Synthesis of a Novel Family of Electrochemically-Doped Vinyl Polymers Containing Pendant Oligothiophenes and Their Electrical and Electrochromic Properties

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ABSTRACT: Novel electrochemically-doped vinyl polymers containing 2,2′:5′,2″:5″,2‴-quaterthiophene, 4′,3‴-dioctyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene, and 4′,3⁗-dioctyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′-sexithiophene as pendant groups were prepared by anodic polymerizations of the corresponding new vinyl monomers in the presence of tetra-*n*-butylammonium perchlorate as a supporting electrolyte, and their electrical and electrochromic properties were investigated. The electrochemically-doped polymers, which were obtained as deeply-colored, lustrous films on the surface of the working electrode, were identified as radical-cation salts of pendant oligothiophenes with ClO_4^- as a dopant, having a partially-cross-linked structure due to the coupling reaction of the radical cation of the pendant oligothiophene moiety. The electrical conductivity of these electrochemically-doped polymers increased with increasing conjugation length of the pendant oligothiophenes; the polymer containing the pendant sexithiophene group exhibited a room-temperature conductivity of *ca.* 10^{-4} S cm^{-1} with an activation energy of 0.25 eV. These polymers undergo a reversible clear color change from green to yellow and *vice versa* on electrochemical dedoping and doping, constituting a novel class of potential electrochromic materials.

Introduction

Electrically-conducting polymers have attracted great attention in view of both academic interest and potential technological applications as materials for use in electronic devices.[1,2] π-Conjugated linear polymers, *e.g.*, polyacetylene, poly(*p*-phenylene), polypyrrole, polythiophene, and polyaniline, have been studied extensively owing to their high electrical conductivities which can be attained by doping.[3−7]

For the purpose of developing a novel class of electrically-conducting polymers, we have studied electrochemical doping of nonconjugated vinyl polymers containing pendant π-electron systems and investigated the properties and applications of doped polymers.[8] They include poly(*N*-vinylcarbazole),[9−13] poly(vinylferrocene),[14] poly[4-(diphenylamino)phenylmethyl methacrylate],[15] poly(1-vinylpyrene),[16] and poly(3-vinylperylene).[17−20]

In order to develop a further new type of electrically-conducting polymers, we have been studying the synthesis, properties, and applications of polymers containing oligothiophenes as pendant groups. α,α′-Oligothiophenes with well-defined structures have recently attracted attention not only as model compounds for electrically-conducting polythiophenes but also as a new family of organic π-electron systems. The synthesis,[21−24] molecular and crystal structures,[25,26] and optical,[27−30] electrochemical,[31−33] electrical,[34−36] and photovoltaic properties,[37−39] of α,α′-oligothiophenes and their application to field-effect transistors[40−43] have been reported. 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. We have reported the synthesis of novel vinyl and methacrylate polymers containing pendant 2,2′:5′,2″-terthiophene, poly(5-vinyl-2,2′:5′,2″-terthiophene) (PV3T),[44−46] and poly[(2,2′:5′,2″-terthiophene-5-yl)methyl methacrylate] (PMA3T)[47] and their electrical and electrochromic properties.

We report here the synthesis of a novel family of electrochemically-doped vinyl polymers containing pendant oligothiophenes with longer conjugation lengths, 2,2′:5′,2″:5″,2‴-quaterthiophene, 4′,3‴-dioctyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene, and 4′,3⁗-dioctyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′-sexithiophene, by anodic polymerizations of the corresponding new vinyl monomers, 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), and 4′,3⁗-dioctyl-5-vinyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′-sexithiophene (VDOc6T), and discuss their electrical and electrochromic properties in relation to the conjugation length of the pendant oligothiophenes. Preliminary results of poly(5-vinyl-2,2′:5′,2″:5″,2‴-quaterthiophene) (PV4T) have been reported as a communication.[44] Related to the present study, the anionic polymerization of 5-vinyl-2,2′:5′,2″-terthiophene[48] and the preparation of polymers having a poly(methyl methacrylate) backbone and polythiophene side chains by chemical oxidation of poly(2-thienylmethyl methacrylate)[49] and by electrochemical and chemical oxidation of a mixture of poly(2,2′-bithienylmethyl methacrylate) and 3-alkylthiophene[50] have recently been reported.

