

PREPARATION AND PROPERTY OF POLYMERIC PENDANT $\text{Ru}(\text{bpy})_3^{2+}$ COMPLEXES*

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ABSTRACT

Polymeric pendant $\text{Ru}(\text{bpy})_3^{2+}$ complexes were prepared from homopolymer and copolymers of 4-methyl-4'-vinyl-2,2'-bipyridine (Vbpy). Vbpy was prepared from 4-methylpyridine. The comonomers were styrene (St), acrylic acid (AA), N-vinylpyrrolidone (Pyr), 4-vinylpyridine (Vpy), methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), acrylonitrile (AN) and N-ethyl-4-vinylpyridium bromide (EQ-Vpy). The fraction of the pendant $\text{Ru}(\text{bpy})_3^{2+}$ repeating unit in the polymeric complex was 0.022 to 0.052. Absorption maximum, molar extinction coefficient, emission maximum and relative emission intensity of the polymeric complexes were studied.

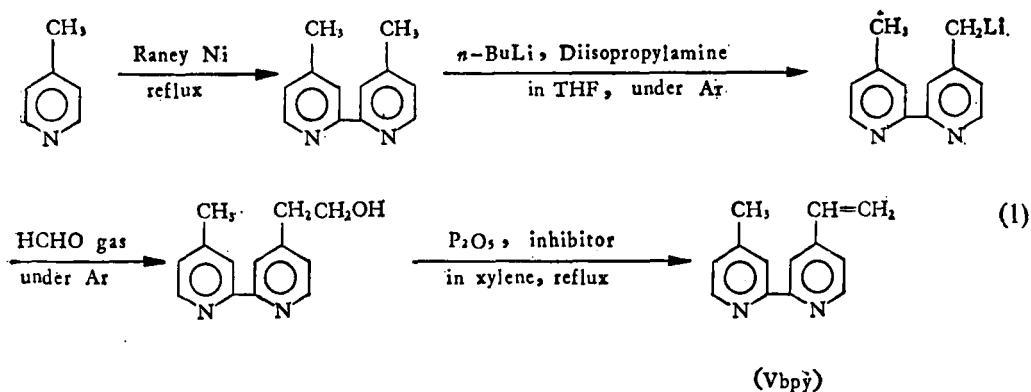
Water photolysis with visible light has attracted much attention in chemical conversion of solar energy. Tris (2, 2'-bipyridine) ruthenium (II) complex $\text{Ru}(\text{bpy})_3^{2+}$ is taken as a photoreaction center for that purpose^[1, 2]. Since the construction of heterogeneous reaction phase is a crucial point for designing photochemical conversion system^[3-5], utilization of synthetic polymer is adequate. The authors have prepared polymeric pendant $\text{Ru}(\text{bpy})_3^{2+}$ complexes starting from poly(styrene)^[6, 7] and poly(styrene-co-vinylbipyridine)^[8] for use as heterogeneous photocatalysts. In this article 4-methyl-4'-vinyl-2,2'-bipyridine (Vbpy) homopolymer and copolymer with seven vinyl monomers were prepared and their properties were studied.

EXPERIMENTAL

1. Preparation of 4-methyl-4'-vinyl-2,2'-bipyridine (Vbpy)

Vbpy was prepared from 4-methylpyridine by a modified literature method^[9]. This process is shown as follows:

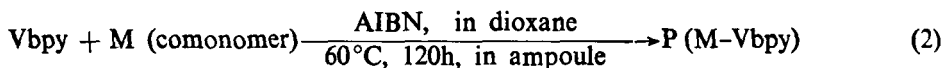
* Received February 24, 1984



Crude yield of the Vbpy was about 70% based on 4-methylpyridine and the Vbpy was purified by recrystallization with *n*-hexane.

