

PARTICLE SIZES OF EMULSION COPOLYMERS OF
12-(*o*-STYRYLOXYDODECYL)TRIMETHYLAMMONIUM BROMIDE,
STYRENE, AND DIVINYLBENZENE

By
MILIND D. CHCUBAL

Bachelor of Science
University of Bombay
Bombay, India
1978

Master of Science
University of Bombay
Bombay, India
1980

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Thesis Approved :

Warren T. Ford

Thesis Adviser

Horacio A. Mottola

Richard A. Bruce

Norman N. Osburn

Dean of the Graduate College

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CHAPTER I

INTRODUCTION

Emulsion Polymerization

Emulsion polymerization¹ is a method of preparing addition polymers. This method is mainly used for the polymerization of unsaturated organic compounds. It can be used to make plastics, elastomers and paints. The emulsion polymers can also be used to support a reagent or a catalyst to carry out polymer supported reactions.

A typical recipe for emulsion polymerization generally includes a monomer, surfactant, free radical initiator and water. Consider an example of polymerization of styrene in water using sodium dodecylsulfate as surfactant and sodium persulfate as initiator. When this mixture is heated, a free radical chain polymerization takes place in three steps.² 1. Decomposition of the persulfate to form free radicals. 2. Attack of radicals on styrene to form oligomeric radicals and propagation of a free radical chain reaction to form high molecular weight polymers. 3. Termination of radicals by combination or disproportionation. At the end of polymerization, a colloidal suspension of polystyrene is obtained. A colloid³ is a suspension of particles that has dimensions between 10^{-8}m (10 \AA) and 10^{-6}m ($10,000 \text{ \AA}$).

The terms that are generally used in emulsion polymerization are as follows. An emulsion is a suspension of microscopic particles that are either monomer droplets or polymer particles in water. The sizes of monomer droplets are greater than 1000 \AA . A latex or polymer colloid is a suspension of polymer particles. The sizes vary from 1 nm to $1 \mu\text{m}$. Colloidally unstable polymer that precipitates is called coagulum. A surfactant is a compound that reduces the surface tension of a liquid. Surfactants have both polar and

nonpolar regions in their structures. A polymerizable surfactant also possesses a reactive double bond. A micelle is an aggregate of surfactant molecules with the polar groups on the outside in contact with water and the nonpolar groups aggregated inside. At lower surfactant concentrations (1-2 wt %) micelles are spherical with diameters of 20-100 Å, while at high concentrations micelles are larger and rodlike, 1000-3000 Å long. The critical micelle concentration (CMC) is the minimum concentration of the surfactant required to form micelles. Below the critical micelle concentration the surfactant molecules are not aggregated while above the critical micelle concentration, the amount of surfactant in excess of the CMC is present in the micelles. When two or more particles combine together to give a bigger particle, the term aggregation or agglomeration is used to describe this phenomenon. When an unstable polymer colloid precipitates, it is said to coagulate.

The main objective of this research is to determine the effects of quantities of a polymerizable quaternary ammonium ion surfactant, styrene and divinylbenzene on the sizes of particles formed during emulsion polymerization. This information will be useful when a polymer of a particular size is required. Before describing this research it is necessary to understand some of the basic concepts behind emulsion polymerization and the factors that can affect the particle size.

Two important theories about the mechanism of emulsion polymerization are those proposed by Smith and Ewart⁴ and by Baxendale and coworkers⁵.

Smith and Ewart⁴ reported the emulsion polymerization of styrene and butadiene and proposed that the radicals formed in the aqueous phase from a water soluble initiator such as persulfate ion, enter the monomer swollen micelles and polymerize the monomer. This results in the formation of small polymer particles that are swollen with monomer and stabilized by adsorbed emulsifier. These particles act as loci for polymerization. As they grow by polymerization, they adsorb more surfactant from unpolymerized micelles until a separate phase of micelles disappears.

The mechanism of an emulsion polymerization varies as polymerization proceeds and is usually described by three intervals⁶.

Interval 1 starts with the first generation of free radicals and ends when the nucleation of polymer particles is completed. LaMer and Dinegar⁷ reported that only when initiation is fast compared to the overall time required for the polymerization are monodisperse latexes obtained. The nucleation of particles lasts for only few minutes as compared to hours or days required for the whole process. Up to 15 % of the monomer is consumed during this interval.

Interval 2 starts when the nucleation of the polymer particle is completed, and ends when all of the monomer droplets are consumed. It is much longer than interval 1 and 30 to 50 % of the monomer is polymerized during this interval. In the case of a slightly soluble monomer such as styrene, a saturated aqueous solution of the monomer is maintained by continuous dissolution of the monomer from droplets into water as the monomer is used up by polymerization. The particle growth takes place by one of the following pathways.

A. The monomer is absorbed into the polymer particles and the particles grow. At equilibrium every particle contains the same relative amounts of polymer and monomer. The probability of trapping a radical per weight of particle is greater for a small particle than for a large particle. Hence small particles grow faster than large ones. This results in the formation of particles of almost uniform size, called a monodisperse latex.

B. Particle growth can also take place by aggregation of two or more particles. Since hydrophilic groups come to the polymer-water interface, aggregation of particles results in more hydrophilic surface groups per unit surface area. As a result, the surface charge density and hence the stability increase.

Interval 3 begins when there are no more monomer droplets. The monomer swollen into the particles polymerizes and the size of the particles stays constant.

According to Smith-Ewart theory,

$$N = \text{constant } (\mathcal{R}/\mathcal{U})^{0.4} (a_s [S])^{0.6} \quad (1)$$

where N is the number of polymer particles formed, \mathcal{R} is rate of formation of free radicals, \mathcal{U} is rate of volume increase of one particle, a_s is the area occupied by an emulsifier molecule in a saturated monolayer at the polymer-water interface and S is the concentration of the surfactant. This equation indicates that the greater the concentration of the surfactant, the greater the number of particles. The more particles formed from given amounts of surfactant and monomers, the smaller the particles. The rate of polymerization is given by the equation.

$$v = k_p [M]_p n N N_A^{-1} \quad (2)$$

where k_p is the polymerization constant, v is the rate of polymerization, $[M]_p$ is a constant monomer concentration in latex particles, n is constant average number of radicals per particle, N is the number of polymer particles, and N_A is Avogadro's number.

Baxandale and coworkers⁵ reported the polymerization of methyl methacrylate in water both in the presence and in the absence of cetyltrimethylammonium bromide. They found that the kinetics of polymerization were unaffected by the presence of surfactant. This indicated that in this case the surfactant micelles were not the loci of the polymerization. Other possible loci for the polymerization are the discontinuous monomer phase, the interface between the monomer and the aqueous phase and the continuous aqueous phase. If either the monomer phase or the water-monomer interface was the locus for the polymerization, the initial rate of polymerization would have depended on the amount of monomer phase present. They found that initial rate of polymerization was independent of the monomer phase. Hence they concluded that nucleation took place in the aqueous phase.

There are several theories of nucleation of particles in emulsion polymerization, according to which the primary particles are formed by one of the following mechanisms.²

1. Primary homogeneous nucleation. An initiator radical attacks a monomer molecule in the aqueous phase and proceeds to form an oligomer. The solubility of this oligomer depends upon the number of monomer units it possesses. The greater the number of monomer units, the more insoluble it is. A particle is formed when the oligomer becomes a separate phase.
2. Aggregate nucleation. Oligomers in the aqueous phase aggregate to form a primary particle. The surfactant concentration determines the number of oligomers that will aggregate. The lower the concentration of surfactant, the greater the number of oligomers that must aggregate to give a colloidally stable primary particle.
3. Micellar nucleation. An oligomeric radical is trapped in the monomer-swollen micelle and initiates the polymerization.
4. Monomer droplet nucleation. A radical is captured by or is formed in a monomer droplet, and initiates the polymerization. The droplets are continuously broken and reformed. The primary polymer particle can escape from the droplet during that period, absorb some more monomer, and continue polymerization.

Colloidal Stability⁸

A polymer latex particle consists of a large number of polymer chains with molecular weights ranging from 10^5 to 10^7 . The surface structure, which is very important to the colloidal properties of the latex, may consist of groups from the initiator, adsorbed surfactants, polymerized surfactants or polyelectrolytes polymerized on the latex particle surface, and adsorbed polymers.

Latex stabilization can be achieved by electrostatic forces. The surface functional groups can be anionic, cationic or neutral. When a surface grouping is acidic or basic, and a medium of a high electrical conductivity is used, the particle surface may be charged due to the ionization of acidic or basic groups. An electrical double layer is formed due to the charge on the particle surface, and oppositely charged ions surrounding the surface. As a

result, the particle has an electrostatic potential which decreases exponentially with the distance from the particle surface. The repulsion of these charged surfaces prevents the particles from aggregating, and the emulsion is stable.

Factors that can decrease this potential will destabilize the latex. The repulsive forces between the charged particles decrease in the presence of an electrolyte, and a charged latex will coagulate at a high concentration of electrolyte. Addition of a solvent that can swell the particle may cause agglomeration of particles. Swelling increases the total surface area of the particles. The number of ionic groups per unit area will decrease, the repulsive force that prevents the particles from aggregating will decrease, and the particles may aggregate. Reduction of the number of ionic sites on the particle surface by chemical means will also cause agglomeration of particles due to the same reason. An example is neutralization of a carboxylate salt to the carboxylic acid.

A latex can also be stabilized by adsorbed or grafted polymers that by themselves would be soluble in the medium. This is called steric stabilization of a colloid. The negative entropy that results from interpenetration of random coils of polymer chains on the surfaces of separate particles prevents the agglomeration of these particles. The lengths of these chains determine the stability of the latex.

Latex stability can also be achieved by a combination of the steric and electronic factors. When the chains of polyelectrolyte are grafted or adsorbed on the particles, they are stabilized to a greater extent due to the combined effect.

Effects of the Emulsifier on the Emulsion Polymerization⁹

The emulsifier used in an emulsion polymerization affects the number of particles formed during the polymerization, which in turn determines the particle size and the molecular weight of the polymer. The surfactant in emulsion polymerization serves to stabilize and solubilize monomer and polymer.

The Smith-Ewart theory can be used only in the case of ionic emulsifiers. Dunn⁹ reported that Ivanova and Yurzhenko in 1958, and Onischenko and coworkers in 1970, found that the latex particle size decreased markedly, and the rate of polymerization increased correspondingly as the alkyl chain length of the emulsifier was increased. The critical micelle concentrations of a homologous series of surfactants decrease as the alkyl chain length increases. Thus with the same concentrations of surfactants of varied chain lengths, the fraction of the surfactant in micellar form increases with the alkyl chain length. When polymerizations are carried out with equal number of micelles using different surfactants, the particle sizes of the product polymers are the same. When the length of an alkyl chain is increased, the size of micelle increases. Hence at a constant weight percent surfactant the number of micelles decreases as the size increases. The rate at which the initiator radicals are trapped depends upon the total surface area of the micelles. The greater the surface area, the greater the number of the radicals trapped. As a result of this, when the total surface area of latex particles becomes greater than that of the micelles in the polymerization, they capture the radicals more efficiently than the micelles.

Particle sizes of 30-200 nm are obtained in emulsion polymerization when an ionic emulsifier is used.⁹ Polymers with particle sizes greater than 200 nm are usually obtained by multistage seeded emulsion polymerizations. The particle size can be increased also by deliberate agglomeration. If the latex is destabilized to a certain extent, agglomeration takes place to gain back the stability. The destabilization can be achieved by different methods. A solvent can be added to swell the polymer, and then removed after the agglomeration. When the emulsifier has a carboxylate group, the partial neutralization of the carboxylate salt to carboxylic acid causes agglomeration. Aggregation can also be achieved by addition of an electrolyte or freezing the emulsion, whereupon some water separates as ice leaving behind an increased concentration of electrolytes.

Emulsion Polymerization with Surface Active Monomers ¹⁰

A surface active monomer has a polymerizable double bond, a surface active head group, and a hydrocarbon chain. With a nonpolar monomer it can form copolymer particles with surfactant head groups on the surface. Particle size can be controlled by changing the concentration of the polymerizable surfactant. Unlike most surfactants, a polymerizable surfactant can be covalently bound to the polymer.

Juang and Krieger¹¹ reported the copolymerization of styrene and sodium styrenesulfonate (NaSS). They found that the number of particles increases very rapidly in the beginning of the polymerization, and then stays constant after about one hour and 8 % conversion. As a result of a short nucleation stage, they obtained a narrow particle size distribution. The numerical value of the particle size distribution was not mentioned. When conventional surfactants are used, the nucleation stage lasts up to 15-20 % conversion. They found that particle diameter varied as 0.64 power of ionic strength to polymerizable comonomer.

$$D = 166[\text{NaSS}/I]^{0.64} [\text{K}_2\text{S}_2\text{O}_8]^{-0.20} [\text{M}]^{0.46} \quad (3)$$

where D is a diameter in A, [NaSS/I] is the ratio of molar concentration of NaSS to ionic strength, [M] is the total molar concentration of styrene in aqueous and organic phase, [K₂S₂O₈] is the molar concentration of potassium persulfate.

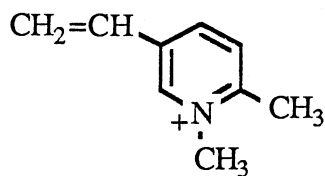
Chen and Chang¹² studied the polymerization of styrene with the sodium salt of undecylenic isethionate (NaUI).



