

Coagulation of Polymer–Cu²⁺ Complexes in Polymer Films and Its Application for Producing Semiconducting CuI Surface Layers

OSAO SUMITA, ATSUO FUKUDA, and EIICHI KUZE, *Tokyo Institute of Technology, Department of Textile and Polymeric Materials, O-okayama, Meguro-ku, Tokyo 152, Japan*

Synopsis

In poly(vinyl alcohol) and polyacrylamide films containing the corresponding polymer–Cu²⁺ complexes, the reason why the films may gain surface electrical semiconductivity as high as 10⁻³ Ω⁻¹ when treated with acetone solution of iodine was investigated. Optical and scanning electron microscope observations indicated that the coagulated polymer–Cu²⁺ complexes favor the appearance of the high conductivity and that the state of coagulation depends on the anions of the copper salts used as well as two parameters, $F_1 \equiv [\text{Cu}^{2+}]/[\text{MU}]$ and $F_2 \equiv [\text{OH}^-]/[\text{Cu}^{2+}]$, where [MU] is the molar concentration of monomeric units of the polymer and [OH⁻] is that of hydroxide ions added. The effectiveness of the anions in causing coagulation decreases in the order of SO₄²⁻ > Cl⁻ > NO₃⁻ ≈ Br⁻. The whitish substance that appears on the film surface after the iodine treatment gives x-ray Debye–Scherrer rings characteristic of γ-CuI. The γ-CuI surface layer adheres to the film rather firmly, at least in polyacrylamide, and is responsible for the conductivity. By controlling the state of coagulation of the complexes and hence the formation of the γ-CuI surface layer, we have produced films with anisotropic surface electrical semiconductivity, i.e., $\sigma_{\parallel} \approx 10^{-4} \Omega^{-1}$ and $\sigma_{\parallel}/\sigma_{\perp} = 1 \sim 10^3$. Optical and ESR spectra are also obtained to understand the mechanism of γ-CuI formation and to clarify the optical properties of the films.

INTRODUCTION

Polymer films containing polymer–metal complexes are of interest to us in view of their electrical properties. In previous papers Kakinoki et al.¹⁻³ reported that poly(vinyl alcohol) and polyacrylamide films (hereinafter abbreviated to PVA and PAAm, respectively) containing the corresponding polymer–Cu²⁺ complexes may become semiconductive when treated with acetone solution of iodine. The conductivity depends on the two parameters, $F_1 \equiv [\text{Cu}^{2+}]/[\text{MU}]$ and $F_2 \equiv [\text{OH}^-]/[\text{Cu}^{2+}]$, where [MU] is the molar concentration of monomeric units of the polymer and [OH⁻] is that of hydroxide ions added. In a previous paper,⁴ on the other hand, we showed that the structure of the complexes and the state of their coagulation in the films also depend on the two parameters, F_1 and F_2 . When $F_1 \approx 1/200$, for example, the PVA–Cu²⁺ complex is monomeric at $F_2 \approx 0$, polymeric at $F_2 \approx 1$, and dimeric at $F_2 \approx 2$; the complex with $F_2 \approx 1$ tends to coagulate as particles about 1 μm in diameter.

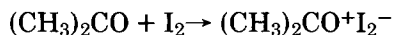
In the present paper we study the relationship between the surface electrical conductivity and the state of coagulation of the polymer–Cu²⁺ complexes in the films, clarifying the reason why the films may become semiconductive after the iodine treatment. In the next section the experimental procedures are briefly explained. In the Results and Discussion section, first optical and electron

microscope observations will be described in detail. It will become clear that the formation of γ -CuI surface layer is responsible for the conductivity. Second, we will study the reaction of the films with iodine in acetone solution by using optical and ESR spectra. Finally, a method is described for producing films that show anisotropic surface electrical conductivity by controlling the state of coagulation of the complexes in the films.

EXPERIMENTAL

Polymers used were PVA with molecular weight (MW) $\sim 6 \times 10^4$, manufactured by Koso Chemical Co. Ltd.; and 10 wt-% aqueous solution of PAAm with MW $(5-7) \times 10^5$ by Sumitomo Chemical Industry Co. Ltd. Polymer-Cu²⁺ complexes in solutions were prepared by mixing aqueous solution of PVA or PAAm; aqueous CuSO₄, CuCl₂, Cu(NO₃)₂, or CuBr₂; aqueous NaOH; and water to give [MU] = 0.508 mole/liter for PVA or 0.211 mole/liter for PAAm, $F_1 = 1/200-1/14$, and $F_2 = 0-2$. Films containing the polymer-Cu²⁺ complexes were made by casting the above prepared solutions on the poly(methyl methacrylate) plate and drying them for about three days at room temperature. These films about 50 μ m in thickness were peeled from the plate and further dried over silica gel in a desiccator for a few days.⁴

The iodine treatment was carried out as follows. First 5 wt-% acetone solution of iodine was spread on the film surface and then the acetone was blown away at room temperature in a few minutes. Unreacted iodine was removed by washing the film with pure acetone. The blowing-away of acetone is essential; if the film was dipped in the acetone solution of iodine for more than 1 hr and then washed with pure acetone immediately after being withdrawn from the solution, the film will not be semiconductive. This is because of the complexation of iodine with acetone pointed out by Mulliken⁵:



The surface electrical conductivity of the films was obtained by observing the current passing through a unit area (1 cm \times 1 cm) by a conventional four-terminal method with aluminum foil electrodes, as described previously.¹⁻³ Optical and scanning electron microscope observations were made by a Nikon Model S-Ut and a Hitachi Model HSM-2. Surface electron diffraction pattern was obtained by a Hitachi Model HS-7 electron microscope with a beam spot about 1 μ m in diameter. Visible and UV spectra of the films were obtained by a Shimadzu Model UV 200 spectrophotometer and ESR spectra by an Electron Optics Lab. Model JES-ME X-band spectrometer with 100-kHz magnetic field modulation.

