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Thermally stimulated depolarization current studies of sulfonated polystyrene ionomers

Thermally stimulated depolarization current studies of sulfonated polystyrene ionomers

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Abstract A detailed study of thermally stimulated depolarization current (TSDC) was carried out to investigate dipolar relaxation and the charge storage phenomenon in films of sulfonated polystyrene (SPS) ionomers having lithium or potassium as counterions. Differential scanning calorimetry measurements were also applied as a complementary technique, mainly to follow the change of the glass transition temperature with the amount of sulfonated groups. It was observed that, since the glass transition does not change significantly with the amount of sulfonated groups, a cluster of multiplets is expected not to be formed in the range used in this work. TSDC of SPS samples polarized at temperatures higher than the glass transition temperature showed three peaks: one at lower temperature (peak β), an intermediate peak (peak α), and a third that appeared at a temperature coincident with the polarization temperature (peak ρ). Quantitative information about trapping–detrapping and dipolar relaxation and their corresponding activation energies was determined by fittings of the deconvoluted peaks with kinetic relaxation processes.

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1 Introduction

Ionomers are ion-containing functional polymers that have a relatively low concentration of pendent ionic groups distributed in a non-ionic and low polar backbone chain. The ionic pair of each ionomer forms a strong dipole when it is chemically bound to the polymer chain, considering that the surrounding medium has a low dielectric constant. On the other hand, for relatively high temperature or for medium to high dielectric constant a dissociation of the ions takes place, generating ionic carriers but destroying the polar groups. Due to their singular chemical and physical properties, ionomers are currently applied in the development of new composite materials and also as proton exchange membranes in fuel cells [1], and as either active or auxiliary layers in organic electronic devices [2, 3]. Most recently, it was shown that a thin film of sulfonated polystyrene (SPS) ionomer, acting as an electron transport layer (ETL) in a polymer light-emitting diode (PLED) structure, improved considerably the electrical performance of the device, by increasing the amount of injected electrons at least by a factor of two [4, 5]. The charge injection phenomenon is relevant for the operation of PLEDs because the recombination process responsible for the light generation is optimized by the number of injected carriers (electrons and holes) and by the equilibrium between them. The mechanism responsible for such high electronic injection provided by the SPS ionomer layer is still not well understood. However, the polarization formed by the alignment of ionic dipoles (in the multiplet regions) combined with the migration of ionic species under an external applied field can facilitate the injection of the electrons. To evaluate quantitatively the role of a SPS thin film in this phenomenon, some fundamental aspects of relaxation processes concerning dipoles and charge migration need to

be enlightened. Relaxation processes depend on the chemical composition and on the morphology of SPS films because they strongly affect the temperature-dependent mobility of bound (dipoles) and free (ions and electronic carriers) charges in the system. Here, we employ the thermally stimulated depolarization current (TSDC) technique, which is an experimental approach widely applied to study thermal relaxation processes of polymers, combined with differential scanning calorimetry (DSC) to investigate the charge storage, charge migration, and dipolar relaxation of SPS ionomers with an $-SO_3^-$ group attached to the backbone, having lithium or potassium as cationic counterions. We are interested in obtaining quantitative information about trapping–detrapping and dipolar relaxation data, such as the values of activation energies and their relation with the glass transition of the ionomer.

2 Materials

Ionomers of polystyrene with sulfonation degree of 6 mol% and 9 mol%, respectively, for lithium and potassium as counterions (Fig. 1) were synthesized by sulfonation of the parent polystyrene (Aldrich) with acetyl sulfate in dichloroethane solution [6, 7]. The sulfonated polystyrene and the parent polymers were characterized by Fourier Transform Infrared spectroscopy (FTIR) (ThermoNicolet Nexus 470) spectroscopy, and sulfonation degrees were estimated from the sulfur content determined by elemental analysis (Carlo Erba). These values are in agreement with those theoretically predicted considering a yield of approximately 100%, as observed in previous work for low sulfonation degree polystyrenes [6]. Differential scanning calorimetry (DSC) experiments were carried out in a Shimadzu TW-50 system, with a heating ratio of 10°C/min, under N_2 environment. The glass transition temperature was determined in the inflection point of the glass transition region; the energy change in the transitions corresponded to approximately 0.05 mW/mg, being weakly dependent on the sulfonation degree. Films of sulfonated polystyrene with 6% of lithium (designated as Li6) were prepared by casting from solution
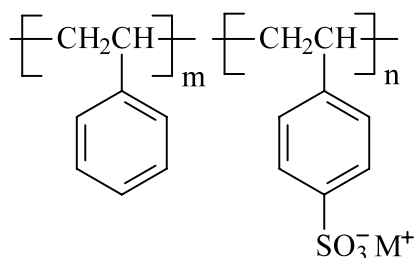
in chloroform and then dried for 24 h at 60°C. The same procedure was used to prepare films of sulfonated polystyrene with 9% of potassium (K9), with the difference that, for these films, a mixture of chloroform with dimethylsulfoxide (DMSO) was used as solvent. Film thicknesses were about 80 μm, and circular aluminium electrodes of 1.57 cm^2 were evaporated on both sides.