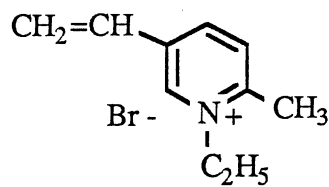
NaUI

Polymerization was carried out in the presence of sodium sulfate. On increasing the concentration of sodium sulfate from 0 to 0.17×10^{-2} g/mL (0.012 M) in water, the particle diameter increased initially, followed by a decrease in the diameter at high concentrations of sodium sulfate. At 0.17×10^{-2} g/mL (0.012 M) of sodium sulfate, the polymer coagulated. They proposed two different mechanisms for particle formation. In the low concentration range of sodium sulfate, the electrostatic repulsive force between the particles decreases with increasing concentration of sodium sulfate due to the screening effect caused by sodium sulfate. This causes agglomeration of primary particles to form stable secondary particles that increase in size with increasing concentration of sodium sulfate. However the critical micelle concentration of NaUI decreases as the sodium sulfate concentration increases. When the critical micelle concentration decreases to less than the concentration of the surfactant, micelles form, and particle nucleation takes place in micelles. The greater the concentration of sodium sulfate, the greater the number of micelles. As a result, higher concentration of sodium sulfate results in the formation of more and hence smaller particles. At very high concentrations of sodium sulfate the particle size is very small, the surface charge density is very low, latex stability is lost due to the screening effect and the latex coagulates.

Liu and Krieger¹⁰ reported the polymerization of styrene with the cationic comonomers, 1,2-dimethyl-5-vinylpyridinium methyl sulfate (DMVS), and 1-ethyl-2-methyl-5-vinylpyridinium bromide (DMVB).



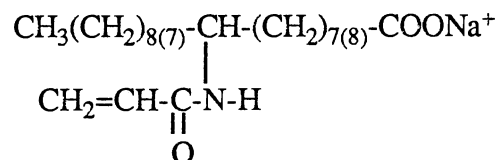
DMVS



DMVB

They found an initial decrease in the particle diameter with increase in comonomer concentration, followed by an increase in the particle diameter at a very high comonomer concentration. The comonomer reacts with an initiator and produces oligomeric radicals. When the particles are formed from these oligomeric radicals, they have higher electrostatic charge as compared to the particles formed without a charged monomer, and this results in smaller particles. At higher comonomer concentration, the oligomeric radicals have more comonomer units, and are soluble in water. When polymer is formed from these radicals, more comonomer units are required for the polymer to precipitate as particles, resulting in the formation of bigger particles. Larger particles were formed with 1-ethyl-2-methyl-5-vinyl pyridinium bromide than with 1,2-dimethyl-5-vinylpyridinium methyl sulfate.

Greene and coworkers¹³ used a mixture of sodium 9-(and 10)-acrylamido stearate (NaAAS) as a surface active agent in the polymerization of styrene and butadiene.



NaAAS

They reported that when percentage of surface coverage of the latex (defined below) was greater than 60 %, more unpolymerized emulsifier was present in the solution than when surface coverage of the latex was less than 60 %. They speculated that up to 60 % coverage the polymer chains were loosely packed, and did not interact with each other, while above 60 % they became more closely packed, and started interacting with each other sterically. The molecular area of NaAAS was 35 \AA^2 and specific surface area of the latex was $4.2 \times 10^{21} \text{ \AA}^2/\text{g}$ of latex solids. The latex can incorporate a maximum of 20 meq/g of latex solids when the monodisperse particle diameter is $0.134 \pm 0.015 \text{ m}$.

$$\% \text{ Surface coverage} = 100 \left[\frac{(\text{meq of NaAAS found}/100 \text{ g of latex solids})}{(20 \text{ meq of NaAAS}/100 \text{ g of latex solids})} \right] \quad (4)$$

Sakota and Okaya,¹⁴ while working on the cationic latexes prepared from styrene and N,N-dimethylaminoethyl methacrylate, found that at a high concentrations of the amine comonomer, only 12-13 % of the total amine groups were found on the surface of the polymer particles, and the rest of the amine monomer was unpolymerized. They found that when ionic comonomer was introduced in the last stages of the polymerization, more than 60 % of the amine groups used were attached to the particle surface.

Vanderhoff and coworkers¹⁵ reported the copolymerization of styrene with sodium styrenesulfonate (NaSS). They found that when all sodium styrenesulfonate was charged initially, even at very high concentrations, its incorporation did not exceed 2.6 % by weight of the final latex. A polyelectrolyte was formed from NaSS in excess of 2.6 % of monomers. The adsorption of this polyelectrolyte on the particle surface resulted in the formation of particles of different sizes. Monodisperse particles with high charge density were obtained by carrying out the polymerization in two stages. In the first stage styrene was polymerized with less than 1 weight % of sodium styrenesulfonate. In the second stage a mixture of styrene and sodium styrenesulfonate with the weight ratio of NaSS:styrene from 0.09 to 0.36 was added. Nearly all of the NaSS was incorporated into 120 to 300 nm particles.

Effect of a Crosslinking Agent¹⁶

Emulsion polymerization of divinylbenzene gives much smaller particles than that of styrene. Obrecht and coworkers¹⁶ reported that under identical polymerization conditions, the particles obtained by polymerization of styrene were twice as large as particles obtained from 1,4-DVB. Their results can be explained on the basis of Smith-Ewart theory as in equation 1.

When more particles are formed from the given quantity of a monomer, particles will be smaller. When the same quantities of styrene and divinylbenzene are polymerized separately at the same a_s and $[S]$, differences in the values of ξ or μ must explain the difference in the particle size. If ξ is the same for styrene and DVB, then μ of DVB must be 100 times smaller than that of styrene to produce six times more particles of poly(divinylbenzene). Although μ for DVB is less than μ for styrene, a 100 fold difference is not possible. It is possible that the value of ξ is much higher in the case of 1,4-divinylbenzene than styrene. During the polymerization of styrene, free radicals are generated by the decomposition of the initiator, while in the case of homopolymerization of divinylbenzene additional free radicals are generated by thermal initiation at 50 °C. Generation of more radicals in the case of divinylbenzene results in the formation of smaller particles.

The thermal initiation of the polymerization of 1,4-divinylbenzene has been proved. Kast and Funke¹⁷ reported the polymerization of 1,4-divinylbenzene in the absence of an initiator. The polymerization was initiated in monomer droplets at low sodium dodecylsulfate (SDS) concentration (0.1 M), and the rate of polymerization was 33.1 % conversion per hour. At high SDS concentrations (0.85 M), most of the monomer was solubilized in emulsifier micelles, and the rate of polymerization was 1.0 % conversion per hour. Under identical conditions the rate of polymerization of styrene, using 0.85 M SDS, was 13.3 % conversion per hour. Thus the rate of polymerization thermally initiated in DVB monomer droplets is 13.3 times the rate of polymerization of styrene. The particle size decreased on increasing the temperature 90 °C to 95 °C. More radicals are formed at a higher temperature that can initiate the polymerization in more micelles, producing more, and hence smaller particles.

Objective of This Project

Catalysts supported on polymer latexes are used in our laboratory to catalyze oxidation reactions of organic compounds. As catalyst supports these latexes should be water insoluble. A large number of ionic sites makes a polymer water soluble unless it is crosslinked. Systematic study of the effects of particle size and charge density on catalytic activity will help understanding of the catalysis mechanism. During this project a polymerizable surfactant 12-(*o*-styryloxydodecyl)trimethylammonium bromide (SDTAB), has been prepared and copolymerized in emulsion with styrene, and divinylbenzene. Particle sizes were determined from thirteen different emulsion polymers prepared with varied relative amounts of styrene, DVB, and surfactant.

CHAPTER II

RESULTS AND DISCUSSION

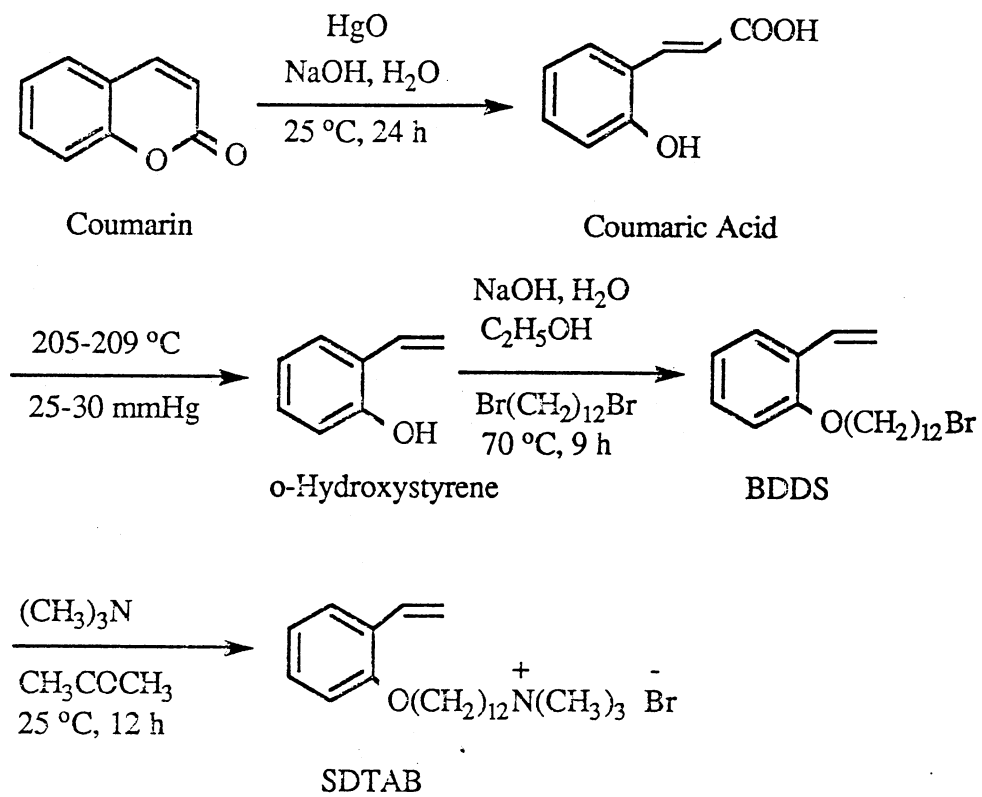
Results

Synthesis of 12-(*o*-Styryloxydodecyl)trimethylammonium Bromide (SDTAB)

The synthetic route used by Tsaur² for the synthesis of 10-(*o*-styryloxydecyl)trimethylammonium bromide was used, as shown on the next page.

Coumaric acid was prepared by an alkaline hydrolysis of coumarin catalyzed by mercuric oxide. Sanjay Srinivasan¹⁸ reported that when the reaction was carried out in the absence of mercuric oxide, it gave back the starting material. The NMR spectrum of coumaric acid showed a coupling constant of 16 Hz for the vinylic protons. This indicates that the phenyl group and the carboxylic acid group are *trans*, and hence *trans*-coumaric acid cannot cyclize back to coumarin. Apparently *cis*-coumaric acid cyclizes back to coumarin in the absence of mercuric oxide. When the crude product was recrystallized from boiling water as in the procedure of Tsaur,² only 50 % yield of coumaric acid was obtained. The solubility of coumaric acid is low in boiling water. When a small quantity of 95 % ethanol was added to the water used for the recrystallization, the volume of the solution was much less than before and the recovered yield was improved to 85 %.

SCHEME I



Coumaric acid was decarboxylated to *o*-hydroxystyrene. It was found that control of the pressure, the quantity of inhibitor, and the apparatus used are very important for efficient decarboxylation. Low yields were obtained when the pressure was greater than 60 mmHg or less than 10 mmHg. The pressure used in the original procedure² was 10-15 mmHg. At 70-80 mmHg the product did not distill and polymerized, while at less than 10 mmHg most of the product was lost as it entered the traps connected to the vacuum pump, and even the vacuum pump. The purity of coumaric acid was also found to be very important. Pure coumaric acid melts at 210 °C. A batch of impure coumaric acid, melting at 163 °C gave only a trace of *o*-hydroxystyrene on decarboxylation. It was also found that when the temperature was increased rapidly to 210 °C as reported in the original procedure of Tsaur,² a lot of solid, which may be coumarin, condensed on the walls of the apparatus. This resulted in only 39 % yield. When the decarboxylation was carried out below 210 °C, the decarboxylation proceeded smoothly and 63 % yield of *o*-hydroxystyrene was obtained.

o-Hydroxystyrene was treated with dibromododecane and sodium hydroxide in ethanol. Out of dichlorododecane, dibromododecane, and diiodododecane the best choice was dibromododecane. Bromide is a better leaving group as compared to chloride. Hence the reaction should be faster with dibromododecane as compared to dichlorododecane. When the surfactant is formed by reacting these dihalides with *o*-hydroxystyrene, the ionic bond between the quaternary nitrogen and iodide will be weaker as compared to the bond between the quaternary nitrogen and bromide. This will give a less stable latex when iodide is used as a counterion.

The thin layer chromatography of the product mixture showed the presence of four compounds, which were separated using a silica gel column. 1,12-Dibromododecane eluted with petroleum ether. When 5 % toluene in petroleum ether was used as an eluant, pure 12-bromododecylstyryl ether was obtained in 38 % yield. The purity of the product was checked by NMR and thin layer chromatography. The low yield of the product might

have been caused by the low solubility of 1,12-dibromododecane in ethanol. An attempt to improve the mixing of two layers by using a mechanical stirrer did not improve the yield. Since the yield obtained was in the range of yields obtained by Tsaur² in the synthesis of 10-bromodecylstyryloxy ether, no further attempt was made to improve the yield.