RESULTS AND DISCUSSION

Optical Microscope Observations

The state of coagulation of the polymer-Cu²⁺ complexes in the films depends on the copper salts used as well as on the two parameters, F_1 and F_2 . Both PVA- and PAAm-Cu²⁺ complexes show the following similar tendencies. When $F_2 = 0$ or $F_2 \geq 2$, no coagulation occurs irrespective of F_1 and the copper salt used. Figure 1 illustrates the variation in the state of coagulation of PVA-Cu²⁺ com-

plexes with increasing F_2 where $F_1 = 1/50$ and CuCl_2 was used. In the films with $F_2 = 1$ and 1.5, the complex coagulates into a number of particles about $1 \mu\text{m}$ in diameter as shown in (b) and (c) of Figure 1. In the film with $F_2 = 2$, however, few particles appear, as in (d). Coagulation also takes place in the film with $F_2 = 0.5$ as shown in (a), though the state of coagulation is different from that in the films with $F_2 = 1$ and 1.5. When F_1 is as small as $1/200$, coagulation was observed only in the films with $F_2 \approx 1$. As is clear in Figure 2, CuSO_4 is more effective than CuCl_2 in causing coagulation under the same conditions of $F_1 = 1/100$

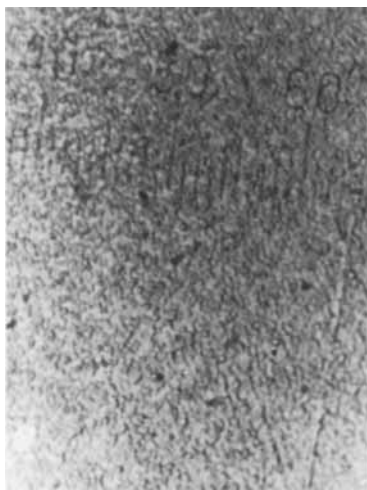
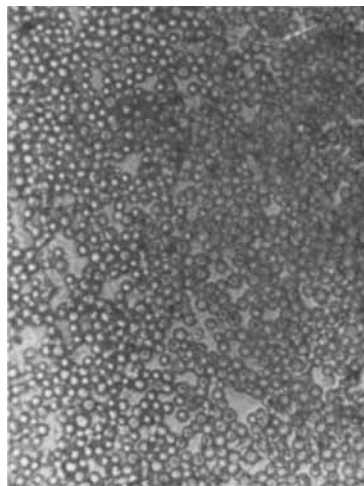
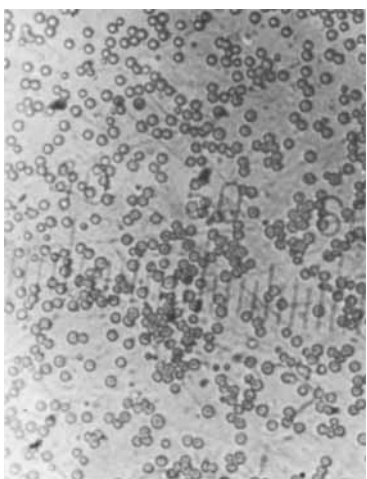
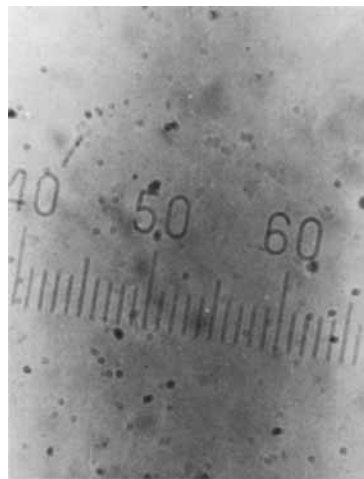
(a) $F_2 = 0.5$ (b) $F_2 = 1.0$ (c) $F_2 = 1.5$ (d) $F_2 = 2.0$ \longleftrightarrow
 $10 \mu\text{m}$

Fig. 1. Optical microscope photographs showing the coagulation of PVA-Cu²⁺ complexes with $F_1 = 1/50$ at indicated F_2 .

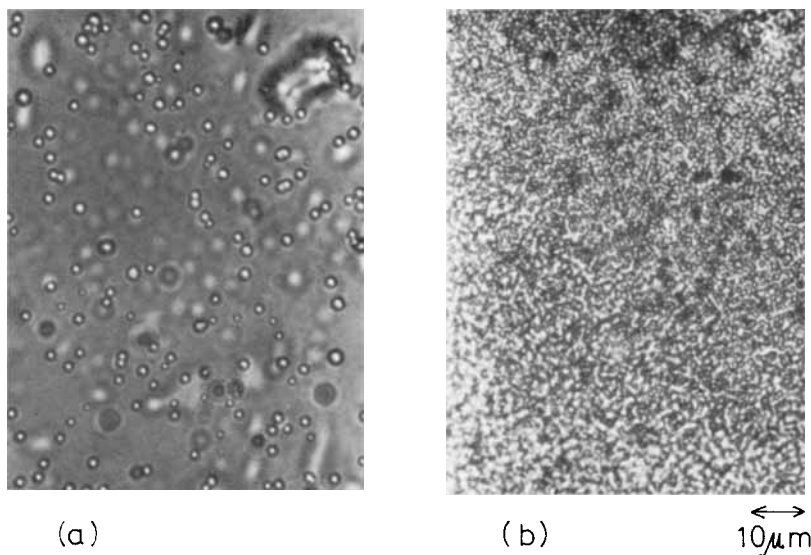


Fig. 2. Optical microscope photographs illustrating the effectiveness of anions in coagulating the PVA-Cu²⁺ complex with $F_1 = 1/100$ and $F_2 = 1$: (a) CuCl₂; (b) CuSO₄.

and $F_2 = 1$. The effectiveness decreases in the order of $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- \approx \text{Br}^-$. When Cu(NO₃)₂ or CuBr₂ was used, the film always appeared to be almost homogeneous. In the following, CuCl₂ is usually used, except when otherwise stated.

