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

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Abstract

Cationic latices, products of emulsion copolymerization of styrene with 3-(methacrylamidinopropyl)trimethylammoniumchloride (MAD), and its homopolymer (PMAD) have been tested as cocatalyst in the autoxidation of 2-mercaptoethanol in the presence of cobalt(II)phthalocyanine tetrasodiumsulphonate (CoTSPc). It was found that all systems studied enhanced the catalytic activity compared with the polymer-free CoTSPc-containing system. The systems examined 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 such immobilization. However, the catalytic activity often decreases on immobilization as a result of mass transport limitations. In the last decade, much 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 their 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 [1].

Polymer colloids have been used to immobilize enzymes [2, 3] for various purposes, sulphonic acid for sucrose inversion [4–6] and for ester hydrolysis

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

We recently reported the immobilization of cobalt(II)phthalocyanine tetrasodiumsulphonate (CoTSPc, **1**, Fig. 1) on latex particles stabilized by block-type copolymers of styrene and quaternized 4-vinylpyridine (PS-*b*-qPVP) for the autoxidation of 2-mercaptoethanol (ME) [23]. The block copolymer stabilizes latex particles, binds CoTSPc and, in addition, the cationic segments of PS-*b*-qPVP act as cocatalyst in the thiol oxidation. Cationic polymers are known accelerators in the CoTSPc-catalyzed oxidation of thiol. The role of the cocatalyst is four-fold: (1) binding of CoTSPc, (2) substrate enrichment, (3) preventing the formation of inactive oxygen-bridged dimers of CoTSPc, and (4) formation of highly active CoTSPc aggregates.

In this paper we describe the effect of the immobilization of CoTSPc on cationic latices on the oxidation of 2-mercaptoethanol. The cationic latices were prepared by emulsion copolymerization of styrene with 3-(methacrylamidinopropyl)trimethylammoniumchloride (MAD, **2**, Fig. 1), as has been described elsewhere [24]. The activity of the homopolymer of 3-(metha-

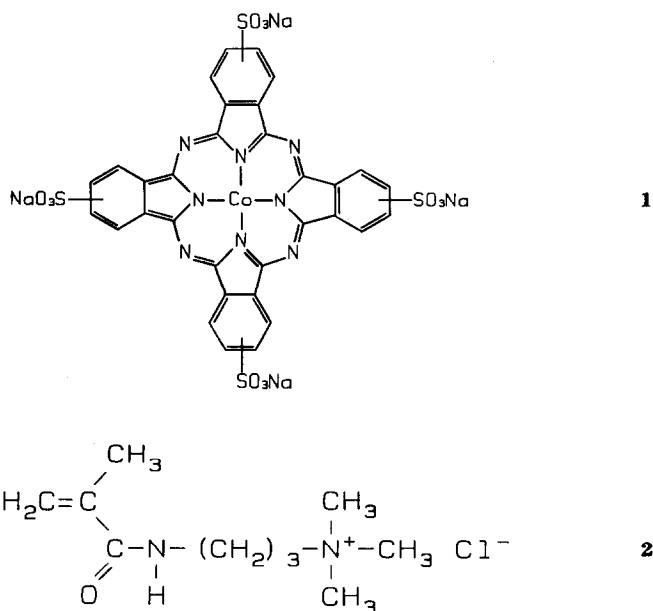


Fig. 1. Structures of CoTSPc (**1**) and MAD (**2**).

crylamidinopropyl)trimethylammoniumchloride (PMAD) has also been measured in order to allow a study on the effect of immobilization.

Experimental

Both latices S5 and SG3 were prepared by emulsion copolymerization of styrene and 3-(methacrylamidinopropyl)trimethylammoniumchloride (MAD) as comonomer and purified as previously described; however, S5 was prepared by batch and SG3 by shot-growth emulsion copolymerization [24]. Data characterizing the produced latices are presented in Table 1. Poly-3-(methacrylamidinopropyl)trimethylammoniumchloride (PMAD) was prepared by polymerization of MAD in methanol, using azobis(isobutyramidine hydrochloride) (AIBA) as initiator.

Vis spectra were recorded on a Hewlett-Packard diode array 8451A spectrophotometer using a 1-cm cell. The Vis reflectance spectra were recorded on a Hitachi 150-20 spectrophotometer using an integrating sphere. All spectra were measured at 25 °C.

The latices were precipitated by ultracentrifugation (20 000–30 000 rpm for 30 min, Centrikon T-2060).

