Effect of Metal Halides on Thermal, Mechanical, and Electrical Properties of Polypyromellitimide Films*

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Synopsis

This paper describes the effect of metal halides (Co^{2+}, Sn^{2+}, and Hg^{2+}) on the properties of polyimides. Low temperature, solution polycondensation reaction of pyromellitic dianhydride and 4,4'-diaminodiphenyl ether was used for preparation of a poly(amide-acid) solution in dimethylformamide ($[\eta] = 2.0$ dL/g). Films containing 1% (w/w) of cobalt (II) chloride, tin (II) chloride, and mercury (II) chloride were prepared by solution casting of poly(amide-acid) from the DMF solution. Cyclodehydration to polyimide was done by heating the films in nitrogen atmosphere for one hour each at 100°, 200°, and 250°C. The color of the films depended on the dopant and was yellow ($HgCl_2$ or $SnCl_2$) or green ($CoCl_2$). Higher percentage weight loss was observed in doped films in nitrogen atmosphere in the temperature range of 250–400°C. No significant difference in thermal behavior of doped and undoped films was observed above 500°C. Doping reduced the tensile strength of polyimide films, maximum reduction was observed in $CoCl_2$-doped film. The electrical conductivity of polyimide films as a function of temperature and field was studied. Undoped polyimide showed ohmic behavior up to 150°C. In doped films at lower voltages Poole-Frenkel mechanism was operative, while at high voltages Richardson-Schottky's mechanism was operative. Dielectric relaxation in polyimide films was also studied.

INTRODUCTION

Considerable research effort has been made in the past to modify the properties of polyimides by incorporation of a variety of metallic dopants into the polymers. Attempts have been made to find metal complex/polyimide combinations which will offer a high temperature-resistant material with semiconductive or conductive properties.

Angelo, for the first time, briefly described the effect of addition of metal ions (in the form of coordination complexes) on the conductivity of polyimides.[1] Superior antistatic properties were reported for polyimide films loaded with LiCl or $LiNO_3$.[2] Metal-doped polyimide films with improved high temperature adhesive properties,[3,4] increased electrical and thermal conductivity,[5] excellent thermal stability,[6] and mechanical properties,[7] have been reported in literature. The potential for enhanced electrical conductivity has been demonstrated by doping with palladium complexes,[8–10] copper[11] (II)

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and lithium. Polyimide films doped with $SnCl_2$. $2H_2O$[12], Co (II) chloride, and Ni (II) chloride have been reported.[13]

Additional work in this area of metal-doped polyimides is necessary to evaluate the extent of polyimide modification by a variety of different dopants. Thermal, mechanical, and electrical properties are of major interest in such modified polyimides. In this paper we report the effect of addition of Co (II) chloride, Sn (II) chloride, and Hg (II) chloride on the properties of polypyromellitimide films.

EXPERIMENTAL

Pyromellitic dianhydride (PMDA) (Fluka) was crystallized from acetic anhydride and dried under vacuum for 24 hr. 4,4′-diaminodiphenyl ether (E) (Fluka) was vacuum dried for 24 hr. *N-N′*-dimethylformamide (DMF) (Glaxo) was used as such. $HgCl_2$, $CoCl_2.6H_2O$, and $SnCl_2.2H_2O$ (BDH) were all vacuum dried for 24 hr and stored in dessicator.

Poly(amide-acid) solution in DMF (10% w/w) was prepared by reacting 0.2 mole of diamine with 0.2 mole of PMDA in nitrogen atmosphere at 0–5°C for 5–6 hr. The intrinsic viscosity of poly(amide-acid) was determined by using Ubbelhode viscometer at 30°C and was found to be 2.0 dL/g. To the poly(amide-acid) in DMF, $CoCl_2$, $HgCl_2$, and $SnCl_2$ (1% w/w with respect to polyamide-acid) were added. The resulting homogeneous solutions were poured on glass plate, spread using doctor's blade, and dried at 60–70°C. Imidization was done by heating in an oven flushed with nitrogen for one hour each at 100, 200, and 250°C. Films were then removed from the glass plates.

A DuPont 1090 thermal analyzer having a 910 DSC module and 951 TG module was used to evaluate the thermal behavior of the films in nitrogen atmosphere. A heating rate of 10°C/min was used.

The tensile strength of polyimide films containing metallic salts was evaluated by using Instron Tensile Tester (model 1120) according to ASTM D-882-80. Gauge length of 5 cm, sample width of 0.5 cm, and crosshead speed of 2 cm/min were used.

For conductivity measurements, the films were sandwiched between two aluminum electrodes and the whole system was kept in a furnace for one hour to attain constant temperature. For better contact, films were coated with silver. Aplab high-voltage-regulated power supply (model 7332) was used for field variation. Current measurements were done on a 610C Keithley electrometer. Temperature was varied from ambient to 150°C. For capacitance and loss measurements 4192 ALF Impedence Analyzer (Hewlett Packard) range 5 Hz–13 MHz bridge was used and frequency was varied from 100 Hz to 13 MHz and temperature from ambient to 100°C.

