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Structure and Dynamics of Plast-Doped Conducting Polyaniline Compounds

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Abstract

The structural properties of polyaniline (PANI) protonated with plasticising dopants, namely diesters of 4-sulphophthalic acid containing linear alkyl or alkoxy substituents (so-called plast-dopants) have been investigated by both wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) measurements. The SAXS measurements were performed at the ESRF (Grenoble) synchrotron facility. Based on the experimental data, we proposed a lamellar-like structure in which a bilayer of plast-dopant anions alternates with a layer of PANI chains. In order to account for the shape of the diffraction curves obtained experimentally, we have used a theoretical model in which statistical fluctuations of the electron density are introduced along the stacking direction of the lamellae. This simple concept of a layered structure in which stacks of polymer chains are separated by dopant anions was taken as the starting point of a model for carrying out molecular dynamics (MD) simulations and geometry optimisation of the PANI/plast-dopant system. These simulations were carried out using the Cerius2 program (Accelrys Inc.), and the interactions of atoms were described by the force field called COMPASS ('Condensed-phase Optimised Molecular Potentials for Atomic Simulation Studies'). As the results of such modelling, we not only established the structural model of the system studied, but also obtained some very important information concerning the dynamical properties of both dopant molecules as well as the polymer chains. Finally the measurements using quasi-elastic neutron scattering technique (QENS) in order to investigate these dynamical properties experimentally were performed. These studies were done in the ILL reactor centre in Grenoble. We obtained a great deal of information concerning the movements of atoms and the groups of atoms in the compounds studied.

Key words: X-ray diffraction, small-angle X-ray scattering, neutron scattering, polyaniline and derivatives, supramolecular structure, molecular dynamics, computer simulations.

Introduction

Polyaniline (PANI) in the oxidation state of emeraldine belongs to one of several macromolecular systems whose physical properties can be tuned via appropriate doping. One consequence of the doping reaction is an increase in the conductivity of the polymer, which may become metallic in character. In recent years it has been shown that in addition to their doping functions, several dopants from the families of sulphonic [1,2] and phosphoric acids [3] as well as phosphoric acid diesters [4] improve the polymer's processibility in its conducting state. Among these bifunctional dopants, diesters of phthalosulphonic and sulphosuccinic acids, which contain long alkyl or alkoxy groups, are particularly interesting because they plasticise PANI. For this reason they are known as plast-dopants. Plast-doped PANI combines the high electrical conductivity of conducting polymers with the excellent mechanical properties of plastics [5,6]. All these interesting properties have their origin in the specific supramolecular structure of the system, and – on the other hand – in the dopant-polymer chain interactions. These were the reasons why we started to eluci-

date the supramolecular organisation and the dynamical properties of plast-doped PANI.

Experimental

Samples

The general formula of the plast-dopants used in this work is shown in Figure 1, where R = *n*-pentyl, *n*-octyl, *n*-decyl, *n*-dodecyl, -butoxyethyl, -butoxyethoxyethyl. The abbreviations used in the following text are also described in Figure 1. The protonation of PANI-EB was carried out in a dichloroacetic acid solution. This solution was then used for casting free-standing films of c. 20-30 m. The stoichiometry PANI(plast-dopant)_{0.5} was kept in each case.

X-ray scattering measurements

X-ray diffraction measurements were carried out with reflection Bragg-Brentano geometry using CuK α_1 radiation. The 800-channel linear multi-detector measured the intensity.

