

# Photoconductivity of Poly(vinyl Alcohol) Films with $\text{Fe}^{3+}$ Complexes and ESR Study of their Structures

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## Synopsis

We have studied whether photoconductivity is observed in polymer films containing the first transition metal complexes. Polymers investigated were poly(vinyl alcohol) (PVA), polyacrylamide, poly(acrylic acid), poly(vinyl pyrrolidone), and polyethylene glycol. Transition metal salts used were  $\text{CrCl}_3$ ,  $\text{MnCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{CoCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{FeBr}_3$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{Fe}_2(\text{SO}_4)_3$ , and  $\text{Fe}(\text{ClO}_4)_3$ . Only in the PVA- $\text{FeCl}_3$  film was relatively large photoconductivity due to the photoreduction of  $\text{Fe}^{3+}$  observed. ESR spectra indicate that an  $\text{Fe}^{3+}$  ion is chelated with two in-plane OH residues of PVA and coordinated with three  $\text{Cl}^-$  ions on the meridian. UV irradiation causes an electron transfer from  $\text{Cl}^-$  to  $\text{Fe}^{3+}$ . The produced chlorine atom extracts an electron from the oxygen of a neighboring OH residue. The unpaired electron thus formed can move from one oxygen to another through hydrogen bonding. In other words, the photoconductivity is due to holes produced in the network of PVA hydrogen bonding by the reduction of  $\text{Fe}^{3+}$ . Finally, we have tried to explain why the photoconductivity is observed only in the PVA- $\text{FeCl}_3$  film.

## INTRODUCTION

In previous articles<sup>1,2</sup> we have studied the structure of  $\text{Cu}^{2+}$  complexes in poly(vinyl alcohol) (PVA) and other analogous polymer films. The ESR study revealed that the polymer- $\text{Cu}^{2+}$  complexes exhibit several structures. Main factors in determining the structure are copper salt used, the two ratios  $F_1 = [\text{Cu}^{2+}]/[\text{MU}]$  and  $F_2 = [\text{OH}^-]/[\text{Cu}^{2+}]$ , and the heat treatment of the films, where the brackets denote the concentrations and MU refers to the monomeric units of PVA, for example. Most of the  $\text{Cu}^{2+}$  ion is chelated by two OH residues and coordinated by two halide ions when  $\text{CuCl}_2$  or  $\text{CuBr}_2$  is used, the ratios are chosen as  $F_1 > 0.015$  and  $F_2 = 0$ , and the film is dried at  $80^\circ\text{C}$  for 15 min. Since the  $\text{Cu}^{2+}$  ions are interacting by the superexchange interaction via the halide ions, there exists a network of the complexes. A hole generated by the electron transfer from halide ions to  $\text{Cu}^{2+}$ , i.e., by the photoreduction of the metal ion, can move through the network. Hence, the photoconductivity is observed by illuminating the charge transfer bands. This is the first example of the photoconductivity due to the photoredox reaction of the polymer-metal complexes in PVA and other analogous polymer films.<sup>3</sup>

To find other examples, we have studied various combinations of polymers and the first transition metal salts. Polymers investigated are PVA, polyacrylamide (PAAm), poly(acrylic acid) (PAAc), poly(vinyl pyrrolidone) (PVPr), and polyethylene glycol (PEG); transition metal salts used are  $\text{CrCl}_3$ ,  $\text{MnCl}_2$ ,

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$\text{FeCl}_3$ ,  $\text{CoCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{FeBr}_3$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{Fe}_2(\text{SO}_4)_3$ , and  $\text{Fe}(\text{ClO}_4)_3$ . Only the combination of PVA and  $\text{FeCl}_3$  is effective in producing the photoconductivity due to the photoredox reaction of the polymer-metal complexes. In the present article we report the characteristic features of the photoconductivity in the PVA- $\text{FeCl}_3$  film together with the optical absorption and ESR spectra of PVA- $\text{Fe}^{3+}$  films prepared by using  $\text{FeCl}_3$ ,  $\text{FeBr}_3$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{Fe}_2(\text{SO}_4)_3$ , and  $\text{Fe}(\text{ClO}_4)_3$ , and of other analogous polymer- $\text{FeCl}_3$  films mentioned above. Optical absorption spectra are also presented for PVA films containing  $\text{CrCl}_3$ ,  $\text{MnCl}_2$ ,  $\text{CoCl}_2$ , and  $\text{NiCl}_2$ . Based on these experimental results, we propose a model for the mechanism of the photoconductivity and the structure of the PVA- $\text{Fe}^{3+}$  complexes. We also try to explain why the photoconductivity due to the photoredox reaction is observed only in the PVA- $\text{FeCl}_3$  film among many other analogous films here investigated.

## EXPERIMENTAL

Table I summarizes the polymers used, together with their manufacturers and the molecular weights. Films of the polymer-metal complexes were made as described in detail in the previous articles.<sup>1-3</sup> The MU concentration used for casting the films was 2.5% by weight. The films were dried in a desiccator at least for five days, being heated at the glass transition temperatures (about 80°C in PVA) for 15 min before each measurement. The same procedures as in the previous articles<sup>1-3</sup> were followed in obtaining the photocurrent and ESR as well as optical absorption spectra. Unless otherwise stated, the photocurrent was obtained by using the surface cell.

### Photoconductivity

The photocurrent  $I_p$  depends on the polymer, on the metal salt, on the two ratios  $F_1$  and  $F_2$ , and on the wavelength of illumination. In PVA films,  $I_p$  is observed only when the films are prepared by using  $\text{FeCl}_3$ ,  $\text{FeBr}_3$ , and  $\text{CrCl}_3$ . Figure 1 illustrates  $I_p$  of these films. As in PVA- $\text{CuCl}_2$  and PVA- $\text{CuBr}_2$  films,<sup>3</sup>  $I_p$  consists of at least two components; one is a fast component that rises or falls quickly when light is turned on or off, and the other is a slow component. The fast component is rather weak and scarcely depends on the wavelength of illumination. The rather strong, slow component is observed only in the PVA- $\text{FeCl}_3$  film and appears to be related to the charge transfer band; hence we designate this component as  $I_{ct}$ . Figure 2 illustrates the wavelength dependence of  $I_p$

TABLE I  
Polymers Used

Polymer	Symbol	Molecular weight (MW)	Manufacturer
Poly(vinyl alcohol)	PVA	$6 \times 10^4$	Koso Chemical Co. Ltd.
Poly(acrylic acid)	PAAc	$1 \times 10^5$	Wako Pure Chemical Industries Ltd.
Polyacrylamide	PAAm	$5 \times 10^5$	Sumitomo Chemical Industry Co. Ltd.
Poly(vinyl pyrrolidone)	PVPPr	$3 \times 10^5$	Tokyo Kasei Kogyo Co. Ltd.
Polyethylene glycol	PEG	$6 \times 10^4$	Iwai Kagaku Co. Ltd.

