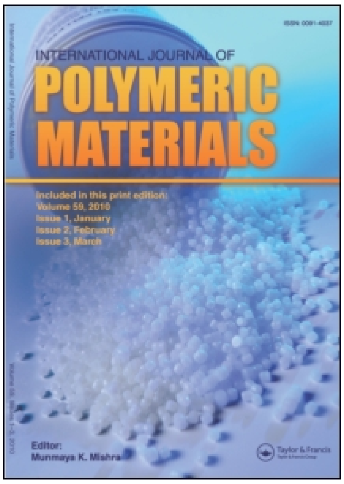

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MOLECULAR WEIGHT STUDIES ON THE GAMMA IRRADIATION DEGRADATION OF POLY(METHYLMETHACRYLATE) IN THE ABSENCE AND PRESENCE OF SULFANILAMIDE DERIVATIVES, PART I: TETRAOXALYLSULFANILAMIDE AND ITS COBALT (II) COMPLEX

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Protection of some poly (methylmethacrylate) samples against gamma rays has been investigated in the absence and presence of Tetraoxalylsulfanilamide and its Cobalt (II) complex. The pure PMMA (without additives), PMMA-Ligand and PMMA - Cobalt (II) complex composite samples were irradiated with gamma rays for different exposure doses (5, 15, 25, 35, 50, 75 and 100 KGy). Viscosity average molecular weight (M_v-values) and thin layer chromatographic measurements were carried out after each irradiation dose.

The maximum protection against gamma ray is found when 3% of the organic ligand or its Cobalt (II) complex is used in the polymer matrix.

The radiation chemical yield for chain scission (G_s) is calculated and has its lower values in the case of the organic ligand, which means that the protection is

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stronger in the case of the organic ligand than its Cobalt (II) complex. From TLC studies, it is noticed that both the R_f-values and polydispersity of the PMMA samples increase with increasing exposure dose.

Keywords: poly(methylmethacrylate), gamma irradiation, degradation, sulfanilamide derivative, γ-rays, thin layer chromatography (TLC)

1. INTRODUCTION

The radiolysis of PMMA has been studied more extensively than any other polymers. This can probably be explained by the fact that irradiation produces striking changes in PMMA, which can be detected by simple visual examination. Color changes are particularly apparent and easy to follow spectroscopically owing to the perfect optical clarity of the polymer. PMMA acquires a faint yellow color after 3–5 merged [1, 2].

Chemical groups differ widely in their sensitivity to radiation, this may be seen, for example, in the different $G_{(S)}$ – values for radical production in simple organic compounds and in the wide range of $G_{(S)}$– values for cross linking and degrading polymers. Bopp and Sisman(3) have listed such groups, in the order of their radiation stability, from the phenyl group in polystyrene (with highest resistance to radiation) to the methacrylate of –CF_2– groups (which decompose most readily).

The sensitivity of a chemical group to radiation is, however, a purely relative term and it may be greatly modified by the presence of other groups either in the same or adjacent molecules. Where 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 could occur due to the resonance effects in low molecular weight compounds such as aromatic derivatives [4, 5]. 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. Where such additives reduce the effect of radiation on the polymer itself, they are often used as protectors.

The concentration of these additives may be quite low, of the order of a few percent [6–9]. Optical and some structural changes were also investigated for PMMA polymer samples [10]. The effect of gamma irradiation on the electrical properties and dosimetric studies have also been studied on some acrylate polymers by Sayyah et al [11–14]. The amount of quantitative data available in this field is as yet limited. In view of the very scant amount of reliable quantitative data published to date on this subject, it is not usually possible to reach firm conclusions as to the precise method by which protection takes place in each case, particularly since the basic mechanisms of cross linking and degradation are themselves uncertain.

In the present work, we intend to investigate the protection of PMMA against gamma rays by using new organic additives containing sulfur. The viscosity average molecular weight and thin layer chromatography of PMMA before and after irradiation with gamma rays are also investigated.

2. EXPERIMENTAL

2.1. Materials

Methylmethacrylate (MMA) monomer was a product of Merck-Schuchardt, yield 99% stabilized with 100 ppm hydroquinone, density 20/4° 0.942–0.944 g/cm^3. Benzene (thiophene free) and methanol were of chemically pure grade from EL-Nasr Pharmaceutical Chemical company, A.R.E. They were distilled twice over a suitable drying agent. Sulfanilamide and oxalic acid were of analytical pure grade (Merck, Germany).

