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Special Polymers

Chelating polymers

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SUMMARY

Chelating polymers were synthesized by polymer analogous reaction of polyethyleneimine with chelating agents: 2-hydroxy-4[2-chloroethanoyl]benzophenone, butanoic-4-oxo-4-(2'-hydroxy-5'-methyl-phenyl)acid and 4,4'-o-o'-succinoyl-bis-resorcylaldehyde. The chelating agents were characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy.

The polychelates are insoluble in water and common organic solvents and they were characterized by IR spectroscopy. These polymers were contacted with an aqueous solution of copper(II), nickel(II) and cobalt(II).

INTRODUCTION

Synthesis of polymer carrying ligands as pendant groups on a polymer chain has been a subject of great interest(1-2). Chelating polymer consist of a polymer backbone and a grafted chelating group. This chelating group may be incorporated in the monomer structure or added to polymer backbone by polymer-analogous reaction. On the other hand, polyethyleneimine(PEI) a functional polymer, is known for their ability for complex with heavy metals (3-10).

In this paper is reported the synthesis of three chelating polymers by addition to polyethyleneimine of the following chelating agents: 2-hydroxy-4-[2-chloroethanoyl]benzophenone(I); butanoic 4-oxo-4-(2'-hydroxy-5'-methyl-phenyl) acid(II) and 4,4'-o-o'-succinoyl-bis-resorcylaldehyde(III).

EXPERIMENTAL PART

Synthesis of 2-hydroxy-4-[2-chloroethanoyl]benzophenone(I).

It was synthesized by Schotten-Baumann reaction. First 36.24 g (0.17 mol) 2,4-dihydroxybenzophenone were dissolved in 20 ml dichloromethane. To this solution, 16 ml pyridine and then 22.59 g monochloroacetic acid were added drop by drop. The reaction was stirred for 2 h. The crude was washed once with HCl 10% and with water till neutral. The organic phase was dried with $CaCl_2$, the solvent evaporated and the product crystallized from carbon tetrachloride. Yield: 75%; m.p.:90°C

Synthesis of butanoic 4-oxo-4-[2'-hydroxy-5'-methyl-phenyl]acid(II).

To solution of 108 g (1.0 mol) p-cresol in 500 ml nitrobenzene, 132 g (1.0 mol) $AlCl_3$ were added. Then 100 g (1 mol) succinic anhydride dissolved in nitrobenzene slowly were added. The reaction mixture was heated to 120-130°C. After 30 min a dark brown solid product is obtained. The reaction is kept for 2 h and it is poured on water-ice-HCl mixture and the organic phase is separated. It is extracted with NaOH 3N and neutralized with HCl 3N. The pure product was obtained by crystallization from water. Yield 30%; m.p.:136°C.

Synthesis of 4,4'-o-o'-succinoyl-bis-resorcylaldehyde (III).

Method A: A solution of 9 g (0.09 mol) succinic anhydride, 10 g (0.09 mol) resorcylaldehyde and acetone was refluxed for 5 h. The solvent was evaporated and the solid was crystallized from chloroform. Yield:25%.

Method B: A mixture of 10 g resorcylaldehyde and 9 g succinic anhydride were dissolved in dichloromethane/pyridine. It was refluxed for 7 h and washed with water, HCl 20%. The product was purified by crystallization from chloroform. Yield: 17.9%; m.p.:92-94°C.

Synthesis of Chelating Polymer A.

To 4 g PEI, 5 g (0.014 mol) 4,4'-o-o'-succinoyl-bis-resorcylaldehyde (III) dissolved in methanol were added with stirring at room temperature . The crude solid was washed with ethanol several times and dried under vacuum Yield: 9.0 g.

Synthesis of Chelating Polymer B.

To a solution of 5.0 g (0.023 mol) butanoic 4-oxo-4'-(2'hydroxy-5'-methyl-phenyl)acid (II) in dichloromethane, 3.57 g (0.03 mol) thionyl chloride were added. After two hours, the solvent and excess of thionyl chloride were evaporated yielding a red solid. To 5.3 g acid-chloride dissolved in CH_2Cl_2, 1.0 g PEI was added. The reaction mixture was stirred for 3 h at room temperature. The brown solid was dried under vacuum. Yield:3.8 g.

