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# Localized and long-distance charge hopping in fresh and thermally aged conductive copolymers of polypyrrole and polyaniline studied by combined TSDC and dc conductivity

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## Abstract

The charge trapping centers in fresh and thermally aged conductive polyaniline–polypyrrole copolymers (starting from pure polyaniline and ending in pure polypyrrole by steps of 10 wt%) were studied by thermally stimulated depolarization current (TSDC) spectroscopy and dc conductivity measurements. One low temperature (115–135 K) relaxation mechanism appears in polyaniline-rich copolymers and disappears after thermal anneal. It is attributed to polaron trapping in the vicinity of chlorine anion dopants. Another relaxation mechanism operates close to room temperature and is related to conformational relaxation, which corresponds to the influence of the annihilation of the conformons on the conduction mechanism. The relaxation is sensitive to thermal aging as a result of the thermal annealing on the conductivity. The temperature derivative of the dc conductivity supports the latter assertion. The activation energy values were obtained as a function of composition for both fresh and heated samples. The TSDC spectroscopy is a sensitive tool which is an alternative to the standard conductivity studies for the characterization of polypyrrole–polyaniline conductive copolymers and the study of the thermal degradation. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** A. Polymers; A. Organic compounds; D. Electrical conductivity; D. Dielectric properties

## 1. Introduction

During the last decade, dielectric studies on conductive polymers have revealed dielectric relaxation mechanisms which have been attributed to the localized motion of charge carriers. Ac-impedance measurements were performed on the polypyrrole family polymers (Fig. 1a) and revealed a dielectric loss mechanism [1–3]. These Debye-type dispersions were attributed to the motion of polaron entities between redox centers and other defect sites situated along the polymer chain [11]. Thermally stimulated current studies of polyaniline (Fig. 2) thin films have also revealed dielectric relaxation mechanisms both in undoped and doped samples [4]. In the present work, conductive

polypyrrole–polyaniline copolymers are studied via thermally stimulated depolarization current (TSDC) spectroscopy [5]. The high resolving power of the TSDC spectroscopy is used in addition to dc conductivity measurements on these copolymers in order to gain alternative insight into the effect of mixing on their dielectric properties and the thermal degradation of their conductivity.

## 2. Experimental

Freshly distilled monomers (Merck) in the proper ratio were used for the preparation of the polypyrrole–polyaniline conductive samples. The polymerization took place in the presence of FeCl<sub>3</sub> (Merck) as oxidant in HCl acid–water solutions at pH 2.00 in an ice bath (monomers/oxidant = 1:1 mol/mol) under nitrogen atmosphere. The copolymers were obtained in the form of black powders and after purification by Soxhlet extraction for 36 h, were pressed by an IR press

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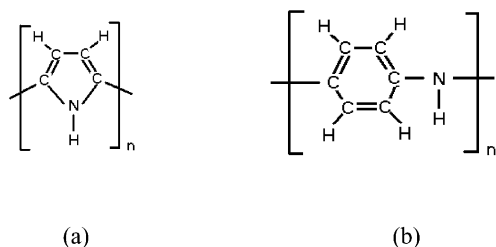


Fig. 1. The chemical formulae of (a) polypyrrole and (b) polyaniline.

in the form of disc shaped specimens 13 mm in diameter and about 1.5 mm thick. The thermal aging of the samples took place in an oven thermostated at 70 °C under room atmosphere, for time intervals ranging from 0 to 600 h.

The TSDC measurements were performed in a vacuum cryostat operating from liquid nitrogen temperature (LNT) to 420 K at a constant heating rate of 2 K/min. The vacuum was maintained at about  $10^{-1}$  Pa. The sample holder consisted of two spring-loaded platinum electrodes. Insulating (blocking) spacers could be placed optionally between the specimen and the standard metal electrodes. More details have previously been given [6]. The TSDC experiments were performed by using insulating electrodes. Teflon foils, which were dielectrically inert, separated the specimen from the standard platinum electrodes of the apparatus, thus making a MISIM (metal–insulator–sample–insulator–metal) structure [7]. The use of blocking electrodes was highly desirable because the specimens were conductive enough to experience extrinsic charge injection from the electrodes and permit the formation of trapped homocharge [8]. On the other hand, the MISIM configuration prohibits the neutralization of intrinsic charge carriers at the electrodes. Polarizing fields of strength ranging from  $10^3$  to  $10^5$  V/m were applied, but no field dependent phenomena were observed in the subsequent TSDC spectra. The field

was applied at room temperature for the time interval  $t_p = 2$  min. The samples were then cooled to LNT.

