Studies on the Preparation and Properties of Conductive Polymers. Part II. Novel Method to Prepare Metallized Plastics from Metal Chelates of Polyamides

CHIH-CHAO YEN, CHUEH-JUNG HUANG, and TEH-CHOU CHANG*

Department of Chemical Engineering, Chung Yuan Christian University, Chung Li, Taiwan 32023, Republic of China

SYNOPSIS

New metallized films were obtained by the reduction of polyamide metal chelate films with reducing agents. Polyamide metal chelates films exhibited excellent surface resistivity around 10^0–10^1 Ω/cm^2 when treated with sodium borohydride aqueous solutions. Aqueous solutions of polyamide–formic acid with metal salts, and films prepared from those solutions, were analyzed by UV-visible and IR spectroscopy, respectively, in order to investigate and identify the structure of the polyamide metal chelates. Factors that include kinds and concentrations of metal salts, kinds and concentrations of reducing agents, and reduction time, which may affect the conductivity of metallized films, were investigated. The surfaces of these films were treated with sodium borohydride aqueous solution to form a definite metallic luster appearance. The surfaces of these conductive films were proved to be metallized, by means of ESCA analysis. The strongly adhered metal on the films was believed to be responsible for the improvement in electrical conductivity. The mechanical properties and scanning electron microscope (SEM) observations were also studied.

INTRODUCTION

Electrically conducting polymers have recently been the subject of intense interest. The doping of neutral polymers with dissolved metal salts or metal complexes for the purpose of imparting electrical conductivity to the polymer has received much attention. The surface electrical conductivity of films of poly(vinyl alcohol)–Cu^{2+} and polyacrylamide–Cu^{2+} have been shown[1,2] to increase by spreading an acetone solution of iodine over the film surfaces. After iodine treatment, a whitish substance identified as γ-CuI is believed to be responsible for the enhanced electrical conductivity. However, these conductive films were very unstable in air, and their surface resistivity only reached about 10^3–10^4 Ω/cm^2, therefore, they are of less practical use.

In order to develop easily processed metallized films, there have been attempts to use polymers as a base for the films and further chemically modify

them so as to obtain good electrical conductivity. A new metallized film with good conductivity obtained from poly(vinyl alcohol) metal chelate film treated with reducing agents was prepared successfully as described in the first paper of this series.[3]

In this investigation, nylon 4 and nylon 6 with amide groups capable of forming metal chelates are used as another class of easily processable polymer. It was found that polyamide metal chelate film reduced by sodium borohydride solution also showed similar conductivity to that of the poly(vinyl alcohol) metal chelate film.

EXPERIMENTAL

Nylon 4 Synthesis

Nylon 4 was synthesized by the CO_2-initiated polymerization of 2-pyrrolidone using potassium 2-pyrrolidonate as the catalyst.[4,5] The molecular weight of the samples, measured in m-cresol at 25°C by a Cannon-Fenske viscometer was about 20,000

to 42,000. In this study, nylon 4 with a molecular weight of about 25,000 was used.

Purification of Nylon 6

Commercially available nylon 6 with a molecular weight of 16,000 was used. Nylon 6 was dissolved in formic acid, and the resulting solution was poured into distilled water. Precipitation of the nylon 6 took place immediately. The precipitate was washed thoroughly with water and dried in a vacuum oven to obtain the refined nylon 6.

Preparation of Polyamide Metal Chelate Film

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

Mixed Method

The nylon–formic acid solution comprised 10–12 wt % nylon in an 88–90 wt % mixture of 4 : 1 (v/v) 90% formic acid solution and n-PrOH. The ratio of the molar concentration of metal ion to that of monomeric units of the nylon ($F = [M^{n+}]/[MU]$) was adjusted by adding the proper amounts of the metal salt aqueous solution to the nylon–formic acid solution. Various conditions used are shown in Table II and Table III.

Solution of the mixtures were stirred at room temperature for 24 h. The resulting viscous solutions were cast on clean glass plates. The films on the glass plates were evaporated at ambient for 5 min and further dried in an oven at 80°C for 30 min. The films were then peeled off and cut into 1 × 3 cm pieces for subsequent uses.

Soak Method

The polyamide solution comprised of 10–12 wt % nylon and 88–90 wt % mixture of 4 : 1 (v/v) 90% formic acid solution and n-PrOH was cast on a clean glass plate. The film on the glass plate was evaporated for 5 min at ambient, heated in an oven at 80°C for 30 min, and then cooled to room temperature for 10 min. The film cast on the glass plate was immersed in a methanol bath at room temperature for 10 min. The film was then peeled off and stored in water for at least 12 h before subsequent use. The film was cut into a 1 × 3 cm test piece. The test piece was soaked in 100 mL of a suitable concentration of aqueous metal salt solution containing 0.04 g of nonionic surfactant (polyethylene glycol mono-p-nonylphenyl ether, $n = 15$) in an oven at

50°C for a suitable time, was dried for a few minutes in air, and further dried in an oven at 80°C for 30 min.

Preparation of Metallized Polyamide Films by Metalhydride Reducing Agents

The test pieces of polyamide metal chelate films were reduced by 25 mL of a 0.2–4.0 wt % sodium borohydride aqueous solution containing 0.04 g of nonionic surfactant (polyethylene glycol mono-p-nonylphenyl ether, $n = 15$) at 40–80°C for a suitable time. The reduced films were washed with water and dried at 100°C for 5 min, then cooled to room temperature and stored in a desiccator for subsequent use. Other reducing agents including lithium aluminum hydride ($LiAlH_4$), lithium hydride (LiH), sodium hydride (NaH), calcium hydride (CaH_2), and sodium (Na) were also tested and were unsuccessful (Table IV).

Electric Measurement

The surface electrical conductivity of the films was measured according to the conventional four-terminal method using aluminum foil electrodes, as described previously.[2]

Instrument Analysis

Visible and UV absorption spectral data of the polyamide metal chelate films were obtained by using a Shimadzu model UV-160 spectrophotometer. IR spectra of polyamide metal chelate films ranging from 4000 to 400 cm^{-1} were obtained by using the Perkin-Elmer 710B spectrophotometer. Electron spectroscopy for chemical analysis (ESCA) spectra were obtained by using a VG Scientific LTD model LAB 5 spectrometer with a Mg K_α X-ray source with radiation generated at 10 kV and 20 mA. The surfaces of unreduced and reduced samples coated with gold film of 150 Å thickness, were measured by a Hitachi Model S570 scanning electron microscope (SEM).

