KINETIC ANALYSIS OF REACTIONS INSIDE ALKYL METHACRYLATE LATEX PARTICLES

By

PAUL DAREN MILLER

Bachelor of Science

Southwest Missouri State University

Springfield, Missouri

1994

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
DOCTOR OF PHILOSOPHY
July, 1999

KINETIC ANALYSIS OF REACTIONS INSIDE ALKYL METHACRYLATE LATEX PARTICLES

Thesis Approved:

Warren T Ford
Thesis Advisor

Penger Tong

Richard A. Bunce

Wayne B. Powell
Dean of the Graduate College

PREFACE

Small spherical polymeric particles on the order of 2 x 10^{-5} cm in diameter, known as polymer latexes, can act as catalytic media for the hydrolysis and neutralization of toxic organic compounds. These particles function as catalysts by absorbing the substrates into the particles, thereby concentrating them inside the polymer phase. By incorporating positively charged sites throughout the particles, we can also increase the concentration of negatively charged reagents in the polymer phase also. Thus, polymer latexes can concentrate neutral organic substrates and reagents in an environment which would lead to more favorable reaction conditions.

Although a number of studies have been conducted on the rates of reactions inside polymer latexes, there has not been an in depth analysis which was designed to determine the rate of reactions based on the local concentrations of reactants in the latex particles. Also, the latexes which have been investigated up to this point have primarily been cross-linked polystyrene latexes and little attention has been given to analysis of reactions inside various aliphatic methacrylate polymer latexes, which can vary widely in their ability to absorb and concentrate various organic substrates.

In this work, we measured the rates of reactions under various conditions and used a statistical approach to determine what factors are responsible for the observed rate enhancements, thus making it possible to design a catalyst which has optimal activity.

ACKNOWLEDGMENTS

I would like to thank Dr. Warren Ford for his guidance, advise, and support throughout this research project. In addition, I would like to extend my appreciation to those with whom I have shared the lab for the past five years for their support, friendship, and patience. I would especially like to thank Stephanie Copeland, Ken Hampton, Jason Kreider, Alanta Lary, Spence Pilcher and Edward Seabolt.

I would also like to thank my committee members Dr. Edward Knobbe, Dr. Richard Bunce, Dr. Penger Tong and Dr. Bruce Ackerson for allowing me access to their equipment and expertise. Without them this work would not have been possible. In addition, I would like to thank Dr. H. Olin Spivey for his assistance and advise throughout this project.

I also want to thank Dr. Reza Sedaghat-Herati at Southwest Missouri State University for his encouragement and support, without which this work would never have taken place.

I would also like to give my special appreciation to my parents Mr. Alvin Ray Miller and Mrs. Rose Lavern Miller for their love, support, and encouragement throughout my life.

Finally, I want to dedicate this work to my wife, Jennifer Ann Williams, who has been unwavering in her support. Thank you all.

TABLE OF CONTENTS

Chapter Page

I. INTRODUCTION 1

Polymer Latexes 2
Advantages of Polymer Latexes as Catalytic Media 3
Systems Studied Using Latexes as Phase Transfer Catalysts 6
Limitations of Polymer Latexes as Catalytic Media 11
Potential Applications of Polymer Latexes 12
Objectives of Research 13
REFERENCES 15

II. PARALLEL SYNTHESIS OF ALKYL METHACRYLATE LATEXES FOR USE AS CATALYTIC MEDIA 18

ABSTRACT 18
INTRODUCTION 19
EXPERIMENTAL 24
  Materials 24
  Parallel Polymerization 25
  Quaternization of Latex Particles 26
  Determination of Conversion to Quaternary Ammonium Chloride Units 26
  Purification 27
  Kinetic Analysis 27
RESULTS AND DISCUSSION 28
  Latexes 28
  Screening Polymer Latexes for Activity 31
  Intraparticle Pseudo First-Order Rate Constants and Binding Constants 34
  Behavior of *p*-Nitrophenyl Esters with Chain Lengths up to C-18 37
  Ability of Latexes to Promote Decarboxylation Reactions 39
CONCLUSION 42
REFERENCES 44

III. SECOND-ORDER INTRAPARTICLE RATE CONSTANTS AND PARTITION COEFFICIENTS FOR THE HYDROLYSIS OF *p*-NITROPHENYL ALKANOATES IN COLLOIDAL POLYMER DISPERSIONS 47

ABSTRACT 47

INTRODUCTION 48
  Kinetic Models 50
 EXPERIMENTAL 53
  Materials 53
  Equipment 54
  Synthesis of Latex Particles 54
  Solid Content of Latexes 55
  Quaternization of Latexes 55
  Partition Coefficients of *p*-Nitrophenyl Alkanoates 56
  Chloride Concentration in Aqueous Phase 57
  Kinetic Measurements 57
  Particle Size Determination 58
  Fitting of the Data 58
 RESULTS 58
  Latexes 58
  Pseudo First-Order Rate Constants and Equilibrium Constants 61
  Partition Coefficients and Second-Order Constants 65
 DISCUSSION 71
 CONCLUSION 73
 REFERENCES 74

IV. CONCLUDING REMARKS 76

 SUMMARY 76

APPENDIX 78

 KINETIC DATA 78

LIST OF TABLES

Chapter I

Table Page

I. Relative Rate Constants of Decarboxylation of 6-Nitrobenzisoxazole-3-Carboxylate at 25°C 8

II. Rate Constants for the IBA-Catalyzed Hydrolysis of PNPDPP in 5.0 mM TAPS Buffer and 0.10 mg/mL Latex at 25.0°C 10

Chapter II

Table Page

I. Compostitions of Quaternary Ammonium Ion Functionalized Latexes 29

II. Sizes of Quaternary Ammonium Ion Functionalized Latexes in 0.002 M, 0.01 M and 0.02 M Borate Buffer 30

III. Observed Rate Constants for the Hydrolysis of PNP-Hexanoate by Alkyl Methacrylate Latexes Quaternized with Trimethylamine 32

IV. Observed Rate Constants for the Hydrolysis of PNP-Hexanoate by Styrene and Alkyl Methacrylate Latexes Quatternized with Trimethylamine and Tributylamine 33

V. Pseudo First-Order Intraparticle Rate Constants and Equilibrium Binding Constants for Trimethylamine and Tributylamine Quaternized Latexes 36

VI. Observed Rates of Decarboxylation of 6-Nitrobenzisoxazole-3-Carboxylate by Polymer Latexes 41

VII. Intraparticle Rate Constants and Equilibrium Binding Constants for the Decarboxylation of 6-Nitrobenzisoxazole-3-Carboxylate by Polystyrene and Poly(2-Ethylhexyl Methacrylate) Latex Particles 42

Chapter III

Table Page

I. Compositions of Quaternary Ammonium Ion Functionalized Latexes....59

II. Sizes of Quaternary Ammonium Ion Functionalized Latexes in 0.002 M, 0.01 M and 0.02 M Borate Buffer....60

III. Relative Rate Constants of Hydrolysis of PNP-Hexanoate....62

IV. Intraparticle Pseudo First-Order Rate Constants and Equilibrium Constants....64

V. Second-Order Rate Constants, Partition Coefficients and Selectivity Coefficients for PNP Ester Hydrolysis in Polystyrene Latexes....68

VI. Second-Order Rate Constants, Partition Coefficients and Selectivity Coefficients for PNP Ester Hydrolysis in Butyl Methacrylate Latexes....69

VII. Second-Order Rate Constants, Partition Coefficients and Selectivity Coefficients for PNP Ester Hydrolysis in 2-Ethylhexyl Methacrylate Latexes....70

LIST OF FIGURES

Chapter II

Figure Page

1. Structure of alkyl methacrylate copolymers 29
2. Dependence of observed rate of hydrolysis of *p*-nitrophenyl esters on the alkanoate chain length 38
3. Dependence of observed rate on the concentration of poly(2-ethylhexyl methacrylate)-TBA in pH 9.4 borate buffer at 30.0°C 39

Chapter III

Figure Page

1. Structure of EHMA-TMA latex 48
2. Basic hydrolysis of *p*-nitrophenyl alkanoates 49
3. Model for determining phase equilibrium constants and pseudo first-order intraparticle rate constants 49
4. Ion exchange model for determination of partition coefficients, intraparticle second-order rate constants and selectivity coefficients 51
5. Plot of observed rate constants versus the quaternary ammonium ion concentration of latexes 63
6. Chloride-selective potentiometric titration of latex 67

LIST OF SCHEMES

Chapter I

Scheme Page

I. Reaction of benzyl bromide with cyanide 7

II. Decarboxylation of 6-nitrobenzisoxazole-3-carboxylate 7

III. IBA-catalyzed reaction of PNPDPP 9

Chapter II

Scheme Page

I. Basic hydrolysis of *p*-nitrophenyl hexanoate 31

II. Menger-Portnoy model for pseudophase catalysis in molecular aggregates 34

III. Decarboxylation of 6-nitrobenzisoxazole-3-carboxylate 40

CHAPTER I

INTRODUCTION

Molecular aggregates, also known as association colloids, have been used as heterogeneous media to enhance the rates of chemical reactions in aqueous solution for many years. This has included the use of micelles,[1-3] ion exchange resins,[4] polyelectrolytes,[1] bilayer vesicles,[5] and polymer latexes.[6-9] These systems work on the same general principle, they concentrate the organic substrate in a lipophilic environment where it will be brought into contact with anionic reagents, which have also been concentrated into the same phase due to the presence of cationic sites. Therefore, the use of these types of heterogeneous catalytic media enables one to carry out organic reactions in an aqueous environment which would not be practical otherwise.

Each of the above methods offers certain advantages and disadvantages over the others, making them more suitable for specific uses. Some of them combine the advantages of the others making them applicable for more general use. In this chapter, I want to examine the use of polymer latexes as catalytic media; to define the importance of polymer latexes in the field of heterogeneous catalysis; to point out some of the advantages of polymer latexes over other types of association colloids; to look at some of the systems that have been studied using polymer latexes; and to look the limitations and potential applications of polymer latexes as catalytic media. But first, what are polymer latexes, and how they are made?

Polymer Latexes

Polymer latexes are sub-micrometer sized particles composed of a polymer matrix dispersed in aqueous solution. They are small enough so as not to fall out of solution due to gravitational forces and they are small enough to scatter light, thus the appearance of a latex ranges from colorless to white depending on the concentration and size of the particles in the solution. The particles are colloidally stable, that is they do not coagulate and fall out of solution, through electrostatic repulsion of charged sites on the surface of the particles. The charges may be the result of ionic sites incorporated into the polymer structure through the use of charged monomers or charged initiator fragments, or they may be the result of charged molecules, such as surfactant molecules, absorbed onto the surface of the particle.

Latexes are synthesized by emulsion polymerization processes. This is the same method as for the commercial production of water-based paints, coatings, and adhesives. A typical emulsion polymerization mixture consists of an aqueous phase into which has been added a surfactant in an amount in excess of its critical coagulation concentration so that micelles are formed, a monomer phase, and a water soluble initiator. Some of the monomer is incorporated into the micelles through diffusion through the aqueous phase. In the aqueous phase some of the monomer is attacked by radicals from the initiator and begins to form oligomers. Once these fragments are incorporated into the micellar structures, polymerization takes place in the micelles with monomer being replenished via diffusion from the monomer droplets through the water phase into the micelles. This process continues until stable polymer particles are formed and all of the monomer is spent. The surfactant used to form the micelles is now absorbed onto the surface of the particles, and helps provide charge stabilization. The emulsion process has been studied in great detail and there are several excellent sources for detailed information.[10]

By incorporating positively charged units into the polymer structure, it is possible have polymer latexes which can behave like ion exchange resins; i.e. they can concentrate anionic species through electrostatic interaction. Due to the hydrophobic nature of the polymer matrix, it is also possible to extract lipophilic substrates from the aqueous environment into the latex particles. Due to the small volume of the particles, the concentration of the species within these particles can be up to several orders of magnitude larger than that in the aqueous phase. Thus, particles can act in the capacity of phase transfer catalysts by bringing substrate and reagent into intimate contact with each other.

Advantages of Polymer Latexes as Catalytic Media

Polymer latexes offer distinct advantages over other types of heterogeneous catalytic media, and these advantages vary depending upon the conditions employed. In order to get a clear idea of how polymer latexes are comparable and in many ways superior to other types of media employed in heterogeneous catalysis, we will look at several different processes and compare them to latex catalysis.

Micellar Catalysis. Cationic surfactant micelles have been investigated as catalytic media for many years.[1-3,5] The surfactant micelles increase the rate at which anions react with neutral organic compounds. The anions bind to the Stern layer, or the region at the outer surface which contains the cationic head groups of the surfactant molecule, of the micelle through electrostatic interactions. The neutral organic substrate binds to the micelle due to the lipophilic nature of the surfactant alkyl chains. Bilayer vesicles also operate in a similar manner. In fact, these species have been called enzyme mimics because of their small size and amphiphilic nature.[5]

Reactions in these systems have been studied using enzyme kinetic and ion exchange models.[11] It has been shown that the hydrolysis of *p*-nitrophenyl diphenyl phosphate (PNPDPP) catalyzed by 5-octyloxy *o*-iodosobenzoate is about 18000 times faster that in the absence of surfactant. However, there is no significant enhancement in the observed rate until the surfactant is present in amounts that exceed the critical coagulation concentration (CMC). Below the CMC there are no micellar structures present to concentrate the reactants.

One of the most important advantages that polymer latexes, as catalysts, have over micelles is that latexes are discrete particles. Micelles are dynamic entities that are constantly undergoing association and dissociation, and they are present only above the critical micellar concentration (CMC) of the surfactant. Catalytic activity of latexes can persist even at very low concentrations.[6-8] In addition, because of the static nature of latex particles, one can accurately determine the volume of the latex phase at any time given the density and mass of the particles in the reaction mixture. Micelles, on the other hand are dynamic particles and the micellar volume must be approximated. Finally, particles can be removed from the reaction mixture through ultrafiltration, whereas surfactant separation requires more tedious and time consuming techniques such as dialysis or precipitation.

Polyelectrolytes. Polyelectrolytes are polymer chains which contain charged units along either the polymer chain or on pendant groups. Due to the large amount of charge, polyelectrolytes are generally soluble in aqueous solution. They will arrange themselves into colloidal species with the charged sites facing out toward the aqueous phase and hydrophobic regions in the core. In this way they act very similar to micelles in that they have a lipophilic core and a hydrophilic surface to concentrate neutral organic substrates and anionic reagents respectiviely.[1]

Like micelles, polyelectrolytes lack structural specificity and their volume can only be approximated. They also present separation problems because of their soluble nature in aqueous solution. Thus polymer latexes have the advantage of definable volumes and ease of isolation.

Microemulsions. Microemulsions have also been extensively studied as catalytic media.[12] Microemulsions are thermodynamically stable dispersions of oil in water or water in oil to which has been added a surfactant, and usually a co-surfactant. The phases are so finely divided that the dispersion does not noticeably scatter light.

Microemulsions can be very sensitive to relative composition and temperature. If either of these exceeds the limits of toleration, the mixture may phase separate. If this occurs, the rate enhancement disappears. Latexes are colloidally stable in a wide range of concentrations and temperatures. In addition, microemulsions can present enormous difficulties when it comes to isolation from reaction mixture.

Ion Exchange Resins. Ion exchange resins are water-swollen polymer gels which can have cationic sites throughout the particle and are very similar to polymer latexes. Like latex particles, resins have a specific structure and their volumes can be calculated accurately. Because anion exchange resins have cationic sites in their core, reactions can occur within the particle itself and not only at the surface. Resins can be easily separated from the reaction mixture by filtration and are routinely recycled.

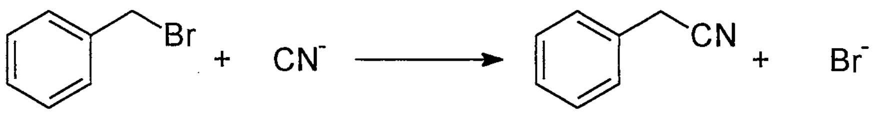
Anion exchange resins are typically on the order of 10 μm up to several hundred μm in diameter. This is 10^3 times larger than latex particles and although this makes separation easier, it does present some problems. As a result of their larger size, ion exchange resins do suffer some mass transport and intraparticle diffusion limitations.[4a] It has been shown that, when the half-life of a polymer supported phase transfer reaction is fairly short (< 1 hr), the rate approaches a limit at large particle size that is inversely proportional to the radius of the particle due to intraparticle diffusional control. Because latexes are 2-3 orders of magnitude smaller than ion exchange resins, diffusion within the particle does not limit the rate of reaction. In addition, the smaller size, and larger surface area per unit weight, of latex particles means that substrate molecules must diffuse through less water to reach a particle than in the case of ion exchange resins.

Systems Studied Using Latexes as Phase Transfer Catalysts

Polystyrene latexes have been investigated as phase transport catalysts for a number of years.[6a,7-9] The kinetics of reactions within these latexes have been analyzed using both enzyme and ion exchange models. Several reactions have been studied and, as will be shown, many have shown that latexes accelerate the reaction several orders of magnitude higher than that observed in the absence of latex particles.

Reaction of Benzyl Bromide with Cyanide. The reaction of benzyl bromide with cyanide (Scheme I) in 100 nm cross-linked polystyrene latex particles revealed a rate enhancement two times that previously observed in 10 μm polystyrene beads which up to that point were the most active.[13]

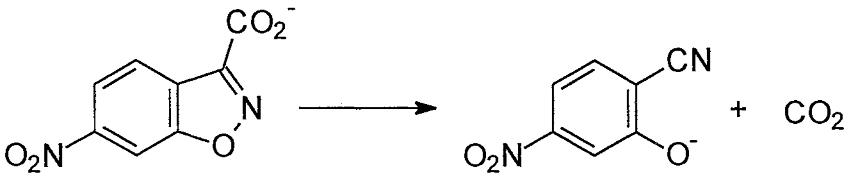
Scheme I. Reaction of benzyl bromide with cyanide.



In this case, the latex particles eventially became colloidally unstable because the anions screened the positive charge on the surface to the particles allowing the particles to coagulate. However, the reaction did serve to show that the latexes could enhance rates above those seen in micrometer-sized particles.

Decarboxylation of 6-Nitrobenzisoxazole-3-Carboxylate. The decarboxylation reaction of 6-nitrobenzisoxazole-3-carboxylate (Scheme II) is a very solvent dependent reaction. For instance, the reaction proceeds 10^8 times faster in hexamethylphosphoramide than in aqueous solution.[14]

Scheme II. Decarboxylation of 6-nitrobenzisoxazole-3-carboxylate.



Due to the solvent-sensitive nature of this reaction, it has been used to study the environment of many colloidal media. Table I presents a comparison of the relative rates in a number of colloidal media.

Table I. Relative Rate Constants of Decarboxylation of 6-Nitrobenzisoxazole-3-Carboxylate at 25.0°C[a]

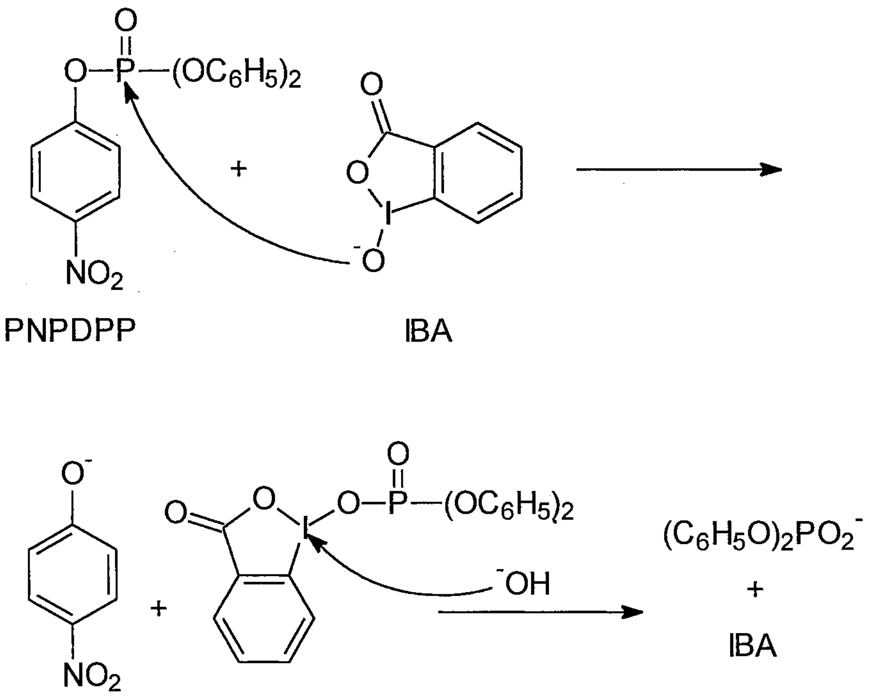
catalyst	k_c/k_w
TMAQ60[b]	310
TMAQ39[b]	340
TBAQ24[b]	21000
cetyltrimethylammonium bromide[c]	130
poly(4-vinylpyridine), 54% octyl substituted[d]	157
IER, 15% cross-linked, 54% N+ TEA[e]	1400
poly(vinylbenzo-18-crown-6)[f]	14000

[a] This table adapted from ref. 8. [b] $k_w = 3.1 \times 10^{-6}\ s^{-1}$. [c] $k_w = 3.0 \times 10^{-6}\ s^{-1}$, ref. 15. [d] $k_w = 7.0 \times 10^{-6}\ s^{-1}$, ref. 16. [e] IER = ion exchange resin with poly(styrylmethyl)triethylammonium groups, $k_w = 6.0 \times 10^{-6}\ s^{-1}$, ref. 17. [f] $k_w = 3.0 \times 10^{-6}\ s^{-1}$, ref. 18.

