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# Synthesis of a Novel Type of Electrochemically Doped Vinyl Polymer Containing Pendant Terthiophene and Its Electrical and Electrochromic Properties

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ABSTRACT: A novel kind of electrochemically doped poly(5-vinyl-2,2′:5′,2″-terthiophene) has been prepared by electrochemical doping of poly(5-vinyl-2,2′:5′,2″-terthiophene) and by electrolytic polymerization of 5-vinyl-2,2′:5′,2″-terthiophene in the presence of tetra-*n*-butylammonium perchlorate as a supporting electrolyte. The electrochemically doped poly(5-vinyl-2,2′:5′,2″-terthiophene), obtained as bluish purple lustrous films, is identified as a partially oxidized radical-cation salt with $ClO_4^-$ as a dopant, having a partially cross-linked structure due to the coupling reaction of the radical cation of the pendant terthiophene moiety. The polymer with a degree of doping of 45% exhibits a room-temperature conductivity of $2 \times 10^{-8}$ S cm$^{-1}$ with an activation energy of 0.5 eV. The polymer undergoes a reversible clear color change from bluish purple to pale yellowish orange and *vice versa* on electrochemical dedoping and doping and functions as a novel class of potential electrochromic material.

## Introduction

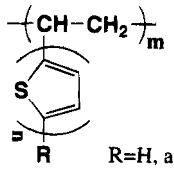
Electrically conducting polymers, including both semiconducting polymers and polymers with metallic conduction, have received attention in view of both academic interest and potential technological applications to materials for use in electronic devices and have been the subject of extensive studies.

Electrically conducting polymers are classified mainly into the following categories from the structural viewpoint: (a) wholly π-conjugated linear polymers, (b) wholly π-conjugated planar polymers, (c) nonconjugated polymers containing pendant π-electron systems, (d) metallomacrocycles, and (e) composite polymers. Among these, wholly π-conjugated linear polymers, *e.g.*, polyacetylene, poly(*p*-phenylene), poly(*p*-phenylenevinylene), polypyrrole, polythiophene, and polyaniline, have drawn attention because of their ability to achieve high electrical conductivity by doping and have been studied extensively.[1] The electrical conduction of these doped polymers has been understood in terms of polaron and bipolaron mechanisms.[1a]

For the purpose of developing a new type of electrically conducting polymers, we have studied electrochemical doping of class c polymers, *i.e.*, nonconjugated vinyl-type polymers containing pendant π-electron systems, and properties and applications of doped polymers.[2−14] They are of interest for the following reasons: the variety of possible pendant molecules, chemical stability, processability, photoconducting properties, and the invariance of the standard oxidation/reduction potential irrespective of the degree of doping.[2] The polymers studied include poly(*N*-vinylcarbazole),[3−7] poly(vinylferrocene),[8] poly[4-(diphenylamino)phenylmethyl methacrylate],[9] poly(1-vinylpyrene),[10] and poly(3-vinylperylene).[11−14] We have shown that insulating polymers are transformed into electrically conducting polymers by electrochemical doping and that electrically conducting polymers can be prepared directly by electrolytic polymerization of vinyl monomers. We have also shown that these electrochemically doped polymers function as photoactive materials for photovoltaic devices[6,9] and electrode materials for secondary batteries.[5,7,13]

For the purpose of developing a further new type of electrically conducting polymers, we have been studying the synthesis and electrochemical doping of nonconjugated vinyl-type polymers containing π-conjugated linear oligomers with well-defined structures as pendant groups. It is expected that these new polymers may have unique properties characteristic of both nonconjugated backbone and pendant π-conjugated linear oligomers. Related to this work, grafted π-conjugated polymers, *e.g.*, polyacetylene and polypyrrole grafted to polystyrene and other polymers, have been reported.[15−17]

We have chosen oligothiophenes,[18−33] which have received attention as models for highly conductive polythiophenes, as pendant groups of vinyl-type polymers. It is of interest to examine the correlation between the length of pendant oligothiophenes and electrochromic and electrical properties of the resulting electrochemically doped polymers. This paper reports the synthesis of electrochemically doped poly(5-vinyl-2,2′:5′,2″-terthiophene) ($n = 3$, R = H), its characterization, and electrical and electrochromic properties.[34] A part of the present work has been reported as a communication.[35] After our communication was published, publications appeared which deal with the anionic polymerization of 5-vinyl-2,2′:5′,2″-terthiophene[36] and with the synthesis of polymers with a poly(methyl methacrylate) backbone and polythiophene side chains.[37]



R=H, alkyl

## Experimental Section

**Materials.** *n*-Hexane, ethanol, methanol, benzene, tetrahydrofuran (THF), dichloromethane, and *N,N*-dimethylformamide (DMF) were purified by ordinary methods, dried, and distilled immediately before use. 2,2′:5′,2″-Terthiophene (terthiophene; Aldrich Chemical Company, Inc.) was purified by

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recrystallization from *n*-hexane, mp 94.0–95.5 °C. 2,2′-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from methanol.

