Indian J.Sci.Res. 13 (1): 194-198, 2017

ISSN: 0976-2876 (Print)
ISSN: 2250-0138 (Online)

SPECTROSCOPIC AND TSL INVESTIGATION OF AMMONIUM SALT OF POLYSTYRENE SULFONATE

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ABSTRACT

Polystyrene (PS) is one of the important commercial aromatic polymer with innumerable applications. Changing the chemical structure of the polymer by different methods, is reported desired to improve its applications. In this context, sulphonic acid groups are incorporated into the aromatic groups of PS side chains to make it as a poly electrolyte (Poly Styrene Sulphonate), (PSS). In the present studies one of its salt i.e. ammonium salt is taken and its spectroscopic, thermal properties are investigated. FTTR spectra of NH_4PSS are recorded and characteristic absorption band around 3450, 2960, 1660,1550, 1250, 1080 & 990 cm^{-1} positions are observed. These groups represent the sulphonic acid, meta phenyl group, methylene group of the salt. DSC thermo grams of the salt show first order transition corresponding to the glass transition point of the salt. With regard to the TSL results, a glow peak around 90°C is observed. The glow peak is analyzed by three methods namely initial rise method, Chen's method and modified initial rise method and trap parameters corresponding to glow peak are evaluated. A correlation of spectroscopic and thermal studies is attempted. The salt is exposed to gamma rays to different radiation doses and changes induced by gamma irradiation are ascertained.

KEYWORDS: PSS Salt, TSL, Glow Peak, Dsc Thermogram, FTIR Spectra

Polystyrene sulphonate (PSS) is a water soluble polymer and find several pharmaceutical applications like self healing agent (Minzhen Cai et al, 2012), Capsules (X. Zheng et al,2011) and sensors (Yi-His Liu et al, 2009). Since PSS is a polyelectrolyte, it can be made into salt form. Therefore several monovalent salts like sodium polystyrene salfonate (Na PSS), potassium polystyrene salfonate (KPSS) and divalent salts like calcium poly styrene sulfonate (Ca PSS) barium Poly styrene Sulfonate (BaPSS) etc have been synthesized and their properties are investigated. However Ammonium Polystyrene Sulphonate (NH_4PSS) has received less attention in literature. Therefore the authors have made an attempt in this regard and investigated the spectroscopic thermal properties of (NH_4 PSS) using FTIR, DSC techniques. Salts of polystyrene of sulphonate also find excellent dosimetric applications (N.Rajeswar Rao et al, 2014. J.S. Prasad et al,2013) has used thermal stimulated luminescence, Electron Spin Resonance, Fourier Transform Infrared techniques and reported that the Na PSS is suitable for dosimetric applications.

Gamma irradiation of polymers is an important way to later the chemical structure causing a change in physical properties to improve their applications. In this context the authors have exposed NH_4 PSS to gamma irradiation and investigated the changes in thermal properties. To characterize the irradiated and non-radiated NH_4PSS, FTIR Spectra and DSC thermogram are recorded. To study thermal properties affected by gamma irradiation TSL technique is used.

EXPERIMENTAL

NH_4PSS in the form of films procured from Pressure chemicals, USA is used in the present studies. FTIR spectra are recorded in Perkin Elmer spectrometer. Thin transparent film of polymer with the thickness equal to 10 μm is used for FTIR measurements. To record DSC thermogram, METTLER calorimeter is used. The sample weighing about 2-5mg is kept in Al pan and sealed; while empty aluminum pan is taken as reference. The sample is heated from 0-350°C with a heating rate of 10°C/min. Thermograms are recorded during first heating cycle of the sample. To avoid oxidation of samples , nitrogen gas is flushed throughout the experiment. To record thermally stimulated luminescence (TSL) spectra, the NH_4PSS is kept in the sample holder kept above a thermocouple and heated with a constant heating rate of 10° C per minute up to 350°C .The light emitted by the sample is fall on the window of photo multiplier tube which is connected to an electrometer cum recorder. Gamma irradiation of the polymer is performed in cobalt 60 gamma source which has at a rate of 15K Gy (0.15M.rad/Hr) at room temperature.