Catalytic measurements

The catalyst was prepared by adding a CoTSPc solution (2×10^{-5} mol dm^{-3}) to the diluted latex solution prior to reaction. The catalytic measurements were described elsewhere [25]. This procedure was adapted in such a way as to minimize latex coagulation. pH was adjusted by the addition of a NaOH solution (0.1 M) to this mixture just before the addition of 2-mercaptoethanol. The initial reaction rate was measured immediately after ME was added. General conditions: stirring speed = 2 600 rpm, reaction volume = 0.1 dm^3 and $T = 25$ °C.

Results and discussion

Catalyst bleeding and stability

The catalytic system under study is extremely susceptible to very low concentrations of cocatalyst (see also Fig. 4). Clearly, in the case of the

TABLE 1
Data of the latices used in the catalytic experiments

Latex	Particle size (nm)	Surface charge density	
		($\mu\text{mol g}^{-1}$)	($\mu\text{mol m}^{-2}$)
S5	162	54.5	1.54
SG3	214	32.6	1.22

heterogeneous CoTSPc-bound latices, the absence of free nonimmobilized polyelectrolyte, an inevitable side product during the synthesis of these latices, must be demonstrated. Moreover, desorption of adsorbed polyelectrolyte and CoTSPc (catalyst bleeding) will lead to deactivation. We earlier reported a spectrophotometric method of detecting low concentrations of cationic polymers ($[N^+] \geq 5 \times 10^{-7}$ M) based on the observation of monomerization or aggregation of CoTSPc in the absence or presence of polyelectrolyte, respectively [26]. A cleaned latex (S5) was stirred under the experimental conditions for 15 min at 2 600 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 was 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 largely determines the possible commercial applicability of catalysts is their activity after reuse. The activity of the systems under study, as depicted in Fig. 2, 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 (Scheme 1), CoTSPc-catalyzed thiol oxidation yielding H_2O_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].



Scheme 1.

In our earlier work on poly(vinylamine) (PVAm) as polymer ligand, it was demonstrated that CoTSPc is deactivated by H_2O_2 via direct oxidation of the phthalocyanine ring, while the polymer backbone is affected by the oxidation by H_2O_2 of thiol and disulphide to sulphur-containing oxo-acids [27]. 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.

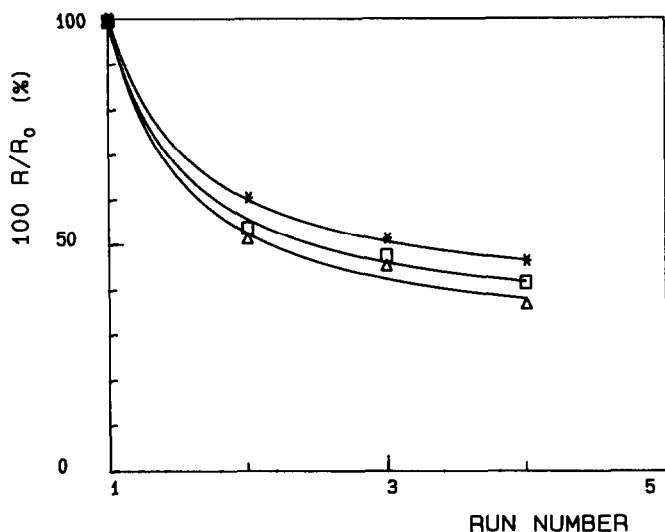


Fig. 2. Relative reaction rate as function of run number. $[\text{CoTSPc}] = 4 \times 10^{-7} \text{ mol dm}^{-3}$, $[\text{N}^+](\text{S5}) = 3.6 \times 10^{-6} \text{ mol dm}^{-3}$, $[\text{N}^+](\text{SG3}) = 4.2 \times 10^{-6} \text{ mol dm}^{-3}$, $[\text{N}^+](\text{PMAD}) = 10^{-5} \text{ mol dm}^{-3}$, $\text{pH} = 9.0$. Every run is started by the addition of 1 ml ME (0.0143 mol); (□) S5, (△) SG3, (*) PMAD.

Colloidal (in)stability may also play a role in the case of the CoTSPc-bound latex system. The colloidal stability is a known problem in catalyst-immobilized latex systems [9, 22, 29]. In the case of CoTSPc-bound latex system stabilized by a block-type copolymer of styrene and quaternized 4-vinylpyridine we also observed some colloidal instability [23]. For the present latex systems (S5 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 differences 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, on raising the pH to 12 some coagulation in the form of coagulum adhering to the reactor wall could be observed. Similar coagulation effects were obtained on increasing the ionic strength of the latex solution (0.1 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 cocatalyst in the CoTSPc-catalyzed oxidation of 2-mercaptoethanol (ME) give rise to an enzyme-like kinetic behaviour. In the present investigation we have studied the catalytic behaviour and kinetics of the colloiddally immobilized systems.

