A study on the stability of n-type conductive polymer

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Abstract. Novel n-type conducting polymer, poly(p-methylpyridinium vinylene), PMePyV were synthesized by using the quaternization of poly(p-pyridyl vinylene), PPyV and several regiochemical consequences in this polymer were proposed. The electrical, optical, and electrochemical properties of n-type conductive polymer were observed. In addition, a possibility of a variety of functional applications of n-type conductive polymer was indicated.

1. Introduction
At present, electronic devices sweeping over a market are inorganic semiconductor devices mainly on the Si, especially Si VLSIs (Very Large-Scale Integrated circuits) which incorporated a lot of ultrafine electronic circuits. When MOS (Metal-Oxide-Semiconductor) transistors are reduced steadily and to 1/k (k is an arbitrary constant), they are packed the tip of the same area, as a result, the degree of integration and the movement speed become k^2 and k times, respectively, and the consumption electricity is controlled by 1/k^2. Therefore, there are no factors which device performance grows to worse due to ultrafine processing. So-called, as shown in figure 1, according to scaling law established by Robert H. Dennard of IBM in 1974 [1], the Si semiconductor industry continued progressing by breaking the limit such as ultrafine processing steadily. However, it is said the in early 21st century, inorganic semiconductor electronics began to sputter due to the physical limit of the ultrafine processing technology. As the reasons, for example,

① The thickness of the gate insulation film becomes thin in the thickness of several atomic layers, as a result the restraint of the tunneling current is difficult.
② Because the density of impurities atom is too low and cannot control it, the unevenness of device properties is caused.
③ Due to various kinds of parasitism effects, the performance enhancements such as speedup based on simple scaling law, low consumption electricity, high integrations, etc cannot be expected.

etc.
Furthermore, development of the extreme ultraviolet ray source of light to use for lithography is an important problem.

If current electronics technologies mainly on the Si have limits, the basic solution is to break the limit by devising replacements. The suggested technique is the concept of the molecular electronic devices which is going to fabricate molecular electronics using molecules. This thought is proposed for the theoretical consideration of the diode device function consisting of one organic molecule by
Arieh Aviram et al. for the first time in 1974 [2], and basically are incorporating a function to control electronic flow to individual molecules and to realize electronic devices of the molecular size.

On the other hand, the ability for complicated information processing based on pattern recognition or the parallel computation in brain and the nervous system of the animal is extremely high and is performed easily. The bio-system has complicated and extremely high function. That is, bioelectronics attracts great interest in making good use for converting information, taking in the function that is going to store, and also limited development of electronics technologies based on a scaling law [3].

At all events, because a variety of the organic materials have much metastable structure, the flexibility is bigger than an inorganic material markedly, and the expectations for the organic materials are particularly high.

In such a background, the world of the electronics which developed mainly on a Si semiconductor is going to change drastically. A paradigm shift which is called organic electronics or printed electronics is finally more likely.

Organic electronics based on Flexible-Organic Semiconductors are called Flexible Electronics or Plastic Electronics. In addition, because a print technology is applicable to fabricate films, the motivations to use polymers are twofold: the possibility to shrink the circuit size to the molecular level and the printing of large-area circuits at extremely low-cost. So-called this is printed electronics. The development research of organic electronic devices having active layers consisting of flexible-organic semiconductor materials such as organic light-emitting devices, organic transistors, organic solar batteries etc. is developed extremely actively [4].

In the organic semiconductors, we often call them p- or n-type materials. This is not a meaning having holes and electrons as majority carriers like an inorganic semiconductor, but the meaning that electrons and holes injection are easy. This is extremely important and should be careful [5].

As one of the most characteristic effect that conductive polymers possess, doping effects are well known. By way called the doping, if acceptor (electron-accepting) or donor (electron-donating) are soaked or put forcibly into conductive polymers, their conductivities can be widely controlled from the insulator region, via the semiconductor region, and finally to the metallic region. As a result, other characterizations such as magnetic and optical properties are also greatly changed. Basically, such doping effects are strongly caused by the change of electronic states of conductive polymers, because of the interaction between dopants and the polymer main chains. As for such conductive macromolecule, the use as the (i) metals, (ii) insulators and semiconductors, (iii) insulator/metal transition phenomena, (iv) reversible doping ability, and so on is possible [6].

