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Preparation of a soluble and neutral alkyl derivative of poly(3,4-ethylenedioxythiophene) and its optical properties

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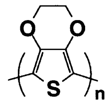
Abstract

Soluble and non-doped poly(3,4-ethylenedioxythiophene) with a hexyl substituent (PEDOTh-C_6 (Ni)), was first synthesized by Ni promoted dehalogenation polycondensation of the corresponding monomer. PEDOTh-C_6 (Ni) exhibited good solubility in common organic solvents such as $CHCl_3$, CH_2Cl_2, and DMF, in contrast to poor solubility of the corresponding polymer synthesized by oxidative polymerization. GPC analysis indicated that PEDOTh-C_6 (Ni) had M_n and M_w of 5400 and 8500 (vs polystyrene standards); ^{1}H NMR analysis gave an M_n value of 11,000. A cast film of PEDOTh-C_6 (Ni) received electrochemical p-doping at 0.20 V vs Ag^+/Ag. Chemical and electrochemical oxidation of PEDOTh-C_6 (Ni) led to appearance of new absorption bands in the near infrared region. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(3,4-ethylenedioxythiophene); Soluble π-conjugated polymer; Optical properties

1. Introduction

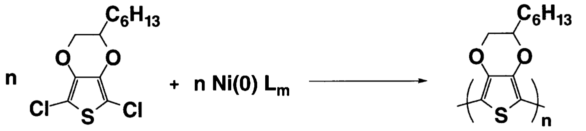
Polythiophene and its derivatives have been investigated intensively in view of their attractive electronic and optical properties [1,2]. Especially, poly(3,4-ethylenedioxythiophene) (PEDOTh), has recently attracted strong attention because of its high conductivity, good electrochemical cyclability, high transparency and high thermal stability in the doped conducting state [3–9].



PEDOTh

Due to the strong interest in poly(3,4-ethylenedioxythiophene) (PEDOTh), several derivatives with alkyl side chains connected to the ethylene bridge have been prepared and their properties have been revealed [7–9]. Up to now, these polymers were synthesized by chemical and electrochemically oxidative polymerization of the corresponding monomers, resulting in polymers that are in a p-doped state. These PEDOTh derivatives are difficult to be completely dedoped owing to stabilization effect of the electron-donating dialkoxy group on the p-doped state. Furthermore, the obtained polymers display a low solubility even in the presence of a long alkyl side chain. Therefore, characterization of the neutral alkylated PEDOTh derivatives, e.g. by NMR spectroscopy, has not been established well. On these bases, obtaining soluble and non-doped PEDOTh derivatives is strongly desired.

We previously reported the preparation of PEDOTh by organometallic polycondensation of 2,5-dichloro-3,4-ethylenedioxythiophene [10,11]. The polymer was obtained as completely non-doped state; however it was insoluble. In order to obtain further information on the PEDOTh type polymer, we have carried out the following polycondensation and obtained a soluble non-doped neutral polymer that is suited to the instrumental analyses. We here report results of the preparation of a non-doped soluble PEDOTh derivative, its characterization, and its chemical properties.



(1)

Ni(0) L_m: a mixture of bis(1,5-cyclooctadiene)-nickel(0), $Ni(cod)_2$ and 2,2'-bipyridyl.
C_6H_{13} = hexyl

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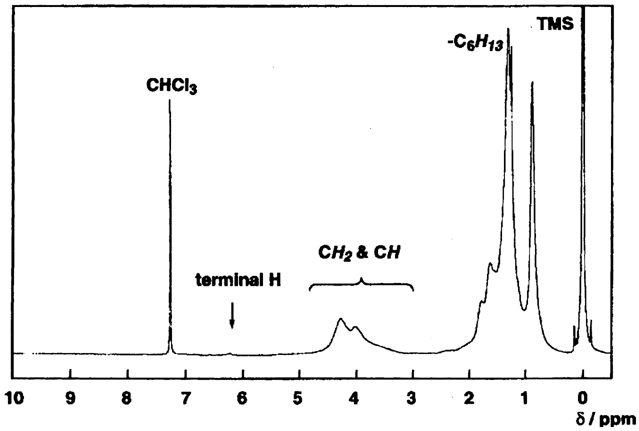

Fig. 1. ^{1}H NMR spectrum of PEDOTh-C_6 (Ni) in $CDCl_3$.

