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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

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SUMMARY:
To overcome mass transport limitations that are usually encountered on immobilizing highly active catalysts, cationic latex particles were used as support for tetrasodium phthalocyaninato-cobalt(II)tetrasulfonate (2). The cationic latex was prepared by emulsion copolymerization of styrene and divinylbenzene in the presence of a block copolymer from styrene and 4-vinyl-*N*-methylpyridinium PS-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 2 as 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 homogeneous homopolymer (qPVP) 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 retaining 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 conformational changes of the polymer chain on immobilization, a comparison between the latex system and the homogeneous system containing either homopolymer or block copolymer remains difficult.

Introduction

Since heterogeneous peptide synthesis was introduced by Merrifield[1], many immobilization studies on Merrifield-type resins have been published[2,3]. The Merrifield 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 received considerable academic and industrial interest.

Beside this gel-type Merrifield resin, a macroreticular (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 using emulsion polymerization techniques.

Several articles have been published on immobilizing enzymes[4-6] or catalysts[7-12] on latex particles. In the paint industry, latices functionalized with fungicides to prevent mildew defacement, have been synthesized[13, 14]. These chemically modified latices are sometimes called reactive latices[15].

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 **1**, *Scheme 1*) on the catalytic oxidative coupling of 2-mercaptoethanol to its corresponding disulfide in the presence of molecular oxygen and the tetrasodium phthalocyaninatocobalt(II)tetrasulfonate **2** *(Scheme 1)*[16, 17].

Scheme 1:

1

2

3
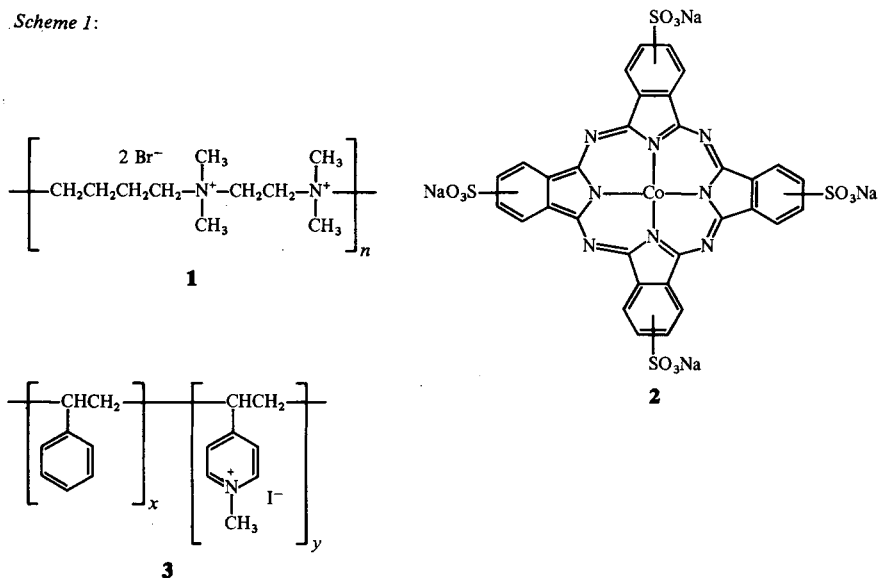
Earlier we reported the immobilization of this very reactive (homogeneous) polymeric catalyst on a macroporous resin[18]. As expected, a lower reaction rate was observed as compared with the homogeneous polyelectrolyte system. This effect was not only due to mass transport limitation of the reactants, but also appeared to be caused by an inhomogeneity of the catalytic support: **2** hardly penetrates into 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 **2** on a cationic latex[19] 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 principal aim of this investigation is anchoring of the highly active 2-polyelectrolyte system onto insoluble supports retaining the high oxidation rate, that is immobilization without the above described disadvantages of conventional immobilization methods. In the present paper we describe (i) the preparation of a cationic latex, containing anchored cationic polyelectrolytes, that will serve as a support for **2** and (ii) 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 1*) as surfactant. The resulting latex was tested as a cocatalyst in thiol oxidation. For comparison, the catalytic activity of systems containing the block copolymer PS-b-qPVP or its homopolymer, quaternized poly(4-vinylpyridine) (qPVP), have also been investigated. A few preliminary results on this system have recently been mentioned in a more comprehensive survey[20]. The complete results will be presented and discussed in the present paper.