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. Tetra-*n*-butylammonium perchlorate (TBAP) (Tokyo Chemical Industry Co., Ltd.) was purified by recrystallization from ethanol and dried.

Synthesis of Vinyl Monomers. 2,2′:5′,2″:5″,2‴-Quaterthiophene and 4′,3⁗-dioctyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′-sexithiophene were prepared according to the literature.[51−53] The new compound, 4′,3‴-dioctyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene, was also synthesized in a similar manner by a

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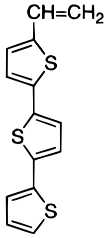
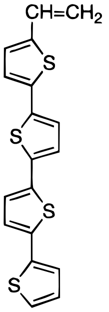
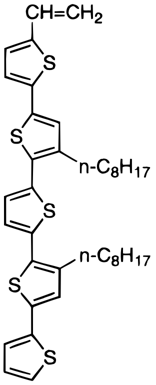


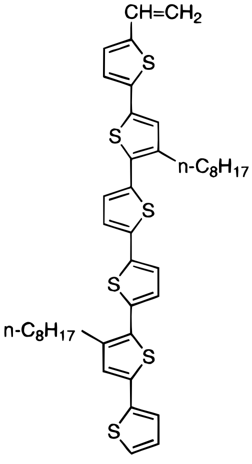
V3T



V4T



VDOc5T



VDOc6T

Ni-catalyzed Grignard coupling reaction of 2-thienylmagnesium 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)thienylmagnesium bromide with 2,5-dibromothiophene. 2,2′:5′,2″:5″,2‴-Quaterthiophene, 4′,3‴-dioctyl-2,2′:5′,2″:5″,2‴:5‴,2′′′′-quinquethiophene, and 4′,3′′′′-dioctyl-2,2′:5′,2″:5″,2‴:5‴,2′′′′:5′′′′,2′′′′′-sexithiophene were purified by silica gel column chromatography followed by recrystallization from *n*-hexane, mp 211, 75, and 128 °C.

The new vinyl monomers, V4T, VDOc5T, and VDOc6T, were synthesized by the Vilsmeier reaction of 2,2′:5′,2″:5″,2‴-quaterthiophene, 4′, 3‴-dioctyl-2,2′:5′,2″:5″,2‴:5‴,2′′′′-quinquethiophene, and 4′,3′′′′-dioctyl-2,2′:5′,2″:5″,2‴:5‴,2′′′′:5′′′′,2′′′′′-sexithiophene followed by the Wittig reaction.

VDOc6T. 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′′′′: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 h. 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′′′′:5′′′′,2′′′′′-sexithiophene (DOc6T-CHO). DOc6T-CHO was purified by recrystallization from *n*-hexane to give a dark red powder (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 h at room temperature. After DOc6T-CHO in the solution disappeared, the solvent was evaporated. The resulting 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 $C_{42}H_{48}S_6$: C, 67.69; H, 6.49; S, 25.82. Found: C, 67.77; H, 6.48; S, 25.71. MS (*m/z*): 744 (M^+). UV (THF, λ_{max}): 426 nm ($\epsilon = 57\,000\ M^{-1}\ cm^{-1}$). IR (KBr pellet, cm^{-1}): 3076 (w, ν_{C-H} thienyl), 3058 (w, ν_{C-H} thienyl), 2952 (m, ν_{asC-H} methyl), 2920 (s, ν_{asC-H} methylene), 2867 (m, ν_{sC-H} methyl), 2851 (s, ν_{sC-H} methylene), 1615 (m, $\nu_{C=C}$ vinyl), 972 (m, δ_{C-H} vinyl), 890 (m, δ_{C-H} vinyl), 833 (m, δ_{C-H} 2-monosubstituted thiophene), 819 (m, δ_{C-H} 2-monosubstituted thiophene), 805 (m, δ_{C-H} 2,3,5-trisubstituted thiophene), 792 (m, δ_{C-H} 2,5-disubstituted thiophene), 687 (m, δ_{C-H} 2-monosubstituted thiophene). ^{1}H-NMR (400 MHz, C_6D_6, 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_2, 4H, t, $J = 6.6$ Hz), 1.62−1.60 (alkyl β-CH_2, 4H, m), 1.40−1.25 (alkyl CH_2, 20H, m), 0.95 (CH_3, 6H, t, $J = 6.6$ Hz).

