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PREPARATION AND CO-CATALYTIC PROPERTIES OF FUNCTIONALIZED LATTICES

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Abstract—Stable cationic latices were prepared by emulsifier-free emulsion polymerization of styrene with
1-methyl-4-vinylpyridinium bromide or 1-methyl-4-vinylpyridinium iodide as comonomers using azo-
bis(isobutyramidine hydrochloride) as initiator. Comonomers were prepared by a new and simple
synthetic procedure. Addition of methanol and especially comonomer increased the surface charge density
of cleaned latices and enhanced the polymerization rate. In the presence of iodide, the polymerization rate
was lowered. The co-catalytic properties of silica-cleaned latices on the oxidative coupling of 2-mercap-
toethanol were tested after cobalt(II)phthalocyanine-tetrasodiumsulphonate (CoTSPc) immobilization
onto the functionalized latex particles. A significant increase in oxidation rate was found as compared
with the polymer-free CoTSPc system.

INTRODUCTION

Clean, monodisperse latices are frequently used as
model systems for studying colloidal stability and for
calibrating instruments, e.g. ultracentrifuges and
light-scattering units. Usually these latices are pre-
pared by emulsion polymerization in which an
emulsifier is used for stabilization of the particles. The
disadvantages of using an emulsifier are the difficulty
of removing any excess of emulsifier and coagulation
of the particles on cleaning the latex [1].

To overcome some of the problems in cleaning
latices, the emulsifier is sometimes left out, as first
done by Matsumoto et al. [2]. Subsequently many
accounts have been published on emulsifier-free poly-
merization systems in which ionic initiators and
comonomers are used for stabilization. These latices
are stabilized by:

(i) chemically bound and charged initiator
groups;
(ii) hydrophilic groups at the particle-water
interface arising from copolymerization of
ionic comonomers;
(iii) in situ formed polyelectrolyte, adsorbed on
the particles or combinations of (i) to (iii).

have been used in the presence of ionic initiators like
azobis(isobutyramidine hydrochloride) and potassium
persulphate to prepare these functionalized lat-
tices. Alcohols as cosolvents have been shown to
improve the polydispersity of the latex particles pre-
pared by emulsion polymerizations [3].

In our laboratory the co-catalytic activity of both functionalized cationic latices and organic supports
on the oxidative coupling of thiols to disulphides in the presence of cobalt(II)phthalocyanine-tetrasodium-
sulphonate (CoTSPc) is investigated (Scheme 1). The oxidation rate is determined from the oxygen
consumption rate and is an indication of catalyst
activity. Immobilization of CoTSPc on organic sup-
ports severely reduced catalytic activity caused by
interparticle and intraparticle diffusion limitations
[7]. To overcome mass transfer limitations, small and
nonporous functionalized cationic latex particles can
be used. Because of the extreme susceptibility of the
CoTSPc catalytic system to low cationic polymer
concentrations, extensive cleaning of the latices is
required. Mainly for this reason, emulsifier-free emul-
sion polymerization is preferred over the conven-
tional process. The co-catalytic effect of cationic
polymers on CoTSPc-catalysed thiol oxidations arises from binding the catalyst, substrate enrichment
and formation of active CoTSPc aggregates. The
linear charge density of the polymer backbone also
appeared to be of crucial importance to the catalytic
activity of these homogeneous polymers [8]. Control
over surface charge density of these functionalized
latices was therefore an important goal.

In this paper we report the use of 1-methyl-4-
vinylpyridinium bromide (qVPBr) and 1-methyl-4-
vinylpyridinium iodide (qVPI) as comonomers in
the emulsifier-free polymerization of styrene (St),
applying azobis(isobutyramidine hydrochloride)
(AIBA·2HCl) as initiator. Problems in the synthesis
of these comonomers [9, 10] have been overcome by
a new and simple synthetic procedure. Effects of
comonomer concentration and methanol addition on
particle size, polymerization rate and surface charge
density have been investigated. Based on the findings
of these experiments, stable monodisperse latex
systems with high surface charge density were se-
lected for catalytic measurements after thorough
cleaning. The initial reaction rates in the oxidative
coupling of 2-mercaptoethanol are reported and dis-
cussed.
**Experimental Procedures**

**Apparatus**

Two reactor types were used for polymerizations. For conversion measurements, a 500 cm³ thermostated glass reactor was used, equipped with a rubber septum for sampling and a gas inlet and outlet. Most reactions were conducted in a 1000 cm³ thermostated glass vessel. All polymerizations were carried out under N₂, using a disc turbine impeller at 300 rpm, keeping temperature at 60° ± 1°.

