

## $\gamma$ -Radiation-Induced Cross-Linking of Polyethylene

Hiroshi MITSUI\* and Fumio HOSOI\*

*Japan Atomic Energy Research Institute, Takasaki Radiation  
Chemistry Research Establishment, Takasaki, Japan.*

Tsutomu KAGIYA

*Faculty of Engineering of Kyoto University, Kyoto, Japan.*

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**ABSTRACT:** The  $\gamma$ -radiation-induced cross-linking of polyethylene was studied *in vacuo* at 30–200°C with a dose rate of  $1.1 \times 10^5$  rad/hr. The gel fraction increased with rising irradiation temperature, and become almost constant above 150°C. The degree of increase was extremely large at near the melting temperature of polyethylene. The dosage to produce gelation decreased with the temperature, but was almost constant above 150°C. The gel fraction was increased by irradiation beyond the gel-point dosage at each temperature, and the relative increment decreased with the radiation dose. The amount of hydrogen formation was found to increase to some extent with temperature. The content of *trans*-vinylene unsaturation increased almost linearly with the dose, and the extent of the increment was little affected by the temperature. At 150 and 200°C, the methyl-group content also increased almost linearly with the dose, and the rate of increase was somewhat higher at 200°C than at 150°C. On the basis of these results, the mechanism of the  $\gamma$ -radiation-induced cross-linking of polyethylene was discussed.

**KEY WORDS**  $\gamma$ -Radiation / Cross-Linking / Polyethylene /  $\gamma$ -Radiation-Induced Cross-Linking / Gel Fraction / Hydrogen Formation / Structural Change / Mechanism of Cross-Linking

It is well known<sup>1,2</sup> that ionizing radiations induce the cross-linking, hydrogen evolution, formation of *trans*-vinylene unsaturation, disappearance of terminal vinyl and vinylidene unsaturations, and slight main-chain scission, in polyethylene. Although a number of mechanisms have been proposed for the radiation-induced cross-linking of polyethylene, it is difficult to find a mechanism to explain perfectly all the observed results.

In this paper, on the basis of the quantitative experimental results for gel formation, hydrogen formation, and structural changes in the polyethylene irradiated by  $\gamma$ -rays *in vacuo* at 30–200°C, the mechanism of the  $\gamma$ -radiation-induced cross-linking of polyethylene is discussed.

### EXPERIMENTAL

#### *Polyethylene*

The powder polyethylene used was obtained by the  $\gamma$ -radiation-induced polymerization of

ethylene in the gas phase. The polymerization was carried out under a pressure of 400 kg/cm<sup>2</sup> at 30°C with a dose rate of  $3.8 \times 10^5$  rad/hr by using a flow-type reactor of 10-l capacity. The ethylene flow-rate was 10.3 kg/hr. The number- and weight-average molecular weights of the polyethylene were found to be  $1.14 \times 10^5$  and  $2.50 \times 10^5$ , respectively, from the intrinsic viscosity in tetralin solution at 130°C by using the Tung's equation<sup>3</sup>, and from the one in decalin solution at 135°C by using the Chiang's equation<sup>4</sup>. The polyethylene melted at about 120°C.

#### *Irradiation Procedure*

About 2 g of polyethylene was weighed out into a stainless steel (SUS-27) cylindrical vessel of 100-ml capacity. The vessel was evacuated to a pressure of  $10^{-4}$  mmHg at the desired temperature for more than 1 hr, and irradiated by  $\gamma$ -radiation from a 5000-Ci <sup>60</sup>Co with a dose rate of  $1.1 \times 10^5$  rad/hr.

#### *Gel-Fraction Measurement*

The polymer sample of about 200 mg was

accurately weighed out into a 100-mesh stainless steel (SUS-27) basket. The sample was extracted with boiling xylene for 48 hr, boiled with methanol for 3 hr to remove the attached xylene, and then dried under reduced pressure at room temperature for more than 40 hr. The operation of extraction and drying was repeated until the weight change of insoluble polymer became less than 1%, and the percentage of the insoluble polymer was defined as the gel fraction. Commercially available reagent grade xylene and methanol were used for the extraction, and the antioxidant 2, 6-di-*t*-butyl-*p*-cresol of 0.5 wt% was added to them. The extraction time varied from 100 to 400 hr.

