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Preparation and Properties of Poly(methylpyridine-2,5-diyl)s

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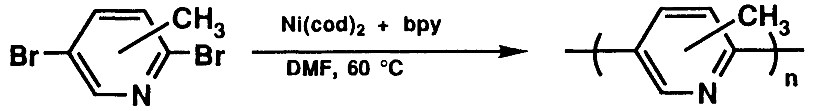
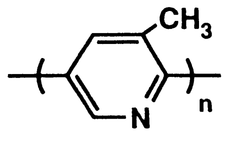
A series of poly(methylpyridine-2,5-diyl)s were synthesized by dehalogenation polycondensation of the corresponding 2,5-dibromo-methylpyridine with zerovalent nickel complexes. The polymers had molecular weight much higher than that of poly(pyridine-2,5-diyl). Poly(methylpyridine-2,5-diyl)s were converted into semiconducting material by chemical and electrochemical reduction (n-type doping).

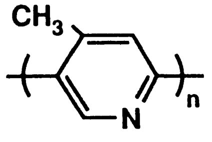
Electrically conducting polymers with π-conjugated systems along the polymer chain have been widely investigated in recent years. As for the π-conjugated electrically conducting polymers, various p-type polymers which are converted into the conducting material by oxidation have been synthesized. However kinds of n-type polymers which are converted into the conducting material by reduction are still limited. We previously reported poly(pyridine-2,5-diyl)[1)](PPy) and poly(2,2'-bipyridine-5,5'-diyl)[2)](PBPy) synthesized by dehalogenation polycondensation of 2,5-dibromopyridine and 5,5'-dibromo-2,2'-bipyridine, respectively, with zerovalent nickel complexes. These polymers were converted into the n-type conductor by the reduction. However, molecular weights of the obtained polymers were not sufficient, and obtaining the n-type poly(pyridine -2,5-diyl) or its derivatives with large molecular weight is desired for further use of the polymer to provide electric (e.g., p-n junction) and optical[3)] devices as well as catalysts like photo-catalyst.[4)] We now report synthesis of methyl-substituted PPy's shown in Eq. 1, which have considerably higher molecular



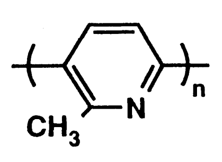
(1)



P3MePy



P4MePy



P6MePy

weight than PPy and are converted into the conducting material by the reduction. Modification of physical(e.g., solubility) and chemical properties of the π-conjugated poly(arylene)s by substitution with alkyl group has been reported.[5)]

Three kinds of 2,5-dibromo-methylpyridines were prepared by modifying a reported method.[6)] Stirring the monomer with a mixture of bis(1,5-cyclooctadiene)nickel(Ni(cod)$_2$), 1,5-cyclooctadiene(cod), and 2,2'-bipyridine(bpy) in N,N-dimethylformamide for 16 h at about 60 °C afforded a precipitate of the polymer. The polymers were isolated by a similar manner applied to the isolation of PPy.[1)] P3MePy and P6MePy were gray, whereas P4MePy was dark brown. Results of the polymerization are summarized in Table 1. As shown in Table 1, PMePy's were obtained in high yield.

Table 1. Polymerization of PMePys[a)]

	Yield / %	Mw[b)]	n[c)]	$[\eta]^{d,e)}$ / dlg^{-1}	λmax[f)] / nm
PPy[g)]	95	3800	50	0.85	375
P3MePy	80	16000	180	1.61	320
P4MePy	80	12000	130	1.01	310
P6MePy	90	27000	300	1.50	340

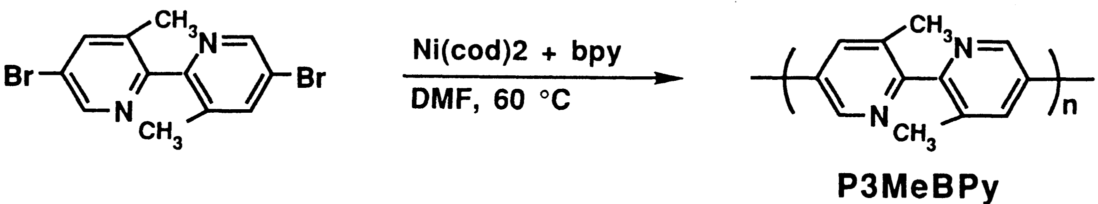
a) Monomer : Ni(cod)$_2$: cod : bpy = 1 : 1.5 : 1.5 : 1.5. b) Measured by the light scattering method. c) The degree of polymerization. d) The inherent viscosity. dlg^{-1}=100 cm^{3}g^{-1}. e) Measured in formic acid at 30 °C. f) Measured in formic acid. g) From Ref. 3.

