Int. J. Chem. Sci.: 10(3), 2012, 1577-1582
ISSN 0972-768X
www.sadgurupublications.com

EVALUATION OF ACTIVATION ENERGY FROM TEMPERATURE DEPENDENT ESR SPECTRA OF IRRADIATED AAAMPS COPOLYMER

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ABSTRACT

Temperature dependent radical decay in gamma irradiated Acrylamide (AA) 2 acrylamid 2-methyl propone salfonic acid. (AAAMPS) copolymer has been investigated by electron spin resonance (ESR) technique.The ESR multiplet spectrum observed at room temperature (RT) is assigned to macro radicals of the type ~ CH_2-CH-CH_2 ~ formed on AMPS part of the copolymer on irradiation. The ESR hyperfine (hf) pattern observed at room temperature gradually reduced on heating and finally the spectrum completely disappeared around 410 K. Bloch analysis is used to evaluate activation energy associated with free radical decay.

Key words: AAAMPS copolymer, Gamma irradiation, ESR technique, Free radicals, Activation energy.

INTRODUCTION

Both polyacrlyamide and poly (AMPS) homopolymer are water soluble and form super abserband gels[1] degree of gelation in this polymer is reported be improved by various methods. When compared to chemical methods, radiation induced cross linking is effective in formation of gels[2]. In order to study radiation induced gelation, a slud of radiolysis in the copolymer is desirable. In this context, the authors attempts a study on radiation induced changes in AAAMPS copolymer, using the ESR technique.

Free radicals formed in irradiated polymers decay upon thermal treatment and the radical decay depends on the nature of polymer matrix or type of radicals formed.

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Therefore radical decay is used as a probe to investigate the nature of surrounding medium. In this context Ohinishi et al.,[3] have used Bloch analysis to obtain activation energy of decay of radicals formed in irradiated polyethylene. Later, Prasad et al.,[4] have applied this method to evaluate activation energy of free radicals formed in irradiated polyethylene terepthalate. The method is based on measurement of values peak separations of ESR spectra. Using this the relaxation time is measured. A plot of (1/T) against log (1/τ) is drawn. The slope of the line gives activation energy. This method has been described in detail by Prasad et al.[4]

EXPERIMENTAL

AAAMPS copolymer used in the present studies is in powder form. Synthesis and characterization of the copolymer has been discussed by Rao et al.[5] The copolymer is exposed to Cobalt 60 gamma source with a dose rate of 0.15 Mrad/hr in air at room temperature. ESR spectra of irriadiated AAAMPS copolymer have been recorded on VARIAN E line spectrometer operating of at X-band frequencies and 100 KHz modulation.

RESULTS AND DISCUSSION

ESR spectrum of gamma irradiated AAAMPS copolymer at room temperature is shown as curve Fig. 1. While the spectra at 320 K, 350 K and 410 K are shown as curves 2, 3 and 4. The spectral parameters are listed Table 1. The parameters indicate that the hyperfine intervals and spread of the spectrum gradually decrease with the increase of temperature. The ESR spectra observed at different temperatures are stimulated by the total curve fitting method[6,7].

The method involve generation of various component spectra resulting from free radicals formed on irradiation of the copolymer. The component spectra are superposed in desired combinations to yield the experimental spectrum. The component spectra are stimulated with the magnetic parameters like line width (a) relative intensity ($y_{max\ i}$) center of spectrum (X_o), hyperfine splitting (A_i,B_i) and number of lines resulting from the adjacent nuclei (n_i,m_i). Out of these parameters the values of n_i and m_i are very important because they yield important information regarding the nature of interacting nuclei at the α and β position of unpaired electron. Therefore using the magnetic parameters it is possible to identify free radicals causing ESR spectrum.

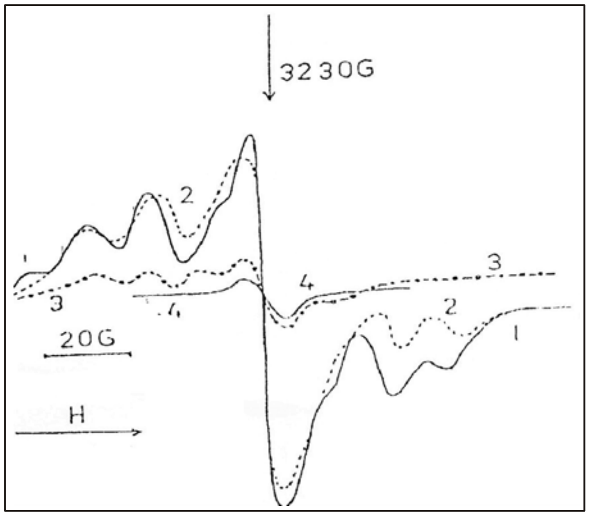

Fig. 1: ESR spectra of irradiated AAAMPS copolymer at different temperatures

Curve 1: ESR spectrum recorded at 300 K

Curve 2: ESR spectrum recorded at 320 K

Curve 3: ESR spectrum recorded at 350 K

Curve 4: ESR spectrum recorded at 420 K

Table 1: Spectral parameters of irradiated AAAMPS copolymer at different temperatures

S. No.	Tempurature (K)	Hyperfine lines	Spread (G)	Hyperfine splitting
1	300	8	140	23,12
2	320	6	130	23,12
3	330	4	100	12
4	400	1	70	-
5	420	1	40	-

