

Particle Size and Size Distribution of Styrene/Sulfopropylmethacrylate/2,2'-Azobis[2-methyl-N-(2-hydroxyethyl) Propionamide] (styrene/SPM/VA-086) and Styrene/N,N-Dimethyl-N-methacryloxyethyl-N-(3-sulfopropyl) Ammonium Betain [Styrene/SPE/Oil-Soluble 1,1-Azo-bis(cyclohexanecarbonitrile)]-Initiated Latices, Using a Zetasizer and Atomic Force Microscopy

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ABSTRACT: The preparation of surface-functional monodisperse nanoparticles with surfactant-free emulsion polymerization using polymerizable functional surface-active monomers was investigated. Crosslinked styrene seed latex to be used in the second-stage polymerization of styrene with SPM or SPE was synthesized. The seed latex was characterized by particle size and size distribution. In the second stage of a starved-feed polymerization of styrene with SPM, a water-soluble azo initiator and an oil-soluble azo initiator were used separately, and the relevant mechanistic characteristics, mainly competitive growth, were compared with data obtained from Zetasizer and atomic force microscopy measurements. The mechanism of competitive growth was the same in both systems. The oil-soluble azo

initiator also was used in the second-stage, starved-feed polymerization of styrene with SPE. Latices were cleaned by the serum replacement technique and ion exchange method. Particle size data clearly suggested a bimodal particle size distribution during the first 2 h of polymerization. The bimodality originated from the fractions of different-sized particles in the seed latex competing for the available monomer. The two particle size fractions in the early stages of polymerization tended to merge after 2 h, a situation that satisfied the conditions of a competitive growth mechanism. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 166–174, 2006

Key words: particle size distribution; particle nucleation; latices; initiators

INTRODUCTION

A seed emulsion is generally employed to control the final properties of the second stage emulsion. By seeding an emulsion, secondary nucleation can be prevented, and the size of the final latex particles can be controlled.¹ The seed latex can also be crosslinked to prevent dissolution of the latex particles in the monomer and also to prevent the migration of chemical groups to the surfaces of the final latex particles.² Calculating the weight of monomer required for the second stage can control the particle size of the second-stage emulsion. If both secondary nucleation and limited flocculation do not occur during the addition of monomer, the equation proposed by Chern and

Lin³ can be used to determine the mass of monomer required:

$$d_f = \left[d_i^3 + \frac{(6 \times 10^{21} W_m)}{\pi \rho N_c} \right]^{\frac{1}{3}} \quad (1)$$

where d_f is the final particle diameter (nm), d_i is the initial particle diameter (nm), W_m is the weight of the monomer (g), ρ is the polymer density (g cm^{-3}), and N_c is the number of particles (cm^{-3}).

The serum replacement technique⁴ is efficient for cleaning an emulsion of aqueous-phase oligomers, adsorbed emulsifier, and electrolytes. This technique involves a simple rinsing of the emulsion with distilled, deionized water, followed by further washing with a dilute HCl solution to replace the Na^+ and K^+ counterions and, finally, with distilled, deionized water again to remove all traces of the acid. An alternative method is to remove the counterions by shaking the emulsion with a suitable ion-exchange resin.

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McCarthy et al.⁵ employed a redox initiator system consisting of $\text{Na}_2\text{S}_2\text{O}_5$, $t\text{-BuOOH}$, and FeSO_4 that was found to be effective in the preparation of self-emulsifying fluoropolymers with a monodisperse particle size distribution and having less than 45% polymer solids in water. They found that the number of particles and the ultimate particle size were linearly related to the quantity of the initial charged redox catalyst. The inclusion of a small amount of acrylic acid (AA) during the semibatch surfactant-free polymerization of butyl acrylate in the presence of carboxylic monomers has been reported⁶ to depress the limited flocculation process, which results in decreased particle size. The final latex size increased initially to a maximum of about 2% AA and then decreased with increasing AA concentration because of the polyelectrolyte effect during particle nucleation. The final particle size was found to have increased significantly with increasing concentration of NaHCO_3 , which was used as a nucleating agent, because of the ionic strength effect. The run with the highest NaHCO_3 concentration showed the worst latex stability, whereas that with 0.2% NaHCO_3 manifested the best stability. Therefore, Chen and Lin⁶ concluded that the incorporation of 5% AA or 5% methacrylic acid into emulsion polymers can greatly improve the chemical stability of the finished latex products, especially with a high pH. The preparation of large monodisperse polystyrene particles (diameter $\approx 3.2 \mu\text{m}$) with no surface roughness using lower stirrer speeds than normally employed and by a one-step surfactant-free emulsion polymerization method was reported by Tuin et al.⁷

By using divinylbenzene-styrene copolymer seed particles, Leendertse and Thoenes⁸ prepared monodisperse polystyrene latex without surfactant adsorption on the particle surface. According to them, by adjusting the seed concentration, any size particle desired in the range 0.5–1.2 μm could be obtained with very good monodispersity. The kinetics of the surfactant-free emulsion polymerization of styrene, applying quantitative theories to the postnucleation stage, was studied by Chainey et al.,⁹ who believed that this was best described by treatments based on a surface polymerization model.

