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ELECTRON CAPTURE BY ACCEPTOR ADDITIVES DURING THE RADIOLYSIS OF POLYVINYL CHLORIDE

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In most works on the radiolysis of polymers, radical mechanisms of radiation-chemical reactions are considered. The possibility of ionic reactions is usually not taken into account, the main argument against a significant role of the latter being the short lifetime of the initially formed ions—according to estimates, 10^{-10}–10^{-13} sec and less—which is insufficient for ordinary (non-chain) ionic reactions to occur. It should be noted, however, that under certain conditions—the presence of electron-acceptor groups in the polymer and sufficiently low temperatures—processes of capture of thermal electrons can occur with appreciable efficiency, which should lead to an increase in the lifetime of the ions formed. A useful method for studying ionic reactions during radiolysis may be the introduction into the irradiated polymer of additives that are electron donors and acceptors ([1–4]).

In the radiolysis of polyvinyl chloride, especially at low temperatures, one may expect electrons to be captured by acceptor Cl-groups. If processes of this kind occur in the irradiated polymer, then the course of radiolysis may be influenced by additives of electron-acceptor substances. The present work is devoted to a study of electron capture by acceptor additives during low-temperature radiolysis of polyvinyl chloride, and also of the effect of the additives on the yield of gaseous radiolysis products (H_2, HCl).

As electron-acceptor additives we used compounds whose absorption spectra of anion-radicals are known in the literature: polynuclear aromatic hydrocarbons ([5])—anthracene, *n*-terphenyl; quinones—*n*-benzoquinone ([6]), tetrachloro-*n*-benzoquinone (chloranil) ([7]). Additives in amounts of 0.03-0.6 mole % were introduced into polymer films obtained by evaporating dichloroethane solutions (the mole of polymer was taken as the gram-molecule of the monomeric unit). Irradiation was carried out in sealed ampoules under vacuum (10^{-4} mm Hg) at 77° K using sources of γ-radiation Co^{60}. The dose rate was 0.6–1.7 Mrad/hr. The formation of anion-radicals was studied from absorption spectra in the visible and ultraviolet regions and from EPR spectra at 77° K. Optical absorption spectra were measured on an SF-4 spectrophotometer in a specially constructed

Fig. 1. Absorption spectra at 77°K of γ-irradiated PVC samples containing anthracene (a) and chloranil (b)

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quartz Dewar cell. A feature of the latter was the absence of liquid nitrogen in the path of the beam and precise magnetic fixation of the samples, which made it possible to obtain reproducible spectra of irradiated samples at the temperature of liquid nitrogen. EPR spectra were recorded on an EPR-2 radiospectrometer. For quantitative measurements, single crystals of $CuCl_2 \cdot 2H_2O$ were used as standards. Samples for EPR measurements were irradiated in ampoules made of "Luch-2" glass. The yield of H_2 was determined volumetrically on a Teppler apparatus, with other gaseous products frozen out. The yield of HCl was determined by titrating an aqueous extract with a solution of $AgNO_3$ using K_2CrO_4 as indicator (Mohr method).

In the absorption spectrum of pure polyvinyl chloride (PVC), irradiated at 77° K, a broad band appears with a maximum at 245 mμ; in the visible region the polymer remains transparent. PVC samples containing acceptor additives became intensely colored after irradiation at 77° K: with additions of chloranil and *n*-benzoquinone—yellow, with anthracene—green, and with *n*-terphenyl—yellowish-green. Spe-

absorption spectra of irradiated PVC with anthracene and chloranil additives are shown in Fig. 1. The shapes of the spectra and the positions of the absorption maxima are almost identical to those reported in the literature for the corresponding anion radicals obtained by chemical methods (5–7). The slight shifts of the absorption maxima are probably due to the influence of the solvent —solid PVC. Prolonged storage of the irradiated samples in vacuum at 77°K did not affect the intensity of the coloration; when warmed to room temperature the characteristic color of the anion radicals rapidly disappeared. Thawed irradiated samples of pure PVC, on prolonged keeping in vacuum (5–10 days), acquired an intense brown coloration associated with the formation of polyene chains (8–10). In the presence of acceptor additives the irradiated samples either did not become colored at all or were only weakly colored.

