Macromolecules **1993,** *26,* 4055–4057

π-Conjugated Soluble Poly(6-hexylpyridine-2,5-diyl) and Poly(6,6'-dihexyl-2,2'-bipyridine-5,5'-diyl) with High Molecular Weights and *n*-Type Conducting Properties. Synthesis, Electrical and Optical Properties, and Chemical Reactivities of the Polymers

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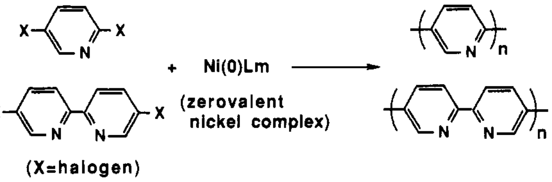
Received December 31, 1992
Revised Manuscript Received April 12, 1993

Electrical and optical properties of π-conjugated polymers have received much attention in recent years. However, detailed investigation of chemical and physical properties of the π-conjugated polymers and their application have often been restricted due to their insolubility in solvents and their infusibility.

It is now recognized that the introduction of appropriate substituents (e.g., the long alkyl or alkoxy side groups) to these polymers generally enhances their solubility[1] and sometimes makes the polymers fusible. However, the introduction of the substituent has been carried out mainly with π-conjugated polymers which are converted into p-type conducting materials by oxidation, e.g., poly(thiophene-2,5-diyl) and poly(pyrrole-2,5-diyl).

Previously, we reported the preparation of n-type electrically conducting poly(pyridine-2,5-diyl) (Ppy)[2] and poly(2,2'-bipyridine-5,5'-diyl) (PBpy),[2d,3] which consist of π-electron-deficient pyridine rings,[4] according to the following polycondensation based on organonickel chemistry.[5,6]

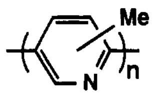


(1a)

(1b)

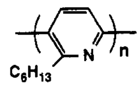
These polymers not only have the n-type conducting properties but also show interesting chemical and physical properties. For example, they exhibit strong fluorescence,[2d] have high thermal stability, serve as catalyst for photoreduction of water,[7] and are useful for making polarizers of light.[2c,e] Furthermore, PBpy serves as a unique electrically conducting polymer chelate ligand.[7c] However, these polymers are soluble only in formic acid among organic solvents. The molecular weights (M_w) of Ppy and PBpy were determined as 3800 (degree of polymerization (DP) = 45) and 3200 (DP = 21), respectively, by a light scattering method in formic acid solutions.

For the purpose of getting the n-type conducting Ppy and PBpy type polymers with higher DP and higher solubility, we carried out a polycondensation similar to eq 1 using three kinds of methyl-substituted 2,5-dibromopyridines and obtained the corresponding polymers (PMepy's) with M_w of 12 000–27 000 (DP = 130–300).[8] These polymers also show n-conducting properties; however, the increase in the solubility by the introduction of a methyl group is not sufficient, and PMepy's are soluble only in formic acid among tested organic solvents.

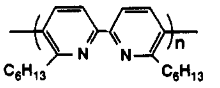


PMepy's

In order to obtain n-type conducting polymers with higher molecular weight and good solubility in common organic solvents, we have introduced longer alkyl chains and now report the preparation of poly(6-hexylpyridine-2,5-diyl) (P6Hpy) and poly(6,6'-dihexyl-2,2'-bipyridine-5,5'-diyl) (P6BHpy), which have high molecular weights, good solubility in organic solvents, and interesting chemical reactivity.