An interesting and important phenomenon frequently encountered in emulsion polymerization is the mechanistic phenomenon of competitive growth. Vanderhoff et al.^{10–15} used a competitive-growth technique to obtain kinetic information for styrene emulsion polymerization. They mixed two monodisperse polystyrene latices of different sizes to form a seed latex with a bimodal particle size distribution, and additional monomer was polymerized in the seed latex under conditions such that no new particles were formed. The different-sized seed particles completed for the available monomer and free radicals, and the

final latex particle size was then measured by electron microscopy.

Water-soluble monomers often polymerize in water, leading to aqueous-phase oligomers and secondary nucleation. This can be avoided by use of an oil-soluble initiator. This study used a styrene seed latex crosslinked with divinylbenzene. Surface-functional monodisperse nanoparticles with surfactant-free emulsion polymerization were prepared using polymerizable functional surface-active monomers.

Recent developments include a comprehensive experimental study of surfactant-free emulsion polymerization of styrene by Taure et al.,¹⁶ who placed special emphasis on particle nucleation, the chemical structure of the nucleating species, the changes in the latex, particle, and polymer properties, and the development of particle morphology with time. Under special conditions with a transmission electron microscope (TEM), they observed less electron-dense, anomalous particles. However, dialysis of the latices changed their properties drastically, as they became unstable to coagulation. Esquena et al.¹⁷ prepared polystyrene (PS) and poly(methyl methacrylate) (PMMA) latex dispersions via surfactant-free emulsion polymerization and studied the stability of these dispersions using photon correlation spectroscopy to obtain the average particle size and polydispersity index, whereas the stability of the latices was detected by the critical coagulation concentration (CCC) of the three electrolytes used: NaCl , CaCl_2 , and Al_2SO_4 .

Recently, Sadiku and Sanderson¹⁸ also reported on the coagulation kinetics and stability of surfactant-free emulsion polymerized styrene/SPM and styrene/SPE latices using NaCl as the electrolyte. They found that the log–log plot of the stability factors of the two latices decreased exponentially with the electrolyte concentration. A conductometric meter was coupled to a calorimetric reactor in order to provide *in situ* and online measurements of conductivity during emulsion polymerization of styrene with sodium dodecyl sulfate as an anionic surfactant and with potassium persulfate as a free-radical initiator.¹⁹ A converted semiempirical model combined with the conductometric signal, conversion, and temperature measurements was therefore able to accurately predict the number of polymer particles in the latex and the surfactant concentrations in the many phases without online measurement of particle size. Dongqi et al.²⁰ monitored the transformation of colloidal crystalline film of styrene/2-hydroethyl methacrylate (St/HEMA) copolymer latex by solvent vapor into a new periodic structure, using an atomic force microscope (AFM). Images from the AFM of the transforming heated films revealed that the PHEMA shells and the colloidal crystalline films shrunk and partially became cores that were dispersed in the polystyrene continu-

ous matrix as the transformation proceeded by an ordered-disordered-ordered sequence.

Using ultrasonic waves to perform suspension polymerization of styrene monomer in the absence of both emulsifier and initiator, Gen et al.²¹ reported that the particle size obtained from TEM and dynamic light scattering was on the order of several tens of nanometers. Tuin and Stein²² investigated the adsorption of an ionic surfactant on polystyrene particles in the presence of a cosurfactant. They reported variation in the surface charge density (scd) and particle size and that differences in the scd only had an effect on the adsorption behavior of the dodecylbenzenesulfonate surfactant at a very high scd. The addition of long-chain fatty alcohols (cosurfactant), such as dodecanol or cetyl alcohol, influenced the adsorption behavior of the dodecylbenzene surfactant.

In this study, the semicontinuous starve-feed method of emulsion polymerization was used in the second-stage polymerization of styrene with sulfopropylmethacrylate (SPM), on the one hand, and *N,N*-dimethyl-*N*-methacryloxyethyl-*N*-(3-sulfopropyl) ammonium betain (SPE), on the other, in a method similar to that employed by Geurts et al.²² For the styrene/SPM emulsion, a water-soluble nonionic azo initiator, 2,2'-azobis[2-methyl-*N*-(2-hydroxyethyl) propionamide] (VA-086), was first used and was later replaced with an oil-soluble nonionic azo initiator, 1,1'-azobis(cyclohexanecarbonitrile). The starve-feed method enables particles of a uniform size with a monodisperse particle size distribution to be produced. Under these conditions, the surface-charge densities of the styrene/SPM and styrene/SPE emulsions can be determined and compared by conductometric and potentiometric titrations, which is the subject of a future report.