Thiol oxidations were carried out in an all-glass double-walled Warburg apparatus, equipped with a mechanical glass stirrer and a pH-electrode (Radiometer GK 2401B). The oxygen uptake rate was measured with an Inacorn digital mass flow controller.

A Cambridge S-200 scanning electron microscope was used to determine particle size and particle size distributions. Nuclear magnetic resonance spectra were recorded with a Bruker 200 MHz spectrometer at 25°, using D₂O as solvent. Spectroscopic measurements were performed with a Hewlett-Packard 8451A diode array spectrophotometer. Conductometric titration curves were recorded on a CDMS-80 conductivity meter, using a PPT042 cell (Radiometer). Centrifugation was done on a Centrikon T-2060 ultracentrifuge. Amicon serum replacement cells were used with 100 or 200 nm pore size polycarbonate membranes (Nucleopore).

**Materials**

Styrene (Merck) was distilled under N₂ at 69°/6·10⁻¹⁰ Pa to remove inhibitor, and stored at 2°. 4-Vinylpyridine (Janssen Chimica) was distilled twice at 31°/5·10⁻¹⁰ Pa and stored in the dark at -18°. 2-Mercaptoethanol (Janssen Chimica) was distilled twice at 31°/5 · 10⁻² Pa and stored in the dark at -18°. 2-Mercaptoacetophenone (Janssen Chimica) and AIBA·2HCl (Polyscience) (Merck), silica (Merck, Kieselgel 60, 63-200 μm), hydroquinone (Janssen Chimica), methanol p.a., acetone p.a. (Merck), styrene (Merck, Kieselgel 60, 63-200 μm), hydroquinone (Janssen Chimica) and AIBA·2HCl (Polyscience) were used without further purification.

**Synthesis and polymerization procedures**

qVPBr was prepared by adding 0.05 mol 4-vinylpyridine, freshly distilled, in 3 hr to a stirred solution of 0.21 mol bromomethane in 50 cm³ acetone at 0°. By slowly adding 4-vinylpyridine to an excess of bromomethane, the product is formed instantly and the nucleophilic attack of 4-vinylpyridine on qVPBr resulting in polymer formation is avoided [9]. After a reaction time of 6 hr, the crude product was filtered off and washed several times with acetone.

**Results and Discussion**

**Emulsion polymerization kinetics**

The key difference between the emulsifier-free emulsion process and conventional emulsion polymerizations is the nucleation period of the polymerization. At the start of the emulsifier-free emulsion polymerization, no monomer swollen micelles are present to absorb the radicals formed by dissociation of the water-soluble initiator. For copolymerization of hydrophilic comonomers, a homogeneous nucleation mechanism has been proposed [13, 14].
The effects of initiator, comonomer and methanol concentrations on polymerization rates and particle size distributions of latices prepared with qVPBr or qVPI as comonomer show agreement with the homogeneous nucleation mechanism. During the nucleation period, the copolymerization of styrene and these comonomers starts in the aqueous phase. Polymer growth continues until the formed oligomeric radicals reach a critical chain length, determined by the solubility of the growing oligomer in the water phase. Precipitation of these oligoradicals results in primary particles. Increasing the comonomer concentration is thought to increase primary particle stability by enhanced comonomer incorporation [15]. The increase in particle number together with the Trommsdorff gel effect causes the polymerization rate enhancement depicted in Fig. 1. The observed decrease in particle size (Table 1) indicates an increase in particle number over the indicated concentration range of Fig. 1. The adsorption of polyelectrolyte formed at higher comonomer concentrations might also increase primary particle stability.

