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Coordination polymers of copper(II) with some dicarboxysiloxane ligands

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Several new coordination polymers of copper(II) with different carboxylate ligands containing siloxane units were synthesized by equilibrium polycoordination reactions of copper(II) acetate with the proper dicarboxylic acid (i.e. 1,3-bis(3-carboxypropyl)tetramethyldisiloxane, α,ω-bis(3-carboxypropyl)oligodimethylsiloxane, and 1,3-bis(sebacomethyl)tetramethyldisiloxane) in solution (methanol), at room temperature. Some variations in the feed molar ratios were made. The resulting polymers having a polycoordination degree between 5 and 71 are soluble in a wide range of common organic solvents. The formation of polymers was proved by IR and UV–VIS absorption spectroscopy. The thermal behaviour of the coordination polymers was analysed by thermogravimetry in air. The silicon and copper contents and inherent viscosities were also determined. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: coordination polymer; polycoordination; siloxane ligand; copper-containing polymers

INTRODUCTION

Interaction between metal ions and some ligands may lead to the formation of metal-containing polymers in which the central metal ions are bound to ligand molecules. Metal-containing polymers are becoming increasingly important for fabrication of high-temperature stable materials, liquid crystalline polymers, superconductive materials, etc.[1–3] In contrast to other kinds of high molecular weight compound, metal-containing polymers can be thermally stable and so maintain their characteristics over a wide range of temperatures (e.g. high radiation stability, hydrolytic and thermo-oxidative stability, high dielectric constants, etc.).[1,4] The incorporation of metals in polymeric materials can be effected by the dispersion of fine metal powders in the polymer, metal salts, or complexes.[4] Also, ligands that selectively form complexes with some metal ions are of particular importance in various applications, such as recycling and refining of metals, purification of solutions, improving the environment, and treatment of pollutant metals, as well as in the qualitative and quantitative analysis of metals.[5]

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Polymers obtained by reaction of dicarboxylic acids with metal ions have been investigated either from the point of view of coordination chemistry or macromolecular chemistry. The polymeric nature of the metal dicarboxylate salts depends mainly on the coordination number of the metal ion and the number of ligands in the system, as well as on steric factors and the method of preparation.[6]

Systematic studies of coordination polymers have been carried out by Korshak and coworkers.[7–11] Copper, Zinc, Cadmium, Cobalt and Nickel ions form polymeric salts easily by coordination with dicarboxylic, α,ω-dioxidicarboxylic, and α,α'-dimethoxydicarboxylic acids.[8] The resulting polymers are infusible, insoluble in common organic solvents, and melt at high temperatures.[9] Their insolubility is due to the formation of coordination networks.[8] The use of polysiloxane ligands could provide improved solubility for coordination polymers. Siloxanes are well known as having low intermolecular forces, which are responsible for the low solubility parameter ($\delta_p = 7.3$).[12,13] The incorporation of some transition metals in siloxane polymers[14] and the catalytic activity of these metal-coordinated polymers have been reported.[15] Also, some polyorganosiloxanes with pendant amino groups can give rise to catalytically active copper(II) complexes.[16]

In the present study, the synthesis and characterization of linear coordination polymers obtained by equilibrium polycoordination reactions between siloxane diacids as

Table 1. The main characteristics of the metal-coordinated polymers

Sample code	Ligand	Molar ratio: Feed siloxane comp./$Cu(CH_3COO)_2{\cdot}H_2O$	Molar ratio: Siloxane comp./Copper(II) in polymer[a]	η[b] (dl/g^{-1})	Si (%)[c] exp. (theor.[d])	Cu (%)[c] exp. (theor.[d])	Polycoordination degree x[e]
CXCu1	CX	1:1	1.40	0.127	17.9 (15.2)	14.2 (17.2)	10
CXCu2	CX	1:2	1.06	0.328	13.7 (15.2)	14.7 (17.2)	71
CXCu3	CX	2:1	1.22	0.076	16.6 (15.2)	15.1 (17.2)	16
COXCu	COX	1:1	1.13	0.130	30.5 (32.2)	3.6 (4.3)	31
SMCu	SM	1:1	1.77	0.157	11.1 (9.0)	7.2 (10.2)	5

[a] Determined on the basis of the silicon content.
[b] Measured in chloroform at 25°C.
[c] Determined according to Ref. 16.
[d] Calculated on the basis of structural unit.
[e] Calculated on the basis of the elemental analysis (silicon, copper) and by assumption that the chain ends are constituted from ligand; the relationship $x = 2a\%\,Cu/(63.5\%\,Si - a\%\,Cu)$, with $a = 56$ for samples CXCu1, 2, 3 and SMCu and $a = 476$ for sample COXCu, was used.

ligand and copper(II) ions are described. These coordination polymers are readily soluble in common organic solvents.

