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We compare in this Communication the HCl doping data for the two recently discovered classes of polyaniline. The EB-II – ES-II system was found to be more difficult to dope in the pH=3 – pH=2 range than the previously studied EB-I – ES-I system. We discuss the influence of the crystallinity of the sample on its doping behavior.

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Protonic acid doping of two classes of the emeraldine form of polyaniline.

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Abstract

We compare in this Communication the HCl doping data for the two recently discovered classes of polyaniline. The EB-II - ES-II system was found to be more difficult to dope in the pH=3 - pH=2 range than the previously studied EB-I - ES-I system. We discuss the influence of the crystallinity of the sample on its doping behavior.

The polyaniline family of polymers has attracted a wide interest recently as a conducting polymer with interesting electronic properties, easy processability and good environmental stability [1, 2, 3, 4]. Recently, we reported that there exist two classes of emeraldine, depending on the method of preparation [5, 6]. Class I materials, initially prepared in the conducting salt form are amorphous in the base form and partially crystalline in the HCl salt form with crystal structure we label ES-I. Class II materials, initially

prepared as base from ES-I (see below), are partially crystalline in the base form with the crystalline structure EB-II and partially crystalline in the salt form with structure ES-II, different than that of ES-I. Detailed descriptions of various means of preparing Class I and Class II materials and their respective crystal structures have been reported earlier [6].

In order to gain information about the evolution of structure of materials belonging to both classes with HCl doping, we studied the doping process in itself, and particularly the pH - doping level relationship. The previously published doping concentration vs pH data [7] were obtained from Class I materials. Therefore, we concentrated on determining a similar relationship for Class II materials.

Class II base powder (EB-II) was obtained as follows. Emeraldine hydrochloride powder (ES-I), synthesized according to the usual procedure [8], was converted into emeraldine base EB-I form by washing it with 0.1M NH_4OH solution (the EB-I material used in the previous doping study was obtained by this procedure [7]). EB-I powder was subsequently transformed to partially crystalline EB-II powder by extracting first with tetrahydrofuran (THF) until the liquid was colorless and then with *N*-methyl-2-pyrrolidone until the liquid was almost colorless [5]. The powder was then dried in dynamic vacuum for 48 hours.

The extraction process removes some low molecular weight and oligomeric materials [3, 9] and converts amorphous EB-I sample into partially crystalline EB-II sample. EB-II obtained in such way was subsequently doped with aqueous solutions of HCl. EB-II powder was stirred with an HCl solution of appropriate pH for 48 hrs, then washed with the same solution and dried under dynamic vacuum for 24 hrs. The polyaniline samples were then analyzed for carbon, nitrogen, hydrogen and chlorine and the doping level x=[Cl]/[N] was calculated.

The [Cl]/[N] versus doping pH data obtained for Class II are plotted on Fig. 1 together

with the previously published data for Class I [7]. The circles (o) represent Class I data and are linked by dashed line (- - - - -) which serves as a guide to the eye. Dots (•) represent Class II data and are linked by solid line (———).

The low pH data, from about pH=2 to pH=0 are very similar for both Classes. However, the intermediate part, from approximately pH=4 to pH=2 is significantly different. The doping level of Class I materials increases steadily as the pH of the doping solutions decreases, starting from about pH=3.5. In contrast, EB-II is only slightly doped (less than 10%) by HCl solutions with pH as low as 2.5, but when still lower pH is applied, the doping level rapidly increases. Treating the EB-II with doping solution of pH=1.5 results in a sample which is 40% doped. Between pH=3 and pH=2, the Class II doping curve is less than that of the Class I doping curve by as much as 15 percentage points.

It is unlikely that the differences in doping level for a given pH are due primarily to some difference in the surface area and morphology of doped EB-I and doped EB-II and differing desorption of HCl after being maintained in vacuum for 24 hours. We see no differences in ES-I and ES-II doping levels at low pH (heavily doped) and earlier studies of ES-I [10] showed that repeated evacuation and exposure to water vapor leads to only very small changes in conductivity (and hence the doping level remains nearly constant).

It is proposed that the cause for these differences in doping behavior between the two forms of emeraldine base lies in the differences in their degree of crystallinity. EB-I is essentially amorphous and, as x-ray data show [6], doping induces a continuous increase in crystallinity in Class I materials, with no dramatic composition changes with varying pH. Both the percent crystallinity and the coherence length of the crystallites increase approximately linearly with the doping level. A continuous doping process may be possible because Class I samples were formed/precipitated in the doped form originally. In contrast,

Class II samples were precipitated in the partially crystalline base form EB-II. X-ray data show [5, 6] that initially EB-II samples are doped into the amorphous regions and only at an approximately 25% doping level the EB-II crystal structure disappears and new ES-II crystalline structure is formed. Apparently, doping in the amorphous part of EB-II is energetically more favorable and the crystalline part is not substantially doped until the material is treated with HCl solution of pH lower than about 2.3. At approximately this pH, the crystalline part is doped and the rapid increase in the doping curve is observed.

To test the hypothesis that the crystallinity of the sample is the primary influence on the doping process we prepared an amorphous EB-II sample. (Doping and dedoping of crystalline EB-II material destroys EB-II crystalline order; the resulting material is however distinct from EB-I material because, when doped, it forms the ES-II structure [6]). We doped this sample with aqueous HCl solution of pH = 2.85. The resulting doping level was 16.4%. This data point is marked (□) on Fig. 1 and it can be readily seen that it lies on the (amorphous) EB-I doping curve. Hence crystallinity of the sample is the major factor determining the final doping level of emeraldine material at intermediate pH values.

