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Reaction Mechanism for Ozone Oxidation of Polyethylene as Studied by ESR and IR Spectroscopies

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In a previous study of graft copolymerization of methyl methacrylate onto polyethylene oxidized with ozone, we clarified that ozone-oxidation reactions produce peroxyl radicals in polyethylene and that the graft copolymerization is assumed to start upon heating, through the decomposition of hydroperoxides which are converted from the peroxyl radicals. A series of reaction processes proposed for the ozone oxidation were examined from the viewpoint of the reaction rate. The time-dependent content of the peroxyl radicals was pursued by observing in situ ESR; the initial evolution rate of the peroxyl radicals and the decay rate after the ozone-stop were discussed on the basis of the proposed ozone-oxidation mechanism, leading to a good agreement between the experiment and theory. The amounts of hydroperoxide and carbonyl species determined from iodometry and the IR spectra, respectively, were also discussed with regard to the oxidation time, showing reasonable linear dependences.

Many investigations regarding polymer degradation have been reported.¹⁾ Free-radical species in polyethylene and polypropylene irradiated by UV light or γ-rays have also been extensively discussed, and a reaction mechanism involving those radical species proposed.²⁻¹⁰⁾ On the other hand, we recently found that the ozone oxidation of polyethylene is very effective for its graft copolymerization with methyl methacrylate.¹¹⁾ The influence of the ozone-oxidation and polymerization times on the total conversion, degree of grafting, and graft efficiency were discussed in detail, and the molecular weight of branch polymers estimated. This graft copolymerization can be initiated by active species on polymers introduced by means of ozone oxidation. Making use of ESR spectroscopy, the active species were determined to be peroxyl radicals, as in the case of polypropylene.¹²⁾

The reaction mechanism for the ozone oxidation of polyethylene was presumed in a previous study,¹¹⁾ based on the detected species in oxidation reactions, such as the peroxyl radical and hydroperoxide. In order to examine the proposed reaction mechanism from the view-point of the reaction rate, we performed in situ ESR measurements and pursued the time-dependent contents of the peroxyl radicals during the initial reaction stage and after stopping the ozone flow (ozone-stop). In addition, the hydroperoxide product was determined from iodometry, and the final inert products were also checked by the IR spectra. The amounts of these products depended on the oxidation time, and were examined on the basis of the proposed reaction mechanism.

Experimental

Polyethylene samples were purchased from Sumitomo Seika Co., Ltd.; 80—100 mesh of low-density type, 0.918 g cm^{-3}, mp 105-111 °C, and molecular weight 4.84×10^4. Polyethylene fibers were obtained from Daiwa Boseki Co., Ltd.; density 0.955—0.961, mp 125—130 °C. Polyethylene films were made by pressing the above-mentioned polyethylene powder at a temperature of 140 °C and a pressure of 10 kg cm^{-2}.

Ozone was produced in a silently discharged oxygen flow (concentration ca. 30 g m^{-3}) and then introduced to a sample tube set in the ESR cavity. For IR measurements polyethylene films were exposed to ozone flow for a prescribed time.

ESR measurements were carried out using a JEOL X-band spectrometer (ME-3X type) with 100-kHz field modulation. Polyethylene fibers of 100—200 mg weight in a quartz glass tube were set inside the ESR cavity and an ozone stream was directly introduced. The decay rate after stopping the ozone was so rapid that the spectral intensity could not be calculated by integration, and was pursued by sitting on the ESR signal; the peak heights were plotted.

The IR spectra were measured for both untreated polyethylene and ozone-exposed polyethylene films using a Shimadzu IR spectrometer (IR-27G type). The absorption intensity was calculated by the usual base-line method.

A determination of hydroperoxide was made according to Chien's method.¹³⁾ Details have been described in the literature;¹¹⁾ data involving the concentration of hydroperoxide vs. the oxidation time were utilized for a rate-process analysis.

Results

The ESR spectrum of polyethylene during ozone oxidation consists of one absorption line with g=2.015 and a line width of ca. 2.4 mT. The radical species was identified as being peroxyl radicals ROO·, as was discussed in a previous paper.¹¹⁾ The spectral intensities of the ESR spectra during ozone oxidation, as well as after stopping ozone flow, are depicted in Fig. 1, which shows a gradual growth of the radical species for ca. 10 min, then reaching a plateau (a stationary radical concentration). After stopping the ozone flow the intensity decreased rapidly, becoming very weak after ca. 6 min.

