Changes of ESR Spectrum of Poly(methyl methacrylate) during Decay of Free Radicals at High Pressures

F. SZŐCS

Institute of Polymers, Slovak Academy of Sciences, Bratislava 9

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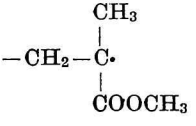
Free radical decay at high pressures in irradiated poly(methyl methacrylate) (PMMA) has been studied. It has been found that by the effect of high pressure the free radical decay is slowed down and, simultaneously, great changes of the line intensity ratio occur in the form of ESR spectrum of free radicals. In this paper the changes of the ESR spectrum appearing during the free radical decay over the temperature range 100—180°C at the pressures of 5000 and 10,000 atm respectively, are discussed.

By the effect of PMMA irradiation or mechanical degradation quite a high concentration of free radicals is attained, giving an intense 9-line spectrum. The interpretation of this spectrum gave rise to many discussions. One group of authors [2—7] supposed the 9-line spectrum to reflect the presence of two types of free radicals, whereas the second group [1, 8, 9, 18] attributed the spectrum to one type of free radicals in various configurations.

The first group of authors was supported by the observation that in the course of free radical decay there appeared changes in the intensity ratio of individual lines of the 9-line spectrum. From that they drew the conclusion that the spectrum originates from superposition of at least two types of free radicals. They ascribed the more intense 5-line part of spectrum to one, whereas the weaker 4-line part of spectrum to another free radical type.

However, the effort to find suitable types of free radicals, which might well fit both the 5- and the 4-line spectrum parts, was not successful.

A new view of the spectrum interpretation is brought by *Fischer*'s papers [10, 11]. In the course of polymerization of methacrylic acid in aqueous medium he observed a 16-line spectrum of growing chain radicals



(*I*)

where the unpaired electron interacts with the three equivalent protons of methyl group and two nonequivalent protons of the methylene group as well. Because of the greater line width, only 9 of the 16 lines may be resolved in the solid state. Further papers [12—14] prove the correctness of this supposition on the basis of the spectra obtained from deuterated PMMA.

This interpretation solved the origin of the 9-line spectrum, but it did not elucidate the changes of the spectrum shape observed in the course of free radical decay. These changes are very striking when observed at high pressures.

Experimental

For this work, commercial samples (Plexiglass 233) of Rhöm and Haas, GmbH, of molecular weight $M_w = 3 \cdot 10^6$ and of $T_g = 108°C$ were used. The samples were irradiated with 1 MeV electrons from a van der Graaf generator at room temperature in nitrogen atmosphere.

The ESR spectra were measured by commercial spectrometer (12X, AEG) at room temperature. After recording the initial spectrum, the samples were subjected to high pressure in nitrogen atmosphere and, after reaching the pressure required, they were heated rapidly up to various temperatures. After 30 minutes of annealing they were cooled and after the pressure relief, they were transferred into the cavity resonator in cooled state. The method used is more thoroughly described elsewhere [15].

Results and Discussion

By the effect of pressure the free radical decay is slowed down. The rate constant of free radical decay at 100°C and 5000 atm proves to be more than 10^2 smaller than at 100°C and at atmospheric pressure. At 10,000 atm, the decay of free radicals is still slower [15]. At this pressure, the free radicals may be observed also after 30 minutes of sample annealing at 200°C. At the pressure of 10,000 atm, the T_g attains the value of 200°C. This is supported by the higher speed of free radical decay over 200°C.

In Fig. 1 PMMA spectra recorded after 30 minutes of sample annealing performed at various temperatures and at the pressure of 5000 atm are shown. With growing decay temperature, the spectrum shape changes gradually. The relative intensity of the 4th

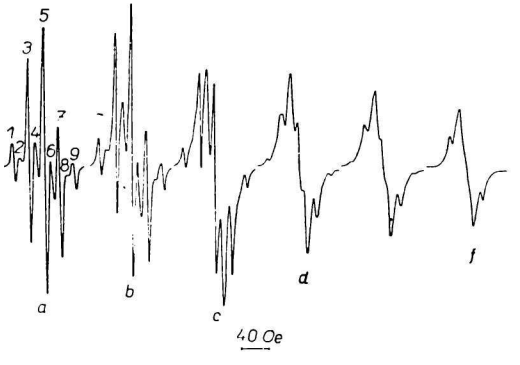


Fig. 1. ESR spectra of PMMA free radicals after 30 minutes' sample tempering at 5000 atm and following temperatures: *a*) starting untempered spectrum, G-1; *b*) 110°C, G-4; *c*) 120°C, G-4; *d*) 130°C, G-4; *e*) 140°C, G-4; *f*) 155°C, G-10. *G* — relative values of spectrometer gain.

