

Macrocomplexes on the basis of functionalized polyethylene glycols and copolymers of ethylene oxide and propylene oxide: synthesis and catalysis

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Abstract

Water soluble catalysts combining the properties of metal complexes and surfactants on the basis of terminally functionalized polyethylene glycols and block-copolymers of ethylene oxide and propylene oxide with various combinations of ethylene and propylene oxide fragments were investigated. Polymers, functionalized by dipyriddy and acetylacetonate were used as ligands for preparation of Fe(III) and Co(II) complexes, which showed a high activity and selectivity in oxidation of cyclohexane and ethylbenzene by both hydrogen peroxide and oxygen. An aqueous phase hydroformylation rhodium catalyst was prepared on the basis of polyethylene glycols functionalized by phosphine groups.

Keywords: Macrocomplexes; Water-soluble catalyst; Oxidation; Hydroformylation; Dipyriddy; Acetylacetonate; Phosphine ligands

1. Introduction

The anchoring of homogeneous metal complexes into various supports often leads to unexpected alterations in the catalytic activities, which are due to changes in the microenvironment of the metal ions, to diffusional limitations, and to the changes in the rigidity of modifying groups. That is why the concept of attaching metal complexes to soluble polymers has recently become the focus of much attention [1]. These exciting new catalytic systems allow to perform various organic reactions due to unique features of conformational non-rigidity

of macroligands which makes them in a certain sense similar to natural catalysts.

We investigated a new type of water-soluble catalysts combining the properties of metal complexes and surfactants prepared from transition metal complexes and terminally functionalized polyethylene glycols (PEGs) of various molecular weights and block-copolymers of ethylene oxide and propylene oxide with different combinations of ethylene oxide (E) and propylene oxide (P) fragments (REP and RPE, R=CH₃, C₄H₉). The properties of functionalized RE, RPE and REP offer the possibility of designing soluble and potentially recoverable catalysts for various reactions. The PEGs and their derivatives are easily precipitated in a number of solvents (acetonitrile, benzene, meth-

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ylene chloride, etc.) by addition of diethyl ether. The catalyst can be located in the aqueous phase, and the substrates and products in the organic phase.

The use of such type of ligands [2](a,b) possessing conformational sensitivity to the reaction conditions (solvent, temperature, pH, etc.) enables to influence the catalytic properties. Bergbreiter et al. recently described the use of oligomers of triblock copolymers of ethylene oxide–propylene oxide–ethylene oxide which are terminally functionalized by phosphine groups as ligands for the synthesis of rhodium hydrogenation catalysts, which possess the ability to regulate reaction temperature by a reversible temperature dependent phase separation [2](c).

We used PEG functionalized by phosphine groups as a ligand to prepare a water-soluble Rh catalyst for the hydroformylation of alkenes. The development of a new water-soluble hydroformylation catalyst active under moderate pressure and temperature is considered to be an important goal [3]. The sulphonated triphenylphosphine–rhodium hydroformylation catalyst was patented by Rhone Poulenc [4] and technically realized by Ruhrchemie.

On the basis of polymers, functionalized by dipyriddy and acetylacetonate, the complexes of iron and cobalt were obtained. These complexes were examined as catalysts for the oxidation of cyclohexane and ethylbenzene by both hydrogen peroxide and oxygen. This choice seems to be interesting also from the point of view of developing of new biomimetic catalysts.

2. Experimental

2.1. Materials and measurements

We used PEG of a molecular weight of 1550, monobutyl ether of PEG of a molecular weight of 5000 and monomethyl ethers of PE (REP, RPE) of a molecular weight of 3000. Ethers were synthesized by anionic polymerization of

ethylene oxide and propylene oxide [5]. ^1H and ^{31}P NMR spectra were recorded on a Varian VXR-400 spectrometer. Products were analyzed by GC on a Chrom-5 gas chromatograph and by HPLC on Gilson-310 and further characterized by GC–MS using a Finnigan-MAT-1125 GC–MS system.

2.2. Preparation of macroligands and complexes

The tosylates were obtained according to a literature procedure [6]. For the synthesis of acetylacetonate derivatives (PEG–acac, RE–acac, REP–acac, RPE–acac) 6.2 mmole of acetyl acetone was dissolved in 10 ml of dry acetone and a solution of 6 mmole of sodium ethylate and 3.1 mmole of tosylate in 25 ml of acetone were added. The mixture was refluxed for 48 h. The acetone was distilled off, the residue was dissolved in dry methylene chloride and precipitated by dry diethyl ether (repeated three times).