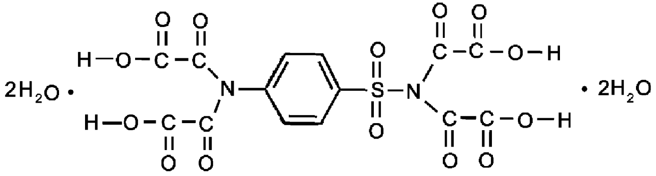
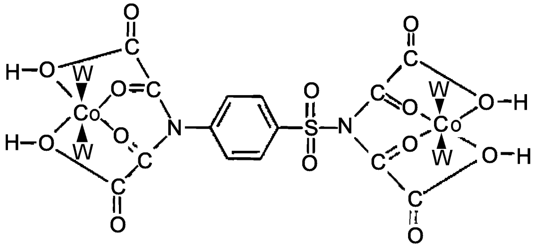
2.2 Preparation and Characterization of Tetraoxalylsulfanilamide and its Cobalt (II) Complex

The new organic chelating agent was prepared by condensation of Sulfanilamide (0.1 mol) and Oxalic acid (0.4 mol) in a Xylene medium, using Dean and Stark apparatus. The theoretical amount of water was removed to produce Tetraoxalylsulfanilamide, which has a melting point of 210 °C. After crystallization from distilled water the yield percentage was found to be 82.5%.

Cobalt (II) complex was prepared by adding 0.2 mol Cobalt (II) Chloride hexahydrate solution in 50 ml distilled water to 0.1 mol of organic ligand (50 ml) and refluxing the solution for one hour. Some analytical data of the prepared ligand and its cobalt (II) complex are tabulated in Tab1e 1.

The ultraviolet-visible absorption spectrum of the prepared ligand were measured using Shimazu UV Spectroscopy M 1601 PC Spectrophotometer. The UV-spectrum of the organic ligand showed an absorption band at $\lambda_{\max} = 279$ nm, which could be attributed to $\pi - \pi^*$ transition (E_2-band) in benzene ring. Another absorption band appearing at $\lambda_{\max} = 210$ nm may be due to $\pi - \pi^*$ transition of carbonyl group ($C=O$).

TABLE 1 Some Analytical Data of the Ligand and its Cobalt (II) Complex

Compound No.	Molecular and structural formula	Color	Elemental analysis Cal./Found					Mol. weight cal./found	Acid value cal./found	$pK_1 - pK_4$
			C%	H%	N%	S%	Co%			
1	 $C_{14}H_{16}N_2SO_{18}$	White	31.67	3.01	5.26	6.01	–	532	421.8	1.86
			32.40	3.5	6.00	6.80	–	539	430.5	2.13
										6.92
										9.70
2	 $C_{14}H_{16}N_2SO_{18}Co_2$	Rose	26.00	1.86	4.30	4.90	18.20	–	–	–
			22.03	2.10	3.90	4.50	18.60	–	–	–

The low % of carbon is due to the metal carbide formation, W = water molecules.

The infrared measurements were carried out using Shimazu FTIR–430 Jasco Spectrophotometer. The IR–spectrum of organic ligand shows the characteristic bands at 838 and 1543 cm^{-1}, which may be attributed to the stretching vibration for the CH out of plane deformation of 1,4–disubstituted benzene ring and $C=C$ in aromatic system, respectively. The broad band at 1157 cm^{-1} and the sharp band at 1399 cm^{-1} could be attributed to the symmetric and asymmetric stretching vibrations of $-SO_2-N$ group, respectively. The sharp band at 1683 cm^{-1} is due to the stretching vibrations of carbonyl group in carboxylic acids. The two sharp bands at 1594 and 1747 cm^{-1} could be attributed to the carbonyl group present in the oxalyl group moiety. A broad band at 3226 cm^{-1} could be attributed to the stretching vibration of the hydrogen bonded OH group in carboxylic acid. (c.f. Tab1e 2).

The IR-spectrum of Cobalt (II) complex shows a sharp band at 493 cm^{-1}, which is attributed to Co – O stretching vibration. Other IR–absorption bands in the region between 400–1014 cm^{-1} appear in case of the prepared ligand and its Cobalt (II) complex. The sharp split band at 1316 and 1360 cm^{-1} could be attributed to the stretching vibration of C–N group and asymmetric stretching vibration of $-SO_2-N$ group respectively. The bands in the region 1750–1500 cm^{-1} in case of the prepared ligand appear as one broad band at 1617 cm^{-1} in case of complex due to the coordination of the carboxylic and carbonyl group with Cobalt (II). The broad band at 3366 cm^{-1} is attributed to hydrogen bonded OH group of coordinated water molecules [15]. Other infrared absorption bands and their assignments are tabulated in Tab1e 2.

