

## **Radiation-Induced Sulfoxidation and Sulfochlorination of Powdery Polyethylene Produced by Radiation Process**

KUNIO KONISHI,\* KOUICHI YAMAGUCHI, and MASAOKI  
TAKEHISA, *Japan Atomic Energy Research Institute, Takasaki Radiation  
Chemistry Research Establishment, Takasaki, Gunma, Japan 370-12*

### **Synopsis**

Gamma radiation-induced sulfoxidation and sulfochlorination of the high specific surface area powdery polyethylene which was produced by radiation-induced polymerization of ethylene at room temperature were studied and were compared with sulfonation by fuming sulfuric acid. In these reactions the effect of surface area on the chemical reactivity was observed to a certain degree. In gamma radiation-induced sulfochlorination, it was elucidated that as the reaction proceeds, the ratio of  $-\text{SO}_2\text{Cl}$  to  $-\text{Cl}$  introduced into the polymer decreases, which can be explained by the difference between the diffusibilities of  $\text{SO}_2$  and  $\text{Cl}_2$  molecules through sulfochlorinated and/or chlorinated polyethylene. Crystallinity, melting temperature, and density of the sulfochlorinated polymers were measured and are discussed.

### **INTRODUCTION**

During the past decade, several studies have been made on  $^{60}\text{Co}$  gamma radiation-induced sulfoxidation and sulfochlorination.

For example, gamma radiation-induced sulfoxidation of polyethylene is described in a U.S.S.R. patent<sup>1</sup> which claims treatment of carbon tetrachloride solution or suspension of polyethylene with  $\text{SO}_2$  and  $\text{O}_2$ . Solution sulfochlorination of polyethylene induced by  $^{60}\text{Co}$  gamma radiation was reported by Dzhagatspanyan and co-workers.<sup>2,3</sup>

Use of gamma radiation in sulfochlorination of polyethylene in a fluidized bed is claimed in a U.S.S.R. patent by the same authors.<sup>4</sup> Wuckel and co-workers<sup>5</sup> studied the radiation-induced sulfochlorination of polyethylene in suspension or in the solid phase. These studies were performed with conventional polyethylenes.

The powdery polyethylene which is obtained by radiation-induced polymerization of ethylene at temperatures between  $30^\circ$  and  $90^\circ\text{C}$  has a very large specific surface area (e.g.,  $20\text{--}130\text{ m}^2/\text{g}$ ) compared with commercially available polyethylene powders ( $0.1\text{--}6\text{ m}^2/\text{g}$ ). Other proper-

\* Present address: Japan Catalytic Chem. Co. Ltd., Suita, Osaka, Japan 564.

ties, for example, density, number of chain branches, and degree of crystallinity, generally take intermediate values between high-pressure and low-pressure polyethylene. The large specific surface area is one of the characteristic features of the powdery polyethylene produced by the radiation process.

It is therefore expected to exhibit higher chemical reactivity in solid form compared with conventional polyethylene powders.

The reactivity of these polyethylene powders was examined as to sulf-oxidation and sulfochlorination induced by gamma radiation and sulfonation by chemicals.

## EXPERIMENTAL

### Apparatus

The reactor was a tubular glass vessel, with an inner diameter of 54 mm and about 300 mm long, equipped with a stirrer, a thermocouple well, a gas inlet tube, and a gas outlet tube. Flow rates of SO<sub>2</sub> and O<sub>2</sub> (or Cl<sub>2</sub>) were measured by rotameters.

Irradiations were performed in the cave-type irradiation facilities of the Takasaki Radiation Chemistry Research Establishment, using either a source which contained approximately 100,000 curies of cobalt 60 or a source containing approximately 5,000 curies of cesium 137.

### Material

Pure-grade sulfur dioxide in a cylinder was obtained from Showa Denko Company and was used as received. The chlorine was of commercial grade. The carbon tetrachloride was reagent-grade material.

The polyethylene powders used are described in Table I.

