STM JOURNALS

Journal of Polymer & Composites
ISSN: 2321-2810(online), ISSN: 2321-8525(print)
Volume 4, Issue 3
www.stmjournals.com

Characterization and Gamma Irradiated MA-EMA Copolymer by ESR and FTIR Techniques

B. Sanjeeva Rao[1], N. Srinivasa Rao[2], B Suresh Babu[3], M. Papi Reddy[4]*

[1]Department of Physics, Government Degree College, Mulugu, Warangal District, Telangana, India
[2]Department of Physics, JVR Government College, Sathupally, Khammam District, Telangana, India
[3]Department of Chemistry, Kakatiya Degree College, Hanumakonda, Telangana, India
[4]Department of Physics, Trinity Degree college, Peddapally, Telangana

Abstract

Gamma irradiation effect of methacrylamide-ethyl methacrylate (MA-EMA) copolymer has been investigated by electron spin resonance (ESR) and Fourier Transform infrared (FTIR) spectroscopic techniques. The ESR spectrum observed for gamma irradiated MA-EMA copolymer has shown resolved hyperfine (hf) pattern at lower temperatures (77K); while at higher temperatures the spectrum is appeared to be broadened. Fourier Transform Infrared spectra of pure and gamma irradiated MA-EMA copolymer have been recorded for the copolymer irradiated to different radiation doses to ascertain chemical changes induced by gamma irradiation. The variation in intensity of 3420, 1660, 1250, 1160 and 1020 cm^{-1} absorption bands is observed, which are attributed cleavage of ester, amide groups on irradiation.

Keywords: *Electron Spin Resonance (ESR), Infrared (IR), Spectroscopy, Gamma irradiation, MA-EMA copolymer, radiation*

****Author for Correspondence*** E-mail: physanjeev@gmail.com

INTRODUCTION

Although various types of polymer materials are widely available, synthesis and characterization of new materials is still needed, to meet various scientific and technological applications. Polyacrylates and acrylarmide polymers and copolymers find applications in industry as well as science [1]. Homopolymer of methacrylamide is known to crosslink; while ethylmethacrylate homopolymer is reported to degrade under the influence of high energy radiation [2]. Thus, it is interesting to note the degradation characteristics of copolymer with methacrylamide and ethylmethacrylate as comonomers.

Electron spin resonance spectroscopy is a useful tool in indentifying the radical species formed on irradiation of polymers [3]. Infrared spectroscopy, together with ESR technique has been successfully used to probe radiation induced changes in polymers and copolymers [4]. In the present studies the authors have made an attempt to characterize gamma irradiation effects in MA-EMA copolymer by ESR and FTIR techniques.

EXPERIMENTAL METHOD

Synthesis and characterization of methacrylamide – ethylmethacrylate MA-EMA copolymer has been described by Sreenivasulu [5]. ESR spectra of irradiated copolymer have been recorded on a GEOL spectrometer operating at X-band frequencies and 100 KHz modulation. Infrared (FTIR) spectra of pure and gamma irradiated MA-EMA copolymer has been recorded on PERKIN-ELMER 283 model spectrometer and intensities of various absorption bands are noted. Potassium Bromide (KBr)-MA-EMA copolymer pellets have been used for IR measurements. Gamma Irradiations were carried out with a cobalt 60, gamma source at a dose rate of 0.2 M.rad/h in air at room temperature (RT).

RESULTS AND DISCUSSION

ESR spectrum of Gamma Irradiated MA-EMA copolymer at liquid nitrogen temperature (LNT) is as shown in Figure 1; whereas the spectrum recorded at RT as shown in Figure 2.

