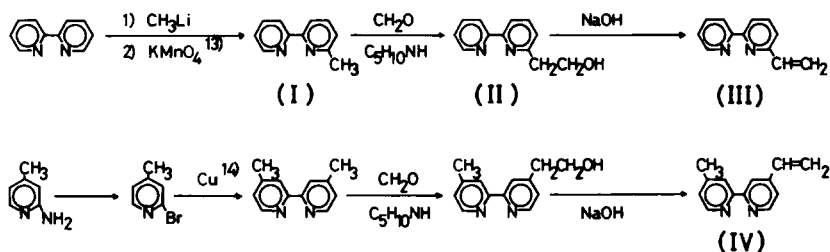


Preparation of Poly(vinyl-2,2'-Bipyridine) and Complex Formation with Various Metal Ions

The photochemistry of 2,2'-bipyridine complexes of transition metal salts has been the subject of recent research activities (1,2). The bipyridine complexes are particularly suitable for light-induced electron transfer processes related to photochemical conversion of solar energy (3-7).

Our effort to explore the role of synthetic polymers as photochemical reaction sites has been directed to the preparation of poly(vinyl-2,2'-bipyridine) which could afford the stable assemblies of transition metal complexes (8). Poly(styryl-2,2'-bipyridine) has been characterized by Card and Neckers (9), in which 2,2'-bipyridine was bound to poly(styrene-co-divinylbenzene) beads. Poly[styryl-Ru(bpy)₃²⁺] has been investigated by Kaneko, Yamada, and Kuri-mura (10). The preparation of 4-vinyl-4'-methyl-2,2'-bipyridine (11) and electrochemical polymerization of its ruthenium (II) and iron (II) complexes (12) have recently been reported.

In this communication, we wish to report the synthesis and the polymerization of 6-vinyl-2,2'-bipyridine (6-vinyl-bpy) and 4-vinyl-4'-methyl-2,2'-bipyridine (4-vinyl-4'-Me-bpy), and the complex formation of these polymers with various transition metal salts.



Scheme I. Preparation of 6-vinyl-bpy and 4-vinyl-4'-Me-bpy.

6-Vinyl-bpy and 4-vinyl-4'-Me-bpy were prepared according to Scheme I. 6-Methyl-2,2'-bipyridine (I) was prepared by the method of Woltermann (46% yield, bp 89°C/0.4 torr) (13). Hydroxymethylation of I (18.8 g, 0.11 mol) with 35% aqueous formalin (15.8 g, 0.18 mol) was carried out in the presence of a catalytic amount of piperidine (0.4 g) under nitrogen pressure at 160-170°C using a magnetic stirring autoclave. The reaction mixture was chromatographed on neutral alumina (Woelm N-Super I) with ethyl acetate to give a viscous liquid, 6-(β-hydroxyethyl)-2,2'-bipyridine (II) (5.66 g) in 26% yield. Treatment of a mixture of II (2.72 g) and p-tert-butylpyrocatechol (trace amount) as a radical inhibitor with powdered sodium hydroxide (0.15 g) under reduced pressure (0.4 torr) at 120°C in a kugelrohr distillation apparatus afforded a clear and viscous liquid, 6-vinyl-bpy (III) (1.92 g), in fairly good yield (78%).

TABLE I

The Extents of Metal Salt Incorporation
in Poly(6-Vinyl-Bpy) (V)

Metal Salts	$[M]_0/[bpy]_0^a$	$[P-M]/[bpy]_0^b$
CoCl ₂	0.958	0.905
	1.916	1.03
CuBr ₂	0.953	0.945
	1.906	0.980
Ni(NO ₃) ₂	0.955	0.693
	1.909	0.79
FeCl ₃	0.969	0.798
	1.62	0.827
	3.03	0.927
FeCl ₃	1.00	0.819
	2.00	0.886

^aInitial molar ratio of metal salts to bipyridine group.

^bMolar ratio of bound metal to bipyridine group in the polymer.

ANAL. Calcd for C₁₂H₁₀N₂: C, 79.35%; H, 5.61%; N, 15.45%; M, 182.
Found: C, 79.10%; H, 5.53%; N, 15.37%; M⁺, 182.

Starting from 4,4'-dimethyl-2,2'-bipyridine (14) using similar procedures, 4-vinyl-4'-Me-bpy (IV) was obtained in 77% yield (mp 85-88°C).

ANAL. Calcd for C₁₃H₁₂N₂: C, 79.56%; H, 6.16%; N, 14.27%; M, 196.
Found: C, 79.42%; H, 6.16%; N, 14.26%; M⁺, 196.

Free radical polymerization of III (1.82 g) was carried out in benzene (10 mL) using 2,2'-azobisisobutyronitrile (4.1 mg) at 60°C for 16 h. Poly(6-vinyl-bpy) (V) (1.20 g) was isolated by precipitation with methanol and purified by two dissolution-precipitation steps, followed by drying under reduced pressure (conversion 66%, $[\eta] = 0.47$ benzene, 30°C). V was soluble in benzene, tetrahydrofuran (THF), chloroform, and dimethylformamide (DMF) and insoluble in water, methanol, ether, and dimethylsulfoxide. However, it turned out that V becomes soluble in water by the complexation with various transition metal salts, such as Co²⁺, Cu²⁺, Fe²⁺, Fe³⁺, Ni²⁺, and Ru²⁺ (15). Similarly IV (1.0 g) gave poly(4-vinyl-4'-Me-bpy) (VI) at 68% conversion. VI was insoluble in common organic solvents because of crosslinking. Crosslinkage could be attributed to the chain transfer to the methyl group of the IV unit or the possible existence of undetectable amount of 4,4'-divinyl-2,2'-bipyridine as a cross-linking reagent.

