Int. J. Chem. Sci.: 7(4), 2009, 2434-2440

ESR AND FTIR STUDY OF GAMMA IRRADIATED POLY (ETHYLENE GLYCOL)

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ABSTRACT

Gamma irradiation effects on poly (ethylene glycol) (PEG) have been investigated by electron spin resonance (ESR) and Fourier transform infrared (FTIR) techniques. The ESR spectrum observed for gamma irradiated PEG is an asymmetric doublet, whose intensity distribution deviated from the expected values. The spectrum is simulated with the superposition of component doublet and component singlet spectra. Magnetic parameters of the component spectra are evaluated. From the values of magnetic parameters, structure of the free radicals has been predicted. As such, the observed spectrum is considered to arise from the free radicals of the type $\sim\dot{C}HO\sim$ (I) and $\sim CH_2\dot{O}$ (II). FTIR spectra of unirradiated and irradiated PEG have been recorded under different conditions. These studies indicate the formation of carbonyl terminated groups. ESR spectra have also been recorded for the PEG irradiated to higher doses of irradiation.

Key words: Poly (ethylene glycol) (PEG), Gamma irradiation, ESR spectra, FTIR spectra, Free radicals.

INTRODUCTION

Poly (ethylene glycol) (PEG) is hydroscopic polymer and find innumerable applications[1,2]. They are used as binders in powder metallurgy and also used in ceramic and lubricant industries.

Ultrasonic degradation of PEG in solution has been reported by Vijayalakshmi and Giridhar[3] using molecular weight measurement and GPC technique. In another paper, Vijayalakshmi and Giridhar[4] have studied thermal and microwave degradation of PEG

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solution and found that temperature and oxidizing agent determine the extent of degradation in PEG.

Sanjeeva Rao and Ramakrishna Murthy have[5,6] observed an ESR doublet spectrum for gamma irradiated PEG and assigned the spectrum to be due to aldehyde terminated groups ~ĊHO~. These authors have simulated the spectrum and magnetic parameters corresponding to the free radicals have been evaluated.

It is reported that addition of heavy metal ion accelerates the degradation of PEG while alcohols mitigates degradation[7]. Berkonsky et al.[8] have reported ultrasonic degradation of PEG and reported that cleavage of PEG accompanies with incorporation of weak bonds into the polymer backbone.

In the present studies, the authors have irradiated the PEG to different radiation doses and recorded the ESR and FTIR spectra. The ESR spectra have been analysed by computer simulations and component spectra at different conditions have been separated. FTIR spectra of unirradiated and irradiated PEG have been compared to ascertain chemical changes induced by gamma irradiation of PEG.

EXPERIMENTAL

Poly (ethylene glycol) in the form of flakes with molecular weight of 20000 supplied by CDH laboratories, New Delhi was used in the present studies. Gamma irradiation have been done by exposing the PEG to Cobalt 60 gamma source having dose of 0.15 Mrad/hour in air at room temperature. ESR spectra of gamma irradiated PEG are recorded on Varian E line spectrometer operating at X- band frequencies and 100 kHz frequency modulation. Fourier transform infrared (FTIR) spectra of PEG are recorded on a Perkin- Elmer spectrometer by making pellets of polymer along with potassium bromide.

RESULTS AND DISCUSSION

ESR spectrum of PEG irradiated to 1 Mrad dose of irradiation is shown as Curve 1 (Fig. 1). The curve is a doublet with a spacing of 12G. Curves 2, 3 and 4 represent the ESR spectra of PEG irradiated to 3, 6 and 9 Mrad doses of irradiation. The spectra at higher doses are also doublets with same hyperfine separation. However, intensity of the spectra gradually increased with increase in radiation dose.

Fig. 1, Curve 1 can be simulated with the component spectra shown in Fig. 2. Curve 1, Fig. 2 is a component doublet and Curve 2 is a component singlet. Magnetic parameters

employed to simulate the component spectra are listed in Table 1. ESR spectra of gamma irradiated PEG at liquid nitrogen temperature (LNT) is shown in Fig. 3. The spectrum is also a doublet but when compared to room temperature (RT) the LNT spectrum is broadened.

