Reports of the Academy of Sciences of the USSR

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1964

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1964, Vol. 156, No. 5

PHYSICAL CHEMISTRY

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E.P.R. SPECTRA OF RADICALS FORMED DURING GAMMA IRRADIATION OF POLYAMIDES

The literature data on the structure of radicals formed in polyamides under the action of radiation are contradictory.

In ([1]) the e.p.r. spectrum of γ-irradiated nylon is explained by the appearance of the radical $R\dot{N}H$. In ([2]), during β-irradiation of capron, the e.p.r. spectrum was attributed to the radical $-CH_2-\dot{C}H-CO-NH-CH_2-$. The structure $-CH_2-CO-NH-\dot{C}H-CH_2-$ was proposed for radicals formed in γ-irradiated polyamide fibers in ([3,4]). The spectrum of ultraviolet-irradiated polycaproamide ([5]) was explained by the formation of three radicals of the structures $-CH_2-CH_2-C=\dot{O}$; $CH_2-\dot{C}H_2-$ and $-CH_2-CO-NH-\dot{C}H-CH_2-$, and by mutual superposition of their signals.

In the present work, e.p.r. spectra were recorded of samples irradiated in vacuum: poly-ε-caproamide, nondeuterated $HO[-CO-CH_2-(CH_2)_4-NH]_{nH}$ (I) and containing deuterium in various positions of the elementary unit: $[-CO-CD_2-(CH_2)_4-NH-]$ (II); $[-CO-CD_2-(CH_2)_3-CD_2-NH-]$ (III) and $[CO-(CH_2)_5-ND]$ (IV). Irradiation and recording of the e.p.r. spectrum were carried out at room temperature on a radiospectrometer constructed in our laboratory, with a klystron wavelength of about 3 cm and high-frequency modulation of the magnetic field. Sample II, containing 60 at.% deuterium, was obtained by polymerization of caprolactam deuterated in the NH group in the presence of D_2O, followed by removal of deuterium from the ND group by back exchange with water. During polymerization at 260°, deuterium of the ND group of caprolactam is exchanged with hydrogen atoms of the methylene group adjacent to the carbonyl group, which facilitates hydrogen exchange at the indicated position ([6]). This exchange may also be accelerated owing to formation of aminocaproic acid ([7]) as an intermediate product of polymerization.

Fig. 1. E.p.r. spectra of nondeuterated (*a*) and deuterated (*b*) polycaprolactam

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Sample III was obtained by polymerization of ε-caprolactam containing deuterium in the $-CH_2$-groups adjacent to the C = O and NH groups, prepared by the Schmidt reaction ([8]) in the presence of D_2SO_4 from deuterated cyclohexanone:

$$\begin{array}{l} CH_2 \quad \begin{array}{l} CH_2-CD_2 \\ \\ CH_2-CD_2 \end{array} \end{array} C=O \; + \; HN_3 \xrightarrow[+D_2SO_4]{-N_2} \begin{array}{l} CH_2 \end{array} \quad \begin{array}{l} CH_2-CD_2-C=O \\ \\ CH_2-CD_2-NH \end{array} \quad |$$

In sample IV, deuterium was introduced by boiling the ordinary polymer with D_2O for 36 hours. The deuterium content in each CD_2 group in samples III and IV was 90 at.%. The presence of deuterium in these groups of the polymer was monitored by IR spectra. In samples containing 90 at.% deuterium, disappearance was observed of the absorption bands corresponding to deformation vibrations of the C–H bonds of the α-methylene groups (1420 and 1200 cm^{-1}), and the appearance of absorption bands in the regions 1020 and 1330 cm^{-1}, as had been found for deuterated polyamide and polyethylene ([9]).

Complete removal of deuterium from the ND groups of the polymer in samples II and III was accompanied by disappearance, in the IR spectra of these samples, of the band of ND stretching vibrations in the region 2500 cm^{-1}.

The EPR spectrum of γ-irradiated poly-ϵ-caproamide is an incompletely resolved quintet 1:2:2:2:1 with a total width of 74 Oe between the outermost maxima (Fig. 1a). The splitting between the outermost pairs of lines 1–2 or 4–5 is 21 Oe and is 1.55 times smaller than the splitting between lines 2–4. This spectrum corresponds to the radical $-CH_2-CO-NH-\dot{C}H-CH_2-$, in which the unpaired electron interacts with one α-hydrogen and two equivalent β-hydrogens with constants $a_\alpha = 33$ Oe and $a_\beta = 21$ Oe. This corresponds to a sextet 1:2:1:1:2:1, in which the two middle lines separated by 8 Oe are merged because of poor resolution. Introduction of deuterium into the NH group (sample IV) does not change the spectrum and its parameters, which contradicts the assumption of the formation of a radical of the $R\dot{N}H$ type ([1]). Likewise, introduction of deuterium into the CH_2 group adjacent to the carbonyl group (sample II) does not change the spectrum. This excludes the assumption that the radical is formed by abstraction of hydrogen from this CH_2 group ([2]).

