

Absorbing Capacity of Accelerated Electrons Flow of Some Polyfunctional Episulphide, Aminothiocarbamide Containing Polyelectrolytes

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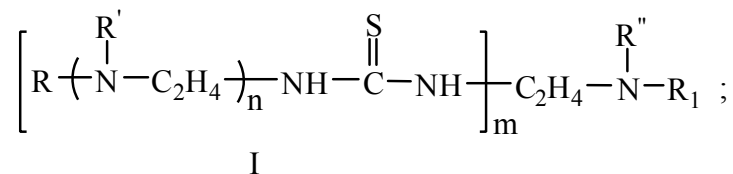
Abstract

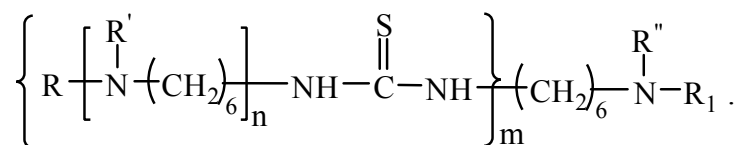
The method of preparation of polyfunctional carbamide and thiocarbamide and amine polymer complexes containing episulphide, nitrile groups and also fragments of quaternary amines and chlorine and possessing properties of cation polymer polyelectrolytes in a wide range of pH has been developed. The capacity of the synthesized polyelectrolytes to absorption of the accelerated electrons flow has been studied and power of the absorbed dose of β -radiation has been determined. It has been shown that the radioimmunity of cooligomers essentially depends on availability of sulphur-containing groups in their composition and is basically determined by availability of three-membered episulphide heterocycles, nitrile and amine fragments.

Keywords: complexes, polyelectrolytes, polyfunctionality, accelerated electrons flow, fragments, electrones

1. Introduction

The synthesis and application of functional episulfides can be judged by known results of study of their physiological activity and technical value (Rachinskiy & Slavachevskaya, 1965). At the same time it is necessary to estimate a possibility of use of polyfunctional episulphides as the semiproducts of synthesis of substances of various purpose (Eyzengart, 1967; Fokin & Kolomiets, 1978; Chew & Harry, 1993; Yuryev & Dyatlovitskaya, 1952, 1959; Talavar et al., 2007). It has been established that with increase of a molecular weight of homologs of ethylenesulphide it is decreased their toxicity which essentially depends on availability of chemically active atom groups in molecule and substituents in cycle. For this reason here are more widely used the products of conversion of episulphides from which, first of all, it should be noted derivatives of 2-aminoethylmercaptane and 2-alkyl(aryl)thioethylmercaptane served as a stimulus for wide study of their properties (Eyzengart, 1967; Fokin & Kolomiets, 1978; Chew & Harry, 1993). The various derivatives of 2-aminoethyl-mercaptane are widely studied basically as the radioprotective means. The condensation products of ethylene sulphide with the primary amines are used for preparation of compounds with heterocyclic structure among of which the substances with radioprotective action and fungicide properties have been found (Yuryev & Dyatlovitskaya, 1952, 1959). It has been previously reported about development of new water-soluble antimicrobial compounds possessing properties of cation polymer electrolytes in a wide range of pH (Talavar et al., 2007; Dzhaferov et al., 2012; Dzhaferov, 1989; Bektashi & Dzhaferov, 2004; Dzhaferov & Bektashi, 2002):