Table 1: Magnetic parameters of component spectra of PEG irradiated to different radiation doses

S. No.	Radiation dose (Mrad)	Line width (a_i)	Relative intensity ($Y_{max\,i}$)	Centre of spectrum (X_{00})	A_i	B_i	n_i	m_i
1	3	10.5	4.5	3470	11	0	2	1
2	6	10.0	5.5	3470	11	0	2	1
3	9	10.3	6.8	3470	11	0	2	1

Fourier transform infrared spectrum of unirradiated PEG is shown in Fig. 4. The spectrum possess various absorption bands as listed in Table 2. The FTIR spectra of PEG have also been recorded by irradiating the polymer to various doses of irradiation. The variation in intensity of 1720 cm^{-1} and 1680 cm^{-1} absorption bands was observed as depicted in Fig. 5.

Table 2: Interpretation of infrared absorption bands of PEG

S. No.	Band position (cm^{-1})	Intensity	Band assignment
1	3450	Strong	OH group
2	2960	Medium	CH_2 / CH_3 group
3	1720	Medium	C-O or C=O group
4	1450	Medium	CH_3 group
5	1380	Medium	CH_3 / CH_2 group
6	1180	Medium	CH_2 / CH group

Computer simulations

ESR spectra of gamma irradiated PEG under different conditions have been analysed by computer simulations. The spectra are basically doublets. The intensity distribution in

ideal case for doublet is 1 : 1. However, the doublets observed in the present case does not possess such ratio. The reasons for the variations in line intensity is thought to be due to two reasons, (i) Either interplay of hyperfine interaction within the protons of the free radicals, or (ii) Superposition of component spectra arising due to various free radicals generated on irradiation of PEG. The component spectra are simulated using the values of magnetic parameters, line width (a_i), relative intensity ($y_{max\ i}$), centre of spectrum (X_{oi}), hyperfine splitting (A_i, B_i) and number of lines resulting from adjacent nuclei (n_i, m_i). The component spectra generated by varying the values of magnetic parameters are superposed to yield experimental spectrum.

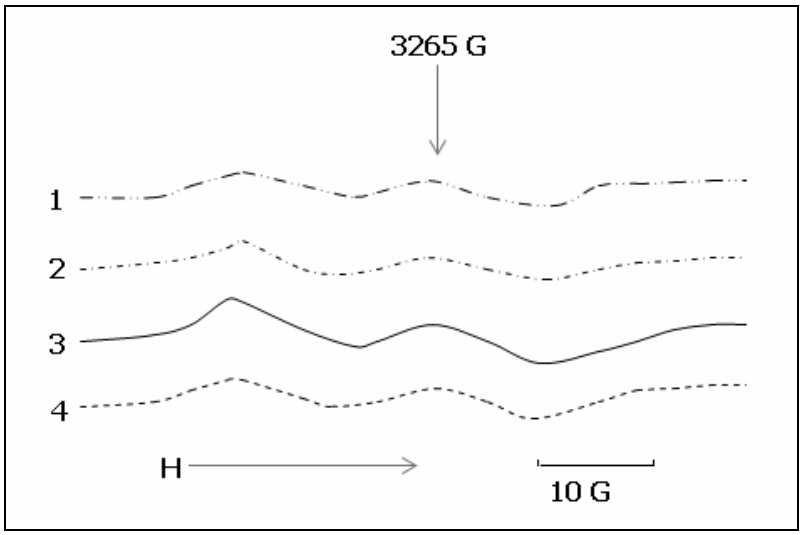

Fig. 1: ESR spectra of PEG radiated to different radiation doses

(1) 1 M rad **(2)** 3 M rad **(3)** 6 M rad **(4)** 9 M rad

ESR spectra of PEG irradiated to 1, 3, 6 and 9 Mrad doses of irradiation are as shown in Fig. 1. The spectrum of PEG irradiated to 1 Mrad dose can be simulated with the component spectra is shown in Fig. 2. Curve 1 is component doublet and Curve 2 is component singlet. Curve 1, Fig. 2 is simulated with the values of $n_i = 2$, $m_i = 1$; $A_i = 12$G and $B_i = 0$ G. The values confirm the presence of one alpha proton and there are no interacting beta protons. Curve 2 is the component singlet spectrum, which can be simulated with the values of $n_i = m_i = 1$ and $A_i = B_i = 0$ indicating that there are neither alpha nor beta protons interacting with the unpaired electron. The superposition of component doublet (Curve 1, Fig. 2) together with component singlet (Curve 2, Fig. 2) gives the superposed spectrum identical to Curve 1, Fig. 1. The free radical responsible for component doublet are assumed to be of the type ~ĊHO~ (I). Considering the chemical structure of radical I, it has

one interacting α- proton, which causes two hyperfine lines. Formation of such type of free radicals have also been reported earlier[9]. The values of magnetic parameters employed to simulate component doublet at various doses are listed in Table 1.