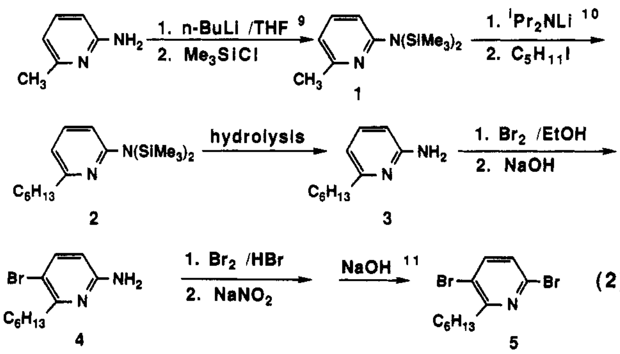


P6Hpy



PB6Hpy

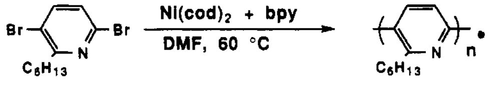
The synthetic route to the starting monomer, 2,5-dibromo-6-hexylpyridine, is outlined in eq 2. The purity of 5 was higher than 99% as determined by GC. Bp: 108–110 °C (1 mmHg). ^{1}H NMR ($CDCl_3$, δ, TMS): 0.87 (t, 3H, $-CH_3$), 1.1–1.9 (m, 8H, $-(CH_2)-_4$), 2.89 (t, 2H, $-(CH_2)-$ attached to the pyridine (Py) ring), 7.13 (d, J = 8.35 Hz, 1H, 3-H of the Py ring), 7.59 (d, J = 8.35, 1H, 4-H of the Py ring). ^{13}C NMR ($CDCl_3$, δ, ppm): 162.29, 142.13, 139.66, 126.56, 120.05, 37.32, 31.50, 29.01, 28.29, 22.50, 14.00. The monomer 5 was converted to 5,5'-dibromo-6,6'-dihexyl-2,2'-bipyridine[12] (6; eq 3) by modifying a method described previously.[3]



(2)

(3)

Stirring 2,5-dibromo-6-hexylpyridine (960 mg, 3.0 mmol) with a mixture of bis(1,5-cyclooctadiene)nickel ($Ni(cod)_2$; 990 mg, 3.6 mmol), 1,5-cyclooctadiene (cod; 390 mg, 3.6 mmol), and 2,2'-bipyridine (bpy; 560 mg, 3.6 mmol) in *N,N*-dimethylformamide (DMF) (20 mL) for 48 h at about 60 °C afforded a precipitate of P6Hpy.



(4)

The precipitate was washed with an aqueous solution containing ethylenediaminetetraacetic acid in a manner[2,6] similar to that previously reported. Brownish-yellow P6Hpy was obtained in high yield (80%). Anal. Calcd

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0024-9297/93/2226-4055$04.00/0

Table I. Solubility of P6Hpy in Various Solvents[a]

	solubility, mg mL^{-1}	λ_{max}, nm		solubility, mg mL^{-1}	λ_{max}, nm
$CHCl_3$	○ (300)	319	NMP	○ (20)	324
THF	○ (300)	323	HMPA	○ (200)	325
benzene	○ (300)	321	Et_2O	△	
toluene	○ (300)	322	hexane	×	
cresol	○ (200)	347	CH_3OH	×	
CF_3COOH	○ (300)	319	C_2H_5OH	×	
CH_3COOH	○ (10)	315	DMF	×	
HCOOH	○ (300)	340	DMSO	×	

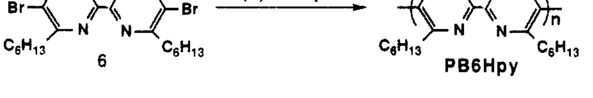
[a] ○: soluble. △: partly soluble (solubility < 10 mg mL^{-1}). ×: insoluble.

for $-(C_{11}H_{15}N)_n-$: C, 81.9; H, 9.4; N, 8.7. Found: C, 80.3; H, 8.9; N, 8.7; Br, 0.0.

