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A Review on Electronic Transport Properties of Individual Conducting Polymer Nanotubes and Nanowires

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1. Introduction

Quasi-one-dimensional nanostructures, such as carbon nanotubes, inorganic semiconducting nanotubes/wires, and conjugated polymer nanotubes/wires, have drawn considerable attention in the past 20 years due to their importance for both fundamental research and potential applications in nanoscale devices (Kuchibhatla et al., 2007; Xia et al., 2003; MacDiarmid, 2002). Since the electrical conductivity of conjugated polymers can be increased by many orders of magnitude from $10^{-10}$ to $10^{3}$ S/cm upon doping (MacDiarmid, 2002), conducting polymer nanotubes and nanowires (e.g., polycarbonate, polyaniline (PANI), polypyrrole (PPY), and poly(3,4-ethylenedioxythiophene) (PEDOT), poly(p-phenylenevinylene) (PPV)), are promising materials for fabricating polymeric nanodevices such as field-effect transistors (Aleshin, 2006), actuators (Jager et al., 2000), bioand chemical sensors (Huang et al., 2003; Ramanathan et al., 2004), nano light emitting diodes, electrochromic displays (Cho et al., 2005), artificial muscles, and solar cells, etc. (Zhang & Wang, 2006)

By now, conducting polymer nanotubes and nanowires can be prepared by various methods such as the template-guided synthesis (Martin, 1994), template-free method (Wan, 1999), interfacial polymerization (Huang et al., 2003), electrospinning (MacDiarmid, 2001), dilute polymerization (Chio & Epstein, 2005), reverse emulsion polymerization method (Zhang et al., 2006), etc. The template method of polymerization proposed by Martin et al. is an effective technique to synthesize polymer micro-/nanotubes and wires with controllable length and diameter (Cai & Martin, 1989; Cai et al., 1991; Parthasarathy & Martin, 1994; Martin, 1994 & 1995). The disadvantage of this method is that a post-synthesis process is needed in order to remove the template. The template-free method developed by Wan et al. Source: Nanowires Science and Technology, Book edited by: Nicoleta Lupu, ISBN 978-953-7619-89-3, pp. 402, February 2010, INTECH, Croatia, downloaded from SCIYO.COM

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is a simple self-assembly method without an external template (Wan et al., 1999 & 2001; Zhang et al., 2004; Huang et al., 2005; Wan, 2008 & 2009; Long et al., 2003). By controlling synthesis conditions such as temperature and molar ratio of monomer to dopant, polyaniline and polypyrrole nanostructures can be prepared by in-situ doping polymerization in the presence of protonic acids as dopants. The self-assembled formation mechanism in this approach is that the micelles formed by dopant and/or monomer-dopant act as soft templates in the process of forming tubes. The interfacial polymerization method proposed by Kaner et al. (Huang et al., 2003; Huang & Kaner, 2004) involves step polymerization of two monomers or agents, which are dissolved respectively in two immiscible phases so that the reaction takes place at the interface between the two liquids. Interfacial polymerization has been used to prepare various polymers, such as polyaniline nanofibers and nanotubes. Electrospinning is an effective approach to fabricate long polymer fibers using strong electrostatic forces (MacDiarmid, 2001; Tan et al., 2008). For instance, submicron fibers of doped polyaniline blended with polyethylene oxide or pure polyaniline have been prepared by this technique (MacDiarmid et al., 2001; Cárdenas et al., 2007). It should be noted that various spectroscopic results have indicated that the polymer micro- and nanostructures produced by these methods are usually partially crystalline; in other words, the small metallic regions of aligned polymer chains are interspersed with amorphous regions where the chains are disordered. The crystalline fraction depends on synthesis methods and synthesis conditions. At present, fabrication of highly crystalline and metallic polymer nanotubes and nanowires is still a challenge.

