APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 614–620
Materials, Nanoscience and Catalysis **AOC**

Chelate polymers. IV. Siloxanes functionalized with chelating groups derived from hydroxy-ketones, their metal complexes and some polymers

M. Vasiliu, M. Cazacu*, M. Marcu, C. Racles and A. Vlad

"Petru Poni" Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A, 700487 Iasi, Romania

Received 7 June 2004; Revised 27 October 2004; Accepted 29 October 2004

New ligands were obtained by the reaction of 1,3-bis(3-aminopropyl)tetramethyldisiloxane, with acetylacetone, 2,4-dihydroxybenzophenone and 2,4-dihydroxyacetophenone. The structures were confirmed by electronic, IR and ^{1}H NMR spectroscopy and elemental analysis. The change of the refractive index of the siloxanes by their chemical modification was also examined. These compounds were used for coordination of some divalent metals. The ligands and their metal complexes were both soluble in common solvents, such as $CHCl_3$, dimethylformamide, dimethylsulfoxide, *N*-methyl-2-pyrrolidone. Some of the bifunctional chelates were inserted into polymeric structures by polycondensation with the diacid chloride of bis(*p*-carboxyphenyl)diphenylsilane. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: azomethines; siloxane ligands; metal–polymer complexes; acetylacetone; benzophenone; acetophenone

INTRODUCTION

Multifunctional ligands are very important from analytical, coordination and environmental chemistry points of view. Such ligands can be useful for removal or selective adsorption of the metal ions due to differences in the stability constants of the complexes formed between ligand and metal ions.[1] Thus, bis-β-diketonate ligands form polymers by complexing with metals that are useful as selective sorbents for gas chromatography. The sorbents are capable of selectively retaining many oxygen- and nitrogen-containing compounds, which can be desorbed for subsequent analysis by heating the metal polymer. The sorbent properties of the complexes depend on both the metal and the ligand types. Temperature also has an effect on the retention properties of the sorbents. It is possible to employ various series of sorbents with different metal polymers.[1,2]

Such organometal complexes have also been synthesized since 1950 for the purpose of obtaining semiconducting organic materials, heat-resistant organic polymers or polymer catalysts.[3] Coordination oligomers and polymers are assembled by the interaction of metal ions with polydentate ligands containing two or more separated metal-binding domains. The simplest structural requirement for such a ligand is two polydentate functionalities linked by a spacer group.[4] The use of polysiloxanes as spacers in such ligands could provide improved solubility for coordination compounds, but another important feature of the siloxanes is their unusually high gas permeability. The high free volume in the siloxanes, compared with hydrocarbons, explains the high solubility and high diffusion coefficient of gases.[5] Siloxanes are well known as having low intermolecular forces, which are responsible for low solubility parameters.[6,7] There are few reports in the literature regarding siloxane-based ligands or their metal complexes synthesis.[8,9] A series of polyazomethines containing pyridine rings and oligosiloxane moieties has been synthesized as macromolecular tridentate ligands and complexed with cobalt in order to obtain highly oxygen-permselective membranes.[10,11]

In our previous papers[12–14] we synthesized siloxane-based ligands having hydroxyl and azomethine as chelating groups. 2,4-Dihydroxybenzaldehyde and 5,5′-methylene-bis-salicylaldehyde were used as carbonylic compounds for azomethines obtained by reaction with siloxane diamines. Three different hydroxy-ketones, (acetylacetone,

---

*Correspondence to: M. Cazacu, "Petru Poni" Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A, 700487 Iasi, Romania.
E-mail: mcazacu@icmpp.tuiasi.ro

Contract/grant sponsor: Romanian Education and Research Ministry; Contract/grant number: CNCSIS 920-41400/2003.

2,4-dihydroxybenzophenone and 2,4-dihydroxyacetophenone) and 1,3-bis(3-aminopropyl)tetramethyldisiloxane (AP_0) were used in this study in order to obtain new ligands, which were complexed with transition metals. Some chelates were polycondensed with bis(*p*-carboxyphenyl)diphenylsilane.