EXPERIMENTAL

Distilled, deionized (DDI) water from a Millipore filtering system was used. Sodium bicarbonate (Saarchem, Johannesburg, South Africa, 99.5% purity) was used as a buffer. The seed emulsion was prepared with a conventional adsorbable surfactant, Polystep B27 (Stepan), a sulfated nonylphenol containing an average of 4 mol of ethylene oxide sodium salt. Potassium persulfate (PPS; Saarchem, 98% purity) was used as a polymerization initiator for the seed emulsion. Styrene monomer was distilled under vacuum at temperatures less than 50°C in order to remove the inhibitor and impurities. Divinylbenzene (DVB; Aldrich, technical grade and 80% purity) was used as the crosslinking agent for the seed emulsion. The monomers sulfopropylmethacrylate (SPM) and 3-[*N,N*-dimethyl-*N*-(methacryloxyethyl) ammonium] propane sulfonate (SPE), both from Raschig AG (Germany), were used as received. VA-086 water-soluble nonionic azo initiator (Wako Pure Chemical Industries, Japan)

TABLE I
Styrene Latex Recipe

Component	Charge (g)
DDI	600
Sodium bicarbonate	1
Polystep B27	5.3
Potassium persulfate (PPS)	4
Styrene (St)	150
Divinylbenzene (DVB)	2

and azobis(cyclohexanecarbonitrile) oil-soluble nonionic azo initiator (Aldrich, 98% purity) were used as received.

Polymerization procedures

All experiments were done in duplicate to ensure the repetitiveness of the results. For the polymerization, the semicontinuous method of emulsion synthesis was followed. The basic polymerization recipe for crosslinked styrene seed emulsion is given in Table I.

PPS (4 g) was dissolved in 200 g of DDI water. A 1-L cylindrical flat-bottomed glass reactor was charged with 400 g of DDI, NaHCO₃ buffer, and Polystep B27 surfactant and then fitted with a twin-blade four-propeller stainless stirrer in a nitrogen gas purge and a condenser and sealed. St/DVB mixture (10 g) was charged to the reactor and allowed to equilibrate to 80°C. Before the initiation reaction, the reaction mixture was stirred vigorously at 500 rpm to emulsify the monomers. An agitation rate of 300 rpm was maintained throughout the remainder of the experiment. A 100-mL aliquot of PPS solution was charged to the St/DVB mixture in a reactor to initiate the reaction. After 15 min, the rest of the monomer mixture was added dropwise over 3 h. The rest of the PPS solution was added over 3 h in aliquots of 8 g of the solution (0.16 g of PPS) every 15 min.

Styrene/SPM second-stage emulsion

The semicontinuous starve-feed method of emulsion polymerization was followed for the second-stage polymerization of styrene and SPM. A major experimental constraint was the absence of a metering pump. Dropping funnels were used to add the monomer, which compromised the accuracy of the addition of monomer. In the developmental stage of the recipe, a water-soluble nonionic azo initiator (VA-086) was used, which was later replaced by an oil-soluble nonionic initiator [1,1'-azobis(cyclohexanecarbonitrile)]. From eq. (1), proposed by Chern and Lin,³ it was found that 102 g of monomer (W_m) was required in the second-stage polymerization to produce a final latex with a particle size (d_p) of 158 nm.

The basic polymerization recipe for the second-stage emulsion is given in Table II. For the first run, 2 g of VA-086 and 10 g of SPM were each dissolved in 100 g of DDI water and placed in separate dropping funnels. The SPM concentration was chosen to achieve a high surface-charge density on the latex particles and for stabilizing the latices. Distilled styrene monomer (87 g) was placed in another dropping funnel. The reactor was charged with 200 g of DDI water, the NaHCO₃ buffer, and styrene seed latex and then sealed and allowed to swell for a 2-h period. Only limited swelling of the styrene seed particles was possible because of the crosslinking agent used. A stirring rate of 300 rpm was maintained throughout the experiment. After the swelling period, a 10-mL aliquot of VA-086 initiator solution was added to the reactor, and the SPM comonomer was then added dropwise. After a further 30 min, the rest of the styrene was added dropwise, and the addition of the initiator continued in 5-mL aliquots every 30 min. The monomers were added dropwise over 8 h.

For the second run, the oil-soluble initiator was dissolved in the remaining 87 g of styrene monomer, and the reactor was correspondingly charged with 300 g of DDI water to compensate for the 100 g of DDI water used to dissolve the VA-086 initiator in the first run. After the swelling period, the dropwise addition of the styrene and SPM monomers was started simultaneously and maintained for 8 h. Samples were drawn from the reactors after 30, 60, 120, 180, and 240 min and at completion of polymerization reactions for particle size analysis by dynamic light scattering and AFM imaging. The pH of the two systems after completion of the reactions was 8.5.

