

## Radiation-Induced Degradation of Poly(Ethylene Oxide) in the Atmosphere of Chlorine Compounds

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The effects of various kinds of chlorine compounds on the  $\gamma$ -ray radiation-induced degradation of poly(ethylene oxide) was studied. The decrease in the molecular weight of the PEO irradiated was accelerated by chlorine compounds. G value for chain scission of the polymer (Gs) was 20 in air, while 50 in  $\text{CCl}_4$ . Various types of carbonyl bands were observed in the IR spectra of the PEO irradiated in air. And by mass spectral measurement,  $\text{CH}_3\text{CHO}$  was detected in the gas evolved under the irradiation in air. While, by gas chromatographic analysis,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CHO}$  and  $\text{HCHO}$  were found to evolve under the irradiation in the atmosphere of  $\text{CCl}_4$ , and  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CHO}$  and  $\text{HCHO}$  were formed in the irradiation in  $\text{CHCl}_3$ . On the basis of these results, degradation mechanism of PEO by  $\gamma$ -ray irradiation was discussed.

### INTRODUCTION

It is well known that poly(ethylene oxide) (PEO) can be easily degraded by exposure to high energy irradiation.<sup>1)</sup> And the radiation-induced degradation of PEO have already been realized with industrial scale as a method of modifying the molecular weight of the high polymer of PEO.

The purpose of the report is to study the acceleration of the degradation of PEO. The effects of various kinds of chlorine compounds on  $\gamma$ -ray radiation-induced degradation of PEO were studied. Changes in molecular weight and chemical structure of the irradiated PEO have been measured. And the determination of the gases evolved under the irradiation in the atmosphere of chlorine compounds have also been made.

On the basis of these results, degradation mechanism of PEO by  $\gamma$ -ray irradiation in the atmosphere of chlorine compounds was discussed.

### EXPERIMENTAL

PEO powder and halogenated methane derivatives were used commercially available materials. Irradiation in the atmosphere of various kinds of chlorine compounds was carried out as follows; PEO powder (approximately 1 gram) was placed in a glass ampule of 30 ml volume. After sufficient evacuation, chlorine compounds were introduced to the ampules. The ampule was irradiated by  $\gamma$ -ray from a  $^{60}\text{Co}$  source with the dose rate of 0.1 Mrad/hr at room temperature.

Viscosity of PEO in 0.1 % aqueous solution was measured by using a Ubbelohde-type viscometer at 45°C. Molecular weight was calculated from the relation;

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$[\eta] = 6.9 \times 10^{-5} \bar{M}_v^{0.81}$ .<sup>2)</sup> PEO film was made by casting method (thickness 0.05 mm). IR spectra of PEO film were obtained on a Nippon-Bunko model DS-403G infrared spectrophotometer. The determination of gases evolved by  $\gamma$ -ray irradiation were made by using a Shimadzu model GC-4A gas chromatography and a Nippon-Denshi model 01-SG mass spectrometer.

As light source for ultraviolet (UV) ray irradiation apparatus, 1.2 KW high pressure mercury lamp was used. The sample was placed at 15 cm distance from UV lamp.

## RESULTS AND DISCUSSION

### $\gamma$ -Ray Irradiation of PEO in the Presence of Air

The relation between irradiation dose and molecular weight of PEO irradiated in air was shown in Fig. 1. The molecular weight remarkably decreased with

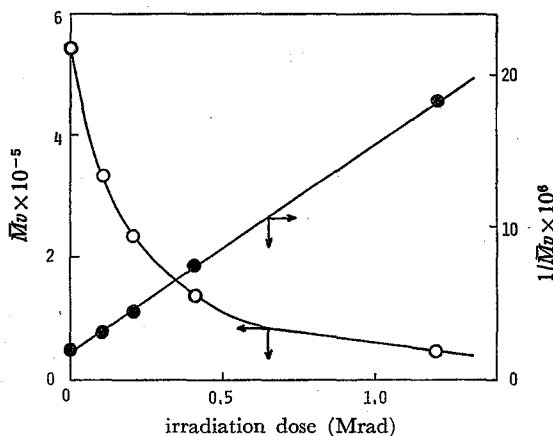


Fig. 1 Effect of irradiation dose on  $\bar{M}_v$  and  $1/\bar{M}_v$  of PEO by  $\gamma$ -ray irradiation