Some results of calculations of the concentrations and radiation-chemical yields of anion radicals, using extinction coefficients available in the literature, are given below.

Fig. 1. Absorption spectra at 77°K of γ-irradiated PVC samples containing anthracene (*a*) and chloranil (*b*)

The ESR spectrum of pure PVC irradiated at 77°K is characterized by a broad singlet-type signal with traces of hyperfine structure (Fig. 2a). In the presence of acceptor additives, a narrower signal of the anion radical appears, superimposed on the signal of the polymer radicals.

Table 1

Additive	Amount of additive, mol.%	Dose, Mrad	ε, L $\cdot$ mol^{-1} $\cdot$ cm^{-1} $\lambda_{\max}$	C, mol $\cdot$ L^{-1}	G_{total}	G_{par}
Benzoquinone	0.1	1.9	$7.4 \cdot 10^3$ (446)	$4.9 \cdot 10^{-4}$	0.257	150
»		9.5	$7.4 \cdot 10^3$ (446)	$1.23 \cdot 10^{-3}$	0.130	75
Chloranil	0.1	1.9	$7.1 \cdot 10^3$ (448)	$8.8 \cdot 10^{-4}$	0.465	123
»		12.7	$7.1 \cdot 10^3$ (448)	$2.11 \cdot 10^{-3}$	0.167	43
»	0.3	1.9	$7.1 \cdot 10^3$ (448)	$1.76 \cdot 10^{-3}$	0.93	80
»		12.7	$7.1 \cdot 10^3$ (448)	$2.93 \cdot 10^{-3}$	0.23	20
Anthracene	0.03	1.7	$9.0 \cdot 10^3$ (725)	$8.9 \cdot 10^{-4}$	0.525	573
»	0.1	1.7	$9.0 \cdot 10^3$ (725)	$1.61 \cdot 10^{-3}$	0.950	313
»	0.3	1.7	$9.0 \cdot 10^3$ (725)	$2.11 \cdot 10^{-3}$	1.25	136
»		3.4	$9.0 \cdot 10^3$ (725)	$2.42 \cdot 10^{-3}$	0.715	78
»		10.2	$9.0 \cdot 10^3$ (725)	$1.8 \cdot 10^{-3}$	0.177	19

G_{total} and G_{par} are the yields per 100 eV absorbed by the whole system and by the additive, respectively.

In some cases (for anthracene) we observed in the spectrum of the anion radical a weakly resolved complex hyperfine structure. At doses of 5–10 Mrad it can be seen that the introduction of acceptor additives suppresses the formation of radicals from the polymer, but the total radiation-chemical yield (G) of polymer radicals and anion radicals is approximately the same as in pure PVC and is ~ 2. With increasing dose, the spectrum of the additive anion radical is increasingly masked by the growing signal of the polymer radicals; however, even at a high dose of 65 Mrad, where the limiting concentration of polymer radicals is reached, the anion-radical signal can be isolated from the total ESR spectrum of a PVC sample with 0.3 mol.% chloranil. It is known that the chloranil anion radical gives an ESR spectrum in the form of a characteristic narrow singlet with a g-factor differing

Fig. 2

Figure 2: Fig. 2

from the value of the g-factor for the free electron (^{11,12}) (Fig. 2c). For quantitative separation of the anion-radical signal from the EPR spectra of irradiated PVC samples containing chloranil, we obtained the paramagnetic K-salt of chloranil semiquinone (^{13}). By graphical subtraction we separated the signals of the polymer radicals (Fig. 2a) and of the chloranil anion-radical (Fig. 2c) in the total spectrum of the irradiated sample (Fig. 2b). A similar separation was also carried out for samples containing anthracene. The yields of anion-radicals, calculated from the EPR spectra, are compared with the data obtained by the spectrophotometric method in Table 2. The agreement of the results obtained by two independent methods must be regarded as satisfactory. The observed discrepancy is due to inaccurate knowledge of the extinction coefficients under the experimental conditions, as well as to errors in the graphical separation and integration of the EPR spectra. The data obtained show that formation of anion-radicals upon irradiation proceeds with yields tens of times greater than would be energetically possible if one starts from an additive scheme of energy absorption.