Experimental part

The quaternization of the block copolymer polystyrene-*block*-poly(4-vinylpyridine) (10:90 mass %) (Polyscience) and poly(4-vinylpyridine) (Polyscience, number-average relative molecular mass $\bar{M}_n$ = 40000) with methyl iodide in *N,N*-dimethylformamide/dimethyl sulfoxide (3:2, by volume) was carried out according to the literature[21, 22]. Both the IR spectra and the quantitative yields indicated a high degree (>99%) of quaternization. The number-average relative molecular 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 $\bar{M}_n$ = 4500 ± 500. The relative molecular mass of the quaternized product (PS-b-qPVP) was calculated to be 10000 ± 1000. $\bar{M}_n$ of the quaternized poly(4-vinylpyridine) (qPVP) was calculated to be 90000 ± 9000. The reduced viscosity (η_i/c) of qPVP and PS-b-qPVP were measured at 25,0 ± 0,1 °C. Styrene (Merck) and divinylbenzene (Merck, 65 wt.-% of divinylbenzene isomers, 33 wt.-% of ethylvinylbenzene isomers) were distilled prior to use. 4,4'-Azodi-4-cyanovaleric acid (ACPA, Fluka) was used as purchased.

0,92 g of styrene and 0,33 g of divinylbenzene were added to a solution containing 8,97 g of distilled deoxygenated water, 60 mg of K_2CO_3, 0,51 g of PS-b-qPVP and 34 mg of ACPA. The emulsion was polymerized at 60 °C during 24 h under nitrogen atmosphere with magnetic stirring. Purification of the latex is described in the text. The sulfonated ion-exchange resin Dowex 50W-X4 was purified and used as described by Vanderhoff et al.[23, 24]. The serum replacement cell (70 cm^3) was equipped with a 50 nm filter (Nucleopore). The average flow through the cell was 15 cm^3/h. 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 solution of 2 (2 · 10^{-5} mol/dm^3) until the desired concentrations of cationic groups (expressed in mol N$^+$ per dm^3) and of cobalt catalyst were reached. The catalytic activity was measured as the initial reaction rate by monitoring the oxygen consumption immediately after the addition of thiol as described earlier[18, 25]. All reactions were performed at an oxygen pressure of 100 kPa, a temperature of 25 °C and a stirring speed of 2600 r. p. m.

VIS (visible light) spectra were recorded with a Hewlett-Packard diode array 8451 A spectrophotometer using a 1 cm cell.

Results and discussion

Latex preparation

In order to prepare a cationic latex that will serve as support for 2, 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 part*. 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 **2** was adsorbed to the cationic surfactant segments on the latex, this system was tested as a catalyst in the oxidative coupling of 2-mercaptoethanol in oxygen atmosphere. Earlier results in our laboratory showed that extremely low concentrations of free cationic polymer have a strongly accelerating effect on the thiol oxidation (polyelectrolyte concentration expressed as nitrogen concentration: $[N^+] = 10^{-5}$ mol/dm³, i. e. 2,6 mg surfactant per dm³ already affects the reaction rate)[25]. 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 ultraviolet method to detect very low concentrations of cationic polymer, based on the occurrence of the easily detectable monomeric or dimeric form of **2** depending on the absence or presence, respectively, of cationic polymer in solution[18, 26]. For PS-b-qPVP, the lowest $N^+/2$ mole ratio, that is the ratio at which the dimeric form of **2** can still be detected, was experimentally determined to be 3, resulting in a detection limit for the polymeric surfactant of $3 \cdot 10^{-7}$ mol/dm³ at $[2] = 10^{-7}$ mol/dm³.

As expected, the unpurified latex did contain an unacceptably high level of free surfactant. It is obvious that after addition of **2**, 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 using 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 ($[N^+] < 3 \cdot 10^{-7}$ mol/dm³). This was double-checked by measuring the catalytic behaviour of the serum in the thiol oxidation, after addition of **2**. The observed serum activity appeared to be identical with that of a surfactant-free solution, i. e. only **2** in water. The latex data are summarised in Tab. 1.