3 TSDC method

The polarization of a dielectric material can be generated by either dipole orientation or charge separation inside the material structure. Both mechanisms are induced by an external electric field, and the structure of the material dictates the relaxation behavior defining the activation energies in which the relaxations take place. TSDC belongs to a great number of relaxation techniques, and is particularly important to investigate dipole orientation and/or storage of charge in dielectric materials. From TSDC thermograms and adequate kinetic theoretical models one can obtain the amount of polarization and the values of the involved activation energies. The technique consists in the application of an external voltage (external polarization electric field, E_p) under a polarization temperature T_p, during a period of time t_p, a time enough to achieve the entire polarization P_o of the material (see Fig. 2). For polymeric materials, the polarization temperature should be higher than its glass transition temperature T_g. The relaxation time τ is an important parameter for TSDC curves that depends on T_p and E_p. After the polarization, determined by t_p, the sample under investigation is cooled to a temperature T_o, short circuited for a brief period

Fig. 1 Sulfonated polystyrene structure where the sulfonation degree is given by molar proportion of sulfonated mers to sulfonated plus non-sulfonated mers, with M^+ being a Li^+ or K^+ counterion
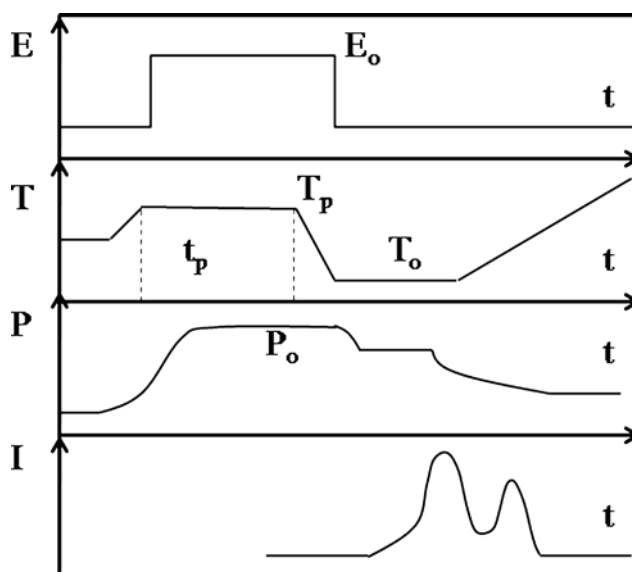

Fig. 2 Schematic process of thermally stimulated depolarization technique

t_s, and then heated with a linear rate ($T = T_o + ct$). During the heating process the electric current $I(t)$ is then recorded. The diameter of evaporated aluminum electrodes was 6 mm.

It is important to stress that, depending on the polarization temperature and on the intensity of the applied field, carriers can be injected from the electrodes (electrons from the cathode, and holes from the anode) and be trapped in the material structure. In general, polymer films have different distributions of traps: in the vicinity of the metal/polymer interface, and in the bulk. When the polarity of stored charges at the interface is the same as the corresponding electrode, the trapped charges are called homocharges. On the other hand, when charges are dissociated inside the bulk and migrate towards the respective opposite electrodes and become blocked at the metal/polymer interfaces, they are called heterocharges. Bucci and Fieschi [8] developed a model to study quantitatively TSDC thermograms, in which the relaxation time obeys an Arrhenius equation, i.e. $\tau(T) = \tau_0 \exp(U/kT)$, where τ_0 is an exponential prefactor (the inverse of the escape frequency s) and U the activation energy of the process. The simplest kinetics is that in which only linear effects are involved (first-order kinetics):

$$I(T) = A \exp(-U/kT) \exp(-s/\beta) \int_{T_o}^{T} \exp(-U/kT') \, dT',$$

(1)

where β is the heating rate; A is equal to $en_o s$ when the TSDC peak is related to the charge-trapping phenomenon, n_o being the amount of stored charge. For processes involving dipolar relaxation, $A = N\mu^2 s\alpha E_p/kT_p$, N being the dipole concentration, μ the dipole moment, and α a dimensionless parameter that depends on the material structure.

