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## Temperature, Dose Dependent Radical Decay in Gamma Irradiated MA AMPS Copolymers.

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### ABSTRACT

Gamma Irradiation effects in methacrylamide (MA) – 2-acrylamido 2- methyl propane sulphonic acid (MA AMPS) copolymers have been investigated using electron spin resonance(ESR) and Fourier transform infrared(FTIR) techniques. Formation of free radicals in gamma irradiated copolymers is found to depend on composition temperature and radiation dose. The ESR spectra observed under various conditions have been analysed by the computer simulation technique and constituent component spectra were assigned to different free radical species produced on irradiation of the copolymer. The copolymer with high AMPS composition preferably undergo degradation through the cleavage of methyl sulphonic acid groups on AMPS part of copolymer leading to the formation of macro radicals ( $\sim\text{CH}_2 - \text{CH} - \text{CH}_2 \sim$ ); while copolymer with less AMPS composition leads to the cleavage on AA part, with the dissociation of amide ( $\text{CONH}_2$ ) groups takes place forming  $\sim\text{CH}_2 - \text{C}(\text{CH}_3) - \text{CH}_2 \sim$  radicals. The free radicals formed in MA copolymer are found to decay with temperature and finally disappear at temperature designated as radical decay temperature. Which depends on composition of co-monomers. Irradiating the copolymer to higher radiation doses had a diminishing effect on the formation of free radicals. The results are further confirmed by recording the FTIR spectra of unirradiated and irradiated copolymers under different condition.

**Keywords:** Methacrylamide-AMPS copolymer, ESR spectra, gamma irradiation, free radicals, computer simulations.

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### INTRODUCTION

AMPS(2-acrylamide-2-methyl Propane Sulfonic acid) homopolymer and copolymers have become a topic of research in view of their application in different branches of science and technology(1). Radiation treatment of polymers and copolymers lead to changes in their chemical structure altering physico-chemical properties. Further, improvement in radiation resistance can also be achieved by copolymerization [2]. Hill et al.[3,4] have reported radiation induced processes in styrene – acrylonitrile copolymers. The radiation stability of the copolymer is found to be in between the two homopolymers. Regarding AMPS copolymer. Sanjeeva Rao et al. [5] have reported that radiation induced changes in acryl amide –AMPS (AA) copolymers depend on composition, temperature and radiation dose. Indira et al.[6] have reported that even in the presence the bulkier guanidine methacrylate (GMA) group, the AMPS copolymer undergo only on the AMPS part of the copolymer. The free radicals formed on irradiation of MAAMPS copolymer with 50:50 and 80:20 compositions have been identified by Sridhar et al.[7] and Reddy et al.[8].The aim of present paper is 1) To study radiation induced changes in MA copolymer of different composition 2) effect of temperature and radiation dose on the free radical produced in MA copolymer.(However effect of composition, temperature and radiation dose on formation of free radicals in irradiated MA copolymers has not been reported) Therefore the authorshave used the electron spin resonance and Fourier transform infrared techniques for this purpose.

### EXPERIMENTAL

Various compositions of Methacrylamide (MA) – AMPS copolymers in powder form were synthesised by Ranga Rao and Ravi Prasad [9]. The designation and properties of the copolymers is as listed in the Table 1. Formation of copolymers has been confirmed by elemental analysis, FTIR and NMR techniques [10]. The chemical formula of copolymer is as shown in Fig 1.

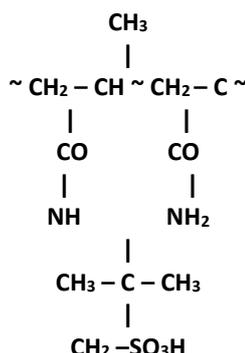


Fig 1: Chemical formula of MA AMPS copolymer

Table-1: Designation of copolymers

| S.NO | Composition of methacrylamide | Composition of AMPS | Designation of copolymer |
|------|-------------------------------|---------------------|--------------------------|
| 1    | 50                            | 50                  | MA55                     |
| 2    | 60                            | 40                  | MA64                     |
| 3    | 70                            | 30                  | MA73                     |
| 4    | 80                            | 20                  | MA82                     |

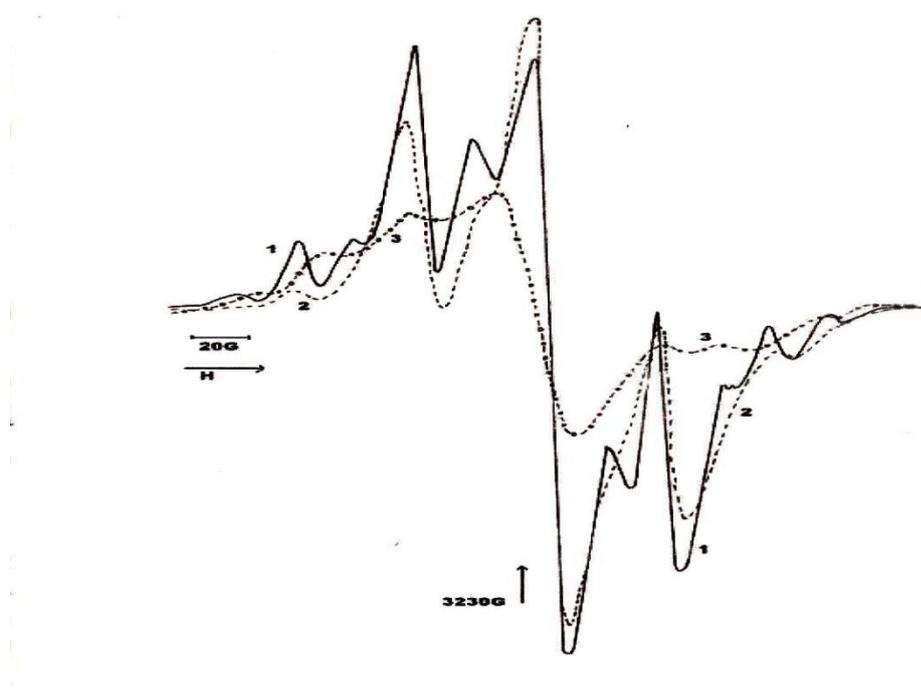
The copolymers are irradiated with Cobalt-60 gamma ray source which delivers radiation dose of adose rate of 15 KGray/hour in air, at room temperature. ESR spectra of irradiated copolymers have been recorded on Varian E-line spectrometer operating at X-band frequencies and 100 KHz modulation. All the spectra are records are identical condition i e, with same receiver gain and power frequency. Necessary accessories are fitted to the spectrometer to record the variable temperature (VT) ESR spectra. FTIR spectra of unirradiated and irradiated copolymer have been recorded on NICOLET 283 model spectrometer for the pellets of copolymer consisting of potassium bromide.

