Preparation of New Main-Chain-Type Polyquinones and Their Electrochemical Response

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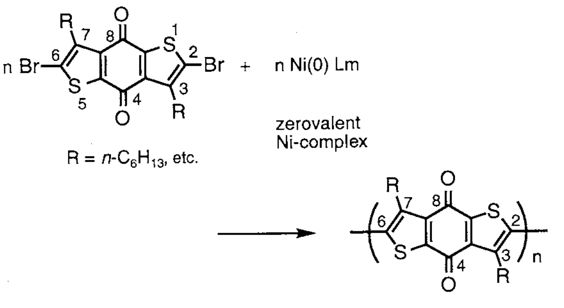
(Received May 27, 1998; CL-980406)

New main chain type polyquinones, poly(3,7-dihexylbenzo[1,2-*b*:4,5-*b*']dithiophene-4,8-dione-2,6-diyl), have been prepared by organometallic polycondensation. In accord with a highly electron-accepting property of the monomeric unit, the polymer receives electrochemical reduction at a higher potential than poly(anthraquinone)s.

π-Conjugated polymers consisted of redox active recurring units are the subject of recent interest.[1] Quinones belong to typical redox active compounds and a huge number of papers have been published on redox behaviors of quinones, however, examples of the polymers consisted of the quinone units are still limited.[2] In order to expand the scope of the redox active main-chain-type polyquinones, we have prepared the following new type of polyquinones by dehalogenation polymerization using a zerovalent nickel complex, which is suited to the preparation of polyquinones,[2a,e] and herein report results of the preparation and electrochemical responses of the polymers.



(1)

Ni(0) Lm: a mixture of bis (1,5-cyclooctadiene) nickel(0) Ni(cod)$_2$ and 2,2'-bipyridyl bpy.

The repeating unit has the fused ring structure with the thiophene subunit at the both sides and modification of the unit by introducing appropriate substituents at the 3- and 7-positions is possible. Modification of the electronic state of polyquinones by substituents[2b,e] and control of self-assembling of aromatic polymers like polythiophene by long R substituents[3] are the subject of recent interest.

The monomer and its hydrogenated compound (with H at the 2- and 6-positions instead of Br: monomeric model compound for the polymer) were prepared from the corresponding thiophene derivatives in manners similar to those previously reported.[4,5]

The organometallic polycondensation of the dihexyl monomer using Ni(cod)$_2$ was carried out in DMF at 60 °C for 48 h, and the obtained polymer, P(2,6-Th$_2$Bq(diHex)), was worked up similarly to the preparation of poly(anthraquinone)s synthesized by an analogous method.[2a,6] The IR spectrum of P(2,6-Th$_2$Bq(diHex)) resembles that of its corresponding monomer except for disappearance of a ν(C-Br) absorption band at 1098 cm^{-1}. Figure 1 exhibits the ^{1}H-NMR spectrum of P(2,6-Th$_2$Bq(diHex)), and the peak area ratios agree with the structure of the polymer. Splitting of the CH$_2$ signal (δ 2.8 - 3.1) attached at the atomatic ring into two peaks is considered to be due to the presence of *s*-cis and *s*-trans bonded monomeric units and/or due to the terminal groups. The analytical data[6] indicate that P(2,6-Th$_2$Bq(diHex)) is H-terminated (not Br-terminated), similar to poly(anthraquinone)s[2a] and poly(pyridine-2,5-diyl).[7] The H-terminal unit is considered to be produced from a Ni-terminated unit during the work-up, and area of the signal of the terminal-H observed at δ 7.33 agrees with the M_n value estimated from GPC.[6] Although the molecular weight of the polymer is not so high, its film can be obtained by casting from solutions and basic electrochemical behavior of the polymer has been revealed by cyclic voltammetry.

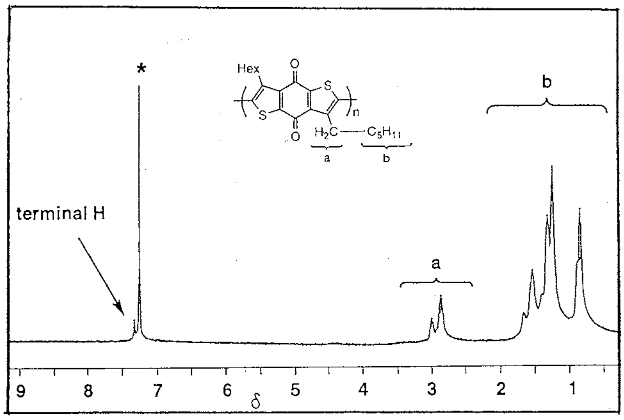
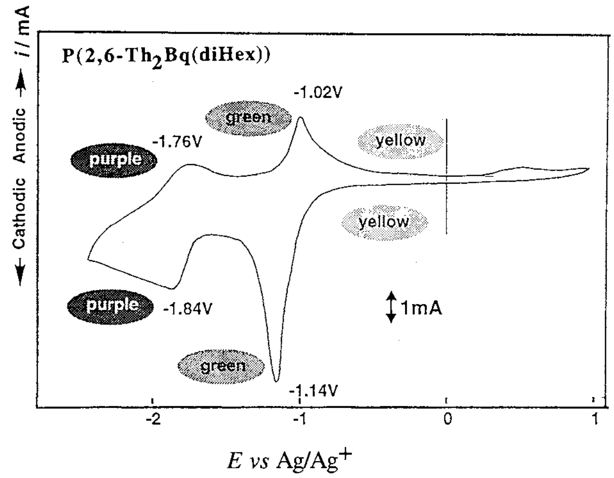


