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Hydrolysis of *p*-Nitrophenyl Esters Promoted by Semi-fluorinated Quaternary Ammonium Polymer Latexes and Films

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Received

Semifluorinated polymer latexes were prepared by emulsion polymerization of 2.5-25% of a fluoroalkyl methacrylate, 25% chloromethylstyrene, 1% styrylmethyl(trimethyl)ammonium chloride, and the remainder 2-ethylhexyl methacrylate under surfactant-free conditions. The chloromethylstyrene units were converted to quaternary ammonium ions with trimethylamine. In aqueous dispersions at particle concentrations of less than 1 mg mL⁻¹ the quaternary ammonium ion latexes promoted hydrolyses of *p*-nitrophenyl hexanoate (PNPH) in pH 9.4 borate buffer and of diethyl *p*-nitrophenyl phosphate (Paraoxon) in 0.1 M NaOH at 30 °C with half-lives of less than 10 minutes. Thin 0.7-2 μm films of the latexes on glass promoted fast hydrolysis of Paraoxon but not of PNPH under the same conditions. Even after annealing the quaternary ammonium ion polymer films at temperatures well above their glass transition temperatures, AFM images of the film surfaces had textures of particles. Contact angle measurements of the annealed films against water and against hexadecane showed that the surfaces were not highly fluorinated.

Introduction

In aqueous-organic mixtures quaternary ammonium ions in the forms of phase transfer agents,¹ surfactant micelles,² soluble polyelectrolytes,³ colloidal particles,⁴⁻⁷ and Merrifield-like resins⁸⁻¹¹ promote reactions between organic-soluble reactants and the nucleophilic or basic anions of water-soluble salts. In a general mechanism, the organic reactants and the reactive anions partition favorably from a large volume of water into a smaller volume of the quaternary ammonium ion polymer or association colloid in which the local reactant concentrations are much higher than in the overall mixture. Consequently the bimolecular reaction rates also are much higher than in water alone. The kinetics of the reactions fit a pseudophase ion exchange model that was derived for micellar catalysis² and also applies to catalysis by quaternary ammonium ion polymers.³⁻⁷

In this paper we report the use of semi-fluorinated latex particles and films to promote hydrolyses of *p*-nitrophenyl hexanoate (PNPH) in pH 9.4 borate buffer and of diethyl *p*-nitrophenyl phosphate (the insecticide Paraoxon) in 0.1 M NaOH. These compounds are structurally similar to, and have rates of hydrolysis similar to, organophosphate chemical warfare agents.¹²⁻¹⁵

Our interest in semi-fluorinated polymer particles continues from a previous investigation in which we examined these same reactions using other polymer particles dispersed both in water and in the fluorous solvent HFE-2200 (perfluorobutyl ethyl ether) to simulate decontamination of fluorous solutions of toxic organic chemicals (TOC).⁷ HFE solvents efficiently extract organic compounds out of the nooks and crannies of electronic equipment.¹⁶ In our work colloidal quaternary ammonium ion polymers, which dispersed into HFE-2200 due to a semifluorinated

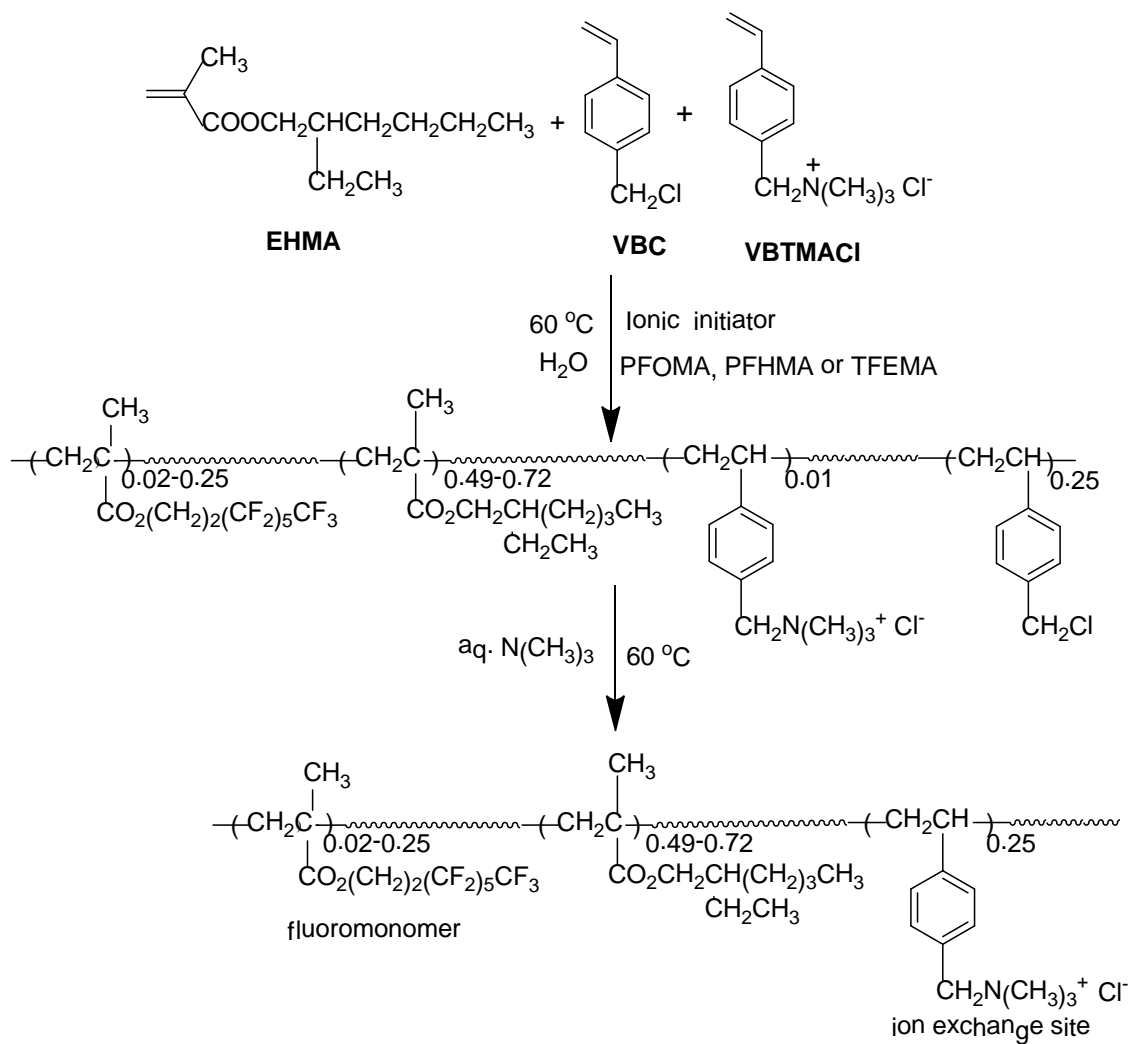
block copolymer stabilizer,¹⁷ proved to be only moderately active for the hydrolyses of PNPB and Paraoxon in two phase HFE/aqueous mixtures. On the other hand polymer particles lacking the fluorinated stabilizer, which dispersed into the aqueous phase, were much more active, comparable with quaternary ammonium ion surfactants such as hexadecyltrimethylammonium bromide, for the same reactions.⁷