RESULTS AND DISCUSSION

The polypyromellitimide (PI) films containing dopants were flexible and deeply colored (i.e., $SnCl_2$, $HgCl_2$, and undoped films were yellow, while $CoCl_2$-doped films were green).

Characteristic imide bands were observed in infrared (IR) spectra of these films (i.e., at 1730 cm^{-1} and 1784 cm^{-1}). The other prominent absorptions arising due to phenyl group (at 1608 cm^{-1} and 1512 cm^{-1}), C—N (at 1384 cm^{-1}) were also observed. An additional absorption band at 1672–1680 cm^{-1}) was observed in doped polyimide films. This may be due to $\nu_{c=o}$ of amido group and is thus indicative of incomplete cyclization (Fig. 1). The presence of various salts in doped PI films did not alter the position of various IR bands, this suggests that no chemical bond was formed between polyimide and dopants.

Effect of dopants on thermal stability of polyimide films was studied by thermogravimetric analysis (TGA) (Fig. 2). A slight loss in weight was observed around 150°C, which may be due to the absorbed moisture in the PI films. Besides this, two prominent regions of weight loss were observed in TGA traces of various doped PI films. From the thermogravimetric scans, the percentage weight losses in the two regions, temperature of maximum rate of weight loss ($T_{\max}$) and char yields (Y_c), at 800°C were recorded (Table I). The weight loss observed in the temperature range 250–400°C may be due to cyclization of residual poly(amide-acid) to polyimide. Only 1% weight loss was observed in polyimide film without dopant. Maximum weight loss in this region was in $SnCl_2$-doped film. This suggests that dopants influence the cyclodehydration reaction of poly(amide-acid) and in presence of $SnCl_2$ the cyclodehydration reaction was affected significantly. Major weight loss due to decomposition of polyimide takes place in the temperature region of 550–700°C. Weight loss in the second region was similar in undoped as well as doped film, thereby indicating that decomposition reaction was not influenced by metal salts.

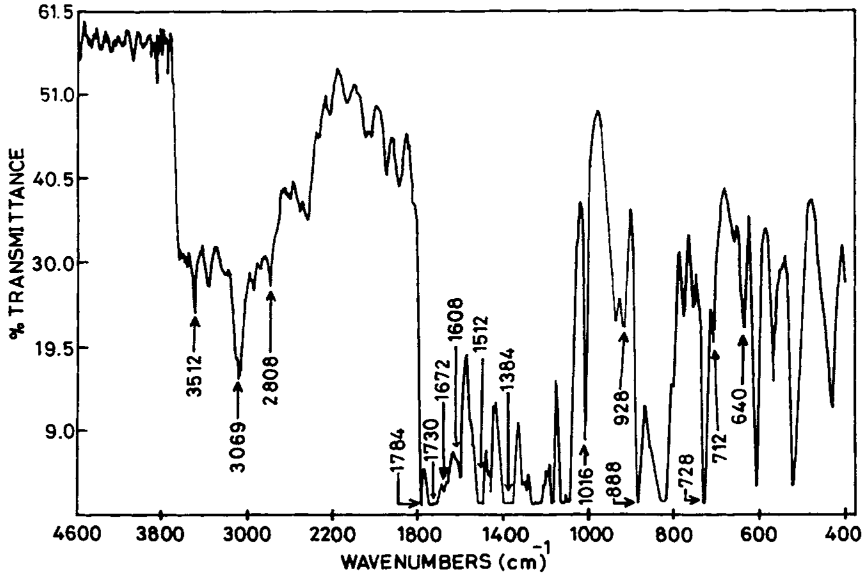

Fig. 1. Infrared spectrum of $SnCl_2$-doped polyimide film.

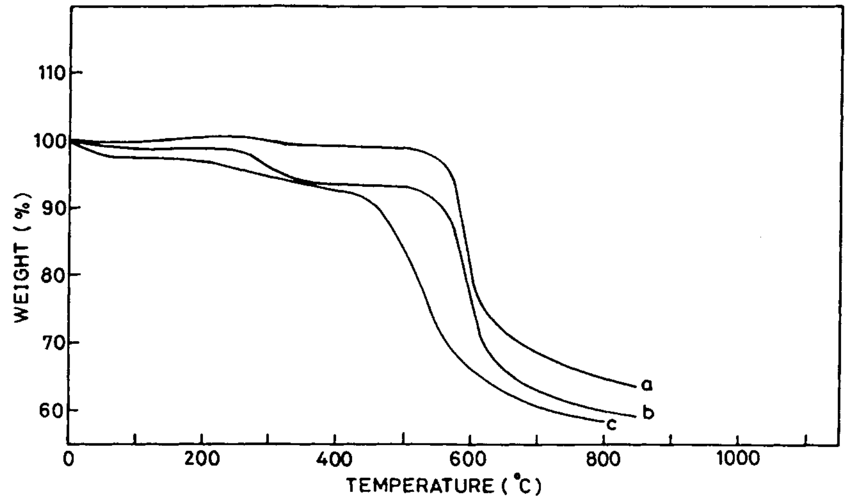

Fig. 2. Thermogravimetric traces for (a) polyimide-, (b) $HgCl_2$-, and (c) $CoCl_2$-doped polyimide films in nitrogen atmosphere.