Coagulation will occur as follows. When $F_2 \approx 1$, the polymers are crosslinked by linear chains that consist of Cu²⁺ ions bridged with OH⁻ ions,⁴ and hence their conformation must be globular. These globular polymers, i.e., colloids of polymer-Cu²⁺ complexes, are positively charged, since Cu²⁺ ions are only partially hydrolyzed. Anions of copper salts will cancel the positive charge and help the colloids to coagulate. Among the four anions stated above, SO₄²⁻ must be most effective since it is divalent. Although it is difficult to explain the order $\text{Cl}^- > \text{NO}_3^- \approx \text{Br}^-$, this order has been observed in other investigations.⁶⁻⁸

The films containing PVA-Cu²⁺ and PAAm-Cu²⁺ complexes are insulators, and their surface conductivity is less than $10^{-10} \Omega^{-1}$ even when F_1 is as large as $1/20$. The iodine treatment increases the surface conductivity provided F_1 and F_2 have proper values. When CuSO₄ or CuCl₂ was used, the maximum surface conductivity is more than $10^{-4} \Omega^{-1}$, as shown in Figure 3; it is two orders of magnitude smaller when Cu(NO₃)₂ or CuBr₂ was used. We may, therefore, reasonably conclude that highly coagulated states of PVA-Cu²⁺ and PAAm-Cu²⁺ complexes are favorable for the high surface conductivity that appears after iodine treatment.

Scanning Electron Microscope Observations

Scanning electron microscope photographs further justify the above conclusion. Photos (a) and (b) in Figures 4 and 5 represent the films before and after iodine treatment, respectively. When $F_1 = 1/50$ and $F_2 = 1$, many particles are seen before the treatment, as shown in (a). The iodine treatment destroys the particles, forming a new reaction product that covers the whole film surface in

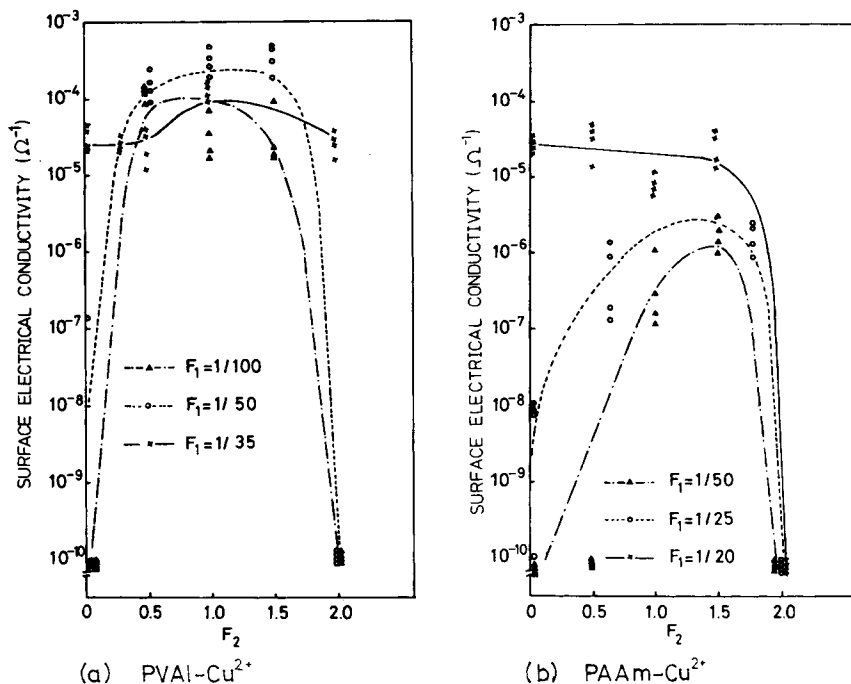


Fig. 3. Influence of F_1 and F_2 on the surface electrical conductivity of the polymer-Cu²⁺ complex films treated with iodine: (a) PVA-Cu²⁺ complex films; (b) PAAm-Cu²⁺ complex films.

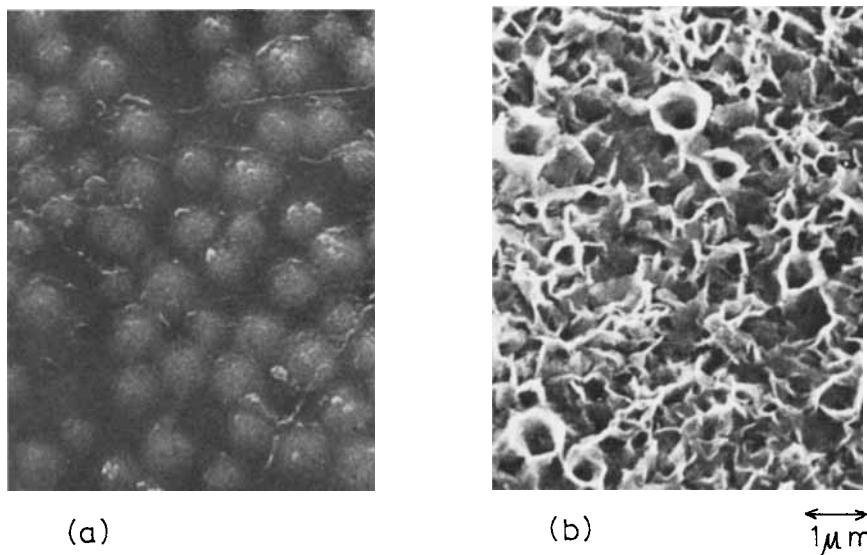


Fig. 4. Scanning electron microscope photographs of PVA-Cu²⁺ complex films with $F_1 = 1/50$ and $F_2 = 1$ showing the change produced by the iodine treatment: (a) before; (b) after iodine treatment.

