

ESR Study of Radiation-induced Solid State Polymerization of Conjugated Dienes

By

Keiji TAKEDA*, Hiroshi YOSHIDA**, Koichiro HAYASHI*
and Seizo OKAMURA*

(Received December 17, 1965)

ESR spectra of free radicals formed from isoprene, 1,3-pentadiene and 2,3-dimethyl-1,3-butadiene were studied at -196°C . Free radicals were formed by several ways, i.e. electron-irradiation, reaction with $\text{HO}\cdot$ and $\text{CH}_3\cdot$ radicals and ultraviolet-irradiation at -196°C . The structure of trapped free radicals formed by electron-irradiation are quite different from that of radicals formed by radical reactions. The mechanism of radiation-induced solid state polymerization is discussed. It is concluded that the trapped free radical formed by radiation is not the propagating radical but an inactive radical end which is formed in the ionic propagation process initiated by an ion-radical.

1. Introduction

Many ESR studies have been so far made on the radiation-induced post-polymerization of acrylamide¹⁻⁵), methacrylamide^{4,5}), acrylic acid⁹) and metal salts of acrylic and methacrylic acids⁶⁻⁸) in the solid state at relatively high temperatures. It was found, for some monomers, that the trapped free radicals at low temperature were formed by addition of a hydrogen atom to monomer molecules and they initiated the post polymerization with rising temperature^{7,9}). On the other hand, the radiation-induced polymerization of acrylonitrile at low temperature was also studied^{10,11}) and non-radical mechanism was proposed, although free radicals were trapped in the polymerizing system¹¹). No definite conclusion was attained on the correlation between the observed free radicals and the active centers responsible for the polymerization reaction. Hirschberger et al reported that the radiation-induced solid state polymerization of isoprene proceeded with the ionic mechanism at low temperature¹²), but its initiation process was not clear. In the present investigation, ESR spectra of free radicals formed from monomers, isoprene,

* Department of Polymer Chemistry

** Research Reactor Institute

1,3-pentadiene and 2,3-dimethyl-1,3-butadiene, at -196°C were studied. Free radicals were formed by the following ways;

- (a) by irradiating monomers with fast electrons,
- (b) by reaction of monomers with $\text{HO}\cdot$ radicals,
- (c) by reaction of monomers with $\text{CH}_3\cdot$ radicals,
- (d) by irradiating monomers with ultraviolet rays.

In the way (a), the reactions involved may be both radical and ionic ones, while they are confined to radical reactions in (b), (c) and (d). As dienes are poly-functional monomers, the type of resulting free radicals may depend upon their formation reactions. By comparing the free radicals in (a) with those in (b), (c) and (d), the reaction mechanism of the radiation-induced solid state polymerization of dienes are discussed.

2. Experimental

Materials.—Isoprene and 1,3-pentadiene obtained commercially were washed by aqueous solution of sodium hydroxide and then pure water. They were dried with calcium chloride and purified repeatedly by fractional distillation in nitrogen atmosphere. 2,3-Dimethyl-1,3-butadiene was synthesised from magnesium and acetone through pinacol¹⁹, and then purified by fractional distillation. The impurities in monomers were examined by gas chromatography, being very little.

Irradiation with fast electrons.—Monomers were sealed in a glass ampoule in vacuum of about 10^{-3} mm Hg, and irradiated at -196°C by Van de Graaff accelerator (1.5 Mev), with the dose of about 10^6 r. (1.5×10^5 r/sec)

Reaction of monomers with $\text{HO}\cdot$ radicals.—Monomers mixed with a small amount of tert-butyl hydroperoxide were sealed in a quartz ampoule in vacuum, which are photo-irradiated at -196°C by a high pressure mercury arc. $\text{HO}\cdot$ radicals were formed by photolysis of the peroxide and they reacted with the monomers. The emission spectra of the mercury arc spread widely from 3000\AA to visible region. When monomers were irradiated without peroxide, no ESR signal was observed. This indicates that monomers are not photolysed directly.

