

# Stabilization of Gamma-Irradiated Poly(vinyl Chloride) by Epoxy Compounds. III. Conjugated Double Bonds and Degree of Unsaturation in Gamma-Irradiated PVC-Stabilizer Mixtures

G. LERKE, I. LERKE, and W. SZYMAŃSKI, *Institute of Chemistry, Nicholas Copernicus University, 87-100, Toruń, Poland*

## Synopsis

The concentration of conjugated polyene sequences was studied in  $\gamma$ -irradiated PVC with 4% admixture of four epoxy stabilizers: diglycidyl ether of 2,2-bis(4-hydroxy-3-methylphenyl)propane (I), styrene oxide (1,2-epoxy ethyl benzene) (IV), epoxidized ricinus oil (VI), and epoxidized soybean oil (Drapex 6.8) (VII). As in the former investigations (Papers I and II), the process of the formation of the polyenes occurs in two stages. The concentration of polyene sequences with  $n$  double bonds,  $H_n$ , the total amount of polyene sequences,  $\Sigma H_n$ , the average length of the polyene sequence,  $\bar{n}$ , and the two extents of reaction  $x$  and  $p$ , were computed. The stabilizing effect of all compounds used agrees with the increasing content of epoxy groups. The addition of stabilizers diminishes the value of  $\bar{n}$ . The decrease of the fraction of long sequences and the increase of short ones occurs. Apart from the binding of evolved HCl, the protective effect towards the macromolecules of PVC consists mainly in the inhibition of growth of chain dehydrochlorination by the epoxy groups.

## INTRODUCTION

The fact of the formation of conjugated double bonds in irradiated PVC, directly connected with the process of dehydrochlorination, causes the appearance of a color. This phenomenon is one of the basic elements of the destruction of polymers. In this situation we have decided to investigate the influence of stabilizers admixture upon this process, in analogy to the investigations of the influence of stabilizers upon the dehydrochlorination process, described in Paper I.

The polyene sequences absorb in the region of 300–600 nm. This property of polyene sequences was exemplified in the investigations of dialkylpolyenes<sup>1–3</sup> with equal number of double bonds and of polyenes of H/CH=CH/H type.<sup>4</sup> The investigations performed till now give correct results for the number of conjugated bonds  $n = 3–10$ . The value of the absorption diminishes, most often, with the increase of the wavelength.<sup>5</sup>

The essential problem, using the UV–VIS spectroscopy, is to attribute the consecutive maxima of spectral fine structure to the respective value of  $n$  of the polyene sequences. The majority of authors base on the works of Braun and Thallmaier<sup>6,7</sup> and on the empirical equations of Hausser and Kuhn<sup>8</sup> and of Bohlman.<sup>3</sup> The question is, however, still open to discussion and quite exact attribution of the bands remains problematic.<sup>1,3,9–12</sup> It seems that the assignment of the number  $n$  to wavelengths, which was done by Popov and Smirnov,<sup>13,14</sup> is most exact.

The absorption maxima in solutions, when compared to solid samples, are shifted slightly (3–5 nm) towards the shorter wavelengths; according to the type of solvent. The data concerning our system (PVC in solution of THF) can be found, among others, in the paper by Shindo and Hirai.<sup>15</sup>

The lack of the data concerning the values of the molar extinction coefficients  $\epsilon_n$  (for the polyenes  $n = 4$ – $12$ ) makes difficult the evaluation of the amount of individual polyene sequence and their statistic distribution. It was, however, stated experimentally<sup>16</sup> and confirmed theoretically<sup>17</sup> that the  $\epsilon_n$  value increases linearly with the increase of the number of the double bonds. On this ground, the following dependence is used  $\epsilon_n = \epsilon_1 + (n - 1)\Delta\epsilon$ , where  $\epsilon_1 = 10,000$  and  $\Delta\epsilon = 20,000$ .<sup>13,18</sup>

In this work (Part III) we have investigated the changes of the degree of unsaturation in the mixtures of PVC with the stabilizers I, IV, VI, and VII. The main investigations are performed in a nitrogen atmosphere, in agreement with the accepted opinion that the oxidation processes make the formation of long polyene sequences impossible. However, since the coloration of the samples was observed also in an oxygen atmosphere, we have performed the supplementary measurements of absorption spectra in this atmosphere too.

## EXPERIMENTAL

The mixtures of PVC with the addition of 4% of a stabilizer {I,  $1.03 \times 10^{-2}$ ; IV,  $1.55 \times 10^{-2}$ ; VI,  $0.34 \times 10^{-2}$ ; VII,  $0.96 \times 10^{-2}$  [mol oxirane groups/mol PVC monomer units (mu)] were irradiated in nitrogen in a dose range of 2.5–19.5 Mrad (25–195 kGy) and in oxygen at doses to about 8 Mrad (80 kGy).

