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Abstract

Full Text

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On the Radiolysis of Polyamides

(Presented by Academician S. S. Medvedev, December 19, 1963)

The work was undertaken in order to obtain information on the primary stages of the radiolysis of polyamides—$CONH(CH_2)_{nCONH}(CH_2)_m$—and—$CONH(CH_2)_{nNHCO}(CH_2)_{mCONH}$—(where n and m could vary from 4 to 10) and of their low-molecular analogs.

During the radiolysis of polyamides, molecular hydrogen and carbon monoxide are formed. Figure 1 gives typical curves for the dependence of the accumulation of H_2 and CO on dose during irradiation of capron ($n = 5$). With increasing dose, as is evident from the graphs in Fig. 1, G_{H_2} does not change (up to 400 Mrad), while G_{CO} decreases. The quantitative composition of the gas changes analogously during irradiation of enanth ($n = 6$), pelargon ($n = 8$), and undecan ($n = 10$) (see Table 1). As the number of $-CH_2-$units between the peptide bonds in the polymer molecule increases, G_{H_2} shows a tendency to increase. The yield of hydrogen formation at −196° and +25° is the same. Under conditions of irradiation of polymers at +100° (capron), it was found that the yield of gas formation decreases sharply, while G_{CO}, in comparison with G_{H_2}, increases somewhat.

Fig. 1. Dependence of gas accumulation on irradiation dose during radiolysis of capron fiber at 25°. 1 —total gas, 2 —hydrogen, 3 —carbon monoxide.

The linear character of the dependence of H_2 accumulation on dose, which is retained under different irradiation conditions, may serve as an indication that H_2 is formed in the primary stages of radiolysis.

Using the EPR method, the nature and kinetics of accumulation of radical radiolysis products were studied under various irradiation conditions. The initial yield of radical accumulation is practically independent either of the type of sample (resin or fiber) or of the temperature of radiolysis (−196° ÷ +20°) and, like G_{H_2}, tends to increase somewhat as the number

Fig. 2

Figure 2: Fig. 2

Table 1

Yield and composition of gas in irradiated polyamides

Sample	Irradiation conditions: temp., °C	Irradiation conditions: dose, Mrad	G_{gas}	Gas composition
Capron, fiber	25	5	3.7	H_2 51%, CO 49%
Capron, fiber	25	15	3.7	H_2 59%, CO 41%
Capron, fiber	25	135	3.7	H_2 66%, CO 34%
Capron, fiber	100	15	1.85	H_2 40.5%, CO 59%
Capron, soluble in alcohol, deuterated $(> ND)$	25	156	1.2	H_2 58%, CO 39%; HD 3%
Enanth, fiber	25	15	–	H_2 61%, CO 39%
Pelargon, fiber	25	15	–	H_2 57%, CO 43%
Pelargon, fiber	25	45	–	H_2 67%, CO 33%
Undecan*, fiber	25	15	–	H_2 59%, CO 40.6%
Undecan*, fiber	25	45	–	H_2 51.5%, CO 40.9%

* In the case of irradiation of undecan at high doses, N_2 was detected.

methylene units in the polymer chain: G_R varies from 1.5 to 2.0 as n increases from 5 to 10 (Fig. 2).

The dependence of radical accumulation on dose correlates with the analogous dependences of CO accumulation (Fig. 1), of color centers (1), and of the increase in the number of crosslinks (1) in irradiated polyamides. The observed effects apparently are explained by the formation and transformation of a radical (colored) that arises as a result of rupture of a C—H bond.

Fig. 3

Figure 3: Fig. 3

Fig. 4. EPR spectra of butyramide of butyric acid irradiated at −196°, recorded at −196°, −170°, −90°

Figure 4: Fig. 4. EPR spectra of butyramide of butyric acid irradiated at −196°, recorded at −196°, −170°, −90°

Fig. 2. Accumulation of radicals as a function of dose during irradiation of polymers with 1.7 MeV electrons. **a** (capron): 1 –resin, −180–160°, 2 –sample 1 after annealing of radicals, −180–160°, 3 –resin, room temperature, 4 –fiber, room temperature. **b**: enanth (1), pelargon (2), undecane (3).

