Characterization of polystyrene latexes
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Abstract: Polystyrene latexes were prepared by emulsion polymerization. Styrene was used as monomer, potassium persulfate was the reaction initiator and sodium hydrogen carbonate was used as buffer. Surfactant may or may not be used. Three types of surfactant, ie sodium dodecylbenzene sulfonate (anionic), Triton X-100 and Vulcastab LW (nonionic), and hexadecyltrimethyl ammonium bromide (cationic), were used. The prepared latexes were characterized according to concentration, density, pH, ionic strength, particle size, particle size distribution and surface charge.

For prepared latexes with anionic surfactant, the effects of temperature, initiator concentration, surfactant concentration and amount of monomer on the latex size were investigated. Scanning electron microscopy was used as a tool for latex characterization. The results show that by increasing temperature, initiator and emulsifier concentration, the latex diameter decreases. However, size increases by increasing the amount of monomer. A potentiometric titration technique was employed for determination of surface charge. It was found that for all latexes, surface charge densities are in the same range.

INTRODUCTION
The preparation and characterization of polystyrene latex have a long history. Traditionally latex preparation needs four essential elements: monomer, initiator, surfactant and dispersion media. All these parameters, together with preparation conditions, affect latex characteristics.

Synthetic polymeric colloids or latexes are usually made by emulsion polymerization of monomers. Emulsion polymerization is a heterogeneous reaction process in which hydrophobic monomers are dispersed in a continuous phase with the aid of an emulsifier system and polymerized with free-radical initiators. The product, a colloidal dispersion of the polymer, is called a latex.

Numerous publications (for example see ref 1 as an old and ref 2 as a new article) describe the preparation procedures and recipes. New preparation techniques for special applications are emerging (see, for example, ref 3 which explains polystyrene latex preparation for use in immunological applications by chemical modification). Recently the preparation time (normally more than 10h) has reduced to less than 1h by employing microwave radiation.4

It is possible to use various monomers to produce latexes. In many works, including this study, styrene has been used as a monomer due to the characteristics of polystyrene latex which is used as a model for various applications.

Initiator affects the latex characteristics. Potassium, sodium and ammonium peroxy disulfates are well-known initiators for polystyrene latex preparation. By variation of the amount and decomposition rate of the initiator, sulfate groups on the surface of latex particles can be controlled.5 Some other chemicals such as dibenzoyl peroxide6 may also be used as initiator.

Surfactant has a unique effect on latex preparation. It performs the dual function of providing sites for particle nucleation, and providing colloidal stability as a result of their adsorption at the particle–water interface. All types of surfactants, including conventional (anionic, cationic and non-ionic), polymerizable and polymeric surfactants, may be used.7 Non-ionic surfactants such as Triton X-405,8 Triton X-1009 and Tween 209 are widely used for latex preparation. Mixed surfactants are also used.10–12 In the latter research, a mixture of anionic/non-ionic surfactants was used. The anionic surfactant imparts repulsive forces while non-ionic surfactant provides steric stabilization. It is also possible to prepare latexes without surfactant.13–15 In the latter work sodium styrene–sulfonate was used as an ionic comonomer to produce latex.

From a colloid chemistry point of view, only particles prepared in the absence of emulsifier can be considered as an ideal colloidal suspension. Latex particles stabilized by surfactants are not ideal colloidal particles. One reason is that the surfactant ions can be arranged in different ways on the particle surface, with the hydrocarbon chain flat on the surface or pointing away from the surface into the surrounding medium. The hydrophobic tail also may be buried in the particle structure.

Latex should be stable for a long time; however, it is...
possible to measure stability time. An excellent review on the stability of colloids has been published. Preparation of stable latexes needs a balanced composition of the polymerization mixture. The dispersions can be stabilized by addition of emulsifying agent (classical emulsion polymerization). In emulsifier-free emulsion polymerization, initiator creates electrostatic repulsion forces between the particles by adding charged groups to the growing macromolecular chains. For particles with charged groups, electrostatic repulsion provides the basis of colloid stability. However, for particles without charged groups to be stable requires steric stabilization. The stabilization mechanisms during particle growth influence the properties (such as particle size, shape and structure) of the final latex dispersion.

