Autoxidation of 1-Decanethiol Catalyzed by Cobalt Phthalocyaninetetrasulfonate on Cationic Latexes

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Cationic latexes 60 nm in diameter have been prepared by emulsion copolymerization of 2% of quaternary ammonium ion surfactant monomers and 1–5% of divinylbenzene with styrene. All of the surfactant monomers were bound to the product latexes, within experimental error. The cationic latexes bound cobalt phthalocyaninetetrasulfonate (CoPcTs) quantitatively from aqueous $CoPcTsNa_4$. The CoPcTs latexes catalyzed autoxidation of 1-decanethiol dispersed in water with zero-order consumption of dioxygen from a gas buret at 1 atm of pressure to at least 65% conversion of thiol. All reactions had an induction time before the start of oxygen consumption. Rates increased with pH in the range 7–9, and the following observations were made at pH 9: The zero-order rate constants with CoPcTs latexes were up to 14 times faster than with $CoPcTsNa_4$ in aqueous solution. Hexadecyltrimethylammonium bromide and one of the surfactant monomers as micellar catalysts gave rate enhancements similar to those with latex catalysts. Rates of autoxidation in the three-phase mixtures of water, latex particles, and thiol droplets were not affected significantly by the method of mixing. The rate of latex-catalyzed oxidation increased with small amounts of added methanol and nonionic surfactant. Varied concentrations of dispersed 1-decanethiol in the range $1-4 \times 10^{-2}$ M gave saturation kinetics. Increasing partial pressures of dioxygen in the range 0.25–1.0 atm gave small increases in rate. The reaction rates increased as CoPcTs concentration in the reaction mixture increased from 1×10^{-7} M to 5×10^{-5} M and then decreased at 1.5×10^{-4} M CoPcTs. At constant concentration of CoPcTs in the reaction mixture, the rate as a function of the weight of latex in the range 0.6–1.5 g of latex per 105 mL of reaction mixture showed a maximum at 0.9 g of latex. The higher activities of the CoPcTs–latex catalysts compared with soluble $CoPcTsNa_4$ are attributed primarily to absorption of the 1-decanethiol by the latexes, which provides a higher concentration of reactant at the active sites.

Catalysis is essential for the vast majority of chemical reactions in living organisms and in industrial production of chemicals. Most of these catalytic processes are heterogeneous. We are exploring a new type of heterogeneous catalysis in which transition-metal complexes are supported on polymer colloids, also known as latexes. Although the catalysts are strictly synthetic, the reaction sites in aqueous colloids are more like the heterogeneous reaction sites in living organisms than in chemical manufacturing plants.

Insoluble polymer-supported catalysts have been developed for promotion and simplification of organic syntheses.[1,2] A principal reason for study of polymer-supported catalysts is their ease of separation from reaction mixtures and reuse. High activity and chemical selectivity also have been attained in some examples. Polymer-supported catalysts often have drawbacks. Their activity is often less than that of soluble catalysts, due to either chemical or diffusional restrictions. When activity is limited in part by external mass transfer or intraparticle diffusion of reactants to the active sites, the activity of heterogeneous catalysts increases as the catalyst particle size decreases because surface area per weight is inversely related to particle diameter.[3] Therefore colloidal polymers with particle sizes of less than 1 μm may have higher activity than conventional polymer-supported catalysts with particle sizes of 20–500 μm. Colloidal catalysts potentially may be used for decontamination of water and for industrial organic chemical syntheses. We aim with colloidal catalysts to take advantage of the specificity of soluble transition-metal catalysts by immobilizing them on high surface area organic polymer supports in free-flowing aqueous dispersions.

Aqueous polymer colloids are a new environment for catalysis. Examples include sulfonic acids for ester hydrolysis[4,5] and inversion of sucrose,[6] a primary amine for ester hydrolysis,[7] imidazoles for ester hydrolysis,[8] an immobilized enzyme,[9] a histamine–Cu(II) complex for oxidation of ascorbic acid,[10] and phase-transfer catalysts.[11] We have reported cobalt catalysts bound to polymer latexes for autoxidation of 1-decanethiol,[12] 2,6-di-*tert*-butylphenol,[13,14] and tetralin.[14,15]

This paper describes kinetics of the autoxidation of 1-decanethiol catalyzed by latex-bound cobalt phthalocyaninetetrasulfonate (CoPcTs). Autoxidation of thiols is important in industry for the sweetening of petroleum[16,17] and in biological systems.[18,19] Previously, CoPcTs bound to soluble cationic polyelectrolytes has shown

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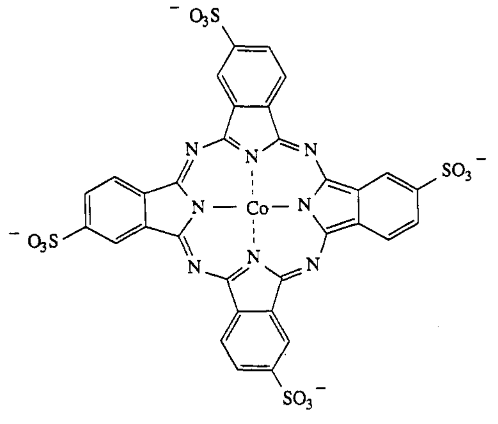
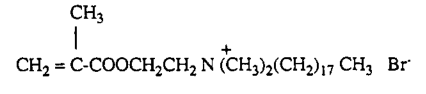


CoPcTs

greater activity than $CoPcTsNa_4$ in water for autoxidation of 2-mercaptoethanol.[20,21] CoPcTs bound to Sephadex ion-exchange resins was less active than soluble $CoPcTsNa_4$ for autoxidation of 2-mercaptoethanol and 1-butanethiol in aqueous and nonaqueous media.[22]

Results

Preparations of Catalysts. Latexes were prepared with polymerizable surfactants **1**–**3**. [12-(4-Styryloxy)dodecyl]trimethylammonium bromide (**3**) was synthesized in three steps: Basic hydrolysis of 4-acetoxystyrene gave 4-hydroxystyrene, alkylation of 4-hydroxystyrene with 1,12-dibromododecane gave 4-styryl 12-bromododecyl ether, and the 4-styryl 12-bromododecyl ether reacted with trimethylamine to give surfactant **3**. (4-Styrylmethyl)hexadecyldimethylammonium chloride (**2**) was prepared by alkylation of hexadecyldimethylamine with vinylbenzyl chloride. [2-(Methacryloyloxy)ethyl]dimethyloctadecylammonium bromide (**1**)[23] was prepared from 1-bromooctadecane and 2-(*N*,*N*-dimethylamino)ethyl methacrylate. Monomeric surfactants **1**–**3** were purified by repeated recrystallization. Their ^1H NMR and IR spectra showed high purity. The critical micelle concentrations (cmc) in water were determined conductometrically to be as follows: **1**, 6×10^{-4} M at 25 °C;[23] **2**, 1.28×10^{-2} M at 25 °C; **3**, 3.6×10^{-2} M at 45 °C.



