Synthesis and Cocatalytic Properties of Polystyrene–Ionene-Stabilized Latices

Eugène T. W. M. Schipper, Ralph P. M. Pinckaers, Pieter Piet, and Anton L. German*

Laboratory of Polymer Chemistry, Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received April 5, 1994; Revised Manuscript Received November 28, 1994⊗

ABSTRACT: Cationic latices with excellent cocatalytic properties were designed by emulsion polymerization of styrene using monodisperse amphiphilic polystyrene–ionene diblock copolymers as surfactant. The amphiphilic block copolymers built in during the emulsion polymerization of styrene, with the water-soluble initiator 2,2′-azobis(2-amidinopropane) dihydrochloride, possess electrostatic as well as steric stabilization properties. A major advantage of the preparative procedure used is that no extensive cleaning procedures need to be applied. After immobilization of the tetrasodium cobalt(II) phthalocyaninetetrasulfonate ($CoPc(NaSO_3)_4$) catalyst onto the latex, reactive latices were obtained which show very high catalytic oxidation rates toward the mercaptoethanol autoxidation. The highest catalytic activity (500 mol of O_2/(mol of Co·s)), 15 times higher as compared with the polymer-free system, was achieved with latices with relatively short ionene blocks with 7 quaternary ammonium groups at their particle surface. Despite relatively low surface charge densities, apparently enough ionene chains of sufficient length are present at the particle surface to stabilize the highly active $CoPc(NaSO_3)_4$ dimers and to achieve substrate enrichment.

Introduction

Polymers can play different roles in catalytic reactions. Initially, polymers were mainly used as a support for many catalysts in order to retain the high activity of the catalyst in combination with the advantages of immobilization, which are improvement of separation, reduced toxicity, and intrinsic possibilities for continuous operation, isolation, and purification. Apart from macromolecular-supported catalysts, the interest in polymer-anchored species increased enormously, and polymers have since been used as polymeric reagents, polymeric protecting groups, and polymeric mediators.[1] In each case a reactive species is bound to a polymer in order to make convenient manipulation possible.

Besides acting as a support for a catalyst or functioning as catalysts themselves, polymers can exert different types of promoting effects on catalytic reactions.[2] When polymers are used as a support for a catalyst, reaction rate, selectivity, and even the reaction mechanism can be changed by polymeric effects. The fact that polymers can be tailor-made offers the opportunity to influence these effects due to specific macromolecular ligation. Applications of polymers have been reported in which polymers achieve site isolation of the catalyst, a change in the chemical microenvironment, steric and structural effects, local concentration effects, and reduction of side reactions, thus resulting in a higher reactivity and/or selectivity of the supported catalyst.[2]

A very interesting system in which polymers have shown a strong influence and exhibit polymeric promoting effects is the cobalt(II) phthalocyanine catalyzed autoxidation of thiols to disulfides (Scheme 1). It appeared that cationic polymers exert large effects on the tetrasodium cobalt(II) phthalocyaninetetrasulfonate ($CoPc(NaSO_3)_4$) (Figure 1) catalyzed thiol autoxidation.[3–6]

Scheme 1[a]

$$4RSH + O_2 \xrightarrow{OH^-,\ CoPc} 2RSSR + 2H_2O$$

[a] RSH = thiol and CoPc = cobalt(II) phthalocyanine.

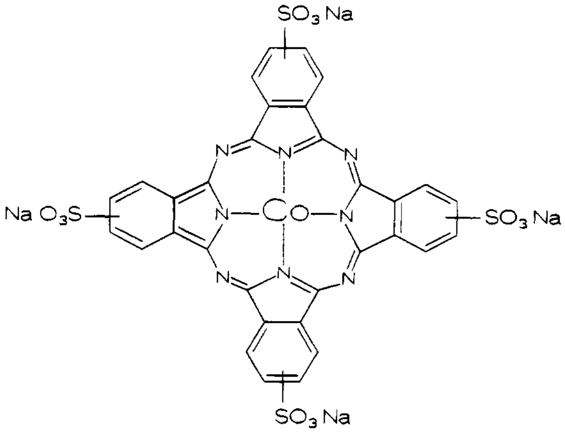


Figure 1. Structure of $CoPc(NaSO_3)_4$.

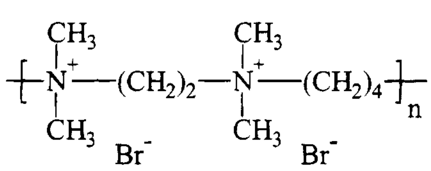


Figure 2. Structure of 2,4-ionene.

In the case of the addition of 2,4-ionene (Figure 2), a poly(quaternary ammonium) salt, the highest rate enhancement is observed, i.e., by a factor of 40, as compared with the polymer-free system.[3] Three effects, induced by polycations, collectively contribute to this increase in the catalytic activity. Recently, we succeeded in separating the different promoting contributions.[6,7] The presence of the polycations, which bind the negatively cobalt catalyst electrostatically, leads to the suppression of catalytically inactive dioxygen-bridged μ-peroxo complexes and leads simultaneously to the formation of highly active dimers of $CoPc(NaSO_3)_4$.[6,8] After studying the influence of the molecular weight of ionene on the catalytic activity, it appeared that oligomeric ionenes show high cocatalytic properties, comparable with those of polymeric 2,4-ionene.[7] Trimeric 2,4-

---

* To whom correspondence should be addressed.

⊗ Abstract published in *Advance ACS Abstracts,* February 1, 1995.

