Electrical Resistance of Long Oligothiophene Molecules

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The electrical resistance of single oligothiophene molecular wires with lengths ranging from 2.2 nm (5-mer) to 9 nm (23-mer) was measured by the break junction method. A linear relationship between the molecular length and resistance was found for molecules longer than 11-mer, whereas an exponential increase in the resistance was observed for molecules shorter than 11-mer. These results indicate that the carrier transport mechanism changes from tunneling to hopping at around 11–14-mer (5.6 nm).

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The mechanism of charge transport through single molecules is a key issue in molecular electronics. It has been demonstrated experimentally as well as theoretically that the resistance of a metal/single-molecule/metal (MMM) junction, R, shows a tunneling behavior expressed as

$$R = R_0 \exp(\beta l), \quad (1)$$

where R_0 is the contact resistance, β is the pre-exponential factor representing the efficiency of charge transmission through molecules, and l is the molecular length.[1–3)]

The parameters R_0 and β are determined by measuring the resistance of MMM junctions as a function of molecular length. Among a variety of measurement techniques,[1)] mechanical break junction (BJ) method using a scanning tunneling microscope (STM) has proven to be one of the most reliable techniques for quantitative analysis of the parameters.[4)] The contact resistance, R_0, is estimated by the BJ method for alkanes connected to gold electrodes via various anchor groups such as –COOH (1800 kΩ),[5)] –NH_2 (370, 350 kΩ),[6)] –S (20 kΩ),[5)] –SMe (270 kΩ),[6)] and –PMe (130 kΩ).[6)] The β value of π-conjugated molecules is also estimated to be 0.004–0.2 $Å^{-1}$,[7–11)] which is much smaller than that of saturated hydrocarbons (0.52–0.96 $Å^{-1}$).[4–6,12,13)]

In addition to tunneling transport, the contribution of the thermally activated process is sometimes evident in the temperature dependence of electrical conductance.[14–19)] The activation energy observed for π-conjugated oligomers, approximately 0.2–0.35 eV,[14,17)] is in good agreement with the energy for the rotational motions, indicating that localized electronic states generated through twisting of the molecule may act as hopping sites.

Theoretical studies have shown that the charge carrier transport is dominated by tunneling for small molecules and hopping for longer ones.[20–24)] Thus, exponential and linear dependences of resistance on molecular length are expected for tunneling and hopping conductions, respectively.

The change of the transport mechanism was experimentally demonstrated in the charge transport measurements of DNA.[25)] Recently, Choi *et al.* reported that the length dependence of the resistance of oligophenyleneimine (OPI) *monolayers* changed from exponential to linear at a thickness of 4 nm on the basis of the results of conductive atomic force microscopy.[26)] It is, however, difficult to conclude from the results of this method that charges are transported through a single molecule, particularly in the hopping conduction regime since approximately 100 molecules were estimated to exist in the junction concerned. We have studied the conductance of a series of single oligothiophene molecules with the lengths ranging from 2 to 9 nm by BJ method.[10,27)] In this paper, we demonstrate the transition of conductance behavior from tunneling to hopping at the molecular length of approximately 5.6 nm.

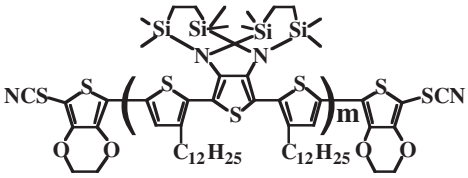

Fig. 1. Oligothiphene molecules used in this study: m = 1–7.

Figure 1 shows the structure of oligothiophenes used in the present study. The molecules were prepared according to the general synthesis protocols described previously.[28–30)] The thiocyanate group attached to both ends of the molecule is known to act as an anchor to gold electrodes.[31–33)] The molecules are described as $(2+3m)$T-di-SCN or $(2+3m)$-mer where $m = 1-7$, i.e., 5–23-mer.

