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Disorder Effects in "Plastic" and Highly Conducting Compounds of Poly(aniline)

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Summary: Numerical methods of molecular dynamics have been combined to measurements of X-ray and neutron scattering in order to obtain a realistic view of structural and dynamical disorder properties of conducting compounds of so called "plastdoped" poly(aniline)s. This combination allowed us to propose for the whole family of these compounds one generic model of a layered structure in which exist statistical fluctuations of the electronic density along the stacking direction of alternating molecular layers. The most part of the dynamics in the 10^{-13}–10^{-9} s time range concerns the motions of protons borne by the flexible tails of doping counter-ions contained in the structure. We found that the molecular dynamics is characterized by both broad time and spatial distributions. These experimental facts coupled to those obtained with electrical conductivity measurements indicate that the high mobility of the counter-ion sublattice seems to be a prerequisite to promote a global metal like electronic behaviour of the polymer films.

Keywords: conducting polymers; molecular dynamics; poly(aniline); structure

Introduction

It is commonly recognized that the transport properties of conducting polymers are highly influenced by both structural and dynamical disorders. In other words, the electron-phonon coupling plays a prominent role in these systems. The balance between the electron-phonon processes, those which promote the conductivity and those which penalize it, is delicate since they are all occurring in the same energy range at temperatures typically comprised between 200 and 320 K [1]. For these reasons, it is of fundamental importance to be able to obtain the most detailed picture of the structure and the molecular dynamics of such systems. In this contribution, we are giving a short description of the structural and dynamical properties of conducting compounds of poly(aniline) (PANI) protonated (or doped) by di-esters of sulfophthalic acid and diesters of sulfosuccinic acid whose chemical formulae are shown in the Figure 1.

Structural Properties of "Plastdoped" PANI [5,6]

These systems are organized as successive layers of stacked PANI chains alternating with bi-layers of doping counter-ions. The structural disorder has been taken into account by considering statistical fluctuations of the electronic density along the stacking direction by writing it as a sum of four Gaussian distributions (equation (1) and Figure 2)

$$\begin{aligned}\rho(z) &= \rho_H\left(\exp-\frac{(z-z_H)^2}{2\sigma_H^2}+\exp-\frac{(z-z_H)^2}{2\sigma_H^2}\right)\\ &\quad+\rho_T\left(\exp-\frac{(z-z_T)^2}{2\sigma_T^2}+\exp-\frac{(z-z_T)^2}{2\sigma_T^2}\right)\end{aligned} \qquad (1)$$

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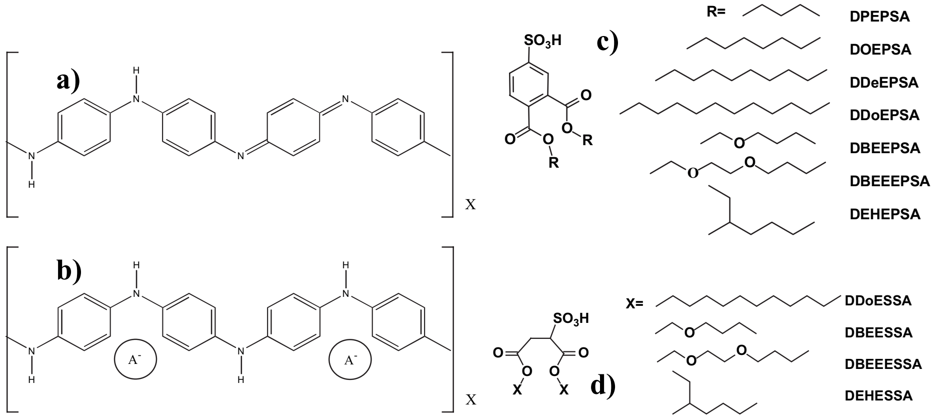

Figure 1.

a) Emeraldine base form of PANI (insulating), b) Emeraldine salt form of PANI (conducting). "Plasdopants": c) diesters of sulfophthalic acid and d) diesters of sulfosuccinic acids. The synthesis and characterization of all these compounds are described in details in the references [2,3] and [4].

