Effect of metal halides on the electrical properties of polyimides

I. K. Varma, Sneh Saxena, Anita Tripathi and D. S. Varma
Centre for Materials Science and Technology, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi-110 016, India
(Received 30 September 1986; revised 28 August 1987; accepted 23 September 1987)

This article describes the effect of metallic salts, Sn (II), Hg (II), Co (II) chlorides, on the electrical properties of polyimide films derived from 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) and 4,4'-diaminodiphenyl ether (E). The effect of temperature/field on the electrical conductivity of the films was studied. An ohmic/sublinear behaviour in undoped film and a non-ohmic behaviour at high field and temperature was observed in doped films. Dielectric characteristics (ε and tan δ) as a function of frequency and temperature were also investigated.

(Keywords: polyimide; poly(amide acid); dopants; dielectric constant; conductivity)

INTRODUCTION

In order to develop polymer films having unique mechanical and electrical properties, doping of poly-(amide acids) with electropositive metal salts and metal complexes has been reported by several workers in the last few years[1-9]. The metal cation is reduced to the metal during the cure cycle to obtain metal-doped polyimide films. The surface electrical resistivity and the volume resistivity are significantly reduced by the incorporation of metal salts and metal complexes. Polyimides having a semiconductive cobalt oxide[10,11] surface or lithium oxide[12] surface have been prepared by the incorporation of soluble metal salts and thermal curing techniques. In an attempt to obtain a lithium-substituted cobalt oxide semiconductive surface, polyimide films have also been co-doped with lithium chloride and cobalt chloride[13]. In our earlier papers[14,15] we described the effect of metal halides on the properties of polypyromellitimide films. In these studies, cyclodehydration of doped polypyromellitamide acid films to polypyromellitimides was done by heating in nitrogen atmosphere. Our studies indicated a non-ohmic behaviour of polyimides in the presence of dopants. Conduction mechanism in these films was deduced from plots of the current as a function of voltage and temperature.

The present studies were undertaken to investigate the effect of doping polyimide films with Sn (II), Co (II) and Hg (II) on their electrical properties. Condensation polyimide was prepared from 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) and 4,4'-diaminodiphenyl ether (E). Investigations on Co (II) chloride doped polyimide films based on BTDA and E have been reported earlier.

EXPERIMENTAL

Materials

3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) (ICN) was crystallized from acetic anhydride and dried in vacuum at 60°C before use. 4,4'-Diaminodipyenyl ether (E) (Fluka), $HgCl_2$ (BDH), $CoCl_2 \cdot 6H_2O$ (BDH), $SnCl_2 \cdot 2H_2O$ (BDH) were all vacuum dried at 60°C for 24 h and stored in a desiccator. *N,N'*-Dimethyl formamide (DMF) (E. Merck) was used as such.

Polymerization

Poly(amide acid) was prepared by the customary low temperature solution polymerization. Diamine (E) (0.04 mol) was dissolved in DMF (10% w/w) followed by addition of a stoichiometric amount of dianhydride. The resulting solution was stirred at 0–5°C for 5–6 h under nitrogen. The solution was finally stored in a refrigerator. The intrinsic viscosity, $[\eta]$, of poly(amide acid) was determined by the Ubbelhode viscometer at 30°C and was found to be 0.69 dl g^{-1}. To the poly(amide acid) in DMF, $SnCl_2$, $HgCl_2$ and $CoCl_2$ (10% w/w with respect to poly(amide acid)) were added. The homogeneous solutions thus obtained were used for film casting. The solution was poured on a glass plate and spread uniformly using a doctor's knife. The solvent was removed by heating the films at 60–70°C (overnight). These films were imidized by heating in an oven flushed with dry nitrogen for 1 h each at 100, 200 and 250°C. Polyimide (PI) films were then removed from the glass plates. No difference in the colour of the film on the glass or exposed sides was observed.

Characterization

I.r. spectra of the doped films were recorded using a Nicolet 5 DX *FT*i.r. spectrophotometer. Analysis of $CoCl_2$, $SnCl_2$ and $HgCl_2$ content in the doped PI films was done by colorimetric method using diphenylthiocarbazone in chloroform, according to the procedure described elsewhere[16].

For the electrical conductivity measurements, a 610C Keithley electrometer and Aplab power supply (model 7331) was used for field variation. Temperature was varied from 40 to 200°C. Dielectric characteristics were evaluated using 4192 ALF Impedence Analyzer (Hewlett Packard). Frequency was varied from 10^2 to 10^6 Hz and temperature from 40 to 200°C. For these measurements,