The ^{1}H-NMR measurements were carried out using Varian EM 360 L, 60 MHz NMR Spectrometer. The proton signals of the organic ligand have been recorded in dimethylsulfoxide with tetramethylsilane as internal reference. The ^{1}H-NMR spectrum shows the following characteristic signals:

1. The two singlet signals at $\delta = 2.5$ ppm and 3.5 ppm are due to solvent protons.
2. The singlet signal at $\delta = 7.2$ ppm may be due to the zwitter ion formation or water of crystallization proton.
3. The doublet-doublet signals at $\delta = 7.6$–7.9 ppm are due to the phenyl ring protons.
4. The singlet signal at $\delta = 11$ ppm is due to carboxylic acid protons.

Thermogravimetric analysis (TGA) of the ligand and Cobalt (II) complex were performed using a thermal analyzer Shimazu DT-30. The weight losses were measured for the ligand and Cobalt (II) complex

TABLE 2 IR-Absorption Band of Tetraoxalylsulfanilamide and its Cobalt (II) Complex and Their Assignment

Name of compound Wave number (cm^{-1})		
Ligand	Cobalt (II) complex	Assignment(15)
–	493	Co – O Stretching vibration
$688^{b,sp}$	589^{w}	C–N bending deformation
$733^{b,sp}$	748^{w}	Wagging deformation –SO_2–N–
838^{s}	826^{s}	Out-of-plane deformation for CH showing 1,4-disubstituted benzene ring.
908^{m}	915^{w}	
953^{vw}		Scissoring bending vibration for –SO_2–N- group
1014^{w}	1014^{w}	
1094^{m}		
1157^{b}	–	Symmetric stretching for –SO_2–N-group
1182^{sh}		
1246^{m}	–	Stretching vibration for C–O
1311^{b}	1316^{s}	Stretching vibration for C–N
1399^{s}	1360^{s}	Asymmetric stretching for –SO_2–N group
1545^{m}		Stretching vibration for C = C in benzene ring or C = O in carboxylic or carboxylate or for –CO–N–CO group
1493^{w}		
1594^{m}	1617^{b}	
1683^{s}		
$1747^{s,sp}$		
3040^{w}	30401^{w}	Symmetric stretching vibration for CH in aromatic
3226^{b}	–	Symmetric stretching for hydrogen bonded hydroxyl group in carboxylic acid.
–	3366^{w}	Strong hydrogen bonded OH group for water molecules.

from ambient up to 500 °C. The weight losses for the ligand and complex were calculated over a temperature range at which H_2O molecules were expelled. The number of water molecules of crystallization are four per one mole of the investigated ligand and the number of coordinated water in the complex are four per one mole of the complex as indicated by the percentage weight loss from TGA curve.

2.3 Preparation of Pure PMMA and Doped PMMA with Cobalt (II) Complex of Tetraoxalylsulfanilamide

The pure PMMA sample and PMMA-doped with Cobalt (II) complex were prepared by mixing the monometer with benzoyl peroxide as initiator (2.668 × 10^{-3} mol/L) in a soda glass tube (2.2 cm diameter and 30 cm length). The tubes were flushed with pure nitrogen gas and then sealed. The sealed tubes were placed in an automatically controlled water bath at 60 °C for several days. Finally, hard plastic samples were obtained.

2.4 Determination of the Viscosity Average Molecular Weights

The doped PMMA samples with organic ligand or its Cobalt (II) complex were separated from the dopant materials by dissolving in benzene, filtering and then the clear polymer solutions were precipitated in excess methanol and finally dried in an electric oven at 105 °C. The intrinsic viscosity (η) was obtained by the usual method of extrapolation. The viscosity average molecular weights M_v 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 [16].

2.5 Preparation of Polymer Thin Film Samples Doped with Organic Ligand

The films were prepared by a solvent casting technique. A flat glass plate provided with four leveling screws and water balance was used as a base for the glass dishes containing polymer solutions to ensure uniform film thickness. The appropriate weight of PMMA and dopant (organic ligand), material which gives the desired concentration of dopant (1, 3, 7, 10 and 15%) in PMMA, were dissolved in acetone /Benzene mixture (1:1 v/v) as a common solvent. The rate of solvent evaporation should not be too rapid and may be controlled by placing an inverted 1000 ml beaker over the casting dish and allowing 1 cm clearance to permit air circulation. The solvent was evaporated over a period of 24 h. A sharp micro spatula was used to score the film around its edges to detach it from the wall of the casting dish. The film was then covered with distilled water and after a few minutes it floated to the surface. The film was gently picked up and laid flat on a non-adhering surface such as a piece of filter paper. The filter paper and film were then placed in a vacuum oven to dry at 60 °C till constant weight. The measured thickness of the films have a high degree of homogeneity.

