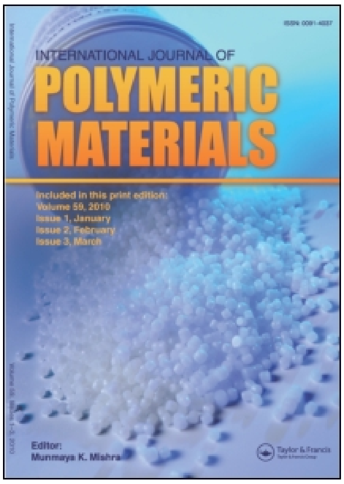

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Infrared Studies on Polymethyl Methacrylate Doped with a Sulphur-Containing Ligand and Its Cobalt (II) Complex During Gamma Radiolysis

S. M. Sayyah[a]; A. B. Khaliel[a]; Z. A. El-Shafiey[b]; B. N. Barsoum[c]
[a] Chemistry Department, Faculty of Science (Beni-Suef branch), Cairo University, Beni-Suef City, Egypt [b] Chemistry Department, Faculty of Science, Al-Azhar University (Girls Branch), Nasr City, Cairo, Egypt [c] Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt

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Infrared Studies on Polymethyl Methacrylate Doped with a Sulphur-Containing Ligand and Its Cobalt (II) Complex During Gamma Radiolysis

S. M. Sayyah
A. B. Khaliel
Chemistry Department, Faculty of Science (Beni-Suef branch),
Cairo University, Beni-Suef City, Egypt

Z. A. El-Shafiey
Chemistry Department, Faculty of Science, Al-Azhar University
(Girls Branch), Nasr City, Cairo, Egypt

B. N. Barsoum
Chemistry Department, Faculty of Science, Cairo University,
Giza, Egypt

Infrared spectroscopic studies were performed for poly(methyl methacrylate) samples doped with an organic ligand (N,N-dioxaloyl benzenesulphonyl-N,N-dioxaloylthiocarbazide) and its cobalt (II) complex during gamma radiolysis after extraction of the dopant. There are no drastic changes in the IR-absorption band positions, but noticeable changes in the intensities are found. The relative transmission of IR-absorption bands such as bands at 750, 840, 1065, and 1388 cm^{-1} were measured relative 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 are suggested by the behavior of the relative transmission data for each group with increasing exposure dose. The tacticity of the PMMA sample was unchanged during radiolysis and was found to be syndiotactic. This fact is confirmed by measuring the IR J-values for different PMMA samples before and after irradiation. The protection efficiency of the organic ligand and its cobalt (II) complex were also investigated and the organic ligand is a more protective material than the cobalt (II) complex

Keywords: PMMA, gamma radiation, degradation, IR-spectroscopy

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Address correspondence to S. M. Sayyah, Faculty of Science, Cairo University, Beni-Suef City, Egypt. E-mail: smsayyah@hotmail.com

INTRODUCTION

The infrared absorption characteristics of poly (methyl methacrylate) (PMMA) have 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], have studies the IR-spectra of PMMA samples doped with some luminescent materials. They found that there are no drastic changes in the position and intensity of the IR-absorption bands in PMMA, except in case of β-naphthol. From this, it is assumed that there is 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 is observed.

The radiolysis of PMMA was studied more extensively than any other polymer. This can probably be 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 be followed spectroscopically, owing to 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 megrad [7–8].

The effect of γ-radiation on the infrared absorption bands of polymers is not adequately studied in the literature. Alexander et al. [9], observed that a new absorption band appears at $888\,\mathrm{cm}^{-1}$ in poly(isobutylene) subjected to heavy doses of reactor radiation. This band was attributed to vinylidene double bonds. A more detailed analysis of the changes in the infrared absorption in gamma irradiated poly(isobutylene) was investigated by Slovokhotova et al. [10].

Gamma degradation and recombination processes, which could be occurring during radiolysis of some MMA-iron acrylate copolymers or MMA-acrylonitrile iron acrylate, were explained by IR-measurements during radiolysis [11]. The degradation and recombination processes, which could be occurring during gamma radiolysis, were established by electrical properties measurements of PMMA-Fe-acrylate-Mn-acrylate terpolymer samples [12].

Protection of PMMA samples against gamma irradiation has been investigated in the absence and presence of N,N-dioxalyl-p-aminobenzene sulponic acid or its iron (II) complex [13] and in the presence of tetraoxaloylsulphanilamide or its cobalt (II) complex [14]. The degradation and recombination processes, which occur in the PMMA sample during gamma radiolysis, were characterized by viscosity average molecular weights and thin layer chromatographic measurements.

The authors found that maximum protection against gamma ray degradation occurs when 7% of the organic ligand or its iron (II) complex is used in the polymer matrix. This is also confirmed by the radiation chemical yield for main chain scission, G_S.

The present study intended to investigated the changes in the band position and intensity of the IR spectra in some PMMA samples doped with sulphur-containing organic ligand and its cobalt (II) complex and exposed to gamma radiation. The IR-measurements for the investigated PMMA samples we carried our for polymer samples after extraction of the dopant materials. The mechanisms of degradation, recombination, and protection of the PMMA samples were also studied.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) monomer was a product of Merck-Schucharedt (yield 99%), stabilized with 100 ppm hydroquinone. It was purified as described before in Reference [15]. All chemicals used throughout this work were of the purest grade available. A Dean and Stark apparatus was used for the preparation of sulphur containing organic ligand as previously described by Sabbah et al. [15]. The cobalt complex of the prepared ligand was prepared as described by Sayyah et al. [14]. The structure and some analytical data of the sprepared ligand and its cobalt (II) complex are given in Table 1.

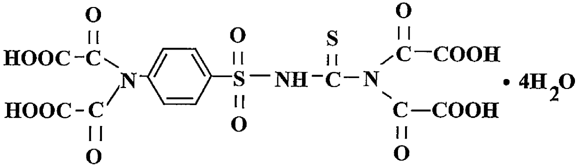
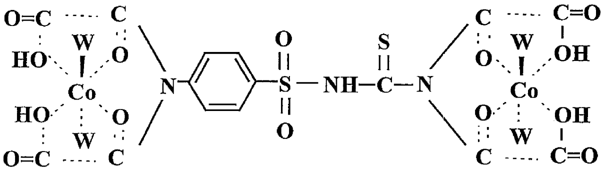
Instrumental

The IR-spectra were obtained via a shimazu FTIR 430 Jasco spectrophotometer, under conditions that would yield the maximum resolution. All the IR measurements were carried out at room temperature. The spectra or pure and doped PMMA films after irradiation and extraction of the dopant material were measured against air for comparison. The films were adjusted to constant thickness (100 μm) by using a cast technique as described by Sayyah et al. [6] Carbon, hydrogen, sulphur, and cobalt were determined for the prepared organic ligand and its cobalt (II) complex by the microanalytical laboratory at Cairo University.

