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Schiff's Base Chelates

Polymeric Schiff's Base Chelates and Their Precursors

5[a] Copolymerization of 2-Hydroxy-5-Vinylbenzaldehyde and Synthesis of Covalently Polymer Bound Cobalt Chelates

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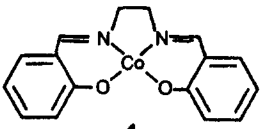
SUMMARY

Covalently polymer bound Schiff's base chelates 8, 12 of the salcomine type were synthesized by copolymerization of 2-butylimino-4-vinylphenol (3) with styrene in different molar ratios, followed by polymer analogous reactions. The copolymerization parameters were determined.

INTRODUCTION

The excellent properties of low molecular Schiff's base chelates like Co(salen) 1a and Co(saldpt) 1b in regard to their ability of binding small molecules like O_2 (Ref. 2-4), CO, CO_2, (Ref. 5,6) (all three reversibly), and also NO (irreversibly) (Ref. 7,8) as well as their catalytic activity for the oxidation of organic compounds like phenoles, indoles, bishydrazones etc. (Ref. 9-11) were the starting point for this work and the following publication (Ref. 12).



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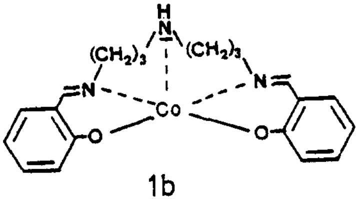

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The objective now was to combine the above mentioned properties of the low molecular chelates with the advantage of polymer immobilization, with respect to the simple separation of the polymer bound catalysts from the reaction mixture, their regeneration and their reinstatement. In this paper we wish to report the results of the synthesis of polymer bound Schiff's base chelates of the type 1.

Covalently polymer bound N,N,O,O-chelates are obtained from 2-hydroxy-5-vinylbenzaldehyd (2) (Ref. 13) and a suitable comonomer followed by polymer analogous reactions.

The copolymerization behaviour of the comonomers was to be examined in order to get information about the structure of the polymer bound catalysts. With the help of the copolymerization parameters it is possible to carry out specific syntheses

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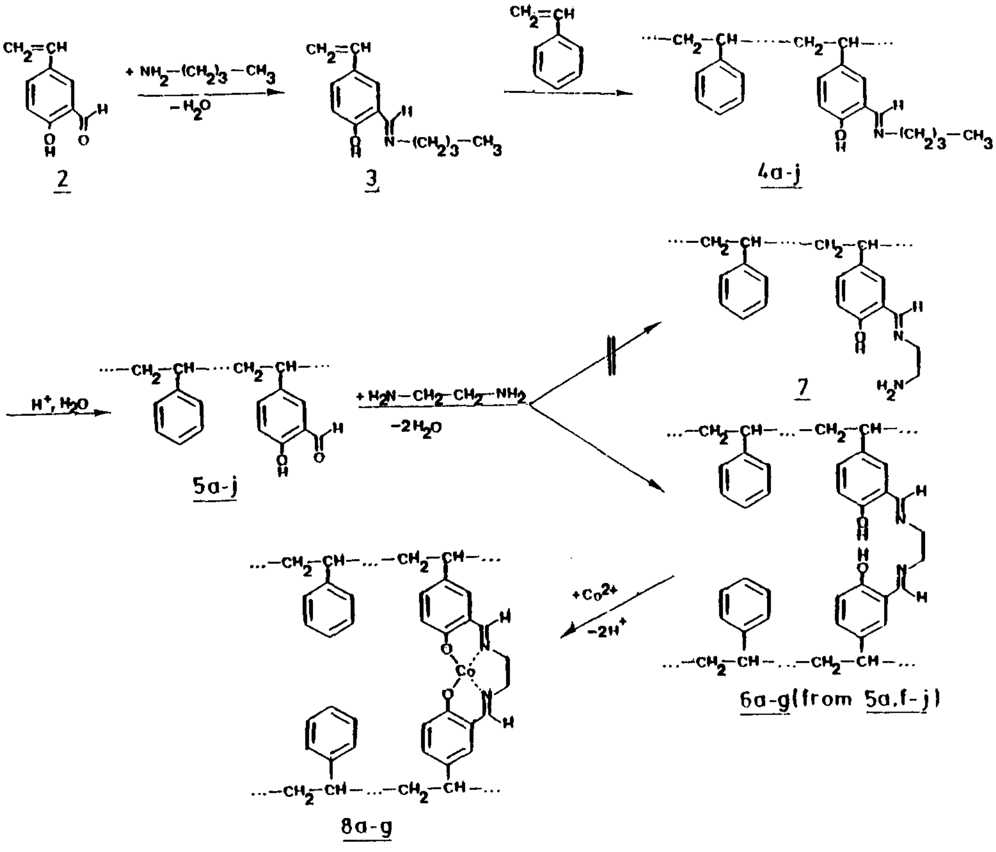
[a] Part 4: Ref. 14)