![Figure 1. Image of scaling law.](image-url)
To date, almost all of the conductive polymers that have been examined for organic devices are good holes conductors and relatively poor electrons conductors. The reason why the stability of the n-type conductive polymers is remarkably low is caused by carbanion (ions of the organic compounds with a negative charge on carbon atoms, that is $\cdot CH\_3$, here $\cdot$ indicated unpaired electron) formed from doping easily reacting with a very small amount of oxygen and water in an atmosphere [7].

In order to fully exploit the potential offered by polymers the device materials have to be processable in its polymeric form. By appropriate modification of the molecular structure of these polymers such as the introduction of long alkyl side chains, conductive polymers which consist of rigidly conjugated double bonds have been found to be soluble in any solvents and even to be fusible at relatively low temperature.

Accordingly, the ability to fabricate organic devices from solution process promises a significant manufacturing advantage. M. J. Marsella et al. [8] have reported the preparation of orange-yellow poly(p-pyridyl vinylene), PPyV using a modification of a synthesis initially developed by R. Galarini et al. [9] Although PPyV can be viewed as an alternating copolymer of pyridine and acetylene and is a conductive polymer having n-type semiconductor natures, its fundamental physical properties have yet to be clarified. In addition, for example, in the presence of trifluoromethanesulfonate (CF$_3$SO$_2$OR, R: alkyl group), PPyV alkylates by heat-treatment using a suitable solvent, and poly(p-alklypyridinium vinylene) is provided.

For example, as shown in figure 2, quaternization of the PPyV to the yellow poly(p-methylpyridinium vinylene), PMePyV is obtained on all isomers (Random, Head-Tail, and Head-Head forms) by reaction in neat methyl triflate in dichloromethane, CH$_2$Cl$_2$ at 40 °C for a week under argon. PMePyV has triflate ions (-CF$_3$SO$_3^-$) as a counter-ion [8].

![Figure 2. Conversion reaction of PPyV to yield alkylated PPyV. Here, quaternization of the PPyV to the yellow poly(p-methylpyridinium vinylene), PMePyV is shown.](image)

To make the stability or conduction mechanisms of positively charged n-type conductive polymer, PMePyV clear, their fundamental physical properties such as electrical, optical and electrochemical properties have been studied and discussed from molecular structures of their reduced states [10].

2. Sample and Experimental Procedure

2.1. Regiocontrol of the PPyV structure

It is well known that while regiocontrol of polymers is an important aspect from synthetic viewpoint, the regiochemical consequences may affect physical properties of polymers [11]. Poly(3-alkylthiophene)s provide for the first time well defined structures for the investigation of structure-property relationships in this class of electronic and photonic materials. Therefore, for similar consideration, since pyridine-vinyl group of PPyV is not a symmetrical molecule, there are three
relative orientations available when two pyridine rings are coupled between the 2- and 5-positions through a vinyl group. PMePyV has three regioisomeric forms: head-to-head (Head-Head) (Here, tail-to-tail (Tail-Tail) is the same as Head-Head), head-to-tail (Head-Tail), and Random (combination of Head-Head and Head-Tail) as shown in figure 3. Of course for similar consideration PPyV has also three regioisomeric forms.

A schematic diagram of the synthetic route to three regioisomeric forms of PPyV is outlined in figure 4. Head-Head, Head-Tail, and Random PPyVs were synthesized via extensive use of palladium catalyzed cross-coupling of vinyl stannanes and pyridine bromides. [8], [9], [12], [13] Random PPyV was prepared via cross-coupling of 2, 5-dibromopyridine and 1, 2-bis(tributylstannyl)ethylene in the presence of palladium phosphine complex essentially according to the procedure reported by Galarini et al. [9] That is, 2, 5-dibromopyridine and tetrakis(triphenylphosphine)- palladium(0) were added to a solution of 1-methyl-2-pyrolidinone and the solution was stirred at 110 °C for 24 hours. The yellowish-orange precipitate was collected and washed with hot tetrahydrofuran (THF). The polymer was purified by Soxhlet extraction with ethanol for 24 hours. As shown in figure 4, the starting monomer for the desired polymer dominated the regiocontrol of the parent PPyV. For example, the synthesis of the Head-Head monomer was accomplished by the high reactivity of the 2-position of 2, 5-dibromopyridine.

Figure 3. Possible regiochemical couplings of PMePyV.
Figure 4. Schematic diagram of the synthetic route to Head-Head, Head-Tail, and Random PPyVs.
2.2. Characterization of PPyV and PMePyV
The PPyV appears a yellowish-orange powder and is not soluble in conventional organic solvents such as chloroform, methylene chloride, etc. However, the polymer is soluble in \textit{m}-cresol, concentrated sulfuric acid and formic acid. These polymer solutions are highly fluorescent. The number-average molecular weight of PPyV was determined by gel permeation chromatography (GPC) against polystyrene standards to be about 7,300.

