ESR Study of the Radiation Chemical Process in Polyethylene

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Several works[1-10] have already been published on the ESR spectrum of irradiated polyethylene (PE). The results of these works have revealed that at least three kinds of radicals are produced in irradiated PE. The short-living component of the radicals (decay: 1 day) gives a sextet spectrum of ΔH_{hfs} (hyperfine separation) = 30 gauss and is assigned to the $-CH_2-\dot{C}H-CH_2-$ radical (FR_{VI})[1,3,4,7,9,10]. The radical of a longer life-time (decay: months) shows a septet spectrum ($\Delta H_{\mathrm{hfs}}=18$ gauss) with further complex splittings, probably a doublet structure ($\Delta H_{\mathrm{hfs}}=7$ gauss) and is identified with the $-CH_2-\dot{C}H-CH=CH-CH_2-$ radical (FR_{VII})[3,9,10]. The interpretation of the septet spectrum is, admittedly, not as well established as the sextet, about which there is no doubt in its identification. Lawton et al.[4] have expressed their view that the spectrum is a quintet with very "fine" struture and perhaps corresponds to the $-CH_2\cdot : \cdot CH_2-$ radical. Their view, however, does not seem to be well supported. The third component of the radicals has a very long life-time (half-life: 30 min. at 150°C) and gives only a singlet spectrum of ΔH_{msl} (line width at maximum slope) = 25 gauss. This is assigned to the polyenyl radical $-CH_2-\dot{C}H-(-CH=CH-)_n-CH_2-$[5,8]. The spectra of these radicals are summarized in Fig. 1.

In the present investigation PE was irradiated in vacuo at −196°C with a variety of doses, and the change in the obtained ESR spectrum with the rising temperature was followed. The results are discussed from the standpoint of the mechanism of the radiation-chemical changes in the irradiated PE.

Experimental

Material. — Marlex 50 inflation film ~30 μ in thickness was used. The inflation film had some internal strain; therefore, it expanded by about 5% in the extruded direction when put into boiling water.

1) $-CH_2-\dot{C}H-CH_2-$
(FR_{VI})
Decay ~days

2) $-CH_2-\dot{C}H-CH=CH-CH_2-$
(FR_{VII})
~months

3) $-CH_2-\dot{C}H-(-CH=CH-)_n-CH_2-$
(FR_I)
half-life 30 min. at 150°C

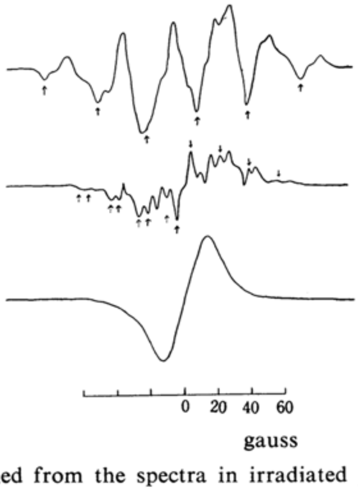

Fig. 1. ESR spectra and free radicals identified from the spectra in irradiated polyethylene.

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1) B. Smaller and M. S. Matheson, *J. Chem. Phys.*, **28**, 1169 (1958).

2) R. J. Abraham and D. H. Whiffen, *Trans. Faraday Soc.*, **54**, 1291 (1858).

3) A. T. Koritzky, Yu. N. Molin, V. N. Shamshev, N. Ya. Bouben and V. V. Voevodsky, *Vysokomolec. Soed.*, **1**, 1182 (1959).

4) E. J. Lawton, J. S. Balwit and R. S. Powell, *J. Chem. Phys.*, **33**, 395 (1960).

5) E. J. Lawton, J. S. Balwit and R. S. Powell, ibid., **33**, 405 (1960).

6) H. Kashiwabara and K. Shinohara, *J. Phys. Soc. Japan*, **15**, 1129 (1960).

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8) S. Ohnishi, Y. Ikeda, S. Sugimoto and I. Nitta, ibid., **47**, 503 (1960).

9) A. G. Kiselev, M. A. Mokul'skii and Yu. S. Lazurkin, *Vysokomolec. Soed.*, **2**, 1678 (1960).

10) S. Ohnishi, Y. Ikeda, M. Kashiwagi and I. Nitta, *Polymer*, **2**, 119 (1961).