The STM-BJ measurement was carried out with mechanically cut gold tips in a 1 mM toluene solution of the molecules at room temperature. The substrate used was epitaxially grown Au(111) on mica. Procedures for BJ measurements have been described previously.[10)] An STM tip is repeatedly brought into and out of the contact with a substrate in the solution with a bias voltage of 100 mV. When the tip is pulled up after contact with the substrate, the measured conductance changes in a stepwise manner at integer multiples of quantum conductance $G_0 = 2e^2/h$ ($= 77.4\,\mu S$) owing to the formation of a quantum point contact of Au. After the atomic contact of metals is broken, a new sequence of conductance steps is observed. These conductance steps are attributed to the conductance of MMM junctions formed between the tip and the gold substrate. The conductance of the MMM junction is determined from a conductance histogram created from 500–1000 measurements.

Figure 2 shows typical conductance transient curves obtained during the retraction of the STM tip after contact with the substrate in the 5T-di-SCN solution. Plateaus

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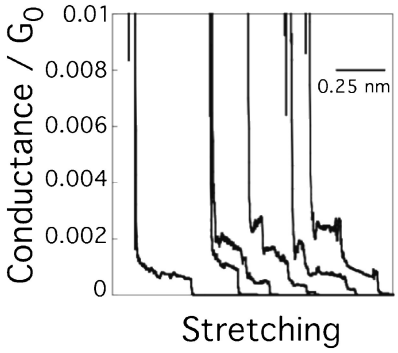

Fig. 2. Conductance transient curve of 5T-di-SCN.

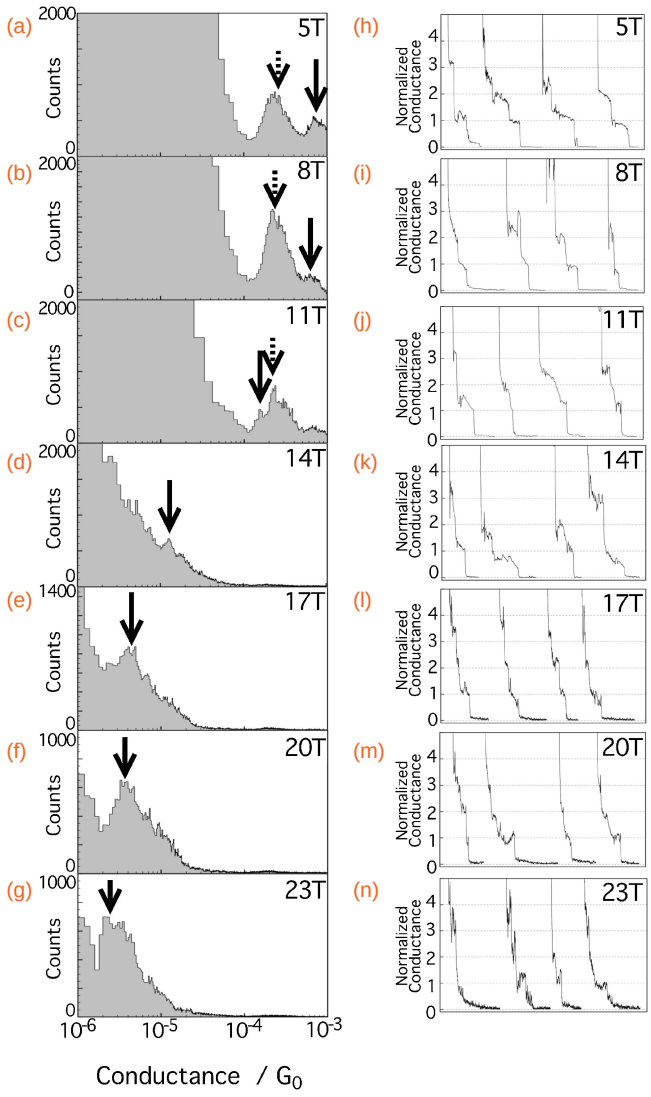

Fig. 3. Conductance histograms of 5T (a), 8T (b), 11T (c), 14T (d), 17T (e), 20T (f), and 23T (g)-di-SCN. (h–n) Conductance transient curves showing plateaus at the integer multiples of the fundamental conductance values determined from the peaks in the histograms. The vertical axis is normalized to the fundamental conductance values of each molecule.

