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Photopolymerization of aniline derivatives by photoinduced electron transfer for application to image formation

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Conductive polyaniline was successfully generated when Flemion film containing tris(2,2-bipyridyl)ruthenium complex ($Ru(bpy)_3^{2+}$) and methylviologen (MV^{2+}) was illuminated in an acidic aqueous solution containing *N*-phenyl-*p*-phenylenediamine (PPD) and aniline or acetone. Aniline or acetone was employed to prepare PPD-incorporating particles in an acidic aqueous solution, which was important for the photopolymerization. The photopolymerization proceeded in the solution rather than on the film when aniline was employed at higher concentration. This is due to the release of $Ru(bpy)_3^{2+}$ from the film by the ion-exchange reaction between $Ru(bpy)_3^{2+}$ and protonated aniline. On the other hand, acetone molecules did not take part in the photopolymerization. Acetone enables PPD to be supplied near $Ru(bpy)_3^{2+}$ in the film without the release of $Ru(bpy)_3^{2+}$. Addition of acetone was revealed to be effective for the photopolymerization of aniline derivatives for the film from the viewpoint of image formation.

Introduction

Photoinduced electron transfer (PIET) between $Ru(bpy)_3^{2+}$ and methylviologen (MV^{2+}) has been studied from the standpoint of photosynthesis, photolysis of water, a photoenergy conversion system and so on.[1] Many studies have been reported to realize effective vectorial electron transfer because the back electron transfer between $Ru(bpy)_3^{2+}*$ and MV^+ is fast. Since the resulting oxidized $Ru(bpy)_3^{2+}*$ has an oxidation potential of about 1.1 V (*vs.* SCE), many electroactive materials can be oxidized by visible illumination. This process can be utilized to oxidize not only low molecular weight molecules but also polymers. Further, oxidative polymerization by photoillumination is also applicable.

Conducting polymers have been the object of keen interest because of their application to electronic devices. These polymers are generally prepared by oxidative polymerization. If conducting polymers are prepared by PIET, patterning with the conducting polymer can be achieved at any place and in any geometry. This process would offer possibilities for the fabrication of molecular electronic and/or optical devices and for micro-patterning (imaging). On the basis of these interests, photopolymerization of pyrrole has already been performed by using $Ru(bpy)_3^{2+}$ and $Cu(dpp)_3^{2+}$ resulting in polypyrrole.[2,3] In view of the wide application of conducting polymers, we have already reported photopolymerization of an aniline derivative, because polyaniline (PAn) is one of the most promising conducting polymers due to its high chemical stability in air. We have demonstrated its photopolymerization for a bilayer film composed of a $Ru(bpy)_3^{2+}$-incorporating Nafion film and a methylviologen pendant polysiloxane film,[4] and for both a $Ru(bpy)_3^{2+}$ and methylviologen-incorporated Flemion single-layer film[5–8] in an aqueous solution containing *N*-phenyl-*p*-phenylenediamine (PPD), *i.e.*, the head-to-tail dimer of aniline, and/or aniline. Since aniline alone was not photopolymerized by $Ru(bpy)_3^{2+}$, PPD should be necessary to induce photopolymerization in the present system. However, PPD showed poor solubility in acidic aqueous solution. Aniline or another solvent such as acetone is necessary as a solvent for PPD. In the case of aniline, ^{1}H-NMR and GPC spectra of the photopolymerized PAn indicated that aniline was involved in the propagation reaction leading to PAn.[9]

In this paper, the effect of aniline and acetone as a solvent for PPD was studied from the viewpoint of image formation. Effective formation of the PAn in the film, rather than in the solution, was discussed.

Experiments

$Ru(bpy)_3^{2+}$ was prepared according to the literature described elsewhere[10] and then purified by recrystallization from water. Reagent grade MV^{2+} (Tokyo Chemical Industry Co., Ltd.), HCl aqueous solution and PPD (Kanto Chemical Co., Inc.) were used as received. Flemion[8] ethanol solution (9 wt%) was given by Asahi Glass Co., Ltd. Flemion is a perfluorosulfonic acid polymer with a similar structure to Nafion. Its ion-exchange capacity is 1.1 meq g^{-1}.

