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International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

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To cite this Article Sayyah, S. M. , Nasser, S. A. , El-naser, G. Ago and Tammam, M. T.(2000) 'Electrical and Spectroscopic Studies on Some Transition Metal Acrylates Methyl Methacrylate Bulk Co and Terpolymers', International Journal of Polymeric Materials, 46: 3, 721 – 741

To link to this Article: DOI: 10.1080/00914030008033910

URL: <http://dx.doi.org/10.1080/00914030008033910>

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Electrical and Spectroscopic Studies on Some Transition Metal Acrylates Methyl Methacrylate Bulk Co- and Terpolymers

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(Received 10 March 1999)

Copolymers of Fe acrylate-methyl methacrylate (MMA), Mn acrylate-MMA and terpolymer of Fe acrylate-Mn acrylate-MMA were prepared by bulk technique. A thorough investigation of the response of the prepared samples to γ -irradiation has been carried out. The frequency dependence of a.c. conductivity data showed that the relaxation frequency depend on the type and concentration of the metal acrylate units. For a wide distribution of relaxation time, the change of slope at the transition in the plot of $\log \sigma_{ac}$ Vs. $\log f$ is hardly noticeable. The change in the position of some absorption bands in the UV-visible spectrum was attributed to the existence of interaction between the transition metal acrylate unit and MMA monomer. From the relationship between the absorption intensity and dosage occurred, the data suggested that MMA-Fe acrylate copolymer could be used as plastic dosimeter for γ -rays in the dose range 1.75–6.41 KG y.

Keywords: Methyl methacrylate co-polymers; spectra; properties

1. INTRODUCTION

Electrically conductive polymers have been widely employed in industrial applications [1, 2]. It is of great importance to correlate the

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physical properties of polymers to its chemical structure. Some investigators have devoted their efforts in studying and improving the electrical properties of polymers doped with metal ions [3–5]. Complexes of unsaturated monomers having free terminal carboxyl groups with transition metal ions are of great industrial importance [6]. As a result of copolymerization of metal acrylate with methyl methacrylate, the structure becomes more rigid and the electrical conduction improves considerably. This has been observed in case of samples prepared by bulk copolymerization of some metal acrylates with methyl methacrylate [6–10]. The electrical conductivity in polymers is generally low since conduction is mainly ionic. However, it increases in polymer composites containing certain particles like metal powder [11], or by doping with suitable charge acceptors [12].

On the other hand various additions to PMMA impact a degree of protection against scission by ionizing radiation. Alexander *et al.* [13] have suggested that added substances reduce the amount of degradation by absorbing energy from the excited polymer molecules. Bovev [14] viewed the effectiveness of these screening as being due to their combination with the free radicals formed during irradiation.

In view of this situation, we intend to prepare a new type of copolymer and terpolymer samples containing iron and manganese in the structural units to improve electrical conduction and thermal resistivity of acrylate polymers. The effect of γ -irradiation upon the conductivity of the prepared samples is investigated. The optical absorption spectra in the UV-visible region before and after γ -irradiation is also studied.

2. EXPERIMENTAL

2.1. Preparation of Materials

Methyl methacrylate (MMA) monomer, (99%) of Merck, was stabilized with 100 ppm hydroquinone, and purified as described before [15]. Acrylic acid, was fractionated using a fractionating column of about 15 theoretical plates. The fraction boiling at 140 to 141°C was collected and used.

Preparation of Fe-acrylate was carried out by adding Iron oxide (Fe_2O_3), (calcinated at 400°C for 4 hours), in stoichiometric amount calculated to the carboxyl groups, to a stirred 20% acrylic acid solution in acetone at room temperature. The reaction mixture was then refluxed with continuous stirring for several hours until complete dissolution of Fe_2O_3 . After the reaction is completed, the excess of the solvent was evaporated using rotatory evaporator at 40°C , and then the residue was dried in vacuum oven at 40°C till constant weight.

A similar procedure was carried out for preparation of Mn-acrylate using MnCO_3 (May and Baker Ltd., England).

Preparation of Methyl Methacrylate-Acrylic acid copolymer was carried out by mixing methyl methacrylate (MMA) and acrylic acid (AA) monomers in different weight ratios in soda glass tube (1.853 cm diameter and 30 cm length) containing 2.688×10^{-3} g mol/L benzoyl peroxide. The tubes were flushed with pure nitrogen gas then sealed. The sealed tubes were put in an automatically controlled water bath at 60°C for several days. A hard transparent yellowish plastic samples were obtained.

Preparation of Methyl Methacrylate-Acrylate copolymer: (Iron or Manganese Acrylate) was carried out by mixing metal acrylate and methyl methacrylate monomers in different weight ratio and follows the same steps as described in the preceding paragraph. A hard transparent reddish-brown plastic samples in case of iron and deep brown in case of manganese were obtained. Finally all samples are then cut into discs of 0.2 cm thickness and polished.