In order to fulfill the potential applications of conducting polymer nanotubes and wires, it is necessary to understand the electronic transport properties of individual polymer tubes/wires. The electrical characterization of individual conducting polymer nanotubes/wires has made significant progress during the last decade. There are several strategies for measuring the conductivity of the template-synthesized fibres. The easiest and usual way is to leave the fibres in the pores of the template membrane and measure the resistance across the membrane (Cai & Martin, 1989; Cai et al., 1991; Parthasarathy & Martin, 1994; Martin, 1995; Granström and Inganäs, 1995; Duchet et al., 1998; Mativetsky and Datars, 2002; Duvail et al., 2002 & 2004). Provided the number and diameter of the fibres are known, the measured trans-membrane resistance can be used to calculate the conductivity of a single fiber. However, this method may result in huge uncertainties on values due to the unknown number of connected fibres. Another way is to measure the resistances of compressed pellet or films (membrane removed) of the polymer nanofibres (Parthasarathy & Martin, 1994; Spatz et al., 1994; Orgzell et al., 1996). In fact, all these approaches did not realized the conductivity measurement of an individual fiber directly. Recently, the conductivity measurement of single polyaniline or polypyrrole tube/wire was achieved based on a conductive tip of an atom-force microscope (Park et al., 2002; Park et al., 2003; Saha et al., 2004; Liu et al., 2006). In this two-probe geometry, the contact resistance can be minimized by applying a significant pressure of the tip onto the nanotube/wire. A common approach was generally realized by dispersing nanotubes/wires on patterned micro- or nanoelectrodes prepared by photo-lithography, electron-beam lithography and focused-ion beam deposition, followed by the subsequent searching of nanofibers just lying on the two or four electrodes only (Kim et al., 1999; MacDiarmid et al., 2001; Park et al., 2001; Park et al., 2003; Lee et al., 2004; Aleshin et al., 2004; Samitsu et al., 2005; Kim et al., 2005; Joo et al., 2005; Aleshin, 2006; Gence et al., 2007 & 2008; Callegari et al., 2009). Particularly, focused-ion beam assisted deposition technique has been employed to attach metal microleads on isolated
nanotubes/wires directly (Long et al., 2003a, 2004b & 2005b; Zhang et al., 2006; Huang et al., 2006; Long et al., 2006c; Duvail et al., 2007; Lu et al., 2007; Long et al., 2008a & 2009b). There are also reports demonstrating a directed electrochemical nanowire assembly technique for the fabrication and measurement of polymer nanowire arrays between pre-patterned electrodes (Ramanathan et al., 2004). All these recent investigations contribute significantly to identify and understand the specific electrical behaviour of conjugated polymer nanowires and nanotubes in comparison to the bulk materials. Though a lot of efforts have been done, there are still some key questions needed to be clarified, for example, the effects of the nanocontacts on the electrical measurements, the differences in electrical properties between that of polymer nanotubes/wires and that of their bulk counterparts, the possibility of tuning and controlling the electrical properties of individual nanotubes/wires and so on. These questions are very important to fabrication and characterization of nanodevices based on individual nanofibers.

In this chapter we provide a brief review of recent advances in the study of electronic transport properties (e.g., size effect in electrical conductivity, nonlinear current-voltage characteristics, small magnetoresistance effect, and nanocontact resistance effect) of individual conducting polyaniline, polypyrrole and PEDOT nanotubes/wires.

2. Experimental

2.1 Preparation and characterization

The results reported in this review have been measured for conducting polymer nanotubes and nanowires prepared by template-free self-assembly method and template-guided method. The protonic acids doped polyaniline and polypyrrole nanotubes/wires were prepared by the template-free self-assembly method. The polyaniline nanotubes are chosen as an example to introduce the synthesis procedure. Aniline monomer was distilled under reduced pressure. Ammonium persulphate as an oxidant and camphor sulfonic acid (CSA) as a dopant were used without any further treatment. In a typical synthesis procedure, aniline monomer (0.002 mol) and CSA (0.001 mol) were mixed in distilled water (10 ml) with stirring. The mixture reacted and formed a transparent solution of CSA-aniline salt. Before oxidative polymerization, the solution was cooled in an ice bath. Then an aqueous solution of ammonium persulphate (0.002 mol in 5 ml of distilled water) cooled in advance was added slowly into the above cooled CSA-aniline salt solution. After all the oxidant was added, the mixture was allowed to react for 15 h in the ice bath. The precipitates were then filtered and washed with distilled water and ethanol for several times, and finally dried at room temperature in a dynamic vacuum for 24 h. It was noted that if the synthesis temperature was changed to -10 °C, polyaniline microspheres would be obtained (Long et al., 2004a). p-toluene sulfonic acid and 8-hydroxyquinoline-5-sulfonic acid doped polypyrrole tubes/wires were carried out along similar lines (Huang et al., 2005). The PEDOT nanowires were prepared in templates of polycarbonate track-etched membranes (Duvail et al., 2002, 2004 & 2008b). After the polymerization, polycarbonate (membrane template) was removed by dissolution with a flow of dichloromethane and the nanowires were dispersed onto a SiO$_2$ wafer.

