A Survey of Alkyl Methacrylate Latexes as Aqueous Catalytic Media

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Cationic polymer latexes serve as catalytic media for the hydrolysis of *p*-nitrophenyl esters by providing a more lipophilic environment into which these compounds can partition from the aqueous phase. The latex quaternary ammonium ions attract high local concentrations of reactive or catalytic anions into the water-swollen particles. We synthesized 32 different methacrylate and styrene latexes via a parallel synthetic route and tested their activities for the hydrolysis of *p*-nitrophenyl hexanoate. The most active latex is a copolymer of 75% 2-ethylhexyl methacrylate and 25% vinylbenzyl chloride that was quaternized with tributylamine. The rate of hydrolysis at 30 °C is 17 times faster using 0.6 mg mL^{-1} of latex in pH 9.4 borate buffer relative to control experiments that lacked polymer latex. Analysis of the kinetics shows that the latex activities depend primarily on the latex/water partition coefficients of *p*-nitrophenyl hexanoate. The latexes also promote the decarboxylation of 6-nitrobenzisoxazole-3-carboxylate (6-NBIC) in aqueous media, and 0.6 mg mL^{-1} of the latex from 75% 2-ethylhexyl methacrylate and 25% vinylbenzyl chloride quaternized with tributylamine gave an observed rate constant 10 400 times that in water alone. The rate accelerations of 6-NBIC decarboxylation are due to both favorable partitioning into the latex and faster intraparticle rate constants.

Introduction

Cationic polymers and colloids, such as polyelectrolytes,[1–4] anion-exchange resins,[5–7] surfactant micelles,[1,2,8–10] and latexes,[11–13] catalyze reactions of anions with uncharged organic compounds in aqueous media. The catalytic activities are due primarily to high local concentrations of the anionic and uncharged reactants in the small volume fraction of the polymer or colloid phase, or pseudophase, in the aqueous mixture, although enhanced intrinsic rate constants sometimes contribute.

Polystyrene latexes containing quaternary ammonium ion exchange sites increase the rate of decarboxylation of 6-nitrobenzisoxazole-3-carboxylate up to 10 000 times and the rate of *o*-iodosobenzoate (IBA)-catalyzed hydrolysis of *p*-nitrophenyl diphenyl phosphate (PNPDPP) up to 6300 times faster than in aqueous solutions with no latex.[12,13] The rate enhancements are as high or higher than those in cationic micelles,[9] and the activity persists at very low particle concentrations, whereas surfactants have high catalytic activity only above the critical micelle concentration. In addition, the small 200 nm diameters of the latexes ensure that reaction rates are not limited by intraparticle diffusion, which often slows rates of reactions using ion-exchange resins and polymer-supported phase transfer catalysts.[5,14]

One potentially important use of colloidal catalysts is hydrolysis of toxic organophosphates, phosphonates, and fluorophosphonates, which are widely used as insecticides and are stockpiled as chemical warfare agents.[15] Attempts to catalyze the hydrolysis of diisopropyl fluorophosphate (DFP) in a polystyrene-based anion exchange latex at pH 11 gave no rate enhancement.[16] One possible reason for lack of activity toward DFP is an unfavorable partition coefficient of the aliphatic DFP into the highly aromatic polystyrene latex particles. Aliphatic latex particles should absorb higher concentrations of aliphatic compounds and be more active than the polystyrene particles for reactions of aliphatic compounds. For this reason we synthesized a family of cationic latexes from copolymers of alkyl methacrylates and tested their activities for basic hydrolysis of *p*-nitrophenyl (PNP) esters and for decarboxylation of 6-nitrobenzisoxazole-3-carboxylate.

