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UNDERSTANDING ESR SPECTRAL DATA OF IRRADIATED MA AMPS COPOLYMER AT DIFFERENT TEMPERATURES

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ABSTRACT

ESR spectra of irradiated methacrylamide (MA) –2–acrylamido, 2-methyl propane sulphonic acid (MA AMPS) copolymer have been recorded in the temperature range of 300 410 K. The observed spectral features have been interpreted in terms of line intensities, line width and spread of the spectra as observed against temperature. Spectral areas and line widths are calculated by integration methods. The observed changes in intensity and line widths are related to radiation induced changes in MA AMPS copolymer.

Key words: MA AMPS Copolymer, ESR Spectra, Line widths, Intensity, Theoretical methods.

INTRODUCTION

AMPS (2-acrylamide, 2-methyl propane sulfonic acid) homopolymer and copolymers find applications as hydrogens, fuel cells and oil field industry[1]. Radiation induced process in these copolymers have been extensively studied by two groups i.e., Aggour *et al*.[2,3] and Sanjeeva Rao *et al.*[4,5] The studies indicate that radiation induced changes most likely occur on AMPS part of copolymer rather than on other commoner. This is attributed to the bulk size and polar mature of AMPS comonomer. In the present studies, the authors have attempted to study the temperature dependent ESR data of irradiated MA AMPS copolymer. Since the spectral intensity is related to free radical concentration,

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attempts have been made to calculate intensity by double integration methods. Since the line width is related to relaxation time, attempts are made to calculate line width by line integration techniques. Similarly, total spread of the spectrum is calculated at different temperatures.

EXPERIMENTAL

MA AMPS Copolymers have been synthesined and charecterised by Rao and Prasad.[6] The samples are in powder form and they are as it is used for ESR measurements. As the pure samples do not have any free radicals, they do not give ESR signal. The samples were exeposed to gamma irradiation and ESR spectra were recorded for MA copolymer irradiated to dose of 3.0 M rad radiation dose. The ESR spectra were recorded on Variation E line spectrometer operating and X-baned frequencies at 100 KHz modulation. Necessary excessories are fitted to the instrument to record the variable temperature spectra.

RESULTS AND DISCUSSION

ESR spectra of irradiated AMPS copolymers have been recorded as shown in Fig. 1. Curves, 1, 2, 3, 4 and 5 represents ESR spectra at 300 K, 330 K, 350 K, 375 K and 400 K. The spectral parameters are as listed in Table 1.

Table 1: Spectral Parameters of irradiated MA AMPS copolymer

Temperature (K)	Line position / Line intensities									
300	3168 4	3180 18	3195 20	3205 86	3115 54	3230 82	3235 120	3245 120	3255 94	3266 94
330	3169 4	3180 20	3195 19	3205 86	3215 49	3230 82	3235 121	3245 58	3255 90	3265 31
350	3170 2	3182 2	3193 4	3205 12	3215 09	3225 3	3235 18	3245 10	3255 12	-
375	-	3182 2	3193 1	3205 3	3215 1	3220 1	3235 10	3245 5	-	-
400	-	-	-	-	-	-	3232 1.0	-	-	-

The total intensity of the spectra at different temperatures have been calculated using double integration methods. The values are as listed in Table 2.

Table 2: Total intensities at different temperatures

Temperature (K)	Intensity	Spread G	Line width G
300	570	138	50
325	550	130	45
350	90	120	19
375	30	90	13
400	8	50	8

Total spread of the spectrum at each temperature was calculated and the values are given in Table 2.

Since the line width is related to relaxation times (τ). These were calculated and are given in Table 3.

Table 3: Temperatures versus relaxation time

Temperature (K)	Line width a_i (G)	Relaxation time (τ)
300	50	0.02
325	45	0.022
350	19	0.0526
375	13	0.0769
400	8	0.125

ESR spectra of gamma irradiated MA AMPS copolymer at room temperature is shown as curve in Fig. 1.

