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Chelate polymers: II. Some novel transition metals complexes with azomethine-containing siloxanes and their polyesters

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New Schiff bases of 2,4-dihydroxybenzaldehyde with siloxane-α,ω-diamines having different numbers of siloxane units in the chain have been synthesized and characterized by spectroscopy, elemental and thermal analyses. These azomethines were found to form complexes readily with copper(II), nickel(II), cobalt(II), cadmium(II) and zinc(II). From IR and UV–Vis studies, the phenolic oxygen and imine nitrogen of the ligand were found to be the coordination sites. Thermogravimetric analysis (TGA) data indicate the chelates to be more stable than the corresponding ligands. The melting points increase with shortening of the siloxane segment from azomethine, as well as the result of complexation. The chelates obtained were covalently inserted in polymeric linear structures by polycondensation through the OH-difunctionalized ligand with 1,3-bis(carboxypropyl)tetramethyldisiloxane. Direct polycondensation, assisted either by acetic anhydride or *N*,*N*′-dicyclohexylcarbodiimide as dehydrating agent and the complex 4-(dimethylamino)pyridinium 4-toluenesulfonate as catalyst, was used for the synthesis of these compound types. The structures of the polymers obtained were confirmed by IR, UV and ^{1}H NMR. Characterization was undertaken by TGA, solubility tests and viscosity measurements. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: siloxane-containing ligands; azomethines; direct polycondensation; siloxane copolymers; chelate polyesters; polymer–metal complexes

INTRODUCTION

Coordination compounds constitute a very important field in chemistry because of their applications in organic synthesis, wastewater treatment, hydrometallurgy, polymer drug grafts, and nuclear chemistry.[1] Transition metal complexes with Schiff bases, in particular, are intensely studied because of their analytical and biological applications.[2,3] The polymer-metal complexes area was developed relatively recently as a multidisciplinary one involving chemistry, metallurgy, environmental and material science.[1]

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Polymer complexes may be classified into different groups according to the metal position on the chain, which is determined by the preparation technique. The methods include complexation between a ligand function anchored on a polymer matrix and metal ion,[4,5] and reaction of a multifunctional ligand with metal ion and polymerization of metal-containing monomers.[1] The first is used in most cases.[4–6]

Systematic studies on coordination polymers were carried out by Korsak and co-workers.[7–11] In general, the resulting polymers were insoluble in common organic solvents, infusible or melted at high temperatures.[9] Their insolubility is explained by formation of coordination networks.[8] The use of polysiloxane-based ligands could provide improved solubility for coordination polymers. Another important feature of siloxane polymers is their unusually high gas permeability. The high free volume in the siloxanes, compared with hydrocarbon polymers, explains the high solubility

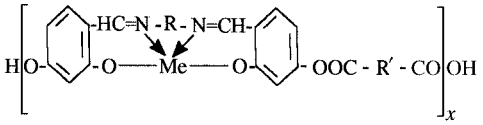
and high diffusion coefficient of gases.[12] Siloxanes are well known as having low-strength intermolecular forces, which are responsible for a low solubility parameter ($\delta_p = 7.3$).[13,14] The incorporation of some transition metals in siloxane polymers,[15] as well as the catalytic activity of these metal-coordinated polymers, has already been reported.[16] Also, it was reported that polyorganosiloxanes with pendant amino groups can give rise to catalytically active copper(II) complexes.[17] Polycondensation of copper, nickel, cobalt resorcylaldehyde-*o*-phenylenediamine complexes with dimethyl- or diphenyl-dichlorosilanes[18] was also studied, but the resulting polymers were insoluble.[19]

Many studies are dedicated to the synthesis of chelating agents based on poly-Schiff bases.[20–23] The literature is incomplete regarding siloxane azomethines synthesis. The synthesis method reported by Madec and Marechal[24] consists of the reaction between siloxanes having aldehyde ends with various aromatic diamines. Azomethine complexes of organotin and organosilicon were synthesized and evaluated for their antimicrobial effects on different species of pathogenic fungi and bacteria *in vivo* and *in vitro*.[3]

Possibilities for preparing polymeric N_2O_2 chelates and their ligands are known.[25] In the present study, we report the synthesis of new N_2O_2 chelates of copper(II), nickel(II), cobalt(II), cadmium(II) and zinc(II) with Schiff bases derived from siloxane diamines. The complexes obtained were then covalently incorporated through the ligands in polymeric linear structures of the type shown in Scheme 1.