EXPERIMENTAL

Materials

Copper(II) acetate monohydrate ($Cu(CH_3COO)_2 \cdot H_2O$), nickel (II) acetate tetrahydrate ($Ni(CH_3COO)_2 \cdot 4H_2O$), and cobalt(II) acetate tetrahydrate ($Co(CH_3COO)_2 \cdot 4H_2O$) were used as received. AP_0 (Fluka AG) was used as received. 2,4-Dihydroxybenzophenone (m.p. 143–145 °C), 2,4-dihydroxyacetophenone (m.p. 143–146 °C) and acetylacetone ($d = 0.972$, b.p. 136–138 °C) were purchased from Fluka AG. Bis(*p*-chlorocarbonyl-phenyl)diphenylsilane (DPClS) was prepared from the appropriate acid, bis(*p*-carboxyphenyl)diphenylsilane, according to Ref.[15]. The solvents methanol (Chimopar) and dimethylformamide (DMF, Fluka) were freshly dried and distilled before using.

Measurements

^1H NMR spectra were obtained with a JEOL C-60 HL spectrometer using tetramethylsilane as internal standard. IR absorption spectra were recorded using 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 $CHCl_3$ or DMF.

Refractive indices were determined with an Abbé refractometer at 25 °C. The reduced viscosities were determined at 25 °C in DMF, using an Ubbelohde suspended level viscometer. Solutions of about $0.5\ g\ dl^{-1}$ samples in DMF were prepared and their flow times by viscometer were measured. The reduced viscosity η_{red} was determined according to the relationship $\eta_{red} = (t/t_0 - 1)/c$, where t, t_0 flow time of the solution and solvent respectively and c ($g\ dl^{-1}$) concentration of the solution. The silicon content was determined according to an adapted procedure.[16] The sample was disintegrated in a platinum crucible by treating with sulfuric acid and then calcined at 900 °C to constant weight, when SiO_2 remained as a residue. For the chelate analysis, the residue consisting of SiO_2 and metal oxide was treated with HF (CARE!), with silicon being removed as SiF_4 and only metal oxide remaining in the crucible.

PROCEDURE

Synthesis of the ligands

A solution of 0.05 mol AP_0 and 0.1 mol of hydroxy-cetone derivative (Table 1) in 40 ml of absolute methanol was stirred

Table 1. The ligands synthesized

Ligand	Starting reactants	Aspect, colour	n_D^{25} ligand (siloxane)	η_{red}^{25} [a]	Elemental analysis found/calc. (wt%) N	Si
$AcAP_0$	$AcAc/AP_0$	Yellow–orange viscous oil	1.5128 (1.4480)	0.027	6.4/6.8	14.1/13.6
$AfAP_0$	Af/AP_0	Yellow powder	—	0.059	4.7/5.4	10.5/10.8
$BfAP_0$	Bf/AP_0	Brown glassy	—	0.046	5.1/4.4	7.8/8.7

[a] Determined in DMF at 25 °C for a concentration of about $0.5\ g\ dl^{-1}$.

Table 2. The synthesis of metal chelates

Chelate	Ligand	Metal	Solvent	Aspect, colour	η_{red}^{25} [a]	Elemental analysis, found/calc. (wt%)[b] N	Si
C1	$AcAP_0$	Cu	CH_3OH	Dark-red glassy	0.030	5.9/5.9	11.8/11.8
C2	$AcAP_0$	Ni	CH_3OH	Green glassy	0.029	5.3/5.9	12.2/11.9
C3	$AcAP_0$	Co	CH_3OH	Dark-green glassy	0.046	5.1/5.9	11.1/11.9
C4	$AfAP_0$	Cu	DMF	Dark-brown powder	0.059	4.9/4.8	10.0/9.7
C5	$AfAP_0$	Ni	DMF	Dark-khaki powder	0.040	4.9/4.9	10.4/9.8
C6	$AfAP_0$	Co	DMF	Khaki powder	0.038	5.0/5.0	9.4/9.8
C7	$BfAP_0$	Cu	CH_3OH	Dark-green powder	0.041	3.3/3.9	7.0/7.9
C8	$BfAP_0$	Ni	CH_3OH	Green–khaki	0.097	3.9/4.0	7.6/8.0
C9	$BfAP_0$	Co	CH_3OH	Dark green powder	0.070	3.8/4.0	8.1/8.0

