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Chelate polymers. VI. New copolymers of the some siloxane containing bis(2,4-dihydroxybenzaldehyd-imine)Me^{2+} with bis(*p*-carboxyphenyl)diphenylsilane

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Abstract

New high complex polymeric structures containing metal chelate sequences alternating, through esteric bridges, with silane units were obtained. The azomethine of 2,4-dihydroxybenzaldehyde with 1,3-bis(aminopropyl)tetramethyldisiloxane has been synthesized and in situ complexed with copper (II), nickel (II), cobalt (II) and cadmium (II). The obtained bis-phenolic chelates were covalently inserted in polymeric linear structures by their polycondensation with bis(*p*-carboxyphenyl)diphenylsilane as a diacid chloride. The structures of the obtained polymers were confirmed by IR, UV, ^{1}H NMR and elemental analysis. The characterization was made by TGA, DSC, solubility tests and GPC. The electrical conductivity of both chelate monomers and their polymers was investigated, all compounds showing typical semiconducting behaviors.

Keywords: Azomethines; Chelate polyesters; Conducting polymers; Metal-polymer complexes; Siloxane ligands; Siloxane–silane copolymers

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1. Introduction

The branch of polymer–metal complexes has been developed as an interdisciplinary area involving chemistry, electrochemistry, metallurgy, environmental protection, and material science [1,2]. The chelate polymers constitute an important category of compounds in this area.

The potential applications of such polymers are, for example, as surface coatings on metals and glasses, adhesives, high-temperature lubricants, electrical insulators, semiconductors [2]. The polymer metal chelates were also found to act as electrochromic materials, since the colour of the polymer varies with the oxidation state of the metal ion present in the chelate [3]. Taking into account these potential applications, the characterization of the chelate polymers and study of their properties are therefore of great importance.

The chelate polymers are, in general, insoluble in common organic solvents, infusible or melted at high temperatures [4–7] and as a result, their application is somewhat limited due to processing difficulties. Their insolubility is explained by formation of coordination networks [5]. Therefore, many efforts have been made to develop structurally modified chelate polymers having increased solubility with retention of the other their good properties. One of way to achieve this goal could be covalently incorporation of the chelate moieties into flexible polymer system. The use of polysiloxane-based ligands could provide improved solubility for coordination polymers. Another important feature of siloxane

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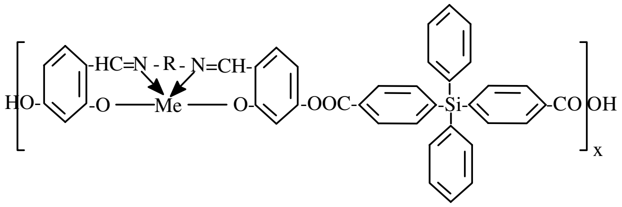
polymers is their unusually high gas permeability. The low intermolecular forces and high free volume in the siloxanes, compared to hydrocarbons are responsible for a low solubility parameter and high diffusion coefficient of gases [8]. The incorporation of some transition metals in siloxane polymers [9], as well as the catalytic activity of these metal-coordinated polymers have already been reported [10,11]. The polycondensation of copper, nickel, cobalt resorcylaldehyde-o-phenylenediamine complexes with dimethyl- or diphenyl-dichlorosilanes [12] also were performed, but the resulted polymers were insoluble [13].

On the other hand, many studies are dedicated to the synthesis of chelating agents based on the poly-Schiff bases [14–16], as semiconductor materials [17]. The electrical properties of Schiff bases and their polymers depend in great measure on the kind of amine and aldehyde from which they were obtained [18]. The literature is poorly regarding siloxane azomethines synthesis [19,20]. A series of polyazomethines containing pyridine ring and oligosiloxane moieties was already synthesized as macromolecular tridentate ligands, and complexed with cobalt in order to obtain highly oxygen permselective membrane [21–23].

The objective of the present study is to synthesize new polymeric materials containing transition metals and evaluate their electrical properties. Thus, we synthesized by a known technique [24,25] the N_2O_2 chelates of copper (II), nickel (II), cobalt (II) and cadmium (II) with Schiff bases derived from 2,4-dihydroxybenzaldehyde and siloxane diamine. The obtained complexes were then polycondensed with bis(*p*-carboxyphenyl)diphenylsilane in order to obtain polymeric linear structures of the type: (Scheme 1).

