Effect of Double Bonds on the γ-Radiation-Induced Crosslinking of Polyethylene

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Synopsis

Various low-density polyethylenes ranging in initial weight-average molecular weight ($\bar{M}_w$) from 7600 to 589000 having a ratio of $\bar{M}_w$ to number-average molecular weight ($\bar{M}_n$) of about 5 were irradiated by γ-rays in vacuo at 30°C. Gel fractions were determined and analyzed by using the equation derived by Charlesby and Pinner. The following relationships were obtained when $\bar{M}_w$ was used as the molecular weight:

$$r_g = 2.85 \times 10^3 \, \bar{M}_w{}^{-1} \, [\mathrm{C}{=}\mathrm{C}]_0{}^{-0.21}$$

$$q_0 = 5.98 \times 10^{-3} \, [\mathrm{C}{=}\mathrm{C}]_0{}^{0.21}$$

$$p_0 = 2.98 \times 10^{-3} \, [\mathrm{C}{=}\mathrm{C}]_0{}^{0.21}$$

where r_g represents the gel point dosage (Mrad), $[\mathrm{C}{=}\mathrm{C}]_0$ is the sum of the initial contents of terminal vinyl and vinylidene unsaturations (mole/g polyethylene), and q_0 and p_0 are the probabilities of crosslinking and main-chain scission per monomer unit for a unit radiation dose in Mrad, respectively. Similar relationships to the equations described above were also obtained when $\bar{M}_n$ was used. From the results, it was concluded that terminal vinyl and vinylidene unsaturations play an important role for the gel formation in the γ-radiation-induced crosslinking of polyethylene in vacuo at room temperature.

INTRODUCTION

It has been pointed out[1,2] that terminal vinyl unsaturation plays an important role in the radiation-induced crosslinking of higher α-olefins and polyethylene. In a previous paper,[3] on the basis of kinetic studies on the double bond contents of polyethylene irradiated by γ-rays, we proposed a mechanism that the disappearance of terminal vinyl and vinylidene unsaturations is concerned with the gel formation.

A few papers[4-6] have been published with respect to the relationship between the gel point dosage and the initial molecular weight in radiation-induced crosslinking of polyethylene. The relationships, however, have been derived without paying any attention to the effect of double bonds.

In this paper, the gel fractions formed in a series of low-density polyethylenes by the irradiation of γ-rays in vacuo at 30°C are analyzed by using the

TABLE I
Polyethylene Samples

Sample no.	Commercial name	Specific gravity	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
1	Sanwax 171-P[a]	0.931	1500	7600	5.07
2	Sanwax 151-P[a]	0.931	2000	8000	4.00
3	Sanwax 131-P[a]	0.931	3500	14800	4.23
4	Sanwax 161-P[a]	0.931	5000	28900	5.78
5	Milason 9[b]	0.923	19600	95000	4.85
6	Sumikathene F 101-1[c]	0.924	34000	171000	5.03
7	Takathene[d]	0.934	114000	589000	5.17

[a] Sanyo Chemical Industries, Ltd.

[b] Mitsui Polychemicals, Co., Ltd.

[c] Sumitomo Chemical, Co., Ltd.

[d] Polyethylene obtained by γ-radiation-induced polymerization of ethylene in the gas phase at 30°C under a pressure of 400 kg/cm² in our laboratory.

equation derived by Charlesby and Pinner,[7] and the results are discussed in connection with the initial double bond contents.

EXPERIMENTAL

Polyethylene

The polyethylenes used are listed in Table I. Samples 1–5 and 7 were prepared into films about 0.2 mm thick by hot-pressing the powder or pellets of polyethylene under a pressure of 200 kg/cm² at 130°C for 10 min, and quenching to room temperature. Sample 6 was a commercial film about 0.3 mm thick.

Woodbrey et al.[8] reported that the contents of terminal vinyl and vinylidene unsaturations of polyethylene polymerized under high pressure decrease with increase in reaction pressure, which results in an increase in the number-average molecular weight.
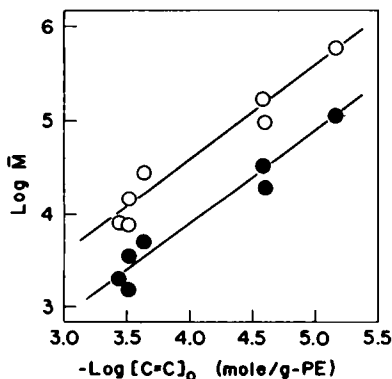

Fig. 1. Relation between initial number-average (●) and weight-average (○) molecular weights ($\bar{M}$) and sum of initial contents of terminal vinyl and vinylidene unsaturations ([C=C]₀) of polyethylene used.

