Infrared Spectroscopic Studies of Poly(methyl methacrylate) Doped with a New Sulfur-Containing Ligand and Its Cobalt(II) Complex during γ-Radiolysis

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ABSTRACT: Infrared (IR) spectroscopy studies were performed for poly(methyl methacrylate) (PMMA) samples doped with an organic ligand or its cobalt(II) complex after the extraction of the dopant during γ-radiolysis. There were no drastic changes in the IR absorption band position, but noticeable changes in the intensities were found. The relative transmission of IR absorption bands, such as those at 750, 840, 1065, and 1388 cm^{-1}, were measured according to the transmission of the carbonyl group band at 1717 cm^{-1}. The degradation and recombination mechanism of different groups in the polymeric chain or backbone during radiolysis could be explained by the behavior of the relative transmission data for each group with increasing exposure dose. The tacticity of the PMMA samples was unchanged during radiolysis, and they were found to be syndiotactic. This was confirmed by the IR J values for different PMMA samples before and after irradiation. The protection efficiency of the organic ligand and its cobalt(II) complex was also investigated, and it was found that the organic ligand was more protective than the cobalt(II) complex for PMMA samples against γ-rays. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1937–1950, 2004

Key words: infrared spectroscopy; calculations; NMR; radiation

INTRODUCTION

The infrared (IR) absorption of poly(methyl methacrylate) (PMMA) has been the subject of several investigations.[1–5] The object of most of these investigations was to describe the dependence of the IR absorption characteristics in terms of the stereoregular nature of the polymer chain. Sayyah et al.[6] studied the IR spectra of PMMA samples doped with some luminescent materials. They found that there were no drastic changes in the position and intensity of the IR absorption bands, except in the case of β-naphthol. From this, they concluded that there was no interaction between the dopant and PMMA with most of the investigated materials, whereas with β-naphthol, hydrogen bonding between adjacent molecules in the polymer matrix was observed.

The radiolysis of PMMA has been studied more extensively than that of any other polymer. This can be probably explained by the fact that irradiation produces striking changes in PMMA that can be detected by simple visual examination. Color changes are particularly apparent and easy to follow spectroscopically because of the perfect optical clarity of the polymer. After fairly low radiation doses, PMMA acquires a faint yellow color. This color is already noticeable after 3–5 Mrad.[7,8]
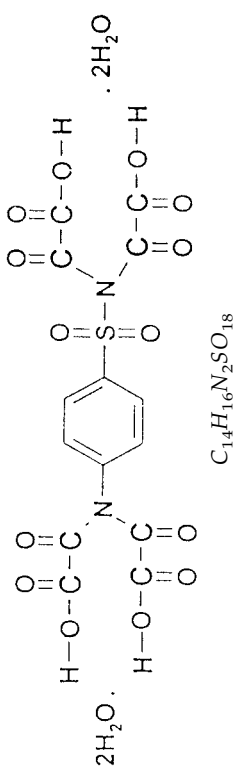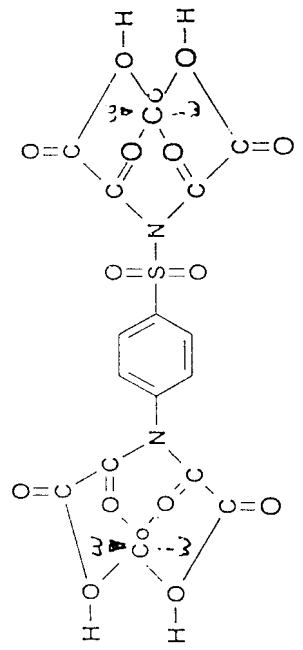
The effect of γ-radiation on the IR absorption bands of polymers has been not adequately studied. Alexander et al.[9] observed that new absorption bands appeared at 888 cm^{-1} in polyisobutylene subjected to heavy doses of reactor radiation. These bands were attributed to vinylidene double bonds. A more detailed analysis of the changes in the IR absorption of γ-irradiated polyisobutylene was presented by Slovokhotova et al.[10]

γ-Degradation and recombination processes, which can occur during the radiolysis of some methyl methacrylate (MMA)/iron acrylate copolymers and MMA/acrylonitrile iron acrylate, can be explained by IR measurements during radiolysis.[11] The degradation and recombination processes, which can occur during γ-radiolysis, have been established by electrical property measurements of PMMA/iron acrylate/manganese acrylate terpolymer samples.[12]

The protection of PMMA samples against γ-rays has been investigated in the absence and presence of N,N-dioxalyl-p-aminobenzene sulfonic acid or its iron (II) complex[13] and in the presence of tetraoxaylsulfanil-amide or its cobalt(II) complex.[14] The degradation and recombination processes, which can occur during

TABLE I
Some Analytical Data of the Ligand and Its Cobalt(II) Complex

| Compound | Molecular and structural formula | Color | Elemental analysis calcd/found | | | | Molecular weight calcd/found | Acid value calcd/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	—	—	—

W = water molecules. The low percentage of carbon was due to metal carbide formation.
PK_1 and pK_4 are equal to $-\log K_1$ and $-\log K_4$ where K_1 and K_4 are the dissociation constant for different protons present in the polybasic acidic ligand.

γ-radiolysis, have been established by viscosity-average molecular weights and thin-layer chromatography measurements of PMMA samples. There is maximum protection against γ-rays when 7% of the organic ligand or its iron (II) complex is used in the polymer matrix; this has also been confirmed by the radiation chemical yield for main-chain scission.

In this study, we investigated the changes in the band position and intensity of the IR spectra of PMMA samples doped with a sulfur-containing organic ligand and its cobalt(II) complex during γ-radiolysis after extraction of the dopant materials. Also, the mechanisms of degradation, recombination, and protection of PMMA were studied.

EXPERIMENTAL

Materials

The MMA monomer was a product of Merck–Schucharedt (Germany) (99% yield) and was stabilized with 100 ppm hydroquinone. It was purified as described in ref. 15. All chemicals used in this work were of the purest grade available. A Dean–Stark apparatus was used for the preparation of the sulfur-containing organic ligand, as previously described by Sabbah et al.[15] A cobalt complex of the prepared ligand was prepared as described by Sayyah et al.[14] The structures and some analytical data of the prepared ligand and its cobalt(II) complex are given in Table I.

Instrumentation

The IR spectra were obtained with a Shimazu FTIR 430 Jasco spectrophotometer (Japan) under conditions yielding the maximum resolution. All the IR measurements were carried out at room temperature. The spectra of pure and doped PMMA films after irradiation with different exposure doses and the extraction of the dopant material were measured against air for comparison. The films were adjusted to a constant thickness (100 μm), and the concentrations of the dopant materials were 1, 3, 5, 7, 10, and 15% with respect to the weight of PMMA. Carbon, hydrogen, sulfur, and cobalt were determined for the prepared organic ligand and its cobalt(II) complex in the microanalytical laboratory at Cairo University.

γ-irradiation of the PMMA films

Egypt's Mega gamma 1 (type J-3600, Canada, Ltd.) for atomic energy, located at the National Center for Radiation Research and Technology (Cairo, Egypt), was used. A ^{60}Co source, with an activity of 137,000 Ci, was used for the γ-irradiation of the PMMA films. The irradiation doses (5, 15, 25, 35, 50, 75, and 100 kGy) were measured with radiochlormic dye film on Per-

spex. The dose rate was 2.76 kGy/h. The overall error in the dose measurements did not exceed ±4%.