The dc conductivity vs temperature from 80 to 310 K was measured with a four-probe method in a cryostat filled with inert He gas.

### 3. Results and discussion

#### 3.1. TSDC experiments

The dielectric relaxation is commonly described through the Arrhenius law:

$$\tau(T) = \tau_0 \exp(E/kT) \quad (1)$$

where  $k$  is Boltzmann's constant,  $E$  denotes the activation energy and  $\tau_0$  is the pre-exponential factor. Eq. (1) governs either the rotation of permanent dipoles or the localized hopping between neighboring potential wells, which may be associated with the presence of defects inside the matrix [9]. The TSDC signal resulting from the rotating dipoles or short-range hopping of charge carriers is [5,8]:

$$I(T) = \frac{SP_0}{\tau_0} \exp\left[-\frac{E}{kT} - \frac{1}{b\tau_0} \int_{T_0}^T \exp\left(-\frac{E}{kT}\right) dT\right] \quad (2)$$

where  $P_0$  is the initial polarization of the dielectric,  $S$  is the surface sample area which is in contact with each of the electrodes,  $b$  is the heating rate, and  $T_0$  is the starting temperature.

##### 3.1.1. Study of the low temperature dispersion

The TSDC spectra of the virgin copolymers consist of two distinct bands with maxima within the temperature region 115–135 K (low temperature (LT) peak) and close to room temperature (high temperature (HT) peak). However, the LT dispersion disappears abruptly when the polypyrrole content is larger than 70 wt%. A typical thermogram of a virgin specimen is depicted in Fig. 2. The temperature

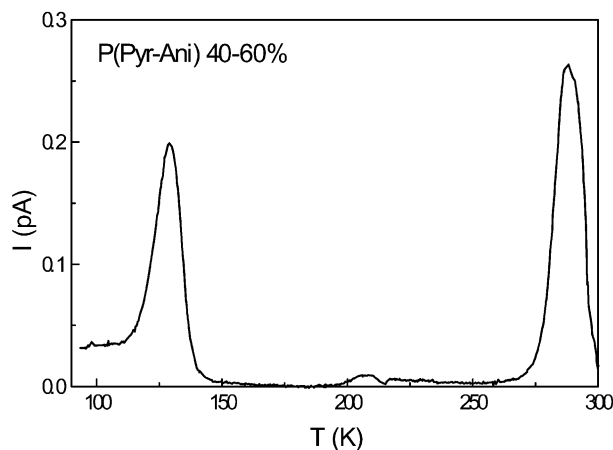


Fig. 2. A typical thermogram of a copolymer containing 60% polyaniline obtained by using blocking electrodes (MISIM structure).

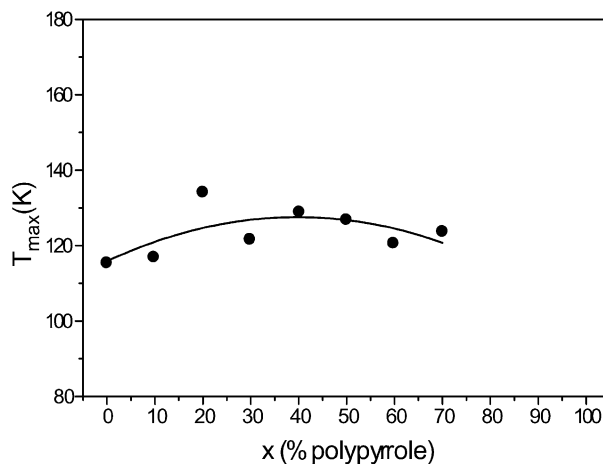


Fig. 3. The temperature  $T_{\max}$  where the LT peak (which is observed in the thermograms of the virgin samples) reaches a maximum as a function of the weight percentage of polypyrrole. Note that the peak is absent in the TSDC spectrum when  $x > 70\%$ .

