Studies on the Preparation and Properties of Conductive Polymer. I. Novel Method to Prepare Metalized Plastic from Metal Chelate of Poly(vinyl Alcohol)

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Synopsis

A novel and easily processed conductive polymer was prepared from poly(vinyl alcohol)(PVA). Metal chelate onto PVA film exhibited excellent surface resistivity around 10^0–10^2 Ω/cm^2 when it was treated with reducing agents. The surface of these films was treated with reducing agents which possessed a definite metallic luster. The conducting surface proved to be metallized by x-ray and ESCA analysis. The strongly adhering metal on the film was believed to be responsible for the enhancement of electrical conductivity. The factors that affect the conductivity of metallized film were also studied.

INTRODUCTION

Electrical conductivity of organic polymers can be introduced by kneading carbon black and metal powders into the polymers. But the amounts of additive required to produce conductivity are large and result in poor mechanical properties for the polymers. Therefore, this method is of limited practical value.

Until now, metallized films or similar metallized polymeric articles have been prepared by using sputtering, vacuum, electroplating, or electroless plating techniques.[1-3] The aforementioned techniques sometimes require preliminary surface treatment, such as mechanical roughing, chemical modification, etching, sensitizing, or activation. These processes are troublesome and tedious.

In order to develop easily processed organic semiconductors, a method is proposed using polymers as a base which can be easily processed and modified. Polyacrylamide (PAAm) and Poly(vinyl alcohol) (PVA) are water-soluble polymers, that can react with metal salts in a aqueous solution to form polymer metal chelates. These metal chelates can be readily moulded into fibers, films, and other mouldings without detriment to the physical properties of the original polymers. Doping with iodine on the chelate film was found by one of the authors to obtain good electric conductivity.[4-6]

Recently, Lee et al.,[7,8] proposed a new method for preparing Ag-Hg alloy metallized PAAm film by holding PAAm–Ag^+ aqueous solution under Hg-

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CCC 0021-8995/90/1-20053-14$04.00

saturated atmosphere at room temperature. However, this method cannot be applied to any other polymer–metal chelate films, including PVA–Ag^+ chelate films.

We report here a novel method for preparing metallized film. PVA metal chelate films were treated with sodium borohydride and other reducing agents in a suitable solvent. Good electrical conducting films can be obtained. The optimal preparative conditions, physical properties, and structures of these conductive polymer films were also studied.

EXPERIMENTAL

Preparation of Poly(vinyl Alcohol) Metal Chelate Film

PVA metal chelate films were prepared by the following two methods:

Mixed Method: By introducing the $AgNO_3$ or $CuCl_2 \cdot 2H_2O$ solution into a 10% (by weight) PVA water solution to adjust the ratio of the molar concentration of metal ions to that of monomeric units of the PVA, ($F = [M^{+n}]/[MU]$). These given conditions are listed in Table I. This mixture was stirred at room temperature for 24 h. The resulting viscous solution was cast on poly(methyl methacrylate) plates and dried under air atmosphere at ambient temperature for three days, and further dried in an oven at 80°C for 1 h. These 50–60 μm thick films were peeled from the plates, and then cut into 1 cm × 3 cm sections for electric measurement.

Soaked Method: A 13% (by weight) PVA water solution was cast onto a poly(methyl methacrylate) sheet and dried by air for about three days at ambient temperature, resulting in a somewhat wet film. The film was peeled off the plate and cut into a 1 × 3 cm test piece. The test piece was soaked in a

TABLE I
Effect of Various Reductive Conditions on the Surface Resistivity of PVA–Metal Chelate Films

PVA metal chelate film			Reductive conditions				Surface resistivity (Ω/cm^2)
Metal salts	Wt %[c]	F value	Reducing agents	Solvent	Temperature	Time	
—	—	—	—	—	—	—	ca. 10^{13}
$AgNO_3$[a]	30.0	0.078	—	—	—	—	ca. 10^{11}
$AgNO_3$[a]	30.0	0.078	$NaBH_4$(0.6%)	H_2O	r.t.	20 s	1.1×10^0
$CuCl_2$[a]	30.0	0.078	$NaBH_4$(2.0%)	H_2O	r.t.	30 s	2.1×10^1
$AgNO_3$[b]	4.0[d]	—	$NaBH_4$(2.0%)	H_2O	r.t.	20 s	4.1×10^1
$CuCl_2$[b]	25.0[d]	—	$NaBH_4$(2.0%)	H_2O	r.t.	20 s	5.0×10^1
$AgNO_3$[a]	25.0	0.065	Fe powder	CH_3COOH	r.t.	120 s	1.1×10^1
$AgNO_3$[b]	4.0[d]	—	Fe powder	CH_3COOH	r.t.	60 s	2.8×10^1
$AgNO_3$[a]	25.0	0.065	Na	C_2H_5OH	78°C	120 s	2.1×10^0
$AgNO_3$[b]	4.0[d]	—	Na	C_2H_5OH	78°C	120 s	4.1×10^1
$AgNO_3$[a]	25.0	0.065	Pd/C	C_2H_5OH	r.t.	4 h	5.6×10^0
$AgNO_3$[b]	4.0[d]	—	Pd/C	C_2H_5OH	r.t.	4 h	1.1×10^2
$AgNO_3$[a]	25.0	0.065	Raney Ni	C_2H_5OH	r.t.	4 h	7.6×10^0
$AgNO_3$[b]	4.0[d]	—	Raney Ni	C_2H_5OH	r.t.	4 h	4.1×10^2