Table 2: Magnetic parameters of irradiated AAAMPS at room temperature

Component	Line width	Relative insanitie	Center of spectrum	A_i B_i	n_i m_i
Macroradical	5	10	3223	23 13	2 5
quartet	10	18	3225	23 0	4 1

This method has been applied to analyze the ESR spectra of irradiated AAAMPS copolymer and the magnetic parameters are as listed in Table 2. The value of magnetic parameters indicate that the main contribution to the ESR spectrum is due to macro radicals with $n_i = 2$ and $m_i = 5$ having a chemical composition of $-CH_2-CH-CH_2-$ at room temperature. The spectra at higher temperature could also be simulated with almost same set of magnetic parameter of $n_i = 2$ and $m_i = 5$, with a small variation in remaining values of parameters, indicating the presence macro radicals at almost all temperatures. However there will be a reduction in concentration of free radicals with the increase of temperature. This suggests that free radicals form on irradiation at RT might have been converted to other radicals or interacted among them selves to form stable cross-linked structures. Since both AA and AMPS homopolymers are cross linkable polymers, the free radicals generated on irradiation might have interacted to form cross linked structure. Thermal energy required to cross link depend on the surrounding matrix and can be estimated Bloch analysis.

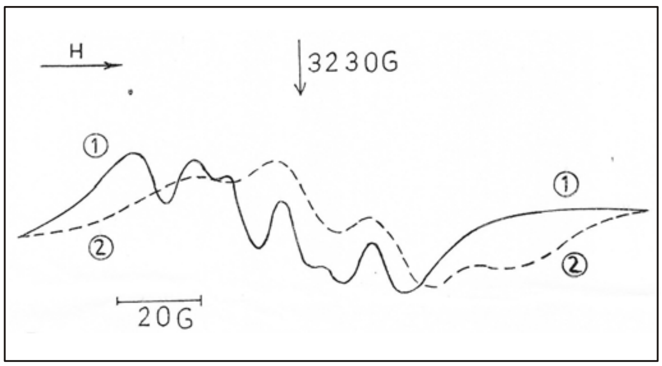

Fig. 2: Component spectra of irradiated AAAMPS copolymer at 300 K

Curve 1: Component spectrum arising due to macro radical

Curve 2: Component quartet spectrum

Ohinishi et al.,[3] and later. Prasad et al.,[4] have reported that the radical interaction are characterized by the separation of peaks in the ESR spectra and obey the following relation.

$$(\Delta\nu / \Delta\nu_0) = \{[1-2\,\pi^2\,\tau^2\,(\Delta\omega_0)^2]^{-1}\}^{-1/2} \qquad \ldots(1)$$

Where τ is relaxation time and τ is related to the life times at sites A and B.

$$\tau_A = \tau_B = 2\tau \qquad \ldots(2)$$

The peaks separation or line width

$$\Delta\nu = 2\beta / h\,(A_{\beta1} - A_{\beta2}) \qquad \ldots(3)$$

Using these equations the values of log (1/τ) are calculated at different temperatures and the values are listed in Table 3.

Table 3: Temperature dependence of (1/T)

Tempurature T (K)	1/T value	Δν value	1/ τ	Log (1/ τ)
300	3.33	15	-	-
320	3.13	10	49.68	1.69
330	2.86	8	56.39	1.75
400	2.38	5	82.85	1.87
420	1.79	2	90.92	1.9

For the AAAMPS the plot of (1/T) and log (1/τ) is as depicted in Fig. 3. The value of activation energy is found to be less when compared to radicals formed in PET.

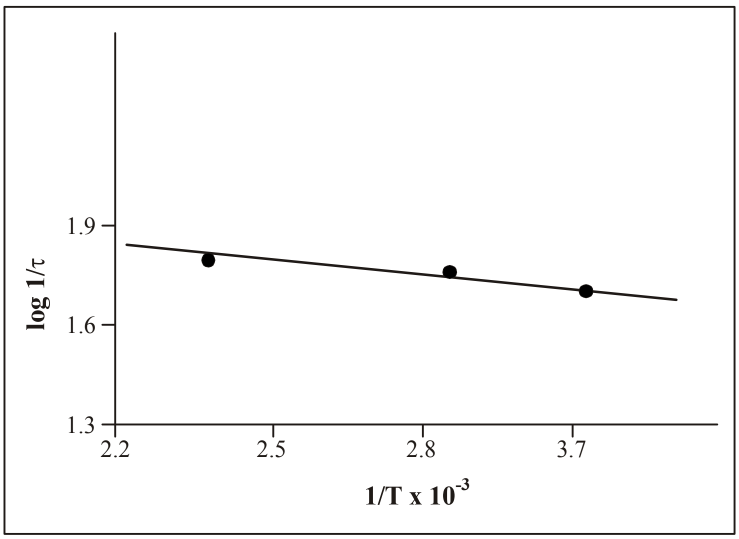

Fig. 3: Plot of 1/T vs log 1/τ of irradiated AAAMPS

CONCLUSION

Irradiation of AAAMPS copolymer results in formation of macro radicals preferabbly on the AMPS part of copolymer. These radicals gain thermal energy upon heating and react causing cross linkings. The energy required for cross linking reaction can be estimated from Block analysis.

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Revised : 19.05.2012 *Accepted : 20.05.2012*