

Monosize Polystyrene Latices Carrying Functional Groups on Their Surfaces

ALI TUNCEL, RIDVAN KAHRAMAN, and ERHAN PIŞKIN*

Department of Chemical Engineering, Division of Bioengineering, Hacettepe University, Beytepe, Ankara, Turkey

SYNOPSIS

In this study, monosize polystyrene (PS) latices were prepared by dispersion polymerization of styrene in isopropanol–water media using poly (acrylic acid) (PAA) as a steric stabilizer and 2,2'-azobisisobutyronitrile (AIBN) as an initiator. The effects of initiator and stabilizer concentrations, alcohol/water and monomer/dispersion medium ratio on the polymerization kinetics, and the size and monodispersity of PS latices were experimented with in a stirred reactor system. Monosize PS beads in the size range of 1.0–3.0 μm were obtained. The PS latex obtained in the first step having a diameter of 2.3 μm were used as the seed latex, and styrene/acrylate monomers, acrylic acid (AA), 2-hydroxyethyl methacrylate (HEMA), and dimethylaminoethyl methacrylate (DMAEMA) were copolymerized onto the PS latex particles. The incorporation of functional groups to the surface and bulk structure of PS was confirmed by IR, FTIR, XPS, and zeta potential measurements. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Monosize polymer particles have found a wide variety of applications in the bioengineering, electronics, and information industries. Monosize polymeric microspheres in the micron-size range were produced first by Ugelstad et al. who developed a method of growing submicron particles using a two-step swelling technique.^{1–4} Vanderhoff and co-workers were able to grow polymeric particles to the micron-size range aboard the space shuttle in microgravity.⁵

Another approach for preparing micron-size particles is dispersion polymerization.^{6–17} In a dispersion-polymerization process, the reaction mixture starts out as a homogeneous solution containing monomer dissolved in an inert medium, and the resulting polymer precipitates as solid spherical particles, stabilized by a steric barrier of dissolved polymer.¹⁸ The final particle size is determined by the inherent polymer aggregation behavior under a given

set of conditions. The dispersion-polymerization method was thoroughly reviewed by Barrett.⁷ Barrett achieved the synthesis of monosize poly (methyl methacrylate) particles by dispersion polymerization.⁸ Almog et al. produced monosize polystyrene and poly (methyl methacrylate) particles up to 5 μm using a quaternary ammonium salt surfactant with a polymeric steric stabilizer.^{9,10} Corner reported a dispersion-polymerization method for production of polystyrene particles in aqueous ethanol media using poly (acrylic acid) as a steric stabilizer.¹¹ Ober and co-workers produced monosize polystyrene particles up to 9 μm by polymerizing styrene in ether/alcohol systems in the presence of different nonionic cellulosic polymers as steric stabilizers.^{18–21} They also achieved large monosize styrene/butyl methacrylate copolymer particles by a single-stage dispersion-polymerization procedure.²⁰ Paine and co-workers reported the production of monosize polystyrene particles up to 18 μm in alcoholic media in the presence of poly (*N*-vinylpyrrolidone) as a steric stabilizer.²² Paine also proposed a simple mathematical model to predict the particle size in dispersion polymerization of styrene in polar solvents.²³ More recently, Okubo et al. reported preparation of micron-size

* To whom correspondence should be addressed.

monosize polystyrene beads having chloromethyl groups by following two-step polymerization in a dispersion medium containing water and ethanol.²⁴ In the first step, they polymerized styrene by dispersion polymerization in the presence of polyacrylic acid as a stabilizer and obtained monosize particles about 2 μm . Then, by seeded copolymerization of styrene and chloromethyl styrene, the final structure was achieved.

Recently, we have also studied dispersion polymerization of styrene in different dispersion media by changing the concentrations of initiator, stabilizer, and monomer.²⁵ In these earlier investigations, we used a shaking reactor and looked only at the effects of different parameters on the average size and size distribution.

In the present study, in the first part, we investigated dispersion polymerization of styrene in an isopropanol/water mixture in a stirred reactor and studied the effects of initiator (i.e., AIBN), stabilizer [i.e., poly(acrylic acid)], and monomer concentrations on both polymerization kinetics and average particle size and size distribution. In the second step of the present study, we incorporated functional groups (i.e., carboxyl, hydroxyl, and dimethylamino) onto polystyrene (PS) latex particles prepared in the first step, by copolymerization of styrene and acrylate comonomers (i.e., AA, HEMA, and DMAEMA; see below for definitions) on the PS latex particles. Incorporation of functional groups was confirmed by IR, FTIR, XPS, and zeta potential measurements.

The size, monodispersity, and surface properties of polymeric microspheres are especially important in biomedical applications. The surface of polymeric microspheres should be derivatized easily for incorporation of proper biological ligands. Plain polystyrene cannot be considered as a proper surface for derivatization. The existence of some basic functional groups (i.e., hydroxyl, carboxyl, or amino) provides important advantages for coupling of ligands onto the polystyrene surface. The aim of the study was to obtain monosize polymeric particles carrying different functional groups in the micron-size range for diverse biomedical applications (i.e., chromatographic separation of biological macromolecules, scintigraphic imaging, cell labeling, and separation). The results of our studies about the biomedical applications of PS-based particles can be found in related articles.²⁶⁻³⁰ Here, we are presenting the method of copolymerization and also results of the experiments that have been performed to confirm the existence of the functional groups on the PS particles.

MATERIALS AND METHODS

Preparation of Monosize PS Latices

Styrene (S) (Yarpet A.S., Turkey) was treated with aqueous NaOH to remove the inhibitor and stored in a refrigerator until use. The initiator was 2,2'-azobisisobutyronitrile (AIBN, BDH Chemicals Ltd., UK). As the dispersion medium, isopropanol (Merck, Germany)/water mixtures were used.

Poly(acrylic acid) (PAA) was used as a steric stabilizer. PAA was prepared by solution polymerization of acrylic acid (AA, BDH) (60 mL) in 1,4-dioxane (BDH) (140 mL) using AIBN (0.06 g) as an initiator at 80°C for 8 h under nitrogen atmosphere in a magnetically stirred, sealed cylindrical polymerization reactor. PAA was precipitated by pouring the final solution into an excess of petroleum ether. The polymer was dried at 70°C for 24 h. The viscosity-average molecular weight measured in 1,4-dioxane at 25°C was 1.5×10^4 .²⁵

The polymerizations were carried out in a magnetic-driven, sealed, cylindrical reactor equipped with a temperature-control system.^{31,32} Polymerizations were conducted at a constant temperature of 75°C. The reaction mixture was stirred with an anchor-type agitator at a speed of 150 rpm. In a typical procedure, PAA was dissolved in 200 mL of dispersion medium containing isopropanol and water. The monomer phase was prepared by dissolving AIBN in styrene monomer. These two phases were mixed in a proper ratio and charged to the reactor. The reactor was purged with nitrogen and then the heating and stirring were started. When the reactor temperature was raised to 75°C, the zero-reaction time was defined, and the polymerization was conducted at 75°C for 24 h. The progress of the polymerization was followed by examination of the samples withdrawn from the sample valve. The solid content of these samples was determined gravimetrically according to the procedure described elsewhere.³¹ In this group of experiments, the effects of initiator and emulsifier concentrations, isopropanol/water, and monomer/dispersion medium volumetric ratios on the polymerization rate, total monomer conversion, average size, and size distribution of the polystyrene particles were investigated. The experimental conditions are given in Table I.