Gamma Irradiation of the PMMA Films

Egypt's Mega gamma 1, supplied as type J-3600 by Atomic Energy of Canada Ltd., and situated at the National Center for Radiation

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	 $C_{15}H_{17}N_3S_2O_{18}$	Yelloish white	30.45 31.4	2.87 3.1	7.1 6.80	10.8 10.2	— —	591 595	379 371	1.65 1.89 5.71 9.75
2	 $C_{15}H_{17}N_3S_2O_{18}\ Co_2$	Rose	25.1 23.00	1.81 2.00	5.8 6.0	8.9 9.1	16.71 17.00	— —	— —	— —

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

Research and Technology, Cairo, was used. The ^{60}Co source having an activity of 137,000 Ci was used for gamma irradiation of the PMMA films. The doses 5, 15, 25, 35, 50, 75, and 100 kGy were measured by radiochromic dye film of Perspex. The does rate was found to be 2.76 kGy/h. The overall error in the dose measurements did not exceed ± 4%.

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

Pure PMMA samples and PMMA doped with cobalt(II) complex were prepared by mixing the monomer with benzoyl peroxide initiator (2.688×10^{-3} mol/L) and the approximate amount of the dopant. The tubes were flushed with pure nitrogen gas and sealed. The sealed tubes were put in an automatically controlled water bath at 60°C for several days. Finally, hard rose plastic or colorless transparent samples were obtained in case of PMMA-cobalt(II) composite and pure PMMA, respectively.

Preparation of PMMA Thin Film Samples (Doped with Organic Ligand)

The films were prepared by a solvent casting technique as described in Reference [6].

Calculation of the J-Values

The IR spectra of the 100 μm thick PMMA films were recorded from 2000 to750 cm^{-1} using Shimazu FTIR-430 Jasco spectrophotomer. A 100% transmission line was drawn between 1950–700 cm^{-1} (5.4–14.5 μ) and the absorbances at 1483 cm^{-1} (6.75 μ), 1388 cm^{-1} (7.2 μ), 1065 cm^{-1} (9.3 μ) and 990 cm^{-1} (10.1 μ) were calculated by using base line method [16–17].

Two sub-parameters, J_1 and J_2, were calculated from this absorbance by means of the equations: [18]

$$J_1 = 179[A_{1065}/A_{990}] + 27 \tag{1}$$

$$J_2 = 81.4[A_{1483}/A_{1388}] - 43 \tag{2}$$

The J-values are the arithmetic average of J_1 and J_2.

Calculation of the Area under the Curve in Case of Relative Transmission Data

For Calculation of the area under the curves, Al-foil sheet was cut into many pieces, which have different areas 5 cm^2 to 100 cm^2. Each piece was weighed and a calibration curve between the weight in gram and foil piece area in cm^2 was plotted.

The curves represented in Figures 4 and 5 (a–d) were retraced on Al-foil and then cut taking into consideration the three zones, which correspond to the degradation zones ((I) and (III) and third piece, which corresponds to the recombination (zone (II)). (c.f. Figure (4). After weighing each such piece, its area was calculated and the results are presented in Table 2.

RESULTS AND DISCUSSION

IR Spectrum of Pure PMMA Sample

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

1. A sharp band at 750 cm^{-1} for α (CH_2) coupled with (C–C) skelctal stretching vibration.
2. Two medium absorption bands at 984 and 950 cm^{-1} for stretching vibration (C–O–C) coupled with rocking vibration of (CH_3–O) and rocking vibration of α (CH_3), respectively.
3. A split band at 1260 and 1220 cm^{-1} for stretching vibration of C–C–O coupled with stretching vibration of C–O (skeletal) and internal CH deformation, respectively.
4. The observed band at 1488 cm^{-1} for δ_a (α-CH_2) group is higher in intensity than the band at 1388^{-1} for δ_s (α-CH_3) group.

From these observations it is clear that the investigated PMMA sample has a syndiotactic structure, as recorded in the literature [18].

Effect of Gamma-Irradiation on the Infrared Absorption Bands of Pure PMMA Sample

The infrared spectra of pure PMMA before and after exposure to different gamma rays doses are represented in Figure 1. From the figure, it can be concluded that, there are no drastic changes in the band positions, but some changes in the band intensities are observed. A variation of the band intensities with an increase in irradiation dose

TABLE 2 Area under the Curves for the Degradation and Recombination Processes in Absence and Presence of Different Additives

	Area in cm^2						
	Additive type and concentration						
		PMMA with ligand			PMMA with complex		
Area type correxponding to the different zones	PMMA without	1%	7%	15%	1%	7%	15%
Degradation (0–25) + (75–100)kGy	236.3^D	216.1^D	176.4^D	213^D	261.9^D	190.3^D	232.6^D
Recombination (25–75)kGy	205.8^R	212.4^R	193.3^R	225^R	257^R	195.4^R	234.5^R
Net area	31^D	3.7^D	16.9^R	12^R	4.9^D	4.7^R	1.9^R

D = Degradation process; R = Recombination process.

for absorption bands appears at 750 cm^{-1}, 840 cm^{-1}, 1065 cm^{-1}, 1388 cm^{-1}, and 1717 cm^{-1} as noted in Figure 2. The changes in the band intensities for each absorption band can be summarized as follows: For the band appearing at 750 cm^{-1}, which could be attributed to CH out of plane deformation in CH_2 group, the intensity decreases from zero up to 25 kGy, increases from 25 up to 75 kGy, and finally decreases from 75 up to 100 kGy.

The decrease in the band intensity from zero up to 25 kGy and from 75 up to 100 kGy can be explained by Schemes 1 and 2. Hydrogen abstraction from the polymeric chain [19] or scission of polymeric chain, respectively.