Measurement of Mechanical Strength

The tensile strengths and elongations of unreduced and reduced samples were measured by the Toyo Baldwin type TENSILON/UTM-III-100 instrument at ambient. The tensile strengths and elongations of samples in their dry states were measured according to ASTM D638 method.[6]
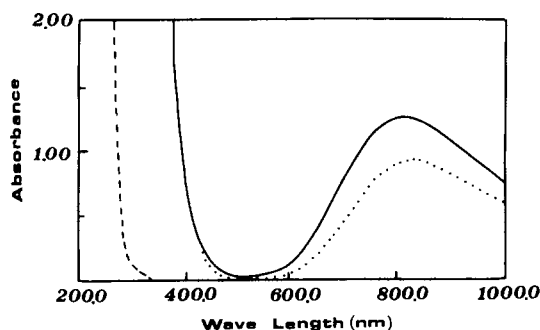
Figure 1 Visible and UV absorption spectra. (a) (– – –) nylon 4–HCOOH solution; (b) (· · ·) CuCl$_2$–HCOOH solution; (c) (——) nylon 4-CuCl$_2$–HCOOH solution.

RESULTS AND DISCUSSION

Visible and UV Spectra Observations

The formation of PVA-Ag$^+$ chelate identified from UV-visible spectra was reported in our previous paper.[3] In this study the formation of polyamide metal chelate can also be identified from UV-visible spectra. Nylon 4 or nylon 6 shows no absorbance in the visible region, as shown in Figure 1(a). The UV-

visible spectral band of the CuCl$_2$-HCOOH solution appears at 825 nm, as shown in Figure 1(b). When the CuCl$_2$-HCOOH solution is added to the nylon 4 (or nylon 6)–formic acid solution and constantly stirred for 24 h, the UV-visible spectral band is shifted to a shorter wavelength, which absorbs at about 800–802 nm, as shown in Figure 1(c). Similarly, the UV-visible spectral band of nylon 4 (or nylon 6)–NiCl$_2$ and nylon 4 (or nylon 6)–CoCl$_2$ solution are also shifted to shorter wavelengths, compared to those of the NiCl$_2$-HCOOH and CoCl$_2$-HCCOH solution, as shown in Table I. From these results the formation of polyamide metal chelate, from metal ion coordinated with the amide group of polyamide, was indicated.

IR Analysis

As mentioned, polyamide metal chelate was formed for metal ion coordinated with polyamide. In order to confirm the chelate formation and further investigate the structure of the metal chelate, IR spectra were measured for polyamide metal chelate films prepared from the mixtures of polyamide solutions and various concentrations of CuCl$_2$ as well as NiCl$_2$.

Table I   Absorption Wavelength of Formic Acid Solution of Metal Salts and Formic Acid Solution of Nylon/Metal Salts

Polymer	Metal Salts	F^a	Wt %^{b}	Absorption Wavelength (nm)
—	CuCl$_2 \cdot$ 2H$_2$O	—	0.30	825
		—	0.50	825
—	NiCl$_2 \cdot$ 6H$_2$O	—	0.28	742, 403, 312
		—	0.70	742, 403, 312
—	CoCl$_2 \cdot$ 6H$_2$O	—	0.43	518, 362
		—	0.70	518, 362
Nylon 4	CuCl$_2 \cdot$ 2H$_2$O	0.03	0.30	800
		0.05	0.50	800
Nylon 4	NiCl$_2 \cdot$ 6H$_2$O	0.02	0.28	733, 394
		0.05	0.70	733, 394
Nylon 4	CoCl$_2 \cdot$ 6H$_2$O	0.03	0.43	523
		0.05	0.53	523
Nylon 6	CuCl$_2 \cdot$ 2H$_2$O	0.03	0.23	802
		0.05	0.38	802
Nylon 6	NiCl$_2 \cdot$ 6H$_2$O	0.02	0.21	735, 394
		0.05	0.53	735, 394
Nylon 6	CoCl$_2 \cdot$ 6H$_2$O	0.03	0.32	523
		0.05	0.53	523

^{a} Molar concentration of metal ions to that of monomeric units of the nylon.
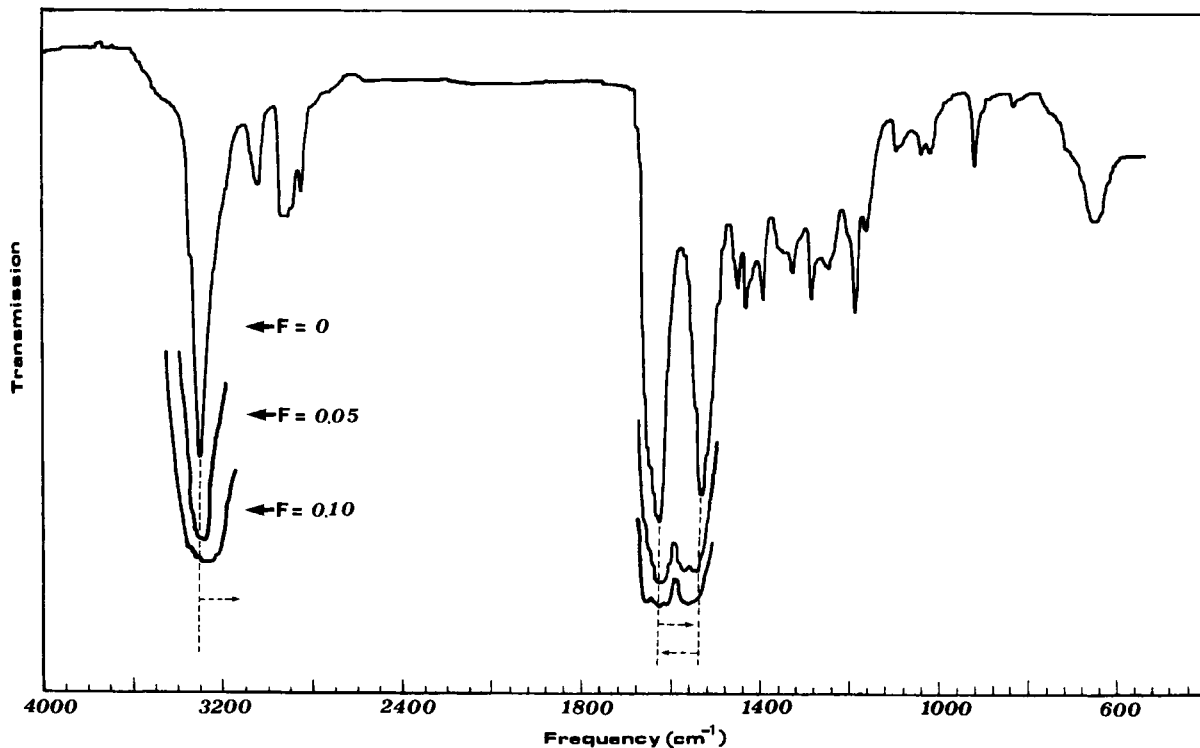^{b} Based on formic acid weight.

