Catalytic activity of cationic latices prepared according to the shot-growth method

Citation for published version (APA):

DOI:
10.1016/0014-3057(93)90138-6

Document status and date:
Published: 01/01/1993

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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CATALYTIC ACTIVITY OF CATIONIC LATTICES PREPARED ACCORDING TO THE SHOT-GROWTH METHOD

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(Received 18 May 1992; accepted 29 May 1992)

Abstract—Stable cationic latices were prepared by the shot-growth method and by use of the ionic copolymer poly(styrene-co-1-methyl 4-vinylpyridinium bromide) (PS-qPVP) as emulsifier. An increase in co-catalytic activity of the shot-growth latices in the cobalt(II)phthalocyanine-tetrasodium-catalysed oxidative coupling of 2-mercaptoethanol was found compared with the batch latex system. Although PS-qPVP was successfully applied as emulsifier only a moderate increase in oxidation rate was found compared with the surfactant-free system. The surface characteristics of both latex systems were investigated by &potential measurement and conductometric titrations. These measurements suggest the presence of a water soluble hairy polymer shell.

INTRODUCTION

Recently we reported on the preparation of stable cationic latices by emulsifier-free emulsion polymerization of styrene (St) and 1-methyl 4-vinylpyridinium bromide (qVPBr). The use of these latices as cocatalyst in the cobalt(II)phthalocyanine-tetrasodium (CoTSPc)-catalysed oxidative coupling of 2-mercaptoethanol (ME) was investigated. Although high surface charge densities were found for these cleaned latices, immobilization of CoTSPc rendered moderate catalyst activities [1]. A possible explanation was thought to be short and inflexible polymer chains at the particle–water interface, arising from the great difference in monomer partition coefficients and unfavourable reactivity ratios. As demonstrated earlier CoTSPc aggregation needed for high activity of this complex is hindered by short and inflexible polymer chains [2]. To obtain sufficiently long hydrophilic groups at the particle surface two alternative routes can be considered.

Introduction of a second charge of monomers during the emulsion polymerization while the first charge is still reacting was shown to effect morphology and to increase surface charge density [3, 4]. Usually the shot has a high ionic comonomer content compared with the feed of the original polymerization. The change in latex properties is attributed to formation of a core-shell structure in which the shell is formed by the shot comonomers. In this line of thought the application of this shot-growth method on emulsifier-free emulsion polymerization of styrene and qVPBr can result in formation of a polymer shell with more hydrophilic polymer chains compared with batch latices. Secondly, copolymers of 4-vinylpyridine (4VP) and St may also exhibit interesting catalytic properties even if they are prepared by radical polymerization. Based on reactivity ratios for radical polymerizations of St and 4VP, relatively long poly(4-vinylpyridine) blocks can be present in these copolymers, when 4VP content of the copolymer is high [5]. For 90 wt% 4VP units in the polymer an average block length of 10 can be expected.

In this paper we report on the shot–growth method in the emulsifier-free emulsion polymerization of St and qVPBr applying azo-bis(isobutyramidine hydrochloride) (AIBA·2HCI) as initiator. The optimum conversion of the batch latex at which to add the second charge monomer mixture was determined. Also poly(styrene-co-1-methyl 4-vinylpyridinium bromide) (PS-qPVP, 10 wt% St units) was used as emulsifier to prepare polystyrene latices. Surface characteristics of cleaned latices were investigated by &potential measurements and conductometric titration. After immobilization of CoTSPc reaction rates in the oxidative coupling of ME were determined. The results are compared with the batch latex system.

EXPERIMENTAL PROCEDURES

Apparatus

Reactors used for polymerizations, conversion measurements and thiol oxidations are described elsewhere [1]. A Cambridge S-200 scanning electron microscope was used to determine particle size and particle size distributions. Spectroscopic measurements were performed with a Hewlett Packard 8451A diode array spectrophotometer. Infrared spectra were recorded on a Mattson Polaris FTIR spectrophotometer. Electrophoretic mobilities were measured using a Malvern Zetasizer 3 and &potentials were corrected according to the Henry equation [6]. Centrifugation was done on Centrikon T-2060 ultracentrifuge. A Knauer vapour pressure osmometer was used for molar mass determinations. Conductometric titration curves were recorded on a CDM80 conductivity meter, using a PP1042 cell (Radiometer). Amicon serum replacement cells were used with 100 or 200 nm pore size polycarbonate membranes (Nucleopore).

