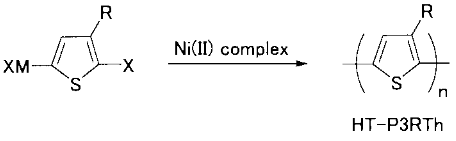
Preparation and Characterization of Regioregular Head-to-Tail π-Conjugated Poly(pyridine-2,5-diyl)s

Takakazu Yamamoto,* Takeshi Nakamura, Hiroki Fukumoto, and Kenji Kubota[†]
Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503
[†]*Department of Biological and Chemical Engineering, Faculty of Engineering, Gunma University, Kiryu, Gunma 376-8515*

(Received March 1, 2001; CL-010171)

Regioregular head–to-tail π-conjugated polypyridines have been prepared for the first time by organometallic polycondensation using Ni(II) complexes as the catalyst. The proportion of the HT-content in poly(6-hexylpyridine-2,5-diyl) was higher than 95%.

π-Conjugated heteroaromatic polymers such as polypyrroles, polythiophenes, and polypyridines are attracting considerable interest not only for their basic interesting electronic and optical properties but also for their practical usefulness.[1] Control of regioregularity of the π-conjugated heteroaromatic polymers is one of the most interesting topics in the field of polymer chemistry, since the regioregulated polymers show attractive electronic and optical properties and assume a π-stacked structure in the solid state.[2–4] For example, the regioregular head-to-tail poly(3-alkylthiophene-2,5-diyl), HT-P3RTh, has been synthesized from regioselectively metallated starting materials using Ni(II) complexes as the catalyst.

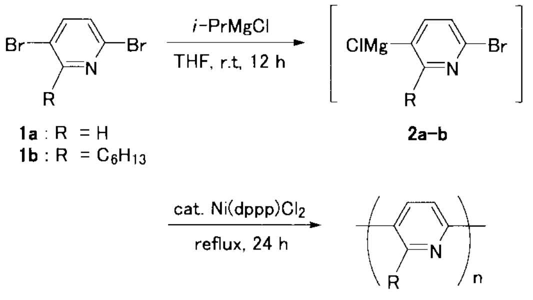


(1)

X = halogen; M = Mg(ref 2) or Zn(ref 3)

In contrast to the success of the synthesis of HT-P3RTh, which consists of electron-donating thiophene units and is easily converted to p-type electrically conducting materials, attmpts to synthesize HT-type polypyridines have not been successful due to difficulty of obtaining the corresponding regioregularly metallated starting materials such as 2,5-XM-C_5H_3N-X.

Due to the electron-accepting nature of pyridine,[5] π-conjugated polypyridines are easily reduced and converted to n-type electrically conducting materials.[1,6] Because of their n-type conductivity, polypyridines are considered to be one of the key materials for constructing polymer electronic devices such as diode and electroluminescent devices.[7] Under these circumstances, the preparation of π-conjugated polypyridines with various regioregularities is considered to be important for the development of polymer devices and the understanding of the basic properties of π-conjugated polymers. In the course of our attempts to prepare HT-polypyridines, we noted recent publications indicating that selective metallation of 2,5-dibromopyridine can be achieved by Grignard exchange reaction with *i*-PrMgCl.[8] We report herein the syntheses of two HT-polypyridines, using the reported results as reference. Head-to-head (HH) type polypyridines have already been synthesized by dehalogenation polycondensation of 5,5′-dibromo-2,2′-bipyridines.[6]



(2)

3a : HT-PPy (R = H)
3b : HT-P6HexPy (R = hexyl)

The occurrence of the selective Grignard exchange reaction of **1a** and **1b** was confirmed by exclusive liberation of the corresponding 2-bromopyridines upon hydrolysis of intermediate **2**. Stirring the reaction mixture under reflux in the presence of 5 mol% of $NiCl_2$(dppp) (dppp = 1,3-bis(diphenylphosphino)propane) afforded a yellow (**3a**) or light yellow (**3b**) precipitate in quantitative crude yield. Workup, including washing successively with aqueous ammonia, diluted hydrochloric acid, and methanol, gave **3a** in 76% yield;[9] a part of the polymer appeared to be lost during the workup. **3a** was soluble in formic acid and hexafluoroisopropanol but not in other organic solvents tested, similar to regiorandom and HH-type poly(pyridine-2,5-diyl)s, rand-PPy and HH-PPy.[6] GPC analysis (eluent = hexafluoro-2-propanol; poly(methyl methacrylate) standards) gave a number average molecular weight, M_n, of 1.1×10^4 ($M_w/M_n = 2.6$), and **3a** showed an $[\eta]$ value of 0.72 dL g^{-1} (dL = 100 cm^3) in formic acid.