Semifluorinated latex coatings have been investigated extensively because their films repel both water and organic compounds due to low surface tensions.¹⁸⁻³⁰ In this work our objective was to create films that both are repellent and contain anion exchange catalytic sites for decomposition of any TOCs that manage to penetrate the surface of the film. Latex particles were designed to have a core-shell morphology with the semifluorinated monomer in the shell, so that upon annealing particle films in air the hydrophobic and oleophobic fluoroalkyl groups could migrate to the surface, and the hydrophilic quaternary ammonium ions could migrate beneath the surface. Here we report the syntheses of the latex particles, their catalytic activities for hydrolyses of PNPB and Paraoxon in the forms of both colloidal dispersions and films, and the characterization of the surfaces of the films by AFM and by dynamic contact angle measurements.

Results

Synthesis of Quaternary Ammonium Ion Latexes. The semi-fluorinated latexes were synthesized by surfactant-free shot-growth emulsion polymerization as shown in Scheme 1. By the shot-growth method the solvent monomer 2-ethylhexyl methacrylate (EHMA) and the functional monomer vinylbenzyl chloride (VBC) were polymerized to incomplete conversion

using the cationic monomer vinylbenzyl(trimethyl)ammonium chloride (VBTMACl) and the cationic initiator 2,2'-azobis(2-methylpropionamide) dihydrochloride for charge stabilization of the colloidal particles. More EHMA, VBC, and VBTMACl, and one of the fluoroalkyl methacrylate monomers (1H,1H,2H,2H-perfluorooctyl methacrylate (PFOMA), 1H,1H,2H,2H-perfluorohexyl methacrylate (PFHMA), or 2,2,2-trifluoroethyl methacrylate (TFEMA)) were added in the second stage to form a particle outer shell that was rich in fluoroalkyl groups. Table 1 reports the products of polymerizations containing 2.5, 5, 10, and 25 wt % of the fluoromonomers and 25 wt% of VBC. Most of the polymerizations gave high yields. The few yields of <50% may have been due to inadequate stirring of the polymerizing mixtures. Dynamic light scattering measurements of the colloidal dispersions showed narrow particle size distributions and average diameters of 88-162 nm. Attempts at similar polymerizations using 10% VBC and 10% of the fluoromonomers gave low yields and colloiddally unstable dispersions.



Scheme 1. Synthesis of cationic polymer colloids.

Table 1. Copolymer Latex Particles

copoly- mer	F monomer	wt % ^a	yield ^b (%)	diameter ^c (nm)
1F	TFEMA	2.5	89	94
2F	PFOMA	2.5	48	94
3F	TFEMA	5.0	84	92
4F	PFOMA	5.0	90	88
5F	TFEMA	10.0	38	98
6F	PFOMA	10.0	32	120
10F	PFHMA	10.0	34	142
11F	PFOMA	25.0	97	105
12F	PFHMA	25.0	97	162
13F	TFEMA	25.0	96	132

^aWeight percent fluoromonomer. The other monomers were 25% VBC, 1% VBTMACl, and the remainder EHMA. ^bCalculated from the weight of copolymer obtained and the weight of monomer mixture used for polymerization. ^cHydrodynamic diameter from dynamic light scattering.

The copolymers were treated with aqueous trimethylamine to convert the vinylbenzyl chloride units to the quaternary ammonium units needed for phase transfer catalysts, as shown in the last step of Scheme 1. The change of chemical structure of the polymers was confirmed by the disappearance of the peak at 1262 cm⁻¹ due to CH₂Cl in the FTIR spectrum of sample 13F. The yields of quaternary ammonium ions, which are reported in Table 2, ranged from 40% to 82%. The higher yields were obtained by repeated additions of trimethylamine to the reaction mixtures. The yields were measured by chloride-selective electrode titration of the chloride

counter ions of the quaternary ammonium ions in the polymers. The diameters of the quaternized particles were substantially larger than those of the starting copolymers, partly due to a gain of mass from the trimethylamine, and mainly due to swelling of the ionic polymers by water. The ratios of the volumes of the quaternized particles to the volumes of the copolymers in aqueous dispersions are listed in Table 2.