Irradiations.—Electron irradiation by a 2 MeV. Van de Graaff accelerator was carried out in vacuo at −196°C as follows: Samples were sealed in a glass ampoule ~4 mm. in diameter under a high vacuum (~10^{-5} mmHg). The glass ampoule was adjusted to float about 1 mm. under the surface of liquid nitrogen so as to be located within the range of the 2 MeV. beam.

In some experiments samples were 'reirradiated'. Samples, preirradiated at a variety of doses, were heated at some high temperature (125°C for FR_{VII} and 250°C for FR_I) so that the free radicals produced by the irradiation could decay almost entirely. After the heat-treatment, the samples were irradiated again at −196°C.

The irradiation dose was calculated by referring to the calorimetry experiment. Hydrogen gas evolved by irradiation from PE was removed by evacuation at −196°C.

ESR Measurement.—ESR signal was recorded at −196°C on a Varian V-4500 spectrometer with Liquid Nitrogen Accessory. All spectra were recorded at a small power level (~1 mW) to avoid the power saturation effect$^{11)}$. The decay curve at room temperature was determined by storing the sample at room temperature for a certain time and then recording the spectrum at −196°C. The concentration of the free radicals was determined by comparing the ESR signal intensity at room temperature with that from a DPPH benzene solution (~1×10^{-5} mol./g.). Sufficient attention was paid to those fractors$^{12)}$ which often lead to an erroneous estimation.

Results and Discussion

Spectrum of Irradiated PE at −196°C.—PE, irradiated at various doses at −196°C, has shown a broad sextet spectrum, as is shown in Fig. 2 (1). Comparing this sextet with that obtained from PE irradiated at room temperature (Fig. 1 (1)), the broadness of the former spectrum can be clearly seen. This arises from the spin-spin interaction and might correspond to the circumstance that such radicals are closely spaced$^{4)}$. It is to be added that, in the irradiated methane, both a broad and a narrow quartet spectrum were obtained and that the interpretation of such differences might be the same$^{13)}$ as has been indicated above.

On warming to room temperature, the broad sextet decayed quickly, and the spectrum remaining after 2.5 hr. was a narrow sextet (see Fig. 2 (2)). After 7 days (Fig. 2 (5)), the sextet spectrum had decayed almost entirely and there only remained the septet spectrum, which hardly decays at all at room temperature.

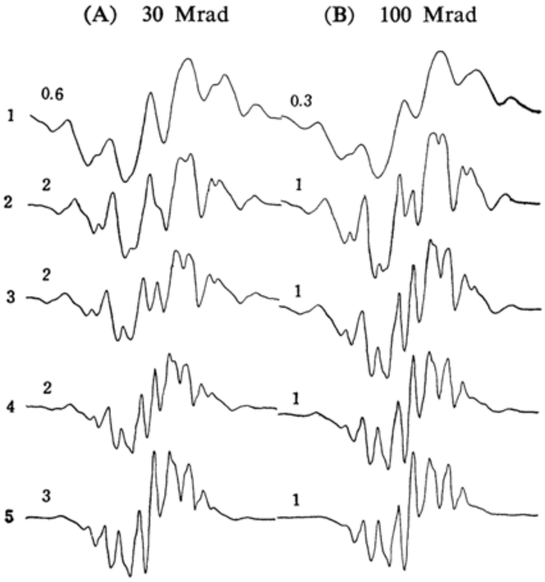

Fig. 2. Change of ESR spectrum of irradiated polyethylene on storage at room temperature. Spectra were recorded at −196°C. Irradiation was carried out in vacuo at −196°C with doses of (A) 30 Mrad and (B) 100 Mrad. The evolved H_2 gas was removed by evacuation. 1) Immediately after irradiation. 2) After 2.5 hr. at room temperature. 3) After 16 hr. 4) After 1 day, 15 hr. 5) After 7 days, 10 hr. Figures show the magnification factor of the amplifier.

