

# Temperature-Induced Transitions in Doped Polyaniline: Correlation between Glass Transition, Thermochromism and Electrical Transport

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Doping (protonation) of polyaniline (PANI) in the oxidation state of emeraldine with diesters of 4-sulfophthalic acid containing flexible alkyl or alkoxy substituents leads to flexible, partially crystalline polymeric conductors which show supramolecular organization of layered-type. Diesters doped PANI exhibits two glass transition temperatures  $T_{g1}$  and  $T_{g2}$  corresponding to the freezing of the movement of the dopant substituents and of the movements of polymer-dopant anion association, respectively. A strong thermochromic effect in the UV-vis-NIR spectra is observed at sub- $T_{g1}$  temperatures indicating increasing charge carriers localization. This thermochromic effect can be correlated with the  $\sigma_{dc} = f(T)$  relationship which unequivocally shows that at low temperatures ( $T < 100$  K) the sample is in the insulating state which is another manifestation of the increasing localization of charge carriers.

## Introduction

Polyaniline (abbreviated as PANI) is one of the most extensively studied conducting polymers because of its high conductivity combined with solution processibility. In particular, free-standing films of this polymer exhibiting metallic-type conductivity can be obtained by casting. With this respect, the solution processing system consisting of PANI, ( $\pm$ )-camphor-10-sulfonic acid (CSA) as the protonating agent, and *m*-cresol (MC) as the solvent turned out to be extremely interesting.<sup>1</sup> More recently other dopants inducing PANI processibility have been developed, for example, 2-acryloamido-2-methyl-1-propanesulfonic acid<sup>2</sup> and other sulfonic acids.<sup>3</sup> We have studied a new family of PANI protonating agents, namely, diesters of 4-sulfophthalic acid, with the goal to improve mechanical properties of this polymer in the doped, i.e., conducting, state. The idea of the use of these dopants was based on the assumption that diesters of 4-sulfophthalic acid must play a double role. First, being sufficiently strong acids, they should protonate PANI rendering it conductive. Second, because they contain strongly plasticizing groups, they should lower the glass transition temperature of the polymer,  $T_g$ , and in this manner improve the flexibility of resulting films.

The use of plasticizing dopants which lower  $T_g$  of doped PANI induces several phenomena previously not observed in this polymer, among them strong thermochromic effect, never registered for PANI at subzero temperatures. Moreover, the

appearance of this effect can be correlated with  $T_g$  and the change of the sign in the slope of the conductivity vs temperature curve.

Other than PANI, conjugated polymers frequently exhibit thermochromism which in the broadest sense can be defined as a reversible change of the optical spectrum with temperature. Thermochromism is especially pronounced in substituted poly-(thiophene)s because of the temperature-induced torsions of the polymer chain.<sup>4</sup> Totally planar geometry of a conjugated polymer gives the widest energy band and the narrowest band gap which in turn leads to the least energetic  $\pi$ - $\pi^*$  transition. As shown by ab initio calculations, the energetic barrier for torsional flexibility is in the case of conjugated polymers of the order of 3.0–6.0 kcal mol<sup>-1</sup><sup>5</sup> which of course is sufficiently low to observe temperature-induced conformational changes. Any deviation from planar geometry will result in a gap widening, shorter conjugation lengths, and a hypsochromic shift of the band corresponding to the  $\pi$ - $\pi^*$  transition.

Thermochromism, although much less pronounced, is also observed in NMP solutions of three principal forms of neutral (i.e., insulating) polyaniline, namely, leucoemeraldine, emeraldine, and pernigraniline<sup>6</sup> as well as in films plasticized with NMP.<sup>7</sup> Thermochromism has also been reported for optically active doped polyaniline, i.e., PANI protonated with (+)-camphor-10-sulfonic acid; however, the effect was observed at a relatively elevated temperature of 413 K at which slow decomposition of doped PANI takes place.<sup>8</sup>

Because spectral changes in polyconjugated systems are caused by changes in the polymer chain conformation, the latter

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can be not only thermally induced but also caused by interactions with solvents. Therefore thermochromic polymers frequently exhibit solvatochromism. An interesting phenomenon of solvent-induced conformational changes in protonated PANI was reported by Xia et al.<sup>9</sup> These authors studied UV–vis–NIR spectra of PANI(CSA)<sub>0.5</sub>, the system initially discovered by Cao et al.<sup>1</sup> It turned out that the spectra are strongly solvent-dependent showing features characteristic of charge carriers delocalization in solvents strongly interacting with CSA doped PANI such as phenols. In noninteracting solvents (chlorobenzene, toluene, chloroform, etc.), different UV–vis–NIR spectra were recorded, characteristic of localized charge carriers. The authors correlated the shape of the spectrum with the crystallinity index of the films after casting and their conductivity.