The other two vinyl monomers, V4T and VDOc5T, were likewise synthesized and identified.

5-Vinyl-2,2′:5′,2″:5″,2‴-quaterthiophene (V4T): orange plate crystals, mp 189−190 °C. Anal. Calcd for $C_{18}H_{12}S_4$: C, 60.67; H, 3.37; S, 35.96. Found: C, 60.87; H, 3.49; S, 35.81. MS (*m/z*): 356 (M^+). UV (THF, λ_{max}): 406 nm ($\epsilon = 31\,000\ M^{-1}\ cm^{-1}$). IR (KBr pellet, cm^{-1}): 3076 (w, ν_{C-H} thienyl), 3062 (w, ν_{C-H} thienyl), 1615 (m, $\nu_{C=C}$ vinyl), 974 (m, δ_{C-H} vinyl), 890 (m, δ_{C-H} vinyl), 832 (m, δ_{C-H} 2-monosubstituted thiophene), 818 (w, δ_{C-H} 2-monosubstituted thiophene), 791 (s, δ_{C-H} 2,5-disubstituted thiophene), 685 (m, δ_{C-H} 2-monosubstituted thiophene). ^{1}H-NMR (400 MHz, C_6D_6, 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 β-CH, 1H, d, $J = 16.9$ Hz), 4.95 (vinyl β-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, λ_{max}): 408 nm ($\epsilon = 42\,000\ M^{-1}\ cm^{-1}$). IR (KBr pellet, cm^{-1}): 3080 (w, ν_{C-H} thienyl), 3065 (w, ν_{C-H} thienyl), 2953 (m, ν_{asC-H} methyl), 2923 (s, ν_{asC-H} methylene), 2869 (m, ν_{sC-H} methyl), 2852 (s, ν_{sC-H} methylene), 1616 (m, $\nu_{C=C}$ vinyl), 974 (m, δ_{C-H} vinyl), 890 (m, δ_{C-H} vinyl), 831 (m, δ_{C-H} 2-monosubstituted thiophene), 819 (m, δ_{C-H} 2-monosubstituted thiophene), 803 (m, δ_{C-H} 2,3,5-trisubstituted thiophene), 798 (m, δ_{C-H} 2,5-disubstituted thiophene), 684 (m, δ_{C-H} 2-monosubstituted thiophene). ^{1}H-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 α-CH, dd, $J = 11.0, 16.9$ Hz), 5.52 (vinyl β-CH, 1H, d, $J = 16.9$ Hz), 4.96 (vinyl β-CH, 1H, d, $J = 11.0$ Hz), 2.75 (alkyl α-CH_2, 4H, t, $J = 6.6$ Hz), 1.63−1.60 (alkyl β-CH_2, 4H, m), 1.40−1.25 (alkyl CH_2, 20H, m), 0.95 (CH_3, 6H, t, $J = 6.6$ Hz).

