A molecular wire containing polypyrrolyl conjugate bonds has been prepared by a chemical adsorption technique using 1,1,1-trichloro-12-pyrrolyl-1-siladodecane (PNN) and an electrooxidative polymerization technique, and the conductivity of the molecular wire without any dopant has been measured by using AFM/STM at room temperature. When sample dimension measured was about 0.3 nm (thickness of the conductive portion in the PNN monomolecular layer) × 100 μm (the average width of an electric path) × 2 mm (the distance between Pt positive electrode and the AFM tip covered with Au), the conductivity of the polymerized PNN molecular wire at room temperature was larger than 1.6 × 10^5 S/cm both in an atmosphere and in a vacuum chamber of 10^-5 Torr. The activation energy obtained by Arrhenius’ plots was almost zero in the temperature range between 320 and 450 K.

1. Introduction

Although there have been numerous investigations into the preparation of conductive polymers and those electric-properties, the conductivity of the conjugate bonds itself has not been measured at present.

W. A. Little reported about forty years ago from a realistic estimation of the matrix elements and density of states in certain organic polymers having a long unsaturated polyene chain that superconductivity should occur even at temperatures well above the room temperature [1]. Nevertheless, the superconductivity has not been confirmed yet at room temperatures on the organic polymer.

Chiang et al. reported that the highest room-temperature results were obtained by doping cis-(CH)x with AsF5+ to yield cis-[CH(AsF5)x]x with σ(300 K) = 560 Ω⁻¹cm⁻¹. The value was comparable to that obtained with single crystals of the organic metal tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) [2]. But the measurement of the conductivity was carried out on the bulk polymer, and the conductivity might contain hopping conduction between polycetylene fibrils. Thus the conductivity of the polycetylenic conjugated bonds itself might no been measured directly.

Moreover Intelmann et al. recently reported the preparation technique of ultrathin polypyrrole films using a chemically adsorbed pyrrolyl monolayer as an adhesion promoter [3].

Thereupon, we have tried to prepare superlong polypyrrole conjugate bonds as a molecular wire by a chemical adsorption technique with 1,1,1-trichloro-12-pyrrolyl-1-siladodecane (PNN) and an electrooxidative polymerization technique and measured the conductivity of the superlong polypyrrole conjugate bonds in the PNN monomolecular layer directly.

2. Experimental

2.1. Materials. A long chain molecule (PNN) having a pyrrolyl group at the molecular end, a trichlorosilyl group
at the other end, and a hydrocarbon group at the middle portion was synthesized. The pyrrolyl group, trichlorosilyl group, and hydrocarbon group were introduced for preparing conjugate bonds by electrooxidative polymerization, chemical adsorbing to a substrate surface having an active hydrogen such as hydroxyl group (–OH), and increasing flexibility and electric resistance of the molecule at electrooxidative polymerization, respectively. The synthesis technique will be reported elsewhere. Although there were some reports of self-assembled monolayer of pyrrole-containing alkanethiol, those were not tried this time, because the self-assembled monolayer of alkanethiol is not so durable for electro-oxidation and it cannot be prepared on an insulator such as a glass plate [4, 5].

2.2. Procedure. Samples were prepared using following steps, and measured: chemically adsorbed monomolecular layers were prepared with PNN on a Tempax (Schott Glas) glass plate (26 × 75 × 1.1 mm$^3$) having two parallel Pt electrodes (deposition thickness was about 50 nm, and gap was about 2 mm) at room temperature, wherein PNN molecules anchored to the substrate surface were aligned at about 45 degrees to the length direction of the electrodes by pulling up from a washing solvent. The monomolecular layer prepared could be confirmed by multiple external reflection (MER) FTIR spectroscopy [6], and it was supported by our studies [7, 8] that monomolecular layers can be prepared on the substrates having active hydrogen such as the hydroxyl group by using chemical adsorption (CA) technique. The CA technique and alignment technique were also reported in some studies [9, 10].

