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Neutral poly(3,4-ethylenedioxythiophene-2,5-diyl)s: preparation by organometallic polycondensation and their unique p-doping behavior

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Abstract

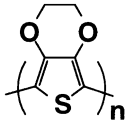
Neutral and non-doped poly(3,4-ethylenedioxythiophene), PEDOTh(Ni), and its hexyl derivative, PEDOTh-C_6(Ni), have been prepared by organometallic dehalogenation polycondensation of 2,5-dichloro-3,4-ethylenedioxythiophene and its hexyl derivative with a zerovalent nickel complex. PEDOTh-C_6(Ni) was soluble in organic solvents and ^{1}H NMR data indicated that it had an M_n of 11,000. MALDI-TOF mass analysis of PEDOTh(Ni) gave M_n and M_w of about 1700 and 2400, respectively. PEDOTh-C_6(Ni) showed a UV–Vis absorption peak at 546 nm in $CHCl_3$. Electrochemical oxidation of PEDOTh-C_6(Ni) started at about −0.40 V vs Ag^+/Ag and gave a peak at 0.20 V vs Ag^+/Ag. Chemical and electrochemical oxidation (or p-doping) of PEDOTh-C_6(Ni), both in solutions and in a solid state, led to weakening of the original π–π^* peaks and rise of new peak(s) in a region of 800–1500 nm. The p-doping of PEDOTh-C_6(Ni) caused not only a decrease in the intensity of ^{1}H NMR signals of the bridging ethylene hydrogens but also a decrease in that of the hexyl side chain, suggesting a strong interaction of the p-dopant with the side chain. NMR data of poly(3-methoxythiophene-2,5-diyl) also supported an assumption that p-doping brings about a severe change in electronic state of the substituent attached to the polythiophene main chain. PEDOTh(Ni) had a density of 1.71 g cm^{-3}; the molecular packing mode of PEDOTh(Ni) is discussed based on the density of the polymer and its XRD data.

Keywords: Poly(3,4-ethylenedioxythiophene) and hexyl derivative; Optical and electronic properties; p-Doping behavior

1. Introduction

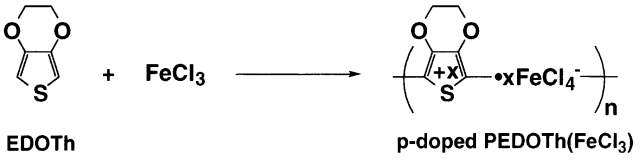
Polythiophene and its derivatives with a π-conjugated system along the polymer backbone have been investigated intensively because of their attractive electronic and optical properties [1–11]. Recently, experimental and theoretical attempts have been focused on the modification of their chemical structures. For example, much attention has been donated to alkoxy substituted polythiophene derivatives such as poly(3-alkoxythiophene) and poly(3,4-dialkoxythiophene) [1–8,12–22].

Among the derivatives of polythiophene, poly(3,4-ethylenedioxythiophene-2,5-diyl) (PEDOTh) has attracted strong attention [15–22]. On the bases of its superior chemical and physical properties, PEDOTh is applied in antistatic coatings and in electrolytic capacitors, for the metallization of insulators, as an active element in thin film transistors, and as a transparent electrode in light emitting diodes [23–30]. Furthermore, p-doped PEDOTh shows more stable electrical conductivity at high temperatures [27] than polypyrrole. Analogues of PEDOTh have also been actively investigated [28].



PEDOTh

In view of these applications of PEDOTh, many investigations have been made on the syntheses of PEDOTh's by the electrochemical and chemical oxidation polymerizations of 3,4-ethylenedioxythiophenes, EDOTh's [15–19,31]. E.g.,



EDOTh p-doped PEDOTh($FeCl_3$)

(1)

However, further investigation seems to be necessitated for characterization and understanding chemical properties of PEDOTh's. PEDOTh's prepared by the electrochemical and oxidation polymerization are obtained in a p-doped state, which sometimes hampers obtaining structural

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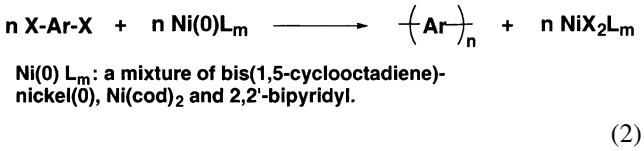
information of neutral PEDOTh's. For new, improved application of PEDOTh's in electronic and optical devices, understanding of neutral PEDOTh's is of importance.

Organometallic dehalogenation polycondensation processes (e.g., that using a zerovalent nickel complex, $Ni(0)L_m$) can produce neutral state polymers; [3,4,32].



(2)

In order to obtain more information on neutral PEDOTh's, we have prepared PEDOTh's by the organometallic dehalogenation polycondensation of 2,5-dichloro-3,4-ethylenedioxythiophene and its hexyl derivative with $Ni(0)L_m$, and investigated chemical properties of the polymers.

2. Experimental

2.1. Materials

Thionyl chloride, thiodiglycolic acid, diethyl oxalate, 1,2-dichloroethane, 2,2′-bipyridyl, 1,5-cyclooctadiene, *N*-chlorosuccinimide, trimethyltin chloride, hydrazine monohydrate, *N*,*N*-diethylhydroxylamine, sodium tetrahydroborate, and sodium dithionite were used as purchased. Bis(1,5-cyclooctadiene)nickel(0) ($Ni(cod)_2$) [33] was synthesized according to the literature. 3,4-Ethylenedioxythiophene, EDOTh (**1a**), was obtained from Bayer AG. Its hexyl derivative, thieno-(3,4-*b*)-2,3-dihydro-2-hexyl-1,4-dioxin, EDOTh-C_6 (**1b**), was synthesized following the previously reported methods of Fager [34] and Guha and Iyer [35]. Barium-promoted copper chromite was obtained from Aldrich Chemical Co., Inc.