EXPERIMENTAL

Materials

Copper(II) acetate monohydrate [$Cu(CH_3COO)_2 \cdot H_2O$], methanol, and chloroform (Chimopar, Romania) were used as received.

1,3-Bis(3-carboxypropyl)tetramethyldisiloxane, [HOOC$(CH_2)_3(CH_3)_2Si]_2O$ (CX), was synthesized by hydrolysis of 1,3-bis(3-cyanopropyl)tetramethyldisiloxane (Fluka) as reported in the literature.[17]

α,ω-Bis(3-carboxypropyl)oligodimethylsiloxane, $HOOC(CH_2)_3(CH_3)_2SiO[(CH_3)_2SiO]_mSi(CH_2)_3COOH$ (COX), with $m = 15$, and 1,3-bis(sebacomethyl)tetramethyldisiloxane (SM) were prepared using previously described methods.[18,19]

Measurements

IR absorption spectra were recorded with KBr pellets on a SPECORD M80 spectrophotometer. Electronic absorption spectra were measured using a SPECORD M42 spectrophotometer with quartz cells of 1 cm thickness in chloroform. Thermogravimetric measurements were performed at a heating rate of 12 °C min^{-1} in air using an MOM Derivatograph. The inherent viscosity was determined with an Ubbelohde suspended-level viscometer at 25 °C in chloroform. The silicon and copper contents were determined as previously reported.[20]

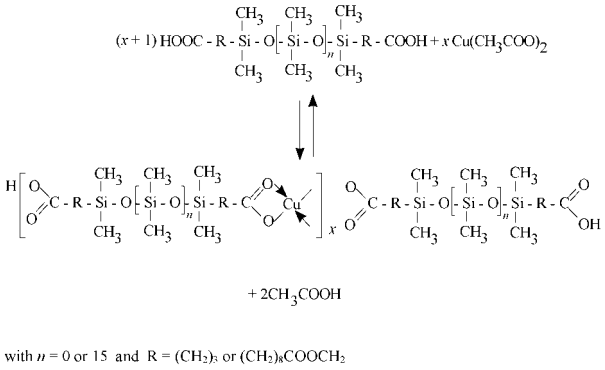
Polycoordination

A typical procedure involved placing 0.07 g (3.5×10^{-4} mol) of copper(II) acetate in a 50 ml glass flask and then 10 ml methanol was added and stirred vigorously for half an hour. 0.1072 g (e.g. 3.5×10^{-4} mol) siloxane diacid (CX) was dissolved separately in 10 ml methanol and this solution was then added dropwise under stirring to the copper(II) acetate solution. The colour of the solution changed slightly from blue to blue–green. The reaction mixture was stirred for 10 h at room temperature, after which the solvent was removed by rotary evaporation. The crude product remained on the bottom and walls of the flask as a transparent high-quality film of blue–greenish colour.

The product was purified by dissolving in chloroform and filtering to remove any unreacted copper(II) acetate, especially when this was used in excess. The solvent was then removed by rotary evaporation.

The same procedure was utilized in all syntheses, with change in the ligand or the molar ratio of ligand/metal ion made according to Table 1.

When the siloxane oligomer COX was used as ligand, the metal-containing polymer separated suddenly on mixing solutions of the two reactants. A very viscous blue–greenish product was obtained.



Scheme 1.

RESULTS AND DISCUSSION

The synthetic procedure leading to the metal-coordinated polymers is outlined in Scheme 1.

Three siloxane diacid types and copper(II) acetate in various ratios were used as reactants (Table 1). The reactions occurred homogeneously in solution, using methanol as solvent. When the oligosiloxane COX was used, the polymer separated from solution as it formed. In contrast to most coordination polymers, which are insoluble, the polymers synthesized here, as expected, were soluble in a wide range of organic solvents, as shown in Table 2.

The improved copolymer solubilities compared with those of most coordination polymers can be explained by the presence of siloxane segments. Owing to these highly flexible and nonpolar units, the packing of macromolecular chains through hydrogen bonding or by ionic–coordinative[10,11] networks is probably reduced, consequently, the solvent molecules can penetrate easily to solubilize the polymer chains.

Elemental analyses (silicon, copper) are presented in (Table 1). Results for silicon and copper were calculated

Table 2. Solubility behaviour[a] of metal-containing polymers

Solvent	CXCu1	CXCu2	CXCu3	COXCu	SMCu
Ethyl ether	+	+	+	++	++
Toluene	+	+	+	+	+
Benzene	+	+	+	−	−
Chloroform	+	+	+	+	+
Tetrahydrofuran	+	+	+		
Acetone	+	+	+		+−
Dimethylformamide	+	+	+		++
Dimethylsulfoxide				+	+
Ethanol				+	+
Methanol	+	+	+	+	−
Water	−	−	−	−	−

[a] ++: very easily soluble; +: soluble; +−: partially soluble; −: insoluble.

