*Thermochimica Acta*, 230 (1993) 129–135
Elsevier Science Publishers B.V., Amsterdam
*SSDI* 0040-6031(93)01350-C

# Preparation, structural characterisation, thermal and electrical studies of cobalt(II) chloride and zinc(II) chloride compounds of poly(acrylamide)

J.R. Allan *, P.C. Beaumont, G.H.W. Milburn and I.J. Wood

*Department of Applied Chemical and Physical Sciences, Napier University, Edinburgh EH10 5DT (UK)*

(Received 31 March 1993; accepted 10 May 1993)

## Abstract

The reaction of poly(acrylamide) with cobalt(II) chloride and zinc(II) chloride produced compounds of stoichiometry $[Co(C_3H_5NO)_{10}Cl_26H_2O]_n$ and $[Zn(C_3H_5NO)_{14}Cl_2H_2O]_n$. In these compounds the metal ions are in tetrahedral environments. Thermal decomposition studies show that these compounds first lose water followed by the organic ligand and halogen to give the metal oxides. Poly(acrylamide) was found to have a glass transition temperature of 168°C. The room temperature electrical conductivities for poly(acrylamide) and its cobalt and zinc polymers lie in the range $9.97 \times 10^{8}$ to $7.71 \times 10^{-7}$ and show ohmic conductivity.

## INTRODUCTION

Metal containing polymers are numerous and include polymer bound coordinating ligands [1–3]. In this paper we discuss this type of polymer system which has been produced from acrylamide and the chlorides of cobalt(II) and zinc(II). Spectral and magnetic studies have been used to obtain information about the environment of the metal ions in this polymer system. We also report thermal analysis and electrical conductivity studies in order to demonstrate the stability and potential semiconductor properties of poly(acrylamide) and its metal polymers.

## EXPERIMENTAL

### *Preparation of compounds*

#### *Preparation of poly(acrylamide)*

Acrylamide (5 g) was purified by recrystallisation from acetone. The acrylamide was then dissolved in acetone (25 cm$^3$), after which recrystallised benzoyl peroxide (0.1 g) was added. This solution was placed in a sealed jar under nitrogen and left in an oven at 60°C for 2 h. The

---

* Corresponding author.

poly(acrylamide) which precipitated out was then filtered and dried in a vacuum oven.

### *Preparation of the metal polymers of poly(acrylamide) with cobalt(II) chloride and zinc(II) chloride*

The polyacrylamide was dissolved in deionised water. Excess metal chloride was added and the mixture was refluxed for 72 h with continuous stirring. The aqueous solution was then poured into three times its volume of methanol. The complexed polymer precipitated immediately and was filtered. This process was repeated to purify the metal polymer.

### *Apparatus and measurement*

The concentration of the metal ion was determined using a Perkin-Elmer 373 atomic absorption spectrophotometer; carbon, hydrogen and nitrogen analyses were carried out on a Carlo Erba elemental analyser; the chloride was estimated gravimetrically [4].

Infrared spectra were obtained using KBr discs (4000–600 $cm^{-1}$ range) and polythene discs (600–200 $cm^{-1}$ range) on a Perkin-Elmer infrared spectrophotometer, model 598.

The electronic spectra for the cobalt compound were obtained as a diffuse reflectance spectra on a Beckman Acta MIV spectrophotometer. The magnetic moment for the cobalt compound was measured using a magnetic balance employing the Gouy method and $Hg[Co(SCN)_4]$ as a calibrant. The thermal analysis measurements were carried out on a Stanton Redcroft Model STA 1500 thermobalance. Thermogravimetric (TG) and differential thermal analysis (DTA) traces were obtained at a heating rate of 6°C $min^{-1}$ in static air. The 20–800°C temperature range was studied.

Electrical measurements were carried out on discs prepared by compressing each powdered sample in a hydraulic press. The current versus voltage characteristics at room temperature were obtained using an electrometer to register current and digital voltmeter for the voltage. Readings of current were obtained for a series of voltages. The thickness of each disc, which was needed for calculating the conductivity was measured using a micrometer.

## RESULTS AND DISCUSSIONS

The experimental results for the elemental analysis of the poly(acrylamide) and its metal polymers are listed in Table 1 and are in good agreement with the given formulae.