a characteristic manner, as shown in (b); iodine attacks selectively the parts rich in complexes. Even when $F_1 = 1/100$ or less and $F_2 = 0$, and hence no coagulation is observed by the microscope, the films are eroded here and there, and some

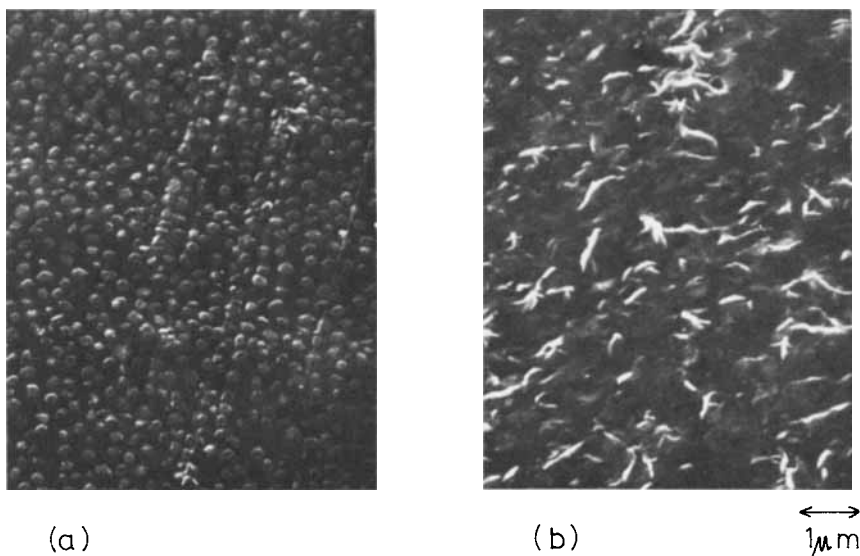


Fig. 5. Photographs similar to Fig. 4 of PAAm-Cu²⁺ complex films with $F_1 = 1/50$ and $F_2 = 1$.

reaction product, which may be slightly different from the previous one, also appears; the product does not cover the whole surface, as seen in Figure 6. The occurrence of inhomogeneous erosion even at $F_1 = 1/200$ seems to indicate that Cu²⁺ complexes are not distributed uniformly but that coagulation of some kind takes place in the films. Low compatibility of PVA or PAAm with the corresponding polymer-Cu²⁺ complex partly contributes to this coagulation. In the film that contains no Cu²⁺ ions, the iodine treatment does not cause any erosion.

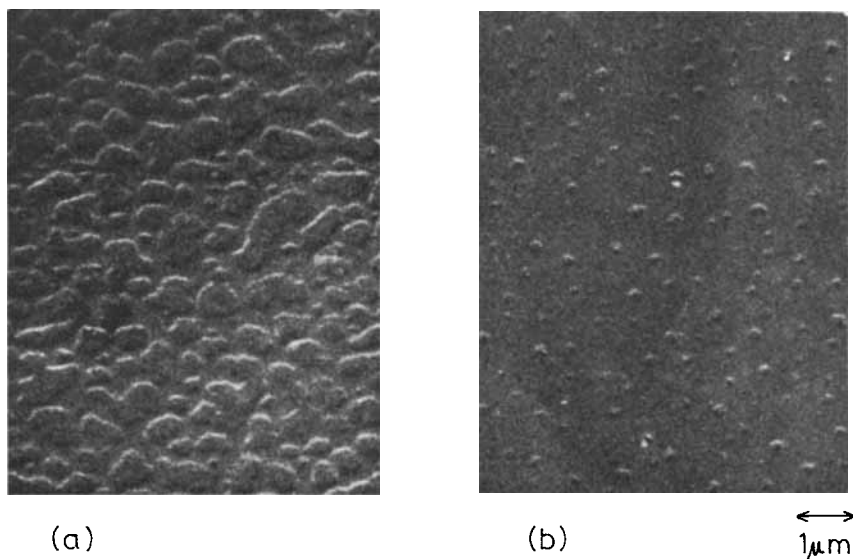


Fig. 6. Scanning electron microscope photographs of the polymer-Cu²⁺ complex films after iodine treatment: (a) PVA-Cu²⁺ complex film with $F_1 = 1/200$ and $F_2 = 0$; (b) PAAm-Cu²⁺ complex film with $F_1 = 1/100$ and $F_2 = 0$.

