



Title	SYNTHESIS OF A NOVEL CLASS OF NONCONJUGATED POLYMERS CONTAINING OLIGOTHIOPHENES AND THEIR ELECTRICAL AND ELECTROCHROMIC PROPERTIES
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**SYNTHESIS OF A NOVEL CLASS OF NONCONJUGATED POLYMERS  
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1997

**ICHIRO IMAE  
OSAKA UNIVERSITY**

SYNTHESIS OF A NOVEL CLASS OF NONCONJUGATED POLYMERS  
CONTAINING OLIGOTHIOPHENES AND THEIR ELECTRICAL AND  
ELECTROCHROMIC PROPERTIES

(オリゴチオフェンを含む新規な非共役型高分子の合成、  
電氣的性質およびエレクトロクロミック特性)

1997

ICHIRO IMAE  
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## Introduction

It is well known that solids are usually classified as metals, semiconductors, and insulators from the standpoint of electronic conduction. Most organic compounds, including polymers, are insulators. Actually, polymers have been used as excellent insulating materials in various ways. Pioneering works on electrical conduction in organic solids were found from the late 1940s to early 1950s for certain classes of organic compounds. Phthalocyanines and highly condensed polycyclic aromatic hydrocarbons (*e.g.*, violanthrene) whose molecular structure resembles that of graphite were found to show electrical conductivity.<sup>1,2</sup> Then it was found that a perylene-bromine charge-transfer complex shows a remarkably higher electrical conductivity of *ca.*  $10^{-2}$  S cm<sup>-1</sup>.<sup>3</sup> These findings have opened up the research field of organic semiconductor.<sup>4</sup> Since then, studies of organic conductors, including polymers, have made remarkable progress over a period of more than 40 years from organic semiconductors to organic metals and to organic superconductors. This field has been the subject of numerous review articles and books.<sup>5</sup>

A variety of charge-transfer complexes have been studied in view of electrical conduction. Since a new electron acceptor, tetracyanoquinodimethane (TCNQ), was synthesized in 1960,<sup>6</sup> there have been extensive studies on TCNQ anion radical salts with various cations. Among them, single crystals of a few TCNQ anion radical salts, for example, quinolinium TCNQ complex salt,<sup>7</sup> acridium TCNQ complex salt,<sup>8</sup> and N-methylphenazinium TCNQ

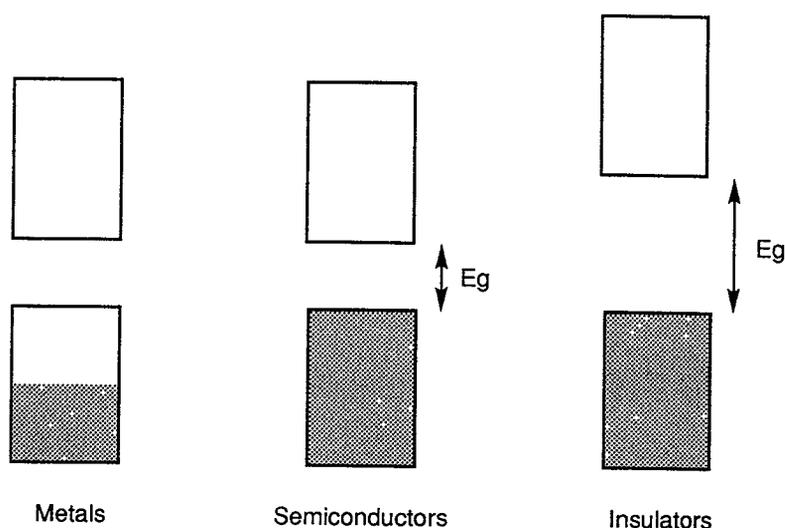
simple salt,<sup>9</sup> have been found to show metallic properties in electrical conduction. In 1970 a new electron donor, tetrathiafulvalene (TTF), was synthesized,<sup>10</sup> and in 1963 single crystals of a TTF-TCNQ charge-transfer complex were found to exhibit a high room-temperature conductivity with metallic properties. The conductivity increases sharply with a decrease in temperature, with maximum conductivity approaching that of mercury.<sup>11,12</sup> These organic metals are characterized by anisotropy in electrical conduction and are termed pseudo-one-dimensional metals. Since then, intensive and extensive studies of pseudo-one-dimensional organic conductors have been made. It was in 1980 that the first known example of organic superconductors was reported: Cation radical salts of tetramethyltetraselenafulvalene (TMTSF),  $(\text{TMTSF})_2\text{PF}_6^-$ , and  $(\text{TMTSF})_2\text{ClO}_4^-$ , prepared by the method of electrocrystallization,<sup>13</sup> have been found to transform from metals to superconductors under a pressure of 12 kbar and at atmospheric pressure with transition temperatures of 0.9 K and 1.4K, respectively.<sup>14,15</sup>

With respect to polymers, a number of polymers (*e.g.*, linear or planar  $\pi$ -conjugated polymers, polymeric charge-transfer complexes, and TCNQ anion radical salts with polymeric cations) have been studied extensively and found to fall into the family of semiconductors. Metallic conductivity in polymers was first found for an inorganic polymer, poly(sulfur nitride), in 1973.<sup>16</sup> In 1975 this polymer was found to transform into a superconductor below 0.3 K.<sup>17</sup> It was found in 1977 that polyacetylene, which itself is a semiconducting polymer, shows metallic properties when heavily doped with dopants such as halogens.<sup>18</sup> Since then intensive studies on organic polymeric metals have

been started. A model for high-temperature polymeric superconductors was proposed in 1964;<sup>19</sup> however, the synthesis of organic polymeric superconductors has not yet been successful. Potential industrial applications for conducting organic solids are also being actively investigated.

The electrical conduction is classified into ionic conduction and electronic conduction, based on whether the charge carriers are ions or electrons. They are essentially different in that ionic conduction is caused by the transport of matter (*i.e.*, ions), whereas electronic conduction involves the transport of electrons. In general, electronic conduction is enhanced with an increase in pressure, whereas the opposite is the case for ionic conduction.

From the standpoint of electronic conduction, solids are classified into metals, semiconductors, and insulators. Certain classes of metals are transformed into superconductors below  $T_c$ . In terms of band structure, a band is



**Figure 0-1.** Band structures for metals, semiconductors, and insulators.

about half-filled with electrons for metals and hence no activation energy is required for the generation of charge carriers. By contrast, the band is completely filled with electrons for both semiconductors and insulators, and hence activation is required for the transition of electrons from the valence band to the conduction band to generate charge carriers. If the band gap is small enough to generate charge carriers by thermal activation, then solids show semiconductive properties. These are termed intrinsic semiconductors. In most cases, however, electron-donating or electron-accepting impurities participate in the generation of charge carriers. In this case, either holes or electrons play the dominant role in transport. These extrinsic semiconductors are termed p-type or n-type semiconductors, where holes or electrons are the major charge carriers, respectively.

The magnitude of electrical conductivity is represented in terms of specific conductivity  $\sigma$  ( $\Omega^{-1} \text{ cm}^{-1}$ ,  $\text{S cm}^{-1}$ ) or its reciprocal, specific resistivity,  $\rho$  ( $\Omega \text{ cm}$ ). The specific conductivity represents the electric current that flows across the unit area ( $1 \text{ cm}^2$ ) of electrode under the unit external electric field ( $1 \text{ V cm}^{-1}$ ) applied to the sample.  $\sigma$  is expressed by eq. 1.

$$\sigma = ne\mu \quad (1)$$

Generally, solids with conductivities of less than  $10^{-12} \text{ S cm}^{-1}$  are termed insulators. Solids with metallic properties in electrical conduction generally show conductivities higher than  $10^2 \text{ S cm}^{-1}$ . Solids with electrical conductivities between  $10^{-12}$  and  $10^2 \text{ S cm}^{-1}$  are referred to as semiconductors. It should be noted that it is the temperature dependence of electrical conductivity instead of its magnitude that distinguishes metals from semiconductors. While

the conductivity increases with a decrease in temperature for metals, the temperature dependence of the electrical conductivity for semiconductors follows the eq. 2.

$$\sigma = \sigma_0 \exp\left(\frac{-\Delta E}{kT}\right) \quad (2)$$

Organic electrical conductors are largely classified into low-molecular-weight organic compounds and polymers. Low-molecular-weight organic compounds can be classified into the following several classes: (a) highly condensed polycyclic aromatic hydrocarbons that resemble graphite in their structures, (b) charge-transfer complexes, (c) ion radical salts, and (d) metal complexes. Ion radical salts include both anion radical salts of electron acceptors and cation radical salts of electron donors. They are either simple salts where cations and anions are 1:1 in stoichiometric proportions or complex salts which additionally contain neutral acceptor or donor molecules. Usually, complex salts are more conductive than simple salts. In general, a high electrical conductivity is found for charge-transfer complexes, ion radical salts, or partially oxidized metal complexes.

Metallic properties in electrical conduction have been found among compounds that form charge-transfer complexes that make segregated stacks of donor and acceptor molecules, ion radical salts mostly with mixed valence interactions, or partially oxidized metal complexes. They are termed organic metals or synthetic metals. Metallic conduction was first found for single crystals of a few TCNQ anion radical salts. Since the finding of metallic conduction for single crystals of a TTF-TCNQ charge-transfer complex, various

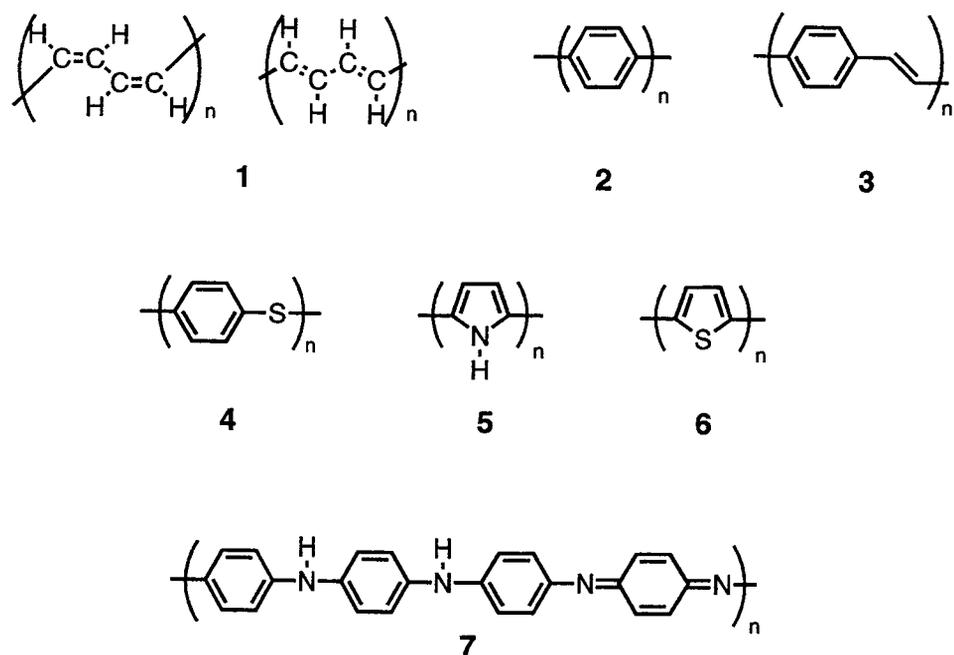
modifications of TTF and TCNQ molecules have been carried out, and electrical conductivities of charge-transfer complexes between these modified TTF molecules and TCNQ, TTF and modified TCNQ molecules, and modified TTF and modified TCNQ molecules, have been examined in order to search for new organic metals with better electrical properties than those of the TTF-TCNQ charge-transfer complex and to gain deeper insight into the origin of metallic conduction. The TTF molecule has been modified in several ways: replacement of the sulfur atom by selenium or tellurium, the introduction of substituents, the synthesis of the molecules having an isoelectronic structure with TTF, and the synthesis of fused TTF rings. Similarly, the TCNQ molecule has been modified by the introduction of substituents or the extension of  $\pi$ -conjugation. Molecules having an isoelectronic structure with TCNQ have also been synthesized. As a result, charge-transfer complexes with electrical properties comparable to or better than those of the parent TTF-TCNQ complex (*e.g.*, the hexamethylene tetraselenafulvalene-TCNQ charge-transfer complex<sup>20</sup>) have been synthesized.<sup>21-24</sup> Synthesis of the derivatives of TTF and TCNQ with isoelectronic structures has enabled the synthesis of organic alloys such as  $\text{TSeF}_{0.03}\text{TTF}_{0.97}\text{TCNQ}^{25}$  or  $\text{TSeF}\cdot\text{TCNQ}_{0.9}\cdot\text{MTCNQ}_{0.1}$ .<sup>26</sup> Metallic conduction has also been found for electrochemically prepared ion radical salts and partially oxidized metal complexes.

From the standpoint of molecular structures, electrically conducting polymers including oligomers can be classified mainly into the following categories; (a)  $\pi$ -conjugated linear polymers, (b)  $\pi$ -conjugated linear oligomers with

well-defined structures, (c)  $\pi$ -conjugated planar polymers (pyropolymers), (d) nonconjugated polymers containing pendant  $\pi$ -electron systems, (e) metallomacrocyclic polymers, and (f) composite polymers. Generally, these polymers and oligomers themselves exhibit very low electrical conductivities, being poor semiconductors or insulators except for pyropolymers. However, they are transformed into conducting materials when they undergo chemical or electrochemical doping. Recently, studies directed toward developing intrinsic semiconducting polymers that exhibit good electrical conductivity without doping, namely, narrow band-gap polymers, are in progress.

Chemical doping of polymers results in the formation of charge-transfer complexes or partially oxidized or reduced ion radical salts, increasing the electrical conductivity many orders of magnitude. Like chemical doping, electrochemical doping of polymers, which produces ion radical salts of polymers, has also proved to be a useful method for producing highly conducting polymers. Metallic properties have been found for chemically or electrochemically doped linear  $\pi$ -conjugated polymers.

Among electrically conducting polymers,  $\pi$ -conjugated linear polymers, such as polyacetylene (1), poly(*p*-phenylene) (2), poly(*p*-phenylene vinylene) (3), poly(phenylene sulfide) (4), polypyrrole (5), polythiophene (6), and polyaniline (7), have attracted a great deal of attention because of their ability to achieve high electrical conductivity by doping.<sup>27-31</sup>



Recently  $\pi$ -conjugated linear oligomers with well-defined structures, *e.g.*, oligophenylenes, oligothiophenes, oligopyrroles, and oligoanilines have been attracting attention as a novel class of organic  $\pi$ -electron systems. In particular, extensive studies have been made of oligothiophenes with well-defined structures. Unsubstituted and substituted oligothiophenes have been synthesized,<sup>32-35</sup> and their structure,<sup>36,37</sup> and optical,<sup>38-41</sup> electrochemical,<sup>42-44</sup> electrical,<sup>45-47</sup> and photoelectrical<sup>48-50</sup> properties, and application to field-effect transistors<sup>51-54</sup> have been studied.

Non-conjugated polymers containing pendant  $\pi$ -electron systems are of interest for the following reasons; the variety of possible pendant molecules, chemical stability, good processability, photoconductivity, and invariance of the standard redox potential with the degree of doping.<sup>55,56</sup> When these polymers are used as electrode materials for secondary batteries, a flat voltage dur-

ing discharge is expected to be maintained owing to the invariance of the standard oxidation/reduction potentials of these polymers with the degree of doping. Photoconductivity coupled with semiconductivity resulting from electrochemical doping may lead to an application of doped polymers as photoactive materials for photoelectrical devices.

For the purpose of developing a novel class of electrically conducting polymers, we have studied electrochemical doping of nonconjugated vinyl polymers containing pendant  $\pi$ -electron systems and investigated the properties and applications of doped polymers.<sup>55</sup> They include poly(*N*-vinylcarbazole),<sup>57-61</sup> poly(vinylferrocene),<sup>62</sup> poly[4-(diphenylamino)phenylmethyl methacrylate],<sup>63</sup> poly(1-vinylpyrene),<sup>64</sup> and poly(3-vinylperylene).<sup>65-68</sup>

In the present study, in order to develop a further new type of electrically conducting polymers, I have studied the synthesis, properties, and applications of polymers containing oligothiophenes as pendant groups. Polymers containing pendant oligothiophenes are expected to form films owing to the presence of the nonconjugated polymer backbone and to exhibit unique properties characteristic of the pendant oligothiophenes. It is of interest to elucidate the relationship between the conjugation length of pendant oligothiophenes and the properties of the polymers containing pendant oligothiophenes.

The thesis consists of three chapters. In chapter 1, the synthesis of new vinyl monomers containing oligothiophenes and a novel vinyl polymer containing pendant terthiophene are described. Chapter 2 deals with electrolytic polymerization of vinyl monomers and electrochemical doping of a vinyl polymer, and characterization and electrical properties of the doped polymers. In chapter 3, electrochromic properties of novel vinyl polymers are discussed.

## Chapter 1

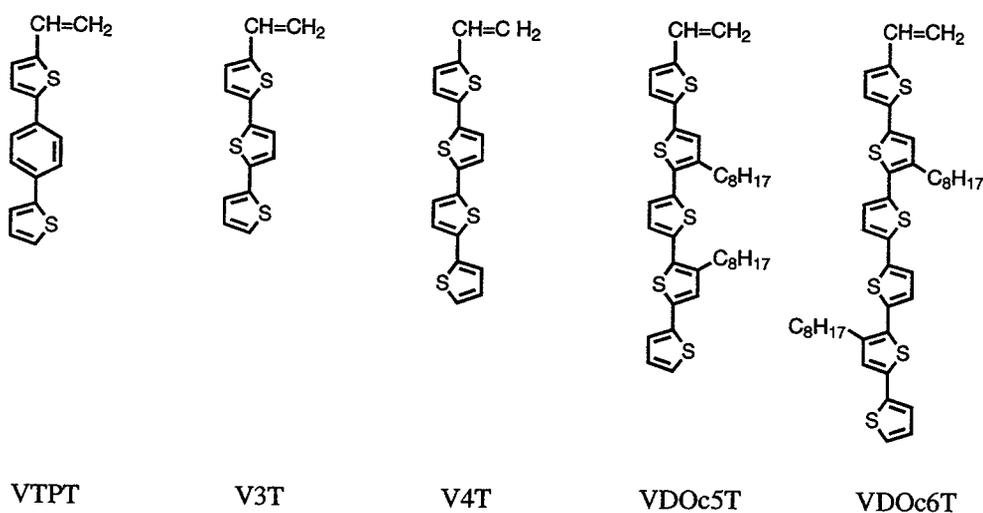
### Synthesis of New Vinyl Monomers Containing Oligothiophenes and a Novel Vinyl Polymer Containing Pendant Terthiophene

#### 1-1 Introduction

Oligothiophenes were originally found as naturally-occurring compounds and then synthesized *via* organochemical routes.<sup>49-51</sup> Recently, various oligothiophenes have been synthesized and developed as model compounds of polythiophenes.<sup>26-44</sup> The major motive for this is that a series of compounds having controllable polymerization degrees can be readily prepared and that their physical properties, as a function of their increasing polymerization degrees, may be extrapolated to those of polythiophene. More recently, oligothiophenes have attracted attention not only as model compounds for polythiophenes but also as a new family of organic  $\pi$ -electron systems, and their application to various devices, such as solar cells and field-effect transistors have been reported.<sup>37-43</sup>

However, oligothiophenes incorporated into nonconjugated polymer backbone have not been synthesized at all. Polymers containing pendant oligothiophenes are expected to form films owing to the presence of the nonconjugated polymer backbone and to exhibit unique properties characteristic of the pendant oligothiophenes. It is also of interest to elucidate the relationship between the conjugation length of pendant oligothiophenes and the properties of the polymers containing pendant oligothiophenes.