The pH dependence of the oxidation rate as depicted in Fig. 3 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 ($\text{pK}_a=9.6$), it can be expected that the oxidation rate will increase on increasing pH. However, the simultaneous increase in ionic strength and hydroxide concentration leads to a competitive ion effect and results in the observed optimum in catalytic activity [30, 31]. Figure 3 also clearly shows the higher activity of free PMAD compared with the latex systems.

The oxidation rate as a function of the cocatalyst concentration shown in Fig. 4 is again typical of cationic polymer cocatalyzed thiol oxidation. Van Welzen *et al.* showed by UV-Vis spectroscopy that highly active aggregates of CoTSPc are formed at $\text{N}^+/\text{Co} \geq 4$ [32]. The optimum experimentally found at higher N^+/Co ratio stems from the fact that, at $\text{N}^+/\text{Co}=4$, the complex is electrostatically neutral (CoTSPc is four-fold negative) and hence no substrate enrichment can occur. After an optimum polymer/CoTSPc ratio is reached, further increase in the cocatalyst concentration (keeping [CoTSPc] constant) will lead to a decrease in the local thiolate anion concentration at the cobalt center. In addition, the increase in polyelectrolyte concentration causes an increase in ionic strength, thus affecting the polymer coil structure, and simultaneously causing substrate competition between polyelectrolyte counter-ions 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 paper.

Before determining the reaction constants of the systems, the absence of mass transfer limitations must be demonstrated. The linear dependence

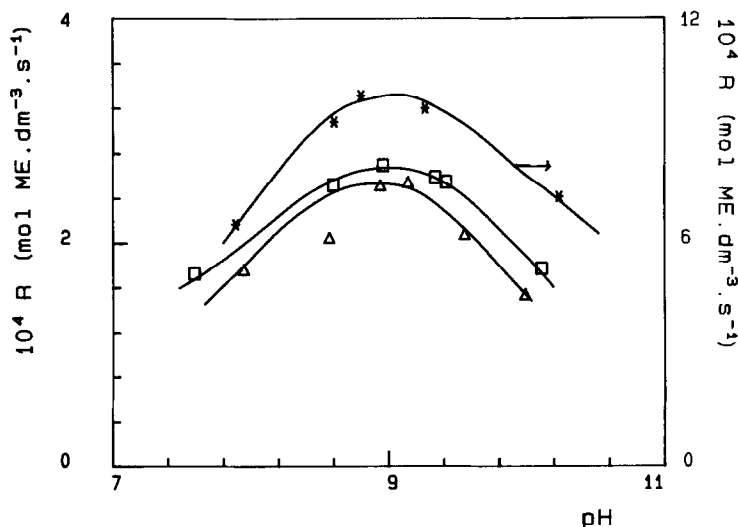


Fig. 3. Catalytic activity as a function of pH. $[\text{ME}] = 0.143 \text{ mol dm}^{-3}$, $[\text{CoTSPc}] = 4 \times 10^{-7} \text{ mol dm}^{-3}$, $[\text{N}^+](\text{S5}) = 3.6 \times 10^{-6} \text{ mol dm}^{-3}$, $[\text{N}^+](\text{SG3}) = 4.2 \times 10^{-6} \text{ mol dm}^{-3}$, $[\text{N}^+](\text{PMAD}) = 10^{-5} \text{ mol dm}^{-3}$; (\square) S5, (Δ) SG3, ($*$) PMAD.