## SIMULATION OF ESR SPECTRA

Since the ESR spectra of irradiated MA copolymers possess ill resolved hyperfine structure analysis of ESR spectra has been made using computer simulation technique [11]. Based on various possibilities of chain cleavages in MA copolymer, presence of different types of free radicals is possible. Such free radicals give respective component spectra, which coal sec to form broadened, ill resolved experimental spectra, as observed in the present studies. Therefore separation of component spectra is desired to assign the total ESR spectrum. Component spectra from all such expected free radicals are simulated theoretically using magnetic parameters like relative intensity ( $Y_{maxi}$ ), line width ( $a_i$ ), centre of spectrum ( $X_{oi}$ ), hyperfine splittings ( $A_i, B_i$ ) and number of hyperfine lines resulting from adjacent nuclei ( $n_i, m_i$ ) the magnetic parameters and their calculations are as described previously(R,T). The component spectra generated by this method are superposed in appropriate proportion to match the experimental spectrum in aspects like intensity and line position. The value of mean square deviation ( $S_e^2$ ) is calculated between the observed and theoretical intensity values. Several trials have been made and the trial with minimum value of mean square deviation is treated as the best fit.

## RESULTS AND DISCUSSION

ESR spectra of irradiated MA copolymers with different compositions are as shown a fig.2Curves 1,2 and 3 refers to the spectra of irradiated MA copolymer with 55,64 and 82 compositions.

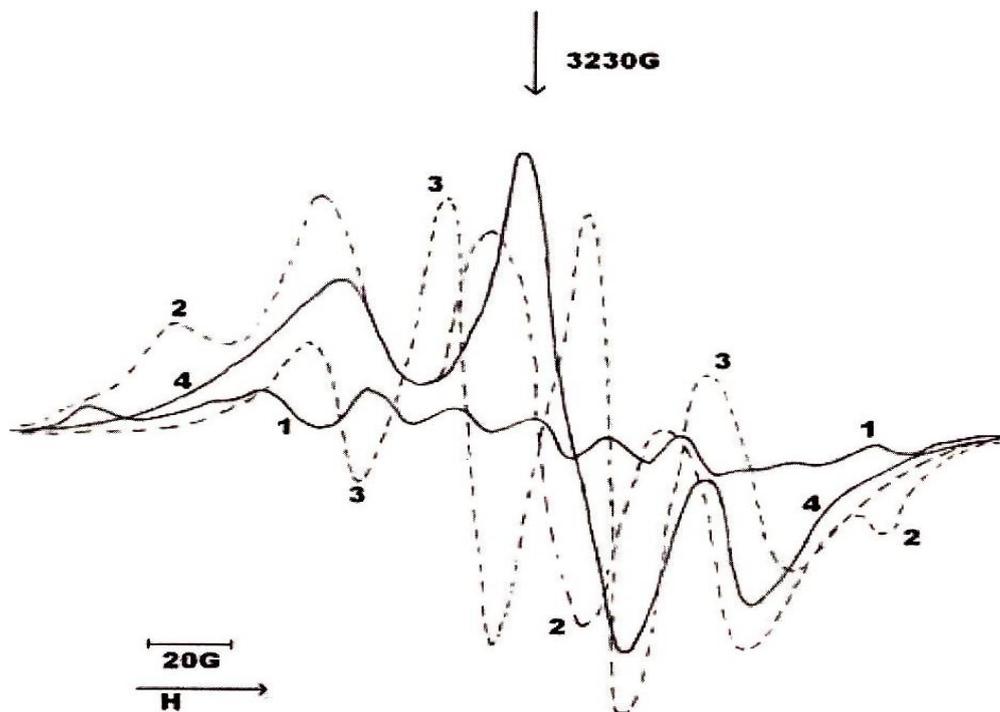


**Fig. 2: ESR spectra of irradiated MA copolymer of different compositions.**  
 Curve 1 50 : 50 composition; Curve 2 60 : 40 composition; Curve 3 80 : 20 composition

### Composition variation.

Curve 1 Fig. 2 (ESR spectrum of irradiated MA55 copolymer at room temperature)is simulated using the component spectra shown in Fig.3. Curve1 is simulated with the values of  $n_i=2, m_i=5, A_i=23G, B_i=12G$ . therefore Free radical responsible for this component should have one alpha and four beta protons i.e.  $\sim CH_2 - CH - CH_2 \sim$  (I). Curve 2 is simulated with the values of  $n_i=1, m_i = 5, A_i = 22G, B_i = 0G$  indicating the presence of only four protons i.e.  $\sim CH_2 - C(CH_3) - CH_2 \sim$ (II)/  $CH_3 - C-CH_3 - C(\sim) - CH_3$  (III). Curve 3 is generated with the values of  $n_i = 4, m_i = 0, A_i = 23G, B_i = 0G$  indicating the presence of three protons and it is assigned to methyl radicals ( $CH_3$ )(IV). Curve 4 is simulated with the value of  $n_i= 3, m_i = 1, A_i = 12G$  which is assigned to methyl sulphonic acid radicals  $CH_2SO_3H$  (IV). The values of magnetic parameters are as listed in Table 2.The methyl sulphonic acid radicals (IV) reduce to form methyl radicals (III)(7,8).The remaining chains of AMPS parts undergo further

reaction to form macro radicals (I) and network structures. The formation network structures was also reported by Aggour et al.[12,13]. Therefore formation of radicals I, II, III and IV is justified. The results suggest that on irradiation the MA 55 copolymer induce chain cleavages on both MA and AMPS parts.



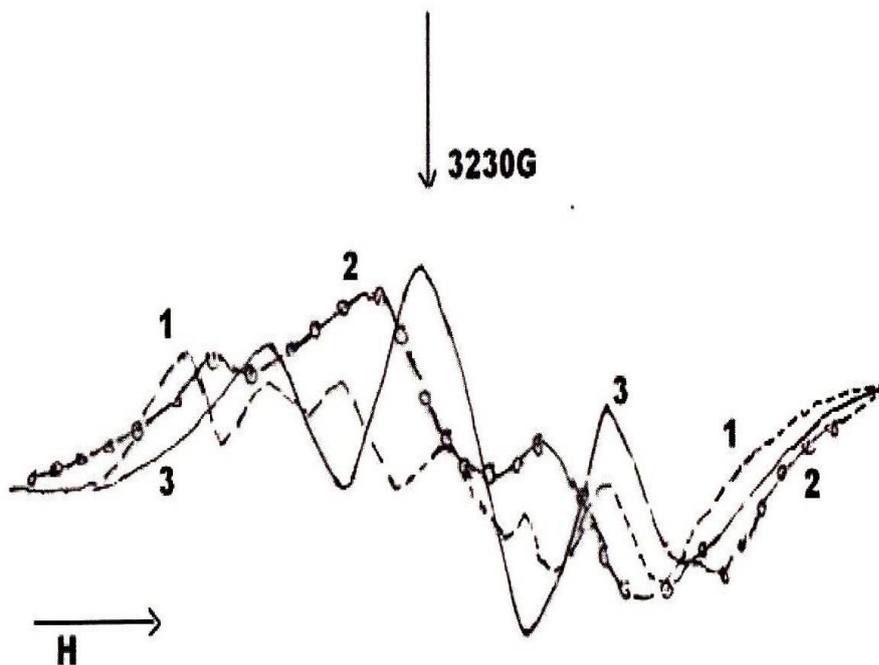
**Fig 3: Component spectra of irradiated MA55 copolymer.**  
**Curve 1 Component multiplet; Curve 2 Component quintet**  
**Curve 3 Component quartet; Curve 4 Component triplet**