An alcoholic solution containing $Ru(bpy)_3^{2+}$ (0.2 wt%), MV^{2+} (0.08 wt%) and Flemion (2.5 wt%) was spread on a glass substrate, and the resulting $Ru(bpy)_3^{2+}+MV^{2+}+$Flemion single layer film was dried at 353 K for 8 h *in vacuo*. 5 M HCl aqueous solution containing PPD (1.0 mM) and aniline (0.3 M) or a given amount of acetone was used as the polymerization solution. The single layer film was immersed in the polymerization solution and was illuminated in the visible region ($\lambda = ca.$ 420–600 nm, 89.5 mW cm^{-2}) from the glass substrate side with a 500 W xenon lamp (Ushio Inc.). The UV-vis spectrum was measured with a UV-vis spectrophotometer (Shimadzu, UV-2200), and its change was monitored at 800 nm.

The photoemission spectrum of $Ru(bpy)_3^{2+}$ (6×10^{-5} M) was measured with a fluorescence photospectrometer F-4500 (Hitachi Co., Ltd.) in HCl aqueous solution containing PPD

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and aniline (0.3 M) or a given amount of acetone under a nitrogen atmosphere. The excitation of $Ru(bpy)_3^{2+}$ was performed at 450 nm, and the photoemission intensity was monitored at 610 nm.

Results and discussion

1. Photopolymerization of An derivatives in the presence of aniline

PAn was easily produced by visible illumination of $Ru(bpy)_3^{2+}+MV^{2+}+$Flemion film in HCl aqueous solution containing PPD and/or aniline. This was confirmed by the increase in the absorption at 800–1000 nm assignable to the polaron band of PAn upon photoillumination as described earlier.[11] The PAn was produced not only in the film but also in the solution. It is favorable to reduce the amount of PAn produced in the solution from the viewpoint of effective image-formation of the conducting polymer. Aniline or another solvent is necessary for the present photopolymerization as a solvent for PPD because of the poor solubility of PPD in an acidic aqueous solution. Namely, in the preparation of the polymerization solution, PPD was first dissolved in aniline or another solvent, and then the resulting solution was mixed with HCl aqueous solution in order to prepare the homogeneous polymerization solution instantly. Fig. 1 shows the change of the absorbance at 800 nm for the film alone upon illumination in the presence of a given concentration of aniline. The increase in absorbance at 800 nm indicates the formation of PAn on the film. Since aniline was expected to work as not only a solvent for PPD but also a monomer for the photopolymerization, the concentration of aniline in the polymerization solution was increased for effective photopolymerization. However, the amount of the photopolymerized PAn on the film decreased with increasing aniline concentration. Particularly, the absorbance in the presence of 2 M of aniline first increases, passes through a maximum, and then decreases upon illumination.

In order to analyze this behavior, the change of the absorbance at 450 nm, which is assignable to $Ru(bpy)_3^{2+}$, for the film alone was monitored upon illumination and is shown in Fig. 2. The absorbance in the presence of 0.05 M of aniline was not changed upon illumination. However, it decreased with increasing concentration of aniline. Particularly, the absorbance in the presence of 2 M of aniline considerably decreased upon illumination and reached nearly zero at 80 min. This indicates that $Ru(bpy)_3^{2+}$ is released from the film when a larger amount of aniline is added in the polymerization solution. A similar decrease in the absorbance was also found without illumination. This is due to the ion exchange reaction between $Ru(bpy)_3^{2+}$ and protonated aniline, because aniline ($pK_a=4.6$) would be fully protonated in the present polymerization solution. Therefore, excessive addition of aniline is not effective for forming the photopolymerized PAn on the film because $Ru(bpy)_3^{2+}$ is released from Flemion film to the solution, leading to PAn formation in the polymerization solution. The FT-IR spectrum of the Flemion film after soaking in HCl aqueous solution containing aniline is shown in Fig. 3. The absorptions at 1600 cm^{-1} and 3000 cm^{-1} in the IR spectrum are assignable to the bending of the C–N bond of protonated aniline and the N–H stretching,