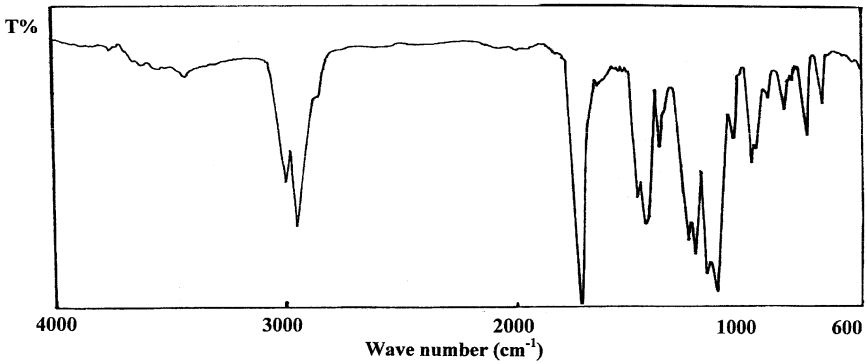


FIGURE 1 Infrared spectrum of pure PMMA sample.

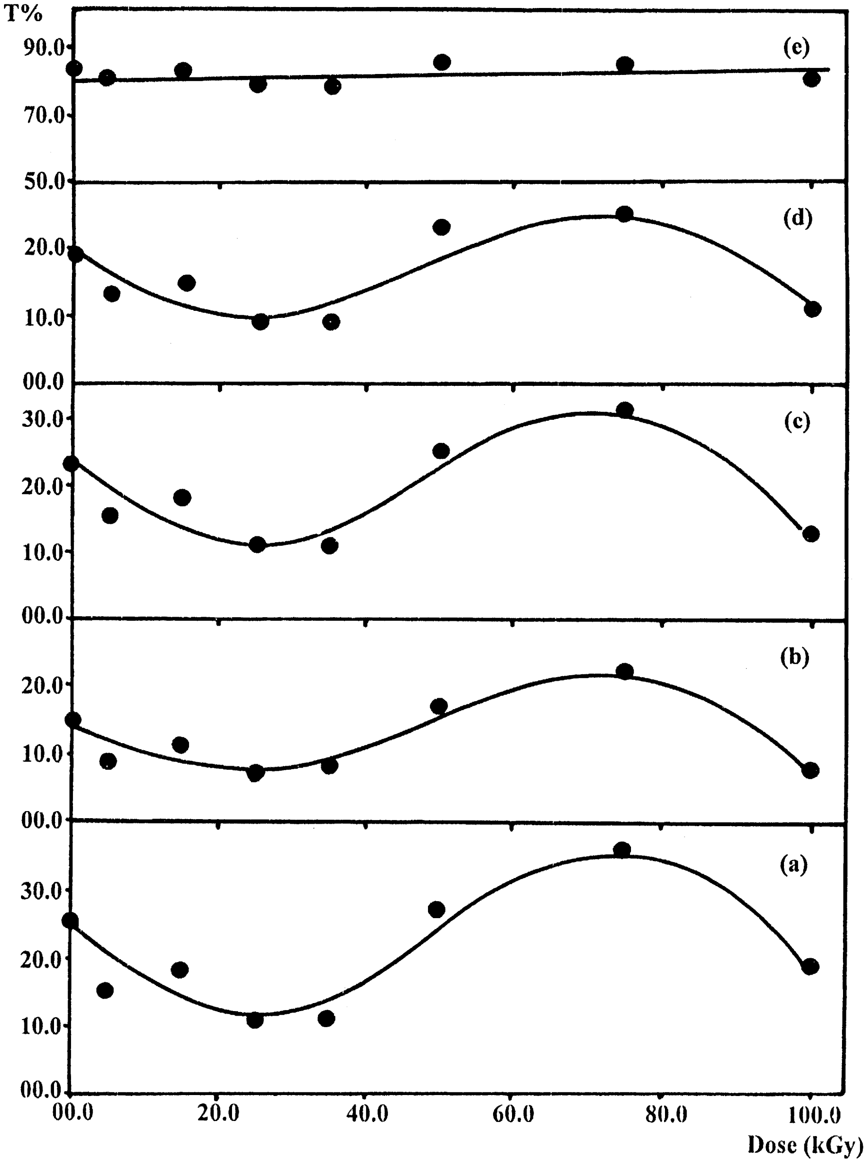
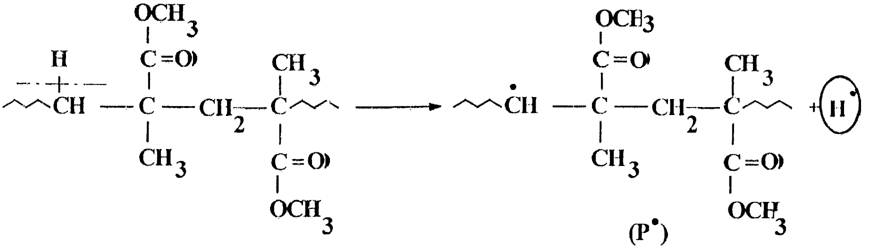
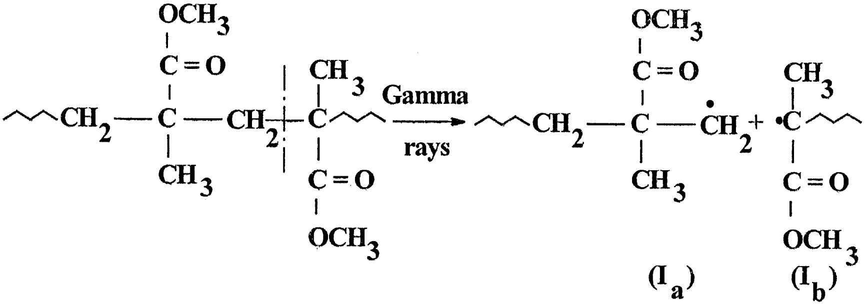


FIGURE 2 Relation between band intensity and the dose quantity for the bands appearing at (a) 750, (b) 840, (c) 1065, (d) 1388, and (e) 1717 cm^{-1} in case of pure PMMA.