Comparing the spectral change at room temperature of samples irradiated at higher doses with those irradiated at lower doses (cf. Fig. 2A with 2B), it can be concluded that FR_{VI} decays faster in those samples irradiated at larger doses. This result might be due to the existence of more 'defects', such as a cross-linked point or a double bond, caused by irradiation in the polymer, defects somewhat facilitating the motion of free radicals in the crystalline region$^{14)}$. It should be remembered in this connection that the ESR spectrum observed on γ-irradiation at room temperature was sextet at small doses <~1 Mrad and septet only in the intermediate dose range (10 ~100 Mrad)$^{10)}$. At higher doses (~3000 Mrad), only a singlet spectrum was observed. The phenomenon might be interpreted, at least in part, on the basis of the increased mobility of the free radicals with increasing doses. In the intermediate doses, for example, FR_{VI} as well as FR_{VII} were produced, but, owing to the increased rate of decay in PE irradiated with larger doses, the sextet spectrum was not observed on ESR recording.

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11) S. Ohnishi, Y. Ikeda, S. Sugimoto and I. Nitta, *Ann. Repts. Japanese Association for Radiation Research on Polymers (JARRP)*, **2**, 215 (1960).

12) S. Ohnishi, Y. Ikeda, S. Sugimoto and I. Nitta, ibid., **2**, 219 (1960).

13) L. A. Wall, D. W. Brown and R. E. Florin, *J. Phys. Chem.*, **63**, 1762 (1959).

14) For example, R. E. Glick, R. P. Gupta, J. A. Sauer and A. E. Woodward, *Polymer*, **1**, 340 (1960).

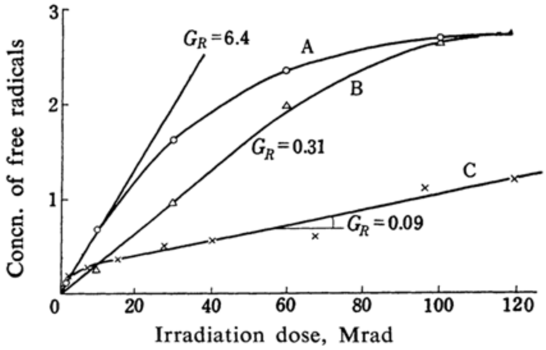

Fig. 3. Free radical formation curve for irradiated polyethylene. Curve A at −196°C by electron irradiation. Curve B for the $-CH_2-\dot{C}H-CH=CH-CH_2-$ radical remaining on storage at room temperature. Curve C at room temperature by γ-irradiation. The ordinate scale for curve A is 10 times larger than that for curves B and C.

$\times 10^{-4}$ mol./g. for ○
$\times 10^{-5}$ mol./g. for △ and ×

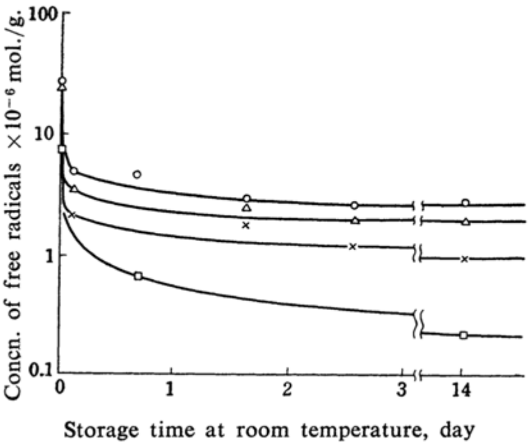

Fig. 4. Free radical decay curve at room temperature for polyethylene irradiated at −196°C with various doses.

—○— 100 Mrad —△— 60 Mrad
—×— 30 Mrad —□— 10 Mrad

Free Radical Formation Curve. — The concentration of free radicals produced by irradiation at −196°C was plotted against the dosage (see Fig. 3 curve A). The curve does not make a straight line, in contrast with the expectation based on a complete trapping of the primary radical at −196°C. This deviation from linearity might suggest that one part of the primary radicals, FR_{VI} showing the broad sextet in our case, reacts during irradiation even at −196°C. This component of FR_{VI} will be referred to as FR^{i}_{VI} (FR_{VI} reacting instantaneously at −196°C) in this paper. The occurrence of the reaction of FR^{i}_{VI} at −196°C might not be unreasonable in view of the fact that most FR_{VI}'s were produced by irradiation in close proximity and also that probably most of them were in 'hot' states.