2.2. Measurements

IR spectra were recorded on a JASCO IR-810 spectrometer. NMR spectra in solutions were taken using a JEOL EX-400 or EX-90 spectrometer. ^{13}C CP-MAS solid NMR spectra were obtained with a JEOL GX-270 NMR spectrometer. X-ray diffraction patterns were recorded on a Philips PS-1051 instrument. Electrical conductivity was measured with a Takeda Riken TR-8651 electrometer. Microanalysis of C, H, and N was carried out by a Leco CHNS-932 or a Yanaco CHN CORDER MT-5. Analysis of halogen and sulfur was carried out on a Leco CHNS-932 (sulfur) or a Yanaco YS-10 (halogen). TGA traces were obtained by a Shimadzu TGA-50 thermogravimetric analyzer.

MALDI-TOF MS analyses were performed using a Thermo Quest LASERMAT 2000 and/or a Hewlett Packard G 2025A, both equiped with a 337 nm nitrogen laser. As matrices we applied α-cyano-4-hydroxycinnamic acid, 2-(4-hydroxyphenylazo)benzoic acid, 5-methoxysalicylic acid, 2,5-dihydroxybenzoic acid, 3,5-dimethoxy-4-hydroxycinnamic acid or 1,8,9-trihydroxyanthracene (dithranol). Analytes were dissolved in DMF or $CHCl_3$. A typical analyte/matrix ratio was 1:500. For more detailed information on sample preparation, see literature [36,37]. Density of the polymers samples were measured by sink and float tests using aqueous solutions of $ZnCl_2$.

2.3. Synthesis of 2,5-dichloro-3,4-ethylenedioxythiophene (*2a*) and its hexyl derivative (*2b*)

3,4-Ethylenedioxythiophene, EDOTh, (**1a**, 2.82 g, 20 mmol) was dissolved in 100 ml of THF under N_2 and cooled to 0°C. *N*-chlorosuccinimide (NCS, 5.87 g, 44 mmol) was added and the mixture was stirred for 5 h. After the reaction was completed, sodium sulfite (2.00 g) was added to the solution, and the solution was concentrated at room temperature. The product was extracted with an excess amount of hexane and the solvent was removed at room temperature. The residue was dissolved in ethanol and crystallized at −20°C to give needles, which were collected by filtration under N_2 and dried under vacuum at 0°C to give 2,5-dichloro-3,4-ethylenedioxythiophene (**2a**, 3.59 g, 17 mmol, 85% yield). This monomer was stored in a refrigerator. Anal. Found: C, 34.3; H, 1.9; Cl, 33.9; S, 15.5%. Calcd for $C_6H_4Cl_2O_2S$: C, 34.1; H, 1.9; Cl, 33.6; S, 15.2%. ^1H NMR (400 MHz, $CDCl_3$): δ: 4.26 (s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ: 64.9, 100.4, 137.2. IR (KBr, cm^{-1}): 2940 (C–H), 1090 (C–O–C), 1050 (C–Cl). Analogous technique was applied to synthesis of 2,5-dichloro-EDOTh-C_6 (**2b**) [34]. Yield = 98%. Anal. Found: C, 48.80; H, 5.46; Cl, 24.25; S, 10.86%. Calcd for $C_{12}H_{16}Cl_2O_2S$: C, 48.82; H, 5.46; Cl, 24.02; S, 10.89%. ^1H NMR (400 MHz, $CDCl_3$): δ: 0.92 (3H, t, $J = 6$ Hz, CH_3), 1.2–1.8 (10H, m, CH_2 of hexyl group), 3.91 (1H, dd, $J = 12$, 8 Hz), 4.15 (1H, m), 4.23 (1H, dd, $J = 12$, 2 Hz). $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ: 14.0, 22.5, 24.9, 29.0, 30.3, 31.6, 68.6, 74.5, 99.5, 99.8, 137.2, 137.6. IR (neat, cm^{-1}): 2928, 2856, 1613, 1518, 1453, 1421, 1366, 1215, 1178, 1127, 1071, 1002, 930, 756.

2.4. Synthesis of PEDOTh(Ni) and PEDOTh-C_6(Ni) by dehalogenation polycondensation

Polymerization was carried out under N_2 using the standard Schlenk technique. To a solution of $Ni(cod)_2$ (0.67 g, 2.5 mmol) in 10 ml of dry DMF were added 0.2 ml of 1,5-cyclooctadiene and 2,2′-bipyridyl (bpy, 0.39 g, 2.5 mmol) at room temperature. After the mixture was stirred for 1 h, a solution of **2a** (0.45 g, 2.1 mmol) in 10 ml of dry DMF was added to the reaction mixture. The solution was stirred for 5 h at room temperature and then for 28 h at 60°C. The black polymer obtained was collected and worked-up in a manner similar to that applied for other polymers reported previously [40], which included removal of Ni compounds using ethylenediaminetetraacetic acid (EDTA). Washing the prepared PEDOTh(Ni) was carried

out with N_2-replaced solutions to avoid oxidation of the polymer with air. PEDOTh(Ni): yield = 0.25 g (82%). Anal. Calcd for $(C_6H_4O_2S)_n$: C, 51.4; H, 2.9; S, 22.9%. Calcd for $(C_6H_4O_2S{\cdot}0.2H_2O)_n$: C, 50.1; H, 3.1; S, 22.3%. Found: C, 49.7; H, 3.0; S, 22.7; Cl, 0,0%. IR (KBr, cm^{-1}): 2940 (C–H), 1450 (skeletal vibration of the thiophene ring), and 1075 (C–O–C). ^{13}C CP-MAS solid NMR: δ: 66, 107 (3,4-C of the thiophene ring), 138 (2,5-C of the thiophene ring). PEDOTh-C_6(Ni) was prepared analogously in 90% yield. Anal. Calcd for $(C_{12}H_{16}O_2S{\cdot}0.5H_2O)_n$: C, 61.8; H, 7.3; S, 13.7%. Found: C, 61.6; H, 6.7; S, 12.9; Cl, 0.0%. A part of the differences between the found and calculated values may be due to high thermal stability of the polymer. ^1H NMR (400 MHz, $CDCl_3$): δ: 0.9–1.8 (13H of hexyl group), 4.0–4.3 (3H, CH_2 and CH). IR (KBr, cm^{-1}): 2918, 2852, 1514, 1458, 1434, 1319, 1205, 1064.