PMePyV is slightly soluble in water, but demonstrates high solubility in dimethyl sulfoxide (DMSO), N,N-dimethyl- formamide (DMF), and 1-methyl-2-pyrrolidone (NMP). At room temperature, DMSO and NMP solutions of PMePyV rapidly turn dark, while after several hours DMF solutions gradually darken. The decomposition of the polymer may occur because of the nucleophilic attack of the solvent.

Protonated poly\textit{(p- pyridyl vinylene)}, PHPyV is positively charged polyelectrolyte like PMePyV and is prepared by treating PPyV with dodecylbenzenesulphonic acid at 100 °C for several days under argon (Ar), as shown in figure 5. Both pyridinium polymer, PMePyV and PHPyV are soluble in common organic solvents, such as chloroform and acetonitrile. PHPyV is yellow-orange in color.

On the other hand, about 20 years ago, a new technique of constructing multilayer assemblies by consecutively alternating adsorption polyelectrolyte was developed [14]. That is, the layer-by-layer molecular self-assembly technique of conductive polymers is based on the spontaneous adsorption of a charged polymer onto a surface from a dilute polymer solution. Both PHPyV and PMePyV are positively charged conjugated polyelectrolytes. These polyelectrolytes can be fabricated into thin self-assembled films via alternating layers of positively and negatively charged polymers. This techniques makes it possible to readily prepare heterostructures with other conjugated or non-conjugated polyions [15].

3. Results and discussions

3.1. Kekulé and non-Kekulé structures of reduced PMePyV
PMePyV, when reduced, should be highly conductive as it is isoelectronic with the highly conductive n-doped poly\textit{(p-phenylene vinylene)}, PPV as shown in figure 6. However, what is not analogous is the fact that the reduced form of PMePyV bears no charge as shown in figure 7: all other known conductive polymers in their doped state bear charge [6]. Such an uncharged highly conductive polymer can be described as an intrinsic conductor. Carriers may be restricted by electrostatic
interactions with dopant ions existing in an imperfect lattice. Accordingly as shown in figure 8, the content of three regioisomeric forms to have a significant effect on the polymer properties has to be considered, since reduction produces a closed shell state for the Head-Head linkages called Kekulé structure and an open shell state for Head-Tail linkages called non-Kekulé structure [8], [16].

Figure 6. Electronic state of n-doped poly(p-phenylene vinylene), PPV.

Figure 7. Reduced form of PMePyV.

Figure 8. Schematic illustration of Kekulé and non-Kekulé states of reduced PMePyV.
3.2. Optical properties of PPyV, PMePyV and PHPyV

Figure 9 shows the optical absorption spectra of PPyV, PMePyV, and PHPyV. In PPyV, only a single absorption peak ($\lambda_{AB\text{max}}$) was observed at about 420 nm due to interband excitation, and the band-gap energy estimated from the absorption edge is about 2.4 eV. Similar optical behaviors are also presented by PMePyV and PHPyV. $\lambda_{AB\text{max}}$s of these polymers corresponding to the interband transition were observed at around 390 nm and 460 nm, respectively and the band-gap energy about 2.8 eV and 2.4 eV, respectively. This band-gap energy in PMePyV, 2.8 eV may be interpreted in terms of change of effective conjugation length due to the introduction of torsion of bonds between nitrogen rings on account of the steric hindrance between N atom and methyl chain.

![Figure 9. Optical-absorption spectra of PPyV, PMePyV and PHPyV.](image)

On the other hand, the photoluminescence (PL) spectra of PPyV, PMePyV and PHPyV are shown in figure 10. For PL spectra these polymers were excited with light at 420 nm. The maximum PL peak wavelength ($\lambda_{PL\text{max}}$) of PPyV and PMePyV shows peaks of 610 nm and 540 nm, respectively.