When 12-bromododecylstyryl ether was treated with trimethylamine in acetone at a room temperature, a white solid was obtained. Recrystallization gave pure 12-(*o*-styryloxydodecyl)trimethylammonium bromide (SDTAB).

Copolymerization of SDTAB with Styrene and Divinylbenzene

12-(*o*-styryloxydodecyl)trimethylammonium bromide (SDTAB) was emulsion polymerized with different molar ratios of styrene and divinylbenzene using azobis(isobutyronitrile) (AIBN) as free radical initiator. A total of thirteen polymers were prepared, as listed in Table I. The latexes with 5 mole % DVB and 1 and 2 mole % surfactant gave more than 10 % coagulum. The latexes were purified by ultrafiltration through 0.1 μ m cellulose acetate/nitrate membrane (Millipore) under a pressure of 70 psi of nitrogen. The initial conductivities of these filtrates, ranging from 11×10^{-6} to $125 \times 10^{-6} \text{ ohm}^{-1}\text{cm}^{-1}$, were much lower than the conductivities of aqueous solutions with the same initial surfactant concentrations, as shown in Figure 2. The graph of concentration of SDTAB vs conductivity (Figure 2) showed two straight lines intersecting at a point. This point is the critical micelle concentration of SDTAB, 16 mM. This indicates that in the cases of 0.5 mole % and 1 mole % SDTAB concentrations, the polymerizations were carried out below critical micelle concentration. The CMC may be affected by styrene and DVB, but to what extent it is affected is not known.

The bromide contents of the latexes were determined by Volhard titration. As shown in Table I, 86-100 % of SDTAB used was incorporated in the polymer.

Particle sizes of the latexes determined from transmission electron micrographs are reported in Table II. Some particles appeared elliptical. In such cases both long and short

axes were measured, and the average diameter was taken. The number average diameter, D_n , and weight average diameter, D_w , were calculated from measurements of 50 particles of each latex. Some of the particles were in the form of small aggregates, but in most of the cases, boundaries of some of the particles can be clearly seen.

TABLE I
BROMIDE CONTENTS OF POLYMERS

mol % SDTAB	mol% DVB	mol % Styrene	Weight of coagulated polymer	mmol SDTAB added	mmol Br in polymer	% Br	Conductivity* of initial filtrate collected x 10 ⁶
0.5	1	98.5	0.6	0.474	0.41	86	11
1	1	98	—	0.932	0.90	97	12.5
2	1	97	—	1.80	1.76	98	30
3	1	96	—	2.65	2.41	91	71
5	1	94	—	4.19	3.9	93	125
1	3	96	0.9	0.932	0.92	99	35
2	3	95	0.4	1.80	1.73	96	36
3	3	94	0.5	2.65	2.65	100	63
5	3	92	0.3	4.19	3.78	90	79
1	5	94	4.5	—	—	—	—
2	5	93	1.4	—	—	—	—
3	5	92	0.4	2.65	2.5	94	47
5	5	90	0.1	4.19	3.88	93	45

* Units of conductivity are $\text{ohm}^{-1}.\text{cm}^{-1}$.

TABLE II
PARTICLE SIZES OF POLYMERS

mol % SDTAB	mol % DVB	D_n^*	D_w^*	U^*
0.5	1	95 ± 10	98	1.02
1	1	92 ± 8	94	1.02
2	1	73 ± 10	78	1.07
3	1	49 ± 12	58	1.18
5	1	43 ± 12	52	1.20
1	3	54 ± 12	61	1.13
2	3	55 ± 16	61	1.12
3	3	39 ± 10	51	1.32
5	3	26 ± 21	51	1.93
1	5	39 ± 16	54	1.39
2	5	39 ± 10	44	1.15
3	5	25 ± 5	28	1.11
5	5	22 ± 5	27	1.26

* U is polydispersity ratio. D_n is number average diameter in nm. D_w is weight average diameter in nm. The number after the sign \pm is one standard deviation.

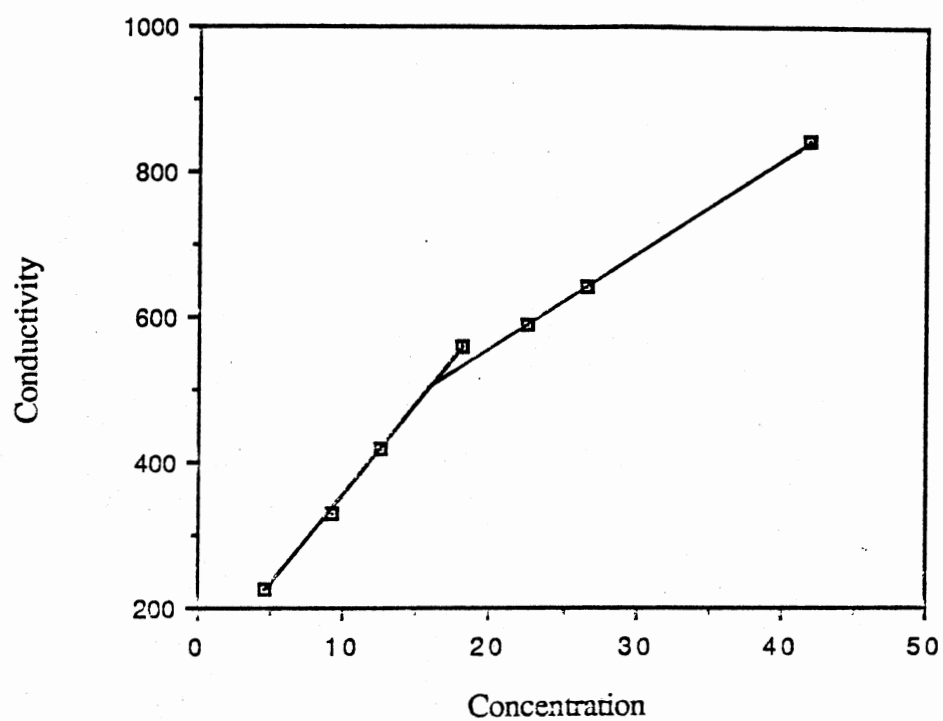


Figure 1. Critical Micelle Concentration Measurement. Unit of concentration is mM while unit of conductivity is $\text{ohm}^{-1} \text{cm}^{-1} \times 10^6$.

Discussion

The conductivities of the ultrafiltrates ranged from 11×10^{-6} to 125×10^{-6} $\text{ohm}^{-1}\text{cm}^{-1}$. The only ionic materials that could be present are monomeric SDTAB and a polyelectrolyte formed during the polymerization. The conductivity of 125×10^{-6} $\text{ohm}^{-1}\text{cm}^{-1}$ is equal to that of a 1.5 mM SDTAB solution, according to extrapolation from Figure 1. The concentration of SDTAB used in that polymerization was 47 mM. This indicates that no more than 3 % $\{(1.5\text{mM}/47\text{mM}) \times 100 = 3 \%\}$ of SDTAB was not bound to the polymer. Volhard titrations of the latexes indicated that 86-100 % of the original bromide ions were present in the latexes. The quaternary ammonium bromide sites may be in the form of a copolymer with styrene and DVB, or a polyelectrolyte adsorbed on particle surface. However, it is not possible to find whether SDTAB is covalently bound or adsorbed on the particles. Both the conductivities of the filtrates and the bromide contents of the ultrafiltered latexes indicate that most or all of the starting SDTAB was bound to latex particles.

We propose a mechanism for the polymerization of SDTAB with styrene and DVB. According to this mechanism the nucleation takes place in monomer droplets, and the primary particles grow by aggregation and polymerization. The mechanism should explain the following results. 1. Smaller particles are obtained on increasing either SDTAB or DVB concentration. 2. The polydispersity ratio increases on increasing SDTAB concentration. 3. Unstable latexes are obtained by using 5 mol % of DVB and either 1 or 2 mol % of SDTAB. 4. The polymer particles are not spherical.

The critical micelle concentration (CMC) of SDTAB is 16 mM. Thus SDTAB concentration was below CMC during polymerization of the 1 and 2 mol % SDTAB latexes. In the absence of micelles the polymerization may nucleate in the aqueous phase or in the monomer droplets. With a monomer such as styrene that has a very low solubility in water, and an oil soluble initiator such as AIBN, the polymerization will start in the monomer droplets. When the reaction mixture is heated, the initiator decomposes in

the monomer droplets, and initiates the polymerization. The sizes of monomer droplets are greater than 100 nm. If a whole droplet was converted into one polymer particle, the size of the resulting particle would be greater than 100 nm. The absence of particles with diameters greater than 100 nm indicates that styrene, SDTAB and DVB dissociate from monomer droplets, and are absorbed by other particles. Polymerization continues in smaller particles. This argument is supported by the literature¹⁹ which indicates that monomers and surfactants are equilibrated between the various phases present in the polymerization mixture on a microsecond time scale, while formation of polymer from monomer takes several minutes. When the total volume of the particles become greater than that of monomer droplets, polymer particles become a major site of polymerization.

Above CMC micelles of SDTAB are present. In micelles the nucleation takes place as follows.¹⁹ The micelles are formed, and a surfactant molecule exchanges with the surrounding medium on a millisecond time scale and during this time a monomer molecule, SDTAB molecule or a radical can be transferred to the micelle from the reaction medium. AIBN is water insoluble and hence cannot be easily transferred to micelles through water. Also the total volume of monomer droplets is much greater than total volume of micelles. Thus even in the presence of micelles the monomer droplets are the major sites of initiation.

Once the primary particles are formed, they can grow further by aggregation and/or further polymerization.

The number average particle diameter D_n decreases on increasing SDTAB concentration for all concentrations of DVB (Table II). The surface area per unit weight of the particles increases on decreasing the particle size. The larger the number of charged groups available for stabilization, the greater the surface area of particles that can be stabilized. As a result, when SDTAB concentration increases, the particle size decreases.

At lower SDTAB concentrations the differences in the number average diameters of the latex particles are not very significant. This can be explained on the basis of stability

of the latex. Even at low concentrations of the surfactants, small primary particles are formed. These particles are not colloidally stable, so they coalesce to form a bigger particles that require fewer charged surfactant groups per weight of latex for stability. This leads to less difference in the diameters of the particles at a low concentrations of the surfactant.

The polydispersity index increases on increasing the surfactant concentration at constant DVB concentration. Vanderhoff¹⁵ has offered an explanation for this phenomenon. At higher concentrations of the surfactant, some of the surfactant homopolymerizes and is adsorbed on the polymer particles. The quantity of surfactant adsorbed on the polymer particles is different for different particles, and monodispersity is lost.

For all surfactant concentrations, smaller particles are obtained on increasing the concentration of divinylbenzene. Divinylbenzene limits the swelling of monomer into polymer particles due to crosslinking. At higher concentrations of DVB, the primary polymer particles formed are very small. Due to their small sizes they require a large quantity of SDTAB for stabilization. At very low SDTAB concentration, the amount of surfactant is insufficient to stabilize small aggregates of the primary particles, and as a result larger aggregates form. In the extreme of 1-2 mol % SDTAB, there was extensive coagulation of particles into a macroscopic precipitate that could be removed from the latex by ordinary filtration. At higher SDTAB concentrations, the primary particles still do not have enough charged groups for stabilization, but aggregation stops at smaller sized particles. The total surface area of the bigger particles is less than that of small particles, and they can be stabilized by the available charged groups. As a result of this aggregation mechanism, at high DVB concentrations the particles are more polydisperse.

Some of the particles were not spherical in shape. In the case of uncrosslinked polymers, motion of the polymer chains allows reformation into the spherical shape that

minimizes polymer-water interfacial free energy. Crosslinking between the chains restricts their motion, and the aggregated particles cannot reform into spheres.

Conclusions

Several stable emulsion polymers were successfully prepared by copolymerization of SDTAB, styrene, and DVB. Particle sizes of the latexes decreased by increasing either the SDTAB or the DVB concentration or both of them. Crosslinking resulted in increased polydispersity and irregularly shaped particles. A mechanism is proposed that involves nucleation in monomer droplets, growth by aggregation, absorption of monomer, and polymerization to produce latexes.

The results of these experiments should enable preparation cationic latexes of controlled particle size for use as supports for heterogeneous colloidal catalysts. Crosslinked latexes can be prepared with different polymerizable surfactants using the same technique. It is thus possible to prepare latexes with a desired particle sizes merely by adjusting the concentrations of a crosslinking agent and surfactant.

CHAPTER III

EXPERIMENTAL

Synthesis and Copolymerization of 12-(*o*-styryloxydodecyl)trimethylammonium bromide

Materials

1,12-Dibromododecane, coumarin, silver nitrate, and potassium thiocyanate were used as received from Aldrich. Styrene was obtained from Aldrich, and purified by distillation at 50 °C and 30 mmHg. Divinylbenzene, as obtained from Dr. Ramachandran, had been purified by vacuum distillation and analyzed by gas chromatography. It contained 55 % by wt divinylbenzene, and 45 % by wt ethylvinylbenzene. Water was distilled under glass after passing through active carbon and a mixed bed ion exchange resin. Conductances were measured on a YSI model 31 conductivity meter with a cell supplied by YSI having a constant of 1.00 ($\pm 1\%$) cm^{-1} . The conductivity of water was always less than $1 \times 10^{-6} \text{ ohm}^{-1}\text{cm}^{-1}$. Melting points were obtained in capillary tubes with a Mel-Temp apparatus and are uncorrected. IR spectra were taken using liquid films on a Perkin-Elmer 681 infrared spectrometer using NaCl plates. NMR spectra were recorded on a Varian- XL-300 instrument at 300 MHz for ^1H , and at 75.4 MHz for ^{13}C .