2.5. Synthesis of PEDOTh($FeCl_3$) by oxidative polymerization

Oxidative polymerization of **1a** (1.43 g, 10.0 mmol) was achieved using anhydrous ferric chloride in acetonitrile according to the literature method [31]. A dark blue powder of p-doped PEDOTh($FeCl_3$) was collected by filtration, washed, and dried to obtained 1.85 g of the polymer (yield = 96% based on the amount of carbon recovered). Anal. Found: C, 37.7; H 2.5; Cl, 16.1; S, 15.6%. The found values roughly agreed with those calculated for ($C_6H_4O_2S{\cdot}0.22$ $FeCl_4{\cdot}0.5H_2O$): C, 37.4; H, 2.6; Cl, 16.2; S, 16.6%.

2.6. Doping of the neutral polymer with iodine

The powdery neutral PEDOTh(Ni) (49.8 mg) was exposed to iodine vapor under vacuum (about 1 Pa) at room temperature. After 3 days of exposure, excess of I_2 was removed by leaving the sample under vacuum for 10 h. The amount of iodine taken into the polymer was 54.4 mg; (wt of iodine)/polymer = 109%.

2.7. Treatment of PEDOTh($FeCl_3$) with reducing reagent

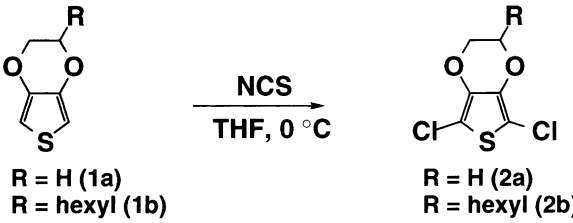
PEDOTh($FeCl_3$) was treated with reducing reagents such as hydrazine monohydrate, *N,N*-diethylhydroxylamine, sodium tetrahydroborate, and sodium dithionite under nitrogen to avoid oxidation of dedoped PEDOTh by air.

A mixture of excess $N_2H_4{\cdot}H_2O$ (5 ml) and dark blue powder of PEDOTh($FeCl_3$) (60 mg) was stirred for 24 h at room temperature under nitrogen. The suspension gradually turned from initial dark blue to black. The black powder was collected by filtration, washed with distilled water, and dried under vacuum to give dedoped PEDOTh($FeCl_3$). The dedoping of PEDOTh($FeCl_3$) with $N_2H_4{\cdot}H_2O$ was also tried in water and CH_3CN ($[N_2H_4] = 3.3$ M, room temperature, 8 h (three times)). The IR spectra of the three samples were essentially identical to each other. By the treatment with N_2H_4, the electrical conductivity of the polymer sample decreased below 10^{-3} S cm^{-1}. Analytical data of the N_2H_4 treated sample: C, 41.6; H, 2.8; S, 20.2; Cl, 0.2; ash 11.5%. The $FeCl_4$-dopant seems to be changed to other iron species, which are difficult to be removed. This N_2H_4-treated sample was used for the IR and NMR measurements. Reduction with other reagents was carried out analogously.

3. Results and discussion

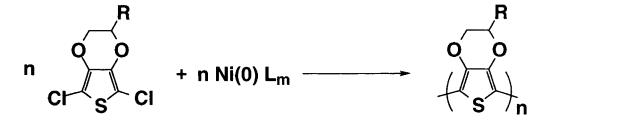
3.1. Syntheses of monomers and polymers

Although 2,5-dichloro-3,4-ethylenedioxythiophene was thermally unstable, careful treatment of the dichlorinated product gave crystals of **2a** (Eq. (3)), which could be stored below 0°C [21]. A hexyl derivative, EDOTh-C_6 [34,35], was also chlorinated with NCS to give a colorless liquid of 2,5-dichloro-3,4-ethylenedioxythiophene with the hexyl substituent, **2b**.



(3)

Neutral poly(3,4-ethylenedioxythiophene)s (PEDOTh(Ni) and PEDOTh-C_6(Ni)) were synthesized from **2a** and **2b** by the dehalogenative polycondensation using Ni(0)L_m as shown in Eq. (4). The polymers were isolated as a black powder of PEDOTh(Ni) in 82% yield and a black purple powder of



(4)

PEDOTh-C_6(Ni) in 90% yield, respectively. The prepared polymers are considered to be Ni-terminated and converted into H-terminated polymers during the work-up including treatment with HCl, since they do not contain chlorine, similar to cases of other polymers prepared analogously [38].

3.2. Instrumental analysis

Chart (a) in Fig. 1 exhibits the IR spectrum of neutral PEDOTh(Ni). It shows ν(C–H) peaks of the ethylene side chain at about 2940 cm^{-1}, and a skeletal vibration peak of the thiophene ring [39] at about 1450 cm^{-1}. p-Doping of this sample with I_2 vapor brings about severe changes in the IR spectrum as shown by chart (b) in Fig. 1. The skeletal