$T_{\max}$ , where the LT peak reaches a maximum, is shown in Fig. 3 as a function of  $x$ , where  $x$  is the weight percentage of the polypyrrole in the copolymer. The dispersion is not detected for  $x > 70\%$ . This composition may be regarded as a percolation limit between trapping and delocalization of charge carriers. It seems that (for  $0 \leq x \leq 70\%$ )  $T_{\max}$  varies on  $x$  upon a second order polynomial law, with its maximum located at  $x = 43\%$ . A TSDC peak is produced when the thermal energy offered to the trapped charges is comparable to their activation energy, i.e.  $kT \approx E$ . Subsequently, to a first approximation, the increase of the temperature where a TSDC peak appears evidences for an increase in the activation energy. In Fig. 4, where the activation energy values are plotted as a function of composition, we see that the activation energy values range from 0.08 to 0.15 eV, but there is no clear dependence of  $E$  on  $x$ . Subsequently, the effective

potential barrier separating two adjusted trapping sites seems independent of composition. However, the maximum in the  $T_{\max}(x)$  plot (Fig. 3) may be explained as a maximum in the distance separating the neighboring trapping sites has a maximum at  $x = 43\%$ . For this composition, the time required for the localized hopping (that is represented by the relaxation time) exhibits a maximum. We note that the position of the LT peak and the activation energy value for pure polyaniline are compatible with those reported in Ref. [4] for thin films ( $T_{\max}$  is around 125 K and  $E = 0.08$  eV).

In Fig. 5, the signal amplitude  $I_{\max}$ , which is proportional to the density of the trapped carriers, is plotted as a function of composition. Recalling that the LT band is absent in the thermograms of pure polypyrrole and polypyrrole-rich composites, we conclude that polyaniline plays a significant role in the formation of the trap centers related to the LT

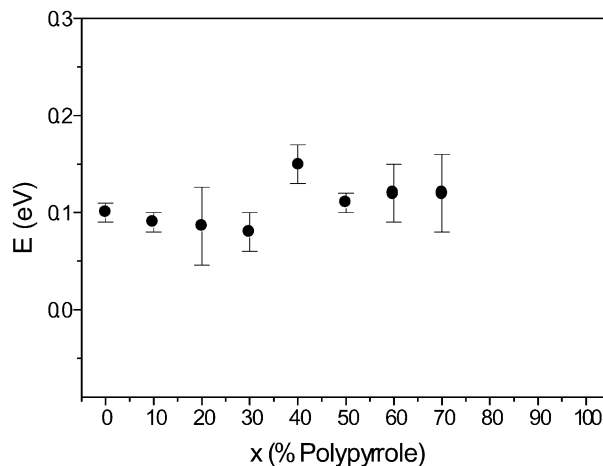


Fig. 4. The activation energy  $E$  obtained from the analysis of the LT signals of the virgin copolymers, as a function of the composition of the sample.

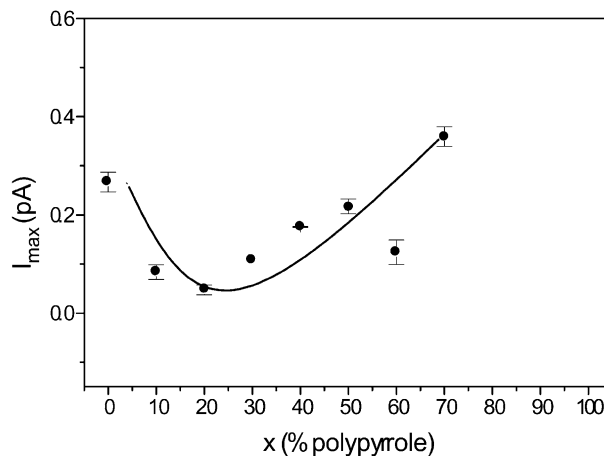


Fig. 5. The peak amplitude  $I_{\max}$ , which is proportional to the amount of trapped charges, of the LT peak as a function of the composition.