Table 2. Quaternized Latex Particles^a

sample	yield (%)	diameter (nm) ^b	volume ratio ^c	N ⁺ Cl ⁻ (mmol/g)	T _g (°C) ^d
1QF	43	140	3.3	0.67	^e
2QF	40	113	1.7	0.58	^e
3QF	42	129	2.8	0.66	^e
4QF	59	140	4.2	0.91	^e
5QF	65	173	5.5	1.00	106
6QF	82	279	12.6	1.25	83
10QF	69	279	3.8	1.06	^e
11QF	53	207	7.6	0.63	102
12QF	56	280	5.2	0.67	94
13QF	56	198	3.4	0.67	91

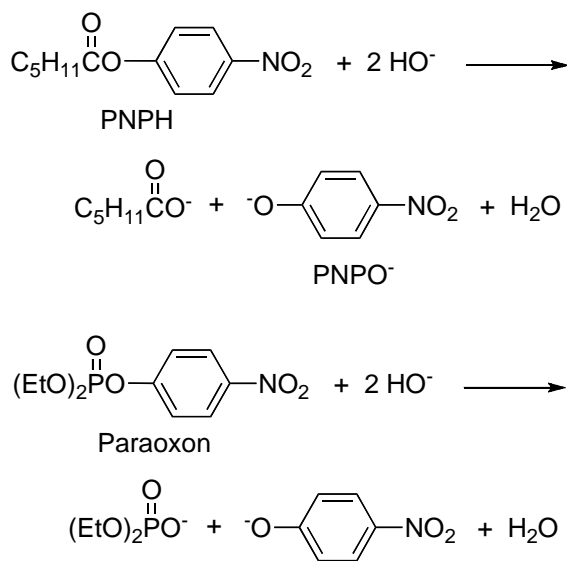
^aDerived from the latexes listed in Table 1. ^bHydrodynamic diameter from dynamic light scattering, ^c(Volume of quaternized polymer particle)/(volume of precursor polymer

particle) calculated from swollen particle diameters. ^dGlass transition temperature of dry particles. ^eNot measured.

In the past we included a cross-linking monomer in the copolymers to insure that none of the polymer produced after quaternization of the VBC units was water-soluble polyelectrolyte.^{5,6} In this work with semi-fluorinated latexes we used no cross-linking monomer because a cross-linked latex might not cure to form smooth coatings.

Preparation of Films. (a) Drop Cast Method. Latex films were prepared on glass cover slips by placing a few drops of the aqueous dispersion onto the glass, spreading the drops with a plastic rod, and allowing the water to evaporate. The thicknesses of the films were 0.9-4.6 μm as calculated from the surface area of the glass, the volume of aqueous dispersion used, and the solid content of the dispersion. Because films that were dried only at room temperature peeled off when the glass was submerged in water, the films were made more robust by annealing at 75-90°C. The weights, thicknesses, and annealing temperatures of the films are reported in Table 1S (Supporting Information). **(b) Spin Coating Method.** To get smoother films, several of the dispersions of quaternized latexes were spin coated onto glass cover slips, dried, and annealed. The thicknesses of the films were 0.7-1.4 μm as calculated from the increase in weight and the surface area of the glass. The samples are reported in Table 1S (Supporting Information).

Kinetics of Hydrolysis of PNPB and Paraoxon in Colloidal Particles. The cationic polymer colloids 1QF - 13QF, which differ by the type and composition of fluoromonomer in the shell (Table 2), were tested as catalysts for the basic hydrolyses of PNPB and Paraoxon. Balanced equations for the reactions are shown in Scheme 2.



Scheme 2. Hydrolyses of PNPB and Paraoxon.

Hydrolyses of PNPB were carried out using particle dispersions in stirred pH 9.4 borate buffer solution in a spectrophotometer cuvette at 30 °C. Graphs of absorbance at 400 nm of the product *p*-nitrophenoxide ion (PNPO⁻) vs. time using many of the particle samples as catalysts are shown in Figure 1. The reaction was very slow in the absence of particles. At weight concentrations of particles in the reaction mixtures of less than 1 mg mL⁻¹, the particles scattered some of the incident light but did not prevent measurement of the intensity of transmitted light. The concentrations of quaternary ammonium ions in the mixtures ([N⁺] = 1.7-3.1 x 10⁻⁴ M) exceeded the initial concentrations of PNPB (8.3 x 10⁻⁵ M). The data were fit to a pseudo-first-order rate equation, and rate constants were calculated from data acquired over the first 60% conversion. The half-lives of PNPB hydrolysis were 2.5-7 minutes using all of the colloidal particle catalysts listed in Table 2. Table 2S (Supporting Information) reports the conditions,

first-order rate constants, half-lives, and second-order rate constants (rate constants per concentration of quaternary ammonium ion exchange sites, $k_2 = k_1/[N^+]$) of the reactions.

