IMMOBILIZATION OF CATIONIC POLYMERS AND ITS EFFECT ON THE COBALT-PHTHALOCYANINE-CATALYZED THIOL OXIDATION

PROEFSCHRIFT

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There are two tragedies in life. One is not to get what your heart desires. The other one is to get it.

Bernard Shaw
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Introduction

Immobilization

The use of insoluble polymer support as carrier for reagents was first introduced by Merrifield\textsuperscript{1}. The principle is basically simple: a partially protected amino acid was attached to a functionalized polymer support. After deprotection, this immobilized amino acid was reacted with a second suitable protected amino acid, and so on. After the desired peptide was synthesized, a decoupling reaction liberated the peptide. Some general advantages of reactive polymers are, (1) simple reaction work-up, (2) reuse of precious reagent, (3) intrinsic possibilities of continuous operation and (4) reduced toxicity. But immobilization also introduces some disadvantages, that is, (1) possible occurrence of diffusional problems resulting in a lower activity, (2) higher costs compared with low molar mass analogues, (3) large quantities of polymer support are needed, (4) possible instability of the polymeric reagent after multiple use and (5) inability to separate polymer-bound impurities. In multistep synthesis as described above, these polymer-bound impurities may be introduced by incomplete reactions. In order to obtain quantitative yields, Merrifield used a large excess of (costly) reagents. The so-called transfer polymeric reagent method provides another way to solve this problem\textsuperscript{2}. In this case the partially protected peptide to be modified is dissolved in the eluent. Reaction with the polymer-bound amino acid releases the desired product. Advantages of this method are that the excess of polymeric reagent needed to obtain quantitative yields can be reused after the reaction, and that the desired product can be purified by the usual methods.

Since the introduction by Merrifield many articles have been published in this field and nowadays reactive polymers are being widely used on a laboratory scale\textsuperscript{3-7}. Due to the above-mentioned problems, polymeric reagents
are still seldom used in industrial processes. However, in future, polymer anchored reagents may be expected to be preferably used in the production of new specialty chemicals, for instance as pharmaceuticals.

Although most of the above advantages and drawbacks of immobilization onto polymer support also hold in the case of catalyst immobilization, polymer anchored catalysts are more widely used than polymeric reagents. Catalysts should be stable and allow multiple use. Obviously, some drawbacks of polymeric reagents do not bear upon polymer-bound catalysts, for instance the often expensive regeneration process is not necessary, and since the catalyst is attached to the polymer matrix, all impurities or contaminants can easily be removed. Moreover, as catalysts are mostly used in small quantities, relatively small amounts of polymer-supported catalysts are needed. Well-known polymer-immobilized catalysts are the ion-exchange resins\(^5\)-\(^10\) used in the synthesis of the petrol additive methyl tert-butyl ether\(^11\). Furthermore, ion-exchange resins are widely used in water softening and deionization.

The insoluble polymer matrix can easily be prepared by suspension-(co)polymerization of a functional monomer and a cross-linker or by post-polymerization modification\(^12\)-\(^16\). Depending on the experimental conditions used during the suspension polymerization, the resulting polymer support (also called beads or resin) is of the gel or macroporous type. Gel-type resins (low degree of cross-linking) exhibit high swellability in suitable solvents, that is good solvents for the polymer matrix, while in the presence of a non-solvent, or in the dry state, the beads become microporous. Macroporous (macroreticular) resins (high degree of cross-linking) exhibit a permanent porosity irrespective of solvent. In many cases, macroporous supports are preferred to gel-type supports as their porosity is hardly affected by solvent and the active sites are more accessible owing to the large pores. Moreover, the macroporous supports are mechanically more stable as a result of a high degree of cross-linking.

Furthermore, soluble polymers can be used as polymeric reagents or
catalysts. Although continuous operation of this type of polymeric support is not possible, reaction work-up can still be achieved by precipitation of the soluble support. Moreover, due to the complete solubilization of the polymer, mass-transport limitations can normally be ruled out, and in basic studies such polymers can therefore be favourable. Soluble polymeric supports can be considered as intermediates between the low molar-mass analogue of a polymeric reagent and a reagent immobilized onto an insoluble polymer matrix.

Immobilization of polymer chains onto insoluble supports combines the advantages of heterogeneous and homogeneous polymer-bound reagents or catalysts. Silica bound initiator was used to immobilize macromolecular copper complexes and macromolecular flavin. Macromolecular flavin was also anchored by adsorption onto silica. Laible et al. outlined some methods to anchor polymers onto silica.

Polymer catalysis

An interesting effect of polymer anchoring is that, in some cases, the support plays an active role in the reactions. Immobilization may cause "site-isolation" of the reactive group or catalyst in the polymer matrix. Due to this restricted motion of the attached groups, self-condensation could be avoided, cyclic peptides synthesized and the formation of lesser active dimers of catalysts prevented. Another example of site-isolation is the increased lifetime of polymer-bound benzene. On the other hand, Koning et al. reported a promoting effect on the desired site-site interactions in the case of the polymer-catalyzed oxidative coupling of 2,6-dimethylphenol.

Polymer-bound catalysts in a way resemble the naturally occurring catalytically active biomacromolecules, i.e. the enzymes. It is therefore not surprising that enzyme-like behaviour was found for some polymer-bound catalysts. Enzyme-like polymers (or polymer catalysts) can be prepared by binding active groups of amino acids, coenzymes, specific binding sites, or
metal ion complexes into or onto a polymer backbone. Another interesting form of polymer catalysis is the introduction of chiral cavities in a polymer matrix\(^{33}\).

During the past decade, the Eindhoven polymer research group studied the effects of binding cobalt(II)phthalocyanine-terrasodiumsulphonate (CoTSPc) to soluble cationic polymers, on the oxidative coupling of thiols in the presence of molecular oxygen\(^{32-35}\). CoTSPc attached to cationic polyelectrolytes appeared to have strongly enhanced the observed catalytic activity and also to have affected reaction kinetics and mechanism. Thiols, present in crude oil, are known to contaminate oil refining catalysts, to enhance corrosion of the apparatus and to pollute the environment after combustion. For that reason, in the petroleum industry, thiols are converted by oxidation via the so-called Merox process (mercaptan oxidation)\(^{36,57}\) to the less harmful disulphide (oil sweetening\(^{30,35}\)) and removed where required.

The oxidative coupling of thiol group also plays an important role in living organisms\(^{40,41}\), where the disulphide linkages is an important element in the structure of proteins.

Outline of this thesis

Most of the research in the field of CoTSPc-catalyzed thiol oxidation has been focused on the elucidation of the polymeric effects of cationic polyelectrolytes on the reaction mechanism and kinetics. As outlined above, insolubilization of catalysts allow continuous operation, which is a prerequisite for possible use in industry. Also, from the scientific point of view, immobilization of this highly active system onto insoluble polymer particles was found to be very interesting, as it leads to a more general insight into the consequences of immobilizing extremely active systems.

In chapter 2 the effect on thiol oxidation of molar mass of the watersoluble and catalytically highly effective polycationic ligand 2,4-ionic is
described.

Chapters 3 and 4 describe the immobilization of 2,4-ionene on poly(styrene-divinylbenzene) macroporous resins and its effect on thiol oxidation.

Chapter 5 deals with the synthesis of latex particles stabilized and modified by a block copolymer of styrene and quaternized N-methyl-4-vinylpyridine. The behaviour of the latex immobilized systems is compared with systems containing homogeneous block copolymers and homopolymers of quaternized N-methyl-4-vinylpyridine.

In chapters 6 and 7 the synthesis and purification of 3-(methacrylamidinopropyl)-trimethylammoniumchloride (MAD) modified latices is described. These latices were also tested as co-catalyst in the thiol oxidation. The insight gained leads to a model description facilitating the design of highly active cationic supports.

The appendix deals with various attempts that have been made to synthesize polyelectrolyte-containing macromonomers, initiators and block copolymers. Although not yet directly applicable in the present investigation, some of these lines of inquiry seem to be of potential interest in future research.

Parts of this thesis have already been published or will be published soon:
* parts of chapter 2 in ref.42
* parts of chapter 3 and 4 in ref.43
* parts of chapter 5 in refs.44,45

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Effect of 2,4-ionenes of different molar masses on the oxidative coupling of thiol catalyzed by cobaltphthalocyanine

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Summary

A photometric method is developed for the determination of the molar mass of 2,4-ionene by attaching a chromophoric moiety to its end groups. Molar mass determination of these polyelectrolytes by acid-base titration of the amine end groups is also possible, and confirms the photometric method. The effects of molar mass of 2,4-ionenes on the oxidative coupling of 2-mercaptoethanol (ME) were studied in the presence of cobalt(II)phthalocyanine-tetra-sodium-sulphonate (CoTSpC). Monomeric analogues of 2,4-ionene showed no increase in reaction rate compared with the polymer-free system. However, relatively low molar-mass ionene (Mn = 1740) showed a dramatic increase in reaction rate. The reactivity showed an optimum around pH = 8. Saturation kinetics (Michaelis-Menten kinetics) was observed. The calculated turnover number was 3300 s\(^{-1}\) and 3700 s\(^{-1}\) for Mn = 6600 and Mn = 1740, respectively. The stoichiometry of the reaction was disturbed at low thiol concentration.

Introduction

In our laboratory we have studied the effect of cationically charged polymers on the so-called Merox-process, that is the oxidative coupling of thiols to disulphides in the presence of the catalyst, cobalt(II)phthalocyanine-tetrasodiumsulphonate (CoTSpC). 1, scheme 1. Polyvinylamine (PVAm) and 2,4-ionene, a poly(quaternary ammonium) salt (2, scheme 2) were found in
particular to give a surprisingly high increase in reaction rate. Experiments showed that an increase in the positive charge density on the polymer chain resulted in an enhancement of the catalytic activity.\textsuperscript{2,3} Two major effects are believed to cause this phenomenon: (1) coulombic interaction between the negative charge of the sulphonate groups of CoTSPc and the positive charge on the polymer backbone and (2) an increase in the degree of dissociation of the thiol in the cationically charged polymer domain, resulting in a locally enhanced thiolate anion concentration. In the case of PVAm, coordinative binding between the metal complex and the polymer is also assumed to occur\textsuperscript{4,5} and Michaelis-Menten kinetics in thiol and oxygen have been observed\textsuperscript{6}. The reaction rates with both PVAm and 2,4-ionene showed an optimum around pH = 8\textsuperscript{3,7}, caused by two opposing effects on increasing the pH; an increase in both thiolate anion concentration and ionic strength. In the case of PVAm, the collapse of the catalytic activity above the pH-optimum is also due to loss of polymer charge (deprotonation). Most interestingly, a molar mass dependence on the catalytic activity was observed in the case of PVAm\textsuperscript{6}. We therefore describe our investigations on molar mass dependence of the catalytic activity and kinetics of ionene containing systems in this chapter. The synthesis of 2,4-ionene involves a step reaction of N,N,N',N'-tetramethyl-ethylenediamine (TMEDA, 2) with 1,4-dibromobutane (4) (Scheme 2). In
Scheme 2 Synthesis of 2,4-iodene

Literature, the molar mass of these types of polymers has been determined by
viscometry, light scattering and ultracentrifugation9-11. However, these
methods are often complicated and laborious, due to the polyelectrolytic
character of these polymers. Therefore, we present in this chapter two
relatively simple methods of determining molar masses of 2,4-iodenes, both
based on the determination of amine end groups of aminated 2,4-iodenes. The
first method measures the UV-absorbance of a chromophore (a benzylic group),
chemically bonded to the amine end-groups. The second method determines the
amount of amine end-groups by direct acid-base titrations. These methods will
be shown to be sufficiently accurate to determine the relatively slight molar
mass dependence of the activity and kinetics of catalytic systems based on
2,4-iodene.

Experimental

All chemicals and solvents were used as purchased unless otherwise
stated. TMEDA, 1,4-dibromobutane and 2-mercaptoethanol were obtained from
Fluka.

Synthesis of 2,4-iodene: 2,4-iodenes were synthesized according to the
method described by Rembaum et al.9 with a few modifications. The reaction
conditions were adapted in such a way as to accomplish the complete solution
of the resulting polymer throughout the reaction. A typical experiment 4.063
g TMEDA (3) and 7.560 g 1,4-dibromobutane (4) (Scheme 2) were dissolved in 70
g water-dimethylformamide (DMF) (1/1, w/w) and placed in a water bath at 40°C under nitrogen atmosphere. After two days or more an excess of TMEDA was added to the reaction mixture in order to aminate the product. After two more days the reaction mixture was precipitated in acetone. After filtration and washing with acetone, the product (5, scheme 3) was dried under reduced pressure (0.1 kPa) at 50°C. Yields, determined by mass, were between 90 and 100%. In order to obtain higher molar masses, reaction times (2-14 days), temperature (20-60°C) and solvent combinations (e.g. DMF/methanol (1/1, w/w) and DMF/water (4/1, w/w) varied. However, the use of these solvent combinations appeared to carry the risk of precipitation of polymer as polymerization proceeds. Only if experimental conditions were used as reported by Brouwer et al.2 (concentrated solutions of TMEDA and 1,4-dibromobutane in DMF/methanol at room temperature and long reaction times) could high molar mass polyelectrolytes be synthesized.

\[
\text{Scheme 3 Amination and benzylolation of 2,4-ionene}
\]

**Determination of molar mass**

**Photometric method:** The aminated 2,4-ionene (5) was reacted with an excess of benzylbromide (6) (scheme 3) in DMF/water (1/1, w/w) at 40°C under nitrogen atmosphere for two days. The product work-up was similar to the procedure used for the aminated 2,4-ionenes. The UV spectra were measured with a Hewlett Packard 8451A diode array spectrophotometer at 25°C in a 0.4 M NaCl solution at \(\lambda = 264\) nm. The slope of the plot of absorbance vs. concentration of ionenes (in g/dm\(^3\)) gives the absorptivity (a, in 10 dm\(^2\)/g).
Titration method: Titration of the aminated 2,4-ionenes was carried out in a 0.4 M NaCl solution under nitrogen atmosphere. A 0.1 M HCl (Merck, Titrisol) solution was added until pH = 3 was reached. Then this solution was titrated with a 0.01 M NaOH solution (Merck, Titrisol). The pH was monitored with a combi-electrode (Radiometer, GK 2401B) connected to a digital pH meter (Radiometer PHM 82). The molar mass can be calculated from the equivalence points and the total mass of 2,4-ionene.

Kinetics of 2,4-ionene: 4.0527 g TMEDA (34.96 mmol) and 7.5596 g 1,4-dibromobutane (35.0 mmol) were dissolved in 70 g DMF/water (1/1, w/w) and stirred under a nitrogen atmosphere at 40°C. At intervals a sample was taken and terminated with an excess of TMEDA for at least 48 hrs at 40°C. After precipitation in acetone and drying under reduced pressure, the molar mass was determined by acid-base titration.

Catalytic experiments

CoTSPc was synthesized according to the method described by Weber and Bush. The substrate, 2-mercaptoethanol (scheme 1, R = CH₂CH₂OH, abbreviated as ME), was distilled before use. Activity measurements were carried out at constant oxygen pressure in an all-glass double-walled Warburg apparatus equipped with a powerful mechanical glass stirrer. The stirring speed was maintained at 2500 rpm during the reaction. The Warburg apparatus was further equipped with a pH-electrode (Radiometer GK 2401B). The catalyst was prepared by adding an aqueous solution of CoTSPc to the reactor containing an aqueous ionene solution. Adjustments of pH were accomplished by adding minor amounts of a 0.01 M NaOH solution (Merck, Titrisol). The mixture was degassed twice and saturated with oxygen. During the reaction, the temperature was maintained at 25°C and the oxygen pressure at 100 kPa. After injecting ME into the reactor, a drop of pH was observed due to the acidity of the thiol. The oxygen uptake rate was monitored with a digital flowmeter (Isacom). The initial reaction rates were determined as the maximum oxygen consumption. The total
reaction volume was 0.1 dm³. The peroxide content of the reaction mixture was determined by iodometry as described by Vogel.14

Results and Discussion

Determination of the molar mass of 2,4-ironene by measuring the UV-absorbance of a chemically bonded chromophore (benzyl bromide, 6, scheme 3) requires the value of the molar absorptivity (ε, in 10 dm³/mol) of the chemically bonded benzyl bromide. In addition, it should be proved experimentally that ε is independent of the length of the attached 2,4-ironene.

Table 1: Molar absorptivity (ε) of various ironene analogues at λ = 264 nm

<table>
<thead>
<tr>
<th>Compound</th>
<th>M</th>
<th>ε (10 dm³/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>250</td>
<td>392</td>
</tr>
<tr>
<td>9</td>
<td>398</td>
<td>346</td>
</tr>
<tr>
<td>10</td>
<td>458</td>
<td>778</td>
</tr>
<tr>
<td>11</td>
<td>708</td>
<td>761</td>
</tr>
</tbody>
</table>

* two chromophoric groups per molecule

Scheme 4: Chemical structure of compounds used in Table 1
chain. In Table 1, where some chromophoric analogues of 2,4-ionene are listed, it is shown that \( \varepsilon \) is relatively insensitive to the chain length. We have chosen compound 11 as reference compound. From Lambert-Beer's law it follows that \( M_{\text{pol}} = \epsilon_{\text{ref}}/a_{\text{pol}} \); where \( M_{\text{pol}} \) is the molar mass of aminated 2,4-ionene (including its chromophoric end groups) and \( a_{\text{pol}} \) is the absorptivity of the unknown ionene, calculated from the slope of the absorbance vs. concentration curve (\( \varepsilon \) in g/dm\(^3\)). The latter measurement requires that 2,4-ionene is first aminated with TMEDA (3) leading to (2) and then reacted with the chromophore benzylbromide (6) (scheme 3). The calculated molar mass minus the molar mass of the benzylbromide groups gives the molar mass of the aminated 2,4-ionene.

As, in fact, the total number of end groups are measured, the calculated molar mass is the number average molar mass (Mn). In Fig. 1 absorbance vs. concentration curves are plotted for several modified 2,4-ionenes. The

![Graphs](image)

**Fig. 1** Absorbance (\( \lambda = 264 \text{ nm} \)) versus concentration of the modified 2,4-ionene (g/dm\(^3\)) at 25°C, K\(_{\text{B}}\)C\(_{11}\) = 0.4 mol/dm\(^3\).

- □: reference compound, \( \Delta: \) Mn = 1800, ○: Mn = 2750, ■: Mn = 8800.
- ■: Mn = 16600

**Fig. 2** Dependence of Mn as a function of time at 40°C.

Reaction conditions are given in the experimental section.
Table 2 Comparison between molar mass (Mn) of aminated 2,4-ionenes determined by the photometric and titration methods

<table>
<thead>
<tr>
<th>Photometric</th>
<th>Titration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1800</td>
<td>1740</td>
</tr>
<tr>
<td>2000</td>
<td>2750</td>
</tr>
<tr>
<td>8600</td>
<td>10100</td>
</tr>
<tr>
<td>16600</td>
<td>13300</td>
</tr>
</tbody>
</table>

Linearity of the curves proves an important prerequisite, i.e. that Lambert-Beer’s law is obeyed in the present case. An alternative method of determining the amount of end groups of aminated 2,4-ionenes is acid-base titration. The molar mass calculated in this manner is again the number average molar mass and can therefore be compared with the results of the photometric method (Table 2). The two methods are in good agreement although the relative discrepancy tends to increase toward higher molar mass. The calculated molar masses of the ionenes, though relatively low, lie within the range of data reported in literature\textsuperscript{9,11}.

The kinetics of the polymerization can now be monitored by one of these determination methods. In Fig. 2 the dependence of molar mass (Mn) as a function of time is depicted (Mn determined by acid-base titration). Assuming that the Flory principle is valid in this case, that is the reactivity of the end-group is independent of the chain length, the theory predicts that the degree of polymerization (Mn = degree of polymerization x molar mass of repeating unit) is linear with time\textsuperscript{15}. The observed deviation from linearity cannot be due to the invalidity of the Flory principle since, in the present case, the molar masses are relatively small. Similar tendencies were also found for other ionenes. In the case of 3,3-ionenes, depolymerization was observed at elevated temperatures\textsuperscript{10} and reaction of 1,5-dibromopentane with DMF was observed in the case of 6,3-ionene\textsuperscript{9}.
Catalytic experiments

In Fig. 3, reactivity vs. pH is shown for 2,4-ionenes of different number average molar mass (Mn=1740 and Mn=6600). Both curves show a broad maximum around pH = 8. The curves indicate an overall lower activity for Mn = 6600.

The pH optimum suggests a dependence of the reactivity on the local thiolate anion concentration (pKa (ME) = 9.6\textsuperscript{18}). The moderate decrease in reactivity above pH = 8 is thought to be caused by an increase of ionic strength of the reaction mixture, including competitive ion effects (RS\textsuperscript{−} and OH\textsuperscript{−}). This effect is less pronounced than in the case of PVAm\textsuperscript{2}. The latter can be explained by the fact that PVAm, in contrast to the ionenes, suffers from coil deprotonation as pH increases\textsuperscript{5}. The reactivity of the monomeric analogues of 2,4-ionene and the conventional system (without polymer) are listed in Table 2.
Table 3 Reactivity of some monomeric analogues of 2,4-dione and of the conventional system

<table>
<thead>
<tr>
<th>System</th>
<th>$10^5$ Reaction Rate $^a$ (Mol. ML/dm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrathylammoniumhydroxide $^b$</td>
<td>1.7</td>
</tr>
<tr>
<td>N,N'-diethyl-N,N',N'-trimethylamide</td>
<td>1.9</td>
</tr>
<tr>
<td>Ethylene diamine dibromide</td>
<td>0.6</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: temperature = 25°C, [CoTSPc] = 2x10^{-7} mol/dm$^3$, [DEA] = 0.1 mol/dm$^3$, [$S^-$] = 10^{-5} mol/dm$^3$ (except for the conventional system), pH = 8.