**Table-2: Magnetic parameters of irradiated MA55 Copolymer at different temperatures**

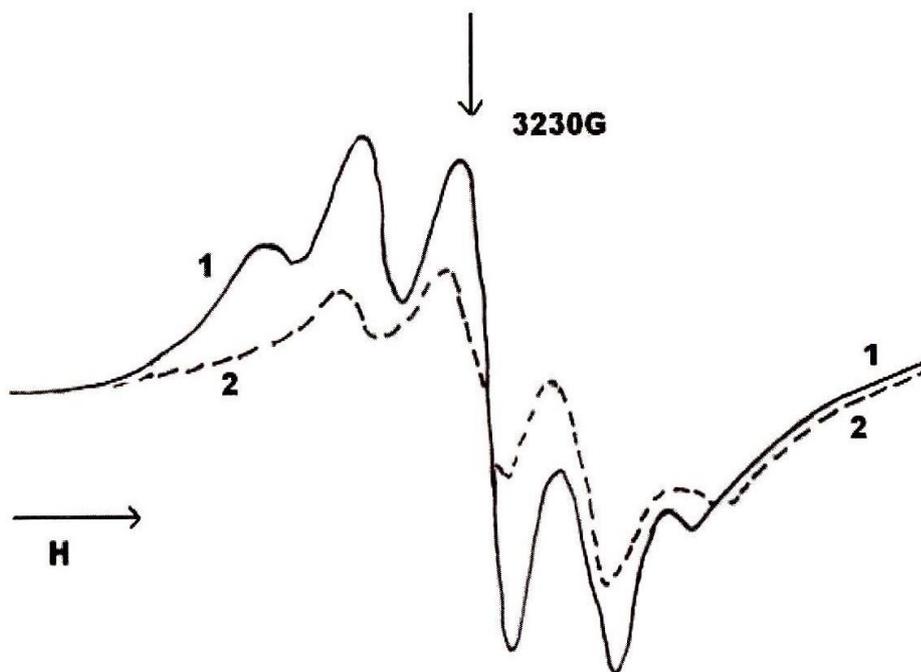
| S.NO | composition | components    | Relative intensity | Line width | Centre of spectrum | H <sub>f</sub> splitting |    | n <sub>i</sub> | m <sub>i</sub> | S <sub>e</sub> <sup>2</sup> |
|------|-------------|---------------|--------------------|------------|--------------------|--------------------------|----|----------------|----------------|-----------------------------|
|      |             |               |                    |            |                    | A                        | B  |                |                |                             |
| 1    | 325         | Macro radical | 2.3                | 7          | 3225               | 13                       | 23 | 2              | 5              | 0.1525                      |
|      |             | Quintet       | 16.5               | 13         | 3230               | 0                        | 22 | 1              | 5              |                             |
|      |             | Quartet       | 10                 | 5          | 3230               | 18                       | 0  | 4              | 1              |                             |
|      |             | Triplet       | 40                 | 15         | 3235               | 24                       | 0  | 3              | 1              |                             |
| 2    | 350         | Macro radical | 2                  | 7          | 3225               | 13                       | 23 | 2              | 5              | 0.133                       |
| 3    | 370         | Macro radical | 1.5                | 15         | 3234               | 12                       | 23 | 2              | 5              | 0.12                        |

ESR spectrum of irradiated MA64 copolymer possess six hyperfine lines as shown in curve 2, Fig. 2. The spectrum can be simulated using the component spectra shown in Fig.4. Curve 1 is the component multiplet which is simulated with values of n<sub>i</sub>=2, m<sub>i</sub>=5 A<sub>i</sub>=23, B<sub>i</sub>=12 and assigned due to macroradical, Curve 2 is component quartet simulated with n<sub>i</sub>=4, m<sub>i</sub>=1 and A<sub>i</sub>=23, B<sub>i</sub>=0 and Curve 3 is component triplet simulated with n<sub>i</sub>=3, m<sub>i</sub>=1 A<sub>i</sub>=23, B<sub>i</sub>=0. The component spectra are attributed to radicals I, III and IV. Regarding MA82 copolymer, the ESR spectrum( curves3 Fig1), it is simulated with the superposition of component quintet with n<sub>i</sub>=1, m<sub>i</sub>=5 A<sub>i</sub>=0 B<sub>i</sub>=23 and quartet spectra simulated with n<sub>i</sub>=4, m<sub>i</sub>=0 A<sub>i</sub>=23, B<sub>i</sub>=0 as shown in Fig.5 [7]. The quintet is assigned to ~CH<sub>2</sub>-C(CH<sub>3</sub>)-CH<sub>2</sub>~ (II) / CH<sub>3</sub>-C(~)-(CH<sub>3</sub>)~(III) and quartet is due to ~CH<sub>3</sub>(IV) radicals .

Further, the existence of macro radicals is ruled out in irradiated MA82 copolymer [7]. Magnetic parameters corresponding to the component spectra of various composition are as listed in Table 2. Therefore it is evident that MA copolymer with high AMPS composition undergoes multiple cleavages on MA and AMPS parts.; whereas the copolymer with less AMPS content preferably undergoes limited cleavages on MA part.



