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New catalytic systems for selective oxidation of aromatic compounds by hydrogen peroxide

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Abstract

Some new water-soluble catalytic systems based on iron complexes of polyethylene oxide and block copolymers of ethylene oxide and propylene oxide functionalized by catechol or β-cyclodextrin have been developed. These complexes were examined as catalysts for biomimetic hydroxylation of benzene and phenol by hydrogen peroxide. It is shown that the introduction of β-cyclodextrin into the polyethylene oxide molecule is favourable for rate and selectivity of hydroxylation of aromatic compounds in a two-phase system. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Water-soluble metal-complex catalysts allow one to perform reactions in two-phase aqueous organic systems and can be easily separated from organic products and reused. Currently, a large number of such catalytic systems are already known. The most striking example is catalysts based on water-soluble ligands for two-phase hydroformylation of unsaturated compounds [1–4]. At the present time, industrial implementation of such catalysts becomes urgent [5].

The basic principle of creating such catalytic systems is the use of water-soluble ligands. This solubility is attained by introducing various polar functional groups (e.g., $-SO_3^-$,$-NR_3^+$,$-CO_2^-$) or fragments of water-soluble polymers (polyethylene oxide, vinyl alcohol, etc.) into a ligand [6]. Such catalytic systems have a phase-transfer ability and allows one to readily separate a catalyst from the reaction products and to reuse it owing to the separation of the aqueous phase, which contains the catalyst, and the organic phase.

We consider that one of the promising trends in creating such catalytic systems is the use of macromolecular ligands based on polyethylene oxide and ethylene oxide–propylene oxide block copolymers. Ligands based on these polymers can be readily functionalized by modifying terminal hydroxyl groups. These polymers are water-soluble, can solubilize various organic substances, and thus can be active phase-transfer catalysts. Catalysts with ligands based on these polymers have demonstrated high catalytic activity in hydroformylation and Wacker oxidation of unsaturated compounds [7,8]. In this

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work, we employed such type of catalysts in hydroxylation of aromatic substances.

Direct oxidation or hydroxylation of aromatic compounds is of current interest both from fundamental and industrial standpoints. Of special interest is the application of hydrogen peroxide as an environmentally friendly oxygen donor. Use of both homogeneous and heterogeneous catalytic systems for direct introduction of a hydroxyl group into an aromatic ring under mild conditions have been described [9–13]. Phenol hydroxylation to hydroquinone (HQ) and catechol (CAT) with titanium silicalite as a catalyst has been industrially implemented [14]. However, in most cases, the hydroxylation selectivity is quite low. To avoid this disadvantage, we developed new water-soluble catalytic systems based on polyethylene oxide and different types of ethylene oxide–propylene oxide block copolymers functionalized by catechol or β-cyclodextrin.

Iron complexes with these ligands were examined as catalysts for hydroxylation of benzene and phenol by hydrogen peroxide. Employment of catechol complexes and the conformation sensitivity of polymers allow one to consider such catalysts as a biomimetic one.

Use of hydroxylating catalytic system – iron(III)–polyethylene oxide, modified by β-cyclodextrin gave grounds to hope that the selectivity of hydroxylation of such a reactant as phenol would be higher owing to formation of β-cyclodextrin–reactant complexes.

2. Experimental

Ligands were prepared from butyl monoether of polyethylene oxide ($C_4H_9E_{67}OH$, E=–OCH_2CH_2–) and butyl monoethers of ethylene oxide–propylene oxide block copolymers ($C_4H_9P_xE_yOH$ and $C_4H_9E_xP_yOH$, P=–$OCH_2CH(CH_3)$–) with the molecular weights 3000 by functionalization with catechol group.

Ligands based on these polymers were synthesized from the corresponding tosylates prepared according to the procedure from [15]. Tetrabutyl ammonium salt of 3,4-hydroxybenzoic acid (protocatechuic acid) was prepared by reaction of 16 mmol of protocatechuic acid and 30% solution of tetrabutyl ammonium hydroxide (16 mmol). This salt was added to a solution of 4 mmol of corresponding tosylate in 75 ml of *N*,*N*-dimethylformamide with intense stirring at 70°C. The reaction was carried out for 4 h, and then *N*,*N*-dimethylformamide was distilled out. The crude product synthesized was dissolved in 50 ml of methylene chloride, and the polymer was precipitated by an excess of diethyl ether in the cold. Reprecipitation was repeated twice.