In this chapter, for the purpose of creation of a novel family of non-conjugated polymers containing pendant oligothiophenes with well-defined structures, corresponding novel vinyl monomers, *i.e.*, 5-vinyl-2,2':5',2''-terthiophene (V3T), 5-vinyl-2,2':5',2''':5'',2''''-quaterthiophene (V4T), 4',3''''-dioctyl-5-vinyl-2,2':5',2''':5'',2''''':5''''',2''''''-quinquethiophene (VDOc5T), 4',3''''-dioctyl-5-vinyl-2,2':5',2''':5'',2''''':5''''',2''''''':5''''''',2''''''''-sexithiophene (VDOc6T), and 2-[4-(2-thienyl)phenyl]-5-vinylthiophene (VTPT), have been synthesized. A new vinyl polymer containing terthiophene as a pendant group, poly(5-vinyl-2,2':5',2''-terthiophene) (PV3T), has been also synthesized by radical and cationic polymerization of 5-vinyl-2,2':5',2''-terthiophene.



## 1-2 Experimental

### *Materials*

*n*-Hexane, ethanol, methanol, benzene, tetrahydrofuran (THF), and *N,N*-dimethylformamide (DMF) were purified by ordinary methods, dried, and distilled immediately before use. 2,2'-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from methanol. Boron trifluoride diethyl etherate was purified by vacuum distillation after addition of diethyl ether and calcium hydride.

### *Synthesis of Vinyl Monomers*

2,2':5',2''-Terthiophene, 2,2':5',2'':5''',2''''-quaterthiophene 4',3''''-dioctyl-2,2':5',2'':5''',2''''':5''''',2''''''-sexithiophene, 1,4-di(2-thienyl)benzene were prepared according to the literatures.<sup>52-55</sup> The new compound, 4',3''''-dioctyl-2,2':5',2'':5''',2''''-quinqethiophene, was also synthesized in a similar manner by a Ni-catalyzed Grignard coupling reaction of 2-thienyl magnesium bromide with 5,5''-dibromo-3,3''-dioctyl-2,2':5',2''-terthiophene, prepared by bromination of 3,3''-dioctyl-2,2':5',2''-terthiophene with *N*-bromosuccinimide. The latter compound was prepared by a Ni-catalyzed Grignard coupling reaction of 2-(3-octyl)thienyl magnesium bromide with 2,5-dibromothiophene. 2,2':5',2''-Terthiophene, 2,2':5',2'':5''',2''''-quaterthiophene 4',3''''-dioctyl-2,2':5',2'':5''',2''''':5''''',2''''''-quinqethiophene, 4',3''''-dioctyl-2,2':5',2'':5''',2''''':5''''',2''''''-sexithiophene, and 1,4-di(2-thienyl)benzene were purified by silica-gel column chromatography, followed by recrystalliza-

tion from *n*-hexane, mp 94 °C, 211 °C, 75 °C, 128 °C, and 212 °C.

The new vinyl monomers, V3T, V4T, VDOc5T, VDOc6T, and VTPT were synthesized by the Vilsmeier reaction of 2,2':5',2''-terthiophene, 2,2':5',2''':5'',2''''-quaterthiophene, 4',3'''-dioctyl-2,2':5',2''':5'',2''''':5''''',2''''''-quinque-thiophene, 4',3''''-dioctyl-2,2':5',2''':5'',2''''':5''''',2''''''':5''''''-sexithiophene, and 1,4-di(2-thienyl)benzene, followed by the Wittig reaction.

As an example, VDOc6T was synthesized as follows. Phosphorus oxychloride (3.0 g, 19.7 mmol) was added to DMF (20 mL) at room temperature, and the mixture was stirred for 20 min. This solution was added to a solution of 4',3''''-dioctyl-2,2':5',2''':5'',2''''':5''''',2''''''-sexithiophene (3.6 g, 5 mmol) in DMF (100 mL) over a period of 5 min at room temperature. The mixture was stirred at room temperature for 30 min and then heated at 75 °C for 12 hr. It was then cooled and poured into water. The resulting precipitate was collected by filtration, washed with water, dried, and separated by silica-gel column chromatography. Elution with benzene gave the starting material and then 4',3''''-dioctyl-5-formyl-2,2':5',2''':5'',2''''':5''''',2''''''-sexithiophene (DOc6T-CHO). DOc6T-CHO was purified by recrystallization from *n*-hexane to give dark red powders (0.65 g, yield 17 %), mp 96-97 °C.

Methyltriphenylphosphonium bromide (0.7 g, 2.0 mmol) was added to THF (50 mL) under a nitrogen atmosphere. *n*-Butyllithium (1.6 mmol) in *n*-hexane was added to this solution, and the resulting solution was stirred for 30 min. This mixture was added to a solution of DOc6T-CHO (0.65 g, 0.87 mmol) in dry THF (200 mL) and stirred for 3 hr at room temperature. After DOc6T-CHO in the solution disappeared, the solvent was evaporated. The re-

sulting solid was purified by silica-gel column chromatography. Elution with benzene gave VDOc6T, which was purified by recrystallization from *n*-hexane to give dark red powders (0.50 g, yield 77 %), mp 96-98 °C. Anal. Calcd for C<sub>42</sub>H<sub>48</sub>S<sub>6</sub>: C, 67.69; H, 6.49; S, 25.82. Found: C, 67.77; H, 6.48; S, 25.71. MS (m/z): 744 (M<sup>+</sup>). UV (THF, λ<sub>max</sub>): 426 nm (ε = 57 000 M<sup>-1</sup> cm<sup>-1</sup>). IR (KBr pellet, cm<sup>-1</sup>): 3076 (w, ν<sub>C-H</sub> thienyl), 3058 (w, ν<sub>C-H</sub> thienyl), 2952 (m, ν<sub>asC-H</sub> methyl), 2920 (s, ν<sub>asC-H</sub> methylene), 2867 (m, ν<sub>sC-H</sub> methyl), 2851 (s, ν<sub>sC-H</sub> methylene), 1615 (m, ν<sub>C=C</sub> vinyl), 972 (m, δ<sub>C-H</sub> vinyl), 890 (m, δ<sub>C-H</sub> vinyl), 833 (m, δ<sub>C-H</sub> 2-monosubstituted thiophene), 819 (m, δ<sub>C-H</sub> 2-monosubstituted thiophene), 805 (m, δ<sub>C-H</sub> 2,3,5-trisubstituted thiophene), 792 (m, δ<sub>C-H</sub> 2,5-disubstituted thiophene), 687 (m, δ<sub>C-H</sub> 2-monosubstituted thiophene). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): 7.09 (thienyl CH, 1H, dd, *J* = 1.5, 3.7 Hz), 7.05 (thienyl CH, 1H, s), 7.04 (thienyl CH, 1H, s), 6.98 (thienyl CH, 1H, d, *J* = 3.7 Hz), 6.97 (thienyl CH, 1H, d, *J* = 3.7 Hz), 6.96 (thienyl CH, 1H, d, *J* = 3.7 Hz), 6.96 (thienyl CH, 1H, d, *J* = 3.7 Hz), 6.93 (thienyl CH, 1H, d, *J* = 3.7 Hz), 6.78 (thienyl CH, 1H, dd, *J* = 1.5, 5.1 Hz), 6.72 (thienyl CH, 1H, dd, *J* = 3.7, 5.1 Hz), 6.59 (thienyl CH, 1H, d, *J* = 3.7 Hz), 6.57 (vinyl α-CH, dd, *J* = 11.0, 16.9 Hz), 5.53 (vinyl β-CH, 1H, d, *J* = 16.9 Hz), 4.97 (vinyl β-CH, 1H, d, *J* = 11.0 Hz), 2.74 (alkyl α-CH<sub>2</sub>, 4H, t, *J* = 6.6 Hz), 1.62-1.60 (alkyl β-CH<sub>2</sub>, 4H, m), 1.40-1.25 (alkyl CH<sub>2</sub>, 20H, m), 0.95 (CH<sub>3</sub>, 6H, t, *J* = 6.6 Hz).

The other three vinyl monomers, V3T, V4T, VDOc5T, and VTPT, were likewise synthesized and identified.

5-Vinyl-2,2':5',2''-terthiophene (V3T) : Yellow leaflets crystals, mp 126-

127 °C. Anal. Calcd for C<sub>14</sub>H<sub>10</sub>S<sub>3</sub>: C, 61.31; H, 3.65; S, 35.04. Found: C, 61.06; H, 3.63; S, 34.92. MS (m/z): 274 (M<sup>+</sup>). IR (KBr pellet, cm<sup>-1</sup>): 3076 (w, ν<sub>C-H</sub> thienyl), 3063 (w, ν<sub>C-H</sub> thienyl), 1612 (m, ν<sub>C=C</sub> vinyl), 979 (m, δ<sub>C-H</sub> vinyl), 898 (m, δ<sub>C-H</sub> vinyl), 833 (m, δ<sub>C-H</sub> 2-monosubstituted thiophene), 794 (s, δ<sub>C-H</sub> 2,5-disubstituted thiophene), 695 (m, δ<sub>C-H</sub> 2-monosubstituted thiophene). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>, ppm): 7.22 (thienyl CH, 1H, dd, *J* = 1.1, 4.9 Hz), 7.17 (thienyl CH, 1H, dd, *J* = 1.1, 3.8 Hz), 7.08 (thienyl CH, 1H, d, *J* = 3.8 Hz), 7.07 (thienyl CH, 1H, d, *J* = 3.8 Hz), 7.03 (thienyl CH, 1H, d, *J* = 3.8 Hz), 7.02 (thienyl CH, 1H, dd, *J* = 3.8, 4.9 Hz), 6.87 (thienyl CH, 1H, d, *J* = 3.8 Hz), 6.76 (vinyl α-CH, 1H, dd, *J* = 10.9, 16.9 Hz), 5.54 (vinyl β-CH, 1H, d, *J* = 16.9 Hz), 5.16 (vinyl β-CH, 1H, d, *J* = 10.9 Hz).

5-Vinyl-2,2':5',2'':5'',2'''-quaterthiophene (V4T) : Orange plate crystals, mp 189-190 °C. Anal. Calcd for C<sub>18</sub>H<sub>12</sub>S<sub>4</sub>: C, 60.67; H, 3.37; S, 35.96. Found: C, 60.87; H, 3.49; S, 35.81. MS (m/z): 356 (M<sup>+</sup>). UV (THF, λ<sub>max</sub>): 406 nm (ε = 31 000 M<sup>-1</sup> cm<sup>-1</sup>). IR (KBr pellet, cm<sup>-1</sup>): 3076 (w, ν<sub>C-H</sub> thienyl), 3062 (w, ν<sub>C-H</sub> thienyl), 1615 (m, ν<sub>C=C</sub> vinyl), 974 (m, δ<sub>C-H</sub> vinyl), 890 (m, δ<sub>C-H</sub> vinyl), 832 (m, δ<sub>C-H</sub> 2-monosubstituted thiophene), 818 (w, δ<sub>C-H</sub> 2-monosubstituted thiophene), 791 (s, δ<sub>C-H</sub> 2,5-disubstituted thiophene), 685 (m, δ<sub>C-H</sub> 2-monosubstituted thiophene). <sup>1</sup>H-NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): 7.01 (thienyl CH, 1H, dd, *J* = 1.5, 3.7 Hz), 6.86 (thienyl CH, 1H, d, *J* = 3.7 Hz), 6.85 (thienyl CH, 1H, d, *J* = 3.7 Hz), 6.85 (thienyl CH, 1H, d, *J* = 3.7 Hz), 6.84 (thienyl CH, 1H, d, *J* = 3.7 Hz), 6.82 (thienyl CH, 1H, d, *J* = 3.7 Hz), 6.75 (thienyl CH, 1H, dd, *J* = 1.5, 5.1 Hz), 6.68 (thienyl CH, 1H, dd, *J* = 3.7, 5.1 Hz), 6.56 (thienyl CH, 1H, d, *J* = 3.7 Hz), 6.55 (vinyl α-CH, 1H, dd, *J* = 11.0,

16.9 Hz), 5.50 (vinyl  $\beta$ -CH, 1H, d,  $J = 16.9$  Hz), 4.95 (vinyl  $\beta$ -CH, 1H, d,  $J = 11.0$  Hz).

4',3'''-Dioctyl-5-vinyl-2,2':5',2'':5'',2''':5''',2''''-quinquethiophene (VDOc5T) : Orange needle crystals, mp 68-70 °C. Anal. Calcd for  $C_{38}H_{46}S_5$ : C, 68.83; H, 6.99; S, 24.18. Found: C, 68.98; H, 7.07; S, 24.23. MS (m/z): 662 ( $M^+$ ). UV (THF,  $\lambda_{max}$ ): 408 nm ( $\epsilon = 42\,000\ M^{-1}\ cm^{-1}$ ). IR (KBr pellet,  $cm^{-1}$ ): 3080 (w,  $\nu_{C-H}$  thienyl), 3065 (w,  $\nu_{C-H}$  thienyl), 2953 (m,  $\nu_{as\ C-H}$  methyl), 2923 (s,  $\nu_{as\ C-H}$  methylene), 2869 (m,  $\nu_s\ C-H$  methyl), 2852 (s,  $\nu_s\ C-H$  methylene), 1616 (m,  $\nu_{C=C}$  vinyl), 974 (m,  $\delta_{C-H}$  vinyl), 890 (m,  $\delta_{C-H}$  vinyl), 831 (m,  $\delta_{C-H}$  2-monosubstituted thiophene), 819 (m,  $\delta_{C-H}$  2-monosubstituted thiophene), 803 (m,  $\delta_{C-H}$  2,3,5-trisubstituted thiophene), 798 (m,  $\delta_{C-H}$  2,5-disubstituted thiophene), 684 (m,  $\delta_{C-H}$  2-monosubstituted thiophene).  $^1H$ -NMR (400 MHz,  $C_6D_6$ , ppm): 7.08 (thienyl CH, 1H, dd,  $J = 1.5, 3.7$  Hz), 7.06 (thienyl CH, 2H, s), 7.05 (thienyl CH, 1H, s), 7.04 (thienyl CH, 1H, s), 6.92 (thienyl CH, 1H, d,  $J = 3.7$  Hz), 6.78 (thienyl CH, 1H, dd,  $J = 1.5, 5.1$  Hz), 6.71 (thienyl CH, 1H, dd,  $J = 3.7, 5.1$  Hz), 6.58 (thienyl CH, 1H, d,  $J = 3.7$  Hz), 6.57 (vinyl  $\alpha$ -CH, dd,  $J = 11.0, 16.9$  Hz), 5.52 (vinyl  $\beta$ -CH, 1H, d,  $J = 16.9$  Hz), 4.96 (vinyl  $\beta$ -CH, 1H, d,  $J = 11.0$  Hz), 2.75 (alkyl  $\alpha$ -CH<sub>2</sub>, 4H, t,  $J = 6.6$  Hz), 1.63-1.60 (alkyl  $\beta$ -CH<sub>2</sub>, 4H, m), 1.40-1.25 (alkyl CH<sub>2</sub>, 20H, m), 0.95 (CH<sub>3</sub>, 6H, t,  $J = 6.6$  Hz).

2-[4-(2-thienyl)phenyl]-5-vinylthiophene (VTPT) : Yellow needle crystals. Anal. Calcd for  $C_{16}H_{12}S_2$ : C, 71.60; H, 4.51; S, 23.89. Found: C, 71.39; H, 4.66; S, 23.52. MS (m/z): 268 ( $M^+$ ). IR (KBr pellet,  $cm^{-1}$ ): 3076 (w,  $\nu_{C-H}$  aromatic), 3063 (w,  $\nu_{C-H}$  aromatic), 1620 (m,  $\nu_{C=C}$  vinyl), 980 (m,  $\delta_{C-H}$  vi-

nyl), 900 (m,  $\delta_{\text{C-H}}$  vinyl), 820 (m,  $\delta_{\text{C-H}}$  1,4-disubstituted benzene), 800 (s,  $\delta_{\text{C-H}}$  2,5-disubstituted thiophene), 690 (m,  $\delta_{\text{C-H}}$  2-monosubstituted thiophene).  $^1\text{H-NMR}$  (400 MHz, 1,4-dioxane-*d*8, ppm): 7.64 (phenyl CH, 2H, d,  $J = 2.4$  Hz), 7.64 (phenyl CH, 2H, d,  $J = 2.4$  Hz), 7.41 (thienyl CH, 1H, dd,  $J = 1.0, 3.9$  Hz), 7.37 (thienyl CH, 1H, dd,  $J = 1.0, 4.9$  Hz), 7.30 (thienyl CH, 1H, d,  $J = 3.9$  Hz), 7.08 (thienyl CH, 1H, dd,  $J = 4.9, 3.9$  Hz), 6.99 (thienyl CH, 1H, d,  $J = 3.9$  Hz), 6.81 (vinyl  $\alpha$ -CH, 1H, dd,  $J = 10.7, 17.6$  Hz), 5.58 (vinyl  $\beta$ -CH, 1H, d,  $J = 17.6$  Hz), 5.15 (vinyl  $\beta$ -CH, 1H, d,  $J = 10.7$  Hz).

#### *Polymerization of 5-Vinyl-2,2':5',2''-terthiophene*

Poly(5-vinyl-2,2':5',2''-terthiophene) was prepared by radical and cationic polymerization of 5-vinyl-2,2':5',2''-terthiophene. Radical polymerization was carried out in an evacuated benzene solution containing the monomer and AIBN at 70 °C for 48 hr. The concentrations of the monomer and AIBN were  $3.7 \times 10^{-1}$  and  $3.7 \times 10^{-3}$  mol dm<sup>-3</sup>, respectively. Cationic polymerization was carried out in an evacuated dichloromethane solution containing the monomer and boron trifluoride diethyl etherate with concentrations of  $5.0 \times 10^{-2}$  and  $9.0 \times 10^{-4}$  mol dm<sup>-3</sup>, respectively, at 0 °C for 8 hr. The polymers obtained by radical and cationic polymerizations were purified by reprecipitation three times from THF / *n*-hexane and benzene / methanol, respectively. The molecular weights of the polymers prepared by radical and cationic polymerizations were determined to be  $M_n = 2,200$  and  $M_w = 3,400$  and  $M_n = 2,500$  and  $M_w = 5,500$ , respectively, by gel permeation chromatography using polystyrene standards.

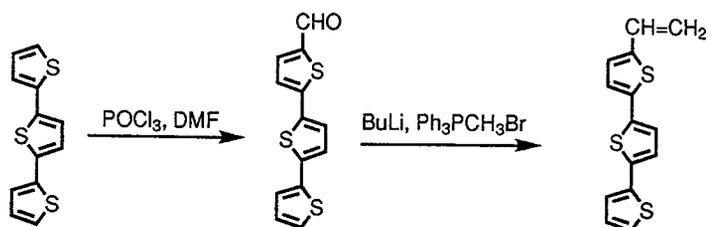
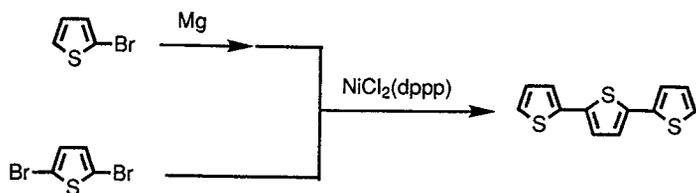
## *Apparatus*

FT-IR, UV-VIS,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectra were measured with a Model FT/IR-300 FT-IR spectrophotometer (Japan Spectroscopic Co., Ltd.), a Model U-3200 double-beam spectrophotometer (Hitachi, Ltd.), a Model JNM-GSX-400 spectrometer (JEOL), and a Model AM-600 (Bruker), respectively. Molecular weights of the polymers were measured with a Model 600 gel permeation chromatography system (waters, Ltd.) using THF as an eluent. The calibration curve was obtained using polystyrene standards.