The decay curve at room temperature is shown in Fig. 4 for samples irradiated with various doses at −196°C (cf. Fig. 2). It shows a quick decay of FR_{VI} and long life-time for the remaining FR_{VII}. This result can be interpreted to show that the free radicals in irradiated PE at −196°C consisted of about 90% FR_{VI} and 10% FR_{VII}. The concentration of the remaining FR_{VII} was plotted against the dosage in Fig. 3 (curve B). It should be noted that the decay curve given in Fig. 4 was for that in vacuo; the evolved hydrogen gas had been removed by reevacuation at −196°C. If the evolved gas was not removed, the decay of FR_{VI} and also of FR_{VII} were accelerated to a small but definite extent, showing a possibility of the backreaction of H_2 with the radicals.

The G_R values were estimated from the initial slope of the formation curve. G_R(total) was found to be 6.4 from curve A, and $G_R(FR_{VII})$ was 0.31 from curve B. It is assumed that $G_R(FR_{VI})=G_R(\text{total})-G_R(FR_{VII})=6.1$. Lawton et al.⁴⁾ obtained $G_R=3.6$ at −196°C calculated at a dose of 40 Mrad. If we calculate the value at the dose of 40 Mrad, where the formation curve deviates from the straight line of slope $G_R=6.4$, our result gives a value of 4.6. Voevodsky et al.³⁾ gave a value of 2.9 ± 0.6 for FR_{VI} at 178°K and 0.16 for FR_{VII} at 323°K. The G_R value, estimated by the scavenger method for the lower aliphatic hydrocarbons¹⁵⁾, ranged from 6 to 8. This range is very close to that for irradiated PE at −196°C and shows that the yield of primary radicals in low and high molecular hydrocarbons is nearly the same.

In Fig. 3 the formation curve in the case of γ-irradiation at room temperatures¹²⁾ is shown for comparison (curve C). The G_R value 1.6 estimated from the initial slope corresponds almost exactly to that for FR_{VI}, and the value 0.09 determined from the slope of the curve in the intermediate dose ranges (10∼100 Mrad), to that for FR_{VII}.

The difference between the straight line with the slope $G_R=6.4$ and the experimentally obtained curve A will correspond to the FR^{i}_{VI} disappearing during irradiation at −196°C. The G_R value for FR^{i}_{VI} was calculated from the amount of deviation to be 2.2 at a dose of 50 Mrad. Therefore, the G_R value for FR_{VI} reacting on being warmed to room temperature should be $G_R(FR_{VI})-G_R(FR^{i}_{VI})=4$. The G_R

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15) See, for example, A. J. Swarrow, " Radiation Chemistry of Organic Compounds ", Pergamon Press, New York (1960), p. 19.

TABLE I. ESTIMATED *G* VALUE

$-CH_2-\dot{C}H-CH_2-$	6.1 (LN)	1.6 (RT)
$-CH_2-\dot{C}H-CH=CH-CH_2-$	0.31 (LN)	0.09 (RT)
$(-CH_2-\dot{C}H-CH_2-)_{\text{Inst}}$	2.2 (LN)*	
Instantaneous crosslinking	1.1 (LN)*	(=2.2/2)
Crosslinking on warming to room temperature	2.0**	$(=1/2(6.1-1.1))$
Total crosslinking	3 (RT)	$(=6.1/2=1.1+2.0)$

* The $-CH_2-\dot{C}H-CH_2-$ radical reacting and disappearing instantaneously during irradiation at −196°C. Estimated from the deviation from linearity in the formation curve at a dose of 50 Mard. *G* (crosslinking) was estimated from G_R $(-CH_2-\dot{C}H-CH_2-)/2$.

** Estimated from the $G_R(-CH_2-\dot{C}H-CH_2-)$ value corresponding to the radical disappearing on warming the sample from −196°C to room temperature.

LN: Liquid nitrogen temperature. RT: Room temperature.

TABLE II. CONCENTRATION OF FREE RADICALS PRODUCED ON 'REIRRADIATION' WITH 30 MRAD AT −196°C

Preirradiation dose (Mrad)	Immediately after irradiation at −196°C*	$-CH_2-\dot{C}H-CH=CH-CH_2-$**
0	1.6×10^{-4} mol./g.	9.6×10^{-6} mol./g.
10	1.2×10^{-4}	8.9×10^{-6}
30	1.3×10^{-4}	9.0×10^{-6}
60	1.3×10^{-4}	1.3×10^{-5}
100	1.1×10^{-4}	1.1×10^{-5}
3000	1.2×10^{-4}	3.5×10^{-5}***

* $-CH_2-\dot{C}H-CH_2-$ + $-CH_2-\dot{C}H-CH=CH-CH_2-$. Corresponds nearly to $-CH_2-\dot{C}H-CH_2-$ except in the case of 3000 Mrad.