Iron complexes were obtained by reaction of the produced macromolecular ligands with anhydrous ferric chloride at the ligand-to-salt ratio 2:1 in a methylene chloride solution. The product was precipitated by ether in the cold.

Oxyethylated β-cyclodextrin (E–β-CD) was synthesized by ethylene oxide oligomerization in the presence of β-cyclodextrin (β-CD) [16].

^1H and ^{13}C NMR spectra were recorded with a Varian WXR-400 spectrometer. FTIR spectra were recorded with a Perkin Elmer 2000 Fourier-transform spectrometer.

Hydroxylation was carried out in intense stirring under mild conditions (20–70°C). A catalyst, a reactant, and a solvent were added successively into a temperature-controlled glass reactor. The reaction was initiated by adding H_2O_2 (30 wt%) at the set temperature. Products were analysed by HPLC (Lichosorb C18, 200×4, eluent methanol/water 1/9).

3. Results and discussion

3.1. Synthesis of catalysts

The structure of the macroligands are shown in Fig. 1.

Catechol-modified macroligands were synthesized as shown in Scheme 1.

Oxyethylated β-cyclodextrin was prepared by the polymerization of ethylene oxide initiated by hydroxyl groups of β-cyclodextrin. Analyses of the structure and composition of the compounds were done using ^1H and ^{13}C NMR spectroscopy. Molecular weight of the molecule was 3000. The number of ethylene oxide fragments (–OCH_2CH_2–) per molecule of β-cyclodextrin is about 53–56 [16].

Ligands based on polymers, modified by catechol, were characterized by NMR and FTIR spectroscopy (Table 1). Along with signals of protons of the

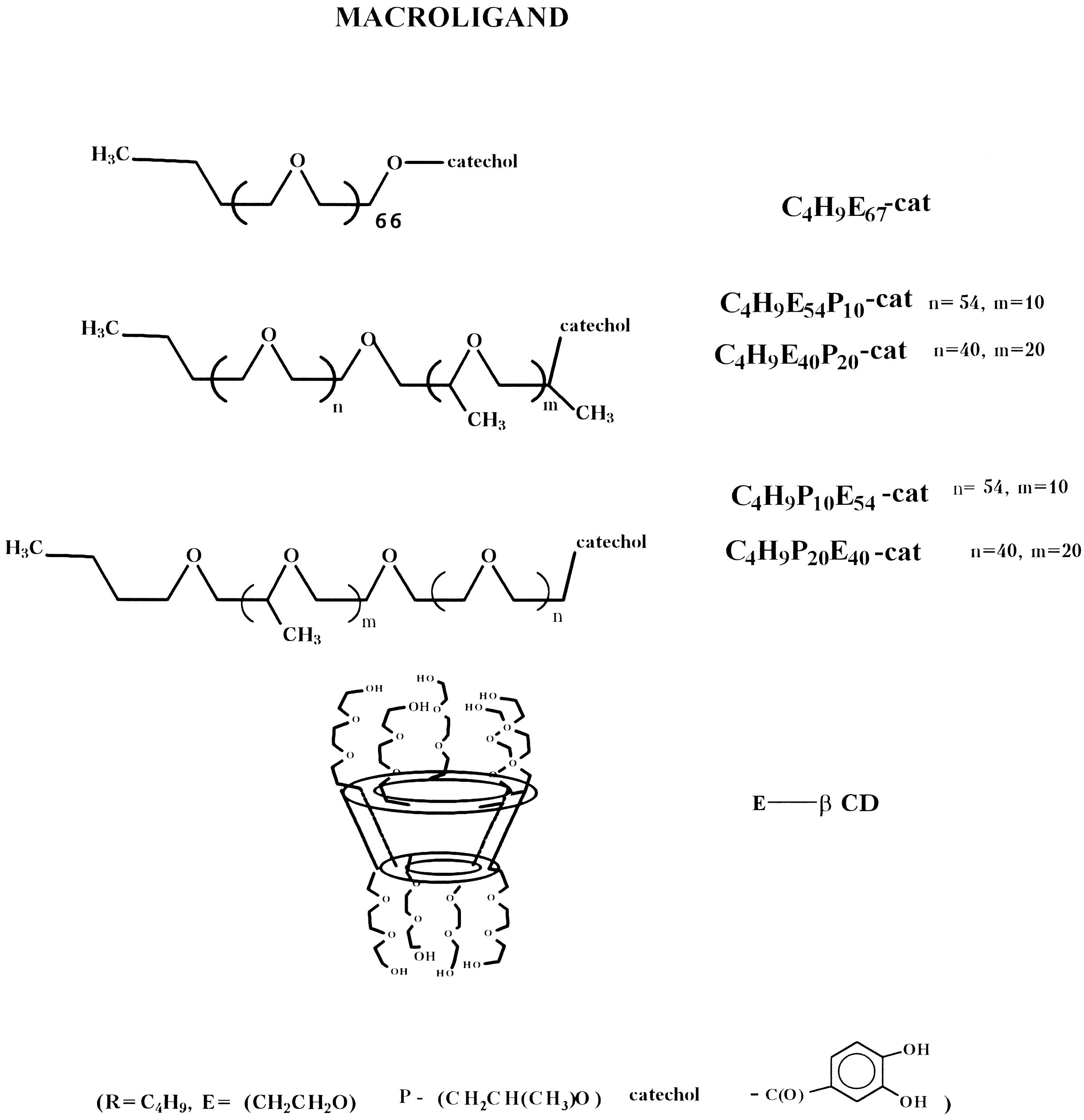
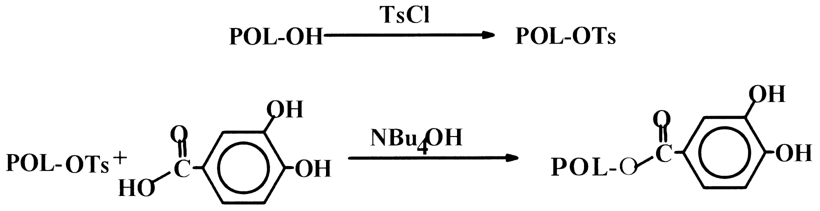