As exhibited in Figure 1, the ^1H NMR spectrum of **3a** is significantly different from those of rand-PPy and HH-PPy, and shows only three main peaks, supporting the formation of the regioregulated polymer. The $^{13}C\{^1H\}$ NMR spectrum of **3a** in DCOOD also gives only five sharp peaks at δ = 128, 132, 142, 146, and 152. Use of other RMgX, instead of *i*-PrMgCl, did not give **3a**.

3b was highly soluble in commonly used organic solvents, and light scattering analysis gave an M_w value of 76000. The ^1H NMR spectrum of **3b** (Figure 2) also shows a simple peak pattern, supporting the formation of the regioregulated polymer. The α-CH_2 peak of **3b** appears at a lower magnetic field than that of HH-P6HexPy, similar to the case of poly(3-hexylthiophene-2,5-diyl)s.[2–4] The HT content of **3b** is higher than 95% as evaluated from the ^1H NMR peak area of α-CH_2 originating from the HT unit.

3a and **3b** gave essentially the same UV–vis data in solutions and electrochemical response (e.g., in cyclic voltammetry) as the corresponding random and HH-homologs. For example,

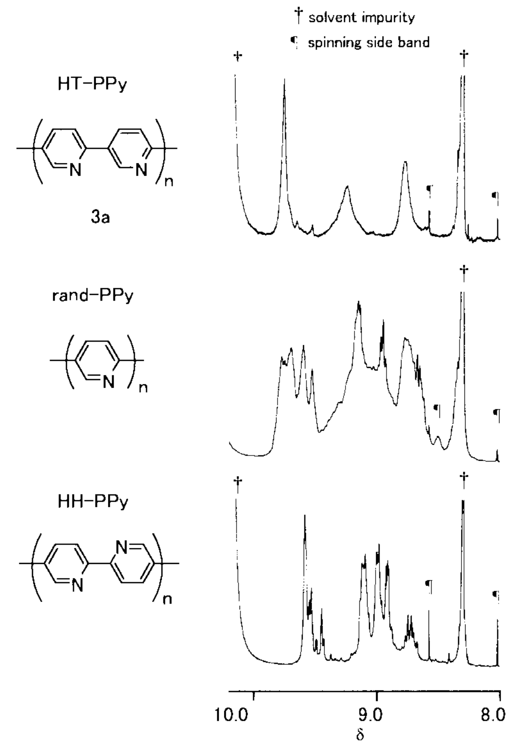


Figure 1. ^{1}H NMR spectra of poly(pyridine-2,5-diyl)s in DCOOD.

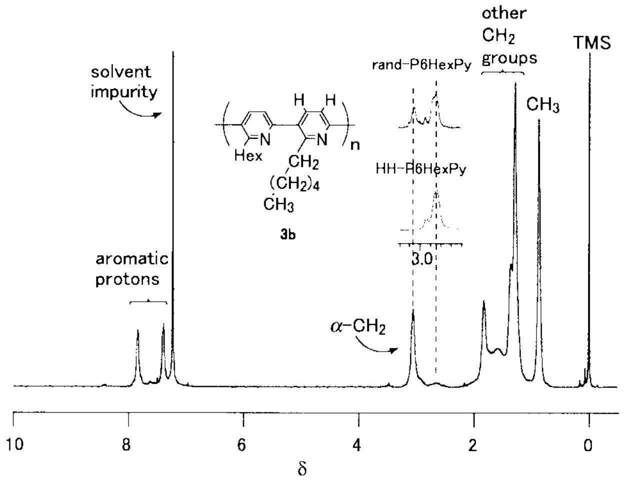


Figure 2. ^{1}H NMR spectrum of HT-P6HexPy in $CDCl_3$. For comparison, the α-CH_2 signals of HH- and rand-P6HexPy[6] are depicted.