The IR spectra shown in Fig. 2 indicate spectral variations with the ozone oxidation time. The spectra are almost the same as those reported earlier.[7,8] The absorption band at 1710 cm^{-1} can be assigned to a streching vibration of carbonyl groups (C=O) and those at 3400 and 3200 cm^{-1} to that of OH groups. The increased absorption by ozone oxidation can also be seen in the area of 900—1400 cm^{-1}, probably due to other vibration modes of the C=O and OH groups. From these spectral variations, a relationship between the oxidation time and the optical density of the carbonyls (Fig. 3) was obtained, showing a good linear dependence of the C=O content on the oxidation time.

In our spectra the absorption at 3555 cm^{-1}, which was assigned to hydroperoxide by Luongo,[8] was not observed. This discrepancy may be attributed to the treated temperatures, that is, room temperature in our case, as compared to 120 or 145 °C in Luongo's experiment. We determined the content of the hydroperoxide by iodometry, the result of which was reported in a previous paper.[11] Like the C=O content, the hydroperoxide concentration increases linearly with the

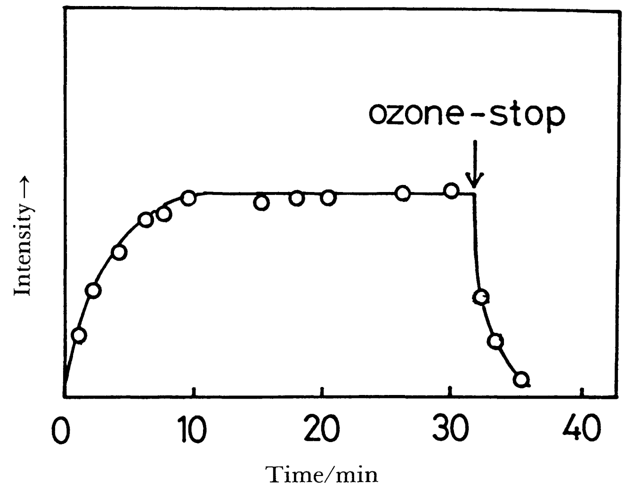


Fig. 1. Variation of the ESR spectral intensities of polyethylene with the ozone-oxidation time and after the ozone-stop.

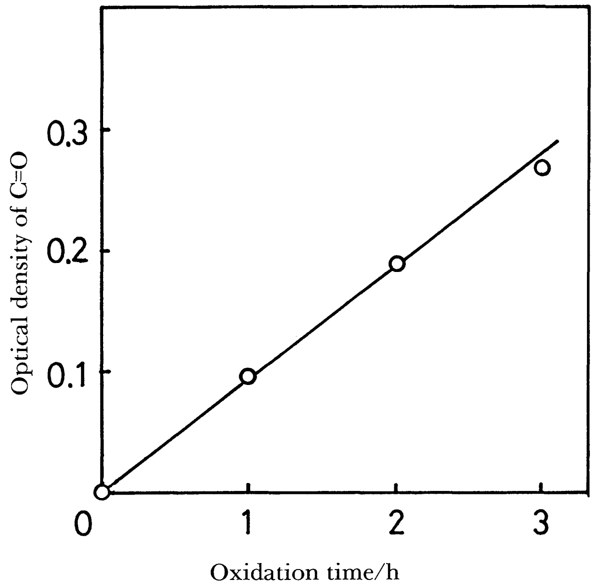


Fig. 3. Relationship between the oxidation time and the optical density of carbonyl groups in polyethylene oxidized with ozone.