Tab. 1.   Data of purified latex

Average particle diameter in nm	Solid content in wt.-%	Elemental analysis of solid latex content in wt.-%	$[N^+]$ of latex[a] in mol/dm³
400 ± 30 nm	0,26	C 86,47 H 8,04 N 1,28	$2,38 \cdot 10^{-3}$

[a] $[N^+]$: concentration of N^+ based on the overall nitrogen content as determined by elemental analysis.

The mechanical strength of the latex was investigated by stirring for 30 min in the reaction vessel (three times the average oxidation reaction time). The resulting mixture was again tested for the presence of free polycation. Only a very low concentration of nitrogen was found in the serum ($1,2 \cdot 10^{-6}$ mol N^+ per 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 as compared with a non-surfactant-containing solution. The average diameter of the latex particles was not affected by continued stirring.

Kinetics

The kinetic behaviour of the latex oxidizing 2-mercaptoethanol (ME) in the presence of 2 was studied: (i) the latex system stabilized by the block copolymer PS-b-qPVP, (ii) the homogeneous block copolymer system that may contain some form of aggregation (described later) and (iii) the homogeneous cationic polyelectrolyte system (qPVP). The difference in relative molecular mass of the surfactant and the homopolymer qPVP (10000 and 90000, respectively) will hardly affect the reaction rate as was observed earlier [25, 28].

In Fig. 1 the catalytic activity of the heterogeneous and homogeneous qPVP systems is shown as a function of pH. For all three systems a distinct optimum was

Fig. 1. Reaction rate R of 2-mercaptoethanol consumption as function of the pH. $[2] = 4 \cdot 10^{-7}$ mol/dm^3; concentration of 2-mercaptoethanol $[ME] = 0{,}143$ mol/dm^3. O: Latex: $[N^+] = 5 \cdot 10^{-5}$ mol/dm^3; □: quaternized poly(4-vinylpyridine) (qPVP): $[N^+] = 10^{-4}$ mol/dm^3; △: PS-b-qPVP (3): $[N^+] = 5 \cdot 10^{-5}$ mol/dm^3
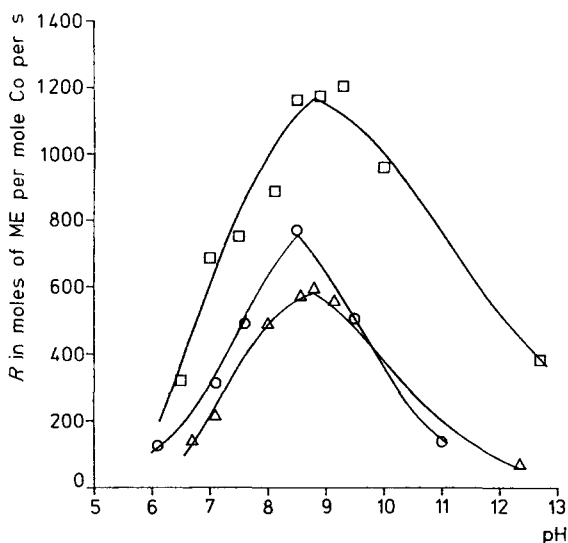
found around pH = 8,7. Also for PVAm- and 2,4-ionene-containing systems we earlier found such a pH-optimum, resulting from the fact that the reactive species in the rate-determining step is the thiolate anion (pK_a(ME) = 9,6) [17]. The difference between the pH-optima for PVAm- as well as 2,4-ionene-containing 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 the charge density on the polymer backbone. The charge density of qPVP, as a result of the presence of aromatic moieties, is lower and more