Particle-size Analysis

Average particle size was evaluated using scanning electron micrographs. The latex solution was spread onto a metal disk and the solvent (i.e., water and

Table I Experimental Conditions in Stirring Reactor System; Temperature: 75°C, Stirring Rate: 150 rpm; Total Reaction Volume: 220 mL; Dispersion Medium: Isopropanol + Water

| Initiator (% mol) | Stabilizer (g PAA/dL Dispersion Medium) | Isopropanol/Water Ratio (mL/mL) | Monomer/Dispersion Medium Ratio (mL/mL) |
|----------------------|--|------------------------------------|---|
| 0.5 | 1.0 | 90/10 | 1.0/10.0 |
| 1.0 | 1.0 | 90/10 | 1.0/10.0 |
| 2.0 | 1.0 | 90/10 | 1.0/10.0 |
| 1.0 | 0.5 | 90/10 | 1.0/10.0 |
| 1.0 | 1.0 | 90/10 | 1.0/10.0 |
| 1.0 | 2.0 | 90/10 | 1.0/10.0 |
| 1.0 | 1.0 | 100/0 | 1.0/10.0 |
| 1.0 | 1.0 | 90/10 | 1.0/10.0 |
| 1.0 | 1.0 | 80/20 | 1.0/10.0 |
| 1.0 | 1.0 | 70/30 | 1.0/10.0 |
| 1.0 | 1.0 | 90/10 | 0.5/10.0 |
| 1.0 | 1.0 | 90/10 | 1.0/10.0 |
| 1.0 | 1.0 | 90/10 | 2.0/10.0 |

alcohol) was evaporated. The dried beads were coated with a thin layer (about 100 Å) of gold in vacuum. Three separate photographs (each containing 100–300 beads) were taken for each latex sample with 2000–2600× magnification using a scanning electron microscope (JEOL, JEM1200EX, Japan). The size of beads was measured on photographs and checked using calibration samples.

Incorporation of Functional Groups

Monosize PS latices prepared with the above method were used as seed particles for copolymerization of styrene with acrylic acid (AA), dimethylaminoethyl methacrylate (DMAEMA), and 2-hydroxyethyl methacrylate (HEMA) (Aldrich Chemical Co., USA) in order to include functional groups, namely, COOH (negatively charged), $-\text{N}(\text{CH}_3)_2$ (positively charged), or $-\text{OH}$ (uncharged) on the monosize PS particles.

Prior to the copolymerization, the relevant comonomer was mixed with styrene, and the initiator was dissolved in this mixture. This monomer phase was added to the PS latex diluted with distilled water, and the resulting mixture was stirred at room temperature for 24 h in order to allow the adsorption of the monomers onto the seed particles. Copolymerizations were then performed at the conditions given in Table II.

The size and size distribution of these copolymer particles were determined by a scanning electron

microscope (JEOL, JEM1200 EX, Japan). The formation of submicron particles during the copolymerization was also checked with higher magnification (e.g., 10,000×).

Incorporation of functional groups into the PS particles was shown by using IR (Hitachi, Model 230, Japan) and FTIR (Shimadzu, FTIR 8000 Series, DR-8001, Japan) spectra. Surface atomic compositions and the related spectra were obtained by using an ESCA (Hewlett-Packard, 5950 B, USA). Electrophoretic mobilities of the polymer latices were measured using a laser-doppler electrophoresis apparatus (Zetasizer 3, Malvern Instruments Ltd., London, UK) with an AZ4 standard cell in 0.01 M KCl at pH 7.0.

Cleaning of Latices

The PS latex was cleaned first using a serum replacement technique. The latex from the reactor was centrifuged and the supernatant was removed. Distilled water (200 mL) was added and a new dispersion was stirred for 24 h at room temperature to remove any stabilizer remaining on the surface of the polymeric particles. This procedure was repeated three times. The PS latex solution was treated with a mixed bed of anion- and cation-exchange resins (H^+ and OH^- type, Amberlite, BDH) at the last step. The serum replacement and ion-exchange methods were not applied for PS latex used for seed preparation. The latices containing functional

Table II The Polymerization Conditions for Incorporation of Functional Groups to PS Latex

| | PS/PDMAEMA | PS/PAA | PS/PHEMA |
|-------------------------------------|------------|--------|----------|
| Polystyrene latex ^a (mL) | 100 | 100 | 100 |
| Water (mL) | 100 | 100 | 100 |
| Styrene (mL) | 2 | 2 | 2 |
| AIBN (g) | 0.12 | 0.12 | 0.12 |
| HEMA (mL) | — | — | 4 |
| AA (mL) | — | 4 | — |
| DMAEMA (mL) | 4 | — | — |
| Conditions | | | |
| Adsorption temp. (°C) | 20 | 20 | 20 |
| Adsorption time (h) | 24 | 24 | 24 |
| Agitation rate (rpm) | 400 | 400 | 400 |
| Temperature program | | | |
| First period | | | |
| Temperature (°C) | 75 | 75 | 75 |
| Time (h) | 8 | 8 | 8 |
| Second period | | | |
| Temperature (°C) | 82 | 82 | 82 |
| Time (h) | 16 | 16 | 16 |

^a The latex suspension contains approximately 18.0% w/v solid latex particles in a solution containing 90% isopropyl alcohol and 10% water by volume.

groups were cleaned by applying only the serum replacement technique after the second-stage polymerization. The ion-exchange method was not used for these latices.

RESULTS AND DISCUSSION

Monosize PS Latices

In the first part of the study, the effects of initiator, stabilizer, and monomer concentrations and alcohol/water ratio on the polymerization rate, total monomer conversion, average particle size, and the size distribution of the PS latices were investigated in a stirred reactor. These effects are separately discussed below.

Effect of Initiator

In this group of experiments, the effects of initiator (i.e., AIBN) concentration on the polymerization of styrene were investigated. These polymerizations were performed with three different AIBN concentrations (i.e., 0.5, 1.0, and 2.0 mol %) in a dispersion medium containing 90% isopropanol and 10% water at a constant stabilizer concentration of 1.0 g/dL and at a constant monomer/dispersion medium ratio of 1/10.

The SEM photographs and variation of monomer conversion with the polymerization time and the average size values of latices obtained with different initiator concentrations are given in Figure 1 and Table III, respectively. As seen in Figure 1, the polymerization rate and final monomer conversion value increased with increasing initiator concentration. The higher rates of free-radical initiation led to faster initial monomer conversion at the high initiator concentrations.

As seen in Figure 1 and Table III, the average particle size increased with increasing initiator concentration. This is an expected behavior that has also been discussed by us and others.^{21,25} The increase in the initiator concentration caused an increase in the number of free radicals for polymerization. In other words, polymerization started with more radicals per unit volume in the case of high initiator concentration. This led to lower molecular weight polymeric chains, which were more soluble in the medium. Note that in dispersion polymerization the nucleation or phase inversion occurs when the polymer chains reach a certain molecular weight in which they become insoluble in the dispersion medium. At high initiator concentration, due to low concentration of high molecular weight chains in the medium, fewer polymerization nuclei were produced, which led to a lower number of particles but with large size.