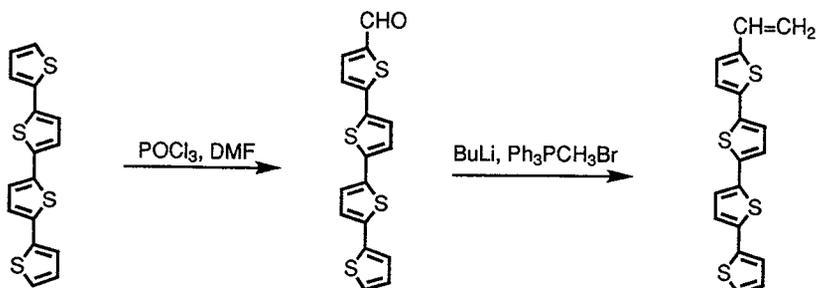
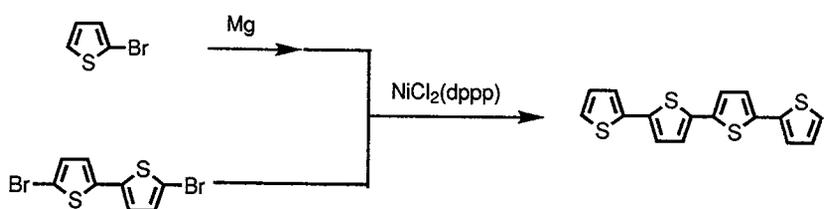
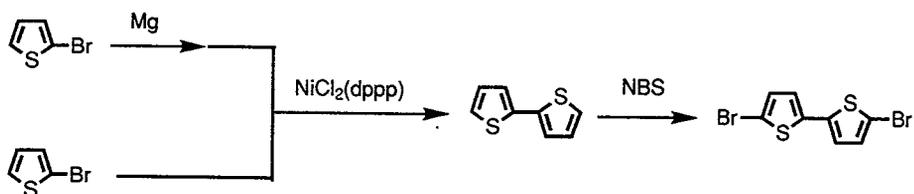
## **1-3 Results and Discussion**

### *Synthesis of New Vinyl Monomers*

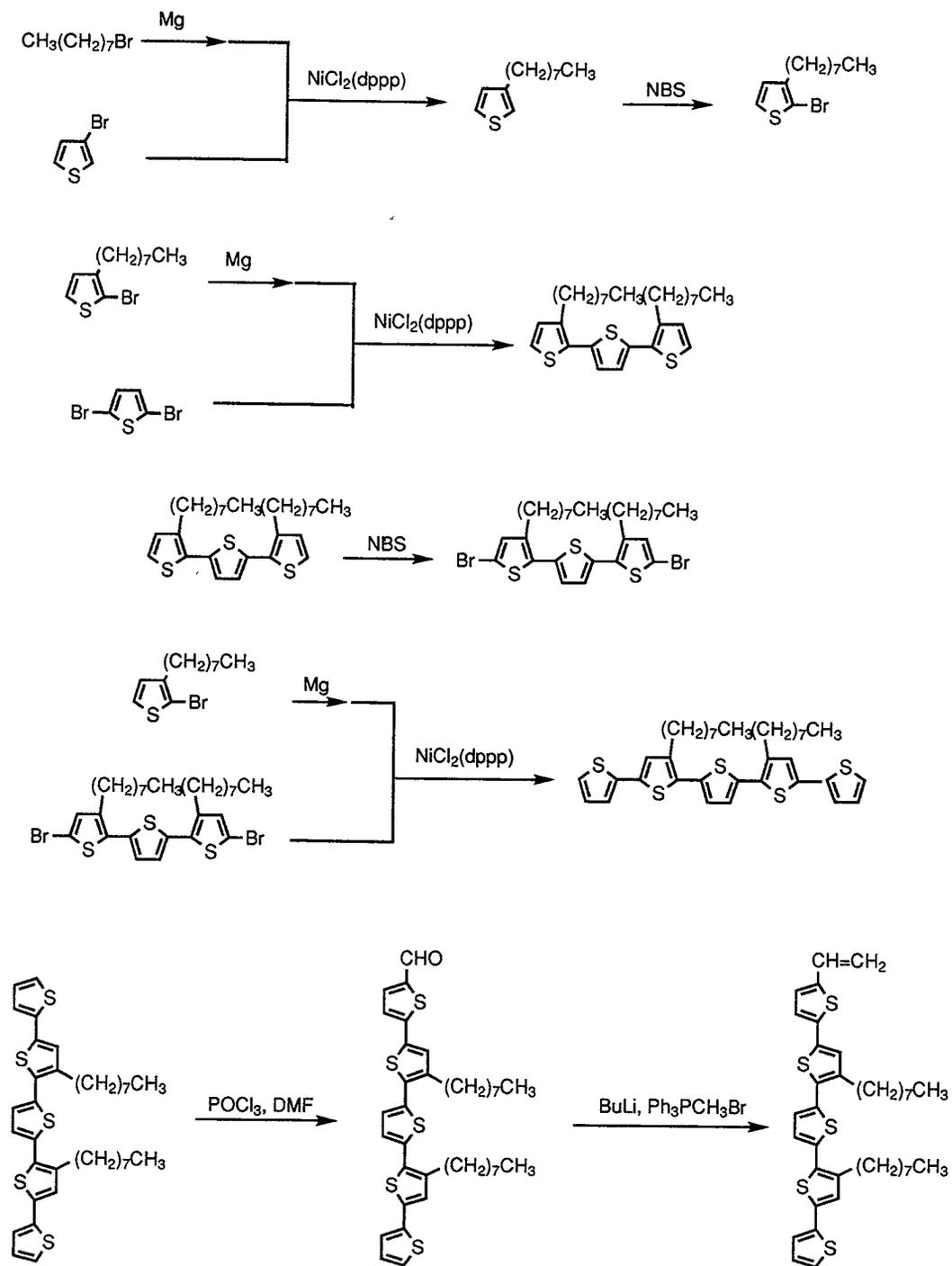
The new vinyl monomers, V3T, V4T, VDOc5T, VDOc6T, and VTPT, were synthesized by the Vilsmeier reaction of 2,2':5',2''-terthiophene, 2,2':5',2'':5''',2''''-quaterthiophene, 4',3'''-dioctyl-2,2':5',2'':5''',2''''-quinque-thiophene, 4',3''''-dioctyl-2,2':5',2'':5''',2''''':5''''',2''''''-sexithiophene, and 1,4-di(2-thienyl)benzene, respectively, followed by the Wittig reaction (Scheme 1-1). The synthesis of vinyl monomers containing unsubstituted  $\alpha$ -linked quinquethiophene and sexithiophene was initially attempted but not successful because of their low solubility in ordinary organic solvents. Therefore, a long-chain alkyl group such as an octyl group was incorporated at the  $\beta$ -position of the thiophene ring of quinquethiophene and sexithiophene in order to enhance the solubility of the monomers as well as the formyl oligothiophenes and the starting oligothiophenes.



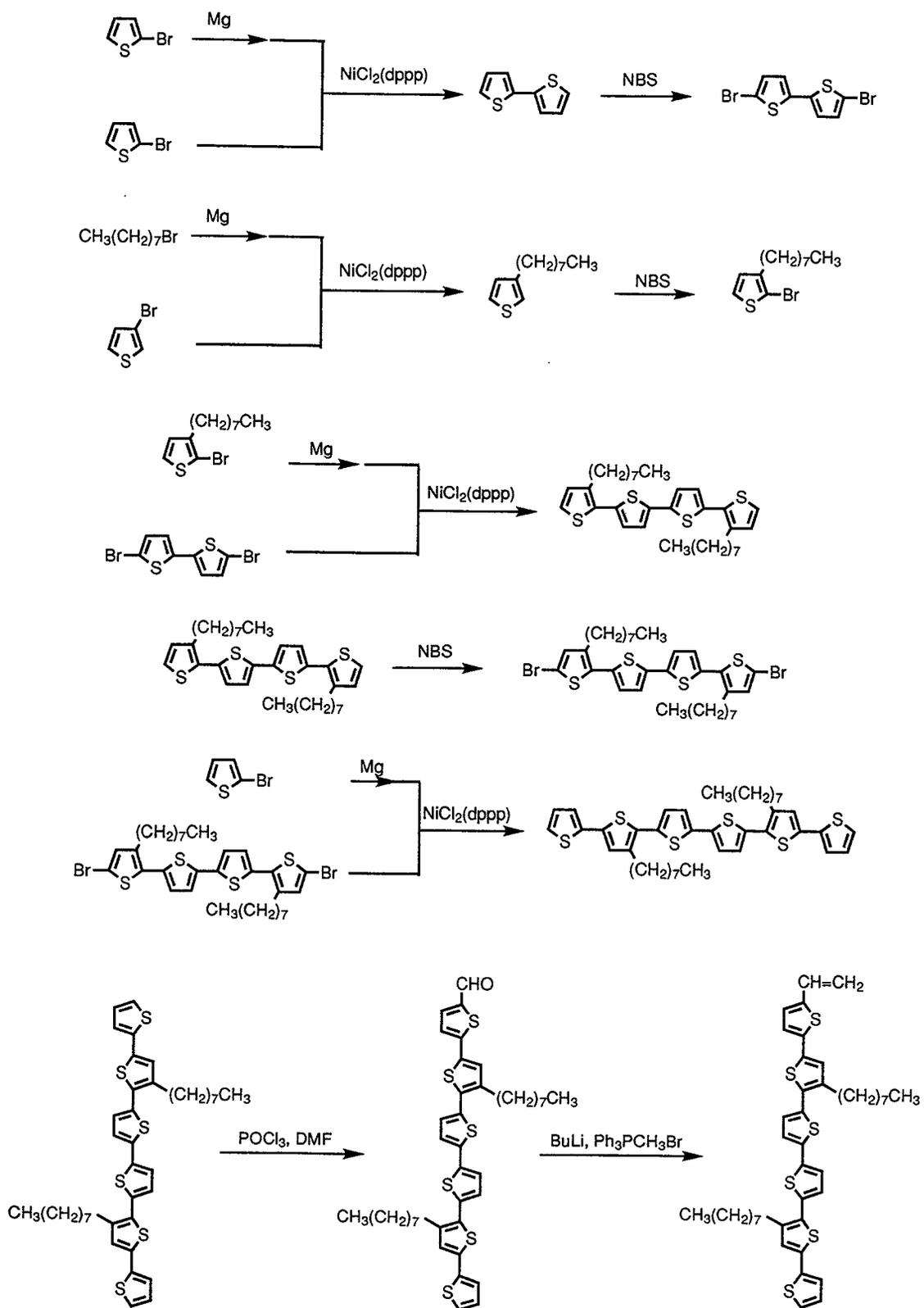
**Scheme 1-1(a).** Synthesis of V3T.



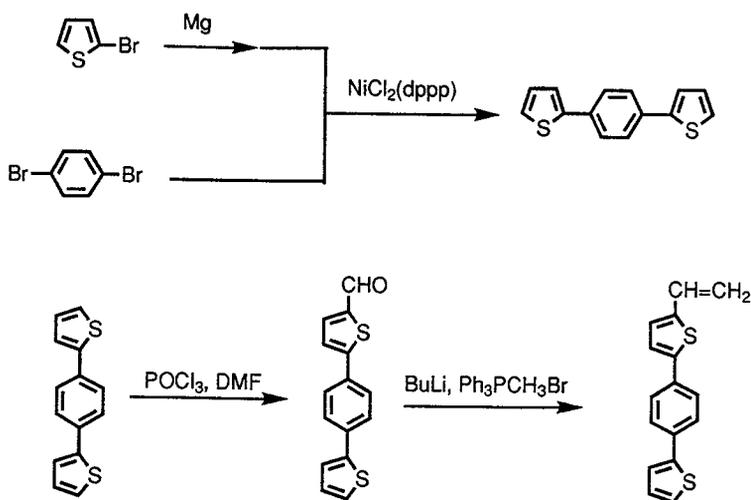
**Scheme 1-1(b).** Synthesis of V4T.



Scheme 1-1(c). Synthesis of VDOc5T.



**Scheme 1-1(d).** Synthesis of VDOc6T.

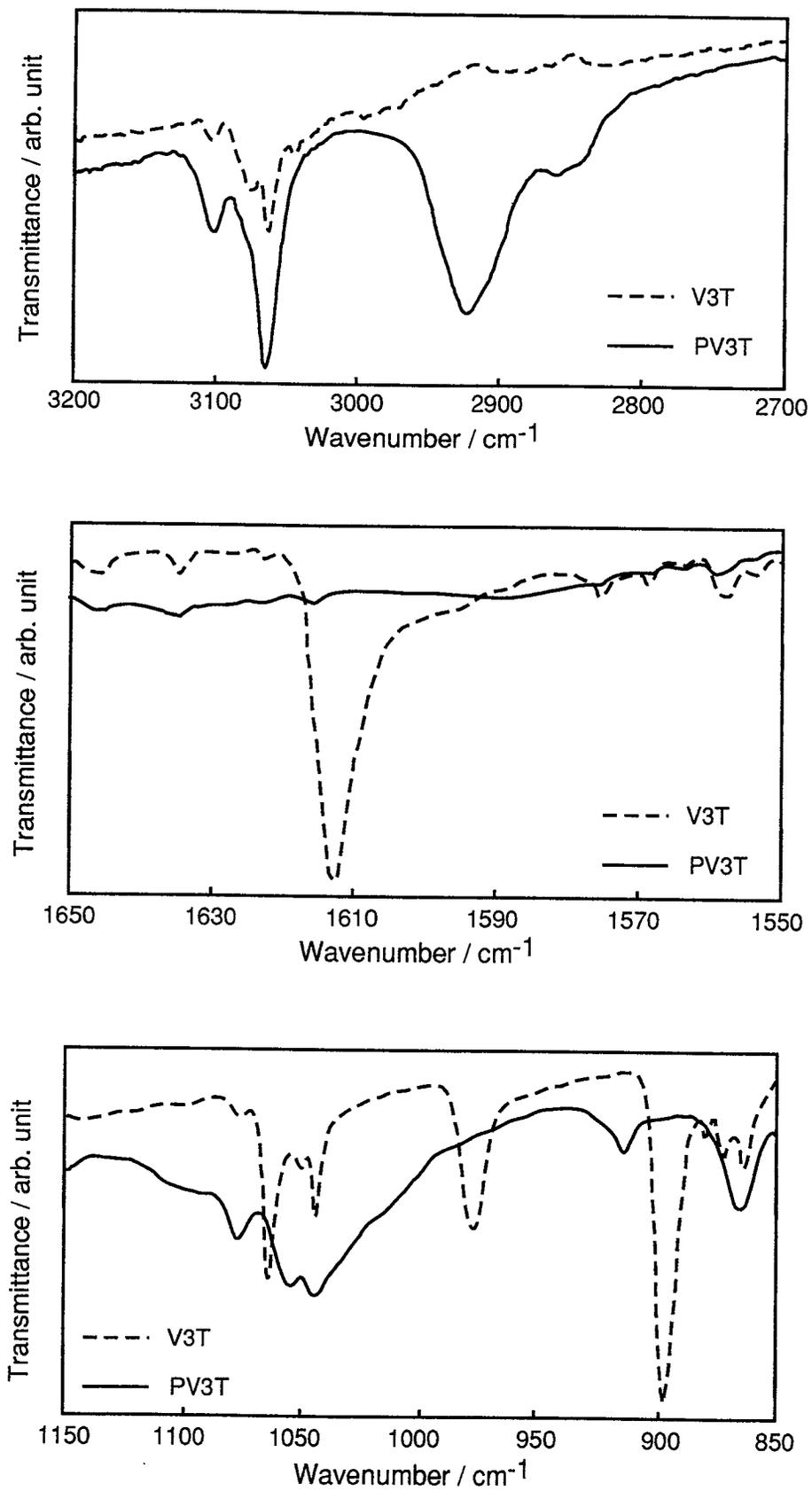


**Scheme 1-1(e).** Synthesis of VTPT.

### *Synthesis of Poly(5-vinyl-2,2':5',2''-terthiophene)*

Poly(5-vinyl-2,2':5',2''-terthiophene) was prepared by radical and cationic polymerizations of 5-vinyl-2,2':5',2''-terthiophene. The polymers are not readily soluble in ordinary solvents but soluble in dichloromethane and THF up to a concentration of *ca.*  $1 \times 10^{-2}$  mol dm<sup>-3</sup>.

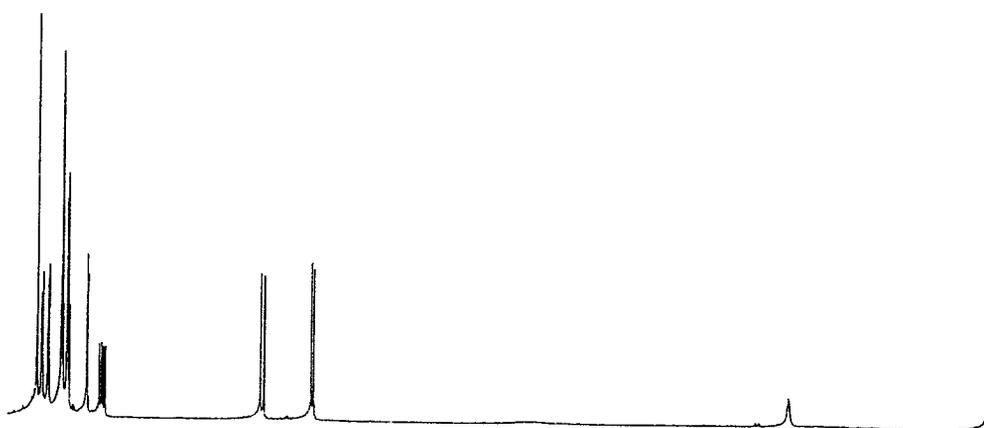
The polymers were characterized by infrared absorption and nuclear magnetic resonance spectroscopies. Figure 1-1 shows the infrared absorption spectra of the vinyl monomer V3T and the polymer PV3T prepared by chemical polymerizations of V3T. The characteristic infrared absorption bands at 1612 cm<sup>-1</sup> and at 979 and 898 cm<sup>-1</sup> observed for V3T, which are due to the stretching vibration of the vinyl C=C and to the C-H out-of-plane deformation vibrations of the vinyl group, respectively, are absent in the spectrum of the polymer prepared by the chemical polymerizations of V3T. Instead, new absorption bands due to the asymmetric and symmetric stretching vibrations of the methylene group appear at 2924 and 2862 cm<sup>-1</sup>, respectively.



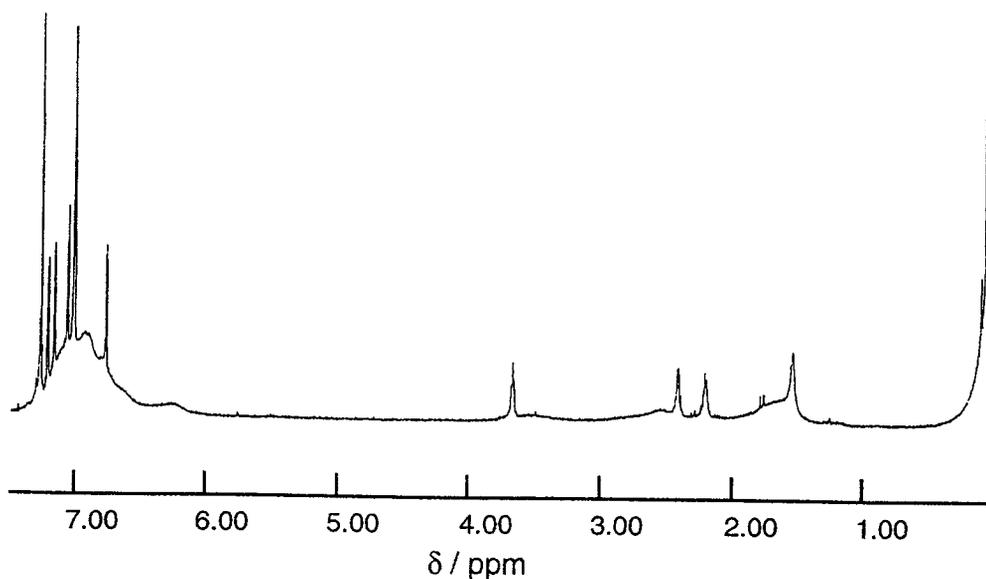
**Figure 1-1.** Infrared absorption spectra of V3T and PV3T.