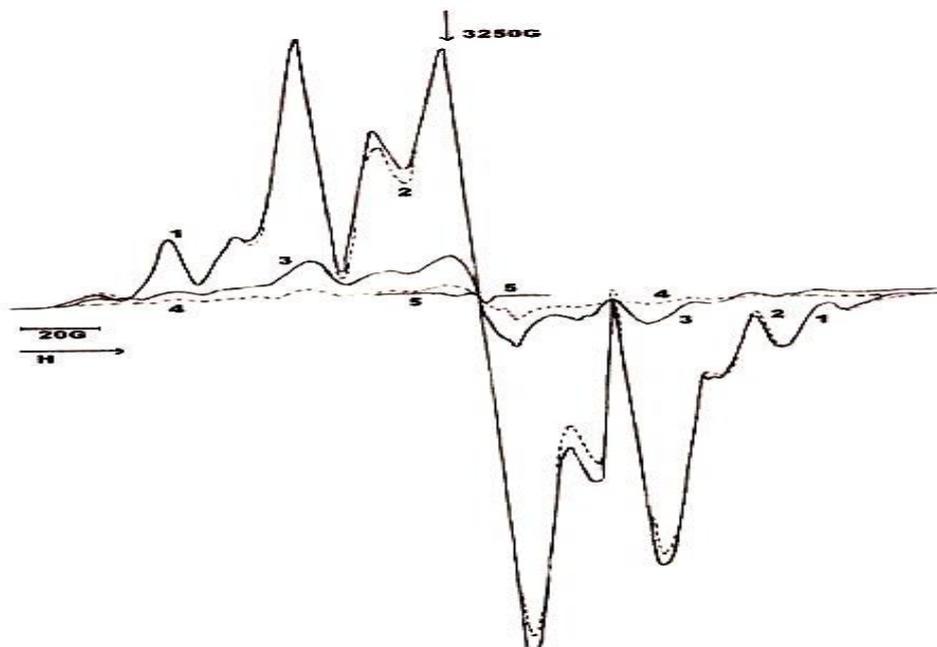
**Fig 4: Component spectra of irradiated MA64 copolymer.**  
 Curve 1 Component multiplet; Curve 2 Component quartet  
 Curve 3 Component triplet



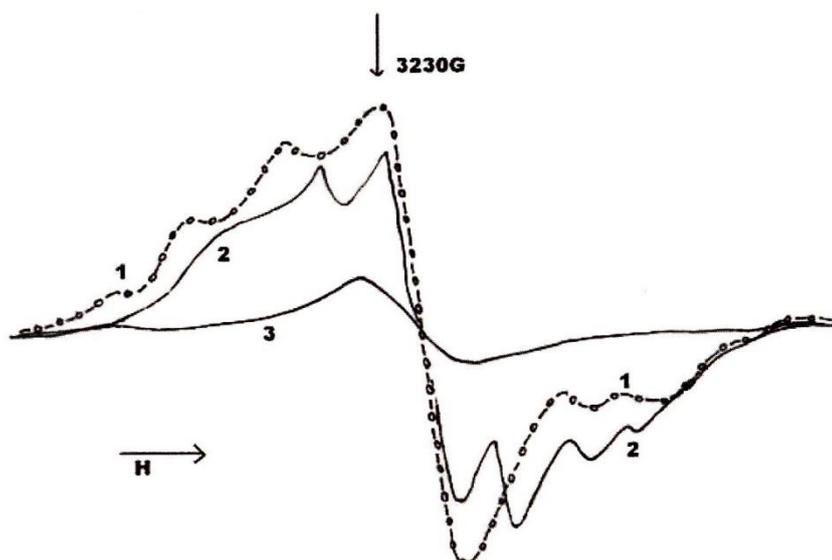
**Fig 5: Component spectra of irradiated MA82 copolymer.**  
 Curve 1 Component quintet; Curve 2 Component quartet

**Temperature variation:**

Area under ESR spectrum represent the free radical concentration. Variation of free radical concentration with temperature for MA55 and MA82 copolymer is as shown in Fig. 6 and Fig. 7 respectively. Intensity of the spectra is found to fall gradually with temperature.



**Fig 6: ESR spectra of irradiated MA55 copolymer at different temperatures. Curve 1 300K; Curve 2 325K; Curve 3 350K; Curve 4 375K; Curve 5 400K**



**Fig 7: ESR spectra of irradiated MA82 copolymer at different temperatures. Curve 1 300K; Curve 2 325K; Curve 3 400K**

**MA55 Copolymer:**

Regarding MA 55 copolymer, the spectrum observed at 325K is similar to that of RT. Hence almost the same component spectra [free radicals I, II, III and IV] are expected to present at 325K also. Beyond 325K a septet spectrum is observed at 350K. The septet transformed to triplet spectrum at 375K finally a singlet is

observed at 400K. The ESR signal completely vanished around 410K, which is designated as radical decay temperature ( $T_R$ ). Such type of radical decay with temperature has also been reported in gamma irradiated Acrylamide – AMPS (AA) copolymer [5]. The spectra observed at other temperatures have been simulated and component spectra are shown in Figs8 and Fig 9. Magnetic parameters corresponding to the component spectra at various temperatures are listed in Table 7. A plot of ESR intensity against temperature is as shown in Fig10.

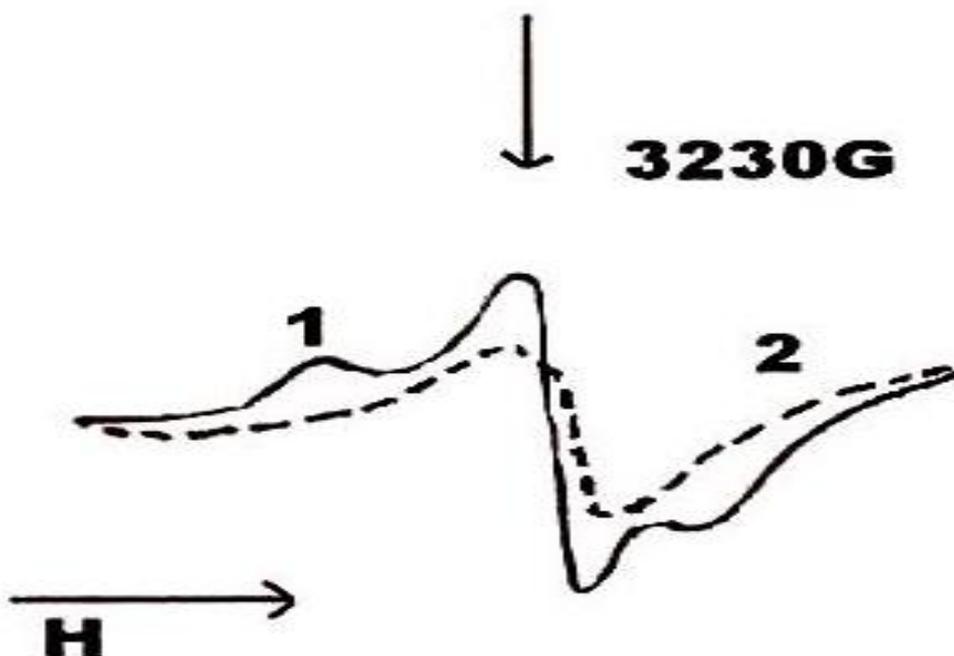


Fig 8: Component spectra of MA55 copolymer at 350K.  
Curve 1 Component multiplet; Curve 2 Component singlet

