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Preparation and Photochemical Behavior of Polystyrene Pendant Tris(bipyridyl)ruthenium(II) Complex

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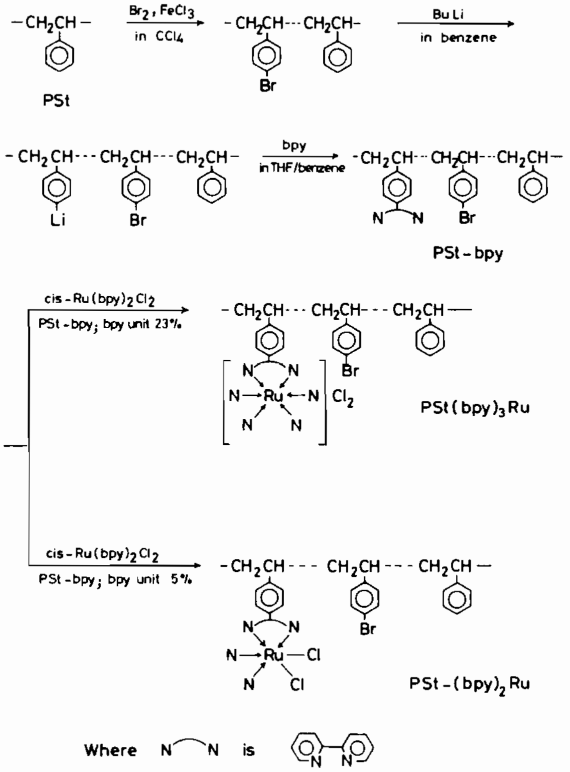
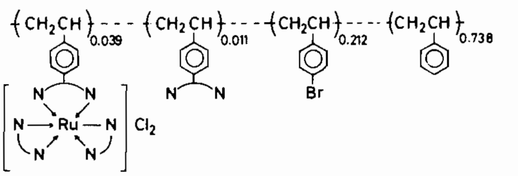
Tris(bipyridyl)ruthenium(II) complex (Ru(bpy)$_3$) is attracting more and more attention as a photocatalyst for decomposing water by solar irradiation [1–4]. In order to construct an efficient photochemical conversion system, the use of a heterogeneous reaction is desirable, since photochemical reaction in a homogeneous solution usually accompanies the backward reaction which consumes the photochemically acquired energy. Thus the backward reaction could be hindered if the reaction products could be separated from each other by using a heterogeneous system. With this point in mind the incorporation of Ru(bpy)$_3$ into monolayer assemblies [5], micells [6] or liposomes [7] has been reported. The immobilization of this complex onto a polymer support must be also usefull for this purpose; however, no polymer supported Ru(bpy)$_3$ has been reported. There has been only a few papers reporting bis(bipyridyl)Ru(II) complex incorporated to poly(4-vinylpyridine) [8]. This polymer supported complex is, however, unstable causing photochemical ligand substitution reaction. In this letter we present the new preparation of polystyrene pendant Ru(bpy)$_3$ complex as well as its photocatalytic reactivity.

Polystyrene (PSt) was used as the backbone polymer. Because it was proved that high molecular PSt gives insoluble polymer complex, relatively low molecular PSt was used in order to prepare soluble polymer complex. PSt (average molecular weight = 4400) was prepared by telomerizing styrene in carbon tetrachloride [9] ((styrene)/(CCl$_4$) = 1/5.13, molar ratio) using 1.1. wt.% 2,2′-azobisisobutyronitrile as initiator under argon at 60 °C for 40 h. The PSt was at first brominated in carbon tetrachloride with FeCl$_3$ as catalyst [10], lithiated with butyl lithium in dry benzene at 80 °C for 2 h, and then bipyridylated by adding the benzene solution dropwise to a refluxed solution of excess 2,2′-bipyridine in dry tetrahydrofurane in 4 h [11]. After cooling air was bubbled to the reaction mixture for 1 h, and the solution was added to a large excess of petroleum ether to give the precipitate of the bipyridylated PSt (PSt-bpy, bipyridylated styrene unti was 23%).