It is known that, the incorporation of diphenylsilyl as well as siloxane groups into a polymeric structure gives soluble products having remarkable thermal stability and good film-forming ability. More recently, silicon-containing aromatic polymers have attracted scientific interest because of their potential applications for the production of opto-electronic materials. The silicon having aromatic neighbours is able to give a σ–π conjugation which facilitates the electrons transport along the macromolecular chain [26]. Therefore, it is expected that, the coexistence of the siloxane, silane, coordinated metal, as well as azomethine and ester bridges within the same chain polymer, would create a superior balance of useful properties and processing capability.



with: R: $(CH_2)_3(CH_3)_2SiOSi(CH_3)_2(CH_2)_3$,

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

Scheme 1.

To the best of our knowledge, such structure has not found in literature.

2. Experimental

2.1. Materials

Copper (II) acetate monohydrate, $Cu(CH_3COO)_2 \times H_2O$, Nickel (II) acetate tetrahydrate, $Ni(CH_3COO)_2 \times 4H_2O$, Cobalt(II) acetate tetrahydrate, $Co(CH_3COO)_2 \times 4H_20$, Cadmium(II) acetate dihydrate, $Cd(CH_3COO)_2 \times 2H_2O$, methanol and chloroform (all purchased from Chimopar, Romania) were used as received.

1,3-Bis(aminopropyl)tetramethyldisiloxane (Fluka AG), (AP_0), was used as received. 2,4-Dihydroxybenzaldehyde was prepared and purified according to a procedure described in literature [27] (yield: 33%, m.p. 135–137 °C).

4-(Dimethylamino)pyridine with m.p. 110–112 °C and Pyridine (Fluka) were used as received.

2.2. Measurements

^{1}H NMR spectra were taken on a JEOL C-60 HL spectrometer using TMS as internal standard.

IR absorption spectra were recorded with KBr pellets on a FT-IR spectrophotometer DIGILAB SCIMITAR (USA).

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 in air using a MOM Derivatograph.

The DSC analyses were performed on a Metler TA DSC 12E instrument.

Gel Permeation Chromatographic analysis (GPC) was carried out on a PL-EMD 950 Evaporative Mass Detector instrument by using DMF as eluant after calibration with standard polystyrene samples.

The silicon content was determined according to an adapted procedure [28]: disintegration with sulphuric acid and ignition at 900 °C to a constant weight. Finally, the residue was treated with HF for silicon removal as SiF_4 and then calculation by difference.

Electrical measurements were performed on the thin films obtained from dimethylformamide solutions onto glass substrates. The substrate temperature during the film growth was about 330 K. Under these conditions, the solvent evaporation was very slowly. The thickness, *d*, of films was determined by Fizeau's method for fringes of equal thickness using an interferential microscope MII-4. Silver films ($d \approx 2$ μm) were used as electrodes [29].

2.3. Procedure

2.3.1. Chelate macromer

2,4-Dihydroxybenzaldehyde (AR), 1,3-bis(3-aminopropyl)tetramethyldisiloxane (AP_0) and metal acetate hydrate in molar ratio 2:1:1.5 were together dissolved in methanol at high dilution (for a 5% w/v solution) and refluxed with stirring for about 6 h. Then, the reaction mixture was concentrated by partial solvent removal in vacuum, and then poured in water. The formed precipitate was separated by filtration, washed with water, dried, first at 100 °C and then over P_2O_5 in vacuum, and then extracted with petroleum ether (yield: in the range 60–80%).

2.3.2. Bis(*p*-carboxyphenyl)diphenylsilane

DPCS, was prepared via a bi-step reaction according to a method described in literature [30]: the reaction of *p*-tolyl lithium with diphenyldichlorosilane afforded diphenylbis(*p*-ditolyl)silane which was further oxidized with chromium trioxide in glacial acetic acid–acetic anhydride–sulphuric acid mixture (yield: 56%, m.p. 248–252 °C).

2.3.3. Synthesis of the diacid chloride: Bis(*p*-chlorocarbonyl-phenyl)diphenylsilane, DPCIS.

5 g DPCS and 50 ml thionyl chloride were refluxed together for about 8 h. Then, 0.5 ml DMF was added in order to finalize the reaction and the refluxing was continued another 0.5 h. Finally, the thionyl chloride excess was removed by vacuum distillation. The remained white product was recrystallized from hexane. Diacid chloride yielded about 55% (m.p. 175–180 °C).