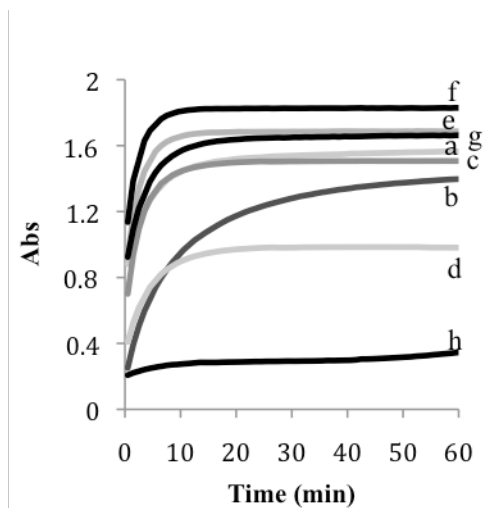


Figure 1. Change of absorbance at 400 nm due to $PNPO^-$ from hydrolysis of PNPB in pH 9.4 borate buffer solution at 30 °C using particle catalysts a = 1QF; b = 2QF; c = 3QF; d = 4QF; e = 5QF; f= 6QF; g=10QF; h = control experiment without particles.

Although all of the reactions followed first-order kinetics, the graphs in Figure 1 show interesting differences. Both the initial absorbance values and the final absorbance values of the experiments vary widely. The varied and non-zero initial absorbance values might be due to differences in the amounts of light scattered by the different particles or to different amounts of $PNPO^-$ present at the start of the experiment. Spectrophotometer baseline was set to 0.00 with a cuvette of water before each experiment. Since the presence of even as much as 10% of $PNPO^-$ in the initial PNPB would account for only 0.15 absorbance units (see next paragraph), most of the differences of initial absorbance must be due to light scattering by the particles. In conclusion, the large initial observed absorbances in Figure 1 are due mainly to turbidity.

If all of the PNPO^- was in the water after complete hydrolysis, and no PNPO^- was present at time = 0, the observed absorbance would increase by 1.50 units over the course of the reaction. ($\text{Abs} = \epsilon cl = (1.8 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1})(8.3 \times 10^{-5} \text{ mol L}^{-1})(1 \text{ cm}) = 1.50$). In no experiment in Figure 1 did the absorbance increase by as much as 1.5 units. Yet all experiments followed first-order kinetics. We attribute the low observed final absorbance values to equilibrium binding of a fraction of the PNPO^- to the quaternary ammonium ions in the particles. PNPO^- in the particles would not contribute to absorbance because light striking the particles is scattered whether or not the particles contain PNPO^- . Constant observed absorbance over the last 40 minutes in most of the experiments in Figure 1 indicates that the amount of light scattered over the course of each experiment was constant. In conclusion, the increases of absorbance of much less than the calculated value over the course of hydrolysis of PNPB are due to binding of PNPO^- to the ion exchange sites in the particles and to light scattering.

Aqueous dispersions of the ion exchange latexes were used to catalyze the hydrolysis of Paraoxon in 0.10 M sodium hydroxide solution at 30 °C by the same experimental method used for PNPB hydrolysis. The data in Figure 2 show at least 80% hydrolysis within 10 minutes using three different quaternized latexes. The kinetic results for all ten of the quaternized polymer dispersions are shown Table 3S. The half-lives of Paraoxon hydrolysis using all of the particles listed in Table 2 were in the range 2.5-6.0 min.

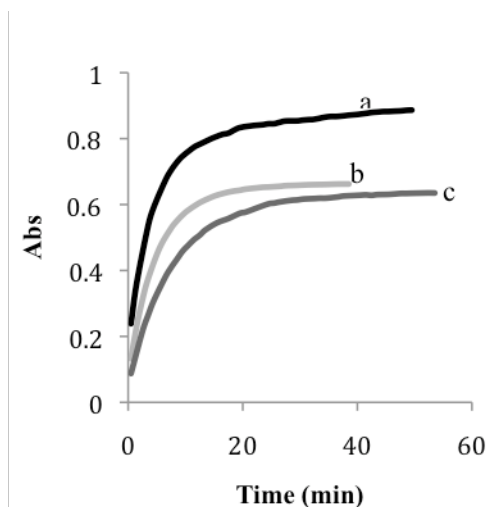


Figure 2. Change of absorbance at 400 nm due to PNPO^- from hydrolysis of Paraoxon in 0.10 M NaOH at 30 °C using particle catalysts: a = 11QF; b = 12QF; c = 13QF.

The rates of hydrolysis of both PNP H^- and Paraoxon do not depend in any systematic way on either the fluorine content or the N^+Cl^- content of the particles. The most catalytically active particles were 3QF, which contained 5% of the least highly fluorinated monomer trifluoroethyl methacrylate (TFEMA). But another sample, 13QF, which contained 25% of TFEMA, was less active than 3QF and also less active than the samples 11QF and 12QF, which contained 25% of fluorinated monomers PFHMA and PFOMA. Latexes of higher N^+ content (>1.00 mmol/g) were no more active than those of lower N^+ content (0.6-0.7 mmol/g). Particles of higher N^+ content generally were more swollen in water, but swelling did not correlate with catalytic activity. What is most remarkable about the ten latexes in Table 2, which differ in type and amount of fluoro monomer, amount of N^+ groups, particle size, and swelling ratio, is that their phase transfer catalytic activities differ so little.

Hydrolysis of Paraoxon in Latex Films. The films on glass cover slips reported in Table 1S were inserted into the solution of 0.1 M NaOH against the side wall of a cuvette out of the light path and with the film side of the cover slip toward the center of the cuvette. Graphs of absorbance at 400 nm vs. time after adding Paraoxon to the cuvette are shown in Figure 3. The kinetic data are in Table 4S.