[a]PVA–metal chelate film prepared from the mixed method.
[b]PVA–metal chelate prepared from the soaked method.
[c]Based on PVA weight.
[d]The concentration (wt%) of metal salts dissolved in methanol.

methanol solution containing 4 wt % silver nitrate for 48 h, and further dried in an oven at 80°C for 1 h.

Preparation of Metallized PVA Film by Reduction Methods

PVA metal chelate films were treated by the following three main reduction methods:

1. Reduction by hydride-transfer reagents:

The test piece of PVA chelate film was reduced by 0.3–2.0 wt % sodium borohydride aqueous solution containing one drop of nonionic surfactant [polyethylene glycol mono-p-nonylphenyl ether ($n = 15$)] at room temperature for 10–45 s. The reduced film was washed with water and dried at 100°C for 15 min, then cooled to room temperature and stored in a desiccator for future use.

2. Reduction by dissolving metal:

(a) Reduction with metal in acidic solution: The test piece of PVA chelate film was reduced at room temperature for 30–120 s in an acetic acid (1 mL)/water (50 mL) solution containing iron powder (4 g). The reduced film was treated in a procedure similar to that mentioned in Method 1.

(b) Reduction with metal in an alcohol solution: The test piece of PVA chelate film was reduced at 78°C for 120 s by dissolving 2.0 g metallic sodium (cut into small pieces) in 25 mL absolute ethanol. The film was washed by absolute ethanol and then treated as in Method 1.

3. Catalytic hydrogenation:

Ethanol (50 mL) and PVA chelate film was placed into a hydrogenation bottle, the air in the bottle was expelled by the H_2 gas immediately after the needed amount of catalyst, palladium on carbon (10%), or Raney nickel (0.2–2.0 g), was added. The bottle was pressurized by H_2 gas to 65 psi, and then shaken 1-5 h at room temperature. The reduced film was treated with the procedure mentioned in method (2b).

Electric Measurement

The surface electrical conductivity of the films was measured according to the conventional four terminal method with aluminum foil electrodes, as described previously.[5]

Instrument Analysis

Visible and ultraviolet (UV) absorption spectra of the PVA metal chelate solutions and films were measured by using Shimadzu model UV-160 spectrophotometer.

X-ray diffraction patterns of metallized PVA film were measured by a diffractometer (Shimadzu XD-3A Diffractometer) using CuKα radiation generated at 30 keV and 20 mA.

Electron spectroscopy for chemical analysis (ESCA) spectra was obtained using a VG Scientific LTD model LAB 5 spectrometer with a Mg Kα x-ray source radiation generated at 10 keV and 20 mA.

These surfaces of unreduced and reduced samples coated with gold of 150 Å thickness, respectively, were measured by a Hitachi Model S-570 Scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Visible and UV Spectra Observations

The formation of a polymer metal chelate can be identified from both the color changes of the solution and the UV-visible spectra of the polymer film.[9] Most commercial poly(vinyl alcohol) absorb strongly in the 200–400 nm region of the ultraviolet spectrum,[10] as shown in Figure 1(a). Silver nitrate aqueous solution is colorless and shows no absorbance in the visible region, as shown in Figure 1(b). When silver nitrate aqueous solution was added to the PVA solution and constantly stirred for 10 h, this colorless mixed solution changed to dark brown. The UV-visible spectral band of the PVA–Ag^+ solution appears at 433 nm, as shown in Figure 1(c). The dark brown solution of PVA–Ag^+ was cast into film, and its UV-visible spectral band appears at 439 nm as shown in Figure 1(d). The PVA films were soaked into $AgNO_3/CH_3OH$ solution for 48 h, the colorless films turned became dark brown, and their UV-visible spectral bands also appear at 439 nm. From the above results, the films prepared by the mixture method and the soaked method demonstrated that Ag chelate formation on the PVA film.

In the soaked method, other polar solvents such as dimethylformamide (DMF) and ethanol, were also used, including methanol. PVA films were soaked in these different solvents containing the same concentration of silver nitrate for the same time period, respectively. The UV-visible spectrum of the film which was soaked in methanol shows the strongest absorbance (Fig. 2). It is obvious that methanol is a suitable solvent for the soaked method.