delocalized than that of e. g. 2,4-ionene, resulting in a lower local thiolate anion concentration at a given pH [17)*)]. 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 [29, 30)]. 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 appears 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 [17)]. The decrease in activity was mainly attributed to the formation of acidic by-products, caused by the
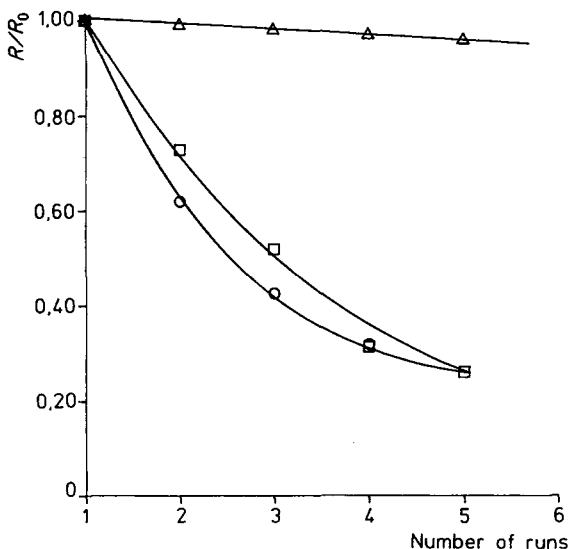

Fig. 2. Ratio of reaction rate R and initial reaction rate R_0 of 2-mercaptoethanol consumption as function of the number of runs. pH = 8,7; [2] = $4 \cdot 10^{-7}$ mol/dm^3; concentration of 2-mercaptoethanol [ME] = 0,143 mol/dm^3. O: Latex: [N$^+$] = $5 \cdot 10^{-5}$ mol/dm^3; □: quaternized poly-(4-vinylpyridine) (qPVP): [N$^+$] = 10^{-4} mol/dm^3; △: PS-b-qPVP (3): [N$^+$] = $5 \cdot 10^{-5}$ mol/dm^3

reaction of the intermediate hydrogen peroxide with disulfide to form sulfur-containing oxo-acids, poisoning the basic sites [31)]. Although decomposition of 2 was found, it was not the primary cause of deactivation. The variation in deactivation for the different cationic complexes is not yet fully understood. Most probably it will be related with a H_2O_2 accumulation in the microenvironment of the catalytic sites. This H_2O_2 accumulation is primarily determined by the intrinsic kinetics of the system but will also depend on 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,

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*) The dimensionless linear charge density parameter (λ) as proposed by Katchalsky [29)] is 1,02, 0,82, and 1,45 for qPVP, 2,10-ionene, and 2,4-ionene, resp.

2-mercaptoethanol was oxidized in the presence of an excess (2 equivalents) of its product: 2,2′-dithiodiethanol. No change in reactivity was observed compared with the regular system, indicating the absence of product inhibition. However, during all catalytic experiments using latex as a support for 2 some coagulation was observed. The colloidal instability is a known problem in catalyst immobilization on latices [32–34]. 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 other qPVP-containing systems will be a subject of future research.

Fig. 3 clearly shows a linear relationship between concentration of 2 and the catalytic activity (at constant [N⁺]). This linear relationship indicates the absence of mass transport limitations. It also shows the absence of a saturation behaviour of 2 at the

Fig. 3.   Reaction rate R' of 2-mercaptoethanol consumption as function of the concentration of 2 (keeping the nitrogen content constant).
pH = 8,7; concentration of 2-mercaptoethanol [ME] = 0,143 mol/dm³; ○: latex: [N⁺] = 5·10⁻⁵ mol/dm³; □: quaternized poly(4-vinylpyridine) (qPVP): [N⁺] = 10⁻⁴ mol/dm³; △: PS-b-qPVP (3): [N⁺] = 5·10⁻⁵ mol/dm³
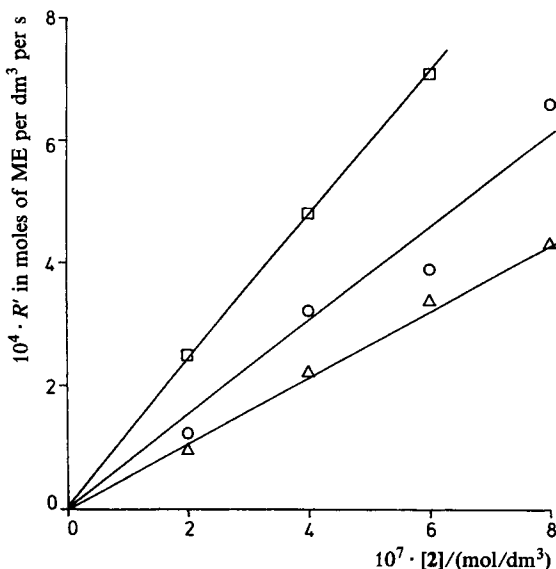
surface of the latex or in the homopolymer domain in the case of the homogeneous systems in this concentration region, otherwise deviations from linearity would have been observed. Again, the findings are in complete agreement with the linear dependencies found for homogeneous PVAm and 2,4-ionene systems.