2. Copolymerization of Vbpy

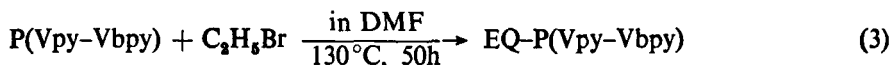
Copolymers, P(M-Vbpy), were prepared from the Vbpy and seven vinyl monomers by the similar method reported^[8]. This process is:



Where M is styrene, acrylic acid, N-vinylpyrrolidone, 4-vinylpyridine, methyl methacrylate, 2-hydroxyethyl methacrylate or acrylonitrile, respectively.

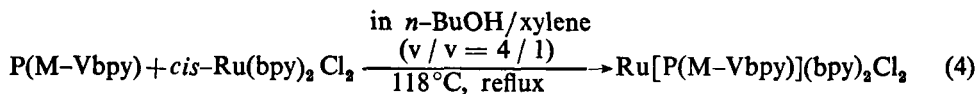
The Vbpy was copolymerized with the vinyl comonomers (M) (molar ratio of M/Vbpy = 20/1 in dioxane) with 2,2'-azobisisobutyronitrile (molar ratio 0.2%) as initiator. The concentration of the Vbpy in dioxane was 0.05M. The obtained copolymers were purified by reprecipitation in petroleum ether.

Cation pendant copolymer, EQ-P(Vpy-Vbpy), quaternized with bromoethane was prepared from the copolymer, P(Vpy-Vbpy), where Vpy is 4-vinylpyridine^[11]. The process is:



3. Preparation of polymeric pendant Ru(bpy)₃²⁺ complexes

Polymeric pendant Ru(bpy)₃²⁺ complexes were formed from the homopolymer and the copolymers by the similar method reported^[8].



The concentration of the Ru complex is 10⁻³ or 10⁻⁴M. The molar ratio of Ru / bpy unit of polymer was 1/2 or 1.

The change of visible spectrum during the formation of Ru(bpy)₃²⁺ type complex with time was measured by the spectrophotometer Hitach 320. The complex formation between P(M-Vbpy) and cis-Ru(bpy)₂Cl₂ was followed by the decrease of the absorption maximum

538 nm due to Ru (bpy)₂Cl₂ and the increase of that 452–457 nm due to polymeric pendant tris(bpy)-type complex. The complex formation was completed after during the range of 2.5 to 216 h, then the complexes were purified by dialysis in water or by extraction.

4. Measurement of the photochemical property

Emission spectra of the polymeric pendant Ru complexes were measured by the Fluoroscpectrophotometer Hitach MPF-4, at the concentration of 10⁻⁵ M under argon.

RESULTS AND DISCUSSION

The IR and ¹H NMR spectra of 4-methyl-4'-vinyl-2,2'-bipyridine (Vbpy) shown in Figs. 1 and 2

These spectra have not been reported yet. IR absorption peaks of Vbpy and their assignment were shown in Table 1. The chemical shift of Vbpy in ¹H NMR spectrum was shown in Table 2.

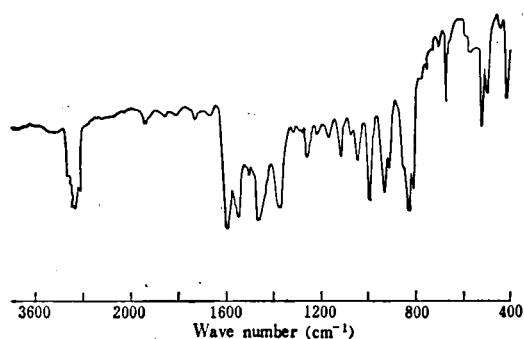


Fig. 1 Infrared spectrum of 4-methyl-4'-vinyl-2,2'-bipyridine (Vbpy)

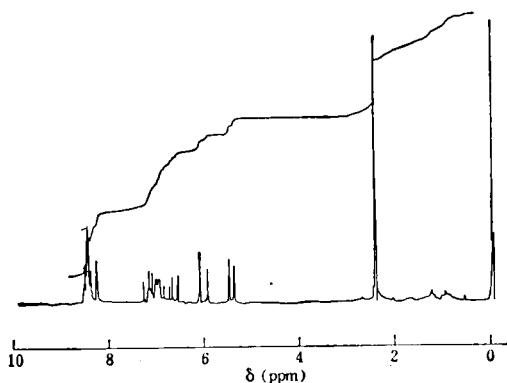


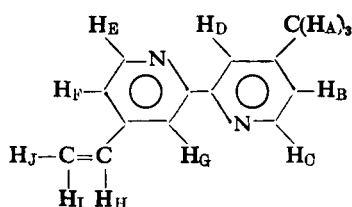
Fig. 2 ¹H NMR spectrum of 4-methyl-4'-vinyl-2,2'-bipyridine (in CCl₄)