As shown in Figure 1, the following relationship was found to hold for the polyethylenes used:

$$[C{=}C]_0 = 7.95 \times 10^{-1}\ \bar{M}_n^{-1}$$
$$= 3.91 \times 10^{-1}\ \bar{M}_w^{-1} \tag{1}$$

where $[C{=}C]_0$ is the sum of initial contents of terminal vinyl and vinylidene unsaturations (mole/g polyethylene), and $\bar{M}_n$ and $\bar{M}_w$ represent the initial number- and weight-average molecular weights, respectively.

Irradiation Procedure

About 0.5 g polyethylene film was weighed out into a stainless steel (SUS-27) cylindrical vessel of 50-ml capacity. The vessel was evacuated to a pressure of 10^{-4} mm Hg at room temperature for more than 1 hr. The vessel was then irradiated by γ-rays from a 8000-Ci ^{60}Co source at 30° ± 1°C.

Gel Fraction Measurement

A 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%. The weight ratio of the insoluble polymer to the original one was defined as the gel fraction.

Commercially available reagent-grade xylene and methanol were used for the extraction, and the antioxidant 2,6-di-*tert*-butyl-*p*-cresol of 0.5 wt-% was added to them.

RESULTS

The measured gel fractions are illustrated in Figure 2 as a function of radiation dose. The relation between the sol fraction (s) and radiation dose (r) has been derived by Charlesby and Pinner[7] for the case of a polymer undergoing simultaneous crosslinking and main-chain scission, and possessing initially a random molecular weight distribution, as follows:

$$s + s^{1/2} = \frac{p_0}{q_0} + \frac{1}{q_0 u_1 r}$$
$$= \frac{p_0}{q_0} + \frac{2}{q_0 u_2 r} \tag{2}$$

where s is given as $(1 - g)$ from the gel fraction (g) obtained experimentally. In eq. (2), p_0 and q_0 are the probabilities of the main-chain scission and crosslinking per monomer unit for unit radiation dose, and u_1 and u_2 represent the initial number- and weight-average degrees of polymerization, respectively.
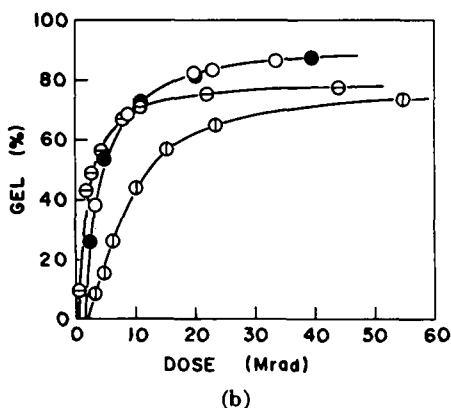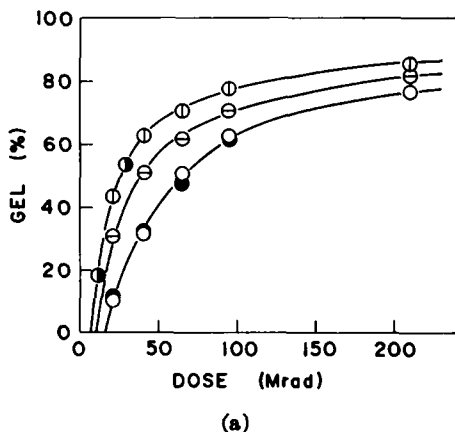
(a)

(b)

Fig. 2.(a) Relation between gel fraction and radiation dose for polyethylene irradiated in vacuo at 30°C. Sample and dose rate: (O) sample 1, 0.42 Mrad/hr; (●) sample 2, 0.42 Mrad/hr; (⊖) sample 3, 0.42 Mrad/hr; (◑) sample 4, 0.0958 Mrad/hr; (⊘) sample 4, 0.42 Mrad/hr. (b) Relation between gel fraction and radiation dose for polyethylene irradiated in vacuo at 30°C. Sample and dose rate: (⊘) sample 5, 0.214 Mrad/hr; (O) sample 6, 0.11 Mrad/hr; (●) sample 6, 0.5 Mrad/hr; (⊖) sample 7, 0.11 Mrad/hr.

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, the plot becomes convex upward if the initial molecular weight distribution is broader than a random one.[7]