New synthesis strategies and techniques for this category of compounds are reported in this paper: viz. azomethine ligands containing siloxane, their chelation with various transition metals and direct polycondensation with siloxane diacids in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC) as the activating agent and 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS) as catalyst. Acetic anhydride was also tested as a dehydrating agent in these reactions. To the best of our knowledge, this is the first time these techniques have been used for the synthesis of such compounds.

It is expected that the insertion of siloxanes can confer improved solubility and ability to form films with high gas permeability useful for purification or as oxygen transport by reversible oxygen binding.



with: R = $(CH_2)_3(CH_3)_2SiO[(CH_3)_2SiO]_nSi(CH_3)_2(CH_2)_3$, $n = 0$ or 8
R′ = $(CH_2)_3(CH_3)_2SiOSi(CH_3)_2(CH_2)_3$
Me = Cu(II), Ni(II), Co(II), Cd(II), Zn(II)

Scheme 1.

EXPERIMENTAL

Materials

Copper(II) acetate monohydrate, $Cu(CH_3COO)_2 \cdot H_2O$, nickel(II) acetate tetrahydrate, $Ni(CH_3COO)_2 \cdot 4H_2O$, cobalt(II) acetate tetrahydrate, $Co(CH_3COO)_2 \cdot 4H_2O$, cadmium(II) acetate dihydrate, $Cd(CH_3COO)_2 \cdot 2H_2O$, zinc(II) acetate dihydrate, $Zn(CH_3COO)_2 \cdot 2H_2O$, methanol and chloroform (all purchased from Chimopar, Romania) were used as received.

1,3-Bis(aminopropyl)tetramethyldisiloxane (AP_0; Fluka AG) was used as received.

α,ω-Bis(3-aminopropyl)oligodimethylsiloxane (AP), having average numerical molecular weights (calculated on the basis of the ^{1}H NMR spectra) $M_n = 890$, $n \approx 8$, was synthesized according to the known procedure:[26] viz. bulk equilibration reactions of octamethylcyclotetrasiloxane, $[(CH_3)_2SiO]_4$ (D_4; Fluka AG), with AP_0 in the presence of the base tetramethylammonium hydroxide (TMAH; Aldrich) as a catalyst.

2,4-Dihydroxybenzaldehyde (resorcylic aldehyde, AR) was prepared and purified according to a procedure described in the literature[27] (yield: 33%; m.p. 135–137 °C). 1,3-Bis(3-carboxypropyl)tetramethyldisiloxane, $[HOOC(CH_2)_3(CH_3)_2Si]_2O$ (CX), was prepared by hydrolysis of 1,3-bis(cyanopropyl)tetramethyldisiloxane[28] (yield: 84%; m.p. 50 °C). The reagent *N*,*N*′-dicyclohexylcarbodiimide (DCC; Fluka) was used as received. The 4-(dimethylamino)-pyridinium 4-toluenesulfonate (DPTS) complex as catalyst was obtained according to a procedure described in the literature,[29,30] starting from 4-(dimethylamino)pyridine and *p*-toluenesulfonic acid. Acetic anhydride (Merck) and methylene chloride (Chimopar) were freshly distilled before use.

Measurements

^{1}H NMR spectra were obtained using a JEOL C-60 HL spectrometer using tetramethylsilane as internal standard. IR absorption spectra were recorded with KBr pellets on a SPECORD M80 spectrophotometer. Electronic absorption spectra were measured using SPECORD M42 spectrophotometer with quartz cells of 1 cm thickness in methanol. Thermogravimetric measurements were performed at a heating rate of 9 °C min^{-1} in air using a MOM Derivatograph.

Thermo-optical analyses were performed on a laboratory-made apparatus, under normal light, with a heating rate of 7 °C min^{-1} in order to determine the melting point.

The silicon content was determined according to an adapted procedure:[31] viz. disintegration with sulfuric acid and ignition at 900 °C to constant weight. Finally, the residue was treated with HF for silicon removal as SiF_4 and then calculation was made by difference.

Procedure

Synthesis of Schiff bases

2.76 g (0.02 mol) AR and 2.42 g (0.01 mol) AP_0 or 8.90 g (0.01 mol) AP were dissolved together in 50 ml methanol. The mixture was refluxed for 9 h. After partial solvent

removal and cooling, the mixture was poured into a large excess of water to precipitate the Schiff base, which was then washed with water and petroleum ether, dried, weighed and analysed.