Coumaric Acid²

Coumarin (73 g, 0.50 mol), sodium hydroxide (73 g, 1.8 mol), mercuric oxide (3.0 g, 0.014 mol), and 800 mL of water were stirred together for 12 h at room

temperature. Sodium sulfide (0.2 g, 0.025 mol) was then added to the solution, and 6M HCl was slowly added until the pH was 6.9. At this pH mercury ions were precipitated as mercuric sulfide. The solid was filtered off, and the filtrate was further acidified to precipitate coumaric acid. Crude coumaric acid was recrystallized from 8 L of distilled water containing 50 mL of 95 % ethanol, and dried to yield 69.4 g (85 %, 0.422 mol) of pale yellow crystals, mp 209-210 °C. ^1H NMR (CD_3OD , $\text{CDCl}_3/\text{Me}_4\text{Si}$): δ 5.03 (s, more than 2H, average of OH from coumaric acid and from CD_3OD), 6.55 (d, $J=16$ Hz, vinylic H, 1H), 6.81 (t, $J=7$ Hz, aromatic H, 1H), 7.20 (t, $J=7$, aromatic H, 1H), 7.46 (d, $J=7$, aromatic H, 1H), 7.99 (d, $J=16$ Hz, vinylic H, 1H); $^{13}\text{C}[^1\text{H}]$ NMR (CD_3OD , $\text{CDCl}_3/\text{Me}_4\text{Si}$): δ 116.2, 118.4, 120.5, 122.4, 129.8, 132.3, 142.4, 157.8, 171.2

o-Hydroxystyrene²

Coumaric acid (40 g, 0.244 mol) was distilled at 25-30 mmHg using a special apparatus. Refer to Figure 2. Decomposition of coumaric acid started when the temperature of the pot was 205-210 °C, and the decomposition products were distilled at around 130 °C. After the decomposition was complete, 50 mL of dichloromethane and 0.05 g of benzoquinone were mixed with the distillate to dissolve the product. The dichloromethane layer was separated and washed four times with saturated sodium bicarbonate solution to remove unreacted coumaric acid. The dichloromethane layer was extracted twice with 50 mL of 4N NaOH solution, leaving organic impurities behind in the organic phase. The aqueous layer was acidified with 3N HCl and extracted with three 20 mL portions of dichloromethane. Dichloromethane extracts and 0.05 g of benzoquinone were combined and dried over anhydrous magnesium sulfate. The solution was filtered, and the solvent was removed on the rotary evaporator to yield 19.1 g of *o*-hydroxystyrene (65 %, 0.159 mol) as a dark brown liquid. IR (neat). 3450 cm^{-1} The NMR spectra of this compound were not taken.

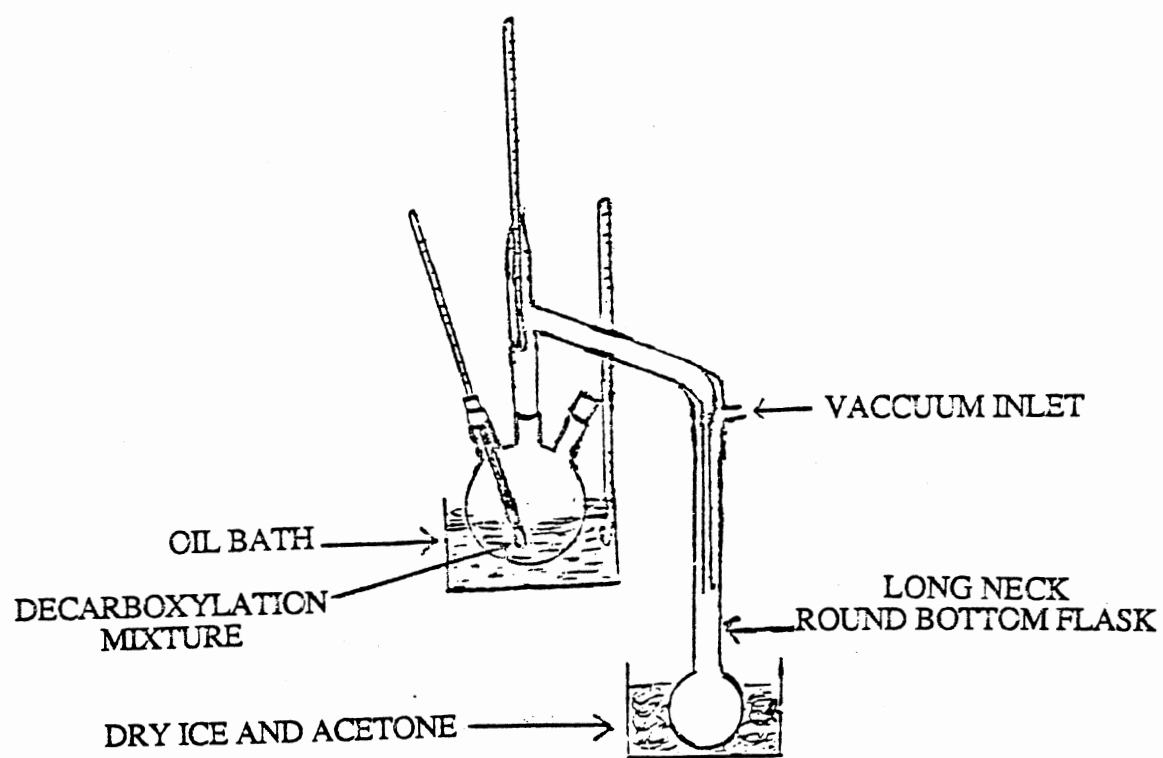


Figure 2. Apparatus for decarboxylation of coumaric acid.

12-Bromododecyl *o*-Styryl Ether

1,12-Dibromododecane (22.4 g, 0.068 mol), and 80 mL of ethanol were mixed in a 250 mL three necked round bottom flask, fitted with a dropping funnel, and a thermometer. *o*-Hydroxystyrene (5.0 g, 0.042 mol), sodium hydroxide (1.9 g, 0.048 mol), and benzoquinone (0.1 g) were dissolved in 15 mL of ethanol. The solution in the flask was heated to 70 °C, and the solution of *o*-hydroxystyrene was slowly added over a period of 1 h. After addition was complete, the temperature was maintained at 70 °C for 9 h. The reaction mixture was cooled and extracted with three 100 mL portions of diethyl ether. The ether extracts were combined, washed with distilled water, and dried over anhydrous magnesium sulfate. The solution was filtered, and the solvent was removed on a rotary evaporator giving 25 g of a brown colored liquid. This liquid was chromatographed through 250 g of 40 μm flash chromatography grade silica gel at atmospheric pressure. With petroleum ether as eluant 1,12-dibromododecane came out in the first 1.8 L, and 2.2 L of 5 % toluene in petroleum ether eluted 5.9 g of 12-bromododecyl *o*-styryl ether (38 %, 0.0161 mol) as colorless solid. ¹H NMR (CDCl₃/Me₄Si): δ 1.25 (m, (CH₂)₈, 16H), 1.76 (m, CH₂-C-Br, CH₂-C-O, 4H), 3.30 (t, J=7 Hz, CH₂Br 2H), 3.89 (t, J=6 Hz, CH₂O, 2H), 5.20 (d, J=10 Hz, vinylic H, 1H), 5.72 (d, J=18 Hz, vinylic H, 1H), 6.77 (d, J=7 Hz, aromatic H, 1H), 6.85 (t, J=7 Hz, aromatic H, 1H), 7.04 (dd, J=11 Hz, 18, vinylic H, 1H), 7.12 (t, J=7 Hz, aromatic H, 1H), 7.42 (d, J=7 Hz, aromatic H, 1H); ¹³C(¹H) NMR (CDCl₃/Me₄Si): δ 26.1, 28.2, 28.8, 29.3, 29.4, 29.4, 29.5, 32.8, 33.7, 68.1, 111.7, 113.8, 120.4, 126.3, 126.6, 128.7, 131.8, 156.2

12-(*o*-Styryloxydodecyl)trimethylammonium Bromide

(SDTAB)

12-Bromododecyl *o*-styryl ether (5.0 g, 0.0136 mol) dissolved in 100 mL of acetone was placed in a 250 mL three necked flask fitted with a dry ice condenser.

Trimethylamine (1.6 g, 0.0272 mol) dissolved in 20 mL of acetone was added to this solution. The reaction mixture was kept under argon and stirred for 12 h at room temperature. At the end of the reaction a white solid precipitated. It was recrystallized from acetone to give 5.5 g of 12-(*o*-styryloxydodecyl)trimethylammonium bromide (95 %, 0.0129 mol). $^1\text{H-NMR}$ (CD_3OD , $\text{CDCl}_3/\text{Me}_4\text{Si}$): δ 1.35 (m, $(\text{CH}_2)_8$, 16H), 1.76 (m, $J=6$ Hz, $\text{CH}_2\text{-C-O}$, $\text{CH}_2\text{-C-N}$, 4H), 3.14 (s, $\text{N}(\text{CH}_3)_3$, 9H), 3.97 (t, $J=6$ Hz, CH_2O , 2H), 5.20 (d, $J=18$ Hz, vinylic H, 1H), 5.74 (d, $J=10$ Hz, vinylic H, 1H), 6.88 (m, $J=7$ Hz, aromatic H, 1H), 7.06 (dd, $J=10$ Hz, vinylic H, 1H), 7.2 (t, $J=8$ Hz, aromatic H, 1H), 7.46 (d, $J=7$ Hz, aromatic H, 1H). $^{13}\text{C}[^1\text{H}]$ NMR (CD_3OD , $\text{CDCl}_3/\text{Me}_4\text{Si}$): δ 23.8, 27.1, 27.2, 30.0, 30.4, 30.4, 30.5, 53.5, 53.5, 67.7, 69.2, 113.0, 114.2, 121.4, 127.2, 129.8, 132.8, 157.4

General Procedure for Polymerization

Calculated quantities of styrene, DVB, and SDTAB were mixed in deionized water in a three necked flask fitted with a condenser, and stirred magnetically under argon for 45 min. The mixture was then deaerated by bubbling argon through it for 10 min. Azobis(isobutyronitrile) (AIBN) was added, and the mixture was stirred for 10 min. The reaction mixture was heated to 65 °C with an oil bath for 20 h, and at 80 °C for 2 h. The reaction mixture was then allowed to cool to room temperature, filtered through cotton, and stored. In some cases a coagulum was obtained as a white solid from filtration. The molar compositions of reagents used to prepare the polymers are reported in Table III.

TABLE III
RECIPES FOR EMULSION POLYMERIZATION

% SDTAB	Wt of SDTAB	% DVB	Wt of DVB	% Styrene	Wt of styrene	Wt of AIBN	Volume of water	Wt of coagulated polymer
0.5	0.202	1	0.123	98.5	9.7	0.0501	90	0.6
1	0.397	1	0.121	98	9.5	0.0500	90	—
2	0.768	1	0.117	97	9.1	0.0500	90	—
3	1.127	1	0.115	96	8.8	0.0503	90	—
5	1.786	1	0.109	94	8.2	0.0505	91	—
1	0.397	3	0.363	96	9.3	0.0503	91	0.9
2	0.768	3	0.351	95	8.9	0.0501	90	0.4
3	1.127	3	0.344	94	8.6	0.0505	91	0.5
5	1.786	3	0.327	92	8.0	0.0507	91	0.3
1	0.397	5	0.606	94	9.1	0.0505	91	4.5
2	0.768	5	0.586	93	8.7	0.0503	90	1.4
3	1.127	5	0.573	92	8.4	0.0505	91	0.4
5	1.786	5	0.540	90	7.8	0.0506	91	0.1

The weights are given in grams, volumes are given in milliliters.

Latexes were purified by ultrafiltration at 70 psi of nitrogen through 0.1 μm cellulose acetate/nitrate membrane (Millipore). Although the pore size of the filter was greater than the particle sizes, the particles were retained on the filter. Probably such filtration is possible due to the specific structure of the filter. However this phenomenon is not yet very clear. The apparatus was shaken continuously using a wrist action shaker. The filtrate was collected, and the conductivity of the filtrate was checked after 40-60 mL of the filtrate was collected. The latexes were washed with deionized water until the conductivity of the filtrate dropped below $10 \times 10^{-6} \text{ ohm}^{-1}\text{cm}^{-1}$. The volumes of deionized water required are 100 to 700 mL depending upon SDTAB concentration. The greater the SDTAB concentration, the greater the volume of deionized water required for washing.