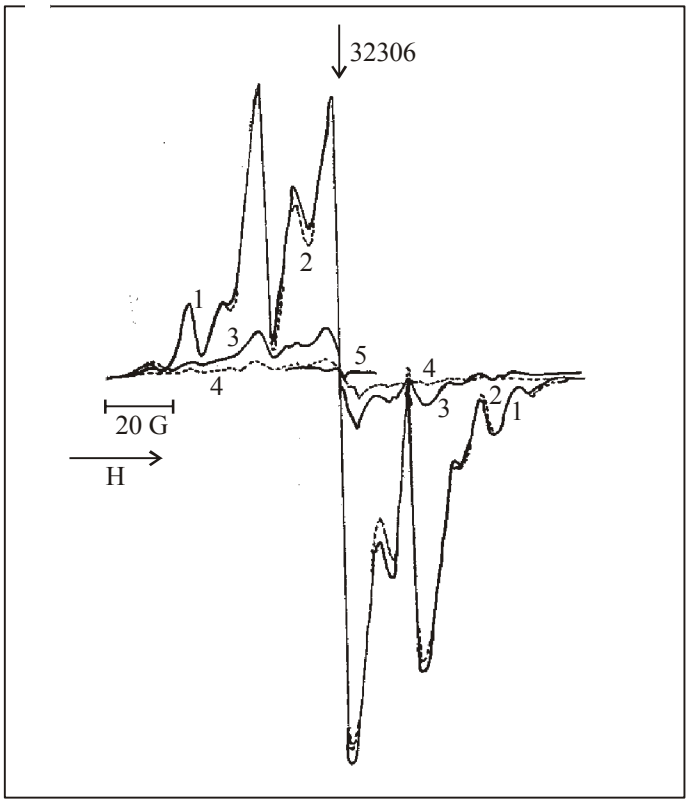

Fig. 1: ESR spectra of gamma irradiated MA AMPS copolymer

The spectrum posses complex hyperfine structure and stimulated to be component spectra arising due to macroradicals (~CH_2-CH-CH_2~), methyl radical (CH_3) and radicals of the type CH_2SO_3H. The superposed spectrum arising due to the combination of component spectra together with the component singlet with result in the experimentally observed spectrum of irradiated MA AMPS copolymer at room temperature[7]. In order to estimate the free radical concentration, the authors have used double integration methods. The average value of intensities obtained by these methods at different temperature are listed in Table 2.

A histogram of intensities against temperature was plotted (Fig. 2). This figure indicates a gradual decrease in intensity with temperature. The decrease in intensity of spectrum with temperature are thought to be associated with the decrease in concentration of free radical on irradiation.

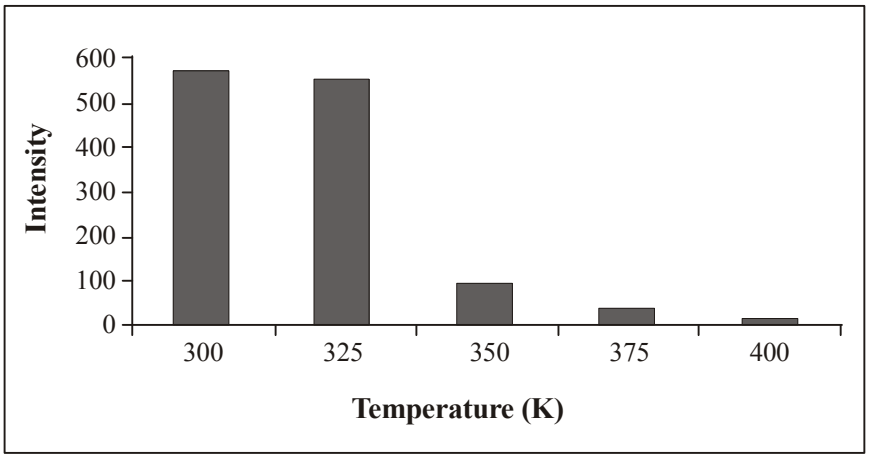

Fig. 2: Temperature versus intensity

Line width of the spectrum at different temperatures has also been calculated using line integration methods. The line widths obtained by these methods are as listed in Table 2. These values indicate a gradual decrease in line width with temperature. The decrease in line width is in consequence to the increase in tumbling rate of free radicals chains at higher temperatures. As the temperatures increases, polymer chains begin to tumble and tumbling rate reaches a maximum value at 400 K in case of MA AMPS copolymer. Since tumbling rate of free radical increase facilitates their recombination, it causes a decrease in their concentration. A plot of line width against temperature was plotted (Fig. 3).