3. Comparing reaction rates in Table 3 and Fig. 3, it can be seen that a cationic charge density together with a minimum polymer chain length are required to increase catalytic activity. Similar molar mass dependence was observed in the case of PVAm$^b$. Only few quaternary ammonium groups are involved in binding the cobalt complex to the polymer backbone. The residual quaternary ammonium groups of the backbone are available to create a cationic polymer domain, thus increasing the local thiolate anion concentration. For PVAm, the dependence of the reaction rate on thiol concentration can be described by Michaelis-Menten kinetics:

$$k_1 [E] \frac{k_2}{k_{-1}}$$

in which $E$ stands for catalyst (CoTSPc), $S$ for substrate (mercaptoethanol) and $P$ for products (disulphide). It can be derived that

$$R = \frac{k_2 [E] [S]}{K_M + [S]}$$

which can be rewritten as
Fig. 4 Catalytic activity as a function of the substrate concentration at 25°C:

\[ \text{ECOTSPcH} \times 2 \times 10^{-7} \text{ mol dm}^{-3}, \ \text{pH} = 8.2, \ \text{[N]} = 10^{-3} \text{ mol dm}^{-3}, \]

\[ \text{C1: Mn} = 1740, \ \Delta: \text{Mn} = 6600 \]

Fig. 5 Lineweaver-Burk plot. Reaction conditions as for Fig. 3.

\[ R^{-1} = (k_3 [E_0])^{-1} + K_M (k_2 [E_0])^{-1} [S]^{-1} \]

where R stands for the reaction rate (expressed in mol ME/dm³ s), \( K_M \) for the Michaelis constant \((k_{-1}+k_2)/k_3 \) and \([E_0]\) for the initial catalyst concentration. \( k_4 \) is the substrate-binding constant \((k_2/k_{-1}) \). \( k_3 \) is also called the turnover number (dimension s⁻¹). In Fig. 4 the reactivity is plotted vs. the thiol concentration. It appears that a plateau is reached at a relatively low thiol concentration, whereas deviations from saturation behaviour are observed for high thiol concentrations (> 0.15 mol dm⁻³). Any possible deviation from Michaelis-Menten kinetics should manifest itself in the nonlinearity of the so-called Lineweaver-Burk plot, i.e. a double reciprocal plot of reactivity vs. thiol concentration as shown in Fig. 5. In spite of some nonlinearity, it seems justified to draw some major conclusions.
Table 4: Comparison between the turnover numbers \( k_2 \) and the Michaelis constants \( K_M \) of 2,4-ionene and PVAm containing systems

<table>
<thead>
<tr>
<th>2,4-ionene</th>
<th>( k_2 ) (s(^{-1}))</th>
<th>( 10^3 K_M ) (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn = 1740</td>
<td>3770 +/- 200</td>
<td>11.3 +/- 2.3</td>
</tr>
<tr>
<td>Mn = 6600</td>
<td>3300 +/- 200</td>
<td>6.8 +/- 1.4</td>
</tr>
<tr>
<td>PVAm</td>
<td>2800 +/- 200</td>
<td>92.0 +/- 20</td>
</tr>
</tbody>
</table>

* Reaction conditions are as in Table 3.

from these curves. The turnover number and Michaelis constant can be estimated from the slope and both are listed in Table 4. Assuming that \( k_3 < k_1 \) i.e. \( K_M \approx K_p^{-1} \), the smaller Michaelis constants for the ionenes indicate a stronger substrate binding compared with PVAm. The reactivity vs. the cobalt complex concentration is shown in Fig. 6. The observed linearity indicates the absence of mass transport limitations (identical reaction conditions were used). The slopes of the curves, i.e. the turnover numbers, are 3600 s\(^{-1}\) and 3200 s\(^{-1}\) for Mn = 1740 and Mn = 6600, respectively, and confirm the \( k_2 \) data from the Lineweaver-Burk plots. The effect of ionene concentration on the catalytic activity is shown in Fig. 7. The ionene concentration is expressed as [N\(^+\)], calculated from the nitrogen content of 2,4-ionene determined by elemental analysis (i.e. 8.37%). Apparently, a minimum ionene concentration is required to enhance the reaction rate. As expected, further increase of the ionene concentration will diminish the thiolate ion concentration locally, i.e. around the active centre. In scheme 1, the overall reaction equation is presented, which according to earlier work in our laboratory\(^6\) results from:

\[
\begin{align*}
2 \text{RSH} + \text{O}_2 & \rightarrow \text{RSSR} + \text{H}_2\text{O}_2 \quad \text{(a)} \\
2 \text{RSH} + \text{H}_2\text{O}_2 & \rightarrow \text{RSSR} + 2\text{H}_2\text{O} \quad \text{(b)} \\
4 \text{RSH} + \text{O}_2 & \rightarrow 2 \text{RSSR} + 2\text{H}_2\text{O}
\end{align*}
\]

The stoichiometry of the reaction can be checked by measuring the peroxide
Fig. 6 Catalytic activity vs CoTSPC concentration at 25°C

\( \text{pH} = 8.2, \ [\text{H}] = 0.14 \text{ mol/dm}^3, \ [\text{CoTSPC}] = 10^{-3} \text{ mol/dm}^3 \)

\( \square: M_\text{n} = 1740, \triangle: M_\text{n} = 6600 \)

Fig. 7 Catalytic activity vs thiol concentration (expressed in \text{mol/dm}^3) at 25°C. (CoTSPC) = 2 \times 10^{-7} \text{ mol/dm}^3, [\text{H}] = 0.14 \text{ mol/dm}^3.

\( \text{pH} = 8.2, \square: M_\text{n} = 1740, \triangle: M_\text{n} = 6600 \)

content after the reaction by iodometry. The results are listed in Table 5. The high residual peroxide content (relative to the initial thiol content) at low thiol concentration is very striking. Apparently, under these conditions, peroxide and thiol concentrations in the bulk are too low for the second oxidation (b) to occur. This unfortunately affects the stoichiometry of the reaction. The observed (apparent) reaction rate, as calculated from the measured oxygen uptake and the assumed stoichiometry of the overall reaction, will be higher than the "true" reaction rate based on thiol conversion, in particular at low thiol concentrations. This will influence the Lineweaver-Burk plot in such a way that the "true" constants, \( k_2 \) and \( K_M \), will be smaller and greater, respectively, than the calculated (apparent) ones. These deviations are negligible at the thiol concentrations used throughout the present kinetic investigation, i.e., 0.14 \text{ mol/dm}^3.
Table 5 Residual hydrogen peroxide content of the reaction mixture

<table>
<thead>
<tr>
<th></th>
<th>Mn = 1740</th>
<th>10^6 mgH_2O_2/mol</th>
<th>10^-6 mgH_2O_2/mol</th>
<th></th>
<th>Mn = 6600</th>
<th>10^-6 mgH_2O_2/mol</th>
<th>10^-6 mgH_2O_2/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>5.15</td>
<td>79.5</td>
<td>5.12</td>
<td>73.2</td>
<td>4.31</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>2.56</td>
<td>2.4</td>
<td>2.60</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Reaction conditions are as described in Table 3
* Percentage of thiol reacting with oxygen only, i.e. thiol consumption during the first step (a)

Conclusions

The photometric and titration techniques developed correspond well and are satisfactory methods of determining the molar mass of 2,4-ionene. The latter polyelectrolyte shows a behaviour similar to PVAm in the catalytic oxidation of thiols in the presence of CoTSPc. Advantages of the ionene-containing system over the PVAm-containing system are: (1) higher turnover numbers (3300-3700 s^{-1}), (2) smaller Michaelis constants ((6.8-11.3)x10^{-3} mol/dm³) indicative of a stronger substrate binding, and (3) a pH independent cationic charge on the polymer backbone, providing high activity over a wider pH range. Monomeric analogues of 2,4-ionene showed no increase in catalytic activity compared with the conventional (polymer-free) system. However, relatively low molar mass ionene (Mn = 1740) appeared to enhance the reaction rate dramatically. Evidently, a cationic charge density on the polymer backbone, together with a minimum polymer chain length are necessary to induce the observed rate accelerations. The residual peroxide content at low thiol concentration, as determined by iodometry, is relatively high, which indicates that the assumed overall stoichiometry of the reaction is disturbed at low thiol concentration.

Acknowledgement
This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

References

Immobilization of 2,4-iodene on a macroporous poly(divinylbenzene-styrene) resin. 1 synthesis and characterization

K.H. van Streun and A.L. German

Summary

2,4-iodene, a poly(quaternary ammonium)salt, has been immobilized on a chloromethylated poly(styrene-divinylbenzene) resin. The iodene content on the resin, determined by CHN elemental analysis, was 50.2 g/kg resin. The most important side effect of the modified resin, catalyst bleeding, can be detected by a spectrophotometric method capable of determining extremely low concentrations of free iodene in the supernatant of the immobilized iodene resin.

Introduction

In our laboratory we have studied the effects of positively charged polymers on the so-called Merox process, that is the oxidative coupling of thiols to disulphides in the presence of cobalt(II)phthalocyanine-tetrasodiumsulphonate(COTSPc) (Scheme 1). Especially polyvinylamine (PVA) and 2,4-iodene a poly(quaternary ammonium)salt (2 and 3 respectively, scheme 2), showed a considerable enhancement compared with the polymer free system.

It is believed that the cationic charge on the polymer backbone has a twofold function: (a) binding the cobalt complex by coulombic interaction, (b) increasing the thiolate anion concentration in the polymer domain, thus bringing the cobalt centre and the substrate together. For both polymers,
Michaelis-Menten kinetics is observed in thiol and oxygen. 2,4-ionene is preferred over PVAm for a number of reasons: (a) its simple synthesis, (b) its cationic charge independent of pH, and (c) the higher overall reaction rate.

In this paper we describe the immobilization of 2,4-ionene on a poly(styrene-divinylbenzene) resin. The advantages of immobilization are several, for instance simple reaction work-up, no loss of the (often) precious catalyst, and intrinsic possibilities for continuous reaction systems.

The strategy for the immobilization of 2,4-ionene on a poly(styrene-divinylbenzene) resin, implies the functionalization of the starting resin by chloromethylation, followed by a reaction of this activated resin with aminated 2,4-ionene (scheme 3). An organic support was preferred to a modified silica resin, as the former is insensitive to pH = 8-12 in contrast to silica, which solubilizes in this pH region.
Experimental

Immobilization

The XAD-2 resin (Rohm&Haas Co., average particle diameter 50-100 μm, specific surface area 300 m²/g and average pore diameter 10 nm) was thoroughly cleaned before use. It was washed twice with water, methanol, 1,4-dioxane and once with methanol and then dried at 50°C (0.1 kPa). The resin was chloromethylated as described by Bootma et al. The number of chloromethyl groups was determined by CHN elemental analysis from the diminishing percentage of carbon compared with the starting resin. CHN elemental analysis was carried out using a Perkin-Elmer 240 CHN elemental analyzer. 2,4-ionene and aminated 2,4-ionene were synthesized and characterized as described previously. In a typical experiment the immobilization proceeds as follows: 2 g chloromethylated resin (Δ, scheme 3) and 1.63 g aminated 2,4-ionene (Δ, scheme 3; Mn = 1630, as determined by titration) in 2 g methanol and 3.3 g water were reacted at 60°C for two weeks. After filtration and washing with water, the resin was extracted with water in a soxhlet-apparatus for at least 48 hrs. Water was added to the resin and the supernatant was tested for the presence of free ionene by the spectrophotometric method based on considerations described in the results. The spectrophotometric measurements

![Scheme 3 Synthetic route to immobilization of 2,4-ionene on a chloromethylated XAD-2 resin](image-url)
were performed on a Hewlett Packard 8451A diode array spectrophotometer in a 1 cm cell at 25°C.

The amount of ionene per gram resin was determined by CHN elemental analysis. Knowing the percentage of nitrogen of the starting ionene (8.37%), the ionene content on the resin is (%N/8.37)×1000 g ionene/kgresin. The resin was stored in water, filtered off and washed with water before use.

Results

For immobilization of 2,4-ionene, a commercially available poly(styrene-divinylbenzene) resin (XAD-2) was used. This XAD-2 resin, a macroporous type of resin, is preferred to a gel type resin (e.g. Merrifield resin) because of its well-defined pore volume, specific area, and being nonswellable (for specifications see experimental). After chloromethylation the chloromethyl content, determined by CHN elemental analysis, was 1.26 mol CH₂Cl/kgresin (Table 1).

The immobilization of 2,4-ionene is accomplished by reacting the chloromethylated resin (4, scheme 3) with the aminated 2,4-ionene (5, scheme 3). The 2,4-ionene content of the resulting product (6, scheme 3), after the product was thoroughly extracted with water, was also determined by CHN

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Elemental analysis of the resin used</th>
<th>C(%)</th>
<th>H(%)</th>
<th>N(%)</th>
<th>mol CH₂Cl/kgresin</th>
<th>ionene/kgresin</th>
</tr>
</thead>
<tbody>
<tr>
<td>XAD-2</td>
<td>91.42</td>
<td>8.35</td>
<td>0.23</td>
<td>-</td>
<td>-</td>
<td>52.0</td>
</tr>
<tr>
<td>XAD-2/5</td>
<td>87.68</td>
<td>7.86</td>
<td>0.26</td>
<td>-</td>
<td>1.26</td>
<td>52.0</td>
</tr>
<tr>
<td>chloromethylated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XAD-2/5</td>
<td>86.72</td>
<td>8.34</td>
<td>0.42</td>
<td>-</td>
<td>50.2</td>
<td>52.0</td>
</tr>
</tbody>
</table>

*a 31 mol ionene/kgresin, based on Mn = 1630, chemical yield = 2.5% based on the chloromethyl groups*
elemental analysis, was 50.2 g ionene/kg resin (Table 1).

Earlier results from our laboratory showed a dependence of the catalytic activity on the ionene concentration (expressed as [N\(^+\)], calculated from the nitrogen content of ionene, 8.37\%)\(^9,9\). Since even very low ionene concentrations ([N\(^+\)] = 10\(^{-2}\) mol/mL\(^2\)) enhance the reaction, we developed a sensitive spectrophotometric method to determine these minor amounts of free ionene in the reaction mixture, based on the clear difference between the VIS-spectra of CoTSPc and the CoTSPc/ionene complex. Van Velzen et al.\(^{10}\) showed that a dimer peak around \(\lambda = 630 \text{ nm}\) was observed for CoTSPc in the presence of low molar mass ionene in a molar ratio (N:Co) of 2:1. If this ratio was less then the monomer peak around \(\lambda = 660 \text{ nm}\) showed up. As the minimum detectable CoTSPc concentration is \(10^{-4} \text{ mol/mL}^2\), the detection limit for ionene is four

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![UV-VIS spectra of CoTSPc in water, 25°C](image)

- (A). CoTSPc in pure water
- (B). Supernatant of immobilized ionene resin before extraction with water (resin present)
- (C). Supernatant of immobilized ionene resin after extraction with water (resin present)
times higher, i.e. 4x10^{-4} \text{ mol/mL}^3.

In Fig. 1, some typical spectra of the supernatant of the resin are shown after addition of CoTSPc. Curve A is the spectrum of CoTSPc in water in the absence of free or resin-immobilized ionene, i.e. pure water. Curve B shows the spectrum of the supernatant of the insufficiently washed, immobilized ionene resin (in the presence of the resin), after addition of CoTSPc. The peak around $\lambda = 630$ nm is indicative of the presence of free 2,4-ionene in the supernatant. No difference in spectra is observed if the resin is removed before adding CoTSPc, indicating that no absorption of CoTSPc on the resin takes place. Curve C shows the spectrum of the supernatant after extracting the resin for 48 hrs with water in a soxhlet apparatus. Evidently all CoTSPc has been bound by ionene on the resin, which indicates that no free ionene is present in the supernatant. If the resin is filtered off before adding CoTSPc, a spectrum identical to curve A is observed.

In order to estimate the amount of quaternary ammonium groups on the resin available for CoTSPc binding, the concentration of CoTSPc in the supernatant was determined spectrophotometrically on increasing the total amount of CoTSPc in the system. The results are shown in Fig. 2. Curve A shows the dependence of the absorbance at $\lambda = 660$ nm as a function of the total amount of added CoTSPc in the presence of the chloromethylated resin. This curve coincides with the curve for CoTSPc alone, indicating there is no adsorption of CoTSPc on the chloromethylated XAD-2 resin. Curve B shows the dependence of the absorbance of CoTSPc on increasing the total amount of CoTSPc in the presence of the resin-containing immobilized ionene. Up to a total concentration of 22x10^{-3} \text{ mol CoTSPc/mL}^3 ([resin] = 4.2 \text{ kg/mL}^3) hardly any absorbance is monitored, indicating that, up to this value, practically all CoTSPc added is being adsorbed on the resin. From these data one can estimate the total amount of CoTSPc on the resin used in the kinetic experiments as 5.2x10^{-3} \text{ mol CoTSPc/kg resin}.

The maximum theoretical amount of adsorption of CoTSPc on the ionene-
modified resin can be calculated from the amine content of the immobilized ionene resin and an assumed N-Co ratio of 4:1 (CoTSPc is fourfold negative) and amounts to $7.5 \times 10^{-3}$ mol/kg$_{resin}$, this means that only 7% of the quaternary ammonium groups is available for CoTSPc complexation. We believe that interaction of CoTSPc with the immobilized ionene at the outer surface of the particles and at the entrance of pores, blocks off the "interior" of the resin, a phenomenon also observed in the case of cross-linked PVAm$^{11}$. 

On the other hand, the proposed CoTSPc distribution on the particles may facilitate substrate accessibility in the kinetic experiments. The effect of the present immobilization on the CoTSPc catalyzed oxidative coupling of thiols will be presented in the next chapter.
Conclusions

The strongly cationic polymer 2,4-ionene can be chemically bonded onto chloromethylated macroporous poly(styrene-divinylbenzene) resins. The ionene content on the resin, determined by CHN analysis, was 50.2 g/kg resin.

Due to limited accessibility of the polymeric quaternary ammonium groups on the macroporous particles, only 7% of these groups are available for complexation with CoTSPc, indicating that CoTSPc is being adsorbed at the outside of the particle.

A spectrophotometric method that has been developed proves the absence of (any possible) traces of ionene in the supernatant, which would highly disturb the kinetic measurements.

Acknowledgement

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Immobilization of 2,4-ionene on a macroporous poly(styrene-divinylbenzene) resin: 2. Effect on the rates of the cobaltphthalocyanine-catalyzed oxidative coupling of mercaptoethanol.

K.H. van Streun, J. Meuldijk and A.L. German

Summary

A poly(quaternary ammonium)salt, 2,4-ionene, has been immobilized on a macroporous chloromethylated poly(styrene-divinylbenzene) resin (XAD-2). The activity of these immobilized 2,4-ionene/cobalt-phthalocyanine-tetrasodiumsulphonate (CoTSPc) complexes towards the oxidative coupling of thiols is much lower than in the homogeneous case, but is still considerably higher than for the polymer-free system. The observed decrease in reaction rate is not caused by mass transfer limitations alone, but is also affected by catalyst properties, such as a very low local N+/Co ratio. The active sites appear to be present only in the outer shell of the resin particles.

Introduction

The effects of positively charged polymers on the oxidative coupling of thiols to disulphides in the presence of cobalt(II)phthalocyanine-tetrasodiumsulphonate (CoTSPc) have been studied intensively in our laboratory.\textsuperscript{1,3}

$$4 \text{RSH} + \text{O}_2 = 2 \text{RSSR} + 2 \text{H}_2\text{O}$$

Special attention was paid to cationic polymers, such as polyvinylamine (PVAm)
and 2,4-ionene, a poly(quaternary ammonium)salt, because both polymers caused a considerable enhancement of the reactivity compared with the polymer-free system. Recent attempts to immobilize PVAm \(^5,6\) often resulted in the collapse of the activity.

Immobilization of soluble precious catalysts is very interesting because it offers the possibility of an easy work-up of the reaction mixtures. Moreover, immobilized systems allow continuous operation\(^5,6\). One of the disadvantages of immobilization may be a decrease in the activity of the immobilized catalyst system compared with the homogeneous system. This can be caused by collapse of the intrinsic reaction rate due to loss of conformational freedom of the catalytic centre, to a microenvironmental effect, to mass transport limitations, or to a combination of these causes.

In this paper we describe the effects of immobilization of 2,4-ionene onto a macroporous chloromethylated XAD-2 resin on the oxidation of 2-mercaptoethanol (ME) in the presence of CoTSpc. Immobilization of the catalyst is achieved by first anchoring the polymer onto reactive support particles and subsequently binding CoTSpc to the immobilized ionenes. The features of the catalyst concerned in the observed reduced activity of the immobilized system will be described.

Experimental

Immobilization

The macroporous XAD-2 resin (Rohm&Haas Co., particle diameter 50-100 \(\mu\)m, specific surface area 300 \(\text{m}^2/\text{g}\) and average pore diameter 10 \(\text{nm}\)) was chloromethylated and characterized as described in our previous paper\(^7\). 2,4-ionene and aminated 2,4-ionene (\(M_n = 1630\)) were synthesized and characterized as described previously\(^8\). The immobilized 2,4-ionene resin was synthesized and thoroughly cleaned by the method described in\(^7\). Characterization of the immobilized ionene resin by CHN elemental analysis showed a nitrogen content
of 0.42 % (i.e. 0.3 mol N⁺/kg resin)

Kinetic runs

CoTSPEC was synthesized by the method described by Weber and Bush. 2-
Mercaptoethanol was used as substrate and distilled before use. Before the
reaction was started, a CoTSPEC solution was added to the reaction vessel
containing the resin. The total reaction volume was 10⁻⁴ m³. The reaction rates
were measured in an all-glass double-walled reactor (diameter = 6.5 x 10⁻² m)
equipped with four symmetrically located baffles (widths = 10⁻² m). A four-
bladed turbine impeller with a diameter of 2.5 x 10⁻² m was used. The stirring
speed was about 2300 rpm (41.7 rps). The reaction was carried out at 0.1 MPa
partial pressure of oxygen and a temperature of 25.0 +/- 0.1 °C. The
monitoring system was identical to that described earlier.