Figure 1-2 shows  $^1\text{H}$  NMR spectra of the vinyl monomer V3T and the polymer prepared by the chemical polymerizations of V3T. The characteristic signals at 5.2, 5.5 and 6.8 ppm observed for V3T, which are due to the protons of vinyl group, respectively, are absent in the spectra of the polymer prepared by the chemical polymerizations of V3T. Instead, new signals due to protons of methylene and methine groups appear at 2.2 and 2.4 ppm and 3.6 ppm.

(a)



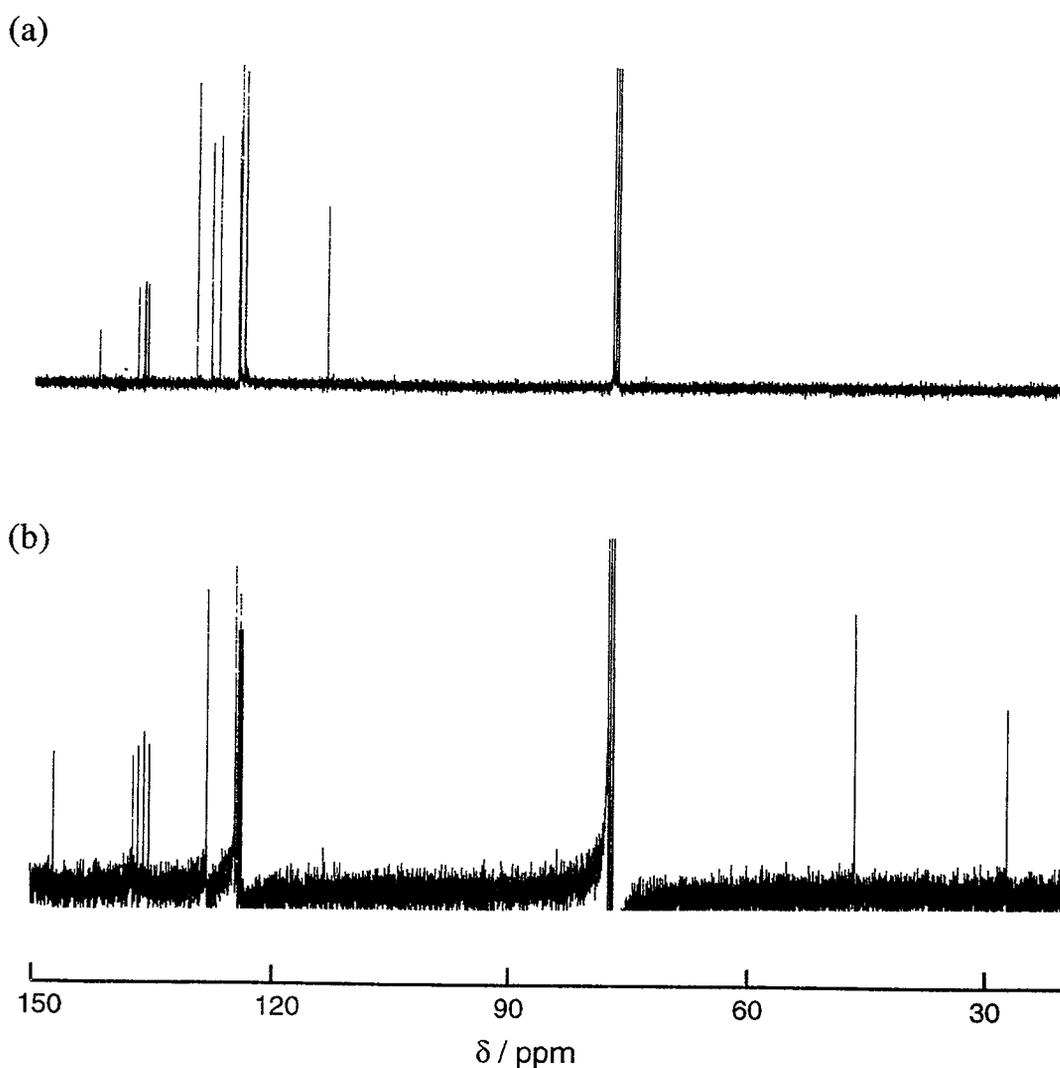
(b)



**Figure 1-2.**  $^1\text{H}$  NMR spectra of (a) V3T and (b) PV3T.

Figure 1-3 shows  $^{13}\text{C}$  NMR spectra of V3T and PV3T. Signals at 113.4 and 129.7 ppm due to carbons of vinyl group observed for V3T disappear in the spectrum of PV3T. Instead, new signals due to carbons of methylene and methine groups appear at 27.2 ppm and 46.0 ppm.

These results indicate that the radical and cationic polymerizations of 5-vinyl-2,2':5',2''-terthiophene take place at the vinyl group.



**Figure 1-3.**  $^{13}\text{C}$  NMR spectra of (a) V3T and (b) PV3T.

## 1-4 Summary

For the purpose of developing a novel family of vinyl polymers containing pendant oligothiophenes, a novel family of vinyl monomers containing oligothiophenes with well-defined structures, 5-vinyl-2,2':5',2''-terthiophene (V3T), 5-vinyl-2,2':5',2'':5'',2'''-quaterthiophene (V4T), 4',3'''-dioctyl-5-vinyl-2,2':5',2'':5'',2'''':5''''-quinquethiophene (VDOc5T), 4',3''''-dioctyl-5-vinyl-2,2':5',2'':5'',2'''':5''''',2''''''-sexithiophene (VDOc6T), and 2-[4-(2-thienyl)phenyl]-5-vinylthiophene (VTPT), and a novel vinyl polymer containing pendant terthiophene, poly(5-vinyl-2,2':5',2''-terthiophene) (PV3T), have been synthesized. The polymer obtained by radical and cationic polymerizations of 5-vinyl-2,2':5',2''-terthiophene was found to have molecular weights of  $M_n = 2,200$ ,  $M_w = 3,400$  and  $M_n = 2,500$ ,  $M_w = 5,500$ . The polymer is soluble in dichloromethane and THF to make spectroscopic measurements and electrochemical doping.

## Chapter 2

### Preparation, Characterization, and Electrical Properties of Electrochemically-doped Vinyl Polymers Containing Pendant Oligothiophenes

#### 2-1 Introduction

$\alpha,\alpha'$ -Oligothiophenes with well-defined structures have been studied as model compounds for electrically conducting polythiophenes as above mentioned. Polythiophenes exhibit high electrical conductivity on doping. Necessarily, it is of interest to investigate the structure and properties of oligothiophenes in the doped state for the sake of understanding such properties of polythiophenes in the doped state. Therefore, chemical and electrochemical doping of oligothiophenes have been attempted and the optical<sup>39,43,44,76-86</sup> and electrical properties<sup>40,45,47,87-92</sup> of the resulting radical-ion salts have been investigated. We have studied the electrochemical doping of 5,5'''-diethyl-2,2':5',2'':5'',2'''-quaterthiophene (DEt4T) and 5,5''''-diethyl-2,2':5',2'':5'',2''':5''',2''''-quinquethiophene (DEt5T) and the electrical conductivity of the resulting radical-cation salts.<sup>47</sup>

It is of great interest to elucidate the correlation between the structures and properties of electrochemically-doped polymers containing pendant oligothiophenes and the conjugation length of pendant oligothiophenes.

In this chapter, preparation, characterization, and electrical properties of electrochemically-doped vinyl polymers containing pendant oligothiophenes with well-defined structures by electrochemical doping of polymer solution and electrolytic polymerization of vinyl monomer has been studied.

## 2-2 Experimental

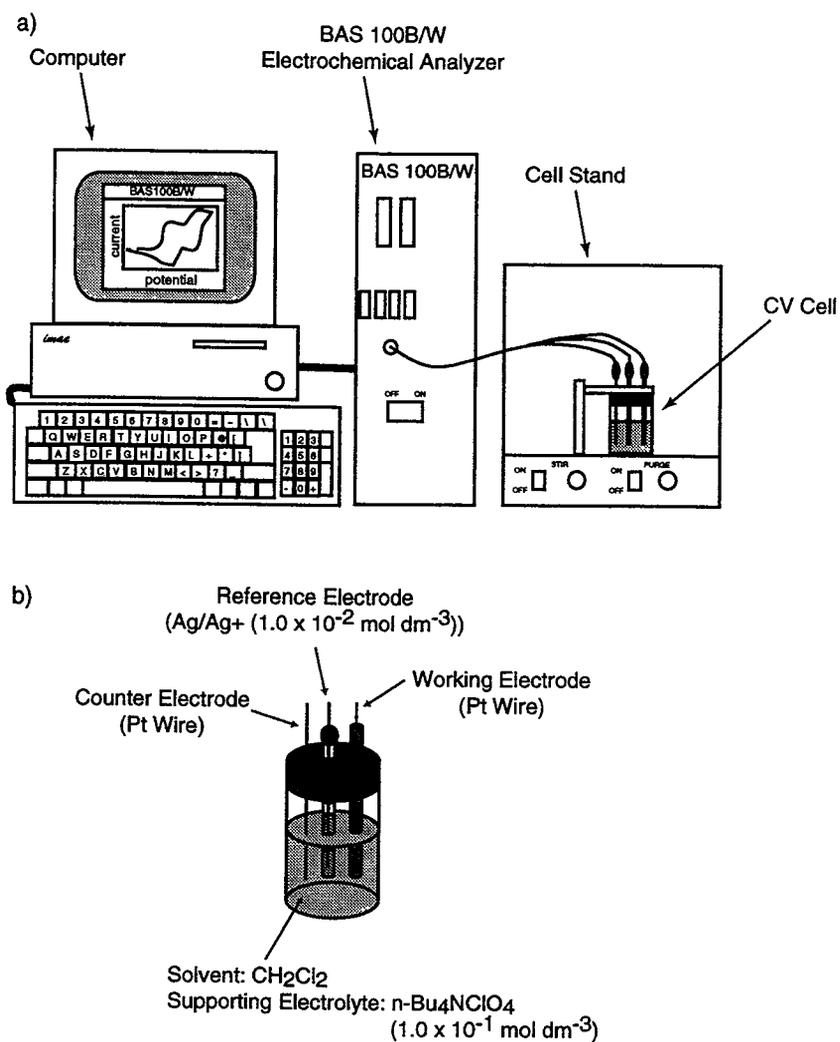
### *Materials*

Dichloromethane was treated with *conc.* sulfuric acid, water, and then distilled over calcium hydride immediately before use. Tetra-*n*-butylammonium perchlorate (Tokyo Kasei, guaranteed reagent) was recrystallized from ethanol three times, dried at 70 °C for 24 hr, stored in a desiccator, and redried *in vacuo* at room-temperature immediately before use.

### *Electrochemical Oxidation*

Cyclic voltammetry was carried out for dichloromethane solutions ( $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) of the vinyl monomers or polymer containing tetra-*n*-butylammonium perchlorate ( $1.0 \times 10^{-1} \text{ mol dm}^{-3}$ ) as a supporting electrolyte using a Ag/Ag<sup>+</sup> ( $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ) reference electrode, which is illustrated in Figure 2-1.

Electrolytic polymerization was carried out potentiostatically in a two-compartment cell with three electrodes for dichloromethane solutions ( $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) of the vinyl monomers or polymers containing tetra-*n*-butylammonium perchlorate ( $1.0 \times 10^{-1} \text{ mol dm}^{-3}$ ) as a supporting electrolyte. Platinum plates were used as the working and counter electrodes, which is illustrated in Figure 2-2.



**Figure 2-1.** Apparatus for cyclic voltammetry. (a) Total scheme of apparatus. (b) Construction of CV cell.

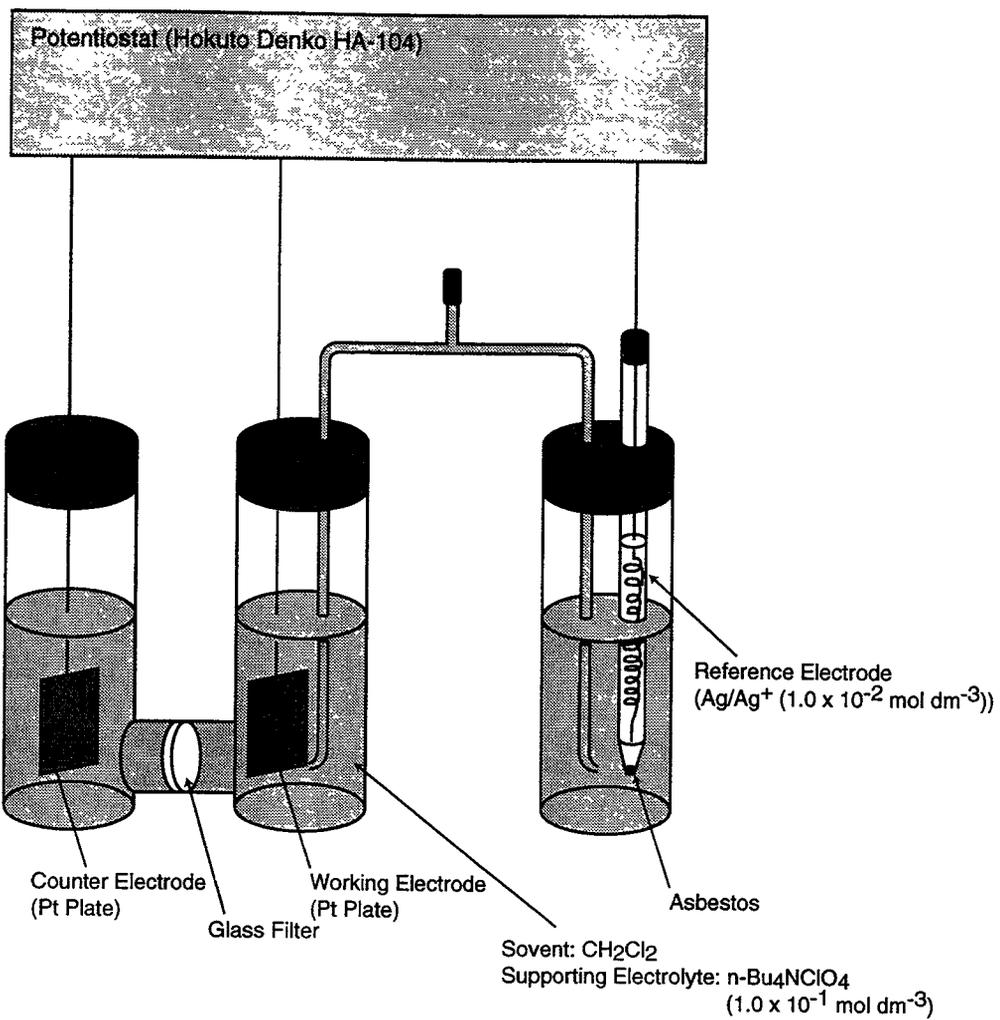
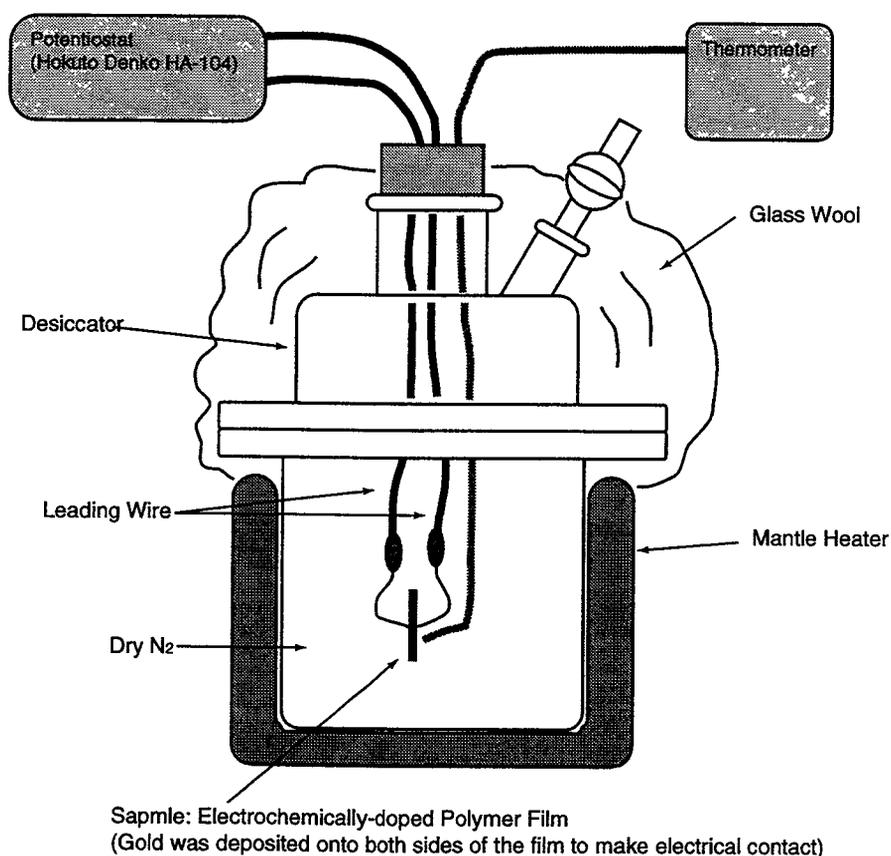


Figure 2-2. Apparatus for anodic oxidation.

## Conductivity Measurement

Electrical conductivity was measured by a two-probe dc method for several film samples obtained by peeling off from the working electrode. Gold was deposited onto both sides of the film by vacuum evaporation to make electrical contact. The activation energy for electrical conduction was determined from the Arrhenius plot of electrical conductivity measured in a temperature range from 20 to 80 °C.