#### Hydrogen Measurement

After the irradiation, the reaction vessel was charged with a desired amount of commercial nitrogen (99.9995 mol% pure) to dilute the gaseous products. Hydrogen was then deter-

mined at 50°C by using a Shimadzu GC-1B gas chromatograph provided with a 3-m column packed with activated alumina. The pure nitrogen of 99.9995 mol% was used as the carrier gas.

#### Infrared Spectra Measurement

The irradiated powder polyethylene was hot-pressed into films of about 0.2 mm thickness under a pressure of 200 kg/cm<sup>2</sup> at 180°C, and quenched to room temperature. The infrared spectra were measured with a Nippon-Bunko model DS-301 infrared spectrophotometer using NaCl optics. The double bond and methyl group contents were determined from the infrared spectrum as described by Cernia, *et al.*,<sup>5</sup> and Bryant, *et al.*,<sup>6</sup> respectively. For the determination of these contents, the densities of films were measured in a gradient tube at 25°C with a methanol-water solution.

Table I. Gel fraction, double bond and methyl group contents

| Temp,<br>°C | Dose,<br>Mrad | Gel,<br>% | Double bond 1/1000C    |                |            | Methyl,<br>1/100C |
|-------------|---------------|-----------|------------------------|----------------|------------|-------------------|
|             |               |           | <i>trans</i> -Vinylene | Terminal vinyl | Vinylidene |                   |
| Blank       | 0.00          | 0.0       | 0.024                  | 0.030          | 0.052      | 0.550             |
| 30          | 1.76          | 1.3       | 0.081                  | 0.029          | 0.052      | 0.543             |
|             | 2.64          | 6.7       | 0.101                  | 0.030          | 0.053      | 0.547             |
|             | 5.28          | 33.7      | 0.180                  | 0.031          | 0.051      | 0.560             |
|             | 9.90          | 61.8      | 0.303                  | 0.023          | 0.047      | 0.530             |
|             | 22.00         | 74.8      | 0.592                  | 0.031          | 0.050      | 0.570             |
| 90          | 0.88          | 2.9       | 0.053                  | 0.034          | 0.049      | 0.550             |
|             | 1.76          | 9.4       | 0.066                  | 0.027          | 0.057      | 0.528             |
|             | 2.64          | 33.7      | 0.105                  | 0.030          | 0.054      | 0.564             |
|             | 5.28          | 63.6      | 0.177                  | 0.027          | 0.050      | 0.555             |
|             | 10.12         | 76.1      | 0.317                  | 0.030          | 0.044      | 0.560             |
| 120         | 0.44          | 5.4       | —                      | —              | —          | —                 |
|             | 1.76          | 53.6      | —                      | —              | —          | —                 |
| 150         | 0.44          | 22.5      | 0.044                  | 0.040          | 0.057      | 0.556             |
|             | 1.76          | 54.7      | 0.072                  | 0.031          | 0.050      | 0.573             |
|             | 2.64          | 60.8      | 0.094                  | 0.024          | 0.051      | 0.585             |
|             | 5.28          | 72.2      | 0.164                  | 0.029          | 0.053      | 0.619             |
| 200         | 0.44          | 20.5      | 0.045                  | 0.041          | 0.054      | 0.556             |
|             | 0.66          | 41.4      | 0.046                  | 0.028          | 0.047      | 0.559             |
|             | 1.76          | 57.5      | 0.067                  | 0.027          | 0.053      | 0.575             |
|             | 5.28          | 73.1      | 0.173                  | 0.024          | 0.054      | 0.629             |
| 250         | 0.44          | 20.3      | —                      | —              | —          | —                 |

## RESULTS AND DISCUSSION

*Gel Fraction*

The gel fraction, and the double bond and methyl group contents in the polyethylene irradiated at various temperatures and doses are listed in Table I.

