TSL Studies of Monovalent and Divalent Salts of Polystyrene Sulfonate

K. Rajendraprasad[1]*, E. Venkateshwar Rao[2], B. Sanjeeva Rao[3]

[1]Department of Physics, Kakatiya Institute of Technology & Science, Warangal, India
[2]Department of Physics, University College, Kakatiya University, Warangal, India
[3]Department of Physics, Govt. Degree College, Mulugu, Warangal, India

Abstract

Thermally stimulated luminescence (TSL) spectra of monovalent and divalent salts of polystyrene sulfonate (PSS) have been recorded to study molecular relaxations and thermally induced processes. Monovalent salts [sodium polystyrene sulfonate (NaPSS) and potassium polystyrene sulfonate (KPSS)] have shown glow peak around 365 K and 369 K while divalent salts [calcium polystyrene sulfonate (CaPSS) and barium polystyrene sulfonate (BaPSS)] have exhibited two glow peaks around 345 K, 385 K (CaPSS) and 350 K, 393 K (BaPSS), respectively. The observed glow peaks are analyzed by initial-rise method and Chen's method. Activation energies associated with the release of traps have been evaluated. Origin of first glow peaks is interpreted to be due to the traps created on decomposition of polymers during thermal stimulation. Reason for shifting of glow peak with the substitute monovalent/divalent anion is explained.

Keywords: monovalent, divalent, glow peaks, thermal stimulation

*Author for Correspondence E-mail: krpkits@gmail.com

INTRODUCTION

Polystyrene sulfonate is an important polyelectrolyte with several applications. As the polymer is unstable, it is usually stored in salt form. Thermal properties of polystyrene (PS) are established; however, very few attempts have been made to study thermal properties of polystyrene sulfonate. In this context, Sanjeeva Rao *et al.* [1] have recorded TSL spectrum of sodium polystyrene sulfonate (NaPSS) and observed a glow peak around 350 K. The glow peak is analyzed by various methods like initial-rise method, Chen method and modified initial-rise method. The observed glow peak is found to shift to low temperatures with increase in dose of irradiation. The glow peak is thought to be associated with the glass transition (T_g) temperature of NaPSS as T_g of PS is around 350 K. ESR spectra of gamma-irradiated NaPSS have been reported by Zhang *et al.* [2] in an attempt to investigate radiolysis of the polymer. The observed ESR singlet spectrum by these authors is assigned to free radicals formed by the cleavage of side chains of

NaPSS. Thimma Reddy [3] has also reported on dose-dependent ESR spectra of irradiated NaPSS. The authors have assigned the ESR spectrum to be due to the free radicals formed by cleavage of sulfonic acid groups on gamma irradiation. With the increase in dose of irradiation, the free radical concentration is found to increase suggesting more number of chain cleavages. Recently, Prasad [4] has reported TSL, FTIR, DSC studies of NaPSS. According to this author, the observed glow peak at 350 K is not due to glass transition [1]. On the basis of DSC studies, this peak is assigned due to dissociation of chemical groups of NaPSS. As there is a first order change in heat flow, instead of second order change, the author [4] proposed the TSL peak to be due to chemical changes rather than glass transition.

TSL studies on sodium polystyrene sulfonate (NaPSS) are available in literature. However, such studies on other monovalent salts like potassium polystyrene sulfonate (KPSS) and divalent salts like calcium polystyrene sulfonate (CaPSS) and barium polystyrene

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sulfonate (BaPSS) are not reported in literature. Therefore, the authors have made an attempt to investigate TSL studies on these systems in the present work.

EXPERIMENTAL

The monovalent salts of NaPSS), KPSS and divalent salts of CaPSS, BaPSS used in the present studies are in powder form supplied by Pressure Chemicals USA. The powders are pressed into pellets, which are placed on the thermocouple of TSL apparatus. The sample holder is fed to a digital temperature indicator and a programmable temperature controller. A heating rate of 10°C/min is maintained and the window of photomultiplier tube (PMT) is exactly placed in front of sample holder to observe luminescence emitted by the sample. The photo current from PMT is measured by a Keithley electrometer.

