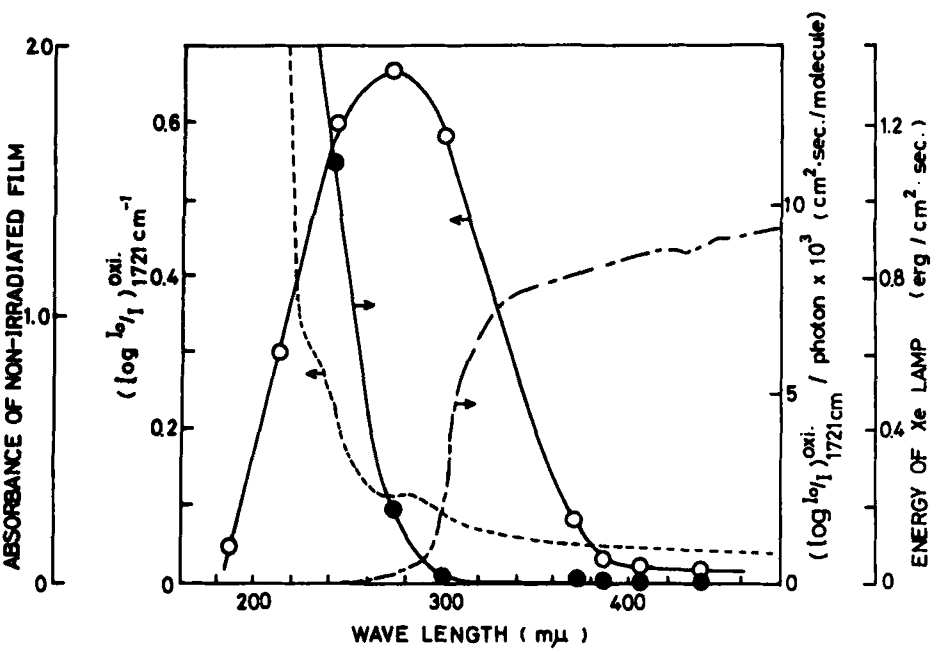

FIG. 2. Effect of wavelength on the formation of >C=O group: (○) >C=O group formation; (●) >C=O group formation on irradiation with same intensity, (—— - ——) UV spectra of nonirradiated 1,2-PBD film (--) spectrum of Xe lamp. Light source: 2-kW xenon lamp (JASCO CRM-FA Spectro-Irradiator); irradiation time: 12 hr; irradiation in air.

absorption bands at 1645, 990, and 910 cm^{-1} assigned to the vinyl endgroup and a shoulder at near 964 cm^{-1} assigned to the trans-vinylene group were observed. Furthermore, shoulders at 1650 and 1600 cm^{-1} assigned to diene and triene, respectively, were also observed.

On the other hand, the ultraviolet spectrum of the nonirradiated film is shown in Fig. 2. The nonirradiated film showed three bands: one at wavelength shorter than 210 nm assigned to the nonconjugated double bond of the branched vinyl group on the main chain and bands

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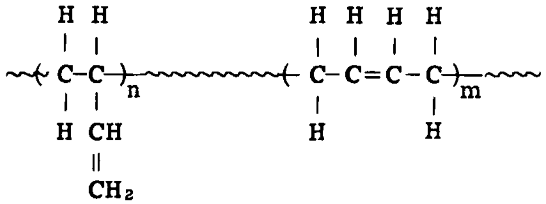
at 230 and 280 nm assigned to diene and triene, respectively. The intensity of the 230 nm band was greater than that of the 280 nm band. These results indicate that the 1,2-PBD polymer is composed mainly of the pendent vinyl structure resulting from 1,2 addition of butadiene to the growing chain end and contains a small amount (3% of total double bonds) of trans-vinylene structures formed by 1,4 addition of butadiene (structure I).