Reaction of monomers with $\text{CH}_3\cdot$ radicals.—Monomers were mixed with a small amount of methyl iodide and irradiated by high pressure mercury arc in the same way as (c). $\text{CH}_3\cdot$ radicals were formed by photolysis of methyl iodide and reacted with the monomers.

Irradiation with ultraviolet rays.—Monomers were sealed in a quartz ampoule in vacuum and irradiated at -196°C by ultraviolet rays from a

medium pressure mercury arc, which emitted mostly the rays of 2537Å wave length.

ESR measurements.—All ESR spectra were recorded at -196°C after irradiation, with the field modulation frequency of 100 Kc. By electron-irradiation, ESR signals were also produced from irradiated glass ampoule. In order to eliminate the contribution of the ampoul signal, it was subtracted from the overlapping signals from both free radicals in question and the ampoule. By ultraviolet and photo-irradiation the signal from the quartz tube was much weaker than that from monomers.

Measurements of the polymer yield and effects of inhibitors of polymerization.—Monomers were sealed in a glass tube in vacuum. After the irradiation with electrons at -196°C , the sample was warmed quickly to room temperature and unreacted monomer was distilled out in vacuum. The residue was weighed as the polymer yield. In order to examine the mechanism of polymerization, radical inhibitor (1,1-diphenyl-2-picryl hydrazyl, or DPPH) and ionic inhibitor (diethylamine) are mixed in monomers. Conversion of polymerization was compared with that of bulk monomers.

3. Relation between the Concentration of Trapped Radicals and Conversion of Polymerization

As shown in Fig. 1, the concentration of free radicals formed and trapped in the solid monomer at -196°C and the conversion of polymerization increase proportionally with the increasing doses of electron-irradiation. This finding indicates that the observed free radicals have a intimate correlation with the polymerization reactions. As the trapped free radicals are very stable at -196°C , no recombination reaction takes place between free radicals at this temperature.

4. Effect of Inhibitors on the Conversion of Polymerization

The effects of inhibitors are shown in Table 1. DPPH gives no inhibiting

Table 1. The effect of inhibitors on the conversion of radiation-induced polymerization at -196°C . (total dose is 4.5×10^7 r.)

inhibitor	conversion of polymerization		
	isoprene	pentadiene	dimethylbutadiene
none	7.9%	6.8%	0.6%
DPPH (1.5 wt.%)	8.7%	8.1%	1.3%
diethylamine (5 wt.%)	—	4.9%	0.5%

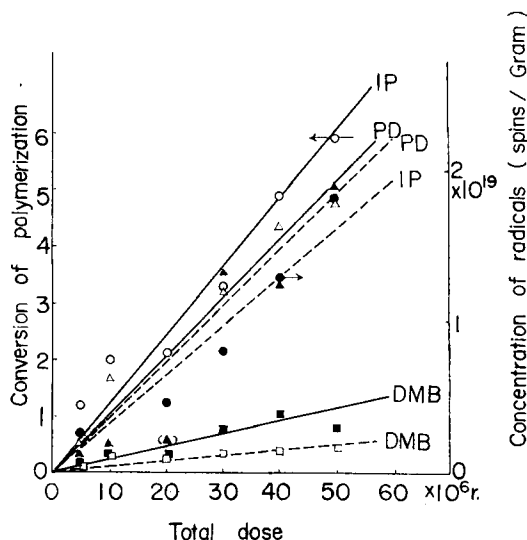


Fig. 1. Variation of conversion of polymerization and concentration of trapped free radicals of dienes with electron-irradiation dose at -196°C . (dose rate 1.5×10^6 r/sec)

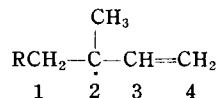
(○) isoprene (IP), (△) pentadiene (PD), (■) dimethylbutadiene (DMB). The solid line is the conversion and dotted line is the concentration of trapped free radicals.

effect but a slight accelerating effect to the polymerization of all monomers. Diethylamine has a slight inhibiting effect on the rate of polymerization.