RESULTS

TSL spectrum of NaPSS is shown in Figure 1 while the glow curve of KPSS is as shown in Figure 2. The figures indicate that the monovalent salts exhibit a single peak only. TSL spectra of divalent salt of polystyrene sulfonate are shown in Figures 3 and 4. Figure 3 corresponds to glow spectrum of CaPSS; while Figure 4 is the spectrum of BaPSS. Divalent salts have shown two glow peaks when compared to the single glow peak of monovalent salts. The TSL data is as shown in Table 1.

Table 1: *Glow Peak Values of Salts of PSS.*

S. No.	Sample	Designation	Glow peak temperature (K)	
1	Sodium polystyrene sulfonate	NaPSS	365	-
2	Potassium polystyrene sulfonate	KPSS	369	-
3	Calcium polystyrene sulfonate	CaPSS	345	385
4	Barium polystyrene sulfonate	BaPSS	350	393
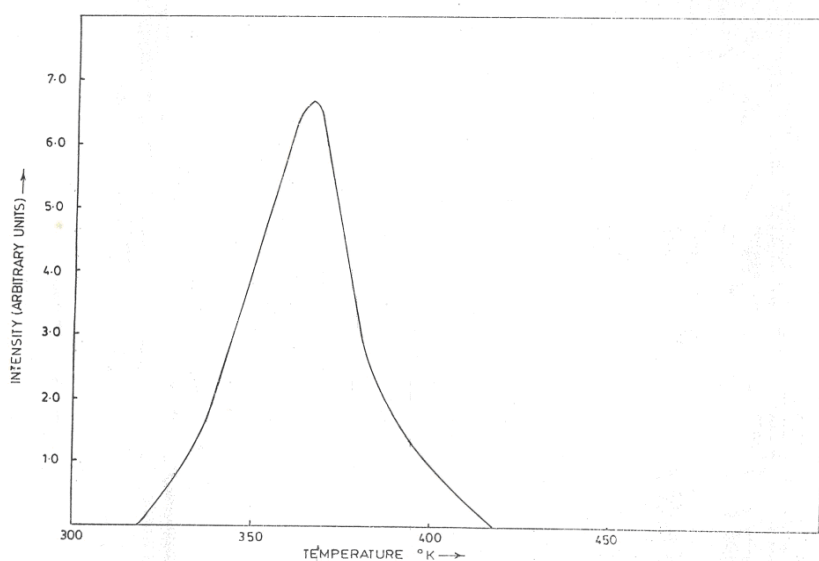
Fig. 1: *TSL Spectrum of NaPSS.*