The wavenumbers of the IR absorption bands, as well as their description and assignments are given in Table 2. In the cobalt compound

TABLE 1

Analysis of compounds in %

| Compound[a] | | M | C | N | H | Cl |
|---|---|---|---|---|---|---|
| $[C_3H_5NO]_n$ | Theory | | 50.69 | 19.70 | 7.09 | |
| | Found | | 49.86 | 19.31 | 7.19 | |
| $[Co(C_3H_5NO)_{10}Cl_26H_2O]_n$ | Theory | 6.21 | 38.00 | 14.77 | 6.59 | 7.47 |
| | Found | 5.59 | 38.36 | 14.26 | 6.43 | 7.09 |
| $[Zn(C_3H_5NO)_{14}Cl_22H_2O]_n$ | Theory | 5.60 | 43.21 | 16.79 | 6.38 | 6.07 |
| | Found | 5.23 | 43.86 | 16.06 | 6.61 | 6.29 |

[a] $C_3H_5NO$ is acrylamide.

the band at 3420 cm$^{-1}$ indicates the presence of water of crystallisation. The change in the position of the $NH_2$ vibration to higher wavenumbers on complexation shows that no bonding has taken place between the nitrogen atom of the $NH_2$ group and the metal ions [5]. The $\nu$(C=O) vibration is found to move to lower wavenumbers on complexation, indicating that bonding is taking place between the oxygen atom of the C=O group and the metal ions [6]. The C=C vibration which is observed in the IR spectrum of acrylamide at 1612 cm$^{-1}$ is absent in the poly(acrylamide) spectrum and in the spectra of its metal polymers. This is consistent with conversion of a double bond to a single bond between carbon atoms on polymerisation. The bands in the far-IR spectra of the metal polymers in the range 290–315 cm$^{-1}$ are assigned to the $\nu$(M–Cl) vibrations and indicate that the metal ions are in a tetrahedral environment [7, 8]. The bands observed in the IR spectra of the metal polymers at 360–390 cm$^{-1}$ have been assigned to the $\nu$(M–O) vibrations.

In the electronic spectrum of the cobalt polymer, bands are observed at 4942, 14 450 and 18 519 cm$^{-1}$ which corresponds to the d–d transitions of $^4A_2(F) \rightarrow {}^4T_2(F)$; $^4A_2(F) \rightarrow {}^4T_1(F)$; $^4A_2(F) \rightarrow {}^4T_1(P)$. The position and intensity of these bands further support the suggestion that the cobalt ions are in the tetrahedral environment in the polymer [7]. The magnetic

TABLE 2

Infrared spectra (4000–200 cm$^{-1}$)

| Compound | $\nu_{O-H}(H_2O)$ | $\nu(NH_2)$ | $\nu$(CO) | $\nu$(M–O) | $\nu$(M–Cl) |
|---|---|---|---|---|---|
| $[C_3H_5NO]_n$ | | 3331s<br>3190s | 1667s | | |
| $[Co(C_3H_5NO)_{10}Cl_26H_2O]_n$ | 3414s | 3338s<br>3202s | 1658s | 360m | 304s |
| $[Zn(C_3H_5NO)_{14}Cl_22H_2O]_n$ | 3412s | 3360s<br>3198s | 1652s | 390m | 315s<br>290s |

Key: s, Strong; m, medium. $C_3H_5NO$ is acrylamide.

moment of the polymer is 4.42 BM and this is further evidence of a tetrahedral environment for the cobalt ions [7].

The cobalt and zinc polymers were obtained as powders and not as single crystals and this means that no complete structural determination can be carried out. However the spectroscopic and magnetic data enable us to suggest possible structures for the metal polymers. The cobalt polymer comprises a repeating unit structure containing two chains each of acrylamide molecules linked through one cobalt ion in a tetrahedral coordination with two chloride ions and two oxygen atoms, one from an acrylamide molecule in each of the chains. Eight acrylamide molecules in each structural unit are not bonded to cobalt ions. The water molecules are attached by hydrogen bonding. The zinc polymer has a similar structural unit except that in this case twelve molecules of acrylamide are not bonded to zinc ions. The water molecules are again attached by hydrogen bonding.

The TG and DTA traces for poly(acrylamide) and the metal polymers are shown in Figs. 1–3. The TG trace for poly(acrylamide) (Fig. 1) shows that the compound begins to decompose at 215°C and finishes its decomposition at 646°C. The DTA trace shows that endothermic and exothermic peaks are associated with the decomposition process. A glass transition ($T_g$) is observed on the DTA trace at 168°C. The TG and DTA traces for the metal polymers (Figs. 2 and 3) show that they each undergo an endothermic reaction with loss of a water molecule followed by endothermic and exothermic reactions and the loss of the organic ligands and halogen to give the metal oxides. The experimental mass losses observed for the decomposition processes are in good agreement with the