4 Results and discussion

Figure 3 shows DSC measurements carried out with PS samples and sulfonated PS ionomer samples having potassium as counterion. The glass transition temperature, T_g, for PS is about 105°C and it shifts to higher temperatures as the amount of ionizing groups increases. T_g for K9 is about 120°C. It is well known from the literature [9] that up to 6 mol% ionomers does not form clusters of multiplets, and for this case the T_g of the ionomer is near to that of the parent polymer [10]. For K9 (9 mol% of ionic groups) a low cluster concentration is expected because is just above the critical concentration of 6 mol%, which was confirmed by our DSC measurements. Similar results were obtained for Li- ionomer samples. The observed T_g shift is most probably caused by the attractive interaction among multiplets, whose interactions tend to decrease the mobility of segment chains during its glass transition (T_g), i.e. the multiplets act as physical cross-linking elements.
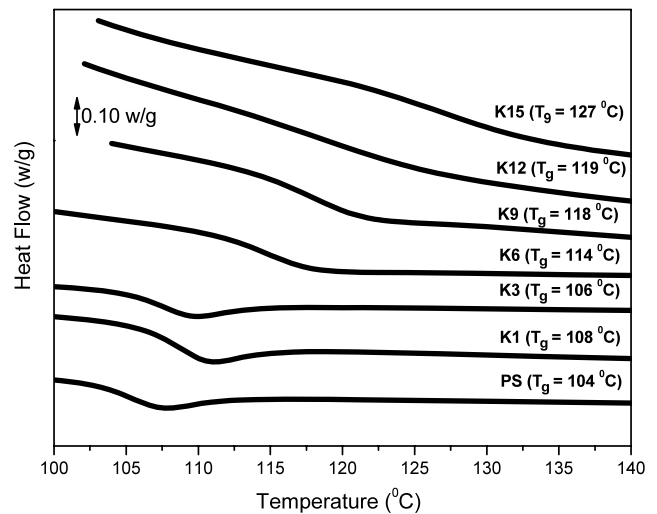

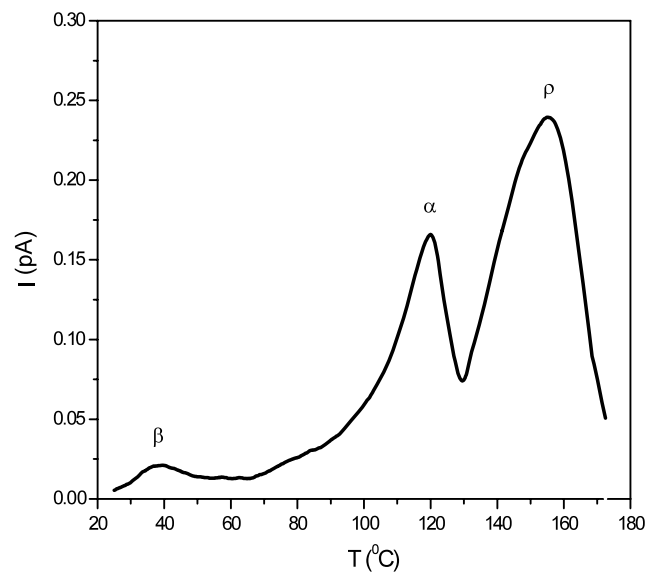**Fig. 3** DSC measurements of PS and potassium sulfonate–PS

Fig. 4 TSDC curve of Li6 ionomer: $T_o = 25°C$, $T_p = 150°C$, and $E_p = 20$ kV/cm