** Remaining component on storage of the samples at room temperature for a week or more.

*** Corresponds to polyenyl radical. Concentration of the $-CH_2-\dot{C}H-CH_2-$ radical 8.8×10^{-5} mol./g.

values obtained in the present investigation are summarized in Table I.

Formation of $-CH_2-\dot{C}H-CH=CH-CH_2-$ Radical.—The $G_R(FR_{VII})$ was found to be 0.31 for electron irradiation at −196°C and 0.09 for γ-irradiation at room temperature. The difference in the values might be due to the decay of FR_{VII} in the presence of evolved H_2 during irradiation, since γ-irradiation takes more time than electron irradiation. On the other hand, it is a well-known fact that irradiation produces a transvinylene group in PE. The *G* value was estimated to be 2.2 by Dole et al.[16] Comparing the values, it may be concluded that FR_{VII} is produced to a lesser extent, about $0.31/2.2=0.14$, than the unsaturated group.

As for the mechanism of FR_{VII} formation, we do not yet have any definite picture. Several possible mechanisms will now be discussed, however,

1) Free radical migration such as

$$-CH_2-\dot{C}H-CH_2-\cdots\cdots-CH_2-CH=CH-$$
$$\rightarrow -CH_2-CH_2-CH_2-\cdots\cdots-\dot{C}H-CH=CH-$$

This mechanism might be essentially the same as that suggested by Voevodsky et al.[3], who had some experimental evidence that 'reirradiation' increased the $G_R(FR_{VII})$ to 3.2. Our result does not seem to support this mechanism strongly. First, FR_{VII} is produced in only 14% of the unsaturated group, as is stated above. Secondly, our results of the reirradiation experiment, summarized in Table II, cannot be interpreted to show that free radical migration is a predominant mechanism for FR_{VII} formation. As the preirradiation dose increased, more unsaturated groups existed in the irradiated polymer. Therefore, on reirradiation at the same dose (30 Mrad), samples preirradiated at higher doses should have a higher FR_{VII} concentration if the migration mechanism prevailed. The results given in Table II show a tendency toward a slightly increasing concentration of FR_{VII}, but it is not certain that the data provide strong evidence for mechanism 1. The

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[16] M. Dole, D. C. Milner and T. F. Williams, *J. Am. Chem. Soc.*, **80**, 1580 (1958).

spectrum obtained from the reirradiated samples was more or less the same as that from the virgin sample except one preirradiated with 3000 Mrad (see Fig. 5). PE irradiated with 3000 Mrad had shown a singlet spectrum. On reirradiation at −196°C with 30 Mrad, the sample (Sample I) gave the spectrum as shown in Fig. 5 (2A), with somewhat different features from those preirradiated with 0 to 100 Mrad. Immediately after being warmed to room temperature, Sample I gave only singlet spectrum (Fig. 5 (2B)). The subtracted curve (A–B) was almost a sextet. That conjugated double bond which exists in Sample I might have something to do with the different features observed.

2) Hydrogen abstraction; $-CH_2-CH=CH- + H \longrightarrow -\dot{C}H-CH=CH- + H_2$. This reaction requires an activation energy of the order of 5 kcal./mol.[17] and hence does not seem to occur easily at −196°C or at room temperature. Hot H atoms could abstract combined H to form FR_{VII} and H_2 even at −196°C, but the probability of H atoms finding double bonds before they cooled or before other reactions, such as the abstraction of H from the neighboring $-CH_2-CH_2-CH_2-$ chain, had occurred, would seem to be very small. Mechanism 3 may also be mentioned as possible:

$$-CH_2-CH_2-CH_2-CH_2-$$
$$\rightsquigarrow (-CH_2-\dot{C}H-CH_2-CH_2-)_{hot}$$
$$\longrightarrow -CH_2-\dot{C}H-CH=CH- + H_2$$

