Polystyrene Latexes Containing Poly(propyleneimine) Dendrimers

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ABSTRACT: Polymerization of styrene in aqueous dispersions of sodium dodecyl sulfate (SDS) and the poly(propyleneimine) dendrimer DAB-*dendr*-$(NH_2)_{64}$ with initiation by potassium persulfate at 80 °C produced latexes with diameters in the range of 26−64 nm and coefficients of variation of diameters of less than 10%. Stable latexes were obtained starting with 1.0 to 4.0 molar ratios of SDS to dendritic primary amine end groups, 5.5 to 11 wt % of SDS relative to styrene, and SDS concentrations below the critical micelle concentration in water at 25 °C. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) showed both individual particles and small clusters. TEM and AFM measurements of particle sizes agreed well. Dynamic light scattering measurements gave larger sizes and large polydispersities, presumably due to the presence of clusters.

Introduction

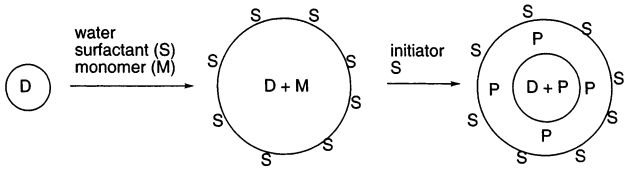
Polymer latexes are used widely in the rubber, coatings, chemical, food, and pharmaceutical industries.[1,2] Emulsion polymerization often produces nearly monodisperse latex particles with diameters in the 0.1−1 μm range.[3,4] Study of monodisperse latex spheres as model colloids has advanced understanding of the physics of particle−particle interactions in colloidal dispersions. The dispersions are stabilized electrostatically by repulsion of particles of the same sign of charge, sterically by the unfavorable entropy of mixing of polymer chains pendant from the surfaces of the particles, or by a combination of the electrostatic and steric mechanisms.[5]

The early formation of electrostatically stabilized particles, and prevention of formation of new particles while the early particles grow, are the keys to achieving monodisperse latexes. A typical batch polymerization mixture initially contains monomer of low solubility in water, which is dispersed by mechanical forces into unstable droplets, and a water-soluble initiator such as potassium persulfate. Usually the mixture also contains either a low molar mass surfactant or a water-soluble monomer. The charged groups on the particle surface can originate from surfactants, initiator end groups, or charged monomers. All three sources of charged groups have led to latexes with narrow distributions of particle sizes, having coefficients of variation (CV = standard deviation/mean diameter) of 3% or less. The particle size distributions can be narrowed even more by seed growth.

Similarly narrow particle size distributions have not been achieved for smaller latexes except in inverse microemulsion polymerization of acrylamide.[6] In general, as diameters of samples decrease from 150 to 20 nm, CV increases markedly. Particles smaller than 20 nm can be produced from oil-in-water microemulsions, but the size distributions are very broad.[7,8] Use of larger amounts of surfactant or charged monomer in conventional emulsion systems (but less than in microemulsions) can produce particles less than 50 nm in diameter, but the CV values generally exceed 10%.

The difficulty of measurement of the particle sizes also increases as the size decreases. Data are reported from either dynamic light scattering (DLS) or transmission electron microscopy (TEM), but seldom from both methods. We rely on TEM for such small sizes because of experimental difficulties in determination of the broader size distributions by DLS.

Scheme 1



In this paper we describe a new strategy for the synthesis of latexes of low polydispersity in the range of 26−64 nm in diameter. The basic idea is illustrated in Scheme 1. If dendrimer−surfactant aggregates are the primary particles for emulsion polymerization, under conditions where no new particles form, and all growth takes place starting from the preformed aggregates, the particle size distribution of the product will depend on the size distribution of the aggregates. Dendrimers are the most nearly monodisperse synthetic polymers available. Here we use the poly(propyleneimine) dendrimer DAB-*dendr*-$(NH_2)_{64}$ (D64), which has a globular conformation about 3 nm in diameter,[9,10] and sodium dodecyl sulfate (SDS) as the surfactant.