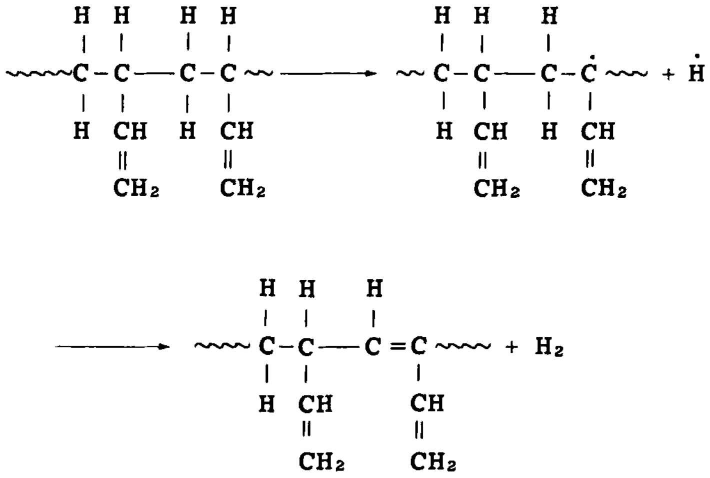


$$\sim\!\left(\mathrm{CH_2{-}CH(CH{=}CH_2)}\right)_n\!\sim\!\left(\mathrm{CH_2{-}CH{=}CH{-}CH_2}\right)_m\!\sim$$

$n/(n + m) = 0.03$

I

Furthermore, the diene and triene structures would result from the dehydrogenation reactions (1) and (2), during either the polymerization or the processing.



$$\sim\mathrm{CH_2{-}CH(CH{=}CH_2){-}CH_2{-}CH(CH{=}CH_2)}\sim \longrightarrow \sim\mathrm{CH_2{-}CH(CH{=}CH_2){-}CH_2{-}\dot{C}(CH{=}CH_2)}\sim + \dot{H} \longrightarrow \sim\mathrm{CH_2{-}CH(CH{=}CH_2){-}CH{=}C(CH{=}CH_2)}\sim + H_2 \qquad (1)$$

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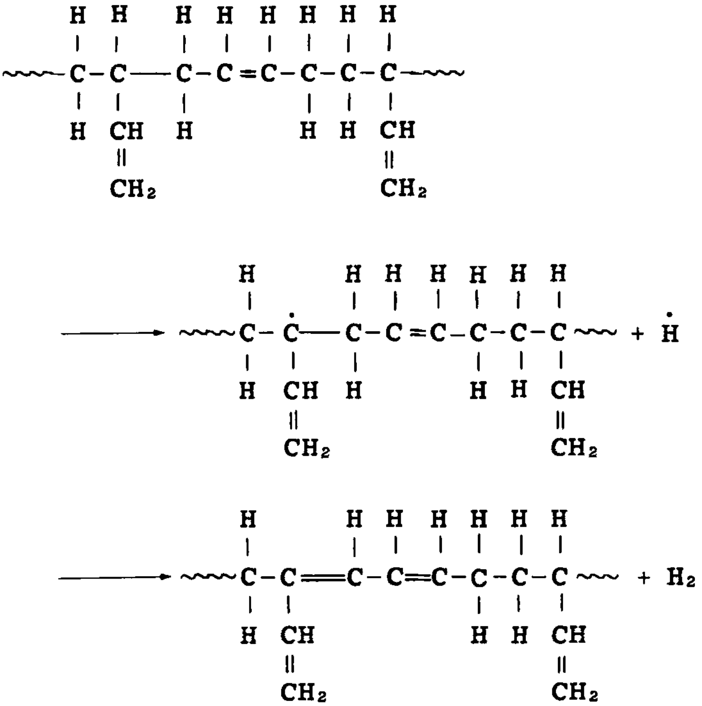

(2)

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Changes in IR and UV Spectra on UV Irradiation