The resulting polyaniline, polypyrrole, and PEDOT nanotubes/wires were characterized by elemental analysis, field-emission scanning electron microscopy (SEM), transmission electron microscopy, infrared and Raman spectroscopy, x-ray diffraction, x-ray photoelectron spectra and electron spin resonance (Zhang et al., 2004; Huang et al., 2005; Duvail et al., 2002 & 2004).
Fig. 1 shows the SEM and TEM images of the obtained polyaniline and polypyrrole nanotubes. The outer diameter is about 80-400 nm for the self-assembled polyaniline and polypyrrole tubes/wires and 20-190 nm for the template-synthesized PEDOT wires. It was found that the polymer tubes/wires prepared by the template-free self-assembly method show a partially crystalline character according to the x-ray diffraction patterns. This partially crystalline feature was also proved by specific heat (Long et al., 2004b) and magnetic susceptibility (Long et al., 2006b) studies on polymer nanotubes/wires.

Fig. 1. Typical SEM images of self-assembled polyaniline nanotubes (a and b) and polypyrrole nanotubes (c and d). Typical TEM images of polyaniline nanotubes (e) and polypyrrole nanotubes (f).

2.2 Fabrication of Pt microleads and electrical measurements
The method used to attach Pt microleads on an isolated polymer nanotube/wire was described in previous publications (Long et al., 2003a & 2005b). First, polymer nanotubes/wires were ultrasonically dispersed in ethanol for template-free prepared nanotubes/wires and in dichloromethane for template-prepared PEDOT nanowires. Then, a drop of solution was placed on an insulating SiO$_2$/Si wafer. After the evaporation of the solvent, an electron microscope was used to find an appropriately isolated nanotube/wire on the wafer. At last, two pairs of Pt microleads typically 0.5 μm in width and 0.4 μm in thickness were fabricated by FIB deposition (Dual-Beam 235 FIB System from FEI Company, working voltage of the system is 5 kV for the electron beam and 30 kV for the focused-ion beam, respectively, current of the focused-ion beam is very small, 1-10 pA, to minimize the modification of the
conjugated polymer). Fig. 2 shows the individual polymer nanotubes/wires and the attached Pt microleads. It was noticed that the resistance of Pt microleads (less than 1 kΩ) is negligibly small compared with that of a single polymer nanotube/wire (several tens or hundreds of kΩ typically).

Fig. 2. Typical SEM images of an isolated polyaniline nanotube/wire (a, b and c) and polypyrrole nanotube/wire (d), and the attached platinum microleads. (Long et al., 2003a & 2005b)

The electrical connection between the Pt microleads and the sample holder was made by highly conductive silver paste and gold wires and the electrical measurements of individual polymer nanotube/wire were carried out using a Physical Property Measurement System from Quantum Design and a Keithley 6487 picoammeter/voltage source, or a Keithley 236 source-measure unit in an Oxford helium gas flow cryostat covering a wide temperature range from 300 down to 2 K. The four-probe resistance was measured by applying a very small current in the linear part of the $I$-$V$ characteristics. The two-probe resistance was determined under $V_{bias} = 0.02$ V, while no rectifying behaviour has been measured in our samples. The $I$-$V$ curves were obtained by scanning the voltage from -4 to 4 V with a step of 0.02 V. The $dI/dV$ curves were numerically derived from the corresponding $I$-$V$ curves. The same polymer nanotube/wire was used for the four-probe measurement first and then for the two-probe measurement. The resistance of the polymer nanotube/wire with a given diameter was measured at least two times, for example, under cooling and during heating with a good reproducibility. In addition, for nanotubes/wires with a given diameter, two or more individual nanowires were measured to check the reproducibility.

3. Electronic transport properties

3.1 Diameter and temperature dependent electrical conductivity

The dependence of electrical conductivity on the diameter of the polymer nanotubes/wires (prepared by the template method) at room temperature has been widely reported (Cai et
It was found that the room-temperature conductivities of nanotubes/wires of conducting polypyrrole, polyaniline et al. can increase from $10^{-1 }$ to about $10^0$ S/cm with the decrease of their outer diameters from 1500 to 35 nm. The possible reason can be ascribed to the enhancement of molecular and supramolecular ordering (alignment of the polymer chains). For PEDOT nanowires prepared by template method, the room-temperature conductivities of the nanowires with diameters of 190, 95-100, 35-40, and 20-25 nm are about 11.2, 30-50, 490-530, and 390-450 S/cm, respectively (Duvail et al., 2007 & 2008a). For polypyrrole nanotubes prepared by template-free method, as shown in Fig. 3, it was found that the polypyrrole tube with a 560-400 nm outer diameter is poorly conductive and the room-temperature conductivity is only 0.13-0.29 S/cm. When the outer diameter decreased to 130 nm, the conductivity of the single nanotube increased to 73 S/cm (Long et al., 2005b). Such conductivity dependence on diameter was observed not only for template-synthesized polymer tubes/wires but also for self-assembled polypyrrole tubes, which indicates that the polymer tubes/wires prepared by these two different methods have similar structural characteristic: the smaller the diameter, the larger the proportion of ordered polymer chains.

