

## Mechanism of Discoloration of Irradiated Polyvinyl Chloride

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A number of researches have been done on the thermal decomposition<sup>1</sup> and radiolysis<sup>2</sup> of polyvinyl chloride (PVC). In thermally degraded PVC, discoloration arises from the formation of a conjugated double-bond system which presumably proceeds through the "zipper" mechanism of allyl-activated molecular elimination of hydrogen chloride.<sup>1</sup> On the other hand, for radiation-induced discoloration, Egorova et al.<sup>3</sup> have postulated the same mechanism. Winkler<sup>4</sup> has put forward a free-radical chain reaction, similar to the zipper mechanism, leading to a conjugated double-bond system. Miller<sup>5</sup> has suggested, in a study of postirradiation effects, a free-radical chain reaction initiated by  $-\text{CHCl}-\dot{\text{C}}\text{H}-\text{CHCl}-$  radical, supporting Winkler's view. Interpretations of experimental results differ somewhat among authors and the mechanism is still not completely understood.

This paper is concerned with the possibility of making a conclusive choice of the mechanism from a study of the free-radical chemistry of irradiated PVC. We employed chiefly the method of electron spin resonance (ESR), since it is very sensitive and also one of the most direct ways of investigating free radicals. Some optical measurements of discoloration of irradiated PVC have been carried out in connection with the behavior of free radicals. As one of the significant parameters for defining the mechanism, gas evolution from irradiated PVC with rising temperature was also measured.

Independently of our work, Gautron,<sup>6</sup> Lawton and Balwit,<sup>7</sup> Atchison,<sup>17</sup> and Loy<sup>8</sup> have very recently published papers on the radiation chemistry of PVC. It might be still of some significance, we suppose, to publish our independent results based on ESR, optical spectroscopy, and gas evolution measurement, with some additional new findings.

### Experimental

The sample was commercially available powder (Shinetsu Chemicals,  $P = 1100$ ). Films 40 to 50  $\mu$  in thickness were prepared by casting a 20% tetrahydrofuran solution on a glass plate. Residual solvent was removed by immersing in carbon disulfide for 4 days and then evacuating at 50°C.

In most cases irradiations were carried out *in vacuo* with 1.5 m.e.v. beams from a Van de Graaff accelerator in liquid nitrogen at doses of  $5 \times 10^6$  up to  $1 \times 10^8$  rad, in steps of  $2 \times 10^7$  rad. Some samples were irradiated with  $\gamma$ -rays from a 1000-c. cobalt-60 source at room temperature. Irradiation doses were measured by means of an air ionization chamber (Radcon, The Victoreen Instrument Co. Model 575) for  $\gamma$ -rays, and a calorimeter especially constructed for electron beams.

ESR measurements were made at  $-196^\circ\text{C}$ . with a standard Varian Model V4500 spectrometer operated at 9400 Mcycles. In order to follow subsequent radical reactions with rising temperature, samples were stored at a certain temperature for a certain period of time and then ESR spectra were measured at  $-196^\circ\text{C}$ .

An ultraviolet and visible spectrometer (Hitachi Model EPS-2) was used to detect color and its changes with rising temperature *in vacuo* on specimen irradiated in a specially designed cell at  $-196^\circ\text{C}$ . In particular, a detailed investigation of discoloration on warming to room temperature of specimens irradiated at  $-196^\circ\text{C}$ . was carried out, and the results were compared with ESR results.

A qualitative and quantitative analysis of gas evolution, which associates with radical reactions and discoloration, was made with rising temperature by the use of a mercury manometer and mass spectrometer (Hitachi Model RMU-5). Thus, after irradiation at  $-196^\circ\text{C}$ ., the sample cell

equipped with a manometer was allowed to effect a gradual temperature rise.

## Results and Discussion

### Change of ESR Spectrum with Rising Temperature

The ESR spectra of PVC irradiated at room temperature or at  $-196^{\circ}\text{C}$ . have been reported by several authors<sup>9-12</sup> to have similar singlet shapes and to show some trace of hyperfine structure (hfs). Our result with PVC irradiated at  $-196^{\circ}\text{C}$ .

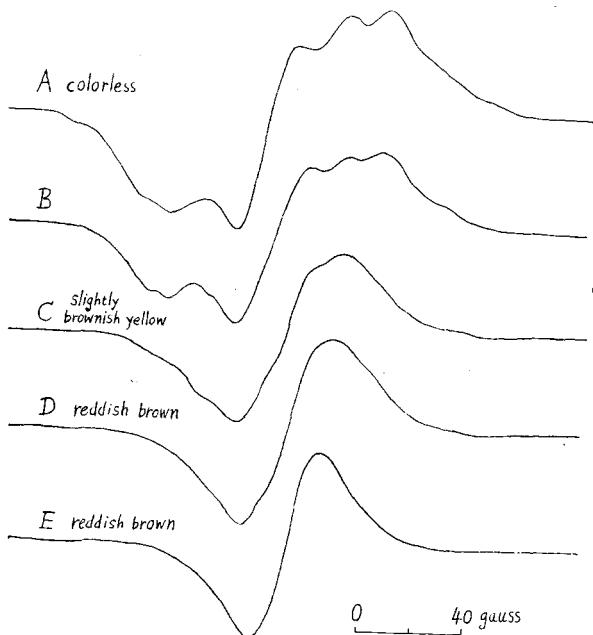


Fig. 1. Change of ESR spectrum of PVC, irradiated *in vacuo* at  $-196^{\circ}\text{C}$ . at a dose of  $5 \times 10^6$  rad with rising temperature all spectra were recorded at  $-196^{\circ}\text{C}$ .: (A) immediately after irradiation; (B) sample immersed in Dry Ice-methanol mixture for 15 hrs.; (C) after 5 min. at  $20^{\circ}\text{C}$ .; (D) after 23 hrs. at  $20^{\circ}\text{C}$ .; (E) after 12 days at  $20^{\circ}\text{C}$ .