Inspired by the above-described research, we asked the question whether it is possible to find a correlation between conformational changes manifested by thermochromic behavior of protonated polyaniline, its glass transition temperature,  $T_g$ , and its electrical transport properties. PANI doped with our new, low- $T_g$ , dopants is almost ideally suited for this type of investigation because in this case segmental movements inducing conformational changes may occur at low temperatures, well below the onset of polymer decomposition, ensuring in this manner the reversibility of the processes studied.

## Experimental Section

**Preparation of Doped-Polymer Films.** 1,2-Di(alkyl) or 1,2-di(alkoxy) esters of 4-sulfophthalic acid, the dopants used for PANI protonation, were synthesized from 4-sulfophthalic acid and the corresponding alcohols. The exact preparation and purification procedure can be found elsewhere.<sup>10,11</sup> They were identified by <sup>1</sup>H NMR, FTIR, mass spectroscopies, and elemental analysis. The following diesters of 4-sulfophthalic acid were tested as PANI dopants:

1,2-(Di-*n*-pentyl) ester of 4-sulfophthalic acid abbreviated as (DPEPSA), 1,2-(di-*n*-octyl) ester of 4-sulfophthalic acid abbreviated as (DOEPSA), 1,2-(di-*n*-dodecyl) ester of 4-sulfophthalic acid abbreviated as (DDOEPSA), 1,2-(di-2-ethylhexyl) ester of 4-sulfophthalic acid abbreviated as (DEHEPSA), 1,2-(di-2-(butoxyethyl)) ester of 4-sulfophthalic acid abbreviated as (DBEEPSA), 1,2-(di-2-(2-butoxyethoxy)ethyl) ester of 4-sulfophthalic acid abbreviated as (DBEEEPSA).

Polyaniline (abbreviated as PANI) was synthesized at −27 °C in HCl/LiCl water/ethanol solution using (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as the oxidizing agent. The obtained polyaniline hydrochloride salt was then converted to the base form by treatment with an excess of 0.3 M NH<sub>3</sub> (aq) solution. The inherent viscosity of the obtained polymer was measured at 25 °C for a 0.1 wt % solution in 96 wt % H<sub>2</sub>SO<sub>4</sub> using an automatic Ubbelohde viscosimeter. The obtained value was 2.25 dL g<sup>−1</sup>. The detailed polymerization procedure can be found elsewhere.<sup>12</sup>

PANI was protonated with the diesters in 2,2′-dichloroacetic acid (abbreviated as DCAA) solution. The concentration of the solution with respect to the PANI base was 0.5 wt %, and the ratio of the dopant molecule to PANI repeat unit was 0.5 in order to give PANI(DEPSA)<sub>0.5</sub> stoichiometry (where DEPSA denotes diester of 4-sulfophthalic acid). This stoichiometry ensures full protonation of imine nitrogens and the formation of a so-called “polaron lattice” in the fully doped polymer. The solutions were magnetically stirred typically for 3–4 weeks until no evolution in their UV–vis–NIR spectrum was observed.

Free-standing films of PANI protonated with diesters of 4-sulfophthalic acid for conductivity and structural studies were cast on the polypropylene substrate at 45 °C under argon flow.

Elemental analysis was routinely carried out for free-standing films (thickness of ca. 20–30 μm) showing the content of ca. 2–3 wt % of the residual solvent (DCAA) even after extending pumping (see discussions in refs 10 and 11). Much thinner films on a glass substrate were prepared in the same manner for UV–vis–NIR studies.

**Characterization Techniques.** Differential scanning calorimetry (DSC) studies were carried out in a constant dry nitrogen flow on a TA Instrument model DSC 2010 analyzer with the rate of heating/cooling of 20 °C min<sup>−1</sup>. Typically, two runs were performed with the following temperature sequence: RT → 143 K → 423 K → 143 K → 473 K. Typical mass of the sample was ca. 15 mg.

Solid-state UV–vis–NIR spectra of PANI protonated with diesters of 4-sulfophthalic acid were recorded on a Perkin-Elmer λ900 spectrometer equipped with a cryostat operating in the temperature range of 77–523 K. Spectra were recorded in the range of 303–170 K both in the decreasing as well as in the increasing temperature mode. In no case was a hysteresis effect observed.

The temperature dependence of dc-conductivity was determined by a four-probe technique.<sup>13,14</sup> To ensure good electrical contacts, four gold lines were evaporated through a mask to which 25 μm golden wires were attached by pressing. The temperature of the sample during the measurement was checked with a rhodium–iron resistance thermometer which was placed in the proximity of the sample. The current was applied by a Keithley model 220 current source, and the voltage was measured independently by two Keithley model 6512 electrometers with an input resistance of 2 × 10<sup>14</sup> ohms. The probe was placed into a continuous flow helium cryostat and pumped for 14 h before the measurement.

