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TRAP LEVEL SPECTROSCOPY AND DIELECTRICAL STUDIES OF ACRYLONITRILE WITH ISOBORNYLACRYLATE AND ISOBORNYLMETHACRYLATE COPOLYMERS

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ABSTRACT

TSC technique has been used to find out the macromolecule relaxations and transitions in the acrylonitrile (AN) with isobornylacrylate (IBA) and isobornylmethacrylate (IBM) copolymers. Static electrical conductivity measurements on these copolymers are studied using four point probe technique with different probe spacing. These results are correlated with physical phenomena derived from TSC spectra. The glass transition temperature, α-relaxation and β-relaxation have been evaluated. Initial Rise and Chin's method have been employed to evaluate activation energies. The dielectric constant (ε) and dielectric loss (tan δ) of AN-IBA and AN-IBM copolymer were evaluated as a function frequency and temperature. The α-relaxation temperature for AN-IBA and AN-IBM copolymer were evaluated using dielectric studies.

Keywords. acrylonitrile, isobornylacrylate, isobornylmethacrylate, dielectric properties and thermally stimulated current

INTRODUCTION

Thermally stimulated relaxation (TSR) by charge transport is a solid- state process mainly deal with electronic and ionic transport phenomena, observed during non-isothermal temperature scans. The occurrence of thermally stimulated current (TSC) of an excited material, during a thermal scan is the most direct evidence of the existence of electronic or ionic trap energy levels.

Thermally stimulated current (TSC) spectrum consists of a number of resolved peaks in electric conductivity as a function of temperature which is attributed to the various species of traps. Electrons or other charged species which are either formed during the process of polymerization of the polymer or may be formed during irradiation with high energy radiation such as ultraviolet, x-ray or γ-rays, the charge carries thus formed are trapped in the macromolecular side or main chain folds in the polymer matrix.Thus, thermal stimulation of the irradiated polymer, results in the release of the charge carries from the traps and these carriers contribute to the conductivity known as TSC. The process of release of charged species on thermal stimulation is associated with the various relaxations in polymers such as secondary and primary relaxations. The appearance of TSC in a polymer represents the escape probability of trapped charge carriers as an increasing function with temperature. Further, with on going thermal stimulation, there will be a decrease in the supply and number of charge carriers.The technique of TSR in polymers has been employed to (i) identify radiation products (ii) study the nature of traps (iii) nature of luminescent centers (radiative re-combinations) (iv) the rate processes of growth and decay of currents due to the release of trapped charges[1-3] etc. Presently, this technique is used to study the macromolecular relaxation and transitions in polymers[4].

The mechanism involves the ionization of the impurities or additives in the polymer, followed by trapping of charged species such as electrons, ions, free radicals, radical ions etc., as a first step. On subsequent thermal stimulation, there will be an on set of macromolecular motions, which leads to a thermally activated detrapping of charge carries from the traps and contribute to the TSR process. The kinetic of the TSC processes are similar to the rate processes of molecular motion. Thus, the factors, which influence the secondary and primary relaxation, also influence the TSR phenomena.The present article describe the TSR experimental investigations on the copolymers (i)Acrylonitrile-isobornylacrylate (Copolymer-I)(ii) Acrylonitrile-isobornylmethacrylate (Copolymer-II) synthesized[5].

EXPERIMENTAL

Thermal stimulated current (TSC)

Copolymer samples are irradiated with 300 watts xenon ultraviolet source at room temperature. The UV irradiated samples are preserved in a black paper to avoid optical bleaching of the charge carriers generated on UV irradiation, prior to taking TSC measurements. The copolymer samples are introduced between two brass metal electrodes to which different voltages may be applied. The samples under investigation are held in good electrical contact with the metal electrodes by a spring loaded mechanism. A copper constant and thermocouple is employed to measure the temperature, which is firmly held so that it measures the sample temperature.

The electrode with thermocouple assembly could be heated to any desired temperature by applying different (a.c) voltages, employing a variac. A. D. C power supply (0-500V) is connected to the electrodes and an electrometer amplifier (Keithley model 610C) connected in series with the electrodes to measure thermally stimulated currents. The temperature of the samples could be varied and set to any desired temperature employing a digital temperature controller. After irradiation the sample is held under the electrodes, specific static D.C voltage is applied and the resulting current is measured. The temperature of the specimen is raised by a pre-set heating rate program.

