



A COMPARISON IN RADIATIVE DEGRADATION OF ACRYLAMIDE POLYMERS

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ABSTRACT

Radiative degradation of polyacrylamide (PAAm) and polymethacrylamide (PMAm) has been compared by spectroscopic techniques. ESR spectrum of gamma irradiated PAAm is a triplet, while irradiated PMAm has shown more than three hyperfine lines. The hyperfine (hf) splittings for PAAm are in the order of 25 G; while hf splittings of PMAm are less than 25 G. The reasons for the variation in number of hf lines and hf splittings is explained. Fourier transform infrared spectra of unirradiated and irradiated PAAm were recorded to ascertain changes induced by gamma irradiation.

Key words: Polyacrylamide, Polymethacrylamide, Gamma irradiation, Free radicals, ESR and FTIR spectra.

INTRODUCTION

Acrylamide polymers find various applications like hydrogel and in oil industry¹. In order to prepare gels of acrylamide polymers, they have been exposed to irradiation². Therefore, radiation induced changes in these polymers is a subject of interest.

PAAm undergo crosslinking reactions, when exposed to gamma rays or electron beam according to Mills *et al.*³ and Alexander *et al.*⁴. Burillo and Ogawa⁵ have observed crosslinking of PAAm on either thermal degradation or gamma irradiation. In order to find routes of crosslinking reactions, ESR technique has been employed by various authors⁶⁻⁹. The observed spectra are either singlet or triplet or quintets, which are assigned to different

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radicals produced on gamma irradiation of PAAm. When compared to PAAm, degradation studies on PMAm are very scanty. These studies indicate random chain scission of PMAm, in contrast to the crosslinking of PAAm.

In the present studies, the authors have attempted to compare degradation behaviour of PAAm and PMAm using spectroscopic techniques. The ESR spectra of the two polymers were recorded under different conditions and the results were compared. FTIR spectra were also recorded to correlate the data.

EXPERIMENTAL

Polyacrylamide and polymethacrylamide used in the present studies are in powder form and are of commercial origin. ESR spectra of irradiated polymers were recorded on Varian E-line spectrometer operating of X-band frequencies and 100 KHz modulation. Gamma irradiations were carried out by cobalt-60 source having a radiation dose rate of 0.15 M.rad/hr in air at room temperature. FTIR spectra are recorded on Perkin-Elmer model spectrometer by making the pellet of polymer along with potassium bromide

RESULTS AND DISCUSSION

ESR spectra of PAAm irradiated to 3 Mrad and 9 Mrad radiation doses are shown as curves 1, 2 in Fig. 1. The spectra are triplets and spectral parameters as listed in Table 1.

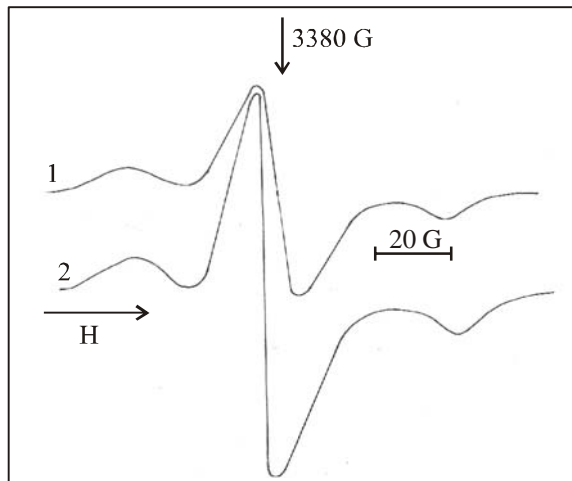


Fig. 1: ESR spectra of irradiated PAAm

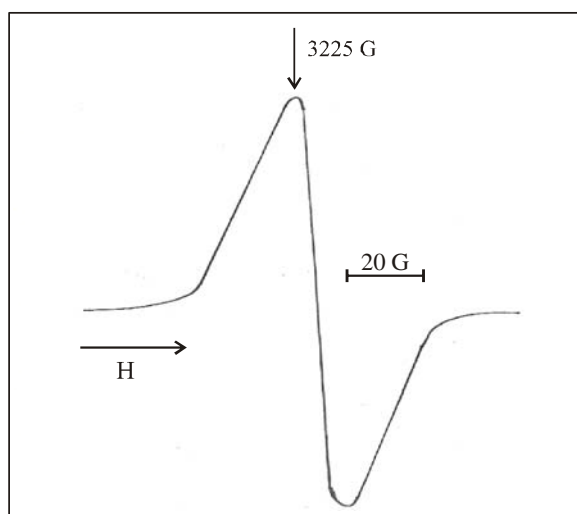
Curve 1: ESR spectrum of PAAm irradiated to 3 Mrad

Curve 2: ESR spectrum of PAAm irradiated to 9 Mrad

Table 1: Spectral parameters of PAAm irradiated to different radiation doses.