And then electrooxidative polymerization was carried out in pure water by applying 40 VDC between the two Pt electrodes with a 2 mm gap at room temperature for about 7 hours. The immersion length in pure water was also 50 mm.

Although Satoh et al. tried electrochemical polymerization in an aqueous medium utilizing various electrolytes, in our experiment, the electrochemical polymerization was carried out in distilled water in order to avoid the electrolytes doping into the monolayer [11], wherein the main current at the electro-oxidation was used for electrolysis of water and a little current was used for polymerization, because many bubbles were generated at two electrode edges during the electrolysis.

For confirming the electric path, polypyrrole decoration was also carried out by applying DC voltages between the third (negative) electrode and the two (positive) Pt electrodes shorted in a pure water-containing pyrrole.

The I-V curves were measured by applying different DC voltages between the two parallel Pt electrodes at room temperature in an atmosphere and in a vacuum chamber of 10$^{-5}$ Torr. Thus the measurements of the I-V curves were carried out using two-probe method. Measurements of activation energies were also carried out at different temperatures in the temperature range between 320 and 450 K by two-probe method in a vacuum chamber of 10$^{-5}$ Torr.

Moreover, for searching electric paths in the monomolecular layer between the two parallel Pt electrodes and measuring the conductivity of these directly, an atomic force microscope (AFM, Type: SPI3800, Seiko Instruments Inc.) combined with a scanning tunneling microscope (STM) for simultaneous operation (AFM/STM) [12] was used. Thus the measurements of the conductivities at the electric path were also carried out using two probes method at room temperature in an atmosphere.

Of course, we know that four probes method should be used to measure correct conductivity of the electric path, but it was hard to attach four electrodes of micron scale to the electric path directly, because the electric path was invisible and too small.

3. Results and Discussion

3.1. Confirmation of the PNN Monomolecular Layer. The MER FTIR spectrum of the PNN monomolecular layer deposited on the SiO$_2$/Al/Glass substrate is shown in Figure 1. Although the absorption peak due to pyrrolyl group was very weak, the split and strong absorption bands due to asymmetric CH$_2$ stretching (ν as) and symmetric CH$_2$ stretching (ν s) vibrations were observed clearly at 2930 cm$^{-1}$ (ν as) and 2860 (ν s) cm$^{-1}$, respectively, indicating that a densely packed PNN monomolecular layer is formed and the PNN molecules in the layer are aligned along a fixed direction [6–8].

![Figure 1: MER FTIR spectrum of the TNN monomolecular layer on a glass plate.](image)

3.2. Electrooxidation Polymerization. Electrooxidation current change is shown in Figure 2. The electric resistivity of the pure water used at the electro-oxidation was about 10$^7$ Ωcm. The electric current was almost 0 mA at the starting point of electro-oxidation. The electro-oxidation current increased gradually from 0 (starting point) to about 5 mA (3.5 hours later) with increasing the electrooxidative polymerization time. The current increased markedly at about 3.7 hours and changed up and down from about 15 mA to 30 mA in a range from several seconds to a few minutes’ cycle in the pure water after the time, as shown in Figure 2.

In this case, although the polypyrrolyl conjugate bonds contributing to electric conduction are formed self-assembly
3.3. Search of Electric Paths. We searched electric paths on the same sample used above by a decoration technique using electrochemical polymerization in an aqueous solution containing pyrrole. After the decoration, several black polypyrrole wires (not molecular wire, and should be only on the electric paths of the polymerized PNN monomolecular layer) connecting two electrodes of 50 nm width (immersed width in water at the electrooxidative polymerization) and 2 mm gap were observed between the two electrodes, as shown in Figures 3(a) and 3(b). All the wires were connected to Pt⁺ electrode, and the widths of wires near the Pt⁺ electrode were wider than those near Pt⁻ electrode, as shown in Figure 3(b), indicating that the polymerization of the PNN monomolecular layer occurred from the Pt⁺ positive electrode.