TABLE I  
Description of Polyethylene Powder Used for Experiments

Polyethylene trade name	Process of production
Takathene-P	gamma radiation-induced bulk polymerization at 30–90°C; polymer is obtained as powder or granule <sup>6</sup>
Takathene-CW	gamma radiation-induced polymerization in an alcohol medium at 30°C; polymer is obtained as a fine powder. <sup>7</sup>
Hizex 5000P, LPPE	Ziegler process (produced by Mitsui Petrochemical Co.)
Sholex 5030, MPPE	Philips process (produced by Showa Denko Co.)
Yukalon PV-30, HPPE	BASF process (produced by Mitsubishi Petrochemical Co.)
Flowthene UF-20, HPPE	ICI-processed polyethylene was reduced to ultra-fine powder by Kothylen process (produced by Seitestu Chemical Co.)

### Procedure

The glass vessel was charged with 5 g polyethylene powder and 230 or 250 ml carbon tetrachloride. The outlet tube was connected with two washing bottles containing water and 20% aqueous NaOH solution. Oxygen in the reaction system was purged by flushing with pure nitrogen for about 10 min prior to irradiation. As soon as the radiation source was lifted into the cave, SO<sub>2</sub> and O<sub>2</sub> (or Cl<sub>2</sub>) were fed into the reaction vessel at constant flow rates. Reactions were carried out at room temperature. After irradiation, the reaction products were flushed with nitrogen for about 10 min, then filtered with a glass filter. No polymer was detected in the filtrate. The polymer was rinsed with methanol or *n*-hexane and dried in vacuo at 50°C. In the case of sulfoxidation, the product polymer was extracted with water containing a small amount of ethanol to remove sulfuric acid.

The titration of the sulfonic acid group was carried out by the usual procedure for ion-exchange resins.<sup>8</sup> Sulfur and total chlorine contents were determined by the Schoeniger combustion method.<sup>9</sup>

In addition, sulfonation by 20% fuming sulfuric acid or by chlorosulfonic acid was attempted. These experiments were performed in Erlenmeyer flasks. The reaction mixtures were allowed to stand at room temperature.

Polymer evaluations were carried out on the following items:

Specific surface area of the original polyethylene powder was measured by means of the Shibata Kagaku BET apparatus Model 600, using nitrogen gas at liquid nitrogen temperature.

Density of the polymer was determined in a gradient tube of carbon tetrachloride-methanol mixture at 24°C. The infrared absorption spectrum was taken with a Nippon-Bunko Model DS 301 infrared spectrophotometer using NaCl optics. For infrared analysis and density measurement, a specimen film of ca. 0.2-mm thickness was prepared by hot pressing the powder at 150°C and quenching at room temperature.

Melting point was measured by a Rigaku Denki Model VKP-32 differential thermal analyzer. The x-ray diffraction was measured by a Rigaku Denki Geigerflex Model DC-2 x-ray diffractometer. The degree of crystallinity was determined by the method of Hendus and Schell.<sup>10</sup>

Gas permeability of chlorinated polyethylene was measured by high-vacuum gas transmission technique at the Industrial Products Research Institute (Tokyo, Japan).

## RESULTS AND DISCUSSION

### Radiation-Induced Sulfoxidation

The results of gamma radiation-induced sulfoxidation of various polyethylene powders are shown in Table II. Apparently, Takathene was more easily sulfoxidized than conventional polyethylene powders. But the

TABLE II  
Radiation-Initiated Sulfoxidation of Polyethylene Powder<sup>a</sup>

Polyethylene powder	Specific surface area, m <sup>2</sup> /g	Increase in weight, %	Sulfur, %	—SO <sub>3</sub> H calcd, meq/g	—SO <sub>3</sub> H titrated, meq/g
Takathene P-8	35	6.6	1.91	0.595	0.464
Takathene CW-21	60	6.4	1.97	0.615	0.362
Sholex 5030, MPPE	0.48	2.8	0.60	0.19	0.017
Sholex 5030, MPPE	1.4	2.2	0.62	0.24	0.020
Yukalon PV-30, HPPE	...	2.2	0.77	0.24	0.019
Hizex 5000P, LPPE	0.69	1.6	0.48	0.15	0.018

<sup>a</sup> Reaction conditions: polymer, 5.0 g; CCl<sub>4</sub>, 230 ml; SO<sub>2</sub>, 180 ml/min; O<sub>2</sub>, 90 ml/min; dose rate, 6 × 10<sup>6</sup> rad/hr; reaction time, 4 hr.

difference in reactivity is as large as the difference in specific surface area. The titration values for the —SO<sub>3</sub>H group are smaller than the values calculated from the sulfur contents (last two columns in Table II).