PMePy's were, similarly to PPy,[1,3a)] soluble in the formic acid, showing λmax at 320 - 340 nm in the formic acid solution. UV-visible absorption peaks of PMePy's showed a blue shift compared with that of PPy presumably due to the steric hindrance of the methyl group on the coplanar pyridine rings. PMePy's gave rise to strong fluorescence both in formic acid and in solid state. A dilute HCOOH solution (2.0x10^{-5} mol of monomer unit / dm^3) of P3MePy showed fluorescence with a peak at about 430 nm when excited at 300 nm, the position being almost the same as that of monomer emission from PPy.[3b)]

The molecular weight of the polymer(Table 1) was measured by the light scattering method with the formic acid solution. The light scattering method revealed that PMePy's took random coil structure in the solution as judged their low degree of depolarization (ρv=0.03±0.02), in contrast to rigid rod-like structure of PPy (ρv=0.30).[1)] The molecular weight of PMePy's was much higher than that of PPy. The inherent viscosity of PMePy's was also higher than that of PPy.

Figure 1(a) shows the 270 MHz ^{1}H-NMR spectrum of P3MePy in CF$_3$COOD. The peak at 11.5 ppm is due to CF$_3$COOH as an impurity in CF$_3$COOD. As shown in Fig. 1(a), The ^{1}H-NMR spectrum of P3MePy showed two peaks at 2.55 and 2.73 ppm assigned to the pyridine ring-attached CH$_3$ protons of head-to-head and head-to-tail units, respectively. Assignment of the peaks was carried out by comparison of the ^{1}H-NMR spectrum with that of P3MeBPy which was constituted of only the head-to-head units and was synthesized in a similar manner applied to synthesis of PBPy (Eq. 2).[2)]

The ^{1}H-NMR spectrum of P3MeBPy showed only one peak at 2.55 ppm (Fig. 1(b)). Comparison of the ^{1}H-NMR spectra of P3MePy and P3MeBPy revealed that P3MePy contained the head-to-tail and the head-to-head units in 65 and 35%, respectively. The two aromatic protons in the pyridine ring appeared at δ=8.5-9.5 ppm. The ratio of the aromatic protons to CH_3 protons peaks was 2:3 in agreement with the structure shown in Eq. 1. The ^{1}H-NMR spectra of P4MePy and P6MePy were also reasonable for the structures shown in Eq. 1.$^{7)}$



(2)

The formic acid solution of P3MePy was spread on a Pt plate and subsequently dried under vacu-