Spectrum code	Radiation dose in M rad	Line position G	Intensity	Spread (G)	Splitting s
Curve 1	3 Mrad	3354 3370 3395	2.4 10 1.0	90	25
Curve 2	9 M rad	3295 3320 3345	2.4 11 0	90	25

ESR spectrum of irradiated PAAm at LNT is shown in Fig. 2. The spectrum is a singlet. Spectral intensities under different conditions are calculated using double integration method and listed in Table 2.

**Fig. 2: ESR spectrum of irradiated PAAm at LNT****Table 2: Spectral intensities of ESR spectra observed for irradiated PAAm**

Temperature (K)	Dose (Mrad)	Spectral intensity
RT 300	3	30
RT 300	9	50
LNT 77	3	20

Fourier transform infrared (FTIR) spectra of unirradiated and irradiated PAAm are shown in Fig. 3 as Curve 1 and Curve 2. The absorption bands and their assignments are as listed in Table 3¹⁰.

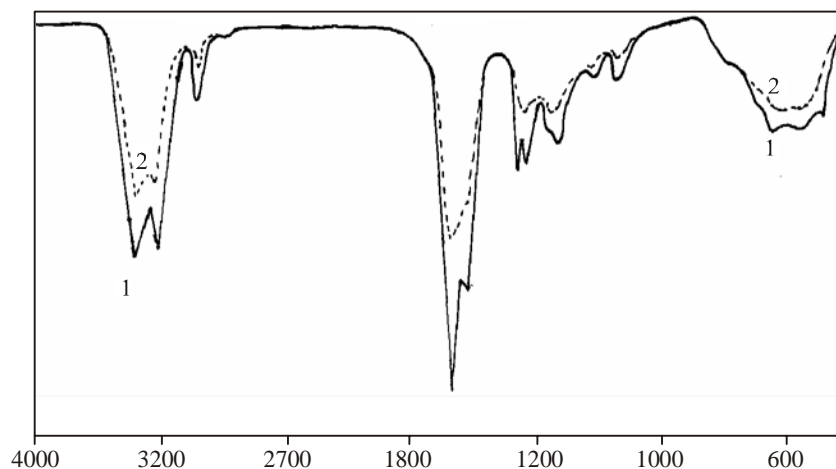


Fig. 3: FTIR spectra of PAAM

Curve 1: FTIR spectrum of unirradiated PAAM

Curve 2: FTIR spectrum of irradiated PAAM

Table 3: FTIR absorption bands observed for PAAM

Band position (cm ⁻¹)	Intensity	Assignment
3350	Strong	NH / NH ₂ group
2926	Medium	CH ₂ group
1700	Medium	C=O group
1350	Weak	CH ₂ / CH group
1250	Medium	CH ₂ / CH moiety
1150	Weak	CH ₂ / CH group

On irradiation, some of these absorption bands have shown a change in intensity. ESR spectrum of PAAM irradiated to 3 Mrad dose is shown in Fig. 4. The spectral parameters are listed in Table 4.

ESR spectrum observed for irradiated PAAM under different conditions i.e. a singlet, triplet or quintet spectrum is assigned to the free radicals of the type^{7,8}.



This type of free radical in PAAM is assumed by the cleavage of bond shown at position at 'a' (Fig. 5).

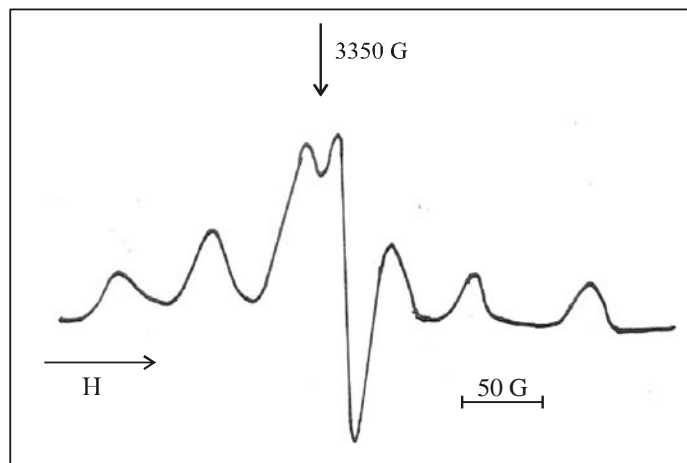


Fig. 4: ESR spectrum of PMAm irradiated 3 Mrad

Table 4: Spectral parameters of irradiated PMAm

S. No.	Line position G	Line intensity	Line separation G
1	3275	1.0	25
2	3300	2.0	20
3	3320	6.0	15
4.	3335	6.2	30
5.	3365	2.5	30
6	3395	2.5	30

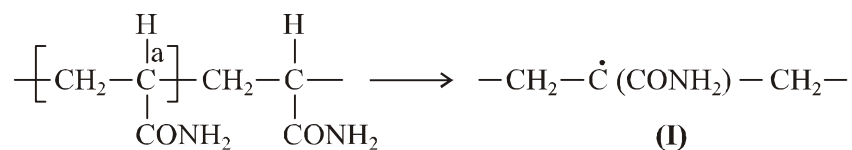


Fig. 5: Chemical formula and cleavage of bond in PAAm

Therefore, the observed triplet in the present investigation is also assigned to free radicals of the type I. When compared to the spectrum of low radiation doses, the spectrum observed of higher doses has more intensity. Therefore, on exposing the PAAm to high radiation doses, more number of cleavages occurs forming more number of free radicals (I). Since the ESR spectral intensity is related to free radical concentration, attempts have been

made to calculate ESR spectral areas. The values are listed in Table 2. It is evident from table that the free radical concentration increases (histogram depicted in Fig. 6 and 7). ESR spectrum of irradiated PAAM at LNT (Liquid nitrogen temperature i.e 77 K) is shown in Fig. 2. Free radical concentrations at RT and LNT are listed in Table 2.