Preparation of pure PMMA and PMMA doped with the cobalt(II) complex

The pure PMMA samples and PMMA doped with the cobalt(II) complex were prepared by the mixing of the monomer with benzoyl peroxide as an initiator (2.688 $\times 10^{-3}$ mol/L) and the calculated amount of the complex in a soda glass tube (2.2 cm in diameter and 30 cm long). The tubes were flushed with pure nitrogen gas and then sealed. The sealed tubes were put into an automatically controlled water bath at 60°C for several days. Finally, hard rose plastic and colorless transpar-
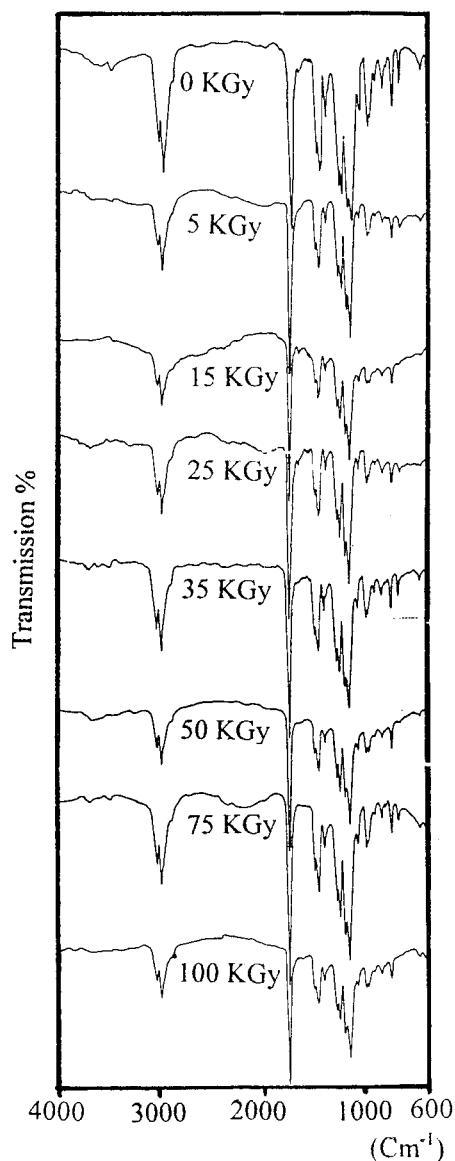
Figure 1 IR spectra of PMMA samples irradiated with different exposure doses.
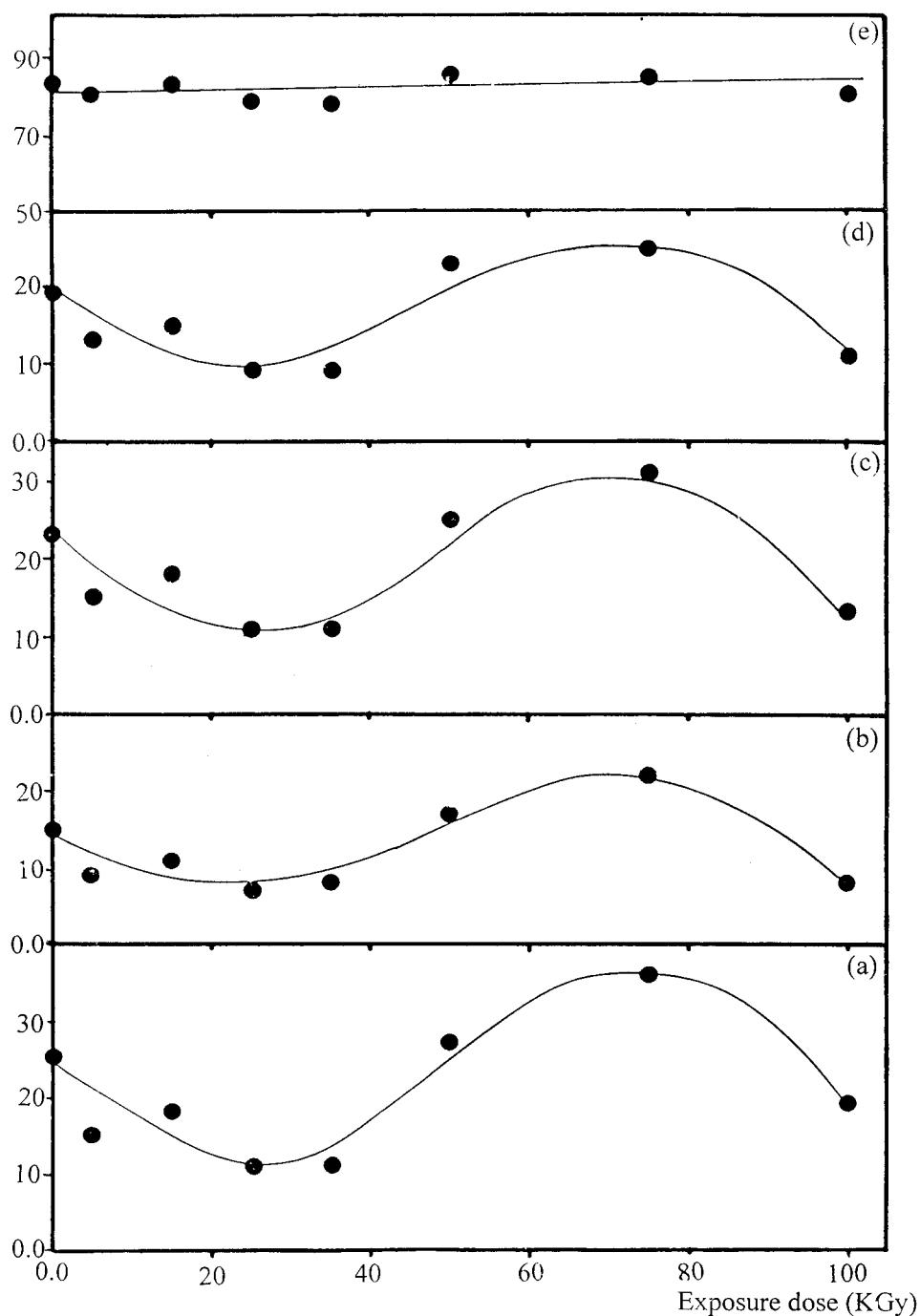
Figure 2   Relationship between the band intensity and the exposure dose for bands at (a) 750, (b) 840, (c) 1065, (d) 1388, and (e) 1717 cm^{-1} for pure PMMA.

ent samples were obtained for PMMA–cobalt(II) composite and pure PMMA, respectively.

Preparation of PMMA thin-film samples (doped with an organic ligand)

The films were prepared by a solvent-casting technique described in ref. 6.

Calculation of the *J* values*

The IR spectra of the PMMA films, which were about 100 μm thick in the range of 2000–750 cm^{-1} (5–15.5 μm), were recorded with a Shimazu FTIR 430 Jasco

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*J value is a relative absorbance value at the mentioned wave numbers in case of PMMA (c.f. equation J, = 179 (A$_{1065}$/A$_{990}$) + 27).

spectrophotometer under standard scanning conditions. A 100% transmission line was drawn between 1950 and 700 cm^{-1} (5.4–14.5 μm), and the absorbances at 1483 (6.75 μm), 1388 (7.2 μm), 1065 (9.3 μm), and 990 cm^{-1} (10.1 μm) were calculated with the baseline method.[16]

Two subparameters, J_1 and J_2, were calculated from this absorbance as follows:[17]

$$J_1 = 179[A_{1065}/A_{990}] + 27$$

$$J_2 = 81.4[A_{1483}/A_{1388}] - 43$$

The J values are the arithmetic averages of J_1 and J_2.

RESULTS AND DISCUSSION

IR spectrum of pure PMMA

The IR spectrum of PMMA is represented in Figure 1. It shows the following characteristic bands:

1. A sharp band at 750 cm^{-1} for α-CH$_2$ coupled to the C—C skeletal stretching vibration.
2. Two medium absorption bands at 984 and 950 cm^{-1} for the stretching vibration of C—O—C coupled to the rocking vibration of CH$_3$—O and the rocking vibration of α-CH$_3$, respectively.
3. Split band at 1260 and 1220 cm^{-1} for the stretching vibration of C—C—O coupled to the stretching vibration of C—O (skeletal) and internal CH deformation, respectively.