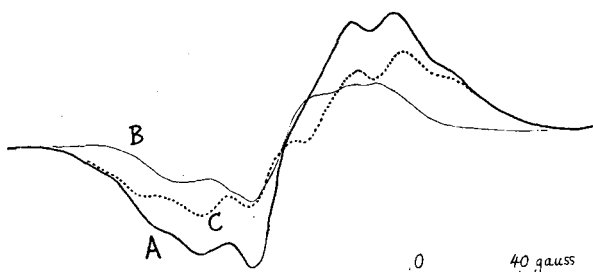


Fig. 2. Subtraction of spectrum B from A. Sample irradiated *in vacuo* at  $-196^{\circ}\text{C}$ . at a dose of  $3 \times 10^7$  rad: (A) immediately after irradiation; (B) sample immersed in Dry Ice-methanol mixture for 15 hrs.; (C) difference of A and B.

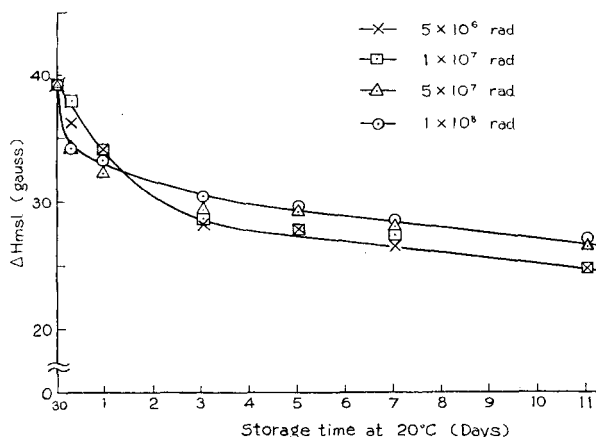


Fig. 3. Change in  $\Delta H_{msl}$  value of the ESR singlet spectrum with storage time at  $20^{\circ}\text{C}$ .; samples irradiated *in vacuo* at  $-196^{\circ}\text{C}$ . with various doses.

is given in Figure 1 (A) which shows some definite hfs. Although the identification of the spectrum A will not be easily made because of the complicated line shape (probably due to chlorine anisotropy) the signal may be interpreted as of a mixture of some radical species such as  $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$ ,  $-\text{CHCl}-\dot{\text{C}}\text{H}-\text{CHCl}-$ ,  $-\text{CH}_2-\dot{\text{C}}\text{Cl}-\text{CH}_2-$ , etc. It changes with rising temperature. Spectrum B was taken after immersing of the sample in a Dry Ice-methanol mixture for 15 hrs. The difference between these resonance signals A and B has been analyzed by subtracting signal B from A. The result reveals the already diminished component at  $-78^{\circ}\text{C}$ . to be a six-line spectrum having separation of approximately 22 gauss (Fig. 2). The relatively fast-decaying six-line spectrum will be due to a radical  $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$  and it might be presumed that the radical combines with a like radical on a near-by chain to form an intermolecular crosslinking in a way analogous to that of polyethylene.<sup>13,14</sup> When the sample had been stood in room temperature at  $20^{\circ}\text{C}$ . for 5 min. it gave spectrum C, showing a drastic change. Spectrum C is nearly a singlet with a slight sign of hfs. The subtraction of the curve C from B is still complex and is not fully interpreted at the present time. Possibly several primary radicals disappeared in this stage. As the sample was further stored at  $20^{\circ}\text{C}$ . the spectrum gradually changed, the line width decreasing (Fig. 3). After 12 days the spectrum tended to a singlet of  $\Delta H_{msl}^* = 25$  gauss (Fig. 1, E), the value being nearly the same as that of the sample  $\gamma$ -ir-

\*  $msl$  means the line width at maximum slope.

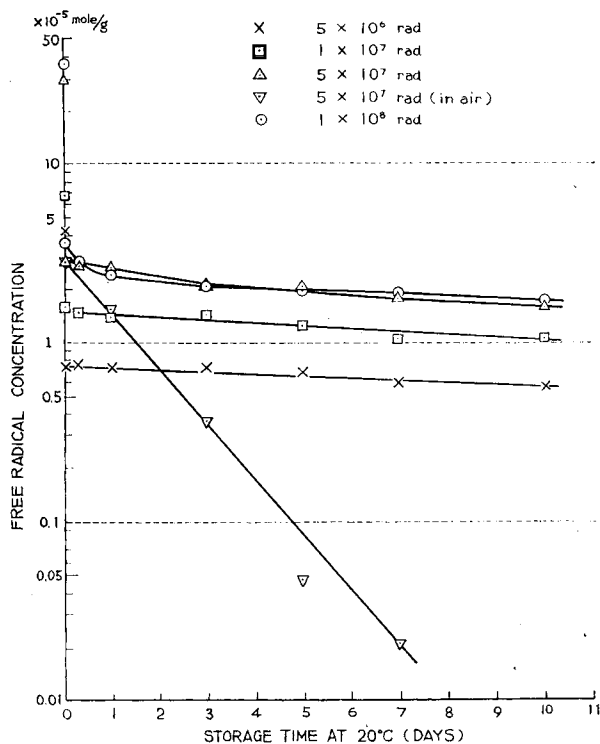


Fig. 4. Free-radical decay at 20°C. *in vacuo*. Samples irradiated *in vacuo* at  $-196^{\circ}\text{C}$ . with various doses.

radiated at room temperature with the same dose ( $5 \times 10^6$  rad).

