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ESR Evidence of Growing Unsaturation in γ-Irradiated Poly (Vinyl Alcohol)

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Abstract

Free radicals present in gamma irradiated PVAL subjected to different degrees oxidation are identified using ESR spectroscopy. The observed ESR spectra are analysed by computer simulations. Gamma irradiated PVAL immediately after irradiation possess ~CH_2–CH–CH_2~ type free radicals (I). Upon oxidation the free radicals transform to ~CH_2–CH=CH–CH_2~ (II) highly oxidized PVAL consist ~CH_2–C=O (III) type free radicals. The results suggest that radical (I) is precursor to radicals (II) and (III). Oxidation induced unsaturation in Gamma irradiated PVAL.

Keywords: *poly (vinyl alcohol), gamma irradiate degree of oxidation, ESR spectra free radicals*

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INTRODUCTION

Free radicals produced in irradiated poly (vinyl alcohol) (PVAL) are appeared to be sensitive to both types of irradiation and degree of oxidation [1]. Some authors [2,3] have reported an ESR triplet spectrum for irradiated PVAL oxidized to lesser extent and a singlet ESR spectrum for highly oxidized PVAL at room temperature (RT). The triplet and singlet spectra were assigned to ~CH_2–C(OH)–CH_2~ and macromolecular unsaturated radicals, respectively.

Sanjeevara Rao *et al.* [4] have reported degradation studies of PVAL irradiated by gamma rays using ESR technique. They have recorded ESR spectra in the temperature range 300– 400 K. The observed ESR spectral changes are reported to be caused by change in magnetic hyperfine interaction of macromolecular radicals of the type ~CH_2–C(OH)–CH_2~.

Considering the ESR spectra of irradiated PVAL at liquid nitrogen temperature (LNT), a quintet spectrum has been reported by Hase *et al.* [5] and Yasunaga *et al.* [6]. Though the spectrum is same, the radicals reported by these authors are different. Thus, the studies on irradiated PVAL at LNT have been once again taken up to arrive at a consistent understanding on free radicals produced in irradiated PVAL at LNT. Therefore, ESR spectra have been recorded at LNT for irradiated PVAL subjected to different degrees of oxidation. The free radicals associated with these spectra are identified by computer simulations employing total curve fitting method [7, 8].

EXPERIMENTAL

Commercially available poly(vinyl alcohol) in the form of powder with a molecular weight of 14000 has been used in the present investigations. The γ-irradiation of PVAL has been carried out in air at RT with Co^{60} source at a dose rate of 0.2 M Rad/h. EPR spectra of irradiated PVAL were recorded on a Varian E-112 spectrometer operating at X-band frequencies and 100 KHz modulation. The spectrometer is fitted with necessary arrangement to record the ESR spectra at low temperature also. The irradiated PVAL samples are sealed in quartz tubes. Three different samples are taken. The first tube contains PVAL immediately after irradiated.

The second and third tubes contain irradiated PVAL oxidized to different extents.

RESULTS AND DISCUSSION

ESR spectra of γ-irradiated PVAL at LNT (77 K) is as shown in Figure 1. Curves 1, 2 and 3 represent the spectra recorded (i) immediately after irradiation, (ii) irradiated PVAL, oxidised for 1 h, (iii) highly oxidized, respectively. Curve 1 is a quintet ESR spectrum which gradually decays to a triplet (Curve 3) as shown in the Figure 1. Considering curves 1 and 2, the number of hyperfine lines and overall spread are same but the spectra differed in their hyperfine (hf) splittings. Computer simulation of curve 1, 2 and 3 has been carried out by total curve fitting method [7,8] employing the magnetic parameters listed in the Figure 1.

