

ESR Analysis of Some Irradiated Polymers: Poly (Acrylic Acid)

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Abstract: Electron Spin Resonance (ESR) spectroscopy is an important tool to investigate radiation induced processes in polymer based materials. The major changes occur in irradiated polymers is through the formation of free radical intermediates. Thus identification of free radicals in irradiated polymers is one of the major tasks. In this context, the authors examine the case of poly (acrylic acid) (PAA), a water soluble polymer. ESR spectra of irradiated PAA are recorded at different temperatures and radiation doses. Hyperfine interactions under different conditions are reported in this article.

Keywords: PAA, ESR spectra, radiation effects, free radicals, hyperfine interactions.

1. INTRODUCTION

Poly acrylic acid (PAA) possess hydroxyl groups which makes it to have hydrophilic nature and they are responsible for inter molecular hydrogen bonding within itself or with any other molecular system. PAA is also soluble in polar solvents like methanol. Thin transparent films of PAA are prepared by dissolving the polymer in above solvent and on slow evaporation. PAA is also proved to be an efficient reducing agent to synthesize silver nano particles (1, 2). The hydroxyl groups (OH) groups of the polymer are capable of reducing metal ions to metal nano particles (1, 2). Such polymer metal composites are reported to retrieve heavy metal particles from polluted water. Glass transition temperature of PAA is well above room temperature making it to use in different applications. PAA can easily co polymerized with poly acryl amide, which is also water soluble, making it to suitable for various applications, including super absorbent hydro gels.

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Thermal degradation studies of PAA (3, 4) (164, 165) indicates that the polymer undergo random chain scission forming different molecular fragments but the monomer yield {i.e., $\sim\text{CH}_2\text{-}\dot{\text{C}}\text{(COOH)}$ type products} was reported to be very low. Kamitakahara et al (5) (166) has reported thermal degradation of PAA with decarboxylation of the polymer at low temperatures; cyclization is predominant at higher temperatures. Effects of ionizing radiations on PAA have been reviewed by Campbell et al (6) (167). Solid state polymerization of acrylic acid monomer to form poly (acrylic acid) (solid state polymerization) and process of polymerization has been monitored by ESR spectroscopy. The process of solid state polymerization of acrylic acid monomer by UV- irradiation, has been reported by Bresler et al (7) (168), employing ESR spectroscopy. An ESR triplet spectrum with hyperfine splitting of 30 G has been reported for PAA, which was assigned to macromolecular free radicals of the type $\sim\text{CH}_2\text{-}\dot{\text{C}}\text{(COOH)-CH}_2\sim$. Shioji et al (8) (169), have reported a double quartet spectrum for irradiated single crystals of acrylic acid (monomer), whose line shape is reported to depend on temperature of observation. The chemical structure of radiation product was identified as $\text{CH}_3\text{-}\dot{\text{C}}\text{(COOH)}$ and the change in line shape was attributed to the rotation of methyl group around the $\text{C}_\alpha\text{-C}_\beta$ bond axis of the free radical. The observed spectrum gradually decayed to a stable triplet spectrum with hyperfine splitting of 24.5 G on warming the sample to room temperature (RT). The quintet and triplet spectra were assigned to chain radicals of the type $(\sim\text{CH}_2\text{-}\dot{\text{C}}\text{(COOH)})_n$ and $\sim\text{CH}_2\text{-CH-CH}_2\sim$ respectively. Ormerod and Charlesby(9) (170), have studied radiation induced reactions in PAA at LNT and proposed the existence of trapped electrons. Charlesby (10) (171), have attributed the ESR spectrum of irradiated PAA (polymerized by gamma irradiation of monomer) to more than one free radical species, which include propagating radicals of the type, $\sim\text{CH}_2\text{-}\dot{\text{C}}\text{(COOH)}$ and $\dot{\text{C}}\text{OOH}$ radicals. The decay of singlet spectrum with a width of 9 G on warming indicates that free electrons are not trapped in the polymer matrix. The additional hyperfine structure observed at 77K reported to disappear gradually on heat treatment to room temperature (RT).

Sanjeeva Rao and Ramakrishna Murthy (11) (172) have reported the ESR studies of gamma irradiated poly acrylic acid. They have (9) observed a ten- line ESR spectrum at RT and well resolved spectrum was observed at liquid nitrogen temperature (LNT). The resolution of the spectrum is reported to be associated with the hindered rotation of adjacent methyl/ (methylene) groups of free radicals $\sim\text{CH}_2\text{-}\dot{\text{C}}\text{(COOH)-CH}_2$ (I). These authors have used computer simulation techniques to analyze the ESR spectra. Based on the magnetic parameters used in computer simulations, cleavage of side (COOH) groups in PAA and formation of macro radicals is reported (9). The results are further confirmed by comparing the IR spectra of irradiated and unirradiated PAA. The observed decrease in intensity of $3400\text{-}3100\text{ cm}^{-1}$ absorption band indicates the decrease in intensity of COOH groups indicating their cleavage on irradiation.