Table I shows that polymer latexes TMAQ60, TMAQ39 and TBAQ24 (TMA refers to (styrylmethyl)trimethylammonium units and TBA refers to (styrylmethyl)-tributylammonium units, the number to mol% quaternary ammonium units) offer rate enhancements equivalent or superior to those observed in other types of colloidal media. In addition it shows that in general, the fewer the quaternary ammonium groups, the more active the latex as a catalyst. Also, the more lipophilic the quaternary ammonium unit, the higher the activity. This suggests that the more lipophilic the environment inside the latex particle, the more active the latex as a phase transfer catalyst. This affects the rate in two possible ways. (1) The more lipophilic environment can extract more of the hydrophobic substrate. (2) The anionic reagents in such an environment are less solvated by water molecules and are more reactive.

Hydrolysis of *p*-Nitrophenyl Diphenyl Phosphate. *p*-Nitrophenyl diphenyl phosphate (PNPDPP) is often used as a model compound for toxic organophosphate compounds such as fluorophosphonate nerve agents and insecticides.[11,19,20] The hydrolysis of PNPDPP is known to be catalyzed by *o*-iodosobenzoate (Scheme III).

Scheme III. IBA-catalyzed reaction of PNPDPP.



The IBA-catalyzed hydrolysis of PNPDPP has been investigated in the presence of cross-linked polystyrene latex particles. Table II shows the second-order rate constants for the hydrolysis reactions performed in the presence of several polymer latexes.

Table II. Rate Constants for the IBA-Catalyzed Hydrolysis of PNPDPP in 5.0 mM TAPS Buffer and 0.10 mg/mL Latex at 25.0°C.

latex	k_{IBA}($M^{-1}s^{-1}$)
TBAQ24[a]	4300
TEAQ32[a]	2120
TMAQ17[b]	1722
TMAQ34[b]	1359

[a] Ref. 6a. [b] Ref. 7.

Again, the more active latexes are those with the fewest quaternary ammonium sites present, as well as those with larger quaternary ammonium ions, indicating that the more lipophilic the core of the latex, the greater the ability of the latex to promote hydrolysis.

Thus, systems that have been studied in micellar media indicate that polymer latexes can be just as active, and in some cases more active, as their surfactant counterparts.

Limitations of Polymer Latexes as Catalytic Media

Although polymer latexes possess advantages over many other forms of heterogeneous catalytic media, they do have their drawbacks. Probably the single most limiting property of latexes is their instability in solutions of high ionic strength. Because latexes are stabilized through surface charge, when they are put into concentrated salt solution, the counterions cause the electric double layer to begin to collapse, decreasing interparticle repulsion leading to particle coagulation.[21]

However, there have been advances in stabilizing polymer latexes in solutions of higher ionic strength. These include the use of poly(ethylene oxide) (PEO) chains which have either been adsorbed onto, or covalently incorporated into, the polymer structure.[22] The PEO chains are extended into the aqueous environment, providing steric stabilization. The particles are prevented from coagulating due to the negative entropy changes associated with the interpenetration of the PEO chains.

Also, there are presently indications that incorporating both positive and negative charge into the polymer structure, creating a polyampholytic latex, provides some stabilization to the latex in solutions at higher electrolyte strengths.[23] The mechanism for this stabilization is not fully understood at this time.

In addition to colloidal instability in solutions of high ionic strength, latexes are not as easily removed from the reaction mixture as larger particles such as anion exchange resins. However, they could find use in flow reactors.

Potential Applications of Polymer Latexes

Because polymer latexes can act as catalytic media, they can enable certain reactions to be carried out in aqueous solution, thereby minimizing the use of organic solvents. By decreasing the use of organic solvents, the cost of many industrial processes can be decreased due to fewer man-hours spent on recycling as well as less money spent on organic waste disposal.

Another possible use of polymer latexes is for the hydrolysis and neutralization of toxic organophosphorous compounds. As was mentioned earlier, PNPDPP, which is widely used as a model for nerve agents and insecticides, undergoes increased rates of reactions with anionic reagents such as IBA in polystyrene latexes. It therefore seems reasonable that latexes could be useful in the neutralization of these types of contaminants.

Finally, because latexes have traditionally been used as coatings and adhesives, it could be possible to synthesize functional latexes which could also be used as coatings. In this way it should be possible to create functional coatings which have active sites incorporated into the polymer matrix. These could be used as protective coatings on human skin as well as on materials. In fact, the U. S. Army Research Laboratories are investigating the potential of functional latexes described in this work as possible additives in a protective skin cream.

Objective of Research

Although it is known that polymer latexes can act as catalytic media, not much is known about the kinetics of reactions that take place within the particles. In addition, most of the investigations of polymer latexes as heterogeneous catalysts have been performed on polystyrene latexes which contain (styrylmethyl)trialkylammonium sites. There has been little investigation into polymer latexes composed of other types of repeat units, i.e. acrylates, methacrylates, etc.

The primary goal of this project is to survey a large number of polymer latexes for their potential to act as heterogeneous catalysts. By examining a large number of potential catalysts, it should be possible to determine which features lead to the highest enhancements in rates. It should therefore be possible to use that information to synthesize catalysts with optimum activity.

In order to achieve this goal we synthesized many latexes through the use of parallel polymerization techniques. We then screened the latexes against a simple reaction in order to compare relative rates. After identifying which latexes had the highest and lowest activity, we then performed kinetic analysis of reactions within the latexes. These analyses were done at different levels leading up to an in-depth analysis which resulted in a statistical analysis of the intraparticle second-order rate constants and the partition coefficients of various substrates.

The long term goal of this project is the synthesis of polymer latexes which can neutralize toxic organophosphorous compounds such as the nerve agents sarin, soman, and VX in the field. This could lead to better protective gear for soldiers in chemically hostile environments, as well as protective coatings for equipment used in testing and demilitarization procedures.

The key result of this project is that the primary factor responsible for the increase in the observed rates of reaction is the partition coefficient which governs the concentration of the substrate inside the latex particle. The intraparticle rate constants may be higher, but their effect on the overall rate is small compared to that of the partition coefficient.

REFERENCES

(1) Fife, W. K. *Trends Polym. Sci.* **1995**, *3*, 214.

(2) Fendler, J. H.; Fendler, E. H. *Catalysis in Micellar and Macromolecular Systems,* Academic Press: New York, 1975.

(3) (a) Cerichelli, G.; Mancini, G.; Luchetti, L.; Savelli, G.; Bunton, C. A. *J. Phys. Org. Chem.* **1991**, *4*, 71. (b) Bunton, C. A.; Cowell, C. P.; Nome, F.; Romsted, L. S. *J. Phys. Org. Chem.* **1990**, *3*, 239. (c) Germani, R.; Ponti, P. P.; Romeo, T.; Savelli, G.; Spreti, N.; Cerichelli, G.; Luchetti, L.; Mancini, G.; Bunton, C. A. *J. Phys. Org. Chem.* **1989**, *2*, 533. (d) Bunton, C. A.; Savelli, G. *Adv. Phys. Org. Chem.* **1986**, *22*, 213.

(4) (a) Ford, W. T.; Tomoi, M. *Adv. Polym. Sci.* **1984**, *55*, 49. (b) Tomoi, M.; Ford, W. T. *Synthesis and Separations Using Functional Polymers*; Sherrington, D. C., Hodge, P., Eds.; Wiley: Chichester, 1988.

(5) (a) Germani, R.; Ponti, P. P.; Savelli, G.; Spreti, N.; Cipicani, A.; Cericelli, G.; Bunton, C. A. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1767. (b) Kunitake, T.; Okahata, Y.; Ando, R.; Shinkai, S.; Hirakawa, S. *J. Am. Chem. Soc.* **1980**, *102*, 7877.

(6) (a) Lee, J. J.; Ford, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 3753. (b) Ford, W. T.; Badley, R. D.; Chandran, R. S.; Babu, S. H.; Hassanein, M.; Srinivasan, S.; Turk, H.; Yu, H.; Zhu, W. *Polymer Latexes; Preparation, Characterization, and Applications;* Daniels, E. S., Sudol, E. D., El-Asser, M. S., Eds.; ACS Symposium Series 492. (c) Ford, W. T.; Lee, J. J.; Yu, H.; Ackerson, B. J.; Davis, K. D.

Macromol. Symp. **1995**, *92*, 333. (d) Sun, Z.; Yan, C.; Kitano, H. *Macromolecules* **1986**, *19*, 984. (e) Wessling, R. A.; Yats, L. D. *Makromol. Chem. Suppl.* **1985**, *10/11*, 319. (f) Kitano, H.; Sun, Z. -H.; Ise, N. *Macromolecules* **1983**, *16*, 1306.

(7) Ford, W. T.; Yu, H. *Langmuir* **1993**, *9*, 1999.

(8) Lee, J. J.; Ford, W. T. *J. Org. Chem.* **1993**, *58*, 4070.

(9) Miller, P. D.; Ford, W. T. *J. Chem. Soc. Chem. Commun.* **1998**, 1152.

(10) (a) El-Asser, M. S.; Sudol, E. D. *Emulsion Polymerization and Emulsion Polymers;* Lovell, P. A., El-Asser, M. S., Eds.; Wiley: Chichester, 1997. (b) Odian, G. *Principles of Polymerization,* Wiley: New York, 1991.

(11) (a) Moss, R. A.; Kotchevar, A. T.; Park, B. D.; Scrimin, P. *Langmuir* **1996**, *9*, 2200. (b) Moss, R. A.; Alwis, K. W.; Shin, J. -S. *J. Am. Soc.* **1984**, *106*, 2651. (c) Moss, R. A.; Alwis, K. W.; Bizzigotti, G. O. *J. Am. Chem. Soc.* **1983**, *105*, 681.

(12) (a) Chaudhuri, A.; Romsted, L. S.; Yao, J. *J. Am. Chem. Soc.* **1993**, *115*, 8362. (b) Germani, R.; Savelli, G.; Cerichelli, G.; Mancini, G.; Luchetti, L.; Ponti, P. P.; Spreti, N.; Bunton, C. A. *J. Coll. Interface Sci.* **1991**,*147*, 152.

(13) Bernard, M.; Ford, W. T.; Taylor, T. W. *Macromolecules* **1984**, *17*, 1812.

(14) Kemp, D. S.; Paul, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 7305.

(15) Bunton, C. A.; Minch, M. J.; Hidalgo, J.; Sepulveda, L. *J. Am. Chem. Soc.* **1973**, *95*, 3262.

(16) Shinkai, S.; Hirakawa, S.; Shimonmura, M.; Kunitake, T. *J. Org. Chem.***1981**, *46*, 868.

(17) Yamazaki, N.; Nakahama, S.; Hirao, A.; Kawabata, J. *Polym. J.* **1980**, *12*, 231.

(18) Shah, S. C.; Smid, J. *J. Am. Chem. Soc.* **1978**, *100*, 1426.

(19) Hammond, P. S.; Forster, J. S.; Lieske, C. N.; Durst, H. D. *J. Am. Chem. Soc.* **1989**, *111,* 7860.

(20) Yang, Y. -C.; Baker, J. A.; Ward, J. R. *Chem. Rev.* **1992**, *92*, 1729.

(21) Hiemenz, P. C. *Principles of Colloid and Surface Chemistry*, Marcel Dekker: New York, 1986.

(22) (a) Vidal, F.; Guillot, J.; Guyot, A. *Polym. for Adv. Tech.* **1995**, *6*, 473. (b) Mura, J. -L.; Riess, G. *Polym. for Adv. Tech.* **1995**, *6*, 497. (c) Filet, A.; Guillot, J.; Hamaide, T.; Guyot, A. *Polym. for Adv. Tech.* **1995**, *6*, 465. (d) Ottewill, R. H.; Satgurunathan, R. *Colloid Polym. Sci.* **1995**, *273*, 379. (e) Ferguson, P.; Sherrington, D. C.; Gough, A. *Polymer* **1993**, *34*, 3281. (f) Ottewill, R. H.; Satgurunathan, R. *Colloid Polym. Sci.* **1988**, *266*, 547. (g) Ottewill, R. H.; Satgurunathan, R. *Colloid Polym. Sci.* **1987**, *265*, 845.

(23) Hampton, K. W. Ph.D. Dissertation, Oklahoma State University, 1999.

CHAPTER II

PARALLEL SYNTHESIS OF ALKYL METHACRYLATE LATEXES FOR USE AS CATALYTIC MEDIA

ABSTRACT

Polymer latexes serve as catalytic media for the hydrolysis of active carboxylate and phosphate esters by providing a more lipophilic environment into which these compounds can partition from the aqueous phase. The quaternary ammonium ions import reactive or catalytic anions into the latex which is swollen by water and the organic substrates. We have synthesized 32 different methacrylate and styrene latexes via a parallel synthetic route and screened their activity for the hydrolysis of *p*-nitrophenyl hexanoate. The most active latex was a copolymer of 75% 2-ethylhexyl methacrylate and 25% vinylbenzyl chloride which had been quaternized with tributylamine. The rate of hydrolysis at 30°C is 17 times faster using 0.6 mg/mL of latex (65 μM N^+ sites) in pH 9.4 borate buffer relative to control experiments which lacked polymer latex. Analysis of the kinetics shows that differences in hydrolysis rates among 6 different latexes are due primarily to latex/water partition coefficients of *p*-nitrophenyl hexanoate and secondarily to higher 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] in aqueous media catalyze reactions of anions with uncharged organic compounds. 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, i.e. pseudophase, in the aqueous mixture, although enhanced intrinsic rate constants sometimes contribute.

We have shown that polystyrene latexes containing quaternary ammonium anion 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 water alone.[12,13] The rate enhancements of these reactions in anion exchange latexes 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 latexes are small enough (approx. 200 nm in diameter) that reaction rates are not limited by intraparticle diffusion which is the case with ion exchange resins and polymer supported phase transfer catalysts.[5,14]

One extremely 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 use these polystyrene latex particles to catalyze the hydrolysis of diisopropyl fluorophosphate (DFP) in pH 11 aqueous media showed no rate enhancement.[16] One possible reason for lack of activity toward DFP could be due to an unfavorable partition coefficient of the aliphatic DFP into the highly aromatic polystyrene latex particles. For reactions of aliphatic compounds, aliphatic latex particles should be more active than the polystyrene particles, because they should absorb higher concentrations of aliphatic compounds. For this reason we have synthesized a family of cationic latexes from copolymers of alkyl methacrylates and VBC and tested their activities for basic hydrolysis of *p*-nitrophenyl esters and for decarboxylation of 6-nitrobenzisoxazole-3-carboxylate.

We chose *p*-nitrophenyl (PNP) esters as a probe to study the ability of the polymer latexes to promote hydrolysis reactions within them for a number of reasons. First, they are commercially available in a wide range of carbon chain lengths; this allows us to investigate substrates which can differ significantly in their hydrophobicity. Second, it is easy to follow the progress of the reaction by monitoring the appearance of *p*-nitrophenoxide by UV/VIS spectrophotometry. And finally, the large amount of literature available on the behavior of PNP esters under a wide range of conditions allows for a more thorough understanding of the processes occurring in our systems.

PNP esters have been the subject of many investigations, not the least of which were concerning the use of PNP esters to study enzyme models.[17] These investigations have looked at PNP alkanoates of various chain lengths in the belief that the alkyl chain of the ester would associate with the enzyme model and lead to an increased rate of hydrolysis via an increase in the local concentration of the reactants. As a result of this increasing interest in the hydrolysis of PNP esters, it became necessary to study the behavior of these compounds in aqueous solutions in order to better understand the uncatalyzed reactions so that comparisons of catalyzed rates could be made, as well as speculations on the nature of the association, or binding, of the subsrates to the enzyme models.

One of the earliest studies of the behavior of PNP esters was done by Scheraga et. al.[18] In this work, it was shown that the alkyl chain of long PNP esters was coiled up in aqueous solution. It then was shown that this coiling up of the alkyl chains increased the steric bulk at the reaction center which resulted in a decreased rate of hydrolysis by hindering the attack of the hydroxide at the carbonyl.[19]. In addition, it was pointed out by Guthrie[20] that if the alkyl chain were long enough it could cause a marked decrease in the polarity around the reaction center, further decreasing the possibility of nucleophilic attack. In that same work, Guthrie showed that the factor responsible for decreased hydrolysis rates at PNP ester concentrations above a critical concentration was due to a solubility limit and not micelle formation.[21]

The mechanism of hydrolysis of PNP esters, specifically PNP-acetate, in aqueous solution has been shown to be through a concerted mechanism using a number of different techniques including Marcus theory,[22] linear free energy relationships,[23] and isotope effects.[24] All of these investigations indicated only the presence of a transition state and no intermediate was suggested. It was then shown that in many cases the enzyme-catalyzed hydrolysis of PNP-acetate also occurred through a very similar concerted mechanism.[25] It has recently been shown that the hydrolysis of phenyl acetate occurs through a stepwise mechanism with a very short-lived tetrahedral intermediate.[26] The reason for the difference in the mechanism for phenyl acetate and the concerted mechanism for PNP-acetate is due to the lower basicity of the PNP leaving group. This is similar to the effect described by Menger in his "*p*-nitrophenyl ester syndrome" paper,[27] in which he related the acceleration of the rate of hydrolysis of an enzyme-substrate complex over the uncatalyzed rate to the pK_a of the leaving group.

Probably most important to the work described herein is the continued interest in micellar catalysis of PNP esters.[2,8-10,28-34] Early investigations looked at hydrolysis of PNP-acetate and PNP-hexanoate in cetyltrimethylammonium bromide micelles[29] and was soon followed by the work by Menger and Portnoy which introduced the pseudophase model of catalysis in molecular aggregates for hydrolysis of PNP-acetate and PNP-octanoate in dodecyltrimethylammonium bromide micelles[30]. This led to the investigation of the effect of surfactant structure on the ability of micelles to catalyze the hydrolysis of PNP esters.[31] These studies led to the conclusion that higher observed rates of hydrolysis are seen when the surfactant has a long alipatic chain as well as when the PNP ester has a long acyl chain. This is a result of the fact that the substrate is partitioned into the latex with the ester near the Stern layer of the micelle where the hydroxide ion is concentrated.[32]

The Menger-Portnoy model for pseudophase catalysis was widely used for several years. However, Chaimovich et. al. realized that at high cetyltrimethylammonium bromide concentration the observed rate of hydrolysis of PNP-acetate and PNP-octanoate decreased because the bromide ion in the Stern layer of the micelle lowered the effective concentration of hydroxide.[33] This led to the need for a more complete model which takes into account ion selectivities. The result was the pseudophase ion exchange model.[33, 34] A modified version of this model has been used by our group to evaluate kinetic data from selected polymer latexes and will be further elaborated on in the discussion section of this paper.[35]

In order to study a number of polymer latexes and assess their potential to promote the hydrolysis of *p*-nitrophenyl esters, we opted to pursue an approach utilizing a diversity strategy. Diversity strategies are now employed at all major pharmaceutical companies for the synthesis of biologically active compounds, and have been used in search of superconducting[36], magnetic[37], and phosphorescent[38] materials. Diversity strategies also have been used to synthesize potential catalysts, including polymer catalysts.[39] These approaches allow for the production and screening of a large number of catalyst candidates in a short time. One widespread approach is the synthesis of different compounds on polymer beads that can be separated and tested individually.

