

# Studies on the Preparation and Properties of Conductive Polymers. V. Analysis of Metallized Polyamide Complex Metal Chelate Films and Precipitates in Metal Chelate Solution

CHIH-CHAO YEN,<sup>1</sup> CHUEH-JUNG HUANG,<sup>2</sup> and TEH-CHOU CHANG<sup>3,\*</sup>

<sup>1</sup>Department of Chemical Engineering, Chung Yuan Christian University, Chung Li, Taiwan, Republic of China, 32023, <sup>2</sup>Shu-Teh Junior College of Technology, Taichung, Taiwan, Republic of China, and <sup>3</sup>Department of Chemical Engineering, Chung Yuan Christian University, Chung Li, Taiwan, Republic of China, 32023

## SYNOPSIS

Metallized films were obtained by the reduction of polyamide metal chelate films with reducing agents. In the preparation of polyamide metal chelate solution, a small amount of precipitate forms when a certain stoichiometric ratio of formic acid, polyamide, and metal salts was mixed. The precipitate formation rate was affected by kinds and concentrations of metal salts, kinds and molecular weight of polyamide, and solution temperature. In addition, the precipitate formation rate affects the conducting surface metallic substance of reduced nylon/CuCl<sub>2</sub>/NiCl<sub>2</sub> complex metal chelate film. The conducting surface is metallic Ni for low-molecular-weight nylon 4/CuCl<sub>2</sub>/NiCl<sub>2</sub> film and metallic Cu for high-molecular-weight nylon 4/CuCl<sub>2</sub>/NiCl<sub>2</sub> film reduced by NaBH<sub>4</sub> aqueous solution. The precipitate consists of polyamide, metal salt, and formic acid. The interaction among the polyamide, metal salt, and formic acid appears to be by means of hydrogen bonds and ionic bonds. The proposed structure of precipitate was also studied. © 1992 John Wiley & Sons, Inc.

## INTRODUCTION

In the previous articles of this series,<sup>1-4</sup> metallized polymer films were prepared from polymer metal chelate films. The polymer metal chelate films were prepared by metal salts mixed with polymers containing functional groups such as poly(vinyl alcohol) (PVA), polyamide, polyamide-imides (PAI), and polyurethane (PU). These polymer metal chelate films were reduced by reducing agents or the retroplating out method.<sup>1-4</sup> Excellent conductive films with long-term stability were obtained.

In this study, instead of the polymer single metal chelate used in the previous works,<sup>1-4</sup> the effect of polymer complex metal chelate was investigated.

Various polyamide metal chelate films with different concentrations of complex metal salts were prepared and reduced to metallized polyamide films by reducing agents. The metallized substance on the surface of films as well as their surface resistivities were also examined.

Some articles report interactions between polymer and small molecules.<sup>5-7</sup> It was of interest to study the molecular weight dependence in the polymer reaction that is characteristic of polymers. Morishima<sup>5</sup> reported that high-molecular-weight PVA forms a soluble complex, and low-molecular-weight PVA forms an insoluble complex. This was attributed to PVA with a degree of polymerization smaller than 160 not being large enough to form the intramolecular complex, resulting in the intermolecular complex and hence in precipitation by cross-linking. Aharoni<sup>6,7</sup> reported the formation of highly crystalline adducts of synthetic aliphatic or aromatic

\* To whom correspondence should be addressed.

polyamides with diacids. Formation is associated with an approximate equivalence between the lengths of the extended diacids and the repeat unit of the polymeric chain.

In this investigation we report a new precipitate formed from polyamide, formic acid, and metal salts. It was found that a small amount of precipitate formed when a stoichiometric amount of formic acid, polyamide, and metal salts was mixed to prepare polyamide metal chelate solution. Factors affecting the formation of precipitate in the polyamide metal chelate solution and the proposed structure of precipitate were also investigated.

## EXPERIMENTAL

### Preparation of Polyamide Complex Metal Chelate Films

Nylon 4 with a molecular weight of about  $1.8 \times 10^4$  to  $8.0 \times 10^4$  and commercially available nylon 6 with a molecular weight of  $1.5 \times 10^4$  were used to prepare the polyamide complex metal chelate films. To the polyamide-formic acid solution was added mixed metal salts by one of the following two methods: (1) The aqueous solution of complex metal salts was added to polyamide-formic acid solution, and the mixture was subsequently stirred for 24 h. (2) One of the metal salt aqueous solutions was first added to polyamide-formic acid solution, stirred for 12 h, and then a second metal salt aqueous solution was introduced and stirred another 12 h. The amount of the metal salts was expressed by the weight percent of metal salt based on nylon 4 weight and the  $F$  value (the ratio of the molar concentration of metal ion to that of monomeric units of nylon 4). Various conditions used are listed in Tables I-IV.

The prepared polyamide complex metal chelate solution was kept a while to clarify; then the resulting viscous solution was cast on a clean glass plate. The film on the glass plate was evaporated at ambient for 5 min and further dried in an oven at  $80^\circ\text{C}$  for 30 min. The film was then peeled off and cut into  $1 \times 3$  cm test pieces.

### Preparation of Metallized Polyamide Films by Metal Hydride Reducing Agents

The test pieces of polyamide complex metal chelate films were reduced by 25 mL of a 0.2-4.0 wt % sodium borohydride aqueous solution at  $35-80^\circ\text{C}$  for a suitable time. The reduced films were washed with

water and dried at  $100^\circ\text{C}$  for 5 min, then cooled to room temperature, and stored in a desiccator for subsequent use.

### Electric Measurement

The surface electrical conductivity of the films was measured according to the conventional four-terminal method using aluminum foil electrodes, as described in a previous study.<sup>1</sup>

### Preparation of Precipitate from Polyamide Metal Chelate Solution

Various precipitates of polyamide metal chelate solution were prepared by dissolving polyamide (nylon 4 or 6 with a molecular weight less than  $2 \times 10^4$ ) in formic acid followed by addition of aqueous solution of a metal salt (such as  $\text{CuCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{CoCl}_2$ , etc.). Whether a precipitate formed or not was affected by the stirring time, the amount of formic acid, and kinds of metal salts, as shown in Table VII and Table VIII. When the precipitate was formed out of the polyamide metal chelate solution, it was filtered and then dried under vacuum at  $80^\circ\text{C}$ .

### Instrument Analysis

The melting point was determined on a YAZAWA Micro Melting Point BY-2 Model. UV-visible absorption spectra of aqueous solutions of the precipitates were measured by using a Jasco Model 7800 spectrophotometer. IR spectra of the precipitates were obtained by the KBr method using a Perkin-Elmer 710 B spectrophotometer. X-ray diffraction patterns of metallized polyamide films were measured by a Shimadzu XD-3A Diffractometer using  $\text{CuK}_\alpha$  radiation generated at 30 kV and 20 mA.

Electron spectroscopy for chemical analysis (ESCA) spectra was recorded using a VG Scientific LTD model LAB 5 spectrometer with a  $\text{MgK}_\alpha$  X-ray source radiation generated at 10 kV and 20 mA.