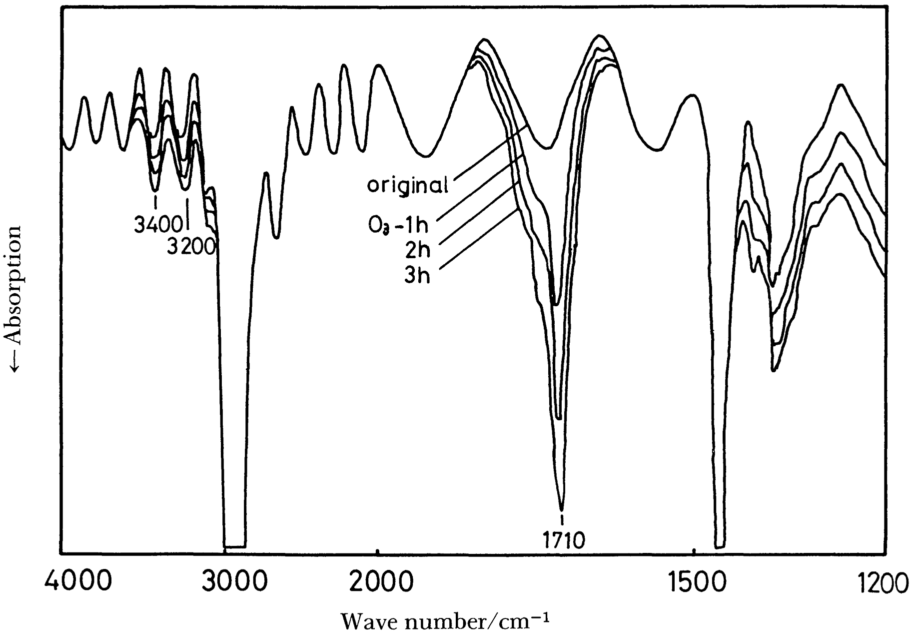


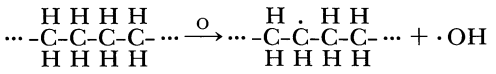
Fig. 2. Variation of the IR spectra of polyethylene with the ozone-oxidation time.

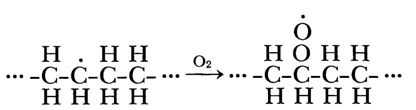
ozone oxidation time.

Discussion

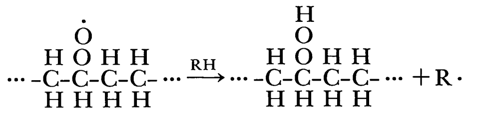
Ozone-Oxidation Mechanism. The presumed ozone-oxidation mechanism[11] is first summarized as follows. An atomic oxygen arising from ozone decomposition attacks polymers, producing carbon and hydroxyl radicals. The carbon radical reacts almost immediately with an oxygen molecule, giving a peroxyl radical:

$$O_3 \longrightarrow O_2 + (O) \qquad (1)$$

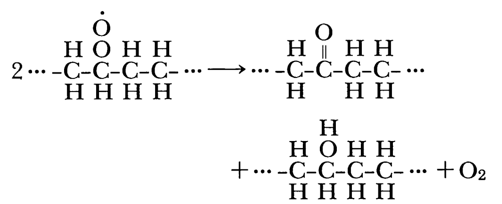

$$\cdots\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\cdots \xrightarrow{O} \cdots\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{\cdot}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\cdots + \cdot OH \qquad (2)$$


$$\cdots\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{\cdot}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\cdots \xrightarrow{O_2} \cdots\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{\overset{\cdot}{O}}{\overset{O}{\underset{H}{C}}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\cdots \qquad (3)$$

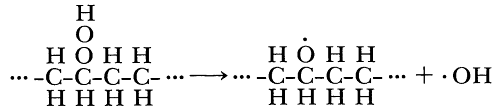
A part of the peroxyl radicals, thus produced, gives hydroperoxide by pulling out a hydrogen atom from polyethylene:


$$\cdots\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{\overset{\cdot}{O}}{\overset{O}{\underset{H}{C}}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\cdots \xrightarrow{RH} \cdots\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{\overset{H}{O}}{\overset{O}{\underset{H}{C}}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\cdots + R\cdot \qquad (4)$$

Another part of the peroxyl radicals gives inert substances, such as ketone and alcohol by recombination:


$$2\cdots\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{\overset{\cdot}{O}}{\overset{O}{\underset{H}{C}}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\cdots \longrightarrow \cdots\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{\overset{O}{\parallel}}{C}\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\cdots$$
$$+\cdots\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{\overset{H}{O}}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\cdots + O_2 \qquad (5)$$

The O-O bond of the hydroperoxide given in reaction (4) is broken by heating:


$$\cdots\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{\overset{H}{O}}{\overset{O}{\underset{H}{C}}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\cdots \longrightarrow \cdots\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{\overset{\cdot}{O}}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\cdots + \cdot OH \qquad (6)$$

The alkoxyl and hydroxyl radicals, thus obtained, are presumed to initiate polymerization as active sites and to give graft copolymers and homopolymers, respectively.