TSDC thermograms obtained with virgin ionomer samples always exhibited three pronounced peaks: one at lower temperature (peak β), an intermediate peak (peak α), and one that appears at higher temperature (peak ρ) [11–13]. As an example, we show a TSDC curve obtained with a sample Li6, polarized under $E_p = 20$ kV/cm at $T_p = 150°C$ (Fig. 4). While the β-peak was registered only for virgin samples—not appearing for subsequent measurements—the other two peaks were recorded for successive TSDC cycles. The β-peak is most probably related to detrapping of carriers, which are stored in shallow traps and during the first TSDC measurement they are swept out of the sample. Such 'residual charges' are responsible for absorption current recorded in isothermal decay measurements [14].
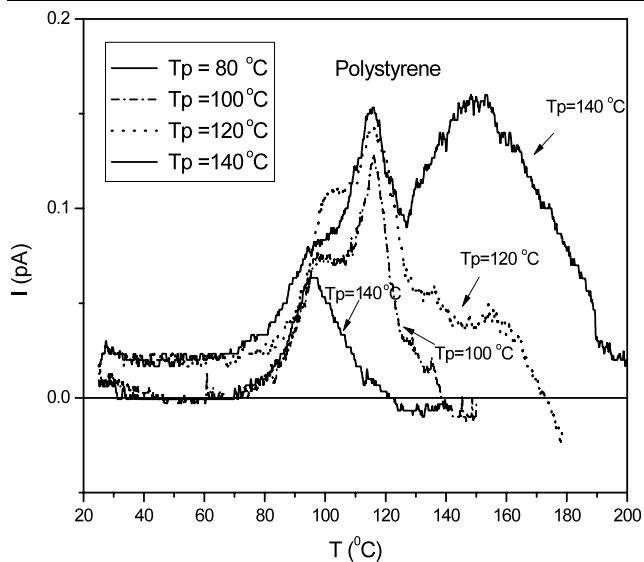
Fig. 5 TSDC curves of a PS film with T_p equal to 80°C, 100°C, 120°C, and 140°C

Fig. 6 TSDC curves of Li6 sample: $E_p = 20$ kV/cm and $t_p = 10$ min at different polarization temperatures T_p

Therefore, our study will be confined to the α- and ρ-peaks, which, as we will see, are phenomena related to the glass transition of the material [15].

Figure 5 shows TSDC thermograms obtained with pure polystyrene, polarized at different temperatures T_p: 80, 100, 120, and 140°C. When T_p is lower than the glass transition temperature T_g, which means below 104°C, only one TSDC peak was recorded. This peak is the α-peak with a maximum at $T_m = 95$°C. For measurements in which T_p was equal to or above 100°C, both α- and ρ-peaks were detected, and the measurements show that the magnitude of the ρ-peak increases with T_p, and that it shifts to higher temperature as T_p increases. The α-peak does not exhibit any T_p dependence being recorded at $T_p = 120$°C, except when $T_p < T_g$. We can, therefore, infer that the single peak recorded at $T_p < T_g$ splits in two peaks for $T_p > T_g$: one due to the dipolar orientation (α-peak) at T_g, and the other generated by detrapped carriers (ρ-peak), which were previously injected from the electrodes during the polarization of the sample.

Figures 6 and 7 show TSDC measurements carried out with Li6 and K9 ionomers. Each series of measurements was obtained from a single sample, which was polarized at different polarization temperatures T_p, always under $E_p = 20$ kV/cm. Before starting the TSDC measurement, the sample was short circuited for one hour at room temperature to eliminate residual and fast polarizations. TSDC curves carried out with SPS are similar to those of PS (Fig. 5); however the magnitudes of the involved polarizations are bigger. For the K9 sample it was observed that the α-peak shifts to higher temperatures as T_p increases, its maximum being recorded at 122°C when the sample was polarized at 120°C, and at 150°C when $T_p = 200$°C. This effect indicates that
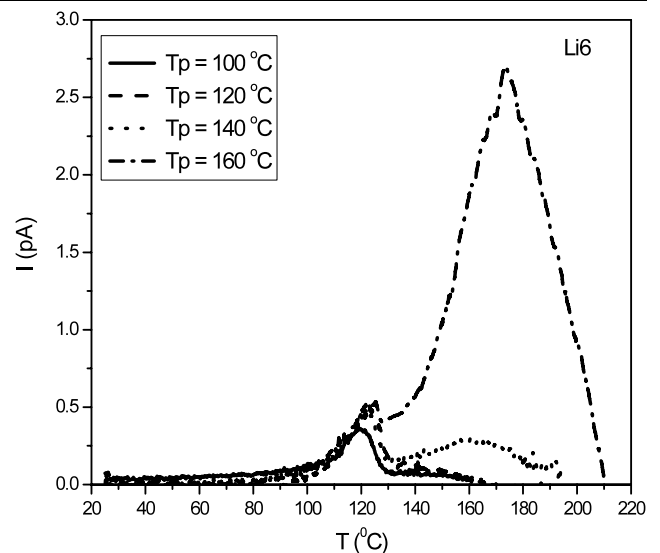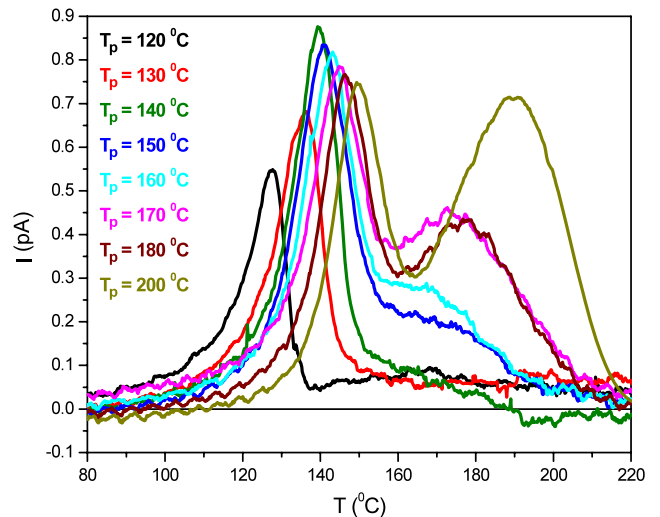