Latex particles <0.5 μm in diameter are too small to be separated, and thus a combinatorial approach is not practical in this instance. In addition, a combinatorial approach would result in particles which were a product of the polymerization of all the monomers employed with little variance from particle to particle. With these considerations, it became apparent that it would be necessary to synthesize the particles in separate batches but in such a way and in a small enough amount that it is practical to analyze a number of latexes at one time. Therefore, we have synthesized a diverse series of alkyl methacrylate-based catalysts by a parallel approach. Once a number of samples have been prepared, it is then possible to screen these latexes for the ability to promote the hydrolysis of active esters.

As a result of this investigation we have concluded that the primary factor responsible for the activity of these cationic latexes to promote hydrolysis of *p*-nitrophenyl esters is how well they are able to extract the substrate out of the aqueous phase into the particle phase where it is concentrated along with anionic reactants. Some of the results were reported in a preliminary communication.[40]

EXPERIMENTAL

Materials

Vinylbenzyl chloride (Scientific Polymer Products) was distilled under vacuum, and filtered through a plug of alumina just prior to use. (*m,p*-Vinylbenzyl)trimethylammonium chloride was prepared previously,[41] and used as a 0.0482 M aqueous solution (as determined with a chloride selective electrode). Divinylbenzene (Aldrich), butyl methacrylate, 2-chloroethyl methacrylate (Scientific Polymer Products), isobutyl methacrylate, tetrahydrofurfuryl methacrylate, 2-ethylhexyl methacrylate, butoxyethoxyethyl methacrylate, ethoxyethoxyethyl methacrylate (all from Aldrich) were distilled and filtered through a plug of alumina prior to use, a solubility test (dripping into hexane) indicated that no polymer was present. The initiator, 2,2'-azobis(*N,N'*-dimethyleneisobutyramidine) dihydrochloride (Wako Pure Chemical Ind. Ltd.), was used as received after ^{1}H and ^{13}C NMR indicated no contamination. Trimethylamine (Eastman) was used as received as a 25% w/w solution in methanol. Tributylamine (Eastman) was used as received. Triply deionized water was used in all experiments. *p*-Nitrophenyl acetate (Pfaltz & Bauer, Inc.), as well as all other *p*-nitrophenyl esters (Sigma) were all used as 2.5 mM solutions in acetonitrile (Aldrich). The preparation of 6-nitrobenzisoxazole-3-carboxylic acid from methyl 6-nitro-1,2-benzisoxazole-3-carboxylate (Pfaltz & Bauer) has been reported previously.[13]

Parallel Polymerizations

The polymerizations were carried out in sets of twelve and seven test tubes, each containing a different monomer mixture. The test tubes were placed in a water bath at 60°C. The tubes were kept stationary by a sheet of polystyrene foam, which had been cut for a snug fit in the bath container and served both to immobilize the tubes and to help insulate the water bath. The water bath was maintained at the desired temperature by a circulating water bath. The polymerization mixture was stirred using a six-plate magnetic stirrer (Lab-Line Instruments, Inc. model 1278) and a 7 mm stirbar in each tube.

The test tubes with stirbars were placed in the water bath as described above. Into each tube was added 3.5 mL of water, through which N_2 had been bubbled. The tubes were allowed to equilibrate to 60°C for 10 min, after which was added 1.0 mL of 2.36×10^{-2} M aqueous (*m,p*-vinylbenzyl)trimethylammonium chloride (this is equivalent to 5 mg). The mixture was stirred for 5 min, at which time 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 as shown in Tables 1 and 2. The monomer mixture was allowed to stir for 5 min before the initiator (5 mg VA044 in 0.5 mL water) was added. The tubes were then covered with stretch film to prevent evaporation of monomer. The polymerization was allowed to continue for 3 h. The latexes were filtered through a plug of cotton in a Pasteur pipette to remove any coagulum. The amount of coagulum collected was always <30 mg (<8% total polymer weight).

Quaternization of Latex Particles

A 4 mL aliquot of the latex was placed in a 10 mL vial and 2 mL of ethanol was added along with 2 mL of 25 wt% trimethylamine and the screw cap was screwed on the vial. Three such vials at a time were placed in the stainless steel reactor and a mixture, consisting of 12 mL of water, 6 mL of ethanol and 6 mL of aqueous trimethylamine was poured into the reactor around the vials. The top was placed on the reactor and the reactor was placed in a 60°C oil bath for 48 hrs.

This process allowed for the quaternization of different latex samples at the same time in the same sealed container. The purpose of adding the water/ethanol/amine solution to the reactor was to allow for internal and external equalization of pressure around the vials containing the quaternization reaction mixtures, thus preventing rupturing the vials.

Determination of Conversion to Quaternary Ammonium Chloride Units

In order to determine the percent conversion of vinylbenzyl chloride groups to quaternized ammonium groups, potentiometric titration with a chloride selective electrode was utilized. To a 50 mL beaker was added 2.000 mL of the latex, 1.000 mL of 5 M $NaNO_3$, and enough water to cover the tip of the electrode (about 20 mL). The solution was adjusted to near pH 2 with 1 M HNO_3. The mixture was then titrated with 0.0500 M solution of $AgNO_3$. A titration curve of mL titrant vs. mV was then constructed and the end point was determined at the point of maximum slope.

Purification

An aliquot (about 2 mL) of each latex sample was drawn into a 5 mL syringe, added to the 50,000 MW cut-off dialysis tubing, and dialyzed for two days against deionized water. After dialysis, the latex sample was again drawn into a 5 mL syringe and the syringe was fitted with a 0.1 μm pore size Millipore brand filter. The volume was reduced to about 0.75 mL by depressing the plunger. The volume was brought back up to about 3 mL by adding deionized water and again the volume was reduced to less than 1 mL, and the process was repeated until the water which was filtered from the latex showed a pH less than 7 (usually about 15-20 mL). At this point the typical solids content was 5-7 mg/mL.

Kinetic Analysis

The latex samples were diluted until they had a solid content of 1.2 mg/mL. A 2 mL aliquot of each latex was diluted to 40 mL with 0.02 M borate buffer (pH 9.38) to give a concentration of N^+ units of approximately 6.15×10^{-5} M. A 3 mL sample of the latex/buffer solution was placed into a polystyrene cuvette. The solution was allowed to equilibrate to 30°C for 20 min, 5 μL of 2.5 mM PNP-hexanoate in acetonitrile was added, and data acquisition was initiated. A UV/VIS spectrum was taken every 0.9 seconds and the average absorbance from 400-410 nm was plotted as a function of time.

The value of k_{obs} was calculated by the kinetics application in the manner of a plot of $\ln[(A_{inf}-A_o)/(A_{inf}-A_t)]$ vs time (from $\ln[(C_o/C_t)]=k_{obs}t$). The values of A_{inf} were determined manually and the calculations were made over a time corresponding to 20%

conversion. The data fit first-order kinetics up to 20% conversion quite well ($R^2 \geq 0.994$) at higher conversion, the correlation coefficient was < 0.990.

The procedure for determining the rate of decarboxylation was performed in a similar manner except that the reaction was carried out in 2.0 mM NaOH solution and the rate was followed at 426 nm.[13]

RESULTS AND DISCUSSION

Latexes

Thirty latex copolymers of 25% w/w vinylbenzyl chloride (70:30 *m:p*) and 73% w/w various aliphatic methacrylates using 1% w/w divinylbenzene as a cross-linking agent (Figure 1). In lieu of a surfactant, 1% w/w (*m,p*-vinylbenzyl)trimethylammonium chloride was used to stabilize the particles during their growth. The latexes differ in the number and combination of aliphatic monomers present. Quaternary ammonium groups were introduced by reacting the vinylbenzyl chloride component with either trimethylamine or tributylamine. The resulting anion exchange latexes consisted of particles which were 124-150 nm in diameter and contained 21-25 wt% (14-24 mol %) of quaternary ammonium units. Some representative latexes are presented in Tables I and II.

conversion. The data fit first-order kinetics up to 20% conversion quite well ($R^2 \geq 0.994$) at higher conversion, the correlation coefficient was < 0.990.

The procedure for determining the rate of decarboxylation was performed in a similar manner except that the reaction was carried out in 2.0 mM NaOH solution and the rate was followed at 426 nm.[13]

RESULTS AND DISCUSSION

Latexes

Thirty latex copolymers of 25% w/w vinylbenzyl chloride (70:30 *m*:*p*) and 73% w/w various aliphatic methacrylates using 1% w/w divinylbenzene as a cross-linking agent (Figure 1). In lieu of a surfactant, 1% w/w (*m,p*-vinylbenzyl)trimethylammonium chloride was used to stabilize the particles during their growth. The latexes differ in the number and combination of aliphatic monomers present. Quaternary ammonium groups were introduced by reacting the vinylbenzyl chloride component with either trimethylamine or tributylamine. The resulting anion exchange latexes consisted of particles which were 124-150 nm in diameter and contained 21-25 wt% (14-24 mol %) of quaternary ammonium units. Some representative latexes are presented in Tables I and II.

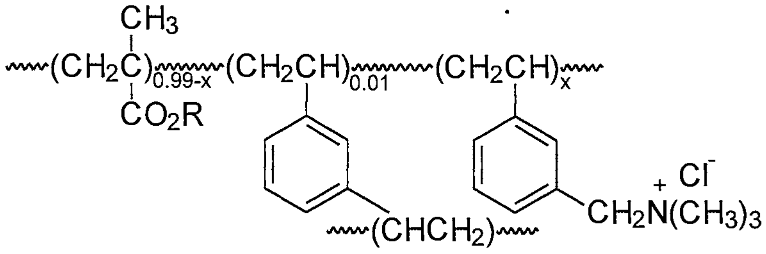


Figure 1. Structure of alkyl methacrylate latex copolymers

Table I. Compositions of Quaternary Ammonium Ion Functionalized Latexes.

composition	quaternization yield (%)	N^+/g^a	N^+/mL^b	N^+(mol %)^c
EHMA-TMA	80.0	1.22	0.419	24.2
EHMA-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] Mol% of N^+ repeat units.

Table II. Sizes of Quaternary Ammonium Ion Functionalized Latexes in 0.002 M, 0.01 M, and 0.02 M Borate Buffer.

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
EHMA-TMA	135.1	135.6	211	203	198	3.8	3.4	3.2
EHMA-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,b] Calculated using measurements of fifty particles from TEM negatives. Number average diameter, $d_n = (\Sigma N_i d_i^3/\Sigma N_i)^{1/3}$ Weight average diameter, $d_w = (\Sigma N_i d_i^6/\Sigma N_i d_i^3)^{1/3}$
[c] Hydrodynamic diameter from dynamic light scattering in various buffer strength solutions. [d] $(d_h/d_w)^3$ in buffer solutions of various strengths.

Screening Polymer Latexes for Activity

To screen the activities of the particles, we have measured the rates of basic hydrolysis of *p*-nitrophenyl (PNP) hexanoate and the rates of decarboxylation of 6-nitrobenzisoxazole-3-carboxylate. PNP-hexanoate was used because it possessed a significant amount of hydrophobicity, but not so much as to create a solubility problem at the concentrations used in this study.

The screening was carried out under conditions that would force the reaction to pseudo first-order conditions. The quaternary ammonium sites were present in a greater than ten-fold excess oversubstrate. Under these conditions all experiments had half-lives in the range of 130-925 s.

Tables III and IV present the results of screening the catalytic activities of alkyl methacrylate latexes for the hydrolysis PNP-hexanoate in pH 9.4 borate buffer solution (Scheme I).

Scheme I. Basic hydrolysis of *p*-nitrophenyl hexanoate.

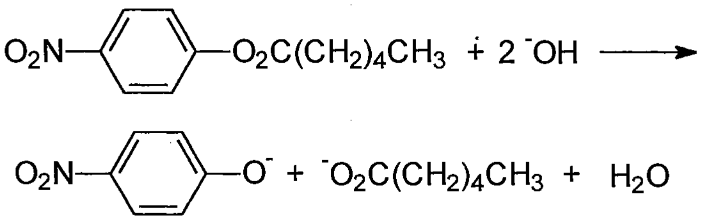


Table III. Observed Rate Constants for the Hydrolysis of PNP-Hexanoate by Alkyl Methacrylate Latexes Quaternized with Trimethylamine.

latex	methacrylate[a]	k_{obs}/k_w
1	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] Latex concentration is 0.6 mg/mL with $[N^+] = 62$ μM and substrate concentration is 4.2 μM in 0.02 M borate buffer pH 9.4 at 30.0°C. Reaction was followed by the formation of *p*-nitrophenoxide at 410 nm over the first 20 % conversion. Data are averages of 2-3 experiments that deviated over a range of ≤ 5 % of the reported k_{obs}.

Table IV. Observed Rate Constants for the Hydrolysis of PNP-Hexanoate by Styrene and Alkyl Methacrylate Latexes Quaternized with Tributylamine.

latex	composition[a]	k_{obs}/k_w
30	2-Ethylhexyl (TBA)	16.5
31	Butyl (TBA)	15.7
32	Styrene (TBA)	12.0

[a]See footnote for Table III.

From Table III, it is evident that 2-ethylhexyl methacrylate (8) shows the highest catalytic activity of all 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 are the most active (latexes 16, 19 and 23).

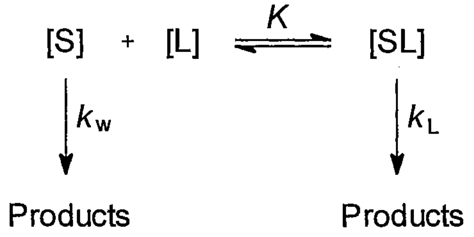
Longer-chained and branched aliphatic methacrylate latexes (2-8) were also investigated. From n-hexyl to n-dodecyl methacrylate there is an increase in the activity, and the magnitude of the change decreases as the chain length is increased. 2-Ethylhexyl methacrylate (8) is much more active than n-octyl methacrylate (3) and n-octyl/2-ethylhexyl methacrylate (16) even though there are the same number of carbons in each latex. In fact, it appears that the presence of n-octyl methacrylate only serves to dilute the effect of 2-ethylhexyl methacrylate in latex 16 since the activity of that sample is between those which are composed solely of the individual monomers.

Finally, Table IV indicates that particles which contain tributylammonium sites are much more active than those which contain trimethylammonium sites. In this table it appears that the difference between the activity of TBA and TMA latexes is much more pronounced in the styrene case than it is in the case of the methacrylates.

Intraparticle Pseudo First-Order Rate Constants and Equilibrium Constants

In order to determine what factor(s) are responsible for the differences in activities between latexes we decided to perform a more in-depth kinetic analysis of representative latexes. The styrene, butyl methacrylate, and the 2-ethylhexyl methacrylate-based latexes quaternized by TMA and TBA were studied at varied particle concentrations. Nonlinear plots of equation 1 have been constructed where k_{obs} is the observed rate constant, k_w is the rate constant in the absence of particles, k_L is the intraparticle pseudo first-order rate constant, and K is the association constant of substrate going from the aqueous phase to the particle phase (see Scheme II). By fitting the data to equation 1 through nonlinear regression analysis, we were able to calculate the pseudo-first order intraparticle rate constants (k_L) and the equilibrium distribution constants (K)[30, 42] for the hydrolysis of PNP-acetate, hexanoate, and octanoate. These results are shown in table V.

Scheme II. Menger-Portnoy model for pseudophase catalysis in molecular aggregates.



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

Table V shows that 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 activities are due to equilibrium distribution constants: the longer the aliphatic chain of the PNP ester, the greater its distribution constant to the latex. In addition, the more aliphatic character that the latex possesses, the higher the value of *K*. Therefore, more aliphatic latex can extract a larger fraction of substrate from the aqueous phase. Comparison of the *K* values in Table V indicate that the TBA latexes extract more of the substrates than the TMA latexes. In general, there is a much larger increase in the distribution constant in going from TMA polystyrene to TBA polystyrene than with the poly(2-ethylhexyl methacrylate) latexes for any given ester. Thus TBA increases the overall aliphatic character of the polystyrene latexes making them more compatible with the substrates. The methacrylates inherently have aliphatic character, so the TBA effect is not as great.

Table V. Pseudo-First Order Intraparticle Rate Constants and Equilibrium Binding Constants for Trimethylamine and Tributylamine Quaternized Latexes.[a]

	S		BMA		EHMA	
PNP ester	$10^3k_L/s^{-1}$	$10^{-3}K/M^{-1}$	$10^3k_L/s^{-1}$	$10^{-3}K/M^{-1}$	$10^3k_L/s^{-1}$	$10^{-3}K/M^{-1}$
TMA-quaternized						
Acetate	11.3	2.0	9.3	2.3	7.4	2.3
Hexanoate	5.7	2.1	5.9	11.8	4.7	21.0
Octanoate	4.7	12.7	5.3	46.0	4.9	70.0
TBA-quaternized						
Acetate	11.9	3.1	9.5	4.1	9.0	5.0
Hexanoate	5.8	15.1	5.8	25.0	5.8	31.0
Octanoate	5.7	39.0	5.3	74.0	5.1	88.0

[a] At 30.0°C in 0.02 M borate buffer (pH 9.38). The pseudo-first order rate constants in the absence of latex, k_w, were 6.0×10^{-4} s^{-1}, 3.26×10^{-4} s^{-1} and 1.22×10^{-4} s^{-1} for PNP-acetate, hexanoate and octanoate respectively.

Behavior of *p*-Nitrophenyl Esters with Chain Lengths up to C_{18}

We also examined the hydrolytic activity of these latexes toward some longer chain PNP esters with chain lengths ranging up C-18. Figure 2 shows that as the chain length is increased k_{obs} increases until a maximum is reached and then k_{obs} begins to decrease. Furthermore, the point at which this maximum is reached depends on the concentration of the polymer. As the concentration of the polymer is increased, the maximum k_{obs} is seen at lower alkanoate chain lengths. This behavior has been observed in other polymer systems which have been used to catalyzed the hydrolysis on PNP alkanoates.[43] We believe this is the result of the longer-chained alkanoates having more favorable equilibrium distribution constants into the particles. The observed rate is the sum of the rate inside the particles and the rate in the aqueous phase. The rate inside the particles is a function of the fraction of substrate in the particles and the intraparticle rate constant. As the data in Table V shows, the longer the alkanoate chain the larger the value of K, and therefore the higher the fraction of substrate in the particles at a given polymer concentration. When the polymer concentration reaches a point that essentially all of a given PNP ester is in the particle phase then the relative rates of hydrolysis of all esters with longer alkanoate chain lengths is a function of the relative intraparticle rate constants. Due to chain-coiling, the intrapartilce rate constants would be expected to decrease and this is supported by the data in Table V. Thus, once the polymer concentration reaches a point that all of the substrate is in the particle phase, then the observed rates would be expected to decrease with increasing alkanoate chain length. Figure 3 shows the dependence of k_{obs} on polymer concentration, and the same conclusion is reached. The rate increases with increasing particle concentration until essentially all of the substrate is in the particle phase and then begins to level off; and the maximum rate is lower for substrates with longer alkanoate chain lengths. A rough analysis of the data in Figure 3 leads to calculated pseudo first-order rate constants of 4.8 x 10^{-3}, 4.5 x 10^{-3} and 4.4 x 10^{-3} s^{-1} and equilibrium constants of 9.0 x 10^4, 9.1 x 10^4 and 9.3 x 10^4 M^{-1} for C_{10}, C_{14} and C_{18}, respectively. These values are not as reliable as those in Table V due to fewer duplicate runs and k_w's that were determined by fit rather than by experiment.

