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

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SYNPOSIS

A new type of polyamide–imides (PAI) was synthesized by direct polycondensation. A series of polyamide–imide metal chelate films was prepared by the transition-metal salts (AgNO$_3$, CuCl$_2$, NiCl$_2$, and CoCl$_2$) mixed with the polyamide–imides in NMP solution. These polyamide–imide metal chelate films were reduced by various reducing agents, and the reduced films exhibited low surface resistivity around 10^0–10^1 Ω/cm^2. The surfaces of these conductive films were proved to be metallized by means of X-ray analysis. The metal adhered on the film was believed to be responsible for the improvement of electrical conductivity. The effects of kinds and concentrations of metal salts, kinds and concentrations of reducing agents, and reduction time on the conductivity of metallized films were investigated. The IR spectra and SEM observations of unreduced and reduced polymer chelate films were also studied.

INTRODUCTION

In the previous papers of this series,[1-3] a novel method was introduced by which metallized polymer films were readily prepared from poly(vinyl alcohol) (PVA), polyacrylonitrile (PAN), and polyamide. These polymer metal chelate films exhibited very low surface resistivity when reduced by various reducing agents or heat treatment. The surfaces of these reduced polymer chelate films were proved to be metallized by means of X-ray and ESCA analysis. These metallized films were very stable in air for a long time.

In the newest of this series,[4] another novel reduction method, retroplating out, for preparing metallized film was reported. PVA, polyamide, polyacrylamide (PAAm), and polyurethane (PU) metal chelate films were reduced by wetted metal plates (or metal powders) whose ionization tendencies were greater than that of the metal of these polymer metal chelate films. These reduced films showed excellent conductivity and long-term stability.

In recent years, polyimides have been accepted and recognized as important thermally stable polymers.[5,6] Aromatic polyimides have been generally recognized as high-performance polymers because of their outstanding thermal stability. However, their utilization is greatly restricted by their poor handling and processing characteristics. This is due to a number of factors: (a) the high glass transition temperature (t_g) of the polyimides makes molding processes troublesome; (b) since polyimides are insoluble in most commercial solvents, solution processing is also impossible; and (c) the prepolymer of polyimides, i.e., polyamic acid, is very corrosive, and, hence, its handling/processing is difficult and requires a special type alloy. To overcome these disadvantages, polyester–imides and polyamide–imides were developed as alternative materials[7-10] without much deterioration in thermal properties and provided better processability.

Direct polycondensation has attracted considerable attention due to its simplicity and efficiency as a synthetic method. Therefore, the purpose of this investigation is to synthesize a new type of poly-

amide–imide by the direct polycondensation of a di-carboxylic acid containing an internal imide group with aromatic diamines by means of triphenyl phosphite (TPP) in N-methyl-2-pyrrolidone (NMP)–pyridine solution containing lithium chloride (LiCl). Use of the direct polycondensation reaction to synthesize polyamide and polyesteramides has been widely utilized and reported by Yamazaki et al.,[11,12] Higashi et al.,[13,14] and one of the authors.[15,16]

One of the major applications of polyimides is for the fabrication of laminated copper/polyimide structures used as electrical connectors, I/O cables, or flexible printed circuit (FPC). Use of a laminate complicates the process since an adhesive is required to adhere copper foil to the polyimide film. To develop easily processable metallized polymer films, a series of polyamide–imide metal chelate films were prepared by transition-metal salts mixed with polyamide–imides NMP solution. Polyamide–imide metal chelate films can be easily processed and reduced to metallized polyamide–imide films by using reducing agents. Therefore, the other purpose of this investigation was to prepare metallized polyamide–imide film. The surfaces of these conductive films were proved to be metallized by means of X-ray analysis. The effects of kinds and concentrations of metal salts, kinds and concentrations of reducing agents, and reduction time on the conductivity of metallized films were also studied.

EXPERIMENTAL

Monomers Synthesis

N-(p-carboxyphenyl)trimellitimide **1**), N-(m-carboxyphenyl)trimellitimide **2**) and N-(carboxymethyl)trimellitimide **3**) were prepared by the condensation of trimellitic anhydride (TMA) with p-aminobenzoic acid, m-aminobenzoic acid, and glycine, respectively, in NMP (N-methyl-2-pyrrolidone) by the method described in the literature.[17]

Polymer Synthesis

The direct polycondensation polymerization was conducted under a nitrogen atmosphere. Dicarboxylic acid containing an internal imide group on the backbone (10 mmol) was added to a four-necked flask (100 mL) equipped with a reflux condenser, a nitrogen inlet tube, a pressure-equalized dropping funnel, and a thermometer. Forty milliliters NMP, 16 mL pyridine, 20 mmol TPP (triphenyl phosphite), and 2.0 g LiCl were charged into the flask

with stirring. After stirring 10 min, aromatic diamine (10 mmol) was added and then heated at 100°C for 3 h. After cooling, the reaction mixture was poured into distilled water, and the precipitated polymer was separated by filtration, ground to a powder, washed well with refluxing methanol for 2 h, and finally dried at 80°C for 24 h. A yellow polymer powder was obtained.