Determination of the Particle Sizes

Sizes Transmission electron micrographs of the diluted latexes with solids contents of 0.3 to 0.5 % by weight were taken on a JEOL TEM-SCAN model 100 CX II instrument in TEM mode at 80 kV. The magnifications were 19,000 and 48,000. The dilute latexes were sprayed onto formvar coated copper grids, dried, and stained with 1 % vinyl acetate for 30 sec before the excess stain was wicked off. Diameters of 50 particles were measured from the photographic negative using a microscope fitted with a vernier scale. Since some of the particles were ellipsoidal in shape, the diameters along both the short and the long axis were measured. An ellipsoid has three axes, but only two can be seen on the micrographs. Hence hypothetical estimates were made for the third axis. Two such estimates are: 1) The third axis is equal to the short axis. 2) The third axis is equal to the average of the long and short axes. For a typical sample of a particle the number average and the weight average lengths, L_n and L_w , were calculated as shown below. The values of both of these lengths should be close to each other for a given particle. The values of the diameters taken for this example are fictitious.

Example. $d_1 = 1.000$ and $d_2 = d_3 = 0.900$

$$L_n = (1.000 + 0.900 + 0.900)/3 = 0.933$$

$$L_w = \left[\frac{(1.000)^2(0.900)^2(0.900)^2}{(1.000)(0.900)(0.900)} \right]^{1/3} = 0.932$$

In the case of $d_1 = 1.000$; $d_2 = 0.900$; $d_3 = 0.950$

$$L_n = 0.950, \text{ and } L_w = 0.949.$$

Thus regardless of which assumption is made for d_3 , the values of L_n , and L_w differ only by 0.933 vs. 0.950.

When the difference between the long and short axes of a particle in the TEM negative was large, the particle was treated as an ellipsoid as well as a sphere, and the corresponding volumes were calculated. When the difference in the volumes was more than 20 %, the particle was rejected. In the other cases an average of the two axes was used for the calculations of D_n , and D_w .

The number average diameter, D_n , a weight average diameter, D_w , and polydispersity index, U , were determined for each set of particles. The formulas are as follows.

$$D_n = (\sum N_i D_i^3 / \sum N_i)^{1/3} \quad (5)$$

$$D_w = (\sum N_i D_i^6 / \sum N_i D_i^3)^{1/3} \quad (6)$$

$$U = D_w / D_n \quad (7)$$

A program was written in Basic on an IBM personal computer to perform the above calculations. The results are reported in Table II.

Determination of the Bromide Contents of the Polymers

The quantity of solids in the latex was determined by drying 10 g of the latex at 68-70 °C for 3-4 h, followed by drying under vacuum at 40 °C for 1 h. Volhard's method²⁰ was used for the determination of the bromide content. The quantity of the latex corresponding to 1 g of the solids was taken, and mixed with 10 mL of 6 M HNO₃, and an excess aliquot of 0.010 M AgNO₃. The mixture was stirred for 15 min, and 5 mL of the indicator was added. This solution was stirred magnetically, and 0.010 M KSCN solution was slowly added to it. The end point of this titration was milky white to pale brown. The results of these titrations are given in Table IV.

TABLE IV
RESULTS OF VOLHARD TITRATIONS

% SDTAB	% DVB	% Styrene	Weight of latex used, g	mL of AgNO ₃ added	mL of KSCN needed	mL of AgNO ₃ reacted	mmoles SDTAB added	mmoles Br in latex	% Br
0.5	1	98.5	136.4	25	20.7	4.3	0.474	0.41	86
1	1	98	60.9	30	21.0	9.0	0.932	0.90	97
2	1	97	54.2	40	22.4	17.6	1.80	1.76	98
3	1	96	50.6	50	25.9	24.1	2.65	2.41	91
5	1	94	54.7	60	21.0	39.0	4.19	3.9	93
1	3	96	153.2	30	20.0	10.0	0.932	0.92	99
2	3	95	37.7	40	22.0	18.0	1.80	1.73	96
3	3	94	96.1	50	22.1	27.9	2.65	2.65	100
5	3	92	59.3	60	21.6	38.4	4.19	3.78	90
1	5	94	—	—	—	—	—	—	—
2	5	93	—	—	—	—	—	—	—
3	5	92	87.4	50	24.2	25.8	2.65	2.5	94
5	5	90	63.7	60	20.8	39.2	4.19	3.88	93

Determination of Critical Micelle Concentration of SDTAB

In order to determine the critical micelle concentration of the surfactant solutions with seven different concentrations were made, and the conductivities of these solutions were measured. The observations are as follows.

Concentration in mM	Conductivity x $10^6 \text{ ohm}^{-1} \text{ cm}^{-1}$
4.7	225
9.3	330
12.5	420
18.0	560
22.5	590
26.5	640
41.9	840

A graph of concentration vs. conductivity was plotted as Figure 1. It showed two straight lines intersecting at one point. The concentration corresponding to this point is the critical micelle concentration of SDTAB.

REFERENCES

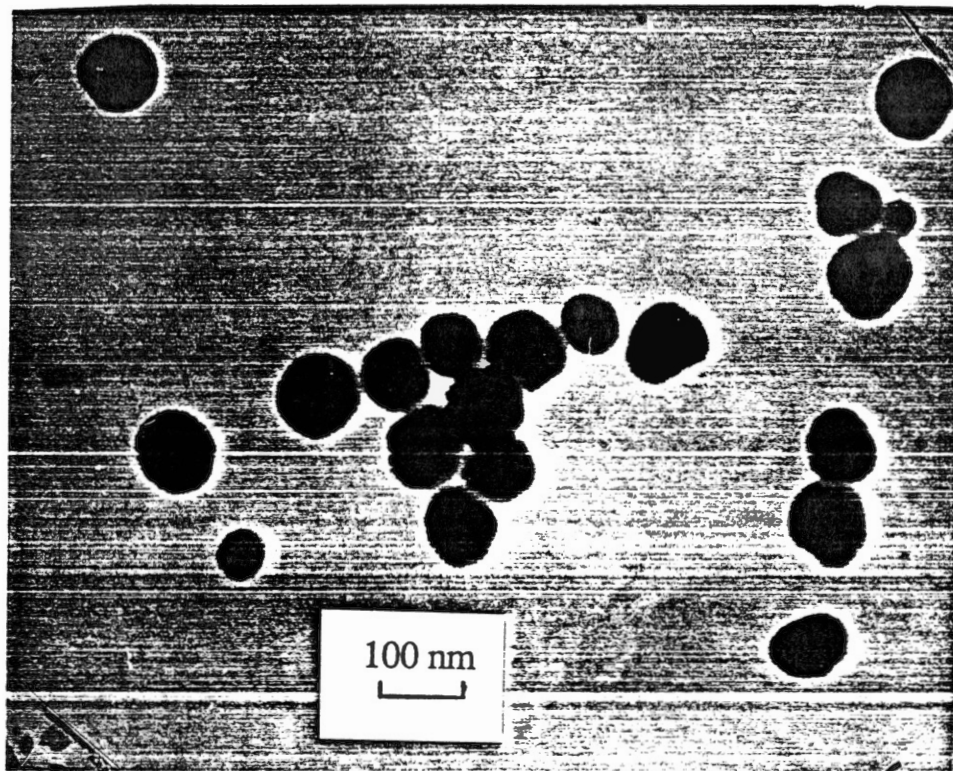
1. Blackley, D. C. *Emulsion Polymerization, Theory and Practice*; John Wiley and Sons, New York, 1975, p 1.
2. Tsaur, S. L. *Synthesis of Surface-active Polymerizable Monomer and Chemically Functional Polymer Colloids Derived Therefrom*; Ph.D. Thesis, 1983, The University of Connecticut.
3. Hiemenz, P. C. *Principles of Colloid and Surface Chemistry*; Marcel Decker Inc: New York., 1977, p 1.
4. Smith, W. V.; Ewart, R. H. *J. Chem. Phys.* **1948**, *16*, 592.
5. Baxandale, J. H.; Evans, M. G.; Kilham, J. K. *Trans. Faraday Soc.* **1946**, *42*, 668.
6. Harding, I. H. *Coll. Polym.Sci.* **1985**, *263*, 58.
7. LaMer V. K.; Dinegar, R. H. *J. Am. Chem. Soc.* **1950**, *72*, 4847.
8. Ottewill, R. H. in *Emulsion Polymerization* ; Piirma, I. Ed.; Academic Press: New York, N. Y., p 1.
9. Dunn, A. S. in *Emulsion Polymerization*; Piirma, I. Ed.; Academic Press : New York, N. Y., p 221.
10. Liu, L.; Krieger, I. M. *J. Polym. Sci.; Polym. Chem. Ed.* **1981**, *19*, 3013.
11. Juang, M. S.; Krieger, I. M. *J. Polym. Sci.: Polym. Chem. Ed.* **1976**, *14*, 2089.
12. Chen, S.; Chang, H. *J. Polym. Sci.: Polym. Chem. Ed.* **1985**, *23*, 2615.
13. Greene, B. W.; Sheetz, D. P.; Fiker, T. D. *J. Coll. Interface Sci.* **1970**, *32*, 90.
14. Sakota, K.; Takuji, O. *J. Appl. Polym. Sci.*, **1976**, *20*, 1725.
15. Kim, J. H.; Chainey, M.; El-Aasser M. S.; Vanderhoff, J. W. *J. Polym. Sci. : Polym.Chem. Ed.* **1988** (In press).

16. Obrecht, W.; Seitz, U.; Funke, W. in *Emulsion Polymerization ; ACS Symp. Ser.* **1975**, *24*, 92.
17. Kast, H.; Funke, W. *Makromol. Chem.*, **1976**, *177*, 1567.
18. Srinivasan, S. S. personal communication; Oklahoma State University, 1987.
19. Hamid, S.; Sherington, D. *J. Chem. Soc., Chem. Commun.* **1986**, 936.
20. Vogel A. I., *A Text-book of Qualitative Inorganic Analysis*; Longmans : 3rd ed., p 258.