**Figure 2-3.** Apparatus for conductivity measurement.

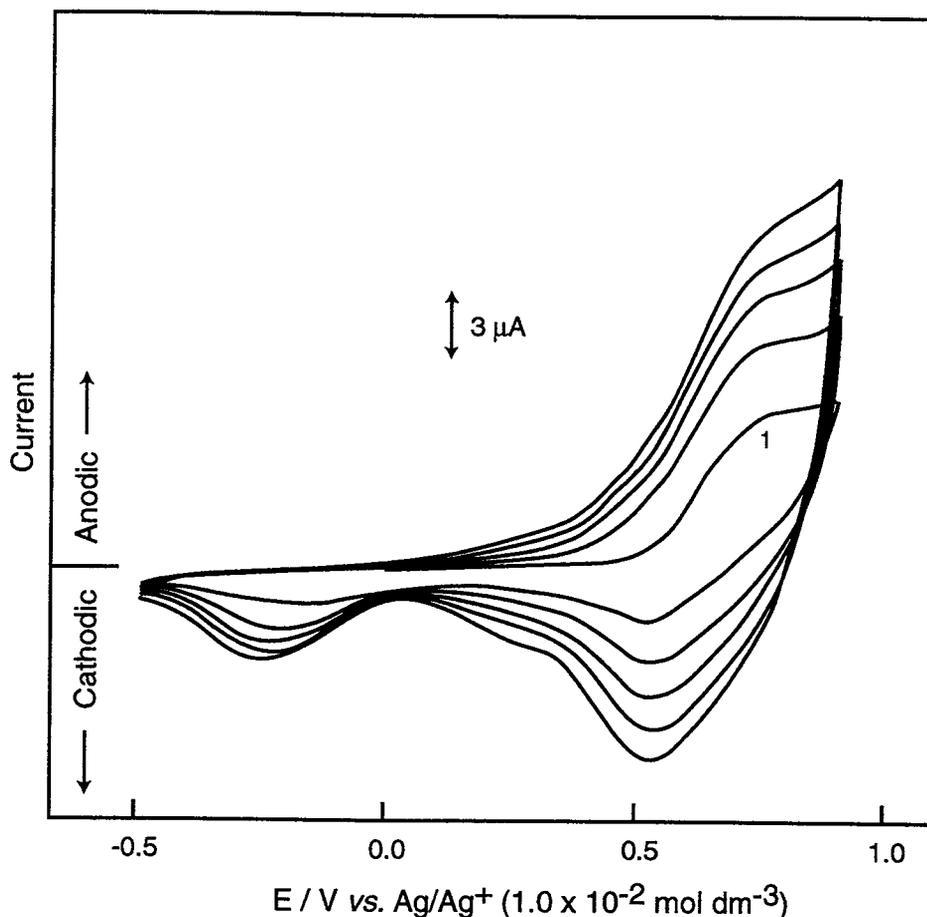
## *Apparatus*

Electrochemical measurements were carried out using a Model BAS 100B/W (Bioanalytical Systems, Inc.), a Model HA-104 potentiostat (Hokuto Denko, Ltd.), a Model HB-104 function generator (Hokuto Denko, Ltd.), and a Model NP-0361 recorder (Rikadenki). FT-IR, UV-VIS, and ESR spectra were measured with a Model FT/IR-300 FT-IR spectrophotometer (Japan Spectroscopic Co., Ltd.), a Model U-3200 double-beam spectrophotometer (Hitachi, Ltd.), and a Model JES-ME-2X (JEOL), respectively.

## **2-3 Results and Discussion**

### *Anodic Oxidation Processes of the Vinyl Monomers and Polymer*

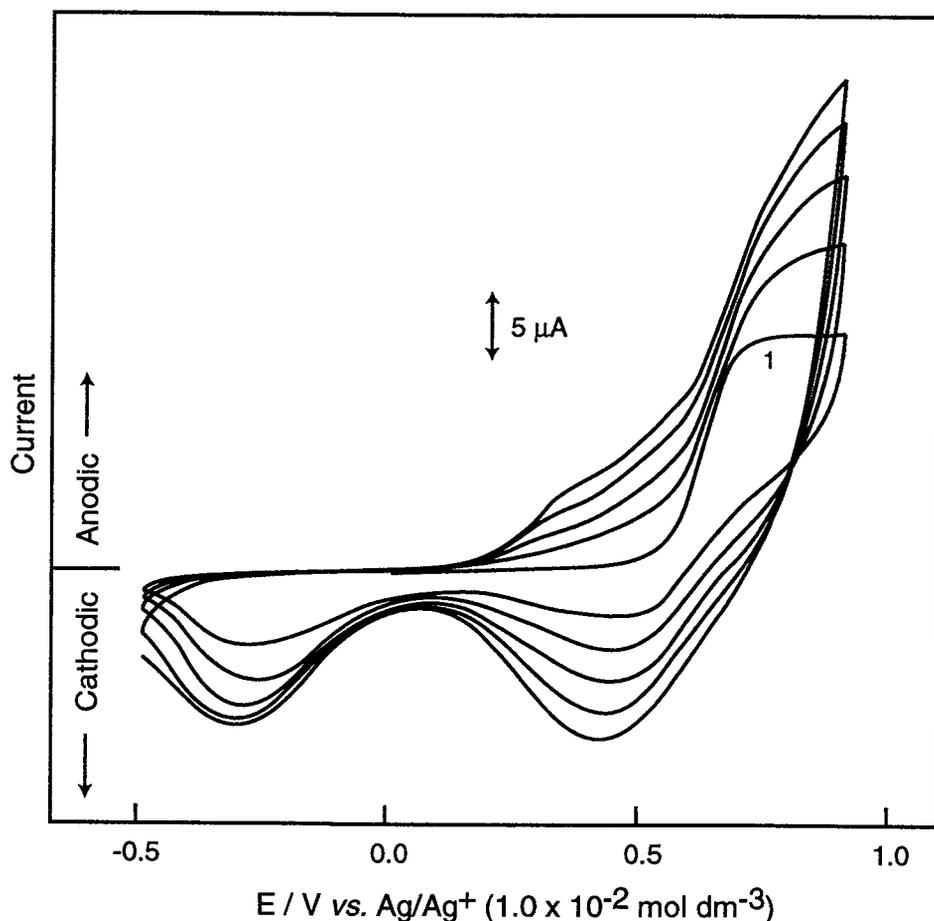
Cyclic voltammetry was carried out in order to obtain information on the anodic oxidation processes of the vinyl monomers and polymer. Figure 2-4 shows cyclic voltammograms for the anodic oxidation of PV3T. The anodic wave due to the oxidation of the pendant terthiophene moiety in the polymer was observed at  $E_{pa/2} = 0.70$  V ( $E_{pa} = ca. 0.80$  V) vs. Ag/Ag<sup>+</sup> ( $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>), but the corresponding cathodic wave was much smaller. In addition, a new cathodic wave was observed at  $E_{pc} = ca. -0.30$  V vs. Ag/Ag<sup>+</sup> ( $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>). This cathodic wave is ascribed to the reduction of H<sup>+</sup>, generated by the deprotonation at the  $\alpha$ -position of the terminal thiophene ring on the coupling reaction of the pendant terthiophene radical cations. In addition to the above anodic and cathodic waves, another new anodic and the corresponding cathodic waves were observed at a potential more negative than 0.60 V.



**Figure 2-4.** Cyclic voltammograms of PV3T ( $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) in dichloromethane containing  $n\text{-Bu}_4\text{NClO}_4$  ( $1.0 \times 10^{-1} \text{ mol dm}^{-3}$ ). 1: First sweep. Sweep rate:  $100 \text{ mV sec}^{-1}$ .

The new anodic and the corresponding cathodic waves at the potential more negative than  $0.60 \text{ V}$  are ascribed to the oxidation of the sexithiophene moiety, generated by the coupling reaction of the pendant terthiophene radical cation, and to the reduction of the sexithiophene radical cation, respectively. The anodic waves ascribed to the pendant terthiophene and the sexithiophene approximately in accord with the literature data for the anodic oxidations of terthiophene and sexithiophene,  $1.05$  and  $0.84 \text{ V} (E_{\text{pa}})$  vs. SCE,<sup>93</sup> *i.e.*,  $0.78$  and  $0.57 \text{ V} (E_{\text{pa}})$  vs.  $\text{Ag}/\text{Ag}^+$  ( $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ), respectively.

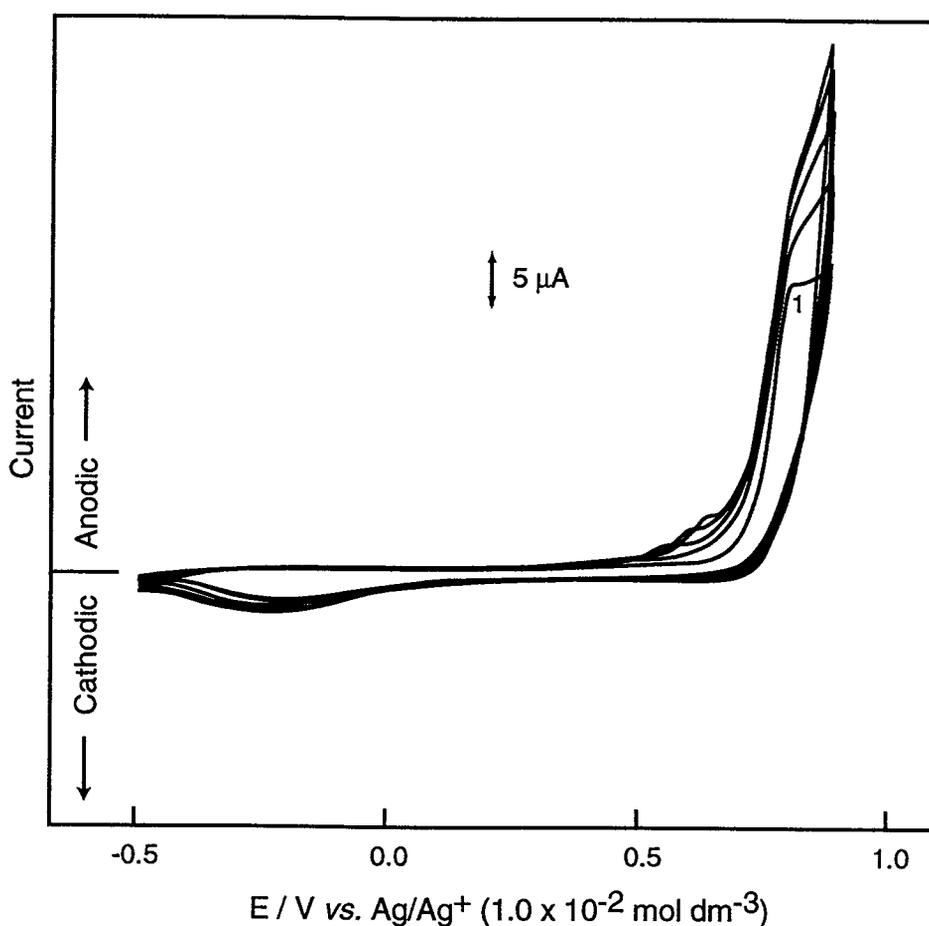
The anodic oxidation process of V3T was totally irreversible (Figure 2-5). In the first sweep, an anodic wave due to the oxidation of V3T was observed at  $E_{pa/2} = 0.67$  V ( $E_{pa} = 0.77$  V) vs. Ag/Ag<sup>+</sup> ( $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>) reference electrode, but the corresponding cathodic wave was much smaller. When the sweep was repeated, the anodic wave shifted slightly to a more positive potential, and the cathodic waves were observed at *ca.* 0.80 and *ca.* 0.50 V. Another new cathodic wave due to the reduction of H<sup>+</sup> generated by deprotonation at the  $\alpha$ -position of terminal thiophene ring on the coupling reaction of pendant terthiophene radical cations. The new anodic wave at a po-



**Figure 2-5.** Cyclic voltammograms of V3T ( $1 \times 10^{-3}$  mol dm<sup>-3</sup>) in dichloromethene containing n-Bu<sub>4</sub>NClO<sub>4</sub> ( $1.0 \times 10^{-1}$  mol dm<sup>-3</sup>). 1: First sweep. Scan rate: 100 mV sec<sup>-1</sup>.

tential more negative than 0.60 V is ascribed to the oxidation of the sexithiophene moiety generated by the coupling reaction of the pendant terthiophene radical cation. These results indicate that the electrochemical doping of PV3T and the electrolytic polymerization of V3T are accompanied by the coupling reaction of the pendant terthiophene moiety to produce partially a sexithiophene moiety.

Figure 2-6 shows cyclic voltammograms of VTPT, which contains three aromatic rings such as V3T. The anodic process of VTPT was irreversible like the case of V3T. An anodic wave due to the oxidation of VTPT was observed

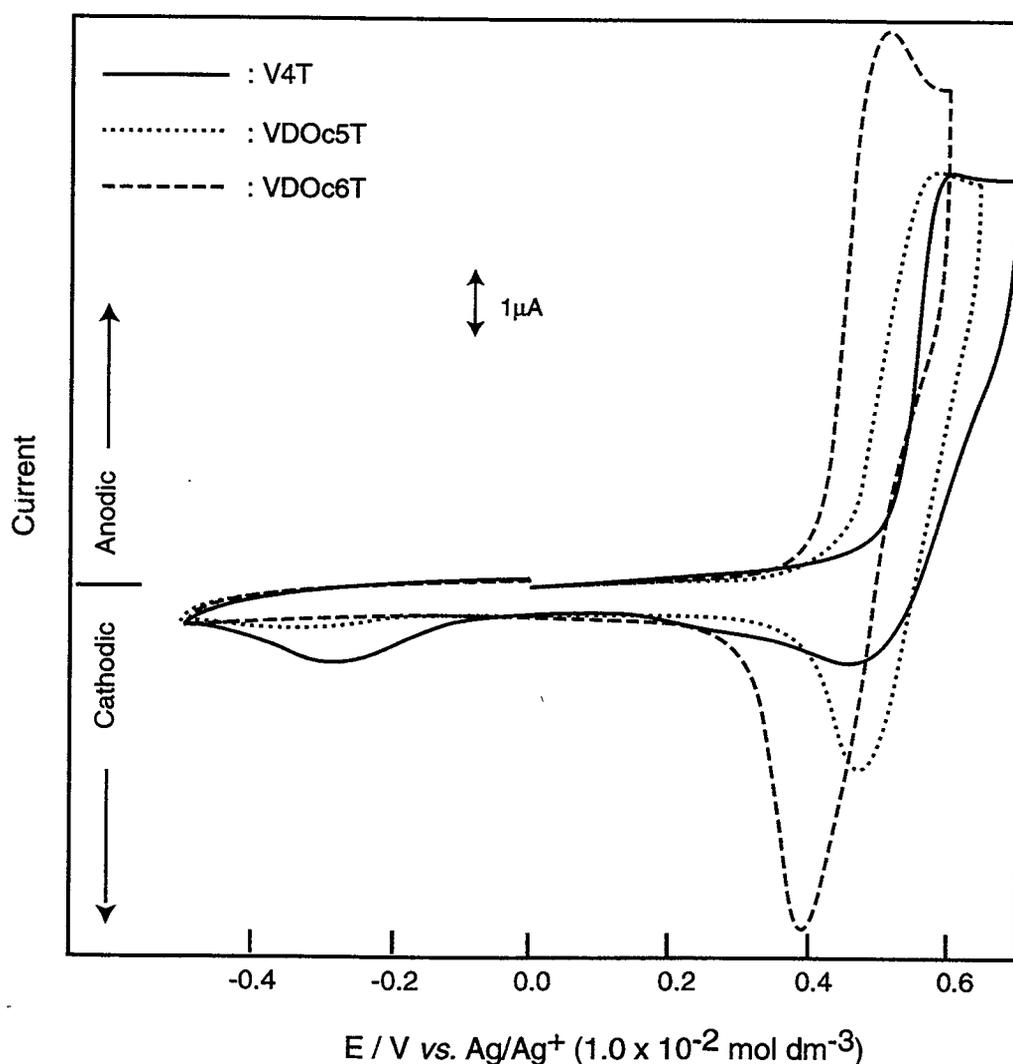


**Figure 2-6.** Cyclic voltammograms of VTPT ( $1 \times 10^{-3} \text{ mol dm}^{-3}$ ) in dichloromethane containing  $n\text{-Bu}_4\text{NClO}_4$  ( $1.0 \times 10^{-1} \text{ mol dm}^{-3}$ ). 1: First sweep. Scan rate:  $100 \text{ mV sec}^{-1}$ .

at  $E_{pa/2} = 0.87$  V ( $E_{pa} = ca. 0.95$  V) vs. Ag/Ag<sup>+</sup> ( $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>), but the corresponding cathodic wave was little observed.

It is of interest to investigate the correlation between the conjugation length of oligothiophenes and the electrochemical properties of vinyl monomers having them. Figure 2-7 shows cyclic voltammograms for the anodic oxidations of V4T, VDOc5T, and VDOc6T in dichloromethane. The anodic oxidation process of V4T, VDOc5T, and VDOc6T were irreversible. The anodic wave due to the oxidation of V4T was observed at  $E_{pa/2} = 0.55$  V ( $E_{pa} = 0.60$  V) vs. Ag/Ag<sup>+</sup> ( $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>), but the corresponding cathodic wave ( $E_{pc} = 0.46$  V vs. Ag/Ag<sup>+</sup> ( $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>)) was much smaller in intensity. In addition to the above anodic and cathodic waves, another cathodic wave was also observed at  $E_{pc} = ca. -0.30$  V vs. Ag/Ag<sup>+</sup> ( $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>), which is ascribed to the reduction of H<sup>+</sup> as above mentioned, generated by the deprotonation at the  $\alpha$ -position of the terminal thiophene ring in the coupling reaction of the pendant quaterthiophene radical cation. These results are similar to those of V3T. Likewise, the anodic waves due to the oxidation of VDOc5T and VDOc6T were observed at  $E_{pa/2} = 0.51$  V ( $E_{pa} = 0.59$  V) and at  $E_{pa/2} = 0.46$  V ( $E_{pa} = 0.52$  V) vs. Ag/Ag<sup>+</sup> ( $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>), respectively, and the corresponding cathodic waves were observed at  $E_{pc} = 0.48$  V and  $0.37$  V vs. Ag/Ag<sup>+</sup> ( $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>), respectively, more definitely than those for V3T and V4T. In addition, the cathodic wave at  $E_{pc} = ca. -0.30$  V vs. Ag/Ag<sup>+</sup> ( $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>) due to the reduction of H<sup>+</sup> was smaller than that observed for V3T and V4T. It is noteworthy that the cathodic wave corresponding to the anodic one due to the oxidation of the vinyl monomer

became larger in intensity and the cathodic wave due to the reduction of  $H^+$  became smaller with increasing conjugation length of the pendant oligothiophenes. These results strongly suggest that the increase in the conjugation length of the pendant oligothiophenes enhances the stability of the oligothiophene radical cation due to the delocalization of charge through the entire molecule,<sup>94</sup> making the coupling reaction of the pendant oligothiophene radical cation less favorable.



**Figure 2-7.** Cyclic voltammograms of V4T, VDOc5T, VDOc6T ( $1.0 \times 10^{-3}$  mol dm<sup>-3</sup>, respectively) in dichloromethane containing  $n\text{-Bu}_4\text{NClO}_4$  ( $1.0 \times 10^{-1}$  mol dm<sup>-3</sup>). Sweep rate: 100 mV sec<sup>-1</sup>.