The small-angle X-ray scattering measurements were performed at the ESRF

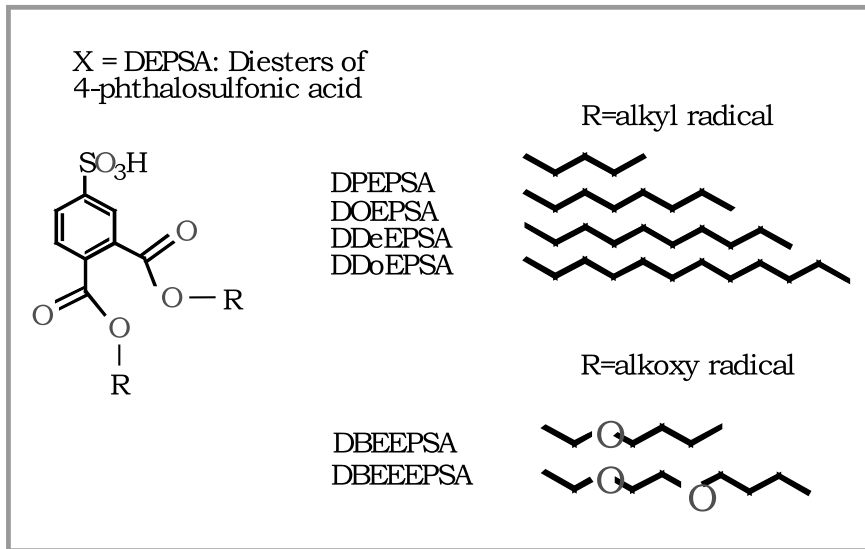


Figure 1. Chemical formulae of the plasticizing dopants.

(Grenoble, France) on the high q resolution French CRG beam line D2AM using a monochromatic beam with a wavelength of 0.12 nm. A two-dimensional detector was placed at 2.2 m from the sample, and the separation between two channels was 4.5 m. The two-dimensional scattering figures were always found to be isotropic within the plane of films, so the one-dimensional profiles were then obtained by executing a 2B radial integration of the total scattered intensity.

Neutron scattering measurements

The neutron scattering measurements were performed at the Institute Laue-Langevin in Grenoble, France. Two different experimental set-ups were used: the IN6 Time of Flight (TOF) Spectrometer and the IN10 Back Scattering Spec-

trometer. We were able to measure the dynamic structure factor $S(q, T)$, thus giving the information on the elastic, inelastic and quasi-elastic components of the scattered intensity as a function of the temperature for all the samples studied.

XRD results – the lamellar-like structure model

The XRD profiles recorded for the PANI/plast-dopants samples are shown in Figure 2. They can be described as consisting of one rather sharp reflection at small q values, one broad diffuse maximum, and a narrower one for higher q value. The position of the small q reflection is strongly dependent on the size of the substituent in the dopant, whereas the position of the higher q maximum, as related

to the repetition distance of 0.35 nm, is independent of the size of the dopant. One can attribute the small q reflection to a chain/dopant bilayer/chain repeat distance, and the high q reflection to the stacking distance of phenylene rings or PANI chains. These observations allowed us to propose the simple structural model of supramolecular organisation of the system studied which is shown schematically in Figure 3.

Small-angle X-ray scattering results

Because in the case of XRD experiments the position of the small q peak is close to the low angle limit of the experiment, which may lead to some incorrectness in determination of the peak features, we undertook the SAXS measurements for the same set of samples. All the scattering profiles obtained are shown in Figure 4. We may conclude that with the increasing length of the substituent, the SAXS peak becomes more intensive and narrower, which indicates increasing ordering. This narrowing is accompanied by a shift of the peak towards lower q values as expected for the increasing dopant size.

We proposed a model for the statistical fluctuations in the multi-lamellar-like structure which enabled us to describe the experimental SAXS curves theoretically with perfect agreement. The details of these calculations and their results were published elsewhere [7]. In order to perform such calculations, we needed to estimate some structural parameters. Therefore we undertook the computer

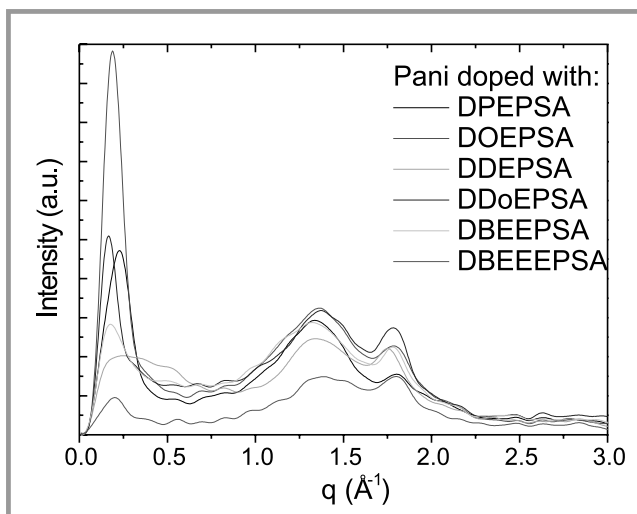


Figure 2. XRD profiles of PANI/plast-dopants samples.