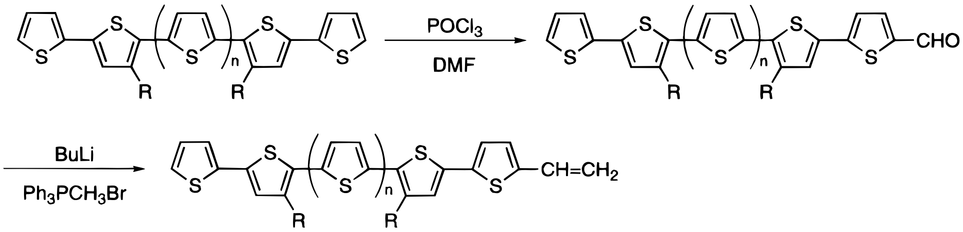
Electrochemical Oxidation. Cyclic voltammetry was carried out for dichloromethane solutions (1.0×10^{-3} mol dm^{-3}) of the vinyl monomers containing tetra-*n*-butylammonium perchlorate (TBAP) (0.1 mol dm^{-3}) as a supporting electrolyte using a Ag/Ag^+ (0.01 mol dm^{-3}) reference electrode.

Electrolytic polymerization was carried out potentiostatically in a two-compartment cell with three electrodes for dichloromethane solutions (1.0×10^{-3} mol dm^{-3}) of the vinyl monomers containing TBAP (0.1 mol dm^{-3}) as a supporting electrolyte. Platinum plates were used as the working electrodes and counterelectrodes.

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.

Measurement of Electrochromic Properties. The electrochemically-doped polymer was deposited onto an indium−tin−oxide (ITO)-coated glass electrode in a film form by the electrolytic polymerization of the monomer in dichloromethane. The resulting ITO electrode was then transferred into an acetonitrile solution containing only the supporting electrolyte

Scheme 1



V4T: R=H, n=0
VDOc5T: R=$(CH_2)_7CH_3$, n=1
VDOc6T: R=$(CH_2)_7CH_3$, n=2

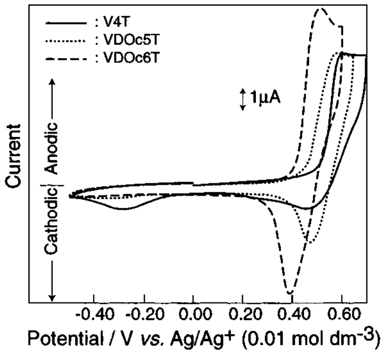


Figure 1. Cyclic voltammograms of vinyl oligothiophenes (1.0 × 10^{-3} mol dm^{-3}) in dichloromethane containing TBAP (0.1 mol dm^{-3}); sweep rate: 100 mV s^{-1}.

(0.1 mol dm^{-3} TBAP) in a silica−glass cell with a platinum counterelectrode and a Ag/Ag^+ (0.01 mol dm^{-3}) reference electrode. The electrode current and optical density were measured *in situ* by applying repetitive pulsed voltages of 0 and 0.65, 0 and 0.55, and 0 and 0.50 V *vs* Ag/Ag^+ (0.01 mol dm^{-3}) for the polymers obtained by electrolytic polymerization of V4T, VDOc5T, and VDOc6T, respectively, for each 10 s in air.

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, ^{1}H-NMR, 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.), a Model JNM-GSX-400 spectrometer (JEOL), and a Model JES-ME-2X spectrometer (JEOL), respectively.

Results and Discussion

The new vinyl monomers, V4T, VDOc5T, and VDOc6T, were synthesized by the Vilsmeier reaction of 2,2′:5′,2″:5″,2‴-quaterthiophene, 4′,3‴-dioctyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene, and 4′,3⁗-dioctyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2′′′′′-sexithiophene, respectively, followed by the Wittig reaction (Scheme 1). The synthesis of vinyl monomers containing unsubstituted α-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 β-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.