0024-9297/95/2228-2194$09.00/0

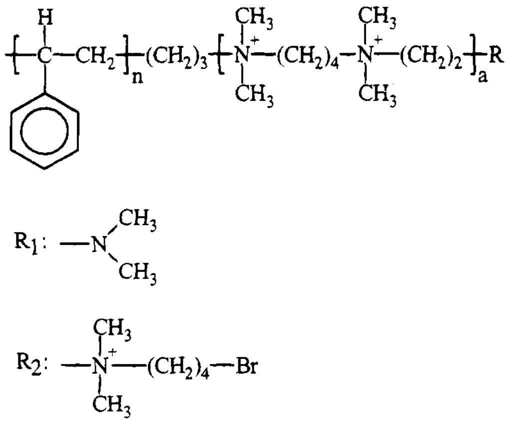
ionenes, containing two quaternary ammonium groups separated by four methylene groups, are already capable of stimulating the formation of active $CoPc(NaSO_3)_4$ dimers. By contrast, the monomeric analogue of 2,4-ionene, tetramethylammonium hydroxide, shows no increase in reaction rate as compared with the polymer-free system. Furthermore, the presence of the polycations leads to substrate enrichment in the polyelectrolyte domain; since the reactive species, i.e., the thiolate anions, and the catalyst are both negatively charged, the presence of ionenes results in higher local concentrations of the reactive species near the catalytically active sites.

The excellent catalytic $CoPc(NaSO_3)_4$/2,4-ionene combination for the autoxidation of thiols to disulfides does not allow continuous operation because of the homogeneity of the system. The disadvantages of this method for industrial applications are the recovery and the reuse of the catalyst. Therefore, it is necessary to apply a support in order to immobilize the highly active system. Several methods have been used before to immobilize the $CoPc(NaSO_3)_4$ catalyst onto polymeric macroporous resins. For example, $CoPc(NaSO_3)_4$ has been covalently bound to polystyrene beads in several ways.[9] Also, the catalyst was electrostatically immobilized to poly(vinylamine) grafted onto macroporous particles,[10] to cross-linked poly(vinylamine),[11] and to cationic resin particles and was subsequently tested in the mercaptoethanol autoxidation.[12] The disadvantages of these systems which are sometimes encountered are transport limitations and the absence of long flexible cationic tails at the particle surface, resulting in lower catalytic activities.

In order to overcome these difficulties polymer colloids proved to be more successful as a support for catalysts, due to their higher specific surface areas and their nonporous character. Mass transport limitations are therefore unlikely because of the better accessibility of the latex surface. More and more attention is being focused on these latex particles which can easily be prepared by emulsion polymerization. Latex-supported catalysts have been successfully applied in hydrolysis reactions,[13] inversion of sucrose,[14] phase-transfer catalysis,[15] and oxidation[16] and epoxidation[17] reactions.

Earlier attempts with $CoPc(NaSO_3)_4$ electrostatically attached to the particle surface of cationic latices have been reported. These latices were used as catalysts in thiol autoxidations. The main problem was that the several preparative procedures did not result in long and flexible cationic chains at the latex particle surface. Mostly, a cationic surfactant with a polymerizable group was used, which was built in during the emulsion polymerization.[18] A few efforts, applying cationic comonomers or poly(styrene-*co*-1-methyl-4-vinylpyridinium bromide) copolymers resulted in positively charged chains at the surface, but in all cases these were too short to stabilize the highly active Co dimers, and as a consequence low thiol oxidation rates were observed as compared with the homogeneous $CoPc(NaSO_3)_4$/2,4-ionene system.[5,19–21] Application of shot-growth techniques improved the activity,[21] but very high catalytic thiol oxidation rates were achieved only when vinylbenzyl-telechelic macromonomers of 2,4-ionene were used.[22]

Monodisperse amphiphilic polystyrene–ionene diblock copolymers (Figure 3), synthesized according to earlier described procedures,[7,23] should allow us to prepare latex particles with well-defined ionene chains at the particle surface extending into the water phase. The preparation of these amphiphilic polystyrene–ionene diblock copolymers with blocks of controlled molecular weights started with the anionic polymerization of styrene using [3-(dimethylamino)propyl]lithium as initiator, which yielded tertiary amino end-functionalized polystyrenes. This was followed by the stepwise coupling of the reactive end group of the polystyrene with bromo and tertiary amino terminated monodisperse oligomeric 2,4-ionenes, resulting in a monodisperse 2,4-ionene block.



diblock copolymer	a	R
A-4	2	R_1
A-7	3	R_2
D-4	2	R_1
D-9	4	R_2
G-7	3	R_2

Figure 3. Structure of polystyrene–ionene diblock copolymer.

During the emulsion polymerization of styrene the tailor-made block copolymers will act as a surfactant, so by the end of the reaction the hydrophobic polystyrene block will extend into the interior of the latex particles and the ionene block will extend into the aqueous phase. In this paper the preparation and properties of polystyrene–ionene-stabilized latices will be presented. Subsequently, the application of these latices as cocatalyst in the $CoPc(NaSO_3)_4$-catalyzed oxidation of mercaptoethanol will be discussed.

Experimental Procedures

Materials. Styrene (Merck, p.a.) was distilled at reduced pressure prior to use. The preparation procedure of the different polystyrene–ionene diblock copolymers has been described previously.[23,7] 2,2′-Azobis(2-amidinopropane) dihydrochloride (AIBA·2HCl) (Polysciences), cetyltrimethylammonium bromide (CTAB) (Fluka, 99%), and 2,2′-azobis(2-methylpropionitrile) (AIBN) (Merck, zur synthese) were used without purification. Deionized water was used throughout the experiments after purging with argon.