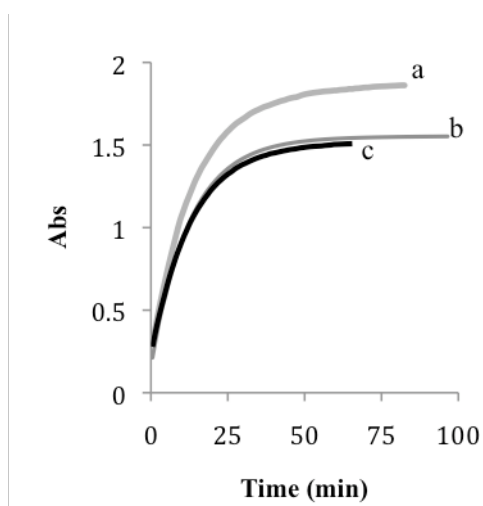


Figure 3. Change of absorbance at 400 nm due to PNPO^- from hydrolysis of Paraoxon in 0.10 M NaOH using spin coated films as catalysts (a = 5QF, b = 6QF, c = 10QF). The films were 0.71-0.76 μm thick and were annealed at 120 $^\circ\text{C}$.

There are several interesting features to the kinetics of hydrolysis of Paraoxon using the latex films as catalysts. First, with the drop cast films the half-lives of hydrolysis (Table 4S) are about twice as long (5.5-10 minutes) as the half-lives of hydrolysis by the same latex particles in dispersions (2.5-6 minutes, Table 3S) even though the amounts of N^+ sites available in the film experiments were slightly larger. The difference is likely due to slower transport of Paraoxon to

the N^+ sites in the 0.75-1.68 μm thick drop cast films than to the sites in the 113-280 nm-diameter dispersed particles. Since the reaction mixtures were magnetically stirred, the slow transport is likely due to slow diffusion of Paraoxon through the films and not to slow transport through the liquid. Second, the observed rates of Paraoxon hydrolysis were slower using the thinner (0.71-1.4 μm) spin-coated films (half-lives of 9-14 minutes) than using the thicker drop cast films (half-lives of 5.5-10 minutes). But when compared as second-order rate constants ($k_2 = k_1/[N^+]$), the spin-coated films actually are more active catalysts by a factor of about 1.3 per ion exchange site. (The median second-order rate constant in Table 4S using six different spin-coated films was $3.1 \times 10^2 \text{ L mol}^{-1} \text{ min}^{-1}$ vs. $2.3 \times 10^2 \text{ L mol}^{-1} \text{ min}^{-1}$ using drop-cast films of the same latexes). Faster hydrolysis using the thinner films further supports the conclusion that the rates of Paraoxon hydrolysis using the films are slightly slower than using the particles because of time required for diffusion of Paraoxon through the films to the ion exchange sites. Third, the drop-cast films and the spin-coated films have different surface textures and were annealed at different temperatures, but those factors do not appear to cause any major differences in the rates of Paraoxon hydrolysis.

Hydrolyses of PNPB in the same borate buffer solution used for particle-catalyzed hydrolyses were carried out with the same types of films used for hydrolysis of Paraoxon, but the rates were much slower.

Surfaces of the Films. The purpose of using a fluoroalkyl methacrylate component in the latexes is to make the film surface both hydrophobic and lipophobic to protect the underlying substrate from toxic organic chemicals (TOCs). The purpose of the quaternary ammonium sites is decomposition of the TOC. If the TOC does penetrate the surface, it would then be decontaminated by hydroxide ions or another reactive counterion of the polymer. The kinetic

experiments demonstrate success in making films that act as phase transfer catalysts beneath the surface. Next we report the characterization of the film surfaces by contact angle measurements and atomic force microscopy (AFM).

Atomic Force Microscopy. Drop-cast films from copolymer dispersions 5F, 6F and 10F (before conversion of VBC units to quaternary ammonium ions, Table 1) by AFM before annealing showed layers of particles about the same size as those measured in dispersions by dynamic light scattering. Since the T_g of the copolymer 6F is 38 °C, and the other copolymers probably have similar T_g values, the particles were not expected to form smooth films at room temperature. Annealing of the drop-cast film of copolymer 6F at 60 °C for 18 hours made its bumpy surface appear smoother in an AFM image.

The surfaces of the spin-coated films of quaternary ammonium ion particles annealed at 120 °C and 165 °C still showed the presence of particles and rough surfaces. Figure 4 shows examples of the AFM images. The latex particles did not coalesce to a continuous film even at 165 °C, which was more than 60 degrees above the T_g .

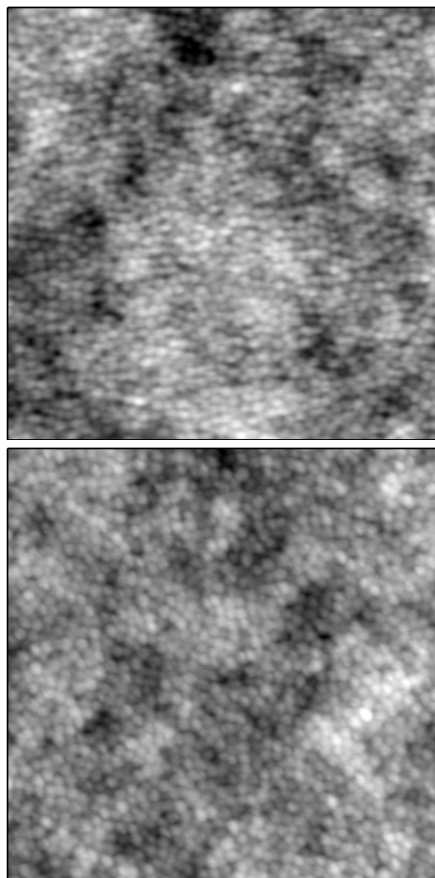


Figure 4. 5x5 μm AFM images of (top) 5QF-S120 and (bottom) 5QF-S165.

