Polarization in polystyrene-chloranil complex

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Thermally stimulated discharge (tsd) current investigations have been carried out for polystyrene-chloranil donor-acceptor complex in the temperature range 34–106°C. Peaks have been observed near 80°C and 130°C in the current spectrum. The lower peak (α) has been correlated with relaxation of dipolar polarization at the glass-rubber transition and the higher peak (ρ) attributed to release of space charges. Comparison of tsd curves of polystyrene complex with pure polystyrene brings out two features: (i) the peaks are at lower temperatures; (ii) the magnitude and area of peaks are larger for the polymer complex. These have been explained on the basis of the increase in free volume and the dipole moment of the polymer on formation of complex. The tsd results have been compared with a.c. bridge measurements and are in good agreement. Polarizations for both α and ρ peaks are shown to be uniform up to field strength 40 kV/cm. Above this field, polarization is non-uniform. This has been explained by two different mechanisms responsible for polarization which give rise to heterocharge and homocharge.

INTRODUCTION

The study of thermally stimulated discharge (tsd) of polymer electrets provides an efficient technique for investigating molecular motions in polymers, because of its high sensitivity and resolving power as it probes the system at a very low frequency ($\sim 10^{-3}$ Hz).[1] The structural changes in polymers such as crosslinking,[2] structural isomerism,[3] degree of crystallinity,[3,4] and substitutions in the polymer molecule[5] are clearly reflected in tsd spectra. Tsd results are expected to show transformations in the dielectric properties of polymers such as change in dipole moment and conductivity because of the formation of donor-acceptor molecular complex[6] with suitable additives. The present work reports investigations on molcular complex of polystyrene and chloranil by tsd technique. The results have been compared with a.c. bridge measurements.

EXPERIMENTAL

Polystyrene (PS) and *p*-chloranil (CA) used in the experiments were supplied by Shri Ram Institute of Industrial Research, Delhi, India, and Merck, Germany respectively. Films were cast from benzene solution of PS containing 1% by weight of CA. After the solvent evaporation at room temperature, films were dried at 50°C for 24 h. Thickness of the samples was about 130 μm and area 6 cm^2.

For thermoelectret[7] formation, samples kept between two polished aluminium electrodes were heated to the required polarization temperative (T_p) and polarized by applying electric field (E_p) for 20 min. The samples were subsequently cooled to room temperature under the applied electric stress. Tsd current was observed by reheating of the shorted samples at a linear rate of 2°C per min from room temperature to 160°C. The discharge current was monitored by a Keithley model 610C electrometer. The tsd data were smoothed by fitting a fifth-order polynomial to the experimental points. The experimental points before smoothing and the smoothed curve, are shown for one of the tsd spectra (see *Figure 1*). Variation of T_p was in the range 60–140°C, and E_p in the range 10–70 kV/cm.

Optical absorption spectra were recorded on a Unicam SP700 A Ultraviolet and Visible Spectrophotometer.

Measurements of loss tangent and dielectric constant were made by means of an *LCR* Bridge in the frequency range 310–9600 Hz and temperature range 30–150°C. Voltage applied to the sample was 20 V r.m.s.

RESULTS AND DISCUSSION

Figure 1 shows tsd curve for pure PS sample polarized at $T_p = 100$°C and $E_p = 40$ kV/cm. A peak is observed at 96°C with current rise at higher temperatures.

Tsd spectrum of unpolarized doped sample (PS-CA)