In the IR spectrum of film irradiated in vacuo, no new band appeared, but intensities of bands at 1460, 1450, and 1440 cm^{-1} assigned to various types of methylene groups such as cyclopentane and cyclohexane and of the band at 1380 cm^{-1} attributed to the methyl group increased with increasing irradiation time. Further, an increase in the intensity of the trans-vinylene group band was observed (Fig. 1). However, the spectrum of the film irradiated in air showed new bands: at near 3450 cm^{-1}, assigned to hydroxyl group; in the region of 1800-1675 cm^{-1}, assigned to various kinds of carbonyl groups; at near 1100 cm^{-1}, assigned to the ether linkage. The intensities of these bands and of the band assigned to methylene increased with increasing irradiation time. In addition, intensities of various kinds of double bonds, such as trans-vinylene, also increased with the increase in irradiation time in air and in vacuo. The mechanism of the increase in concentration of methylene group will be discussed in connection with gel formation in a later section.

On the other hand, new bands were not observed in the UV spectra of films irradiated in vacuo and in air, while bands in the region shorter than 300 nm assigned to the carbonyl group formed on photooxidation and increased in intensity with increasing irradiation time in air.

Mass Spectrum of the Gas Evolved by UV Irradiation

The mass spectral compositions of the gases generated by UV irradiation for 75 hr in vacuo and in the presence of 1 Torr oxygen are listed in Table 1. In both cases, H and H_2 were observed, and the quantities of hydrogen produced in vacuum irradiation were much greater than those produced in an atmosphere of oxygen. A large quantity of H_2O was observed only in the gas formed by irradiation with oxygen.

On the other hand, large quantities of hydrocarbons such as C_3H_6 and C_3H_7 were generated in the vacuum irradiation, while small

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TABLE 1. Mass Spectra of Gaseous Products Evolved on UV Irradiation in Vacuo and in Oxygen for 45 Hr

	Relative intensity		
m/e	In O_2	In vacuo	Assignment
1	0	7	H
2	3	4	H_2
15	1	18	CH_3
16	35	38	O, CH_4
17	13	0	OH
18	57	0	H_2O
28	14	100	CO, C_2H_4
40	100	12	C_2O
42	1	7	C_3H_6
43	0	11	C_3H_7
44	95	62	CO_2, C_3H_8

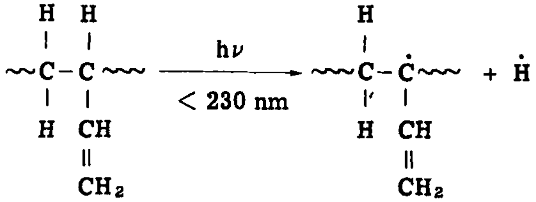
quantities of various kinds of hydrocarbons were obtained by irradiation in an atmosphere of oxygen. In addition, various fragments assigned to oxygen-containing compounds such as H_2O, C_2O, and CO_2 were observed in the irradiation with oxygen, and a small amount of hydrocarbon fragments was also detected. These results indicate that dehydrogenations such as shown in Eqs. (1) and (2) were induced by UV irradiation and the diene and triene structures formed by the dehydrogenation play an important role in the basic photochemical reaction in photooxidation and crosslinking of 1,2-PBD.

Crosslinking of 1,2-Polybutadiene by UV Irradiation

To clarify the effect of the energy of photons on the oxidation in air, the optical density of the ketone group formed (1721 cm^{-1}) was plotted against the wavelength of monochromatic UV rays. The UV spectrum of nonirradiated 1,2-PBD and the spectrum of the xenon lamp are also shown in Fig. 2. The xenon lamp emitted very little radiation shorter than 300 nm and emitted mostly visible rays longer than 350 nm. On the other hand, 1,2-PBD absorbed only UV rays shorter than 300 nm.

Gel formation and ketone group formation were induced by irradiation with UV rays shorter than ca. 350 nm. Both reactions were accelerated markedly by the irradiation with UV rays of wavelength near 280 nm. However, in film irradiated by UV rays of the same intensity, the formation of gel and ketone groups increased with increasing photon energy, that is, with shortening of the wavelength.

