Solvent compatible cobalt ion species as additives to polyimides

E. KHOR*, H. S. O. CHAN, T. S. ANDY HOR,
Chemistry Department, National University of Singapore, Singapore

A series of solvent compatible cobalt compounds have been synthesized as additives to polyimides. The resultant cobalt doped polyimide films are smooth, flexible and shiny. The doped films display lowered electrical resistivities by 3 to 4 orders of magnitude compared to the undoped polyimide. Additive migration to the surface of the film generating a cobalt oxide layer has been observed.

1. Introduction

In recent years the study of metal doping into polyimide films has been pursued with fervor as part of a concerted effort in the field of conductive polymers. While success has only occurred with one particular palladium additive [1], a whole series of compounds with differing metal systems have been investigated [2]. One of the more promising systems is based on the cobalt metal ion [3], which has been reported to give polyimide films that display a semiconductive surface [4]. In these studies however, many additives were rejected because of their solvent incompatibility [2], limiting the choice of cobalt precursor to $CoCl_2$. In view of the promising semiconductivity of cobalt ion generated polyimide films, it would be interesting if more cobalt ion based additives could be obtained to further investigate such semiconductive nature of cobalt doped polyimide films. We recently communicated our approach in the choice of additives into polyimides based on a more thorough consideration of the criteria that a potential dopant should possess [5]. We have found that solvent compatible metal additive systems can be devised. In this regard we would like to report on our study of generating more solvent compatible cobalt(II) ion additives and their resultant polyimide films.

2. Experimental procedure

All chemical reagents were obtained from commercial sources and used without further purification except for oxydianiline (ODA) which was vacuum sublimed before use and dimethylacetamide (DMAc) which was stored under N_2 and molecular sieves.

Cobalt complexes were synthesized by adding equimolar quantities of cobalt chloride hexahydrate and ligand under conditions summarized in Table I. Typical cobalt doped polyimide films were prepared by dissolving equal moles of diamine and dianhydride in DMAc to give a solution containing 25% solids. This solution was stirred under N_2 for 6 h and the metal dopant (mole ratio metal to polymer summarized in

Table II) added as a solid and stirred for a further 18 h. The polyamic acid solution was cast on a clean glass plate and cured at 80° C for 20 min, 100, 200, 300° C for 1 h each. Films were peeled off the glass plate upon cooling.

Elemental analyses were performed by the Microanalytical Laboratory, Chemistry Department, National University of Singapore. Thermogravimetry were performed on a Dupont 9900 Thermal Analyzer System in air (75 cc min^{-1}) and a heating rate of 10 deg min^{-1}. Electrical measurements were performed following the standard ASTM D257 method using a 3 point probe with a Keithley 617 electrometer/source. An electrification time of 5 min was used. X-ray photoelectron spectroscopy was performed on Kratos 300 spectrometer using Mg as an X-ray source.

3. Results and discussion
3.1. Dopants

Cobalt complexes have been synthesized with the following ligands: 4-aminophenylsulfone (APS), 4-aminophenyldisulfide (APDS), 4,4′-methylenedianiline (MDA),1,4-phenylenediamine (PDA) and 1,6-hexanediamine (HDA). The syntheses are very simple and except for the HDA complex (which was dissolved in dimethylformamide), all complexes were found to be soluble in the reaction solvent DMAc. The poor solubility of the HDA complex could be due to the aliphatic character of the ligand, which would make it less suited to a polar environment present when using DMAc.

Figs 1 and 2 show the thermograms of the complexes in air. For comparison, $CoCl_2 \cdot 6H_2O$ was used as reference. The $CoCl_2 \cdot 6H_2O$ thermogram shows the loss of water in 3 steps by 200° C. Above this point, the loss of chloride appears to take place giving at 600° C a residue corresponding to Co_3O_4 as the experimental percent residue of 34% agrees well with that calculated for cobalt oxide (34%) as opposed to that based on cobalt metal alone (Table II). It is not unreasonable to suggest that the oxide is the species