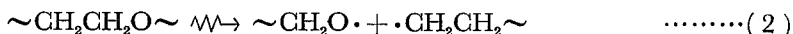
the increase in irradiation dose. Further, Fig. 1 also showed that the plot of  $\bar{M}_v$  against irradiation dose gave a straight line. With the use of this relation, 20 of G value for chain scission of the polymer (Gs) was calculated from the equation<sup>3)</sup>;

$$G_s = \frac{0.96 \times g(a)}{R} \left( \frac{1}{\bar{M}_v} - \frac{1}{(\bar{M}_v)_0} \right)$$

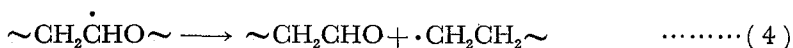
where  $g(a)$  is the ratio of viscosity average molecular weight ( $\bar{M}_v$ ) to number average molecular weight ( $\bar{M}_n$ ) of the polymer, when  $a$  is 0.81,  $g(a)$  is 1.92,<sup>4)</sup>  $R$ ; irradiation dose,  $(\bar{M}_v)_0$ ; molecular weight of the polymer before irradiation.

This Gs value for PEO was much higher than that of the other polymer (for example, Gs for PTFE was 3). In order to explain the higher Gs value, a following mechanism for the degradation can be considered. The initiation reactions of the degradation can be divided into three types such as main chain scission of C-C (reaction 1) and C-O (reaction 2), and chain side scission of C-H (reaction 3).

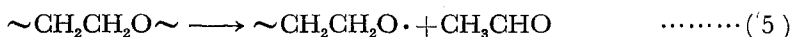
Radiation-Induced Degradation of poly(Ethylene Oxide)



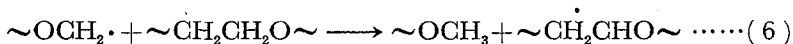
A chain side radical formed by reaction (3) is so unstable that main chain scission occurs, and produces two kinds of polymer chain having an aldehyde end and an alkyl end radical (reaction 4).



A polymer with alkoxy end radical formed by reaction (2) depropagates (zippering) and produces acetaldehyde (reaction 5).



A polymer with alkyl end radical formed by reaction (1) and (4) abstracts hydrogen atom from the polymer, and produces methoxy end polymer and a polymer having chain side radical (reaction 6).



Further, the polymer with chain side alkyl radical, which was formed by reaction (6), brings about repeatedly main chain scission reaction (4).

**γ-Ray Irradiation of PEO in Various Kinds of Chlorine Compounds**

Table I shows that changes in molecular weight of PEO irradiated in vacuum or in the atmosphere of various kinds of chlorine compounds and G value for chain

Table I. Changes in Molecular Weight and G Value for Chain Scission of PEO by γ-ray Irradiation

atmosphere	Mv × 10 <sup>-5</sup>	Gs
non-irradiated	5.42	—
air	1.33	20.0
vacuum		gel formation
CH <sub>2</sub> Cl <sub>2</sub>	1.45	19.5
CHCl <sub>3</sub>	1.04	27.8
CCl <sub>4</sub>	0.63	50.0
BrCCl <sub>3</sub>	0.55	57.4

irradiation dose 0.4 Mrad

scission (Gs). In the irradiation in vacuum, cross linking of the polymer took place. While, the molecular weight of PEO irradiated in various kinds of chlorine compounds remarkably decreased without gel formation. Gs for PEO irradiated in the atmosphere of chlorine compounds increased in the following order; CH<sub>2</sub>Cl<sub>2</sub> < CHCl<sub>3</sub> < CCl<sub>4</sub> < BrCCl<sub>3</sub>. And Gs in CHCl<sub>3</sub> was 1.4 times as high as that in air, CCl<sub>4</sub> was 2.5 times and BrCCl<sub>3</sub> 2.9 times.

A chain mechanism for the acceleration effect of chlorine compounds on degradation can be considered as follows; chlorine compounds reacts with the polymer radical, which was formed by reaction (1) and (3), and formed chlorine compounds radical. This chlorine compounds radical thus produced abstracts hydrogen atom from the polymer, and produces a polymer chain side alkyl radical, which leads to main chain scission reaction (4). Chlorine compounds is considered to act as a chain transfer reagent to form polymer with chain side radical and lead to the increase in Gs value.