**Synthesis of 5-Vinyl-2,2′:5′,2″-terthiophene and Poly(5-vinyl-2,2′:5′,2″-terthiophene).** 5-Vinyl-2,2′:5′,2″-terthiophene (5-vinylterthiophene) was synthesized starting from terthiophene by the Vilsmeier reaction, followed by the Wittig reaction. Phosphorus oxychloride (3.22 g, 0.02 mol) was added to ice-cooled DMF (20 mL), and the mixture was stirred for 15 min. To this solution was added a solution of terthiophene (4.96 g, 0.02 mol) in DMF (20 mL) over a period of 30 min at 0 °C. The mixture was gradually warmed to room temperature and then heated at 70 °C for 1 h. It was then cooled and poured into ice water. The resulting precipitate was collected by filtration, washed with water, dried, and separated by silica gel column chromatography. Elution with carbon tetrachloride and then with benzene gave the starting material and 5-formyl-2,2′:5′,2″-terthiophene (5-formylterthiophene), respectively. 5-Formylterthiophene was purified by recrystallization from carbon tetrachloride to give yellow needles (3.04 g, yield 55%), mp 141.5–142.5 °C (lit.[38] mp 140–141 °C).

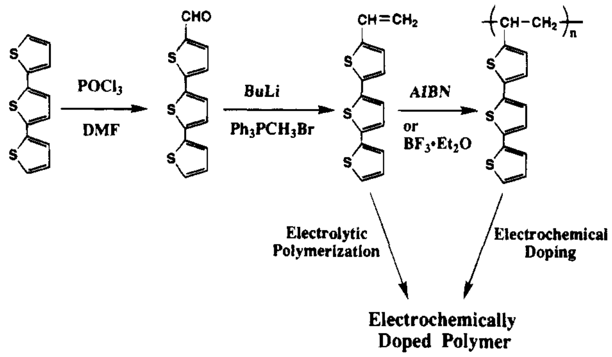
Methyltriphenylphosphonium bromide (2.0 g, 5.6 mmol) was added to THF (27 mL) under a nitrogen atmosphere. *n*-Butyllithium (5.6 mmol) in *n*-hexane was added to this solution, and the resulting solution was stirred for 3 h. 5-Formylterthiophene (1.2 g, 4.5 mmol) in dry THF (83 mL) was then added and the solution stirred for 24 h. The reaction solution was poured into excess ice water, and the product was extracted several times with diethyl ether. The ether solution was washed with water and evaporated. The resulting solid was purified by silica gel column chromatography. Elution with *n*-hexane/benzene gave 5-vinyl-2,2′:5′,2″-terthiophene (5-vinylterthiophene). The monomer was purified by recrystallization twice from ethanol to give yellow leaflets (0.75 g, yield 61%), mp 126.5–127.5 °C. Anal. Calcd for $C_{14}H_{10}S_3$: C, 61.31; H, 3.65; S, 35.04. Found: C, 61.06; H, 3.63; S, 34.92.

Poly(5-vinyl-2,2′:5′,2″-terthiophene) (poly(5-vinylterthiophene)) was prepared by radical or cationic polymerization of 5-vinylterthiophene. Radical polymerization was carried out in an evacuated benzene solution containing the monomer and AIBN at 70 °C for 48 h. The concentrations of the monomer and AIBN were $3.7 \times 10^{-1}$ and $3.7 \times 10^{-3}$ mol dm$^{-3}$, respectively. Cationic polymerization was carried out in an evacuated dichloromethane solution containing the monomer and $BF_3 \cdot Et_2O$ with concentrations of $5.0 \times 10^{-2}$ and $9.0 \times 10^{-4}$ mol dm$^{-3}$, respectively, at 0 °C for 8 h. 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 $M_n = 2200$ and $M_w = 3400$ and $M_n = 2500$ and $M_w = 5500$, respectively, by gel permeation chromatography using polystyrene standards.

**Electrochemical Oxidation.** Cyclic voltammetry was carried out for a dichloromethane solution ($1.0 \times 10^{-3}$ mol dm$^{-3}$) of 5-vinylterthiophene or poly(5-vinylterthiophene) containing tetra-*n*-butylammonium perchlorate ($Bu_4NClO_4$) ($1.0 \times 10^{-1}$ mol dm$^{-3}$) as a supporting electrolyte with a Ag/Ag$^+$ (0.01 mol dm$^{-3}$) reference electrode.