---

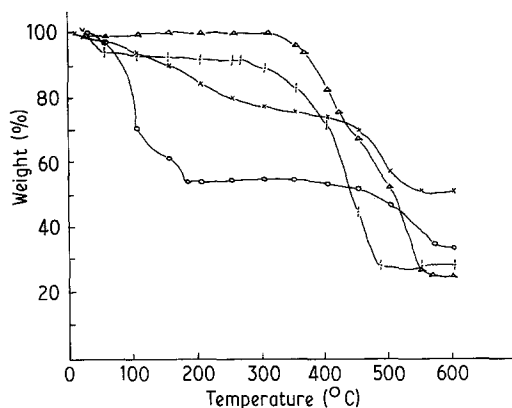*Figure 1* Thermograms of cobalt H₂O, MDA, PDA, HDA complexes (in an airflow of 75 cc/min and a heating rate of 10°C/min. MDA, (—△—△—); PDA, (—│—│—); HDA, (-x-x-); 6H₂O (-○-○-).

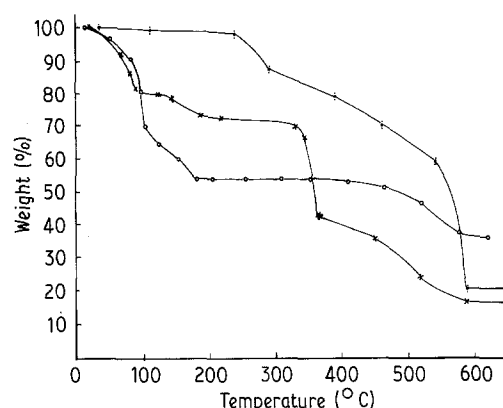*Figure 2* Thermograms of cobalt H₂O, APS, APDS complexes (in an airflow of 75 cc/min and a heating rate of 10°C/min). APS, (-x-x-); APDS, (—·—·—); 6H₂O, (—○—○—).

generated since the decomposition was performed in air.

Turning to the thermograms of the complexes, it can be seen immediately that the complexes do not exhibit a straightforward decomposition pattern compared to $CoCl_2 \cdot 6H_2O$. The MDA and APDS based complexes appear to decompose to cobalt oxide. Their residues of 24 and 22% agree well with that calculated for cobalt oxide 24.5 and 20% respectively. The other 2 complexes (APS and PDA) appear to decompose beyond the oxide stage but not completely to the metal. This is easily seen when a comparison is made between the calculated and observed values of their percent residues (Table II). The HDA complex on the other hand displays characteristics of incomplete decomposition (the percentage residue is higher even for that calculated for the oxide). In summary, these

$CoCl_2$ based complexes do exhibit the general trend of decomposing to Co_3O_4 and would then be expected to behave like $CoCl_2$ upon doping. It should be noted that at 300°C, the temperature of imidization, decomposition to the oxide is incomplete and suggests that in the cobalt doped polyimide films, curing environment plays a role in generating cobalt oxide like species.

3.2. Polyimide films

Polyimide films derived with the monomer combination of 3,3',4,4'-benzophenonetetracarboxylicacid-dianhydride (BTDA) and oxydianiline (ODA) doped with the above five different solvent compatible cobalt complexes have been prepared. The films are typically smooth, flexible and shiny dependent on the amount of cobalt present.

As an example, the $CoCl_2 \cdot MDA$ doped film with highest metal content (2:1 polymer/metal ratio) is

TABLE I Syntheses procedure for cobalt complexes

Complex	Synthesis procedure	C	H	N
CoCl₂6H₂O	dried *in vacuo* 120°C, 12 h		–	
[CoCl₂ · MDA]	CoCl₂/MDA/MeOH, stir 16 h	47.90 (47.56)	4.41 (4.27)	8.65 (8.54)
[CoCl₂ · APS · 2H₂O]	CoCl₂/MeOH, APS/CH₃CN stir 16 h	34.59 (34.78)	3.15 (3.86)	6.96 (6.76)
[CoCl₂ · APDS · 2H₂O]	CoCl₂/MeOH, APDS/hot MeOH stir 16 h	34.76 (34.78)	2.84 (3.86)	6.78 (6.76)
[CoCl₂ · PDA]	CoCl₂/PDA/MeOH stir 16 h	29.24 (30.26)	2.92 (3.36)	11.63 (11.77)
[Co₂Cl₄ · HDA · 4H₂O]	CoCl₂/MeOH, HDA/CH₃CN stir 16 h	15.53 (16.07)	4.51 (5.36)	6.32 (6.25)

MDA 4, 4'-methylenedianiline, APS 4-aminophenylsulfone, APDS 4-aminophenyldisulfide, PDA 1, 4-phenylenediamine, HDA 1, 6-hexanediamine.