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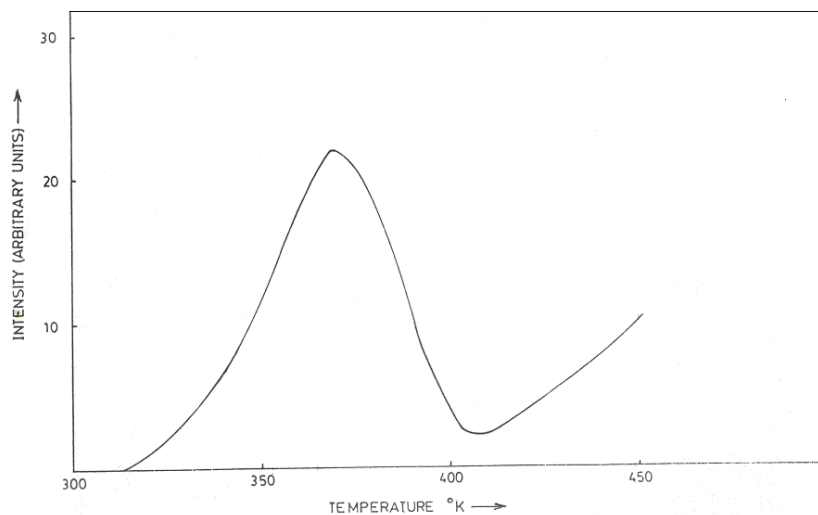
Fig. 2: *TSL Spectrum of KPSS.*
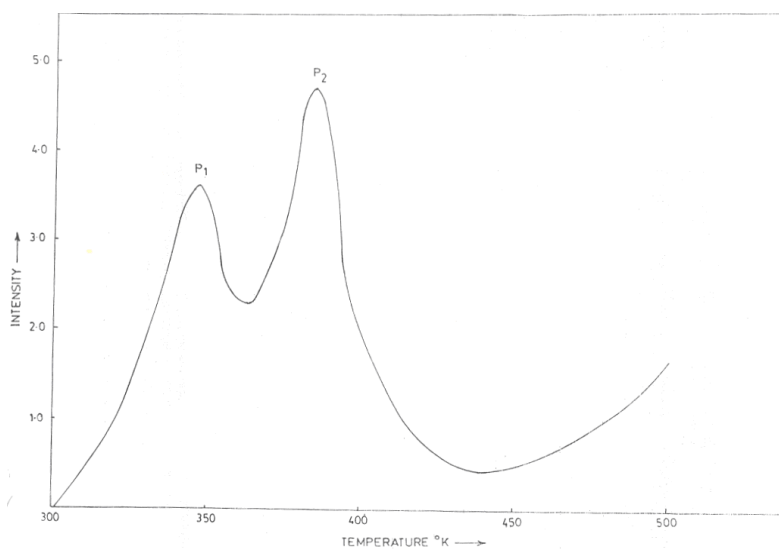
Fig. 3: *TSL Spectrum of CaPSS.*
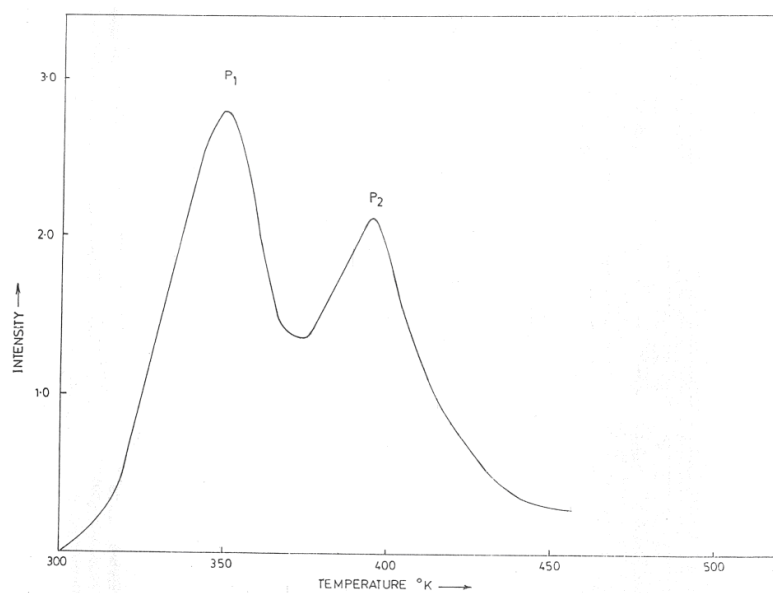
Fig. 4: *TSL Spectrum of BaPSS.*
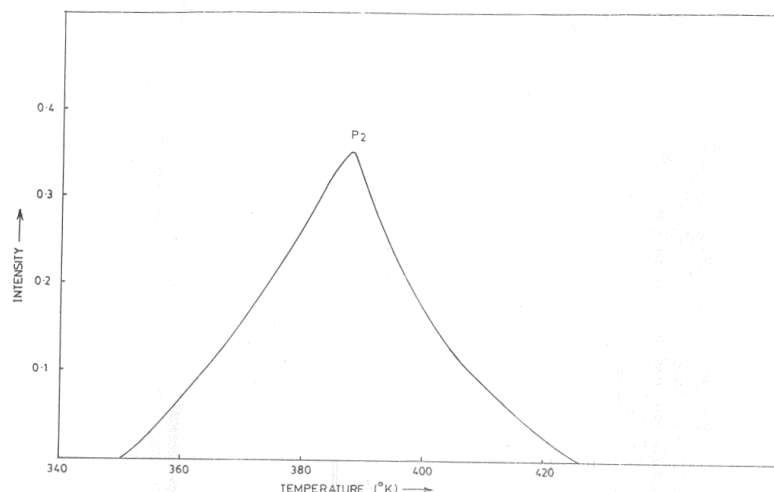
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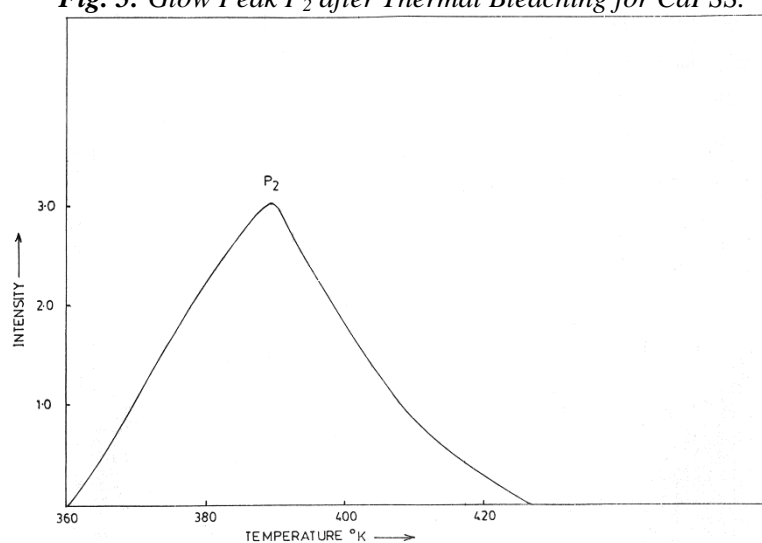**Fig. 5:** *Glow Peak P₂ after Thermal Bleaching for CaPSS.*