2.6 Gamma Irradiation of the Prepared PMMA Samples

The new irradiation facility Egypt's Mega-Gamma I, supplied as type J-6300 by atomic energy of Canada Ltd., at the National Center for Radiation Research and Technology, Cairo, has been furnished with a ^{60}Co source having an activity of 137,000 Ci at the time of the present measurement. The radiation doses (5, 15, 25, 35, 50, 75 and 100 KGy) were measured by radio chromic dye film and Perspex. The overall error in the dose measurement did not exceed ±4%.

2.7 Thin Layer Chromatography

TLC technique has been applied for characterization of poly (methylmethacrylate) (PMMA) samples before and after irradiation with gamma rays. The TLC experiments were carried out as previously mentioned by Sayyah et al [16]. The spot area measurements was carried out using aluminum foil weighing technique [17].

3. RESULTS AND DISCUSSION

3.1 Effect of the Complex Concentration on the Viscosity Average Molecular Weight of PMMA Samples

Cobalt (II) complex of Tetraoxalylsulfanilamide was prepared and purified as mentioned in the experimental section. The Cobalt complex and methylmethacrylate (MMA) were mixed in different weight percentage of the Cobalt complex based on MMA-monomer weight in soda glass tubes (2.2 cm diameter and 30 cm length) containing 2.688×10^{-3} mol/L benzoyl peroxide.

The tubes were flushed with pure nitrogen gas, then scaled. The sealed tubes were placed in an automatically controlled water bath at 60°C for several hours. When the viscosity of the polymers in monometer solution increased, stirring of the contents was necessary to make the complex homogeneously suspended in the polymer matrix.

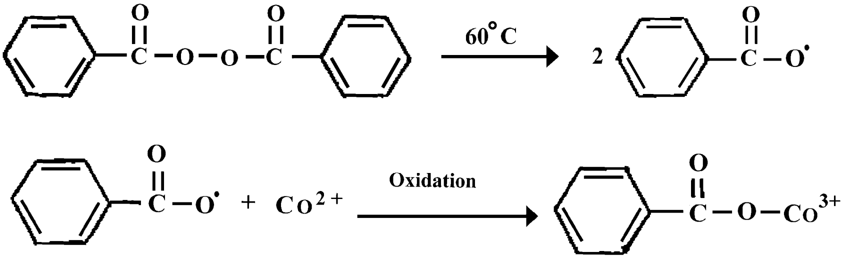
The tubes were flushed again with nitrogen gas and resealed, then the reaction was continued at 60 °C till the polymer complex composite sample solidified. Finally, hard, pink, plastic samples were obtained, cut into discs of 0.2 cm thickness and polished. Six samples were prepared under the above mentioned conditions, which contain 1, 3, 5, 7, 10 and 15% by weight of the Cobalt (II) complex, respectively. A standard sample (pure PMMA) was prepared under the same condition without addition of Cobalt (II) complex.

A small piece of each polymer sample (0.5 g) was dissolved in benzene (thiophene free) at room temperature. After the complete dissolution of the polymer sample in benzene, the solution was filtered to remove the inorganic Cobalt (II) complex. The solution was poured into a glass Petri dish of 5 cm diameter to obtain a thin film of pure PMMA sample. The viscosity measurements were carried out for each sample.

In order to show the effect of Cobalt (II) complex concentration on the molecular weight of the obtained PMMA during polymerization, a relationship was graphically drawn between Cobalt (II) complex weight percentage and the M_v-values (Figure 1).

From this relationship, it is clear that the viscosity average molecular weight of the PMMA samples increases up to 3%, then decreases up to 15%, which means that the reaction is inhibited by the presence of Cobalt (II) complex up to 3% in the reaction medium.

The increase in the molecular weight of the PMMA with increasing Co^{2+} complex concentration may be explained by the presence of Cobalt (II) in the reaction medium which attract the free radicals obtained from the initiator as follows:



The above mentioned equation leads to a decrease in the effective concentration of the free radicals up to 3% of the Cobalt (II) complex and subsequently leads to an increase in the viscosity average molecular weight of the prepared PMMA samples. The presence of Cobalt (II) complex in a concentration higher than 3% leads to a decrease in the viscosity average molecular weight, which may be explained by the loss of the coordinated water molecules to the reaction medium and these water molecules act as transfer agent in the polymerization reaction, leading to a decrease in the viscosity average molecular weight. The above discussion is based on the experimental observations during polymerization, where the color of the complex changes from pale pink to blue at the beginning of the polymerization reaction, then turns to pink at the end of the reaction.

