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Effect of copolymerization with chloranil on the polarization processes in polystyrene

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Polarization processes in polystyrene–chloranil copolymer have been investigated by the thermally stimulated discharge (TSD) technique. The observed TSD current peak consists of contributions from two different processes having activation energies 0.78 and 1.29 eV. The single peak could not be resolved into its constituents due to experimental limitations. Comparison of the TSD results for the copolymer with those of pure polystyrene and chloranil suggests that dipolar and space charge types of polarization are playing a role in the polarization of the copolymer.

1. Introduction

The dielectric properties of a polymer can be tailored to the required extent by suitable modification of its chemical or physical structure. Structural modification may be introduced by doping, substitution, copolymerization, blend formation, crosslinking and orientation. The effect of doping polystyrene with chloranil on its dielectric properties has been reported earlier [1, 2]. The dielectric relaxations were shifted to lower temperatures along with an increase in the total polarization, dielectric constant and dielectric loss. This paper presents a study of polarization processes in polystyrene–chloranil copolymer (PSCA) by thermally stimulated discharge (TSD) technique. On doping polystyrene (PS) with chloranil (CA), the dopant molecules interact with the phenyl groups of PS, forming a donor–acceptor complex which is responsible for the observed changes in the dielectric properties. In the PSCA copolymer, the CA groups exist in the main chain of the polymer. Thus, the present studies would help to understand how a particular chemical unit, when incorporated at different sites in a polymer structure, affects the dielectric behaviour of the system.

2. Experimental details

2.1. Preparation of the copolymer

PSCA copolymer was prepared by bulk polymerization of styrene and chloranil (in equimolar ratio) at 60° C using benzoyl peroxide (1 mol%) as initiator [3]. The copolymer was purified by repeated precipitation using methanol as a non-solvent to remove unreacted monomers. The molecular weight ($\bar{M}_v$) of the copolymer was calculated to be 6×10^3.

2.2. Thermal stability

Thermogravimetric analysis (TGA) of PSCA was carried out with a Stanton Redcraft TG-750 thermobalance in static air at a heating rate of $10^\circ\,\mathrm{C\,min^{-1}}$. The thermogram shown in Fig. 1 indicates the initial degradation temperature (IDT) of the copolymer as 153° C.

2.3. Infrared spectrum

Infrared absorption spectra were recorded on a Unicam SP-1200 IR spectrophotometer. The IR spectrum of PSCA is shown in Fig. 2 along with those of PS and CA for comparison. Copolymerization is expected to affect the vibration frequencies of the CH_2 and CH groups of PS. The stretching mode $\nu_a(CH_2)$ at $2925\,\mathrm{cm^{-1}}$ and the bending mode $\delta(CH_2)$ at $1460\,\mathrm{cm^{-1}}$ of PS [4] have shifted to 2940 and $1430\,\mathrm{cm^{-1}}$ respectively in the spectrum of the copolymer. The stretching mode $\nu_s(CH_2)$ is not observed at all. Two new absorption bands have appeared at 990 and $1045\,\mathrm{cm^{-1}}$, which may be assigned

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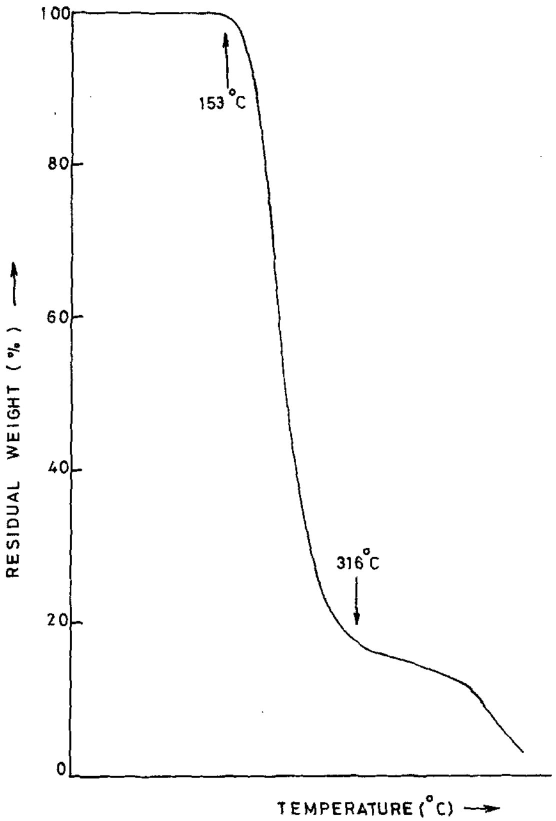

