Specific heat and magnetic susceptibility of polyaniline nanotubes: inhomogeneous disorder

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Abstract
We report on the specific heat and magnetic susceptibility of polyaniline (PANI) nanotubes, which were self-assembled by a template-free method. It is interestingly found that an electronic specific heat is not observed from present data, and the lattice specific heat of PANI nanotubes can be interpreted in terms of the contributions from both the crystalline and the amorphous phases. The magnetic susceptibility includes a Pauli-like susceptibility and a Curie-type susceptibility. The results reveal an inhomogeneous disorder picture of PANI nanotubes (i.e., PANI nanotubes are composed of crystalline regions and amorphous regions). The crystallinity fraction D_g obtained from the specific heat is about 15% for the measured PANI nanotubes, which indicates that most of the polymer chains in the nanotubes are disordered.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In recent years, conducting polymer nanostructures such as polyaniline (PANI) and polypyrrole (PPy) nanotubes/wires have attracted much attention because of their novel properties (e.g. high conductivity) and potential applications in molecular electronics [1]. Various methods such as template synthesis [2–5] and self-assembly [6–10] have been used for the synthesis of polymer nanostructures. The template synthesis method is an effective route to preparation of micro/nanotubes and nanowires of conducting polymers [2–5]. The main advantage is that the length and diameter of the resulting tubes can be controlled by the selected porous membrane.

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Recently, Professor Wan, one of the authors developed a template-free method [6–10]. It is found that micro/nanotubes of PANI and PPy can be easily obtained using ammonium persulfate as an oxidant in the presence of protonic acid as a dopant without an external template. It has been proved that the essence of the template-free method is a self-assembly process [8, 9]. The reliability and practicability of the method have also been proved by successfully synthesizing PANI (or PPy) nanotubes/wires doped with different protonic acids (e.g., naphthalene sulfonic acid (NSA) [9], HCl, H_2SO_4 and HBF_4 [8]). Compared with the template synthesis method, the self-assembly method is much simpler and cheaper without a template membrane and other expensive instruments. In addition, it is very easy to mass-produce polymer nanotubes by this method. Therefore, it provides us with an opportunity to measure the specific heat of PANI nanotubes.

The electrical properties of PANI nanotubes have already been extensively reported [11–14]. For example, Long *et al* [11, 12] studied the effects of temperature, doping concentration, different dopants and crystallinity on the conductivity of PANI nanotubes. In particular, it is reported that the intrinsic conductivity of an individual PANI nanotube is very high ($32 \ S \ cm^{-1}$) [13] and the contact resistance of crossed PANI nanotubes is much larger than the resistance of an individual nanotube [14]. However, the thermal and magnetic properties of PANI nanotubes have not been extensively explored yet.

In this paper, conducting PANI nanotubes have been prepared by the template-free method. We have measured the specific heat and magnetic susceptibility. The experimental data reveal an inhomogeneous disorder picture of PANI nanotubes.

2. Experimental details

Aniline monomer was distilled under reduced pressure. Ammonium persulfate as an oxidant and camphor sulfonic acid (CSA) as a dopant were used without any further treatment. PANI nanotubes were synthesized by *in situ* doping polymerization in the presence of CSA. The self-assembly that essentially happened during the process of this method was that aniline–CSA salt precipitate or micelles acted as templates in the formation of PANI nanotubes [8, 9]. In particular, these micelles do not need to be removed after polymerization since they act as dopants at the same time. In a typical synthesis procedure, aniline monomer and CSA were mixed in deionized water with stirring, and then oxidant was also dissolved in deionized water and was added slowly into previously cooled mixture. After all the oxidant was added, the reaction mixture was stirred for 24 h. The precipitate was then washed with deionized water, methanol and ethyl ether several times, and finally dried at room temperature in a dynamic vacuum for 24 h. Production of other protonic acid doped PANI nanotubes could be carried out along similar lines.