This tendency is more remarkable in the case of conventional polyethylene powders. The reason for this might be the poor wettability of such polyethylene powders containing a relatively small number of sulfonic acid groups.

#### Sulfonation by 20% Fuming Sulfuric Acid and Chlorosulfonic Acid

The results of sulfonation of various polyethylene powders by 20% fuming sulfuric acid are shown in Table III. In this case, the high-pressure

TABLE III  
Sulfonation of Polyethylene Powder by 20% Fuming Sulfuric Acid<sup>a</sup>

Polyethylene powder	Increase in weight, %	—SO <sub>3</sub> H titrated, meq/g	No. of chain branches per 1000 CH <sub>2</sub>
Yukalon PV-30, HPPE	24.0	0.647	ca. 20
Takathene CW-21	13.7	0.530	2.6
Takathene P-8	13.5	0.453	4.3
Sholex 5030, MPPE	8.3	0.332	ca. 1.5
Hizex 5000P, LPPE	4.8	0.121	ca. 1.0

<sup>a</sup> Reaction conditions: polymer, 5.0 g; 20% fuming sulfuric acid, 30 ml; temperature, room temperature; reaction time, 72 hr.

polyethylene is the most reactive one, and the effect of specific surface area is not observed.

The results of sulfonation by chlorosulfonic acid and the titration of sulfonic acid groups produced by hydrolysis are shown in Table IV. The results are similar to those of Table III. The effect of the specific surface area on reactivity is not found.

TABLE IV  
Sulfonation of Polyethylene Powder by Chlorosulfonic Acid<sup>a</sup>

Polyethylene powder	Increase in weight, %	—SO <sub>3</sub> H titrated, meq/g	No. of chain branches per 1000 C
Yukalon PV-30, HPPE	14.9	0.704	ca. 20
Takathene P-8	9.4	0.436	4.3
Sholex 5030, MPPE	6.9	0.323	ca. 1.5
Hizex 5000P, LPPE	4.3	0.155	ca. 1.0

<sup>a</sup> Reaction conditions: polymer, 5 g; chlorosulfonic acid, 30 ml; temperature, room temperature; time, 68 hr.

The reaction probably proceeds at the tertiary carbon atoms of polyethylene by ionic mechanism.<sup>11</sup> As is evident from Tables III and IV, the polymer reacts more easily as its chain branches increase in number.

### Sulfochlorination

The experimental conditions and results are summarized in Table V. Figure 1 shows the results of sulfochlorination of Takathene P-8. The rate of sulfochlorination decreases with time. But the rate of chlorination (a side reaction) is constant at least during 4 hr. Similar result are shown in Figure 2 for Takathene CW-28. The sulfonyl chloride group seems to be introduced mainly near the surface of the polyethylene powder. This might be due to the smaller diffusibility of sulfur dioxide molecules compared with chlorine molecules through the amorphous region of the polyethylene. The permeation or diffusion of sulfur dioxide and chlorine molecules through the polymer will be retarded as the sulfochlorination reaction proceeds. To elucidate the above hypothesis, diffusibility of sulfur dioxide and chlorine gases through polyethylene film of various degrees of chlorination was measured by the method described previously.

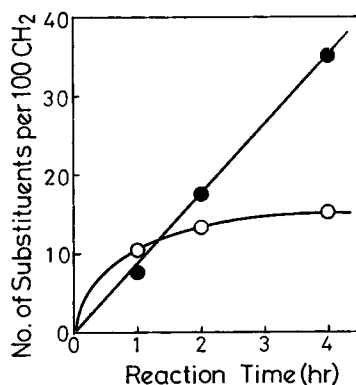


Fig. 1. Number of substituents vs. reaction time. Reaction conditions: polymer Takathene P-8, 5.0 g; CCl<sub>4</sub>, 250 ml; SO<sub>2</sub>, 94 ml/min; Cl<sub>2</sub>, 47 ml/min; dose rate,  $2.7 \times 10^4$  rad/hr; temperature, 31–25°C; (O) —SO<sub>2</sub>Cl; (●) —Cl.