Fig. 1. Macroligands.

ethylene oxide- and propylene oxide-containing parts of polymer and terminal butyl groups, ^1H NMR spectra of catechol-modified ligands exhibited shifts of protons of the aromatic ring of catechol in the range 7.1–7.9 ppm. From ^1H NMR spectra of polymers it was found that the signal of tosyl group (7.72 and 7.41 ppm) completely diminished and signals of catechol group (7.55, 7.05 and 6.95 ppm) appeared. The degree of modification of terminal groups was determined from the ratio between the intensities of the



POL$^-$ = $C_4H_9E_{67}$-, $C_4H_9E_{54}P_{10}$-, $C_4H_9P_{10}E_{54}$-, $C_4H_9E_{40}P_{20}$-, $C_4H_9P_{20}E_{40}$-

TsCl- tosyl cloride

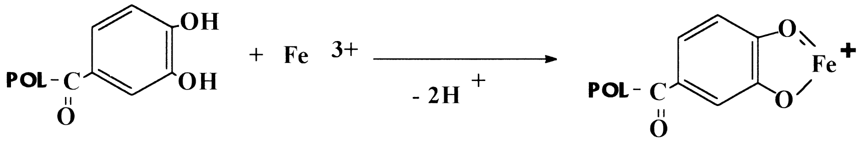
Scheme 1.

Table 1
^{1}H NMR chemical shift data and FTIR frequencies of macroligands, based on polyethylene oxide and block copolymer of ethylene oxide and propylene oxide