Aggregates form when the dendrimer and the surfactant have opposite charge: protonated polyamine dendrimers aggregate with anionic surfactants, and dendrimers with carboxylate end groups aggregate with cationic surfactants.[11,12] Mixtures of oppositely charged dendrimers without surfactants form well-defined aggregates.[13,14] Dendrimers form complexes with linear polyelectrolytes of opposite charge.[15−18] Aggregates of poly(amideamine) (PAMAM) dendrimers and SDS bind more of a hydrophobic dye than either the dendrimer or the surfactant alone (at a concentration less than the cmc).[19] Poly(propyleneimine) dendrimers with up to 64 primary amine end groups bind SDS starting at SDS concentrations lower than 10^{-5} M. Increased binding is observed until the dendrimer surface is saturated, and then separate SDS micelles form in solution.[12] At concentrations of anionic surfactants below the cmc, aggregates with PAMAM dendrimers form a variety of complexes, in which the microenvironments have been characterized by a solvatochromic fluorescent probe.[20]

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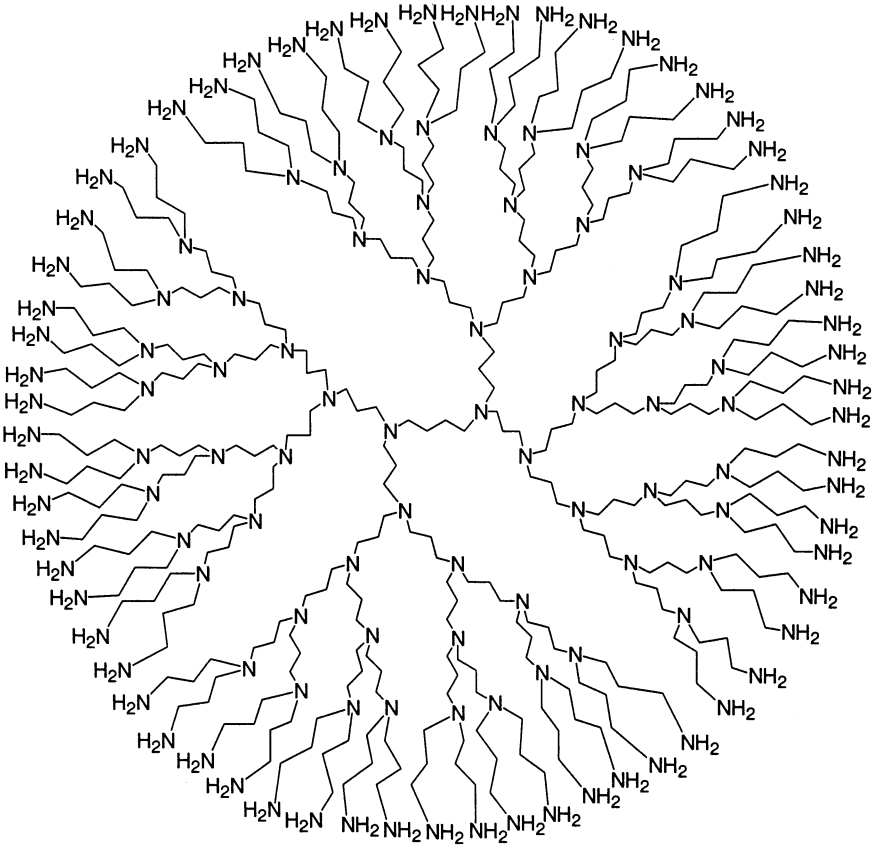

D64

In the only previous report of emulsion polymerization in dendrimer solutions of which we are aware, latexes were prepared from 100 mg of PAMAM generation 5 dendrimer (128 end groups) and 0.1 mL of monomers in 20 mL of water using the oil-soluble initiator azobis(isobutyronitrile) (AIBN).[21] The products from methyl methacrylate and from vinyl acetate were transparent dispersions. A TEM image of the PVAc sample showed particles 6−7 nm in diameter in clusters. Initiation with potassium persulfate (KPS) gave similar results. Our conditions differ markedly from the previous experiments by the use of only 1−2 wt % of dendrimer and 5.5−44 wt % of SDS relative to styrene monomer.

Experimental Section

General. Water was deionized using a Barnstead water purification system. Styrene (Aldrich) was distilled under vacuum and stored at 4 °C. Azobis(isobutyronitrile) (AIBN) from Aldrich was recrystallized from ethanol. All other chemicals including sodium dodecyl sulfate (SDS, 99%), dendrimer DAB-*dendr*-$(NH_2)_{64}$ (D64), potassium persulfate (KPS, 99+%), 2,2′-azobis(2-methylpropionamidine) dihydrochloride (V50, 97%), and sodium bicarbonate (Aldrich) were used as received. D64 had ^{1}H and ^{13}C NMR spectra consistent with its structure.