Differential scanning calorimetry (DSC) (Fig. 3) in the temperature range 100–500°C indicated an endotherm around 100°C in all the four samples, suggesting the removal of moisture associated with the films (Table II). An exothermic transition in the temperature range of 260–400°C was observed in DSC scans. Weight loss in this region was also indicated by TGA results. Loss of solvent (DMF) and water (perhaps due to cyclodehydration of amide-acid intermediate) was indicated by gas chromatography-mass spectroscopy (GC-MS) studies of these samples at 250°C. Loss of solvent is expected to lead to an endothermic transition, whereas an exotherm would be obtained for cyclodehydration reaction where one C—O (~ 81 kcal/mole) and N—H (~ 84 kcal/mole) are broken and a new C—N bond (~ 62 kcal/mole) is formed and water (O—H 110 kcal/mole) is eliminated. Heat of reaction was calculated from the area under the exothermic curve and was found to be maximum in $SnCl_2$-doped polyimide film. From the DSC scans the temperature of onset of exotherm (T_1), temperature of end of exotherm (T_2), the exothermic peak temperature (T_{exo}) and heat of reaction (ΔH) were noted down (Table II).

TABLE I
Results of Thermogravimetric Analysis in Nitrogen Atmosphere of PI Films Doped with Metal Salts

Dopant	Temp. range (°C)	Weight loss (%)	T_{max} (°C)	Y_c (%)
None	250–340	1.1	310	
	563–624	35.5	591.3	63.4
$CoCl_2$	250–400	3.5	324	
	525–637	35.7	583.7	60.8
$HgCl_2$	257–335	5.3	297.2	
	560–634	34.2	593.7	60.5
$SnCl_2$	200–400	6.6	276.2	
	566–643	36.7	594.2	56.7

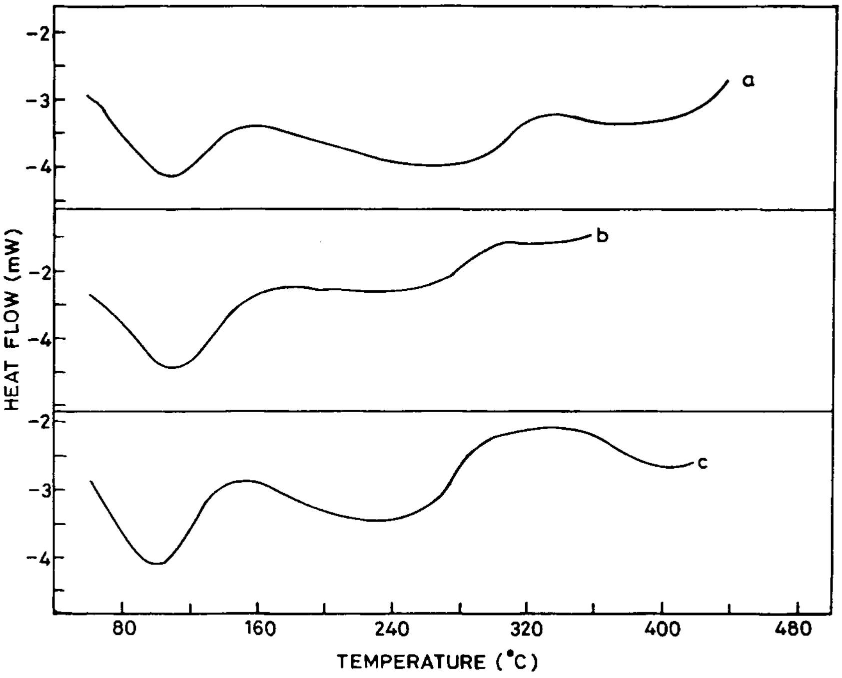

Fig. 3. DSC scans of (a) polyimide-, (b) $CoCl_2$-, and (c) $SnCl_2$-doped polyimide films.

Stress–strain plots of various polyimide films are shown in Figure 4. The tensile strength, modulus, and percentage elongation was calculated from these curves and has been tabulated in Table III. The tensile strength of polyimide films was reduced in the presence of dopants.