On the basis of these results, the initiation mechanism in the irradiation with far-ultraviolet rays, is presumed to follow Eq. (3), with the pendent vinyl group absorbing the energy of the light.



$$\sim\!\sim\mathrm{CH_2{-}CH(CH{=}CH_2)}\sim\!\sim \xrightarrow[< 230\ \mathrm{nm}]{h\nu} \sim\!\sim\mathrm{CH_2{-}\dot{C}(CH{=}CH_2)}\sim\!\sim + \dot{\mathrm{H}} \qquad (3)$$

In the case of irradiation with near-ultraviolet rays, conjugated double bonds such as diene and triene are considered to absorb the energy, according to Eqs. (4) and (5):

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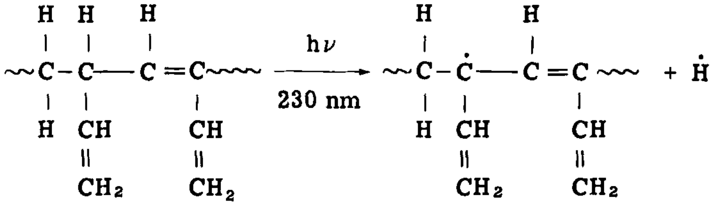
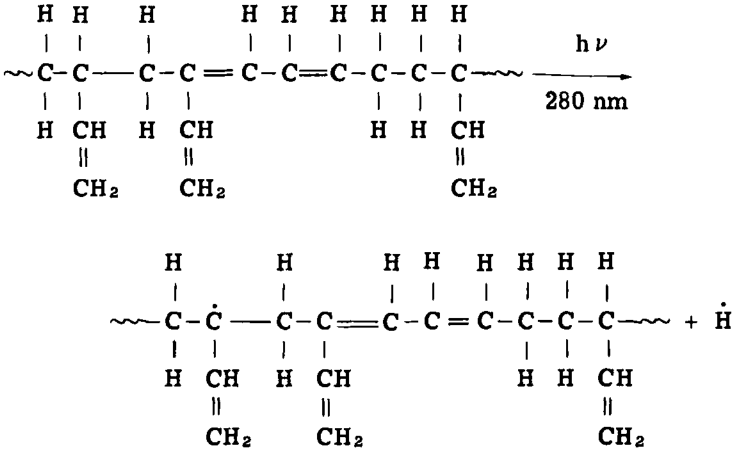


$$\sim\mathrm{CH_2{-}CH(CH{=}CH_2){-}CH{=}C(CH{=}CH_2)}\sim \xrightarrow[230\ \mathrm{nm}]{h\nu} \sim\mathrm{CH_2{-}\dot{C}(CH{=}CH_2){-}CH{=}C(CH{=}CH_2)}\sim + \mathrm{\dot{H}} \qquad (4)$$



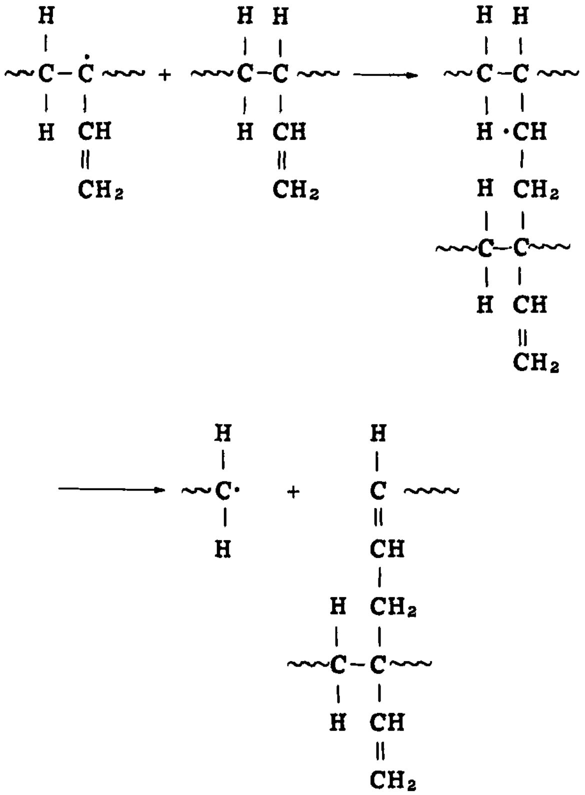
$$\sim\mathrm{CH_2{-}CH(CH{=}CH_2){-}CH_2{-}C(CH{=}CH_2){=}CH{-}CH{=}CH{-}CH_2{-}CH_2{-}CH(CH{=}CH_2)}\sim \xrightarrow[280\ \mathrm{nm}]{h\nu}$$