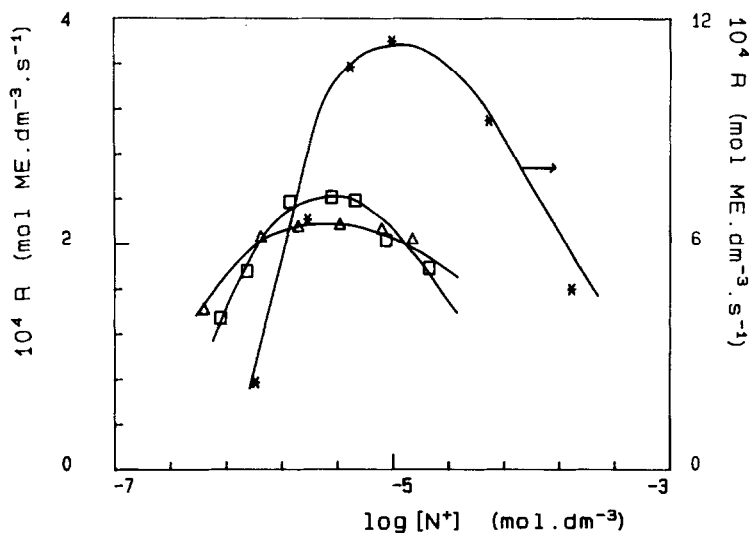


Fig. 4. Effect of the N^+/Co ratio on the reaction rate. $[ME] = 0.143 \text{ mol dm}^{-3}$, $[CoTSPc] = 4 \times 10^{-7} \text{ mol dm}^{-3}$, $\text{pH} = 9.0$; (\square) S5, (\triangle) SG3, ($*$) PMAD.

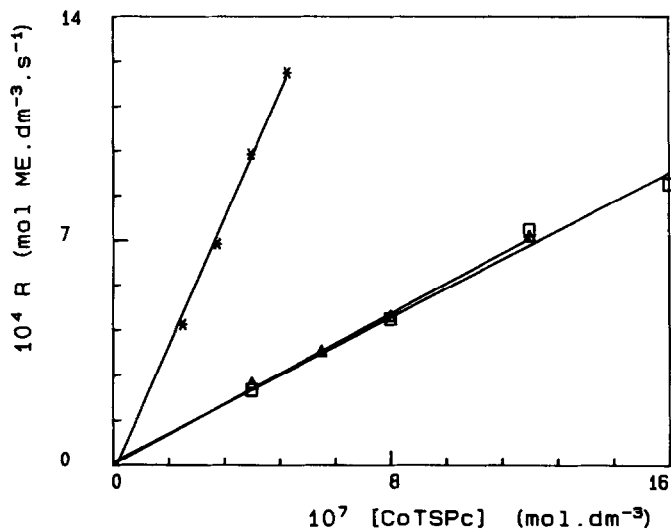


Fig. 5. Reaction rate as a function of catalyst concentration (keeping N^+/Co ratio constant). $[ME] = 0.143 \text{ mol dm}^{-3}$, $\text{pH} = 9.0$, $N^+/Co(S5) = 9$, $N^+/Co(SG3) = 10.4$, $N^+/Co(PMAD) = 25$; (\square) S5, (\triangle) SG3, ($*$) PMAD.

of the catalytic activity on the catalyst concentration ($N^+/Co = \text{constant}$) clearly demonstrates the absence of mass transport limitations in the present case (Fig. 5).

For the three catalytic systems under study, a saturation behaviour typical of enzyme-like kinetics was found on measuring the reactivity as a function

of the substrate concentration (Fig. 6). This type of kinetics can be described by a two-substrate Michaelis–Menten model [30] presented in Scheme 2.



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 by assuming steady-state kinetics in both ES_1 and ES_1S_2 . At constant oxygen concentration, eqn. (7) results:

$$R = \frac{k'[\text{CoTSPc}][\text{ME}]}{K_M' + [\text{ME}]} \quad (7)$$

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

From the double reciprocal plot of reactivity *vs.* substrate concentration (the so-called Lineweaver–Burk plot, Fig. 7) the turnover frequency and Michaelis constant can be determined (Table 2).