Ligand	^{1}H NMR	FTIR
$C_4H_9E_{67}$-cat	1 ppm (CH_3–, 3 H), 1.4, 1.6 ppm (–CH_2–CH_2, butyl, 4 H), 3.7 ppm (–CH_2CH_2O, ethylene oxide block, 282 H) 6.95, 7.05, 7.55 ppm (aromatic ring, 3 H)	3400–3550 cm^{-1} (–OH catechol) 2870–2890 cm^{-1} (C–H aromatic ring), 1720 cm^{-1} (C=O), 1548, 1511, 1492,1469, 1234 cm^{-1} (ν_v C–C aromatic ring), 906, 879, 788, 753 cm^{-1} (ν_d C–C aromatic ring)
$C_4H_9E_{40}P_{20}$-cat	1.05 ppm (CH_3–, butyl, 3 H), 1.2 (CH_3–, propylene oxide block, 60 H), 1.4, 1.6 ppm (–CH_2–CH_2, butyl, 4 H), 3.7 ppm (–CH_2CH_2O, ethylene oxide block, 220 H) 7.05, 7.2, 7.68 ppm (aromatic ring, 3 H)	
$C_4H_9E_{54}P_{10}$-cat	1.5 ppm (CH_3–, butyl, 3 H), 1.19 (CH_3–, propylene oxide block, 30 H), 1.4, 1.6 ppm (–CH_2–CH_2, butyl, 4 H), 3.67 ppm (–CH_2CH_2O, polyethylene oxide, 250 H) 7.05, 7.2, 7.68 ppm (aromatic ring, 3 H)	
$C_4H_9P_{10}E_{54}$-cat	1.0 ppm (CH_3–, butyl, 3 H), 1.22 (CH_3–, propylene oxide block, 60 H), 1.4, 1.6 ppm (–CH_2–CH_2, butyl, 4 H), 3.65 ppm (–CH_2CH_2O, ethylene oxide block, 220 H) 7.0, 7.1, 7.55 ppm (aromatic ring, 3 H)	
$C_4H_9P_{20}E_{40}$-cat	1.03 ppm (CH_3–, butyl, 3 H), 1.2 (CH_3–, propylene oxide block, 60 H), 1.4, 1.6 ppm (–CH_2–CH_2, butyl, 4 H), 3.7 ppm (–CH_2CH_2O, ethylene oxide block, 220 H) 7.0, 7.1, 7.55 ppm (aromatic ring, 3 H)	

signals of the polymer chain, butyl groups and the aromatic protons and ranged from 90% to 100%. IR spectra of ligands displayed bands of the hydroxyl groups of catechol (3400–3500 cm^{-1}), –C(O)–O group of ester (1720, 1170 cm^{-1}), and aromatic ring (1603, 1548, 1511, and 1240–1280 cm^{-1}).

Iron complexes were synthesized with all catechol containing ligands. Signals in ^{1}H NMR spectra in 7.1–7.9 ppm of complexes were quite diffuse. FTIR spectra showed frequency shift from 1603 to 1585 and from 1548 to 1530 cm^{-1}. Electron spectra of the complexes produced in an aqueous solution showed an absorption band at 680 nm, which indicates the formation of a complex of Fe^{3+} with a terminal catechol group. The polymer-to-metal molar ratio is 1:1 [17,18]:



POL = $C_4H_9E_{54}P_{10}$, $C_4H_9E_{40}P_{20}$, $C_4H_9P_{10}E_{54}$, $C_4H_9P_{20}E_{40}$, $C_4H_9E_{67}$

Table 2
Hydroxylation of benzene by H_2O_2

Catalyst	Phenol (%)	Hydroquinone (%)	Catechol (%)
Two-phase system (benzene–water)			
β-CD+Fe^{3+} [β-CD]=0.008 mol/l	25	4	2
E–β-CD+Fe^{3+} [E–β-CD]=0.008 mol/l	69	6	$\gg$1
$C_4H_9E_{67}$-cat-Fe^{3+}	5	1	1
$C_4H_9E_{54}P_{10}$-cat-Fe^{3+}	8	1	2
Homogeneous system (CH_3CN/H_2O_2=4/1)			
C_4H_9 E_{67}OH+Fe^{3+}+3,4-di- hydroxobenzoic acid[a]	17	2	3
$C_4H_9E_{54}P_{10}$OH+Fe^{3+}+3,4-di-hydroxobenzoic acid[a]	8	1	1
C_4H_9 E_{67}-cat-Fe^{3+}	30	2	5
$C_4H_9E_{54}P_{10}$-cat-Fe^{3+}	20	2	4
$C_4H_9P_{10}E_{54}$-cat-Fe^{3+}	15	1	3
$C_4H_9E_{40}P_{20}$-cat-Fe^{3+}	14	1	2
$C_4H_9P_{20}E_{40}$-cat-Fe^{3+}	8	1	3

50°C, 30 min [H_2O_2]=1.54 mol/l, [Fe^{3+}]=0.0021 mol/l, [C_6H_6]=0.77 mol/l.
[a] Mixture of polymer, 3,4-dihydroxobenzoic acid and $FeCl_3$.

Quantitative analysis of macrocomplexes showed the same polymer-to-metal molar ratio of 1:1.

3.2. *Benzene hydroxylation*

Hydroxylation was conducted under both homophase (acetonitryl–water) and heterophase conditions. Table 2 presents the results of benzene hydroxylation after 30 min of reaction.

Catalysts based on catechol containing iron macrocomplexes represent the analogue of Hamilton's hydroxylating system, where the complex of catechol and iron(III) is the active site [11,19,20].

