Electrochemical Synthesis of Soluble Poly(n-alkylphenylene)s

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Electrochemical oxidation of n-alkylbenzenes (alkyl =
butyl, hexyl, octyl, and dodecyl) in 0.1 mol dm^{-3} n-Bu_4NBF_4-
nitromethane with a catalytic amount of $NiCl_2[P(allyl)_2Ph]_2$
affords poly(n-alkylphenylene)s soluble in common organic
solvents. n-Alkylbenzene with a longer alkyl chain gives a
soluble polymer with higher molecular weight, more positive
oxidation potential and larger band gap.

Soluble organic conducting polymers have been of recent absorbing
interest because of their high processability useful to various
technological applications. Extensive studies have been carried out on
preparation and properties of soluble polythiophene and polypyrrole
derivatives,[1] while reports on soluble poly(p-phenylene) derivatives are
rather limited.[2] Most of soluble poly(p-phenylene)s have been prepared
not by oxidative polymerization of benzene derivatives but by reductive
coupling of aryl halides. This should be ascribed to much difficulty in
oxidation of benzene than thiophene and pyrrole. We have previously
reported an electrochemical method effective to prepare high-quality
poly(p-phenylene) films using a nickel complex catalyst.[3] In this study
we applied this method to synthesize poly(n-alkylphenylene)s, where alkyl
is butyl, hexyl, octyl and dodecyl, in order to obtain polyphenylenes
soluble in organic solvents. This paper presents electrochemical synthetic
conditions and electrochemical and optical properties of their soluble
components.
    A typical procedure of the electrochemical synthesis of poly(n-
alkylphenylene) is as follows. Controlled potential electrolysis of 0.3
mol dm^{-3} n-dodecylbenzene was carried out at an SnO_2-coated glass electrode

in 0.1 mol dm^{-3} $n-Bu_4NBF_4$ / nitrobenzene + nitromethane (1:1 in volume)
with 3 mmol dm^{-3} $NiCl_2[P(allyl)_2Ph]_2$ at 4.5 V vs. Ag/Ag^+ (10 mmol dm^{-3}
$AgClO_4$ in CH_3CN) for 18 h. The electrode surface was covered with some
fragile film, but most of the products were dissolved in solution. A
considerable part of the electrode film was dissolved in solution by the
following electrochemical dedoping at -1.0 V until the cathodic current
decreased to the background level. Solvents were distilled off under
vacuum and acetonitrile was added to the dark-brown residue. The
precipitate including films were collected, washed thoroughly with
acetonitrile, and extracted with chloroform. Average molecular weight of
the extract measured by GPC based on polystylene molecular weight standards
was 7600, and thus the polymerization degree was 31. This number is 50%
higher than that prepared in the absence of the Ni complex. The obtained
polymer in the undoped form is soluble in organic solvents with low
polarity such as dichloromethane, benzene or tetrahydrofuran but insoluble
in polar solvents such as acetonitrile or propylene carbonate.

Effects of electrochemical conditions on the yield, average molecular

Table 1. Electrochemical Synthetic Conditions[a] and Properties of Soluble
Poly(n-alkylphenylene)s

Run	Alkyl in monomer	Electrolyte solution[b]	Amount of charge /C	Yield[c] /%	Average m.w.	Elemental anal.[d] C	H	N/%
1	dodecyl	$[BF_4]$-NB	930	53	5900	86.2	10.4	0.9
2	dodecyl	$[BF_4]$-NB[e]	770	18	6000	86.7	10.3	0.6
3	dodecyl	$[ClO_4]$-NB	600	0	-	-	-	-
4	dodecyl	$[BF_4]$-NM,NB	1100	24	5200	87.7	10.4	0.5
5	dodecyl	$[BF_4]$-NM,NB[e]	1550	10	7600	86.1	10.0	1.0
6	dodecyl	$[BF_4]$-MeCN,NB	1760	0.2	1550	-	-	-
7	dodecyl	$[BF_4]$-MeCN,NB[e]	1350	0.1	1500	-	-	-
8	dodecyl	$[BF_4]$-DCE	110	6.3	2650	86.4	10.8	0.1
9	dodecyl	$[BF_4]$-DCE[e]	210	19	2350	88.2	10.9	0.1
10	octyl	$[BF_4]$-NM[e]	570	8.7	2235	88.3	9.2	1.2
11	hexyl	$[BF_4]$-NM[e]	800	23	1700	89.4	9.1	0.3
12	butyl	$[BF_4]$-NM[e]	1760	17	1550	89.6	8.0	0.4