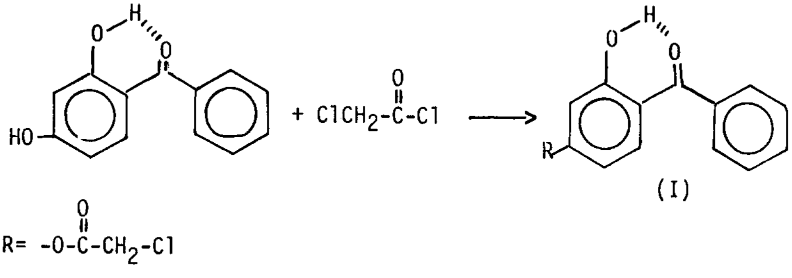
Synthesis of Chelating Polymer C.

One g PEI and 6.7 g 2-hydroxy-4-(2-chloroethanoyl)benzophenone(I) were dissolved in CH_2Cl_2 and heated and stirred for two hours. Yield: 0.54 g.

Measurements. The IR spectra were recorded on a Perkin Elmer 577 spectrophotometer. The ^1H NMR and ^{13}C NMR spectra were recorded in a 60 MHz Varian T-60 A, and 20 MHz Varian CFT spectrometer respectively. Copper, cobalt and nickel were analyzed on a Perkin Elmer 306 Atomic absorption spectrometer.

RESULTS AND DISCUSSION

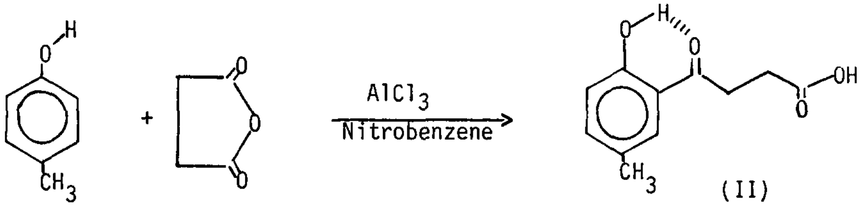
The chelating agents were synthesized from resorcinol, p-cresol and succinic anhydride. The structure of 2-hydroxy-4-(2-chloroethanoyl) benzophenone is similar to LIX reagents which are α-hydroxyketoximes used in the selective extraction of copper. This compound(I) has a hydroxy and carboxylic group in positions 1 and 2, respectively, which allow condensation with primary amine groups. Besides, the 2-chloroethanoyl group allows the grafting of polyethyleneimine.



(I)

The IR spectrum of (I) presents characteristic absorption bands corresponding to $\nu_{C=O}$ at 1702 cm^{-1} and ν_{O-H} at 3300 cm^{-1}.

Butanoic 4-oxo-4'-(2'-hydroxy-5'-methyl-phenyl) acid (II) was synthesized by Friedel Crafts acylation of p-cresol with succinic anhydride (11). The reaction occurs only at the orto position as the p-position is occupied.



(II)

The ^{1}H NMR spectrum of (II) ($CDCl_3$, room temperature, 60 MHz and TMS) shows a singlet at δ=2.3 ppm assigned to methyl protons. The triplet at δ=3.0 ppm is attributed to methylene protons (2H) attached to carboxilic acid group; the triplet at 3.4 ppm (2H) is assigned to methylene protons attached to the carbonyl group and multiplet between 7.0-8.0 ppm corresponds to the aromatic protons (3H).

The ^{13}C NMR spectrum ($CDCl_3$, 20MHz, room temperature) shows signals that corroborate this structure. Signals at 178.12 and 170.89 ppm were assigned to -C=O and O=C-OH respectively. Four signals at 148.53, 135.54, 128.82 and 120.02 ppm were assigned to aromatic carbons. The signal at 28.72 ppm was assigned to the two methylene carbons which are accidentally equivalent. The signal of the sp^3 carbon (CH_3) is at 20.80 ppm (See fig.1)