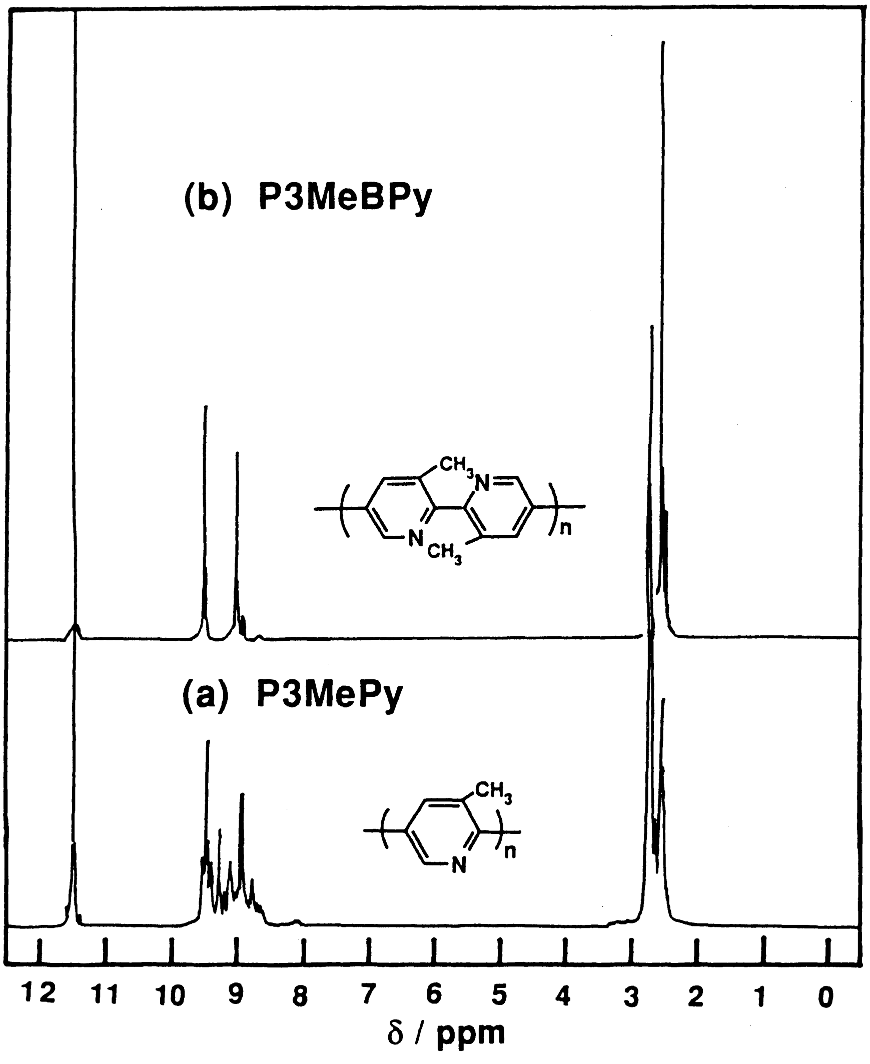
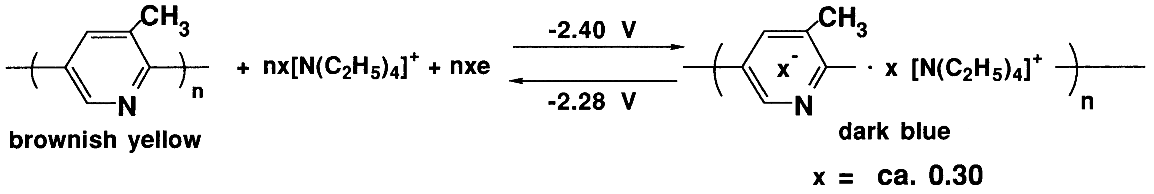


Fig. 1. ^{1}H-NMR spectra of P3MePy and P3MeBPy.

um. The cast film thus obtained had good mechanical strength. The cyclic voltammogram of the polymer film (in dry acetonitrile containing 0.10 M $[N(C_2H_5)_4]ClO_4$ at a scan rate of 20 mVs^{-1}; amount of P3MePy = ca. 0.01 $mgcm^{-2}$) showed electrochemically active peaks at -2.40 V and -2.28 V vs. Ag/Ag^+ ascribed to n-doping and undoping (Eq. 3), respectively. The doping level x was about 0.30 per the monomer unit. The redox processes were accompanied by color change of the film between brownish yellow and dark blue. These doping and undoping processes were repeated with no observable change for 50 cycles. In the oxidation (p-doping) region, P3MePy was electrochemically inactive. P4MePy and P6MePy also afforded essentially the same cyclic voltammograms (at a scan rate of 20 mVs^{-1}; amount of these polymers = ca. 0.01 $mgcm^{-2}$), giving rise to a couple of doping and undoping peaks at -2.46 V and -2.32 V for P4MePy and those at -2.44 V and -2.30 V for P6MePy, respectively. The doping and undoping potentials of PMePy's were not essentially affected by changing of the scanning rate in range of 10-100 mVs^{-1}. Treatment of PMePy's with a THF solution of sodium naphthalide at room temperature caused a color change from brownish yellow to reddish purple, and the insulating PMePy's (electrical conductivity $\sigma < 10^{-14}$ S cm^{-1}) became a semiconducting material having an electrical conductivity of about 1.0×10^{-4} S cm^{-1} by the chemical reduction.



(3)

TGA analysis of PMePy's showed that they were thermally stable without any observable weight loss up to 250 °C in nitrogen.

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7) ^1H-NMR(CF_3COOD). P4MePy: δ 2.8-3.3(br, 3H, $-CH_3$), 8.6(br, 1H, 3-H at pyridine(Py)-ring), 9.7(br, 1H, 6-H at Py-ring). P6MePy: δ 2.6-3.4(br, 3H, $-CH_3$), 8.1-9.4(m, 2H, 3-H and 4-H at Py-ring).

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