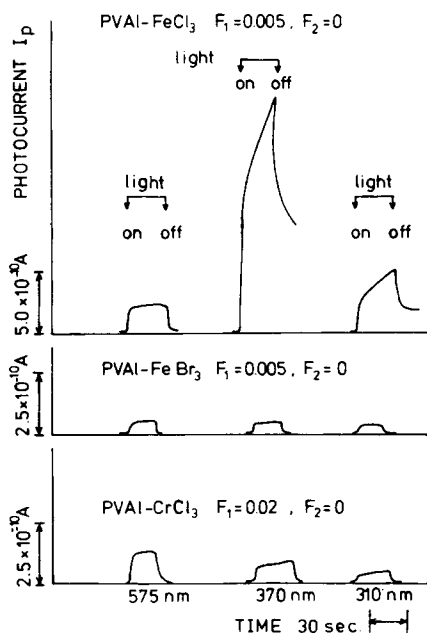


Fig. 1. Photocurrent in PVA-FeCl<sub>3</sub>, PVA-FeBr<sub>3</sub>, and PVA-CrCl<sub>3</sub> films produced by illumination at indicated wavelengths. Incident light intensities correspond to nearly equal numbers of photons; applied electric field is  $E = 270$  V/mm.

measured after 30 sec of illumination;  $I_p$  begins to increase at about  $20 \times 10^3$  cm<sup>-1</sup>. The observed increase is chiefly due to  $I_{ct}$ .

Contrary to the case of PVA-CuCl<sub>2</sub> and PVA-CuBr<sub>2</sub> films,  $I_{ct}$  is observed even when the Fe<sup>3+</sup> concentration is as low as  $F_1 = 0.002$ , becoming zero when  $F_1$  decreases further. Moreover, we have to distinguish two kinds of  $I_{ct}$ , since the response time of  $I_{ct}$  depends on  $F_1$ , as shown in Figure 3. When  $F_1 \gtrsim 0.02$ ,  $I_{ct}$  increases with time very slowly and hardly exhibits saturation even after 20 min of illumination. When  $F_1 \lesssim 0.02$ , on the other hand,  $I_{ct}$  rises rather quickly and is saturable. Since ESR spectra described below indicate that no interaction occurs among Fe<sup>3+</sup> complexes when  $F_1 \lesssim 0.02$ , we designate  $I_{ct}$  due to these monomeric Fe<sup>3+</sup> complexes as  $I_{ct,m}$  and mainly study it in this article. With increasing  $F_2$ ,  $I_{ct,m}$  naturally decreases and becomes zero when  $F_2 \gtrsim 3$ , for coagulation favors the occurrence of interactions among Fe<sup>3+</sup> complexes.<sup>1,2</sup>

To determine whether electrons or holes are responsible for the observed photocurrent,  $I_p$  was measured after illumination for 30 sec by using a sandwich cell in a longitudinal electric field.<sup>3</sup> The result is shown in Figure 4. In the charge transfer bands, where  $I_p$  chiefly consists of  $I_{ct,m}$ , illumination of the positive electrode produces larger  $I_p$  than illumination of the negative electrode, i.e.,  $I_p^+ > I_p^-$ .

We tried to measure  $I_p$  in PAAM, PAAc, and PEG films containing FeCl<sub>3</sub> complexes with  $F_1 = 0.02$  and  $F_2 = 0$ , but no photocurrent was observed even when the films were directly illuminated with a 250-W high-pressure mercury arc. In the PVPr-FeCl<sub>3</sub> film, UV irradiation produced  $I_{ct}$ , but it was very small as compared with that in the PVA-FeCl<sub>3</sub> film.

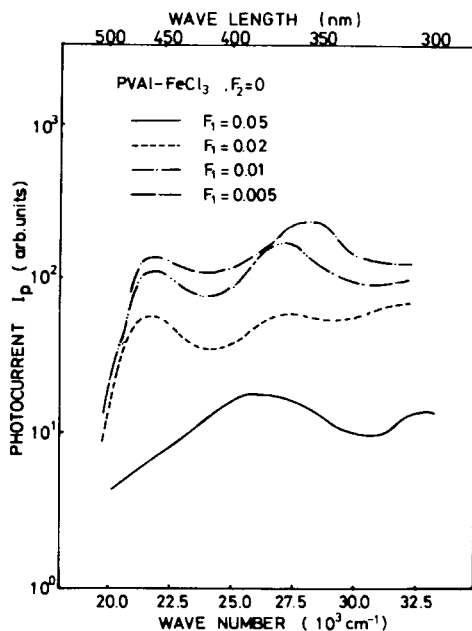


Fig. 2. Photocurrent spectra after 30 sec of illumination of PVA-FeCl<sub>3</sub> films with indicated  $F_1$  values and  $F_2 = 0$ ;  $E = 360 \text{ V/mm}$ .

### Optical Absorption Spectra

Figures 5 and 6 show the optical absorption spectra of PVA films containing one of the  $\text{Fe}^{3+}$  salts,  $\text{CrCl}_3$ ,  $\text{MnCl}_2$ ,  $\text{CoCl}_2$ , or  $\text{NiCl}_2$ . No charge transfer band is observed in the region below  $35 \times 10^3 \text{ cm}^{-1}$  in PVA-CrCl<sub>3</sub>, PVA-MnCl<sub>2</sub>,

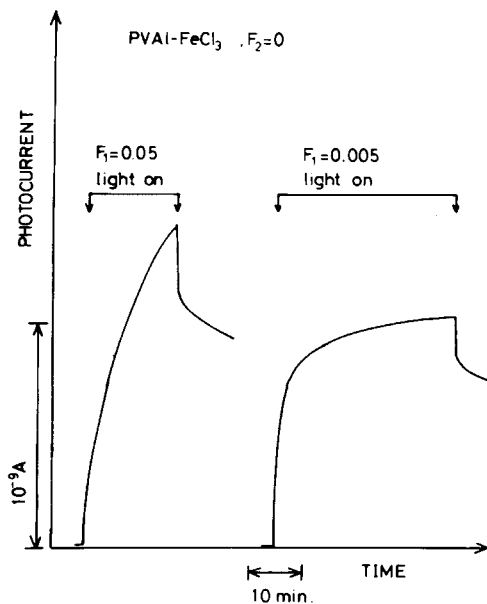


Fig. 3. Effect of  $F_1$  on  $I_p$  in PVA-FeCl<sub>3</sub> film with  $F_2 = 0$  produced by illumination at  $370 \text{ nm}$ ;  $E = 360 \text{ V/mm}$ .