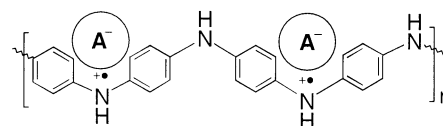
Wide-angle X-ray diffraction (WAXD) studies were carried out in reflection geometry (Bragg–Brentano) using Cu Kα<sub>1</sub> radiation (1.5406 Å). The scan step was 0.06° (in 2θ) with the counting time of 15 s/step. The diffractometer was equipped with an 800 channels linear detector with a step of 0.02°. The crystallinity index was calculated from the ratio of the integrated intensity of the reflections corresponding to the crystalline phase over the total integrated intensity.

Small-angle X-ray scattering (SAXS) studies were performed at ESRF Grenoble on Beam Line D2AM using a monochromatic beam of 15 keV energy (wavelength of 1.2 Å). A two-dimensional detector was located 0.6 m from the sample position. The separation between two channels was 4.5 μm.

## Results and Discussion

PANI(DEPSA)<sub>0.5</sub> can be schematically depicted as follows, assuming that polaron lattice is formed upon the protonation (Chart 1):

CHART 1



Polymers doped either electrochemically or chemically with anions containing long alkyl or alkoxy substituents have the tendency to form lamellar or more generally layered-type structures. The lamellar-type of structural organization was observed for example in poly(pyrrole) doped electrochemically with *n*-alkyl sulfates.<sup>15</sup> It was also found in polymers containing basic centers in their backbone such as polyaniline,<sup>16</sup> poly-

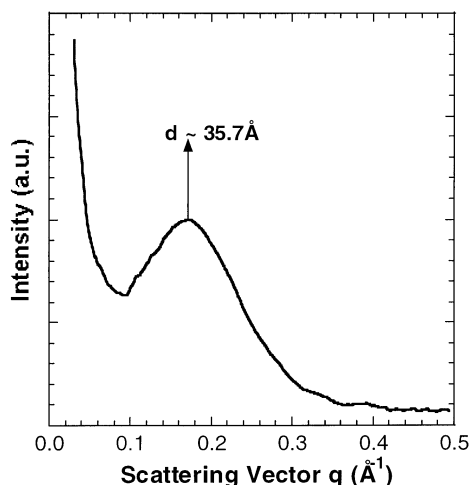


Figure 1. SAXS profile of PANI(DBEPPSA)<sub>0.5</sub>.

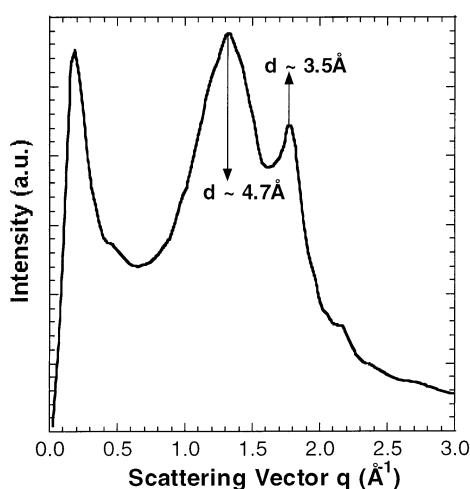


Figure 2. WAXD pattern of PANI(DBEPPSA)<sub>0.5</sub>.

(ethyleneimine),<sup>17</sup> and poly(vinylpyridine)<sup>18</sup> which were doped via protonation with anions of *n*-dodecylbenzenesulfonic acid as well as in doped-PANI gels containing surfactant-type dopants.<sup>19–21</sup>

Layered-type structure can also be postulated for PANI-(DEPSA)<sub>0.5</sub>. Figures 1 and 2 show SAXS and WAXD profiles

of free-standing films of PANI(DBEPPSA)<sub>0.5</sub> whose diffraction patterns are typical of this group of PANI-based conductors. The SAXS profile was fitted with the sum of two exponential functions and a Gaussian one in order to determine accurately the position of the peak found at a scattering vector ( $q$ ) value of  $0.176 \text{ Å}^{-1}$  which corresponds to a  $d$  spacing of  $35.7 \text{ Å}$ . This feature can be regarded as a Bragg peak of a layered structure and can be attributed to chain-dopant-chain repeat distance. In our previous paper,<sup>11</sup> we have demonstrated that the position of the SAXS reflections can be correlated with the length of the alkyl group for a series of PANI samples doped with diesters of 4-sulfophthalic acid containing *n*-alkyl substituents with increasing length. To the contrary, the positions of the two maxima observed in WAXD, a relatively narrow one at  $q = 1.8 \text{ Å}^{-1}$  and a broader one at  $q = 1.4 \text{ Å}^{-1}$ , corresponding to  $d = 3.5$  and  $4.7 \text{ Å}$  respectively, are dopant-independent. The first  $d$  spacing is characteristic of the van der Waals distances between stacks of phenylene rings, and the second one corresponds to the distance between the aliphatic chains of the substituents. On the basis of these data, we are tempted to postulate for PANI(DEPSA)<sub>0.5</sub> a layered-type structure which is schematically depicted in Figure 3. It should be noted that the absence of higher order reflections along the  $b$  direction of Figure 3 may indicate the existence of high degree of positional disorder along the dopant molecules.