Preparation of Polyamide–imide Metal Chelate Films

Metal salts dissolved in NMP were mixed with polyamide–imide (0.5 g)–NMP (5 g) solutions to make viscous polyamide–imide metal chelate solutions. The resulting viscous solutions were cast on glass plates and dried at 120°C for 30 min. These films were peeled from the plates and then cut to a size of 1 × 3 cm for subsequent use.

Reduction of Polyamide–imide Metal Chelate Films

The test pieces of polyamide–imide chelate films were reduced by sodium borohydride in aqueous solution.[2] The reduction conditions are listed in Table II.

The procedures to reduce PAI/AgNO$_3$ chelate films by metal powders (such as Fe, Mg, and Zn) in dilute protonic acid solution, or sodium in ethanol, were similar to those of the first paper of this series.[1]

Another reduction method, "retroplating out," as described in our previous paper, was used.[4] The PAI/AgNO$_3$ chelate films were put onto the surface of wetted iron plate (or iron powders), which was preheated to 100°C for about 2 min.

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 paper.[18]

Instrument Analysis

Visible and UV absorption spectral data of polyamide–imide metal chelate films were obtained by using a Jasco model 7800 spectrophotometer. IR spectra of polyamide–imide metal chelate films ranging from 4000 to 400 cm^{-1} were obtained using a Perkin-Elmer 710B spectrophotometer.

The tensile strengths of polyamide-imide films were measured by the Hung Ta microcomputer uni-

versal tester at ambient. The tensile strengths of samples in their dry states were measured according to ASTM D638 method.[19]

The thermogravimetric analyses (TGA) were obtained on a DuPont 2100 at a heating rate 10°C/ min under nitrogen atmosphere. X-ray diffraction patterns of metallized polyamide–imide films were measured by a diffractometer (Shimadzu XD-3A diffractometer) using CuK_α radiation generated at 30 KV and 20 mA.
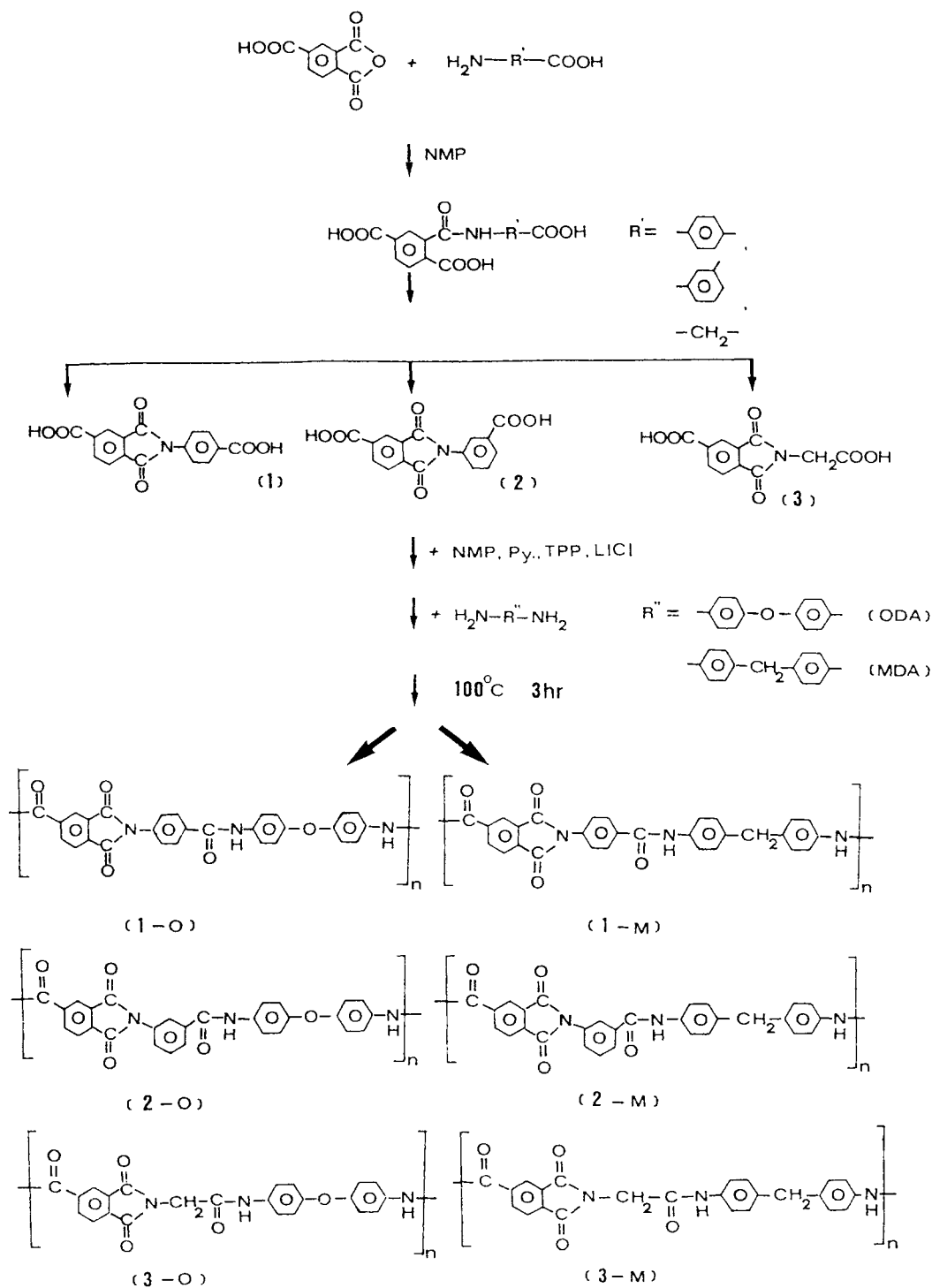
Scheme 1