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RESULTS AND DISCUSSION

FTIR Studies

FTIR spectrum of NH_4 PSS is as shown in Fig. 1.PSS posses various absorption bands corresponding to the chemical structure of polymer. Prominent among these bands are (1) sulfonic acid groups which show absorption bands in the region of 3490-3150, 1260-1150, 1090 -1010 Cm^{-1} . (2) meta phenyl group, with absorption bands, at 1640-1570, 1530-1470, 1192-1140, 1100-1070 and 1062-1030cm $^{-1}$ (3) methyl/methylene group gives characteristic absorption bands in the region of 2960-2840cm^{-1} (6) .These bands are listed in table(1)

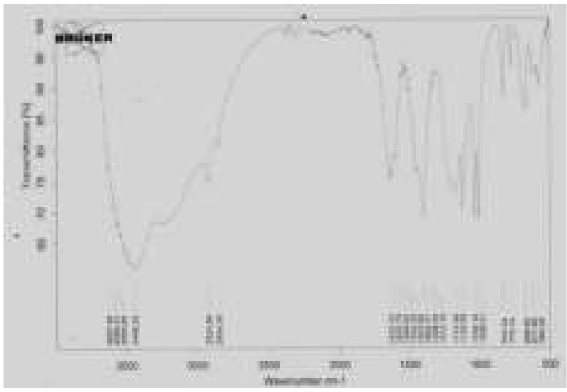

Figure 1: FTIR Spectrum of NH_4PSS

Table: 1 FTIR assignments of NH_4PSS

S. No	Absorption band position cm^{-1}	Intensity	Assignment
1	3446	Broad/ Intense	Cat I
2	2924,2854	Small/ medium	Cat III
3	1632	Sharp/ Intense	Cat II
4	1503	Medium/intense	Cat II
5	1174	Broad	Cat II,II
6	1036	Medium	Cat III
7	1008	Intense	Cat I
8	833	Medium	Cat II
9	775	Medium	Cat I

DSC Studies

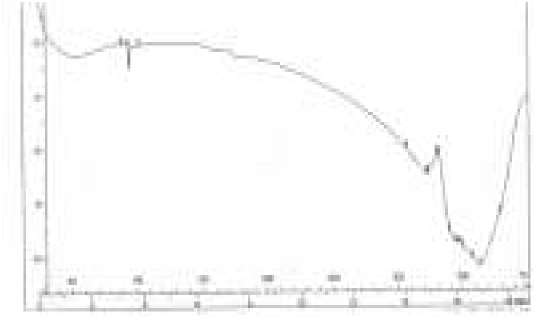

Figure 2: DSC Thermogram of NH_4PSS

Thermogram consists of first order transition cum small endothermic around 80^{o}C and an exothermic peak around 360^{o}C. The glass transition temperature Tg of polystyrene is around 85^{o}C. The glass transition temperature in a DSC thermogram is DSC thermogram of NH_4 PSS is as shown in Fig.2. Thermogram consists of first order accompanied with a first order transition. Together with a baseline shifts, a small endothermic peak at 90^{0}C are observed .In the presence of such endothermic transition in the glass transition region is reported previously (Z.Bashir et al, 1994). Due to the presence of moisture together with enthalpy relation effects, the endothermic transition is accompanied with base line shift (J.R.Prescott et al, 1998).Therefore the first order transition observed for NH_4PSS of 360^{0}K is assigned to be due to the Tg of polymer. The Tg of PS is 100^{o}C; while for NH_4 PSS the Tg is of 80^{o}C. The decrease of Tg is to be due to the presence of polar groups due to which chain stiffness increases causing an decrease of Tg. The second peak at 360^{o}C is assigned to be due to chemical decomposition of polymer at higher temperatures.

TSL Studies

TSL spectra of unirradiated and irradiated NH_4PSS are shown as curve 1 and curve 2 in Fig.3. The spectrum posses two glow peaks centered around 90^{o}C (peak1) and 120^{o}C (Peak2). On irradiation both the peaks are shifted to low temperature (84^{o}C and 105^{o}C); while peak intensity is slightly decreased. With the regard to the origin of peak1, the peak is observed near the glass transition temperature of the polymer i.e, 80^{0}C. By incorporating sulphonic acid groups, Glass transition temperature (Tg) of polystyrene is around 100^{o}C. The Tg of polymer may shift to either low or higher temperature depending on the nature of incorporated functional groups. Due to the presence of sulphonic acid groups in the NH_4PSS, the first order transition is observed near the Tg of PS. Therefore peak 1 is thought to be associated with the glass transition temperature of NH_4PSS.

