ESR Study of free radicals trapped in mechanically destructed polyamide 6

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Free radicals formed from polyamide 6 during its mechanical destruction have been studied. By analysis of the e.s.r. spectra it has been elucidated that three types of free radicals, namely $-\mathrm{CONH\dot{C}HCH_2}-$, $\mathrm{\dot{C}H_2CONH}-$, and $\mathrm{\dot{C}H_2NHCO}-$, are present in the system over the temperature range −50 to 0°C. The structure of these radicals as well as the proportion of their spectra in the total spectrum has been determined.

In preceding papers [1, 2] we studied free radicals stabilized in nonoriented and oriented samples of polyamide 6 subjected to γ-irradiation. In correspondence with other authors [3, 4] it was found that the radical $-\mathrm{CONH\dot{C}HCH_2}-$ predominated over the other radicals, as *e.g.* $-\mathrm{CH_2\dot{C}(OH)NHCH_2}-$ and $-\mathrm{CH_2\dot{C}HCH{=}CHCONH}-$, the e.s.r. spectrum of which is a triplet and a singlet* respectively. The concentration of the latter radicals in the system was very small [1]. As the mechanical destruction represents a different kind of generation of free radicals, the e.s.r. spectra are often different from the spectra recorded after γ-irradiation of polymers [6, 7]. In this paper we present the results of the e.s.r. study of the free radicals trapped after mechanical destruction of polyamide 6.

Experimental

Measurements were performed on samples of polyamide 6 of commercial mark Silamide produced by alkaline polymerization in Chemical Works in Žilina. The samples had the following parameters: density 1.15 g cm^{-3}, melting point 220°C, specific heat 0.51 kcal kg^{-1} K^{-1}, and T_g 57°C. Molecular weight $\overline{M}_n = 40\,000$ was determined viscosimetrically at 25°C for solutions of polymer in the mixture consisting of formic acid (80%) and water [8]. The samples were of cylindrical shape with both the diameter and the length 7 mm.

Mechanical destruction was carried out by a special vidium drill in vacuum and at liquid nitrogen temperature in an equipment described elsewhere [9].

The e.s.r. spectra were measured by X-band spectrometer ER-9 (Zeiss, Jena) in the temperature range from −50 to 0°C.

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* Singlet e.s.r. spectrum was by some authors attributed to the radical $-\mathrm{CON{=}CH\dot{C}HCH_2}-$ (see [5] and references therein).

Results and discussion

Fig. 1 shows the e.s.r. spectra of the radicals trapped after mechanical destruction of polyamide 6. The shape of the spectrum changes with temperature only slightly and all radicals disappear at 0°C. For each experimental spectrum the corresponding theoretical spectrum was constructed*.

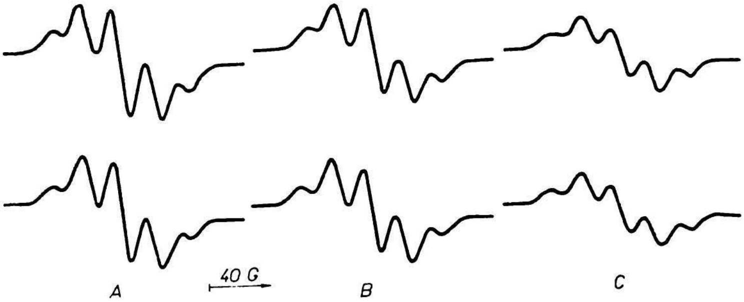

Fig. 1. The e.s.r. spectra of free radicals trapped in polyamide 6 after its mechanical destruction.
A. −50°C; *B.* −30°C; *C.* −15°C.
Spectra were recorded after 16.8 min of sample heating to a given temperature. Experimental spectrum is in the upper part and the theoretical one in the lower part of the picture.

To achieve an agreement between theoretical and experimental spectra we had to assume that the overall spectrum is a superposition of spectra of several free radicals. Since primary radicals arising in mechanical destruction are mainly the products of the main chain scissions [6], their e.s.r. spectrum at −50°C should differ from that obtained by γ-irradiation of polymers. In the latter case, according to an exciton model, the primary radicals should be, as a result of radiation interaction with polymers, formed on side groups of polymer chains [10]. The e.s.r. spectra of irradiated and destructed polyamide 6 are given in Fig. 2. At first sight it is clear that the e.s.r. spectra observed are composed of spectra of several radicals which are present at this temperature in the system.

