

Free Radicals in X-Ray Irradiated Poly(methylmethacrylate) from the Point of View of ESR Dosimetry

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Received 12 February 1998

Free radicals were generated in atactic poly(methylmethacrylate) by the effect of X-ray radiation. The resulting changes in ESR spectra were investigated in the course of 11 weeks in air at room temperature. The overall ESR spectrum is formed by superposition of the effects of some types of free radicals decaying at different rates. For this reason, the form of spectrum changes with time. It is pointed out that the change in relative intensity of spectral lines gives information about the time elapsed between irradiation of polymer and recording of ESR spectrum. The possibility of using the decay of free radicals for retrospective ESR dosimetry is discussed.

Poly(methylmethacrylate) (PMMA) is one of the polymers which were most thoroughly studied by the method of ESR. As early as in the first stage of development of the ESR spectroscopy it was observed that X-ray irradiated PMMA gives intensive 9-line spectrum of free radicals. The interpretation of this spectrum evoked many discussions [1]. This circumstance was due to the fact that the form of the spectrum significantly changed in the course of decay of free radicals. The interpretation was approached from two different points of view. The proponents of the presence of one radical type assumed different conformation states of terminal radicals. The second group of authors supposed at least the presence of two types of free radicals owing to which the observed composite spectrum was considered to arise by superposition of the contributions of terminal radicals and radicals on polymer chains. From the viewpoint of this study it is important that the character of spectrum changes with time. The longer is the time interval between irradiation and the moment of ESR spectrum measurement, the greater are the changes in intensity ratios of lines. One could figuratively say that the hands of clockwork start at different speed in the moment of polymer irradiation. Provided it is feasible to estimate the height ratio of spectral lines immediately after sample irradiation and the temporal progress of the changes in individual spectral lines, the time interval between sample irradiation and the record of ESR spectrum can be determined. In the scope of this work this process is demonstrated and estimated from the viewpoint of retrospective ESR dosimetry.

EXPERIMENTAL

The measurements were carried out with a sample

of atactic PMMA (product of Röhm and Haas, brand name PMMA 8N, $\theta_g = 105^\circ\text{C}$). The PMMA 8N granulate was used for moulding a sample of $2 \times 3 \times 6$ mm size at the temperature of 200°C under pressure. The sample was irradiated with X-rays for 210 min in air at room temperature by using a Co-lamp operating in the regime of 30 kV and 20 mA. The total absorbed dose of radiation was 28 kGy. The ESR measurements were performed on an X-band spectrometer (Varian E-4) at room temperature.

RESULTS AND DISCUSSION

The PMMA sample irradiated at laboratory temperature gives a characteristic 9-line composite spectrum of free radicals. The spectrum taken immediately after sample irradiation is represented in Fig. 1*a*. The concentration of free radicals corresponding to this spectrum is 7.4×10^{17} spin cm^{-3} . Further spectrum in Fig. 1*b* reflects the stage of advanced decay of free radicals. This spectrum was recorded after the annealing of the sample lasting 43 days. The corresponding concentration of free radicals is 4.7×10^{16} spin cm^{-3} .

The method of evaluation of line ratio is depicted in Fig. 1*a*. The lines of spectrum are numbered in the sense of increasing magnetic field. The peak-peak deflection of the middle (fifth) spectral line is denoted by letter *A*, while the peak-peak deflection of the fourth and sixth line is denoted by letter *B*.

The temporal course of the values *A* and *B* is represented in Fig. 2. The ratio of these values (*A/B*) is given in Fig. 3. A review of the ESR spectrum of irradiated PMMA has been presented in literature [1]. The ESR spectrum of PMMA irradiated by X-rays does not practically differ from the spectrum of gamma-irradiated sample. Small differences in the ra-

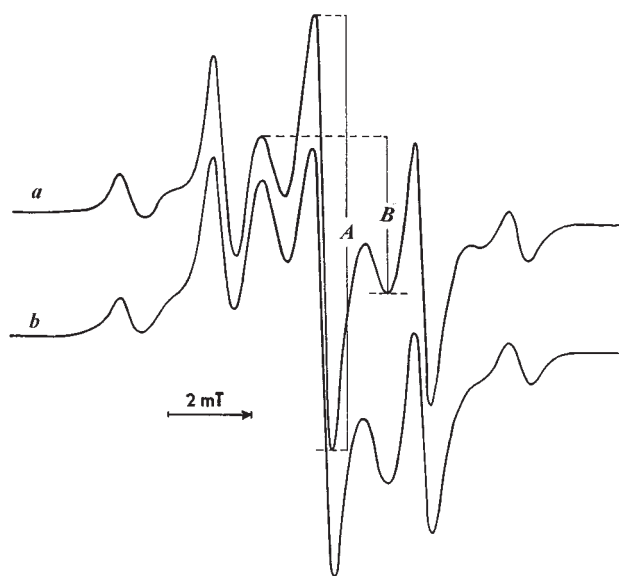


Fig. 1. ESR spectrum of X-ray irradiated polymethylmethacrylate: a) shortly after irradiation, gain 63; b) after 43 d annealing at 21 °C, gain 1000.

ratio of lines of 9-line spectrum may occur and thus signalize some differences in relative representation of free radicals. Small differences in efficiency of formation of individual types of free radicals due to the difference in wavelength of applied radiation may appear. The ratio A/B is, to a small degree, affected by intensity and persistence of irradiation as well. This effect results from the fact that a part of free radicals decays already during irradiation. Besides these effects the ratio of lines is especially affected by the pres-

ence of monomer in sample. That may be the residual monomer of the process of polymer production or the monomer arisen by the effect of radiation and depolymerization of chains. The present monomer units can thus react with radicals on chains to give terminal radicals. If the polymer is carefully deprived of monomer, the relative intensity of the fourth and sixth line is greater and the ratio A/B decreases. In samples containing high content of monomer the middle spectral line is stronger [2].