Figure 1. ^{1}H-NMR spectrum of P(2,6-Th$_2$Bq(diHex)) in CDCl$_3$. * is due to impurity in CDCl$_3$.

Figures 2 shows cyclic voltamogram of a film of P(2,6-



E vs Ag/Ag$^+$

Figure 2. Cyclic voltammogram of P(2,6-Th$_2$Bq(diHex)) film laid on a Pt plate (1 cm x 1 cm). In a CH$_3$CN solution of [Bu$_4$N]PF$_6$ (0.10 M). At 100 mVs^{-1}.

Th_2Bq(diHex)) cast on a Pt plate. The polymer receives the first and second reduction with E_{pc} values of -1.14 and -1.84 V *vs* Ag/Ag^+, and the electrochemical reduction is accompanied with the color changes shown in Figure 2.

The first-step electrochemical reduction of P(2,6-Th_2Bq(diHex)) proceeds at higher potential by about 0.3 V than that of poly(anthraquinone-1,4-diyl)s. This more facile electrochemical reduction of P(2,6-Th_2Bq(diHex)) is considered to be a reflection of higher first reduction potential of the monomeric model compound of the polymer (3,7-dihexylbenzo[1,2-*b*: 4,5-*b'*]dithiophene: E_{pc} = -1.12 V *vs* Ag/Ag^+) than that of anthraquinone[2a] by about 0.2 V. The electrochemically reduced polymer becomes partly soluble in CH_3CN, and the smaller anodic peak at -1.02 V than the cathodic peak at -1.14 V is attributed to partial dissolution of the polymer in the solution.

Powder X-ray diffraction pattern of P(2,6-Th_2Bq(diHex)) is similar to those of regioregular poly(3-hexylthiophene-2,5-diyl) and poly(4,4'-dialkyl-2,2'-bithiazole-5,5'-diyl),[3] suggesting occurrence of stacking of P(2,6-Th_2Bq(diHex)), similar to cases of the previously reported polymers. The long alkyl chains seem to assist the stacking, however, the *d*-values (13.0 Å and 4.1 Å)[8] are somewhat different from those of head-to-tail type poly(3-hexylthiophene-2,5-diyl) (*d* = 16.7 and 3.84 Å)[3] due to the difference in steric effect around the core aromatic rings. Preliminary experiments indicate that P(2,6-Th_2Bq(diDod)) (R = dodecyl) analogously prepared also takes a similar self-assembled structure, showing X-ray diffraction peaks at *d* = 21.0, 10.6, 7.0 (d = 21.0/n; n = 1, 2, 3), and about 4 Å.

References and Notes

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5 For example, 2,6-dibromo-3,7-dihexylbenzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (monomer for P(2,6-Th_2Bq(diHex))) was obtained by treating 3-(dimethylamino-carbonyl)-4-hexyl-2,5-dibromothiophene with butyllithium in 33% yield. Anal. Found: C, 48.8; H, 4.7%. Calcd for $C_{22}H_{26}Br_2O_2S_2$: C, 48.4; H, 4.8%. mp = 132 °C. ^1H-NMR($CDCl_3$): δ: 0.89 (6H, CH_3), 1.31-1.55 (16H, CH_2), 2.95 (4H, CH_2). Other compounds were prepared analogously.

6 P(2,6-Th_2Bq(diHex)): 98% yield. Anal. Found: C, 67.0, H, 6.6; Br, 0%. Calcd. for $H(C_{22}H_{26}O_2S_2{\cdot}0.3H_2O)_9H$: C, 67.4; H, 6.9%. GPC ($CHCl_3$; polystyrene standards): M_n = 3500, M_w = 4700. The polymer is soluble in $CHCl_3$ and partly soluble in THF and toluene. λ_{max} = 398 nm (in $CHCl_3$).

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8 The 13.0 Å peak is accompanied with a peak at 6.5 Å (= 13.0 Å/2).