As the two last-named polymers showed Michaelis-Menten kinetics in thiol and oxygen [16,35] the dependence of the 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 provides a zeroth-order reaction in oxygen, and pseudo single-substrate Michaelis-Menten kinetics is observed [16] according to Eq. (1).

$$v = \frac{k_2 \, [2] \, [ME]}{K_M + [ME]} \tag{1}$$

with v = initial oxidation rate, k_2 = turnover number (in s^{-1}) and K_M = Michaelis constant (in mol/dm³). From the double reciprocal of the reactivity versus thiol concentration, the so-called Lineweaver-Burk plot, these constants were determined as listed in Tab. 2. For comparison the data of PVAm and 2,4-ionene are also listed in Tab. 2 [16, 25]. As can be seen from Tab. 2, 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
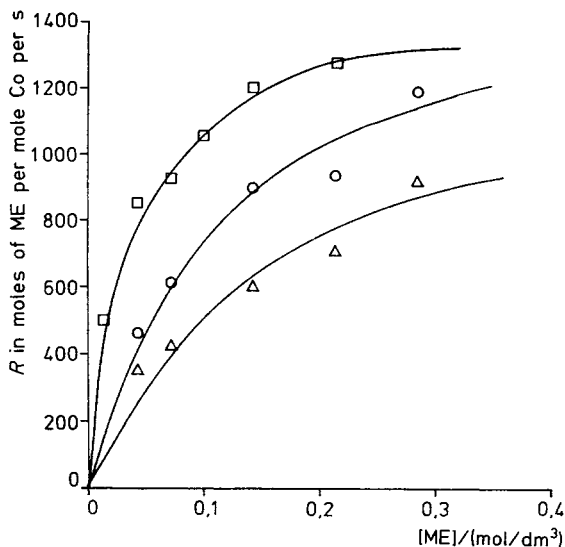

Fig. 4. Reaction rate R of 2-mercaptoethanol consumption as function of 2-mercaptoethanol (ME) concentration.
pH = 8,7; [2] = $4 \cdot 10^{-7}$ mol/dm³; ○: latex: [N⁺] = $5 \cdot 10^{-5}$ mol/dm³; □: quaternized poly(4-vinylpyridine) (qPVP): [N⁺] = 10^{-4} mol/dm³; △: PS-b-qPVP (3): [N⁺] = $5 \cdot 10^{-5}$ mol/dm³

are the differences between the Michaelis constant of the observed systems. In contrast with the turnover number, the Michaelis constant is only slightly affected by the

Tab. 2. Turnover numbers (k_2) and Michaelis constant (K_M) of several cationic polymer-containing systems

Polymer[a]	k_2/s^{-1}	$10^2 \cdot K_M/(mol/dm^3)$
qPVP	1 400[b] ± 110	2,6 ±0,4
PS-b-qPVP/latex	1 700[b] ± 150	12 ± 2
PS-b-qPVP	1 100[b] ± 210	11 ± 4
PVAm	2 800[c] ± 200	9,0 ± 2,0
2,4-ionene	3 300[c] ± 200	0,68 ± 0,14

[a] qPVP = quaternized poly(4-vinylpyridine); PS-b-qPVP = block copolymer of styrene and quaternized 4-vinylpyridine (3); PVAm = poly(vinylamine); 2,4-ionene = polyquaternary ammonium salt 1.
[b] pH = 8,7.
[c] pH = 8,0.

immobilization of PS-b-qPVP while K_M of the qPVP system is significantly lower than that of the block copolymer-containing systems. In Michaelis-Menten kinetics the constant (k_2) of decomposition of the Michaelis complex into product is assumed to be small in relation to the constant (k_{-1}) of the backward reaction in the complex formation from substrate and catalyst[28]. In case of $k_2 \lll k_{-1}$, the Michaelis constant $(K_M = (k_{-1} + k_2)/k_1)$ equals the reciprocal of the binding constant $K_s(=k_1/k_{-1}$, that is the binding of the thiolate anion to the cobalt centre).