[a] Determined in DMF at 25 °C for a concentration of about $0.5\ g\ dl^{-1}$.
[b] Calculated for the idealized structural unit.

at room temperature for about 20 h. Then, the reaction mixture was processed in different ways depending on their form. Thus, in the case of acetophenone derivative synthesis, the resulting ligand was insoluble in the reaction medium and it was separated by filtration, washed with methanol and dried at 100 °C. A yellow powder was obtained. The acetylacetone and benzophenone derivatives resulted in soluble products in the reaction medium. Therefore, the solvent and the other volatile components (residual reactants and water) were removed by vacuum distillation. The remaining products, a yellow viscous oil in the case of acetyl-acetone and a brown glassy solid in the case of benzophenone, were characterized and used as such.

Synthesis of metal chelates

For a typical procedure, 3.5×10^{-4} mol siloxane ligand was dissolved in 10 ml methanol or DMF in a 50 ml round-bottom, Pyrex flask. The metal(II) acetate (3.5×10^{-4} mol) was separately dissolved in 10 ml solvent and the resulting solution was added under stirring to the ligand solution. The colour of the reaction mixture modified quickly, depending on the involved metal. The reaction mixture was stirred for about 5 h at reflux, after which the solvent was partially removed by rotary evaporation. The concentrated mixture was precipitated in water, filtered, washed with water and petroleum ether, and dried.

The same procedure was utilized in all syntheses, except for changes in ligand or metal salt, according to Table 2.

The isolated chelates were soluble in $CHCl_3$, DMF, and methanol.

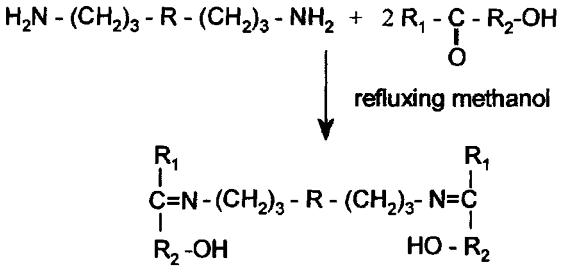
Polycondensation of bisphenolic chelates with diacid chloride

This occurred according to a procedure already described:[14] diacid chloride (CDPClS), bis-phenol chelate, 4-dimethyl aminopyridine and pyridine in 1 : 1 : 2 : 2 molar ratios were introduced in a well-dried one-necked flask equipped with a magnetic stirrer and nitrogen inlet. Freshly dried *N*-methyl-2-pyrollidone (NMP) was added as a solvent for a 50 wt% solution. The reaction flask containing a clear solution was immersed in a water-ice bath and stirred for about 1 h. Stirring was then continued for 24 h at room temperature even though the chlorohydrate appeared as a white precipitate in the first 2–3 h. Finally, the reaction mixture was poured into, a large excess of water, filtered, washed with water and dried, first at 100 °C and then over P_2O_5 in vacuum.

RESULTS AND DISCUSSION

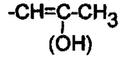
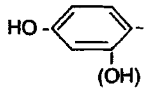
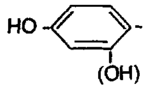
Ligands synthesis

New ligands were obtained by chemical modification of AP_0 with acetylacetone, 2,4-dihydroxybenzophenone or 2,4-dihydroxyacetophenone.



with R: $(CH_3)_2Si\text{-}OSi(CH_3)_2$

R_1, R_2:

Ketone	$-R_1$	$-R_2$
Acetylacetone	$-CH_3$	 $-CH=\underset{(OH)}{C}-CH_3$
2,4-Dihydroxyacetophenone	$-CH_3$	
2,4-Dihydroxybenzophenone	$-C_6H_5$	

Scheme 1.

