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Catalysis of a nucleophilic reaction by cationic latexes

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Polystyrene latexes 200 nm in diameter and containing quaternary ammonium ions have the internal structure of anion exchange resins and the surface of surfactant micelles. They increase the *o*-iodosobenzoate (IBA) anion-catalyzed rate of hydrolysis of *p*-nitrophenyl diphenyl phosphate (PNPDPP) up to 6300 times in dilute aqueous dispersions by providing a phase of the reaction mixture in which the products of the PNPDPP and IBA concentrations are up to 630 times higher than in the aqueous phase, and in which the intrinsic second-order rate constants are up to ten times faster than in water. As in phase transfer catalysis, highest activity is achieved with the most lipophilic tetraalkylammonium ions.

INTRODUCTION

Because most organic compounds are insoluble in water, and many inorganic reagents are insoluble in nonpolar organic solvents, numerous organic synthetic methods have been devised to get organic and inorganic reactants into the same phase. The traditional method is use of a polar protic or aprotic organic solvent that dissolves both reactants to give a homogeneous solution. However, many reactions do proceed in heterogeneous mixtures at the phase interface, or more commonly in the phase in which one reactant is highly soluble and the other slightly soluble. Phase transfer catalysts promote the solubility of anions in organic solvents by providing a lipophilic counterion, such as a tetraalkylammonium ion or the crown ether complex of a sodium or potassium ion, to partially extract the reactive anion into the organic phase.[1,2] Although phase transfer catalysis was one of the first applications of crown ethers,[2–4] tetraalkylammonium and tetraalkylphosphonium salts are generally preferred because of their lower cost.

Closely related to phase transfer catalysis are many uses of polymers and colloids containing quaternary onium ions as catalysts in aqueous media. Sizeable enhancements of rates of reaction over the rates in aqueous solution are common in colloids, polymer solutions, and suspensions of insoluble polymer beads.[5–7] In most of these examples the polymer or colloid is a second phase of the reaction mixture, so the term phase transfer catalysis is appropriate. A colloid is a heterogeneous mixture in which one phase remains dispersed indefinitely. In a colloid composed of solid particles in a liquid of low viscosity such as water, the particles are in Brownian motion and mutually repel one another electrostatically or via unfavorable mixing of amphiphilic polymers adsorbed or grafted to the surface. Colloids also form by association of small molecules into aggregates such as surfactant micelles and vesicles. As catalysts association colloids have been called enzyme mimics because of their structural similarity to biological membranes, having polar surfaces and lipophilic interiors, and because the kinetics usually follow a Michaelis-Menten mechanism. The structures of some of the association colloids most widely studied as catalysts, micelles,[8–13] microemulsions,[14] and bilayer vesicles,[15] are illustrated in Figure 1. Spherical micelles 3–5 nm in diameter are composed of surfactant molecules having ionic or nonionic head groups exposed to water and a disordered lipophilic core. Microemulsions usually are about the same size as micelles but consist of water pools dispersed in oil with surfactant head groups in the water and tails in the oil to stabilize the interface. Bilayer vesicles are ordered annular spheres of 2-tailed surfactants arranged with head groups at the inner and outer surfaces and approximately parallel tails in the lipophilic interior. The overall diameters of vesicles may vary from about 10 nm to >1 µm, and they may have multilayered structures, but the thickness of each bilayer is a constant equal to twice the length of a surfactant molecule in an extended conformation.

The types of quaternary onium ion polymers used for catalysis are illustrated in Figure 2. Polyelectrolyte structures in water are less ordered than those of association