Cyclic voltammetry was carried out in order to obtain information on the anodic oxidation processes of the vinyl monomers. Figure 1 shows cyclic voltammograms for the anodic oxidations of V4T, VDOc5T, and VDOc6T in dichloromethane. The anodic oxidation processes 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^+ (0.01 mol dm^{-3}), but the corresponding cathodic wave (E_{pc} = 0.46 V *vs* Ag/Ag^+ (0.01 mol dm^{-3})) 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^+ (0.01 mol dm^{-3}). This cathodic wave is ascribed to the reduction of H^+, generated by the deprotonation at the α-position of the terminal thiophene ring in the coupling reaction of the pendant quaterthiophene radical cation. These results are similar to those of V3T.[46] 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 $E_{pa/2}$ = 0.46 V (E_{pa} = 0.52 V) *vs* Ag/Ag^+ (0.01 mol dm^{-3}), respectively, and the corresponding cathodic waves were observed at E_{pc} = 0.48 and 0.37 V *vs* Ag/Ag^+ (0.01 mol dm^{-3}), respectively, more definitely than those for V4T. In addition, the cathodic wave at E_{pc} = *ca.* −0.30 V *vs* Ag/Ag^+ (0.01 mol dm^{-3}) due to the reduction of H^+ was smaller than that observed for 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,[54] making the coupling reaction of the pendant oligothiophene radical cation less favorable.

Electrochemically-doped polymers were prepared by anodic polymerization of the vinyl monomers, based on the information obtained by cyclic voltammetry for the anodic oxidation of the vinyl monomers. Electrolytic polymerizations of V4T, VDOc5T, and VDOc6T were carried out by controlled-potential anodic oxidation at 0.65, 0.55, and 0.50 V *vs* Ag/Ag^+ (0.01 mol dm^{-3}), 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.[36]

The electrochemically-doped polymers, 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), and poly(4′,3⁗-dioctyl-5-vinyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2′′′′′-sexithiophene) (PVDOc6T), obtained by the electrolytic polymerization of the vinyl

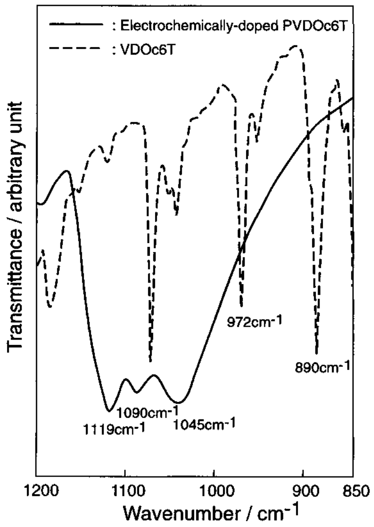


Figure 2. Infrared absorption spectra of vinyl monomer VDOc6T and electrochemically-doped PVDOc6T.

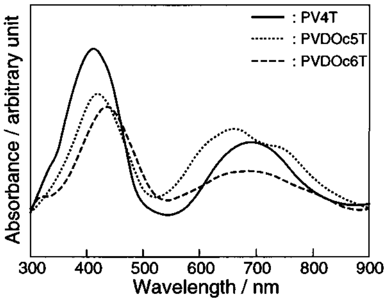


Figure 3. Electronic absorption spectra of electrochemically-doped polymer films.

monomers were characterized by infrared absorption, electronic absorption, and electron spin resonance spectroscopies and elemental analysis. Figure 2 shows the infrared absorption spectra of the vinyl monomer VDOc6T and the film formed by the anodic polymerization of VDOc6T. The characteristic infrared absorption bands at 972 and 890 cm^{-1} observed for VDOc6T, 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 VDOc6T. The case was the same for PVDOc5T and PV4T. Furthermore, a new absorption band in the wavelength region from 2800 to 3000 cm^{-1}, which was not observed for V4T, appeared in the spectrum of the electrochemically-doped PV4T. This band is ascribed to the methine and methylene groups of the polymer backbone formed by the electrolytic polymerization. These results indicate that the electrolytic polymerization of each vinyl monomer takes place at the vinyl group to give the polymer. The polymer films show strong infrared absorption bands at 1119, 1090, and 1045 cm^{-1} due to the ClO_4^- ion. Thus, the polymers produced by the electrolytic polymerization concurrently undergo anodic oxidation to give electrochemically-doped polymers with ClO_4^- as a dopant. These results are similar to those for PV3T prepared by the electrolytic polymerization of V3T.[46]

Figure 3 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 λ_{max} at 690 nm along with the absorption band with λ_{max} at 400 nm due to the π−π* transition of the neutral quaterthiophene chromophore. When the electrochemically-doped PV4T was dedoped by cathodic reduction at 0 V *vs* Ag/Ag$^+$ (0.01 mol dm^{-3}), the characteristic absorption band with λ_{max} at 690 nm disappeared and a new absorption band in the wavelength region from 500 to 600 nm appeared instead. The absorption band with λ_{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.