2.3.4. Synthesis of the coordination polymers

In an well-dried one-necked flask equipped with a magnetic stirrer and nitrogen inlet, diacid chloride (CDPC1S), bis-phenol chelate, 4-dimethyl aminopyridine and pyridine were introduced in 1:1:2:2 molar ratio. Freshly dried *N*-methyl-pyrollidone 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 in these conditions. Then, stirring was continued 24 h at room temperature even though the chlorohydrate as a white precipitate appeared just in the first 2–3 h. Finally, the reaction mixture was poured in a large excess of water, filtered, and washed with water.

Purification was made by repeated precipitation with water from NMP. Finally, the polymer was dried, first at 100 °C, and then over P_2O_5 in vacuum.

3. Results and discussion

The chelate macromers were prepared (Table 1), according to an already reported procedure [25]. The siloxane involving and by working in the polar medium (methanol) at high dilution permitted us to obtain soluble chelates. By using the di-OH functionalized starting aldehyde, the difunctional chelates are obtained, which can be used as monomers for polycondensation.

Chelate formation is proved by IR (Fig. 1(a)) and UV–Vis (Fig. 2) spectrometries. Thus, in IR spectra the stretching vibration frequency of the complexed C=N group at 1614 cm^{-1} (enveloping also the aromatic band) can be seen together with the other characteristic bands (cm^{-1}): 1254 (δ Si–CH_3 sym.), 1051 (Si–O–Si asym.), 795 (rocking asym. Si–C), 463 ($\nu_{Me \rightarrow N}$), 631 ($\nu_{Me \rightarrow N}$) [25,31,32]. The UV–Vis spectra, show specific bands for λ_{max} assigned to aromatic and azometinic π–π* transitions (at about 280 and 350 nm, respectively) [25].

In general, the obtained chelates are soluble in THF, DMF, DMSO, methanol, and ethanol. These chelates were inserted as sequences in polymeric structure. The polymerization of the metal containing monomers has already been applied to the synthesis of chelate polymers [1]. These types of polymer–metal complexes are known for their well-defined coordination structures. Polymerization can occur by radical or ionic initiation. Interfacial polycondensation of bifunctional low molecular chelates dissolved in NaOH with bifunctional aromatic acid chlorides dissolved in CH_2Cl_2 also was reported [1,33], to give polyesters, polyethers or polyamides. Polyesters can be obtained by either direct or activated polycondensation. Direct polycondensation requires high temperature which often leads to side reactions that limit

Table 1
The synthesized chelate and their polymers

Chelate	Contained metal	Resulted polymer	Polymer yield (%)	Polymer aspect
C_1	Cu	P_1	95	Green powder
C_2	Ni	P_2	85	Yellow powder
C_3	Co	P_3	85	Yellow powder
C_4	Cd	P_4	81	Yellow powder