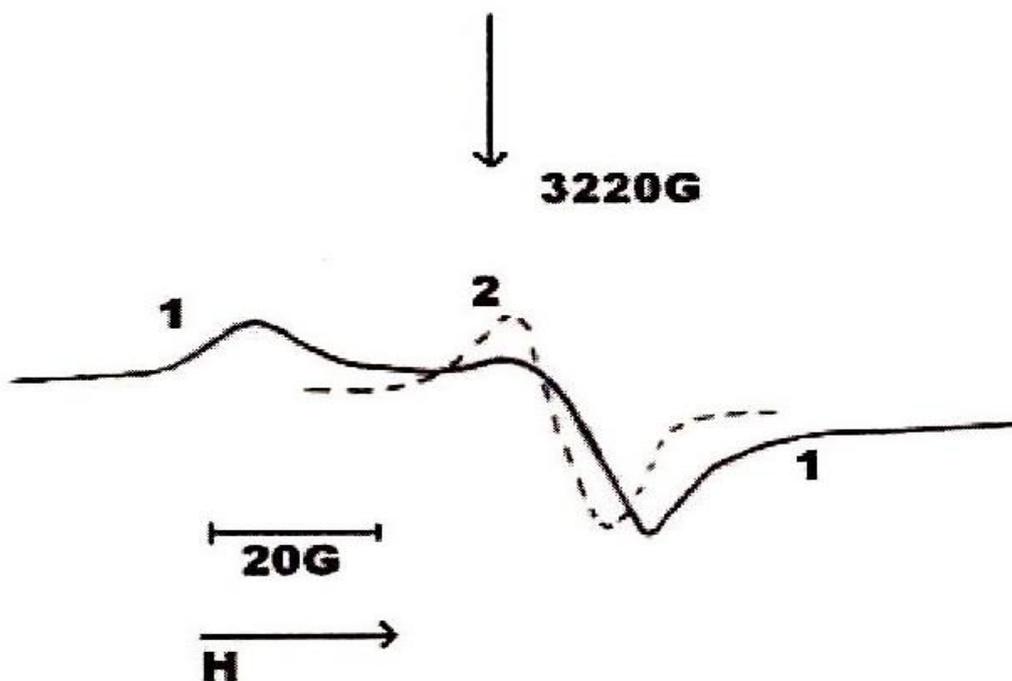


Fig 9: Component spectra of MA55 copolymer at 375K.  
Curve 1 Component multiplet; Curve 2 Component singlet

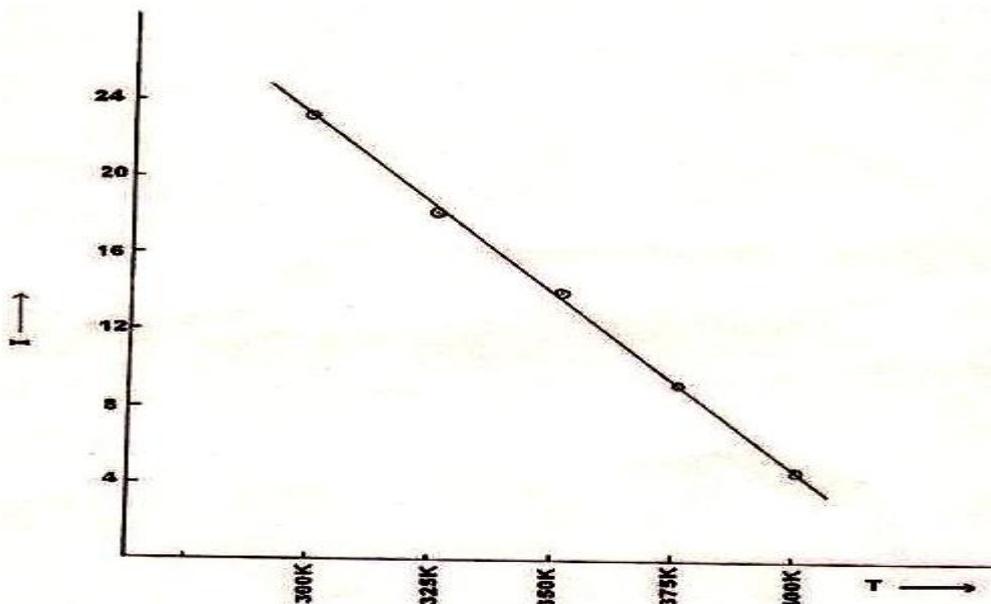


Fig 10: Variation of ESR intensity against temperature of MA55 copolymer

**MA 82 Copolymer:**

Variable temperature (VT) ESR spectra of gamma irradiated MA 82 copolymer have also been recorded as shown in Fig 7. The hyperfine pattern is stable up to 350K and spectral changes are appeared beyond this temperature. The ESR signal completely vanished around 420K. Sridhar et al.[7] have simulated the ESR spectra of MA 82 copolymer at RT and proposed the existence of chain radicals  $\sim \text{CH}_2 - \text{C}(\text{CH}_3) - \text{CH}_2 \sim / \text{CH}_3 - \text{C}(\sim) -$  giving component quintet; while methyl radicals  $\dot{\text{C}}\text{H}_3$  gives component quartet spectrum. The spectra observed at different temperatures are also simulated using the quartet – quintet combination. The component spectra of RT spectrum are as shown in Fig11. Magnetic parameters corresponding to the component spectra at different temperatures are as listed in Table 3. The radical decay temperature ( $T_R$ ) of MA 82 copolymer is found to be around 420K.

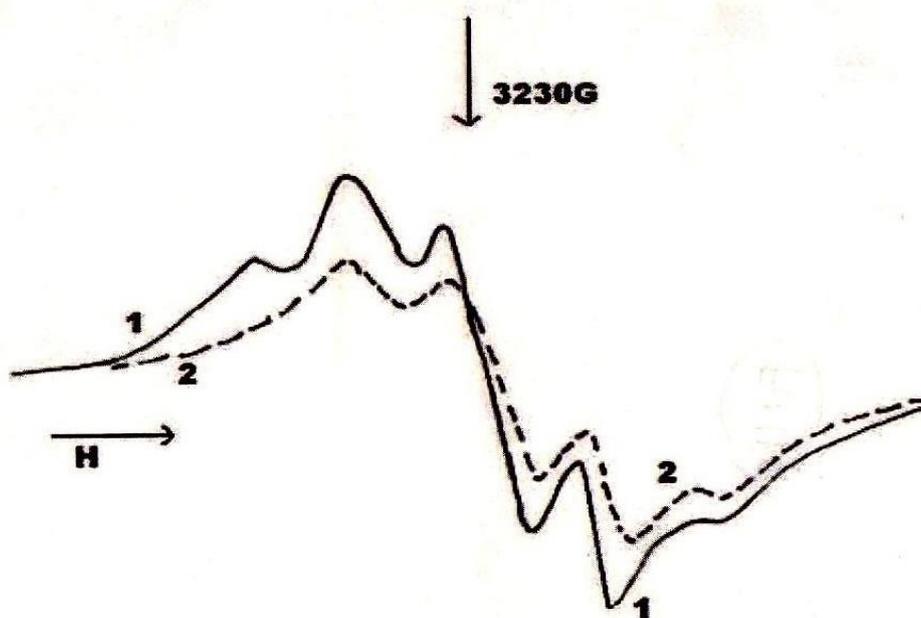


Fig 11: Component spectra of MA82 copolymer.  
Curve 1 Component quintet Curve 2 Component quartet