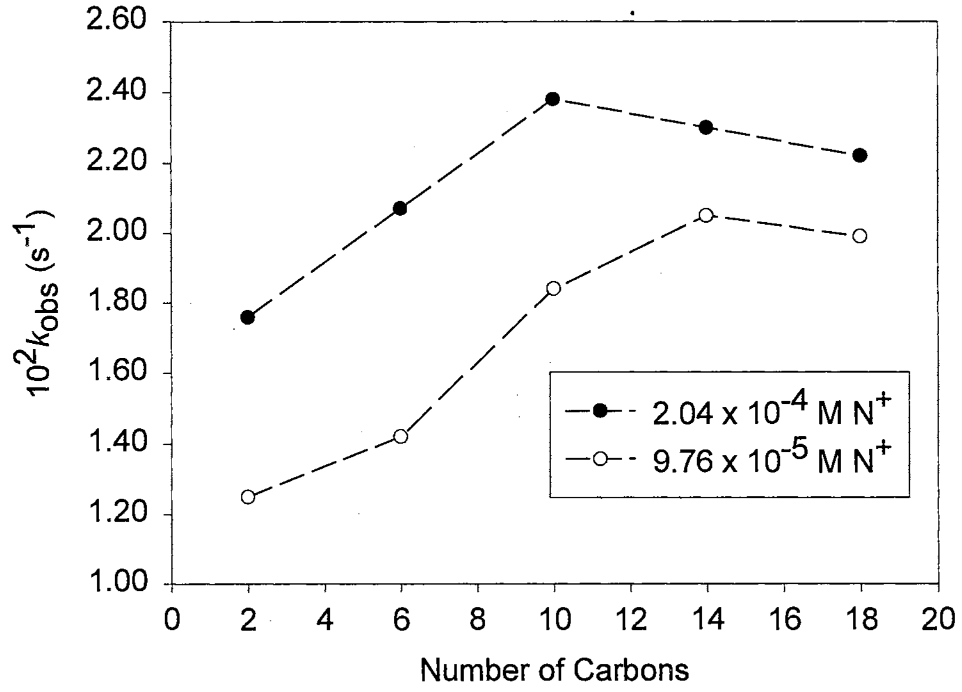


Figure 2. Dependence of the observed rate of hydrolysis of *p*-nitrophenyl esters on the alkanoate chain length. The catalyst used was poly(2-ethylhexyl methacrylate) quaternized with tributylamine at 30.0°C.

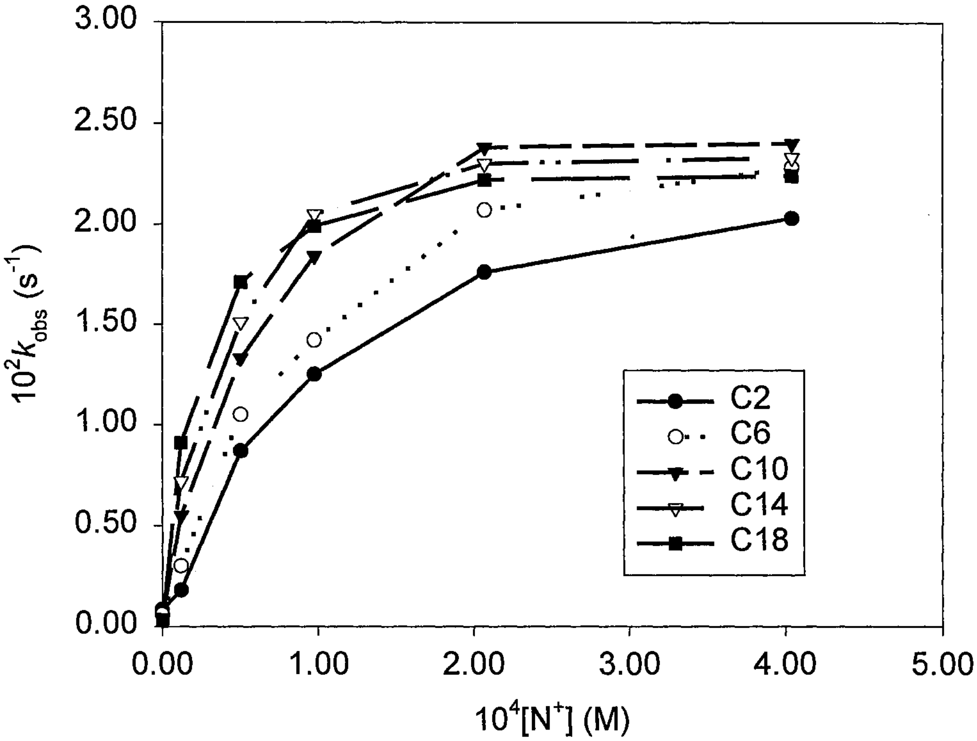


Figure 3. Dependence of observed rate on the concentration of poly(2-ethylhexyl methacrylate)-TBA in pH 9.4 borate buffer at 30.0°C. .

Ability of the Latexes to Promote Decarboxylation Reactions

Some of the latexes were screened for the ability to promote the decarboxylation of 6-nitrobenzisoxazole-3-carboxylate (Scheme III). The results are presented in Table VI. Again, 2-ethylhexyl methacrylate is the most effective monomer for producing active copolymers, and the tributylamine quaternized latexes are more active than their trimethylamine quaternized analogues. The reactions were performed under conditions that forced pseudo first order kinetics. The $[N^+]$ was a factor of ten greater than the substrate concentration (Scheme II). It is important to note that the λ_{max} for the product, 2-cyano-5-nitrophenoxide shifts from 398 nm in water to 426 nm in the latexes. The reaction followed first-order kinetics throughout the first 20 % conversion.

Scheme III. Decarboxylation of 6-nitrobenzisoxazole-3-carboxylate.

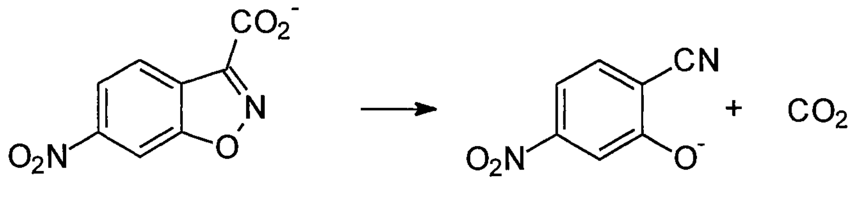


Table VII shows a comparison of the intraparticle rate constants and the equilibrium binding constants for the decarboxylation reaction promoted by polystyrene and poly(2-ethylhexyl methacrylate) copolymer latexes quaternized with tributylamine. Even though the k_L for the polystyrene-TBA latex is larger than that for the methacrylate latex, K is much smaller resulting in an observed rate which is lower than that for the methacrylate latex. Also, when comparing the polystyrene-TBA latex to the polystyrene-TMA latex it becomes apparent that the enhanced activity of polystyrene-TBA (by a factor of 10.6 noted in Table VI) is a result of both higher k_L and K values (the k_L value is higher by a factor of 3.8 and the K is higher by a factor of 3.0, 3.8 x 3.0 = 11.4 a difference of less than 8% of the experimental value of 10.6, close to error limits).

It should be pointed out that in the case of the decarboxylation reaction, it appears that the intraparticle rate constants play a more important role in determining the overall rate of reaction. This was not the case in the PNP hydrolysis reaction where the intraparticle rate constants had virtually no effect on the observed rate.

Table VI. Observed Rate of Decarboxylation of 6-Nitrobenzisoxazole-3-Carboxylate by Polymer Latexes.

latex	composition[a,b]	k_{obs}/k_w[c]
1	2-Ethylhexyl (TBA)	10400
2	Styrene (TBA)	9600
3	2-Ethylhexyl	8300
4	n-Octyl/2-ethylhexyl	7400
5	Butyl (TBA)	6000
6	n-Decyl	4400
7	n-Octyl	4100
8	Isobutyl	3300
9	Tetrahydrofurfuryl	3200
10	Butyl	2900
11	Styrene	900
12	Butoxyethoxyethyl	400
13	Ethoxyethoxyethyl	200

[a] All latexes are quaternized with trimethylamine except 1, 2 and 5 which are quaternized with tributylamine. [b] Latex concentration is 0.6 mg/mL with $[N^+] = 62$ μM and substrate concentration is 1.00×10^{-6} M in 2 mM NaOH at 30°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}.

Table VII. Intraparticle Rate Constants and Equilibrium Binding Constants for the Decarboxylation of 6-Nitrobenzisoxazole-3-Carboxylate by Polystyrene and Poly(2-Ethylhexyl Methacrylate) Latex Particles.

latex	composition	10^3k_L (s^{-1})	k_L/k_w	K (M^{-1})
1	2-Ethylhexyl methacrylate (TBA)	44	13000	4200
2	Styrene (TBA)	58	17000	2930
3	2-Ethylhexyl methacrylate (TMA)	39	11000	3600
11	Styrene (TMA)	15	4000	980

CONCLUSION

Methacrylate latexes give higher observed rates of reaction of aliphatic substrates than do polystyrene latexes, and the magnitude of the increase is greater for the more aliphatic latexes and substrates. Furthermore, especially in the case of PNP ester hydrolysis, this increase in the observed rate is the result of a more favorable equilibrium binding constant. 2-Ethylhexyl methacrylate latex particles show the most favorable equilibrium constant of the latexes studied. Another factor which affects the ability of the latexes to extract more of the substrate out of the aqueous phase is the nature of the quaternary ammonium groups; the tributylamine quaternized latexes are more effective than the trimethylamine latexes because the tributylamine moiety tends to increase the "aliphaticity" of the latex.

A diversity strategy has resulted in the synthesis and screening of a large number of potential latex catalysts in a time efficient manner. This approach can be used to further identify even more active catalysts for the neutralization of toxic organophosphorous compounds.

As was mentioned in the introduction, this model does not account for ion selectivities. As a result, we have performed a more detailed kinetic analysis with six of the latexes discussed here. A more detailed analysis reveals that the partition coefficient is indeed correlated to the aliphatic character of the latexes and the nature of the quaternary ammonium groups due to reasons stated above. In addition, the partition coefficient is also dependent upon the ionic strength of the reaction medium. This appears to be due to two factors: contraction of the latex particle resulting in a smaller intraparticle volume and also to salting the substrate out of the aqueous phase. This is discussed in more detail in the next chapter.

REFERENCES

(1) Fife, W. K. *Trends Polym. Sci.* **1995**, *3*, 214.

(2) Fendler, J. H.; Fendler, E. H. *Catalysis in Micellar and Macromolecular Systems*, Academic, New York, 1975.

(3) Zheng, Y.; Knoesel, R.; Galin, J. *Polymer* **1987,** *28*, 2297.

(4) Yang, Y.; Engberts, J. *J. Org. Chem.* **1991**, *56*, 4300.

(5) Ford, W. T.; Tomoi, M. *Adv. Polym. Sci.* **1984**, *55*, 49.

(6) Tomoi, M.; Ford, W. T. *Synthesis and Separations Using Functional Polymers,* ed. Sherrington, D. C.; Hodge, P., Wiley, Chichester, 1988, 181-207.

(7) Yamazaki, N. *Polym. J.* **1980**, *12*, 231.

(8) Bunton, C. A.; Savelli, G. *Adv. Phys. Org. Chem.* **1986**, *22*, 213.

(9) Moss, R.; Alwis, K.; Bizzigotti, G. *J. Am. Chem. Soc.* **1983**, *105*, 681.

(10) Moss, R.; Kotchevar, A.; Byeong, D. *Langmuir* **1996**, *12*, 2200.

(11) Lee, J. J.; Ford, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 3753.

(12) Yu, H.; Ford, W. T. *Langmuir* **1993**, *9*, 1999.

(13) Lee, J. J.; Ford, W. T. *J. Org. Chem.* **1993**, *58*, 4070.

(14) Tomoi, M.; Ford, W. T. *J. Am. Chem. Sci.* **1981**, *103*, 3821.

(15) Yang, Y. -C.; Baker, J. A.; Ward, J. R. *Chem. Rev.* **1992**, *92*, 1729.

(16) Walker, J.; Hoskins, F. US Army Natick Research Development and Engineering Center, personal communication.

(17) Blyth, C. A.; Knowles, J. *J. Am. Chem. Soc.* **1971**, *93*, 3017. (b) Blyth, C. A.; Knowles, J. R. *J. Am. Chem. Soc.* **1971**, *93*, 3021. (c) Hershfield, R.; Bender, M. L. *J. Am. Chem. Soc.* **1972**, *94*, 1376. (d) Kunitake, T.; Okahata, Y.; Sakamoto,

T. *J. Am. Chem. Soc.* **1976**, *98*, 7799. (e) Breslow, R.; Trainor, G.; Uleno, A. *J. Am. Chem. Soc.* **1983**, *105*, 2739. (f) Cram, D. J.; Lam, P. Y.; Ho, S. P. *J. Am. Chem. Soc.* **1986**, *108*, 839. (g) Broo, K. S.; Brive, L.; Ahlberg, P.; Baltzer, L. *J. Am. Chem. Soc.* **1997**, *119*, 11362.

(18) Nemethy, G.; Scheraga, H. *J. Chem. Phys.* **1962**, *36*, 3382.

(19) Maugh II, T.; Bruice, T. C. *J. Am. Chem. Soc.* **1971**, *93*, 6584.

(20) Guthrie, J. P. *Can. J. Chem.* **1973**, *51*, 3494.

(21) Murakami, Y.; Aoyama, Y.; Kida, M. *J. C. S. Perkin Trans. 2* **1977**, 1947.

(22) Guthrie, P. J. *J. Am. Chem. Soc.* **1991**, *113*, 3941.

(23) Stefanidis, D.; Cho, S.; Dhe-Paganon, S.; Jencks, W. P. *J. Am. Chem. Soc.* **1993**, *115*, 1650.

(24) Hengge, A. C.; Hess, R. A. *J. Am. Chem. Soc.* **1994**, *116*, 11256. (b) Hess, R. A.; Hengge, A. C.; Cleland, W. W. *J. Am. Chem. Soc.* **1997**, *119*, 6980.

(25) Hess, R. A.; Hengge, A. C.; Cleland, W. W. *J. Am. Chem. Soc.* **1998**, *120*, 2703.

(26) Tantillo, D. J.; Houk, K. N. *J. Org. Chem.* **1999**, *64*, 3066.

(27) Menger, F. M.; Ladika, M. *J. Am. Chem. Soc.* **1987**, *109*, 3145.

(28) Berezin, I. V.; Martinek, K.; Yatsimirski, A. K. *Russ. Chem. Rev. Eng. Trans.* **1973**, *42*, 787. (b) Bunton, C. A. *In the Chemistry of Enzyme Action*, Ed. Page, M. I., Elsevier, Amsterdam, 1984, 461-500.

(29) Behme, M. T. A.; Fullington, J. G; Noel, R.; Cordes, E. H. *J. Am. Chem. Soc.* **1965**, *87*, 265.

(30) Menger, F. M.; Portnoy, C. E. *J. Am. Chem. Soc.* **1967**, *89*, 4698.

(31) Romsted, L. R.; Cordes, E. H. *J. Am. Chem. Soc.* **1968**, *90*, 4404.

(32) Al-Awadi, N.; Williams, A. *J. Org. Chem.* **1990**, *55*, 2001.

(33) Quina, F. H.; Politi, M. J.; Cuccovia, I. M.; Baumgarten, E.; Martins-Frachetti, S. M.; Chaimovich, H. *J. Phys. Chem.* **1980**, *84*, 361. (b) Quina, F. H.; Chaimovich, H. *J. Phys. Chem.* **1979**, *83*, 1844.

(34) Bunton, C. A.; Nome, F.; Quina, F. H.; Romsted, L. S. *Acc. Chem. Res.* **1991**, *24*, 357.

(35) Miller, P. D.; Copeland, S. L.; Sanders, R.; Woodruff, A.; Gearhart, D.; Spivey, H. O.; Ford, W. T. *Langmuir*, submitted May 7, 1999.

(36) Xiang, X. -D.; Sun, X.; Briceno, G.; Lou, Y.; Wang, K. -A.; Chang H.; Wallace-Freedman, W. G.; Chen, S. -W.; Schultz, P. G. *Science* **1995**, *268*, 1738.

(37) Briceno, G.; Chang, H.; Sun, X.; Schultz, P. G. *Science* **1995**, *270*, 273.

(38) Sun, X. -D.; Gao, C.; Wang, J.; Xiang, X. -D. *Appl. Phys. Lett.* **1997**, *70*, 3353.

(39) Menger, F. M.; Eliseev, A. V.; Migulin, V. A. *J. Org. Chem.* **1995**, *60*, 6666. (b) Shimizu, K. D.; Cole, B. M.; Krueger, C. A.; Kuntz, K. W.; Snapper, M. L.; Hoveyda, A. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1704.

(40) Miller, P. D.; Ford, W. T. *J. Chem. Soc. Chem. Commun.* **1998**, 1151.

(41) Ford, W. T.; Yu, H.; Lee, J. J.; El-Hamshary, H. *Langmuir* **1993**, *9*, 1698.

(42) Tee, O. S.; Federtchenko, A. A. *Can. J. Chem.* **1997**, *75*, 1434.

(43) Wang, G. -J.; Fife, W. K. *J. Am. Chem. Soc.* **1998**, *120*, 883.

CHAPTER III

SECOND-ORDER INTRAPARTICLE RATE CONSTANTS AND PARTITION COEFFICIENTS FOR THE HYDROLYSIS OF *p*-NITROPHENYL ALKANOATES IN COLLOIDAL POLYMER DISPERSIONS

ABSTRACT

Rates of hydrolyses of *p*-nitrophenyl acetate, hexanoate, and octanoate in borate buffer solutions at 30°C are 2.3-16.5 times faster in the presence of 1.2 mg/mL of quaternary ammonium ion exchange latex particles than in water alone. The latexes were synthesized by emulsion copolymerization of styrene, butyl methacrylate, or 2-ethylhexyl methacrylate with 25 wt% of vinylbenzyl chloride (VBC), 1 wt% divinylbenzene, and 1 wt% (*m,p*-vinylbenzyl)trimethylammonium chloride followed by quaternization of the VBC units with either trimethylamine or tributylamine. Analysis of the kinetics of hydrolysis as a function of particle concentration, pH, and buffer concentration using an ion exchange model allowed for the calculation of second-order intraparticle rate constants, partition coefficients of substrates, and ion selectivity coefficients. This analysis showed that the major factor governing the rate of hydrolysis in these systems was the partition coefficient of the substrate from the aqueous phase into the particle phase. In addition, the hydroxide concentration inside the particles was up to ten times that in the aqueous phase. The intraparticle rate constants were similar to those in the aqueous phase.

INTRODUCTION

The previous chapter described the synthesis and preliminary screening of various alkyl methacrylates for the ability to promote hydrolysis of *p*-nitrophenyl hexanoate. As was mentioned earlier, polymers and colloids such as polyelectrolytes,[1-4] anion exchange resins,[5-7] surfactant micelles[1,2,8-10] and latexes[11-14] catalyze the reactions of anions with organic compounds. Here, we conduct a detailed investigation into the factors responsible for the rate increases observed in a representative few of the latexes surveyed.

We chose to concentrate on polystyrene (S), poly(butyl methacrylate) (BMA), and poly (2-ethylhexyl methacrylate) (EHMA) latexes which have been quaternized with trimethylamine (TMA) and tributylamine (TBA). These particular latexes were chosen because they represented the entire range of activities observed with EHMA-TBA being the most active, S-TMA being one of the least active, and BMA latexes in the intermediate ranges.

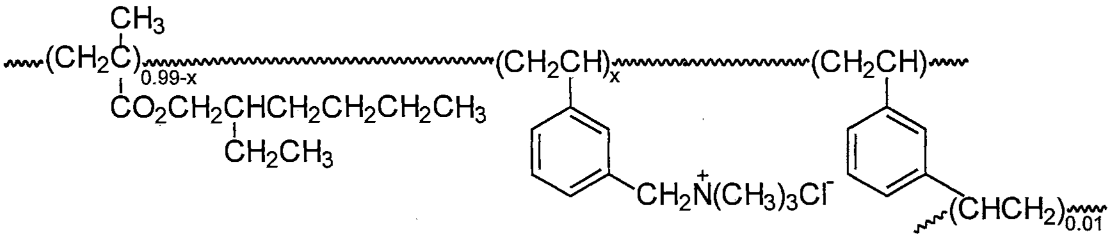


Figure 1. Structure of EHMA-TMA latex.

Hydrolyses of *p*-nitrophenyl esters have been studied in numerous micellar and polymer systems.[15.16] In this work, we measured rate constants of hydrolysis as functions of particle concentration, ester chain length, pH, and borate buffer concentration using only esters with chain lengths of eight or fewer carbons to avoid solubility limitations and self-aggregation of the substrates (Figure 2). We analyzed the results first by a simple binding model (Figure 3) and then by a detailed ion exchange model to obtain values for the intraparticle second-order rate constants, partition coefficients of the substrates into the particle phase, and selectivity coefficients for exchange of hydroxide and borate ions into the particles.