$$\sim\mathrm{CH_2{-}\dot{C}(CH{=}CH_2){-}CH_2{-}C(CH{=}CH_2){=}CH{-}CH{=}CH{-}CH_2{-}CH_2{-}CH(CH{=}CH_2)}\sim + \mathrm{\dot{H}} \qquad (5)$$

The absorbed energy resulting in the $\pi \rightarrow \pi^*$ electronic transition activates the C–H bond at the allyl position and that, in turn, the tertiary hydrogen atom on the main chain. As a result of the energy absorption, the C–H bond is weakened, and polymer radicals, as shown in Eqs. (3), (4) and (5), are formed by cleavage of the C–H bond.

On the other hand, nonirradiated film and film irradiated for a short time, in which an increase in methylene group formation was not detected, were soluble in benzene. On the other hand, film irradiated for long time, in which increases in methylene group content and in ether linkages, were observed, was insoluble in benzene. The increase in the gel fraction with irradiation in vacuo brought about an increase in trans-vinylene groups and a decrease in pendent vinyl groups.

On the basis of these results, the mechanism of gel formation may be supposed to follow the reaction (6). That is, the polymer radical formed on the main chain by reactions (3), (4), and (5) reacts with the pendent vinyl group branched on the main chain; the radical thus formed leads to the formation of methylene groups and β-scission of the C–C bond of the main chain.



(6)

The increase in the concentrations of methylene and trans-vinylene groups with the increase in gel fraction and the concomittant decrease in the concentration of the pendent vinyl group support this mechanism. Further, it can be considered from this mechanism that the methylene radical formed on the polymer and end groups as in Eq. (6) abstracts the hydrogen from the allyl position of another polymer chain as shown in Eq. (7). The methyl groups increased as a result of this transfer reaction.

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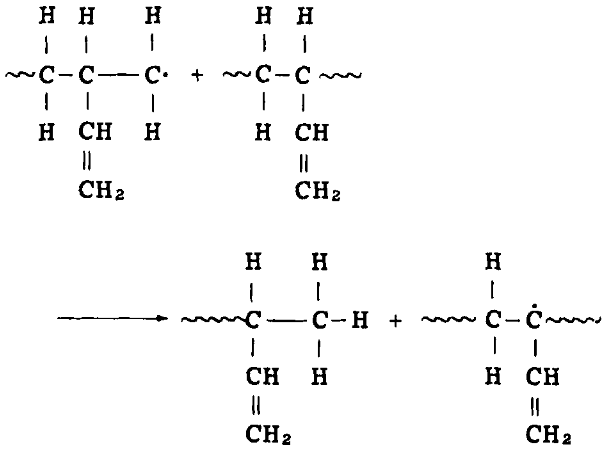
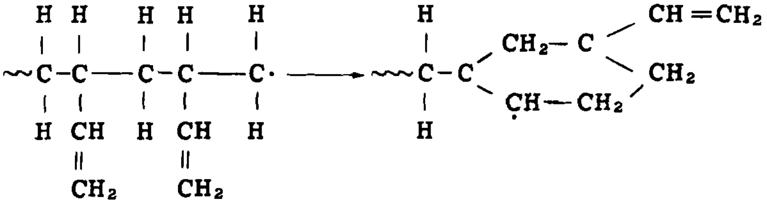


(7)

II

The fact that the intensity of the methyl group band increased with the increase in gel fraction is a result of the chain reaction mechanism of initiation reactions (3), (4) and (5) and the chain transfer reactions (6) and (7). The increase in the band at 1450 cm^{-1} assigned to the methylene group of cyclohexane with the increase in gel fraction may be caused by intramolecular cyclization of the chain end methylene radical as shown in Eq. (8).