Effect of Reducing Agents on the Conductivity of PVA Metal Chelate Films

PVA metal chelate films can be prepared easily by the following two methods: (1) the mixed method and (2) the soaked method, which are mentioned in the Experimental section. The PVA film itself exhibited high surface resistivity, ca. 10^{13} Ω/cm^2. In order to prevent ionic conduction caused by the presence of water or solvent, before the PVA chelate film is treated by reducing agents, it was further dried in an oven at 80–100°C for 1 h. Its
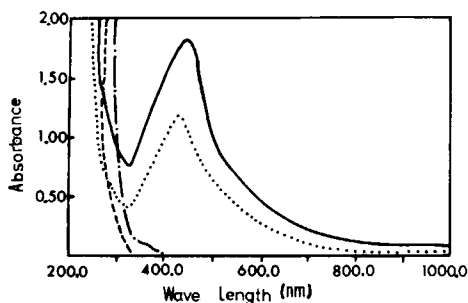

Fig. 1. Visible and UV adsorption spectra. (a) (— · —) PVA solution; (b) (- - - - -) AgNO₃ solution; (c) (· · ·) PVA–Ag^+ solution; (d) (———)PVA–Ag^+ film.
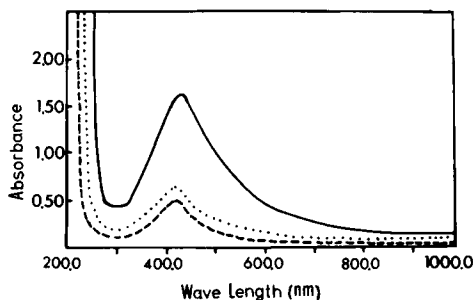
Fig. 2. Visible and UV adsorption spectra. (a) (——) PVA film soaked in AgNO$_3$/CH$_3$OH; (b) (· · ·) PVA film soaked in AgNO$_3$/C$_2$H$_5$OH; (c) (-----) PVA film soaked in AgNO$_3$/DMF.

surface resistivity exhibited ca. 10^{11} Ω/cm^2 at that time. When the PVA chelate film was treated by one of the given reducing agents and dried at 80–100°C, the film showed low surface resistivity of 10^0–10^2 Ω/cm^2 as shown in Table I. The conductivity of PVA chelate film rises from that of an insulator to the metallic region. An increase in conductivity value of 9 to 11 orders of magnitude is obtained.

The effect of reducing agents on the conductivity of PVA metal chelate film is shown in Table I. The most appropriate reductive conditions for preparing an excellent conductivity of the films are also listed in Table I. Using sodium borohydride as reducing agent for PVA chelate film, surfactant was added to facilitate complete wetting of the film by sodium borohydride solution. Consequently, the reduction rate was extremely fast, taking only 20 s. The original film was immediately converted into a shiny, metallic appearing, and opaque film.

Using iron powder in acidic solution as a reducing agent, the PVA–Ag$^+$ chelate film possessed a definite silvery, metallic appearance, which is similar to that of films treated with sodium borohydride solution. Similar results were also obtained by using zinc as a reducing agent.

The PVA–Ag$^+$ chelate film was also dipped into a solution of metallic sodium dissolved in ethanol as reducing agent and the metallic luster on the film surface formed when the reduction temperature was raised to 78°C. The film was washed further to completely remove sodium ethoxide on the film surface. In general, methanol could take the place of ethanol and the same result is obtained.

Catalytic hydrogenation was also available for the reduction of PVA-Ag$^+$ chelate film. Reduction was easily effected by simply shaking the chelate film with the catalyst in a suitable solvent. Here, reduction is used in the sense of addition of hydrogen to the PVA–Ag$^+$ chelate film. Palladium on activated carbon and Raney nickel were chosen as catalysts for this catalytic hydrogenation. The reduction condition was mild, at low pressure (65 psi) and room temperature. The PVA–Ag$^+$ chelate film after these reducing agents treatments exhibited excellent conductivity as shown in Table I. From Table I, with metallized film prepared from the mixed method, the conductivity represented a 1–2 order of magnitude enhancement compared with that of the soaked method when the same reducing agent was used.
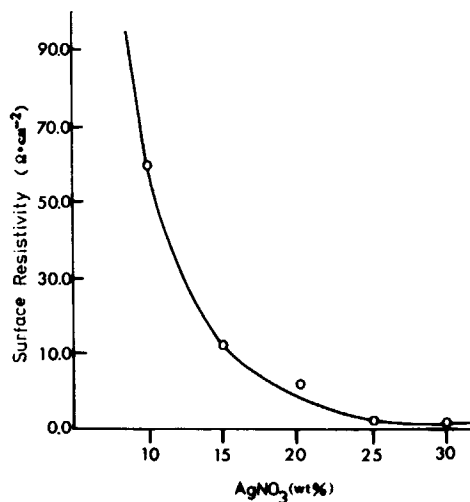
Fig. 3.   Variation of surface resistivity of PVA–Ag$^+$ chelate film after NaBH$_4$ treatment with the amount of AgNO$_3$ (PVA; DP = 2000, NaBH$_4$ = 0.6 wt%).