The TSC spectrum is obtained by plotting the current against temperature. TSC curves may be either well isolated obtained or there may be an overlapping of the curves as the temperature is scanned. In respect of overlapping TSC peaks (curves) thermal cleaning of the peaks would result in isolation of peaks (separated from the remaining TSC curves) which enabled the analysis of the TSC curves in the present investigations. TSC curves resulted for different static voltages also may be recorded. Samples are irradiated to different doses of UV irradiation. The TSC curves of higher intensity are obtained as the dose of irradiation is increased, without much change in the form or shape of the curves.

Measurements of electrical conductivity by four probe method

Electrical conductivity in thin films of the copolymers at different temperatures has been measured employing four-point probe techniques.[6-7] The four contacts used to measure conductivity are of point contact type, arranged as a linear array. The thickness of the film should be very much less than the probe spacing. Probe spacing of 0.2 and 0.8 cm are employed in the experimental set up.

The four-probe arrangement consists of four spring type, collinear and equally spaced probes, which are coated with zinc to ensure good electrical contact. These probes are mounted in a Teflon bush for good electrical insulation. The entire arrangement is mounted on a suitable stand and leads are provided for current and voltage measurements. The sample holder with four probes may be kept in an oven to vary the temperature of the specimen. A thermocouple kept in contact with the specimen is used in conjunction with a digital temperature controller to monitor the temperature of the sample to an accuracy of $\pm 1^0$C.The temperature controller may be set to any desired temperature and the sample is stabilized to these temperatures, for at least half an hour before the actual measurement. Voltage is applied to the outer two probes and the resulting

current in the inner two probes is measured by employing a Keithley Model 610C by connecting the electrometer in series with the inner two probes. Conductivity (σ) is evaluated from these measurements.

Dielectric Properties

Several methods are available for the measurement of dielectric constant and dielectric loss. Nature of specimen and the frequency range are the governing factors for the adoption of a particular method. In the present work, a capacitance bridge model GR 1620 (WG) is used. This assembly consist of an audio oscillator (Type-13114), a transformer ratio arms capacitance bridge (Type-1615A) and a tuned amplifier and null detector (Type-1232A). An external oscillator (Agronic 72) is used for frequencies beyond 10 KHz. Measurements have been carried out in the frequency range of 0.5 - 100 KHz using a laboratory built cell. Temperature of the samples is varied from 30 - 240^{o}C with the help of a heater. The temperature is measured using a copper constant thermocouple and a digital panel meter.

RESULTS AND DISCUSSION

The TSC spectra of AN-IBA copolymer (I) and AN-IBM copolymer (II) has been recorded with a heating rate of 5^{o}min^{-1}. The TSC curves (Fig.1) for IBA shows three maxima at 85, 115 and 167 ^{o}C. The intensity of the TSC curves is found to increase with the dose of UV irradiation. The curves a, b and c (Fig.1) represents the spectra for the samples irradiated for 50, 90 and 120 minutes respectively. The peaks are designated as P_1, P_2 and P_3 with increase in the order of the peak temperature maxima respectively. Similarly IBM curves are shown in. Fig.2 The curves show maximum temperature at 42, 95 and 177^{o}C respectively and are given in Table 1

Thermally stimulated relaxation (TSR) phenomena is very much related the electric conduction phenomena and hence the electrical conductivity (σ) measurements of these copolymers have been made as a function of increase in temperatures. The electrical conductivity (σ) of the copolymer (I) film was studied with probe spacing of 0.2cm employing four-point probe method[6]. The (Fig.3) shows the logσ vs. I/T plot for the copolymer (I) which shows three distinct regions named as I, II and III. In the lower temperature region (I) there is a slow but linear increase in electrical conductivity with temperature. In the region II, there is a relatively fast increase in conductivity with a change in slope relative to region I. In the high temperature region III, the electrical conductivity is relatively higher than region I and II, but remained almost constant as the temperature is increased and there is temperature saturation in the conductivity. The transition temperature at 65, 85 and 102^{o}C separates the three regions I, II and III Fig.3. The Fig.4 shows electrical conductivity (σ) measurements of the copolymer (I) with probe spacing of 0.8 cm. The σ values are lower than the values obtained from probe spacing of 0.2cm at all the temperatures of observation, indicating that some of the charge carriers either decay or recombine during the transit. However, the three regions I, II and III are still distinctly observed. Table 2.