Results and discussion

Influence of pH

Fig. 1 shows the effect of pH on the rate of the oxidative coupling of 2-
mercaptoethanol (ME) catalyzed by CoTSPEC/ionene immobilized on XAD-2 resin
(2,4-ionene/XAD catalyst). The optimum pH for this catalyst is found to be
7.3, being significantly lower and less pronounced than in the case of the
homogeneous system. For the latter system the pH optimum around 8 was found.
The relatively weak pH dependence of the reaction rates in slurries of the
immobilized system probably originates from the adsorption of the substrate at
the resin surface. In the case of an almost complete saturation of ammonium
groups on the resin particle with the thiolate anions, a pH variation will
hardly affect the concentration of reactive thiolate anions at the surface.
This saturation effect is also clearly demonstrated in Fig. 2. In this figure
the oxygen consumption rates are plotted as a function of the mercaptoethanol
concentration. The relatively slight increase in the rate of the oxygen
Fig. 1 Oxygen consumption rate as function of pH

$[\text{CoTSPE}] = 2 \times 10^{-4} \text{ mol/kg resin}$, $[\text{ME}] = 143 \text{ mol/m}^3$,

[Resin] = 1.0 kg/m$^3$, $V_L = 10^{-4} \text{ m}^3$

Fig. 2 Oxygen consumption rate as function of the mercaptoethanol concentration

$[\text{CoTSPE}] = 4 \times 10^{-4} \text{ mol/kg resin}$, $[\text{resin}] = 0.5 \text{ kg/mL}$,

$pH = 8.3, V_L = 10^{-4} \text{ m}^3$

correlation on increasing the substrate concentration indicates a tendency towards saturation with the thiolate anion for mercaptoethanol concentrations above 50 mol/mL. This saturation effect results in a relatively slight influence of the pH on the substrate concentration above 50 mol/mL. The rather low activity of the immobilized system compared with the homogeneous system will be explained in due course.

Influence of catalyst loading

The reaction rates, $-r_{O_2}$, expressed in mol O$_2$/($k_S$ * $c_{resin}$) as a function of the mean CoTSPE concentration in the resin are collected in Fig. 3. This figure shows that, for CoTSPE concentrations below $2 \times 10^{-4}$ mol/kg resin, there is an almost linear relationship between the reaction rate and the CoTSPE
concentration. For CoTSPc concentrations above $4 \times 10^{-4}$ mol/kg resin, the reaction rate is almost independent of [CoTSPc] resin. According to the Michaelis-Menten mechanism which holds for the homogeneous CoTSPc/ionene-catalyzed oxidative coupling of thiols, a linear relationship is to be expected between reaction rate and CoTSPc concentration. The observed deviation from linearity for CoTSPc concentrations above $2 \times 10^{-4}$ mol/kg resin may be attributed to a limited number of residual sites on the 2,4-ionene/XAD resin after the binding of a relatively small number of CoTSPc molecules. In that case, excess CoTSPc would only have a relatively small contribution to the observed catalytic activity. The influence of catalyst loading on the reaction rate can also be caused by mass transfer limitations. A detailed discussion of the importance of various possible mass transfer resistances will therefore be presented.

![Graph](image)

*Fig. 3. Reaction rate ($\log \text{mol} \cdot \text{kg resin}^{-1} \cdot \text{s}^{-1}$) as a function of the CoTSPc concentration in the resin

$[\text{Co}] = 143 \text{ mol/kg}$, $pH = 8.3$*
Mass transfer

Only mass transfer of molecular oxygen has to be considered because the initial concentration of ME ([ME] = 143 mol/mL\(^2\)) is much higher than the equilibrium concentration of oxygen in the bulk liquid ([O\(_2\)]\(_b\) = 1.4 mol/mL\(^2\) at 0.1 MPa partial pressure of oxygen). As a result of the macroporous character of the 2,4-iodine/XAD resin, it is quite obvious that mercaptoethanol is present in large excess over oxygen in the resin phase also. The resistance to oxygen transport from the gas phase to the liquid phase is negligible under the experimental conditions. This can be derived from the homogeneous ionene system where no mass transport limitation was observed at even much higher oxygen consumption rates than those occurring in the present study.\(^6,10\)

Hence, possible remaining barriers are oxygen transport from the bulk liquid to the outer surface of the resin (film diffusion limitation) and the oxygen conversion in the resin particle (pore diffusion limitation). These two effects constitute resistances in series, leading to a relation between \(\text{-}r_{\text{O}_2}\) and the difference between the oxygen concentrations in the bulk liquid ([O\(_2\)]\(_b\)) and the outer surface of the resin ([O\(_2\)]\(_s\)), given by

\[
\text{-}r_{\text{O}_2} = k_{\text{LS}} \ a_{\text{LS}} \ ([\text{O}_2]_b - [\text{O}_2]_s) \quad (1)
\]

where \(k_{\text{LS}}\) (expressed in m\(^3\)/s) stands for the oxygen mass transfer coefficient between the liquid and the outer catalyst surface, and \(a_{\text{LS}}\) for the outer catalyst surface per unit of mass of the water-swollen resin. A value for \(a_{\text{LS}}\) can be obtained from

\[
a_{\text{LS}} = \frac{6}{(d_p \ \rho_{\text{resin}})} \quad (2)
\]

where \(d_p\) is the mean diameter of the resin particles and \(\rho_{\text{resin}}\) is the density of the water-swollen resin. For \(d_p = 80 \times 10^{-6}\) m and \(\rho_{\text{resin}} = 10^2\) kg/m\(^3\), \(a_{\text{LS}}\) becomes 75 m\(^2\)/kg\(_{\text{resin}}\). \(k_{\text{LS}}\) can be estimated with an accuracy of about 30 %
from the experimental relation derived by Sano et al for mass transport to
spherical ion-exchange resin particles in a stirred tank reactor\textsuperscript{11}:

$$k_{LS} d_P/D_{O2} = 2 + 0.4 (\varepsilon d_P^2/\nu)^{1/4} \left( \nu/D_{O2} \right)^{1/8} \quad (3)$$

where $D_{O2}$ stands for the molecular diffusion coefficient of oxygen in the free
liquid ($D_{O2} = 2 \times 10^{-9}$ m$^2$/s \textsuperscript{12}$), $\nu$ for the kinematic viscosity of the liquid
($\nu_{H2O/25^{\circ}C} = 0.9 \times 10^{-6}$ m$^2$/s) and $\varepsilon$ (expressed in m$^2$/s$^2$) for the energy input
rate per unit of mass due to stirring. For agitated vessels, $\varepsilon$ can be obtained
from\textsuperscript{11}

$$\varepsilon = N_p d_L^5 N^3/V_L \quad (4)$$

For our experimental setup, a power number $N_p = 5$ is reasonable\textsuperscript{11,12} and $\varepsilon = 35.2$ W/kg (the values of the impeller diameter ($d_L$), the stirring speed ($N$)
and the reaction volume ($V_L$) are given in the experimental section).

Substitution of the values of $\varepsilon$, $d_P$, $\nu$ and $D_{O2}$ into equation (3) leads to $k_{LS}$
$= (5.6 \pm 1.7) \times 10^{-4}$ m$^2$/s$^2$.

From the observed values of $-r_{O2}^W$ and equation (1) the oxygen
concentrations at the outer surface of the resin ($[O2]_S$) can now be
calculated. $[O2]_S$ decreases from 0.95 +/- 0.14 mol/m$^3$ for [CoTSPc] = 10$^{-4}$
mol/kg$_{resin}$ to 0.53 +/- 0.27 mol/m$^3$ for [CoTSPc] = 2.0 \times 10^{-4}$ mol/kg$_{resin}$.

Although the values of $[O2]_S$ decreases on increasing catalyst loading, there
is a linear relationship between $-r_{O2}^W$ and $[CoTSPc]_{resin}$ for $[CoTSPc]_{resin} \leq 2 \times 10^{-4}$ mol/kg$_{resin}$. This linear relationship between $-r_{O2}^W$ and $[CoTSPc]_{resin}$ is
only possible for a reaction order in oxygen close to zero and the absence
of intraparticle diffusion limitation of the reaction rate. A reaction order
in oxygen close to zero for the $[O2]_S$ values found for $[CoTSPc]_{resin} \leq 2 \times 10^{-4}$
mol/kg$_{resin}$ agrees with the dependence of the rates on the oxygen
concentration as observed for the homogeneous CoTSPc/ironene systems\textsuperscript{10}. It will
later be shown that, on the basis of a homogeneous distribution of CoTSPc over the resin particles, a linear relationship between \(-r_{O_{2}}\) and \([\text{CoTSPc}]_{\text{resin}}\) for \([\text{CoTSPc}]_{\text{resin}} < 2 \times 10^{-4} \text{ mol}/\text{kg}_{\text{resin}}\) cannot be expected. Therefore, most probably CoTSPc will only be present in the outer shell of the 2,4-icocene/XAD catalyst. Assuming a homogeneous distribution of the active sites through the particle, the catalyst effectiveness factor can be obtained from observed reaction rates using the Weisz modulus. The modulus can be estimated from the observed rates\(^{15}\). The Weisz modulus (Φ) for an nth-order irreversible reaction in a spherical catalyst is defined as

\[
Φ = \frac{(n+1) (-r_{O_{2}}^W) \rho_{\text{resin}} (d_{p}/6)^2}{2 \, D_{O_{2}(e)} [O_{2}]_{\text{in}} \, \lambda}
\]  

where \(n\) stands for the reaction order in oxygen, \(D_{O_{2}(e)}\) for the effective diffusion coefficient in the resin particle and \(\lambda\) for the partition coefficient of oxygen between the resin phase and the surrounding liquid. For oxygen \(\lambda\) is taken as unity. \(D_{O_{2}(e)}\) can be estimated from the molecular diffusion coefficient of oxygen \(D_{O_{2}}\) according to\(^{14}\)

\[
\frac{D_{O_{2}(e)}}{D_{O_{2}}} = \frac{F}{\alpha \, \lambda}
\]  

where \(F\) is the "drag" factor representing the reduction of the mobility of a spherical molecule in a cylindrical pore and \(\alpha\) is a parameter depending on the porosity and tortuosity of the resin. For diffusion of oxygen in the XAD-2 resin \(F = 1\), because the mean pore diameter (10 nm) is much greater than the diameter of the oxygen molecule (0.46 nm as calculated from the Van der Waals equation\(^{15}\)). For poly(styrene-divinylbenzene) resins \(\alpha = 4\) seems to be a reasonable value\(^{14}\). Substitution of the values into equation (6) gives

\(D_{O_{2}(e)} = 5 \times 10^{-10} \text{ m}^2/\text{s}\). For \(-r_{O_{2}}^W = 1.73 \times 10^{-4} \text{ mol } O_{2}/(\text{kg}_{\text{resin}} \cdot \text{s})\) (as
determined for \([\text{CoTSPc}]_{\text{resin}} = 10^{-4} \text{ mol/kg}_{\text{resin}}\) and \(n = 0, \Phi = 3.2\). For these values of \(\Phi\) the effectiveness factor \(\eta\) can be calculated on the basis of \(^{18}\)

\[
\eta = 1/\Phi \quad (7)
\]

resulting in \(\eta = 0.31\). For zeroth-order reaction in catalyst particles with a homogeneous distribution of active sites and \(\Phi > 1\), an increase in the number of active sites by a factor of \(m\) results in the following expression for the ratio before \((-r_{\text{O}_2}^{W}(1))\) and after \((-r_{\text{O}_2}^{W}(2))\) the change of catalyst activity\(^{18}\), that is

\[
\frac{-r_{\text{O}_2}^{W}(1)}{-r_{\text{O}_2}^{W}(2)} = \frac{1}{\sqrt{m}} \sqrt{\frac{[\text{O}_2]_{\text{L},1}}{[\text{O}_2]_{\text{L},2}}} \quad (8)
\]

In equation (8) \([\text{O}_2]_{\text{L},1}\) and \([\text{O}_2]_{\text{L},2}\) stand for the oxygen concentration at the outer surface of the particles before and after changing the number of active sites. Relation (8) shows that, for a homogeneous distribution of active sites, a rate increase from \(1.73 \times 10^{-4} \text{ mol O}_2/(\text{kg}_{\text{resin}} \cdot \text{s})\) \(([\text{CoTSPc}]_{\text{resin}} = 10^{-4} \text{ mol/kg}_{\text{resin}}, [\text{O}_2]_{\text{L}} = 0.95 \text{ mol/m}^3\) to \(3.29 \times 10^{-5} \text{ mol O}_2/(\text{kg}_{\text{resin}} \cdot \text{s})\)

\(([\text{CoTSPc}]_{\text{resin}} = 2 \times 10^{-4} \text{ mol/kg}_{\text{resin}}, [\text{O}_2]_{\text{L}} = 0.53 \text{ mol/m}^3\) should only be reached for an increase of \([\text{CoTSPc}]_{\text{resin}}\) from \(10^{-4} \text{ mol/kg}_{\text{resin}}\) to 6.5 mol/kg\(_{\text{resin}}\). Experimentally, the rate of \(3.29 \times 10^{-5} \text{ mol O}_2/\text{kg}_{\text{resin}}\) has already been found for \([\text{CoTSPc}]_{\text{resin}} = 2 \times 10^{-4} \text{ mol/kg}_{\text{resin}}\). The measured behaviour of the rates as a function of the catalyst loading for \([\text{CoTSPc}]_{\text{resin}} \leq 2 \times 10^{-4} \text{ mol/kg}_{\text{resin}}\) strongly suggests that the diffusion rates of oxygen in the pores of the resin do not have a significant influence on the observed rates. The experimentally found linear relationship between the reaction rate and \([\text{CoTSPc}]_{\text{resin}}\) for \([\text{CoTSPc}]_{\text{resin}} \leq 2 \times 10^{-4} \text{ mol/kg}_{\text{resin}}\) could only be obtained for a reaction order in oxygen close to zero and an effectiveness factor \(\eta = 1\).

On the basis of these arguments, the intrinsic activity of the CoTSPc sites on
the XAD/ionene catalyst in terms of the turnover frequency can now be calculated from the rates as a function of the \([\text{CoTSPC}]_{\text{resin}}\) for \([\text{CoTSPC}]_{\text{resin}} \leq 2 \times 10^{-4} \text{ mol/kg}_{\text{resin}}\). For a mercaptoethanol concentration of 143 mol/m\(_3\), a pH value of 8.3 and a temperature of 25°C a turnover frequency of 175 mol O\(_2\)/(mol CoTSPC.s) is found for the XAD/ionene catalyst. Later in this chapter the difference between this turnover frequency and those of other CoTSPC catalyst systems used for the oxidative coupling of 2-mercaptoethanol will be discussed.

CoTSPC loading

An effectiveness factor \((\eta)\) of almost unity, indicating an almost complete use of the active sites, can only be achieved when active CoTSPC is present in the outer shell of the resin particle. This is confirmed by the adsorption experiments of CoTSPC on an ionene-XAD catalyst, as shown in the

\[
\text{Radial position}
\]

Fig. 4 Schematic representation of the immobilized CoTSPC/ionene system on XAD-2 and the concentration profile for oxygen as a function of the particle radial position.
previous chapter. The sudden change of the reaction rate dependence on increasing the catalyst loading above [CoTSPc] > 4x10^{-4} mol/kg resin into a more saturation type of behaviour cannot be explained by mass transport effects alone. In that case a much slower change in the reaction rate dependence on increasing the catalyst loading would have been observed. These considerations allow the conclusion that another feature must, in any case, be at least partially responsible for this rapid change.

Apparently the reaction rate is hardly influenced by increasing the already high catalyst loading above 4x10^{-4} mol/kg resin. This is probably caused by less accessibility of the immobilized 2,4-ionene to CoTSPc molecules due to the already high local CoTSPc concentration. From the considerations described above, the oxygen concentration profile in the liquid and resin phases can be represented as shown in Fig. 4. The film layer around the resin particle, the region between $R_f$ and the particle radius $R$ (= 0.5 $d_p$), has a considerable influence on the concentration of oxygen. As the outer shell of the spheres between $R$ and $R_c$ of the particle contains most of the reactive CoTSPc moieties, oxygen conversion will take place in this shell. The proportions of the layers are not properly scaled. In the interior of the support, where no CoTSPc is present, there will be no change in oxygen concentration.

**Influence of immobilization of ionenes on the activity**

The catalytic activity of some CoTSPc catalysts at the optimum pH and 25°C expressed in the turnover frequencies are given in Table 1. This table shows that attaching 2,4-ionene to the XAD-2 resin results in a considerably lower activity compared with that of homogeneous solution of 2,4-ionene. However, the activity of the immobilized system is still much higher than that of the polymer-free system. The difference in activity between a solution of 2,4-ionene and the 2,4-ionene/XAD-2 catalyst can be explained in terms of the $N^+/Co$ ratio in these catalysts. For solutions of 2,4-ionene, optimum activity
Table 1 Turnover frequencies in the oxidative coupling of mercaptoethanol

<table>
<thead>
<tr>
<th>system</th>
<th>pH</th>
<th>( N^+ )</th>
<th>Turnover frequency (mol O_{2}/(mol CoTSPc.s))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co^II</td>
<td>8.2</td>
<td>1</td>
<td>7.5^g</td>
</tr>
<tr>
<td>PVA^a</td>
<td>8</td>
<td>0.1^b</td>
<td>700</td>
</tr>
<tr>
<td>2,4-ionene</td>
<td>8</td>
<td>0.3^c</td>
<td>825^c</td>
</tr>
<tr>
<td>2,4-ionene/</td>
<td>7.5</td>
<td>0.3^c</td>
<td>175^d</td>
</tr>
<tr>
<td>XAD-2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

^a [CoTSPc] = 2x10^-4 mol/mL
^b in mol/mL, [CoTSPc] = 2x10^-4 mol/mL
^c in mol/kg resin, [CoTSPc] = 2x10^-4 mol/kg resin
^d as determined by the slope of the reaction rate vs. catalyst loading

(Fig. 3), for [CoTSPc] = 2x10^-4 mol/kg resin

is observed for 300 < \( N^+/Co < 800^c \). Lowering this ratio will dramatically reduce the reaction rate. Since the CoTSPc appears to be present in the outer shell of the ionene-modified resin particles only, the local concentration of CoTSPc is much higher than the overall concentration in the resin. Following this train of thought, the rather low activity of the 2,4-ionene/XAD-2 catalyst can probably be explained in terms of low \( N^+/Co \) ratios in the outer shell of the resin particles compared with homogeneous solutions of 2,4-ionene/CoTSPc.

Conclusions

Immobilization of 2,4-ionene/CoTSPc on a macroporous polystyrene-divinylbenzene (XAD-2) results in a considerable reduction of the reaction rate of the oxidative coupling of 2-mercaptopethanol compared with the homogeneous 2,4-ionene/CoTSPc systems. Although there is a significant resistance to oxygen from the bulk liquid to the active sites, this decrease at higher catalyst loadings is not a result of the limited rate of mass transfer alone, but is also affected by the rather low \( N^+/Co \) ratio around the
active centres which are localized in the outer shell of the resin particle. The number of binding sites for CoTSPc in the 2,4-lonene-modified resin is rather limited resulting in only a slight increase of the activity on increasing the CoTSPc concentration on the resin for [CoTSPc] > 4x10^{-4} mol/kg resin. A more reactive catalyst may be prepared by a strong enhancement of the N⁺ groups in the resin phase. These ammonium groups should be available to CoTSPc binding and are thus preferably located at the outer shell of the catalyst particle. This leads to the conclusion that the reaction rates per unit mass of catalyst can be considerably increased by drastically reducing the particle size. In this way the complete volume of the support may become accessible to the CoTSPc moieties.

Acknowledgement

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Immobilization of a block copolymer of styrene and quaternized 4-vinylpyridine on latex and its effect on the cobaltphthalocyanine-catalyzed oxidation of 2-mercaptoethanol.

Karel H. van Streun, Ronald Tennebroek, Pieter Piet and Anton L. German

Summary

To overcome mass transport limitations that are usually encountered on immobilizing highly active catalysts, cationic latex particles were used as support for cobalt(II)phthalocyanine-tetrasodiumsulphonate (CoTSpC). The cationic latex was prepared by emulsion copolymerization of styrene and divinylbenzene in the presence of a block copolymer of styrene and 4-vinyl-N-methylpyridinium iodide (PS-β-qPVP) serving as surfactant. The latex-bound system was found to considerably increase the reaction rate of the oxidation of 2-mercaptoethanol in the presence of CoTSpC compared with the conventional polymer free system. Michaelis-Menten kinetics was observed for all three systems investigated, that is the block copolymer-stabilized latex system, the homogeneous block copolymer system and the quaternized 4-vinylpyridine (qPVP) homogeneous homopolymer system. Although the stability of the latex and qPVP containing systems after successive runs is rather poor, this immobilization method shows the great potential value of anchoring highly active systems while retaining the high catalytic activity. The turnover number is increased on immobilizing the block copolymer compared with the homogeneous block copolymer solution. The Michaelis constant is hardly affected by immobilization. Due to concentration of the polycations at the particle surface on immobilization, comparison between the latex system and the homogeneous system containing either homopolymer or block copolymer remains
difficult.

Introduction

Since the heterogeneous peptide synthesis introduced by Merrifield, many immobilization studies on Merrifield-type resins have been published. This method not only offers a simple separation of product and unused reactants, but also the possibility of continuous operation. For these reasons, immobilization of catalysts has met with considerable academic and industrial interest.

In addition to this gel-type Merrifield resin, a macroporous (macroporous) resin, which has a solvent-independent pore structure was introduced. However, because of reactions with large substrate molecules or very fast reactions, or in immobilization studies, another type of support was needed to exclude mass transfer limitations. This kind of carrier should not only have a large specific surface area, but also contain no pores. For larger particles (usually a product of suspension polymerization with a minimal size of 10 μm) these are contradictory requirements. But latex particles, products of emulsion polymerization, combine these two features. Moreover, monodisperse particles can be made by emulsion polymerization techniques.

Scheme 1 Chemical structure of G0TPC (1) and 2,4-tionene (2)
Several articles have been published on immobilizing enzymes or catalysts on latex particles. In the paint industry, latices have been synthesized functionalized with fungicides to prevent mildew defacement. These chemically modified latices are sometimes called reactive latices.

In the past years we have studied the cocatalytic behaviour of several cationic polymers, like poly-vinylamine (PVAm) and a polyquaternary ammonium salt (the so-called 2,4-ionene, \( \mathcal{L} \), scheme 1) on the catalytic oxidative coupling of 2-mercaptoethanol (ME) to its corresponding disulphide in the presence of molecular oxygen and cobalt(II)phthalocyanine-tetrasodiumsulphonate (CoTSPc, \( \mathcal{L} \), scheme 1).

We earlier reported the immobilization of this very reactive (homogeneous) polymeric catalyst on a macroporous resin. As expected, a lower reaction rate was observed compared with the homogeneous polyelectrolyte system. This effect was not only due to mass transport limitation of the reactants, but also appeared to be caused by an inhomogeneity of the catalytic support; CoTSPc scarcely penetrates the porous resin. A different immobilization strategy was therefore required to retain the high intrinsic catalytic activity of the system.

Recently, Ford et al. reported the immobilization of CoTSPc on a cationic latex and its effect on the oxidation of 1-decanethiol. A rate enhancement in the presence of the latex was observed compared with the conventional polymer-free system.