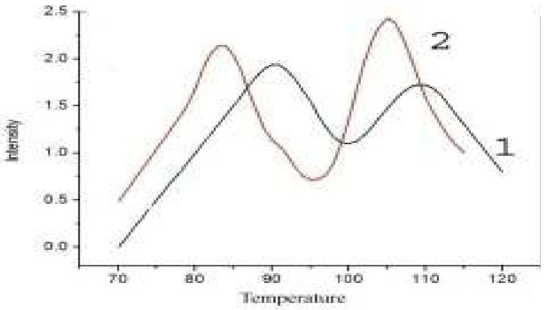

Figure 3: TSL Spectra of un-irradiated (curve1) and irradiated (curve 2) NH_4 PSS

On irradiation, the glow peak1 is shifted to low temperature i.e., 84°C; While peak intensity is increased. WuJi-Lan et al,1981 have investigated gamma irradiation effects in NaPSS using ESR technique. Formation of SO_4 radicals and macro radicals is reported. Gamma irradiation of PSS causes cleavage of sulphonic acid group; which inturn forms -SO^{-}_4 (5) radicals resulting in the formation of macro radicals. The G values for formation of these free radicals is calculated(J.S.Prasad et al,2013) and the results suggest that the G value for formation SO_4— radicals nearly 1000 times larger than the G values of free radicals with long life. i.e, macroradicals. They have further reported that the incident gamma energy is dissipate through the side chains of the NaPSS forming radicals 1 and 2. With the cleavage of polar groups, the decrease of Tg is expected as observed in the present studies. With regard to radiation effects in polymers and copolymers MA AMPS(B.Sanjeeva Rao et al, 2002), AA AMPS (B.Sanjeeva Rao et al, 2005) containing sulphonic acid groups, chain cleavages preferably occurs through the cleavage of sulphonic acid groups only. The So_4^- radicals may lose and or trap free electrons to form different types of ions, which in turn recombine to produce observed luminescence peaks of NH_4PSS.

With regard to peak2 observed at 120°C, to the peak is assigned to be due to the chemical transformation occurring in the polymer on irradiation and further thermal treatment. Due to the chain cleavage a decrease in chain lengths and decrease of molecular weight is expected. Therefore NH_4PSS with lesser molecular weight and chain length, the chemical transformation may occurs at a lower temperature than the unirradiated polymer.

Activation energy corresponding to the glow peaks has been calculated by three methods namely 1. Initial rise method 2. Chen's method and3. Modified Initial rise method. Method of analysis the glow peaks by the three methods and evaluation of activation energy is described in detail by the authors previously (B.Sanjeeva Rao et al, 1993). With regard to the initial rise method a plot of inverse of temperature(1/T) and log I is drawn and shown as curve 1(is for peak1) and curve 2 peak2 fig 4. From the slope of the straight line the values of activation is calculated and the values are as listed in the Table 2.

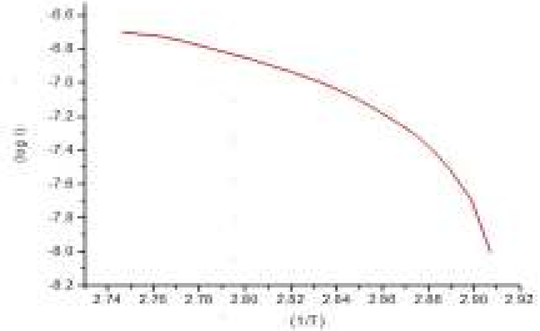

Figure 4: plot of 1/T Vs log I (initial rise method) for peak P_1

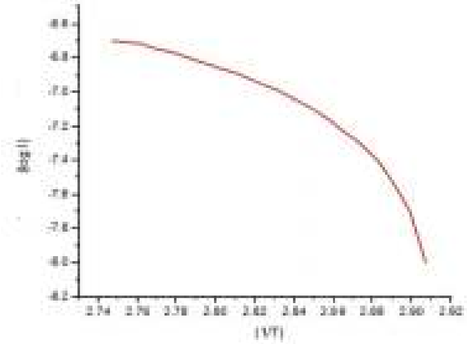

Figure 5: plot of 1/T Vs log I by (initial rise Method) for peak P_2

With regard to analysis of glow peaks by Chen's method the values of ω ,τ and δ are calculated from the experimental glow peaks and the values are substituted in equation given by Chen's (R .Chen, 1969) to calculate activation energy using first and second order kinetics of trap decay. The values of the E_a are listed in the table 3 (peak1) and table 4 (peak 2).