The log σ Vs l/T plot for the UV irradiated copolymer AN-IBA (I) is shown in Fig.5. The electrical conductivity is found to increase on UV-irradiation at all the temperatures of observation. However, there are only two regions I and II. In region I, there is a slow increase of conductivity with temperature. But above 64^{o}C, there is a fast increase in conductivity with temperature. Thermal stimulation of UV-excited polymer charged species may result in an increase in the number of charge carriers and their mobilities. The decay of current for fixed voltage of 120V as grown films with time for the unirradiated copolymer (I) and irradiated copolymer (I)are shown in Fig 6 and 7 respectively. These curves indicated a faster decay of the charged species in UV irradiated samples relative to unirradiated sample.

The Fig.8 shows log σ vs I/T plot for the AN-IBM (II) copolymer with probe spacing of 0.8 cm. The three regions I, II and III with varied slopes at temperatures 68^{o}C and 108^{o}C have been observed. The electrical conductivity of copolymer I is found to be more than copolymer II at all the temperatures of observation. The UV-irradiated copolymer II showed increase in the electrical

conductivity with temperature as shown in Fig. 9, but the changes in slopes of the straight line plots occurred at transition temperatures 67°C and 130°C. Table 2.

Relaxation transitions for polymers in the amorphous states are often labeled with the Greek letters α, β, γ and δ etc. As per this nomenclature, the α transition corresponds to the relaxation observed at the highest temperature, while the β, γ etc. apply to the relaxation regions, in the order of decreasing temperature. The α - relaxation is referred to as primary relaxation, which is the most pronounced relaxation. The β, γ, δ etc. result from molecular motion with in the polymer and are referred to as secondary relaxations.

The high temperature TSC peak (P_3) in both the copolymers in the present studies is due to the large scale macromolecular motion, involving the main or back - bone chains of the polymer. The detrapping of the charge carries (which are trapped on irradiation) is facilitated by the molecular motion, which occur on thermal stimulation. The TSC peak (P_3) observed for the copolymer I occur at 167°C, while that for copolymer II occur at a higher temperature 177°C indicating that the α relaxation correspond to the glass transition temperature of copolymer II is higher than for copolymer I, which may be due to methyl group substitution in the main chain. This conclusion is further evidenced by the steep increase in electrical conductivity of these materials around the glass transition temperature Fig5 and 9. The single glass transition for both the copolymers, indicate that these copolymers belong to the class of random copolymers.

The TSC peak (P_2) observed at 115°C for copolymer I and at 95°C for copolymer II, is considered to be due to the β-relaxation, which is a secondary relaxation and is associated with the motion of the side group or pendent groups. The charge carriers, which are trapped at a different energy level, are detrapped on thermal stimulation and contribute to the conductivity, in the region of β transition and showed relatively lower values of electrical conductivity.

The TSC peak (P_1) recorded at 85°C for copolymer I and at 45°C for copolymer II is attributed to secondary relaxation associated with internal motion within a side group or small molecules in the polymer matrix. Thus, the electrical conductivity (σ) measured for the copolymers at different temperatures, could be correlated with the TSC peaks recorded and the macromolecular relaxation and transitions. The transition temperatures in the conductivity plots represent the on-set of molecular motion on thermal stimulation. The TSC peaks are analyzed by the initial rise method[8]and Chen's method[9] and the activation energies are evaluated Table 3

Initial rise method:

The initial rising portion of a well isolated glow curve of TSC curve bears an exponential relation with temperature (T) and is represented by the equation

$$I = Io \exp^{-E/kT}$$

Where k is the Boltzmann constant and E is the activation energy, viz. minimum energy required exciting the TSC curve on thermal stimulation and 'T' is temperature. Thus, for a well isolated TSC curve during the initial rising part of the curve, the values of currents with different temperature are noted on the experimental curve. Io being the maximum current for the entire curve, a plot of log (I/Io) vs. 1/T yields a straight line. From the slope of this straight line the activation energy (E) is evaluated in electron volts Table 3.

Chen's method: Chen has proposed a non-iterative way of evaluating the activation energy of the TSC curves after modifying a method proposed by Halperin[10], Lushchick[11] and Abdul Khader.[12]This method is based on the measurement of the TSC curve. Chen's equations is $E_\alpha = C_\alpha kT^2_m/\alpha - B_\alpha (2kT_m)$

where E is the activation energy k is the Boltzmann's constant and α can be determined by earlier method[10]

Table-3 summarizes the results of these calculations and thermal cleaning of the TSC peaks enabled the application of Chen's method to evaluate the activation energies.

