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Polymer-Supported Transition Metal Clusters

1. Copolymers Containing Tricobalt Carbonyl Clusters

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SUMMARY

The synthesis of appropriate monomers bearing alkylidyne tricobaltnonacarbonyl cluster or sulfido tricobalt heptacarbonyl cluster is described. Organometallic copolymers are obtained by free-radical copolymerisation with other vinyl monomers. Direct metallation of macromolecules containing the dithioester or the thioamide functional groups was also studied. We show that the copolymerisation method is more convenient for the synthesis of pure materials containing a variable amount of definite cluster units. The potentiality of these new organometallic polymers with regard to homogeneous catalysis and for the modification of electrode surfaces is also discussed.

INTODUCTION

In the last two decades considerable efforts have been made to combine the advantages of homogeneous catalysis (selectivity, mild operating conditions) and of heterogeneous catalysis (duration, easy separation of the products from the reactants). This might be done by attaching homogeneous catalysts either to organic polymers or to inorganic supports in a way such as the ligand sphere is preserved around the metal and the complex is kept in contact with the solvent and reactants (PITTMAN, 1980). In the field of organometallic complexes possessing a real or a potential activity in homogeneous catalysis the synthesis and chemistry of polynuclear compounds (or clusters) have been recently widely studied following the suggestion that they can act as small portions of metal surfaces

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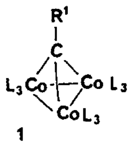
(MUETTERTIES, 1980). We have recently described the synthesis and structure of the tricobalt carbonyl clusters 1 and 2 by reacting $Co_2(CO)_8$ on dithioesters or thioamides respectively. (PATIN et al., 1979 and 1981). On the other hand, some of us have developed the preparation of various monomers and polymers bearing the required functionalities to allow the direct incorporation of clusters on the macromolecules. (HARAOUBIA et al. 1975 and 1981, LEVESQUE et al. 1982). Owing to the easy access of monomers such as 1 or 2 containing an organic ligand able to polymerise or copolymerise, obtention of macromolecules with a variable amount of clusters became possible either by a direct metallation procedure or by the indirect route.

We wish to report here the synthesis of the monomers 1 and 2 of several copolymers which are to the best of our knowledge the first examples of macromolecules containing trimetallic cobalt clusters of known structures.



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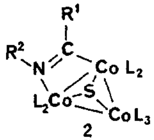

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$R^1 = p.C_6H_4\text{-}CH{=}CH_2$; $R^2 = C_6H_{11}\text{-}$; L = CO

EXPERIMENTAL

The monomers 1 (R^1=p.C_6H_4-CH=CH_2) and 2 (R^1=p.C_6H_4-CH=CH_2, R^2=C_6H_{11}) are prepared according to the described procedures. To a solution of p.vinyldithiobenzoïc methylester or N-cyclohexyl 4-vinyl-thio-benzamide (10^{-2}mole) in anhydrous THF (30 ml) was added $Co_2(CO)_8$($1.8.10^{-2}$mole).

The mixture was stirred under N_2 for 2 h at 70°C (compound 1) or 3 h at room temperature (compound 2) until complete reaction of the starting materials (TLC control). Removal of the solvent was followed by chromatographic separation on silica gel (elution with hexane) to afford black crystals which were recristallized from methanol or pentane.

Compound 1 : m.p. 73°C ; yield 40% ; IR (CCl_4) 2010, 2030 and 2095 cm^{-1} (terminal carbonyls) ; ^{1}H-NMR ($CDCl_3$, TMS) δ= 7.5 (4H) ; 5.40, 5.85 and

6.80 ppm (3H), Anal., calc'd for $C_{18}H_7O_9Co_3$: C, 39.74 ; H, 1.30 ; Co, 32.50% ; found C, 39.72 ; H, 1.95 ; Co, 32.47.

Compound 2 : m.p. 126°C ; yield 30% ; IR (CCl_4) 2010, 2030 and 2080 cm^{-1} (terminal carbonyls) ; ^{1}H-NMR ($CDCl_3$, TMS) δ=6.8 and 7.5 (4H), 5.3, 5.8 and 6.8 (3H), 3.0 (1H) and 1.5 ppm (10H) ; Anal. calc'd for $C_{22}H_{18}NO_4SCo_3$: Co, 28.62 ; found Co, 28.64.

Copolymerisation of 1 and 2

Free-radical initiated copolymerisation of 1 and 2 with styrene, methyl methacrylate and N-[tris-1,1,1 (hydroxymethyl) methyl] acrylamide (Tris-A) has been studied in the following conditions : monomer concentration 0.2 $mole.l^{-1}$ with 1% (mole %) of cluster 1 or 2, AIBN 5% (mole %) ; 5 h under N_2 at 60°C with stirring ; the solvent used is benzene except for "Tris-A" for which N-methyl pyrrolidone was employed. The reactions were carried out with 2.10^{-2} mole of monomers. After cooling the solution was poured in methanol and the precipitate was isolated and purified using the dissolution-precipitation technique (CH_2Cl_2/CH_3OH). The yields of copolymers are 40-60% and their characteristics are listed in the table. In all cases the presence of the cluster units are proved by IR analysis showing strong absorptions at 2020, 2040 and 2080 cm^{-1} (terminal carbonyls) and the amount of cluster in the polymer is deduced from the microanalytical data (Co%).

Chemical modification of polymers by reaction with $Co_2(CO)_8$

Previously described homopolymers and copolymers of 3, 4, 5 bearing the dithiocarboxylate or the thioamide functional group have been studied.