Polymerization Procedures. The polymerizations were carried out in a thermostated stirred glass batch reactor (1 dm^3, no baffles) equipped with a disk turbine impeller under an argon atmosphere. First, the polystyrene–ionene diblock copolymer was dissolved in 6 mL (7.8×10^{-2} mol) of *N,N*-dimethylformamide (DMF) (Janssen Chimica, p.a.). This block copolymer solution was poured into the reactor and, subsequently, the styrene and then the water were added. When the reaction temperature (70 °C) was reached, initiator

Table 1. Characteristics of the Amphiphilic Polystyrene–Ionene Diblock Copolymers Used

diblock copolymer	polystyrene block $\bar{M}_n$ (10^3 g·mol^{-1})	ionene block $\bar{M}_n$ (10^3 g·mol^{-1})	number of N^+ per ionene block
A-4	1.1	0.71	4
A-7	1.1	1.18	7
D-4	2.6	0.71	4
D-9	2.6	1.51	9
G-7	9.2	1.18	7

(AIBA·2HCl) dissolved in 5 mL of water was introduced by means of a syringe. Unless stated otherwise, the emulsion polymerizations were carried out with 5 g (4.8×10^{-2} mol) of styrene, 0.1 g (3.7×10^{-4} mol) of AIBA·2HCl, and 2.1×10^{-4} mol of N^+ of diblock copolymer or of CTAB. The total reaction volume was always 0.5 dm^3. For the kinetic measurements, samples were taken from the reactor, the polymerizations were stopped with hydroquinone (Janssen Chimica), and the conversions were determined gravimetrically. Finally, after a polymerization time of 15–24 h at 300 rpm (at this point the conversions were always, unless stated elsewhere, 90% or more), the product was filtrated in order to remove any coagulum (the amount of coagulum was always less than 3%). With respect to the catalytic experiments it was not necessary to purify the latex any further.

Characterization Procedures. Particle size distributions were determined by dynamic light scattering (DLS) (Malvern Autosizer 2C) and transmission electron microscopy (TEM) (JEOL 2000 FX). The latices were further characterized by determining the N^+ content present at the surface of the latex particles by conductometric titration. Before titration, the latices (±250 mL) were washed with 6 dm^3 of 0.001 M NaOH solution in a serum replacement cell (Amicon) equipped with a 100 nm pore size polycarbonate membrane (Nucleopore) in order to replace all counterions by hydroxide anions. Next, after washing with 6 dm^3 of deionized water in order to remove excess of base, the latices were conductometrically titrated with 0.01 M HCl under an argon atmosphere using a Radiometer CDM80. From the solids content, the particle diameter, determined by TEM, and the titration data the surface charge density was calculated.

Catalytic Activity Measurements. The catalytic thiol autoxidations were carried out batchwise as reported previously[6,24] in an all-glass double-walled Warburg apparatus (250 mL) equipped with a powerful mechanical glass stirrer (the stirring speed was 2600 rpm) and thermostated at 25.0 ± 0.1 °C. First, the latex was charged into the reaction vessel and diluted with water. Next, the catalyst was prepared by addition of a $CoPc(NaSO_3)_4$ solution to the diluted latex, followed by adjustment of the pH by the addition of a concentrated KOH (Merck, p.a.) solution (total reaction volume was always 0.10 dm^3). The reaction vessel was degassed, followed by saturation of the solution with oxygen. After repeating this procedure twice, the mixture was stirred vigorously for 5 min. The reaction was started by addition of 2-mercaptoethanol (ME) by means of a syringe into the reactor. Reaction rates were monitored by measuring the oxygen uptake. Prior to use ME (Janssen Chimica, 98%) was distilled in an argon atmosphere, stored in the dark, and kept under argon in sealed flasks at 5 °C.

Results and Discussion

Emulsion Polymerization of Polystyrene–Ionene Diblock Copolymer Stabilized Polystyrene Latices. First, we studied the kinetics of the emulsion polymerization of styrene in the presence of the ionic diblock copolymer in order to find the answer to the question whether these amphiphilic block copolymers really act as stabilizers in the emulsion polymerization. The characteristics of the monodisperse polystyrene–ionene diblock copolymers used during the emulsion polymerizations are presented in Figure 3 and Table 1.

Table 2. Effects of Stabilizer, Initiator, and Cosolvent Concentrations on the Particle Size Distributions of Polystyrene Latices[a]

	surfactant					
latex	type	$10^4[N^+]$ (mol·dm^{-3})	10^4[AIBA·2HCl] (mol·dm^{-3})	$\bar{d}_n$ (TEM) (nm)	$\bar{d}_w/\bar{d}_n$	$\bar{d}_z$ (DLS) (nm)
R1[b]			7.4	117	1.04	112
R2	**D-9**	4.4	7.4	58	1.10	71
E1[c]	**D-9**	2.2	18.5	207	1.01	
E2[c]	**D-9**	4.4	18.5	70	1.27	74
E3[c]	**D-9**	11	18.5	54	1.19	75
R3[d]	CTAB	4.4	7.4	85	1.18	
R4	CTAB	4.4	7.4	92	1.02	102
R5[e]	CTAB	4.4	7.4	95	1.02	104
R6	**D-4**	4.4	7.4	*f*		32
R7	**A-4**	4.4	7.4	*f*		40
R8	**A-7**	4.4	7.4	*f*		45

[a] Conditions: [styrene] = 9.6×10^{-2} mol·dm$^{-3}_{water}$, [DMF] = 1.6×10^{-1} mol·dm$^{-3}_{water}$, 70 °C. [b] Maximum conversion 35%. [c] [Styrene] = 9.6×10^{-1} mol·dm$^{-3}_{water}$. [d] No DMF. [e] [DMF] = 7.8×10^{-1} mol·dm$^{-3}_{water}$. [f] No reliable diameters could be determined with TEM.

