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Radiation-chemical degradation of cellulose and other polysaccharides

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Abstract. Results of studies on the radiation-chemical transformations of cellulose, its ethers, and some other polysaccharides (xylan, starch, dextran, chitin, chitosan, and heparin) are discussed. Ionising radiation causes the degradation of these compounds accompanied by decomposition of the pyranose ring and formation of compounds with carbonyl and carboxy groups, as well as formation of hydrogen, carbon dioxide, and carbon monoxide. The efficiency of degradation increases considerably with temperature and depends on the structure of the polysaccharide and the nature of its substituents. A mechanism of the radiation-chemical transformations of cellulose and other polysaccharides is suggested. The prospects of using radiation-chemical methods for processing of cellulose and other polysaccharides in industry and agriculture are considered. The bibliography includes 213 references.

I. Introduction

Cellulose is the most widespread natural polymer, the main component of plants. Products based on cellulose are widely used in everyday life. In many technological processes, cellulose undergoes radiation treatment. They include: sterilisation of cellulose-based dressings; degradation of plant raw materials aimed at the intensification of industrial hydrolysis of raw materials and production of foodstuff, forage, and technical products (alcohols, furfural, *etc*.); preliminary treatment of cellulose for subsequent production of its various derivatives (nitrates, xanthates, *etc*.), and a number of other processes.

The prospects for the successful adoption of radiation technology for preliminary cellulose treatment stem from the possibility of replacing ecologically hazardous chemical steps by pure treatment with ionising radiation, reduction of the number of technological stages, and decrease in energy consumption. These factors encourage the studies in the field of radiation chemistry of cellulose and related compounds, in particular, on the elucidation of the detailed mechanism of radiation-induced chemical transformations. Furthermore, depending on the area of cellulose application, opposite problems are targeted: on the one hand, increase in the radiation stability of cellulose, and on the other hand, intensification of its degradation.

Preliminary destructive treatment of cellulose by ionising radiation may turn out to be particularly important for the industrial production of viscose and nitrate esters. The manufacture of these compounds generally includes a preliminary stage of cellulose treatment in order to decrease its molecular mass. Radiation treatment can eliminate this stage or simplify it considerably. In addition, radiation-induced degradation of cellulose-containing plant materials favours their subsequent acid hydrolysis, which is particularly important for the intensification of industry based on hydrolysis. It has also to be taken into consideration that cellulose and a number of other polysaccharides (chitin, starch, *etc*.) are the constituents of biological structures. Therefore, systems based on these polysaccharides are rather convenient models for studying the effect of radiation on biological structures.

We discussed the problems of the radiation chemistry of cellulose in a previous review[1] in which the results published before 1984 were systematised. Since that time, new experimental results on the mechanism of cellulose radiation-induced degradation have been obtained. This mechanism has the form of a local explosion of the pyranose ring in the polymeric chain, which results in its scission with formation of diverse products. To date, quantitative relationships for the radiation-chemical yields of degradation and major products † have been determined and ways for intensifying the degradation of cellulose and plant

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† The radiation-chemical yields refer to 100 eV of energy absorbed. For example, the yield of degradation is the number of bonds cleaved per 100 eV of energy absorbed, the yield of gaseous products is the number of gas molecules per 100 eV of energy absorbed, the yield of the oxidised groups is the number of these groups per 100 eV of energy absorbed, *etc*.

materials by combined ionising radiation and thermal treatment as well as by mechanical treatment (grinding) have been established. The present review includes data on the radiation-induced degradation and chemical transformations of other polysaccharides (starch, xylan, chitin, *etc.*), which make it possible to reveal general regularities of the interaction of ionising radiation with this important class of natural compounds.

II. Random degradation of polymers

The main result of the action of ionising radiation on cellulose (as well as on other polysaccharides) is scission of the polymeric chain, *i.e.* the degradation changing the physicochemical properties of the polymer (structural state, mechanical strength, solubility in different media, reactivity, *etc.*).[1]

Let us consider degradation in which a macromolecule undergoes random scission without cross-linking.[2–5] It will be shown below that this process predominates on irradiation of cellulose and other polysaccharides.

The degradation of polymers is described using the statistical method. If the initial molecular-mass distribution (MMD) of the polymer is the most probable one and the chain scission occurs randomly, the MMD will be maintained with a decrease in the average molecular mass of the fragments. The following equation relating the number of scissions (S) per initial polymeric molecule to the number-average (P_n) and weight-average (P_w) degrees of polymerisation is valid

$$S = \frac{P_n^0 - P_n}{P_n} = \frac{P_w^0 - P_w}{P_w}, \quad (1)$$

where P_n^0 and P_w^0 are the starting number-average and weight-average degrees of polymerisation, respectively. For the most probable distribution, $P_w = 2P_n$.

The number of scissions can also be calculated from the radiation-chemical yield of degradation according to the following equation:

$$S = \frac{DP_n^0 mG^0}{10^2 N_A}, \quad (2)$$

where D is the absorbed dose, eV; m is the molecular mass of a polymer monomeric unit (which equals 162 for cellulose); and N_A is the Avogadro number.

Combining Eqns (1) and (2) we obtain the dependence of the number-average (or weight-average) degree of polymerisation on the absorbed dose of ionising radiation

$$\frac{1}{P_n} - \frac{1}{P_n^0} = \frac{G^0 mD}{10^2 N_A}. \quad (3)$$

Thus, the quantitative determination of the efficiency of radiation-chemical degradation of cellulose expressed through the yield G^0 is reduced to finding the dependence of P_n or P_w on the absorbed dose according to Eqn (3).

Experimental determination of the number-average degree of polymerisation P_n of cellulose is carried out rarely. This is usually performed using osmometry, which gives a considerable error. In practice, the degree of polymerisation of cellulose is most commonly determined by measuring the viscosity of its dilute solutions. The empirical Mark–Kuhn–Houwink equation, which relates the characteristic viscosity of a solution $[\eta]$ to the viscosity-average degree of polymerisation P_v, is valid in this case:

$$[\eta] = KP_v^\alpha. \quad (4)$$

For a given polymer, the K and α coefficients are constants provided the measurement conditions and solvents are the same. The dependence of P_v on P_n is given by the equation[3]

$$P_v = P_n[(\alpha + 1)\Gamma(\alpha + 1)]^{1/\alpha} = P_n^0 k, \quad (5)$$

where $\Gamma(\alpha+1)$ is the gamma-function of α and k is a coefficient. Depending on the shape of the polymer macromolecule in solution and the character of the solvent effect, the value of $1/\alpha$ varies from 0.6 to 1.0, which corresponds to a variation of the term in brackets in Eqn (5) just from 1.82 to 2.0.[3] Thus, one can determine the yield of polymer degradation G^0 from the experimental values of P_v using the equation

$$\frac{1}{P_v} - \frac{1}{P_v^0} = \frac{G^0 mD}{10^2 N_A k}, \quad (6)$$

where the k coefficient takes account of the actual ratio of P_v and P_n determined from Eqn (5).

In determination of the radiation-chemical yield of cellulose degradation, one makes certain assumptions on the character of its molecular-mass distribution and the random chain scission; also, one takes into consideration the use of different experimental methods for the measurement of its molecular mass with different inherent errors. The degradation of cellulose has been dealt with in a number of studies.[6–24] The yields of degradation have a considerable scatter from 1.8–2.0 (see Refs 6 and 7) to 25 (see Ref. 8). Let us consider in more detail the effect of the main factors on the determination of the radiation-chemical yield of cellulose degradation.

Molecular-mass distribution factor. Equations (3) and (6) were obtained for the most probable molecular-mass distribution. However, this is generally not the case for the MMD of the original celluloses. One cannot state *a priori* that radiation-induced degradation results in the most probable distribution. Therefore, it is necessary to follow the changes of cellulose MMD during irradiation and to find the relationship between P_n and P_v. If the MMD differs from the most probable one, the k coefficient in Eqn (6) should differ from the value corresponding to the most probable distribution (~ 2). However, it was assumed groundlessly that $P_n = P_v$.[6, 7, 9–14, 17–19] The radiation-chemical yield was generally close to 3.

This approach is based on the assumption on the monodispersive MMD and its retention during the irradiation, *i.e.* it is assumed that the radiation-induced cleavage of polymer chain bonds is not random. Then it should follow that the yield of degradation is underestimated considerably. If this process is random and the cellulose MMD is nonuniform before the irradiation, it will tend to reach uniformity during the irradiation. It will be shown below that the ratio $P_v \simeq 2P_n$ is established in the case of uniform MMD. Therefore, the yield of degradation should be twice as high as that measured under the assumption that $P_n = P_v$.

Assuming a random character of cellulose degradation, it is easy to show that with virtually any initial MMD, the most probable distribution is reached during the irradiation. The dose required for this may vary from 30 to 80 kGy depending on the initial MMD. For the first time, this conclusion seems to have been confirmed experimentally by Kusama *et al.*[20] It was shown that during γ-irradiation of cotton cellulose whose initial MMD was close to the monodisperse one ($P_v/P_n = 1.26$), the most probable distribution was reached at an absorbed dose of 30–50 kGy ($P_v/P_n = 2.0 \pm 0.1$). Hence, when the molecular mass of cellulose is determined by viscosimetry, the use of Eqn (6) for the description of degradation is justified at doses exceeding the above value.

Chemical stability of irradiated cellulose in different solvents. In early studies, the viscosity of cellulose was measured mostly in aqueous solutions of copper complexes with ammonia or ethylenediamine.[6, 7, 9–12, 14, 16, 21–24] In some cases, the radiation-chemical yields of degradation differed considerably. As to the yield of carbonyl groups, it was unreasonably high (*e.g.*, 58 in Ref. 22). This fact may be regarded as an indication of the chain character of degradation. However, it became clear later that cellulose in the presence of bivalent copper underwent spontaneous oxidative alkaline degradation. This process was initiated

by the existing terminal carbonyl groups,[25] whose concentration in cellulose increases significantly after irradiation. Therefore, one has to consider critically the results obtained without taking account of the possible spontaneous alkaline degradation of cellulose in the solvents specified above.

A quantitative estimate of possible errors resulting from the use of alkaline solutions of copper complexes with ammonia or ethylenediamine for the analysis of cellulose was made in by Sakurada *et al.*[13] As shown in later studies, the optimum solvent for cellulose is cadoxen, *i.e.* an aqueous solution containing cadmium oxide and ethylenediamine.[26–28] In this solvent, cellulose undergoes no noticeable spontaneous degradation. It was extensively used in studies of the radiation-induced degradation of cellulose. In some cases, cellulose was nitrated first, and the viscosity of the resulting nitrates was then measured in acetone.[13, 15, 20] All these methods made it possible to avoid the errors caused by the chemical degradation of irradiated cellulose during the preparation of its dilute solutions.

III. Radiation-chemical degradation of cellulose

The radiation-chemical degradation of cellulose of different origins in different solvents has been studied.[16, 20, 29, 30] Changes in the degree of polymerisation of cotton cellulose upon γ-irradiation as measured by viscosimetry in cadoxen were shown to be a function of the absorbed dose.[29]

Dose /kGy	0	5	10	32	170	480	680	800	1680
P_v	2537	827	723	314	138	32	30	28	14

It is seen that the degree of polymerisation decreases with an increase in the dose, *i.e.* cellulose undergoes degradation. It was noted[29] that the crystallinity index remains virtually unchanged at all absorbed doses and equals 73%. The amount of the fraction soluble in ethanol increases from 10.3% in non-irradiated cellulose to 43.7% at an absorbed dose of 1680 kGy. Figure 1 presents the dependence of $1/P_v - 1/P_v^0$ on the absorbed dose. Unless specified otherwise, it was dry cellulose that was subject to γ-irradiation *in vacuo* or in an inert gas. The cellulose was dried at 105 °C over P_2O_5.

The characteristic viscosity of cotton cellulose has been measured in a solution of copper–ethylenediamine complex.[16] Freshly prepared solutions were used, and the possible spontaneous alkaline degradation of cellulose was taken into account. In another study,[30] the sulfite cellulose with an initial degree of polymerisation of 920 was used; the characteristic viscosity was measured in cadoxen solutions. Finally, Kusama *et al.*[20] studied Mexican cotton with an initial degree of polymerisation of 3265, whose characteristic viscosity was measured in acetone following nitration of the irradiated material.

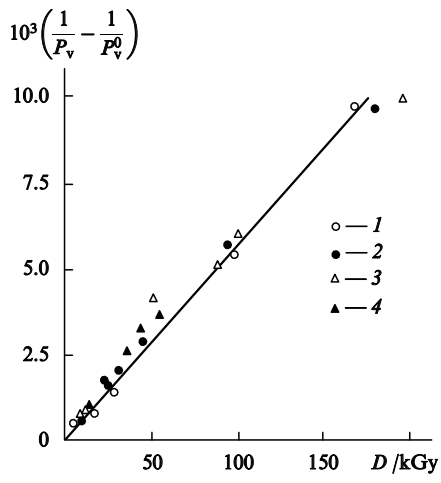


Figure 1. Dependence of $1/P_v - 1/P_v^0$ in cellulose on the absorbed dose; (*1–4*) data from Refs 29, 16, 30, and 20, respectively.

At doses above ~50 kGy, all experimental data from these works[16, 20, 29, 30] fit on a linear plot, which passes through the origin. Hence, Eqn (6) actually gives a good quantitative description of the dependence of the degree of polymerisation on the absorbed dose for celluloses from various sources. It turned out to be insignificant in practice what solvent was used for the determination of the characteristic viscosity of dilute cellulose solutions and what kind of cellulose was used. A detailed analysis of data for doses below 50 kGy showed some deviations of the $(1/P_v - 1/P_v^0) - D$ dependence from linearity, which is due to nonuniform MMD of the starting celluloses and to the fact that the most probable distribution is reached at doses above 50 kGy.

Thus, the validity of Eqn (6) confirms the random character of degradation and the attainment of the most probable molecular-mass distribution. When determining the radiation-chemical yield of degradation, one has to take into account the relationship between the viscosity-average and number-average degrees of polymerisation as a function of the α factor involved in Eqn (5). For cadoxen, the α factor is 0.94 (see Refs 26–28), and the corresponding relationship is $P_v = 1.96P_n$. For a copper–ethylenediamine complex solution, the α factor is considered to be 0.9 (see Ref. 16), and $P_v = 1.9P_n$. Finally, for solutions of nitrocellulose in acetone, the α factor is considered to be 1 (see Ref. 20), and $P_v = 2P_n$. Taking the errors inherent in the viscosimetric method into account, one has grounds to assume that the following relationships are valid for all of the solvents mentioned: $P_v = 2P_n$ and $P_v = P_w$. Hence, the k coefficient in Eqn (6) may be considered to be ~2. Given the slope of the linear plot in Fig. 1, one can find the yield of cellulose degradation from Eqn (6); it equals 6.0 ± 1.0. In Refs 16, 20, and 30, whose experimental data we used for the determination of the degradation yield, it was assumed that $P_v = P_n$. The yield determined under this assumption was about two times smaller than that determined by us.

It was noted[12] that the yield of degradation of various kinds of cellulose materials changed from 7.6 to 3.1 with an increase in the absorbed dose from 12 to 120 kGy. The yields were calculated assuming that $P_n = P_v$. This dependence of the yield on the dose can be explained as follows. At small doses, uniform MMD is not established yet, hence it is improper to use Eqn (6) for calculation of the yield. At large doses, uniform MMD is reached, so it is necessary to bear in mind that $P_v = 2P_n$. In this case, we find that the yield of degradation is 6.2, *i.e.* it agrees with the value determined above.

The viscosimetric method in copper–ammonia solutions was used to measure the degradation yields, which were found to be 4.5 (Ref. 24) and 5.0 (Refs 3 and 21), account being taken of the partial degradation of cellulose. The actual dependences of P_n and P_v on the characteristic viscosity according to Eqns (4) and (5) were used in these calculations. The P_n values of nitrocelluloses were determined by the osmometric method, and the degradation yields were calculated to be 3.3 (Ref. 13) and 2.9 (Ref. 15). These low yields might be due to the low accuracy of the method used and the small absorbed doses at which the uniform MMD was not achieved.

The discrepancies between the literature data for the radiation-chemical yields of cellulose degradation are explained by different interpretations of viscosimetric data for the molecular mass determination and by differences in the absorbed doses. Given a random pattern of radiation-induced degradation, it is only at a certain absorbed dose that the most probable distribution is reached, where $P_v = 2P_n$. In this case, Eqn (6) can be used for the yield determination. Analysis of experimental data from numerous works shows that, taking account of the factors specified above, the yields are very similar and are equal to 6.0 ± 1.0.

Cellulose materials differ markedly in their initial molecular masses and in the MMD.[31–34] For instance, the weight-average degree of polymerisation (P_w) changes from several thousand for

cotton linter to ~400 for viscose fibres.[34] As a rule, the MMD differs noticeably from the most probable distribution, and the non-uniformity factor $U = P_w/P_n$ for the majority of natural and industrial celluloses varies over the range 1.2–3.0.[33]

Let us evaluate the effect of the MMD non-uniformity factor of the starting cellulose on the dependence of $1/P_v$ on the absorbed dose assuming a random degradation pattern. At absorbed doses D_c where the most probable distribution is reached, the following equation is valid:

$$\frac{1}{P_v} = \frac{G^0 m D_c}{10^2 N_A k} + \frac{U^0}{2P_v^0},$$

where $U^0 = P_w^0/P_n^0$.

According to this equation, the radiation-chemical yield of degradation can be calculated from the slope of the plot of $1/P_v$ *versus* the absorbed dose, while the intercept with the *y*-axis allows one to determine U^0. This approach was used in a study of the radiation-induced degradation of wood and cotton cellulose.[35] The yield of degradation was 5.6 for both celluloses. The calculated U^0 value was in good agreement with the measured one.