We chose PNP esters as probes for a number of reasons. First, they are available in a wide range of carbon chain lengths which differ significantly in hydrophobicity. Second, it is easy to follow the appearance of *p*-nitrophenoxide ion by UV–visible spectrophotometry. And finally, extensive literature on the behavior of PNP esters allows for a more thorough understanding of the processes occurring in our systems. They have been used as model substrates for enzyme mimics for many years,[2,17] although their value is dubious because in many cases hydrolyses of esters having more basic leaving groups are not catalyzed.[18] The mechanism of alkaline hydrolysis of PNP

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acetate in aqueous solution is concerted according to an extension of Marcus theory,[19] linear free energy relationships,[20] isotope effects,[21] and ab initio calculations.[22]

Hydrolyses of PNP alkanoates were among the first reactions discovered to be catalyzed by alkyltrimethylammonium ion micelles,[23,24] and Menger and Portnoy introduced an enzyme-like model for the kinetics.[24] Ion exchange models were developed to analyze the kinetics in greater detail.[8,25] We have applied a modified version of the pseudophase ion exchange model of micellar catalysis to the kinetics of hydrolysis of PNP esters in selected polymer latexes.[26]

To study a variety of polymer latexes as catalytic media, we devised a diversity strategy for latex synthesis.[27] Diversity strategies are employed at all major pharmaceutical companies for the synthesis of biologically active compounds, and have been used in search of superconducting, magnetic, and phosphorescent materials.[28] They also have been used to synthesize potential catalysts, including polymer catalysts, for the production and testing of a large number of catalyst candidates in a short time.[29] Since latex particles <0.5 μm in diameter are too small to be separated, we synthesized a series of alkyl methacrylate-based latex catalysts simultaneously in separate containers by a parallel approach.

Experimental Section

Materials. Vinylbenzyl chloride, butyl methacrylate, and 2-chloroethyl methacrylate (all from Scientific Polymer Products) and divinylbenzene (55−60% active), isobutyl methacrylate, tetrahydrofurfuryl methacrylate, 2-ethylhexyl methacrylate, butoxyethoxyethyl methacrylate, and ethoxyethoxyethyl methacrylate (all from Aldrich) were distilled and filtered through a plug of alumina prior to use. A solubility test (dripping into hexane and examining for insoluble solid polymer) shortly before use indicated that no polymer was present. (*m,p*-Vinylbenzyl)-trimethylammonium chloride was used as a 0.0482 M aqueous solution (as determined with a chloride selective electrode).[30] 2,2′-Azobis(*N,N*-dimethyleneisobutyramidine) dihydrochloride (VA044, Wako) was used as received after ^{1}H and ^{13}C NMR indicated no contamination. Trimethylamine (Eastman, 25 wt % in methanol) and tributylamine (Eastman) were used as

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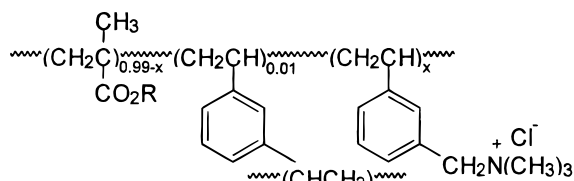
received. Triply deionized water having resistivity >1 × 10^6 Ω cm was used in all experiments. *p*-Nitrophenyl acetate (Pfaltz & Bauer) and all other *p*-nitrophenyl esters (Sigma) were used as 2.5 mM solutions in acetonitrile (Aldrich). 6-Nitrobenzisoxazole-3-carboxylic acid was prepared as before.[13]

Parallel Polymerizations. The polymerizations were carried out in sets of 12 and 7 test tubes, each containing a different monomer mixture. The test tubes were placed in a water bath at 60 °C, through holes in a sheet of polystyrene foam, which both immobilized the tubes and insulated the water bath. The polymerization mixtures were stirred using a six-plate magnetic stirrer (Lab-Line Instruments, Inc., model 1278) and a 7 mm stirbar in each tube. To each tube was added 3.5 mL of nitrogen-purged water. After 10 min at 60 °C, 1.0 mL of the (*m,p*-vinylbenzyl)trimethylammonium chloride solution (5 mg of monomer) was added. The mixture was stirred for 5 min, and 5 μL of divinylbenzene, 175 μL of vinylbenzyl chloride, and either 320 μL of a single monomer or 160 μL each of two monomers were added. The monomer mixture was stirred for 5 min, and 5 mg of VA044 in 0.5 mL of water was added. The tubes were covered with Durafilm to prevent evaporation of monomer and kept for 3.0 h at 60 °C. The latexes were filtered through a plug of cotton in a Pasteur pipet to remove any coagulum, which was always <30 mg (<8% of total polymer weight).