SCHEME 1



SCHEME 2

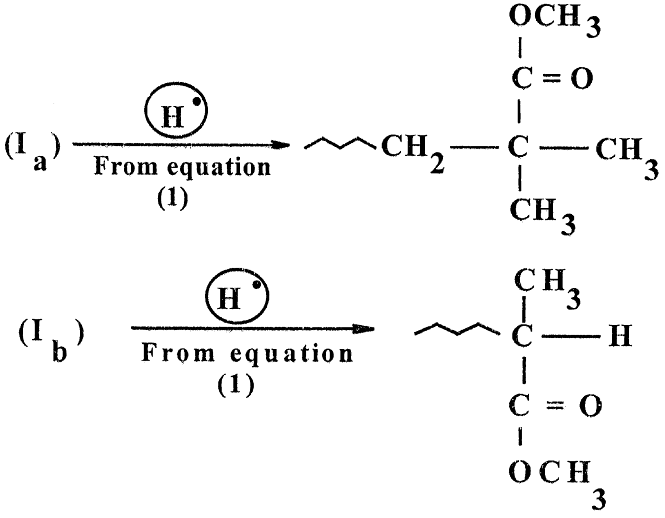
Recombination of the formed polymeric radical I_a and I_b with hydrogen radical is shown in Scheme 3.

The increase in the band intensity from 25 up to 75 kGy can be explained by the recombination process represented by scheme 4.

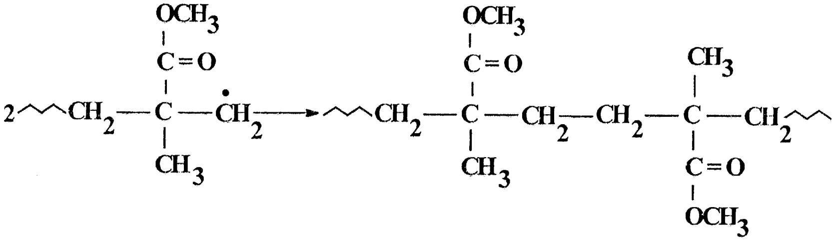
The band appearing at 840 cm^{-1} may be attributed to the deformation of C–O–C in the (OCH_3) group, the band intensity decreases from zero up to 25 kGy, and from 75 up to 100 kGy. This behavior can be explained by Schemes 5–9.

The increase in the band intensity from 25 upto 75 kGy is explained by the recombination process (schemes 10 and 11).

The band appearing at 1065 cm^{-1} may be attributed to intramolecular interaction in the (C–C) skeletal mode; the intensity shows the same behavior as mentioned for the bands appearing at 750 and 840 cm^{-1}.The band appearing at 1388 cm^{-1} may be attributed to δ_s (α–CH_3). The band intensity decreases from zero dose up to 25 kGy, increases from 25 up to 75 kGy, and finally decreases from 75 up to 100 kGy. The decrease in the band intensity from zero up to 25 kGy



SCHEME 3

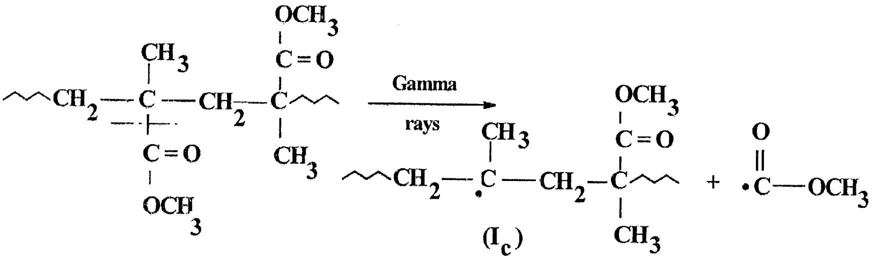


SCHEME 4

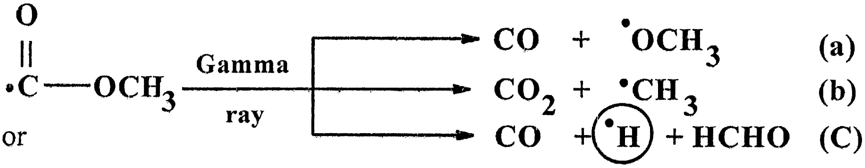
and from 75 up to 100 kGy can be discussed on the basis of Schemes 12–15.

The increase in the band intensity from 25 up to 75 kGy is attributed to the recombination process of ${}^{\bullet}CH_3$ produced from Scheme 7 with any polymeric radicals ($P^{\bullet}$), I_a, I_b, I_c, I_d or the recombination of the formed ($P^{\bullet}$) radical with each other to form P-P (Scheme 11).

The band appearing at 1717 cm^{-1}, which is attributed to the carbonyl stretching vibration in ester group shows a slight increase in band intensity with an increase in the irradiation dose. This is in good agreement with what was found by Subrahmanyam et al. [20] in dose range from zero to 500 kGy.



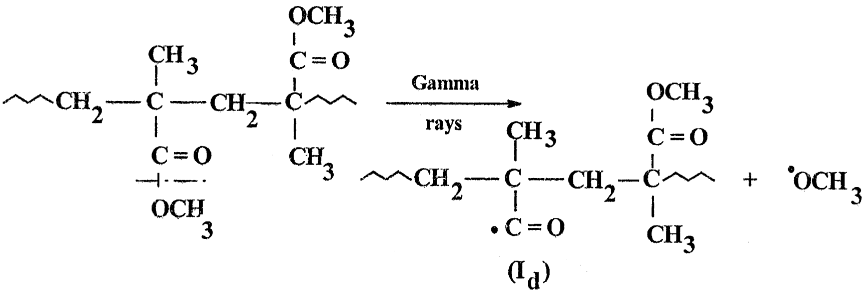
SCHEME 5



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

or

SCHEME 6



SCHEME 7

$$\textcircled{H}^{\bullet} + {}^{\bullet}OCH_3 \xrightarrow[\text{rays}]{\text{Gamma}} CH_3OH$$