The dried powders of PANI nanotubes (28 mg) were pelletized by a hydraulic press. The specific heat was measured in the range between 1.8 and 45 K using a PPMS (Physical Property Measurement System, made by Quantum Design, USA) which operated by the thermal relaxation method. The magnetic susceptibility was also measured using the PPMS from 3 to 300 K under a dc magnetic field of 1.0 T.

3. Results and discussion

3.1. The inhomogeneous disorder picture of PANI nanotubes

The structure of the resulting PANI nanotubes was identified by means of UV–visible, infrared and Raman spectra, as well as x-ray diffraction [15]. The morphology of the nanotubes was
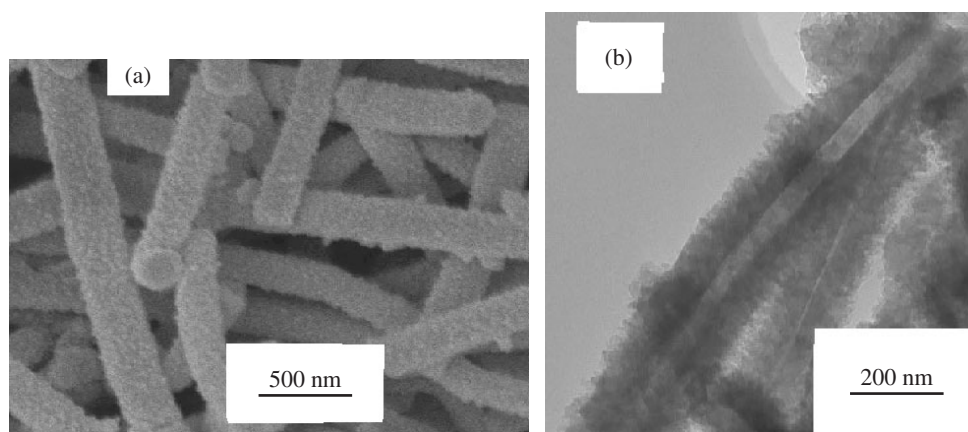
Figure 1. (a) SEM and (b) TEM images of PANI nanotubes synthesized by the template-free method.

confirmed by field-emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figures 1(a) and (b) show the typical SEM and TEM images of PANI nanotubes synthesized by the template-free method. The average outer diameter of the PANI nanotubes is about 180 nm.

According to x-ray structure studies, PANI nanotubes show only partial crystallinity just like granular or fibrillar morphology PANI [16–18], i.e., the polymer chains are not aligned with each other over their whole length, only in small crystallite regions. It is worth noting that a template-synthesized conductive polymer tube has a layer of ordered polymer chains at its outer surface and the polymer chains become progressively disordered toward the centre of the nanotube [19, 20]. Therefore, we propose that self-assembled APNI nanotubes can also be considered as composed of two kinds of regions: crystalline (ordered) regions and amorphous (disordered) regions, and the ordered regions are interconnected by amorphous regions [16–18]. It is easy to see that crystalline and amorphous components of PANI nanotubes will all contribute to the physical properties, but their relative weightings may be different.

3.2. Specific heat

For metals, the specific heat can be written as $C_p(T) = \gamma T + \beta T^3$; here, γT and βT^3 are the electronic and lattice contributions, respectively, to the specific heat. Recently, Kahol *et al* [21, 22] studied the low temperature specific heat of *p*-toluene sulfonic acid (PTSA) doped PANI film and PTSA doped polyaniline–polymethylmethacrylate (PANI–PMMA) blends. They found that the specific heat was represented at low temperatures (0.4–16 K) by the expression $C_p(T) = A + \gamma T + \beta T^3$ for PANI and by the expression $C_p(T) = \gamma T + \beta T^3$ for PANI–PMMA blends; here, the origin of the constant term, A, is not clear. According to the free-electron model, they calculated the corresponding density of states at the Fermi level, $N(E_F)$ (in states eV^{-1} mol^{-1}) $= 0.212\gamma$ (in mJ mol^{-1} K^{-2}), the values of $N(E_F)$ are 3 states $eV^{-1}/(2\text{-rings})$ for PANI film, and 17 states $eV^{-1}/(2\text{-rings})$ for PANI–PMMA blends.