Cationic or anionic initiators are used to produce stable latexes. An anionic or uncharged initiator should be used with anionic emulsifiers, and a cationic or uncharged initiator with cationic emulsifiers. A stable latex may be obtained with an initiator of opposite charge to the emulsifier when a high enough emulsifier concentration is used. Particle size may also affect the colloid stability. It has been shown that colloid stability increases, reaches a maximum and then decreases as the particle size increases.

Thirumalai examined the crystalline states of aqueous suspensions of uniform polystyrene spheres (polyballs). He found that for low density dispersions (low volume fraction) the inherent structure was a cubic crystal. However, at high density (high volume fraction) the latex spheres undergo a transition from a disordered state to an ordered crystalline structure. Palberg et al. introduced a reproducible method for preparation of ordered colloidal suspensions at very low salt concentrations. Shaw and Marshall employed infrared spectroscopy to study the nature of the structural changes which occurred during the emulsion polymerization of styrene. Nakashima et al. studied the surface characteristics of polystyrene latex particles. They found that the latex surface is flat and smooth on a molecular scale. However, although the surface of dry particles appears smooth in scanning electron micrographs, this may be less true for particles in water with hydrophilic end-groups on their surface.

The important characteristics of a latex are particle size, particle size distribution and surface charge. These characteristics are a function of preparation phenomena, ie raw materials, techniques and conditions. In the present work, a systematic study has been organized to elucidate the effect of variable parameters (temperature, monomer, initiator and surfactant concentration) on polystyrene latex characteristics, with emphasis on size and charge. For this purpose, practical techniques rather than theoretical aspects are considered. This article, which is unique in using sodium dodecylbenzene sulfonate as emulsifier, provides information for preparation of polystyrene latex with a desired size and charge.

**MATERIALS AND METHODS**

**Reagents**

Materials used in this work were styrene; sodium hydrogen carbonate, NaHCO₃, d = 2.159 g ml⁻¹ which is used as a buffer; sodium dodecylbenzene sulfonate, C₁₃H₂₇C₆H₄SO₃Na⁺, critical micelle concentration = 5 × 10⁻⁵ M = 0.18%, which is an anionic surfactant; Triton X-100, C₃₈H₇₇O₁₁, critical micelle concentration around 10⁻⁴ M, d = 1.05 g ml⁻¹, which is a non-ionic surfactant; chloroform, CHCl₃, d = 1.47 g ml⁻¹; hydrochloric acid 37%, HCl, and potassium peroxydisulfate, K₂S₂O₈, used as initiator (all from Merck); hexadecyltrimethyl ammonium bromide, [CH₃(CH₂)₁₅N(CH₃)₃]Br, critical micelle concentration = 1.5 × 10⁻² M, which is a cationic surfactant; methanol, CH₃OH, d = 0.79 g ml⁻¹ (from BDH); and Vulcastab LW (ethoxylated linear alcohol), d = 1.06 g ml⁻¹, which is a nonionic surfactant (from ICI).

**Apparatus**

The pH and potential of samples were determined with a Methrom 692pH meter using a combined electrode. A Cambridge scanning electron microscope with resolution of 2.5 nm was used for visualization of the size and shape of particles.

In electron microscopy, preparation of samples is a crucial step and must be performed with attention to the aim of the study. If the sample is not electrically conductive, a thin film of a metal or carbon is coated on its surface. The coating is performed using evaporation in vacuum. The thickness of the coating is about 100 nm. The usual coats are Au, Au–Pd alloy, Al and carbon. For scanning electron microscopy (SEM), samples of the dialysed latexes were diluted with distilled water 20–30 times and dried in refrigerator for a week. The samples were coated with gold and viewed under the scanning electron microscope.