Chelate macromer

Although the proper ligands were synthesized in the above step in order to characterize them, they could also be made if the components were mixed together and heated. Thus, AR, AP_0 or AP and metal acetate hydrate in molar ratios 2:1:1 were dissolved together in methanol (for a 10% w/v solution) and refluxed with stirring for about 6 h. The reaction mixture was then concentrated by partial solvent removal and poured into water. The precipitate formed was separated by filtration, washed with water until the result was a colourless wastewater, dried first at 100 °C and then over P_2O_5 in vacuum, weighed and analysed.

Synthesis of the coordination polymers

Procedure A

For a typical procedure, both dicarboxylic acid (4 mmol) and diol–chelate macromer (4 mmol), were added to a two-necked flask equipped with a magnetic stirrer, a Dean–Stark trap with reflux condenser and gas inlet. Excess acetic anhydride (for a 0.02 M solution) was added. The reaction mixture was refluxed under a slow stream of nitrogen with stirring for 2 h. During the process, acetic acid was removed as it formed. Finally, introduction of nitrogen was stopped and high vacuum was applied to remove the excess acetic anhydride from the reaction mixture. A very viscous yellow–brown polymer in the form of a transparent coating remains in the reaction vessel. Purification was made by repeated precipitation with water from acetone. Finally, the polymer was dried first at 100 °C and then over P_2O_5 in vacuum.

Procedure B

Dicarboxylic acid (4 mmol), diol–chelate macromer (4 mmol), DPTS (0.04 mmol) and 30 ml dried CH_2Cl_2 were added to a one-necked, round-bottom flask, equipped with a magnetic stirrer. DCC (6 mmol) dissolved in 10 ml CH_2Cl_2 was added and the mixture was stirred at room temperature. A fine, white precipitate appeared at the surface of the reaction mixture in the first hour. However, the mixture was maintained under these conditions for about 48 h. The *N,N′*-dicyclohexyl urea (DCU) formed was filtered off. The solvent was then removed by rotary evaporation. The crude product was treated with acetic acid by stirring at room temperature for about 1 h in order to hydrolyse the residual DCC. At the end, the polymer was dissolved in CH_2Cl_2 and insoluble DCU was removed by filtration. The solvent was again removed by rotary evaporation and the remaining polymer was washed with water and dried at 100 °C and then over P_2O_5 in vacuum. The yields of all polymers were around 70–80%.

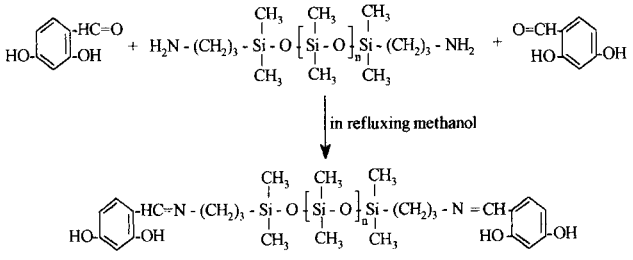
RESULTS AND DISCUSSION

Synthesis of the ligands (Schiff bases)

The Schiff bases were prepared by condensation of AR with AP_0 or AP in 2:1 molar ratio (Table 1), according to Scheme 2.

The IR spectra of the azomethines formed (Fig. 1: L1) show all the characteristic absorption bands: 1660 cm^{-1} (CH═N), 1000–1100 cm^{-1} (Si–O–Si), 800, 1260 cm^{-1} (Si–CH_3). Significant modifications appear in the ^1H NMR spectra of the azomethine compared with the reactants (Fig. 2). So, chemical shifts corresponding to the protons from azomethine are: 8.3–8.2 ppm (CH═N–), 6.2–6.0 and 7.0–6.8 (aromatic CH), 3.6–3.1 (Si$(CH_2)_2$–CH_2–N═C) compared with 11.0–10.8 (CH═O), 6.5–6.3 and 7.6–7.4 (CH aromatic) in AR and 2.7–2.4 for (Si$(CH_2)_2$–CH_2–N═C) in AP_0.

Bathochromic shift were observed in the UV–Vis spectra both for the λ_{max} at 320 to 370 nm (assigned to $\pi-\pi^*$ transitions of the carbonyl to azomethine groups respectively) and λ_{max} at 270 to 300 nm (assigned to the aromatic ring as a result of the reaction occurrence); see Fig. 3 (AR, L1, L2).