Fig. 6: *Glow Peak P₂ after Thermal Bleaching for BaPSS.*

DISCUSSION

TSL spectra are analyzed by two methods – they are (i) initial-rise method [5] and (ii) Chen method [6]. The initial-rise method involves plotting of logarithmic value of intensity against inverse of temperature (1/T). The curve is a straight line, whose slope directly gives the value of activation energy. To apply initial-rise method, the TSL intensity values during initial-rise point should be known accurately. However, second glow peak of divalent salts are overlapped. Therefore, resolution of the peak is very important. For this purpose, two methods are proposed in literature. They are (i) thermal-cleaning method [7, 8], which requires experimentation, and (ii) modified initial-rise method, which makes use of theory [9]. In the present studies, thermal-cleaning method is employed. The intensity points for monovalent salts and for the first peak of divalent sulfonate overlapped. Therefore, thermal-cleaning method is applied for these peaks. The glow peaks obtained after this method are as shown in Figures 5 and 6 for CaPSS and BaPSS respectively. As such all the glow peaks are analyzed by initial-rise method and activation energy is evaluated. Plots of (1/T) versus log (I) for different glow peaks are shown in Figures 7 (NaPSS), 8 (KaPSS), 9 (CaPSS), 10 (CaPSS), 11 (CaPSS) and 12 (BaPSS). Activation energy is also calculated by Chen's method. To calculate activation energy, Chen considered both first- and second-order kinetics. These equations involve parameters like ω, τ and δ, which could be calculated from the glow curves. The method is already described [7]. The values of activation energies by both the methods are as given in Table 2.
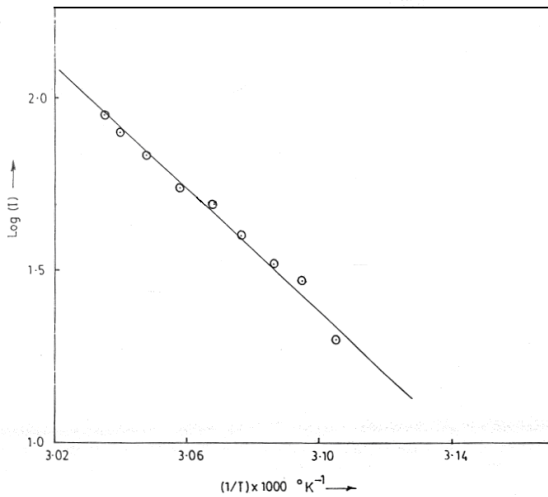
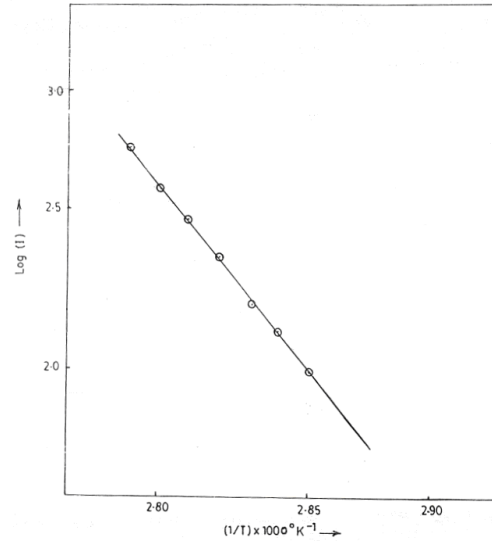***Fig. 7:*** *Initial-Rise Method for Glow Curve of NaPSS.*