The initiation of the emulsion polymerization will most probably proceed according to a homogeneous nucleation mechanism. The water-soluble initiator AIBA·2HCl forms two radicals, which will initiate the polymerization of styrene in the aqueous phase. Initially, the amphiphilic block copolymer is most probably present in the monomer droplets, due to the extremely low solubility in the water phase, but during the growth of the latex particles the block copolymer will be incorporated into the latex particles. Consequently, the copolymer acts as a stabilizer as the ionene part will be located at the particle surface. In fact, these block copolymers have all the prerequisites to function as highly efficient stabilizers, because the nature of the polystyrene block is similar to that of the latex particle and the ionene block is perfectly soluble in the continuous phase.

We have to keep in mind that a significant part of the electrostatic stabilization of the latex particles originates from the initiator. AIBA generates two cationic water-soluble radicals which will end as covalently bound charged initiator residues at the particle surface. In order to investigate this effect, we tried to prepare latices with only AIBA (R1) (see Table 2) and without surfactant. The conversion never exceeded 35% and the latex particle size was significantly larger as compared with latex (R2) prepared with block copolymer **D-9**. As a consequence, we may conclude that a polystyrene–ionene diblock copolymer exhibits stabilizing properties in the emulsion polymerization of styrene.

Furthermore, in order to examine the stabilization efficiency we studied the effect of the concentration of block copolymer **D-9** on the particle size distributions of the latices (E1, E2, and E3). As can be seen in Table 2, increasing the block copolymer concentration results in an increase in the number of particles, leading to a decrease in the particle diameters. A monodisperse latex was obtained with a large diameter only when a low block copolymer concentration was used.

Additionally, we performed an experiment (R4) with the cationic surfactant cetyltrimethylammonium bromide (CTAB) with an equal amount of charged groups (N^+ groups) as latex R2. A comparison between the two latices is only possible if the soap concentration is below the critical micelle concentration (cmc$_{CTAB}$ = 9.2×10^{-4} M).[25] Although at higher ionic strengths the cmc will be shifted to lower values, the CTAB concentration used here will still be lower than its cmc. By comparing the two latices, it appears that using the ionic block copolymer results in a smaller diameter. Hence, it can be assumed that amphiphilic polystyrene–ionene diblock copolymers possess electrostatic as well as steric stabilization properties.

The fact that AIBA contributes to the stabilization of the latex to a considerable extent gives reason to prepare latex particles of which the stabilization results purely from ionene chains, because AIBA residues at the interface are assumed to be unable to bind the cobalt catalyst in its catalytically active dimeric form. In order to overcome the problem of AIBA binding the monomeric form of $CoPc(NaSO_3)_4$, which is less catalytically active, a noncharged water-soluble or an oil-soluble initiator should be used. Applying the water-insoluble initiator AIBN in the emulsion polymerization of styrene with block copolymer **D-9** resulted in a colloidally unstable latex and in low maximal conversion (47%).

It has been reported before that cosolvents added during an emulsion polymerization influence the nucleation of the polymerization.[26] In our case DMF is used as a cosolvent to dissolve the block copolymer, because the copolymer is only sparingly soluble in water.[23] In order to study the effect of DMF we performed three emulsion polymerizations with 0, 6, and 30 mL of DMF (R3, R4, and R5) using CTAB as surfactant. Slightly smaller particle diameters were obtained if the amount of DMF was decreased and the polydispersity decreased if DMF was added.

Several block copolymers were used to examine the influence of both block lengths on the properties of the latices. In the case of nonionic diblock copolymers, the molecular weights of both blocks and the hydrophobic/hydrophilic ratio appeared to have large effects on their behavior in emulsion polymerizations.[27] First of all, we investigated the influence of the ionene block length on the latex properties. By reducing the ionene block length from 9 to 4 quaternary ammonium groups, keeping the total concentration of quaternary ammonium groups constant in the polymerization reactions (R2 vs R6), latices were obtained with a smaller particle size. By comparing latices R7 and R8, prepared with an amphiphilic block copolymer with a smaller polystyrene block and with 4 and 7 N^+, respectively, similar results were obtained. From these experiments it becomes evident that with increasing surfactant concentration, the amount of surfactant to contribute to the stabilization of the latex also increases. The fact that with CTAB with similar N^+ concentrations no smaller diameters were obtained again emphasizes the possibility of steric stabilization by the polystyrene–ionene diblock copolymers. However, it should be remarked that the latices prepared with copolymers consisting of 4 quaternary ammonium groups, exhibited a lower colloidal stability with respect to the latices with ionene chains with 7 and 9 N^+. This resulted in partial coagulation during the catalytic experiments.

In order to study the influence of the length of the polystyrene block we also performed polymerizations with **G-7**, which has a relatively high polystyrene content and contains 7 quaternary ammonium groups. Even with very high block copolymer concentrations no colloidally stable latices could be derived. Due to the high molecular weight of the polystyrene block, difficulties arise in its solubility during the emulsion polymerization and a part of the block copolymer precipitates.

Table 3. Surface Charge Densities (σ) of the Latices Used in the Catalytic Measurements[a]

latex	surfactant	$\bar{d}_n$ (nm)	$\bar{d}_w/\bar{d}_n$	$\bar{d}_z$ (nm)	σ ($\mu C \cdot cm^{-2}$)
R1		117	1.04	112	11.6
E3	**D-9**	54	1.19	75	1.1
R2	**D-9**	58	1.10	71	7.4
R8	**A-7**			45	5.0[b]

[a] For experimental conditions, see Table 2. [b] Surface charge density is based on $\bar{d}_z$.