Figure 2 Infrared absorption spectra of nylon 4–$CuCl_2$ films with different F value.
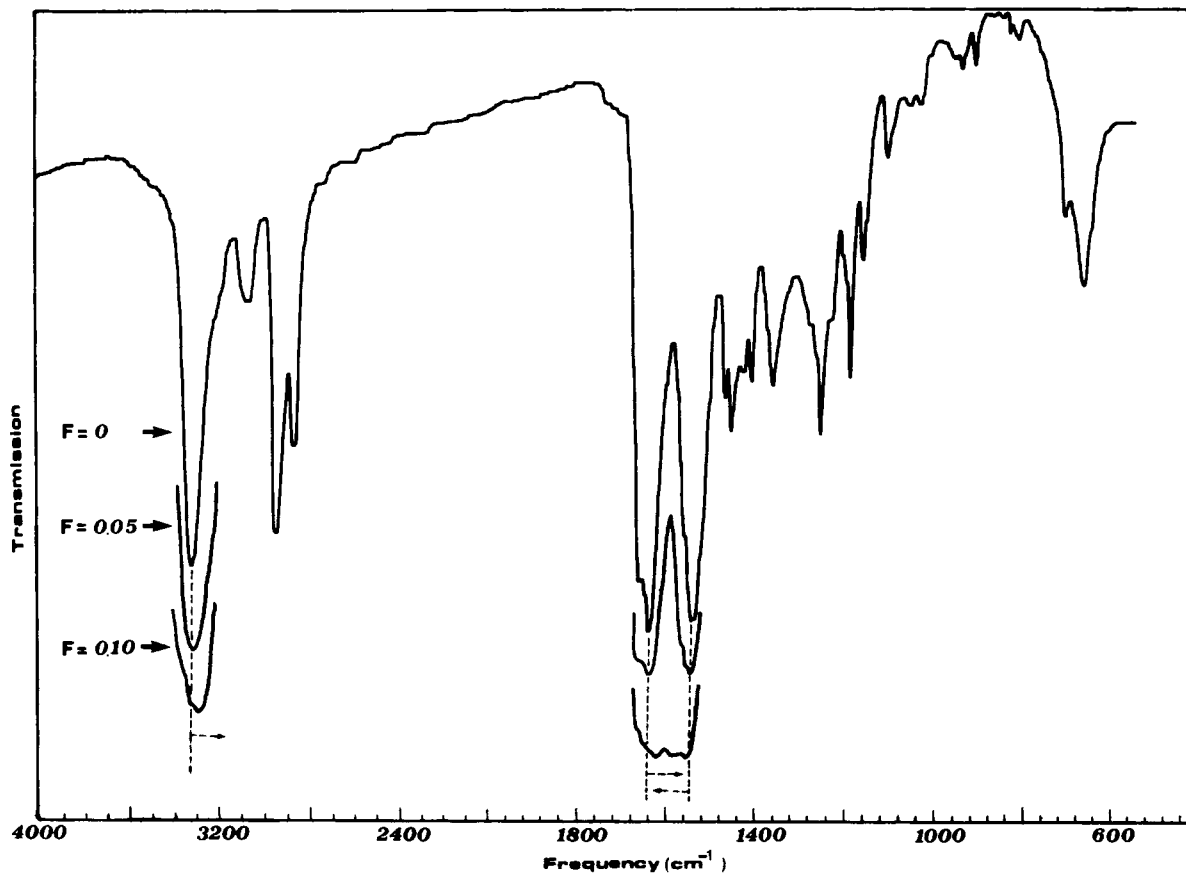

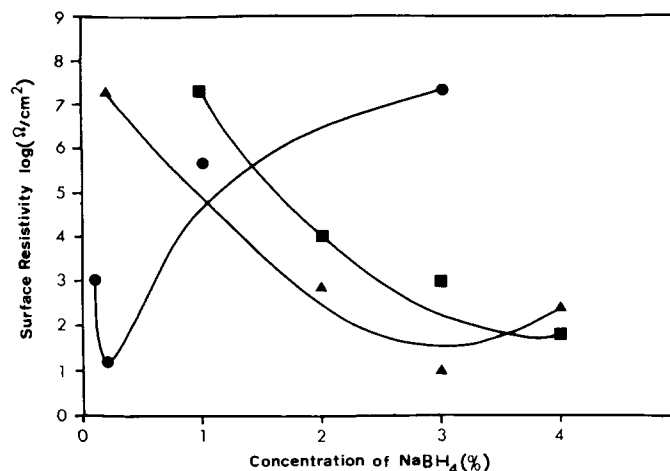**Figure 3** Infrared absorption spectra of nylon 6–$CuCl_2$ films with different F value.

Figure 4   Variation of surface resistivity of nylon 4 metal chelate films with the concentration of $NaBH_4$ aqueous solution. (■) nylon $4-CoCl_2 \cdot 6H_2O$; (▲) nylon $4-CuCl_2 \cdot 2H_2O$; (●) nylon $4-NiCl_2 \cdot 6H_2O$.

The IR spectra for nylon 4 and nylon 6 with $CuCl_2$ of $F = 0$, 0.05, and 0.1 are shown in Figures 2 and 3, respectively. It should be noticed that a peak due to the C=O stretching band at 1640 cm^{-1} shifts to shorter frequency with increasing F value, and another peak due to the C—NH stretching band at 1540 cm^{-1} shifts to longer frequency with increasing F value. Another spectral change is also observed in the peak due to the N—H stretching band at 3290 cm^{-1}, which shifts to a lower frequency with increasing F value. Moreover, these absorption bands get broader with increasing F value. The IR spectra

for nylon $4-NiCl_2$ and nylon $6-NiCl_2$ chelate films are similar to those of nylon $4-CuCl_2$ and nylon 6-$CuCl_2$ chelate films. From these results chelate formation is confirmed for Cu^{2+} or Ni^{2+} coordinated with amide group of nylon 4 and nylon 6.