in order to obtain specific polymer bound N,N,O,O-chelates which can be easily adapted to the respective binding of small molecules and catalytic reactions for further investigations (Ref. 14).

RESULTS AND DISCUSSION

2 cannot be polymerized via radicalic copolymerization with styrene to the copolymer 5 since the chain transferring effect of the monomeric aldehyde proton leads to crosslinking, resulting in insoluble products. Corresponding to work by Ringsdorf (Ref. 15), the aldehyde group in 2 must be protected before copolymerization. In our case 1-aminobutane was employed as protecting agent. The azomethine 3 from 2 and 1-aminobutane can react radically in varying concentrations with styrene without any difficulties, leading to linear soluble copolymers 4 (scheme 1). In contrast to our short note (Ref. 16) the polymerizations were carried out in solution instead of in bulk because of the easier work up (reaction time 2h: 4a-e; 144 h:

Scheme 1



4f-j (Tab. 1). The light yellow compounds 4a-j are soluble in toluene and DMF. In addition to the polystyrene absorptions the IR spectra of the copolymers 4 exhibit at 1625 cm^{-1} the ν(C=N)- and at 1275 cm^{-1} the phenolic ν(C-O)-absorption, thus confirming that the monomer 3 is build in.

The next reaction step is the splitting off of the protecting group in order to get back the free aldehyde group that is necessary for the construction of the N,N,O,O-ligand. The saponification of 4a-j to 5a-j in ethanolic H_2SO_4 (Ref. 16) does not always achieve the intended objective (rest of ν(C=N) at 1625 cm^{-1}). However the reaction is quantitative when conducted in 20 % acetic acid in toluene. The characteristic absorption of the aldehyde group of 5 appears at 1650 cm^{-1} ν(C=O). No azomethine ν(C=N)-absorption occurs any more at 1625 cm^{-1}. The copolymers are of light yellow color just as the starting materials and are soluble in toluene and DMF.

The reaction of the copolymers 5a,f-j with 1,2-diaminoethane leads to the formation of the polymer bound N,N,O,O-ligands. Owing to their high reactivity, both amino groups condense with polymer bound salicylaldehydes under construction of the thermodynamically more stable N,N,O,O-chelates, so that crosslinking occurs. The products 7 that are condensed one-sidely at the diamine are not formed. The yellow colored copolymers 6 are not soluble in toluene and DMF, however they are swellable in these solvents. The IR absorption at 1650 cm^{-1} ν(C=O) has disappeared, however a strong absorption appears at 1630 - 1625 cm^{-1} ν(C=N) . Besides the polystyrene absorption the phenolic ν(C-O) -absorption can be found at 1275 cm^{-1}. There is no indication of free amine groups in the IR-spectrum (Fig. 1).

Since an after-treatment with salicylaldehyde of the substances reacted with ethylenediamine does not alter the IR-spectrum, it can be assumed that a nearly quantitative crosslinking takes place in the reaction of 5 to 6. The existance of salicylaldehyde in the filtrate can be proven almost quantitatively.

