Molecular Weight Studies of the γ-Irradiation Degradation of Poly(methyl methacrylate) Doped with Poly(*p*-sulfanilamide)

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ABSTRACT: The protection of some poly(methyl methacrylate) (PMMA) samples against γ rays was investigated in the absence and presence of poly(*p*-sulfanilamide). Pure PMMA (without additives) and PMMA–poly(*p*-sulfanilamide) blend samples were irradiated with γ rays for different exposure doses (5, 15, 25, 35, 50, 75, and 100 kGy). The viscosity-average molecular weights were determined and thin-layer chromatography measurements were carried out after each irradiation dose. The maximum protection against γ rays was found when 1% poly(*p*-sulfanilamide) was used. The radiation chemical yield for main scission (G_s) was calculated and had lower values in the case of 1% poly(*p*-sulfanilamide). The energy absorption per scission was maximum for 1% poly(*p*-sulfanilamide), and this con-firmed the obtained G_s data. From thin-layer chromatography studies, it was observed that both the retention factor (R_f) values and polydispersity of the PMMA samples increased with an increasing exposure dose. The effect of γ irradiation on PMMA films doped with 1% poly(*p*-sulfanilamide) was investigated with UV spectroscopy after the extraction of the additives. A change in the intensity of the absorption bands with an increasing irradiation dose was recorded. It is suggested that PMMA films doped with this type of polymer can be used as dosimeters. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1294–1300, 2007

Key words: degradation; radiation; chromatography; NMR; UV spectroscopy; conducting polymer blend

INTRODUCTION

The vigorous development of polymer science and the extensive utilization of polymeric materials in technology have led in recent years to an increased interest in various problems of the chemistry and physics of conducting polymers. This is evident from the fact that not only physicists but also synthetic chemists, technologists, and structural engineers have become more and more interested in the numerous problems of the chemistry and physics of polyaniline and its derivatives as good conducting polymers.[1–11]

The radiolysis of poly(methyl methacrylate) (PMMA) has been studied more extensively than that of any other polymer. This can probably be explained by the fact that irradiation produces striking changes in PMMA that can be detected by a simple visual examination. Color changes are particularly apparent and easy to follow spectroscopically because of the perfect optical clarity of the polymer. Chemical groups differ widely in their sensitivity to radiation; this may be seen, for example, in the different values of the radiation chemical yield for main scission (G_s) for radical production in simple organic compounds and in the wide range of G_s values for crosslinking and degrading polymers. The sensitivity of a chemical group to radiation is, however, a purely relative term and may be greatly modified by the presence of other groups in either the same or adjacent molecules. When the effect is to reduce the reactivity of a major component of the system by the presence of another component or additives, one refers to radiation protection. Generally, there are two types of radiation protection. The first is internal radiation protection, which can occur because of resonance effects in low-molecular-weight compounds such as aromatic derivatives.[12–16] The second type of radiation protection is external protection; marked changes in the sensitivity of a polymer to radiation may be obtained by the use of additives, which do not form part of the polymer chain itself. When such additives reduce the effect of radiation on the polymer itself, they are often used as protectors.[16–18]

The concentration of these additives may be quite low, of the order of a few percent.[17,18] Optical and some structural changes have been also investigated in PMMA samples.[17,19–22] The effects of γ irradiation on the electrical properties of some ac-

rylate polymers were studied and dosimetric investigations were performed by Sayyah and co-workers.[23–26] The amount of quantitative data available in this field is limited. Because of the very small amount of reliable quantitative data published to date on this subject, it is not usually possible to reach definite conclusions about the basic mechanisms of crosslinking and degradation. To the best of our knowledge, there is no one who has discussed or investigated in the literature the use of conducting polymers as protective materials for PMMA against γ rays.

In this work, we investigated the protection of PMMA against γ rays by using a new conducting polymer. The viscosity-average molecular weight (M_v) and thin-layer chromatography (TLC) of PMMA before and after irradiation with γ rays were also investigated. It was of great interest to investigate in this study the use of these additives in the PMMA matrix as dosimeters.