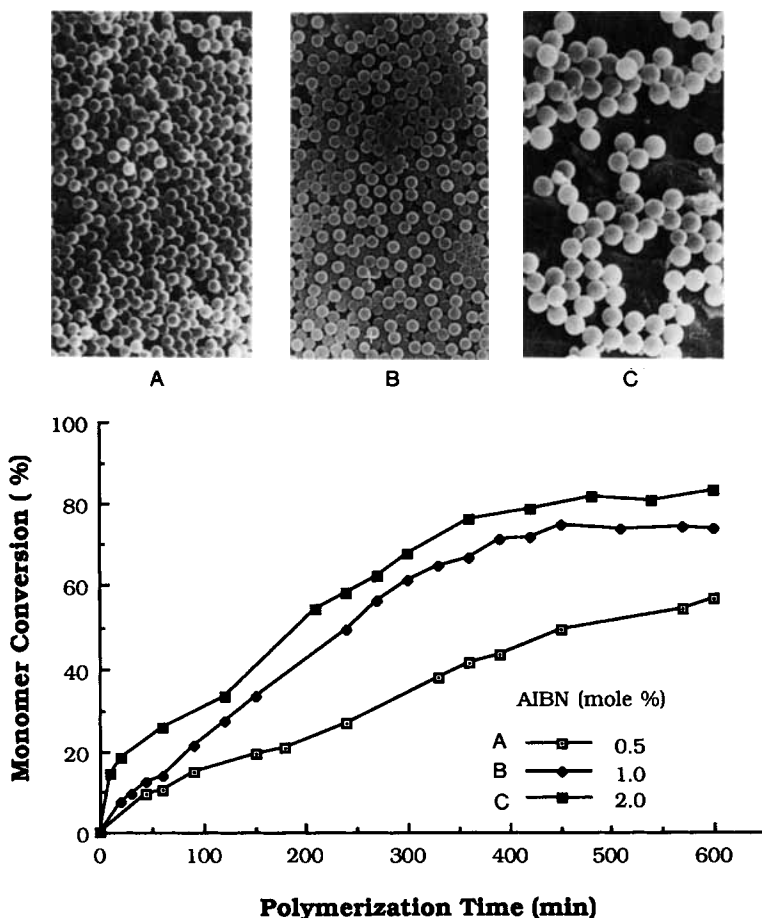


Figure 1 SEM photographs of the latices and the variation of the monomer conversion with the polymerization time at different initiator concentrations. Initiator concentration (mol %): (A) 0.5; (B) 1.0; (C) 2.0. The original SEM photographs were taken with 2600 \times , 2000 \times , and 2600 \times magnifications for (A), (B), and (C), respectively, and reduced at a proper ratio to place the figure.

The amount of initiator remained on the surface of the PS particles should be another important consideration, especially in biomedical applications of latex particles. As will be discussed in a later part of this paper, the nitrogen content of the surface

observed in the ESCA spectrum of PS is not very significant, but may be an indication of the AIBN molecules on the surface of the PS particles. Note that it is really difficult to obtain the exact amount of AIBN molecules on the particle surface. The monomer phase is dissolved completely in the dispersion medium at the beginning of dispersion polymerization. Then, a homogeneous polymerization medium is obtained initially. The phase separation begins when the polymer chains reach to a certain length. After phase separation, the monomer molecules diffuse from the dispersion medium to the more hydrophobic solid phase. Therefore, the initiator molecules accompany the monomer molecules and enter into the forming particles. Note that the solubilities of AIBN in the monomer (i.e., styrene) and in the dispersion medium (i.e., isopropanol/water 90/10), which are determined by us, are 6.35

Table III The Variation of Average Size of PS Latices with Initiator Concentration

| Initiator Concentration (% mol) | Average Size (μm) | Size Range (μm) |
|---------------------------------|--------------------------------|------------------------------|
| 0.50 | 1.50 | MD |
| 1.00 | 2.00 | MD |
| 2.00 | 2.50 | 1.40-3.60 |

MD: monosize sample (CV < 1%).

and 1.80% w/v (at 25°C), respectively. The amount of AIBN on the particle surface is not only related to the solubilities of AIBN in the respective phases and the amount of AIBN used in the polymerization, but are also related to the kinetics of the polymerization.

Effect of Stabilizer

In this group of experiments, the effects of stabilizer (i.e., PAA) concentration on the dispersion polymerization of styrene were investigated. The polymerizations were performed with three different PAA concentrations (i.e., 0.5, 1.0, and 2.0 g/dL) at a constant initiator concentration of 1% (by mol) and at a constant monomer/dispersion medium ratio of 1/10 in a dispersion medium containing 90% isopropanol and 10% water.

Table IV The Variation of Average Size of PS Latices with Stabilizer Concentration

| Stabilizer Concentration (g/dL) | Average Size (μm) | Size Range (μm) |
|---------------------------------|--------------------------------|------------------------------|
| 0.50 | 2.30 | 2.25–2.40 |
| 1.00 | 2.00 | MD |
| 2.00 | 1.70 | MD |

MD: monosize sample (CV < 1%).

The SEM photographs and variation of monomer conversion with the polymerization time and the average size values of latices obtained with different stabilizer concentrations are given in Figure 2 and Table IV, respectively. As seen in Figure 2, the po-

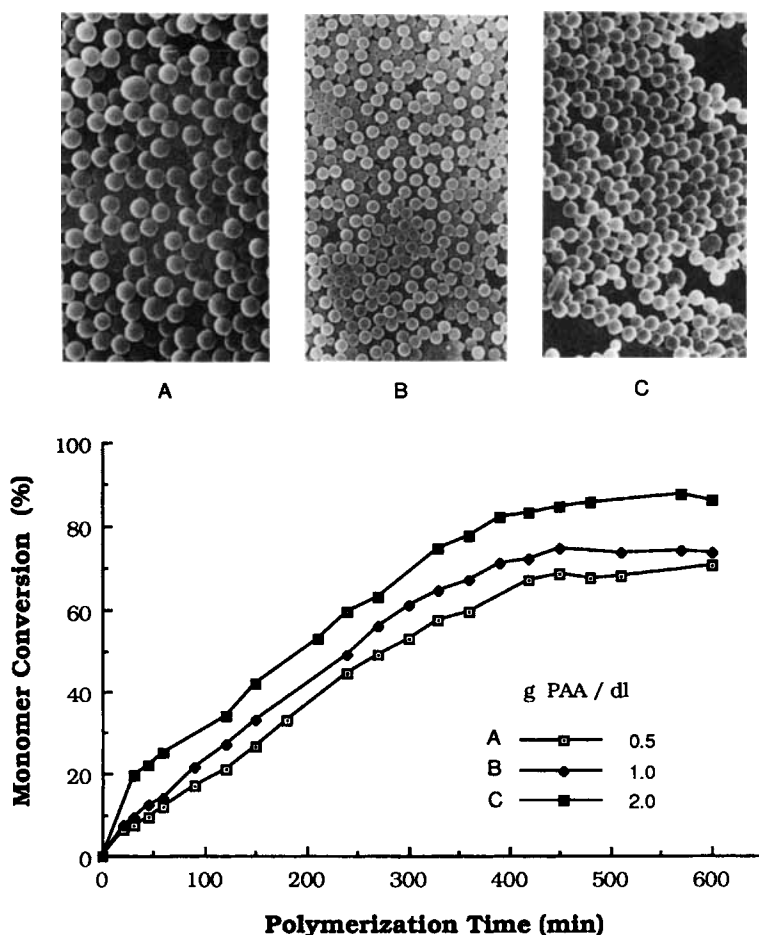


Figure 2 SEM photographs of the latices and the variation of the monomer conversion with the polymerization time at different stabilizer concentrations. Stabilizer concentration (g/dL): (A) 0.5; (B) 1.0; (C) 2.0. The original SEM photographs were taken with 2600 \times , 2000 \times , and 2600 \times magnifications for (A), (B), and (C), respectively, and reduced at a proper ratio to place the figure.

lymerization rate and final monomer conversion value slightly increased with increasing stabilizer concentration. This may be explained in that the number of forming particles increased with increasing stabilizer concentration, which led to an increase in the apparent polymerization rate.