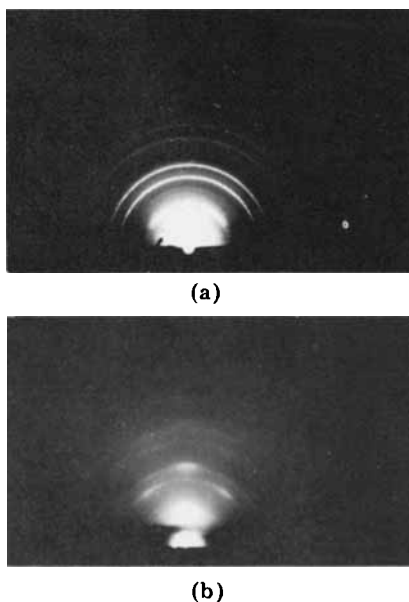


Fig. 7. Surface electron diffraction patterns of the polymer-Cu²⁺ complex films after iodine treatment: (a) PVA-Cu²⁺ complex film with $F_1 = 1/20$ and $F_2 = 0$; (b) PAAm-Cu²⁺ complex film with $F_1 = 1/14$ and $F_2 = 0$.

When the coagulation is observed, the reaction product on the film surface gives the surface electron diffraction pattern shown in Figure 7. The pattern suggests that the product is crystalline. Moreover, Figure 7(b) shows that the crystals in PAAm are oriented partially. To identify the reaction product, we scratched the product and obtained its x-ray Debye-Scherrer rings. Figure 8 clearly demonstrates that the main product is γ -CuI; the formation of the γ -CuI surface layer is responsible for the conductivity. When the coagulation is not clear, polymer-Cu²⁺-iodine-iodide complexes of some kind also appear to be formed, as will become clear in the ESR spectra.

Optical Absorption Spectra

We now consider the optical properties of the films. Absorption spectra of PVA films treated with acetone solution of iodine are shown in Figure 9. When the films contain no Cu²⁺ ions, i.e., $F_1 = 0$, four absorption bands are observed at 220, 295, 365, and 460 nm as indicated in Figure 9(a). By taking account of the assignments made for the absorption bands of an aqueous iodine-iodide solution, three species, I⁻, I₃⁻, and I₂, are considered to be responsible for these four absorption bands: I⁻ for 220 nm, I₃⁻ for 295 and 365 nm, and I₂ for 460

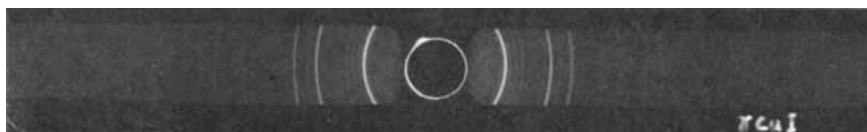
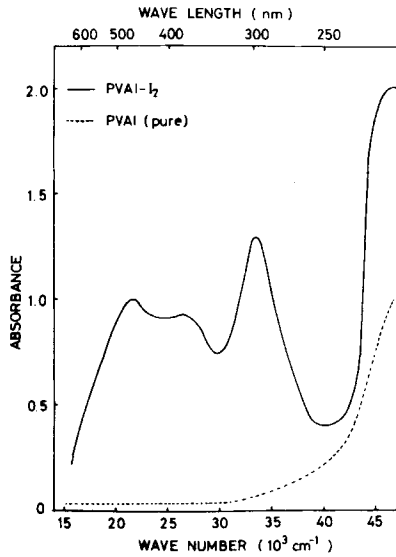


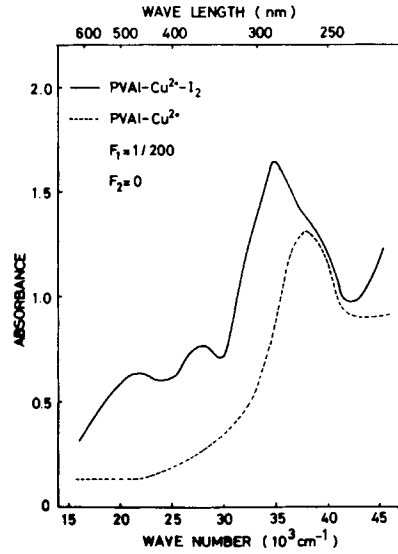
Fig. 8. X-Ray Debye-Scherrer rings of the reaction product on the surface of the PVA-Cu²⁺ complex film treated with iodine.

nm.⁹⁻¹² According to Tanizaki et al.,¹³ however, who studied the absorption bands of iodine-iodide complexes in uniaxially extended PVA films by using linearly polarized light, the 295- and 365-nm bands may be due to different species. An electron transfer from oxygen of PVA to iodine must produce PVA-I⁻ and PVA-I₃⁻ complexes.¹³

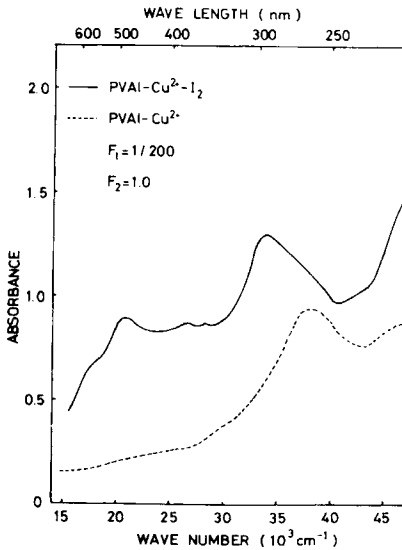
PVA-Cu²⁺ complexes contained in the films bring about two types of changes in the absorption spectra shown in Figure 9(a) depending on the state of coagu-



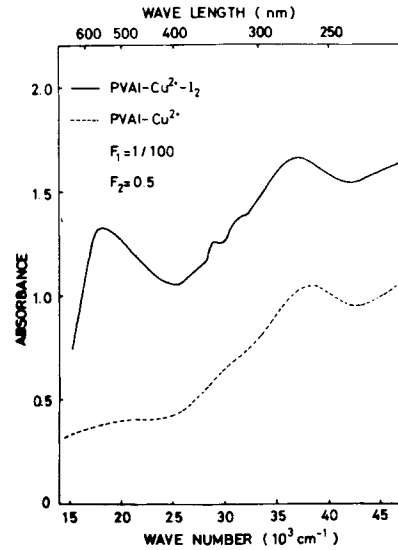
(a)