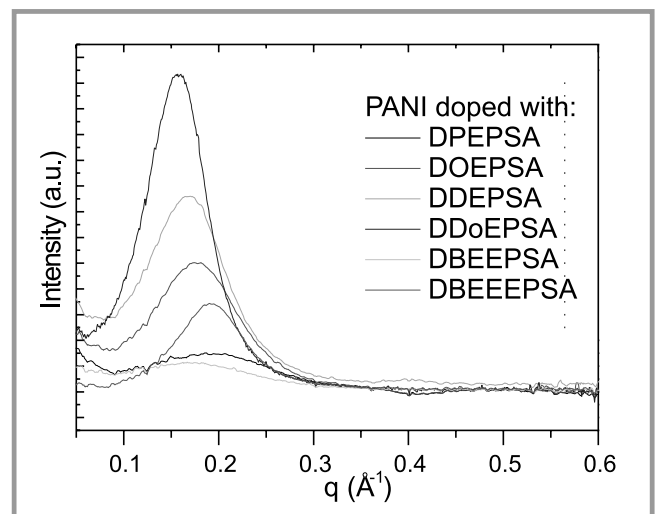


Figure 4. SAXS curves for PANI/plast-dopants samples.

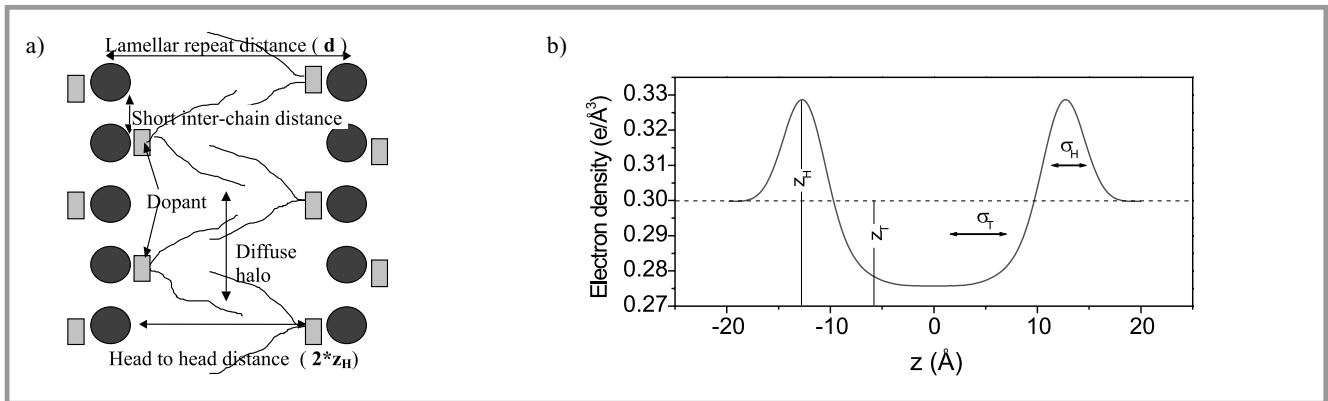


Figure 3. a) Schematic view of the simple model of PANI/plast-dopant system; b) Electron density distribution of a single bilayer, calculated theoretically (see text).

simulation study of the system investigated.

Computer simulations of the PANI/plast-dopants system by use of the molecular dynamics technique

The simulations were carried out using the *Cerius2* program (Accelrys Inc.). The calculations were performed following the steps described below:

- Initial configuration of atoms (taken from the simple model based on experimental XRD and SAXS data);
- The force field (all interactions within the system – see below);
- The conditions of simulation (*NVT* versus *NpT* ensemble);

- Optimisation of the system – searching for energy minimum ;
- Initial simulation – searching for equilibrium;
- Main simulation – recording the trajectory;
- Analysis of the trajectory.

The calculations were performed in a simulation box with periodic boundary conditions. For the PANI/DB3EPSA system, this box contained 776 atoms (4 PANI chains with 4 phenylene rings, each + 8 counterions). The interactions of atoms are described by Coulomb forces, Van der Waals interactions, and so-called cross terms, related to bond-angle, bond-stretch and bond-torsion phenomena. These lead to the second-generation po-

tential known as COMPASS ('Condensed-phase Optimised Molecular Potentials for Atomic Simulation Studies') used in this work.