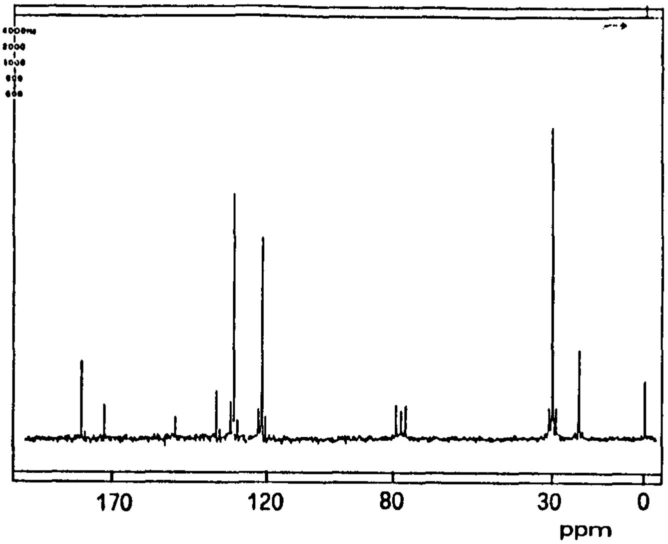
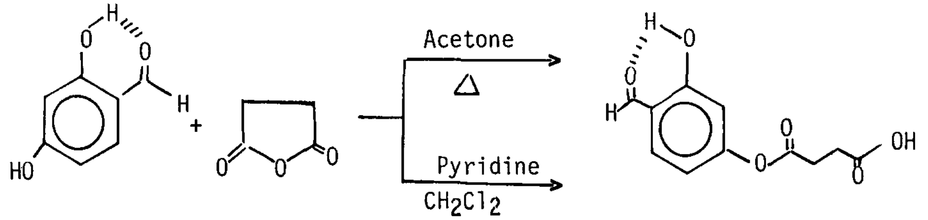
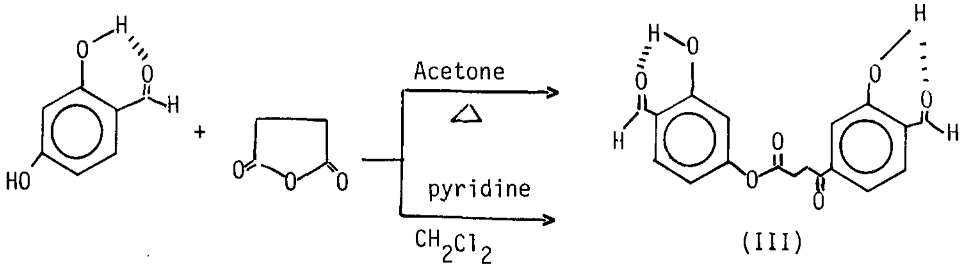


Figure 1.- ^{13}C NMR ($CDCl_3$, 20MHz, room temperature) spectrum of butanoic 4-oxo-4'-(2'-hydroxy-5'-methyl-phenyl)acid.

With respect to the chelating agent (III) we wanted to obtain the compound (III)*;two methods were attempted but in both cases the end product was 4,4'-o-o'-succinoyl-bis-resorcylaldehyde (III).



(III)*



(III)

The ^1H NMR spectrum shows a singlet (4H) at 2.55 ppm assigned to methylene protons. In the region between 5.6 to 7.0 ppm there is a multiplet (6H) corresponding to aromatic protons and a singlet 9.1 ppm assigned to the aldehyde proton that forms a hydrogen bridge with the hydroxy group.

The ^{13}C NMR spectroscopy supports structure(III) which has a plane of symmetry which is not present in structure(III)*. The ^{13}C NMR spectrum shows 9 signals. The signal at 216.47 ppm is assigned to the carbonyl carbon that forms a hydrogen bridge with the hydroxy group. At 181.48 ppm appears a signal corresponding to carboxy carbon (ester group). The six signals at 174.72, 173.39, 145.30, 124.12, 117.94 and 111.62 ppm were assigned to sp^2 carbons of the aromatic ring and that at 38.23 ppm was assigned to the methyl carbon (see figure 2).