Dielectric studies of AN-IBA and AN-IBM copolymers:
A capacitance bridge model GR1620 (WG) is used to measure the dielectric constant (έ) and dielectric loss (tan δ) of the AN-IBA and AN-IBM copolymers[13]. All samples are annealed prior to use for the measurements. The results of variation of έ and tan δ with frequency for IBA_1 and IBA_3 copolymers are given in Table 4
The results shows that as the frequency decrease from 100 to 5 KHz, the έ values increases from 1.84 to 3.30 for IBA_1 and 1.79 to 3.14 for IBA_3 copolymer, while tanδ values increases from 0.01 to 0.056 for IBA_1 and 0.016 to 0.062 for IBA_3 copolymer. The effect of temperature on έ and tan δ has been explained by taking AN-IBA_2 copolymer at 1 KHz and the values are given in Table 5. The results shows that a slight variation έ with increase of temperature, but tan δ values increases with increase in temperature, reaches a maximum value at 120°C and then decreases with further increase in temperature. A peak due to relaxation is observed in tan δ, known as α-relaxation, at about 120°C in the rubbery state of the polymer [14-16]. At lower temperature, molecular chains are not only immobile but also tightly bound at some points because of dipole-dipole interactions[17]As the temperature is raised, more and more dipole groups are released and the mobility of polymer segments increases. Similar results were observed with AN-IBM are given in Tables 6,7. For IBM2 copolymer the α-relaxation is observed at 180°C

CONCLUSION

Thermally stimulated relaxation (TSR) studies have been made for the copolymers which are synthesized in this laboratory. Thermally stimulated current (TSC) technique has been employed to elucidate the macromolecular relaxations and transitions in the copolymers. Static electrical conductivity (σ) measurements on copolymer films are employed using four point probe technique at different temperatures. These results are correlated with the physical phenomena derived from TSC spectra. The detrapping of charge carriers (which are formed on UV irradiation and are trapped in the polymer matrix) is facilitated by the large scale macromolecular motions near glass transition temperature (α-relaxation) and the secondary side chain motions of the copolymer (β-relaxation) that occur on thermal stimulation have been identified. Analysis of the TSC spectra employing, initial rise and Chen's method have been made to evaluate the activation energies. The single α-relaxation observed for copolymer I and copolymer II indicate the copolymers are random. The dielectric constant (έ) and dielectric loss (tan δ) of AN-IBA and AN-IBM copolymer were evaluated as a function frequency and temperature. The α-relaxation temperature for AN-IBA and AN-IBM copolymer were evaluated.

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Table-1:TSC spectra of copolymers

Copolymer	P_1	P_2	P_3
AN-IBA (I) Fig (1)	85°C	115°C	167°C
AN-IBM (II) Fig (2)	42°C	95°C	177°C

Table - 2 :Electrical conductivity (σ) data of copolymers
*UV-irradiated polymer

(A) Acrylonitrite – isobornylacrylate (I)			
Region I–II Transition Temperature	**Region II – III** Transition Temperature	**Probe Spacging**	**Reference**
65°C	102°C	0.2 cm	Figure 3
62°C	82°C	0.8 cm	Figure 4
64°C	----	0.2cm*	Figure 5
(B) Acrylonitrile – isobornyl methacrylate (II)			
68°C	108°C	0.2cm	Figure 8
67°C	130°C	0.2cm*	Figure 9

Table– 3: Activation energies evaluated by different methods for TSC curves of copolymer**s**

Polymers	**Method**	**Activation energy (ev)**		
		P1	**P2**	**P3**
Copolymer I	Chen's	E_ω = 0.49 E_τ = 0.48 E_δ = 0.49	0.73 0.75 0.68	1.13 1.16 1.10
	Initial rise	0.5	0.7	1.2
Copolymer II	Chen's	E_ω = 0.73 E_τ = 0.38 E_δ = 0.75	0.85 0.87 0.88	1.62 1.82 1.46
	Initial rise	0.75	0.89	1.50

Table – 4 : Variation of dielectric constant (έ) and dielectric loss (tan δ) with frequency for AN-IBA copolymer