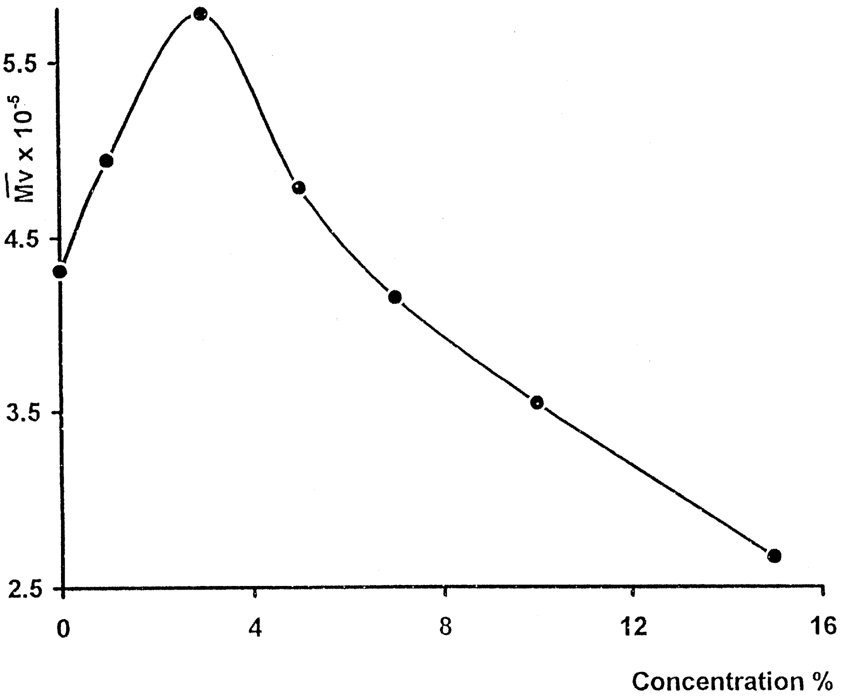


FIGURE 1 Relation between viscosity average molecular weight and complex concentration during polymerization.

3.2 Effect of Gamma Rays upon the Viscosity Average Molecular Weight of Pure PMMA Samples and Samples Containing Ligand or its Cobalt (II) Complex

The pure PMMA sample (without additives), PMMA ligand and PMMA Cobalt (II) complex composite samples were irradiated with gamma rays for different exposure doses (5, 15, 25, 35, 50, 75 and 100 KGy). The intrinsic viscosity $[\eta]$ for each polymer sample was obtained by the usual method of extrapolation [18].

The viscosity average molecular weight M_V for each sample before and after different irradiation doses was calculated. It was found that the viscosity average molecular weight of the PMMA samples decreases with increasing irradiation dose in all cases. It was also noticed that the area under the curves of the relation between M_V and irradiation doses are different for each sample, according to the additives concentrations. Therefore, these areas were calculated with the Microsoft Excel™ computer program.

A graphic representation between the area under the M_v vs dose curves and the concentrations of the organic ligand or its Cobalt (II) complex is shown in Figure 2. The highest values of the area are 23.815 and 19.855 cm^2 for the organic ligand and its Cobalt (II) complex, respectively, when 3% of ligand or its Cobalt (II) complex was used. The change in the obtained average molecular weight (dM_v) relative to the original viscosity average molecular weight M_v (i.e. dM_v/M_v) was found to increase with increasing irradiation does in a linear way, but with different slopes depending on the additive type and concentration. The slopes of the obtained linear relationship's between dM_v/M_v vs. exposure dose of gamma rays were calculated for each sample and the relations between the slope values and the concentration of additives are graphically represented in Figure 3, from which it is clear that the slope of the straight line has its minimum value at 3% concentration for both cases (i.e., in the case of ligand and Cobalt (II) complex). The obtained data are in accordance with that obtained from the area under the curve (c.f. Figure 2), which may be considered as an indication of the extent of degradation.

From the above mentioned data, it is clear that the molecular weights of the PMMA samples decrease with increasing irradiation