In a two-phase condition the yield of the main product, phenol, in the presence of the catalytic system E–β-CD/Fe^{3+} was considerably higher than that with systems based on both unmodified β-cyclodextrin and macromolecular metal complexes. Note that these results were obtained in pH-neutral media, where the phenol yield is low and typically does not exceed 5% [10].

In our opinion, this is caused by the specific mechanism of hydroxylation in the presence of water-soluble E–β-CD/Fe^{3+}. This catalyst with phase-transfer ability forms inclusion complexes with aromatic molecules (Fig. 2) [16,21,22], and benzene readily passes into the water phase, where hydroxylation occurs. The catalytic cycle is closed by the decomposition of the complex with phenol and its passage into the organic phase.

In the presence of macromolecular metal complexes, the phenol yield was low in heterophase system and considerably increased under homophase conditions. In this case the recycling can be achieved

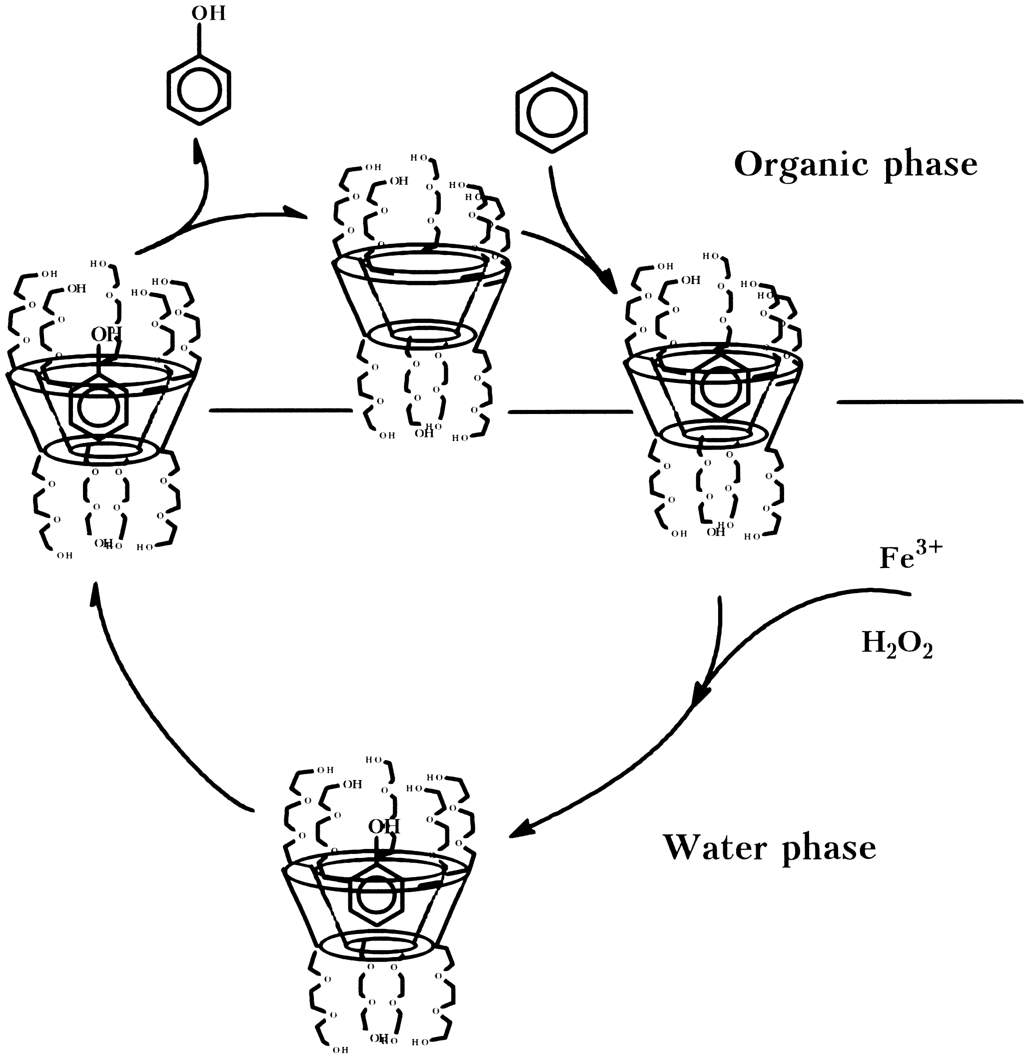


Fig. 2. Hydroxylation of benzene in two-phase system in the presence of ethoxylated β-cyclodextrin.

by adding a "bad" solvent (diethyl ether). The reaction products remain in the ether solution, and the catalyst is retained in an aqueous phase.