a) Controlled potential electrolysis at an SnO_2-coated glass electrode (2
cm^2) at 4.5 V vs. Ag/Ag^+ for n-dodecylbenzene and 3.5 V for others for 18
h. b) Electrolyte concn: 0.1 mol dm^{-3}, $[BF_4]$: $n-Bu_4NBF_4$, $[ClO_4]$: n-
Bu_4NClO_4, NB: nitrobenzene, NM: nitromethane, DCE: 1,2-dichloroethane. c)
Based on the amount of charge passed during electrolysis. d) Calcd for
$C_{18n}H_{28n}$ (poly(n-dodecylphenylene)): C, 88.5; H, 11.5%; $C_{14n}H_{20n}$ (poly(n-
octylphenylene)): C, 89.3; H, 10.7%; $C_{12n}H_{16n}$ (poly(n-hexylphenylene)): C,
89.9; H,: 10.1%; $C_{10n}H_{12n}$ (poly(n-butylphenylene)): C, 90.9; H, 9.1%. e)
Added 3 mmol dm^{-3} $NiCl_2[P(allyl)_2Ph]_2$.

weight and elemental analysis data of soluble components of the polymers prepared from alkylbenzenes are given in Table 1. Solvents with low donor numbers such as nitrobenzene and/or nitromethane are effective and a BF_4^- salt is a better electrolyte than a ClO_4^- salt for the electro-polymerization. Addition of the Ni complex decreases the yield of the soluble product but increases that of insoluble one. Infrared spectra of the soluble and insoluble components were almost identical, suggesting that there is no difference in the fundamental structure between the soluble and insoluble ones. Thus, the solubility should depend on the molecular weight simply. Amounts of the insoluble component increases and the average molecular weight of the soluble part decreases according to the shortening of the alkyl chain in the monomer. This indicates that low solubility of poly(n-alkylphenylene) with short alkyl side chains limits the molecular weight of the soluble component. It should be noted that quite positive potentials, 3.5 - 4.5 V vs. Ag/Ag^+ are requisite for the polymerization of n-alkylbenzenes. This condition causes some undesirable decomposition of the solvent (nitro compounds), which might be the reason of the contamination of nitrogen in the product (see Table 1).

Poly(n-dodecylphenylene) with different molecular weights can be easily separated by silicagel column chromatography with $EtOAc-CH_2Cl_2$-hexane as an eluent. The component with m.w. = 2500 is a viscous oil, and that with m.w. = 8200 is a fusible solid (mp 150 °C) processable as a flexible free-standing film. An infrared spectrum of the component with m.w. = 8200 is displayed in Fig. 1. A peak at 822 cm^{-1} due to out-of-plane CH deformation vibration and two peaks in the 2000-1600 cm^{-1} region indicate the structure of 1,2,4-substituted benzene, implying the ortho- or para-phenylene configuration. Paraphenylene configuration is more likely since the steric hinderance is crucial in the ortho-configuration.