The absorption spectra, in the solution of  $0.15 \pm 0.0002$  g PVC in  $10 \text{ cm}^3$  of tetrahydrofuran (THF), were performed in the region of  $1.4$ – $3.5 \times 10^4 \text{ cm}^{-1}$ , using Specord UV-VIS spectrophotometer. The solutions were prepared in an oxygen-free atmosphere and were protected against the action of light. The reference solution was pure or stabilized, unirradiated PVC in THF.

On the basis of the analysis of absorption spectra the presence of polyene sequences, from five to ten double bonds, was ascertained. The character of the obtained spectra is entirely consistent with the majority of spectra described in the literature. In the whole analyzed region of wavelengths, visible and near UV, we have stated no influence of stabilizers on the character of spectra. We have not found an absorption in the solutions of unirradiated material either for pure PVC or for PVC with the admixture of a stabilizer. We have also not observed the change in the position of successive maxima for the irradiated mixtures of PVC with a stabilizer.

The attribution of maxima to the number  $n$  is presented in Table I. It is very close to that of Shindo and Hirai.<sup>15</sup>

## RESULTS AND DISCUSSION

### $\text{N}_2$ Atmosphere

From the spectral data we have computed<sup>15,18–20</sup> the concentration of polyene sequences with  $n$  double bonds in conjugation,  $H_n$ ,

$$H_n = A_n / cd\epsilon_n$$

TABLE I  
Attribution of Absorption Maxima to Number of Conjugated Double Bonds in the Solution of PVC in THF

Number of conjugated double bonds $n$	5	6	7	8	9	10
$\bar{V} (cm^{-1} \times 10^{-4})$	3.10	2.78	2.59	2.44	2.32	2.23
$l(nm)$ (our results)	323	360	387	410	432	450
$l(nm)$ (Shindo and Hirai <sup>15</sup> )	334	364	390	410	428	447

where  $A_n$  = the absorption corresponding to particular value of  $n$ ,  $c$  = concentration of the solution (monomeric units/dm<sup>3</sup>),  $d$  = thickness of absorbing layer (cm),  $\epsilon_n$  = the molar absorption coefficient (dm<sup>3</sup>·mol<sup>-1</sup>·cm<sup>-1</sup>), calculated from the dependence given above.<sup>13,18</sup> The  $H_n$  value is evaluated in moles of polyene sequences per monomeric unit.

The concentration of polyene sequences  $H_n$  vs.  $\gamma$ -irradiation dose, drawn for each (I, IV, VI, VII) epoxy compound, are represented by similar curves. Thus we give only Figure 1 for the pure PVC and Figure 2 for the mixture of PVC with stabilizer I. Our conclusions are based on quantitative comparison of these similar curves.

The amount of formed polyene sequences  $H_n$  increases with the dose for all values of  $n$ . The fraction of individual sequences decreases with the increase of  $n$ . As in all investigations carried previously by us, the process goes in two stages. In the early stage of radiolysis the dependences have a linear character. The dependence of  $H_n$  value on a dose is different for the stabilizers with aro-

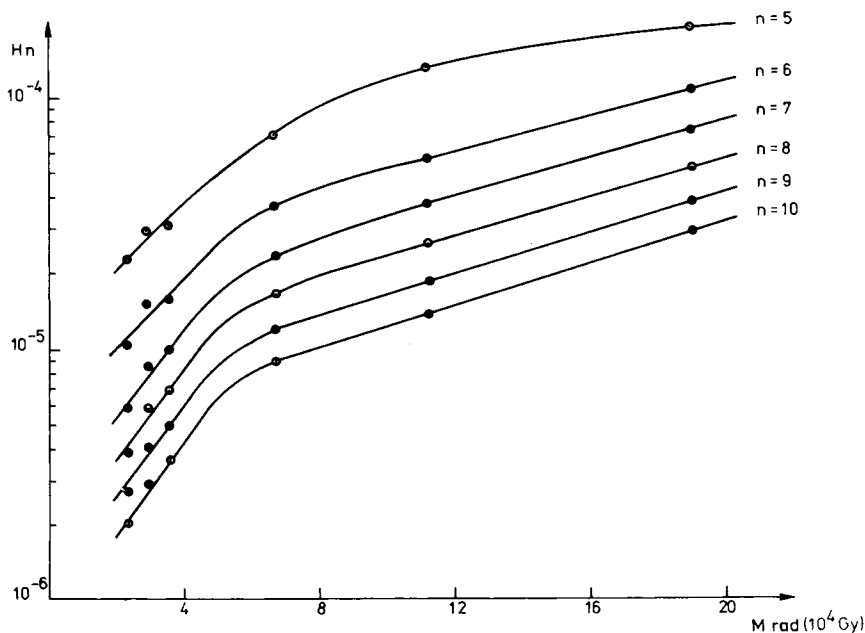


Fig. 1. The concentration of polyene sequences  $H_n$  vs.  $\gamma$ -irradiation dose, in pure PVC. Dose rate  $4.73 \times 10^{17}$  eV·cm<sup>-3</sup>·min<sup>-1</sup>.