Quaternization of Latexes. A 4 mL aliquot of the latex was placed in a 10 mL screw cap vial, 2 mL of ethanol and 2 mL of 25 wt % trimethylamine were added and the vial was capped tightly. Three such vials at a time were placed in a stainless steel pressure reactor. A mixture of 12 mL of water, 6 mL of ethanol, and 6 mL of aqueous trimethylamine was poured into the reactor outside the vials to balance the pressure. The reactor was sealed and kept in a 60 °C oil bath for 48 h.

Purification of Latexes. About 2 mL of each latex sample was dialyzed for 2 days in 50 000 MW cutoff tubing against deionized water. After dialysis the latex was drawn into a 5 mL syringe, the syringe was fitted with a 0.1 μm Millipore filter, and the volume was reduced to about 0.75 mL. The volume was brought back up to about 3 mL by adding water and was reduced to less than 1 mL repeatedly until the filtrate had a pH less than 7. Usually about 15−20 mL of water was needed. The typical solids content was 5−7 mg/mL, determined by drying 1.00 mL samples to constant weight in a 130 °C oven. The percent conversion of vinylbenzyl chloride groups to quaternary ammonium groups was determined by potentiometric titration with a chloride selective electrode.[12]

Kinetics. The latex samples were diluted to a solid content of 1.20 mg/mL. A 2.00 mL aliquot of each latex was diluted to 40 mL with 0.02 M borate buffer (pH 9.38) to give about 6.2 × 10^{-5} M of N$^+$ units. A 3.00 mL sample of the latex/buffer solution was placed into a polystyrene cuvette. The solution was equilibrated at 30 °C for 20 min, 5 μL of 2.5 mM PNP−hexanoate in acetonitrile was added, and a UV−vis spectrum was taken every 0.9 s. The average absorbance from 400 to 410 nm was plotted as a function of time, and k_{obs} was calculated from data over the first 20% conversion using $\ln[(A_{inf} - A_o)/(A_{inf} - A_t)] = k_{obs}t$]. A_{inf} was chosen by the experimenter. Correlation coefficients were ≥0.994.

The procedure for measuring rate constants of decarboxylation of 6-NBIC was reported before.[13]

Results and Discussion

Latexes. Thirty latex copolymers were prepared from monomer mixtures containing by weight 25% of vinylbenzyl chloride (70:30 *m:p*), 73% of various aliphatic methacrylates, and 1% of divinylbenzene (0.55−0.60% of active DVB) as a cross-linking agent. In lieu of a surfactant, 1% of (*m,p*-vinylbenzyl)trimethylammonium chloride was used as a comonomer to stabilize the particles during growth. The latexes differed in the number and combination of aliphatic monomers present. Reaction of the vinylbenzyl chloride units with either trimethylamine (TMA) or tributylamine (TBA) produced anion exchange latexes having the structure in Figure 1. The latex particles were 124−150 nm in diameter and contained 21−25 wt

Figure 1. Structure of latex copolymers.

Table 1. Compositions of Quaternary Ammonium Ion Functionalized Latexes

| composition	quaternization yield (%)	N$^+$/g[a]	N$^+$/mL[b]	N$^+$ (mol %)[c]
2EHMA−TMA	80.0	1.22	0.419	24.2
2EHMA−TBA	78.8	1.04	0.369	23.8
BMA−TMA	82.2	1.25	0.509	19.5
BMA−TBA	77.4	1.03	0.453	18.4
S−TMA	77.1	1.17	0.677	14.3
S−TBA	78.2	1.03	0.540	14.5

[a] mmol of N$^+$ per gram of dry latex. [b] mmol of N$^+$ per mL of swollen latex in 0.02 M pH 9.4 borate buffer. [c] Mole percent of N$^+$ repeat units.