**Table 3: Magnetic parameters of MA82Copolymer temperatures**

| S.NO | Composition | Components | Magnetic parameters             |            |                    |                           |    |       |       |         |        |
|------|-------------|------------|---------------------------------|------------|--------------------|---------------------------|----|-------|-------|---------|--------|
|      |             |            | Relative intensity<br>$Y_{max}$ | Line width | Centre of spectrum | H <sub>f</sub> splittings |    | $n_i$ | $m_i$ | $S_e^2$ |        |
|      |             |            |                                 |            |                    | A                         | B  |       |       |         |        |
| 1    | 325         | Quartet    | 7                               | 6          | 3211               |                           | 14 | 0     | 4     | 1       | 0.3687 |
|      |             | Quintet    | 8                               | 5          | 3203               |                           | 0  | 1     | 1     | 5       |        |

The observed differences in radical decay temperatures of MA55 and MA82 copolymers is expected to be associated with molecular relaxations. Several polymers and copolymers exhibited similar decay characteristics around the transition temperatures [14,15]. The free radicals formed at room temperature, become reactive due to increase of thermal energy and approach each other to recombine with themselves or react with polymer chain forming networks structures. As the temperature approaches relaxation temperature, the decay/recombination of radicals becomes fast resulting in vanishing of ESR signals. Such type of free radical decay has also been observed in irradiated poly (ethylene terephthalate) [14] and poly (methyl methacrylate) [15].

Considering the radical decay temperatures ( $T_R$ ) of AMPS copolymer, the MA82 copolymer has a value around 420K while for MA55 copolymer the  $T_R$  is 410K. The difference in  $T_R$  value is considered to be due to the presence of AMPS groups. Since the AMPS groups are considered to have polar nature, with the increase in composition of these groups; the free volume increase causing a reduction in glass transition temperatures[16]. In contrast copolymer with less AMPS content has less free volume and  $T_g$  will be more for it. Therefore the MA82 copolymer with less number of AMPS groups is anticipated to possess higher values of transition temperatures than MA55 copolymer. Hence radical decay temperature is more for it. Thermally stimulated luminescence (TSL) studies of MA copolymers have also supported these views. The TSL glow peak temperatures of MA82 and MA55 copolymers is reported to be around 415K and 405K respectively [17,18]. The results suggest that the MA55 copolymer with more number of bulkier polar AMPS groups, the glow peak temperature is less, when compared to the MA82 copolymer with less number of AMPS groups. The glow peaks are thought to be associated with transition temperatures. Therefore it is likely that, the free radicals formed on irradiation may decay around transition temperatures.

**Dose Dependency:**

Effect of radiation dose on free radical formation has been investigated by recording ESR spectra of the copolymer irradiated to different radiation doses. The spectra are shown in Fig12. The spectra observed at different doses have been simulated and magnetic parameters corresponding to component spectra are as listed in Table 4. The component spectra are as shown in Fig 13.

**Table-4: Magnetic parameters of MA55 Copolymer irradiated to different Radiation doses**

| S.NO    | Radiation Dose(Mrad) | components    | Relative intensity<br>$Y_{max}$ | Line width (a <sub>i</sub> )G | Centre of spectrum (X <sub>oi</sub> ) | H <sub>f</sub> splitting |                | $n_i$ | $m_i$ | $S_e^2$ |
|---------|----------------------|---------------|---------------------------------|-------------------------------|---------------------------------------|--------------------------|----------------|-------|-------|---------|
|         |                      |               |                                 |                               |                                       | A <sub>i</sub>           | B <sub>i</sub> |       |       |         |
|         |                      |               |                                 |                               |                                       | 1                        | 4              |       |       |         |
| Quartet | 15                   | 18            | 3245                            | 23                            | 0                                     |                          |                | 4     | 1     |         |
| Triplet | 18                   | 11            | 3232                            | 22                            | 0                                     |                          |                | 3     | 1     |         |
| 2       | 10                   | Macro radical | 2.3                             | 7                             | 3225                                  | 13                       | 23             | 2     | 5     | 0.1525  |
|         |                      | Quintet       | 16.5                            | 13                            | 3230                                  | 0                        | 22             | 1     | 5     |         |
|         |                      | Quartet       | 10                              | 5                             | 3230                                  | 18                       | 0              | 4     | 1     |         |
|         |                      | Triplet       | 40                              | 15                            | 3225                                  | 24                       | 0              | 3     | 1     |         |
| 3       | 20                   | Triplet       | 2                               | 14                            | 3234                                  | 12                       | 23             | 2     | 5     | 0.124   |
| 4       | 30                   | Triplet       | 1.3                             | 10                            | 3234                                  | 10                       | 22             | 2     | 5     | 0.143   |

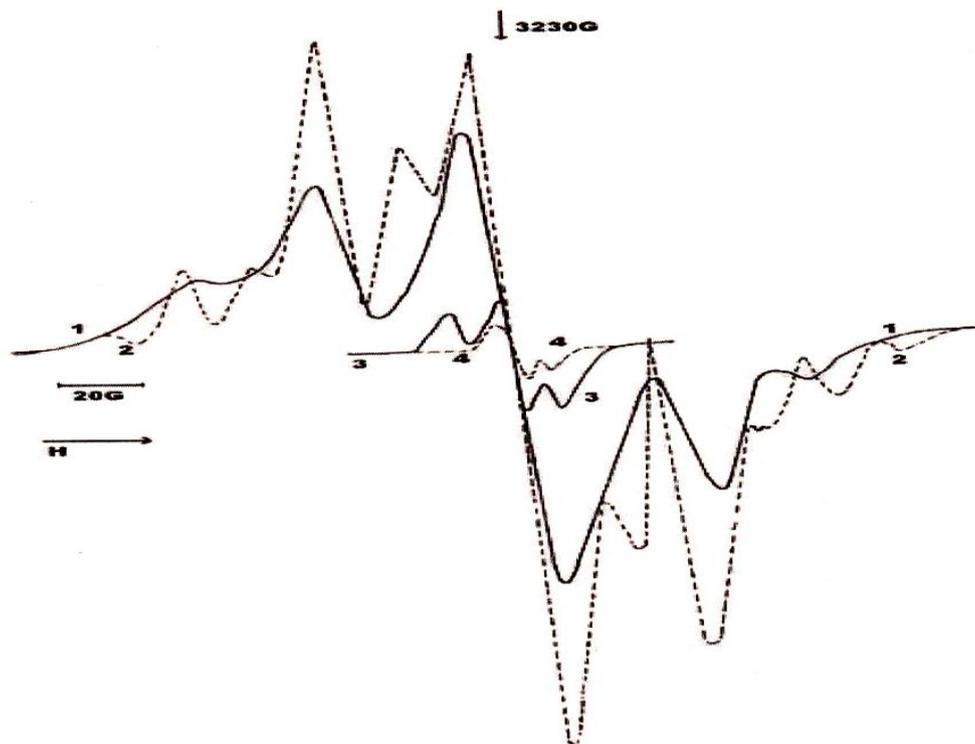


Fig 12: ESR spectra of MA55 copolymer irradiated to different radiation doses.  
 Curve 1 3 Mrad; Curve 2 10 Mrad; Curve 3 20 Mrad; Curve 4 30 Mrad