$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}\text{-}COOCH_2CH_2\overset{+}{N}(CH_3)_2(CH_2)_{17}CH_3\ Br^-$

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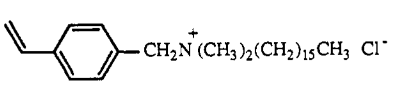

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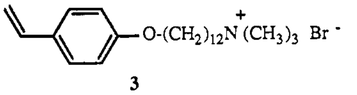

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Table I. Monomer Mixtures Polymerized and Bromide Ion Contents of Latexes[a]

latex[b]	styrene, g	55% active DVB, g	surfactant monomer, g	Br^-,[c] mequiv/g
L-1	30.264	0.711	**1**, 2.940	0.174
L-2	10.08	0.236	**2**, 0.843	0.173
L-3	10.08	0.236	**3**, 0.852	0.179
L-4	9.57	1.203	**1**, 0.981	0.174

[a] All product latexes contained 10 wt % solids. [b] All latexes contained 2.0 mol % surface active monomer. L-1, L-2, and L-3 contained 96.2 mol % styrene, 1.0 mol % divinylbenzene (DVB), and 0.80 mol % ethylvinylbenzene (EVB). L-4 contained 5 mol % DVB, 4 mol % EVB, and 89 mol % styrene. [c] Bromide content of latex in milliequivalents per gram of dry solid polymer determined by the Volhard method.

Table II. Particle Sizes of Latexes

latex	d_n,[a] nm	d_w/d_n[b]
L-1	58.5	1.16
L-2	64.5	1.04
L-3	58.5	1.12
L-4	56.5	1.16
LC-1	60.1	1.14
LC-2	67.4	1.04
LC-3	59.2	1.09

[a] Number average diameter of 50 particles with standard deviation ±1.0 nm. [b] Polydispersity; d_w = weight average diameter.

Emulsion copolymerizations of styrene with 2.0 mol % of **1**, **2**, or **3** and 1.0 mol % of divinylbenzene (DVB) using azobisisobutyronitrile initiator at 65 °C produced latexes L-1, L-2, and L-3 containing 10 wt % solids (Table I). A 5.0 mol % DVB latex (L-4) also was prepared from **1**. The quaternary ammonium groups of the polymerizable surfactants serve both to stabilize the colloid and to bind CoPcTs. Cross-linking with DVB insured that the polymer remained insoluble during all subsequent experiments. The latexes were ultrafiltered through 0.1-μm membranes to remove water-soluble constituents. Conductivities of the filtrates collected initially ranged from 25 to 30×10^{-6} $ohm^{-1}\ cm^{-1}$, compared with 440×10^{-6} $ohm^{-1}\ cm^{-1}$ for the aqueous solution of monomer **1** before copolymerization. The reduced conductivity of the aqueous phase after polymerization indicates that most of the ionic constituents of the original reaction mixture were bound to particles. Further washing of the particles with water and ultrafiltration gave final ultrafiltrates with conductivities of 6×10^{-6} $ohm^{-1}\ cm^{-1}$. Titrations of the ultrafiltered latexes by the Volhard method detected 95–97% of the bromide ion initially charged as surfactant (Table I). IR analysis of coagulated latexes showed no bands at 1630–1640 cm^{-1} for the carbon–carbon double bonds of the monomers **1**–**3**. Thus no free surfactants were detected in the aqueous dispersions. Catalysts LC-1, LC-2, LC-3, and LC-4 were prepared by addition of aqueous $CoPcTsNa_4$[24] to the latexes L-1, L-2, L-3, and L-4. Ultrafiltration of each catalyst revealed no blue CoPcTs in the filtrate. Since less than 1×10^{-7} M $CoPcTsNa_4$ in water can be detected by the human eye, and 5×10^{-5} M $CoPcTsNa_4$ was used in the preparation, at least 99.8% of the CoPcTs was bound to the particles. $CoPcTsNa_4$ is soluble in water alone and in the presence of surfactants. Transmission electron micrographs of the latex L-1, freshly prepared colloidal catalyst LC-1, and LC-1 recovered after use (Figure 1) show a narrow distribution of particle sizes. No precipitation or coagulation of latexes was observed. Particle sizes of the latexes and colloidal catalysts measured from the

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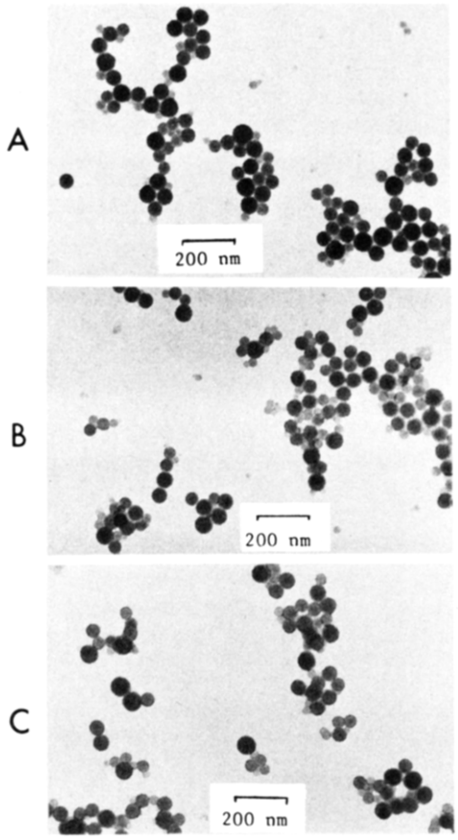

Figure 1. Transmission electron micrographs of (A) latex L-1, (B) catalyst LC-1 containing 0.0175 mmol of CoPcTs/g of solids before use, and (C) LC-1 after use.

Table III. Activities of CoPcTs Catalysts for Autoxidation of 1-Decanethiol[a]

catalyst	R_4N^+, mmol	CoPcTs, mmol	k_{rel}[b]
none	0.0	0.0	1.0
L-1	0.105	0.0	1.2
$CoPcTsNa_4$	0.0	0.0105	2.1
LC-1	0.105	0.0105	24.2
LC-2	0.105	0.0105	9.0
LC-3	0.105	0.0105	30.4
LC-4	0.105	0.0105	22.3

[a] All experiments were carried out at 35 ± 0.1 °C and O_2 pressure of 720 mmHg with magnetic stirring of 1.54 mmol of 1-decanethiol dispersed in 105 mL of reaction mixture containing 600 mg of latex particles. The pH was adjusted to 9.0 by using amounts of $Na_2B_4O_7$ and HCl that left 4.8×10^{-4} M borate and 1.75×10^{-4} M chloride in the reaction mixture. [b] Relative zero-order rate constants calculated from the plot of volume of dioxygen consumed vs time as in Figure 2.

micrographs are in Table II.