Table 1 IR absorption peaks and their assignment of Vbpy

Absorption peak (cm) ⁻¹	Assignment
3045, 2900	ν_{CH} (arom)
2910, 2840	ν_{CH} (aliph)
1590, 1545	$\nu_{\text{C}=\text{C}}, \text{C}=\text{N}$
1460, 1365	δ_{CH} (CH ₃)
1250	ν_{CN} (arom)
1110, 1070	δ_{CH} (in plane)
930*	δ_{CH} (vinyl)
850*, 830*, 810*	δ_{CH} (1,2,4-substituted)

* Specific to Vbpy.

Table 2 Chemical shift of Vbpy



δ (ppm)		Assignment
2.40	(s)	H _A
5.42	(d)	H _I
6.00	(d)	H _J
6.68	(q)	H _H
6.96	(d)	H _B
7.10	(q)	H _F
8.24	(s)	H _D
8.36	(q)	H _G
8.42	(d)	H _O
8.48	(d)	H _E

s: singlet d: doublet q: quartet

These IR and NMR data show that Vbpy has been prepared. The purity of the Vbpy calculated to be about 98% from the NMR spectrum. The yield and the composition of the copolymers obtained from Vbpy and vinyl comonomers were shown in Table 3. The composition was obtained from elementary analysis and NMR spectrum.

Table 3 The yield and the composition of Vbpy copolymers $-M_x-(Vbpy)_y-$

Copolymer	Comonomer (M)	Polymer yield(%)	X	Y
P(St-Vbpy)	styrene	30.8	0.956	0.044
P(AA-Vbpy)	acrylic acid	17.5	0.924	0.076
P(Pyr-Vbpy)	N-vinylpyrrolidone	76.6	0.980	0.110
P(Vpy-Vbpy)	4-vinylpyridine	58.1	0.941	0.059
P(MMA-Vbpy)	methylmethacrylate	90.2	0.958	0.042
P(HEMA-Vbpy)	2-hydroxyethyl methacrylate	91.6	0.972	0.028
P(AN-Vbpy)	acrylonitrile	41.7	0.917	0.083
EQ-P(Vpy-Vbpy)	N-ethyl-4-vinylpyridinium bromide	50.4	0.930*	0.059*

* The repeating unit, $-(Vpy)_{0.011}-$ is added

Intrinsic viscosities of the prepared homopolymer and copolymers of Vbpy were determined, and the molecular weights of the copolymers was estimated from the known K and α values of the corresponding homopolymer listed in Table 4.

Table 4 Intrinsic viscosities and estimated molecular weights of the homopolymer and copolymers of Vbpy

Polymer	Solvent	$[\eta]$ (dl/g)	K	α	Molecular weight *
P(Vbpy)	DMF	0.4			
P(St-Vbpy)	Benzene	0.28	22.7×10^{-5}	0.72	2×10^4
P(AA-Vbpy)	H_2O (NaOH 2M)	0.09	44.2×10^{-5}	0.64	4×10^3
P(Pyr-Vbpy)	H_2O	0.19	67.6×10^{-5}	0.55	3×10^4
P(Vpy-Vbpy)	EtOH	0.50	25×10^{-5}	0.68	7×10^4
P(MMA-Vbpy)	Benzene	1.06	7.24×10^{-6}	0.76	3×10^5
P(HEMA-Vbpy)	DMF	0.46**			
P(AN-Vbpy)	DMF	0.35	24.3×10^{-5}	0.75	2×10^4
EQ-P(Vpy-Vbpy)	H_2O	0.16			

Measured at 25°C.