Fractionation was used[35,36] to determine the MMDs of various types of intact and irradiated celluloses, and the values of P_w and P_n were calculated. The integral MMD curves prior to and after irradiation are shown in Fig. 2. After irradiation, the integral MMD curve becomes considerably narrower and is shifted toward smaller P_w. For example, the major part of macromolecules in non-irradiated cellulose has P_w values in the region from 600 to 1500, whereas after irradiation to the absorbed dose of 40 kGy, more than 90% of the macromolecules have P_w from 250 to 400. The percentage of the α-fraction measured by the solubility of cellulose in a 17.5% alkali solution decreases as the absorbed dose increases, hence the content of a low-molecular-weight fraction having enhanced solubility increases. The results of mathematical treatment of the integral MMD curves are presented in Table 1. It is seen that both the number-average and weight-average degrees of polymerisation decrease as the dose increases, while the non-uniformity factor increases after irradiation to reach the value of ~2, which corresponds to the most probable distribution. The pattern of U variation is similar to that found by Kusama *et al.*[20] who used gel permeation chromatography. The most probable MMD was observed[20] at somewhat smaller doses. This difference is probably due to the fact that the fractionation of irradiated celluloses results in a loss of some portion of the low-molecular-weight fraction, which in turn affects the P_w/P_n ratio.

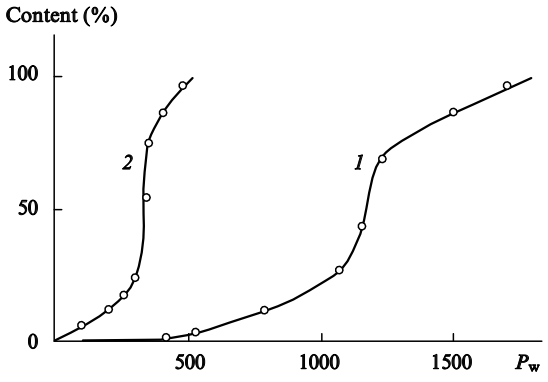


Figure 2. Integral MMD curves for cotton cellulose.[35,36] (*1*) before irradiation, (*2*) after irradiation; the absorbed dose was 40 kGy.

Thus, the experimental data from many studies on cellulose degradation are described satisfactorily by equations derived assuming a random cleavage of the polymeric chain. As a result of irradiation, the most probable MMD is attained. The average

Table 1. Molecular-weight characteristics of celluloses exposed to γ-irradiation.[35,36]

Dose /kGy	P_v	P_w	P_n	P_w/P_n
Wood cellulose				
0	974	987	700	1.41
50	302	300	195	1.55
100	196	197	96	2.05
150	150	185	87	2.13
Cotton cellulose				
0	1220	1160	1060	1.1
40	330	340	240	1.4
100	190	182	124	2.0

radiation-chemical yield of degradation is generally 6.0 ± 1.0. This yield is virtually independent of the dose rate of γ-irradiation or accelerated electrons, on the initial degree of polymerisation, and on whether the irradiation was carried out in a vacuum, in an inert gas, or in air. The absence of a noticeable effect of air on the degradation efficiency is most probably due to the dense crystalline packing of cellulose, which hinders the diffusion of oxygen to the reaction centres. Oxygen has only a slight effect on the formation of carbonyl and carboxy groups, which should be due to the partial radiation-induced oxidation of the surface layer of the material. Special studies showed that the presence of moisture has a slight inhibiting effect on the cellulose degradation.[20]

The degradation of cellulose is well described by Eqn (6) up to an absorbed dose of ~200 kGy. At higher doses, $1/P_v - 1/P_v^0$ tends to a steady value. Since

$$\frac{1}{P_v} - \frac{1}{P_v^0} = \frac{1}{P_v^0}\left(\frac{P_v^0}{P_v} - 1\right) = \frac{S}{P_v^0},$$

where S is the number of bonds cleaved in one macromolecule, the rate of accumulation of cleaved bonds decreases, *i.e.* the efficiency of degradation decreases. This phenomenon, which is rather common for radiation-chemical processes, results from the accumulation of radiolysis products with an increase in the absorbed dose; these products then accept the energy of the ionising radiation. For cellulose, this phenomenon may be due to the fact that the cleavage of bonds in macromolecules is accompanied by the formation and accumulation of radicals stable at room temperature and new functional groups. Compounds with carbonyl and carboxy groups are, along with radicals, efficient acceptors of electrons and excited species formed upon irradiation. Therefore, the accumulation of these compounds during radiolysis hinders subsequent degradation of cellulose. In fact, the degradation of cellulose-based materials containing carboxy groups (monocarboxylcellulose) is much slower.[37] It should be noted that up to very large absorbed doses (>1000 kGy), the degradation of cellulose can be described by an empirical equation similar to Eqn (6) in which the value of D has an exponent q equal to 0.83 (see Refs 16 and 19) or 0.73 (see Ref. 12).

IV. Products of radiation-chemical transformations of cellulose

The action of ionising radiation on cellulose results in profound chemical transformations and produces carbonyl and carboxy groups at the sites of bond cleavage and gases, namely, H_2, CO_2, and CO.[38–42] The dependences presented in Fig. 3 demonstrate the change in the content of >C=O and −COOH groups in the γ-irradiation of cotton cellulose at room temperature. The yields of formation of these groups are 6.5 ± 0.5 and 1.8 ± 0.2, respectively. Hence, the process of cellulose degradation is accompanied by preferential formation of compounds with carbonyl groups. The yields presented here are in good agreement with the values found by Imamura *et al.*[16] The yields of formation of the carboxy

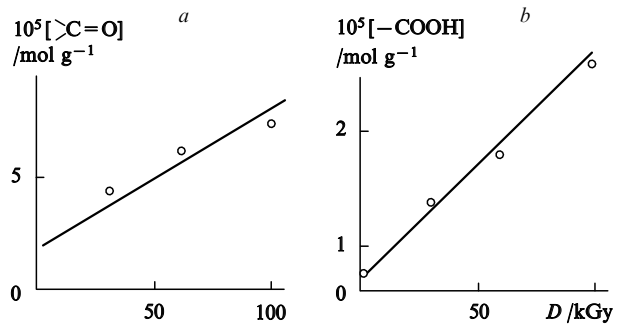


Figure 3. Dependence of the accumulation of carbonyl (*a*) and carboxy (*b*) groups in cellulose on the absorbed dose.[42]

group[10, 12, 22, 23, 43–46] range from 0.9 to 1.4. Commercial brands of cellulose differ in the content of carbonyl and carboxy groups. However, this does not affect markedly the yields of these groups under γ-irradiation. Irradiation of cellulose increases their content in comparison with the initial concentrations (Table 2). To decrease the degree of polymerisation of commercial celluloses to ~300–400, which is an optimum value for their conversion into viscose, nitrate esters, and other products, an irradiation dose of ~50 kGy is required. Such an absorbed dose produces ~3 mmol of carbonyl groups and 1 mmol of carboxy groups per 100 g of cellulose.

Table 2. Initial concentrations and radiation-chemical yields of oxidised groups upon γ-irradiation of cellulose.[35, 36]

Cellulose	Concentration /mmol per 100 g		Yield /mmol per 100 eV	
	−CHO	−COOH	−CHO	−COOH
Sulfite wood	0.13	0.24	6.0	2.0
Sulfite wood, high viscosity	0.53	3.16	5.4	1.8
Cotton	0.10	0.45	5.9	2.5

In the initial stage of γ-irradiation, the dependence of the accumulation of carbonyl and carboxy groups in cellulose on the absorbed dose is linear (see Fig. 3). At greater doses, the concentration (*c*) of these groups increases with the absorbed dose according to the equation

$$c = BD^q ,$$

i.e. it obeys the same law as the degradation of cellulose at similar doses. The *B* coefficient is 6.8×10^{-7} and 1.8×10^{-7} mol (g kGy)$^{-1}$ for carbonyl and carboxy groups, respectively.[16] The *q* exponent was found to be ~0.5 for both groups. In a discussion of data by Blouin and Arthur[10] for the accumulation of carboxy groups,[12] the *q* exponent was determined to be 0.69. Obviously, as in the case of degradation, the existence of a limiting concentration of functional groups in cellulose is explained by their involvement in radiation-chemical transformations.

The gaseous products of cellulose radiolysis were studied by several authors.[22, 23, 47–50] The yields of hydrogen, carbon dioxide, and carbon monoxide measured in a vacuum in the γ-irradiation of cellulose were 1.3, 1.6, and 0.8, respectively.[22, 23] Carbon dioxide predominates in the products of radiation-chemical transformations of cellulose. A systematic study of gas formation in the irradiation of cellulose in vacuum has been carried out.[40, 42] Linear dependences of the H_2, CO_2, and CO accumulation on the absorbed dose were found up to doses of ~300 kGy. The yields determined from these linear plots were 3.2 (H_2), 6.0 (CO_2), and 0.9 (CO). In addition to the gases mentioned, a trace amount of methane was also detected. The reported yields and ratio of the gases formed agree with other data.[49]

Because of the high molecular mass of macromolecules of cellulose and other polysaccharides, the use of traditional analytical methods such as chromatography and mass spectrometry for the determination of the final products of their radiation-chemical transformations is virtually impossible. It was noted[48, 51, 52] that irradiated cellulose contains water-soluble and water-insoluble fractions. Components that dissolve well in ethanol can be isolated from the water-soluble fraction. They include cellobiose, glucose, arabinose, glyoxal, 2-oxogluconic acid, and a number of other acids.[48] Hydrolysis of the water-soluble fraction results in xylose, arabinose, glucuronic and formic acids, and malondialdehyde.[43–45, 53] The following radiation-chemical yields were determined for some of these compounds: 48.7 ± 2.4 for glucose, 10.1 ± 2.0 for xylose, 2.3 ± 0.2 for formic acid, and 0.016 for malondialdehyde.[44] The formation of pentosans upon irradiation of cellulose was also reported.[16]

V. The nature of radical products in cellulose

There are plenty of data on free radicals formed under the action of ionising radiation on cellulose.[54–64] However, the generally accepted concept of their nature has been settled only after a series of publications.[65–69] Figure 4 shows the ESR spectra of several types of cellulose (absolutely dry, moistened with H_2O, and moistened with D_2O) γ-irradiated at 77 K. All of the irradiated samples are blue (the dry cellulose is weakly coloured, while the colour of moist samples is rather intense) and decolourise upon illumination. This is accompanied by disappearance of narrow singlet signals of ~1.0–1.2 mT (in the case of H_2O) or 0.3–0.5 mT (D_2O) widths in the central part of ESR spectra of moistened celluloses. In the spectrum of dry cellulose, the signal intensity is much lower, and photobleaching does not change noticeably the ESR spectrum. These singlets are due to captured electrons.[66, 70]

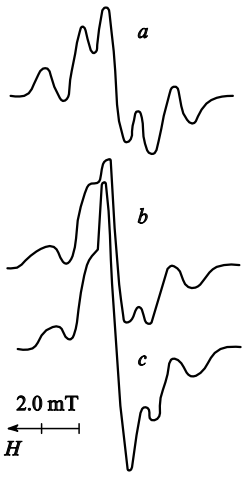


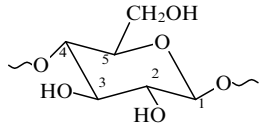
Figure 4. ESR spectra of cellulose γ-irradiated at 77 K;[70] (*a*) absolutely dry cellulose; (*b*) moistened with H_2O (40%); (*c*) moistened with D_2O (40%).

After photoannealing of the captured electrons by visible light, the ESR spectra of dry and moistened celluloses become identical with the spectrum shown in Fig. 4*a*. The latter is a superposition of a triplet signal, in which the intensity ratio of the components is 1:2:1 and the splitting is 3.0 ± 0.2 mT, with a doublet signal with 2.6 ± 0.1 mT splitting (Fig. 4*a* shows the hyperfine structure of ESR signals of the radicals). The triplet and doublet signals are due to radicals in which the unpaired electron interacts with β-protons, *viz.* with one proton to form a doublet

and with two protons to form a triplet. The doublet signal can belong only to the radical formed upon abstraction of a hydrogen atom from the C(1) atom of the glucopyranose ring, while the triplet signal can be identified with any radical containing an unpaired electron at positions C(2), C(3), or C(4). Such interpretation of ESR spectra of irradiated cellulose has been suggested in a series of publications.[65–69]

Subsequent analysis of the radical centre conformations made it possible to draw a fundamental conclusion that the radicals with doublet and triplet hyperfine structures (HFS) are terminal and appear due to the cleavage of the glucosidic bond in the polymeric chain of cellulose.[70]

Let us discuss this approach in more detail. The monomer units of cellulose consist of pyranose rings in the chair conformation with axial hydrogen atoms.



The polymer and its fragments are characterised by high rigidity, which restricts considerably the conformational transitions.

In valence-saturated organic compounds, the carbon atom has four sp^3-hybrid orbitals. Cleavage of one C–H bond results in sp^2-hybridisation, while the unpaired electron in the radical centre occupies a $2p_z$ orbital perpendicular to the plane of the three sp^2-orbitals. In this arrangement, it interacts efficiently with the β-protons. It is obvious that such radical centres at positions C(1) and C(4) of the pyranose ring cannot be obtained without cleavage of the polymeric chain of cellulose. The HFS coupling constants indicate that terminal radicals are formed. This conclusion is supported by calculations of HFS constants for "cellulose" radicals carried out with the assumption of complete sp^2-hybridisation.[70] Figure 5 shows a projection of a radical fragment.

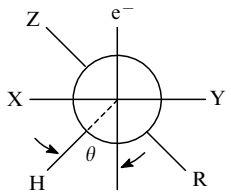


Figure 5. Frontal projection of the $C_\alpha-C_\beta$ radical fragment. X, Y, Z, and R are substituents. The angle θ between the axis of the $2p_z$ orbital of the unpaired electron and the projection of the $C_\alpha-H$ on the plane perpendicular to the $C_\alpha-C_\beta$ bond characterises the conformation of the radical centre.

The dependence of the HFS coupling constant for β-protons, a_H, on the angle of rotation around the $C_\alpha-C_\beta$ bond is expressed by the equation[71]

$$a_H = Q_\beta \rho_\alpha \cos^2\theta ,$$

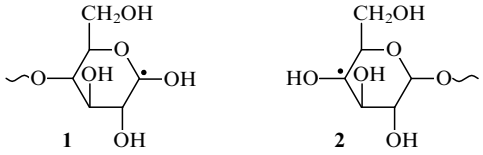
where Q_β is a constant equal to 5.86 mT for alkyl-substituted radicals,[72] and ρ_α is a coefficient that takes into account the change in the spin density of the unpaired electron at the α-carbon atom caused by substituents. In radicals of the X–C–Y type, the value of ρ_α is calculated by the formula[72,73]

$$\rho_\alpha = (1-\Delta x)(1-\Delta y)(1-\Delta z).$$

The Δx, Δy, and Δz values show the fraction of spin density withdrawn by the X, Y, and Z substituents, respectively. The coupling constants of radical centres in cellulose were calculated with the use of data for substituents that best match the actual ones in the radicals in question. It was found that the calculated constants (2.72 mT for the triplet and 3.04 mT for the doublet) fit those observed experimentally (2.6 and 3.0 mT, respectively) if one assumes that the θ angle for the axial β-hydrogen atoms with respect to the C(1) and C(4) atoms is 30°. This value agrees with that expected for the actual structure of the radical centres where they are localised at these positions of the pyranose ring at the ends of the polymeric chain.

Calculations for the radical centres at positions C(2) and C(3) with the expected triplet structures can be carried out less accurately due to the absence of data on the electronegativity of the closest substituents. Nevertheless, it is believed that the coupling constants for them (triplets) would also be close to the experimental value of 2.6 mT. Therefore, it cannot be ruled out that radicals with an unpaired electron at the C(2) or C(3) atoms also appear on irradiation of cellulose. However, the fact that the C(1)–H and C(4)–H bonds are the weakest makes them most susceptible to hydrogen abstraction.

The conclusion on the formation of radicals at these positions of the pyranose ring due to the polymeric chain cleavage is in good agreement with data on chain degradation and formation of products of radiation-chemical transformations. Moreover, considering the rigid structure of cellulose, sp^2-hybridisation could be formed only due to the cleavage of the glucosidic bonds. Otherwise, due to the strong dependence of a_H on the angle θ, one could expect a considerable deviation of the HFS coupling constants from those found experimentally. Thus, the radical states in irradiated cellulose are localised in the terminal fragments of the polymeric chain.



An estimate[70] shows that the yields of radicals **1** and **2** are approximately the same, *i.e.* the radiation-induced cleavage of the C(1)–H and C(4)–H bonds occurs with about the same probability even at the liquid nitrogen temperature.

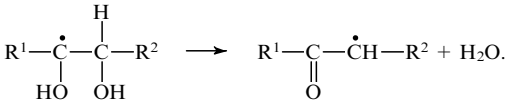
When a considerable amount of water (up to 50 mass%) was present in cellulose samples, an ESR signal was found in the temperature range corresponding to unfreezing of the vibration-rotational mobility of the pyranose ring fragments. This signal is a triplet (2.5–2.7 mT splitting) of quadruplets (0.5–0.7 mT splitting).[74] It belongs to the radical **2**, whose ESR spectrum displays the hyperfine coupling on γ-protons at C(6) and C(2) due to the narrowing of the triplet signal components.

As mentioned above, γ-irradiation of cellulose at the liquid nitrogen temperature results in the formation of trapped electrons with low yield; which cause the blue colour of the samples.[66,67,70] The colour intensity increases with the humidity of the samples. If heavy water is used, the ESR signal of trapped electrons becomes much narrower, and its intensity increases (Fig. 4 *b*,*c*). The reason is that the stabilisation of electrons occurs in intermolecular traps in the field of oriented dipoles of water molecules.[75] The ESR signal of trapped electrons is an envelope of unresolved HFS due to the coupling of an unpaired electron with the closest protons (deuterons in the case of heavy water). The magnetic moment of the deuteron is *ca.* three times smaller than that of the proton, hence the HFS constant decreases, and narrowing of the ESR signal occurs.