As can be seen in Figure 1, the gel fraction increases with the rise of irradiation temperature, and subsequently becomes almost constant above 150°C. The scale of the increment is remarkable at near 120°C, which corresponds approximately to the melting temperature of polyethylene. This shows that the rate of gel formation is markedly increased when polyethylene is irradiated in the molten state.

In Figure 2, the gel fractions are plotted against the radiation dose. In this figure, the

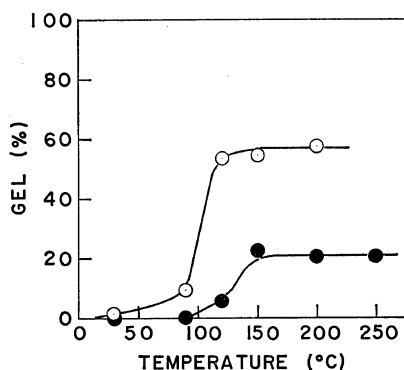


Figure 1. Relation between gel fraction and irradiation temperature: ●, 0.44 Mrad; ○, 1.76 Mrad; dose rate,  $1.1 \times 10^5$  rad/hr.

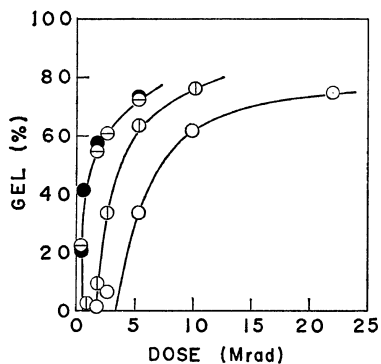


Figure 2. Relation between gel fraction and radiation dose: ○, 30°C; ⊕, 90°C; ⊖, 150°C; ●, 200°C; dose rate,  $1.1 \times 10^5$  rad/hr.

intercepts on the abscissa of the curves represent the gel-point dosage, that is, the critical dose for incipient gel-formation. It is clear from this figure that the gel-point dosage decreases with the temperature, and becomes almost the same at 150 and 200°C.

The gel fraction increases remarkably in each case when the irradiation dose exceeded the gel-point dosage, and the scale of the increment decreases with the dose. The rate of gel formation at near the gel-point dosage increases with temperature, and becomes almost the same at 150 and 200°C.

*Hydrogen Formation*

As shown in Table II, the amount of hydrogen formation tends to increase gradually with the rise of irradiation temperature. The activation energy is given to be 0.4 kcal/mol from the Arrhenius plot of the values given in Table II.

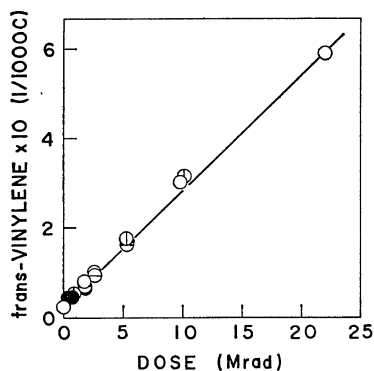
Table II. Hydrogen yield

| Temp, °C | Hydrogen yield, $\times 10^6$ mol/g-PE·Mrad |
|----------|---|
| 30       | 2.89  |
| 90       | 3.39  |
| 150      | 3.30  |
| 200      | 3.78  |

It is well known in general that the primary radiation-chemical reactions are only brought about by the radiation energy absorbed in the reaction system, that the rates depend on the amount of the absorbed energy, and that the activation energies are almost 0 kcal/mol. It seems reasonable, therefore, from the small value of observed activation energy of 0.4 kcal/mol for hydrogen formation, to assume that hydrogen is formed mainly by the primary radiation-chemical reactions. Thus, when polyethylene is irradiated by ionizing radiation, hydrogen is assumed to be formed by the hydrogen radical (itself formed by the side-chain C—H bond scission), which abstracts a hydrogen atom from methylene group.

