RELATION BETWEEN FREE RADICALS AND ULTRAVIOLET ABSORPTION IN IRRADIATED POLYMETHYL METHACRYLATE DOPED WITH SQUALENE

M. Trihi1*, J. L. Duroux2, A. Hoummada1

1Laboratoire de Physique Nucléaire, Faculté des Sciences Ain Chock, Université Hassan II, B.P. 5366, Casablanca, Maroc
2Laboratoire de Biophysique Pharmaceutique, Faculté de Pharmacie, 2, rue du Dr Marcland, 87025 Limoges, France

* Corresponding author. E-mail: TRIHI@facsc-achok.ac.ma

Received 20 November 2000; revised version accepted 08 June 2001

Abstract

A relation between the radiation-induced nine-line electron spin resonance signal and the unstable component of the optical absorption in the near ultraviolet of Polymethyl methacrylate doped with squalene is made on the basis of the radiation dose relationship. It is concluded that this correlation is applicable several days following irradiation.

This good correlation shows that the absorption and the ESR (Electron Spin Resonance) spectrum of irradiated PMMA doped with squalene are due to the same species or two species having the same radiochemical precursor.

The best model for the ESR response as a function of the spectrophotometric response is a linear regression.

Keywords: Polymethyl Methacrylate; Squalene; Ionizing radiation; Dosimetry.

1. Introduction

The effects of ionizing radiation on Polymethyl methacrylate (PMMA) doped with squalene have been studied by our research team for many years. Free radicals formation has been examined extensively by using electron spin resonance (ESR) [1].

The irradiation-induced optical absorption in irradiated PMMA doped or undoped with squalene has also been studied extensively [2-6]. It was discovered that the irradiated PMMA doped with squalene, presented spectrophotometric responses changing in time allowing us to find the absorbed dose and the delay separating the irradiation and the measurement.

In this paper the relation between the change in optical density per unit thickness (ΔDO/mm) and the ESR signal will be verified in order to check if a relation exists between the UV-visible absorption and the ESR spectrum of irradiated PMMA doped with squalene.

2. Materials and Methods

In order to make the spectrophotometric response of our dosimeter unstable in time, we have added 2,5 % of squalene to monomer (methyl methacrylate) before polymerization. The steps of polymerization are the same as for normal PMMA [7]. Dosimeters sheets of 1,8 mm thickness were cut to size of 11x45 mm² to fit the holder of the spectrophotometer.

Irradiation of samples was carried out using a 60Co source (IBL 460, Faculty of Pharmacy, Limoges, France) with a nominal activity of 8000 Ci and with absorbed dose rate of the order of 3 kGy/h. The samples were irradiated at doses of : 0.665 ; 1.33 ; 2.66 ; 5.32 ; 10.64 kGy.

The dosimetry of source was carried out using alanine/ESR dosimetry [8,9] by the constructor and in routine using the Fricke method [10]. During the irradiation, at ambient temperature, the dosimeters for each γ-ray irradiation were held in a PMMA cylinder, which provided electron equilibrium conditions.

The absorption spectra and optical densities (O.D.) before and after irradiation were measured at 299 nm using an UVIKON 930 double beam spectrophotometer of KONTRON.

ESR spectra were taken with a BRUCKER Spectrometer (ESP 300 E) using the following parameters :
- Microwave power : 0.402 mW
- Modulation amplitude : 0.88 G
- Time constant : 10.24 ms
- Scan range : 200 G

The measurements were done on the basis of peak to peak spectrum heights.

The measurements of O.D. and ESR signal were carried out at ambient temperature and at the following times :
- just before irradiation (for optical density)
- 1 h after irradiation (D+0)
- then in days : D+1, D+2, D+5, D+7, D+9, D+12, D+16, D+22.
The samples were stored between the measurements in a controlled enclosure at 20 °C sheltered from light [11,12].

3. Results

From results obtained using ESR spectroscopy [1] and spectrophotometric method [2, 3], we have searched for a good model between the ESR signal and the change in optical absorption per unit thickness ($\Delta DO/mm$), $\Delta DO$ corresponds to the difference between the optical density measured at D+i (i : number of days after irradiation) and that measured before irradiation, on the basis of the radiation dose relationship for all days of measurements.

Many regressions have been tested ; the model giving the best results is a linear regression (ESR) response = $a + b (\Delta DO/mm)$.

The coefficients $a$ and $b$ are given in Table 1, with the correlation coefficients obtained for all the days of measurements.

<table>
<thead>
<tr>
<th>Days</th>
<th>D+0</th>
<th>D+1</th>
<th>D+2</th>
<th>D+5</th>
<th>D+7</th>
<th>D+9</th>
<th>D+12</th>
<th>D+16</th>
<th>D+22</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>342,111</td>
<td>131,244</td>
<td>-98,664</td>
<td>-268,585</td>
<td>-120,266</td>
<td>-153,252</td>
<td>-274,710</td>
<td>-350,917</td>
<td>-458,506</td>
</tr>
<tr>
<td>b</td>
<td>11181,099</td>
<td>9627,821</td>
<td>7442,623</td>
<td>5732,581</td>
<td>6821,692</td>
<td>6283,158</td>
<td>6438,637</td>
<td>5961,711</td>
<td>5443,224</td>
</tr>
<tr>
<td>r</td>
<td>0,992</td>
<td>0,997</td>
<td>0,999</td>
<td>0,999</td>
<td>0,998</td>
<td>0,998</td>
<td>0,999</td>
<td>0,999</td>
<td>0,999</td>
</tr>
</tbody>
</table>

Table 1 : coefficients of the linear regression characterizing the evolution of the ESR response as a function of $DO/mm$ for different days following irradiation, with the correlation coefficient $r$.

It should be noted that the coefficients of correlation varied between 0,992 and 0,999 for all regressions obtained.

The essential fact to emphasize in Table 1 is the very good correlation obtained.

Figs. 1, 2, 3 and 4 show the correlation between the unstable O.D. development at 299 nm per unit thickness and production of free radicals with the radiation dose, as parameter for these days : D+0, D+1, D+7, D+22.

The correlation for the straight line shown is $r = 0.992$ for D+0, 0,997 for D+1, 0,999 for D+2, 0,999 for D+7, 0,999 for D+12 and 0,999 for D+22.

The curves show a linear and regular evolution at any days (D+i), in addition there is a perfect correlation between the ESR response and the spectrophotometric response, we concluded that the absorption and the ESR spectrum are due to the same species or two species having the same radiochemical precursor.

Figure 1 : Correlation between a change of O. D. per unit thickness at 299 nm and ESR response with the radiation dose as parameter at D+0.
Figure 2: Correlation between a change of O. D. per unit thickness at 299 nm and ESR response with the radiation dose as parameter at D+1.

Figure 3: Correlation between a change of O. D. per unit thickness at 299 nm and ESR response with the radiation dose as parameter at D+7.
4. Conclusion

In this study, we have demonstrated the existence of a clear correlation between the nine-line ESR spectrum and the unstable optical density at 299 nm of irradiated and squalene doped Polymethyl Methacrylate.

From the best correlation obtained in this work, we can conclude that the radicals giving the nine-line ESR spectrum also give the unstable optical density component, immediately following irradiation.

References