Though gamma irradiation effects on PAA have been attempted previously, little is known about temperature and radiation dependent changes. The present studies devoted to these aspects. Hyperfine interactions of free radicals at different temperatures are studied and activation energy associated with free radical decay is calculated.

2. EXPERIMENTAL

Poly acrylic acid (PAA) in powder form was procured from BDH laboratory. Polymer films have been prepared by solution casting method. 1 gm of PAA is dissolved in 10 ml water/ methanol and stirred for few hour and resultant mixture is vacuum dried at 60°C for several hours to obtain thin films of polymer. Gamma irradiation is performed using Cobalt 60 gamma source with a dose rate of 0.15 M rad (15 K Gy)/hr in air at room

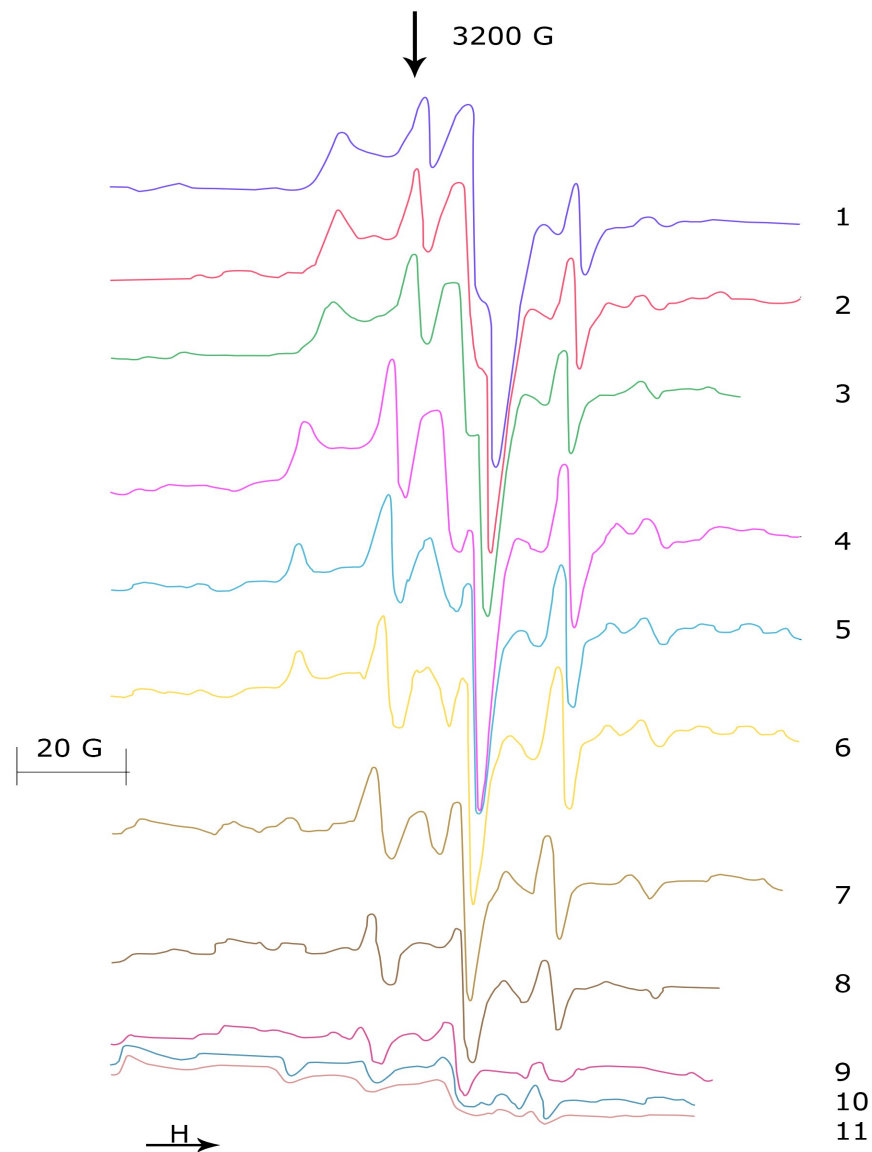
temperature. ESR spectra of irradiated polymer are recorded on VARIAN E-112 spectrometer operated at X-band frequency and 100 KHz modulation.