Table I Properties of the Polyamide-imide Films[d]

Polymer	Yield (%)	η_{inh}[a]	Tensile Strength (kg/cm²)[b]	Elongation (%)	T_d (°C)[c]
1—O	99	1.27	815.2	7.4	523
1—M	99	2.26	810.8	7.5	470
2—O	99	1.14	731.9	8.0	488
2—M	99	2.70	709.9	6.8	483
3—O	99	1.05	768.5	6.9	416
3—M	99	0.83	672.8	6.5	430

[a] Measured at a concentration of 0.5 g/dL in NMP solution at 30°C.

[b] Drawing rate: 5.0 mm/min; drawing temperature = room temperature; load cell: 10 kg.

[c] T_d: Temperature of start of decomposition (10% weight loss in N_2); thermogravimetric analyses conducted at a heating rate of 10°C/min in nitrogen.

[d] All films were flexible.

Morphology of the unreduced and reduced poly-amide–imide metal chelate films surface were observed under a Hitachi model S-570 scanning electron microscope (SEM). SEM specimens were prepared by evaporating gold onto the films surface after drying under vacuum.

RESULTS AND DISCUSSION

Polymer Synthesis

The general reaction scheme and the structure of the various polyamide–imides (PAI) are given in Scheme I. A series of polyamide–imides were prepared by the direct polycondensation of a dicarboxylic acid containing an internal imide group with aromatic diamines by means of triphenyl phosphite (TPP) in NMP–pyridine solution containing lithium chloride. The IR spectrum of the dicarboxylic acid containing an internal imide group showed disappearance of the strong and broad absorption near 3400 to 2400 cm⁻¹ due to the acid group and appearance of the absorption near 3290 and 1640 cm⁻¹ due to the N—H stretching and the C=O stretching of amide group of polyamide–imides. The IR spectra of polyamide–imides were consistent with those for the expected structures. The characteristic IR bands of the polymer are observed near 1770 and 1720 cm⁻¹ due to symmetrical and asymmetrical carbonyl stretching of imides, and another peak is observed due to the C—N imide stretching vibration band at 1370 cm⁻¹.

Properties of Polymers

As shown in Table I, the new type of polyamide–imides had a high inherent viscosity in the range of

0.83–2.70 dL/g. All of polyamide–imides were obtained in high yield, and all of the polyamide–imide films exhibited excellent flexibility. The tested polyamide–imide films demonstrate high tensile strengths from 672 to 815 kg/cm², at elongations of 6.5–8.0%. As shown in Table I, thermogravimetry conducted in an atmosphere of nitrogen indicates that polyamide–imides have a 10% loss of weight in the range of 416–523°C. The temperature at which
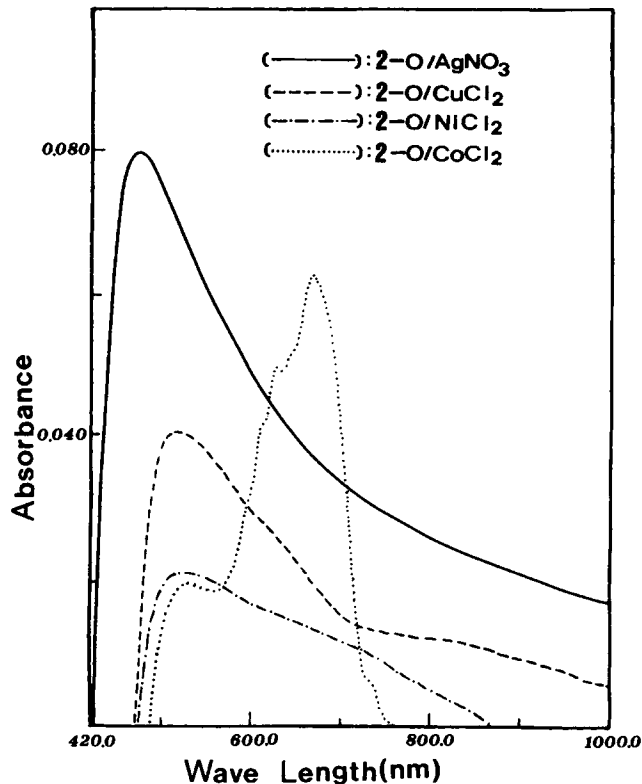

