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Evaluating the Temperature Dependence on Activation Energy of Free Radical Decay in Irradiated Polyacrylamide Using Bloch Analysis

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Abstract: ***Gamma irradiation of polymer is convenient method to alter the physico-chemical properties. To attain the desired properties, it is desirable to know about the radiation induced changes in the concerned polymeric systems. Formation of free radicals is the most obvious effect of gamma irradiation. The generation of free radicals depends on the chemical structure and environmental conditions. In this context the authors have studied radiation effects in irradiated polyacrylamide (PAAm) using Electron Spin Resonance (ESR) spectroscopy. The free radicals generated in PAAm are appeared to decay with increase of temperature causing the decay of ESR signal. To study the decay characteristics of free radicals and to calculate activation energy associated with free radicals decay, Bloch analysis is used in literature. Bloch analysis is based on measurement of line width and Hyperfine splitting accurately. For this purpose Computer simulation are employed by the authors to reconstruct the ESR spectra. Using the values of Hyperfine splitting, correlation time (τ) is measured at different temperatures (T). A plot of log(1/τ) and (1/T) is drawn. The slope of the straight line gives the activation energy corresponding to free radical decay***.

Keywords: polyacrylamide (PAAm), Gamma irradiation, ESR spectra, Activation Energy.

1. Introduction

Polyacrylamide (PAAm) is a water soluble non-biodegradable polymer. It is used in various branches of science and technology. To increase the dry strength of paper, copolymers of PAAm are used (1). The polymer undergo cross linking under the action of high energy radiation. Cross linked PAAm is a hydrogel. Therefore to study the PAAm as hydrogel, radiation effects on it are to be investigated. Mills etal (2) have irradiated PAAm with 80kev electron beam and observed cross linking of polymer. Radiation effects on PAAm are found to be concentration dependent (3). In low concentrations, the polymer degrades; while in higher concentrations, cross linking predominates. Radiolysis of PAAm has been reported by Sanjeeva Rao etal (4) using ESR spectroscopy. These authors have observed an ESR triplet at room temperature (RT); while at low temperature i.e. at Liquid Nitrogen Temperature (LNT) an ESR singlet is observed. The triplet is assigned to ~$\dot{C}H_2$-$C(CONH_2)$-CH_2~ free radicals produced by the cleavage of proton. Only two of the four adjacent methylene protons contributes to hyperfine interaction giving rise to the observed triplet at RT. While at LNT, an inter-convertible form of I gives singlet spectrum. This radical is designated as II. Since the spectra at RT and LNT have inter-convertible nature, radical transformation is proposed. Burillo etal (5) have also investigated radiative and thermal degradation of PAAm under different conditions using thermal methods.

ESR spectra of irradiated PAAm have been recorded by Sanjeeva Rao etal (6) for PAAm irradiated to different radiation doses. The observed ESR spectra with a hyperfine splitting of 25G is attributed to radical (I). These authors have recorded Fourier Transform Infrared (FTIR) spectra of unirradiated and irradiated PAAm and reported the cleavage proton of CH group. The ESR spectra of irradiated PAAm is compared with the spectra of poly (methacrylamide) (PMAm).

Considering the literature, temperature dependent radiation changes in PAAm has not been attempted. In this context the authors have recorded ESR spectra of irradiated PAAm in high temperatures i.e. RT to melting point (T_m). The authors have used Bloch analysis (line width) to evaluate activation energy associated with decay of free radicals (7).

2. Experimental Study

Powders of polyacrylamide supplied by BDH chemicals is used in the present studies. PAAm is irradiated with gamma rays from cobalt 60 source with dose rate of 15kGy/hr in air at room temperature. ESR spectra of irradiated PAAm are recorded on Varian E-112 spectrometer operating at X-band frequencies and 100 KHz modulation. The ESR spectrometer is fitted with necessary accessories to record the spectra at high temperatures. accuracy in measurement of temperature is $\pm 1^0$C.

3. Results & Discussions

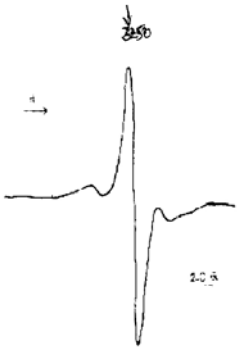


Fig. 1: ESR Spectra of -irradiated Polyacrylamide At room temperature

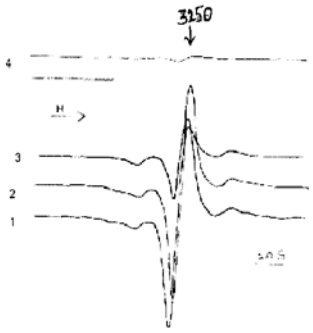


Fig.2: ESR Spectra of -irradiated polyacrylamide at different temperature
Curve 1 : 310 K, Curve 2 : 330 K
Curve 3 : 350 K, Curve 4 : 360 K

Non-irradiated PAAm has not shown any ESR signal, indicating the absence of free radicals. ESR spectrum of PAAm irradiated to 4 M.Rad radiation dose at room temperature is shown as curve 1 of Fig1.