relaxation. This may be attributed to the intervention of nitrogen atoms between adjacent rings along the polyaniline chain. However, the variation of  $T_{\max}$  (and  $E$ ) with varying composition indicates that the polypyrrole phase perturbs the LT centers induced by the polyaniline phase and yields the critical value for the composition ( $x = 70\%$ ), which serves as a threshold for the trapping.

The disappearance of the LT dispersion after the thermal treatment may be attributed to the removal of dopant anions, which are introduced between the polymer chains during oxidation and protonation with hydrochloric acid. Their negative charge acts like trapping centers for positive polarons, impeding their motion. In polyaniline, heating removes  $H^+$  from the chains, which combines with  $Cl^-$  to form gaseous HCl which, leaves finally the sample. This removal of  $H^+$  is one of the causes of the thermal degradation, as it reduces the quantity of the conductive phase of the polymer,

making the conduction more difficult, although the simultaneous departure of  $Cl^-$  decreases the number of the trapping centers and enhances the carrier mobility. The simultaneous disappearance of the LT band and the departure of  $H^+$  and  $Cl^-$  (recombined to HCl gas) from the polymer indicate that the LT band can be attributed to the trapping of positively charged polarons by chlorine anions positioned between the polymer chains.

### 3.1.2. Study of the HT dispersion

In the virgin samples, the HT peak reaches its maximum close to room temperature, and shifts towards lower temperature after thermal degradation of the conductivity (Fig. 6). The only exception is observed for  $x = 20$  and 50%, where  $T_{\max}$  moves toward higher temperature after the thermal treatment. The shift is of the order of 10 K. It

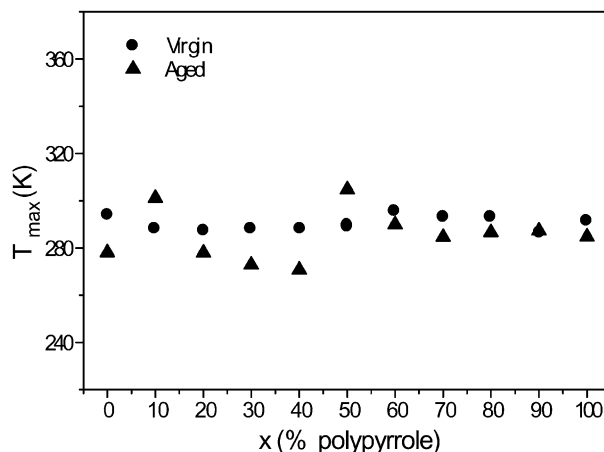


Fig. 6. The temperature  $T_{\max}$  where the HT signal has its maximum against the polypyrrole content. The circles correspond to the virgin specimens and the triangles to the thermally treated ones.

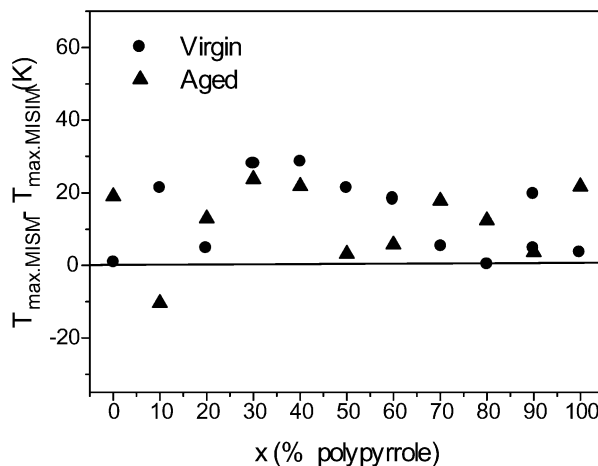


Fig. 7. The alteration of the temperature  $T_{\max}$  of the HT band when changing the nature of the electrodes. Details are given in the text.

seems that thermal aging induces structural changes, which reduce the relaxation time that governs the HT relaxation.