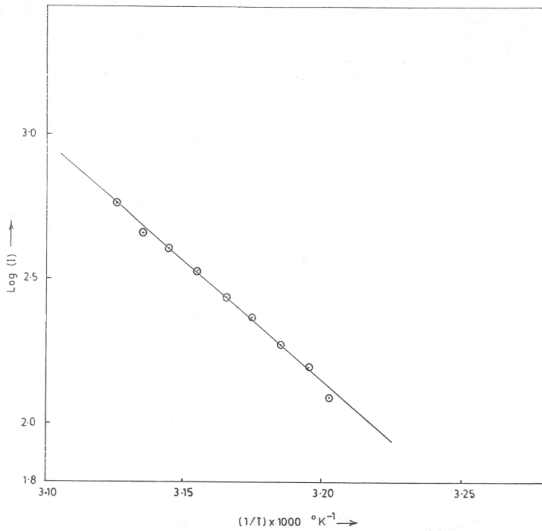***Fig. 10:*** *Initial-Rise Method for Glow Curve P_2 of CaPSS.*

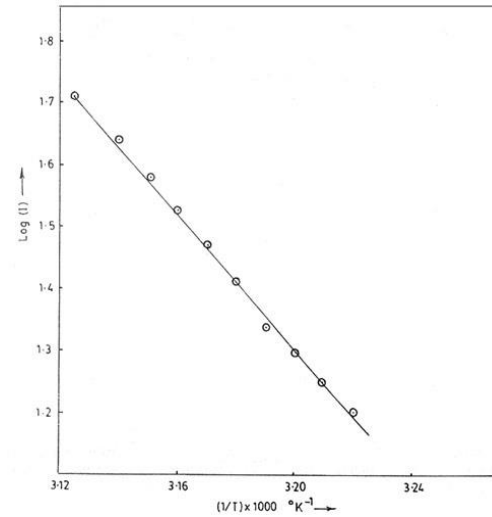***Fig. 8:*** *Initial-Rise Method for Glow Curve of KPSS.*
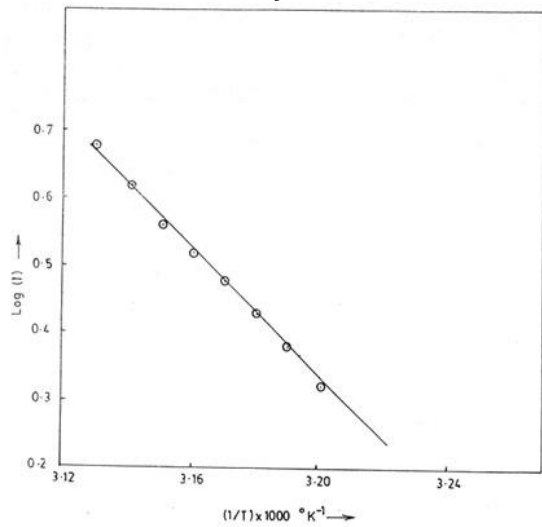