0032-3861/88/030559-07$03.00

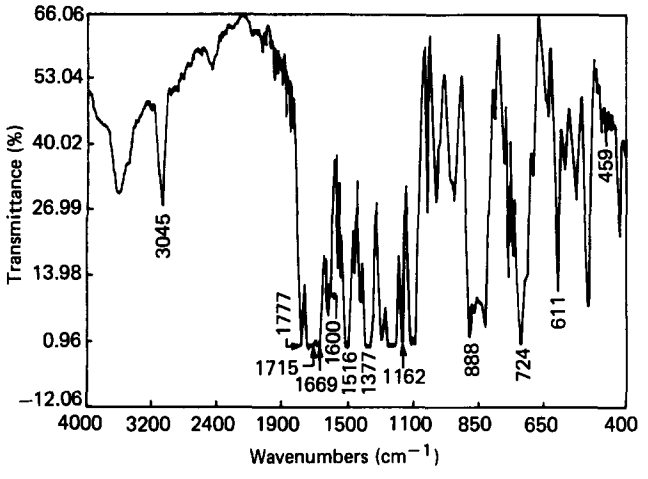

Figure 1 Infra-red spectrum of $HgCl_2$ doped polyimide film

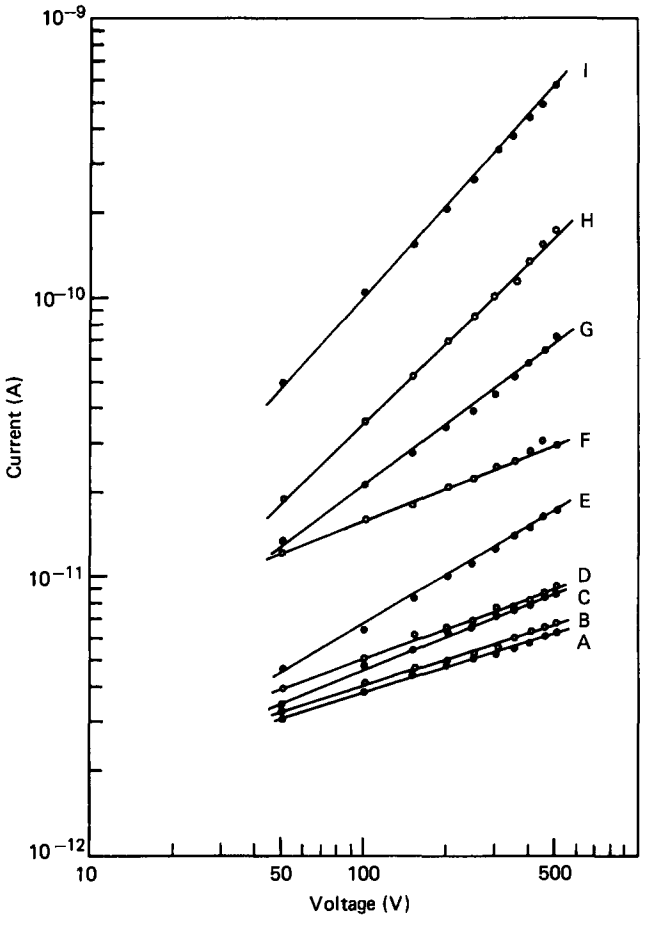

Figure 2 Logarithmic plots of current *versus* voltage of undopd polyimide film at different temperatures: A, 40; B, 60; C, 80; D, 100; E, 120; F, 140; G, 160; H, 180; I, 200°C

aluminium was deposited in vacuum on both sides of the films and the PI films were then sandwiched between two aluminium electrodes. The whole system was kept in an electrically controlled measurement cell for 1 h to attain the desired temperature. The temperature of the measurement cell was maintained at ± 2°C by using a contact thermometer and an electric relay.

RESULTS AND DISCUSSION

The PI films containing dopants were flexible and deeply coloured. The colour of these films was similar to that observed in doped polypyromellitimide films, i.e. yellow ($SnCl_2$ and $HgCl_2$) and green ($CoCl_2$ doped films). The thicknesses of the undoped and $SnCl_2/CoCl_2/HgCl_2$ doped films were 5×10^{-5}, 5×10^{-5}, 3×10^{-5} and 4×10^{-5} m, respectively. Metal analysis using dithizone as the reagent showed partial loss of the metal in the films. The percentage of $HgCl_2$, $CoCl_2\cdot6H_2O$ and $SnCl_2\cdot2H_2O$ in the films was found to be 8.37, 5.49 and 11.4%, respectively.

In the i.r. spectra of the various films, typical absorption bands associated with imide groups (at 1715 and 1777 cm^{-1}) were observed. Other absorption bands associated with aromatic groups (1516 and 1600 cm^{-1}), C–N (1377 cm^{-1}) and C=O groups of the BTDA moiety at 165 ± 10 cm^{-1} were observed. A typical i.r. spectrum of doped PI film is given in *Figure 1*. The incorporation of various salts in PI films did not alter the position of various i.r. bands thereby suggesting that no chemical bond was formed between PI and dopants.

The electrical resistivities of neat and doped PI films were evaluated at temperatures ranging from 40 to 200°C. High temperature measurements are necessary to evaluate variation in the electrical resistivity of these films at temperatures which may be encountered during the service life. The curves of current–voltage characteristics for undoped PI film (*Figure 2*) and metal salt doped PI film (*Figure 3*) show some differences. A linear relationship between log I and log V was observed in PI

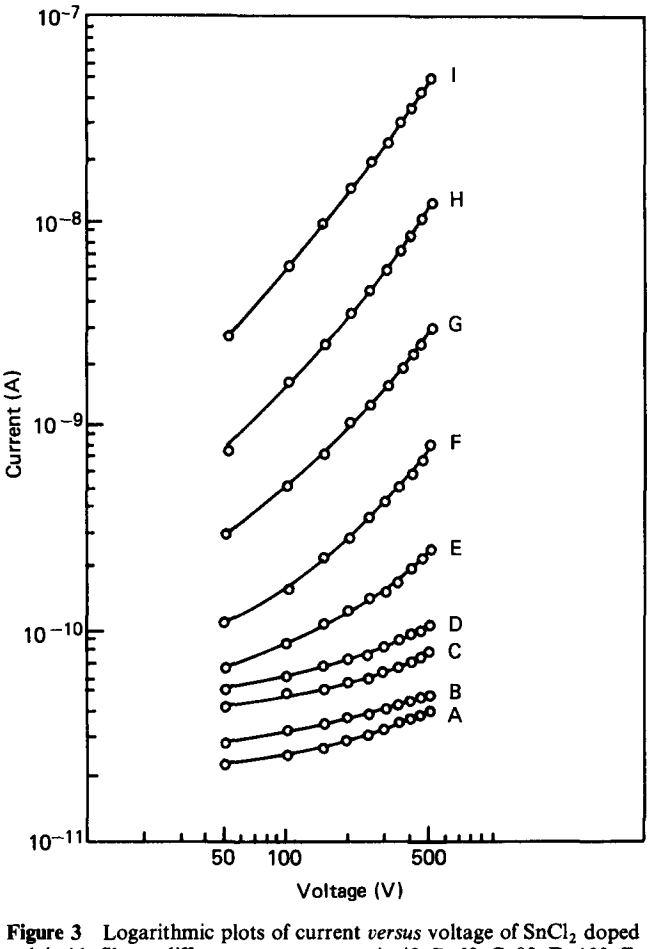

Figure 3 Logarithmic plots of current *versus* voltage of $SnCl_2$ doped polyimide film at different temperatures: A, 40; B, 60; C, 80; D, 100; E, 120; F, 140; G, 160; H, 180; I, 200°C