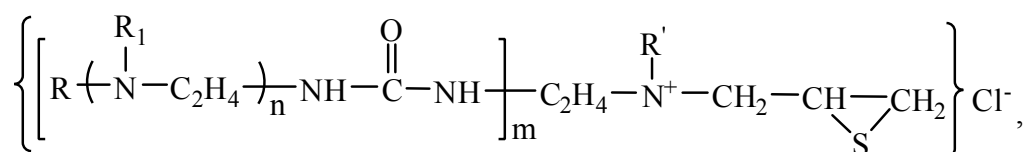




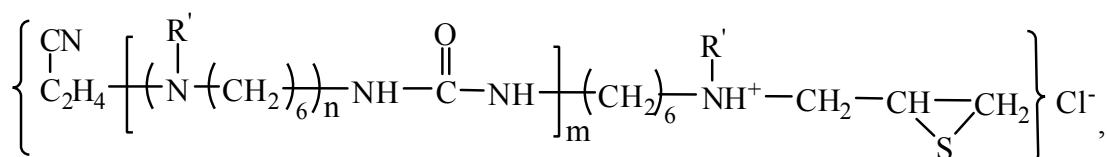
II

2. Materials and Methods

In this investigation the method of preparation of the polyfunctional carbamide and thiocarbamide amine polymer complexes containing episulphide, nitrile groups and also fragments of quaternary amines and chlorine has been developed. It has been shown that the interaction of epichlorhydrin with thiocarbamide containing amine compounds—polyethylenepolyamine or hexamethylenediamine—leads to formation of carbamide containing oligomer complexes with the supposed structures (III–VI):



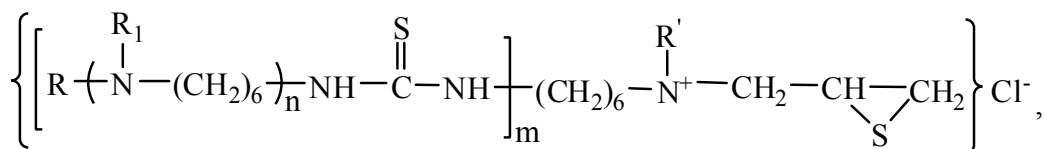
III-V



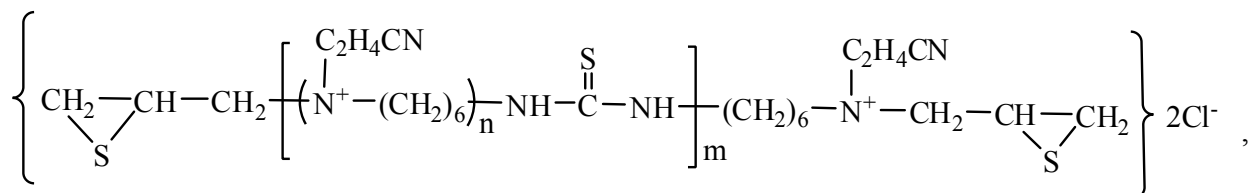
VI

where $n = 1-3$; $m = 1-8$; $R, R', R'' = H, R_1 = \text{C}_2\text{H}_4\text{CN}$ (I); $R, R', R'', R_1 = \text{C}_2\text{H}_4\text{CN}$ (II);
 $R_1 = H, R, R' = \text{C}_2\text{H}_4\text{CN}$ (III); $R, R_1, R' = H$ (IV); $R, R_1, R' = \text{C}_2\text{H}_4\text{CN}$ (V); $R' = H$ (VI)

An interaction of epithiochlorhydrin with thiocarbamide containing hexamethylenediamine fragments leads to the formation of thiocarbamide containing polymers with structures:



VII-IX



X

$R, R_1 = H, R' = \text{C}_2\text{H}_4\text{CN}$ (VII); $R, R_1 = \text{C}_2\text{H}_4\text{CN}, R' = H$ (VIII); $R, R_1, R' = \text{C}_2\text{H}_4\text{CN}$ (IX)

The structure of the prepared oligomers I-XI has been confirmed with the IR- and PMR-spectral methods, chemical conversions, elemental analysis.