However, at low temperatures (especially when T is lower than 10 K), applicability of the free-electron model to polyaniline is questionable, because early studies on dc conductivity, frequency-dependent conductivity and thermoelectric power indicate that charge carriers in PANI are strongly localized at low temperatures due to disorder and electron–electron
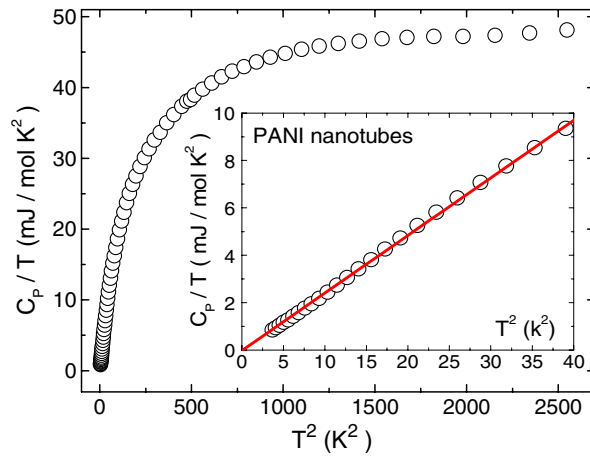
Figure 2. The specific heat of PANI nanotubes, plotted as C_p/T versus T^2. The inset shows the low temperature data (1.8–6.3 K).

interactions [23, 24]. PANI cannot be simply considered as a homogeneously disordered metal or Fermi glass [23, 24].

Figure 2 shows the specific heat $C_p(T)$ of PANI nanotubes between 1.8 and 45 K in the form of a C_p/T versus T^2 plot. The inset shows the low temperature data (1.8–6.3 K). We notice in particular that an electronic specific heat (γT) is not observed from the present data, which is very different from the result of Kahol *et al* [21]. The possible reason is that our sample is much more disordered and less conductive; charge carriers are strongly localized to PANI chains. This result indicates that the free-electron model is not suitable for our self-assembled PANI nanotubes. This point of view is consistent with the Curie-type susceptibility at low temperatures (see the remainder of this paper).

In view of the inhomogeneous disorder picture, we suggest that the lattice specific heat $C_p(T)$ of PANI nanotubes can be expressed as a linear overlap of the heat capacities from the crystalline (C_{cr}) and amorphous (C_{am}) regions weighted by a parameter which expresses the corresponding crystallinity fraction D_g [25]:
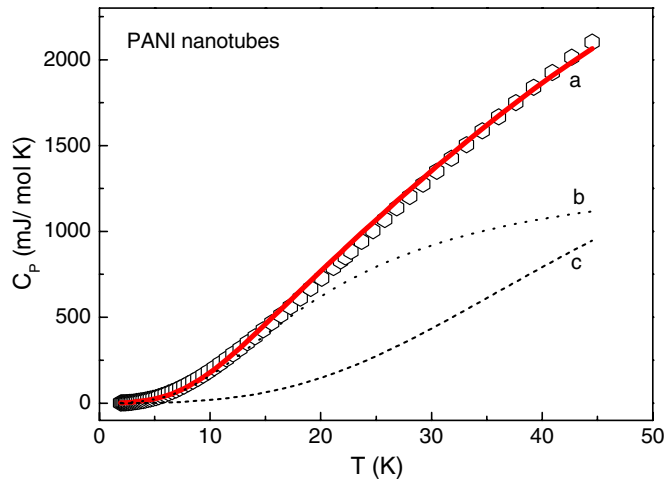
$$C_p(T) = D_g C_{cr}(T) + (1 - D_g)C_{am}(T). \tag{1}$$