3. RESULTS AND DISCUSSION

Temperature Dependency:

ESR spectra of PAA irradiated to 5 M rad radiation dose at different temperatures of 30,40,60,70,80,90,100 and 110, 120,130,140⁰ C are shown as curves 1,2,3,4,5,6,7,8,9,10 and 11 in **Figure 1**. The spectrum at RT (30 C) consists of ten hyperfine lines with splitting of, 23 G and 10-12 G (Listed in Table 1) is shown as curve 1 **Figure 1**. With the increase of temperature intensities of some of the hyperfine lines (lines 3, 5, 7 and 9) increase at the expense of others (lines 2, 4, 6, 8). A shift in line positions is also observed. The peak to peak separation and spread of the spectrum gradually decreased with temperature. The ESR spectra observed at other temperatures are shown as curves 2,3,4,5,6,7,8,9,10 and 11 in **Figure 1**. At the temperature of 140⁰C (curve 10) quintet spectrum corresponding to hyperfine line, 2,4,6,8 appeared. Finally the quintet also reduced and the ESR signal totally vanished above 140⁰C. ESR spectra under different conditions are assigned to the following types of free radicals.

They are (i) $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$ I (macro radical) (ii) $\text{CH}_2-\dot{\text{C}}\text{H}(\text{COOH})$ (iii) $\dot{\text{C}}\text{H}_2-\text{CH}(\text{COOH})-\text{CH}_2$. The hyper fine lines arising due to these free radicals depend on the hyper fine interaction of alpha and beta protons with the unpaired electron as observed in case of irradiated poly acrylates [poly (methyl methacrylate), Poly methyl acrylate etc] which are reported to give doublet of quintet ESR spectrum] (12). Formation of radical I is reported in most of the cases. Chemical constitution of (I) indicate the presence one proton in α -position (which gives two hyperfine lines) and four protons in β position (five lines are expected). Therefore radical I have to give (2x5=10) ten-line hyperfine spectrum in case of isotropic interaction of alpha and beta protons. The proton in alpha position give doublet spectrum with an intensity distribution of 1 : 1 and four protons in beta protons results in quintet spectrum with an intensity distribution of 1:4:6:4:1. When the quintet superpose on the doublet, the intensity distribution of resultant ESR spectrum is 1:1:4:4:6:6:4:4:1:1 and it appear as ten-line spectrum. However in most of the observed ESR spectra, the hyperfine pattern deviate from the theoretical values due to the variations in line width to hyperfine splitting constant ratio (13). Due to in - equivalency of protonic interaction, the hyperfine lines due to radical I will vary. Consequently the ESR spectrum of irradiated PAA also resemble double quintet shape with 2,4,6,8,10 lines as first quintet with a hyper fine splitting of 20-22 G while hyperfine lines 1,3,5,7,9 giving quintet II with splitting of 20-22 G. It is observed that intensity of first quintet increased while quintet II decreased with increase of temperature. With regard to other free radicals II to give quintet spectrum and radical III gives quintet spectrum. In view of hyper fine line separation and intensity distribution presence of II and III is ruled out and radical I is proposed in the present studies. Spread of the spectrum is related to chain length of the free radical (14 Indira).



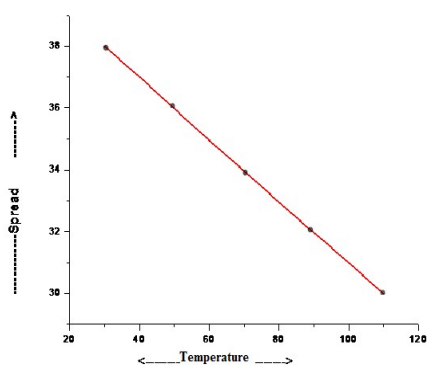
Curve 1:30 °C, Curve 2:40 °C, Curve 3:60 °C, Curve 4:70 °C,
 Curve 5:80 °C, Curve 6:90 °C, Curve 7:100 °C, Curve 8:110 °C,
 Curve 9:120 °C, Curve 10:140 °C, Curve 11: above 140 °C.

Figure 1: ESR spectrum of irradiated PAA at different temperatures.

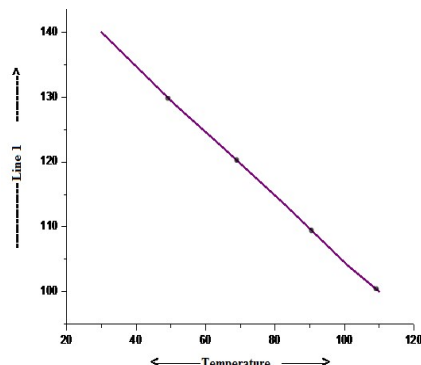
As the spread decrease with temperature, length of the free radical I is thought to decrease as shown in **Figure 2**. With regard to peak to peak separation, it also found to decrease with temperature as shown in **Figure 2**. In order to study the hyperfine interaction of spectral lines their intensity variation against temperature has been plotted as shown in **Fig 2**.

