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Radiation effects in n BA - AMPS Copolymer using ESR method

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Abstract

Radiation induced effects in n BA-AMPS copolymer has been investigated by Electron spin resonance (ESR) spectroscopy. An attempt has been made in this regard, to study the effect of gamma ray irradiation on AMPS copolymer. The ESR spectra of n BA-AMPS copolymer suggest the formation of free radicals and trapped charge carriers, reasons for these changes are explained based on chemical changes induced by gamma irradiation.

Key words: Electron spin resonance(ESR), gamma irradiation, nBA-AMPS copolymer (ButylAcrylite acrylamido methyl propane sulfonic acid)

Introduction

Many of the AMPS homo polymers and copolymers are water soluble. Due to this property they are used in different branches of science and technology. Therefore several AMPS polymers have been synthesized and their applications have been reviewed (1). On the other hand degradation studies of MA AMPS (2,3) acryl amide(AA), AMPS (4) and guanidine methacrylate(GMA) AMPS copolymer (5) has been reported. These authors have reported ESR spectra of polymers under different conditions. When the copolymers are irradiated with gamma rays, chain cleavages are reported to be induced on acryl amide part of the copolymer with less AMPS content. Upon increase of AMPS content, chain cleavages are reported to occur on AMPS part. Since the AMPS group is having sulfonic acid

group, they are reported to be interact with gamma rays initially. Therefore cleavage of sulfonic acid groups initially takes place, during gamma irradiation. On further increase of radiation dose, entire side groups of AMPS part will be affected by gamma irradiation. Same results have been observed for MA AMPS copolymers. Chain cleavages preferably take place on MA part for copolymer with more MA content, while for the copolymer with more AMPS content, gamma irradiation induce cleavage on AMPS part. These results are conformed by measuring ESR spectra of irradiated copolymer at different temperatures, radiation dose and post irradiation time.

With regard to thermally stimulated luminescence (TSL) studies, Sanjeeva Rao et al (6) have used TSL technique to investigate radiation damage and molecular relaxations in methyl methacrylate (MMA) AMPS copolymers. These authors have observed a TSL glow peak for gamma irradiated MMA-AMPS at 408 K. The authors have analyzed the glow peaks by different methods namely initial rise method, Chens method and modified initial rise method.

Activation energy corresponding to the glow peaks has been calculated. The value of activation energy by the three methods is found to be almost same. Further the glow peak is shifted to low temperature by irradiation of copolymer to high radiation doses. The results suggest that the glow peak is thought to be due to release of traps near the transition temperature. The glow peak is shifted to high temperature with the increase of radiation dose . The glow peak is assigned to α-relaxation temperature of copolymer

The glow peak shift towards high temperature is assigned to be due to the cleavage of side groups. As a result the available free volume increase, causing an increase of transition temperature. Therefore the TSL technique has successfully explained the radiation damage and molecular relaxation of MMA AMPS copolymer.

Sanjeeva Rao et al (7) in another paper reported on high temperature molecular relaxations and degradation studies of ethyl methacrylate–AMPS copolymer using the TSL technique. With the increase of side substitution of comonomer, the glow peak is shifted to 411 K. The result in increase of glow maximum temperature for EMA AMPS, when compared to MMA AMPS, is assigned to the increase in molecular weight of copolymer. The author evaluated activation energies and trap parameters corresponding to the glow peaks by different methods namely initial rise

method, Chen's method and modified initial rise method . In case of EMA AMPS also the glow maximum increased with the increase of radiation dose used to irradiate the copolymer. Correspondingly these authors, have recorded ESR spectra of irradiated copolymer and assigned the ESR signal to be due to various free radicals and ions.

Super absorbent hydrogels based on AMPS – acrylic amide grafted on sodium alginate have been synthesized by Noor Mohammed et al (8). The hydrogels have been characterized by different experimental techniques like FTIR and SEM technique. Influence of PH on hydrogel has been investigated. Waterabsorbency of hydrogels is found to be high. Incorporation of titanianano particles in to polymerizable ionic liquids has let to the generation of UV- imprint resists.

The resultant microstructures are reported resistant to cracking and shrinkage (9).

Bio degradable polymers have been used in tumor treatment. When drug implemented polymer is at tumor site it let to exposure locally (10).

Gamma irradiation is used to prepare hydrogel of poly (AMPS). viscosity measurements were conducted to study crosslinking effects . The resultant gels are characterized by DSC, XRD and SEM techniques (11).Articles and coatings can be made from water soluble polymers like AMPS polymer and copolymer Systems(12).