5. Assignment of ESR Spectra

(1) Isoprene

Electron-irradiation.—The ESR spectrum of the trapped free radical in isoprene irradiated by electrons at -196°C is shown in Fig. 2(a). The spectrum consists of equidistant seven lines and its hyperfine coupling constant is about 14 Gauss. Therefore six equivalent protons contribute to the hyperfine structure of the spectrum. The coupling constant, 14 Gauss, shows that the trapped free radicals are allylic ones and the spectrum is assigned to the free radicals,



It looks like a free radical formed by addition of alkyl radical, R·, to the 1-position of isoprene. The spin density in an allylic radical is 0.62 on the

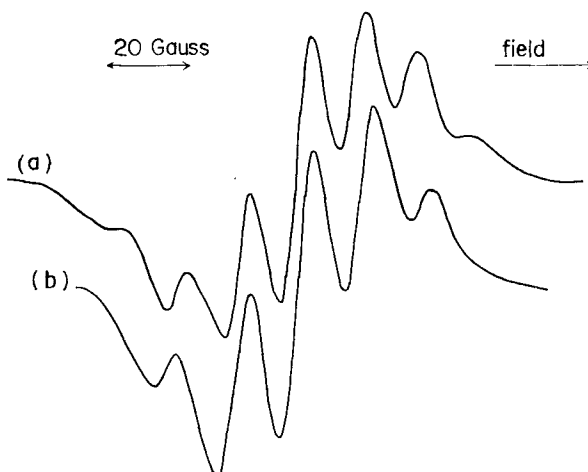


Fig. 2. ESR spectra of isoprene, measured at -196°C , (a) electron-irradiated to 3.15×10^6 r. at -196°C by Van de Graaff accelerator (dose rate 1.5×10^5 r/sec), (b) photo-irradiated with a small amount of methyl iodide for 4 hours at -196°C by high pressure mercury arc.

end carbon atoms and -0.24 on the central carbon atom¹⁴). From these values and the following equation¹⁵,

$$a_{\text{H}\alpha} = Q_{\alpha}\rho \quad (1)$$

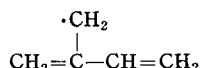
where a constant, Q_{α} , is 23 Gauss¹⁶), the coupling constant of the proton on the 3-carbon and 4-carbon atom is about 5 Gauss and 14 Gauss, respectively. The coupling constant of β -protons is expressed by the equation,

$$a_{\text{H}\beta} = Q_{\beta}\rho \cos^2 \theta \quad (2)$$

where a constant, Q_{β} , is about 50 Gauss¹⁷) and θ is an angle between the 1-carbon atom-H bond and p_z orbital of the odd electron, when seen from the direction of the 1-carbon-2-carbon bond. By assuming that the methyl group is rotating rapidly, its three protons are equivalent and have a coupling constant of about 15 Gauss. The coupling constants of each proton on the 1-carbon are 15 Gauss and 2 Gauss respectively, corresponding to the values of $\theta_1=45^{\circ}$ and $\theta_2=75^{\circ}$. Considering these values, the septet spectrum with a coupling constant of 15 Gauss is expected. Alternatively the septet spectrum would be attributed to the free radicals formed by addition of a hydrogen atom to the 4-carbon atom of isoprene. However, this is improbable from an energetical consideration.

Reaction with $\text{HO}\cdot$ radicals.—After the reaction with $\text{HO}\cdot$ radicals at

−196°C, isoprene gives an ESR spectrum consisted of 5 lines of a coupling constant 14 Gauss. The asymmetry of the spectrum may be caused by the spectrum from peroxy radicals overlapping on the quintet one. But the peroxy radical spectrum can be isolated with the power saturation technique, because the hydrocarbon radical has a longer spin lattice relaxation time than the oxy-radical. Considering the observed coupling constant of 14 Gauss, the trapped free radicals are also allylic, in which four equivalent protons are involved. Therefore, the spectrum is assigned to the hydrogen atom-deficient radical,



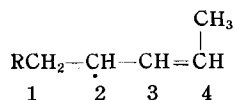
formed by the abstraction of a hydrogen atom from the methyl group.

Reaction with $\text{CH}_3\cdot$ radicals.—After reacting with $\text{CH}_3\cdot$ radicals, isoprene gives a quintet spectrum as shown in Fig. 2 (b). The spectrum is assigned to the same free radicals as those formed by $\text{HO}\cdot$ radicals.