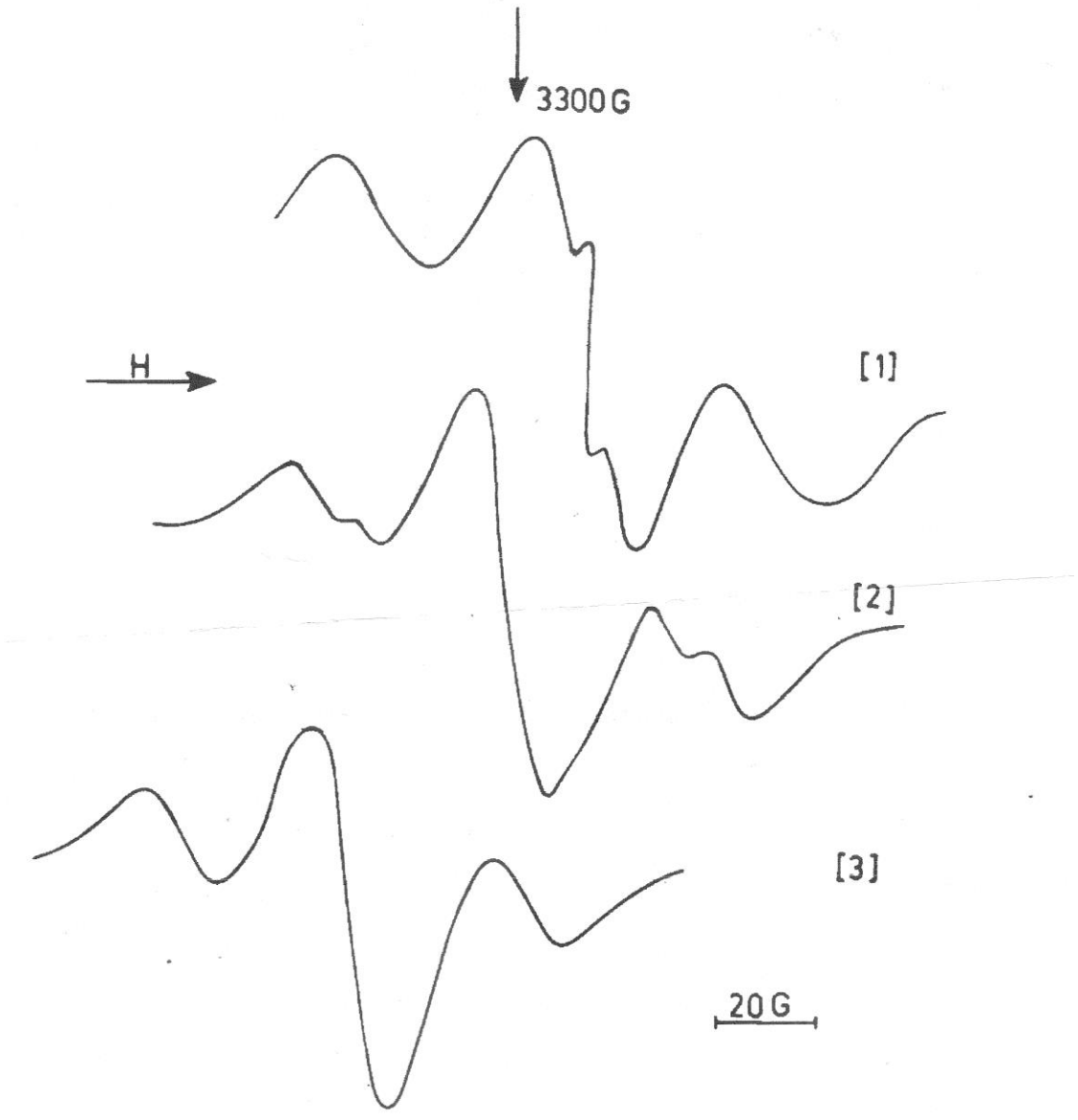

Fig. 1: *ESR Spectra of γ-irradiated PVAL at LNT.*

The ESR spectra of γ-irradiated PVAL at LNT are analyzed by computer simulations assuming Lorentzian line shape function. The method of simulating the ESR spectra by the above method has already been described [7,8]. Curve 1, Figure 1 could be simulated using the magnetic parameters n = 2, m = 5 and with hyperfine splitting of A = 13.67 G,

B=33 G. Magnetic parameters employed simulate curve I indicate that the free radical responsible for curve I has one interacting alpha proton and four Beta protons. Free radicals corresponding to the above parameters may be of the type ~CH_2–CH–CH_2~ or ~CH_2–C(OH) –CH_2~ (I). This type of free radical is formed by abstraction of hydroxyl groups /proton from PVAL main chain. This assignment is in good agreement with the infrared studies of Oyabu [9], who have reported the decrease in the concentration of protons of (CH) groups during initial stages of irradiation of PVAL.

Table 1: *Magnetic Parameters of Irradiated PVAL at LNT.*

Component	Line width a	Relative intensity Y_{max}	Centre of spectrum X_0	Hyperfine coupling constants		n_1	m_1
				A	B		
Curve 1 Quintet	9.55 G	13.55	3310 G	13.67 G	33 G	2	5
Curve 2 Quintet	12.50 G	19.20	3308 G	13.50 G	35 G	2	4
Curve 3 Triplet	13.05 G	19.77	3268 G	0 G	35 G	1	3

Curve 2, Figure 1 has been simulated using the values of n = 2, m = 4 and with splitting of A = 13.5 G, B = 35 G. Therefore free radical responsible for curve 2 has one interacting Alpha proton and three Beta protons. Free radicals having such a structure are of the type ~CH_2–CH=CH–CH_2~. (ii) These radicals may be formed in PVAL by assuming, a chemical transformation in radical I. Formation of radical (II) is also proposed previously [3, 5, 6]. Thus, the process of oxidation in irradiated PVAL enhances unsaturation, as also evidenced from the UV absorption studies [10].

Curve 3, is generated with the 'values of n = 1, m = 3 and A = 0 G, B = 35 G is ~CH_2–C=O (III). Therefore free radicals responsible for curve three will have only two interacting beta protons. i.e., ~CH_2–C=O (III). Formation of radicals (III) is also proposed by various authors previously [2–6].

CONCLUSION

In conclusion, computer simulation of the ESR shown in Figure 1, indicate that the free radicals causing curve 1 (I) are precursor to the (II) and (III). Oxidation of irradiated PVAL enhance unsaturation of PVAL chain.

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