or

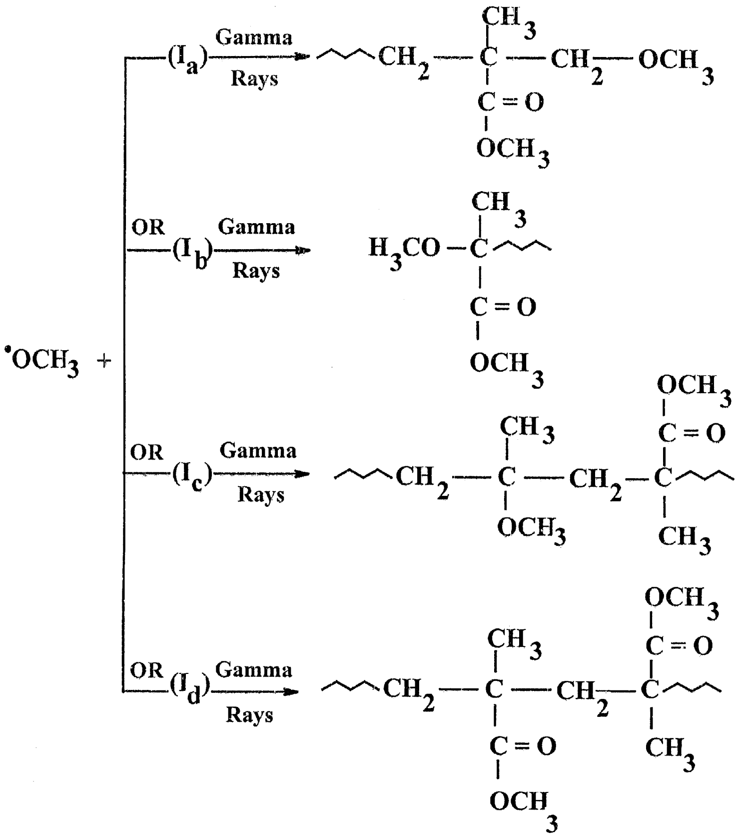
SCHEME 8

$$PH + {}^{\bullet}OCH_3 \longrightarrow P^{\bullet} + CH_3OH$$

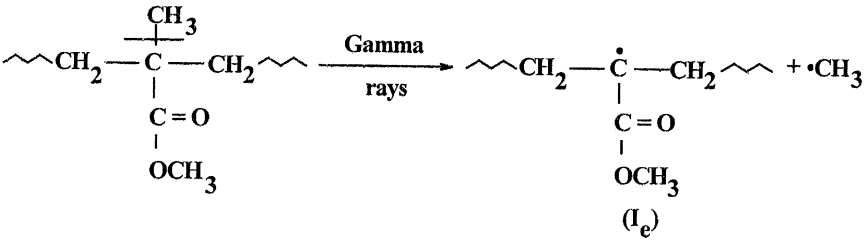
SCHEME 9

$$P^{\bullet} + P^{\bullet} \longrightarrow P - P$$

SCHEME 10

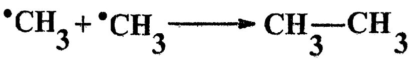


SCHEME 11

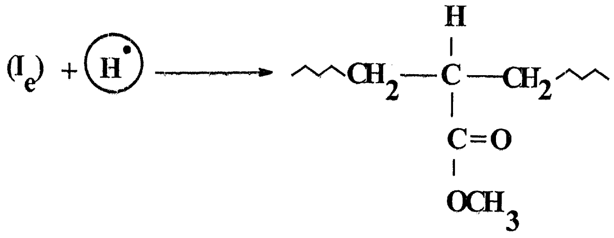


SCHEME 12

SCHEME 13



SCHEME 14



SCHEME 15

Effect of Gamma Irradiation on Infrared Absorption Bands of PMMA-Organic Ligand and PMMA-Cobalt Complex Composite Samples

From the infrared spectra of PMMA–N.N-dioxaloylbenzene sulphonyl-N,N-dioxaloylthiocarbazide composite, and PMMA cobalt(II) complex composite samples before and after irradiation, it is clear that there are no drastic changes in the band positions, but the band intensities do fluctuate between maximum and minimum or slightly increase with an increase of irradiation dose (c.f. Figure 3).

From these observations, there is not enough data to determine the changes produced in the polymer samples during radiolysis. Therefore, the decomposition of different groups in PMMA was investigated by calculating the transmission of the carbonyl group at 1717 cm^{-1}, which has an approximately constant band intensity during radiolysis, relative to the transmission of the bands at 1388, 1065, 840, and 750 cm^{-1}, attributed to (α–CH_3), (C–C), (C–O–C) stretching vibration and (CH_2) out of plane deformation, respectively. The relations between the relative transmission (T_{1717}/T_{750}), (T_{1717}/T_{840}), (T_{1717}/T_{1065}), and (T_{1717}/T_{1388}) with the dose for pure PMMA-samples are represented in Figure 4 (a, b, c, and d). From the figure, it is clear