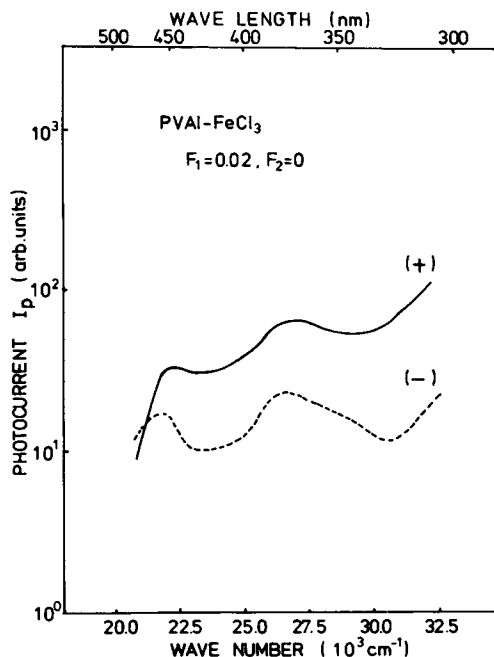


Fig. 4. Photocurrent spectra of PVA-FeCl<sub>3</sub> film with  $F_1 = 0.02$  and  $F_2 = 0$  for illumination of the positive (+) or negative (-) electrode of the sandwich cell for 30 sec.

PVA-CoCl<sub>2</sub>, and PVA-NiCl<sub>2</sub>; these transition metal ions are not easily photo-reducible. In PVA-Fe<sup>3+</sup> complexes, on the other hand, at least one characteristic peak or shoulder is observed between  $25 \times 10^3 \text{ cm}^{-1}$  and  $35 \times 10^3 \text{ cm}^{-1}$ ; PVA-FeBr<sub>3</sub> has the longest wavelength peak at about  $25 \times 10^3 \text{ cm}^{-1}$ . As  $F_1$  decreases and/or  $F_2$  increases, the effect of anions gradually becomes vague, as illustrated in Figure 6; the spectra of the complex films with  $F_1 = 0.002$  or less are almost similar to those of the complex solutions.

The spectra of PVA-Fe<sup>3+</sup> complex solutions do not depend on the salt anions unless  $F_1$  is very high. Figure 7 shows the  $F_2$  dependence of the spectra; the absorption intensity around  $(25-35) \times 10^3 \text{ cm}^{-1}$  increases with  $F_2$ . The potentiometric titration curve indicates the existence of a buffer region  $0 \leq F_2 \leq 3$ ; protons are dissociated from the PVA-FeCl<sub>3</sub> complex. The viscosity of the solution increases in the buffer region.

In PVA-Fe<sup>3+</sup> films, UV irradiation changes the absorption spectra, as illustrated in Figure 8; illumination was by a 250-W high-pressure mercury arc with a Toshiba UVD2 filter. The two characteristic peaks around  $(25-35) \times 10^3 \text{ cm}^{-1}$  clearly decrease with UV dosage. In PVPr-FeCl<sub>3</sub>, an analogous but slight change is also observed. The spectra of PAAm, PAAc, and PEG films containing FeCl<sub>3</sub>, and PVA films containing CrCl<sub>3</sub>, MnCl<sub>2</sub>, CoCl<sub>2</sub>, or NiCl<sub>2</sub>, on the other hand, are scarcely affected by UV irradiation.

### ESR Spectra

An ESR study is suitable for understanding the local environment of an Fe<sup>3+</sup> ion, since it has the  $d^5$  electron configuration. Figures 9 and 10 illustrate the influence of anions on the ESR spectra of PVA-Fe<sup>3+</sup> films with  $F_1 = 0.02$  and

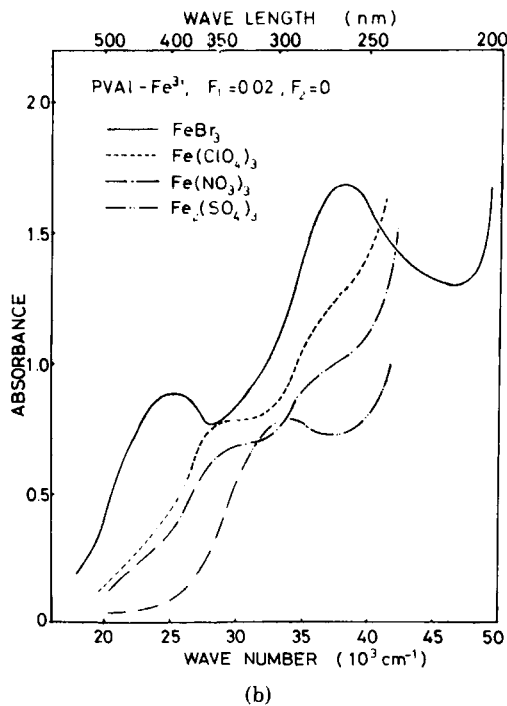
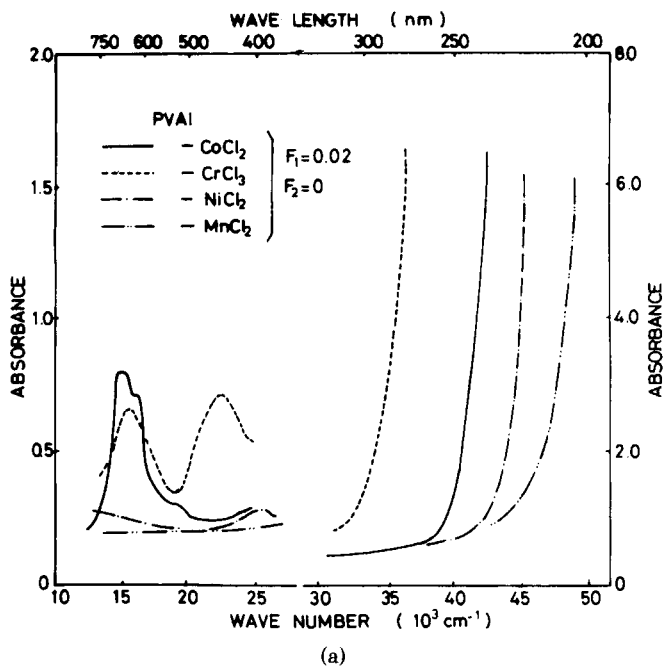