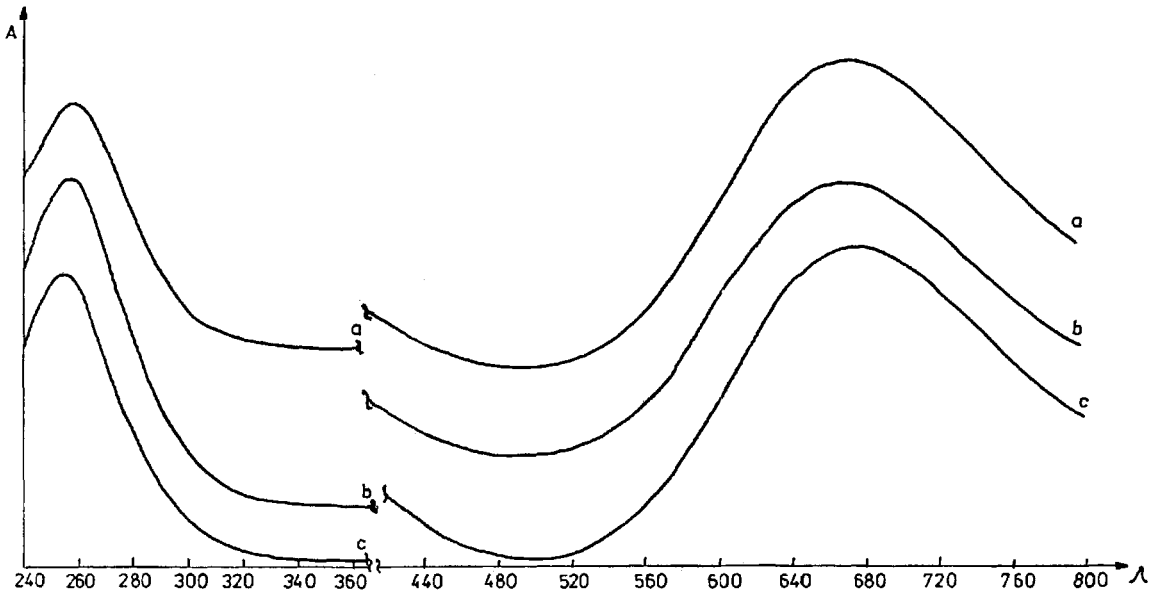


Figure 1. Illustrative UV–VIS absorption spectra for the coordinated polymers: (a) CXCul; (b) COXCu; (c) SMCu.

considering the structural unit of the polymer, where length varies, and neglecting chain end units.

Viscometric results are also presented in Table 1. The inherent viscosity of the metal-coordinated polymers increased slightly with increasing copper content in the siloxane compound/copper(II) acetate ratio and reached a higher value for polymer CXCu2. The enhancement of the molecular weights may be responsible for the enhancement of the polymer viscosities and also for lowering of the flexibility of the polymer chains. The use of copper(II) acetate in excess leads to increases in the polycoordination degree in the resulting polymer, providing higher values for the