### *Anodic Oxidation of Vinyl Monomers and Polymer*

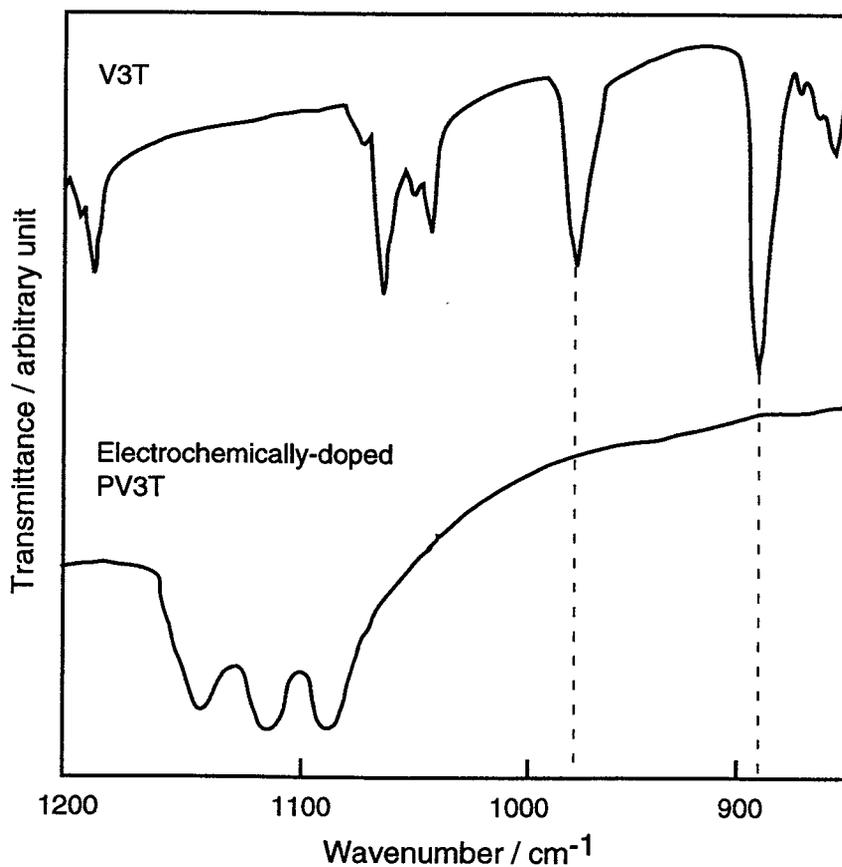
Electrochemically-doped polymers were prepared by electrochemical doping of neutral polymer and by electrolytic polymerization of the vinyl monomers, based on the information obtained by cyclic voltammetry for the anodic oxidation of the vinyl monomers and polymer. Electrochemical doping of PV3T and electrolytic polymerization of V3T were carried out by controlled-potential anodic oxidation at 0.80 V vs. Ag/Ag<sup>+</sup> ( $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>) reference electrode. Electrolytic polymerizations of VTPT, V4T, VD0c5T, and VD0c6T were carried out by controlled-potential anodic oxidation at 0.95, 0.65, 0.55, and 0.50 V vs. Ag/Ag<sup>+</sup> ( $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>), respectively. A deeply colored, smooth and lustrous film was deposited onto the surface of the working electrode in each case. The formation of the films of the electrochemically-doped polymers is due to the presence of a nonconjugated polymer backbone, since electrochemical doping of 5,5''-diethyl-2,2':5',2'':5'',2'''-quaterthiophene and 5,5''''-diethyl-2,2':5',2'':5'',2'''':5''',2''''-quinquethiophene produces only black powders instead of smooth films.<sup>47</sup>

### *Characterization of Electrochemically-doped Polymers*

The electrochemically-doped polymers, poly(5-vinyl-2,2':5',2''-terthiophene) (PV3T), poly(5-vinyl-2,2':5',2'':5'',2'''-quaterthiophene) (PV4T), poly(4',3'''-dioctyl-5-vinyl-2,2':5',2'':5'',2''':5''',2''''-quinquethiophene) (PVDOc5T), poly(4',3''''-dioctyl-5-vinyl-2,2':5',2'':5'',2''':5''',2''''':5''''',2''''''-sexithiophene) (PVDOc6T), and poly[2-[4-(2-thienyl)phenyl]-5-vinylthiophene] (PVTPT), obtained by the electrolytic polymerization of the vinyl monomers

and by the electrochemical doping of the vinyl polymer were characterized by infrared and electronic absorption, and electron spin resonance spectroscopies and elemental analysis.

Figure 2-8 shows the infrared absorption spectra of the vinyl monomer V3T and the film formed by the anodic polymerization of V3T. The characteristic infrared absorption bands at  $1612\text{ cm}^{-1}$  and at  $979$  and  $898\text{ cm}^{-1}$  observed for V3T, which are due to the stretching vibration of the vinyl C=C and to the C-H out-of-plane deformation vibrations of the vinyl group, are absent in the spectrum of the film prepared by the electrolytic polymerization of V3T.



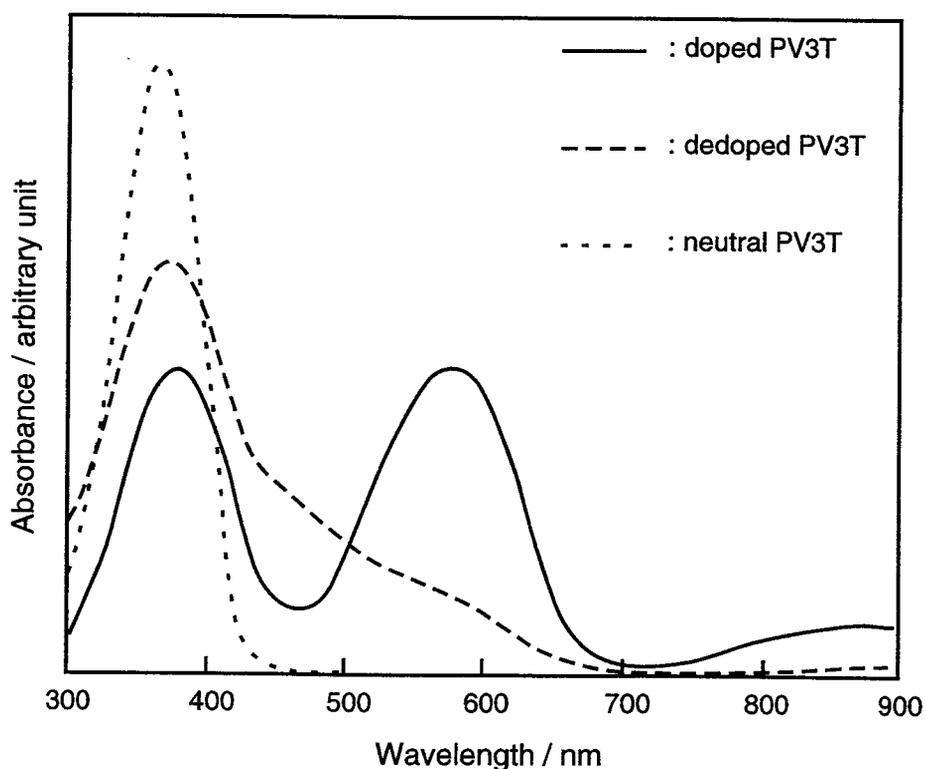
**Figure 2-8.** Infrared absorption spectra of starting vinyl monomer V3T and electrochemically-doped PV3T.

Instead, a new band due to the asymmetric stretching vibration of the methylene group appeared at  $2922\text{ cm}^{-1}$ . These results indicate that the electrolytic polymerization of V3T takes place at the vinyl group to give the polymer. The polymer films show strong infrared absorption bands at 1090, 1120, and  $1150\text{ cm}^{-1}$  due to the  $\text{ClO}_4^-$  ion. Thus, the polymers produced by the electrolytic polymerization concurrently undergo anodic oxidation to give electrochemically-doped polymers with  $\text{ClO}_4^-$  as a dopant. The characteristic IR absorption bands at  $795$  and  $695\text{ cm}^{-1}$  observed for the starting materials, V3T and undoped PV3T, are assigned to the C-H out-of-plane deformation vibrations of 2,5-disubstituted and 2-monosubstituted thiophenes, respectively.<sup>95</sup> The relative intensity of the latter band decreased for the electrochemically-doped PV3T prepared by both methods; this suggests that the pendant terthiophenes are partially transformed into sexithiophene moiety due to the coupling reaction of the pendant terthiophene radical cation. A new doping-induced band was observed at  $1400\text{ cm}^{-1}$ , which is attributed to the band due to radical-cation species. A similar band has been observed for 2,2':5',2'':5'',2''':5''',2''''':5''''',2''''':5'''''-sexithiophene doped with  $\text{FeCl}_3$ .<sup>39</sup> When the polymer was dedoped by controlled-galvanostatic reduction of the doped polymer, the intensities of the bands at 1090, 1120, and  $1150\text{ cm}^{-1}$  due to  $\text{ClO}_4^-$  and the doping-induced band at  $1400\text{ cm}^{-1}$  decreased significantly.

For the sake of getting information on the mechanism of electrolytic polymerization of the vinyl monomer, anodic oxidation of V3T in dichloromethane containing 10 vol% methanol was carried out. As a result, there were

no film deposited onto the working electrode. It is shown that the electrolytic polymerization of vinyl monomer proceeds by a cationic mechanism.

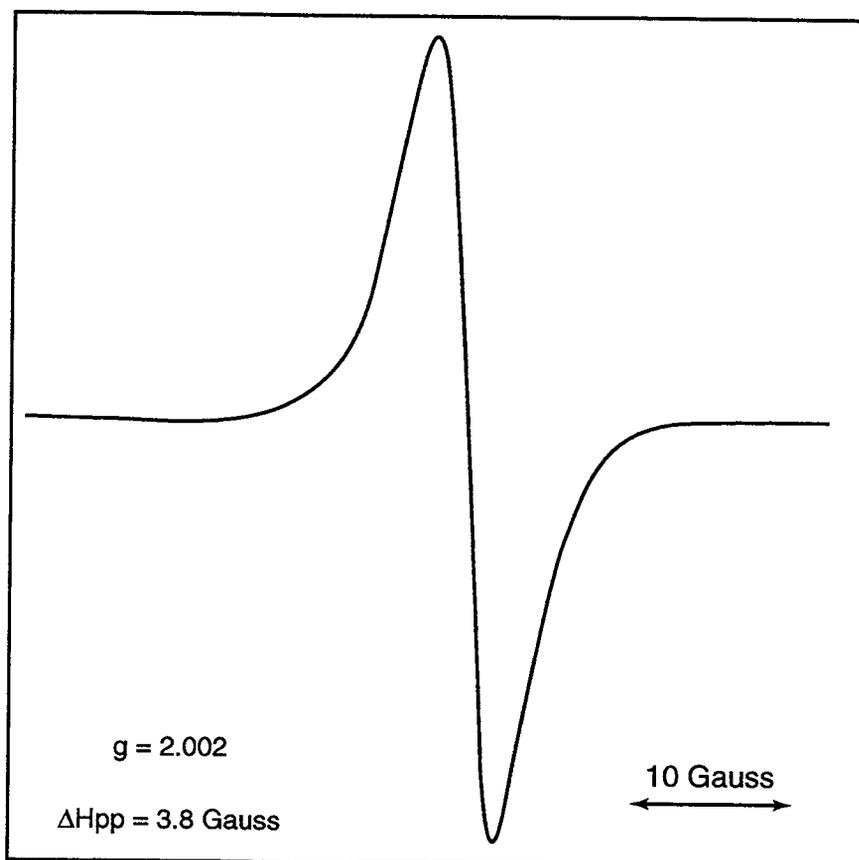
Figure 2-9 shows the electronic absorption spectra of transparent thin films of electrochemically-doped PV3T deposited onto the indium-tin-oxide (ITO)-coated glass electrode by the electrolytic polymerization of V3T and the dedoped polymer. The electrochemically-doped polymer obtained by the anodic oxidation of PV3T also shows essentially the same electronic absorption spectrum as that of the polymer obtained by the electrolytic polymerization of V3T. The electronic absorption spectrum of a dichloromethane solution of the undoped, neutral PV3T is also given for reference in the figure.



**Figure 2-9.** Electronic absorption spectra of electrochemically-doped PV3T film, dedoped film, and neutral PV3T in dichloromethane solution.

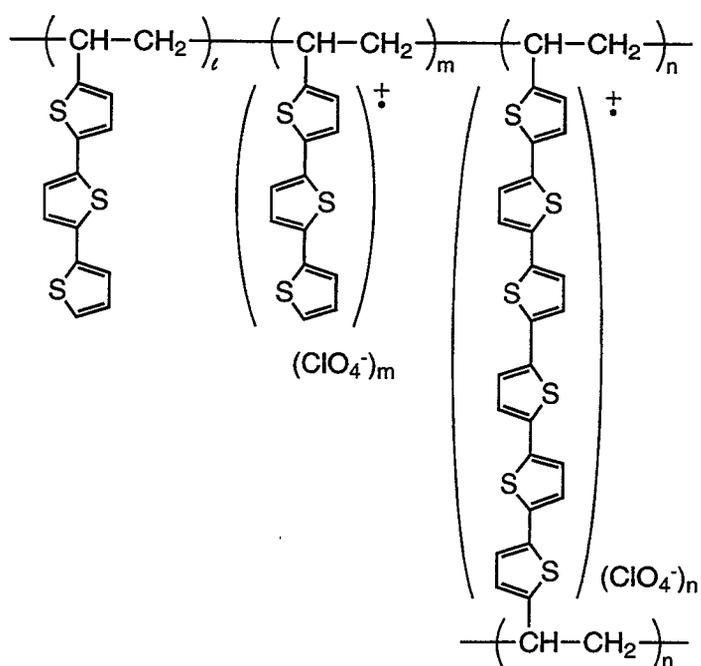
The thin film of the electrochemically-doped polymer shows new absorption bands with  $\lambda_{\text{max}}$  at 577 nm and in the wavelength region from 750 to 900 nm, along with the absorption band with  $\lambda_{\text{max}}$  at 374 nm due to the  $\pi-\pi^*$  transition of the neutral terthiophene chromophore. On the other hand, in the electronic absorption spectrum of the dedoped polymer, which was obtained by the cathodic reduction of the doped polymer, the characteristic absorption band with  $\lambda_{\text{max}}$  at 577 nm and the band in the wavelength region from 750 to 900 nm observed for the electrochemically-doped polymer disappeared, but instead a new absorption band in the wavelength region from 400 to 550 nm appeared. The absorption band with  $\lambda_{\text{max}}$  at 577 nm observed for the electrochemically-doped PV3T film is ascribed to the pendant terthiophene radical-cation species. Likewise, the absorption band in the wavelength region from 750 to 900 nm observed for the electrochemically-doped PV3T film is assigned to the sexithiophene radical-cation species. In fact, the electronic absorption spectra of the radical-cation species of terthiophene and  $\alpha$ -methyl-disubstituted terthiophene produced by laser flash photolysis in methanol and by anodic oxidation in acetonitrile have been reported to show a band with  $\lambda_{\text{max}}$  at 535 nm and at 572 nm, respectively.<sup>76,79</sup> The absorption band in the wavelength region from 400 to 550 nm observed for the dedoped polymer film, which was not observed before electrochemical doping was carried out, is attributed to the neutral sexithiophene chromophore generated by the coupling reaction of the pendant terthiophene radical cation. The result is in accord with the literature data that sexithiophene shows an absorption band with  $\lambda_{\text{max}}$  at 432 nm in benzene.<sup>96</sup>

The presence of unpaired electrons for the electrochemically-doped polymers was evidenced by electron spin resonance spectroscopy. Figure 2-10 shows the electron spin resonance spectrum of the electrochemically-doped PV3T prepared by the electrolytic polymerization of V3T. A strong single line with a  $g$ -value of 2.002 and a line width of 3.8 Gauss due to the radical-cation species was observed.



**Figure 2-10.** Electron spin resonance spectrum of electrochemically-doped PV3T.

Based on the spectroscopic results together with the results of cyclic voltammetry, the electrochemically-doped polymers prepared by the electrolytic polymerization of V3T and by the electrochemical doping of PV3T are identified as partially oxidized radical-cation salts with  $\text{ClO}_4^-$  as a dopant. Both electrochemically-doped polymer and dedoped polymer become insoluble. Furthermore, the fact that the dedoped polymer film clearly shows an electronic absorption band due to the sexithiophene moiety together with the results of cyclic voltammetry indicates that the electrochemically-doped and dedoped polymers have a partially cross-linked structures due to the interpolymer coupling reaction of the radical cation of the pendant terthiophene moiety.



**Scheme 2-1.** Structure of electrochemically-doped PV3T.

The degree of cross-linking, *i.e.*, the molar fraction of the sexithiophene chromophore, can be roughly estimated from the electronic absorption bands of the electrochemically-dedoped polymer. That is, when the electrochemically-doped polymer is dedoped, both pendant terthiophene and sexithiophene radical-cation species are reduced to their neutral states. The molar extinction coefficients of 2,2':5',2''-terthiophene ( $\epsilon_{\max} = 21,900$  at 355 nm in benzene)<sup>38</sup> and trimethylsilyl disubstituted thiophene hexamer ( $\epsilon_{\max} = 40,600$  at 430 nm in chloroform)<sup>41</sup> were used as model compounds for the pendant terthiophene and sexithiophene chromophores in the dedoped polymer, respectively. The ration of the pendant terthiophene and sexithiophene chromophore is given by the following equation:

$$\text{terthiophene} / \text{sexithiophene} = \frac{\left( \frac{I_{3T}}{\epsilon_{\max 3T}} \right)}{\left( \frac{I_{6T}}{\epsilon_{\max 6T}} \right)}$$

where  $I_{3T}$  and  $I_{6T}$  stand for the intensities of the absorption bands due to the pendant neutral terthiophene and sexithiophene chromophores of the dedoped polymer ( $\lambda_{\max}$  at 374 and 490 nm, respectively) and  $\epsilon_{\max 3T}$  and  $\epsilon_{\max 6T}$  for the molar extinction coefficients of the model compounds for the pendant terthiophene and sexithiophene chromophores, respectively.

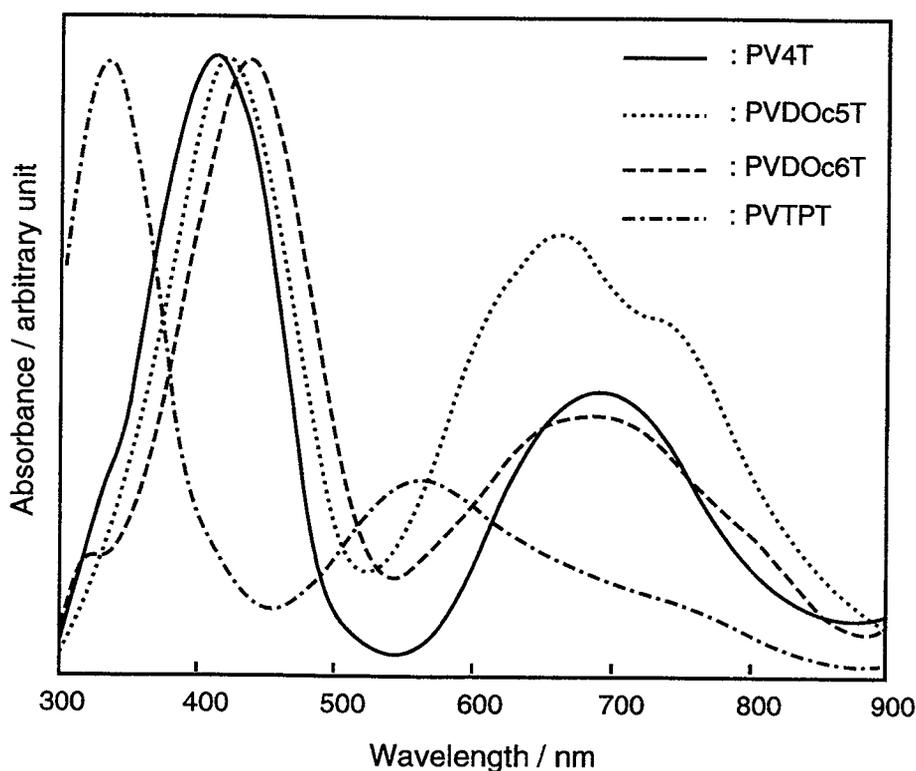
The degree of cross-linking, *i.e.*, the molar fraction of the sexithiophene chromophore, was estimated to be in the range from *ca.* 10 to 20 %, when the electrochemical doping of PV3T and the electrolytic polymerization of V3T were carried out for a period from 1 to 5 min. The value of the degree of cross-

linking tended to increase gradually with increasing electrolysis time from 1 to 5 min.

Likewise, the characteristic infrared absorption bands observed for V4T, VDOc5T, VDOc6T, and VTPT, which are due to the C-H out-of-plane deformation vibrations of the vinyl group, are absent in the spectrum of the film prepared by the electrolytic polymerization of these vinyl monomers. Furthermore, a new absorption band in the wavelength region from 2800 to 3000  $\text{cm}^{-1}$  due to stretching vibration of the methylene C-H, which was not observed for V4T and VTPT, appeared in the spectrum of the electrochemically-doped PV4T and PVTPT. The polymer films show three strong infrared absorption bands around *ca.* 1100  $\text{cm}^{-1}$  due to the  $\text{ClO}_4^-$  ion. Thus, the polymers produced by the electrolytic polymerization concurrently undergo anodic oxidation to give electrochemically-doped polymers with  $\text{ClO}_4^-$  as a dopant. These results are similar to those for PV3T prepared by the electrolytic polymerization of V3T.

