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Preparation and Properties of Highly Electron-accepting Poly(pyrimidine-2,5-diyl)

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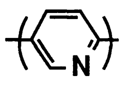
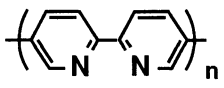
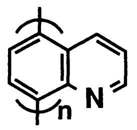
Reaction of 2,5-dibromopyrimidine with a zero-valent nickel complex affords poly(pyrimidine-2,5-diyl). This new polymer is easily converted into electrical conducting materials by chemical and electrochemical reductions, the latter reduction occurring at the highest potential (-1.75 V *vs.* Ag/Ag^+) among reported π-conjugated polymers.

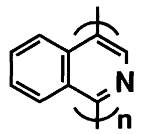
Preparation and electrical properties of poly(arylene)s having π-conjugation system along the polymer chain are the subject of recent interest. However, most of reported poly(arylene)s such as poly(pyrrole-2,5-diyl)1) and poly(thiophene-2,5-diyl)2) show p-type electrically conducting properties, and preparation of n-type electrically conducting poly(arylene)s has been limited.

Recently, preparation of poly(pyridine-2,5-diyl),3) poly(2,2'-bipyridine-5,5'-diyl)3c,d) and poly(quinolinediyl)s4) by dehalogenation polycondensation of corresponding dihalogenated aromatic compounds with zero-valent nickel complex has been reported. Poly(quinolinediyl) derivatives also have been prepared by Friedlander reaction.5) These polymers exhibit n-type electrically conducting properties, which is considered to originate from π-deficient nature of the aromatic units containing an electron-withdrawing imine nitrogen.6) On these bases, it is considered to be of interest to design and prepare poly(arylene)s constituted of higher electron-accepting aromatic units having more imine nitrogens.

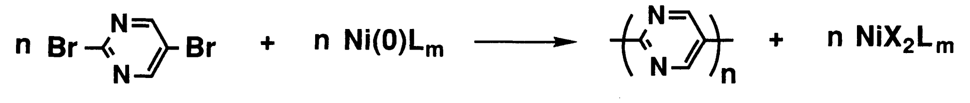

poly(pyridine-
2,5-diyl)


poly(2,2'-bipyridine-
5,5'-diyl)


poly(quinoline-
5,8-diyl)


poly(isoquinoline-
1,4-diyl)

We now report preparation of new poly(arylene), poly(pyrimidine-2,5-diyl) PPym, by dehalogenation polycondensation of 2,5-dibromopyrimidine with a zero-valent nickel complex.7) This polymer has two electron-withdrawing imine nitrogens in main chain ring, and shows highly electron accepting properties to be converted into n-type semiconducting materials.



(1)

$Ni(0)L_m$: zero-valent nickel complex (a mixture of bis(1,5-cyclooctadiene)nickel(0), $Ni(cod)_2$, and 2,2'-bipyridine, bpy)

2,5-Dibromopyrimidine was prepared by a method reported by Arantz and Brown.[8] Stirring 2,5-dibromopyrimidine (360 mg, 1.51 mmol) with a mixture of bis(1,5-cyclooctadiene)nickel $Ni(cod)_2$ (510 mg, 1.85 mmol), 1,5-cyclooctadiene (0.35 cm^3), and 2,2'-bipyridine (300 mg, 1.92 mmol) in N,N-dimethylformamide (25 cm^3) for 48 h at about 60 °C afforded a precipitate of a reddish yellow polymer. Work up of the polymer, involving removal of nickel compounds with ethylenediaminetetraacetic acid, was carried out in a manner similar to that reported previously.[3,4] Reddish yellow PPym was obtained in high yield (85%). Elemental analysis of the polymer showed negligible halogen content. Anal : Found: C, 57.7; H, 2.7; N, 32.1; Br, 0.0%. Calcd for $(C_4H_2N_2 \cdot 0.3\ H_2O)_n$: C, 57.6; H, 3.1; N, 33.6%. The analytical data and absorption bands at 3450 and 1640 cm^{-1} in the IR spectrum indicate addition of H_2O to the polymer.

PPym is soluble in concd HCl, HNO_3, and H_2SO_4. UV-visible spectrum of a concd H_2SO_4 solution of PPym shows a π-π^* absorption peak at 361 nm. The light scattering technique applied for a concd H_2SO_4 solution of PPym shows that the polymer has molecular weight of 82000.[9]

Figure 1 shows IR spectra of 2,5-dibromopyrimidine and PPym. The IR spectrum of PPym is essentially similar to that of 2,5-dibromopyrimidine, and ν(C-Br) band (428 cm^{-1} for 2,5-dibromopyrimidine) is almost negligible.