(b)



(c)



(d)

Fig. 9. Dependence on F_1 and F_2 of optical absorption spectra of PVA-Cu²⁺ complex films before and after the iodine treatment.

lation. When no coagulation apparently exists, the change observed is mainly a decrease of the I⁻, I₃⁻, and I₂ absorption bands as illustrated in Figure 9(b); the presence of PVA-Cu²⁺ complexes prevents the formation of pure PVA-I⁻, -I₃⁻, and -I₂ complexes. Iodine selectively attacks structurally disordered regions around Cu²⁺ complexes, forming PVA-Cu²⁺, -I⁻, -I₃⁻, and -I₂ complexes. Several reactions may further occur among PVA-Cu²⁺, -I⁻, -I₃⁻, and -I₂ complexes.

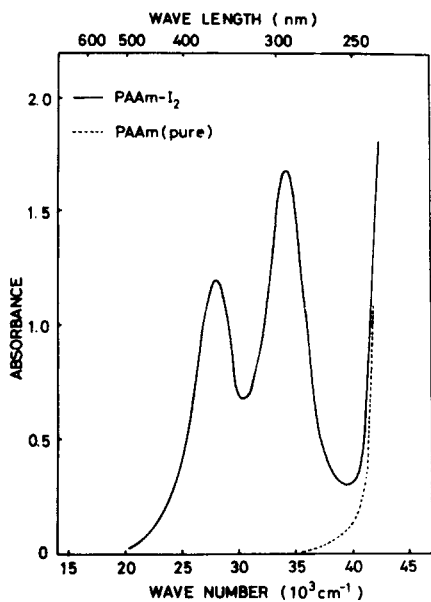
When the PVA-Cu²⁺ complex coagulates into a number of particles, on the other hand, new absorption bands grow at about 320, 345, and 550 nm with the increase of γ -CuI, as illustrated in Figures 9(c) and 9(d). The peak positions of these bands are slightly different from sample to sample. The 320- and 345-nm bands may originate from γ -CuI formed on the film surface and may relate to the formation of excitons, which produce two bands, i.e., the 335- and 395-nm bands at 4 K in pure γ -CuI crystals.¹⁴ In view of the success in explaining the blue color of PVA-boric acid-iodine in aqueous solution,^{11,12} the 550-nm band must be due to associated iodine molecules which may be helically enveloped by PVA chains. The crosslinking of a PVA molecule by Cu²⁺ chains bridged with OH⁻ ions may help to form a helical structure of some kind that meets the associated iodine molecules, as the boric acid does in aqueous solutions.

In the case of PAAM films treated with acetone solution of iodine, the situation is simpler, as shown in Figure 10. When the films contain no Cu²⁺ ions, i.e., $F_1 = 0$, only the I₃⁻ absorption bands are observed at 290 and 360 nm. When the complex coagulates into a number of particles, the two exciton bands of γ -CuI are clearly seen at 360 and 410 nm; the visible band due to associated iodine molecules does not appear, and hence the films remain colorless even after the iodine treatment.

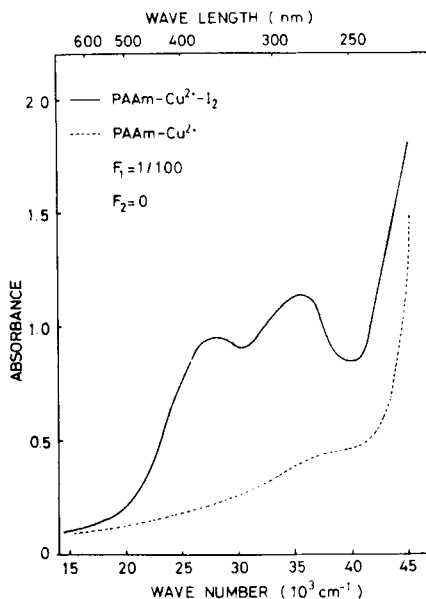
ESR Spectra

With $F_1 \lesssim 1/100$, we can obtain the information by means of changes in ESR signals about the way in which the iodine attacks the PVA-Cu²⁺ complexes and about the state of their coagulation. Figure 11 illustrates these changes with $F_1 = 1/200$. One extreme is the case shown in Figure 11(a), where no coagulation of PVA-Cu²⁺ complex is observed by the microscope. Before the iodine treatment the film shows the typical signal due to the monomeric Cu²⁺ complex as studied in detail in the previous paper⁴; this signal is designated as A signal. After the iodine treatment, an additional ESR signal is observed at $g \approx 4$, i.e., about 1600 G. The appearance of the $g \approx 4$ line indicates the formation of a dimeric Cu²⁺ complex⁴ probably bridged via iodine or iodide ions. The formation at low concentration of the complexes, i.e., $F_1 = 1/200$, indicates that some complexes lie close to one another even at $F_2 = 0$. This indication agrees with that made previously in connection with the inhomogeneous erosion observed by the scanning electron microscope.