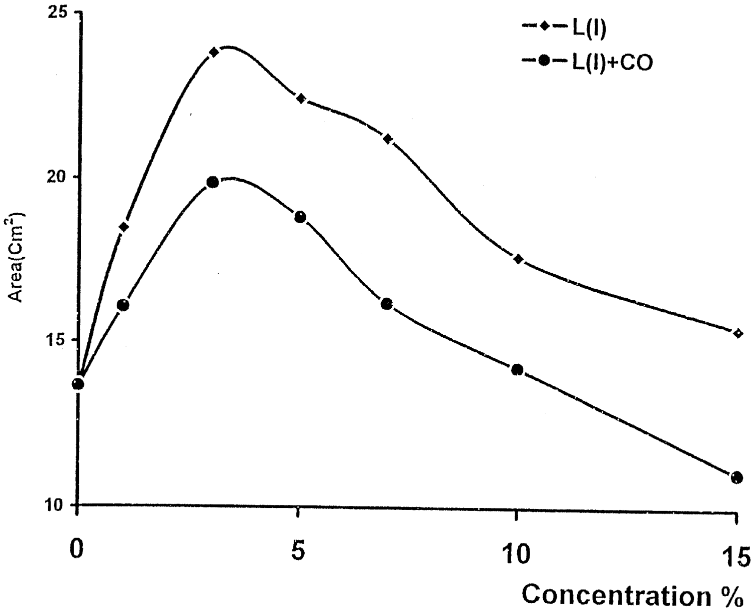


FIGURE 2 Relation between area under the curve and the concentration of the additives during radiolysis.

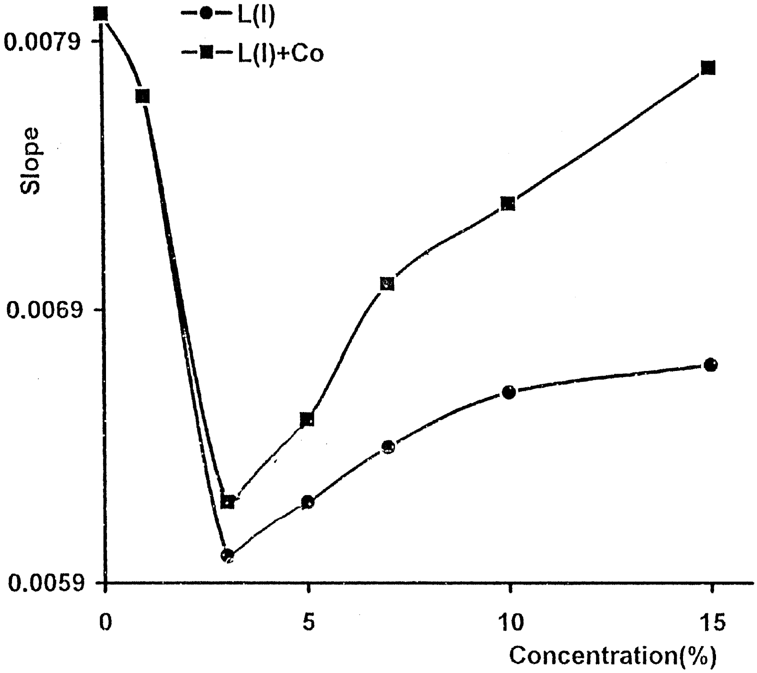


FIGURE 3 The slope of the relation between dM_v/M_v vs. concentration of additives.

dose. But, if $(1/M_v)$ is plotted against exposure dose, the $(1/M_v)$ values increase in a linear manner with increasing irradiation dose. The slope of the straight lines in the above relation are the radiation chemical yields for main-chain scission, $G_{(scission)}$. The degradation of PMMA by gamma rays gives a G_s value of about 2 (calculated by using M_n) when the irradiation was in air and in the absence of any additives [19].

A graphic representation of the relationship between $(1/M_v)$ and irradiation dose in each case is given in Figure 4 and the straight line was adjusted between the points by means of a computer program (Excel Fitting). The slope of each relation was calculated to obtain the G_s – values. The relation between G_s – values and the concentration of ligand or its Cobalt (II) complex in the polymer samples is represented in Figure 5, from which it is clear that the chemical yield for the main chain scission has its lowest value at 3% of the prepared ligand or its Cobalt (II) complex in the polymer matrix, but the G_s – values have lower values in the case of the ligand than in the case of the Cobalt (II) complex. This means that the ligand has a more protective effect on PMMA samples against gamma rays than its Cobalt (II) complex.