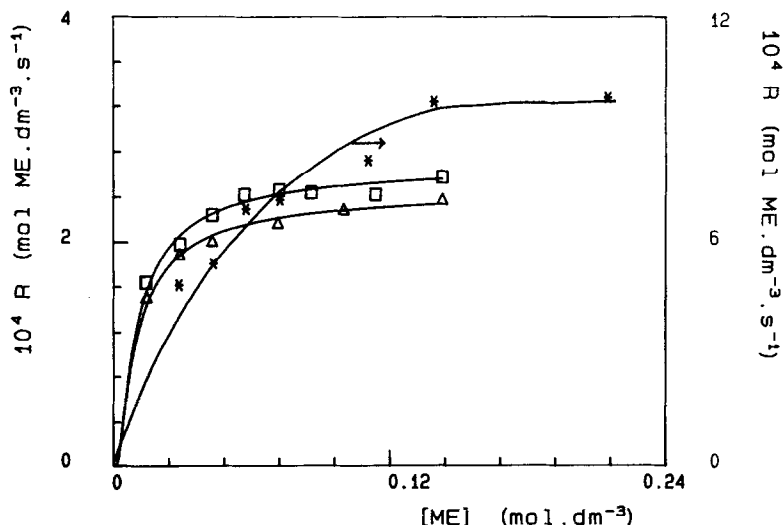


Fig. 6. Catalytic activity as a function of substrate (ME) concentration. $\text{pH} = 9.0$, $[\text{CoTSPc}] = 4 \times 10^{-7} \text{ mol dm}^{-3}$, $[\text{N}^+](\text{S5}) = 3.6 \times 10^{-6} \text{ mol dm}^{-3}$, $[\text{N}^+](\text{SG3}) = 4.2 \times 10^{-6} \text{ mol dm}^{-3}$, $[\text{N}^+](\text{PMAD}) = 10^{-6} \text{ mol dm}^{-3}$, (\square) S5, (Δ) SG3, ($*$) PMAD.

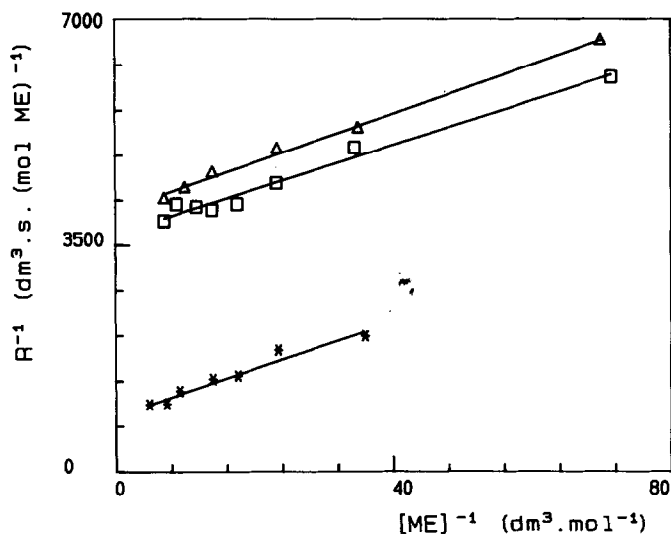


Fig. 7. Lineweaver-Burk plots of the catalytic systems under study. For experimental conditions see Fig. 6.

TABLE 2

Turnover frequencies and apparent Michaelis constants of the catalytic systems under study. Experimental conditions as in Fig. 6

	k' (mol ME (mol Co s) ⁻¹)	$10^2 K_M'$ (mol ME dm ⁻³)
PMAD	2900 ± 190	4.53 ± 0.72
S5	690 ± 10	0.95 ± 0.09
SG3	630 ± 10	0.95 ± 0.05

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 polymer systems, for example 2,4-ionene and PVAm. Due to the long side groups carrying the cationic groups, the linear charge density parameter [33] (σ) cannot be calculated accurately. The estimated linear charge density ($\sigma \approx 1.15$) lies in the same region as those calculated for PVAm ($\sigma = 0.99$) and 2,4-ionene ($\sigma = 1.44$). Since it has been shown that the catalytic activity of these polyelectrolytes is proportional to the linear charge density parameter [34, 35], the observed activity for PMAD closely agrees with the estimated linear charge density.

However, not only charge density (in terms of the linear charge density of polymers or surface charge density of latices) dominates the catalytic activity. This was clearly demonstrated by van Welzen *et al.* who compared

TABLE 3
Reaction rates of several CoTSPc-containing systems

System	R/R_0^a	pH
<i>homogeneous</i>		
OH ⁻	1	8.9
PVAm [35]	41.1	8.0
2,4-ionene [25]	59.3	9.0
qPVP [23]	20.5 ^b	8.7
PS-b-qPVP [23]	16.1 ^b	8.7
PMAD	42.5	9.0
oleyl-3,3-ionene	57.5	9.0
<i>heterogeneous</i>		
2,4-ionene/XAD-2 [26]	10.3	7.3
qPVP/latex [23]	24.9 ^b	8.7
MAD/latex S5	10.0	9.0
MAD/latex SG3	9.1	9.0

^a $R_0 = 2.73 \times 10^{-5}$ mol thiol $\text{dm}^{-3} \text{s}^{-1}$, [CoTSPc] = 4×10^{-7} mol dm^{-3} , [ME] = 0.143 mol dm^{-3} .

^bMeasured when saturation in [ME] is reached.

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 $N^+/\text{Co} \geq 4$ 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 four-fold 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 $N^+/\text{Co} \geq 4$ disappeared again on further increasing polyelectrolyte concentration. This phenomenon was attributed to the formation of micelle-like hydrophobic domains above the critical micelle concentration, which favoured the CoTSPc monomerization. Interestingly, on diluting these micelle-containing solutions (keeping N^+/Co constant), aggregation of CoTSPc occurred 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. On further addition of 2,10-ionene, more micelles will be formed and, as a consequence, more monomerization will be observed.