Figure 1 Visible and UV absorption spectra of polyamide–imide metal chelate films.
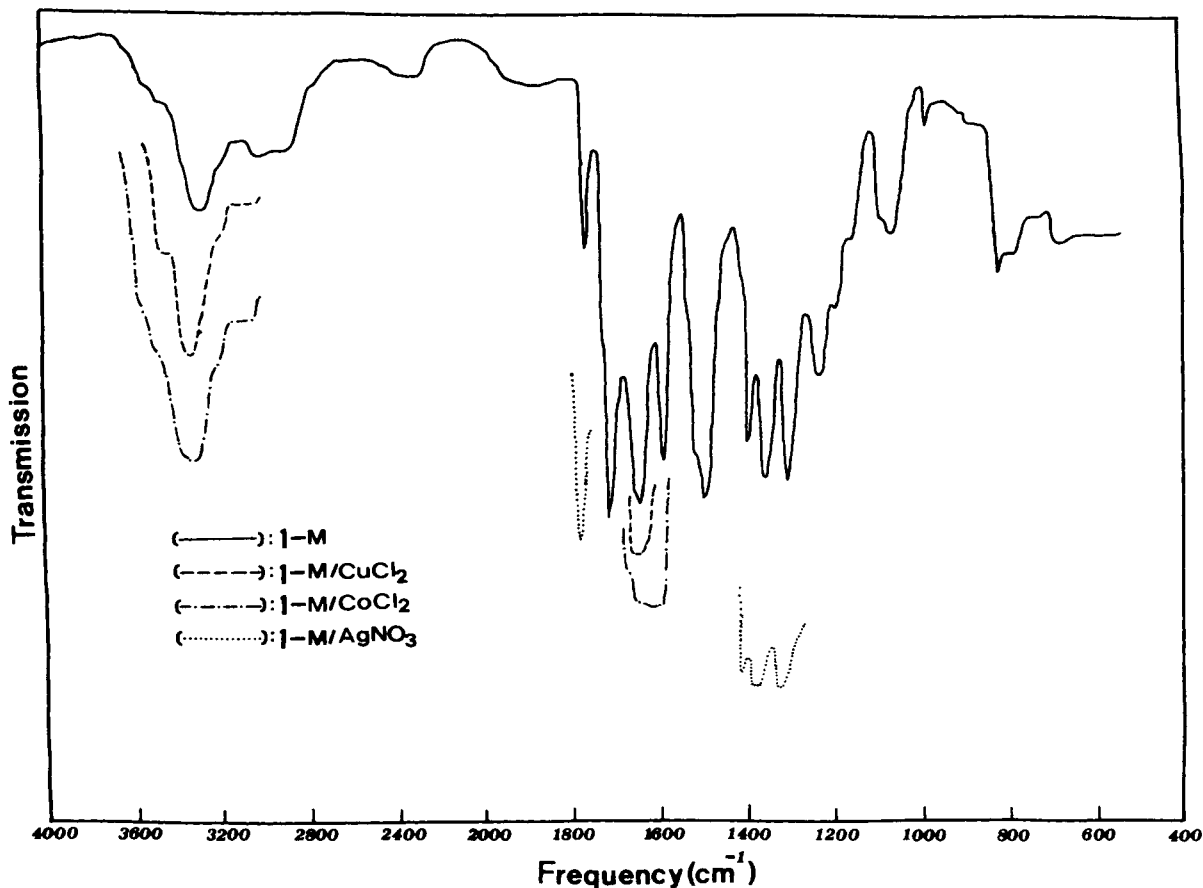
Figure 2   Infrared absorption spectra of polyamide–imide metal chelate films.

there is a 10% loss of weight clearly indicates the beginning of significant thermal degradation.[20] It is demonstrated that these polymers have good mechanical properties and thermal stabilities.

Visible and UV Spectra Observations

In this study, the formation of polyamide–imide metal chelates can be identified from UV-visible spectra by a similar method to that described in the previous papers of this series.[1-3] When $AgNO_3$/NMP solution was added to the PAI/NMP solution and constantly stirred for several hours, the color of this mixed solution changed from brown to black. The NMP black solution of PAI/$AgNO_3$ was cast and dried to a film, and the film exhibited a maximum absorption band at 480 nm (PAI film as reference), as shown in Figure 1(a). Similarly, as shown in Figure 1(b)-(d), the UV-visible spectral band of PA1/$CuCl_2$, PAI/$NiCl_2$, and PAI/$CoCl_2$ appear at 523, 527, and 668 nm, respectively. These results indicate the formation of polyamide–imide

metal chelates from metal ion coordinated with the amide group or imide group of polyamide–imides.

IR Analysis

The UV-visible spectral observations mentioned above indicate the formation of polyamide–imide metal chelates, but cannot provide information about which functional groups of polyamide–imides coordinate with the metal ion. To identify whether the metal ion coordinates with the amide or imide group of polyamide–imides, IR spectra of polyamide–imide metal chelate films were measured.