4. The observed band at 1488 cm^{-1} for the δ_a (α-CH$_2$) group is higher in intensity than the band at 1388 cm^{-1} for the δ_s (α-CH$_3$) group.
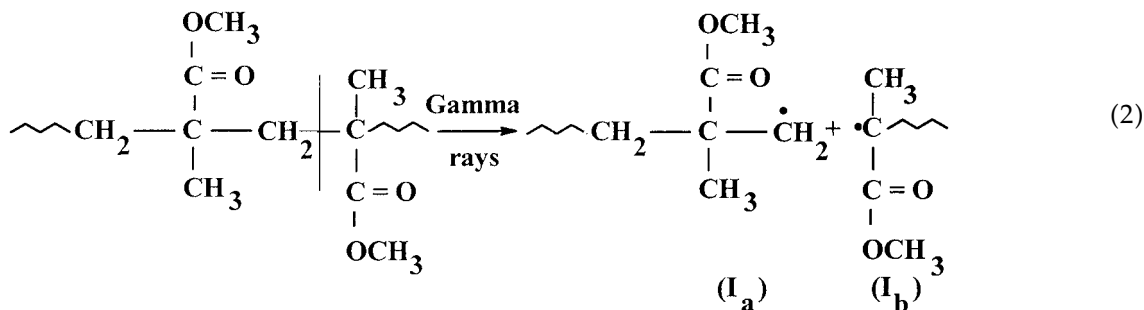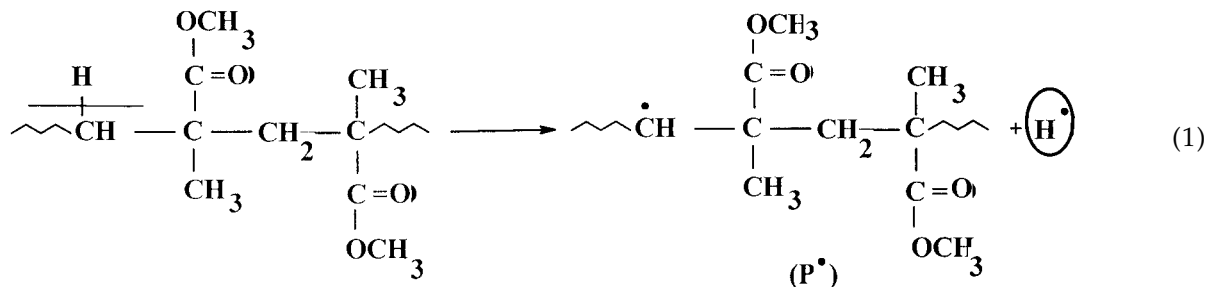
From these observations, it is clear that the investigated PMMA sample had a syndiotactic structure, and this agreed with the findings in the literature.[17]
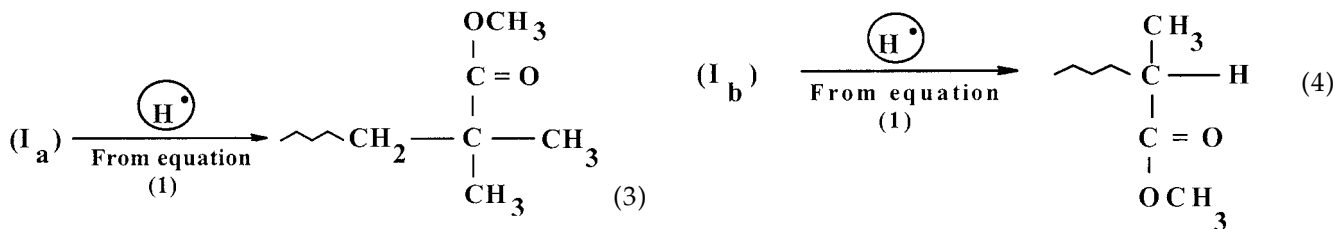
Effect of γ-irradiation on the IR absorption bands of pure PMMA

The IR spectra of pure PMMA before and after exposure to different γ-ray doses are shown in Figure 1. There were no drastic changes in the band positions, but some changes in the band intensities could be observed. The variation of the band intensities as the irradiation dose increased for absorption bands appearing at 750, 840, 1065, 1388, and 2950 cm^{-1} is graphically represented in Figure 2. The changes in the band intensities for each absorption band can be summarized as follows.

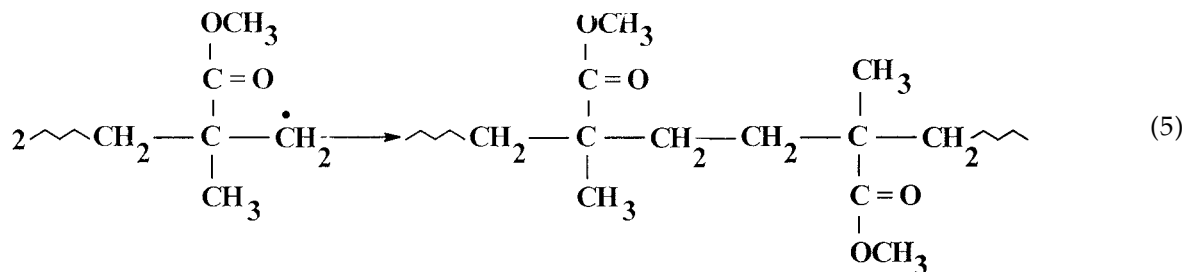First, for the band appearing at 750 cm^{-1}, which could be attributed to CH out-of-plane deformation in the CH$_2$ group, the band intensity decreased from 0 to 25 kGy, increased from 25 to 75 kGy, and finally decreased from 75 to 100 kGy.

The decrease in the band intensity from 0 to 25 kGy and from 75 to 100 kGy can be explained by eqs. (1)–(4). Equation (1) describes hydrogen abstraction from the polymeric chain, eq. (2) describes scission of the polymeric chain, and eqs. (3) and (4) describe the recombination of the formed polymeric radicals I$_a$ and I$_b$ with the hydrogen radical:

(1)

(2)

$$(I_a) \xrightarrow[\text{From equation} \ (1)]{\enclose{circle}{H^\bullet}} \sim\!\!\sim CH_2 - \underset{\underset{CH_3}{|}}{\overset{\overset{OCH_3}{|}}{\underset{|}{\overset{|}{C}}}} - CH_3 \quad (3)$$

$$(I_b) \xrightarrow[\text{From equation} \ (1)]{\enclose{circle}{H^\bullet}} \sim\!\!\sim \underset{\underset{OCH_3}{|}}{\overset{\overset{CH_3}{|}}{\underset{|}{\overset{|}{C}}}}\!\!-\!\!H \quad (4)$$
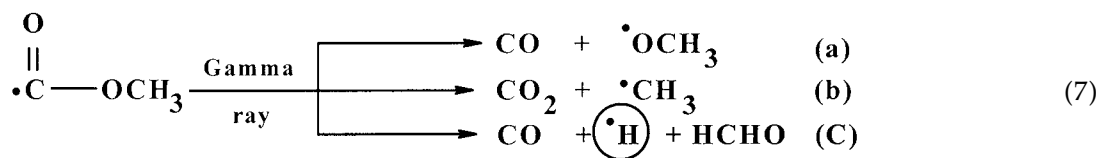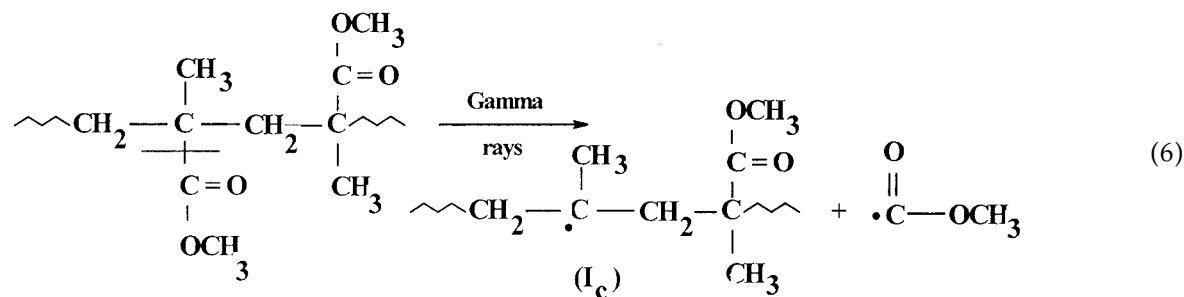
The increase in the band intensity from 25 to 75 kGy can be explained by the recombination process shown by the following equation:

$$2 \sim\!\!\sim CH_2 - \underset{\underset{CH_3}{|}}{\overset{\overset{OCH_3}{|}{\overset{|}{C=O}}}{\underset{|}{C}}} - \overset{\bullet}{C}H_2 \longrightarrow \sim\!\!\sim CH_2 - C - CH_2 - CH_2 - C - CH_2\sim\!\!\sim \quad (5)$$
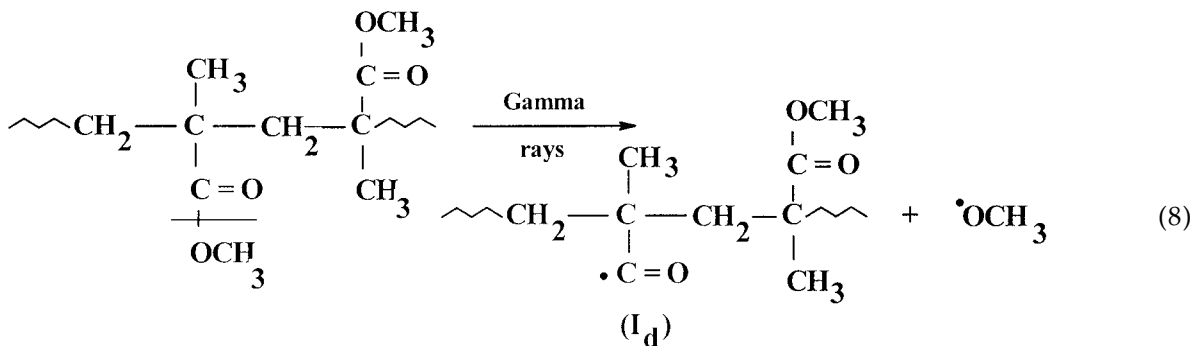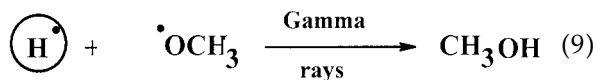
Second, for the band appearing at 840 cm^{-1}, which could be attributed to the deformation of C—O—C in the OCH$_3$ group, the band intensity decreased from 0 to 25 kGy and from 75 to 100 kGy. This behavior can be explained by the following equations:
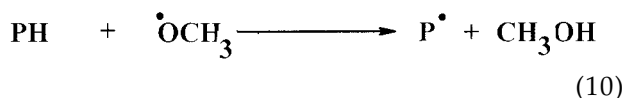
$$\sim\!\!\sim CH_2 - C - CH_2 - C \sim\!\!\sim \xrightarrow[\text{rays}]{\text{Gamma}} \sim\!\!\sim CH_2 - \overset{\bullet}{C} - CH_2 - C\sim\!\!\sim \ + \ \overset{O}{\overset{\|}{\bullet C}}\!\!-\!\!OCH_3 \quad (6)$$

$$(I_c)$$

$$\overset{O}{\overset{\|}{\bullet C}}\!\!-\!\!OCH_3 \xrightarrow[\text{ray}]{\text{Gamma}} \begin{cases} CO \ + \ {}^\bullet OCH_3 & (a) \\ CO_2 \ + \ {}^\bullet CH_3 & (b) \\ CO \ + \enclose{circle}{{}^\bullet H} + HCHO & (C) \end{cases} \quad (7)$$

or

$$\sim\!\!\sim CH_2 - C - CH_2 - C\sim\!\!\sim \xrightarrow[\text{rays}]{\text{Gamma}} \sim\!\!\sim CH_2 - C - CH_2 - C\sim\!\!\sim \ + \ {}^\bullet OCH_3 \quad (8)$$

$$(I_d)$$

$$\overset{\bullet}{(H)} + \overset{\bullet}{}OCH_3 \xrightarrow[\text{rays}]{\text{Gamma}} CH_3OH \quad (9)$$

or

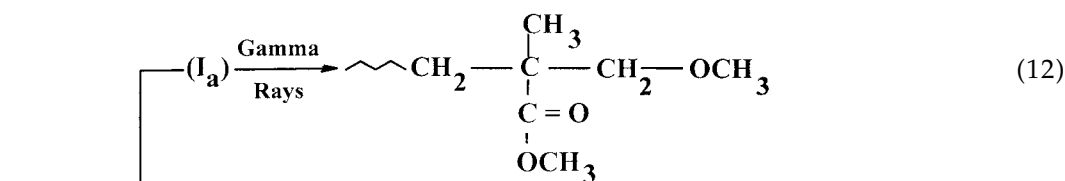$$PH + \overset{\bullet}{}OCH_3 \longrightarrow P^{\bullet} + CH_3OH \quad (10)$$
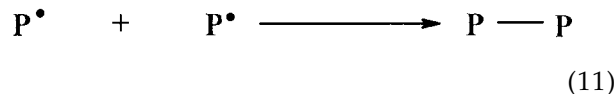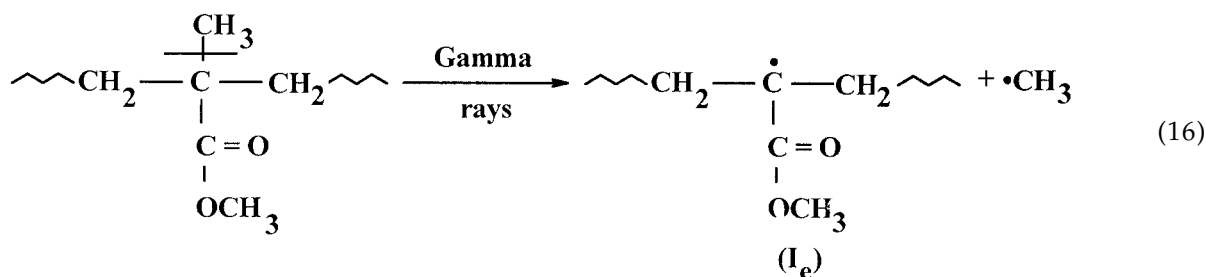
The increase in the band intensity from 25 to 75 kGy can be explained by the recombination process as follows:

$$P^{\bullet} + P^{\bullet} \longrightarrow P \text{—} P \quad (11)$$

$$\overset{\bullet}{}OCH_3 + \begin{cases} \text{—}(I_a)\xrightarrow[\text{Rays}]{\text{Gamma}} \sim\!\!\sim CH_2\text{—}\underset{\underset{OCH_3}{\overset{|}{\underset{|}{C=O}}}}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}\text{—}CH_2\text{—}OCH_3 \quad (12) \\[2em] \text{OR —}(I_b)\xrightarrow[\text{Rays}]{\text{Gamma}} H_3CO\text{—}\underset{\underset{OCH_3}{\overset{|}{\underset{|}{C=O}}}}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}\sim\!\!\sim \quad (13) \\[2em] \text{OR —}(I_c)\xrightarrow[\text{Rays}]{\text{Gamma}} \sim\!\!\sim CH_2\text{—}\underset{OCH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}\text{—}CH_2\text{—}\underset{CH_3}{\overset{\overset{OCH_3}{|}}{\overset{C=O}{\overset{|}{\underset{|}{C}}}}}\sim\!\!\sim \quad (14) \\[2em] \text{OR —}(I_d)\xrightarrow[\text{Rays}]{\text{Gamma}} \sim\!\!\sim CH_2\text{—}\underset{\underset{OCH_3}{\overset{|}{\underset{|}{C=O}}}}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}\text{—}CH_2\text{—}\underset{CH_3}{\overset{\overset{OCH_3}{|}}{\overset{C=O}{\overset{|}{\underset{|}{C}}}}}\sim\!\!\sim \quad (15) \end{cases}$$
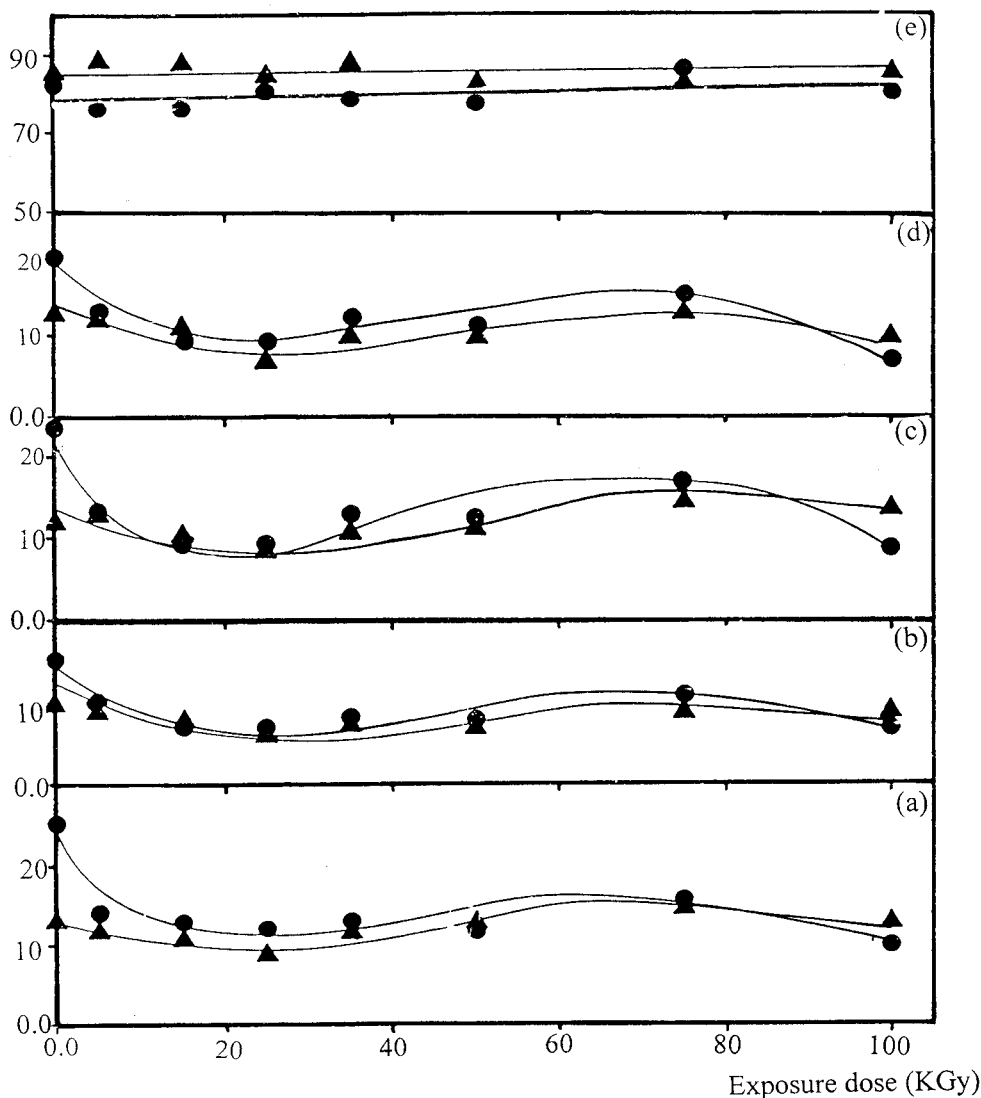
Third, for the band appearing at 1065 cm^{-1}, which could be attributed to the intramolecular interaction C—C skeletal mode, the intensity showed the same behavior as mentioned for the bands appearing at 750 and 840 cm^{-1}.
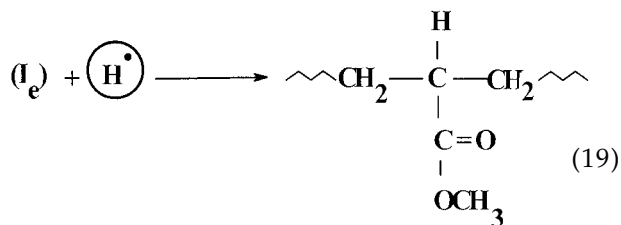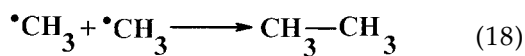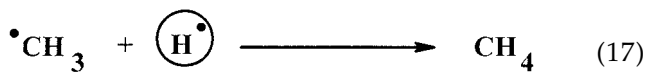
Fourth, for the band appearing at 1388 cm^{-1}, which could be attributed to δ_s (α-CH$_3$), the band intensity decreased from 0 to 25 kGy, increased from 25 to 75 kGy, and finally decreased from 75 to 100 kGy. The decrease in the band intensity from 0 to 25 kGy and from 75 to 100 kGy can be discussed on the basis of the following equations:

$$\sim\!\!\sim CH_2\text{—}\underset{\underset{OCH_3}{\overset{|}{\underset{|}{C=O}}}}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}\text{—}CH_2\sim\!\!\sim \xrightarrow[\text{rays}]{\text{Gamma}} \sim\!\!\sim CH_2\text{—}\underset{\underset{OCH_3}{\overset{|}{\underset{|}{C=O}}}}{\overset{\bullet}{\overset{|}{\underset{|}{C}}}}\text{—}CH_2\sim\!\!\sim + {}^{\bullet}CH_3 \quad (16)$$

$$(I_e)$$

Figure 3 Relationship between the band intensity and the exposure dose for bands at (a) 750, (b) 840, (c) 1065, (d) 1388, and (e) 1717 cm^{-1} for (●) an organic ligand and (▲) a cobalt(II) complex of the organic ligand.

$$\bullet CH_3 + \textcircled{H^\bullet} \longrightarrow CH_4 \quad (17)$$

$$\bullet CH_3 + \bullet CH_3 \longrightarrow CH_3—CH_3 \quad (18)$$

$$(I_e) + \textcircled{H^\bullet} \longrightarrow \wedge\wedge CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OCH_3}{|}}{\underset{\displaystyle C=O}{|}}}—CH_2 \wedge\wedge \quad (19)$$

The increase in the band intensity from 25 to 75 kGy can be attributed to the recombination process of CH$_3$

produced from eq. (7b) with any polymeric radicals (P$\cdot$), I$_a$, I$_b$, I$_c$, or I$_d$, or the recombination of the formed P$\cdot$ radicals with one another to form P—P.

Fifth, for the band appearing at 1717 cm^{-1}, which could be attributed to the carbonyl stretching vibration in the ester group, there were no drastic changes, and it remained approximately constant with an increase in the irradiation dose.

Effect of γ-irradiation on the IR absorption bands of PMMA/organic ligand and PMMA/cobalt complex composite samples

The IR spectra of the PMMA–tetraoxaloylsulfanilamide composite and PMMA cobalt complex composite samples before and after irradiation with γ-rays were measured. From the IR spectra, it is clear that

there was no drastic changes in the band positions, but the band intensities fluctuated between the maximum and minimum or remained approximately constant with an increase in the irradiation dose (cf. Fig. 3).

These observations do not provide enough data to determine the changes produced in the polymer samples during radiolysis. Therefore, the decomposition of different groups in PMMA had to be investigated by the calculation of the relative transmission of the carbonyl group at 1717 cm^{-1}, which had an approximately constant band intensity during radiolysis, and the transmission of bands at 1388, 1065, 840, and 750 cm^{-1}, which were attributed to α-CH$_3$, C—C, and C—O—C stretching vibrations and CH$_2$ out-of-plane deformation, respectively. The relationship between the relative transmissions T_{1717}/T_{750}, T_{1717}/T_{840}, T_{1717}/T_{1065}, and T_{1717}/T_{1388} and the dose quantity for pure PMMA samples are shown in Fig 4(a–d). T_{1717}/T_{750} increased as the irradiation dose increased up to 25 kGy, decreased as the irradiation dose increased up to 75 kGy, and increased once more as the irradiation dose increased from 75 to 100 kGy. This behavior [Fig. 4(a)] can be explained by eqs. (1)–(5).

The formed polymeric radical (I$_a$) could be recombined with other simple radicals such as the $\cdot$ CH$_3$ radical produced from eq. (7b) or (16). The variation in the relative transmission data for other groups can be explained, as mentioned previously, in the case of band intensity behavior with an increasing irradiation dose.