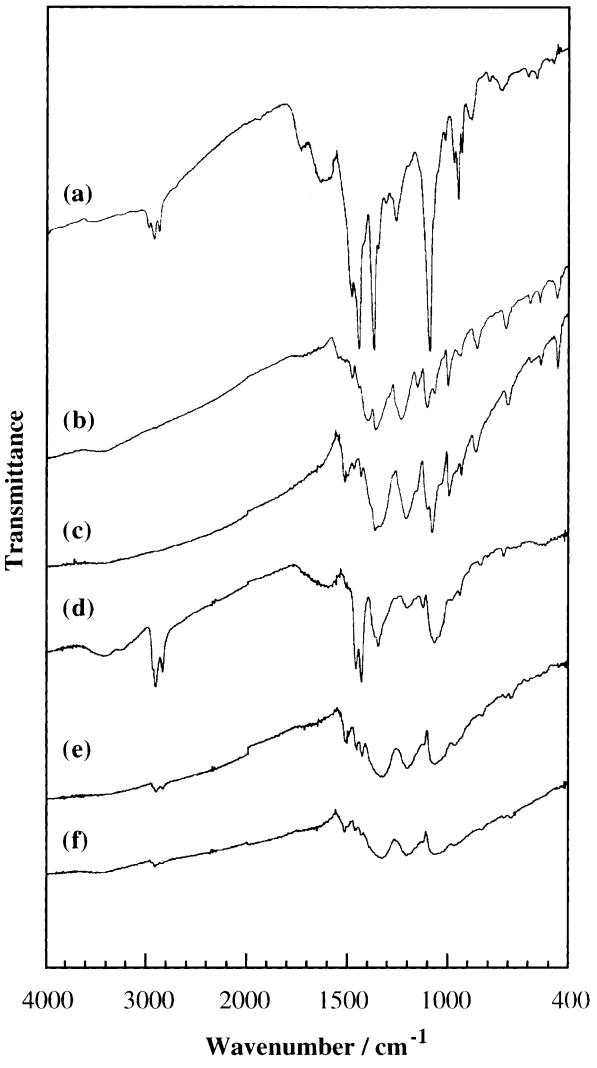


Fig. 1. IR spectra of (a) PEDOTh(Ni), (b) PEDOTh(Ni), after I_2 doping, (c) PEDOTh($FeCl_3$), after treated with hydrazine, (d) PEDOTh-C_6(Ni), (e) PEDOTh-C_6(Ni) after I_2 doping (4 wt%), and (f) PEDOTh-C_6(Ni) after I_2 doping (9 wt%).

vibration peak is shifted to a lower frequency [39,40]. The aliphatic ν(C–H) absorption peaks of the ethylenedioxy unit disappear, suggesting that the p-doping leads to a great change in electronic state of the ethylenedioxy unit.

Similar severe IR changes in the ν(C–H) absorption peaks have been reported for p-doped poly(3-alkoxythiophene) [13] and poly(3-alkylthiophene) [41], and Miller and Mann reported, based on X-ray crystallography, that a p-dopant (PF_6^-) can locate near an alkyl side chain of a p-doped alkyl-substituted oligothiophene [42].

PEDOTh($FeCl_3$) was not transparent toward the IR light presumably due to its electrically conducting properties. Treatment of this polymer with hydrazine resulted in a sample that gave rise to the IR spectrum shown by chart (c) in Fig. 1. However, this chart (c) resembles chart (b) in Fig. 1, indicating that complete dedoping of the p-doped PEDOTh with hydrazine does not take place due to a strong electron donating nature of the ethylenedioxy substituent. A similar stabilization effect has been reported for the methoxy group in poly(3-methoxythiophene) [14]. To the contrary, treatment of p-doped non-substituted polythiophene with hydrazine leads to complete dedoping of the polymer [40]. Treatment of the p-doped PEDOTh($FeCl_3$) with stronger reducing reagents [43] (Et_2NOH, $NaBH_4$, and $Na_2S_2O_4$; cf. experimental) did not lead to complete dedoping, either, as judged from IR data.

Chart (d) in Fig. 1 exhibits the IR spectrum of PEDOTh-C_6(Ni). To avoid oxidation of the polymer in the air, the KBr pellet for the IR measurement was prepared under Ar gas. On exposure the KBr pellet to air for few days, the IR peaks were somewhat broadened, suggesting partial oxidation (or p-doping) of the polymer by oxygen.

Charts (e) and (f) in Fig. 1 show changes in the IR spectrum on p-doping of PEDOTh-C_6(Ni) with iodine. p-Doping also leads to a strong changes both for the ν(C–H) peaks and the skeletal vibration peaks of the thiophene ring.

3.3. Solubility, NMR, and molecular weight information

PEDOTh(Ni) was hardly soluble in commonly used organic solvents such as $CHCl_3$, DMF, DMSO and NMP, similar to PEDOTh prepared by oxidative polymerizations.

PEDOTh-C_6(Ni) possessed good solubility in organic solvents such as $CHCl_3$, CH_2Cl_2 and DMF. These results surprised us since oxidative polymerization taught us that one required at least a decyl ($C_{10}H_{21}$) substituent at each EDOTh unit to keep the corresponding polymer soluble. This observation strengthens the idea that alkyl chain cleavage occurs upon oxidative polymerization conditions as observed from NMR analyses.

Due to the insoluble character of PEDOTh(Ni), we applied MALDI-TOF MS for evaluation of the molecular weight of this polymer. All MALDI-TOF MS spectra measured with various matrices showed a GPC-like shape to give M_n and M_w of about 1700 and 2400, respectively. The high insolubility of PEDOTh may be the reason for the lower molecular weight of PEDOTh(Ni) than PEDOTh-C_6(Ni). M_n of PEDOTh-C_6(Ni) was evaluated from its NMR data described below.

Fig. 2(a) shows the ^{1}H NMR spectrum of PEDOTh-C_6(Ni) in $CDCl_3$. The two broad peaks in the range of δ 3.4–4.5 are attributed to the O–CH_2 and O–CH protons of the O–CH_2–CH(C_6H_{13})–O bridge. The small ^{1}H NMR signal at δ 6.3 can be assigned to terminal thiophene-H protons, that are formed from a Ni-terminated unit (polymer-NiL_m) as discussed above. Integration of the ^{1}H NMR peaks indicated that PEDOTh-C_6(Ni) had an M_n of 11,000 corresponding to a degree of polymerization of about 50. On the other hand, GPC analysis gave M_n and M_w of 5400 and 8500, respectively (vs polystyrene standards).

