

ESR STUDY OF THE GENERATION AND DECAY OF PEROXY RADICALS IN MECHANICALLY DESTRUCTED POLYAMIDE 6

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Abstract—Polyamide 6 has been mechanically destructed *in vacuo*. At -70° , the ESR spectrum corresponds to the sum of the component spectra of three radicals $\text{—NH}\dot{\text{C}}\text{HCH}_2\text{—}$, $\cdot\text{CH}_2\text{NHCO—}$, and $\cdot\text{CH}_2\text{CONH—}$. After introducing air into the ampoule, the spectrum changes even at -70° ; the changes have been studied up to 0° . The spectrum of the peroxy radical $\text{ROO}\cdot$ (with line width 1.57 mT, $g_{\perp} = 2.0089$ and $g_{\parallel} = 2.0301$) predominates.

INTRODUCTION

The specific feature of the mechanical destruction of polymers is the generation of free radicals on the surface of the sample. The radicals thus formed readily react with oxygen and change into peroxy radicals [1]. When investigating macroradicals are trapped after mechanical destruction of polymers, conditions have to be chosen to avoid effects on the spectrum by O_2 [1–4]. On the other hand, if we are interested in the ESR spectrum of the peroxy radical for a certain polymer and the change of the original spectrum into the spectrum of the peroxy radical, O_2 can be introduced into the ampoule with the destructed sample. At -170° , $\text{ROO}\cdot$ radicals are formed and in a certain temperature region they show anomalous behaviour [5, 6] viz. increase of the total radical concentration. The anomaly is accounted for by decay of the non-paramagnetic associates at higher temperatures. Sakaguchi *et al.* [5] assume that non-paramagnetic particles are formed by adding free electrons to the radicals obtained by mechanical destruction in polypropylene and Pilař and Ulbert assume formation of the non-paramagnetic polymeric tetroxides in PGMA [6].

At -70° and higher, such effects have not been observed [5, 6]. Therefore the concentration changes of the peroxy radicals being formed may be related to decay of alkyl radicals formed by mechanical destruction.

The aim of the present paper is to study between -70° and 0° the changes of the ESR spectrum of free radicals trapped after mechanical destruction of polyamide 6, resulting from the interaction of these radicals with O_2 and to characterize the ESR spectrum of the peroxy radical in this polymer.

EXPERIMENTAL

The samples of polyamide 6 were produced in Chemical Works (Považské chemické závody, Žilina) under the trade name "Silamid". The parameters were: density 1.15 g/cm^3 , softening point 220° , specific heat $0.51 \text{ kcal kg}^{-1} \text{ deg}^{-1}$, $T_g = 57^{\circ}$. Molecular weight

($\bar{M}_n = 40,000$) was determined viscometrically in a mixture of formic acid (80%)–water at 25° [7]. The samples were cylindrical, their dia and length being 7 mm. Mechanical destruction was carried out by drilling with a special vidium drill *in vacuo* (10^{-4} mmHg) in a device described elsewhere [8]. The ampoule in which the mechanical destruction took place was dipped in liquid nitrogen.

ESR spectra were measured by an X-band ER-9 (Carl Zeiss, Jena) spectrometer. After measuring the spectrum at -70° , air was introduced into the ampoule and the changes of the spectrum were observed over the range -70 – 0° . The ESR spectra were evaluated by simulation of the experimental spectra [9] assuming that the shape of the spectrum was Gaussian.

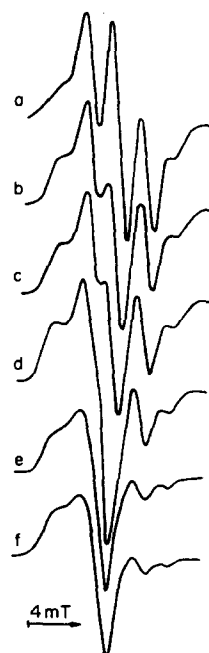


Fig. 1. ESR spectra of the free radicals trapped in mechanically destructed polyamide 6 *in vacuo* (a) and after introducing air (b–f). Temperature, ($^{\circ}\text{C}$), time at the given temperature (min), gain; a: -70° , 5.6, 1; b: -70° , 5.6, 1; c: -70° , 8.4, 1; d: -70° , 36.4, 1; e: -30° , 2.8, 0.8; f: -15° , 8.4, 2.