Table 1: Hyperfine parameters of irradiated PAA at different temperatures 2,4,6,8 decrease 3,5,7,9 increases

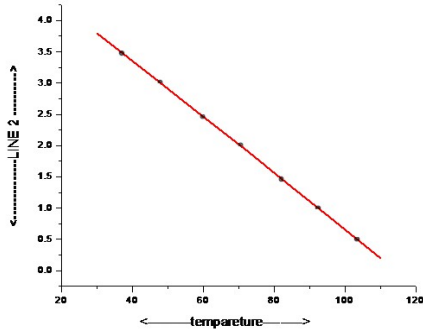
Temperature	dV	Spread	Line – 2	Line - 3	Line - 4	Line - 5	Line – 6	Line – 7
30	38	140	3.8	-	4.2	9.0	10	5.2
40	37	130	3.4	0	4.0	8.0	9.5	5.2
60	36	120	3.2	-	3.8	4.0	9.0	4.6
80	35	110	1.2	-	3.5	2.2	8.0	4.4
90	33	110	0.8	0.3	3.0	1.4	6.6	4.0
100	32	100	0.5	0.35	2.5	1.2	4.4	3.2
110	30	100	0.2	-	2	-	4	2



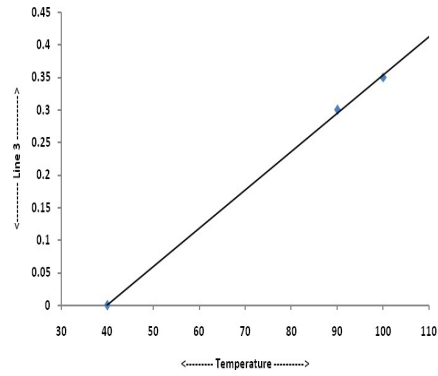
Curve 1



Curve 2



Curve 3



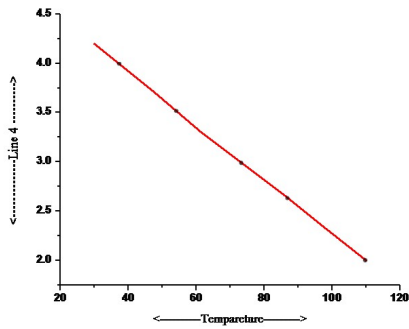
Curve 4

Curve 1: Variation of Spread against Temperature.

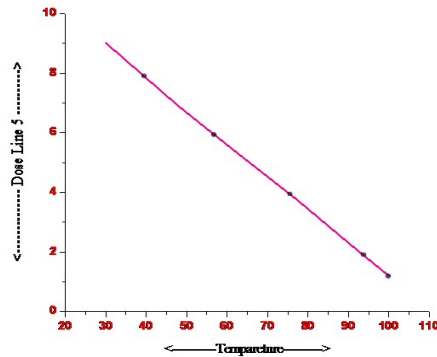
Curve 2: Temperature vs Intensity of line 1.

Curve 3: Temperature vs Intensity of line 2.

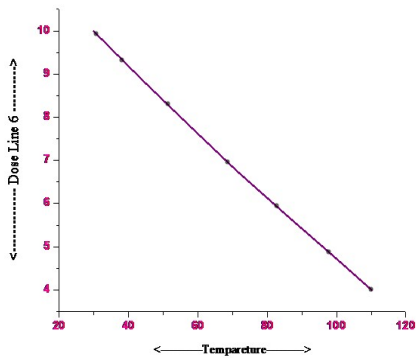
Curve 4: Temperature vs Intensity of line 3.



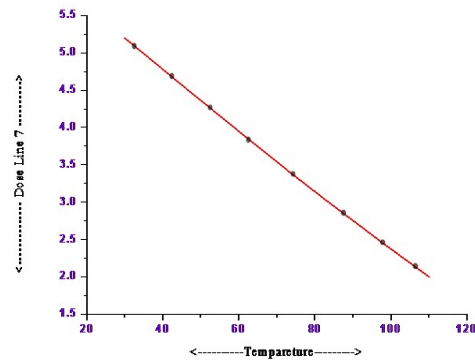
Curve 5



Curve 6



Curve 7



Curve 8

- Curev 5: Temperature vs Intensity of line 4.
- Curev 6: Temperature vs Intensity of line 5.
- Curev 7: Temperature vs Intensity of line 6.
- Curev 8: Temperature vs Intensity of line 7.

Figure 2: Variation of hyperfine parameters with temperature

The results suggest that hyper fine interactions also cease to exist with increase of temperature. Melting temperature (T_m) of PAA is reported to be around $200^{\circ}C$ (15 Srinivas). ESR signal decay of irradiated PAA below the T_m indicates that the free radicals are trapped in amorphous region of polymer. Such type of free radical decay below the T_m has also been observed for several semi - crystalline polymers (Rajesh)(16). Free radical formed on gamma irradiation of PAA gain thermal energy with the increase of temperature and initiate reaction with un - fragmented parts of polymer chains to form stable cross linked structures.