Electrolytic polymerization of 5-vinylterthiophene and electrochemical doping of poly(5-vinylterthiophene) were carried out potentiostatically in a two-compartment cell with three electrodes, at 0.80 V *vs* Ag/Ag$^+$ (0.01 mol dm$^{-3}$) reference electrode, for a dichloromethane solution ($(1.0-5.0) \times 10^{-3}$ mol dm$^{-3}$) of 5-vinylterthiophene or poly(5-vinylterthiophene) containing $Bu_4NClO_4$ ($1.0 \times 10^{-1}$ mol dm$^{-3}$) as a supporting electrolyte. Platinum plates were used as the working and counter electrodes. When the electrolysis of 5-vinylterthiophene (27 mg, $5 \times 10^{-3}$ mol dm$^{-3}$) started, a current of 0.44 mA flowed, and it gradually decreased to 0.17 mA during electrolysis. After electrolysis for 250 min, during which *ca.* 8.2 C of electricity flowed, 29 mg of electrochemically doped polymers was obtained. Likewise, when the electrochemical doping of poly(5-vinylterthiophene) (27 mg, $5 \times 10^{-3}$ mol dm$^{-3}$) started, a current of *ca.* 2.6 mA flowed, and it gradually decreased to 0.15 mA during electrochemical doping. After electochemical doping for 270 min, during which *ca.* 9.1 C of electricity flowed, 25 mg of electrochemically doped polymers was obtained. Dedoping of the electrochemically doped polymer was carried out by controlled-galvanostatic reduction of the doped polymer at a current of 0.3 mA.

**Scheme 1. Synthesis of 5-Vinylterthiophene, Poly(5-vinylterthiophene), and Electrochemically Doped Poly(5-vinylterthiophene)**



**Conductivity Measurement.** Electrical conductivity was measured by a two-probe dc method for several film samples which were peeled off from the working electrode. Gold was vacuum deposited onto both sides of the film 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.

**Measurement of Electrochromic Properties.** The electrochemically doped poly(5-vinylterthiophene) was deposited onto an ITO (indium tin oxide) electrode in a film form by the electrochemical doping of poly(5-vinylterthiophene) or by the electrolytic polymerization of 5-vinylterthiophene in dichloromethane for 120 s. The resulting ITO electrode was transferred into an acetonitrile solution containing only supporting electrolyte (0.1 mol dm$^{-3}$ $Bu_4NClO_4$) in a silica-glass cell with a platinum counter electrode and a Ag/Ag$^+$ (0.01 mol dm$^{-3}$) reference electrode. The electrode current and optical absorbance (monitored at 570 nm) were measured *in situ* by applying repetitive pulsed voltages of 0 and 0.80 V *vs* Ag/Ag$^+$ (0.01 mol dm$^{-3}$) for each 10 s in air.

**Apparatus.** Electrochemical measurements were carried out using a Model HA-104 potentiostat (Hokuto Denko, Ltd.), a Model HB-104 function generator (Hokuto Denko, Ltd.), and a Model NP-0361 recorder (Rikadenki). IR, FT-IR, electronic absorption, and $^1$H-NMR spectra were measured with a Model A-102 diffraction grating IR spectrophotometer (Japan Spectroscopic Co., Ltd.), a Model FT/IR-3 FT-IR spectrophotometer (Japan Spectroscopic Co., Ltd.), a Model U-3200 double-beam spectrophotometer (Hitachi, Ltd.), and a Model JNM-GSX-400 spectrometer (JEOL), 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.

## Results and Discussion

The vinyl monomer, 5-vinylterthiophene, was synthesized starting from terthiophene by the Vilsmeier reaction, followed by the Wittig reaction. Poly(5-vinylterthiophene) was prepared by radical and cationic polymerizations of 5-vinylterthiophene (Scheme 1). The polymers produced were found to be oligomers; however, we refer to these oligomers as poly(5-vinylterthiophene) or polymer for the sake of convenience. 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$^{-3}$.

Electrochemically doped poly(5-vinylterthiophene) was prepared by two methods, *i.e.*, electrochemical doping of poly(5-vinylterthiophene) and electrolytic polymeri-