Elemental analyses were performed at Huffman Laboratories, Golden, CO. Size exclusion chromatographic analyses of molecular weights were measured relative to polystyrene standards of molecular weights 17 500−1 800 000 using a series of 10 mm particle size 10^6, 10^5, and 10^4 Å PLgel columns (Polymer Laboratories, Amherst, MA). The solvent was THF at 40 °C, and the flow rate was 1.0 mL/min. Data were fitted by a first-order polynomial using a GPC macro supplied by Hewlett-Packard Co.

Emulsion Polymerization. The general procedure is illustrated with sample 6 (Table 1). To a 100 mL three-neck round-bottom flask equipped with a condenser, a magnetic stirrer, and a nitrogen inlet were added 20.0 mg of D64 and 20.0 mL of water. The stirrer was started, 100.0 mg of SDS in 5.00 mL of water was added, and 5 min later 1.00 mL of styrene was added. The air in the flask was replaced by nitrogen, and the mixture was kept under nitrogen until polymerization was finished. After stirring for 1.5 h, 2.00 mL of KPS stock solution (1.50 g of KPS in 100.0 mL of water) and 0.50 mL of $NaHCO_3$ solution (1.00 g of $NaHCO_3$ in 40.0 mL of water) were added. The mixture was stirred for 0.5 h and then was placed in an oil bath at 80 °C. After 0.5 h an additional 100.0 mg of SDS in 5.00 mL of water was added, and the polymerization was continued for 0.5 h to produce a latex. The pH of the emulsion was measured with a pH meter.

For elemental and molecular weight analyses the latex was filtered with cotton, and the filtrate was dialyzed (Spectrum, Spectra/Por^R 7 membrane, 50 000 molecular weight cutoff) with daily change of the water for 30 days. The latex became unstable and began to precipitate after 12 days. Precipitation was completed by adding methanol and allowing the mixture to stand overnight. The precipitated polymer was filtered, washed with water, and dried in a vacuum for 24 h at 60 °C to obtain a pale yellow solid.

TEM. To prepare an unstained specimen, the emulsion was diluted 1:15 with water. A drop of this sample was placed on a Formvar-coated copper grid for 2 min, the excess emulsion was removed by touching a piece of filter paper to the drop, and the grid was dried in air. The TEM images were obtained at 80 keV with a JEOL JEM 100 CX II instrument at 29 000, 58 000, 72 000, or 100 000× magnification.

Diameters of at least 100 particles from photographic images of three or four areas of the grid were measured using an optical microscope whose stage was equipped with a vernier scale. Although some of the particles were in clusters, we measured every particle with a clearly identifiable diameter in a cluster. Diameters were calculated from the nominal instrument magnification. Calibration of the instrument showed

Table 1. Compositions of Emulsion Polymerization Mixtures and Latex Stabilities

sample	water (mL)	D64 (mg)	initial SDS (mg)	mol of SDS/mol of NH_2	styrene (mL)	$K_2S_2O_8$ (mg)	pH[b]	stability[c]
A. Increasing Amount of D-64 at 11 wt % Initial SDS								
26	27.5	0.0	100		1.00	30	7.0	good
13	27.5	10.0	100	4.0	1.00	30	7.3	good
6 (25)[a]	27.5	20.0	100	2.0	1.00	30	7.6	good
12	27.5	30.0	100	1.33	1.00	30	8.8	poor
B. Increasing Amount of D-64 at 5.5 wt % Initial SDS								
28	30.0	0.0	50	1.00	30	6.9		good
15 (29)[a]	30.0	10.0	50	2.0	1.00	30	7.1	good
11 (27)[a]	30.0	20.0	50	1.0	1.00	30	7.6	good
18	30.0	25.0	50	0.8	1.00	30	9.3	poor
14	30.0	30.0	50	0.67	1.00	30	bad	
C. Varied Amount of Styrene at Constant SDS/D-64								
21	30.0	10.0	50	2.0	0.50	30	7.1	good
20	30.0	10.0	50	2.0	1.50	30	6.9	good
D. Varied Amount of KPS								
22	30.0	10.0	50	2.0	1.00	15	7.8	good
23	30.0	10.0	50	2.0	1.00	45	4.7	good
E. Acidified Initially to pH 3.9								
17[d]	30.0	20.0	50	1.0	1.00	30	2.3	fair

[a] Duplicate experiments. [b] After polymerization. [c] Good: no coagulum was observed for at least 30 days. Fair: there was some visible coagulated latex. Poor: there was substantial coagulum. Bad: all of the latex precipitated. [d] The pH was adjusted with HCl before heating.

only random deviations of ±2% from the nominal values. The number-, weight-, and *z*-average diameters and the coefficient of variation (CV) were calculated using eqs 1−4, where D_i is the diameter of a particle and N_i is the number of particles measured.