As seen in Figure 2 and Table IV, the average particle size slightly decreased with increasing stabilizer concentration. Dispersion polymerization begins and progresses around the stabilizer chains. During the nucleation period, the stabilizer chains form a structure that acts as a skeleton for particle growth. The number of forming nuclei increases with increasing stabilizer concentration, which leads to more particles but with smaller size. It should be noted that the increase in the average size is not directly proportional to the stabilizer concentration in the studied conditions.

Alcohol/Water Ratio

Monosize polymer latices can be prepared in a wide variety of solvent combinations by dispersion polymerization. This type of polymerization requires that the monomer, initiator, and stabilizer are all soluble in the starting medium. Solubility of the monomer in the dispersion medium strongly depends on the polarity of the medium, which controls the size and size distribution of the resultant polymer particles.^{18,19,22-24,25,32}

In our earlier studies, we investigated several alcohol/water mixtures to arrange the polarity of the dispersion medium in the styrene polymerization.²⁵ In this study, we used an isopropanol/water mixture since both the dispersion and polymerization media were homogeneous and provided monosize PS latices. To have dispersion media with different polarities, the alcohol/water ratio was changed. The calculated solubility parameters of the dispersion media

used in the polymerizations were given in Table V.^{33,34}

In this group of experiments, the effects of the isopropanol/water volumetric ratio on the dispersion polymerization of styrene were investigated. The polymerizations were performed with four different isopropanol/water ratios (i.e., 100/0, 90/10, 80/20, 70/30) at a constant initiator concentration of 1% (by mol), with a constant stabilizer concentration of 1.0 g/dL at a constant monomer/dispersion medium ratio of 1/10.

The SEM photographs and variation of monomer conversion with the polymerization time and the average size values of latices obtained with different alcohol/water ratios are given in Figure 3 and Table V, respectively. As seen in Figure 3, the polymerization rate and final monomer conversion value increased with increasing water content or the polarity of dispersion medium. Both the monomer and AIBN solubilities in the dispersion medium decrease with increasing water content of this medium. In other words, more monomer and initiator molecules transfer to the forming particles when the water content of the medium is high, so that the concentration of styrene and AIBN in the forming particles increases as the water content of the continuous phase increases. Therefore, higher polymerization rates are observed. Another factor that may be effective on the polymerization rate is the total surface area of the forming particles. An increase in the polarity of the dispersion medium results in formation of smaller particles having a higher total surface area at the nucleation step. In the initial period, the polymerization reaction progresses in the dispersion medium. But after nucleation (approximately 30% conversion), the monomer and the initiator molecules diffuse from the dispersion medium to the forming particles. The monomer and initiator diffusion rate will be higher in the presence of smaller particles due to their higher total surface area.

As seen in Figure 3 and Table V, the alcohol/water ratio (or polarity of the medium) significantly changed the size and size distribution of the polymer latices. The polymer particles obtained by using pure isopropanol as the dispersion medium were larger but not monosize. However, monosize latices but smaller in size were produced with other alcohol/water ratios. The general trend was that the average particle size decreased with increasing water content (or polarity) of the dispersion medium. This behavior may be explained as follows: Styrene is more apolar than is isopropanol. Therefore, the oligomer chains forming during the polymerization of styrene are more apolar relative to the isopropanol/water

Table V The Variation of Average Size PS Latices with Alcohol/Water Ratio

| Alcohol/Water Ratio | Solubility Parameter ^a (cal/cm ³) ^{1/2} | Average Size (μm) | Size Range (μm) |
|---------------------|---|-------------------|-----------------|
| 100/0 | 11.50 | 2.80 | 1.00-3.80 |
| 90/10 | 13.18 | 2.00 | MD |
| 80/20 | 14.67 | 1.25 | MD |
| 70/30 | 16.03 | 1.50 | MD |

MD: monosize sample (CV < 1%).

^a The solubility parameters of the isopropanol water media were calculated based on the information in Refs. 33 and 34.

mixture having a certain water content. Therefore, longer oligomer chains (i.e., chains with higher molecular weights) can be obtained in the medium that is more apolar (containing more isopropanol), before the nucleation occurs. In other words, nucleation occurs at relatively higher molecular weights due to the higher solubility of polymer chains in relatively apolar dispersion medium. Thus, fewer nuclei are produced, which leads to fewer polymeric particles but larger in size.

Monomer/Dispersion Medium Ratio

In this group of experiments, the effects of the monomer/dispersion medium ratio on the average particle size and polymerization rate were studied. The polymerizations were performed with three different monomer/dispersion medium ratios (i.e., 0.5/

10, 1/10, and 2/10) at a constant initiator concentration of 1% (by mol) and at a constant stabilizer concentration of 1.0 g/dL in a dispersion medium containing 90% isopropanol and 10% water.

The SEM photographs and variation of monomer conversion with the polymerization time and the average size values of latices obtained with different monomer/dispersion medium ratios are given in Figure 4 and Table VI, respectively. As seen in Figure 4, both the polymerization rate and final monomer conversion value increased with increasing monomer/dispersion medium ratio. As also discussed by us and others,^{22,24,25} high monomer concentration leads high polymerization rates both in the initial polymerization period and in the period after nucleation.