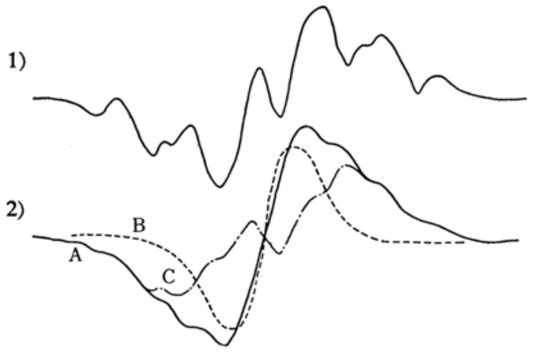

Fig. 5. Spectrum of polyethylene 'reirradiated' with 30 Mrad at −196°C. 1) For sample preirradiated with 100 Mrad. 2) For sample preirradiated with 3000 Mrad. A: Immediately after irradiation. B: After storage at room temperature for 25 min., spectrum being recorded at −196°C. C: Subtracted curve A–B, showing the decayed component to be nearly a sextet spectrum.

or

$$-CH_2-CH_2-CH_2-CH_2-$$
$$\rightsquigarrow -CH_2-\overset{+}{C}H-CH_2-CH_2- + H + e$$
$$-CH_2-\overset{+}{C}H-CH_2-CH_2-$$
$$\longrightarrow -CH_2-\overset{+}{C}H-CH=CH- + H_2$$
$$-CH_2-\overset{+}{C}H-CH=CH- + e$$
$$\longrightarrow -CH_2-\dot{C}H-CH=CH-$$

The molecular elimination reaction of H_2 from the thermal $-CH_2-\dot{C}H-CH_2-CH_2-$ radical requires an activation energy of about 30 kcal./mol.[18] Some hot radicals could overcome the barrier and could produce FR_{VII} even at −196°C.

Other mechanisms than these three could be thought of, but as yet we have no experimental background available for further discussion.

Radiation Chemical Process in Polyethylene; a Concluding Remark.—The present ESR result could be interpreted to suggest the following features of the radiation chemical process in PE. Primarily irradiation produces the $-CH_2-\dot{C}H-CH-$ radicals (FR_{VI}) clustered in a spur with a G value of 6.4; it also produces the trans-vinylene unsaturated group by the molecular H_2 detatchment process with a G value of 2.2. The $-CH_2-\dot{C}H-CH_2-$ radicals are 'hot', and the excess energy might distribute over a certain range. Most of the $-CH_2-\dot{C}H-CH_2-$ radicals are produced in close proximity, giving the broad sextet spectrum, and the distance distribution among the radicals might be given by a certain function. The excess energy of the hot radicals would cool very rapidly ($\sim 10^{-12}$ sec.). Some hot radicals with sufficient excess energy decompose before cooling to give $-CH_2-\dot{C}H-CH=CH-$ and H_2, with a G value of 0.31. Other hot radicals located very closely within a certain range can react with each other during irradiation even at −196°C and form crosslinks. The rest of the hot radicals will only cool without reacting and so be trapped. They will, however, react to form crosslinks as the temperature is raised. Thus the reaction process can be represented as:

$$-CH_2-CH_2-CH_2-CH_2-$$
$$\underset{G=6.4}{\overset{1)}{\rightsquigarrow}} (-CH_2-\dot{C}H-CH_2-CH_2-)_{hot} + H$$
$$\underset{G=2.2}{\overset{2)}{\rightsquigarrow}} -CH_2-CH=CH-CH_2- + H_2$$
$$(-CH_2-\dot{C}H-CH_2-CH_2-)_{hot}$$

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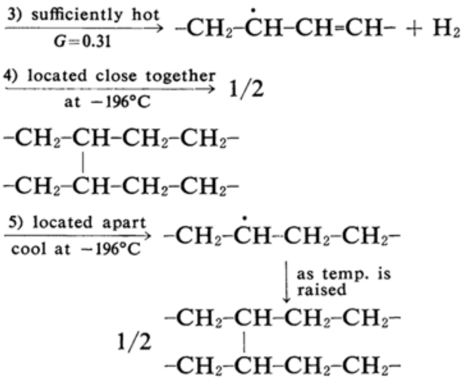
[17] See, for example, E. W. R. Steacie, "Atomic and Free Radical Reactions", 2nd Ed. Vol. 1, Reinhold Publishing Corporation, New York (1954).

