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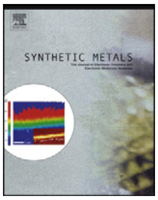

Equilibrium doping of polyaniline by dodecylbenzenesulfonic acid

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ABSTRACT

We study a wide-range doping of polyaniline by dodecylbenzenesulfonic acid, carried out by a prolonged equilibration of the undoped polymer powder with aqueous solution of the dopant. While the resulting material is always amorphous, the corresponding dopant content – determined by a nuclear spectroscopy – indicates two doping regimes. When the amount of the dopant in the solution is smaller than that of the protonation sites, the dopant is completely absorbed by the protonation. At larger amounts of the dopant, a two-phase system is obtained. It consists of the completely protonated polymer and unbound dopant captured between the chains. This conclusion is supported by the room temperature magnetic susceptibility of selected samples. The room temperature dc electrical conductivity increases with increasing dopant content even in the two-phase system, extending over $\sim 10^{-10}$ to ~ 10 S/cm. This increase in the single-phase system can be understood in terms of the creation of the conducting charge by the protonation, whereas its underlying cause is for the two-phase system discussed with regard to the nature of the charge transport at the microscopic scale.

1. Introduction

Polyaniline (PANI) is a polymer comprising z reduced ($-C_6H_4-NH-C_6H_4-NH-$) and $(1-z)$ oxidized ($-C_6H_4-N{=}\,C_6H_4{=}N-$) repeat units. The interest in PANI was boosted when it was found that there is a dopant (HCl) which can make it electrically conducting with a conductivity σ comparable to that of conventional semiconductors [1]. Since then, PANI has held a prominent position among conducting polymers (CPs) because of its advantageous properties—a number of which we mention here. The polymerization methods are rather simple and involve inexpensive chemicals while the final product is stable both in its insulating and conducting forms [2]. PANI is converted into a conductor by an uncomplicated protonation [3] of the thermodynamically favored symmetric form ($z = 1/2$) called the emeraldine base (EB), which in practice permits easy control of σ over around ten orders of magnitude. Not only HCl but also a number of other acids are effective in the protonation. Recently, for instance, camphorsulfonic acid [4,5] and dodecylbenzenesulfonic acid (DBSA) [4] have often been used, sometimes even combined mutually [6] or with HCl [7] in order to produce polymeric blends. From the point of view of exploring the mechanisms of charge transport in CPs, doped PANI has served as a system suitable for testing different theoretical models [8].

Technological applications in many cases require that a CP can be dissolved in some common solvent, for example when one wants to use standard processing methods such as spin coating or molding. Insulating EB is soluble in N-methyl-2-pyrrolidinone [9] but no commercially useful solvent is known for the "classically doped" PANI–HCl, which sets restrictions to its wider technological use. On the other hand, doping of EB by DBSA results in PANI–DBSA which conducts well and at the same time is soluble in common solvents such as chloroform, xylene or *m*-cresol [4]. The mechanisms behind this property relate to the efficiency of DBSA, $C_{12}H_{25}C_6H_4SO_3H$, in protonating EB due to its $-C_6H_4SO_3H$ "head" while the $C_{12}H_{25}-$ "tail" gives rise to a surfactant effect. This convenient combination has incited numerous studies – particularly in recent years – involving PANI–DBSA as such or combined with other materials [4,6,7,10]. However, full σ vs doping-level characteristics (i.e., over a wide doping range) for PANI–DBSA has not been studied systematically, in contrast to PANI–HCl where this curve is well known [11] and used in understanding the underlying chemistry, physics, and consequent perspectives for applications.

In this paper, we present results of a doping of EB by DBSA over a wide range, which leads to the room temperature (RT, 295 K) dc conductivity σ_{RT} extending from $\sim 10^{-10}$ to ~ 10 S/cm. The obtained material is studied further by carrying out an elemental analysis

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and measurements of magnetic susceptibility. Analysis of these results shows that DBSA efficiently protonates EB, and also that DBSA can be captured between the polymer chains. The dopant first occupies the protonation sites, and if these are saturated, the material is stabilized in a two-phased form consisting of fully protonated PANI–DBSA and chemically unbound DBSA in the interchain space.

Where appropriate, we compare properties of our PANI–DBSA material to PANI–HCl (generic to the doped-PANI class) produced from the same EB. Therefore, the abbreviations EB, PANI–DBSA and PANI–HCl are henceforth used to refer explicitly to these materials prepared by us (as described).

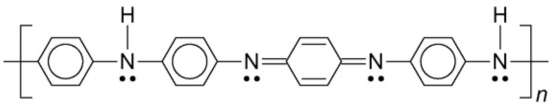
2. Experimental details

Chemicals were purchased either from Merck (aniline) or Alfa Aesar (DBSA, ammonium peroxydisulfate). Since our results could be of interest for research in different fields (e.g., physics, chemistry, materials science), we have attempted to maintain simplicity by avoiding any untraceable post-processing of the chemicals. EB was produced by deprotonation of PANI–HCl synthesized by the oxidative polymerization of aniline, using ammonium peroxydisulfate as the oxidant, in an aqueous HCl solution of pH ~0, and a ~1 M aqueous solution of NH_4OH for the deprotonation [12]. This material was subsequently doped by DBSA as described later, and also by HCl using a standard procedure [11].