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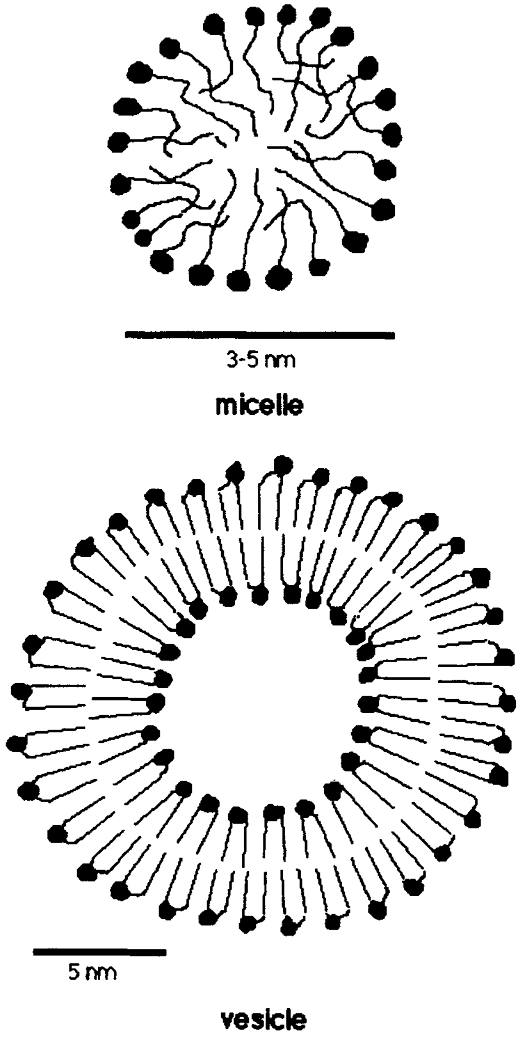

Figure 1 Representations of a spherical surfactant micelle and a small synthetic bilayer vesicle. The dark spots indicate surfactant head groups.

colloids, and the polymer chain is a highly expanded random coil whose volume consists mostly of water.[16–18] The insoluble polymers used as catalysts come in many shapes and sizes. The most common are spherical ion exchange resins (0.5–1 mm in diameter) and derivatives of the Merrifield resins (37–75 μm) used for solid phase peptide synthesis. These polymers are gels through which organic and inorganic reactants must diffuse to meet at the active sites. Their practical advantage is ease of separation of the polymer beads from reaction mixtures by filtration. We are studying cationic polymer latexes as catalysts. (Latex is another name for polymer colloid). These latexes are polystyrene networks containing quaternary ammonium ions, the same as those of anion exchange resins and of many polymer-supported phase transfer catalysts, and their sizes are colloidal, 50–500 nm in diameter.

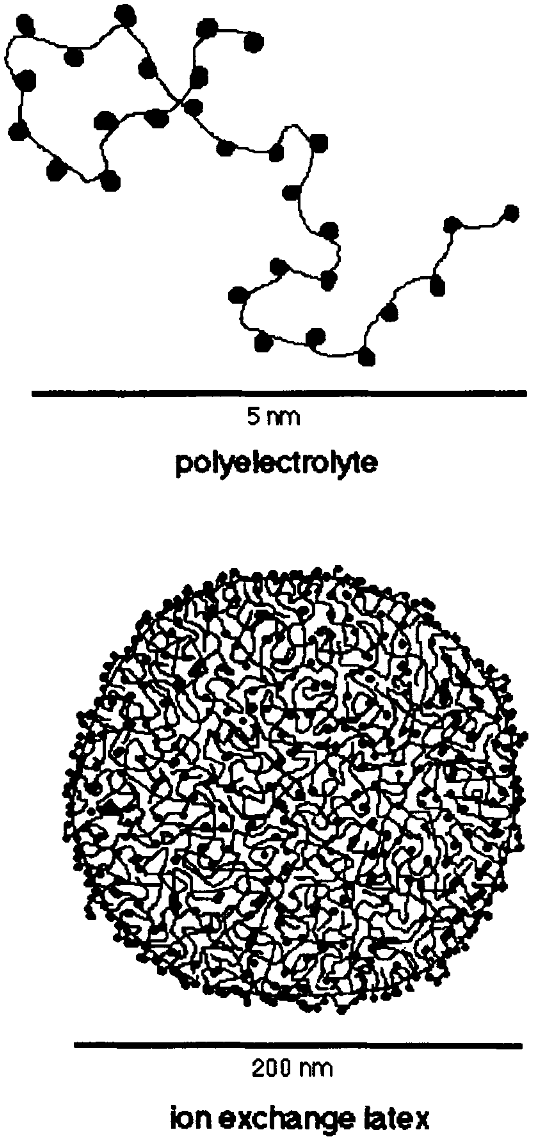

Figure 2 Representations of a polyelectrolyte and an ion exchange latex. The dark spots represent ionic functional groups. Ion exchange resins and polymer supported phase transfer catalysts have structures similar to that of the ion exchange latex except that the particle sizes typically are 0.5–1 mm and 37–75 μm respectively.

