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SHORT COMMUNICATION

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Nano-sized dendrimer PAMAM/polystyrene composite polymer emulsion

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Abstract Single state emulsion polymerization of styrene with aggregates of generation 4.5 polyamideamine dendrimer and sodium dodecyl sulfate as templates produces lattices with diameters in the range 33–66 nm and polydispersity indices of less than 10%.

Keywords Polystyrene · Latex · Emulsion polymerization · Dendrimer · Starburst dendrimer polyamideamine

Introduction

Polymer emulsions are extensively used in the coatings, rubber, lubricants, food, and pharmaceutical industries. Many of their properties depend on the particle size and particle size distribution, as well as on their chemistry. In emulsion polymer science, the control of the morphology, size and distribution of emulsion particles has been an intensive area of research for over 40 years [1]. Various emulsion polymerization methods are capable of yielding spherical colloids of high uniformity; these involve seeding techniques, emulsifier-free methods, mixtures of ionic and nonionic surfactants, ionic copolymers, and steric stabilizers. However, particle sizes are more than 100 nm from all these methods at present [2]. On the other hand, microemulsion polymerization can yield nano-sized stable emulsions that are not easily obtained from other systems [3], but the polymer emulsion particles are polydisperse. Moreover, the amount of surfactant, which is fundamental in the stabilization of the starting emulsion as well as of the final latex [1, 4, 5], is much larger than for conventional emulsion polymerization. During film formation when the polymer coalesces, the surfactant is able to migrate toward the surface of the film; this causes phase separation in the resulting film. In the process of polymer recovery via coagulation, the surfactants are wastewater pollutants that increase the chemical oxygen demand and the biological oxygen demand. The preparation of monodisperse polymer emulsion particles is most difficult in the size range from about 10 to 100 nm, but a coefficient of variation (CV = standard deviation/mean diameter) of a few percent is needed for many applications. Therefore, there is a need for innovative synthesis routes for producing polystyrene spheres of lower polydispersity in the size range 10–100 nm [6].

The structure and properties of several poly(amidoamine) dendrimers have been studied extensively. A dendrimer can be regarded as a large molecule similar to "normal" polymer but with precise molecular weight and structure. The higher generation dendrimers have approximately spherical shape [7]. The so-called dual-

natured properties of dendrimers involve the internal core, which is often large enough to host small molecules, and the external periphery, which contains multiple functional groups that can provide sites for binding. The host-guest systems made from dendrimers have enormous possibilities in the areas of molecular encapsulation, membrane transport and drug delivery [8, 9, 10]. Tomalia et al. [11] found that sodium dodecyl sulfate (SDS) binds to poly(amidoamine) dendrimers, and that binding proceeds until the dendrimers become fully saturated with bound SDS molecules. The interactions of these dendrimers with anionic surfactants generate supramolecular assemblies which greatly enhance their ability to accommodate small molecules.

Polymer synthesis in confined environments can lead to unusual structures and properties. We reported recently the preparation of polystyrene lattices of < 100 nm in diameter with *CV*s of less than 10% with complexes of the poly(propyleneimine) dendrimer DAB-*dendr*-$(NH_2)_{64}$ or dodecanamide-modified DAB-*dendr*-$(NH_2)_{64}$ and the anionic surfactant SDS in water [12, 13]. Now we report the use of a polyamideamine (PAMAM) dendrimer to prepare small, monodispersed polystyrene lattices.

Materials and methods

General All water was deionized and boiled under N_2 before use. Styrene was distilled under vacuum, and the distilled styrene was refrigerated. Starburst PAMAM dendrimer (generation 4.5, having 128 carboxylate end groups) was used as received from Aldrich (methanol solution, 5 wt%). All other chemicals including SDS, potassium persulfate (KPS), and sodium bicarbonate were used as received.

Emulsion polymerization Typical compositions of emulsions that have been polymerized are given in Table 1. The general procedure is illustrated by example 21 in Table 1.