$$D_n = \sum N_i D_i / \sum N_i \quad (1)$$

$$D_w = \sum N_i D_i^4 / \sum N_i D_i^3 \quad (2)$$

$$D_z = \sum N_i D_i^5 / \sum N_i D_i^4 \quad (3)$$

$$CV = [\sum (D_i - D_n)^2 / \sum N_i]^{1/2} / D_n \quad (4)$$

AFM. Measurements were performed in air using a Nanoscope IIIa instrument (Digital Instruments Inc., Santa Barbara, CA) operating in the tapping mode. TESP silicon tips with a cantilever length of 125 μm and a characteristic frequency of 300−330 kHz were employed for image acquisition. The substrates were polished silicon wafers coated as follows with aminopropyl silica. A clean wafer was held in a 1 mM toluene solution of 3-aminopropyl(triethoxy)silane for 1 h and then dried at 110 °C for 10 min. The coated substrate was immersed in a dilute solution of a latex dispersion, rinsed with water, and dried in air.

DLS. Particle sizes were measured at 22 ± 1 °C using a Brookhaven Instruments 200SM goniometer and 900AT multi-τ-digital correlator equipped with a coherent INNOVA-90 argon laser (514.5 nm) at a 90 °C scattering angle. The samples were filtered with a MILLEX-VV 0.1 μm filter (Millipore) and diluted with water. The method of cumulants was used to calculate the translational diffusion coefficient *D*, and the Stokes−Einstein equation (eq 5), where k_B is the Boltzmann constant, η is the viscosity of water, and T is the absolute temperature, was used to calculate the hydrodynamic radius R_h. We report diameters from quadratic fits to the data. The diameters calculated from quadratic and cubic fits differed by no more than 2% and usually by ≤1%.

$$R_h = k_B T / 6\pi\eta D \quad (5)$$

Results

Latex Synthesis. Particles were prepared by emulsion polymerization of styrene in solutions of SDS surfactant at less than its critical micelle concentration and poly(propyleneimine) dendrimer D64. The molar ratio of SDS to primary amine end groups of D64 in the heterogeneous reaction mixture was varied from 0.67 to 8.0. For example, 100 mg of SDS and 20 mg of D64 make a 2:1 ratio of surfactant anions to primary amines. In preliminary experiments we obtained stable polydisperse latexes from 22 to 44 wt % of SDS relative to styrene in a batch process. We also investigated semicontinuous processes in which the styrene, or more SDS solution, or both, were added dropwise over 0.5, 1.0, or 8 h to a solution of D64, SDS, and KPS at 80 °C. Both the batch and the semicontinuous processes produced polydisperse latexes with average diameters of <100 nm. (These compositions and particle size distributions are not shown in the tables.)

We obtained the most nearly monodisperse latexes by mixing dendrimer, surfactant, initiator, and styrene in water at room temperature, heating to 80 °C, and adding more surfactant 0.5 h later to increase the final amount of SDS to 22 wt % relative to polystyrene. The compositions are reported in Table 1. Initial molar ratios of SDS to primary amines from 0.8 to 2.0 and initial amounts of SDS from 5.5 to 11 wt % relative to polystyrene gave stable latexes with CV of diameters of less than 10% measured by TEM. When no dendrimer was used under otherwise identical conditions, the product latexes were polydisperse, as shown in Figure 1. *The dendrimer was necessary to produce the least polydisperse latexes.*

The initial reaction mixtures contained a small amount of sodium bicarbonate but not enough to buffer the mixture throughout the polymerization. Usually the initial pH was 8.6−9.5 due to the bicarbonate and the amine groups of the dendrimer, and the pH decreased to about 7 during the polymerization, presumably due to hydrolysis of SDS and of sulfate end groups to alcohols and hydrogen sulfate ion. When the initial molar concentration of dendrimer primary amines was more than twice the initial molar concentration of persulfate ion, the pH of the product mixture was 8.8 or higher, and the latexes were not stable. With no sodium bicarbonate in the reaction mixture, the initial pH was about 8, the final pH was about 4, and the latex was stable but polydisperse. When the initial mixture was acidified to pH 3.9 before polymerization, the final