When the polymerization is not complete in connecting between two electrodes, pure water acts as a conductor connecting between the conjugate bonds, which was formed by the polymerization of monomolecular layer from the Pt⁺ electrode and connected to the Pt⁺ electrode but not connected to the Pt⁻ electrode, and the Pt⁻ electrode. When the polymerization of the PNN monomolecular layer becomes completed in connecting between two electrodes, most of the electric current of about 30 mA runs through the several electric paths at the electro-oxidation time of about 3.7 hours. Then the electric current decreases or increases depending on the connection of the electric paths between two electrodes. That is, when some of the electric paths are destroyed by overconcentration of the electric current, the electric current decreases, and when the electric paths are recompleted by the electro-oxidation, the electric current increases again. This may indicate that some PNN molecular wires connected between two Pt electrodes at the current of 30 mA.

3.4. Measurement of the I-V Curves. On another sample after the polymerization, I-V curves were measured. The I-V curves measured in an atmosphere and in a vacuum chamber of 10⁻⁵ Torr were similar to each other, as shown in Figure 4. Currents increased linearly with applied voltages, indicating that the sample and circuits for measuring are ohmic and the effects of adsorbed water may be neglected in an atmosphere. Thus it is easy to calculate the electric resistance of the sample, regardless of the contact resistance. However, it was difficult to calculate the electric conductivity of the electric paths (portions of the polymerized PNN monomolecular layer), because the electric paths were invisible and too small, and the number of paths and widths was unknown.

3.5. Estimation of the Activation Energy. Electric currents at temperatures in the range between 320 and 450 K were measured in a vacuum chamber of 10⁻⁵ Torr and plotted as a function of 1/T to estimate the activation energies of conductivity using Arrhenius's plots under three applied voltages of 0.01, 0.1, and 0.5 V DC, as shown in Figure 5. Slopes of three plots at applied voltages of 0.01, 0.1, and 0.5 V were almost zero, indicating that all the activation energies were almost zero between 320 and 450 K.

Accordingly, this material may be neither metallic nor semiconductor like, because if the material was metallic, the activation energy should be negative and if the material was semiconductor like, the activation energy should be positive.

3.6. Direct Measuring of Conductivity of the Polymerized PNN Monomolecular Layer. For searching the electric paths in the monomolecular layer directly and measuring the conductivity of these directly, an atomic force microscope (AFM) combined with scanning tunneling microscope (STM) for simultaneous operation (AFM/STM) [12] was used.

A topographical and a current were simultaneously obtained on the other sample without the decoration by AFM and using an AFM tip covered with Au, respectively, as shown in Figures 6(a) and 6(b). The sample used here was also one after 7 hours of electrolysis. The topographical image (Figure 6(a)) and the current image (Figure 6(b)) were obtained at the same position corresponding to the positions indicated by B (near Pt⁺ electrode) in Figure 3(b).

On the topographical image (Figure 6(a)) obtained by AFM, there was no boundary between pp and p portions, because there was a PNN monomolecular layer on these portions and there was no difference of thickness. On the other hand, a boundary of the Pt⁺ electrode and the PNN monomolecular layer (pp and p) could be distinguished clearly, because there was a large difference of thickness.

On the current image (Figure 6(b)) obtained using an AFM tip covered with Au, a boundary of the PNN monomolecular layer pp and the PNN monomolecular layer p could be distinguished clearly, because there were large differences in currents. But a boundary of the Pt⁺ electrode and the PNN monomolecular layer pp could not be distinguished, because these currents were similar to each other, wherein the difference between the portion pp and the portion p was caused by the current differences of the monomolecular layer. I-V curves pp and p measured at black and white cross-points in Figure 6(b) are shown in Figure 6(c), respectively.
Figure 3: A schematic view (a) of a sample after electrooxidative polymerization. A micrograph taken after the polypyrrole decoration (b) at the position A indicated in (a). It is observed that the electric path composed of polypyrrolyl conjugate bonds grew from the Pt⁺ electrode by electrooxidative polymerization.