TABLE V  
 Sulfochlorination of Polyethylene Powders<sup>a</sup>

Run no.	Trade name	Polyethylene powder, specific surface area, m <sup>2</sup> /g	Degree of crystallinity, %	Yield, g	S, %	Cl, %	-SO <sub>2</sub> Cl, g	-Cl, g	No. of -SO <sub>2</sub> Cl per 100 CH <sub>2</sub>	No. of -Cl per 100 CH <sub>2</sub>
41	Takathene P-2	22	67.3	12.0	10.0	39.0	3.72	3.28	9.2	25.8
42	Takathene P-8	35	63.5	13.8	11.5	42.2	4.92	3.88	13.8	31.2
44	Takathene P-8	35	58.7	14.61	11.6	43.7	5.26	4.35	14.8	35.7
43	Takathene P-12	47	61.9	11.8	10.4	38.8	3.8	3.0	10.7	23.7
10	Takathene CW-21		74	13.47	12.9	39.1	5.40	3.07	15.2	42.6
30	Takathene CW-20	69.7	73.4	11.04	12.8	33.5	4.39	1.65	12.3	13.0
31	Takathene CW-28	56.7	72.2	11.52	12.4	34.5	4.44	2.08	12.5	16.1
48	Takathene CW-24	37.2	72.6	11.5	11.5	34.9	4.1	2.4	11.5	18.9
27	Hizex 5000P			6.23	3.77	13.7	0.73	0.50	2.1	3.9
45	Hizex 5000P <sup>b</sup>	13.2	80.4	7.20	5.8	19.3	1.3	0.9	3.7	7.1
6	Sholex 5030	0.48		6.47	3.69	15.7	0.74	0.73	2.2	5.8
7	Sholex 5030 <sup>b</sup>	10.4	77.9	7.99	5.28	28.9	1.31	1.68	3.7	12.7
8	Sholex 5030	1.4		7.81	5.84	26.0	1.41	1.41	4.0	11.1
35	Flowthene UF-20	5.8	57.0	13.1	11.8	39.6	4.79	3.3	13.5	26.0
29	Yukalon PV-30			10.8	9.75	35.1	3.26	2.54	9.2	20.0
46	Yukalon PV-30 <sup>b</sup>	1.3	53.3	15.2	11.3	14.6	5.33	4.9	15.0	38.7
34	Yukalon PV-30 <sup>b</sup>		52.0	13.47	11.4	40.1	4.76	3.71	13.4	26.0

<sup>a</sup> Reaction conditions: polymer, 5 g, CCl<sub>4</sub>, 240 ml; SO<sub>2</sub>, 94 ml/min; Cl<sub>2</sub>, 47 ml/min; dose rate, 2.7 × 10<sup>4</sup> rad/hr; temperature, 13–25°C; time, 4 hr. <sup>b</sup> Powders obtained by recrystallization of commercially available powder (solvent, xylene; precipitant, methanol).

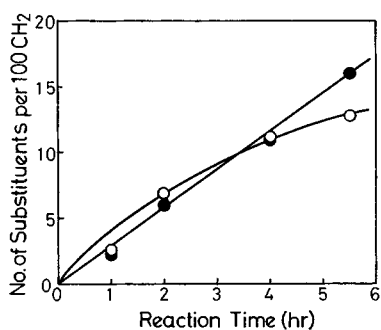


Fig. 2. Number of substituents vs. reaction time. Reaction conditions: polymer Takathene CW-28, 5.0 g; CCl<sub>4</sub>, 250 ml; SO<sub>2</sub>, 47 ml/min; Cl<sub>2</sub>, 24 ml/min; dose rate,  $2.7 \times 10^4$  rad/hr; temperature, 13–25°C; (O) –SO<sub>2</sub>Cl; (●) –Cl.