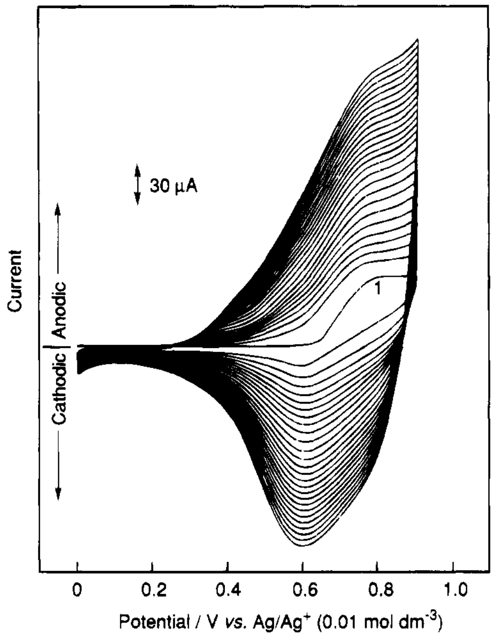


**Figure 1.** Cyclic voltammograms of poly(5-vinylterthiophene) ($1.0 \times 10^{-3}$ mol dm$^{-3}$) in dichloromethane containing $Bu_4NClO_4$ (0.1 mol dm$^{-3}$). 1: First sweep. Sweep rate: 100 mV s$^{-1}$.

zation of the vinyl monomer, 5-vinylterthiophene, with concurrent deposition of a doped polymer (Scheme 1).

First, cyclic voltammetry of the polymer and the vinyl monomer was carried out. Figure 1 shows cyclic voltammograms for the anodic oxidation of poly(5-vinylterthiophene). 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$^+$ (0.01 mol dm$^{-3}$), but the corresponding cathodic wave was much smaller. When the sweep was repeated, two cathodic waves began to be observed at *ca.* 0.80 and 0.60 V. 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. The intensity of these waves gradually increased as the sweep was repeated. The new anodic and the corresponding cathodic waves at the potential more negative than 0.60 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 are approximately in accord with the literature data for the anodic oxidations of terthiophene and sexithiophene, 1.05 and 0.84 V ($E_{pa}$) *vs* SCE,[25] *i.e.*, 0.78 and 0.57 V ($E_{pa}$) *vs* Ag/Ag$^+$ (0.01 mol dm$^{-3}$), respectively. The two cathodic waves at *ca.* 0.80 and 0.60 V may be due to the reduction of the pendant terthiophene radical-cation species with different rates of electron transfer. The wave at *ca.* 0.8 V might also be due to the reduction of sexithiophene dication in the light of the literature that the second anodic oxidation wave of a sexithiophene derivative to form the dication species was observed at 1.08 V ($E_{pa}$) *vs* SCE,[31] *i.e.*, 0.81 V ($E_{pa}$) *vs* Ag/Ag$^+$ (0.01 mol dm$^{-3}$).

The anodic oxidation process of 5-vinylterthiophene was totally irreversible. In the first sweep, an anodic wave due to the oxidation of 5-vinylterthiophene was observed at $E_{pa/2} = 0.67$ V ($E_{pa} = 0.77$ V) *vs* Ag/Ag$^+$ (0.01 mol dm$^{-3}$) 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. In addition, another new anodic and the corresponding cathodic waves were observed at a potential more negative than 0.60 and 0.50V, respectively. The intensity of these waves gradually increased with the repetition of sweep. Like the case of poly(5-vinylterthiophene), the cathodic waves at *ca.* 0.80 and *ca.* 0.50 V may be attributed to the reduction of the pendant terthiophene radical-cation species with different rates of electron transfer or to the reductions of sexithiophene dication and terthiophene radical cation, respectively. The new anodic wave at a potential 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 poly(5-vinylterthiophene) and the electrolytic polymerization of 5-vinylterthiophene are accompanied by the coupling reaction of the pendant terthiophene moiety to produce partially a sexithiophene moiety.

Based on the information obtained by the cyclic voltammetry for the anodic oxidations of poly(5-vinylterthiophene) and 5-vinylterthiophene, electrochemical doping of poly(5-vinylterthiophene) and electrolytic polymerization of 5-vinylterthiophene were carried out by controlled-potential anodic oxidation at 0.80 V *vs* Ag/Ag$^+$ (0.01 mol dm$^{-3}$) reference electrode. Deeply colored, smooth, lustrous films were deposited onto the surface of the working electrode in both cases.