Figure 1 TGA thermogram of PSCA, heating rate 10° C min^{-1}.

to the vibration modes of CO groups. The other vibration modes of the CA group in the copolymer can be analysed by considering them as substituted benzene groups. The vibration modes at 410, 842 and 1027 cm^{-1} (these are the ν_{16A}, ν_{10A}, and ν_{18A} fundamental modes, respectively, of benzene molecules) and some others have appeared at the same frequencies in the spectrum of PSCA as these do not depend on substitution in the ring.

2.4. TSD experiment

Samples for TSD experiment were prepared in the form of pellets (thickness 480 μm; diameter: 1.3 cm). The experimental procedure for polarization and observation of TSD current has been described earlier [1].

TSD currents were recorded in the temperature range 34 to 100° C. Above this temperature, the copolymer probably starts degrading, although the IDT observed by TGA was much higher. The degradation was reflected in the TSD thermogram of an unpolarized sample by a rapid increase of the current above 100° C and is shown in Fig. 3. On heating the copolymer in a capillary tube and directly examining through a microscope, the material was observed to turn brownish above 100° C before finally melting in the temperature range 110 to 120° C. Thermally stimulated current due to polymer degradation has been observed for polyacrylonitrile also at temperatures above 200° C [5].

3. Results

The TSD thermograms of PSCA samples polarized under different conditions are shown in Figs. 4 to 6. A common feature of all the thermograms is a current peak in the investigated range of temperature. The peak temperature (T_m) depends on the polarizing temperature (T_p) (Fig. 4). The peak value of the current (J_m) increases linearly with the polarizing field (E_p) (Fig. 5). The effect of increasing the polarizing time (t_p) above 20 min is not appreciable. Resistance of a PSCA sample was measured as a function of temperature (Fig. 7). A sharp decrease in the resistance is observed at about 65° C.

4. Discussion

In the TSD thermograms of polymers current peaks are generally observed at various polymeric transitions. Different modes of polarization, such as dipolar orientation and space charge, are able to relax with different types of molecular motions of the polymer. Generally, molecular motions which occur at sub-T_g and T_g transitions are concerned with dipolar type of polarization, whereas above-T_g transitions involving molecular movement of complete chains are linked to polarization due to charges trapped at various sites such as crystalline amorphous boundaries or accumulated near the electrodes.

The TSD thermograms of PSCA show only one current peak. Before analysing the origin of this peak, we consider that the resistance of PSCA shows a sharp decrease at about 65° C (Fig. 7). This type of variation is characteristic of polymers, where resistivity decreases sharply as temperature is increased above the T_g [6]. This suggests that the T_g of PSCA is about 65° C.

The TSD thermograms of PSCA may be analysed by comparing them with those of pure PS [1, 7, 8] and CA [9]. In the case of PS two peaks were observed, namely the α peak at 96° C (T_g) and the ρ peak at 160° C (T_{ll}). The α peak has its origin in