Increasing initiator and comonomer concentrations initially reduce particle diameter, because of the increase in the number of particles formed during the nucleation period. For both parameters, an increase in particle diameter is observed at high concentrations (Tables 1 and 2). The increase in ionic strength which accompanies increasing initiator and comonomer concentrations is believed to dominate the initial concentration effects. Coagulation of primary particles results in enhancement of number-average particle diameter [16]. At comonomer concentrations exceeding 25·10⁻³ mol/dm³, bridging was observed by scanning electron microscopy resulting in heterodisperse latices, thus setting a maximum to the use of qVPBr to control particle properties.

Addition of methanol results in increased styrene incorporation in the water-soluble oligomeric radicals, caused by increased styrene solubility in the continuous phase [17]. Polyelectrolyte formation is therefore partially prevented. The change in solubility of the formed polymers in the presence of methanol results in formation of an increased number of particles. From Fig. 2 and Table 3 it can be seen that the increase in polymerization rate (and decrease in particle diameter) lasts up to a concentration of about 3.1 mol/dm³. Additional effects of methanol addition were commented upon by Homola et al. [16]. The reported lower polydispersity on methanol addition was also noticed in the present study.

A clear difference was found between the use of qVPBr and qVPI as comonomer. Conversion measurements showed a retardation of polymerization when qVPI was used (Fig. 3). The capability of iodide to retard the polymerization is also indicated.
Table 3. Effect of methanol concentration on number-average particle diameter

<table>
<thead>
<tr>
<th>Methanol (mol/dm³)</th>
<th>Dₐ (nm)</th>
<th>Dₛ/Dₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>285</td>
<td>1.01</td>
</tr>
<tr>
<td>2.8</td>
<td>265</td>
<td>1.01</td>
</tr>
<tr>
<td>3.7</td>
<td>210</td>
<td>1.01</td>
</tr>
<tr>
<td>4.9</td>
<td>190</td>
<td>1.01</td>
</tr>
</tbody>
</table>

[AIBA·2HCl] = 2.3·10⁻³ mol/dm³, [St] = 1.05 mol/dm³, [qVPBr] = 1.2·10⁻³ mol/dm³, [NaCl] = 8.6·10⁻³ mol/dm³.

by the experiments shown in Fig. 4. An equimolar amount of sodium iodide clearly lowered the polymerization rate as compared with systems involving sodium chloride and sodium bromide. Preliminary results of experiments seem to indicate that the initiator AIBA·2HCl is capable of reacting with iodide, so forming iodine. The yellowish colour of some latices prepared with qVPi supports iodine formation as is the decolouration on addition of sodium thiosulphate. This iodine formation could explain the retarding effect found in the polymerizations, as iodine is known to be a radical scavenger.

Surface charge density

The cationic comonomer and initiator residues present at the particle–water interface are responsible for the surface charge of latices prepared by emulsifier-free emulsion polymerization. Surface charge density measurements by determination of the counterion concentration at the particle surface is best accomplished by conductometric titration after replacing the ions with hydroxyl ions. Potentiometric titration of chloride, bromide and iodide ions in cleaned latices with silver nitrate did not give reproducible values. Possibly, replacement of these counterions during latex handling and cleaning by counterions not detectable with silver nitrate must be taken into account. Such problems were not encountered in the conductometric titration with HCl of the hydroxyl counterions.

A typical titration curve is given by Fig. 5. Initially the conductivity hardly changes on addition of titrant. When all hydroxyl ions in the electrical double layer are replaced, the conductivity rises rapidly as a result of excess acid added. A more accurate determination of equivalence point is possible by using the back titration technique. Removal of traces of carbon dioxide at low pH has been indicated to cause this effect [18].