In all IR-spectra of oligomers I-II the found absorption bands at ~ 3410 , 1560 , 1450 , 1310 , 1100 cm^{-1} are referred to thiocarbamide group, at 3400 cm^{-1} —to the secondary amide groups of thiocarbamides. The found frequencies of the compounds III–IV at 3440 , 1680 , 1680 , 1655 cm^{-1} are referred to the secondary carbamide fragments. In compounds I, IV and VII the absorption bands in the field of valence vibrations at $\sim 3510\text{ cm}^{-1}$ and in the field of deformation vibrations 1640 – 1565 cm^{-1} are characteristic for the primary amines, the frequencies 3360 – 3320 cm^{-1} are characteristic for the secondary amines in compounds III and VI. In the spectra of substances I–X the frequencies 2260 – 2230 cm^{-1} are referred to nitrile groups. The found sufficiently narrow "Ammonium band" in the field of 2700 – 2260 cm^{-1} is referred to ammonium salt in compounds III–X. In all IR-spectra of III–IX the absorption bands in the field of 660 – 620 cm^{-1} characteristic for three-membered episulphide groups have been found (Dzhafarov, 1989).

The PMR-spectra of III–X consist of some groups of the resonance absorptions. The resonance signals with the chemical shifts 2.13 ppm and 2.38 ppm are referred to heminal protons of methylene group of episulphide ring. The doubling has been connected with spin-spin interaction of episulphide ring with CH-group. Multiplet having chemical shift $\sim 2.96\text{ ppm}$ corresponds to proton of CH-group of episulphide cycle. The multiplicity has been stipulated with the fact that this proton interacts both with protons of methylene group of episulphide ring and with protons of methylene group connected with amines. The signals with 2.80 – 4.10 ppm as a multiplet correspond to the rest groups in oligomers. The resonance absorption 1.45 ppm is referred to 4 protons of methylene (CH_2 , CH_2) groups. The resonance absorptions as a multiplet with 2.10 – 2.60 ppm are referred to protons of methylene groups in tertiary amines of polymers V, VIII–X.

The molecular-weight distribution (MWD) has been studied by example of polyethylenepolyaminethiocarbamide (I). The optimal conditions of formation of the products I–X have been found and it has been established that the prepared oligomers, basically consist of two fractions with molecular weights 250 – 300 (in this case $m = 1$ – 2) and 3000 – 4000 , a ratio of which is changed depending on conditions of synthesis. It has been shown that by change of ratio of the taken components the oligomers with various content of functional groups are prepared. So, in a case of compound I with the reaction temperature rise to 433 K and at reaction duration 3 h a content of low-molecular fractions is decreased to minimum (10%) and the product basically consist of oligomer molecules with M_w and M_n equal to 4000 and 4200 respectively. In this case a coefficient value of polydispersity ($M_w/M_n = 1.05$) is close to one. This index is one of the important characteristics for polyelectrolytes used as the preparations with narrow MWD. The study of MWD was carried out by the method of exclusion chromatography on high-effective liquid chromatograph of firm "KOVO" (detector—refractometric). Two columns with size $3.3 \times 150\text{ mm}$ filled with sorbent separon SGX have been used. Eluent-dimethylformamide.

It should be noted that three-membered saturated heterocyclic episulphide compounds are differed with clearly expressed dual reactivity. Their characteristic feature consists of sufficiently easy opening of cycle skeleton both with electrophilic and nucleophilic reagents. It testifies that the episulphide cycles have high-reactive nucleophilic and electrophilic centers, i.e. filled electron-donor and unoccupied electron-acceptor orbitals strongly differing according to the energetic state. An availability of three-membered episulphide heterocycles in polymer complexes at irradiation of the latter ones with the accelerated electrons flow favors increase of valency of sulphur atoms which leads to the absorption of radiation. The other reason favoring increase of absorbing capacity of β -radiation can be a close spatial disposition of sulphur atoms of episulphide cycle and amine groups similarly to that as it takes place in the known radiative-resistance compounds (Rachinskiy & Slavachevskaya, 1965; Dzhafarov et al., 2012; Dzhafarov, 1989). At radioactive decay of atom nuclei the high-energetic particles (Akulov, 1984), energy of which in this experiment is in the ranges of 0.5 – 10 MeV are beamed. At such decay the basic views of radiation are: β -particles (electrons), α -particles (helium nucleus) and photons (electromagnetic radiation of γ -beams), and at fission of atomic nuclei the fission fragments, neutrons and γ -beams are formed. These beams accompany almost all nuclear processes (Dzhafarov & Bektashi, 2002; Akulov, 1984; Radiation chemistry of polymers, 1966; Alexander, 1953; Pikaev, 1987; Asthana & Nukundan, 2002) and their basic characteristic is penetrating power through substance which depends on particle energy. In the field of average energies of photons (approximately to 10 MeV) the photoeffect, Compton effect and formation effect of vapors have the most essential value. In all these processes the electrons which, first of all, interact with substance are formed. Therefore a determination of penetrating power of electrons is of great interest. Due to small density and thickness of materials used for protection, for determination of their absorbing capacity the accelerated electrons flow with nominal energy of 0.8 MeV close to threshold energy of β -particles has been used. The absorbing capacity of the polymer complexes shows how efficiently this material is subjected to radiation as a result of which energy and flow of penetrating particles is decreased.