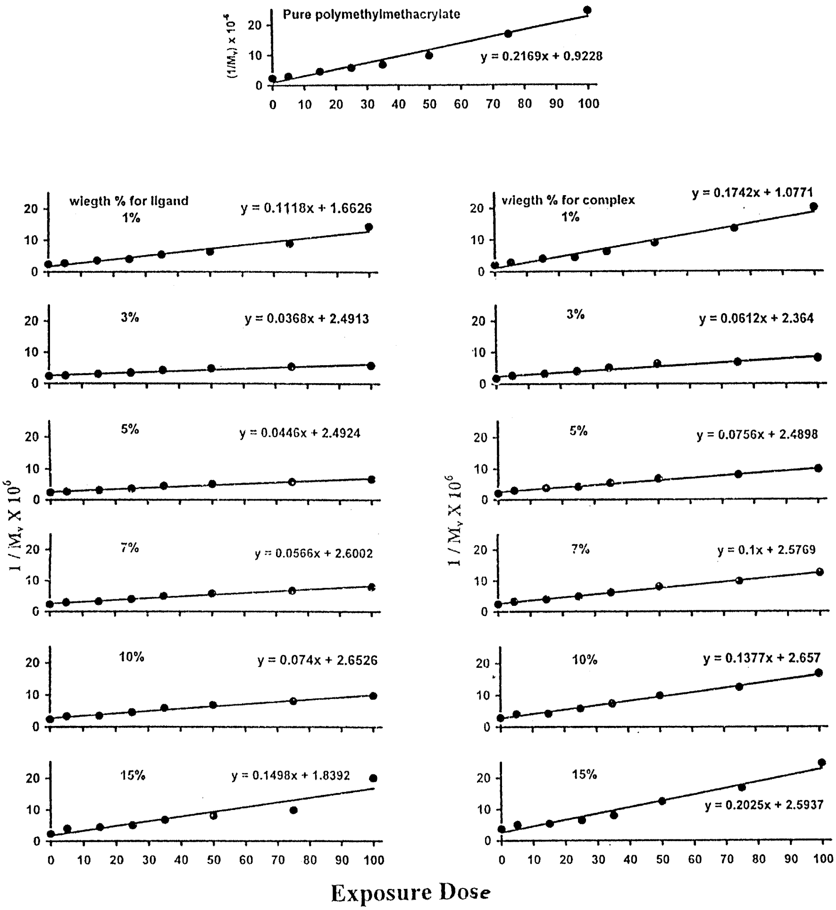


FIGURE 4 ($1/M_v$) vs. exposure dose.

In other words, the Tetraoxalylsulfanilamide compound and its Cobalt (II) complex have a protective effect on the PMMA samples, especially at 3% concentration. This protective efficiency could be attributed to the presence of sulfur [20]. in the organic ligand and its Cobalt (II) complex.

3.3 Thin Layer Chromatographic Analysis

Thin layer chromatographic analysis (TLC) is a good and rapid technique for characterization of samples, especially in determination

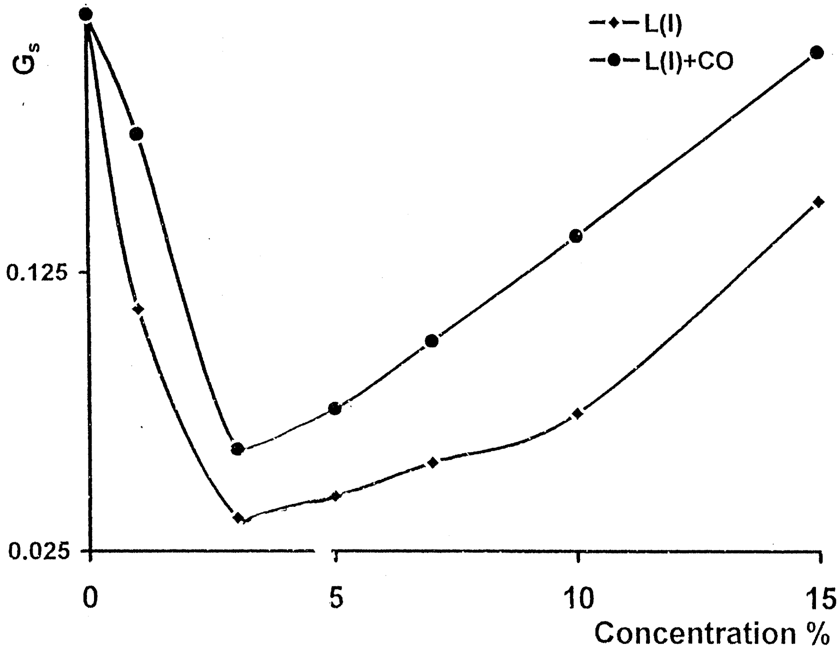


FIGURE 5 Gs vs. concentration of additives.

of molecular weight, and gives an idea about the polydispersity of the obtained polymer samples [21–24]. The separation of different PMMA samples on thin layer chromatographic plates was investigated after each irradiation dose. From the chromatograms obtained after development in a normal saturation system at 25 °C by using a binary mixture of benzene and methanol (1:1.5 v/v), the R_f-values and the spot area values are calculated. The relations between the R_f or spot area values and exposure dose in absence and presence of the organic ligand or its Cobalt complex are represented in Figure 6.