Fig. 7 TSDC curves of K9 sample: $E_p = 20$ kV/cm and $t_p = 10$ min at different polarization temperatures T_p

this shift is related to the influence of T_p on the glass transition of the ionomer. We are considering that the amount of sulfonated groups in this case has only a slight influence on the glass transition of the polystyrene, i.e. clusters of multiplets are not formed. The displacement to higher temperatures, caused by T_p, is more prominent over the ρ-peak. In addition, the ρ-peak's magnitude increases considerably with the polarization temperature, and for Li6 samples polarized at 160°C this increase was extremely high.

From the results shown in Figs. 6 and 7, we infer that the two peaks (α and ρ) are always present: α being the result of dipolar relaxation originating due to glass transition which includes the destruction of the multiplets during the
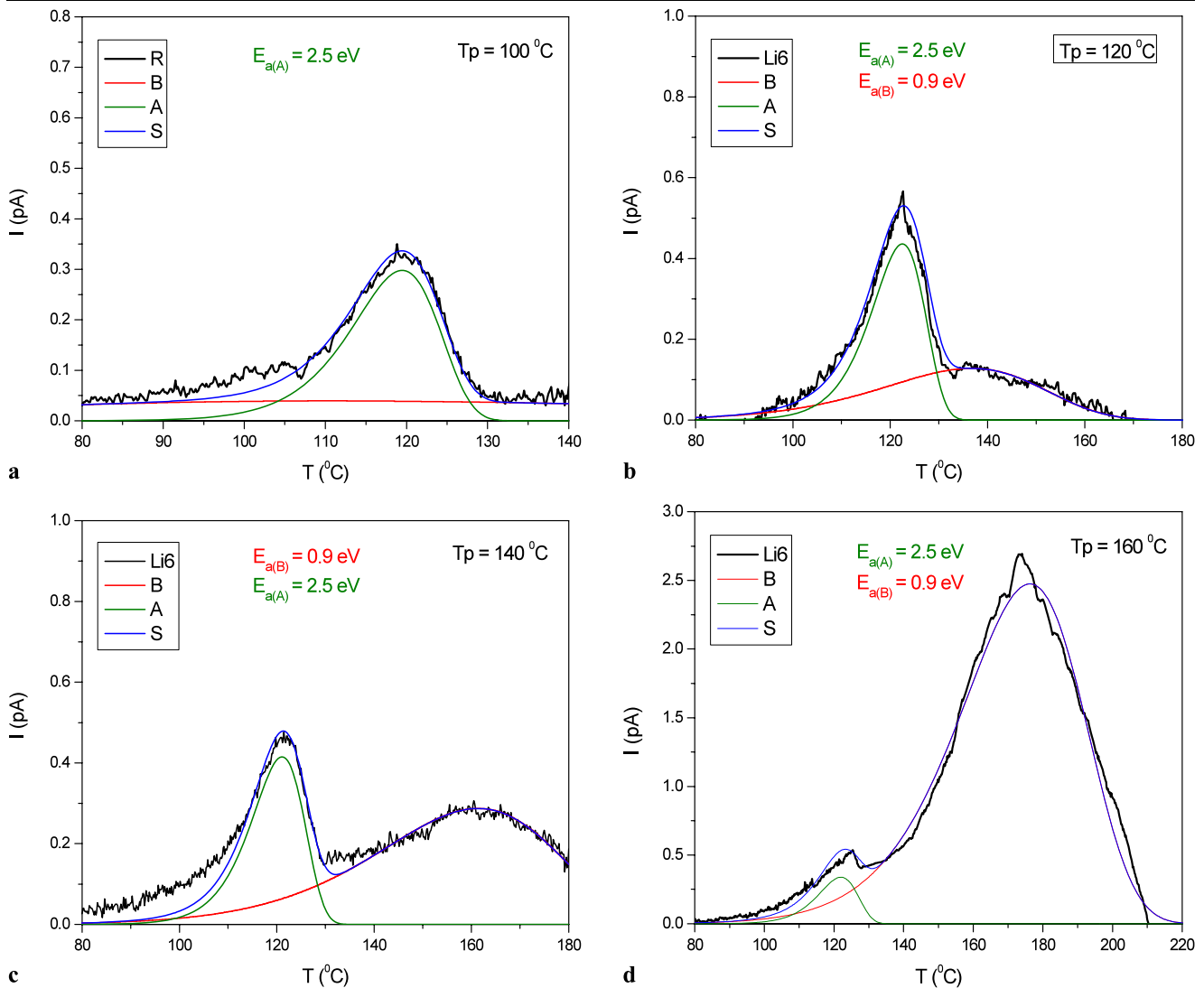
Fig. 8 Fittings of the deconvoluted TSDC thermograms obtained with a Li6 sample: (**a**) $T_p = 100°C$, (**b**) $T_p = 120°C$, (**c**) $T_p = 140°C$, and (**d**) $T_p = 160°C$