Frequency (KHz)	**έ**		**tanδ**	
	IBA_1	**IBA_3**	**IBA_1**	**IBA_3**
100	1.84	1.79	0.010	0.016
50	2.01	1.99	0.028	0.031
30	2.32	2.13	0.037	0.042
20	2.88	2.41	0.048	0.051
10	3.17	2.99	0.054	0.059
5	3.30	3.14	0.056	0.062

Table-5: Variation of dielectric constant (έ) and dielectric loss (tan) with temperature for AN-IBA_2 copolymer at a constant frequency of 1 KHz

Temperature	30	60	90	120	150	180	210	240
Έ	3.52	3.54	3.57	3.61	3.66	3.71	3.80	3.92
Tanδ	0.061	0.063	0.066	0.071	0.069	0.064	0.062	0.059

Table – 6: Variation of dielectric constant (έ) and dielectric loss (tanδ) with frequency for AN-IBM copolymer

Frequency (KHz)	έ		tanδ	
	IBM_1	IBM_3	IBM_1	IBM_3
100	1.98	1.89	0.015	0.017
50	2.08	12.06	0.029	0.033
30	2.20	2.17	0.040	0.042
20	2.31	2.25	0.053	0.055
10	2.61	2.40	0.058	0.062
5	2.75	2.60	0.062	0.073

Table – 7: Variation of dielectric constant (έ) with frequency for AN-IBM_2 copolymer at a constant frequency of 1 KHz

Temperature	30	60	90	120	150	180	210	240
Έ	2.32	2.37	2.41	2.48	2.54	2.57	2.62	2.67