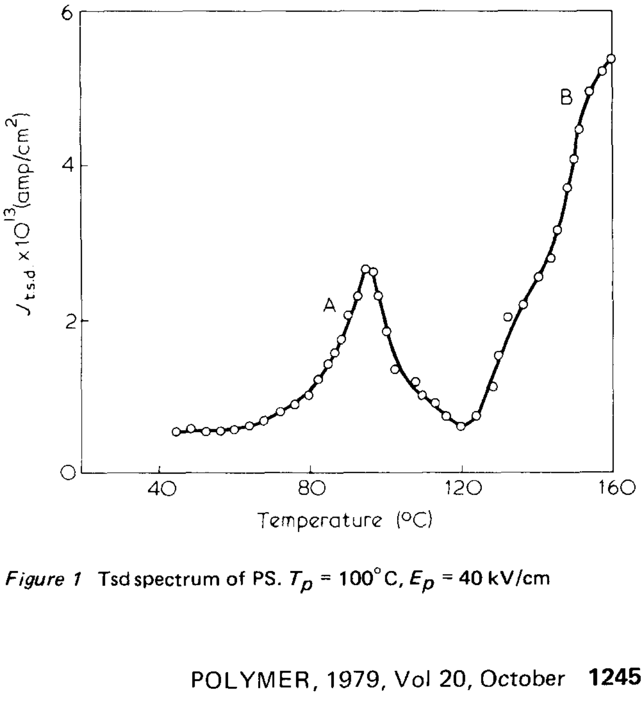

Figure 1 Tsd spectrum of PS. $T_p = 100$°C, $E_p = 40$ kV/cm

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shows a small peak at 120°C (*Figure 2*), which disappears on reheating. Tsd results for polarized PS-CA samples (*Figures 3* and *4*) show two maxima in current near 80°C and 130°C.

The influence of T_p at a constant E_p = 40 kV/cm can be seen in *Figure 3*. The lower temperature peak (peak A) shows relatively less variation than the peak at higher temperature (peak B). Peak A gradually increases and shifts to higher temperatures and reaches saturation at T_p = 100°C, whereas peak B is not significant until T_p is 80°C. At T_p = 100°C, its maximum value of current is an order of magnitude higher than peak A (*Figure 5*). Above T_p = 100°C, peak B decreases and at 140°C it is insignificant again. Changes in peak A are small above T_p = 100°C.

The influence of E_p at a constant polarization temperature of 100°C is shown in *Figure 4*. Both the peaks increase in magnitude with increase in E_p up to 40 kV/cm, the intensity of peaks falls. Further increase in E_p causes renewed rise in the peak heights. The current values for peak B were not reproducible very accurately from sample to sample, but the trend was same as shown in *Figures 3* and *4*.