Styrene/SPE second-stage emulsion

Procedures and recipe identical to those used for the styrene/SPM emulsion were used for the styrene/SPE emulsion. The oil-soluble initiator, 1,1-azobis(cyclohexanecarbonitrile), was used in order to obtain the desired particle size. SPE was used in equimolar amounts to SPM in order to ensure that the recipes used for both latices were identical. The buffer was

TABLE II
Styrene/SPM Emulsion Recipe

Component	Charge (g)—	
	Run 1	Run 2
DDI	400	400
Sodium bicarbonate	0.5	0.5
VA-086	2	
Oil-soluble azo		2
Styrene	92	92
Styrene seed latex	100 mL	100 mL
Potassium persulfate (PPS)	10	10

TABLE III
Styrene/SPE Emulsion Recipe

Component	Charge (g)
DDI	400
Oil-soluble azo	2
Styrene	92
Styrene latex seed	100 mL
SPE	11.34

excluded because the latex was found to coagulate under high ionic strength. The basic polymerization recipe for the second-stage emulsion is shown in Table III. Following the completion of the reaction, the pH of the system was adjusted from 2.5 to 6.5 in order to convert the SPE to zwitterionic form.

Latex purification procedure

The styrene/SPM and styrene/SPE latices were cleaned by serum replacement, using a 100 000 nominal molecular mass cutoff UltraSep membrane (Micon Separations Incorporated). The serum replacement cell used was similar to the type used by Ahmed et al.⁴ The conductivity of the supernatant was recorded until it reached a constant value similar to the conductivity of the DDI water. After the replacement of the serum, the counterions were replaced by ion exchange with an Amberlite MB-1 mixed-bed ion-exchange resin from ICN Biochemicals, Inc. The amount of exchange resin used was five times greater than the solid content of the latices, and the mixtures were stirred for 2 h. Finally, the latices were again purified by serum replacement.

Samples of styrene/SPM and styrene/SPE latices were diluted to a particle-number concentration of 10⁹ particles/m³ because at this concentration, the aggregation rate constant was independent of the particle-number concentration.¹⁷ The low particle concentration would ensure the absence of multiple scattering and particle-particle interactions. All dilutions were performed using distilled, deionized (DDI) water that had been filtered through a 0.45- μ m Millipore filter. Reagent-grade NaCl was used.

Photon correlation spectroscopy (PCS)

Particle size analysis was carried out by dynamic light scattering on a Malvern Zetasizer 4S from Malvern Instruments Ltd. Photon correlation spectroscopy was used to follow the coagulation kinetics of the latices at different electrolyte concentrations. The measurements were made at 25°C and at a scattering angle of 90°. Equal volumes of latex and salt solution were mixed in the sample cuvette, and measurements started as soon as possible. Data acquisition typically

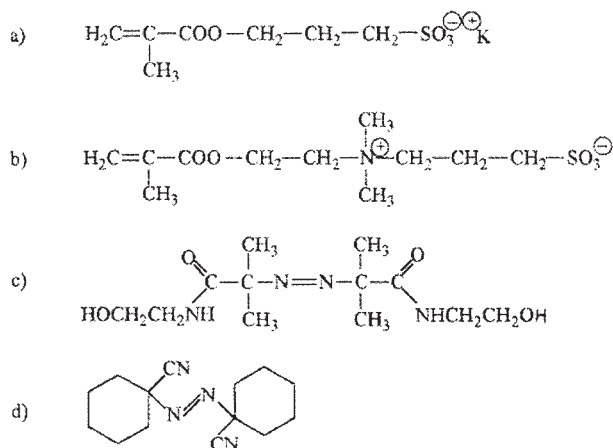


Figure 1 Chemical structures of (a) SPM, (b) SPE, (c) VA-086, and (d) 1,1'-azobis(cyclohexanecarbonitrile).

lasted about 1000 s. A fractional analysis of the size-intensity table revealed the diameters of the growing aggregates at certain time intervals. The chemical structures of SPM, SPE, VA-086, and 1,1'-azobis(cyclohexanecarbonitrile) are shown in Figure 1(a-d).

Atomic force microscopy

All samples were prepared by drying a drop of the latex on a polished silicon plate. The samples were dried in an air-conditioned room at 18°C, which revealed the particle matrix had a clearly defined structure. The atomic force microscope was a Topometrix TMX 2000 Explorer, using a silicon tip with a radius of 20 nm and a low-resonance frequency cantilever that had a manufacturer's spring constant of 35–65 N/m. Scans of $1.8 \times 1.8 \mu\text{m}$ were obtained for each sample. The images were recorded in the noncontact mode by which the probe operated in the attractive region. All recordings were made in air under ambient conditions to produce 3-D images.