One should underline here the close resemblance of the layered structure of the DEPSA doped-PANI structure to the structure characteristic of neutral poly(3-alkylthiophene)s which are strongly thermochromic.<sup>4</sup> Poly(3-alkylthiophene)s frequently reveal lamellar ordering, and for long alkyl substituents, the crystallization of side-chains takes place.<sup>22,23</sup> The main difference between neutral poly(3-alkylthiophene)s and PANI doped with diesters of 4-sulfophthalic acid consists of the fact that in the former case the side-groups are covalently bonded to the main chain, whereas in the latter one, they are introduced via protonation reaction as an inherent part of the dopant anion.

PANI doped with DEPSA are, in reality, only partially crystalline materials showing, for example, the crystalline index of ca. 30% in the case of PANI(DBEPPSA)<sub>0.5</sub>. These doped-PANI films are therefore heterogeneous materials in which better ordered crystalline domains coexist with less ordered amorphous ones. In such partially crystalline polymers, the value of the glass transition temperature,  $T_g$ , is of crucial importance and

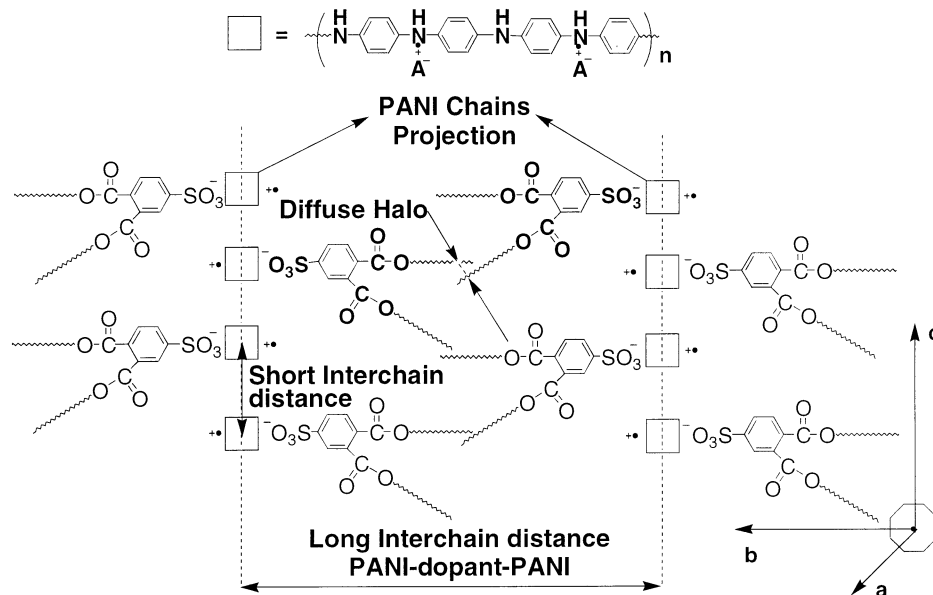
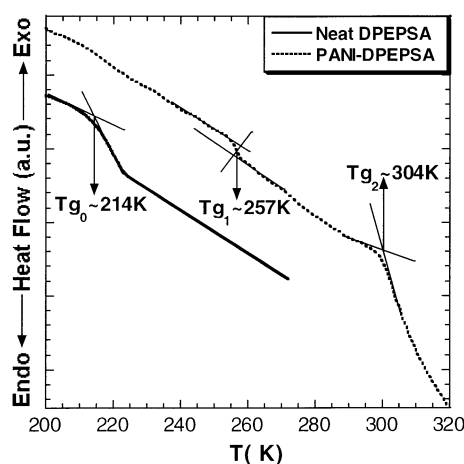


Figure 3. Model of layered-type structure in PANI(DEPSA)<sub>0.5</sub> conductors.