P6Hpy is soluble in formic acid and many common organic solvents. The solubility and UV-visible absorption peak of P6Hpy in various solvents are summarized in Table I. The UV-visible spectrum shows one sharp peak at 340–350 nm in cresol and formic acid and at 320 nm in other common organic solvents. In formic acid the absorption peak was shifted to a shorter wavelength by 30 nm compared with that of Ppy[2a,d] (373 nm) and PBpy[3] (373 nm). A similar hypochromic effect of the bulky substituent has been reported for poly(thiophene-2,5-diyl) derivatives.[13] P6Hpy gives rise to strong fluorescence both in formic acid and in chloroform. When excited with 310-nm light, P6Hpy (2.0 × 10^{-5} M) gives rise to fluorescence bands with peaks at 362 and 417 nm in chloroform and formic acid, respectively.

The weight-average molecular weights (M_w) of P6Hpy determined by light scattering[14] in formic acid and chloroform are 37 000 (DP = 230) and 36 000 (DP = 220), respectively, which are considerably higher than those of Ppy and PBpy. The degrees of depolarization, ρ_v,[14] determined by light scattering were 0.015 and 0.065 in formic acid and chloroform, respectively. The ρ_v value was much smaller than those observed for Ppy and PBpy ($\rho_v = 0.33$), which are regarded as taking a rigid-rod-like linear structure[2,3] and are comparable to that of PMepy's ($\rho_v = 0.03 \pm 0.02$).[8] However, the nonzero ρ_v value of P6Hpy in chloroform, which is comparable to that (ρ_v = 0.026) of $-(p\text{-}C_6H_4CONH)-_n$ with high molecular weight (M_w = 38 400),[15] indicates that P6Hpy still takes a rather linear structure, although the rigidity of the linear structure is considerably lower than that of Ppy.

Figure 1a shows the ^{1}H-NMR spectrum of P6Hpy in $CDCl_3$. As shown in Figure 1a, the ^{1}H-NMR spectrum shows two resonances at 2.66 and 3.05 ppm for the pyridine ring-attached CH_2 proton. These two peaks for the methylene protons are explained by the presence of head-to-head and head-to-tail linkages along the polymer chain. Poly(6,6′-dihexyl-2,2′-bipyridine-5,5′-diyl)[16] (PB6Hpy) prepared by an analogous dehalogenation polycondensation (eq 5) gives rise to a methylene peak at 2.66 ppm (Figure 1b), and thus the peaks at 2.66 and 3.05 ppm of P6Hpy are assigned to head-to-head and head-to-tail units, respectively. The peak area ratio indicates that P6Hpy consists of approximately 55% head-to-tail configuration. P6Hpy and PB6Hpy give rise to almost the same IR spectrum (Figure 2). A C–H out-of-plane vibration characteristic of 2,5,6-trisubstituted pyridine appears at about 830 cm^{-1}.



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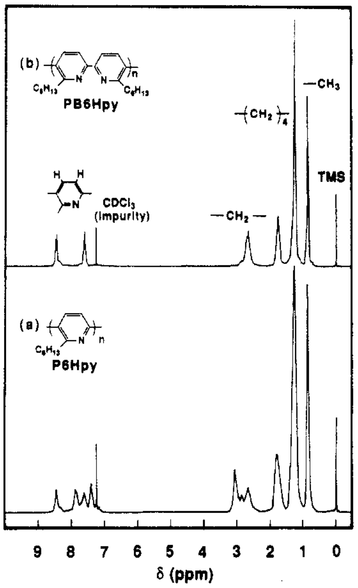

Figure 1. ^{1}H-NMR spectra of (a) P6Hpy and (b) PB6Hpy in $CDCl_3$.

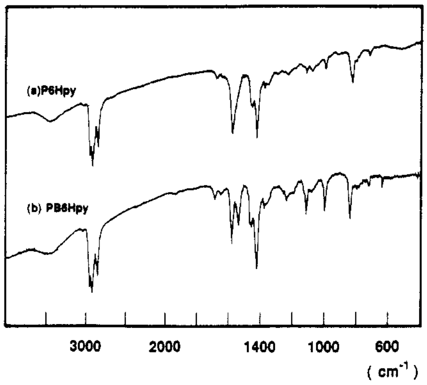

Figure 2. IR spectra of (a) P6Hpy and (b) PB6Hpy.

