(4) Yarusso, D. J.; Cooper, S. L. *Macromolecules* **1983**, *16*, 1871; *Polymer* **1985**, *26*, 371.
(5) Fujimura, M.; Hashimoto, T.; Kawai, H. *Macromolecules* **1982**, *15*, 136; **1981**, *14*, 1309.
(6) Weiss, R. A.; Lefelar, J. A. *Polymer* **1986**, *27*, 3. Lefelar, J. A.; Weiss, R. A. *Macromolecules* **1984**, *17*, 1148.
(7) Peiffer, D. G.; Weiss, R. A.; Lundberg, R. D. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1503.
(8) For example, see: Kao, J.; Stein, R. S.; MacKnight, W. J.; Taggart, W. P.; Cargill, G. S., III *Macromolecules* **1974**, *7*, 95.
(9) Chu, B.; Wu, D.-Q.; Wu, C. *Rev. Sci. Instrum.* **1987**, *58*, 1158.

† State University of New York at Stony Brook.
‡ University of Massachusetts.
§ State University of New York at Buffalo.
⊥ BNL.
∥ Exxon Chemical Co.

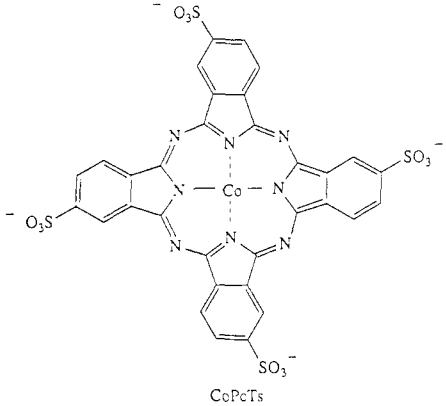
Benjamin Chu,*† Dan-Qing Wu,† W. J. MacKnight,‡ Chi Wu,† J. C. Phillips,§,⊥ A. LeGrand,⊥ C. W. Lantman,‡ and R. D. Lundberg∥

Chemistry Department, State University of New York at Stony Brook, Long Island, New York 11794-3400
Department of Polymer Science and Engineering University of Massachusetts Amherst, Massachusetts 01003
Chemistry Department, State University of New York at Buffalo, Buffalo, New York 14214
SUNY X3 Beamline, NSLS, BNL Upton, New York 11973
Paramins Division, Exxon Chemical Company Linden, New Jersey 07036

Received August 24, 1987; Revised Manuscript Received October 19, 1987

Cationic Latexes with Bound Cobalt Phthalocyaninetetrasulfonate Catalyze Autoxidation of 1-Decanethiol

The activity of heterogeneous catalysts normally increases as the catalyst particle size decreases because surface area per unit weight is inversely related to particle diameter. We report that a 60-nm diameter cationic latex with bound cobalt phthalocyaninetetrasulfonate (CoPcTs)



CoPcTs

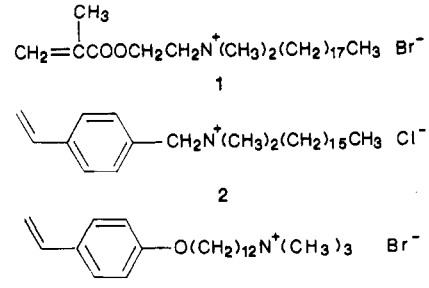
is 11 times more active than soluble $CoPcTsNa_4$ for autoxidation of 1-decanethiol in water. Previously CoPcTs bound to soluble polymers has shown greater activity than $CoPcTsNa_4$ for autoxidation of 2-mercaptoethanol.[1-3] CoPcTs bound to Sephadex ion-exchange resins was less active than soluble $CoPcTsNa_4$ for autoxidations of 2-mercaptoethanol and 1-butanethiol in aqueous and nonaqueous media.[4] Autoxidation of thiols is important in industry for the removal of thiol odors (such as the "sweetening" of petroleum)[5,6] and in living organisms (such as for changes in protein structure).[7,8]

Table I
Autoxidation of 1-Decanethiol with CoPcTs Catalysts[a]

	latex 1, mg	R_4N^+, mmol	CoPcTs, mmol	1-decanethiol, mmol	pH[b]	k_{obsd},[c] mL of O_2 min^{-1}
1	0	0.0	0.0105	1.53	9.0	0.060
2	600	0.105	0.0	1.53	9.0	0.034
3	600	0.105	0.0105	1.53	9.0	0.678
4	600	0.105	0.0105	1.53	8.0	0.444
5	600	0.105	0.0105	1.53	7.0[d]	0.129
6	900	0.158	0.0158	1.53	9.0	0.724
7	79	0.014	0.0014	1.53	9.0	0.301
8	600	0.105	0.0105	0.75	9.0	0.371
9	600	0.105	0.0105	3.14	9.0	0.601
10	600	0.105	0.0105	1.53	9.0	0.20

[a] All experiments were carried out at 35.0 ± 0.1 °C and O_2 pressure of 720 mmHg (about 20 mmHg less than atmospheric pressure) with magnetic stirring of 105 mL of reaction mixture. [b] Adjusted with 4 mL of 0.0125 M $Na_2B_4O_7$ and HCl buffer. [c] Initial zero-order rate constants calculated from the plot of oxygen consumption during oxidations of decanethiol. [d] Buffered with Na_2HPO_4 and HCl.