EXPERIMENTAL

Materials

The methyl methacrylate monomer was a product of Merck–Schuchardt (Germany) (yield = 99%, stabilized with 100 ppm hydroquinone, density at 20 ± 4°C = 0.942–0.944 g/cm^3). Benzene (thiophene-free) and methanol were chemically pure grades from El-Nasr Pharmaceutical Chemical Co. (Cairo, Egypt). They were distilled twice over a suitable drying agent. p-Sulfanilamide was provided by Merck Chemical Co. (Schucharolt, Germany). Concentrated hydrochloric acid and an ammonia solution (33%) were chemically pure grade products provided by Prolabo Chemical Co. (London, England). Twice distilled water was used as a medium for the polymerization reactions. The sodium dichromate was a product of Merck Chemical.

Preparation of poly(p-sulfanilamide)

The polymer was prepared as mentioned in a previous article by Sayyah et al.[11]

Determination of M_v

The PMMA samples doped with poly(p-sulfanilamide) were separated from the dopant material poly(p-sulfanilamide) by dissolution in benzene and filtration, and then the clear polymer solutions were precipitated in a certain amount of methanol and finally dried in an electric oven at 105°C. The intrinsic viscosity ([η]) was obtained by the usual method of extrapolation.[27] The M_v values were calculated from the corresponding [η] values with the following equation:

$$[\eta] = 0.94 \times 10^{-4} M_v^{0.76}$$

The viscosity measurements were carried out in thiophene-free benzene at 25°C.[27]

Preparation of the PMMA thin-film samples doped with poly(p-sulfanilamide)

The films were prepared by a solvent-casting technique with a benzene/acetone mixed solvent (50 vol %) as a common solvent for the polymers, as mentioned in a previous article.[18]

γ irradiation of the prepared PMMA samples

Egypt's new irradiation facility, Mega-γ I (type J-6300), supplied by Atomic Energy of Canada, Ltd., at the National Center for Radiation Research and Technology (Cairo, Egypt) had been furnished with a ^{60}Co source having an activity of 137,000 Ci at the time of the measurement. The radiation doses (5, 15, 25, 35, 50, 75, and 100 kGy) were measured with a radio chromic dye film and Perspex. The overall error in the dose measurements did not exceed ±4%. The dose rate was 27.77 krad/h. The irradiation of the polymer samples was carried out in an air atmosphere.

TLC

The TLC technique was applied for the characterization of the PMMA samples before and after irradiation with γ rays. The TLC experiments were carried out as previously mentioned by Sayyah et al.[18] The spot area measurements were carried out with an aluminum foil weighing technique.[28]

RESULTS AND DISCUSSION

Effect of γ rays on M_v of pure PMMA samples and samples containing poly(p-sulfanilamide)

The pure PMMA sample (without additives) and PMMA–poly(p-sulfanilamide) blends were irradiated with γ rays for different exposure doses (5, 15, 25, 35, 50, 75 and 100 kGy). [η] for each polymer sample was obtained by the usual method of extrapolation.[27]