## RESULTS AND DISCUSSIONS

### Effects of Mixing Methods of Complex Metal Salts on the Surface Resistivity of Metallized Films

To study whether the addition order of the metal salts to the polyamide-formic acid solution in preparing the chelate films affected the conductivity of chelate films, three modes of addition of  $\text{CuCl}_2$  (15 wt %) and  $\text{NiCl}_2$  (15 wt %) to nylon 4-formic acid

solution were employed for the preparation of nylon 4 complex metal chelate films: (1) the aqueous solution of  $\text{CuCl}_2$  and  $\text{NiCl}_2$  was well mixed and then added; (2)  $\text{CuCl}_2$  aqueous solution was added first followed by  $\text{NiCl}_2$  aqueous solution; and (3)  $\text{NiCl}_2$  aqueous solution was added first, then  $\text{CuCl}_2$  aqueous solution was introduced. Films prepared from these methods all exhibited low surface resistivity, around  $10^1 \Omega/\text{cm}^2$ , when reduced with 3%  $\text{NaBH}_4$  aqueous solution at  $80^\circ\text{C}$  for 1 min. Therefore, the addition order of complex metal salts did not affect the conductivity of metallized films. Similar results were investigated in the complex metal chelate films prepared by mixing  $\text{CuCl}_2$  (15 wt %) and  $\text{CoCl}_2$  (15 wt %) as well as by mixing  $\text{NiCl}_2$  (15 wt %) and  $\text{CoCl}_2$  (15 wt %), the surface resistivities of which were around  $10^2 \Omega/\text{cm}^2$ , as shown in Table I.

#### Effects of the Concentrations of Complex Metal Salts on the Surface Resistivity of Metallized Films

In the course of the previous study,<sup>2</sup> it was shown that nylon 4 single metal chelate films, such as nylon

4/ $\text{CuCl}_2$ , nylon 4/ $\text{NiCl}_2$  or nylon 4/ $\text{CoCl}_2$  metal chelate films, show excellent conductivity after  $\text{NaBH}_4$  reduction, with  $F > 0.05$ ,  $F > 0.02$ , and  $F > 0.04$ , respectively. The concentration of the metal salts appears to play an important role in producing an excellent conductivity polymer film. Consequently, the effects of the concentrations of complex metal salt systems were investigated in this study. Effects of the concentrations of  $\text{CuCl}_2/\text{NiCl}_2$  mixture,  $\text{NiCl}_2/\text{CoCl}_2$  mixture, and  $\text{CuCl}_2/\text{CoCl}_2$  mixture in nylon 4 complex metal chelate films on the conductivity of metallized films are listed in Tables II, III, and IV, respectively. For nylon 4/ $\text{CuCl}_2/\text{NiCl}_2$  or nylon 4/ $\text{CuCl}_2/\text{CoCl}_2$  complex metal chelate films, when  $F = 0.05$  for  $\text{CuCl}_2$ , the surface resistivity of the reduced films decreased with increasing concentration of  $\text{NiCl}_2$  or  $\text{CoCl}_2$ . For nylon 4/ $\text{CuCl}_2/\text{NiCl}_2$  or nylon 4/ $\text{NiCl}_2/\text{CoCl}_2$  complex metal chelate films, when  $F = 0.02$  for  $\text{NiCl}_2$ , low surface resistivity can be obtained with  $F > 0.04$  for  $\text{CuCl}_2$ , while the surface resistivity decreased with  $F > 0.05$  for  $\text{CoCl}_2$ . For nylon 4/ $\text{NiCl}_2/\text{CoCl}_2$  or nylon 4/ $\text{CuCl}_2/\text{CoCl}_2$  complex metal chelate films,

**Table I** Effect of the Addition Order of Metal Salts on the Conductivity of Nylon 4 Complex Metal Chelate Film Reduced by  $\text{NaBH}_4$  Aqueous Solution

Metal Salts	Reduction	Surface Resistivity ( $\Omega/\text{cm}^2$ )
$\text{NiCl}_2 + \text{CuCl}_2^{\text{a}}$ (15 wt %) <sup>d</sup> (15 wt %)	$\text{NaBH}_4$ : 3.0% Temp.: $80^\circ\text{C}$ Time: 1 min	$1.0 \times 10^1$
$\text{CuCl}_2 / \text{NiCl}_2^{\text{b}}$ (15 wt %) (15 wt %)	$\text{NaBH}_4$ : 3.0% Temp.: $80^\circ\text{C}$ Time: 1 min	$5.0 \times 10^1$
$\text{NiCl}_2 / \text{CuCl}_2^{\text{c}}$ (15 wt %) (15 wt %)	$\text{NaBH}_4$ : 3.0% Temp.: $80^\circ\text{C}$ Time: 1 min	$2.5 \times 10^1$
$\text{CuCl}_2 + \text{CoCl}_2$ (15 wt %) (15 wt %)	$\text{NaBH}_4$ : 3.0% Temp.: $80^\circ\text{C}$ Time: 1 min	$1.0 \times 10^2$
$\text{NiCl}_2 + \text{CoCl}_2$ (15 wt %) (15 wt %)	$\text{NaBH}_4$ : 1.2% Temp.: $50^\circ\text{C}$ Time: 1 min	$1.0 \times 10^2$

<sup>a</sup>  $\text{CuCl}_2$  and  $\text{NiCl}_2$  were added together, and the solution was stirred for 24 h.

<sup>b</sup>  $\text{CuCl}_2$  was added first; the solution was stirred for 12 h; then  $\text{NiCl}_2$  was added and the mixture was stirred for another 12 h.

<sup>c</sup>  $\text{NiCl}_2$  was added first; the solution was stirred for 12 h; then  $\text{CuCl}_2$  was added and the mixture was stirred for another 12 h.

<sup>d</sup> Base on nylon 4 weight.

**Table II Effect of the Concentrations of CuCl<sub>2</sub> and NiCl<sub>2</sub> on the Surface Resistivity of Nylon/CuCl<sub>2</sub>/NiCl<sub>2</sub> Complex Metal Chelate Films Reduced by NaBH<sub>4</sub> Aqueous Solution**

Run No.	CuCl <sub>2</sub>		NiCl <sub>2</sub>		$R_s^c$ ( $\Omega/\text{cm}^2$ )	$R_s^d$ ( $\Omega/\text{cm}^2$ )
	$F^a$	wt % <sup>b</sup>	$F$	wt %		
Cu-Ni-1	0.05	10.0	0.02	2.8	$2.0 \times 10^7$	$5.0 \times 10^4$
Cu-Ni-2	0.05	10.0	0.02	5.6	$2.0 \times 10^7$	$1.0 \times 10^4$
Cu-Ni-3	0.05	10.0	0.03	8.4	$2.0 \times 10^7$	$1.0 \times 10^3$
Cu-Ni-4	0.05	10.0	0.04	11.2	$1.0 \times 10^5$	$4.0 \times 10^2$
Cu-Ni-5	0.01	2.0	0.02	5.6	$2.0 \times 10^7$	$2.0 \times 10^7$
Cu-Ni-6	0.02	4.0	0.02	5.6	$2.0 \times 10^7$	$2.0 \times 10^7$
Cu-Ni-7	0.03	6.0	0.02	5.6	$2.0 \times 10^7$	$2.0 \times 10^7$
Cu-Ni-8	0.04	8.0	0.02	5.6	$2.0 \times 10^7$	$1.0 \times 10^5$
Cu-Ni-9	0.05	10.0	0.02	5.6	$2.0 \times 10^7$	$1.0 \times 10^4$
Cu-Ni-10	0.06	12.0	0.02	5.6	$1.0 \times 10^5$	$5.0 \times 10^2$
Cu-Ni-11	0.06	12.0	0.03	8.4	$1.0 \times 10^3$	$5.0 \times 10^1$
Cu-Ni-12	0.075	15.0	0.054	15.0	$1.0 \times 10^1$	$5.0 \times 10^1$

<sup>a</sup> Molar concentration of metal ions to that of monomeric units of the nylon 4.

<sup>b</sup> Base on the nylon 4 weight.

<sup>c</sup>  $R_s$ : Surface resistivity; concentration of NaBH<sub>4</sub> solution = 3.0 wt %, temperature = 75°C.