As seen in Figure 4 and Table VI, the average particle size increased with increase in the volu-

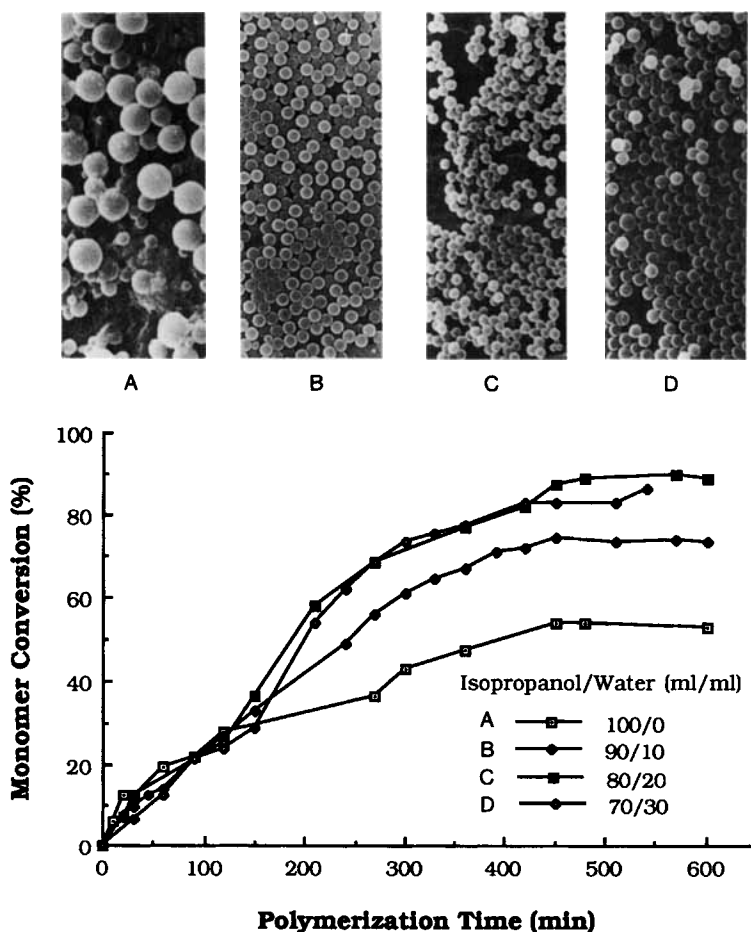


Figure 3 SEM photographs of the latices and the variation of the monomer conversion with the polymerization time at different alcohol/water ratios. Alcohol/water ratio (mL/mL): (A) 100/0; (B) 90/10; (C) 80/20; (D) 70/30. The original SEM photographs were taken with 2600 \times , 2000 \times , 2600 \times , and 2600 \times magnifications for (A), (B), (C), and (D), respectively, and reduced at a proper ratio to place the figure.

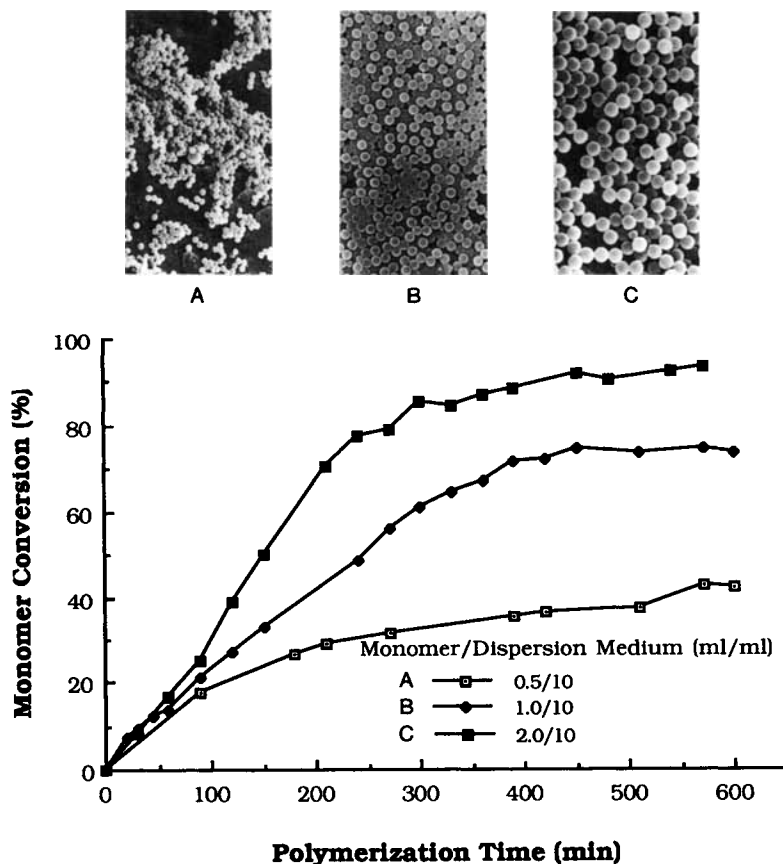


Figure 4 SEM photographs of the latices and the variation of the monomer conversion with the polymerization time at different monomer/dispersion medium ratios. Monomer/dispersion medium (mL/mL): (A) 5/100; (B) 10/100; (C) 20/100. The original SEM photographs were taken with 2600 \times , 2000 \times , and 2600 \times magnifications for (A), (B), and (C), respectively, and reduced at a proper ratio to place the figure.

metric ratio of the monomer/dispersion medium. This can be explained as follows: As discussed above, polymer particle size can be controlled by changing three polymerization parameters, which are the initiator and stabilizer concentrations and the polarity of the dispersion medium. All these parameters cause a change in the number of nucleation points and

therefore affect the final particle size. In these groups of experiments, these three parameters were constant; therefore, one does expect approximately the same number of nucleation points in the polymerization media containing monomer at different concentrations. At the high monomer concentration, more monomer molecules are available for each nucleation point, which leads to an increase in the particle size.

Table VI The Variation of Average Size of PS Latices with Monomer/Dispersion Medium Ratio

| Monomer/Dispersion Medium Ratio (% v/v) | Average Size (μm) | Size Range (μm) |
|---|--------------------------------|------------------------------|
| 5/100 | 1.15 | MD |
| 10/100 | 2.00 | MD |
| 20/100 | 2.30 | MD |

MD: monosize sample (CV < 1%).

Monosize PS Latices with Functional Groups

Monosize PS latices with functional groups were prepared by a two-step polymerization. In the first step, which is discussed above in detail, PS latices with different sizes were prepared. In the second step, monosize PS latex (i.e., 2.3 μm in diameter) was used as a seed latex. Mixtures of styrene with acrylic comonomers (i.e., AA, HEMA, and DMAEMA) were adsorbed on the seed latex parti-

cles and then were polymerized. Note that the abbreviations PS/PAA, PS/PHEMA, and PS/PDMAEMA were used to specify these copolymer latices. Polymerization conditions are shown in Table II. The SEM micrographs of the latex particles containing functional groups were taken with higher magnification to check the formation of submicron particles during the second stage (i.e., copolymerization). The electron micrographs given in Figure 5 clearly showed that PS/PAA, PS/PHEMA, and PS/PDMAEMA latices were obtained without producing new particles in the second stage. As seen here, no significant change in the size and monodispersity occurred.