The IR spectra of PAI/$CuCl_2$, PAI/$CoCl_2$, and PAI/$AgNO_3$ chelate films are shown in Figure 2. For PAI/$CuCl_2$ and PAI/$CoCl_2$ chelate film, a peak due to the NH stretching band at 3290 cm^{-1} shifts to the longer frequency side, and another peak due to the amide carbonyl group C=O stretching band at 1640 cm^{-1} shifts slightly to the longer frequency side and gets broader for PAI/$CuCl_2$ chelate film, but shifts to the shorter frequency side and gets broader for PAI/$CoCl_2$ chelate film. The peaks due

Table II   Effect of the Amount of Silver Nitrate on the Conductivity of Various PAI/AgNO₃ Chelate Films Reduced by Sodium Borohydride Aqueous Solution

Film	F	Wt %[a]	Property[b]	Conc (wt %)	Temp (°C)	Time (min)	Surface Resistivity (Ω/cm^2)
1—M—Ag⁺	1.0	35.92	+	1.0–4.0	50–85	3	$> 2 \times 10^7$
	1.5	53.88	+	2.5	65	3	2.0×10^2
	2.0	71.84	+	2.5	65	3	1.0×10^1
2—M—Ag⁺	1.0	35.92	+	1.0–4.0	50–85	3	$> 2 \times 10^7$
	1.5	53.88	+	1.0–4.0	50–85	3	$> 2 \times 10^7$
	2.0	71.84	+	1.0–4.0	50–85	3	$> 2 \times 10^7$
	2.5	89.80	+	3.5	85	3	1.0×10^3
	3.0	107.76	+	3.5	85	3	2.5×10^1
2—O—Ag⁺	1.0	35.76	+	1.0–4.0	50–85	3	$> 2 \times 10^7$
	1.5	53.64	+	3.5	85	3	1.0×10^5
	2.0	71.52	+	3.5	85	3	1.0×10^3
	2.5	89.40	+	3.5	85	3	5.0×10^1
1—O—Ag⁺	1.0	35.76	+	1.0–4.0	50–85	3	$> 2 \times 10^7$
	1.5	53.64	−	—	—	—	—
	2.0	71.52	−	—	—	—	—

[a] Based on polyamide–imide weight.
[b] +, flexible; −, brittle.

to imide group stretching (1770, 1720, and 1370 cm⁻¹) do not shift. Thus, Cu^{2+} and Co^{2+} ions coordinate only with the amide groups and not with the imide groups of polyamide–imides.

For PAI/AgNO₃ chelate film, a peak due to the imide $C=O$ stretching band at 1770 cm⁻¹ shifts to the shorter frequency side, a peak due to the imide $C=O$ stretching vibration coupled band at 1720 cm⁻¹ shifts slightly to the longer frequency side, and an-

other peak due to the C—N imide stretching vibration band at 1370 cm⁻¹ shifts to a longer frequency and gets broader. The peaks due to amide group stretching (3290 and 1640 cm⁻¹) do not shift. Therefore, it appears that Ag⁺ ions coordinate with imide groups and not with amide groups of polyamide–imides. When AgNO₃ is mixed with a formic acid solution of aliphatic polyamide (nylons 4 and 6), the polyamide is degraded by AgNO₃; thus,

Table III   Effect of the Amount of Silver Nitrate on the Conductivity of Various PAI/AgNO₃ Chelate Films Reduced by Magnesium (Mg) Powders in Dilute Hydrochloric Acid Aqueous Solution

Film	F	Wt %[a]	Surface Resistivity (Ω/cm^2)	Reduction Time (s)
1—M—Ag⁺	1.0	35.92	1.68×10^0	20
	1.5	53.88	2.12×10^0	20
	2.0	71.84	4.50×10^0	20
2—M—Ag⁺	1.0	35.92	3.40×10^1	60
	1.5	53.88	4.10×10^0	20
	2.0	71.84	5.90×10^0	20
	2.5	89.80	1.40×10^1	20
	3.0	107.76	6.90×10^0	20
2—O—Ag⁺	1.0	35.76	5.80×10^0	120
	1.5	53.64	6.00×10^0	20
	2.0	71.52	9.00×10^0	20
	2.5	89.40	1.80×10^0	20

[a] Based on polyamide–imide weight.

Table IV   Effect of the Amount of Silver Nitrate on the Conductivity of Various PAI/AgNO₃ Chelate Films Reduced by Iron (Fe) Powders in Dilute Acetic Acid Aqueous Solution[a]

Film	F	Wt %[b]	Surface Resistivity (Ω/cm^2)
1—M—Ag⁺	1.0	35.92	$> 2 \times 10^7$
	1.5	53.88	1.36×10^1
	2.0	71.84	6.72×10^0
2—M—Ag⁺	1.0	35.92	$> 2 \times 10^7$
	1.5	53.88	1.97×10^1
	2.0	71.84	4.91×10^1
	2.5	89.80	4.30×10^1
	3.0	107.76	4.80×10^0
2—O—Ag⁺	1.0	35.76	1.48×10^1
	1.5	53.64	1.02×10^1
	2.0	71.52	9.50×10^0
	2.5	89.40	7.90×10^0
3—O—Ag⁺	1.0	41.14	3.96×10^1

[a] Iron (Fe) powders in dilute acetic acid aqueous solution temp: 60°C, reduction time: 20 s.
[b] Based on polyamide–imide weight.

formic acid solutions of polyamide/AgNO₃ cannot be cast into film. In the aromatic polyamide–imides, the Ag⁺ ions are coordinated with imide groups of polyamide–imides and the amide groups of poly-amide–imides cannot degrade; thus, the PAI/AgNO₃ formic acid solution can be cast to film and reduced to metallized film by various reducing agents.