**Procedures**

**Preparation of polystyrene latexes**

Firstly, styrene was distilled under vacuum using a water pump. All the polymerization reactions were carried out in a 50 ml round-bottomed flask. A typical preparation procedure was as follows. Surfactant, styrene and sodium hydrogen carbonate were added to the flask and brought to the reaction temperature (60–90°C) in an oil bath and emulsified by continuous stirring for 15 min. The surfactant is an emulsifying agent, and NaHCO₃ was used as a buffer. Potassium persulfate dissolved in water was also added to the mixture; its role is as reaction initiator. A water-cooled reflux condenser was connected to the flask. The mixture was stirred for 24 h to facilitate the complete conversion of monomer to polymer. At the end of the reaction time, the flask was removed from the oil bath and allowed to cool for a few minutes. Obtaining a single-phase suspension indicates preparation of a latex (positive result). However, in many cases the
prepared suspension formed two phases (negative result). Vigorous stirring is required to disperse the monomer in small droplets and to provide rapid transfer of the monomer from the droplets to the water in order to maintain a monomer-saturated aqueous phase.

The prepared latex must be purified. For latex purification, various techniques have been employed. The methods include filtration, ion exchange and centrifugation. In the present work, the latexes were dialysed against distilled water using a cellophane membrane from Phywe. This is for removal of unreacted monomer, initiator, surfactant and potassium sulfate formed in the reaction. The latex was dialysed for 24 h and then decanted through a filter packed with glass wool. This stage removed both unreacted monomer and any coagulum formed. All dialysis membranes were prepared before use by heating in EDTA (0.1%) solution for 10 min to remove small oligomers.

Latex can be prepared by emulsifier-free emulsion polymerization of styrene in the presence of potassium peroxydisulfate. In this technique, 25 ml of styrene was dispersed in 180 ml of twice-distilled water, in a round-bottomed flask. The mixture was heated to 100°C. The desired amount of potassium peroxydisulfate (0.01–2.0 g) and 45 ml of water were added to the solution. The dispersion was held at 100°C for 6 h, cooled and dialysed against water, then filtered through glass wool. Potentiometric titration of latexes

Acid–base potentiometric titration is a method for determining the charge characteristics of colloidal particles. The potential measurement determines the equivalent point of titration. After addition of NaOH, a time is needed to establish equilibrium. Often, good stirring is effective for reaching equilibrium. For finding the end-point, a potentiometric titration can be organized in different procedures. The easiest way is to plot the potential versus volume of base added. Another way is to calculate \( \frac{DE}{DV} \), in which \( DV \) is the change in NaOH volume and \( DE \) is the corresponding change of potential due to the addition of the base. Plotting \( \frac{DE}{DV} \) versus volume of base provides a sharp maximum at the equivalence point.

For titration experiments a known volume of latex (1 ml) was added to 5 ml of HCl (0.1 M). The sample was stirred for 30 min and filtered. The potential of the solution was measured using a pH meter. A certain volume of NaOH (0.5 M) was added to the sample and the potential was recorded after 2 min.

RESULTS AND DISCUSSION

Polystyrene latex preparation

The anionic surfactant sodium dodecylbenzene sulfonate was used with various amounts of initiator (K\(_2\)S\(_2\)O\(_8\)), monomer and buffer (sodium hydrogen carbonate). Polymerization was carried out at four different temperatures. The details of the recipes and

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<tr>
<th>Sample no</th>
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<th>Surfactant (g)</th>
<th>K(_2)S(_2)O(_8) (g)</th>
<th>H(_2)O (ml)</th>
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\(^a\) See text.
\(^b\) Solvent is CH\(_3\)OH.

Table 1. Emulsion polymerization recipe (anionic surfactant: sodium dodecylbenzene sulfonate)
the results are shown in Table 1. A positive result means that latex was formed and a negative result indicates no formation of latex suspension.

In emulsion polymerization of styrene, water is used as solvent. In sample 24, methanol was used as solvent. No latex was formed, because the initiator (potassium peroxysulfate) may not have been soluble enough in methanol to be effective. Water is a chief ingredient in emulsion polymerization, acting as the medium for transfer of monomer from droplets to particles, the locus for initiator decomposition, and the medium of dynamic exchange of surfactant between the phases. Buffers, such as sodium hydrogen carbonate, are often added to a latex formulation to regulate the pH of the reacting system. The decomposition rate of initiators is also influenced by pH.

For latex preparation, using sodium dodecylbenzene sulfonate as anionic surfactant, suitable conditions are: NaHCO₃, 5.41 × 10⁻³ M; styrene, 5.455 M; surfactant, 1.47 × 10⁻² M and initiator, 1.68 × 10⁻³ M. These quantities were the basis for investigation of the effects of variations of ingredients on latex characteristics.