*Contents of Double Bonds and Methyl Group*

As shown in Figure 3, the content of *trans*-vinylene unsaturation increases almost linearly with the radiation dose, and the rate of the



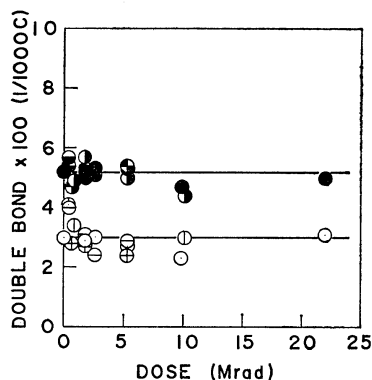
**Figure 3.** Relation between the content of *trans*-vinylene unsaturation and radiation dose: ○, 30°C; ⊙, 90°C; ⊖, 150°C; ●, 200°C; dose rate,  $1.1 \times 10^5$  rad/hr.

increase is almost independent of the irradiation temperature.

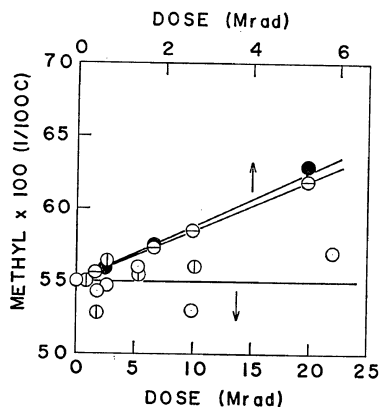
When polyethylene is irradiated by ionizing radiation, *trans*-vinylene unsaturation is assumed to be formed by the reaction due to the hydrogen radical formed by the primary radiation-chemical reaction which abstracts the hydrogen atom of the adjacent methylene group in the same molecule. Since the activation energy of hydrogen-radical formation by the irradiation is about 0 kcal/mol (as described above), the fact that the rate of formation of *trans*-vinylene unsaturation is little affected by the temperature, is considered to suggest that the activation energy of the hydrogen abstraction reaction to form *trans*-vinylene unsaturation is about 0 kcal/mol.

The contents of terminal vinyl and vinylidene unsaturations of polyethylene remain almost unaltered by the irradiation at all temperatures (Figure 4).

As shown in Figure 5, the methyl-group content is little affected by the radiation dose at 30 and 90°C, while the content increases almost linearly with the dose at 150 and 200°C, and the extent of the increment is somewhat larger at 200°C than at 150°C. This result may indicate that, at high temperatures where the polyethylene is in a molten state, the hydrogen abstraction reaction takes place from methylene group by the main-chain polymer radical ( $-\text{CH}_2-\dot{\text{C}}\text{H}_2$ ), which is formed by the main-chain C—C bond scission under  $\gamma$ -irradiation.



**Figure 4.** Relation between the terminal vinyl and vinylidene unsaturation contents and radiation dose: terminal vinyl, ○, 30°C; ⊙, 90°C; ⊖, 150°C; ⊕, 200°C; vinylidene, ●, 30°C; ⊙, 90°C, ⊖, 150°C, ⊕, 200°C; dose rate,  $1.1 \times 10^5$  rad/hr.



**Figure 5.** Relation between the methyl-group content and radiation dose: ○, 30°C; ⊙, 90°C; ⊖, 150°C; ●, 200°C; dose rate,  $1.1 \times 10^5$  rad/hr.

The activation energy of 0.6 kcal/mol for the methyl-group formation is obtained from the Arrhenius plot of the *G*-values obtained from the slopes of the straight lines at 150 and 200°C in Figure 5. The value is considered to represent the activation energy for the diffusion of the main-chain polymer radical, because the methyl group is only formed in the molten state.

#### *G*-Values of Cross-Linking and Main-Chain Scission

The initial molecular distribution of polyethylene used can be considered to be random, since the ratio of the weight-average molec-

ular weight to the number-average ( $M_w/M_n$ ) is about 2.2.