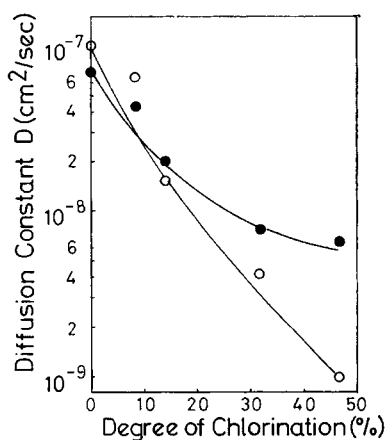


Fig. 3. Diffusion constant vs. degree of chlorination. Low-density polyethylene was chlorinated in acetic anhydride solvent at 60°C: (O) –SO<sub>2</sub>; (●) –Cl<sub>2</sub>, temperature, 23°C.

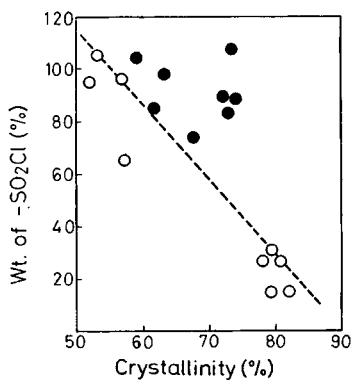


Fig. 4. Weight of sulfonylchloride vs. polymer crystallinity. Reaction conditions same as in Figures 1 and 2: (●) Takathene; (○) conventional polyethylene.

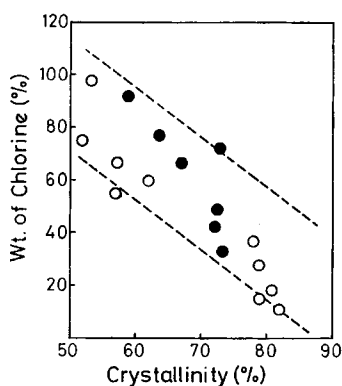


Fig. 5. Weight of chlorine vs. polymer crystallinity. Reaction conditions and symbols same as in Figure 4.

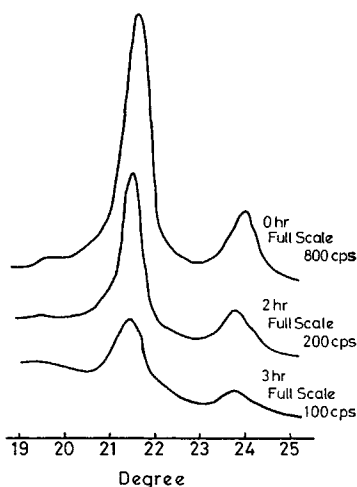


Fig. 6. Relation of x-ray diffraction intensity to reaction time.

Figure 3 shows the diffusion constants which were calculated from gas permeation measurement of  $\text{SO}_2$  and  $\text{Cl}_2$  through chlorinated, low-density polyethylene. Both the diffusion constants  $D$  of  $\text{SO}_2$  and  $\text{Cl}_2$  through chlorinated polyethylene decreased with increase in chlorine content. In the case of  $\text{SO}_2$  gas, the rate of diffusion decreases more markedly than in the case of  $\text{Cl}_2$  as the chlorine content of the polymer increases.

The results of sulfochlorination of various polyethylene powders are summarized in Figure 4. The ordinate indicates the percentage by weight of  $-\text{SO}_2\text{Cl}$  groups introduced into the original polyethylene. The abscissa shows the degree of crystallinity of polyethylene powders which was determined by x-ray diffraction measurement. The points in the right region are the results for high-density polyethylenes. The points in the left region are the results for low-density polyethylenes. The broken



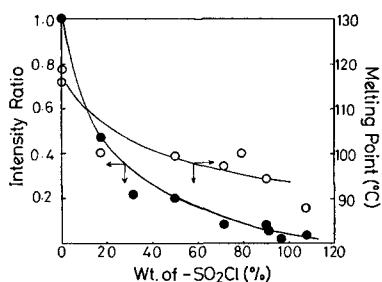


Fig. 7. Dependence of x-ray diffraction intensity ratio (●) and polymer melting point (○) on weight of sulfonyl chloride.