[18] A. S. Gordon and S. R. Smith, *J. Chem. Phys.*, **34**, 331 (1961).



$$\xrightarrow[G=0.31]{\text{3) sufficiently hot}} -CH_2-\dot{C}H-CH=CH- + H_2$$

$$\xrightarrow[\text{at }-196^\circ\text{C}]{\text{4) located close together}} 1/2 \begin{array}{l} -CH_2-CH-CH_2-CH_2- \\ \qquad\quad\ \ | \\ -CH_2-CH-CH_2-CH_2- \end{array}$$

$$\xrightarrow[\text{cool at }-196^\circ\text{C}]{\text{5) located apart}} -CH_2-\dot{C}H-CH_2-CH_2- \xrightarrow{\text{as temp. is raised}} 1/2 \begin{array}{l} -CH_2-CH-CH_2-CH_2- \\ \qquad\quad\ \ | \\ -CH_2-CH-CH_2-CH_2- \end{array}$$

The G value for the instantaneous crosslinking at -196°C (Eq. 4) can be calculated from $G_R(FR^i_{VI})$ divided by 2 and so becomes 1.1. The G value for crosslinking (G(X)) resulted from being warmed to room temperature (Eq. 5) is calculated to $1/2(G_R(FR_{VI})-G_R(FR^i_{VI}))=2$. On irradiation at room temperature the G(X) will then become $2+1.1=3.1$.

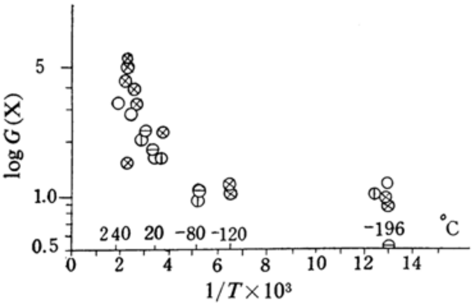


Fig. 6. An Arrhenius plot of the crosslinking yields obtained by various authors, compiled by A. Chapiro[19].

⊖ Black 1956
⊗ Charlesby Davison 1957
⦶ Pravednikov Medvedev 1958
○ Lawton et al. 1958

Comparing the crosslinking G value expected from the present ESR result with those obtained experimentally by several other authors, the agreement is found to be satisfactory. Chapiro[19] has summarized the G(X) values by several authors as in Fig. 6. The data show the G(X) at -196°C to be nearly 1 and the value at 40°C to be 3, in agreement with the present suggestion. Such agreement may well show the reasonableness of the present picture of the radiation chemistry of PE. As Fig. 6 suggests, the crosslinking reaction below -40°C proceeds with an activation energy of nearly zero. In order to explain this particular nature of the crosslinking reaction, some authors have suggested an 'ionic' mechanism[19,20]. Pravednikov et al.[21], on the other hand, proposed a 'hot' radical mechanism. Our result is in favor of the latter opinion. Production of the 'hot' $-CH_2-\dot{C}H-CH_2-$ radicals in close proximity is a characteristic of chemical reaction caused by ionizing radiation. They cannot react with oxygen, as has been revealed by us[22], and cannot react with radical scavengers such as DPPH, because, before the arrival of such scavengers, they react with each other almost instantaneously. The $-CH_2-\dot{C}H-CH_2-$ radicals produced apart from each other or diffused out of the spur, thus making 'background' radicals in Magee's sense[23], behave in a way similar to the so-called free radical reaction or photochemical reaction. They may react with oxygen or radical scavengers.

In irradiated poly(vinyl chloride)[24], poly(vinyl alchohol)[12], and nylon[12], the free radical formation curves deviated from straight line in a way quite similar to that of PE. This might suggest, as in the case of PE, the occurrence of the reaction of some hot radicals at -196°C. The G_R values were estimated from the initial slope to be 7.1, 8.0 and 10 respectively, Irradiated polypropylene[25] was an exceptional case where the free radical formation curve at -196°C was nearly a straight line ($G_R=6.2$) up to 100 Mrad, showing an almost complete trapping of the primary radicals. This rather exceptional behavior might have something to do with the shrinkage of the spiral main chain on scission.

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