Table V   Effect of the Amount of Silver Nitrate on the Conductivity of Various PAI/AgNO₃ Chelate Films Reduced by Wetted Fe Powders[a]

Film	F	Wt %[b]	Surface Resistivity (Ω/cm^2)
1—M—Ag⁺	1.0	35.92	$> 2 \times 10^7$
	1.5	53.88	$> 2 \times 10^7$
	2.0	71.84	$> 2 \times 10^7$
2—M—Ag⁺	1.0	35.92	4.10×10^2
	1.5	53.88	1.03×10^4
	2.0	71.84	$> 2 \times 10^7$
	2.5	89.80	7.36×10^2
	3.0	107.76	5.02×10^2
2—O—Ag⁺	1.0	35.76	$> 2 \times 10^7$
	1.5	53.64	2.79×10^4
	2.0	71.52	$> 2 \times 10^7$
	2.5	89.40	$> 2 \times 10^7$
3—O—Ag⁺	1.0	41.14	$> 2 \times 10^7$

[a] Wetted Fe powders temp: 100°C; reduction time: 2 min.
[b] Based on polyamide–imide weight.

Table VI   Effect of the Amount of Silver Nitrate on the Conductivity of Various PAI/AgNO₃ Chelate Films Reduced by Na in C₂H₅OH[a]

Film	F	Wt %[b]	Surface Resistivity (Ω/cm^2)
1—M—Ag⁺	1.0	35.92	$> 2 \times 10^7$
	1.5	53.88	$> 2 \times 10^7$
	2.0	71.84	1.30×10^2
2—M—Ag⁺	1.0	35.92	$> 2 \times 10^7$
	1.5	53.88	$> 2 \times 10^7$
	2.0	71.84	$> 2 \times 10^7$
	2.5	89.80	5.80×10^1
2—O—Ag⁺	1.0	35.76	$> 2 \times 10^7$
	1.5	53.64	$> 2 \times 10^7$
	2.0	71.52	$> 2 \times 10^7$
	2.5	89.40	1.32×10^1
3—O—Ag⁺	1.0	41.14	$> 2 \times 10^7$

[a] Two grams Na in 25 mL C₂H₅OH.
[b] Based on polyamide–imide weight.

Effect of the Amount of Silver Nitrate in Polyamide–imide Metal Chelate Films on the Conductivity of Metallized Films

As shown in Table II, when $F = 1.0$ of PAI/AgNO₃ chelate film was treated with NaBH₄ aqueous solution, it exhibited high surface resistivity ($> 2 \times 10^7$ Ω/cm^2). The surface resistivity decreases drastically with increasing F value when the film was treated with NaBH₄ aqueous solution. Therefore, suitable F values for 1—M/AgNO₃, 2—O/AgNO₃, and 2—M/AgNO₃ chelate films to prepare metallized films were 2.0, 2.5, and 3.0, respectively. When the F value of the 1—O/AgNO₃ chelate film was higher than 1.0, the film exhibits brittleness so that it is not suitable to treat with reducing agents.

As shown in Table III, the various PAI/AgNO₃ chelate films exhibited low surface resistivity around 10^0–10^1 Ω/cm^2 when these films were reduced by magnesium (Mg) powders in dilute aqueous hydro-chloric acid. Similarly, the various F values of PAI/ AgNO₃ chelate films, except $F = 1.0$ of 1—M/ AgNO₃ and 2—M/AgNO₃ films, showed excellent conductivity when these films were reduced by iron (Fe) powders in dilute aqueous acetic acid solution, as shown in Table IV. Similar results were also obtained by using zinc powders in acidic solution as reducing agents.
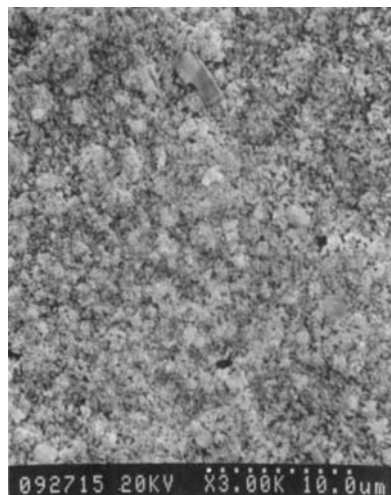
In retroplating out, as mentioned in the previous paper,[3] polymer metal chelate films were reduced by wetted metal plates or metal powders whose ionization tendencies were greater than that of the
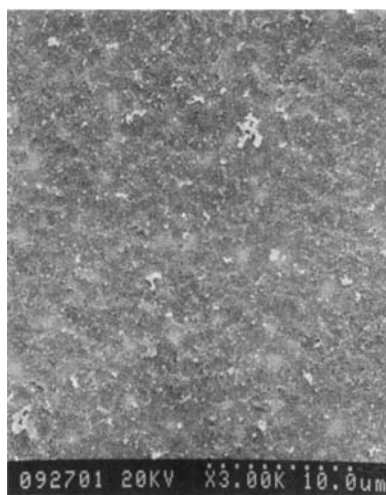
(a) F=2.5 2-M-PAI/AgNO₃
unreduced film
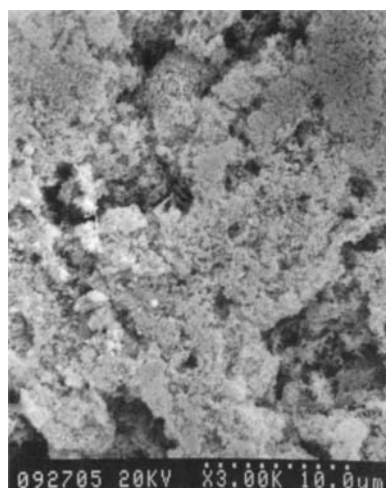
(b) F=2.5 2-M-PAI/AgNO₃ film after
NaBH₄ aqueous solution treatment