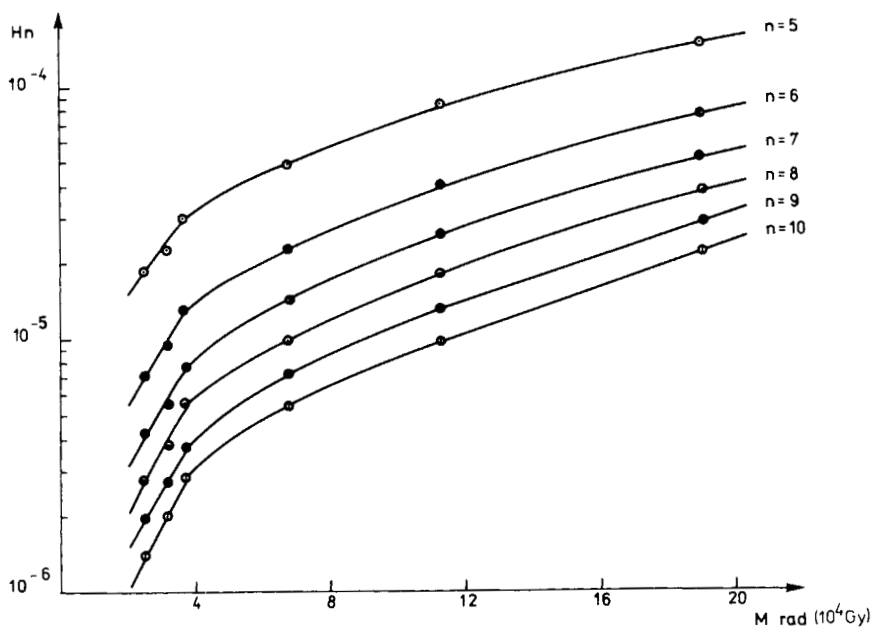


Fig. 2. The concentration of polyene sequences  $H_n$  vs.  $\gamma$ -irradiation dose, in PVC with stabilizer I ( $1.03 \times 10^{-2}$  mol oxirane groups/mol PVC  $\mu$ ). Dose rate  $4.73 \times 10^{17}$  eV $\cdot$ cm $^{-3}\cdot$ min $^{-1}$ .

matic ring (I, IV) and for the stabilizers VI and VII. A nonlinear segments of this dependence indicate the appearance of secondary reactions.<sup>18,21,22</sup>

On purpose, to illustrate better the action of a stabilizer on the formation of the conjugated polyene sequences, the total amount of polyene sequences,  $H_n$  vs dose, for the pure and stabilized PVC, is presented in Figures 3 and 4. There

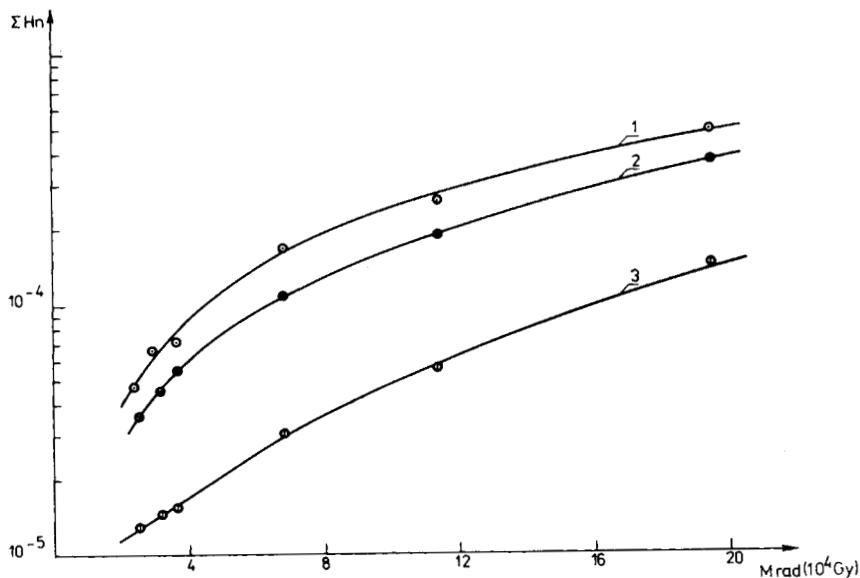


Fig. 3. The total amount of polyene sequences  $\Sigma H_n$  vs.  $\gamma$ -irradiation dose; designations 1, 2, 3 refer to PVC, PVC + stabilizer I, PVC + stabilizer IV, respectively. Dose rate  $4.73 \times 10^{17}$  eV $\cdot$ cm $^{-3}\cdot$ min $^{-1}$ .