The stabilisation of electrons occurs most efficiently in hydrated cellulose, which contains much more water than natural and industrial celluloses. Due to the transparency of the material, it was possible to record the optical spectrum of the trapped electrons. It is a single wide band with a maximum at 540 nm and a half-height width of ~1.3 eV,[66] which are close to the parameters of optical spectra of trapped electrons in glassy polyatomic alcohols[76–78] and in concentrated aqueous solutions of carbohydrates.[79,80] However, even in hydrated cellulose, the yield of electrons was estimated to be only ~0.3. In cotton and industrial

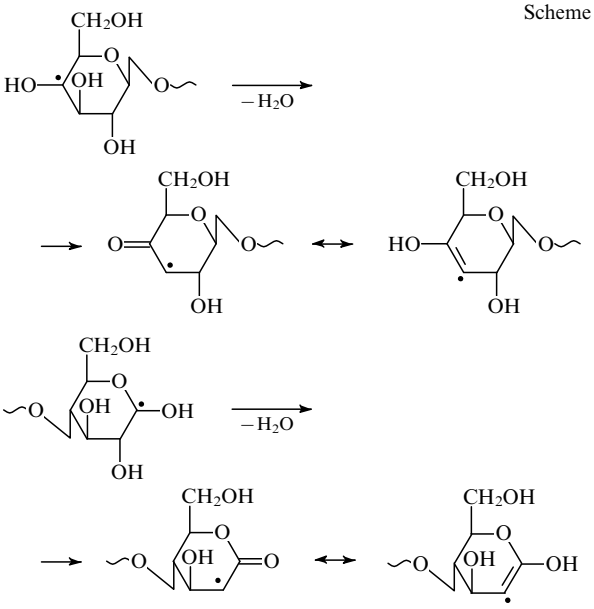
celluloses, this yield is even smaller, specifically only a few per cent of the overall yield of radicals. Thus, the stabilisation of electrons preferentially occurs in the water microphase. Efficient stabilisation takes place if a system has a glassy (amorphous) structure.[74,81] It may therefore be believed that the water present in cellulose exists in the glassy state when it is frozen.

The presence of moisture and ammonia in cellulose accelerates the thermal decay of radicals after γ-irradiation at 77 K.[22,55–58,63,68] Most probably, this is due to the plasticising effect of the admixtures that weaken the intermolecular bonds in the polymer.[68] It was noted[70] that radicals in which the unpaired electron is located at position C(1) (the doublet signal in the ESR spectrum) have the lowest thermal stability. In dry cellulose, such radicals gradually disappear at temperatures above 233 K. The disappearance of doublet and triplet signals occurs at 320–370 K, and a new doublet signal with a 1.4 ± 0.1 mT splitting becomes distinct in the ESR spectrum. Such a coupling constant is characteristic of allylic-type radicals in which the unpaired electron forms a conjugated structure with π-electrons of a double bond.[82] Radicals of this type are formed in the dehydration of polyatomic alcohols,[83,84] mono- and poly-saccharides[85] according to the reaction



Obviously, dehydration of radicals in the irradiated cellulose (Scheme 1) is also the main process in thermal transformations.

Scheme 1



Because of the distortion of the pyranose ring conformation and the decrease in the spin density ρ_α, hyperfine coupling with β-protons is not detected ($a_H < 0.8$ mT). Admixtures of lignin in the irradiated cellulose can cause a new signal to appear in the ESR spectrum (a symmetrical singlet with a width of ~1.0 mT).[67] No RO•-type radicals have been detected in the irradiated cellulose.[74]

The irradiation of cellulose at room temperature produces the same radicals as the irradiation at the liquid nitrogen temperature does. However, the concentration ratio of different radicals changes somewhat (the proportion of more thermally stable radicals with a triplet HFS increases). The yield of radicals is ~3.0–4.0. The yield increases approximately twofold if the irradiation is carried out at room temperature.[63] The kinetics of the accumulation[63] and thermal decay[68] of radicals as a function of the accumulated dose were considered. The observed polychromatic kinetics of radical decay is caused by the physical non-uniformity of the polymeric matrix. Therefore, the chemically identical processes occurring in the matrix have different rate constants of their limiting steps, *i.e.* a distribution of rate constants over the activation energy exists. The diffusion mobility of macroradicals increases by several orders when a polymer is plasticised with water. The elementary act of their diffusion apparently includes the migration of the pyranose unit, in which the radical is localised, relative to other polymer units. The presence of water weakens the bonds between the polymer chain segments.

VI. Mechanism of radiation-chemical transformations of cellulose

The first step of action of an ionising radiation on a material, *e.g.*, on cellulose (RH), is reduced to ionisation of its components

$$RH \rightsquigarrow RH^+ + e^- .$$

The Coulomb interaction of the electrons kicked out by irradiation and the parent positive ions after their thermalisation leads eventually to their recombination

$$RH^+ + e^- \longrightarrow RH^* .$$

This process is favoured considerably by a crystal-like and rigid structure of the polymer. The recombination of opposite charges formed in the physical step of the interaction of the irradiation with cellulose predominates, as follows from the extremely low yield of stabilised electrons, which does not exceed 5% of the overall yield of radicals after γ-irradiation at 77 K.[70] Recombination is probably preceded by charge migration, which is completed on defects of the crystal structure (mainly in amorphous regions). As a result, excited fragments of the polymer are formed. These fragments decompose with preferential cleavage of the C(1)–H and C(4)–H bonds of the glucopyranose ring

$$RH^* \longrightarrow R^\bullet + H.$$

The hydrogen atoms formed abstract hydrogen from other carbon atoms at the corresponding positions

$$RH + H \longrightarrow R^\bullet + H_2 .$$

The resulting R• radicals are unstable. Because their structures are strained, they decompose with the cleavage of the glucosidic bond to give radicals **1** and **2** and with scission of the glucopyranose ring (Scheme 2).

In our opinion, the available data do not make it possible to infer the detailed mechanism of intermediate reactions. Probably, a substantial role in the radiation-induced decomposition of cellulose belongs to the excited states. The scission of the glucopyranose ring results in CO_2 (or CO) and polymeric compounds containing terminal carbonyl or carboxy groups. Some possible ways for the chemical transformation of irradiated cellulose have been reviewed in detail.[1]

According to the general scheme suggested for the radiation-chemical transformations of cellulose, the following ratio of yields of the main products should be expected:

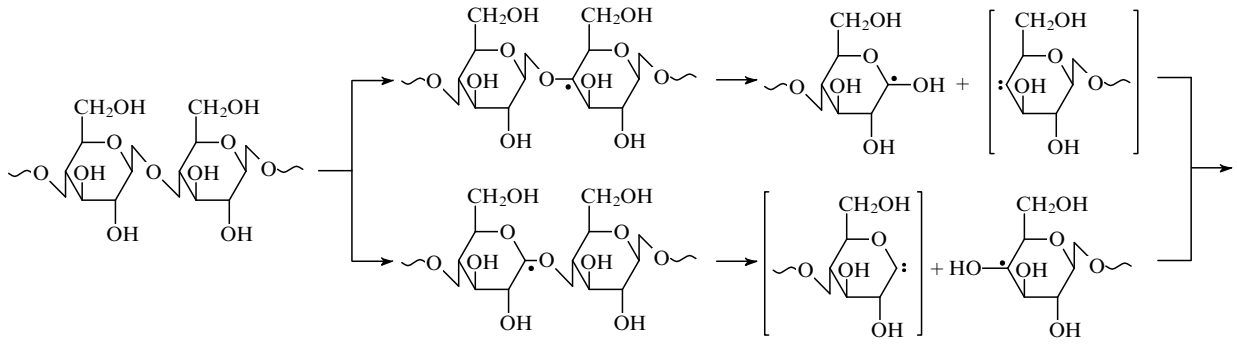
$$2G_{H_2} = G_d \simeq G_{RCHO} \simeq G_{CO_2} + G_{CO} ,$$

where G_d is the degradation yield.

In fact, this ratio is fulfilled well in the γ-irradiation of celluloses at room temperature. This can be regarded as a confirmation of the general scheme suggested for the initial step of the radiation-induced degradation of cellulose. The yield of carbonyl groups is quite close to the degradation yield and the yield of carbon dioxide, *i.e.* each act of cleavage of the polymeric chain is accompanied by the formation of one CO_2 molecule and one carbonyl group.

It was found[40,42] that the degradation of cellulose in the γ-irradiation at the liquid nitrogen temperature is described by the same equations as at room temperature. However, the degradation yield decreases from 6.0 to 3.4. The yields of carbonyl and

Scheme 2



carboxy groups decrease from 6.5 and 1.8 to 3.3 and 1.3, respectively, while the yield of carbon dioxide decreases from 6.0 to 3.1. The yield of molecular hydrogen is about the same as that at room temperature.

Since the yield of hydrogen is used as a measure of the efficiency of radiation-induced cleavage of the C–H bonds in the polymer, it can be concluded that this process is not affected considerably by a decrease in temperature. The formation of CO_2 shows that deep radiation-chemical transformations of cellulose occur which lead to decomposition of the glucopyranose ring. The decrease in the CO_2 yield indicates that this process is hampered as the temperature is decreased. It should be emphasised that the gas analysis[40,42] has been carried out after the temperature was increased to 210 or 300 K. This was done in order to ascertain the role of radicals in the formation of CO_2 since the primary radicals partially disappear only at temperatures above 233 K.

The yields of gases were found to be independent of the temperature used for the determination of the gaseous products. Hence, the formation of CO_2 does not result from secondary reactions of radicals. Most likely, it is formed even at the liquid nitrogen temperature through decomposition of the glucopyranose ring in a single process, which involves the formation of radicals and cleavage of the glucosidic bond. This also occurs with the same ratio of yields of the main products ($G_d \simeq G_{CO_2} \simeq G_{RCHO}$) determined for the irradiation at room temperature and confirming that the acts of degradation and formation of carbon dioxide and carbonyl groups occur simultaneously. The decrease in the yields of cellulose degradation on passing from room temperature to liquid nitrogen temperature is probably due to the hindrance of intramolecular mobility at lower temperatures causing a decrease in the efficiency of degradation of the pyranose ring.

We have already mentioned the difficulties inherent in the determination of the yield of cellulose degradation by viscosimetry. This yield is calculated with a number of assumptions, such as the Gaussian distribution of molecular masses, the known dependence of viscosity on the degree of polymerisation, account of chemical reactions in the dissolution of cellulose, *etc*. Therefore, it is necessary to measure this most important characteristic of the efficiency of radiation-chemical transformation of the polymer by additional, independent methods. The formation of CO_2 and CO in the irradiated cellulose suggests that scission of the glucose fragment occurs. The overall yield of CO_2 and CO determines the yield of polymer degradation by this mechanism. Within the experimental error, the yield of gases coincides with the degradation yield found by viscosimetry. On the one hand, this confirms that the degradation of cellulose mainly involves the degradation of the glucose unit, and, on the other hand, this justifies the applicability of the viscosimetric method for characterisation of cellulose degradation.

The mechanism of formation and chemical transformations of radicals in cellulose can be determined more accurately by using the data available for similar processes in cellobiose.[86] Cellobiose is a structural element of cellulose and is used in studies of model reactions of hydrogen atoms with carbohydrates and polysaccharides.[87,88] Analysis of these reactions indicates that degradation of polysaccharides can involve not only the glucosidic bond, but also the C–O bond in the pyranose ring. Pentoses (arabinose, xylose, *etc*.) were found among the hydrolysis products of radiation-chemical transformations of cellulose.[44–46,52] The suggested radiolysis scheme shows that they are formed through removal of one carbon atom as CO_2 and CO from the glucose fragment. Deeper degradation of the glucopyranose ring gives low-molecular-weight products (formaldehyde, formic acid, malondialdehyde, and others). Deoxy- and deoxyoxo-sugars (hexoses) are probably formed through disproportionation of the radicals **1** and **2**.

VII. Degradation of cellulose in plant tissues

Preliminary irradiation of plant raw materials (*e.g*., wood) changes its properties substantially: it increases the solubility in various media of the constituent cellulose, and, most importantly, enhances its ability to undergo acid hydrolysis.[89–96] It is natural to relate the latter property to the degradation of cellulose in plant tissues, which contain 60% – 80% of cellulose. Studies of the effect of irradiation on the physicochemical state of a lignin – carbohydrate complex from plant materials have confirmed this conclusion. They also demonstrated that the efficiency of cellulose degradation *in situ* is much lower than that in the pure state.[97–99] This is due to the presence of lignin in plant tissues, which protects cellulose from the radiation-induced degradation.

Systematic studies of the degradation of cellulose within plant tissues have been carried out for aspen wood.[100,101] It was found that the yield of cellulose degradation *in situ* is actually about half that of cellulose isolated from this source and subjected to irradiation. However, this comparison is insufficient to draw a final conclusion on the effect of lignin on the efficiency of radiation-induced degradation of cellulose in plant tissues, because the approach used[100,101] for the yield determination did not take into account the possible additional hydrolytic degradation of cellulose during its isolation from the plant material. The degree of such degradation is the larger the higher the absorbed dose.

The hydrolytic degradation of cellulose in acidic media depends on the content of carbonyl and carboxy groups, which affect the hydrolysis rate. Therefore, cellulose degradation was studied in the course of its one-step delignification[102] carried out according to Seifert.[103] The latter method involves treatment of a plant material with a solution containing acetylacetone, dioxane, and aqueous hydrochloric acid. It was shown that the dependence of $1/P_v$ on the duration of treatment with the delignifying solution is described by a first-order equation.[104,105] The rate constants of hydrolysis calculated from the slope of the $1/P_v - \tau$ plot increase with the absorbed dose (Table 3). Extrapolation of the kinetic straight line to the ordinate axis (*i.e*. to $\tau = 0$) makes it possible to

determine the degree of cellulose polymerisation in the plant tissue after irradiation, but before its isolation by the delignification process. As noted above, the latter process leads to additional hydrolysis of cellulose. The P_v values obtained are listed in Table 3. The dependence of $1/P_v$ on the absorbed dose is described well by Eqn (6). The degradation yield of aspen wood cellulose was calculated to be 1.8 ± 0.2, *i.e.* one-third that for pure cellulose. The yield of CO_2 in the radiolysis of aspen wood, which can be related to the degradation of the constituent cellulose, is ~ 2.0. Hence, like in the irradiation of pure cellulose, aspen wood decomposition also involves the degradation of glucopyranose rings.

Table 3. Change in viscosity-average degree of polymerisation of cellulose isolated from irradiated wood on the duration of delignification.[102]

Dose /kGy	Degree of polymerisation at τ /min			
	30	40	50	60
0	360	350	340	330
50	200	180	165	150
100	160	150	140	120
150	135	120	110	100

Thus, cellulose irradiated *in situ* is decomposed to a much lesser extent than pure cellulose due to the protective effect of lignin. This effect is probably due to the transfer of the excitation energy from the cellulose complex to lignin. Lignin contains complex aromatic groups, which are known[106, 107] to act as protectors in the radiolysis in a mixture with other organic compounds.

The protective effect of lignin in the radiation-induced degradation of cellulose as a component of wood is detected when analysing the quantitative and qualitative composition of radicals at 77 and 300 K. It was shown that the same cellulose radicals **1** and **2** are formed as from pure cellulose, along with a lignin-type radical. The latter is observed in the ESR spectrum as a narrow symmetrical singlet with a *g*-factor 2.003 and a width 1.0 ± 0.1 mT.[101] It was assumed that this is a phenoxyl radical formed upon cleavage of the ether lignin–carbohydrate bond. Analysis of the ESR spectrum of this radical in the 2-mm region confirmed the above assignment.[74] At absorbed doses < 60 kGy, the signal of the lignin radical predominates in the ESR spectrum, although the content of carbohydrates (cellulose and hemicellulose) is $\sim 70\%$ of the plant tissue weight. The yield of formation of cellulose radicals upon γ-irradiation of aspen wood at 77 K was found to be 0.8. In pure cellulose, this yield is 2.7. The yield of lignin radicals is 1.7.

Thus, the efficiency of *in situ* degradation of cellulose changes noticeably over a wide temperature range in which the plant tissue is irradiated; this can be explained by the protective effect of lignin present in it.

VIII. Radiation-thermal degradation of cellulose

Cellulose processing, primarily the manufacture of esters (viscose, nitrates, *etc.*), is preceded by a stage of its preliminary degradation in order to achieve the required average molecular mass and the optimum MMD. This is commonly done by hydrolysis or thermal treatment. Acidic or alkaline hydrolysis of cellulose makes it possible to achieve this goal. However, the disadvantages of this method (it is laborious, involves inevitable and considerable losses of material, and requires chemicals hazardous to the environment) necessitate the search for alternative ways for decreasing the molecular mass of cellulose. Thermolysis of the polymer also results in its degradation. The degree of polymerisation achievable by this method is limited to $\sim 200-250$. Subsequent treatment leads only to pyrolysis with the formation of gaseous products, levoglucosan, and resins.[108, 109] Comparison of the above methods with radiation-induced degradation shows the attractiveness of the latter for industrial application. Such treatment of cellulose results in its deep and bulk-uniform degradation to the required and controlled molecular masses without using chemical reagents and without considerable decomposition. Combination of the radiation and thermal treatments makes it possible to decrease the energy consumption for cellulose degradation.

The radiation-induced degradation of cellulose is accelerated markedly with temperature.[38] The decrease in the degree of polymerisation in the γ-irradiation is more significant the higher the temperature. The dependence of P_v on the absorbed dose is well described in the coordinates of Eqn (6). Figure 6 demonstrates the dependence of the calculated yields of degradation on temperature in the Arrhenius equation coordinates; Table 4 lists the yields of degradation and the yields of the carbonyl and carboxy groups in the temperature range from 303 to 463 K. It is seen that two temperature ranges of the radiation-induced degradation of cellulose exist: < 380 K, where the yields do not change much, and > 380 K, where the yields increase markedly with temperature. It should be noted specially that the contribution of thermal degradation in the γ-irradiation was taken into account in the calculation of the yields, although it is insignificant.