Scheme 2.

Table 1. The synthesized chelating Schiff bases containing siloxane

Ligand	Starting diamine	Aspect, colour	Yield, (%)	M.p.[a] (°C)	Elemental analysis: found (calc.) (%)			
					C	H	N	Si
L1	AP_0	Brown, fine powder	91	104	59.8 (59.3)	6.8 (7.0)	5.1 (5.8)	10.8 (11.5)
L2	AP	Yellow, transparent film	89	63–92	43.3 (44.0)	6.9 (7.6)	3.1 (2.5)	25.4 (26.5)

[a] Determined by thermo-optical analysis.

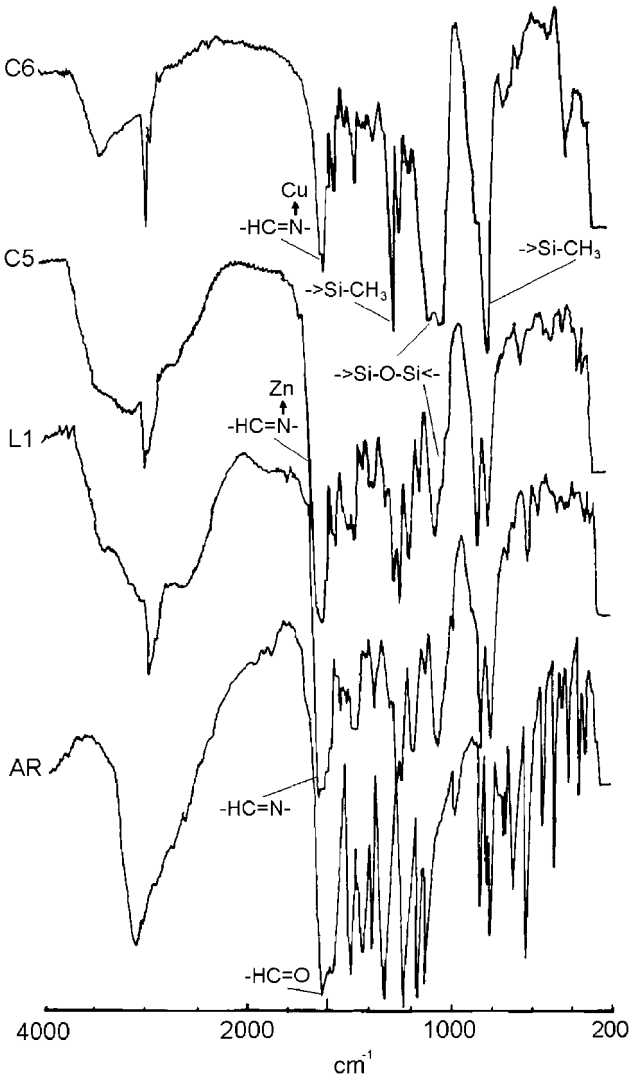


Figure 1. IR spectra of the starting reactants (AR), Schiff base (L1) and some related chelates (C5 and C6).

Table 2. The comparative solubilities[a] of the two ligands synthesized

Solvent	CH_2Cl_2	$CHCl_3$	Acetone	THF	DMF	DMSO	MeOH
L1	—[a]	+[b]	+	++[c]	++	++	+
L2	++	+	+	++	+	+	+

[a] Insoluble (—); [b]Soluble (+); [c]Very easily soluble (++).

The relative solubilities of the siloxane-based azomethine ligands obtained are listed in Table 2.

Thermogravimetric studies revealed that the ligand L2, containing an oligosiloxane segment, has higher thermal stability than the ligand L1, which contains a disiloxane segment (Fig. 4: L1, L2). This agrees with the known[14] increase of the thermostability of the siloxanes as their chain length increases.

The decrease in melting temperature for ligand L2 compared with that of ligand L1 can be explained by the presence of longer siloxane segments, which probably disturb the packing of molecules through hydrogen bonding.