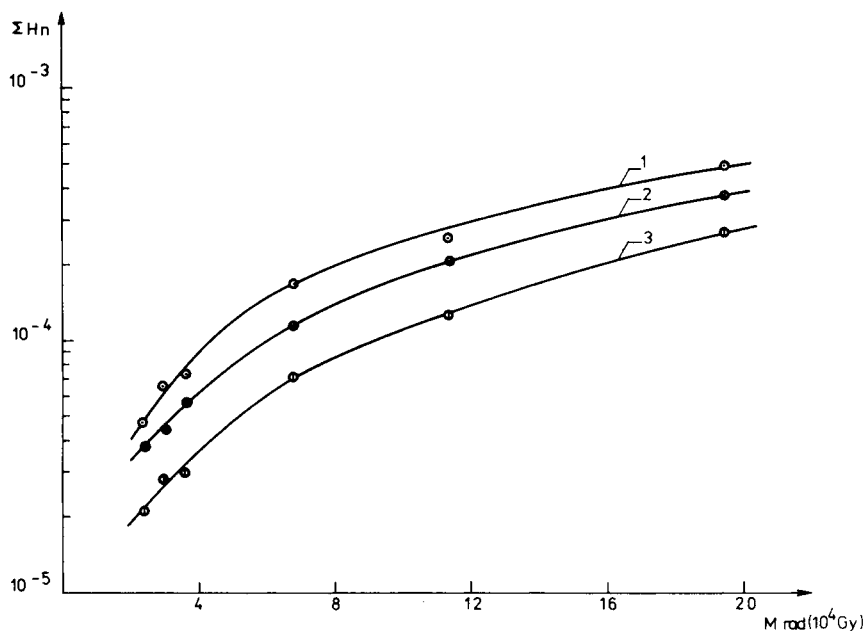


Fig. 4. The total amount of polyene sequences  $\Sigma H_n$  vs.  $\gamma$ -irradiation dose, designations 1, 2, 3 refer to PVC, PVC + stabilizer VI, PVC + stabilizer VII, respectively. Dose rate  $4.73 \times 10^{17}$  eV·cm<sup>-3</sup>·min<sup>-1</sup>.

is a pronounced stabilizing effect. This effect for both types of stabilizers, I, IV and VI, VII, agrees with the increasing content of epoxy groups.

The decrease of  $H_n$  value with the increase of  $n$  is especially rapid in the case of styrene oxide (IV). The percent decrease of  $H_n$  value relative to pure PVC, for the extreme values of  $n$  and extreme doses, is presented in Table II. The content of epoxy oxygen in the stabilizers is also given in Table II, for comparison. For two stabilizers, for which the contents of epoxy oxygen are 2% and 9.5%, the decrease of  $H_n$  for  $n = 10$  reaches 100%. The stabilizer I does not follow this general regularity, and we believe that its different reactivity, connected with the structure of the molecule, is responsible for this effect. After all, this stabilizer does not inhibit the formation of polyene sequences in an oxygen atmosphere also.

The average length of the polyene sequence,  $\bar{n} = (\sum_{n=5}^{10} n)H_n / \Sigma H_n$ , vs. dose, for the mixtures of PVC with stabilizers, is presented in Table III.

The value of  $\bar{n}$  increases with the dose. In general, after the addition of a

TABLE II  
Decrease of Concentration of Polyene Sequences  $H_n$  Relative to Pure PVC (%) for Extreme Values of  $n$  and of the Doses

Stabilizer	Epoxy oxygen (%)	Dose 3.6 Mrad (36.4 kGy)		Dose 19.6 Mrad (195.7 kGy)	
		$n = 5$	$n = 10$	$n = 5$	$n = 10$
VI	2.08	10	42	29	19
VII	5.9	47	77	41	51
I	6.3	3	33	21	24
IV	9.54	64	100	60	86

TABLE III  
Average Length of Polyene Sequences  $\bar{n} = \left( \sum_{n=5}^{10} n \times \frac{H_n}{\sum H_n} \right)$  in  $\gamma$ -Irradiated Mixtures of PVC  
with Stabilizers