2.2. Measurements

The elemental analysis of carbon and hydrogen in the prepared samples are determined by mass spectrometer. Metal contents were carried out by atomic absorption. Bulk density measurements are carried out by dividing the weight of the disk in air by its volume. Hardness measurements are carried out using wolpert hardness tester (HT 2004). The ultraviolet absorption spectra are measured using superscan spectrophotometer at room temperature in the range 200–800 nm. Irradiation of samples was carried out using A^{60}Co source. The a.c. conductivity measurements was carried out on disks

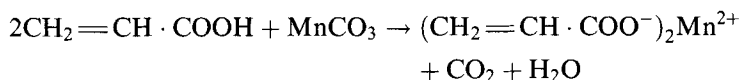
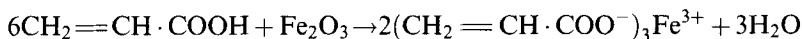
painted on both sides with silver paste. Philips RLC bridge (digital and computerized) are used at a frequency range 100 Hz – 10⁵ Hz and in the temperature range 30–100°C.

3. RESULTS AND DISCUSSION

3.1. Structural Determination

The introduction of Fe-acrylate or Mn-acrylate units in the MMA polymeric chains produces changes in their chemical reaction may be represented by the following steps:

- (i) The pattern of the initial step of the reaction between acrylic acid and iron oxide or acrylic acid and manganese carbonate in molar ratio 6:1 and 2:1, respectively occurs as follows:

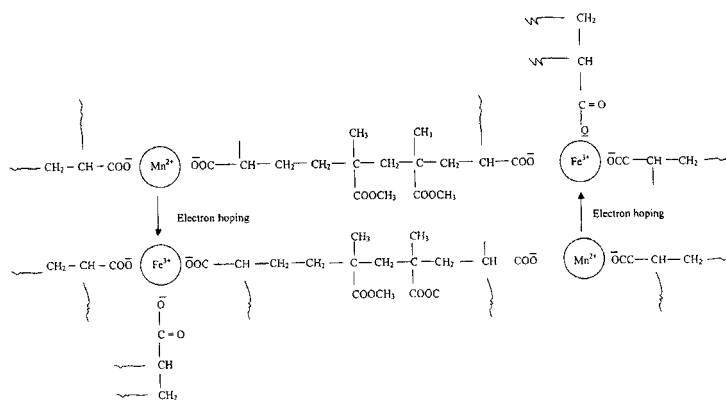


This step involves ionic or ionic dipolar associations.

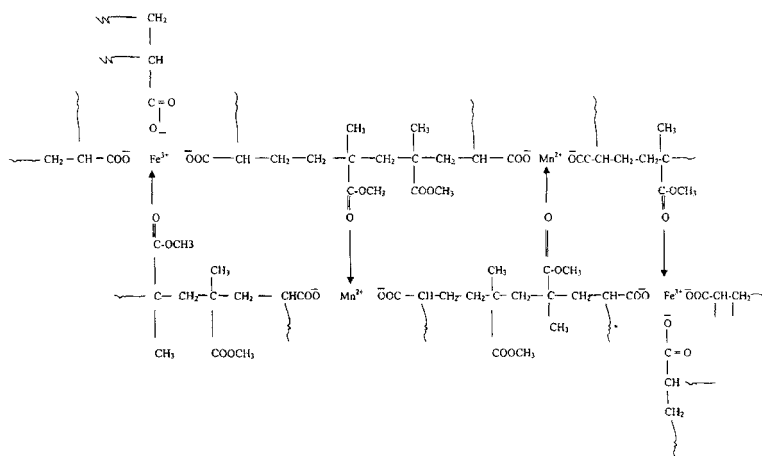
- (ii) The bulk copolymerization of MMA and Fe- or Mn-acrylate salts was carried out by free radical mechanism. This type of copolymerization reaction led to random structures as previously reported in case of Cu-acrylate-MMA copolymer [6]. The proposed structures of the Fe-acrylate or Mn-acrylate-MMA copolymer samples are the same as described in our previous articles [6–10].

The introduction of Mn-acrylate and Fe-acrylate units in the MMA polymeric chains produces some changes in their chemical and physical properties. This type of terpolymerization led to the random structure as illustrated in Scheme (1). The possibility of the chain side connections is illustrated in Scheme (2).

The elemental analysis of the produced terpolymer samples is in good agreement with the proposed structure [*cf.* Tab. I].