The scission in the polymeric chain could also take place in side groups, such as the ester group or α-methyl group, and this affected the relative transmissions of different groups present in the polymeric structure. The scission of the backbone chain was more predominant and had a marked effect in the case of pure PMMA. However, a lower effect was observed in the case of the presence of the prepared ligand or its cobalt(II) complex. In the case of PMMA/organic ligand composite samples, the IR data may throw some light on the protective effect of the organic ligand (3%), the ester group, and the main chains of the polymeric structure, which was confirmed by viscosity measurements.[14] In other words, sharp changes were observed in the relative transmission values of the carbonyl group band to different selected bands as the irradiation dose increased for 1 and 15% ligand concentrations. However, slight changes occurred for a 3% concentration (cf. Fig. 5).

For the PMMA/cobalt complex composite sample, the relative transmission data showed a maximum peak at 25 kGy and a minimum peak at 75 kGy for the degradation and recombination process, respectively. The relative transmission data showed the lowest values for 3 wt % cobalt complex in the PMMA matrix. In other words, the protection of different bonds in the polymeric main and side chain occurred at 3% (cf. Fig. 6). As shown by the aforemen-
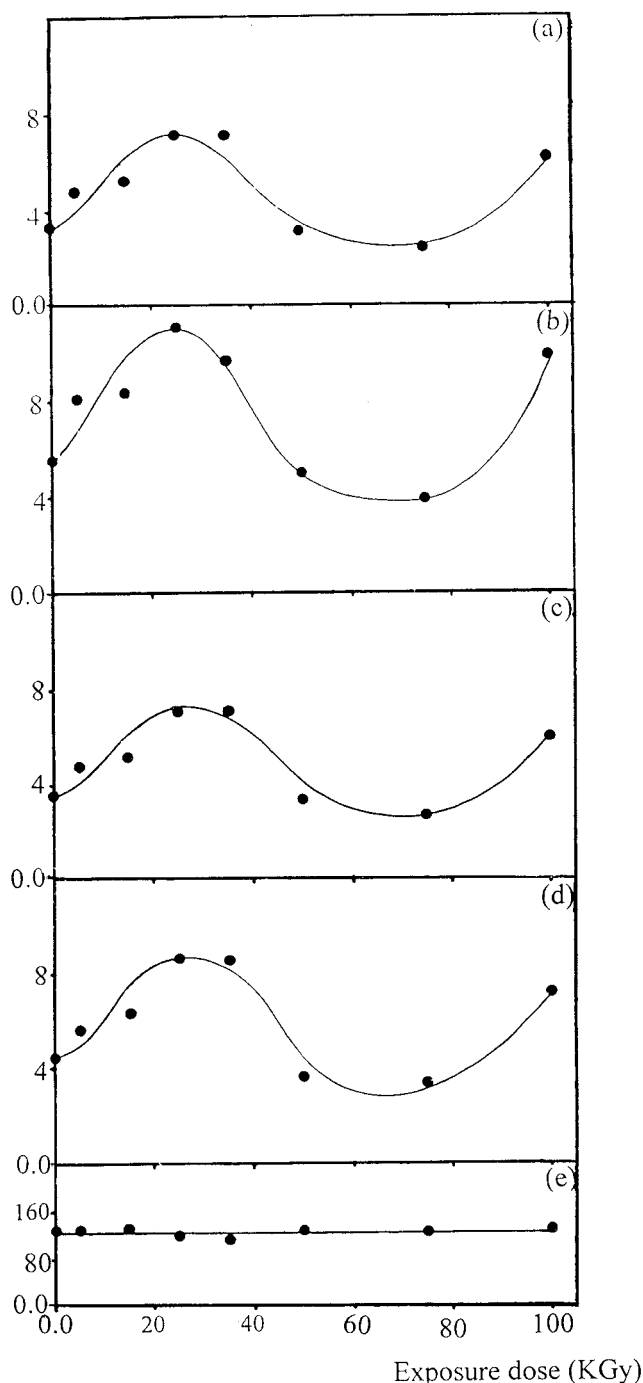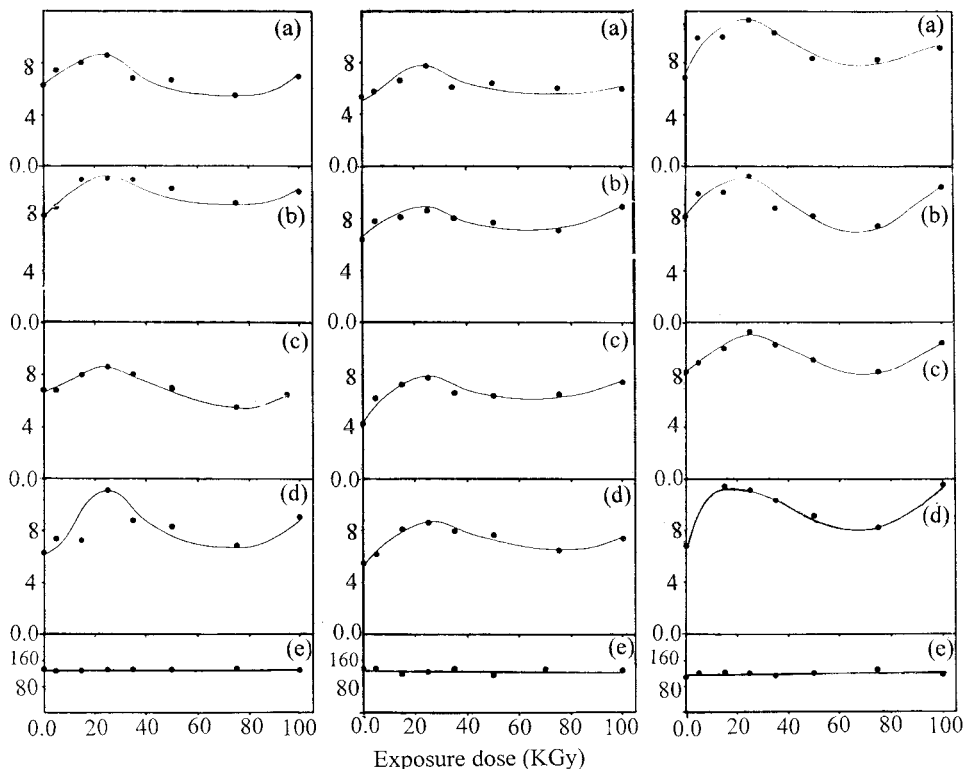

Figure 4 Relationship between the relative transmission [(a) T_{1717}/T_{750}, (b) T_{1717}/T_{840}, (c) T_{1717}/T_{1065}, (d) T_{1717}/T_{1388}, and (e) IR J values] and the exposure dose for pure PMMA.

tioned relations between the relative transmissions of the carbonyl group band and other groups present in the polymeric structure, the area under the curve could be divided into three zones. Two zones were for the degradation process between 0 and 25 kGy and 75 and 100 kGy. The third zone was an indication of the recombination process between 25 and 75 kGy. The area under the curve was calculated for each zone, and the data are summarized in Table II. For the calculation of the area under the curves, an aluminum foil sheet was cut into
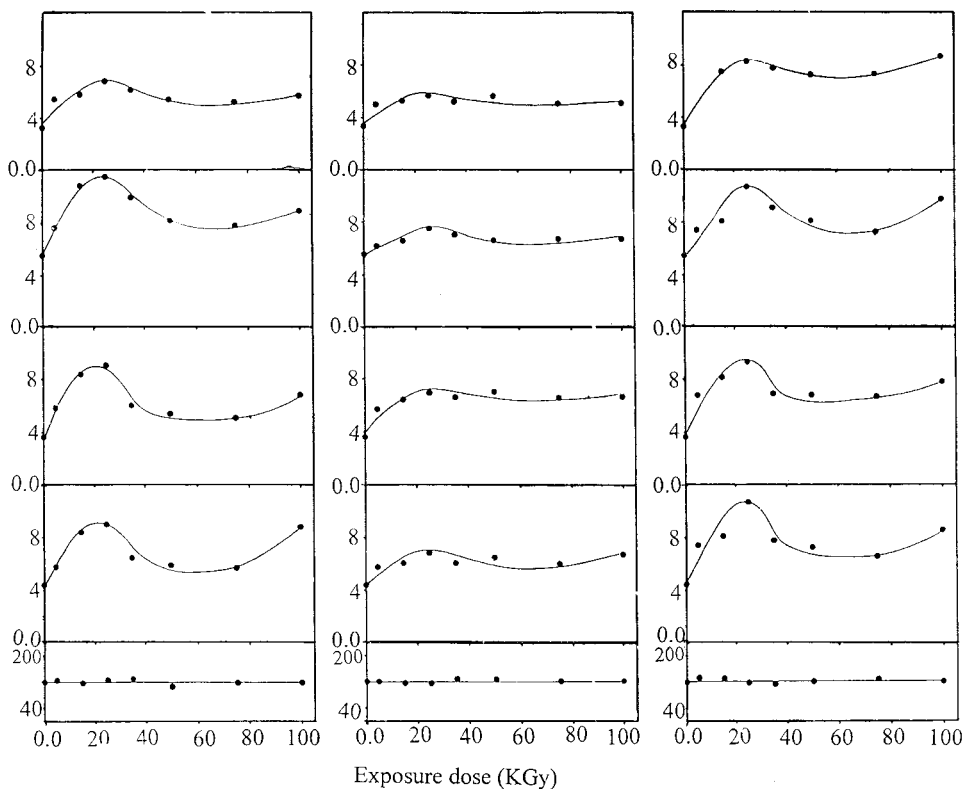
Figure 5 Relationship between the relative transmission [(a) T_{1717}/T_{750}, (b) T_{1717}/T_{840}, (c) T_{1717}/T_{1065}, (d) T_{1717}/T_{1388}, and (e) IR J values] and the exposure dose for an organic ligand.