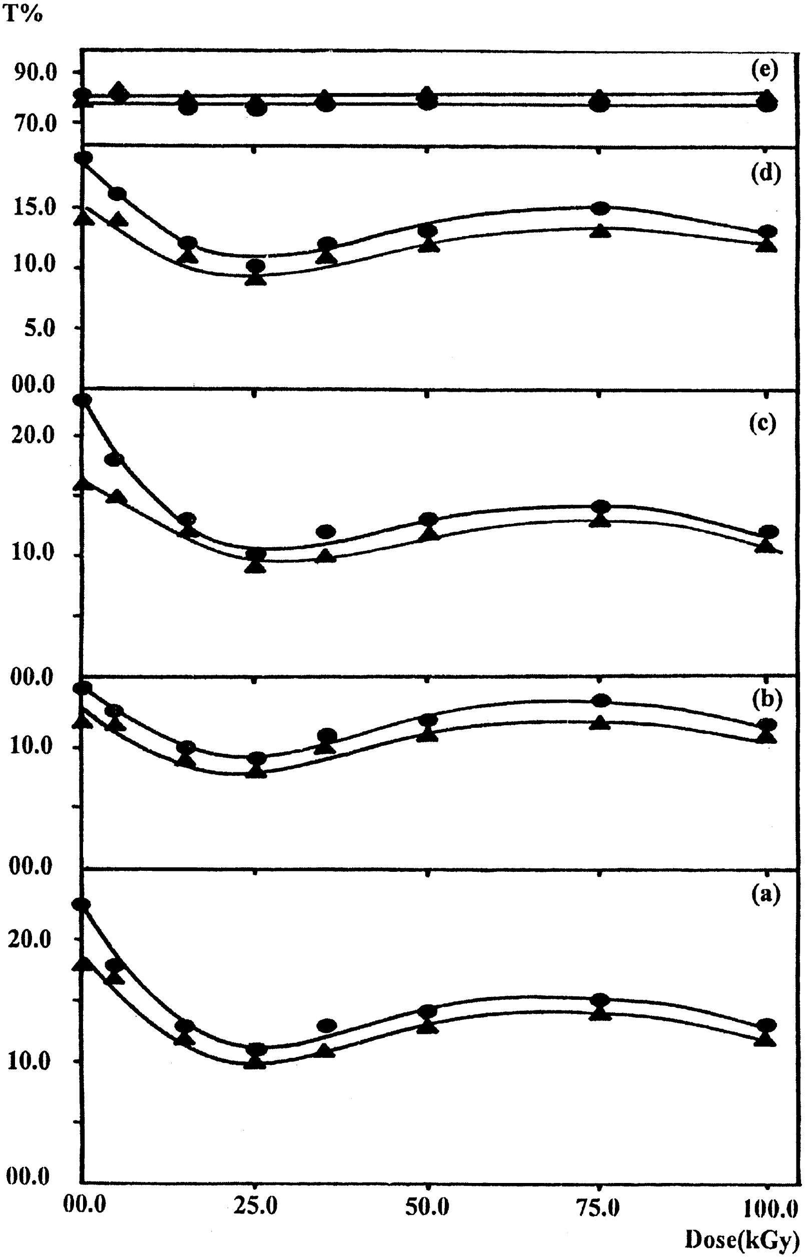


FIGURE 3 Relation between the band intensity and the dose quantity for the bands appearing at (a) 750, (b) 840, (c) 1065, (d) 1388, and (e) 1717 cm^{-1} in case of: (●) Organic ligand. (▲) Cobalt (II) complex of the organic ligand.

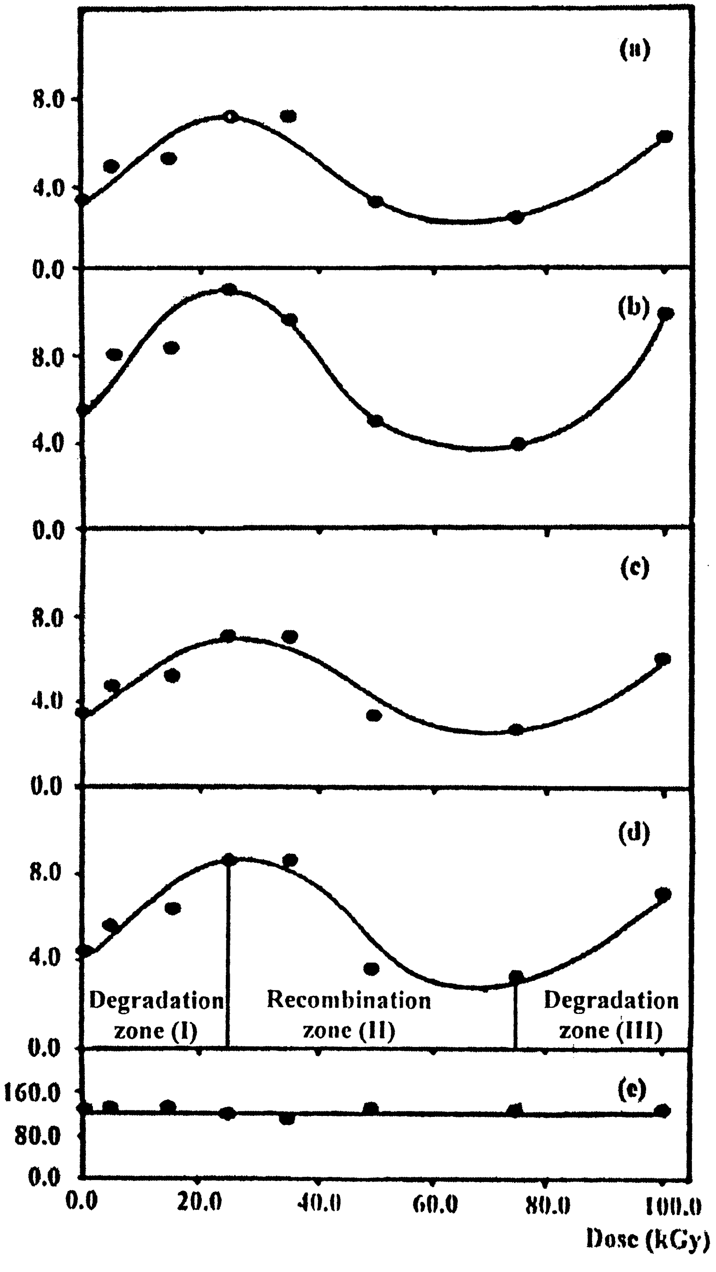


FIGURE 4 Relation between the relative transmission (a) T_{1717}/T_{750}, (b) T_{1717}/T_{840} (C) T_{1717}/T_{1065}, (d) $T_{1717};T_{1388}$, (e) IR J-values vs. dose quantity in PMMA.

that the value of the relative transmission (T_{1717}/T_{750}) increases with the increasing irradiation dose up to 25 kGy, then decreases up to 75 kGy, and increases once more from 75 up to 100 kGy. This behavior can be explained by Schemes 1–4.

The formed polymeric radical (Ia) can be recombined with other simple radicals such as ($^{\bullet}CH_3$) radical produced from Schemes 6b or 12. The variation in the relative transmission data for other groups can be explained as mentioned earlier in the case of band intensity behavior with increasing of the irradiation dose.

Scission of the polymeric chain may also take place in the side groups such as the ester group or α-methyl group and this affects the relative transmission of different groups present in the polymeric structure. Scission of the backbone chain is more predominant and has a clear effect in case of pure PMMA, but a lower effect is observed in the presence of the ligand or its cobalt (II) complex. In the case of the PMMA-organic ligand composite samples, the infrared data may throw some light on the protective effect of the organic ligand (7%) on the ester group and the main chains of the polymeric structure, which was confirmed by G_s-values calculations (G_s being the radiation chemical yield for chain scission), that is, the lowest G_s-values are found when using 7% ligand in the polymer matrix[21]. In other words, sharp changes are observed in the relative transmission values of the carbonyl group band relative to different selected bands with increasing dose in case of 1% and 15% ligand concentration. However, much smaller changes occurred in the case of the 7% concentration (c.f. Figure 5).