On the other hand, no conduction region corresponding to pp' was observed near the Pt⁻ electrode. These results may indicate that the PNN monomolecular layer at pp and pp' was polymerized and became conductive, but the PNN monomolecular layer at p and p' was not polymerized and was kept nonconductive, and conductivity at the portion of pp' is larger than that of Pt, because the thickness of Pt⁺ electrode is much thicker than that of the PNN monomolecular layer and currents of these were similar to each other. The polymerization of the PNN monomolecular layer grew from the positive electrode, and the polypyrrolyl conjugate bonds contributing to electric conduction are formed on the substrate from the positive electrode to negative electrode self-assemblly perpendicular to the two electrodes by the applied electric field, but the polymerization did not occur from the negative electrode.

Moreover, we found the electric path (molecular wire) in the monomolecular layer and measured the conductivity of the polymerized PNN monomolecular layer directly. Figures 7(a), 7(b), and 7(c), respectively, show topographical images, current images and the I-V curves. They were obtained simultaneously on the electric path of the same sample which was used for obtaining Figure 6 by the same technique. The topographical images D1, E1, and F1, and the currents images, D2, E2, and F2, and the I-V curves D3, E3, and F3 were simultaneously obtained at the same positions corresponding to the positions indicated by D, E, and F in Figure 3(b), respectively.
On the topographical images D1 and F1 in Figure 7(a), boundaries of the polymerized portion of the PNN monomolecular layer (pp) and the Pt electrodes (Pt$^+$ and Pt$^-$) could be distinguished clearly, but no boundary was observed on the current images D2 and F2 in Figure 7(b).

On the other hand, on the topographical image E1 in Figure 7(a), the boundary of the polymerized portion of the PNN monomolecular layer (pp) and the unpolymerized portion (p) could not be distinguished, but, on the current image E2 in Figure 7(b), black and white portions were observed clearly. This indicates that the PNN monomolecular layer is polymerized at the bottom portion (pp$'$) in the image E2, and the PNN monomolecular layer is unpolymerized at the top portion (p$'$).

Accordingly, the electric path (molecular wire), which was composed of the polymerized PNN monomolecular layer containing polypyrrolyl conjugate bonds and similar to that confirmed by the above decoration technique, was observed directly by the current images. When the width of electric path without the decoration was measured directly using the AFM tip covered with Au, the average of the width was about 100 $\mu$m.

Moreover, we tried to measure conductivity at the electric path (three points on the polymerized portion of the PNN monomolecular layer indicated by cross-marks on the images D2, E2, and F2 in Figure 7(b)) using the AFM tip covered with Au in an atmosphere at room temperature. The I-V curves D3, E3, and F3 observed at the three cross marks in Figure 7(b) are shown in Figure 7(c). The slopes of the three I-V curves obtained were very similar to each other, as shown in Figure 7(c).

Although the I-V curves D3, E3, and F3 are a little different from each other, it is thought that the differences were caused by the timing silt. As the slopes of the three I-V curves were very similar to each other, the resistances calculated with the slope of the three curves were almost the same.

When the applied voltage between Pt$^+$ electrode and the AFM tip covered with Au was 0–2 mV, the slopes were about 250 nA/mV at the cross-mark on the image F2. That is, electric resistance at the F2 point was about 4 k$\Omega$, and since the dimension of the electric path was about 0.3 $\times$ 10$^{-9}$ cm$^2$ (cross-sectional area of the electric path; average width of the electric path: about 100 $\mu$m and thickness of the conjugate bonds: 0.2 nm) $\times$ 2 mm (length from the Pt electrode to the tip at the cross-mark in the image F2), the conductivity calculated was about 1.6 $\times$ 10$^5$ S/cm. When the measurements were carried out in a vacuum chamber of 10$^{-5}$ Torr, very similar result was also obtained. This conductivity is similar to that of Au.

On the other hand, when the measurement points of the resistance (indicated by the cross-marks) were moved from the cross-mark in F2 to the cross marks in E2 and D2 (the lengths measured from the Pt$^+$ electrode to the tip on the cross marks in E2 and D2 were about 0.6 mm and 100 $\mu$m, resp.), two similar I-V curves E3 and D3 were obtained, as shown in Figure 7(c). This indicates that the electric resistance of the electric path is smaller than the contact resistance (between the polypyrrolyl conjugate bonds and the AFM tip covered with Au) and another contact resistance (between the polypyrrolyl conjugate bonds and the Pt$^+$ electrode) and the circuit resistance of our setup.