The rate enhancements in colloidal and polymeric media, as well as in phase transfer catalysis, arise from both kinetic and thermodynamic contributions. Kinetically the polymer or colloid plays the same role as the solvent in homogeneous catalysis. Solvation affects the energies of the ground state and the transition state of a reaction by electrostatic, ion-dipole, dipole-dipole, and van der Waal's forces. Stabilization of the transition state, destabilization of the ground state, or both can increase the rate of reaction. Thermodynamically the colloid or polymer acts as a second phase or a pseudophase. Reactants equilibrate between the aqueous and organic phases, and overall rates of reaction depend upon the concentrations of reactants in the two phases. For bimolecular reactions the observed second-order rate constant is a sum of contributions from the two phases and depends on the concentrations of reactants and the rate constant in each phase, as shown in eq 1, in which *S* (substrate) and *N* (nucleophile) are the reactants, and the concentrations are based on the total reaction mixture.

$$\text{rate} = k_{2\text{w}}[S]_\text{w}[N]_\text{w} + k_{2\text{c}}[S]_\text{c}[N]_\text{c} \qquad (1)$$

In surfactant micelles, the type of colloidal medium most thoroughly investigated by kinetics of catalysis, the major factors affecting rates of bimolecular reactions are the concentrations of the reactants in the micelles. Reactions of micelle counter ions with organic substrates are promoted by much higher concentration of those anions at the micelle surface than in water, and by much higher concentration of the organic reactant in the micelle than in water. Thus reactions of anions with organic substrates are promoted by cationic micelles, and conversely are retarded by anionic micelles from which the reactant anions are repelled.

Polymer latex diameters are 10–100 times larger than micelles and 1000–10000 times smaller than ion exchange resins. Their internal structures are entangled polymer coils with hydrated ionic functional groups, the same as those of ion exchange resins and polymer-supported phase transfer catalysts, and their surfaces are ionic, the same as the surfaces of micelles. We began study of polymer latexes as catalytic media because the rates of fast polymer-supported phase transfer catalyzed reactions are limited by the rates of intraparticle diffusion of one or both reactants to the active sites in the gel phase.[19] The mean time $t_{1/2}$ required for diffusion of a molecule or ion having diffusion coefficient D from the surface of a particle to 50% of the active sites depends on the spherical particle radius r_0 according to[20]

$$t_{1/2} = 0.030\, r_0^2/D \qquad (2)$$

Smaller particles reduce the time required for diffusion. In the limit of short diffusional paths the observed rate depends only on the intraparticle and solution phase rate constants and on concentrations in the two phases. Increasing rates of reaction with decreasing particle size are known for many cases of polymer-supported phase transfer catalysis.

Numerous reactions promoted by latexes are known.[21–23] Here we focus on the bimolecular reaction for which the kinetics are understood best, and on the properties of a family of anion exchange polystyrene latexes in which the members differ by numbers of quaternary ammonium groups ranging from 1 to 60 mol-% of (styrylmethyl)trimethylammonium ion repeat units and by the size of the quaternary ammonium ions constructed with tertiary amines ranging from trimethylamine to tributylamine. We show that reactivity is greater within the core than at the surface of the latexes, that the counter ions of large (styrylmethyl)tributylammonium ions are more reactive than those of smaller (styrylmethyl)trimethylammonium ions, and that high concentrations of reactants in the particles are the major factor responsible for the faster reaction.

RESULTS AND DISCUSSION

Latexes. The cationic latexes used for catalysis were prepared by a surfactant-free method of emulsion copolymerization of styrene, chloromethylstyrene (CMS), and divinylbenzene (DVB) shown in Figure 3.[24] All latexes were crosslinked with 1.0 mol-% DVB to insure that even polymers with high ion content were insoluble in water. The number average diameters D_n of the various samples measured by transmission electron microscopy (TEM) are 137–162 nm. Each sample has a narrow distribution of particle sizes with the ratio of weight average to number average diameter $D_\text{w}/D_\text{n} < 1.02$. Treatment of the copolymers with trimethylamine led to quaternary ammonium ion particles larger than the starting particles due to the amine incorporated. Some properties of the quaternary ammonium ion latexes are reported in Table 1. Quaternization of the copolymer prepared with 50 wt-% CMS with different tertiary amines led to another family of monodisperse particles also reported in Table 1.[25]