Since the electrical properties of conducting polymers are strongly influenced by the effect of disorder and temperature, three different regimes (namely, insulating, critical, and metallic regimes close to the metal-insulator transition) have sorted out based on the extent of disorder and conductivity dependence on temperature (Yoon et al., 1994; Menon et al., 1998; Heeger, 2002). In the insulating regime, for a three-dimensional system, the temperature dependent resistivity usually follows Mott variable-range hopping (VRH) model: $\rho(T) = \rho_0 \exp(T_{M}/T)^{1/4}$. At lower temperatures, when the Coulomb interaction between charge carriers is significant, $\rho(T)$ usually follows Efros-Shklovskii (ES) VRH: $\rho(T) = \rho_0 \exp(T_{ES}/T)^{1/2}$. In the critical regime, for a three-dimensional system close to the metal-insulator transition, the resistivity follows the power-law dependence: $\rho(T)\propto T^{\beta}$, where $\beta$ lies within the range of $0.3<\beta<1$. In the metallic regime, the sample shows a positive temperature coefficient of the resistivity at low temperatures (for example, below 10-20 K for metallic polypyrrole films, Menon et al., 1998).
Fig. 4. The dependence of resistance on temperature of a single polyaniline nanotube ($\sigma_{RT} = 47$ S/cm) and a single polypyrrole nanotube ($\sigma_{RT} = 0.8$ S/cm) in the insulating regime of the metal-insulator transition: (a) and (c) plotted as $\ln R(T)$ versus $T^{-1/4}$; (b) and (d) plotted as $\ln R(T)$ versus $T^{-1/2}$; the temperature dependence of resistance follows 3D-VRH at higher temperatures and ES-VRH at lower temperatures. (Long et al., 2005b)

Long et al. reported temperature dependent resistivity of a single polyaniline nanotube with average outer and inner diameters of 120 nm and 80 nm, which falls in the insulating regime of metal-insulator transition (Long et al., 2005b). The tube’s room-temperature conductivity is 47 S/cm. It was found that the resistivity follows three-dimensional (3D) Mott-VRH above 66 K, and follows ES-VRH model below 66 K, as shown in Figs. 4a and 4b. Here it is noted that from the viewpoint of electrons, the polymer tube/wire with an outer diameter of 120 nm is still three dimensional because the localization length of carriers ($L_C < 20$ nm) is much smaller than the wall thickness or the diameter of the submicrotube. Similar smooth crossover from Mott-VRH to ES-VRH has also been observed in a single polypyrrole microtube (room-temperature conductivity, 0.8 S/cm) at around 96 K (as shown in Figs. 4c and 4d, Long et al., 2005b). However, the crossover temperature ($T_{cros} \sim 66-96$ K) and the characteristic ES temperature ($T_{ES} \sim 316-780$ K) of a single polymer tube/wire are much higher than those of a polyaniline pellet or a polypyrrole film ($T_{cros} < 15$ K and $T_{ES} \sim 29-56$ K), which could be possibly due to enhanced strong Coulomb interaction in polymer nanotubes/wires at low temperatures.
In addition, with the decrease of disorder or diameter of polymer nanotubes/wires, Long et al. found that a 130-nm polypyrrole nanotube with room-temperature conductivity of 73 S/cm is lying close to the critical regime of metal-insulator transition (Long et al., 2005b). Its resistivity follows the power-law dependence: $\rho(T) \propto T^\beta$, as shown in Fig. 5. The fit yields a $\beta$ value of 0.488. Duvail et al. reported that a 100-nm PEDOT nanowire ($\sigma_{RT} \sim 50$ S/cm) fell in the critical regime with a $\beta$ value of ~ 0.78 (Duvail et al., 2007). Furthermore, the 35-40 nm template-prepared PEDOT nanowire ($\sigma_{RT} \sim 490$ S/cm) displays a metal-insulator transition at about 32 K, indicating that the nanowire is lying in the metallic regime (Duvail et al., 2007). However, for a PEDOT nanowire with a diameter of 20-25 nm, though its conductivity is relatively high at room temperature (~ 390-450 S/cm), the nanowire shows very strong temperature dependence ($R(10 K)/R(300 K) \sim 10^5$) or insulating behavior at low temperature. This is possibly due to a confining effect since the value of the diameter (20-25 nm) becomes equal or close to the localization length of electrons ($L_c \sim 20$ nm). In such a case, localization of electrons induced by Coulomb interaction or small disorder must be taken into account for explaining this insulating behavior at low temperatures.

