Photoreduction of Ferric Chloride in Poly(vinyl Alcohol) Film

It is well known that poly(vinyl alcohol) forms a blue-colored complex with iodine.[1] On the other hand, iodide is oxidized to iodine by ferric chloride, which loses its oxidizing ability by the photoreduction to ferrous salt. A photosensitive paper was designed on the basis of a combination of the above photochemical and thermal reactions.[2] After drying a paper coated with an aqueous solution of poly(vinyl alcohol) containing ferric chloride, it was irradiated with UV light, followed by dipping into a KI solution. A clear image appeared on the paper by formation of a poly(vinyl alcohol)–iodine complex only at the part unexposed to UV light. The photosensitivity of the paper, however, was not satisfactory because of a low quantum yield for the photoreduction of ferric chloride. In this paper, we wish to report studies on the photoreduction of ferric chloride in poly(vinyl alcohol) film, which is of great importance in relation to an improvement of the photosensitivity of the photosensitive paper.

EXPERIMENTAL

A commercially available poly(vinyl alcohol) (PVA, $P_n = 500$) was used after extraction with methanol. Anhydrous ferric chloride was used after purification by sublimation. Lithium hydroxide, ammonium thiocyanate, o-phenanthroline, benzophenone, and benzhydrol were of reagent grade and used without further purification. To adjust pH, a small amount of 0.1N—LiOH was added to 15 mL of aqueous solution containing PVA (0.40 eq/L), ferric chloride (1.0×10^{-3} mol/L), and HCl (9.6×10^{-3} mol/L). The pH of the solution was measured by using a pH meter (Toadempa HM-5B). The solution was placed in a polystyrene container ($6.1 \times 5.5 \times 1.0$ cm), and dried to a film at 40°C for 40 h in the dark. The thickness of the film was 40–60 μm. The pH value in PVA film means hereinafter the pH value of the aqueous solution for the preparation of PVA film at room temperature.

A film (4.0×4.5 cm) containing ferric chloride was irradiated at room temperature under air with a 100-W high-pressure mercury lamp (Toshiba SHL-100 UV) which was powered by a regulated ac power supply (100 V ± 1.5%). A filter (Toshiba UV-D36B) was employed to isolate 366-nm light. The intensity ($I_0 = 1.2 \times 10^{-8}$ einstein/s·cm^2) of the irradiation light was determined with a chemical actinometer, benzophenone–benzhydrol, according to the method of Moore and Ketchum.[3] The quantum yield (Φ) for the photoreduction of ferric chloride in PVA film was determined as $\Phi = -\Delta[Fe^{3+}]/I_{abs}$. The photoreduction of ferric chloride was followed by observing the decrease in the absorbance at 370 nm. The conversion was always less than 8%. A Shimadzu UV-200S recording spectrophotometer was used.

RESULTS AND DISCUSSION

Ferric chloride shows a charge transfer band from ligand to iron in aqueous solution. The wavelength of the charge transfer band changes with pH of the solution, showing that the ligand of ferric ion changes with pH. A similar phenomenon was observed for ferric chloride in PVA film. As shown in Figure 1, the absorption spectrum of ferric chloride in PVA film was influenced by pH of the aqueous solution for the preparation of film. At pH 2.31, the absorption peaks were observed at 360 and 320 nm, which have been reported to be characteristic of $FeCl_4^-$.[4] The absorption peak at 230 nm can be attributed to Fe_{aq}^{3+}.[5] The absorption spectrum became structureless at pH 3.35, suggesting the formation of association species of Fe^{3+} and OH^- such as $FeOH^{2+}$, $Fe(OH)_2^+$, and $Fe_2(OH)_2^{4+}$.[5]

The initial step following the photoexcitation of ferric complexes of the type FeX^{2+}, where X is OH or Cl, is the production of ferrous ion and free radical species in solution.[6] The recombination of radical X with ferrous ion

$$FeX^{2+} \underset{}{\overset{h\nu}{\rightleftarrows}} Fe^{2+} + X\cdot$$
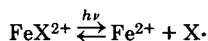
results in a lowering of the quantum yield for the photoreduction of ferric complexes. The quantum yield increases in the presence of a radical scavenger like alcohols.[5] In the previous paper,[7] it was
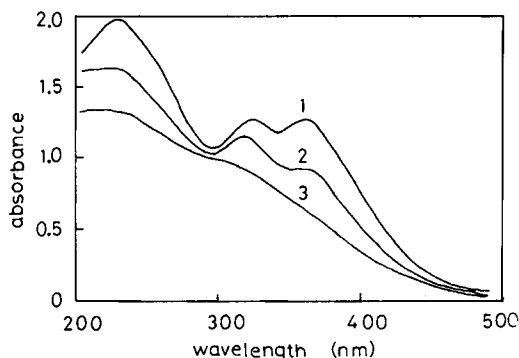
Fig. 1. Effect of pH on the absorption spectrum of ferric chloride in PVA film: (1) pH 2.31; (2) pH 2.78; (3) pH 3.35.