(8)

A radical formed on the ring may abstract hydrogen from the allyl position of the main chain or react with a pendent vinyl group. As a result of hydrogen abstraction from the allyl group, [Eq. (6)], crosslinking takes place at an increasing rate with irradiation time. time.

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Photoinduced Oxidation of 1,2-Polybutadiene

When the 1,2-PBD film was irradiated in air, the optical density of the ketone group increased markedly with increasing irradiation time, and the gel fraction also increased (Fig. 3). In order to elucidate the effect of wavelength of light on the photooxidation, the film was irradiated in air with monochromatic light. From Fig. 2, it is found that the UV radiation of 280-290 nm wavelength was most effective for formation of ketone groups; on irradiation with light in the visible range (longer than 350 nm) of the same intensity (as shown by the broken line in Fig. 2), the ketone group increased with increasing energy of the photons, that is, with light of shorter wavelengths.

When the 1,2-PBD film was irradiated in vacuo, ketone groups were not produced, while gel formation was observed. The optical density of the pendent vinyl group decreased gradually with increasing irradiation time. However, in the film irradiated in vacuo, the optical density of methylene groups only increased with increasing irradiation time. In the case of irradiation in air, the optical densities of both the methylene group and the ether linkage increased. The increase in the optical density of the ether linkage was greater than that of the methylene group. The relationship between the decrease in the optical density of the pendent vinyl group and the increase in the ketone group and the gel fraction is plotted in Fig. 4. The optical density of the ketone group increased linearly with the decrease in optical density of the pendent vinyl group, while the gel fraction showed an accelerating increase with decreasing concentration of the pendent vinyl group.

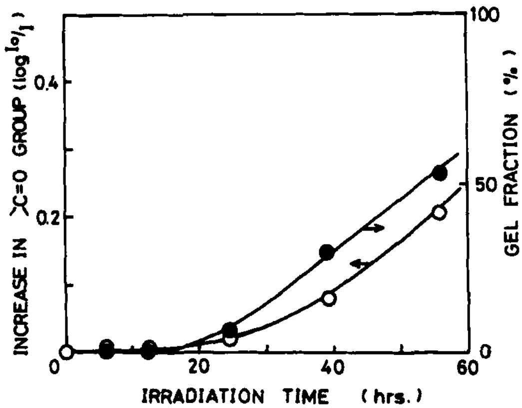

FIG. 3. Relation between UV irradiation time and increase in ketone group absorbance and gel fraction: (○) $>C=O$ formation; (●) gel fraction.

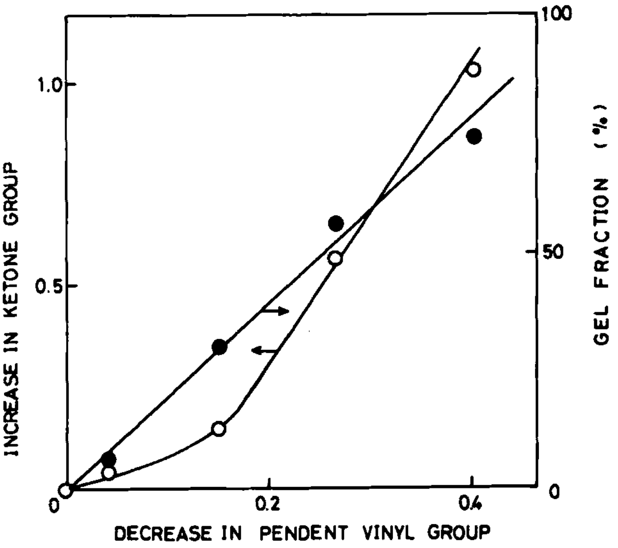

FIG. 4. Relation between decrease in pendent vinyl group and (○) increase in ketone groups and (●) gel fraction.