![Fig. 5. The dependence of resistance on temperature (ln $R$ versus ln $T$ plot) for a single 130-nm polypyrrole nanotube in a conductive state close to the critical regime of the metal-insulator transition. (Long et al., 2005b)](image)

### 3.2 Nonlinear I-V characteristics

The current-voltage ($I$-V) characteristics of individual polymer nanowires/tubes such as the polycetylene, polyaniline, polypyrrole, and PEDOT have been explored extensively in the past ten years (Park et al., 2001; Park et al., 2003; Kaiser et al., 2002, 2003 & 2004; Aleshin et al., 2004; Long et al., 2005b). With lowering temperature, a transition from linear to nonlinear $I$-$V$ characteristics is usually observed (Fig. 6a), and a clear zero bias anomaly (i.e., Coulomb gap-like structure) gradually appears on the differential conductance ($dI/dV$) curves (Fig. 6b). Similar transition has also been reported in carbon nanotubes (Kang et al., 2002) and inorganic compound nanowires such as CdS nanoropes (Long et al., 2005a & 2008b), $K_0.27\text{MnO}_2\cdot0.5\text{H}_2\text{O}$ nanowires (Long et al., 2008c), ZnO (Ma et al., 2005) and $\text{SnO}_2$ (Ma et al., 2004) nanowires.

Up to now, several theoretical models such as the space-charge limited current, fluctuation-induced tunneling (Kaiser et al., 2003 & 2004; Kaiser and Park, 2005), Coulomb gap (Kang et
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Fig. 6. I-V characteristics (a) and the corresponding differential conductance (dI/dV) curves (b) of a single polypyrrole nanotube at low temperatures.

al., 2002; Ma et al., 2004; Long et al., 2005b & 2008c), Coulomb blockade (Saha, 2002; Aleshin et al., 2005; Long et al., 2008b), Lüttinger liquid (Aleshin et al., 2004), Wigner crystal (Rahman and Sanyal, 2007) models, etc. have been considered to explain the conduction mechanism of quasi-one dimensional nanofibers. Saha and Aleshin et al. reported single-electron tunneling or Coulomb-blockade transport in conducting polypyrrole and helical polyacetylene nanofibers (Saha, 2002; Aleshin et al., 2005) separately. In addition, power-law behaviors for both I-V characteristics and electrical conductance \( G(T) \) have been reported recently in polyacetylene fibers (Aleshin et al., 2004) and polypyrrole wires/tubes (Rahman and Sanyal, 2007), which are characteristics of one-dimensional systems composed of several Lüttinger liquids or Wigner crystals connected in series, owing to electron-electron interactions (repulsive short-range electron-electron interactions or long-range Coulomb interactions). Particularly, Kaiser et al. (Kaiser et al., 2004; Kaiser and Park, 2005) recently proposed a generic expression (extended fluctuation-induced tunneling and thermal excitation model) for the nonlinear I-V curves based on numerical calculations for metallic conduction interrupted by small barriers:

\[
G = I/V = G_0 \exp(V/V_0) / \{1 + h[\exp(V/V_0) - 1]\} \tag{1}
\]

where \( G_0, V_0 \) and \( h \) are parameters: \( G_0 \) is the temperature-dependent zero-bias conductance; \( V_0 \) is the voltage scale factor, which strongly depends on the barrier energy. Kaiser et al. showed that this expression could give a very good description of the observed nonlinearities in polyacetylene nanofibers, vanadium pentoxide nanofibers, etc. Here, one question arises for the Kaiser expression: Is it still appropriate to fit the nonlinear I-V characteristics of individual polymer nanowires/tubes if the Coulomb interactions are strong and should be taken into account?