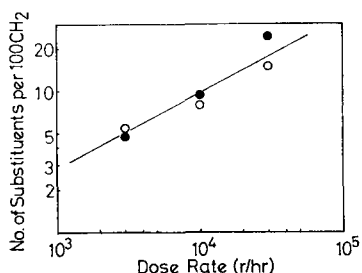


Fig. 8. Number of substituents vs. dose rate. Reaction conditions and symbols same as in Figure 2.

line can be drawn by connecting the highest points of these two regions. The results for Takathene are represented by the black dots. These dots, with one exception, are all above the broken line. This may be due to the effect of surface area, but it is not apparent in the low crystallinity region.

Figure 5 shows the chlorine atoms introduced by side reaction (chlorination) as percentages by weight of the original polyethylene. In this case, the effect of surface area cannot be observed. The infrared spectrum of the product indicates a strong absorption peak which was assigned to sulfonylchloride groups.

There is a gradual breakdown of crystalline structure during the radiation sulfochlorination of polyethylene, as shown in Figure 6. However, it is very difficult to determine the quantity of crystalline phase from the absolute intensity of the x-ray diffraction peak. Therefore, as a measure of crystallinity, it is better to use the ratio of the intensity of the (110) peak in the sulfochlorinated specimen to the intensity of the same peak in the original polyethylene. The positions of the peak did not change after the sulfochlorinated phase. However, the intensity of the (110) x-ray diffraction peak decreased markedly with increase in the number of sulfonyl chloride groups in the polyethylene, as shown in Figure 7.

The melting temperature was determined at the intersection of the baseline and the tangent line of the DTA peak. The melting point determined

by the DTA method is the crystalline fusion temperature of the sulfochlorinated polyethylene. A high-conversion specimen did not show any clear DTA peak, nor an x-ray diffraction peak, because of breakdown of the crystalline structure. The density increased from 1.20 to 1.50 g/cm<sup>3</sup> with increasing sulfonyl chloride content.

The relation between dose rate and quantity of substituent is shown in Figure 8 in the case of Takathene CW-21. With smaller dose rate, fewer chlorine atoms are introduced by the side reaction. As to sulfochlorination, the rate seems to be proportional to the square root of the dose rate, suggesting that the reaction proceed by the free-radical chain mechanism with bimolecular termination.

### References

1. R. V. Dzhagatspanyan, V. I. Zetkin, and E. N. Zykova, U.S.S.R. Pat. 135,639 (Feb. 15, 1961).
2. R. V. Dzhagatspanyan and V. I. Zetkin, *Plast. Massy*, **10**, 5 (1964).
3. R. V. Dzhagatspanyan, V. I. Zetkin, E. N. Zykova and M. T. Filippov, U.S.S.R. Pat. 128,142 (Apr. 28, 1960).
4. R. V. Dzhagatspanyan, L. M. Yakimenko, A. I. Gershimovich, and V. I. Zetkin, U.S.S.R. Pat. 150,625 (1963).
5. L. Wuckel, L. Sawtchenko, and A. Seidel, *Proceedings of the 1962 Tihany Symposium on Radiation Chemistry*, Hungary, 1964, pp. 301-306.
6. M. Takehisa, S. Machi, and S. Sawayanagi, *Hydrocarbon Processing*, **47**, 169 (1968).
7. M. Takehisa et al., *Proceedings of 9th Radioisotope Conference Japan*, 1969, p. 286.
8. G. M. Kline, Analytical Chemistry of Polymers, in *High Polymers*, Vol. 12, part 1, H. Mark et al., Ed., Interscience, New York, 1959, p. 520.
9. W. Schoeniger, *Mikrochim. Acta*, (1955), 123, (1956) 869.
10. H. Hendus and G. Schell, *Kunststoffe*, **51**, 69 (1961).
11. G. F. Lisk: *Ind. Eng. Chem.*, **40**, 1671 (1948).

Received August 14, 1970

Revised October 13, 1970