Table 1 Slope (m) values from log I *versus* log V plot of polyimide films

Dopant	Temperature (°C)	Slope (m) Low field	Slope (m) High field
None	40	0.32	
	80	0.39	
	120	0.52	
	160	0.76	
	200	1.10	
$SnCl_2$	40	0.18	0.54
	80	0.21	0.57
	120	0.36	1.13
	160	0.74	1.20
	200	1.15	1.94
$HgCl_2$	40	0.19	0.33
	80	0.33	0.61
	120	–	1.00
	160	0.84	2.10
	200	1.10	2.00
$CoCl_2$	40	0.85	1.84
	80	0.84	1.39
	120	0.79	1.22
	160	0.86	1.48
	200	1.05	1.80

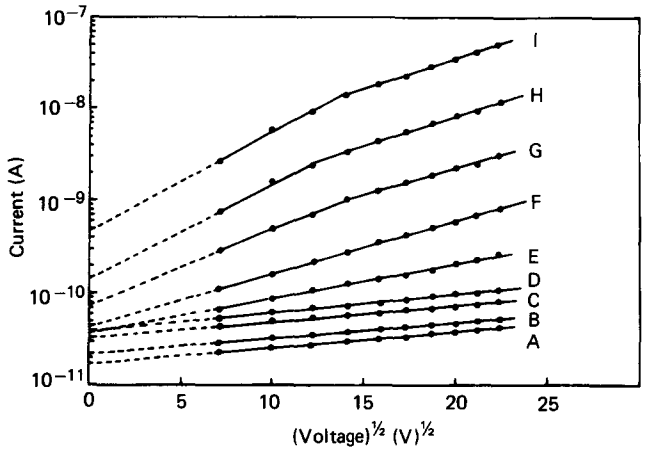

Figure 4 Dependence of current on the square root of voltage of $SnCl_2$ doped polyimide film at different temperatures: A, 40; B, 60; C, 80; D, 100; E, 120; F, 140; G, 160; H, 180; I, 200°C

films. In doped films, on the other hand, an increase in current at high fields was observed which resulted in two different slopes of the log I–log V plots (*Figure 3*). The slopes of these plots were calculated at different temperatures and these results are given in *Table 1*. In undoped PI film, ohmic behaviour was observed above 160°C. At lower temperatures, however, a sublinear behaviour was observed. Incorporation of metallic halides in PI resulted in a non-ohmic behaviour at high fields and high temperatures. However, at low fields around 200°C or at high fields in the temperature range around 120°C an ohmic behaviour was observed in doped PI films.

The resistivity of both doped and undoped PI films was very high at low temperatures and low fields. On increasing the temperature or field, an increase in conductivity was observed. The conductivity of a polymer, σ, is described by the following equation:

$$\sigma = ne\mu$$

where n is the charge carrier concentration, e is the charge and μ is the charge carrier mobility. An increase in charge carrier mobility is expected at high temperature/field. Therefore, the observed increase in the conductivity of PI films on increasing the temperature/field may be attributed to the increase in charge carrier mobility.

A plot of log I vs. $V^{1/2}$ of $SnCl_2$ doped PI film (*Figure 4*) indicated a linear relationship in the temperature range 40–200°C. The slopes of these lines were similar. Further increase in temperature resulted in a significant increase in the slope. At higher temperatures (i.e. above 120°C) a voltage-dependent variation in the slope was observed. At lower fields, the slope of log I vs. $V^{1/2}$ plot was higher than at higher fields. Similar behaviour was observed when $HgCl_2$ was used as a dopant. On the other hand, in undoped and $CoCl_2$ doped films, a voltage dependent variation, in the slopes of log I vs. $V^{1/2}$ plot, was observed at all temperatures. The slope values of the undoped and the various doped PI films are given in *Table 2*. The Schottky coefficient, β, was also calculated using the equation:

$$\beta = 1/kT(e^3/4\pi\varepsilon\varepsilon_0 d)^{1/2}$$

where k is the Boltzmann's constant, T is the temperature in Kelvin, e is the electronic charge, ε_0 is the permittivity of the free space, ε is the dielectric constant and d is the thickness of the film. The slopes of log I vs. $V^{1/2}$ plots at two temperatures have been compared with the theoretical β in *Table 3*. These results show that in undoped PI films only few charge carriers are generated at low temperatures. At high temperature and field the observed slope value is almost double the theoretical β value indicating the possibility of a Poole–Frenkel type of

Table 2 Slope values from log I *versus* $V^{1/2}$ plot of polyimide films

Temperature (°C)	Dopant None	$CoCl_2$	$HgCl_2$	$SnCl_2$
40	0.07 (0.06)	0.23 (0.17)	0.05	0.03
120	0.13 (0.11)	0.25 (0.15)	0.27 (0.10)	0.09
160	0.15 (0.11)	0.29 (0.18)	0.22 (0.21)	0.18 (0.13)
200	0.22 (0.13)	0.33 (0.23)	0.30 (0.25)	0.22 (0.15)

Figures in parentheses are the slope values at high fields

Table 3 β values calculated from the log I *versus* $V^{1/2}$ plot of polyimide films