* Estimated from $[\eta] = KM^{\alpha[10]}$.

** Soluble part in DMF.

Conditions for the preparation of polymeric pendant $\text{Ru}(\text{bpy})_3^{2+}$ from P(M-Vbpy) and *cis*- $\text{Ru}(\text{bpy})_2\text{Cl}_2$, and the results were shown in Table 5.

Table 5 Preparation conditions of polymeric pendant $\text{Ru}(\text{bpy})_3^{2+}$ complexes and their yields

Polymer complex	Starting polymer	Solvent	Vbpy unit/Ru (mol. ratio)	$\text{Ru}(\text{bpy})_2\text{Cl}_2$ (M)	Reaction time (h)	Yield (wt. %)
$\text{Ru}(\text{PVbpy})(\text{bpy})_2^{2+}$	P(Vbpy)	mix. *	1 / 1	10^{-3}	48	49.6
$\text{Ru}[\text{P}(\text{St-Vbpy})](\text{bpy})_2^{2+}$	P(St-Vbpy)	mix. *	2 / 1	5×10^{-4}	48	96.2
$\text{Ru}[\text{P}(\text{AA-Vbpy})](\text{bpy})_2^{2+}$	P(AA-Vbpy)	<i>n</i> -BuOH	2 / 1	5×10^{-4}	2.5	75.2
$\text{Ru}[\text{P}(\text{Pyr-Vbpy})](\text{bpy})_2^{2+}$	P(Pyr-Vbpy)	mix. *	2 / 1	5×10^{-4}	30	66.4
$\text{Ru}[\text{P}(\text{Vpy-Vbpy})](\text{bpy})_2^{2+}$	P(Vpy-Vbpy)	<i>n</i> -BuOH	2 / 1	5×10^{-4}	216	51.4
$\text{Ru}[\text{P}(\text{MMA-Vbpy})](\text{bpy})_2^{2+}$	P(MMA-Vbpy)	mix. *	2 / 1	5×10^{-4}	20.5	93.3
$\text{Ru}[\text{P}(\text{HEMA-Vbpy})](\text{bpy})_2^{2+}$	P(HEMA-Vbpy)	<i>n</i> -BuOH	2 / 1	5×10^{-4}	3	76.9
$\text{Ru}[\text{P}(\text{AN-Vbpy})](\text{bpy})_2^{2+}$	P(AN-Vbpy)	mix. *	2 / 1	5×10^{-4}	14.5	92.8
$\text{Ru}[\text{EQ-P}(\text{Vpy-Vbpy})](\text{bpy})_2^{2+}$	EQ-P(Vpy-Vbpy)	<i>n</i> -BuOH	2 / 1	5×10^{-4}	80	30.0
$\text{Ru}(\text{Vbpy})(\text{bpy})_2^{2+}$	Vbpy	<i>n</i> -BuOH	2 / 1	10^{-3}	5	

Reaction temperature is 118°C.

* Mixture solvent xylene / *n*-BuOH = 1 / 4 (v / v).

The change of visible spectrum accompanying the complex formation of P(St-Vbpy) with *cis*-Ru(bpy)₂Cl₂ in xylene / *n*-butanol was shown in Fig.3 as a typical example. At the initial stage of the reaction, the absorption peak ($\lambda_{\max} = 538$ nm) of Ru(bpy)₂Cl₂ was observed. When the reaction proceeded, the absorption peak of $\lambda_{\max} = 538$ nm decreased, and the absorption at 452 nm gradually increased. At the end of the reaction, the absorption of 538 nm almost entirely disappeared, and only the absorption peak at 452 nm remained. During the preparation of Ru[P(Vpy-Vbpy)](bpy)₂²⁺, an interesting phenomenon was observed as reported previously [11].