Irradiation with ultraviolet rays.—Isoprene irradiated by ultraviolet rays gives the same ESR spectrum as shown in Fig. 2 (b). It is assigned to the same hydrogen atom-deficient radical.

(2) 1,3-Pentadiene

Electron-irradiation.—1,3-Pentadiene irradiated by electrons gives a spectrum shown in Fig. 3 (a). The spectrum consists of eight lines with a coupling constant 14 Gauss. The trapped free radical is an allylic one, having seven equivalent protons as following,



This looks like a type of free radicals formed by addition of an alkyl radical, $\text{R}\cdot$, to the 1-position of pentadiene. Two protons on the 1-carbon atom are equivalent, giving a coupling constants of 15 Gauss.

Reaction with $\text{HO}\cdot$ radicals.—The spectrum, as shown in Fig. 3 (b) are observed from the reaction between 1,3-pentadiene and $\text{HO}\cdot$ radicals. The sample being warmed from −196°C to the melting point, showed no change of the spectral shape. Therefore, it may be only one radical species which gives the complex spectra. The spectra are composed of overlapping two spectra;

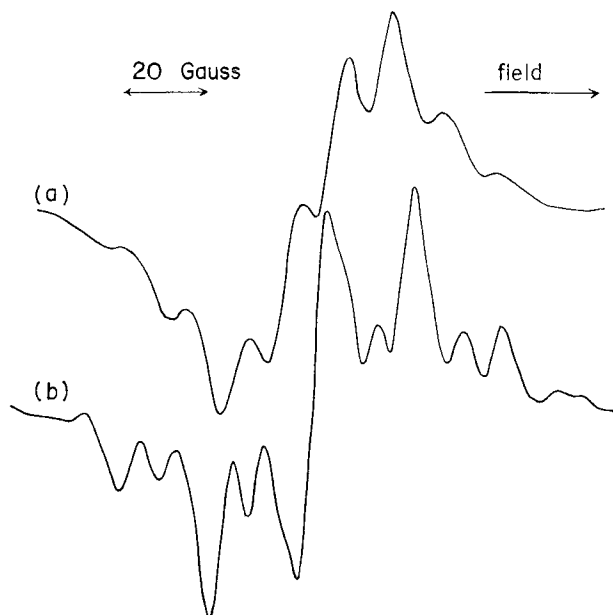
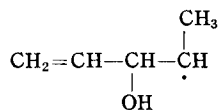


Fig. 3. ESR spectra of 1,3-pentadiene, measured at -196°C , (a) electron-irradiated to $3.15 \times 10^6 \text{r.}$ at -196°C by Van de Graaff accelerator (dose rate $1.5 \times 10^3 \text{r./sec}$), (b) photo-irradiated with a small amount of tert-butyl hydroperoxide for 5 hours at -196°C by high pressure mercury arc.

(A) a quintet with a coupling constant about 22 Gauss,

(B) a sextet with a coupling constant about 22 Gauss.

This value of the coupling constant 22 Gauss indicates that the trapped free radical is not an allylic or dienyl ones, but an saturated free radical. Therefore, the spectra are assigned to the radical as following,



This is formed by addition of $\text{HO}\cdot$ radical or propagating radical, $\text{R}\cdot$, to the 3-carbon atom of pentadiene. The spectral shape of the above free radicals depends on the rotational conformation along the 3-carbon-4-carbon atom bonding. The coupling constant of the proton on the 3-carbon atom is determined according the equation (2), being 22 Gauss for $\theta=47^{\circ}$. and less for $\theta \gg 47^{\circ}$. By assuming the free rotation of the methyl group, three methyl protons are equevalent, giving the same coupling constant of about 23 Gauss. Therefore two spectra result from two rotational isomers of the radical;