Dopant	Temperature (°C)	β_S (Theoretical)	β Lower field	β Higher field
None	40	0.095	0.07	0.06
None	200	0.064	0.22	0.13
$SnCl_2$	40	0.076	–	0.03
$SnCl_2$	200	0.052	0.22	0.15
$CoCl_2$	40	0.075	0.23	0.17
$CoCl_2$	200	0.05	0.33	0.23
$HgCl_2$	40	0.076	–	0.05
$HgCl_2$	200	0.052	0.30	0.25

Table 4 Dielectric constants calculated from the Schottky and Poole–Frenkel equations

Dopant	Temperature (°C)	ε_S	ε_{PF}	ε_{AC}
None	40	8.82 (8.32)	35.28 (33.2)	4.33
	200	0.97 (0.34)	3.93 (1.38)	4.03
$SnCl_2$	40	32.3	129.3	6.70
	200	0.73 (0.34)	2.95 (1.37)	6.08
$CoCl_2$	40	2.23 (1.28)	8.93 (5.12)	11.69
	200	0.53 (0.25)	2.15 (1.02)	10.46
$HgCl_2$	40	19.87	79.52	8.37
	200	0.34 (0.23)	1.38 (0.92)	7.82

Figures in parentheses are the values at low field

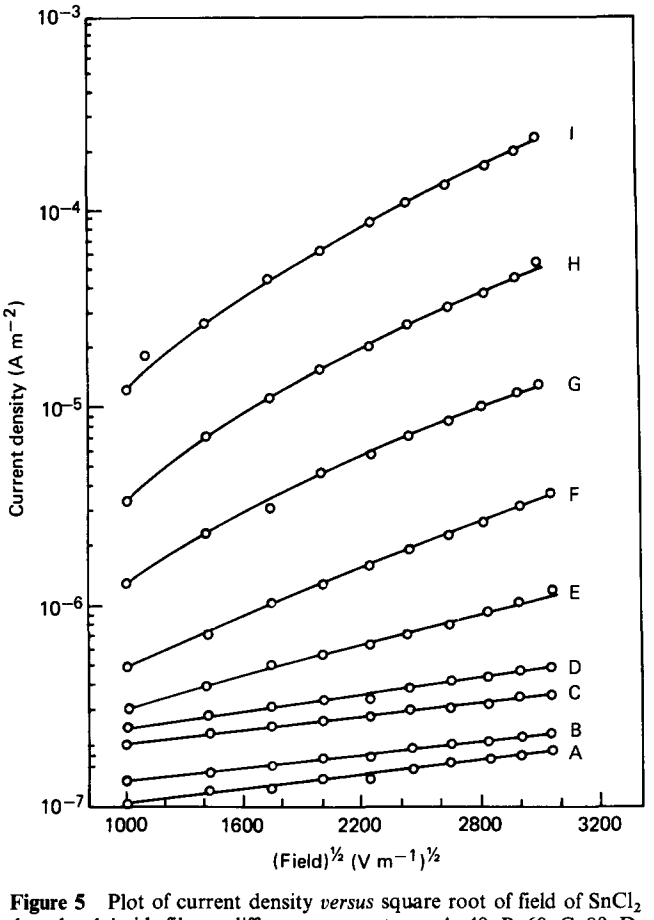

Figure 5 Plot of current density *versus* square root of field of $SnCl_2$ doped polyimide film at different temperatures: A, 40; B, 60; C, 80; D, 100; E, 120; F, 140; G, 160; H, 180; I, 200°C

electronic conduction. In doped films too at low temperature/field the concentration of charge carriers and their mobility is low. The slope values are four to five times the β theoretical values at high temperaure. The mechanism of conduction might be a combination of electronic and ionic types.

From these values of the slopes, it is possible to calculate the dielectric constants, ε_S and ε_{PF}, assuming that Richardson–Schottky or Poole–Frenkel mechanisms for condution are applicable according to the following equation:

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

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

where J_{RS} and J_{PF} are the current densities in Richardson–Schottky and Poole–Frenkel mechanisms of conduction, respectively, ϕ is the potential barrier at metal–polymer contact, A^* is the Richardson's constant and A is the constant independent of field and temperature. These values together with the dielectric constant obtained from the alternating current (AC) studies are given in *Table 4*.

An almost perfect straight line was observed in the plot of $\log J$ vs. $E^{1/2}$, in the various PI films under investigation (*Figure 5*). This too suggests a Schottky or Poole–Frenkel mechanism of conduction. Both are electronic processes.

The activation energy for conduction, independent of field may be found by plotting the extrapolated zero-field current I_0 obtained from the $\log I$ vs. $V^{1/2}$ plots, against reciprocal temperature as shown in *Figure 6*. Two distinct regions were observed in these plots for all the PI films. The ϕ_S values have been calculated using the Schottky equation[17] (*Table 5*).

Figure 7 shows the variation of conductivity as a function of reciprocal temperature. Two distinct regions were observed in both doped and undoped PI films. All films showed low conductivity below 120°C and an activation energy in the range of 1.4–3.5 kcal mol^{-1}. Above 120°C there was a sharp increase in the activation energy for conduction (11–21 kcal mol^{-1}) (*Table 6*). Similar values were observed in our previous work on polypyromellitimide films. This may be due to the

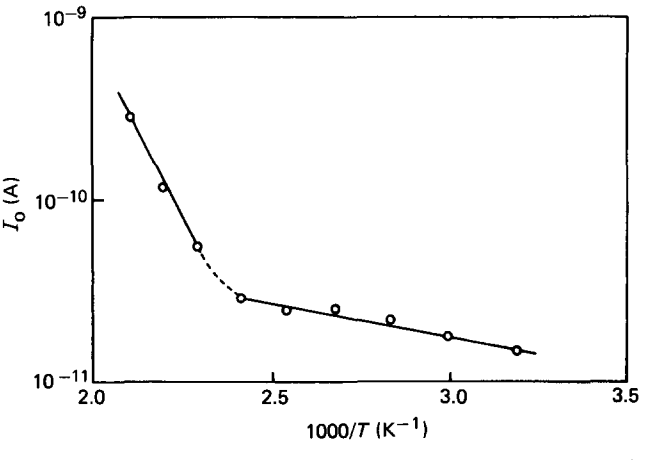

Figure 6 The extrapolated zero-field current (I_0) in $SnCl_2$ doped polyimide film as a function of reciprocal temperature

