

Chemical Insertion of Transition Metals Into Some Silicone-Based Polymer Structures

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Some new iron (II)-polymer complex structures having siloxane units included either in ligand structure or as co-monomer partner with an already metal (Fe^{2+}) complexed structure were prepared and characterized by the spectral and elemental analysis. Solubility tests and viscosity measurements have also been performed.

Keywords: siloxane, iron complexes, azomethine, ferrocene

The incorporation of transition metals into a polymer main chain offers unique potential for the preparation of processable materials with properties, which differ significantly from those of conventional organic polymers [1].

Particularly, the organometallic chemistry of iron is dominated by complexes that contain cyclopentadienyl and/or carbonyl ligands [2]. The chemistry of ferrocene-based structures has been receiving increasing attention because of their importance in many fields such as electrochemistry, materials science, organic synthesis and catalysis. This is because the ferrocene unit has proved to be a versatile structural moiety with excellent thermal and photochemical stability, as well as with unique and valuable redox properties. Poly(ferrocenyl)-based macromolecules are of interest for their useful application in the chemical modification of electrodes, as electrode mediators, electrochemical sensors, as materials for the construction of liquid crystals, electronic devices, non-linear optical (NLO) systems and as chiral ligands for asymmetric catalysis [3].

On the other hand, the field of Schiff base complexes was fast developed on account of the wide variety of possible structures for the ligands depending upon the aldehydes and amines. Many attempts were done to prepare symmetric polydentate ligands in order to achieve rare coordination number with divalent metal ions whose importance was mainly due to their ability to form metal chelates. Even though many Schiff bases using salicylaldehyde and substituted salicylaldehydes and amines were studied as ligands, no work was done with salicylaldehyde and amino-siloxanes as the basic nucleus of Schiff bases. Schiff base metal complexes constitute a widely studied subject due to their industrial and biological applications found in the field of pesticides and medicine [4].

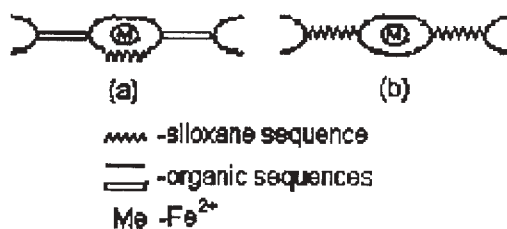
Complexes that contain Fe(II) and Fe(III) can show a wide range of magnetic behaviors [2].

Three polyester structures containing Fe complexed units in the main chain and siloxane sequences, either in ligand (a) or in co-monomer structure (b) (scheme 1), are reported in this paper.

Experimental part

Materials

1,3-Bis(3-aminopropyl)tetramethyldisiloxane (AP_0), (Fluka AG), and 1,3-Bis(hydroxypropyl) tetramethyl-



Scheme 1

disiloxane (HP_0) (ABCR GmbH & Co) were used as received.

1,1'-Di(chlorocarbonyl)ferrocene (CEN) was prepared by a three-step procedure starting from the ferrocene, according to methods described in literature [5,6].

Iron(II) sulphate heptahydrate, $Fe(SO_4)_2 \cdot 7H_2O$, purchased from Chimopar, Romania was used as received.

2,4-Dihydroxybenzaldehyde (Ar) was prepared and purified according to known procedure described in literature (m. p. 135-137 °C).

2,4-Dihydroxybenzophenone (Bf), m. p. 143-145° was purchased from Fluka AG.

Bis(p-chlorocarbonyl-phenyl)diphenylsilane (CA) was prepared by a three-step reaction according to a method described in literature [7].

Iron bis-phenol chelates were prepared, according to an already reported procedure [8-10]: Siloxane diamine, (AP_0), carbonylic compounds (Ar or Bf), and Fe(II) sulphate heptahydrate, in molar ratio 2:1:1.15 were mixed together in methanol solution (about 10%) and refluxed with stirring for about 5 h. After partial removing of the solvent, the filtrate was poured in water, filtered, washed with water and petroleum ether, and finally, dried in vacuum over P_2O_5 , at room temperature.

Pyridine (Fluka) was used as received.