The electrochemically doped polymers obtained by the electrochemical doping of poly(5-vinylterthiophene) and by the electrolytic polymerization of 5-vinylterthiophene were characterized by IR and electronic absorption spectroscopies and elemental analysis. The characteristic IR absorption bands at 1620 cm$^{-1}$ and at 980 and 900 cm$^{-1}$ observed for 5-vinylterthiophene, 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, were absent in the spectrum of the electrochemically doped polymer prepared by the electrolytic polymerization of the monomer. Instead, a new band due to the asymmetric strectching vibration of the methylene group appeared at 2922 cm$^{-1}$. These results idnicate that the electrolytic polymerization of 5-vinylterthiophene takes place at the vinyl group to give electroactive poly(5-vinylterthiophene), which concurrently undergoes electrochemical doping. The electrochemically doped polymers prepared by both methods show strong IR absorption bands at 1090, 1120, and 1150 cm$^{-1}$ due to $ClO_4^-$. This indicates that the electrochemically doped polymer contains $ClO_4^-$ as a dopant. The characteristic IR absorption bands at 795 and 695 cm$^{-1}$ observed for the starting materials, 5-vinylterthiophene and undoped poly(5-vinylterthiophene), are assigned to the C−H out-of-plane deformation vibrations of 2,5-disubstituted and 2-substituted thiophenes, respectively.[22] The relative intensity of the latter band decreased for the electrochemically doped poly(5-vinylterthiophene) prepared by both methods; this suggests that the pendant terthiophenes are partially transformed into the sexithiophene moiety due to the coupling reaction of the pendant terthiophene radical cation. A new doping-induced band was observed at 1400 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‴″-sexithiophene doped with $FeCl_3$.[27] When the polymer was dedoped by

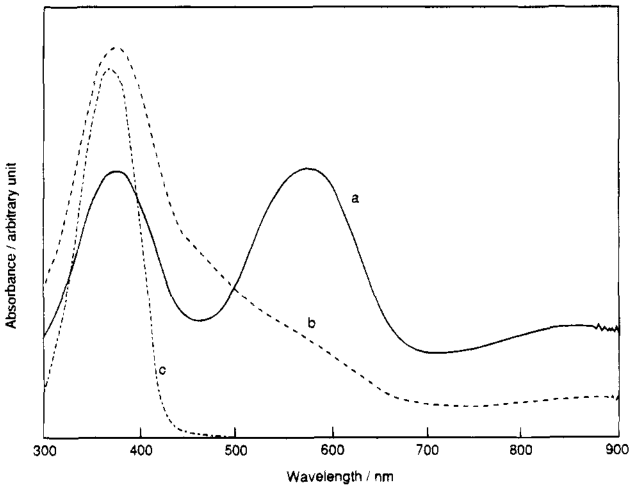


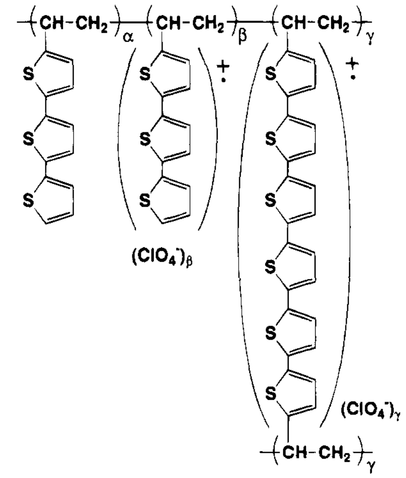
**Figure 2.** Electronic absorption spectra of (a) electrochemically doped poly(5-vinylterthiophene) film, (b) dedoped polymer film, and (c) undoped, neutral poly(5-vinylterthiophene) in dichloromethane. The doped polymer film was obtained by the electrolytic polymerization of 5-vinylterthiophene at 0.8 V *vs* Ag/Ag$^+$ (0.01 mol dm$^{-3}$) for 2 min, and the dedoped polymer film was obtained by the controlled-galvanostatic reduction at a current of 0.3 mA for 4 min.

controlled-galvanostatic reduction of the doped polymer, the intensities of the bands at 1090, 1120, and 1150 cm$^{-1}$ due to $ClO_4^-$ and the doping-induced band at 1400 cm$^{-1}$ decreased significantly.

Figure 2 shows the electronic absorption spectra of transparent thin films of electrochemically doped poly(5-vinylterthiophene) deposited onto the ITO glass by the anodic polymerization of 5-vinylterthiophene and the dedoped polymer. The electrochemically doped polymer obtained by the anodic oxidation of poly(5-vinylterthiophene) also shows essentially the same electronic absorption spectrum as that of the polymer obtained by the anodic polymerization of 5-vinylterthiophene. The electronic absorption spectrum of a dichloromethane solution of the undoped, neutral poly(5-vinylterthiophene) is also given for reference in the figure.