Higher concentrations of comonomer result in an increase in the surface charge density as depicted by Fig. 6. An increasing comonomer content of the copolymer as indicated before is the determining factor. The measured surface charge densities originate both from comonomer and initiator residues. All polymerizations depicted in Fig. 6 reached final conversion in 2–5 hr depending on comonomer concentration. With the k₄ [19] for AIBA·2HCl at 60°
being $3.2 \times 10^{-1}$ sec$^{-1}$, only 20–60% of the initiator will have decomposed during the reaction time. Assuming 60% initiator efficiency, the surface charge densities reported in Fig. 6 would exceed maximum initiator built-in by 10–90%. Therefore, the unaccounted surface charge must result from comonomer units at the particle-water interface. If initiator residues buried in the latex particles and polyelectrolyte formation are considered, even higher comonomer surface coverage must be assumed. Surface charge density control by comonomer addition is limited, however, as mentioned before because of polyelectrolyte formation, resulting in bridging. Although the reported surface charge densities in Fig. 6 are of cleaned latices with serum $N^+$ concentrations below $8 \times 10^{-7}$ mol/dm$^3$, adsorbed polyelectrolyte has to be expected when the values are compared with surface charge densities of silica-treated latices in Table 4. This point clearly indicates the ambiguity of the term ‘cleaned latex’ frequently encountered in the literature.

Finally, methanol addition results in a constant surface charge density (Fig. 7). Up to a methanol concentration of about 3.1 mol/dm$^3$, increase in surface charge density is found. In agreement with the effect on particle diameter and polymerization rate (Table 3 and Fig. 2), increase in the number of stable primary particles formed during the nucleation period is most probably responsible for these effects. However, the effect of methanol addition on surface charge density is relatively small as compared with the effect of comonomer.

**Catalytic measurements**

The CoTSPc-catalysed oxidative coupling of ME using cationic polymers gives rise to an enzyme-like kinetic behaviour as indicated earlier in our laboratories. The coupling can be described by a two-substrate Michaelis–Menten model [20] presented in Scheme 2, with $E = \text{CoTSPc}$, $S_1 = \text{ME}$, $S_2 = \text{O}_2$ and $P = 2,2'$-dithiodiethanol. An expression for the rate of ME consumption ($R$) can be derived assuming pseudo steady-state kinetics in both $E\text{S}_1$ and $E\text{S}_2$. At constant oxygen concentration equation (1) results, with $k' = 4 \times (k_3 [O_2])/(C_2 + [O_2])$ the turnover frequency at 0.1 MPa $O_2$ and saturation in thiol, $K' = (C_2 + [O_2])/(C_3 + [O_2])$ the apparent Michaelis constant, $C_2 = (k_2 + k_3)/k_2$, $C_3 = k_3/k_2$ and $C_4 = k_4/k_1$.

In Fig. 8 dependence of catalytic activity on pH of latices described in Table 4 is given. Because the reactive species in oxidative coupling of thiols are thiolate anions, increase in rate on increasing pH is expected [$pK_a(ME) = 9.6$]. The simultaneous increase in ionic strength, however, is believed to give rise to a competitive ion effect, resulting in the depicted optimum [21, 22]. The dependence of reaction rate on co-catalyst concentration is shown in Fig. 9. For $N^+/Co \leq 4$, no substrate enrichment can occur because of the negative electrostatic charge of the immobilized CoTSPc. For $N^+/Co > 4$, active aggregates of CoTSPc are formed [23]. The optimum here arises from thiolate anion depletion at the active cobalt centre at high co-catalyst concentration. The saturation behaviour typical of enzyme-like kinetics at optimum pH and $[N^+]$ conditions is depicted in Fig. 10. Both turn-over frequency and apparent Michaelis constant have been calculated from the Lineweaver–Burk plot (Fig. 11) constructed from

![Image](image-url)

**Table 4. Characteristics of latices used in catalytic measurements**

<table>
<thead>
<tr>
<th>Latices</th>
<th>$[\text{qVPBr}]$ (10$^{-3}$ mol dm$^{-3}$)</th>
<th>$D_1$ (mm)</th>
<th>$D_2/D_1$</th>
<th>Surface charge density (μC cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latex 101</td>
<td>12.4</td>
<td>265</td>
<td>1.02</td>
<td>21.4</td>
</tr>
<tr>
<td>Latex 104</td>
<td>18.4</td>
<td>250</td>
<td>1.02</td>
<td>22.6</td>
</tr>
</tbody>
</table>

$[\text{AIBA-2HCl}] = 2.3 \times 10^{-3}$ mol dm$^{-3}$, $[\text{St}] = 1.05$ mol dm$^{-3}$, $[\text{NaCl}] = 8.6 \times 10^{-3}$ mol dm$^{-3}$, $[\text{methanol}] = 2.8$ mol dm$^{-3}$.