![Figure 10. Photoluminescence spectra of PPyV, PMePyV and PHPyV.](image)

As evident from figures 9 and 10, both the optical absorption ($\lambda_{AB\text{max}}$ at 390 nm) and PL ($\lambda_{PL\text{max}}$ at 540 nm) spectra of PMePyV are blue-shifted relative to PPyV to lower the energy of the filled
orbits significantly, this blue-shift may be affected by the methyl substitution too. On the other hand, the situation for PHPyV is different from that observed for PMePyV. Interestingly, the optical-absorption spectrum of PHPyV is red-shifted relative to PPyV, while the PL spectrum has two peaks evolved at around 540 nm and 570 nm. Both these two features are blue-shifted relative to PPyV. Though the mechanism of this anomaly is not clear at this stage, however the degree and uniformity of the protonation reaction may influence the PL spectrum. Detailed experimental studies of these unique phenomena will be carried out in the future.

Moreover, unfortunately, the significant difference was not recognized in optical properties for three regioisomers of PPyV, PMePyV and PHPyV. Though the detailed mechanism of this unique phenomenon is not clear at this stage, probably it is considered that optical measurements such as absorption and photoluminescence spectra are relatively structure insensitive properties.

3.3. Electrical conductivities of three regioisomeric PMePV

Electrical conductivity measurements have not been carried out in situ during electrolysis doping, because of loss of any reversible electrolysis behavior of PMePyV. In other word, reduced state of three regioisomeric forms was not so stable and the evaluation of intrinsic conductivity of these polymers was a little bit difficult, especially the temperature dependence of conductivity. Therefore, maximum electrical conductivities measured at room temperature for the reduced forms with three regioisomers of PPyV and PMePyV are summarized in Table 1.

Table 1. Electrical conductivities for the reduced forms with three regioisomers of PPyV and PMePyV.

|          | Random (S/cm) | Head-to-Head (S/cm) | Head-to-Tail (S/cm) |
|----------|---------------|---------------------|---------------------|
| PPyV     | 2.8 × 10⁻³    | 4.2 × 10⁻⁴          | 1.8 × 10⁻²           |
| PMePyV   | 1 × 10⁻⁷      | 1 × 10⁻⁷            | 2.4 × 10⁻⁵           |

at room temperature

The PPyV and PMePyV polymers are easily reduced and resisted oxidation. The electrochemical cycle between the desired doping potential and the neutral state was repeated for 2 or 3 times to obtain more uniformly doped samples. The doping conditions such as the film thickness (approximately 200 nm) and the composition of electrolyte (0.1 mol/L Bu₄NPF₆ in THF), are almost the same as electrochemistry explained in 3.4. The films thus obtained were washed immediately with THF for several times and cut into appropriate pieces to measure the electrical conductivity. These procedures were carried out in an Ar–filled dry box without exposure to air. The electrical conductivity was measured using either a standard four-probe or two-probe technique in an evacuated chamber.

The conductivity of Head-Tail PPyV shows one to two order of magnitude higher than those of both Random and Head-Head PPyV. On the other hand, methylation to form PMePyV caused a remarkable decrease of the conductivity. However, the conductivity of Head-Tail PMePyV shows a high value compared with those of other two regioisomeric forms. These results reflect both “carrierless” reduced forms of Head-Head PMePyV and the destruction of the highly reactive carriers generated on reduction of the Head-Tail PMePyV. A similar consideration may be observed for the conductivity of Random PMePyV. Moreover, the high conductivity of Head-Tail PMePyV and Head-Tail PPyV may be related to their non-Kekulé structure as shown in figure 8, if those are stable at room temperature. However, lengthy and careful consideration should be given to the origin of these unique phenomena.
3.4. Electrochemistry of random PMePyV and its regioisomers

Figure 11. Cyclic voltammetry of the three regioisomeric forms of (a) Random, (b) Head-to-Head, and (c) Head-to-Tail PMePyV.
The cyclic voltammetry of three regioisomeric forms of PMePyV during electrochemical redox reaction was studied using a three-electrode cell in which the working electrode consisted of an about 200 nm thick film of samples deposited on an ITO (indium-tin oxide) glass substrate. The counter and reference electrodes were Pt plate and Ag wire, respectively. The composition of electrolyte used for the cyclic voltammetry is 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as the supporting electrolyte in THF. In this study, the reduction of these polymers were easy, but the oxidation difficult.

As shown in figure 11 (a), the cyclic voltammogram of the Random PMePyV demonstrated high coulombic reversibility. Two well defined reduction waves are centered at about -0.35 and -1.26 volts vs. Ag/Ag⁺. And then, two oxidation waves slightly overlap, showing current peaks at -0.6 and 0 volts.