Fig. 2. EPR spectra of poly-ω-undecanamide *(a)* and hexamethylenedipamide *(b)*

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Figure 2: Fig. 2. EPR spectra of poly-ω-undecanamide (a) and hexamethylenedipamide (b)

Sample III, with deuterium in two CH_2 groups adjacent to the carbonyl and to the NH group, gives a completely resolved triplet 1:2:1 with splitting $a_\beta = 28$ Oe and a total width of 56 Oe between the outermost maxima (Fig. 1b). This spectrum corresponds to the radical $-CD_2-CO-NH-\dot{C}D-CH_2-$, in which for splitting on α-D one should expect the value

$$a_{\alpha\text{-D}} = a_{\alpha\text{-H}} \cdot \gamma_D/\gamma_H = 33 \text{ (Oe)}/6.5 = 5 \text{ Oe},$$

not resolved because of the large line width (about 18 Oe) characteristic of solid samples.

Gradual heating of sample III from 30 to 100° leads to a decrease in the signal intensity with preservation of the shape, total width, splitting magnitude, and ratio of line intensities until complete disappearance of the signal. This confirms that the polymer spectrum is not a superposition of signals from two or several radicals ([3-5]).

The spectra of irradiated polyamides containing 8 and 10 CH_2 groups in the elementary unit are incompletely resolved quadruplets 1:3:3:1 with the same splitting of 21 Oe between adjacent lines. Figure 2a shows the EPR spectrum of γ-irradiated poly-ω-undecanamide. It should be assigned to a radical of the same structure as in poly-ϵ-caproamide, with splitting on α- and β-hydrogens, but with $a_\alpha/a_\beta = 21$ Oe. The difference in the ratio a_α/a_β for different polyamides may be connected with polymorphism and the degree of crystallinity of the sample ([10]).

The spectrum of irradiated, completely crystalline hexamethylenedipamide (AG salt)
$COOH—(CH_2)_4—CO—NH—(CH_2)_6—NH_2$ is a well-resolved quintet $1:2:2:2:1$ with a total width between the outer maxima of 84 Oe, with $a_\beta = 21$ Oe and $a_\alpha/a_\beta = 2.0$ (see Fig. 2 b). It corresponds to a radical in which hydrogen is detached from the CH_2 group in the α-position to NH, as in the radical of poly-ε-caproamide. The better resolution, in comparison with the latter, is apparently due to the absence of a polymer chain.

Irradiated monomeric ε-caprolactam gives a poorly resolved spectrum similar to that observed in (11) and (12). Upon introducing deuterium into the methylene groups of nondeuterated and deuterated NH in caprolactam, $[COCD_2—(CH_2)_3CD_2NH]-V$ and $CO—CD_2(CH_2)_3CD_2ND-VII$, a sharp change in the shape of the spectrum is observed. The spectrum of sample VI (Fig. 3 b) corresponds to a quadruplet with an intensity ratio of $1:1:1:1$.

The spectral parameters agree with those theoretically calculated from the atlas of EPR spectra (13). The intensity ratio found is due to the formation of a radical of the same structure as in the polymer, with nonequivalent interaction of the unpaired electron with two β-protons: $a_{\beta 1}/a_{\beta 2} = 2$. This nonequivalence is apparently connected with the cyclic structure of caprolactam. Splitting by deuterium of the α-methylene group, as in the case of deuterated poly-ε-caproamide, is not manifested in the spectrum. In (11) the EPR spectrum of irradiated caprolactam is also explained by the formation of the radical —CH_2CO—$NH\dot{C}HCH_2$—.

Fig. 3. EPR spectra of caprolactam deuterated in the CH_2 groups (a) and in the CH_2 and NH groups (b)

Labels in the figure:
a. CO—CD_2—$(CH_2)_3$—CD_2—NH; b. CO—CD_2—$(CH_2)_3$—CD_2—ND; $a_{\beta 1}$; $a_{\beta 2}$.

The spectrum of sample V (Fig. 3 a) is resolved more poorly, probably because of the participation of hydrogen of the NH group in the splitting. This spectrum, apparently, may also be considered as a quadruplet with an intensity ratio of $1 : 1 : 1 : 1$.

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Received
9 III 1964

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Note: Figure translations are in progress. See original paper for figures.