Kinetic data of latex-immobilized catalytic systems unfortunately are scarce. Therefore, a comparison is only possible with effect 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[4, 12]. If a neutral substrate was used, the Michaelis constant was hardly affected by immobilization[4].

In our latex system, the styrene part of the block copolymer is strongly absorbed to, or embedded in the polymer particles and as a consequence may not play a role in the oxidation process that takes place in the aqueous boundary layer rich in qPVP blocks. It therefore seemed justified to compare the latex system with the homogeneous qPVP system. If the important prerequisite $(k_2 \lll k_{-1}, K_M \approx K_s^{-1})$ still holds after immobilization, immobilization of PS-b-qPVP (3) on latex particles, that is concentration of cationic charge on the latex surface, might lower the Michaelis constant compared with the qPVP system, seemingly in contrast to our present findings as can be seen in Tab. 2. The Michaelis constant for the latex system is higher than for the homogeneous qPVP system. The higher value of K_M for the immobilized system cannot be due to diffusional problems as was suggested by Brouwer et al. in the case of cross-linked PVAm[36] 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[4]. 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. Increasing the polymer concentration affects the polymer coil structure, that is immobilization (concentration) of polyelectrolyte on latex particles may directly influence the binding constant, as is seen in Fig. 5, where the reduced viscosity of qPVP is measured as a function of 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.
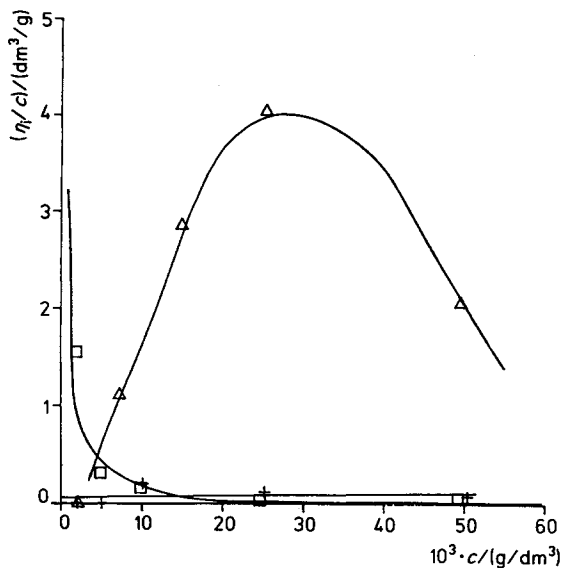
Fig. 5. Reduced viscosity (η_i/c) of PS-b-qPVP (3) and quaternized poly(4-vinylpyridine) (qPVP). $\triangle$: qPVP in pure water; $\square$: PS-b-qPVP in pure water; $+$: PS-b-qPVP in 0,02 M KBr

On these grounds, a 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 [37, 38]. It was reported that a small hydrophobic block in the block copolymer of styrene and 2-vinyl-N-methylpyridinium [39] and low concentrations of block copolymer of styrene and 4-vinyl-N-ethylpyridinium already influenced (increased) the viscosity in water. This anomalous behaviour was attributed to the formation of supramolecular structures as a result of incomplete solubilization [40]. In order to investigate the presence or absence of aggregated structures during the catalytic experiments, reduced viscosities (η_i/c) of both 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 case of the block copolymer the reduced viscosity increased on increasing its initial 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 [41]. The decrease of the reduced viscosity of the block copolymer at higher concentrations may be attributed to the increase of ionic strength. Fig. 5 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^{-4} mol/dm^3). The addition of a low concentration of 2 ($4 \cdot 10^{-7}$ mol/dm^3) did not affect the reduced viscosity.

We tried to demonstrate the presence or absence of the aggregated structures using light scattering. Unfortunately, the block copolymer concentrations used (simulating

the low concentrations used in the catalytic experiments) are too low by this technique to prove unambiguously the presence or absence of these structures.