It has been evidenced that the 9-line ESR spectrum of free radicals observed at room temperature comes into existence by superposition of the spectra belonging to 4 types of free radicals [3]. Two types of free radicals exhibiting odd number of lines contribute to the fifth line. This couple of radical types includes the free radicals occurring at the end of polymer chain responsible for the 9-line spectrum and the radicals on side groups ($-\dot{\text{C}}\text{H}_2$) responsible for the triplet spectrum [4]. The radicals giving rise to even number of lines contribute to the fourth and fifth line. It is the doublet [5] of radicals on the main chain ($-\dot{\text{C}}\text{H}-$) and the quartet [6] of allyl radicals. It was succeeded in obtaining a good agreement of experimental spectrum with simulated spectrum of PMMA by using superposition of the spectra of these 4 types of free radicals.

The enhancement of the fourth and sixth line was observed if the free radicals decayed under high pressure [5]. The effect of pressure results in retardation of the decay of free radicals and the line ratio A/B decreases. The radicals on the main chain decay more slowly than the radicals at the end of chains or the radicals on side groups. The reduction of free volume due to pressure increase retards the transport of rad-

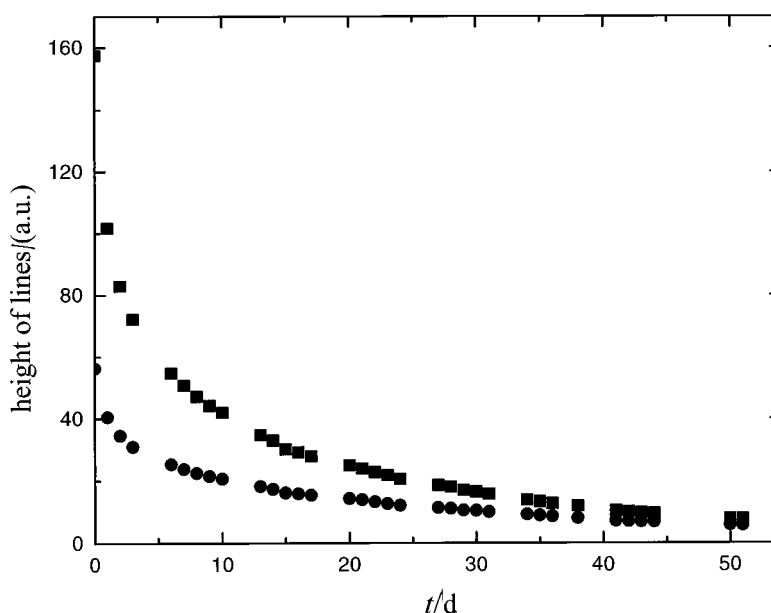


Fig. 2. Dependence of the values A (■) and B (●) on the time of annealing at 21 °C.

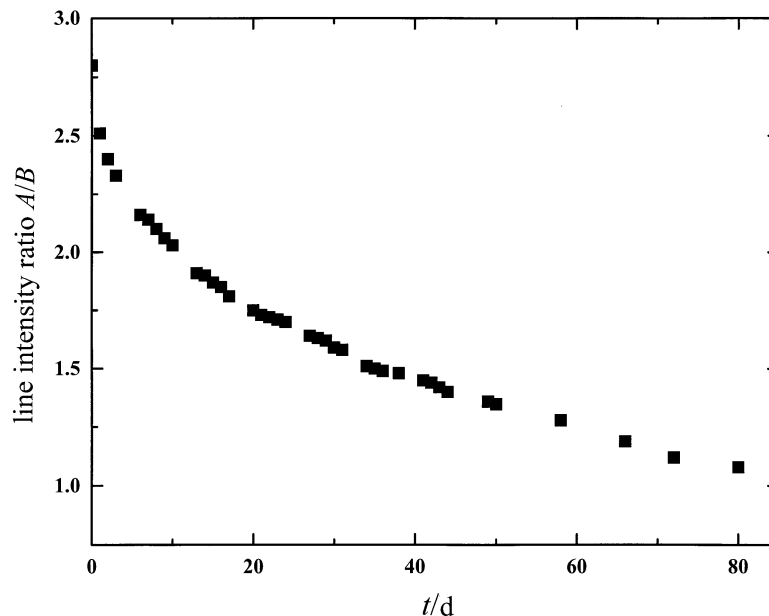


Fig. 3. Dependence of the line intensity ratio A/B on the time of annealing at 21 °C.

ical centres. A similar effect can also be observed if the mobility of segments of polymer chains is reduced owing to extensive cross-linking.

The variations resulting from different influence of individual types of radiation or different content of monomer in sample can, to a great extent, be eliminated by recording the decay curve of sample of the used type. On the basis of the knowledge of circumstances connected with the investigated radiation event we can estimate the dose, intensity, and kind of radiation. Then we could irradiate with the estimated dose a sample similar to the sample present at the place of radiation incident. By measuring the time dependence of the decay of free radicals or the change in the form of spectrum it could be possible to come to such form of the spectrum which might be identical with the spectrum recorded immediately after radiation incident. At this basis it could be feasible to determine the interval of time between irradiation and record of the spectrum.

Acknowledgements. Partial support of this work by the Grant Agency VEGA, No. 2/404/97, is gratefully acknowledged.

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