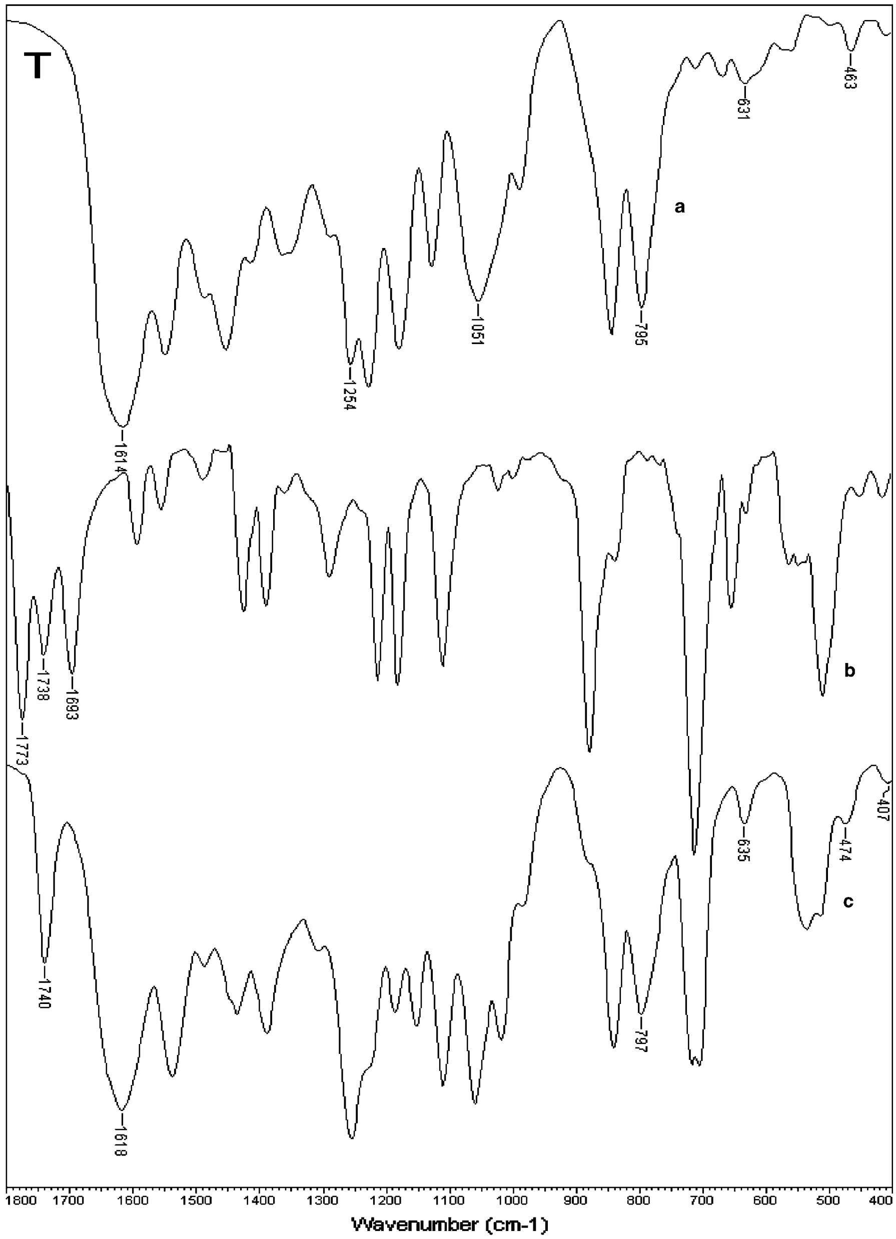


Fig. 1. Comparative IR spectra of the: (a) chelate C_2, (b) bis(*p*-chlorocarbonyl-phenyl)diphenylsilane, and (c) copolymer P_2.

the molecular weights of the polymers. Diacid chloride was used as activating agent in this study, in order to insert the chelate monomers in the polyester structures (Table 1) by working under mild conditions. The equimolecular amounts of bis-phenolic chelate and diacid chloride in NMP as a solvent, at high concentration (about 50%) were used. Two hydrochloric acid acceptors were added in order to assure the neutrality of the reaction medium and, as a result, to protect the coordination linkages. Also, the reaction occurred at low temperature in order to prevent undesirable side reactions. The resulted copolymers were isolated by precipitation with water from NMP (Scheme 2).

Some characteristics of the resulted polymers are given in Table 2. As it can be seen there is a satisfactory concordance between the found values and those calculated for the silicon and nitrogen contents taking into account the low molecular polymeric structure where the chain ends influence is significant in the case of the low polycondensation degrees.

All obtained polymers are soluble in: THF, DMF, NMP, DMSO. These good solubilities are due to the flexible siloxane presence but also to the diphenylsilane groups that introduce an asymmetry factor and steric hindrance that prevent a dense packing of the chains. The disturbed packing of macromolecular chains facilitates