If a surfactant containing long cationic tails, for example oleyl-3,3-ionene [37] (Fig. 8), is used as cocatalyst instead of soap-like 2,10-ionene, contrasting results are observed. The micellar surface of this polymeric surfactant contains hydrophilic polymer segments of sufficiently high charge density and sufficient length, extending into the water phase. The soap-like behaviour of oleyl-3,3-ionene can be described in terms of a critical micelle concentration

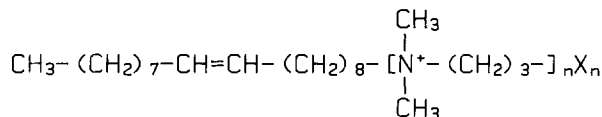


Fig. 8. Structure of oleyl-3,3-ionene ($\text{X} = \text{Cl}^-$ or I^-).

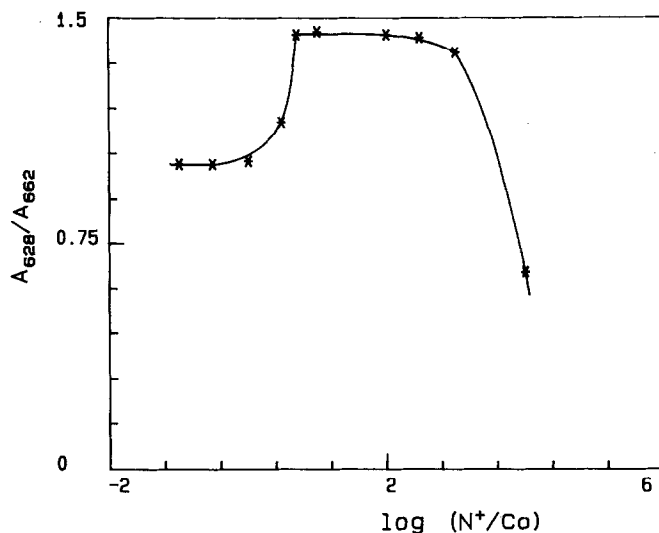


Fig. 9. Ratio of absorbances at 628 nm and 662 nm as a function of the N^+/Co ratio for oleyl-3,3-ionene; $[\text{CoTSPc}] = 10^{-5} \text{ mol dm}^{-3}$.

($\text{cmc} = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$) [38]. To obtain information about the presence of CoTSPc aggregates in oleyl-3,3-ionene-containing solutions, visible light experiments were carried out over a wide range of N^+/Co ratios for oleyl-3,3-ionene (Fig. 9). It appeared from earlier experiments that the ratio of the absorbances at 628 nm and 662 nm is a measure of the relative amount of aggregated cobalt species [32]. At N^+/Co ratios between 4 and 10^3 a relatively high A_{628}/A_{662} ratio is found, indicating aggregation of CoTSPc. This implies that for oleyl-3,3-ionene, in contrast with the soap-like 2,10-ionene, even above the critical micelle concentration considerable aggregation is present. The deaggregation at high N^+/Co ratios must be ascribed to diluting effects of the CoTSPc rather than micellization.

The cocatalytic properties of oleyl-3,3-ionene (Figs. 10 and 11) in terms of intrinsic activity, pH optimum and N^+/Co optimum are comparable with those of the analogue polyelectrolyte 3,3-ionene (or 2,4-ionene) [35, 36]. Apparently, under catalytic conditions oleyl-3,3-ionene behaves like 3,3-ionene. To obtain high catalytic activities, it can be concluded that it is necessary to use polymeric surfactants (or latex particles) with long cationic tails of a sufficiently high charge density.

Table 3 shows that all immobilized systems exhibit much higher catalytic activities than the polymer-free system. It is interesting to compare the MAD-