TABLE II
Results of DSC Analysis of Polyimide Films Doped with Metal Salts

Dopant	T_{endo} (°C)	T_1 (°C)	T_{exo} (°C)	T_2 (°C)	ΔH (J/g)
None	108	299.8	334.3	390	12.8
$CoCl_2$	110	274.1	301.7	356	17.2
$HgCl_2$	99.9	322.2	340	390	
$SnCl_2$	98.5	262.8	317.1	400	54.8

TABLE III
Mechanical Properties of Polyimide Films (Figures Given in the Brackets are the Standard Deviation Values)

Dopant	Elongation (%)	Tensile strength (kg/cm^2)	Tensile modulus (kg/cm^2)
None	8.8 (0)	711 (6.18)	16,640 (703)
$CoCl_2$	2.1 (0.4)	233 (105)	10,996 (3925)
$HgCl_2$	15 (5.1)	657 (12.9)	21,267 (4318)
$SnCl_2$	5 (1.4)	549 (64.3)	15,770 (2882)

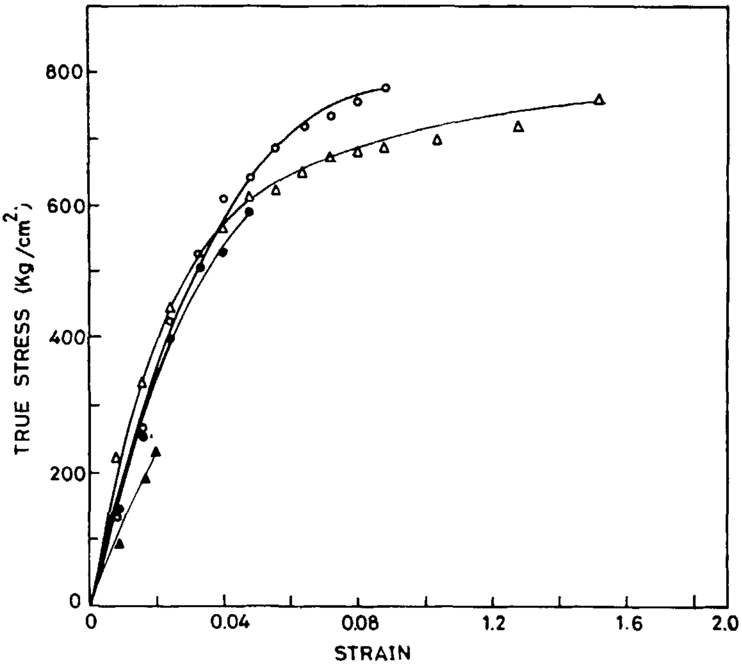

Fig. 4. Stress–strain curves of (○) polyimide-, (●) $SnCl_2$-, (△) $HgCl_2$-, (▲) $CoCl_2$-doped polyimide films.

Variation of current (*I*) as a function of voltage (*V*) was determined for the various doped films at different temperatures (ambient to 150°C). Linear relationship between log *I* vs. log *V* was obtained. However, a direct relationship between *I* and *V*, indicative of ohmic behavior, was observed only in neat polyimide film (Fig. 5). In doped polyimide films the slopes of log *I* vs. log *V* plots were greater than one (Table IV), indicating nonohmic behavior (Fig. 6).

I-V data was further found to obey a linear log *J* (*J* = current density) vs. $\sqrt{E}$ (*E* = field) relation suggesting Richardson-Schottky (RS) or Poole-Frenkel (PF) mechanism of conduction in doped polyimide films (Figs. 7, 8). The current voltage relationship for these mechanisms are given by:[14,15]

$$J_{RS} = A^* T^2 \exp(-\phi/kT) \exp[(e/kT)(eE/4\pi\varepsilon\ \varepsilon_0 d)^{\frac{1}{2}}]$$

$$J_{PF} = AE \exp(-\phi/kT) \exp[(e/kT)(eE/\pi\varepsilon\ \varepsilon_0 d)^{\frac{1}{2}}]$$

TABLE IV
Slope (m) Values from the Log *I* vs. log *V* Plot of Polyimide Films

Temperature (°C)	Neat polyimide	$CoCl_2$-doped PI	$HgCl_2$-doped PI	$SnCl_2$-doped PI
50	1.1	1.5	1.5	2.1
75	1.1	1.5	1.5	2.1
100	1.0	1.5	1.4	2.0
125	1.0	1.5	1.8	1.83
150	1.0	1.5	1.8	1.73