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Materials

Styrene (Merck) was distilled under nitrogen atmosphere at 69°/6·10³ Pa to remove inhibitor, after which it was kept at 2° until usage. 4-Vinylpyridine (Janssen Chimica) was distilled twice at 31°/5·10³ Pa and kept dark at −18° until used. 2-Mercaptoethanol (Janssen Chimica) was distilled at atmospheric pressure and kept dark until used. Deionized water was used for all polymerizations after purging with argon. AIBA·2HCl, poly(styrene-co-4-vinylpyridine) with 10 wt% St units was supplied by Polyscie ne, bromomethane (Fluka), dimethyl sulfoxide p.a. (DMSO), methanol p.a., acetonitrile p.a., silica (Kieselgel 60, 63-200 μm) by Merck. Iodomethane, N,N-dimethylformamide p.a. (DMF) and hydroquinone (Janssen Chimica) were used without further purification.

Synthesis and polymerization procedures

Synthesis of qVPBr was carried out as reported [1].

The number average molar mass of poly(styrene-co-4-vinylpyridine) is 4.500 ± 500, determined by vapour pressure osmometry in methanol at 45°. Methylation of this copolymer with iodomethane was carried out according to literature in DMF/DMSO (3:2 by volume) [7]. Complete quaternization was demonstrated by i.r. spectroscopy [8].

The polymerizations were carried out in a reactor heated to 60°, in which 360 cm³ water and 0.42 mol St were placed. The mixture was stirred at 300 rpm for 10 min with nitrogen passing through the reactor. 5·10⁻³ mol qVPBr dissolved in 5 cm³ of water was added and washed in with an additional 20 cm³ water. When the reaction temperature (60°) was reached 9·10⁻⁴ mol initiator in 5 cm³ of water was added and washed in with 10 cm³ water. After the desired conversion was reached, shots of St, qVPBr and AIBA·2HCl in water were added through a neoprene septum. After a reaction time of 18-20 hr, the product was heated to 90° for 2 hr to decompose residual initiator. Finally the latex was filtered to remove any coagulum present. Samples for polymerization rate measurements were short stopped with hydroquinone and conversions were determined by weight based on amount of polystyrene present.

Cleaning procedures

Latices were cleaned by centrifuging twice for 30 min at 20,000-30,000 rpm, depending on particle size, to reduce both soluble cationic polymer concentration and ionic strength. After each run the supernatants were replaced by water of low conductance (<0.6 μS/cm) and the latices were redispersed. Latices cleaned according to the described combination of ultracentrifugation and serum replacement still contained adsorbed polyelectrolyte. Desorption during catalytic measurements clearly influenced the oxygen consumption rate [9]. Therefore latices were treated with three portions of silica (2 g/100 cm³ latex) after centrifugation. After shaking the latices with silica for 6-8 hr the silica was filtered off. Centrifugation of these latices was finally employed to remove possible impurities arising from silica treatment. 30 cm³ samples were placed in serum replacement cells and washed with water of low conductance. Samples of the serum were checked for presence of polyelectrolyte with a VIS spectrophotometric method [10]. In the presence of a CoTSPE solution N⁺ concentrations of 8·10⁻⁷ mol/dm³ and up result in an absorbance maximum at 630 nm, originating from the dimeric structure of CoTSPE. If no N⁺ was detectable, the latices were washed with 1000 cm³ 0.001 N NaOH solution to replace all counter ions by hydroxyl ions. After washing with 1000 cm³ of water to remove excess of base the latices were conductometrically titrated with 0.001 N HCl under an argon atmosphere.

Catalytic measurements

Catalyst preparation and oxidation rate measurements were described earlier [1].