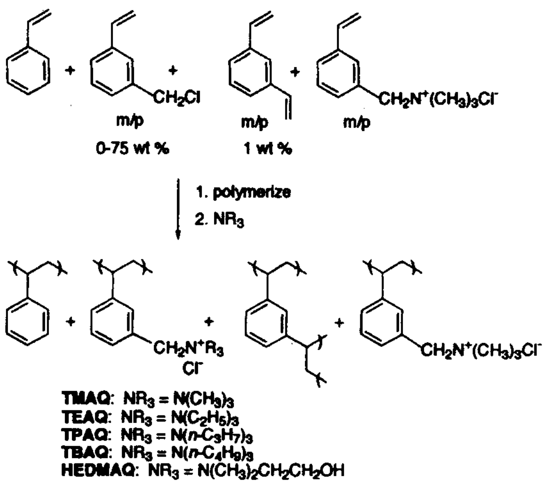

Figure 3 Synthesis of latexes used as catalytic media.

Table 1 Properties of Latexes Used As Catalysts

Latex [a]	*N^+ sites, mol-%*	D_n, *nm, by TEM*	D_h, *nm, by DLS*
TMAQ1HY	0.6	149	166
TMAQ5HY	1.3	154	172
TMAQ10HY	6.2	155	183
TMAQ25HY	17	175	217
TMAQ50HY	34	168	274
TMAQ75HY	60	181	379
TMAQ25JJL	14	184	225
TMAQ50JJL	39	169	300
TMAQ75JJL	61	212	423
TEAQ50JJL	32	164	314
TPAQ50JJL	13	162	208
TBAQ50JJL	24	184	258
HEDMAQ50JJL	25	165	275

[a] Numbers in the latex names refer to wt-% of CMS in the emulsion copolymerization. Data are from refs 24 and 25.

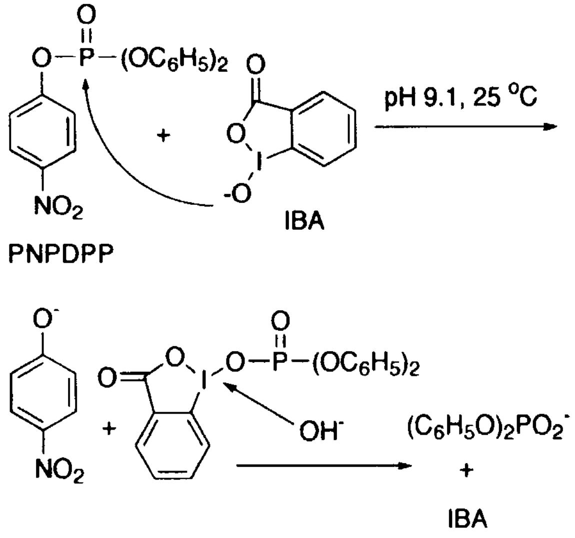

Figure 4 Mechanism of IBA-catalyzed hydrolysis of PNPDPP.

The particles vary widely in their internal structures due to variation of the fraction of ionic polymer repeat units. A particle containing only 1% of ionic repeat units can have nearly all of its charged groups on the surface and have an interior consisting of 1% crosslinked polystyrene with few charged groups. With increasing numbers of charged repeat units most of the quaternary ammonium ions must be inside, for less than 2% of them can be in the surface monolayer of a 200 nm diameter particle. The internal ionic groups are hydrated, and the particles are swollen gels in water. The degree of swelling depends on the number of ionic groups, the structure of the ionic group, and the degree of crosslinking of the polymer. The particle diameters reported in Table 1 were measured under dry conditions by TEM and in water by dynamic light scattering (DLS). The most swollen particles, TMAQ75, have a swelling ratio of 8, meaning they contain 7/8 water by volume. Hydrophilicity of the quaternary ammonium ions and swelling of the particles decrease with increasing ionic radius from methyl to butyl. Because of the high ion content and the low degree of crosslinking, the particles TMAQ75 and TMAQ50 contain long polyelectrolyte chains, some of which are anchored to the polymer network at only one end, leaving the other end free to dangle out into the aqueous phase. These hydrophilic particles may be described as hairy balls.