observed at values smaller than G_0 were attributed to the conductance of the MMM junctions since no plateaus were observed in this region in pure solvent. As the molecules became longer, the following phenomena were observed in

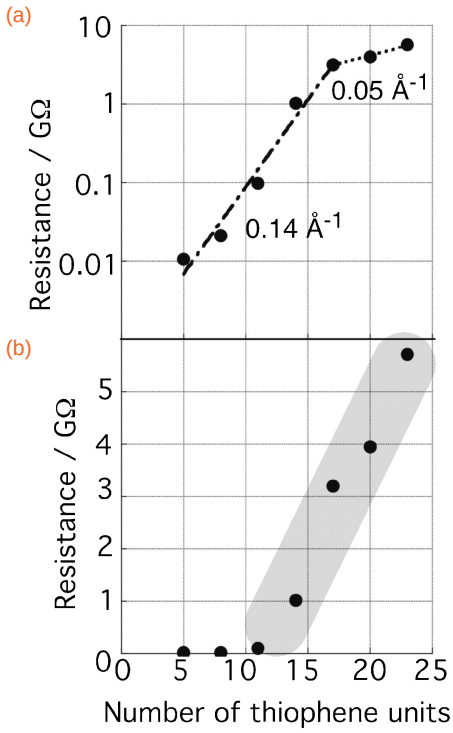

Fig. 4. Semilog (a) and linear (b) plots of the resistance as a function of the number of thiophene units.

the conductance transient curves. First, the possibility of the appearance of plateaus indicating the formation of the desired MMM junctions decreases, probably due to the decrease in the number of molecules in the unit area and in the mobility of molecules. Second, the signal-to-noise ratio became worse indicating that the wide variety of conformation of long molecules resulted in the fluctuation of conductance. These factors reduced the contrast in the histograms, as shown below.

Figures 3(a)–3(g) show the conductance histograms of 5, 8, 11, 14, 17, 20, and 23T-di-SCN, respectively.[34] The solid arrows in Fig. 3 indicate the peak values observed. The peaks indicated by the dashed arrows are not related to the conductance of oligothiophene molecules because these peaks were observed in the solution of CH_3SCN and mono-5T-SCN molecules, as reported previously.[10]

In the conductance transient curves, a clear stepwise decrease was sometimes observed, indicating that the number of molecules between the STM tip and the substrate decreases one by one in the retracting process as shown in Figs. 3(h)–3(n). On the basis not only of the histogram but also of the transient curves, we have estimated the fundamental values of conductance of each molecules.

Figure 4(a) shows a semilog plot of the resistance as a function of the number of thiophene units. The tunneling transport was evident from the exponential increase in the resistance with molecular length up to 17T-di-SCN (6.7 nm). The β value calculated from the slope is 0.16 $Å^{-1}$, which is in good agreement with the previous result.[10,35]

A much weaker dependence of the resistance on molecular length ($\beta = 0.05$ $Å^{-1}$) was observed for molecules longer than 17T-di-SCN. The transition of β to the extremely small

value suggests that the transport mechanism changes to hopping. As shown in Fig. 4(b), the linear relationship between the resistance and the molecular length, which is expected for hopping conduction, is observed for molecules longer than 14T-di-SCN. We concluded that the transport mechanism changed at the molecules with the length of approximately 5.6 nm (14-mer)–6.8 nm (17-mer).

The change of the slope observed in Fig. 4(a) clearly indicates the transition of the major transport mechanism. The β (0.16 $Å^{-1}$) observed for the short oligothiophene molecules is comparable to that observed for OPIs in the hopping regime (0.09 $Å^{-1}$).[26] It seems possible that the hopping conduction has some contributions to the carrier transport in the short oligothiophene molecules.

In summary, the resistance of single oligothiophene molecules with lengths from 5-mer (2.2 nm) to 23-mer (9 nm) was measured. The conduction mechanism was found to change from tunneling to hopping at around 14-mer (5.6 nm) in the oligothiophene molecules used in this study.

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35) The length of a thiophene unit is estimated to be 0.4 nm.