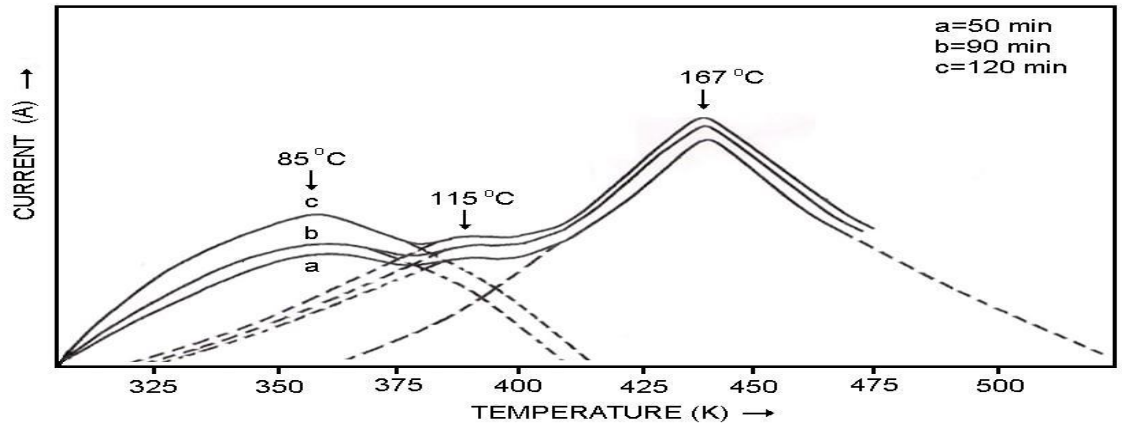

Fig.-1 :TSC Spectrum of acrylonitrile – isobornylacrylate

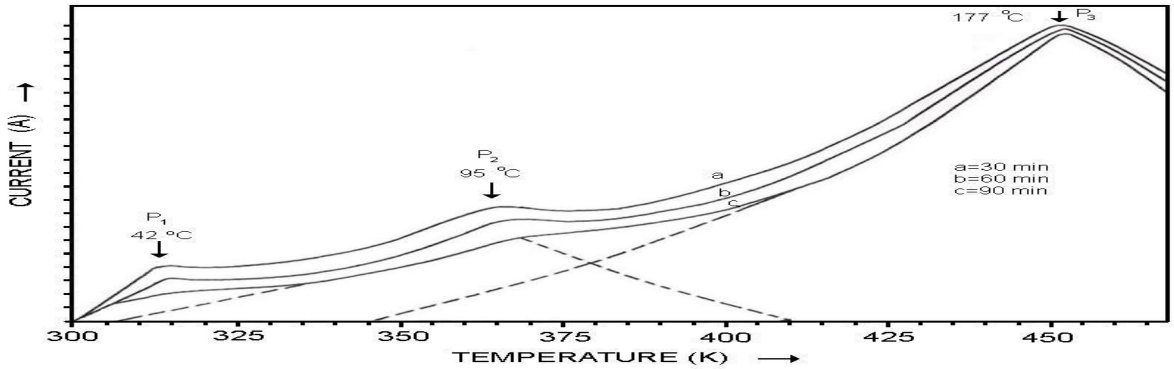

Fig.-2:TSC Spectrum of acrylonitrile – isobornylmethacrylate

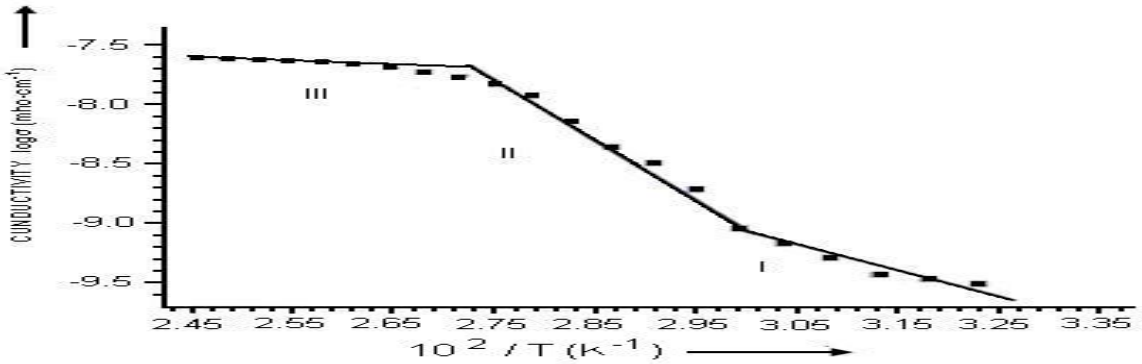

Fig.-3: Electrical conductivity (σ) Vs Temperature plot for (probe spacing 0.2 cm) AN-IBA copolymer(I)

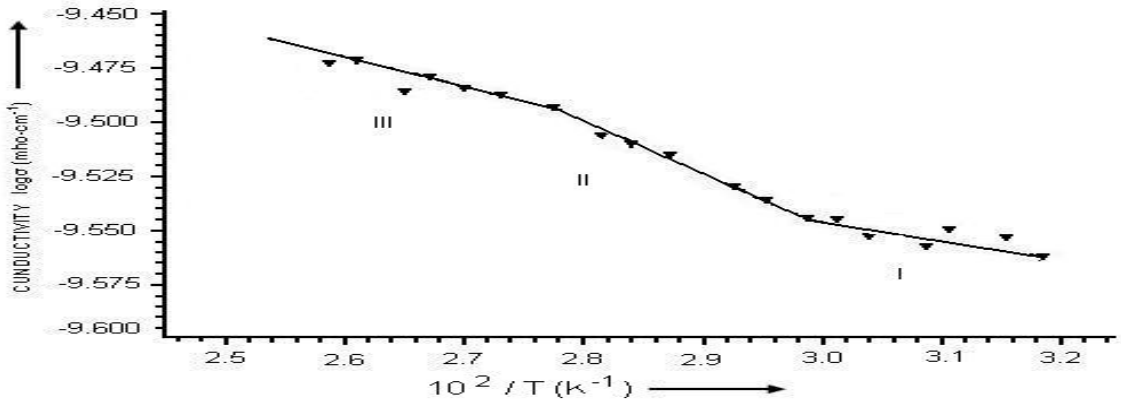

Fig. -4: Log σ Vs 1/T Plot for AN-IBA copolymer (I) (Probe spacing 0.8 cm)