Gamma irradiation is used to produce superabsorbent formulation consisting of two layers of hydrogel. The first layer is based on AMPS / hydrogel. Thermal stabilities of gels is studied by TGA method . The material is found to be promising in the field of diaper (13). AMPS systems are used in enhanced oil recovery (14)

Heavy metal ions in waste water are more hazards. AMPS copolymers are used to remove these metal ions from the waste water. In this context Zhengkui et al (15) have made an attempt to remove Pb,

Cd, Fe, Cr from water using these Copolymers N Vinyl pyrrollidone – AMPS hydrogels have been synthesized and their floe to remove heavy metals has been investigated by Kok(16). The resultant copolymer have been characterised by different experimental techniques using this copolymers Cu, Cd, Fe metals particles have been removed from waste water (16).

Hybrid polymers based on silver nano particles with AMPS copolymers are used for corrosion protection of steel pipe lines. These molecular system are synthesized and characterized by different techniques (17).

Through the TSL studies of copolymers containing AMPS and several acrylates as co monomers is available, such studies on n-butyl acrylate – AMPS copolymer are not previously attempted. Although degraded action mechanism of other poly acrylates is available, very few studies on nbA AMPS copolymer are available. Further degradation studies and molecular relaxation of nbA AMPS has also not been attempted previously. Therefore the authors have made an attempt in this regard. nbA-AMPS copolymer of 50:50 composition and 60:40 composition are taken and the TSL spectra are recorded. To identify degradation effects in nbA-AMPS copolymer, the copolymer is exposed to gamma rays and resultant TSL glow curves are recorded. A comparison of unirradiated and irradiated glow curves has been made.

Experimental

nbA – AMPS copolymer with different composition have been synthesized and characterized by different experimental techniques. Formation of copolymers has been confirmed by FTIR, NMR techniques (Rangarao).

The copolymer obtained by this method are in powder form and they are used in ESR studies .ESR spectra of irradiated nba AMPS copolymer are recorded on Varian E line spectrometer operating at X band frequencies and 100 K Hz modulation.

Gamma irradiation are carried out in air at room temperature with Cobalt 60 radiation source with a dose rate of 0,2 M rad / hr.

Dose absorbed by the copolymer is measured in terms of time of exposure the copolymer to the source.

Results and Discussions

ESR Studies: ESR spectra irradiate nbA AMPS at different doses are as shown in Fig. 1. Curve 1 is the ESR spectrum of copolymer irradiated to 3 M.rad radiation dose; while Curves 2,3 reported the ESR spectra of copolymer of irradiated to 6 and 9 M.rad radiation doses. The spectra are asymmetric triplets with spacing of 20 - 25 G. Though the spectra appears to be triplet,

their intensity distribution appreciably deviated from the anticipated values of a triplet.

Considering the chemical structure of nbA AMPS, nether nbA groups nor AMPS groups does not gives triplet spectrum with the observed intensity distribution. If chain cleaves occur on nbA or AMPS groups, macro radicals might have produced and gives component multiplet spectra. In this context, the observed ESR spectra can be compared with the poly nbA or poly AMPS. It is reported in literature that poly acrylates like poly acrylic acid, poly methyl methacrylate gives ten – line ESR spectrum. The ten – line ESR spectrum is thought to arise due to macro radicals of the type $CH_2 – CH – CH_2$ which usually give doublets of quintet. Poly (AMPS) when copolymerized with acrylates like acrylamide, methacrylamide also produce macro radicals, which gives component multiplet together with component singlet arise due to several radical species produced on irradiation of copolymer. One important result of these studies is the hyperfine interaction of macro radicals.