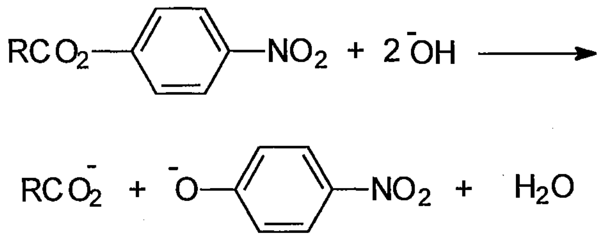


Figure 2. Basic hydrolysis of *p*-nitrophenyl alkanoates.

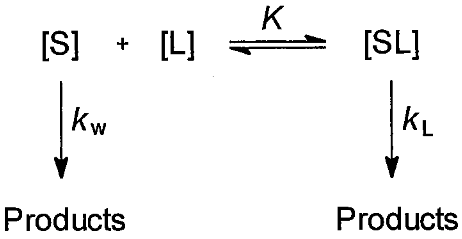


Figure 3. Model for determining phase equilibrium constants and pseudo-first order intraparticle rate constants.

Kinetic Models

Using the Menger-Portnoy model for pseudophase catalysis in molecular aggregates,[17] we assume that the substrate is distributed between the aqueous and the polymer phase according to an equilibrium constant, K (Figure 3), where [S] is the concentration of the substrate in the aqueous phase, [L] is the latex concentration, and [SL] is the concentration of the substrate in the latex based on total volume. Hydrolysis of the ester can then occur either in the aqueous phase with a first-order rate constant k_w, or inside the latex particle with a rate constant k_L. K is an equilibrium constant based on the total volume of the reaction mixture and does not adequately describe the concentration of the substrate in the latex particle itself. Likewise, k_L, is a pseudo-first order rate constant that incorporates the unknown intraparticle hydroxide ion concentration and the second-order intraparticle rate constant: $k_L = k_{2L}[OH^-]$. The values of the first-order rate constants k_w and k_L are extremely valuable for determining a partition coefficient for the substrate into the latex particle based on local volumes, as well as for applying a more complicated model for the determination of the second-order rate constant for hydrolysis.

In order to calculate the intraparticle second-order rate constant, we modified the pseudophase ion exchange model of micellar catalysis (Figure 4).[8,18-20]

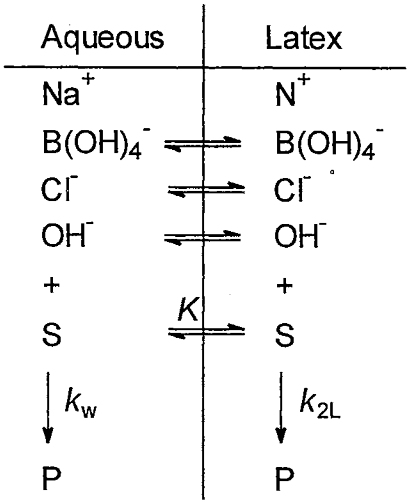


Figure 4. Ion exchange model for determination of partition coefficients, intraparticle second-order rate constants, and selectivity coefficients.

$$k_{obs}[S]_T = k_w[S]_w[OH^-]_wV_w + k_{2L}[S]_L[OH^-]_LV_L \tag{1}$$

$$[N^+] = [Cl^-]_w + [Cl^-]_L \tag{2}$$

$$[S]_T = [S]_w + [S]_L \tag{3}$$

$$[B]_T = [B(OH)_3]_w + [B(OH)_4^-]_w \tag{4}$$

$$[N^+]_L = [Cl^-]_L + [OH^-]_L + [B(OH)_4^-]_L \tag{5}$$

$$K_{OH/Cl} = [OH^-]_L[Cl^-]_w/[OH^-]_w[Cl^-]_L \tag{6}$$

$$K_{B/Cl} = [B(OH)_4^-]_L[Cl^-]_w/[B(OH)_4^-]_w[Cl^-]_L \tag{7}$$

$$K_{B/OH} = [B(OH)_4^-]_L[OH^-]_w/[B(OH)_4^-]_w[OH^-]_L \tag{8}$$

$$K = [S]_L/[S]_w \tag{9}$$

$$pK_a\,[B(OH)_3] = 9.23 \tag{10}$$

$$[H^+][OH^-] = 1.00 \times 10^{-14} \tag{11}$$

The total rate of reaction is the sum of the rates of reaction in the water and latex phases, as shown in eq 1 where V_w and V_L are the volume fractions of the water and latex phases and the concentrations and rate constants are based on the volumes of each phase. Although the volume fraction of the latex phase is generally ≤ 0.002, reaction mostly proceeds in the latex, for the rate enhancements observed in Chapter II are factors of 2.3-16.5 greater than the rate in water alone. To understand more easily the distributions of the substrate and the other species in the dispersions, the rest of the equations of the model use concentrations in the latex phase based on the total volume. Equations 2-4 are mass balances. The chloride ion in the dispersions comes only from the quaternary ammonium chloride latex (eq 2), the substrate PNP ester partitions between the water and latex phases (eq 3), and the total borate in the mixture can be approximated as the amount in the water (eq 4). The charge balance (eq 5) assumes no dissociation of counter ions from the latex particles. Of course this is an approximation, but measurements of the degree of dissociation of sodium ions from charged arenesulfonate latexes of about the same size as ours and having charged groups only on the surface, show ≤ 0.04 mol fraction of sodium ions dissociated.[21] Because of the large number of internal ionic sites in the gel phase of our quaternary ammonium ion latexes, the degree of dissociation of counter ions should be much smaller than that of the arenesulfonate latexes. Equations 6-8 are selectivity coefficients for ion exchange of chloride, hydroxide, and borate between the quaternary ammonium ion particles and the water phase. The selectivity coefficients are interdependent, so that determination of two of them gives the third. Equation 9 is an equilibrium association constant for substrate in latex based on concentrations in the overall mixture. After taking the volume fraction of the latex into account, it will be transformed into a partition coefficient. Equations 10-11 are the known acid association constant of boric acid and the autoprotolysis constant of water.

In eqs 1-9 the concentrations in the aqueous phase can be measured directly, but the concentrations in the latex phase and the intraparticle second-order rate constant k_{2L} cannot. Thus in any one experiment $[Cl^-]_L$, $[OH^-]_L$, $[B(OH)_4^-]_L$, $[S]_L$ and k_{2L} must be determined by regression analysis of kinetic data. The volume of the latex phase can be calculated from the mass of polymer employed and the average hydrodynamic diameter of the nearly monodisperse spherical particles, which is determined by dynamic light scattering.

The major differences between the ion exchange model for latex catalysis and the pseudophase ion exchange model for micellar catalysis are (1) the fraction of counter ions dissociated from the latex is negligibly small, (2) the volume of the latex particle can be measured directly, whereas the volume of the Stern layer at the surface of a micelle must be approximated, and (3) all structural units are in the particles, while monomeric surfactant molecules are in equilibrium with micelles.

EXPERIMENTAL

Materials

Vinylbenzyl chloride (VBC, 70/30 *m/p,* Scientific Polymer Products), divinylbenzene (80% mixture of isomers), butyl methacrylate (BMA), 2-ethylhexyl methacrylate (EHMA), and styrene (Aldrich) were distilled under vacuum and filtered through a plug of alumina just prior to use. (*m,p*-Vinylbenzyl)trimethylammonium chloride (VBTMACl) was prepared previously,[22] and used as a 0.0482 M aqueous solution (as determined by potentiometric titration with a chloride selective electrode). 2,2'-Azobis(*N,N*'-dimethyleneisobutyramidine) dihydrochloride (Wako Pure Chemical Ind. Ltd.), and tributylamine (Aldrich) was used as received. Trimethylamine (Eastman) was used as received as a 25% w/w solution in methanol. Triply deionized water was used in all experiments. The buffers were prepared from aqueous boric acid titrated to the appropriate pH with sodium hydroxide.

Equipment

Potentiometric titrations were carried out with an Orion combination chloride electrode (model 9617B). Kinetic experiments were performed on a Hewlett Packard diode array UV/VIS spectrophotometer (model 8452A) equipped with a thermostatted cell block and circulating water bath.

Synthesis of Latex Particles

Emulsion polymerization of the latex particles was carried out using the shot-growth method.[23] The following procedure was used for the preparation of EHMA-VBC copolymers with 25% w/w VBC units (EHMA). BMA and styrene latexes were prepared in a similar manner.

A three-necked round bottomed flask containing 200 mL of water was fitted with an overhead stirrer, a condenser, and a nitrogen inlet and placed into a 60°C oil bath. Nitrogen was bubbled through the water for 30 min, and a solution of (*m,p*-vinylbenzyl) trimethylammonium chloride (14 mL, 0.140 g of monomer) was added. The solution was stirred for 5 min, and 18.00 g of 2-ethylhexyl methacrylate, 6.00 g of vinylbenzyl chloride, and 0.300 g of divinylbenzene were added. After 10 min 1 mL of water containing 0.240 g of 2,2'-azobis(*N,N'*-dimethyleneisobutyramidine) dihydrochloride was added. After stirring for 60 min a second shot of monomers and initiator consisting of 6.00 g EHMA, 2.00 g VBC, 0.300 g VBTMACl, 0.100 g DVB, and 0.080 g of initiator was added. The reaction mixture was stirred for 4 h, cooled, and filtered through a plug of cotton to remove a trace of coagulum.

Solid content of Latexes

The solid content of all latexes was determined by accurately weighing 1 mL of the latex and drying to constant weight in a 130°C oven. Determinations performed in triplicate were reproducible to within 3% of the mean.

Quaternization of Latexes

Quaternization with trimethylamine was carried out in a sealed stainless steel reactor with magnetic stirring. A mixture of 50 mL of EHMA (5.31 g solid, 8.68 mmol VBC groups) diluted with 35 mL water and 6.17 g of 25 wt % aqueous trimethylamine (26.1 mmol) was sealed in the reactor and stirred for 48 h at 60°C. The excess trimethylamine was evaporated by bubbling nitrogen through the latex for 4 h. The latex was dialyzed in 50,000 MW cut-off regenerated cellulose Spectra/Por dialysis tubing for

1 week. Quaternization with tributylamine was carried out by refluxing the latex with 10% methanol and a three-fold excess of tributylamine.

The percent conversion of VBC groups to quaternary ammonium chloride groups was measured by potentiometric titration with a chloride selective electrode. To a 50 mL beaker was added 2.000 mL of the latex, 1.000 mL of 5 M $NaNO_3$, and 20 mL of water to cover the tip of the electrode. The solution was adjusted to pH 2 with 1 M HNO_3 and titrated with a 0.0500 M $AgNO_3$. A titration curve of mL titrant vs. millivolts was constructed and the end point was taken as the point of maximum slope.

Partition Coefficients of *p*-Nitrophenyl Alkanoates

The latex, 5 mL of the appropriate dilution to give a concentration of N+ units of 5.00 mM, was added to a 20 mL scintillation vial along with 200 μL of 2.5 mM PNP ester in acetonitrile. The mixture was stirred for 20 min, and drawn into a 5 mL syringe. The syringe tip was fitted with a 0.1 μm filter, and the dispersion was filtered into a polystyrene UV cuvette until about 1.7 mL of filtrate had been collected. Identical results were obtained when using quartz cuvettes, which indicates that the disposable cuvettes did not absorb any of the PNP ester. The concentration of the PNP-substrate in the aqueous phase was calculated from the absorbance at 290 nm, the molar extinction coefficient $\varepsilon = 5722$ of the PNP-alkanoate, and Abs = εbc. The ratio of the PNP ester concentration in the filtrate to PNP ester concentration in the original dispersion is the fraction in the aqueous phase, and the remainder is the fraction in the particle phase.

These experiments were reproducible to within 10% of the mean and were performed in triplicate. The results were used to calculate *K* in Figures 3 and 4.

Chloride Concentration in Aqueous Phase

The latex was diluted to $[N^+]$ = 5.00 mM, and filtered through a 0.1μm filter-tip syringe until enough was collected to allow 5.00 mL of filtrate to be transferred to a 50 mL beaker. The filtrate was analyzed by the method used to determine the chloride content of the original latexes.

Kinetic Measurements

The latex samples were diluted to a solid content of 1.2 mg/mL. A 2.00 mL aliquot of latex was diluted to 40.00 mL with 0.0200 M borate buffer (pH 9.38) to give $[N^+] = 6.15 \times 10^{-5}$ M. A 3.00 mL sample of the latex/buffer solution in a polystyrene cuvette was equilibrated at 30.0°C for 20 min, 30 μL of 2.5 mM PNP-hexanoate in acetonitrile was added, and a UV/VIS spectrum was taken every 0.9 s. The average Abs from 400-410 nm was plotted as a function of time.

The value of k_{obs} was calculated by the Hewlett Packard kinetics application from $\ln[(A_{inf}-A_o)/(A_{inf}-A_t) = k_{obs}t$. The value of A_{inf} was determined manually and the calculations were made from data over the first 20% conversion. Rate constants were measured in triplicate and the results were reproducible to within 5% of the mean.

Particle Size Determination

Diameters of unswollen particles were measured from TEM negatives on a microscope equipped with a micrometer scale. Diameters of particles under reaction conditions were determined from dynamic light scattering experiments. Both methods are reported in the literature.[13]

Fitting of the Data

The equations were solved numerically by a nonlinear least squares program based on the Marquardt-Levenberg algorithm. Equations which generate cubics were solved by a Newton-Raphson algorithm inserted into the problem dependent part of the least squares program.

RESULTS

Latexes

Six different latexes were synthesized for kinetic analysis. The latexes differed in the major component of the latex, either 2-ethylhexyl methacrylate (EHMA), butyl methacrylate (BMA) or styrene (S), and the quaternary ammonium group trimethylammonium (TMA) or tributylammonium (TBA). The latexes were analyzed by transmission electron microscopy (TEM) and dynamic light scattering (DLS) in order to determine the sizes under dry and swollen conditions respectively. The compositions and sizes of the latexes are presented in Tables I and II.

Table I. Compositions of Quaternary Ammonium Ion Functionalized Latexes.

composition	quaternization yield (%)	N^+/g^a	N^+/mL^b	N^+(mol %)^c
EHMA-TMA	80.0	1.22	0.419	24.2
EHMA-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] Mol% of N^+ repeat units.

Table II. Sizes of Quaternary Ammonium Ion Functionalized Latexes in Solutions of Buffer Strengths of 0.002 M, 0.01 M, and 0.02 M.

			d_h(nm)[c]			swelling ratio[d]		
composition	d_n[a] (nm)	d_w[b] (nm)	0.002	0.01	0.02	0.002	0.01	0.02
EHMA-TMA	135.1	135.6	211	203	198	3.8	3.4	3.2
EHMA-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,b] Calculated using measurements of fifty particles from TEM negatives. Number average diameter, $d_n = (\Sigma N_i d_i^3/\Sigma N_i)^{1/3}$. Weight average diameter, $d_w = (\Sigma N_i d_i^6/\Sigma N_i d_i^3)^{1/3}$. [c] Hydrodynamic diameter from dynamic light scattering in various buffer strength solutions. [d] $(d_h/d_w)^3$ in buffer solutions of various strengths.

Pseudo-First Order Intraparticle Rate Constants and Equilibrium Constants

Most of the hydrolysis rates were measured at pH 9.38 and 30.0°C. The observed psuedo-first-order rate constants, k_{obs}, for the hydrolysis of PNP-hexanoate in 1.2 mg/mL dispersions of the six latexes relative to the rate constant in the absence of latex are reported in Table III.

The activities of the styrene butyl methacrylate and 2-ethylhexyl methacrylate-based latexes were measured at 5-6 different particle concentrations. Using the Menger-Portnoy model for pseudophase catalysis in molecular aggregates,[16,17] the data were plotted according to eq. 12 as shown in Figure 5.

$$k_{obs} = (k_w/K + k_L[N^+])/(1/K + [N^+]) \qquad (12)$$

K is the association constant of the substrate from the aqueous phase into the particle phase, and k_w is the independently measured rate constant for hydrolysis in the absence of latex. Pseudo-first order intraparticle rate constants (k_L) and equilibrium constants (K) can then be calculated graphically. The results are reported in Table IV.

Table III. Relative Rate Constants of Hydrolysis of PNP-Hexanoate.[a]

latex	k_{obs}/k_w
EHMA-TBA	16.5
BMA-TBA	15.7
EHMA-TMA	12.5
S-TBA	12.0
BMA-TMA	6.1
S-TMA	2.3

[a] At 30.0°C in 0.02 M pH 9.38 borate buffer at a latex concentration of 1.2 mg/mL with $[N^+]$ = 62 μM and substrate concentration of 4.2 μM. k_w for the reaction in the absence of latex was 3.26×10^{-4} s^{-1}.

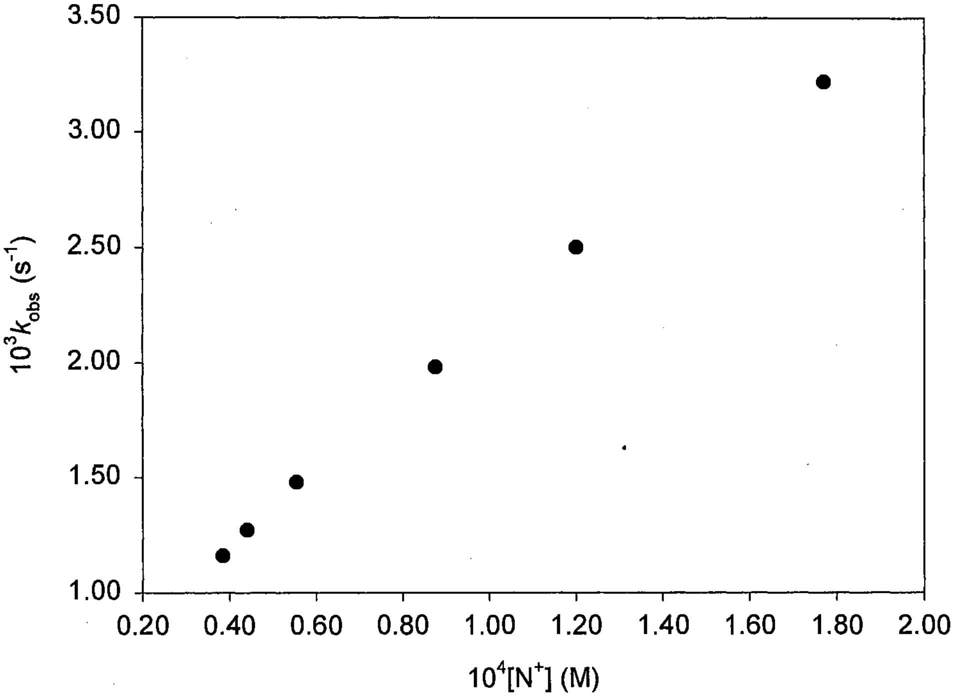


Figure 5. Plot of observed rate constants versus the concentration of quaternary ammonium ion in the latexes.

Table IV. Intraparticle Pseudo-First Order Rate Constants and Equilibrium Constants.[a]

	S		BMA		EHMA	
PNP ester	$10^3 k_L/s^{-1}$	$10^{-3} K/M^{-1}$	$10^3 k_L/s^{-1}$	$10^{-3} K/M^{-1}$	$10^3 k_L/s^{-1}$	$10^{-3} K/M^{-1}$
TMA-quaternized						
Acetate	11.3	2.0	9.3	2.3	7.4	2.3
Hexanoate	5.7	2.1	5.9	11.8	4.7	21.0
Octanoate	4.7	12.7	5.3	46.0	4.9	70.0
TBA-quaternized						
Acetate	11.9	3.1	9.5	4.1	9.0	5.0
Hexanoate	5.8	15.1	5.8	25.0	5.8	31.0
Octanoate	5.7	39.0	5.3	74.0	5.1	88.0

[a] At 30.0°C in 0.02 M pH 9.38 borate buffer. The pseudo-first order rate constants in the absence of latex, k_w, were 6.0×10^{-4} s^{-1}, 3.26×10^{-4} s^{-1} and 1.22×10^{-4} s^{-1} for PNP-acetate, hexanoate and octanoate respectively.

