Photopolymerization of aniline with a tris(2,2′-bipyridyl)ruthenium complex–methylviologen polymer bilayer electrode system

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Aniline is photopolymerized by illuminating a bilayer electrode composed of tris(2,2′-bipyridyl)ruthenium complex [Ru(bpy)$_3$$^{2+}$] incorporated Nafion film and methylviologen pendant poly(siloxane) (PSiO-MV^{2+}) film in aniline solution in the presence of *N*-phenyl-*p*-phenylenediamine (PPD); the role of PPD on photopolymerization of aniline is also discussed.

It is well known that an interactive reaction takes place between photoexcited Ru(bpy)$_3$$^{2+}$ and electroactive molecules[1] such as methylviologen. This kind of photoinduced electron transfer is fundamental to photosynthesis, photoenergy conversion *etc.* Photoinduced electron transfers with higher efficiency can be observed in inorganic semiconductor particles or deposits.[2] However, a system employing photoinduced electron transfer between functional molecules would be useful for the easier fabrication of molecular function systems. Conducting polymers are also attracting keen interest regarding their use in some electronic devices. Conducting polymers prepared by photoinduced electron transfer are of use in molecular electronics. On this basis, photopolymerization of pyrrole has already been performed using Ru(bpy)$_3$$^{2+}$, n-TiO$_2$ and Cu(dpp)$_2$$^+$ resulting in poly(pyrrole).[3] From the electronic device viewpoint poly(aniline) is one of the most promising conducting polymers due to its high chemical stability in air. However, the photopolymerization of aniline has not yet been reported. Here we report a photopolymerization of aniline by illuminating the bilayer electrode composed of Ru(bpy)$_3$$^{2+}$ incorporated Nafion film and PSiO-MV^{2+} film in aqueous solution containing PPD and/or aniline.

PSiO-MV^{2+} was synthesized according to the previously described procedure.[4] Firstly, PSiO-MV^{2+} film was prepared on the indium–tin oxide (ITO) electrode from its methanol solution, and was left for 12 h under a moist atmosphere at 353 K to make it insoluble in alcohol. It was then dried for 2 h *in vacuo* at 353 K. Secondly, an alcoholic solution containing Ru(bpy)$_3$$^{2+}$ and Nafion was spread on the ITO/PSiO-MV^{2+} electrode and then dried. The resulting electrode was confirmed to have a clear ITO/PSiO-MV^{2+}/Nafion + Ru(bpy)$_3$$^{2+}$ bilayer structure by SEM. An aqueous solution of HCl (2 mol dm^{-3}) containing aniline (0.3 mol dm^{-3}), PPD (1.0 mmol dm^{-3}), or both was used as the polymerization solution. The bilayer electrode was illuminated in the visible region in the polymerization solution (λ = *ca.* 420–600 nm, 89.5 mW cm^{-2}) from the ITO electrode side with a 500 W xenon lamp (Ushio INC.).

Fig. 1 shows the absorption spectrum of the bilayer electrode in the solution containing both the PPD and aniline monomer under continuous illumination conditions. The absorption peaks at around 800 and 400 nm were enhanced with illumination time. These peaks can be assigned to the conjugated polaron structure and semiquinone cation radical structure of poly(aniline), respectively.[5] In the FTIR spec- trum of the product, peaks at 3200, 1585, 1500 and 800 cm^{-1} were assigned to the stretching of the N–H bond, the stretching of the C=N bond and C=C quinoid form, the stretching of the C=C benzenoid form and the out of plane bending of the C–H bond in poly(aniline), respectively.[6] Furthermore, an increase in the electrode mass during illumination was observed and measured by an electrochemical quartz crystal microbalance (EQCM). From these results, the photopolymerization of aniline was brought about by photoinduced electron transfer, and poly(aniline) was revealed to be formed on or in the bilayer film upon illumination.

In order to estimate the photopolymerization mechanism, especially the role of PPD, the illumination was carried out for the bilayer electrode in acidic aqueous solution containing only aniline (0.3 mol dm^{-3}). No change in the absorption spectrum was observed upon illumination as shown in Fig. 2(*a*). This strongly indicates that the photoinduced electron transfer from aniline, followed by photopolymerization, does not occur by illumination of the solution containing only aniline.