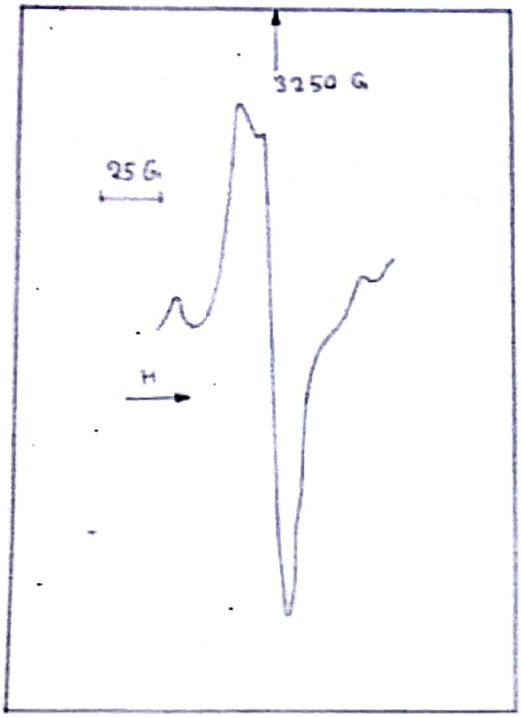

Fig. 1: *ESR Spectra of Irradiated MA EMA Copolymer at LNT.*

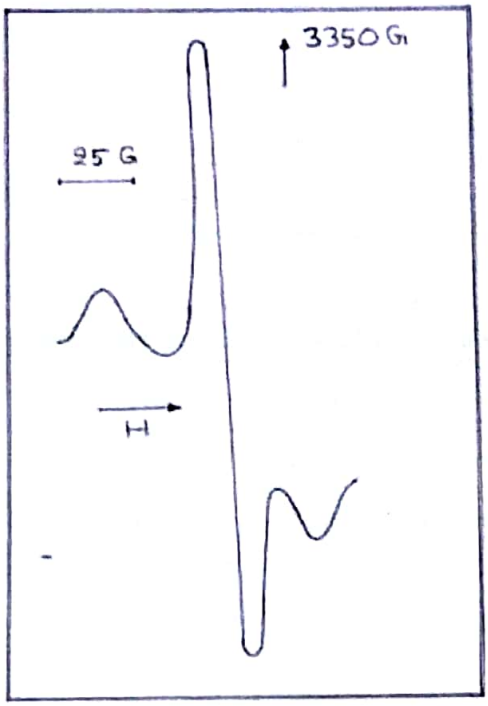

Fig. 2: *ESR Spectra of Irradiated MA EMA Copolymer at RT.*

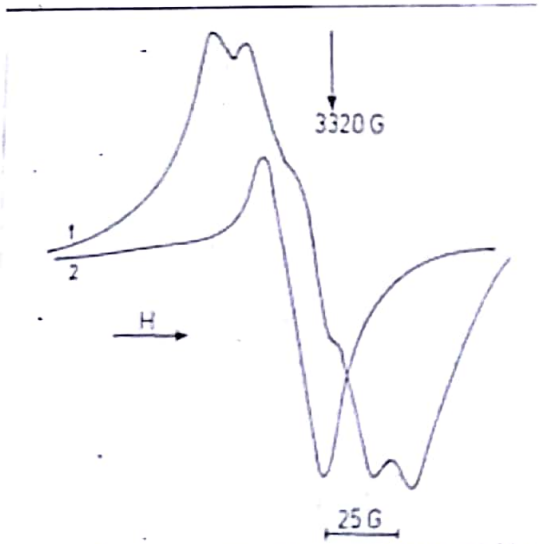

Fig. 3: *Component ESR Spectra of MA-EMA at LNT.*

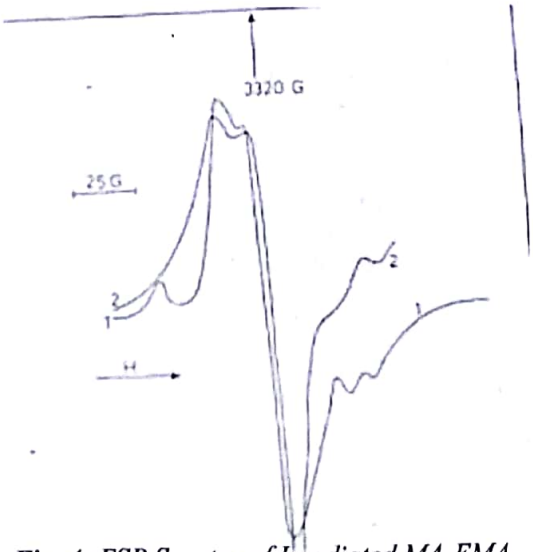

Fig. 4: *ESR Spectra of Irradiated MA-EMA Copoly Copolymer at LNT.*

These spectra composed of inherent hyperfine lines and resemble the spectra observed for several acrylates, i.e., poly(methyl methacrylate) (PMMA), poly(acrylic acid) (PAA), poly(methacrylic acid) (PMAA) [6–8]. Further when compared to the observed spectrum at lower temperatures (LNT), the spectrum at RT is observed to be broadened.

The ESR spectra observed for polyacrylates are reported to be a superposition of component spectra arising from macro-radicals and free radicals giving components singlet spectrum [6–8]. As such ESR spectra of irradiated MA-EMA copolymer are also supposed to have contributions from same type of free radicals.

Table 1: Magnetic Parameters of Gamma Irradiated MA-EMA Copolymer.

Temperature	Line Width a_{iG}	Relative Intensity $Y_{max\,i}$	Centre of spectrum X_{oi} G	Hyperfine Splitting G		n_i	m_i
				A_i	B_i		
LNT	13.0	12.0	3220	23.0	12.0	2	5
LNT	3.5	12.0	3220	23.0	12.0	2	5
RT	4.0	11.0	3220	23.0	10.0	2	5

For singlet $n_i=m_i=1$ $A_i=B_i=0$

The spectra observed at LNT and RT are simulated by ~~metal curve fitting method~~ discussed earlier [9, 10]. As such the spectrum observed at LNT can be simulated with the component spectra shown in Figure 3, Curve-1. Figure 3 is the component multiplet; while Curve-2 is component singlet.