Table 2. Sizes of Quaternary Ammonium Ion Functionalized Latexes in Borate Buffer Solutions

composition	d_n[a] (nm)	d_w[b] (nm)	d_h (nm)[c] 0.002	0.01	0.02	swelling ratio[d] 0.002	0.01	0.02
2EHMA−TMA	135.1	135.6	211	203	198	3.8	3.4	3.2
2EHMA−TBA	146.9	149.2	222	217	214	3.5	3.2	3.1
BMA−TMA	138.2	140.7	202	195	192	3.1	2.8	2.7
BMA−TBA	143.3	144.4	205	199	194	2.9	2.7	2.5
S−TMA	128.7	129.5	171	164	160	2.4	2.1	1.9
S−TBA	124.0	124.8	168	162	169	2.5	2.2	2.1

[a] Calculated using measurements of 50 particles from TEM negatives. Number average diameter, $d_n = (\sum N_i d_i^3 / \sum N_i)^{1/3}$. [b] Weight average diameter, $d_w = (\sum N_i d_i^6 / \sum N_i d_i^3)^{1/3}$. [c] Hydrodynamic diameter from dynamic light scattering in various buffer strength solutions at pH 9.4. [d] $(d_h/d_w)^3$ in buffer solutions of various strengths.

Scheme 1
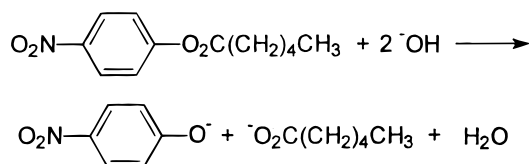
% (14−24 mol %) of quaternary ammonium units. Properties of some representative latexes are presented in Tables 1 and 2.

Influence of Latex Structure on Rates of PNP Alkanoate Hydrolysis. To test catalytic activities of the particles, we measured the rates of basic hydrolysis of *p*-nitrophenyl (PNP) hexanoate (shown in Scheme 1) in pH 9.4 borate buffer solutions with the quaternary ammonium sites in a greater than 10-fold excess over substrate. PNP hexanoate is hydrophobic but still completely soluble at the concentration needed for kinetic measurements. All experiments had half-lives in the range of 130−930 s. The ratios of rate constants in latex dispersions to rate constants in buffer alone are in Tables 3 and 4.

Table 3 shows that the 2-ethylhexyl methacrylate latex (**8**) has the highest catalytic activity of all of the TMA quaternized latexes. All of the methacrylate latexes have higher activity than the styrene-based TMA latex (**29**). Latexes **15**−**28** contain combinations of monomers, and those containing 2-ethylhexyl methacrylate (latexes **16**, **19**, and **23**) are the most active.

Table 3. Relative Rate Constants of Hydrolysis of PNP−Hexanoate in Latexes Quaternized with Trimethylamine

latex	methacrylate[a]	k_{obs}/k_w
1	*n*-butyl	6.1
2	*n*-hexyl	6.5
3	*n*-octyl	9.5
4	*n*-decyl	10.2
5	*n*-dodecyl	10.7
6	isobutyl	6.5
7	2-ethylbutyl	6.1
8	2-ethylhexyl	12.5
9	2-chloroethyl	5.6
10	butoxyethoxyethyl	5.8
11	ethoxyethoxyethyl	5.5
12	tetrahydrofurfuryl	7.1
13	tetrahydropyranyl	5.6
14	furfuryl	5.8
15	*n*-hexyl/2-ethylbutyl	6.5
16	*n*-octyl/2-ethylhexyl	10.7
17	butyl/butoxyethoxyethyl]	6.5
18	isobutyl/ethoxyethoxyethyl	6.2
19	2-ethylhexyl/butoxyethoxyethyl	10.5
20	2-chloroethyl/ethoxyethoxyethyl	5.6
21	2-chloroethyl/butyl	6.2
22	2-chloroethyl/tetrahydrofurfuryl	6.5
23	2-chloroethyl/2-ethylhexyl	9.9
24	tetrahydrofurfuryl/ethoxyethoxyethyl	6.6
25	tetrahydrofurfuryl/butyl	6.4
26	tetraydrofurfuryl/butoxyethoxyethyl	7.0
27	tetrahydrofurfuryl/isobutyl	7.1
28	tetrahydrofurfuryl/2-ethylhexyl	11.2
29	styrene	2.3

[a] 0.6 mg/mL of latex with [N$^+$] = 62 μM and 4.2 μM PNP hexanoate in 0.02 M borate buffer at pH 9.4 and 30.0 °C. Data are averages of two to three experiments that deviated over a range of ≤5% of the reported k_{obs}. $k_w = 3.26 \times 10^{-4}$ s^{-1}.