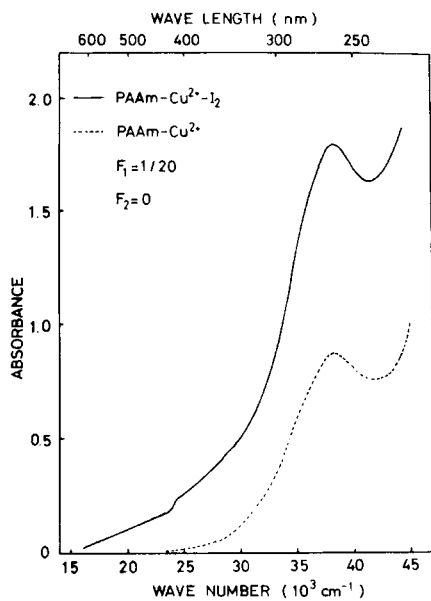
The other extreme is the case shown in Figure 11(c), where the coagulation of PVA-Cu²⁺ complex is complete. Before the iodine treatment the films show the single line due to the polymeric Cu²⁺ complex as studied in detail in the previous paper⁴; this signal is designated as B signal. After the iodine treatment, the A signal appears to be recovered. The B signal originates from the linear



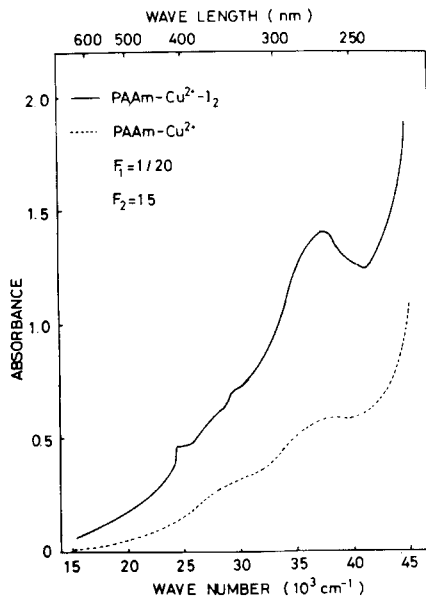
(a)



(b)

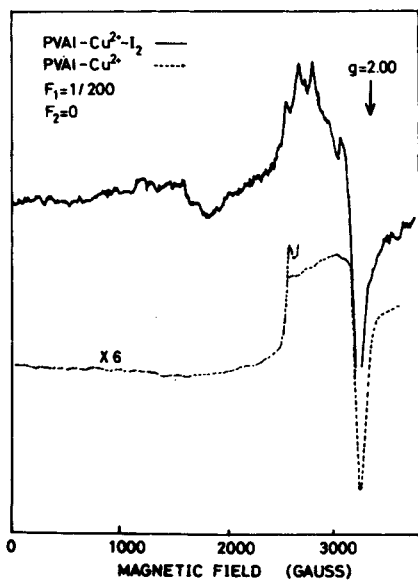


(c)

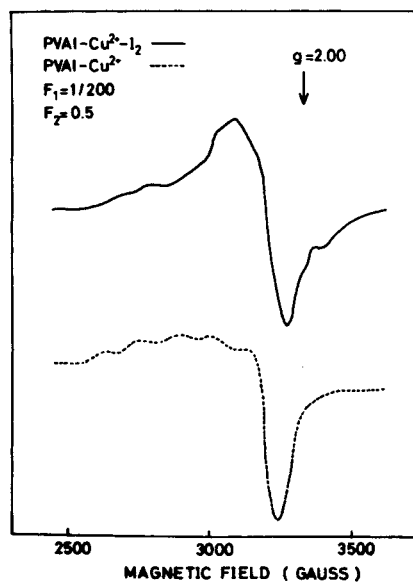


(d)

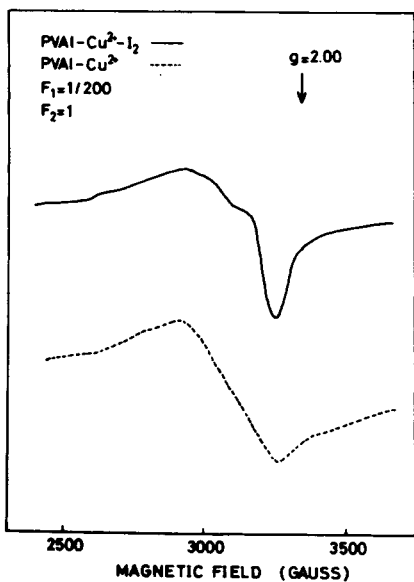
Fig. 10. Figures similar to Fig. 9 in PAAm-Cu²⁺ complex films.



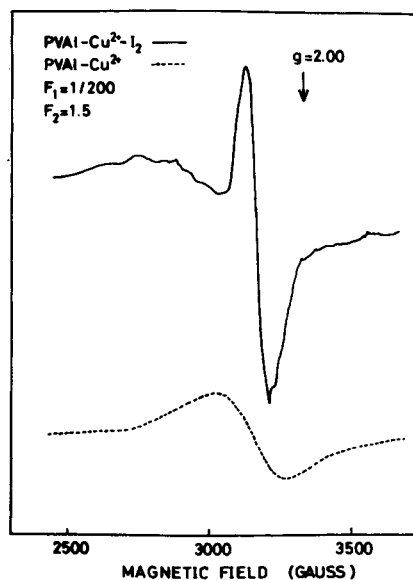
(a)



(b)



(c)



(d)

Fig. 11. Dependence on F_1 and F_2 of ESR spectra of PVA-CuCl₂ complex films before and after iodine treatment.

