Temperature dependence of the resistance of self-assembled polyaniline nanotubes doped with 2-acrylamido-2-methyl-1-propanesulfonic acid

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Abstract

Hollow polyaniline (PANi) nanotubes doped with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) have been synthesized and their electrical resistance measured as a function of temperature. The average length of the nanotubes was in the range 2–5 μm and the average diameter was in the range 200–400 nm. Longer reaction times did not affect the morphology of the nanotubes. The resistance of AMPSA doped nanotubes were measured as a function of temperature and compared to emeraldine base PANi doped with AMPSA in the solid state. Dissolving the PANi nanotubes in dichloroacetic acid leads to better polymer chain ordering.

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1. Introduction

The synthesis and electrical characterization of polyaniline has been the subject of extensive research during the past two decades since it was discovered that polyaniline could be made conducting (PANI-ES) via doping with acids like for e.g. HCl and then dedoped to the insulating state (PANI-EB) via treatment with a base like for e.g. NH₄OH [1]. The ease of synthesis with high yield, good stability in air and the ability to reversibly tune the conductivity to any value from the insulating to the metallic regime (several orders of magnitude) have made polyaniline a very desirable and the most investigated conducting polymer. The use of functionalized protonic acids like for e.g. 10-camphorsulfonic acid (CSA) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) have resulted in PANi-ES being soluble in common organic solvents[2,3] . Depending on the choice of the solvent, the conductivity of polyaniline doped with these acids increases dramatically and also exhibits metallic behavior. These features are attributed to the expanded coil like conformation in such solvents which facilitates charge transport [4].

In recent years there has been renewed interest in the preparation and electrical characterization of doped polyaniline nanofibers. Various methods have been utilized for their preparation and include the use of templates [5], self-assembly [6,7], interfacial polymerization [8,9] or electrospinning [10,11]. In the electrospinning technique, the process begins with the synthesized emeraldine base form of polyaniline (PANI-EB) to prepare the spin dope from which fibers are spun, while the other methods involve the polymerization of the monomer into polymer nanofibers. The advantage of the electrospinning technique is the ability to spin, in a matter of minutes, centimeter long nanofibers of the desired polymer. The other methods yield short (few microns long) conducting nanofibers, but in gram size quantities. One of the reasons for preparing PANi nanofibers is to investigate charge transport in conducting organic polymers that are one-dimensional in nature.
In the last few years, M. Wan and coworkers have described a self-assembly technique to prepare PANi nanotubes directly during the polymerization process using a number of different dopant acids [6, 12–14]. The probability of nanotube formation during the synthesis depended on various factors like the dopant/monomer ratio, oxidant/monomer ratio, dopant concentration, reaction temperature and reaction time. In the self-assembly technique, the acid and the monomer react to form micelles which in turn was believed to act as templates so that upon addition of the oxidant the polymerization took place at the micelle water interface and progressed via elongation to yield nanotubes. We have synthesized PANi doped with AMPSA using the above method. The purpose was to ascertain if indeed nanotubes of PANi doped with AMPSA could be prepared via the self-assembly technique and if the metallic characteristics of PANi-EB doped with AMPSA in the solid state and cast from dichloroacetic acid (DCA) were also present in the AMPSA doped PANi nanotubes. Our results indicate that doping PANi with AMPSA during the synthesis did not reveal metallic characteristics, however the barriers to conduction were very much reduced when the polymer was dissolved and cast from DCA.

2. Experimental

Aniline monomer (An) was distilled under reduced pressure prior to polymerization. AMPSA, DCA and the oxidant ([NH4]2S2O8) were purchased from Aldrich and used as received. PANi-EB was purchased from SFST Inc. and used as received. The polymerization of PANi nanotubes was carried out at a fixed temperature of 0°C and the dopant/monomer ratio was fixed at 1:1. The synthesis was carried out in a manner analogous to that reported for D-CSA doped PANi nanotubes [6]: 4 × 10^-3 mol (0.829 g) AMPSA was dissolved in 20 ml of distilled water containing 4 × 10^-3 mol (364.8 µl) An, and cooled to 0°C. In a separate beaker, 4 × 10^-3 mol (0.9128 g) ([NH4]2S2O8) was dissolved in 10 ml of distilled water and also cooled to 0°C. The solution with the oxidant was then added drop wise to the solution with the monomer/dopant solution and the reaction allowed to proceed at 0°C without stirring for a specified time. The solution was then filtered and the polymer washed with 500 ml of distilled water and 250 ml of methanol and left to dry in vacuum for 24 h prior to characterization. A portion of the polymer was then ground to a fine powder and used to prepare a pressed pellet while another portion was dissolved in DCA (2 wt%) to prepare a thin film via drop casting. Since AMPSA is a linear and more flexible acid that CSA we expect that longer nanotubes will be formed during the synthesis. For comparison, PANi was also doped with AMPSA in the solid state as follows [3]: commercial PANi-EB (0.38 g) and AMPSA (0.52 g) were mixed in air manually with a glass rod to obtain a thick deep green viscous solution. A thin (15 µm) free standing film was prepared by placing a drop of this solution on a glass slide that was then kept in an oven at 80°C for 48 h.