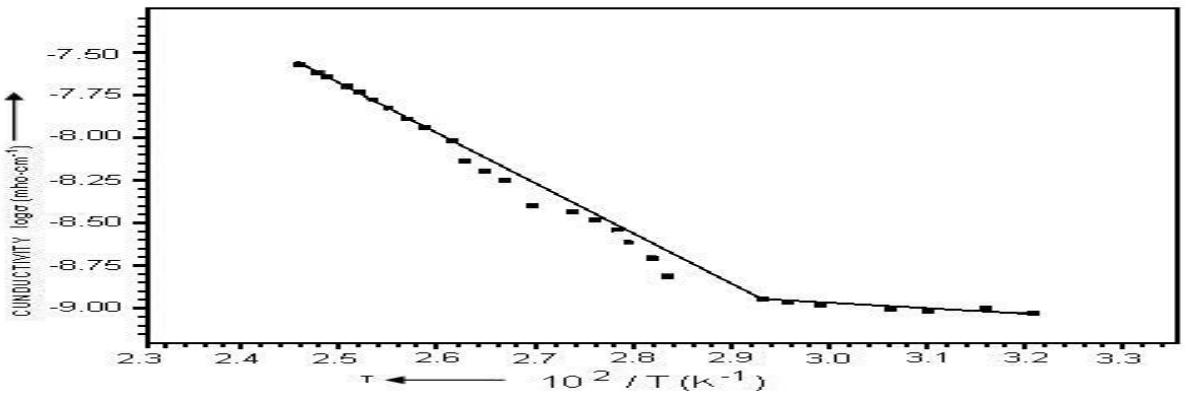

Fig-5 : Log σ Vs 1/T Plot for UV – irradiated AN-IBA copolymer

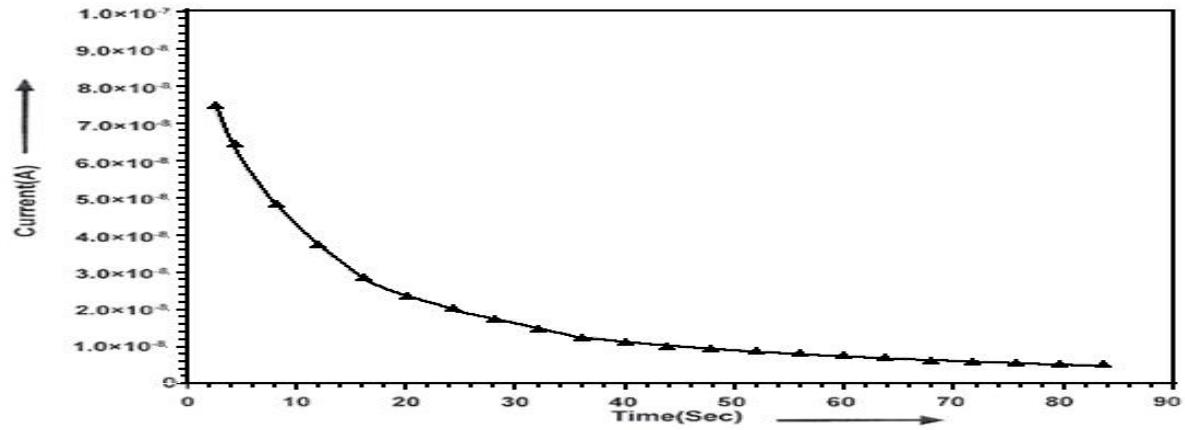

Fig.-6 : Decay of current with time for potential applied to the unirradiated (Voltage 120V) film of AN-IBA copolymer

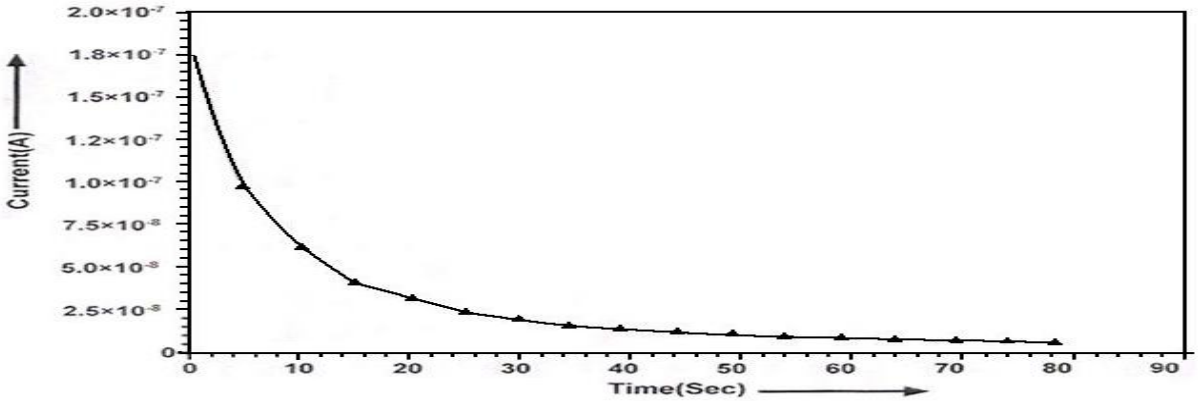

Fig.-7: Decay of current with time for potential applied to an irradiated (Voltage 120V) film of AN-IBA copolymer