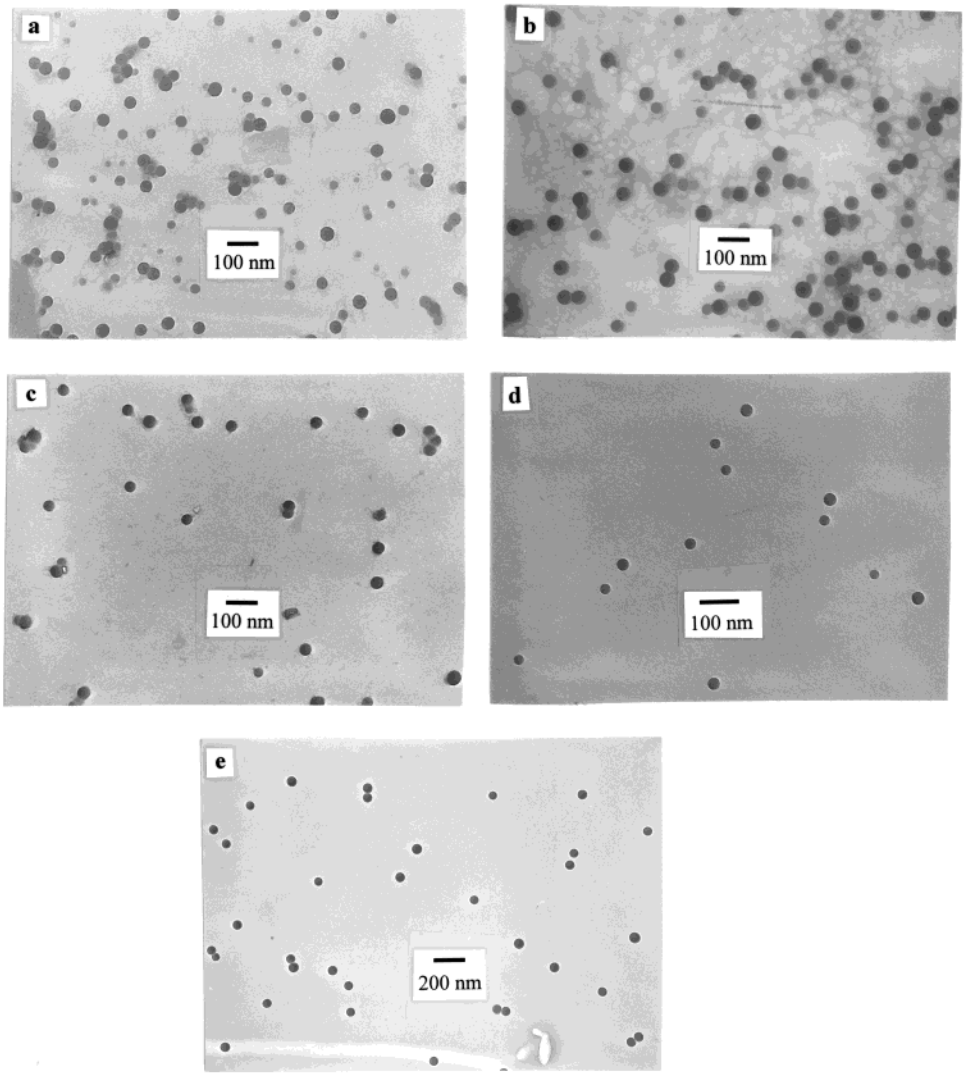

Figure 1. TEM images of (a) sample 26 (made by the same method as sample 6 but without dendrimer, (b) sample 28 (made by the same method as sample 11 but without dendrimer), (c) sample 6, (d) sample 11, and (e) sample 15.

pH was 2.3, and the latex was not stable. At pH ≤ 4 the branch point tertiary amines as well as the end group primary amines of PPI dendrimers are protonated.[22,23] Stable latexes were obtained at final pH values from 4.7 to 7.8.

Dynamic Light Scattering Measurements of Initial Reaction Mixtures. A mixture of dendrimer, SDS, and water, but no styrene, was stirred for 5 min, exactly as in the polymerization experiments. The solution was transferred quickly to a cuvette, and the average diameter of the scattering species was measured by DLS to be 42, 36, and 22 nm for mixtures having the same compositions of samples 6, 11, and 15, respectively. Then styrene was added and mixed. The average diameter increased to >100 nm and continued to increase over time. These sizes do not correlate with the sizes of the product latexes. The scattering species in the mixtures are aggregates containing styrene, dendrimer, and SDS, or styrene droplets. Such aggregates would contain many dendrimer molecules. (A sphere 20 nm in diameter consisting of a uniform composition like that of sample 11 of styrene, dendrimer, and SDS would contain seven dendrimer molecules.)