Autoxidation of 1-Decanethiol. The colloidal catalysts showed high activity for autoxidation of 1-decanethiol to di-1-decyldisulfide in magnetically stirred mixtures (Table III), even though the solubility of 1-decanethiol in water at 35 °C is estimated to be about 5×10^{-4} M. (The solubility of 1-dodecanethiol in water is 3×10^{-5} M at 50 °C,[25a] and the free energy of transfer of alkanes from water to hydrocarbon decreases by 884 cal/mol of CH_2 groups.[25b]) Under standard conditions of pH 9.0 and slightly less than 1 atm of dioxygen at 35 °C, the catalyst LC-1 gave 95% conversion of thiol in 30 min according to GLC analysis. Oxygen consumption was measured with a gas buret. Slightly more than 1 mol of dioxygen/4 mol of 1-decanethiol was consumed, which corresponds with the stoichiometry of eq 1.

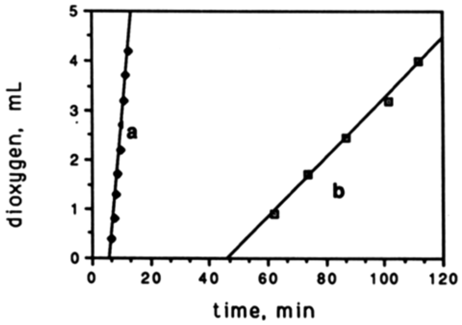

Figure 2. Dioxygen consumption with time during autoxidation of 1-decanethiol catalyzed by (a) LC-1 and (b) aqueous $CoPcTsNa_4$. For conditions, see Table III. Zero-order rate constants in milliliters of dioxygen per minute were calculated from the slopes, and induction periods were calculated by extrapolation to the x axis.

Table IV. Effects of pH and Amount of Latex Catalyst LC-1 on Rates of Autoxidation[a]

L-1, mg	R_4N^+, mmol	CoPcTs, mmol	pH	k_{obsd},[b] mL of O_2/min
600	0.105	0.0105	7.0[c]	0.129
600	0.105	0.0105	8.0[d]	0.444
600	0.105	0.0105	9.0[e]	0.678
79	0.014	0.0014	9.0[e]	0.301
900	0.158	0.01575	9.0[e]	0.724

[a] All experiments were carried out under conditions reported in Table III unless noted otherwise. [b] Initial zero-order rate constants calculated from the plot of oxygen consumption vs time. [c] Phosphate, 6.0×10^{-4} M; chloride, 4.3×10^{-4} M. [d] Borate, 4.8×10^{-4} M; chloride, 7.8×10^{-4} M. [e] Borate, 4.8×10^{-4} M; chloride, 1.75×10^{-4} M.

$$4CH_3(CH_2)_9SH + O_2 \rightarrow 2[CH_3(CH_2)_9S]_2 + 2H_2O \qquad (1)$$

Rate constants were determined with the gas buret and are expressed in either milliliters of dioxygen per minute or moles of 1-decanethiol per liter per second. All molar concentrations are based on total volume of heterogeneous reaction mixture. After an induction period, the volume of dioxygen consumed was linear with time to about 65% conversion of 1-decanethiol. Figure 2 illustrates the faster reaction and shorter induction period achieved with latex catalyst LC-1 compared with soluble $CoPcTsNa_4$. The relative zero-order rate constants in Table III show that the latex catalyst LC-1 is 11 times more active than soluble $CoPcTsNa_4$ and 20 times more active than cobalt-free latex L-1. The reaction with LC-1 is 24 times faster than in the absence of catalyst. The most active latex catalyst, LC-3, was 14 times as active as soluble $CoPcTsNa_4$.

Because surfactant 1 was easier to prepare and purify than 2 or 3, colloidal catalyst LC-1 was chosen for more detailed study. The rate of autoxidation increased with pH in the range 7.0–9.0 (Table IV). Experiments were not performed at higher pH because the latexes were less colloidally stable at pH 10–11. The pK_a of 1-decanethiol in water is estimated to be 10.7, the same as that of 1-heptanethiol.[26] The rate also increased with increasing amount of catalyst LC-1 at a constant CoPcTs loading of N$^+$/Co = 10.0 (Table IV). Figure 3 shows the effect of varied amounts of CoPcTs supported on a fixed amount of latex L-1. The rate constants increased linearly with the amount of CoPcTs at $<2.5 \times 10^{-5}$ M and decreased as

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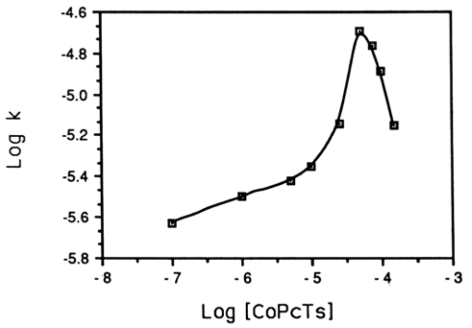

Figure 3. Dependence of autoxidation rate constants on CoPcTs concentration in the reaction mixture. All experiments used 1.47 × 10^{-2} M 1-decanethiol in 105 mL of water containing 600 mg of L-1 at pH 9.0 and 35 °C. The concentration of CoPcTs was 1.00 × 10^{-4} M for the rate constants in Tables III–VII.

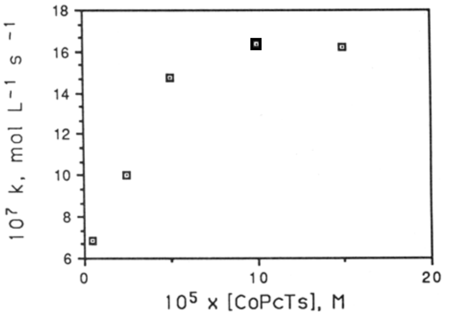

Figure 4. Dependence of autoxidation rate constants on concentration of $CoPcTsNa_4$ in aqueous solution. Conditions are the same as in Figure 3.

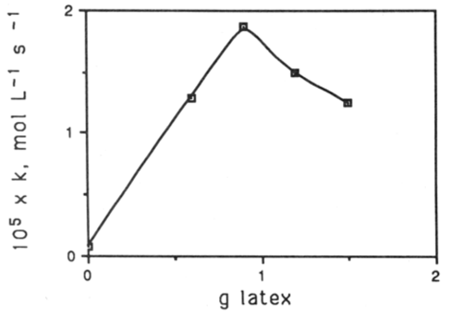

Figure 5. Dependence of autoxidation rate constants on varied amounts of latex L-1 containing a constant amount of 1.00 × 10^{-4} M CoPcTs in the reaction mixture. Conditions are the same as in Figure 3.