Hydrolysis of *p*-Nitrophenyl Diphenyl Phosphate Moss and coworkers[26] discovered the *o*-iodosobenzoate (IBA) ion to be a highly active catalyst for the hydrolysis of phosphate esters. Its activity is enhanced by micelles and polymer colloids. The hydrolysis of $\leq 10^{-4}$ M *p*-nitrophenyl diphenyl phosphate (PNPDPP) with $<10^{-4}$ M IBA at 25°C has a half-life of 10 s or less in hexadecyltrimethylammonium chloride micelles at the critical micelle concentration[26] and in 0.2–0.6 mg mL^{-1} of several of our latexes.[27,28] The iodoso oxygen atom of the cyclic IBA structure shown in Figure 4 attacks phosphorus.[29] Phosphate ester hydrolysis has been investigated widely in micelles, microemulsions, ion exchange resins, and other heterogeneous media because of its potential as a method of decontamination of organophosphorus insecticides and chemical warfare agents.[30–34]

Pseudo-first-order kinetic experiments with varied IBA concentrations were analyzed for the second-order rate constants k_{IBA} according to

$$-d[PNPDPP]/dt = (k_0 + k_{IBA}[IBA]_t)\,[PNPDPP] \qquad (3)$$

in which all concentrations are based on total volume of aqueous dispersion. The rate constants are reported in Table 2. The most active media are the latex TBAQ50 which contains 24 mol % of (styrylmethyl)tributylammonium ion repeat units and the polyelectrolyte PE44

Table 2 Rate Constants of Hydrolysis of PNPDPP with Latexes and Polyelectrolytes[a]

Latex	k_{IBA}, *M^{-1} s^{-1}*	k_{2L}, *M^{-1} s^{-1}*
TBAQ50JJL	3190	5.5
PE44P[b,c]	2050	d
TPAQ50JJL	1700	2.6
TEAQ50JJL	1630	5.7
TMAQ25JJL	1410	3.7
TMAQ50JJL	1200	1.8
PE50N[b,c]	850	d
HEDMAQ50JJL	770	2.2
TMAQ75JJL	370	0.57
PE75N[b,c]	190	d
TMAQ5HY[b]	184	d
TMAQ2HY[b]	167	d
none	0.51	

[a] pH 9.10 TAPS {N-(tris[hydroxymethyl]methyl-3-aminopropanesulfonic acid} buffer, 5.0 *mM*, *[IBA]* $\leq 5.9 \times 10^{-6}$ M, *0.2 mg of latex per* mL, 25.0 °C. Data are from ref 28. [b] pH 8.00, 0.4 mg particles or polyelectrolyte mL^{-1}, and otherwise the same conditions. Data are from ref 27. [c] The polyelectrolytes are designated by the wt-% of CMS used in copolymerization, N for quaternization with trimethylamine, and P for quaternization with tributylphosphine. [d] Not determined.

which contains 44 mol % of (styrylmethyl)tributylphosphonium ion repeat units. Activity of the (styrylmethyl) trimethylammonium ion latexes decreases in the order butyl > propyl > ethyl > methyl. Polyelectrolytes prepared from copolymers having the same chloromethyl content but lacking the DVB crosslinks are slightly less active than the corresponding latexes.

The kinetic data were analyzed by the ion exchange model of Figure 5. In the model the PNPDPP and the IBA are distributed between the particle and the aqueous phases with second-order reaction occurring in both phases. For most latex dispersions reaction in the aqueous phase is negligible, and the rate of reaction depends on the concentrations of PNPDPP and IBA and the second-order rate constant k_{2L} in the particle phase. Measurements of the rates of hydrolysis over a range of particle concentrations showed that all of 2×10^{-5} M PNPDPP was bound to particles at >2 mg particles mL^{-1}.

Concentrations of IBA in the particles in the absence of PNPDPP but otherwise under the same conditions used for kinetics were calculated from spectrophotometric measurements of the IBA concentration in the aqueous phase, from which the particles were removed by ultrafiltration. The relative amounts of chloride and buffer anions bound to the particles were calculated from measurements with an ion-selective electrode of the chloride ion concentration in the ultrafiltrate of mixtures that contained no IBA. These combined data enabled calculation, via quadratic equations, of the ion exchange selectivity coefficients defined by eq 4, and the results are reported in Table 3.

$$K_{X/Cl} = [X]_b[Cl]_w / [X]_w[Cl]_b \qquad (4)$$

Table 3 Ion Exchange Selectivity Coefficients in Latexes at 25°C[a]

Latex	$K_{IBA/Cl}$[b)]	$K_{TAPS/Cl}$[c)]
TMAQ75JJL	2.4	0.58
TMAQ50JJL	1.4	0.37
TBAQ50JJL	1.7	0.27

[a] Ref 28. [b] 5.0 mM pH 9.10 TAPS, 2.5×10^{-4} M IBA, Cl^- from 0.1 mg latex mL^{-1}. [c] 5.0 mM pH 9.10 TAPS, Cl^- from 0.1 mg latex mL^{-1}.