Figure 2 shows ^{13}C CP/MAS NMR spectrum of PPym in the solid state at room temperature. The peaks for the carbon groups

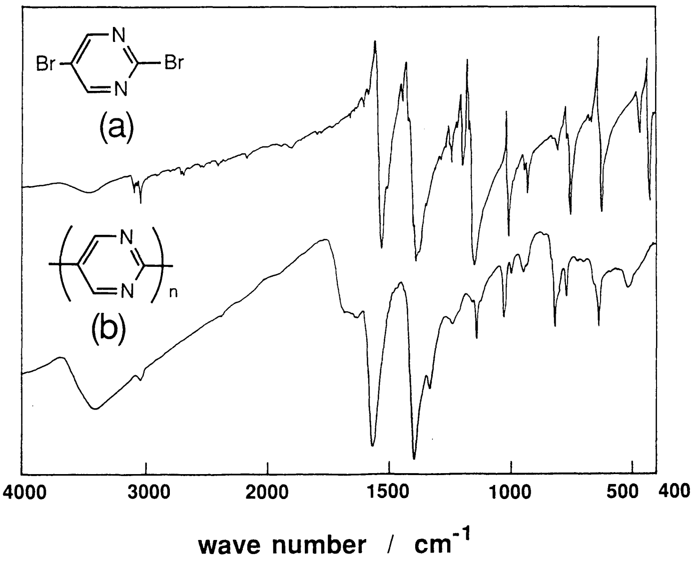


Fig. 1. Infrared spectra of (a) 2,5-dibromopyrimidine and (b) poly(pyrimidine-2,5-diyl) (PPym).

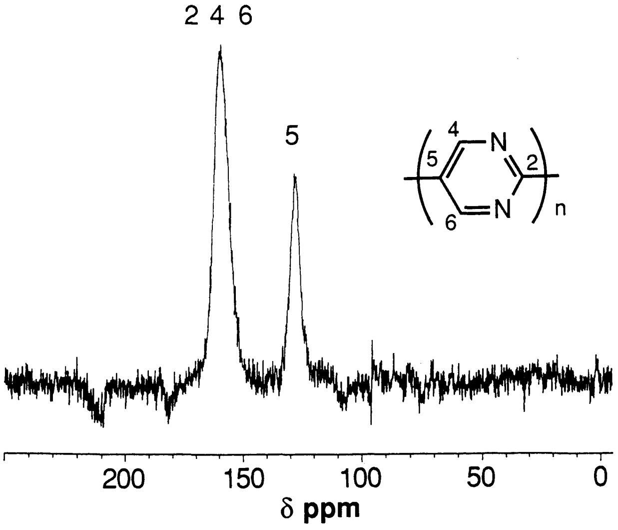


Fig. 2. ^{13}C CP/MAS spectrum of poly(pyrimidine-2,5-diyl) (PPym).

have been assigned on the basis of solution ^{13}C-NMR data of pyrimidine and 2,5-dibromopyrimidine. A peak at δ 160-145 ppm is assigned to an overlapped peak of 2-C, 4-C, and 6-C carbons of pyrimidine ring, and another peak assigned to 5-C carbon is observed at δ 135-120 ppm.

The elemental analysis, molecular weight measurement, and IR and NMR data shown above indicate that the present preparation method affords the proposed poly(pyrimidine-2,5-diyl).

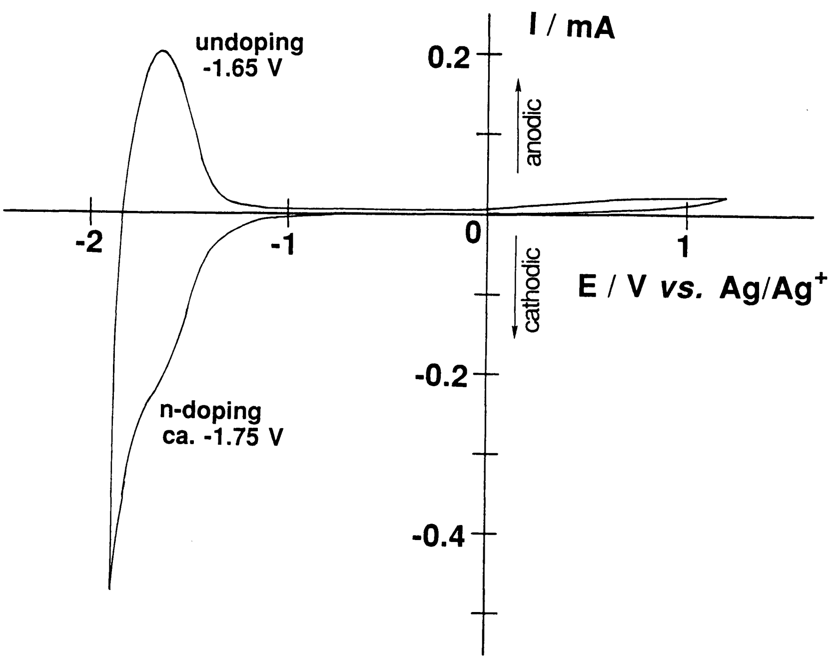
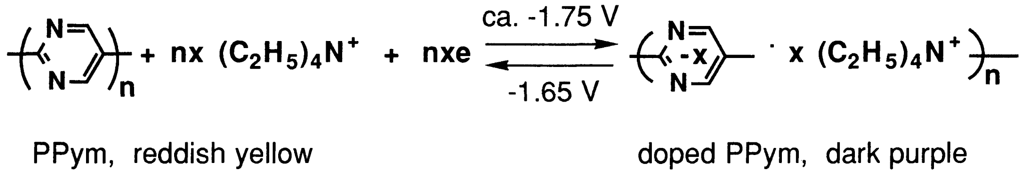