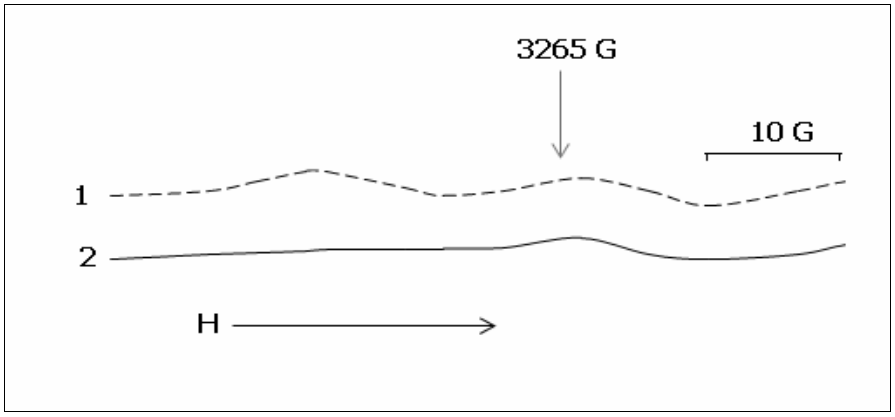

Fig. 2: Component ESR spectra of PEG irradiated to 1 M rad.

(1) Component doublet **(2)** Component singlet

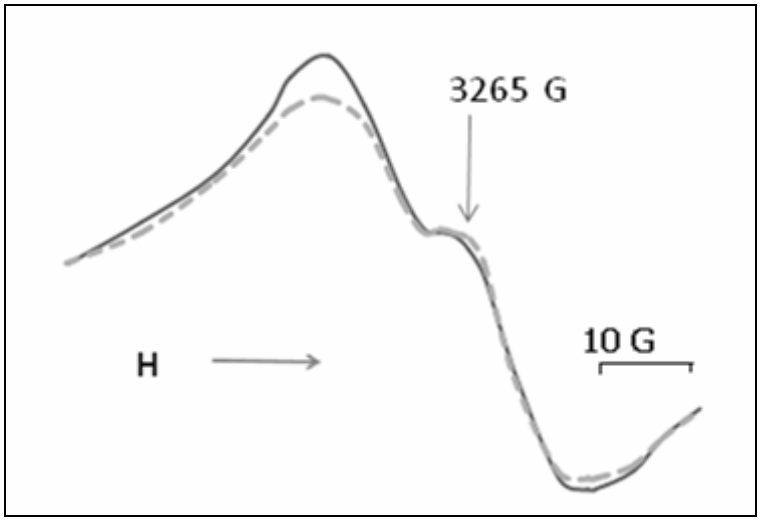

Fig. 3: ESR spectrum of irradiated PEG

--------- at RT ——— at LNT

Regarding the ESR spectra of PEG irradiated to higher doses of irradiation, the shape and pattern of the spectrum is almost same, but a change in intensity has been observed. Therefore, presence of almost same type of free radicals are expected at higher

doses. Thus, ESR spectra at higher doses can also be simulated with almost same set of magnetic parameters.