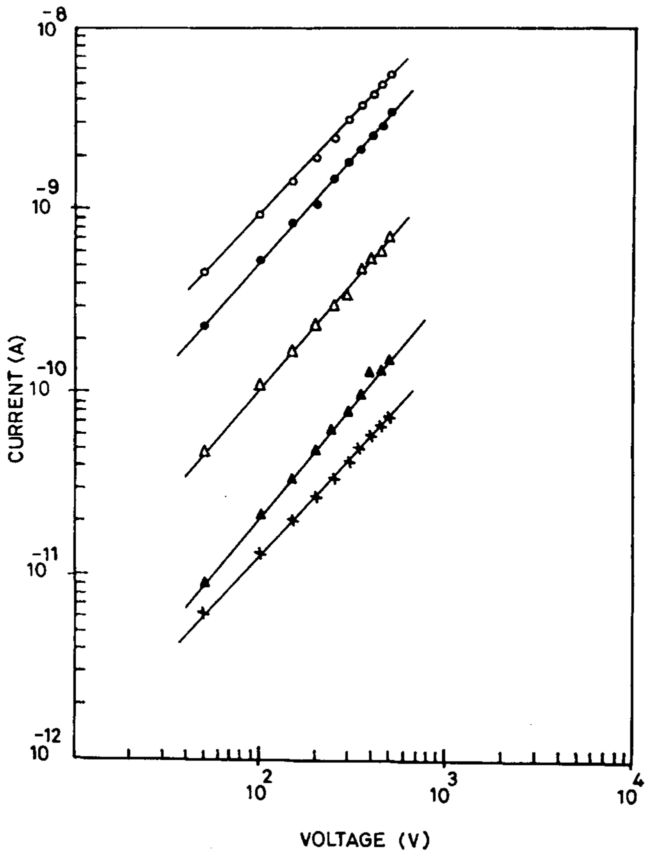

Fig. 5. Logarithmic plots of current (*I*) vs. voltage (*V*) of undoped polyimide film at different temperatures (×) 50°C, (▲) 75°C, (△) 100°C, (●) 125°C, and (○) 150°C.

Where J_{RS} and J_{PF} are the current densities in Richardson-Schottky & Poole-Frenkel mechanism of conduction, respectively, ϕ is the potential barrier at metal polymer contact, A* is the effective Richardson's constant, *A* is the constant independent of field and temperature, *k* is the Boltzmann's constant, *T* the absolute temperature, *e* is the electronic charge, *E* is the field,

TABLE V

β Values Calculated from log J vs. $\sqrt{E}$ Plots of Polyimide Films

Temperature (°C)	Dopant	β (theoretical)	β (calculated)	
			Lower field	Higher field
50	None	.073	.154	.062
50	$CoCl_2$	.086	.171	.074
50	$SnCl_2$	.098	—	.084
50	$HgCl_2$	.077	—	.09
150	None	.056	.105	.048
150	$CoCl_2$	.066	.127	.060
150	$SnCl_2$	.075	.15	.097
150	$HgCl_2$	.058	.119	.083

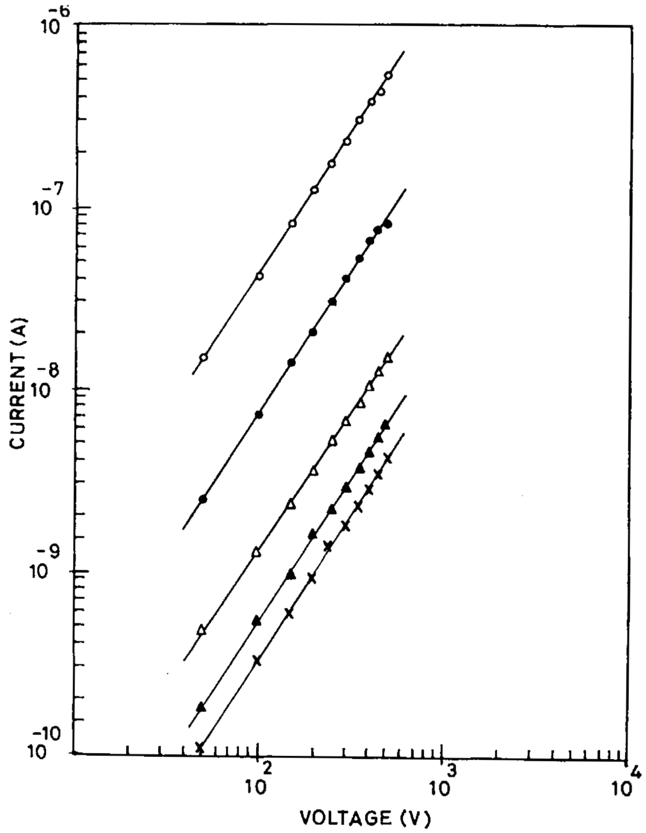

Fig. 6. Logarithmic plots of current (I) vs. voltage (V) of $CoCl_2$-doped polyimide film at different temperatures, (×) 50°C, (▲) 75°C, (△) 100°C, (●) 125°C, and (○) 150°C.

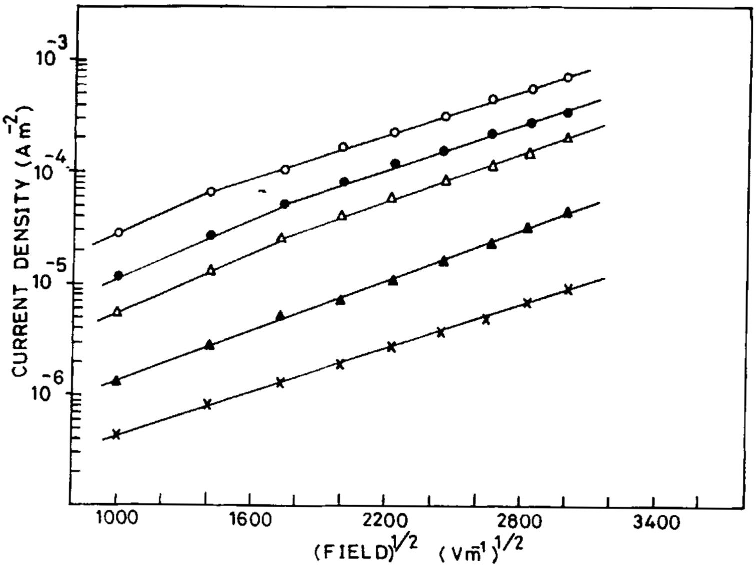

Fig. 7. Plot of current density (J) vs. square root of field ($\sqrt{E}$) of $SnCl_2$-doped polyimide film at different temperatures, (×) 50°C, (▲) 75°C, (△) 100°C, (●) 125°C, and (○) 150°C.