\[ E + S_1 \overset{k_1}{\underset{k_1^{-1}}{\rightleftharpoons}} E\text{S}_1 \]

\[ E\text{S}_1 + S_2 \overset{k_2}{\underset{k_2^{-1}}{\rightleftharpoons}} E\text{S}_1\text{S}_2 \]

\[ E\text{S}_1\text{S}_2 \overset{k_3}{\longrightarrow} E + P \]

Scheme 2. Two substrate Michaelis–Menten model.
Equation (1). Rate of ME consumption at constant oxygen concentration.

\[ R = \frac{k' \cdot [\text{CoTSPc}] \cdot [\text{ME}]}{K'_{\text{H}} + [\text{ME}]} \]

Fig. 10. These constants are indicative of the activity of the immobilized system. In Table 5 these constants are listed together with reported values for the polymer-free system, the homogeneous quaternized poly (4-vinylpyridine) (qPVP) system and the emulsifier-free copolymerized system of styrene and 3-(meth-acrylamidino-propyl)trimethylammonium-chloride(MAD) [24]. Compared with the polymer-free system, the immobilization of CoTSPc on qVPBr latices showed no considerable acceleration of the oxidation rate. Because the absence of mass transport limitations was demonstrated for the latex system, mass transport limitations could not be the cause of the difference in oxidation rates between the homogeneous qPVP system and the qVPBr latex system. Possibly a low linear charge density of the polymer chains is responsible. It has been demonstrated that low linear charge density of polymer chains prevents CoTSPc aggregation necessary for high catalytic activity [8]. Also short hydrophilic blocks of cationic polymer could be present on the particle surface originating from two phenomena. If a high percentage of the \( N^+ \) on the particle surface arises from initiator-capped polystyrene fragments, these charges could be fairly isolated from other cationic groups. This charge isolation would result in CoTSPc isolation instead of aggregation. Also the relatively low qVPBr/St ratio, the difference in monomer partition coefficients in combination with unfavourable reactivity ratios of styrene with qVPBr could contribute to a relatively short hydrophilic block length. Considering the reported dependencies of surface charge density of cleaned latices on methanol, initiator and comon-
Table 5. Turn-over frequencies (mol RSH/mol CoTSPc) and apparent Michaelis constants in oxidative coupling of ME

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( k' ) (sec(^{-1}))</th>
<th>( K_M ) (mol/dm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latex 101</td>
<td>169 ± 31</td>
<td>0.10 ± 0.01</td>
</tr>
<tr>
<td>Latex 104</td>
<td>128 ± 16</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>Latex MAD</td>
<td>690 ± 10</td>
<td>0.95 ± 0.09 [7]</td>
</tr>
<tr>
<td>qPVP</td>
<td>1400 ± 110</td>
<td>2.6 ± 0.4 [24]</td>
</tr>
</tbody>
</table>

omer concentrations, variation of these parameters is not expected to affect significantly cationic block length. Comparison of MAD with qVPBr latices (surface charge density 14.8 μC/cm\(^2\) and 22.6 μC/cm\(^2\), respectively) finally indicates that surface charge density is not a dominant factor in the preparation of an active co-catalyst. The distribution of charge along the polymer chains seems more important than the total amount of charge present on the particle surface.

**CONCLUSIONS**

Comonomers qVPBr and qVPI can be synthesized easily and are used to prepare stable, monodisperse polystyrene latices under emulsifier-free polymerization conditions. Comonomer concentration, initiator concentration and methanol addition are all versatile tools in controlling particle size and polydispersity of this emulsifier-free polymerization system. The surface charge density can be controlled by comonomer and to a less extent by methanol addition. Although methanol addition results in almost monodisperse latex systems, the surface charge density is only increased slightly. Comonomer addition has a much clearer effect and surface charge densities up to 150 μC/cm\(^2\) were found. Significant acceleration was found for the CoTSPc-catalysed coupling of 2-mercaptoethanol after immobilization on the qVPBr latices.

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**REFERENCES**