The results of the simulations confirmed that the layered structure proposed above is indeed quite stable, mainly because of the strong interactions of the dopant molecules' interdigitating tails. Furthermore, we were able to evaluate the electron density parameters, which are needed to perform the theoretical calculation described in the previous section. And finally, we obtained much information concerning the dynamic properties of the systems studied, which can be well correlated with the experimental data from the neutron scattering measurements.

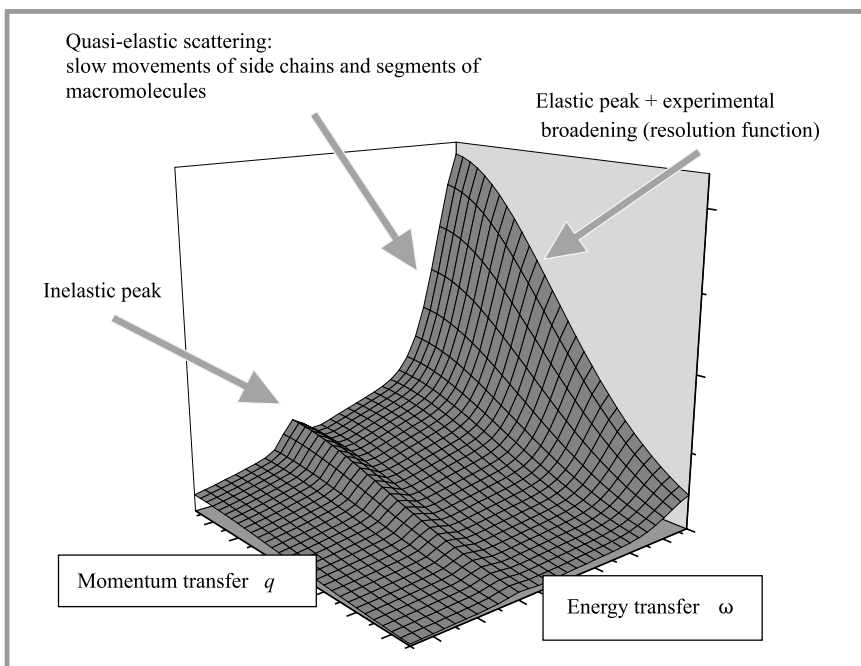


Figure 5. Typical shape of the dynamic structure factor $S(q, T)$ and its main features.

The dynamic properties of PANI/plast-dopants system studied by the neutron scattering techniques

It is well known that the dynamical properties of condensed matter studied by the neutron scattering techniques are well described in terms of the dynamic structure factor $S(q, T)$, where q is the scattering wave vector equal to $4B \sin^2 / \lambda$, and T describes the energy transfer between the neutron and the particle (atom, molecule, etc.) of a sample. This quantity $S(q, T)$ is the weighted sum of two components, incoherent and coherent; it describes the dynamic of single particles in the system, and their relative (longitudinal) motion in terms of the particle density respectively. On the otherhand, both incoherent and coherent dynamic structure factors are the Fourier transformation of two components of the time-space pair correlation function $G(r, t)$. The func-

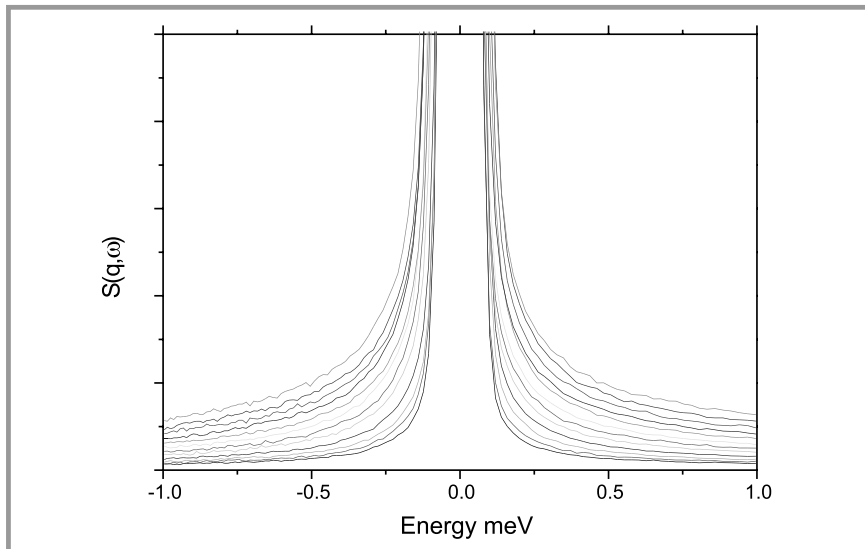


Figure 6. Dynamic structure factor $S(q, T)$ (its quasi-elastic component) measured for PANI/DB3EPSA sample.