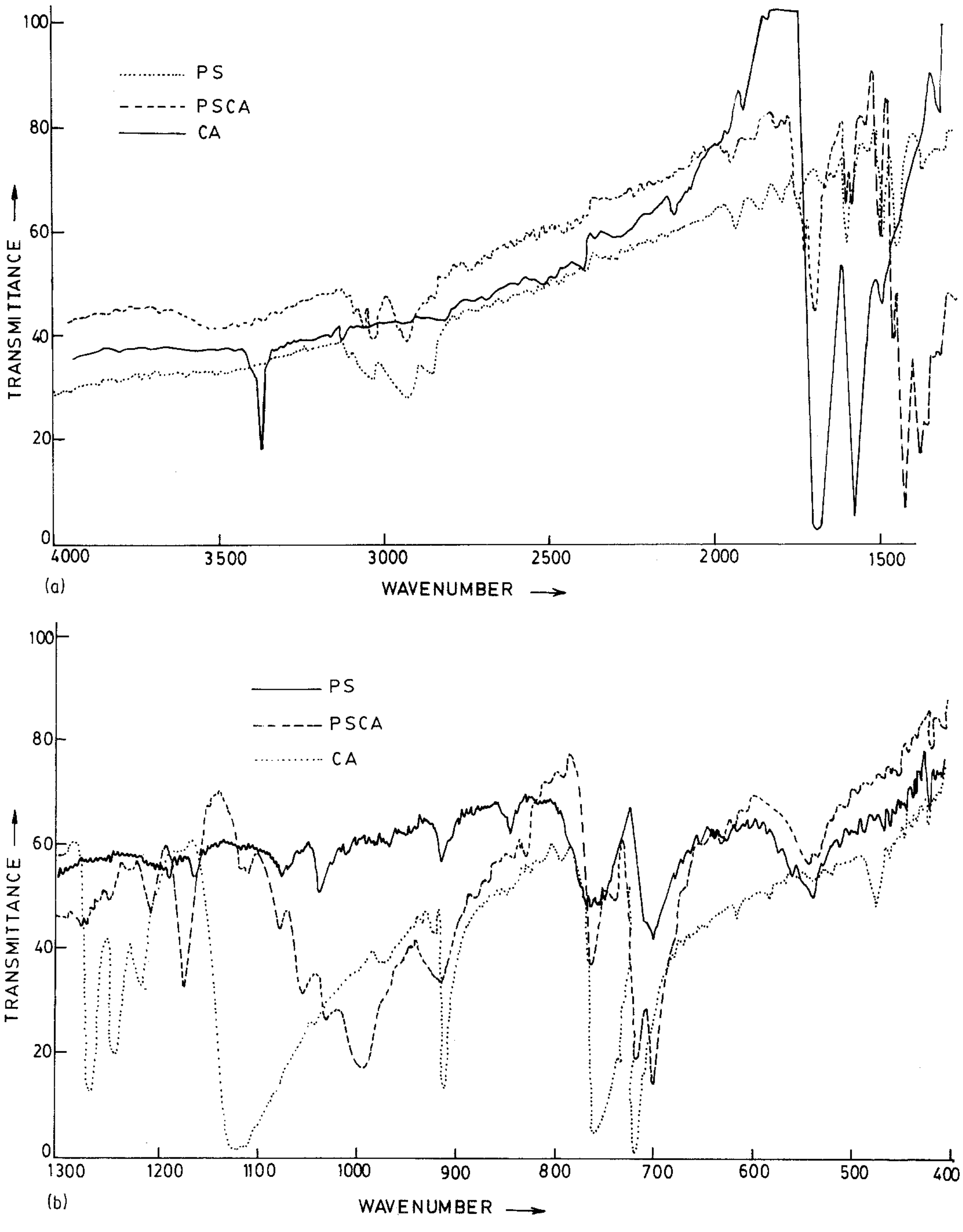

Figure 2 IR absorption spectra of PSCA, PS and CA (samples as KBR pellets). (a) 4000 to 1500 cm^{-1}, (b) 1300 to 400 cm^{-1}.

small dipolar polarization contributed by the weakly polar phenyl groups of PS and the ρ peak is due to space charges. The chloranil pellets are found to exhibit polarization which is a contribution of dipolar as well as of charges trapped at various sites including grain boundaries.