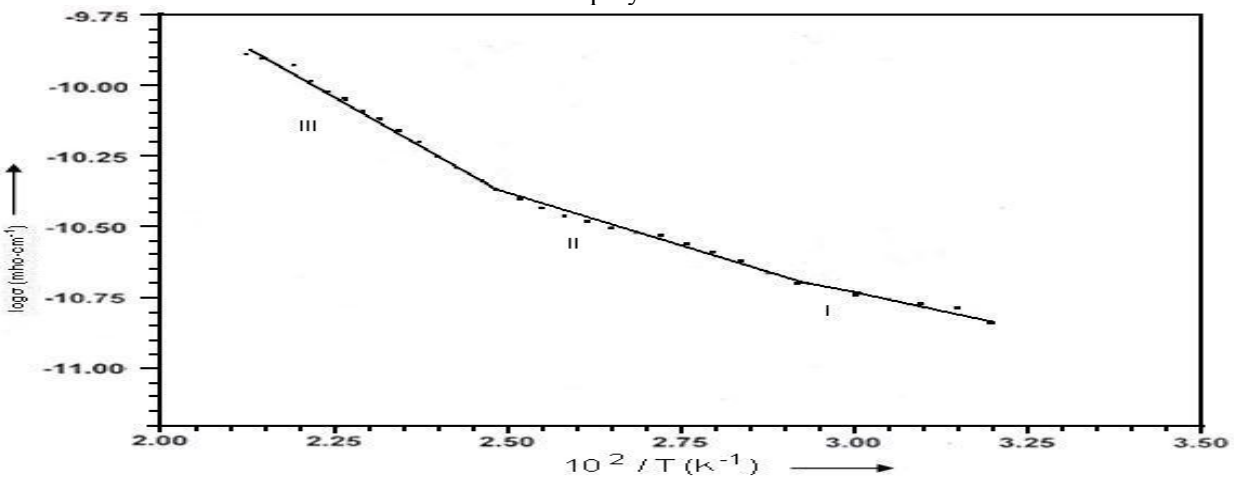

Fig.-8: Log σ Vs 1/T Plot for AN-IBM copolymer (II) (Probe spacing 0.8 cm)

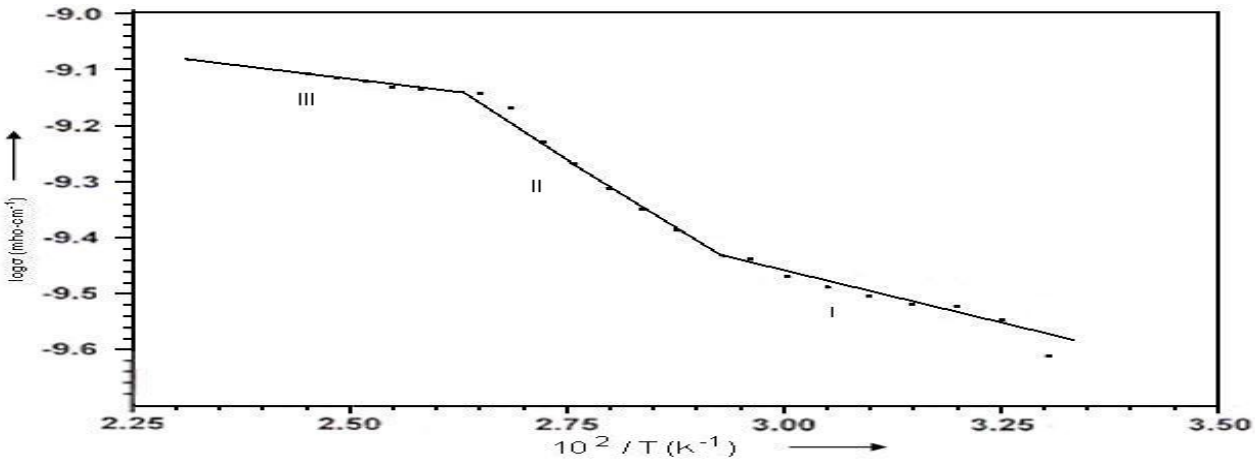

Fig.-9:Log σ Vs 1/T Plot for UV – irradiated AN-IBM copolymer (II) film

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