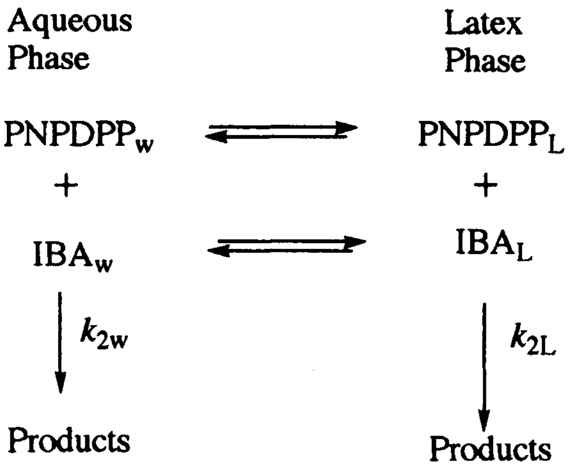

Figure 5 Kinetic scheme for IBA-catalyzed hydrolysis of PNPDPP in a latex dispersion.

The remaining analysis of the kinetic data depends on two approximations. (1) Exchange of IBA, chloride, and buffer ions is much faster than chemical reaction. Equation 2 and diffusion coefficients of 10^{-7} to 10^{-5} cm^2 $s.^{-1}$ for ions in ion exchange resins show that a time of 1–100 μs is required for 50% exchange of ions in particles of 200–400 nm diameter. This verifies the approximation, since all reactions had half-lives of at least 10 s. (2) The sum of concentrations of bound anions equals the concentration of polymer quaternary ammonium ions. This is the electroneutrality approximation of conventional ion exchange resins.[35] It is supported by measurements of the fraction of H^+ dissociated from poly(styrenesulfonic acid) latexes to be ≤0.04,[36] but measurements have not been reported for quaternary ammonium ion latexes.

The concentration of IBA in mols per L of particles ($[IBA]_L$) was calculated from mols IBA bound in particles per L of dispersion ($[IBA]_b$), the molar concentration of quaternary ammonium ions in the dispersion ($[N^+]$), and the particle volume per mol of N^+ ions using eq 5. Particle volume was calculated from the weight of particles per unit volume and the diameter measured by light scattering. The second-order rate constant in the particle k_{2L} was calculated from k_{IBA} and $[IBA]_L$ via eq 6, and the results are reported in Table 2.

$$[IBA]_L = [IBA]_b / [N^+]V \qquad (5)$$

$$k_{IBA} = k_{2L}[IBA]_L \qquad (6)$$

The k_{2L} values show that the reactivity of IBA in the most lipophilic latex, TBAQ50, is 10 times that in water, and that the remaining factor of 630 in the k_{IBA} enhancement of 6300 times is due to the higher concentrations of IBA and PNPDPP in the particle phase than in aqueous solution. Analysis of the results for the most hydrophilic latex TMAQ75 shows that the rate acceleration of 370 relative to water is due entirely to higher intraparticle concentrations of reactants. Thus the major factor responsible for faster reaction of IBA with PNPDPP in latex dispersions is the extraction of high concentrations of reactants from water into the particles. The more lipophilic latexes cause an additional rate acceleration due to higher activity of the IBA anion, which we attribute to less stabilization of IBA by hydrogen bonding to water.

The higher activity in more lipophilic latex particles shown by intraparticle rate constants in Table 2, and the very low activity of the latexes TMAQ2 and TMAQ5, which have almost all of their quaternary ammonium ions on the particle surface, prove that the cores, not the surfaces, of the ion exchange particles are responsible for the larger rate enhancements. High intraparticle activity and high activity of more lipophilic quaternary ammonium ions are consistent with the performance of polymer-supported phase transfer catalysts derived from ion exchange and Merrifield resin beads.[19]