### Changes in IR Spectra of PEO by $\gamma$ -Ray Irradiation

Changes in IR spectra of PEO irradiated in air at 10 Mrad was shown in Fig. 2. Various kinds of carbonyl bands were observed at 1750~1700  $\text{cm}^{-1}$ , and the band at 1715  $\text{cm}^{-1}$  was the strongest absorption one. The band at 1750  $\text{cm}^{-1}$  has been assigned to ester type carbonyl, 1733  $\text{cm}^{-1}$  to aldehyde, 1721  $\text{cm}^{-1}$  to ketone and 1715  $\text{cm}^{-1}$  to carboxyl. A hydroxyl group was also observed at 3400  $\text{cm}^{-1}$ . The absorption of these carbonyl groups increased with the irradiation dose.

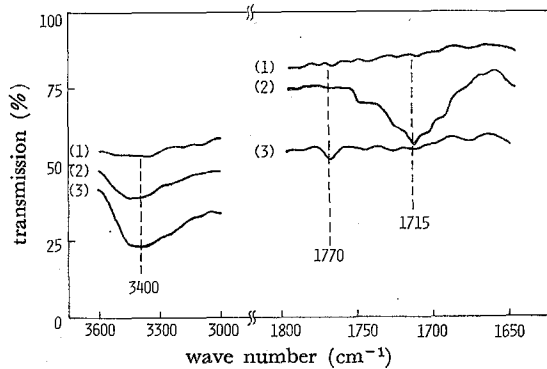
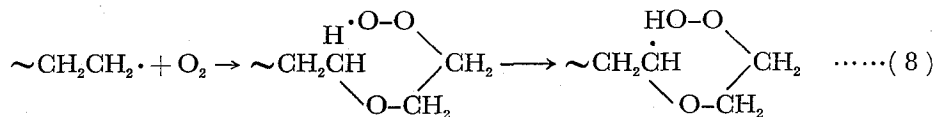
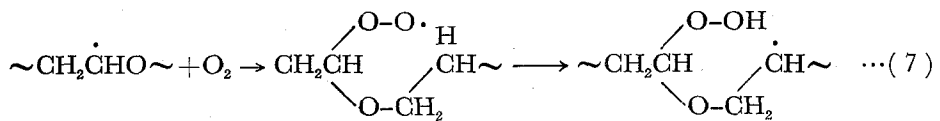
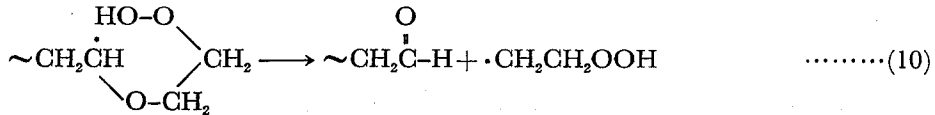
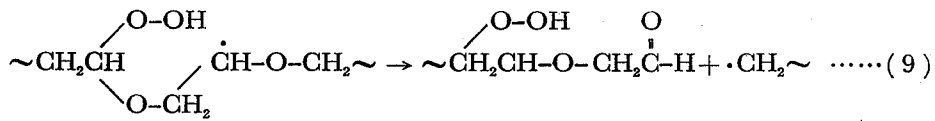


Fig. 2 IR spectra of  $\gamma$ -ray irradiated PEO  
 (1) non-irrad. (2) 10 Mrad irrad. in air  
 (3) 10 Mrad irrad. in  $\text{CCl}_4$

On the basis of these results, oxidative mechanism for the degradation in the presence of air can be considered as follows; the polymer radical formed by reaction (1) and (3) reacts with oxygen and formed a polymer with chain side and chain end peroxy radical. These peroxy radicals abstract intramolecularly a hydrogen atom from the polymer, and produces a polymer with chain side and chain end hydroperoxide and chain side alkyl radical (reaction 7 and 8).



These resulted polymer radicals are considered to lead to main chain scission as follows (reaction 9 and 10);



On the other hand, there was little change in IR spectra of PEO irradiated in the presence of  $\text{CCl}_4$  at 10 Mrad in the region of the carbonyl, but the band at  $1770\text{ cm}^{-1}$ , which may be attributed to acid chloride was observed. From these results, the degradation of PEO irradiated in the atmosphere of  $\text{CCl}_4$  is considered to take place without oxidation.