Fig. 2. EPR spectrum at 77°K of γ-irradiated PVC containing 0.3 mol.% chloranil, dose 5.1 Mrad (b); EPR spectra of polymer radicals (a) and of the chloranil anion-radical (c), separated from (b).

The yield of anion-radicals does not depend on the irradiation temperature in the interval studied, 77—133°K; nevertheless, at room temperature they are not stabilized. Probably, on warming, the anion-radicals recombine with positive ions directly, and not by thermal release of electrons. The dependence of the concentration of chloranil anion-radicals on dose has a limiting character; saturation is reached at doses of 12–15 Mrad. In the case of anthracene and n-terphenyl, the dependence on dose has an unusual form: rapidly, at 3–4 Mrad, the maximum concentration of anion-radicals is reached; then, with increasing dose, a slow decrease is observed (Fig. 3). It may be assumed that the anion-radicals slowly react by electron donation with some intermediate compound accumulating during irradiation, possibly with free radicals. The yield of anion-radicals reaches a limiting value with increasing concentration of the additive (Fig. 4).

Table 2

Additive	Amount of additive, mol.%	Dose, Mrad	G_{tot} by EPR	G_{tot} from absorption spectra
Chloranil	0.3	5.1	0.19	0.46
»	0.1	5.1	0.09	0.18

Fig. 3

Figure 3: Fig. 3

Additive	Amount of additive, mol.%	Dose, Mrad	G_{tot} by EPR	G_{tot} from absorption spectra
Anthracene	0.3	5.1	0.18	0.40
»	0.1	5.1	0.16	0.32

The efficient formation of anion-radicals upon irradiation is difficult to imagine as occurring otherwise than through the capture of thermal electrons by acceptor molecules. However, direct capture of free electrons by the additives can hardly explain the high yields of anion-radi-

···radicals. We assume that initially the electrons are captured by macromolecules and only then pass into deeper traps—the additive molecules.

The yield of H_2 in irradiated PVC does not depend on the presence of acceptors and is ~ 0.2 at 77°K.

The principal product of PVC radiolysis, in terms of radiation-chemical yield, is HCl (10). Its elimination from the polymer chains leads to the formation of conjugated double bonds and to the appearance of characteristic absorption in the visible region (8–10). As noted above, the introduction of acceptor additives inhibits the coloration of the thawed irradiated polymer.

Fig. 3. Dependence of the concentration of anthracene anion-radicals on dose: *a*—0.1 mole%; *b*—0.3 mole%; *v*—0.6 mole% anthracene.

Measurement of the HCl yield, carried out several hours after thawing the irradiated PVC, gives approximately identical values both for the pure polymer and for samples with additives ($G_{HCl} \approx 1.6$—1.7). The samples at this stage are practically uncolored. Upon further keeping of the irradiated samples in vacuum for 5–10 days at room temperature, an additional amount of HCl is evolved in pure PVC (total $G_{HCl} \approx 2.4$) and the polymer becomes intensely brown, whereas PVC samples with additives did not become colored and no additional evolution of HCl occurred. Thus, acceptor additives inhibit the dehydrochlorination of irradiated PVC, which leads to the formation of polyene chains. We suppose that the process of chain dehydrochlorination is associated with capture of an electron by the polymer molecule and occurs as a “post-effect” upon thawing by successive elimination of HCl molecules from the macromolecular anion-radical with regeneration of the active center. We intend subsequently to study this process in greater detail.

Fig. 4. Dependence of the yield of anthracene anion-radicals on the concentration in the film

Fig. 4

Figure 4: Fig. 4

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