The relation between the sol fraction ( $s$ ) and radiation dose ( $r$ ) has been derived by Charlesby, *et al.*,<sup>7</sup> for the case of a polymer undergoing simultaneous cross-linking and main-chain scission, and possessing initially a random molecular weight distribution as follows

$$s + s^{1/2} = \frac{p_0}{q_0} + \frac{1}{q_0 u_1 r} \quad (1)$$

where  $p_0$  and  $q_0$  are the probabilities of the main-chain scission and cross-linking per monomer unit per unit dose, respectively, and  $u_1$  represents the initial number-average degree of polymerization. When  $r$  is represented by the unit of Mrad, eq 1 is given as

$$s + s^{1/2} = \frac{G(S)}{2G(X)} + \frac{1.602 \times 10^{-18} N_A}{G(X) M_w r} \quad (2)$$

where the sol fraction ( $s$ ) is given as  $(1 - g)$  from the gel fraction ( $g$ ) obtained experimentally. In eq 2,  $G(S)$  and  $G(X)$  are the  $G$ -values (events per 100 eV absorbed) of main-chain scission and cross-linking, respectively,  $N_A$  is the Avogadro's number, and  $M_w$  represents the initial weight-average molecular weight.

According to eq 2, the plot of  $(s + s^{1/2})$  against  $(1/r)$  gives a straight line when the initial molecular weight distribution of polymer is random. On the other hand, it has been theoretically demonstrated<sup>8</sup> that the plot becomes convex upward when the intramolecular cross-linking, that is, cyclization occurs simultaneously with the intermolecular one.

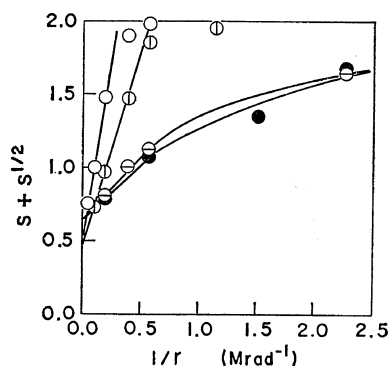


Figure 6. Plots of  $(s + s^{1/2})$  as a function of the reciprocal of dose for irradiated polyethylene: ○, 30°C; ⊙, 90°C; ⊖, 150°C; ●, 200°C.

As can be seen in Figure 6, the relationship of eq 2 is satisfied at 30 and 90°C, since a linear relation is found to hold between  $(s + s^{1/2})$  and  $(1/r)$ . The plot, however, gives a convex upward curve at 150 and 200°C. The results are considered to indicate that the intramolecular cross-linking occurs very little at low temperatures where the polyethylene is in the solid state, but this reaction occurs at the same time as the intermolecular cross-linking at high temperatures where the polyethylene is in the molten state.

Since the initial molecular weight distribution of polyethylene used is considered to be random (as described above), the value of  $G(S)/2G(X)$  in eq 2 is given from the intercepts on the ordinate when the straight lines and curves in Figure 6 are back-extrapolated to  $1/r=0$ . The  $G$ -values are calculated as shown in Table III,

Table III.  $G$ -values

| Temp. °C                   | 30   | 90   | 150  | 200  |
|----------------------------|------|------|------|------|
| $G(\text{cross-linking})$  | 0.76 | 1.44 | 4.55 | 5.06 |
| $G(\text{scission})$       | 0.77 | 1.34 | 5.87 | 6.51 |
| $G(\text{H}_2)$            | 2.79 | 3.27 | 3.18 | 3.64 |
| $G(\text{trans-vinylene})$ | 2.04 | 2.00 | 1.83 | 1.93 |
| $G(\text{terminal vinyl})$ | 0.00 | 0.00 | 0.00 | 0.00 |
| $G(\text{vinylidene})$     | 0.00 | 0.00 | 0.00 | 0.00 |
| $G(\text{methyl})$         | 0.00 | 0.00 | 9.05 | 9.72 |

by using eq 2 from the slopes of straight lines and the tangents of curves at  $1/r=0$  in Figure 6, and from the values of  $G(S)/2G(X)$ . In this table, the  $G$ -values for the formation of hydrogen, unsaturations, and methyl group are calculated on the basis of the results described before.