On the other hand, cyclic voltammetry of both the regiochemically Head-Head and Head-Tail PMePyV show a rapid decrease in activity after the first reduction cycle. As shown in figure 11 (b), Head-Head PMePyV shows two reduction waves centered at about -0.25 and -0.75 volts. And two oxidation waves which show considerably less coulombic activity than their corresponding reduction waves are centered at about -0.25 and +0.12 volts. A similar cyclic behavior is also presented by Head-Tail PMePyV. As shown in figure 11 (c), two reduction waves centered at about -0.4 and -1.3 volts. And two oxidation waves which show considerably less coulombic activity than their corresponding reduction waves are centered at about -0.3 and +0.8 volts. The continued cycling of these two PMePyV resulted in loss of electrolysis activity.

![Polaron state](image1) ![Bipolaron state](image2)

(a) head-to-head PMePyV

![Polaron state](image3) ![Bipolaron state](image4)

(b) head-to-tail PMePyV

**Figure 12.** Speculated polaron and bipolaron states of (a) Head-Head and (b) Head-to-Tail PMePyV generated on reduction.

In Head-to-Head and Head-to-Tail PMePyV, though the cause of the inactivating phenomenon by the repetition of the cyclic voltammetry measurement is not clear at this stage, the Kekulé and non-Kekulé structures of reduced regioisomeric form described in figure 8 might also contribute to the loss of reversible electrochemical behavior. Because, for example, polaron and bipolaron states of (a) Head-to-Head and (b) Head-to-Tail PMePyV generated on reduction is estimated as shown in figure...
12, the non-Kekulé structures are formed and the high reactivity of them may affect to the physical properties of regioisomeric forms of PPyV.

4. Conclusion
In order to clarify the stability of n-type conductive polymers, fundamental physical properties of three regioisomeric forms of PPyV (Random, Head-Head, and Head-Tail) have been investigated. The structural change (reduced states) of Head-Head PMePyV and Head-Tail PMePyV, that is, Kekulé and non-Kekulé structures, may strongly affect to the stability.

Reference
[1] Dennard R H, Gaensslen F H, Rideout V L, Bassous E and LeBlanc A R 1974 IEEE Journal of Solid-State Circuits 9(5) 256-268
[2] Galarini R, Musco A, Pontellini R, Bolognesi A, Destri S, Catellani M, Mascherpa M and Zhuo M 1991 Journal of the Chemical Society, Chemical Communications (6) 364-365 Aviram A and Ratner M A 1974 Chemical Physics Letters 29(2) 277-283
[3] Onoda M, Kaneto K, Ohsawa T and Yoshino K 2016 Organic Iontronics (Tokyo: Morikita Publishing Co., Ltd.) in Japanese
[4] Onoda M (Supervisor) 2012 Physical properties and evaluation of conductive polymers for high performance organic electronic devices (Tokyo-Osaka: CMC Publishing Co., Ltd.) in Japanese
[5] Onoda M 2013 in New Developments in Polymer Composites Research (edited Laske S and Witschnigg A New York: Nova Publishers) 67-88
[6] Yoshino K and Onoda M 1996 Polymer Electronics (Tokyo: Corona Publishing Co., Ltd.) in Japanese
[7] de Leeuw D M, Simonen M M J, Brown A R and Einerhand R E F 1997 Synthetic Metals 87 (1) 53-59
[8] Marsella M J, Fu D-K and Swager T M 1995 Advanced Materials 7(2) 145-147
[9] Galarini R, Musco A, Pontellini R, Bolognesi A, Destri S, Catellani M, Mascherpa M and Zhuo M 1991 Journal of the Chemical Society, Chemical Communications (6) 364-365
[10] Onoda M 2015 International Conference & Exhibition on Advanced & Nano Materials OPHM-1
[11] McCullough R D, Lowe R D, Jayaraman M and Anderson D L 1993 The Journal of Organic Chemistry 58(4) 904-912
[12] Stille J K 1986 Angewandte Chemie International Edition in English 25(6) 508-524
[13] Beddoes R L, Cheeseright T, Wang J and Quayle P 1995 Tetrahedron Letters 36(2)283-286
[14] Decher G, Hong J D and Schmitt J 1992 Thin Solid Films 210-211(2) 831-835
[15] Onoda M 2013 in New Developments in Polymer Composites Research (edited Laske S and Witschnigg A New York: Nova Publishers) 89-149
[16] Vollhardt K P C and Schore N E 1999 Organic Chemistry, Structure and Function 3rd Edition (New York and Oxford: W. H. Freeman and Company)