We conclude that emeraldine base exhibits different doping behaviour depending on the method of preparation. Partially crystalline emeraldine form (EB-II) is doped to significantly lower levels than amorphous form EB-I at intermediate pH of doping solutions. We note that percent crystallinity of the various EB-II samples can vary from about 0% for dedoped ES-II and 5% for NMP cast films [11] to about 50% for the powders we studied. With the varying degree of crystallinity it is likely that the doping curve of EB-II samples will vary from sample to sample. Therefore it is very important when studying the emeraldine materials with intermediate doping levels that cognizance is taken of both

the crystallinity and the doping level of the sample.

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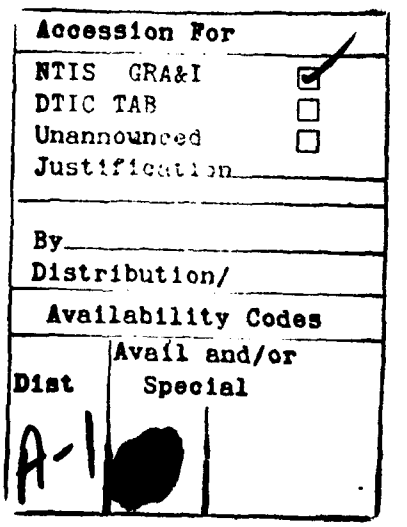

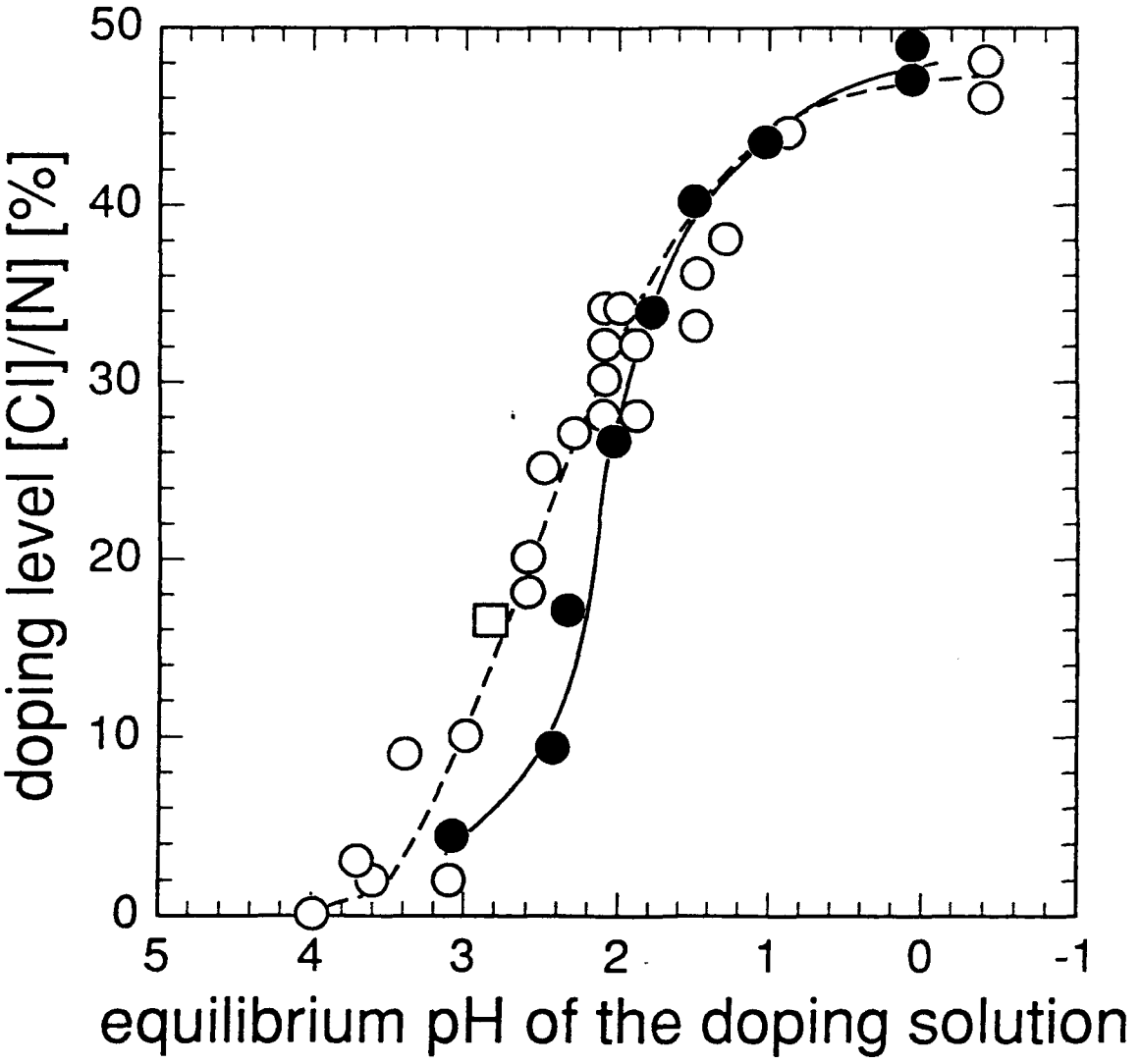

Figure 1 Plot of the doping level $x = [Cl]/[N]$ of emeraldine versus pH. The circles (o) represent Class I data [7] and dots (•) represent Class II data. (□) represents doping level o[redacted]orphous EB-II sample (see text). Lines serve as guides to the eye.