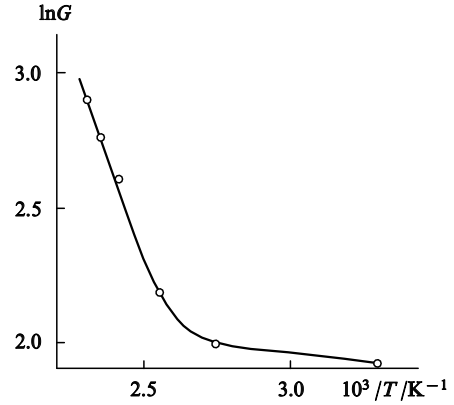


Figure 6. Dependence of the yield of cellulose degradation (bonds per 100 eV of absorbed energy) on temperature in the Arrhenius equation coordinates.[38]

The activation energy determined in the second temperature range is 23.4 ± 1.6 kJ mol^{-1}. It is most probable that the activation energy corresponds to the diffusion of radicals in the polymer. An increase in temperature initiates the transfer of the radical state to the nearest polymeric chain and causes its degradation. This explanation is based on the fact that the activation energy measured corresponds to the energy of conformational vibrations of the glucopyranose ring.[109] One can see from Table 4 that the degradation yield coincides with the yield of formation of carbonyl groups. It was also found[38] that the

Table 4. Yields of products upon radiation-thermal degradation of cellulose.[38]

T /K	G_d	G_{CHO}	G_{COOH}
303	5.1	5.4	1.8
363	6.0	5.8	1.8
393	7.4	7.1	1.8
413	10.7	11.1	1.9
423	11.4	–	–
433	16.8	17.1	2.3
443	18.1	–	–
463	27.7	26.0	3.3

radiation-induced degradation at high temperatures is accompanied by the formation of hydrogen and carbon dioxide. The yield of the latter is about two times higher.

These facts indicate that the radiation-induced degradation of cellulose at temperatures above 380 K occurs by a chain mechanism, which is initiated by radicals formed upon irradiation. The ratio of the yields of the main products is the same as that in the irradiation under ordinary conditions. This indicates the similarity of processes of radiation-induced degradation occurring in different temperature ranges that are accompanied by degradation of glucopyranose rings with evolution of carbon dioxide and formation of compounds with carbonyl groups.

IX. Degradation of cellulose upon sequential irradiation and thermal treatment

Takeshi and Shosaki [110] were the first to observe that degradation of cellulose exposed to γ-irradiation and thermal treatment depends considerably on the ordering of these processes. After irradiation or thermal treatment, the degree of polymerisation of cellulose decreases, while the amount of reducing sugar obtained on its acid hydrolysis increases (Table 5). In the heating–irradiation mode, the increase in the amount of reducing sugar is approximately the sum of the increments corresponding to each of the effects. When treatment is carried out in the irradiation–heating mode, a different picture is observed: the increase in the amount of reducing sugar is markedly greater than that expected for the additive degradation processes. A similar situation was observed when analysing the changes in the number of chain scissions (S). It was found that the total number of bond scissions ($S_{\gamma T}$) in a macromolecule upon consecutive γ-irradiation of cellulose (S_γ) and heating (S_T) can be represented as follows:[40, 111–113]

$$S_{\gamma T} = S_\gamma + S_T + \beta D\,,$$

where β is a coefficient which takes account of the increase in the cellulose thermal degradation and D is the absorbed dose. It was also shown that the result of thermal treatment followed by irradiation is additive, *i.e.* the number of chain scissions observed ($S_{\gamma T}$) equals the sum of scissions obtained separately, *i.e.* S_γ and S_T.

Figure 7 shows plots of the number of bond scissions in wood cellulose as a function of the absorbed dose for different modes of irradiation and thermal treatment. In all cases, the dependence of $1/P_v$ on the absorbed dose is described by the simple Eqn (6). The slopes of straight lines *1* and *2* characterising the efficiency of degradation are the same, which confirms the above fact that preliminary thermal treatment does not affect the efficiency of subsequent radiation-induced degradation. On the other hand, the higher slope for consecutive radiation and thermal treatment corresponds to the more efficient polymer degradation. The β factor is determined from the difference between the slopes of dependences of $1/P_v$ *vs.* the absorbed dose for each temperature. It is equal to 0.4×10^{-2}, 2.0×10^{-2}, and 3.8×10^{-2} scissions per 1 kGy at 423, 443, and 463 K, respectively.[40, 112]

Table 5. Viscosity-average degrees of polymerisation (P_v) and amount of reducing sugar in cellulose after different types of treatment.[110]

Treatment	P_v	$P_v/P_v^0 - 1$	Total sugar [a]	Increase in sugar content [a]
Without treatment	408	–	130	–
Irradiation (100 kGy)	71	4.7	167	37
Heating (473 K, 1 h)	190	1.1	155	25
Heating and irradiation	62	5.6	184	54
Irradiation and heating	43	8.5	311	181

[a] In mg of sugar per 1 g of cellulose.

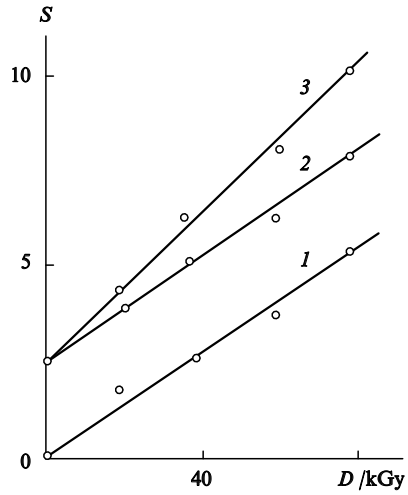


Figure 7. Dependence of the number of bond scissions (S) in wood cellulose on the absorbed dose;[112] (*1*) radiation treatment; (*2*) successive thermal and radiation treatment; (*3*) successive radiation and thermal treatment. In all cases, the thermal treatment was carried out at 463 K for 3 h to reach a steady state.

Hence, the efficiency of degradation of irradiated cellulose increases with temperature. Enhancement of degradation in the irradiation–heating mode probably results from the formation of defects such as weakened bonds, reactive groups, and radicals in cellulose upon irradiation. On heating, these defects activate scission of the polymeric chain. The Arrhenius-type dependence of the β factor on temperature made it possible to determine the activation energy, which is about 96 kJ mol^{-1}. This value corresponds to the activation energy of super-slow transmolecular motion of the cellulose macromolecule on its thermal treatment.[68]

Thus, combination of irradiation and heating can lead to much deeper degradation of cellulose than that resulting from irradiation or thermal treatment separately. The most energetically favourable mode is the simultaneous action of irradiation and heat or successive irradiation and heating. It was shown [114, 115] that electron accelerators can be used to implement successfully the destructive treatment of cellulose without the application of additional heating devices. Because of the very poor heat transfer properties of cellulose materials, their intense radiation-induced heating occurs on irradiation with accelerated electrons with dose intensity >0.4 kGy s^{-1}. Under convective heat exchange conditions, the temperature increased nonuniformly across the depth and reached 430 K, thus providing an efficient degradation mode. Under these conditions, radiolysis products formed in cellulose impregnated with iron salts efficiently reduce the metal ions to produce pyrophoric compounds.[116, 117]

X. Radiation-chemical transformations of polysaccharides

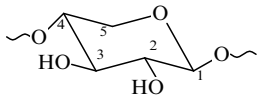
In addition to cellulose, plant materials include other polysaccharides, such as starch and xylan. A number of physicochemical properties and the biological role of cellulose and chitin are similar. Like cellulose, chitin is among the most abundant natural polymers. It constitutes the basis of the outside skeleton (cuticle) of insects, crustaceans, and other Arthropoda, and is a substitute of cellulose in lower plants (*e.g.*, in fungi). Deacetylation of chitin gives chitosan. In recent years, the radiation-chemical transformations of the above polysaccharides have been studied inten-

sively. Below, we discuss the results of the relevant studies and compare these with the data for cellulose.

1. Radiation-chemical transformations of xylans

The study of xylans has received much less attention than that of cellulose.[118–123] It was reported[118–120] that irradiation of xylan results in transformations that decrease the viscosity of its solutions and give products with carbonyl and carboxy groups. The degradation of xylans and the nature of the resultant radicals and final products have been studied systematically.[121–123] 4-*O*-Methylglucuronoxylan isolated from beech holocellulose by extraction with 10% alkali was used. This compound contains 4-*O*-methyl-D-glucuronic acid residues glycosidically linked at position O(2) of about every eighths xylose unit.

The ESR spectra of xylan γ-irradiated at 77 K[121] are shown in Fig. 8 for different absorbed doses. It is seen that the shape of the spectrum changes as the dose increases, which indicates that several types of radicals are formed, which accumulate at different rates. In the initial stage, a narrow singlet signal of trapped electrons predominates. At higher absorbed doses, two signals predominate in the spectrum: a triplet with 2.6 mT splitting and a doublet with 3.0 mT splitting, *i.e.* almost the same signals as those observed in irradiated cellulose. The doublet signal can belong only to the radical formed on abstraction of the hydrogen atom from position C(1) followed by cleavage of the glycosidic bond. The triplet signal can belong to any of the radicals formed upon abstraction of hydrogen from positions C(2), C(3), or C(4).



For positions C(2) and C(3), both β-protons are equivalent, which explains the observed structure of the ESR signal. When the radical state is localised at C(4), the two β-protons at C(5) are nonequivalent. The coupling constants with one of the β-protons at C(5) and with the β-proton at C(3) are approximately the same, while that with the other β-proton at C(5) is much smaller. In this case, a triplet ESR signal can be expected, and its components can be further sub-splitted into doublets due to the weaker coupling with one of the β-protons at C(5). However, considering that the C(1)–H and C(4)–H bonds are the weakest, it may be assumed that the formation of radicals in γ-irradiated xylan is due to the localisation of the unpaired electron at positions C(1) and C(4) and cleavage of the glycosidic bond. Hence, radicals of the same type as in the case of cellulose are formed.

Theoretical analysis of the ESR spectra[121] agrees with this interpretation. The spin densities for radicals with localisation of the unpaired electron at positions C(1) and C(4) are 0.696 and 0.619, and the coupling constants are 3.04 and 2.72 mT, respectively. The role of the glucuronic acid residue was found to be insignificant and not to affect significantly the nature of radicals formed. The radicals are accumulated linearly up to an absorbed dose of 300 kGy. The overall yield of radicals measured in this range is ~4.0.

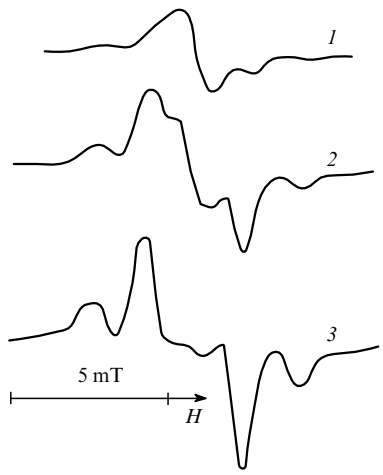


Figure 8. ESR spectra of xylan γ-irradiated at 77 K.[121] Absorbed dose /kGy: (*1*) 10; (*2*) 30; (*3*) 240.

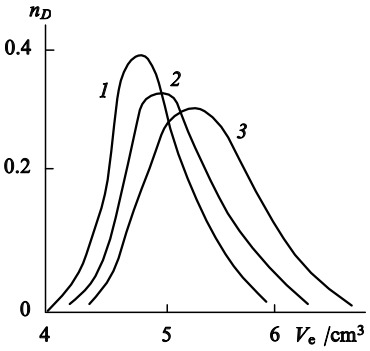


Figure 9. Gel-permeation chromatograms of xylan;[123] (*1*) original sample; absorbed dose /kGy: (*2*) 50; (*3*) 125.

The irradiation of xylan is accompanied by its intense degradation.[122, 123] Figure 9 shows the gel-filtration curves of xylans γ-irradiated to different doses (the molecular-mass characteristics were monitored with a refractometer). It is seen that the peak height decreases, while the distribution curve broadens. Table 6 lists the experimental molecular masses M_v and the calculated number-average M_n and weight-average M_w molecular masses. The decrease in the molecular mass with an increase in the absorbed dose is the consequence of the radiation-induced degradation of the polysaccharide. This fact was pointed out by Beinart *et al.*,[118] who also observed a noticeable decrease in the viscosity-average degree of polymerisation of glucuronoxylan after γ-irradiation and an increase in its solubility in water. In fact, the content of a water-soluble fraction in xylan increased from 35.7% to 54.5% at an absorbed dose 125 kGy (see Table 6). The degradation of xylan occurs in a random way, which follows from the change in the M_w/M_n ratio from 1.53 in the starting sample to 1.9 after irradiation to a 125 kGy dose. The latter ratio is close to 2.0, which corresponds to the most probable molecular-mass distribution of polymers. As indicated above, such MMD can result from random scissions of an infinite polymeric chain. This allows the use of Eqn (6) for the determination of the degradation yield. In fact, the dose dependence of $1/M_n$ (or $1/P_n$) predicted by this equation is linear in the high dose region, and the calculated degradation yield is 8 ± 1.

It was also found that xylan, like cellulose, produces hydrogen and carbon dioxide, whose radiation-chemical yields are 2.8 and 4.4.[122, 123] The presence of carbon dioxide indicates that the formation of radicals actually does not occur directly upon cleavage of the glycosidic bond but involves rupture of the

Table 6. Molecular-weight characteristics and solubility of irradiated xylan.[123]

Dose /kGy	Extraction with water (%)	$10^{-3}M_w$	$10^{-3}M_n$	$10^{-3}M_v$	M_w/M_n
0	35.7	22.1	14.4	21.8	1.53
12.5	40.7	20.1	12.6	19.8	1.59
25	51.2	18.5	11.2	18.2	1.65
50	49.6	16.0	9.4	15.8	1.70
87.5	49.1	12.7	7.2	12.5	1.76
125	54.5	12.2	6.6	12.0	1.90

pyranose ring resulting in the formation of a carbon dioxide molecule. Hence, the mechanisms of radiation-induced degradation of xylan and cellulose are fairly similar.

2. Radiation-chemical transformations of chitin and chitosan

Chitin is a polysaccharide built of 1,4-linked 2-acetamido-2-deoxy-β-D-glucose moieties. It can be regarded as cellulose in which the OH groups at C(2) are replaced by acetamido groups. Deacetylation of chitin produces chitosan. The difficulty of studying the radiation-chemical transformations of chitin is due to its extraordinary chemical stability: γ-irradiation of chitin with even rather high doses does not cause a noticeable change in the IR spectra and is not accompanied by a decrease in the adsorption properties toward metal ions from aqueous solutions.[124–127] The conclusion made as to the high radiation stability can hardly be considered proven because of the inadequacy of the methods used in the study. These methods are too insensitive to determine the destructive role of the ionising radiation. Moreover, the application of such methods to cellulose would lead to the same conclusions, since chemical changes are reflected in IR spectra at much higher doses where the number of new chemical bonds is comparable to that present in the material. In fact, the pattern and intensity of IR absorption spectra of cellulose is retained during its irradiation up to an absorbed dose of 1000 kGy, but the conclusion as to its high radiation stability cannot be made on this basis.[23]

The difficulties of studying the degradation of chitin are associated primarily with the selection of an appropriate solvent for this compound and determination of the viscosimetric properties as a function of the absorbed dose. The molecular mass of chitin was determined from the characteristic viscosity in a solution in *N*,*N*-dimethylacetamide containing 5% lithium chloride[128] according to the procedure suggested by Terboevich *et al.*[129] Chitin samples from various sources were studied. During the irradiation, the molecular masses of chitins decreased, and the content of the amino and carboxy groups increased (Table 7). The dependence of $1/P_v$ on the absorbed dose predicted by Eqn (6) for random degradation was obeyed well (Fig. 10). The radiation-chemical yields of degradation of chitins obtained from crab and krill shells were almost the same (1.8 ± 0.2), while the yield for chitin from shrimp shells was 1.1 ± 0.1. It is seen that the yields of degradation decrease markedly on going from cellulose to chitin. Up to high absorbed doses, degradation occurred without changes in the crystalline structure and without violation of the intermolecular packing, as was shown by X-ray diffraction analysis.[128] Similar dependences were reported for irradiated cellulose.[29, 130, 131]

Table 7. Changes in molecular mass and functional composition of chitin from various sources exposed to γ-irradiation.[128]

Dose /kGy	Amino groups $/10^{-6}$ mol g^{-1}	Carboxy groups $/10^{-6}$ mol g^{-1}	P_v
Chitin from crab shells			
0	2.2	3.6	806
25	23.8	–	600
50	35.3	–	567
137	29.8	26.7	247
181	–	–	152
275	25.7	24.3	140
550	–	–	100
Chitin from shrimp shells			
0	3.8	4.0	1356
25	10.4	14.7	977
50	63.3	11.4	937
137	39.1	40.0	455
275	33.4	38.0	247
550	–	–	144
Chitin from krill shells			
0	4.7	–	720
25	22.8	13.4	470
50	21.7	43.6	442
137	–	35.6	288
275	18.4	–	144
550	–	–	84

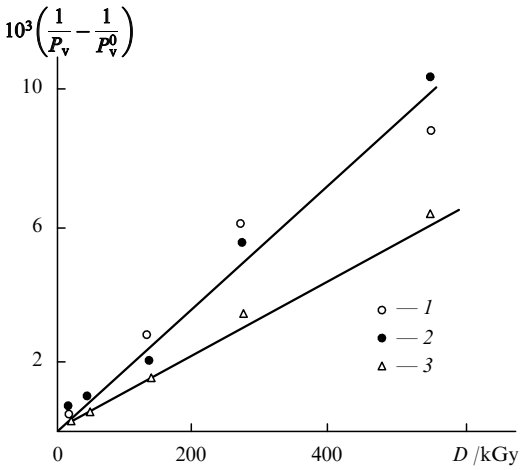


Figure 10. Dependence of the $1/P_v - 1/P_v^0$ difference in chitin on the absorbed dose;[128] chitin source: (*1*) crab shells; (*2*) krill shells; (*3*) shrimp shells.