Dose [Mrad (kGy)]	PVC	PVC + stab. I	PVC + stab. IV	PVC + stab. VI	PVC + stab. VII
2.4 (24.3)	6.161	—	—	6.093	5.880
2.6 (25.5)	—	6.080	5.370	—	—
3.0 (29.6)	6.220	—	—	6.101	5.883
3.2 (31.9)	—	6.145	5.396	—	—
3.6 (36.4)	6.310	6.183	5.416	6.150	5.934
6.8 (68.3)	6.337	6.267	5.720	6.315	6.015
11.4 (113.8)	6.374	6.311	5.760	6.408	6.182
19.6 (195.7)	6.434	6.418	5.961	6.545	6.345
$\Delta\bar{n}$	0.273	0.338	0.591	0.452	0.465

stabilizer a diminution of  $\bar{n}$ , at a particular dose, takes place. The fraction  $H_n/\sum H_n$  of short sequences ( $n = 5$ ) is, for all investigated stabilizers, greater than for the pure PVC; the fraction of long sequences is smaller. The fraction of long sequences, for less effective stabilizers I and VI, is somewhat greater than for the pure PVC, at higher doses only. The decrease of the average length of polyene sequence is caused by the reaction between polymer chain and the epoxy groups. We have suggested such a mechanism based on the results of the investigations of the decay of epoxy groups (Paper I). The most probable is the reaction of the stabilizer with the allylic chlorine at the end of polyene sequence.

For comparison of the radiation yield of HCl and of the amount of polyene

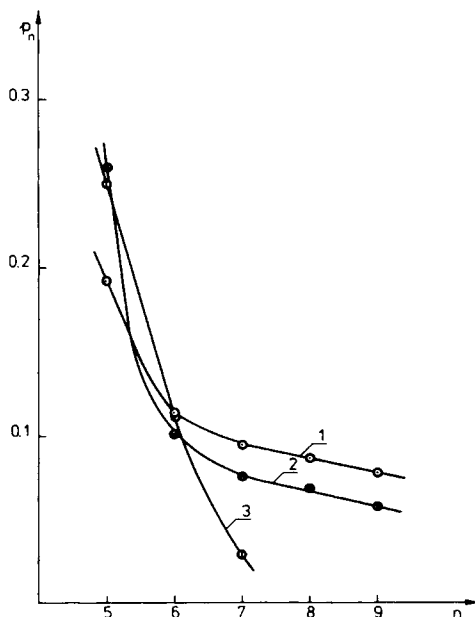


Fig. 5. The extent of reaction  $p_n$  vs. the number  $n$  of polyenes; designations 1, 2, 3 refer to PVC, PVC + stabilizer I, PVC + stabilizer IV, respectively. Dose of 3.6 Mrad (36.4 kGy).

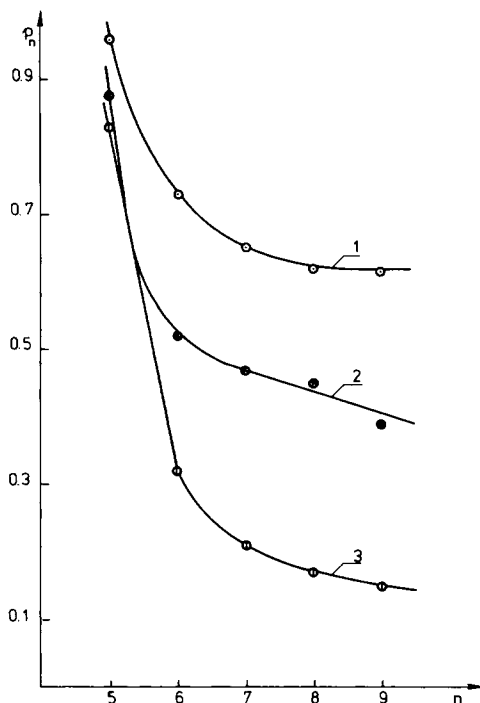


Fig. 6. The extent of reaction  $p_n$  vs. the number  $n$  of polyenes; designations 1, 2, 3 refer to PVC, PVC + stabilizer I, PVC + stabilizer IV, respectively. Dose of 19.6 Mrad (195.7 kGy).

sequences we have computed the two extents of reaction:  $x = (x_{\text{exptl}}/x_0) \times 100$ , where  $x_{\text{exptl}}$  is the determined amount of HCl evolved from the polymer and  $x_0$  is the possible amount of HCl evolved when the total dehydrochlorination takes place; and  $p = \sum_{n=5}^9 p_n$ , where  $p_n$  is the extent of reaction computed by the method of Boyer.<sup>23</sup>

The extent of reaction  $p_n$  vs. the length of the polyene sequences  $n$  is presented in Figures 5–8. With increasing  $n$  a decrease of the extent of reaction  $p_n$  takes place; it is more intensive in the presence of the stabilizers than in the pure polymer. For the small doses the linear stabilizers prefer the formation of short polyene sequences in a less degree (Figs. 5 and 7). For the high doses, a much greater decrease of  $p_n$  value, for the stabilizers with aromatic groups, occurs (Figs. 6 and 8). These stabilizers diminish the  $p_n$  value more effectively for the longest sequences.

The changes of the total extent of reaction,  $p$ , are presented in Table IV, for two doses. These data, as compared with correlations in Figures 5–8, permit us to formulate the following conclusions.