2. Experimental part

2.1. Monomer synthesis

Thieno-(3,4-*b*)-2,3-dihydro-2-hexyl-1,4-dioxin [3] (EDOTh-C_6, 0.41 g, 1.8 mmol) and 0.49 g (3.7 mmol) of *N*-chlorosuccinimide was dissolved in 20 ml of dry THF. The solution was stirred for 2 h at −5°C and subsequently for 6 h at room temperature. After the reaction, aqueous $Na_2S_2O_3$ was added. The organic fraction was separated, and aqueous layer was extracted with $CHCl_3$ (3 × 20 ml). The combined organic fraction was washed with aqueous $Na_2S_2O_3$ and dried with $MgSO_4$. Column chromatography on silica gel (eluent = 1:1 mixture of $CHCl_3$ and hexane) gave a colourless liquid, pure [2,5-dichlorothieno-(3,4-*b*)]-2,3-dihydro-2-hexyl-1,4-dioxin, monomer-1. 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%. ^{1}H NMR ($CDCl_3$, ppm):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, $J = 12$ Hz, 8 Hz), 4.15 (1H, m), 4.23 (1H, dd, $J = 12$ Hz, 2 Hz). ^{13}C NMR ($CDCl_3$, ppm):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.

2.2. Polymer synthesis

A mixture of [2,5-dichlorothieno-(3,4-*b*)]-2,3-dihydro-2-hexyl-1,4-dioxin (0.30 g, 1.0 mmol), $Ni(cod)_2$, (0.55 g, 2.0 mmol), 2,2′-bipyridyl, (0.31 g, 2.0 mmol), and 1,5-cyclooctadiene (0.21 g, 2.0 mmol) in dry DMF (15 ml) was stirred for 48 h at 60°C. The obtained black mixture was washed in a manner similar to those previously applied for the preparation of PEDOTh [10]. Reprecipitation of a $CHCl_3$ solution of the product to methanol gave a deep purple powder of poly{2,5-thienylene-(3,4-*b*)-[2,3-dihydro-2-hexyl-1,4-dioxin]}, PEDOTh-C_6 (Ni). Yield = 90%. All manipulations were carried out under N_2, and the obtained polymer was stored under N_2. Anal. Found: C 61.6%; H 6.7%; S 12.9; Cl 0.0%. Calcd. for $(C_{12}H_{14}O_2S{\cdot}0.5H_2O)_n$: C 61.8%; H 7.3%; S 13.7%; Cl 0.0%. ^{1}H NMR ($CDCl_3$, ppm): δ: 0.9–1.8 (13H of hexyl group), 4.0–4.3 (3H of methylene and methine). IR (KBr disk, cm^{-1}): 2918, 2852, 1514, 1458, 1434, 1319, 1205, 1064.

2.3. Analyses

NMR and IR spectra were recorded on a JEOL EX-400 spectrometer and a JASCO IR-810 spectrometer, respectively. GPC analysis was carried out with a Tosoh HLC 8210 equipped with polystyrene gel columns (TSK gel G2500, G4000, and G5000), using a DMF solution of LiBr (0.006 M) as an eluent. UV–Vis spectra were measured with a Shimadzu UV-3100PC spectrometer. Cyclic voltammograms were obtained with a Hokuto Denko HA-501 galvano/potentiostat and a Hokuto Denko HB-104 function generator using an CH_3CN solution of $[NBu_4]PF_6$ (0.10 M) at 100 mV s^{-1}. Changes in the absorption spectrum of PEDOTh-C_6 (Ni) (1.0×10^{-4} M) by chemical doping were investigated by addition of I_2 as an oxidant. A cast film of PEDOTh-C_6 (Ni) on an indium/tin oxide (ITO) glass substrate was used for studies on electrochromic behaviour of the polymer in an acetonitrile solution with tetrabutylammonium hexafluorophosphate $[NBu_4]PF_6$ (0.10 M).