Rate-Process Analyses. For simplicity, the following rate processes are taken into consideration. Reactions (2) and (3) can be expected to take place almost concurrently; that is,

$$RH + O_3 \xrightarrow{k_1} ROO\cdot + \cdot OH. \qquad (7)$$

The rate constants in reaction (4) and the following chain reaction are set to be k_2 and k_3, respectively:

$$ROO\cdot + RH \xrightarrow{k_2} ROOH + R\cdot \qquad (8)$$

and

$$R\cdot + O_2 \xrightarrow{k_3} ROO\cdot. \qquad (9)$$

The chain reaction is terminated as in reaction (5):

$$2ROO\cdot \xrightarrow{k_4} \text{inert products.} \qquad (10)$$

We assume a steady state of R· in reactions (8) and (9). Then, the production rate of ROO· is obtained as

$$\frac{d[ROO\cdot]}{dt} = k_1[RH][O_3] - k_4[ROO\cdot]^2. \qquad (11)$$

Here, we use two parameters, $I = k_1[RH][O_3]$ and $K = (I/k_4)^{1/2}$, and then obtain a solution of the Eq. 11 as[14]

$$\ln\frac{K+[ROO\cdot]}{K-[ROO\cdot]} = \frac{2I}{K}t \qquad (12)$$

or

$$[ROO\cdot] = \frac{e^{(2I/K)t}-1}{e^{(2I/K)t}+1} \times K. \qquad (13)$$

One can see that the saturated concentration of product ROO· is given by the parameter K, where

$$[ROO\cdot]_s = K = (I/k_4)^{1/2}. \qquad (14)$$

If we assume a small concentration of intermediate R·, as compared to that of ROO·, the observed ESR intensity becomes proportional to the concentration of ROO·.[15]

Figure 4 shows the time-dependent ESR intensities in the form

$$\ln\{([ROO\cdot]_s + [ROO\cdot])/([ROO\cdot]_s - [ROO\cdot])\},$$

which was calculated from the observed ESR intensity and the saturated value given in Fig. 1. A good linear correlation with the oxidation time given in Fig. 4 is

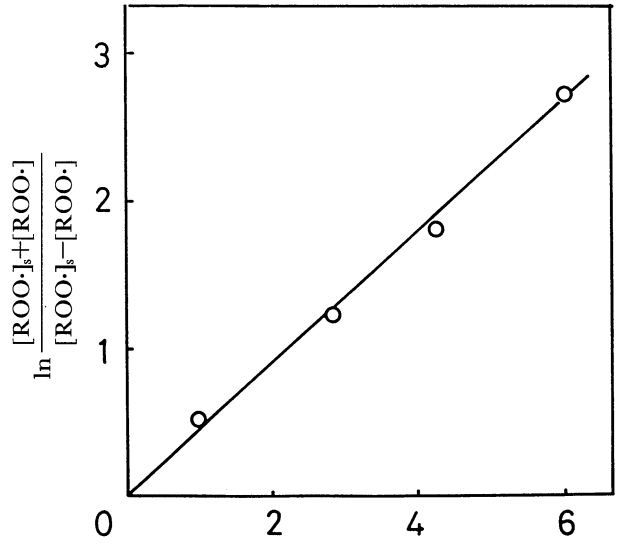


Fig. 4. Plot of $\ln\{([ROO\cdot]_s + [ROO\cdot])/([ROO\cdot]_s - [ROO\cdot])\}$ against ozone-oxidation time.

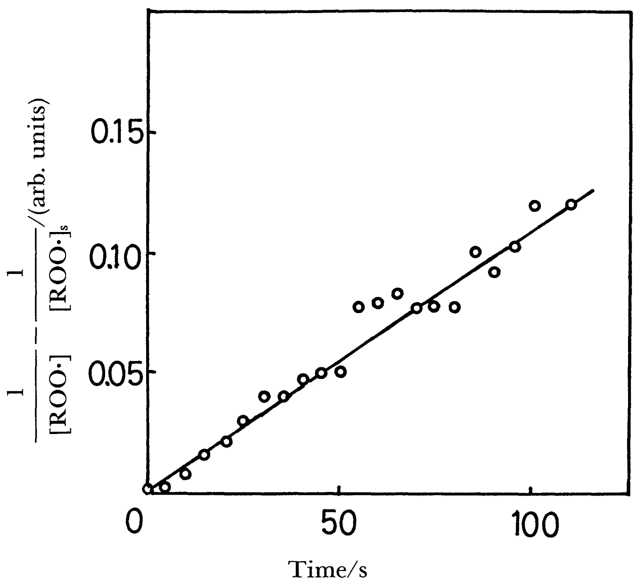


Fig. 5. Plot of 1/[ROO·]−1/[ROO·]$_s$ against time after the ozone-stop.