These results indicate that crosslinking induced by irradiation in air would result from both mechanisms: addition of the radical on the main chain to the pendent vinyl group and addition of the oxide radical on the side chain by the reaction with an oxygen molecule. That is to say, it is suggested that photooxidation accelerated the crosslinking in the film.

To examine the effect of concentration of oxygen on the oxidation rate and crosslinking, film placed in a quartz test tube was irradiated in the presence of a mixture of oxygen and nitrogen. Both optical density of the ketone group and gel fraction were plotted against the oxygen concentration, as shown in Fig. 5.

In the case of film irradiated in vacuo, the ketone group was not observed, but a gel fraction was formed. The optical density of the ketone group increased with increasing oxygen concentration, while the gel formation increased only slightly and even decreased slightly at high concentrations of oxygen.

On the basis of these results, the mechanism for the photooxidation can be presumed to be as follows. First, polymer radicals formed by dehydrogenation as in reactions (3), (4), and (5) react with triplet oxygen molecule in excited and/or ground state [Eq. (9)],

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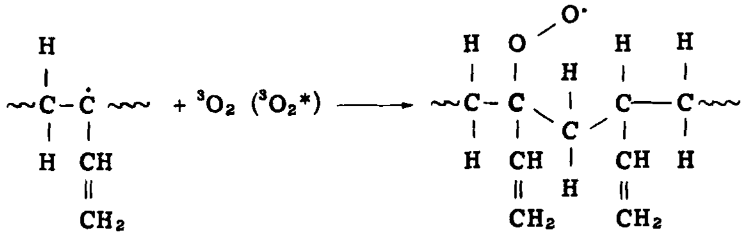
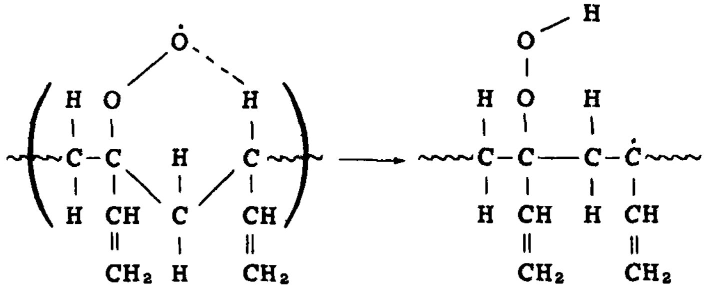


(9)

III

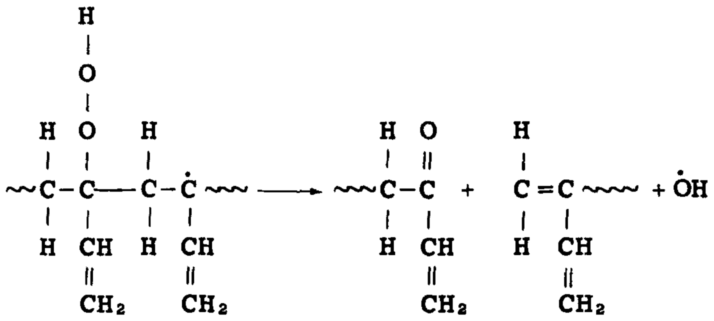
then, the peroxide radical of the polymer forms a six-membered cyclic intermediate (III) and abstracts the tertiary hydrogen atom on a γ-carbon as [Eq. (10)], resulting in formation of hydroperoxide and an allyl radical on the main chain (structure IV);



(10)

III IV

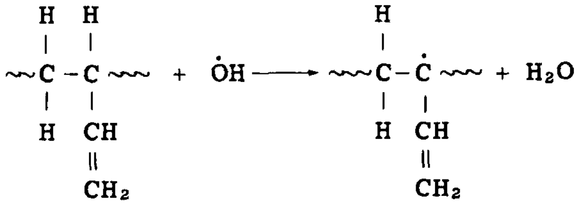
both decomposition of the hydroperoxide and β-scission result in formation of a derivative of butadiene (V) and vinyl ketone (VI) as shown in Eq. (11).