The thin film of the electrochemically doped polymer shows new absorption bands with $\lambda_{max}$ at 577 nm and in the wavelength region from 750 to 900 nm, along with the absorption band with $\lambda_{max}$ 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 $\lambda_{max}$ 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 $\lambda_{max}$ at 577 nm observed for the electrochemically doped poly(5-vinylterthiophene) 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 poly(5-vinylterthiophene) film is assigned to the sexithiophene radical-cation species. In fact, the electronic absorption spectra of the radical-cation species of terthiophene and α-methyl-disubstituted terthiophene produced by laser flash photolysis in methanol and by anodic oxidation in acetonitrile have been reported to show a band with $\lambda_{max}$ at 535 nm and at 572 nm, respectively.[39,40] The electronic absorption band of the sexithiophene radical cation has been reported to show a band with $\lambda_{max}$ at *ca.* 780 nm in a dichloromethane solution.[27,33] Recent studies have revealed that radical cations of oligothiophenes, *e.g.*, terthiophene and sexithiophene, in solution are in reversible equilibrium between the monomeric and dimeric radical cations, and that the formation of dimeric radical cations, the electronic absorption bands of which are blue-shifted relative to those of monomeric radical cations, is favored at low temperature.[33,40] With regard to the present electrochemically doped polymers, however, it is not clear from the electronic absorption spectrum whether the dimeric radical-cation species is involved in equilibrium with the monomeric radical cations. 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 $\lambda_{max}$ at 432 nm in benzene.[24]

Based on the spectroscopic results together with the results of cyclic voltammetry, the electrochemically doped polymers prepared by the electrolytic polymerization of 5-vinylterthiophene and by the electrochemical doping of poly(5-vinylterthiophene) are identified as partially oxidized radical-cation salts with $ClO_4^-$ 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 structure due to the interpolymer coupling reaction of the radical cation of the pendant terthiophene moiety.



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)[18] and trimethylsilyl-disubstituted thiophene hexamer ($\epsilon_{max}$ = 40 600 at 430 nm in chloroform)[32] were used as model compounds for the pendant terthiophene and sexithiophene chro-

**Table 1. Room-Temperature Conductivities and Activation Energies of Electrochemically Doped Poly(5-vinylterthiophene)**

| sample | doping method[a] | doping time/min | degree of doping/% | conductivity/ (S cm$^{-1}$) | activation energy/eV |
|---|---|---|---|---|---|
| 1 | A | 1 | 35[b] | $7 \times 10^{-9}$ | 0.49 |
| 2 | A | 2 | 45[b] | $2 \times 10^{-8}$ | 0.50 |
| 3 | A | 3 | 37[b] | $1 \times 10^{-8}$ | 0.35 |
| 4 | A | 250 | 100[c] | $5 \times 10^{-10}$ | 0.60 |
| 5 | B | 2 | 29[b] | $5 \times 10^{-9}$ | 0.45 |
| 6 | B | 5 | 34[b] | $4 \times 10^{-9}$ | 0.42 |
| 7 | B | 318 | 86[c] | $4 \times 10^{-10}$ |  |

[a] A: Prepared by electrolytic polymerization of 5-vinylterthiophene in dichloromethane at 0.8 V *vs* Ag/Ag$^+$ (0.01 mol dm$^{-3}$). B: Prepared by electrochemical doping of poly(5-vinylterthiophene) in dichloromethane at 0.8 V *vs* Ag/Ag$^+$ (0.01 mol dm$^{-3}$). [b] Estimated from electronic absorption spectra. Degree of doping = $(\beta + \gamma)/(\alpha + \beta + 2\gamma)$, where $\alpha$, $\beta$, and $\gamma$ represent the molar fractions of the pendant neutral terthiophene, terthiophene radical cation, and sexithiophene radical cation, which are estimated from molar extinction coefficients and the intensities of the electronic absorption bands due to the neutral terthiophene and terthiophene radical cation in the electrochemically doped polymer and due to neutral sexithiophene in the electrochemically dedoped polymer. The molar extinction coefficients of 2,2′:5′,2″-terthiophene ($\epsilon_{\max}$ = 21 900 at 355 nm in benzene),[18] its radical cation ($\epsilon_{\max}$ = 29 000 at 535 nm in methanol),[39] and trimethylsilyl-disubstituted thiophene hexamer ($\epsilon_{\max}$ = 40 600 at 430 nm in chloroform)[32] were used for those of the corresponding pendant chromophores. [c] Calculated from the chlorine content.

mophores in the dedoped polymer, respectively. The ratio of the pendant terthiophene to sexithiophene chromophore is given by the following equation:

$$\text{terthiophene:sexithiophene} = I_{3T}/\epsilon_{\max 3T}{:}I_{6T}/\epsilon_{\max 6T}$$

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 poly(5-vinylterthiophene) and the electrolytic polymerization of 5-vinylterthiophene 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.