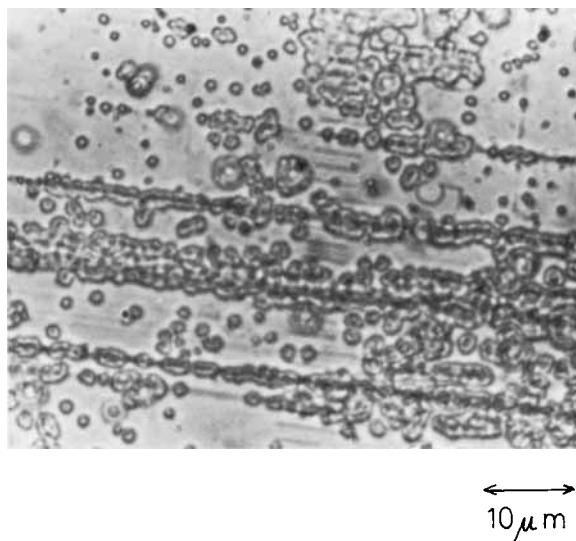


Fig. 12. Optical microscope photograph of the PVA-Cu²⁺ complex film with $F_1 = 1/100$ and $F_2 = 0.5$ made on grooved poly(methyl methacrylate) plate.

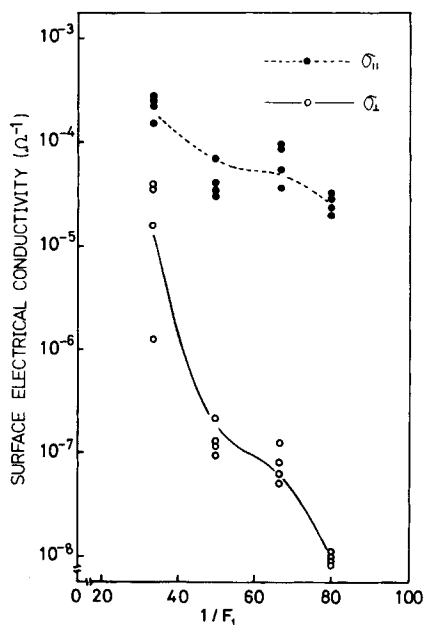


Fig. 13. Surface electrical conductivities, parallel (σ_{\parallel}) and perpendicular (σ_{\perp}) to the grooves, of PVA-Cu²⁺ complex films with $F_2 = 0.5$, made on grooved poly(methyl methacrylate) plate and treated with acetone solution of iodine.

chain of Cu²⁺ ions bridged with OH⁻ ions, both ends of the chain being chelated by PVA chains. The iodine treatment destroys the linear chain of Cu²⁺ ions. Since there exist enough iodide and Cu²⁺ ions in a concentrated region because of the coagulation of PVA-Cu²⁺ complex, the most stable γ -CuI is produced as a result of several reactions among PVA-Cu²⁺, I⁻, I₃⁻, and I₂ complexes.

Some of the Cu²⁺ ions chelated by PVA chains, however, remain unreacted and are responsible for the A signal.

Intermediate cases are shown in Figures 11(b) and 11(d), where the coagulation of the PVA-Cu²⁺ complexes is not complete. Though the formation of γ -CuI is not complete, some polynuclear Cu²⁺ complexes bridged via iodine or iodide ions will be produced, which may be responsible for the rather narrow line shown in Figures 11(b) and 11(d). A similar narrow single line is also observed in PAAM.

Films with Anisotropic Surface Conductivity

As often observed, the interface between a colloidal solution and its container will influence coagulation.¹⁵ Actually, we noted a tendency for the coagulation to occur along a scratch that existed accidentally on the poly(methyl methacrylate) plate used. Hence we cut grooves on the plate with a razor and tried to coagulate the polymer-Cu²⁺ complexes along the grooves. Figure 12 shows an optical microscope photograph of a film thus obtained. We can see linear arrays of polymer-Cu²⁺ complex. When treated with iodine, the film shows anisotropic surface conductivity as shown in Figure 13. To facilitate the coagulation, we chose $F_2 = 1$ and used CuCl₂. Both conductivities, parallel (σ_{\parallel}) and perpendicular (σ_{\perp}) to the grooves, decrease with decreasing F_1 . Since σ_{\perp} decreases rapidly, however, the anisotropy $\sigma_{\parallel}/\sigma_{\perp} \approx 10^3$ with reasonable conductivity $\sigma_{\parallel} \approx 10^{-4} \Omega^{-1}$ was obtained when $F_1 \approx 60$.

The authors would like to thank Professor H. Iwanaga in Nagasaki University for taking the x-ray photograph of the Debye-Scherrer rings.

References

1. H. Kakinoki, O. Sumita, C. S. Cho, and F. Higashi, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 407 (1976).
2. F. Higashi, C. S. Cho, H. Kakinoki, and O. Sumita, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 2303 (1977).
3. H. Kakinoki, C. S. Cho, F. Higashi, and O. Sumita, *J. Polym. Sci., Polym. Chem. Ed.*, in press.
4. O. Sumita, A. Fukuda, and E. Kuze, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 1801 (1978).
5. R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950).
6. B. Jirgensons and M. E. Straumanis, *A Short Textbook of Colloid Science*, Pergamon Press, London, 1962, Chap. XIII.
7. A. E. Alexander and P. Johnson, *Colloid Science*, Clarendon, Oxford, 1949, Chap. XX.
8. A. Sheludko, *Colloid Chemistry*, Elsevier, Amsterdam, 1966, Chap. XII.
9. L. L. Katzin, *J. Chem. Phys.*, **21**, 490 (1953).
10. A. D. Awtrey and E. Connick, *J. Am. Chem. Soc.*, **73**, 1842 (1951).
11. M. M. Zwick, *J. Appl. Polym. Sci.*, **9**, 2393 (1965).
12. J. G. Pritchard and D. A. Akintola, *Talanta*, **19**, 877 (1972).
13. Y. Tanizaki, J. Kobayashi, and N. Ando, *Nippon Kagaku Kaishi*, **80**, 445 (1959).
14. M. Cardona, *Phys. Rev.*, **129**, 69 (1968).
15. Reference 6, Chap. V.

Received May 2, 1978