The bulk structures of polymer latices containing functional groups were characterized by IR and FTIR spectroscopy. Cleaned latices were dried in vacuum at 60°C for 24 h and used in the spectro-

photometric measurements. To show clearly the hydroxyl groups on the latices, IR spectra were taken between 3000 and 4000 cm^{-1} by preparing the tablets containing only the latex particles (i.e., no KBr was used in these tablets). Figure 6 shows the IR spectra of PS, PS/PHEMA, and PS/PAA latices. The strong hydroxyl band in the spectrum of the PS/PHEMA latex can easily be seen, which is expected. The hydroxyl band coming from PAA in the spectrum of the PS/PAA latex is also visible. The interesting finding is the existence of a weak hydroxyl band in the spectrum of the PS reference latex, which is unexpected. However, PAA was also used as a steric stabilizer in the polymerization of styrene. PAA stabilizer molecules act as a skeleton during the polymer formation in the first step. Therefore, the weak hydroxyl band in the IR spectrum of PS originated from the stabilizer molecules is strongly

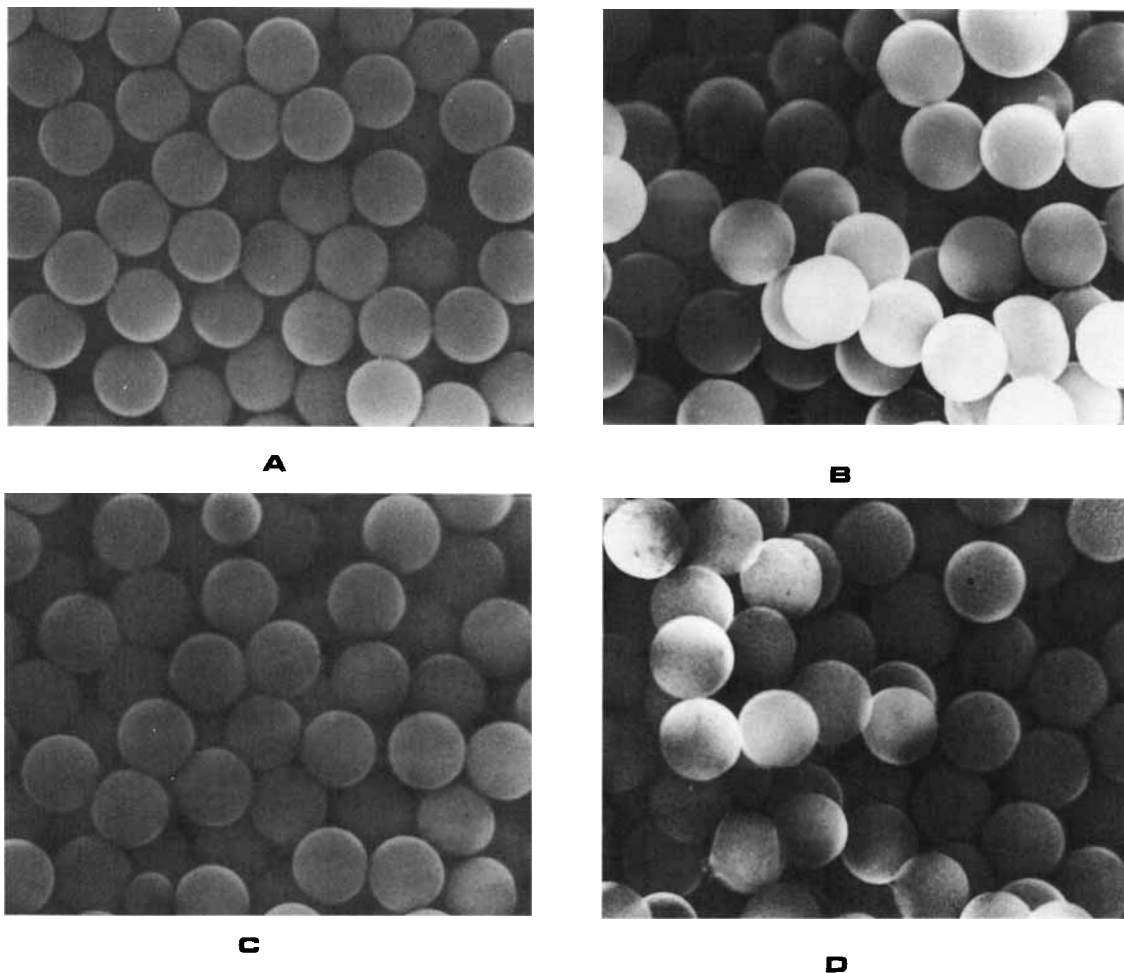


Figure 5 SEM photographs of PS latices carrying functional groups after the second-stage polymerization: (A) PS; (B) PS/PAA; (C) PS/PHEMA; (D) PS/PDMAEMA. The original SEM photographs were taken with 10,000 \times magnification and reduced at a proper ratio to place the figure.

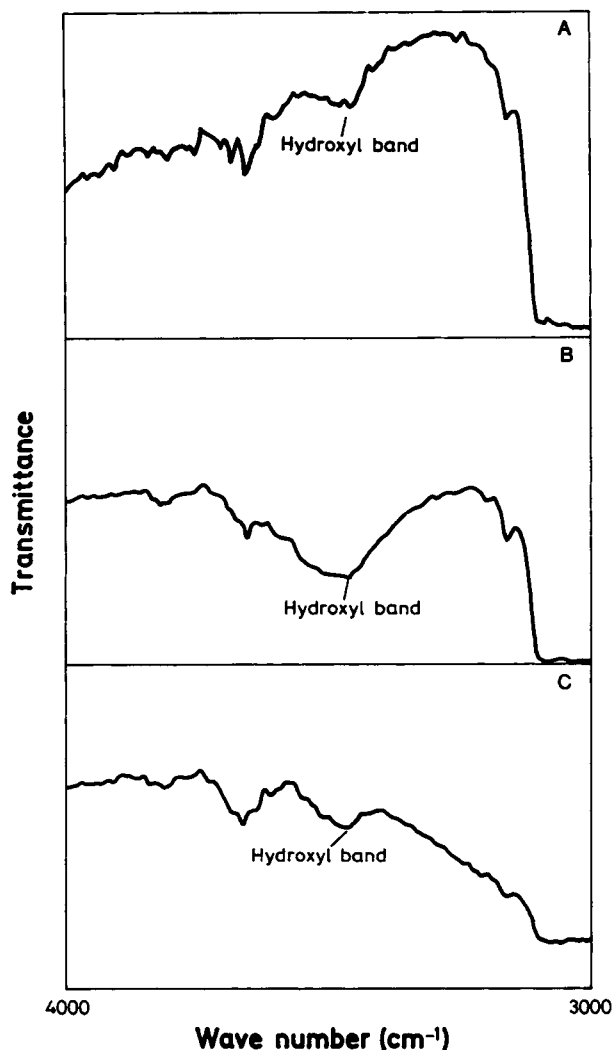


Figure 6 IR spectra of PS latices carrying functional groups: (A) PS; (B) PS/PHEMA; (C) PS/PAA.

entrapped in the forming polymer chains. However, it should also be noted that the hydrophilic carboxyl groups should be located on the outer surface of the PS latex particles.

FTIR spectra of the PS and PS/polyacrylate copolymer latices were also obtained. The tablets for FTIR spectroscopy were prepared by diluting the dried polymer particles with KBr. FTIR spectra were obtained by taking the difference spectrum according to the KBr tablet. They are given in Figure 7. Hydroxyl bands at 3500 cm^{-1} in the spectrum of PS/PHEMA and PS/PAA are shown here. However, these bands are weaker than those observed in the IR spectra given in Figure 6. This is due to the dilution of the latices with KBr in the FTIR spectrophotometric measurements. The carbonyl band at 1750 cm^{-1} may be considered as another indication of the incorporation of functional groups

to the PS latex at the second copolymerization step. Note that the spectrum of the PS latex also contains a carbonyl band that is coming from the PAA stabilizer molecules as discussed above. However, the relative intensity of the carbonyl band is stronger in the FTIR spectra of PS/PHEMA and PS/PAA latices, due to the carbonyl groups coming from PHEMA and PAA. The increase in the relative intensity of the carbonyl band is less significant in the FTIR spectra of PS/PDMAEMA latex. This may be due to the less amount of incorporation of DMAEMA into the polymeric structure.