TABLE II Calculated percentage composition of cobalt complexes

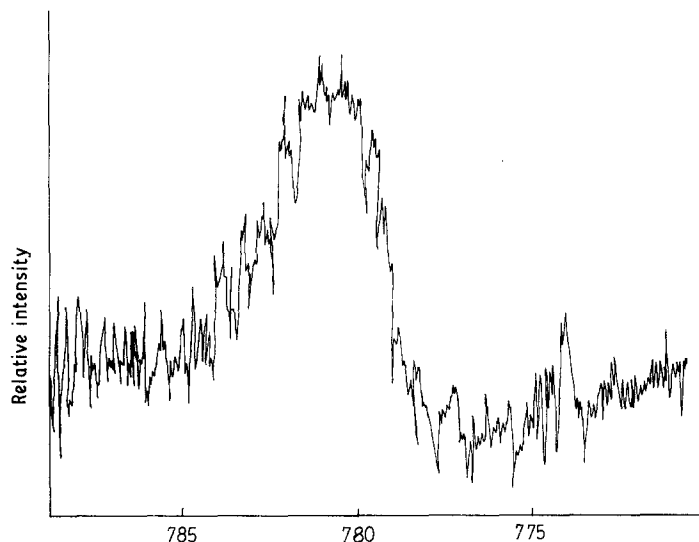| Dopant	Calculated				Found
	% H₂O	% Ligand	% Cl	% Co (as oxide)	% Residue
CoCl₂ · 6H₂O	45%	–	30%	25% (33%)	32%
[CoCl₂ · MDA]	–	61%	21%	18% (24.5%)	24%
[CoCl₂ · APS · 2H₂O]	9%	60%	17%	14% (20%)	17.5%
[CoCl · APDS · 2H₂O]	9%	60%	17%	14% (20%)	22%
CoCl₂PDA]	–	45%	30%	25% (34%)	28%
[Co₂Cl₄ · HDA · 2H₂O]	16%	26%	32%	26% (36%)	42%

Figure 3 XP spectrum of cobalt $2P_{3/2}$ Region of the $CoCl_2 \cdot$ MDA doped polyimide film.

tough, more brittle and very shiny black. This shiny feature probably indicates a semiconductive cobalt oxide layer. The next film in the series (i.e. the 4:1 ratio) is more flexible and less shiny. The film with a 16:1 ratio of polymer to metal exhibits essentially the undoped polymer characteristics being yellow-brown in colour and very flexible.

These features are exhibited by the other doped films stated in Table III i.e. the heavier doped films being darker, shinier and more brittle than their lighter doped counterparts.

3.3. Thermogravimetry

The results of thermogravimetric analysis are shown in Table III. As would be expected, the procedural decomposition temperatures (PDT) (the temperature corresponding to a 10% weight loss) of all doped films are lower than that of the undoped polyimide films. This trend is also followed when one considers the polymer metal ratio. The heavier the doping, the more detrimental the thermal stability.

Using the $CoCl_2 \cdot$ MDA doped polyimides again as example, it can be seen that the film having 3.66% cobalt has the lowest PDT of 430° C. This increases to 465° C when the metal content is decreased to 2.18%. Finally, the films having 1.26 and 0.86% metal have the same PDT of 480° C. This last point suggests that at dilute concentrations of doping, the metal is dis-

persed well enough not to create a concentration effect, only a lowering of the PDT.

The $CoCl_2 \cdot$ APDS $\cdot H_2O$ doped films appear to give unique results. Considering the high metal content in these two films, the PDTs are exceptionally high. The film with 3.31% cobalt has a PDT of 490° C while the film having 1.96% cobalt has a PDT of 520° C. One possible answer may lie in the fact that the metal probably concentrates on the surface of the film, as evident in its electrical data (vide infra). This would mean that there is less metal in the bulk of the film, leading to a reduced influence of additive on the polymer thermal character, giving rise to the higher observed PDTs.