Fig. 2(b) shows changes of the ^{1}H NMR spectrum of PEDOTh-C_6(Ni) on addition of I_2 to the $CDCl_3$ solution of PEDOTh-C_6(Ni). At an early stage of the p-doping (curve

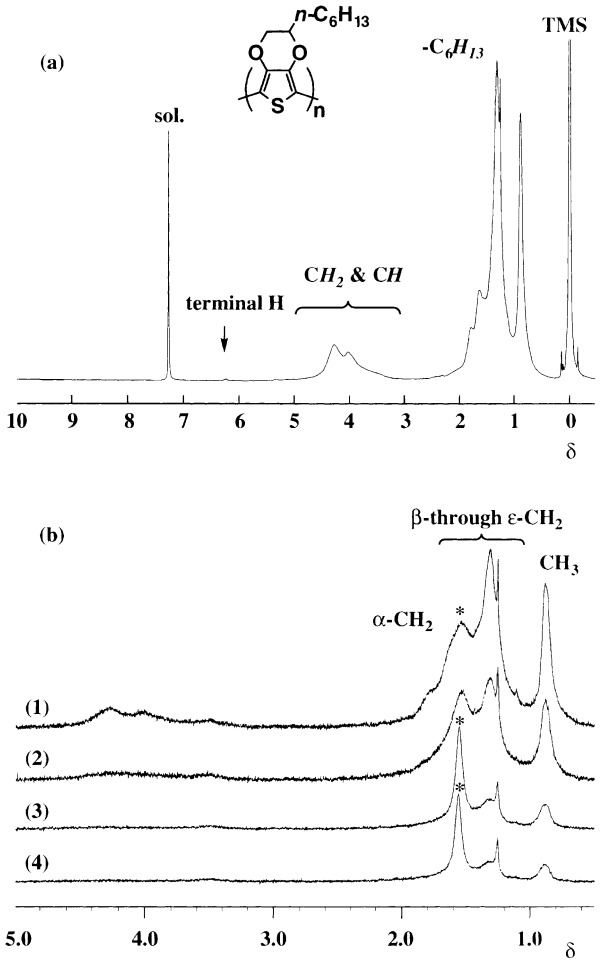


Fig. 2. (a) ^{1}H NMR spectrum of PEDOTh-C_6(Ni) in $CDCl_3$. (b) Changes of the ^{1}H NMR spectrum on addition of I_2 to a $CDCl_3$ solution of PEDOTh-C_6(Ni) (concentration of the monomer unit = 10 mM). Concentration of I_2: (1) 0 mM, (2) 0.9 mM, (3) 4.4 mM, and (4) 8.9 mM. The peak with a * mark is overlapped with a peak of water contained. This peak is weakened on addition of D_2O.

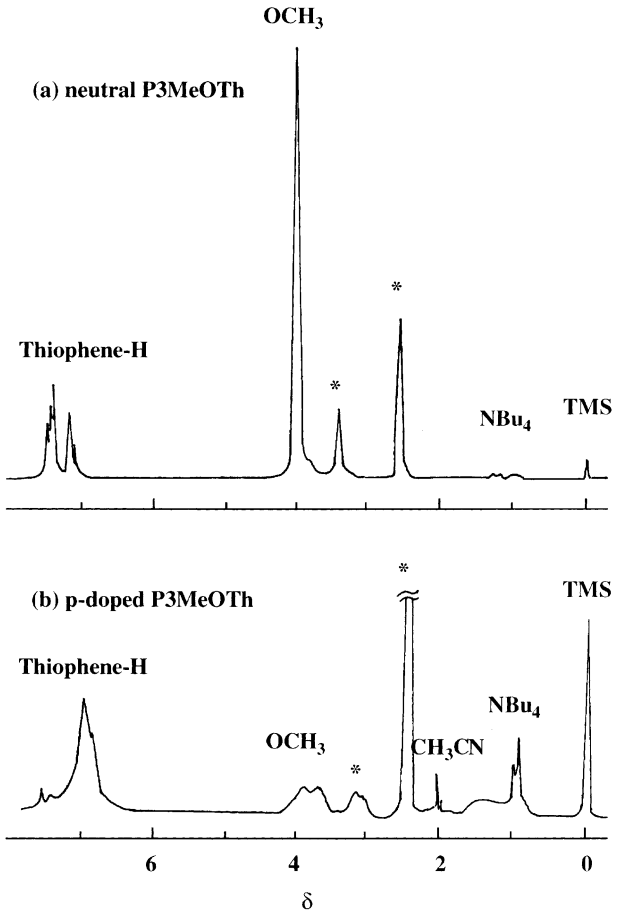
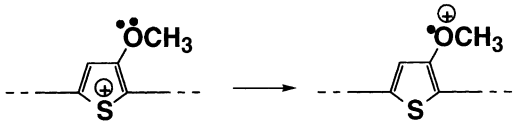


Fig. 3. (a) ^{1}H NMR spectrum of dedoped P3MeOTh in DMSO-d_6. The sample was prepared by electrochemical polymerization of 3-methoxythiophene in an CH_3CN solution containing $[Bu_4N]PF_6$ (Bu = butyl) and dedoped with N_2H_4. Peaks with a * mark are due to impurities (DMSO-d_6 and H_2O) of the solvent. (b) Electrochemically as-prepared, p-doped P3MeOTh (before the dedoping) (in DMSO-d_6).

(2) in Fig. 2(b)), peaks of the ethylenedioxy group in a range of δ 3.4–4.5 disappear, similar to the CH_3 peak of poly(3-methoxythiophene), P3MeOTh [13], however, the signals of the hexyl group in a range of δ 0.7–2.0 essentially remain.

For P3MeOTh, p-doping gives only a smaller effect on the thiophene-H signal, however, the p-doping brings about a severe decrease in the OCH_3 signal [13]. Fig. 3(a) and (b) compares ^{1}H NMR spectra of neutral, dedoped P3MeOTh and p-doped P3MeOTh, respectively. The severe effect of the p-doping on the OCH_3 signal may be accounted for by migration of one of the lone pair electrons on OCH_3 to the p-doped polythiophene main chain, which will render a paramagnetic nature to the OCH_3 groups to decrease the intensity of the original OCH_3 peak.