M_v for each sample before and after different irradiation doses was calculated. M_v of the PMMA samples decreased with an increasing irradiation dose in all cases (cf. Fig. 1). Moreover, the areas under the curves of the relation between M_v and the irradiation doses were different for each sample according to the additive concentrations. Therefore, these areas were calculated with the Microsoft Excel Fitting computer program. A graphical representation of the area under the curves of Figure 1 and
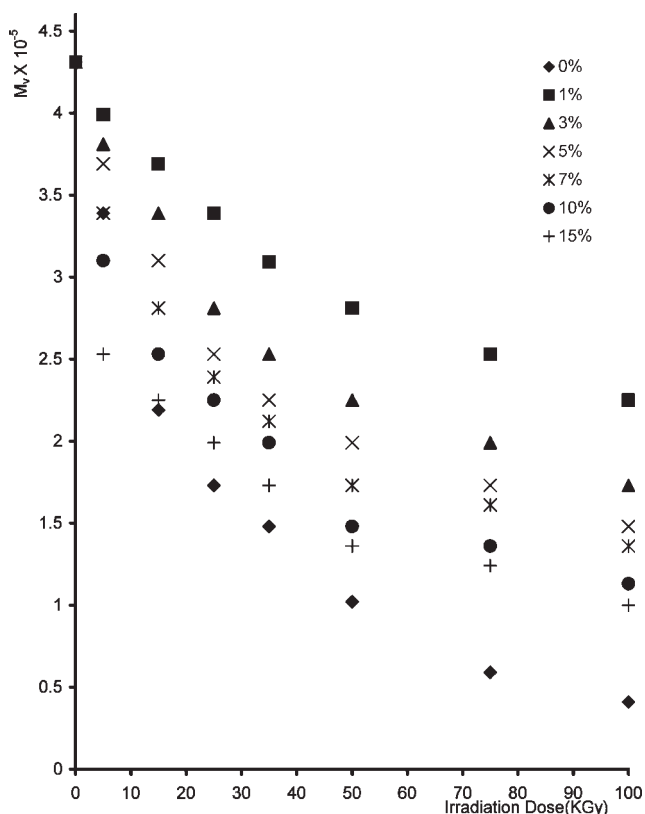
Figure 1 M_v versus the irradiation dose (kGy).

1% concentration. This protective efficiency could be attributed to the presence of sulfur or phenyl rings in the poly(p-sulfanilamide) as follows.

Poly(p-sulfanilamide) has many sulfur atoms and phenyl rings in its structure. The radicals that can be formed during the γ radiolysis of PMMA doped with poly(p-sulfanilamide) can be represented as follows:

$$(1)$$

$$(2)$$

the additive concentration (wt %) is shown in Figure 2. The highest value of the area was 33.08 cm^2 for poly(p-sulfanilamide) when 1% poly(p-sulfanilamide) was used.

From the aforementioned data, it was clear that the molecular weights of the PMMA samples decreased with the irradiation dose. However, when $1/M_v$ was plotted against the exposure dose, the $1/M_v$ values increased in a linear manner with an increasing irradiation dose. The slope of the straight lines in the aforementioned relation was G_s. The degradation of PMMA by γ rays gave a G_s value of about 2 (calculated with the number-average molecular weight) when the irradiation was performed in air and in the absence of any additives.[29]

A graphical representation between $1/M_v$ and the irradiation dose in each case is given in Figure 3, and the straight line was adjusted between the points with a computer program (Excel Fitting). The slope of each relation was calculated to obtain the G_s values. The relation between the G_s values and the concentration of poly(p-sulfanilamide) in the polymer blend samples is graphically represented in Figure 4, from which it is clear that the chemical yield for the main-chain scission had its lowest value at 1% poly(p-sulfanilamide).