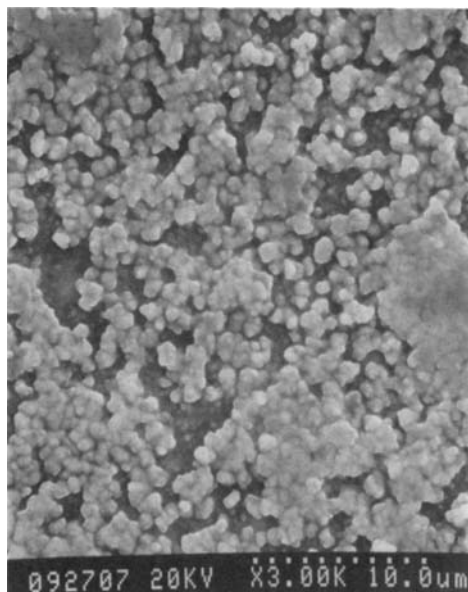(c) F=2.5 2-M-PAI/AgNO₃ film after
treatment with Mg powder in dil.
HCl

(d) F=2.5 2-M-PAI/AgNO₃ film after
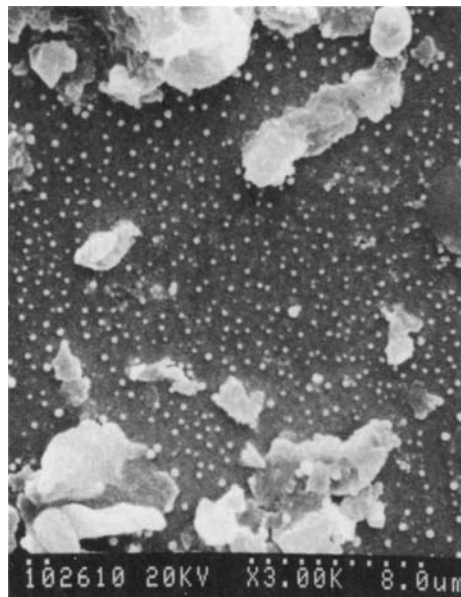treatment with Fe powder in dil.
acetic acid

metal in the polymer metal chelate films and excellent conductivity and long-term stability were obtained. However, when PAI/AgNO₃ chelate films were reduced by wetted iron plate (or iron powders), some treated films exhibited low surface resistivity and some treated films exhibited high surface resistivity, as shown in Table V. When the F values were higher than 2.0 or 2.5, all the PAI/AgNO₃ chelate films exhibited a low surface resistivity after treatment with sodium in ethanol (Table VI).

Effect of Metal Salts and Reductive Conditions on the Conductivity of Polyamide–imide Metallized Films

When various polyamide–imide metal chelate films, such as PAI/CuCl₂, PAI/NiCl₂, and PAI/CoCl₂ chelate films are reduced by NaBH₄ aqueous solution, low surface resistivities, around 10^1–10^3 Ω/cm^2, are found as shown in Table VII. In general, the PAI/CuCl₂ metallized film shows lower surface re-

(e) F=1.0 2-M-PAI/CuCl₂ film after NaBH₄ aqueous solution treatment

(f) F=1.0 2-M-PAI/AgNO₃ film after treatment with Fe powder in dil. acetic acid

Figure 3 (*Continued from the previous page*)

sistivity than do those of the PAI/NiCl₂ and PAI/CoCl₂ metallized films. Suitable reduction concentration of NaBH₄, reduction temperature, and reduction time to prepare metallized polyamide–imide films were 2.0–4.0 wt %, 50–80°C, and 1–3 min, respectively.

X-ray Analysis

To identify whether the surface of the reduced film is metallized or not, the polyamide–imide metal chelate films, after treatment with various reducing agents, were examined by X-ray diffraction. From the results of X-ray diffraction analysis, shown in Table VIII, the metallized film clearly demonstrates that the main product on the film surface was metallic silver for PAI/AgNO₃ chelate films. Similarly, for PAI/CuCl₂ films treated by NaBH₄ aqueous solution, the film surface was also reduced, to metallic copper as shown in Table IX. The formation of these metallic silver and copper surface layers were responsible for the conductivity.