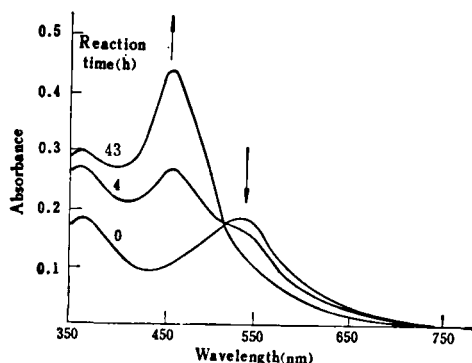


Fig. 3 The change of visible spectrum during the formation of Ru[P(St-Vbpy)](bpy)₂²⁺ complex with time

Reaction time of the formation of polymeric pendant Ru(bpy)₃²⁺ complexes was usually longer than that of the low molecular Ru(bpy)₃²⁺ complex probably due to steric hindrance as Table 5 showed. But in the cases of P(AA-Vbpy) and P(HEMA-Vbpy) the reaction time was about 1 / 2 of that of low molecular one. It is because of a solvation of hydrophilic group in polymeric chains with *n*-butanol. This made the polymeric chains more extended and so decreased the reaction time of formation of the polymeric complexes.

Composition of the polymeric pendant Ru(bpy)₃²⁺ complexes were determined from the composition of the starting polymer and the degree of the complex formation measured by the visible spectrum of the product. They were shown in Table 6.

The solubility of the polymeric complex is dependent on the property of the comonomer. The polymeric complex composed of water-insoluble comonomer, e.g., St, is insoluble in water contrary to the low molecular Ru(bpy)₃²⁺ which is easily soluble in water. The polymeric pendant complex, Ru[P(St-Vbpy)](bpy)₂²⁺ can therefore be used as a stable film or powders in water.

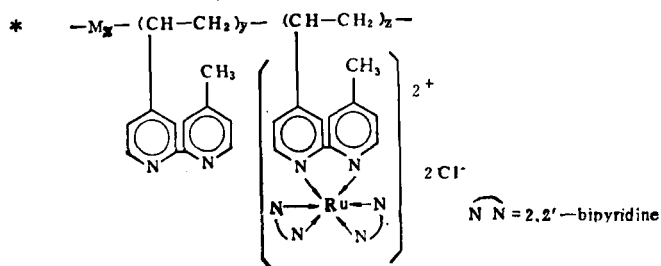
Absorption maximum ($\lambda_{\max}$), molar extinction coefficient (ϵ), emission maximum ($E_{\max}$) and relative emission intensity of the polymeric pendant Ru(bpy)₃²⁺ complexes were measured and listed in Table 7.

The absorption and emission maxima of the polymeric pendant Ru(bpy)₃²⁺ complexes were 452 to 457 nm, and 606 to 625 nm respectively. They are slightly higher than those of Ru(bpy)₃²⁺ (450 and 605 nm, respectively). They might be caused by stabilization of the excited state due to a delocalization by the extended ligand system involving polymeric chain. The relative emission intensity of the polymeric pendant Ru(bpy)₃²⁺ complex was about 0.18

Table 6 Composition of the polymeric complexes, RuP(M-Vbpy)(bpy)₃²⁺

Complex	X*	Y*	Z*
Ru(PVbpy)(bpy) ₃ ²⁺	0	0.088	0.912
Ru[P(St-Vbpy)](bpy) ₃ ²⁺	0.956	0.020	0.024
Ru[P(AA-Vbpy)](bpy) ₃ ²⁺	0.924	0.054	0.022
Ru[P(Pyr-Vbpy)](bpy) ₃ ²⁺	0.890	0.085	0.025
Ru[P(Vpy-Vbpy)](bpy) ₃ ²⁺	0.941	0.034	0.025
Ru[P(MMA-Vbpy)](bpy) ₃ ²⁺	0.958	0.018	0.024
Ru[P(HEMA-Vbpy)](bpy) ₃ ²⁺	0.972	0.005	0.023
Ru[P(AN-Vbpy)](bpy) ₃ ²⁺	0.917	0.041	0.042
Ru[EQ-P(Vpy-Vbpy)](bpy) ₃ ²⁺	0.930**	0.007**	0.052**