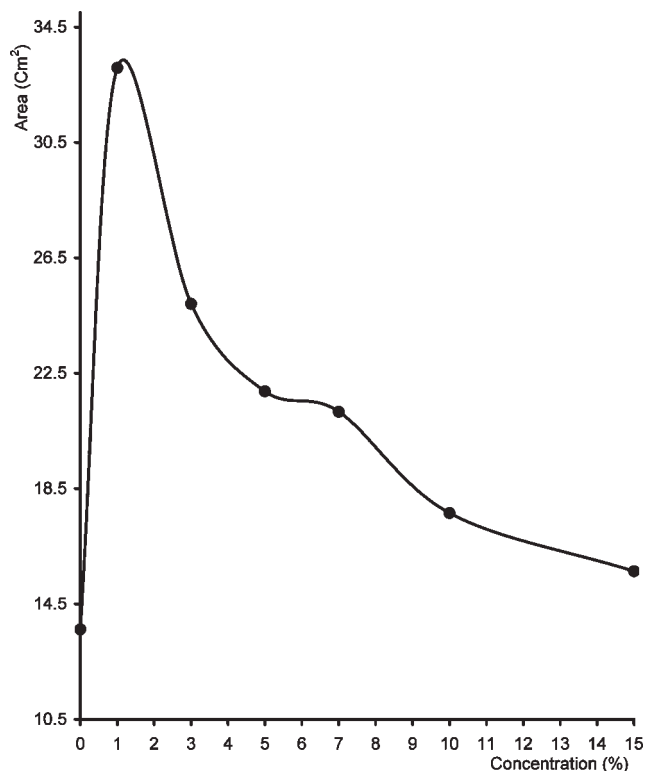In other words, poly(p-sulfanilamide) had a protective effect on the PMMA samples, especially at a
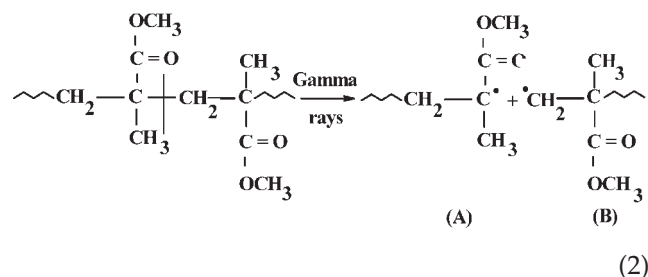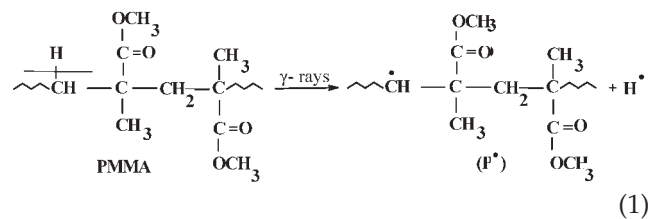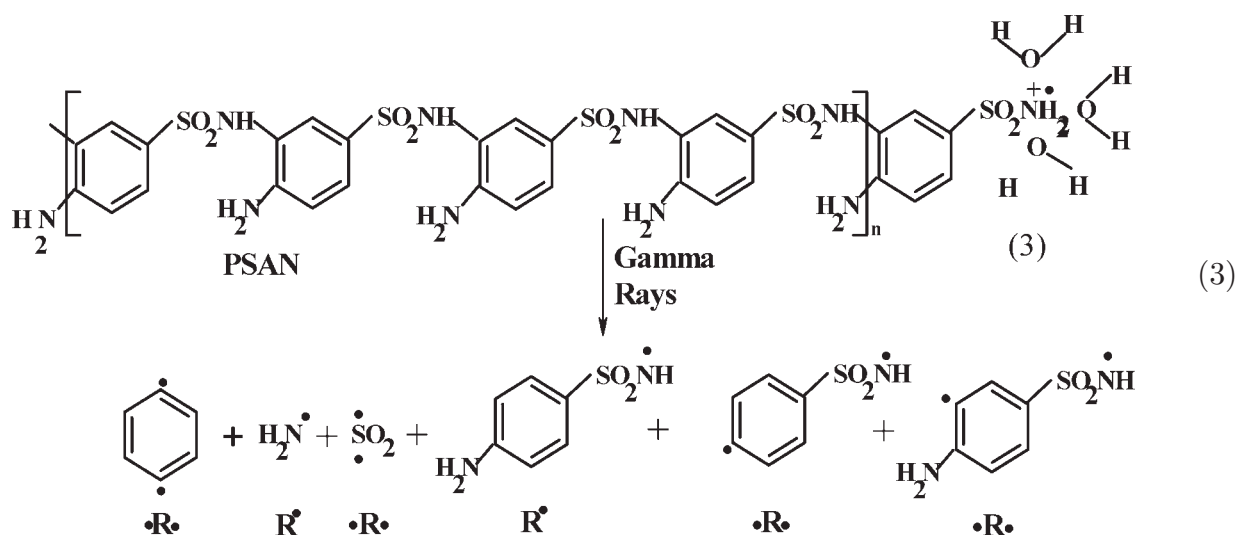

Figure 2 Relation between the area under the curve and the concentration of the additives during radiolysis.

$$(3)$$

Radiation protection by the additives may be considered to operate through the following alternative mechanisms. The formed biradical from the additives during the γ radiolysis [cf. eqs. (1)–(3)] may repair the damage caused by radiation. In PMMA polymers, the major reaction is a loss of a hydrogen atom leaving a polymer radical (P·), which is protected by a combination of the monoradicals of the additives and P·.