<sup>d</sup>  $R_s$ : Surface resistivity; concentration of NaBH<sub>4</sub> solution = 0.2 wt %, temperature = 40°C.

when  $F = 0.05$  for CoCl<sub>2</sub>, the surface resistivity also decreased with an increase in  $F$  values of NiCl<sub>2</sub> or CuCl<sub>2</sub>.

#### Effects of the Reductive Conditions on the Surface Resistivity of Metallized Nylon 4 Complex Metal Chelate Films

In order to get a good conducting film, milder conditions had to be used in the reduction of the above

complex metal chelate films with NaBH<sub>4</sub> aqueous solution as compared with the reduction of the single metal chelate films of high concentration of NaBH<sub>4</sub> aqueous solution. For example, in order to obtain films with high conductivity, the metal chelate films were treated with an aqueous NaBH<sub>4</sub> solution of lower concentration at lower temperature for the films prepared in Tables II, III, and IV. If the reduction conditions were too strong, the internal structure of metal chelate films would be destroyed

**Table III Effect of the Concentrations of NiCl<sub>2</sub> and CoCl<sub>2</sub> on the Surface Resistivity of Nylon 4/NiCl<sub>2</sub>/CoCl<sub>2</sub> Complex Metal Chelate Films Reduced by NaBH<sub>4</sub> Aqueous Solution**

Run No.	NiCl <sub>2</sub>		CoCl <sub>2</sub>		$R_s^a$ ( $\Omega/\text{cm}^2$ )	$R_s^b$ ( $\Omega/\text{cm}^2$ )
	$F$	wt %	$F$	wt %		
Ni-Co-1	0.02	5.6	0.03	8.4	$2.0 \times 10^7$	$2.0 \times 10^7$
Ni-Co-2	0.02	5.6	0.04	11.2	$2.0 \times 10^7$	$2.0 \times 10^7$
Ni-Co-3	0.02	5.6	0.05	13.4	$2.0 \times 10^7$	$5.0 \times 10^4$
Ni-Co-4	0.02	5.6	0.07	19.6	$2.5 \times 10^4$	$7.0 \times 10^1$
Ni-Co-5	0.03	8.4	0.05	13.4	$2.0 \times 10^7$	$1.0 \times 10^3$
Ni-Co-6	0.04	11.2	0.05	13.4	$2.0 \times 10^7$	$4.0 \times 10^2$
Ni-Co-7	0.05	13.8	0.05	13.4	$2.0 \times 10^7$	$3.0 \times 10^2$
Ni-Co-8	0.06	16.8	0.05	13.4	$4.0 \times 10^4$	$6.0 \times 10^1$

<sup>a</sup>  $R_s$ : Surface resistivity; concentration of NaBH<sub>4</sub> solution = 3.0 wt %, temperature = 65°C.

<sup>b</sup>  $R_s$ : Surface resistivity; concentration of NaBH<sub>4</sub> solution = 0.5 wt %, temperature = 35°C.

**Table IV Effect of the Concentrations of CuCl<sub>2</sub> and CoCl<sub>2</sub> on the Surface Resistivity of Nylon 4/CuCl<sub>2</sub>/CoCl<sub>2</sub> Complex Metal Chelate Films Reduced by NaBH<sub>4</sub> Aqueous Solution**

Run No.	CuCl <sub>2</sub>		CoCl <sub>2</sub>		$R_s^a$ ( $\Omega/\text{cm}^2$ )	$R_s^b$ ( $\Omega/\text{cm}^2$ )	$R_s^c$ ( $\Omega/\text{cm}^2$ )
	$F$	wt %	$F$	wt %			
Cu-Co-1	0.05	10.0	0.03	8.4	$2.0 \times 10^7$	$2.0 \times 10^7$	$2.5 \times 10^2$
Cu-Co-2	0.05	10.0	0.04	11.2	$2.0 \times 10^7$	$2.0 \times 10^7$	$1.1 \times 10^2$
Cu-Co-3	0.05	10.0	0.05	13.4	$1.5 \times 10^4$	$3.0 \times 10^3$	$3.5 \times 10^1$
Cu-Co-4	0.05	10.0	0.06	16.8	$2.0 \times 10^3$	$1.4 \times 10^3$	$2.5 \times 10^1$
Cu-Co-5	0.0	0.0	0.05	13.4	$2.0 \times 10^7$	$2.0 \times 10^7$	$1.0 \times 10^4$
Cu-Co-6	0.03	6.0	0.05	13.4	$1.0 \times 10^5$	$2.0 \times 10^2$	$1.0 \times 10^2$
Cu-Co-7	0.04	8.0	0.05	13.4	$1.0 \times 10^4$	$3.8 \times 10^2$	$7.5 \times 10^1$
Cu-Co-8	0.06	12.0	0.05	13.4	$9.0 \times 10^1$	$1.8 \times 10^2$	$2.0 \times 10^1$

<sup>a</sup>  $R_s$ : Surface resistivity; concentration of NaBH<sub>4</sub> solution = 4.0 wt %, temperature = 70°C.

<sup>b</sup>  $R_s$ : Surface resistivity; concentration of NaBH<sub>4</sub> solution = 3.0 wt %, temperature = 60°C.

<sup>c</sup>  $R_s$ : Surface resistivity; concentration of NaBH<sub>4</sub> solution = 0.5 wt %, temperature = 35°C.

by high temperature and high concentration of NaBH<sub>4</sub>. Therefore, the tiny metal particles formed on the surfaces of films would be damaged and cause the films to exhibit high surface resistivity. In addition, the metal layer on the complex metal chelate films with higher concentrations of metal salts, was much more uniform since more surplus metal salts in the activated complex could be reduced to form a thick metal layer on the film surface. Thus the internal structure of such metal chelate films was more stable, and was not easily destroyed by high temperature and high concentration of NaBH<sub>4</sub>.

#### Analysis of the Surface Composition of Metallized Complex Metal Chelate Films and Investigation of the Conductive Mechanism

According to the previous studies,<sup>1-4</sup> the surfaces of single metal chelate films after reaction with reducing agents form a metal layer that binds tightly to the films through chelation. This adhered metal layer is responsible for the conductivity of the metallized films. The surface of complex metal chelate films prepared by mixing two kinds of metal salts followed by treatment with aqueous NaBH<sub>4</sub> could be analyzed by ESCA and X-ray. The electron binding energies and the relative atom concentrations of nylon 4/NiCl<sub>2</sub>/CoCl<sub>2</sub> and nylon 4/CuCl<sub>2</sub>/NiCl<sub>2</sub> complex metal chelate films measured by ESCA are given in Table V. In principle, Ni<sup>2+</sup> should be reduced to Ni<sup>0</sup> much easier than Co<sup>2+</sup> to Co<sup>0</sup> since the reduction potential of Ni<sup>2+</sup> is higher than that of Co<sup>2+</sup> for Ni-Co-4 complex metal chelate film.