It was mentioned earlier in this paper that cationic polymers induced aggregation of 2. 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 Welzen et al. [42] showed that this aggregation is irreversible, whereas in the case of more soap-like polyelectrolytes, like 2,10-ionene, monomerization of 2 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 Figs. 6 and 7 the visible light (VIS) spectra of 2 in the presence of qPVP and PS-b-qPVP are shown for $[2] = 2 \cdot 10^{-6}$ mol/dm^3 and $[N^+] = 2 \cdot 10^{-4}$ mol/dm^3 (curve A) and $2 \cdot 10^{-3}$ mol/dm^3 (curve B). As can be expected, qPVP
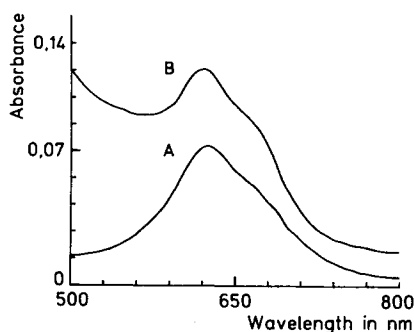

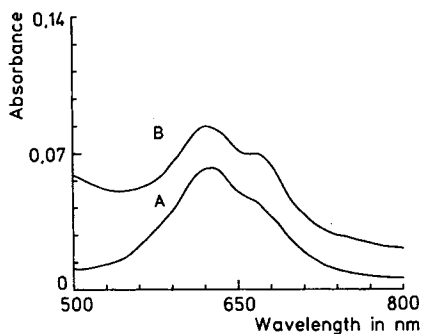Fig. 6.   Fig. 7.

Fig. 6.   VIS spectrum of 2 in the presence of quaternized poly(4-vinylpyridine) (qPVP); $[2] = 2 \cdot 10^{-6}$ mol/dm^3; A: $[N^+] = 2 \cdot 10^{-4}$ mol/dm^3, B: $[N^+] = 2 \cdot 10^{-3}$ mol/dm^3

Fig. 7.   VIS spectrum of 2 in the presence of PS-b-qPVP (3); $[2] = 2 \cdot 10^{-6}$ mol/dm^3; A: $[N^+] = 2 \cdot 10^{-4}$ mol/dm^3; B: $[N^+] = 2 \cdot 10^{-3}$ mol/dm^3

exhibits the behaviour of a common cationic polymer, i. e. strong aggregation of 2 that is hardly disturbed at high $[N^+]$ (628 nm, Fig. 6). In the case of the block copolymer, aggregation of 2 is also observed at $[N^+] = 2 \cdot 10^{-4}$ mol/dm^3 (Fig. 7, curve A). However, at higher polymer concentration ($[N^+] = 2 \cdot 10^{-3}$ mol/dm^3, curve B) the shoulder in the VIS spectrum of 2 at 660 nm suggests partial monomerization of the aggregated 2 indicating the presence of micelle-like structures. The nearly identical catalytic activity for both qPVP and PS-b-qPVP systems (see Tab. 2) confirms the absence of the less reactive, monomeric 2 in the case of PS-b-qPVP during the catalytic reactions (reaction conditions: $[N^+] = 5 \cdot 10^{-5}$ mol/dm^3, $[2] = 4 \cdot 10^{-7}$ mol/dm^3).

The data presented in this paper 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 suggests a similarity between the microenvironment of the catalytic centres of 2 in the block copolymer and the block copolymer-stabilized latex system.

Conclusions

PS-b-qPVP can be immobilized on latex particles by using the block copolymer as a surfactant in the emulsion copolymerization of styrene and divinylbenzene. As compared with the conventional polymer-free 2-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 activity of both the latex- and the qPVP-containing system after successive runs is rather poor, this immobilization method demonstrates its potential value for anchoring highly active systems with retaining high catalytic activity. The turnover number is increased on an 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 by immobilization. Due to conformational changes of the polymer domain on the immobilization of PS-b-qPVP, the observed differences between the three systems cannot be fully elucidated. The K_M values of the latex system and the block copolymer system suggest a similarity in structure between the two.

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