In the case of the degradation of PMMA by main-chain scission, as shown in eq. (2), protective additive monoradicals may combine with these radicals to form stable side chains.

Additionally, any monoradical that can be formed from the γ degradation of poly(p-sulfanilamide) can react instead of R· in eqs. (4) and (5):
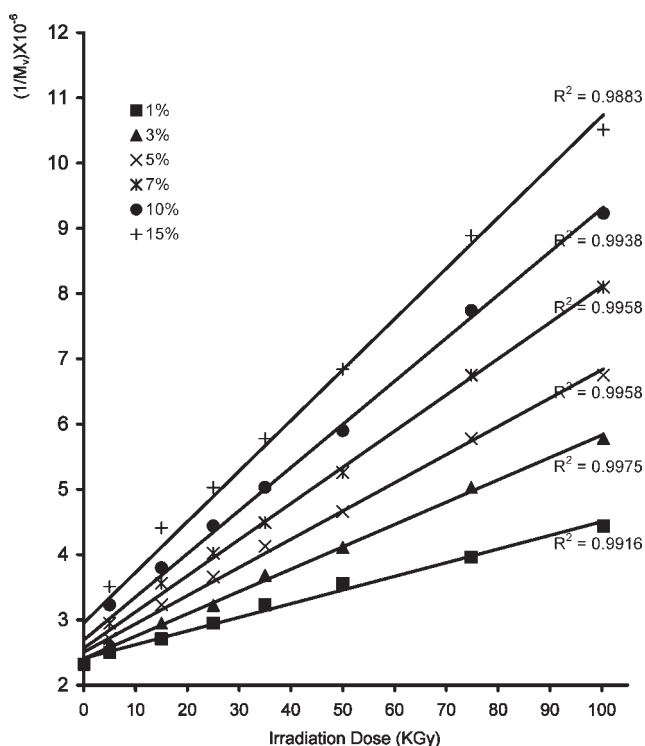