The contribution from the crystalline phase $C_{cr}(T)$ has been evaluated by the usual Debye theory, and that from the amorphous phase $C_{am}(T)$ has been analysed in terms of a phonon-fraction model proposed by Avogadro *et al* [26]:

$$C_{cr}(T) = 9\nu R\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 \exp(x)}{[\exp(x) - 1]^2}\, dx, \tag{2}$$

$$C_{am}(T) = 9\nu R\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_{co}/T} \frac{x^4 \exp(x)}{[\exp(x) - 1]^2}\, dx + 9\nu R\left(\frac{T}{\theta_D}\right) Q \int_{\theta_{co}}^{\theta_M/T} \frac{x^2 \exp(x)}{[\exp(x) - 1]^2}\, dx \tag{3}$$

where ν is the number of atoms per formula unit, R is the molar gas constant, Q is a dimensionless constant, θ_D is the Debye temperature, θ_{co} and θ_M are the crossover frequency temperature and the maximal frequency temperature, respectively.

As shown in figure 3, the data can be well fitted using equation (1). The corresponding parameters are obtained as follows: θ_D is 218.5 K, θ_{co} is 84.7 K and θ_M is 318.6 K. In particular, the crystallinity fraction D_g is obtained: about 15%. The value is small compared with that

Figure 3. The temperature dependence of the specific heat of PANI nanotubes; curve (a) shows the fit to $C_p(T) = D_g^* C_{cr}(T) + (1 - D_g)^* C_{am}(T)$, curve (b) shows the contribution from amorphous regions and curve (c) shows the contribution from crystalline regions of PANI nanotubes.

of PANI films ($D_g \sim$ 40–50%) [16, 27]. It demonstrates that most of polymer chains in the present nanotubes are very disordered and the charge delocalization length is small, because the structural coherence length decreases with decreasing percentage of crystallinity [27]. This result provides strong evidence to support the inhomogeneous disorder picture of PANI nanotubes. Figure 3 also shows the contributions from the amorphous phase (curve (b)) and the crystalline phase (curve (c)) to the specific heat. It is evident that at low temperatures the contribution from the amorphous regions is dominant, and much larger than that from the crystalline regions.
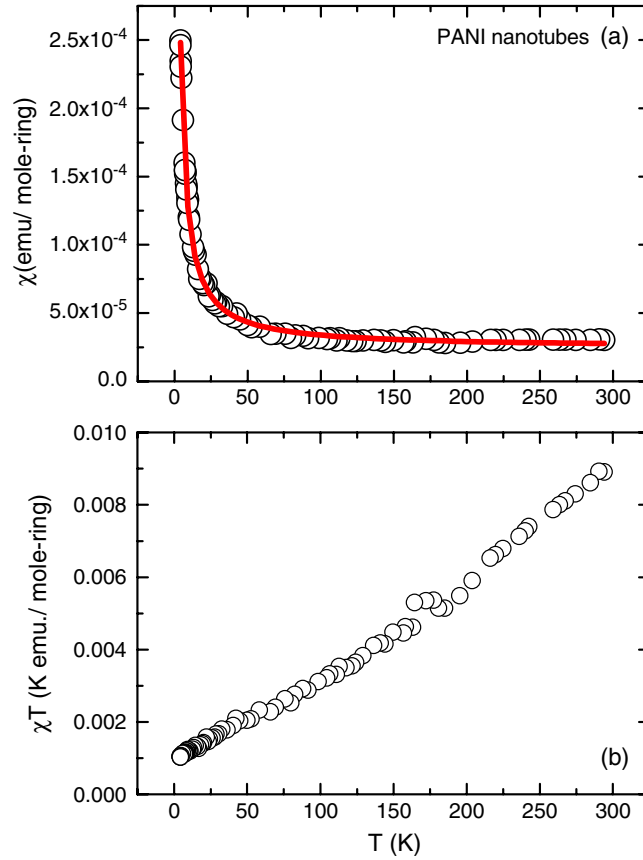
3.3. Magnetic susceptibility