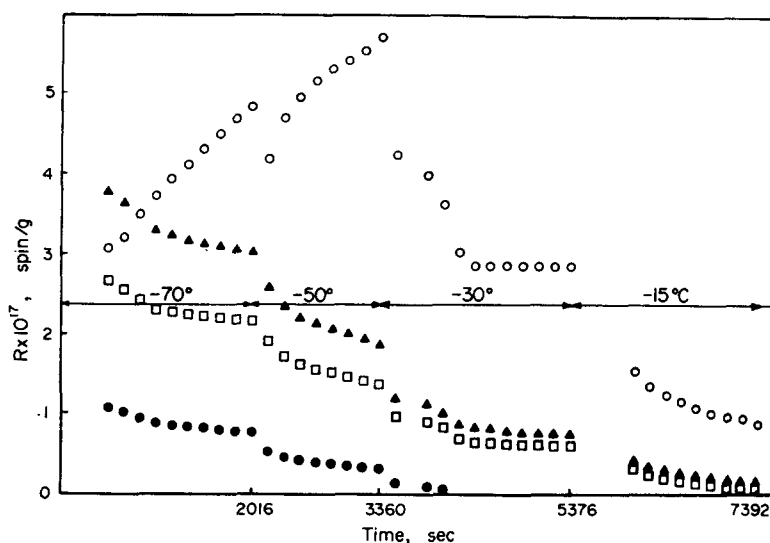


Fig. 2. Dependence of concentration of free radicals on time and temperature. \square —Radical (I); \bullet —Radical (II); \blacktriangle —Radical (III); \circ —ROO· Radical.

RESULTS AND DISCUSSION

As found in the study of free radical formed during mechanical destruction of polyamide [6, 9], the total ESR spectrum at -50° is a sum of three component spectra corresponding to the $\sim\text{CONH}\dot{\text{C}}\text{HCH}_2\sim$ (I), $\dot{\text{C}}\text{H}_2\text{CONH}\sim$ (II) and $\dot{\text{C}}\text{H}_2\text{NHCO}\sim$ (III) radicals. The shape of the spectrum undergoes no substantial change in the temperature region between -50 and -30° .

Air was introduced into the ampoule at -70° . In the next few minutes, the spectrum changed markedly. Peroxy radicals began to appear and the total spectrum was asymmetrized (Fig. 1). The original alkyl radicals (I)–(III) were preserved at 0° at a certain concentration. At the same temperature, all the radicals gradually vanished. This made it possible to study the change of the alkyl radicals to peroxy radicals at -70 and -50° as well as the decay of all the radicals at temperatures from -30 to 0° .

As pointed out earlier [2, 9], the concentration of the radicals (I)–(III) does not change at -50 and -30° in the absence of oxygen. Although the total concentration of radicals (I)–(III) at -70° changed in the presence of oxygen, the number of radicals in the system remained unaltered. Alkyl radicals changed to peroxy radicals.

When the temperature is changed from -70° to -50° , the concentration of both the ROO· and the alkyl radicals will decrease (Fig. 2). Later, at -50° the number of ROO· radicals increases with time accompanied by a decrease in radicals (I)–(III). Decrease in the number of the peroxy radicals is observed also as the temperature is raised from -50 to -30° . At -30° , the concentration of peroxy radicals neither increases nor decreases (Fig. 2). The effect

of a rapid decrease in the concentration of ROO· radicals resulting from rise of temperature is probably due to change in the mobility of the polymer matrix; this leads to a possibility of the interaction of more distant radicals. As soon as most of the radicals react in the given surroundings, there should be an increase in the concentration of ROO· radicals resulting from the continuing interaction of oxygen with alkyl radicals. At -30° , there is dynamic equilibrium. After elevation of the temperature from -30° , rapid decay of all the radicals in the system is observed.

The ESR spectrum of the peroxy radical is an asymmetric singlet. Its parameters were found from agreement between the theoretical and experimental spectra, assuming the axial symmetry. The best agreement between these spectra was achieved with line width 1.57 mT, $g_\perp = 2.0089$ and $g_\parallel = 2.0301$.

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