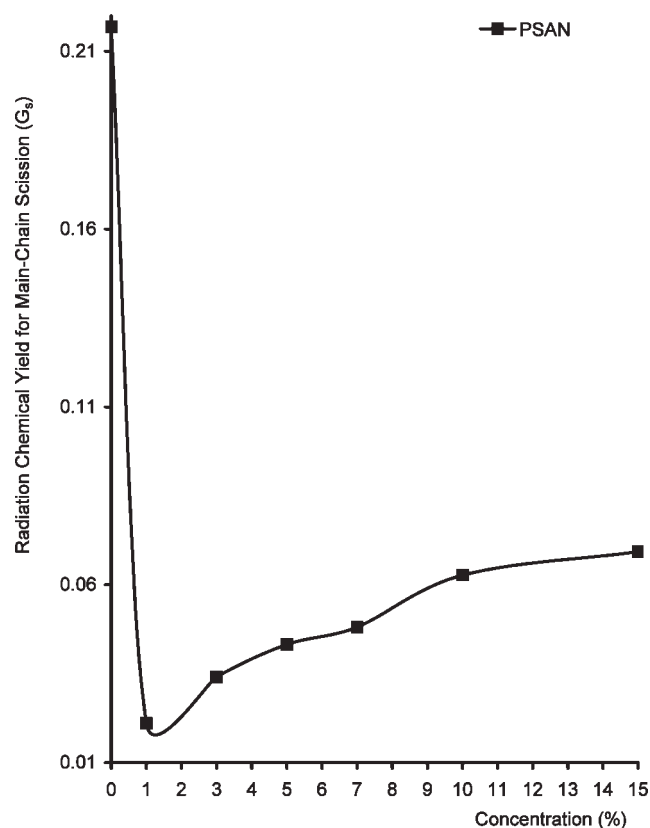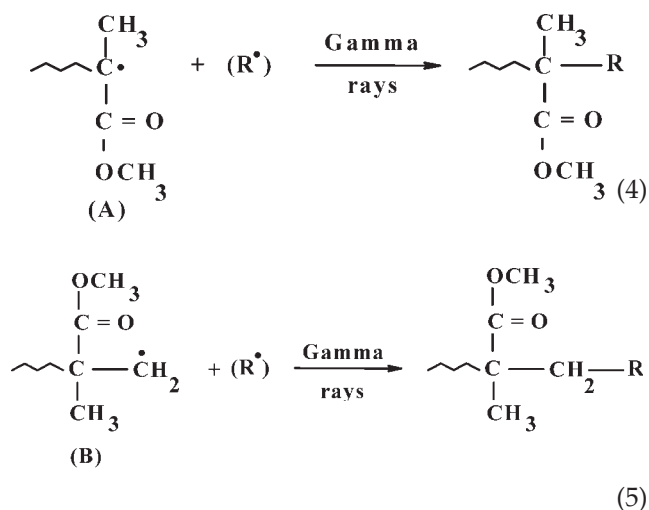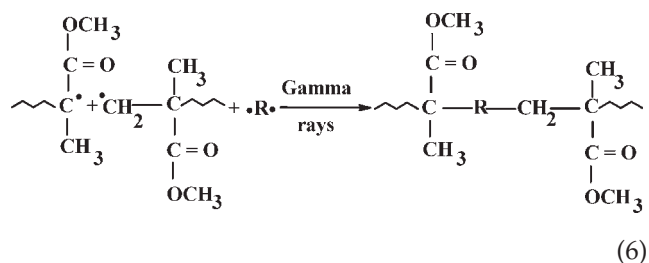**Figure 3** Relation between $1/M_v$ and the irradiation dose.

Figure 4 G_s versus the concentrations of the additives.

$$\text{(4)}$$

$$\text{(5)}$$

The additives can link the two polymer radicals together and thereby heal a radiation-induced scission. This means that there will be no significant change in the average molecular weight in the following equation:

$$\text{(6)}$$

The aforementioned mechanisms were confirmed by the ^{1}H-NMR spectroscopy measurements. The ^{1}H-NMR spectra were measured after irradiation with 50 kGy and the extraction of the additives by Soxhlet solvent extraction and filtration. This is represented in Figure 5, which shows two doublet signals in the region at $\delta = 7.3$ ppm that indicate the presence of a benzene ring; also, the diamide protons appear as two singlet signals at $\delta = 5.6$ ppm and at $\delta = 6.0$ ppm from poly(p-sulfanilamide) in the PMMA chains, which heal a radiation-induced fracture. This is in good agreement with what was found by Sayyah et al.[18] in the case of the protection of PMMA against γ rays by some sulfanilamide organic ligands.