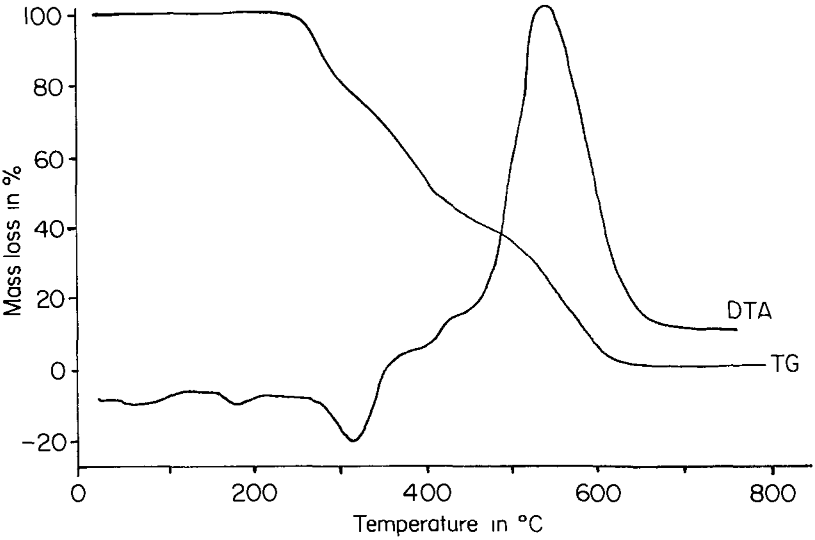

Fig. 1. TG and DTA traces for $[C_3H_5NO]_n$; sample mass, 6.42 mg.

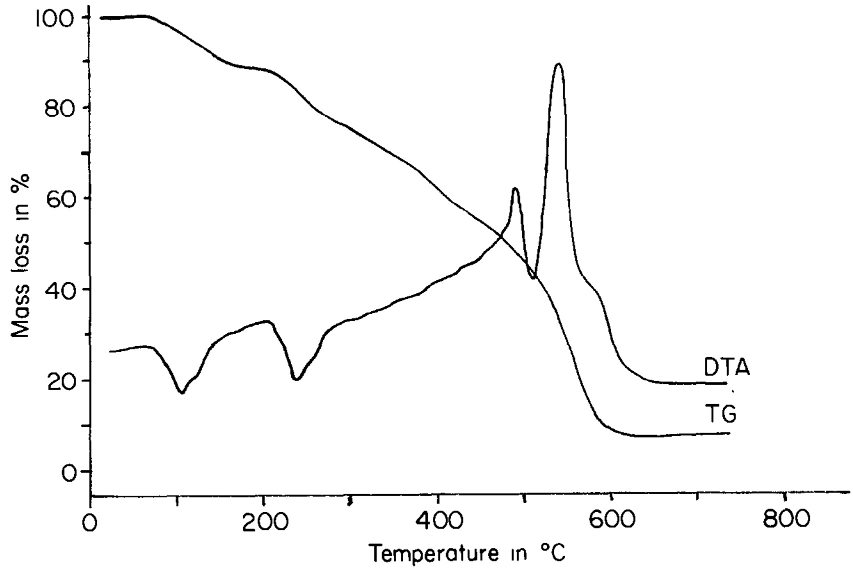

Fig. 2. TG and DTA traces for $[Co(C_3H_5NO)_{10}Cl_2 6H_2O]_n$; sample mass, 11.65 mg.

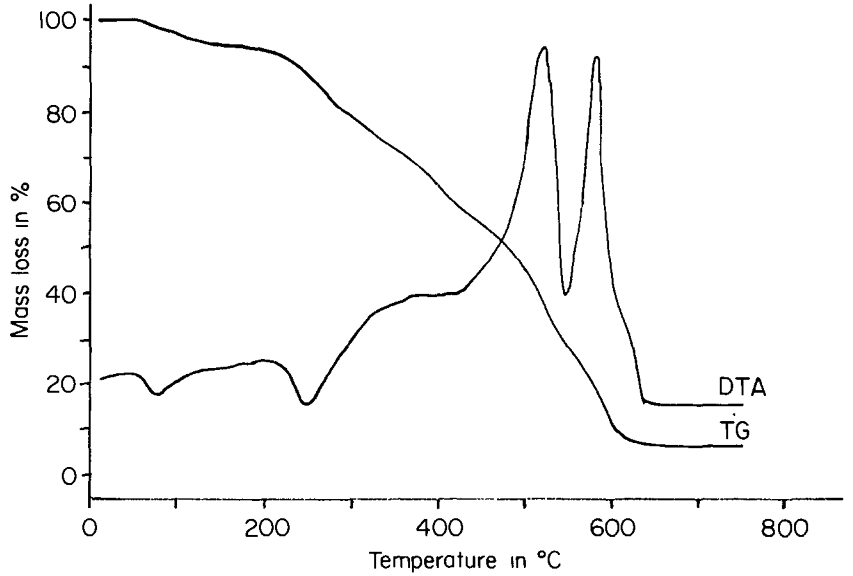

Fig. 3. TG and DTA traces for $[Zn(C_4H_5NO)_{14}Cl_2 2H_2O]_n$; sample mass, 11.19 mg.