To a three-neck 100 mL round-bottom flask equipped with a condenser, a magnetic stirrer and a nitrogen inlet, 0.10 mL of PAMAM methanol solution and 25.0 mL of water were added, and the stirrer was started. Then 40 mg of SDS was dissolved in 2.0 mL water, and 5 min later 0.50 mL of styrene was added. The air in the flask was replaced by a stream of nitrogen, and the mixture was kept under nitrogen until polymerization was finished. The mixture was stirred magnetically for 2.0 h. KPS stock solution (1.50 g of KPS dissolved in 100.0 mL of water) was then added (1 mL). The sample was stirred for 15 min, and the flask then placed in 80 °C oil bath. Additional SDS (40 mg dissolved in 2.0 mL water) was added after the sample had been held at 80 °C for 0.5 h, and the polymerization was continued for 0.5 h to produce a dispersion.

Transmission electron microscope To prepare unstained specimen for the transmission electron microscope (TEM), the emulsion was diluted 1:15 with deionized 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 kV with a JEOL JEM 100 C×II instrument (Tokyo, Japan).

Table 1 Compositions of emulsion polymerization mixtures using dendrimer PAMAM as template. All samples contained 30.0 mL of water and 15 mg of KPS

Sample	PAMAM (5%, mL)	SDS[a] (mg)	SDS[b] (mg)	Styrene (mL)
9	0.20	100	200	0.50
10	0.10	100	200	0.50
21	0.10	40	80	0.50
22	0.30	40	80	0.50
23	0	40	80	0.50
24	0.30	40	80	1.00
25	0.30	60	80	0.50
35[c]	0.30	60	80	0.50
26	0.30	60	80	1.00
27	0.50	60	80	1.00
37[c]	0.50	60	80	1.00
28	0.30	40	80	0.80
29	0	60	80	1.00
30	0.30	60	80	0.80

[a]Amount of SDS used at the start of emulsion polymerization
[b]The total amount of SDS used in emulsion polymerization
[c]Duplicate of the preceding experiment

Diameters of at least 100 particles were measured directly from the micrograph negatives using an optical microscope with a calibrated stage. Sizes were calculated from the nominal instrument magnification. The number (D_n), weight (D_w), z-average (D_z) diameters, and the coefficient of variation (CV) were calculated with Eq. 1, Eq. 2, Eq. 3,and Eq. 4, where N_i is the number of particles having diameter D_i.

$$D_n = \sum N_i D_i / \sum N_i \tag{1}$$

$$D_w = \sum N_i D_i^4 / \sum N_i D_i^3 \tag{2}$$

$$D_z = \sum N_i D_i^5 / \sum N_i D_i^4 \tag{3}$$

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

Dynamic light scattering Diffusion coefficients D of particles in diluted dispersions were measured at 25.0 °C with a coherent INNOVA-90 argon laser (514.5 nm), a BI-200SM goniometer and a BI-900AT multi-τ-digital correlator (Brookhaven Instruments) at a 90° scattering angle. The hydrodynamic radius R_h was calculated from Eq. 5:

$$R_h = k_B T / (6\pi\eta D) \tag{5}$$

where k_B, η, and T are the Boltzmann constant, the solvent viscosity, and the absolute temperature, respectively. Samples were not filtered before measurement to prevent bias of the results by exclusion of large particles.

Results and discussion

Emulsion polymerization

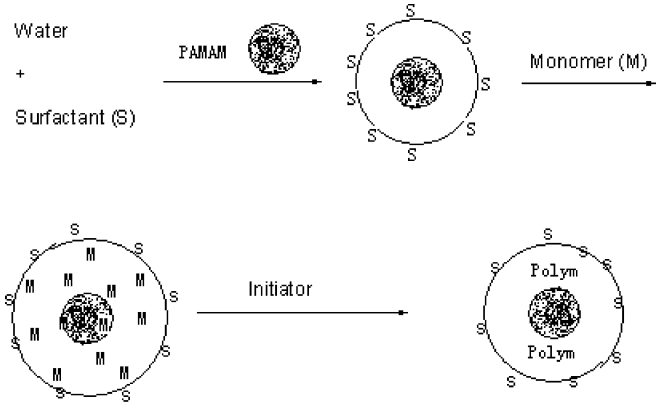
The difficulty in preparation of < 100 nm polymer latexes of low polydispersity lies in the mechanism of formation of colloidally stable primary particles during emulsion polymerization [1, 14, 15]. In conventional