Table 1 lists room-temperature conductivities and activation energies for electrical conduction for several samples of electrochemically doped poly(5-vinylterthiophene) with varying degrees of doping. The polymer with a doping degree of 45% exhibited a room-temperature conductivity of $2 \times 10^{-8}$ S cm$^{-1}$, while the conductivity dropped to less than $4 \times 10^{-10}$ S cm$^{-1}$ for samples with a doping degree of *ca.* 86–100%. Unsubstituted oligothiophenes such as trimer, tetramer, and pentamer have been reported to exhibit room-temperature conductivities of $10^{-11}$, $10^{-10}$, and $10^{-8}$ cm$^{-1}$, respectively.[29] The room-temperature conductivities of the charge-transfer complexes of unsubstituted thiophene trimer or tetramer with TCNQ have been reported to be *ca.* $10^{-10}$–$10^{-9}$ S cm$^{-1}$.[26] $\beta$-Alkyl-substituted thiophene heptamer ($n = 7$) doped with iodine has been reported to exhibit a room-temperature conductivity of $10^{-2}$ S cm$^{-1}$.[28] The low conductivity for the present polymer is attributed to poor intermolecular overlap of $\pi$-conjugation in a pendant terthiophene moiety in the light of the facts that 2,2′:5′,2″-terthiophene and its charge-transfer complex with TCNQ exhibit low conductivity. It is expected that electrical conductivity will increase as the length of pendant oligothiophenes increases.

Applications of electrically conducting polymers to functional materials have been a subject of interest. They include secondary batteries, photovoltaic devices, field-effect transistors, electrochromic displays, *etc.*

Electrochromic organic polymers are attractive because they may exhibit a memory effect in addition to a multicolor display and because they have a good cycle life owing to their ability to be cast in a film form. Electrically conducting polymers such as polypyrrole,[41] polythiophene,[41,42] and polyisothianaphthene[43] have been reported to be potential electrochromic materials. With regard to polythiophenes, for example, the color switches from blue (oxidized state) to red (reduced state). However, $\pi$-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. By contrast, the present polymers containing oligothiophenes with well-defined structures as pendant groups have the following attractive characteristics. That is, the starting polymers are expected to be soluble in ordinary solvents in their neutral states and cast in films. The polymers are expected to exhibit clear color changes on electrochemical doping and dedoping owing to the well-defined structures of the pendant oligothiophenes.

As Figure 3 shows, the thin lustrous films of electrochemically doped poly(5-vinylterthiophene) obtained both by the electrolytic polymerization of 5-vinylterthiophene and by the electrochemical doping of poly(5-vinylterthiophene) were found to undergo a reversible clear color change from bluish purple to pale yellowish orange on electrochemical dedoping and *vice versa* when the cycle of dedoping and doping is repeated.

The formation of a smooth film and the insolubility of the doped and dedoped polymers as well as a reversible clear color change enable the application of the polymer as an electrochromic display material. Electrochromic properties of the poly(5-vinylterthiophene) film were examined. When repetitive pulsed voltages of 0 and 0.80 V *vs* Ag/Ag$^+$ (0.01 mol dm$^{-3}$) were applied for each 10 s to the electrochemically doped poly(5-vinylterthiophene) prepared by the electrolytic polymerization of 5-vinylterthiophene, the electrode current and optical absorbance (monitored at 570 nm) changed in such a way as shown in Figure 4. The response times for doping (coloration) and dedoping (decoloration) were 3.4 and 1.5 s, respectively. In the case of the electrochemically doped poly(5-vinylterthiophene) prepared by the electrochemical doping of poly(5-vinylterthiophene), the response times were 4.7 s for doping and 2.0 s for dedoping. The response time is here defined as the time required for the absorbance change from 10% to 90%. When the redox cycle of dedoping at 0 and doping at 0.8 V *vs* Ag/Ag$^+$ (0.01 mol dm$^{-3}$) for each 2 s was repeated over 500 times, a reversible color change was observed.

A series of polymers containing oligothiophenes with well-defined structures as pendant groups may constitute a novel class of potential electrochromic materials with memory effect. It is expected that the color can be controlled by varying the length of linear $\pi$-conjugated oligothiophenes. Performance characteristics such as cycle life and response time as well as adhesion of