RESULTS AND DISCUSSION

The multimodal graph of the particle size distribution of the styrene seed latex is shown in Figure 2, whereas the graph of the final particle size distributions of the second stage styrene/SPM emulsions (styrene/SPM/VA-086 and styrene/SPM/oil-soluble azo latices) after the completion of the reactions is shown in Figure 3. Following completion of the reactions, the final particle size of the styrene/SPM/VA-086 emulsion was about 104 nm and that of the styrene/SPM/oil-soluble azo emulsion was 162 nm. The final particle size of the styrene/SPE/oil-soluble azo was also found to be 162 nm. Therefore, equal-sized particles were obtained for the two latices, which was essential for comparing their surface-charge densities and colloidal stabilities,

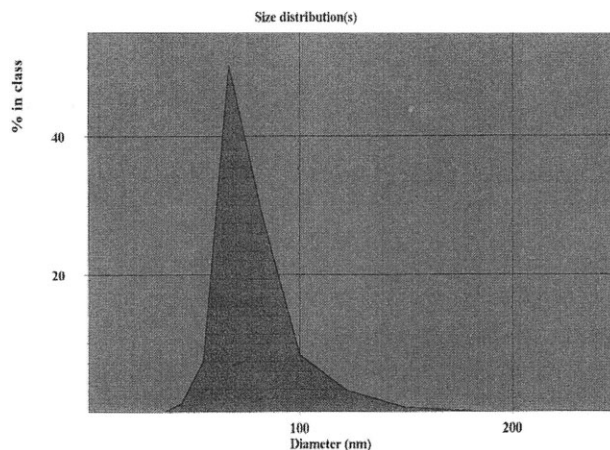


Figure 2 Multimodal curve of the particle size distribution of styrene seed latex.

reported elsewhere.¹⁸ The plot of the particle size distribution of the styrene/SPE latex is shown in Figure 4. It was found that the particle number from the seed latex remained constant in the styrene/SPM latices, which proved that the bimodal particle size distributions, shown in Figure 5, could be attributed to competitive growth. This effectively ruled out secondary nucleation. During the first 4 h, a characteristic feature of both styrene/SPM systems was a definitely bimodal particle size distribution, as was apparent from the two peaks obtained in the multimodal mode of analysis. The two particle size fractions at various times from Zetasizer measurements are given in Figure 5 and in Table IV.

Atomic force microscopy (AFM) were also used to measure the dried latex samples, which showed a particle size distribution similar to those from Zetasizer measurement. AFM measurements of the two particle sizes at various times are shown in Table V and the relative AFM images and particle size measurements are shown in Figure 6.

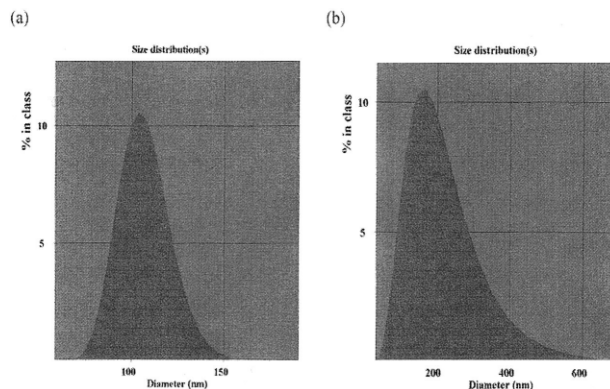


Figure 3 Particle size distribution in the monomodal mode of (a) styrene/SPM/VA-086 latex and (b) styrene/SPM/oil-soluble latex.

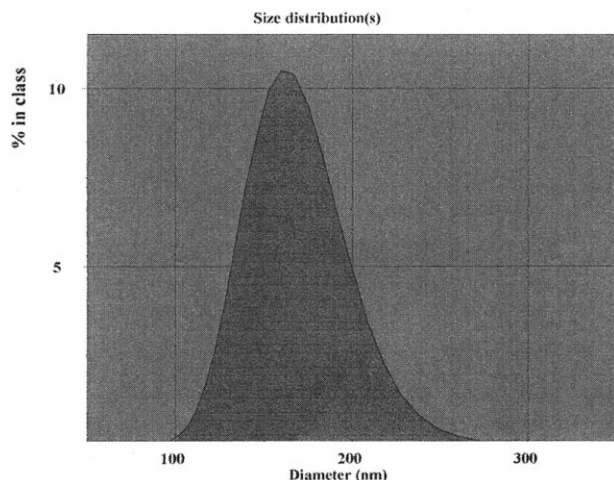


Figure 4 Monomodal curve of the particle size distribution of the styrene/SPE/oil-soluble azo emulsion.