Partition Coefficients and Second-Order Rate Constants

Neither the local concentrations of OH^- and $B(OH)_4^-$ inside the latex particle nor the intraparticle second-order rate constants can be measured directly. They must be calculated from a statistical analysis of k_{obs} as a function of buffer strength, pH, and particle concentration. The results of these experiments are presented in tabular form in the Appendix. However, the analysis can only be done if one knows the partition coefficient, K_P, of the substrate into the latex particles. This can be determined from the ratio of the concentration of substrate in the latex to the total volume concentration of the substrate in the aqueous phase S_L/S_w, which can be determined by combining eqs. (13) and (14), where $[N^+]$ is the concentration of the quaternary ammonium sites in the latex particle and all concentrations refer to the total volume of the dispersion. An expression for K_P can then be derived from eq. (15), by relating it to the total volume, V_T, and the particle volume, V_L, eq. (16), where S_L' is the local concentration of the substrate inside the particle.

$$S_L/S_T = K[N^+]/(1 + K[N^+]) \tag{13}$$

$$S_w/S_T = 1/(1 + K[N^+]) \tag{14}$$

$$S_L/S_w = K[N^+] \tag{15}$$

$$K_P = S_L'/S_w = S_L/S_w(V_T/V_L) \tag{16}$$

The value for K_P obtained by the above approach was used as the initial value for statistical analysis of the data and was entered as an adjustable parameter. The initial value for the intraparticle second-order rate constant, k_2, was estimated as $k_L/[OH^-]_w$, where k_L is the intraparticle pseudo-first order rate constant, and $[OH^-]$ is the external hydroxide ion concentration. In addition to K_P and k_2, the ion exchange selectivity coefficients $K_{B/Cl}$ and $K_{OH/Cl}$ were also entered as adjustable parameters because neither of these constants were known. By comparison of titrations of latexes in excess sodium nitrate and nitric acid which force all of the chloride ion into the aqueous phase, with those performed on the reaction mixture from which the latex had been filtered, we determined that >98% of the chloride was displaced from the particles (Figure 6). Thus experimental data entered into the analysis were: observed rate constant, weight concentration of latex (mg dry latex/mL), anion exchange capacity (mmol/g dry latex), swelling factor (mL wet latex/mL dry latex), substrate and buffer concentration based on total reaction volume. The second-order rate constant in the absence of latex, k_{2w}, the pK_a of boric acid, and pK_w were entered as system constants.

The data were fitted to the equations at first by masking K_P and $K_{B/Cl}$ at the initial values and allowing the values of k_{2L} and $K_{OH/Cl}$ to float. Once a solution was reached, all four variables were allowed to float in order to ensure that a false solution was not forced. The results of minimization of the above data are presented in Tables V-VII for each latex.

The selectivity coefficients were also allowed to adjust during the minimization process. The values of $K_{OH/Cl}$ agrees with those reported in literature.[18-20] The value for $K_{B/Cl}$ also agrees with earlier work.[24] Once a selectivity coefficient was determined for a given latex at a given buffer concentration, it was not allowed to vary among the three esters.

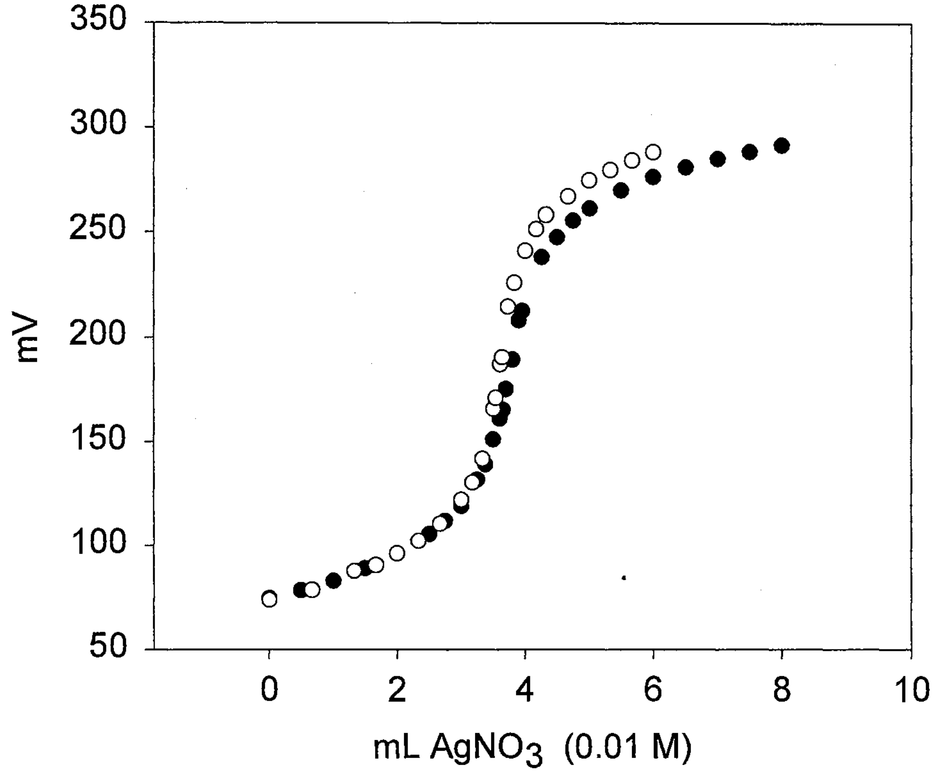


Figure 6. Chloride-selective potentiometric titration of latex in 5 M $NaNO_3$ at pH 2 (solid circles, endpoint = 3.64 mL titrant corresponding to 0.0728 M chloride ion) and reaction medium filtered through 0.1μm membrane to remove latex particles (hollow circles, endpoint = 3.60 mL corresponding to 0.0720 M chloride ion).

Table V. Second-Order Rate Constants, Partition Coefficients, and Selectivity Coefficients for PNP Ester Hydrolysis in Polystyrene Latexes.[a]

buffer strength/ ester	TBA quaternized		TMA quaternized	
	k_{2L} ($M^{-1}s^{-1}$)[b]	$10^{-3}K_P$	k_{2L} ($M^{-1}s^{-1}$)	$10^{-3}K_P$
0.002 M borate				
PNP-Acetate	24.2	0.449	23.1	0.323
PNP-Hexanoate	21.1	1.57	18.4	1.04
PNP-Octanoate	19.3	2.29	19.5	1.38
0.01 M borate				
PNP-Acetate	26.1	0.801	24.9	0.509
PNP-Hexanoate	23.0	2.91	21.8	1.59
PNP-Octanoate	19.9	3.51	20.1	1.73
0.02 M borate				
PNP-Acetate	25.4	1.33	25.7	0.635
PNP-Hexanoate	21.1	4.69	22.7	2.42
PNP-Octanoate	19.3	5.02	19.1	2.91

[a] In borate buffer at pH 9.38 and 30.0°C. [b] The second-order rate constants for hydrolysis in the absence of latex, k_{2w}, were 23.7 $M^{-1}s^{-1}$, 13.0 $M^{-1}s^{-1}$ and 4.9 $M^{-1}s^{-1}$ for PNP acetate, hexanaote, and octanoate respectively. The calculated selectivity coefficients were $K_{OH/Cl} = 0.06$ and $K_{B/Cl} = 0.16$.

Table VI. Second-Order Rate Constants, Partition Coefficients, and Selectivity Coefficients for PNP Ester Hydrolysis in Butyl Methacrylate Latexes.[a]

	TBA quaternized		TMA quaternized	
buffer strength/ ester	k_{2L} ($M^{-1}s^{-1}$)	$10^{-3}K_P$	k_{2L} ($M^{-1}s^{-1}$)	$10^{-3}K_P$
0.002 M borate				
PNP-Acetate	22.4	1.98	20.3	1.56
PNP-Hexanoate	14.9	20.3	12.5	11.2
PNP-Octanoate	13.7	27.7	11.1	25.1
0.01 M borate				
PNP-Acetate	21.1	4.13	22.3	2.94
PNP-Hexanoate	17.4	31.8	15.2	19.0
PNP-Octanoate	13.7	42.0	12.6	31.2
0.02 M borate				
PNP-Acetate	22.4	6.93	22.8	4.88
PNP-Hexanoate	18.0	57.7	17.5	43.3
PNP-Octanoate	15.5	77.1	13.5	63.9

[a] See footnotes of Table 4. The calculated selectivity coefficients were $K_{OH/Cl}$=0.10 and $K_{B/Cl}$=0.18.

Table VII. Second-Order Rate Constants, Partition Coefficients, and Selectivity Coefficients for PNP Ester Hydrolysis in 2-Ethylhexyl Methacrylate Latexes.[a]

	TBA quaternized		TMA quaternized	
buffer strength/ ester	k_{2L} ($M^{-1}s^{-1}$)	$10^{-3}K_P$	k_{2L} ($M^{-1}s^{-1}$)	$10^{-3}K_P$
0.002 M borate				
PNP-Acetate	20.5	2.11	19.7	1.87
PNP-Hexanoate	18.0	25.9	17.4	19.8
PNP-Octanoate	16.8	38.1	16.1	30.1
0.01 M borate				
PNP-Acetate	23.0	4.66	23.5	3.98
PNP-Hexanoate	19.9	36.2	19.2	30.5
PNP-Octanoate	18.0	51.8	17.3	44.7
0.02 M borate				
PNP-Acetate	25.5	7.93	26.1	7.49
PNP-Hexanoate	21.7	67.7	20.8	64.2
PNP-Octanoate	19.9	90.0	19.2	88.6

[a] See footnotes for Table 4. The calculated selectivity coefficients were $K_{OH/Cl}$=0.10 and $K_{B/Cl}$=0.17.

DISCUSSION

The most important and general result of this investigation is that the partitioning of the PNP ester between the aqueous and latex phases is by far the biggest factor responsible for the varied activities of the latexes. Thus the experimental parameters that affect the partition coefficients can be optimized for catalytic activity. By comparison, the second order rate constants for attack of hydroxide on the PNP esters vary only slightly. The wide range of equilibrium constants and narrow range of intraparticle first-order rate constants are clear in the initial analysis of the rates in Table IV and are supported by all of the partition coefficient and intraparticle second-order rate constant data in Tables V-VII.

Several parameters affect the partition coefficients: (1) K_p increases with increasing chain length of the PNP alkanoate as expected because of decreasing solubility in water. Since the molar solubilities of homologous aliphatic compounds in water decrease by a factor of at least 2 per CH_2 group,[25] and the K_p values increase by smaller factors per alkyl group, the solubilites of the PNP alkanoates in latexes must also decrease with increasing chain length, but by a smaller factor than their solubilities in water. (2) K_p increases with increasing "aliphaticity" of the latex in the order polystyrene << poly(butyl methacrylate) < poly(2-ethylhexyl methacrylate). The branched 2-ethylhexyl methacrylate also is more active than linear octyl methacrylate in analogous catalysts,[26] probably because the branched structure creates more free volume for solutes. (3) K_p is larger for tributylamine- than for trimethylamine-quaternized latexes because the ammonium ion with the larger ionic radius is less hydrophilic. The larger ionic radius of the tributylammonium increases K_p over that for the trimethylammonium ion latex for the polystyrene latexes by factors of 1.5-2.0, but that factor is smaller for the BMA latexes and still smaller for the EHMA latexes. Apparently the environment for the PNP alkanoates in a EHMA latex that is already highly aliphatic is not improved as much by increasing the size of alkyl groups on positive nitrogen. (4) K_p increases with increasing buffer concentration. This is due to two factors. First, increasing ionic strength of the aqueous phase tends to decrease the solubility of ("salt out") organic solutes in water. Second, increasing ionic strength due to increasing buffer concentration osmotically reduces the swollen volume of the latex.

The values of the intraparticle second order rate constants k_{2L} cover only a narrow range. (1) k_{2L} decreases with increasing chain length of the PNP alkanoate, as has been reported for hydrolyses in homogeneous solutions and attributed to coiling of the aliphatic chain that hinders attack of nucleophiles at carbonyl carbon.[27] The values of k_{2L} of PNP octanoate are up to a factor of four larger than those of k_{2w} in the absence of latex. This is probably due to the polymer matrix acting as a better solvent for the uncoiling of the alkyl chain of the ester, allowing the hydroxide ion easier access to the carbonyl carbon atom. (2) k_{2L} does not depend on the identity of the amine which was used to introduce the quaternary ammonium functionality into the latex. This result is surprising because one would expect the more lipophilic ammonium ion to be more reactive because a hydroxide ion associated with such a group would have fewer water molecules solvating it, making it react more readily. (3) In most examples k_{2L} increases slightly in the order BMA < EHMA < S, but many of the data are within experimental uncertainty of one another.

The ion exchange selectivity coefficient $K_{OH/Cl}$ was determined to be 0.06 in the polystyrene latexes and 0.10 in the methacrylate ester latexes. The resulting lower intraparticle concentration of hydroxide ion also contributes to the lower activity of the polystyrene latexes.

CONCLUSION

The ion exchange model fits well the kinetic data for basic hydrolysis of PNP-esters in buffered dispersions of polymer latexes. Cationic polymer latexes of styrene, butyl methacrylate, and 2-ethylhexyl methacrylate are active phase transfer catalysts for the hydrolysis of PNP-acetate, hexanoate, and octanoate. Partition coefficients for the esters into the latex particle of up to 9×10^4, and intraparticle hydroxide concentrations ten times higher than in the external aqueous solution are responsible for the observed rate enhancements. Intraparticle second-order rate constants are slightly higher than the rate constant for hydrolysis in water alone. The most active latex studied was a copolymer of 2-ethylhexyl methacrylate and vinylbenzyl chloride with 25% w/w VBC units which was quaternized with tributylamine.

REFERENCES

(1) Fife, W. K. *Trends Polym. Sci.* **1995**, *3*, 214.

(2) Fendler, J. H.; Fendler, E. H. *Catalysis in Micellar and Macromolecular Systems,* Academic, New York, 1975.

(3) Zheng, Y.; Knoesel, R.; Galin, J. *Polymer* **1987,** *28*, 2297.

(4) Yang, Y.; Engberts, J. *J. Org. Chem.* **1991**, *56*, 4300.

(5) Ford, W. T.; Tomoi, M. *Adv. Polym. Sci.* **1984**, *55*, 49.

(6) Tomoi, M.; Ford, W. T. *Synthesis and Separations Using Functional Polymers*, ed. Sherrington, D. C.; Hodge, P., Wiley: Chichester, 1988, 181-207.

(7) Yamazaki, N. *Polym. J.* **1980**, *12*, 231.

(8) Bunton, C. A.; Savelli, G. *Adv. Phys. Org. Chem.* **1986**, *22*, 213.

(9) Moss, R.; Alwis, K.; Bizzigotti, G. *J. Am. Chem. Soc.* **1983**, *105*, 681.

(10) Moss, R.; Kotchevar, A.; Byeong, D. *Langmuir* **1996**, *12,* 2200.

(11) Lee, J. J.; Ford, W. T. *J. Am. Chem. Soc.* **1994,** *116*, 3753.

(12) Yu, H.; Ford, W. T. *Langmuir* **1993**, *9*, 1999.

(13) Lee, J. J.; Ford, W. T. *J. Org. Chem.* **1993**, *58*, 4070.

(14) Tomoi, M.; Ford, W. T. *J. Am. Chem. Soc.* **1981,** *103*, 3821.

(15) (a) Blyth, C. A.; Knowles, J. R. *J. Am. Chem. Soc.* **1971**, *93*, 3017. (b) Bhattacharya, S.; Snehalatha, K. *Langmuir* **1997**, *13*, 378. (c) Wang, G. -J.; Fife, W. K. *Langmuir* **1997**, *13*, 3320. (d) Wang, G. -J.; Fife, W. K. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1543. (e) Wulff, G.; Gross; T.; Schonfeld, R. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1962. (f) Wang, G. -J.; Fife, W. K. *J. Am. Chem. Soc.* **1998,** *120*, 883.

(16) Tee, O. S.; Fedortchenko, A. A. *Can. J. Chem.* **1997**, *75*, 1434.

(17) Menger, F.; Portnoy, C. *J. Am. Chem. Soc.* **1967**, *89*, 4698.

(18) Quina, F. H.; Chaimovich, H. *J. Phys. Chem.* **1979**, *83*, 1844.

(19) Quina, F. H.; Politi, M. J.; Cuccovia, I. M.; Baumgarten,E.; Martins-Franchetti, S. M.; Chaimovich, H. *J. Phys. Chem.* **1980**, *84*, 361.

(20) Romsted, L. S. *Surfactants in Solution,* ed. Mittal, K. L.; Lindman, B. Plenum: New York, 1984, 1015-1068.

(21) Ito, K; Ise, N; Olubo, T. *J. Chem. Phys.* **1985**, *82*, 5732.

(22) Ford, W. T.; Yu, H.; Lee, J. J.; El-Hamshary, H. *Langmuir* **1993**, *9*, 1698.

(23) Kim, J. H.; Chainey, M.; El-Asser, M. S.; Vanderhoff, J. W. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 3187.

(24) Jung, W. N. Ph.D. dissertation, Korea Advanced Institute of Science and Technology 1992.

(25) Tanford, C. *The Hydrophobic Effect*, 2nd ed.; Wiley: New York, 1980.

(26) Miller, P. D.; Ford, W. T. *J. Chem. Soc. Chem. Commun.* **1998**, 1151.

(27) (a) Blyth, C. A.; Knowles, J. R. *J. Am. Chem. Soc.* **1971**, *93*, 3021. (b) Hershfield, R.; Bender, M. L. *J. Am. Chem. Soc.* **1972**, *94*, 1376. (c) Guthrie, J. P. *Can. J. Chem.* **1973**, *51*, 3494.

CHAPTER IV

CONCLUDING REMARKS

SUMMARY

This work has shown that poly(alkyl methacrylate) latex particles are more effective catalytic media than polystyrene latexes for the hydrolysis of aliphatic substrates. The primary factor responsible for the enhanced activity is the more favorable partition coefficient of aliphatic substrates into the methacrylate latex particles than into polystyrene particles. The intrinsic intraparticle rate constant for hydrolysis does not differ significantly from that in the aqueous phase.

The most active polymer latex examined in this study was a copolymer composed of 74 wt% poly(2-ethylhexyl methacrylate) and 25 wt% poly((vinylbenzyl)trimethylbutyl ammonium chloride) cross-linked with 1 wt% divinylbenzene. This latex concentrated *p*-nitrophenyl octanoate up to 9 x 10^4 times that in the aqueous phase in 0.02 M borate buffer at pH 9.4.

As a result of this study, samples of the poly(2-ethylhexyl methacylate) have been sent to the U. S. Army Research Laboratory at Aberdeen Proving Grounds, MD for testing against nerve agent simulants, and nerve agents themselves. These latexes have been looked at as possible additives to a protective skin cream that the army is developing. At this point, we are trying to make the latex compatible with the perfluorinated polyether which is the major component of the cream. It remains to be seen whether or not latexes will prove useful for the catalyic neutralization of chemical warfare agents. At any rate, the information which has come out of this investigation has provided researchers with a more in depth understanding of reactions that occur within polymer latex particles, and the equilibrium constants and the microscopic rate constants that drive those reactions.

APPENDIX

KINETIC DATA

The following tables contain the kinetic data collected on the analysis of rates for hydrolysis of *p*-nitrophenyl (PNP)-acetate, PNP-hexanoate, and PNP-octanoate by polystyrene (PS), poly(butyl methacrylate) (BMA) and poly(2-ethylhexyl methacrylate) (EHMA) latexes which were quaternized by trimethylamine (TMA) and tributylamine (TBA). The experimental details of data acquisition are outlined in Chapter III.

In addition to the observed rates of hydrolysis, which are experimental observations, the tables also contain values for the fraction of substrate bound to the particles. These were calculated after the data was analyzed by a nonlinear least squares approach. They are included in these tables for both clarity and convienence.

In all of the following tables, the avg. k_{obs} is the mean of two or more individual experiments (usually three). The reported rate constants have a relative error of <5%. The value of V_L was calculated from the anion exchange capacity (in mmol N^+/g), the density of the latex (taken to be 1.10 g/mL), the swelling factor of the latex in the reaction medium and the concentration of latex in the reaction mixture.

Table I. Observed Rate Constants for the Hydrolysis of PNP-Acetate by EHMA-TBA in 0.002M Borate Buffer[a]

concentration 10^4 [N^+][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
3.95	12.1	0.72	0.421	2.30	5.90	10.8
1.15	3.52	0.43	0.310	1.59	4.45	7.91
0.677	2.07	0.30	0.264	1.30	3.86	6.73
0.320	0.979	0.17	0.214	0.980	3.21	5.42
0.204	0.624	0.12	0.193	0.849	2.94	4.89

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.