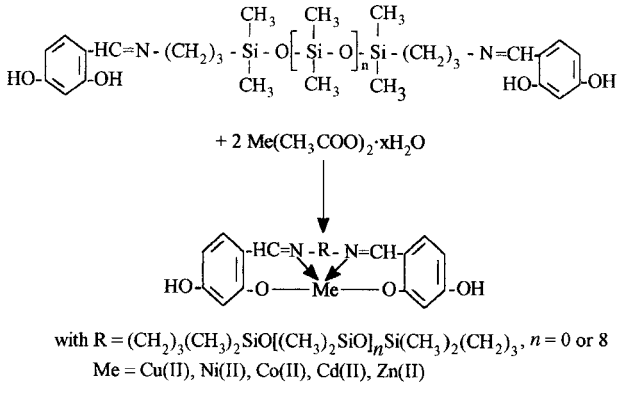
Obtaining the chelate macromer

The Schiff bases were converted to chelates of the divalent metals copper, cobalt, zinc, nickel and cadmium. Complex formation is achieved easily and simply by mixing and slow heating of methanolic solutions of the reaction partners (Table 3). The complexation reaction taking place between the metal ion and the above-prepared or *in situ* formed ligand is expected to occur according to Scheme 3.

When the ligand contains a large number of atoms, a network structure is expected to result. However, in our case, we could presume that the formation of cyclic compounds is also possible because of the high flexibility of the siloxane chain and the reaction occurring in a polar solvent at high dilution. Under such conditions, intramolecular polymer–polymer contacts are favourable and, as a result, the macromolecular chain is coiled.[13] Thus, chelating groups that belong to a molecule could be close enough to participate in the same chelating ring. This fact is sustained by the solubility of the product complexes.

Chelate formation is proved by IR spectra (Fig. 1: C5, C6): the stretching vibration frequency of the C=N group of the free ligand at 1660 cm^{-1} is shifted to lower frequency in the case of the proper complex (1630–1640 cm^{-1}) as a result of bond formation between the nitrogen atom of the ligand and the metal atom.[32,33] In the UV–Vis spectra, λ_{max} at about 370 nm (assigned to $\pi - \pi^*$ transitions of the azomethine) are displaced to lower values (about 350 nm) as a result of nitrogen atom coordination (Fig. 3: C5, C6). A hypsochromic shift is also evidenced for the aromatic transition (λ_{max} at about 300 nm in azomethine to 290 nm in the complex).

The ^1H NMR spectra do not show displacements of specific signals. In general, a broadening of the spectrum is observed, which, as has already been shown,[34] is due to complexation of the ligands with metal ions. Therefore, proton magnetic resonance was not used for structural analysis here.



Scheme 3.