It is expected that the small dipole moment of phenyl groups of PS as well as that of CA will contribute towards dipolar polarization in the case of PSCA. The magnitude of contribution from the CA groups may be different because of restriction of their molecular movement in the polymer chain. The contribution of the phenyl groups in PSCA should not be different from that

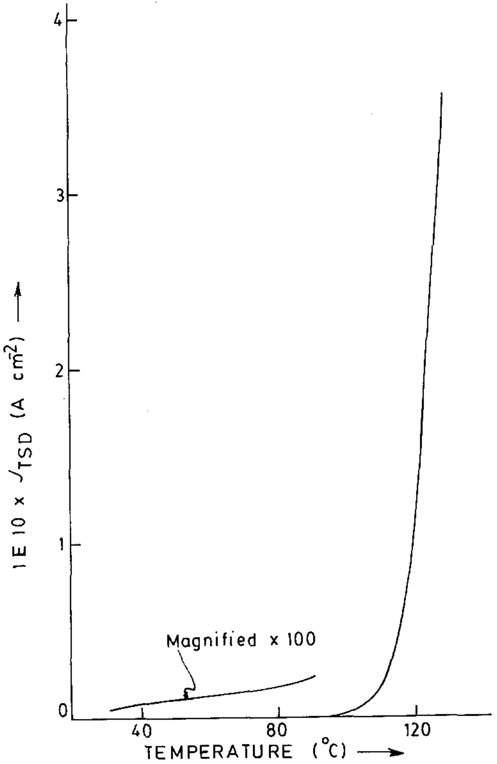

Figure 3 TSD thermogram of an unpolarized PSCA sample.

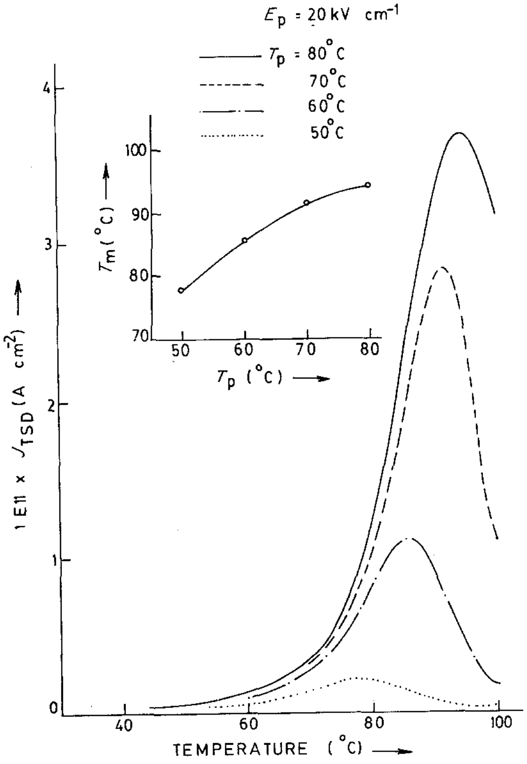

Figure 4 TSD thermograms of PSCA samples polarized at various temperatures. Inset: Variation of peak temperature with polarization temperature.

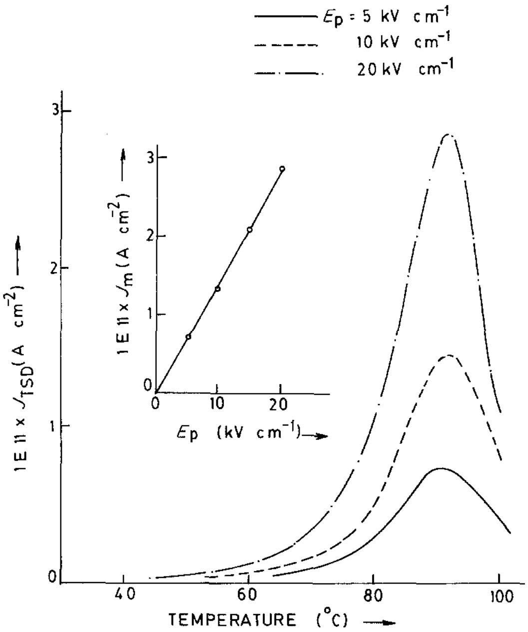

Figure 5 TSD thermograms of PSCA samples polarized at various electric fields. Inset: Variation of peak current with polarization field.