The narrowing of the bimodal particle size distributions obtained during the first 4 h of the second-stage polymerizations was attributed to the mechanistic phenomenon of competitive growth. This was deduced from the number of particles of the styrene seed latex in the styrene/SPM latices being unchanged after 30 min, which proved that the bimodality was not a result of secondary nucleation. From the size-intensity table supplied with the Zetasizer, it was deduced that the seed latex was not completely monodisperse. The reason for this was not clearly understood. The phenomenon of competitive growth was the result of competition by seed particles of different sizes for the available monomer and free radicals. Because of the higher free-radical entry rate of the small particles, the fraction of small particles grew faster than the fraction of large particles. This caused the bimodality to disappear after the reaction time had lasted 4 h. This competitive particle growth process continued until the particle sizes of the two fractions became equal.

The characteristic features of competitive growth are clear from the plots of particle size distributions after 30, 60, and 120 min, shown in Figure 5. After 30 min, the two peaks were visibly separated, corresponding to the two fractions (A and B). After 60 min, the two peaks were starting to overlap as the smaller size fraction, A, was approaching the size of the larger size fraction, B, because of competitive particle growth. After 240 min, the two peaks had largely merged, which seemed to indicate that the size difference between the two fractions was diminishing. The resolution of the AFM images, as shown in Figure 6, was insufficient to accurately determine particle size distribution, raising doubt about the accuracy of using AFM to measure particle size distribution. The obvious similarity in the particle size data of the styrene/SPM/VA-086 and styrene/SPM/oil-soluble azo sys-

tems implies that the same mechanisms of polymerization, that is, the mechanism of competitive growth, can be applied to both systems.

The main difference between the two systems lay in the site at which polymerization took place. In the styrene/SPM/VA-086 system, in which water-soluble initiator was used, polymerization could have been initiated in the aqueous phase, resulting in aqueous phase oligomers not associated with the particles. Polymerization could also have occurred on the particle surface with the styrene monomer preferentially diffusing into the hydrophobic surface of the crosslinked seed particle. The hydrophilic SPM monomer, which was present and which polymerized preferentially in the water phase, therefore did not diffuse readily into or onto the particle surface, negatively affecting particle stability. The possibility of formation of aqueous phase oligomers and grit on the stirrer blades explain the resulting particle size of 104 nm for this latex, which was far below the expected value of 158 nm.

With the styrene/SPM/oil-soluble azo system, the hydrophobic initiator radicals were expected to be preferentially located in the styrene seed particles and polymerization to occur mainly on the particle surface or in the particles as monomer diffused in. It can be inferred, therefore, that the SPM monomer polymerized mainly on the particle surface, with further adsorption of the oligomers on the particles, thus contributing toward the stability of the particles. The resulting particle size of 162 nm correlated well, within experimental error, with the expected particle size of 158 nm. The oil-soluble initiator performed as desired and was therefore chosen as the initiator for the second-stage polymerization of styrene with the zwitterionic SPE.

The styrene/SPE/oil-soluble azo system also yielded a final particle size of 162 nm. Apart from achieving the objective of equal particle sizes for the styrene/SPM and styrene/SPE systems, it also suggested that the same mechanism probably applied to the styrene/SPE system. This would be expected because of the similar hydrophilic nature of SPM and SPE.

CONCLUSIONS

Crosslinked styrene seed latex was synthesized for second-stage polymerization of styrene with SPM and SPE. The seed latex was crosslinked with divinylbenzene in order to prevent the migration of surface groups during the second-stage polymerization. In this way, the sulfate end groups from the potassium persulfate initiator used in the seed latex could not migrate to the surfaces of the final second-stage particles. This was done to prevent the sulfate weak-acid groups from interfering with the conductometric titration during determination of the surface charge density, as reported elsewhere.¹⁸