Contact Angles. The contact angle of a drop of liquid on a solid surface depends on the liquid-solid, air-liquid, and air-solid interfacial free energies.³⁰ The lower the surface energy of the solid, the higher is the contact angle of water on the solid. Dynamic contact angle measurements indicate qualitatively the homogeneity of the chemical coating and the topology of the films.³¹ Dynamic contact angles of water on drop cast films of the both the copolymers and the quaternized polymers, even after annealing at 90 °C, were difficult to measure because of pinning of the contact line of the water drop at the surface of the film. (Pinning means that the

contact line did not move when the volume of the drop was increased or decreased). We attribute the pinning of water drops to the roughness of the surface.

To obtain smoother films, the quaternized polymers were spin-coated and annealed at 120 °C. Even so dynamic contact angle measurement were difficult to obtain due to pinning of the contact line; the advancing contact angles of water were in the range of 94°-105°, and the receding contact angles of water were in the range of 64°-82°. The data are reported in Table 3. The films were annealed at a still higher temperature, 165 °C, in an attempt to bring more of the fluoroalkyl groups to the surface and to increase the contact angle against water, but no increase of advancing contact angle was observed.

Films of samples 5QF and 6QF, which contained 10% of the fluoromonomer, annealed at 75-90 °C and at 120 °C had contact angles of less than 15° against hexadecane, which spread rapidly over the surface and over time soaked into the polymer. Films of sample 12QF, which contained 25% of the fluoromonomer, had contact angles against hexadecane of 25.5° after annealing at 120 °C and 23° after annealing at 165 °C respectively. Samples 11QF, 12QF, and 13QF, which contained 25% of the three different fluoromonomers and were annealed at 165 °C had contact angles against hexadecane that increased with the fluorine content of the fluoromonomer. The data, which are reported in Table 3, correspond to increasingly oleophobic surfaces with increasing fluorine content of the polymers.

Table 3. Contact Angles on the Quaternized Polymer Films

polymer film	thickness ^a (μm)	θ_A ^b ($^\circ$)	θ_R ^c ($^\circ$)	θ_{Hex} ^d ($^\circ$)
5QF-S120	0.71	94	71	4
6QF-S120	0.76	102	82	5
10QF-S120	0.76	96	^e	8
11QF-S120	1.41	102	65	35
12QF-S120	0.95	101	72	23
13QF-S120	1.21	105	73	14

^aMeasured after annealing at 120 $^\circ\text{C}$. ^bAdvancing contact angle ($\pm 2^\circ$) against water. ^cReceding contact angle ($\pm 2^\circ$) against water. ^dStatic contact angle ($\pm 2^\circ$) against hexadecane of films annealed at 165 $^\circ\text{C}$. ^ePinning prevented measurement.

Discussion

The particles and films of this investigation were designed by two stage emulsion polymerization to have most of the quaternary ammonium sites beneath the surface. A typical 200-nm-diameter particle had about 20% of quaternary ammonium ion repeat units, of which only a small fraction could possibly reside on the surface. More than 90% of the quaternary ammonium ion sites in the particles arise from reaction of trimethylamine with the hydrophobic VBC units, and less than 10% come from the ionic monomer VBTMACl. The particles were synthesized using no low molar mass surfactant, because cationic surfactant micelles have catalytic activity similar to that of the cationic particles, and consequently could blur the

distinction between micellar and latex catalysis. The intrinsic catalytic activity of the ion exchange sites in the water-swollen polymers is not high. In a previous kinetic analysis, using particles that were cross-linked with 1% divinylbenzene and contained no fluoruous monomer but were otherwise the same, the rate of PNPB hydrolysis in the 0.117 mg mL⁻¹ of latex particles was 14.4 times the rate of hydrolysis in the borate buffer because of an intraparticle PNPB concentration 4690 times that in water, an intraparticle hydroxide ion concentration 8.5 times higher, and an intraparticle second-order rate constant 1.62 times higher.⁶ The high PNPB concentration in the small volume fraction of particles was the biggest contributor to the enhanced rate of hydrolysis.

The shot-growth emulsion polymerization method with the fluoroalkyl methacrylate added only in the second stage was designed to localize the fluoruous monomer units in the shell of the core-shell latex near the surface and to minimize the amount of fluoruous monomer needed to attain films with surfaces that were both hydrophobic and oleophobic. This synthetic method for EHMA-VBC copolymer particles with a cross-linking monomer and without a fluoruous monomer yields monodisperse polymer spheres of high colloidal stability.^{4,6} Of course, during emulsion polymerization the particle surface consists of mainly ionic sites, which stabilize the colloidal dispersion in water. Thus from the amounts of fluoruous monomer and VBC used in the two stages of the shot-growth polymerization, our model for the structure of a quaternary ammonium ion latex particle is (a) a surface of ionic VBTMACl units, (b) an outer shell comprised of 25 wt % of the particle that is rich in the fluoruous monomer but also contains EHMA and quaternary ammonium ion units, and (c) a core that is almost all EHMA and quaternary ammonium ion units. We were concerned that the larger (up to 25 wt %) amounts of fluoroalkyl methacrylates might lead to colloidal instability or to a barrier to diffusion of organic

reactants and ions through the outer shell of the particles that would reduce the phase transfer catalytic activity of the internal quaternary ammonium ions. Note that the VBC and VBTMACl contents of the latexes were constant, and the sum of the EHMA and fluoroalkyl methacrylate contents was constant. Only the relative amounts of EHMA and fluoroalkyl methacrylate were varied in the syntheses of particles.