ESR singlet spectra frequently observed in irradiated polymers at a large dose have been identified with a radical of the polyenyl type, a  $-\text{CHCl}-\dot{\text{C}}\text{H}-(-\text{CH}=\text{CH}-)_n-\text{CHCl}-$  radical in the case of PVC, and we have concluded that the radiation-induced coloration of PVC was due to the formation of such polyenyl radicals or polyene molecules.<sup>15</sup> The  $\Delta H_{\text{msl}}$  value of the singlet becomes smaller, the longer the conjugation. We have estimated the number of conjugations to be approximately 11 when  $\Delta H_{\text{msl}} = 17$  gauss, according to results with irradiated  $\beta$ -carotene.<sup>15</sup> The present value of  $\Delta H_{\text{msl}} = 25$  gauss for the singlet spectrum of irradiated PVC should be interpreted as that, in the sample, polyenyl radicals of various lengths were produced and the one having a length corresponding to  $\Delta H_{\text{msl}} = 25$  gauss was the richest. The slight sign of hfs observable in spectrum C might be due to the formation of an unsaturated radical such as  $-\text{CHCl}-\dot{\text{C}}\text{H}-\text{CH}=\text{CHCl}-$ , judging from smaller hfs splitting. Curve E subtracted from C was almost a doublet (hyperfine separation, 34 gauss) and it

might be imagined that, in this stage, the  $-\text{CHCl}-\dot{\text{C}}\text{H}-\text{CHCl}-$  radical, etc., has reacted.

On the other hand, visually observable coloration started at stage C (see Fig. 1) and the sample was reddish brown after 12 days at 20°C. On examining free-radical decay on storage of the sample at 20°C. (see Fig. 4), it is found that free radicals hardly decay after the initial, quick decaying period of 2 or 3 days.

These results suggest that the free radical  $-\text{CHCl}-\dot{\text{C}}\text{H}-\text{CHCl}-$  converted to  $-\text{CHCl}-\dot{\text{C}}\text{H}-(-\text{CH}=\text{CH}-)_n-\text{CHCl}-$  radicals of various lengths of conjugation. And on storage at 20°C., the conjugation becomes gradually longer and the polyenyl radicals of considerable length give rise to discoloration.

#### Discoloration of Irradiated PVC

For confirmation of the ESR result, discoloration phenomena were studied by means of optical spectroscopy. Figure 5 represents the change in the UV-visible spectrum after the warming to room temperature *in vacuo* of PVC irradiated at  $-196^{\circ}\text{C}$ . In the first several minutes, when the ESR spectrum was singlet with a slight shoulder on the line, a few characteristic absorption bands were seen in the ultraviolet region (250, 290, 330  $\text{m}\mu$ ). As time elapsed other bands developed at longer wavelengths (368, 400, 430, 460, 485, 510  $\text{m}\mu$ , etc.), the sample becoming colored a reddish brown. These characteristic bands might be attributed to polyenyl radicals as observed in the ESR spectrum, each band corresponding to a polyenyl radical of a definite length. In fact, Morokuma<sup>16</sup> has calculated electronic absorption bands of polyenyl radicals of various lengths. According to him, each band of the characteristic spectrum of irradiated PVC could be assigned as shown in Figure 6. A recognizable absorption band of the longest wavelength, 510  $\text{m}\mu$ , will correspond to a polyenyl radical of conjugation length 9. Figure 7 gives a plot of optical density versus wavelength as time elapses, showing a gradual emergence of these characteristic absorption bands. This optical result also suggests that the coloration arises from the development of a longer conjugated system on storage of irradiated PVC at room temperature.

#### Gas Evolution from Irradiated PVC with Rising Temperature

Gas evolved from irradiated PVC at  $-196^{\circ}\text{C}$ . was examined as a function of temperature and compared with the ESR and optical results. Fig-



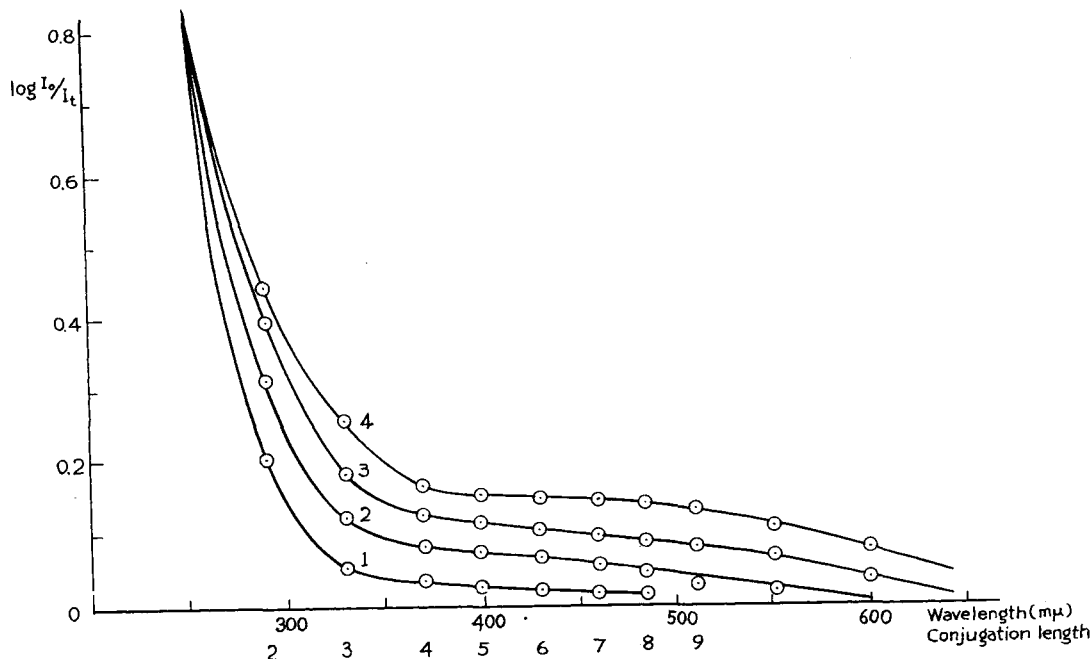
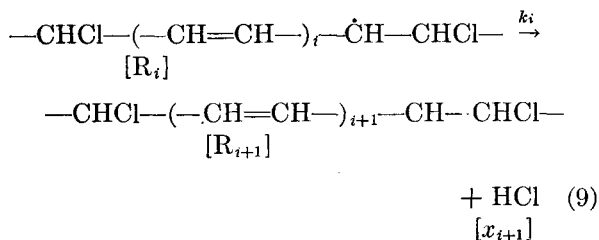