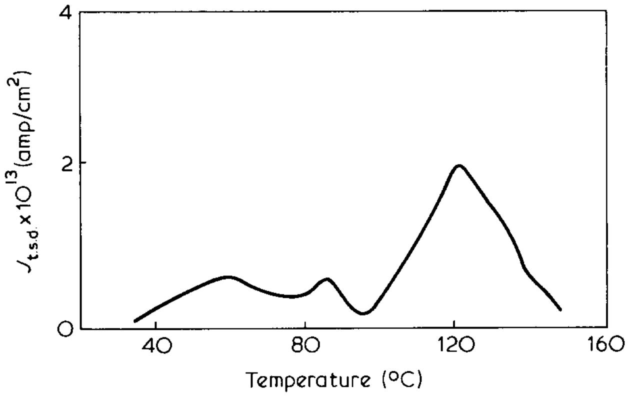

Figure 2 Tsd spectrum of unpolarized PS-CA

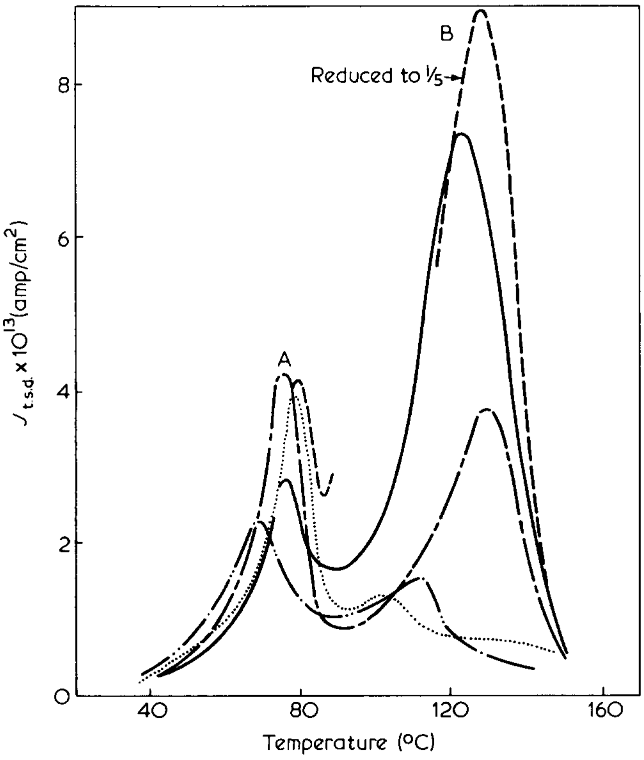

Figure 3 Influence of polarization temperature on tsd spectra of PS-CA. E_p = 40 kV/cm. T_p = 60°C, — — — — ; 80°C, ———— ; 100°C, — — — — — ; 120°C. —— —— —— ; 140°C, ... Current for peak B is reduced to 1/5 for T_p = 100°C

Figure 6 shows the tsd curve obtained from a PS-CA sample subjected to heat treatment at 160°C for 15 min, prior to polarization. Polarization conditions were T_p = 100°C, E_p = 40 kV/cm. Only peak A is observed at 80°C.

Peak A at 96°C in tsd spectrum of pure PS (*Figure 1*) is in the glass transition temperature (T_g) region of PS.[8] It is associated with the relaxation of dipolar polarization due to the onset of main-chain segmental motion which starts at T_g and is called the α peak. Dipolar polarization in PS is due to small dipole moment (~0.2 D)[9] of the phenyl group. The position of the α peak in the tsd spectrum is in agreement with the results of Marchal *et al.*[3]

The small peak at 120°C in the tsd curve of unpolarized PS-CA sample (*Figure 2*) can be due to release of charge carriers initially trapped in the polymer. Thus, this peak should not appear in second heating, and this was the case.

The α peak, which is related to the T_g, occurs at a lower temperature for PS-CA sample compared to pure PS and is approximately 1.5 times more intense (*Figure 3*, peak A for T_p = 100°C compared to *Figure 1*, peak A). The lowering of the glass-transition temperature is due to the increase in the free volume of the polymer system on addition of low molecular weight CA. Glass-transition temperature of polymers decreases with an increase in the free volume.[10] Broens and Muller[9] also have observed lowering of T_g in PS on doping with benzyl benzoate. They explained this as being due to a loosening of the polymer structure by dopant molecules. The lowering of T_g due to the presence of low molecular weight additives is in contrast to increase in T_g of PS due to crosslinking[11,12] and substitutions in the polymer molecule.[13–15] The last two have been explained

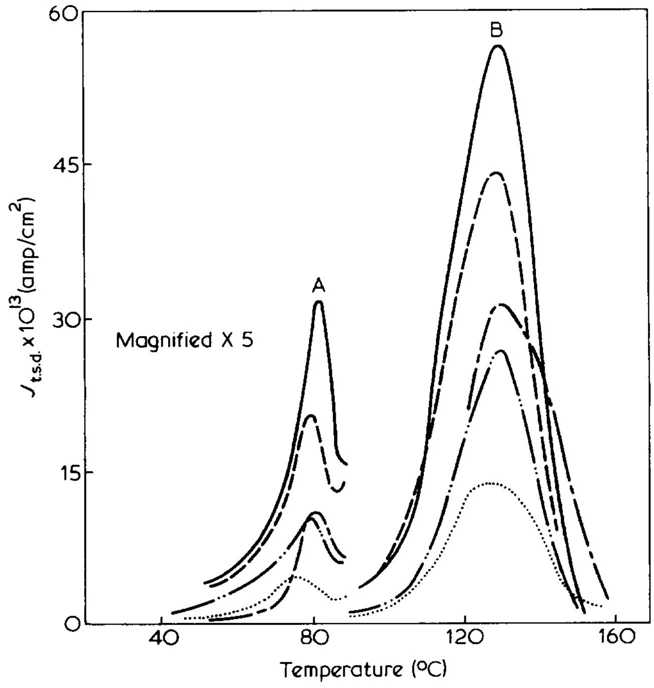

Figure 4 Influence of polarizing field on tsd spectra of PS-CA, T_p = 100°C. E_p = 10 kV/cm, ... ; 20 kV/cm, ——— — — ——— ; 40 kV/cm, — — — — ; 48.5 kV/cm, ——— — ——— ; 70 kV/cm, ————. Peak A is magnified ×5