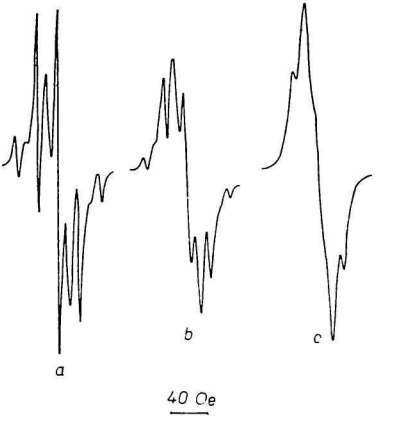


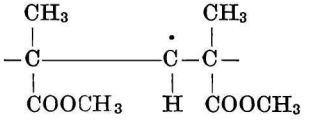
Fig. 2. ESR spectra of PMMA free radicals after 30 minutes' sample tempering at 10,000 atm and following temperatures: *a*) 130°C, G-1; *b*) 150°C, G-1.5; *c*) 180°C, G-3. *G* — relative values of spectrometer gain.

and 6th lines increases; the lines themselves are numbered in the direction of the decreasing magnetic field from 1 to 9. At the pressure of 10,000 atm (Fig. 2) similar changes of spectrum shape as at 5000 atm occur at higher temperatures. The original 9-line spectrum decays gradually leaving behind the 4th and 6th spectral lines only.

Certain intensity ratio changes occur also during the decay at the atmospheric pressure; they are, however, not very marked. At high pressures the changes of the line relation proved to be substantially greater. These changes of the spectrum shape may in no case be explained by the presence of one radical type. It has to be presumed that the intensity of the 4th and 6th lines relatively increases due to the fact that at least another radical has its lines overlapped in these positions.

By PMMA irradiation several types of free radicals are formed. Primary radicals partly recombine and partly react with polymer matrix. Hence, several types of free radicals exist, the most stable one being the end radical observable at room temperature. The end radicals decay gradually at room temperature, reacting with macromolecular segments. During this type of decay, the unpaired electron disappears at the original place where the reaction with the matrix took place and appears in some next position. This transfer process is terminated by recombination after the meeting of two free radicals. Due to the displacement of the unpaired electron new types of free radicals may be formed. Most of them are unstable, reacting further with polymer matrix. But there are conditions under which these unstable radicals decay very slowly, thus attaining relatively high concentrations.

In the spectra shown in Figs. 1 and 2, respectively, striking changes in positions of the 4th and 6th lines occur. It may well be presumed that in these positions, doublet spectrum due to the radical



(*II*)

is overlapped with the original spectrum, diminished in intensity. The spectrum of the radical *II* is the consequence of the interaction of the unpaired electron with one α-proton, the interaction with further γ-protons being negligible.

In free radical decay, taking place at lower pressures, the contribution of radical *II* manifests itself in a slight change of the line ratio. Other effects appear, however, if the polymer is subjected to high pressure. The segmental motions are considerably hindered what reflects itself also in T_g shift toward higher temperature. The radicals located on the chain become then more stable than the end radicals. After the decay of most of free radicals (Figs. 1*d*–*f* and Fig. 2*c*) the resultant spectrum shape is influenced, apart from lines of radicals *I* and *II*, also by another singlet derived probably from polyene radicals.

Similar changes of spectrum shape were observed also in irradiated poly(glycol methacrylate) (PGMA) [16, 17]. In samples with high cross-linking degree a well resolved doublet [16] was observed after weakening the nine-line spectrum. Owing to crosslinking, chain radicals in PGMA get more stable if compared with end radicals. A similar effect may be evoked in the PMMA by high pressure.

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