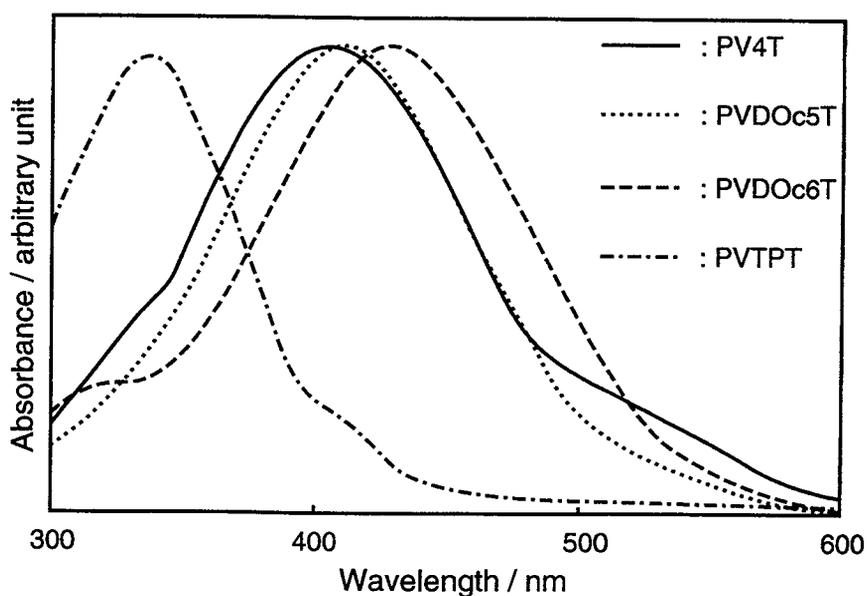
Figure 2-11 shows the electronic absorption spectra of the transparent thin films of electrochemically-doped polymers deposited onto the ITO-coated glass by the electrolytic polymerization of each vinyl monomer. The electrochemically-doped PV4T shows a new absorption band with  $\lambda_{\text{max}}$  at 690 nm along with the absorption band with  $\lambda_{\text{max}}$  at 400 nm due to the  $\pi-\pi^*$  transition of the neutral quaterthiophene chromophore. When the electrochemically-doped PV4T was dedoped by cathodic reduction at 0 V *vs.* Ag/

$\text{Ag}^+$  ( $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ), the characteristic absorption band with  $\lambda_{\text{max}}$  at 690 nm disappeared and a new absorption band in the wavelength region from 500 to 600 nm appeared instead (Figure 2-12). The absorption band with  $\lambda_{\text{max}}$  at 690 nm observed for the electrochemically-doped PV4T film is ascribed to the pendant quaterthiophene radical-cation species and the absorption band in the wavelength region from 500 to 600 nm observed for the dedoped polymer film is attributed to the neutral octithiophene chromophore generated by the coupling reaction of the pendant quaterthiophene radical cation.



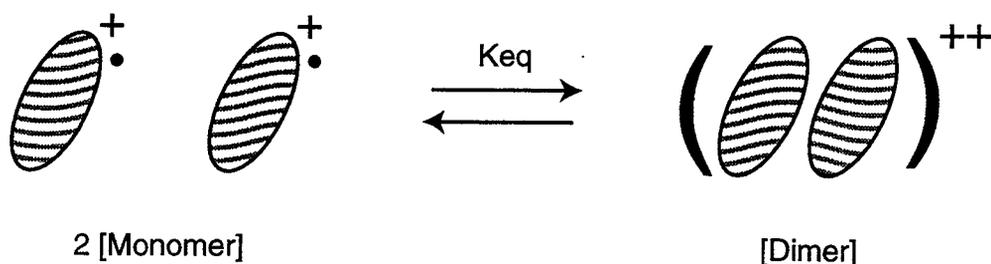
**Figure 2-11.** Electronic absorption spectra of electrochemically-doped PV4T, PVDOc5T, PVDOc6T, and PVTPT films.

Likewise, the electrochemically-doped PVDOc5T and PVDOc6T show new broad absorption bands in the wavelength region from 550 to 800 nm and from 550 to 850 nm, along with the absorption bands with  $\lambda_{\text{max}}$  at 415 nm and 430 nm due to the  $\pi$ - $\pi^*$  transition of the neutral quinquethiophene and sexithiophene chromophores, respectively. In the electronic absorption spectra of the dedoped films of PVDOc5T and PVDOc6T obtained by the cathodic reduction of the doped polymers at 0 V vs. Ag/Ag<sup>+</sup> ( $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>), the characteristic absorption bands in the wavelength regions from 550 to 800 nm and from 550 to 850 nm disappeared. Therefore these new absorption bands are attributed to radical-cation species of the pendant oligothiophenes. We have found that radical cations of oligothiophenes, that is, 5,5'''-diethyl-2,2':5',2'':5'',2'''-quaterthiophene, 4',3'''-dioctyl-2,2':5',2'':5'',2''':5''',2''''-quinque-thiophene, and 4',3''''-dioctyl-2,2':5',2'':5'',2''':5''',2''''':5''''',2''''''-sexithiophene, in solution are in reversible equilibrium between the monomeric radical cation



**Figure 2-12.** Electronic absorption spectra of electrochemically-dedoped PV4T, PVDOc5T, PVDOc6T, and PVTPT films.

and the dimeric radical cation, *i.e.*, associated radical-cation  $\pi$ -dimer (Scheme 2-2),<sup>44,79-81,83,84</sup> and that the absorption bands of the monomeric and dimeric radical cations of 5,5'''-diethyl-2,2':5',2'':5'',2'''-quaterthiophene, 4',3'''-dioctyl-2,2':5',2'':5'',2'''-quinquethiophene, and 4',3''''-dioctyl-2,2':5',2'':5'',2'''-sexithiophene appear at 672 and 543 nm, 733 and 600, 646 nm, and 794 and 648, 700 nm, respectively, in dichloromethane.<sup>97</sup> With regard to the present electrochemically-doped polymer



**Scheme 2-2.** Dimerization of oligothiophene radical cations.

**Table 2-1.** Absorption maxima of monomer and dimer of oligothiophene radical cations.<sup>97</sup>

	$\lambda_{\text{max}} / \text{nm}$	
	Monomer	Dimer
	672	543
	733	600, 646
	794	648, 700

films, radical-cation species of PV4T appear to be almost the monomeric radical cation. On the other hand, the electronic absorption bands due to the radical-cation species of PVDOc5T and PVDOc6T in particular seem to consist of the two bands due to the monomeric radical cation and the dimeric radical cation, *i.e.*, associated radical-cation  $\pi$ -dimer. This is because PVDOc5T and PVDOc6T have longer pendant oligothiophenes than PV4T. Unlike PV3T, PV4T, the new absorption bands due to decithiophene and dodecithiophene which can be generated by the coupling reaction of the pendant quinquethiophene and sexithiophene radical cations were not definitely observed in the electronic absorption spectra of the dedoped PVDOc5T and PVDOc6T (Figure 2-12). The absence of the new absorption bands due to the decithiophene and dodecithiophene chromophores suggests that the radical cations of the pendant quinquethiophene and sexithiophene are more stable than that of the pendant terthiophene and quaterthiophene and hence undergo coupling reaction only slightly. These results are in accord with those obtained from cyclic voltammetry. It is indicated that the increase of the conjugation length of the pendant oligothiophenes make the pendant oligothiophene radical cations more stable, leading to the decrease in the degree of cross-linking in the resulting polymers.

Based on the spectroscopic results together with the results of cyclic voltammetry, the electrochemically-doped polymers prepared by the electrolytic polymerizations of vinyl monomers were identified as radical-cation salts of pendant oligothiophenes with  $\text{ClO}_4^-$  as a dopant, having partially cross-

linked structures. With increasing conjugation length of the pendant oligothiophenes, the extent of cross-linking was found to decrease, and the pendant oligothiophene radical cation readily form  $\pi$ -dimer.

Table 2-2 lists room-temperature conductivities and activation energies for electrical conduction for the electrochemically-doped polymers containing pendant oligothiophenes. Although the extent of doping varied depending upon the polymer, the room-temperature conductivity was found to increase with increasing conjugation length of the pendant oligothiophenes. Whereas the electrochemically-doped PV3T, PV4T, PVTPT were poor conductors, PVDOc5T and PVDOc6T exhibited room-temperature conductivities in the range from *ca.*  $10^{-5}$  to  $10^{-4}$  S cm<sup>-1</sup>. We have reported that the electrochemically generated oligothiophene radical-cation salts of 5,5''-diethyl-2,2':5',2'':5'',2'''-quaterthiophene with a doping degree of *ca.* 100 % and 5,5''''-

**Table 2-2.** Room-temperature conductivities and activation energies for electrochemically-doped polymers.

Polymer	Degree of Doping <sup>a</sup> [%]	Conductivity [S /cm]	Activation Energy [eV]
PVTPT	50	$6 \times 10^{-10}$	—
PV3T	35	$7 \times 10^{-9}$	0.49
PV4T	68	$2 \times 10^{-8}$	0.48
PV5T	66	$2 \times 10^{-5}$	0.32
PV6T	94	$1 \times 10^{-4}$	0.25

<sup>a</sup> Calculated from elemental analysis

diethyl-2,2':5,2":5",2"":5""-quinguethiophene with a doping degree of *ca.* 50 % exhibit room-temperature conductivities of  $10^{-7}$  and  $5 \times 10^{-3}$  S cm<sup>-1</sup> with activation energies of *ca.* 0.5 and 0.1 eV, respectively.<sup>47</sup> The polymers containing pendant oligothiophenes exhibit poorer electrical conductivity relative to oligothiophenes themselves.

## 2-4 Summary

Electrochemically-doped vinyl polymers were prepared by the electrolytic polymerization of vinyl monomers and electrochemical doping of PV3T in a dichloromethane solution containing tetra-*n*-butylammonium perchlorate as a supporting electrolyte. The electrochemically-doped polymers are identified as partially oxidized radical-cation salts of pendant oligothiophenes with  $\text{ClO}_4^-$  as a dopant, having partially cross-linked structure. The degree of cross-linking in the polymers decreased with increasing conjugation length of the pendant oligothiophenes.

The electrical conductivity of the electrochemically-doped polymers increased with increasing conjugation length of the pendant oligothiophenes. The room-temperature conductivity of the polymer containing the pendant sexithiophene group exhibited a room-temperature conductivity of *ca.*  $10^{-4}$  S  $\text{cm}^{-1}$ .

## Chapter 3

### Electrochromic Properties of a Novel Family of Polymers Containing Pendant Oligothiophenes

#### 3-1 Introduction

Electrochromism has received attention for application to display devices, which have characteristics of low operation voltage, a wide viewing angle, and good optical contrast owing to the non-emitting nature of the materials.<sup>98,99</sup> Organic electrochromic materials are of interest for a variety of chromophores and for their potential capability of multicolor display. In particular, polymeric materials are attractive since they may exhibit a memory effect and have a good cycle life.

Polymers containing redox systems such as tetrathiafulvalene or 1,3,5-triaryl-2-pyrazoline as pendant groups have been reported to function as electrochromic materials.<sup>100</sup> Recently, electrically conducting polymers such as polypyrrole,<sup>101</sup> polythiophene,<sup>101-103</sup> and polyisothianaphthene<sup>104</sup> have received attention as potential electrochromic materials, since they undergo reversible color changes on electrochemical doping and dedoping. With regard to polythiophene, for example, the color switches from blue (oxidized state) to red (reduced state).  $\pi$ -Conjugated linear polymers in general are not normally processable. In addition, the electronic absorption bands of  $\pi$ -conjugated linear polymers such as polypyrrole and polythiophene are generally broad.

Chapter 3 deals with the application of a novel family of nonconjugated vinyl polymers containing pendant oligothiophenes with well-defined structures as electrochromic materials. Polymers containing pendant oligothiophenes have the following attractive characteristics. The starting polymers are expected to be soluble in ordinary solvents in their neutral states. It is also expected that they exhibit clear color changes on electrochemical doping and dedoping, owing to the well-defined structures of the pendant oligothiophenes, and that the color can be controlled by varying the length of  $\pi$ -conjugated linear oligothiophenes.

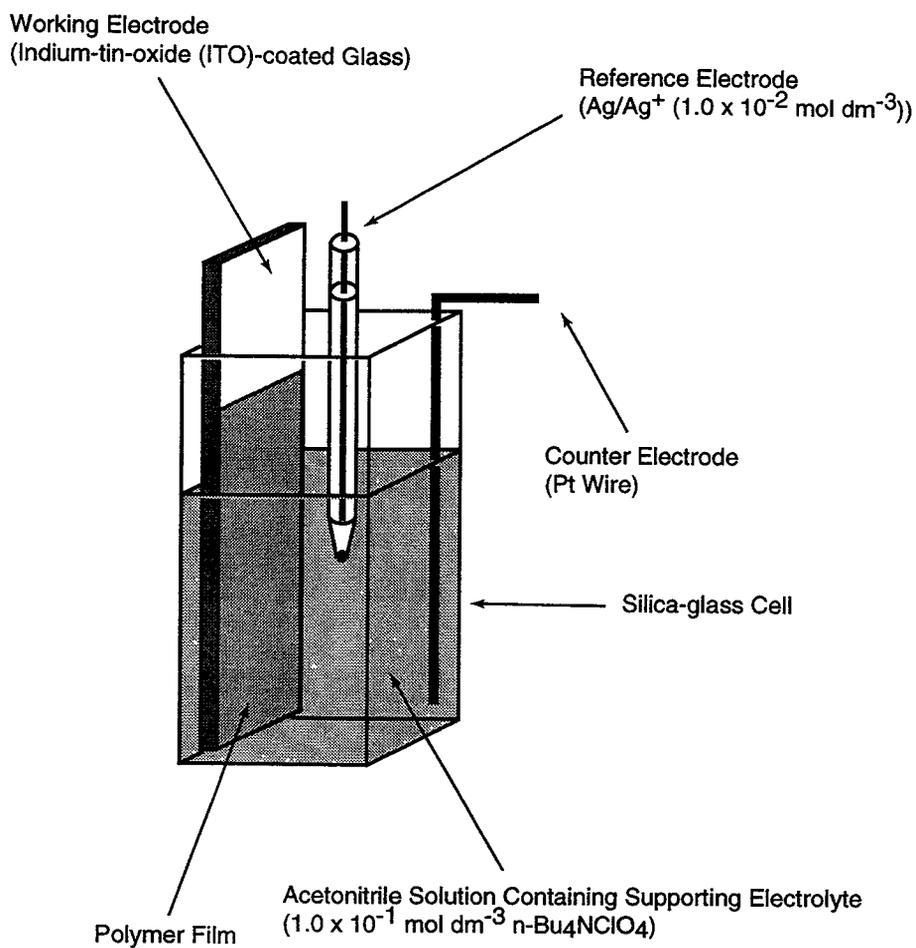
## 3-2 Experimental

### *Materials*

Acetonitrile was purified by column chromatography. Dichloromethane was treated with *conc.* sulfuric acid, water. Then, they were dried, and distilled immediately before use. Tetra-*n*-butylammonium perchlorate (Tokyo Chemical Industry Co., Ltd.) was recrystallized from ethanol three times, dried at 70 °C for 24 hr, stored in a desiccator, and redried *in vacuo* at room-temperature immediately before use.

### *Measurement of Electrochromic Properties*

The electrochemically-doped polymer was deposited on to an indium-tin-oxide (ITO)-coated glass electrode in a thin film form by the electrolytic polymerization of the monomer and the electrochemical doping of the polymer in dichloromethane. The resulting ITO electrode was then transferred into acetonitrile solution containing only the supporting electrolyte ( $1.0 \times 10^{-1} \text{ mol dm}^{-3}$  tetra-*n*-butylammonium perchlorate) in a silica-glass cell with a platinum counter electrode and a Ag/Ag<sup>+</sup> ( $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ) reference electrode. The electrode current and optical density were measured *in situ* by applying repetitive pulsed voltages of 0 and 0.80 V, 0 and 0.65 V, 0 and 0.55 V, 0 and 0.50 V, and 0 and 1.0 V *vs.* Ag/Ag<sup>+</sup> ( $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ) for the polymers obtained by electrolytic polymerization of V3T, V4T, VDOc5T, VDOc6T, and VTPT, respectively, for each 10 sec in air.



**Figure 3-1.** Measurement of electrochromic property.

### 3-3 Results and Discussion

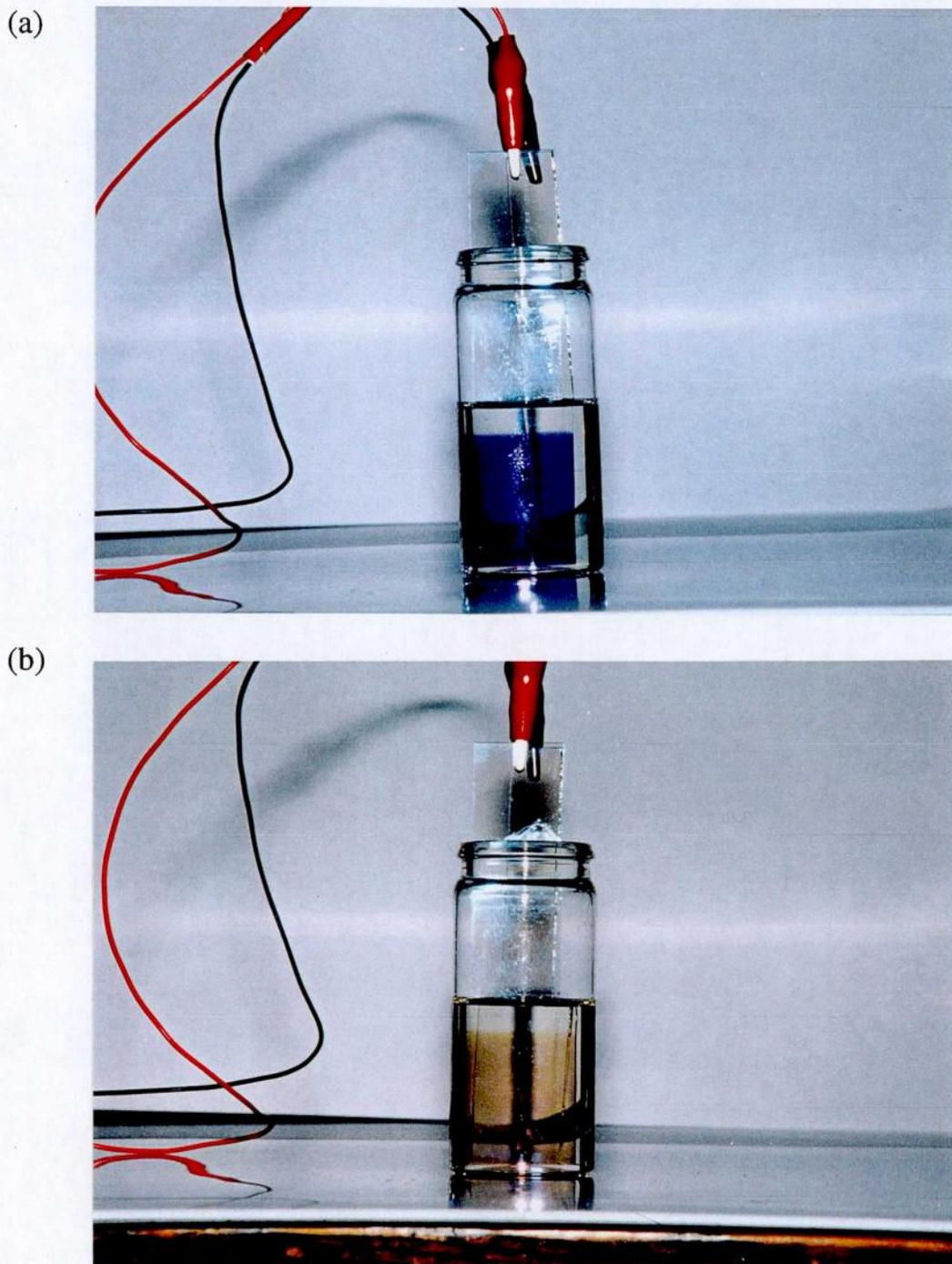
As Figure 3-2 shows, the thin transparent films of electrochemically-doped PV3T obtained both by the electrolytic polymerization of V3T and by the electrochemical doping of PV3T were found to undergo a reversible clear color change from bluish purple to pale yellowish orange and *vice versa* on electrochemical dedoping and doping.