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 λ_{max} at 415 and 430 nm due to the π−π* 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$^+$ (0.01 mol dm^{-3}), 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. It has been reported that radical cations of oligothiophenes in solution are in reversible equilibrium between the monomeric radical cation and the dimeric radical cation, *i.e.*, associated radical-cation π-dimer.[24,33,55−59] The absorption bands of the monomeric and dimeric radical cations of quaterthiophene,[33] quinquethiophene,[33] and sexithiophene[58] have been reported to appear at 693 and 551, 756 and 611, and 775 and 685 nm, respectively, in dichloromethane. With regard to the present electrochemically-doped polymer 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 π-dimer. This is because PVDOc5T and PVDOc6T have longer pendant oligothiophenes than PV4T. Unlike 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. 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 quaterthiophene and hence undergo the 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 makes the pendant oligothiophene radical cations more stable, leading to the decrease in the degree of cross-linking in the resulting polymers.

The presence of unpaired electrons for the electrochemically-doped polymers was evidenced by electron spin resonance spectroscopy. Figure 4 shows the electron spin resonance spectrum of the electrochemically-

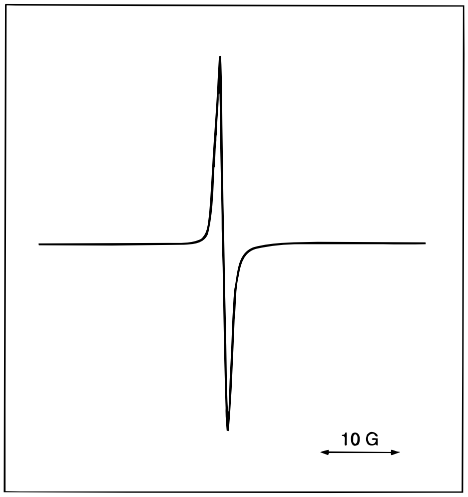


Figure 4. Electron spin resonance spectrum of electrochemically-doped PVDOc6T film.

doped PVDOc6T prepared by the electrolytic polymerization of VDOc6T. A strong single line with a *g*-value of 2.002 and a line width of 1.2 G due to the radical-cation species was observed.

On the basis of the spectroscopic results together with the results of cyclic voltammetry, the electrochemically-doped polymers prepared by the electrolytic polymerizations of V4T, VDOc5T, and VDOc6T were identified as radical-cation salts of pendant oligothiophenes with ClO_4^- as a dopant, having partially-cross-linked structures. The extent of cross-linking was found to decrease with increasing conjugation length of the pendant oligothiophenes.