The irradiation of chitin leads to its deacetylation, which results in free primary amino groups and acetic acid; the degradation of the polymer produces compounds with carboxy groups. Table 7 presents the concentrations of the amino groups and the total concentrations of the carboxy groups. The radiation-chemical yields of these groups in chitins from various sources are 9 ± 2. The yield of chitin degradation is rather low (1.1–1.8); this fact allows one to assume that the major part of carboxy groups determined by chemical analysis is due to acetic acid. This may be regarded as an indication that the free amino groups and the carboxy groups (acetic acid) are mainly formed as a result of deacetylation upon γ-irradiation. At high absorbed doses, the chitin shows the tendency to undergo deamination and decarboxylation. Hydrogen and carbon dioxide are the major gaseous products of chitin radiolysis. Their yields for chitin from crab shells at an absorbed dose of 150 kGy are $\sim 1.1 \pm 0.3$ and $\sim 1.4 \pm 0.4$, respectively (which are considerably smaller than those found for cellulose radiolysis, *viz.*, 3.2 and 6.0, respectively).

The radiation-chemical transformations of deacetylated chitin (chitosan), which is now widely used in various fields of industry, agriculture, and medicine, are perhaps of particular interest.[132] Chitosan undergoes degradation under irradiation, both in aqueous solutions and in the dry state.[133, 134] However, the quantitative estimation of the degradation efficiency has not been made. This problem has been studied for chitosan with degree of deacetylation 85%.[135] Viscosimetric analysis was carried out in aqueous 2% acetic acid containing 0.2 M AcONa according to the published procedure.[136] The radiation-chemical yield of chitosan degradation was found to be 4.2 ± 0.3, which is markedly higher than that for chitin and lower than that for cellulose. The yields of hydrogen and carbon dioxide were 1.3 and 1.5, respectively. The irradiation of chitosan results in its partial deamination. For example, at an absorbed dose 600 kGy, the content of amino groups decreases by ~4%, which corresponds to a radiation-chemical yield of deamination of ~3.

The nature of radical products of low-temperature radiolysis of chitin and chitosan is the same as in the case of cellulose. Both in chitin[128] and in chitosan,[135] terminal radicals appear with localisation of the unpaired electron at C(1) and C(4). These radicals appear in the ESR spectra as a doublet with a ~3.0 mT splitting

and a triplet with 2.6 mT splitting. The ESR spectra of chitin have some specific features, namely, the doublet components have a slight additional splitting. This splitting can be caused by an anisotropy of the hyperfine structure due to the amino group adjacent to the C(1) position or by overlapping with another doublet signal with a higher HFS coupling constant ($\sim$2.9 mT). The latter may be due to the different positions of pyranose rings in the crystal structure of chitin (two nonequivalent positions) resulting in a slight nonequivalence of the two radical centres. The radiation-chemical yields of radicals in the γ-irradiation of chitin and chitosan at the liquid nitrogen temperature are 2.3 (see Ref. 128) and 3.0 (see Ref. 135), respectively.

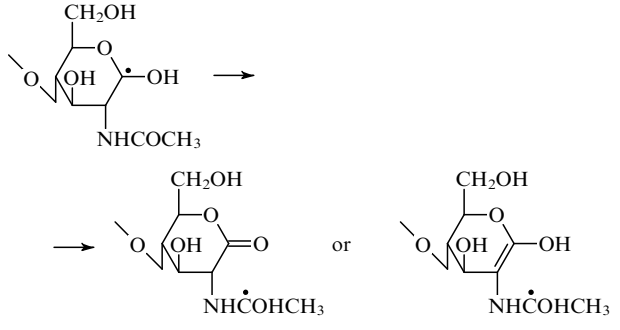
Of interest are specific features of thermal transformations of radicals in chitin. It was found[128] that a decrease in their concentration starts from $\sim$200 K. The radical at C(1) is more stable than that at C(4). Furthermore, as the primary radicals disappear (even at room temperature), an ESR signal appears as a quartet with a 1 : 3 : 3 : 1 intensity ratio of the components and a $\sim$1.4 mT splitting between them. This signal can be assigned rather definitely to the $GlcNH\dot{C}(OH)CH_3$ radical, where Glc is the glucose residue. The quartet structure of the signal of this radical is due to splitting of the unpaired electron with three protons of the CH_3 group. The parameters of the ESR signal of the $NH_2\dot{C}(OH)CH_3$ radical formed upon γ-irradiation of acetamide[137] are similar to those of the radical indicated above.

Calculations show that the presence of the amino group at C(2) in chitin and chitosan instead of the hydroxy group in cellulose scarcely affects the coupling constant of the doublet signal. For cellulose, the triplet ESR signal might be due to the localisation of the radical centre not only at C(4) but also at C(2), which is not the case for chitin and chitosan. If the radical were localised at C(2), the HFS of the signal would be different due to coupling of the unpaired electron with the nitrogen nucleus (nuclear spin 1). Thus, the conclusion that terminal radicals are preferentially formed at the C(1) and C(4) atoms in the irradiation of polysaccharides appears to be well substantiated.

The similarity of the nature of radicals formed upon γ-irradiation of chitin, chitosan, and cellulose indicates that the initial processes of their radiation-chemical transformations are similar. However, the yields of scission of the polymeric chain in chitin (1.1 – 1.8) and chitosan (4.2) are much lower than those in cellulose ($\sim$6.0). The yields of gaseous products are also much lower. The predominating process is the deacetylation of chitin leading to the formation of free primary amino groups and acetic acid, as well as the deamination in the case of chitosan. In a general form, the formation of acetic acid under γ-irradiation of chitin can be represented as hydrolytic deacetylation

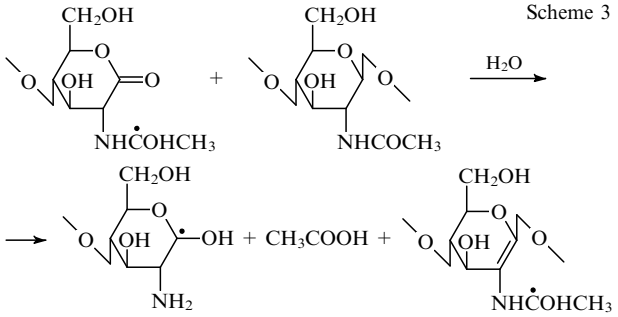
$$GlcNHCOCH_3 + H_2O \longrightarrow GlcNH_2 + CH_3COOH.$$

In fact, agreement between the yields of the formation of amino and carboxy groups has been found.[128] In addition, ESR studies indicate that the deacetylation mechanism involves the following transformations of radicals at C(1):



These transformations may involve both intra- and intermolecular hydrogen shift. Subsequent reactions of the $GlcNH\dot{C}(OH)CH_3$ radicals result in chitin deacetylation. The considerably higher yield of deacetylation products in comparison with the yield of radicals and degradation yield can be explained by the chain character of the process (Scheme 3).

Scheme 3



The reason why the origin of chitin affects the nature of the radicals formed and the degradation efficiency remains unclear. This may be due to the different structures of the materials themselves.

Thus, the replacement of the OH groups in cellulose with the NH_2 (chitosan) or $NHCOCH_3$ groups (chitin) increases markedly the radiation stability of materials against degradation. Along with degradation, deamination (in the case of chitosan) and deacetylation (in the case of chitin) occur in these polysaccharides.

3. Radiation-chemical transformations of starch and dextran

Like cellulose, starch consists of d-glucose residues linked by 1,4-α- rather than β-glucosidic bonds. Cellulose is a cellobiose-type and starch is a maltose-type polysaccharide. The interest in the study of radiation-chemical transformations of starch is partially caused by the wide use of irradiation for sterilisation of food. It was found[138 – 144] that the action of γ-irradiation on starch from different sources (from waxy and amilose corn, potatoes, manioc, rice, beans, wheat, and other plant products) results in the accumulation of carbonyl groups,[138] organic acids,[139] and hydrogen peroxide[140] and is accompanied by degradation.[141 – 144] The accumulation of new functional groups depends on the source of the starch; this is explained by differences in its structure. The acidity increased during storage of the samples, whereas the content of hydrogen peroxide decreased. The content of water-soluble dextrins increased linearly with the absorbed dose. The moisture present in starch inhibited the formation of dextrins and reducing groups. Unfortunately, the authors of the works cited did not report quantitative data on the efficiency of radiation-chemical degradation of starch (*i.e.*, the yields).

According to the degradation mechanism common for polysaccharides, it may be believed that a degradation act is accompanied by the cleavage of a pyranose ring to produce one carbon dioxide molecule and a carbonyl-containing compound. Therefore, the yields of these products can also, to some degree, serve as an indication of the efficiency of the polysaccharide degradation. In fact, this rule was valid for all of the polysaccharides considered. It was found for potato starch[145] that, in addition to hydrogen, whose yield is 4.5 molecules per 100 eV of the energy adsorbed, CO_2 and CO are formed in 5.5 and 1.5 yields, respectively, while the yield of carbonyl groups is 6.5.[146] It is also worthy of note that the yields of reducing compounds upon the radiolysis of various starches also do not exceed 6 – 10.[147, 148] Therefore, taking into account the possible errors in the chemical analysis of products of the radiation-chemical transformations of starch, it can be assumed that the yield of its degradation is within 5 – 7. The yields of gaseous products that formed upon γ-irradiation of potato starch were also measured.[146] The resulting $G(H_2)/[G(CO_2) + G(CO)]$ ratio was approximately the same as that found by Ershov and Isakova.[145] However, the absolute yields were by about an order of magnitude lower (0.5 for H_2, 0.5 for CO_2, and 0.2 for CO). They did not correlate with the yields of carbonyl and carboxy groups (6.5 and 5.0, respectively) measured in the same study, which also characterise the efficiency of the

radiation-chemical degradation of starch. It should be noted that this low yield of hydrogen is generally untypical for irradiation of saturated compounds.[149] An unusual (oscillating) dependence of the formation of products of radiolysis of potato starch and dextran on the absorbed dose was observed.[146] It was also found that the presence of moisture in starch resulted in an almost 30-fold increase in the hydrogen yield, while the yields of other gases remained the same. It is unlikely that this fact can be reduced only to the specific radiolytic behaviour of water structured by polysaccharides.

The radicals formed upon the action of radiation on starch at the liquid nitrogen temperature have the same nature as those in other polysaccharides: they are terminal with localisation of the unpaired electron at positions C(1) and C(4) of the pyranose ring.[144, 145] Therefore, there is reason to assume that the nature of the linkage between the glucose residues (α-linkage in the case of starch and β-linkage in the case of cellulose) does not affect markedly the mechanism or the efficiency of bond cleavage.

A systematic analysis of the products of radiation-chemical degradation of corn starch in the presence of oxygen was carried out.[150] It was shown that the main products include oxo compounds and water; carboxy and aldehyde groups are also accumulated in about an order of magnitude smaller yields. The efficient radiation-chemical oxidation of starch is explained by the involvement of peroxide radicals in the reaction. The latter are formed due to trapping of oxygen molecules by radicals formed in the irradiation. Low-molecular-weight dicarboxylic acids are found among the products of starch radiolysis at high absorbed doses (up to 1000 kGy): tartaric (42.4%), citric (33.5%), malic (16.4%), succinic (4.6%), lactic (1.8%), and fumaric acids (1.3%). The formation of a dicarboxylic acid molecule implies the insertion of two additional oxygen atoms into a monomeric unit, which presumes the formation and subsequent transformation of two peroxide radicals. The possibility of a chain mechanism of the reaction is not ruled out.[150] The suggested schemes of the formation of dicarboxylic acids take into account that the isomerisation and dehydration of a polysaccharide occur at high rates and that the reaction of radicals with an oxygen molecule is by an order of magnitude faster than recombination.

The dextran chain comprises mainly α-1,6-glucosidic units. It also contains branches, [mainly at C(3)] built of mono- and disaccharides. Early studies[151–157] of radiation-chemical transformations of dextrans were carried out for aqueous solutions. The possibility of decreasing the molecular mass of this polysaccharide was studied with the aim of using it as plasma extender.[151] A stronger decrease in characteristic viscosity was noted for solutions than for the solid polymer. This indicated the degradation of dextran in which radical products of water radiolysis played the decisive role. Thus, irradiation turns out to be an efficient tool for directed decreasing the molecular masses, making it possible to lower them by a factor of tens and hundreds.

It was found that in the radiolysis of dry dextran[152–155] the molecular mass and viscosity decrease, the rate of cleavage of molecular chains depending on the molecular mass. The degradation was accompanied by narrowing of MMD,[156, 157] and radiation-chemical modification.

Different polysaccharides differ in the degree of crystallinity and in the content of bound water. These factors can affect markedly the direction and efficiency of their radiation-chemical degradation. These factors can be revealed with sufficient reliability only in rare cases. However, their important role is obvious. In this respect, a study by Petrov *et al.*[153] that dealt with the radiolysis of potato starch deserves special attention. Starch granules contain linear amylose molecules along with branched amylopectin. The crystallinity index of potato starch is only ~20%. The adsorbed water in it is distributed nonuniformly among the units and is mainly located in structural channels and cavities of amorphous regions of amylopectin. A study of fractions of irradiated potato starch by gel-permeation chromatography showed that amylopectin is the component which is destroyed preferentially. At a dose of 200 kGy, the content of amylopectin is 15% (as compared to 75% for the native starch), while that at a dose of 600 kGy is only 2%. The considerable increase in the reducing power of fractions along with the decrease in their molecular masses[157] confirm the formation of low-molecular-weight aldehydes and acids in the radiation-chemical transformations of amylopectin.

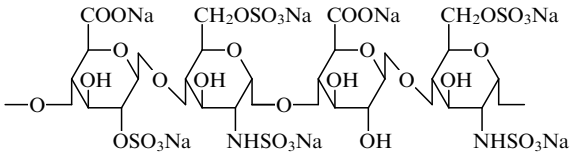
The effect of the structural factor on the radiation-chemical degradation and chemical transformations of native polysaccharides, which differed considerably in their degree of crystallinity and in the content of bound water, was studied under normal conditions and in a wide range of absorbed doses.[158] Cellulose, potato starch, amylopectin, and dextran were studied. Dextran macromolecules do not form a crystalline phase but exist as disordered coils with high density in the centre and low density at the periphery. The yields of reducing compounds and carboxy groups reach ~32 and ~14, respectively, for dextran, as compared to 4–7 and 3–5 for other polysaccharides. The yields are determined by the density and type of distribution of amorphous regions, which provide free access of water and oxygen to the macroradicals and access of the H$^{\bullet}$ and $^{\bullet}$OH radicals formed due to water decomposition to one or another carbon atom of the glucopyranose ring. The considerable yields of radiolysis products in dextran may indicate a chain mechanism of its radiation-oxidative decomposition.

The paper cited[158] also reports very low degradation yields of starch and dextran, namely, 0.3 and 1.0, respectively. These values disagree with the much higher yields of CO_2 and CO formation and the yields of reducing compounds and carboxy groups. Therefore, the conclusion is made about the possibility that these compounds are formed without the decomposition of the pyranose ring. However, this seeming contradiction is explained by the inapplicability of the approach used to describe degradation, which is valid only for linear polymers with the most probable MMD and random chain scission. This circumstance was noted even in early studies of the degradation of these polysaccharides in aqueous solutions. Native starch and dextran have very wide and nonuniform MMD, and the different nature of bonds in these branched polysaccharides does not presume *a priori* their equal proneness to radiation-induced degradation.

Numerous studies dealt with the action of radiation on aqueous solutions of such polysaccharides as agar-agar, alginic acids, pectins, glycogen, and some others. The results of these studies and the mechanism of the radiation-chemical transformations have been considered in sufficient detail by Bovey[2] and Kochetkov *et al.*[159] It was shown that degradation accompanied by a decrease in the molecular mass of the polymer is the dominating process.

4. Radiation-chemical transformations of heparin

Heparin is a natural acidic polysaccharide. It is a nonbranched heteropolysaccharide built mainly of two types of sulfated disaccharide residues linked through 1,4-α-glucosidic bonds. The structural formula of the repeating tetrameric unit of heparin can be written in the form:



Several studies were devoted to the radiolysis of heparin solutions.[160–165] The degradation of macromolecular chains is the main radiolysis process. Specific features of the degradation of a dry polymer were studied by Kudryavtsev *et al.*[166] for the sodium salt of heparin in the form of a powder with a starting viscosity-average molecular weight (M_v) of 10,325 as an example. The reciprocal of M_v varied linearly with an increase in the absorbed dose according to Eqn (6); the calculated degradation

yield was 3.1 ± 0.4. This is about half the degradation yields for cellulose, dextran, and starch. It can be concluded that the presence of sulfamino and sulfo groups in heparin, like the presence of acetamido groups in chitin, increases the resistance of the polysaccharide against radiation-induced degradation. Irradiation resulted in partial desulfation of heparin. Analysis of ESR spectra[166–169] showed that radicals of the same types as those commonly observed in polysaccharides were present in irradiated heparin. These radicals appeared upon cleavage of glycosidic bonds, and their unpaired electrons are localised at positions C(1) and C(4). Chromatography of gaseous products did not detect carbon dioxide. It was concluded[166] that the radiolysis of heparin does not involve the degradation of the pyranose ring. However, it is hardly possible to agree with this conclusion. The observed formation of terminal radicals could not occur without rupture of the pyranose ring. Most likely, the sensitivity of the chromatographic method was insufficient to measure the concentration of CO_2 when using a small amount of the starting material. The yield of molecular hydrogen (~ 0.6 for dried heparin and 0.9 for non-dried heparin) was also low, which is difficult to explain.

It should be noted that the radiation-induced degradation of heparin is a convenient method for controlled variation of its molecular mass and for directed change of its properties.