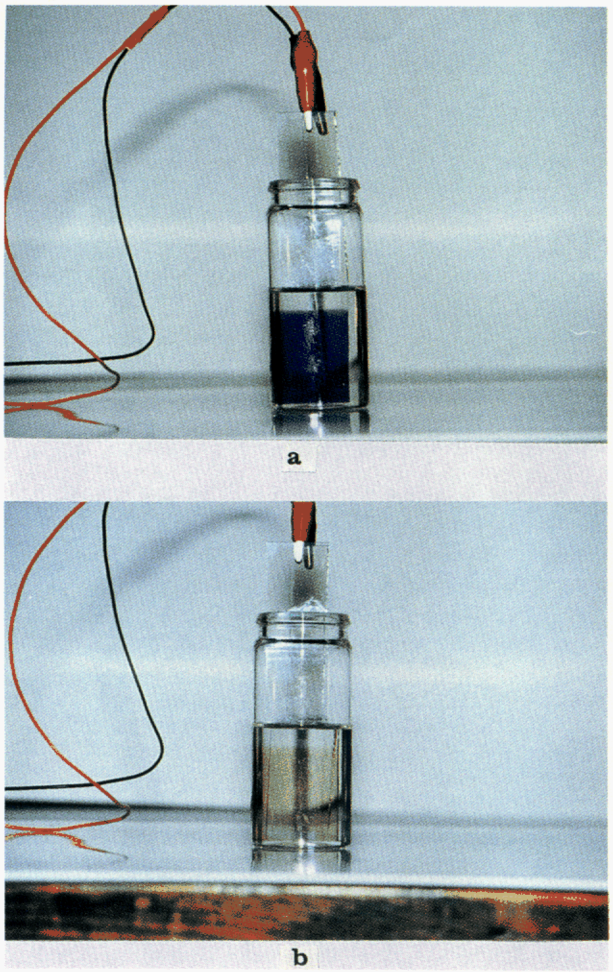


**Figure 3.** Reversible color change for a poly(5-vinylterthiophene) film on (a) electrochemical doping at 0.80 V and (b) dedoping at −0.10 V *vs* Ag/Ag$^+$ (0.01 mol dm$^{-3}$).

the electrochromic film to the substrate will be improved by optimization of film thickness, solvent, electrode, *etc.*, and by modification of the polymers. It will also be of interest to examine how the electrical conductivity or the electrochromic behavior is affected by the length of pendant oligothiophenes. Further studies on the synthesis, electrochemical doping, and properties of a series of novel polymers containing pendant oligothiophenes are in progress.

## Conclusion

For the purpose of developing a novel type of electrically conducting polymer, a nonconjugated, vinyl-type polymer containing $\pi$-conjugated terthiophene as a pendant group has been studied. A new vinyl monomer, 5-vinylterthiophene, and its polymer, poly(5-vinylterthiophene), have been synthesized and electrolytic polymerization of the monomer and electrochemical doping of the polymer carried out. Characterization of the resulting electrochemically doped polymers and their electrical and electrochromic properties have been examined. Electrochemically doped poly(5-vinylterthiophene), obtained as a bluish purple lustrous film, is identified as a partially oxidized radical-cation salt with $ClO_4^-$ as a dopant. The doped polymer is partially cross-linked due to the coupling reaction of the pendant terthiophene radical cation.

The polymer film with a doping degree of 45% exhibited a room-temperature conductivity of *ca.* 2 × $10^{-8}$ S cm$^{-1}$ with an activation energy of 0.5 eV. The polymer film undergoes a reversible clear color change from bluish purple to pale yellowish orange on electrochemical dedoping and *vice versa*. Electrochromic properties have been examined, and the polymer is found to be a candidate for a novel class of electrochromic material.

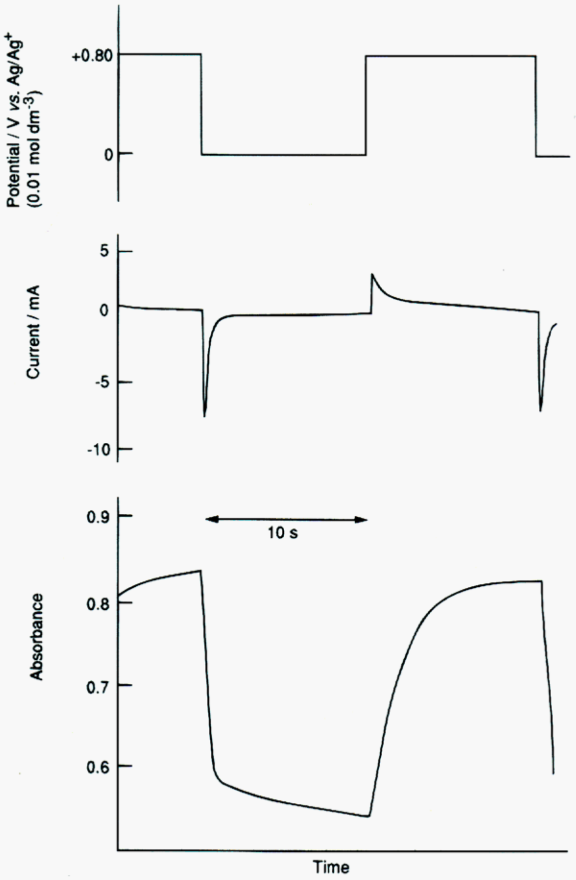


**Figure 4.** Changes of electrode current and optical absorption (monitored at 570 nm) as a function of time for a poly(5-vinylterthiophene) film under applications of repetitive voltages of 0 and 0.8 V *vs* Ag/Ag$^+$ (0.01 mol dm$^{-3}$).

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