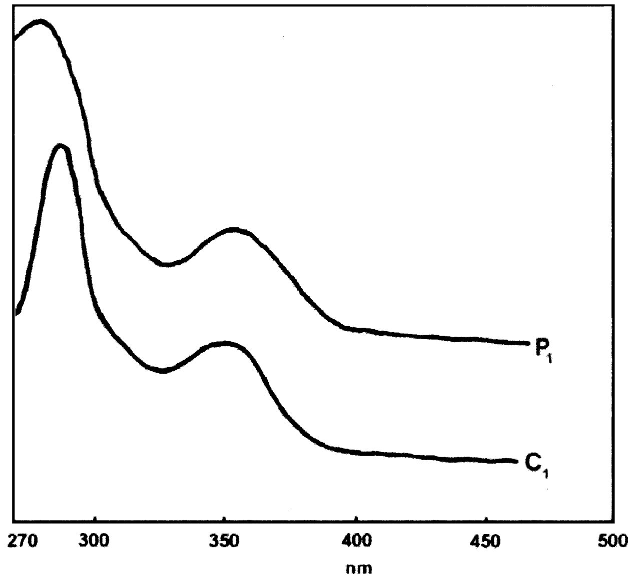
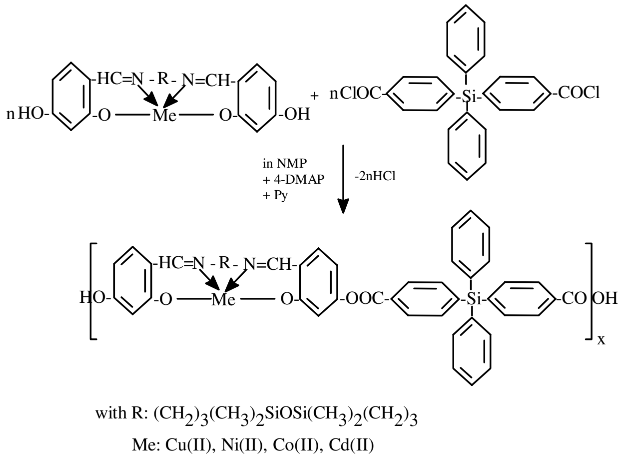


Fig. 2. Illustrative UV spectra for chelate C_1 and related copolymer P_1, in DMF, at 20° C.



with R: $(CH_2)_3(CH_3)_2SiOSi(CH_3)_2(CH_2)_3$
Me: Cu(II), Ni(II), Co(II), Cd(II)

Scheme 2.

the diffusion of small molecules of solvents between the polymer chains, which leads to better solubility [26].

In the IR spectra (Fig. 1(c)) an intense band at 1740 cm^{-1} assigned to the esteric groups formed as a result of the polycondensation reaction appears beside the other characteristic bands. The IR spectrum of the partially hydrolyzed diacid chloride also was recorded for comparison in Fig. 1(b).

When comparing the UV spectra of the obtained polymers with the corresponding chelates (namely, the copper based compounds, Fig. 2), a slight hypsochromic shifting of the aromatic transitions could be noted, probably due to the presence of the new neighbourhoods, as a result of the polycondensation.

As is known [34], proton magnetic resonance is not well applicable for chelate compounds because a broadening of the spectrum appeared as a result of the ligand complexation with metal ions (with copper, in special). However, in the ^1H NMR spectra of the polymers containing Ni, Co or Cd, the following large signals can be distinguished: 0.0–0.5 ppm (CH_3SiO) and 7.5–8.25 ppm (aromatic protons), which agree with the presumed structures.

The polymers have average gravimetric molecular weights (measured by GPC with evaporative mass detector) in the range 3000–5800 (Table 2). A very approximative estimation on the basis of these values revealed a maximum polycondensation degree of about 6, indicating rather the oligomeric structures formation.

The thermo-oxidative stability was estimated by TGA. The thermal decomposition profiles of the copolymers containing various metals compared to some chelate monomers are shown in Fig. 3. Some data derived from TG curves are summarized in Table 3 where the thermal stability in terms of onset and offset temperatures and 10-wt% losses are given. Although a modification of the thermal stability by polycondensation or depending on the metal cation electronegativity is expected [35] this is rather unsignificantly. Both chelate monomers and polymers show onset temperature values in the range 230–290 °C. The transition metal and silicon presences are reflected in high percent of the thermal decomposition residue. The water presence is also evidenced in TGA curves of some chelates (Fig. 3) which showed until 2% weight losses in the range 100–200 °C assigned both crystallization (100–150 °C) and coordination water (150–200 °C) removal [3,36]. This can also explain the differences appeared between the found and calculated elemental analysis values.

Table 2
Some analytical data for the synthesized chelate polymers

Sample	Elemental analysis (%), Found/Calc.[a]		M_w[c]
	N	Si[b]	
P_1	3.3/3.0	10.3/9.0	5500
P_2	3.1/3.0	10.1/9.0	3600
P_3	3.1/3.0	9.8/9.0	3000
P_4	2.7/2.8	8.2/8.5	5800

[a] Calculated for the presumed structural unit.
[b] Determined according to [30].
[c] Estimated by GPC.