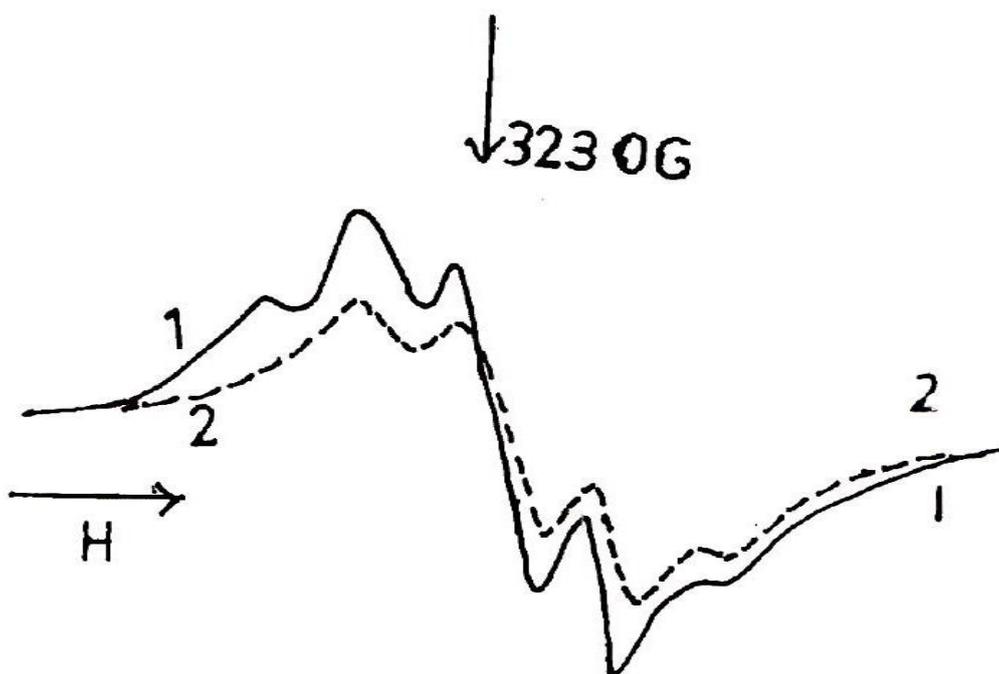


Fig 13: Component spectra of MA55 copolymer irradiated to 20 Mrad dose.  
 Curve 1 Component multiplet; Curve 2 Component singlet

ESR spectra of irradiated MA copolymer indicate that the spectra at low doses possess more number of hyperfine (hf) lines whose at higher and intermediate doses, number of hf lines is less. The reduction in hf pattern at higher doses is attributed to two factors (i) either the radicals formed during initial stages may crosslink to mitigate further degradation of copolymer, or(ii) a change in physical state induced by irradiation might have played a diminishing effect for formation of free radicals. Charlesby[19] and Harris et al.[20] have proposed that the MA homopolymer undergoes degradation during initial stages; while at higher doses the polymer undergo crosslinking. These crosslinks might have halted further degradation of copolymer, as has been evidenced in propylene-ethylene copolymer(21,22). Jenilang et al(21)and Jenshuan et al.[22] have observed a decrease in amorphous content of PE copolymer at higher doses leading to an increase in crystallinity. With the increase of crystalline content, the degradation of PE copolymer is reported to be reduced. The reduction in ESRhf structure at higher doses is attributed to the decrease of disordered regions and formation of crosslinked structures at higher doses.

**FTIR studies:**

Fig 14 shows the FTIR spectra of MA copolymer together with the spectra of MA and AMPS homopolymers. The spectrum possesses characteristic absorption bands of both the co-monomers confirming the formation of copolymer. Considering the chemical structure of MA copolymer, the constituent chemical absorption bands corresponding to chemical structure of different regions are as given in Table 5. As more than one group is giving absorption at same position, spectrum of the copolymer possesses broadened shapes(23). On irradiation intensity of some of these bands have shown a variation, indicating the change in concentration of corresponding functional group.