Effects of the Concentration of Reducing Agents on the Conductivity of Nylon 4 Metal Chelate Films

In this study sodium borohydride ($NaBH_4$) is shown to be a suitable reducing agent to reduce polyamide
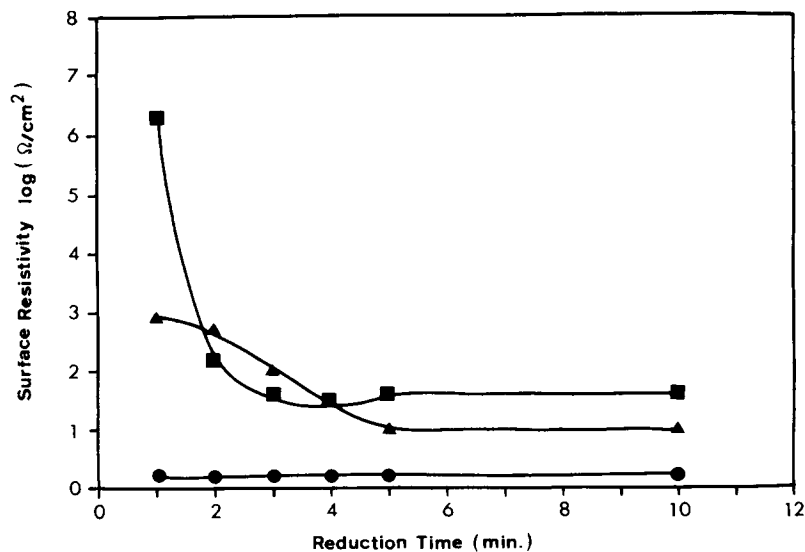

Figure 5   Effect of reduction time of $NaBH_4$ aqueous solution on the surface resistivity of nylon $4-CuCl_2$ chelate film (reduction temperature = 75°C). (■) $F = 0.06$; (▲) $F = 0.10$; (●) $F = 0.20$.

metal chelate films. The effects of various concentrations of $NaBH_4$ on the conductivity of nylon 4 metal chelate films are shown in Figure 4. These metal chelate films were prepared by the mixed method as mentioned in the experimental section. Nylon 4–Cu^{2+} chelate film was treated with 0.2 wt % $NaBH_4$ aqueous solution and showed a surface resistivity over 2×10^7 Ω/cm^2. The surface resistivity of this film is decreased with increasing concentration of $NaBH_4$ aqueous solution up to a concentration of 3.0 wt %. When nylon 4–$CuCl_2$ chelate film was reduced by 3.0 wt % $NaBH_4$ aqueous solution, it showed a low surface resistivity of about 1.0×10^1 Ω/cm^2. Therefore, a suitable concentration of $NaBH_4$ to reduce nylon–Cu^{2+} chelate film is 3.0 wt %. Similarly, suitable concentrations of $NaBH_4$ to reduce nylon–Ni^{2+} and nylon–Co^{2+} are 0.2 and 4.0 wt %, respectively.

Effects of Reduction Time on the Conductivity of Polyamide-Metallized Films

The nylon 4 metal chelate films are treated with $NaBH_4$ aqueous solution at different reduction times ranging from 10 s to 10 min. As shown in Figure 5, when $F = 0.06$ for nylon 4–Cu^{2+} chelate film treated with $NaBH_4$ aqueous solution for 4 min, the film shows excellent conductivity. When $F = 0.1$ and $F = 0.2$ for nylon 4–Cu^{2+} chelate films, suitable reduction times for preparing excellent conductivity films are 5 and 1 min, respectively. Similarly, the most appropriate reduction time for preparing the

nylon 4–Ni^{2+} chelate films ($F = 0.05$ and $F = 1.0$) having excellent conductivity are 3 to 5 min, which is shown in Figure 6.

Effects of the Amount of Metal Salts in Polyamide Metal Chelate Films on the Conductivity of Metallized Films

As shown in Table II, when $F = 0.05$ of nylon 4–Cu^{2+} chelate film is treated with $NaBH_4$ aqueous solution, surface resistivity shows still over 2×10^7 Ω/cm^2. When $F > 0.05$, the surface resistivity of films treated with $NaBH_4$ aqueous solution decreases with increasing F values. When $F > 0.1$, the films exhibited low surface resistivity, about 10^0 Ω/cm^2 after the $NaBH_4$ aqueous solution treatment. The nylon 4–Ni^{2+} and nylon 4–Co^{2+} chelate films shows excellent conductivity after the $NaBH_4$ aqueous solution treatment, with $F > 0.03$ and $F > 0.06$, respectively. Similarly, the surface resistivity of nylon 6 metal chelate films after $NaBH_4$ aqueous solution treatment show a decrease with an increase of F values, as shown in Table III. In general, the films with $F > 0.2$ did not improve the electrical conductivity and had unsatisfactory effects on the mechanical properties.

Effects of the Solvents on the Reduction of Polyamide Metal Chelate Films

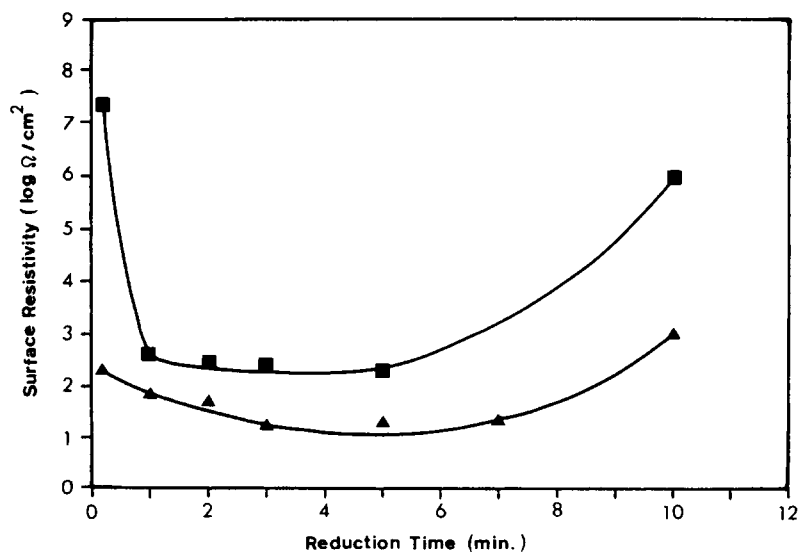In this study polyamide metal chelate films were reduced by certain agents in various solvents. As

Figure 6   Effect of reduction time of $NaBH_4$ aqueous solution on the surface resistivity of nylon 4–$NiCl_2$ chelate film (reduction temperature = 40°C). (■) $F = 0.05$; (▲) $F = 0.10$.