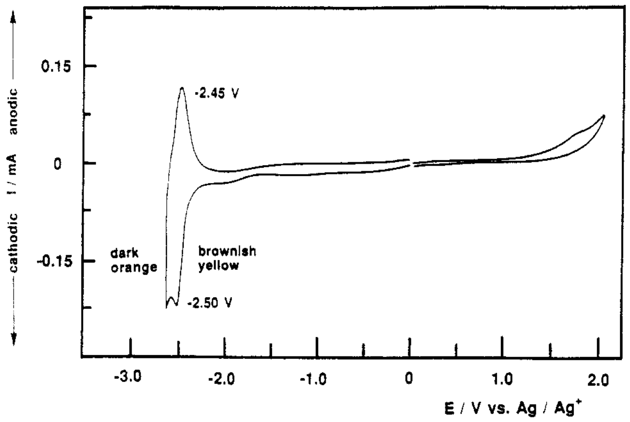

Figure 3. Cyclic voltammogram of the P6Hpy film on a Pt electrode in a CH_3CN solution of $[Bu_4N]BF_4$ (0.10 M). Sweep rate = 20 mV s^{-1}.

Casting chloroform solutions of P6Hpy and PB6Hpy on a platinum plate and removing chloroform by evaporation gave good free-standing films of the polymers. A cyclic voltammogram (CV) of the P6Hpy film on the Pt plate (Figure 3) clearly indicates that P6Hpy behaves as an n-type electrically conducting material. The CV shows a cycle with peaks at −2.50 and −2.45 V *vs* Ag/Ag$^+$ ascribed to n-doping and n-undoping, respectively. The doping and undoping processes can be repeated without any observable change in the CV curve for 50 cycles. The P6Hpy film reversibly changes color from brownish yellow (undoped state) to dark orange (doped state) during the redox processes. A P6Hpy film coated on an ITO glass (indium–tin oxide coated glass, 100 ohm/square) plate shows two new absorption bands appeared at 465 and 1100 nm on the electrochemical n-doping in $[(C_4H_9)_4N]BF_4/CH_3CN$. The color of the n-doped P6Hpy film gradually changed from dark orange of the n-doped state to brownish yellow of the undoped state in a few minutes after exposure to air, indicating that the n-doped state of P6Hpy does not have enough stability against moisture and oxygen in air.

The n-doping and n-undoping potentials of P6Hpy are comparable to those of Ppy (n-doping, 2.40 V; n-undoping, −2.00 V *vs* Ag/Ag^+) and PMepy's (−2.43 V; −2.30 V). However, the color of the n-doped P6Hpy is somewhat different from those of n-doped Ppy (reddish purple) and PMepy's (dark blue). Like Ppy and PMepy's, P6Hpy is electrochemically inactive in the oxidation region.

Thermogravimetric analysis (TGA) of P6Hpy under N_2 shows a 5% weight loss at 450 °C and 47% residual weight even at 900 °C under N_2.

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(12) Mp: 61–63 °C; Anal. Calcd for $C_{22}H_{30}N_2Br_2$: C, 54.80; H, 6.30; N, 5.8; Br, 33.1. Found: C, 55.0; H, 6.2; N, 5.7; Br, 32.9. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.91 (t, 3H, $-CH_3$), 1.2–1.9 (m, 8H, $-(CH2)-_4$), 3.01 (t, 2H, $-(CH_2)-$ attached to the pyridine (Py) ring), 7.86 (d, $J = 8.35$ Hz, 1H, 3-H of the Py ring), 8.13 (d, $J = 8.35$, 1H, 4-H of the Py ring). ^{13}C NMR ($CDCl_3$, δ, ppm): 159.71, 153.65, 140.74, 121.56, 119.65, 37.32, 31.72, 29.07, 28.14, 22.63, 14.10.

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