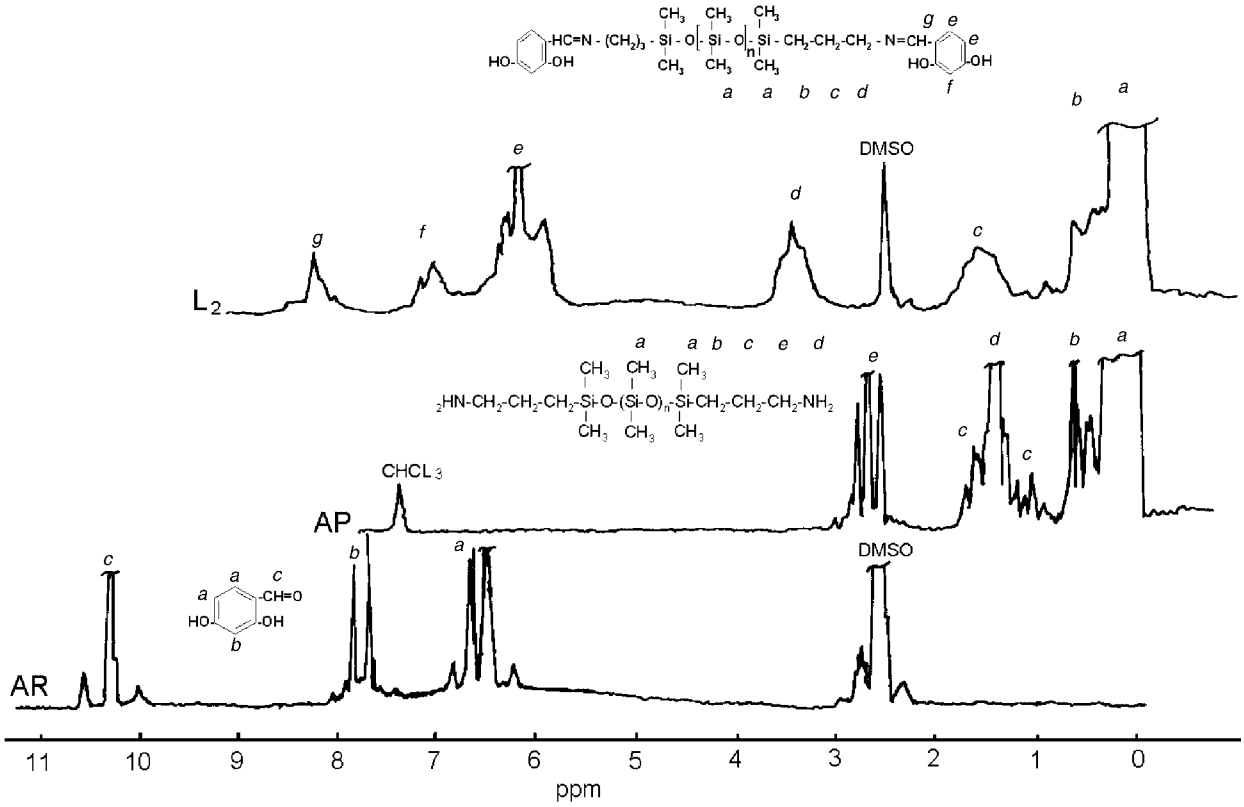


Figure 2. ^{1}H NMR spectra of the ligand L2 compared with those of the starting compounds (AR and AP).

Table 3. Some characteristics of the chelates synthesized

Sample	Ligand	Metal	Aspect, colour	Yield (%)	M. p.[a] (°C)	Elemental analysis: found (calc.) (%) N	Si
C1	L1	Cu	Grey–black	87	>330	5.5 (5.1)	9.9 (10.2)
C2	L1	Ni	Dark green	89	>330	5.1 (5.1)	10.7 (10.3)
C3	L1	Co	Dark red	79	>330	5.0 (5.1)	9.7 (10.3)
C4	L1	Cd	Yellow, fine powder	68	>330	4.9 (4.7)	10.5 (9.4)
C5	L1	Zn	Yellow, fine powder	78	>330	4.7 (5.1)	10.3 (10.2)
C6	L2	Cu	Dark brown	83	100–125	2.3 (2.4)	23.8 (25.1)
C7	L2	Ni	Dark green	81	<250	2.3 (2.4)	26.1 (25.2)
C8	L2	Co	Dark red	78	100–125	2.5 (2.4)	25.7 (25.2)
C9	L2	Cd	Yellow–brown, transparent film	75	123	2.2 (2.3)	24.4 (24.1)
C10	L2	Zn	Orange, bright, transparent film	82	112	2.1 (2.3)	22.8 (25.1)

[a] Determined by thermo-optical analysis.

In general, the chelates obtained are soluble in methylene chloride, acetone, tetrahydrofuran (THF), dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and methanol.

The thermal oxidative stability of the chelates formed increases compared with those of the corresponding ligand (Fig. 4). The higher char yields of the chelate compared with the starting ligand are due to the metal presence in the compound. The chelates have higher melting points than the ligands themselves (Tables 2 and 3).

Synthesis of the chelate polymer

The polymerization of metal-containing monomers has already been applied to the synthesis of chelate polymers.[1] These types of polymer–metal complex are known for their well-defined coordination structures. Polymerization can occur by radical or ionic initiation. Interfacial polycondensation of bifunctional low molecular weight chelates dissolved in NaOH with bifunctional aromatic acid chlorides dissolved in CH_2Cl_2 have also been reported,[1,35] giving polyesters, polyethers or polyamides.

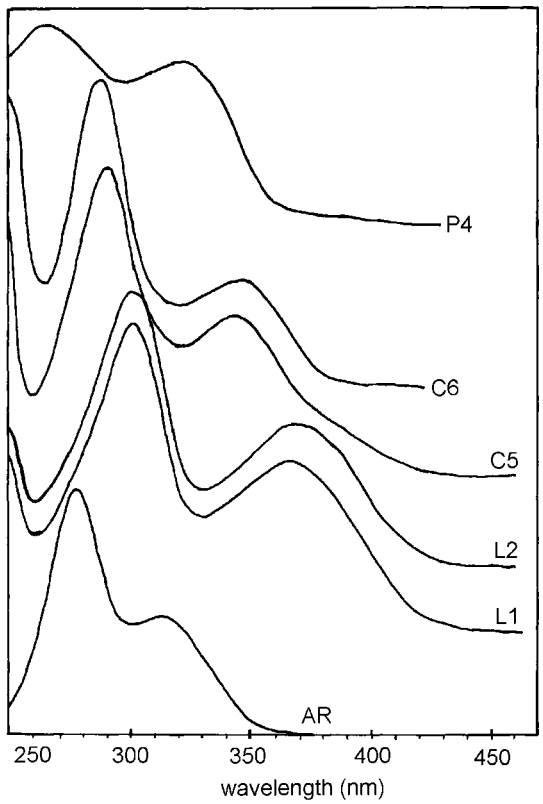


Figure 3. Modification of the UV spectra for the compounds obtained in each step of the synthesis starting from AR to ligands L1 and L2, chelate macromers (C5, C6) and chelate polymer P4, in methanol, at 20 °C.