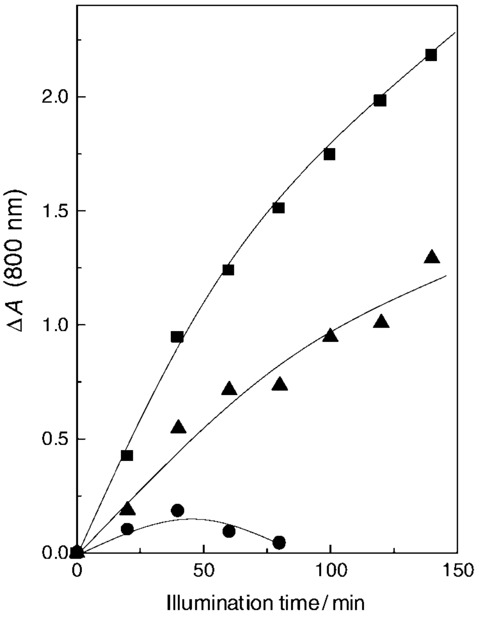

Fig. 1 Change of absorbance at 800 nm of $Ru(bpy)_3^{2+}+MV^{2+}+$ Flemion film alone induced by visible light illumination (420–600 nm) in 5 M HCl aqueous solution containing 1.0×10^{-3} M PPD and 0.05 (■), 0.5 (▲), and 2 M aniline (●).

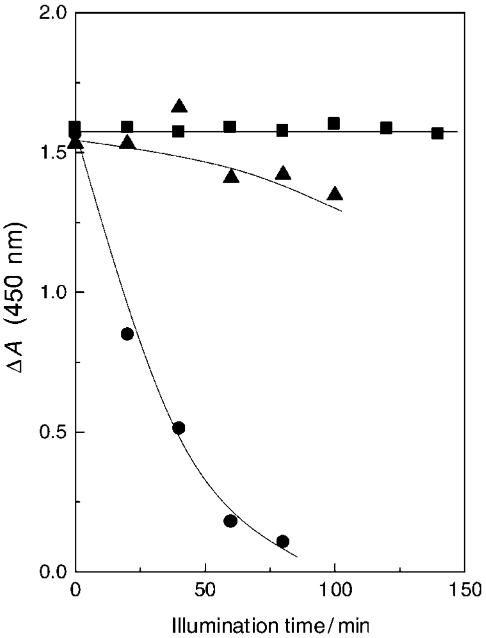

Fig. 2 Change of absorbance at 450 nm of $Ru(bpy)_3^{2+}+MV^{2+}+$ Flemion film alone induced by visible light illumination (420–600 nm) in 5 M HCl aqueous solution containing 1.0×10^{-3} M PPD and 0.05 (■), 0.5 (▲), and 2 M aniline (●).

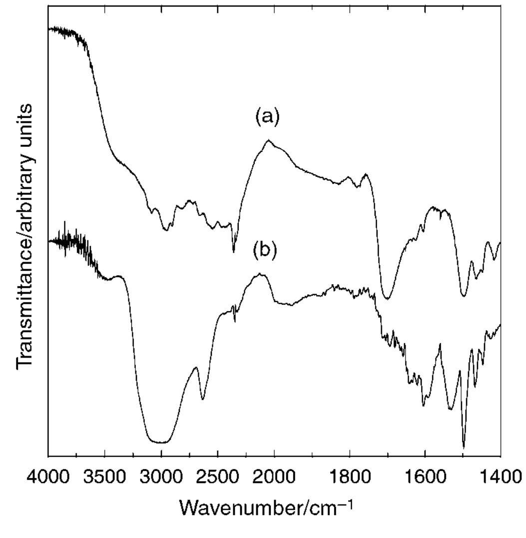

Fig. 3 FT-IR spectrum of Flemion film (a) before and (b) after soaking in HCl aqueous solution containing aniline.

respectively. This indicates that protonated aniline was incorporated into Flemion film by ion-exchange between the protonated aniline ion and $Ru(bpy)_3^{2+}$.

2. Effect of acetone as solvent for PPD

As already described, effective polymerization induced by photoinduced electron transfer between $Ru(bpy)_3^{2+}$ and PPD depends on the concentration of PPD. Therefore, it is important to increase the PPD concentration in the polymerization solution, resulting in an increase of the amount of photopolymerized PAn for the Flemion film. We employed acetone, instead of aniline, in order to increase the PPD concentration in the polymerization solution as well as to eliminate the release of $Ru(bpy)_3^{2+}$ from the Flemion film. Fig. 4 shows the change of absorbance at 800 nm in the polymerization solution containing $Ru(bpy)_3^{2+}$ and PPD upon illumination as a function of acetone content. This measurement was carried out in the solution without film. The absorbance at a given illumination time increased with increase in acetone content. As reported previously,[5,9] aniline which was employed instead of acetone worked to form PPD–aniline particles in the polymerization solution. This makes PPD disperse molecularly in the solution and is effective in inducing photoinduced electron transfer between $Ru(bpy)_3^{2+}$ and PPD. Although acetone does not take part in the photopolymerization, the result in Fig. 4 indicates that acetone works in a similar manner to aniline to form PPD-containing particles. This is also supported by the fact that the solubility parameter of PPD for acetone $\delta = 10.0\ (\mathrm{cal\ cm^{-3}})^{\frac{1}{2}}$ (rt) is comparable to that for aniline $\delta = 10.3\ (\mathrm{cal\ cm^{-3}})^{\frac{1}{2}}$ (rt).