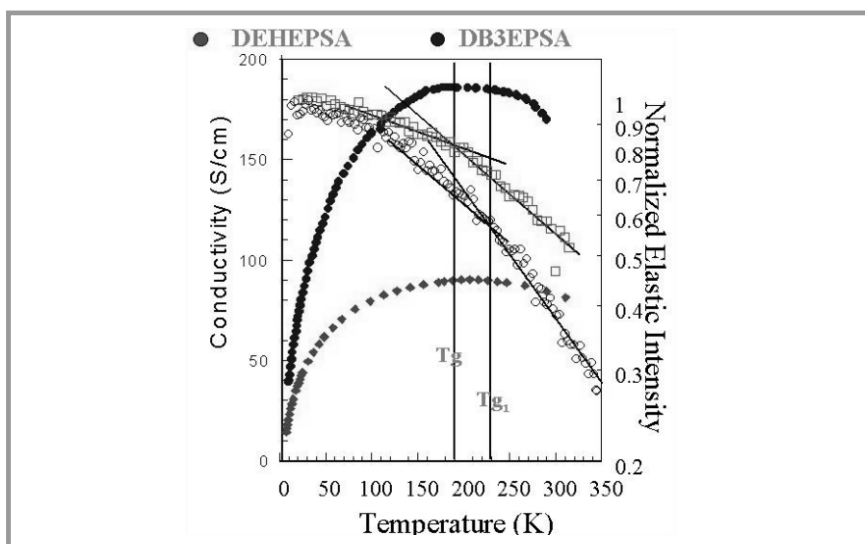


Figure 7. Intensity of the elastic peak and the electric conductivity of PANI/DEHEPSA and PANI/DB3EPSA samples, as the functions of the temperature.

tion $S(q, T)$ is accessible from the neutron scattering experiments, whereas the function $G(r, t)$ may be calculated from the results of the computer simulation, so we can compare both sets of data in order to obtain useful information concerning the dynamics and movements of the atoms and groups of atoms within the system studied.

The typical shape of the dynamic structure factor with the description of its main feature is shown in Figure 5. We were able to obtain some important information from the following sources:

- the characteristics of an elastic peak;
- the quasi-elastic component of the recorded intensity;
- the characteristics of an inelastic peak.

The example results of the $S(q, T)$ measured for the PANI/DB3EPSA sample is shown in Figure 6. The intensity of the elastic peak as a function of the temperature (for two samples) is shown in Figure 7. We can conclude that the slope of the elastic intensity curve changes in the glass transition points; moreover, the type of conductivity changes simultaneously.

More detailed results of molecular dynamics measurements and simulations, as well as the influence of the dynamics of the molecules on the structural and transport properties of the PANI/plast-dopant samples, will be explained elsewhere [8, 9].

Main conclusions

Concerning the structure properties of the PANI/plast-dopant samples, we may draw the following conclusions:

- The molecular stacking existing in plast-doped polyaniline may be described by a lamellar-like arrangement with statistical disorder;
- The approach allowed important structural parameters (repetition distance, average number of layers involved in crystallite) to be extracted, and quantitative analysis of SAXS data to be performed;
- The important role of the interdigitation of dopant tails in structural properties has been underlined.

As regards the dynamical properties:

- Structural analysis allowed us to prepare a model with starting configuration ready for the molecular dynamics (MD) computer simulations;
- MD simulations justified the stability of proposed structures;
- The good agreement between simulated scattering functions and the dynamic structure factor $S(q, T)$ as experimentally obtained gives evidence of good force field parametrisation;
- The study of the MD trajectories of single atoms and groups of atoms allows different types of particle motion to be separated and analysed.

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