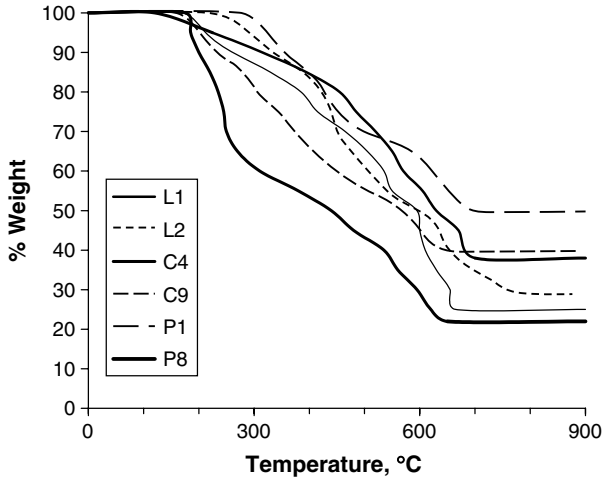


Figure 4. Comparative thermogravimetric curves for ligand L1, chelate C4 and proper polymer P8 and for ligand L2, chelate C9, and proper polymer P1.

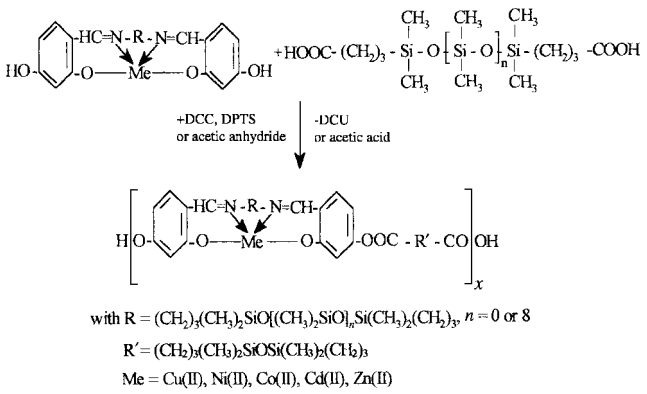
Polyesters can be obtained by either direct or activated polycondensation. Direct polycondensation requires high temperatures, which often leads to side reactions that limit the molecular weights of the polymers. Reactive monomers, like acid chlorides, which permit one to work at lower temperatures, can be used.[30] However, by treatment of certain monomers, such as siloxanes with thionyl chloride, the risk of cleavage of siloxane bonds exists.

Two different activating agents were used for polycondensation in this paper (acetic anhydride and DCC) in order to insert the chelate monomer in polyesteric structures.

Acetic anhydride was used as a reaction environment starting directly from the two co-monomers. The reaction takes place in a homogeneous medium. In fact, in this case, the polycondensation is a transesterification procedure. Acetic anhydride used in excess acts not only as solvent for the easy dissolution of co-monomers, but also as an acetylation agent.[33] The pre-polymer (mixed anhydride) is formed *in situ* during refluxing, and polycondensation occurs as the acetic acid formed is removed from the system. In this way, acetylation and polycondensation take place in one step and in the same reaction medium. The resulting copolymer is isolated by precipitation with water from acetone.

The successful use of DCC as an activating agent and DPTS as a catalyst for synthesis of both aromatic and aliphatic polyesters was been reported.[29,30] This method was also used with good results in the synthesis of polyesters having reasonable degrees of polymerization by condensation of bis(carboxypropyl)dimethylsiloxane with various dihydroxy-functionalized compounds containing azomethines.[36] The use of the special dehydrating agent DCC offers a low-temperature and mild alternative.[30] Also, it was reported that, by use of DPTS, the side reactions that convert carboxylic acids to unreactive *N*-acylureas are avoided, thus allowing formation of high molecular weight polymers.[29,30] In this paper we describe the first use of this method for the synthesis of new polymer–metal complexes by reaction of an OH-difunctionalized preformed chelate with a carboxylic diacid containing siloxane units (Scheme 4).