Fig. 3. E.p.r. spectra of radicals in irradiated polyamides. **a**: 1 –capron, irradiated after annealing, 2 –enanth, 3 –pelargon, 4 –undecane, $t^\circ = -170^\circ$; **b** –butyramide of butyric acid, $t^\circ = -196^\circ$; **c** –N-(ethyl-2d_3)-butyramide of butyric acid, N-d-(ethyl-2d_3)-butyramide of butyric acid, $t = -196^\circ$.

Analysis of the e.p.r. spectra of irradiated polyamides* and their low-molecular analogs (Fig. 3) shows that the recorded radical may be assigned the formula

$$-\mathrm{CO}-\mathrm{NH}\dot{\mathrm{C}}^{\alpha}\mathrm{HC}^{\beta}\mathrm{H}_2- \qquad (I).$$

* The e.p.r. spectra of an irradiated series of polyamides are identical in their basic structure (Fig. 3).

The hyperfine structure (h.f.s.) of the EPR spectrum of this radical is explained by the interaction of the unpaired electron with the nuclei of the α- and β-hydrogen atoms (or of deuterium) (if one takes into account that the unpaired electron does not interact (^{2}) with the nuclei $> \mathrm{N-H}$).

It may be assumed that, in the radiolysis of polyamides, cleavage of the $\mathrm{C-H}$ bond in the methylene groups proceeds according to the law of probability. The atomic hydrogen formed subsequently enters into reactions with polymer molecules and removes mainly H atoms from α-methylene units* (with respect to the peptide bond), as the most mobile in the molecule. There are indications in the literature that H atoms at α-C near a carbonyl group have a greater (by a factor of two to three) reactivity than H atoms of an aliphatic chain (^{3}).

Fig. 4. EPR spectra of butyramide of butyric acid irradiated at −196°, recorded at −196°, −170°, −90°

Under the experimental conditions, the EPR method apparently makes it possible to record mainly only radical I**, which is stable owing to the structural features of polyamides: crystallinity (in fibers, for example, the stationary concentration of radicals is considerably smaller than in resins, Fig. 2a) and the presence of hydrogen bonds. Hence, for involving these radicals in reactions and, consequently, for rearranging their structure, a larger activation energy is required than in the case of alkyl radicals of the polymer chain.

Upon illumination of the irradiated samples with visible light (SVDSh-250 lamp, BS-6 light filter, transmission > 365), it was found that over a short illumination interval (15–20 min.) the EPR spectrum changes sharply: the amplitudes of the side components of the spectrum decrease by approximately a factor of two, and a singlet line is clearly revealed at the center of the spectrum; the total concentration of radicals, within the accuracy of the measurements, does not change. Further illumination of the irradiated samples (up to 5 hr.) does not affect the appearance of the spectrum. The initial change in the EPR spectrum upon illumination with visible light is accompanied by an increase in the intensity of the color of the sample; no gas is evolved. The radical formed during radiolysis probably exists in two conformations (I and I′).

Under the action of light, I′ undergoes isomerization, as a result of which one of the β-H atoms jumps to the oxygen of the carbonyl group. Then the system of conjugated bonds responsible for the color of the sample and for the singlet EPR absorption line takes the form $-\mathrm{CH_2CONCH=CHCH_2}-$. The number of chromophoric groups (and, consequently, the color) in the radical is preserved, but their arrangement changes.

It may be imagined that radicals of this type are formed directly during radiolysis. In studying the thermal stability of radical products, as also in work (^{4}), a temperature reversibility of the EPR spectrum was found (at low temperature —a quintet h.f.s.; at 40-60°—a quartet), which is connected with anisotropy of the h.f.s.