The yield was 90%. NMR: $\text{CH}_3(\text{acac})$, 2.2 ppm; $\text{CH}_2\text{--CH}_2\text{--O(PEG)}$, 3.61 ppm; $\text{CH}_3(\text{Bu})$, 1.1 ppm; CH_2 , 1.4 ppm. NMR analysis indicated 90% substitution for PEG, RPE and 70% for REP.

The synthesis of polymers modified by dipyriddy groups (PEG–dipy, REP–dipy) was performed in the following way: 5.25 mmole of triethylamine was added to a solution of 1.5 mmole of polymer in 50 ml of methylene chloride at room temperature, thereafter a solution of 1.6 mmole of chloroanhydride of 2,2'-dipyriddy-3,3'-dicarboxylic acid in 15 ml of methylene chloride was added. The mixture was stirred for 6 h, filtered, and the product was precipitated by dry diethyl ether on cooling. The modified polymer was purified by double precipitation from methylene chloride. NMR spectra: C–H(dipy), 8.65, 8.96 ppm; $\text{CH}_2\text{--CH}_2\text{--O(PEG)}$, 3.61 ppm; $\text{CH}_3(\text{Bu})$, 1.1 ppm. The degree of modification in case of REP was 80% and in case of PEG not more than 20%.

The synthesis of complexes with cobalt

(RE-acac-Co³⁺) was performed as follows: equimolar amounts of 0.4 N KOH was added to 10 ml of stirred aqueous 0.1 N Co(NO₃)₂ solution. On appearance of the precipitate of Co(OH)₂ simultaneously with adding of the alkali a double excess of the aqueous solution of the polymer, modified by acetylacetonate groups, was added. The mixture was stirred for 48 h. Then the water was removed by distillation, the residue was dissolved in dry methylene chloride, filtered and precipitated by dry diethyl ether. The yield was 65%. The Co content was estimated by emission spectroscopic analyses, and found to be 0.2%.

The synthesis of terminally functionalized PEG by phenylphosphine was performed in inert atmosphere according to [6]. The structure of the ligand obtained was proved by the ¹H and ³¹P NMR. The amount of terminal groups was determined on the basis of ¹H NMR (0.5 mmole/g).

2.3. Catalytic experiments

The oxidation of hydrocarbons was performed in homogeneous and in heterophase systems using a three-neck thermostated reactor provided with a stirrer and a reflux condenser.

The uptake of oxygen was measured with a gas buret. The complexes of polymers with iron were not isolated, but were introduced into the reaction mixture as water solutions, obtained by dissolving equimolar amounts of FeCl₃ and modified polymer.

Hydroformylation was performed in a steel autoclave. Rh-acac(CO)₂, the required amount of polymer and 2 ml of anhydrous toluene were inserted in autoclave. After careful cooling in liquid nitrogen the autoclave was degassed and then filled by 1 atm CO + H₂ (1:1). The solution was stirred at room temperature and atmospheric pressure for 3 h, and 1.5 ml of water, 1.5 mmole of dodecene-1 and 5 (10 or 15) atm/CO + H₂ were added. Under mechanical stirring a temperature of 50°C was maintained for 6 h. The water phase with the catalyst was separated and was re-used. The organic phase was dried and analyzed.

3. Results and discussion

3.1. H₂O₂ oxidation of cyclohexane

The oxidation of cyclohexane by hydrogen peroxide was conducted in the temperature range

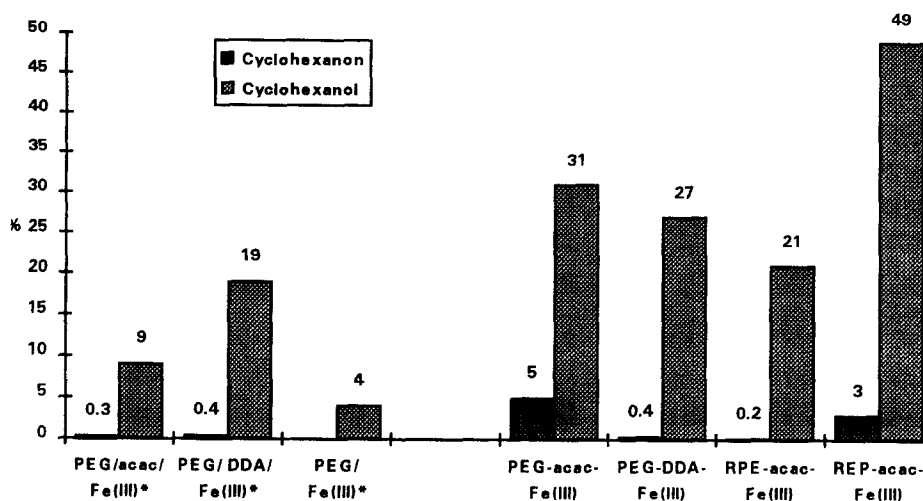


Fig. 1. Oxidation of cyclohexane. [C₆H₁₂] = 0.209 mol/l, [H₂O₂] = 0.93 mol/l, [Fe(III)] = 4.4 mmol/l, * mixture: PEG + ligand + FeCl₃, CH₃CN:H₂O = 3.5:1.