Table II   Effect of the Concentration of Metal Salts on the Surface Resistivity of Nylon 4 Metal Chelate Films Reduced by NaBH$_4$ Aqueous Solution

Metal Salts	F^a	Wt %[b]	Surface Resistivity (Ω/cm^2)
CuCl$_2 \cdot$ 2H$_2$O[c]	0.05	10.0	> 2 × 10^7
	0.06	12.0	3.0 × 10^1
	0.08	16.0	2.6 × 10^1
	0.09	18.0	2.0 × 10^1
	0.10	20.0	1.0 × 10^1
	0.125	25.0	4.0 × 10^0
	0.150	30.0	3.0 × 10^0
	0.175	35.0	3.0 × 10^0
	0.200	40.0	1.6 × 10^1
NiCl$_2 \cdot$ 6H$_2$O[d]	0.02	5.6	> 2 × 10^7
	0.03	8.4	1.0 × 10^5
	0.04	11.2	3.2 × 10^2
	0.05	14.0	2.4 × 10^2
	0.07	19.6	8.0 × 10^1
	0.10	28.0	1.7 × 10^1
	0.125	35.0	1.8 × 10^2
	0.150	42.0	1.8 × 10^2
	0.175	49.0	1.8 × 10^2
CoCl$_2 \cdot$ 6H$_2$O[e]	0.04	11.2	> 2 × 10^7
	0.06	16.8	3.0 × 10^4
	0.08	22.4	2.5 × 10^2
	0.10	28.0	1.8 × 10^1
	0.15	42.0	9.0 × 10^0
	0.175	49.0	9.0 × 10^0

[a] Molar concentration of metal ions to that of monomeric units of the nylon 4.
[b] Based on the nylon 4 weight.
[c] Concentration of NaBH$_4$ solution = 3.0 wt %, temperature = 75°C.
[d] Concentration of NaBH$_4$ solution = 0.2 wt %, temperature = 40°C.
[e] Concentration of NaBH$_4$ solution = 4.0 wt %, temperature = 80°C.

shown in Table IV, polyamide metal chelate films showed excellent electrical conductivity when they were reduced by NaBH$_4$ aqueous solution. Other agents, such as lithium aluminum hydride (LiAlH$_4$) in tetrahydrofuran (or diethyl ether), sodium (Na), lithium hydride (LiH), sodium hydride (NaH), and calcium hydride (CaH$_2$) in ethanol were used, but these films show high surface resistivity (> 2 × 10^7 Ω/cm^2). When these metal chelate films were dipped into water, the metal ions in the metal chelate films diffused out and were detected by a UV-visible spectrophotometer. When these metal chelate films were also dipped into other solvents such as tetrahydrofuran, diethyl ether, and ethanol, metal ions

did not diffuse out and showed no absorbance by UV-visible spectroscopy. These results can be explained by metal ions of the polyamide metal chelate films not being able to diffuse out of the nonaqueous solvents used for reducing agents other than the water solution of NaBH$_4$. Therefore, no reduction is happening even though these reducing agents are more reactive than NaBH$_4$.

Effects of the Concentrations of Metal Salt Solutions on the Electrical Conductivity of Metallized Films Prepared by the Soak Method

The polyamide metal chelate films used were prepared by the soak method. As shown in Table V, when the concentration of metal salt is less than 30 wt %, such as 10 and 20 wt %, the nylon films shows unsatisfactory conductivity after treatment with NaBH$_4$ aqueous solution. Nylon 4 or nylon 6 films were soaked in 30 wt % metal salts solution for 60 h to produce the metal chelate films. These films exhibited surface resistivity around 10^1–10^2 Ω/cm^2

Table III   Effect of the Concentration of Meta Salts on the Surface Resistivity of Nylon 6 Metal Chelate Films Reduced by NaBH$_4$ Aqueous Solution

Metal Salts	F^a	Wt %[b]	Surface Resistivity (Ω/cm^2)
CuCl$_2 \cdot$ 2H$_2$O[c]	0.06	9.0	> 2 × 10^7
	0.08	12.0	5.0 × 10^4
	0.10	15.0	4.8 × 10^1
	0.15	22.6	2.5 × 10^1
	0.20	30.1	4.0 × 10^0
NiCl$_2 \cdot$ 6H$_2$O[d]	0.02	4.2	> 2 × 10^7
	0.03	6.3	2.0 × 10^6
	0.05	10.5	3.4 × 10^3
	0.10	21.0	1.5 × 10^2
	0.15	31.6	6.0 × 10^1
CoCl$_2 \cdot$ 6H$_2$O[e]	0.04	8.4	> 2 × 10^7
	0.06	12.6	> 2 × 10^7
	0.08	16.8	4.0 × 10^3
	0.10	21.0	8.0 × 10^2
	0.15	31.6	6.5 × 10^1

[a] Molar concentration of metal ions to that of monomeric units of the nylon 6.
[b] Based on the nylon 6 weight.
[c] Concentration of NaBH$_4$ solution = 3.0 wt %, temperature = 75°C.
[d] Concentration of NaBH$_4$ solution = 0.2 wt %, temperature = 40°C.
[e] Concentration of NaBH$_4$ solution = 4.0 wt %, temperature = 80°C.

Table IV   Effect of Reducing Agents in Various Solvents on the Surface Resistivity of Polyamide Metal Chelate Film

Reducing Agents	Solvents	Concentration (Wt %)	Reduction Temp. (°C)	Surface Resistivity (Ω/cm^2)
$NaBH_4$	Water	0.2–4.0	40–80	10^0–10^1
$LiAl_4$	Tetrahydrofuran	1.0–3.0	0–10	$> 2 \times 10^7$
$LiAl_4$	Diethyl ether	1.0–3.0	0–10	$> 2 \times 10^7$
Na	Ethanol	8.0–10.0	78	$> 2 \times 10^7$
LiH	Ethanol	1.0–3.0	20–50	$> 2 \times 10^7$
NaH	Ethanol	1.0–3.0	20–50	$> 2 \times 10^7$
CaH_2	Ethanol	1.0–3.0	20–50	$> 2 \times 10^7$

after treating with $NaBH_4$ aqueous solution. When the concentration of metal salt is higher than 30 wt %, nylon films show some cracks after being soaked for 60 h. Therefore, the suitable concentration of metal salts for preparing metallized film is 30 wt %.