In the case of the PMMA cobalt (II) complex-composite sample, the relative transmission data show a maximum at 25 kGy and a minimum peak at 75 kGy due to the degradation and recombination process, respectively. The relative transmission data have the lowest values in case of 7% weight of the cobalt (II) complex in PMMA matrix. In other words, the protection of different bonds in the polymeric main and side chain occurs best in case of 7% (c.f. Figure 5). As shown from the aforementioned relations between the relative transmission of carbonyl group band and other groups present in the polymeric structure, it is clear that the area under each curve is divided into three zones. Two zones are due to the degradation process between 0–25 kGy and 75–100 kGy. The third zone is an indication of a recombination process between 25–75 kGy. The area under the curve was calculated for each zone and the data are summarized in Table 2.

From Table 2, it is clear that during the radiolysis of pure PMMA or PMMA-1% ligand and PMMA-1% complex the degradation process

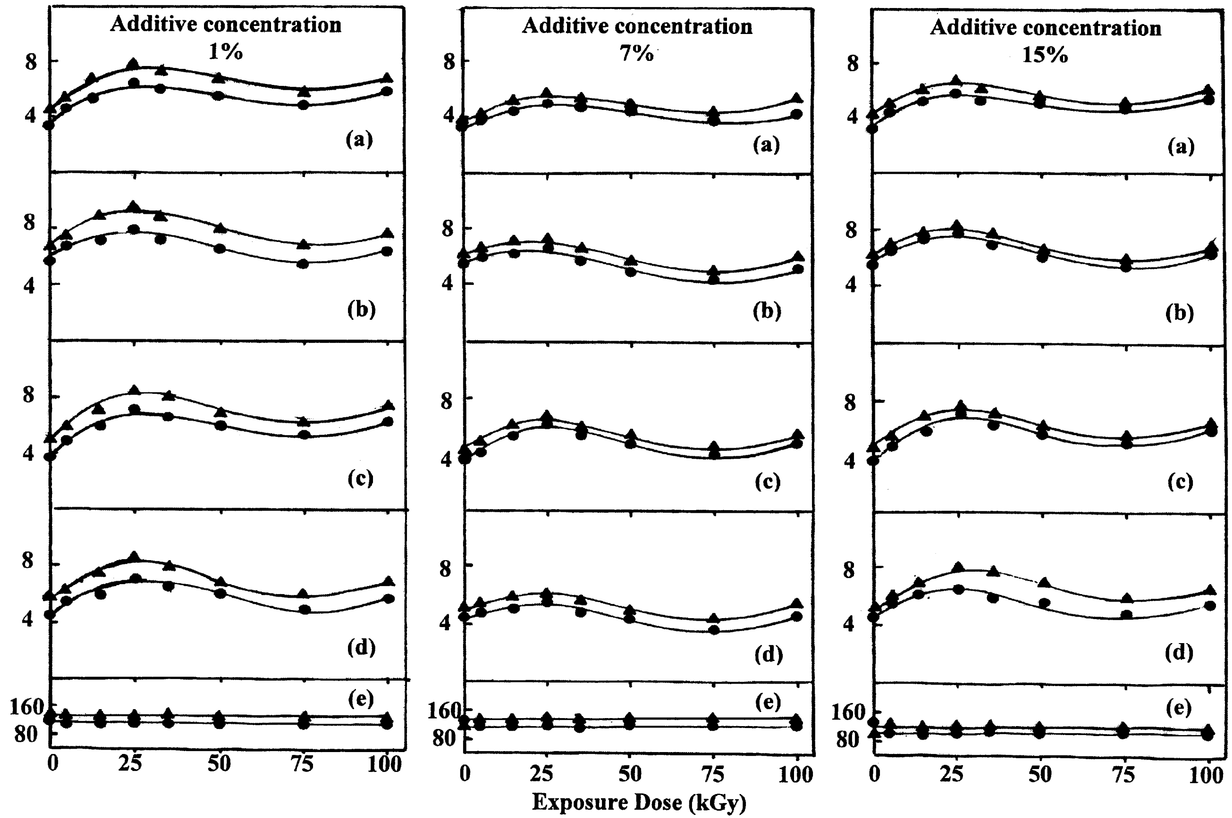


FIGURE 5 Relation between the relative transmission: (a) T_{1717}/T_{750}, (b) T_{1717}/T_{840} (C) T_{1717}/T_{1065}, (d) T_{1717}sol;T_{1388}, (e) IR J-values vs. dose in case of (●) Prepared organic ligand. (▲) Cobalt (II) complex of the prepared organic ligand.

predominates. The amount of degradation in different polymeric samples is as follows:

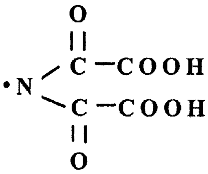
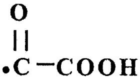
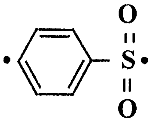
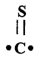
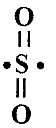
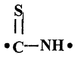
$$\text{Pure PMMA} > \text{PMMA}_{1\%\ \text{complex}} > \text{PMMA}_{1\%\ \text{ligand}} > \text{PMMA}_{15\%\ \text{complex}} > \text{PMMA}_{7\%\ \text{complex}} > \text{PMMA}_{15\%\ \text{ligand}} > \text{PMMA}_{7\%\ \text{ligand}}$$

This means that the most protective additive is the organic ligand present at 7% concentration in the polymeric matrix. The IR data are in good agreement with the obtained data by Sayyah et al. [16] from viscosity average molecular weight measurements of different PMMA samples during gamma radiolysis.

Protection Mechanism of the Organic Additive

The ligand has two sulphur atoms, one phenyl ring and four carboxylic groups, one sulphonyl and one thiocarbonyl group in its structure. The radicals, which may be formed during gamma irradiation, are tabulated in Table 3.