Effect of the Amount of Silver Nitrate in PVA–Ag$^+$ Chelate on the Conductivity of Metallized Film

As shown in Figure 3, as the amount of silver nitrate increased in the PVA–Ag$^+$ chelate film, the surface resistivity decreased. When the amount of silver nitrate reached the range of 25–30 wt %, the film after sodium borohydride treatment exhibited a limiting value of about 10^0 Ω/cm^2. Addition of silver nitrate did not improve the conductivity, but gave unsatisfactory effects such as loss of flexibility of the metallized film.

Effect of Hydrolysis and Degree of Polymerization ($\overline{DP}$) of PVA on the Conductivity of Metallized Film

One of the authors reported that a degree of polymerization ($\overline{DP}$) of PVA of more than 500 was sufficiently effective for the conductivity of PVA–Cu^{+2} chelate film after iodine treatment. Here, degrees of polymerization of PVA ranging from 500 to 2400 were used. When the PVA–Ag$^+$ chelate film was

TABLE II
Effect of Various Degrees of Polymerization ($\overline{DP}$) and Hydrolysis on the Surface Resistivity of PVA–Ag$^+$ Chelate Films[a] Modified with Na/C$_2$H$_5$OH

Item	$\overline{DP}$	Hydrolysis (%)	Surface resistivity (Ω/cm^2)
105	500	98–99	9.1×10^0
205	500	87–89	7.2×10^0
110	1000	98–99	6.4×10^0
210	1000	87–89	8.3×10^0
117	1700	98–99	7.1×10^0
217	1700	87–89	6.4×10^0
124	2400	98–99	6.3×10^0
224	2400	87–89	6.2×10^0

[a]AgNO$_3$ = 25 wt% based on the PVA weight.

treated with Na/C_2H_5OH, no substantial changes in the conductivity were found, (Table II).

The complex formation of partially acetylated PVA was reported by Hojo and Shirai.[11] The formation of four-coordinated Cu chelate was hindered in PVA derivatives with a degree of acetylation above 16%. Here, two degrees of hydrolysis of PVA from poly(vinyl acetate) were obtained, 87–89% and 98–99%. The data in Table II, also indicate that steric hindrance has no effect on the conductivity of metallized film prepared from PVA–Ag^+ chelate.

Effect of Oxygen During Film Formation on the Conductivity of Metallized Film

Films of polyimide–$Pd(S(CH_3)_2)_2Cl_2$ complex possessed noticeably different surfaces state and surface resistivity.[12] These different results were dependent upon whether the film had been exposed to the glass or to the air during imidization procedure. The air-side possessed a definite silvery, metallic appearance and exhibited excellent conductivity, but the glass-side had a dark red-brown appearance and low conductivity. Obviously, the presence of oxygen during the imidization appears crucial for the conductivity.

One of the authors[5] reported semiconducting polymer prepared from PAAm–Cu^{+2} chelate and iodine, as mentioned in the Introductory section. There was no difference between conductivities of PAAm–Cu^{+2} chelate film prepared under air and under nitrogen atmosphere.

When the PVA–Ag^+ chelate was prepared in oxygen-free water, the film was dried at room temperature over silica gel in a desiccator under nitrogen atmosphere. Higher surface resistivity of this PVA–Ag^+ chelate film, 18.0 Ω/cm^2, compared with that of the film prepared under air, 6.5 Ω/cm^2. No substantial changes of surface resistivity were observed. The effect of air (oxygen) on the conductivity of this film is insignificant.

The Stability of Metallized Film Exposure to Air Atmosphere

Although the PVA–Ag^+ chelate film after reducing agent treatments exhibited excellent conductivity, the stability of metallized film was also very important. As shown in Table III, whether using $NaBH_4$ or Na/C_2H_5OH as the reducing agent, the surface resistivity of metallized films shows only a

TABLE III
The Stability of PVA–Ag^+ Chelate Film[a] After Reducing Agent Treatments
and Exposure to Air Atmosphere

Time (month)	$NaBH_4$ treatment Surface resistivity (Ω/cm^2)	Na/C_2H_5OH treatment Surface resistivity (Ω/cm^2)
Start	6.50×10^0	4.20×10^0
1	7.00×10^0	5.30×10^0
2	6.80×10^0	5.50×10^0
3	8.70×10^0	7.90×10^0
4	9.80×10^0	1.18×10^1
5	3.21×10^1	1.50×10^1
6	4.43×10^1	1.92×10^1

[a] DP of PVA = 2000; $AgNO_3$ = 25 wt% based on the PVA weight.