Table 4. Relative Rate Constants of Hydrolysis of PNP Hexanoate in Latexes Quaternized with Tributylamine

latex	composition[a]	k_{obs}/k_w[b]
30	2-ethylhexyl methacrylate	16.5
31	*n*-butyl methacrylate	15.7
32	styrene	12.0

[a] See footnotes of Table 1. [b] See footnotes of Table 3.

Longer-chained and branched aliphatic methacrylate latexes (**2**−**8**) were also investigated. Activity increased with alkyl methacrylate chain length from *n*-hexyl to *n*-dodecyl methacrylate, and the magnitude of the change decreased with each two additional carbon atoms. The 2-ethylhexyl methacrylate latex (**8**) is more active than the *n*-octyl methacrylate (**3**), and the *n*-octyl/2-ethylhexyl methacrylate (**16**) has intermediate activity.

Table 4 indicates that particles containing tributylammonium ions are more active than those containing trimethylammonium ions. The difference between the activity of TBA and TMA latexes is much more pronounced for polystyrene than for polymethacrylates.
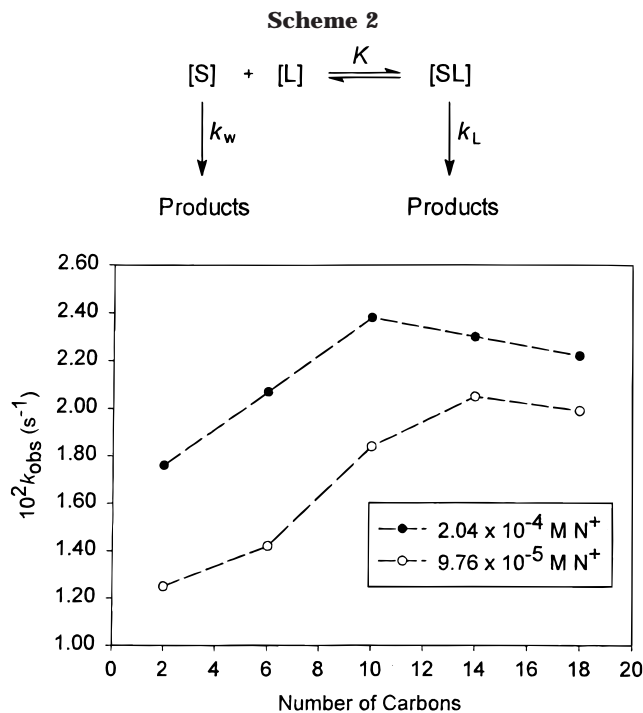
To determine what factors are responsible for the differences in activities between latexes, we analyzed details of the kinetics of hydrolysis of *p*-nitrophenyl acetate, hexanoate, and octanoate using the styrene, butyl methacrylate, and 2-ethylhexyl methacrylate latexes quaternized by TMA and TBA. The data were analyzed by eqs 1 and 2, which come from Scheme 2, where

$$k_{obs}[S]_t = k_w[S]_w + k_L[S]_L \qquad (1)$$

$$k_{obs} = (k_w/K + k_L[N^+])/(1/K + [N^+]) \qquad (2)$$

k_{obs} is the observed rate constant, k_w is the rate constant

Scheme 2

$$[S] \quad + \quad [L] \quad \overset{K}{\rightleftharpoons} \quad [SL]$$

$$\downarrow k_w \qquad\qquad\qquad \downarrow k_L$$

Products　　　　　　　　Products

Figure 2. Dependence of observed rate constant of hydrolysis of *p*-nitrophenyl esters at 30 °C on the alkanoate chain length. The catalyst was a poly(2-ethylhexyl methacrylate) quaternized with tributylamine in pH 9.4 borate buffer.

in the absence of particles, k_L is the intraparticle pseudo-first-order rate constant, and K is a distribution constant of substrate between the aqueous phase and the particle phase. (K is the binding constant of the Menger–Portnoy model).[24] Nonlinear regression analysis of rate constants at varied particle concentrations gave values of k_L and K.[31] The details of the data analysis are reported elsewhere.[26]