In homogeneous conditions the activity of macrocomplexes, based on terminally modified polymers, was higher than that of systems based on a mixture of 3,4-dihydroxybenzoic acid, polymer and iron salt. This can be explained as follows: in the macrocomplexes the active sites are located in polymer coil where the concentration of benzene is high [10,23]. For mixture systems the part of active sites are located outside.

The activity of catalysts changed in a homogeneous system in the order

$$\mathrm{C_4H_9E_{67}\text{-}cat\text{-}Fe^{3+}} > \mathrm{C_4H_9E_{54}P_{10}\text{-}cat\text{-}Fe^{3+}} > \mathrm{C_4H_9P_{10}E_{54}\text{-}cat\text{-}Fe^{3+}} > \mathrm{C_4H_9E_{40}P_{20}\text{-}cat\text{-}Fe^{3+}} > \mathrm{C_4H_9P_{20}E_{40}\text{-}cat\text{-}Fe^{3+}}$$

Such an order, probably, is connected with the different accessibility of active sites. The greater the content of propylene oxide part in block copolymer, the higher the extent of aggregation, which leads to

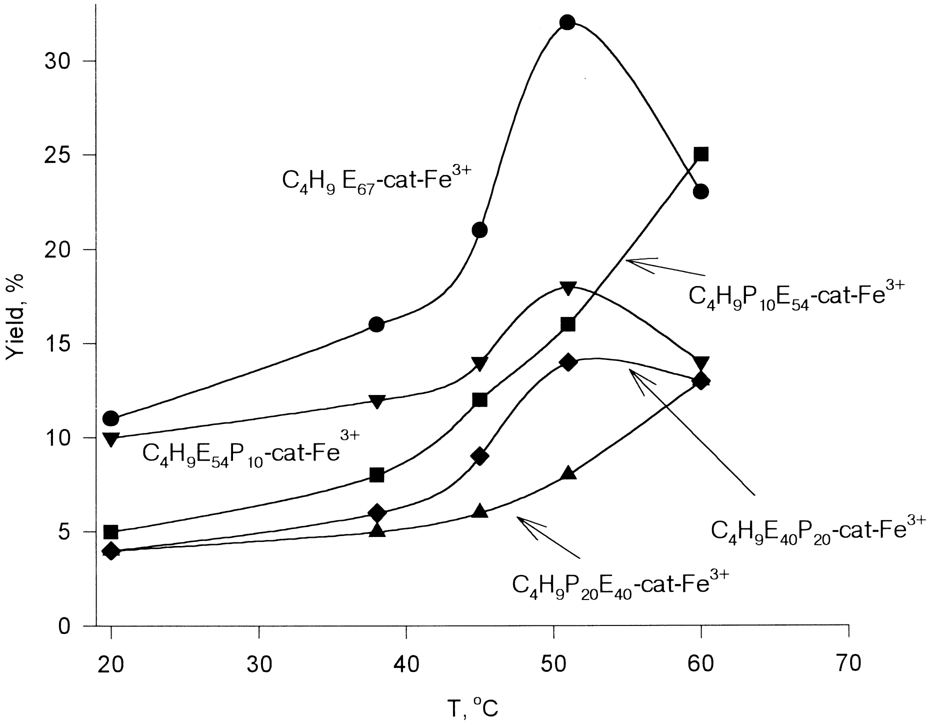


Fig. 3. Hydroxylation of benzene under different temperatures: (30 min $[H_2O_2]$=1.54 mol/l, $[Fe^{3+}]$=0.0021 mol/l, $[C_6H_6]$=0.77 mol/l).

the decrease of availability of catalytic centres. The aggregation is minimal in the case of $C_4H_9E_{67}$-cat-Fe^{3+}.

Macrocomplexes, whose active sites are in the propylene oxide (lipophilic) part of a molecule (e.g. $C_4H_9E_{54}P_{10}$-cat-Fe^{3+}) were more active than block copolymer based systems whose active sites are in the ethylene oxide (hydrophilic) part. For such block copolymers the main quantity of benzene in water solution is known to be located in the apolar propylene oxide-containing part [24,25].