[b] Anion exchange capacity = 1.04 mmol N^+/g

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 2.57 x 10^{-5} M, 1.45 x 10^{-4} M, 3.55 x 10^{-4} M and 6.61 x 10^{-4} M for pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table II. Observed Rate Constants for the Hydrolysis of PNP-Hexanoate by EHMA-TBA in 0.002M Borate Buffer[a]

concentration 10^4 [N$^+$][b] (M)	10^4 V$_L$[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
3.95	12.1	0.97	0.451	2.54	6.23	11.6
1.15	3.52	0.90	0.424	2.37	5.87	10.9
0.677	2.07	0.84	0.403	2.25	5.59	10.4
0.320	0.979	0.72	0.355	1.96	4.95	9.11
0.204	0.624	0.62	0.317	1.73	4.45	8.14

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.

[b] Anion exchange capacity = 1.04 mmol N$^+$/g

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 2.57 x 10^{-5} M, 1.45 x 10^{-4} M, 3.55 x 10^{-4} M and 6.61 x 10^{-4} M for pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table III. Observed Rate Constants for the Hydrolysis of PNP-Octanoate by EHMA-TBA in 0.002M Borate Buffer[a]

concentration 10^4 $[N^+]$[b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1}) pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
3.95	12.1	0.98	0.423	2.39	5.85	10.9
1.15	3.52	0.93	0.403	2.27	5.56	10.4
0.677	2.07	0.89	0.387	2.18	5.35	9.94
0.320	0.979	0.79	0.347	1.94	4.80	8.91
0.204	0.624	0.70	0.313	1.75	4.35	8.05

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.

[b] Anion exchange capacity = 1.04 mmol N^+/g

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 2.57 x 10^{-5} M, 1.45 x 10^{-4} M, 3.55 x 10^{-4} M and 6.61 x 10^{-4} M for pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table IV. Observed Rate Constants for the Hydrolysis of PNP-Acetate by EHMA-TBA in 0.01M Borate Buffer[a]

concentration 10^4 [N$^+$][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1}) pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
3.95	11.0	0.84	0.660	3.36	10.0	18.1
1.15	3.22	0.60	0.517	2.58	7.87	14.1
0.677	1.89	0.47	0.436	2.13	6.65	11.8
0.320	0.895	0.29	0.329	1.55	5.06	8.81
0.204	0.571	0.21	0.278	1.27	4.30	7.37

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.

[b] Anion exchange capacity = 1.04 mmol N$^+$/g

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 3.31 x 10^{-5} M, 1.70 x 10^{-4} M, 5.01 x 10^{-4} M and 9.12 x 10^{-4} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table V. Observed Rate Constants for the Hydrolysis of PNP-hexanoate by EHMA-TBA in 0.01M Borate Buffer[a]

concentration 10^4 [N^+][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
3.95	11.0	0.98	0.643	3.30	9.73	17.7
1.15	3.22	0.92	0.614	3.14	9.29	16.9
0.677	1.89	0.87	0.584	2.99	8.85	16.1
0.320	0.895	0.76	0.522	2.65	7.91	14.3
0.204	0.571	0.67	0.471	2.38	7.15	12.9

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.04 mmol N^+/g

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 3.31×10^{-5} M, 1.70×10^{-4} M, 5.01×10^{-4} M and 9.12×10^{-4} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table VI. Observed Rate Constants for the Hydrolysis of PNP-Octanoate by EHMA-TBA in 0.01M Borate Buffer[a]

concentration 10^4 $[N^+]^b$ (M)	10^4 $V_L{}^c$	$\chi_L{}^d$	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
3.95	11.0	0.98	0.584	3.00	8.84	16.1
1.15	3.22	0.94	0.564	2.90	8.54	15.5
0.677	1.89	0.91	0.543	2.78	8.21	14.9
0.320	0.895	0.82	0.495	2.53	7.49	13.6
0.204	0.571	0.75	0.454	2.32	6.87	12.5

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.
[b] Anion exchange capacity = 1.04 mmol N^+/g
[c] Volume fraction of latex in reaction mixture.
[d] Fraction of substrate bound to particles.
[e] Intraparticle hydroxide concentration was 3.31×10^{-5} M, 1.70×10^{-4} M, 5.01×10^{-4} M and 9.12×10^{-4} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table VII. Observed Rate Constants for the Hydrolysis of PNP-Acetate by EHMA-TBA in 0.02M Borate Buffer[a]

concentration 10^4 $[N^+]$[b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
3.95	10.7	0.89	1.10	4.71	17.6	25.5
1.15	3.12	0.71	0.910	3.87	14.5	21.1
0.677	1.83	0.59	0.780	3.31	12.4	18.1
0.320	0.867	0.41	0.584	2.46	9.29	13.6
0.204	0.553	0.30	0.475	1.98	7.55	11.2

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.
[b] Anion exchange capacity = 1.04 mmol N^+/g
[c] Volume fraction of latex in reaction mixture.
[d] Fraction of substrate bound to particles.
[e] Intraparticle hydroxide concentration was 4.77 x 10^{-5} M, 2.04 x 10^{-4} M, 7.59 x 10^{-4} M and 1.10 x 10^{-3} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table VIII. Observed Rate Constants for the Hydrolysis of PNP-Hexanoate by EHMA-TBA in 0.02M Borate Buffer[a]

concentration 10^4 $[N^+]$[b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
3.95	10.7	0.99	1.02	4.37	16.3	23.6
1.15	3.12	0.95	0.993	4.25	15.8	22.9
0.677	1.83	0.93	0.962	4.11	15.3	22.2
0.320	0.867	0.85	0.897	3.83	14.3	20.7
0.204	0.553	0.79	0.834	3.56	13.3	19.3

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.04 mmol N^+/g

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 4.77×10^{-5} M, 2.04×10^{-4} M, 7.59×10^{-4} M and 1.10×10^{-3} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table IX. Observed Rate Constants for the Hydrolysis of PNP-Octanoate by EHMA-TBA in 0.02M Borate Buffer[a]

concentration 10^4 [N$^+$][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
3.95	10.7	0.99	0.940	4.02	15.0	21.7
1.15	3.12	0.97	0.919	3.93	14.6	21.2
0.677	1.83	0.94	0.895	3.83	14.2	20.6
0.320	0.867	0.89	0.845	3.61	13.4	19.5
0.204	0.553	0.83	0.795	3.40	12.7	18.3

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.

[b] Anion exchange capacity = 1.04 mmol N$^+$/g

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 4.77 x 10^{-5} M, 2.04 x 10^{-4} M, 7.59 x 10^{-4} M and 1.10 x 10^{-3} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table X. Observed Rate Constants for the Hydrolysis of PNP-Acetate by EHMA-TMA in 0.002 M Borate Buffer[a]

concentration 10^4 $[N^+]$[b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
4.01	11.4	0.68	0.393	2.13	5.53	10.1
1.22	3.45	0.39	0.289	1.46	4.18	7.37
0.680	1.93	0.26	0.244	1.18	3.60	6.21
0.325	0.920	0.15	0.202	0.905	3.05	5.11
0.200	0.566	0.10	0.184	0.788	2.81	4.63

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.
[b] Anion exchange capacity = 1.22 mmol N^+/g.
[c] Volume fraction of latex in reaction mixture.
[d] Fraction of substrate bound to particles.
[e] Intraparticle hydroxide concentration was 2.57×10^{-5} M, 1.45×10^{-4} M, 3.55×10^{-4} M and 6.61×10^{-4} M for pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XI. Observed Rate Constants for the Hydrolysis of PNP-Hexanoate by EHMA-TMA in 0.002 M Borate Buffer[a]

concentration 10^4 $[N^+]$[b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
4.01	11.4	0.96	0.433	2.44	5.99	11.1
1.22	3.45	0.87	0.399	2.23	5.53	10.3
0.680	1.93	0.79	0.372	2.07	5.17	9.56
0.325	0.920	0.65	0.318	1.74	4.45	8.15
0.200	0.566	0.53	0.275	1.48	3.87	7.04

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.
[b] Anion exchange capacity = 1.22 mmol N^+/g.
[c] Volume fraction of latex in reaction mixture.
[d] Fraction of substrate bound to particles.
[e] Intraparticle hydroxide concentration was 2.57×10^{-5} M, 1.45×10^{-4} M, 3.55×10^{-4} M and 6.61×10^{-4} M for pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XII. Observed Rate Constants for the Hydrolysis of PNP-Octanoate by EHMA-TMA in 0.002 M Borate Buffer[a]

concentration 10^4 [N^+][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
4.01	11.4	0.97	0.404	2.28	5.58	10.4
1.22	3.45	0.91	0.378	2.13	5.23	9.73
0.680	1.93	0.85	0.358	2.01	4.96	9.21
0.325	0.920	0.73	0.312	1.75	4.33	8.02
0.200	0.566	0.63	0.272	1.51	3.78	6.99

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.22 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 2.57×10^{-5} M, 1.45×10^{-4} M, 3.55×10^{-4} M and 6.61×10^{-4} M for pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XIII. Observed Rate Constants for the Hydrolysis of PNP-Acetate by EHMA-TMA in 0.01 M Borate Buffer[a]

concentration 10^4 $[N^+]^b$ (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
4.01	10.2	0.80	0.655	3.33	9.94	18.0
1.22	3.09	0.55	0.496	2.46	7.56	13.5
0.680	1.72	0.41	0.405	1.96	6.19	10.9
0.325	0.823	0.25	0.305	1.41	4.69	8.11
0.200	0.507	0.17	0.255	1.14	3.95	6.72

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.22 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 3.31×10^{-5} M, 1.70×10^{-4} M, 5.01×10^{-4} M and 9.12×10^{-4} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XIV. Observed Rate Constants for the Hydrolysis of PNP-Hexanoate by EHMA-TMA in 0.01 M Borate Buffer[a]

concentration 10^4 $[N^+]^b$ (M)	10^4 V_L^c	χ_L^d	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
4.01	10.2	0.97	0.620	3.18	9.39	17.1
1.22	3.09	0.90	0.582	2.98	8.82	16.0
0.680	1.72	0.84	0.546	2.79	8.27	15.0
0.325	0.823	0.72	0.478	2.42	7.25	13.1
0.200	0.507	0.61	0.418	2.11	6.35	11.4

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.22 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 3.31×10^{-5} M, 1.70×10^{-4} M, 5.01×10^{-4} M and 9.12×10^{-4} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XV. Observed Rate Constants for the Hydrolysis of PNP-Octanoate by EHMA-TMA in 0.01 M Borate Buffer[a]

concentration 10^4 $[N^+]$[b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
4.01	10.2	0.98	0.563	2.89	8.52	15.5
1.22	3.09	0.93	0.536	2.75	8.12	14.8
0.680	1.72	0.89	0.509	2.61	7.71	14.0
0.325	0.823	0.79	0.457	2.34	6.92	12.6
0.200	0.507	0.69	0.407	2.08	6.17	11.2

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.22 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 3.31×10^{-5} M, 1.70×10^{-4} M, 5.01×10^{-4} M and 9.12×10^{-4} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XVI. Observed Rate Constants for the Hydrolysis of PNP-Acetate by EHMA-TMA in 0.02 M Borate Buffer[a]

concentration 10^4 [N^+][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
4.01	9.56	0.88	1.11	4.74	17.7	25.6
1.22	2.91	0.69	0.900	3.83	14.3	20.9
0.680	1.62	0.55	0.750	3.18	11.9	17.4
0.325	0.775	0.37	0.552	2.32	8.78	12.9
0.200	0.477	0.26	0.438	1.82	6.96	10.3

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.

[b] Anion exchange capacity = 1.22 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 4.77 x 10^{-5} M, 2.04 x 10^{-4} M, 7.59 x 10^{-4} M and 1.10 x 10^{-3} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XVII. Observed Rate Constants for the Hydrolysis of PNP-Hexanoate by EHMA-TMA in 0.02 M Borate Buffer[a]

concentration 10^4 $[N^+]$[b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
4.01	9.56	0.98	0.977	4.18	15.5	22.5
1.22	2.91	0.95	0.946	4.04	15.1	21.8
0.680	1.62	0.91	0.912	3.90	14.5	21.1
0.325	0.775	0.83	0.841	3.59	13.4	19.4
0.200	0.477	0.75	0.769	3.28	12.2	17.8

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.22 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 4.77×10^{-5} M, 2.04×10^{-4} M, 7.59×10^{-4} M and 1.10×10^{-3} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XVIII. Observed Rate Constants for the Hydrolysis of PNP-Octanoate by EHMA-TMA in 0.02 M Borate Buffer[a]

concentration 10^4 [N$^+$][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
4.01	9.56	0.99	0.905	3.87	14.4	20.9
1.22	2.91	0.96	0.883	3.77	14.0	20.4
0.680	1.62	0.93	0.858	3.67	13.7	19.8
0.325	0.775	0.87	0.805	3.44	12.8	18.6
0.200	0.477	0.81	0.747	3.19	11.9	17.2

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.22 mmol N$^+$/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 4.77×10^{-5} M, 2.04×10^{-4} M, 7.59×10^{-4} M and 1.10×10^{-3} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XIX. Observed Rate Constants for the Hydrolysis of PNP-Acetate by BMA-TBA in 0.002 M Borate Buffer[a]

concentration 10^4 $[N^+]^b$ (M)	10^4 V_L^c	χ_L^d	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.75	4.48	0.47	0.350	1.83	5.00	8.96
1.20	3.07	0.38	0.311	1.58	4.48	7.93
0.875	2.24	0.31	0.280	1.39	4.09	7.14
0.560	1.43	0.22	0.243	1.16	3.60	6.18
0.435	1.11	0.18	0.226	1.05	3.37	5.73

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.03 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 2.57×10^{-5} M, 1.45×10^{-4} M, 3.55×10^{-4} M and 6.61×10^{-4} M for pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XX. Observed Rate Constants for the Hydrolysis of PNP-Hexanoate by BMA-TBA in 0.002 M Borate Buffer[a]

concentration 10^4 [N^+][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1}) pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.75	4.48	0.90	0.498	2.79	6.90	12.8
1.20	3.07	0.86	0.479	2.68	6.63	12.3
0.875	2.24	0.82	0.459	2.56	6.37	11.8
0.560	1.43	0.74	0.424	2.35	5.89	10.9
0.435	1.11	0.69	0.400	2.21	5.58	10.3

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.

[b] Anion exchange capacity = 1.03 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 2.57 x 10^{-5} M, 1.45 x 10^{-4} M, 3.55 x 10^{-4} M and 6.61 x 10^{-4} M for pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XXI. Observed Rate Constants for the Hydrolysis of PNP-Octanoate by BMA-TBA in 0.002 M Borate Buffer[a]

concentration 10^4 [N^+][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.75	4.48	0.93	0.329	1.85	4.55	8.46
1.20	3.07	0.89	0.318	1.79	4.40	8.18
0.875	2.24	0.86	0.308	1.73	4.26	7.91
0.560	1.43	0.80	0.287	1.61	3.97	7.37
0.435	1.11	0.76	0.273	1.52	3.78	7.01

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.03 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 2.57×10^{-5} M, 1.45×10^{-4} M, 3.55×10^{-4} M and 6.61×10^{-4} M for pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XXII. Observed Rate Constants for the Hydrolysis of PNP-Acetate by BMA-TBA in 0.01 M Borate Buffer[a]

concentration 10^4 [N^+][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.75	4.17	0.63	0.497	2.48	7.56	13.6
1.20	2.86	0.54	0.447	2.20	6.81	12.1
0.875	2.09	0.46	0.404	1.97	6.17	10.9
0.560	1.33	0.36	0.344	1.64	5.27	9.23
0.435	1.04	0.30	0.315	1.48	4.84	8.41

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.

[b] Anion exchange capacity = 1.03 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 3.31 x 10^{-5} M, 1.70 x 10^{-4} M, 5.01 x 10^{-4} M and 9.12 x 10^{-4} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XXIII. Observed Rate Constants for the Hydrolysis of PNP-Hexanoate by BMA-TBA in 0.01 M Borate Buffer[a]

concentration 10^4 $[N^+]$[b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1}) pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.75	4.17	0.93	0.542	2.77	8.20	14.9
1.20	2.86	0.90	0.527	2.70	7.98	14.5
0.875	2.09	0.87	0.512	2.62	7.76	14.1
0.560	1.33	0.81	0.481	2.45	7.28	13.2
0.435	1.04	0.77	0.462	2.35	7.01	12.7

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.
[b] Anion exchange capacity = 1.03 mmol N^+/g.
[c] Volume fraction of latex in reaction mixture.
[d] Fraction of substrate bound to particles.
[e] Intraparticle hydroxide concentration was 3.31×10^{-5} M, 1.70×10^{-4} M, 5.01×10^{-4} M and 9.12×10^{-4} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XXIV. Observed Rate Constants for the Hydrolysis of PNP-Octanoate by BMA-TBA in 0.01 M Borate Buffer[a]

concentration 10^4 $[N^+]^b$ (M)	10^4 V_L^c	χ_L^d	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.75	4.17	0.95	0.431	2.21	6.52	11.9
1.20	2.86	0.92	0.421	2.16	6.37	11.6
0.875	2.09	0.90	0.411	2.11	6.22	11.3
0.560	1.33	0.85	0.388	1.99	5.88	10.7
0.435	1.04	0.81	0.376	1.92	5.69	10.3

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.03 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 3.31×10^{-5} M, 1.70×10^{-4} M, 5.01×10^{-4} M and 9.12×10^{-4} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XXV. Observed Rate Constants for the Hydrolysis of PNP-Acetate by BMA-TBA in 0.02 M Borate Buffer[a]

concentration 10^4 $[N^+]^b$ (M)	10^4 $V_L{}^c$	$\chi_L{}^d$	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.75	3.86	0.73	0.817	3.48	13.0	18.9
1.20	2.65	0.65	0.745	3.16	11.9	17.3
0.875	1.93	0.57	0.675	2.86	10.7	15.7
0.560	1.24	0.46	0.575	2.42	9.14	13.4
0.435	0.960	0.40	0.517	2.17	8.22	12.1

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.03 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 4.77×10^{-5} M, 2.04×10^{-4} M, 7.59×10^{-4} M and 1.10×10^{-3} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XXVI. Observed Rate Constants for the Hydrolysis of PNP-Hexanoate by BMA-TBA in 0.02 M Borate Buffer[a]

concentration 10^4 [N$^+$]^b (M)	10^4 V$_L$^{c}	χ_L^{d}	10^3 k_{obs} (s^{-1})			
			pH 8.8^e	pH 9.4	pH 10.0	pH 10.2
1.75	3.86	0.96	0.824	3.52	13.1	19.0
1.20	2.65	0.94	0.812	3.47	12.9	18.7
0.875	1.93	0.92	0.795	3.40	12.6	18.3
0.560	1.24	0.88	0.765	3.27	12.2	17.7
0.435	0.960	0.85	0.740	3.16	11.8	17.1

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.03 mmol N$^+$/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 4.77×10^{-5} M, 2.04×10^{-4} M, 7.59×10^{-4} M and 1.10×10^{-3} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XXVII. Observed Rate Constants for the Hydrolysis of PNP-Octanoate by BMA-TBA in 0.02 M Borate Buffer[a]

concentration 10^4 [N$^+$][b] (M)	10^4 V$_L$[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.75	3.86	0.97	0.715	3.06	11.4	16.5
1.20	2.65	0.95	0.707	3.02	11.3	16.3
0.875	1.93	0.94	0.695	2.97	11.1	16.0
0.560	1.24	0.91	0.674	2.88	10.7	15.5
0.435	0.960	0.88	0.655	2.80	10.4	15.1

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.
[b] Anion exchange capacity = 1.03 mmol N$^+$/g.
[c] Volume fraction of latex in reaction mixture.
[d] Fraction of substrate bound to particles.
[e] Intraparticle hydroxide concentration was 4.77 x 10^{-5} M, 2.04 x 10^{-4} M, 7.59 x 10^{-4} M and 1.10 x 10^{-3} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XXVIII. Observed Rate Constants for the Hydrolysis of PNP-Acetate by BMA-TMA in 0.002 M Borate Buffer[a]

concentration 10^4 [N$^+$][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
3.90	8.79	0.58	0.365	1.94	5.16	9.33
1.25	2.82	0.31	0.263	1.29	3.85	6.70
0.760	1.71	0.21	0.228	1.07	3.39	5.78
0.455	1.03	0.14	0.201	0.898	3.04	5.09
0.384	0.866	0.12	0.194	0.851	2.95	4.90

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.25 mmol N$^+$/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 2.57×10^{-5} M, 1.45×10^{-4} M, 3.55×10^{-4} M and 6.61×10^{-4} M for pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XXIX. Observed Rate Constants for the Hydrolysis of PNP-Hexanoate by BMA-TMA in 0.002 M Borate Buffer[a]

concentration 10^4 [N^+][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
3.90	8.79	0.91	0.299	1.67	4.14	7.68
1.25	2.82	0.76	0.264	1.45	3.69	6.78
0.760	1.71	0.66	0.239	1.30	3.36	6.12
0.455	1.03	0.53	0.211	1.12	2.99	5.39
0.384	0.866	0.49	0.200	1.05	2.84	5.11

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.