TLC analysis

TLC analysis is a good and rapid technique for the characterization of polymer samples, especially for the determination of the molecular weight, and it gives an idea about the polydispersity of the obtained polymer samples.[30–34] The separation of
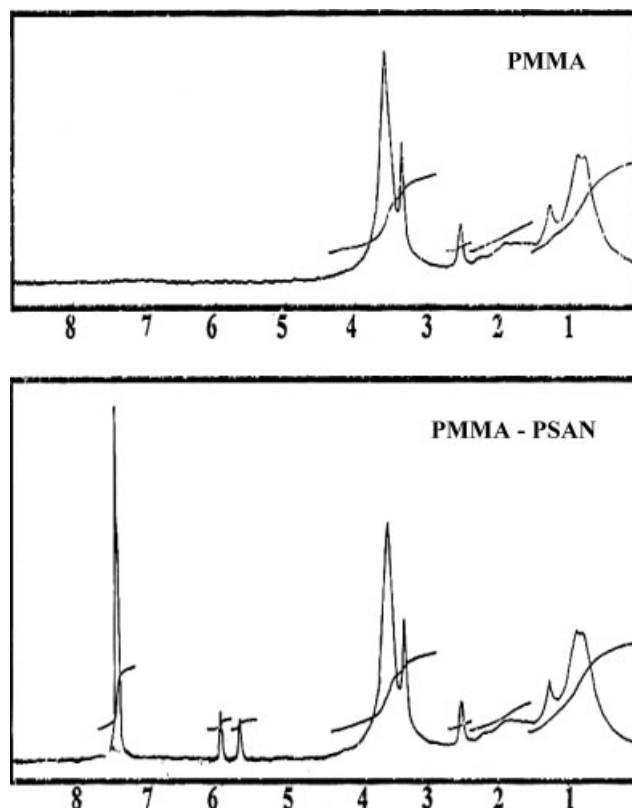

Figure 5 ^{1}H-NMR spectra of pure PMMA and PMMA after irradiation with 50 kGy and the extraction of additives by solvent extraction and filtration.

different PMMA samples on TLC plates was investigated after each irradiation dose. From the TLC chromatograms obtained after development in a normal saturation system at 25°C with a binary mixture of benzene and methanol (1 : 1.5 v/v), it is clear that both the R_f values and the spot area values increased with an increasing exposure dose in the absence and presence of poly(p-sulfanilamide) (cf. Fig. 6). This means that the polydispersity of the PMMA samples increased with the increasing irradiation dose, but M_v decreased in the same direction.

Dosimetric studies: UV spectra of a pure PMMA film and PMMA doped with poly(p-sulfanilamide) during γ radiolysis

The UV spectra of a pure PMMA film before and after γ irradiation with different accumulated exposure doses (5, 15, 25, 35, 50, 75, and 100 kGy) was investigated by Sayyah et al.[35] They found that the absorbance increased with increasing γ ray doses, and the linear part of the relationship between the absorbance and γ-exposure dose lay between 0 and 50 kGy. This means that a pure PMMA film can be used as a dosimeter in this range of exposure doses.[36,37]
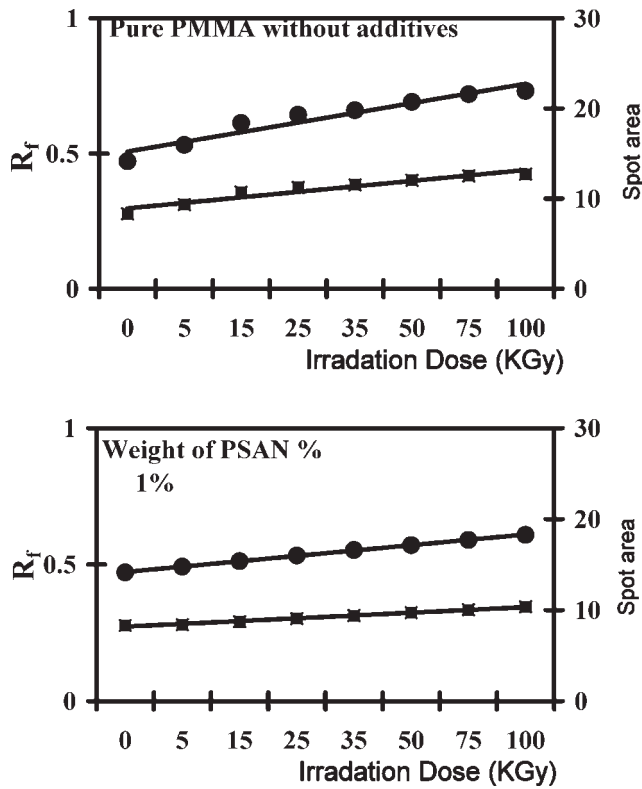
Figure 6 Relation between the spot area and R_f values and the irradiation dose: (●) R_f and (■) spot area.