Both the values of  $G(X)$  and  $G(S)$  increase with the rise of irradiation temperature, and the scale of the increment is extremely large between 90 and 150°C (Table III). From the results, it is supposed that the rise in temperature leads to the increase in the intermolecular cross-linking between the polymer radicals, which are formed by the scission of the side-chain C—H and main-chain C—C bonds of polyethylene caused by the irradiation, and then reduced by the recombination hence producing the original polymer molecule at 30°C. In addition, the result also shows that

the increase in the intermolecular cross-linking is remarkable at near the melting temperature of polyethylene, and the increase may be ascribed to the change in the physical state of polyethylene.

The activation energies of cross-linking and main-chain scission are calculated for each temperature range from the Arrhenius plots of  $G(X)$  and  $G(S)$  given in Table III, and listed in Table IV.

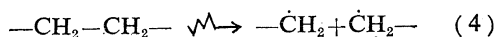
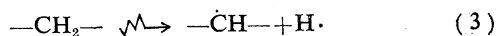
Table IV. Activation energies of  $G$ -values of cross-linking and main-chain scission

|                           | Activation energy, kcal/mol |           |
|---------------------------|-----------------------------|-----------|
|                           | 80—90°C                     | 150—200°C |
| $G(\text{cross-linking})$ | 2.3                         | 0.8       |
| $G(\text{scission})$      | 2.0                         | 0.8       |

#### Mechanism of Cross-Linking

In the calculation of  $G(X)$  and  $G(S)$  by using eq 2 from Charlesby—Pinner plot (Figure 6), the two processes have been assumed as occurring consecutively rather than simultaneously. At first, only main-chain scission, that is, degradation takes place to the extent corresponding to the radiation dose  $r$ , and result in a modified molecular weight distribution. The second step then consists of cross-linking this new distribution, likewise to an extent depending on the radiation dose  $r$ . This separation of the two processes, which normally occur simultaneously, is only justified by the random nature of the two processes.

In the case of polyethylene, the side-chain C—H and main-chain C—C bonds may be broken at random as the primary radiation-chemical event (eq 3 and 4).



As shown in Table III, the occurrence of cross-linking and main-chain scission due to the irradiation are measured by the formation of hydrogen and *trans*-vinylene unsaturation. In addition, the methyl group is formed at 150 and 200°C. The contents of terminal vinyl and vinylidene unsaturations, however, remain

unaltered.

On the basis of these results, the following reactions can be expected to occur after the reactions of eq 3 and 4.

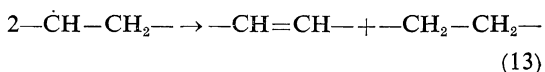
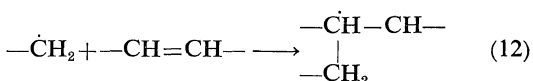
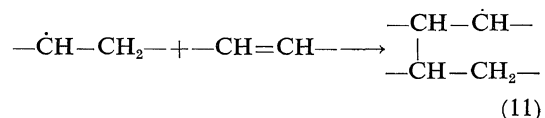
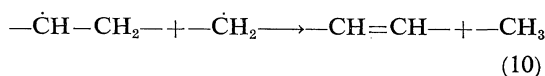
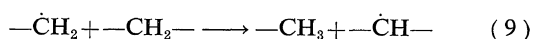
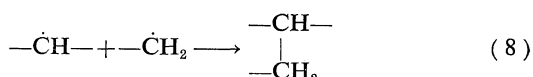
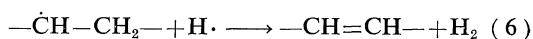


Figure 3 shows the content of *trans*-vinylene unsaturation increases almost linearly with the radiation dose, and the rate of the increment is little affected by the irradiation temperature. Furthermore, it is shown in Figure 5 that the methyl-group content remains unaltered at 30 and 90°C. These results are considered to indicate that the reactions of eq 10, 11 and 12 occur to a very small extent, since *trans*-vinylene unsaturation and methyl group are simultaneously formed by the reaction of eq 10, and *trans*-vinylene unsaturation is removed by the reactions of eq 11 and 12. In addition, the disproportionation of eq 13 may be also very unlikely to occur, because of the low probability of the disproportionation of eq 10 as mentioned above.