In Fig. 2, further addition of I_2 to the $CDCl_3$ solution of PEDOTh-C_6(Ni) leads to weakening of the hexyl signals as exhibited by curves (3) and (4) in Fig. 2(b). These ^{1}H NMR data support the above described assumption based on IR data that alkyl side chain can have a strong interaction with the p-dopant and the p-doping gives a strong change (presumably by endowing the alkyl chain with a paramagnetic nature which often leads to severe decrease in NMR intensity) in the electronic state of the alkyl side chain. The FT-^{1}H NMR spectra were usually observed with a pulse repetition time of 5 s, and no significant change in the signals of the hexyl groups was observed with longer pulse repetition times (e.g. 50 s) in the FT-^{1}H NMR measurement, revealing that the decrease in the ^{1}H NMR signal of the hexyl group is not due to elongation of the relaxation time of the hexyl protons on the p-doping. As discussed below, iodine-doping of PEDOTh-C_6(Ni) is reversible and the iodine-doped PEDOTh-C_6(Ni) can be completely dedoped on addition of $N_2H_4{\cdot}H_2O$.

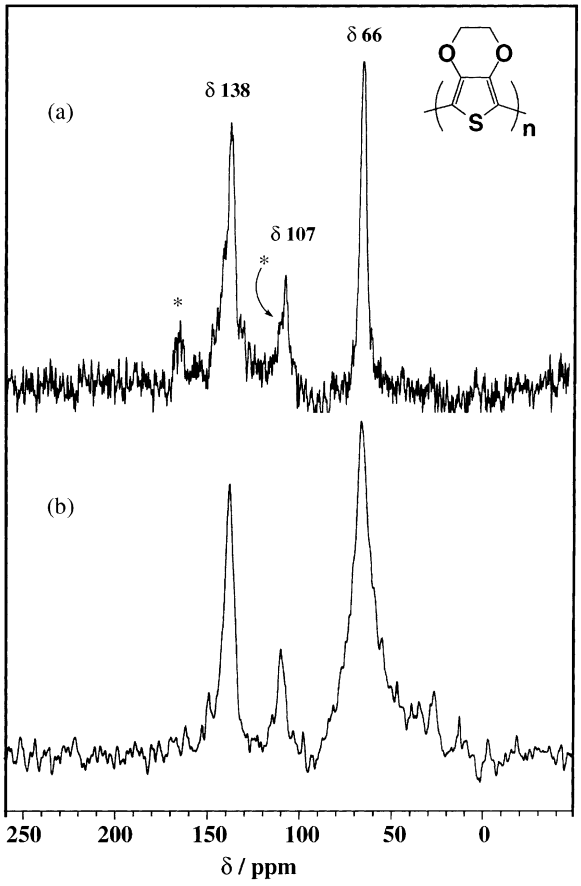


Fig. 4. ^{13}C CP-MAS solid NMR spectra of (a) PEDOTh(Ni) and (b) PEDOTh($FeCl_3$), after treatment with hydrazine. Peaks with a * mark are due to the spinning side bands.

The ^{13}C CP-MAS solid NMR spectrum of the neutral PEDOTh(Ni) (chart (a) in Fig. 4) shows one peak (δ 66) in the aliphatic carbon region and two peaks at δ 107 and 138 which are assigned to the 3,4-C and 2,5-C of the thiophene ring, respectively. Non-substituted neutral polythiophene shows the ^{13}C NMR signals of 3,4- and 2,5-carbons at δ 126 and 137, respectively [39].

The p-doped PEDOTh($FeCl_3$) is not suited to the ^{13}C CP-MAS solid NMR because of its electrically conducting properties. On the other hand, the hydrazine-treated PEDOTh($FeCl_3$) does not have high conductivity and is susceptible to the NMR spectroscopy; its ^{13}C CP-MAS solid NMR chart is exhibited in the lower part of Fig. 4. As seen in this NMR chart, the ethylenedioxy peak is considerably broadened from a half width of 220 Hz of the neutral PEDOTh(Ni) to a half width of 750 Hz. However, the half width of the aromatic carbon signals is almost the same for the two samples, revealing that the p-doping brings about severer changes in the NMR signals of the side chain than in the NMR signals of polythiophene main chain, similar to the case of P3MeOTh. These results also support the strong effect of the p-doping on the side chain alkoxy group (ethylenedioxy group in this case), as described above.

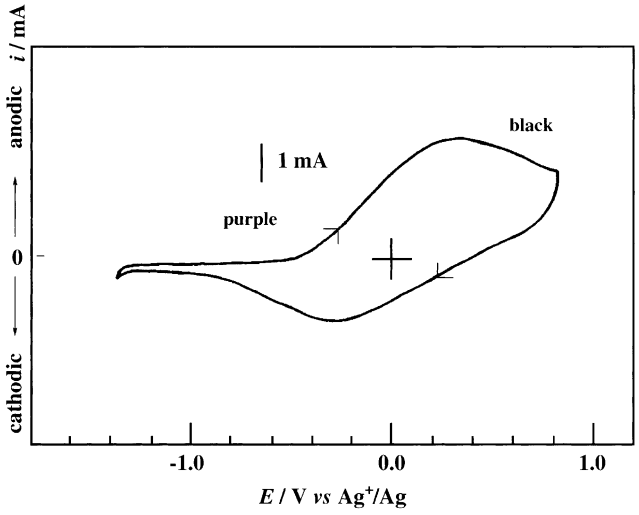


Fig. 5. CV chart for PEDOTh-C_6(Ni) film cast on a Pt plate. In a CH_3CN solution of $[Bu_4N]PF_6$ (0.10 M) at 100 mV s^{-1}.

3.4. Electronic and optical properties of PEDOTh-C_6(Ni)

Fig. 5 exhibits cyclic voltammogram (CV) of an as-cast film of PEDOTh-C_6(Ni) on a Pt plate. The CV curve shows that electrochemical oxidation (or p-doping) starts at -0.40 V vs Ag^+/Ag and gives E_{pa} at about 0.20 V. The corresponding p-dedoping gives a peak at -0.24 V vs. Ag^+/Ag. The p-doping peak locates at a lower potential by about 0.5 V than that of non-substituted polythiophene, reflecting the electron-donating properties of the ethylenedioxy substituent. The color of the film changed from purple to black on oxidation. The film revealed stable upon repeated scanning of CV, giving same CV curves. The doping level (stored positive charge/thiophene unit) is evaluated as 0.30 from the doping current. Sweeping to a higher potential 0.80–1.50 V vs Ag^+/Ag gave no peak, revealing high stability of PEDOTh-C_6(Ni) in this oxidative region.