Fig. 5. Optical absorption spectra: (a) PVA- $\text{CrCl}_3$ , PVA- $\text{MnCl}_2$ , PVA- $\text{CoCl}_2$ , and PVA- $\text{NiCl}_2$  films ( $F_1 = 0.02$  and  $F_2 = 0$ ); (b) PVA- $\text{FeBr}_3$ , PVA- $\text{Fe}(\text{ClO}_4)_3$ , PVA- $\text{Fe}(\text{NO}_3)_3$ , and PVA- $\text{Fe}_2(\text{SO}_4)_3$  films ( $F_1 = 0.02$  and  $F_2 = 0$ ).

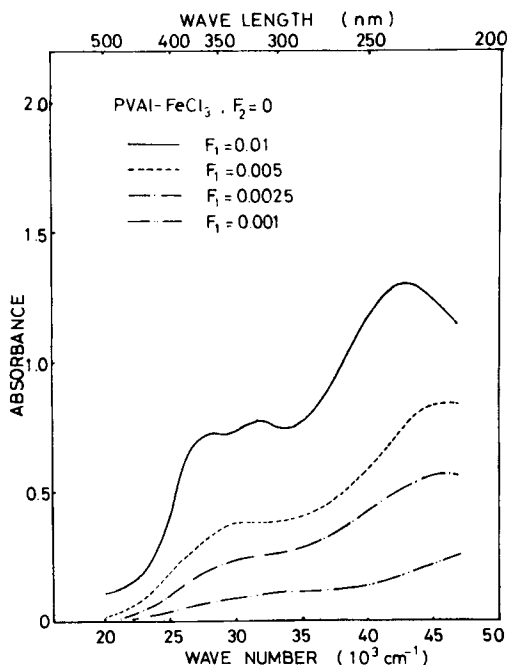


Fig. 6. Optical absorption spectra of PVA-FeCl<sub>3</sub> films with indicated  $F_1$  values and  $F_2 = 0$ .

$F_2 = 0$ . For Cl<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup> anions, two signals are observed; one is a single line at  $g = 4.3$ , and the other is a very broad background absorption with a shoulder at  $g = 10$ . For Br<sup>-</sup> anion, the  $g = 6$  signal is stronger than the  $g = 4.3$  signal. The ratio between these signals depends on the heat treatment; the  $g = 6$  signal will disappear almost completely after prolonged, say, 45-min, heat treatment. For SO<sub>4</sub><sup>2-</sup> anion, a  $g = 2$  broad signal is observed in addition to the  $g = 4.3$  signal. When the PVA-FeCl<sub>3</sub> film is dialyzed for 1 hr, the analogous  $g = 2$  broad signal grows, while the  $g = 4.3$  signal almost completely disappears.

Figure 9 also shows the  $F_1$  dependence of the ESR spectra in the PVA-FeCl<sub>3</sub> film with  $F_2 = 0$ . With decreasing  $F_1$ , the  $g = 4.3$  signal becomes weak and narrow, and, at the same time, another signal seems to appear at  $g = 2$ . Note that the threshold for the appearance of the  $g = 4.3$  signal in the ESR spectra is about  $F_2 = 0.002$ , which nearly coincides with that of  $I_{ct,m}$  in the photocurrent. With increasing  $F_2$ , a broad single line grows at  $g = 2$ , whereas the  $g = 4.3$  signal gets smaller, disappearing almost completely when  $F_2 = 1.5$ . This  $g = 2$  broad single line, illustrated in Figure 11, also appears in other PVA-Fe<sup>3+</sup> films investigated when  $F_2 > 0$ .

The intensity of the  $g = 4.3$  signal, together with the  $g = 10$  shoulder in the PVA-FeCl<sub>3</sub> film with  $F_1 = 0.002$ -0.05 and  $F_2 = 0$ , is inversely proportional to the absolute temperature. The  $g = 2$  broad single-line intensity of the film with  $F_2 > 0$ , on the other hand, decreases with lowering temperature, as shown in Figure 11; this decrease indicates that a strong exchange interaction exists among the complexes responsible for the signal.

Figure 12 shows the ESR spectra of the PVA-FeCl<sub>3</sub> film with  $F_1 = 0.01$  and  $F_2 = 0$  uniaxially stretched by 200% at about 80°C. The  $g = 4.3$  signal is insen-

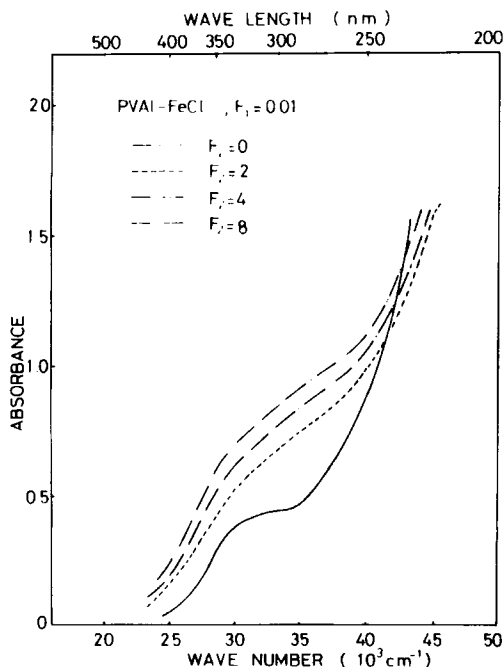


Fig. 7. Optical absorption spectra of PVA-FeCl<sub>3</sub> aqueous solutions with  $F_1 = 0.01$  and indicated  $F_2$  values.

sitive to the angle between the applied magnetic field and the stretching direction; this signal is isotropic. The broad signal with the shoulder at  $g = 10$ , on the other hand, depends on the angle  $\alpha$ ; its intensity at  $\alpha = 0^\circ$  is smaller than that at  $\alpha = 90^\circ$ .