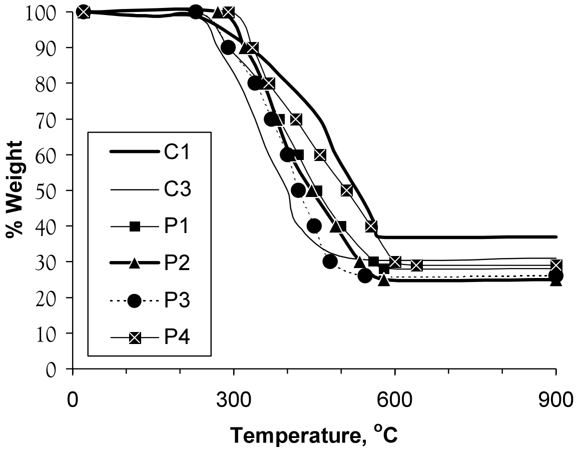


Fig. 3. The thermogravimetric curves for the obtained chelate polymers as comparing to some monomers.

The DSC traces of the copolymers do not evidence any transition in the temperature range 20–200 °C.

The electrical conductivity of the metal complexes containing siloxane and their polyesters with silane has been measured using the thin films having thickness, d, between 0.52 and 1.36 μm. It was experimentally established that the stable structures of films can be obtained if, after preparation, they are submitted to a heat treatment within a given temperature range ΔT, indicated for each compound/polymer in Table 4. In these temperature domains the chelates and polychelates loss the water molecules. An exponential increase of the electrical conductivity with the temperature has been observed in all temperature range ΔT. The intrinsic conduction domain begins at a certain temperature T_c, characteristic for every sample (Table 4). In the intrinsic domain, the temperature dependence of the electrical conductivity is given by the expression:

$$\sigma = \sigma_0 \exp(-\Delta E/2KT),$$

where ΔE is thermal energy of electrical conduction, K denotes Boltzman constant and σ_0 is a parameter depending on the semiconductor nature. The values of ΔE depend on the molecular structure of the compounds. The found conductivities were in the range 10^{-9}–10^{-7} Ω^{-1} cm^{-1}.

The chelate monomers have increased electrical conductivities and lower activation energy values as comparing with the similar compounds without silicon [17]. Excepting the cobalt containing compounds these increasing trends are emphasized by polycondensation with the silane diacid as a result of the extended conjugation favoured by the presence of aromatic rings.

Table 3
The main thermogravimetric data for synthesized structures

Sample	T_{on}[a]	10% Weight Losses	T_{of}[b]	% Weight residue
C_1	230	330	570	37
C_2	260	290	500	27
C_3	240	270	515	31
C_4	290	300	605	29
P_1	230	290	580	28
P_2	270	320	580	25
P_3	230	290	545	26
P_4	290	335	640	29

[a] The onset temperature.
[b] The offset temperature.

Table 4
Some electrical parameters of the chelates and their polymers

Sample	d (μm)[a]	ΔT[b]	σ_T (Ω^{-1} cm^{-1})[c]	T_c (K)[d]	ΔE (eV)[e]
C_1	0.75	300–475	$8.55.10^{-8}$	385	1.82
C_2	0.55	300–460	$2.25.10^{-8}$	370	2.36
C_3	0.78	300–470	$6.67.10^{-7}$	355	1.40
C_4	0.66	300–480	$7.56.10^{-9}$	380	2.40
P_1	0.83	300–465	$8.10.10^{-7}$	355	1.50
P_2	1.36	300–450	$9.00.10^{-7}$	370	2.35
P_3	0.52	300–450	$4.17.10^{-7}$	370	1.80
P_4	1.25	300–455	$6.15.10^{-7}$	357	1.20

[a] Film thickness.
[b] Temperature range in which the heat treatment of respective sample was performed.
[c] Electrical conductivity at room temperature after heat treatment.
[d] Characteristic temperature for heat-treated samples (for $T > T_c$ samples possess an intrinsic conduction).
[e] Thermal activation energy of electrical conduction.

4. Conclusions

Four new polymers were obtained by polycondensation of the siloxane containing bis-phenolic chelates with a bifunctional silane. The resulted structures were confirmed by IR, UV and elemental analysis. The siloxane and silane presences in such structures confer the improved solubility. The chelate monomers have conductivities typically for semiconducting materials. Excepting the case of the cobalt compounds, the conductivity increases by polycondensation with silane and also depends on the metal from their structure.

Acknowledgements

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References

[1] T. Kaliyappan, P. Kannan, Progr. Polym. Sci. 25 (2000) 343.

[2] W. Kaminski, Z. Modrzejewska, Sep. Sci. Technol. 32 (1997) 2659.