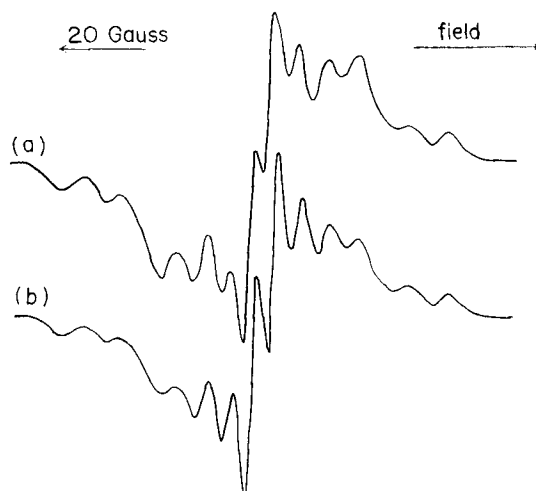


Fig. 4. ESR spectra of 1,3-pentadiene, ultraviolet-irradiated for (a) 2 hours and (b) 4 hours at -196°C by medium pressure mercury arc and measured at -196°C .

(A) a quintet for $\theta \gg 47^{\circ}$,

(B) a sextet for $\theta \approx 47^{\circ}$.

The overlapping of these spectra gives the recorded spectral shape.

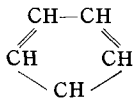
Reaction with $\text{CH}_3\cdot$ radicals.—The ESR spectrum, observed from the reaction of $\text{CH}_3\cdot$ radicals with pentadiene, is complex and cannot be assigned.

Irradiation with ultraviolet rays.—Pentadiene, irradiated with ultraviolet rays, gives the spectrum shown in Fig. 4. The spectral shape depends on the irradiation time. This fact shows that the recorded spectral line are composed of two overlapping spectra corresponding to different radical species;

(A) the same spectrum to that observed from the reaction with $\text{HO}\cdot$,

(B) a sextet with a coupling constant about 6 Gauss.

The spectrum (A) is assigned to the free radical formed by addition of some primary radicals to the 3-carbon atom of pentadiene. The spectrum (B) is assigned to the cyclopentadienyl radical¹⁸⁾,



(3) 2,3-Dimethyl-1,3-butadiene

Electron-irradiation.—The spectrum, observed for the electron-irradia-

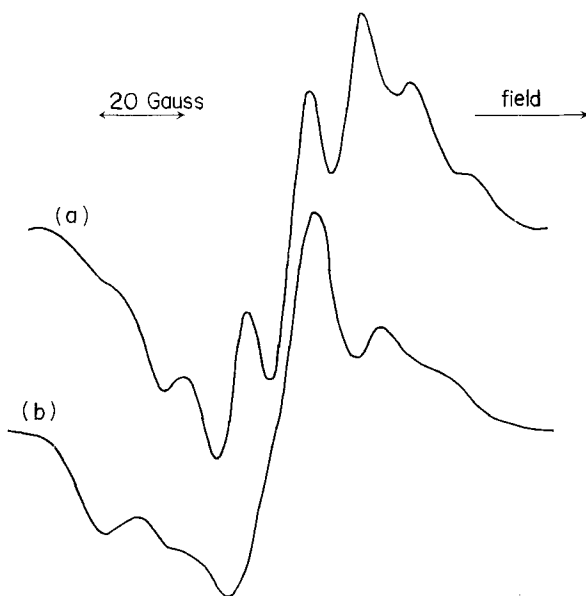
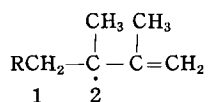


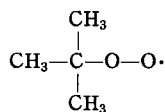
Fig. 5 (a). ESR spectrum of 2,3-dimethyl-1,3-butadiene, electron-irradiated to 3.15×10^6 r. at -196°C (dose rate 1.5×10^5 r./sec) by van de Graaff accelerator and measured at -196°C .
 (b). ESR spectrum of dimethylbutadiene-tert-butyl-hydroperoxide solution, photo-irradiated for 5 hours at -196°C by high pressure mercury arc and measured at -196°C . (The horizontal position of this spectrum is arbitrary.)

tion of dimethyl butadiene is composed of seven lines of the coupling constant 14 Gauss, as shown in Fig. 5 (a). This is due to an allylic radical,

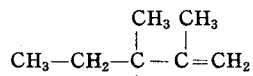


It looks like a free radical formed by addition of alkyl radical to the end carbon of the monomer. Here, only one of two protons on the 1-carbon atom couples with an odd electron, giving a coupling constant of 14 Gauss as the free radical formed from electron-irradiated isoprene.