CoPcTs concentration increased from 5 to 15 × 10^{-5} M (Figure 3). When soluble $CoPcTsNa_4$ was used, the rate constants increased with catalyst concentration and leveled off at about 1.0 × 10^{-4} M CoPcTs (Figure 4). Dependence of the rate constants on the amount of particles of latex L-1 at a constant CoPcTs concentration is shown in Figure 5. Figure 6 shows the dependence of the rate constants on concentration of 1-decanethiol. A similar effect of 1-decanethiol concentration was observed for the autoxidation catalyzed with soluble $CoPcTsNa_4$. The temperature dependence of the rate constants from 15 to 45 °C with catalyst LC-1 under standard conditions gave an Arrhenius activation energy of 10.8 kcal mol^{-1} (Figure 7).

To test for possible external mass transfer limitation of the overall reaction rate, the reaction was conducted with vigorous shaking of the mixture instead of magnetic stirring under the standard conditions of Table III (except for 0.016 mmol of CoPcTs). Magnetic stirring gave a reaction 1.2 times as fast as vigorous shaking. The rate constants are considered identical within experimental error, since variation in the rate constant was typically ±10% with LC-1 under the conditions of Table III.

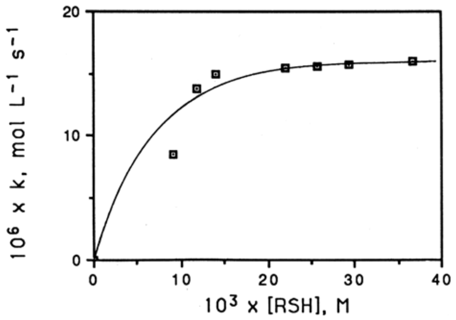

Figure 6. Dependence of zero-order rate constant of consumption of dioxygen on 1-decanethiol concentration in colloidal dispersions. Reaction conditions are in Table III.

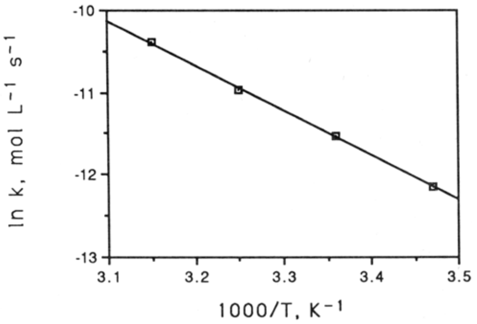

Figure 7. Arrhenius plot of zero-order rate data at 15–45 °C under the conditions of Table III.

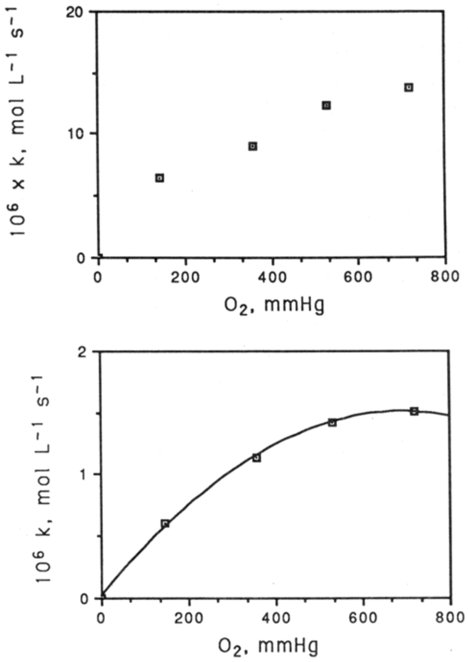

Figure 8. Dependence of rate constant of autoxidation of 1-decanethiol on partial pressure of dioxygen. Above: catalyzed by LC-1. Below: catalyzed by soluble $CoPcTsNa_4$. Reaction conditions are in Table III.

To test for possible intraparticle diffusional limitation of the overall reaction rate, a catalyst with 5% instead of 1% divinylbenzene cross-linking in the latex (colloidal catalyst LC-4, Table III) was tested. LC-1 and LC-4 gave rate constants that differed by less than 10%.

The effect of the partial pressure of dioxygen was investigated by using oxygen/nitrogen mixtures to obtain reduced partial pressures at 1 atm total pressure on the reaction mixture. Oxygen/nitrogen mixtures behave as ideal gases.[27] Figure 8b shows that the reactions catalyzed

Table V. Effects of Methanol on Autoxidation Rates and Induction Times[a]

catalyst	methanol, vol fractn	inductn time, min	k_{rel}
CoPcTsNa$_4$	0.0	48	1.00
CoPcTsNa$_4$	0.076	40	1.17
LC-1	0.0	4	11.0
LC-1	0.14	1.5	37.0

[a] All experiments were carried out under the conditions of Table III.

Table VI. Effects of Surfactants on Rates of Autoxidation Catalyzed by CoPcTsNa$_4$[a]

surfactant or latex	concn,[b] M	cmc,[c] M	inductn time, min	k_{rel}
none	–	–	40	1.0
LC-1	1.1×10^{-3} (600 mg)	–	4	11.0
1	1.00×10^{-3} (51.5 mg)	6.0×10^{-4}	1	5.6
CTAB	1.00×10^{-3} (38.3 mg)	9.2×10^{-4}	3	11.9
Triton X-100	4.5×10^{-4} (30 mg)	3.0×10^{-4}	7	2.2

[a] All reactions were carried out with 0.0105 mmol of CoPcTs under conditions reported in Table III. [b] Concentrations of surfactant head groups and/or ammonium ions in the reaction mixture. [c] The cmc of 1 is from ref 23. Other cmc values are from the following: Fendler, J. H. *Membrane Mimetic Chemistry*; Wiley: New York, 1982; p 8. Data are at 25 °C.

by soluble CoPcTsNa$_4$ approach saturation kinetic conditions at about 1 atm of dioxygen. The data with latex catalyst LC-1 in Figure 8a show only a 2-fold increase in rate constant with a 4-fold increase in pressure, but it is not clear that a maximum rate was reached at 1 atm of dioxygen.