As a result of these considerations, when polyethylene is irradiated by  $\gamma$ -rays, it can be concluded that hydrogen is formed by the reactions of eq 5 and 6, *trans*-vinylene unsaturation

by eq 6, methyl group by eq 9, and the three-dimensional networks to form an insoluble gel by the intermolecular cross-linking and end-linking expressed by eq 7 and 8, respectively.

The intermolecular cross-linkage is directly formed by the intermolecular cross-linking between the side-chain polymer radicals ( $-\dot{\text{C}}\text{H}-$ ) formed by the reaction of eq 3 (eq 7). When the main-chain scission of eq 4 occurs at two places in the same polyethylene molecule to form the main-chain polymer radical possessing an unpaired electron at both ends, and the reaction is followed by the intermolecular end-linking of eq 8 at both ends, the intermolecular cross-linkage makes a long chain. The contribution to the formation of three-dimensional structure of the intermolecular end-linking of eq 8, therefore, can be considered to be half of the intermolecular cross-linking of eq 7. On the basis of this assumption and the stationary state hypothesis (with respect to the concentrations of hydrogen and polymer radicals), the  $G$ -values of the reactions of eq 3–9 are calculated at each temperature from the  $G$ -values given in Table III, and listed in Table V.

Table V.  $G$ -values of proposed reactions

| Reaction no. | $G$ -value |      |       |       |
|--------------|------------|------|-------|-------|
|              | 30°C       | 90°C | 150°C | 200°C |
| 3            | 2.79       | 3.27 | 3.18  | 3.64  |
| 4            | 0.77       | 1.34 | 5.87  | 6.51  |
| 5            | 0.75       | 1.27 | 1.35  | 1.71  |
| 6            | 2.04       | 2.00 | 1.83  | 1.93  |
| 7            | 0.00       | 0.00 | 4.53  | 4.92  |
| 8            | 1.52       | 2.61 | 2.69  | 3.30  |
| 9            | 0.00       | 0.00 | 9.05  | 9.72  |
| Cyclization  | 0.00       | 0.00 | 1.33  | 1.51  |

In Table V, the term cyclization refers to the intramolecular cross-linking and end-linking given by eq 7 and 8, respectively, which are not considered to form the three-dimensional networks, and the  $G$ -values calculated from following equation.

$$G(\text{cyclization}) = G(\text{eq 7}) + \frac{1}{2} G(\text{eq 8}) - G(\text{X}) \quad (14)$$

As can be seen in Table V, the cyclization takes place at 150 and 200°C, while the reaction occurs very little at 30 and 90°C. The result

is consistent with the result of consideration obtained from the Charlaby—Pinner plot (Figure 6) described before.

In general, the bond dissociation energy of  $\text{R}_1-\text{R}_2$  bond [ $D(\text{R}_1-\text{R}_2)$ ] is given as

$$D(\text{R}_1-\text{R}_2) = \Delta H_f^0(\text{R}_1\cdot) + \Delta H_f^0(\text{R}_2\cdot) - \Delta H_f^0(\text{R}_1-\text{R}_2) \quad (15)$$

where  $\Delta H_f^0(\text{R}_1\cdot)$ ,  $\Delta H_f^0(\text{R}_2\cdot)$ , and  $\Delta H_f^0(\text{R}_1-\text{R}_2)$  represent the standard heats of formation for radicals  $\text{R}_1\cdot$  and  $\text{R}_2\cdot$ , and for stable molecule  $\text{R}_1-\text{R}_2$ , respectively. The standard heats of formation can be calculated according to the method<sup>9</sup> proposed by the authors, which is based on the group-contribution method for the estimation of thermochemical properties proposed by Andersen, *et al.*<sup>10</sup>

By using eq 15, the bond dissociation energies are found to be 94.51 kcal/mol for side-chain C—H bond, and 81.66 kcal/mol for main-chain C—C bond of polyethylene, respectively. This shows the main-chain scission of eq 4 is more likely to occur than the side-chain scission of eq 3. At 150 and 200°C, the experimental result is consistent with the consideration, since the  $G$ -value of eq 4 is higher than that of eq 3 (Table V). The situation in the  $G$ -values, however, is reversed at 30 and 90°C, and the  $G$ -value of eq 4 is significantly larger at 150 and 200°C than at 30 and 90°C. In addition, the methyl group is shown in Table V to form by eq 9 at 150 and 200°C.