Fig. 3. Cyclic voltammogram of a film of poly(pyrimidine-2,5-diyl) (PPym) on platinum plate in an acetonitrile solution of $[(C_2H_5)_4N]ClO_4$ (0.1 M). Sweep rate = 5 mV s^{-1}.

Figure 3 shows cyclic voltammogram (CV) of PPym. Platinum plates coated with film of PPym is prepared by spreading the concd HCl solution of PPym on platinum plate and ensuing evaporation of the solvent under vacuum. As shown in Fig. 3, the PPym film gives rise to an electrochemically active cycle in the reduction region, showing an n-doping peak at about *ca.* -1.75 V *vs.* Ag/Ag$^+$ and an undoping peak at -1.65 V. Color of PPym changes from reddish yellow to dark purple during reduction. However, the polymer film was electrochemically inert in an oxidation region up to +1.0 V *vs.* Ag/Ag$^+$. The polymer film electrode is stable during repeated scanning, showing essentially the same CV and color change. These results suggest the n-type doping properties of PPym.



(2)

The CV result and color change resemble to those of poly(pyridine-2,5-diyl),$^{3)}$ poly(2,2'-bipyridine-5,5'-diyl),$^{3d)}$ poly(quinoline-5,8-diyl)$^{5)}$ and poly(isoquinoline-1,4-diyl).$^{5)}$ Table 1 summarizes potentials for the n-doping and undoping of these polymers estimated by the cyclic voltammetry measurement. As shown in Table 1, PPym gives rise to the electrochemical reduction potential with smallest absolute value. These results reveal that the introduction of two electron-withdrawing imine nitrogens in the main chain ring raises an electron accepting property of the poly(arylene).

Non-doped PPym was essentially an insulator with electrical conductivity (σ) of 7.1×10^{-11} S cm^{-1}. Doping of PPym with sodium and iodine afforded electrically conducting material. Sodium-doped sample was obtained by treatment of the polymer with sodium naphthalide in THF at room temperature, whereas an exposure of the polymer to vapor of iodine gives iodine-doped samples. Sodium-doped PPym shows electrical conductivity of 1.2×10^{-4} S cm^{-1}. Iodine-doped samples also show electrically conducting properties, but the σ values are not so high (1.5×10^{-5} S cm^{-1}).

Table 1. n-Doping and undoping peak potentials of poly(arylene)s[a)]

Polymer	$E_{red}{}^{b)}$ / V	$E_{ox}{}^{c)}$ / V
Poly(pyrimidine-2,5-diyl) (PPym)	ca. -1.75	-1.65
Poly(pyridine-2,5-diyl)[d)]	-2.24	-1.98
Poly(2,2'-bipyridine-5,5'-diyl)[d)]	-2.40	-2.00
Poly(quinoline-5,8-diyl)[e)]	-2.46	-2.29
Poly(isoquinoline-1,4-diyl)[e)]	-2.08	-1.96

a) *vs.* Ag/Ag^+ in an acetonitrile solution of $[(C_2H_5)_4N]ClO_4$. b) Cathodic peak potential for n-doping. c) Anodic peak potential for undoping. d) From Ref. 3. e) From Ref. 4.

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9) K. Kubota and B. Chu, *Biopolymers*, **22**, 1461 (1983). Since linear rod-like polymers like PPym may coagulate with each other, further examination of the solution may be necessitated for obtaining accurate value of the molecular weight.

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