From Fig. 4, one can see that the photopolymerization is facilitated with increasing acetone content. Almost all of the PPD molecules would be incorporated in PPD–acetone particles because the solubility of PPD in acidic aqueous solution is very low.[12] Therefore, the concentration of PPD in the PPD–acetone particles should decrease with increasing acetone concentration in the polymerization solution. On the other hand, $Ru(bpy)_3^{2+}$ molecules should be solubilized in the aqueous phase because the solubility of $Ru(bpy)_3^{2+}$ in acetone is very low. This could be assumed by the fact that the emission intensity of $Ru(bpy)_3^{2+}$ in the present solution was independent of acetone content as shown in Fig. 5. Therefore, the photoinduced electron transfer between $Ru(bpy)_3^{2+}$ and PPD should proceed at the interface between the aqueous phase and PPD–acetone particles. This reminds us that the possibility of incorporation of PPD molecules in the core of the PPD–acetone particles would be increased with increasing PPD concentration in the particle. Namely, these incorporated PPD can not easily participate in the photoinduced electron transfer. The photopolymerization in the presence of higher acetone content was thought to show higher absorption at 800 nm at a given illumination time. Since a photopolymerization generally consists of the initial reaction and the following propagation reaction, we cannot discuss the present photopolymerization only from the viewpoint of the photoinduced electron transfer between PPD and $Ru(bpy)_3^{2+}$ (initial reaction). However, taking into account that PAn with molar mass lower than 1000 also showed the absorbance at 800 nm, the difference in the absorbance at a given illumination time as shown in Fig. 4 seems to be due to the initial reaction.

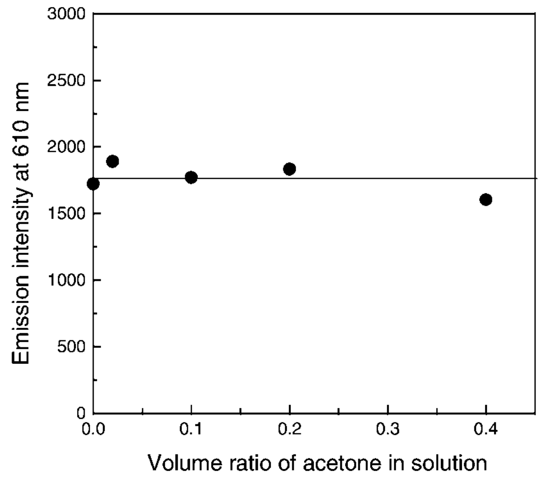

Fig. 5 Change of emission intensity at 610 nm of HCl aqueous solution containing 6.0×10^{-5} M $Ru(bpy)_3^{2+}$ as a function of acetone content.

In order to investigate the mechanism of the initial reaction of the present photopolymerization, Stern–Volmer plots for $Ru(bpy)_3^{2+}$ quenched by PPD in HCl aqueous solution containing 0.3 M aniline or 0.2 vol% acetone were evaluated and are shown in Fig. 6. The plot in the presence of aniline showed a curved relationship due to the electrostatic repulsion between $Ru(bpy)_3^{2+}$ and PPD–aniline particles as reported earlier.[5] On the other hand, that in the presence of acetone showed a linear relationship, indicating that the electron transfer between $Ru(bpy)_3^{2+}$ and PPD obeyed a dynamic mechanism and there is no remarkable interaction between $Ru(bpy)_3^{2+}$ and PPD–acetone particles. This may be explained by the particle density which is estimated by light scattering. In