Table 5 ϕ_S values calculated from I_0 (extrapolated zero-field current) *versus* reciprocal temperature

Dopant	ϕ_S (eV)	
	Low temp. (°C)	High temp. (°C)
None	–	0.11
$SnCl_2$	0.07	1.39
$CoCl_2$	0.19	0.42
$HgCl_2$	0.24	0.73

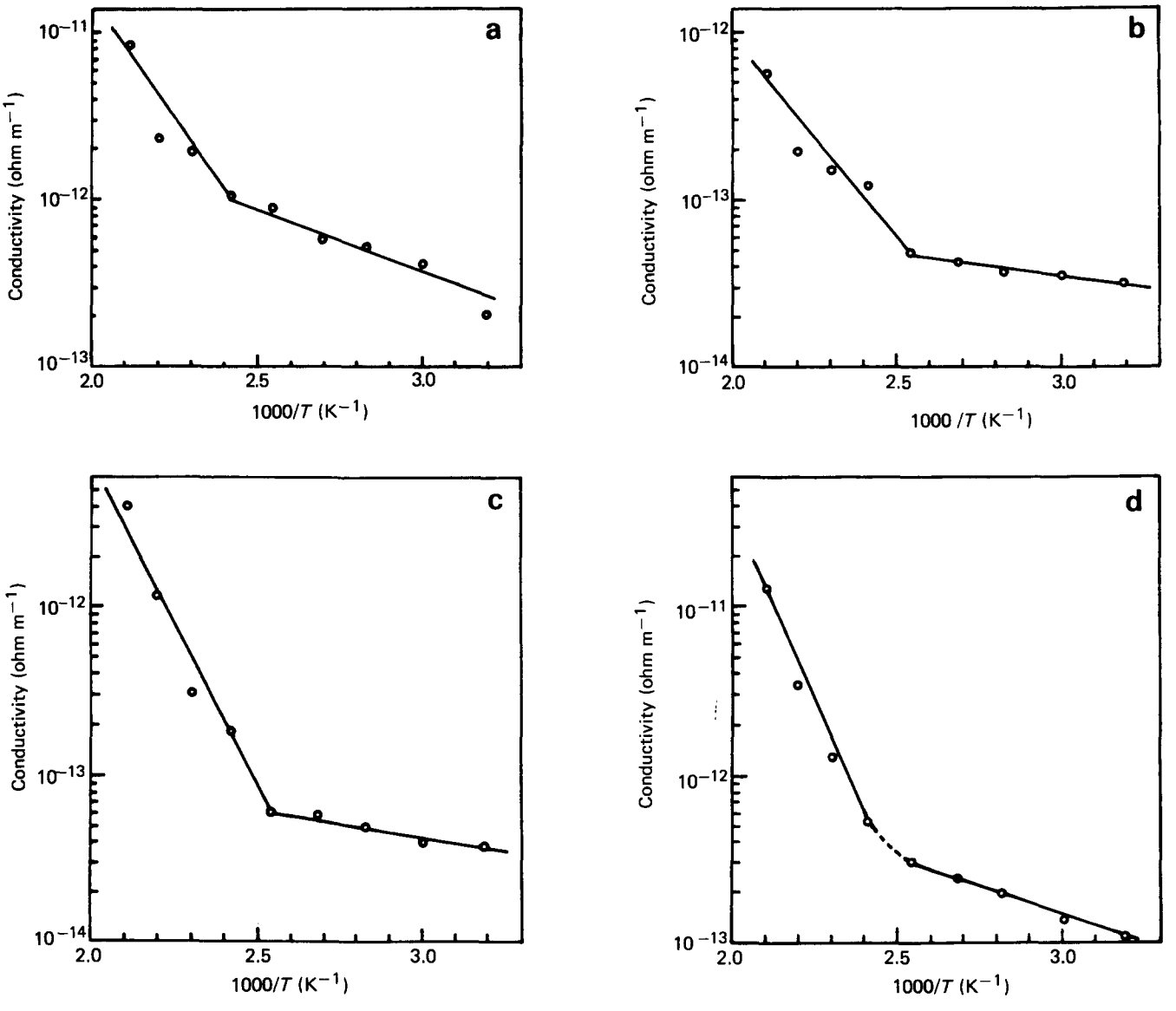

Figure 7 Plot of conductivity *versus* reciprocal temperatures of polyimide films. (a) $CoCl_2$, (b) undoped, (c) $HgCl_2$ and (d) $SnCl_2$ doped polyimide films

Table 6 Activation energies calculated from log (conductivity) *versus* reciprocal temperature plot

Dopant	Voltage (V)	Activation energy (eV)	
		Low temp. (°C)	High temp. (°C)
None	50	0.06	0.48
$SnCl_2$	50	0.13	0.89
$CoCl_2$	50	0.15	0.54
$HgCl_2$	40	0.07	0.75

dissociation of loosely bound water from these films at high temperatures. A change in conduction mechanism (from electronic to ionic) may take place at higher temperatures[18].

The frequency dependence of dielectric constant for polyimide films (undoped and doped with $HgCl_2$) is shown in *Figures 8* and *9*, respectively. Increasing the frequency at a given temperature resulted in a decrease in dielectric constant. Similar behaviour was observed in polypyromellitimide films. The dielectric constant of PI film increased by doping with metallic halides (*Table 7*). Incorporation of cobalt chloride resulted in a maximum increase of dielectric constant ($\varepsilon = 11.8$). Similarly a higher conductivity was observed in doped PI films in d.c. measurements. Temperature dependence of dielectric constant at a fixed frequency of 10^5 Hz is shown in *Figure 10*.