Bloch analysis is used to calculate activation energy associated with free radical decay (11 EvRao) (17). This analysis requires measurement of line width (μ) at different temperatures, which can be calculated using the Lorentzian and Gaussian line shape properties (18 Sanjeevarao). Using the values of line width (μ), the values of τ are calculated (18). Then by plotting $1/T$ on X- axis and $\log 1/\tau$ on Y-axis a straight line is obtained as shown in **Figure3**. Using the slope of straight line, the value of activation energy associated with free radical decay is calculated. The values of μ , τ and other parameters are as listed in **Table 2**. Using this method the activation energy is around 145 KJ/ Mole.

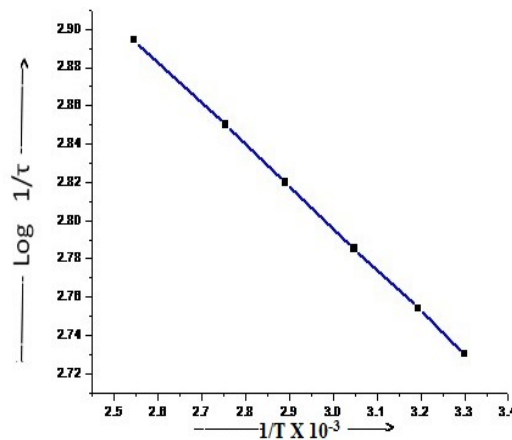


Figure 3: Bloch analysis of irradiated PAA [1/T vs. log 1/τ graph]

Table 2 : Parameters used in Bloch analysis for evaluation of activation energy.

S. No	Temp(t) in °C	T	$\Delta\theta$	τ	$1/T \times 10^{-3}$	$\text{Log}(1/\tau)$
1	30	303	29	-	3.300	-
2	40	313	27	2.83	3.194	2.532
3	60	333	25.5	2.74	3.003	2.560
4	70	343	24.25	2.29	2.915	2.593
5	80	353	23.5	2.24	2.832	2.640
6	90	363	22.85	2.16	2.754	2.657
7	100	373	21.97	1.71	2.680	2.681
8	110	383	21.15	1.21	2.610	2.763

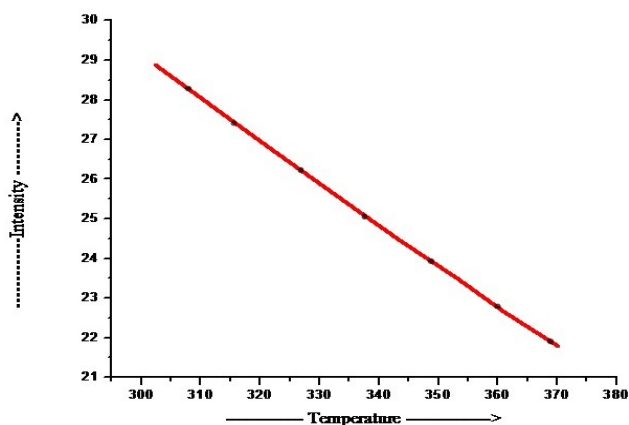


Figure 4: Intensity variation of gamma irradiated PAA with temperature.

Variation of overall intensity of ESR spectra at different temperatures is also plotted as shown in **Figure 4**. Linear of the graph indicate homogeneous decay of free radicals.

Radiation Dose Dependency

ESR spectra of PAA irradiated to different radiation dose rate (1, 1.5 and 2 M rad dose) are as shown curves 1, 2, 3 in **Figure 5**. The intensity and spread of the spectra gradually increases with the radiation dose. Therefore more number of chain cleavages occurs

increasing the free radical concentration. Hyperfine parameters are listed in **Table 3**. Variation of hyperfine parameters with radiation dose is as depicted in **Figure 6**.

