

On the Temperature Dependent ESR of Gamma Irradiated Polyacrylamide



Physics

KEYWORDS : Gamma irradiation, PAAm, ESR, DSC, free radical

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ABSTRACT

Radiation induced chemical changes in PAAm have been studied by the electron spin resonance (ESR) technique. ESR spectra of irradiated PAAm have been recorded in the temperature range of 300-400 K. An ESR quintet was observed at 300 K (Room temperature). The quintet gradually decreased to triplet and then to a singlet by heating the irradiated polymer. Finally the ESR signal decayed around 420 K. The spectrum is assigned to the free radicals of the type $CH_2-C(CONH_2)-CH_2$, formed by cleavage of proton from the main chains of the polymer. Reason the decay of ESR signal has been explained in terms of molecular mobility of the polymer. DSC thermograms of irradiated and irradiated, heated PAAm are also recorded to study the thermal properties.

INTRODUCTION

Polyacrylamide (PAAm) is a water soluble polymer and form hydrogels upon irradiation. Although radiation effects in PAAm are available in literature, temperature dependent phenomena are not reported.

Radiation effects in PAAm have been reported by various authors. Ueda *et al* (1) and Chachaty *et al.* (2) have assigned the observed ESR spectrum is due to the free radicals of the type $\sim CH_2-CH(CONH_2)$. Harris *et.al* (3), Remelow and Baysal (4) have reported photodegradation of PAAm and observed an ESR quintet at LNT, which was assigned to $\sim CH_2-C(CONH_2)-CH_2\sim$ radicals formed by cleavage of proton. This radical in principle should give an ESR quintet. However when irradiated PAAm is heated to RT the quintet transform to triplet. The formation of triplet from quintet has been explained by free radical transformation, in which the spin density delocalises to side amide groups. Later Sanjeeva Rao *et al.* (5) have reported an ESR triplet for the gamma irradiated PAAm at room temperature. The spectrum reduced to a singlet when the temperature is lowered to liquid nitrogen temperature (77K). The spectrum at room temperature is assigned to $\sim CH_2-C(CONH_2)-CH_2\sim$ radicals, in which only two β -protons out of four methylene protons interact with unpaired electron, resulting in the triplet spectrum. When the temperature is lowered, the free radical transforms to type $\sim CH_2-C(CONH_2)-CH_2$ (II) so that in second form(II) there are no protons in neither α nor β positions resulting in ESR signal with hyperfine lines. It was not known, whether the radical transformation is possible at high temperature also. In order to investigate this and to study the thermal stability of the free radicals, the authors have recorded the ESR spectra from RT to high temperatures. Further apart from the ESR techniques differential scanning calorimetry is also employed to study the thermal properties

Experimental method

Commercially available PAAm in the form of fine powder is procured from CDH labs. The polymer is irradiated with cobalt 60 gamma source, with a dose rate of 0.15 M rad / hr in air at room temperatures. ESR spectra are recorded on a VARIAN-E line spectrometer operating at X-band frequencies and 100 K Hz modulation. DSC thermograms are recorded on METTLER Star SW instrument using a heating rate 10°C/ min.

RESULTS AND DISCUSSION

ESR spectrum of PAAm irradiated to 3 M rad radiation dose at RT is shown as Fig.1, Curve 1 2, 3, 4. Fig 2 represent the spectra

observed at 310, 330, 350 and 365 K. The spectral parameters at different temperatures are as listed in Table 1.

Table 1 : Spectral parameters of irradiated PAAm at different temperatures.

S.No.	Temperature K	No. of hyperfine lines	Hf splitting G	Spread G	Spectral areas
1	300	5	20	120	17.60
2	310	5	20	120	13.68
3	330	3	15	100	9.44
4	350	3	15	80	5.48
5	365	1	--	40	1.00

Since area under the ESR spectrum represent the free radical concentration, attempts have been made to calculate the spectral areas (6). The area values under ESR spectra at different temperatures are as listed in Table 1. A plot of ESR intensity against temperature is plotted in Fig. 3. Free radical decay is found to be non-linear.