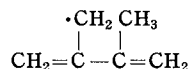
Reaction with $\text{HO}\cdot$ radicals.—Fig. 5 (b) shows the spectrum observed at -196°C from the photolysis of the solid solution of tert-butyl hydroperoxide in monomer. This spectrum is the same as that observed from the photolysis of pure peroxide. The spectrum may be due to the peroxy-radical, and no monomer radical is formed.



Reaction with $\text{CH}_3\cdot$ radicals.—Reacting with $\text{CH}_3\cdot$ radicals, dimethylbutadiene gives the same spectrum as that observed for electron-irradiation, shown in Fig. 5 (a). The spectrum is assigned to the free radicals formed by addition of methyl radicals to an end carbon atom of dimethylbutadiene,



Irradiation with ultraviolet rays.—The spectrum, observed for ultraviolet-irradiation of dimethylbutadiene, consists of a quintet with a coupling constant 14 Gauss. This is assigned to the radicals formed by loss of a methyl hydrogen atom,



6. Discussions

The structure of free radicals and the type of reactions, through which the radicals are formed, are summarized in Table 2. For isoprene and pentadiene, the structure of trapped free radicals formed by electron-irradiation is quite different from that of radicals formed by radical reactions. From these data, the characteristics of the radiation-induced reaction of monomers is discussed below, in contrast with radical reactions. Then the formation process of trapped free radicals by electron-irradiation is discussed, in relation to the polymerization mechanism.

(1) Isoprene

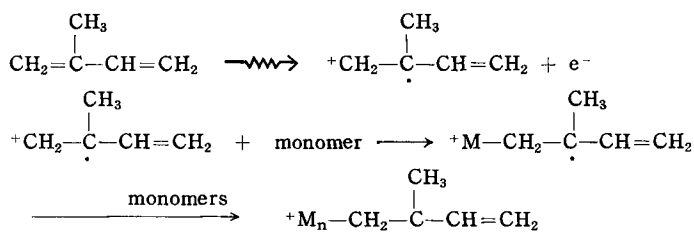
Free radicals such as $\text{HO}\cdot$ and $\text{CH}_3\cdot$ abstract a hydrogen atom from the methyl group of isoprene and no addition reaction occurs to the conjugated double bond. By ultraviolet-irradiation, also a hydrogen atom of the methyl group is abstracted. The reactions are probably radical ones, because no ionization following u. v.-irradiation occurs by light of the wave length 2537Å. It follows from these facts that the isoprene molecule loses a hydrogen atom of the methyl group by radical reactions.

On the other hand, the free radical formed by radiation gives such an ESR spectrum that is expected for a propagating chain end of radical polymerization. The propagating type free radical is not formed, however,

Table 2. The structure of trapped free radicals and the types of reactions of conjugated dienes.
(assigned from electron spin resonance spectra)