It can be concluded that the preparation of colloidally stable latex particles requires the use of amphiphilic polystyrene–ionene diblock copolymers with a restricted polystyrene content and an ionene chain length of at least 7 N^+. When block copolymers with 4 N^+ are utilized, relatively high emulsifier concentrations should be applied in order to obtain stable latices. Before examining whether these short ionene chains are of sufficient length to exhibit cocatalytic properties, it is necessary to know the total positive charge at the particle surface which can bind the $CoPc(NaSO_3)_4$ catalyst.

The concentration of the positive charges from AIBA initiator residues and ionene at the latex surfaces was determined by conductometric titration. In Table 3 the surface charge densities of four different latices are presented. Latex R1, where AIBA residues solely contribute to the stabilization, shows the highest surface charge density. After a polymerization time of 15–24 h, nearly all AIBA (k_d of 1.2×10^{-4} s^{-1} at 70 °C) has decomposed. Present at the particle surface is 23% of the initial amount of AIBA. Also, a significant part of the initiator residues is buried in the latex particles during the emulsion polymerization.

By contrast, latex E3 has a low surface charge density, because a relatively high styrene/block copolymer ratio was used in the emulsion polymerization. A high surface charge density so far has been assumed to be a very important cocatalytic parameter in the catalytic thiol oxidation.[5] In order to prepare latex particles with high surface charge densities, we reduced the styrene/surfactant ratio, which will lead to higher ionene concentrations at the latex surface. As can be seen in Table 3, indeed higher surface charge densities were obtained with latices R2 and R8 as compared with latex E3. In general, the charge densities determined are low in comparison with systems using ionic comonomers.[19,21] Nevertheless, besides a high concentration of positive charges at the latex surface, the other prerequisite for an efficient cocatalytic system is the presence of flexible cationic tails. The latter effect can be studied by performing catalytic experiments with latices with different ionene lengths at their surface.

Catalytic Activities of Latex-Supported $CoPc(NaSO_3)_4$ Catalysts in the Mercaptoethanol Autoxidation. One of the major problems encountered when reactive latices are applied in the thiol oxidation is the presence of free polyelectrolyte, which is an inevitable side product.[20–22] Desorption of polyelectrolyte, formed during the preparation, from the latex drastically affects the thiol oxidation rate and should therefore be avoided. Extensive and elaborous cleaning techniques, like ultrafiltration, serum replacement, and treatment with silica, are necessary before performing catalytic experiments.[20–22] In our case no ionene-containing block copolymer could be detected in the water phase after polymerization, because of its ex-

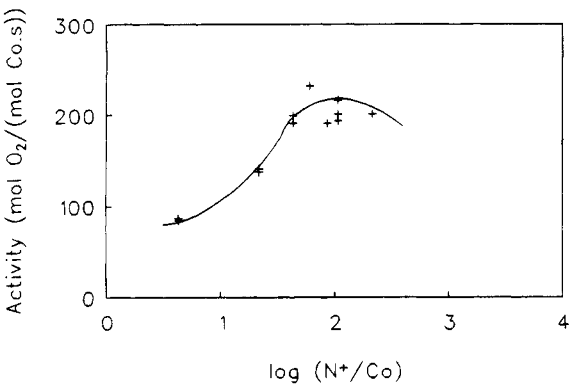


Figure 4. Catalytic mercaptoethanol oxidation rate as a function of [N^+] (latex R2). [$CoPc(NaSO_3)_4$] = 4 × 10^{-7} mol·dm^{-3}, pH = 9.0, [ME] = 7.1 × 10^{-2} mol·dm^{-3}.

tremely low water solubility. Hence, latices stabilized by polystyrene–ionene diblock copolymers can be applied directly after preparation as cocatalysts in the thiol autoxidation.

After electrostatic immobilization of the $CoPc(NaSO_3)_4$ catalyst, we first examined the effect of N^+ concentration on the catalytic mercaptoethanol oxidation rate. In Figure 4 the catalytic activity is plotted as a function of the N^+/Co ratio for latex R2, prepared with a block copolymer with 9 quaternary ammonium groups. The oxidation rate rises if the N^+ concentration is increased due to the fact that $CoPc(NaSO_3)_4$ dimers are formed and simultaneously substrate enrichment occurs, leading to a maximum in the catalytic activity. After this point the activity decreases because the local RS^- concentration near the catalytic sites is reduced. The fact that ionene chains at the latex surface are responsible for the cocatalytic properties is demonstrated by the activities measured for the cobalt catalyst bound to latex R1, where only AIBA residues are present at the surface. In the latter case only a slight increase by a factor of 2–3 in the oxidation rate was observed as compared with the polymer-free system. These AIBA residues are incapable of stimulating dimerization of the catalyst. Therefore, this enhancement can be ascribed to substrate enrichment of thiolate anions at the active sites.

We also determined the pH dependence of the mercaptoethanol oxidation rate for the latex R2 (Figure 5). As can be seen, at low pH low activities are measured because of the absence of thiolate anions, the reactive species. After increasing the pH, a maximum occurs, which has also been observed for other polycation-containing systems.[5,20–22]

An important parameter in the homogeneous $CoPc(NaSO_3)_4$/2,4-ionene system is the chain length of the ionene.[28] In immobilized systems the effects of ionene chains cooperating collectively are difficult to determine, because the ionene chains are linked to the surface. Nevertheless, we tried to investigate the effect of the length of ionene tails at the particle surface. In Figure 6 the influence of the latex concentration on the oxidation rate is depicted for two latices R7 and R8 prepared with cationic tails consisting of 4 N^+ and 7 N^+, respectively. It should be noted here that coagulation occurred on a small scale due to some colloidal instability of latex R7 during the catalytic experiments. Consequently, determination of the surface charge density was impossible.