However, when the concentration of Ni<sup>2+</sup> was very low ( $F = 0.02$ ), the relative atom concentration of Co<sup>0</sup> was 72.2 while the atom concentration of Ni<sup>2+</sup> was 27.8, after NaBH<sub>4</sub> reduction, as detected by ESCA. This result indicates that the Ni<sup>2+</sup> was not reduced to Ni metal because there was only a very limited amount of Ni<sup>2+</sup> present due to chelation of most of the Ni<sup>2+</sup> ions by nylon 4. As a result, Co<sup>2+</sup> was reduced preferentially to metallic Co on the surface of the film due to its higher concentration. Since Co metal was formed on the surface of the film, the surface resistivity reduced to  $7.0 \times 10^1 \Omega/\text{cm}^2$ . When the concentration of CoCl<sub>2</sub> was decreased to  $F = 0.05$ , for such as the Ni-Co-3 complex metal chelate film, the quantity of reduced metallic Co decreased accordingly, and its relative atom concentration (Co<sup>0</sup>) lowered to 2.0. Since less metal was formed on the surface of the film, the surface resistivity jumped to  $5.0 \times 10^4 \Omega/\text{cm}^2$ . When the concentration of NiCl<sub>2</sub> increased to  $F = 0.05$ , for example, for the Ni-Co-7 complex metal chelate film, an even layer of Ni metal was formed on the surface of the film, since the reduction of Ni<sup>2+</sup> was not limited by its concentration and Ni<sup>2+</sup> was reduced preferentially. Under this condition, the concentration of atom (Ni<sup>0</sup>) was 100% after reduction and the film displayed a higher conductivity. Similar results were also investigated for nylon 4/CuCl<sub>2</sub>/NiCl<sub>2</sub> complex metal chelate films. When the  $F$  values of CuCl<sub>2</sub> and NiCl<sub>2</sub> were lower than 0.03 and 0.02, respectively, no extra metallic ions were available for reduction since most of the metal ions were coordinated with polyamide through chelation. The

**Table V Electron Binding Energies and Relative Concentrations of Atoms Corresponding to Peaks Observed in ESCA Analysis for the Surfaces of Metallized Nylon 4 Metal Complex Metal Chelate Films Reduced by NaBH<sub>4</sub> Aqueous Solution**

Nylon 4 Complex Metal Chelate Films Run No.	Surface Resistivity ( $\Omega/\text{cm}^2$ )	Binding Energy ( $2p_{3/2}$ ), eV		
		934 <sup>a</sup> Cu <sup>0</sup>	852 <sup>b</sup> Ni <sup>0</sup>	781 <sup>c</sup> Co <sup>0</sup>
Ni-Co-4	$7.0 \times 10^1$		856 Ni <sup>2+</sup> (27.8) <sup>d</sup>	781 Co <sup>0</sup> (72.2)
Ni-Co-3	$5.0 \times 10^4$		856 Ni <sup>2+</sup> (98.0)	781 Co <sup>0</sup> (2.0)
Ni-Co-7	$3.0 \times 10^2$		853 Ni <sup>0</sup> (100)	
Cu-Ni-6	$2.0 \times 10^7$	937 Cu <sup>2+</sup> (23.1)	860 Ni <sup>2+</sup> (76.8)	
Cu-Ni-4	$4.0 \times 10^2$	933 Cu <sup>0</sup> (1.0)	856 Ni <sup>2+</sup> (99.0)	
Cu-Ni-11	$5.0 \times 10^1$	932 Cu <sup>0</sup> (44.3)	856 Ni <sup>2+</sup> (55.6)	
Cu-Ni-112	$1.0 \times 10^1$	932 Cu <sup>0</sup> (100)		

<sup>a</sup> Cu<sup>0</sup> ( $2p_{3/2}$ ) electron binding energy.

<sup>b</sup> Ni<sup>0</sup> ( $2p_{3/2}$ ) electron binding energy.

<sup>c</sup> Co<sup>0</sup> ( $2p_{3/2}$ ) electron binding energy.

<sup>d</sup> Relative concentrations of atoms.

films prepared under these conditions, such as Cu-Ni-6 complex metal chelate film, exhibited extremely high surface resistivity after reduction. In addition, when the concentration of metal ion was increased, the metal layer formed on the surface of the film became much more uniform, and the surface resistivity of the film decreased considerably. It is evident from our results above that the concentration of the metal ions is crucial, not only as to which metal can be deposited on the surface, but also to the conductivity of the polymer. To demonstrate the importance of ion concentration further, reduction of complex metal salts film was carried out in high metal ion concentrations, such as Cu-Ni-12 complex metal chelate film, which afforded a uniform layer

of Cu metal. The surface resistivity reduced dramatically to  $1 \times 10^1 \Omega/\text{cm}^2$ , which is at the limit of our detection.

For nylon 4/CuCl<sub>2</sub>/NiCl<sub>2</sub> complex metal chelate films with high metal ion concentration, the addition order of metal salts in the preparation of film did not affect the conductivity and the metallized substance on the surface of the film. The reduced films prepared in three different modes of addition of metal salts were analyzed by X-ray and their surfaces were all identified to be Cu metal, as shown in Table VI.

#### Effect of the Amount of Formic Acid on the Time Required to Form Precipitate in Nylon 6 Metal Chelate Formic Acid Solution

In the preparation of nylon 6/NiCl<sub>2</sub>/HCOOH solution, as shown in Table VII, when the amount of formic acid was increased in the nylon 6 metal chelate solution, the time required for a precipitate to appear increased and the amount of precipitate decreased. No precipitation occurred when the amount of formic acid in the nylon 6 metal chelate solution was over a certain quantity. Furthermore, when the

**Table VI Diffraction Angles ( $2\theta$ ) and Plane Distances ( $d$ ) Corresponding to Peaks Observed in X-ray Analysis for Nylon 4/CuCl<sub>2</sub> (15 wt %)/NiCl<sub>2</sub> (15 wt %) Complex Metal Chelate Film Reduced by NaBH<sub>4</sub> Aqueous Solution**

Peaks	Film A <sup>a</sup> Experiment		Film B <sup>b</sup> Experiment	
	$2\theta$	$d$	$2\theta$	$d$
1	43.3	2.088	43.3	2.088
2	50.4	1.809	50.5	1.807
3	74.1	1.279	74.1	1.279
Peaks	Film C <sup>c</sup> Experiment		Pure Cu Experiment	
	$2\theta$	$d$	$2\theta$	$d$
1	43.3	2.088	43.30	2.088
2	50.5	1.807	50.43	1.808
3	74.2	1.277	74.13	1.278

<sup>a</sup> CuCl<sub>2</sub> was added first; the solution was stirred for 12 h; then NiCl<sub>2</sub> was added and the solution stirred for an additional 12 h.

<sup>b</sup> NiCl<sub>2</sub> was added first; the solution was stirred for 12 h; then CuCl<sub>2</sub> was added and the solution stirred for an additional 12 h.

<sup>c</sup> CuCl<sub>2</sub> and NiCl<sub>2</sub> added together, and solution stirred for 24 h.

**Table VII Effect of the Amount of Formic Acid on the Time Required to Appear Precipitate in Nylon 6/NiCl<sub>2</sub>/HCOOH Solution**

Nylon 6 (g)	NiCl <sub>2</sub> (g)	<i>F</i> <sup>a</sup>	HCOOH (g)	wt % <sup>b</sup>	Precipitate (g)	Time (h) <sup>c</sup>
5.0	1.573	0.15	15	25	0.40	2.5
5.0	1.573	0.15	35	12.5	0.21	4.0
5.0	1.573	0.15	57.5	8.0	0.12	9.0
5.0	1.573	0.15	95.0	5.0	0.022	168
5.0	1.573	0.15	161.6	3.0	None	—

<sup>a</sup>  $F = [\text{molar conc. of NiCl}_2]/[\text{molar conc. of monomeric unit of nylon 6}]$ .

<sup>b</sup>  $\text{wt \%} = [\text{nylon 6 (g)}/(\text{HCOOH (g)} + \text{Nylon 6 (g)})] \times 100\%$ .

<sup>c</sup> The time required to appear precipitate.

metal chelate solution was at a higher temperature, it required much more time to form a precipitate, but the amount of precipitate was the same as with a lower temperature system.