The kinetics of PNPB hydrolysis and Paraoxon hydrolysis depend both on intrinsic activity at the N^+ sites and on transport of both the *p*-nitrophenyl ester and of hydroxide ion through the shell of the particle. The kinetic results indicate that diffusion through a fluorinated layer does not limit catalytic activity, for there was no correlation between the rates of PNPB and Paraoxon hydrolysis and the fluorine content of the polymer, either in the form of colloidal particles or in the form of a thin film.

To form a coherent thin film from a latex dispersion, the particles must deform and fill the interstitial spaces as the water evaporates.³² This requires that the temperature at which the film is cured be substantially higher than the T_g of the polymer. Although homopolymers of EHMA and of the fluoroalkyl methacrylates have low T_g , the large number of ionic repeat units in the quaternary ammonium ion latex particles raises T_g to around 100 °C (Table 2). Consequently the films as prepared at room temperature had the surface textures of particles as shown by AFM images. Even after annealing at 120 °C and 165 °C, the surfaces retain their particle history, as seen in Figure 4. Our intent was to create films with a highly fluorinated surface in order to repel both water and organic liquids. The lowest surface energy morphology of a dry polymer film would have a fluoroalkyl surface, and all ions would be located beneath the surface to avoid contact with air. The contact angles of the films against water and against hexadecane show the annealed surfaces of all films to be hydrophobic, but only the films

prepared with 25% of a fluoroalkyl monomer behaved at all oleophobic. Advancing contact angles against water as high as 115-120° have been reported for perfluoroalkyl acrylate copolymers, in some cases even with only minor amounts of the fluoruous monomer.^{33,34} Perfluoroalkyl surfactants and polymers have the lowest critical surface tensions of any known smooth surfaces.^{35,36} (Roughness is required for an ultrahydrophobic surface.)^{37,38} The advancing contact angles of our spin-coated films were 94-105° against water, which is consistent with a hydrocarbon or a mixed hydrocarbon-fluorocarbon surface, not a purely fluorocarbon surface. Likewise contact angles of <10° against hexadecane indicate a hydrocarbon-like surface of all films prepared with 10% of a fluoromonomer. The larger contact angles against hexadecane of films with 25% of a fluoromonomer indicate that only those films had sizeable fluoroalkyl content on the surface. The resistance to rearrangement of the surface morphology by annealing probably is due not only to the high ion content of the polymers but also to the random-copolymer structures. Block or graft copolymers of fluoroalkyl methacrylates would likely develop fluoruous surfaces at lower annealing temperatures.

In conclusion, the semifluorinated quaternary ammonium ion latexes have the same high phase transfer catalytic activity as the non-fluorinated analogs for basic hydrolysis of PNPB and Paraoxon in particle dispersions, and the films are almost as catalytically active as the particles for hydrolysis of Paraoxon. A small dependence of hydrolysis rates on film thickness indicates that diffusion through the >0.7 μm thick films slightly limits the rates. The AFM images show that the particle texture of the film surface is retained even after annealing at 165 °C. Contact angles of the annealed films against water and hexadecane show that the perfluoroalkyl repeat units have very limited mobility, which is attributed to the random copolymer structure and to the strong electrostatic attractions of the ionic repeat units to one another. To attain more highly

fluorinated surfaces of copolymer latex films and still use only minor fractions of the fluororous monomers, lesser ion content, particularly in the shell of the core-shell emulsion polymer particles, will likely be necessary.

Experimental Section

Materials. Vinylbenzyl chloride (VBC, 96%, *m/p* isomeric mixture, Scientific Polymer Products, Inc.), 2-ethylhexyl methacrylate (EHMA, 98%, Aldrich), 1H,1H,2H,2H-perfluorooctyl methacrylate (PFOMA, Top Fluorochem), 1H,1H,2H,2H-perfluorohexyl methacrylate (PFHMA, Top Fluorochem, Shanghai, China), trifluoroethyl methacrylate (TFEMA, Aldrich) were purified before use by passing through basic aluminium oxide. Vinylbenzyl(trimethylammonium) chloride (VBTMACl, Aldrich), 2,2'-azobis(2-methylpropionamide) dihydrochloride (Aldrich), trimethylamine 25% (w/w) solution in water (Aldrich), diethyl *p*-nitrophenyl phosphate (Paraoxon, Aldrich), *p*-nitrophenyl hexanoate (TCI Chemicals), aluminum oxide (Al₂O₃, activated, basic, ~ 150 mesh, 58 Å, Aldrich) and acetonitrile (Aldrich) were used as received. Triply deionized water was used in all experiments.

Instrumentation. DSC analyses were performed with a TA Instruments DSC Q2000 over a temperature range of -100 °C to 150 °C with the ramp of 5 °C per minute. T_g data are from the second heating cycle. Morphologies of the 120-165 °C annealed latex particles were studied by atomic force microscopy using an Asylum Research Molecular Force Probe 3D. Some AFM images of copolymers and films annealed at 75-90 °C were obtained with a Veeco Multimode III instrument. The samples for AFM images were prepared by spreading 45 μL of the dispersion on a 1 cm² glass cover slip that was cleaned with deionized water and acetone.

The film was annealed at the indicated temperature for 18 h. Particle sizes and size distributions in aqueous dispersions at 25 °C were measured by dynamic light scattering using a Malvern HPSS 3.1 instrument equipped with a 3.0 mW, 633 nm He-Ne laser. One drop of aqueous dispersion of copolymer was diluted with 3 mL of water for DLS measurement. Dynamic contact angles were measured using a long-range microscope computer analysis package from First Ten Angstroms (FTA 100Series). The expansion and retraction of sessile drops of water from a negligible volume to a maximum volume of 15 μL during the dynamic contact angle measurements were performed using a Kent Scientific Genie Plus syringe pump. The advancing contact angle of the films annealed at 120°C represents an average of all advancing angles between 3-10 μL , with the exception of sample 6QF-S120, where 9.2 μL was the maximum volume obtained in the experiment. Likewise for the average of the receding contact angle, volumes between 2-6 μL were used with the exceptions being samples 11QF-S120 and 13QF-S120, where only 2-4 μL were available for measurement.