Component multiplet is be simulated with the values of n_i=2, m_i=5, A_i=23.0G and B_i=12.0G. The values of magnetic parameters indicate the presence of one α- and four β-protons. The free radical having such a structure is of the type .~CH_2-CH-CH_2~. Component singlet spectrum is simulated to the values of n_i=1, m_i=1, A_i= B_i= 0G and is assigned to $COOCH_2C_3H$ and $CONH_2$ free radicals. The superposition of singlets arising due to ester radicals ($COOCH_2CH_3$) and amide radicals ($CONH_2$) together with the component spectra arising macro-radicals give the observed ESR spectrum of Gamma irradiated MA-EMA copolymer at LNT. In order to verify the goodness of the fit, a comparison of experimental and simulated ESR spectra is made as shown in Figure 4. Curve 1 is experimental spectrum while Curve 2 is superposed or theoretical spectrum. The magnetic parameter employed to simulate the component spectra are as listed in Table 1.

The macro-radicals may give more than three hyperfine lines depending on the magnetic environment around the unpaired electron brought by physical conditions like temperature and morphology [11]. The broadening of the ESR spectrum at RT is thought to be associated with hindered motion of end methylene/ methyl groups of macro-radicals [12]. Formation of ester and amide radicals have been confirmed by measuring the FTIR spectra of pure gamma irradiated MA-EMA copolymer. Fourier Transform Infrared spectra of pure MA-EMA copolymer has shown absorption bands at various positions. Among them the 3420 cm^{-1} absorption band is assigned to amide groups (N-H stretching vibration), 1720 cm^{-1} absorption band is assigned to ester carbonyle functional groups, while 1660 cm^{-1} absorption bands is due to amide carbonyl vibrations.

The methyl/methylene groups give characteristic absorption band at 2920 and 1250 cm^{-1}. The absorption bands at 1160 and 1020 cm^{-1} position arise due to C-O-C vibrations [11]. With the increase in radiation dose, Intensity of the absorption bands is changed with radiation dose as depicted in Figures 5 and 6.