ESCA Analysis

Electron spectroscopy chemical analysis (ESCA) was used to analyze the surface of the metallized

films. The ESCA spectrum of nylon 4 metallized film after argon sputtering for 5 min is shown in Figures 7 and 8. In Figure 7 the electron binding energies of Cu $2p_{3/2}$ is 933.15 eV and Cu $2p_{1/2}$ is 952.95 eV. In Figure 8 the electron binding energies of Ni $2p_{3/2}$ is 853.25 eV and Ni $2p_{1/2}$ is 870.65 eV. These results are consistent with the ESCA handbook.[7] From these results Cu^{2+} and Ni^{2+} have been reduced to metallic Cu and metallic Ni on these films as indicated.

Table V   Variation of Surface Resistivity of Metallized Nylon Films Prepared from Nylon Films Soaked in Various Concentrations of Metal Salts Aqueous Solution for 60 h

Species	Metal Salts	Concentration (%)	Surface Resistivity (Ω/cm^2)
Nylon 4	$CuCl_2 \cdot 2H_2O$[a]	10.0	1.0×10^6
		20.0	7.0×10^1
		30.0	4.0×10^1
	$NiCl_2 \cdot 6H_2O$[b]	10.0	4.0×10^3
		20.0	1.7×10^2
		30.0	7.0×10^1
	$CoCl_2 \cdot 6H_2O$[c]	10.0	$> 2 \times 10^7$
		20.0	1.0×10^3
		30.0	2.5×10^1
Nylon 6	$CuCl_2 \cdot 2H_2O$[d]	10.0	1.0×10^2
		20.0	7.0×10^1
		30.0	2.0×10^1
	$NiCl_2 \cdot 6H_2O$[e]	10.0	1.3×10^2
		20.0	1.0×10^2
		30.0	3.5×10^1
	$CoCl_2 \cdot 6H_2O$[f]	10.0	$> 2 \times 10^7$
		20.0	1.0×10^5
		30.0	5.1×10^2

[a] Concentration of $NaBH_4$ solution = 2.0 wt %, temp. = 70°C, time = 30 s.
[b] Concentration of $NaBH_4$ solution = 0.8 wt %, temp. = 45°C, time = 30 s.
[c] Concentration of $NaBH_4$ solution = 4.0 wt %, temp. = 65°C, time = 30 s.
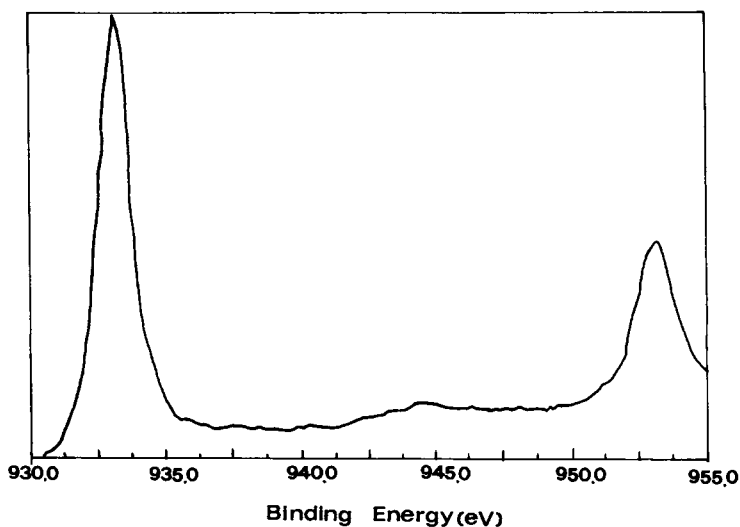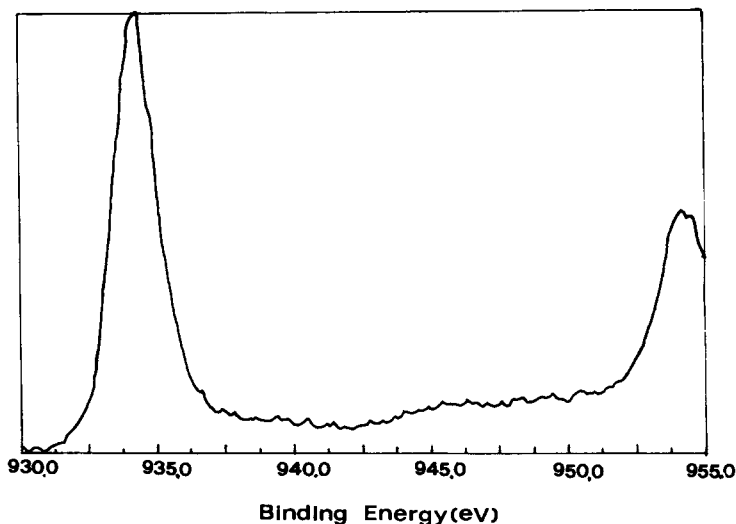[d] Concentration of $NaBH_4$ solution = 2.0 wt %, temp. = 70°C, time = 10 s.
[e] Concentration of $NaBH_4$ solution = 0.8 wt %, temp. = 45°C, time = 10 s.
[a] Concentration of $NaBH_4$ solution = 4.0 wt %, temp. = 65°C, time = 10 s.

Figure 7(a)   ESCA spectrum of unreduced nylon 4-Cu^{2+} chelate film.
Figure 7(b)   ESCA spectrum of nylon 4-Cu^{2+} chelate film reduced by $NaBH_4$ aqueous solution.

A 50/50 by weight mixture of cupric chloride and nickel chloride solutions was added to the polyamide–formic acid solution. The mixture was stirred at room temperature for 24 h and dried to a film as reported in the experimental section. The film was then reduced by $NaBH_4$ aqueous solution to provide excellent conductivity. The results of ESCA indicate only Ni^{2+} has been reduced to Ni on the film surface. It indicates that Cu^{2+} first formed a metal chelate with the amide group of polyamide and Ni^{2+} was then connected with Cu^{2+} by Cl^- in the outer position. Therefore, only Ni^{2+} was reduced by $NaBH_4$

solution to Ni on the film surface. A precise study is now in progress and will be reported in the near future.