The reaction of PSt-bpy (0.936 g) and *cis*-Ru(II)(bpy)$_2$Cl$_2$·4H$_2$O [12] (0.242 g) was carried out in the mixture of 100 ml THF and 100 ml MeOH at a reflux temperature for 72 h. After concentration the reaction mixture was added to a large excess of water to give PSt pendant Ru(bpy)$_3$ complex (PSt-(bpy)$_3$Ru). This polymer complex is brown in color, soluble in DMF, DMSO or THF, but insoluble in water, alcohols or ether. The complexation of the PSt-bpy with Ru(bpy)$_2$Cl$_2$ was dependent upon the bpy content in the polymer. When a PSt-bpy sample containing less bpy (bipyridylated styrene unit 5%) and Ru(bpy)$_2$Cl$_2$ were reacted under similar conditions, precipitation in water gave PSt pendant bis(bipyridyl)Ru complex (PSt-(bpy)$_2$Ru) because of some ligand exchange reaction. Such a PSt pendant bis(bpy) complex could be changed to a tris(bpy) type complex by reaction with excess bipyridine in dimethylformamide at 153 °C for 24 h. PSt-(bpy)$_3$Ru was then obtained as a precipitate by adding the DMF solution to a large excess of water. These reaction schemes are described as follows:



The formation of PSt-bpy was confirmed by IR spectrum and elemental analysis. The IR spectrum of PSt-(bpy)$_3$Ru complex showed almost the same absorptions as PSt-bpy, overlapped with weak absorptions (1465, 1424 and 738 cm^{-1}, s) due to $Ru(bpy)_3$ complex. One example of the composition of the PSt-(bpy)$_3$Ru obtained by elemental analyses was as follows:



	C	H	N	Halogen
Found (wt.%):	75.76	6.25	2.68	12.78
Calcd. (wt.%):	75.57	5.95	2.44	13.34

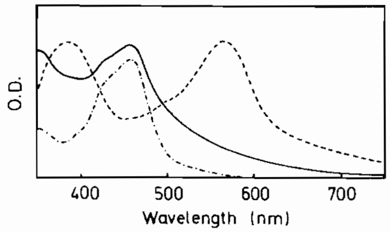


Fig. 1. Visible spectra of PSt-(bpy)$_3$Ru (——), $Ru(bpy)_3Cl_2$ (—.—.—.) and *cis*-$Ru(bpy)_2Cl_2$ (– – – –) in DMF/H_2O = 9/1 (v./v.).

The visible spectrum of PSt-(bpy)$_3$Ru in DMF was shown in Fig. 1 with those of $Ru(bpy)_3$ and $Ru(bpy)_2Cl_2$ as references. The polymer complex shows absorption maximum at 456 nm which is characteristic of tris(bpy) complex. Although the polymer complex shows a rather strong absorption in the region below 400 nm, the PSt backbone does not affect the maximum absorption which is due to charge transfer from metal to ligand of the attached $Ru(bpy)_3$. The polymer complex in DMF solution showed also luminescence at 597 nm, which is a little higher than that of $Ru(bpy)_3$ at 586 nm.

Photochemical reduction of methyl viologen (MV^{2+}) is now attracting attention as a means of solar energy conversion [4, 6, 7], because its cation radical ($MV^{\dot{+}}$) can reduce protons to give hydrogen [13]. The PSt pendant $Ru(bpy)_3$ complex also showed catalytic activity for the photoreduction of MV^{2+} like the known $Ru(bpy)_3$ complex. Figure 2 shows the photochemical formation of $MV^{\dot{+}}$ catalyzed by PSt-(bpy)$_3$Ru in DMF/H_2O = 9/1 (v./v.) using triethanolamine (see ref. 14) as electron donor. EDTA was also effective as electron donor for the PSt-(bpy)$_3$Ru catalyzed photoreduction of MV^{2+}.

The effect of molecular weight of the polymer incorporating $Ru(bpy)_3$ complex upon its photochemical reactivity as well as the application of the polymer complex for photoenergy conversion such as the use of its film or solid phase catalyst, are now being studied.

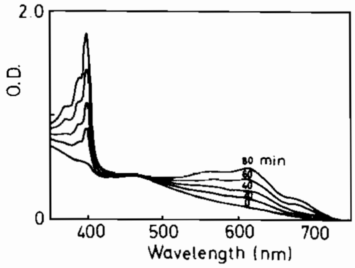


Fig. 2. Photochemical formation of $MV^{\dot{+}}$ catalyzed by PSt-(bpy)$_3$Ru using triethanolamine as electron donor. PSt-(bpy)$_3$Ru; 10^{-5} Ru g ion/l, MV^{2+}; 10^{-3} *M*, Triethanolamine; 5 × 10^{-2} *M*. Irradiated with halogen lamp (12 V, 100 W) through UV and IR cutoff filters under argon at 30 °C.

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