** The repeating unit, $-(\overline{\text{Vpy}})_{0.011}-$ is added.

**Table 7** Absorption maximum (λ_{max}), molar extinction coefficient (ϵ), emission maximum (E_{max}) and relative emission intensity of the polymeric pendant Ru complexes

Complex	Solvent	λ_{max} (nm)	ϵ (M ⁻¹ cm ⁻¹)	E_{max} (nm)	Relative emission intensity
Ru(bpy) ₃ ²⁺	H ₂ O	450	1.49×10^4	605	1.00
Ru(PVbpy)(bpy) ₃ ²⁺	H ₂ O	453	1.16×10^4	625	0.22
Ru[P(St-Vbpy)](bpy) ₃ ²⁺	CH ₃ CN / H ₂ O = 1/9	452	1.40×10^4	608	0.70
Ru[P(AA-Vbpy)](bpy) ₃ ²⁺	H ₂ O (pH 9)	456	1.43×10^4	608	0.69
Ru[P(Pyr-Vbpy)](bpy) ₃ ²⁺	H ₂ O	456	1.23×10^4	607	0.66
Ru[P(Vpy-Vbpy)](bpy) ₃ ²⁺	MeOH / H ₂ O = 1/9	457	0.85×10^4	610	0.18
Ru[P(MMA-Vbpy)](bpy) ₃ ²⁺	Dioxane / H ₂ O = 1/9	455	1.01×10^4	610	0.66
Ru[P(HEMA-Vbpy)](bpy) ₃ ²⁺	H ₂ O	455	1.13×10^4	606	0.78
Ru[P(AN-Vbpy)](bpy) ₃ ²⁺	DMF / H ₂ O = 1/9	456	1.13×10^4	608	0.45
Ru[EQ-P(Vpy-Vbpy)](bpy) ₃ ²⁺	H ₂ O	457	1.51×10^4	611	0.18

to 0.78 of that of $\text{Ru}(\text{bpy})_3^{2+}$. The especially low emission intensity of $\text{Ru}(\text{PVbpy})(\text{bpy})_2^{2+}$ would be due to quenching by concentration because of the high content of the Ru complex on a polymeric chain. The low emission intensity of $\text{Ru}[\text{P}(\text{Vpy-Vbpy})](\text{bpy})_2^{2+}$ would be due to the quenching effect by the Vpy groups, and that of $\text{Ru}[\text{EQ-P}(\text{Vpy-Vbpy})](\text{bpy})_2^{2+}$ due to the heavy atom effect of the bromine.

The study on the photochemical reaction of the polymeric complexes is now in progress.

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REFERENCES

- [1] Creutz C. and Sutin, N., *Proc. Natl. Acad. Sci. U. S.*, **1975**, 72, 2858.
- [2] 金子正夫, 山田 瑛, 高分子(日), **1979**, 28, 85.
- [3] 山田瑛, 戸嶋直樹, 金子正夫編著, 光エネルギー変換, **1983**, 学会出版センター.
- [4] Matsuo T., Sakamoto, T., Takuma K., Sakura K. and Ohsako T., *J. Phys. Chem.*, **1981**, 85, 1277.
- [5] Sumi, K. Furue M. and Nozakura S., *Polym. Prepr. Jpn.*, **1982**, 31, 2033.
- [6] Kaneko M., Nemoto S., Yamada A. and Kurimura Y., *Inorg. Chim. Acta*, **1980**, 44, L 289.
- [7] Kaneko M., Ochiai M., Kinoshita K., Jr., and Yamada A., *J. Polym. Sci., Polym. Chem. Ed.*, **1982**, 20, 1011.
- [8] Kaneko M., Yamada A., Tsuchida E. and Kurimura Y., *J. Polym. Sci., Polym. Lett. Ed.*, **1982**, 20, 593.
- [9] Ghosh P. K. and Spiro T. G., *J. Am. Chem. Soc.*, **1980**, 102, 5543.
- [10] Brandrup J. and Immergut E. H. (Ed.), "Polymer Handbook", **1967**, Interscience.
- [11] 後曉淮, 金子正夫, 山田 瑛, 高分子論文集(日), **1984**, 41, 311.