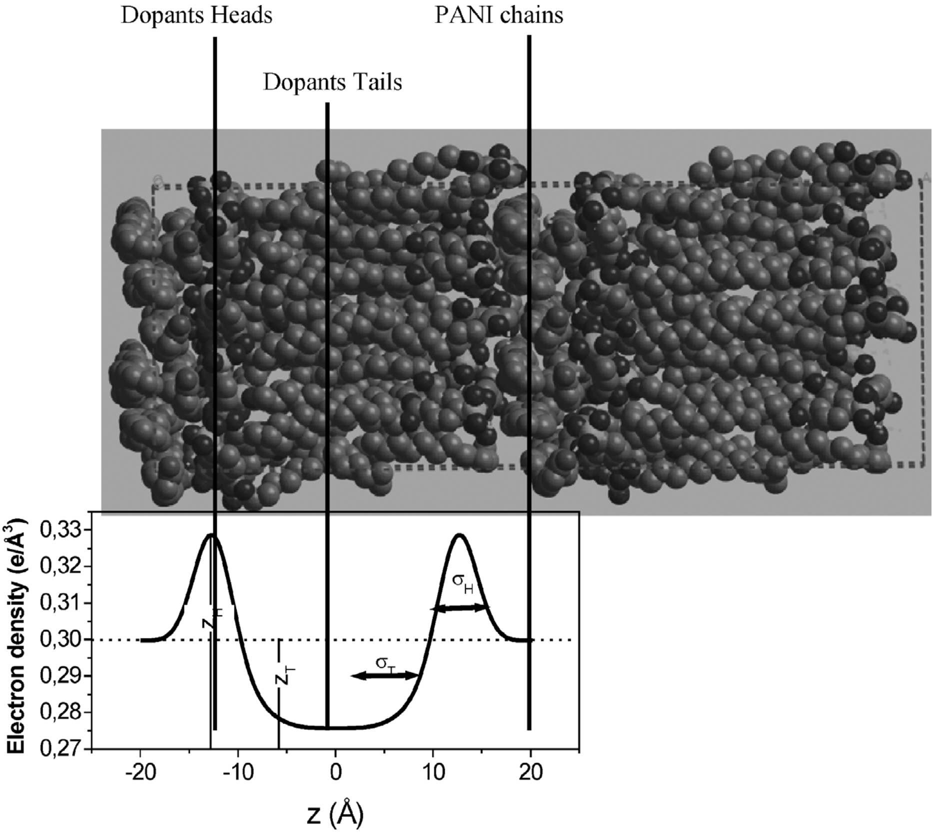

Figure 2.

A view along the PANI chain direction of the layered structure of plastdoped PANI's. The profile of the electron density used for calculating the form factor entering in the expression of the scattered intensity is also shown.

By using a force field based method (force field Compass as available in the Cerius^2 Accelrys® package), a triclinic simulation box consisting of 4 PANI chains and 8 counter-ions molecules was built according to this model. The stabilization procedure (geometry optimization) performed in the NPT ensemble was a combination of several steps repeated until the total energy of the system reached a constant value [5]. Once this structure proved to be stable it was then easy to extract the local electron densities (see equation (1)) needed for calculating the form factor while the other distance parameters were also used for the calculation of the structure factor [6]. By following this procedure, we could calculate the X-ray scattering profiles and obtain a very good agreement between experiments and simulations [6]. From this analysis it is worth to note that we found a longer coherence length along the stacking direction for the systems with long counter-ions (coherence length is corresponding to 5 consecutive stacking sequences) compared to those having the shortest ones (coherence length is corresponding to only 3 consecutive stacking sequences). This result indicates that the mutual interaction of flexible tails is very effective for such a structure to be stabilized.

The Geometry of Molecular Dynamics in "Plastdoped" PANI [7–10]

We studied the molecular dynamics in plastdoped PANI's by using incoherent quasi-elastic neutron scattering techniques [7–9]. We showed that most of the dynamics in the 10^{-9}–10^{-13} s characteristic time range was due to the motion of protons borne by the flexible aliphatic tails of doping counter-ions. We coupled this approach with numerical simulations carried out either in the small box already described or in a bigger one made of two consecutive bi-layers of 12 PANI segments of 8 benzene rings giving 9312 atoms in the case of PANI-DB3EPSA [5].

From this extensive study carried out at 110, 210, 235, 280, 310 and 340 K, it could be established that the most mobile protons are those placed at the end of the tails while those attached to the heads of dopants were mostly immobile. The space explored by these protons was modelled as limited spheres in which the protons can diffuse and the radii of these spheres can be considered as distributed according to a gamma function as a function of the respective position of the protons along the flexible molecules [8]. In this way it appears that the parts of the structure comprising the PANI chains in interaction with the heads of dopants are quite rigid while the centre of the bilayer composed of the dopants tails is much softer and flexible.

Interestingly enough, the numerical simulations gave very similar results as it is shown in the Figure 3. In this figure, we are considering the mean square displacements of protons along the tails of dopants. Low numbers are labels for groups of protons attached to the head of dopants and higher numbers are designing those which are attached to their ends. We considered independently all the same protons of all the counter-ions and we calculate the average value of their mean squared displacements.

In the same figure it can be seen the evolution of these trajectories as a function of the temperature and it can be noted that the simulated system is reproducing the glass transition around 220K which could be measured for most of these systems [10].

Moreover, the simulations also proved that the spatial distribution of these local motions does not apply only for protons belonging to a same dopant molecule but also to equivalent protons belonging to different counter-ions [5].