The chelates 8a-g are obtained by the reaction of the crosslinked copolymers 6a-g with Co(II)-acetate$\cdot H_2O$ in DMF. An excess of metal salt leads to higher cobalt contents of the products 8b,c,e-g (Tab. 1). The cobalt content can be reduced by an after-treatment of these chelates with boiling water, followed by extraction with methanol. The differences between theoretical and experimental value then still amount to about 50 %. The metallization reaction takes place quantitatively at the ligand even in the case of an equimolar amount of Co-salt (Tab. 1; 8a,d). Treatment of the metallized polymer 8d with an excess of Co(II)-acetate$\cdot H_2O$ (around 5 fold excess additional to the present Co of 2.25 %) leads to an additional incorporation (Co found 7.44 %) after cleaning. The nature of this incorporation is still unknown.
Besides the styrene absorptions, the resulting brown products 8a-g show the characteristic absorptions of 1: 1610 cm^{-1} ν(C=N) , 1525 cm^{-1} ν(C=C) , 1300 cm^{-1} (C-O-Co) and 1130 cm^{-1} ν(C=N) . Metal free portions cannot be recognized at 1275 cm^{-1}

ν(C-O) (Fig. 1).

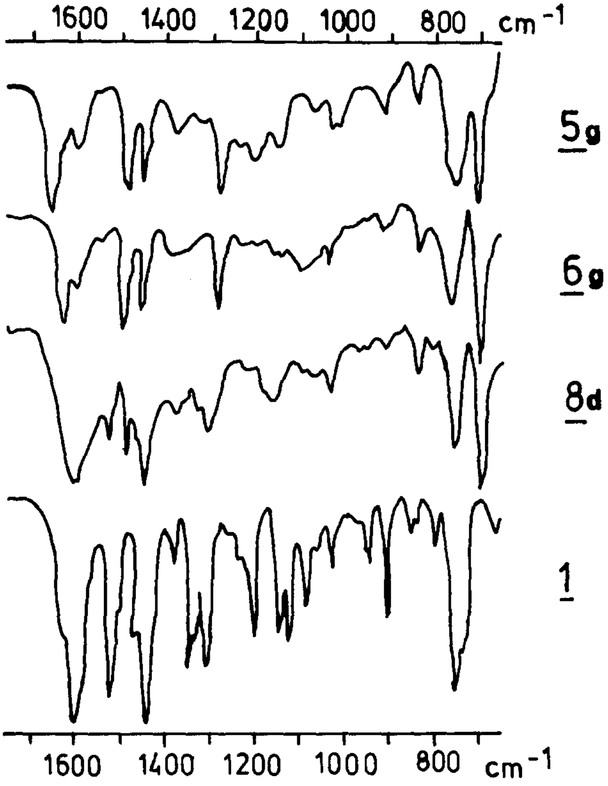
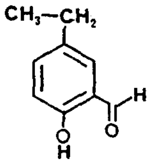


Fig. 1. IR-spectra (KBr) of low molecular chelate 1 and copolymers 5g, 6g and 8d (prepared from 4g).

In our further work the metal containing products 8b-g were employed for catalytic reactions as phenol oxidation and reversible oxygen uptake (Ref. 14). In these experiments the copolymers with higher Co-contents show the same effectivity as metal containing copolymers with defined Co-content. Therefore excess cobalt in the polymer does not have any influence on the results of the catalysis reaction and the oxygen uptake. Only the ligand bound cobalt is active.

DETERMINATION OF THE BUILT IN RATIO OF THE MONOMERS

The built in ratios were determined by employing appropriate model substances 9-10 with the aid of UV-spectroscopic extinction coefficients.