TABLE IV
Effect of Heat Treatment[a] Time on the Conductivity
of PVA–Cu^{+2} after NaBH$_4$ Treatment

Heat treatment time	Surface resistivity (Ω/cm^2)
Start	1.90×10^2
40 min	4.00×10^1
2 h	1.50×10^1
4 h	4.00×10^0

[a] Heated in an oven at 100°C.

slight change with time, indicating that the metallized films were very stable in the air.

Effect of Heat Treatment on the Conductivity of Metallized Film

The PVA–Cu^{+2} chelate film after NaBH$_4$ treatment is unstable in air. In order to improve the stability of the metallized film, it was heated in an oven at 100°C. As shown in Table IV, after 4 h heat treatment of the polymer film, both the conductivity and the stability of the metallized film are improved.

X-Ray Analysis

In order to identify whether the surface of film is metallized or not on the PVA film after reducing agent treatment, these films were examined by means of x-ray diffraction. From the results of x-ray diffraction analysis, as shown in Table V, the metallized films clearly demonstrate that the main product on the film surface was Ag. The formation of the metallic silver surface layer was responsible for the conductivity. Similar results were obtained from PVA–Cu^{+2} chelate film after NaBH$_4$ treatment, the main product on the film surface being Cu as shown in Table VI. The results of the x-ray analysis were in good agreement with the standard samples. From these above results, it indicates that an appreciable amount of silver nitrate or cupric chloride has been reduced to the elemental state on these films.

ESCA Analysis

In order to further analyze the surface of the metallized film which is prepared from PVA–Ag$^+$ chelate film, this metallized film was measured by

TABLE V
Diffraction Angles (2θ) and Plane Distances (d) Corresponding to Peaks Observed in
X-Ray Analysis for PVA–Ag$^+$ Chelate Film Modified with Reducing Agents

Peaks	Film A[a] experiment		Film B[b] Experiment		Pure Ag reference	
	2θ	d	2θ	d	2θ	d
1	38.1	2.360	38.2	2.354	38.14	2.359
2	44.4	2.039	44.3	2.043	44.33	2.043
3	64.4	1.442	64.4	1.442	64.50	1.445
4	77.5	1.231	77.4	1.232	77.61	1.230

[a] Film A prepared from PVA–Ag$^+$ chelate film modified with NaBH$_4$ solution.
[b] Film B prepared from PVA–Ag$^+$ chelate film modified with Na/C$_2$H$_5$OH.

TABLE VI
Diffraction Angles (2θ) and Plane Distances (d) Corresponding to Peaks Observed in
X-Ray Analysis for PVA–Cu^{2+} Chelate Film Modified with Reducing Agents

Peaks	Film C[a] experiment		Pure Cu reference	
	2θ	d	2θ	d
1	43.3	2.088	43.30	2.088
2	50.4	1.809	50.43	1.808
3	74.1	1.279	74.13	1.278

[a] Film C prepared from PVA–Cu^{2+} chelate film modified with $NaBH_4$ solution.

TABLE VII
Silver and Metallized Film Electron Binding Energies

Electron level	Binding energy (ev) (this work)	Binding energy (ev) (Ag foil)[a]	FWHM (ev) (this work)	FWHM (ev) (Ag foil)[a]
$Ag_{3d5/2}$	368.25	368.1 ± 0.1	1.15	1.15
$Ag_{3d3/2}$	347.15	374.2 ± 0.1	1.15	1.15

[a] Reported by G. Schön (Ref. 13).

electron spectroscopy chemical analysis (ESCA). The results of $3d_{5/2}$, $3d_{3/2}$ electron binding energies and FWHM (full width half maximum) in metallized film are shown in Table VII and Figure 4. The results are consistent with ESCA data of Ag foil (0.013 mm thick) taken from Schön.[13] The electron binding energy of Ag $3d_{5/2}$ is 368.1 ± 0.1 eV, Ag $3d_{3/2}$ is 374.2 ± 0.1 eV and FWHM for Ag $3d_{5/2}$, Ag $3d_{3/2}$ is 1.15 eV. The results of ESCA analysis also indicate that silver nitrate has been reduced to metallic silver on these films.
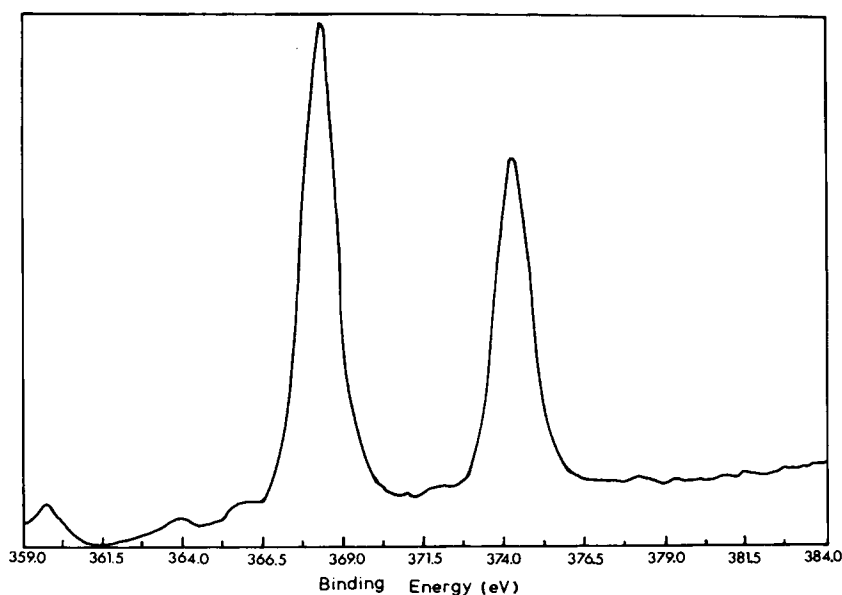