The cationic surfactant (hexadecyltrimethyl ammonium bromide) did not result in any suitable latex (Table 2). This can be attributed to the dissimilarity of initiator (anionic) and emulsifier (cationic) charge.

Two types of non-ionic surfactant were used in this work. For Triton X-100 (Table 3) by changing the amount of surfactant, a suitable latex may be obtained (sample 3). This shows the importance of the ratio of the amount of surfactant to the other ingredients. Using another non-ionic surfactant (Vulcastab LW, Table 4) latex may (sample 26) or may not (sample 27) be formed. This also shows the importance of the amount of ingredients. Even a small change (0.1 g compared to 0.09 g of Vulcastab LW) may result in negative or positive results.

Latex may be prepared without using surfactant (Table 5). If the amount of initiator is high enough, latex may be formed; shortage of initiator means that free radicals for nucleation of particles cannot be provided.

**Preliminary characteristics**

The concentrations of polystyrene latexes were obtained by drying the samples at room temperature and measuring the weight of the dried samples. The pH and density of each sample were measured by pH meter and picnometer. The ionic strength of each latex suspension was calculated. The results are shown in Table 6.

**Particle size determination**

Various techniques are used for measuring the size of latex particles. This includes hydrodynamic chromatography, ultracentrifugation and electron microscopy. Electron microscopy was used for the first time.

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**Table 2. Emulsion polymerization recipe (cationic surfactant: hexadecyltrimethyl ammonium bromide)**

<table>
<thead>
<tr>
<th>Sample no</th>
<th>NaHCO₃ (g)</th>
<th>Styrene (ml)</th>
<th>Surfactant (g)</th>
<th>K₂S₂O₈ (g)</th>
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* See text.

**Table 3. Emulsion polymerization recipe (non-ionic surfactant: Triton X-100)**

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* See text.

**Table 4. Emulsion polymerization recipe (non-ionic surfactant: Vulcastab LW)**

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* See text.

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**Table 5. Emulsifier-free emulsion polymerization**

<table>
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<td>31</td>
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* See text.
in 1949 by Backus and Williams\textsuperscript{29} and after that by Bradford and Vanderhoff\textsuperscript{30} to determine the particle diameter of polystyrene latexes.

In this study, scanning electron microscopy was used for the determination of particle size and particle-size distribution. The technique is to take two or three micrographs of each sample and measure the size of the particles from the micrographs. A representative micrograph is shown in Fig 1.

Normally it is desired to produce latex particles with narrow size distribution. Kinetic factors influence the uniformity of latexes.\textsuperscript{31} However, it has been found that polydispersity decreases with increasing surfactant concentration or agitation speed.\textsuperscript{32} The particle size distributions of polystyrene latexes were measured using the micrographs. A representative sample is presented in Fig 2 (the others show the same trend). The mean particle size for each sample was obtained from the figure.

<table>
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<th>(w/w%)</th>
<th>pH</th>
<th>Density (g/ml)</th>
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Table 6. Preliminary characteristics of latexes

**Effect of temperature on particle size**

The effect of temperature in the range 60–90 °C on the final particle size was investigated. The other factors such as initiator, monomer, surfactant and ionic strength were held constant. The results are shown graphically in Fig 3.

It is not convenient to work at temperatures below 60 °C because of the slow rate of initiator decomposition. Figure 3 shows that the diameter decreases as the temperature of the reaction is raised. The temperature must be high enough to give a reasonable rate of initiator decomposition. High temperature provides a large number of radicals, and therefore a large number of nuclei. Solubility is increased by increasing temperature. This means that more monomer dissolves in the solvent which results in an increase in the number of polymer nuclei. More nuclei produce more particles; hence particle size is decreased. However, temperature is a useful variable which can be employed to control particle size.