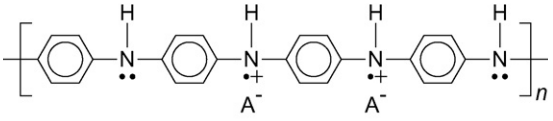
Elemental analysis was performed by the Elastic Backscattering Spectroscopy technique using 1.6 MeV protons – produced by the Tandetron electrostatic accelerator at the Rudjer Bošković Institute – as probing ions. Owing to the large probing depth of protons and high cross sections due to the nuclear component of the interaction, this is a well established tool in the analysis of light elements in materials, the basic principles being equivalent to the widely known Rutherford Backscattering Spectroscopy [13]. In particular, this method is appropriate for quantifying the content of S and N (by using evaluated elastic backscattering cross sections available through the online SIGMACALC calculator [14]), which is of importance for the main topic of this work. A full account of the amounts of all elements present in our samples – including impurities – was obtained by combining the above method with the Particle Induced X-Ray Emission technique [15], which is not addressed in this paper.

Magnetic susceptibility was measured using a commercial Quantum Design magnetometer with a Superconducting Quantum Interference Device for detecting magnetic moment at a resolution down to 10^{-8} emu. Samples were produced by pressing the polymer powder of a mass 80–100 mg into cylinders under ~90 MPa. Over the range of the applied magnetic field, up to 2 T, the magnetic moment vs magnetic field curves were linear, i.e., χ was a proper parameter of the magnetic response. $\chi(T)$ was always measured over the range ~10–300 K, and χ_{RT} was taken from these curves.

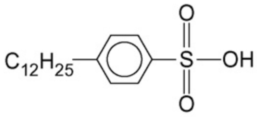
Resistance measurements were carried out using a Yokogawa 7651 dc source in the constant-current mode, and an Agilent 34420A nanovoltmeter with a 10 G Ω input resistance and a maximum input voltage of 12 V. Polymer powder was pressed into ~8 mm × 5 mm × 1 mm pellets under ~90 MPa. Electrical contacts in the four-point configuration were made by first depositing a thin graphite layer onto the contact area and then applying a silver paste. This resulted in contact resistances that did not exceed the sample resistance irrespective of its value. A constant current I in the range 0.01–1 μA was passed between the current contacts, leading to an Ohmic response of the measured voltage. The σ_{RT} presented is a part of $\sigma(T)$ measured down to the lowest (doping dependent) temperature where the resistance was still measurable with the available equipment.



(a) EB (undoped PANI)



(b) fully protonated PANI-H$^+$A$^-$



(C) DBSA molecule

Fig. 1. (a) Mer of EB (undoped PANI). The dots represent electron lone pairs on the N atoms. (b) Fully protonated mer of EB. The protonation by an acid H^+A^- results in PANI-H^+A^-. The "+" symbols on the protonated N atoms depict holes. (c) DBSA molecule. The $C_{12}H_{25}$– "tail" points outwards from the polymer backbone and causes a surfactant effect in an appropriate solvent.

3. Equilibrium doping of EB in aqueous DBSA solution

Although direct polymerization of aniline in aqueous DBSA solution can yield PANI–DBSA in a one-step procedure [16], it is difficult to control the doping this way. Instead, in our work we employ another method, i.e., equilibrium DBSA doping of independently synthesized EB powder. More precisely, we use the term "equilibrium" in connection with the following procedure: EB powder and aqueous DBSA solution are equilibrated for two weeks, the only perturbation being occasional stirring. Due to the prolonged reaction time and absence of external disturbances, the system can reach a state close to its thermodynamic equilibrium. This method is standard in doping of EB by HCl, and we have deliberately avoided any further modifications because the effects of these can be elucidated only if the simplest approach is understood well enough.

For clarity of the discussion, in Fig. 1 we show schematically: (a) one mer of EB, (b) this mer fully protonated by an acid H^+A^- [17], and (c) the DBSA molecule.

3.1. Preparation of aqueous DBSA solutions

Preparation of the doping solutions required a consideration of the complexity of DBSA. As shown in Fig. 1(c), DBSA molecule consists of a $-C_6H_4SO_3H$ "head" and a long $C_{12}H_{25}-$ "tail". Being an anionic surfactant, DBSA shares common properties with these materials in aqueous solutions. For temperatures $T < T_K$, where T_K is the Krafft temperature, there are no micelles regardless of the surfactant concentration, so single surfactant molecules dispersed in water aggregate only as crystalline hydrates if the amount of the former exceeds the value given by the solubility curve. For $T > T_K$, at surfactant concentrations above the critical micelle concentration (CMC), which depends on T only weakly, micelles appear [18]. Since the most efficient doping of EB by DBSA is expected to occur by single DBSA molecules, their aggregation should be suppressed but – as we argue below – this mainly applies to the formation of micelles.

Namely, at a low binding degree of H^+ counterions to a micelle of DBSA, H^+ can protonate EB, and the resulting PANI-H^+ can then attract the charged micelle. This attraction is strong, as it originates in the electrostatic force. Since micellization is a fast and reversible reaction [19], the mere presence of micelles should not be an obstacle to the doping, but the chains may wrap around the micelles,