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REFERENCES

1 Starks, C.M.; *J. Am. Chem. Soc.* **1971**, *93*, 195.
2 Starks, C.M.; Liotta, C.L., Halpern, M.; *Phase Transfer Catalysis*; New York: Chapman and Hall, 1994.
3 Sam, D.; Simmons, H.E.; *J. Am. Chem. Soc.* **1972**, *94*, 4024.
4 Liotta, C.L.; Grisdale, E.; Hopkins, H.P., Jr.; *Tetrahedron Lett.* **1975**, 4205.
5 Fendler, J.H.; Fendler, E.J.; *Catalysis in Micellar and Macromolecular Systems*; Academic Press, New York 1975.
6 Fendler, J.H.; *Membrane Mimetic Chemistry*; John Wiley and Sons, New York 1982.
7 Grätzel, M.; Kalyanasundaram, M.K.; *Kinetics and Catalysis in Microheterogeneous Systems*; Marcel Dekker Inc., New York 1991.
8 Menger, F.M.; Portnoy, C.E.; *J. Am. Chem. Soc.* **1967**, *89*, 4698.
9 Cordes, E.H.; Dunlap, R.B.; *Acc. Chem. Res.* **1969**, *2*, 329.
10 Quina, F.H.; Chaimovich, H.J.; *J. Phys. Chem.* **1979**, *83*, 1844.
11 Romsted, L.S. in *Surfactants in Solution*, K.L. Mittal, B. Lindman, Eds., Plenum, New York, 1984, pp 1015–1068.
12 Bunton, C.A.; Savelli, G.; *Adv. Phys. Org. Chem.* **1986**, *22*, 213.
13 Bunton, C.A.; Nome, F.; Quina, F.H.; Romsted, L.S.; *Acc. Chem. Res.* **1991**, *24*, 357.
14 Mackay, R.A.; Hermansky, C.; *J. Phys. Chem.* **1981**, *85*, 739.
15 Fendler, J.H.; Hinze, W.L.; *J. Am. Chem. Soc.* **1981**, *103*, 5439.
16 Overberger, C.G.; Salamone, J.C.; *Acc. Chem. Res.* **1969**, *2*, 217.
17 Morawetz, H.; *Acc. Chem. Res.* **1970**, *3*, 354.
18 Ise, N.; Okubo, R.; Kunugi, S.; *Acc. Chem. Res.* **1982**, *15*, 171.
19 Ford, W.T.; Tomoi, M.; *Adv. Polym. Sci.* **1984**, *55*, 49.
20 Helfferich, F.; *Ion Exchange*; McGraw-Hill, New York 1962, pp 261–262.
21 Kitano, H.; Sun, Z.-H.; Ise, N.; *Macromolecules* **1983**, *16*, 1306.
22 Sun, Z.; Yan, C.; Kitano, H.; *Macromolecules* **1986**, *19*, 984.
23 Ford, W.T.; Badley, R.C.; Chandran, R.S.; Babu, S.H.; Hassanein, M.; Srinivasan, S.; Turk, H.; Yu, H.; Zhu, W.; *Am. Chem. Soc. Symp. Ser.* **1992**, *492*, 423, *and references therein.*
24 Ford, W.T.; Yu, H.; Lee, J.-J.; El-Hamshary, H.; *Langmuir* **1993**, *9*, 1698.
25 Lee, J.-J.; Ford, W.T.; *J. Org. Chem.* **1993**, *58*, 4070.
26 Moss, R.A.; Alwis, K.W.; Bizzigotti, G.O.; *J. Am. Chem. Soc.* **1983**, *105*, 681.
27 Ford, W.T.; Yu, H.; *Langmuir* **1993**, *9*, 1999.
28 Lee, J.-J.; Ford, W.T.; *J. Am. Chem. Soc.* **1994**, *116*, 3753.
29 Moss, R.A., presented at the U.S. Army Edgewood Research, Development and Engineering Center Scientific Conference, November 1993, and personal communication.
30 Hammond, P.S.; Forster, J.S.; Lieske, C.N.; Durst, H.D.; *J. Am. Chem. Soc.* **1989**, *111*, 7860.
31 Mackay, R.A.; Longo, F.R.; Knier, B.L.; Durst, H.D.; *J. Phys. Chem.* **1987**, *91*, 861.
32 Moss, R.A.; Chung, Y.-C.; Durst, H.D.; Hovanec, J.W. *J. Chem. Soc. Perkin Trans. I* **1989**, 1350.
33 Moss, R.A.; Chung, Y.-C.; *J. Org. Chem.* **1990**, *55*, 2064.
34 Moss, R.A.; Chung, Y.-C.; *Langmuir* **1990**, *6*, 1614.
35 Helfferich, F. *Ion Exchange*; McGraw-Hill, New York, 1962, pp 133–136.
36 Ito, K.; Ise, N.; Okubo, T.; *J. Chem. Phys.* **1985**, *82*, 5732