Figure 6 Relationship between the relative transmission [(a) T_{1717}/T_{750}, (b) T_{1717}/T_{840}, (c) T_{1717}/T_{1065}, (d) T_{1717}/T_{1388}, and (e) IR J values] and the exposure dose for a cobalt(II) complex of an organic ligand.

TABLE II
Area Under the Curves for the Degradation and Recombination Processes
in the Absence and Presence of Different Additives

Area type corresponding to the different zones	Area (cm^2)						
		Additive type and concentration					
		PMMA with ligand			PMMA with complex		
	PMMA	1%	3%	15%	1%	3%	15%
Degradation	236.3	277	233.8	323.1	325.6	275.1	380.5
Recombination	205.8	265	246.4	312.5	306.6	279.8	363.5
Net area	31^D	12^D	12.6^R	10.6^D	19^D	4.7^R	17^D

D = degradation process; R = recombination process.

different pieces, which had different areas of 5–100 cm^2. Each aluminum foil piece was weighed, and a calibration curve between the weight (g) and foil piece area (cm^2) was plotted. A straight line was obtained with Microsoft Excel 5. The equation for this line was $Y = 126.14X + 0.165$, where Y is the area and X is the weight. Cutting the curves represented in Figures 5 and 6(a–d), we took into consideration the three zones. We weigh each aluminum foil piece, which was equal to a degradation zone, and a third piece, which was equal to recombination. By entering the weight data into a computer with the aforementioned equation, we obtained the area under the curve for each zone.

From Table II, it is clear that during the radiolysis of pure PMMA, PMMA/1% ligand, PMMA/15% ligand, PMMA/1% cobalt(II) complex, and PMMA/15% cobalt(II) complex, the degradation process predominated. The order of the degradation process in the different polymeric samples was as follows: pure PMMA > PMMA$_{1\% \text{ complex}}$ > PMMA$_{15\% \text{ complex}}$ > PMMA$_{1\% \text{ ligand}}$ > PMMA$_{15\% \text{ ligand}}$ > PMMA$_{3\% \text{ complex}}$ > PMMA$_{3\% \text{ ligand}}$. This means that the most protective additive was the organic ligand that had a 3% concentration in the polymeric matrix. The IR data were in good agreement with the data obtained by Sayyah et al.[14] from the viscosity-average molecular weights of different PMMA samples during γ-radiolysis.

Protection mechanism of the organic additives

The prepared ligand has one sulfur atom, one phenyl ring, and four carboxylic groups in its structure. The radicals that can form during γ-irradiation, are listed in Table III.

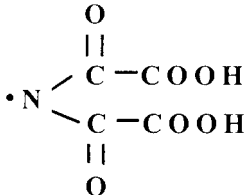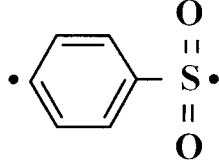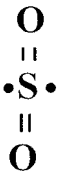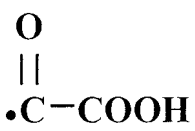Radiation protection by the prepared additives may be considered to operate through the following two alternative mechanisms:

1. Some form of energy transfer may take place from PMMA to the additive, with the polymer being chemically unaltered. The additive either may dissipate the energy without suffering any permanent chemical change or may itself be modified and cease to be active. In the latter case,

the protection will cease when all the additive has been destroyed or modified.
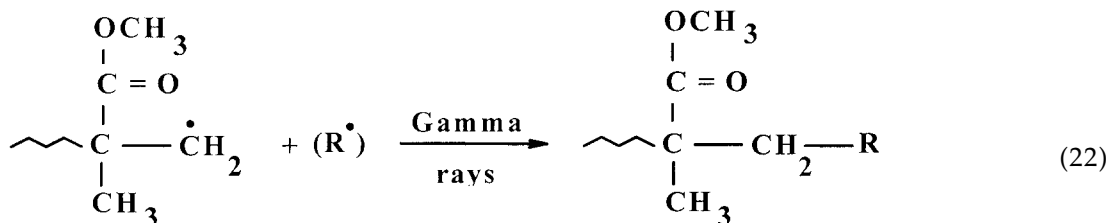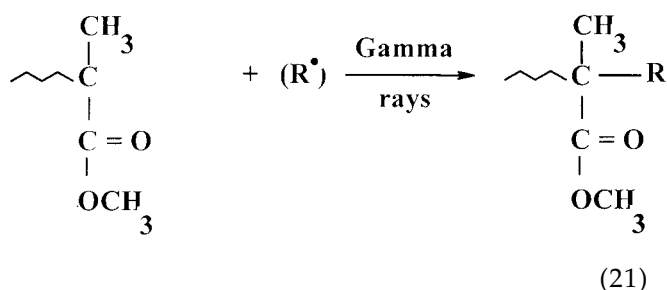
2. The additive may repair the damage caused by radiation. Here again, the additive may not itself suffer as a result. In PMMA polymers, the major reaction is the loss of a hydrogen atom leaving a polymer radical (P ·), as in eq. (16). Protection against further reactions can occur if the additive can itself furnish a hydrogen atom and remain a radical with new activity.