Cyclic voltammograms of a poly(n-octyl-phenylene) film coated on an ITO electrode in 0.1 mol dm^{-3} KPF_6-propylene carbonate are shown in Fig. 2. Although anodic current due to oxidation accompanying with anion doping flows, any obvious anodic peak does not appear up to 1.2 V vs. Ag/Ag^+. Similar voltammograms were obtained for other poly(n-alkylphenylene)s and their cathodic peak potentials of rereduction, E_{pc}, are given in Table 2. The E_{pc} value becomes more positive for the polymer with longer alkyl chains.
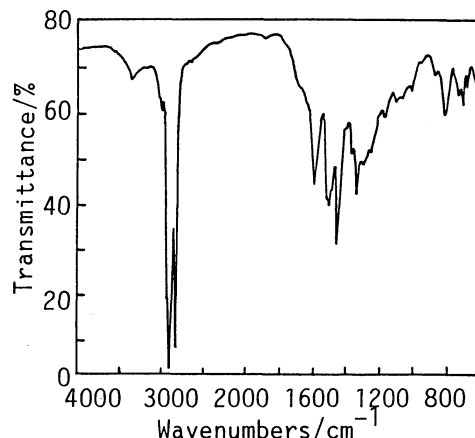
VIS-NIR spectra of poly(n-octyl-

Fig. 1. An infrared spectrum of poly(n-dodecylphenylene) with m.w. = 8200.

phenylene) at various potentials are displayed in Fig. 3, which represents a decrease in absorbance in the short wavelength region and an increase in the long wavelength region characteristic of a polaronic state formation.[4] An isobestic point appears at 460 nm, from which band gap, E_g, is estimated at 2.7 eV. The E_g values of poly(n-alkylphenylene)s obtained in this way and listed in Table 2 are smaller than E_g of unsubstituted poly(p-phenylene), 3.2 eV.[4] A possible rationale of this phenomenon is that the electron donation by the alkyl group increases the double bond character of the phenylene-phenylene bond and lessens the tortion angle between the phenylene rings, of which largeness is the cause of the large E_g value of poly(p-phenylene). The E_g value of poly(n-alkylphenylene), however, increases with lengthening the alkyl side chain as shown in Table 2. We speculate that the electronic effects of alkyl groups to decrease E_g are overcome with their steric effects; the motion of phenylene rings to change the tortion angle upon oxidation might be restricted by the strong interaction between long alkyl side chains.
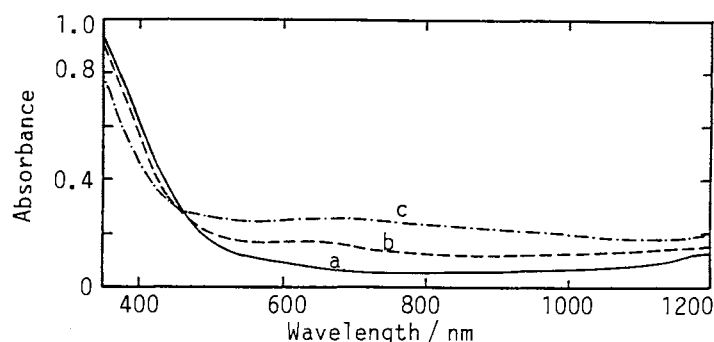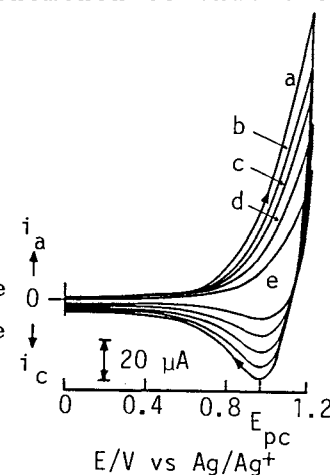

Fig. 2. Cyclic voltammetry of poly(n-octylphenylene)/ITO in 0.1 mol dm^{-3} KPF$_6$-propylene carbonate at 100, 80, 60, 40, and 20 mV s^{-1} for (a), (b), (c), (d), and (e), respectively.

Fig. 3. VIS-NIR spectra of poly(n-octyl-phenylene)/ITO in 0.1 mol dm^{-3} n-Bu$_4$NClO$_4$-MeCN at 0, 0.8 and 1.1 V vs. Ag/Ag$^+$ for (a), (b), and (c), respectively.

Table 2. Properties of Poly(n-alkylphenylene)s

Alkyl	E_{pc} /V vs. Ag/Ag$^+$	E_g /eV
butyl	0.62	2.4
hexyl	0.84	2.6
octyl	0.96	2.7
dodecyl	0.99	2.8

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