Intensity of 3420 and 1660 cm^{-1} bands is found to decrease with the increase of radiation dose (Curve 1, Curve 3 in Figure 5), indicating the disassociation of $-NH_2$ and amide carbonyl groups (-$CONH_2$), from the main chain, on irradiation. Dissociation of these groups may lead to the formation of amide type free radicals ($CONH_2$) which may give component singlet spectrum. Intensity variation of 1720 cm^{-1} absorption band (ester carbonyl), 2920, 1250 cm^{-1} absorption bands (methyl/methylene groups) 1160 and 1020 cm^{-1} absorption bands (-C-O-C groups) with radiation dose are as shown in Curve 2 Figure 5, curve 2 and curve 3 in Figure 6. The results indicate cleavage of ester groups (-$COOCH_2CH_3$) from the main chain of the copolymers, leading to the formation of $COOCH_2CH_3$ radicals. The ester radicals may also give an ESR singlet spectrum. The remaining chains of the copolymer may give macro-radicals CH_2-CH-CH_3, which may give component multiplet ESR spectrum.

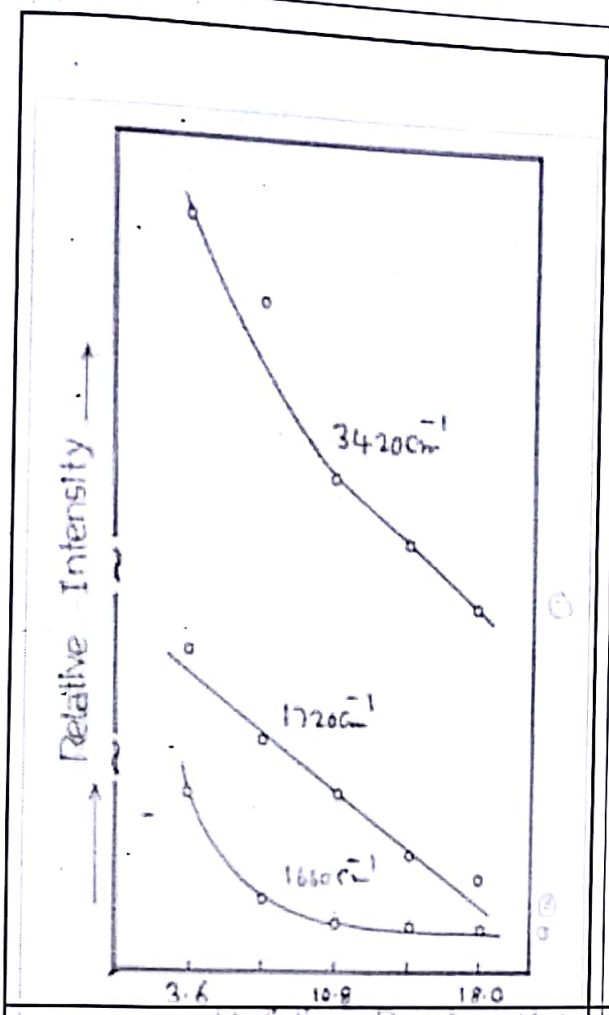

Fig. 5: Intensity Variation of FTIR with Radiation dose

Curve 1 3420cm^{-1}, Curve 2 1720cm^{-1}

Curve 3: 1660 cm^{-1}

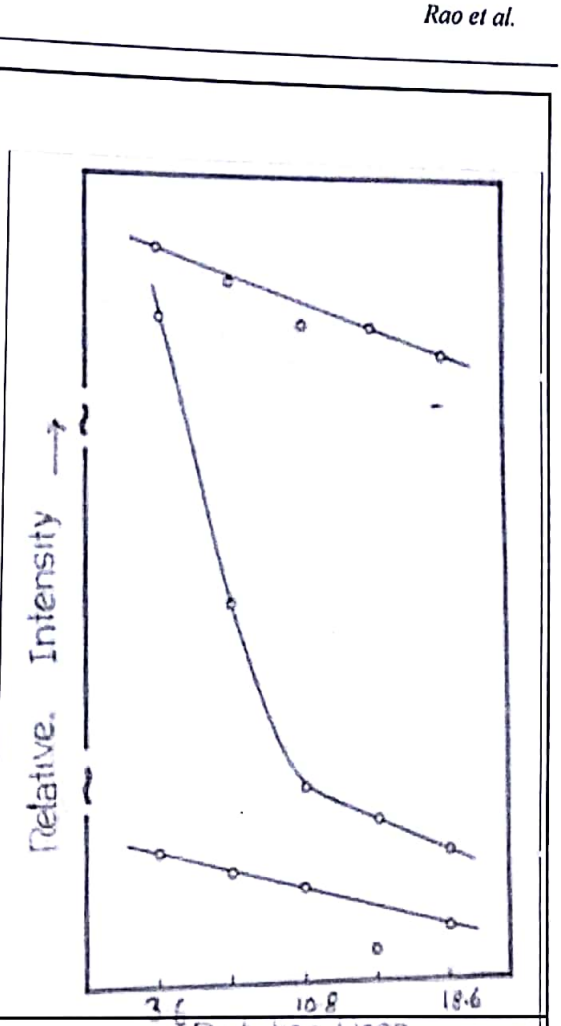

Fig. 6: Intensity Variation of FTIR Absorption Bands Absorption Bands with Radiation Dose

Curve 1 1250cm^{-1}, Curve 21160cm^{-1}

Curve 3: 1020 cm^{-1}

CONCLUSION

In conclusion, the irradiated MA-EMA copolymer may contain at least three types of free radicals species; (i) macro-radicals of the type CH_2-CH-CH_3, (ii) ester radicals ($COOCH_2CH_3$), and (iii) amide radicals ($CONH_2$). The ESR spectra arising from these components may be superposed to