#### Effects of Kinds of Metal Salts on the Formation of Precipitates

The concentration of metal salt was fixed at 20.0 wt % of nylon 6–formic acid solution and precipitate formation occurred in the sequence of CoCl<sub>2</sub> first, then NiCl<sub>2</sub>, but no precipitate occurred for CuCl<sub>2</sub>. When low-molecular-weight nylon 4 was used in nylon 4–formic acid metal chelate solution, precipitate formation occurred in the sequence of CoCl<sub>2</sub> first, CuCl<sub>2</sub> second, and NiCl<sub>2</sub> last. The time required for precipitation to occur decreased as the quantity

**Table VIII Effect of Metal Salts on the Time Required for Precipitate to Appear in Polyamide–Metal Salts–HCOOH Solution**

Polymer	Metal Salts	wt % <sup>a</sup>	Time <sup>b</sup>
Nylon 6 <sup>c</sup>	CoCl <sub>2</sub>	20.0	6 h
	NiCl <sub>2</sub>	20.0	18 h
	CuCl <sub>2</sub>	20.0	— (no precipitate)
Nylon 4 <sup>d</sup>	CoCl <sub>2</sub>	20.0	5/3 h
	CuCl <sub>2</sub>	20.0	19 h
	NiCl <sub>2</sub>	20.0	29 h
Nylon 4 <sup>d</sup>	CoCl <sub>2</sub>	40.0	5 min
	CuCl <sub>2</sub>	40.0	80 min
	NiCl <sub>2</sub>	40.0	200 min

<sup>a</sup> Weight percent of metal salt based on polyamide weight.

<sup>b</sup> Time required for precipitate to appear.

<sup>c</sup>  $M_w$  of nylon 6 =  $1.5 \times 10^4$ .

<sup>d</sup>  $M_w$  of nylon 4 =  $2.6 \times 10^2$ .

of metal salt increased in polyamide–formic acid solution, as shown in Table VIII.

#### Effects of the Molecular Weight of Polyamide on the Formation of Precipitate

The molecular weight of polyamide was found to be an important factor in the formation of precipitate. Precipitation conditions for polyamide–formic acid metal chelate solution with polyamide of lower molecular weight after addition of metal salts are summarized in Table VIII. It seems that the higher the molecular weight of polyamide the longer the time required for the precipitate to appear. Therefore, nylon 4 samples with different molecular weights were used to examine the effect. As shown in Table IX, no precipitate formed when the molecular weight of nylon 4 was greater than  $1.8 \times 10^4$ .

#### Effects of Solvents Used to Dissolve Metal Salt on the Formation of Precipitate

In the preparation of polyamide metal chelate solution, the rate of formation of precipitate was different when metal salts were dissolved in either water or formic acid (90%). As demonstrated in Table X, in preparing nylon 6/NiCl<sub>2</sub>/HCOOH chelate solution, the precipitate formation required 5 days

**Table IX Effect of Molecular Weight of Nylon 4 on the Precipitate in Nylon 4/NiCl<sub>2</sub>/HCOOH Solution**

$M_w$ of Nylon 4	NiCl <sub>2</sub> , wt %	Solution
$1.8 \times 10^4$	20.0	Precipitate
$4.0 \times 10^4$	20.0	No precipitate
$8.0 \times 10^4$	20.0	No precipitate

**Table X Effect of Solvent on the Time Required for Precipitate to Appear in Nylon 6/NiCl<sub>2</sub>/HCOOH Solution**

Run No.	Nylon 6 (g)	NiCl <sub>2</sub> /Solvent (g)/(g)	HCOOH (g)	wt % <sup>a</sup>	Precipitate (g)	Time <sup>b</sup> (h)
1.	5.0	10.5/10.0 H <sub>2</sub> O	35.0	12.5	0.63	120
2.	5.0	10.5/20.4 HCOOH	14.6	12.5	1.13	48

<sup>a</sup> wt % = nylon 6 (g)/[HCOOH (g) + Nylon 6 (g)] × 100%.

<sup>b</sup> Time required for precipitate to appear.

when NiCl<sub>2</sub>/H<sub>2</sub>O solution was used. On the other hand, it took only 2 days to form precipitate when NiCl<sub>2</sub>-formic acid was used, and much more precipitate was formed.

### Instrumental Analysis of Precipitate

#### Melting Point Analysis

When nylon 6/NiCl<sub>2</sub>/HCOOH precipitate was heated at 280°C, significant discoloration occurred, indicating possible degradation. The melting point of pure nylon 6 was 256°C. This indicates that the structure of precipitate was different from that of the parent polymer. Similar phenomena were observed for the nylon 6/CoCl<sub>2</sub>/HCOOH precipitates ( $T_d = 320^\circ\text{C}$ ).

#### UV-Visible Spectra Observations

The color of nylon 6/NiCl<sub>2</sub>/HCOOH precipitate was light green. Upon immersion in distilled water, the precipitate was destroyed, a white powder formed, and the aqueous solution changed to light green. The melting point and infrared spectra of this white powder were the same as that of nylon 6, indicating the polymer was regenerated. The UV-visible absorption spectrum of the light green aqueous solution after the white powder had been filtered out are given in Table XI. The presence of absorption wavelengths at 204.0, 209.0, 393.0, and 721.0

**Table XI Absorbance Wavelength of Precipitate Dissolved in H<sub>2</sub>O<sup>a</sup>**

Sample	Absorption Wavelength (nm)
HCOOH/H <sub>2</sub> O	204.0, 209.0
NiCl <sub>2</sub> /H <sub>2</sub> O	393.0, 721.0
Precipitate/H <sub>2</sub> O	204.0, 209.0, 393.0, 721.0

<sup>a</sup> Precipitate appears in nylon 6/NiCl<sub>2</sub>/HCOOH solution.

nm indicate that the light green aqueous solution contained HCOOH and NiCl<sub>2</sub>. Therefore, the precipitate was composed of nylon 6, NiCl<sub>2</sub>, and HCOOH. Similar results were observed for nylon 4 (or nylon 6, 6)/NiCl<sub>2</sub>/HCOOH precipitates.