Since the initial molecular weight distribution of the polyethylenes used is broader than a random one (Table I), when $(s + s^{1/2})$ is plotted against $(1/r)$, the plot becomes a convex upward curve (Fig. 3). As shown by the curves of samples 4 and 6 given in Figures 2 and 3, even if the samples are irradiated at different dose rates, the plots ride on the same curve. From the results, it can be concluded that, when polyethylene is irradiated by γ-rays in vacuo at room temperature, the gel formation is proportional to the radiation dose and independent of the dose rate. The conclusion is consistent with the result reported by Atchison et al.[9]
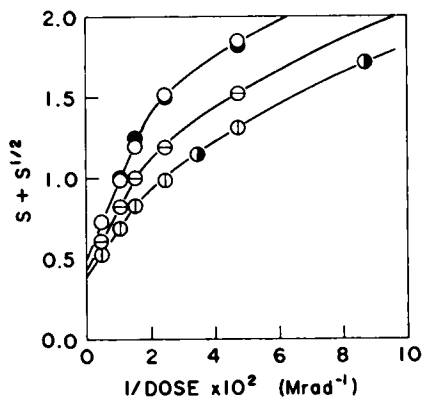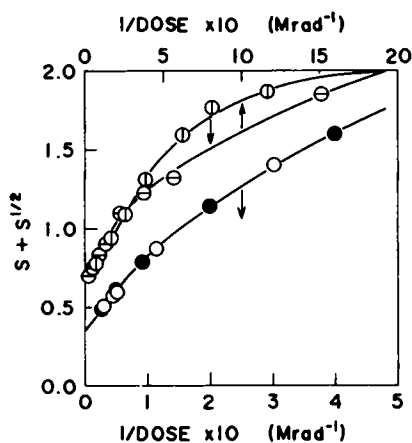
Fig. 3.(a) Plots of $(s + s^{1/2})$ as a function of reciprocal of dose. Irradiation conditions and symbols same as in Fig. 2a. (b) Plots of $(s + s^{1/2})$ as a function of reciprocal of dose. Irradiation conditions and symbols same as in Fig. 2b.

The sol fraction can be assumed to be unity at the gel point, that is, the critical point for incipient gel formation. The gel point dosage (r_g), therefore, can be estimated by back-extrapolating the curves given in Figure 3 to $s + s^{1/2} = 2$. This method is not very satisfactory, owing to the small angle with which $(s + s^{1/2})$ approaches the value of 2. The estimated r_g values by this method, however, are approximately equal to the one estimated from the intercept on the abscissa of the curve in Figure 2.

From the result shown in Figure 4, which is a plot of the logarithms of r_g estimated by the methods described above against $-\log [C{=}C]_0$, r_g (Mrad) is given as follows:
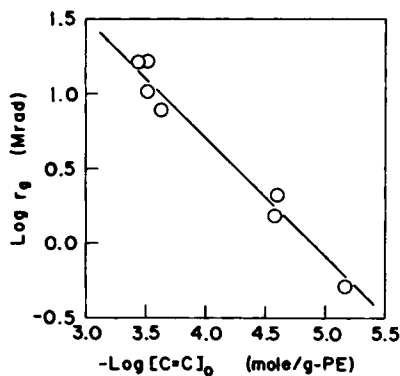
$$r_g = 7.28 \times 10^3 \, [C{=}C]_0^{0.79}. \qquad (3)$$

Fig. 4. Relation between gel point dosage (r_g) and sum of initial contents of terminal vinyl and vinylidene unsaturations ($[C=C]_0$).

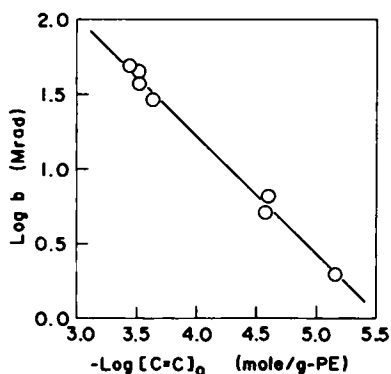Fig. 5. Relation between slope of linear portion (b) in high dose region of curves in Fig. 3 and sum of initial contents of terminal vinyl and vinylidene unsaturation ($[C=C]_0$.

In the derivation of eq. (2), the two processes have been assumed as occurring consecutively rather than simultaneously. At first, only random main-chain scission takes place to the extent corresponding to the radiation dose r, resulting in a modified molecular weight distribution. The second step then consists of random crosslinking this new distribution, likewise to an extent depending on the radiation dose r.

On the basis of this assumption, when a polymer having an initial molecular weight distribution which is not random is irradiated by γ-rays up to a sufficiently high dose, the molecular weight distribution after the first step may be assumed to be random, because of the random main-chain scission. This means that a linear relation can be found to hold between $(s + s^{1/2})$ and $(1/r)$ in the high-dose region. Accordingly, from the slope and the intercept on the ordinate of the linear portion, the values of q_0 and p_0 may be evaluated by combining with eq. (2) if u_1 or u_2 can be assigned a value. In this case, the use of u_1 has been presented to be the most reliable.[7]
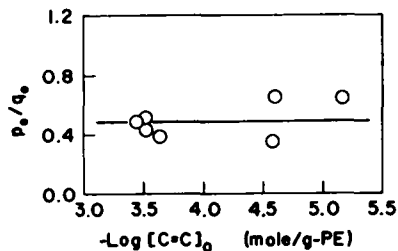
Fig. 6. Relation between (p_0/q_0) and sum of initial contents of terminal vinyl and vinylidene unsaturations ($[C{=}C]_0$).