XI. Radiation-chemical degradation of ethers and esters of cellulose and other polysaccharides

It is known[22] that the presence of aromatic groups (benzyl, benzoyl, naphthoyl, *etc.*) in cotton cellulose increases considerably the tensile strength of fibres exposed to ionising radiation. Taking into consideration the decrease in the strength of cellulose materials upon degradation, it may be assumed that aromatic groups in cellulose favour a decrease in the degradation yield. It is also known[106, 107] that aromatic molecules are efficient energy acceptors.

Deactivation of excited states occurs with high probability without cleavage of chemical bonds.

The results of studies of the effect of irradiation on cellulose ethers and esters show that they also undergo degradation, although to a smaller extent.[170–183] The efficiency of polymeric chain scission is determined by the nature of the substituent and the degree of substitution. The following cellulose derivatives have been studied:[175, 181] hydroxyethylcellulose (HEC), sodium salt of carboxymethylcellulose (Na-CMC), allyloxyethylcellulose (AOEC), allyloxycarbonylmethylcellulose (ACMC), and (methacryloyl)carboxymethylcellulose (MCMC). Samples with various degrees of substitution by allyl (j_a) and methacryloyl (j_m) groups (the number of groups per 100 anhydroglucose units) were used in the experiments. It was found that the solubilities of the ethers (ether-esters) before and after γ-irradiation differ greatly. For example, HEC, Na-CMC, ACMC ($j_a = 5$) and MCMC ($j_m = 4$) remain water-soluble at any absorbed dose (up to 120 kGy). However, AOEC ($j_a = 4$), AOEC ($j_a = 30$), and ACMC ($j_a = 40$) lose solubility even at a dose 10 kGy. This shows unambiguously that degradation processes dominate in derivatives of the first group, while cross-linking of polymeric chains resulting in the formation of a three-dimensional structure dominate in the second group. Table 8 demonstrates the dependence of the degree of polymerisation of various cellulose ethers and esters on the absorbed dose. It was found[175] that the dependence for Na-CMC is described well by Eqn (6). The degradation yield is almost the same within the experimental error and equals 2.5 ± 0.5. This is consistent with the value of 2.8 calculated by us on the basis of other data.[182] The yield for HEC is 1.5 ± 0.2. Thus, the presence of functional groups in ethers determines their much lower degradation yield in comparison with cellulose.

Table 8. Change in the viscosity-average degree of polymerisation (P_v) of cellulose ethers (esters) as a function of the absorbed dose.[175]

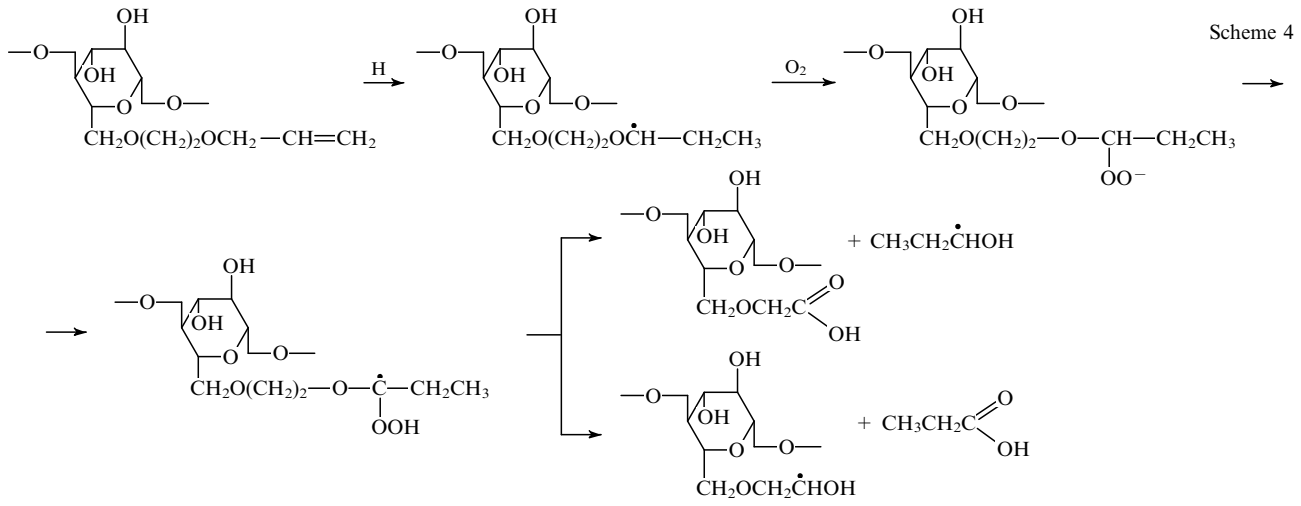
Cellulose derivative	Degree of polymerisation for absorbed dose /kGy						
	0	10	20	40	60	80	100
HEC	1995	–	1485	1187	908	617	565
Na-CMC	460	–	220	206	164	169	147
ACMC ($j_a = 5$)	359	213	185	196	–	157	140
MCMC ($j_m = 4$)	348	219	224	219	–	160	–

Analysis for carboxy and peroxide groups and double bonds showed[175] that their content is primarily determined by the nature of substituent in the ether. For instance, no formation of double bonds or peroxide and carboxy groups is observed in HEC, unlike in the other ethers. According to IR spectroscopic data, only accumulation of carbonyl groups occurs with an increase in the absorbed dose. On the other hand, in AOEC with $j_a = 4$ and especially with $j_a = 30$, the number of double bonds decreases, while peroxide and carboxy groups are accumulated. These changes are probably caused by the addition of hydrogen atoms (formed due to radiation-induced cleavage of C–H bonds) to the allyl group followed by chemical transformations (Scheme 4).

The suggested scheme of radiation-chemical transformations makes it possible to explain the inverse character of changes in the concentrations of double bonds and peroxide groups observed for allylic derivatives of cellulose.

In Na-CMC, as well as in ACMC with $j_a = 5$ and 40, the number of carboxy groups decreases. In addition, a decrease in the number of double bonds and accumulation of peroxide groups is observed in the latter two samples. The process in MCMC with $j_m = 4$ occurs similarly, the differences being that peroxide groups

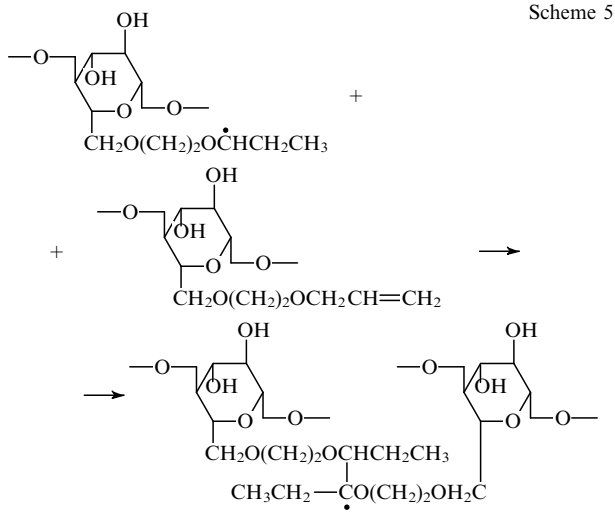
Scheme 4



are detected only at a dose of 120 kGy and that the change in the number of double bonds is less distinct.

Cross-linking of allyl ethers and methacryloyl esters occurs through double bonds (Scheme 5).

Scheme 5



This process depends on the concentration of double bonds in the macromolecule and on the mobility of groups containing these bonds, *i.e.* on various steric factors. The probability of cross-linking of macromolecules increases with an increase in concentration of double bonds in the starting ether and with an increase in the length of the substituent, which is characteristic of AOEC where the reactive double bond is located at the end of a grafted chain of ethylene oxide units. Therefore, AOEC forms a three-dimensional insoluble structure at a lower content of allyl groups than ACMC.

The ESR spectra of γ-irradiated HEC and AOEC exhibit mainly superpositions of the spectra of cellulose-type radicals. The predominant signal in the spectra of Na-CMC, ACMC, and MCMC is a triplet with 2.1 mT splitting, which overlaps with additional signals of cellulose radicals. The presence of a triplet signal indicates most likely that the radicals are localised on the carboxymethyl group, which protects cellulose from degradation.

Thus, the introduction of allyl groups in HEC and CMC affects substantially the chemical transformations that occur, on the one hand, and does not affect the nature of the radicals formed, on the other hand. This apparent contradiction may be explained by that the formation of radicals due to the addition of hydrogen atoms or other radicals to the allyl group is the reason for the chain cross-linking of polymers. However, the concentration of allyl radicals is either much lower than that of radicals formed in hydroxyethyl and carboxymethyl derivatives of cellulose (and allyl radicals are therefore not detected by ESR), or these radicals are transformed into more stable ones, which are observed in the ESR spectra.

In the case of cellulose nitrate, a decrease in molecular non-uniformity upon γ-irradiation is observed.[176,178] At a dose of 20 kGy, the polydispersity index (M_w/M_n) is 2.8 (*cf.* 8.3 for the original sample).[177] The polydispersity index approaches the value of 2, which corresponds to the most probable MMD, at high degrees of degradation. The calculated radiation-chemical degradation yield is 2.5, which is close to 1.8 found in another study.[171] The decrease in molecular mass with simultaneous narrowing of the MMD of cellulose nitrate leads to the conclusion that no efficient cross-linking of macromolecules under γ-radiolysis occurs. An interesting feature of the radiolysis of cellulose nitrate is that a signal of the $NO_2^{\bullet}$ radical predominates in the ESR spectrum obtained after radiolysis at 77 K. It can be concluded on this basis that mobile electrons formed in the initial ionisation step are mostly trapped by electrophilic nitro groups in the reaction

$$GlcONO_2 + e^- + H^+ \longrightarrow GlcOH + NO_2^{\bullet}.$$

Annealing of cellulose nitrate results in the appearance in the ESR spectrum of a triplet anisotropic signal stable up to 370 K when the NO_2 radicals disappear completely. This signal was assigned[171] to the terminal radical at C(1) of the pyranose ring. It was assumed that the unpaired electron interacted with one α- and one β-proton. The formation of a macroradical was explained by the polymeric chain scission. However, as was shown later,[184] this radical is formed due to the thermal degradation of cellulose nitrate even without preliminary irradiation due to $RNO_2^{\bullet}$ or $RNO_2H^{\bullet}$ radicals. These radicals are formed in the reaction

$$RH + NO_2^{\bullet} \longrightarrow RNO_2^{\bullet} \text{ (or } RNO_2H^{\bullet}) + H^+.$$

The role of oxygen in the radiation-induced degradation of cellulose nitrate macromolecules was found to be insignificant. It is manifested in a post-effect, which is observed as a reaction of macroradicals with an oxygen molecule to give peroxide radicals.

Cellulose acetate also undergoes degradation under γ-irradiation.[172–174,180,183] The yield for diacetate[171] was found to be unexpectedly low (0.8), which indicates the high protective effect of the acetyl groups against the polymeric chain scission. Benzyl groups also possess high protective ability.

Unfortunately, there are only scant data on the radiation-induced degradation of the ethers of other polysaccharides. Only studies on the radiation-chemical transformations of allylchitosan can be mentioned.[181,185] As in the case of analogous cellulose derivatives, the tendency of allylchitosan to cross-linking increases with an increase in the degree of substitution. However, this is also accompanied by polymeric chain degradation, which is evident from the increase in the content of carboxy groups as the absorbed dose increases.

Thus, cellulose ethers and esters, like cellulose itself, undergo degradation. However, this process is less distinct due to the protective action of substituents, which can serve as centres for localisation of the excitation energy or primary radical-ion radiolysis products.

XII. Conclusion

Analysis of data on radiation-chemical transformations of cellulose and some other polysaccharides shows a similarity of the mechanisms of the formation of the final radiolysis products. Radiation-induced degradation is the process which determines changes in the physicochemical properties of these compounds. By itself, this is not a new fact, which was already known in the 1950s. The achievements of recent years include accurate quantitative estimation of degradation yields, the finding that this mechanism is common for many other polysaccharides, and the elucidation of the nature of the primary radicals and of the mechanism of polymeric chain scission and formation of the main final products. Both in cellulose and in other polysaccharides, ionising radiation causes preferential abstraction of hydrogen atoms from the C(1) and C(4) atoms of the pyranose ring, rupture of the latter, and scission of the polymeric chain to produce a carbon dioxide molecule and a carbonyl compound.

This mechanism implies approximately equal yields of the main products ($G_d \simeq G_{CO_2} \simeq G_{RCHO}$), which is obeyed well for almost all linear polysaccharides. The unusual degradation mechanism involving pyranose ring opening is due to the fact that cellulose and other polysaccharides are polymers with chains rigidly fixed by a system of hydrogen bonds. Under these conditions, abstraction of hydrogen atoms from the C(1) and C(4) atoms leads to the formation of metastable radical states in which the stable conformation with sp^2-hybridisation can be formed only through cleavage of a glycosidic bond and rupture of the adjacent pyranose ring. Thus, radiation-induced cleavage of one C–H bond initiates subsequent explosion of a pyranose ring and a cascade of splittings of other chemical bonds. This unusual degradation mechanism is probably characteristic of not only polysaccharides but also other polymers and compounds with

rigidly fixed conformations in which the formation of metastable radicals is initiated by some factor.

The degradation yields for cellulose, xylan, and starch are in the range from 5 to 7 bonds per 100 eV of absorbed energy of the ionising radiation. Taking the possible errors into account, it may be believed that the degradation yields for these polysaccharides are approximately equal. Starch, like cellulose, consists of D-glucose residues. However, they are linked by 1,4-α-glycosidic bonds in starch and by 1,4-β-glycosidic bonds in cellulose. This does not affect noticeably the efficiency of the radiation-induced degradation. On going to chitin, which, unlike cellulose, contains the CH_3CONH group at position C(2) instead of the OH group, the degradation yield decreases 4–5-fold, and deacetylation rather than degradation becomes the dominating process. The same effect is observed on replacing the OH group with an NH_2 group in the case of chitosan. However, this conclusion is not indisputable. It cannot be ruled out that the enhanced radiation stability of chitosan is also due to the presence of residual acetyl groups. The problem is that it is practically impossible to deacetylate chitin completely to prepare chitosan. The degree of deacetylation in chitosan used by Ershov *et al.*[135] for the study of its radiation-induced degradation was 85%. Probably, the presence of chitin admixture in chitosan increases the radiation resistance of the latter. The degradation efficiency of cellulose and chitosan ethers decreases the more strongly the higher the degree of substitution. In the case of unsaturated mixed ethers-esters, two competing processes occur, namely, cross-linking at unsaturated bonds and degradation; their ratio depends on the number of unsaturated groups in the ether and on their structure.

One has to admit that the mechanism of radiation-chemical transformations of cellulose and other polysaccharides has not yet been studied sufficiently. This is hindered by difficulties in chemical determination of the composition of the products (compounds with carbonyl and carboxy groups, sugar isomers, *etc.*) localised in the polymeric chain. Probably, studies of the transformations occurring in them may involve the data obtained in studies of the radiation-chemical transformations of simple saccharides that are the fragments of complex polysaccharides.

Radiolysis of monosaccharides has been studied much more thoroughly.[159] In particular, a number of interesting regularities found for these compounds, which can also hold for polysaccharides, deserve steady attention. For example, it has been shown that irradiation of frozen aqueous solutions of monosaccharides results in their epimerisation the nature of which is determined by the structure of the original saccharide. The formation of isomeric saccharides is attributed to reactions of electrons with radicals localised in the matrix. Undoubtedly, this process can also play an important role in the irradiation of polysaccharides in which the mobility of carbohydrate radicals is limited and they themselves act as acceptors of the electrons formed upon irradiation. It was also found that simple aminosaccharides have low stability against radiation.[159] For example, the radiation-chemical yield of decomposition of glucosamine (a fragment of chitosan) is certainly an evidence that chain processes occur. Acetylation of the amino group decreases considerably the degradation yield. On the other hand, methyl glycosides of both aminosaccharides, which do not have an open glycosidic centre, have degradation yields typical of usual monosaccharides without amino groups. Therefore, one can agree with the authors of the monograph cited[159] that on going to biopolymers much higher radiation stability of these compounds should be expected in comparison with the monosaccharide constituents. The results of studies of radiation-chemical transformations of chitin, chitosan, and heparin discussed in the present review confirm this important conclusion.

The ability of ionising radiation to cause cellulose degradation is extensively used for the development of original techniques for the isolation of cellulose from raw plant materials and for its preliminary treatment for subsequent manufacture of various products. It was shown[186–190] that irradiation of wood chips in air to relatively small doses absorbed (5–20 kGy) increases their stability in storage and increases the yield of cellulose in the sulfite pulping of wood. It is promising to use irradiation for the preparation of powdered cellulose and fillers from cotton linter.[191, 192] The possibility of producing microcrystalline cellulose by irradiating usual cellulose is being considered.[193]

Radiation pretreatment of high-molecular-weight, highly viscous sulfite cellulose with very low reactivity to an absorbed dose of 5–10 kGy changes its physicochemical properties and enhances the reactivity to such an extent that it becomes possible to use this cellulose in the production of viscose fibres.[194] Irradiation makes it possible to decrease the amount of CS_2 required for xanthation from 30%–40% to 10%–15% and to elaborate a process for molding films from cellulose hydrate.[195] It was found that irradiation affects strongly the rate of cellulose nitration and the degree of substitution.[36, 196, 197] The content of bound nitrogen increases from 12.9% to 13.5% as the absorbed dose increases from 0 to 40 kGy. Nitration of pre-irradiated cotton cellulose (10–40 kGy) results in esters with practically uniform MMD. This improves considerably their physicomechanical parameters. Optimum conditions for the radiation pretreatment of cellulose from various sources using modern electron accelerators were developed for the manufacture of nitrates.