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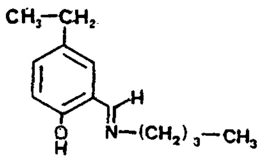

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The built in ratios were determined in the concentration range of $2\text{-}5\cdot10^{-4}$ mol/l in DMF, taking the law of Lambert-Beer into consideration. The following values apply for λ/nm (ε) $l\cdot mol^{-1}$ cm^{-1}): 9: 332 ($3{,}8\cdot10^{3}$); 10: 322 ($4{,}2\cdot10^{3}$). The examined copolymers absorb as follows: 4: 322; 5: 332. Table 1 contains the values of the monomer concentrations $[M_1]/[M_2]$ and the calculated concentrations $[m1]/[m2]$ of the monomers in the copolymers. After graphic evaluation to the methods of Fineman and Ross (Ref. 17) the following situation arises:

For the copolymerization of styrene (M_1)/3 (M_2) to 4 parameters of r_1= 1,2 and r_2= 0,8 are found. The definition of the parameters permits the conclusion that with this pair of monomers a polymerization to high yield is possible without a significant change in the composition of the copolymer. Comparison of the reactions leading to 4f-j (144h; Tab. 1) with those leading to 4a-e (2h; Table 1) confirms this. The built in ratios found for 2 in 5 and 3 in 4 are almost identical. Additional the composition of the copolymers was checked by treating 5g (from 4g) with 2,4-dinitrophenylhydrazine in DMF at 353 K to get polymer bound hydrazone. The N-value is in agreement with the theor. value: Hydrazone from 5g N= 3,9 % (calc. 4,1 %).

Tab. 1. Composition of copolymers 4 and 8.

Copolymer 4 from styrene (M_1) and 3 (M_2)					copolymer 8 from 6			
	polymerisation conditions		resulting polymer					
No. 4	t (h)	$[M_1]/[M_2]$	yield 4(%)	$[m_1]/[m_2]$	Nº 8,	inserted molar ratio Co/6	Co cal (%)	Co fd (%)
a	2	5	16	7.3	a	1	3.36	3.80
b	2	10	16	12.1				
c	2	20	15	25.8				
d	2	40	16	52.3				
e	2	80	16	94.2				
f	144	5	49	7.2	b	9	3.10	7.75
g	144	10	50	12.1	c	4	2.05	7.60
					d	1	2.05	2.25
h	144	20	55	24.1	e	4	1.07	2.38
i	144	40	55	50.0	f	4	0.55	1.12
j	144	80	56	94.0	g	4	0.30	0.64

EXPERIMENTAL

Used instruments: IR (Perkin Elmer 577), UV-VIS (Perkin-Elmer 544).

Cobalt analyses of 8: The chelates were destroyed in a Perkin-Elmer autoclav no. 3 with 6 ml conc. HNO_3 and 3 ml conc. H_2SO_4 at 423 K. The determination of Co(III) was accomplished with 1-nitroso-2-naphthol through absorption at 410 nm in $CHCl_3$ (Ref. 18,19).

All reactions are carried out under dry argon or nitrogen, with dry solvents and reagents free of molecular oxygen. AIBN is

recrystallized from ether and dried at reduced pressure. Styrene was destabilized and destilled before use (Ref. 20).
2-Butyliminomethyl-4-vinylphenol 3: From 2-hydroxy-5-vinylbenzaldehyde (2) and 1-aminobutane (Ref. 16).
Polymerization of 3 and styrene to poly[2-phenylethylene-co-2-(3-butyliminomethyl-4-hydroxyphenyl)ethylene] (4): A polymerization tube was charged with 20 mmol styrene and the desired amount of 3 (Tab. 1), 0.5 mol % of AIBN and toluene, degassed by three freeze-thaw cycles at 10^{-2} torr. The sealed ampoule was heated at 373 K for 2 or 144 h (Tab. 1). Precipitation of the contents in methanol yielded the copolymers 4a-j as light yellow powders. The products are soluble in DMF and toluene. After reprecipitation the products were treated with methanol in a Soxhlet apparatus for 24 hours and dried in vac. at 333 K.

IR (KBr, cm^{-1}): 1625 (s; C=N); 1275 (m; C-O), absorption of polystyrene.
UV (DMF): λ_{max}/nm= 322).