An increase in frequency resulted in a decrease in the loss value (tan δ) at all temperatures and for all the films. Variation of tan δ *versus* frequency at all temperatures for $HgCl_2$ and $CoCl_2$ doped films has been shown in *Figures 11* and *12*. At 10^5 Hz, tan δ has been plotted against temperature for all the films (*Figure 13*). Around 140°C a small peak was observed which might be due to the loss of water at this temperature. Variation of tan δ with temperature at different frequencies for $SnCl_2$ doped film is shown in *Figure 14*. It is very clear from the figure that the value of tan δ is maximum for highest frequency at low temperature while minimum for highest frequency at high temperature. This is also supported by conductivity measurements in which at low temperatures the conductivity is low (because the loss is maximum) while at high temperature the conductivity is high (because the loss is minimum).

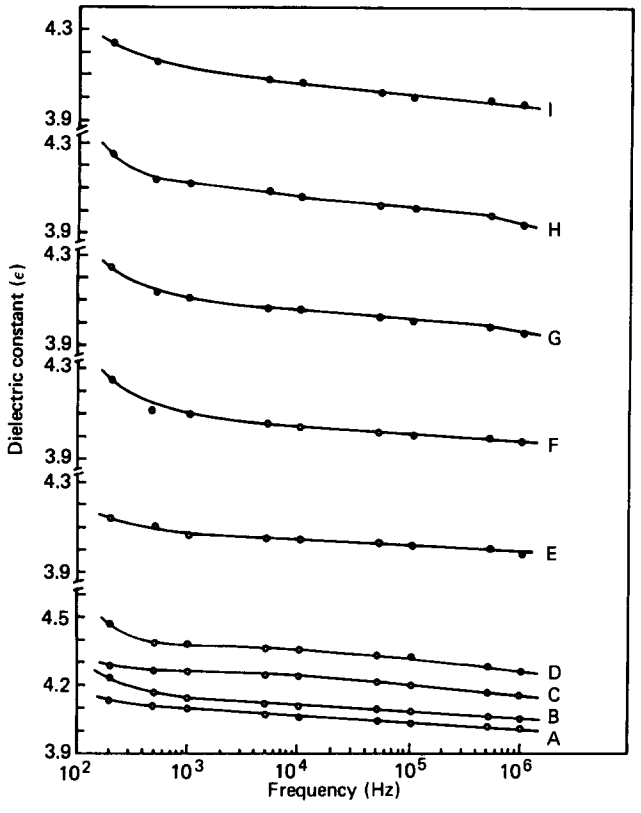

Figure 8 Dependence of dielectric constant on frequency of undoped polyimide film at different temperatures: A, 40; B, 60; C, 80; D, 100; E, 120; F, 140; G, 160; H, 180; I, 200°C

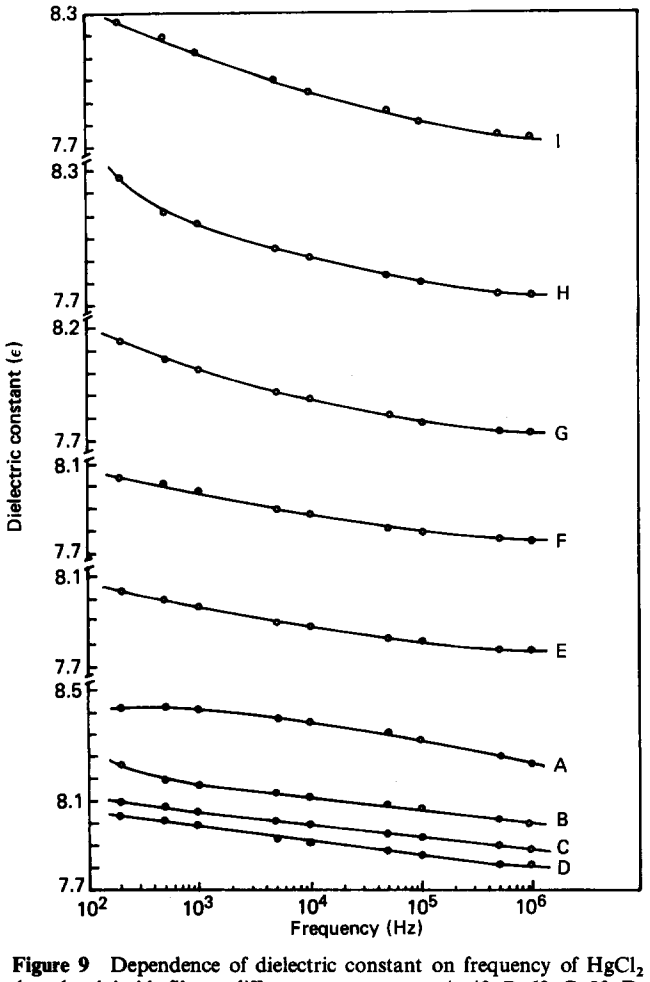

Figure 9 Dependence of dielectric constant on frequency of $HgCl_2$ doped polyimide film at different temperatures: A, 40; B, 60; C, 80; D, 100; E, 120; F, 140; G, 160; H, 180; I, 200°C

Table 7 Dielectric constant of polyimide films at given temperatures and frequencies

Temperature (°C)	Frequency (Hz)	Dopant			
		None	$CoCl_2$	$HgCl_2$	$SnCl_2$
40	10^3	4.39	13.23	8.51	6.81
	10^4	4.36	12.42	8.46	6.77
	10^5	4.33	11.70	8.37	6.70
120	10^3	4.07	10.46	7.97	6.14
	10^4	4.05	10.09	7.88	6.09
	10^5	4.03	9.83	7.82	6.06
200	10^3	4.47	11.94	8.13	6.25
	10^4	4.08	11.09	7.95	6.16
	10^5	4.02	10.46	7.82	6.08