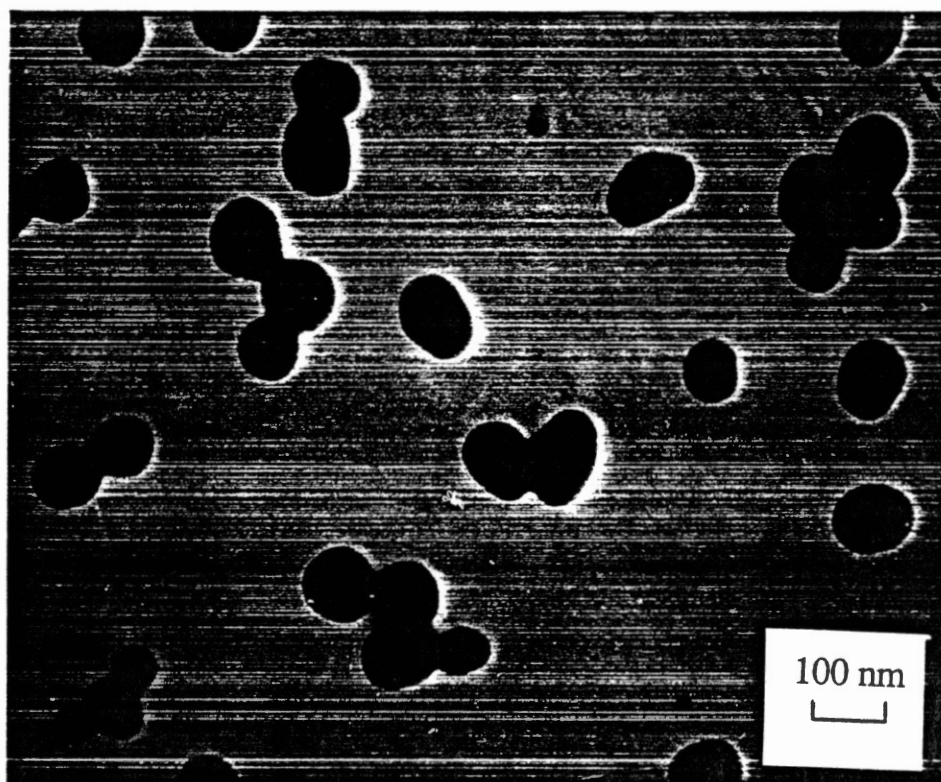
APPENDIXES

APPENDIX A

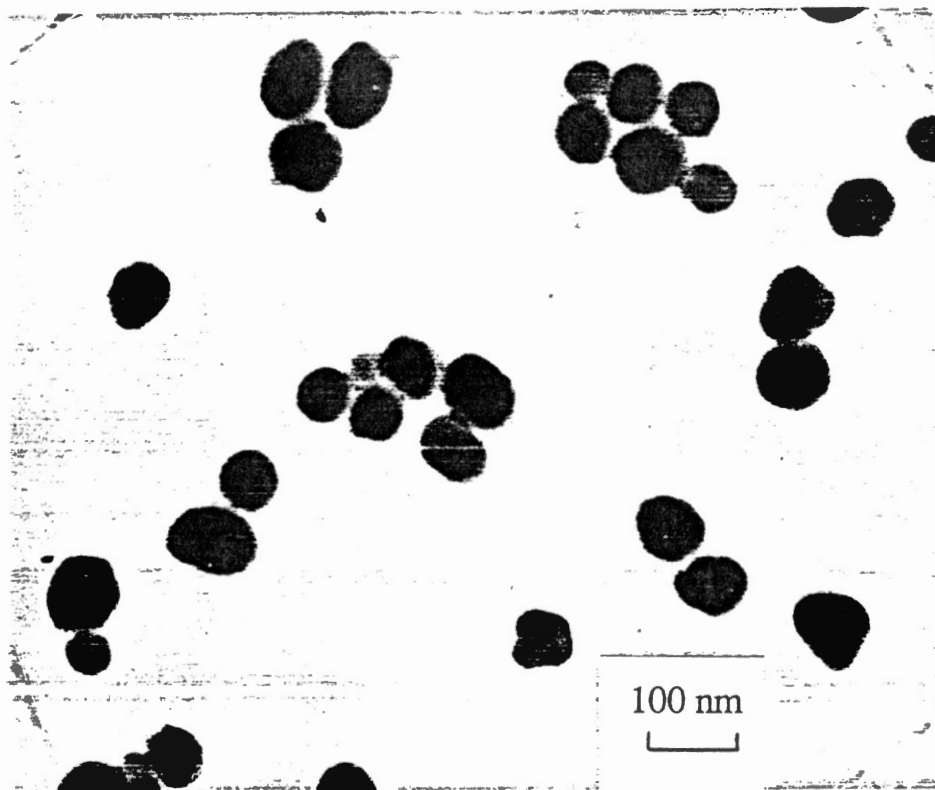
TEM PHOTOGRAPHS OF POLYMER PARTICLES



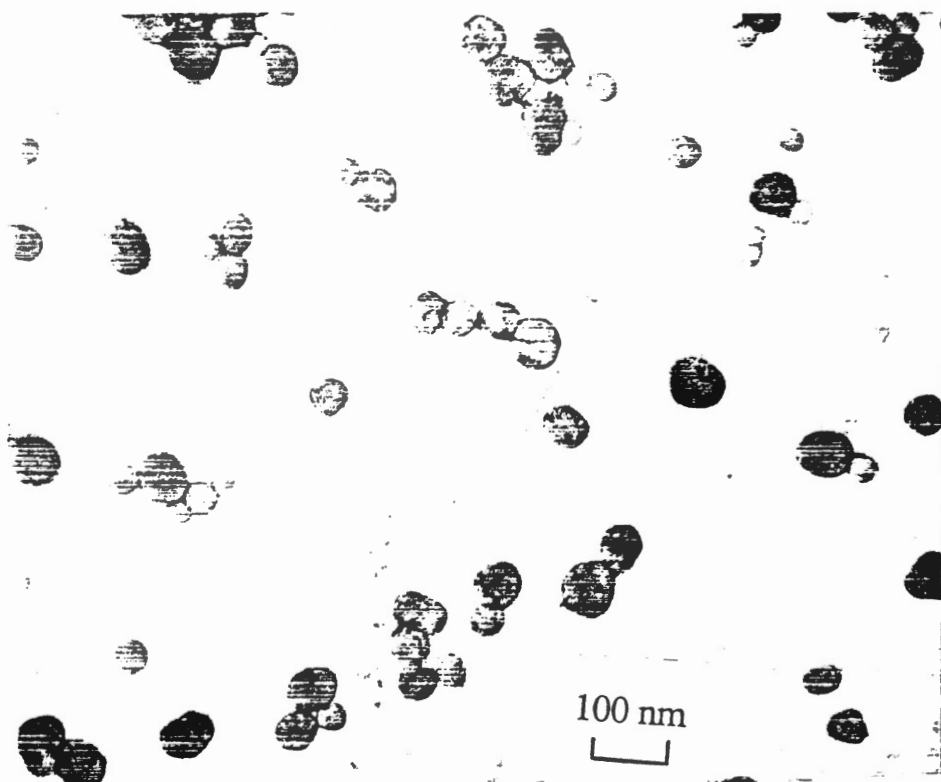
0.5 % SDTAB, 1 % DVB



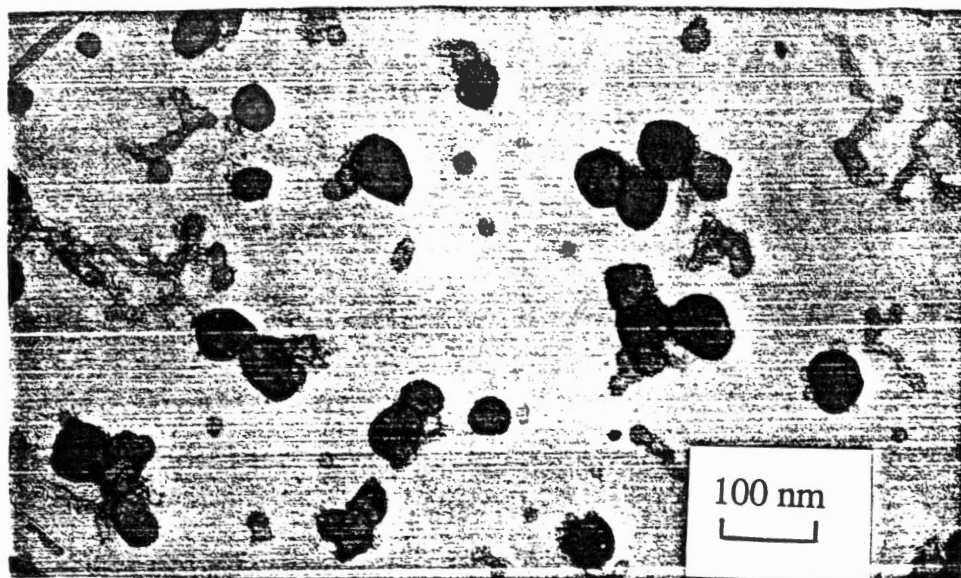
1 % SDTAB, 1 % DVB



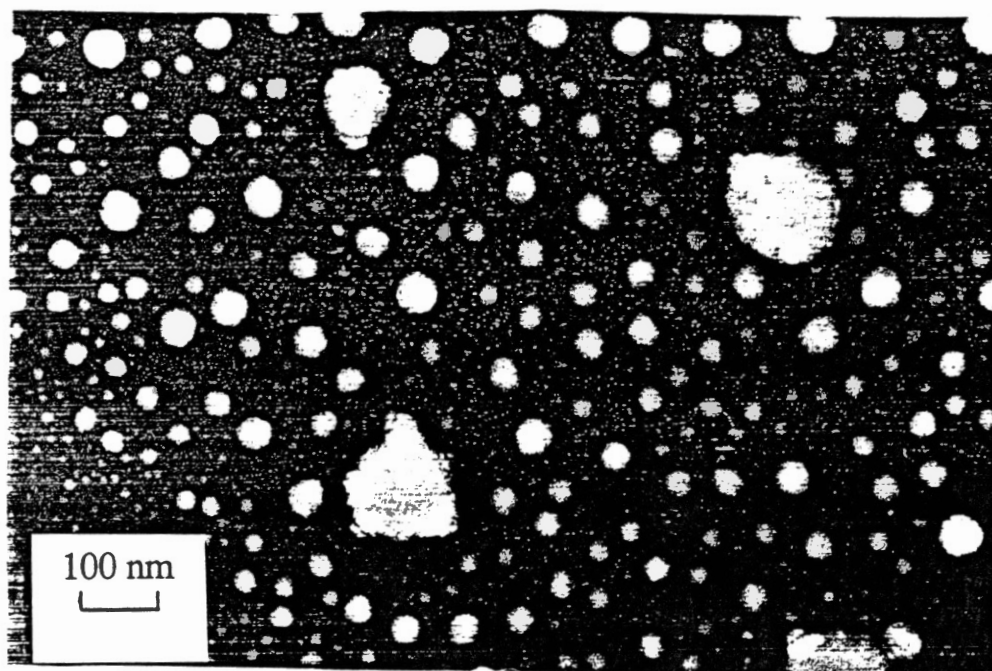
2 % SDTAB, 1 % DVB



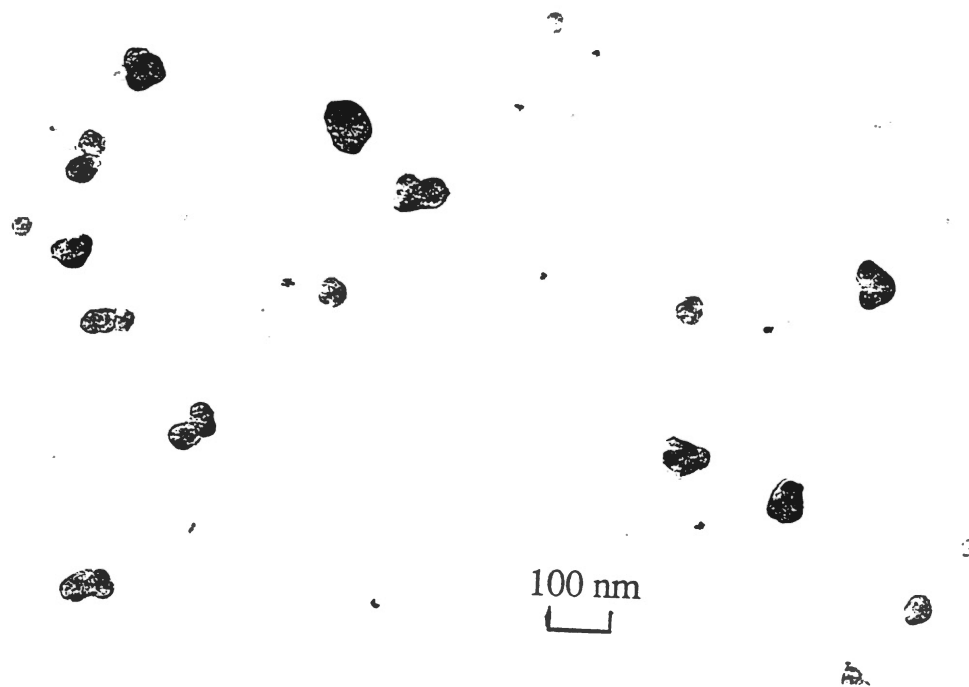
3 % SDTAB, 1 % DVB



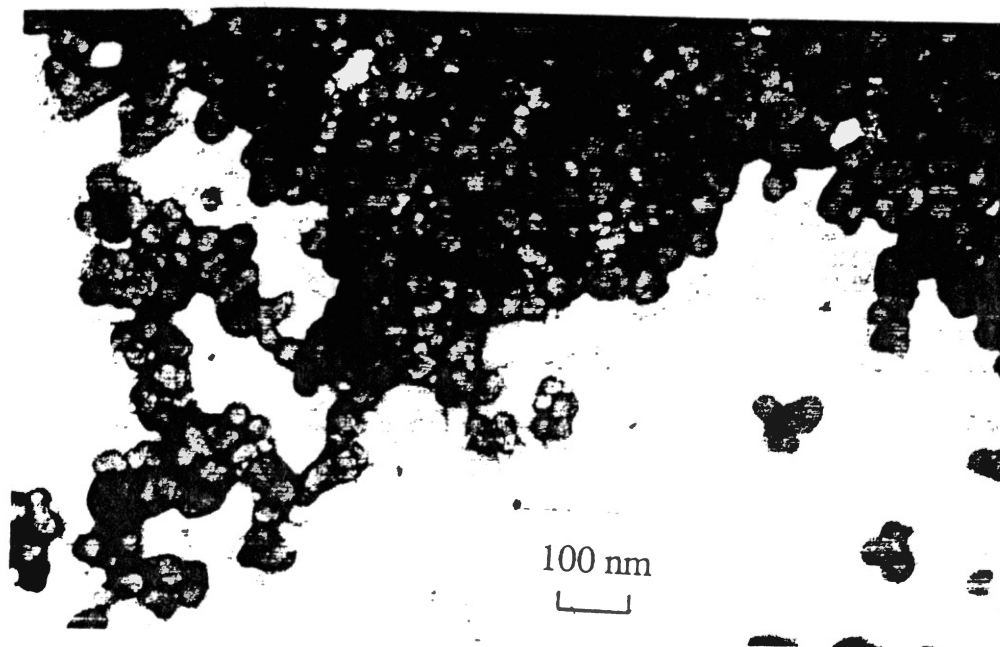
5 % SDTAB, 1 % DVB



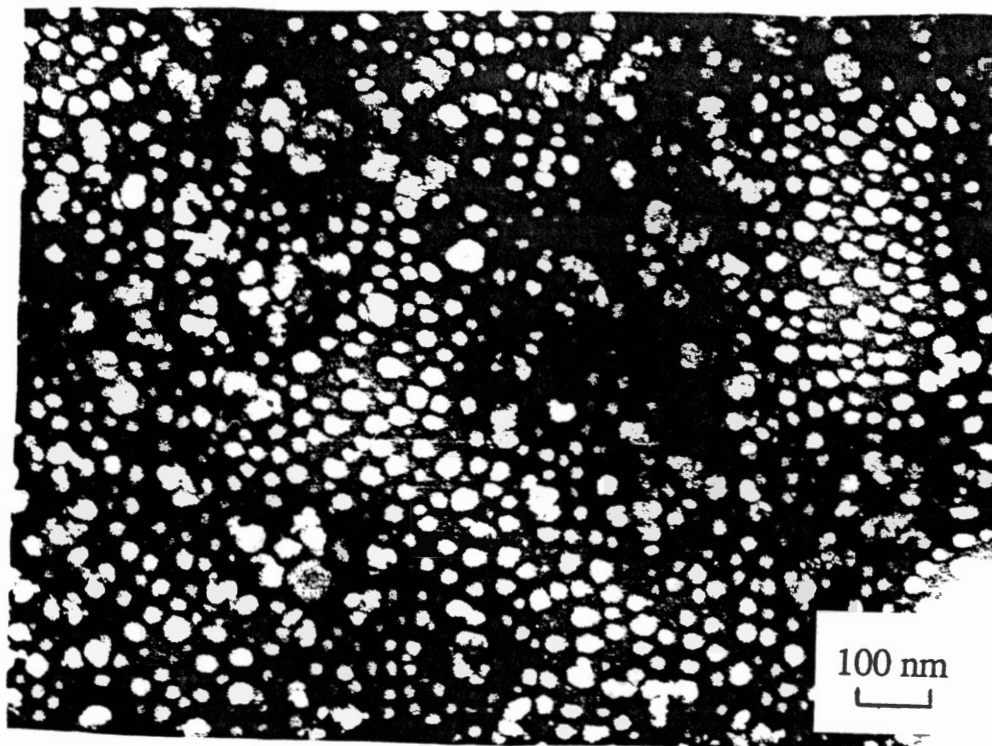
1 % SDTAB, 3 % DVB



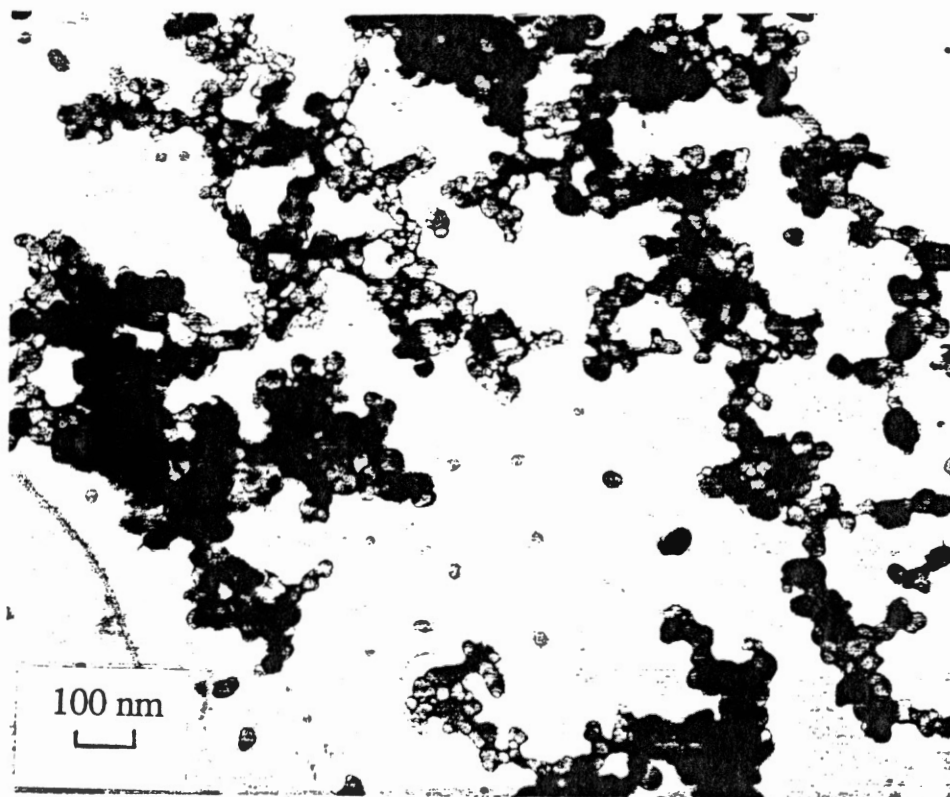
2 % SDTAB, 3 % DVB



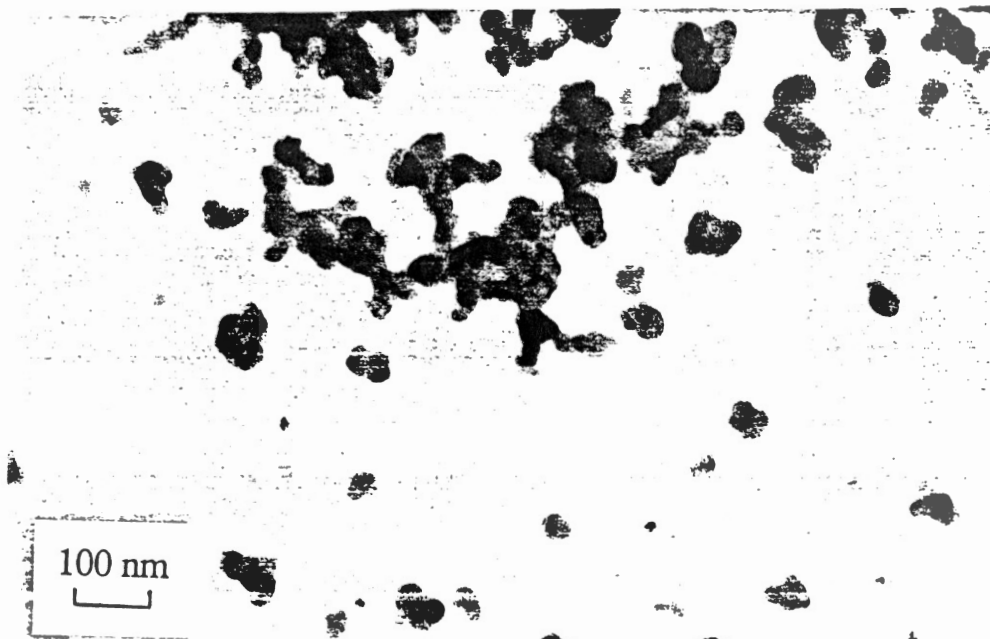
3 % SDTAB, 3 % DVB



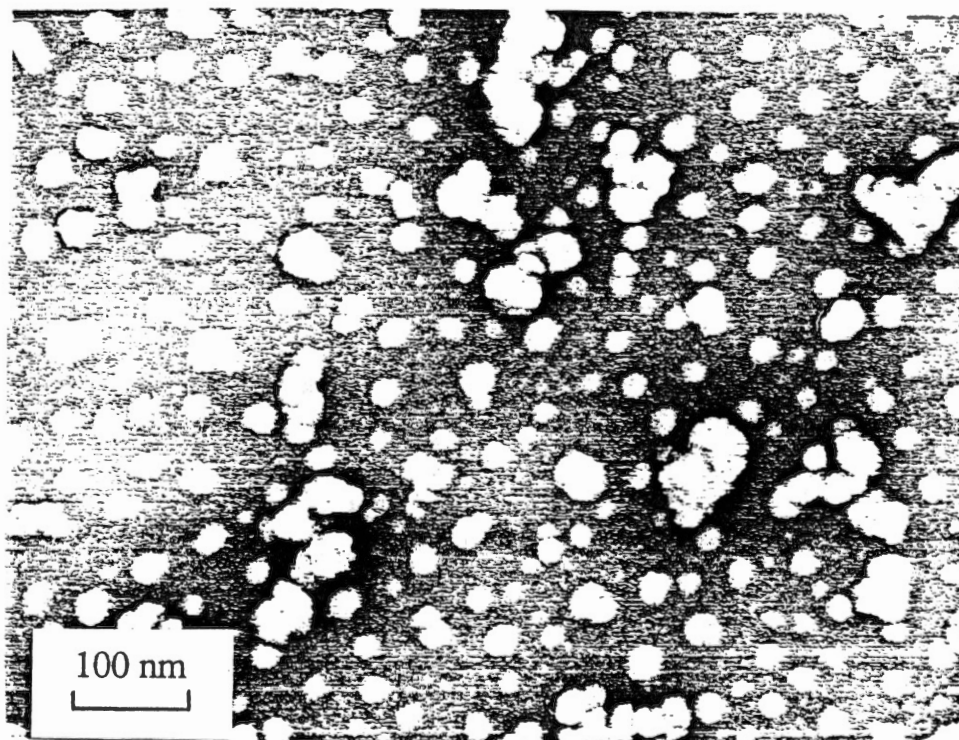
5 % SDTAB, 3 % DVB



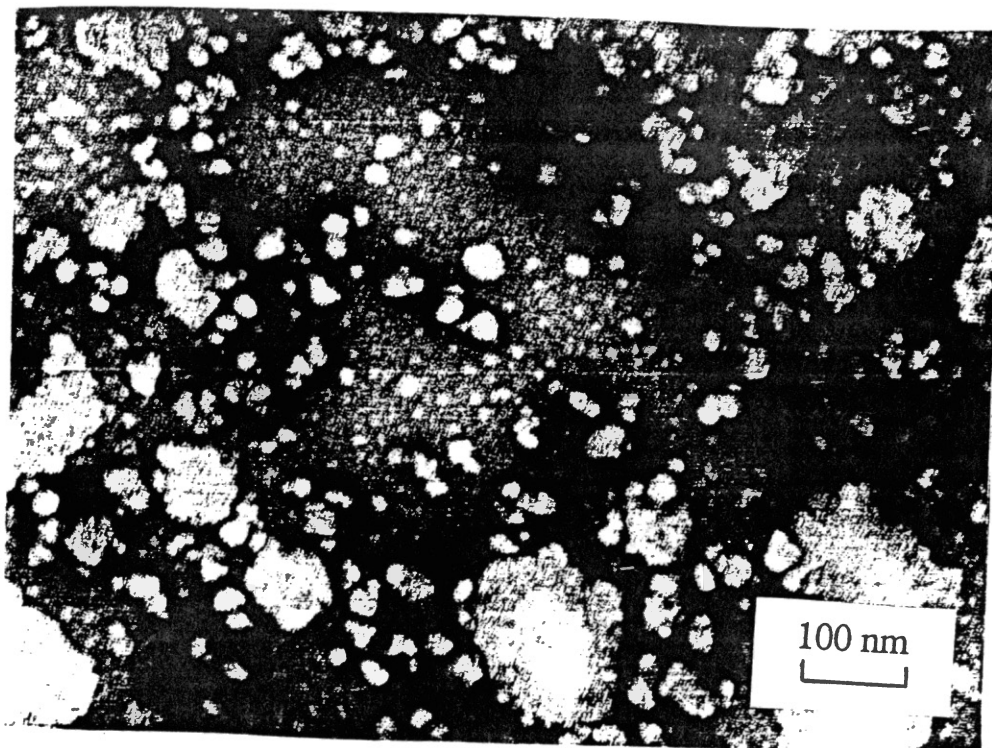
1 % SDTAB, 5 % DVB



2 % SDTAB, 5 % DVB

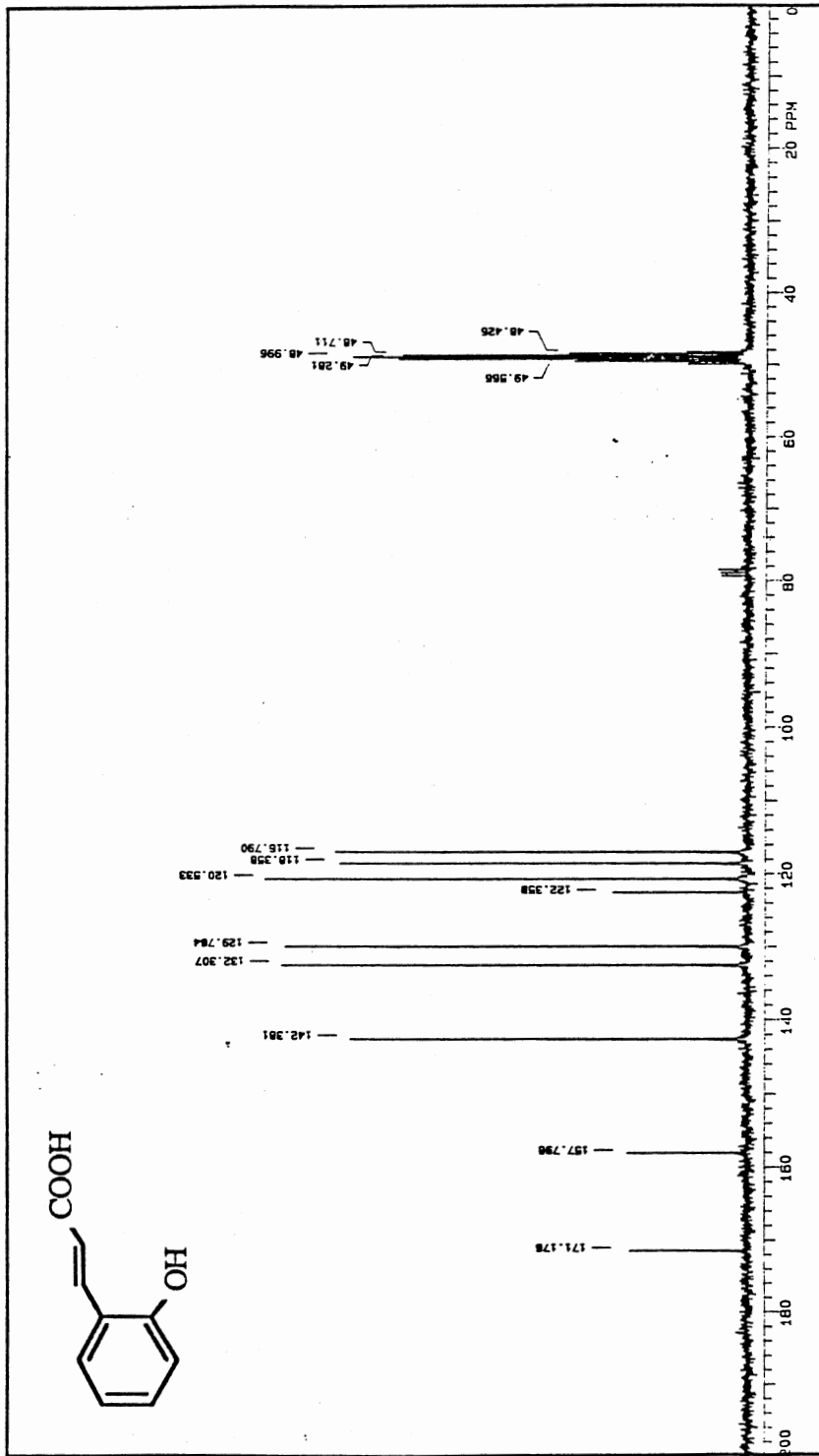


3 % SDTAB, 5 % DVB

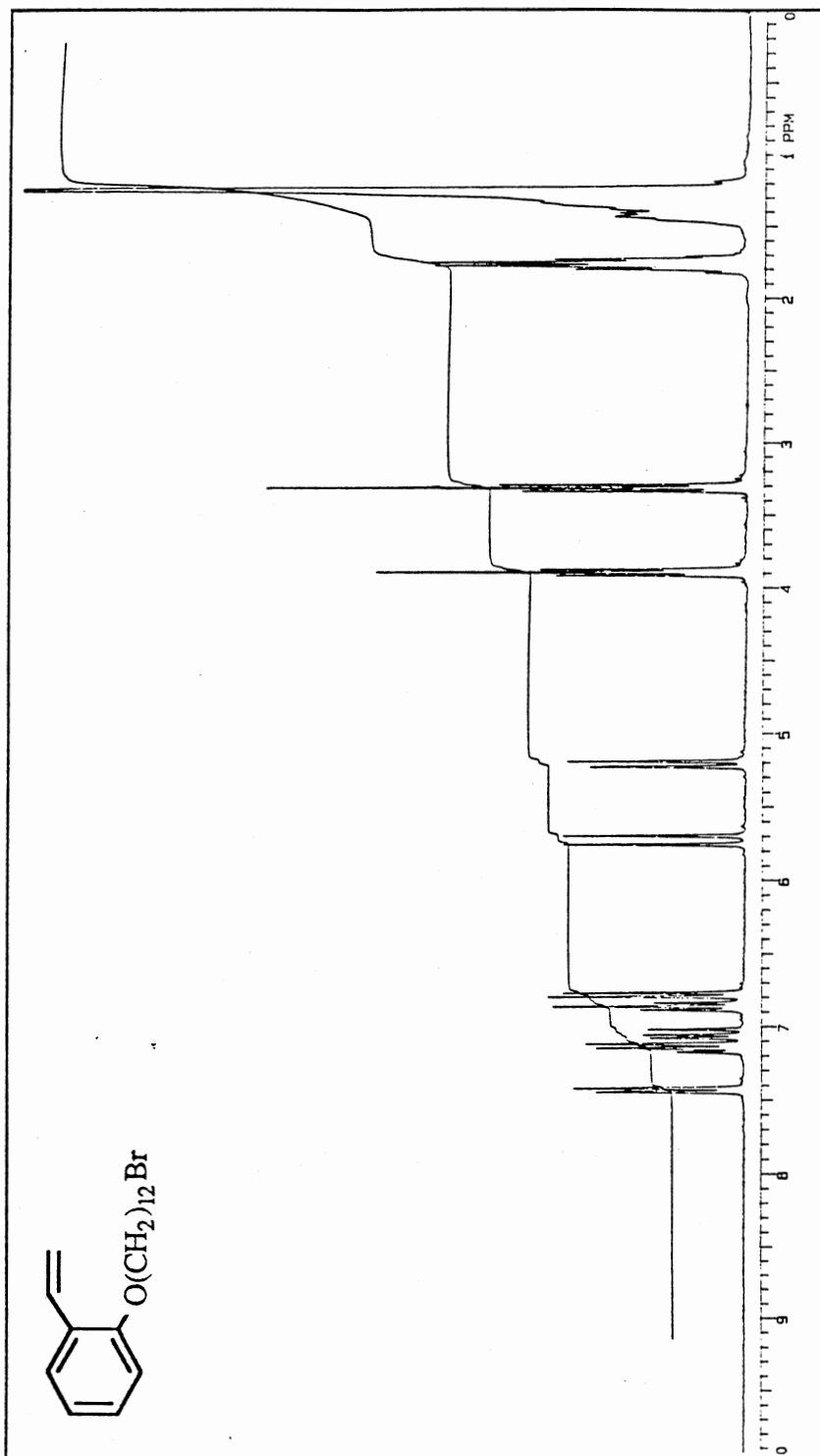


5 % SDTAB, 5 % DVB

APPENDIX B
SELECTED NMR SPECTRA



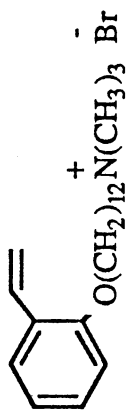
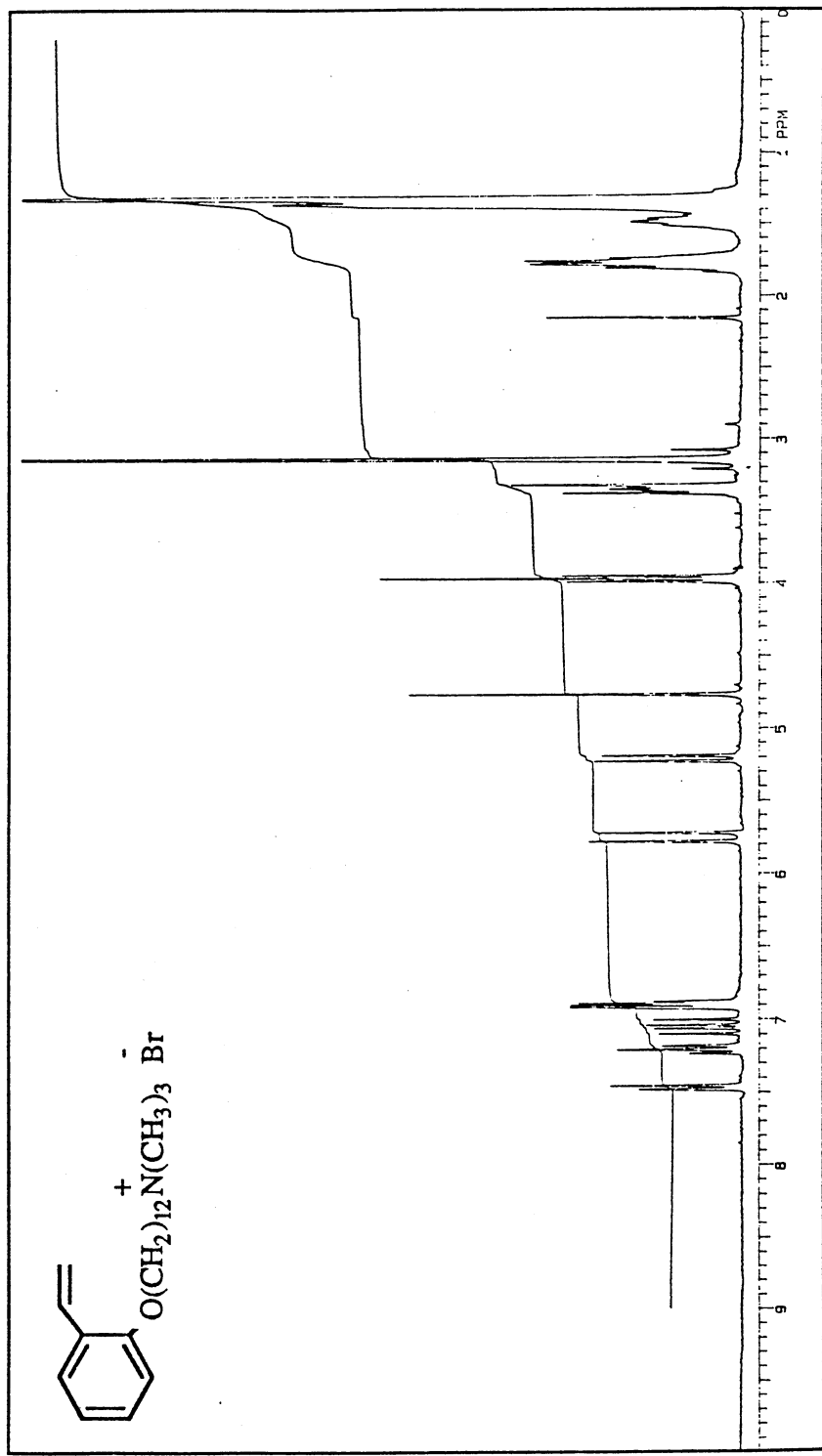
PREPARED: _____
 Nucleus: ^{13}C Freq: 125.76 MHz
 Spec Mod: 0000.0 Hz Offset: 130.0 Hz
 Acq Freq: 125.76 MHz Delay: 3.000 sec
 Pulse Width: 12.0 μs Transp: 60
 RECEIVED: _____
 Nucleus: ^{13}C P1: 1.500 s P2: 120.0 μs
 Mod: VXX Power: 0 dB
 Acquisition: 5 s Freq: 125.76 MHz
 Pulse Width: 12.5 μs Power Mode: _____
 REFERENCE: _____