In the PVA-FeCl<sub>3</sub> film with  $F_2 = 0$ , UV irradiation at the charge transfer bands changes the ESR spectra, as illustrated in Figure 13. The irradiation produces a new triplet signal at  $g = 2$ , reducing the  $g = 4.3$  signal. The production rate depends on  $F_1$ ; it is fast when  $F_1$  is small. When the irradiation is made at  $-100^\circ\text{C}$ , a single broad signal first grows, and then the triplet signal appears, as shown in Figure 14. The  $g = 2$  single broad signal is strong and slightly asymmetric at low temperatures; it becomes weak and narrow with rising temperature and is hardly detected above  $-20^\circ\text{C}$ , as shown in Figure 15. UV irradiation also produces the  $g = 2$  triplet signal in PVA-FeBr<sub>3</sub>, PVA-Fe(ClO<sub>4</sub>)<sub>3</sub>, and PVA-Fe(NO<sub>3</sub>)<sub>3</sub> films, as illustrated in Figure 16. However, more than three times the dosage is needed to obtain the same signal intensity as in the PVA-FeCl<sub>3</sub> film. Moreover, the  $g = 2$  single broad signal could not be observed in these films, even at low temperatures. Note that the  $g = 2$  triplet signal is asymmetric in the PVA-Fe(NO<sub>3</sub>)<sub>3</sub> film.

The  $g = 4.3$  signal is also observed in PAAM-FeCl<sub>3</sub> and PAAc-FeCl<sub>3</sub> films with  $F_1 = 0.02$  and  $F_2 = 0$ . In PVPr-FeCl<sub>3</sub> and PEG-FeCl<sub>3</sub> films, on the other hand, the  $g = 2$  broad signal is observed as in the PVA-Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> film. In PAAM-FeCl<sub>3</sub>, PAAc-FeCl<sub>3</sub>, PVPr-FeCl<sub>3</sub>, and PEG-FeCl<sub>3</sub> films, UV irradiation does not efficiently produce the  $g = 2$  triplet signal.



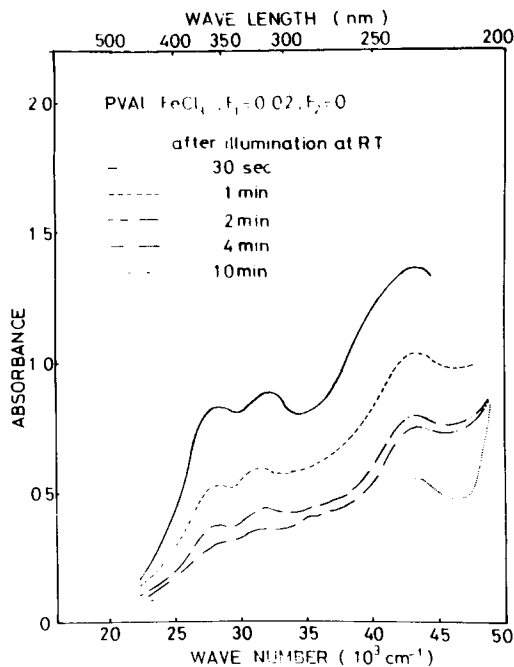


Fig. 8. Effect of UV irradiation on optical absorption spectra of PVA-FeCl<sub>3</sub> film with  $F_1 = 0.02$  and  $F_2 = 0$ .

DISCUSSION

Interpretation of ESR Spectra

There are many ESR studies of Fe<sup>3+</sup> complexes in view of their importance in biochemistry. So far as we know, however, no systematic ESR study has been made for PVA-Fe<sup>3+</sup> complexes in films. Following the treatment by Castner et al.,<sup>4</sup> Griffith,<sup>5,6</sup> Wickman et al.,<sup>7</sup> Dowsing and Gibson,<sup>8</sup> and Aasa,<sup>9</sup> we shall

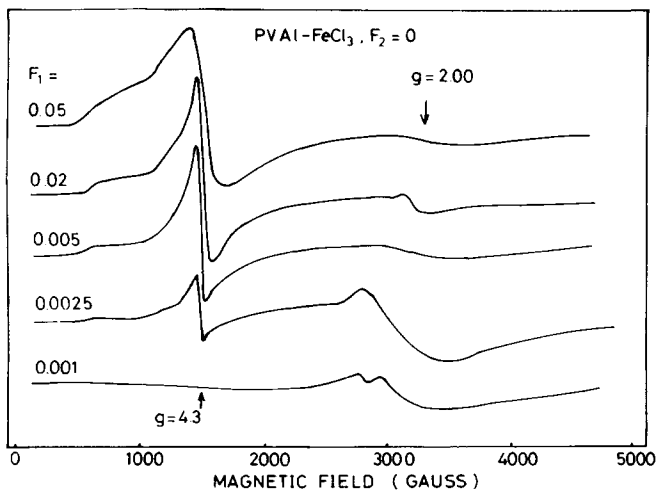


Fig. 9. ESR spectra of PVA-FeCl<sub>3</sub> films with indicated  $F_1$  values and  $F_2 = 0$ .

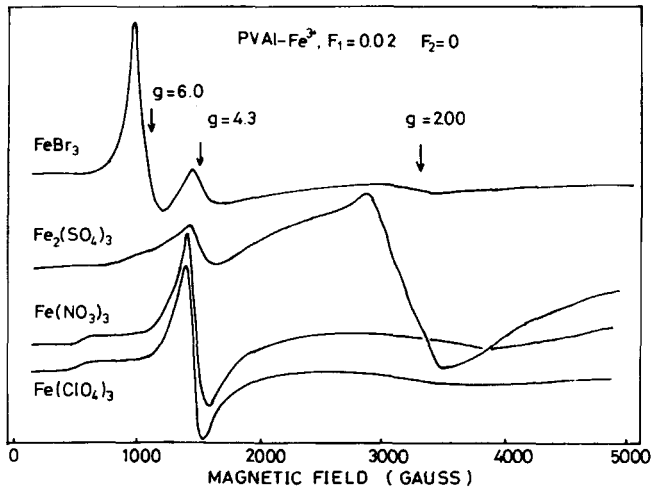


Fig. 10. ESR spectra of PVA-FeBr<sub>3</sub>, PVA-Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, PVA-Fe(NO<sub>3</sub>)<sub>3</sub>, and PVA-Fe(ClO<sub>4</sub>)<sub>3</sub> films with  $F_1 = 0.02$  and  $F_2 = 0$ .

analyze the observed ESR spectra to elucidate the structure of the PVA-Fe<sup>3+</sup> complexes. When the ligand field is weak, a single line appears at  $g = 2$  because the ground state of a free Fe<sup>3+</sup> ion is  ${}^6S_{5/2}$  with a  $3d^5$  electron configuration. Actually, the ligand field is strong, and the effective  $g$ -value largely depends on the symmetry of the complexes; three Kramers' doublets exist. The spin Hamiltonian is given by

$$\mathcal{H}_S = g\beta S \cdot H + D\{S_z^2 - \frac{1}{3}S(S+1)\} + E(S_x^2 - S_y^2) \quad (1)$$

where  $D$  and  $E$  are fine-structure constants.