glass transition, and ρ due to the detrapping phenomenon of the carriers that were injected during the sample polarization. Carrier injection depends strongly on the temperature (Schottky effect); then the amount of injected carriers, and consequently the charges stored in traps, is bigger for higher T_p. For relatively low T_p (below 120°C for Li6 and 140°C for K9), only the α-peak is recorded. However, as T_p increases, the ρ-peak becomes more and more prominent as it displaces to higher temperatures. To fit both peaks with the kinetic equation shown in (1), we make a deconvolution of each TSDC thermogram using two Lorentzian curves, coherent with the first-order kinetic shapes. Figures 8 and 9 show fittings of the curves displayed in Figs. 6 and 7, respectively. This procedure allowed us to fit α- and ρ-peaks making use of (1). The use of a first-order kinetics is chosen because the peaks exhibit non-symmetric shapes. From the

fittings, we obtained 0.9 eV and 1.3 eV as activation energies for the ρ-peak, respectively, for Li6 and K9 samples, while, for the α-peak, the adjusted values for the activation energies were 2.5 and 2.7 eV. Such values are the same as obtained by the initial rise time, which reinforce the correctness of (1) to explain the TSDC thermograms.

5 Conclusions

TSDC measurements carried out with samples of sulfonated polystyrene ionomers previously polarized at temperatures higher than the glass transition temperature show basically two important peaks: one at a temperature close to T_g (peak α), and another in which the peak was coincident with the polarization temperature T_p (peak ρ). The amount of sul-