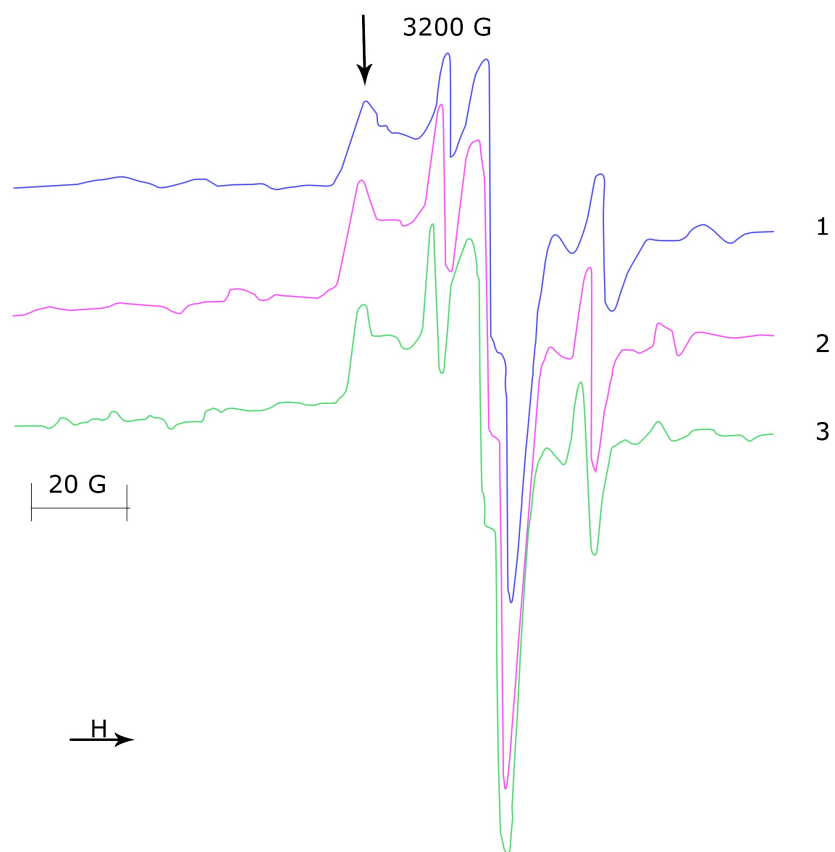
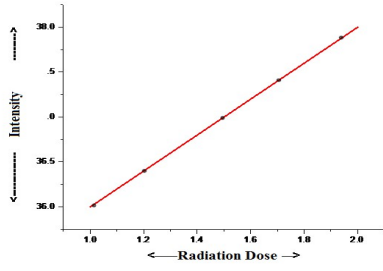


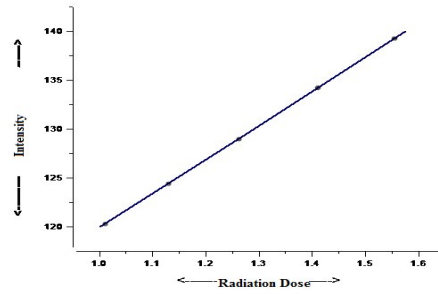
Figure 5: ESR spectrum of PAA irradiated to different radiation doses (1) 1.0 M rad (2) 1.5 M rad (3) 2.0 M.rad.

Table 3: Hyperfine parameters at different radiation doses

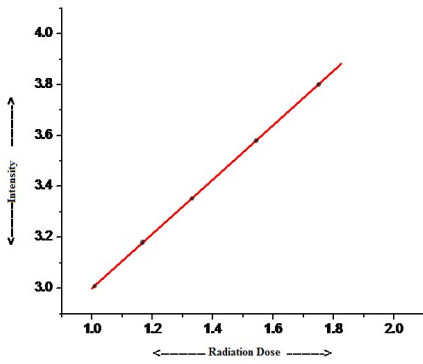
Dose M rad	dV	Spread	Line - 1	Line - 2	Line - 3	Line - 4	Line - 5	Line - 6	Line - 7
1.0	36	120	3.0	3.2	3.0	8.0	7.0	0.5	4.0
1.5	37	130	3.5	3.9	5.0	9.0	10.0	0.6	5.0
2.0	38	140	4.2	4.3	4.4	9.2	10.0	0.8	6.0