[3] B.L. Rivas, G.V. Seguel, C. Acatripai, Polym. Bull. 44 (2000) 445.

[4] V.V. Korsak, E.S. Krongauz, P.N. Gribkova, V.A. Vasnev, Vysokomol. Soedin. 4 (1962) 815.

[5] V.V. Korsak, S.V. Rogojin, V.I. Volkov, Vysokomol. Soedin. 4 (1962) 20.

[6] V.V. Korsak, S.V. Vinogradova, V.S. Artemova, Vysokomol. Soedin. 4 (1961) 492.

[7] V.V. Korsak, S.V. Vinogradova, V.S. Artemova, T.N. Babciniter, S.A. Pavlova, Vysokomol. Soedin. 3 (1961) 1116.

[8] W. Noll, Chemistry and Technology of Silicones, Academic Press, New York and London, 1968 p. 437.

[9] I.V. Blagodatskikh, O.I. Shchegolikhina, T.A. Larina, A.A. Zhdanov, V.G. Vasil'ev, Vysokomol. Soedin. A 38 (1996) 1876.

[10] R. Ophir, Y. Shvo, J. Mol. Catal. 140 (1999) 259.

[11] N. Nemoto, T. Yotsuya, S. Aoyagi, Y. Ueno, K. Ikeda, N. Takamiya, Polym. Commun. 31 (1990) 65.

[12] M. Marcu, M. Spiratos, Patent Romania 66034, (1977).

[13] M. Marcu, S.E. Lazarescu, G.E. Grigoriu, Mater. Plast. 26 (1989) 196.

[14] S. Samal, R.R. Das, D. Sahoo, S. Acharya, R.L. Panda, R.C. Rout, J. Appl. Polym. Sci 62 (1996) 1437.

[15] S. Samal, R.R. Das, R.K. Dey, S. Acharya, J. Appl. Polym. Sci. 77 (2000) 967.

[16] S. Samal, N.K. Mohapatra, S. Acharya, React. Funct. Polym. 42 (1999) 37.

[17] G.I. Rusu, Ann. Sci. Univ. Iassy, Cond. Matt. Phys, 45/46 (1999–2000) 229.

[18] I. Kaya, S. Koyuncu, Polymer 44 (2003) 7299.

[19] P.J. Madec, E. Marechal, Polym. Prepr. 34 (1993) 814.

[20] S. Belwal, R.V. Singh, Appl. Organomet. Chem. 12 (1998) 39.

[21] K. Shin, T. Aoki, E. Oikawa, Macromol. Rapid Commun. 16 (1995) 599.

[22] T. Aoki, K. Shin, E. Oikawa, Polym. J. 28 (1996) 106.

[23] T. Aoki, Progr. Polym. Sci. 24 (1999) 951.

[24] D. Woehrle, Adv. Polym. Sci. 50 (1983) 45.

[25] M. Marcu, M. Cazacu, A. Vlad, C. Racles, Appl. Organomet. Chem. 17 (2003) 693.

[26] E. Hamciuc, M. Bruma, B. Schultz, T. Kopnick, High Perform. Polym. 15 (2003) 347.

[27] M. Bisagni, N.P. Bun-Hoiet, R. Roger, J. Chem. Soc. 11 (1955) 3688.

[28] M.D. Gaul, N.C. Angelotti, in: A.L. Smith (Ed.), The Analytical Chemistry of Silicones, Wiley, 1991, p. 181.

[29] G.I. Rusu, G.G. Rusu, M.E. Popa, Mater. Res. Innovat. 7 (2003) 372.

[30] I.K. Varma, K. Chander, R.C. Anand, Die Angew. Makromol. Chem. 168 (1989) 217.

[31] M. Gabryszewski, Spectrosc. Lett. 34 (2001) 57.

[32] D. Dong, R. Zhang, G. Li, Y. Ni, Polym. J. 31 (1999) 37.

[33] M. Spiratos, A. Airinei, A. Ciobanu, Rev. Roum. Chim. 25 (1980) 1083.

[34] M. Kaneko, E. Tsuchida, J. Polym. Sci.-Macromol. Rev. 16 (1981) 397.

[35] A.H. Basta, H. El-Saied, Polym.-Plast. Technol. Eng. 39 (2000) 887.

[36] V. Banerjie, A.K. Dey, Makromol. Chem. Rapid Commun. 1 (1980) 41.