obtain the spectrum at LNT. The broadening of the RT spectrum is assigned to be due to hindered rotation of methyl/methylene groups brought out by the change of the temperature from LNT to RT. This can be confirmed by measuring FTIR spectra of copolymer.

REFERENCES

1. Baijal MD. *Plastics, Polymer Science and Technology*, Wiley-interscience, 21, 1982.
2. Charlesby A. *Atomic Radiation and polymers*, International Series of Monographs on Radiation Effects in

Materials, Pergamon Press, 1, 1960, 426–440p.

3. Subbarami Reddy N., Sudarsan Reddy Y, Sanjeeva Rao B. *Radiation Effects and Defects in Solids*, Taylor & Francis, *1994;* 129: 273–278p.
4. Sanjeeva Rao B, Indira S, Sridhar V,and G.Punnaiah *Radiation Effects and Defects in Solids*, Taylor & Francis, 2005; 160: 245p.
5. Sreenivaslu B. Synthesis and Characterization of Some Polymers, and Exploring Chapter-II [*Ph.D. Dissertation*], Kakatiya University, Warangal, 1992.
6. Tatar L, Kaptan HY. *J Polym Sci. B.* 1997; 35: 2195p.
7. Sanjeeva Rao B, Ramakrishna Murthy M. *J Polym Sci B.* 1989; 27: 1187p.
8. Sanjeeva Rao B, Md. Fasiul Hasan, Subbarami Reddy N,Y.Sudarsan Reddy. *J Polym Sci B.* 1994; 32: 1289p.

9. Sanjeeva Rao B, Ramakrishna Murthy M. *J Polym Sci B.* 1987; 25: 1897p.
10. Ramakrishna Murthy M, Sanjeeva Rao B. *J Polym Sci B.* 1990; 28: 133p.
11. Iwasaki M, Sakai I. *J Polym Sci.* 1969; A7: 1537p.
12. Ranby B. *Experimental Methods in Polymers*, John Wiley, New York, 1980.

Cite this Article
Sanjeeva Rao B, Srinivasa Rao N, Suresh Babu B, *et al.* Characterization and Gamma Irradiated MA-EMA copolymer by ESR and FTIR Techniques, *Journal of Polymer & Composites.* 2016; 4(3):