Mixtures of the same amounts of D64 and SDS as in sample 6 (Table 1) but without KPS or styrene were dialyzed for 2 days and for 15 days. After 2 days the mixture contained suspended white solid, and after 15 days the solid had precipitated. The solids were isolated by filtration and analyzed by ^{1}H NMR spectroscopy to contain 1.65 and 1.67 dodecyl sulfate ions per D64 end group, assuming no sodium ions and one ammonium ion per dodecyl sulfate ion, which corresponds with electrical neutrality. The amounts of solid isolated and their compositions were the same after 2 days and after 15 days.

Measurement of Particle Sizes. The diameters of particles were measured by TEM and DLS and in a few cases by AFM. The data are reported in Table 2. The TEM images show both individual and clustered spherical particles, as in Figure 1a. We measured every possible sphere in each cluster as well as the isolated spheres and calculated the number-, weight-, and *z*-average diameters. The CV was less than 10% for most of the samples.

Experiments 6, 11, and 15 were duplicated at a time several months later. The diameters of the products of the later experiments (25, 27, and 29) measured by TEM agreed well with those of the earlier experiments, as shown in Table 2. Moreover, the numbers of clustered particles in samples 6, 11, and 15 did not change when new TEM images were obtained after 9 months.

Table 2. Diameters of Particles (nm)

	TEM				
sample[a]	D_n	D_w	D_z	CV	DLS
A. Increasing Amount of D64 at 11 wt % Initial SDS					
26	~28		polydisperse		47
13	29	31	31	15.7	49
6	34	35	35	7.4	80
25[b]	38	39	39	8.0	90
12	~45		polydisperse		108
B. Increasing Amount of D64 at 5.5 wt % Initial SDS					
28	~47		polydisperse		57
15	57	57	57	4.1	78
29[b]	54	55	55	5.6	75
11	27	27	28	9.8	36
27[b]	29	30	30	9.1	46
18	49	50	50	7.1	42
C. Varied Amount of Styrene at Constant SDS/D64					
21	50	51	51	8.5	125
15	57	57	57	4.1	78
20	64	65	65	6.7	76
D. Varied Amount of KPS					
22	49	50	50	4.1	83
15	57	57	57	4.1	78
23	67	68	68	5.5	76
E. Acidified Initially to pH 3.9					
17	93	96	97	10.8	126

[a] See Table 1 for the compositions. [b] Duplicate of the preceding experiment.

The diameters calculated from DLS were much larger than those from TEM, and there was no consistent difference between the TEM and the DLS results. We suspect that aggregates of particles are responsible for the differences. The clusters seen in the TEM could have been formed either during polymerization or during preparation of the TEM samples. Diameters are expected to be a few nanometers larger from DLS than from TEM because DLS measures a hydrodynamic size. In an attempt to reduce the thickness of the shell of associated counterions around the particles (which is part of the hydrodynamic size), sample 6 was diluted with 1.0 mM NaCl solution before DLS measurement. The diameter was 85 nm in the NaCl solution compared with 80 nm in pure water. This rules out any large contribution of a shell of counterions and water to the diameter measured by DLS. Sample 6 also was diluted with 70 mM SDS (in excess of the critical micelle concentration), and the diameter measured by DLS was 90 nm. Thus, excess SDS failed to break up aggregates. The most likely reason for the inconsistent DLS results is the presence of clusters of small numbers of particles. Consequently, we will discuss further only the diameters measured by TEM.

The sizes of selected particles were measured by AFM under ambient conditions. Figure 2 shows an image and a height profile of sample 15 on a silicon wafer, which was pretreated with 3-aminopropyl(triethoxy)silane to make the anionic latex stick to the surface. As in the TEM images, there are both individual and clustered particles. The shapes of the particles are distorted in the horizontal plane by the motion of the sample under the tapping probe, and consequently size measurements are considered to be reliable only in the vertical direction.[24,25] The profile of three particles in Figure 2b gives a height of 53 ± 3 nm, in good agreement with the diameter of 57 nm measured by TEM. By the same method, the height of particles of sample 11 was 26 ± 3 nm by AFM compared with 27 nm by TEM.