![Figure 1. Scanning electron micrograph of a prepared latex.](image)

![Figure 2. Size distribution of a prepared latex.](image)
Effect of initiator concentration on particle size

The result for the variation of particle diameter as a function of the initial concentration of initiator at 80°C and constant monomer, surfactant and solvent concentrations is given in Fig 4. The result clearly shows that a decrease in the initiator concentration, under constant conditions (monomer concentration 5.455 M, surfactant concentration 0.0147 M), results in an increase in the particle size. The same trend (decreasing particle size with increasing initiator concentration) has been reported in previous works.33

Potassium persulfate dissociates into two sulfate radical anions which can initiate the polymerization.34 These radicals may propagate in the aqueous phase to form oligoradicals by adding monomer molecules dissolved in the aqueous phase. Particle nucleation begins at this point via one mechanism or another, forming polymer particles, which swell with monomer by diffusion of monomer from monomer droplets. These monomer swollen polymer particles become the main sites for further propagation reactions which result in particle growth. The number of these polymerization sites is within a few orders of magnitude of the number of radicals generated over a wide range of temperatures and initiator concentrations. This is responsible for the ability to simultaneously increase the polymerization rate. By increasing polymerization rate, the number of particles increases and their size decreases.

Effect of amount of monomer on particle size

The effect of the amount of the monomer on the particle size was examined at constant temperature and other variables. The details are listed in Table 7. By increasing the amount of monomer, the particle size is increased. This is due to the formation of large size nuclei which results in large size particles. Another explanation is that the time during which the viscosity of the latex particles permits coalescence is increased, producing larger particles.

Effect of surfactant concentration on particle size

Sodium dodecyl benzene sulfonate was used as surfactant. Under constant conditions (temperature 90°C, initiator concentration 0.0019 M and monomer concentration 6.234 M), the effect of surfactant concentration on the particle size was examined. The results are shown in Fig 5. The same trend (decreasing particle size with increasing surfactant concentration) has been observed by other researchers.12,33,35,36

It is well known that the emulsifier concentration has a strong effect on average particle diameter, and number of polymer particles (Nt) formed in the emulsion polymerization. According to the Smith–Ewart37 micellar theory, the relation between these parameters can be expressed mathematically as

\[
N_t \approx [\text{emulsifier}]^{0.6}
\]  

This equation has been proved to be valid for emulsion polymerization of water-insoluble monomers such as styrene using anionic surfactant.12 By
increasing emulsifier concentration, the number of polymer particles \( N_t \) increases\(^36\) and the average particle diameter decreases. Increasing emulsifier concentration accelerates the rate of polymerization because of the increased number of latex particles. This reduces the particle size. A mathematical model for prediction of particle growth in emulsion polymerization has been developed.\(^38\)

**Summary of effect of conditions on particle size**

A linear log-log relationship was obtained over the range of conditions examined. They are fitted in eqns \((2-4))\, where \( T \) is the temperature, \([I]\) the potassium peroxodisulfate concentration (M), \([S]\) is the sodium dodecyl benzene sulfonate concentration (M) and \( D \) is the particle diameter.

\[
\log D = -0.02 \, T + 3.86 \tag{2}
\]
\[
\log D = -2.13 \log[I] - 3.66 \quad \text{at } 80^\circ C \tag{3}
\]
\[
\log D = -2.25 \log[S] - 1.47 \quad \text{at } 90^\circ C \tag{4}
\]

These parameters (temperature, monomer, initiator and surfactant concentrations) influence the ultimate size of the particles produced in a polymerization reaction.

In summary, to obtain small latex particles, the conditions are high initiator concentration, low monomer concentration, high emulsifier concentration and high temperature. These conditions provide a large number of radicals at the early stage of the reaction, producing surface active oligomers which colloidal stabilize the small particles formed and thus provide a large number of nuclei.

**Estimation of surface charge**

The latex particles carry functional groups chemically bound to the particle surface. Surface charge develops via absorption of complex ions derived from the electrolyte and from the particle itself, and dissociation of surface groups.\(^39\) Surface charge depends on electrolyte concentration,\(^1,39\) surfactant concentration,\(^1,39\) and pH.\(^39\)

Surface charge estimation is a vital step in latex characterization. Kesavamoorthy\, et al\(^40\) used Raman scattering to estimate in situ the charge of polystyrene particles in aqueous suspension. Potentiometry and conductometry are other techniques used to estimate charge.\(^1,41-44\)

A fundamental quantity for any charged surface is the surface charge density\(^34\) \( \sigma_0 \), the subscript zero denoting that this is the location of the surface. The formal definition is

\[
\sigma_0 = \nu e N_s \tag{5}
\]

where \( N_s \) is the number of charged sites per unit area, and \( e \) represents the electrostatic charge on each charged site, such that \( e \) is the charge on the electron \((1.6 \times 10^{-19} \text{ coulomb}) \) and \( \nu \) is the magnitude of the charge, ie 1, 2 or 3 depending on its chemical nature.