A JEOL 6500 scanning electron microscope (SEM) was used for morphological studies while resistance measurements were made via two in-line and four-in-line contacts and measured with a Keithley Model 6517A electrometer. The current–voltage characteristics of the sample were recorded in a dynamic vacuum and the resistance extracted from the Ohmic region of the curve. Measurements were taken after the sample had been pumped for at least 30 min and with a stable current flowing through it, to ensure minimal effect of adsorbed water. A closed cycle helium refrigerator was used to lower the sample temperature that was controlled with a temperature controller.

3. Results and discussion

Fig. 1a shows an SEM image of the nanotubes of AMPSA doped PANi prepared as described in Section 2 with a reaction time of 4 h. The formation of these tubes is assumed to take place through a self-assembly process similar to that described by M. Wan in the case of D-CSA doped PANi viz. the formation of micelles of the AMPSA/An salt prior to the initiation of the polymerization process via the addition of the oxidant. As the polymerization proceeded on their surface the micelles grow in size and form polymer tubes via elongation [6]. As seen in Fig. 1a, the PANi nanotubes are for the most part hollow with rough surface features. Two more samples were prepared using the same technique and with the same molar ratio (1:1) of the monomer/dopant and monomer/oxidant but with reaction times of 15 and 24 h and also yielded nanotubes. These nanotubes exhibited similar features as with a 4 h reaction time as seen in Fig. 1b and c. The average length of the nanotubes was in the range 2–5 µm and the average diameter was in the range 200–400 nm. Some fine granular regions of the polymer did exist as random distributions within the bulk material that comprised of nanotubes. The nanotubes appeared to be formed in clusters remaining packed within the micron size polymer granules that were dispersed in the aqueous solution. In an attempt to isolate these clusters we have electrosprun a dilute dispersion of these polymer granules in water. Fig. 1d shows an SEM image of one such cluster using a spinning voltage of 30 kV. While there appears to be some separation of the nanotubes from the bulk material, the process also leads to their fragmentation.

Fig. 2 shows the temperature dependence of the normalized resistance of AMPSA doped PANi. In order to compare charge transport in PANi prepared via two distinct routes, the molar concentration of dopant to monomer and the monomer to oxidant ratio during synthesis of PANi nanotubes was fixed. Three samples were investigated and include a pressed pellet of AMPSA doped PANi nanotubes (sample A), a thin film cast from a 2 wt% of AMPSA doped PANi nanotubes dis-
solved in DCA (sample B) and a 10 wt% of AMPSA doped PANi prepared via solid state doping (sample C). The inset to Fig. 2 shows the room temperature normalized current flowing through each sample at a fixed voltage as a function of pump down time. There is an increase in the resistance (reduced current) with time as any adsorbed water is slowly removed from the sample and which in turn leads to localization of charge [15]. After the current stabilized to a relatively steady value, the temperature was varied and the current recorded at a small fixed voltage in the case of the two in-line leads measurement. For the four in-line leads measurement, a small constant current was passed through the outer two leads and the voltage measured across the two inner leads. Resistance measurements via two in-line and four in-line contacts
are shown in Fig. 2 for the case of sample A. No significant
difference due to contact resistance is observed for
$T > 100 \text{K}$
due to the high conductivity of the sample. It is generally
accepted that charge transport in conducting polymers is of
the variable range hopping type.

Fig. 2 shows the normalized
resistance as a function of inverse square root of the temper-
ature according to the quasi one-dimensional hopping model
\[ R(T) = R_0 \exp \left( \frac{T_0}{T} \right) \]
(1)

where $T_0$ is related to the barriers to hopping conduction and
is a measure of the disorder present. The data for samples A
and B is seen to apply while sample C shows metallic behavior
with weak temperature dependence in the temperature range
170–300 K and for which this model is inappropriate. From
the slope of the curves for samples A and B we calculate the
value of $T_0$ to be $1.1 \times 10^4 \text{K}$ and $2.8 \times 10^3 \text{K}$, respectively.

Doping the polymer during the synthesis possibly introduces
disorder that cannot be completely removed when dissolved
in DCA as opposed to solid state doping and dissolving PANi
as in the case of sample C. This can explain the absence of
metallic features in samples A and B. Another possibility
could be that the doping level during the synthesis of the
PANI nanotubes was not complete ($y < 0.5$). Elemental anal-
ysis of sample A yielded 55.76, 5.71 and 10.18% for carbon,
hydrogen and nitrogen with corresponding values calculated
as 58.75, 5.71 and 10.82%, respectively. This suggests that
while AMPSA is incorporated into the polymer there is an ex-
cess of unreacted AMPSA also present and that could hinder
charge transport. Further evidence of this was the color of the
nanotube/DCA solution which appeared brownish-green in-
dicating the presence of oligomers which would increase the
order. Nevertheless, the weaker temperature dependence of the resistance at high temperatures and the lower value of $T_0$ indicate better polymer chain ordering in DCA when compared to that of the pressed pellet.

**4. Conclusions**

AMPSA doped PANi nanotubes were prepared via a
template free method at a fixed dopant/monomer and
monomer/oxidant ratio. The morphology of the nanotubes
were not affected by the reaction time. The average length
of the nanotubes was in the range 2–5 μm and the average
diameter was in the range 200–400 nm. The resistance of the
as prepared polymer was compared with a cast film of the
same polymer after dissolving in DCA and with AMPSA
doped PANi cast from DCA and doped in the solid state. It
was found that the polymer nanotubes did not exhibit metallic
characteristics, however, when dissolved in DCA, the barriers
to charge transport were reduced. This reduction is attributed
to the solvent induced structural order in DCA.

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