The product yield and the reaction selectivity in using soluble metal complexes were substantially temperature-dependent (Fig. 3). Three of these complexes ($C_4H_9E_{67}$-cat-Fe^{3+}, $C_4H_9E_{54}P_{10}$-cat-Fe^{3+} and $C_4H_9E_{40}P_{20}$-cat-Fe^{3+}) were characterized by the existence of the temperature (50°C) that was optimum to perform the reaction, i.e., at which the yield and the selectivity with respect to phenol were maximum. At the higher temperatures aggregation of polymer coils occurs [26], as a result the active sites become less accessible.

In block copolymer macrocomplexes ($C_4H_9P_{10}E_{54}$-cat-Fe^{3+}, $C_4H_9P_{20}E_{40}$-cat-Fe^{3+}) whose active sites are located in the hydrophilic part of a molecule, an increase in temperature levelled the differences between polymer blocks. This leads to an increase in the concentration of the substrate near the active site and consequently the reaction product yield increases. Note that a similar phenomenon has been observed in using block copolymer-based systems in cyclohexane oxidation [23].

With ethoxylated cyclodextrin, an increase in temperature from 25°C to 50°C increased the phenol yield from 25% to 65%. This can be explained by the inverse temperature dependence of the solubility of E–β-CD, which enabled it to act as a temperature-dependent phase-transfer catalyst.

Fig. 4 presents the relationship between the phenol yield and the H_2O_2 consumption. Under the reaction conditions, virtually the entire amount of hydrogen peroxide was consumed in hydroxylation.

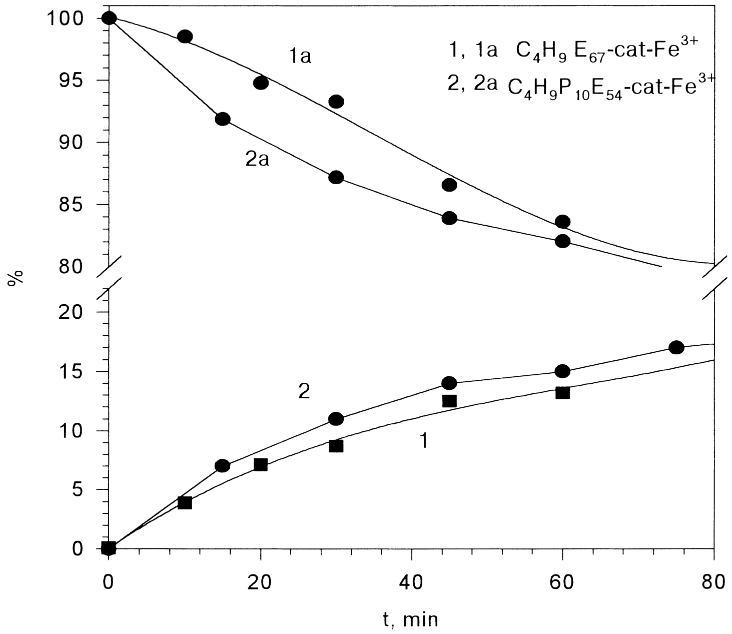


Fig. 4. Relationship between phenol yield (1) and (2) and consumption of H_2O_2 (1a) and (2a). $[H_2O_2]$=1.54 mol/l, $[Fe^{3+}]$=0.0021 mol/l.

Table 3
Hydroxylation of phenol by H_2O_2

Catalyst	Phenol conversion (%)	Hydroquinone (%)	Benzoquinone (%)	Catechol (%)
Two-phase system (solvent – dichloroethane, $C_2H_4Cl_2/H_2O$=1/4)				
β-CD+Fe^{3+} [β-CD]=0.5 mmol/l	19	11	5	3
E–β-CD+Fe^{3+} [E–β-CD]=0.5 mmol/l	40	37	2	1
Water system				
$C_4H_9E_{67}$-cat-Fe^{3+}	75	25	1	54
$C_4H_9E_{54}P_{10}$-cat-Fe^{3+}	33	10	3	20
$C_4H_9P_{10}E_{54}$-cat-Fe^{3+}	29	9	3	17
$C_4H_9E_{40}P_{20}$-cat-Fe^{3+}	48	12	2	24
$C_4H_9P_{20}E_{40}$-cat-Fe^{3+}	29	10	2	17

50°C, 30 min ($[H_2O_2]$=0.1 mol/l, $[Fe^{3+}]$=0.5 mmol/l, $[C_6H_5OH]$=0.05 mol/l).