Fig. 4. ESCA spectrum of PVA–Ag^+ chelate film after $NaBH_4$ solution treatment.
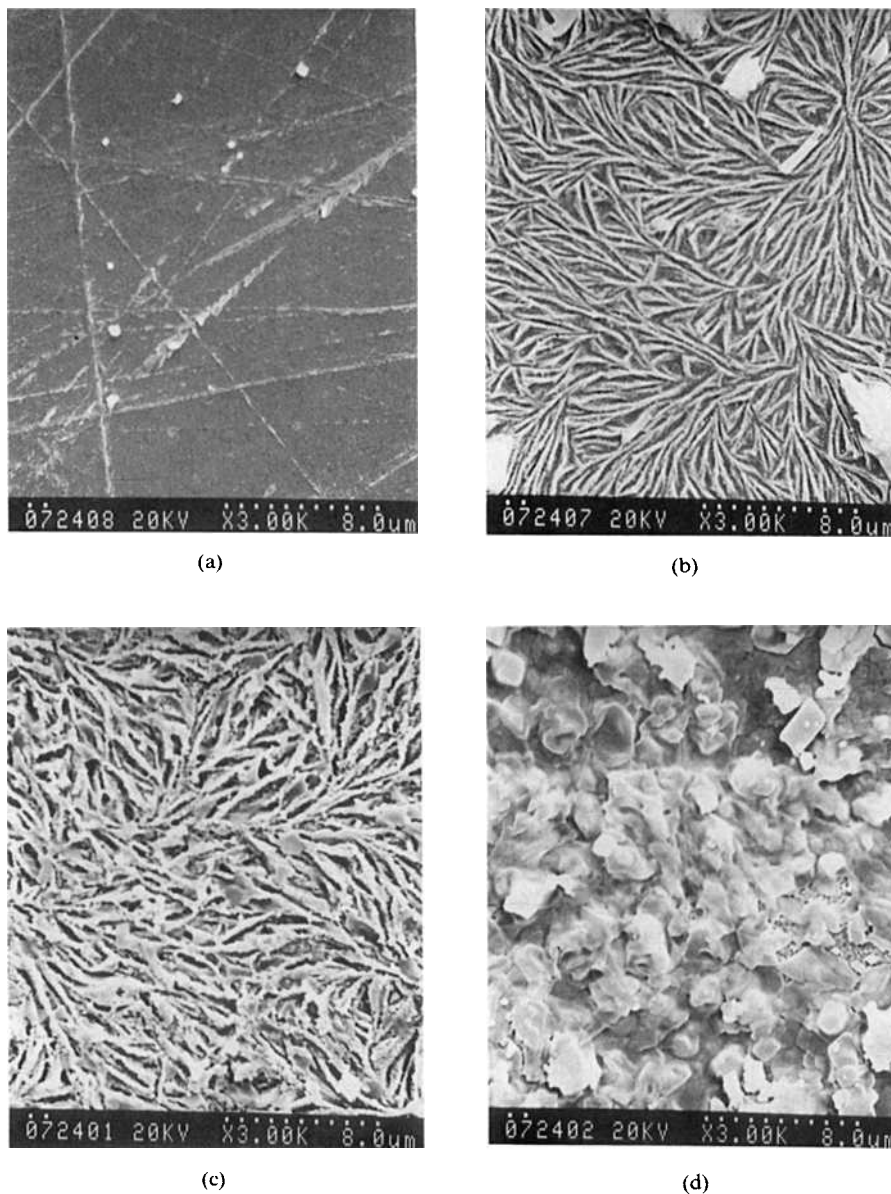
(a)

(b)

(c)

(d)

Fig. 5. Scanning electron microscope photographs of the PVA–Ag$^+$ chelate films. Before Na/C$_2$H$_5$OH treatment: (a) PMMA-side; (b) air-side. After Na/C$_2$H$_5$OH treatment: (c) PMMA-side; (d) air-side. After NaBH$_4$ treatment: (e) PMMA-side, (f) air-side. After Raney Ni/H$_2$ treatment: (g) PMMA-side, (h) air-side.