Alternatively, we had to estimate the surface charge density of latex R7. Based on the measured surface charge density of latex R8 (Table 3) and the assumption that all block copolymer is present at the exterior of the particles, it is possible to calculate the amount of AIBA residues at the outside of the particle: 20% of the initial amount of AIBA is present at the surface of latex R8. This value is comparable with the percentage AIBA (23%) present at the particle surface of latex R1, prepared with only AIBA. Performing an analogous estimation for latex R2, a value of 28% of the initial amount of AIBA was calculated. Next, the N^+ concentration at the surface of latices R7, E1 and E2 could be estimated, assuming an equivalent percentage AIBA present at the surface as of latex R1 and assuming all block copolymer is present at the surface of the latex particles.

The assumption that all block copolymer will be built in at the particle surface also implies that we are able to attribute the N^+ at the particle surfaces to block copolymer or initiator residues. It appears that about 40% of the N^+ present at the surface of latex R8 can be ascribed to AIBA residues. In the case of latex R2 this value is 45%. These high percentages explain the fact that no colloidally stable latices were obtained without AIBA as initiator. This also means that about 60% of the N^+ at the particle surface can be ascribed to the ionene.

Despite a large amount of AIBA residues at the surface, very high oxidation rates (Figure 6) are obtained applying latex R8 with ionene chains consisting of 7 N^+ at their surface. The maximum catalytic activity observed is a factor of 15 higher as compared with the polymer-free system. Even more important is that this heterogeneous catalytic system is able to compete with the highly active homogeneous $CoPc(NaSO_3)_4$/2,4-ionene

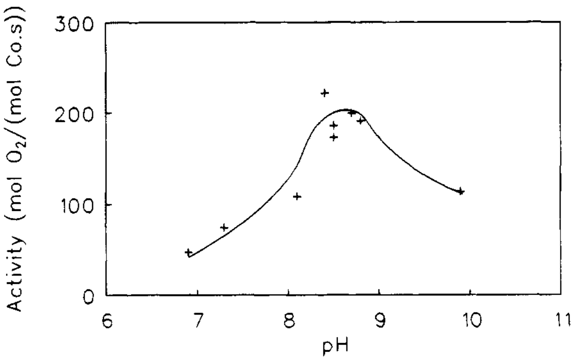


Figure 5. Catalytic mercaptoethanol oxidation rate as a function of pH (latex R2). [$CoPc(NaSO_3)_4$] = 4 × 10^{-7} mol·dm^{-3}, [ME] = 7.1 × 10^{-2} mol·dm^{-3}; [N^+](R2) = 2 × 10^{-5} mol·dm^{-3}.

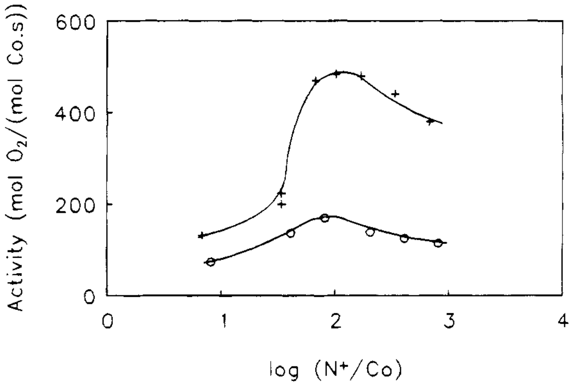


Figure 6. Catalytic mercaptoethanol oxidation rate as a function of [N^+]. [$CoPc(NaSO_3)_4$] = 4 × 10^{-7} mol·dm^{-3}, pH = 9.0, [ME] = 7.1 × 10^{-2} mol·dm^{-3}; (○) R7, (+) R8.

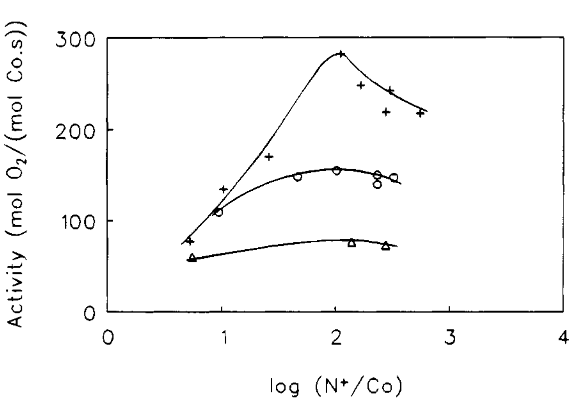


Figure 7. Catalytic mercaptoethanol oxidation rate as a function of [N$^+$]. [CoPc(NaSO$_3$)$_4$] = 4 × 10^{-7} mol·dm^{-3}, pH = 9.0, [ME] = 7.1 × 10^{-2} mol·dm^{-3}; (△) E1, (○) E2, (+) E3.

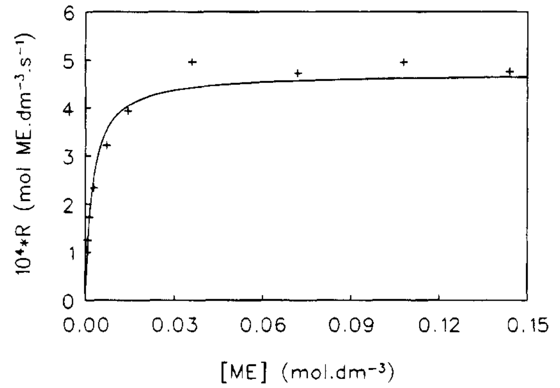


Figure 8. Catalytic thiol oxidation rate (R) as a function of substrate (ME) concentration (latex E3). N$^+$/Co = 100, [CoPc(NaSO$_3$)$_4$] = 4 × 10^{-7} mol·dm^{-3}, pH = 9.0.

system.[3] Furthermore, when shorter ionene chains are present at the surface (latex R7) catalytic activities are realized which are a factor of 3 lower than measured for latex R8. With respect to latex R7, the cationic tails are fixed onto the particle surface and cannot contribute collectively to the stabilization of the Co dimers.