Fig. 7. Change with storage time *in vacuo* at 20°C. in optical density of characteristic absorption bands observed in UV-visible spectrum of irradiated PVC (cf. Fig. 5); sample irradiated *in vacuo* at -196°C. with  $3 \times 10^7$  rad and then warmed to 20°C.: (1) after 3-8 min. at 20°C.; (2) after 45-50 min.; (3) after 65 hrs.; (4) after 11 days.  $I_0$  and  $I_t$  are intensities of transmission light at zero (unirradiated) and after  $t$  hours of storage at 20°C., respectively.



$$x_i = [\text{R}_0]_0 \left\{ 1 - \sum_0^i \left[ \left( \prod_{\substack{n=0 \\ n \neq 1}}^i \frac{k_n}{(k_n - k_i)} \right) e^{-k_i t} \right] \right\}$$

$$\sum_0^{N-1} x_i = \sum_0^{N-1} [\text{R}_0]_0 - [\text{R}_0]_0$$

$$\sum_0^{N-1} \left\{ \sum_0^i \left[ \left( \prod_{\substack{n=0 \\ n \neq 1}}^i \frac{k_n}{(k_n - k_i)} \right) e^{-k_i t} \right] \right\}$$

$$P = \int_0^T \sum_0^{N-1} x_i dT$$

$$= N[\text{R}_0]_0 T - [\text{R}_0]_0 \int_0^T \sum_0^{N-1} \left\{ \sum_0^i \left[ \left( \prod_{\substack{n=0 \\ n \neq 1}}^i \frac{k_n}{(k_n - k_i)} \right) e^{-k_i t} \right] \right\} dT \quad (10)$$

The crosslinking reaction (5) occurs even at low temperature (-78°C.). ESR and optical results showed that the zipper reaction, (7), (8), (9), proceeds at relatively high temperatures; e.g., rather quickly at 20°C. Gas evolution data clearly showed the zipper reaction to proceed at above -70°C.

A kinetic treatment of the zipper reaction gives a relation between gas yield and reaction temperature as follows (see the above reaction scheme for notation used):

$$d[x_0]/dt = k_0[\text{R}_0] \quad [\text{R}_0] = [\text{R}_0]_0 - [x_0]$$

$$d[x_1]/dt = k_1[\text{R}_1] \quad [\text{R}_1] = [x_0] - [x_1]$$

.....  
.....

$$d[x_i]/dt = k_i[\text{R}_i] \quad [\text{R}_i] = [x_{i-1}] - [x_i]$$

$P$  is measured pressure of hydrogen chloride at temperature  $T$  at the time the zipper reaction has proceeded to a length  $N$ . An actually observed experimental behavior, that the gas yield increased proportionally to temperature above -20°C. may be explained by the first term of the solution, eq. (10). This may be considered as justifying a consequence of HCl evolution under the zipper mechanism.

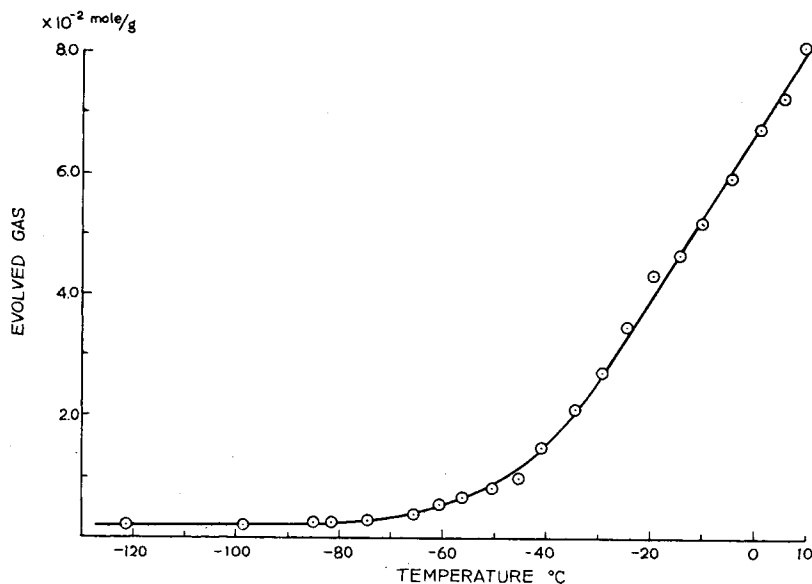


Fig. 8. Gas yield vs. temperature of reaction. Sample irradiated *in vacuo* at  $-196^{\circ}\text{C}$ . with  $2 \times 10^7$  rad and then warmed gradually. Rate of temperature rise was about  $2^{\circ}\text{C./min.}$  at  $-40^{\circ}\text{C}$ . and  $0.3^{\circ}\text{C./min.}$  at  $-20^{\circ}\text{C}$ .