Scanning Electron Microscope Observations

Scanning electron microscopy (SEM) on the metallized films have shown rather interesting features. The PMMA-side of the PVA–Ag$^+$ chelate film was smooth, and the air-side was in the dendritic state as shown in Figure 5(a) and 5(b), respectively. A drastic change of surface features occurs, by the reducing agents treatment, as shown in Figure 5(c) to 5(h). The morphology of the metallized films are shown in Table VIII. The aggregation of particles on
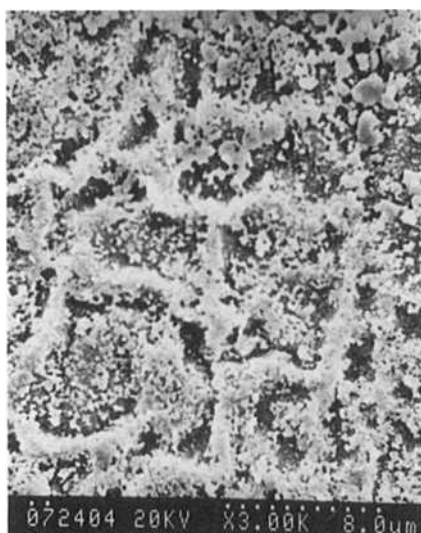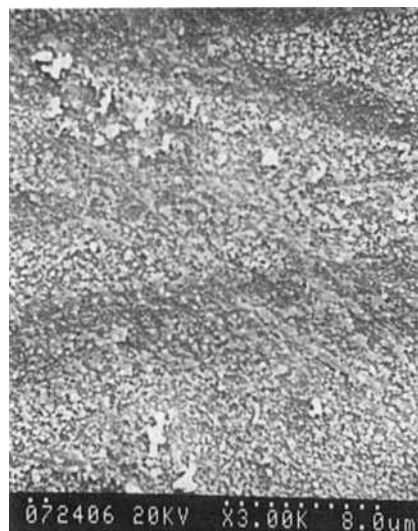
(e)
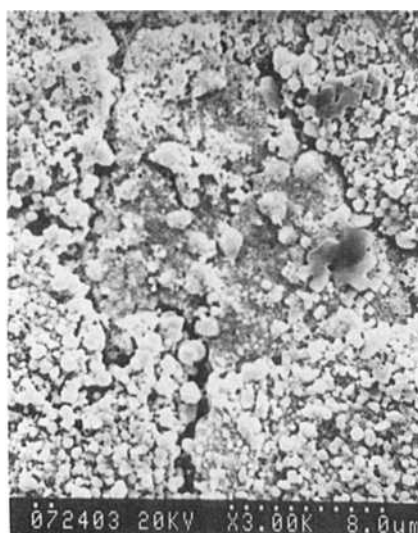
(f)
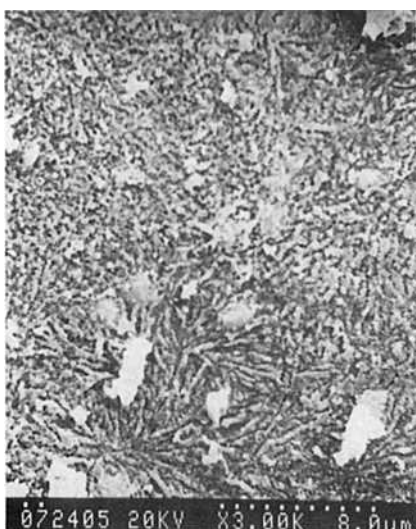
(g)

(h)

Fig. 5. (*Continued from the previous page.*)

the surface of both sides of the reduced film is revealed by the SEM photo. Although the SEM photos show a great deal of different features appearing on the film surface after reducing agents treatment, the products on the film surface were revealed by the x-ray analysis and ESCA analysis to be the same substance.

Effect of Chelate Formation on the Conductivity of the Metallized Film

In this study, $AgNO_3$ was dissolved in PVA water solution and stirred over 4 h, then the solution was cast into the PVA chelate film. After treatment by

TABLE VIII
Morphology of PVA–Ag$^+$ Chelate Film[a] after Reducing Agent Treatment

Sample[b]	Morphology	Reducing agent treatment
c	Dendritic	Na/C_2H_5OH
d	Block	Na/C_2H_5OH
e	Fibrillar/globular	$NaBH_4$
f	Globular	$NaBH_4$
g	Short fibrils	Raney Ni/H_2
h	Globular	Raney Ni/H_2

[a] DP of PVA = 2000; $AgNO_3$ = 25 wt% based on the PVA weight.
[b] As designated in Fig. 5.

reducing agents, the silver ions in the chelate film were reduced to metallic silver on the surface of film. The film exhibits excellent conductivity. Ag sols prepared by the method of Nakao and Kaeriyama[14] was mixed with PVA water solution and then cast into film. However, this film exhibited high resistivity (over 2×10^7 Ω/cm^2).