SCHEME 1



SCHEME 2

3.2. A.C. Electrical Conductivity

Figure (1) represents the temperature dependence of a.c electrical conductivity for the samples with different compositions. It is observed that σ_{ac} decreases with the increase of temperature. The graph approximately, behaves in a linear fashion so that an electronic conduction mechanism dominates [8]. This indicates a semiconducting behaviour of the copolymer and terpolymer samples. Moreover, the

9	66.700 (4)	-	-	33.300 (1)	Deep Brown colour	52.190	6.352	9.299	-	1.2300	95
10	75.000 (6)	-	(0)	25.000 (1)		50.200	6.100	9.102	-	1.0150	105
11	80.000 (8)	-	(0)	20.000 (1)	intensity	54.140	6.763	6.975	-	1.0010	115
12	83.300 (10)	-	(0)	16.700 (1)	decrease	52.300	7.010	5.580	-	0.9500	125
13	71.770 (60)	-	(0)	11.961 (1)	Deep brown	53.300	7.173	4.650	-	0.9500	110
14	77.220 (80)	-	(1)	9.653 (1)	Deep brown	56.080	7.500	3.340	3.550	0.9210	120
						54.400	6.680	3.200	3.400		
						52.050	6.500	2.690	2.860		
						54.760	6.930	2.510	2.700		
						53.100	6.600				

The low % of carbon in the found data is due to metal carbide information (in case of metal acrylate polymers).

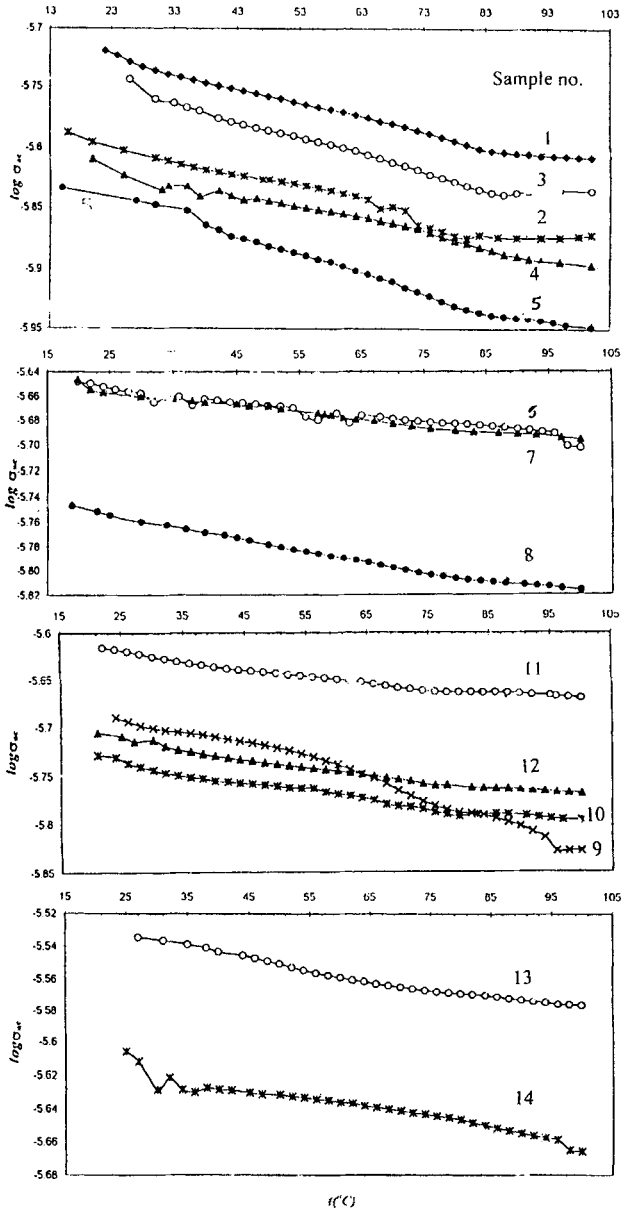


FIGURE 1 Temperature dependence of the A.C. electrical conductivity for different polymeric samples (*cf.* Tab. I).

attenuation of $\log \sigma_{ac}$ Vs. temperature curves with the thermal expansion of the hopping pathes between metal ions was the main conduction mechanism for all copolymers and terpolymers.

The frequency dependence of the a.c conductivity at 40°C for the samples are shown in Figure (2) at different metal acrylate contents. Two straight lines have been obtained (which are similar to the PMMA sample) with a change of slope occuring at frequency higher than the critical frequency. This relaxation frequency was found to be function of the type and concentration of the acrylic acid and metal acrylate as shown in Table (II).

This behaviour of the a.c conductivity is in coincidence with a finite distribution of relaxation time [16] which is detected by Narula *et al.* [17] in case of PMMA. For a very wide distribution of relaxation time, the change of slope at the transition in the plot of σ_{ac} Vs. $\log f$ is hardly noticeable.

3.2.1. Effect of γ -irradiation on A.C. Conductivity

Figure 3 shows the effect of γ -irradiation on the a.c conductivity of some investigated samples. The irradiation of polymers with γ -rays affect greatly on the chemical structure and consequently the electrical conductivity.

It may expected that γ -rays can generate photoelectrons and possibly displacement of atoms from their sites in the lattice of the solids. The produced photoelectrons will go back and forth and then become freely or loosely bound to trapping centers somewhere in the materials structure. This new electronic configuration, besides the displacement of atoms would cause a change in the electrical properties of material [18].