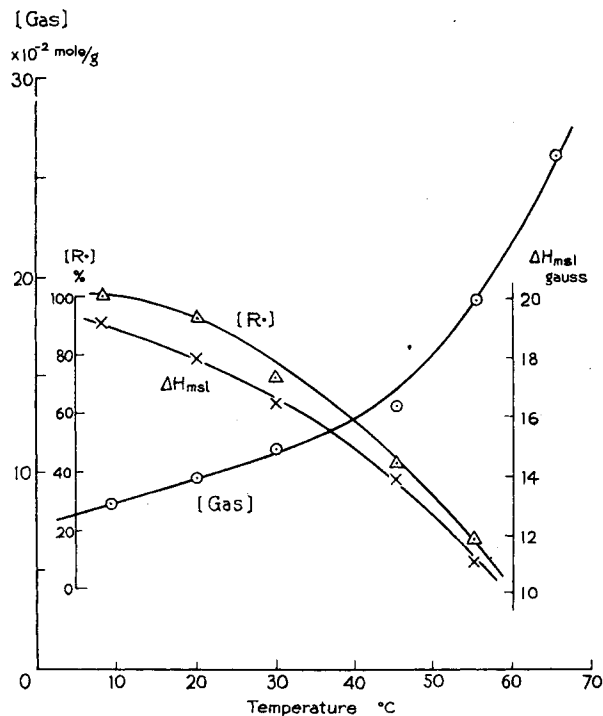


Fig. 9. Effect of heat-treatment at various temperatures on gas evolution ( $\odot$ ), free-radical concentration ( $\Delta$ ), and  $\Delta H_{msl}$  value of ESR singlet spectrum ( $\times$ ). Sample irradiated at  $-196^{\circ}\text{C}$ . with  $2 \times 10^7$  rad and then warmed to each temperature for enough time to attain equilibrium.

#### Effect of Heat Treatment on Discoloration

When the sample preirradiated at  $-196^{\circ}\text{C}$ . was heated at higher temperatures than  $20^{\circ}\text{C}$ ., the gas yield curve deviated from the linear relationship and the free-radical concentration as well as  $\Delta H_{msl}$  value of the singlet spectrum decreased, as shown in Figure 9. These phenomena are in contrast with the above-mentioned behavior at less than  $20^{\circ}\text{C}$ . and they suggest some additional, less simple mechanism of coloration, such as an ordinary pyrolytic one.

On the other hand, our pyrolytic experiment with unirradiated specimen showed that coloration and the ESR signal could hardly be observed below  $150^{\circ}\text{C}$ . Pyrolysis at  $200^{\circ}\text{C}$ . gave color and a quite narrow singlet spectrum of  $\Delta H_{msl} = 8$  gauss, showing formation of polyenyl radicals of very long conjugation. At first sight there seems to be some inconsistency between these observations. However, it might be supposed that irradiation leaves some sites to facilitate pyrolytic reaction.

In passing, change of UV-visible spectrum on heating at  $60^{\circ}\text{C}$ . is shown in Figure 10. The sample had been  $\gamma$ -irradiated at room temperatures with  $6.3 \times 10^6$  rad. Figure 11 shows a plot of optical density versus wavelength. The data show an acceleration of discoloration on heating at  $60^{\circ}\text{C}$ .

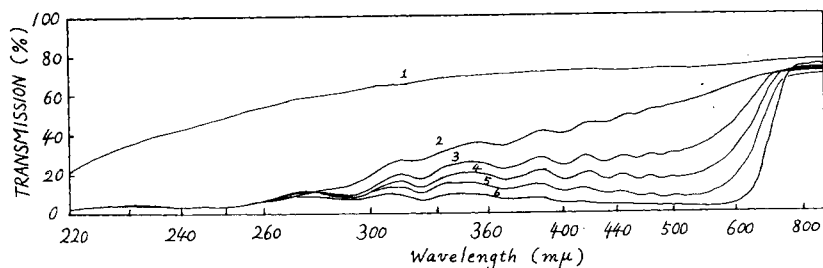


Fig. 10. Change in UV-visible spectrum of irradiated PVC on heating *in vacuo* at 60°C.; sample  $\gamma$ -irradiated at room temperature with a dose of  $6.3 \times 10^6$  rad: (1) unirradiated; (2) immediately after irradiation; (3) after 2 hrs. at 60°C.; (4) after 6 hrs.; (5) after 22 hrs.; (6) after 10 days.