3.4. X-ray photoelectron spectroscopy

Fig. 3 shows the X-ray photoelectron spectrum of the $CoCl_2 \cdot$ MDA doped polyimide film air side (the side which was exposed to air during imidization) for the
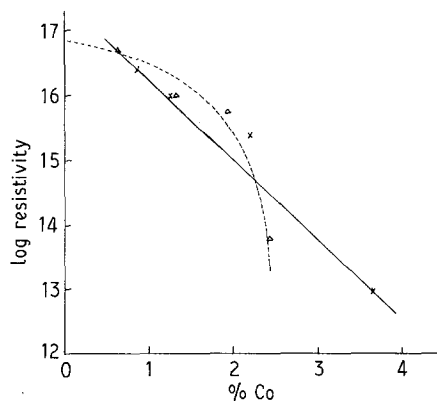

Figure 4 Volume electrical resistivity against % cobalt profile for $CoCl_2$ MDA and PDA doped polyimide films. MDA, (x); PDA, (Δ).

TABLE III PDT* for cobalt doped BTDA–ODA derived polyimide films

Dopant	Polymer/metal ratio	PDT(°C)	% Cobalt found (calc.)
undoped	–	540	–
$CoCl_2$	2:1	460	3.59 (4.90)
	4:1	478	1.51 (2.85)[†]
[$CoCl_2 \cdot$ MDA]	2:1	430	3.66 (4.19)
	4:1	465	2.18 (2.37)
	8:1	480	1.26 (1.28)
	16:1	480	0.86 (0.60)
[$CoCl_2 \cdot$ APS $\cdot H_2O$]	2:1	420	3.54 (4.05)
	4:1	480	2.78 (2.32)
[$CoCl_2 \cdot$ APDS $\cdot H_2O$]	2:1	490	3.31 (3.97)
	4:1	520	1.96 (2.35)
[$Co_2Cl_4 \cdot$ HDA $\cdot H_2O$]	2:1	410	6.18 (4.48)
	4:1	450	2.21 (2.64)
[$CoCl_2 \cdot$ PDA]	2:1	440	2.42 (4.47)
	4:1	490	1.93 (2.46)
	8:1	490	1.30 (1.28)
	12:1	480	0.66 (0.67)

*PDT: Procedural decomposition temperature in air, the temperature corresponding to a 10% weight loss.
[†] See [3].

Co $2P_{3/2}$ region. The peak is referenced to the C 1s peak taken as 285.0 eV. This gives the Co $2P_{3/2}$ peak a binding energy of 780.2 eV, which is much higher than the reported binding energy if 777.9 eV for cobalt (O). This suggests that the cobalt is in an electropositive environment probably of Co(II)/Co(III) as has been previously suggested to arise from Co_3O_4 [6]. The experimentally determined carbon to cobalt ratio found was 100:2.35 (after correcting for the sensitivity factor for cobalt). This is higher than the calculated ratio of 100:1.7241 based on a molar ratio of 2:1 polymer to cobalt additive. This suggests that the air surface is cobalt rich. It is not unreasonable to suggest that migration of cobalt to the surface of the film had occurred during imidization which is a typical characteristic of doped polyimide systems. Upon scanning the glass surface of the film, only trace amounts of cobalt at best, could be detected. Therefore the distribution of cobalt in these films appear to be concentrated at the top due to dopant migration, falling off the trace levels as the bulk of the film is progressed.

3.5. Electrical resistivities

Room temperature electrical resistivity measurements have been performed on all cobalt derived polyimide films and are reported in Table IV. All doped films appear to exhibit lowered volume electrical resistivity compared to its undoped counterpart. In general, films that have lowered volume resistivity exhibit a corresponding lowering of surface resistivities. This is exemplified by the $CoCl_2$ doped film which displays similar volume and surface resistivities.

A general trend observed with the additives employed in this study is that there appears to be slight improvement in the lowering of resistivities by all additives compared to $CoCl_2$. For example, the MDA, APS and APDS complexes all have similar percentages of cobalt to the $CoCl_2$ film and yet are one order of magnitude lower in resistivity. A possible explanation could lie in the fact that the new cobalt additives are larger in size than $CoCl_2$, and thus are more readily trapped

between the polymer chains during imidization, which could provide a more efficient conduction path than cobalt chloride as being smaller they would tend to rise to the top. This is not to say that migration of dopant had not occurred as suggested earlier in the XPS discussion, only that when compared to $CoCl_2$, there is a relatively higher dopant content in the bulk of the film.