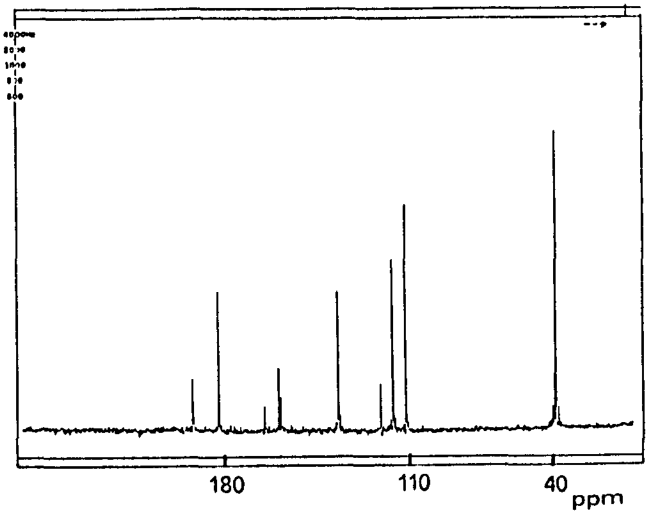


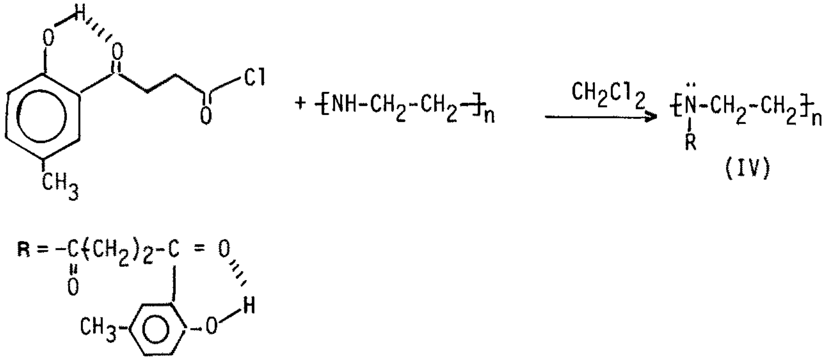
Figure 2.- ^{13}C NMR of 4,4'-o-o-succinoyl-bis-resorcylaldehyde(III).

A possible explanation for obtaining(III) is that resorcylaldehyde reacts with succinic anhydride forming(III)* which then reacts with an other succinic anhydride molecule to give a mixed anhydride; the latter by nucleophilic attack reacts with an other resorcylaldehyde molecule forming compound(III) and succinic acid.

Synthesis of Chelating Polymers.

To obtain chelating polymers the chelating compounds were incorporated as pendant groups to branched polyethyleneimine. Polychelates are insoluble in water and common organic solvents. As an example, the polymer analogous reaction for chelating agent(II) is shown. PEI is a commercial product (Aqueous solution, 40% from Aldrich Chem.Co.)

Polymer A was synthesized by condensation between the primary amine group of PEI with the aldehyde group of the chelating agent forming a Schiff base. This polymer is yellow and insoluble in water and organic solvents.



(IV)

Polymer B contains ketoimine and amide groups. This polymer as brown. The IR spectrum shows absorption bands at 3400 cm^{-1} (ν_{OH} associated), at 1640 cm^{-1} ($\nu_{C=N}$), at 1290 cm^{-1} (ν_{OH} phenolic).

Polymer C is formed by reacting the primary and secondary amine groups pf PEI with chelating agent(I) forming an α-hydroxyketoimine. It is a white solid, insoluble in water and organic solvents. The IR spectrum shows a broad absorption band between 3400 and 3200 cm^{-1} assigned to the H bridge between OH and NH groups. The spectrum shows further absorption at 1630 cm^{-1} ($\nu_{C=N}$), at 1560 cm^{-1} ($\nu_{C=O}$) from ester, and at 1280 cm^{-1} a characteristic absotption band of phenolic hydroxyl group.

Extraction properties of Chelating Polymers.

Chelating polymers were contacted with aqueous solutions of copper (II), nickel(II) and cobalt(II).

Chelating polymer A-Cu(II). One g chelating polymer was contacted for 5h with a solution containing 15.3 g copper sulphate pentahydrate. The polychelate was dark blue.

Chelating polymer A-Ni(II). Chelation was carried out in similar way but the contact time was 22 h.

Chelating polymer A-Co(II). In this case the contact time was 22 h and the complex polymer was black.

Chelating polymer B-Cu(II), Ni(II) and Co(II). The polymer was contacted with different aqueous solutions for 24 h but there was no complex formation.

Chelating polymer C-Cu(II), Ni(II) and Co(II). One g polymer was contacted for 24 h with a solution of 3.5 g/l in copper. No complex formed with Co(II) and Ni(II).

The extraction results are summarized in Table 1.-

Table 1.- Extraction properties for chelating polymers.

Chelating Polymer	Extracted ion(meq/g)		
	Cu(II)	Co(II)	Ni(II)
A	4.0	2.5	2.5
B	-	-	-
C	2.0	-	-

Only chelating polymer A forms complexes with all metallic ions. Chelating polymer B does not form stable complex with copper(II), nickel(II) and cobalt(II) and polymer C does not form complexes with nickel(II) and cobalt (II).

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