The autoxidation of 1-decanethiol catalyzed by soluble CoPcTsNa$_4$ was slower and had a longer induction time than that catalyzed by colloidal catalyst LC-1 (Figure 2). Since this could be due to low solubility of 1-decanethiol in water, we tried methanol/water mixtures to increase the solubility. Rates of dioxygen consumption were measured after adding solutions of 1-decanethiol in methanol to the aqueous colloid LC-1 and to aqueous CoPcTsNa$_4$ (Table V). After addition of the solution of thiol in methanol to aqueous CoPcTsNa$_4$, the reaction mixture turned cloudy, indicating that the 1-decanethiol was incompletely miscible with 0.076 vol fraction methanol in water. The methanol had little effect on the rate or the induction time with soluble CoPcTsNa$_4$ as catalyst. In contrast, the rate catalyzed by LC-1 was enhanced by a factor of 3.4 by 0.14 vol fraction methanol (Table V).

The test the activity of surfactant 1 as a soluble catalyst, we performed the reaction with a solution of 1 and CoPcTsNa$_4$ at the same concentrations and reaction conditions as with the latex catalyst LC-1. A solution of surfactant 1 was 0.5 times as active as LC-1 (Table VI). However, the latex preparations contained less than 5% of the initial surfactant in free form, so the contribution to catalysis by surfactant not bound to latex particles to the rates in Table III is negligible. Effects of the conventional cationic surfactant hexadecyltrimethylammonium bromide (CTAB) and the nonionic surfactant Triton X-100 on the rate constants also are in Table VI. All of the reactions catalyzed by micelles and by LC-1 had much shorter induction times than the reaction catalyzed only by CoPcTsNa$_4$. The rate of reaction catalyzed by colloidal catalyst LC-1 was almost as fast as that catalyzed by CoPcTsNa$_4$ and CTAB and twice as fast as that catalyzed by CoPcTsNa$_4$ and surfactant 1.

Table VII. Effects of Inhibitors on Kinetics of Autoxidation[a]

catalyst	inhibitor (I)	inductn time, min		k_{rel}[b]
		with I	without I	
CoPcTsNa$_4$	TBMP[c]	35	36	0.66
LC-1	TBMP[d]	4.0	4.5	0.82
LC-1	*p*-benzoquinone[e]	1.0	1.0	0.31

[a] All experiments were carried out by using 1.54 mmol of 1-decanethiol and 0.0105 mmol of CoPcTs under the standard conditions of Table III. [b] Rate constant of oxygen consumption with inhibitor relative to rate constant without inhibitor. [c] 2,6-Di-*tert*-butyl-4-methylphenol (0.2 mmol) was added in 8 mL of methanol. [d] Solid TBMP, 0.20 mmol, was added to the reaction mixture. [e] *p*-Benzoquinone (0.20 mmol) was added in 15 mL of methanol.

To determine if the kinetics behaved like those of typical free-radical chain reactions, we added the inhibitors 2,6-di-*tert*-butyl-4-methylphenol and *p*-benzoquinone to reaction mixtures catalyzed by soluble CoPcTsNa$_4$ and by LC-1. Table VII shows that no change within experimental error occurred in the induction times, and the rate constants were reduced by factors of 3 or less.

Since there is evidence for the formation of hydrogen peroxide during the CoPcTsNa$_4$-catalyzed autoxidations of water-soluble thiols,[28,29] we added 0.02 mmol of hydrogen peroxide to reaction mixtures that contained 1.54 mmol of 1-decanethiol using soluble CoPcTsNa$_4$ and LC-1 as catalysts. Neither the rate nor the induction time was affected by using either catalyst. Oxidation of 1-decanethiol in a nitrogen atmosphere with a stoichiometric amount of hydrogen peroxide (0.5 mol/mol of 1-decanethiol) at pH 9 gave 36% conversion of thiol in 15 min at 35 °C both in the presence and in the absence of CoPcTsNa$_4$. The amount of thiol consumed was determined by GLC. The amount of 1-decanethiol oxidized by hydrogen peroxide under nitrogen during 15 min was less than by dioxygen using LC-1. No reaction was observed after 15 min with aqueous CoPcTsNa$_4$ in dioxygen due to a long induction period. We did not determine if the oxidation with hydrogen peroxide had an induction period.

Reuse of catalyst LC-1 was tested as follows. Autoxidation under the standard conditions of Table III was followed by dioxygen uptake. When dioxygen absorption stopped after 100% conversion, another 1.54 mmol of 1-decanethiol was injected, and the catalyst was reused without separation of reaction products. The reused catalyst was 0.33 times as active as the fresh catalyst. In another experiment using the same reaction conditions, products were extracted with diethyl ether, traces of ether in the aqueous dispersion were removed by sparging with nitrogen at room temperature, another 1.54 mmol of 1-decanethiol was injected, and the rate of dioxygen consumption was measured again. The rate constant with the extracted, recycled catalyst was 0.5 times that with the fresh catalyst. The color of the completed reaction mixtures was still phthalocyanine blue, but its intensity had faded. The transmission electron micrograph of catalyst LC-1 recovered from a reaction mixture appeared identical with that of the starting catalyst, as shown in Figure 1.

Discussion

Mechanism of Autoxidation. All of the colloidal catalysts were more active than aqueous CoPcTsNa$_4$.

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Since 1-decanethiol has very low solubility in water, and $CoPcTsNa_4$ is insoluble in nonpolar organic solvents, catalysis by $CoPcTsNa_4$ requires that the water-soluble catalyst react either with the small amount of thiol that is dissolved in the water or with the thiol at the thiol–water interface. Thus qualitatively the higher activity of the CoPcTs bound to latex particles may be attributed to a higher concentration of 1-decanethiol in organic polymer particles, the phase that contains the CoPcTs. With this qualitative conclusion in mind, let us now interpret the effects of many experimental parameters on the kinetics of autoxidation.

First consider the possibility that the rate of consumption of 1-decanethiol is limited by slow mass transfer of either dioxygen from the gas phase or 1-decanethiol from the insoluble droplets to the active sites on the latex particles.[3] Since the pK_a of 1-decanethiol is about 10.7 in water, at pH 9.0 in the aqueous phase only about 2% of it is present as the thiolate ion. Part of the 268 mg of thiol in a standard reaction mixture is absorbed into the 600 mg of latex particles. The degree of ionization of thiol may be greater in latexes than in water. This point is discussed later. The rest of the thiol is present as dispersed insoluble droplets. When stirring of a reaction mixture is stopped, a film of the lipophilic thiol can be seen on top of the aqueous dispersion. The independence of the rate of dioxygen consumption on the vigor of agitation (stirring vs shaking) of the reaction mixture is evidence against rate-limiting mass transfer of dioxygen, the thiol, or the disulfide. The rate constants depend slightly on dioxygen pressure at 1 atm with the latex catalyst but not with the soluble catalyst (Figure 8), which suggests a small dioxygen mass transfer limitation to the rate when the latex catalyst is used. With latex the rate was enhanced by 0.14 vol fraction methanol (Table V), which could both promote mass transfer and increase the solubility of the thiol in the aqueous and latex phases. We attribute the faster reactions with added methanol to increased solubility of thiol in catalyst particles because varied mixing methods do not affect the rates in the absence of a cosolvent. The rate of dioxygen consumption was not affected by increasing the degree of cross-linking of the latex from 1% to 5% (Table III). This indicates that the rate also is not limited by intraparticle diffusion. We aim to study the kinetics of autoxidation in the absence of mass transfer and diffusional limitations. Since the only apparent mass transfer limitation to the rates is a small dependence on dioxygen pressure at 1 atm, the pressure used for all other experiments, we believe that the neglect of mass transfer effects in the rest of our qualitative discussion is justified and that the remaining experimental variables affect mainly intrinsic catalytic activity.