The Time Distribution of Molecular Dynamics in "Plastdoped" PANI [9]

One of the most surprising features we found for the dynamics of these systems is the very broad distribution of their characteristic times. Indeed, several spectrometers with different energy resolutions were used in order to span the broadest time range possible (10^{-13} to 10^{-9}s) and whatever the resolution of the spectrometer, we found the same values for the elastic

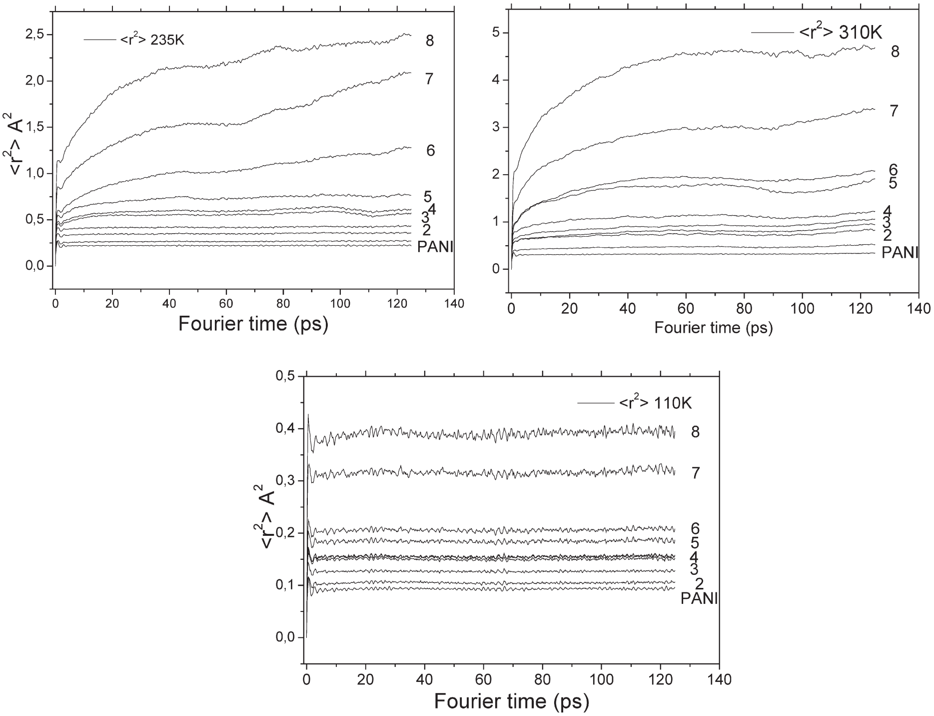

Figure 3.

Calculated mean squared displacements of protons at different temperatures for PANI-DB3EPSA. Protons on the PANI chains and on the head of dopants are found immobile in the simulated time window while others are more mobile. It can be noted that all the motions are frozen at 110K while they are visible at 235K to reach high amplitudes at 310K (see text for explanation about the numbering).

incoherent structure factors (EISF) [9] (see Figure 4). This result means the observed motion of protons has a broad range of time characteristics. In other words, whatever the spectrometer which is used (we used spectrometer whose energy resolutions were ranging from 1 μev to 100 μeV), one population of these protons experience a dynamics whose characteristic times is fully entering the corresponding energy window. Thus, we are dealing with systems in which all the protons are experiencing the same geometry of motion but with very different characteristic times. In some respect, we might speak about a kind of "time fractality" since whatever the observation time scale a same motion could be observed somewhere in the system. We believe that this behaviour is a direct consequence of the structural mode of these systems. The short chains are in fact confined in two dimensional galleries delimited by stiffer molecular walls (PANI chains stacks) to which the more flexible counter-ions are tightly bounded via a strong ionic interaction.

Conclusion: About the Correspondence of Dynamical Transition and Electrical Transition

The zero frequency electronic conductivities of several samples have been measured as a function of the temperature and the results are shown in the Figure 5a.

Also, in the Figures 5b and 5c are shown so called "elastic scans" of compounds with long counter-ions. These scans are representing the intensity of elastically scattered neutrons as measured as a function of the temperature on high resolution backscattering spectrometers. These curves have the advantage to reveal at which temperatures local diffusive motions are entering the

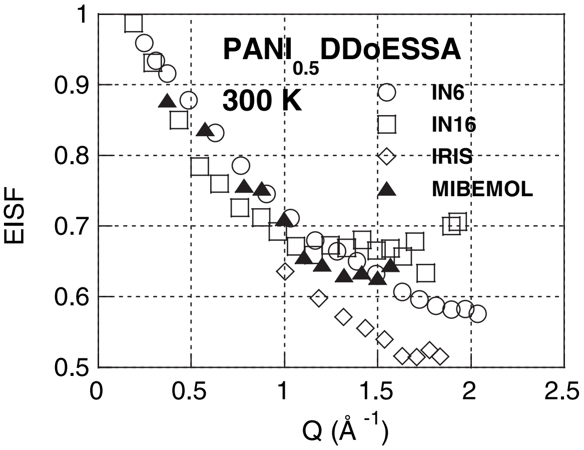

Figure 4.
Experimental EISF at 300K for PANI-DDoESSA measured on four different spectrometers with energy resolutions of 100 μeV, 1 μeV, 15 μeV and 42 μeV from top to bottom.