It should be noticed that higher maximal activities are achieved with latex R8 with ionene chains consisting of 7 N$^+$ than for latex R2 with ionene chains of 9 N$^+$ at the surface. The difference in activities could be explained by the length of polystyrene block of the copolymers used. Apparently, using copolymer **D-9** instead of **A-7**, more block copolymer should be embedded inside the particle, because of its higher polystyrene content and its higher hydrophobic/hydrophilic ratio. However, this should affect the surface charge density, which is similar in both cases. Therefore, the reason for this discrepancy is not yet clear.

Additionally, we investigated the cocatalytic properties of a series of latices prepared with different concentrations of the polystyrene−ionene block copolymer **D-9**. In Figure 7 the effect of the N$^+$/Co ratio of latices E1, E2, and E3 on the mercaptoethanol oxidation rate is presented. It clearly shows that increasing the amount of block copolymer present during the emulsion polymerization leads to a higher concentration of ionene tails at the surface and as a result higher oxidation rates are observed. It can be noticed further that the use of latex R2, with a higher surface charge density than E3, did not result in better cocatalytic properties (see also Figure 4). Apparently, in both cases the cationic tails sticking into the water phase are capable of achieving aggregation of the cobalt species.

It can be seen (Figures 4, 6, and 7) that a similar value of the optimal N$^+$/Co ratio of about 100 can be observed for the three well-characterized latices (E3, R2, and R8) with relatively long ionene chains. This value is slightly higher than those found for the homogeneous counterparts, but also in the homogeneous system the optimal N$^+$/Co ratio is shifted to larger values when relatively short ionene chains are used.[28]

The oxidative coupling of mercaptoethanol to its corresponding disulfide gives rise to an enzyme-like kinetic behavior. It has been shown before that in the homogeneous as well as in several latex-supported catalytic systems Michaelis−Menten kinetics were observed.[5,20,21,29] The kinetics of the oxidative coupling of ME can be described as a Michaelis−Menten kinetic model. At a constant oxygen concentration the rate of thiol oxidation (R) is given by

$$R = \frac{k'[\mathrm{CoPc(NaSO_3)_4}][\mathrm{ME}]}{K'_\mathrm{M} + [\mathrm{ME}]} \qquad (1)$$

with k' the minimum turnover frequency for thiol conversion at 0.1 MPa O$_2$ and saturation in thiol and K'_M the apparent Michaelis constant. In Figure 8 the ME consumption rate is depicted as a function of the ME concentration using latex E3. These results point to simple Michaelis−Menten kinetics according to eq 1 (zeroth reaction order in O$_2$).[29]

The minimum turnover frequency for thiol conversion, k', and the apparent Michaelis constant, K'_M, calculated by plotting 1/R vs 1/[ME], a so-called Lineweaver−Burk plot, are (1.2 ± 0.2) × 10^3 mol ME·(mol of CoPc(NaSO$_3$)$_4$·s)$^{-1}$ and (2.4 ± 0.8) × 10^{-3} mol of ME·dm^{-3}, respectively. Therefore, we can conclude that the polystyrene−ionene-stabilized latices exhibit Michaelis−Menten kinetics in the mercaptoethanol autoxidation.

Conclusions

Monodisperse amphiphilic polystyrene−ionene diblock copolymers act as effective stabilizers during the emulsion polymerization of styrene. Colloidally stable latices with well-defined ionene chains at the particle surface are obtained when diblock copolymers are used with a low polystyrene content and a 2,4-ionene block consisting of at least 7 quaternary ammonium groups. A large part of the N$^+$ at the latex surfaces consists of AIBA residues, which contribute to the stabilization of the latices.

After immobilization of CoPc(NaSO$_3$)$_4$, a heterogeneous catalytic system is obtained which is highly active in the autoxidation of mercaptoethanol. Compared with the polymer-free system a 15-fold oxidation rate enhancement was observed. Furthermore, it appeared that surface charge density is an important factor, but the predominant factor determining the promoting properties is the length of the cationic tails present at the particle surface.

The polystyrene−ionene-stabilized latices should be preferred to other latex systems because no leaching of polyelectrolyte of the support occurs. Hence, there is no necessity to perform extensive cleaning techniques: after preparation the reaction latices can immediately be applied in catalysis.

References and Notes

(1) Sherrington, D. C. *Chem. Ind.* **1991**, *1*, 15.

(2) (a) Ford, W. T. *Polymeric Reagents and Catalysts*; ACS Symp. Ser. 308; American Chemical Society: Washington, DC, 1986. (b) Sherrington, D. C.; Hodge, P. *Synthesis and Separations Using Functional Polymers*; Wiley: Chichester, 1988. (c) Sherrington, D. C. *Pure Appl. Chem.* **1988**, *60*, 401. (d) Ciardelli, F.; Carlini, C.; Pertici, P.; Valentini, G. *J. Macromol. Sci., Chem.* **1989**, *A26*, 327.

(3) van Welzen, J.; van Herk, A. M.; German, A. L. *Makromol. Chem.* **1989**, *190*, 2477.

(4) Hari Babu, S.; Ford, W. T. *J. Polym. Sci., Polym. Chem.* **1992**, *30*, 1917.