Irradiation of plant raw materials decreases the content of difficultly hydrolysable polysaccharides and increases the content of readily hydrolysable ones.[90–100] The enhancement of hydrolysability occurs due to the radiation-induced degradation of polysaccharides. The rate constants for polysaccharide hydrolysis increase markedly with the dose. The adoption of radiation technology can simplify the existing manufacture of valuable technical compounds (ethanol, furfural, xylitol, and others) from plant raw materials. Radiation pre-treatment of cellulose-containing wood materials and agricultural waste (straw) facilitates their subsequent high-temperature acid or enzymic hydrolysis to give glucose.[198–205]

A promising field of the use of radiation technology is the production of high-quality food additives from waste of plant origin (primarily, the waste of agricultural production, *i.e.* straw, corn cobs, *etc.*).[206] It was found[206–209] that an increase in the absorbed dose in these plant materials decreases the content of indigestible cellulose and increases the fraction of polysaccharides assimilable by ruminant animals. As a result of such a treatment, a plant material acquires the properties of a high-quality food additive (foraging sugar). Unfortunately, the radiation treatment is still rather expensive.[210, 211]

The radiation technology for the production of composite materials from polymers and wood or compressed waste of cellulose industry (see, *e.g.*, Refs 212 and 213), which is rather widespread, remains of current interest. The method involves impregnation of these materials with a monomer or oligomers (most commonly, methyl methacrylate is used) followed by ionising radiation-induced polymerisation. The resulting materials are used for the manufacture of high-quality parquet and other items.

The value of plant biomass, whose main components include cellulose and other polysaccharides, as a reproducible source of bound carbon for the industrial production of valuable technical, forage and food products will increase with time. It can also be believed that the role of radiation methods for the processing of plant biomass aimed at extraction of cellulose and other polysaccharides from it and for imparting to them the required properties will also increase.

References

1. B G Ershov, A S Klimentov *Usp. Khim.* **53** 2056 (1984) [*Russ. Chem. Rev.* **53** 1195 (1984)]
2. F Bovey *The Effects of Ionising Radiation on Natural and Synthetic High Polymers* (New York: Interscience, 1958)
3. A Charlesby *Atomic Radiation and Polymers* (New York: Pergamon Press, 1960)

4. M Dole *The Radiation Chemistry of Macromolecules* (New York: Academic Press, 1972)
5. F A Makhlis *Radiatsionnaya Khimiya i Fizika Polimerov* (The Radiation Chemistry and Physics of Polymers) (Atomizdat: Moscow, 1970) p. 327
6. J F Saeman, M A Millet, E J Lowton *Ind. Eng. Chem.* **44** 2848 (1952)
7. J T Guthrie, M B Huglin, G O Phillips *J. Appl. Polym. Sci.* **16** 1077 (1972)
8. J T Guthrie, M B Huglin, G O Phillips *J. Polym. Sci., Part C, Polym. Lett.* **37** 205 (1972)
9. A H Ahmed, W H Rapson *Nucl. Sci. Appl. A* **5** 33 (1969)
10. F A Blouin, J C Arthur *Textile Res. J.* **29** 198 (1958)
11. R Y-M Huang *J. Appl. Polym. Sci.* **10** 325 (1966)
12. I Sakurada, T Okada, K Kaji *J. Polym. Sci., Part C, Polym. Lett.* **37** 1 (1972)
13. I Sakurada, K Kaji, T Okada, A Tsuchiya *Cellul. Chem. Technol.* **9** 503 (1975)
14. F L Dalton, M R Houlton *Radiat. Res.* **28** 576 (1966)
15. W M Dziedziela, J Rosiak *Cellul. Chem.Technol.* **11** 261 (1977)
16. R Imamura, T Uena, K Murukami *Bull. Inst. Res. Kyoto Univ.* **50** 51 (1972)
17. K Sultanov, U A Azizov, in *6-ya Vsesoyuz. Konf. po Fizike i Khimii Tsellyulozy* (*Tez. Dokl.), Minsk, 1990* [The Sixth All-Union Conference on Physics and Chemistry of Cellulose (Abstracts of Reports), Minsk, 1990] p. 156
18. K Sultanov *Vysokomol. Soedin., Ser. B* **32** 296 (1990) [a]
19. K Sultanov, U A Azizov, Kh U Usmanov *Dokl. Akad. Nauk SSSR* **309** 907 (1989) [b]
20. Y Kusama, E Kageyama, M Shimada, Y Nakamura *J. Appl. Polym. Sci.* **20** 1679 (1976)
21. A Charlesby *J. Polym. Sci.* **15** 263 (1955)
22. J C Arthur, in *Cellulose and Cellulose Derivatives* Vol. 2 (Eds N Bikales, L Segal) (New York: Wiley-Interscience, 1971)
23. J Arthur, F A Blouin, R Demint *J. Am. Dyes Rep.* **49** 383 (1960)
24. C G Delides, C Z Panagiotalidis, O S Lega-Panagiotalidis *Textile Res. J.* **51** 311 (1981)
25. G N Richards, in *Cellulose and Cellulose Derivatives* Vol. 2 (Eds N Bikales, L Segal) (New York: Wiley-Interscience, 1971)
26. L S Bolotnikova, T I Samsonova *Vysokomol. Soedin., Ser. A* **6** 533 (1964) [a]
27. W I Brown, J Winkstrom *Eur. Polym. J.* **1** 1 (1965)
28. L S Bolotnikova, L S Danilov, T I Samsonova *Zh. Prikl. Khim.* **39** 176 (1966) [c]
29. A S Klimentov, A L Fedorov, N E Kotel'nikova, G A Petropavlovskii, L A Volkova, B G Ershov *Zh. Prikl. Khim.* **54** 686 (1981) [c]
30. N T Rychko, A P Meleshevich, L L Gordienko, N M Lepalovskaya *Khim. Drevesiny* 28 (1980)
31. R E Glegg, L J Tanghe, R J Brewer, in *Cellulose and Cellulose Derivatives* Vol. 1 (Eds N Bikales, L Segal) (New York: Wiley-Interscience, 1971)
32. M Marx-Figini, G V Schulz *Makromol. Chem.* **62** 49 (1963)
33. T O Bykova, Candidate Thesis in Chemical Sciences, Institute of Chemistry of Wood, Academy of Sciences Latvian Republic, Riga, 1991
34. S E Sobolev, V M Nikitin *Khim. Drevesiny* (3) 74 (1977)
35. V B Komarov, Candidate Thesis in Chemical Sciences, Institute of Physical Chemistry, Russian Academy of Sciences, Moscow, 1992
36. V B Komarov, S D Samuilova, L S Kirsanova, V A Morozov, T M Kuleshova, A G Smirnov, B G Ershov *Zh. Prikl. Khim.* **66** 393 (1993) [c]
37. F N Kaputskii, V E Kaputskii, T P Mortina, A V Mogulenko, S I Gol'din, S V Markevich *Zh. Prikl. Khim.* **48** 2045 (1975) [c]
38. B G Ershov, S D Samuilova, G A Petropavlovskii, G G Vasil'eva *Dokl. Akad. Nauk SSSR* **274** 102 (1984) [b]
39. B G Ershov, O V Isakova, E P Matyushkina, S D Samuilova *Cellul. Chem. Technol.* **21** 331 (1987)
40. B G Ershov, V B Komarov, S D Samuilova *Cellul. Chem. Technol.* **21** 457 (1987)
41. A S Klimentov, G A Petropavlovskii, N E Kotel'nikova, S V Skvortsov, L A Volkova *Cellul. Chem. Technol.* **19** 251 (1985)
42. B G Ershov, O V Isakova, E P Matyushkina, S D Samuilova *Khim. Vys. Energ.* **20** 142 (1986) [d]
43. K Burczak, W Pekala, J Rosiak *Wiad. Chem.* **37** 193 (1983)
44. B Bludovsky, V Duchacek *J. Radiochem. Radioanal. Lett.* **38** 21 (1979)
45. V Duchacek, R Bludovsky *J. Radiochem. Radioanal. Lett.* **38** 31 (1979)
46. R Bludovsky, M Prochazka, J Kopoldova *J. Radioanal. Nulc. Chem.* **87** 69 (1984)
47. M Horio, R Imamura, K Murukami *Bull. Inst. Res. Kyoto Univ.* **43** 117 (1965)
48. S Dilli, J L Garnet *Chem. Ind. (London)* 409 (1963)
49. A D Nekhaichuk, A M Evdokimov, S Kh Kitaev, V E Moskaleva, A A Yatsenko-Khmelevskii *Khim. Drevesiny* (1) 32 (1974)
50. A S Freidin *Deistvie Ioniziruyushchei Radiatsii na Drevesinu i ee Komponenty* (The Effects of Ionising Radiation on Wood and Its Components) (Nauka: Moscow, 1961) p. 75
51. F A Blouin, J C Arthur *J. Chem. Eng. Data* **5** 470 (1960)
52. M Horio, R Imamura, K Muzukami *Bull. Inst. Res. Kyoto Univ.* **41** 17 (1963)
53. B Bludovsky, V Duchacek *Prûm. Potravin* **30** 534 (1979)
54. R Florin, L Wall, D Brown *Trans. Faraday Soc.* **56** 1304 (1960)
55. V N Makatun, A K Potapovich, N N Ermolenko *Vysokomol. Soedin., Ser. A* **5** 467 (1963) [a]
56. P J Baugh, O Hinojosa, J Arthur *J. Appl. Polym. Sci.* **11** 1139 (1967)
57. J Arthur, O Hinojosa, V W Tripp *J. Appl. Polym. Sci.* **13** 1497 (1969)
58. J C Arthur, T Mares, O Hinojosa *Textile Res.* **36** 630 (1966)
59. S Dilly, J T Ernst, J Garnet *Aust. J. Chem.* **20** 911 (1967)
60. K Worlungton, P Baugh *Cellul. Chem. Technol.* **5** 23 (1971)
61. O Hinojosa, Y Nakamura, J Arthur *J. Polym. Sci., Part C, Polym. Lett.* **37** 27 (1972)
62. Cr Simionescu, R Butnaru, Gh Rosmarin *Cellul. Chem. Technol.* **7** 153 (1973)
63. D S Khamidov, U A Azizov, V K Milinchuk, Kh U Usmanov *Vysokomol. Soedin., Ser A.* **14** 838 (1972) [a]
64. M Shimada, Y Nakamura, T Kusama, O Matsuda, E Kageyama *J. Appl. Polym. Sci.* **18** 3387 (1974)
65. I S Gaponova, G P Pariiskii, D Ya Toptygin *Vysokomol. Soedin., Ser. B* **19** 706 (1977) [a]
66. B G Ershov, A S Klimentov *Vysokomol. Soedin., Ser. A* **19** 808 (1977)
67. A S Klimentov, B G Ershov, A E Bykov *Khimiya drevesiny* (2) 74 (1977) [a]
68. O V Plotnikov, A I Mikhailov, E L Rayavee *Vysokomol. Soedin., Ser. A* **19** 25 (1977) [a]
69. N-S Hon *J. Macromol. Sci., Chem.* **A10** 1175 (1976)
70. B G Ershov, O V Isakova *Izv Akad. Nauk SSSR, Ser. Khim.* 1277 (1984) [e]
71. H Heller, H M McConnell *J. Chem. Phys.* **32** 1535 (1960)
72. R W Fessenden, R M Schuler *J. Chem. Phys.* **39** 2147 (1963)
73. H Fischer Z *Naturforsch. A, Phys. Sci.* **20** 420 (1965)
74. S I Kuzina, S V Demidov, A Yu Brezgunov, O G Poluektov, O Ya Grinberg, A A Dubinskii, A I Mikhailov, Ya S Lebedev, in *Fizika i Khimiya Elementarnykh Khimicheskikh Protsessov (Tez. Dokl. 5 Vseros. Konf.), Chernogolovka, 1997* [The Physics and Chemistry of Elementary Chemical Processes (Abstracts of Reports at the Fifth All-Russian Conference), Chernogolovka, 1997] p. 310
75. B G Ershov, A K Pikaev *Zh. Fiz. Khim.* **41** 2573 (1967) [f]
76. B G Ershov, I E Makarov, A K Pikaev *Khim. Vys. Energ.* **1** 472 (1967) [d]
77. H J Hase *J. Phys. Soc. Jpn.* **24** 579 (1967)
78. I E Makarov, B G Ershov, A K Pikaev *Izv Akad. Nauk SSSR, Ser. Khim.* 2170 (1969) [e]
79. I E Makarov, B G Ershov, A K Pikaev *Izv Akad. Nauk SSSR, Ser. Khim.* 477 (1968) [e]
80. I E Makarov, B G Ershov, A K Pikaev *Izv Akad. Nauk SSSR, Ser. Khim.* 106 (1972) [e]
81. B G Ershov, Doctoral Thesis in Chemical Sciences, Institute of Physical Chemistry, Academy of Sciences of the USSR, Moscow, 1971
82. S Ya Pshezhetskii, A G Kotov, V K Milinchuk, V A Roginskii, V I Tupikov *EPR Svobodnykh Radikalov v Radiatsionnoi Khimii* (ESR of Free Radicals in Radiation Chemistry) (Moscow: Khimiya, 1972)
83. R Livingston, H Zeldes *J. Am. Chem. Soc.* **88** 4333 (1966)
84. A L Buley, R O Norman, R J Pritchett *J. Chem. Soc., B* 849 (1966)
85. V A Sharpatyi *Radiatsionnaya Khimiya Biopolimerov* (Radiation Chemistry of Biopolymers) (Moscow: Energoatomizdat, 1981)
86. E Yu Kozlova, A G Shostenko, S V Ermolaev *Khim. Vys. Energ.* **29** 23 (1995) [d]
87. G V Abagyan *Arm. Khim. Zh.* **34** 809 (1981)
88. G V Abagyan *Arm. Khim. Zh.* **35** 8 (1982)
89. Y W Han, A Ciegler *Annu. Rep. Ferment. Proces.* **6** 299 (1983)