Scanning Electron Microscope Observations

An SEM photograph shows a very flat surface on the nylon 4-$CuCl_2$ chelate film [Fig. 9(a)]. A drastic change of surface features occurs upon treatment with reducing agents, as shown in Figure 9(b). An extremely rough surface for the nylon 4-$CuCl_2$ chelate film results after $NaBH_4$ treatment. In Figure
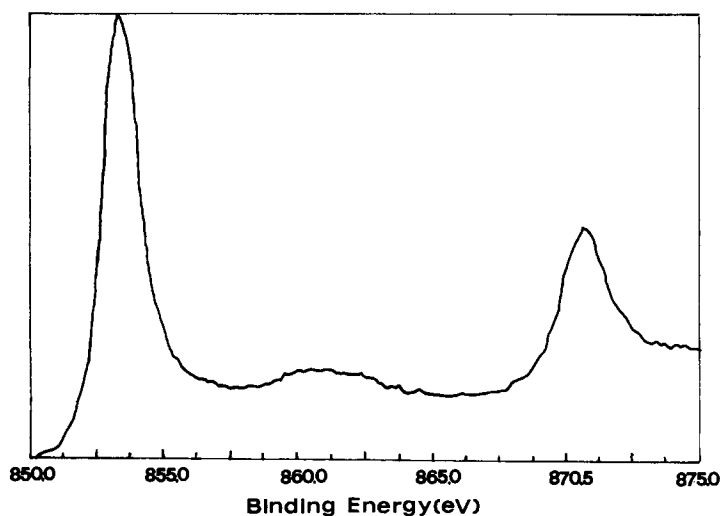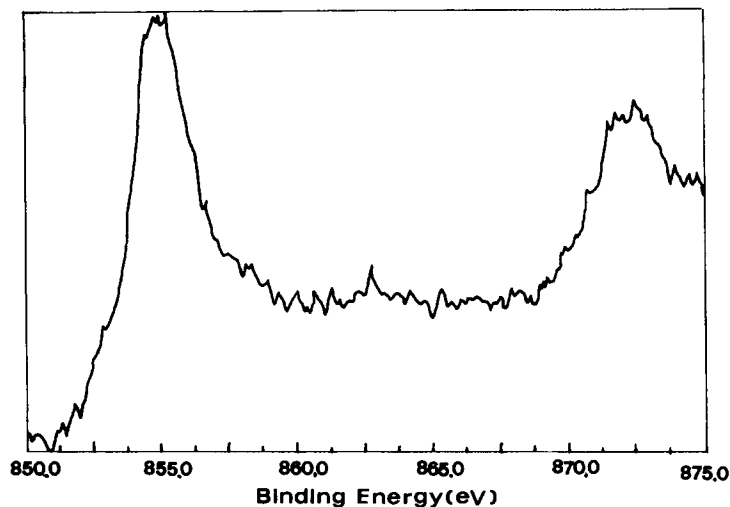
Figure 8(a)   ESCA spectrum of unreduced nylon 4–Ni^{2+} chelate film.
Figure 8(b)   ESCA spectrum of nylon 4–Ni^{2+} chelate film reduced by NaBH$_4$ aqueous solution.

9(c) and Figure 9(d), a "network" morphology is shown for the surface of the nylon–NiCl$_2$ and nylon–CoCl$_2$ metal chelate film, respectively. The continuous aggregation of metal particles on the surface of the reduced film is responsible for the conductivity of the metallized film.

Effects of Metal Salts and Reducing Agents on the Tensile Properties of Polyamide Metal Chelate Films

As shown in Table VI, the tensile strength of unreduced nylon 4 (or nylon 6) chelate films was higher than for control nylon 4 (or nylon 6) film, but the elongation was much lower than for the control nylon film. The increase in tensile strength of polyamide metal chelate films could be attributed to the interpolymer chelates. The tensile strengths of reduced nylon 4 (or nylon 6)–CuCl$_2$ chelate films were slightly lower than for the unreduced nylon 4 (or nylon 6)–CuCl$_2$ chelate film, and the elongation was higher than for the unreduced polyamide metal chelate films. On average, there were no observable differences between the tensile properties of reduced polyamide metal chelate films and the control polyamide films. Therefore, these reduced polyamide
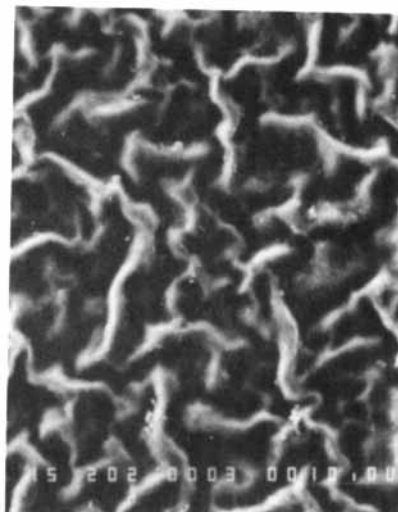
(a) Nylon 4-CuCl$_2$ Film
   before NaBH$_4$ Treatment
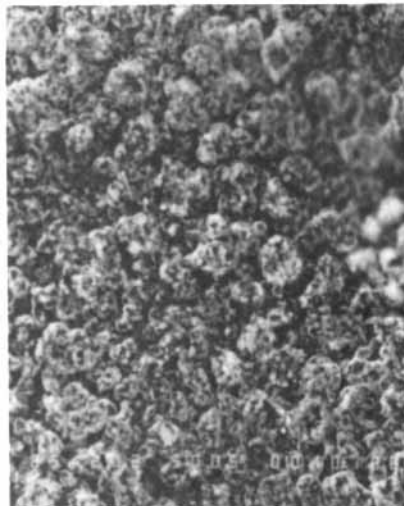
(b) Nylon 4-CuCl$_2$ Film
   after NaBH$_4$ Treatment
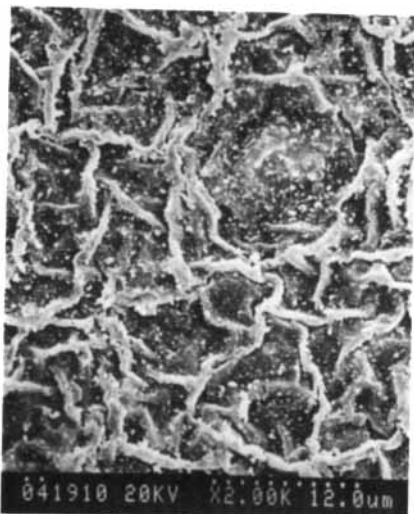
(c) Nylon 4-NiCl$_2$ Film

   after NaBH$_4$ Treatment

(d) Nylon 4-CoCl$_2$ Film

   after NaBH$_4$ Treatment

Figure 9   Scanning electron microscope photographs of nylon films.