(5) van Streun, K. H.; Belt, W. J.; Schipper, E. T. W. M.; Piet, P.; German, A. L. *J. Mol. Catal.* **1992**, *71*, 245.

(6) Schipper, E. T. W. M.; Heuts, J. P. A.; Piet, P.; Beelen, T. P. M.; German, A. L. *J. Mol. Catal.* **1994**, *87*, 161.

(7) Schipper, E. T. W. M.; van Hest, J. C. M.; Roelofs, A. H. C.; Piet, P.; German, A. L. *Polym. Int.* **1993**, *33*, 317.

(8) van Welzen, J.; van Herk, A. M.; German, A. L. *Makromol. Chem.* **1987**, *188*, 1923.

(9) (a) Rollmann, L. *J. Am. Chem. Soc.* **1975**, *97*, 2132. (b) Ledon, H.; Brigandat, Y. *J. Organomet. Chem.* **1979**, *165*, C25. (c) Skorabogaty, A.; Smith, T. D. *J. Mol. Catal.* **1982**, *16*, 131. (d) Shirai, H.; Maruyama, A.; Kobayashi, K.; Hojo, N.; Urushido, K. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 661. (e) Gebler, M. *Inorg. Nucl. Chem.* **1981**, *43*, 2759. (f) Shirai, H.; Higaki, S.; Hanabusa, K.; Kondo, Y.; Hojo, N. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1309.

(10) Schutten, J. H.; van Hastenberg, C. H.; Piet, P.; German, A. L. *Angew. Makromol. Chem.* **1980**, *89*, 201.

(11) Brouwer, W. M.; Traa, P. A. M.; de Weerd, T. J. W.; Piet, P.; German, A. L. *Angew. Makromol. Chem.* **1984**, *128*, 133.

(12) Ratering, M. T.; Meuldijk, J.; Piet, P.; German, A. L. *React. Polym.* **1993**, *19*, 233.

(13) (a) Arai, K.; Maseki, Y.; Ogiwara, Y. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 655. (b) Hopkins, A.; Williams, A. *J. Chem. Soc., Perkin Trans. 2* **1983**, 891. (c) Kitano, H.; Sun, Z.-H.; Ise, N. *Macromolecules* **1983**, *16*, 1306. (d) Ruckenstein, E.; Hong, L. *J. Catal.* **1992**, *136*, 378. (e) Ford, W. T.; Yu, H. *Langmuir* **1993**, *9*, 1999.

(14) (a) Kim, J. H.; El-Aasser, M. S.; Klein, A.; Vanderhoff, J. W. *Polym. Mater. Sci. Eng.* **1987**, *57*, 819. (b) Kim, J. H.; El-Aasser, M. S.; Klein, A.; Vanderhoff, J. W. *J. Appl. Polym. Sci.* **1988**, *35*, 2117.

(15) Bernard, M.; Ford, W. T.; Taylor, T. W. *Macromolecules* **1984**, *17*, 1812.

(16) (a) Sun, Z.; Yan, C.; Kitano, H. *Macromolecules* **1986**, *19*, 984. (b) Chandran, R. S.; Srinivasan, S.; Ford, W. T. *Langmuir* **1989**, *5*, 1061. (c) Zhu, W.; Ford, W. T. *J. Mol. Catal.* **1993**, *78*, 367. (d) Turk, H.; Ford, W. T. *J. Org. Chem.* **1988**, *53*, 460.

(17) (a) Srinivasan, S.; Ford, W. T. *New J. Chem.* **1991**, *15*, 693. (b) Turk, H.; Ford, W. T. *J. Org. Chem.* **1991**, *56*, 1253.

(18) (a) Hassanein, M.; Ford, W. T. *Macromolecules* **1988**, *21*, 525. (b) Hassanein, M.; Ford, W. T. *J. Org. Chem.* **1989**, *54*, 3106.

(19) van Streun, K. H.; Belt, W. J.; Piet, P.; German, A. L. *Eur. Polym. J.* **1991**, *27*, 931.

(20) Twigt, F.; Piet, P.; German, A. L. *Eur. Polym. J.* **1991**, *27*, 939.

(21) Twigt, F.; Broekman, J.; Piet, P.; German, A. L. *Eur. Polym. J.* **1993**, *29*, 745.

(22) van Beek, H.; Leclercq, J.-W.; Piet, P.; German, A. L. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 371.

(23) Schipper, E. T. W. M.; van Hest, J. C. M.; Piet, P.; German, A. L. *Makromol. Chem.* **1992**, *193*, 2807.

(24) Brouwer, W. M.; Piet, P.; German, A. L. *Makromol. Chem.* **1984**, *185*, 363.

(25) Fendler, J. H.; Fendler, E. J. *Catalysis in Micellar and Macromolecular Systems*; Academic Press: New York, 1975.

(26) (a) Chonde, Y.; Krieger, I. M. *J. Appl. Polym. Sci.* **1981**, *26*, 1819. (b) Kawaguchi, H.; Nakamura, M.; Yanagisawa, M.; Hishino, F. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 315. (c) Homola, A. M.; Inoue, M.; Robertson, A. A. *J. Appl. Polym. Sci.* **1975**, *19*, 3077.

(27) (a) Piirma, I. *Makromol. Chem., Macromol. Symp.* **1990**, *35/36*, 467. (b) Jialanella, G. L.; Firer, E. M.; Piirma, I. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 1925.

(28) Schipper, E. T. W. M.; Roelofs, A. H. C.; Piet, P.; German, A. L. *Polym. Int.* **1994**, *33*, 79.

(29) van Herk, A. M.; van Streun, K. H.; van Welzen, J.; German, A. L. *Br. Polym. J.* **1989**, *21*, 125.

MA9413195