**TABLE 1: Glass Transition Temperatures for Neat Diesters of 4-Sulfophthalic Acid ( $T_{g0}$ ) vs DEPSA Protonated PANI Films ( $T_{g1}$  and  $T_{g2}$ ) and Elongation at Break for Doped-PANI Films**

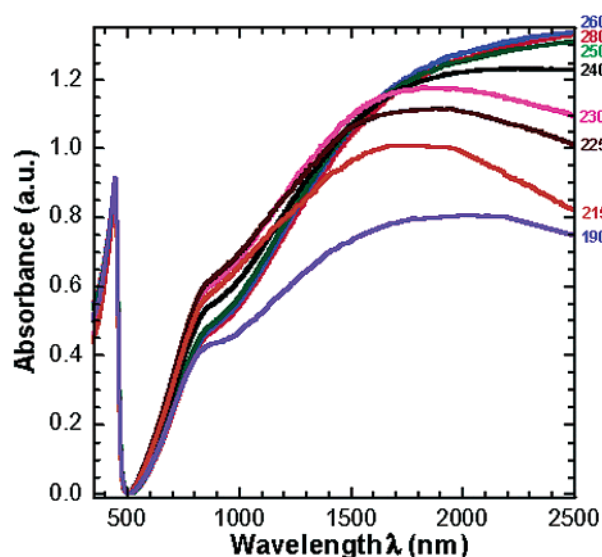
neat diester of 4-sulfophthalic acid	$T_{g0}^a$ (K)	DEPSA and CSA protonated PANI films	$T_{g1}^a$ (K)	$T_{g2}^a$ (K)	elongation at break <sup>b</sup> $\Delta l/l_0$ (%)
DPEPSA	214 $\pm$ 10	PANI(DPEPSA) <sub>0.5</sub>	257 $\pm$ 10	304 $\pm$ 10	17
DEHEPSA	202 $\pm$ 10	PANI(DEHEPSA) <sub>0.5</sub>	c	283 $\pm$ 10	26
DOEPSA	199 $\pm$ 10	PANI(DOEPSA) <sub>0.5</sub>	c	299 $\pm$ 10	39
DDOEPSA	204 $\pm$ 10	PANI(DDOEPSA) <sub>0.5</sub>	243 $\pm$ 10	c	78
DBEEPSA	236 $\pm$ 10	PANI(DBEEPSA) <sub>0.5</sub>	d	301 $\pm$ 10	29
DBEEEPSA	218 $\pm$ 10	PANI(DBEEEPSA) <sub>0.5</sub>	231 $\pm$ 10	281 $\pm$ 10	72
		PANI(CSA) <sub>0.5</sub>		403–423 <sup>e</sup>	4

<sup>a</sup> Determined on the second heating scan. <sup>b</sup> At RT. <sup>c</sup> Too small changes in the slope to be accurately detected. <sup>d</sup>  $T_{g1} = 260 \pm 10$  K on the first heating scan but vanishes on the second run. <sup>e</sup> Data from ref 28–30.

**Figure 4.** DSC thermograms (second heating scan) of the neat diester DPEPSA and of PANI(DPEPSA)<sub>0.5</sub> recorded at a scan rate of 20 °C min<sup>-1</sup>.

influences several physical properties. Because DSC is the most convenient method for the determination of  $T_g$ , we have undertaken such studies for PANI doped with plasticizing esters. A representative DSC thermogram of diester doped PANI, i.e., PANI(DPEPSA)<sub>0.5</sub>, together with the DSC thermogram of the corresponding neat diester (DPEPSA) is presented in Figure 4. The DSC curves of other systems are very similar. All DSC results are summarized in Table 1. In the majority of cases, we observe two glass transitions, at lower temperatures ( $T_{g1}$ ) and at higher temperatures ( $T_{g2}$ ). The observation of two transitions at two distinctly different temperatures is not unexpected because doped PANI is a complex system in which different types of segmental movements can occur either in flexible substituents present in the dopant anion or in the polymer chain. We are tempted to attribute  $T_{g1}$  to the freezing of the movements of the dopant branches. In general, neat diesters of phthalic acid show lower  $T_g$ , typically in the temperature range from 170 to 190 K,<sup>24</sup> whereas neat diesters of 4-sulfophthalic acid tested in our study show  $T_g$  between 199 and 236 K ( $T_{g0}$  in Table 1). An increase in the value of  $T_g$  observed in the diesters doped PANI with respect to the  $T_g$  of neat diesters is caused by the fact that the dopant anion is inserted into the polymer matrix and interacts with the chain via  $SO_3^-$  group. This of course makes the movements of the substituents more difficult.  $T_{g2}$  is associated with the polymer-dopant association because above this temperature doped PANI can be mechanically stretched and shows stress-strain curves typical of plasticized polymers. Typical  $\Delta l/l_0$  values (elongation at break) for films of diesters doped PANI studied in this research are listed in Table 1.