Previously, autoxidations of water-soluble thiols catalyzed by $CoPcTsNa_4$ have been studied in water,[29] in aqueous solutions of cationic polyelectrolytes such as poly(vinylamine) and ionenes (polymeric quaternary ammonium ions prepared from α,ω-dialkylaminoalkanes and α',ω'-dibromoalkanes),[20-21] and in Sephadex ion-exchange resins.[22] The reactions are thought to proceed according to eq 2 and 3 with rate-limiting autoxidation (eq 2).[21]

$$2RSH + O_2 \rightarrow RSSR + H_2O_2 \quad (2)$$

$$2RSH + H_2O_2 \rightarrow RSSR + 2H_2O \quad (3)$$

In our CoPcTs latex-catalyzed autoxidations of 1-decanethiol, hydrogen peroxide in catalytic amounts did not increase the rate of reaction, and stoichiometric hydrogen peroxide under nitrogen did not oxidize the thiol faster than latex LC-1 under dioxygen. The latex-catalyzed reactions are zero-order in dioxygen to greater than 65% conversion of thiol. These observations are consistent with either a mechanism that does not require hydrogen peroxide as an intermediate or a mechanism in which dioxygen and CoPcTs have a synergistic effect on the rate of oxidation of thiol by hydrogen peroxide.

In both previous kinetic studies and ours, increasing rates of thiol autoxidation with increasing pH indicate either that the thiolate anion is the reactive species or that both hydroxide ion and thiol belong in the rate equation. The explanation proposed before is that the cationic polyelectrolyte binds the thiolate ion, and the thiolate ion is oxidized.[21]

An intriguing aspect of the latex kinetics is the increasing rate constants of thiol oxidation with increasing amounts of CoPcTs bound to a constant amount of polymer latex up to 5.0×10^{-5} M overall CoPcTs in the reaction mixture followed by decreasing rate constants at $>5.0 \times 10^{-5}$ M CoPcTs (Figure 3). The maximum rate constant was at 0.008 75 mmol of CoPcTs/g of latex, which contained 0.18 mmol of quaternary ammonium sites per gram. This corresponds with maximum activity at 0.05 CoPcTs per N^+ site. The zero-order rate constants at 10^{-7}–10^{-5} M CoPcTs are proportional to the 0.1 power of CoPcTs concentration. If the rate constants were reported as amount of thiol oxidized per mole of CoPcTs per unit time, they would decrease with increasing CoPcTs concentration over the entire concentration range. Two major causes are believed to be responsible for the CoPcTs concentration effects:[21,28b] (1) aggregation of CoPcTs and (2) decrease of the number of residual quaternary ammonium sites on the polymer available for thiolate binding with increasing CoPcTs concentration. Figure 4 shows that in the 5–15 $\times 10^{-5}$ M concentration range, soluble $CoPcTsNa_4$ gives rate constants approximately independent of concentration, which might be attributed to increasing aggregation of $CoPcTsNa_4$ and to lesser activity of aggregated species. Therefore, the decreasing rate constants of Figure 3 must be due either to a lesser amount of thiolate on the latex or to a greater depression in rate constants with aggregation of CoPcTs on the latex than with aggregation of CoPcTs in solution. Spectroscopic analysis of $CoPcTsNa_4$ indicates that it is more highly aggregated in the presence of 2,4-ionenes than in water alone.[30] Surprisingly the more aggregated CoPcTs in the presence of the ionene polymer was also the more active for 2-mercaptoethanol autoxidation.[28b]

The maximum in the graph of rate constant vs weight of catalyst support at constant CoPcTs concentration shown in Figure 5 has been observed with $CoPcTsNa_4$ in ionenes,[29] and with cationic micellar catalysts.[26,31-33] The increase in rate with up to 0.9 g of latex in 105 mL of reaction mixture can be attributed to increasing concentration of 1-decanethiol in the catalyst phase. The decrease in rate with 1.5 g of latex can be attributed to a decreased concentration of CoPcTs in the latex phase.

Figures 6 and 8 indicate that the rate constants of autoxidation of 1-decanethiol catalyzed by soluble $CoPcTsNa_4$ and by the CoPcTs–latex reach maxima with respect to both thiol concentration and pressure of dioxygen. Similar results have been reported for aut-

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oxidations of low concentrations of 2-mercaptoethanol in water catalyzed by $CoPcTsNa_4$ and soluble cationic polymers[34] and have been explained by a Michaelis–Menten mechanism. Our reactions were performed with the aqueous phase and the latex saturated with thiol, conditions not appropriate for analysis by a Michaelis–Menten mechanism.

Catalysis of 1-decanethiol autoxidation by CoPcTs latexes strongly resembles catalysis by cationic micelles. Both involve binding of reactive anionic species to a cationic colloidal species. The diameters of typical spherical cationic micelles are 3–5 nm, compared with 60 nm for our latexes. The surface area per quaternary ammonium ion of our latexes is about 1.0 nm^2 compared with about 0.45 nm^2 for a hexadecyltrimethylammonium bromide micelle. Both have a highly charged surface surrounding a lipophilic core that is composed of aliphatic hydrocarbon in micelles and of cross-linked polystyrene in latex particles. Catalysis of thiol autoxidation requires binding of two anions, $CoPcTs^{4-}$ and 1-decanethiolate, to the cationic latex or micelle. Binding to a polycation overcomes the electrostatic repulsion of the two anions that makes such reactions slow in solution. Table VI shows that the catalytic activity of the standard cationic micellar catalyst CTAB is about the same as that of the latex catalyst LC-1, and that the surfactant monomer 1 is about half as active as LC-1, using 1×10^{-3} M ammonium ions. The activities of micellar catalysts vary widely with relative concentrations of anionic reactants, co-ions, and binding sites.[31-33] The activities in Table VI are not maximized, for the micellar catalysis experiments are intended only for comparison with latexes at the same quaternary ammonium ion concentration.

