

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

Tsutomu KAGIYA, Norio YOKOYAMA, and Katsuo TAKEMOTO*

Received December 8, 1975

The effects of various kinds of chlorine compounds on the γ -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 CCl_4 . Various types of carbonyl bands were observed in the IR spectra of the PEO irradiated in air. And by mass spectral measurement, CH_3CHO was detected in the gas evolved under the irradiation in air. While, by gas chromatographic analysis, CHCl_3 , CH_2Cl_2 , CH_3CHO and HCHO were found to evolve under the irradiation in the atmosphere of CCl_4 , and CH_2Cl_2 , CH_3CHO and HCHO were formed in the irradiation in CHCl_3 . On the basis of these results, degradation mechanism of PEO by γ -ray irradiation was discussed.

INTRODUCTION

It is well known that poly(ethylene oxide) (PEO) can be easily degraded by exposure to high energy irradiation.¹⁾ 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 γ -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 γ -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 γ -ray from a ^{60}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;

* 鍵谷 勤, 横山 憲夫, 武本 勝雄: Department of Hydrocarbon Chemistry, Kyoto University, Kyoto, Japan.

$[\eta] = 6.9 \times 10^{-5} \bar{M}_v^{0.81}$.²⁾ 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 γ -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

γ -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

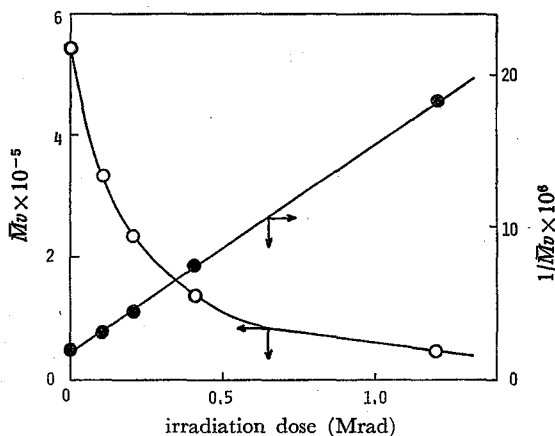


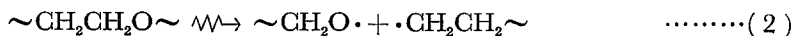
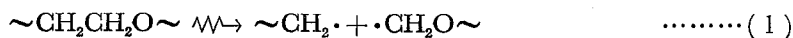
Fig. 1 Effect of irradiation dose on $\bar{M}_v$ and $1/\bar{M}_v$ of PEO by γ -ray irradiation

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 equation³⁾;

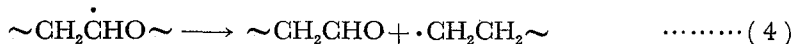
$$Gs = \frac{0.96 \times g(a)}{R} \left(\frac{1}{\bar{M}_v} - \frac{1}{(\bar{M}_v)_0} \right)$$

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 1.92,⁴⁾ R ; irradiation dose, $(\bar{M}_v)_0$; molecular weight of the polymer before irradiation.

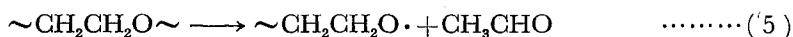
This Gs value for PEO was much higher than that of the other polymer (for example, Gs for PTFE was 3). In order to explain the higher Gs value, a following mechanism for the degradation can be considered. The initiation reactions of the degradation can be divided into three types such as main chain scission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



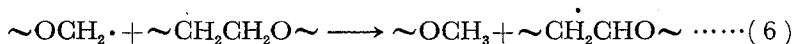
A chain side radical formed by reaction (3) is so unstable that main chain scission occurs, and produces two kinds of polymer chain having an aldehyde end and an alkyl end radical (reaction 4).



A polymer with alkoxyl 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	$M_v \times 10^{-5}$	Gs
non-irradiated	5.42	—
air	1.33	20.0
vacuum	gel formation	
CH_2Cl_2	1.45	19.5
CHCl_3	1.04	27.8
CCl_4	0.63	50.0
BrCCl_3	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; $\text{CH}_2\text{Cl}_2 < \text{CHCl}_3 < \text{CCl}_4 < \text{BrCCl}_3$. And Gs in CHCl_3 was 1.4 times as high as that in air, CCl_4 was 2.5 times and BrCCl_3 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 γ -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 $1750\sim 1700\text{ cm}^{-1}$, and the band at 1715 cm^{-1} was the strongest absorption one. The band at 1750 cm^{-1} has been assigned to ester type carbonyl, 1733 cm^{-1} to aldehyde, 1721 cm^{-1} to ketone and 1715 cm^{-1} to carboxyl. A hydroxyl group was also observed at 3400 cm^{-1} . The absorption of these carbonyl groups increased with the irradiation dose.