3. Results and discussions

Organometallic polycondensation of monomer-1 using the zero valent nickel complex gave PEDOTh-C_6 (Ni) in 90% yield. The deep purple powder of the neutral polymers was

$$n\ \text{Monomer-1} + n\ \text{Ni(0)L}_m \rightarrow \underset{\text{deep purple}}{\text{PEDOTh-C}_6\ \text{(Ni)}} \qquad (2)$$

somewhat unstable when exposed to air. It was gradually oxidized by oxygen from the air as judged from a colour change to a black powder. Thus, all manipulations and measurements were carefully carried out under N_2. All analytical data supported the structure of PEDOTh-C_6 (Ni), including that the polymer did not contain any Cl. The polymer exhibited good solubility in organic solvents such as $CHCl_3$, CH_2Cl_2, and DMF. The latter surprises us since oxidative polymerization (e.g. with $FeCl_3$) have taught us that one requires at least a decyl ($C_{10}H_{21}$) substituent at each EDOTh unit to keep the corresponding polymer soluble [3]. This observation strengthens the idea that alkyl chain cleavage occurs upon oxidative polymerization conditions as observed from NMR analyses. The reductive polymerization using $Ni(0)L_m$ (Eq. 2) does not show this cleavage. GPC analysis furthermore indicated that PEDOTh-C_6 (Ni) had a number average molecular weight (M_n) of 5400 and a weight average molecular weight (M_w) of 8500.

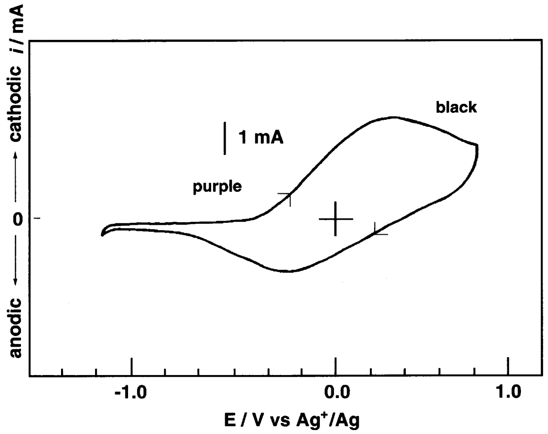

Fig. 2. CV chart for the PEDOTh-C_6 (Ni) film cast on a Pt plate. In an CH_3CN solution of $[NBu_4]PF_6$ (0.10 M) at 100 mV s^{-1}.

Fig. 1 shows the ^1H NMR spectrum of PEDOTh-C_6 (Ni) in $CDCl_3$. The two broad peaks in the range of δ 4.0–4.2 are attributed to the O–CH_2 and O–CH protons of the O–CH_2–$CH(C_6H_{13})$–O bridge. The small ^1H NMR signal at about δ 6.3 can be assigned to terminal thiophene-H protons, that are formed from a Ni-terminated unit (polymer-$NiL_{m'}$) during the work-up including treatment with acidic media [11,12]. Based on the integration of these peaks an M_n of 11,000 (ca. 50 EDOTh units) can be calculated. The IR peaks of PEDOTh-C_6 (Ni) are sharp, which supports that the polymer is in the expected non-doped state; p-doping of polythiophenes usually brings about broadening of the IR peaks. The peaks at 1434 and 1458 cm^{-1} (cf. experimental part) are assigned to ring vibrations of the thiophene ring. Two absorption peaks at 1205 and 1064 cm^{-1} are assigned to $\nu(COC_{asym})$ and $\nu(COC_{sym})$, respectively.

Casting a $CHCl_3$ solution of PEDOTh-C_6 (Ni) onto a Pt plate gave a deep purple film. The cyclic voltammogram (CV) of the film in an CH_3CN solution of $[NBu_4]PF_6$ reveals that electrochemical oxidation of the film started at about −0.40 V vs Ag^+/Ag as shown in Fig. 2. The CV curve gave a p-doping peak at 0.20 V vs Ag^+/Ag and a p-dedoping peak at −0.24 V at 100 mV s^{-1}. The colour of the film changed from deep purple to black upon oxidation. The polymer film appears stable upon repeated scanning, giving the same CV curve and colour changes each time. The doping level of the oxidized polymer is about 0.3 as measured from the doping current.