Fig. 11: *Initial-Rise Method for Glow Curve P_1 of BaPSS.*

Fig. 9: *Initial-Rise Method for Glow Curve P_1 of CaPSS.*
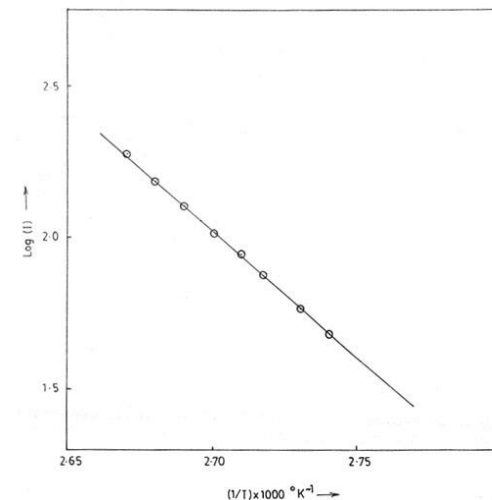

Fig. 12: *1/T – Log (I) Graph for Glow Curve P_2 of BaPSS.*

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Table 2: *Activation Energy Values Obtained by Different Methods.*

Salt	Glow peak temp.(Tp)	Activation energy (eV)	
		Initial-rise method	Chen's method
NaPSS	365	0.75	$E_\omega = 0.81$ $E_\tau = 1.30$ $E_\delta = 0.80$
KPSS	369	0.87	$E_\omega = 0.90$ $E_\tau = 1.00$ $E_\delta = 0.86$
CaPSS	345	0.50	$E_\omega = 0.71$ $E_\tau = 0.65$ $E_\delta = 0.72$
	385	0.96	$E_\omega = 1.10$ $E_\tau = 1.20$ $E_\delta = 1.10$
BaPSS	350	0.59	$E_\omega = 0.76$ $E_\tau = 0.94$ $E_\delta = 0.76$
	393	1.05	$E_\omega = 1.15$ $E_\tau = 1.18$ $E_\delta = 1.22$

Note: It can be observed from Table 2 that the value of activation energy obtained by both the methods is almost comparable.

Analysis of Glow Peaks

Initially, it was thought that the glow peak observed for NaPSS at 365 K is due to glass transition temperature [1, 3]. Later, Prasad [4] has proved that the glow peak is not due to glass transition (Tg) as Tg is reflected by a second-order change in enthalpy (heat rate) of DSC thermogram. The DSC thermogram has shown a first-order change only. The first-order changes are usually accompanied by chemical group dissociations (or) crosslinking reactions. In this context, Zhang *et al.* [3] have reported that the sulfonic acid groups of polystyrene sulfonate dissociate around 350 K. Therefore, the observed glow peak (P$_1$) of both monovalent and divalent salts of PSS is attributed to chemical dissociation of groups rather than glass transition. Regarding the second glow peak (P$_2$) observed for divalent salts, it is due to molecular relaxations.

With regard to the difference in glow peak temperatures, the monovalent salts have more T$_p$ value than divalent salts. This is due to difference in ionic content of the polymers. As the divalent salts have more ionic content/ion size in side chain rather than monovalent salts, a reduction in the chain stiffness is caused. Therefore, the T$_p$ value decreases in case of CaPSS and BaPSS.

Origin of Glow Peak

As the salts contain ions, heating of the salts causes a dissociation of ions leading to the formation of different types of charges. These ions/charges recombine to give the observed luminescence. The photomultiplier tube converts photoenergy into electrical current as observed in the present studies.

Further, with the incorporation of heavy ions, molecular weight of polymer increases, then decreasing the decomposition temperature.

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