emulsion polymerization, by the homogeneous and heterogeneous nucleation mechanisms, the primary particles are never perfectly monodisperse. However, dendrimers are perfectly monodisperse, and seed emulsion polymerization methods are capable of yielding spherical colloids of high uniformity. The basic concept for synthesis of monodisperse emulsion particles from dendrimer cores is shown in Scheme 1. Using the dendrimer PAMAM as a template, the molecules of sodium alkyl sulfate surfactant are attached as ligands on the dendrimer periphery [16]. In the present seed emulsion polymerization system, dendrimers and SDS were mixed with styrene monomer, and the styrene was polymerized. The dendrimer-polystyrene composite particles have diameters of much less than 100 nm and contain tens of dendrimer molecules, not one dendrimer molecule as shown in the simplified Scheme 1.

We followed the methods of seed emulsion polymerization to prepare the PAMAM/polystyrene composite latexes. Typical compositions of emulsions that have been polymerized are given in Table 1. Nearly monodisperse and stable dendrimer/polystyrene composite nanoparticle emulsions have been obtained by emulsion polymerization using dendrimer as template.

During the emulsion polymerization, if the initial amount of SDS was ≥0.2 times (w/v) the amount of styrene and ≥9 times the molar amount of primary surface carboxylate groups of the dendrimer (Table 1; samples 9, 10), a stable emulsion was easily obtained, but the particles were polydisperse. The free micelles of SDS might be formed due to many more SDS molecules. Stable emulsions of nearly monodisperse particles smaller than 100 nm were obtained when the initial amount of SDS was 0.04–0.12 times the amount of styrene and 2.2–3.6 times the molar amount of primary surface carboxylate groups of the dendrimer (Table 1; samples 24, 25, 27, 22).

Figure 1 shows TEM images of different nanoparticles with or without PAMAM according to recipes given in Table 1. The images show that the particles (sample 22, 25, 27) are monodisperse if dendrimer PAMAM is used in emulsion polymerization (Fig. 1a, b, c); however, the particles (sample 23) are polydisperse if the emulsion polymerization is carried out without dendrimer PAMAM (Fig. 1d). The results indicate that the dendrimer PAMAM certainly does act as a template in emulsion polymerization.



Scheme 1 Synthesis of a dendrimer core-polystyrene shell nanosized particle emulsion. *PAMAM* Polyamideamine

Morphology and size of nanoparticles

Figure 1a, b, c shows TEM images of different dendrimer/polystyrene composite nanoparticles obtained by emulsion polymerization using PAMAM as template under different polymerization conditions (Table 1). The nanoparticles have a spherical morphology with number-average particle diameters smaller than 100 nm and low polydispersity. But there are some regions in which two or three particles are clumped, although we diluted the emulsion to very low concentration. We measured the size of particles excepting the clumps. The mean diameters of particles along with the CV are listed in Table 2. It shows that the size of particles is smaller than 100 nm and that the particles have low polydispersity when the PAMAM is used as a template.

The results of dynamic light scattering (DLS) show the sizes of emulsion particles are less than 100 nm (Table 2). In most cases the particles sizes measured by DLS do not agree well with the results of TEM: sizes from DLS are larger than the sizes from TEM. It may be that tails or loops of the polymer slow down the diffusion of particles significantly, while they collapse on the particle when dried for TEM. Moreover, aggregates or clusters are counted in the DLS measurement [17]. The light scattering data are inherent z-averages and $D_z = \sum N_i D_i^7 / \sum N_i D_i^6$.