Table 2: Trap Parameters of unirradiated NH_4PSS

SNo	peak	ω	τ	δ	Tp	Activation energy (eV)					
						I Order			II Order		
						E_ω	E_τ	E_δ	E_ω	E_τ	E_δ
1	P_1	20	11	9	95	1.19	1.18	1.19	1.28	1.26	1.34
2	P_2	18.4	10.8	7.6	120	1.31	1.29	1.34	1.46	1.35	1.60

Table 3: Trap Parameters of irradiated NH_4PSS

SNo	peak	ω	τ	δ	Tp	Activation energy (eV)					
						I Order			II Order		
						E_ω	E_τ	E_δ	E_ω	E_τ	E_δ
1	P_1	13.6	7.6	6	84	1.25	1.25	1.25	1.36	1.33	1.44
2	P_2	12.8	5.8	7	110	1.43	1.56	1.33	1.62	1.66	1.59

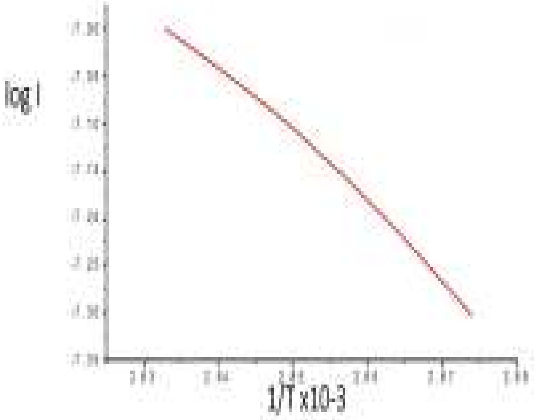

Figure 6: Plot of 1/T Vs log I by (modified initial rise method) Peak P_1

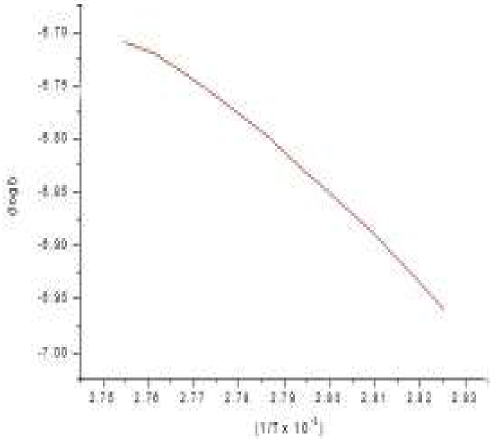

Figure 7: Plot of 1/T Vs log I by (modified initial rise method) peak P_2

The values suggest that the activation energy of irradiated NH_4PSS is less than the values of unirradiated polymer. Due to the cleavage of chain by gamma irradiation, the degradation of polymer occur reducing the molecular weight. Therefore traps may be released at a earlier temperature than the unirradiated polymer. Since the plot of 1/T - log(I) graphs of initial rise method are far from linear shape, modified initial rise method is applied to evaluate activation energy (B.Sanjeeva Rao et al, 1993). For this purpose the glow peaks are simulated using values listed in the table 4.

Table 4: Parameters employed to stimulate glow peak (p_1)

SNo	Condition	Ymax	SA I	T0I
1	Unirradiated	3.0	6.2	95
2	Irradiated	4.0	6.5	84

The theoretical intensity values obtained by computer simulation techniques are taken to plot 1/T – log(I) graph, curve 1 Fig 5 and Correspond to unirradiated polymer, while curve 2 Fig. 5 correspond to irradiated polymer. From the slope of the straight line, the value of activation energy is calculated as listed in Table 5.

A Comparison in values of activation energy (Ea) by the three methods is made and the values are listed in table 5. The data suggest that (Ea) is almost same by the three methods.

Table 5: Evaluation of Activation energy by different methods

SNo	Sample	Peak	Activation energy (eV)				
			Initial rise method (eV)	Chen's Method (eV)			Modified Initial rise method (eV)
				E_{ω}	E_{τ}	E_{δ}	
1	Unirradiated NH_4PSS	P_1	1.33	1.28	1.26	1.34	1.14
		P_2	1.65	1.40	1.35	1.60	1.85
2	Irradiated NH_4PSS	P_1	1.16	1.36	1.33	1.44	1.09
		P_2	1.86	1.62	1.66	1.59	1.58

CONCLUSION

In conclusion spectroscopic, thermal properties of NH_4PSS have been investigated by FTIR, DSC and TSC techniques. FTIR studies indicate the presence of sulphonic acid group, meta phenyl groups suggesting the formation of PSS . Presence of amide groups is also proved by the FTIR technique.DSC studies suggest that Tg of polymer is around 95°C and on gamma irradiation the Tg shifted to low temparature . The TSL of unirradiated NH_4PSS show a glow peak around 95°C, and 105°C. The first peak is assigned to glass transition temperature of polymer, while the second peak is due to chemical transformation. On irradiation the glow peak shift has been observed. Trap parameters corresponding to the both the peaks are evaluated.

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