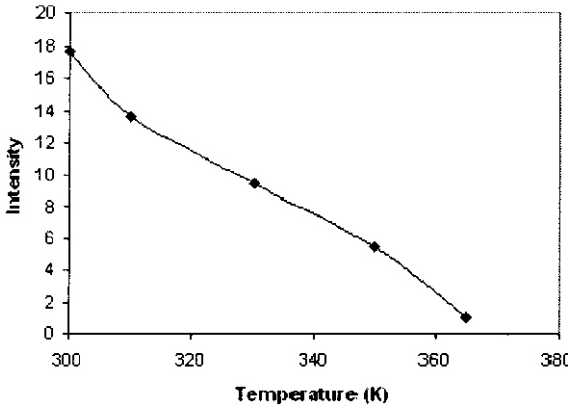
Spectra observed at 315K, 330K, 350K and 390K are shown as curves 2, 3, 4 and 5 in Fig1. Beyond 390K the ESR signal vanished. Spectrum observed RT is a quintet with hyperfine splitting of 20G and spread of 110G. Intensity distribution of spectrum has not followed any particular pattern. The ESR quintet is stable up to 330K and then it transformed to triplet at 350K. Triplet retained its shape up to 360K and around 365K, it converted to a singlet. The ESR signal is vanished at 370K. Spectral parameters corresponding to ESR spectra as different temperatures are as listed in Table 1.

Table1. Spectral parameters of irradiated PAAm at different temperatures

S.No.	Temperature in K	Number of Hyperfine lines	Hyperfine Splitting	Spread of Spectrum
1	300	Quintet	20-22	110
2	315	Quintet	20-22	110
3	330	Quintet	20	90
4	350	Triplet	20	70
5	360	Triplet	20	40

ESR spectra observed for irradiated PAAm at different temperatures are analysed by Computer simulations (8). As such the spectrum observed at RT is simulated with the magnetic parameters of n_i =1 m_i=5; A_i=0 and B=22G. The magnetic parameters indicate that there are four interacting beta protons. Therefore free radicals of the type ~ $\dot{C}H_2$-$C(CONH_2)$-CH_2~ are expected to present in irradiated PAAm at RT. Cleavage of proton from quaternary carbon is expected to give radical I. Since the quintet is stable up to 330K, radical I is expected to stable up to this temperature. But a change in overall spread of the spectrum indicate that the magnetic environment at 330K is not the same as that at RT.

The observed triplet at 350K is simulated with the same set of magnetic parameters of n_i=1, m_i=5 indicating the presence of radical (I) even at 350K. But decrease in overall spread indicate that radical (I) might have involved in some of reactions causing a decrease in chain length. As the temperature is further increased, the hyperfine structure gradually diminished around 370K. Since PAAm is preferably a crosslinking type of polymer(9), radical (I) might have interacted with themselves to form cross linked structures Variation of ESR intensity against temperature is as shown in Fig3. Figure



: Variation of ESR intensity against temperature **F**

Figure:3 3

To evaluate activation energy associated with recombination free radicals Bloch analysis is applied (8). The analysis requires computation of accurate values of line width and hyperfine splittings. Therefore the authors have used the values of magnetic parameters to stimulate the ESR spectra. The Bloch analysis is successfully applied to measure temperature dependent radical decay of irradiated polymers and copolymers (7). From the values of line widths/hyperfine splittings the values of correlation time(τ) is measured as given in Table2. A plot of 1/T against log ($1/\tau$) is drawn. The slope of the straight line gives the value of activation energy (E_a) in KJ/mole.

Table 2: Correlation times at different temperatures of irradiated PAAm.

SNo	*Temperature in K*	*1/T Values*	*$\Delta\upsilon$*	*$1/\tau$*	*log(1/ τ)*
1	300	$3.33x10^{-3}$	20	-	-
2	315	$3.17x10^{-3}$	18	6.0	7.78
3	330	$3.03x10^{-3}$	16	5.8	7.63
4	350	$2.85x10^{-3}$	13	4.7	6.72
5	360	$2.77x10^{-3}$	10	3.6	5.56

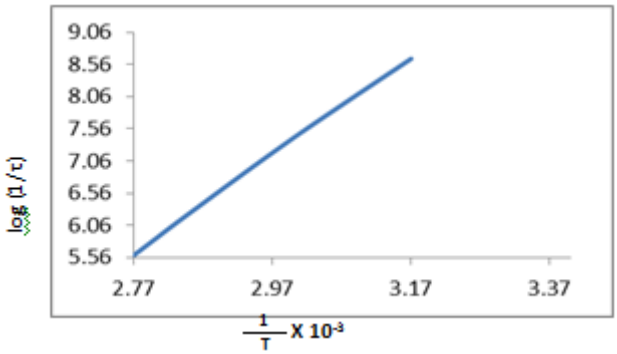


Figure 4: Plot of 1/T - log (1/τ). The slope gives the value of activation energy (E_a)

A plot of 1/T against log (1/ τ) is drawn as shown in Fig 4. From the slope of straight, the value of activation energy is found to be around E_a = 5.55 KJ/mol. The value of E_a is observed to very less when compared to the other acrylics.

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