In a typical experiment 2g of polymer dissolved in THF (20ml) was reacted with $Co_2(CO)_8$ (20% excess) at 70°C for 2h under N_2.

The solution was poured in methanol and the purple-black precipate filtered and purified using the dissolution-precipitation technique (CH_2Cl_2/CH_3OH) or washed with acetone and methylene chloride in the case of cross-linked polymers. The polymers are characterized as described before and the data are listed in the table.

Table : Characteristics of cobalt cluster-containing copolymers.

Cluster unit in the copolymer	Obtention mode (a)	Starting Material (b)	Analysis Co% (w/w)	Cluster unit in copolymer (mole%)	$\overline{Mn}$; $\overline{Mw}$ (GPC)	Ref of copolymer
6	I	Styrene/1 (99/1)	5.45	3.7	6400, 14720	6a
	I	Methyl methacrylate/1 (99/1)	1.78	1.0	21300, 44700	6b
	I	Tris A/1 (99/1)	1.65	1.6	-	6c (c)
	II	Styrene/3 (85/15)	18.91	13.0 (d)	5320, 12600	6d
	II	Homopolymer 3	20.33	37.8	4300, 8650	6e
7	I	Styrene/2 (99/1)	2.26	1.3	7200, 16800	7a
	I	Methylmethacrylate/2 (99/1)	3.13	1.8	24600, 41300	7b
	I	Tris A/2 (99/1)	1.60	1.6	-	7c (c)
8	II	Styrene/5 (91.3/8.7)	11.08	8.5	Cross-linked	8a

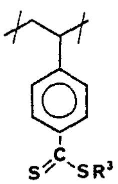
(a) I copolymerisation ; II chemical modification.
(b) in case I : in brackets, percentage of the comonomer and cluster monomer in the comonomers mixture (mole%)
in case II : in brackets, percentage (mole%) of each units in the starting copolymer.
(c) Water-soluble.
(d) dithioester unreacted : 2.0% (mole%) ; CoS adsorbed on polymer 7.4% (w/w) give the best correlation with analytical data.

Results and discussion

Chemical modification of polymers such as 3, 4 and 5 which appeared at first glance to be the more convenient way to prepare supported cobalt clusters has proved to be of low reliability if one wish to be sure of the purity and of the definite structure of the cluster units on the polymer chain. In the case of polymer 3 and 5 which contain the dithioester function, formation of cluster-containing polymers respectively 6 and 8 with a high content of tricobalt nonacarbonyl groupings is proved by IR spectroscopy and determination of the cobalt percentage. However purification of these polymers was difficult because the clusterisation reaction involving at least two desulfurization steps lead to sulfur-containing organocobalt species (or colloïdal cobalt sulfide) which are not easily removed from the macromolecules. This is proved for instance in the case of 6d for which an excess of metal is found by comparison to the theoretical value available by the known composition of the starting material (Co% = 18.91 vs. 15.58% calculated for 100% reaction).For polymers 4 and 9 bearing the thioamide functional group as well as for the bifunctional models of 9, reaction with $Co_2(CO)_8$, even at room temperature, lead to insoluble materials resulting from cross-linking. Important structural modifications in this particular case are proved by IR studies showing that the carbonyl ligands are no longer present in the polymer. It is obvious that $Co_2(CO)_8$ does not react on a single thioamide group but rather plays the role of a cross-linking reagent giving rise to polymers with a high metal content, the structure and properties of which are currently under investigation.

Since tricobaltcarbonyl clusters have been shown to be active catalysts for hydroformylation of olefins (PITTMAN et al. 1978), in the purpose of stúdying the catalytic activity of such clusters anchored on polymers, it appears more convenient to prepare them by the copolymerisation method which offers in addition to a high degree of purity, the advantage of preserving the integrality of the cluster units. This method allows also the synthesis of a large variety of copolymers simply by modifying the nature of the comonomer or the ratio of cluster 1 or 2 versus the comonomer. In addition, the copolymerisation method has proved to be general and for instance water soluble polymers such as 6c and 7c are easily prepared in excellent yield. These macromolecules are also of interest for the modification of electrodes owing to the original behaviour of clusters 1 and 2 which can be reduced reversibly into the corresponding paramagnetic species in the potential range -0.5 to -0.7 volt S.C.E. (MAHE, 1982). Preliminary experiments show that a polymer film can be deposited on a platinum electrode and that the monoelectronic reversible reduction is observed at the same potentials.

Direct metallation on the surface of various resins (cross-linked polymers bearing dithioesters functions prepared according to LEVESQUE and al. 1981) can also be performed by addition of $Co_2(CO)_8$ to a suspension of the resins in THF.



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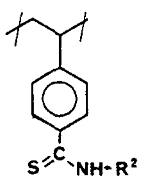

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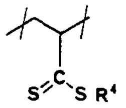

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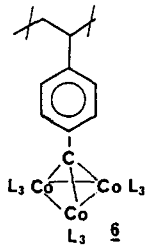

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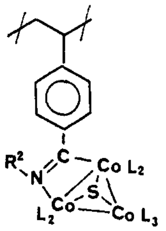

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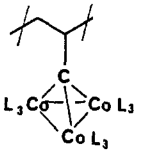

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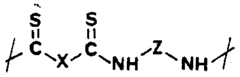

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$L = CO$; $R^2 = C_6H_{11}-$; $R^3 = CH_3-$; $R^4 = C_2H_5-$; $X, Z = -(CH_2)_n-$ $4 \leqslant n \leqslant 10$

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