### The Determination of Gases Evolved by Mass Spectral and Gas Chromatographic Measurement

Mass spectra of the gases evolved under the irradiation of PEO in vacuum at 10 Mrad was shown in Table II. Major product detected at  $m/e=44$  was assigned to  $\text{CH}_3\text{CHO}$ , and the others were various kinds of oxygen compounds. From these results, it is concluded that depropagation (zippering) reaction (5) occurred and produced acetaldehyde.

Table II. Mass Spectra of the Gases Evolved under the Irradiation in Vacuum of PEO

m/e	assignment	relative
28	CO	22
29	CHO	13
42	$\text{C}_2\text{H}_2\text{O}$	12
44	$\text{C}_2\text{H}_4\text{O}$ , $\text{CO}_2$	100
59	$\text{C}_2\text{H}_3\text{O}_2$	54

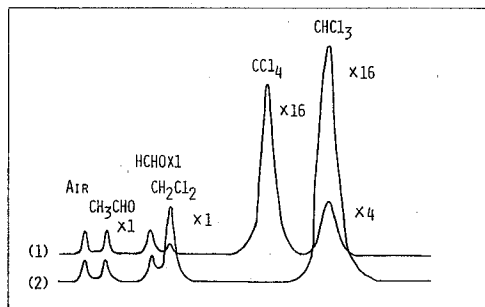
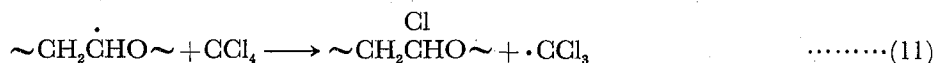


Fig. 3 Gas chromatograph of gases evolved by  $\gamma$ -ray irradiation of PEO in  $\text{CCl}_4$  or in  $\text{CHCl}_3$   
 (1) 2.5 Mrad irradiation in  $\text{CCl}_4$  (2) 2.5 Mrad irradiation in  $\text{CHCl}_3$

By gas chromatographic analysis,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CHO}$  and  $\text{HCHO}$  were detected in the gases evolved under the irradiation in the atmosphere of  $\text{CCl}_4$  (Fig. 3). From the results, a following mechanism for the degradation in  $\text{CCl}_4$  can be considered. The polymer radical, which was formed by  $\gamma$ -ray irradiation (reaction 3) reacted with  $\text{CCl}_4$  and produced  $\cdot\text{CCl}_3$  radical (reaction 11).

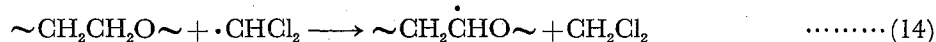


The  $\cdot\text{CCl}_3$  radical abstracted hydrogen atom from the polymer, and produced  $\text{CHCl}_3$  and a polymer having chain side radical (reaction 12).



The formation of  $\text{CH}_3\text{CHO}$  and  $\text{HCHO}$  showed that the reaction (5) occurred.

While,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CHO}$  and  $\text{HCHO}$  were formed in the case of  $\text{CHCl}_3$ . The polymer radical, which was formed by reaction (3) reacted with  $\text{CHCl}_3$  and formed  $\cdot\text{CHCl}_2$  radical (reaction 13). This  $\cdot\text{CHCl}_2$  radical abstracted hydrogen atom from the polymer and produced  $\text{CH}_2\text{Cl}_2$  (reaction 14).



### UV Irradiation of PEO in Various Kinds of Chlorine Compounds

Changes in molecular weight and  $(\bar{M}_0/\bar{M}) - 1$  were shown in Table III. In the UV-irradiation in air, degradation took place, but cross linking in vacuum. While, the decrease in the molecular weight of PEO UV-irradiated and the increase in the value of  $(\bar{M}_0/\bar{M}) - 1$  was accelerated by various kinds of chlorine compounds.

In the UV-irradiation in the atmosphere of chloroacetone ( $\text{CH}_3\text{COCH}_2\text{Cl}$ ) containing  $\text{C}=\text{O}$  structure, which is able to absorb UV light, the molecular weight remarkably decreased and liquid polymer was obtained. Further, in the case of  $\text{Cl}_2$ , the degradation occurred rapidly and the value of  $(\bar{M}_0/\bar{M}) - 1$  was the largest

Table III. Changes in Molecular Weight of PEO UV-irradiated in the Atmosphere of Chlorine Compounds

atmosphere	$M_v \times 10^{-5}$	$(M_0/M) - 1$
non-irrad.	2.34	—
air	1.32	0.77
vacuum		
$\text{CCl}_4$	0.33	cross linking 6.07
$\text{CH}_3\text{COCH}_2\text{Cl}$	0.033	69.7
$\text{CCl}_2=\text{CCl}_2$	0.40	4.88
$\text{Cl}_2^*$	0.004	522.5
$\text{Cl}_2\text{-O}_2^*$	0.055	41.5

irradiation time 4 hr (\* 0.5 hr)

of all the irradiation.