As can be seen in Figure 3, the curve for each sample can be approximated to a straight line in the high-dose region. When the logarithms of the slopes of the linear portion ($b = 1/q_0u_1$ or $2/q_0u_2$) are plotted against $-\log [C{=}C]_0$, a straight line is obtained having a slope of approximately -0.79 (Fig. 5). From the result, q_0 (Mrad^{-1}) is given as follows:

$$q_0 = 1.17 \times 10^{-3} \, \bar{M}_n^{-1} \, [C{=}C]_0^{-0.79}$$

$$= 2.34 \times 10^{-3} \, \bar{M}_w^{-1} \, [C{=}C]_0^{-0.79}. \tag{4}$$

Figure 6 shows that the ratios p_0/q_0 given by the intercepts on the ordinate of the linear portion in the high-dose region of the curves in Figure 3 are almost independent of $[C{=}C]_0$. From this result and eq. (4), p_0 is represented by eq. (5):

$$p_0 = 0.58 \times 10^{-3} \, \bar{M}_n \, [C{=}C]_0^{-0.79}$$

$$= 1.16 \times 10^{-3} \, \bar{M}_w \, [C{=}C]_0^{-0.79}. \tag{5}$$

DISCUSSION

According to the mechanism presented in the previous paper,[3] when polyethylene is irradiated by γ-rays in vacuo at 30°C, the disappearance of the terminal vinyl and vinylidene unsaturations contributes to gel formation. On the other hand, it can be considered that gel formation is little affected by the *trans*-vinylene unsaturation, because the content increases almost linearly with irradiation time.[3]

Figure 2 shows that the rate of increase in the gel fraction after r_g decreases with increasing radiation dose. The contents of terminal vinyl and vinylidene unsaturation have been reported[3] to decrease exponentially with increase in the dose. From this result, it can be said that the decrease in the rate of gel formation is partly brought about by the decrease in the content of terminal vinyl and vinylidene unsaturations.

The consideration is consistent with the result that the absolute value of exponent of $[C{=}C]_0$ in eq. (3) is equal to those in eqs. (4) and (5).

Since the sol fraction can be assumed to be unity at r_g as described before, r_g is given from eq. (2) as follows:

$$r_g = \frac{1}{(2q_0 - p_0)u_1}$$

$$= \frac{2}{(2q_0 - p_0)u_2}. \tag{6}$$

Assuming r_g is proportional to the reciprocal of $\bar{M}_n$ or $\bar{M}_w$ on the basis of eq. (6), r_g can be represented by eq. (7) when eq. (1) is substituted in eq. (3):

$$r_g = 5.76 \times 10^3\, \bar{M}_n{}^{-1}\, [C{=}C]_0{}^{-0.21}$$

$$= 2.85 \times 10^3\, \bar{M}_w{}^{-1}\, [C{=}C]_0{}^{-0.21}. \tag{7}$$

By combination of eq. (1) with eqs. (4) and (5), q_0 and p_0 are expressed by eqs. (8) and (9), respectively, as a function of $[C{=}C]_0$ when the molecular weight is given as the number-average molecular weight:

$$q_0 = 1.47 \times 10^{-3}\, [C{=}C]_0{}^{0.21} \tag{8}$$

$$p_0 = 0.73 \times 10^{-3}\, [C{=}C]_0{}^{0.21} \tag{9}$$

In the case of the weight-average molecular weight, these are represented as follows:

$$q_0 = 5.98 \times 10^{-3}\, [C{=}C]_0{}^{0.21} \tag{10}$$

$$p_0 = 2.98 \times 10^{-3}\, [C{=}C]_0{}^{0.21}. \tag{11}$$

From the relationships of eq. (7) and eqs. (8)–(11), it can be concluded that the increase in the initial contents of terminal vinyl and vinylidene unsaturations results in a decrease in r_g, if the molecular weight of polyethylene is the same, and an increase in both q_0 and p_0.

The results appear to indicate that the increase in crosslinking is brought about by the increase in the main-chain scission under γ-irradiation, and the crosslinking increases partly by a reaction involving the terminal vinyl and vinylidene unsaturations. Accordingly, it seems reasonable to conclude that terminal vinyl and vinylidene unsaturations play an important role in the gel formation in γ-radiation-induced crosslinking of polyethylene in vacuo at room temperature.

The conclusion is consistent with the mechanism proposed in a previous paper[3] that the terminal vinyl and vinylidene unsaturations disappear by the addition reactions of the polymer radicals, which are formed by the main-chain scission of polyethylene under γ-irradiation, to these unsaturations, resulting in the formation of endlinkage and crosslinkage, respectively.

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