The stabilizing action of the investigated epoxy compounds, in a low dose range, consists mainly of the inhibition of the kinetic growth of chain dehydrochlorination (the increase of the fraction of short sequences,  $n = 5$ , and decrease of long sequences). The total extent of reaction is, in this range, less affected. For the high doses the total extent of reaction diminishes and simultaneously the stabilizers I and IV (aromatic) inhibit more the increase of long sequences.

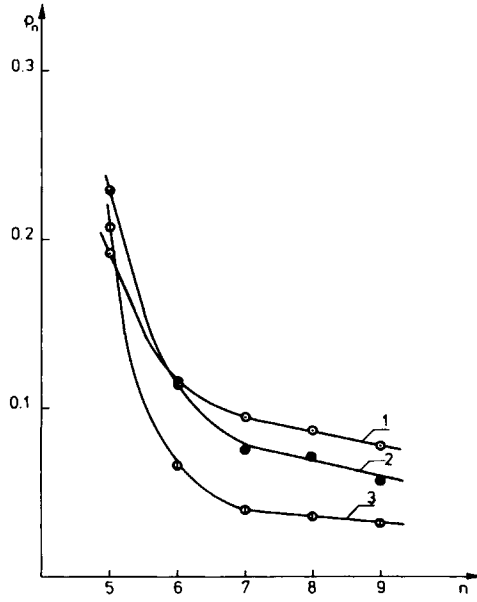


Fig. 7. The extent of reaction  $p_n$  vs. the number  $n$  of polyenes; designations 1, 2, 3 refer to PVC, PVC + stabilizer VI, PVC + stabilizer VII, respectively. Dose of 3.6 Mrad (36.4 kGy).

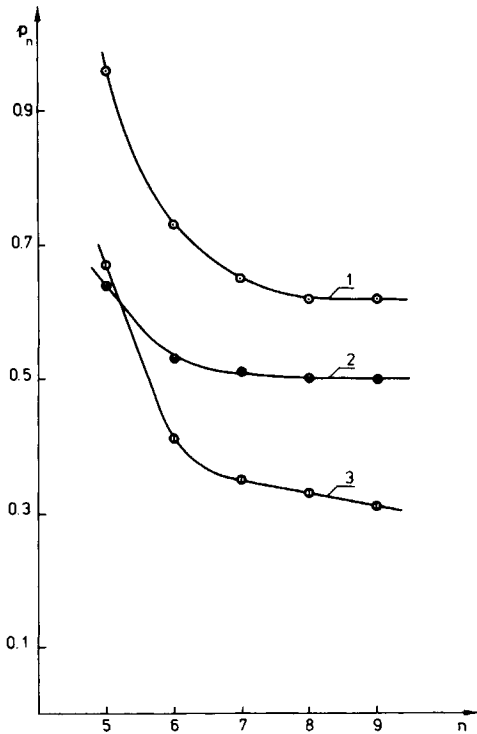


Fig. 8. The extent of reaction  $p_n$  vs. the number  $n$  of polyenes; designations 1, 2, 3 refer to PVC, PVC + stabilizer VI, PVC + stabilizer VII, respectively. Dose of 19.6 Mrad (195.7 kGy).



TABLE IV  
Changes in Total Extent of Reaction,  $p = \sum_{n=5}^9 p_n$ , in  $\gamma$ -Irradiated pure and stabilized PVC

System	3.64 Mrad (36.4 kGy)	19.6 Mrad (195.7 kGy)
PVC	0.57	3.64
PVC + I	0.57	2.71
PVC + IV	0.39	1.68
PVC + VI	0.55	2.70
PVC + VII	0.38	2.07

Some authors<sup>5</sup> affirm that the agreement between the extent of reaction  $x$  and the value of  $p$  takes place for small values of  $x$  to about 0.2 only. In our investigations there is ascertained that this agreement goes a little further: At the dose 3.6 Mrad (36.4 kGy) we have obtained, for the pure PVC,  $p = 0.57$  and  $x = 0.53$ . For the same dose and for all stabilizers used the values of  $x$  and  $p$  are compared in Table V.

The much greater decrease of the extent of reaction  $x$ , which is computed from HCl yield, in comparison to the extent of reaction  $p$ , which is the measure of the concentration of the formed conjugated double bonds, shows that the stabilizers used demonstrate a great ability to bind the evolved HCl. On the other hand, the diminishing of  $p$  value, relative to pure PVC, demonstrates the protective effect towards the macromolecules of PVC, and this is more clearly seen at high doses (see Table IV).

### O<sub>2</sub> Atmosphere

The spectra of investigated systems of PVC with stabilizers, irradiated in an oxygen atmosphere, do not demonstrate any fine structure, which is characteristic for conjugated polyene sequences. In these spectra, only a slight deformation at 323 nm appears, which corresponds to the absorption of the sequence with  $n = 5$ . On this ground we have measured the absorption at the wavelengths corresponding to the sequences  $n = 4, 5, 6$ . The absorption corresponding to the sequence  $n = 7$  was not observed.