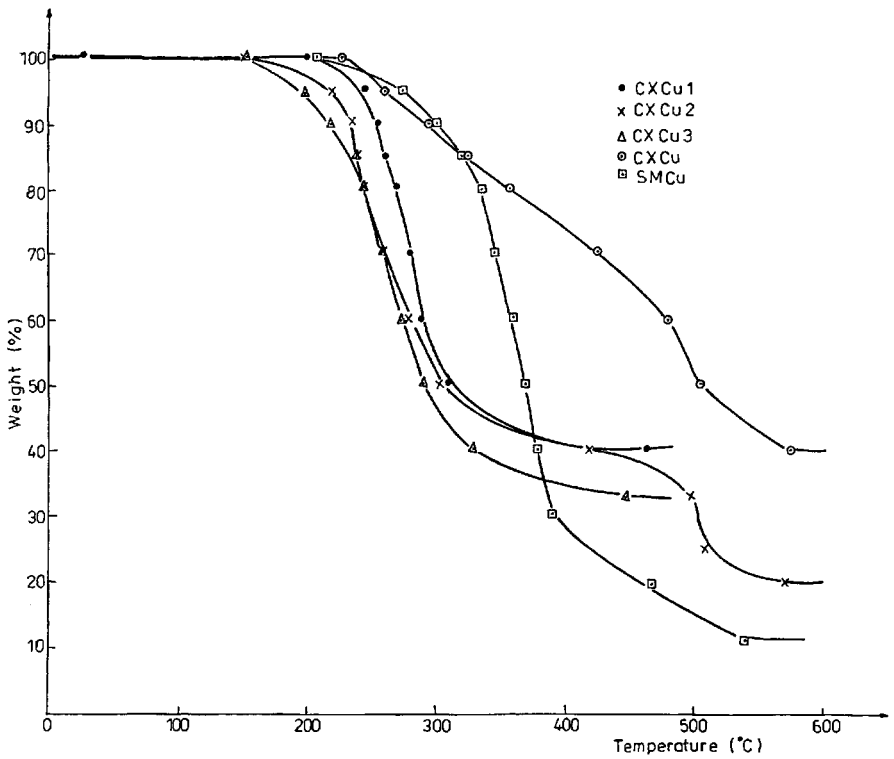


Figure 2. Thermogravimetric curves for the coordination polymers synthesized.

Table 3. Thermogravimetric data of metal-coordinated polysiloxanes

Sample	T_d (°C)	T_m (°C)	Weight loss at different temperatures (%)				
			250 °C	300 °C	350 °C	400 °C	450 °C
CXCu1	200	285	9.7	47.2	52.8	58.3	59.7
CXCu2	150	255	20.7	50.0	52.0	59.0	62.0
CXCu3	152	262	22.7	53.0	62.5	66.0	66.5
COXCu	227	290	5.0	11.5	19.0	26.5	35.0
SMCu	207	362	3.0	10.0	35.0	71.0	78.5

inherent viscosity.

The analysis of IR absorption spectra allows us to identify some structural changes due to the polycoordination reaction. Thus, new absorption bands appear at about 1600, 1545, and 1460 cm^{-1}, which correspond to symmetrical and antisymmetrical stretching vibrations of the carboxylate groups as the carbonyl groups of the siloxane component complex with the metal ions. The IR absorption spectrum of the SM polymer exhibits a strong band at 1745 cm^{-1} arising from the stretching vibration of C═O ester groups. The absorption at 1720 cm^{-1} arising from the carboxylic acid groups disappears. In the IR spectra of the other polymers, both absorption bands at 1745 and 1720 cm^{-1} are seen. The absorption bands at 1425 cm^{-1} are characteristic of methylene groups bonded to the carboxyl groups. Si—O—Si stretching bands appear in all spectra at about 1070 cm^{-1}. Two strong absorption bands at 2980 and 2910 cm^{-1} are due to aliphatic C—H stretching vibrations.

The electronic absorption spectra of the coordination polymers are presented in Fig. 1. In the presence of copper ions, three absorption bands appear at about 255, 375 and 674 nm in chloroform solutions. The broad absorption band at 674 nm can be assigned to a d–d transition of copper(II) coordinated by carboxylate groups.[21] The absorption bands at 255 nm have high intensities and can be attributed to a charge transfer transition between the carboxylate ligand and the copper ion.[21] The band around 375 nm as a shoulder of low intensity may be associated with a copper(II) acetate dimeric structure.[22]

The absorption bands at 674 and 255 nm are likely shifted to lower wavelengths for SMCu and COXCu polymers, due to conformational changes in the polymer chain determined by the nature of the R segment.

Representative thermogravimetrical curves of the metal-containing polymers are shown in Fig. 2, from which a series of thermal degradation parameters are obtained and presented in Table 3. The values of the decomposition temperature T_d and weight loss at different temperatures, and the temperature at the maximum weight-loss rate T_m, are given in Table 3. The polymers CXCu2 and COXCu showed two decomposition steps. The maximum rate of weight loss in the first step occurred at higher temperatures for COXCu and SMCu polymers relative to the CXCu polymers.

CONCLUSIONS

Starting from copper(II) acetate and the three different siloxane diacids CX, COX, and SM in various ratios, several coordination polymers were obtained. The presence of siloxane moieties within the polymeric backbones confers a higher solubility. The structural changes due to the polycoordination reaction were emphasized in the IR and UV–VIS absorption spectra. Thus, new absorption bands appear at about 1600, 1545, and 1460 cm^{-1}; these correspond to symmetrical and antisymmetrical stretching vibrations of the carboxylate groups, as the carbonyl groups of the siloxane component complex with the metal ions. In the presence of copper ions, three absorption bands also appear in the electronic absorption spectra at about 255, 375 and 674 nm in chloroform solutions. The polymers obtained have reasonable thermal stabilities. The inherent viscosity values are higher for a polymer containing the flexible siloxane segments in the backbone, revealing a good degree of polycoordination as determined on the basis of silicon content.

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