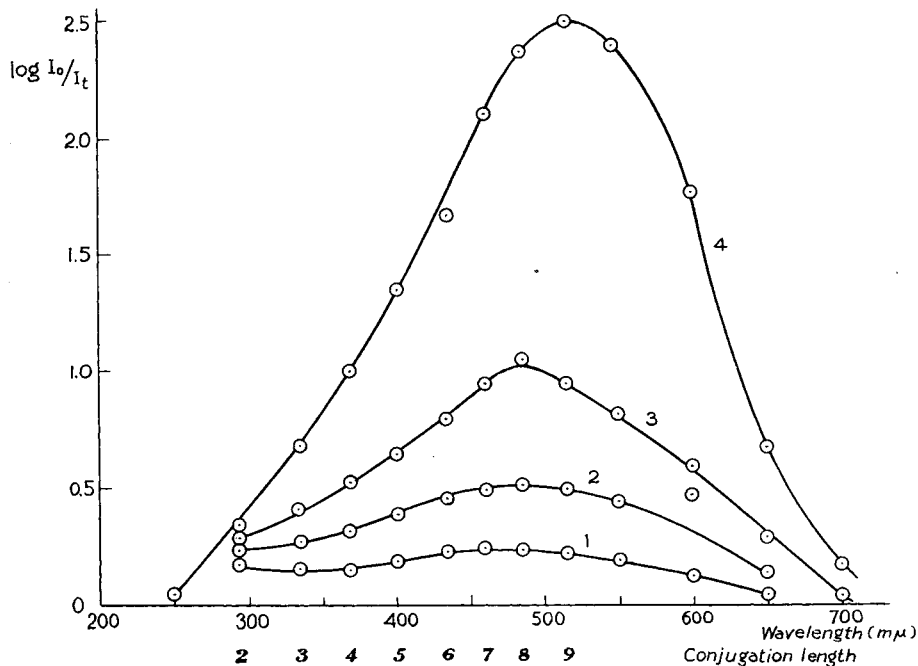


Fig. 11. Change with storage time at 60°C. in optical density of characteristic absorption bands in irradiated PVC (cf. Fig. 10); sample  $\gamma$ -irradiated *in vacuo* at a room temperature with  $6.3 \times 10^6$  rad and then heated *in vacuo* at 60°C. for: (1) 2 hrs.; (2) 6 hrs.; (3) 22 hrs.; and (4) 10 days.

After 1 day the polyenyl radical of conjugation length 8 was found richest, while after 10 days the conjugation peak changed to 9. Careful analysis of such data (Figure 11) would enable us to estimate the activation energy of the zipper reaction as a function of  $i$  (see reaction scheme).

#### Effect of Increasing Dose on Discoloration

On irradiation at room temperature PVC becomes discolored more and more as the dose increases. (This is the basis of dosimetry by means of PVC coloration.) Figure 12 shows the change in the UV-visible spectrum with increasing dose of

$\gamma$ -rays, and Figure 13 is a plot of optical density versus wavelength (or conjugation length).

An abnormal discoloration behavior was observed when PVC was irradiated at  $-196^\circ\text{C}$ . with increasing dose. After warming to room temperature, samples irradiated with lower doses, below  $\sim 3 \times 10^7$  rad, became colored to reddish brown immediately; similar behavior stated above. On the other hand, the coloration of samples irradiated with relatively high doses ( $> 5 \times 10^7$  rad) proceeded to a less extent so that these were colored only deep green after 1 day although they became gradually brownish after 10 days. This can be

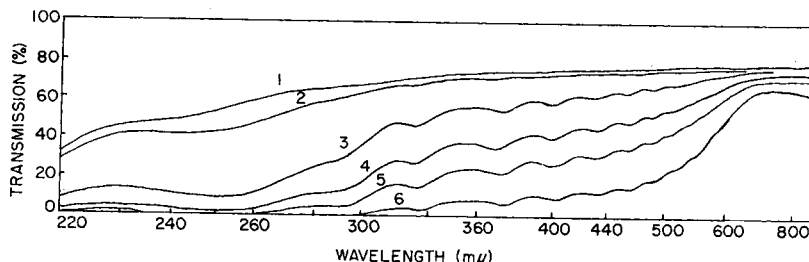


Fig. 12. Change with increasing dose in UV-visible spectrum of irradiated PVC;  $\gamma$ -irradiation *in vacuo* at room temperature with  $2.7 \times 10^5$  rad/hr.: (1) unirradiated; (2)  $2.1 \times 10^6$  rad; (3)  $4.4 \times 10^6$  rad; (4)  $6.0 \times 10^6$  rad; (5)  $9.7 \times 10^6$  rad; (6)  $1.7 \times 10^7$  rad.

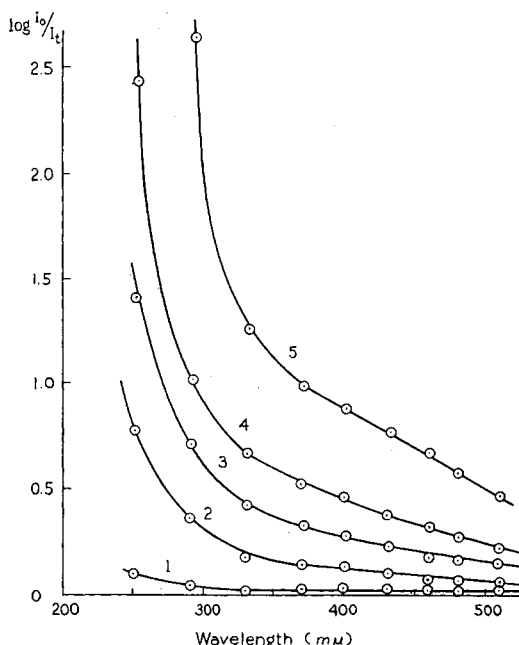


Fig. 13. Change with increasing dose in optical density of characteristic absorption bands (cf. Fig. 12): (1)  $2.1 \times 10^6$  rad; (2)  $4.4 \times 10^6$  rad; (3)  $6.0 \times 10^6$  rad; (4)  $9.7 \times 10^6$  rad; (5)  $1.7 \times 10^7$  rad.

seen in Figure 14 which shows the UV-visible spectrum after 10 days' storage at  $20^\circ\text{C}$ . It is noticeable that in samples irradiated at  $-196^\circ\text{C}$ . with doses higher than  $5 \times 10^7$  rad lack absorptions at longer wavelengths. The abnormal discoloration might have something to do with the formation of crosslinks; it might restrain the development of polyenyl radicals.