The intraparticle rate constants for hydrolysis of the three PNP esters are very similar for each of the six latexes. The major differences in the latex activities are due to the distribution constants: the longer the aliphatic chain of the PNP ester, the greater its affinity for the latex, and the longer the aliphatic chain of the methacrylate latex, the higher the value of K. Thus a more aliphatic latex extracts a larger fraction of substrate from the aqueous phase. The TBA latexes extract more of the substrates than the TMA latexes, and the difference in values of intraparticle rate constants k_L for TBA and TMA latexes is much larger for polystyrene than for poly(butyl methacrylate) or poly(2-ethylhexyl methacrylate). The methacrylates already have aliphatic character, so the TBA effect is not as great.

The model of Scheme 2 does not account for ion selectivities. We have performed a more detailed kinetic analysis of hydrolyses of PNP acetate, hexanoate, and octanoate using the six latexes reported in Table 2 by an ion exchange model.[26] The results of the analysis were that the intraparticle second-order rate constants for reaction of hydroxide with PNP esters were almost the same for all latexes, so that differences in partition coefficients of the substrates between the particle and water phases were completely responsible for the differences in observed rate constants. The overall rate accelerations also were promoted by approximatedly 10-fold higher concentration of hydroxide ion in the particles than in the external buffer solution.

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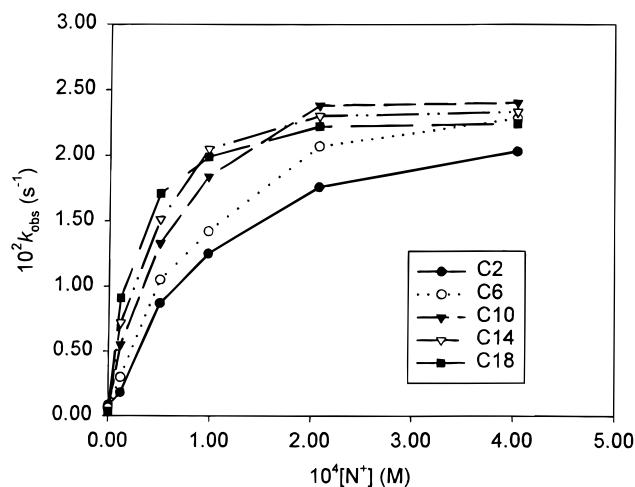
Figure 3. Dependence of observed rate constant on the concentration of poly(2-ethylhexyl methacrylate)−TBA in pH 9.4 borate buffer at 30.0 °C.

Table 5. Intraparticle Rate Constants and Distribution Constants for Hydrolysis of Long Chain PNP Alkanoates[a]

PNP ester	$10^3 k_L$, s^{-1}	$10^{-4}K$, M^{-1}
decanoate	4.8	9.0
tetradecanoate	4.5	9.1
octadecanoate	4.4	9.3

[a] k_L and K are defined in Scheme 2.

Dependence of Rate of Hydrolysis on PNP Alkanoate Chain Length. We also measured the activity of the latexes for hydrolysis of PNP esters with chain lengths up to C_{18}. Figure 2 shows that as the chain length increases, k_{obs} increases to a maximum and then decreases. The chain length at which this maximum k_{obs} is reached decreases as the concentration of the polymer increases. Such dependence of rates of hydrolysis on chain length of PNP alkanoates also has been observed with soluble 4-dialkylaminopyridine-containing polysiloxanes as catalysts in 50/50 methanol/water.[32] The observed rate constant is the sum of the rate constant inside the particles and the rate constant in the aqueous phase (eq 1). The rate inside the particles is a function of the fraction of substrate in the particles and the intraparticle rate constant. The longer the alkanoate chain, the larger is the value of K and, therefore, the higher the fraction of substrate in the particles at a given polymer concentration.[26] When the polymer concentration is high enough that essentially all of a given PNP ester is in the particle phase, the relative rates of hydrolysis of all esters with longer alkanoate chain lengths depend only on the relative intraparticle rate constants, which decrease with increasing chain length because chain coiling slows attack of hydroxide ion at the ester group.[31,33]