The Kaiser expression has been used by Long et al. (Long et al., 2009b; Yin et al., 2009) to numerically calculate the I-V characteristics of individual polyaniline nanotube, polypyrrole nanotubes, PEDOT nanowires, CdS nanorope, and K\(_{0.27}\)MnO\(_2\) nanowire, as shown in Fig. 7a. The fitting results indicate that except at low temperatures and low bias voltages, the Kaiser generic expression can give a good description of the I-V characteristics of individual nanotubes/wires, because the Kaiser expression (extending the Sheng model or fluctuation-induced tunneling and thermal excitation model) has well included the microstructure feature and the conduction feature of conjugated polymer nanofibers (quasi-one-
dimensional metallic conduction interrupted by small barriers). Apparent deviation from the Kaiser expression has been evidenced in the low-temperature \( I-V \) curves as shown in Fig. 7b).

![Figure 7a](image1.png)  
![Figure 7b](image2.png)  

**Fig. 7.** \( I-V \) characteristics of single polypyrrole nanotube with fits to expression (2), at temperatures (a) ranging from 300 K to 100 K and (b) from 80 K to 10 K. (Long et al., 2009b)

![Figure 8](image3.png)  

**Fig. 8.** Zero-field conductance versus temperature, where \( G_0 \) is determined from the fitting data and \( G'_0 \) is determined from the experimental data. (Long et al., 2009b)

Particularly, we compare the values of zero-bias conductance determined from the fitting parameter (\( G_0 \)) with that determined from experimental measurements (\( G'_0 \), obtained from the \( I-V \) curve or the differential conductance). As shown in Fig. 8, the fitting parameter \( G_0 \) decreases smoothly with temperature lowering, but the experimental value \( G'_0 \) sharply decreases below 80-100 K and deviates from \( G_0 \) although it becomes superposable to \( G_0 \) for temperature equal and larger to 100 K. We note that the deviation temperature (about 80 K) is close to and consistent with the crossover temperature (66-96 K) for the crossover from Mott-VRH to ES-VRH, as shown in Fig. 4.

We propose that one possible reason for the deviation is that the Kaiser expression does not include the contributions from the Coulomb-gap occurring in density of states near Femi
level and/or enhanced Coulomb interactions due to nanosize effects, which become important at low temperatures and voltages. (Long et al., 2009b & 2005b; Yin et al., 2009)

### 3.3 Magnetoresistance

The magnetoresistance (MR, defined as MR=$\frac{\Delta R(H)}{R(0)}=\frac{[R(H)-R(0)]}{R(0)}$) of bulk films of conducting polymers have been extensively studied in the past 20 years (Menon et al., 1998). For example, polyaniline, polypyrrole, PEDOT films, and polyaniline composites usually exhibit a positive magnetoresistance at low temperatures (T<10 K) and MR$\propto H^2$ (H is not very large). The mechanism generally involved is the shrinkage of localised wavefunctions of electrons in the presence of a magnetic field or electron-electron interactions (Menon et al., 1998). Whereas highly conductive polyaniline films usually show a negative magnetoresistance at low temperatures, which is mainly attributed to the weak localization effects (Menon et al., 1998; Kozub et al., 2002). Up to date, only a few papers have reported the magnetoresistance of polymer nanotubes/wires (Kim et al., 1999; Park et al., 2001; Kozub et al., 2002; Long et al., 2006a, 2006c & 2009c).

![Fig. 9.](https://www.intechopen.com) The magnetoresistance curves for different temperatures of (a) a single polyaniline nanotube and (b) a pellet of polyaniline nanotubes. (Long et al., 2006a)