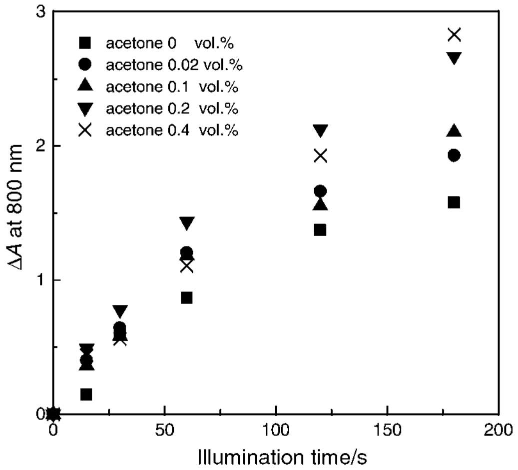

Fig. 4 Change of absorbance at 800 nm of HCl aqueous solution containing 6.0×10^{-5} M $Ru(bpy)_3^{2+}$ and 1.0×10^{-3} M PPD induced by visible light illumination as a function of acetone content.

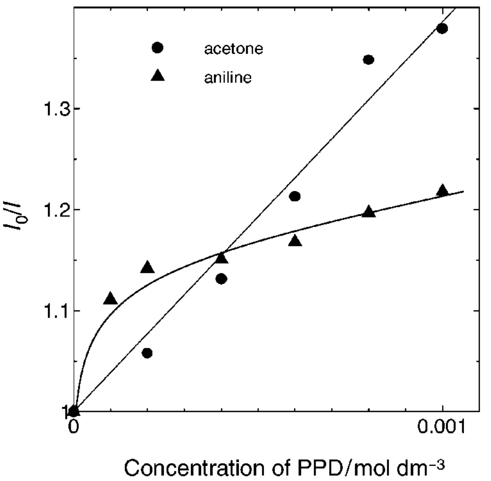

Fig. 6 Stern–Volmer plots for quenching of $Ru(bpy)_3^{2+}$ emission by PPD in 5 M HCl aqueous solution containing 6×10^{-5} M $Ru(bpy)_3^{2+}$, 0.3 M aniline (▲) and 0.2 vol% acetone (●), $\lambda_{ex} = 450$ nm.

fact, an increase in absorbance of 0.1 was observed at the wavelength range between 300 nm and 500 nm in the solution by adding 1 mM of PPD when aniline was employed as the solvent for PPD. Furthermore, the absorbance proportionally increased with PPD concentration in the 0–1 mM region. On the other hand, the increase of absorbance was within 0.02 at the same PPD concentration range for the acetone-containing solution. If the increase in the absorbance reflected the amount and the size of the particles, PPD did not seem to be incorporated in acetone particles but to be solvated by acetone molecules in acetone-containing solution. This may support the dynamic photoinduced electron transfer in acetone-containing solution, indicating that smaller particles with no specific interactions with $Ru(bpy)_3{}^{2+}$ are likely to show a dynamic electron transfer mechanism. Neither solution showed a change in those spectra within at least half a day after preparation. From these results, we assume that the solution containing aniline or acetone contains stable colloidal particles under the present experimental conditions. One can note from Fig. 6 that the photoinduced electron transfer at a PPD concentration of 1 mM proceeds more effectively in the solution containing acetone, leading to the effective initial reaction of the present photopolymerization. Therefore, acetone-containing polymerization solution is effective from the viewpoint of coloration, meaning the increase of the absorption at around 800 nm.

3. Photopolymerization of PPD–acetone system for imaging

When acetone was employed as the solvent for PPD, only PPD should participate in the photopolymerization. The incorporation of PPD into the Flemion film is important for the photopolymerization to proceed for the film. Since acetone can swell Flemion film, PPD would be incorporated into the Flemion film to induce photoinduced electron transfer between $Ru(bpy)_3{}^{2+}$ and PPD at the Flemion film. Fig. 7 shows the change in the absorbance at 800 nm for the Flemion film alone and that for the resulting polymerization solution containing 0.2 vol% acetone and 1 mM PPD. In contrast to the aniline-containing system, the photopolymerization for the Flemion film proceeded effectively in the solution containing acetone even at 0.2 vol%. In fact, $Ru(bpy)_3{}^{2+}$ was not confirmed to be released during the photopolymerization. In view of this fact, the amount of PAn photopolymerized in the solution was one-eighth of that for the Flemion film. The polymerization in the presence of acetone is not effective for obtaining PAn with higher molar mass.[9] However, since PPD–acetone particles did not release $Ru(bpy)_3{}^{2+}$ from the film because of the lower charge on the particle surface, PAn was formed for the film effectively. Namely, the employment of acetone is advantageous for preparing the photopolymerized PAn for the Flemion film leading to PAn image formation.