reported that PVA was an efficient scavenger for the radical X in aqueous solution. The primary photoreaction for $FeCl_4^-$ is also shown as follows[6]:

$$FeCl_4^- \overset{h\nu}{\rightleftarrows} FeCl_2 + Cl^- + Cl\cdot$$

The change in the absorption spectra of PVA film containing ferric chloride with irradiation is shown in Figure 2. The absorbance over the range 200–400 nm simply decreased with irradiation time and almost completely disappeared by the prolonged irradiation. No isosbestic point was observed. Although the absorption spectrum of the PVA—ferric chloride film changes with pH, a similar spectral change with irradiation was observed. The film after irradiation was dissolved in $0.1N$—H_2SO_4 under nitrogen atmosphere at 60°C. The amounts of Fe^{3+} and Fe^{2+} in the solution were determined by the thiocyanate and o-phenanthroline methods,[8] respectively. The amount of Fe^{3+} which disappeared was in good agreement with that of Fe^{2+} formed. Furthermore, a decrease in Fe^{3+} determined from the change in absorption spectra was in good agreement with that obtained from thiocyanate method.

As shown in Figure 3, the Φ value was dependent on pH of the solution for the preparation of film. In the range of pH 2–3.5, Φ increased with an increase in pH, passed through a maximum at pH 2.25, and decreased at higher pH's. The maximum Φ value was 0.17, which was about 2.5 times higher than the Φ value without pH adjustment. Although the Φ value (0.17) was smaller than that (0.25) in aqueous solution of PVA,[7] the dependence of Φ value on pH was almost the same in the film and in aqueous solution. According to David and David[9] and Langford and Carey,[5] the order of activity for the photoreduction of ferric complexes in aqueous solution is $FeOH^{2+} > FeCl^{2+} > Fe_{aq}^{3+} \gg Fe(OH)_2^+$ and $Fe_2(OH)_2^{4+}$. The primary quantum yield for the photoreduction of $FeCl_4^-$ reported by Dainton and Jones[10] is almost the same as that of $FeCl^{2+}$. If the relative reactivity of the ferric complexes in PVA film is the same as that in aqueous solution, the pH effect on the Φ value in PVA
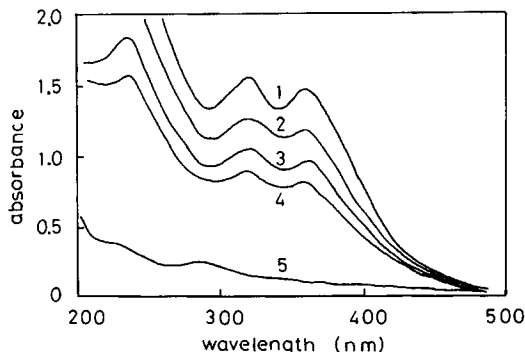

Fig. 2. Change in the absorption spectrum of ferric chloride in PVA film with UV light irradiation: (1) initial; (2) 1 min; (3) 2 min; (4) 3 min; (5) 60 min. pH 2.48.
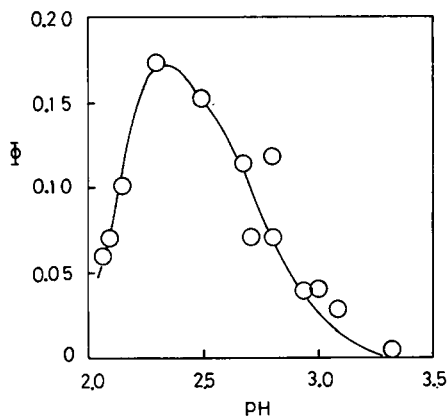
Fig. 3. Effect of pH on the quantum yield (Φ) for the photoreduction of ferric chloride in PVA film.

film may be explained as follows. At pH about 2, the main light absorbing species is $FeCl_4^-$, which is photochemically less reactive than $FeOH^{2+}$. The increase in pH (2 to 2.25) may cause an increase in $FeOH^{2+}$, resulting in an increase in Φ value. The decrease in Φ value with an increase in pH (2.25 to 3.5) may be due to the formation of $Fe(OH)_2^+$ and/or $Fe_2(OH)_2^{4+}$, which are photochemically less reactive than $FeOH^{2+}$.

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