Curve (a) in Fig. 6 shows the UV–Vis spectrum of PEDOTh-C_6(Ni) in $CHCl_3$. Due to expansion of the π-conjugation system, the spectrum exhibits an absorption peak at 546 nm with a molar absorption coefficient ε (based on the repeating unit) of 5300 $M^{-1}\,cm^{-1}$. As shown in Fig. 6, addition of I_2 causes a decrease in the intensity of the π–π^* absorption band at 546 nm, accompanied with the appearance of a new absorption band at about 950 nm and another absorption band in a longer wavelength region, which are characteristic of p-doped polythiophenes. Addition of 20 mol% of I_2 per the thiophene unit (curve (f) in Fig. 6) is sufficient for complete disappearance of the original peak at 546 nm.

Increase in the amount of I_2 results in lowering of these two absorption bands and a rise of a new absorption band, presumably due to a change of a polaron state to a bipolaron state. The former state usually gives two absorption peaks whereas the latter does only one peak. Similar spectroscopic

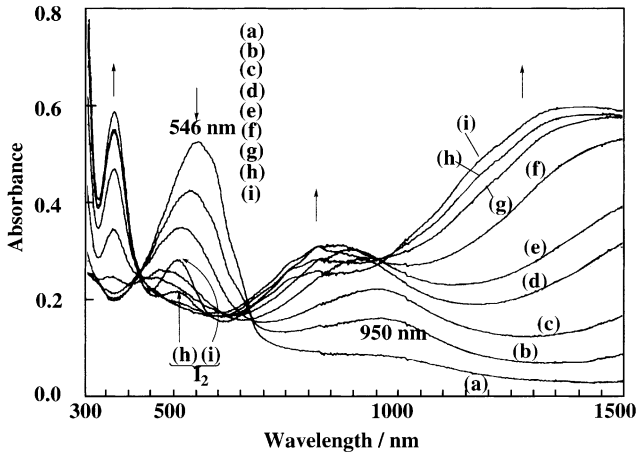


Fig. 6. Changes in UV–Vis spectrum of a $CHCl_3$ solution of PEDOTh-C_6(Ni) (concentration of the monomer unit = 1.0×10^{-4} M) on addition of I_2. Concentration (M) of I_2: (a) 0, (b) 1.0×10^{-6}, (c) 2.0×10^{-6}, (d) 5.0×10^{-6}, (e) 1.0×10^{-5}, (f) 2.0×10^{-5}, (g) 5.0×10^{-5}, (h) 1.0×10^{-4}, (i) 2.0×10^{-4}. The peak at 505 nm observed with (h) and (i) is due to free I_2.

changes were reported for oxidatively prepared and dedoped PEDOTh-C_{14}, on doping with $SbCl_5$ in $CHCl_3$ [30]. On addition of $N_2H_4{\cdot}H_2O$ to the solution containing p-doped PEDOTh-C_6(Ni), the spectrum immediately returned to the original UV–Vis spectrum of non-doped PEDOTh-C_6(Ni). p-Doping of PEDOTh-C_6(Ni) with $FeCl_3$ in $CHCl_3$ gave analogous changes in the UV–Vis spectrum.

As shown by curve (a) in Fig. 7, the as-cast film of PEDOTh-C_6(Ni) on an indium–tin-oxide (ITO) glass plate exhibits an absorption peak at essentially the same position as the $CHCl_3$ solution of PEDOTh-C_6(Ni). However, the absorption band has substructures at 620 and 410 nm, suggesting the presence of intermolecular interaction in the solid [44]. Fig. 7 shows changes of the absorption spectrum of the film of PEDOTh-C_6(Ni) during electrochemical oxidation. The polymer film appears inert on applying a reduction potential of −1.0 V vs Ag^+/Ag. To the contrary, at −0.4 V vs Ag^+/Ag, the π–π^* absorption peak at 540 nm starts to decrease in accordance with the cyclic voltammographic data shown in Fig. 5. At −0.2 V, new absorption bands are clearly observed at about 850 and 1400 nm. Application of higher potentials of −0.1–0.4 V enhanced the changes of the UV–Vis spectrum, similar to the case of chemical oxidation with I_2, although positions of the new absorption bands are somewhat different from those observed with the p-doping with I_2 in the solution system (Fig. 6). The electrochromic behavior was only partly reversible. On applying −0.6 V vs Ag^+/Ag, the curve (h) in Fig. 7 did not returned to the curve (b). On applying the reverse potential, the UV–Vis spectrum changed to that similar to curve (e) in Fig. 7. These results suggest a strong interaction of PEDOTh-C_6(Ni) with the dopant. When the cast film of PEDOTh-C_6(Ni) was exposed to I_2 vapor, the film showed the analogous color change, giving the spectrum comparable to that of Fig. 7(d).

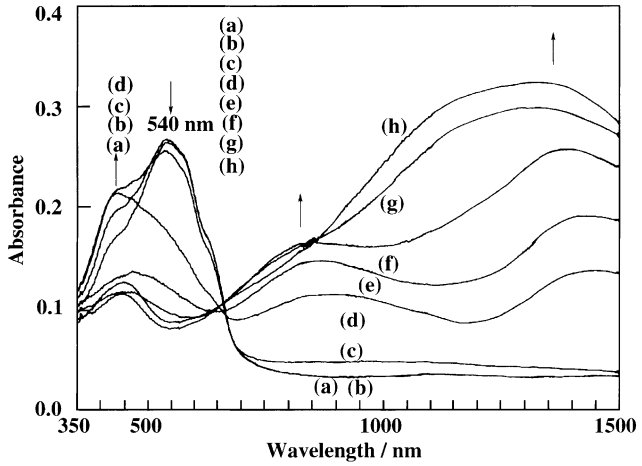


Fig. 7. Changes in the UV–Vis spectrum of a film of PEDOTh-C_6(Ni) on an ITO glass electrode at various applied potentials vs Ag^+/Ag. The curve (a) shows the UV–Vis spectrum of the as-cast film. The film gives the same UV–Vis spectrum at a potential of −1.0 V vs Ag^+/Ag. Applied potential (V): (b) −0.6, (c) −0.4, (d) −0.2, (e) −0.1, (f) 0, (g) 0.2, (h) 0.4. In a CH_3CN solution of $[Bu_4N][PF_6]$ (0.10 M).