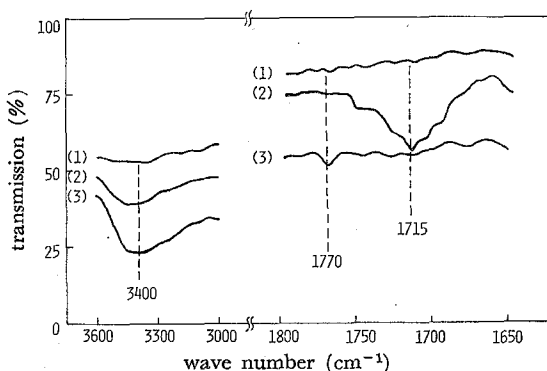
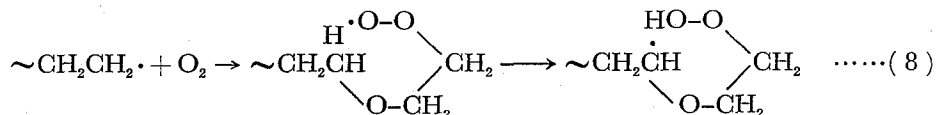
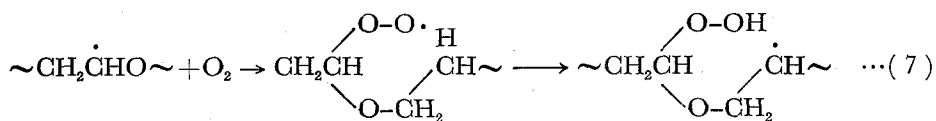
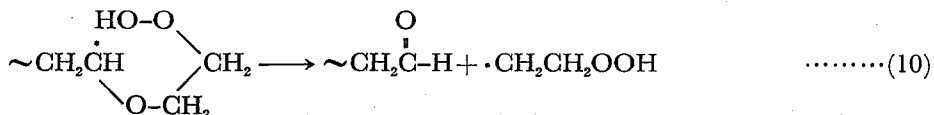
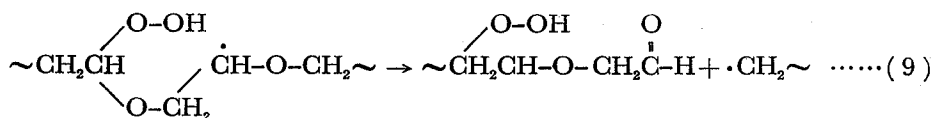


Fig. 2 IR spectra of γ -ray irradiated PEO
(1) non-irrad. (2) 10 Mrad irrad. in air
(3) 10 Mrad irrad. in CCl_4

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 CCl_4 at 10 Mrad in the region of the carbonyl, but the band at 1770 cm^{-1} , which may be attributed to acid chloride was observed. From these results, the degradation of PEO irradiated in the atmosphere of 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 CH_3CHO , 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	$\text{C}_2\text{H}_4\text{O}$, CO_2	100
59	$\text{C}_2\text{H}_3\text{O}_2$	54

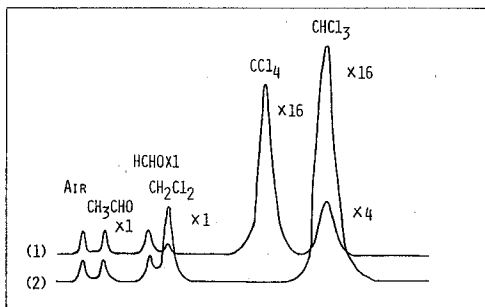
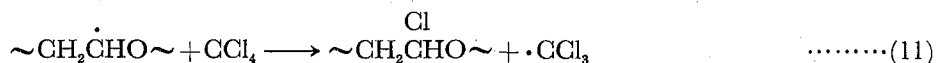


Fig. 3 Gas chromatograph of gases evolved by γ -ray irradiation of PEO in CCl_4 or in CHCl_3
(1) 2.5 Mrad irr. in CCl_4 (2) 2.5 Mrad irr. in CHCl_3

By gas chromatographic analysis, CHCl_3 , CH_2Cl_2 , CH_3CHO and HCHO were detected in the gases evolved under the irradiation in the atmosphere of CCl_4 (Fig. 3). From the results, a following mechanism for the degradation in CCl_4 can be considered. The polymer radical, which was formed by γ -ray irradiation (reaction 3) reacted with 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 CHCl_3 and a polymer having chain side radical (reaction 12).