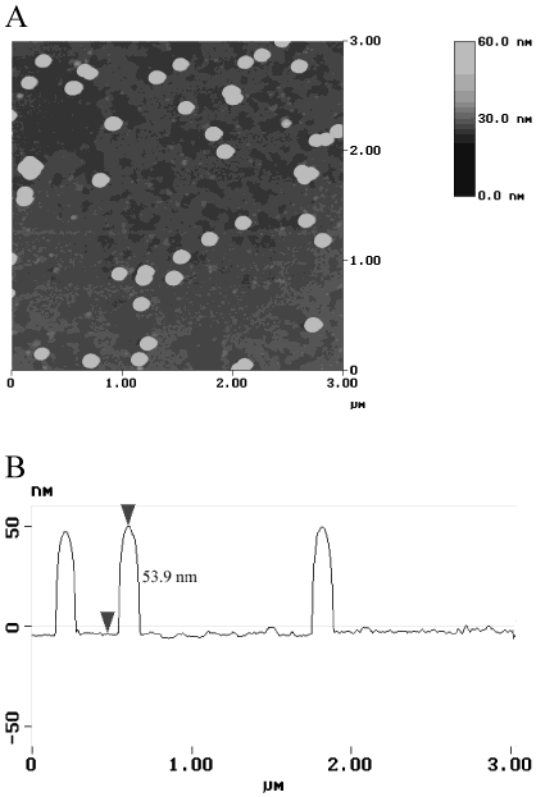

Figure 2. (a) AFM height image of sample 15. (b) Profile of three particles of sample 15.

Effects of Surfactant, Dendrimer, and Initiator Concentrations. Amounts of SDS of 5.5 and 11 wt % relative to styrene and molar ratios of 1.0−2.0 SDS to dendrimer primary amines produced the most stable latexes. The data in Tables 1 and 2 are grouped to compare one experimental parameter at a time. Group C shows that, at constant molar ratio of SDS to D64 of 2.0, increasing concentration of styrene increased the particle size of the product. It is normal for increasing amount of monomer relative to the surfactant in emulsion polymerization to increase the size of the polymer particles. Group D shows that increasing concentration of KPS increased the particle size. The effects of the relative amount of SDS and D64 are not clear. In group A a decrease in the SDS to D64 molar ratio (sample 13 vs samples 6 and 25) increased the particle size. In group B the same decrease in the SDS to dendrimer molar ratio (samples 15 and 29 vs samples 11 and 27) markedly decreased the particle size. We have no explanation for these results.

We tested the oil-soluble initiator AIBN and the cationic water-soluble initiator 2,2′-azobis(2-methylpropionamidine) dihydrochloride in place of KPS by the standard conditions of sample 6. AIBN produced a stable latex with a larger polydispersity than sample 6. The cationic initiator produced a latex that was less stable and still more polydisperse than sample 6.

Amount of Dendrimer in the Particles. Samples 6 and 11 were dialyzed against water for 30 days using a 50 000 molecular weight cutoff membrane. The purified latexes were dried and analyzed by the Kjeldahl method to contain 0.67 and 0.25% of nitrogen, compared with a calculated value of 0.44 wt % nitrogen based on the total weight of D64, SDS, and styrene in the starting mixtures. The analyses prove that the latexes contain dendrimer, because there is no other source of nitrogen

Table 3. Polymer Molecular Weights

sample[a]	M_w	M_n
6	790 000	120 000
11	250 000	63 000
26	450 000	130 000
28	400 000	160 000

[a] See Table 1 for compositions.

in the reaction mixtures. The differences between experimental and calculated nitrogen contents may be within experimental error and in any case are not quantitatively informative.

Polymer Molecular Weights. The molecular weights, measured by size exclusion chromatography relative to polystyrene standards, of samples 6 and 11, and those of analogous samples 26 and 28, which were made by the same method but without dendrimer, are reported in Table 3.

Discussion

Dendrimer Contents of Particles. If all dendrimer is incorporated into particles, the average number of dendrimer molecules per particle is large. For example, a latex made from the composition of sample 11 and having only one dendrimer per particle would have a diameter of 10.1 nm. (This value is calculated from $R = (3V/4\pi)^{1/3}$, where R is the radius of the particle and V is the volume of a sphere that has a density of 1.04 g cm^{-3}, and the sphere contains one dendrimer molecule and the same relative amounts of SDS and styrene as the initial reaction mixture.) The 27 nm diameter of sample 11 corresponds with an average of 18 dendrimer molecules per particle. Similarly, the 57 nm diameter of sample 15 corresponds with an average of 170 dendrimer molecules per particle.