Latexes L-1, L-2, and L-3 were prepared by emulsion copolymerization of 96.2 mol % styrene, 1.0 mol % active divinylbenzene (technical 55% active), 0.8 mol % ethylvinylbenzene, and 2.0 mol % of monomer **1**,[9] **2**, and **3** as



surfactant with azobis(isobutyronitrile) as initiator. Cross-linking with divinylbenzene ensured that the polymer remained insoluble during all subsequent experiments. Number-average particle diameters of the three latexes measured on transmission electron micrographs were 58, 64, and 58 nm (±1-nm standard deviation), respectively. The conductivity of the aqueous solution of **1** was 440 Ω^{-1} cm^{-1} before copolymerization. Ultrafiltration of the copolymer latex gave an initial filtrate with conductivity of 20–25 Ω^{-1} cm^{-1} and a final filtrate with 6 Ω^{-1} cm^{-1}. Titration of the ultrafiltered latex by the Volhard method detected 96% of the bromide ion initially charged as surfactant. IR analysis of coagulated latex showed no detectable band at 1635 cm^{-1} for the double bond of **1**. Thus the polymer colloids contained little, if any, free surfactant.

Addition of aqueous $CoPcTsNa_4$[10] to the latexes completely bound the CoPcTs to form the latex catalysts LC-1, LC-2, and LC-3. Ultrafiltration of each catalyst with a 0.1-μm cellulose acetate/nitrate membrane (Millipore) revealed no blue CoPcTs in the filtrate; 0.1 μM CoPcTs can be detected by the human eye. $CoPcTsNa_4$ is soluble in water alone or in the presence of surfactant **1**. The colloids used as catalysts contained no detectable CoPcTs in solution.

Autoxidation of 1-decanethiol at pH 9.0 in 1 atm of dioxygen with LC-1 gave 95% conversion of thiol in 30 min at 35 °C (experiment 3 in Table I), even though 1-decanethiol is immiscible with water. The catalyst suspension was held in air for 15 min before addition of thiol. The amount of thiol consumed was determined by GLC

0024-9297/88/2221-0525$01.50/0

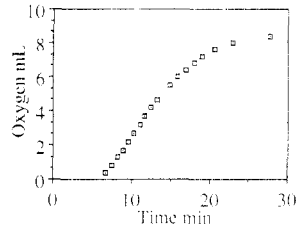


Figure 1. Dioxygen consumption with time during autoxidation of 1-decanethiol catalyzed by LC-1 (experiment 3). One mole of dioxygen per 4 mol of thiol corresponds to 8.6 mL.

analysis. Slightly more than 1 mol of O_2 per 4 mol of 1-decanethiol was consumed, which corresponds with the stoichiometry of eq 1.

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

After an induction period the volume of dioxygen consumed was linear with time to about 65% conversion of 1-decanethiol, as shown in Figure 1, which indicates a zero-order rate dependence on 1-decanethiol. The relative zero-order rate constants in Table I show that the latex catalyst LC-1 is 11 times more active than either soluble CoPcTs or cobalt-free latex L-1 (experiments 1–3). Increased oxidation rates with increasing pH in the range 7.0–9.0 (experiments 3–5) indicate that the thiolate ion is the likely reactive species, as found with other polymer-bound CoPcTs catalysts.[1,2] The increase of rate constants with increasing amounts of latex (at constant loading of CoPcTs in the latex, experiments 3, 6, and 7) and with decreasing amounts of initial thiol (at constant weight and loading of LC-1, experiments 3, 8, and 9) may be attributed to absorption of thiol and thiolate ion into the latexes. Higher initial thiol concentration (experiment 9) showed a decrease in the rate of consumption of dioxygen at >65% conversion. This may be due to accumulation of the didecyl disulfide as well as 1-decanethiol in the polymer. We have not determined yet the kinetic order in dioxygen, but in one experiment (10, Table I) the rate of oxidation was 0.30 times as fast under air as it was under oxygen (experiment 3) at atmospheric pressure. A solution of surfactant 1 and $CoPcTsNa_4$ at the same concentrations as in experiment 3 was 0.5 times as active as the latex catalyst. However, the latex preparations contained less than 5% of the initial surfactant in free form (according to conductometric analysis), so the contribution of micellar catalysis to the rates in Table I is negligible. Under the conditions of experiment 3 (except for 0.016-mmol of CoPcTs) magnetic stirring, shaking, and sonication of reaction mixtures gave 79%, 86%, and 90% conversion of thiol, respectively, in 40 min. Increased conversion with more vigorous agitation of reaction mixtures suggests a partial mass transfer limitation to the reaction rates.