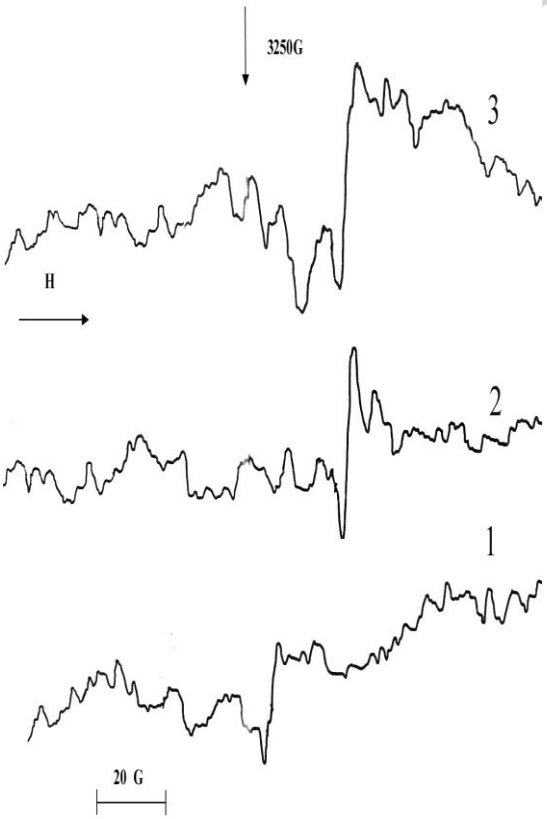

Fig.1 ESR Spectra of nbA AMPS irradiated to different radiation doses

Usually the macro radicals gives component multiplet with ten – hyperfine lines. However depending on the interplay of hyperfine interaction of adjacent methylene protons number of hyperfine lines resulting from macro radicals may not be ten instead they are 1 - 10

Based on these concepts, efforts have been made to simulate the observed ESR spectra at different radiation doses. Magnetic parameters used to simulate the ESR spectra are given as Table1. Component spectra for copolymers irradiated to 3 M rad. radiation dose are as shown in Fig. curve 1 is component

multiplet which curve 2 is component singlet. Variation of ESR intensity with radiation dose is as shown in Fig. 3.

Table 1. Magnetic parameters used to simulate the ESR spectra

Radiation Dose M.rad	Relative Intensity Y_{max}	Line Width G ai	Centre of Spectrum G Xoi	Hyperfine Splitting G A	B	n_i	m_i
3	5	3.5	3240	23	12	2	5
6	7.5	4.2	3240	23	12	2	5
9	9.3	5.7	3240	23	12	2	5

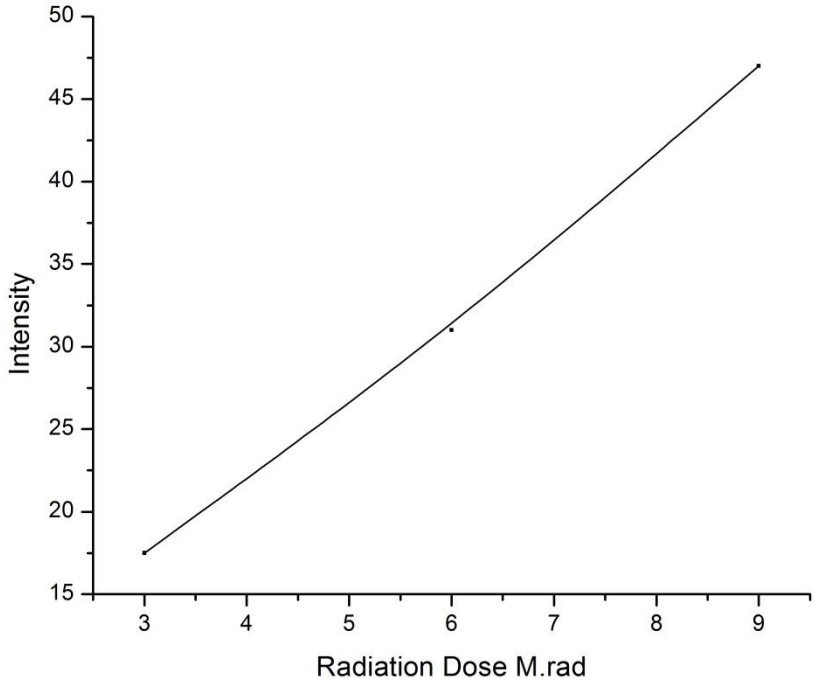

Fig. 3 Variation of ESR intensity against radiation dose

Curve 1 Fig 4.9 is simulated with the values of n_o= 2: m_o = 5, A = 23 , B = 12 G Magnetic parameters indicate the presence of one alpha proton and four methylene protons. Hyperfine couplings constraints are also in the range of expected values. In

principle above magnetic parameters might have resulted in ten – line ESR spectra is observed experimentally. The results suggest that all the protons are not contributing to the hyperfine interaction equally. Such type of hindered hyperfine interactions were also observed experimentally earlier in several polymers and copolymers (R R) . The component singlet is assigned to other free radical species formed on irradiation of polymers and or trapped charge carriers.

Conclusion

The ESR spectra of n BA- AMPS copolymer suggest the formation of free radicals and trapped charge carriers. The charge carriers trapped in polymers matrices release on thermal stimulation gives TSL emission. Usually TSL emission occur around transition temperature . Therefore the glow observed for nbA AMPS at 148 ^{o}C and 136^{o}C is thought to due to molecular relaxations.

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