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Preparation and Properties of Poly(2,2'-bipyridine-5,5'-diyl)

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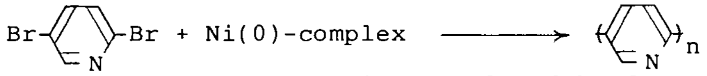
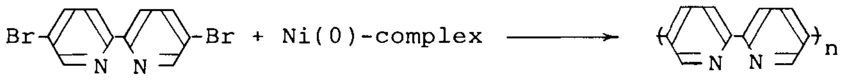
A reaction of 5,5'-dibromo-2,2'-bipyridine with a zero-valent nickel complex affords poly(2,2'-bipyridine-5,5'-diyl), which has physical and electrically conducting properties similar to those of poly(2,5-pyridinediyl) and forms complexes with Fe^{2+} and Ru^{2+}.

Dehalogenation polycondensation of 2,5-dibromopyridine with Ni(0)-complexes affords thermally stable and n-type electrically conducting poly(2,5-pyridinediyl) (PPy), which is soluble in formic acid and has linear rod-like structure.1)



(PPy) (1)

PPy is considered to consist mostly of head-to-tail units; content of head-to-head unit corresponding to 2,2'-bipyridine (bpy) in PPy is small and PPy does not show apparent coordinating ability toward Fe^{2+}. As an extension of our studies on poly(arylene)s, we have applied such dehalogenation polycondensation with Ni(0)-complex to obtain a new electrically conducting polymer, poly(2,2'-bipyridine-5,5'-diyl), which serves polymer chelate ligand.



(PBpy) (2)

5,5'-Dibromo-2,2'-bipyridine (bpy-Br_2) was prepared by modifying a method reported for the preparation of 5,5'-dichloro-2,2'-pyridine.2) Stirring bpy-Br_2 (584 mg, 1.87 mmol) with a mixture of bis(1,5-cyclooctadiene)nickel (639 mg, 2.32 mmol), 1,5-cyclooctadiene (0.8 cm^3), and bpy (348 mg, 2.23 mmol) in N,N-dimethylformamide (12 cm^3) for 20 h at about 70 °C afforded a precipitate of a yellow polymer. Work up of the polymer in a similar manner applied to the isolation of PPy1) gave 278 mg (yield = 97%) of a yellow polymer. Elemental analytical results of the polymer were reasonable for PBpy and showed containing of 1.2% of Br due to the terminal unit(s).

Table 1 summarizes comparison of properties of PPy and PBpy thus obtained. PBpy is also soluble in formic acid, showing λ_{max} at 372 nm in the formic acid solution, and the light scattering technique3) shows that the polymer has molecular weight of about 1400. Use of higher amount of $Ni(cod)_2$ (2.0 mol/mol of bpy-Br_2) gave the polymer with higher molecular weight (3200). PBpy was not soluble in other usual organic solvents tested. PBpy gives rise to relatively sharp diffraction bands in the powder X-ray diffraction pattern. On the other hand, X-ray diffraction pattern of Ppy showed only broad diffraction bands presumably due to contamination with the head-to-head unit. IR spectrum of PBpy was essentially the same as that of PPy except for some difrerence in a δ(C-H) region (600-1100 cm^{-1}; peaks (in cm^{-1}): 1072s, 1025s, 995s, 926w, 831vs, 795m, 741s, 651w, 634w). $^{13}C\{^{1}H\}$-NMR spectrum of PBpy showed reasonable aromatic carbon signals from 125 to 149 ppm (main peaks at 124.1, 125.4, 138.9, 143.4 and 147.8 ppm with additional peaks which may be due to presence of both cis- and trans-microstructures in the polymer chain).

Treatment of PBpy with sodium naphthalide in THF at room temperature gave a reddish black n-doped PBpy which showed electrical conductivity of 1.6×10^{-1} S cm^{-1} as measured with a pellet obtained by pressing the doped polymer powder at 200 kg cm^{-2}.

Table 1. Comparison of Properties of PPy and PBpy

	Solvent	λ_{max}/nm	Thermal staBility[a]	Powder X-ray diffraction	Doping
PPy	HCOOH	372	ca. 260 °C	broad	n-type(σ=1.1x10^{-1} S cm^{-1})
PBpy	HCOOH	374	ca. 270 °C	relatively sharp[b]	n-type(σ=1.6x10^{-1} S cm^{-1})

a) Temperature where weight loss of the polymer starts (measured by TGA).
b) Two strong diffractions at 5.377 and 7.561 A, respectively, were observed.

Treatment of PBpy with $FeSO_4$ and $RuCl_3$ (in a 3 : 1 ratio) in an aqueous and ethanolic solutions, respectively, afforded a reddish brown and dark brown precipitates, respectively, presumably due to gelation through formation of intermolecular chelate complexes. The color of the precipitate obtained in the treatment with Fe^{2+} resembled wine red color of $[Fe(bpy)_3]^{2+}$. However, the color of the precipitate obtained in the treatment with $RuCl_3$ was different from that of $[Ru(bpy)_3]^{2+}$, suggesting that the electronic state of Ru or the ligand in the polymer complex was different from those in $[Ru(bpy)_3]^{2+}$. Treatment of PPy with $FeSO_4$ did not cause apparent color change.

We are grateful to Professor Kubota of Gunma University for measuring molecular weight of PBpy.

References

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2) S. Oae, T. Kawai, and N. Furukawa, Phosphorus and Sulfur, 34, 123 (1987).
3) K. Kubota and B. Chu, Biopolymers, 22, 1461 (1983). The special refractive index increment of PBpy in formic acid (n_0 = 1.37) was 0.55 cm^3 g^{-1} at 488 nm (Ar laser).

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