3.5. XRD, TGA, and conductivity

Neutral PEDOTh(Ni) and the hydrazine-treated PEDOTh($FeCl_3$) give analogous powder X-ray diffraction patterns as shown in Fig. 8. They show two diffraction peaks at 2θ (Cu Kα) = 11.3 and 23.5° corresponding to d_1 of 7.83 Å and d_2 of 3.79 Å, respectively. The d_2 distance of 3.79 Å is normal for a face-to-face distance between polythiophene planes of π-stacked poly(alkylthiophene)s

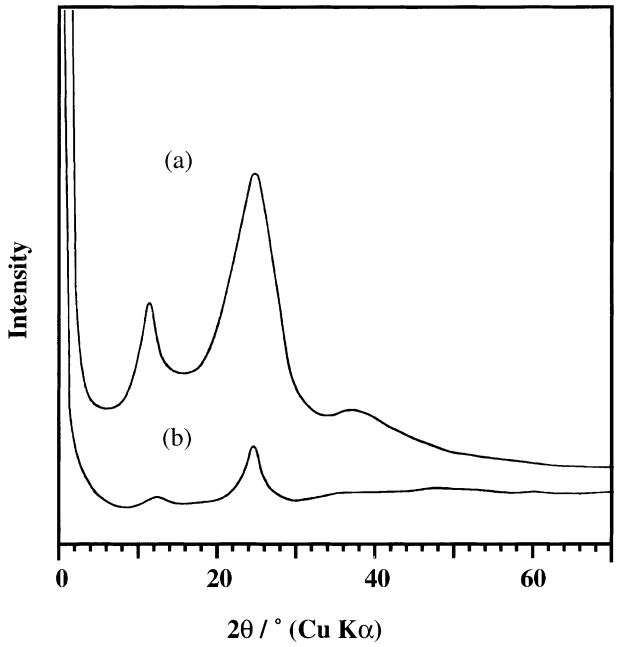


Fig. 8. Powder X-ray diffraction patterns of (a) PEDOTh(Ni) and (b) PEDOTh($FeCl_3$), after treatment with hydrazine.

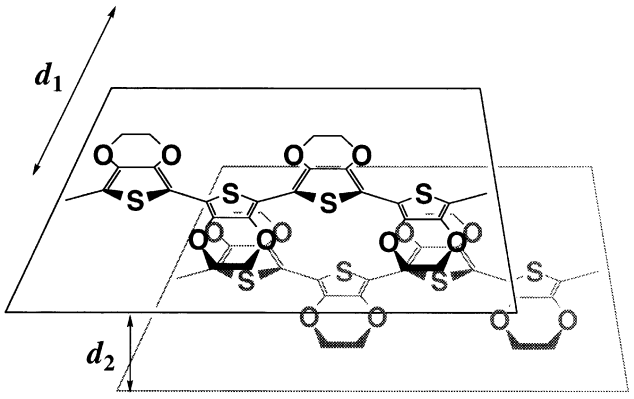


Chart 1. A packing model of PEDOTh.

[45–47] and oligomeric thiophene derivatives [48]. If PEDOTh also takes a similar π-stacked structure, the d_1 value of 7.83 Å may correspond to the distance between the polythiophene main chain separated by the side chain [45–47], the ethylenedioxy group in this case (Chart 1).

According to the previously reported XRD analysis of polythiophene [49,50] and a low-molecular-weight derivative of ethylenedioxythiophene [51],[1] the 3,4-ethylenedioxythiophene-2,5-diyl unit seems to have a repeating height of 4.0–4.2 Å, and use of a value of 4.2 Å in the above shown packing model gives a calculated density of $(140/6.02 \times 10^{23})/(4.2 \times 7.83 \times 3.79 \times 10^{-24}) = 1.87\ \mathrm{g\ cm^{-3}}$ for PEDOTh. A lower observed density of 1.71 g $\mathrm{cm^{-3}}$ seems to be due to containing of an amorphous part and insufficient chain length of the polymer, if the polymer takes the proposed packing structure. Hydrazine treated PEDOTh($FeCl_3$) gave a similar XRD pattern as shown in Fig. 8(b). The lightly p-doped state of PEDOTh does not seem to have a large influence on the packing mode of the polymer in the solid; similar results have been reported for p-doped head-to-tail poly(3-hexylthiophene) [52]. PEDOTh-C_6(Ni) gave only one broad X-ray diffraction peak at 2θ (Cu Kα) = 21.2° ($d = 4.2$ Å), which is considered to originate from loose packing of the hexyl chains in the solid. PEDOTh-C_6(Ni) had a density of 1.31 g $\mathrm{cm^{-3}}$.

Thermolysis of PEDOTh(Ni) started at about 200°C with $Td_{5\%}$ at 300°C and there was no residual weight at about 600°C. Thermolysis of as-prepared p-doped PEDOTh($FeCl_3$) started at about 250°C, and the residue at 900°C (40%) was considered to be due to Fe-based ash.

The neutral PEDOTh's were essentially an insulator with an electrical conductivity lower than $10^{-7}\ \mathrm{S\ cm^{-1}}$. p-Doping of PEDOTh(Ni) and PEDOTh-C_6(Ni) with I_2 raised the electrical conductivity to $10^{-3}\ \mathrm{S\ cm^{-1}}$, respectively, as measured with compressed powder.

As described above neutral PEDOTh(Ni) and PEDOTh-C_6(Ni) can be prepared by the organometallic polycondensation, and the obtained polymers give basic data for the doping behavior of PEDOTh and alkylated PEDOTh which are now expected to have important application.

[1] The ethylenedioxythiophene unit may have a longer repeating height than the thiophene unit due to the presence of ethylenedioxy group.

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