cast films of **3a**, rand-PPy, and HH-PPy, are electrochemically reduced with E_{pc} of –2.58, –2.52, and –2.62 V vs Ag^+/Ag, respectively. However, as shown in Figure 3, the powder XRD patterns of **3b** and HH-P6HexPy clearly indicate that they take significantly different packing modes. The peaks in the low angle region (peaks at d = 21.3 and 11.3 Å in Figures 3a and 3b, respectively) are considered to be assignable to the distance between polypyridine main chains separated by hexyl groups; similar assignment has been made for various alkylated regioregular π-conjugated poly(arylene)s.[1–4,6] The sharper diffraction peak of HH-P6HexPy suggests a higher order of packing in the solid. Regioirregular P6HexPy with an HT content of 55%[6] gives relatively broad XRD peaks at d = 14.1 and 4.40 Å. Due to the molecular assembly, the UV–vis peak position of **3b** at 309 nm in $CHCl_3$ is shifted to 327 nm in film, which is presumably caused by π–π interaction between the π-stacked HT-P6HexPy molecules. Cast films of regioirregular and HH-P6HexPy show absorption peaks at 326 and 324 nm, respectively.

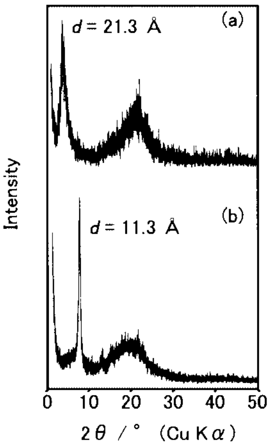


Figure 3. Powder XRD patterns of (a) **3b** and (b) HH-P6HexPy.

Reference and Notes

1 H. S. Nalwa, "Handbook of Organic Conductive Molecules and Polymers Vol. 2," Wiley, Chichester (1997); T. Yamamoto, *Bull. Chem. Soc. Jpn.*, **72**, 621 (1999); *Kagaku*, **56**, 24 (2001).
2 R. D. MaCullough, S. Tristam-Nagle, S. P. Lowe, R. D. Lowe, and M. Jayaraman, *J. Am. Chem. Soc.*, **115**, 4910 (1993).
3 T. Chen, X. Wu, and R. D. Rieke, *J. Am. Chem. Soc.*, **117**, 233 (1995).
4 T. Yamamoto, D. Komarudin, M. Arai, B.-L. Lee, H. Suganuma, N. Asakawa, K. Kubota, S. Sasaki, T. Fukuda, and H. Matsuda, *J. Am. Chem. Soc.*, **120**, 2047 (1998).
5 G. R. Newkome and W. W. Paudler, "Contemporary Heterocyclic Chemistry," Wiley, New York (1982).
6 T. Yamamoto, T. Maruyama, Z.-H. Zhou, T. Ito, T. Fukuda, Y. Yoneda, F. Begum, T. Ikeda, S. Sasaki, H. Takezoe, A. Fukuda, and K. Kubota, *J. Am. Chem. Soc.*, **116**, 4832 (1994); T. Yamamoto, M. Takeuchi, and K. Kubota, *J. Polym. Sci., Part B: Polym. Phys.*, **38**, 1348 (2000).
7 D. D. Gebler, Y. Z. Wang, J. W. Blatchford, S. W. Jessen, L. -B. Lin, T. L. Gustafson, H. L. Wang, T. M. Swager, A. G. MacDiarmid, and A. J. Epstein, *J. Appl. Phys.*, **78**, 4264 (1995).
8 F. Trécourt, G. Breton, V. Bonnet, F. Mongin, F. Marsais, and G. Quéguiner, *Tetrahedron*, **56**, 1349 (2000).
9 Analytical data for **3a**: Anal. Found: C, 75.33; H, 4.57; N, 16.85; Br, 1.39%. Calcd for $Br(C_5H_3N{\cdot}0.1H_2O)_{150}Br$: C, 74.73; H, 4.52; N, 17.43; Br, 1.33%. UV–vis spectrum (HCOOH) λ_{max}/nm: 365.