The used reactants and some characteristics of the ligands obtained are presented in Table 1. All reactions occurred in solution using methanol as a solvent.

The condensation of the aliphatic organic diamine (ethylenediamine, trimethylenediamine) with β-diketones, particularly with acetylacetone, has already been reported.[17] Here, we used a siloxane diamine, namely AP_0. Acetylacetone and the two dihydroxy-ketones 2,4-dihydroxybenzophenone and 2,4-dihydroxyacetophenone (Table 1) were used as carbonylic compounds in order to prepare the Schiff base (Scheme 1). The reaction occurred in methanol at room temperature, as in the case of the organic amine.[17,18]

The Schiff base formation was verified by elemental (Table 1) and spectral (IR, UV–Vis and ^{1}H NMR) analyses. The differences between the elemental analysis values found and calculated are in agreement with those reported in the literature for these product types and their complexes.[19]

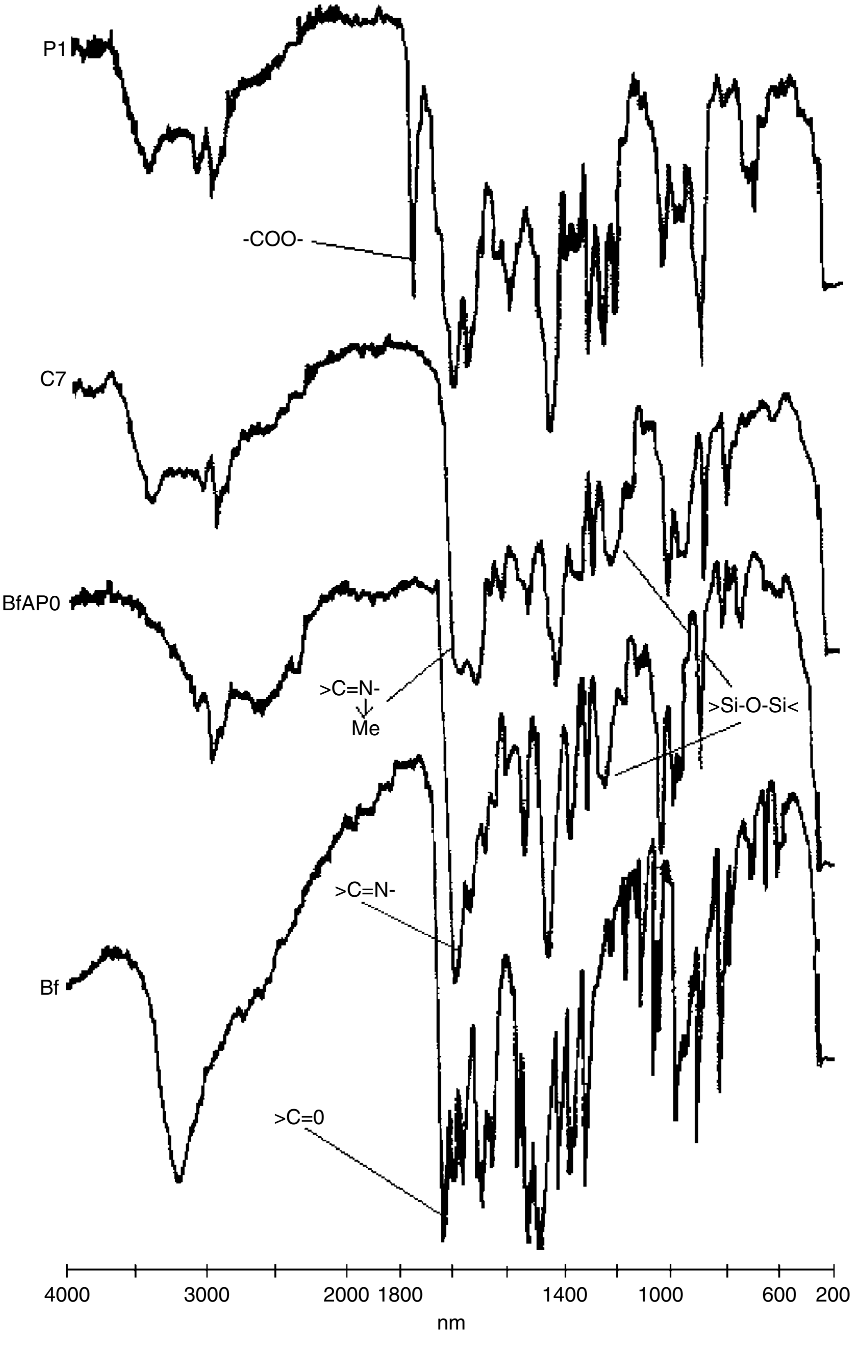


Figure 1. Modification of IR spectra as a result of the successive transformations from 2,4-dihydroxybenzophenone (Bf) to Schiff base ligand ($BfAP_0$), metal chelate (C7), and polycondensation polymer (P1).

Some characteristic absorption bands can be identified in the IR spectra of the resulting azomethines. The acetylacetone derivative presents an intense band at 1610 cm^{-1} that is assigned to the stretching vibration frequency of the azomethine group, $\nu(-C{=}N-)$, having in close vicinity, at 1580 cm^{-1}, another intense band assigned to the stretching vibration frequency of the double bond, $\nu(-C{=}C-)$. In the 2,4-dihydroxybenzophenone derivative (Fig. 1, $BfAP_0$), the azomethine band appears at 1600 cm^{-1} overlapping the stretching aromatic band at the same wavenumber. The absorption band at about 1350 cm^{-1} in the IR spectra of the 2,4-dihydroxybenzophenone is assigned to $\nu(-C-O-)$ phenolic. Other characteristic bands at 1260 cm^{-1} $\delta_s(Si-CH_3)$, 1050 cm^{-1} $\nu_{as}(Si-O-Si)$, and 800 cm^{-1} $\delta_{as}(Si-CH_3)$ are present in all products.