To have a comparison, the spectral intensities are also compared (Fig. 6 and 7). The free radical concentration at low temperature is found to be less; indicating that the formation of free radicals is less, when compared to RT.

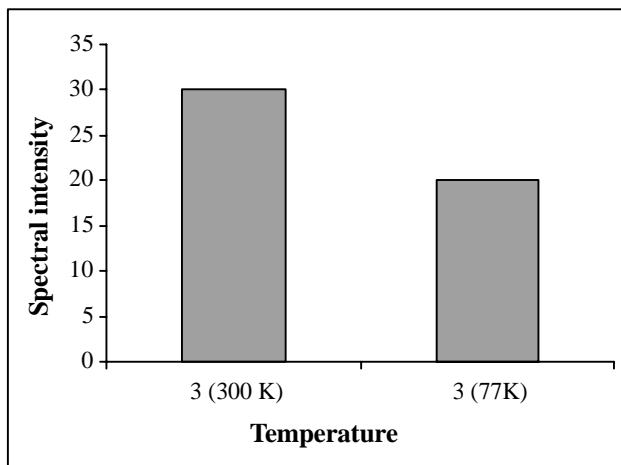


Fig. 6: Comparison of spectral intensities in the form of histogram at various temperatures

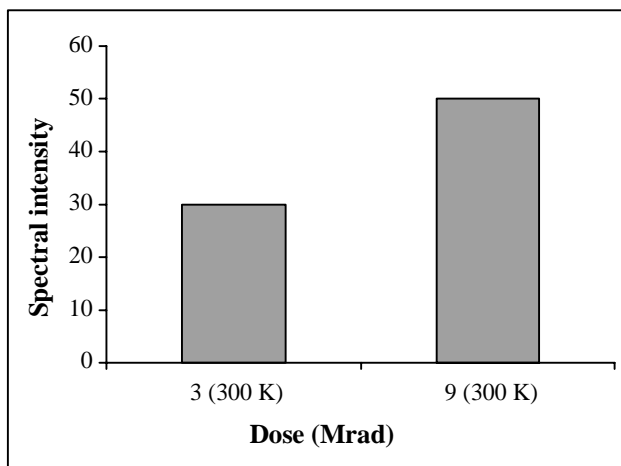


Fig. 7: Comparison of spectral intensities in the form of histogram at various doses

Fourier transform infrared spectrum of unirradiated PAAM is shown in Fig. 3. The spectrum possesses various absorption bands, whose positions are listed in Table 3. Assignment of the absorption bands to various chemical groups in PAAM is also given in Table 3. Among the various absorption bands, it is found that the band at 1250 cm^{-1} and 1150 cm^{-1} are immediately affected by irradiation. Then a decrease in 3350 cm^{-1} and 1700 cm^{-1} absorption bands has occurred, indicating that the C-H band (marked as a) is cleaved initially; afterwards, the CONH_2 group may be dissociated from the main chains of PAAM to a small extent.

Regarding polymethacrylamide, on irradiation, the number of hf lines in PMAM are large when compared to PAAM.

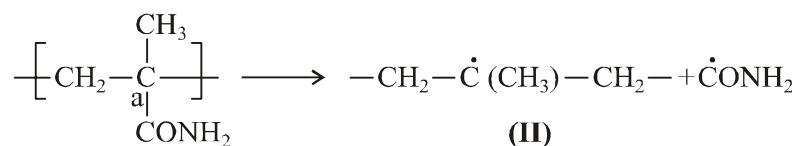


Fig. 8: Cleavage of chain in PMAM

Considering the chemical formula of PMAM, cleavage of bond at position 'a' is more preferable, when compared to the other bonds. When this cleavage occurs, the formation of radical (II) takes place.

Radical (II) has no protons in ' α ' position; while there are seven ($4 + 3 = 7$) protons in β -position. In the event of all beta protonic interaction, an octet ($7 + 1$) spectrum might have resulted in. However, the observed ESR spectrum of irradiated PMAM contains six hyperfine lines only. The reduction in number of hf lines is attributed to the interplay of hyperfine interaction in macroradicals^{11,12}. Therefore, formation of radicals of type II is more probable in PMAM.

CONCLUSIONS

In conclusion, irradiation of PAAM results in the cleavage of C-H bond leading to the formation of free radicals of the type (I), which gives the observed ESR triplet spectrum. In contrast to PAAM, the PMAM undergoes side chain cleavage to form radicals of the type II, which gives the ESR singlet spectrum.

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