The pseudophase ion-exchange model of micellar catalysis[26,31-33] analyzes the kinetics in terms of concentrations of reactive anions bound in the micelle phase. The model should be applicable to latex particles as well as to micelles, and we consider the term colloid to include both latexes and micelles for the rest of this paragraph. In our case, CoPcTs, a tetraanion, is completely bound to the colloid. Substrate, 1-decanethiol, is absorbed to an unknown extent by polystyrene, for which decanethiol is not a good solvent. The concentration of absorbed 1-decanethiol in latexes is probably smaller than in cationic micelles. The degree of ionization of the thiol in the colloid may be either higher or lower than in the aqueous phase.[26] The ionization constant of bound thiol varies with concentrations of thiol, quaternary ammonium ions, and anions such as chloride, bromide, borate, and hydroxide. Highly lipophilic counterions such as decanethiolate are bound by specific adsorption in addition to electrostatic forces.[32-34] 1-Decanethiolate in our reaction mixtures occupies most of the binding sites not taken by CoPcTs, leaving almost all of the more weakly binding bromide, chloride, borate, and hydroxide ions in the surrounding solution. Even in the presence of an excess of the lipophilic 1-decanethiolate, not all latex sites would have counterions. Otherwise, the latex would not be colloidally stable. Specific binding of a lipophilic anion such as a thiolate reduces the net charge on the colloid by reducing the degree of overall dissociation of counterions, but the total negative charge of bound anions is always less than the total positive charge of quaternary ammonium ions. Although is seems reasonable that the pseudophase ion-exchange model should apply to catalysis by latex particles, it has not been tested.

Numerous mechanisms could be proposed for the role of the CoPcTs in thiol autoxidations. The reaction could involve the successive binding of thiolate and dioxygen to either Co(II) or Co(III). Since inhibitors of free-radical chain reactions do not affect the induction period (Table VII), a free-radical chain mechanism is unlikely, although some other free-radical mechanism is possible. The reduced rates in the presence of inhibitors suggest that 2,6-di-*tert*-butyl-4-methylphenol and benzoquinone retard the reaction by reacting with the catalyst.

Recycling of latex catalyst LC-1 showed reduced activity during the second run. Since this occurred both with and without extraction of reaction products between kinetic runs, deactivation cannot be attributed entirely to accumulation of reaction products in the polymer. Possibly byproducts convert the CoPcTs to some catalytically inactive species. The latexes prepared from surfactant monomers 1–3 were not colloidally stable at pH 10 or 11 and were not indefinitely stable even at pH 9. Although the recovered catalyst LC-1 shown in Figure 1c does not appear to be coagulated, we also cannot rule out some change in colloidal structure during the reaction as the source of the reduced activity on reuse. We plan to continue autoxidation studies with more colloidally stable cationic latexes.

Experimental Section

Reagents. Hexadecyldimethylamine was prepared from hexadecylamine by reductive methylation with formic acid and formaldehyde[36] and was distilled under vacuum before use. 4-Acetoxystyrene (Maruzen Petrochemical Co.) was distilled under vacuum before use. 4-Hydroxystyrene was obtained by hydrolysis of 4-acetoxystyrene.[37] Styrene (Aldrich) and divinylbenzene (DVB, Aldrich) were distilled under vacuum and stored under argon at −10 °C until use. Azobisisobutyronitrile (AIBN, Aldrich) was recrystallized from methanol. [2-(Methacryloyloxy)ethyl]dimethyloctadecylammonium bromide (1)[23] was recrystallized several times from acetone; mp 168–170 °C (lit.[23] mp 168 °C). Triton X-100 (Sigma) and hexadecyltrimethylammonium bromide (CTAB, certified 99.6%, Fisher) were used as supplied. $CoPcTsNa_4$ was synthesized by the method of Weber and Busch.[24] All other reagents were used as received unless stated otherwise. Water used in the emulsion polymerizations and ultrafiltrations was purified by treatment with active charcoal and a mixed-bed ion-exchange resin and distillation in a glass apparatus. Its conductivity was typically 0.25×10^{-6} ohm^{-1} cm^{-1} after sparging with nitrogen.

Analyses. Melting points were determined on a Mel-Temp apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer Model 681 instrument. ^1H NMR spectra at 300 MHz and ^{13}C NMR spectra at 75.4 MHz were obtained on a Varian XL-300 instrument. GLC analyses were performed on a Varian 4100 chromatograph with a flame-ionization detector. The GC was modified to fit a 30-m Megabore capillary column having bonded methyl silicone as the stationary phase. Decane was used as internal standard. Conductances were measured with a YSI Model 31 conductivity bridge having a cell constant of 1.00 cm^{-1}. Critical micelle concentrations were determined conductometrically.

Compounds 2 and 3 were hygroscopic and difficult to purify, so the structures of 2, 3, and 12-bromododecyl-4-styryl ether (the precursor of 3) were assigned on the basis of ^1H and ^{13}C NMR spectra which are available as supplementary material.

(4-Styrylmethyl)hexadecyldimethylammonium Chloride (2). In a 100-mL flask, 3.05 g (0.020 mol) of vinylbenzyl chloride (Dow Chemical Co., a 70/30 meta/para mixture) was mixed with 5.4 g (0.020 mol) of hexadecyldimethylamine and 100 mg (0.45 mmol) of 2,6-di-*tert*-butyl-4-methylphenol. The mixture was heated overnight at 50 °C. The solid product was washed several times with dry ether and dried under vacuum at room temper-

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ature. Recrystallization from acetone/ether gave 6.3 g (75%) of **2**, which is estimated to be 97% pure on the basis of its ^{1}H NMR spectrum. ^{1}H NMR ($CDCl_3/Me_4Si$): δ 0.88 (t, 3 H), 1.24 (m, 26 H), 1.78 (m, 2 H), 2.75 (m, 1.4 H, unidentified impurity), 3.30 (s, 6 H), 3.53 (m, 2 H), 5.08 (s, 2 H), 5.32 (d, J = 10.8 Hz, 1 H), 5.84 (d, J = 18 Hz, 1 H), 6.7 (dd, 1 H), 7.3–7.7 (m, 4 H). ^{13}C NMR ($CDCl_3/Me_4Si$): δ 14.1, 22.7, 22.9, 26.3, 29.3, 29.4, 29.4, 29.6, 29.7, 29.7, 31.9, 49.7, 63.6, 67.3, 115.7, 116.1 (minor), 126.8 (minor), 127.9, 128.0, 129.4, 131.0, 132.5, 135.5 (minor), 135.6, 138.5, 139.7 (minor). IR (KBr): 3020, 2920, 1640 cm^{-1}.