Figure 4 shows the magnetic susceptibility $\chi(T)$ of PANI nanotubes as a function of temperature. Though the conductivity of PANI nanotubes (10^{-2}–10^0 S cm^{-1}) is much smaller than that of fibrillar PANI film (10^2 S cm^{-1}), it is interesting to find that the susceptibility data for PANI tubes can also be written as a sum of a Pauli-like susceptibility χ_P and a Curie-type susceptibility χ_C, which is similar to the case for PANI films [18, 23, 28–30]:

$$\chi(T) = \chi_P + \chi_C = \chi_P + \frac{C}{T} \tag{4}$$

where C is the Curie constant. Figure 4(a) shows the best fit using the above equation. At higher temperatures ($T > 65$ K), the temperature-independent χ_P is about 3×10^{-5} emu mol^{-1}/ring; below 65 K, $\chi(T)$ increases rapidly—the Curie constant $C = 1 \times 10^{-3}$ emu K mol^{-1}/ring.

Although the transport properties such as conductivity and temperature dependence are strongly affected by the morphology of polyaniline, the magnetic properties are less dependent on the morphology, which demonstrates that the magnetic susceptibility of PANI nanotubes also includes contributions from the crystalline and amorphous parts. Since the charge carriers in the amorphous regions are expected to be strongly localized to single polymer chains, the amorphous regions probably give rise to the Curie spins and Curie-type susceptibility. For highly conducting and ordered PANI films (D_g is about 45%), the Pauli-like part is usually attributed to the delocalized or mobile Pauli spins in metallic crystalline regions [18, 23, 29, 30].

Figure 4. The temperature dependence of the magnetic susceptibility of PANI nanotubes: (a) plotted as χ versus T—the curve shows the best fit to $\chi(T) = \chi_P + C/T$; (b) plotted as χT versus T.

However, Kahol *et al* [21] pointed out that the simple interpretation of the 'linear' part of the χT versus T plot in terms of Pauli-like susceptibility may not be correct especially for PANI and other less conducting polymeric materials, because most of the spins are localized. Considering the spin interactions, they proposed a simple exchange coupled pairs model [21, 31]: for an ensemble of $N/2$ spin pairs with a random distribution of exchange couplings up to a maximum value of J_0, $\chi(T)$ can be expressed as

$$\chi(T)T = (Ng^2\mu_B^2/k_BT) \int_0^{J_0} [3 + \exp(-2J/k_BT)]^{-1} P(J)\, dJ. \tag{5}$$

Assuming the distribution function $P(J)$ is constant, the above equation is

$$\chi(T)T = Ng^2\mu_B^2/3k_B + (Ng^2\mu_B^2/6J_0)T\{\ln[3 + \exp(-2J_0/k_BT)] - \ln 4\} + B \tag{6}$$
$$\approx A_1 T + A_2 \qquad (J_0 \leqslant k_BT).$$

Here a constant B has been added to this equation to account for Curie spins in the samples. This model has successfully explained the ageing or moisture effect on PANI and its derivatives [31–33], and may be applicable to our PANI nanotubes due to their small percentage of crystallinity.

4. Conclusions

Polyaniline (PANI) nanotubes have been self-assembled by a template-free method. We have explored the specific heat and magnetic susceptibility of PANI nanotubes. The main conclusions obtained in this paper are summarized as follows:

(1) PANI nanotubes are composed of crystalline regions and amorphous regions. The crystallinity fraction D_g, which depends on the synthesis method and the morphology of PANI, is about 15% for the present nanotubes.
(2) An electronic specific heat of PANI nanotubes has not been observed due to the strong localization of spins. The lattice specific heat can be interpreted in terms of the contributions from both the crystalline and the amorphous phases.
(3) The magnetic susceptibility of PANI nanotubes includes a Pauli-like susceptibility and a Curie-type susceptibility, which can be explained by an exchange coupled pairs model.

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