In order to identify whether metal chelate formation is necessary or not to obtain excellent conductivity after treatment with reducing agents, the following experimental procedures were performed. The PVA solution was added to a silver nitrate solution and the mixture was stirred for 2 min. The mixture solution shows no absorbance in the UV-visible spectra. The resulting viscous solution was immediately cast onto a poly(methyl methacrylate) plate, and dried at room temperature, at a pressure less than 1 torr for 4 h. The dried film is colorless and shows no absorbance in the UV-visible spectra, indicating that no chelate is formed.

The film was treated with $NaBH_4$ solution, the reduction product was very easily peeled from the film, due to no chelate formation with PVA. The film was found to exhibit high surface resistivity (over 2×10^7 Ω/cm^2).

When the PVA–Ag$^+$ solution wa stirred at room temperature, this solution showed no absorbance at 433 nm within 30 min. One hour later, the absorption increased gradually with increasing stirred time and remained unchanged after 4 h. It could be considered that Ag chelate with PVA is formed completely within 4 h. The film exhibited excellent conductivity when treated with reducing agents as shown in Table I, compared with the conductivity of the film with no chelate formation as mentioned above. Obviously, the chelate formation plays an important role to the conductivity.

When the film with no chelate formation was prepared by the same procedure as mentioned above, it exhibited conductivity (7.8 Ω/cm^2) after treatment with Na/C_2H_5OH. The different results between $NaBH_4$ treatment and Na/C_2H_5OH treatment would be explained if the process using Na dissolved into C_2H_5OH was much more exothermic than $NaBH_4$. The Ag chelate formation with PVA was very rapid and the metallic substance was formed on the film surface simultaneously. Therefore, the reason the metallic substance layer adhered to the film rather firmly was due to the Ag chelate formation, which like an "anchor" held onto the metallic substance.

According to the results of x-ray, ESCA, SEM and identification of PVA-Ag$^+$ chelate formation mentioned above, and the articles provided by Sumita
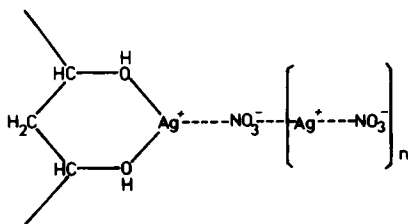
Fig. 6.   Proposed structure for the PVA–Ag^+ chelate responsible for conductivity.

et al.,[15] Burkstand,[16,17] and Basolo and Johnson,[18] it appears that when the amount of $AgNO_3$ in the PVA–Ag^+ chelate film is over 10 wt% ($F \geq 0.026$), most of Ag^+ ions are not chelated by PVA but coordinated by NO_3^-. The NO_3^- is considered to be the bridging atom to form the activated complex. Therefore, the surplus $AgNO_3$ in the activated complex can be easily reduced to metallic Ag on the film surface. It is emphasized again that Ag chelate formation can lead to enhanced adhesion with the metallic Ag. A proposed structure of this chelate is shown in Figure 6. Since the relative reduction potential of Ag^+ is 0.799 V, it is easily reduced to Ag by different reducing agents as mentioned in Table I and exhibits excellent conductivity.

Hojo et al.[19] pointed out that the stability constants increase in the order of $Co^{+2} < Ni^{+2} < Cu^{+2}$ for the PVA metal chelate solution. The lesser stability of PVA–Co^{+2}, PVA–Ni^{+2} chelate and the negative relative reduction potentials of $Co^{+2}(-0.277$ V), $Ni^{+2}(-0.250$ V), indicate that they are not easily reduced. This is consistent with the fact that the PVA–Co^{+2} and PVA–Ni^{+2} chelate films were not reduced by the $NaBH_4$ solution and the surface resistivities of these films were over $2 \times 10^7 \ \Omega/cm^2$.

CONCLUSIONS

This novel method is defined by the following steps to obtain electrically conducting polymer: (1) dissolve metal salts into PVA, (2) form the PVA metal chelate film, (3) reduce by using reducing agents. The main purpose of using reducing agents to treat the PVA metal chelate film is to reduce monovalent silver ions or bivalent copper ions into metallic silver or copper, respectively. This method is relatively fast and simple and obtained excellent metal-like conductivity. The PVA–Ag^+ conducting films show very good stability in the air for at least 6 months. This novel method also can be applied to polymers with functional group such as polyamides, polyacrylonitrile, polyamic acid, polyamide-imide, polyurethane, etc. as will be reported in the near future.

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