reaction method	isoprene	pentadiene	dimethyl-butadiene
	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \\ 1 \quad 2 \quad 3 \quad 4 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{CH}-\text{CH}=\text{CH} \\ 1 \quad 2 \quad 3 \quad 4 \end{array}$	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_2=\text{C}-\text{C}=\text{CH}_2 \\ 1 \quad 2 \end{array}$
electron-irradiation	R-addition type (1-carbon) $\begin{array}{c} \text{CH}_3 \\ \\ \text{RCH}_2-\dot{\text{C}}-\text{CH}=\text{CH}_2 \end{array}$	R-addition type (1-carbon) $\begin{array}{c} \text{CH}_3 \\ \\ \text{RCH}_2-\dot{\text{C}}\text{H}-\text{CH}=\text{CH} \end{array}$	R-addition type (1-carbon) $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{RCH}_2-\dot{\text{C}}-\text{C}=\text{CH}_2 \end{array}$
reaction with HO·	abstraction of H·atom $\begin{array}{c} \cdot\text{CH}_2 \\ \\ \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \end{array}$	addition of HO· (3-position) $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{CH}-\text{CH}-\dot{\text{C}}\text{H} \\ \\ \text{OH} \end{array}$	no radical observed
reaction with CH ₃ ·	abstraction of H·atom $\begin{array}{c} \cdot\text{CH}_2 \\ \\ \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \end{array}$	complicated spectra not to be assigned	addition of CH ₃ ·(1-position) $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{CH}_2-\dot{\text{C}}-\text{C}=\text{CH}_2 \end{array}$
ultraviolet-irradiation	loss of H·atom $\begin{array}{c} \cdot\text{CH}_2 \\ \\ \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \end{array}$	(A) addition of R·(3-position) $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{CH}-\text{CH}-\dot{\text{C}}\text{H} \\ \\ \text{R} \end{array}$ (B) $\begin{array}{c} \cdot\text{CH} \\ / \quad \backslash \\ \text{CH} \quad \text{CH} \\ \backslash \quad / \\ \text{CH}=\text{CH} \end{array}$	loss of H·atom $\begin{array}{c} \cdot\text{CH}_2 \quad \text{CH}_3 \\ \quad \\ \text{CH}_2=\text{C}-\text{C}=\text{CH}_2 \end{array}$

actually by addition of R· radical to isoprene, as R· radical probably abstracts a hydrogen atom from the methyl group of isoprene. Therefore, the trapped free radicals formed by electron-irradiation is formed through another process rather than the addition of R· radicals to the isoprene molecule. The process is probably an ion-molecule reaction involving an ion-radical as a reaction intermediate:

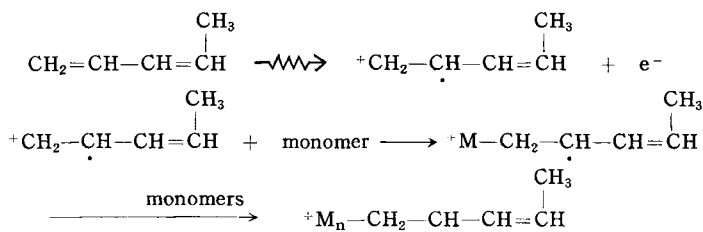


The ion-radical is primarily formed by loss of a π -electron from isoprene molecule by the effect of ionizing radiation. This molecule-ion then adds to a monomer and so initiates the polymerization from its ionic end. The radical end of parent ion-radical, so isolated from the ion end by ionic propagation, is thought to be unreactive at this temperature and trapped stable in solid monomer molecules. This unreactive radical gives the observed ESR spectrum.

(2) 1,3-Pentadiene

$\text{HO}\cdot$ radical adds to the 3-carbon atom of pentadiene. By ultraviolet irradiation, radicals are also formed by addition of some primary radical to 3-carbon atom. In addition to this, the cyclopentadienyl radical is formed probably by a photochemical process. It follows that radicals add to the 3-carbon atom of pentadiene.

On the other hand, the radical formed by electron-irradiation is quite different from that formed by radical reactions, giving an ESR spectrum expected for the radical of propagating end of radical polymerization. However, this radical is not identical to one formed by actual addition of $\text{R}\cdot$ radical to the 1-carbon of pentadiene as stated above. The radical is probably formed through the following mechanism similar to that of isoprene:



The radical thus trapped as an inactive end of an ion-radical gives the observed spectrum.

(3) 2,3-Dimethyl-1,3-butadiene

$\text{CH}_3\cdot$ radicals added to the 1-carbon atom of dimethylbutadiene. A hydrogen atom is lost from a methyl group of dimethylbutadiene by the

irradiation of ultraviolet rays. By electron-irradiation, the addition type radical is formed, as if an alkyl radical, $R\cdot$, adds to the 1-carbon of the monomer. In this case, it cannot be determined whether the radicals for electron-irradiation are formed by a similar ion-radical mechanism as that of isoprene and pentadiene or by actual addition of the propagating radical, $R\cdot$, to the monomer, as radicals such as $CH_3\cdot$ add to the 1-carbon atoms.