 P1: 64.1 s P2: 10.0 μs CD: _____
 Mod: 0000.0 Hz Offset: 0.0 Hz
 Acquisition: 5 s Freq: 125.76 MHz
 Pulse Width: 12.5 μs Power Mode: _____
 EXPERIMENT: _____
 File Name: 510130-0130
 Tube ID: NUC-1-1C
 Temp: _____ $^{\circ}\text{C}$
 Solvent: CDCl_3
 SAMPLE: _____
 Number: _____
 Date: 01-04-88
 File: NUC1C
 VFA
 X-174-300
 V1818



RECEIVED **EXPERIMENT** **PLATE/PROCESSING** **NAME**
 Nucleus: 1.500 MHz Freq: 300 MHz Nucleus: 1.500 MHz Freq: 300 MHz Nucleus: 1.500 MHz Freq: 300 MHz
 Spc. Wdh: 4000.0 Hz Offset: 100 Hz Spc. Wdh: 4000.0 Hz Offset: 100 Hz Spc. Wdh: 4000.0 Hz Offset: 100 Hz
 Acq. Time: 1.000 sec Delay: 0 sec Acq. Time: 1.000 sec Delay: 0 sec Acq. Time: 1.000 sec Delay: 0 sec
 Pulse Width: 2.0 sec Transm: 15 Pulse Width: 2.0 sec Transm: 15 Pulse Width: 2.0 sec Transm: 15

REFERENCE **PARAMETERS** **EXPERIMENT** **SAMPLE**
 Ref: 0.1 Hz Wdth: 2555.0 Hz/gm Sfr: 0 Hz/gm Ref: 0.1 Hz Wdth: 2555.0 Hz/gm Sfr: 0 Hz/gm
 Modulation: 0 Hz Modulation: 0 Hz Modulation: 0 Hz Modulation: 0 Hz
 Pulse Seq: 1234 Pulse Seq: 1234 Pulse Seq: 1234 Pulse Seq: 1234
 Tube ID: 00 Tube ID: 00 Tube ID: 00 Tube ID: 00
 Temp: 0 °C Temp: 0 °C Temp: 0 °C Temp: 0 °C
 Solvent: CDCl3 Solvent: CDCl3 Solvent: CDCl3 Solvent: CDCl3

Name: _____
 File: 030301
 Date: 01-01-00
 A: PHN-000 Version: _____



ACQUIRE
 Nucleus: 1,500 MHz
 Spec. Vols: 4000.0 Hz
 Acq. Time: 1.000 sec