The final goal of our investigations is the anchoring of the highly

\[
\text{scheme 2: Chemical structure of the surfactant, PS-b-gPV (3)}
\]

48
active CoTSPc-polyelectrolyte system onto insoluble supports while maintaining the high oxidation rate, that is immobilization without the above described disadvantages of conventional immobilization methods. In the present chapter we describe (1) the preparation of a cationic latex, containing anchored cationic polyelectrolytes, that will serve as a support for CoTSPc and (2) the effect of catalyst immobilization on the oxidation of 2-mercaptoethanol. The cationic latex was prepared by the emulsion copolymerization of styrene and divinylbenzene using a block copolymer of styrene and quaternized 4-vinylpyridine (PS-b-qPVP, 3, scheme 2) as surfactant. The resulting latex was tested as a cocatalyst in the thiol oxidation. A few preliminary results on this system have recently been mentioned in a more comprehensive survey. The complete results will be presented and discussed in the present chapter.

Experimental section

The quaternization of the block-copolymer styrene-b-4-vinylpyridine (Polyscience, PS-PVP=1:9) and poly-4-vinylpyridine (Polyscience, Mn=40,000) with methylidide in DMF/DMSO (3:2, by volume) was carried out according to literature. Both the IR spectra and the quantitative yields indicated a high degree (>99%) of quaternization. The number average molar mass of the unquaternized copolymer was determined by vapour pressure osmometry in methanol at 45°C with a Knauer vapour pressure osmometer, and amounted to 4,500 +/- 500. The molar mass of the quaternized product (PS-b-qPVP) was calculated to be 10,000 +/- 1,000. The number average molar mass of the quaternized PVP was calculated to be 90,000 +/- 9,000. The reduced viscosity (ηr) of qPVP and PS-b-qPVP were measured at 25.0 +/- 0.1°C. Styrene (Merck) and divinylbenzene (Merck, technical grade) were distilled prior to use, 4,4'-azo-bis-4-cyanopentanoic acid (ACPA, Fluka) was used as purchased. 0.92 g styrene and 0.33 g divinylbenzene were added to a solution containing 8.97 g distilled deoxygenated water, 60 mg K2CO3, 0.51 g PS-b-qPVP
and 34 mg ACPA. The emulsion was polymerized at 60°C for 24 hrs under nitrogen atmosphere with magnetic stirring. The purification of the latex is described in the text. The sulphonated ion-exchange resin Dowex 50W-X4 was purified and used as described by Vanderhoff et al.23,24. The serum replacement cell (70 cm²) was equipped with a 50 nm filter (Nuclepore). The average flow through the cell was 15 cm³/hr. The particle size was determined by dynamic light scattering and scanning electron microscopy (SEM).

The latex was diluted in the reaction vessel by adding water and a CoTSPE solution (2x10⁻⁵ mol/dm³) until the desired concentrations of cationic groups (expressed in mol N⁺/dm³) and of cobalt catalyst were obtained. The catalytic activity was measured as the initial reaction rate by monitoring the oxygen consumption immediately after the addition of thiol as described earlier.25,26 All reactions were performed at an oxygen pressure of 100 kPa, a temperature of 25°C and a stirring speed of 2600 rpm.

VIS spectra were recorded at a Hewlett-Packard diode array 8451A spectrophotometer using a 1-cm cell.

Results and discussion

Latex preparation

In order to prepare a cationic latex that will serve as support for CoTSPE, an emulsion copolymerization of styrene and divinylbenzene was carried out in the presence of the block copolymer PS-b-qPVP, as described in the experimental section. The block copolymer serves as surfactant, stabilizing the latex particles by its charged, hydrophilic qPVP part. The hydrophobic polystyrene block acts as an anchoring group. This anchoring is achieved by insertion of the hydrophobic polystyrene blocks into the latex particles. The resulting product is a latex stabilized by immobilized cationic qPVP.

After CoTSPE was adsorbed to the cationic surfactant segments on latex,
this system was tested as a catalyst in the oxidative coupling of 2-mercaptopethanol (ME) in oxygen atmosphere. Earlier results in our laboratory showed that extremely low concentrations of free cationic polymer had a strongly accelerating effect on the thiol oxidation (polyelectrolyte concentration expressed as nitrogen concentration: $[N^+] = 10^{-5}$ mol/dm$^3$, i.e. 2.6 mg surfactant/dm$^3$ already affects the reaction rate)$^{27}$. Before measuring the catalytic activity of the latex, it is therefore of essential importance to examine the serum of the latex for the presence of even minor traces of free surfactant. We developed a sensitive VIS method to detect very low concentrations of cationic polymer, based on the occurrence of the easily detectable monomeric or dimeric form of CoTSpC depending on the absence or presence respectively of cationic polymers in solution$^{18,36}$. For PS-b-qPVP, the lowest $N^+/CoTSpC$ ratio, that is the ratio at which the dimeric form of CoTSpC can still be detected, was experimentally determined to be 3, resulting in a detection limit for the polymeric surfactant of $3 \times 10^{-7}$ mol/dm$^3$ at $[CoTSpC] = 10^{-7}$ mol/dm$^3$.

As expected, the unpurified latex did contain an unacceptably high level of free surfactant. It is obvious that, after addition of CoTSpC, such a latex would show the same kinetic features as a homogeneous, surfactant solution. Even after washing the latex with water for several days by the serum-replacement technique$^{27}$ the serum still contained considerable amounts of surfactant. Only a combination of the ion-exchange method reported by Vanderhoff et al.$^{23,24}$ followed by a serum-replacement procedure resulted in a
surfactant-free serum ([N⁺]c = 3x10⁻⁷ mol/dm³). This was double-checked by measuring the catalytic behaviour of the serum in the thiol oxidation, after addition of CoTSPC. The observed serum activity appeared to be identical to that of a surfactant-free solution, i.e., only CoTSPC in water. The latex data are summarised in Table 1.

The mechanical strength of the latex was investigated by stirring for 30 minutes in the reaction vessel (three times the average oxidation reaction time). The resulting mixture was again tested on the presence of free polycations. Only a very low concentration of nitrogen was found in the serum (1.2x10⁻⁴ mol N⁺/dm³, i.e., about 2.5% of the pyridinium groups of the block polymer did desorb from the latex). The resulting serum still did not contain enough free surfactant to show an increase in reaction rate compared with a solution containing no surfactants. The average diameter of the latex particles was not affected by the continued stirring.

**Kinetics**

The kinetic behaviour of the latex oxidizing 2-mercaptoethanol (ME) in the presence of CoTSPC was studied: (1) the latex system stabilized by the block copolymer (PS-b-qPVP), (2) the homogeneous block copolymer system that may contain some form of aggregation (described later) and (3) the homogeneous cationic polyelectrolyte system (qPVP). The difference in molar mass of the surfactant and the homopolymer qPVP (10,000 and 90,000, respectively) will scarcely affect the reaction rate as was observed earlier.²⁸,²⁹

In Fig. 1 the catalytic activity (expressed in mol ME·dm⁻³·s⁻¹) of the heterogeneous and homogeneous qPVP systems is shown as a function of pH. For all three systems a distinct optimum was found around pH=8.7. Such a pH optimum had already been found for PVAm and 2,4-ionene-containing systems as well, resulting from the fact that the reactive species in the rate-determining step is the thiolate anion (pKₐ(ME) = 9.6).³⁷ The difference between the pH optima for PVAm and 2,4-ionene containing systems (pH = 8) on
the one hand, and the qPVP-containing systems on the other, is striking however. This may be explained by a difference in charge density on the polymer backbone. The charge density of qPVP is lower and more delocalized, as a result of the presence of aromatic moieties, than that, for instance of 2,4-ionene, resulting in a lower local thiolate anion concentration at a given pH. This line of thought is confirmed by the earlier observed shift of the pH optimum towards higher pH for 2,10-ionene, that also has a lower charge density than 2,4-ionene. Surprisingly, the concentration of the block copolymer at the latex surface, likely to result in an increase of the apparent charge density, does not affect the pH optimum.

The stabilities of the qPVP containing systems are shown in Fig. 2. The catalytic activity of the latex and qPVP systems were found to decrease after
successive runs. Surprisingly, the reactivity of the block copolymer containing solution is hardly affected at all. A similar independence was also found for 2,4-ionene. However, in the case of PVAm a decrease in oxidation rate was also observed\textsuperscript{17}. The decrease in activity was mainly attributed to the formation of acidic by-products, caused by the reaction of the intermediate hydrogen peroxide with disulphide to form sulphur-containing oxo-acids, poisoning the basic sites\textsuperscript{22}. Decomposition of CoTSPc was also observed, but this was not the primary cause of deactivation. Although these oxo-acids are only formed in very low concentrations (less than 1% of the total oxygen consumption) substantial accumulation of disulphide after successive runs will enhance their formation. The variation in deactivation of the different cationic complexes is not yet fully understood. Most probably, it will be related to the \( \text{H}_2\text{O}_2 \) accumulation in the microenvironment of the catalytic sites. The peroxide accumulation is primary determined by the intrinsic kinetics of the system, but it will also be dependent of the hydrophobicity of the polymer domain.

In the case of the latex system, product inhibition, caused by a relatively slow desorption of the product from the latex surface could not be ruled out. Therefore, mercaptoethanol was oxidized in the presence of an excess (2 equivalent) of its product: 2,2'-dithiodiethanol. There was no change in reactivity observed compared with the regular system, indicating the absence of product inhibition. However, during all catalytic experiments using latex as support for CoTSPc some coagulation was observed. The colloidal instability is a known problem in catalyst immobilization\textsuperscript{33-35}. Latex coagulation will likely affect the catalytic activity after successive runs, but it will hardly influence the catalytic activity measured as the initial oxygen uptake. The deactivation of the latex and qPVP containing systems will be a subject for future research.

Fig. 3 clearly shows a linear relationship between CoTSPc concentration and the catalytic activity (at constant \([\text{N}^\circ]\)). This linear relationship
Fig. 3 Reaction rate as a function of the CoTSFc concentration ([N⁺] = constant) 
$\text{pH} = 8.7$, $[\text{M}] = 0.143 \text{ mol/dm}^3$, symbols see Fig. 1

Fig. 4 Reaction rate as a function of the thiol concentration 
$\text{pH} = 8.7$, $[\text{CoTSFc}] = 4 \times 10^{-7} \text{ mol/dm}^3$, symbols see Fig. 1

indicates the absence of mass transport limitations. It also shows the absence of a saturation behaviour of CoTSFc at the surface of the latex or in the homopolymer domain in the case of the homogeneous systems in this concentration region, otherwise deviations from linearity would have been observed. Again, these findings are in complete agreement with the linear dependencies found for homogeneous PVAm and 2,4-iodene systems. The observed reaction rate was not affected when the Co/N⁺ ratio was kept constant$^{26}$.

As the two last-named polymers showed Michaelis-Menten kinetics in thiol and oxygen$^{16,36}$ the dependence of reaction rate on thiol concentration was also measured for the present systems (Fig. 4). All three qPVP-containing systems showed saturation-type behaviour in thiol concentration, but in the case of the homogeneous block copolymer system it was less pronounced.

Maintaining a high oxygen concentration brings a zeroth-order reaction in oxygen, and pseudo single-substrate Michaelis-Menten kinetics is observed
according to eq. 1

\[ v = \frac{k_2[\text{CoTSPc}] \cdot [\text{ME}]}{K_M + [\text{ME}]} \quad (1) \]

with \( k_2 \) = turnover number (s\(^{-1}\)) and \( K_M \) = Michaelis constant (mol dm\(^{-3}\)). From the double reciprocal of reactivity versus thiol concentration, the so-called Lineweaver-Burk plot, these constants were determined as listed in Table 2.

For comparison, the data of PVAm and 2,4-ionene are also listed in this table\(^{16,23}\). As can be seen from the table, the turnover number \( (k_2) \) for the PS-b-qPVP (latex) system is increased on immobilization of the block copolymer (the saturation levels of the curves in Fig. 4 are determined by the turnover number, as can be deduced from eq. 1). The turnover number of qPVP lies in between these values. Very striking are the differences between the Michaelis constants of the observed systems. In contrast with the turnover number, the Michaelis constant is only slightly affected by immobilization of PS-b-qPVP while the \( K_M \) of the qPVP system is significantly lower than that of the block copolymer-containing systems. Assuming \( k_2 \ll k_1 \), the Michaelis constant \((= k_1 k_2/k_4)\) equals the reciprocal of the binding constant \( K_M (= k_1/k_4) \), i.e., the binding of thiogluconate anion to the cobalt centre.

Table 2: Turnover numbers \( (k_2) \) and Michaelis constants \( (K_M) \) of several cationic polymer containing systems.

<table>
<thead>
<tr>
<th>Cationic polymer containing systems</th>
<th>( k_2 ) (1/s)</th>
<th>( 10^5 \times K_M ) (mol/dm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>qPVP</td>
<td>( 1.5 \times 10^3 ) ±/− 110</td>
<td>2.6 ±/− 0.4</td>
</tr>
<tr>
<td>PS-b-qPVP/latex</td>
<td>( 1.7 \times 10^3 ) ±/− 150</td>
<td>12 ±/− 2</td>
</tr>
<tr>
<td>PS-b-qPVP</td>
<td>( 1.1 \times 10^3 ) ±/− 210</td>
<td>11 ±/− 4</td>
</tr>
<tr>
<td>PVAm</td>
<td>( 2.0 \times 10^3 ) ±/− 200</td>
<td>9.0 ±/− 2.0</td>
</tr>
<tr>
<td>2,4-ionene</td>
<td>( 3.3 \times 10^3 ) ±/− 200</td>
<td>0.66 ±/− 0.14</td>
</tr>
</tbody>
</table>

\( ^{a} pK_a = 7 \)

\( ^{b} pK_a = 8.0 \)
Kinetic data of latex-immobilized catalytic systems are unfortunately scarce. Therefore comparison is only possible with effects of latex immobilization on the Michaelis constants of enzymes. In these studies, an increase of $K_M$ was found after immobilizing enzymes, indicating a weaker substrate-enzyme binding. This was explained by an electrostatic repulsion between the negatively charged substrate and the anionic latex particles.\(^5,12\) When a neutral substrate was used, the Michaelis constant was hardly affected by immobilization.\(^6\)

In our latex system, the styrene part of the block copolymer is strongly adsorbed to, or embedded in the polymer particles and in consequence may not play a role in the oxidation process that takes place in the aqueous boundary layer which is rich in $q$PVP blocks. It therefore seemed justified to compare the latex system with the homogeneous $q$PVP system. If the important prerequisite ($k_\text{diss} < k_\text{diss}, K_M \approx K_B^{-1}$) still holds after immobilization, immobilization of PS-$b$-$q$PVP on latex particles, that is concentration of cationic charge on the latex surface, might lower the Michaelis constant as compared with the $q$PVP system, seemingly in contrast to our present findings as can be seen in Table 2. The Michaelis constant for the latex system is higher than for the homogeneous $q$PVP system. The higher value of $K_M$ for the immobilized system can not be due to diffusional problems, as was suggested by Brouwer et al. in the case of cross-linked PVAc\(^7\) because mass transfer limitations can be ruled out here (see Fig. 2).

However, the most important difference between immobilized enzymes and immobilized macromolecules is the extent of conformational change on immobilization. The rather rigid three-dimensional structure of enzymes will hardly be affected by immobilization. A completely different situation occurs when polyelectrolytes are being immobilized. In a homogeneous catalytic system the polymer concentration is very diluted whereas, in the case of the immobilized system, the polymer is concentrated at the surface of the latex particles. In addition, the increase of the polymer concentration affects the
polymer coil structure, that is immobilization (concentration) of polyelectrolyte on latex particles may directly influence the binding constant, as will be seen in Fig. 5, where the reduced viscosity of qPVP is measured as a function of its concentration. Besides this concentration effect, the mobility of the polymer chain will decrease on immobilization. Moreover, this binding constant is actually determined by the local thiolate concentration (and not by the overall thiol concentration) and is therefore an apparent constant. This local anion concentration depends on electrostatic interactions between polymer and substrate and remains unknown. Therefore changes in local substrate concentration due to the immobilization of the polycation, will affect the apparent binding constant.

On these grounds, comparison of the two homogeneous systems, that is PS-b-qPVP and qPVP seems justified, although it must be emphasized that the block copolymer may hold an exceptional position due to its amphiphilic character. It was reported that a small hydrophobic block in the block copolymer of styrene and 2-vinyl-N-methylpyridine and low concentrations of block copolymer of styrene and 4-vinyl-N-ethylpyridine already influenced (increased) the viscosity in water. This anomalous behaviour was attributed to the formation of supramolecular structures as a result of incomplete solubilization. In order to investigate the presence or absence of aggregated structures during the catalytic experiments, reduced viscosities ($\eta_{s} / c$) of PS-qPVP and qPVP-containing solutions were measured at low polymer concentrations (2.50 mg/dm$^3$) as used under the experimental conditions (Fig. 5). In the case of the block copolymer, the reduced viscosity rose on increasing its concentration, indicating that some kind of supramolecular structure may be formed at low polymer concentrations. For comparison, the reduced viscosity of the homopolymer (qPVP) is also shown in Fig. 5 and its concentration dependence is typical of a common polyelectrolyte. The decrease of the reduced viscosity of the block copolymer at higher concentrations may be attributed to the increase of ionic strength. Fig. 5
Fig. 5 Reduced viscosity ($\eta_{red}$) of PS-b-GVP and GVP

□ : GVP in pure water, △ : PS-b-GVP in pure water,
+ : PS-b-GVP in 0.02 M KBr

clearly shows that increasing the ionic strength by the addition of a low
concentration of salt ([KBr] = 0.02 mol/dm$^3$) had a similar effect on the
reduced viscosity of the block copolymer. This sensitivity to ionic strength
may play a role in the catalytic experiments, where varying the thiol
concentration, or the basicity, will have a strong effect on the ionic
strength of the reaction mixture ($10^{-1} - 10^{-1}$ mol/dm$^3$). The addition of low
concentration of CoTSPc (4x10$^{-7}$ mol/dm$^3$) did not affect the reduced viscosity.

We tried to demonstrate the presence or absence of these aggregated
structures by light scattering. Unfortunately, the block copolymer
concentrations used (simulating the low concentrations used in the catalytic
experiments) are too low in this technique to prove unambiguously the presence
or absence of these structures.
It was mentioned earlier in this chapter that cationic polymers induced aggregation of CoTSPc. This aggregated form of the catalyst is believed to be responsible for the dramatic increase in reactivity. Extensive studies on several polyelectrolytes, like 2,4-, 2,6- and 2,8-ionene by van Welse et al. showed that this aggregation is irreversible, whereas in the case of more soap-like polyelectrolytes, like 2,10-ionene, monomerization of CoTSPc was observed at high polymer concentrations (expressed as [N\(^+\)]\[^{26}\]) This phenomenon was attributed to the hydrophobic character of the polymer backbone generating micelle-like structures. In Fig. 6 and 7 the VIS spectra of CoTSPc in the presence of qPVP and PS-b-pPVP are shown at [CoTSPc] = 2x10^{-6} mol/dm\(^3\) and [N\(^+\)] = 2x10^{-4} mol/dm\(^3\) (curve A) and 2x10^{-3} mol/dm\(^3\) (curve B). As can be expected, qPVP exhibits the behaviour of a common cationic polymer, that is strong aggregation of CoTSPc that is hardly disturbed at high [N\(^+\)] (628 nm, Fig. 6). In the case of the block copolymer, aggregation of CoTSPc is also observed at [N\(^+\)] = 2x10^{-4} mol/dm\(^3\) (Fig. 7, curve A). However, at higher polymer

![Fig. 6 VIS spectrum of CoTSPc in the presence of qPVP](image)

\[ [\text{CoTSPc}] = 2 \times 10^{-6} \text{ mol/dm}^3, \text{ A: [N}^+\text{]} = 2 \times 10^{-4} \text{ mol/dm}^3, \]

\[ \text{B: [N}^+\text{]} = 2 \times 10^{-3} \text{ mol/dm}^3 \]

![Fig. 7 VIS spectrum of CoTSPc in the presence of PS-b-pPVP](image)

\[ [\text{CoTSPc}] = 2 \times 10^{-6} \text{ mol/dm}^3, \text{ A: [N}^+\text{]} = 2 \times 10^{-4} \text{ mol/dm}^3, \]

\[ \text{B: [N}^+\text{]} = 2 \times 10^{-3} \text{ mol/dm}^3 \]

60
concentration ([N⁺] = 2 \times 10^{-8} \text{ mol/dm}^3, \text{ curve B}) the shoulder in the VIS spectrum of CoTSPc at 660 nm suggests partial monomerization of the aggregated CoTSPc indicative for the presence of micelle-like structures. The nearly identical catalytic activity for both the qPVp and PS-b-qPVp systems (see Table 2) confirms the absence of the less reactive, monomeric CoTSPc in the case of PS-b-qPVp during the catalytic reactions (reaction conditions: [N⁺] = 5 \times 10^{-6} \text{ mol/dm}^3, [CoTSPc] = 4 \times 10^{-7} \text{ mol/dm}^3).

The data presented in this chapter indicate the absence of multi-molecular micelle-like structures. However, the discrepancy between the K_M values for these two homogeneous systems and the similarity of the constants of the block copolymer and the latex systems suggest a similarity between the micro-environment of the catalytic CoTSPc centres of the block copolymer and the block copolymer-stabilized latex system.

Conclusions

Emulsion copolymerization of styrene and divinylbenzene with PS-b-qPVp as surfactant was found to be a successful method to prepare a cationic latex that serves as support for CoTSPc without the decrease in reactivity that is usually encountered on immobilizing this highly active system. As compared with the conventional polymer-free CoTSPc-containing system all three systems, qPVp, PS-b-qPVp and block copolymer-stabilized latex, show a strong enhancement of the oxidation rate of 2-mercaptoethanol. Although the stability of the latex and qPVp-containing systems after successive runs is rather poor, this immobilization method shows the great potential value of anchoring highly active systems retaining the high catalytic activity. The turnover number is increased on immobilization of the block copolymer. The turnover number of the qPVp system lies in between the values of these systems. The Michaelis constant for the block copolymer-containing systems is hardly affected on immobilization. The observed differences between the three systems can not be
fully elucidated, due to conformational changes of the polymer domain on
immobilization of PS-b-qPVP and the high local polycation concentration at the
particle surface. The $K_M$ values of the latex system and the block copolymer
system suggest a similarity in structure between the two.