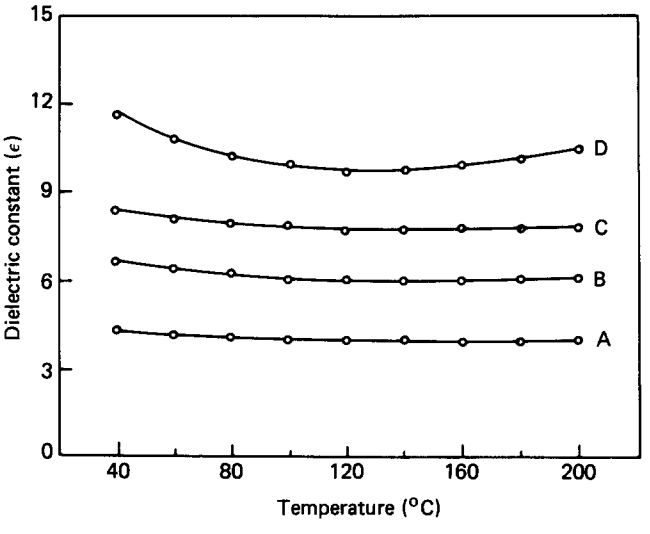

Figure 10 Dependence of dielectric constant on temperature at a fixed frequency of 10^5 Hz. A, undoped; B, $SnCl_2$; C, $HgCl_2$; D, $CoCl_2$ doped polyimide films

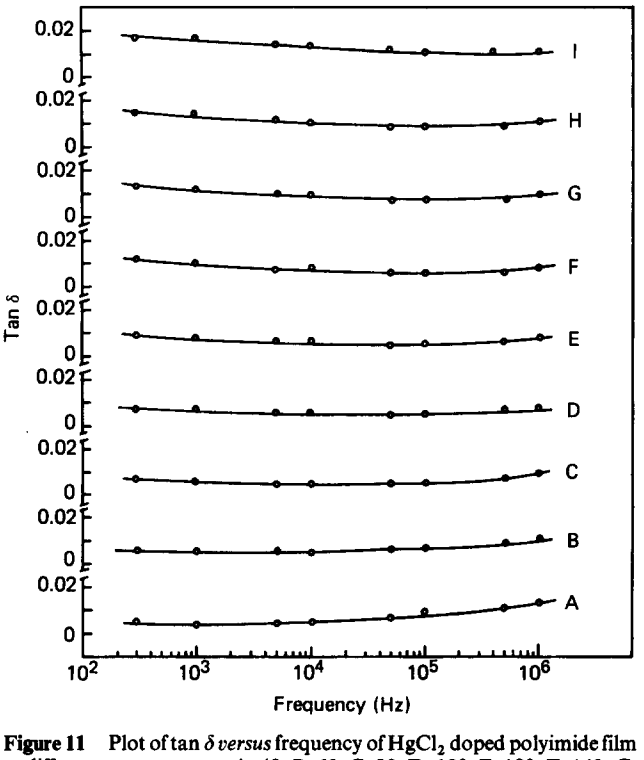

Figure 11 Plot of tan δ *versus* frequency of $HgCl_2$ doped polyimide film at different temperatures: A, 40; B, 60; C, 80; D, 100; E, 120; F, 140; G, 160; H, 180; I, 200°C

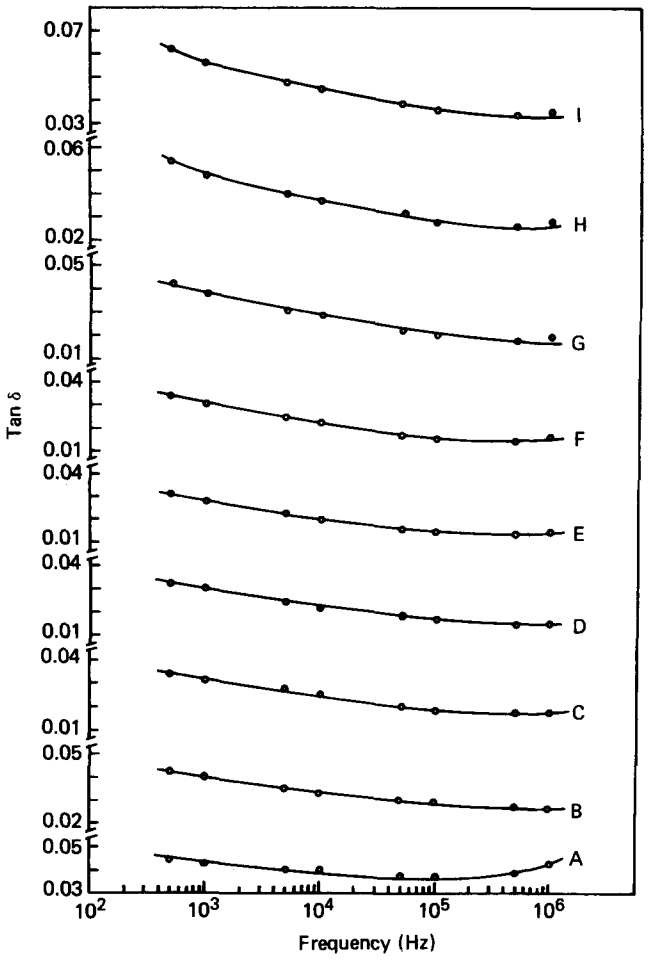

Figure 12 Plot of tan δ *versus* frequency of $CoCl_2$ doped polyimide film at different temperatures: A, 40; B, 60; C, 80; D, 100; E, 120; F, 140; G, 160; H, 180; I, 200°C