In papers [11] and [12] dealing with the e.s.r. spectra of radicals in mechanically destructed polyamide 6 *Zakrevskii et al.* came to the conclusion that most likely the bonds 3 and 6 in the structure

$$-\mathrm{CO}\overset{1}{-}\mathrm{NH}\overset{2}{-}\mathrm{CH_2}\overset{3}{-}\mathrm{CH_2}\overset{4}{-}\mathrm{CH_2}\overset{5}{-}\mathrm{CH_2}\overset{6}{-}\mathrm{CH_2}\overset{7}{-}\mathrm{CO}\overset{8}{-}\mathrm{NH}-$$

are split whereas the bonds 1 and 2 retain. As a consequence, one may expect the formation of three types of free radicals. The first type is represented by the radical

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* For the construction of theoretical spectra the modified *Heuvel—Lind* method was used [14]. It was assumed that the shape of the line was Gaussian.

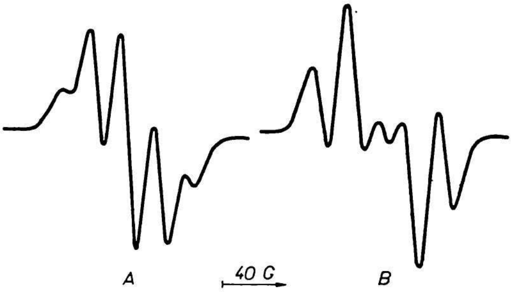

Fig. 2. The e.s.r. spectra of mechanically destructed (*A*) and irradiated (*B*) polyamide 6 at −50°C.

$$\dot{C}H_2CH_2CH_2- \qquad (1)$$

which was by the authors observed at lower temperatures. In our investigations we did not observe the spectrum of this radical at −50°C which was obviously due to its fast decay. On the other hand, the radicals

$$\dot{C}H_2CONH- \qquad (2)$$

$$\dot{C}H_2NHCO- \qquad (3)$$

contribute to the total spectrum. They give a triplet with the constants of hyperfine splitting of 20 G (radical (*2*)) and 22 G (radical (*3*))*. The nitrogen atom contributes differently to the hyperfine structure of the e.s.r. spectra of radicals (*2*) and (*3*). Therefore these spectra must differ in the line width which enables us to determine their proportion in the total spectrum at various temperatures. The working line width (real width extended by the additional unresolved splitting from nitrogen atom) in the spectrum of radical (*2*) is 11 G while in the spectrum of radical (*3*) 16 G.

From the secondary radicals which might arise after mechanical destruction of polyamide 6 we observed only one, *i.e.*

$$-CONH\dot{C}HCH_2- . \qquad (4)$$

The spectrum of this radical was described in detail elsewhere [1]. By using the theoretical spectra of radicals (*2*), (*3*), and (*4*)** we succeeded in constructing the total theoretical spectra which were in very good agreement with the spectra found experimentally. The proportion of individual component spectra in the total spectrum was determined

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* According to the calculation by the McLachlan method [13] ($h_O = 1$, $k_{C-O} = 0.8$, $h_N = 1.5$, $k_{C-N} = 1$, $|Q| = 28$ G) a_H in the radical $\dot{C}H_2CONH_2$ equals 19.6 G and in the radical $\dot{C}H_2NHCOH$ 21.7 G.

** For the synthesis of the theoretical spectra the broad singlet coming from the teflon tube of the heating device was taken into account because it was not negligible at the sensitivity of the spectrometer used.

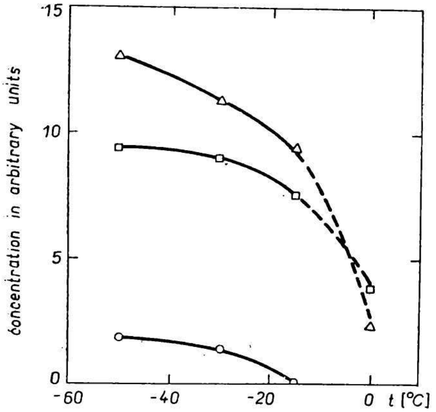

Fig. 3. The concentration dependence of the corresponding free radicals trapped in polyamide 6 after its mechanical destruction.
○ radical (*2*); △ radical (*3*); □ radical (*4*).

for 4 different temperatures 16.8 min after heating the samples to those temperatures (Fig. 3). Only for the temperature of 0°C, the spectrum recorded 2.8 min after heating the sample was interpreted because all radicals decayed in a few minutes. (In Fig. 3 the corresponding sections are denoted by dashed lines.)

In conclusion, mainly the bonds 3 and 6 appear to be broken down in the mechanical destruction of polyamide 6. With respect to the used method of the interpretation of spectra we were able to determine not only the corresponding types of free radicals contributing to the overall spectrum but also to characterize these radicals by their ratio in the resulting spectrum. We established that the radical (*1*) was absent in the system even at −50°C. At this temperature the overall spectrum is a superposition of three spectra corresponding to radicals (*2*), (*3*), and (*4*), respectively. The radical (*2*) vanishes at −15°C. The radical (*4*), which is a secondary radical and has also been observed in irradiated samples, decays along with radical (*3*) at 0°C.

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