Acknowledgment

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Synthesis, purification and characterization of cationic latices produced by the emulsion copolymerization of styrene with 3-(methacrylamidinopropyl)-trimethylammoniumchloride.

Karel H. van Straun, Wil J. Belt, Pieter Piet and Anton L. German

Summary

The effect was investigated of varying the amount of 3-(methacrylamidinopropyl)trimethylammoniumchloride (MAD) on the emulsion copolymerization of styrene and MAD with azo-bis(isobutyramidine hydrochloride) (AIBA) as initiator. The addition of MAD accelerated the polymerization and decreased the particle size. Cleaning of these latices in order to remove the undesired polyelectrolyte not incorporated in the latex particles, was found to be tedious. Serum replacement, diafiltration and centrifugation appeared to be unsatisfactory, since desorption of polyelectrolyte was still observed after standing or stirring. A combination of centrifugation and treatment with silica appeared to clean the latices to a satisfactory level (expressed as $[N^+] < 5 \times 10^{-7} \text{ mol/dm}^3$). Surface charge density, as determined by conductometric acid-base titrations, rose slightly on increasing the initial MAD concentration. Shot-growth (two-step) emulsion polymerization or the use of a cross-linking agent (divinylbenzene) hardly affected the surface charge density.

Introduction

The immobilization of catalytic systems onto insoluble supports has received considerable academic and industrial attention over the last few
decades. Most of these investigations focused on organic supports that can be functionalized by chemical reactions. Generally, after immobilization the activities of intrinsically highly reactive catalytic systems have been disappointing. In most cases this is due to mass transfer limitations to the support particles (interparticle diffusion) or within these particles (intraparticle diffusion). To overcome these problems smaller, nonporous particles are needed. However, a drawback of particle size reduction is the need for more sophisticated separation techniques to purify the resulting products.

Emulsion polymerization offers the possibility of synthesizing these small, organic, nonporous particles in the submicron region. This polymerization technique also allows the synthesis of particles with narrow particle size distribution (monodispersity). Functionalization of these latices can then be achieved by emulsion polymerization in the presence of a functional monomer, a functional surfactant, a functional initiator or by a post-polymerization modification.

In a conventional emulsion polymerization latices are stabilized by surfactants. The removal of stabilizer after polymerization is difficult, and coagulation may result. In the case of surfactant-free emulsion polymerization of styrene, particles are stabilized by ionic initiator residues. Potassium persulphate as initiator has been studied extensively and was found to result in sulphate stabilized latices. In order to obtain a better control of both particle size and surface charge density, ionic comonomers can be used. Most studies are concerned with the stabilization by anionic groups introduced by sulphonate-containing monomers. Other types of ionic monomers frequently used are monomers containing carboxyl groups, and nonionic hydrophilic monomers like acrylamide and acrylamide derivatives. Surprisingly, the use of cationic comonomers is less common. Also, the use of surfactant-like monomers has been reported. Our goal is to prepare stable, cationic latices with a high surface
charge density as supports for cobalt(II) phthalocyanine-tetrasodium sulphonate (CoTSPc). In this chapter we describe the synthesis, purification and characterization of cationic latices prepared by emulsion polymerization of styrene in the presence of the functional cationic comonomer, 3-(methacrylamidinopropyl)trimethylammonium chloride (1, MAD) and azobis(isobutyramide hydrochloride) (2, AIBA) as initiator. The immobilization of CoTSPc on these colloidal particles by coulombic interaction and the activity of these functionalized latices in the oxidation of 2-mercaptoethanol will be presented in the next chapter.

Scheme 1 Structures of MAD (1) and AIBA (2)

**Experimental Part**

**Emulsion polymerization**

Styrene (Merck) and divinylbenzene (DVB, technical grade, Merck) were distilled before use. AIBA (Polyscience) was used as purchased. MAD (Merck) was received as a 50% aqueous solution. The inhibitor was removed by extraction with diethyl ether. The remaining solution was flushed with nitrogen and stored at -18°C. A double-wall all-glass reactor, thermostated at 60°C and equipped with a mechanical stirrer, was filled with 350 ml of distilled deoxygenated water and flushed with argon for 20 minutes. Styrene (30 g) was then added to the reactor and after 5 minutes the desired amounts of MAD and AIBA were added to this mixture together with 50 ml of water. The emulsion polymerization was carried out under argon atmosphere and the stirring speed was maintained at 300 rpm. All polymerizations were stopped after approx. 16 hrs and the product was filtered over glass wool to remove any possible coagulum.
Shot-growth experiments. The first step was identical to S2 (see Table 2) i.e. 400 ml water, 30 g styrene, 0.5 g MAD and 0.5 g AIBA. A second batch of monomers was added after 3 hrs, to wit 6 g styrene, 150 mg AIBA, a varying amount MAD and 50 ml of water.

In the case of kinetic experiments, samples were taken in order to monitor conversion and the polymerization was stopped by the addition of hydroquinone–monomethylether. After evaporation of the volatile components by heating at 90°C and drying of the sample under reduced pressure, the styrene conversion was gravimetrically determined as given below.

\[
\text{Styrene conversion(\%)} = \frac{\text{s}_t - \text{s}_{t=0}}{\text{s}_{t=0} - \text{s}_{t=0}} \times 100
\]

where \( s_t \) stands for solid content of the sample (grams solid/gram solution) at time \( t \), \( s_{t=0} \) = solid content at the beginning of the reaction, and \( s_{t=0} \) = solid content at 100% styrene conversion.

Cleaning procedure

The latex (ca 100 ml) was centrifuged twice (20,000 – 30,000 rpm for 30 minutes, Centrkon T-2060), decanted, redispersed in water and then treated with 2 – 5 g silica (Merck, Kieselgel 60 for column chromatography, 63–200 µm). After every treatment the silica was filtered off through a paper filter. Silica treatment, followed by filtration was repeated twice. The latex was subsequently centrifuged twice before rinsing with NaOH solution (pH = 11) in a serum-replacement cell. After the passage of at least 15 cell volumes of diluted base, the cell was connected to water (Millipore, Milli-Q). After rinsing with at least 20 cell volumes the latex was titrated.

VIS spectra were recorded at a Hewlett-Packard diode array 8451A spectrophotometer using a 1-cm cell. Average particle size and dispersity were determined by Scanning Electron Microscopy (SEM).
Titration

An amount of latex was weighed and, where necessary, water was added to make up to a volume of 25 ml. The latex solution was flushed with argon for at least 30 minutes. The inert atmosphere was maintained during the titration. The latex was titrated with 0.001 N HCl solution. The conductivity was monitored using a Radiometer CDM80 conductivity meter. The surface charge density was calculated as given below.

\[
surface\ charge\ density = \frac{v_t \times D \times 1.753}{S_c \times w_{latex}} \ \mu\text{mol/m}^2
\]

\(v_t\) = added volume of acid (ml), \(D\) = average particle diameter (nm), \(S_c\) = solid content latex solution and \(w_{latex}\) = weight of titrated latex solution (g).

Results and discussion

Kinetics of emulsion polymerization

Surfactant-free emulsion copolymerization with ionic comonomers is not as straightforward as it may seem. This is particularly due to the great difference between water-solubility of the two monomers. In a classical emulsion polymerization, that is the polymerization of a scarcely water-soluble monomer (e.g. styrene) in the presence of a water-soluble initiator and a surfactant, the kinetics may be described by the Smith-Ewart theory\(^3\). The most important mechanistic difference between a classical and a surfactant-free emulsion polymerization is the nucleation stage, so-called stage I. In the case of conventional emulsion polymerization, particles may originate from monomer-swollen micelles activated by initiator radicals (micellar nucleation). Particle production stops when all surfactant molecules have been adsorbed to the already existing particles. This is the end of stage
I. In the case of a surfactant-free emulsion polymerization, copolymerization of the scarcely water-soluble styrene with the water-soluble 3- (methacrylamidinopropyl)-trimethylammoniumchloride (MAD) the homogeneous nucleation mechanism is likely to occur. Thermal decomposition of the water-soluble initiator starts copolymerization of MAD with styrene in the water phase. Copolymerization in the water phase will proceed until the oligomer (1) is captured by already existing particles, (2) reaches a critical chain length after which it will "precipitate" to form a primary particle or (3) terminates before it can be adsorbed or can nucleate. These processes are dependent on the solubility (hydrophobic - hydrophilic balance) of the formed oligomer, the capturing ability of the already existing particles and the rate of termination of the oligomers in the water phase. Primary particles coalesce to larger particles until their surface charge provides sufficient colloidal stability. Particle production stops when all oligomeric radicals are captured by already existing stable particles before nucleation can occur.

The effect of MAD concentration on the styrene conversion as a function of time is shown in Fig. 1.

![Graph](image)

**Fig. 1** Effect of MAD concentration on the styrene conversion

- : [MAD] = 0 mol/dm³,
- : [MAD] = 2.8x10⁻³ mol/dm³,
- : [MAD] = 5.7x10⁻³ mol/dm³

**Fig. 2** Effect of MAD concentration on the particle size
of time is shown in Fig. 1. An increase of the initial MAD concentration accelerates the rate of styrene conversion. Since the rate of polymerization is affected by the number of particles, the particle size of the resulting latices was measured as a function of the MAD concentration (Fig. 2). Indeed, the particle size drops on increasing the MAD concentration; it will be shown below that this is due to the increase of surface charge density.

To eliminate any possible influence of (very small concentrations of) polyelectrolyte that is present in the commercially available MAD, unquaternized amine was treated with iodomethane. The ammonium salt formed in this manner appeared to be free of polyelectrolyte, and increased particle size in emulsion copolymerization with styrene, compared with MAD under identical experimental conditions. In order to determine whether the origin of

![Graph](image)

**Fig. 3** Effect of the presence of iodine on the polymerization rate of styrene

\[(\text{MAD}) = 1.15 \times 10^{-2} \text{ mole/dm}^3, (\text{AM}) = 4.61 \times 10^{-3} \text{ mole/dm}^3, \]
\[(\text{styrene}) = 0.72 \text{ mole/dm}^3 \text{ (based on water)}, T = 60^\circ \text{C and } V = 0.4 \text{ dm}^3 \]
\[(\text{Iodine}) = [\text{NaCl}] = 1.0 \times 10^{-2} \text{ mole/dm}^3, \Delta: \text{NaCl}, *= \text{MAD}\]
this unexpected phenomenon was due to the absence of polyelectrolyte or to the
introduction of iodide, two emulsion polymerizations were carried out in the
presence of MAD: one in the presence of NaCl and the other in that of
equimolar NaI. The kinetics as depicted in Fig. 3 clearly shows that the
retardation of styrene conversion is not caused by the presence of low
concentrations of polyelectrolyte, but stems from the presence of the iodide
salt. We are not aware of any publication reporting this effect. It appears
that unstable iodine reacts as a radical scavenger, thereby reducing the
overall efficiency of the initiator and resulting in an increase of particle
size. This effect is still under investigation.

Latex purification

Earlier work in our laboratory showed that the CoTSPc-catalyzed thiol
oxidation in the presence of cationic polymer is dependent on the linear
charge density on the backbone of the polyelectrolyte. In this line of thought
the catalytic activity of the lattices will also be affected by its surface
charge density. It is therefore necessary to determine the surface charge
density of the produced lattices.

Due to the very great difference between the partition coefficients of
both monomers, the formation of free water-soluble polyelectrolyte, that is
copolymer of styrene and MAD not anchored onto the latex particles, is likely
to occur. In order to determine the surface charge density in a reliable
manner, these polymeric side products, together with low molar mass
contaminants, must be removed prior to surface charge determination.

In addition, the CoTSPc catalytic system is extremely susceptible to very
low concentrations of cationic polymer, for instance in the case of 2,4-
ionene, a poly-(quaternary ammonium salt), a reaction-rate enhancement was
still observed at \([N^+] = 10^{-5} \text{ mol/dm}^3\) (i.e. \(\approx 0.12 \text{ mg/dm}^3\) homopolymer)\(^9\). It
will be shown in the next chapter that, for the present homopolymer (PMAD),
the thiol oxidation is still affected at free polyelectrolyte levels.
corresponding to \([N^\text{+}] = 10^{-6} \text{ mol/dm}^3\). In order to measure the true activity of the immobilized PMAD/latex system only, it is thus of essential importance to clean the latex to such an extent as to obtain a polyelectrolyte concentration of the serum of the latex lower than \([N^\text{+}] = 10^{-9} \text{ mol/dm}^3\). Aiming at the detection of extremely low concentrations of cationic polymer, we developed a VIS spectrophotometric method based on the occurrence of the dimeric or monomeric structure of CoTSPc in the presence or absence of these charged polymers, respectively. Due to the very high extinction coefficient of CoTSPc and to the clear difference between the VIS spectra of these two structures, this technique provided an excellent and sufficiently sensitive method of determining trace amounts of polycations.

As a result of the smaller particle diameter, purification of the latex requires more sophisticated cleaning techniques than those available for resin particle cleaning. Recently, El-Aasser reviewed various latex-cleaning techniques, for example dialysis, ion-exchange, serum replacement, microfiltration and diafiltration. Low molar mass impurities can generally be removed by one of these methods. On the other hand, the removal of polyelectrolyte by one of these methods will usually be more difficult.

The often used ion-exchange method alone is known to be insufficient to clean latices from polyelectrolyte. Moreover, the purification of the commercially available ion-exchange resin itself, that is the removal of charged polymeric contaminants, is laborious. In chapter 5 we therefore purified polystyrene latices, stabilized by a block copolymer of styrene and quaternized 4-vinylpyridine, by using the ion-exchange method followed by serum replacement. In that case, the combination of these two techniques appeared to be sufficient to cleanse the latex of polymeric contaminants. Unfortunately, a small amount of copolymer (polymeric surfactant) was found to desorb after these cleaning steps, but its concentration was too low to induce an accelerating effect on the thiol oxidation. Before developing a cleaning technique by ourselves, we tested three well-known purification methods for
cleaning MAD stabilized polystyrene latices, to wit serum replacement, diafiltration and ultracentrifugation.

In the case of the serum replacement, Ahmed et al.\textsuperscript{40} showed that the removal of salt from a diluted latex-containing low molar mass electrolyte is somewhat slower than expected on grounds of theoretical considerations implying interaction of the electrolyte with the polymer particle. It can be expected that in the present case, where interaction of polymeric contaminants with the latex is very likely to occur, the cleaning process will be even more time consuming. Indeed we observed that the cleaning procedure could take days or weeks, depending on the water flow through the cell and on the conditions used during the emulsion polymerization, that is the concentration of the charged monomer. The total volume of cleaning water ranged between 30 and 100 times the cell volume before the polyelectrolyte concentration in the effluent of the serum replacement cell was less than $5 \times 10^{-7}$ N$^+$ mol/dm$^3$ as determined by the CoTSPc-VIS method.

Diafiltration, a technique very similar to serum replacement was also investigated. Instead of pumping water through the cell containing a latex solution, the latex is continuously circulated in a tangential flow pattern through channels over a membrane by the use of a pump, because of which, shear-induced coagulation may occur. In our case this method did not appear to be faster than the serum-replacement technique as was claimed by others\textsuperscript{40} and indeed, in some cases coagulation was observed.

Latices cleaned by serum replacement and diafiltration were tested under the conditions used in the catalytic reactions. As was pointed out earlier in this chapter, it is of extreme importance that the serum of the latex contains polyelectrolyte concentrations of less than $10^{-8}$ mol N$^+$ /dm$^3$. Of course, this stipulation also applies to the serum after the thiol oxidation. We therefore stirred a dilute latex solution for 15 minutes at 2600 rpm at 25°C, simulating the experimental conditions of the thiol oxidation. The resulting solution was centrifuged and the serum tested for the presence of polyelectrolyte by the
CoTSPEC-VIS method. In latices cleaned by serum replacement or diafiltration, unacceptably high levels of polyelectrolyte appeared to be desorbed after stirring. Apparently, both techniques purified the latex to such an extent as to leave some polyelectrolyte adsorbed to the latex surface. This polyelectrolyte desorbs at such a slow rate, that its concentration in the effluent is too low to be detected by the CoTSPEC-VIS method \( ([N^+] < 5 \times 10^{-7} \text{ mol/dm}^3) \). But if these cleaned latices were left to stand for approximately one week, or were subjected to vigorous stirring, the sera of the latices were found, after centrifugation, to contain detectable concentrations of polyelectrolyte.

Some authors claim the “complete” removal of polymeric contaminants by centrifugation\(^{15,24,31} \). We also tried to clean latices this way, that is, repeated centrifugation, followed by decantation and redispersion in water. Unfortunately, even after six centrifugations, the serum of the resulting

Table 1 Effect of ionic strength on the desorption of polyelectrolyte as measured by the occurrence of monomeric or dimeric structure of CoTSPEC in the sera of the precipitated latices

<table>
<thead>
<tr>
<th>Number of centrifugations</th>
<th>Serum of sample A</th>
<th>Serum of sample B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>-(^a)</td>
<td>+</td>
</tr>
<tr>
<td>3</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>4</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

\(^a\) - absence of polyelectrolyte according to CoTSPEC-VIS method
\(^b\) - presence of polyelectrolyte according to CoTSPEC-VIS method

Sample A: (1) centrifugation, (2) redispersion in distilled water followed by centrifugation, (3) redispersion in 0.1 M KNO\(_3\) followed by centrifugation and (4) redispersion in distilled water followed by centrifugation. Sample B: as sample A, except for step (3) where distilled water was used instead of 0.1 M KNO\(_3\).
latex still contained, at least for our catalytic systems, an unacceptably high level of polyelectrolyte. Above all, the technique is very laborious.

This cleaning method clearly demonstrated the effect of ionic strength of the serum on the desorption rate of polyelectrolyte (Table 1). As can be seen from Table 1, the CoTSPc-VIS method suggested, after one centrifugation of the latex, the absence of free polyelectrolyte (both samples A and B). Much to our surprise, after redispersion of the remaining solid in pure water, followed by a second centrifugation, the CoTSPc-VIS method indicated the presence of polyelectrolyte (both samples A and B). After redispersion of the solid in a salt solution (0.1 M KNO₃) and subsequent centrifugation, the CoTSPc-VIS method again suggested the absence of polyelectrolyte (sample A), while the serum, after redispersion of the same solid in pure water, followed by centrifugation, contained polyelectrolyte according to our detection method (sample B). These findings are in good agreement with the theoretical considerations put forward by Hesslink. The effect that the adsorption isotherm of charged polymers onto charged surfaces is determined by a coulombic and a nonionic adsorption term. If the charges have the same sign, as in our case, the latter effect must predominate, otherwise no adsorption would take place (the coulombic term has a negative effect on the adsorption isotherm due to the identical sign of the charges). Addition of salt will decrease the desorption rate as a result of a decrease in the electrostatic repulsion between the polyelectrolyte and the charged latex surface.

From all the above attempts to clean the cationic lattices, it becomes clear that, as far as we have been able to test the common cleaning techniques, none of these methods will suffice for our catalytic system, that is after using one of the known purification methods, the cleaned lattices will contain unacceptably high levels of polyelectrolyte. This becomes understandable when we bear in mind the uttermost sensitivity of the CoTSPc catalyzed thiol oxidation to extremely low concentrations of cationic polymers. For example, if a latex of 10% solid content and a specific surface
charge of 50 μmol N⁺/g(solid) (i.e. 5x10⁻³ mol N⁺/dm³(latex), see Table 2) would desorb 0.01% of its charged groups i.e. polyelectrolyte, this can be detected by the CoTSPc-VIS method and the latex will be denoted as unsuitable for a catalytic experiment. On the basis of these considerations, we believed it was necessary to develop a purification method to clean latices to such an extent as to render polymer colloids suitable for the support of CoTSPc in catalytic systems.

It was found in our laboratory that cationic polymers like 2,4-ionene adsorb strongly to silica. Following this line of thought, we also tried to purify the cationic latices by this adsorption medium. In order to simultaneously reduce the amount of soluble charged polymer and the ionic strength of the latex solution, the latex was centrifuged twice before treatment with silica. Fig. 4 shows the effect of silica treatment on the presence of polyelectrolyte in the sera of these latices as determined by the CoTSPc-VIS method. A treatment with silica consists of shaking the latex with silica for at least 12 hours, followed by filtration. Curve A shows the presence of polyelectrolyte in the serum after two centrifugations (presence of dimeric structure of CoTSPc at 630 nm). Curve B clearly shows that after one treatment with silica the serum still contained polyelectrolyte. Curve C and D show that after 2 and 3 treatments of latex with silica the serum contained polyelectrolyte in concentrations of less than 5x10⁻⁷ mol N⁺/dm³ (monomeric structure of CoTSPc at 660 nm). To rid the latex of any possible further impurities that can not be detected by the CoTSPc-VIS method, the latex was centrifuged 2 times after being treated with silica. Most important of all, the sera of the latices remained free of polyelectrolyte after stirring at 2600 rpm for 15 minutes, nor could any polyelectrolyte be detected in the sera after the latex was left to stand for more than one week. The major difference between this cleaning technique and the common techniques is that, in the former case, the desorption of polyelectrolyte from the latex surface is enhanced by the addition of another strongly absorbing material.
Fig. 4 The effect of cleaning latex with silica on the presence of polyelectrolyte in the serum. A) after two centrifugations, B) one treatment with silica followed by centrifugation, C) two treatments with silica followed by centrifugation and D) three treatments with silica.

during the collision of latex particles with the silica spheres whereas, in traditional cleaning techniques, the desorption is purely controlled by the adsorption–desorption equilibrium. The disadvantage of adding strongly adsorbing material is that, in a few cases, coagulation of the latex was observed during the cleaning process, probably initiated by the adsorption of cationic particles to the silica surface.

**Latex characterization**

Only a few techniques and few data appear to be available to characterize surface charge densities of cationic latices. We tried to determine the surface charge by potentiometric titration of the latex with silver nitrate immediately after the silica cleaning procedure. All ammonium groups on the surface of the latex particles should have chloride as counterion. It was
found that the surface charge density of various lattices determined in this way showed no relation to the initial MAD concentration. We therefore tried another, although more time-consuming technique, that is replacement of the counterion with hydroxide by the serum replacement technique, rinsing the latex with dilute sodium hydroxide solution (pH ≈ 11). This was followed by extensively washing of the latex with pure water to remove excess of base and by subsequent conductometric acid-base titration of the resulting latex. The surface charge densities determined in this way showed a satisfactory relation to the MAD content and were quite different from those determined by the silver nitrate method. These experiments suggest that cleaning of lattices with silica replaces the chloride ion by an unknown counterion that does not precipitate on the addition of silver nitrate.