TABLE II Values of slopes of σ_{ac} Vs. frequency curves for all samples

Sam- ple no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
S ₁	2.325	1.180	1.864	2.733	3.049	2.315	2.499	2.446	2.659	2.833	2.4	2.181	1.881	3.189
S ₂	1.195	1.176	1.193	1.174	1.548	1.154	1.159	0.897	1.884	1.848	1.193	1.181	1.164	1.787

S₁ Slope at low frequency.

S₂ Slope at high frequency.

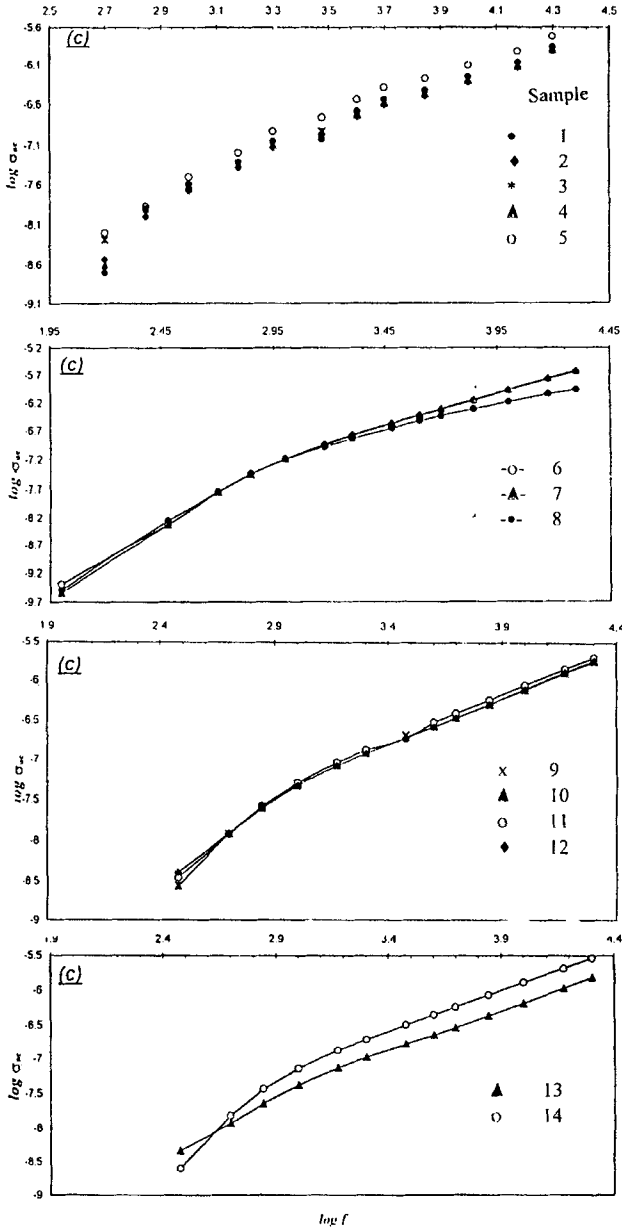


FIGURE 2 Frequency dependence of the A.C. electrical conductivity for different polymeric samples (*cf.* Tab. I).