90. A S Klimentov, I F Vysotskaya *Khim. Drevesiny* (5) 30 (1979)
91. A S Klimentov, R K Shakhanova, I F Vysotskaya, L N Kraev, S V Skvortsov *Khim. Drevesiny* (3) 47 (1980)
92. A S Klimentov, S V Skvortsov, Yu V Bulatenkov, B G Ershov *Khim. Drevesiny* (1) 101 (1981)
93. A S Klimentov, Yu A Komkov, S V Skvortsov, E I Pokrovskii, I F Vysotskaya, B G Ershov *Khim. Drevesiny* (1) 33 (1983)
94. A S Klimentov, I F Vysotskaya, R K Shakhanova, I N Stepanova, P D Evdokimov, V F Bystrov *Khim. Drevesiny* (5) 83 (1983)
95. B G Ershov *Khim. Drevesiny* (1) 6 (1988)
96. V B Komarov, S D Samuilova, B G Ershov *Khim. Drevesiny* (2) 76 (1991)
97. I N Arnapal'skii, A I Skrigan, N S Kuprina *Khim. Drevesiny* (1) 126 (1975)
98. V N Sergeeva, Z N Kreitsberg, M Ya Yakobsone *Khim. Drevesiny* (5) 58 (1976)
99. K Fischer, W Goldberg, M Wilke *Lenzinger Ber*. 33 (1985); *Chem. Abstr*. **104** 11 607 (1986)
100. S V Skvortsov, A S Klimentov *Khim. Drevesiny* (3) 31 (1986)
101. B G Ershov, O V Isakova, V B Komarov, E P Matyushkina *Khim. Drevesiny* (1) 6 (1986)
102. V B Komarov, S D Samuilova, B G Ershov *Khim. Drevesiny* (1) 68 (1992)
103. K Seifert *Papier (BRD)* **13**–**14** 301 (1956)
104. A Sharples, in *Cellulose and Cellulose Derivatives* Vol. 2 (Eds N Bikales, L Segal) (New York: Wiley-Interscience, 1971)
105. I F Zorin, O I Shapovalova, R I Zorina, in *5-ya Vsesoyuz. Konf. po Fizike i Khimii Tsellyulozy (Tez. Dokl.), Tashkent, 1982* [The Fifth All-Union Conference on Physics and Chemistry of Cellulose (Abstracts of Reports), Tashkent, 1982] Vol. 2, p. 27
106. F J Campbell *Radiat. Phys. Chem*. **18** 109 (1981)
107. V K Milinchuk, V I Tupikov (Eds) *Radiatsionnaya Stoikost' Organicheskikh Materialov* (Radiation Resistance of Organic Materials) (Moscow: Energoatomizdat, 1986)
108. N I Nikitin *Khimiya Drevesiny i Tsellyulozy* (The Chemistry of Cellulose and Wood) (Moscow: Izd. Akad. Nauk SSSR, 1962)
109. O P Golova *Usp. Khim*. **44** 1454 (1975) [*Russ. Chem. Rev*. **44** 687 (1975)]
110. S Takeshi, K Shosaki *Nucl. Eng. (Jpn.)* **23** 41 (1977)
111. B G Ershov, V B Komarov *Vysokomol. Soedin., Ser. B* **27** 132 (1985) [a]
112. B G Ershov, V B Komarov, S D Samuilova *Vysokomol. Soedin., Ser. B* **27** 430 (1985) [a]
113. B G Ershov, V B Komarov, S D Samuilova, in *Vsesoyuz. Konf. po Teoreticheskoi i Prikladnoi Radiatsionnoi Khimii (Tez. Dokl.), Moscow, 1984* [The All-Union Conference on Theoretical and Applied Radiation Chemistry (Abstracts of Reports), Moscow, 1984] p. 183
114. V B Komarov, B G Ershov, V A Morozov, T M Kuleshova, A G Smirnov, in *Vtoraya Vsesoyuz. Konf. po Teoreticheskoi i Prikladnoi Radiatsionnoi Khimii (Tez. Dokl.), Moscow, 1990* [The Second All-Union Conference on Theoretical and Applied Radiation Chemistry (Abstracts of Reports), Moscow, 1990] p. 130
115. B G Ershov, V B Komarov *Khim. Vys. Energ*. (1998) (in the press) [d]
116. I V Aleksandrov, Yu V Gavrilov, V B Komarov, B G Ershov, Yu B Voitkovskii, K V Tyurin, in *6-ya Vsesoyuz. Konf. po Fizike i Khimii Tsellyulozy (Tez. Dokl.), Minsk, 1990* [The Sixth All-Union Conference on Physics and Chemistry of Cellulose (Abstracts of Reports), Minsk, 1990] p. 199
117. V B Komarov, B G Ershov *Khim. Vys. Energ*. (1998) (in the press) [d]
118. I I Beinart, T N Tochilovskaya, E L Rayavee *Khim. Drevesiny* (6) 39 (1978)
119. K Fischer, W Goldberg, I Schmidt *Makromol. Chem*. **12** 303 (1987)
120. A Ebringerova, M Kacurakova, Z Hromadkova *J. Radioanal. Nucl., Chem. Lett*. **136** 141 (1989)
121. B G Ershov, N L Sukhov, A Ebringerova *Cellul. Chem. Technol*. **24** 351 (1990)
122. T V Eremeeva, O E Khinoverova, A Ebringerova, B G Ershov *Khim. Vys. Energ*. **25** 91 (1991) [d]
123. A Ebringerova, T E Eremeeva, B G Ershov *Carbohydr. Polym*. **15** 255 (1991)
124. R A Muzzarelli *Water Res*. **4** 451 (1970); *Chem. Abstr*. **73** 136 575 (1970)
125. R A Muzzarelli, B Spalla *J. Radioanal. Chem*. **10** 27 (1972)
126. R A Muzzarelli, O Tubertini *J. Radioanal. Chem*. **12** 431 (1972)
127. R A Muzzarelli *Chitin* (Oxford: Pergamon Press, 1977) p. 300
128. B G Ershov, N L Sukhov, L A Nud'ga, Yu G Baklagina, L G Kozhevnikova, G A Petropavlovskii *Zh. Prikl. Khim*. **66** 649 (1993) [c]
129. M Terboevich, G Garrano, A Cosani, E Marsano *Carbohydr. Res*. **180** 73 (1988)
130. N Sultanov, Sh Tuichiev, N Nizamidinov, B N Narzullaev, in *1-ya Vsesoyuz. Konf. po Pizike i Khimii Tsellyulozy (Tez. Dokl.)* [The First All-Union Conference on Physics and Chemistry of Cellulose (Abstracts of Reports)] (Riga: Zinatne, 1975) Vol. 2, p. 75
131. A P Sinitsyn, A A Klesov *Prikl. Biokhim. Mikrobiol*. **17** 682 (1981)
132. Proizvodstvo i Primenenie Khitozana (Tez. Dokl. 4-oi Vsesoyuz. Konf.) [Production and Application of Chitosan (Abstracts of Reports at the Fourth All-Union Conference)] (Moscow: Izd. VNIRO, 1995)
133. T Kumi, M Takibiza, in *Proceedings of International Conference of Chitin and Chitosan, Sapporo, 1982* p. 66
134. E A Plisko, L I Shchelkunova, L A Nud'ga *Zh. Prikl. Khim*. **50** 2040 (1977) [c]
135. B G Ershov, O V Isakova, S V Rogozhin, A I Gamzazade, E Yu Leonova *Dokl. Akad. Nauk SSSR* **295** 1152 (1987) [b]
136. A I Gamzazade, V M Shlimak, A I Sklyar, S V Rogozhin *Acta Polym*. **36** 420 (1985)
137. S Sivilla *J. Phys. Chem*. **74** 669 (1970)
138. J Raffi, J-P Agnef, B Dauberte, M d'Urbal, L Saint-Lebe *Stärke* **33** 188 (1981)
139. J Raffi, C Frejaville, J F Dauphin, B Dauberte, M d'Urbal, L Saint-Lebe *Stärke* **33** 235 (1981)
140. J Raffi, J-P Agnef, B Dauberte, L Saint-Lebe *Stärke* **33** 269 (1981)
141. J P Michel, J Raffi, L Saint-Lebe *Stärke* **32** 295 (1980)
142. J Raffi, B Dauberte, M d'Urbal, C Pollin, L Saint-Lebe *Stärke* **33** 301 (1981)
143. J Raffi, J-P Agnef, C Thiery, P Vincent *Stärke* **37** 228 (1985)
144. J Raffi, J-P Agnef *J. Phys. Chem*. **87** 2369 (1983)
145. B G Ershov, O V Isakova *Izv Akad. Nauk SSSR, Ser. Khim*. 2337 (1987) [e]
146. G A Fedorova, A A Ivko, N T Bondarenko, V A Sharpatyi *Dokl. Akad. Nauk SSSR* **297** 902 (1987) [b]
147. M Sultanhodjaeva, K A Korotschenko, M Ja Jakubova, V A Sharpatyi, in *Proceedings of the Vth Tihany Symposium on Radiation Chemistry, Budapest, 1982* p. 1079
148. K A Korotchenko, M A Nadzhafova, V A Sharpatyi *Radiobiologiya* **18** 661 (1978)
149. G Foldiak *Radiation Chemistry of Hydrocarbons* (Budapest, 1981)
150. K A Korotchenko, V A Sharpatyi *Khim. Vys. Energ*. **27** 50 (1993) [d]
151. F P Price, W D Bellamy, E J Lawton *J. Phys. Chem*. **58** 821 (1954)
152. P T Petrov, V M Evdokimenko, S V Markevich *Dokl. Akad. Navuk BSSR* **23**, 639 (1979)
153. P T Petrov, G A Fedorova, S V Markevich *Vestsi Akad. Navuk BSSR, Ser. Fiz.-Energ. Navuk* 84 (1980)
154. V M Evdokimenko, M P Lapkovskii, A V Martsul', P T Petrov, S V Markevich *Vestsi Akad. Navuk BSSR, Ser. Fiz.-Energ. Navuk* 14 (1980)
155. I G Gulis, V M Evdokimenko, M P Lapkovskii, A V Martsul', P T Petrov, S V Markevich *Vestsi Akad. Navuk BSSR, Ser. Fiz.-Energ. Navuk* 46 (1977)
156. P T Petrov, B B Sevruk, S V Markevich *Dokl. Akad. Navuk BSSR* **26** 632 (1982)
157. G A Fedorova, N T Bondarenko *Khim. Prir. Soedin*. (6) 691 (1984) [g]
158. G A Fedorova, N T Bondarenko, S M Berlin, S V Volkovich, V A Sharpatyi *Khim. Vys. Energ*. **26** 423 (1992) [d]
159. N K Kochetkov, L I Kudryashov, M A Chlenov, in *Radiatsionnaya Khimiya Uglevodov* (Radiation Chemistry of Carbohydrates) (Moscow: Nauka, 1978) p. 175
160. E A Balazs, T C Laurent, A F Howe, L Varga *Radiat. Res*. **11** 149 (1959)
161. F Jooyandch, J S Moore, R F Morgan, G O Phyllips *Radiat. Res*. **45** 455 (1971)
162. L Sundblad, E A Balazs, in *Amino Sugars* Vol. 2B (New York: Academic Press, 1966) p. 244
163. P G Baugh, R F Morgan, K Kershaw, G O Phillips *Radiat. Res*. **46** 217 (1971)
164. A S Chawla, C Hayward *Pharmacology* **20** 224 (1980)

165. A A Gonchyarov, I N Manina, I V Isaeva, V I Trofimov, V L Talrose, in *The 3th Working Meeting on Radiation Interaction (Abstracts of Reports), Leipzig, 1984* p. 158
166. V N Kudryavtsev, L N Grushevskaya, T K Yurik, V Ya Kabanov *Khim. Vys. Energ.* **27** 41 (1993) [d]
167. J S Moore, G O Phillips, O Rhys *Radiat. Res.* **50** 479 (1972)
168. Ch Baquey, Ch Darnez *C. R. Hebd. Seances Acad. Sci., Ser. C* **277** 132 (1973)
169. M Piazzi *Energ. Nucl.* **9** 355 (1962)
170. B N Nazrullaev, M K Kurbanaliev, A Kh Khukmatov *Dokl. Akad. Nauk Tadzh. SSR* **7** 14 (1964)
171. E K Pasal'skii, N S Moshkovskii, A G Staren'kii, Ya I Lavrentovich *Khim. Vys. Energ.* **11** 363 (1977) [d]
172. E P Petryaev, O I Shadyro, V V Bontroshenok *Vestsi Akad. Navuk BSSR, Ser. Fiz.-Energ. Navuk* (3) 84 (1984)
173. B G Timofeeva, V D Senyukov, I V Borisenko, A N Bazhenov, N V Ivchenko *Vysokomol. Soedin., Ser. B* **21** 586 (1979) [a]
174. A L Karasev, A N Bajenov, Y A Boldusev, E E Jelessov, N V Vannikov, in *The 3th Working Meeting on Radiation Interaction, Leipzig, 1984* p. 183
175. L A Nud'ga, G A Petropavlovskii, E A Plisko, O V Isakova, B G Ershov *Zh. Prikl. Khim.* **60** 1864 (1987) [c]
176. S I Kuzina, S V Stovbun, A G Salina, V A Kochukov, N Ya Kuznetsova, A I Mikhailov *Khim. Vys. Energ.* **21** 413 (1987) [d]
177. S V Stovbun, S I Kuzina, A G Silina, A I Kuzaev, A I Mikhailov *Khim. Vys. Energ.* **23** 337 (1989) [d]
178. S I Kuzina, A I Mikhailov *Vysokomol. Soedin., Ser. A* **32** 681 (1990) [a]
179. L I Volkhonskaya, G E Sokolova, A T Govorkov, in *6-ya Vsesoyuz. Konf. po Fizike i Khimii Tsellyulozy (Tez. Dokl.), Minsk, 1990* [The Sixth All-Union Conference on Physics and Chemistry of Cellulose (Abstracts of Reports), Minsk, 1990] p. 205
180. E A Bannova, A T Govorkov, in *6-ya Vsesoyuz. Konf. po Fizike i Khimii Tsellyulozy (Tez. Dokl.), Minsk, 1990* [The Sixth All-Union Conference on Physics and Chemistry of Cellulose (Abstracts of Reports), Minsk, 1990] p. 206
181. L A Nud'ga, V A Petrova, G A Petropavlovskii, A F Seliverstov, N L Sukhov, B G Ershov, in *Khimiya i Reaktsionnaya Sposobnost' Tsellyulozy i ee Proizvodnykh (Tez. Dokl. Vsesoyuz. Konf.), Cholpon-Ata, 1991* [The Chemistry and Reactivity of Cellulose and Its Derivatives (Abstracts of Reports at the All-Union Conference), Cholpon-Ata, 1991] p. 121
182. A S Turaev, B Dusniyazov, N D Burkhanova, Kh Peremkulova, in *Khimiya i Reaktsionnaya Sposobnost' Tsellyulozy i ee Proizvodnykh (Tez. Dokl. Vsesoyuz. Konf.), Cholpon-Ata, 1991* [The Chemistry and Reactivity of Cellulose and Its Derivatives (Abstracts of Reports at the All-Union Conference), Cholpon-Ata, 1991] p. 119
183. E I Kasymova, E Boimuradov, F F Niyazi, Z Ya Kuznetsova, I Ya Kolontarov, in *Khimiya i Reaktsionnaya Sposobnost' Tsellyulozy i ee Proizvodnykh (Tez. Dokl. Vsesoyuz. Konf.), Cholpon-Ata, 1991* [The Chemistry and Reactivity of Cellulose and Its Derivatives (Abstracts of Reports at the All-Union Conference), Cholpon-Ata, 1991] p. 121
184. A L Kon'kin, B G Ershov, Yu M Kargin, A A Chicherov, M N Agafonov *Izv. Akad. Nauk SSSR, Ser. Khim.* 2641 (1989) [e]
185. L A Nud'ga, V A Petrova, G A Petropavlovskii, A F Seliverstov, N L Sukhov, B G Ershov, *Zh. Prikl. Khim.* **64** 617 (1991) [c]
186. G Becker, A Burmester *Materialprümfung* **4** 416 (1962)
187. A S Hoffman, in *Proceedings of the Vth International Congress of Radiation Research* (New York: Academic Press, 1975) p. 65
188. A P Meleshevich, in *Metody Radiatsionnoi Khimii v Proizvodstve i Modifikatsii Bumagi* (The Methods of Radiation Chemistry in Production and Modification of Paper) (Moscow: Energoatomizdat, 1983) p. 53
189. W Brenner, B Bugg, C Rogers *Radiat. Phys. Chem.* **9** 389 (1977)
190. A A Ryazantsev, V V Khakhinov, O D Naidanov, V R Namsaraeva, in *6-ya Vsesoyuz. Konf. po Fizike i Khimii Tsellyulozy (Tez. Dokl.), Minsk, 1990* [The Sixth All-Union Conference on Physics and Chemistry of Cellulose (Abstracts of Reports), Minsk, 1990] p. 204
191. M U Sadykov, A Yuldashev, N Bakhramov, U N Islamov, in *6-ya Vsesoyuz. Konf. po Fizike i Khimii Tsellyulozy (Tez. Dokl.), Minsk, 1990* [The Sixth All-Union Conference on Physics and Chemistry of Cellulose (Abstracts of Reports), Minsk, 1990] p. 203
192. E L Matukhin, Z T Valishina, G G Garifzyanov, A A Grigorenko, D S Nusinovich, in *Khimiya i Reaktsionnaya Sposobnost' Tsellyulozy i ee Proizvodnykh (Tez. Dokl. Vsesoyuz. Konf.), Cholpon-Ata, 1991* [The Chemistry and Reactivity of Cellulose and Its Derivatives (Abstracts of Reports at the All-Union Conference), Cholpon-Ata, 1991] p. 124
193. B G Nagavi, B M Mithal, J S Chawla *Cellul. Chem.Technol.* **18** 353 (1984)
194. A N Sokira, T P Belasheva, T Yu Sizova, L I Barsova, S D Samuilova, V B Komarov, B G Ershov *Khim. Volokna* 30 (1988)
195. A K Stavtsov, A N Meleshevich, V I Drozdovskii, N D Morozova, in *2-ya Vsesoyuz. Konf. po Teoreticheskoi i Prikladnoi Khimii (Tez. Dokl.), Obninsk, 1990* [The Second All-Union Conference on Theoretical and Applied Chemistry (Abstracts of Reports), Obninsk, 1990] p. 249
196. V A Morozov, V B Komarov, T M Kuleshova, S D Samuilova, L S Kirsanova, A G Smirnov, B G Ershov, in *6-ya Vsesoyuz. Konf. po Fizike i Khimii Tsellyulozy (Tez. Dokl.), Minsk, 1990* [The Sixth All-Union Conference on Physics and Chemistry of Cellulose (Abstracts of Reports), Minsk, 1990] p. 198
197. B G Ershov, V B Komarov, S D Samuilova, Z Sh Shershenalieva, L S Kirsanova, V A Morozov, T M Kuleshova, G N Marchenko, G G Garifzyanov, in *Khimiya i Reaktsionnaya Sposobnost' Tsellyulozy i ee Proizvodnykh (Tez. Dokl. Vsesoyuz. Konf.), Cholpon-Ata, 1991* [The Chemistry and Reactivity of Cellulose and Its Derivatives (Abstracts of Reports at the All-Uniion Conference), Cholpon-Ata, 1991] p. 111
198. D Beardmore, L T Fan, Y H Lee *Biotechnol. Lett.* **2** 435 (1980)
199. L T Fan, Y H Lee, D Beardmore *Biotechnol. Bioeng.* **23** 419 (1981)
200. M Kumakura, I Kaetsu *Biotechnol. Bioeng.* **20** 1309 (1978)
201. M Kumakura, I Kaetsu *Int. J. Appl. Radiat. Isot.* **30** 139 (1979)
202. I Kaetsu, M Kumakura *Radiat. Phys. Chem.* **18** 827 (1981)
203. W Brenner, B Bugg, C Rogers *Radiat. Phys. Chem.* **9** 389 (1977)
204. K Kojima, S Miyake, I Uda *Radiat. Phys. Chem.* **22** 901 (1983)
205. M Kumakura, I Kaetsu *Radiat. Phys. Chem.* **23** 523 (1984)
206. B G Ershov *Radiatsionnaya Tekhnologiya i Kormoproizvodstvo* (Radiation Technology and Production of Feeds) (Moscow: Energoatomizdat, 1986)
207. J W Leonhardt, G Arnold, M Baer, in *Radiation Degradation of Cellulose (Abstracts of Reports of the 5th International Meeting on Radiation Processing). San Diego, 1984* p. 24
208. J W Leonhardt, A Hennig, K Nehring, M Baer, G Flachowsky, I Wolf *Radiat. Phys. Chem.* **21** 397 (1983)
209. J W Leonhardt, G Arnold, M Baer, G Flachowsky *Radiat. Phys. Chem.* **25** 899 (1985)
210. J G Trump, in *Nuclear Techniques for Assessing and Improving Feeds* (Vienna: Inter. Atomic Energy, 1983) p. 203
211. G S Smith, H E Kiesling, M L Galyean, J R Bader *Radiat. Phys. Chem.* **25** 27 (1985)
212. E A Borisov, F Z Raichuk, G V Shiryaeva *Tekhnologiya Radiatsionno-Khimicheskogo Proizvodstva Betonno-Polimernykh i Drevesno-Plastmassovykh Materialov* (The Technology of Radiation Chemical Production of Concrete-Polymer and Wood-Plastics Materials) (Moscow: Energoatomizdat, 1982)
213. A K Pikaev *Sovremennaya Radiatsionnaya Khimiya. Tverdoe Telo i Polimery. Prikladnye Aspekty* (Modern Radiation Chemistry. Solids and Polymers. Applied Aspects) (Moscow: Nauka, 1987) p. 345

[a] — *Polym. Sci. (Engl. Transl.)*
[b] — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*
[c] — *Russ. J. Appl. Chem. (Engl. Transl.)*
[d] — *High Energy Chem. (Engl. Transl.)*
[e] — *Russ. Chem. Bull. (Engl. Transl.)*
[f] — *Russ. J. Phys. Chem. (Engl. Transl.)*
[g] — *Chem. Nat. Compd. (Engl. Transl.)*