To obtain the surface atomic compositions of the latices produced in this study, XPS spectra were

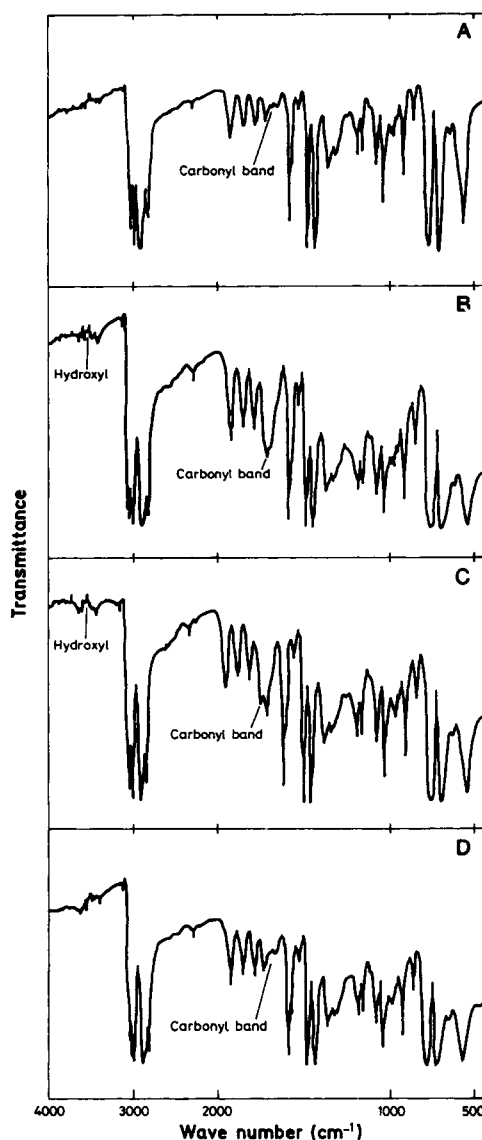


Figure 7 FTIR spectra of PS latices carrying functional groups: (A) PS; (B) PS/PHEMA; (C) PS/PAA; (D) PS/PDMAEMA.

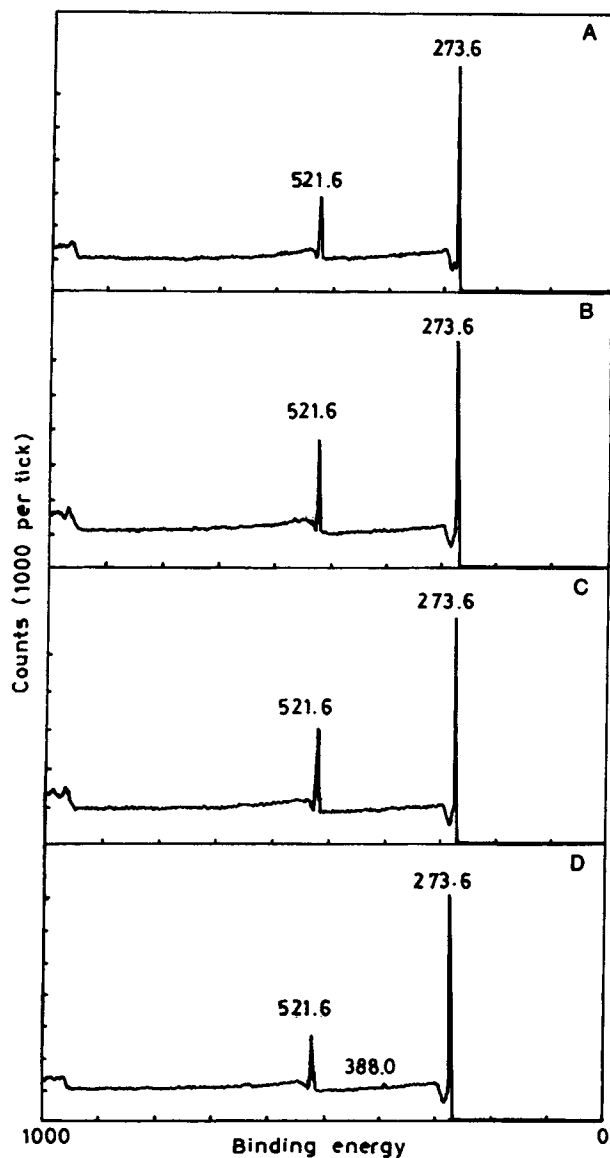


Figure 8 Wide-scan XPS spectra of PS latices carrying functional groups: (A) PS; (B) PS/PHEMA; (C) PS/PAA; (D) PS/PDMAEMA.

obtained. Figure 8 shows the wide-scan XPS spectra of the PS latex and PS latices containing functional groups. As seen in this figure, two peaks belonging to C(1s) and O(1s) are shown at 273.6 and 521.6 eV in the wide-scan XPS spectra of all latices. As discussed above, the O(1s) peak at 521.6 eV in the XPS spectra of the PS latex originated from the carboxyl group of the PAA stabilizer molecules entrapped on the surface. However, due to incorporation of the comonomers, HEMA and AA, the intensities of O(1s) peaks at 521.6 eV increased in the XPS spectra of the PS/PHEMA and PS/PAA latices. The O(1s) peak is also seen in the wide-

scan XPS spectrum of PS/PDMAEMA latex. But the intensity of this peak is very close to that of observed in the XPS spectrum of the PS latex.

The only source for the nitrogen atoms on the surface of these copolymer particles (except PS/PDMAEMA) is the initiator molecules. The solubility of AIBN in the first-stage dispersion medium (i.e., 90/10 isopropanol/water) was determined as 1.80% w/v. The initiator solubility in the dispersion medium used at the second stage (i.e., 40/60 isopropanol/water) was 0.68% w/v at 25°C. But the seed monomer/dispersion medium ratio was very low (i.e., 3/100 v/v) at this stage. Therefore, the amount of AIBN introduced into the latex particles at the second stage might be expected to be insignificant. But it is very difficult to guess the exact amount of AIBN that is introduced during the copolymerization step just by considering relative solubilities of AIBN in the dispersion medium and comonomer mixtures alone. The mechanism of the polymerization and also the kinetics should be well defined.

A small N(1s) peak at 388 eV is detected in the wide-scan XPS spectrum of the PS/PDMAEMA latex. Therefore, the high resolution N(1s) spectra of latices were obtained (Fig. 9). An appreciable N(1s) peak cannot be detected in the spectrum obtained with PS/PAA. But the N(1s) peak originated from the initiator is observed clearly in the spectrum of PS/PHEMA. As expected, a nitrogen peak having the strongest intensity, relative to N(1s) peaks of other latices, is observed at 389.1 eV in the high-resolution N(1s) spectrum of the PS/PDMAEMA latex. This peak clearly indicated incorporation of the nitrogen-carrying comonomer, DMAEMA, onto the PS latex particles.