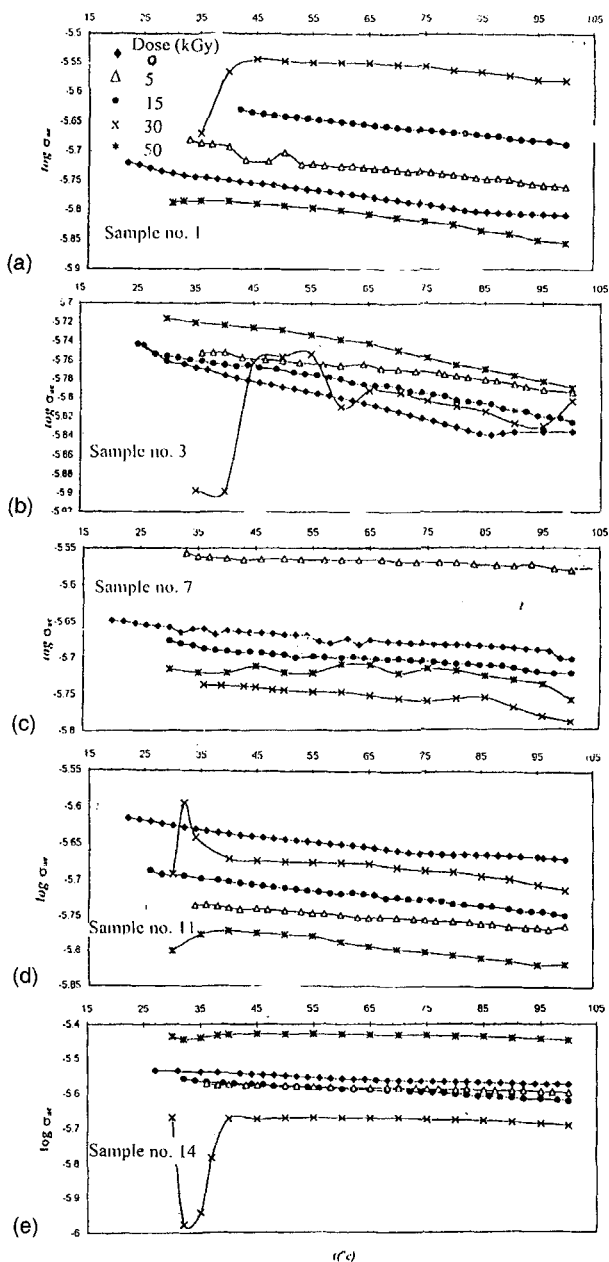


FIGURE 3 Temperature dependence of the A.C. electrical conductivity of: (a) PMMA at different γ -doses. (b) MMA acrylic acid copolymer (Sample 3 Tab. I) at different γ -doses. (c) MMA-Fe acrylate (Sample 7 Tab. I) at different γ -doses. (d) MMA-Mn acrylate copolymer (Sample 11 Tab. I). (e) MMA-Fe & Mn acrylate terpolymer (Sample 14 Tab. I) at different γ -doses.

Cross-linking and degradation are non-equilibrium radiation-chemical processes that change the structure and hence the physical properties of the polymer. Cross-linking transforms a linear polymer into a three dimensional molecule resulting in a significant increase in molecular mass, lower solubility in organic solvents and improving mechanical properties. Degradation results in a decrease in molecular mass and has the opposite effect on the physical properties of the polymer.

As a rule cross-linking and degradation occur simultaneously. However, the ratio of their rates depends on the chemical structure of the polymers, its physical state and the irradiation conditions [19].

(PMMA) is a typical polymer that degrade at room temperature with irradiation results in scission of the main chain to give two end macroradicals [20]. As a result of the irradiation of polymers with γ -radiation, the initial chemical structure is disrupted, the probability of the formation of the double bond increases with increasing dose rate [21] and consequently the electrical conduction can be affected.

The behaviour of σ_{ac} with irradiation dose would be explained as follows. For low doses the increase in σ_{ac} may arise from the presence of electrons and holes which are trapped in the polymer or move under an external field to produce a radiation induced charge. At high irradiation dose recombination of holes and electrons and the formation of space charges may occur resulting in an appreciable decrease in σ_{ac} .

However, for all modified PMMA samples the same features could be detected but with different sensitivities to γ -dose. All samples show a peak in their σ_{ac} *Vs.* temperature at around 30 KGy, except both PMMA modified by the addition of the mixed ratio (1:1) of iron and manganese acrylates and the modified PMMA with iron acrylates (*cf.* Fig. 3).

Also, Figure (3) illustrates the ac conductivity (σ_{ac}) of pure PMMA and modified PMMA at different γ -doses as a function of temperature in the range 25–100°C. All samples (except PMMA modified by iron acrylates) show anomalous behaviour in their temperature dependence of σ_{ac} around 30 KGy radiation dose in the temperature range 29–60°C. Moreover, samples of PMMA modified by the mixing ratio (1:1) of iron and manganese acrylates (sample No. 14) show an anomalous

behaviour appears as a minimum in its temperature dependence of σ_{ac} at about 32°C upon irradiation by 30 KGy γ -dose which reflects the mutual existence of the degradation and branching process.

3.2.2. Frequency Dependence of A.C. Conductivity of γ -Irradiated Samples

The frequency dependence of the a.c conductivity for samples is shown in Figure (4) at different γ -doses. Two distinct straight lines have been also obtained with a change of slope. Moreover, the values of the slope of the two distinct straight lines and the intersected point depend largely on both the type of modified MMA samples and the irradiation γ -dose as shown in Table (III).

The behaviour of frequency dependence of a.c conductivity of these samples could be represented by an electric circuit similar to that suggested by Kawamoto [22]. If we consider that the metal ions form small aggregates through the PMMA polymer matrix. A circuit representation of this system is shown in Figure (5). At low frequencies, the current flows through the contact resistance since it is blocked at the contact capacitance. The net resistance of the metal ions aggregate in series with the contact region is $(R_C + R_A)$, where R_A is the resistance with the metal ion aggregate and R_C is the resistance of the gap resistance between the metal ion.

At high frequencies, the impedance of the contact capacitance is much lower than the contact resistance, and the current flows through the contact resistance. Furthermore, since the capacitor's impedance is much lower than the metal ions aggregate resistance, the net resistance at the higher frequencies is equal R_A , which is lower than the net resistance $(R_C + R_A)$ for the low frequencies.