TABLE II

The Extents of Metal Salt Incorporation
in Poly(4-Vinyl-4'-Me-Bpy) (VI)

Metal Salts	$[M]_0/[bpy]_0^a$	$[P-M]/[bpy]_0^b$
$CoCl_2^c$	1.24	0.79
$CuBr_2^c$	1.89	0.95
$Ni(NO_3)_2^c$	2.01	0.31
$FeCl_3^c$	1.28	0.77
$FeCl_2^d$	1.25	0.22

^aInitial molar ratio of metal salts to bipyridine group.

^bMolar ratio of bound metal to bipyridine group in the polymer.

^cIn DMF.

^dIn H₂O-THF (1:1 v/v).

The complexation of V with transition metal salts such as $Co(II)Cl_2$, $Cu(II)Br_2$, $Fe(II)Cl_2$, $Fe(III)Cl_3$, and $Ni(II)(NO_3)_2$ was studied in THF. In the standard procedure, a THF solution of V was mixed with a THF solution of metal salt at 25°C. The complexation was remarkably facile and the polymer complex precipitated out after a short period of stirring. The amount of metal ion bound to V was determined from the spectrophotometric analysis of the residual metal ion in the supernatant solution. The results are summarized in Table I. When the initial concentration of metal ion was altered from one to three times that of bpy unit of V, the extent of metal ion incorporation went up to almost one. It is clear that the bpy ligand on V readily forms stable 1:1 complexes with these metals.

The stability of the polymer (V) complex was compared with a model complex of Cu^{2+} . The electronic absorption spectrum of the polymer complex showed maxima at 304 and 318 nm, while $Cu(bpy)^{2+}$ had maxima at 300 and 310 nm. Assuming the formation of 1:1 complex, the stability constant of the polymer complex $\log K = 5.5$ was obtained on the basis of the change of absorbance at 318 nm. Compared with $\log K = 6.33$ for the 2,2'-bipyridine- $Cu(II)Cl_2$ system (16), the difference may be derived from the sterical disadvantage of the polymer backbone, i.e., the 6-substituent will hinder the coordination of metal ion.

VI was found to swell to a voluminous gel in DMF. The complexation of VI with $Co(II)Cl_2$, $Cu(II)Br_2$, $Fe(III)Cl_3$, and $Ni(II)(NO_3)_2$ was much slower than that of V. The extent of metal ion incorporation varied with metals as shown in Table II. For Cu^{2+} , 1:1 complex was formed. For Ni^{2+} , Co^{2+} , and Fe^{3+} , 1:1 stoichiometry was not achieved.

Fe^{2+} ion is known to form a reddish tris(2,2'-bipyridine) complex as an equilibrium mixture of 1:1, 1:2, and 1:3 complexes (17). Fe^{2+} formed only

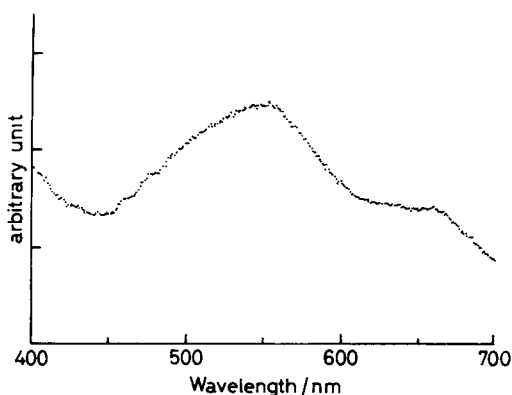


Fig. 1. Photoacoustic spectrum of poly(4-vinyl-4'-Me-bpy) (VI)-Fe²⁺ complex.

1:1 complex with V and there was no spectral evidence for the existence of tris-bpy (Table I). On the other hand, when the polymer VI, swollen in THF/H₂O (1:1 v/v) solution, was mixed with an excess of FeCl₂, the gel turned red. The ratio $[P\text{-Fe}^{2+}]/[\text{bpy}]_0$ was found to be 0.22. The photoacoustic spectrum (18) of the precipitated polymer VI-Fe²⁺ complex exhibited a maximum at ca. 550 nm, which corresponds to 520 nm of Fe(bpy)₃²⁺ (19) (Fig. 1), thus indicating the existence of tris(bipyridine)-type complexation in the polymer VI.

Compared with V, VI has no sterical disadvantage of the polymer backbone to the coordination sites. Furthermore, VI can also facilitate the high local concentration of the ligand because of crosslinking. The stoichiometry which was found for Fe³⁺, Ni²⁺, and Co²⁺ in the polymer VI system may be interpreted in terms of the formation of poly-bpy complexes.

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