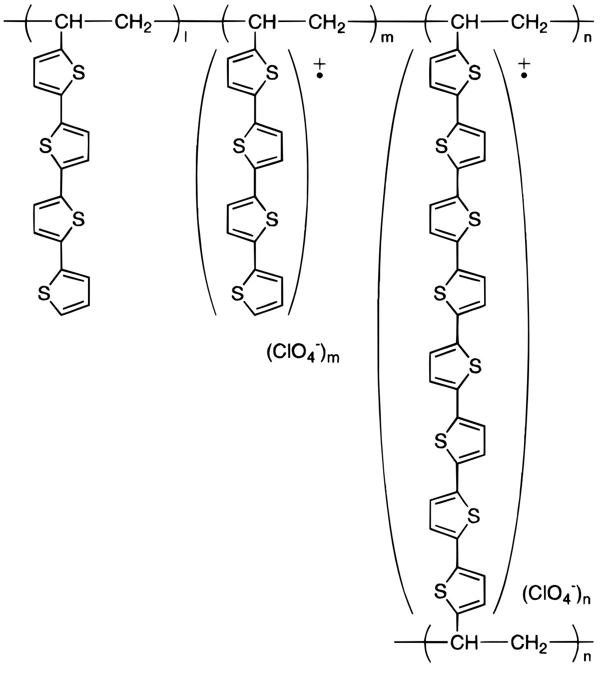


Table 1 lists room-temperature conductivities and activation energies for electrical conduction for the electrochemically-doped polymers containing pendant oligothiophenes. Although the extent of doping varied depending upon the polymer, the room-temperature conductivity was found to increase with increasing conjugation length of the pendant oligothiophenes. Whereas the electrochemically-doped PV3T and PV4T were poor conductors, PVDOc5T and PVDOc6T exhibited room-temperature conductivities in the range from *ca.* 10^{-5} to 10^{-4} S cm^{-1}. 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⁗-diethyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene with a doping degree of *ca.* 50% exhibit room-temperature conductivities of 10^{-7} and 5×10^{-3} S cm^{-1} with activation energies of *ca.* 0.5 and 0.1 eV, respectively.[36] The polymers containing pendant oligothiophenes exhibit poorer electrical conductivity relative to the oligothiophenes themselves. It is suggested that hole transport takes place over pendant oligothiophenes both intramolecularly along the polymer backbone and intermolecularly. However, the data of conductivity and activation energy alone do not allow us to discuss in detail conductivity mechanisms for the doped polymers because the extent of doping for each sample is different and because the nature of the charge transport varies depending upon the extent of doping, particularly in the case of a high extent of doping.

Table 1. Room-Temperature Conductivities and Activation Energies for Electrochemically-Doped Polymers

polymer	degree of doping[a] (%)	conductivity (S/cm)	activation energy (eV)
PV3T[b]	35	7×10^{-9}	0.49
PV4T	68	2×10^{-8}	0.48
PVDOc5T	66	2×10^{-5}	0.32
PVDOc6T	94	1×10^{-4}	0.25

[a] Calculated from elemental analysis. [b] Quoted from ref 46.

Interesting applications of electrically-conducting polymers include electrode materials in secondary batteries,[8,11,13,19] photoactive materials in photovoltaic devices,[8,12,15] and electrochromic materials in display devices and smart windows.[44,46,47] With regard to electrochromic materials, polymers are attractive because they may exhibit a memory effect in addition to the capability of multicolor 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,[60] polythiophene,[60,61] and polyisothianaphthene[62] have been reported to act as potential electrochromic materials. However, π-conjugated linear polymers are in general not normally processable, and their electronic absorption bands are generally broad. In contrast to π-conjugated linear polymers, the present vinyl polymers containing oligothiophenes with well-defined structures as pendant groups are expected to exhibit clear color change on electrochemical doping and dedoping owing to the well-defined structures of the pendant oligothiophenes.

As Figure 5 shows, the thin lustrous film of electrochemically-doped PV4T obtained by the electrolytic polymerization of V4T was found to undergo a reversible clear color change from green to yellow and *vice versa* on electrochemical dedoping and doping. The color change for PV4T contrasts with that for PV3T, which switches from bluish purple (oxidized state) to pale yellow (reduced state).[46] The PVDOc5T and PVDOc6T films were also found to undergo a reversible clear color change from green to pale yellow and *vice versa* on electrochemical dedoping and doping. It is thought that the incorporation of the two octyl groups at the β-position of the pendant α,α'-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