Long et al. reported that the magnetoresistance of single polyaniline nanotube and single PEDOT nanowire is positive below 10 K and increases as $H^2$ up to 9 T. Typically, a positive magnetoresistance is expected for hopping conduction, because applying a magnetic field results in a contraction of the overlap of the localized state wavefunctions and thus an increase in the average hopping length. This corresponds to a positive magnetoresistance at sufficiently low temperatures. The theory of positive magnetoresistance has been developed for two cases, without and with electron-electron interactions. In both cases the weak-field MR with strong temperature dependence can be expressed as $\ln(R(H)/R(0)) \propto H^2T^{-3/4}$ (Shklovskii & Efros 1984). However, the magnetoresistance of a single nanotube/wire is much smaller than that of the nanotube/wire pellet at 9 T: MR<5% (2K) for the single nanotube/wire (Fig. 9a), and MR ~ 90% (3K) for the polyaniline nanotubes’ pellet (Fig. 9b, Long et al., 2006a). In addition, when the temperature increases, the magnetoresistance of the single nanotube/wire becomes smaller and close to zero. No evident transition from positive magnetoresistance to negative one was observed. In contrast to that of single nanotube/wire, pellets of polyaniline and polypyrrole nanotubes/wires show a relatively...
larger positive magnetoresistance at low temperatures. With temperature increasing, there is a transition from a positive magneto-resistance to a small negative magnetoresistance at about 60 K. The results indicate that the magnetoresistance in the bulk pellet samples made of polymer nanotubes/wires is dominated by a random network of inter-fibril contacts. The small magnetoresistance effect in individual polymer nanotube/wire has been confirmed in other samples. For example, the low-temperature magnetoresistance (MR~0.1%) in a polyacetylene nanofiber network is rather smaller than that in a bulk polyacetylene film (Kim et al., 1999; Park et al., 2001). A single gold/polyaniline microfiber shows a small positive magnetoresistance (MR<4.1%) below 6 K (Long et al., 2006c). The reason for this weak magnetoresistance effect in individual polymer nanotube/wire is possibly due to the elimination of inter-nanotube/wire contacts, small size and, relatively high conductivity of individual polymer nanotube/wire. (Park et al., 2001; Long et al., 2006a)

3.4 Nanocontact resistance

The contact resistance is often encountered when we study electronic transport in an individual polymer nanowire/tube or polymer nanofiber-based nano-devices. As we know, there are two major factors responsible for the contact resistance magnitude: geometry and insulating layers (potential barriers) between the contacting surfaces. The resistance of a contact is inversely proportional to its area, and is dependent on the surface stiffness and the force holding the two surfaces together. The insulating layers (potential barriers) between the polymer nanowire and the metal electrode are usually formed due to their different energy levels or work functions. A bad (insulating or semiconducting) electronic contact may possess a strongly temperature dependent contact resistance, and thus can seriously complicate or even dominate the measured resistance. In this section, we discuss two kinds of nanocontact resistance: between two crossed polymer nanowires/tubes and between polymer nanowire/tube and metal microlead.

![SEM images showing two crossed polyaniline nanotubes and their attached Pt microleads. (Long et al., 2003c)](image)

Fig. 10. SEM images showing two crossed polyaniline nanotubes and their attached Pt microleads. (Long et al., 2003c)

The nanocontact resistance between two crossed polymer nanotubes/wires has been studied by Long et al. (Long et al., 2003c & 2009a). It was found that the inter-tubular junction resistance of two crossed polyaniline nanotubes (Fig. 10) is very large, about 500 kΩ at room temperature, which is nearly 16 times larger than the intra-tube (intrinsic) resistance of an individual PANI nanotube (about 30 kΩ, Long et al., 2003c). This result explains straightforwardly why an individual polyaniline nanotube has a much higher room-
temperature conductivity (30.5 S/cm) than that of a pellet of polyaniline nanotubes where the measured resistance is dominated by the inter-fibril resistance (0.03 S/cm). For crossed PEDOT nanowires, the junction resistance (between the two nanowires) at room temperature can vary from 885-1383 kΩ for one sample and to 370-460 MΩ for another sample, which is respectively comparable or much larger than the intrinsic resistance of the PEDOT nanowires. In addition, the contact resistance shows a stronger temperature dependence ($R(72K)/R(300K)$ is about $120 \sim 141$) and could be fitted by a thermal fluctuation-induced tunneling (FIT) model (Long et al., 2009a). It should be noted that the nanojunction resistance is comparable to the intrinsic resistance of polymer nanotube/wire and shows large sample-sample variations. The possible reasons could be attributed to the contamination of the nanotube/wire surfaces (polycarbonate for template-prepared PEDOT nanowires, solvent impurities or water adsorption), the variation of the junction area between the two nanotubes/wires, and the self-formation conditions of the junction. It has to be mentioned that no special effort was made to control the formation of the junction between the two crossed nanotubes/wires during fabrication.