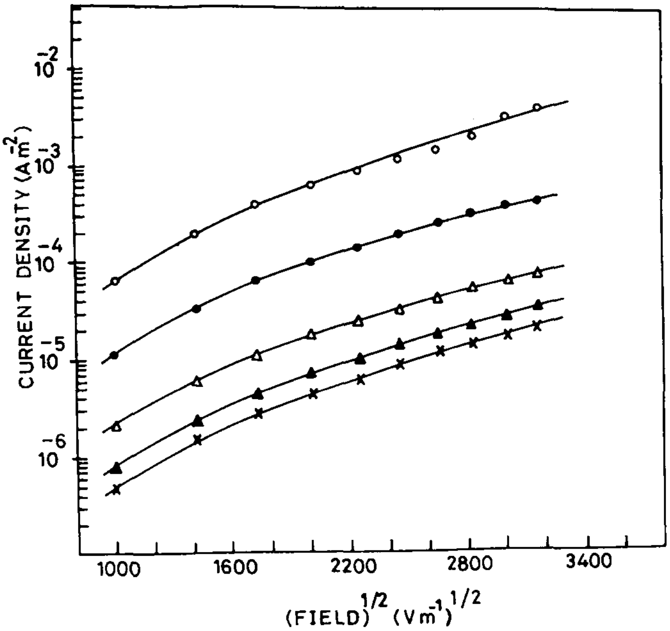

Fig. 8. Plot of current density (J) vs. square root of field ($\sqrt{E}$) of $CoCl_2$-doped polyimide film at different temperatures, (×) 50°C, (▲) 75°C, (△) 100°C, (●) 125°C, and (○) 150°C.

ε_0 is the permittivity of free space, ε the dielectric constant, and d is the thickness of the film. At constant temperature both equations give:

$$\log J = \beta E^{\frac{1}{2}} + C$$

Where β is the exponent such that

$$2\beta_{RS} = \beta_{PF}$$

TABLE VI
Activation Energies Calculated from log σ vs. 1000/T Plot of Polyimide Films

Dopant	Voltage (V)	Activation energy (kcal/mole)	
		Low temperature	High temperature
None	100	4.39	18.53
None	250	4.02	18.5
None	450	5.07	18.79
$CoCl_2$	100	4.53	22.87
$CoCl_2$	250	4.06	22.5
$CoCl_2$	450	4.13	23.17
$HgCl_2$	100	2.88	18.17
$HgCl_2$	250	4.32	17.52
$HgCl_2$	450	5.35	17.8
$SnCl_2$	100	—	12.24
$SnCl_2$	250	—	11.96
$SnCl_2$	450	—	10.23

On calculating the values of β it has been observed that at lower voltages PF mechanism is dominant while at higher voltages RS mechanism is operative. Experimental and theoretical values of β are given in Table V.

Figure 9 shows the variation of log σ (σ = conductivity) as a function of reciprocal temperature. Two distinct regions were observed in undoped and doped PI films. From these plots activation energy was calculated (Table VI). It can be concluded on the basis of the above results that in the given temperature range polyimide showed ohmic behavior while doped films followed RS or PF mechanism of conduction.

The dielectric constant, ε of polyimide film was in the range of 3.4–3.7. This value is comparable to the values reported in the literature. Addition of $SnCl_2$ resulted in an increase in ε values of polyimide film to 3.9–4.2. A decrease in ε was observed in presence of $CoCl_2$ and $HgCl_2$ dopants.

The detailed temperature-frequency dependences of the dielectric characteristics (ε and tan δ) for various polyimide films are shown in Figures 10–14. As seen from these figures ε and tan δ show only marginal dependence on temperature or frequency in polyimide films. In all cases, tan δ is approximately equal to 0.005–0.105. An increase in temperature resulted in significant drop in tan δ values of $CoCl_2$-doped film.