#### IR Analysis

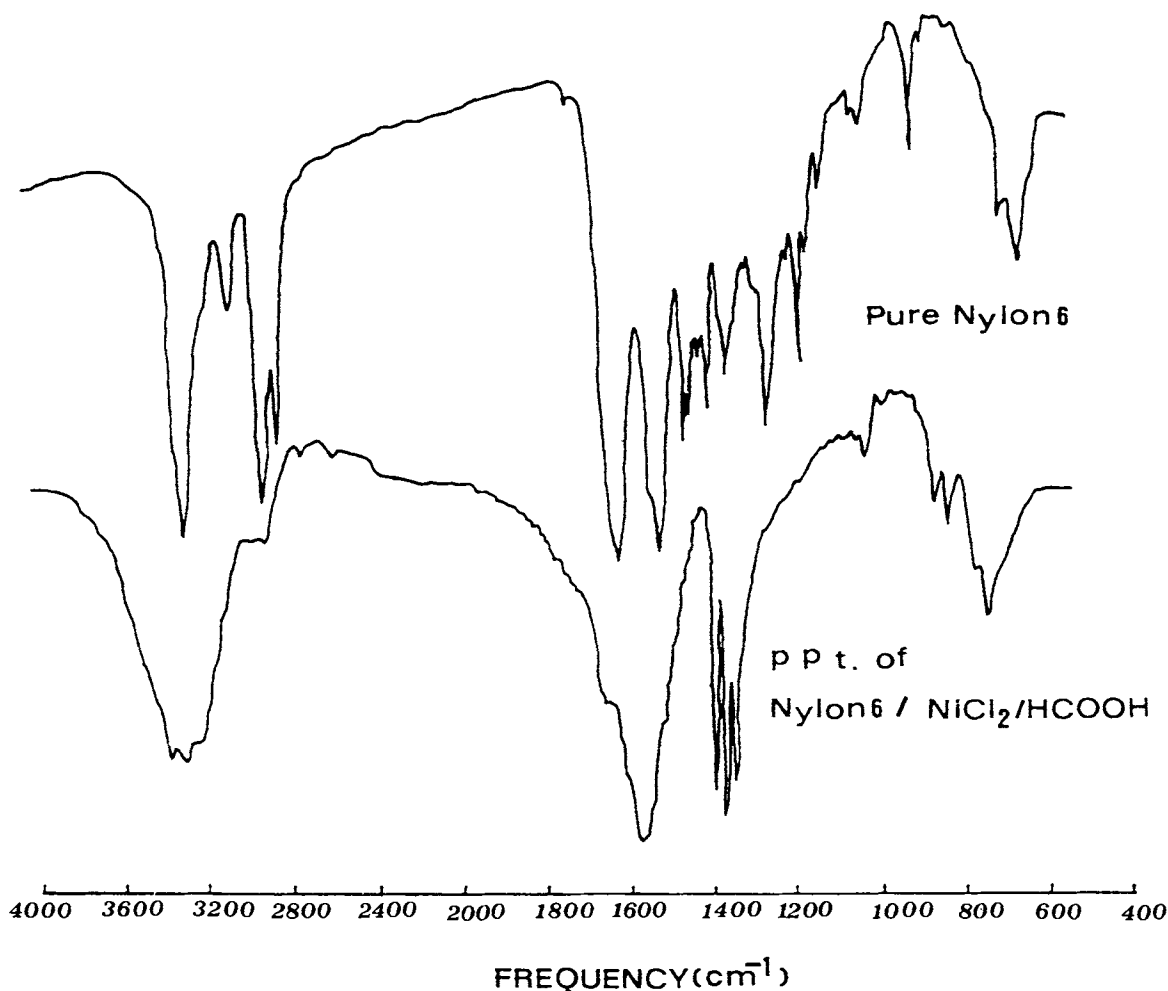
The IR spectrum of nylon 6 is shown in Figure 1. Characteristic absorption peaks of nylon 6 appear at 3305 cm<sup>-1</sup> (N-H stretching), 1640 cm<sup>-1</sup> (amide carbonyl group C=O stretching band) and 1554 cm<sup>-1</sup> (C-N stretching). The precipitate from nylon 6/NiCl<sub>2</sub>/HCOOH solution has IR absorption peaks at 3370 cm<sup>-1</sup>, 3270 cm<sup>-1</sup>, 1560 cm<sup>-1</sup>, and 1300–1400 cm<sup>-1</sup>, as shown in Figure 1. The absorption peak at 3305 cm<sup>-1</sup> due to N-H stretching of nylon 6 was affected by the formation of hydrogen bonding of HCOOH with nylon 6 and was shifted to lower frequency, 3270 cm<sup>-1</sup>, since the energy required for N-H stretching decreases.<sup>8</sup> A shoulder at 3370 cm<sup>-1</sup> is probably caused by the OH stretching band of HCOOH. The peak responsible for the amide C=O stretching band at 1640 cm<sup>-1</sup> almost disappeared with only a shoulder left, while a strong and broad absorption peak appeared at 1560 cm<sup>-1</sup> due to the COO<sup>-</sup> stretching of ionic bonding for HCOOH and Ni<sup>2+</sup>. Three absorption peaks between 1300 and 1420 cm<sup>-1</sup> are probably due to the COO<sup>-</sup> stretching and symmetrical vibrations, which are affected by the formation of ionic bonding of HCOOH and Ni<sup>2+</sup>.

The above result suggests that nylon 6 and HCOOH are held by hydrogen bonding, while HCOOH and metal ions (Ni<sup>2+</sup>) form ionic bonding. It is apparent from the UV-visible and IR spectra that nylon, HCOOH, and metal salt constitute the precipitate.

#### Proposed Structure of Precipitate

Ahoroni<sup>6,7</sup> reported the formation of highly crystalline adducts of polyamides with diacids, but in





**Figure 1** IR absorption spectra of nylon 6 and the precipitate of nylon 6/ $\text{NiCl}_2$ / $\text{HCOOH}$  solution.

no case was a crystalline adduct formed from polyamide with monoacid. Formation is associated with an approximate equivalence between the lengths of the extended diacids and the repeat unit of the polymeric chain. The interaction between the polyamides and diacids appears to be by means of hydrogen bonds. In this study precipitate was still formed although polyamide was dissolved in monoacid-formic acid. Therefore, metal salt plays a very important role here. The metal ions coordinated with formic acid. The anion of metal salt is considered as a bridging atom to form the activated complex, and make formic acid act as diacid. According to the instrumental analysis results and Aharoni's papers, a proposed structure for nylon 6/ $\text{NiCl}_2$ / $\text{HCOOH}$  precipitate is shown in Figure 2. The interaction among the polyamide, formic acid, and metal salt appears to be by means of hydrogen bonds and ionic

bonds. Therefore, the precipitate formed only in cases where there was a reasonable match between the activated complex and the polymer repeat unit. This indicates that once the precipitates are formed and precipitate out of solution, most of the activated complex lies parallel to the polymer chain in the precipitate, with four formic acid molecules forming four hydrogen bonds with two consecutive amide groups in each of two adjacent polymer chains.

The proposed structure of precipitate can be supported from the experimental results listed in Tables VII and X. As shown in Table VII, the greater the amount of formic acid added in the metal chelate solution, the less amount of precipitate was formed. From the viewpoint of collision theory, it is not easy for polyamide, metal salt, and formic acid to form precipitate in a large volume at the same time. Furthermore, the higher the metal chelate solution