TABLE 3

Dehydration processes of the metal complexes

| Process | Initial decomposition temp./°C | Thermal nature of transformation [a] | Mass loss/% | |
|---|---|---|---|---|
| | | | Calc. | Found |
| $[Co(C_3H_5NO)_{10}Cl_2 6H_2O]_n \rightarrow [Co(C_3H_5NO)_{10}Cl_2]_n$ | 64 | endo | 11.40 | 11.24 |
| $[Zn(C_3H_5NO)_{14}Cl_2 2H_2O]_n \rightarrow [Zn(C_3H_5NO)_{14}Cl_2]_n$ | 56 | endo | 3.08 | 3.24 |

[a] endo, Endothermic (from DTA trace).

TABLE 4

Decomposition processes of poly(acrylamide) and its metal polymers

| Process | Temperature range/°C | Thermal nature of transformation [a] | Mass loss/% | |
|---|---|---|---|---|
| | | | Calc. | Found |
| $[C_3H_5NO]_n \rightarrow$ pyrolytic process | 215–660 | endo/exo | 100.00 | 100.00 |
| $[Co(C_3H_5NO)_{10}Cl_2]_n \rightarrow Co_3O_4$ | 204–636 | endo/exo | 80.14 | 79.85 |
| $[Zn(C_3H_5NO)_{14}Cl_2]_n \rightarrow ZnO$ | 182–652 | endo/exo | 89.95 | 88.97 |

[a] endo, Endothermic; exo, exothermic (from DTA traces).

expected theoretical mass losses (Tables 3 and 4). No glass transitions were observed for the metal polymer systems because of their low initial decomposition temperatures.

The measured room temperature electrical conductivities $\sigma$ of poly(acrylamide) and its metal polymers are listed in Table 5. The room temperature current $I$ versus voltage $V$ characteristics were obtained under conditions of rising and falling voltage in both polarities. The $I$–$V$ relationship for all the polymers was found to be linear throughout the voltage range studied, indicating that the electrical conduction was ohmic. The electrical conductivities reported in Table 5 are calculated from the

TABLE 5

Electrical conductivity of compounds

| Compound | $\sigma$ [a]$/(\Omega^{-1}\ m^{-1})$ |
|---|---|
| $[C_3H_5NO]_n$ | $7.71 \times 10^{-7}$ |
| $[Co(C_3H_5NO)_{10}Cl_2 6H_2O]_n$ | $9.84 \times 10^{-8}$ |
| $[Zn(C_3H_5NO)_{14}Cl_2 2H_2O]_n$ | $9.97 \times 10^{-8}$ |

[a] Room temperature (22°C) conductivity. $C_3H_5NO$ is acrylamide.

gradients of the $I$–$V$ plots and with the assumption that the current flow is perpendicular to the electrodes. The measured conductivities show that complexation of the acrylamide with cobalt and zinc chloride yields compounds whose conductivities are lower when compared to the uncomplexed poly(acrylamide). This would suggest that the metal and its stereochemistry are not involved in the conduction process and that the conduction pathway is via ligand molecules. It is postulated that the electrical conduction pathway is due predominantly to suitable orbitals of the ligand in close proximity to one another. On complex formation the presence of the metal ion will hinder the coordination pathway by increasing the intermolecular distance between the ligand orbitals, hence producing lower values for the electrical conductivities of the metal complexes listed in Table 5.

## REFERENCES

1 J.R. Allan, J. Birnie, B.R. Carson, D.L. Gerrard, A. Paton and K. Turvey, Plast. Rubber Process. Appl., 16 (1991) 79.
2 J.R. Allan, J. Birnie, B.R. Carson, D.L. Gerrard and K. Turvey, Eur. Polym. J., 27 (1991) 665.
3 J.R. Allan, J. Birnie, B.R. Carson, D.L. Gerrard and K. Turvey, Thermochim Acta, 180 (1991) 39.
4 A.I. Vogel, Qualitative Inorganic Analysis, Longmans, London, 1964, p. 266.
5 J.R. Allan, B.R. Carson, D.L. Gerrard and S. Hoey, Thermochim Acta, 153 (1989) 173.
6 J.R. Allan, A.D. Paton and K. Turvey, Thermochim Acta, 186 (1991) 293.
7 J.R. Allan and G.M. Baillie, J. Therm. Anal., 14 (1978) 291.
8 J.R. Allan, D.H. Brown, R.H. Nuttall and D.W.A. Sharp, J. Chem. Soc., (1966) 1031.