At the start of this research we hypothesized that one dendrimer−surfactant complex might produce one polymer particle, and so we designed the relative amounts of SDS and D-64 to contain one or two dodecyl sulfate ions per end group of the dendrimer. At pH 7 the primary amine end groups of poly(propyleneimine) dendrimers are protonated, and most of the internal tertiary amines are in free base form.[22,23] As pH increases, the fraction of protonated end groups decreases. Both electrostatic and hydrophobic forces drive aggregation of the anionic surfactant with the dendrimer. The dodecyl sulfate anion probably intercalates its hydrophobic tail into the nonpolar core of the dendrimer and keeps its anionic head among the ammonium ions on the hydrophilic surface of the dendrimer. The precipitate formed by dialysis of a mixture of SDS and D64 contains 1.66 dodecyl sulfate ions per dendrimer end group and must be electrically neutral. The counterions of dodecyl sulfate could be ammonium ions of D64 and/or sodium ions. At the starting pH of 8.6−9.5 of the polymerization mixtures in the absence of SDS, only a fraction of the primary amine end groups and few or none of the branch point tertiary amines are protonated. Therefore, the excess of dodecyl sulfate has sodium counterions, some of which are dissociated to give the aggregate negative charge. The DLS measurements of the mixtures of D64 and SDS in the absence of styrene indicate aggregates with average diameters of 22−42 nm. In the presence of styrene the DLS measurements indicate much larger aggregates (>100 nm). Since the diameters of the product latexes do not correlate with the diameters of the aggregates of D64 and SDS and are much smaller than the diameters measured in the reaction mixtures containing styrene, the styrene and the SDS must equilibrate among the aggregates, particles, and monomer droplets during the polymerization.

Initiation and Chain Transfer Reactions. Reactions of amines, especially tertiary amines such as tetramethylethylenediamine (TMEDA), and persulfate generate radicals of the amines by redox reactions and initiate polymerizations in water at temperatures in the range of 25−50 °C.[26] The rate of initiation of acrylamide polymerization in water at 25 °C by persulfate and TMEDA is convenient for the preparation of polyacrylamide gels.[27,28] The radicals from primary and secondary amines have the unpaired spin mainly on nitrogen. From tertiary amines the unpaired spin is on the carbon bound to the nitrogen. Thus, redox reactions of persulfate with the poly(propyleneimine) dendrimer may initiate the polymerizations, and polystyrene chains may graft onto the dendrimer. In our polymerizations the KPS was added to the mixture of dendrimer, SDS, and styrene at 25 °C, stirred for 0.5 h, and heated rapidly to 80 °C. The cloudy appearance of a polymerized latex usually did not appear until the mixture had reacted for 10 min at 80 °C.

Comparison of the temperature dependences of polymerization by redox initiation and by thermal initiation using persulfate is important to this discussion. The rates of polymerizations of acrylamide in water initiated by persulfate and amines have Arrhenius activation energies in the range of 16−36 kJ mol^{-1}, whereas that for polymerization initiated by persulfate alone is 62 kJ mol^{-1}.[26] Reported activation energies for the decomposition of persulfate ion in water range from 83 to 140 kJ mol^{-1}.[29] Of course, the activation energy of polymerization is $E_a = E_p + E_i/2 - E_t/2$, where the subscripts p, i, and t refer to the activation energies of propagation, initiation, and termination, respectively. Extrapolations of these data suggest that at 80 °C the thermal decomposition of persulfate may produce radicals faster than the redox reaction of persulfate with TMEDA. We cannot predict clearly from the literature whether initiation under our conditions occurs by a redox reaction or by thermal decomposition of the persulfate. Both mechanisms might proceed at the same time. Analysis for polystyrene chains grafted to the dendrimer would be necessary to determine whether polystyrene chains were initiated from the dendrimer.

If several amine sites on one D64 molecule initiated long polystyrene chains, ultrahigh molecular weight polystyrene might be formed. On the other hand, if the amines caused chain transfer reactions, a broader distribution of molecular weights would result. The molecular weight distributions (Table 3) of the polystyrene samples 6 and 11 are broader than those of control polymerizations in which there was no D64. The breadth of the distributions is due to both higher and lower molecular weight components. This supports the hypothesis of chain transfer to dendrimer. All of the molecular weights reported in Table 3 are $<10^6$, which is typical of polystyrene from emulsion polymerization under pseudobulk conditions using SDS at less than the critical micelle concentration.[30]

Small Monodisperse Latexes. The most important result of this investigation is the formation of polystyrene latexes in the 24−64 nm diameter range that are more nearly monodisperse than those reported previ-

ously.[31] In 11 comparisons of the particle diameters of our samples with those listed in the catalogs of commercial suppliers[32−34] for polystyrene particles of almost the same size, ours had the smaller CV (coefficient of variation) in nine cases, the commercial sample had the smaller CV in one case, and the CV values were almost equal in one case. All of the data were from TEM measurements. We do not know whether the commercial samples contained clusters like ours or how the clusters were counted for calculation of the average diameter and the CV. If we counted the diameters of the clusters instead of the diameters of particles within the clusters, our average diameters and CV values would be larger.

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