Combined optical and electrical conductivity studies have established the influence of conformational defects (conformons) on transport mechanisms [10]. Conformons are actually defects of the conjugation of the polymer chains that partition the polymer chain into sub-chains with shorter conjugation length. Conformational defects are created on cooling as the conformational ordering, which is a slow rate process, may not yield an ordered state on temperature reduction. The conformons will disappear when the polymeric chains are flexible enough to restore the conformational disorder; i.e. when the temperature of the sample is raised above its glass transition. The conformational order–disorder transition dependence on temperature or pressure modification yields the appearance of anomalies in the conductivity and thermopower plots against temperature or pressure. Recent investigations in polypyrrole [10–12] showed that the anomaly in the conductivity due to the disappearance of conformons on heating appears in the temperature range 250–310 K. The latter temperature range is above the glass transition  $T_g = 250$  K, where the polymer is in its rubber state and conformons are destroyed more easily [10]. The above-mentioned range 250–310 K coincides with the temperature range where the HT band appears in the TSDC spectra.

A critical question that arises is whether the HT band is related to the localized motion of charge carriers. If the HT dispersion stems from long-distance charge transport within the volume of the specimen, the assertion that the appearance of the HT band is related to the effect of conformon disappearance on the charge drift will be strengthened. The blocking strength of the electrodes was altered by constructing the MISM (metal–insulator–sample–metal) configuration, where a single insulating spacer is placed between one surface of the sample and the adjacent metal electrodes. The position of the HT peak was altered significantly (Fig. 7).

The sensitivity of the band to the nature of the interface suggests that the relaxation mechanism involves extended hopping of charge carriers along the sample thickness influenced by space and time correlations [8]. A portion of the charges can reach the metal electrode where they discharge. Thus, the HT relaxation is likely to occur due to the influence of the disorder to order transition (as conformational defects are destroyed during the heating stage of the TSDC scan) on the traveling charge entities. The TSDC spectroscopy serves as an alternative method for studying the modification of conformational defect state and can monitor the degree of protonation of the copolymers through the detection of the HT band.

The activation energy values are actually large (Fig. 8) but comparable with those reported for the space charge peaks ( $\rho$ -peaks) in polymers, and are of the same order of magnitude as the activation energy values corresponding to other type of transitions such as the glass transition ( $\alpha$ -peak) [8]. The activation energy values are significantly larger than the potential barrier separating the protonated conductive islands in the polymer matrix (e.g.  $0.064 \pm 0.003$  and  $0.087 \pm 0.003$  eV for the fresh and the annealed polypyrrole, respectively [13]) and can hardly be related to the transport mechanism involved by the HT relaxation. We speculate that the charge drift operates from a trapping site (i.e. a defect center) to a neighboring one.

The thermal degradation of the conductivity has been attributed to the decrease of the conductive grains through dedoping and thermo-oxidative modifications of the polymer backbone by oxidation/hydrolysis/chain scission and chemical crosslinking [14–16]. These processes reduce the density of polarons in the copolymers [13] and affect the flexibility of the polymer chains, which may cooperatively assist the charge transport provided that they are mobile enough. Subsequently, the relaxation time characterizing the HT dispersion is modified and the position of the HT band shifts.

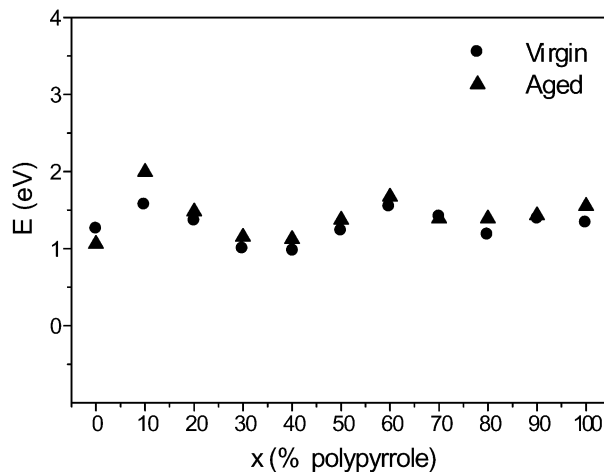


Fig. 8. The activation energy of the HT dispersion for the virgin (circles) and the aged (triangles) samples.