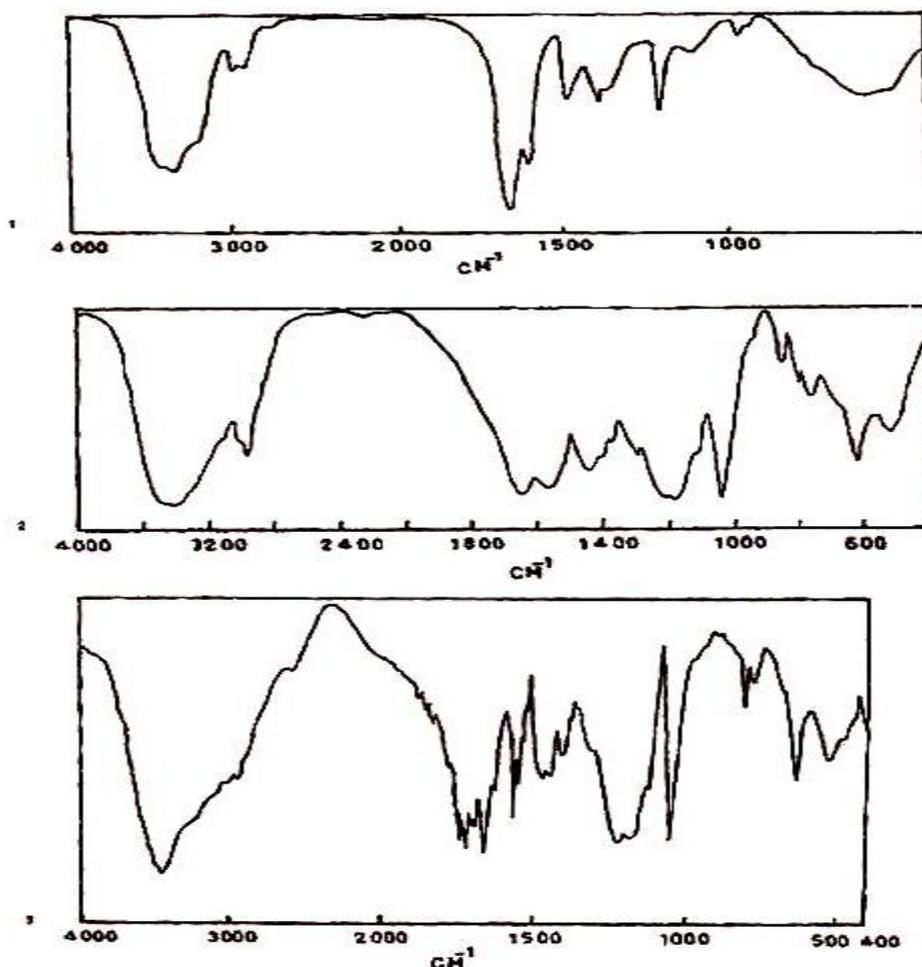
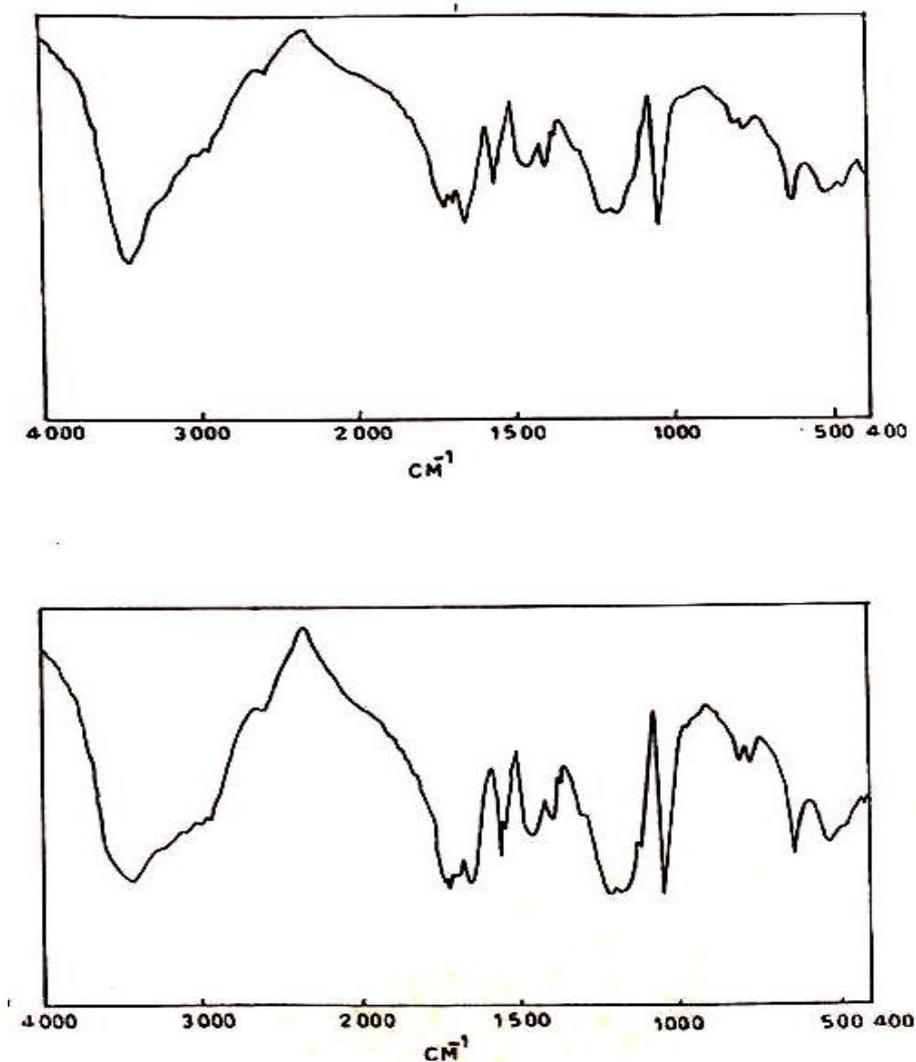


Fig 14: FTIR spectra  
Curve 1 MA homopolymer; Curve 2 AMPS homopolymer; Curve 3 MA copolymer

**Table 5: Characteristic absorption bands of various chemical groups in MA Copolymer**

| S.NO | Chemical group                     | Wavelength range Cm <sup>-1</sup> |           |           |         |
|------|------------------------------------|-----------------------------------|-----------|-----------|---------|
|      |                                    | 3470-3100                         | 1261-1150 | 1080-998  | 700-600 |
| I    | SO <sub>3</sub> H                  | 3470-3100                         | 1261-1150 | 1080-998  | 700-600 |
| II   | CONH <sub>2</sub>                  | 3500-3030                         | 1728-1600 |           |         |
| III  | CONHR                              | 3400-3050                         | 1728-1650 | 1620-1530 |         |
| IV   | CH <sub>3</sub>                    | 3010-2850                         | 1490-1440 | 1400-1350 |         |
| V    | CH <sub>2</sub>                    | 3000-2800                         | 1490-1440 | 750-700   |         |
| VI   | CH                                 | 2965-2800                         |           |           |         |
| VII  | CH <sub>3</sub> -C-CH <sub>3</sub> | 3000-2800                         | 1495-1438 | 1400-1350 |         |

FTIR spectra of MA copolymer irradiated to different radiation doses are shown as Curve 1 and Curve 2 Fig 15. A decrease in intensity of some absorption bands is observed. The reduction in intensity of 3400-3000cm<sup>-1</sup> absorption band is due to cleavage of sulfonic acid groups. The increase in intensities of 3010 – 2850 cm<sup>-1</sup>absorption band is assigned to be due to the increase in concentration of methyl groups. While the decrease in intensity of 1620 cm<sup>-1</sup> absorption band is indicative of cleavage of carbonyl groups (C = O) on irradiation. Therefore FTIR data of irradiated MA copolymer indicate the cleavage of sulphonic acid groups, carbonyl groups and increase in concentration of methyl groups( 2933 cm<sup>-1</sup>).These results supports the ESR results of cleavage of methyl sulfonic acid groups and carbonyl groups.



**Fig 15: FTIR spectra of irradiated MA copolymer**  
 Curve 1 Spectra at lower dose; Curve 2 Spectra at higher dose

## CONCLUSION

In conclusion MA copolymer with less AMPS content groups undergo cleavages on MA part, while copolymer with high AMPS content undergo multiple cleavages on irradiation. The AMPS groups are the primary sets of radiation attack resulting in cleavage of  $\text{CH}_2\text{SO}_3\text{H}$  group forming in  $\text{H}_2$  radicals. Subsequent degradation reaction involves formation of macro radicals and network structures. ESR simulation studies enable identification of free radicals under different conditions. FTIR studies suggest the cleavage of sulfonic acid groups and carbonyl groups [The radical decay temperature depends on composition of copolymer].

## ACKNOWLEDGEMENTS

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