(11)

V VI

Because of products such as V and VI, according to reaction (11), are also photosensitive species, crosslinking would be accelerated by these species on UV irradiation. Furthermore, the hydroxyl radical formed by reaction (11) abstracts a tertiary hydrogen atom and produces a polymer radical (II) on the main chain plus water [Eq. (12)].



$$\begin{array}{c}H\\|\\\sim\!\sim C\\|\\H\end{array}\!-\!\begin{array}{c}H\\|\\C\sim\!\sim\\|\\CH\\\|\\CH_2\end{array} + \dot{O}H \longrightarrow \begin{array}{c}H\\|\\\sim\!\sim C\\|\\H\end{array}\!-\!\begin{array}{c}\\\\\dot{C}\sim\!\sim\\|\\CH\\\|\\CH_2\end{array} + H_2O \qquad (12)$$

II

The increases in various kinds of double bonds such as trans-vinylene group, diene, and triene (except for the vinyl endgroup) and of gel formation also support the mechanism, proposed above.

Postreaction of the film irradiated with UV rays was carried out in the dark in the presence of oxygen. The increase in the optical density of the ketone group and the gel fraction induced by postreaction were plotted against the reaction time (Fig. 6). The gel

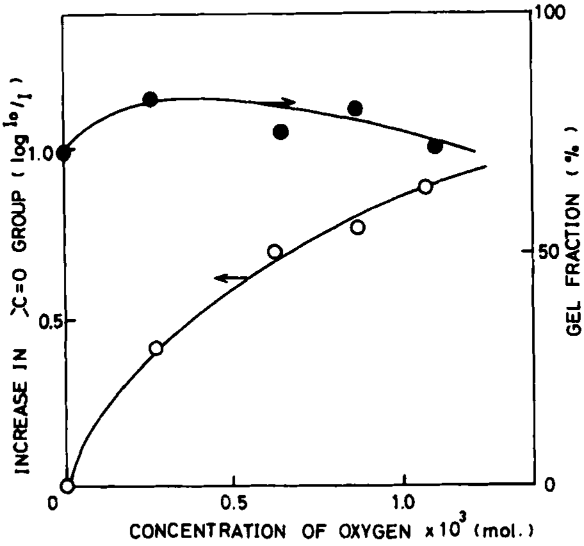


FIG. 5. Effect of oxygen concentration on (○) formation of ketone group and (●) gel formation.

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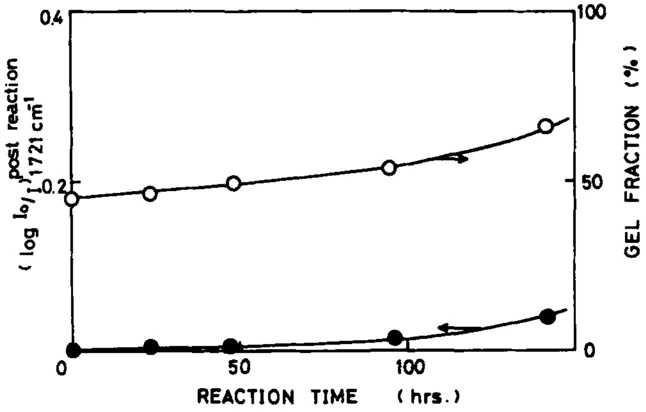

FIG. 6. Relation between reaction time in dark and (○) optical density of >C=O group and (●) gel fraction after postreaction of film irradiated for 30 hr.

fraction increased markedly with the increase in reaction time, while the optical density of the ketone group increased only slowly up to 100 hr irradiation. In addition, an increase in the various types of double bonds such as trans-vinylene, diene, and triene were observed in 1,2-PBD on postreaction.

When the film was subjected to radical reaction with AIBN, a gel fraction of 96% was obtained, compared with 3% without AIBN. These results suggest that hydroxy and perhydroxy radicals formed by reaction (11) or polymer radicals initiated the postreaction. From the results of the postreaction, it may be concluded that the oxidation and crosslinking induced by UV irradiation result from radical reaction induced by a photoinitiation reaction.

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