The transition from a disordered (conformon-rich) state to an ordered one (where conformal defects are absent) is sensitive to the density of polarons. The activation energy values are plotted in Fig. 8. In general,  $E$  is augmented after the thermal treatment and therefore the effective potential barrier increases. The variation is less than about 25%. The experimental results indicate that it is hard to distinguish between two different types of conformon creation and annihilation corresponding to each phase (i.e. polyaniline and polypyrrole). A common mode of relaxation probably describes the disorder to order transition both in polyaniline and polypyrrole chains. However, the sensitivity of the HT band to the degree of protonation indicates that the TSDC experiments are capable of monitoring the conductivity degradation through the conformational transition.

### 3.2. Dc conductivity vs temperature experiments

The dc conductivity change with the time  $t$  of the heat treatment follows for all the samples the relation

$$\sigma = \sigma_0 \exp(-(t/\tau^*)^{1/2}) \quad (3)$$

where  $\sigma_0$  is the conductivity of the unaged sample and  $\tau^*$  is a time-constant which characterizes the aging rate. This is consistent with an inhomogeneous structure of the copolymers, in which highly conducting grains are separated by insulating material [17,18]. Thermal degradation is attributed to a corrosion-like reduction of the grain size [19]. The dc conductivity is a macroscopic quantity arising from many complex microscopic processes, from the intrachain and interchain conduction to the charge carrier transfer between highly conducting grains. The exact structure of these grains and of the intermediate material, the mechanism of charge transport at each of the conductivity stages, as well as the thermal annealing mechanism have been intensively considered [14,20,21].

The question which arises now is how the processes that

give the LT and HT dispersions can affect the dc conductivity of the copolymers. In Fig. 9 we show the  $\sigma = f(T)$  curve for pure polypyrrole after a rapid (5 K/min) cooling to LNT. It appears smooth along the entire temperature range 80–310 K. However, the  $d\sigma/dT$  vs  $T$  curve, shown in Fig. 10, being much more sensitive to changes of  $\sigma$  with  $T$ , reveals two regions, in which a scattering of points is observed, one in the temperature range 100–120 K and another between 250 and 310 K, where this phenomenon is more intense.

This scattering of points in the  $d\sigma/dT$  vs  $T$  curves appear in the same temperature ranges as the TSDC signals, giving the impression that the two phenomena are correlated. However, for the LT range such an association exists only for the fresh polyaniline-rich copolymers (with polypyrrole content less than 70%). For all the other compositions before heat treatment and for all the thermally aged copolymers the scattering of points remains, although the TSDC signal, which is associated with localized carriers, disappears. This makes the origin of the LT points scattering in the  $d\sigma/dT$  vs  $T$  curves obscure. The fact that this scattering appears between 100 and 120 K and then stops until 250 K suggests that it is probably connected to internal changes of the polymer structure. Moreover, the LT TSDC peak corresponds to that portion of charge carriers, which gets trapped and does not contribute to the dc conductivity.

On the other hand, the correlation between the HT TSDC peak and the 250–310 K scattering of points of the  $d\sigma/dT$  vs  $T$  diagrams, which is much more intense than the one at LTs, can be easily understood. As we proved the HT TSDC peak is related to long-distance charge transport, facilitated by the destruction of conformons on heating, which is expected to affect intensely the dc conductivity producing the 250–310 K scattering of points in the  $d\sigma/dT$  vs  $T$  diagrams. A possible explanation for the appearance of a scattering of points instead of a steady increment of  $\sigma$  may be that the relaxation of the polymeric chains accompanying the destruction of conformons affects the carrier mobility.