Surprisingly, we have found that in the case of PANI doped with plasticizing dopants the strongest thermochromic effect is observed below  $T_{g0}$ . In Figure 5, UV-vis-NIR spectra of PANI-

**Figure 5.** UV-vis-NIR spectra of PANI(DBEEPSA)<sub>0.5</sub> registered for the temperature range of 303–170 K.

(DBEEPSA)<sub>0.5</sub> registered at the temperature zone covering all transitions ( $T_{g0}$ ,  $T_{g1}$ , and  $T_{g2}$ ) are presented. First, we observe that above  $T_{g0}$  thermally induced spectral changes are minimal. To the contrary, below this temperature, the changes are very pronounced. At 280 K, DBEEPSA doped PANI shows one sharp peak at 440 nm and an extremely broad absorption tail extending toward NIR. This last spectral feature is usually regarded as the manifestation of charge carriers delocalization in metallic-like PANI.<sup>9</sup> One can also notice, in the vicinity of 800 nm, a localized absorption peak of small intensity superimposed on the tail of monotonically increasing absorbance. This peak is indicative of localized charge carriers also present in the system in a small quantity. Spectral changes, clearly observed at  $T < 240$  K, consist of the narrowing of the NIR absorption tail which is indicative of increasing charge localization with decreasing temperature. The same behavior is registered for PANI-(DEHEPSA)<sub>0.5</sub> although the onset of the thermochromism is shifted to  $T < 208$  K (see Figure 6) consistent with its lower value of  $T_{g0}$  of ca. 202 K.

The temperatures of the onset of the thermochromism coincide not only with  $T_{g0}$  but also with a dynamical transition clearly observed in the incoherent quasielastic neutron scattering (IQNS) studies of PANI doped with DEPSA.<sup>25,26</sup> The analysis of the temperature dependence of the IQNS profiles unequivocally shows that below  $T_{g0}$  both polymer chains and dopant anions behave like rigid objects whose dynamics is out of the investigated time scale. Above  $T_{g0}$  the polymer chains still remain rigid, but the dopant anions undergo diffusive motion which is manifested by the broadening of the scattering function. Very close values of  $T_{g0}$  and of the temperature of the dynamical



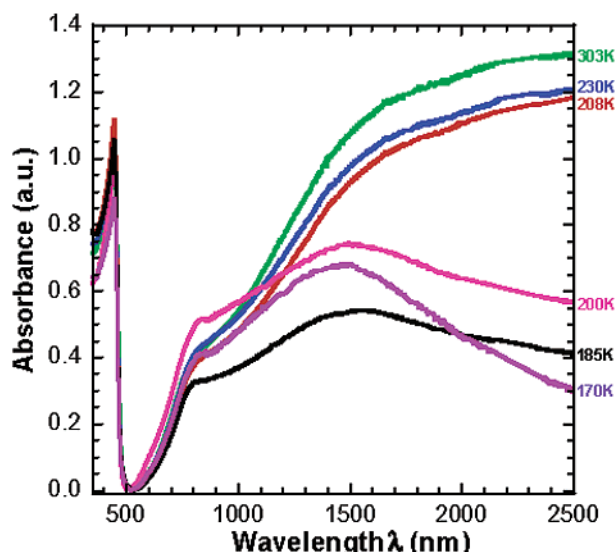
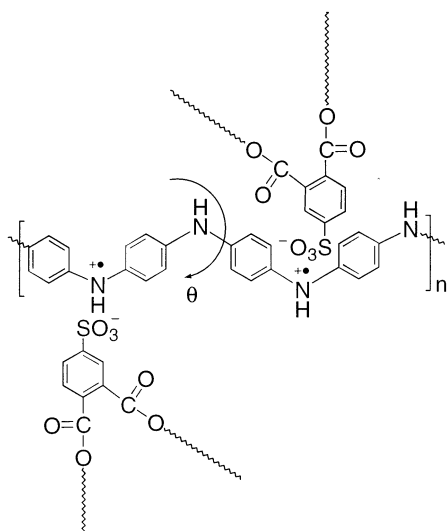


Figure 6. UV-vis-NIR spectra of PANI(DEHEPSA)<sub>0.5</sub> registered for the temperature range of 280–190 K.

#### SCHEME 1



transition detected by IQNS seem to indicate that the activation energy for the motion in the glass of neat DEPSA and in DEPSA forming a layer between two layers of PANI chains must be similar.