The correlation between the absorption  $A$  and a dose is presented in Figures 9–11, for the stabilizers with aromatic ring ( $n = 4, 5, 6$ ). We do not present the data for the linear stabilizers (VI and VII) since the picture is similar. The basis for our conclusions was the quantitative comparison of these results.

As can be seen from the data presented, when the process of radiation oxidation occurs, the markedly different behavior of used stabilizers takes place. The stabilizer I does not inhibit but enforces the formation of polyene sequences, namely those with  $n = 5$  and 6. Stabilizer IV inhibits the growth of longer chains.

TABLE V  
Comparison of the extents of reactions  $x$  and  $p$ , for Pure and Stabilized PVC, Irradiated with Dose of 3.6 Mrad (36.4 kGy) in Nitrogen

System	PVC	PVC + I	PVC + IV	PVC + VI	PVC + VII
$x$ (%)	0.53	0.105	0.053	0.217	0.184
$p$	0.57	0.57	0.39	0.55	0.38

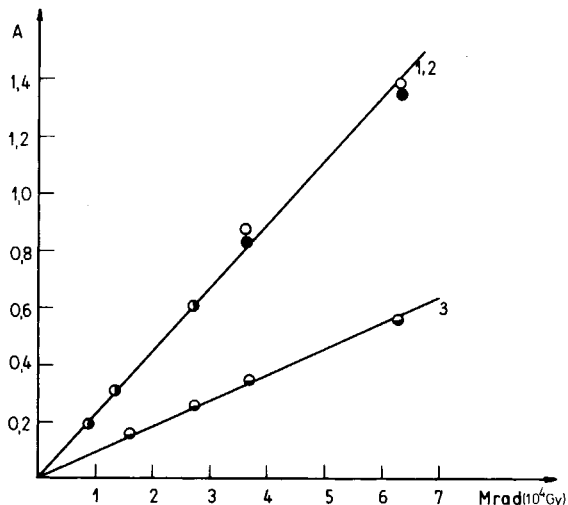


Fig. 9. The absorption  $A$  at the wavenumber  $3.3 \times 10^4 \text{ cm}^{-1}$  ( $n = 4$ ) vs.  $\gamma$ -irradiation dose; designations 1, 2, 3 refer to PVC, PVC + stabilizer I, PVC + stabilizer IV, respectively. Dose rate  $4.73 \times 10^{17} \text{ eV} \cdot \text{cm}^{-3} \cdot \text{min}^{-1}$ .

The linear stabilizers prevent the formation of a color, even at the doses exceeding 8 Mrad (80 kGy). The stabilizer VI, which to a smaller degree affects  $G_{\text{HCl}}$  proves to be the worse inhibitor of the polyene formation.

The action of stabilizer I, being antioxidant, consists, it seems, of the inhibition of an addition of oxygen to double bonds. Then the antioxidative action of styrene oxide (stabilizer IV) must go according to other mechanism, than the one mentioned above, since this epoxy compound stabilizes effectively the processes of dehydrochlorination, of the formation of hydroperoxides and of the formation of polyene sequences.

In the recapitulation of the results obtained in the presented cycle of investi-

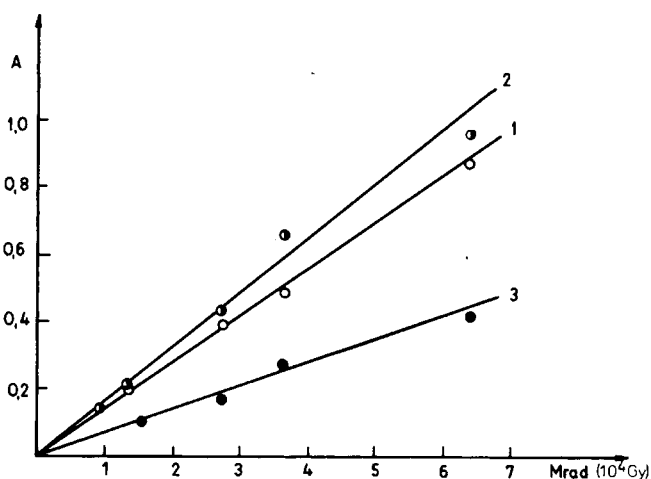


Fig. 10. The absorption  $A$  at the wavenumber  $3.1 \times 10^4 \text{ cm}^{-1}$  ( $n = 5$ ) vs.  $\gamma$ -irradiation dose; designations 1, 2, 3 refer to PVC, PVC + stabilizer I, PVC + stabilizer IV, respectively. Dose rate  $4.73 \times 10^{17} \text{ eV} \cdot \text{cm}^{-3} \cdot \text{min}^{-1}$ .