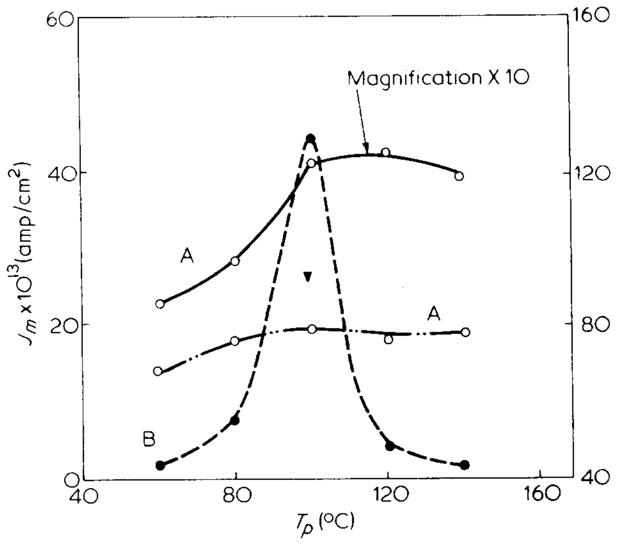

Figure 5 Peak current and peak temperature *versus* polarization temperature for PS-CA, E_p = 40 kV/cm. J_m, peak A, o—o—o magnification 10 x; T_m, peak A, o—··—o; J_m, peak B, ●———●; J_m, peak A, ▼ (of PS)

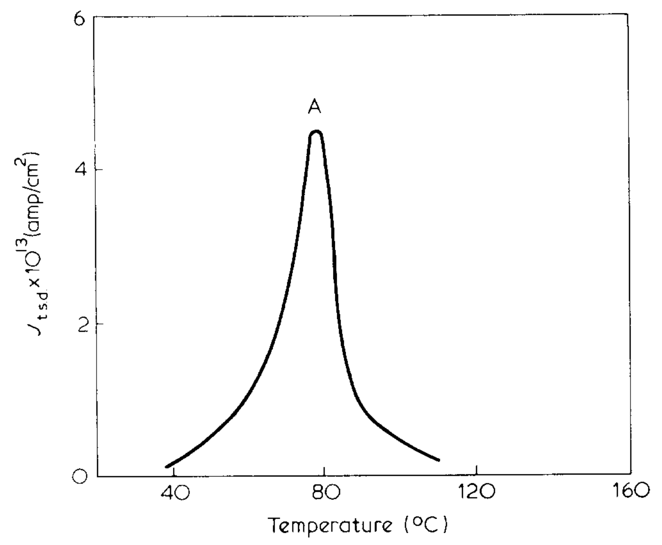

Figure 6 Tsd spectrum of PS-CA. Sample heated at 160°C for 15 min, T_p = 100°C, E_p = 40 kV/cm