As it has already been stated, the different shape of the UV-vis-NIR spectrum registered for the polymer containing frozen (rigid) dopants as compared to that containing the mobile ones reflects different chain conformations in both cases. Charge carriers (polaron) localization observed for the frozen dopants implies shorter conjugation length. In the poly(semiquinone radical) structure (polaron lattice) of doped-PANI chain, the extent of the conjugation depends on the value of the torsional angle between the phenylene ring and the plane of the PANI chain zigzag (angle  $\theta$  in Scheme 1). We believe that the freezing of the dopant leads to an increase of the average value of this angle through a modulation of the ionic interactions between  $-\text{SO}_3^-$  and the  $-(\text{NH})^+$ -doping site of the PANI chain.

The onset of the dopant mobility significantly alters the dopant-chain interactions leading to more planar chain conformations which favor the conjugation and facilitate charge carriers delocalization. To our knowledge, this dopant motion induced delocalization of charge carriers observed in our low- $T_g$  polyaniline has not been observed for other types of doped

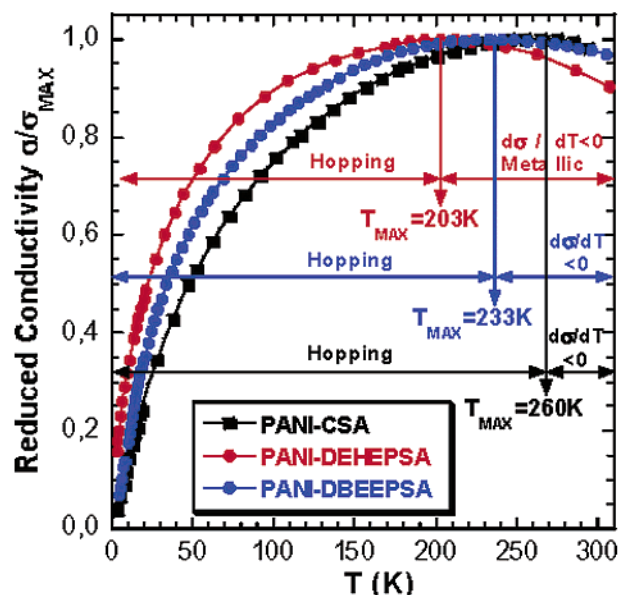


Figure 7. Conductivity vs temperature for the films of PANI-(DBEEPSA)<sub>0.5</sub>, PANI(DEHEPSA)<sub>0.5</sub>, and PANI(CSA)<sub>0.5</sub>.

PANI, and it constitutes another example of the role of the inserted dopants nature in the engineering of the properties of the doped-polymer.

It should be stressed that in the proposed model our thermochromic, low- $T_g$ , doped polyaniline can be formally considered as a comb-like supramolecular polymer in which the pending groups (dopants) are ionically bonded to the main PANI chain via protonation. Such a picture implies a strong resemblance to thermochromic poly(3-alkylthiophene)s<sup>4</sup> which can be also regarded as a comb-like supramolecular polymer of a stiff-conjugated main chain and covalently bonded flexible aliphatic groups.

In any comparative discussion involving UV-vis-NIR, IQNS, and DSC, one must be aware of the fact that the former two methods probe both the crystalline and amorphous parts of the polymer, whereas the latter one, in the temperature range investigated, detects only the transitions in the amorphous part. For this reason, strongly correlated changes in UV-vis-NIR and IQNS profiles are not reflected in the DSC curves of doped PANI. In fact, they occur at sub- $T_{g1}$  temperatures. These findings underline again the strongly heterogeneous nature of the doped PANI.

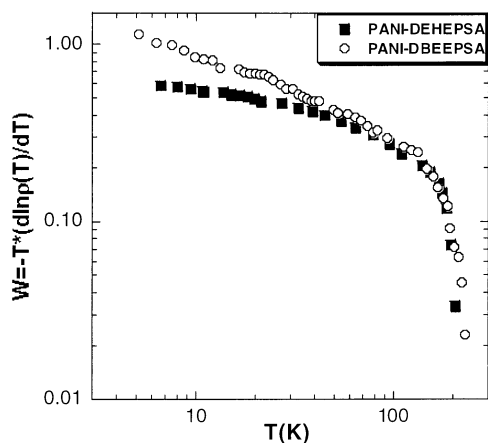
The changes in UV-vis-NIR and IQNS profiles can however be correlated with the temperature dependence of the macroscopic dc-conductivity of the doped-polymer (compare Figures 5–7). The sign of  $d\sigma/dT$  in the  $\sigma_{dc} = f(T)$  curve changes from negative to positive at the temperature of abrupt modifications in UV-vis-NIR spectra and IQNS profiles. This correlation is not unexpected because macroscopic conductivity must embrace contributions from both amorphous and crystalline parts of the polymer similarly as UV-vis-NIR and IQNS.

Increasing charge localization observed in the UV-vis-NIR spectra with decreasing temperature implies that at low temperatures previously metallic sample reaches insulating regime.