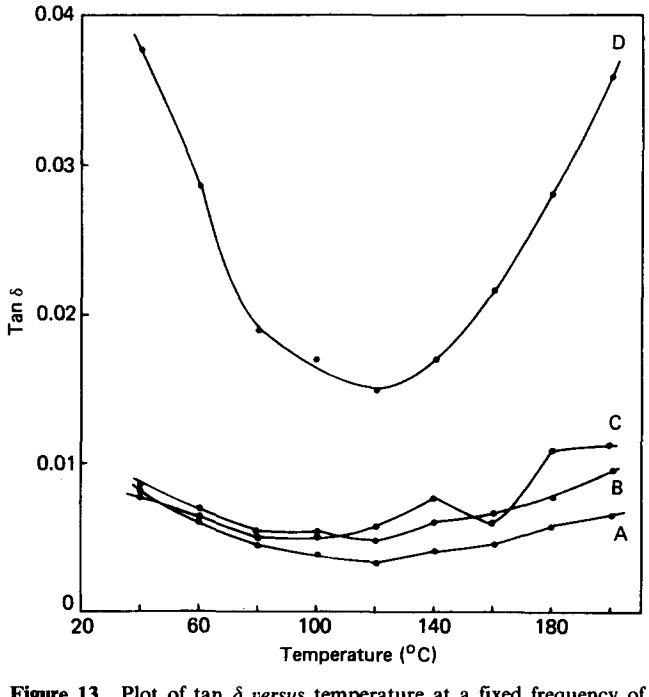

Figure 13 Plot of tan δ *versus* temperature at a fixed frequency of 10^5 Hz. A, $SnCl_2$; B, $HgCl_2$; C, undoped; D, $CoCl_2$ doped polyimide film

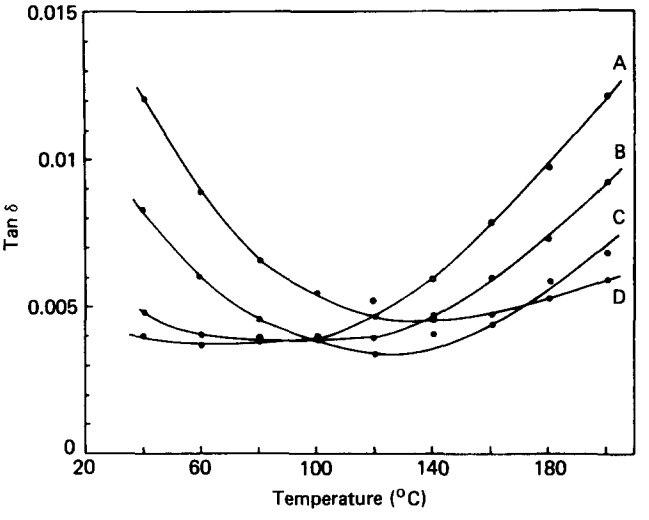

Figure 14 Plot of tan δ *versus* temperature of $SnCl_2$ doped polyimide film at different frequencies: A, 10^3; B, 10^4; C, 10^5; D, 10^6 Hz

On the basis of the above studies, it is concluded that in the presence of dopants the current–voltage characteristics of PI are altered and dependent on field and temperature. No significant increase in conductivity is observed in the presence of metallic halides. The dielectric constant of PI film increased by doping with metallic halides. The loss factor is also affected in the presence of dopants.

REFERENCES

1 Ezzell, S. A., Furstch, T. A., Khor, E. and Taylor, L. T. *J. Polym. Sci., Polym. Chem. Edn.* 1983, **21**, 865
2 Ezzell, S. A. and Taylor, L. T. 'Polyimides: Synthesis, Characterisation and Applications' (Ed. K. L. Mittal), Vol. 1, Plenum Press, New York, 1984, p. 189
3 Furstch, T. A., Taylor, L. T., Fritz, T. W., Fortner, G. and Khor, E. *J. Polym. Sci., Polym. Chem. Edn.* 1982, **20**, 1287
4 Khor, E. and Taylor, L. T. 'Metal Containing Polymeric Systems' (Eds. J. E. Sheats, C. E. Carraher and C. U. Pittman), Plenum Press, New York, 1985, p. 367
5 Taylor, L. T. and St Clair, A. K. 'Polyimides: Synthesis, Characterisation and Applications' (Ed. K. L. Mittal), Vol. 2, Plenum Press, New York, 1984, p. 617
6 Auerback, A. *J. Electrochem. Soc.* 1984, **131**, 937
7 Ezzell, S. A. and Taylor, L. T. *Macromolecules* 1984, **17**, 1627
8 Boggess, R. and Taylor, L. T. *ACS Polym. Prepr.* 1985, **26**(1), 94
9 Madeleine, D., Spillane, S. and Taylor, L. T. *ACS Polym. Prepr.* 1985, **26**(1), 92
10 Rancourt, J. D., Boggess, R. K. and Taylor, L. T. *Polym. Mater. Sci. Eng.* 1985, **53**, 74
11 Boggess, R. K. and Taylor, L. T. *J. Polym. Sci., Polym. Chem. Edn.* 1985, **23**
12 Khor, E. and Taylor, L. T. *Macromolecules* 1982, **15**, 379
13 Rancourt, J. D. and Taylor, L. T. *Polym. Mater. Sci. Eng.* 1986, **54**, 124
14 Varma, I. K., Saxena, S., Tripathi, A., Goel, T. C. and Varma, D. S. *J. Appl. Polym. Sci.* 1986, **32**, 3987
15 Varma, I. K., Saxena, S., Tripathi, A., Goel, T. C. and Varma, D. S. *ACS Polym. Prepr.* 1985, **26**(2), 168
16 Charlot, G. 'Colorimetric Determination of Elements', Elsevier Publishing Co., Amsterdam, 1964, p. 104
17 Hanscomb, J. R. and Calderwood, J. H. *J. Phys. D: Appl. Phys.* 1973, **6**, 1093
18 Nevin, J. H. and Summe, G. L. *Microelectron. Reliab.* 1981, **21**(5), 699