The dielectric losses in the polyimides are caused by the polar CO group

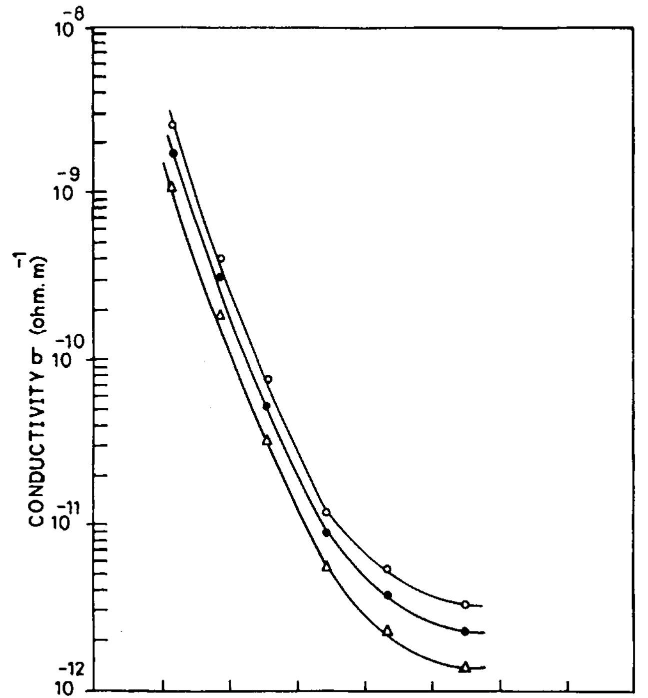

Fig. 9. Plot of conductivity (σ) vs. reciprocal temperature of $CoCl_2$-doped polyimide film at different voltages (△) 100v, (●) 250v, and (○) 450v.

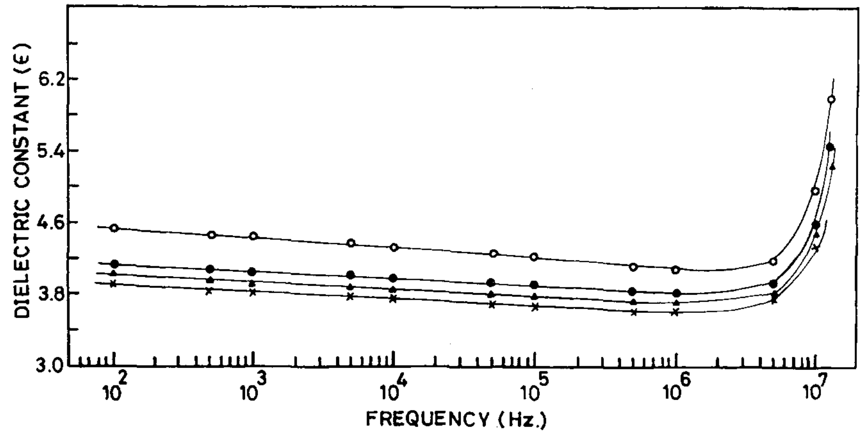

Fig. 10. Dependence of dielectric constant on frequency of $SnCl_2$-doped polyimide film at different temperatures, (×) 90°C, (▲) 70°C, (●) 50°C, and (○) 25°C.

of the imide ring. A symmetrical location of these two groups is responsible for a low loss level. The tan δ values were maximum for $CoCl_2$-doped film and minimum for undoped film (Fig. 14). The difference in tan δ values of various doped films was maximum at low temperature (i.e., 25°C). The low temperature loss values have been attributed in polyimide films to the terminal —COOH and —NH_2 groups. Since the same polyimide was used

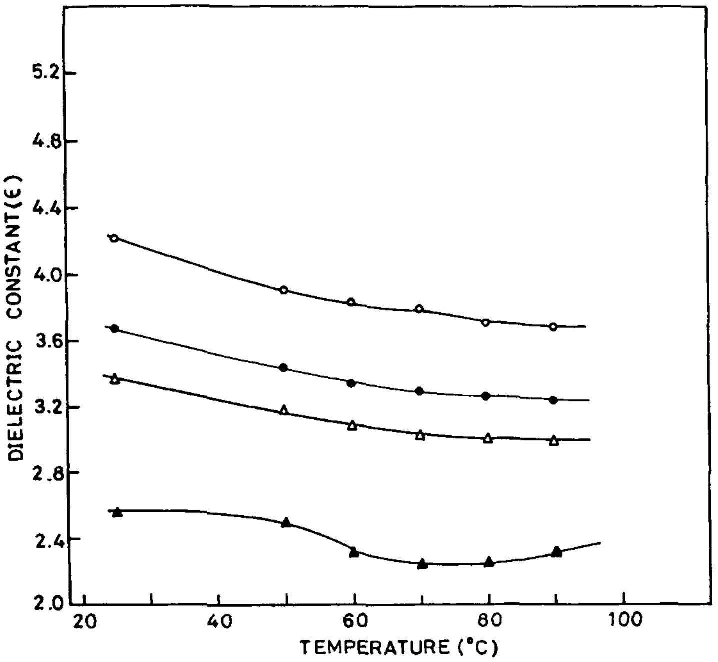

Fig. 11. Dependence of dielectric constant on temperature at a fixed frequency of 10^5 Hz, (●) polyimide-, (○) $SnCl_2$-, (△) $HgCl_2$-, and (▲) $CoCl_2$-doped polyimide film.