3. Result and Discussion

As a result of the carried out investigations on study of properties of polyfunctional episulphide polymer complexes—electrolytes—in a wide range of pH medium their capacity to absorption of the accelerated electrons flow depending on availability of the functional fragments and their structure has been revealed and quantitatively determined. The investigated polymer complexes I–XI were irradiated in cells from mica with cross-linked sizes $20 \times 25 \text{ mm}^2$, which are greater than diameter of the accelerated electrons beam. The cells thickness was changed in the ranges from 1.0 to 1.5 mm. The absorption of the accelerated electrons flow was determined according to the change of beam current of the latter ones. The beam current was measured by means of Faraday cylinder directly before and behind preparation (J_0 and J_1) respectively (see Figure 1).

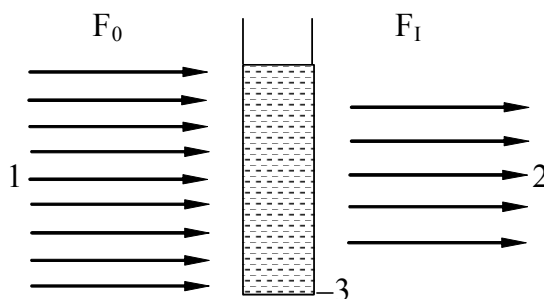


Figure 1. Accelerated electrons flow falling on cell with preparation (3); 2 – weakened electrons flow after absorption with preparation; the tests have been carried out on device ELU-4

The relative absorption of flow has been determined on formula:

$$K (\%) = \frac{J_0 - J_1}{J_0} \times 100 \quad (1)$$

F_0 and F_1 —powers of the accelerated electrons flow falling on preparation and passing through it, respectively. An absolute power value of the absorbed flow is determined as a difference between F_0 and F_1 i.e. as $\Delta F = F_0 - F_1$. The power of the absorbed dose has been calculated on formula:

$$D = \frac{\Delta F \cdot \epsilon}{\rho \cdot L} \times 1.58 \times 10^{-8} \text{ (rad / sec)} \quad (2)$$

ΔF – absolute power value of the absorbed flow of particles ($\text{el/cm}^2 \cdot \text{sec}$); ϵ – particles energy (MeV), in our case $\epsilon = 0.8 \text{ MeV}$; ρ – density of sample (g/cm^3) for complexes I–IX is changed in the ranges from 1.145 to 1.195; L —thickness of the irradiated layer (mm).

In Table the results of study of the relative absorbing capacity of the accelerated electrons flow calculated on the basis of experimental data on formula (1) (K , %), and also power values of the absorbed dose of the accelerated electrons flow falling on cell with preparation determined on Formula (2) (D , rad/sec.).