The reversible color change observed for PVTPT, which has three aromatic rings as PV3T, is slightly different from that of PV3T. That is, the color of PVTPT switched from purple to colorless and *vice versa* on electrochemical dedoping and doping (Figure 3-3).

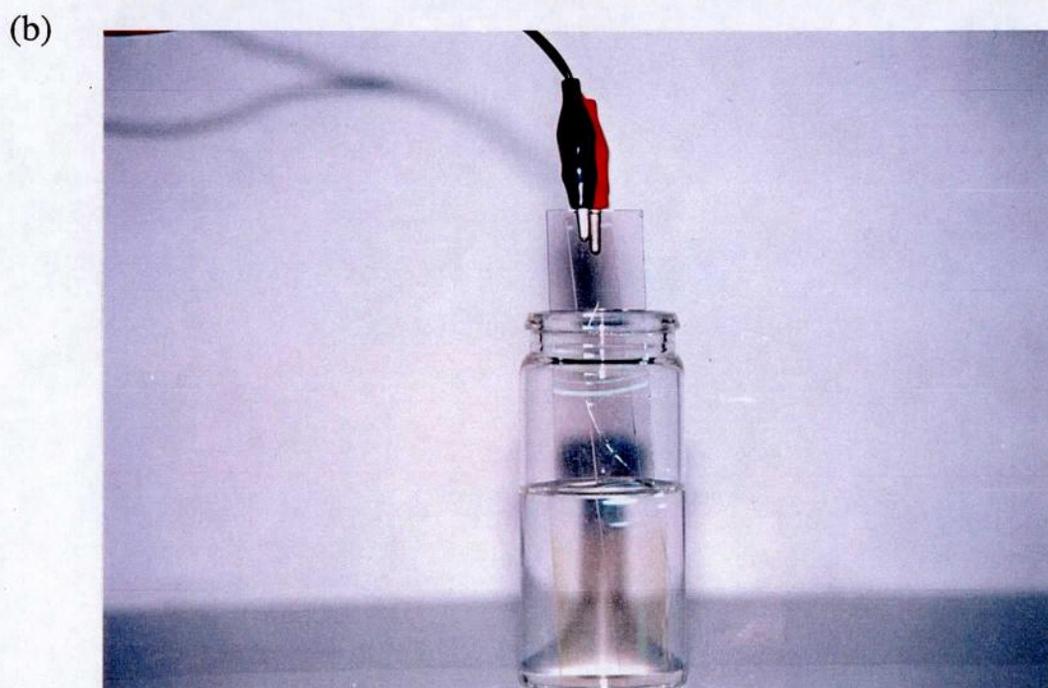
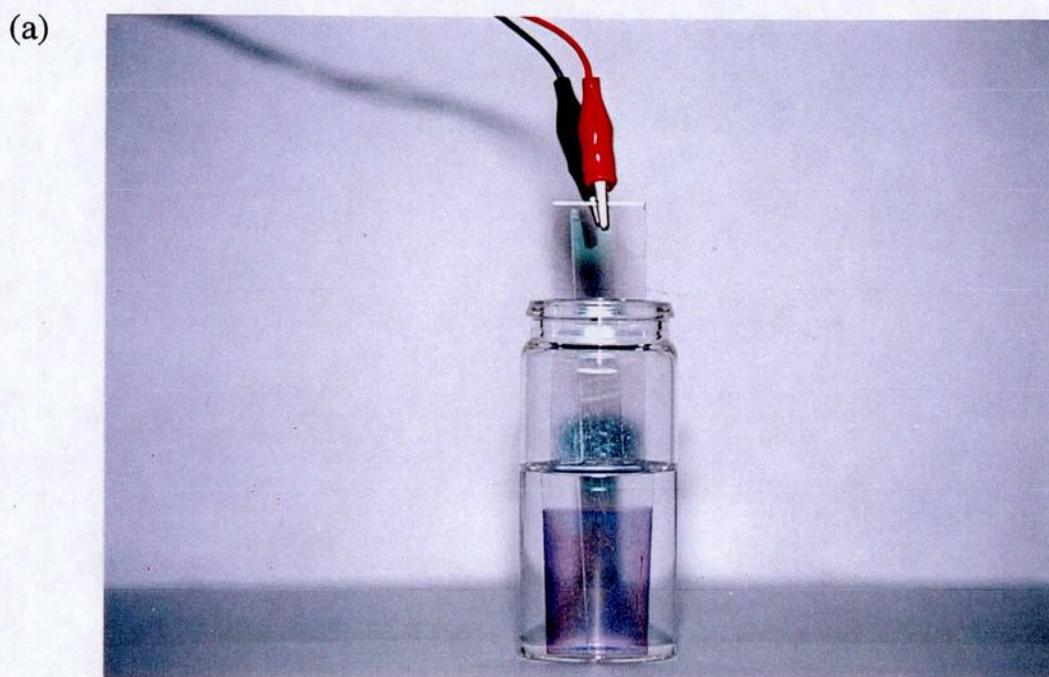
In the case of PV4T, which contains only one more thiophene ring than that of PV3T, *i.e.*, four thiophene rings, the color was remarkably different compared with PV3T and PVTPT. That is, the PV4T film was found to undergo a reversible color change from green to pale yellow and *vice versa* on electrochemical dedoping and doping (Figure 3-4).

However, PVDOc5T and PVDOc6T containing longer oligothiophenes than that of PV4T were also found to undergo a reversible clear color change from green to pale yellow like PV4T and *vice versa* on electrochemical dedoping and doping. It is thought that the incorporation of the two octyl groups at the  $\beta$ -position of the pendant  $\alpha,\alpha'$ -oligothiophenes in PVDOc5T and PVDOc6T causes blue shift of the electronic absorption spectra.

These polymers were insoluble in organic solvents even on electrochemical dedoping; this is due to the partially cross-linked structure of the pendant oligothiophenes and hence these polymers have a memory effect.

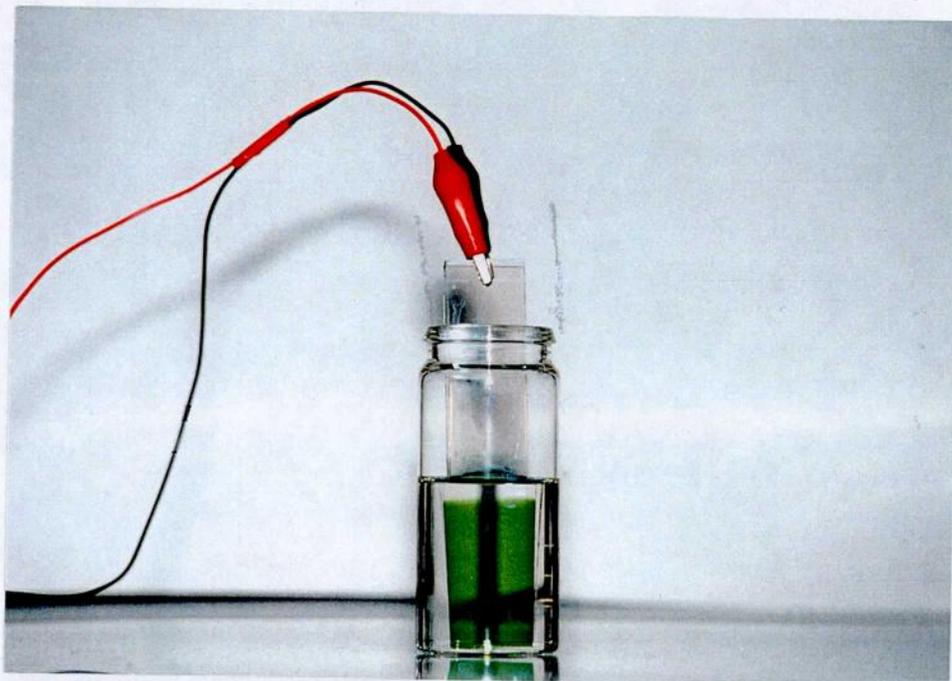


**Figure 3-2.** Reversible color change observed for (a) an electrochemically-doped PV3T film and (b) dedoped PV3T film.

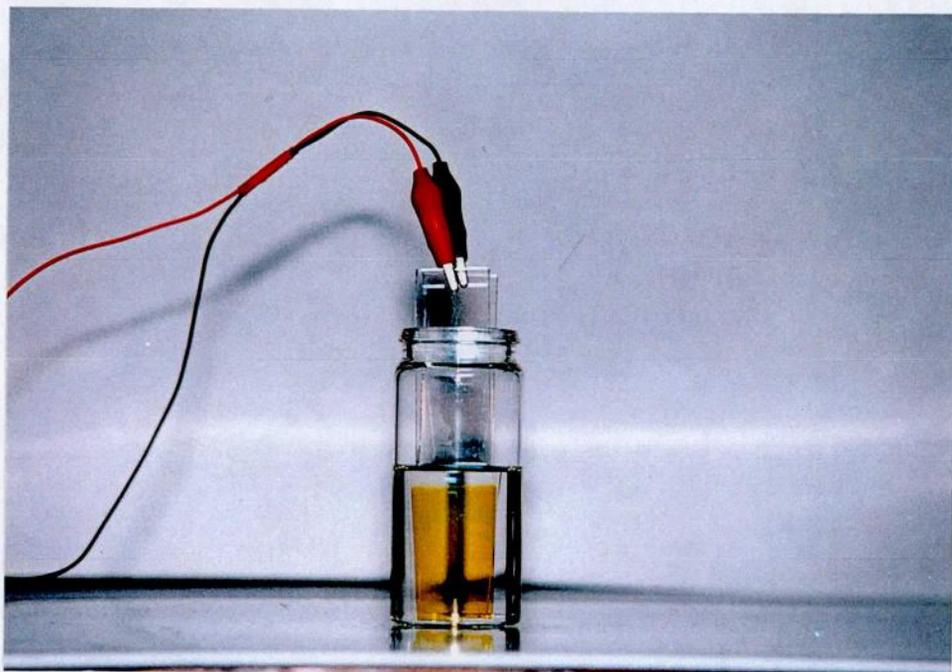


**Figure 3-3.** Reversible color change observed for (a) an electrochemically-doped PVTPT film and (b) dedoped PVTPT film.

(a)

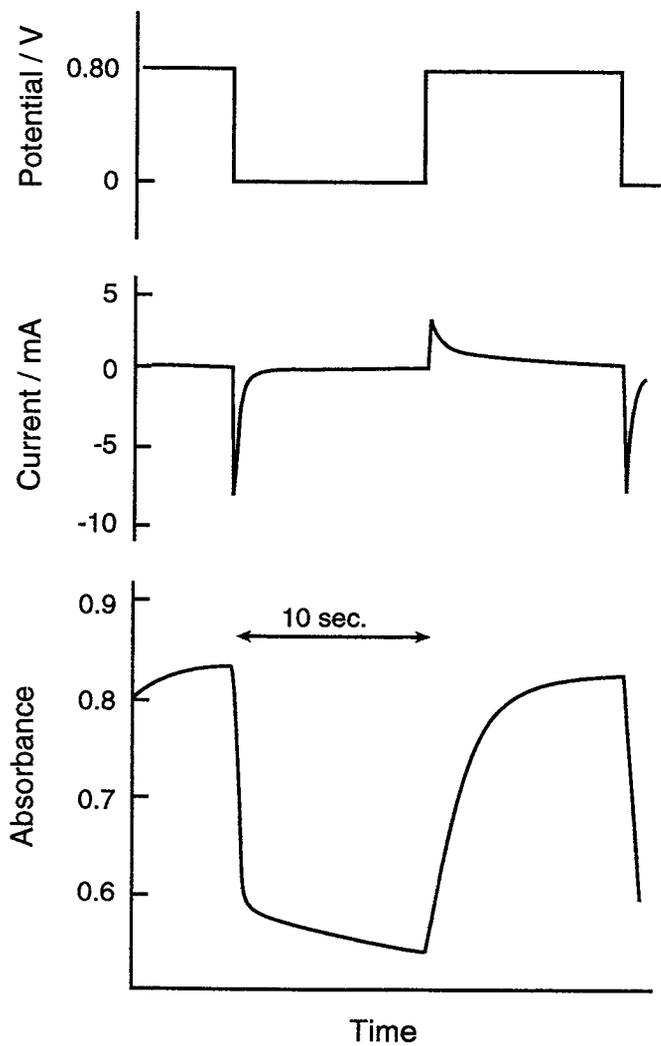


(b)



**Figure 3-4.** Reversible color change observed for (a) an electrochemically-doped PV4T film and (b) dedoped PV4T film.

The response times for coloration and decoloration and the cyclability of the color change were measured by monitoring the optical density on application of repetitive pulsed voltages. The response time was defined as the time required for the absorbance change of 90%. When the repetitive pulsed voltages of 0 and 0.80 V vs. Ag/Ag<sup>+</sup> ( $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>) were applied for each 10 sec to the electrochemically-doped PV3T prepared by the electrolytic polymerization of V3T, the electrode current and optical density (monitored at 570 nm) changed in such a way as shown in Figure 3-7. The response times for doping (coloration) and dedoping (decoloration) were 3.4 and 1.5 sec, respectively. Likewise, the response times for doping and dedoping for PV4T, PVDOc5T, PVDOc6T, and PVTPT films were 4.0 and 0.9 sec, 6.5 and 0.5 sec, 4.8 and 0.3 sec, and 1.2 and 6.3 sec, respectively. When the redox cycle of dedoping and doping for each 2 sec was repeated over 500 times, a reversible color change was observed.



**Figure 3-7.** Changes of electrode current and optical density as a function of time for a PV3T film by application of repetitive voltages.

### **3-4 Summary**

The present study shows that a series of nonconjugated polymers containing oligothiophenes with well-defined structures as pendant groups constitute a novel class of potential electrochromic materials with a memory effect, showing reversible clear color change on electrochemical doping and de-doping, and that the color can be controlled by varying the conjugation length of the pendant oligothiophenes.

## Summary

For the purpose of developing a novel class of electrically conducting polymers, novel vinyl polymers containing pendant oligothiophenes with well-defined structures have been studied. The synthesis of novel vinyl monomers and polymer having oligothiophenes, electrochemical doping of the polymers, and characterization, electrical properties, and application of doped polymers are discussed.

Chapter 1 describes the synthesis and characterization of novel vinyl monomers containing oligothiophenes, 5-vinyl-2,2':5',2''-terthiophene (V3T), 5-vinyl-2,2':5',2''':5'',2''''-quaterthiophene (V4T), 4',3'''-dioctyl-5-vinyl-2,2':5',2''':5'',2''''':5''''',2''''''-quinquethiophene (VDOc5T), 4',3''''-dioctyl-5-vinyl-2,2':5',2''':5'',2''''':5''''',2''''''':5''''''',2''''''''-sexithiophene (VDOc6T), and 2-[4-(2-thienyl)phenyl]-5-vinylthiophene (VTPT), and a novel vinyl polymer containing pendant terthiophene, poly(5-vinyl-2,2':5',2''-terthiophene) (PV3T). The polymer obtained by radical and cationic polymerizations of 5-vinyl-2,2':5',2''-terthiophene was found to have molecular weights of  $M_n = 2,200$ ,  $M_w = 3,400$  and  $M_n = 2,500$ ,  $M_w = 5,500$ . The polymer is soluble in dichloromethane and THF to make spectroscopic measurement and electrochemical doping.

In Chapter 2, preparation, characterization, and electrical properties of electrochemically-doped polymers containing pendant oligothiophenes are studied. A new type of electrochemically-doped polymers have been prepared by electrolytic polymerization of vinyl monomers and electrochemical doping of PV3T. Electrochemically-doped polymers were identified as partially oxi-

dized radical-cation salts of pendant oligothiophenes with  $\text{ClO}_4^-$  as a dopant. The doped polymers are partially cross-linked due to the coupling reaction of the pendant oligothiophene radical-cations. The degree of cross-linking in the polymers decreased with increasing conjugation length of the pendant oligothiophenes. The electrical conductivity of the electrochemically-doped polymers increased with increasing conjugation length of the pendant oligothiophenes. The room-temperature conductivity of the polymer containing sexithiophene group exhibited a room-temperature conductivity of *ca.*  $10^{-4} \text{ S cm}^{-1}$ .

Chapter 3 deals with applications of a novel vinyl polymers containing pendant oligothiophenes as electrochromic materials. The polymer films were found to undergo a reversible clear color change on electrochemical doping and dedoping, owing to the well-defined structures of pendant oligothiophenes. The color of polymers can be controlled by varying the length of pendant oligothiophenes.

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## List of Publications

- (1) Polymers Containing Pendant Oligothiophenes as a Novel Class of Electrochromic Materials

Nawa, K.; Miyawaki, K.; Imae, I.; Noma, N.; Shirota, Y.

*J. Mater, Chem.* **1993**, *3*, 113.

- (2) A Novel Type of Semiconducting Polymers: Synthesis and Properties of Electrochemically-doped Polymers Containing Pendant Oligothiophenes

Nawa, K.; Miyawaki, K.; Imae, I.; Noma, N.; Shirota, Y.

*Synth. Met.* **1993**, *55-57*, 1176.

- (3) Synthesis of a Novel Type of Electrochemically Doped Vinyl Polymer Containing Pendant Terthiophene and Its Electrical and Electrochromic Properties

Nawa, K.; Imae, I.; Noma, N.; Shirota, Y.

*Macromolecules* **1995**, *28*, 723.

- (4) Synthesis and Electrical Properties of Novel Electrochemically-doped Vinyl Polymers Containing 'End-capped' Quaterthiophene and Quinquethiophene as Pendant Groups

Imae, I.; Moriwaki, K.; Nawa, K.; Noma, N.; Shirota, Y.

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- (5) Electrochromic Properties of a Vinyl Polymer Containing Pendant 1,4-Di(2-thienyl)benzene

Imae, I.; Noma, N.; Shirota, Y.

*Synth. Met.* in press.

- (6) Synthesis of a Novel Family of Electrochemically-doped Polymers Containing Pendant Oligothiophenes and their Electrical and Electrochromic Properties

Imae, I.; Nawa, K.; Ohseido, Y.; Noma, N.; Shirota, Y.

*Macromolecules* in press.

### **List of Supplementary Publications**

- (1) Electrochemical Doping of  $\alpha$ -Ethyl-disubstituted Oligothiophenes and Electrical Conductivities of the Resulting Radical-cation Salts

Noma, N.; Kawaguchi, K.; Imae, I.; Nakano, H.; Shirota, Y.

*J. Mater. Chem.* **1996**, *6*, 117.

- (2) Synthesis and Electrochromic Properties of a Methacrylate Polymer Containing Pendant Terthiophene

Ohseido, Y.; Imae, I.; Noma, N.; Shirota, Y.

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