The four different concentrations of the MDA complex display differences in the resistivities in their resultant polyimide films. The most heavily doped film displays the lowest volume resistivity. As the dopant concentration is decreased, there appears to be a tapering off effect as the resistivity values approach that typical for the undoped polymer (Fig. 4). This effect is also displayed with the PDA based dopant.

The APDS based film deserves particular mention as the resistivities are relatively low considering that its metal percent is typical to the other films. It was noted earlier that these films had atypical PDTs. It was suggested that the reason for the abnormal PDT was that there was a concentration of metal on the surface. The electrical data also indicates that such an occurrence had taken place i.e. the APDS additive more than any other dopant, concentrates predominantly at the air surface of the films. Hence the differences in surface resistivities between the air and glass surfaces (two orders of magnitude).

4. Conclusion

Polyimide films using five new dopants have been synthesized at several polymer:metal ratios. Thermal, spectral, elemental and electrical characterizations have been performed. All dopants appear to be compatible additives which display lowering of electrical resistivities comparable or better than $CoCl_2$ doped polyimides.

Acknowledgements

TABLE IV Electrical resistivities for cobalt doped polyimide films

Dopant	Polymer/metal ratio	% Co	Resistivities		
			Volume (Ohm-cm)	Surface	
				air (Ohm)	glass (Ohm)
undoped	–	–	8×10^{16}	5×10^{15}	2×10^{16}
$CoCl_2$	2:1	3.59	5×10^{14}	2×10^{14}	7×10^{14}
[$CoCl_2 \cdot$ MDA]	2:1	3.66	1×10^{13}	1×10^{14}	3×10^{14}
	4:1	2.18	4×10^{15}	1×10^{14}	1×10^{14}
	8:1	1.26	1×10^{16}	5×10^{15}	1×10^{16}
	16:1	0.86	4×10^{16}	6×10^{15}	4×10^{16}
[$CoCl_2 \cdot$ APS $\cdot 2H_2O$]	2:1	3.54	8×10^{13}	5×10^{13}	3×10^{13}
	4:1	2.78	3×10^{14}	4×10^{12}	2×10^{15}
$CoCl_2 \cdot$ APDS $\cdot 2H_2O$]	2:1	3.31	2×10^{12}	3×10^{11}	3×10^{13}
	4:1	1.96	2×10^{14}	1×10^{12}	1×10^{14}
[$Co_2Cl_4 \cdot$ HDA $\cdot 4H_2O$	2:1	6.36	3×10^{13}	4×10^{13}	6×10^{13}
	4:1	2.21	2×10^{16}	1×10^{16}	2×10^{16}
[$CoCl_2 \cdot$ PDA]	2:1	2.42	8×10^{13}	4×10^{12}	3×10^{13}
	4:1	1.93	9×10^{15}	2×10^{16}	3×10^{16}
	8:1	1.30	1×10^{16}	1×10^{16}	3×10^{15}
	16:1	0.66	7×10^{16}	4×10^{15}	2×10^{16}

References

1. L. T. TAYLOR, A. K. ST. CLAIR, U.S. Patent 284 (1981) 461.
2. L. T. TAYLOR, and A. K. ST. CLAIR, in "Polyimides, Synthesis, Characterization and Applications," edited by K. L. Mittal, (Plenum Press, New York, 1984) p. 617.
3. E. KHOR, and L. T. TAYLOR, in "Metal Containing Polymer Systems," edited by J. E. Sheats, C. E. Carraher Jr. and C. U. Pittman, Jr. (Plenum Press, New York, 1985) p. 367.
4. J. D. RANCOURT, R. K. BOGGESS and L. T. TAYLOR, *Polym. Mater. Sci. Engr.* **55** (1986) 328.
5. E. KHOR, H. S. O. CHAN, T. S. A. HOR and J. R. LUSTY, *J. Polym. Sci., Part C, Polym. Lett.* **25** (1987) 471.
6. R. K. BOGGESS and L. T. TAYLOR, *J. Polym. Sci., Part A, Polym. Chem.* **25** (1987) 685.