Synthesis of Aqueous Polymer Colloid 1F. A 50 mL three-necked round bottom flask fitted with an addition funnel, a mechanical stirrer with a Teflon blade, and a reflux condenser was purged with nitrogen for 10 min. Deionized water (20 mL) was charged to the flask, and the head space was flushed with nitrogen for 30 min at 60 °C under continuous stirring. Solid VBTMACl (10. mg) was added, and the solution was stirred for 5 min. Nitrogen-purged EHMA (0.740 g) and VBC (0.250 g) were added and stirred for 10 min. Initiator (10. mg) dissolved in 1.0 mL of water was added, and the mixture was heated to 60 °C. The mixture turned cloudy due to nucleation of the particles within 35-40 min. After 1.0 h a mixture of EHMA (0.215 g), VBC (0.073 g), VBTMACl (9.0 mg), and TFEMA (33 mg) followed by initiator (3.0 mg) were added. The reaction mixture was stirred for 4 h at 60 °C, cooled, and filtered through a cotton plug to

remove traces of coagulum to give stable dispersion 1F. The same procedure was repeated using different amounts of PFHMA, PFOMA, and TFEMA and of VBC to give the stable polymer colloids in Table 1.

Quaternization of Copolymer 1F. A mixture of 10 mL of 1F (0.550 g of solid, 0.90 mmol of VBC groups) diluted with 7 mL of deionized water and 0.160 g of 25 wt% aqueous trimethylamine (2.7 mmol) was transferred to a 50 mL round bottom flask. The reaction mixture was stirred magnetically at 60 °C. More trimethylamine (0.160 g) was added two times per day. After 48 h the excess trimethylamine was removed by bubbling nitrogen through the latex for 2 h to give stable cationic dispersion of BK-1QF. The same procedure was applied using the other copolymers in Table 1 to give the cationic polymer colloids in Table 2. Quaternary ammonium chloride contents of the latexes were measured by potentiometric titration with an Orion 9617 chloride-selective electrode.⁷

Solid Content of Latexes. The solid content of all colloidal dispersions was measured by weighing 1.0 mL of the latex accurately and drying to constant weight at 110 °C. Determinations performed in triplicate were reproducible within 3% of the mean.

Preparation of Films. (a) Drop cast films. To a rectangular glass cover slip having an area of 3.2 cm², 25 μL of 1QF (0.85 mg of particles, [N⁺] = 2.4 x 10⁻⁴ M in the whole mixture) dispersion was applied at room temperature. The polymer was spread using a syringe plunger and then dried in air. The film was annealed at 75 °C for 18 h. The thickness of the final film was calculated from the weight of particles, the surface area, and an assumed polymer density of 1.0 g cm⁻³. Data for amounts of particles and thicknesses of films are in Table 1S. **(b) Spin-coated films.** The glass cover slips were treated with a mixture of potassium hydroxide and isopropyl alcohol for 1.0 h and were washed with water and dried. Polymer dispersions (90 μL) were

applied and spun at 1200 rpm. The films were dried in air, and the spin-coating process was repeated several times. The film thickness was calculated from the increase in weight and the surface area of the glass. Amounts of particles and thicknesses of films are reported in Table 1S.

Kinetic Measurements. Stock solutions of 2.5 mM *p*-nitrophenyl hexanoate and 2.5 mM Paraoxon in acetonitrile were prepared on the day of use. The 0.10 M NaOH solution was prepared in nitrogen-purged water and stored in an air-tight container. Borate buffer solution (pH 9.40, 0.020 M) was prepared from aqueous boric acid solution by titration with sodium hydroxide.

Hydrolysis of PNP. (a) Colloidal Particles. Colloidal particles as a dispersion of 1QF (0.60 mg in 25 μ L) and 2.2 mL of helium-purged borate buffer solution were added to a polystyrene cuvette. The solution was equilibrated at 30 ± 1 °C for 20 min with magnetic stirring in the thermostated cell compartment of a Varian Cary 5000 spectrophotometer. Then 74 μ L of the PNP stock solution in acetonitrile was added by syringe to make the reaction mixture concentrations $[\text{PNP}] = 8.3 \times 10^{-5}$ M and $[\text{N}^+] = 1.7 \times 10^{-4}$ M. The absorbance of the solution at 400 nm was recorded every 0.9 s with continued stirring. Hydrolyses using the other colloidal particles listed in Table 2 were carried out by the same procedure. The amounts and concentrations of quaternary ammonium ion exchange catalysts are shown in Table 2S.

Hydrolysis of Paraoxon. The procedures were identical to those used for hydrolysis of PNP except for 0.10 M NaOH in place of the borate buffer. The data for particle catalysis are in Table 3S, and data for catalysis by films are in Table 4S.

Kinetics calculations. First-order observed rate constants k_{obs} were calculated using the equation

$$k_{\text{obs}}t = \ln[(A_{\infty}-A_0)/(A_{\infty}-A_t)]$$

where t = time, A_0 = measured absorbance at $t = 0$, A_∞ = measured absorbance after at least 98% conversion, A_t = measured absorbance at time t . The slope k_{obs} was calculated by the linear least squares method from the data over the first 60% conversion.

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TOC graphic