12-Bromododecyl 4-Styryl Ether. A mixture of anhydrous potassium carbonate (27.6 g, 0.200 mol), 1,12-dibromododecane (36.1 g, 0.110 mol), 4-hydroxystyrene (12.0 g, 0.100 mol), hydroquinone (0.25 g, 0.0023 mol), and 100 mL of acetone was heated for 48 h at 60 °C. After cooling, insoluble salts were filtered from the reaction mixture, and acetone was evaporated. The product was chromatographed over 250 g of 40-mm flash chromatography grade silica gel. 1,12-Dibromododecane was eluted with petroleum ether, and 8.0 g of 12-bromododecyl 4-styryl ether (22%, mp 57–58 °C) was eluted with 10% toluene/90% petroleum ether. It was estimated to be >98% pure on the basis of its ^{1}H and ^{13}C NMR spectra. ^{1}H NMR ($CDCl_3/Me_4Si$): δ 1.25–1.50 (m, 16 H), 1.84 (m, 4 H), 3.39 (t, J = 7 Hz, 2 H), 3.97 (t, J = 6.6 Hz, 2 H); 5.11 (d, J = 10.8 Hz, 1 H), 5.59 (d, J = 17.6 Hz, 1 H), 6.65 (dd, J = 11 Hz, 17.4 Hz, 1 H), 6.85 (d, J = 8.7 Hz, 2 H), 7.33 (d, J = 8.7 Hz, 2 H). ^{13}C NMR ($CDCl_3/Me_4Si$): δ 26.0, 28.2, 28.8, 29.3, 29.4, 29.5, 32.8, 34.0, 68.0, 111.3, 114.4, 127.3, 130.2, 136.2, 158.9. IR (KBr): 1630, 1250 cm^{-1}.

[12-(4-Styryloxy)dodecyl]trimethylammonium Bromide (3). 12-Bromododecyl 4-styryl ether (2.0 g, 0.0055 mol) and 30 mL of dichloromethane were placed in a 100-mL, three-necked flask fitted with a dry-ice condenser. Trimethylamine (0.6 g, 0.010 mol) in 15 mL of acetone was added. While the reaction mixture was kept under argon at room temperature and allowed to reflux for 20 h, a white solid precipitated. Excess trimethylamine and solvents were removed under vacuum. The solid was washed several times with dry ether and recrystallized from dichloromethane/acetone to give 2.1 g (90%) of **3** which was estimated to contain by weight 70% **3**, 7% unknown impurity, and 23% water from its ^{1}H NMR spectrum. ^{1}H NMR ($CDCl_3/Me_4Si$): δ 1.25–1.50 (m, 16 H), 1.72 (m, 4 H), 3.1 (s, 1.2 H, unidentified impurity), 3.43 (s, 9 H), 3.55 (m, 2 H), 3.6 (s, 16 H, impurity assumed to be water), 3.95 (t, J = 6.6 Hz, 2 H), 5.11 (d, J = 10.8 Hz, 1 H), 5.60 (d, J = 17.6 Hz, 1 H), 5.96 (s, 3 H, unidentified impurity), 6.65 (dd, J = 11 Hz, 17.6 Hz, 1 H), 6.85 (d, J = 8.7 Hz, 2 H), 7.33 (d, J = 8.7 Hz, 2 H). ^{13}C NMR ($CDCl_3/Me_4Si$): δ 23.2, 26.0, 26.2, 29.2, 29.3, 29.4, 29.5, 29.5, 51.7, 53.3 (unidentified impurity), 66.9, 68.0, 70.3 (unidentified impurity), 111.4, 114.5, 127.3, 130.2, 136.2, 158.9; the heights of the impurity peaks were about the same of those of **3**. IR (KBr): 1630, 1250 cm^{-1}.

Polymerizations. Latexes L-1, L-2, L-3, and L-4 listed in Table I were prepared as follows: A mixture of styrene, monomeric surfactant **1**, **2**, or **3**, DVB, and deionized water in a three-necked flask fitted with a condenser was stirred magnetically under argon for 20 min. The mixture was deaerated with bubbling argon for 15 min, and AIBN (0.5% wt of total monomers) was added. The mixture was stirred for 10 min and heated at 65 °C for 20 h and at 80 °C for 2 h. The cool mixture was filtered through cotton to remove a trace of coagulum (<0.1 g). All latexes were purified by ultrafiltration through a 0.1-μm cellulose acetate/nitrate membrane (Millipore) under pressure of 60 psig of nitrogen. The conductivity of the initial filtrate was 25–30 × 10^{-6} ohm^{-1} cm^{-1}. About 100 mL of each latex was washed with about 800 mL of deionized water until the conductivity of the filtrate was 6–8 × 10^{-6} ohm^{-1} cm^{-1}. All latexes were stored at a concentration of 6% solids.

A carefully measured volume of latex corresponding to 1 g of solids was mixed with 2 mL of 6 M nitric acid and an aliquot of excess 0.010 M silver nitrate. The mixture was stirred for 15 min, and ferric ammonium sulfate indicator was added. The dispersion was titrated with 0.010 M KSCN solution[38] to measure the bromide content of the latexes reported in Table I. IR analyses of coagulated latexes showed no detectable bands at 1630–1640 cm^{-1} for the carbon–carbon double bond stretch of the monomers **1**–**3**. Particles sizes of the latexes were measured from transmission electron micrographs as detailed elsewhere.[15b]

Autoxidation of 1-Decanethiol. The colloidal catalysts were prepared by addition of aqueous $CoPcTsNa_4$ solution dropwise with stirring to the latexes and sonication for 20 min at room temperature. Each catalyst was ultrafiltered through a 0.1-μm membrane. No blue CoPcTs was detected in the filtrate. Oxidations of 1-decanethiol were performed with vigorous magnetic stirring of 105 mL of aqueous suspension in a 250-mL round-bottomed flask fitted with a condenser attached to a gas buret and a side arm with rubber septum and stopcock for introduction of reactant. The pH was adjusted by using borate or phosphate buffer. All experiments were carried out at 35.0 ± 0.1 °C and at constant dioxygen pressure. The catalyst suspension was held in air for 15 min, connected to the gas buret, degassed under vacuum three times, and saturated with dioxygen while being stirred. The catalyst mixture was held under dioxygen for 10 min before addition of thiol. 1-Decanethiol (Aldrich, distilled before use) was added to the reaction flask by using a syringe. After completion of the reaction, the mixture was extracted with ether and dichloromethane, and the extract was analyzed by gas chromatography and thin-layer chromatography for unreacted 1-decanethiol.

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Registry No. **1**, 120789-06-2; **2**, 87810-16-0; **3**, 112068-68-5; 1-decanethiol, 143-10-2; 12-bromododecyl 4-styryl ether, 120789-07-3.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of **2**, **3**, and 12-bromododecyl 4-styryl ether (6 pages). Ordering information is given on any current masthead page.

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