RESULTS AND DISCUSSION

Shot–growth latices

The effect of shot addition on particle properties in the emulsifier-free emulsion copolymerization of styrene and sodium sulphonate [4] and the overcoating of St and St/isoprene latices with acrylamide monomers [3, 11, 12] has been considered in some detail. In all cases particle properties strongly depended on time of addition of the second charge. Usually only addition at about 90% conversion rendered satisfactory results. This dependence on conversion is thought to be related to the residual St concentration in the core particles. The capture efficiency of the core particles for oligomeric radicals formed after shot addition, determined by both swelling rate and polymerization rate [13], increases on the presence of residual St in the batch latex particles [4]. On the other hand the high viscosity inside the particles hinders diffusion of shot monomers into the particle. Because of these considerations polymerization of the shot monomers is thought to take place at the particle–water interface. Shell formation as well as the covalent attachment of the shell to the core support this suggestion.

In the case of qVPBr latices shot addition at 85% conversion, based on the polymerization of batch latex B1, depicted in Fig. 1 rendered best results (Table 1). Addition at 0% conversion resulted in the formation of a coagulated latex as reported earlier [1]. For shot addition around 60% conversion a heterodisperse latex was observed. At this conversion St is captured by the monomer droplets still present, which makes uptake by the monomer swollen particles unlikely. Because of the increase in ionic comonomer concentration and initiator concentration in the water phase upon shot addition polyelectrolyte formation and secondary homogeneous nucleation can be expected, resulting in a heterodisperse latex system. At almost complete conversion polydispersity increased. Possibly complete absorption of the shot St fraction by the starved polymer particles is the problem in this case. The

![Fig. 1. Conversion–time curve of St for batch latex B1. [St] = 1.05 mol/dm³, [qVPBr] = 12·10⁻³ mol/dm³, [AIBA·2HCl] = 2.3·10⁻³ mol/dm³.](image-url)
lowest polydispersity was found with shot addition at 85\% for a relatively low qVPBr concentration of the shot. Recipes for latex preparation with PS-qPVP are depicted in Table 2. Although colloidal stability was good, polydispersity was relatively high.

Characterization

The surface charge of the latices originates from ionic groups at the particle–water interface of the initiator, cationic comonomer or emulsifier. Potentiometric titration of bromide ions in cleaned qVBBr latices with silver nitrate, gave no reproducible values. Replacement of bromide ions during latex handling and cleaning with counter ions not detectible with silver nitrate is thought to cause this problem. These problems were not encountered with conductometric titration with HCl after replacing the ions with hydroxyl in serum replacement cells.

The titration curve of latex SG5 typical for these shot–growth latices is depicted in Fig. 2. Initially the conductivity hardly changes on addition of 0.001 N HCl. When all hydroxyl ions in the electrical double layer are replaced, the conductivity rises as a result of excess acid added. Back titration with 0.001 N NaOH was shown to increase the accuracy of equivalence point determination, because of a decreased carbon dioxide solubility at low pH [14]. However, for the shot–growth latices an interesting discrepancy was found for the equivalence point determination of the HCl and NaOH titration. On back titration more surface groups were detected. A similar effect was reported for the conductometric titration of acrylic acid copolymer latices with a pH dependent surface charge [15, 16]. The presence of water soluble polyelectrolyte at the particle surface was suggested to explain the reported results [17]. At high pH electrostatic repulsion between deprotonated acrylic acid groups resulted in extension of the surface polymer chains in solution. Shrinkage of the polymer shell for lower pH values, accompanied by burying part of the endgroups, was held responsible for the decrease in surface charge density. The number of acidic groups determined by direct titration with NaOH was smaller than the amount determined by back titration with HCl.

In the present case pH independent groups account for the surface charge of the particles. The effect of ionic strength on a hydrophilic polymer shell at the particle surface has to be considered since it is the only parameter changing on titration of the latex. On HCl addition the increase in ionic strength could shrink the polymer shell thereby trapping part of the excess HCl. For back titration with NaOH a fictional increase in surface charge density is found. Also for latex E1 this discrepancy was established although less pronounced. On numerous titrations of qVPBr batch latices this behaviour was not encountered. Latices characteristics are given in Table 3.