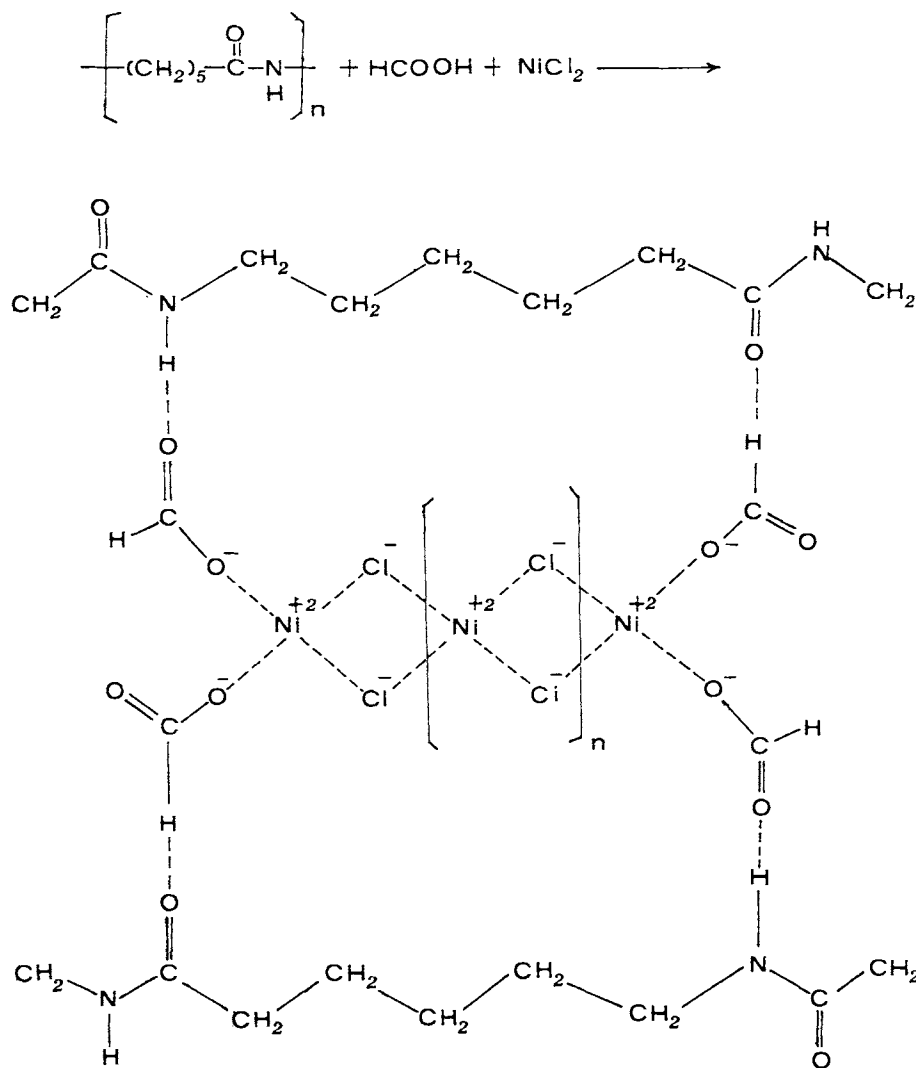


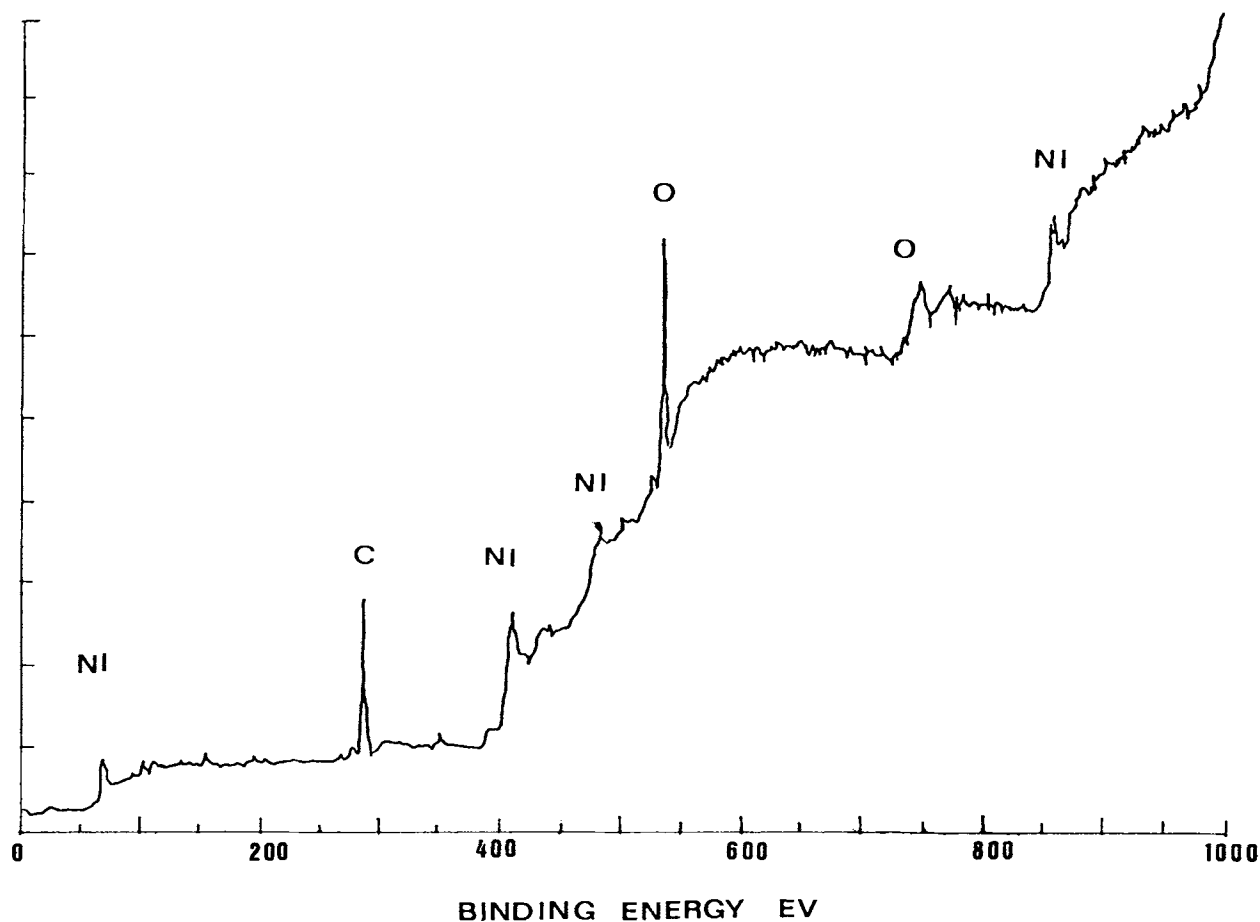
Figure 2 Proposed structure of precipitate of nylon 6/NiCl<sub>2</sub>/HCOOH solution.

temperature was heated, the longer the time required to form precipitate. Because the hydrogen bonding of precipitate was destroyed at higher temperature, it was more difficult to form precipitate and required much more time.

Water is a polar solvent and is capable of solvating metal salts. Water is also a good hydrogen bonding donor and acceptor that can form strong hydrogen bonding with both the amide bond and formic acid. These factors lead to destruction of the precipitate. When water was added, the precipitate dissociated into nylon, HCOOH, and NiCl<sub>2</sub>. This might be the reason the formation of precipitate is more difficult and the quantity of precipitate becomes less when NiCl<sub>2</sub> is dissolved in water, as shown in Table X.

#### Analysis of the Surface Substance on Metallized Nylon 4/CuCl<sub>2</sub>/NiCl<sub>2</sub> Complex Metal Chelate Films with Different Molecular Weight

When molecular weights of nylon 4 higher than  $1.8 \times 10^4$ , NiCl<sub>2</sub>, or/and CuCl<sub>2</sub> were used in the nylon 4-formic acid solution, no precipitate was formed. Since the reduction potential of Cu<sup>2+</sup> was higher than Ni<sup>2+</sup>, 6 Cu<sup>2+</sup> was easier to reduce to metal than Ni<sup>2+</sup>. Therefore, when nylon 4/CuCl<sub>2</sub>/NiCl<sub>2</sub> complex metal chelate films were reduced by aqueous NaBH<sub>4</sub> solution, the surface of the reduced films was metallic Cu. This result seems to be contrary to our previous report.<sup>2</sup> It was reported that nylon 4/CuCl<sub>2</sub>/NiCl<sub>2</sub> complex metal chelate films were reduced to metallic Ni on the film surface. These



**Figure 3** ESCA spectrum (wide scan) of nylon 4 (low  $M_w$ )/ $\text{CuCl}_2$ / $\text{NiCl}_2$  complex metal chelate film after  $\text{NaBH}_4$  aqueous solution treatment.