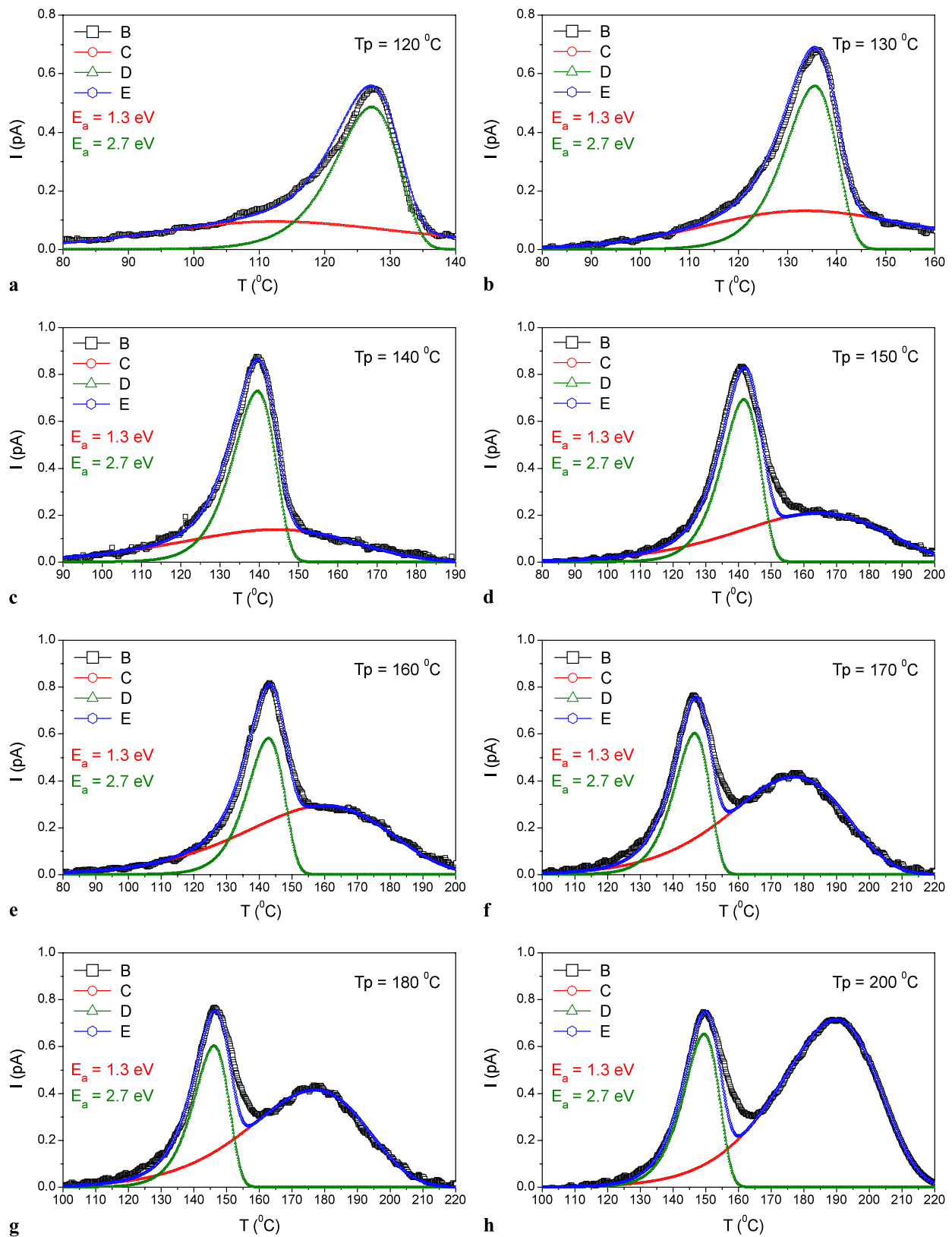
Fig. 9 Fittings of the deconvoluted TSDC thermograms obtained with a K9 sample: (**a**) $T_p = 120°C$, (**b**) $T_p = 130°C$, (**c**) $T_p = 140°C$, (**d**) $T_p = 150°C$, (**e**) $T_p = 160°C$, (**f**) $T_p = 170°C$, (**g**) $T_p = 180°C$, and (**h**) $T_p = 200°C$

fonated groups certainly generates multiplets in the ionomer structure, but it was not enough to form clusters. The existence of multiplets does not change too much the glass transition of the SPS, but a slight shift of the α-peak to higher temperature was observed following the polarization temperature. On the other hand, the position of the ρ-peak follows T_p with a reasonable accuracy, and it was identified as detrapping of injected charges from the electrodes. The amount of such thermally released charges increases with T_p, in agreement with the Schottky injection effect. When T_p is low, the amount of injected charges is relatively small, being trapped in traps at the surface of the sample. As the amount of injection increases, i.e. for higher T_p, the superficial traps are totally filled and the charges move towards the bulk of the sample, being captured by bulk traps. Considering that the superficial traps are shallower than the bulk traps, the shift of the ρ-peak is expected. The fitting of the deconvoluted peaks provided us with the activation energy for both peaks. For the ρ-peak we found 0.9 eV and 1.3 eV, respectively, for Li6 and K9, and for the α-peak 2.5 and 2.7 eV, respectively, for Li6 and K9.

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