Colloidal catalyst LC-3 was more active and catalyst LC-2 was less active than LC-1. The higher activity of the colloidal catalysts than of $CoPcTsNa_4$ suggests that many other autoxidations of organic compounds, such as alkyl aromatic hydrocarbons[11] and phenols,[12] in water may be strongly catalyzed by transition-metal catalysts bound to polymer latexes. We are continuing study of the kinetics of the 1-decanethiol oxidations to gain a better understanding of the mechanisms and to prepare more active catalysts.

Acknowledgment. We thank the U.S. Army Research Office for support of this research and H. Turk for providing the cobalt phthalocyaninetetra(sodium sulfonate).

Registry No. $HS(CH_2)_9CH_3$, 143-10-2; $(H_3C(CH_2)_9S)_2$, 10496-18-1.

References and Notes

(1) Zwart, J.; van der Weide, H. C.; Bröker, N.; Rummens, C.; Schuit, G. C. A. *J. Mol. Catal.* **1977–1978**, *3*, 151.
(2) (a) Schutten, J.; Zwart, J. *J. Mol. Catal.* **1979**, *5*, 109. (b) Brouwer, W. M.; Piet, P.; German, A. L. *Polym. Bull.* **1982**, *8*, 245. (c) Brouwer, W. M.; Piet, P.; German, A. L. *Polym. Commun.* **1983**, *24*, 216. (d) Brouwer, W. M.; Piet, P.; German, A. L. *Makromol. Chem.* **1984**, *185*, 363. (e) Brouwer, W. M.; Piet, P.; German, A. L. *J. Mol. Catal.* **1984**, *22*, 297. (f) Brouwer, W. M.; Piet, P.; German, A. L. *J. Mol. Catal.* **1985**, *29*, 335. (g) Brouwer, W. M.; Piet, P.; German, A. L. *J. Mol. Catal.* **1985**, *31*, 169.
(3) Knudo, N. N.; Keier, N. P. *Russ. J. Phys. Chem. (Engl. Transl.)* **1968**, *42*, 707.
(4) Skorobogaty, A.; Smith, T. D. *J. Mol. Catal.* **1982**, *16*, 131.
(5) Oswald, A. A.; Wallace, T. J. In *The Chemistry of Organic Sulphur Compounds*; Kharasch, N., Meyers, C. Y., Eds.; Pergamon: London, 1966; Vol. 2, Chapter 8.
(6) Frame, R. R. US Patent 4 298 463, 1981.
(7) Tarbell, D. S. In *Organic Sulphur Compounds*; Kharasch, N., Ed.; Pergamon: London, 1961; Vol. 1, Chapter 10.
(8) Jocelyn, P. C. *Biochemistry of the SH Group*; Academic: London, 1972; Chapter 4.
(9) Nagai, K.; Ohishi, Y.; Inaba, H.; Kudo, S. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 1221.
(10) Weber, J. H.; Busch, D. H. *Inorg. Chem.* **1965**, *4*, 469.
(11) Chandran, R. S.; Ford, W. T. *J. Chem. Soc., Chem. Commun.*, in press.
(12) Turk, H.; Ford, W. T. *J. Org. Chem.*, in press.
(13) Permanent address: Department of Chemistry, Faculty of Science, Tanta University, Tanta, Egypt.

M. Hassanein[13] and Warren T. Ford*
Department of Chemistry, Oklahoma State University
Stillwater, Oklahoma 74078

Received September 3, 1987

Orientation and Second Harmonic Generation in Doped Polystyrene and Poly(methyl methacrylate) Films

Doped polymeric films have the potential to become important in many industrial uses requiring nonlinear optical materials with wide-ranging physical and chemical properties.[2-3] Many of these uses involve materials capable of second harmonic generation (SHG), conversion of light of frequency ν to light of frequency 2ν. Materials combining the advantages of efficient SHG dopants with glassy polymers can have good optical and physical properties. Orienting these dopants in the polymeric matrix not only gives material capable of highly efficient SHG but will also allow the use of SHG as a probe of dopant orientation and polymer relaxation phenomena. The long-term stability of these oriented materials, along with their physical and mechanical properties, will ultimately determine their practical commercial value. In the present study, glassy polymers such as polystyrene (PS) and poly(methyl methacrylate) (PMMA) doped with optically characterized second harmonic generating dyes[4-6] were examined for their nonlinear optical properties as determined by sample treatment and physical aging.

The nonlinear optical properties of the guest–host polymer plus dye films are observed when highly conjugated, aromatic dyes with electron-donor and electron-acceptor substituents are oriented noncentrosymmetrically in a polymeric matrix.[4-6] The dopants have excellent nonlinear optical properties when aligned in such a way as to prevent their dipole moments from cancelling out. Our approach has been to dope PS and PMMA films with 4-(dimethylamino)-4′-nitrostilbene (DANS),[4] 2-methyl-4-nitroaniline (MNA),[6] or 4-[ethyl(2-hydroxyethyl)-amino]-4′-nitroazobenzene (disperse red-DR)[5] and align

0024-9297/88/2221-0526$01.50/0