Fig. 11. The temperature dependence of the four-probe resistance ($R_{4P}$) and the two-probe resistance ($R_{2P}$) of (a) an individual PEDOT nanowire with a diameter of 35 nm, which falls in the metallic regime of the metal-insulator transition, and (b) an individual PEDOT nanotube with a diameter of 190 nm, which falls in the insulating regime of the metal-insulator transition (Long et al., 2010). The nanocontact resistance between a polymer PEDOT nanowire and a platinum microlead prepared by FIB deposition has also been studied by Long et al. (Long et al., 2010). It was found that the nanocontact resistance (determined from four-probe resistance and two-probe resistance of the same nanowire) is in the magnitude of 10 kΩ at room temperature and can reach 10 MΩ at low temperatures, which, in some cases, is comparable to the intrinsic resistance of the PEDOT nanowires. For a semiconducting polymer nanowire in the insulating regime of the metal-insulator transition, the four-probe resistance is quite close to the two-probe resistance because the contact resistance is much smaller than the intrinsic resistance of the polymer nanowire as shown in Fig. 11a (Long et al., 2008a & 2010). However, for a nanowire that falls in the metallic regime of the metal-insulator transition (for example, the 35 nm PEDOT nanowire as shown in Fig. 11b, Long et al., 2010), the metallic nature of the measured polymer fibers could be over shadowed by the two-probe measurement although the nanowire shows a relatively high electrical conductivity at room
temperature (390-450 S/cm). It can be attributed to the nanocontact resistance is much larger than the intrinsic resistance of the nanowire especially at low temperatures. We note that, for individual RuO$_2$ nanowires (Lin et al., 2008), the temperature dependence of the two-probe resistance indicates that the nanowire is semiconducting, whereas the four-probe resistance dependence of the same nanowire shows the measured nanowire is metallic. So, in order to explore the intrinsic electronic transport properties of individual nanowires, especially in the case of metallic nanowires, the four-probe electrical measurement is necessary because nanocontact resistance cannot be excluded in a two-probe measurement.

4. Conclusion

During the past 15 years, significant progress has been made in synthesis, structural and electrical characterizations, and applications of conducting polymer nanotubes/wires. In this chapter, a brief review of the recent advances in electronic transport properties of individual conducting polymer nanotubes/wires prepared by both the template-free self-assembly method and the template method is presented. Results with broad interest have been discussed. For example, it was found that the electrical conductivity of the individual polymer tubes/wires increases by several times of magnitudes with decreasing outer diameter (size effect in electrical conductivity). The crossover from Mott to Efros-Shklovskii variable-range hopping conduction was observed at a relatively high transition temperature in single nanotubes/wires (enhanced Coulomb interaction effect). The low-temperature magnetoresistance of a single polymer tube/wire is positive and quite smaller than those of the nanotube/wire pellets (small magnetoresistance effect). The intrinsic resistance of an individual nanotube is much smaller than the contact resistance of two crossed nanotubes (nanocontact resistance effect). In addition, individual polymer tubes/wires show obvious transition from linear to nonlinear $I$-$V$ curves at low temperature, and a clear zero-bias anomaly with Coulomb gap-like structure appeared on the differential conductance curves at low temperatures. These results indicate that the electrical properties of isolated conducting polymer tubes/wires are different from those of bulk polymer pellets or films in some cases due to their nanoscale diameters. However, in order to eliminate nanocontact resistance and reveal the intrinsic electronic transport properties of an individual nanotube/wire, it is still quite important to develop new or improved conductivity measurement approaches on a single nanofibre. Furthermore, due to the complicated microstructures of conducting polymers, there are still problems and challenges to fulfill their applications in nanoscale devices, such as whether fully metallic conducting polymer nanotubes/wires, which show metallic behavior from room-temperature down to low temperatures, can be prepared through improving their molecular or supramolecular ordering. In addition, reproducibility and/or controllability of individual polymer nanotubes/wires are also a problem, since their electrical properties are sensitive to many factors such as doping level, extent of disorder, diameter, temperature, aging effect, etc.

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6. References


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A Review on Electronic Transport Properties of Individual Conducting Polymer Nanotubes and Nanowires


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This book describes nanowires fabrication and their potential applications, both as standing alone or complementing carbon nanotubes and polymers. Understanding the design and working principles of nanowires described here, requires a multidisciplinary background of physics, chemistry, materials science, electrical and optoelectronics engineering, bioengineering, etc. This book is organized in eighteen chapters. In the first chapters, some considerations concerning the preparation of metallic and semiconductor nanowires are presented. Then, combinations of nanowires and carbon nanotubes are described and their properties connected with possible applications. After that, some polymer nanowires single or complementing metallic nanowires are reported. A new family of nanowires, the photoferroelectric ones, is presented in connection with their possible applications in non-volatile memory devices. Finally, some applications of nanowires in Magnetic Resonance Imaging, photoluminescence, light sensing and field-effect transistors are described. The book offers new insights, solutions and ideas for the design of efficient nanowires and applications. While not pretending to be comprehensive, its wide coverage might be appropriate not only for researchers but also for experienced technical professionals.

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