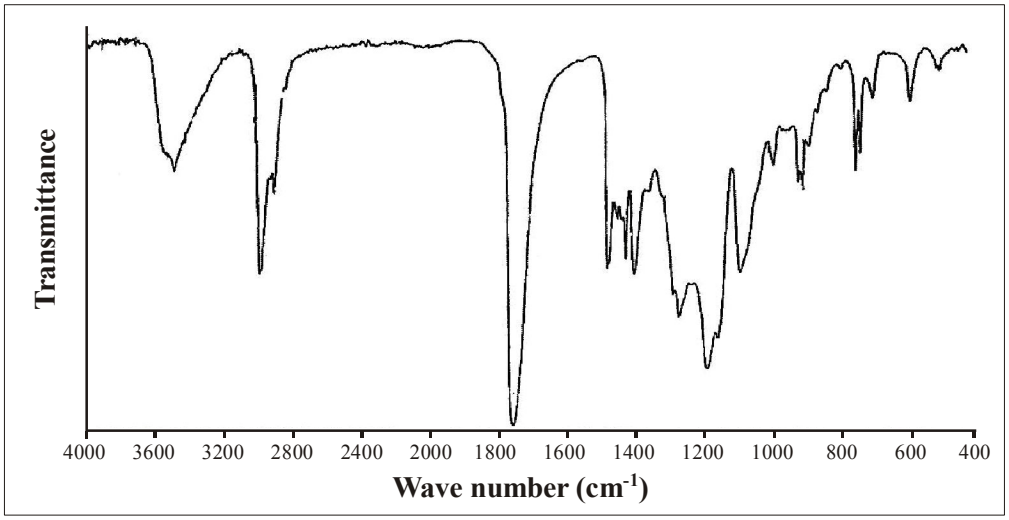

Fig. 4: FTIR spectrum of PEG

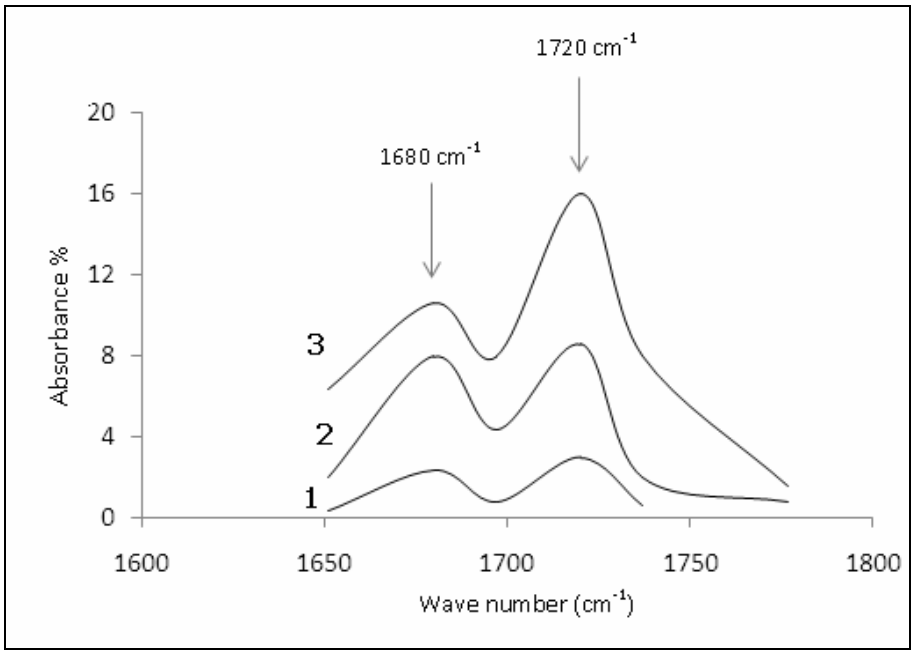

Fig. 5: Variation in intensity of FTIR absorption band with radiation dose

(1) 1 M rad **(2)** 3 M rad **(3)** 6 M rad

ESR spectrum of gamma irradiated PEG has also been recorded at liquid nitrogen temperature at 77 K (LNT). The spectrum is also a doublet. However, the spectrum at LNT was found to be broadened than the spectrum observed at RT. The broadening of the spectrum was observed to be reversible and hence, it is attributed to the molecular relaxation occurring in the macromolecular free radical chains[9].

Considering the FTIR spectra of pure and irradiated PEG, the absorption bands are observed at 3600-3450 cm^{-1}, 2950 cm^{-1}, 2880 cm^{-1}, 1720 cm^{-1}, 1450 cm^{-1}, 1380 cm^{-1} and 1180 cm^{-1} regions. These bands are attributed to various chemical groups present in the polymer as listed in Table 2. On irradiation, a change in intensity of 1720 cm^{-1} and 1680 cm^{-1} absorption bands was observed (Fig. 5). The figure indicates a gradual increase in intensity of the absorption band with an increase in dose of irradiation. Presence of these two groups indicate the formation of carbonyl group on irradiation.

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Accepted: 31.07.2009