3.3. Ultraviolet-Visible Spectroscopic Studies of MMA-Homopolymer, its Copolymers and Terpolymers (Before and After γ -Irradiation)

The UV-visible absorption spectra of some samples before and after γ -irradiation with different doses are shown in Figures 6 and 7. The

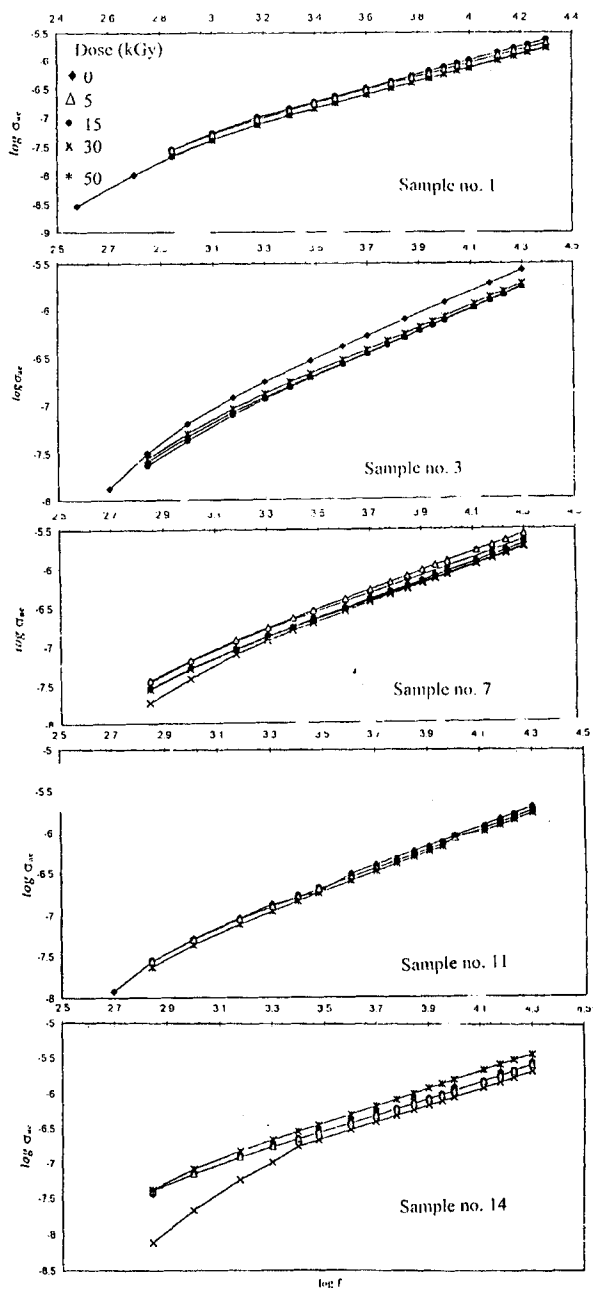


FIGURE 4 Frequency dependence of the A.C. electrical conductivity of the Samples 1, 3, 7, 11 and 14 (*cf.* Tab. I) at different γ -doses.

TABLE III Values of slopes of σ_{ac} Vs. frequency curves for all samples and the values of the critical frequency

Additive	Pure PMMA (Sample 1)	Acrylic acid (Sample 3)	Iron acylate (Sample 7)	Manganese acrylate (Sample 11)	Mn & Fe-acrylates (Sample 14)
S_1	1.5208	1.4782	1.4434	1.581	1.5775
S_2	1.1724	1.1576	1.1676	1.1745	1.2246
f_c (Hz)	1995	2011	2454	2020	2450

S_1 is the slope at low frequencies;

S_2 is the slope at high frequencies, and f is the critical frequency.

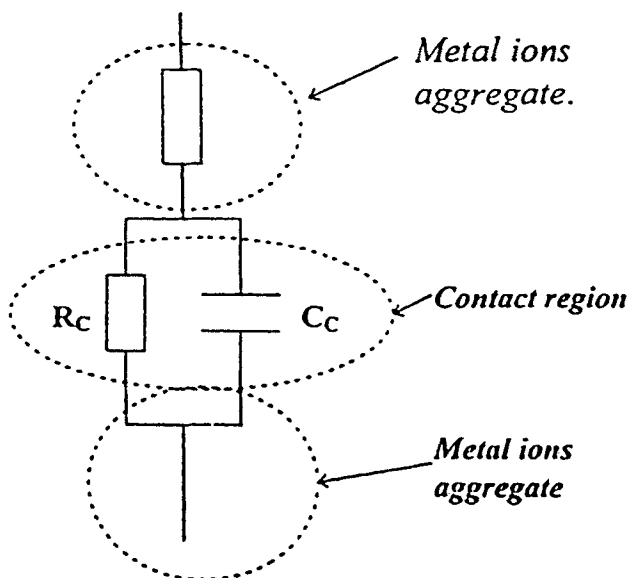


FIGURE 5 Equivalent resistor-capacitor circuit in the contact region of metal ions aggregate.

UV-visible absorption maxims of pure PMMA and the prepared copolymers and terpolymer samples are summarized in Table (IV).