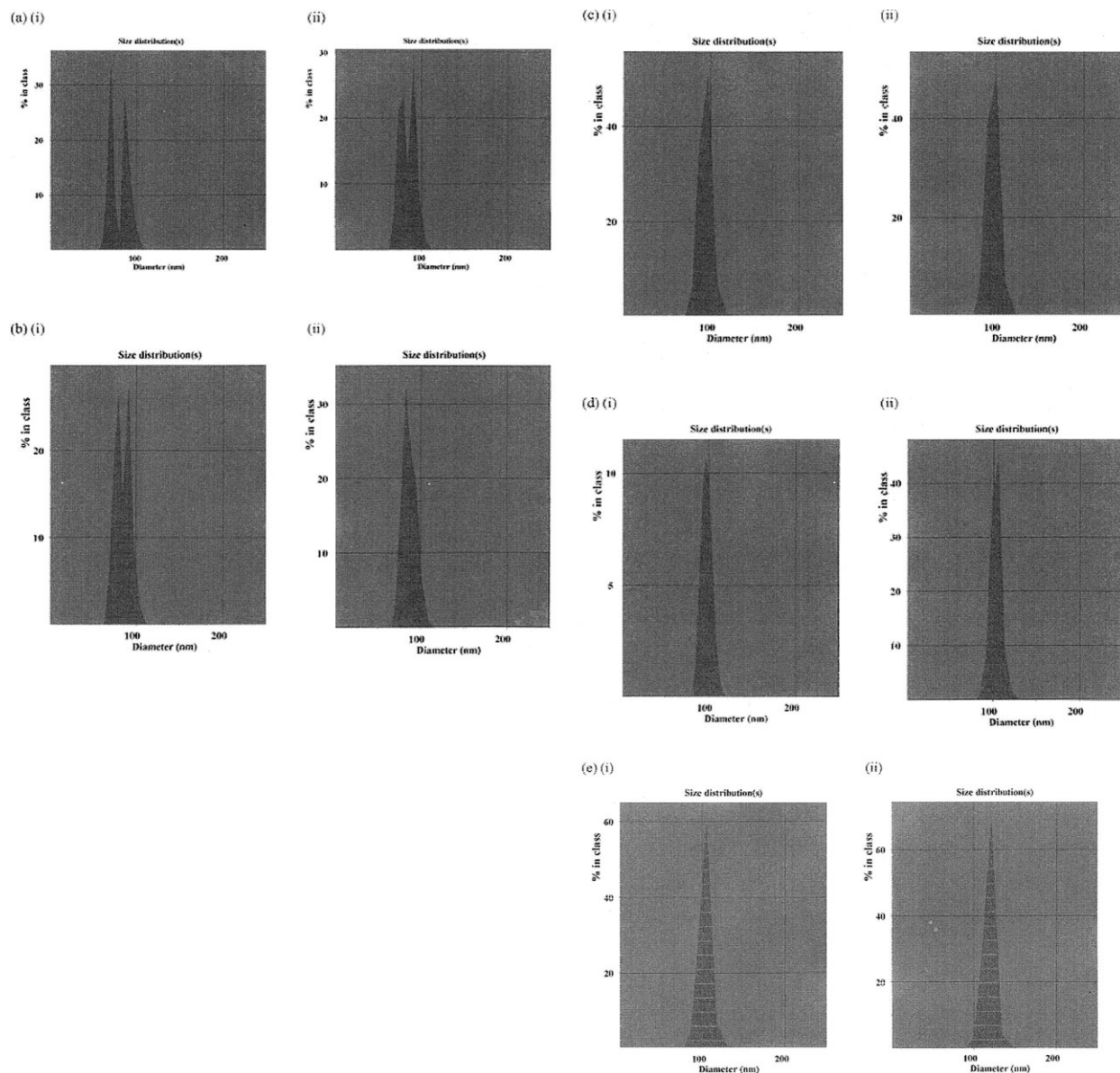


Figure 5 Particle size distributions in the multimodal mode of the respective (i) styrene/SPM/VA-086 and (ii) styrene/SPM/oil-soluble azo latices, indicating different particle size fractions after: (a) 30 min, (b) 60 min, (c) 120 min, (d) 180 min, (e) 240 min.

In the second-stage starved-feed polymerization of styrene with SPM, a water-soluble azo initiator and oil-soluble azo initiator were used separately. The oil-

soluble azo initiator performed as desired, yielding the particle size calculated for the second-stage emulsion. For this reason, the oil-soluble azo initiator was

TABLE IV
Zetasizer Data or Particle Size Fraction at Various Times

Time (min)	VA-086		Oil-soluble azo	
	Fraction A (nm)	Fraction B (nm)	Fraction A (nm)	Fraction B (nm)
Seed latex	70	75	70	75
30	70	86	79	91
60	79	91	83	95
120	87	97	91	100
180	98	105	98	105
240	108	113	121	128

TABLE V
AFM Data on Particle Size at Various Times

Time (min)	VA-086		Oil-soluble azo	
	Particle A (nm)	Particle B (nm)	Particle A (nm)	Particle B (nm)
30	70	90	80	90
60	80	90	80	100
120	90	100	90	100
180	90	110	100	110
240	90	120	100	130