Table 1. Study of absorbing capacity of the accelerated electrons flow of episulphide polymer complexes

№ Comp.	Preparat. thickness L (mm)	Density of sample ρ (g/cm ³)	J_0 (mcA)	J_1 (mcA)	$F_0 \cdot 10^{-10}$ el/cm ² ·sec	$F_1 \cdot 10^{-10}$ el/cm ² ·sec	$\Delta F \cdot 10^{-9}$ el/cm ² ·sec	D rad/sec	K (%)
I	1.0	1.158	0.048	0.047	3×10^{10}	2.94×10^{10}	0.6×10^9	0.48×10^2	2.08
II	1.0	1.160	0.05	0.047	3×10^{10}	2.75×10^{10}	2.5×10^9	2.72×10^2	6.00
III	1.0	1.158	0.048	0.043	3×10^{10}	2.65×10^{10}	3.5×10^9	3.82×10^2	10.42
IV	1.0	1.160	0.048	0.044	3×10^{10}	2.78×10^{10}	2.2×10^9	2.42×10^2	8.33
V	1.0	1.168	0.048	0.042	3×10^{10}	2.55×10^{10}	4.5×10^9	4.87×10^2	12.5
VI	1.0	1.170	0.11	0.095	3×10^{10}	2.40×10^{10}	6.0×10^9	6.48×10^2	13.63
VII	1.38	1.168	0.05	0.042	6.88×10^{10}	5.86×10^{10}	10.2×10^9	8.01×10^2	16.0
VIII	1.38	1.175	0.05	0.040	6.88×10^{10}	5.90×10^{10}	9.8×10^9	7.64×10^2	20.0
IX	1.0	1.176	0.11	0.082	6.88×10^{10}	5.88×10^{10}	10×10^9	10.8×10^2	25.45
X	1.38	1.195	0.11	0.075	6.88×10^{10}	5.40×10^{10}	14.8×10^9	11.34×10^2	31.82

The tests showed that the radioimmunity of the prepared complexes essentially depends on availability of the functional groups in their composition. So, for ex., an availability three-membered episulphide heterocycles, amine and nitrile fragments in molecules of the polymer complexes III–X increases relative absorbing capacity (K) of their polymers from 8.33 to 31.82%. It means that each 1 cm² of the polymer complex with thickness of 1.38 mm (VII, VIII, X) for 1 sec. absorbs almost one of third part of dose β -radiation falling on preparation. In this case the power of the absorbed dose (D , rad/sec) is increased to 11.34×10^{-2} . It has been shown that with increase of the absorbing capacity of the products (I–X) the power of the absorbed dose from 0.48×10^{-2} to 11.34×10^{-2} rad/sec (Table 1) is changed. It is seen from of Table that polyethylenepolyaminothiocarbamide (XI) doesn't show capacity for absorption of the accelerated electrons flow, in spite of the fact that it is sulphur-containing compound. However, unlike compounds (XI) nitrile-containing thiocarbamides I and II show absorbing capacity ($K = 2.08$ and 6.00). In this case the compounds III–X are sufficiently effective in this relation. It has been shown that with increase of content of three-membered episulphide and thiocarbamide groups (compounds VII–X), instead of carbamide (compounds III–VI) and also nitrile groups in macromolecules of the polymers an increase of capacity for absorption of the accelerated electrons flow with the compounds is observed (see Table 1).

4. Conclusions

We have established that the polymers formed on the basis of epithiochlorhydrin, thiocarbamide and hexamethylenediamine (VII, VIII, X) possess more high efficiency to electrons capture ($K = 16.0$ –31.82%) than the polymers on the basis of epichlorhydrin, thiocarbamide of polyethylenepolyamine (III–V) or hexamethylenediamine (VI) ($K = 8.33$ –13.03%). Unlike the known (Rachinskiy & Slavachevskaya, 1965; Eyzengart, 1967; Dzhaferov et al., 2012; Pikaev, 1987) used episulphide (ethylenesulphide) preparations the prepared new polyfunctional polymers of episulphide electrolytes have not odor nuisance and don't possess toxicity and also show antibactericide properties (Talavar et al., 2007; Asthana & Nukundan, 2002). These polyfunctional oligomer complexes can be used in special technology (Pikaev, 1987) for making of protective materials from β -radiations and antibactericide preparations, flocculants and binding components for space technology (Talavar et al., 2007; Pikaev, 1987; Asthana & Nukundan, 2002).

It has been also revealed that the prepared thiocarbamide-containing oligomers are the efficient binder for nanodispersed powder which is used in space technologies (Dzhaferov & Guseinov, 2012).

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