From Figure 6 it is clear that the R_f-values increase with increasing exposure dose, which confirms the obtained viscosity average molecular weight data. The relation between the spot area of the developed samples and the exposure dose. (c.f. Figure 6b) shows an increase of the spot area with increasing exposure dose in all cases, (i.e., in absence and presence of additives). This means that the polydispersity of PMMA samples increases with increasing irradiation dose.

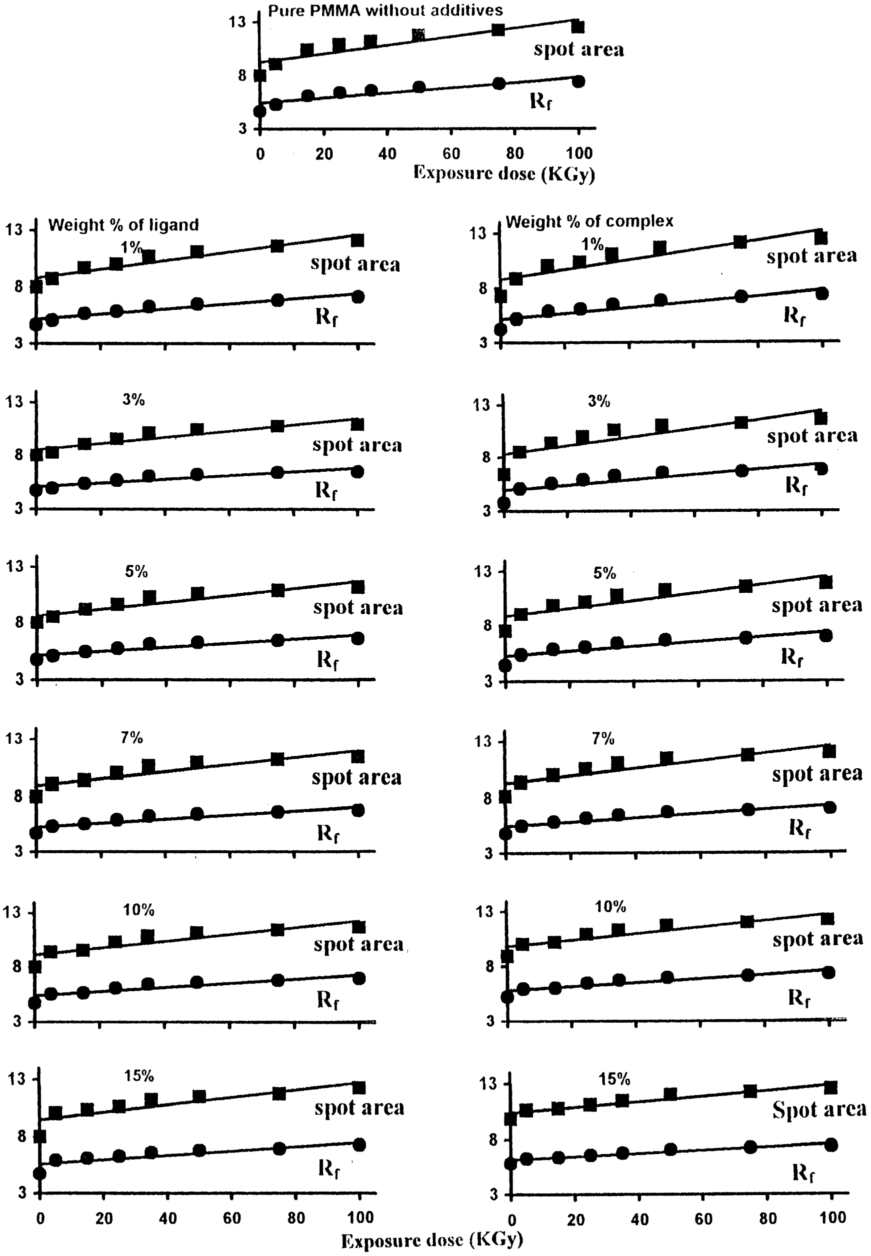


FIGURE 6 R_f and spot area values vs. exposure dose (KGy).

4. CONCLUSIONS

The present study leads to the following conclusions:

1. The prepared ligand and its Cobalt (II) complex have a protective effect on PMMA against gamma rays.
2. The organic ligand is more protective than its Cobalt (II) complex.
3. The best protective concentration of the ligand or its Cobalt (II) complex is 3% by weight of the polymer matrix.
4. Both R_f values and polydispersity of PMMA samples increase with increasing irradiation dose in all cases (i.e., absence and presence of additives).
5. Further spectroscopic investigations must be done for elucidation of the protection mechanism.

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