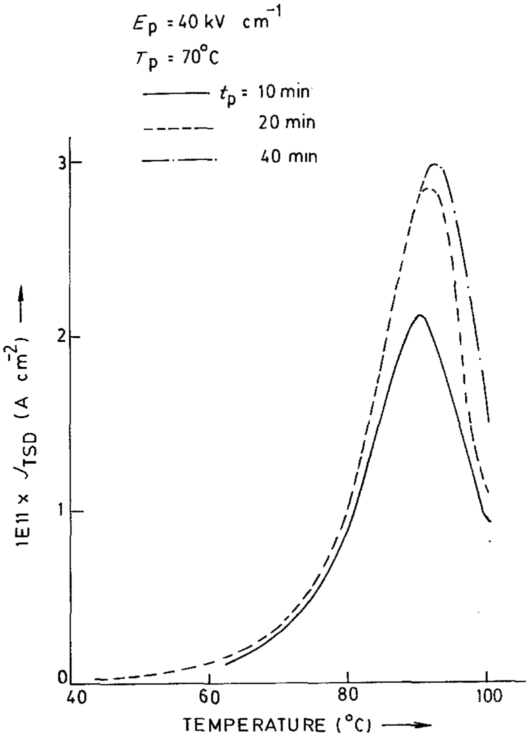

Figure 6 Effect of polarization time on TSD thermograms of PSCA samples.

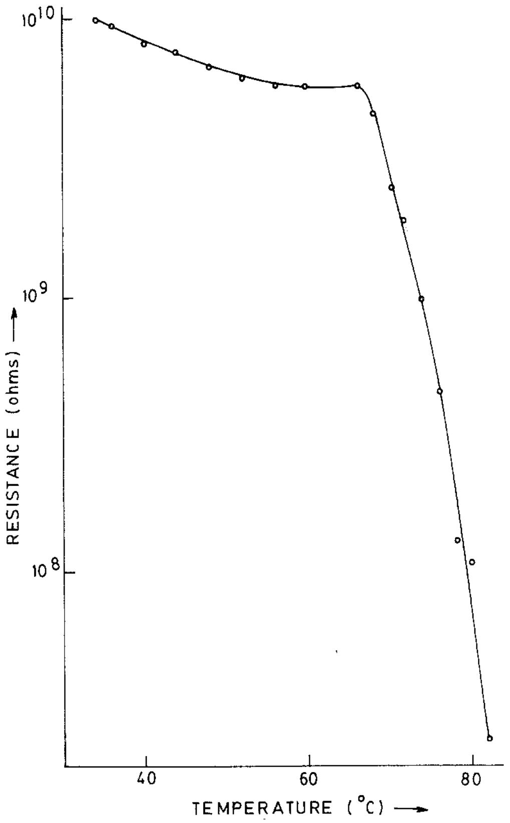

Figure 7 Variation of resistance of a PSCA sample with temperature.

in PS. The phenyl groups in PS give a dipolar relaxation peak below T_g (β) also, but its magnitude is small and was not observed in our experiments. Thus, it is expected that the dipolar polarrization in PSCA will give a relaxation peak at the T_g of the polymer.

Space charge polarization should be higher in PSCA mainly due to a lower resistivity of PSCA ($\sim 10^{10}$ ohm cm) as compared to PS [10] and CA [11]. Carrier trapping at grain boundaries is definitely playing a role, as in the case of CA, due to pellet form of the samples.

Therefore, both dipolar and space charge polarization contribute towards polarization of PSCA and should give rise to two different peaks in a well-resolved TSD thermogram. However, in the present studies it was not possible to resolve the observed peak into its constituents due to experimental limitations in the values of T_p and E_p. It may be possible to resolve the peak at higher values of T_p and E_p as was done for CA.

Further support for two different polarization processes in PSCA is obtained from calculation of activation energy (AE) from the TSD data. Following the method of Bucci *et al.* [12], instead of a single straight line characteristic of a single uniform process, two straight lines are obtained giving two values of AE at 0.78 and 1.29 eV. The change in slope occurs at 65° C, which from the resistance against temperature curve is the T_g of the copolymer.

Thus the single current peak in the TSD thermograms of PSCA is due to two different processes having activation energies of 0.78 and 1.29 eV. These polarization processes may be dipolar orientation, trapping of charges carriers and space formation.

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