#### *Free-Radical Formation Curve; Occurrence of Crosslinking Reaction at $-196^\circ\text{C}$ .*

The ESR spectrum of PVC irradiated at  $-196^\circ\text{C}$ . changes as the dose increases (Figure 15). Samples irradiated with higher doses have spectra with little sign of hfs. This may be a situation in which  $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$  radicals are produced in less proportion in samples irradiated with higher doses. Free-radical concentration was plotted against dose (Figure 16). The  $G_R$  value was estimated from the initial slope to be 7.1. The curve does not make a straight line but deviates at higher doses, as in the case of polyethylene.<sup>14</sup> Both results suggest the occurrence of a radical

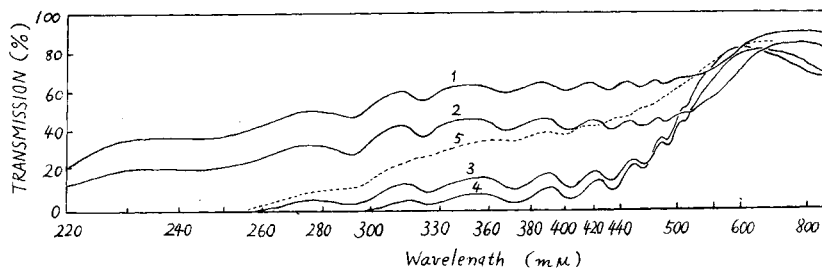


Fig. 14. UV-visible spectrum of PVC irradiated *in vacuo* at  $-196^\circ\text{C}$ . with various doses: (1)  $10^6$  rad; (2)  $10^7$  rad; (3)  $5 \times 10^7$  rad; (4)  $10^8$  rad. The samples were kept at  $20^\circ\text{C}$ . *in vacuo* for 10 days after irradiation. Measurements of the spectra were made immediately after opening vacuum. Curve (5) shows a special example in which the sample was irradiated *in vacuo* at  $-196^\circ\text{C}$ . with  $3 \times 10^7$  rad and then stored at  $20^\circ\text{C}$ . for 10 days in air.



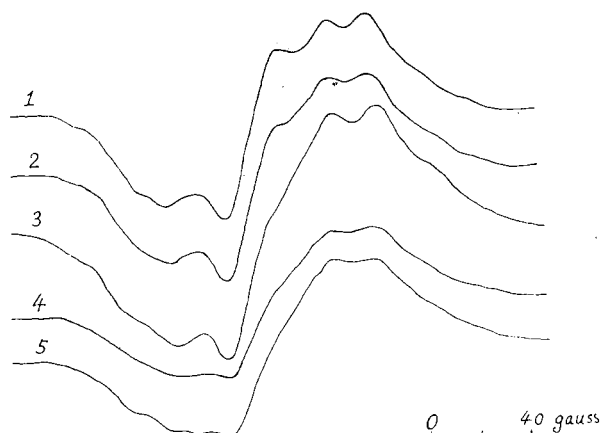


Fig. 15. ESR spectrum of PVC irradiated *in vacuo* at  $-196^{\circ}\text{C}$ . with various doses: (1)  $5 \times 10^6$  rad; (2)  $1 \times 10^7$  rad; (3)  $3 \times 10^7$  rad; (4)  $5 \times 10^7$  rad; (5)  $1 \times 10^8$  rad. Measurements were made at  $-196^{\circ}\text{C}$ . immediately after irradiation.

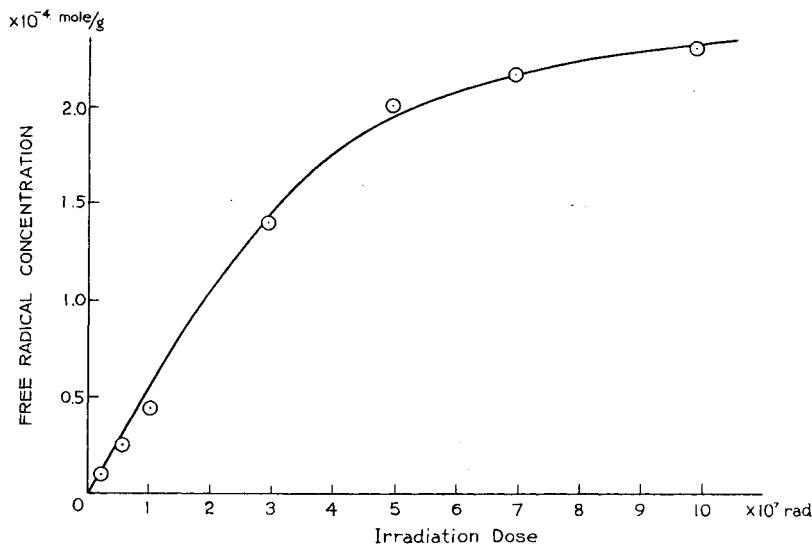


Fig. 16. Free-radical formation curve at  $-196^{\circ}\text{C}$ . in PVC. Electron irradiation by a 2 m.e.v. Van de Graaff accelerator.

reaction during irradiation at  $-196^{\circ}\text{C}$ . It would be a crosslinking reaction due to a recombination of "hot"  $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$  radicals produced in close proximity, similar to the case of polyethylene.<sup>14</sup> An experimental result giving a crosslinking reaction at  $-78^{\circ}\text{C}$ . would not be unreasonable from this standpoint.