Wickman et al.<sup>7</sup> obtained the effective  $g$ -values of three crystal-field Kramers' doublets as a function of  $\lambda = E/D$  by numerically solving the Hamiltonian given in eq. (1);  $\lambda = 0$  represents the axial symmetry and  $|\lambda| = \frac{1}{3}$  corresponds to the "complete" orthorhombic symmetry. More elaborate calculations have been made by Dowsing and Gibson<sup>8</sup> and Aasa.<sup>9</sup> These calculated results suggest the

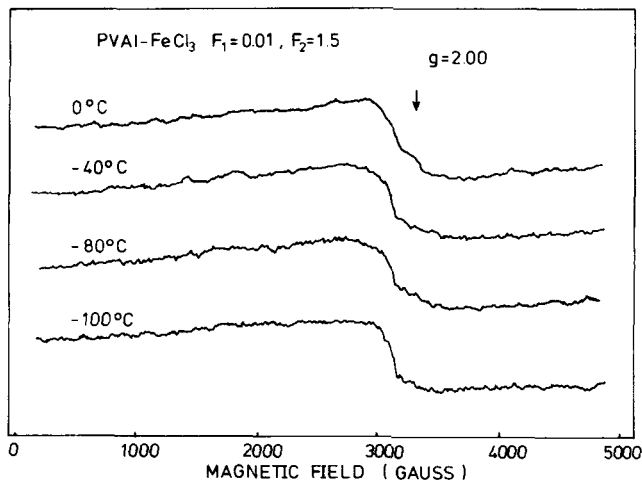


Fig. 11. ESR spectra of PVA-FeCl<sub>3</sub> film with  $F_1 = 0.01$  and  $F_2 = 1.5$  at several temperatures.

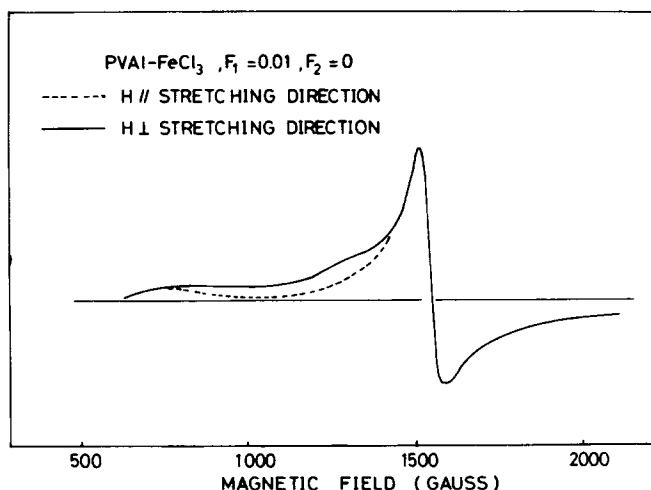


Fig. 12. ESR spectra of PVA-FeCl<sub>3</sub> film with  $F_1 = 0.01$  and  $F_2 = 0$  uniaxially stretched ca. 200% at 80°C.

following interpretation: first, complexes with  $|\lambda| = \frac{1}{3}$  produce the  $g = 4.3$  signal with the  $g = 10$  shoulder; secondly, complexes with  $\lambda = 0$  produce the  $g = 6$  signal; thirdly, the resonance field will be distributed broadly when  $0 < |\lambda| < \frac{1}{3}$ .

### Structure of Fe<sup>3+</sup> Complexes in Polymer Films

The above interpretation makes it possible to deduce the structure of PVA-Fe<sup>3+</sup> complexes. In PVA-FeCl<sub>3</sub>, PVA-Fe(NO<sub>3</sub>)<sub>3</sub>, and PVA-Fe(ClO<sub>4</sub>)<sub>3</sub> films, the symmetry of the Fe<sup>3+</sup> ion must be "completely" orthorhombic, since a  $g = 4.3$  signal is observed. As in the PVA-Cu<sup>2+</sup> complexes,<sup>1</sup> there exists a relatively strong interaction between PVA and Fe<sup>3+</sup>, since most Fe<sup>3+</sup> ions still remain in the film after the 1-hr dialysis. The ESR spectra of uniaxially stretched films shown in Figure 12 suggest that an Fe<sup>3+</sup> ion is chelated with two in-plane OH

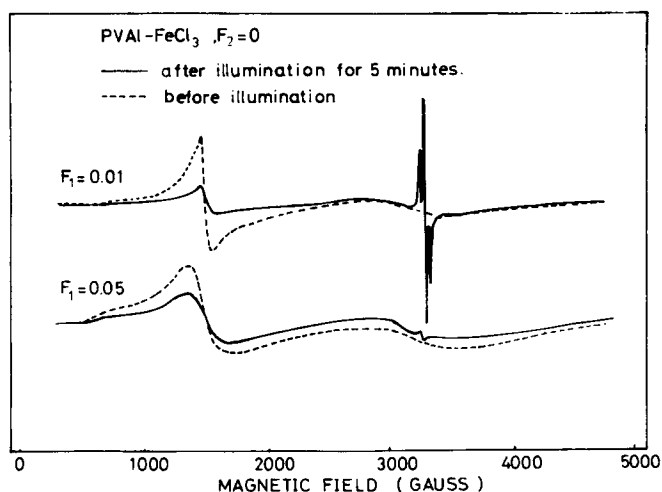


Fig. 13. Effect of UV irradiation on ESR spectra of PVA-FeCl<sub>3</sub> films with indicated  $F_1$  values and  $F_2 = 0$ .