The effect of water soluble polyelectrolyte at the particle surface on the \( \zeta \)-potential of anionic latices also was studied in the case of acrylic acid copolymer latices [17]. A maximum in the \( \zeta \)-potential dependence on electrolyte concentration was depicted in Fig. 3. Shell shrinkage due to increase in electrolyte concentration has been thought to locate the slipping plane in the electrical double layer closer to the particle surface [17]. The accompanied increase in \( \zeta \)-potential gives rise to the depicted optimum. At higher electrolyte concentrations coagulation decreases the \( \zeta \)-potential. As shown both latex E1 and SG5 gave rise to an optimum in \( \zeta \)-potential in contrast to latex B1. We therefore suggest the presence of a hairy water soluble polyelectrolyte shell in these cases.

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

<table>
<thead>
<tr>
<th>Latex</th>
<th>( D_n ) (nm)</th>
<th>( D_n/D_s )</th>
<th>Surface charge density (( \mu C/cm^2 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>250</td>
<td>1.02</td>
<td>21.4</td>
</tr>
<tr>
<td>SG5</td>
<td>240</td>
<td>1.02</td>
<td>9.8</td>
</tr>
<tr>
<td>E2</td>
<td>190</td>
<td>1.22</td>
<td>12.6</td>
</tr>
</tbody>
</table>

*Excess HCl added, back titration with 0.001 N NaOH.

Table 1: Effect of conversion of batch latex B1* and shot comonomer concentration on number average particle diameter. Shot: 0.4 \( 10^{-3} \) mol AIBA-2HCl, 57.6 \( 10^{-3} \) mol St, 1.1 mol water

<table>
<thead>
<tr>
<th>Latex</th>
<th>qVPBr ( 10^{-3} ) mol</th>
<th>Shot addition % conversion</th>
<th>( D_n ) (nm)</th>
<th>( D_s ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG1</td>
<td>6.0</td>
<td>0</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>SG2</td>
<td>6.0</td>
<td>60</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>SG3</td>
<td>6.0</td>
<td>85</td>
<td>250</td>
<td>1.03</td>
</tr>
<tr>
<td>SG4</td>
<td>6.0</td>
<td>95</td>
<td>260</td>
<td>1.10</td>
</tr>
<tr>
<td>SG5</td>
<td>4.0</td>
<td>85</td>
<td>240</td>
<td>1.02</td>
</tr>
<tr>
<td>SG6</td>
<td>4.0</td>
<td>&gt; 98</td>
<td>280</td>
<td>1.06</td>
</tr>
</tbody>
</table>

*Experimental conditions for latex B1 are given in the legend to Fig. 1.

Table 2: Preparation conditions PS-qPVP emulsifier latices at 60\°C.

<table>
<thead>
<tr>
<th>Latex</th>
<th>AIBA -2HCl (g)</th>
<th>PS-qPVP (g)</th>
<th>( D_n ) (nm)</th>
<th>( D_s ) (nm)</th>
<th>( D_s/D_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>1.00</td>
<td>3.5</td>
<td>180</td>
<td>1.24</td>
<td></td>
</tr>
<tr>
<td>E2</td>
<td>0.75</td>
<td>6.5</td>
<td>190</td>
<td>1.22</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Characteristics of latex systems

<table>
<thead>
<tr>
<th>Latex</th>
<th>( D_n ) (nm)</th>
<th>( D_s ) (nm)</th>
<th>( D_s/D_n )</th>
<th>HCl ( cm^3 )</th>
<th>NaOH* ( cm^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>250</td>
<td>1.02</td>
<td>21.4</td>
<td>21.4</td>
<td></td>
</tr>
<tr>
<td>SG5</td>
<td>240</td>
<td>1.02</td>
<td>9.8</td>
<td>10.6</td>
<td></td>
</tr>
<tr>
<td>E2</td>
<td>190</td>
<td>1.22</td>
<td>12.6</td>
<td>13.7</td>
<td></td>
</tr>
</tbody>
</table>
two-substrate Michaelis–Menten model [18] presented below