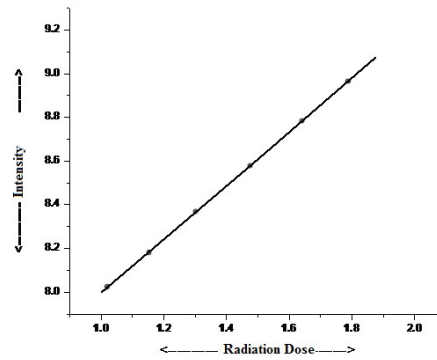
Curve 1



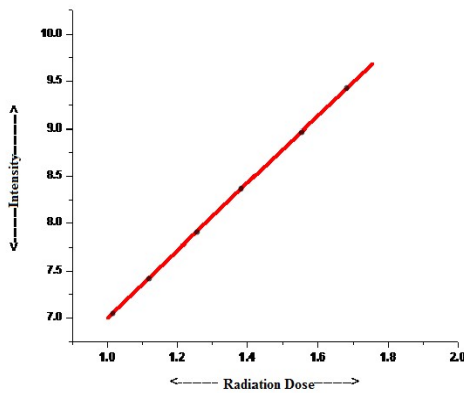
Curve 2



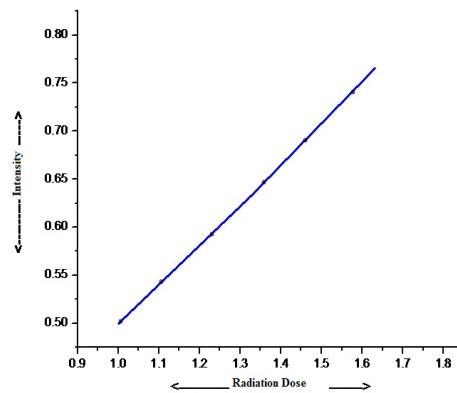
Curve 3



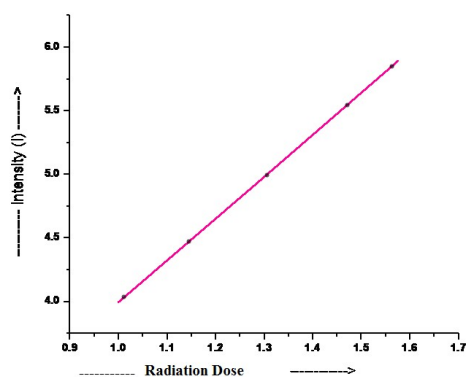
Curve 4



Curve 5



Curve 6



Curve 7

Curve 1: Variation of Intensity of line 1 against Radiation Dose.

Curve 2: Variation of Intensity of line 2 against Radiation Dose.

Curve 3: Variation of Intensity of line 3 against Radiation Dose.

Curve 4: Variation of Intensity of line 4 against Radiation Dose.

Curve 5: Variation of Intensity of line 5 against Radiation Dose.

Curve 6: Variation of Intensity of line 6 against Radiation Dose.

Curve 7: Variation of Intensity of line 7 against Radiation Dose.

Figure 6: Variation of hyperfine parameters with radiation dose.

Micro-Structure Analysis (SEM STUDIES)

Change in surface morphology of PAA has been investigated by Scanning Electron Microscope technique. PAA is a water soluble polymer. Hence treatment of PAA with radiation induces several interesting changes. These changes are observed by SEM micrographs. Surface of un irradiated PAA is shown in **Figure 7**; while surface of irradiated PAA is as shown in **Figure 8**. SEM pictures indicates that, irradiation brought cracks and bores on the surface of PAA as shown in **Figure 8**.

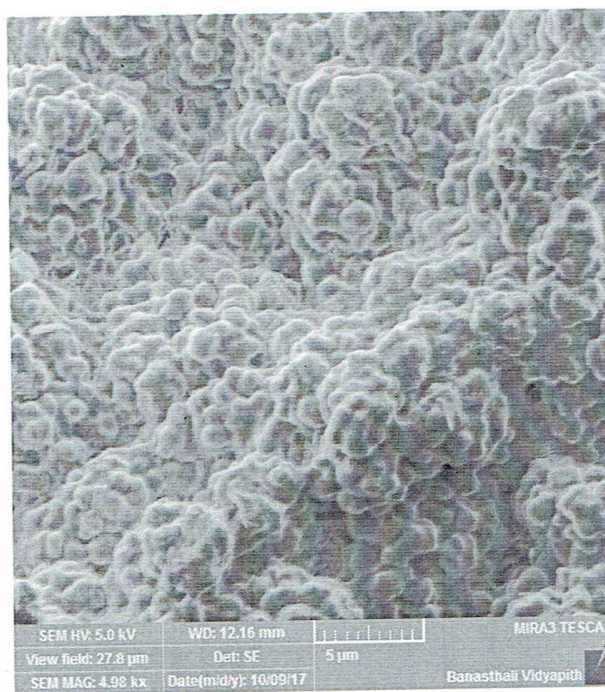


Figure 7: SEM micrograph of unirradiated PAA.

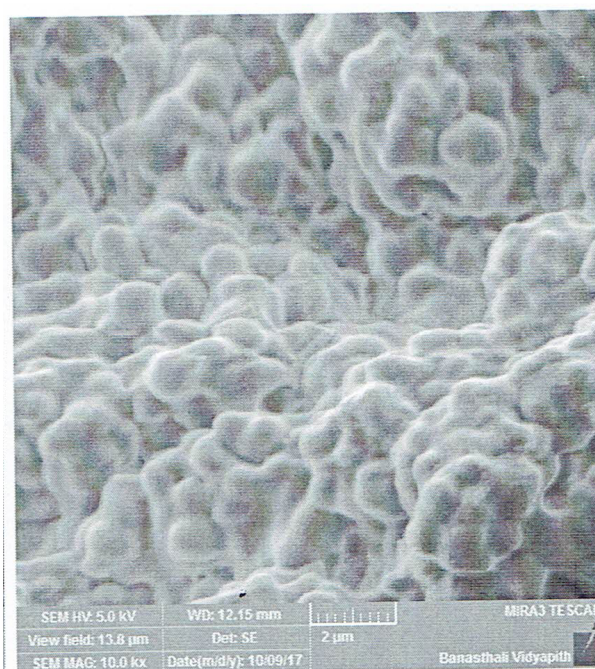


Figure 8: SEM micrograph of irradiated PAA.