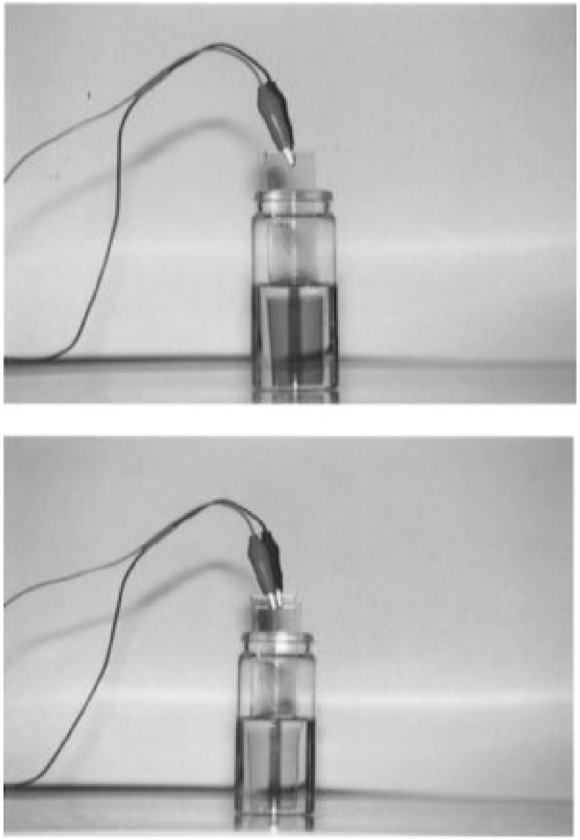


Figure 5. Reversible color change observed for (top) an electrochemically-doped PV4T film and (bottom) a dedoped PV4T film.

to the partially-cross-linked structure of the pendant oligothiophenes, and hence these polymers have a memory effect.

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 0.65 V *vs* Ag/Ag$^+$ (0.01 mol dm^{-3}) were applied for each 10 s to the electrochemically-doped PV4T prepared by the electrolytic polymerization of V4T, the electrode current and optical density (monitored at 690 nm) changed in such a way as shown in Figure 6. The response times for doping (coloration) and dedoping (decoloration) were *ca.* 4 and 0.9 s, respectively. Likewise, the response times for doping and dedoping for PVDOc5T and PVDOc6T films were 6.5 and 0.5, and 4.8 and 0.3 s, respectively. When the redox cycle of dedoping and doping for each 2 s was repeated over 500 times, a reversible color change was observed.

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 dedoping. It is expected that performance characteristics such as cycle life and response time as well as adhesion of the polymer film to the substrate can be improved by optimization of the film thickness, solvent, electrode, *etc.*, and by modification of the polymer chain structure, *e.g.*, the use of a polyacrylate or polysiloxane backbone.

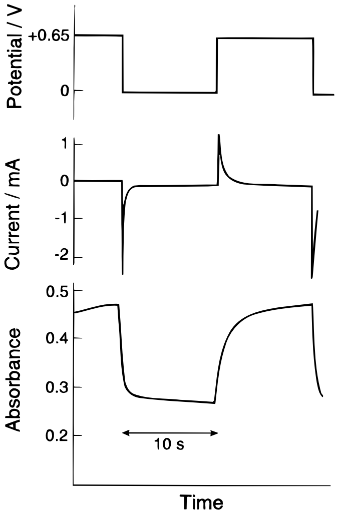


Figure 6. Changes of electrode current and optical density as a function of time for a PV4T film by application of repetitive voltages.

Conclusion

For the purpose of developing a novel type of electrically-conducting polymers, electrochemically-doped vinyl polymers containing π-conjugated oligothiophenes with well-defined structures, 2,2′:5′,2″:5″,2‴-quaterthiophene, 4′,3⁗-dioctyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene, and 4′,3⁗′-dioctyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′-sexithiophene, as pendant groups were synthesized by the electrolytic polymerizations of the corresponding vinyl monomers, and their electrical and electrochromic properties were investigated in relation to the π-conjugation length of the pendant oligothiophenes. The electrochemically-doped polymers, which were obtained as deeply-colored, smooth, and lustrous films, were identified as radical-cation salts of pendant oligothiophenes with 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 the pendant sexithiophene group exhibited a room-temperature conductivity of *ca.* 10^{-4} S cm^{-1}. The polymer films were found to undergo a reversible clear color change from green to yellow and *vice versa* on electrochemical dedoping and doping. The present study shows that a series of polymers containing pendant oligothiophenes with well-defined structures constitute a novel class of potential electrochromic materials.

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