Wherein if real resistance of the electric path without contact resistance was assumed to be 100 $\Omega$ at the cross-mark on the electric path in F2 (length: 2 mm), the resistances at the cross-mark E2 and D2 were calculated to be 30 $\Omega$ (length: 0.6 mm) and 5 $\Omega$ (length: 100 $\mu$m), respectively. Differences between the resistances at F2 and E2 and the resistances at F2 and D2 were 70 and 95 $\Omega$, respectively. These values are larger than that of 1% of 4 K$\Omega$, and as the resolution accuracy of our setup is higher than 1%, it should be easy

![Figure 6: A topographical image (a), a current image (b), and I-V curves (c) simultaneously obtained at the same position corresponding to the positions B in Figure 2(b). Wherein portions pp and pp$'$ are polymerized layer and portions p and p$'$ are unpolymerized layer of the PNN monomolecular layer, and regions Pt$^+$ and Pt$^i+$ are Pt electrodes. The I-V curves ppi and pi were obtained using the AFM tip covered with Au at the black and white cross-mark in (b), respectively.](image-url)
to distinguish the difference on our setup. But any difference was not observed on the three I-V curves obtained at the cross-marks in D2, E2, and in F2. This indicates that if the contact resistance was removed, the real resistance of the electric path at 2 mm was below 100 Ω. If this assumption is correct, the conductivity of the monomolecular layer containing polypyrrolyl conjugate bonds might be larger than \(1 \times 10^7\) S/cm. This assumption may be also supported by Figure 6(b) and Figure 7(b), because the thickness of Pt\(^+\) and Pt\(^-\) electrodes (50 nm thickness), is about two hundred
fifty times thicker than that of the conductive portion in the PNN monomolecular layer (0.2 nm thickness) and currents contrast obtained at Pt+, Pt−, and pp′ were similar to each other, as shown in Figure 6(b) and Figure 7(b).

3.7. Reasonable Electric Conduction Path. The conduction mechanism of this material may be different from semiconductors and metals. Electric conductance at the electric path is extraordinary high, as mentioned above. It is unlikely that all the PNN molecules at the electric path were polymerized to connect between the Pt+ electrode and the tip covered with Au.

Accordingly, although it was difficult to confirm by our technique that the conjugated bond chains (molecular wires) connecting between Pt+ electrode and the tip covered with Au were prepared in the PNN monomolecular layer, it may be reasonable to conclude that some of the molecular wires in the polymerized PNN monomolecular layer connect between Pt+ electrode and the tip covered with Au, and these contribute mainly to the electric conductance. Thus reasonable electric conduction path at the current measurement may be schematically shown in Figure 8.

4. Conclusions

We have confirmed three times on three different samples made by the same technique using three different AFM/STM tips and obtained similar data. The conductivity of the molecular wire containing polypyrrol conjugate bonds should be larger than $1.6 \times 10^5$ S/cm, and there may be a possibility of $1 \times 10^7$ S/cm. The value is much larger than that of Au.

On the other hand, at the electric path (molecular wire), it is unlikely that all the PNN molecules were polymerized linearly to connect between Pt+ electrode and the tip covered with Au. The polypyrrol conjugate bonds have no dopant. Accordingly, it may be reasonable to conclude that only a few molecular wires made of continuous polypyrrol conjugate bonds were prepared in the electric path made of the polymerized PNN monomolecular layer to connect between Pt+ electrode and the AFM tip covered with Au, and these contribute mainly to the electric conductance. The conduction mechanism of this molecular wire might be also different from semiconductors and metals.

Acknowledgment

The authors wish to thank Dr. M. Takenaga, Matsushita Electric Industrial Co., Ltd. for his helpful comments.

References