4. CONCLUSIONS

In conclusion radiation induced change in PAA has been investigated using ESR technique. Homo polymer contains more number of hyper fine lines than the copolymer. Free radical decay temperature of PAA is more than the copolymer. Since the copolymer poses more number of free radicals, they can form intermediate structures by cross linking reactions, so that number of hyperfine lines in ESR spectra is less. SEM studies suggest that due to irradiation, cracks and bores are created on PAA due to gamma irradiation.

5. REFERENCES

- [1] Rivas, B.L.and Mariadel C. A., "Synthesis and characterization of new water-soluble metal-polymer complex and its application for arsenite retention". *J. Appl. Polym. Sci*, 111, 2720–2730 (2009).
- [2] Yahya H.F.Al-qudah, Ghad A.Mahmoud and M.A.Abdel Khalek G. A.Mamond, "Radiation cross linked poly (vinyl alcohol)/acrylic acid copolymer for removal of heavy metal ions from aqueous solutions", *J.Rad. Res and Appl Sci.*, 7, 135-145 (2014).
- [3] S. Francis, M. Kumar and L. Varshney, " Radiation Synthesis of super absorbent Poly (acrylic acid)z) – carrageenan hydro gels", *Rad. Phys. Chem.*, 69, 481 -485 (2004).
- [4] Lv Long Nan Chen Chuan ping Feng, Jing Jhang and Miao Li, "Heavy metal ion removal from aqueous solution by xanthane modified crosslinked magnetic chitosan / Poly(vinyl alcohol) particles", *Roy. Soc. Chem. Adv.*, 7, 27992 – 28000 (2017).
- [5] H. Kamitakahara, Y. Enomoto, C. Hasegawa, P. Nakatsubo, " Synthesis of diblock copolymers with cellulose derivatives 2 Charecterization and thermal properties of cellulose triacetate –block –oligoamide -15", *Cellulose*, 12(5), 527 –554 (2005).
- [6] W. Tod, D. Campbell, S. Veronika and Foldi, "Condensation Polymers from diisocyanates with dihydrazides and hydrazine", *J. Appl. Polym. Sci.*, 2, 155 – 162 (1959).
- [7] Bresler, S. E., and E. N. Kazbekov. "Macroradical reactivity studied by electron spin resonance." *Fortschritte Der Hochpolymeren-Forschung*. Springer, Berlin, Heidelberg, 688-711 (1964).
- [8] YuJi Shioji Shun Ichi Ohinishi zand Isamu Nitta, "ESR study of irradiated acrylic acid and reaction of the product radical", *J. Polym. Sci. A*, 11, 3373- 3384 (1963).
- [9] Ormerod, M. G., and A. Charlesby, "The radiation chemistry of some polysiloxanes: an electron spin resonance study." *Polymer*, 4, 459-470 (1963).
- [10] Charlesby, "Atomic Radiation and Polymers," Pergamon Press, New York, N. Y, 198 and 467 (1960).
- [11] B. Sanjeeva Rao and M. Ramakrishna Murthy, "ESR study of Irradiated poly (acrylic acid)", *J. Polym. Sci. B*, 27, 1187- 1192 (1989).
- [12] N. Subbarami Reddy, B. Sanjeeva Rao, A. Parashuram Jhadav, G. Punnaiah and V. Sridhar & S. Veerabhadraiah, "Identification of free radicals in irradiated MA – AMPS copolymer", *Radiat Effect & Defect in Solid*, 157, 411 – 415 (2002).
- [13] M. Igarshi, "Free Radical identification by ESR in Polyethylene and Nylon", *J. Polym. Sci. A*, 21, 2405- 2425 (1983).
- [14] B. Sanjeeva Rao, S. Indira, V. Sridhar, G. Punnaiah, T. V. Appa Rao, "Temperature and Dose Dependency of free radicals in irradiated Poly (ethylene terephalate)", *Radiation Effect & Defect Solids*, 161, 31 – 39 (2006).
- [15] Ch. Srinivas, S. Kalahasti, B. Sanjeeva Rao, K. Rajendra Prasad and S. Ramesh, "A Study on thermal properties of AA copolymer – Silver metal particle Complexes", *Research J Pharm Biolog and Chem Sciences*, 8, 481-485 (2017).
- [16] N. Rajeshwar Rao, S. V. Ramana Reddy, T. V. Appa Rao and B. Sanjeeva Rao, "The Study of gamma irradiation effects in Poly (glycolic acid)", *Radiation Effect and Defect in Solid*, 170, 439 – 450 (2015).
- [17] E. Venkateswar Rao, B. Sanjeeva Rao and K. Rajendra Prasad, "Evaluation of activation energy from temperature dependent ESR spectra of irradiated AA AMPS copolymer", *Int. J. Chem. Sci.*, 10, 1577 – 1582(2012).
- [18] B. Sanjeeva Rao and M. Ramakrishna Murthy, "Electron spin resonance and UV absorption studies of gamma irradiated Poly (vinyl alcohol)", *J. Polym. Sci. B*, 25, 1897 (1987).