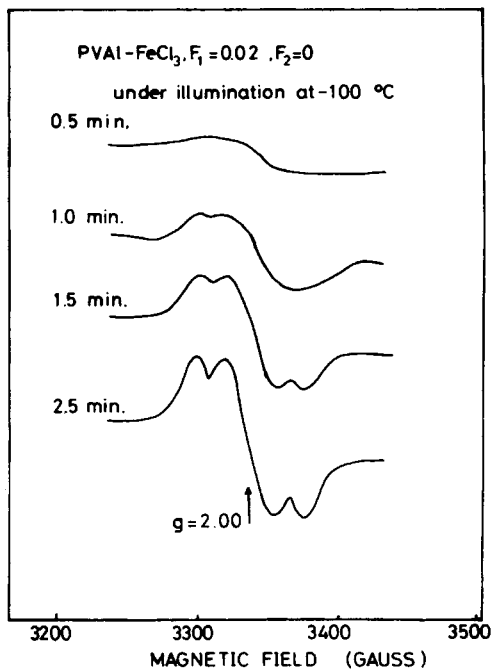


Fig. 14. ESR spectra of PVA-FeCl<sub>3</sub> film with  $F_1 = 0.02$  and  $F_2 = 0$  after UV irradiation at -100°C for indicated periods.

residues of PVA.<sup>3</sup> Because of the heat treatment, the three anions, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, or ClO<sub>4</sub><sup>-</sup>, must exist in the first coordination sphere to compensate 3+ charges.<sup>3</sup> Taking account of the fact that the coordination number is 6, we obtain Figure 17 as a probable configuration in the first coordination sphere; it is of the orthorhombic ( $C_{2v}$ ) symmetry and has the three anions on the meridian.

In the PVA-FeBr<sub>3</sub> film, some complexes show the  $g = 6$  signal and hence have uniaxial symmetry; others produces the  $g = 4.3$  signal and hence are "completely" orthorhombic. With the uniaxial symmetry, two of the three Br<sup>-</sup> ions occupy the ligand sites in the axial direction, whereas the remaining one is not located in the first coordination sphere. When the film is sufficiently heat treated, the remaining Br<sup>-</sup> ion enters the first coordination sphere and the three Br<sup>-</sup> ions are on the meridian; the symmetry becomes "completely" orthorhombic ( $C_{2v}$ ). In the PVA-Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> film, the molar ratio of Fe<sup>3+</sup> to SO<sub>4</sub><sup>2-</sup> ions is not an integer. We reasonably suppose that the complex does not have a well-defined structure or symmetry. The broad  $g = 2$  signal is attributable to the widespread  $|\lambda|$  between 0 and  $\frac{1}{3}$ .

The  $g = 4.3$  signal in PAAm-FeCl<sub>3</sub> and PAAc-FeCl<sub>3</sub> films may suggest a complex structure similar to that in the PVA-FeCl<sub>3</sub> film. In the PVPr-FeCl<sub>3</sub> and PEG-FeCl<sub>3</sub> films, the rather large side chains may hinder the formation of the complex structure shown in Figure 17; these complexes have no well-defined symmetry, and hence the parameter  $|\lambda|$  is widespread between 0 and  $\frac{1}{3}$ . The  $g = 2$  broad signals are explained by this widespread  $|\lambda|$  as in the PVA-Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> film.

Dialysis appears to replace some Cl<sup>-</sup> ions with OH<sup>-</sup>, making the symmetry of the first coordination sphere indefinite as in the PVA-Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> complex.

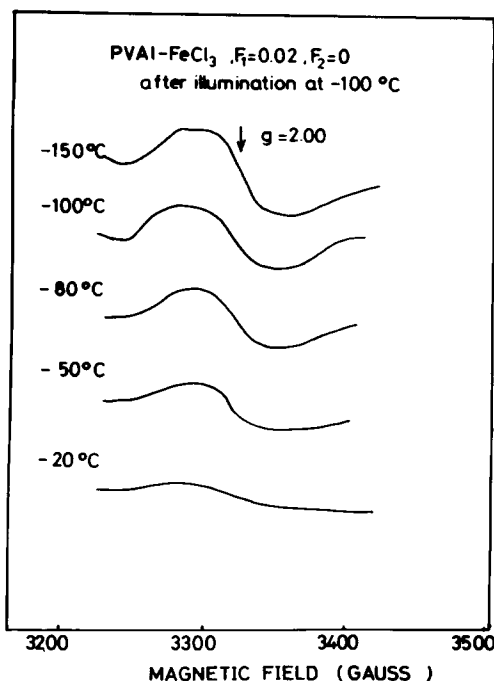


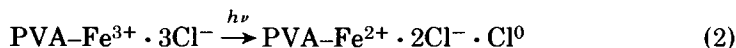
Fig. 15. ESR spectra of PVA-FeCl<sub>3</sub> film with  $F_1 = 0.02$  and  $F_2 = 0$  obtained at indicated temperatures after UV irradiation at  $-100^\circ\text{C}$  for 30 sec.

The replacement results in the disappearance of the  $g = 4.3$  signal in the ESR spectra and of the two characteristic peaks or shoulders in the optical absorption spectra. Moreover, the resulting indefinite symmetry can explain the growth of the  $g = 2$  broad signal as in the PVA-Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> film.

The  $g = 4.3$  signal must be due to the middle-energy Kramers' doublet, because the stretching of the film does not affect the signal; note that the effective  $g$ -values in this Kramers' doublet  $g_x$ ,  $g_y$ , and  $g_z$  have the same value 4.3 when  $|\lambda| = \frac{1}{3}$ , as is clear in Figure 5 of ref. 7. Either of the lowest or highest Kramers' doublet has an effective  $g$ -value  $g_y \approx 10$  or  $g_z \approx 10$ . Because of its temperature variation, we have to assign the  $g = 10$  shoulder to the lowest one; it is anisotropic when the film is stretched as shown in Figure 12. This anisotropy suggests the proposed complex structure where two OH residues occupy the in-plane ligand sites.<sup>3</sup>

### Mechanism of the Photoconduction

The UV absorption bands are known to be charge transfer bands, where an electron is transferred from the ligands to a metal ion. Namely, UV irradiation causes the following reduction reaction:



Usually, chlorine atoms extract hydrogens from polymer molecules to produce alkyl radicals, which show the  $g = 2$  triplet signal in the ESR spectra.<sup>3</sup> In the PVA-FeCl<sub>3</sub> film, however, there exists another process than the formation of