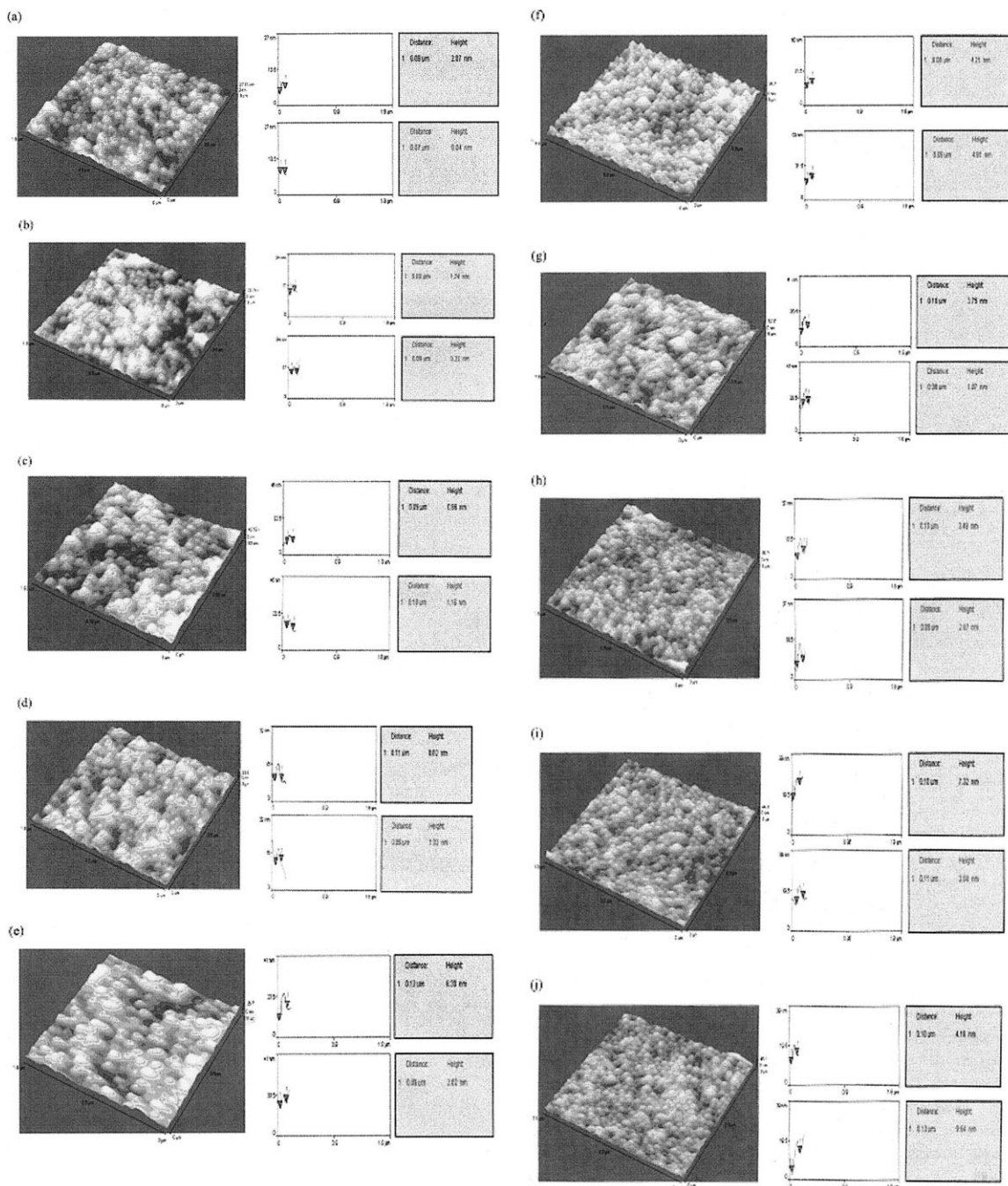


Figure 6 3-D AFM images ($1.8 \times 1.8 \mu\text{m}$) and measurements of dried polystyrene/SPM latices with VA-086 and an oil-soluble initiator: (a) VA-086 after 30 min, (b) VA-086 after 60 min, (c) VA-086 after 120 min, (d) VA-086 after 180 min, (e) VA-086 after 240 min, (f) oil-soluble azo after 30 min, (g) oil-soluble azo after 60 min, (h) oil-soluble azo after 120 min, (i) oil-soluble azo after 180 min, and (j) oil-soluble azo after 240 min.

chosen as the initiator for the second-stage polymerization of styrene with the zwitterionic SPE.

Both systems showed the prevailing mechanism to be competitive growth. The reasons for this mechanism were monitored by gathering particle size data from Zetasizer and AFM measurements. The particle size data clearly suggested a bimodal particle size distribution during the first 240 min of polymeriza-

tion. The bimodality originated from fractions of different-sized particles in the seed latex that competed for the available monomer. Zetasizer measurement indicated that the two particle-size fractions present in the early stages of polymerization tended to merge after 240 min, thereby satisfying the conditions for a competitive growth mechanism. Styrene/SPM and styrene/SPE latices with particles equal in size were

successfully synthesized by the use of identical polymerization recipes, showing that one criterion for comparing the two systems, equal particle size, had been achieved.

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