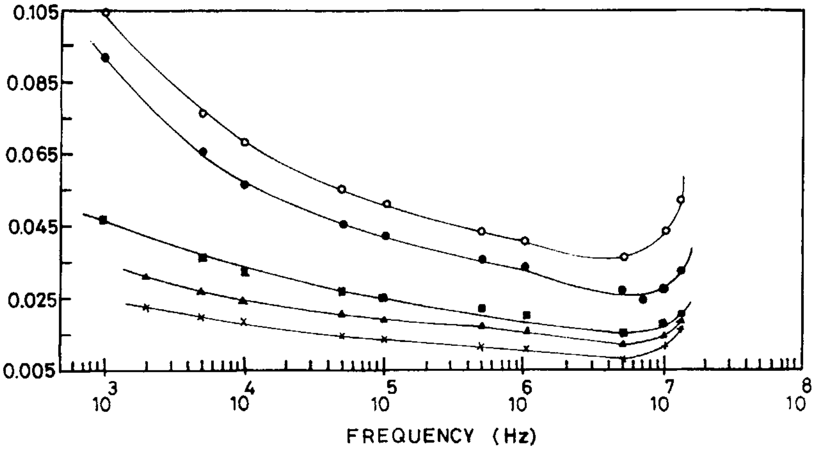

Fig. 12. Plot of tan δ vs. frequency of $CoCl_2$-doped polyimide film at different temperatures, (○) 25°C, (●) 50°C, (■) 60°C, (▲) 70°C, and (×) 90°C.

for doping with different dopants, therefore, the concentration of end groups is expected to be similar in various samples. The TGA studies have indicated the existence of uncyclized poly(amide-acid) in these films. The carboxylic group of these amide-acid are perhaps responsible for variation of tan δ values at low temperatures in various doped PI films.

CONCLUSIONS

The following conclusions can be drawn about the effect of Co (II), Hg (II), and Sn (II) halides on the properties of polyimide films cured in nitrogen atmosphere:

1. The cyclodehydration reactions of poly(amide-acid) are influenced by the presence of metallic salts and incomplete cyclodehydration is observed.

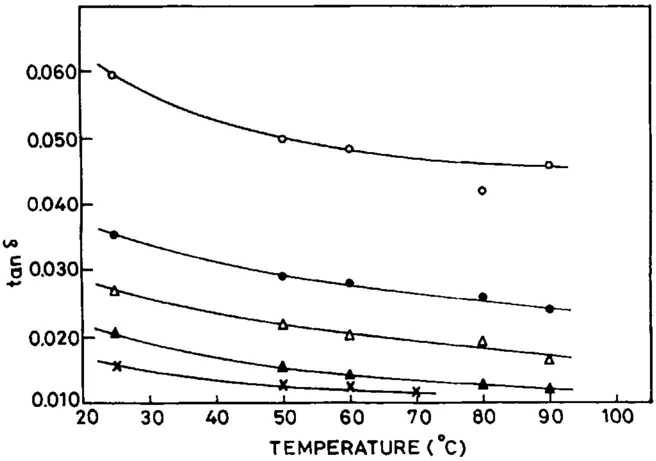

Fig. 13. Plot of tan δ vs. temperature of $SnCl_2$-doped polyimide film at different frequencies, (○) 10^7 Hz, (●) 5×10^6 Hz, (△) 10^6 Hz, (▲) 10^5 Hz, and (×) 10^4 Hz.

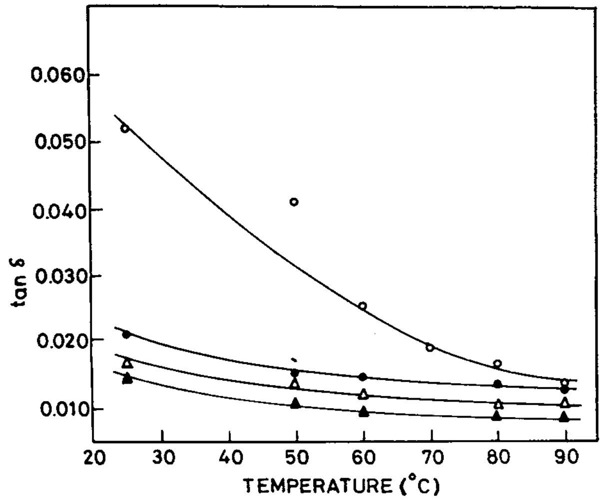

Fig. 14. Plot of tan δ vs. temperature at a fixed frequency of 10^5 Hz, (▲) polyimide, (△) $HgCl_2$-, (●) $SnCl_2$-, and (○) $CoCl_2$-doped polyimide films.

2. Thermal decomposition of polyimides is not affected by the presence of Sn (II), Co (II), or Hg (II) halides.
3. The tensile strength of polyimide films is reduced in the presence of dopants.
4. Nonohmic behavior of polyimides is observed in presence of dopants.
5. In the temperature range of 50–150°C in doped PI films, Richardson-Schottky (RS) mechanism of conduction is operative at higher voltages while Poole-Frenkel (PF) mechanism is dominant at lower voltages or field.
6. An increase in the dielectric constant (ε) values is observed by the addition of $SnCl_2$ while a decrease is observed in presence of $CoCl_2$ and $HgCl_2$ dopants.
7. The dielectric characteristics (i.e., ε and tan δ) show only marginal dependence on temperature or frequency in various doped PI films.

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