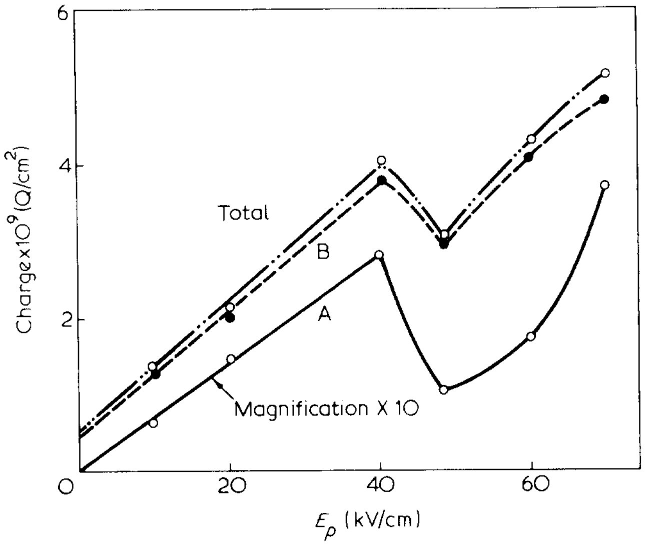

Figure 7 Charge released *versus* polarization field for PS-CA. Total charge, o——··——o; charge from peak A, o————o, magnification 10 x; charge from peak B ●— — —●

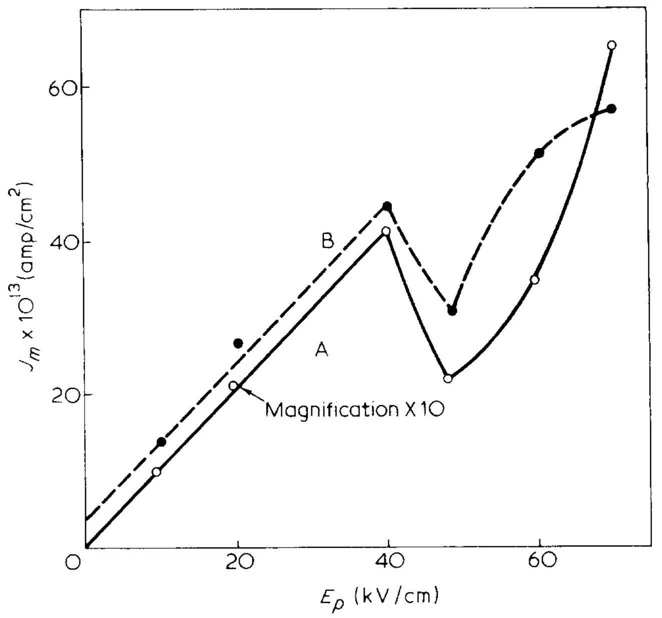

Figure 8 Peak current *versus* polarization field for PS-CA. Peak A o————o, magnification 10 x; peak B, ●— — —●

in terms of chain rigidity, steric hindrance to rotation and intermolecular forces of attraction.

The increase in peak intensity and area (i.e. charge released) can be related to increase in dipole moment of PS-CA over pure PS due to donor-acceptor (D-A) interaction between PS and CA molecules. The D-A complex formation is evidenced by the appearance of a new absorption band at about 3400 Å in the absorption spectrum which corresponds well with the D-A absorption band of benzene-CA complex.[16] This correspondence indicates that, in the polymer complex, the CA molecule is bonded to the phenyl group of the PS molecule.

The increase in peak value of current with T_p before reaching saturation is characteristic of incomplete filling of dipolar polarization. Shift in peak temperature (T_m) with T_p indicates a distribution in relaxation times,[17] (*Figure 5a*). For a single dipolar relaxation, T_m is independent of T_p, only peak height increases before reaching saturation value. For a distribution of relaxations, for low T_p, all subpolarizations are not filled. As T_p is increased, more and more subpolarizations are filled giving rise to shift in T_m towards higher temperature.

The peak above T_g in the tsd spectra of polymer electrets has been associated by Turnhout[18] with the release of space charges and is called the ρ peak. Marchal *et al.*[3] have observed a peak in the 160°C region for PS which was found to be very sensitive to the structure of the polymer. This peak was related to T_{ll} transition[21] in PS facilitating space charge release via long-range molecular motion. In our tsd spectrum for pure PS, there is an indication of this peak, but unfortunately all the tsd experiments in present studies were terminated at 160°C as above this temperature samples were distorted. For PS-CA samples, space charge seems to be released at a lower temperature, giving rise to a peak at about 130°C (*Figures 3* and *4*, peak B).