Scanning Electron Microscope Observations

Scanning electron microscope (SEM) photographs display a flat surface of the unreduced polyamide–imide metal chelate films as shown in Figure 3(a). A drastic change of surface features occurs after treatment with various reducing agents. As shown in Figure 3(b)–(e), particles of metallic Ag or Cu are aggregated on the surfaces of reduced films to form a continuous distribution. Therefore, these reduced films exhibited excellent conductivity. The metal adhered to the film was believed to be responsible for the improvement of electrical conductivity. When the F value of PAI/AgNO₃ chelate film was not large enough, e.g., $F = 1.0$, for PAI/AgNO₃ films reduced by Fe powders in dilute acetic acid aqueous solution, the reduced films exhibited high surface resistivity ($> 2 \times 10^7$ Ω/cm²) due to the metallic silver being distributed on the surface of the PAI film in "islands," as shown in Figure 3(f).

CONCLUSION

Polyamide–imides are well-known thermally stable polymers. In this study, a new type of polyamide–imide was synthesized by the direct polycondensation of a dicarboxylic acid containing an internal imide group with aromatic diamines by means of triphenyl phosphite (TPP) in NMP–pyridine solution containing LiCl. Introduction of transition-

Table VII Effect of the Amount of Various Metal Salts on the Conductivity of Polyamide–imide Metallized Films[b]

Run No.	PAI	Metal Salts	F	Wt %[a]	Reductive Conditions			Surface Resistivity (Ω/cm^2)
					Conc of $NaBH_4$	Temp (°C)	Time (min)	
1	1—O	$CuCl_2 \cdot 2H_2O$	1.0	35.91	3.0	80	3	1×10^2
2		$NiCl_2 \cdot 6H_2O$	1.0	50.04	2.5	60	3	1×10^2
3		$CoCl_2 \cdot 6H_2O$	1.0	50.06	4.0	80	3	2×10^3
4	1—M	$CuCl_2 \cdot 2H_2O$	1.0	36.04	3.0	80	1	5×10^1
5		$NiCl_2 \cdot 6H_2O$	1.0	50.26	2.5	60	1	2×10^2
6		$CoCl_2 \cdot 6H_2O$	1.0	50.29	4.0	80	1	1×10^3
7	2—O	$CuCl_2 \cdot 2H_2O$	1.0	35.91	3.0	80	3	1×10^1
8		$NiCl_2 \cdot 6H_2O$	1.0	50.04	2.0	60	3	1×10^2
9		$CoCl_2 \cdot 6H_2O$	1.0	50.06	4.0	80	3	2×10^2
10	2—M	$CuCl_2 \cdot 2H_2O$	1.0	36.04	3.0	80	1	1×10^2
11		$NiCl_2 \cdot 6H_2O$	1.0	50.26	2.5	60	1	1×10^2
12		$CoCl_2 \cdot 6H_2O$	1.0	50.29	4.0	80	1	3×10^4
13	3—O	$CuCl_2 \cdot 2H_2O$	1.0	41.27	3.0	80	3	1×10^2
14		$NiCl_2 \cdot 6H_2O$	1.0	57.56	2.0	65	3	1×10^2
15		$CoCl_2 \cdot 6H_2O$	1.0	57.58	4.0	80	3	1×10^2
16	3—M	$CuCl_2 \cdot 2H_2O$	1.0	41.48	3.0	80	1	3×10^2
17		$NiCl_2 \cdot 6H_2O$	1.0	57.83	2.5	50	1	5×10^2

[a] Based on polymer weight.
[b] All films were flexible.

Table VIII Diffraction Angles (2θ) and Plane Distances (d) Corresponding to Peaks Observed in X-ray Analysis for Polyamide–imide Chelate Film Reduced by Reducing Agents

Peaks	Film A[a] Experiment		Pure Ag Reference	
	2θ	d	2θ	d
1	38.2	2.354	38.14	2.359
2	44.4	2.039	44.33	2.043
3	64.6	1.442	64.50	1.445
4	77.6	1.229	77.61	1.230

[a] Film A prepared from 2—M—Ag^{1+} ($F = 2.5$) chelate film reduced by sodium borohydride aqueous solution, magnesium powder in dilute hydrochloric acid aqueous solution, or iron powder in dilute acetic acid aqueous solution.

metal salts into the polyamide–imides provides metal chelate films. These polyamide–imide metal chelate films exhibit excellent electrical conductivity when treated with reducing agents. Moreover, these polymer films maintain satisfactory mechanical properties and thermal stability and might be useful as processable heat-resistant conductive polymers.

Table IX Diffraction Angles (2θ) and Plane Distances (d) Corresponding to Peaks Observed in X-ray Analysis for Polyamide–imide Chelate Film Reduced by Sodium Borohydride Aqueous Solution

Peaks	Film B[a] Experiment		Pure Cu Reference	
	2θ	d	2θ	d
1	43.3	2.088	43.30	2.088
2	50.2	1.816	50.43	1.808
3	74.2	1.277	74.13	1.278

[a] Film B prepared from 1—O—Cu^{2+} ($F = 1.0$) chelate film reduced by sodium borohydride aqueous solution.

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