Compared with the UV spectrum of acetylacetone, which shows a specific large band for $\lambda_{max} = 277$ nm, a bathochromic shift at $\lambda_{max} = 310$ nm occurred as a result of the azomethine formation (Fig. 2a). In the case of the other azomethines, hypsochromic shifts of the two original bands in the starting ketones, as well as the appearance of a third band, were noticed. Thus, in $BfAP_0$ (Table 1), the absorption bands were at λ_{max} 283, 315 and 390 nm, instead of at 293 and 330 nm in Bf (Fig. 2b), but in $AfAP_0$ the absorption bands appeared at 273 and 296 nm instead of at 277 and 315 nm in Af, and a new band was visible at about 373 nm.

Azomethine formation was also proved by the modification of the ^{1}H NMR spectra compared with those of the reactants.[12,13] The strong signal at 1.2–1.3 ppm assigned to NH_2 protons of AP_0 disappeared due to the transformation of the primary amine group into an azomethine group.

An increase in the refractive indices of the newly formed azomethine towards those of the starting reactants can be observed (Table 1), probably as a result of the incompatibility between the siloxane and organic (ketone) moieties.

The ligands are soluble in $CHCl_3$, DMF, dimethylsulfoxide, and in hot methanol and acetone.

Coordination reactions

The above synthesized ligands (telechelic functionalized siloxanes) were tested as chelating agents for some divalent transition metals. Either low-molecular or macromolecular chelates, of the type N_2O_2, could be formed. Taking into account the high dilution of the reaction mixture, the high solubility and the low values of the reduced viscosities of the reaction products (Table 2), we presume that intramolecular chelating has occurred.

The general method used for the preparation of the metal chelates consisted of methanol refluxing of the stoichiometric quantities of the hydrated metal inorganic salt and ligand, according to the procedure described in Ref.[17] Although a colour change indicating complex formation usually began immediately, the refluxing was prolonged to 5 h in order to ensure a definite reaction. The synthetic procedure leading to the metal complex is outlined in Scheme 2.