Table 1
Oxidation of cyclohexane by hydrogen peroxide

Catalyst	Yield, %							
	20°C		30°C		50°C		70°C	
	Ket.	Alc.	Ket.	Alc.	Ket.	Alc.	Ket.	Alc.
PEG-acac-Fe(III)	–	–	5	31	0	24	1	16
RPE-acac-Fe(III)	–	–	<1	21	<1	41	<1	20
REP-acac-Fe(III)	0	21	3	49	0	24	2	20
PEG-dipy-Fe(III)	–	–	<1	25	<1	23	<1	20
REP-dipy-Fe(III)	–	–	<1	14	<1	40	<1	28

$[C_6H_{12}] = 0.206$ mol/l, $[H_2O_2] = 0.93$ mol/l, $[Fe(III)] = 4.4$ mmol/l, $CH_3CN:H_2O = 3.5:1$.

of 20–70°C in the presence of synthesized macroligands and iron salts (Fig. 1, Table 1).

The maximum rate of the reaction was achieved in the solvent acetonitrile/water (1/3.5). The major product of the reaction was cyclohexanol, while the yields of cyclohexanone were less than 5%.

It is worth mentioning that under the reaction conditions used cyclohexanol was not oxidized, which testifies the fact that the route of products formation is different — cyclohexanone and cyclohexanol are independently formed in parallel reaction paths.

It follows from the results shown in Fig. 1 that macrocomplexes exhibit significantly higher activity than systems consisting of mixtures of polymer and iron salt. This fact can be explained as follows: the oxidation of cyclohexane is likely to proceed via radical mechanisms in polymer micelles. In the complexes metal ions are coordinated both to terminal ligands and to oxygen atoms in the chain of PEG. The latter has a significant lability and are not bound strongly to iron. The micelles formed can be regarded as microreactors in which the reaction proceeds. Free Fe(III) can easily be hydrolyzed and poorly absorbed by the polymer globules. The macromolecular structure of the catalysts hinders the hydrolysis of Fe(III) ions. At the same time iron coordinated to terminal groups of the ligand penetrates more easily to the inside of micelles where the concentration of cyclohexane is high. The oxidation of cyclohexane at

different temperatures proves that the reaction proceeds inside the micelles. Extremes in yields of products were noticed at certain temperatures for every type of macrocomplexes. Apparently, this fact points to the change of conformation of polymers during the formation of micelles under alteration of the temperature.

Micelles of block copolymers RPE and REP differ in the location of the modified groups. The hydrophilic part of the micelles consists of ethylene oxide blocks and nuclei of the micelles — blocks of propylene oxide. The fixed metal ions in REP are located in the center of the micelle, meanwhile in case of RPE they are on the surface. Consequently, it is necessary to overcome the conformational and steric hindrances to facilitate the reaction in the second case.

The decrease of the yield of the product with further increase of temperature is connected with the decrease of the affinity of the polymer chains to the solvent and the formation of big conglomerates.

There is an optimal ratio of $[H_2O_2]/[Fe(III)]$. Increasing this ratio the rate of decomposition of hydrogen peroxide increases and becomes predominant when the ratio gets higher than 225.

3.2. Oxidation of ethylbenzene

The macrocomplexes obtained showed high activity and selectivity in the oxidation of ethylbenzene by hydrogen peroxide. The results are

Table 2
Oxidation of ethylbenzene by hydrogen peroxide at 75°C

Catalyst	Yield, %	
	Acetophenon	Methylphenylcarbinol
PEG-acac-Fe(III)	71	2
PEG/acac/Fe(III) ^a	40	2
REP-acac-Fe(III)	37	<1
REP/acac/Fe(III) ^a	17	1

$[C_6H_5C_2H_5] = 0.36$ mol/l, $[H_2O_2] = 0.93$ mol/l, $[Fe(III)] = 3.6$ mmol/l, $CH_3CN:H_2O = 3.5:1$.

^a Mixture of polymer + acac + FeCl₃.