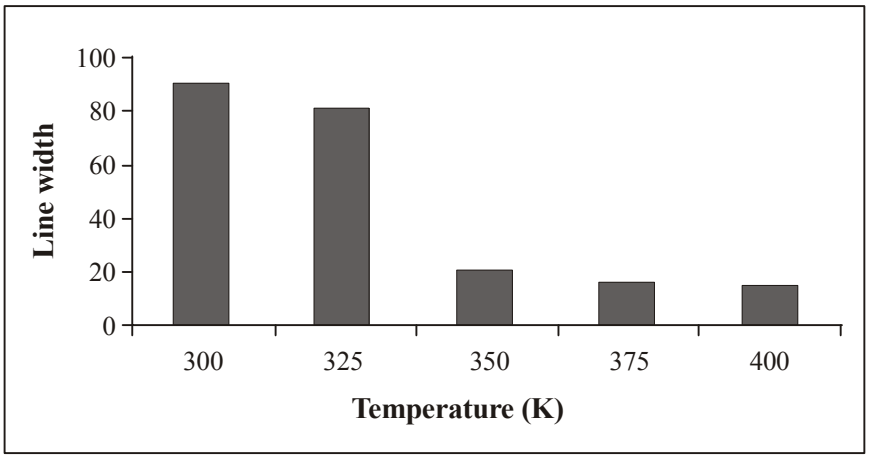

Fig. 3: Temperature versus line width

The decrease in line width is also understood in terms of dissociation of polar groups in MA MPS copolymer. Sanjeeva Rao *et al.*[8] have reported that on irradiation, sulphonic acid groups will be cleaved from the AMPS part of copolymer during initial stage. During further courses of degradation, entire side groups may be cleaved from the main chain of copolymer. Therefore, free volume available for the radical increase, causes an increase in mobility of radical chains[9]. Therefore, tumbling rate of radical chains will increase and it causes a decrease in line width as observed in the present investigation.

A plot of total spread of the spectrum against temperature is shown (in the form of histogram) in Fig. 4. Spread of spectrum was found to decrease with the increase in temperature. Decrease in spread of the spectrum is thought to be caused by decrease in extent of hyperfine interaction.

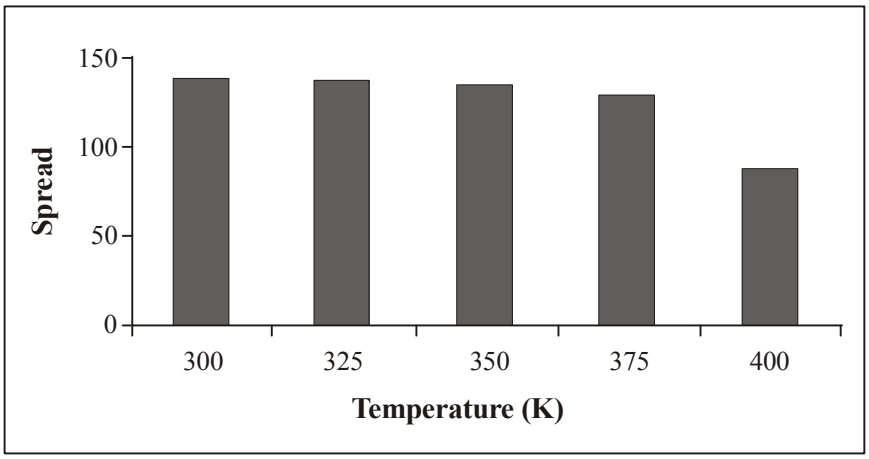

Fig. 4: Temperature versus spread

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