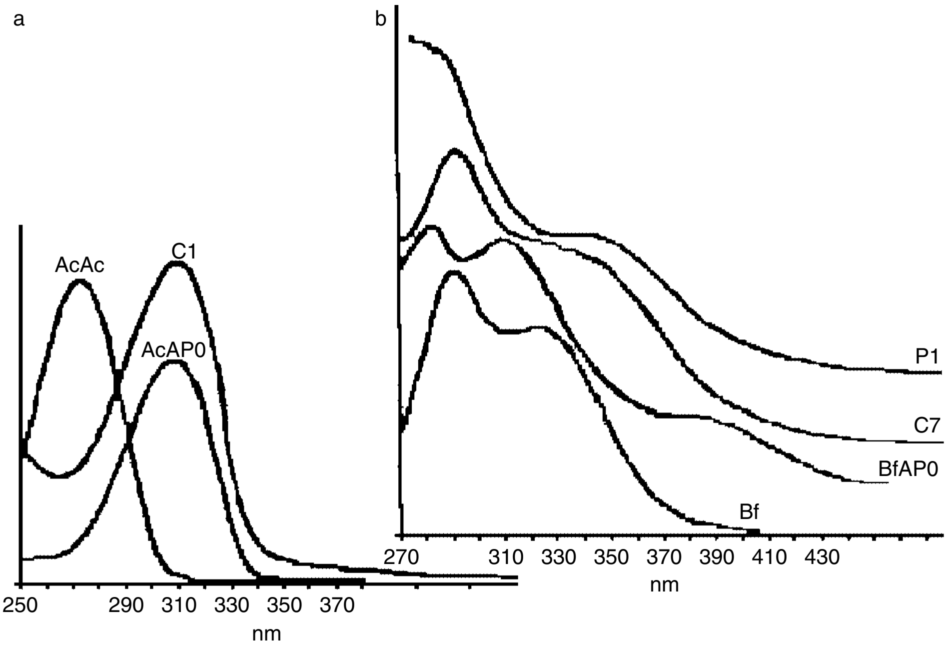
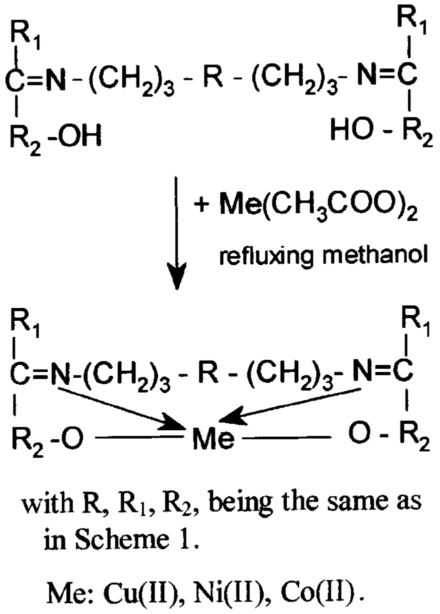


Figure 2. Comparative UV spectra (in $CHCl_3$) of some reactants and their products: (a) acetylacetone (AcAc), Schiff base with 1,3-bis(3-aminopropyl)tetramethyldisiloxane ($AcAP_0$), and relating copper chelate (C1); (b) 2,4-dihydroxybenzophenone (Bf), Schiff base with 1,3-bis(3-aminopropyl)tetramethyldisiloxane ($BfAP_0$), copper chelate (C7) and derived copolymer with bis(*p*-carboxyphenyl)diphenylsilane (P1).



with R, R_1, R_2, being the same as in Scheme 1.

Me: Cu(II), Ni(II), Co(II).

Scheme 2.

As expected, the chelates synthesized were soluble in a wide range of organic solvents. The siloxane moieties' presence within the structure confers a higher solubility.