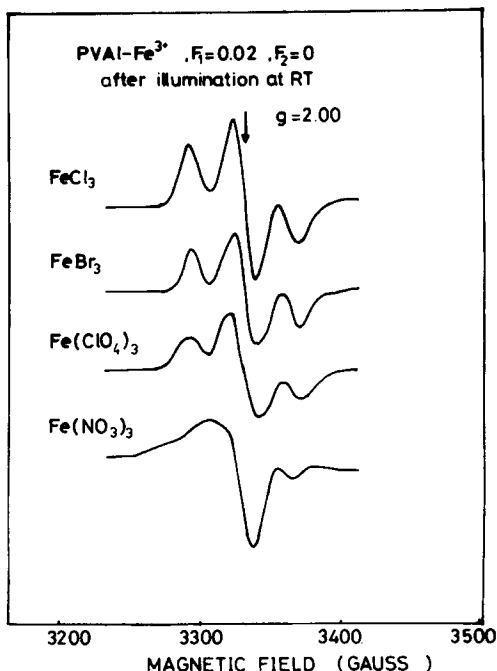


Fig. 16. ESR spectra of PVA-FeCl<sub>3</sub>, PVA-FeBr<sub>3</sub>, PVA-Fe(ClO<sub>4</sub>)<sub>3</sub>, and PVA-Fe(NO<sub>3</sub>)<sub>3</sub> films with  $F_1 = 0.02$  and  $F_2 = 0$  after UV irradiation at room temperature.

alkyl radicals; this process forms the unpaired electron responsible for the  $g = 2$  single broad signal shown in Figures 14 and 15. Since the signal exhibits motional narrowing, the produced unpaired electron must move here and there. We tentatively assign the signal to the alkoxy radical associated with the OH residue of the PVA<sup>10</sup> because of the following three reasons: first, the signal width is relatively broad; secondly, the signal becomes asymmetric at low temperatures; and thirdly, it is unstable at room temperature. The chlorine atom extracts an electron from the oxygen of a neighboring OH residue.

The unpaired electron thus produced can move from one oxygen to another through hydrogen bonding, as illustrated in Figure 18. After moving some distance, the unpaired electron will become stabilized by forming an alkyl radical. In view of solid-state physics, we can say that the photoconductivity is due to

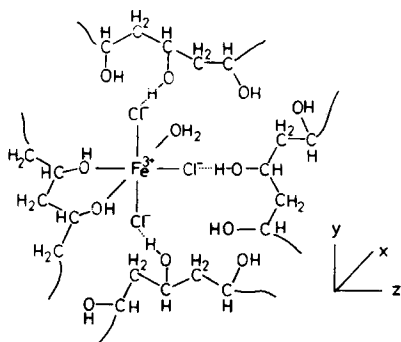


Fig. 17. Probable structure of PVA-FeCl<sub>3</sub> complex with  $F_2 = 0$ .

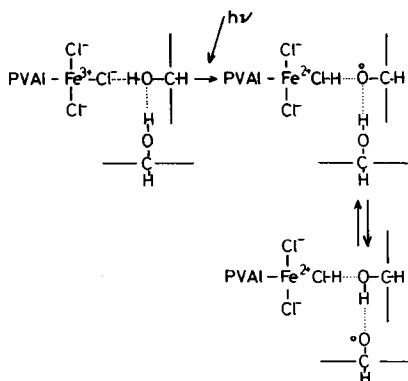


Fig. 18. Proposed mechanism of photoconductivity. Holes are produced in the network of PVA hydrogen bonding by the reduction of  $\text{Fe}^{3+}$ .

holes produced in the network of PVA hydrogen bonding by the reduction of  $\text{Fe}^{3+}$ . This conclusion is consistent with the dependence of  $I_{ct,m}$  on the polarity of the illuminated electrode, i.e.,  $I_{ct,m}^+ > I_{ct,m}^-$ .

The  $g = 4.3$  signal becomes broader with increasing  $F_1$  as shown in Figure 9. The width appears to be due to the magnetic dipolar interaction because of the following three reasons: first,<sup>11</sup> the width is proportional to the square root of  $F_1$ ; secondly, a similar broadening is observed even in  $\text{PVA-Fe}(\text{NO}_3)_3$  and  $\text{PVA-Fe}(\text{ClO}_4)_3$  where exchange interaction is hardly considered to be operative; finally, the temperature dependence of the signal intensity is independent of  $F_1$ . In  $\text{PVA-CuCl}_2$  and  $\text{PVA-CuBr}_2$  films, on the other hand, only the exchange interaction via intervening halide ions is effective in transporting holes through the films. Since this mechanism can be regarded as an impurity conduction in solid-state physics, the photocurrent rises slowly as compared with that in the  $\text{PVA-FeCl}_3$  film. The transportation of carriers must be partly assisted by the exchange interaction even in the  $\text{PVA-FeCl}_3$  film when  $F_1$  is as large as 0.02 or more. The assistance can explain the lowered production rate of alkyl radicals illustrated in Figure 13 and the prolonged rise time of the photocurrent shown in Figure 3.

In this way,  $I_{ct}$  depends on the production rate of mobile unpaired electrons as well as their Schubweg. The production rate critically depends on the efficiency of transferring the excitation energy from the complex to the polymer itself. Hence, the structure of the outer coordination sphere is as important as that of the inner coordination sphere. The simple atomic ligands,  $\text{Cl}^-$  or  $\text{Br}^-$ , are more favorable for the transformation than the molecular ligands,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{ClO}_4^-$ . In fact,  $\text{NO}_3^-$  appears to capture the produced unpaired electron<sup>12</sup> and to prohibit the excitation energy in the complex from transferring to the polymer; even the simple atomic ligand,  $\text{Br}^-$ , is not enough for the appearance of the photoconductivity. Note that the chlorine atom is more effective in extracting hydrogen than the bromine atom.<sup>13</sup> Other first transition metal ions investigated are less reducible than  $\text{Fe}^{3+}$ ; reverse reaction, i.e., oxidation of the metal ions, must occur before excited energy is transferred from the complex to the polymer and hence no photocurrent is observed. When carriers are transported in the polymer itself, its electronic structure must influence the photocurrent. In the  $\text{PAAc-FeCl}_3$  film, no photocurrent is observed, though

the coordination sphere of the complexes appears to be similar to that of the PVA-FeCl<sub>3</sub> film. This suggests that carbonyl residues are malignant to the transportation of carriers, because holes are probably trapped on the carbonyl oxygens.

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