Methylene chloride and NMP were dried according to the known procedures.

Measurements

IR absorption spectra were recorded with KBr pellets on a Specord M80 Carl Zeiss Jena, Germany spectrophotometer.

The silicon content was determined according to a known procedure [11]: disintegration with sulphuric acid and ignition at 900 °C to constant weight. When a chelate is analyzed, the residue was treated with HF for silicon removal as SiF_4 and then calculated by difference. The iron content was also determined from the residue.

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Procedure

a. Polycondensation of the iron *bis*-phenol chelates with a diacid chloride

In a well-dried installation consisting in one-necked flask equipped with a magnetic stirrer and nitrogen inlet, diacid chloride (CA), *bis*-phenol chelate, 4-dimethyl aminopyridine and pyridine were introduced in 1:1:2:2 molar ratio. Freshly dried N-methyl-pyrrolidone 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 hour in these conditions. Then, stirring was continued for 24 h at room temperature even, though the chlorohydrate as a white precipitate appeared just in the first two-three hours. 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 P₂O₅ in vacuum.

b. Polycondensation of the 1,1'-Di(chlorocarbonyl)-ferrocene (CEN) with 1,3-Bis(hydroxypropyl)tetramethyl-disiloxane (HP₀)

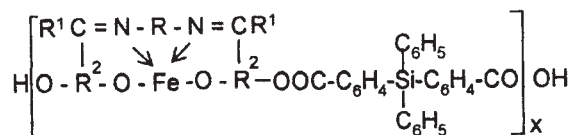
In the same above described installation, CEN and HP₀ in molar ratio 1:1 were dissolved together in freshly dried CH₂Cl₂ for a solution of about 50 wt.-% concentration.

Pyridine in molar ratio 2:1 related to ferrocene was added. The reaction mixture was stirred at refluxing temperature for about 4h and then, until 24h at room temperature. Finally, the reaction mixture was filtered in order to separate the pyridine chlorohydrate. The filtrate was washed with water in a separation funnel, dried on anhydrous sodium sulfate, filtered and the solvent was removed by vacuumation. The polymer was dried over P₂O₅ in vacuum. An orange, viscous oil was obtained and characterized.

Results and discussions

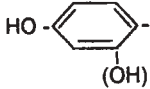
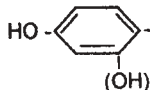
a. Metal-containing polyesters having siloxane enclosed in the ligand structure

The polymerization of the metal containing monomers has already been applied to the synthesis of the chelate polymers [12]. These types of polymer-metal complexes are known for their well-defined coordination structures. Polyesters can be obtained by either direct or activated polycondensation. Diacid chloride was used as an activating agent in this study, in order to obtain the polyesteric structures by working in mild conditions. The equimolecular amounts of *bis*-phenolic chelate and diacid chloride in NMP as a solvent, at high concentration (about 50%) were used.



with R: (CH₂)₃(CH₃)₂SiOSi(CH₃)₂(CH₂)₃

Me: Fe(II)

Sample/Carbonylic compound	-R ₁	-R ₂
P1/ 2,4-Dihydroxybenzaldehyde	-H	
P2/2,4-dihydroxybenzophenone	-C ₆ H ₅	

Scheme 2

Table 1
POLYMERS CONTAINING SILOXANE UNITS IN THE LIGAND STRUCTURE

Code	Reactants	^a η _{red} ²⁵	Aspect	Solubility	Elemental analysis, %wt, found/calc.	
					N	Si
P1	Ar, APo, CA, iron salt	0.075	Brown-redish	DMF, DMSO	3.5/2.8	7.1/7.7
P2	Bf, APo, CA, iron salt	0.055	Brown	DMF, NMP, CHCl ₃	3.0/3.2	8.6/9.5

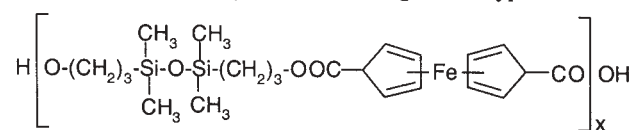
^a Determined in DMF at 25°C for a concentration of about 0.5g/dl.