Typically, with polymeric colloids the surface groups are singly charged, \( |\nu| = 1 \).

In order to obtain the total number of sites on the particle surface, potentiometric titration was performed. This will give in the volume of NaOH required to neutralize the acid end-groups in the polystyrene latex. The latex was potentiometrically titrated with a standard alkali solution (Fig 6). The equivalence point was obtained using the first order derivatization method (Fig 7). Using these curves the number of equivalents of base required to neutralize the \( H^+ \) can be obtained. Based on the equivalence point, the number of charged sites \( (N) \) can be calculated:

\[
N = [(\text{mole of } H^+) N_{Av}] / \text{number of particles per unit volume} \tag{6}
\]

where \( N_{Av} \) is the Avogadro constant \((6.023 \times 10^{23} \text{ molecules mol}^{-1})\). The number of particles per unit volume can be estimated from the total volume of particles and the volume of a single particle.

\[
\text{Mean volume of a particle } = v_i = \frac{4}{3} (\pi R_i^3) = 1/6(\pi D_i^3) \tag{7}
\]
in which $D_i$ is the particle diameter (m).

$$V = \frac{W(g)}{\text{Density (g ml}^{-1})} \times 10^{-3} \tag{8}$$

in which $W$ is the dried weight of latex in 1 ml of latex suspension, and $V$ is the total volume of latex particles per unit volume of suspension (m$^3$). The number of particles per unit of volume equals $V/V_i$. The number of charged sites per unit area ($N_i$) is obtained by dividing $N$ by the particle surface area. Using eqn (5), surface charge density was obtained for each latex. A typical calculation is as follows:

$$\text{mole of } H^+ = [(N_{\text{HCl}} \cdot V_{\text{HCl}}) - (N_{\text{NaOH}} \cdot V_{\text{NaOH(consumed)}})] \times 10^{-3} \tag{9}$$

where $V_i$ is given in ml.

As an example, using the first order derivatization curve for latex no 2, $V_{\text{NaOH(consumed)}} = 0.476$ ml, thus:

$mole of V_i (m^3) = [(0.1 \times 5) - (0.5 \times 0.476)] \times 10^{-3} = 2.62 \times 10^{-4}$. By dividing this parameter by the surface area ($\pi D_i^2$) of each latex, $\sigma_i$ (C cm$^{-2}$) is obtained. The results are presented in Table 8 and show that the surface charge density ($\sigma_i$) varies within a comparatively narrow range for different sized particles. This can be explained as resulting from the similarity of the syntheses. For polystyrene latex, charge is due to $SO_4$ groups from the initiator ($K_2S_2O_8$); however, the $SO_4$ group density is almost the same for all latexes prepared.

The data for surface charge given in the literature are more and less in agreement with the results of the present study. Using sodium dodecyl sulfate and sodium dodecyl sulfonate as the surfactant, surface charges of around 1 $\mu$C cm$^{-2}$ and 1.5 $\mu$C cm$^{-2}$, respectively, have been reported. For particles with average size of 286 nm, surface charge density was reported as 3 $\mu$C cm$^{-2}$. For 2 nm polystyrene latex particles, the surface charge density has been estimated to be around 6 $\mu$C cm$^{-2}$.

### CONCLUSIONS

For polystyrene latexes prepared with sodium dodecylbenzene sulfonate as surfactant, the effects of temperature, initiator concentration, surfactant concentration and amount of monomer on the latex size were investigated. To obtain small latex particles, the conditions are high initiator concentration, low monomer concentration, high emulsifier concentration and high temperature. These conditions provide a large number of radicals at the early stage of the reaction to produce surface active oligomers which colloidally stabilize the small particles formed and thus provide a large number of nuclei.

A potentiometric titration technique was employed for determination of surface charge. It was found that for all latexes, surface charge densities vary within a comparatively narrow range.

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