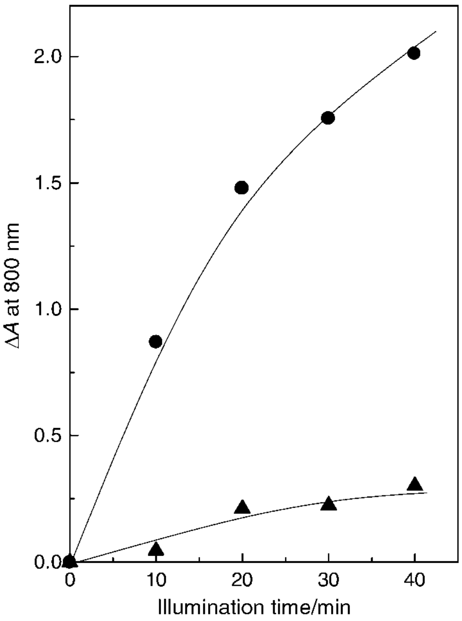

Fig. 7 Change of absorbance at 800 nm of $Ru(bpy)_3{}^{2+} + MV^{2+} +$ Flemion film (●) and polymerization solution (▲) induced by visible light illumination (420–600 nm) in 5 M HCl aqueous solution containing 1.0×10^{-3} M PPD and 0.2 vol% acetone.

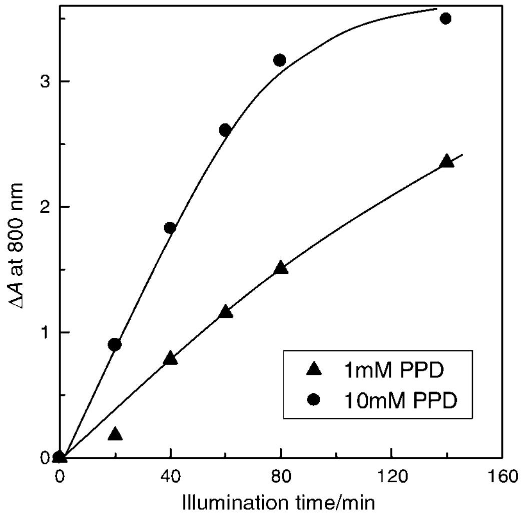

Fig. 8 Change of absorbance at 800 nm of $Ru(bpy)_3{}^{2+} + MV^{2+} +$ Flemion film induced by visible light illumination (420–600 nm) in 5 M HCl aqueous solution containing 0.2 vol% acetone and 1.0×10^{-3} (▲) and 1.0×10^{-2} M PPD (●).

We employed a PPD concentration of 1 mM for the measurement described above. Larger amounts of PPD should be dissolved in the polymerization solution containing acetone. PPD concentration was increased to 10 mM, and the Flemion film immersed in its solution was illuminated. More effective photopolymerization for the Flemion film was performed as shown in Fig. 8. This suggests that acetone would be the preferred solvent for PPD for the present photopolymerization from the viewpoint of PAn imaging.

Conclusion

An ITO/Flemion + $Ru(bpy)_3{}^{2+} + MV^{2+}$ electrode was illuminated in acidic aqueous solution containing various concentrations of aniline and 1 mM PPD to form conductive PAn effectively. However, higher concentrations of aniline in the polymerization solution brought about the release of $Ru(bpy)_3{}^{2+}$ from the Flemion film due to an ion exchange reaction between $Ru(bpy)_3{}^{2+}$ and anilinium ion. On the other hand, when acetone was employed instead of aniline, effective photopolymerization for the Flemion film was performed. This seems to be explained by differences in the PPD-containing particles in the solution. Acetone did not participate in the present photopolymerization, and the resulting photopolymerized PAn showed lower molar mass compared with the aniline-containing system. However, acetone is revealed to have an advantage from the viewpoint of image formation on the Flemion film.

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12 1 mM of PPD is dispersed in 2 M HCl solution containing no acetone or aniline with 200 W sonication over 30 min. However, crystallization of PPD from the solution was observed within a few hours. The experiment with no acetone or aniline was done within this time scale.