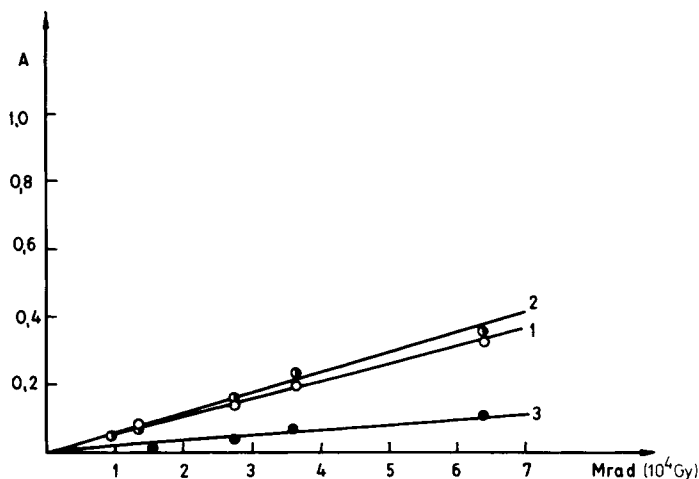


Fig. 11. The absorption  $A$  at the wavenumber  $2.7 \times 10^4 \text{ cm}^{-1}$  ( $n = 6$ ) vs.  $\gamma$ -irradiation dose; designations 1, 2, 3 refer to PVC, PVC + stabilizer I, PVC + stabilizer IV, respectively. Dose rate:  $4.73 \times 10^{17} \text{ eV} \cdot \text{cm}^{-3} \cdot \text{min}^{-1}$ .

gations one can state that the epoxy groups, in the stabilization of PVC towards ionizing radiation, play the twofold role.

The epoxy groups bind the evolved HCl and inhibit the formation of conjugated double bonds. The joint action of epoxy compound is wider and, in the case of the presence of aromatic groups, extends on the reactions of radiation oxidation.

### References

1. P. Nayler and M. C. Whiting, *J. Chem. Soc.*, **1955**, 3037 (1955).
2. F. Bohlman, *Chem. Ber.*, **86**, 265 (1957).
3. F. Bohlman and H. J. Mannhard, *Chem. Ber.*, **89**, 1309 (1958).
4. F. Sondheimer, D. A. Ben-Efraim, and R. Volovsky, *J. Am. Chem. Soc.*, **83**, 1675 (1961).
5. K. S. Minskier and E. O. Krac, *Vysokomol. Soed.*, **13**, 1205 (1971).
6. D. Braun and M. Thallmaier, *Makromol. Chem.*, **99**, 59 (1966).
7. M. Thallmaier and D. Braun, *Makromol. Chem.*, **108**, 241 (1967).
8. K. W. Hausser and R. Kuhn, *Z. Phys. Chem., B*, **29**, 363 (1935).
9. W. C. Geddes, *Rubber Chem. Technol.*, **40**, 177 (1967); *Eur. Polym. J.*, **3**, 747 (1967).
10. W. J. Bengough and J. K. Varma, *Eur. Polym. J.*, **2**, 61 (1966).
11. K. Hirayama, *J. Am. Chem. Soc.*, **77**, 379 (1955).
12. K. S. Minskier, E. O. Krac, and J. K. Pachomova, *Vysokomol. Soed.*, **12**, 483 (1970).
13. K. R. Popov and L. W. Smirnov, *Optik. Spektrosk.*, **14**, 787 (1963).
14. L. W. Smirnov and K. R. Popov, *Vysokomol. Soed.*, **A13**, 1204 (1971).
15. Y. Shindo and T. Hirai, *Makromol. Chem.*, **155**, 1 (1972).
16. K. W. Hausser, R. Kuhn, A. Smakula, and M. Hoffer, *Z. Phys. Chem.*, **B29**, 371 (1935).
17. J. R. Platt, *Radiation Biol.*, **3**, 176 (1956).
18. K. B. Abbas, *J. Macromol. Sci., Chem.*, **A12**, 479 (1978).
19. L. W. Smirnov, N. W. Platonova, and K. R. Popov, *Zh. Prikl. Spektrosk.*, **7**, 94 (1967).
20. Y. Shindo and B. E. Read, *Makromol. Chem.*, **118**, 272 (1968).
21. W. J. Bengough and H. M. Sharp, *Makromol. Chem.*, **66**, 31 (1963).
22. K. B. Abbas and E. M. Sorvik, *J. Appl. Polym. Sci.*, **17**, 3577 (1973); **19**, 2991 (1975).
23. R. F. Boyer, *J. Phys. Chem.*, **51**, 80 (1947).

Received June 1, 1981

Accepted August 19, 1982