3.3. *Phenol hydroxylation*

Table 3 shows that the activities of macromolecular metal complexes in aqueous solutions (without other solvents) increased in the order

$$C_4H_9E_{67}\text{-cat-}Fe^{3+} > C_4H_9E_{40}P_{20}\text{-cat-}Fe^{3+} > C_4H_9E_{54}P_{10}\text{-cat-}Fe^{3+} > C_4H_9P_{10}E_{54}\text{-cat-}Fe^{3+} = C_4H_9P_{20}E_{40}\text{-cat-}Fe^{3+}$$

This order suggested a correlation between the position of modifying groups and the catalyst activity. The degree of phenol conversion was highest (73%) when $C_4H_9E_{67}$-cat-Fe^{3+} was used as a catalyst. The selectivity was low with all catalysts. The results of phenol hydroxylation by H_2O_2 show that along with the main products (*p*- and *o*-dihydroxybenzenes), benzoquinone (BQ) also formed. The hydroquinone-to-catechol ratio

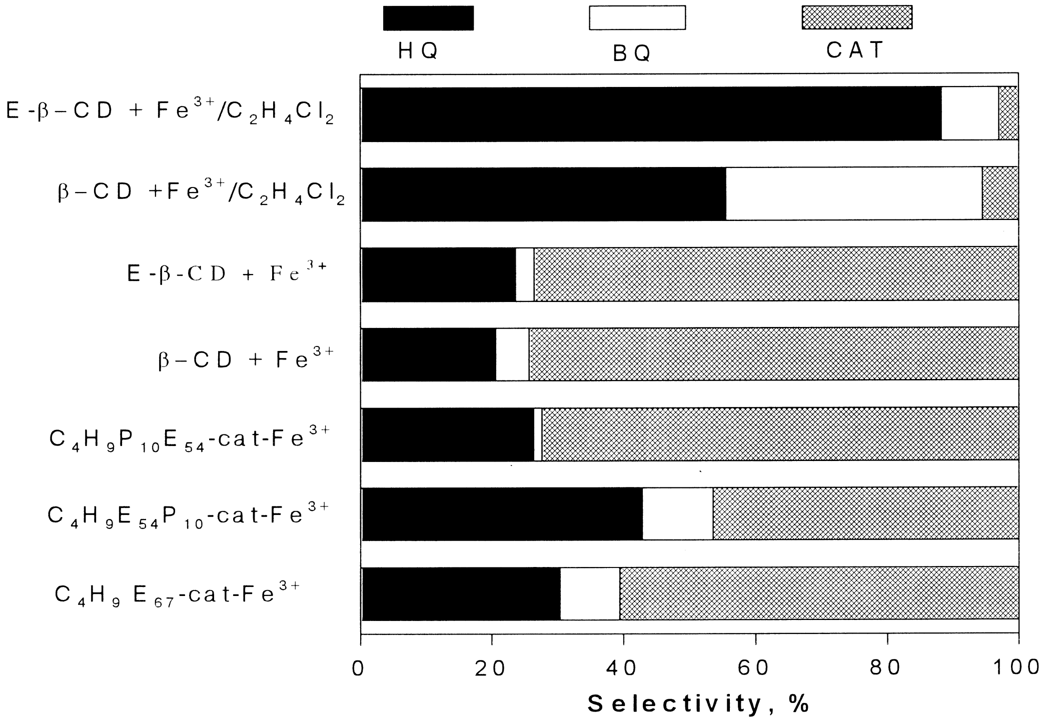


Fig. 5. Selectivity of phenol hydroxylation by H_2O_2 (1 h). $[H_2O_2]$=0.1 mol/l, $[Fe^{3+}]$=0.5mmol/l, $[C_6H_5OH]$=0.05 mol/l.

(near 1:2) is typical for the chemistry of Hamilton hydroxylation.

To increase the hydroxylation selectivity, cyclodextrin-containing catalysts in a two-phase system were used. β-Cyclodextrin introduction into a polyethylene oxide molecule was found to favour hydroxylation at the *p*-position. The selectivity with respect to hydroquinone was about 95% (Fig. 5). This can be tentatively explained as follows: in a two-phase system ethoxylated β-cyclodextrin forms an inclusion complex with phenol [27]. All carbon atoms of phenol, except for *p*-position, are enclosed in the cavity of β-cyclodextrin and the *p*-position of phenol is preferentially attacked by active hydroxylation species.

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