TABLE III.
Different Radicals that can Form During γ-Radiolysis

Radical type	Number of radicals
	2
	1
	1
	1
	4
	4

$$
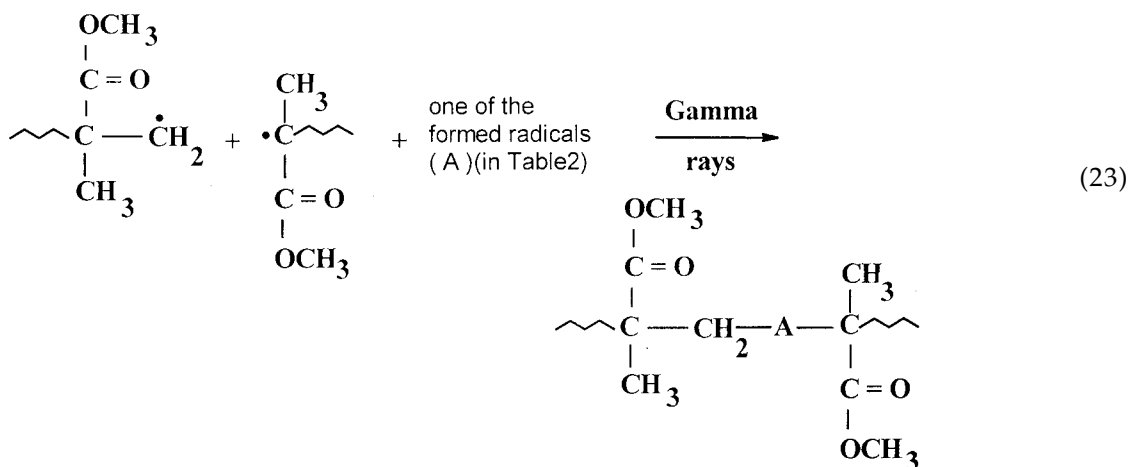\text{(structure)} + \underset{\text{Gamma rays}}{\overset{\text{}}{\longrightarrow}} \quad (20)
$$
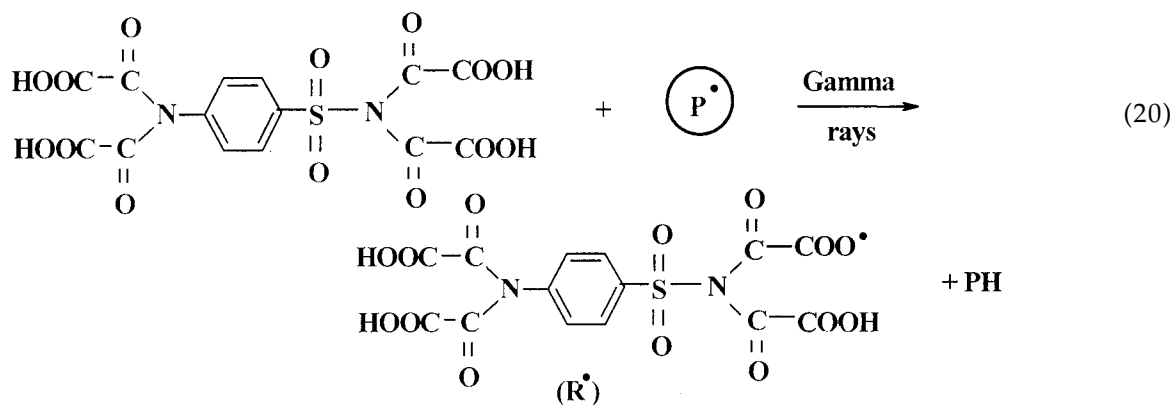
In the case of the degradation of PMMA by main-chain fracture, as shown in eq. (2), a protective additive molecule may combine with these radicals to form a stable side chain or less reactive radicals:

$$
\text{(structure)} + (R^\bullet) \xrightarrow[\text{rays}]{\text{Gamma}} \text{(structure)} \quad (21)
$$

$$
\text{(structure)} + (R^\bullet) \xrightarrow[\text{rays}]{\text{Gamma}} \text{(structure)} \quad (22)
$$

Any monoradical that can be formed through the γ-degradation of the organic ligand may take the place of R · in eqs. (21) and (22).

The protective additives may link the two polymer radicals together and thereby heal a radiation-induced fracture. This means that there will be no significant change in the average molecular weight. These radicals are the biradicals listed in Table III:
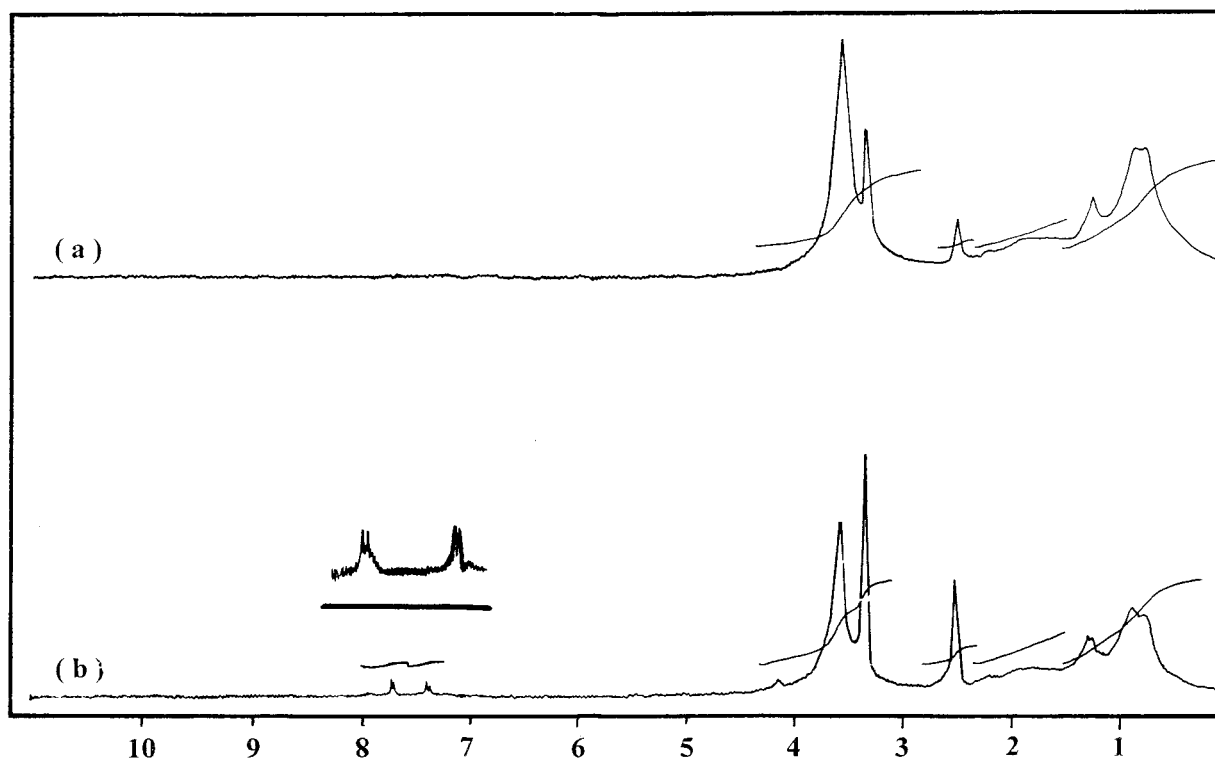
$$
\text{(structure)} + \text{•C} + \begin{array}{c}\text{one of the}\\\text{formed radicals}\\\text{(A)(in Table2)}\end{array} \xrightarrow[\text{rays}]{\text{Gamma}} \quad (23)
$$

Figure 7 ^{1}H-NMR spectra of (a) pure PMMA and (b) PMMA, after the extraction of an organic ligand (3%), that was irradiated as a composite with a γ-ray dose of 50 kGy.

The aforementioned mechanisms were confirmed by the appearance of absorption bands at 3200–3500 cm^{-1} for different groups combined with PMMA chains during radiolysis. Other absorption bands of these groups may be superimposed with the PMMA absorption bands. Also, the ^{1}H-NMR spectrum, given in Figure 7, shows two doublet signals in the region of $\delta = 7.3$–7.7 ppm, which indicate the presence of a benzene ring from the organic ligand in the PMMA chains, which heal a radiation-induced fracture.

IR *J* values of PMMA

The IR *J* values constitute a convenient parameter for isotacticity and syndiotacticity as an arbitrary measure of the difference in the IR absorption spectra observed for the different structures of PMMA. The method for determining this parameter is described in the Experimental section of this study. Goode et al.[18] reported that syndiotactic PMMA had *J* values of greater than 100, whereas isotactic PMMA had *J* values of about 30. Thus, the *J* values could be used as a diagnostic parameter for the structure. A graphical representation of the *J* values and irradiation doses are shown in Figure 4–6. It is clear that all the values are greater than 100, and this mean that all the PMMA samples had a syndiotactic structure. However, γ-irradiation of

the pure PMMA or PMMA composite samples up to 100 kGy had no effect on the tacticity of PMMA.

CONCLUSIONS

IR measurements can be used for the determination of the efficiency of the protection of PMMA against γ-rays in the presence of an organic ligand or its cobalt complex at different concentrations. The use of a combined technique of transmission data of OCH$_3$, α-CH$_3$, CH$_2$, and C—C skeletal vibration bands with respect to the transmission band of the carbonyl group and the measurements of the area under the curve is a good technique for obtaining an idea of the protection efficiency of the additives. The presence of a phenyl ring in the polymeric chains of PMMA during γ-radiolysis was confirmed by ^{1}H-NMR spectroscopy.

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