[b] Anion exchange capacity = 1.25 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 2.57 x 10^{-5} M, 1.45 x 10^{-4} M, 3.55 x 10^{-4} M and 6.61 x 10^{-4} M for pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XXX. Observed Rate Constants for the Hydrolysis of PNP-Octanoate by BMA-TMA in 0.002 M Borate Buffer[a]

concentration 10^4 $[N^+]^b$ (M)	10^4 $V_L{}^c$	$\chi_L{}^d$	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
3.90	8.79	0.96	0.274	1.54	3.79	7.04
1.25	2.82	0.88	0.254	1.43	3.52	6.53
0.760	1.71	0.81	0.237	1.33	3.28	6.09
0.455	1.03	0.72	0.215	1.20	2.99	5.52
0.384	0.866	0.69	0.205	1.14	2.85	5.27

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.

[b] Anion exchange capacity = 1.25 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 2.57 x 10^{-5} M, 1.45 x 10^{-4} M, 3.55 x 10^{-4} M and 6.61 x 10^{-4} M for pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XXXI. Observed Rate Constants for the Hydrolysis of PNP-Acetate by BMA-TMA in 0.01 M Borate Buffer[a]

concentration 10^4 [N^+][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
3.90	7.94	0.70	0.562	2.83	8.54	15.4
1.25	2.55	0.43	0.402	1.95	6.14	10.9
0.760	1.55	0.31	0.334	1.58	5.13	8.94
0.455	0.927	0.21	0.276	1.26	4.26	7.30
0.384	0.782	0.19	0.259	1.17	4.01	6.84

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.

[b] Anion exchange capacity = 1.25 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 3.31 x 10^{-5} M, 1.70 x 10^{-4} M, 5.01 x 10^{-4} M and 9.12 x 10^{-4} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XXXII. Observed Rate Constants for the Hydrolysis of PNP-Hexanoate by BMA-TMA in 0.01 M Borate Buffer[a]

concentration 10^4 [N$^+$][b] (M)	10^4 V$_L$[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
3.90	7.94	0.94	0.477	2.44	7.23	13.1
1.25	2.55	0.83	0.432	2.20	6.54	11.9
0.760	1.55	0.75	0.397	2.01	6.02	10.9
0.455	0.927	0.64	0.351	1.76	5.33	9.59
0.384	0.782	0.60	0.333	1.67	5.07	9.10

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.

[b] Anion exchange capacity = 1.25 mmol N$^+$/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 3.31 x 10^{-5} M, 1.70 x 10^{-4} M, 5.01 x 10^{-4} M and 9.12 x 10^{-4} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XXXIII. Observed Rate Constants for the Hydrolysis of PNP-Octanoate by BMA-TMA in 0.01 M Borate Buffer[a]

concentration 10^4 $[N^+]^b$ (M)	10^4 V_L^c	χ_L^d	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
3.90	7.94	0.96	0.402	2.07	6.09	11.1
1.25	2.55	0.89	0.374	1.92	5.67	10.3
0.760	1.55	0.83	0.352	1.80	5.32	9.67
0.455	0.927	0.74	0.318	1.62	4.82	8.74
0.384	0.782	0.71	0.304	1.55	4.61	8.37

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.

[b] Anion exchange capacity = 1.25 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 3.31 x 10^{-5} M, 1.70 x 10^{-4} M, 5.01 x 10^{-4} M and 9.12 x 10^{-4} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XXXIV. Observed Rate Constants for the Hydrolysis of PNP-Acetate by BMA-TMA in 0.02 M Borate Buffer[a]

concentration 10^4 [N^+][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
3.90	7.66	0.88	0.973	4.15	15.5	22.5
1.25	2.45	0.54	0.660	2.79	10.5	15.4
0.760	1.49	0.42	0.544	2.29	8.65	12.7
0.455	0.893	0.30	0.434	1.81	6.90	10.2
0.384	0.754	0.27	0.402	1.67	9.39	9.49

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.
[b] Anion exchange capacity = 1.25 mmol N^+/g.
[c] Volume fraction of latex in reaction mixture.
[d] Fraction of substrate bound to particles.
[e] Intraparticle hydroxide concentration was 4.77 x 10^{-5} M, 2.04 x 10^{-4} M, 7.59 x 10^{-4} M and 1.10 x 10^{-3} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XXXV. Observed Rate Constants for the Hydrolysis of PNP-Hexanoate by BMA-TMA in 0.02 M Borate Buffer[a]

concentration 10^4 [N^+][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
3.90	7.66	0.98	0.822	3.51	13.1	18.9
1.25	2.45	0.91	0.769	3.29	12.2	17.7
0.760	1.49	0.87	0.732	3.13	11.7	16.9
0.455	0.893	0.79	0.680	2.90	10.8	15.7
0.384	0.754	0.77	0.659	2.81	10.5	15.2

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.25 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 4.77×10^{-5} M, 2.04×10^{-4} M, 7.59×10^{-4} M and 1.10×10^{-3} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XXXVI. Observed Rate Constants for the Hydrolysis of PNP-Octanoate by BMA-TMA in 0.02 M Borate Buffer[a]

concentration 10^4 $[N^+]^b$ (M)	10^4 $V_L{}^c$	$\chi_L{}^d$	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
3.90	7.66	0.99	0.636	2.72	10.1	14.7
1.25	2.45	0.94	0.606	2.59	9.65	14.0
0.760	1.49	0.91	0.584	2.50	9.30	13.5
0.455	0.893	0.85	0.552	2.36	8.79	12.7
0.384	0.754	0.83	0.539	2.30	8.58	12.4

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.25 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 4.77×10^{-5} M, 2.04×10^{-4} M, 7.59×10^{-4} M and 1.10×10^{-3} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XXXVII. Observed Rate Constants for the Hydrolysis of PNP-Acetate by PS-TBA in 0.002 M Borate Buffer[a]

concentration 10^4 [N^+][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.77	3.91	0.15	0.220	1.01	3.30	5.58
1.20	2.65	0.11	0.200	0.882	3.03	5.05
0.875	1.93	0.08	0.187	0.803	2.87	4.72
0.555	1.22	0.05	0.174	0.721	2.69	4.38
0.441	0.973	0.04	0.169	0.692	2.63	4.26

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.

[b] Anion exchange capacity = 1.03 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 2.57 x 10^{-5} M, 1.45 x 10^{-4} M, 3.55 x 10^{-4} M and 6.61 x 10^{-4} M for pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XXXVIII. Observed Rate Constants for the Hydrolysis of PNP-Hexanoate by PS-TBA in 0.002 M Borate Buffer[a]

concentration 10^4 $[N^+]$[b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.77	3.91	0.38	0.258	1.36	3.66	6.60
1.20	2.65	0.29	0.217	1.12	3.11	5.53
0.875	1.93	0.23	0.189	0.953	2.74	4.83
0.555	1.22	0.16	0.159	0.755	2.30	3.97
0.441	0.973	0.13	0.143	0.677	2.12	3.63

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.03 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 2.57×10^{-5} M, 1.45×10^{-4} M, 3.55×10^{-4} M and 6.61×10^{-4} M for pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XXXIX. Observed Rate Constants for the Hydrolysis of PNP-Octanoate by PS-TBA in 0.002 M Borate Buffer[a]

concentration 10^4 [N$^+$][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1}) pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.77	3.91	0.47	0.251	1.39	3.50	6.44
1.20	2.65	0.38	0.207	1.13	2.89	5.30
0.875	1.93	0.31	0.173	0.939	2.44	4.45
0.555	1.22	0.22	0.132	0.703	1.88	3.39
0.441	0.973	0.18	0.116	0.606	1.65	2.96

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.03 mmol N$^+$/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 2.57×10^{-5} M, 1.45×10^{-4} M, 3.55×10^{-4} M and 6.61×10^{-4} M for pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XL. Observed Rate Constants for the Hydrolysis of PNP-Acetate by PS-TBA in 0.01 M Borate Buffer[a]

concentration 10^4 [N^+][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.77	3.44	0.21	0.303	1.40	4.67	8.06
1.20	2.34	0.16	0.262	1.18	4.05	6.89
0.875	1.70	0.12	0.235	1.03	3.65	6.15
0.555	1.08	0.08	0.206	0.877	3.22	5.34
0.441	0.856	0.06	0.195	0.816	3.05	5.03

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.
[b] Anion exchange capacity = 1.03 mmol N^+/g.
[c] Volume fraction of latex in reaction mixture.
[d] Fraction of substrate bound to particles.
[e] Intraparticle hydroxide concentration was 3.31×10^{-5} M, 1.70×10^{-4} M, 5.01×10^{-4} M and 9.12×10^{-4} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XLI. Observed Rate Constants for the Hydrolysis of PNP-Hexanoate by PS-TBA in 0.01 M Borate Buffer[a]

concentration 10^4 $[N^+]$[b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.77	3.44	0.50	0.423	2.11	6.43	11.5
1.20	2.34	0.40	0.357	1.77	5.44	9.72
0.875	1.70	0.33	0.307	1.51	4.69	8.32
0.555	1.08	0.24	0.245	1.17	3.75	6.58
0.441	0.856	0.20	0.217	1.03	3.34	5.83

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.03 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 3.31×10^{-5} M, 1.70×10^{-4} M, 5.01×10^{-4} M and 9.12×10^{-4} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XLII. Observed Rate Constants for the Hydrolysis of PNP-Octanoate by PS-TBA in 0.01 M Borate Buffer[a]

concentration 10^4 $[N^+]^b$ (M)	10^4 $V_L{}^c$	$\chi_L{}^d$	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.77	3.44	0.54	0.374	1.90	5.67	10.3
1.20	2.34	0.45	0.314	1.59	4.77	8.62
0.875	1.70	0.37	0.265	1.33	4.02	7.25
0.555	1.08	0.27	0.203	1.01	3.09	5.54
0.441	0.856	0.23	0.176	0.872	2.68	4.78

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.03 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 3.31×10^{-5} M, 1.70×10^{-4} M, 5.01×10^{-4} M and 9.12×10^{-4} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XLIII. Observed Rate Constants for the Hydrolysis of PNP-Acetate by PS-TBA in 0.02 M Borate Buffer[a]

concentration 10^4 [N^+][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1}) pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.77	3.28	0.30	0.473	1.97	7.50	11.1
1.20	2.23	0.23	0.394	1.62	6.24	9.28
0.875	1.62	0.17	0.338	1.38	5.36	8.02
0.555	1.03	0.12	0.278	1.12	4.41	6.66
0.441	0.817	0.10	0.255	1.02	4.04	6.14

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.

[b] Anion exchange capacity = 1.03 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 4.77 x 10^{-5} M, 2.04 x 10^{-4} M, 7.59 x 10^{-4} M and 1.10 x 10^{-3} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XLIV. Observed Rate Constants for the Hydrolysis of PNP-Hexanoate by PS-TBA in 0.02 M Borate Buffer[a]

concentration 10^4 $[N^+]^b$ (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.77	3.28	0.61	0.644	2.73	10.2	15.0
1.20	2.23	0.51	0.556	2.50	8.81	12.8
0.875	1.62	0.43	0.482	2.03	7.63	11.2
0.555	1.03	0.33	0.385	1.61	6.10	8.94
0.441	0.817	0.28	0.339	1.42	5.37	7.92

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.03 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 4.77×10^{-5} M, 2.04×10^{-4} M, 7.59×10^{-4} M and 1.10×10^{-3} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XLV. Observed Rate Constants for the Hydrolysis of PNP-Octanoate by PS-TBA in 0.02 M Borate Buffer[a]

concentration 10^4 $[N^+]^b$ (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.77	3.28	0.62	0.586	2.49	9.29	13.5
1.20	2.23	0.53	0.503	2.13	7.97	11.6
0.875	1.62	0.45	0.432	1.83	6.85	9.96
0.555	1.03	0.34	0.335	1.34	5.31	7.73
0.441	0.817	0.29	0.290	1.23	4.60	6.72

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.03 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 4.77×10^{-5} M, 2.04×10^{-4} M, 7.59×10^{-4} M and 1.10×10^{-3} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XLVI. Observed Rate Constants for the Hydrolysis on PNP-Acetate by PS-TMA in 0.002 M Borate Buffer[a]

concentration 10^4 $[N^+]$[b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.77	3.29	0.10	0.192	0.836	2.93	4.85
1.20	2.24	0.07	0.180	0.756	2.76	4.52
0.875	1.63	0.05	0.172	0.708	2.66	4.32
0.555	1.03	0.03	0.164	0.658	2.56	4.12
0.441	0.823	0.03	0.161	0.641	2.52	4.04

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.

[b] Anion exchange capacity = 1.17 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 2.57 x 10^{-5} M, 1.45 x 10^{-4} M, 3.55 x 10^{-4} M and 6.61 x 10^{-4} M for pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XLVII. Observed Rate Constants for the Hydrolysis on PNP-Hexanoate by PS-TMA in 0.002 M Borate Buffer[a]

concentration 10^4 [N^+][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.77	3.29	0.25	0.182	0.913	2.63	4.63
1.20	2.24	0.19	0.156	0.757	2.29	3.96
0.875	1.63	0.15	0.139	0.653	2.06	3.52
0.555	1.03	0.10	0.120	0.540	1.81	3.03
0.441	0.823	0.08	0.113	0.498	1.71	2.85

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.17 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 2.57×10^{-5} M, 1.45×10^{-4} M, 3.55×10^{-4} M and 6.61×10^{-4} M for pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table XLVIII. Observed Rate Constants for the Hydrolysis on PNP-Octanoate by PS-TMA in 0.002 M Borate Buffer[a]

concentration 10^4 [N^+][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.77	3.29	0.31	0.178	0.964	2.50	4.56
1.20	2.24	0.24	0.142	0.757	2.01	3.63
0.875	1.63	0.18	0.117	0.615	1.67	3.00
0.555	1.03	0.12	0.0894	0.455	1.29	2.28
0.441	0.823	0.10	0.0789	0.394	1.15	2.01

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.

[b] Anion exchange capacity = 1.17 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 2.57 x 10^{-5} M, 1.45 x 10^{-4} M, 3.55 x 10^{-4} M and 6.61 x 10^{-4} M for pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table IL. Observed Rate Constants for the Hydrolysis on PNP-Acetate by PS-TMA in 0.01 M Borate Buffer[a]

concentration 10^4 [N^+][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.77	2.88	0.13	0.236	1.04	3.66	6.17
1.20	1.96	0.09	0.211	0.901	3.29	5.47
0.875	1.43	0.07	0.195	0.818	3.06	5.03
0.555	0.905	0.04	0.179	0.730	2.81	4.58
0.441	0.720	0.04	0.173	0.698	2.73	4.42

[a] All reactions performed at 30°C. Substrate concentration was 2.50 x 10^{-5} M.

[b] Anion exchange capacity = 1.17 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 3.31 x 10^{-5} M, 1.70 x 10^{-4} M, 5.01 x 10^{-4} M and 9.12 x 10^{-4} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table L. Observed Rate Constants for the Hydrolysis on PNP-Hexanoate by PS-TMA in 0.01 M Borate Buffer[a]

concentration 10^4 $[N^+]^b$ (M)	10^4 $V_L{}^c$	$\chi_L{}^d$	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.77	2.88	0.31	0.283	1.38	4.32	7.65
1.20	1.96	0.24	0.234	1.12	3.59	6.29
0.875	1.43	0.18	0.201	0.941	3.08	5.36
0.555	0.905	0.13	0.162	0.739	2.51	4.30
0.441	0.720	0.10	0.148	0.661	2.29	3.89

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.17 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 3.31×10^{-5} M, 1.70×10^{-4} M, 5.01×10^{-4} M and 9.12×10^{-4} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table LI. Observed Rate Constants for the Hydrolysis on PNP-Octanoate by PS-TMA in 0.01 M Borate Buffer[a]

concentration 10^4 [N^+][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1}) pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.77	2.88	0.33	0.242	1.21	3.67	6.61
1.20	1.96	0.25	0.192	0.953	2.92	5.22
0.875	1.43	0.20	0.157	0.772	2.39	4.26
0.555	0.905	0.14	0.117	0.564	1.79	3.15
0.441	0.720	0.11	0.101	0.483	1.55	2.72

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.17 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 3.31×10^{-5} M, 1.70×10^{-4} M, 5.01×10^{-4} M and 9.12×10^{-4} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table LII. Observed Rate Constants for the Hydrolysis on PNP-Acetate by PS-TMA in 0.02 M Borate Buffer[a]

concentration 10^4 $[N^+]^b$ (M)	10^4 $V_L{}^c$	$\chi_L{}^d$	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.77	2.61	0.14	0.303	1.23	4.81	7.23
1.20	1.77	0.10	0.258	1.04	4.10	6.22
0.875	1.29	0.08	0.231	0.923	3.67	5.60
0.555	0.819	0.05	0.203	0.800	3.22	4.96
0.441	0.651	0.04	0.192	0.754	3.05	4.72

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.17 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 4.77×10^{-5} M, 2.04×10^{-4} M, 7.59×10^{-4} M and 1.10×10^{-3} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table LIII. Observed Rate Constants for the Hydrolysis on PNP-Hexanoate by PS-TMA in 0.02 M Borate Buffer[a]

concentration 10^4 [N$^+$][b] (M)	10^4 V$_L$[c]	χ_L[d]	$10^3\ k_{obs}$ (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.77	2.61	0.39	0.469	1.98	7.46	10.9
1.20	1.77	0.30	0.382	1.61	6.08	8.93
0.875	1.29	0.24	0.320	1.34	5.09	7.50
0.555	0.819	0.17	0.248	1.03	3.93	5.84
0.441	0.651	0.14	0.218	0.900	3.47	5.17

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.17 mmol N$^+$/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 4.77×10^{-5} M, 2.04×10^{-4} M, 7.59×10^{-4} M and 1.10×10^{-3} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

Table LIV. Observed Rate Constants for the Hydrolysis on PNP-Octanoate by PS-TMA in 0.02 M Borate Buffer[a]

concentration 10^4 [N^+][b] (M)	10^4 V_L[c]	χ_L[d]	10^3 k_{obs} (s^{-1})			
			pH 8.8[e]	pH 9.4	pH 10.0	pH 10.2
1.77	2.61	0.43	0.411	1.75	6.53	9.50
1.20	1.77	0.34	0.330	1.40	5.25	7.65
0.875	1.29	0.27	0.271	1.15	4.31	6.29
0.555	0.819	0.19	0.200	0.845	3.19	4.67
0.441	0.651	0.16	0.171	0.720	2.72	4.00

[a] All reactions performed at 30°C. Substrate concentration was 2.50×10^{-5} M.

[b] Anion exchange capacity = 1.17 mmol N^+/g.

[c] Volume fraction of latex in reaction mixture.

[d] Fraction of substrate bound to particles.

[e] Intraparticle hydroxide concentration was 4.77×10^{-5} M, 2.04×10^{-4} M, 7.59×10^{-4} M and 1.10×10^{-3} M at pH 8.8, 9.4, 10.0 and 10.2 respectively.

VITA

Paul Daren Miller

Candidate for the Degree of

Doctor of Philosophy

Thesis: KINETIC ANALYSIS OF REACTIONS INSIDE ALKYL METHACRYLATE LATEX PARTICLES

Major Field: Chemistry

Biographical:

Personal Data: Born in Mansfield, Missouri, USA on March 23, 1968, son of Alvin R. Miller and Rose L. Miller.

Education: Recieved Bachelor of Science Degree in Chemistry from Southwest Missouri State University, Springfield Missouri in May 1994. Completed the requirements for the Doctor of Philosophy degree with a major in Chemistry at Oklahoma State University, Stillwater Oklahoma in July, 1999.

Experience: Enlisted in the United States Army in 1985 and recieved an honorable discharge in 1993. Employed by Southwest Missouri State University, Department of Chemistry as teaching assistant and research assistant from 1992-1994. Employed by Oklahoma State University, Department of Chemistry as teaching assistant and research assistant from 1994-1999.

Professional Memberships: American Chemical Society, Phi Lambda Upsilon Honorary Chemical Society.