Changes in IR spectra of PEO UV-irradiated in air or in  $\text{Cl}_2$  were shown in Fig. 4. Various kinds of carbonyl were observed under the UV-irradiation in air and oxidative degradation took place. On the other hands, in the case of  $\text{Cl}_2$ , the band at  $1760\text{ cm}^{-1}$  was observed, which may be assigned to acid chloride

$$\begin{array}{c} \text{O} \\ || \\ (-\text{C}-\text{Cl}) \end{array}$$
 and the C-Cl band at  $800\sim 600\text{ cm}^{-1}$  was also observed.

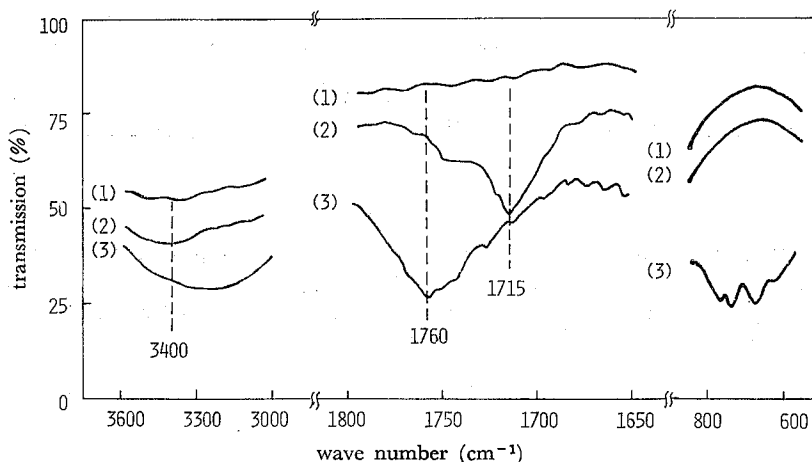


Fig. 4 IR spectra of UV-irradiated PEO  
(1) non-irrad. (2) 96 hr irrad. in air (3) 0.5 hr irrad. in  $\text{Cl}_2$ .

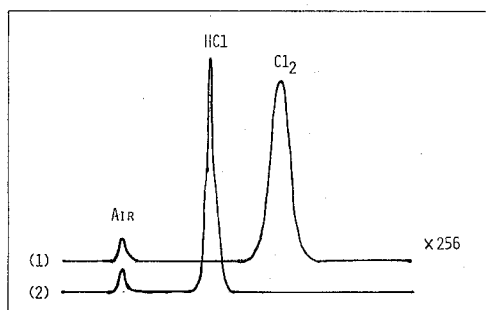
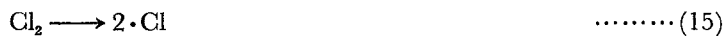
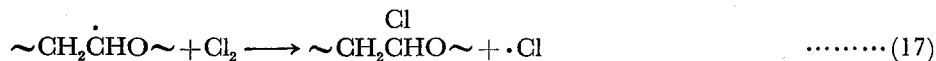


Fig. 5 Gas chromatograph of the gas evolved by UV-irradiation of PEO in the presence of  $\text{Cl}_2$   
(1) non-irrad. (2) UV-irrad. for 3 min.

Figure 5 showed that HCl was detected by gas chromatographic analysis in the gas evolved under the UV-irradiation in the presence of  $\text{Cl}_2$ . On the basis of these results, a chain mechanism for the degradation of PEO UV-irradiated in the presence of  $\text{Cl}_2$  can be considered as follows;  $\text{Cl}_2$  decomposes into two chlorine radicals by UV-irradiation (reaction 15). Chlorine radical abstracts hydrogen atom from the polymer, and produces HCl and a polymer having chain side radical (reaction 16).



This chain side radical reacts with  $\text{Cl}_2$ , and produces the chlorinated PEO and chlorine radical (reaction 17). Further, chlorine radical formed by reaction (17) brings about the reaction (16) again.



#### ACKNOWLEDGMENT

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