The reaction was monitored by the IR spectra where an intense band appears at 1740 cm^{-1} assigned to the esteric group formed as a result of the polycondensation reaction. The absorption assigned to the complexed azomethine at about 1610 cm^{-1} , as well as the absorption at 800 cm^{-1} for Si-CH₃ are visible. The Si-O-Si ($1050\text{-}1100\text{ cm}^{-1}$) and Si-CH₃ (1260 cm^{-1}) characteristic absorption bands are overlapped with another bands. The metal presence is proved by the bands at $407\text{ and }474\text{ cm}^{-1}$ ($\nu_{\text{Me}\rightarrow\text{N}}$), and 635 cm^{-1} ($\nu_{\text{Me}\rightarrow\text{O}}$) [8].

Some characteristics of the two obtained polymers are presented in table 1.

b. Metal-containing polyesters having siloxane in the comonomere structure

The difunctional ferrocene derivative, namely 1,1'-Ferrocenedicarboxylic acid was proved to be a convenient intermediary for polyester obtaining of the type:



The used siloxane precursor was 1,3-Bis(3-hydroxypropyl)tetramethyldisiloxane (HP₃). The polycondensation reaction occurred in solution using methylene chloride as a solvent. The resulted polymer as an orange viscous oil was characterized by spectral and elemental analysis.

The spectroscopic data confirm the formation of the polyester. Thus, the acid chloride C=O peak seen at 1760 cm^{-1} disappears coincidentally with the appearance of an ester resonance at 1720 cm^{-1} . The bands at 3100 cm^{-1} assigned to 1,1'-disubstituted ferrocene ring and at 1050 cm^{-1} assigned to Si-O-Si bond are also present in the IR spectrum. Elemental analysis (Found/Calc.): C: 50.5/52.8; H: 7.6/8.8; Si: 10.2/11.2; Fe: 11.5/ 11.2. The polymer is soluble in all common solvents.

Conclusion

New polyester structures containing iron complexed units and siloxane sequences in the backbone were synthesized by using activated polycondensation technique, in which a diol and a diacid chloride are involved. The esteric linkage formation was well evidenced by IR spectra.

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References

1. MANNERS, I., Pure Appl. Chem., **71**, **8**, 1999, p. 1471
2. FRYZUK, M. D., LEZNOFF, D. B., MA, E. S. F., RETTIG, S. J., AND YOUNG, JR V. G., Organometallics, **8**, **17**, 1998, p. 2313
3. ALONSO, B., GONZALEZ, B., GARCIA, B., RAMIREZ-OLIVA, E., ZAMORA, M., CASADO, C. M., CUADRADO, I. J. Organomet. Chem., **637-639**, 2001, p. 642
4. MOHAMED G. G., AND ABD EL-WAHAB, Z. H., J. Therm. Anal. Calorim., **73**, 2003, p. 347
5. VOGEL, M., RAUSCH, M., ROSENBERG, H., J. Organomet. Chem. **22**, 1957, p. 1016
6. KNOBLOCH, F. W., RAUSCHER, W. H., J. Polym. Sci. **51**, 1961, p. 651
7. VARMA, I. K., CHANDER, K., ANAND, R. C., Die Angew. Makromol. Chem., **168**, 1989, p. 217
8. CAZACU, M., MARCU, M., VLAD, A., RUSU, G. I., AVĂDANEI, M. J. Organomet. Chem., **689**, **19**, 2004, p. 3005
9. MARCU, M., CAZACU, M., VLAD, A., RACLES, C., Appl. Organomet. Chem., **17**, 2003, p. 693
10. VASILIU, M., CAZACU, M., MARCU, M., RACLES, C., VLAD A., Appl. Organomet. Chem. **19**, 2005, p. 614
11. GAUL, M. D., ANGELOTTI, N. C. Chemical Analysis. In: The Analytical Chemistry of Silicones, 1991, p. 181, Smith A. Lee (Ed.), Wiley.
12. KALIYAPPAN T, KANNAN P., Progr. Polym. Sci., **25**, 2000, p. 343

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