Pure PMMA sample is transparent in the range from 200 to 800 nm. An absorption hump starts at 300 nm with absorption value 0.12. At 290 nm the absorption increases with a high rate and shows a maximum in the range of 250–280 nm. It is possible to say that PMMA shows two absorption bands at nearly 280 nm with high intensity and another with low intensity at 250 nm to 265 nm.

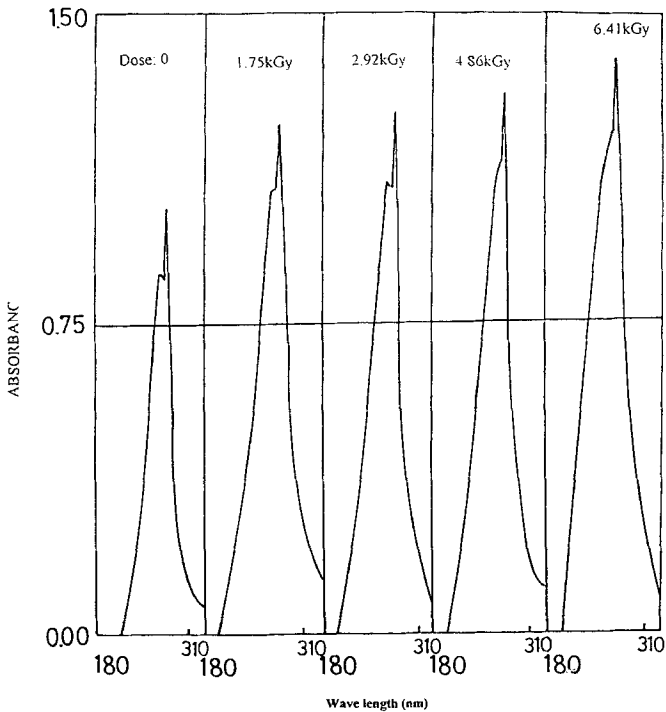


FIGURE 6 UV spectra of PMMA at different γ -exposure doses.

The high intensity absorption band in the 250–280 nm region could be attributed to the π - π^* transition superimposed with the absorption bands of MMA monomer and initiator. This agrees well with the work of Fleming [23] on the effect of different initiators and monomer concentration on the UV spectrum of PMMA. The PMMA without monomer and initiator residues is transparent to UV. The UV-visible absorption characteristics of poly methyl methacrylate (PMMA) have been reported by different authors [24, 25]. The influence of self-absorption in some organic dyes doped within PMMA as an optical wave guide on the light transmission efficiency have been evaluated by Sansegret *et al.* [26]. The transmission of light through PMMA as optical wave guide have been reported by Kagami *et al.* [27].

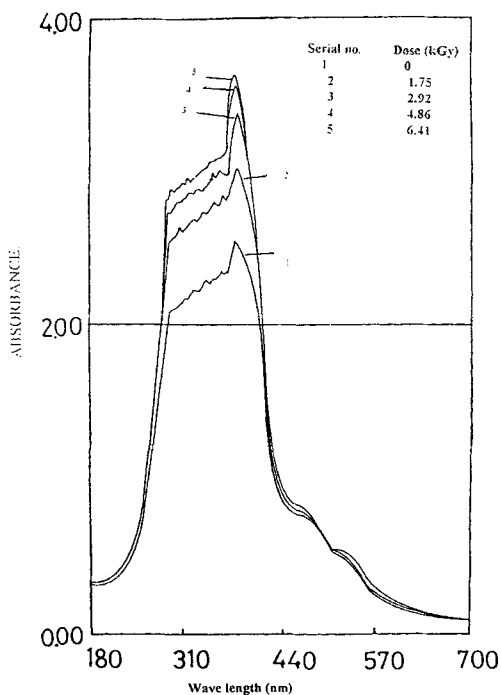


FIGURE 7 UV-Visible spectra of MMA-Fe acrylate (8:1 molar ratio) copolymer at different γ -exposure doses.

The PMMA-acrylic and copolymer sample is transparent in the visible region 400 to 800 nm, meanwhile MMA-Fe-acrylate, MMA-Mn-acrylate copolymer and MMA-Fe-acrylate-Mn-acrylate terpolymer show an low absorption band at 468–511, 490 and 410–569 nm (*cf.* Tab. IV). The absorption bands of the copolymer and terpolymer samples appear with change in the band position in the spectra of copolymer and terpolymer samples. This change in the position of the absorption band allow to predict that there is an interaction between the transition metal acrylate unit and the MMA monomer units. An absorption band of low intensity in the region 290–360 nm, is the most typical absorption band for carbonyl compounds usually indicates an $n-\pi^*$ transition.