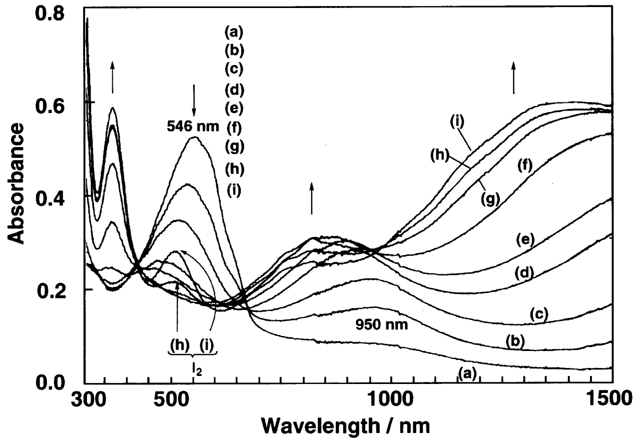

Fig. 3. Changes in UV–Vis spectrum of a $CHCl_3$ solution of PEDOTh-C_6 (Ni) (1.0×10^{-4} M) on addition of I_2. Concentration of I_2: (a) 0, (b) 1.0×10^{-6}, (c) 2.0×10^{-6}, (d) 5.0×10^{-6}, (e) 1.0×10^{-5}, (f) 2.0×10^{-5}, (g) 5.0×10^{-5}, (h) 1.0×10^{-4}, (i) 2.0×10^{-4} M.

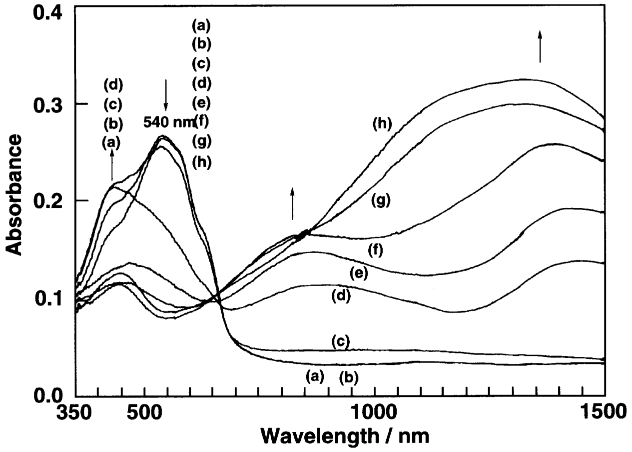

Fig. 4. Changes in the UV–Vis spectrum of a film of PEDOTh-C_6 (Ni) on an ITO glass electrode at various applied potentials vs. Ag^+/Ag. The curve (a) shows the UV–Vis spectrum of the as-cast film. The film gives the same UV–Vis spectrum at a potential of −1.0 V vs Ag^+/Ag. Applied potential = (b) −0.6, (c) −0.4, (d) −0.2, (e) −0.1, (f) 0, (g) 0.2, (h) 0.4 V. In a CH_3CN solution of $[Bu_4N][PF_6]$ (0.10 M).

Fig. 3(a) shows the UV–Vis spectrum of PEDOTh-C_6 (Ni) in $CHCl_3$. Due to expansion of π-conjugation system, the spectrum exhibits a broad absorption band at about 546 nm with a molar absorption coefficient ϵ (based on the repeating unit) of 5300 M^{-1} cm^{-1}. As shown in Fig. 3, addition of I_2 causes decrease in the intensity of a 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. Increase in the amount of I_2 results in lowering of these two absorption bands and 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 [1,2]. Similar spectroscopic changes were reported for oxidatively prepared and dedoped PEDOTh-C_{14}, on doping with $SbCl_5$ in $CHCl_3$ [8].

As shown in Fig. 4, the as-cast film of PEDOTh-C_6 (Ni) exhibits an absorption peak at essentially the same position as the $CHCl_3$ solution of PEDOTh-C_6 (Ni). However, the absorption bands has substructures at 620 and 410 nm, suggesting the presence of intermolecular interaction in the solid. Fig. 4 depicts changes of the absorption spectrum of the cast film of PEDOTh-C_6 (Ni) on the ITO glass substrate 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. At −0.2 V, new absorption bands are clearly observed at about 850 and 1400 nm. Application of higher potentials of −0.1 through 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. 3). The electrochromic behaviour is reversible, and it is essentially similar to that of the electrochemically prepared films of PEDOTh derivatives. When the cast film of PEDOTh-C_6 (Ni) was exposed to I_2 vapour, the film showed the analogous colour change, giving the spectrum comparable to that of Fig. 4(d).

As described above, Ni-promoted dehalogenation polycondensation gives neutral non-doped PEDOTh-C_6 (Ni) in good yield. The polymer had good solubility in organic solvents, and the cast films of the non-doped polymer were easily obtained. The results obtained in this study will contribute to a better understanding of chemistry of PEDOTh and its derivatives.

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