 Pulse Width: 2.0 sec
 Relax: 300 sec
 Offset: 130.2 Hz
 Power: 20 dB
 Frequency: 200 MHz
 Pulse Width: 32 sec

PROCESSE
 FI: 8.1 Hz
 LB: 1.0 Hz
 WH: 2399.8 Hz
 Reference:

EXPERIMENT
 Name Sequence: 31311L
 Tube ID: MOC-I-4H
 Temp: °C
 Solvent: CDCl3

SAMPLE
 Number: 1111
 File: 31311L
 Date: 01-04-88
 XL: 16 3100 V011011

VITA ²

Milind D. Choubal

Candidate for the degree of

Master of Science

**Thesis: PARTICLE SIZES OF EMULSION COPOLYMERS OF
12-(*o*-STYRYLOXYDODECYL)TRIMETHYLAMMONIUM BROMIDE,
STYRENE, AND DIVINYLBENZENE**

Major Field: Chemistry

Biographical:

Personal Data: Born in Pune, India, January 4, 1958, the son of Dattatraya S. and Pushpa Choubal.

Education: Graduated from Raja Shivaji Vidyalaya, Bombay, India, In March, 1974; received Bachelor of Science Degree in Chemistry from University of Bombay in April, 1978; received Master of Science in Organic Chemistry from University of Bombay in October, 1980; completed requirements for the Master of Science Degree at Oklahoma State University in December, 1988.

Professional Experience: Teaching Assistant, Department of Chemistry, Western Carolina University, August 1982 to August 1985; Teaching Assistant, Department of Chemistry, Oklahoma State University, August, 1985 to December, 1987; Teaching Assistant, Department of Chemistry, Western Carolina University, January, 1988 to August, 1988.