The large difference in magnitude of the peaks A and B is also expected as space-charge polarization is much more effective than dipolar polarization. Significant tsd peaks are observed for a relatively small number of space charges.[19]

The ρ peak is very small for $T_p = 60°C$ as the formation temperature is too low. At $T_p = 80°C$, it is already twice as large as the α peak and at $T_p = 100°C$, it is almost 10 times as large (*Figure 5*). Decrease in intensity of this peak for T_p above 100°C can possibly be due to (i) stronger unnoticed dissipation of space charges by increased ohmic condition at high temperatures;[20] (ii) loss of trapping sites due to increased molecular motion.[5]

To further investigate the behaviour of the ρ peak at high T_p, a tsd spectrum of a sample heated at 160°C was taken (*Figure 6*). The ρ peak was missing. The α peak was reproducible on repeated polarization and tsd cycles, but the ρ peak was observed only in the first cycle. This suggests that the fall in the ρ peak for $T_p > 100°C$ is not due to mechanisms (i) or (ii). It could be due to loss of charges themselves which are responsible for space-charge polarization, or due to the loss of trapping sites because of change in the structure on heating above 100°C. The ρ peak is not due to absorbed water as the tsd peaks were observed at 91°C and 141°C for PS-CA samples exposed to humid atmosphere. Moreover, these peaks were not reproducible on repeated tsd runs as some water was lost in each heating.

For uniform volume polarization, released charge (Q) and peak value of current (J_m) increase linearly with field. Linear variations has been observed for both Q and J_m up to $E_p = 40$ kV/cm for both the peaks (*Figures 7* and *8*). Above this, the field variation is not linear. Such variation is possible if polarization is due to two different mechanisms. One is uniform volume polarization (heterocharge) produced by dipole alignment and migration of charge carriers with uniform trapping. The other is non-uniform volume polarization (homocharge) produced by charge injection from electrodes and space-charge build up near electrodes.

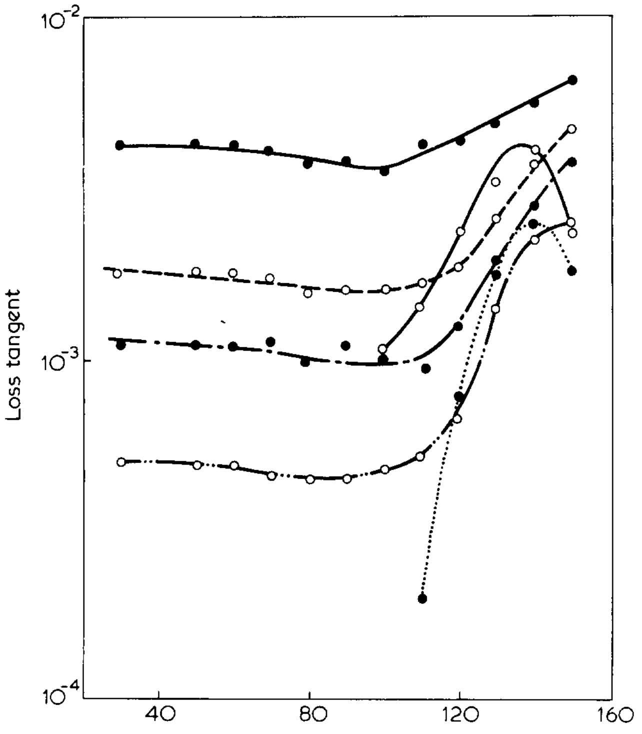

Figure 9 Loss tangent *versus* temperature for PS. 310 Hz, o——o; 660 Hz, •·········•; 1500 Hz, o——··——o; 3100 Hz, •——·——•; 4500 Hz, o— — —o; 9600 Hz, •———•