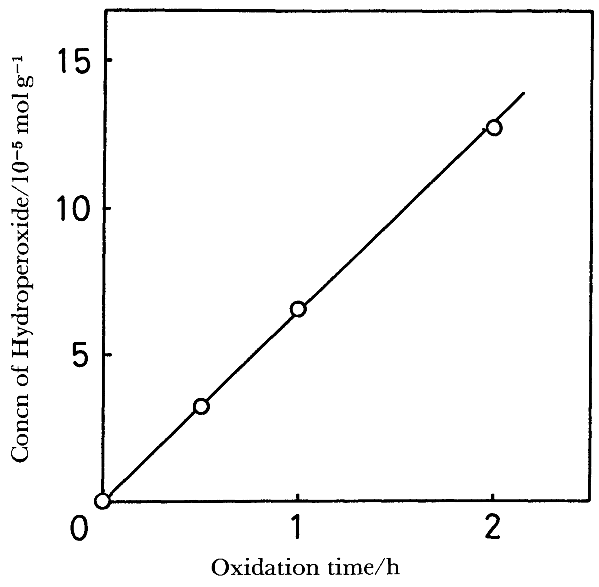


Fig. 6. Relationship between oxidation time and concentration of hydroperoxide in polyethylene oxidized with ozone.

indicative of the validity of Eqs. 12 or 13.

After stopping the ozone flow, the decomposition of ROO· can be expressed by Eq. 10, giving

$$\frac{1}{[\mathrm{ROO}\cdot]}-\frac{1}{[\mathrm{ROO}\cdot]_s}=k_4t. \qquad (15)$$

Using this equation, the decay process is plotted in Fig. 5, which also exhibits a linear time dependence of 1/[ROO·]−1/[ROO·]$_s$, supporting Eq. 15.

Products of Hydroperoxide and Ketone. In order to obtain more evidence for the ozone-oxidation mechanism we measured the amounts of products, such as hydroperoxide and ketone, depending on the ozone-oxidation time. From Eq. 8,

$$\frac{\mathrm{d[ROOH]}}{\mathrm{d}t}=k_2[\mathrm{ROO}\cdot][\mathrm{RH}]. \qquad (16)$$

Here, we use the saturated value, [ROO·]$_s$, for [ROO·] in the case of a longer oxidation time than 10 min. Then, [ROOH] becomes proportional to time:

$$\begin{aligned}[\mathrm{ROOH}]&=k_2[\mathrm{ROO}\cdot][\mathrm{RH}]t\\ &=k_2k_1^{1/2}k_4^{-1/2}[\mathrm{RH}]^{3/2}[\mathrm{O_3}]^{1/2}t. \qquad (17)\end{aligned}$$

The iodometry disclosed the content of hydroperoxide, as shown in Fig. 6.[11] It is concluded that hydroperoxide is increasingly yielded with the oxidation time, as is predicted by Eq. 8. This is compatible with reactions (1)—(4).

One of the inert products in reaction (5), the ketone, can be monitored from the IR spectra (Fig. 2). From Eq. 10,

$$\frac{\mathrm{d[C{=}O]}}{\mathrm{d}t}=k_4[\mathrm{ROO}\cdot]^2. \qquad (18)$$

Here, we again discuss the process after the saturation of ROO·; Eq. 18 then becomes

$$\frac{\mathrm{d[C{=}O]}}{\mathrm{d}t}=k_4[\mathrm{ROO}\cdot]_s^2. \qquad (19)$$

Since [ROO·]$_s$ can be replaced by $(Ik_4)^{1/2}$ from Eq. 14 we obtain

$$[\mathrm{C{=}O}]=It. \qquad (20)$$

The optical density of the C=O groups in the IR spectra for the various oxidized polyethylenes again shows a linear relation with the oxidation time, as in Fig. 3, indicating the decomposition process of ROO·, like Eqs. 5 or 10.

In this paper concerning the ozone oxidation of polyethylene we pursued the time-dependent radical species ROO· by ESR spectroscopy; the influence of the oxidation time upon such products as hydroperoxide and ketone were clarified by iodometry and IR spectroscopy, respectively. The radical evolution in the initial stage and the radical decay after stopping ozone flow were kinetically analyzed on the basis of several assumptions, affording supporting evidence concerning the reaction mechanism involved in reactions (1)—(5).

The final product, hydroperoxide, which is useful for graft-copolymerization, has a reasonable linear dependence on the oxidation time; the inert product, the ketone, which arises from the decomposition of ROO·, shows the same dependence on the oxidation time. These two findings also support the proposed oxidation mechanism.

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14) In the present rate analyses we assumed a constant ozone concentration $[O_3]$ and vast excess of RH.

15) In the case of $k_3 \gg k_2$ this assumption may be plausible. Even if this is not the case, in the steady state approximation about R·, [R·] is related to [ROO·] so that the ESR intensity due to R· and ROO· is eventually proportional to [ROO·].