The surface elemental compositions of latices estimated from XPS data are given in Table VII. These compositions were found by using the wide scans, except for nitrogen where a C/N ratio was utilized from the open aperture narrow scan data to obtain a more accurate value for its composition. The expected elemental compositions of these surfaces were also calculated from the initial amounts of the ingredients in the polymerization medium. Note that these calculations were made in the weight basis and by assuming complete monomer conversion and complete adsorption of stabilizer molecules by forming polymeric particles. These calculated values were also included in Table VII in the parentheses. The calculated values were placed in this table only to give an idea about the order of magnitude of the elemental composition values expected from ESCA measurements.

As discussed above, by copolymerization (at the

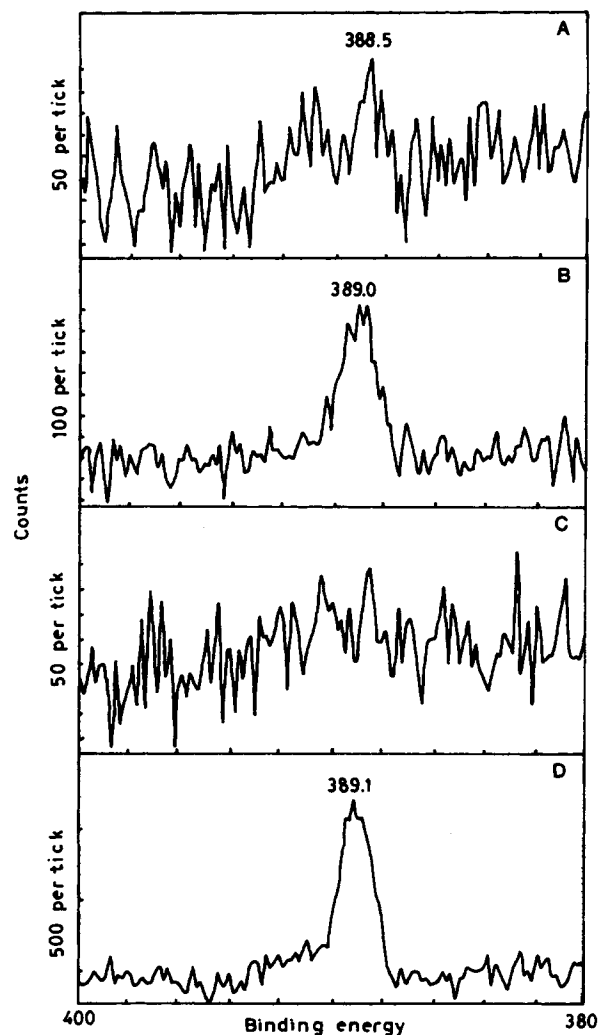


Figure 9 High-resolution XPS spectra of PS latices carrying functional groups: (A) PS; (B) PS/PHEMA; (C) PS/PAA; (D) PS/PDMAEMA.

second step), we were able to incorporate carboxyl, hydroxyl, and dimethyl amino groups onto the PS latices. Table VII confirms once again these findings, numerically. Oxygen on the surfaces of the copolymer latices comes from the comonomers, AA, HEMA, and DMAEMA, and also from the PAA stabilizer molecules, whereas the oxygen on the surface of the PS latex is coming from the stabilizer. As seen in Table VII, the surface oxygen contents of PS/PAA and PS/PHEMA latex particles are higher relative to the surface oxygen content of the PS sample. This result indicated that the introduction of carboxyl and hydroxyl functional groups onto the PS surface was achieved by using AA and HEMA as comonomers in the second-stage polymerizations, respectively. As expected, the highest surface nitrogen content was obtained with PS/PDMAEMA la-

Table VII Calculated and Determined Surface Atomic Compositions

| Latex | Atom (%) | | |
|------------|-------------|------------|-----------|
| | Carbon | Oxygen | Nitrogen |
| PS | 89.0 (97.0) | 10.0 (2.5) | 0.1 (0.5) |
| PS/PHEMA | 86.0 (90.9) | 13.0 (8.6) | 0.7 (0.6) |
| PS/PAA | 86.0 (89.6) | 14.0 (9.8) | — (0.6) |
| PS/PDMAEMA | 89.0 (92.7) | 9.50 (5.2) | 1.3 (2.0) |

The values in parentheses were calculated on hydrogen free base.

tex, due to the existence of dimethyl amino groups on the surface. But some part of the surface nitrogen content of the PS/PDMAEMA latex may come from the initiator molecules on the particle surface.

The electrophoretic mobilities of the latices were also measured in 0.01 M KCl solution at pH 7.0, and these values with the mean zeta potentials are given in Table VIII. It can be seen that all these latices have negative charges at pH 7.0. The order of the zeta potentials is as follows:

$$\text{PS} < \text{PS/PDMAEMA} < \text{PS/PHEMA} < \text{PS/PAA}$$

The PS latex exhibits the smallest value. Note that the negative charge of PS latex particles arises from the carboxylic acid groups of the stabilizer. The important point to be discussed here is the magnitude of zeta potentials of the latices produced by us in this study. Notice that it changes between -38 and -45 . However, the PS latices produced by conventional emulsion polymerization and seeding techniques exhibit zeta potentials around -70 .³⁵⁻³⁷ These conventional PS latices contain strong acidic groups arising from the initiator. Note that the high negative charge may be a disadvantage in, especially, surface-related biomedical applications of these latices.^{26,27}

Table VIII The Electrophoretic Mobilities and Mean Zeta Potentials of Latices

| Latex | Electrophoretic Mobility (mV) | Mean Zeta Potential (mV) |
|------------|-------------------------------|--------------------------|
| PS | -2.823 | -37.73 |
| PS/PDMAEMA | -2.985 | -39.89 |
| PS/PHEMA | -3.136 | -41.91 |
| PS/PAA | -3.384 | -45.23 |

CONCLUSION

The results of the dispersion polymerization study carried out in the isopropanol/water medium indicated that monosize PS latices can be obtained in the size range of 1.0–3.0 μm by changing the initiator, stabilizer, alcohol, and monomer concentrations. Monosize PS latices carrying functional groups on their surfaces (i.e., carboxyl, hydroxyl, and dimethylamino) can be produced by a simple two-step polymerization technique without producing new particles during the second-stage polymerization. The incorporation of functional groups onto the surface of PS particles is especially important for biomedical applications of these latices. Monosize PS latices have already been used as sorbents in the specific and nonspecific protein adsorption studies and as a tracer in the monitoring of phagocytosis.^{26–28} The PS latex carrying DMAEMA (labeled by with ^{99m}Tc) has been used, clinically, as a radionuclid for imaging of human gastrointestinal system by gamma scintigraphy.^{29–30} The incorporation of DMAEMA onto the surface of PS increased significantly the ^{99m}Tc binding and stability of the label relative to those observed with PS latex.

We would like to thank Prof. Joseph D. Andrade and Paul Dryden (The Department of Bioengineering, University of Utah) and Prof. Jeff Schakenraad (Biomedical Technology Center, University of Groningen, The Netherlands) for the ESCA measurements. The electrophoretic mobility measurements were done at the Department of Metallurgical Engineering, University of Utah. It is a pleasure to thank Prof. Jan D. Miller and Jaroslaw Drellich for their respective contributions in the electrophoretic mobility measurements.

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Received March 2, 1993

Accepted July 31, 1993