Table VI   Mechanical Properties of Nylon Films and Nylon Metal Chelate Films[a]

Species	F	Tensile Strength (kg/cm^2)		Elongation (%)	
		Unreduced	Reduced	Unreduced	Reduced
Nylon 4	0	722.6	—	66.67	—
Nylon 4–CuCl$_2$	0.05	733.3	682.1	65.83	59.17
	0.10	759.0	753.2	18.33	65.00
	0.125	1006.7	658.8	10.00	49.17
	0.15	916.7	584.6	15.42	17.92
Nylon 6	0	561.7	—	44.00	—
Nylon 6–CuCl$_2$	0.06	511.1	440.0	10.83	13.33
	0.10	716.4	619.4	10.83	26.70
	0.15	654.8	584.4	12.50	30.00
	0.20	720.7	524.2	5.83	21.67

[a] Drawing rate = 5.0 mm/min; drawing temperature = room temperature; load cell = 5.0 kg.

chelate films still maintained excellent tensile properties.

Proposed Structures for the Polyamide Metal Chelates

UV-visible and IR spectra confirmed metal chelate formation with metal ion coordinated with the amide groups of polyamide. Grant and Hay[8] have shown that copper(II) could coordinate with the nitrogen atom of the amide group. Furthermore, according to investigations by Sumita[9] and Taube,[10] if the amount of CuCl$_2$ in the nylon 4–Cu^{2+} chelate film is over 10 wt % ($F > 0.05$), most of the Cu^{2+} ions are not chelated by nylon 4 but coordinated by Cl$^-$. The Cl$^-$ is considered as a bridging atom to form the activated complex. A proposed structure of this chelate is shown in Figure 10. Therefore, the surplus CuCl$_2$ in the activated complex can be easily reduced to metallic Cu on the film surface by NaBH$_4$ aqueous solution and results in excellent electrical conductivity.

As mentioned, only when the polyamide metal chelate film was reduced by NaBH$_4$ aqueous solution can these surplus metal ions in these films diffuse out by water and be further reduced to the metallic state by NaBH$_4$. But in the first paper of this series, poly(vinyl alcohol) (PVA) metal chelate film was shown to be reduced in various combinations of solvents and reducing agents, such as NaBH$_4$ in water, sodium (Na) in ethanol, etc., and all showed excellent electrical conductivity. The two different results, for polyamide metal chelate films and PVA metal chelate film, can be explained by the assumption that metal ions in the PVA-activated complex are oriented on the film surface, pointing toward the air. Therefore, the surplus metal ions in the PVA-activated complex can easily diffuse out in a variety of reducing agent solvents. The metal ions in the polyamide-activated complex were distributed throughout the interior of the film surface. Only strongly polar solvents such as water can cause metal ions in the polyamide metal chelate to diffuse out and then be reduced to the metallic state by NaBH$_4$.
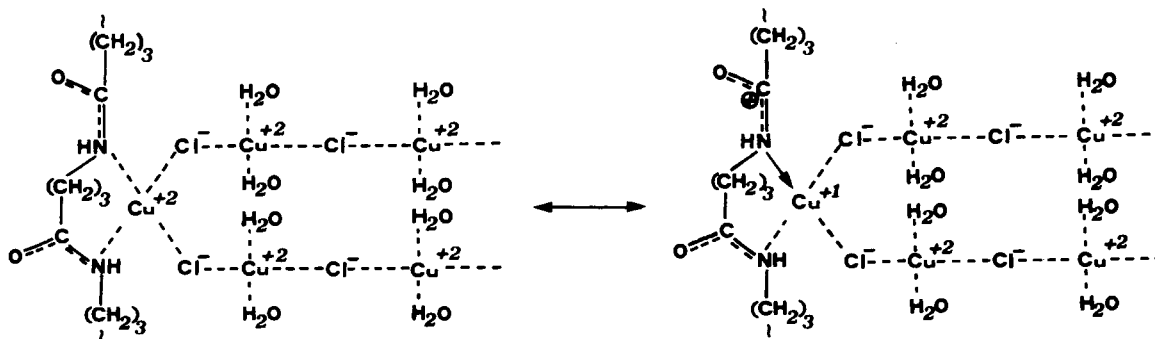

Figure 10   Proposed structure for the nylon 4–Cu^{2+} chelate responsible for conductivity.

Therefore, the affinity between solvents and metal ions plays an important role in the reduction to form conductive polymer films.

CONCLUSION

Electrically conducting polymer by this novel method can be prepared by the following steps:

1. Choose functional group-containing polymers such as polyamides, poly(vinyl alcohol), polyacrylonitrile, polyacrylamide, polyurethanes, polyamide-imides, etc.[11]
2. Introduce metal salt solutions into the polymer solutions or soaking blank polymer films in metal salt solutions.
3. Form the polymer metal chelate films.
4. Treat with reducing agents in suitable solvents.
5. Reduce metal ions to metallic states on the polymer film surfaces.
6. Form polymer films with excellent electrical conductivity.

These processes are relatively simple and fast, and commercially available polymers can be used in this novel method. The mechanism of conduction will be reported in the near future.

REFERENCES

1. O. Sumita, A. Fukuda, and E. Huge, *J. Appl. Polym. Sci.*, **23**, 2279 (1979).
2. F. Higashi, C. S. Cho, H. Kakinoki, and O. Sumita, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 2303 (1977).
3. C. C. Yen, T. C. Chang, and H. Kakinoki, *J. Appl. Polym. Sci.*, to appear.
4. J. Y. Lai, T. C. Chang, Z. J. Wu, and T. S. Heish, *J. Appl. Polym. Sci.*, **26**, 1135 (1981).
5. A. Jong, T. C. Chang, and J. Y. Lai, *J. Appl. Polym. Sci.*, **36**, 87 (1988).
6. L. E. Nilsen, Ed., *Mechanical Properties of Polymers and Composites*, Dekker, New York, 1974, vol. I.
7. C. D. Wagner, W. N. Riggs, L. E. Davis, J. F. Moulder, and G. E. Muilenberg, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Co., Eden Prairie, Minnesota, 1979.
8. I. J. Grant and R. W. Hay, *Aust. J. Chem.*, **18**, 1189 (1965).
9. O. Sumita, A. Fukuda, and E. Kuze, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 1801 (1978).
10. F. Basolo and R. C. Johnson, *Coordination Chemistry, The Chemistry of Metal Complexes*, Benjamin, New York, 1964.
11. Jpn. Pat. 88 314208 (1988).