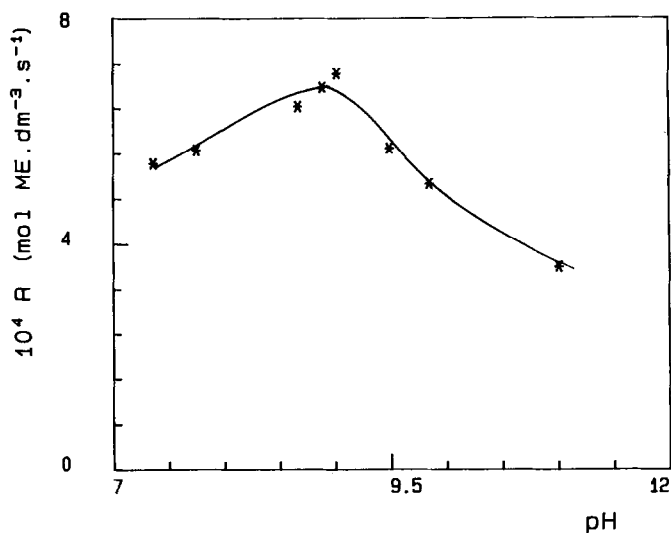


Fig. 10. Catalytic activity of oleyl-3,3-ionene as function of pH. $[ME]=0.143$ mol dm⁻³, $[CoTSPc]=2 \times 10^{-7}$ mol dm⁻³, $[N^+]=1.5 \times 10^{-5}$ mol dm⁻³.

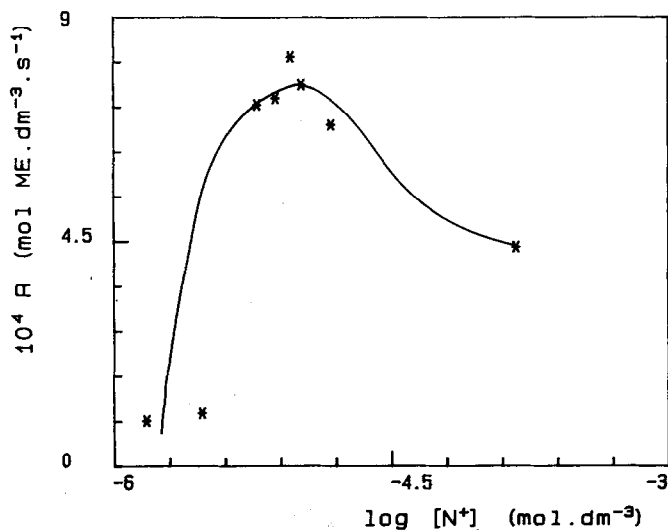


Fig. 11. Effect of varying N^+/Co ratio on catalytic activity of oleyl-3,3-ionene. $[ME]=0.143$ mol dm⁻³, $[CoTSPc]=2 \times 10^{-7}$ mol dm⁻³, pH=9.0.

stabilized latices with those stabilized by an amphiphilic block-type copolymer. The PS-b-qPVP-stabilized latex shows a much higher activity than the MAD/latex systems. However, the methods of preparing these two latex systems hardly allow any comparison to be made. The block-type copolymer-stabilized latex system is prepared by emulsion polymerization of styrene in the presence of an amphiphilic polymeric emulsifier, whereas the MAD-stabilized latices

are prepared by emulsion copolymerization of styrene in the presence of a cationic comonomer. As was pointed out in our previous paper, MAD-rich oligomeric radicals will not likely be trapped by highly (positively) charged latex particles before they terminate [24]. 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 in the particles. Consequently, the linear charge density parameter and molar mass of such anchored polymer chains will be lower than those of the homopolymer (PMAD).

The observed low reactivities of the MAD latex systems are also in line with the Vis reflectance spectra of latex SG3 at different N^+/Co ratios (Fig. 12). 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. Apparently the length of the cationic tails is insufficient and induces little aggregation.

Another striking point is the increase in monomerization on increasing latex concentration ($[\text{CoTSPc}] = \text{constant}$), 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 ($[\text{N}^+] = 8.28 \mu\text{mol dm}^{-3}$, $[\text{CoTSPc}] = 4 \mu\text{mol dm}^{-3}$, curve A in Fig. 12) was found to contain free CoTSPc after centrifugation. About 70% of CoTSPc was bound to the latex surface, that is $N^+/\text{Co}(\text{surface}) = 3$. On doubling the latex