From the results for solid polyethylene, it appears that the most of the main-chain polymer radicals formed by the main-chain scission of eq 4 are trapped within the polyethylene, and then gradually removed by recombination to form the original molecule. On the other hand, in the case of polyethylene in molten state, the main-chain polymer radicals can be considered to diffuse within the system, and abstract the hydrogen atoms of methylene groups to form methyl groups (eq 9). It may be reasonable to assume that the polymer radical formed by the reaction of eq 9 disappears by either intermolecular or intramolecular cross-linking and end-linking (eq 7 and 8).

#### Activation Energy

From the mechanism mentioned above, the activation energies of  $G(\text{X})$  given in Table IV

appear to represent the summarization of the reactions of eq 3—9. On the other hand, those of  $G(S)$  can be simply considered to represent activation energy of the reaction of eq 4.

As mentioned before, both the activation energies of side-chain and main-chain scissions (eq 3 and 4) are considered to be 0 kcal/mol, because these reactions are the primary radiation-chemical ones induced by  $\gamma$ -rays. On the other hand, from the Arrhenius plot of the  $G$ -values given in Table V, the activation energy of the side-chain scission of eq 3 is found to be 0.4 kcal/mol, which is equal to that of hydrogen formation. As described above, the activation energy of the reaction of eq 4 is equal to the one of  $G(S)$  given in Table IV.

Since the intermolecular cross-linking and end-linking expressed by eq 7 and 8, respectively, are due to the recombination between polymer radicals, the activation energies of these reactions can be considered to be approximately 0 kcal/mol. From the Arrhenius plot of the  $G$ -values listed in Table V, however, the activation energies are calculated to be 0.7 kcal/mol for the reaction of eq 7 at 150—200°C, 2.0 kcal/mol at 30—90°C and 1.6 kcal/mol at 150—200°C for eq 8, respectively.

The activation energies thus calculated on the basis of the analyses of the experimental results are in conflict with the predicted ones. The discrepancy is considered to mean that the  $G$ -values of the reactions of eq 3, 4, 7, and 8 involve the change in the reaction rates brought about by the alteration in the physical state of polyethylene with the rise of irradiation temperature, such as the degree of crystallinity, crystal structure, and phase.

The reactions of eq 5, 6, and 9 are the radical substitution reactions. The following equation has been proposed by Kagiya, *et al.*,<sup>11</sup> for estimating the activation energy of elementary reactions ( $E_a$ )

$$E_a = \frac{D_i \{ (1 - 2\alpha) D_f + \alpha^2 D_i \}^2}{(D_f - \alpha^2 D_i)^2} \quad (16)$$

where  $D_i$  and  $D_f$  represent the bond dissociation energies of the bonds removed and formed by the reaction, respectively, and these can be calculated from eq 15 by using the estimated

standard heats of formation according to the method described before.  $\alpha$  is a function of reaction heat ( $Q$ ) represented by eq 17.

$$\alpha = \exp(\beta Q) \quad (17)$$

Here  $\beta$  is a constant depending on the type of reaction, and has been given<sup>11</sup> to be 0.0190 for the radical substitution reaction. The value of  $Q$  is given as

$$Q = D_f - D_i \quad (18)$$

By using eq 16, the activation energies of the reactions of eq 5, 6, and 9 are calculated to be 8.57, 1.96, and 6.43 kcal/mol, respectively. On the other hand, from the Arrhenius plot of the  $G$ -values listed in Table V, the activation energies are given to be 1.3 kcal/mol for the reaction of eq 5 and 0 kcal/mol for eq 6 at 30—200°C, and 0.6 kcal/mol for eq 9 at 150—200°C, respectively. Thus, the all activation energies predicted for these reactions are higher than the ones calculated on the basis of the analyses of experimental results. This seems to suggest the possibility that both of the polymer molecules and radicals in the system are somewhat excited under  $\gamma$ -irradiation.

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