In order to identify the free radicals present at different temperature, computer simulations are employed to resolve the component spectra. Each component spectrum is characterized by magnetic parameters relative intensity (Y_{max}), line width like (a_i), center of spectrum (X_{c_i}), hyperfine splittings (A_i, B_i) and number of lines resulting from alpha and beta protons (n_i, m_i) (7). Based on the chemical constitution, the values of n_i, m_i will depend; while initial values of other remaining magnetic parameters are taken from the experimental ESR spectrum (7). As such the spectrum observed at RT could be simulated with the component spectra shown in Fig. 4 Curve 1 is component multiplet, while curve 2 is singlet. The superposition of both the component spectra results in the experimental spectrum at RT shown as Fig. 1. Magnetic parameters employed to simulate the component spectra are as listed in Table 2.

Table 2: Magnetic parameters of component spectra at room temperature

S.No.	Component	Line width (a_i) (G)	Relative intensity Y_{max}	Centre of spectrum (X_{c_i}) G	Hyperfine splittings A_i, B_i	n_i	m_i
	Quintet	9.0	6.0	3251	0 20	1	5
	Singlet	6.0	4.5	3251	0 0	1	1

Considering the magnetic parameters of component spectra, curve 1 Fig. 4 can be simulated with the values of $n_i=1$ $m_i=5$ and $A_i=0$ and $B_i=20G$. Therefore the radical responsible for curve 1 will have interacting β -protons only. Free radicals having such configuration in PAAm may be of the type $\sim CH_2-C-CH_2\sim$. These radicals may be formed by the cleavage of proton on irradiation of the polymer. The proton may interact themselves or with other radicals forming stable products. The protons in the α - position of alkyl radicals, will usually have a splitting of 20-23G (8). However in the present studies a splitting of only 20G, is observed indicating that hf interaction is not due to α - proton but arise only due to β -protons. Such type of β -hyperfine interactions are also observed earlier (9).

With the increase of temperature to 330K, the quintet observed at RT reduced to a triplet with a hf splitting of 20G. The triplet could also be simulated with same set of $n_i=2$ $m_i=5$ values; however the values of remaining magnetic parameters are changed. It indicate that the free radical remains unchanged; while the hyperfine contribution arising from neighboring β - protons will change. Such type of hyperfine interaction of alkyl radicals were also reported previously (9). With the increase of temperature to 365K, the triplet reduced to a singlet and finally at 370K the signal completely vanished. The disappearance of ESR signal with temperature is thought to be associated with recombination of free radicals. Polyacrylamide is preferably crosslink upon irradiation (10). Therefore the macroradicals formed at RT might have reacted and cross-linked by heating the irradiated samples to higher temperatures (370K), resulting in decay of ESR signals.

DSC thermo grams of irradiated PAAm are recorded as shown in fig5. curve 5(a) represent the irradiated and thermally treated at (370K) PAAm while Curve 5(b) represent the irradiated and thermally treated at (370K) PAAm. Unirradiated PAAm has exhibited two peaks P_1 (around 65°C) and P_2 (around 250°) which corresponds to dissociation of chemical groups and melting point of the polymer. On irradiation, P_1 has shifted to 52°C while P_2 appeared at 295°C. For the irradiated and heated polymer the peaks appeared at (120°C) sample, 62°C and 247°C. Comparing these peaks, it can be observed that the peak P_1 at 62°C became very broad indicating chemical reaction occurred in the polymer heavily.

CONCLUSIONS

In conclusion irradiation of PAAm produces macro radicals, generating ESR quintent spectrum. Heating of irradiated PAAm increases molecular mobility causing reduction in ESR hf interactions. Finally the free radicals crosslink and ESR signal vanishes.