Rate constants for the hydrolysis of various PNP alkanoates up to C_{18} at varied concentration of the 2-EHMA-TBA latex are shown in Figure 3. The observed rate constants increase with increasing particle concentration until essentially all of the substrate is in the particle phase and then level off. The maximum rate constant occurs at lower particle concentration as the alkanoate chain length increases. Analysis of the data in Figure 3 using eqs 1 and 2 leads to the calculated intraparticle pseudo-first-order rate constants and distribution con-

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Scheme 3
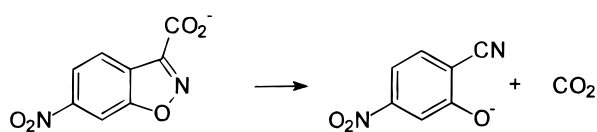
Table 6. Relative Rate Constants of Decarboxylation of 6-Nitrobenzisoxazole-3-carboxylate in Polymer Latexes

composition[a,b]	k_{obs}/k_w[c]	composition[a,b]	k_{obs}/k_w[c]
2-ethylhexyl (TBA)	10400	isobutyl	3300
styrene (TBA)	9600	tetrahydrofurfuryl	3200
2-ethylhexyl	8300	*n*-butyl	2900
n-octyl/2-ethylhexyl	7400	styrene	900
n-butyl (TBA)	6000	butoxyethoxyethyl	400
n-decyl	4400	ethoxyethoxyethyl	200
n-octyl	4100		

[a] All latexes were quaternized with trimethylamine except those designated TBA. [b] 0.6 mg/mL of latex with $[N^+] = 62\ \mu M$ and 1.00×10^{-5} M substrate in 2 mM NaOH at 30.0 °C. Reaction was followed by the appearance of 2-cyano-5-nitrophenoxide at 426 nm. [c] $k_w = 3.4 \times 10^{-6}\ s^{-1}$.

stants listed in Table 5. The intraparticle rate constants decrease slightly with increasing chain length, and the distribution constants are all the same within experimental error.

Decarboxylation of 6-Nitrobenzisoxazole-3-carboxylate. Some of the latexes were tested for the ability to promote the unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate (Scheme 3). The latex quaternary ammonium ion concentration was greater than 10-fold excess over the substrate concentration (Scheme 2). The reaction followed first-order kinetics for >3 half-lives, but only data from the first 20% conversion were analyzed. The ratios of rate constants in latex dispersions vs water alone are presented in Table 6. Again the

Table 7. Intraparticle Rate Constants and Distribution Constants for the Decarboxylation of 6-Nitrobenzisoxazole-3-Carboxylate in Latexes at 30.0 °C

latex	composition	$10^3 k_L$, s^{-1}	k_L/k_w	K, M^{-1}
1	2-ethylhexyl methacrylate (TBA)	44	13 000	4200
2	styrene (TBA)	58	17 000	2930
3	2-ethylhexyl methacrylate (TMA)	39	11 000	3600
11	styrene (TMA)	15	4 000	980

2-ethylhexyl methacrylate latexes were most active, and the tributylamine quaternized latexes were more active than their trimethylamine quaternized analogues.

The rate constants at varied particle concentrations were analyzed by eqs 1 and 2. Table 7 shows a comparison of the intraparticle rate constants and the distribution constants for the decarboxylation promoted by polystyrene and poly(2-ethylhexyl methacrylate) copolymer latexes quaternized with tributylamine. Even though the k_L for the polystyrene–TBA latex is larger than that for the methacrylate latex, K is much smaller, resulting in an observed rate that is lower than that for the methacrylate latex (Table 6). Comparing the polystyrene–TBA latex with the polystyrene–TMA latex, the decarboxylation in the TBA latex is 10.7 times faster (Table 6) as a result of both higher k_L and K values by factors of 3.8 and 3.0, respectively. Thus the intraparticle rate constants are more important contributors to the overall rates of the decarboxylation than to the rates of PNP alkanoate hydrolyses, where the intraparticle first-order rate constants depended very little on the polymer composition.[26]