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* It is not excluded, however, that the initial cleavage of the $\mathrm{C-H}$ bond in the polymer molecule is preceded by a stage of migration of the excitation energy along the molecule, with subsequent localization of it on the $\mathrm{C-H}$ bonds.

** In the EPR spectra of undecane irradiated at temperatures close to that of liquid nitrogen, along with the main absorption line there is clearly manifested a broader one, apparently due to the presence of alkyl radicals. According to an estimate, the concentration of these radicals amounted to 15–20% of the total radical concentration.

In the case of irradiation of a low-molecular-weight analogue of a polyamide —butyramide of butyric acid—at -196°, warming the sample to approximately -90° leads to an irreversible change in the EPR spectrum: instead of a spectrum with a complex structure* at -90°, a triplet $1:2:1$ with a splitting of 69 oersteds is clearly manifested, which can be assigned to the propyl radical (^{5}).

Mass-spectrometric analysis of the radiolysis products of butyramide of butyric acid showed that, under the action of radiation, H_2, CO, $CH_3CH_2CH_3$, and $CH_3CH:CH_2$ are formed. The formation yields of the latter two in the frozen model are approximately equal and amount to about half the value of G_{CO}. Taking this into account, the following scheme of radiolysis may be proposed for a low-molecular-weight analogue of polyamides:

$$\mathrm{C_3H_7-C=O-NH-CH_2-C_3H_7 \rightarrow C_3H_7CO-NH-\dot{C}H-C_3H_7 \rightarrow}$$

$$\mathrm{\rightarrow C_3H_7-\dot{C}O+NH=CHC_3H_7,}$$

$$\mathrm{C_3H_7\dot{C}O \rightarrow C_3H_7^{\bullet}+CO, \quad 2C_3H_7^{\bullet}=CH_3CH_2CH_3+CH_3CH=CH_2.}$$

In the case of radiolysis of polyamides, apparently, the radical I that is formed is subsequently transformed with rupture of the peptide bond.

It should be noted that $G_{\mathrm{H_2}}$, both in the case of radiolysis of polyamides and in the radiolysis of butyramide of butyric acid, exceeds the value of G_{CO} required by the balance of radical products according to the scheme given. At the same time, the yield of cross-link formation in the polymer (0.35 according to the data of ([6])) does not cover the difference between G_{CO} and $G_{\mathrm{H_2}}$. Apparently, in the radiolysis of polyamides, as in the radiolysis of their low-molecular-weight analogues, along with the radical mechanism of H_2 formation, a process of molecular elimination of H_2 is possible. It might have been expected that H_2 is eliminated from two neighboring carbon atoms or from NC groups located near the carbonyl group. Replacement of the H atom bonded to the N atom by deuterium (50% enrichment, according to IR spectroscopy data) in a polymer of composition $-[\mathrm{CONH(CH_2)_5}][\mathrm{CONH(CH_2)_6NHCO\cdot(CH_2)_4}]_n$ showed that detachment of an HD molecule from NC atoms, if it occurs at all, proceeds with a very small yield (< 0.06). The IR spectra of irradiated samples indicate the formation of trans-vinylene double bonds. In contrast to polyamides, the yield of H_2 formation observed upon irradiation of their low-molecular-weight analogues (as also G_{CO}) depends on the irradiation dose and on the temperature of the irradiated sample. With increasing irradiation dose (from 40 to 200) at an irradiation temperature of 25°, $G_{\mathrm{H_2}}$ and G_{CO} decrease by approximately a factor of two. Transition to the temperature of liquid nitrogen leads to an increase in $G_{\mathrm{H_2}}$. G_{CO}, on the contrary, decreases. From this one may conclude that the processes of formation of H_2 and CO during radiolysis of polyamides and their low-molecular-weight analogues are to some extent independent.

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* The EPR spectrum of the irradiated polyamide model at −196° could be interpreted as the result of superposition of absorption lines of propyl and imino radicals. The latter corresponds to a sextet 1 : 4 : 7 : 7 : 4 : 1 with splitting between components of approximately 25 oersteds (Fig. 4).

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