PPD is the head-to-tail coupling dimer of aniline having a lower oxidation potential than aniline. It has already been reported that the electrochemical polymerization of aniline is facilitated in the presence of an aniline dimer such as PPD.[7] Therefore, PPD was used in the preparation of poly(aniline) photoelectrochemically. The illumination was carried out for the solution containing only PPD (1.0 mmol dm^{-3}). In spite of the lower concentration of PPD, the absorbance at 800 nm was observed upon illumination [Fig. 2(*b*)]. In contrast to the system containing only aniline, active PPD cation radicals are formed by the photooxidation, because the oxidative potential of PPD is comparatively lower than the redox potential of the ruthenium complex. The electron is transferred from PPD to the ruthenium

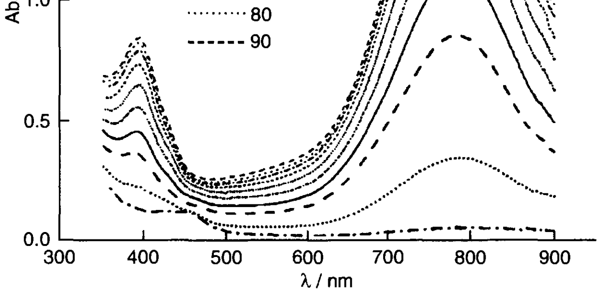

Fig. 1 Absorption spectrum changes of ITO/PSiO-MV^{2+}/Nafion + Ru(bpy)$_3$$^{2+}$ bilayer electrode in 2.0 mol dm^{-3} HCl aqueous solution containing 0.3 mol dm^{-3} aniline and 1 mmol dm^{-3} PPD upon continuous illumination

complex and to MV^{2+}, and then consequently to O_2 by photoinduced electron transfer. This continuous and unidirectional photoinduced electron transfer produced PPD cation radicals, and the resulting cation radicals form the poly(aniline) chain. A further improvement in the photopolymerization rate of PPD could be expected if PPD were more soluble. For the mixed solution containing both aniline (0.3 mol dm^{-3}) and PPD (1.0 mmol dm^{-3}), a larger enhancement (*ca.* four times) in the absorbance at 800 nm was observed in comparison with the PPD solution system, Fig. 2(*c*). In this system, photooxidation of aniline itself is also difficult. It is presumed that the PPD cation radical reacted with aniline monomer. Wei *et al.* reported that the oxidation of aniline monomers to the dimeric species was the rate-determining step in the polymerization of aniline.[7] They also suggested that the dimer of aniline effectively functioned as an initiator in the polymerization process in the presence of aniline dimer, and proposed that the dimeric species generated from the aniline dimer cation radicals electrophilically attacked the aniline monomer.[7] This proposed mechanism was directly supported by the present photopolymerization of aniline in the presence of PPD. Namely, photooxidized PPD attacked aniline monomer to yield aniline trimer. As the oxidation potential of the aniline trimer should be lower than that of the dimer, the trimmer can be easily photooxidized by the photoactivated ruthenium complex. This reaction proceeds successively to yield poly(aniline).

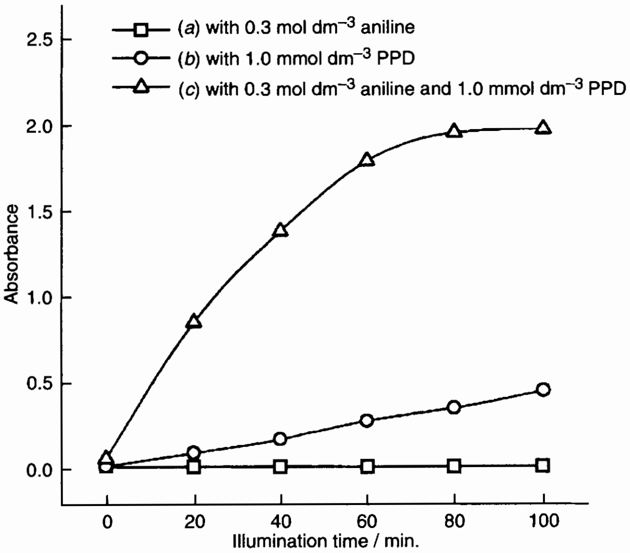

Fig. 2 Changes in absorbance at 800 nm of ITO/PSiO-MV^{2+}/Nafion + $Ru(bpy)_3^{2+}$ bilayer electrode in the polymerization solution upon continuous illumination

Since the photopolymerization proceeds only when illuminated, poly(aniline) must be obtained as a clear image by illumination through a mask. Actually, a clearly defined image (*ca.* 200 μm interval, depending on the mask and/or light source) was formed on or in the bilayer electrode by illumination through a mask.

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