# A Novel Photo-sensitized Polymerization of Pyrrole

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A novel photo-sensitized polymerization of pyrrole by the use of tris(2,2′-bipyridine)ruthenium(II) as a photo-sensitizer has been investigated in aqueous solution and in polymer matrix for the fabrication of fine conducting polymer patterns.

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The fabrication of conducting polymers is an important subject in the construction of organic electronics devices.[1] Among conducting polymers, polypyrrole (ppy) has been extensively studied in a variety of applications owing to its stability and superiority in redox process.[2] Although chemical[3] and electrochemical[4] polymerization has mostly been used so far for the synthesis of ppy, photochemical polymerization should have great advantages for the fine fabrication of ppy. The fine fabrication of ppy, ppy patterning, has been studied on photoelectrochemical and photocatalytic polymerizations by the use of semiconductors.[5] The ppy pattern was formed on the semiconductor surface. On the other hand the fabrication of the conducting polymer on an insulating organic material is also important for the utilization of its conducting behaviour and the development of a new field of conducting polymers. In this paper, we report a novel photo-sensitized polymerization of pyrrole with the intention

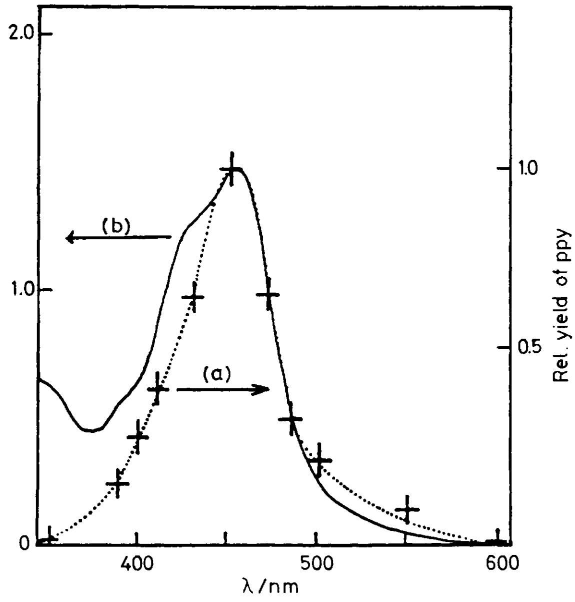
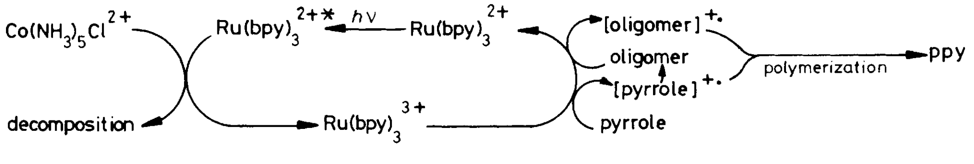


**Figure 1.** (a) Wavelength dependence of photo-sensitized polymerization of pyrrole by $Ru(bpy)_3^{2+}$ and (b) absorption spectrum of $Ru(bpy)_3^{2+}$. Relative yield of ppy was obtained from the absorbance change at 800 nm due to ppy formation.

Firstly, the photo-sensitized polymerization of pyrrole was investigated in aqueous solution. Tris(2,2′-bipyridine)ruthenium(II) $[Ru(bpy)_3^{2+}]$ having an intense absorption at 452 nm and high stability to photo-irradiation was used as photosensitizer.[6] Penta-amminechlorocobalt(III) $[Co(NH_3)_5Cl^{2+}]$ which does not directly oxidize pyrrole was used as a sacrificial oxidant. A pyrrole saturated aqueous solution containing $[Ru(bpy)_3]Cl_2$ and $[Co(NH_3)_5Cl]Cl_2$ was deoxygenated by bubbling argon and was photo-irradiated by a 500 W Xe lamp through a u.v. cut-off filter (L-42, Toshiba). As the photo-irradiation proceeded, a broad absorption from the visible to the near-i.r. region was produced and the solution became turbid and then a precipitate was observed. The i.r. spectrum of the product showed bands at 1560, 1380, 1040, and 940 $cm^{-1}$. These bands coincided with those of $Cl^-$-doped ppy synthesized by electrochemical polymerization in 0.1 mol $dm^{-3}$ KCl. Elemental analyses of the photoreaction product indicated the formula $C_{4.0}N_{1.0}Cl_{0.14}$ (normalized to four carbon atoms). These results support the product being $Cl^-$-doped ppy.The powdery ppy was shaped into a tablet by pressing at 200 kg $cm^{-1}$, and gave a conductivity of $3 \times 10^{-4}$ S $cm^{-1}$. The relatively low conductivity of the photo-polymerized ppy compared to electrochemically synthesized ppy was considered to be due to the poor packing of ppy chain or the low dopant concentration.

The wavelength dependence of the polymerization is similar to the absorption spectrum of $Ru(bpy)_3^{2+}$ (Figure 1). This result shows that the $Ru(bpy)_3^{2+}$ acted as photo-sensitizer for the polymerization of pyrrole. Since the phosphorescence at 610 nm of the triplet excited-state of $Ru(bpy)_3^{2+}$ was strongly quenched by $Co(NH_3)_5Cl^{2+}$ ($k_q$ $2.6 \times 10^8$ $dm^3$ $mol^{-1}$ $s^{-1}$) compared to that by pyrrole, the first step of the photoreaction is considered to be generation of $Ru(bpy)_3^{3+}$ through oxidative quenching. Since the $Ru(bpy)_3^{3+}$ has sufficient oxidizing power $[E_{\frac{1}{2}}(3+/2+)$ 1.27 V *vs.* normal hydrogen electrode$]$[6] for the oxidation of pyrrole and its oligomer, the polymerization is considered to proceed through the oxidation of pyrrole and its oligomer by the photo-generated $Ru(bpy)_3^{3+}$. In the absence of either the sensitizer or the oxidant, the polymerization did not proceed. It was concluded that the photo-sensitized polymerization proceeded through the oxidative electron transfer process shown in Scheme 1.



**Scheme 1.** Representation of photo-sensitized polymerization of pyrrole.

On the basis of the above result the photo-sensitized polymerization was performed using a polymer membrane, Nafion. The anionic Nafion can adsorb both the photosensitizer and the oxidant, and can take the part of dopant of ppy. The Nafion membrane (187 μm thick) adsorbing $Ru(bpy)_3^{2+}$ was dipped into a saturated pyrrole solution containing $[Co(NH_3)_5Cl]Cl_2$ and photo-irradiated by a dye laser at 490 nm through a photomask. The present preliminary study gave a fine polypyrrole pattern with 10 μm line width directly on the Nafion membrane. In the absence of either the sensitizer or the oxidant, the ppy pattern was not formed.

The present photo-sensitized polymerization is useful for the fabrication of fine conducting polymer patterns on insulating materials. Further fine fabrications of conducting polymers on insulating materials are in progress.

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