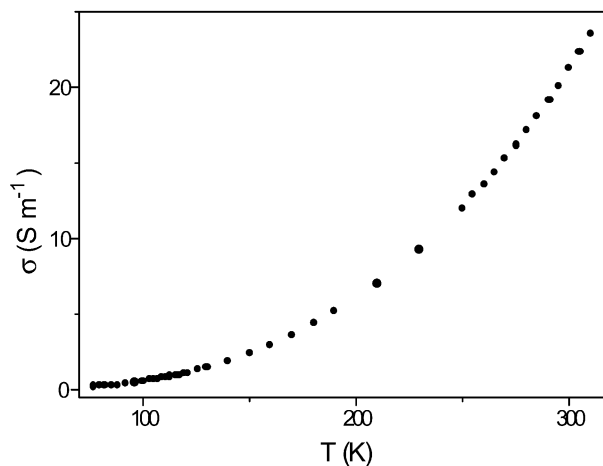


Fig. 9. The dc conductivity  $\sigma$  of a polypyrrole sample vs  $T$  after rapid cooling (5 K/min) from 300 to 80 K. The curve appears smooth for the entire temperature range.

#### 4. Conclusions

An alternative insight into the problem of thermal instability of conductive polypyrrole–polyaniline copolymers is given by using combined TSDC spectroscopy and conductivity measurements vs temperature. The results are summarized as follows:

- (i) In general, a couple of a LT and HT peaks are detected in the TSDC thermograms. The  $d\sigma/dT$  vs  $T$  curves exhibit a scattering of points in the same temperature regions.
- (ii) The LT peak is present in fresh samples with polypyrrole content equal or less than 70 wt%. This composition seems to be a threshold for trapping, above which the polypyrrole-rich phase provides percolation paths to the charge carriers. The dispersion, which disappears after the thermal treatment, corresponds to trapping centers

probably related to the presence of  $\text{Cl}^-$  between the polymer chains. The density of these centers is reduced by the recombination of  $\text{H}^+$  and  $\text{Cl}^-$  and the simultaneous removal of HCl from the copolymer during the heat treatment. On the other hand, the LT scattering of the  $d\sigma/dT$  vs  $T$  points is exhibited by all the samples before and after the heat treatment. This makes questionable its direct association with the LT TSDC peak.

(iii) The HT peak is present in all samples and shifts towards lower temperature after the thermal treatment. Its position coincides with another scattering of points in  $d\sigma/dT$  vs  $T$  diagrams. Both these phenomena are related to the conformon disorder to order transition on heating.

(iv) The HT peak exhibits typical features of space charge relaxation and reflects the influence of the conformational modification on the conductivity mechanisms.

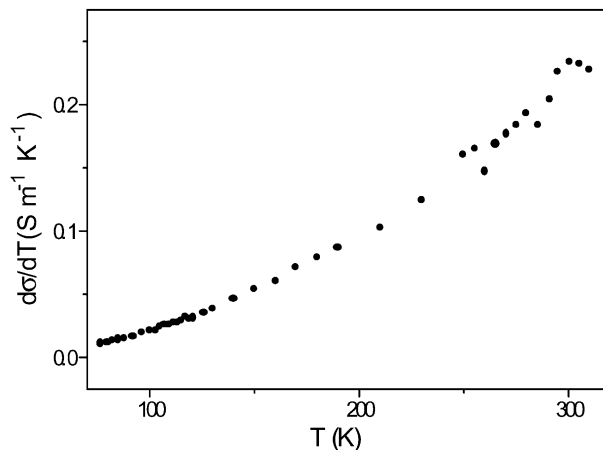


Fig. 10. The  $d\sigma/dT$  vs  $T$  curve derived from the data shown in Fig. 8. Scattering of points appears in two regions, a minor one between 100 and 120 K and a major one between 250 and 310 K, where the LT and HT peaks of the TSDC are also observed.

The TSDC spectroscopy might well be an alternative tool for the indirect investigation of the thermal degradation of the conductivity in conductive polymers. In comparison with the dc measurements, TSDC proves to be sensitive enough to monitor the thermal instability of conductive polymers.

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