Fig. 5 shows a typical titration curve of a latex-containing hydroxide as counterion. At first the conductivity of the latex solution hardly changes on the addition of the hydrochloric acid (0.001 mol/dm³) indicative for the reduced mobility of the counterion. When all the hydroxide ions have been replaced, the conductivity rises steeply as a result of the excess of acid.

![Graph](image)

**Fig. 5** Conductivity as a function of the amount of added acid to latex 62

\[ [\text{HCl}] = 0.001 \text{ mol/dm}^3, 0.321 \text{ g (solid) in } 25 \text{ ml water} \]

**Fig. 6** Surface charge density (\(\mu\text{mol/m}^2\)) as a function of the initial MAD concentration
The number of basic groups on the particle surface can be calculated from the intersection of these two lines. The results of the titration are shown in Fig. 6 and Table 2. It can be seen that the surface charge density increases slightly on raising the initial MAD concentration which confirms the conversion-time curves previously presented in this chapter. Considering the high affinity-type adsorption isotherm of polymers, it seems reasonable to assume that, during the emulsion polymerization, polyelectrolyte is adsorbed by the growing particles and, in consequence, increases the colloidal stability of the growing particles. On further increasing the comonomer (MAD) concentration, more MAD-rich copolymer or even homopolymer formation is likely to occur. The presence of more polyelectrolyte may result in (1) bridging between particles resulting in a broadening of the particle size distribution (Dw/Dm) (2) continuous formation of primary particles resulting in a polydisperse latex system.

The formation of nonanchored polyelectrolyte may be decreased by reducing

The formation of polyelectrolyte may be decreased by reducing the polyelectrolyte concentration.

<table>
<thead>
<tr>
<th>Table 2 Surface charge densities as a function of the MAD concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^3 (MAD) (mol/dm³)</td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>s0</td>
</tr>
<tr>
<td>s1</td>
</tr>
<tr>
<td>s2</td>
</tr>
<tr>
<td>s3</td>
</tr>
<tr>
<td>s4</td>
</tr>
<tr>
<td>s5</td>
</tr>
<tr>
<td>s6</td>
</tr>
<tr>
<td>s7₉₁</td>
</tr>
<tr>
<td>s7₁⁺</td>
</tr>
</tbody>
</table>

a Latex cleaned by serum replacement, followed by AuNPs titration.
b not determined

Addition of 0.5 mol/dm³ [Styrene], [Styrene] = 0.72 mol/dm³ and T = 60°C (see experimental section)
the critical chain length of the growing water-soluble oligomeric radical. A possible way to reduce the critical chain length without affecting the charge density is the addition of the cross-linking agent (divinylbenzene, DVB). Moreover, the cationic charges anchored this way are chemically truly bonded to the latex particles. The results depicted in Table 2 clearly show that the surface charge density decreases on the addition of DVB (compare S2 with SDVB1 and SDVB2). Moreover, the addition of cross-linker caused a broadening of the particle size distribution. Apparently, cross-linker addition causes a dual particle-formation mechanism.

Although many articles have been published in the field of surfactant-free emulsion polymerization in the presence of an ionic comonomer, only few studies report surface charge densities. A review is given in Table 3. We should like to emphasize that the different cleaning techniques used in these

Table 3 Surface charge densities of several latexes produced by the surfactant-free emulsion polymerization in the presence of an ionic comonomer

<table>
<thead>
<tr>
<th>system</th>
<th>D (nm)</th>
<th>surface charge density</th>
<th>( \text{mmol/g} )</th>
<th>( \text{mmol/m}^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1/MASS (^{11})</td>
<td>236</td>
<td>21.2</td>
<td>0.87</td>
<td></td>
</tr>
<tr>
<td>S1/MAVAC/MAA (^{15})</td>
<td>272</td>
<td>15.7</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>S1/MAVAC/MAA (^{18})</td>
<td>288</td>
<td>104.9</td>
<td>5.02</td>
<td></td>
</tr>
<tr>
<td>S1/MAVAC (^{10})</td>
<td>165</td>
<td>35.2</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>S1/MAVAC (^{10})</td>
<td>86</td>
<td>36.1</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>S1/MAVAC (^{16})</td>
<td>67</td>
<td>93.0</td>
<td>1.09</td>
<td></td>
</tr>
<tr>
<td>S1/MAVAC (^{16})</td>
<td>390</td>
<td>15.5</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>S1/MAVAC (^{16})</td>
<td>280</td>
<td>19.7</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>S1/MAVAC (^{16})</td>
<td>280</td>
<td>40.7</td>
<td>1.99</td>
<td></td>
</tr>
<tr>
<td>S1/MAVAC (^{16})</td>
<td>151</td>
<td>80.6</td>
<td>2.13</td>
<td></td>
</tr>
</tbody>
</table>

S1: styrene, MAVAC: butylacrylate, MAA: methacrylic acid, Na2S: sodium styrene sulphonate, NaVTS: sodium vinyltrimethylethyl sulphonate, AA: acrylic acid, \( \text{EMPS}: \) 1-ethyl 2-methy 5-vinylpyridinium bromide, DVB: 1,2-dimethyl 5-vinylpyridinium methylsulphate, ANPS: 2-acylamido-2-methyl propane sulphonic acid
studies, together with the different extent of cleaning, will certainly affect the reported surface charge densities. In the case of emulsion polymerization of styrene with butylacrylate and methacrylic acid, the authors in fact suggest the incomplete removal of adsorbed polyelectrolyte.

The surface charge densities as depicted in Table 2 constitute cationic monomeric units and initiator residues at the end of polymeric chains that have not been buried. Since immobilization of the slightly acidic protonated initiator residues (pKₐ = 12.5⁴⁸,⁴⁹) on the latex surface will certainly decrease its pKₐ, a difference in basicity between the two types of cationic groups both having hydroxide as the counterion was to be expected.⁵⁰ The titration curve (Fig. 5), however, clearly demonstrates that this distinction cannot be made. Although the concentration of initiator residues at the latex surface cannot be determined, an estimation can be made. Even at low MAD concentrations ([MAD] = 5.66 x 10⁻⁵ mol/dm³) the polymerization is completed within three hours (see Fig. 1), which means that approx. 30% of the initiator has thermally decomposed (kₐ(AIBA) = 3.22 x 10⁻⁶ s⁻¹, at 60°C⁵¹). From the polymerization conditions, as given in the experimental section, the maximum charge density per unit of weight due exclusively to initiator residues can now be calculated. They amount to 37 μmol/g. It must be noted that this can only be the case if all decomposed initiator radicals induce polymerization, no free polyelectrolyte is formed and no initiator residues are being buried in the latex particles. Clearly, these prerequisites do not hold in the present case; the efficiency of the initiator will be less than unity (for solution polymerization this value usually ranges between 0.6-1⁴³), polyelectrolyte is formed and initiator residues will be buried inside latex particles. Assuming an efficiency of 0.7, the maximum concentration of initiator molecules at the latex surface is 26 μmol/g. The surface charge density of S₀ is much lower than this theoretical value ([MAD] = 0, Table 2. It should be noted that the reaction time in this case was much longer than 3 hrs). Liu et al. reported a surface charge density due to AIBA residues of
Table 4: Surface charge density of latexes produced by the shot-growth method

<table>
<thead>
<tr>
<th>Latex</th>
<th>$10^2 \text{ unmol/g}$</th>
<th>D (nm)</th>
<th>$2\pi r_{w1}$</th>
<th>Surface charge density $\mu$mol/g</th>
<th>$\mu$mol/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>S01</td>
<td>12.6</td>
<td>220</td>
<td>1.91</td>
<td>26.9</td>
<td>1.00</td>
</tr>
<tr>
<td>S02</td>
<td>25.2</td>
<td>204</td>
<td>1.02</td>
<td>28.8</td>
<td>1.03</td>
</tr>
<tr>
<td>S03</td>
<td>59.3</td>
<td>214</td>
<td>1.01</td>
<td>32.6</td>
<td>1.22</td>
</tr>
<tr>
<td>S04</td>
<td>75.5</td>
<td>218</td>
<td>1.16</td>
<td>30.9</td>
<td>1.18</td>
</tr>
</tbody>
</table>

*experimental details are given in the experimental section.*

(0.3 $\mu$mol/g in the case of EMVPB (total charge density is 15.3 $\mu$mol/g, see Table 3).

Although the addition of charged comonomer results in latexes having a higher solid content and a greater surface charge density than in the absence of ionic monomer, the surface charge may be further increased by the so-called seeded-growth method and shot-growth emulsion polymerization. The difference between these two methods is that in the latter case, a second charge of monomer is added to the emulsion while the first charge is still reacting. In a seeded-growth experiment the latex (seed) is purified before a second emulsion polymerization is carried out. It is claimed that a better morphology as well as an increase of surface charge density⁵⁴,⁵⁵ can be achieved in the case of the shot-growth method compared with the seeded-growth technique⁵⁹. This phenomenon has been explained by a difference in swelling behaviour between a purified (i.e. monomer free) and unpurified latex⁵⁵,⁶⁰-⁶⁶ or by the presence of oligomeric radicals in the slightly monomer-swollen particles⁵⁷,⁵⁸. The results of the shot-growth method are given in Table 4.

The experimental conditions that were used during first charge of the shot-growth reaction were identical to the conditions used to synthesize latex S2 (see Table 2 and experimental section). After three hours (conversion > 80%) a second charge of monomer, comonomer, initiator and water is added. It can be concluded that the surface charge density increases slightly by using the shot-growth technique. In the case of high concentration of MAD, the resulting latex was less monodisperse. The production of polydisperse latices by the
addition of a second charge at low conversion (50%) agrees closely with the findings of Sakai.46

From the batch and shot-growth experiments (Table 2 and 4) it can be concluded that in both cases the addition of comonomer slightly increases the surface charge density. Increasing the comonomer concentration will increase the total surface (as a result of particle-size reduction) and therefore more comonomer can be built in (increase of total charge per unit of weight, μmol/g). We postulate that MAD can be built into the latex surface only up to a certain level of charge density. As soon as this level is reached, the incoming comonomer-rich oligomeric radicals are prevented from entering and inducing polymerization in the particles as a result of coulombic repulsion. The shot-growth experiments confirm this line of thought. The quasi indifference of surface charge densities presented in Table 3 to changing the comonomer, despite the great difference between ionic comonomers and the various experimental conditions used to prepare these functionalized latices, can also be understood on these grounds.

A possible alternative route in synthesizing highly charged latices and simultaneously avoiding the formation of free polyelectrolyte is the post-polymerization method.4 However, some drawbacks are introduced by this technique, (1) large (unstable) particles are produced in the case of surfactant-free emulsion copolymerization of a hydrophobic monomer, (2) large quantities of comonomer will be buried inside the polymer particles and thus be unavailable for functionalization and (3) functionalization may be incomplete as a result of the formation of highly charged surface during the modification.

Conclusion

3-(methacrylamidopropyl)trimethylammonium chloride (MAD) can be used as a comonomer in the emulsion polymerization of styrene with azo-
bis(isobutyramidine hydrochloride) (AIBA) as initiator. Increasing comonomer concentration appeared to increase the conversion rate of styrene, which can be attributed to particle size reduction. Since the latices will be used as a support for cobalt(II) phthalocyanine-tetrasodiumsulphonate (CoTSPh), a catalyst in the thiol oxidation, and since this catalytic system is extremely sensitive to low concentrations of inevitably produced free polyelectrolyte, the latices must be thoroughly cleaned prior to their use in the catalytic reaction. Conventional purification techniques like serum replacement, dialfiltration and centrifugation were found to be insufficient and continuous desorption could be observed on standing or after stirring. Centrifugation of latices, followed by treatment with silica, was found to clean the latices to such an extent as to lead to serum-containing polyelectrolyte concentrations lower than \( [N^+] < 5 \times 10^{-7} \) mol/dm\(^3\). Surface charge density as determined by conductometric acid-base titrations increased on increasing MAD concentration. Addition of cross-linking agent (divinylbenzene) decreased the surface charge density and broadened the particle size distribution. So-called shot-growth emulsion polymerization hardly increased the surface charge density.

**Acknowledgement**

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Cationic latices as co-catalyst in the cobaltphthalocyanine-catalyzed oxidation of 2-mercaptoethanol

Karel H. van Streun, Wil J. Belt, Pieter Piet and Anton L. German

Summary

Cationic latices, products of emulsion copolymerization of styrene with 3-(methacrylamidinopropyl)trimethylammoniumchloride (MAD), and its homopolymer (PMAD) have been tested as co-catalyst in the autoxidation of 2-mercaptoethanol in the presence of cobalt(II)phthalocyanine-tetrasodiumsulphonate (CoTSPc). It was found that all systems enhanced the catalytic activity compared with the polymer-free CoTSPc containing system. The systems under study invariably showed an enzyme-like behaviour. Unfortunately, the stability after successive runs is still not quite satisfactory. From the observed catalytic activities and spectrophotometric measurements, it can be concluded that, in addition to a high surface charge density, flexible polymeric cationic chains of sufficient length are also necessary to enhance the activity of CoTSPc-bound latex systems in thiol oxidation.

Introduction

Catalysts play a major role in many biochemical reactions and industrial processes. To allow continuous operation, an important requirement for industrial processes, many catalysts have been immobilized onto insoluble, often porous supporting particles. In addition, economics and environmental legislation favour immobilization. However, the catalytic activity often
decreases on immobilization as a result of mass transport limitations. In the last decade, attention has been paid to the immobilization of catalysts without the loss of reactivity. Polymer colloids (latices) offer interesting possibilities of combining these two requirements. Latex particles, products of emulsion polymerization, in spite of low porosity, exhibit a high surface area due to the small particle size (submicron region). Latices can be functionalized during their synthesis by the addition of functional monomers or by post-polymerization functionalization. Functionalized latices are sometimes called reactive latices.

Polymer colloids have been used to immobilize enzymes\textsuperscript{12} for various purposes, sulphonic acid for sucrose inversion\textsuperscript{4-6} and for ester hydrolysis\textsuperscript{6,7}. cobalt complexes for the autoxidation of 1-decanethiol\textsuperscript{8,9}, 2,6-di-tert-butylphenol\textsuperscript{10} and tetralin\textsuperscript{11}, imidazole for ester hydrolysis\textsuperscript{12} and histamine-Cu complex for the oxidation of ascorbic acid\textsuperscript{13}. Functionalized latices have also been used in diagnostic tests\textsuperscript{14} and paints\textsuperscript{15,16}. Cross-linked polymer colloids, so-called microgels\textsuperscript{17}, allow operations in organic solvents. For example microgels were used to immobilize sulphonic acid for ester\textsuperscript{18,19} and sucrose hydrolysis\textsuperscript{10}, hydroxamic acid for ester hydrolysis\textsuperscript{20}, primary amines for ester hydrolysis\textsuperscript{21}, and phase-transfer catalysts\textsuperscript{22} in various applications.

We recently reported the immobilization of cobalt(II)phthalocyanine-tetrasodiumsulphonate (CoTSPc, 1, scheme 1) on latex particles stabilized by block copolymers of styrene and quaternized 4-vinylpyridine (PS-b-qPVP) for the autoxidation of 2-mercaptoethanol (ME)\textsuperscript{23}. The block copolymer stabilizes latex particles, binds CoTSPc and, in addition, the cationic segments of PS-b-qPVP act as co-catalyst in the thiol oxidation. Cationic polymers are known accelerators in the CoTSPc-catalyzed thiol oxidation. The role of the co-catalyst is fourfold, (1) binding CoTSPc, (2) substrate enrichment, (3) preventing the formation of inactive oxygen-bridged dimers of CoTSPc and (4) formation of highly active CoTSPc aggregates. The catalytic activity observed
polymers ([N\(^n\)] \geq 5 \times 10^{-7} \text{ M}) based on the observation of monomerisation or aggregation of CoTSPc in the absence or presence of polyelectrolyte, respectively\(^{36}\). A cleaned latex (55) was stirred under the experimental conditions for 15 minutes at 2600 rpm. The presence of free polyelectrolyte could not be demonstrated by spectrophotometric measurements after centrifugation. This was also verified by measuring the catalytic activity of the serum after addition of CoTSPc and pH adjustment. The oxidation rate observed in the serum was almost identical to that found in the polymer-free, i.e. conventional CoTSPc system, thus indicating the absence of polyelectrolyte. A similar experiment was carried out, but now CoTSPc was added prior to stirring. In this case, too, after stirring and centrifugation, desorption of CoTSPc or polyelectrolyte could not be demonstrated by UV-VIS spectrophotometry. The catalytic activity of this serum (only pH adjustment) was too low to be detected by our monitoring system, as is also the case in the oxidation of 2-mercaptoethanol catalyzed by base only. From these experiments it may be inferred that any possible desorption of CoTSPc and/or polyelectrolyte will be highly improbable during the measurements of the catalytic activity of the latex systems.

A feature that predominately determines the possible commercial applicability of catalysts is their activity after reuse. The activity of the systems under study, as depicted in Fig. 1, clearly shows a decrease in activity after successive runs. It has been shown in our laboratory that hydrogen peroxide accumulation is responsible for this behaviour. The overall thiol oxidation comprises two reactions, CoTSPc catalyzed thiol oxidation yielding H\(_2\)O\(_2\) as side product (step 1), that will oxidize a second thiol in a consecutive reaction (step 2). The second step is not affected by the presence of CoTSPc or polyelectrolyte\(^{27,28}\).
\[
\begin{align*}
2 \text{RSH} + O_2 & \rightarrow \text{RSSR} + H_2O_2 \quad (1) \\
2 \text{RSH} + H_2O_2 & \rightarrow \text{RSSR} + 2 H_2O \quad (2) \\
4 \text{RSH} + O_2 & \rightarrow 2 \text{RSSR} + 2 H_2O
\end{align*}
\]

In our earlier work on PVA-m as polymer ligand, it was demonstrated that CoTSPc is deactivated by H₂O₂ by direct oxidation of the phthalocyanine ring, while the polymer backbone is affected by the oxidation by H₂O₂ of thiol and disulphide to sulphur-containing oxo-acids. Although these oxo-acids are only formed in very low concentrations (less than 1% of the total oxygen consumption) substantial accumulation of disulphide after successive runs will enhance their formation.

Colloidal (in)stability may also play a role in the case of the CoTSPc-

![Graphs showing initial reaction rate and catalytic activity as a function of pH](image)

**Fig. 1** Initial reaction rate after successive runs at 25°C

\[\text{[CoTSPc]} = 4 \times 10^{-7} \text{mol/cm}^3,\]
\[\text{[H}^+\text{]}(\text{SS}) = 3.6 \times 10^{-6} \text{mol/cm}^3,\]
\[\text{[H}^+\text{]}(\text{SS}) = 4.2 \times 10^{-6} \text{mol/cm}^3,\]
\[\text{[H}^+\text{]}(\text{PMAD}) = 10^{-6} \text{mol/cm}^3, \text{pH} = 9.0. \text{ Every run is started by the addition of 1 ml ME (0.0143 mol), CI: 85, Δ: SS3, *: PMAD} \]

**Fig. 2** Catalytic activity as a function of pH at 25°C

\[\text{[ME]} = 0.143 \text{mol/cm}^3, \text{[CoTSPc]} = 4 \times 10^{-7} \text{mol/cm}^3,\]
\[\text{[H}^+\text{]}(\text{SS}) = 3.6 \times 10^{-6} \text{mol/cm}^3,\]
\[\text{[H}^+\text{]}(\text{SS}) = 4.2 \times 10^{-6} \text{mol/cm}^3,\]
\[\text{[H}^+\text{]}(\text{PMAD}) = 10^{-6} \text{mol/cm}^3, \text{CI: 85, Δ: SS3, *: PMAD} \]
bound latex system. The colloidal stability is a known problem in catalyst-immobilized latex systems\textsuperscript{9,22,26}. In the case of CoTSPc-bound latex system stabilized by a block copolymer of styrene and quaternized 4-vinylpyridine (PS-b-qPVP) we also observed some colloidal instability\textsuperscript{23}. For the present latex systems (SS and SG3) we have investigated this undesired phenomenon in more detail. Unfortunately, due to the low latex concentrations, only qualitative information can be obtained. The difference observed between the scanning electron micrographs (SEM) of latices before and after stirring were too small to reveal any significant information. Both latex systems did not show any coagulation after stirring at 2600 rpm for 15 minutes. However, raising the pH to 12 some coagulation in the form of coagulum adhering to the reactor wall could be observed. Similar coagulation effects were observed on increasing the ionic strength of the latex solution (0.01 M). On addition of CoTSPc or 2-mercaptoethanol, no further coagulation was observed. Although this deactivation of the catalytic systems may affect the activity in the reuse experiments, it hardly influences the initial reaction rate measured.

**Kinetics**

It was shown earlier in our laboratory that cationic polymers as co-catalyst in the CoTSPc-catalyzed oxidation of 2-mercaptoethanol (ME) give rise to an enzyme-like kinetic behavior. In the present investigation we have studied the catalytic behavior and kinetics of the colloidally immobilized systems.

The pH dependence of the oxidation rate as depicted in Fig. 2 is typical of a polyelectrolyte-catalyzed thiol oxidation. It is believed that the reactive species is not thiol, but its anion. Since 2-mercaptoethanol is slightly acidic (pK\textsubscript{a} = 9.6), it can be expected that the oxidation rate will increase on increasing pH. However, the simultaneous increase of ionic strength and hydroxide concentration leads to a competitive ion effect and results in the observed optimum in catalytic activity\textsuperscript{26,31}. Fig. 2 also
Fig. 3 Reaction rate vs. co-catalyst concentration (expressed as [N°])
at 25°C
[MHE] = 0.143 mol/dm³, [CoTSPe] = 4×10⁻⁷ mol/dm³,
ph = 9.0, □: 55, △: 65, *: PMAD

Fig. 4 Reaction rate as a function of the catalyst concentration
(keeping N°/Co ratio constant) at 25°C
[MHE] = 0.143 mol/dm³, ph = 9.0,
N°/Co(55) = 9, N°/Co(65) = 10.4, N°/Co(PMAD) = 25,
□: 85, △: 65, *: PMAD
clearly shows the higher activity of free PMAD compared with the latex systems.