For the analysis of this problem, it is convenient to use the approach proposed by Heeger and co-workers.<sup>27</sup> If the so-called reduced activation energy is defined as the logarithmic derivative of  $\rho(T)$  as shown by equation 1<sup>28</sup>

$$W = -T^*(d \ln \rho(T)/dT) = d \ln \rho(T)/d \ln T \quad (1)$$

then three regimes for the temperature dependence of  $W$  are



**Figure 8.** Log-log plot of reduced activation energy  $W(T)$  vs temperature for PANI(DBEEPSA)<sub>0.5</sub> and PANI(DEHEPSA)<sub>0.5</sub>.

expected at  $T < 100$  K: in the insulating regime,  $W$  has a negative temperature coefficient, in the critical one,  $W$  is temperature independent, and finally, in the metallic regime,  $W$  has a positive temperature coefficient.

In heterogeneously disordered systems, the temperature dependence of the conductivity for the samples being in the metallic regime can be described by eq 2:<sup>29</sup>

$$\sigma_{dc}^{-1} = f_c \rho_m^* \exp(-T_m/T) + f_n \rho_t^* \exp(T_l/T + T_s) \quad (2)$$

where the first term describes the resistance in a quasi-one-dimensional metal and the second term originates from Sheng model of fluctuations-induced tunneling between metallic regions,<sup>30</sup>  $f_c$  and  $f_n$  are constants depending on the morphology of the system,  $T_m$  corresponds to the energy of phonons which backscatter the charge carriers, and  $(T_l, T_s)$  are the so-called tunneling parameters.

For samples being in the insulating regime, the second term of eq 2 is replaced by the term describing hopping-type conductivity in disordered semiconductors:

$$\sigma_{dc}^{-1} = f_c \rho_m^* \exp(-T_m/T) + f_n \rho_t^* \exp(T_0/T)^\gamma \quad (3)$$

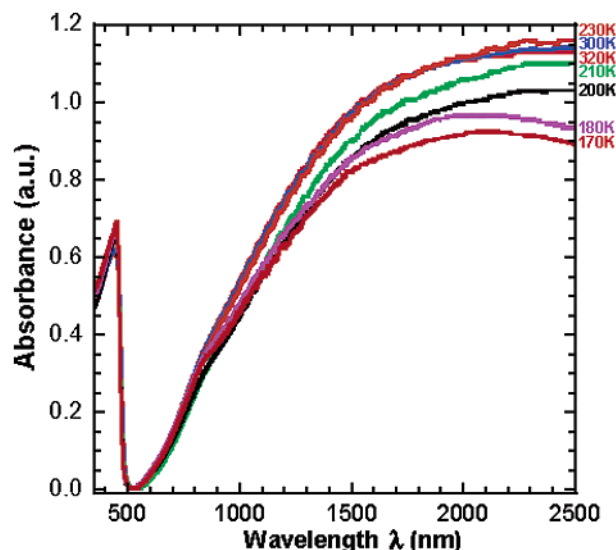
At low temperatures, the resistivity due to the hopping mechanism dominates, and the  $\gamma$  coefficient can be calculated from the low-temperature limit of  $\log W(T) = \text{constant} - \gamma \log T$  relationship.

As seen from Figure 8 for both PANI(DEHEPSA)<sub>0.5</sub> and PANI(DBEEPSA)<sub>0.5</sub>, the slope is negative. Linear regression for  $T < 100$  K leads to  $\gamma$  equal to 0.23 and 0.45 for PANI-(DEHEPSA)<sub>0.5</sub> and PANI(DBEEPSA)<sub>0.5</sub>, respectively. The first value is close to 0.25 expected for Mott's variable range hopping, whereas the second one close to 0.50 represents rather 1D hopping. Anyhow, the conductivity vs temperature data unequivocally show that at low  $T$  both samples of doped PANI are in the insulating regime.

At the end it, should be noted that the low temperature thermochromism described in this research is quite unique and requires the preparation of doped PANI with low  $T_g$ . In the same temperature range, PANI(CSA)<sub>0.5</sub> which exhibits  $T_g \sim 403$ – $423$  K<sup>31–33</sup> shows only minimal changes in their UV-vis-NIR spectra (see Figure 9).

## Conclusions

To summarize, using doped PANI of low glass transition temperature,  $T_g$ , we have demonstrated new, never reported



**Figure 9.** UV-vis-NIR spectra of PANI(CSA)<sub>0.5</sub> registered for the temperature range of 320–170 K.

previously for PANI-based conductors, phenomenon of low-temperature thermochromism occurring at sub- $T_g$  temperatures. The onset of this thermochromism can be correlated with a dynamical transition observed in IQNS experiments and with the maximum of the dc-conductivity vs temperature curve.

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