To analyze the effect of γ -irradiation on these samples. The relation between the absorption values and the exposure doses are

TABLE IV UV-visible absorption bands of MMA homo-,co-and terpolymer samples

Sample no.	Polymer name & composition in molar ratio	Maximum absorption $\gamma_{max}(nm)$	Assignment
1	PMMA	280	$\pi-\pi^*$ - transition
3	MMA-AA Copolymer (8:1)	278 ^{sh} 280 ^s	$\pi-\pi^*$ - transition $\pi-\pi^*$ - transition
7	MMA-Fe Acr. Copolymer (8:1)	(275 - 324) ^b 371 ^s 468 ^{sh} & 511 ^{sh}	$\pi-\pi^*$ - transition n- π^* - transition in the visible region due to the colour of the transition metal acrylate unit.
11	MMA-Mn Acr Copolymer (8:1)	285sh & 297s 310s 490sh	$\pi-\pi^*$ - transition n- π^* - transition in the visible region due to the colour of the transition metal acrylate unit.
14	MMA-Fe Acr -Mn Acr. Terpolymer MMA:Fe & Mn acrylates (8:1)]	274 ^{sh} & 297 ^s 339 ^{sh} 410 ^{sh} , 475 ^b & 569 ^b	$\pi-\pi^*$ - transition n- π^* - transition in the visible region due to the colour of the transition metal acrylate unit

N.B: S = Sharp; b = broad & sh = sholder.
AA = Acylic Acid.

shown in Figure (8) and are summarized in Table V. The slopes of this linear relationship are calculated and shown in Table V. It is clear from this data that a distinct increase in the absorption of MMA-Fe acrylate copolymer is observed with increasing the γ -irradiation dose.

This suggests that MMA-Fe acrylate copolymer is the more sensitive polymer composition to be used as plastic dosimeter in the dose range used.

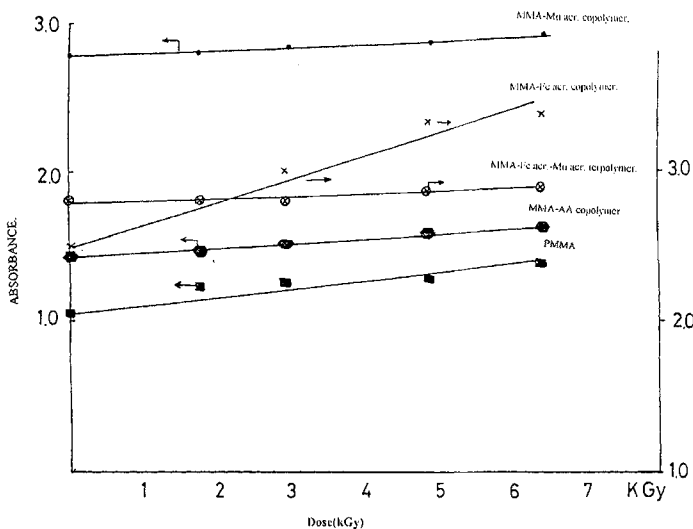


FIGURE 8 The relation between γ -exposure doses and absorption at λ_{\max} for different polymer samples

TABLE V Relation between absorbance and exposure dose quantity at maximum absorption band with the increasing of the γ -irradiation dose for different polymer samples

Polymer name	λ_{\max} (nm)	Absorbance Dose Quantity (K.Gy)					Slope $\times 10^4$
		0	1.75	2.92	4.86	6.41	
PMMA	280 ^s	1.04	1.23	1.26	1.32	1.39	4.80
MMA-AA Copolymer	280 ^s	1.43	1.48	1.52	1.59	1.64	3.00
MMA-Fe Acr. Copolymer	371 ^s	2.52	2.79	3.01	3.33	3.38	15.80
MMA-Mn Acr. Copolymer	297 ^s	2.78	2.80	2.84	2.87	2.91	1.70
MMA-Mn Acr.-Fe Acr. Terpolymer.	297 ^s	2.81	2.81	2.82	2.87	2.89	1.53

NB: S = strong.

4. CONCLUSIONS

1. Copolymers of Fe acrylate-methyl methacrylate MMA, Mn acrylate-MMA and terpolymer of Fe acrylate-Mn acrylate-MMA

- were prepared by bulk technique using benzoyl peroxide as free radical initiator under nitrogen atmosphere at 60°C.
2. A.C electrical conductivity measurements of the prepared modified PMMA showed that the electronic conduction mechanism dominates in the temperature range 35–100°C for the copolymer and terpolymer samples.
 3. The frequency dependence of a.c conductivity data showed that the relaxation frequency depends on the type and concentration of the metal acrylate units.
 4. The shift in the position of some absorption bands in the UV-visible spectrum of the modified PMMA was attributed to the interaction between the transition metal acrylate unit and MMA monomer.
 5. The data suggests that, MMA-Fe acrylate copolymer samples could be used as plastic dosimeter for γ -rays in the dose range 1.75–6.41 KGy as deduced from UV-visible absorption spectra.

Acknowledgments

The authors would like to thank Dr. M. A. El-Ahdal, Department of Radiation Protection and Dosimetry, National Center for Radiation Research and Technology, Nasr City, Cairo, Egypt for irradiation the samples. Also we acknowledge the use of facilities in the center for microanalysis, Cairo University, Cairo, Egypt, for elemental analysis and optical measurements.

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