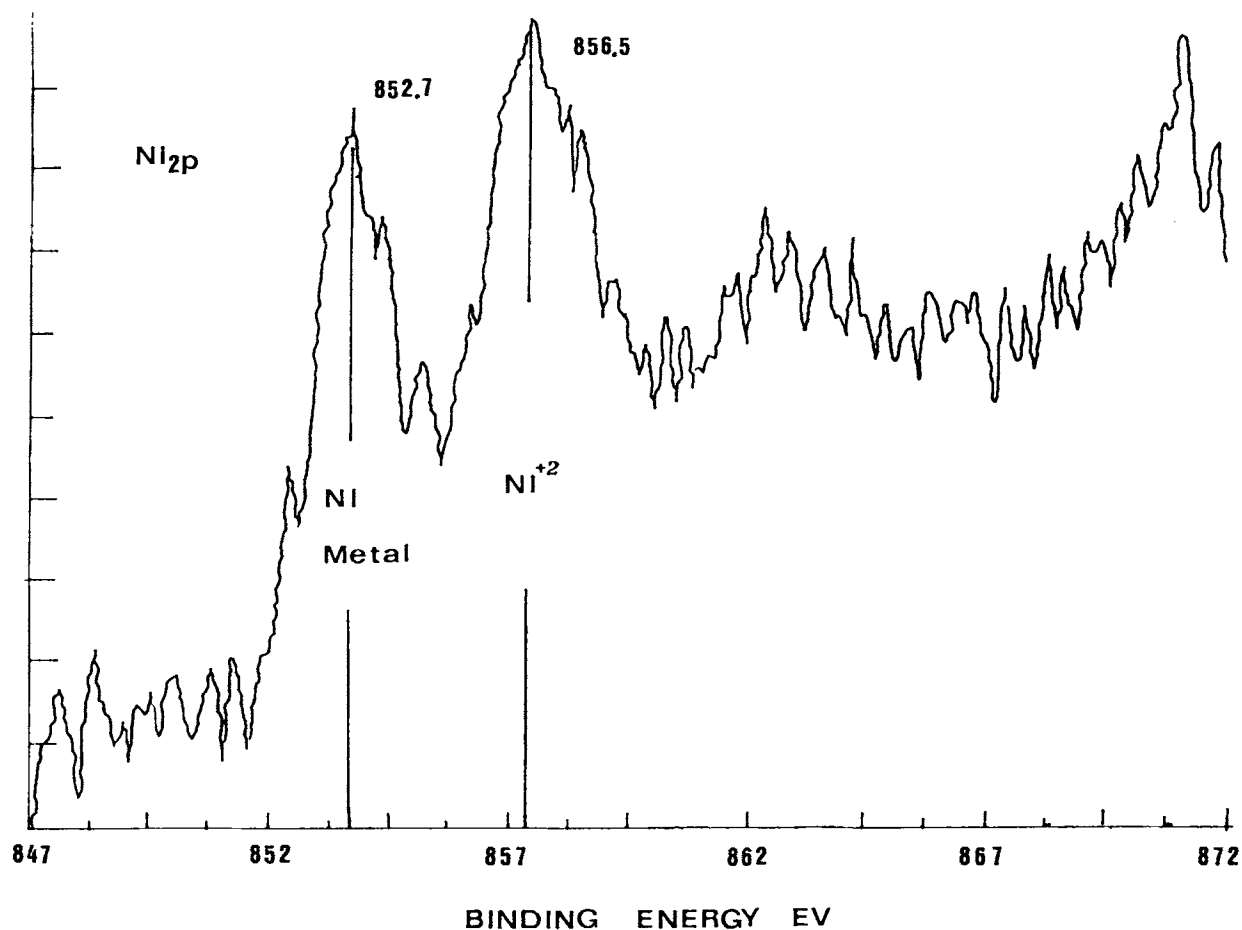
different results were dependent on the molecular weight of nylon 4. It was noticed that when  $\text{CuCl}_2$ ,  $\text{NiCl}_2$ , or  $\text{CoCl}_2$  were in formic acid solution of low-molecular-weight nylon 4, precipitation occurred in the sequence of  $\text{CoCl}_2$  first,  $\text{CuCl}_2$  second, and  $\text{NiCl}_2$  last, as demonstrated in Table VIII. This difference in precipitation rates caused differential precipitate formation when mixed metal salts were utilized with low-molecular-weight nylon 4. Thus, when a mixture of  $\text{CuCl}_2$  and  $\text{NiCl}_2$  was used to prepare complex metal chelate film, the precipitate was formed almost entirely from  $\text{CuCl}_2$  in the nylon 4/ $\text{CuCl}_2$ / $\text{NiCl}_2$  chelate solution. Hence most of the film formed by casting the clear upper chelate solution was composed of nylon 4- $\text{Ni}^{2+}$  chelate. Therefore, more  $\text{NiCl}_2$  could be reduced to metallic Ni on the surface of film, as shown in Figures 3 and 4. From these results the molecular weight of nylon 4 plays a very important role on the conducting surface metallic

substance of reduced nylon 4 complex metal chelate film.

## CONCLUSION

Some conclusions might be drawn from the preceding results and discussions.

1. When the polyamide complex metal chelate films were treated with reducing agents, metallized films with excellent electrical conductivity were obtained. When compared with the polyamide single metal chelate metallized films, these films showed little difference, as shown in Table XII.
2. The precipitate consists of polyamide, formic acid, and metal salts through hydrogen bonding and ionic bonding, as indicated by the UV-visible and IR spectra.



**Figure 4** ESCA spectrum ( $\text{Ni}_{2p}$ ) of nylon 4 (low  $M_w$ )/ $\text{CuCl}_2$ / $\text{NiCl}_2$  complex metal chelate film after  $\text{NaBH}_4$  aqueous solution treatment.

3. Factors that affected the conducting surface metallic substance of reduced complex metal chelate films.
  - a. When using polyamide with lower molecular weight ( $M_w = 1.8 \times 10^4$ ) as base materials,

**Table XII** Surface Resistivities of Polyamide Complex Metal Chelate and Single Metal Chelate Films Reduced by  $\text{NaBH}_4$  Aqueous Solution

Sample	Surface Resistivity ( $\Omega/\text{cm}^2$ )
Nylon 4/ $\text{CuCl}_2$ / $\text{NiCl}_2$	$1.0 \times 10^1$
Nylon 6/ $\text{CuCl}_2$ / $\text{NiCl}_2$	$3.5 \times 10^2$
Nylon 6/ $\text{CuCl}_2$	$2.5 \times 10^1$
Nylon 6/ $\text{NiCl}_2$	$1.5 \times 10^2$
Nylon 4/ $\text{CuCl}_2$	$2.0 \times 10^1$
Nylon 4/ $\text{NiCl}_2$	$8.0 \times 10^2$

- one metal salt formed precipitate easily in polyamide complex metal chelate solution; then the other metal salt could be reduced on the surfaces of films as conductive metallic layers.
  - b. When using polyamide with higher molecular weight as base materials, precipitate did not occur easily in polyamide-formic acid solution for most of the metal salts. The amount of metallized particles on the surfaces of films was influenced by the concentrations of mixed salts. When the concentrations of complex metal salts were low, the metal salt with the higher concentration was preferentially reduced to metal on the surface of film. When the concentrations of complex metal salts were high, the metal salt with higher reduction potential was reduced to metal on the surface of film.

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## REFERENCES

1. C. C. Yen, T. C. Chang, and H. Kakinoki, *J. Appl. Polym. Sci.*, **40**, 53-66 (1990).
2. C. C. Yen, C. J. Huang, and T. C. Chang, *J. Appl. Polym. Sci.*, **42**, 439-451 (1991).
3. C. J. Huang, C. C. Yen, and T. C. Chang, *J. Appl. Polym. Sci.*, **42**, 2237-2245 (1991).
4. C. J. Huang, C. C. Yen, and T. C. Chang, *J. Appl. Polym. Sci.*, **42**, 2267-2277 (1991).
5. Y. Morishima, K. Fujisawa, and S. Nozakura, *J. Polym. Sci. Polym. Lett. Ed.*, **16**, 141 (1978).
6. S. M. Aharoni, *J. Polym. Sci. Polym. Phys. Ed.*, **19**, 1827-1836 (1981).
7. S. M. Aharoni, and E. Wasserman, *Macromolecules*, **15**, 20-25 (1982).
8. D. J. Skrovanek, S. E. Howe, P. C. Painter, and M. M. Coleman, *Macromolecules*, **18**, 1676-1683 (1985).

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