The structural changes due to the coordination reaction were emphasized by the IR spectra (Fig. 1, C8), where a broadening to low frequencies of the azomethine band occurred as a result of the complexation. The intensity of the band assigned to the stretching vibration frequency of the phenolic group, $\nu(=C-O-)$, at 1350 cm^{-1} decreased significantly as a result of the complexation and a new band (shoulder) developed at higher wavenumber, namely at 1375 cm^{-1}, in the benzophenone derivatives. New characteristic absorption bands also appeared at 450 nm and 631 nm, assigned to ν_{Me-N} and ν_{Me-O} respectively.[20,21]

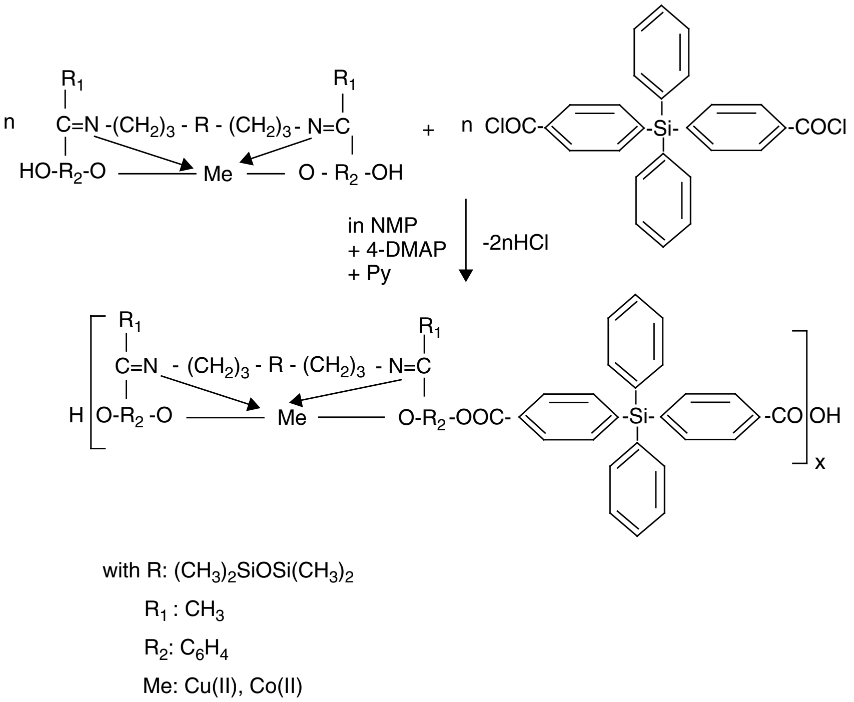
The UV spectra remain almost unchanged as a result of the complexation in the case of the acetylacetone derivatives (Fig. 2a). Instead, bathochromic shifts of the bands were observed as a result of the copper complexation of $AfAP_0$ (Fig. 2b) and $BfAP_0$.

Polycondensation

An already published procedure[14] was also applied in this case in order to obtain chelate polymeric structures by activated polycondensation of the bifunctional chelate monomer with a diacid chloride (Scheme 3) in the presence of 4-dimethyl aminopyridine and pyridine as hydrochloric acid acceptors (Table 3).

The resulting copolymers were isolated by precipitation with water from NMP. They are soluble in $CHCl_3$, THF, DMF, and NMP. It can be appreciated that an acceptable concordance is obtained between the elemental analysis values found and calculated (Table 3) for polymeric structures with low polymerization degrees (as indicated by viscosity), when the chain end influence is important.

An intense absorption band appears in the IR spectra of the polymer (Fig. 1, P1) at 1740 cm^{-1} assigned to the formed ester groups. The absorption bands assigned to the complexed



with R: $(CH_3)_2SiOSi(CH_3)_2$
R_1 : CH_3
R_2: C_6H_4
Me: Cu(II), Co(II)

Scheme 3.