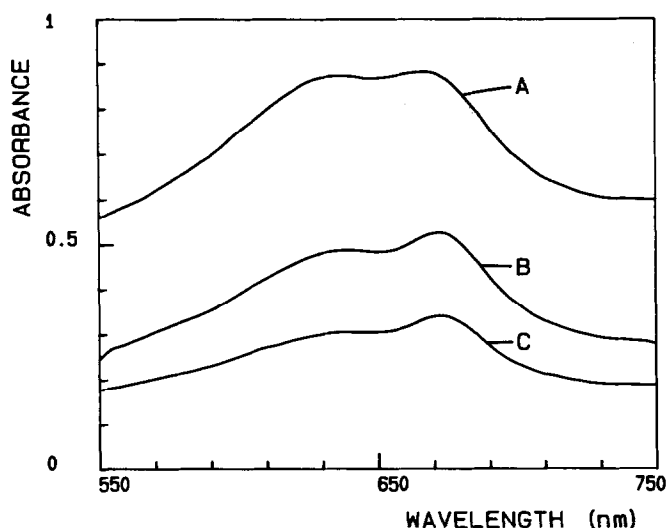


Fig. 12. Vis reflectance spectra of SG3/CoTSPc. $[\text{CoTSPc}] = 4 \times 10^{-6} \text{ mol dm}^{-3}$; (A) $N^+/\text{Co} = 3$, (B) $N^+/\text{Co} = 10.4$, (C) $N^+/\text{Co} = 41.4$.

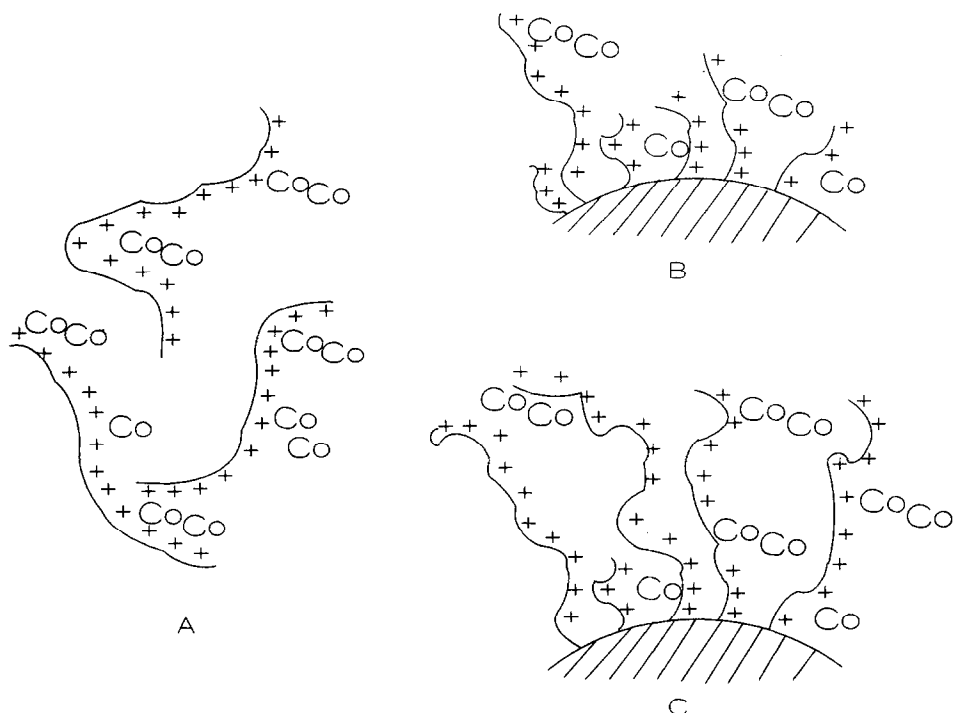


Fig. 13. Structures of CoTSPc in the presence of different cocatalysts. (A) cationic polymer, (B) MAD/latex, (C) ideal system.

concentration ($[N^+] = 18.56 \mu\text{mol dm}^{-3}$, $[\text{CoTSPc}] = 4 \mu\text{mol dm}^{-3}$), CoTSPc could not be detected in the serum 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. 4). 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 frequency and the Michaelis constant for the two MAD-containing latices implies that the differences between the preparation methods hardly affected the catalytic activity.

However, these results are in contrast with those obtained by Twigt *et al.* [39], whose preparation technique had a large effect on the catalytic properties. Styrene/qVP latices prepared by shot-growth emulsion polymerization exhibited 10 times higher activity than latices, prepared by batch emulsion copolymerization, despite of a 2 times lower surface charge density. In this case ζ -potential measurements demonstrated differences in the surface morphology of the particles.

On these grounds we picture the aggregation of CoTSPc as drawn in Fig. 13. 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. Structure B 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 contains both monomeric and aggregated forms of CoTSPc and a moderate activity is therefore observed. Structure C exhibits the most ideal 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 should be similar to that in the homogeneous polymer 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 still unsatisfactory. All three systems showed Michaelis–Menten type of kinetics. The differences between the two copolymeric (styrene-MAD) latex systems, prepared according to different techniques, do not affect the catalytic activity. The observed reaction rates, and also spectrophotometric measurements, indicate 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.

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