\[
E + S_1 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES_1
\]

\[
ES_1 + S_2 \underset{k_{-2}}{\overset{k_{2}}{\rightleftharpoons}} ES_1S_2
\]

\[
ES_1S_2 \overset{k_3}{\rightarrow} E + P
\]

with \( E = \text{CoTSPc}, \ S_1 = \text{ME}, \ S_2 = \text{O}_2 \) and \( P = 2,2'\text{-dithiodiethanol} \). An expression for the rate of ME consumption (\( R \)) can be derived assuming pseudo steady-state kinetics in both \( ES_1 \) and \( ES_1S_2 \). At constant oxygen concentration equation (1) results, with

\[
k' = \frac{4 \cdot k_{2} \cdot [O_2]}{(C_2 + [O_2])} \] the turn-over frequency at 0.1 MPa \( \text{O}_2 \) and saturation in thiol, \( K_M = \frac{(C_2 \cdot [O_2] + C_4)}{(C_3 + [O_2])} \) the apparent Michaelis constant, \( C_3 = \frac{k_2 \cdot k_3}{k_1} \) and \( C_4 = \frac{k_{-1}}{k_1} \).

\[
R = \frac{k' \cdot [\text{CoTSPc}] \cdot [\text{ME}]}{K_M + [\text{ME}]} \quad (1)
\]

Figures 4 and 5 depict the pH and \([N^+] \) dependence of the oxidation rate for the three systems described in Table 3 respectively. Consideration to the occurrence of maxima in these curves is given elsewhere [19, 20]. The dependence of reaction rate on thiol concentration at optimum pH and \([N^+] \) conditions is depicted in Fig. 6. The saturation behaviour typical of enzyme-like kinetics is observed. Both turn-over frequency and apparent Michaelis constant were determined from the Lineweaver–Burk plot (Fig. 7). These constants are indicative of the activity of the catalytic system and are listed in Table 4 together with results obtained earlier.

No significant difference in the turn-over frequency of the homogeneous methylated poly(4-vinylpyridine)(qPVP) and the shot-growth latex system was found. The shift in pH optimum from 8.5 to 9.0 is too small to be related to a difference in linear charge density as was done for ionene systems [9]. CoTSPc aggregation responsible for the catalytic properties of this system was shown to be dependent on linear charge density [21]. The increase in turn-over frequency of the shot-growth latex system compared with the batch latex indicates that surface characteristics of these systems differ. The difference seems to stem from the applied shot and could be attributed to dissimilarities in nature or length of cationic blocks at the particle interface. Additional evidence of this phenomenon comes from
Catalytic activity of cationic latices

Fig. 7. Lineweaver-Burk plot of immobilized latex systems at 25°C. Latex B1 (+), SG5 (▲) and E2 (●). Conditions as depicted in Fig. 6.

Table 4. 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>B1</td>
<td>128 ± 16</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>SG5</td>
<td>1100 ± 190</td>
<td>0.15 ± 0.02</td>
</tr>
<tr>
<td>E2</td>
<td>165 ± 17</td>
<td>0.09 ± 0.02</td>
</tr>
<tr>
<td>Latex MAD</td>
<td>690 ± 10</td>
<td>0.95 ± 0.09</td>
</tr>
<tr>
<td>qPVP</td>
<td>1400 ± 110</td>
<td>2.6 ± 0.4</td>
</tr>
</tbody>
</table>

- and conductometric titration support these assumptions. The use of a methylated copolymer of St and 4VP as emulsifier also suggested a hairy particle surface. CoTSPc aggregation was not sufficiently stimulated by this copolymer however.

CONCLUSIONS

Shot-growth latices were successfully prepared by emulsifier-free emulsion polymerization of St and 1-methyl-4-vinylpyridinium bromide. The increase in co-catalytic properties of the latices are attributed to formation of a hydrophilic shell of the shot comonomer. -Potential measurements and conductometric titration support these assumptions. The use of a methylated copolymer of St and 4VP as emulsifier also suggested a hairy particle surface. CoTSPc aggregation was not sufficiently stimulated by this copolymer however.

REFERENCES