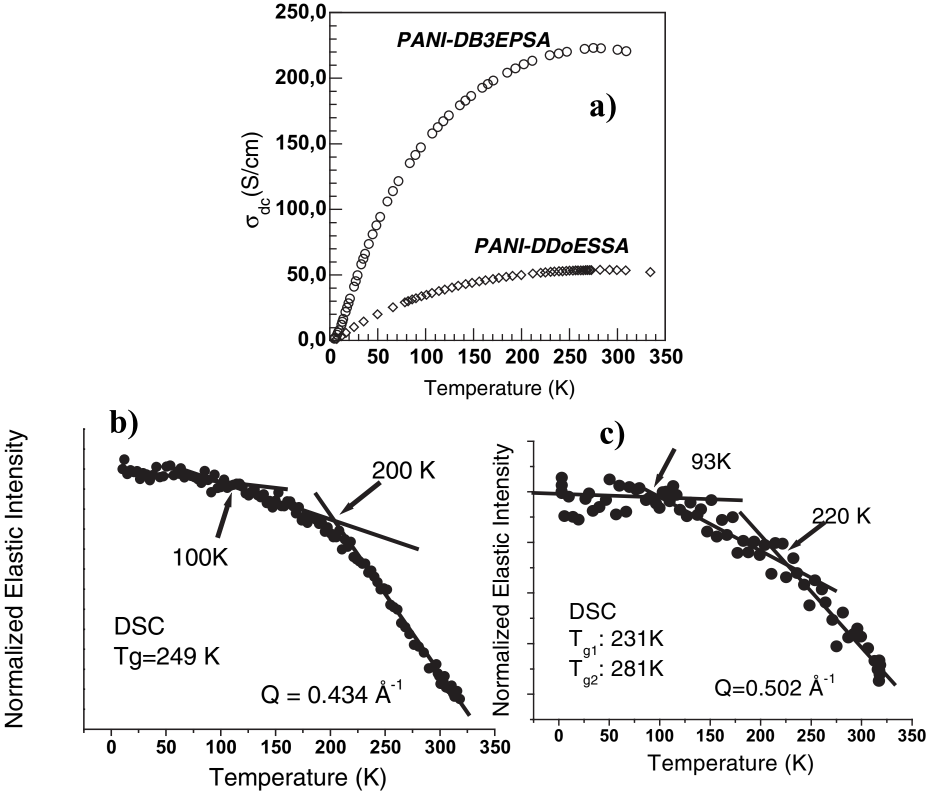

Figure 5.
a) DC conductivity curves as a function of the temperature for two plastdoped PANI's, b) & c) "elastic scans"of PANI DDoESSA and PANI-DB3EPSA for one scattering vector. The transition around 100K corresponds to the methyl rotation while those at higher temperatures correspond to glass transition(s).

experimental window of the measurements since their appearance produce a change of slope of the obtained curves [11,12]. From all these curves, it is clear that dynamical transitions and electrical transitions are occurring in the same temperature range. Would that mean that metal like electronic conductivity along the PANI chains exist only when the counter-ion sublattice is mobile enough? At first glance such a correlation would be surprising since the expected orders of magnitude of respective characteristic times of electronic scattering processes (10^{-14}–10^{-15} s) and lattice dynamics (10^{-9} to 10^{-13}s) should be very different. However, in these systems the situation differs notably from classical inorganic metals. Many authors have pointed out that the conduction in these systems can be due to excited states as polarons [13]. The effective mass and the mobility of these excitations may differ of several orders of magnitude from those of free electrons.

Moreover, several contributions in the literature pointed out that in these systems metallic contribution to the conductivity might be due to a very small number of carriers whose scattering times would be surprisingly low ($<10^{-12}$ s) [14,15]. In such conditions, and taking into account the broad time distribution which exists in the molecular dynamics, the possibility of decisive influence of the mobility of the lattice on the electronic process of conduction does not seem so unlikely. The next step of this study would consist to find further experimental evidence of this coupling. We are carrying out additional electronic measurements (impedance measurements, ESR, conductivity as a function of the frequency) and we plan to undertake calculations of the electronic structures using a DFT based method in order to progress in our understanding of these systems.

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