The oxidation rate as a function of the co-catalyst concentration shown in Fig. 3, is again typical of cationic polymer co-catalyzed thiol oxidation. Van Welzen et al. showed by UV–VIS spectroscopy that highly active aggregates of CoTSPe are formed at N°/Co ≥ 4⁹⁰. The optimum experimentally found at higher N°/Co ratio stems from the fact that, at N°/Co = 4, the complex is electrosstatically neutral (CoTSPe is fourfold negative) and hence no substrate enrichment can occur. After an optimum polymer/CoTSPe ratio is reached, further increase of the co-catalyst concentration (keeping [CoTSPe] constant) will lead to a decrease in the local thiolate anion concentration at the cobalt centre. In addition, the increase in polyelectrolyte concentration
Fig. 5 Catalytic activity as a function of the substrate (ME) concentration at 25°C:

- pH = 9.0, [CoTNPc] = 4 x 10^{-7} \text{ mol/dm}^3,
- \{W\} ([SS]) = 3.6 x 10^{-6} \text{ mol/dm}^3, \{W\} ([SSS]) = 4.2 x 10^{-6} \text{ mol/dm}^3,
- \{W\} ([PMSD]) = 1 x 10^{-5} \text{ mol/dm}^3, \bullet: \text{SS}, \Delta: \text{SSS}, \ast: \text{PMSD}.

Fig. 6 Lineweaver-Burk plots of the catalytic systems under study, for experimental conditions see Fig. 5.

Causes an increase of ionic strength, thus affecting the polymer coil structure, and simultaneously causing substrate competition between polyelectrolyte counterions and thiolate anions. The observed catalytic activities of the latex containing systems as a function of the latex concentration are dealt with elsewhere in this chapter.

Before determining the reaction constants of the systems, the absence of mass transfer limitations must be demonstrated. The linear dependence of the catalytic activity on the catalyst concentration (N'/Co = constant) clearly demonstrates the absence of mass transport limitations in the present case (Fig. 4).

For the three catalytic systems under study, a saturation behavior typical of enzyme-like kinetics was found on measuring the reactivity as a function of the substrate concentration (Fig. 5). This type of kinetics can be described by the Michaelis-Menten kinetics.
\[ R = \frac{k_2[CoTS\text{Pc}][\text{ME}]}{K_M + [\text{ME}]} \]

where \( k_2 \) stands for the turnover number, \( K_M \) for the Michaelis constant and [ME] for the 2-mercaptoethanol concentration. From the double reciprocal plot of reactivity vs. substrate concentration (the so-called Lineweaver-Burk plot, Fig. 6) the turnover number and Michaelis constant can be determined (Table 2).

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Turnover numbers and Michaelis constants of the catalytic systems under study. Experimental conditions as in Fig. 5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( s_2(\text{s}^{-1}) )</td>
</tr>
<tr>
<td>PMAD</td>
<td>2000 +/- 100</td>
</tr>
<tr>
<td>95</td>
<td>690 +/- 10</td>
</tr>
<tr>
<td>903</td>
<td>630 +/- 10</td>
</tr>
</tbody>
</table>

**Relation between structure and catalytic activity**

The present systems, together with those studied earlier in our laboratory, are listed in Table 3. The activity of the homopolymer PMAD agrees closely with other homogeneous cationic polymers systems, for example 2,4-iodene and PVAm. Due to the long side groups carrying the cationic groups, the linear charge density parameter \( \sigma \) cannot be calculated accurately. The estimated linear charge density (\( \sigma = 1.13 \)) lies in the same region as those calculated for PVAm (\( \sigma = 0.99 \)) and 2,4-iodene (\( \sigma = 1.44 \)). Since it has been shown that the catalytic activity of these polyelectrolytes is proportional to the linear charge- density parameter \( \sigma \), the observed activity for PMAD closely agrees with the estimated linear charge density.

However, charge density (in terms of the charge density of polymers or surface charge density of lattices) does not only dominate the catalytic
Table 5: Reaction rates of several CoTSPc-containing systems

<table>
<thead>
<tr>
<th>System</th>
<th>$R/R_0^a$</th>
<th>$\phi\hbox{m}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>homogenous</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DH-5</td>
<td>1</td>
<td>8.0</td>
</tr>
<tr>
<td>PVAm 35</td>
<td>41.1</td>
<td>8.1</td>
</tr>
<tr>
<td>2,4-ionene/Ca 2-26</td>
<td>48.3</td>
<td>8.3</td>
</tr>
<tr>
<td>qVP/polymer 23</td>
<td>20.5  b</td>
<td>8.7</td>
</tr>
<tr>
<td>PS-b-qVP 23</td>
<td>16.1  b</td>
<td>8.7</td>
</tr>
<tr>
<td>PMMA</td>
<td>42.5</td>
<td>9.0</td>
</tr>
<tr>
<td>heterogenous</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAm/silica 23</td>
<td>9.7</td>
<td>8.1</td>
</tr>
<tr>
<td>2,4-ionene/Ca 2-26</td>
<td>10.3</td>
<td>7.3</td>
</tr>
<tr>
<td>qVP/later 23</td>
<td>24.9  b</td>
<td>8.7</td>
</tr>
<tr>
<td>MAD/latex 85</td>
<td>16.0</td>
<td>9.0</td>
</tr>
<tr>
<td>MAD/latex 505</td>
<td>9.1</td>
<td>9.0</td>
</tr>
</tbody>
</table>

$^a$ $k_3 = 2.75 \times 10^{-5}$ mol thiol/cm$^3$s, $[\text{CoTSPc}] = 4 \times 10^{-7}$ mol/cm$^3$.
$[\text{Me}] = 0.145$ mol/cm$^3$, $T = 25^\circ C$

$^b$ measured at $10^\circ C$ when saturation is reached

activity. This was clearly demonstrated by van Velzen et al., who compared the reactivities of 6,6-ionene and 2,10-ionene, both having the same linear charge-density parameter ($\sigma = 0.82$)$^{36}$.

6,6-ionene behaved like a (common) polyelectrolyte. Aggregation of CoTSPc at $N^+/Co \geq 4$ was not disturbed at high polymer concentrations. This strong aggregation of CoTSPc, responsible for the observed increase in reactivity, was attributed to the suppression of charge repulsion between the fourfold negatively charged CoTSPc molecules on addition of cationically charged polymers. The presence of polymer of considerable chain length is, however, of essential importance to CoTSPc aggregation, since monomeric analogues of PVAm and 2,4-ionene hardly affect the catalytic activity$^{34}$.

In the case of the soap-like 2,10-ionene, aggregation occurring at $N^+/Co \geq 4$ disappeared again on further increasing polyelectrolyte concentration. This phenomenon was attributed to the formation of micelle-like hydrophobic domains, favoring CoTSPc monomerization. Interestingly, on diluting these micelle-containing solutions (keeping $N^+/Co$ constant), aggregation of CoTSPc
showed up again. It was concluded that monomerization of CoTSPc is not directly induced by the hydrophobic segments on the polymer backbone, but indirectly through the formation of micelle-like structures. Apparently the polymeric effect that causes the observed rate enhancement is destroyed as a result of reduction of the mobility of cationic charge on micellization. On further addition of 2,10-loneness, more micelles will be formed and, in consequence, more monomerization will be observed.

If surfactants containing long cationic tails, for example block copolymers of styrene and quaternized 4-vinylpyridine (PS-b-qPVP)\textsuperscript{28} or oleyl-3,3-lonene\textsuperscript{27}, are used as co-catalysts instead of soap-like 2,10-lonenes contrasting results are observed. The micellar surface of these polymeric surfactants contains hydrophilic polymer segments of sufficiently high charge density, extending into the water phase. The presence of CoTSPc aggregates in

![Graphical representation](image)

**Fig. 7** VIS spectra of CoTSPc in the presence of oleyl-3,3-lonene

[CotSPc] = 10^{-5} \text{ mol/dm}^3, T = 25^\circ C

A: \text{Co}^+/\text{Co} = 100, B: \text{Co}^+/\text{Co} = 5000, C: \text{Co}^+/\text{Co} = 10000

**Fig. 8** VIS spectra of CoTSPc in the presence of CTAB

[CotSPc] = 10^{-5} \text{ mol/dm}^3, T = 25^\circ C

A: \text{Co}^+/\text{Co} = 100, B: \text{Co}^+/\text{Co} = 1000, C: \text{Co}^+/\text{Co} = 10000
PS-b-oPVP\textsuperscript{28} and oleyl-3,3-ionene containing solutions (absorbance at 628 nm, Fig. 7) indicates that these polymer charges have sufficient mobility and charge density to allow aggregation and agrees closely with the similarity of the observed catalytic activities when comparing both block copolymers with their homopolymer. Only at relatively high polymeric surfactant concentration is CoTSPc deaggregation observed due to the presence of large numbers of micelles (absorbance at 660 nm).

The effect of highly charged co-catalysts lacking the essential polymeric character on the catalytic activity is also clearly demonstrated by the oxidation of 2-mercaptoethanol catalyzed by hexadecyltrimethylammoniumbromide (CTAB)\textsuperscript{28}. In spite of the high surface-charge density of the micelles formed by CTAB (surface-charge density: 3.69 $\mu$mol/m$^2$), the observed reactivity (at [CTAB] > cmc) was even lower than for the polymer-free system. This observed decrease in catalytic activity can be understood by the VIS spectrum of CoTSPc in the presence of CTAB (Fig. 8). The addition of surfactant hardly affects the equilibrium between monomer and aggregate of CoTSPc, even though $N^+/Co >> 4$ (curve A, [CTAB] = $10^{-4}$ mol/dm$^3$, is nearly identical to the soap-free CoTSPc spectrum). At the onset of micelle formation (cmc = 9x$10^{-4}$ mol/dm$^3$),\textsuperscript{28} the shoulder at 628 nm disappears, which is indicative of CoTSPc deaggregation. The presence of micelles in the catalytic system induces the formation of the less active monomeric CoTSPc and, in consequence, a lower activity is observed. Interestingly, Ford et al. recently reported the CoTSPc-catalyzed oxidation of the more hydrophobic 1-decanethiol in the presence of cationic lattices prepared by emulsion polymerization of styrene with polymerizable surfactants.\textsuperscript{9} The observed rate enhancement was found to be equal to that in experiments using only CTAB. In view of the above considerations, the observed rate enhancement is likely due to the partial solubilization of the water-insoluble 1-decanethiol. Similar results were found for the oxidation of 1-dodecanethiol catalyzed by CTAB\textsuperscript{28}.

The observed reactivity of the MAD/latex systems is in line with the VIS
Fig. 9 VIS reflection spectra of SG3/CoTSPc at 25°C

A: $\frac{N^+}{Co} = 2.1\),  B: $\frac{N^+}{Co} = 10.4$,  C: $\frac{N^+}{Co} = 41.4$

reflection spectra of latex SG3 at different N⁺/Co ratios (Fig. 9). The shoulder at 628 nm is indicative of the presence of the highly active CoTSPc aggregate. However, the absorbance at 660 nm demonstrates the presence of the less active CoTSPc monomer. This monomerization is likely to be the reason for the observed lower reactivity compared with PMAD. It appears that the surface charge density of the lattices under study is too low and induces little aggregation. Very striking is the increase of monomerization on increasing latex concentration ([CoTSPc] = constant), an effect that agrees closely with the above-mentioned considerations. The latex particles can be regarded as microreactors. On increasing the latex concentration (keeping CoTSPc concentration constant) the number of CoTSPc molecules per latex particle will decrease and monomerization will result. The serum of the latex ([N⁺] = 8.28 µmol/dm³, [CoTSPc] = 4 µmol/dm³, curve A in Fig. 9) was found to contain free CoTSPc after centrifugation. About 70% of CoTSPC was bound to the latex surface, i.e. $\frac{N^+}{Co}$ (surface) = 3. On doubling the latex concentration ([N⁺] = 18.56 µmol/dm³, [CoTSPc] = 4 µmol/dm³), CoTSPc could not be detected in the
scrum after centrifugation. A 3:1 ratio implies an overall negatively charged latex surface, in good agreement with the observed lower reactivity compared with higher latex concentration (Fig. 3). The presence of the more reactive aggregates of CoTSPc at this low latex concentration is counteracted by the overall negatively charged latex surface that will prevent substrate enrichment. Increasing the latex concentration will allow substrate enrichment, but will also favour the undesirable CoTSPc monomerization. At even higher latex concentration, this monomerization will cause a decrease in the observed reactivity. The close resemblance between both the turnover number and the Michaelis constant for the two MAD containing latices implies that the differences in both particle size and surface-charge density within this range hardly affect the catalytic activity.

Table 3 shows that all immobilized systems exhibit a greater catalytic activity than the polymer-free system. It is interesting to compare the MAD-stabilized latices with those stabilized by a block copolymer PS-b-qPVP. The PS-b-qPVP-stabilized latex shows a much higher activity than the MAD/latex systems. Moreover, the increase in activity on immobilizing the block copolymer is striking. However, the methods of preparing these two latex systems hardly allow any comparison to be made. The block copolymer-stabilized latex system is prepared by emulsion polymerization of styrene in the presence of PS-b-qPVP as an emulsifier, whereas the MAD stabilized latices are prepared by emulsion polymerization of styrene in the presence of the cationic comonomer. As was pointed out in our previous paper, MAD-rich oligomeric radicals will scarcely be trapped by highly (also positively) charged latex particles before they terminate. It is more probable that more hydrophobic styrene-rich oligomeric radicals of low molar mass will be captured by the monomer-swollen particles and initiate polymerization. Consequently, the linear charge-density parameter and molar mass of such anchored polymer chains will be lower than those of the homopolymer (PMAD).

On these grounds we picture the aggregation of CoTSPc as drawn in scheme.
2. Structure A shows the aggregation of CoTSPc induced by common cationic polyelectrolytes. The flexibility of the polymer backbone, a sufficiently high charge density and a considerable chain length are needed to allow CoTSPc aggregation. The micellar structure as drawn in B lacks these mobile charges; the less mobile charges at the micelle surface, together with the absence of sufficient chain length, prevent CoTSPc aggregation. Structure C reflects the MAD-stabilized latex systems; some cationic charge is spread over the latex surface (mainly initiator residues) and cationic charge is present as part of immobilized oligomeric chains of low molar mass. This structure, that can be regarded as intermediate between structures B and D, contains both monomeric and aggregated forms of CoTSPc and a moderate activity is therefore observed. The PS-b-qPVP-stabilized latex (D) exhibits a truly immobilized
polyelectrolyte system. Aggregation of CoTSPc can readily occur due to the presence of flexible, long polyelectrolyte chains at the latex surface and, in consequence, the observed catalytic activity is similar to that in the homogeneous system.

From the experiments with PMAD and MAD/latices we derived further supporting evidence for our assumption that anchored cationic polymers solvated in the interfacial boundary layer must combine a high charge density with a not too low chain length.

Conclusions

The colloidal support systems under study showed an accelerating effect on the CoTSPc catalyzed oxidation of 2-mercaptoethanol compared with the polymer-free system. The observed stability after successive runs is rather poor. All three systems showed Michaelis-Menten type of kinetics. The differences between the two copolymeric (styrene-MAD) latex systems (particle size and surface charge density) do not affect the catalytic activity. The observed reaction rates and also spectrophotometric measurements suggest that charge density alone does not determine the catalytic activity. It appears that flexible cationic polymer chains of sufficient chain length are also needed to suppress charge repulsion between CoTSPc molecules, thus allowing the formation of the catalytically highly active CoTSPc aggregates.

Acknowledgement

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Appendix

Attempts to synthesize functional macromonomers, macroinitiators and block copolymers

Introduction

In chapter 7, experimental evidence indicates that charge density, that is surface charge density for particles or linear charge-density parameter for linear polymers is not the only important factor in the design of a highly active co-catalyst in the CoTSPr-catalyzed oxidation of 2-mercaptoethanol. The formation of CoTSPr aggregates, responsible for the observed increase in reactivity, is found to be severely hindered if the cationic charges of the polymer backbone are fixed to the surface of micelles or particles in such a way as to diminish the mobility of the backbone. In addition, the chain length of the anchored polyelectrolyte must not be too small to allow CoTSPr aggregation.

In order to design a CoTSPr-immobilized system that will be successful in the catalytic oxidation of 2-mercaptoethanol, viz. a highly active immobilized system exhibiting intrinsic kinetics (absence of mass transport limitation), we believe that the catalyst support has to fulfill two requirements (1) absence of pores and (2) presence of cationic polymers on the surface. It can be concluded from chapter 4 that porous supports of comparatively low catalytic activity and homogeneously distributed CoTSPr will certainly exhibit mass transport limitation. Above all, it is very unlikely that the fourfold negatively charged CoTSPr will penetrate into the porous support.

The reduced specific surface area (m²/g support) as a result of low porosity or diminished accessibility of the pores can be counterbalanced by particle size reduction. An important disadvantage of particle size reduction is the need for more sophisticated separation techniques, like membrane
filtration. It has already been stated that particles produced by emulsion polymerization may fulfill these (high) expectations and requirements.

On the basis of chapters 6 and 7 it can be concluded that emulsion copolymerization of styrene and a water-soluble comonomer leads to most interesting results and to the best solution feasible to date, but it was realised that, in principle, this is not the best route for synthesizing highly active systems. Despite a high surface charge density, the absence of long flexible cationic polymer chains at the latex surface gives rise to a relatively low catalytic activity. The very great difference in monomer partition coefficients, together with unfavourable reactivity ratios (often unknown for systems exhibiting big differences in partition coefficients) are the main reasons for the partial success of this approach. In order to synthesize a latex system that will be more active, we believe it is necessary to use tailor-made and separately synthesized polyelectrolytes during the emulsion polymerization. In this appendix we describe attempts that have been undertaken to synthesize these polyelectrolytes. Approaches that have not yet led to successful systems, but in our opinion, have a high potential value in future research.

Experimental

2,4-Ionene and aminated 2,4-ionene were synthesized according to the method described in chapter 2. 3-N,N-dimethylamino-α-propylchloride (d, scheme 2, DMAPCI) was isolated from its salt (Merck) according to literature1. All polymerizations were carried out under a nitrogen atmosphere.

Emulsion polymerizations were carried out in a way similar to that described in chapter 6.

FT-IR spectra were recorded at a Mattson Polaris FT-IR spectrophotometer. 
1H-NMR spectra were measured using a Bruker 200MHz instrument.
Block copolymers (I, scheme 1)

Block copolymer of styrene and ionene

Prior to the anionic polymerization of styrene in toluene, the usual precautions were taken to avoid contamination by water or oxygen. All reactants were distilled before use and stored under nitrogen atmosphere. The polymerization was initiated at -80°C by the addition n-butyllithium. The temperature was raised to 0°C and after 30 minutes, to 30°C. After 6 hrs the temperature was lowered to -80°C. Before terminating the living polymer with an excess of 1,4-dibromobutane, a sample was taken and precipitated in 2-propanol. After the addition of 1,4-dibromobutane, the colour of the reaction mixture changed from deep red to light yellow. The product (PS-Br) was precipitated in 2-propanol. GPC measurements showed a slight increase in molar mass after termination with 1,4-dibromobutane.

4 g PS-Br (Mn = 7800) and 0.9 g aminated 2,4-ionene (Mn = 1700) were suspended in 35 ml toluene and 2 ml water. After reacting at 40°C for 26 days, the polymer mixture was precipitated in acetone. The resulting product was twice boiled in toluene followed by filtration. Two products were obtained, toluene soluble and toluene-insoluble polymer. The toluene soluble product was found to be polystyrene (^1H and ^13C NMR, IR and elemental analysis). Similar results were obtained using DMF/water (4/1) at 54°C for 20 days.

The polymerization of DMAPCI in the presence of functionalized polystyrene (R = 6, scheme 2) was carried out under different experimental conditions. (1) 6 g functionalized polystyrene (Mn = 3200) and 5.7 g DMAPCI were dissolved in 35 ml DMF. After 5 days stirring at 55°C the reaction mixture was precipitated in acetone and treated as described above. (2) 3.1 g functionalized polystyrene and 8.2 g DMAPCI were dissolved in 1.6 ml DMF and 0.4 ml water. After 48 hrs at 55°C the reaction product was precipitated in acetone. (3) 3 g functionalized polystyrene was dissolved in 8.2 g DMAPCI and 0.8 ml water. The product was precipitated in acetone after reacting at 100°C for 24 hrs.
Macromonomers (2, scheme 1)

4-styryloxydodecyl-3,3-ionone

The coupling of 4-vinylphenol with 1,12-dibromododecane was carried out according to literature. The product (R = 2, scheme 2) was chromatographically separated over silica. The product was first eluted with petroleum-ether (40-60) to isolate 1,12-dibromododecane. After elution with tetrachloromethane the desired product was isolated (chemical yield 48%).

The solubility of the product in DMF was very low. To improve DMF and water solubility, the product was reacted with N,N,N',N'-tetramethylethylenediamine (TMEDA) in refluxing acetone for 2 hrs. After evaporating the solvent, the remaining solid was washed with hexane. After recrystallisation in diisopropylether/dichloromethane the chemical yield was 73%. Polymerization of DMAPCI in the presence of this product was carried out under experimental conditions similar to those described above. After freeze-drying and washing the remaining solid with acetone the product was identified by 1H-NMR (D2O). The coupling efficiency could be calculated from the ratio O-C-(CH2)6-C-N(δ=1.2,m) / N-C-CH2-C-N(δ=2.2,m)

oleyl-3,3-ionone

Synthesis of oleyloxytlate (CH3(CH2)7CH=CH(CH2)7CH2OSO2C6H5CH2) n 5.0 g distilled oleylalcohol and 3.91 g tosyl chloride were dissolved in 50 ml pyridine and stored for one night at 0°C. A precipitate was formed during the reaction. The reaction mixture was poured onto ice and extracted several times with dichloromethane. The combined organic fractions were washed with a 5% HCl solution, followed by washing with water. After drying the organic solution over MgSO4, the solvent was removed under reduced pressure. The yield was nearly quantitative. 1H-NMR (CCl4) showed the absence of the starting oleylalcohol (C-CH2-OH: δ=3.6,t), (C-CH2-OSO2-: δ=3.8,t).

Synthesis of oleyloxydodecyl (CH3(CH2)7CH=CH(CH2)7CH2): 5.5 g of unpurified
oleyltosylate together with 2.1 g NaI, were dissolved in 75 ml acetone and refluxed under nitrogen atmosphere for three hours, during which a precipitate was formed. After filtration and evaporation of acetone, a yellow oil remained (yield approx. 95%). $^1$H-NMR showed the absence of the tosylate group (–C–CH$_2$–I: δ = 3.2, t). The quality of the iodide was found to be satisfactory for the next step.