It is concluded, from the above discussions, that the trapped free radicals in electron-irradiated isoprene and pentadiene are inactive ones not involved in the propagating reaction. They are formed in the ionic polymerization process initiated by primary ion-radicals, though their ESR spectra are the same as those expected for the propagating free radical ends in the polymerization proceeded by the radical mechanism. In the proposed scheme, where the free radicals giving the observed ESR spectra are formed, only a cation is considered as an active species responsible for the polymerization reaction, but not an anion. It is not determined, however, which ion is responsible for the polymerization involved, at the present stage of research.

The effect of inhibitors of polymerizations, shown in Table 1, gives an evidence that the polymerization involved proceeds by ionic mechanism. The intimate correlation between the concentration of the trapped free radicals and the conversion of polymerization, shown in Fig. 1, may also support the proposed scheme of the reactions where one free radical end should correspond to one polymer chain.

Morawetz²⁾ and Ayscough²²⁾ proposed that the solid state polymerization of acrylamide²⁾ and hexadecene-1²²⁾ might involve radical-ions, though the definite conclusion has not yet been attained by ESR. Wagner et al¹⁹⁻²¹⁾ found in their research on the radiolysis of olefins, that radical-cations are primarily formed and radical ends are separated from cation ends by addition reactions. In the present research, radical-ions primarily formed were not observed by ESR. This indicates that the radical-ions are unstable and reactive even at -196°C .

References

- 1) T. A. Fadner, I. Rubin, H. Morawetz, *J. Polymer Sci.*, **37**, 549 (1959).
- 2) T. A. Fadner, H. Morawetz, *ibid*, **45**, 475 (1960).
- 3) B. Baysal, G. Adler, D. Ballantine, P. Colombo, *ibid*, **44**, 117 (1960).
- 4) G. Adler, D. Ballantine, B. Baysal, *ibid*, **48**, 195 (1960).
- 5) H. Ueda, Z. Kuri, *ibid*, **61**, 333 (1962).
- 6) H. Morawetz, I. D. Rubin, *ibid*, **57**, 669 (1962).
- 7) J. H. O'Donnell, B. McGarvey, H. Morawetz, *J. Am. Chem. Soc.*, **86**, 2322 (1964).
- 8) J. B. Lando, H. Morawetz, *J. Polymer Sci.*, **C**, No. 4, 789 (1964).

- 9) Y. Shioji, S. Ohnishi, I. Nitta, *ibid*, **A1**, 3373 (1963).
- 10) R. Bensasson, R. Marx, *ibid*, **48**, 53 (1960).
- 11) I. M. Barkalov, V. I. Coldanskii, N. S. Enikolopyan, S. F. Terekhova, G. M. Trofimova, *ibid*, **C**, No. 4, 897 (1964).
- 12) A. Hirschberger, J. Marchal, *Compt. rend.*, **358**, 2329 (1964).
- 13) *Org. Synth.*, *Coll. Vol.* **1**, 459, **3**, 312.
- 14) H. C. Lefkvitz, J. Fain, F. A. Matsen, *J. Chem. Phys.*, **23**, 1690 (1955).
- 15) H. M. McConnell, D. B. Chesnut, *ibid*, **27**, 984 (1957), **28**, 107 (1958).
- 16) R. W. Fessenden, R. H. Schuler, *ibid*, **39**, 2147 (1963).
- 17) R. W. Fessenden, R. H. Schuler, *ibid*, **38**, 773 (1963).
- 18) S. Ohnishi, I. Nitta, *ibid*, **39**, 2848 (1963).
- 19) P. C. Chang, N. C. Yang, C. D. Wagner, *J. Am. Chem. Soc.*, **81**, 2060 (1959).
- 20) C. D. Wagner, *Tetrahedron* **14**, 164 (1961).
- 21) C. D. Wagner, *J. Phys. Chem.*, **65**, 2275 (1961).
- 22) P. B. Ayscough, A. P. McCann, C. Thomson, D. C. Walker, *Trans. Faraday Soc.*, **57**, 1487 (1961).