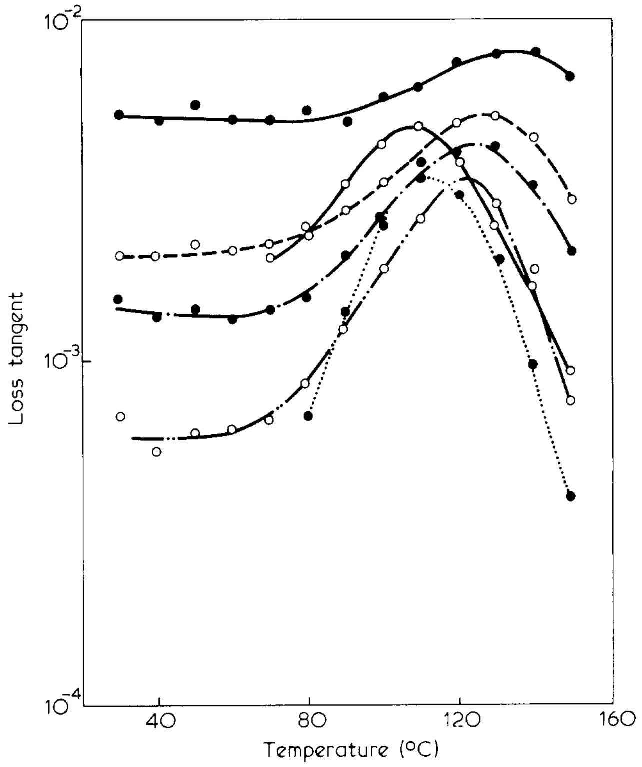

Figure 10 Loss tangent *versus* temperature for PS-CA. 310 Hz, o——o; 660 Hz, •·········•; 1500 Hz, o——··——o; 3100 Hz, •——·——•; 4500 Hz, o— — —o; 9600 Hz, •———•

The results shown in *Figures 7* and *8* indicate that up to $E_p = 40$ kV/cm, heterocharge is dominant and above this field homocharge is also appreciable. The dipolar peak also may have a contribution from the space-charge polarization as this peak also shows nonlinear variation for Q and J_m.

Figures 9 and *10* show the variation of dielectric loss tangent with temperature at different frequencies for PS and PS-CA samples respectively. The loss peak observed is due to α relaxation which shifts to higher temperatures with increases in frequency. The tsd ρ peak does not appear in a.c. bridge experiments; instead, increasing conduction losses are observed above the dipolar peak due to the presence of an external voltage. In the present investigations, these conduction losses have not been observed till 150°C, but are expected to occur above this temperature. At a measuring frequency of 310 Hz, a loss peak is observed at 137°C for PS and at 108°C for the PS-CA-complex. The temperatures are higher compared to those obtained in tsd experiments. This is to be expected as the equivalent frequency of tsd experiment is very low.

On comparison of the results shown in *Figures 9* and *10*, it is observed that (i) loss peaks occur at lower temperatures; (ii) the peaks are broader; and (iii) the magnitude of the loss tangent is larger for PS-CA complex compared to pure PS. The lowering of the peak temperature is due to an increase in the free volume of the polymer, as already explained. The increase in the peak width and magnitude imply an increase in the area under the loss peak, i.e. more absorption of energy. This is due to the larger dipole moment of the complex. The magnitude of the loss tangent is also higher for the complex at temperatures well away from the peak. This is due to the larger conductivity of the complex.

The capacitance, and hence dielectric constant values, were found to be independent of frequency for both PS and PS-CA samples within the range of investigations. Dielectric constant at 30°C was 2.93 for PS and 3.03 for PS-CA, and decreased slightly at temperatures above 80°C. The increase in the dielectric constant of PS-CA is comparable with the increase in area under the tsd peak (i.e. charge stored).

The dielectric α relaxation for PS has been studied by several other workers by the alternating-field method.[9,22] The tan δ peak has been observed in the range 120-125°C for a frequency of 1 kHz, which is lower than the value obtained in this investigation. The dielectric constant for PS is also higher than the value generally accepted (2.4-2.7).[9,23] These discrepancies can be due to the presence of some trace impurities in the PS used.

Thus the results from tsd experiments for dipolar relaxation in PS and PS-CA complex are in agreement with a.c. dielectric measurements. The tsd technique is to be preferred as information about space-charge polarization is not obtained from a.c. bridge experiments.

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