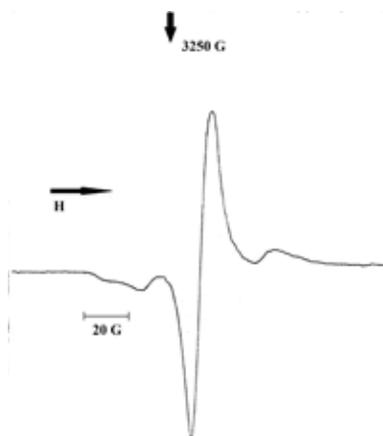


Fig. 1: ESR Spectra of γ -irradiated Polyacrylamide At room temperature

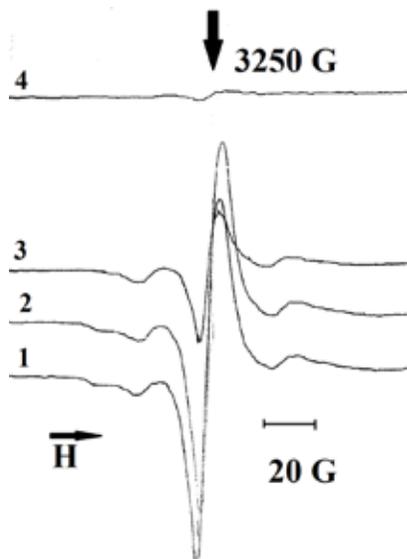


Fig.2: ESR Spectra of γ -irradiated polyacrylamide at different temperature

Curve 1 : 310 K, Curve 2 : 330 K
Curve 3 : 350 K, Curve 4 : 360 K

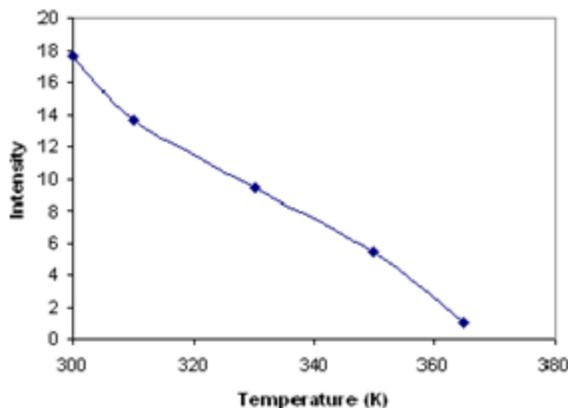


Fig.3: Variation of ESR intensity against temperature

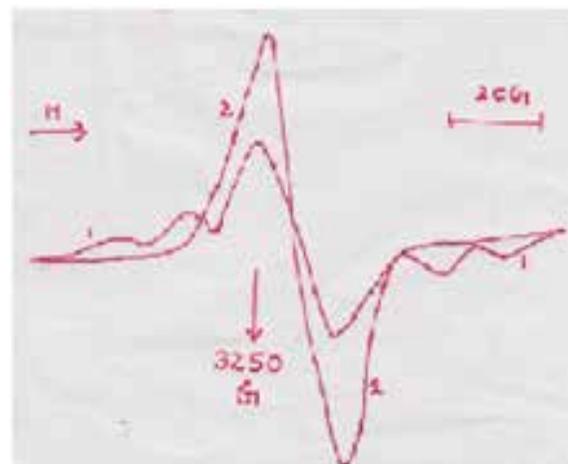


Fig.4:Component spectra of irradiated Polyacrylamide

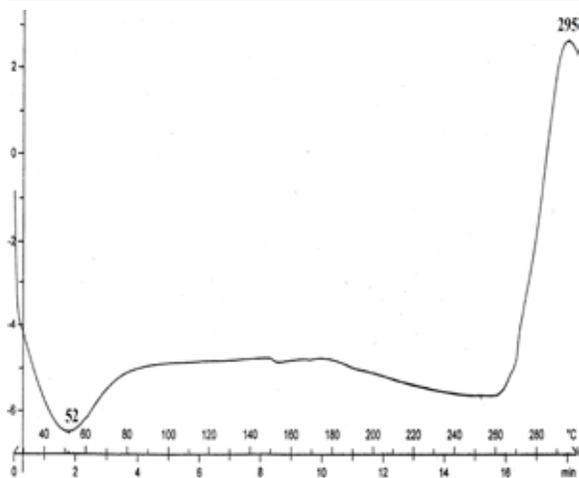


Fig: 5(a)

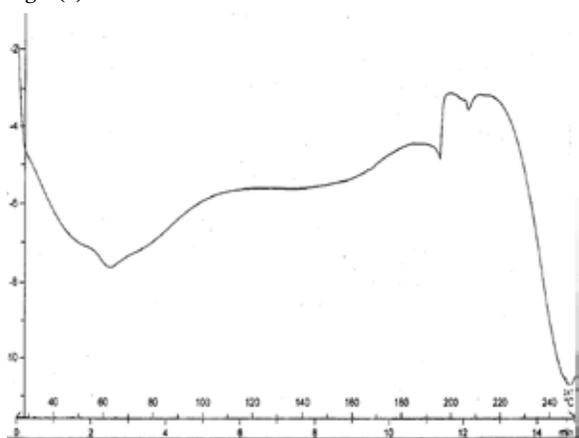


Fig: 5(b)

Fig. 5: DSC thermograms of PAAm

- (a) Irradiated and heated
(b) Irradiated

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