$[(C_8H_8)_{12,1} \cdot C_{13}H_{17}NO]_n$	$(1459,37)_n$	calc.	C 90.1	H 7.84
		found	C 88.9	H 7.8

Saponification of 4 to poly[2-phenylmethylene-co-2-(3-formyl-4-hydroxyphenyl)ethylene] (5): 0.5 g - 1 g of the copolymers 4 were dissolved in 20 - 30 ml 20 % acetic acid in toluene. After stirring for 24 h at 293 K the copolymers were precipitated in methanol and washed extensively with water. After treatment with methanol in a Soxhlet apparatus for 24 h and drying in vacuo at 333 K the light yellow polymers were obtained quantitatively.

IR (KBr, cm^{-1}): 1650 (s; C=O), 1280 cm^{-1} (m; C-O), absorptions of polystyrene.
UV (DMF): λ_{max}/nm= 332.

$[(C_8H_8)_{12,1} \cdot C_9H_8O_2]_n$	$(1403,41)_n$	calc.	C 90.28	H 7.44
		found	C 88.7	H 7.99

Poly 2-phenylethylene-co-2-(2,2'-ethylenebis(nitrolomethylidyne)-diphenol) (6): 0.5 g - 1 g of the copolymers 5 were refluxed for 24 h in 30 - 65 ml toluene with a 10fold amount of 1,2-diaminoethane. The polymers were treated with methanol, filtered off and treated with methanol for 24 h in a Soxhlet apparatus. After drying in vacuo the yellow products were obtained in quantitative yields. The products are highly swellable in DMF. Treatment of the polymers 6 with the double amount of salicylaldehyde and working up as described in the method above yielded similar products without any differences in IR spectra.
IR (KBr; cm^{-1}): 1630 (s; C=N), 1275 (m; C-O), absorptions of polystyrene.

$[(C_8H_8)_{12,1} \cdot C_{10}H_{10}NO]_n$	$(1416,28)_n$	calc.	C 90.3	H 7.58	N 0.99
		found	C 89.17	H 7.6	N 0.4

[Poly{2-phenylethylene-co-2-(2,2'ethylene}bis(nitrilomethylidyne)-diphenolato)cobalt(II)-4-yl]-ethylene (8): Approximately 1 g of copolymer 6 was treated with an excess or stöichiometric amount of cobalt(II)acetate·$4H_2O$ (Tab. 1) in 50 ml oxygen-free DMF for 24 h at 353 K. The precipitated swollen polymers were filtered off, treated with methanol in a Soxhlet apparatus under inert conditions and dried at 353 K.

IR (KBr, cm^{-1}):1610 (C=N); 1625 (C=C); 1300 (C-O); 1130 (-C-N).

$[(C_8H_2)_{12,1}C_{10}H_9NOCo/2]_n$ $(1444,74)_n$

calc.	C 88.52	H 7.36	N 0.97	Co 2.05
found	C 85.4	H 7.3	N 0.5	Co 1.96

2-Hydroxy-5-ethylphenol (9) (Ref. 21): yield 22.3 %
UV (DMF): λ_{max}/nm= 332.

2-Butyliminomethyl-4-ethylphenol (14): 7.5 g (0.1 mol) 1-aminobutan was added to a solution of 7.5 g (0.05 mol) 13 in 75 ml benzene. The mixture was heated under reflux for 2h. After washing the benzene solution twice with water the benzene was destilled off in vac. yielding 8.8 g (87 %) of a yellow oil.

UV (DMF): λ_{max}/nm= 322.
IR (KBr, cm^{-1}): 3600 - 3200 cm^{-1} (OH), 2950 cm^{-1} (s; CH_2)
1625 cm^{-1} (s; C=N), 1580, 1430 cm^{-1} (m; ar), 1280 cm^{-1} (s; C-O)
830 cm^{-1} (m; CH).
^1H-NMR ($CDCl_3$) δ= 13.23 (COH), 8.2 (CH=N), 7.2 - 6.8 (ar),
3.53 (NCH_2), 2.4 - 2.75 (CH_2) 1.7 - 0.9 ($-CH_2-CH_3$).

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