The formation of CH_3CHO and HCHO showed that the reaction (5) occurred.

While, CH_2Cl_2 , CH_3CHO and HCHO were formed in the case of CHCl_3 . The polymer radical, which was formed by reaction (3) reacted with 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 CH_2Cl_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 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	$\text{Mv} \times 10^{-5}$	$(\text{Mo}/\text{M}) - 1$
non-irrad.	2.34	—
air	1.32	0.77
vacuum		
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
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 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 Cl_2 , the band at 1760 cm^{-1} was observed, which may be assigned to acid chloride



and the C-Cl band at $800\sim 600\text{ cm}^{-1}$ was also observed.

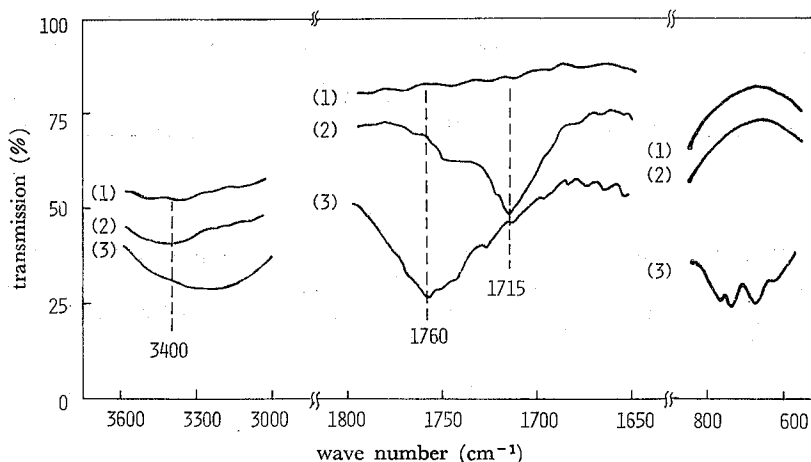


Fig. 4 IR spectra of UV-irradiated PEO
(1) non-irrad. (2) 96 hr irrad. in air (3) 0.5 hr irrad. in Cl_2 .

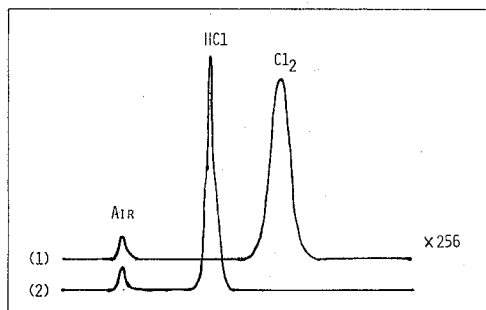
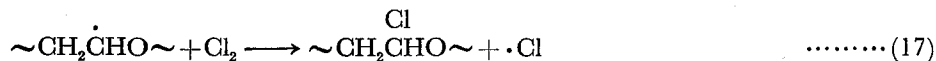


Fig. 5 Gas chromatograph of the gas evolved by UV-irradiation of PEO in the presence of Cl_2
(1) non-irrad. (2) UV-irrad. for 3 min.

Figure 5 showed that HCl was detected by gas chromatographic analysis in the gas evolved under the UV-irradiation in the presence of Cl_2 . On the basis of these results, a chain mechanism for the degradation of PEO UV-irradiated in the presence of Cl_2 can be considered as follows; 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 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

The authors wish to thank the Institute for Chemical Research of Kyoto University for permitting us to use the ^{60}Co γ -ray irradiation apparatus.

REFERENCES

- (1) P. A. King, "Irradiation of Polymers", American Chemical Society, (1967) p. 113.
- (2) F. E. Baily, *et al.*, *J. Apply Polymer Sci.*, **1**, 56 (1959).
- (3) A. Charlesby, "Radiation Effects in Materials", Pergamon Press, (1960) p. 137.
- (4) A. Charlesby, *ibid.*, p. 132.