Table 3
Oxidation of ethylbenzene by hydrogen peroxide

Catalyst	30°C		50°C		75°C	
	Ketone	Alcohol	Ketone	Alcohol	Ketone	Alcohol
PEG-acac-Fe(III)	24	3	44	3	71	2
PEG/acac/Fe(III) ^a	18	1	30	2	40	2

[C₆H₅C₂H₅] = 0.36 mol/l, [H₂O₂] = 0.93 mol/l, [Fe(III)] = 3.6 mmol/l, CH₃CN:H₂O = 3.5:1.

^a Mixture of polymer + acac + FeCl₃.

summarized in Tables 2 and 3. The main product is acetophenone, the minor is methylphenylcarbinol. As in the case of cyclohexane macrocomplexes were more active than the catalytic systems consisting of mixture of FeCl₃, acetylacetone, and PEG in equimolecular amounts.

With rising temperature the yields of products grow and reach 73% in 2 h (Table 2). The results can be explained by increasing the affinity of ethylbenzene to PEG with rise of temperature.

Macrocomplexes PEG-acac-Co exhibited significant activity in the oxidation of ethylbenzene by dioxygen. From the data shown in Table 4 it is obvious that under the same temperature and even at smaller concentrations of cobalt macrocomplexes turned out to be more active than their non-polymeric analogues. The only product was acetophenone. The rise of oxygen and catalyst concentration resulted in the increase of reaction rates. The reaction is likely to go through the activation of dioxygen by the cobalt macrocomplex. Cobalt remains fixed at the end of the polymer and is sur-

rounded by oxygen atoms of the PEG chain. Such surrounding is labile and does not preclude from activation of dioxygen:

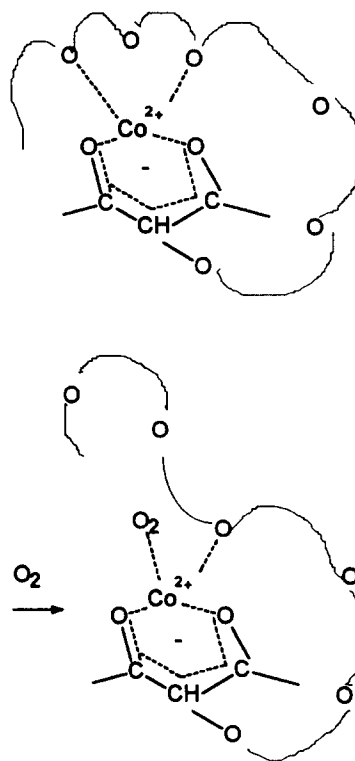


Table 4
Oxidation of ethylbenzene by dioxygen

Catalyst	Oxidant	[Co ²⁺], mmol/l	T, °C	Acetophenon yield, %
RE/Co ²⁺ *	air	10.5	100	9
RE/acac/Co ²⁺ **	air	14	100	4
RE-acac-Co ²⁺	air	2.3	100	16
RE/Co ²⁺ *	dioxygen	2.3	120	2
RE-acac-Co ²⁺	dioxygen	2.3	120	21

[C₆H₅C₂H₅] = 8.18 mol/l, reaction time 2 h.

* mixture: RE + ligand + Co(NO₃)₂.

** mixture: RE + ligand + Co(NO₃)₂.

3.3. Hydroformylation

The hydroformylation catalyst was obtained in situ from Rh-acac(CO)₂ and the functionalized polymer (RE)₂-PPh under the atmosphere of the synthesis gas. The catalytic properties of the complex were investigated in the model reaction of hydroformylation of dodecene-1 in the aqueous two-phase system (Table 5). The

Table 5
Hydroformylation of dodecene-1 in toluene/water

Pressure atm.	Ratio P/Rh	Conversion, %	Ratio n/i-aldehyde
1 *	5	< 1	–
10	15	50	2.3
15	5 *	20	1.3
15	10	38	2.3
15	15	80	1.5
15	20	42	2.5

$[C_{12}H_{22}]/[Rh] = 150$, $CO/H_2 = 1$, $T = 50^\circ C$, reaction time = 6 h.

* Reaction time = 12 h.

polymer chain of the ligand plays the role of phase transfer agent.

The rise of the pressure of the synthesis gas caused the increase of total yield of aldehyde. Using catalysts with different P/Rh ratio for hydroformylation showed that the optimum is around 15:1. It was shown that at the end of the reaction the catalyst practically completely remains in the water phase and can be easily separated from the products. The catalyst proved to be active in the hydroformylation of a new portion of dodecene.

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