The polymers obtained are soluble in a large range of solvents: methylene chloride, chloroform, acetone, DMF, DMSO, methanol, ethanol. Their analytical characterizations given in Table 4 are all as expected for the resulting polymers.



Scheme 4.

Table 4. Some characteristics of the chelate polymers synthesized

Code	Starting chelate	Synthesis procedure (activating agent)	Yield (%)	Aspect	η_{inh}[a] (dl g^{-1})	$A_{COO(1770)}/A_{ref.(1260)}$[b]
P1	C9	B (DCC)	68	Yellow, soft crosslinked film	—	0.86
P9	C9	A ($(CH_3CO)_2O$)	75	Yellow, soft crosslinked film	—	0.95
P2	C4	B (DCC)	71	Yellow–brown, transparent, hard film	0.13	0.36
P8	C4	A ($(CH_3CO)_2O$)	78	Yellow–brown, transparent, hard film	0.27	1.08
P3	C5	B (DCC)	70	Brown viscous paste	0.09	0.30
P4	C5	A ($(CH_3CO)_2O$)	80	Yellow–brown, transparent, hard film	0.12	0.83
P5	C6	A ($(CH_3CO)_2O$)	82	Yellow–brown, transparent, hard film	0.33	0.42
P7	C10	B (DCC)	75	Brown viscous paste	0.17	0.20

[a] In DMF, at 25 °C for about 0.2 wt% solution.
[b] The ratio $A_{COO(1770)}/A_{ref.(1260)}$ was estimated from IR spectra,[37] taking a base line from 500 to 2000 cm^{-1}, free of any absorption. The absorption band at 1260 cm^{-1} assigned to the stretching vibrations of the Si–CH_3 group in the siloxane units was considered as a reference.

When comparing the UV spectra of the polymers obtained with those of the corresponding chelates and azomethines (Fig. 3), a hypsochromic shift of the aromatic transitions could be noted, probably due to the presence of the newly formed ester groups.

From the thermogravimetric analysis (TGA) curves it can be seen that the polyesters obtained (Fig. 4: P1 and P8) were generally less stable then the starting chelates (C9 and C4 respectively), as also reported in the literature.[38] Polyesters with longer siloxane chains in the chelate monomer exhibit better thermal oxidative stability in the first stages than their disiloxane-containing homologues. Therefore, we assume that the ester groups are the first to decompose, since their number per mass unit decreases as the siloxane length increases.

The absorbance ratios $A_{COO(1770)}/A_{ref.(1260)}$ of the polyesters synthesized were used (Table 4) to estimate the polycondensation degrees for polymers based on the same ligand. As can be seen, there are concordances between absorbance ratios and inherent viscosity values when comparing P2 with P8, P3 and P4 or P5 with P7. Even though the activation by the acetylation method is aggressive, this is more effective than activation with DCC. So, higher polycondensation degrees are obtained in shorter times. In addition, polymer purification is easier. The residual DCU formed as a side product by procedure B is very difficult (and often impossible) to remove completely.

CONCLUSION

The preparation of new siloxane-based ligands, chelates and their polymers by new synthesis strategies for this category of compounds are presented. Two Schiff bases of AR with siloxane-α,ω-diamines have been synthesized, separately or *in situ*, and complexed with five transition metals, viz. copper(II), nickel(II), cobalt(II), cadmium(II) and zinc(II). The chelates obtained were transformed into polyester structures using CX as a co-monomer. Two different activating agents were used for polycondensation of the preformed chelate macromers: acetic anhydride and DCC. The DPTS complex was used as a catalyst in the latter case. Acetic anhydride proved to be the more effective activating agent, permitting easy and rapid synthesis of the polyesters with a high degree of polycondensation.

The ligand, complex and polymer structures were confirmed by their IR, UV and ^{1}H NMR spectra. The TGA data revealed increases in thermal stability by complexation as well as by increases in the length of the siloxane segment. The polyesters were less stable than the starting chelate macromers. Comparative information related to the degree of polycondensation was obtained by estimation of the absorbance ratios $A_{COO(1770)}/A_{ref.(1260)}$ and inherent viscosities. The siloxane component in such structures confers improved solubility, lower melting points and, as a result, good processability.

Acknowledgements

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