TABLE 3 Different Radicals, which may Form During Gamma Radiolysis

Radical type	Number of radicals	Radical type	Number of radicals
	2	 $\bullet\overset{\text{O}}{\overset{\|\|}{\text{C}}}\text{—COOH}$	4
	1	•COOH	4
	1	 $\bullet\overset{\text{S}}{\overset{\|\|}{\text{C}}}\bullet$	1
 $\bullet\overset{\text{O}}{\overset{\|\|}{\underset{\underset{\text{O}}{\|\|}}{\text{S}}}}\bullet$	1	 $\bullet\overset{\text{S}}{\overset{\|\|}{\text{C}}}\text{—NH}\bullet$	1

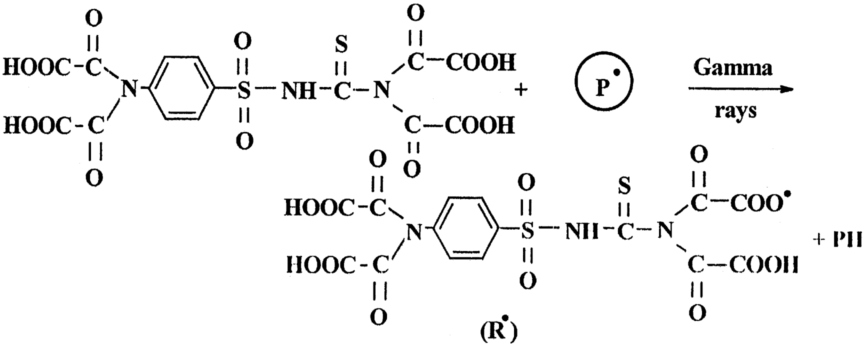
Radiation protection by the additives may be considered to operate through the following two alternative mechanisms:

1. Some form of energy transfer may take place from PMMA to the additive, wherein the polymer is chemically unaltered. The additive may either dissipate the energy without suffering any permanent chemical change or it 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 any consequence. In PMMA polymers, the major reaction is a loss of hydrogen atom leaving a polymer radical ($P^\bullet$) as in Scheme 2. Protection against further reactions may occur if the additive can itself furnish a hydrogen atom and remain as a radical with new activity as is shown, for example, in Scheme 16.

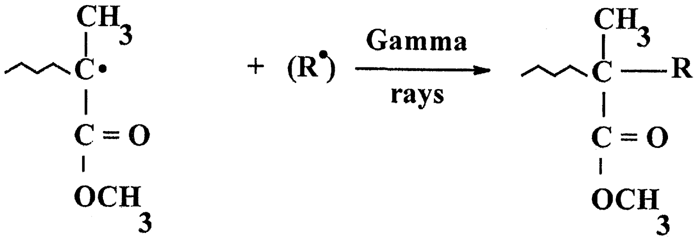
In case of degradation of PMMA by main chain scission as shown in Scheme 2, a protective additive molecule may combine with these radicals to form stable side chain or less reactive radicals (c.f. Scheme 16).

Additionally, any monoradical that may be formed from the gamma degradation of the organic ligand, may react instead of ($R^\bullet$) in Schemes 17 and 18.

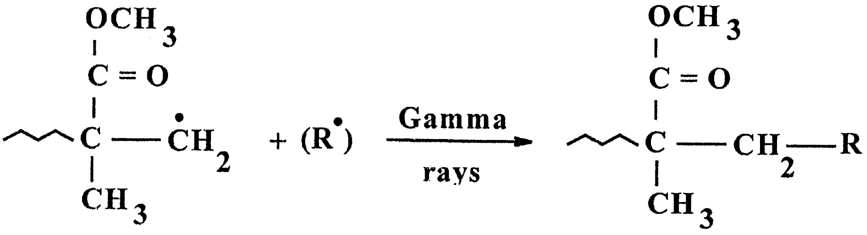
The protective additives may link the two polymer radicals together and thereby heal a radiation-induced scission as shown in Scheme 19. This means that there will be no significant change in the average molecular weight. These radicals are the biradicals listed in Table 3 (c.f. Scheme 19).



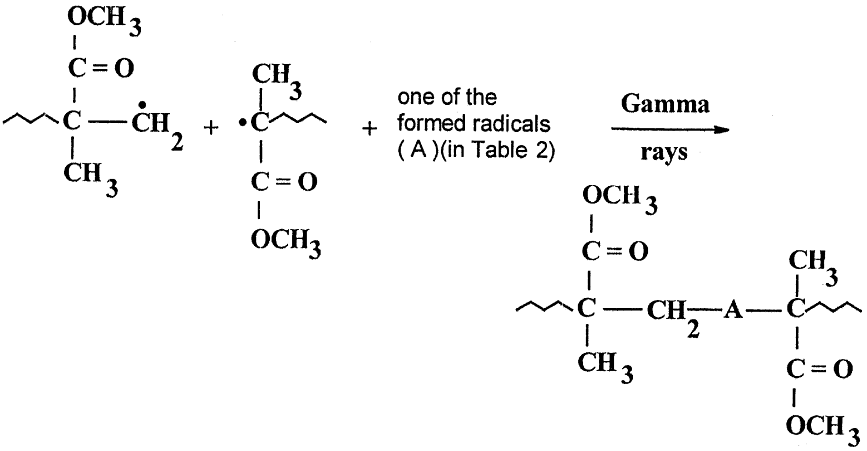
SCHEME 16



SCHEME 17



SCHEME 18



SCHEME 19

The aforementioned mechanisms are 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 on the PMMA absorption bands.

Infrared J-Values of the PMMA Samples

Infrared J-values constitute a convenient parameter for measuring isotactic and syndiotactic contents in PMMA. The method for determining this parameter is described in the experimental part of the present study. Goode et al. [22] have reported that syndiotactic PMMA has J-values greater than 100, whereas isotactic PMMA has J-values of about 30. Thus, the J-value method can be used as a diagnostic parameter for the structure. A graphical representation between J-values and irradiation doses are shown in Figs (3, 4, & 5e). It is clear that all values are more than 100, which means that the our PMMA samples have a syndiotactic structure. Importantly, gamma irradiations of pure PMMA or PMMA composite samples up to 100 kGy have no effect on the tacticity of the poly(methyl methacrylate).

CONCLUSION

Infrared measurements can be used for the determination of the efficiency of the protection of PMMA against gamma rays in the presence of organic ligand or its cobalt complex, using different concentrations. The use of a combined technique of transmission data for OCH_3, $\alpha{-}CH_3$, CH_2, and C–C skeletal vibration bands relative to the transmission band of the carbonyl group and the measurements of the area under the curve is a good technique to give an approximation of the protection efficiency of the additives.

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