The UV spectra of PMMA films doped with poly(p-sulfanilamide) before and after irradiation with different accumulated γ doses (5, 15, 25, 35, 50, 75, and 100 kGy) were measured after the extraction
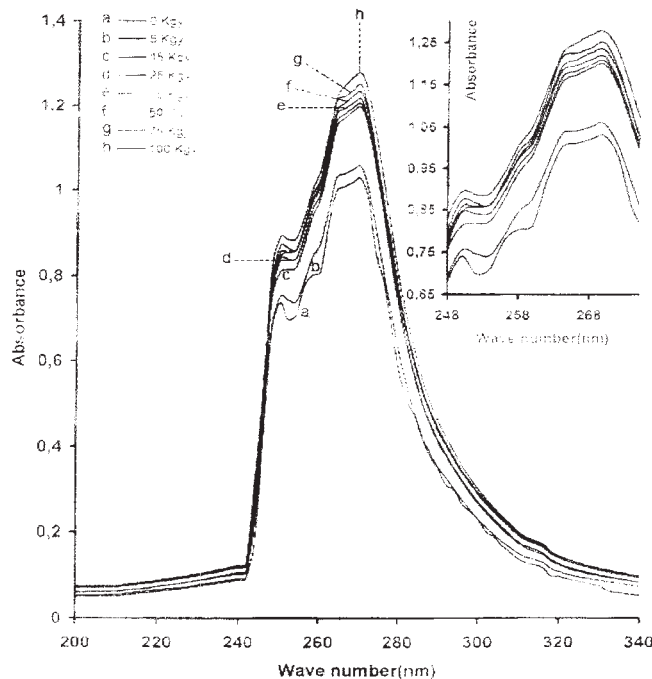

Figure 7 The UV-Spectra of PMMA irradiated with different exposurer doses of poly(p-sulfanilamide).
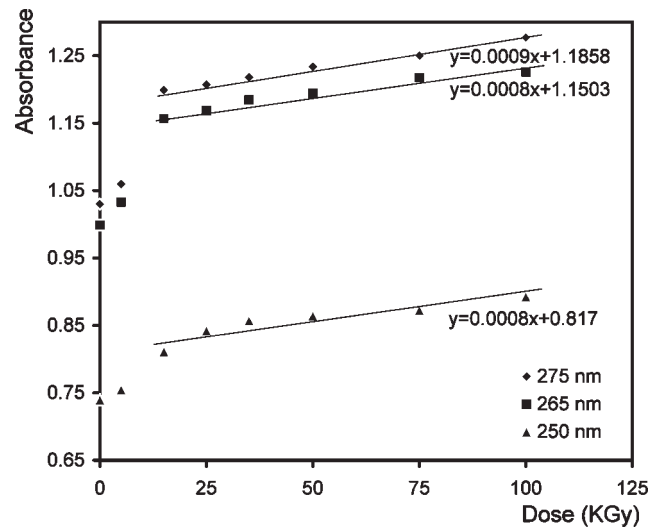

Figure 8 Relation between the exposure dose (kGy) and absorbance at different wavelengths for PMMA membranes after the extraction of poly(p-sulfanilamide).

of the dopant (Fig. 7). The absorbance of the band at 250, 265 and 275 nm increased with the increase of the γ-exposure doses. The relationship between the absorbance and the γ-exposure dose is presented in Figure 8 from which it is clear that the response of the PMMA film used to measure the γ-ray dose increased in the presence of poly(p-sulfanilamide) from 50 to 100 kGy.

CONCLUSIONS

This study led to the following conclusions:

1. The prepared poly(p-sulfanilamide) had a protective effect on PMMA against γ rays.
2. The protective concentration of poly(p-sulfanilamide) was 1 wt % of the polymer matrix.
3. Both the R_f values and polydispersity of the PMMA samples increased with an increasing irradiation dose in all cases (i.e., the absence and presence of additives).

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