Synthesis of oleyl-3,3-ionone (R = Φ, scheme 2): 3.65 g DMAPCl and 0.69 g oleyl iodide were refluxed in 5 ml water under a nitrogen atmosphere for 48 hours. The iodide dissolved rapidly after the polymerization had started and a viscous reaction mixture resulted. After freeze-drying and washing the product with acetone the chemical yield was found to be nearly quantitative.

Macroinitiators

Di-(a-bromo-4-methylbenzoyl)peroxide

Di-(a-bromo-4-methylbenzoyl)peroxide (9, scheme 3) was synthesized according to literature.$^{6,9}$ Polymerization of DMAPCl in the presence of this peroxide coloured the solution deep brown. This discoloration was also observed when triethylamine was added to the acylperoxide instead of DMAPCl.

ACPA derivatives

ACPA–Cl was synthesized in a way similar to that described in literature.$^{60}$ 4.5 g ACPA (4,4’-azo-bis-(cyanopentanoic acid, Fluka) was dispersed in 45 ml benzene and cooled in an ice bath to 0–5°C. 9.0 g PCl$_5$ was added in small portions. Moisture was excluded from the reaction mixture by using a CaCl$_2$-tube. After 13 minutes the ice bath was removed and the reaction mixture was stirred for 2–3 hrs at ambient temperature. After evaporation of the solvent under reduced pressure, the precipitate was dissolved in dichloromethane. A precipitate was formed on the addition of hexane. After filtration and washing with hexane this procedure was repeated. The melting point, after drying under reduced pressure for at least 30 minutes, was 74-
75°C (lit.93–95°C). Therefore, the 1H-NMR spectrum (CDCl₃) was measured after the addition of excess of methanol. The purity of the acid chloride, calculated from the ratio CH₂-O / CH₂-C(CN)–C, was in all cases > 90%. The chemical yield was 70%. This product was reacted with dimethylaminopropylamine (resulting in \( R = 10 \), scheme 3) or aminopropylbromide (resulting in \( R = 11 \), scheme 3) in acetonitrile at 0-5°C. Polymerization of DMAPCI in the presence of these products gave no satisfactory results even under very moderate conditions.

Di-i-butyl-4,4'-azo-bis(cyanoperoxypentanate) (\( R = 12 \), scheme 3) was synthesized according to literature⁷. Polymerization in the presence of this initiator with 3-(methacrylamidinopropyl)trimethylammoniumchloride (\( 13 \), scheme 3, MAD) was catalyzed by the addition of tetraethylpentamine (TEPA) as described by Piirma et al.⁸. 0.5 g of \( 12 \) and 15 g aqueous MAD solution (50%) were dissolved in 30 ml methanol. 0.25 g TEPA was added after flushing with nitrogen for at least 15 minutes. After polymerization for 5 hrs the mixture was precipitated in acetone, filtrated, dissolved in a little water, filtrated and the remaining solution again precipitated in acetone. After drying under reduced pressure, the chemical yield was 54%. The cyano-group (2260 -2200 cm⁻¹) could not be detected by FT-IR.

Results and discussion

The cationic polymers under consideration (scheme 1) must somehow be attached to the latex surface. Although physical adsorption by the addition of block copolymers (1) has been shown to be successful (see chapter 5) the chemical attachment is to be preferred. The addition of macromonomers (2) or macroinitiators (3) may lead to the desired product.

Ford recently reported the synthesis of cationic latices by the use of polymerisable low molar mass cationic surfactants, for example 4-styryloxododecyl-trimethylammoniumbromide, a product of Z (scheme 2) with trimethylamine⁹. It is important to note that considerable amounts of coagulum
were reported to be formed during emulsion polymerizations. Above all, the resulting latices were polydisperse. These experiments already showed the difficulties encountered when applying polymerizable surfactants. On copolymerization with styrene, the dynamic behaviour of the surfactant molecules is strongly reduced as the result of chemical anchoring. The equilibrium of adsorption/desorption is disturbed and polydisperse latices will result.

It can be expected that the use of macroinitiators will also give rise to some difficulties. Macroinitiators will most likely exhibit a very low initiator efficiency because of the occurrence of the cage effect. The process of initiation in the water phase may then lead to the continuous formation of new particles as a result of strongly stabilizing effects of the charged polymers (both steric and charge stabilization). Consequently, polydisperse latices will result. It should be noted that the experimental conditions for surfactant-free emulsion polymerizations or for using polymerizable surfactants are not as straightforward as for conventional emulsion polymerizations. In the first-named cases, conditions like stirring
speed, type of stirrer and reactor design may determine the outcome of the polymerization. The outcome of a standard emulsion polymerization, for instance to test whether a coupling reaction has been successful, is rather arbitrary. Any possible success of coupling reactions can therefore not be determined by such standard emulsion-polymerization tests, but requires elaborate optimization of emulsion-polymerization conditions.

A way to synthesize block copolymers is the coupling of end-group-functionalized polystyrene with functionalized 2,4-ionene. The complete synthesis of these types of block copolymers by anionic polymerization is not possible, as different polymerization mechanisms are required for the two blocks. Functionalized polystyrene was synthesized by anionic polymerization to low molar mass chains terminated with 1,4-dibromobutane. After purification, this product was reacted with aminated 2,4-ionenes in various solvent combinations and at various temperatures. One of the major problems is the insolubility of the hydrophobic polystyrene in polar solvents and the

\[
\text{Scheme 2 Synthesis of 3,3-ionene derivatives}
\]
insolubility of 2,4-ionene in apolar solvents. Common solvents for both
segments of the block copolymer are thus not available.

Another approach to the synthesis of these types of block copolymers is
outlined in scheme 2. Since the outlined route is not possible for 2,4-ionene,
a product of the step reaction of N,N',N',N''-tetramethylenealamine (TMEDA)
and 1,4-dibromobutane, a bifunctional monomer for 3,3-ionene (5, scheme 2), 3-
N,N-dimethylini-mino-n-propylchloride (4, scheme 2, DMAPC), was used (2,4-ionene
and 3,3-ionene both have the same linear charge density). All attempts to
synthesize this type of block copolymer (6, scheme 2) turned out to be
unsuccessful. Probably the extremely hydrophobic polystyrene has a too low
reactivity to allow coupling.

Another approach is the synthesis of macromonomers (2, scheme 1). Of
course, polyelectrolytes containing one polymerisable end group will be
completely soluble in water and it is therefore to be expected that problems
similar to those encountered in using low molar mass hydrophilic comonomers
will be encountered (chapter 6). To avoid these problems, polyelectrolytes
were synthesized to contain polymerizable hydrophobic segments followed by a
cationic segment. Several attempts were made to synthesize these types of
polymers. It turns out that the reaction presented in scheme 2 is not as
straightforward as it seems. In fact, we have the same problem here as was met
earlier in the attempts to synthesize block copolymers of styrene and ionene.
The reactivity of the added monofunctional group is too low compared with the
homopolymerization of DMAPC. In the case of 4-styryloxydodecyl-3,3-ionene (7,
scheme 2) a small quantity of functional groups was embodied. Only the
coupling of oleyl chloride with 3,3-ionene (8, scheme 2) turned out to be
successful. Unfortunately, the oleyl-3,3-ionene was found to be too unreactive
to be built in during an emulsion polymerization of styrene and
divinybenzene.

Attempts have also been made to synthesize macroinitiators (2, scheme 1).
Coupling of 2 (scheme 3) with DMAPC did not succeed because the acylperoxide
readily oxidized the amine group, like the results reported on peroxides. Attempts to polymerize DMAPCI in the presence of 10 and 11 were not successful (scheme 3). Attempts to polymerize 3-(methacrylamidinopropyl)-trimethylammoniumchloride (12, MAD) with 12 as initiator gave no satisfactory results (scheme 3). The thermolabile groups are very susceptible to temperature and therefore only moderate reaction conditions can be used.

All the attempts to couple functional groups to 3,3-ionene by polymerization of DMAPCI in the presence of a functionalized monomer or initiator were unsuccessful (except for oleyl-3,3-ionene). Apparently, the synthesis as depicted in scheme 2 is not as straightforward as it seems. This is probably due to the insolubility of the functionalized monomers and initiators in polar solvents, the extreme hydrophilic character of the 3,3-ionene so formed that makes the polymer only soluble in water-containing solvents, and the moderate experimental conditions needed to avoid polymerization of the polymerisable surfactants or decomposition of the functional initiators during their syntheses. In addition, the purification of
the products appears to be extremely difficult. Since we aim at the synthesis of functionalyzed cationic polymers of high purity (> 90%) none of the described attempts (except for oleyl-3,3-ionene) were successful.

Conclusions

Difficulties are encountered in synthesizing block copolymers, macromonomers or macrorinitiators. A combination of lack of reactivity of the functionalyzed precursors in the synthetic routes outlined, the high rate of homopolymerization of DMAPCl, and the occurrence of chemically unstable functional groups are the main reasons for the lack of success. However, it may be inferred that the principles of the approaches presented are of great potential value and interest and should be the subject of further future research.

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12. see e.g. J. March, "Advanced organic chemistry: reactions, mechanisms and
Summary

This thesis describes the immobilization of cobaltphthalocyaninetetrasodiumsulphonate (CotSPc) and cationic polymers acting as co-catalyst onto organic supports and its effect on the oxidation of 2-mercaptoethanol to its corresponding disulphide in the presence of molecular oxygen. The aims of the investigation are threefold, (1) the synthesis of an immobilized CotSPc/polyelectrolyte system, (2) study of the effect of immobilization on oxidation reaction and, (3) determination of the key factors controlling the catalytic activity of immobilized CotSPc-containing systems.

Relatively low molar mass 2,4-ionene, a poly-quaternary ammonium salt, strongly enhances the thiol oxidation. On the other hand, monomeric analogues hardly affect the oxidation rate in the presence of CotSPc. The thiol oxidation appeared to be extremely susceptible to low concentration of cationic polymer (expressed as N+: [N+] = 10^{-9} - 10^{-10} mol/dm^3). Michaelis-Menten kinetics was observed (chapter 2).

The immobilization of low molar mass 2,4-ionene on chloromethylated XAD-2 resin, a macroporous poly-(styrene–divinylbenzene) resin, is described in chapter 3. A method has been developed to detect very low concentrations of free ionene ([N+] > 4x10^{-7} mol/dm^3).

The observed reaction rate decreased on immobilizing 2,4-ionene on XAD-2 resin. Calculations showed that this decrease cannot be exclusively ascribed to mass transport limitations. It was also shown that CotSPc is mainly adsorbed to the outer surface of the resin particles and does not penetrate the (small) pores. This diminishes the N+/Co ratio, which also plays an important role in the thiol oxidation and may contribute to the observed decrease in catalytic activity (chapter 4).

To avoid the above difficulties, nonporous latex particles with a high specific surface area (as a result of the small particle size) were used as organic supports (chapter 5). Quaternized polyvinylpyridine (qPVP)-stabilized
latex particles were synthesized by the emulsion polymerization of styrene and
divinylbenzene in the presence of a block copolymer of styrene and quaternized
vinylpyridine (PS-b-qPVP) as a surfactant. The latex cleaning was found to be
tedious. The latex system exhibited a catalytic activity that is even somewhat
higher than both homogeneous qPVP or PS-b-qPVP-containing systems. For all
three systems enzyme-like kinetics was observed. The difference in Michaelis
constant (K_M) between the three systems is striking. Concentration of
polyelectrolyte at the latex surface by immobilization will affect the
conformation of the polymer chains and an explanation for the observed
difference in K_M between the qPVP-containing systems and the block copolymer-
 stabilized system therefore remains difficult. Even the comparison between the
two homogeneous systems remains difficult owing to the dual character of the
block copolymer.

A more generally applicable way of synthesizing cationic latices is
eulsion polymerization in the presence of a cationic comonomer, for example
3-(methacrylamidinopropyl)trimethylammonium chloride (MAD) (chapter 6).
Monodisperse latices could be prepared in this manner. The addition of the
water-soluble MAD strongly enhanced the rate of emulsion polymerization thanks
to the particle size reduction. Several latex cleaning techniques were
investigated, but no available technique was found capable of removing traces
of free polyelectrolyte. A novel technique, centrifugation, followed by
shaking with silica appeared to clean the latices to a satisfactory level. The
surface charge density of the latices increased on increasing the initial
[MAD]. Other emulsion polymerization techniques did not further increase the
surface charge density. There seems to be an intrinsic maximum to the number
cationic groups incorporated at the surface when polymerizing in this
manner.

Two latices stabilized by MAD and the homopolymer of MAD (PMAD) were
tested as co-catalyst in the thiol oxidation (chapter 7). PMAD behaved as a
polycation giving a large enhancement of the oxidation rate. The observed
catalytic activity of the MAD-stabilized latex systems was much lower compared with the oxidation rate of the system containing free PMAD. Enzyme-like kinetics were observed for all three systems. The origin of the observed lower activity was revealed by VIS reflection spectroscopy of CoTSPc-bound lattices. In contrast to homogeneous cationic polymer-containing systems, in the latex systems the highly active aggregated form of CoTSPc was only present at low concentrations. The presence of the less active CoTSPc monomers was attributed to the presence of relatively short cationic chains at the latex surface exhibiting low linear charge density and low flexibility.

The key factors that may lead to a highly active support are: high surface charge density, flexible, not too short cationic polymer chains and nonporosity of the supporting particles.

In order to synthesize still more active supports, some promising synthetic routes are outlined in the appendix. Block copolymers, macromonomers and macroinitiators are believed to indicate many intrinsic opportunities for preparing functionalized lattices. Some synthetic attempts are described. Generally speaking, the extreme water-solubility of the cationic polymers, the difficulty in separating products from starting material and undesired side products, and the chemolability and thermolability of the materials greatly hindered the synthesis of the desired components. However, the principles proposed are believed to be of great potential value and deserve more specific attention in future research.
Samenvatting

Dit proefschrift beschrijft de immobilisatie van kobaalftalocyanine tetra-natriumsulfonaat (CoTSpC) en kationische polymeren, die als katalysator dienen, op organische dragermaterialen en het effect hiervan op de autoxidatie van 2-mercaptopethanol tot het overeenkomstige disulfide. Het onderzoek had een drieledig doel: (1) de synthese van een CoTSpC/polyelektroliet systeem, (2) de bestudering van het effect van immobilisatie op de thioloxidatie en (3) de bepaling van de factoren die de katalytische aktiviteit van de geimmobiliseerde CoTSpC bevattende systemen bepalen.

2,4-ionene, een polyquaternair ammoniumzout, met een relatief laag molekulargewicht versnelt de thioloxidatie aanzienlijk. Analoge, monomere verbindingen hebben daarentegen nauwelijks invloed op de oxidatiesnelheid in aanwezigheid van CoTSpC. Het bleek dat de thioloxidatie zeer gevoelig was voor lage concentraties polyelektroliet (uitgedrukt in quaternaire ammoniumgroepen: \( [N^+] = 10^{-6} \rightarrow 10^{-5} \) mol/dm\(^3\)). Het polymeresysteem vertoond Michaelis-Menten kinetiek (hoofdstuk 2).

In hoofdstuk 3 wordt de immobilisatie van 2,4-ionene met een laag molekulargewicht op gechloormethyleerde XAD-2 deeltjes beschreven. Allereerst werd een methode ontwikkeld om zeer lage concentraties niet gebonden ionene aan te kunnen tonen (\( [N^+] > 4 \times 10^{-7} \) mol/dm\(^3\)).

Immobilisatie van 2,4-ionene op XAD-2 deeltjes vertraagde de reactiesnelheid. Berekeningen toonden aan dat de verlaging niet alleen toegeschreven kon worden aan limitatie van het stoftransport. Tevens bleek dat CoTSpC voornamelijk aan de buitenkant van de deeltjes geabsorbeerd zit en niet doordringt in de kleine poriën. Dit verlaagt de N\(^+\)/Co verhouding welke een belangrijke rol in de thioloxidatie speelt en hier waarschijnlijk bijdraagt tot de gevonden verlaging van de katalytische activiteit (hoofdstuk 4). Om de bovengenoemde problemen te vermijden werden niet poreuze
latexdeeltjes met groot specifiek oppervlak (als gevolg van de geringe deeltjesgrootte) gebruikt als dragermateriaal (hoofdstuk 3). Door gequaterniseerde poly-4-vinylpyridine (qPVP) gestabiliseerde latexdeeltjes werden gemaakt door middel van een emulsiepolymerisatie van styreen en divinylbenzeen in aanwezigheid van een blokkopolymer van styreen en gequaterniseerde 4-vinylpyridine (PS–b–qPVP). Het schoonmaken van de latex bleek zeer moeilijk te zijn. Het latexsysteem vertoonde een katalytische activiteit die zelfs iets hoger was dan die van de homogene qPVP of PS–b–qPVP bevattende systemen. Alle drie systemen vertoonden enzymachtige kinetiek. Het verschil in Michaels konstante ($K_M$) voor de drie systemen was opvallend. Het concentreren van polyelektroliet op het latexoppervlak als gevolg van de immobilisatie zal de conformatie van de polymer ketens beïnvloeden. Een vergelijking van de $K_M$ van de qPVP bevattende systemen met die van de door blokkopolymer gestabiliseerde systemen blijft daardoor moeilijk. Zelfs de vergelijking tussen de twee homogene systemen is moeilijk door het amfifiele karakter van het blokkopolymer.

Een meer algemeen toepasbare manier om kationische latices te synthetiseren is emulsiepolymerisatie in aanwezigheid van een kationisch comonomer bijv. 3-(methacrylamlidinopropyl)trimethylammoniumchloride (MAD) (hoofdstuk 6). Op deze manier konden monodisperse latices gemaakt worden. Toevoeging van het wateroplosbare MAD verhoogde de emulsiepolymerisatiesnelheid met als gevolg een toenemen van het aantal deeltjes. Verschillende technieken om latices schoon te maken werden onderzocht, maar de beschikbare methoden konden sporen polyelektroliet niet verwijderen. Een nieuwe procedure, centrifugeren gevolgd door schudden met silica, bleek de latices afdoende te zuiveren. De oppervlakteopwaardingsdichtheid nam toe met stijgende MAD concentratie. Andere emulsiepolymerisatietechnieken konden de oppervlakteopwaardingsdichtheid niet verder verhogen. Deze resultaten wijzen op het bestaan van een intrinsiek maximum voor het aantal kationische groepen dat ingehouwd wordt op het latex oppervlak.
Twze door MAD gestabiliseerde latices en het homopolymer van MAD (PMAD) werden getest als kokatalysator in de thioloxidatie (hoofdstuk 7). De gevonden katalytische activiteit van de door MAD gestabiliseerde latexystemen was veel lagere dan die van het PMAD bevattende homogene systeem. Alle drie de systemen vertoonden enzymachtige kinetiek. De reden voor de gevonden lagere activiteit werd opgehelderd met behulp van VIS-reflectie spektroskopie van de aan latexes gebonden CoTSPc. In tegenstelling tot homogene kationisch polymere bevattende systemen bezitten de latex systemen slechts lage concentraties van de katalytisch aktieve geaggregeerde vorm van CoTSPc. De aanwezigheid van de minder aktieve CoTSPc monomeren wordt toegeschreven aan de relatief korte kationische ketens op het latex oppervlak die een lage ladingdichtheid en een beperkt bewegelijkheid hebben.

De sleutelfactoren die mogelijk leiden tot een zeer reaktief dragermateriaal zijn: hoge ladingdichtheid, bewegelijkheid, niet te korte kationische ketens en dragermateriaal zonder poriën.

Om nog reaktieve dragermaterialen te syntetiseren zijn in de appendix enkele veelbelovende strategieen uitgetippeld. Blokkopolymeren, maktromonomeren en makronalinitiatoren bieden mogelijkheden om functionele latices te maken. Enkele synthetische routes zijn beschreven. Algemeen gesproken wordt de syntese van de gewenste stoffen bemoedigd door de extreem hoge wateroplosbaarheid van de kationische polymeren, de chemische en thermische gevoeligheid van de tussenprodukten en de problematiek bij het isoleren van het eindproduct. De voorgestelde principes zijn dermate interessant dat ze speciaal aandacht verdienen in toekomstig onderzoek.
Curriculum vitae

STELLINGEN

behoorende bij het proefschrift van K. H. van Streun

IMMOBILIZATION OF CATIONIC POLYMERS AND ITS EFFECT ON THE
COBALTPTHALOCYANINE-CATALYZED THIOL OXIDATION

1. De zuivering van latices, die gemaakt zijn in aanwezigheid van een ionisch
monomere, blijkt in veel gevallen te worden onderschat.

Hoofdstuk 6 van dit proefschrift

2. De aannemer dat de kinetiek van de door geimmobiliseerde sulfonzuur
gekatalyseerde sucreose-inversie door adsorptie bepaald wordt, is niet terug
tevinden in de experimenteel gevonden relaties.

35, 2117 (1988)

3. Gezien de manier van bereiding van de reactieve latices als drager voor
kobalt katalysators, is het aantonen van de afwezigheid van "intrapartiele
diffusion" tijdens de betreffende modelreactie overbodig.


4. Bij het bepalen van de oppervlakteladingsdichtheid van methacrylzuur
gestabiliseerde styreen-butylacrylaat latices wordt door onderstaande
auteur onvoldoende rekening gehouden met de zweefbaarheid van de deeltjes.

26, 1937 (1988)

5. In het door de auteur aangegrepen voorstel tot het verklaren van de gevonden
relatie tussen deeltjesgrootte en monomere concentratie wordt onvoldoende
rekening met de sterke adsorptie van polymeren aan oppervlakten.

6. Gezien het geringe effect van de algemene periodieke keuring van auto's (APK) op de verkeersveiligheid, dient deze keuring ook meer gezien te worden als een indirecte subsidieregeling voor de autobranche.

7. Diegenen, die bijdragen tot het steeds maar uitstellen van een goede euthanasieregeling, houden onvoldoende rekening met de moderne medische ontwikkelingen en dragen als zodanig, morele verantwoordelijkheid voor veel menselijk leed.

8. Bij het toekennen van de term “milieu-vriendelijk” aan een produkt wordt, naast de schadelijkheid aan het milieu door produktion en gebruik, onvoldoende rekening gehouden met de schaal waarop de produktion cq. konsumption van het doelbetreffende produkt plaatsvindt.

Eindhoven, 26 januari 1990