Table 3. The representative polymers based on bisphenolic chelates

Sample	Starting chelate	Aspect, colour	$\eta_{\text{red}}^{25\ \text{a}}$	Elemental analysis, found/calc.[b] (wt%) Si	N
P1	C7	Olive powder	0.071	7.1/7.7	2.8/2.6
P2	C6	Dark-khaki powder	0.075	9.2/8.7	2.7/2.9

[a] Determined in DMF at 25 °C for a concentration of about 0.5 g dl^{-1}.
[b] Calculated for the idealized structural unit.

azomethine, $\nu(-C{=}N-)$ at 1580–1600 cm^{-1} and $\delta(Si-CH_3)$ at 800 cm^{-1} are also visible. The band assigned to $\nu(\equiv C-O-)$ phenolic is shifted to about 1390 cm^{-1} as a result of its involvement in chelating and polycondensation processes.

CONCLUSIONS

AP_0 was modified by reaction with three different hydroxyketones, i.e. acetylacetone, 2,4-dihydroxybenzophenone, and 2,4-dihydroxyacetophenone. The obtained compounds were complexed with transition metals (copper, nickel, and cobalt) resulting in low-viscosity, soluble chelates. Some of the OH-bifunctionalized chelates served as co-monomers for obtaining the polyester structures. The structures obtained in every step were verified and characterized by using spectral techniques, elemental analysis, refractive index and viscometric measurements.

Acknowledgements

This work was financially supported by the Romanian Education and Research Ministry by grant CNCSIS 920-41400/2003.

REFERENCES

1. Kaneko M, Tsuchida E. *J. Polym. Sci. Macromol. Rev.* 1981; **16**: 397.
2. Wenzel TJ, Yarmaloff LW, St Cyr L, O'Mcara LJ, Donatelli M. *J. Chromatogr. A* 1987; **396**: 51.
3. Woehrle D, Schnurpfeil G. In *Comprehensive Polymer Science*, 2nd Supplement, Aggarwal SL, Russo S (eds). Elsevier: Oxford, 1996; 577.
4. Constable EC, Cargill Thompson AMW, Tocher DA. *Polym. Prepr.* 1993; **34**(1): 110.
5. Noll W. *Chemistry and Technology of Silicones*. Academic Press: New York, 1968.
6. Voronkov MG, Mileshkevich VP, Yuzhelevski YuA. *The Siloxane Bond—Physical Properties and Chemical Transformations*. Consultants Bureau: New York, 1978; 47.
7. Barry AJ, Beck HN. Siloxane polymers. In *Inorganic Polymers*, Stone FGA, Graham WAG (eds). Academic Press: New York, 1962; 272.
8. Belwal S, Singh RV. *Appl. Organometal. Chem.* 1998; **12**: 39.
9. El-Nasser AA, Parish RV. *J. Chem. Soc. Dalton Trans.* 1999; 3463.
10. Aoki T, Shin K, Oikawa E. *Polym. J.* 1996; **28**: 106.
11. Aoki T. *Progr. Polym. Sci.* 1999; **24**: 951.
12. Marcu M, Cazacu M, Vlad A, Racles C. *Appl. Organometal. Chem.* 2003; **17**: 693.
13. Cazacu M, Marcu M, Vlad A, Toth A, Racles C. *J. Polym. Sci. Part A Polym. Chem.* 2003; **41**: 3169.
14. Cazacu M, Marcu M, Vlad A, Rusu GhI, Avadanei M. *J. Organometal. Chem.* 2004; **689**: 3005.
15. Varma IK, Chander K, Anand RC. *Angew. Makromol. Chem.* 1989; **168**: 217.
16. Gaul MD, Angelotti NC. Chemical analysis. In *The Analytical Chemistry of Silicones*, Smith A.L. (ed.), Wiley: 1991; 181.
17. McCarthy PJ, Hovey RJ, Ueno K, Martell AE. *J. Am. Chem. Soc.* 1955; **77**: 5820.
18. Hovey RJ, O'Connell JJ, Martell AE. *J. Am. Chem. Soc.* 1959; **8**: 3189.
19. Manecke G, Wille WE. *Makromol. Chem.* 1970; **133**: 61.
20. Gabryszewski M. *Spectrosc. Lett.* 2001; **34**: 57.
21. Dong D, Zhang R, Li G, Ni Y. *Polym. J.* 1999; **31**: 37.