### Conclusion

Several primary radicals such as  $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$ ,  $-\text{CHCl}-\dot{\text{C}}\text{H}-\text{CHCl}-$ , etc., are produced in PVC on irradiation. Among them, some  $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$  radicals may recombine to

form crosslinks during irradiation even at  $-196^{\circ}\text{C}$ ., since most of them probably would be produced in the "hot" state and in close proximity. This is a characteristic reaction in radiation chemical processes, as pointed out in the case of polyethylene.<sup>14</sup> Some primary radicals such as  $-\text{CHCl}-\dot{\text{C}}\text{H}-\text{CHCl}-$  participate in a thermally induced secondary reaction above  $-70^{\circ}\text{C}$ ., leading to the formation of polyenyl radicals by hydrogen chloride detachment. Polyenyl radicals of considerable lengths, some as long as 9 conjugated double bonds, thus formed, cause coloration. Finally, it may be added that results from the present investigation would be of significant use in radiation dosimetry by discoloration.

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### Synopsis

The radiation chemical process in polyvinyl chloride has been studied by means of electron spin resonance, optical spectroscopy, and measurement of gas evolution. The chief technique was to irradiate samples at  $-196^{\circ}\text{C}$ . and then follow the change or changes with rising temperature. Resonance results showed that, on irradiation, several primary radicals, such as  $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$ ,  $-\text{CHCl}-\dot{\text{C}}\text{H}-\text{CHCl}-$ , etc., were produced. Among them some  $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$  radicals could recombine to form crosslinks during irradiation even at  $-196^{\circ}\text{C}$ . A mechanism for the discoloration of PVC, based upon results obtained by these three different methods, has been postulated. Discoloration is caused by the formation of polyenyl radicals or polyene molecules of considerable conjugation lengths, some as long as 9 conjugated double bonds. Polyenyl radicals are produced as a result of a thermally induced secondary reaction of the  $-\text{CHCl}-\dot{\text{C}}\text{H}-\text{CHCl}-$  radical, above  $-70^{\circ}\text{C}$ ., thereby accompanied by hydrogen chloride detachment following the so-called "zipper" mechanism. An equation relating the pressure of evolved HCl to the reaction temperature has been derived by a simple kinetic treatment of the zipper reaction. Some effect of heat treatment and increasing dose on discoloration was discussed.

### Résumé

On étudie le processus chimique d'irradiation du chlorure de polyvinyle par résonance électronique paramagnétique (ESR) par spectroscopie optique et par mesure du dégagement gazeux. La technique principale consiste à irradier les échantillons à  $-196^{\circ}\text{C}$  et de suivre alors le ou les changements qui s'opèrent par augmentation de température. Les résultats obtenus par E.S.R. montrent que l'irradiation produit plusieurs radicaux primaires tels que  $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$ ,  $-\text{CHCl}-\dot{\text{C}}\text{H}-\text{CHCl}-$  etc. Parmi ceux-ci certains

radicaux  $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$  peuvent se recombinaer pour former des pontages durant l'irradiation même à  $-196^{\circ}\text{C}$ . On propose un mécanisme pour la coloration foncée du PVC en se basant sur les résultats obtenus par les trois méthodes précédemment citées. Cette coloration est provoquée par formation de radicaux polyényles ou de molécules de polyène possédant un grand nombre de doubles liaisons conjuguées (jusqu'à 9 liaisons doubles conjuguées). Les radicaux polyényles sont produits par réaction thermique induite secondairement, du radical  $-\text{CHCl}-\dot{\text{C}}\text{H}-\text{CHCl}$  au dessus de  $-70^{\circ}\text{C}$ , accompagnée de détachement d'HCl suivant le mécanisme de propagation progressive. Une équation, reliant la pression d'HCl dégagé à la température de réaction, a été dérivée par une étude cinétique simple de réaction de dépropagation progressive. On discute certains effets de la chaleur et de l'augmentation de la dose sur la coloration.

### Zusammenfassung

Der durch Bestrahlung in Polyvinylchlorid hervorgerufene chemische Prozess wurde mittels Elektronenspinresonanz (ESR), optischer Spektroskopie und Messung der Gasentwicklung untersucht. Das hauptsächlich angewandte Verfahren bestand darin, die Proben bei  $-196^{\circ}\text{C}$  zu bestrahlen und dann die darauffolgenden Veränderungen bei steigender Temperatur zu verfolgen. Die ESR-Ergebnisse zeigten, dass bei der Bestrahlung verschiedene Primärradikale, wie  $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$ ,  $-\text{CHCl}-\dot{\text{C}}\text{H}-\text{CHCl}-$ , usw. gebildet werden. Unter diesen können gewisse  $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$  Radikale rekombinieren und sogar bei  $-196^{\circ}\text{C}$  während der Bestrahlung Vernetzungsstellen bilden. Auf Grund der mit den drei angeführten verschiedenen Methoden erhaltenen Ergebnisse wurde ein Mechanismus für die Verfärbung von PVC angegeben. Die Verfärbung wird durch die Bildung von Polyenylradikalen oder Polyenmolekülen mit beträchtlicher Konjugationslänge verursacht (bis zu 9 konjugierten Doppelbindungen). Polyenylradikale werden als Produkt einer thermisch induzierten Sekundärreaktion des  $-\text{CHCl}-\dot{\text{C}}\text{H}-\text{CHCl}-$  Radikals oberhalb  $-70^{\circ}\text{C}$  gebildet, durch welche eine Chlorwasserstoffabspaltung nach dem sogenannten "Zipper"-Mechanismus eingeleitet wird. Eine Beziehung zwischen dem Druck des entwickelten HCl und der Reaktionstemperatur wurde durch eine einfache kinetische Behandlung der Zipperreaktion abgeleitet. Der Einfluss der Wärmebehandlung und der steigenden Bestrahlungsdosis auf die Verfärbung wurde diskutiert.

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