We duplicated preparation of samples 25 and 27 and obtained reproducible diameters of the particles, which are shown in Table 2 (samples 35 and 37).

The average number of dendrimer molecules per latex particle in representative samples was calculated from the weight-average volume of a particle, $V = (\pi D_w^3/6)$, the density of polystyrene (1.05 g cm^{-3}), the formula weight of the dendrimer (26,258), Avogadro's number, and the weight of dendrimer and styrene (SDS was not counted) in the starting mixture. The results in Table 2 indicate as few as 13 dendrimer molecules in 33-nm particles to as many as 26 dendrimer molecules in 46-nm particles.

Effects of concentrations of mixture components on latex size and polydispersity

Particles obtained by emulsion polymerization both at a high content of styrene (samples 24 and 26) or a low

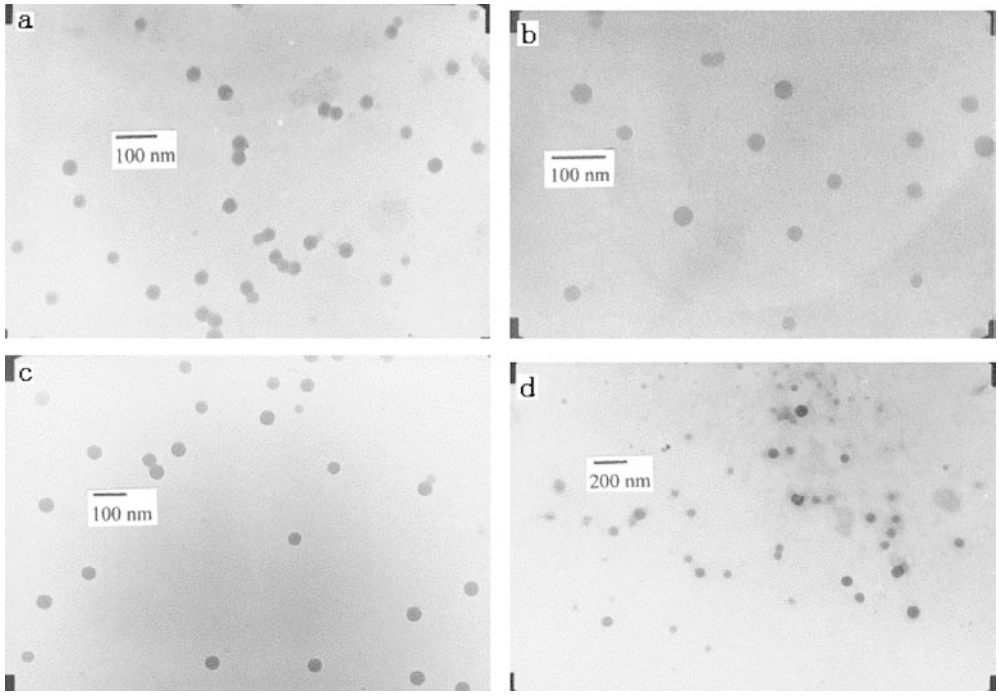


Fig. 1a–d Transmission electron microscope images of dendrimer polyamideamine (PAMAM)/polystyrene composite emulsion particles. **a** Sample 22. **b** Sample 25. **c** Sample 27. **d** Sample 23

Table 2 The properties of dendrimer/polystyrene composite emulsions

Sample[a]	TEM				DLS	N_d[c]	pH[b]
	D_n (nm)	D_w (nm)	D_z (nm)	CV (%)	D_h (nm)		
22	39.5	40.6	40.9	9.4	47.0	21	7.45
25	33.3	33.8	34.0	7.7	46.6	12	7.08
35[d]	34.3	34.7	35.0	7.4	48.2		7.11
24	51.5	52.8	53.2	9.7	57.4	24	7.14
26	48.7	49.8	50.1	9.2	55.0	20	7.12
29	54.2	59.7	63.4	19.6	73.6		7.05
26	48.7	49.8	50.1	9.2	55.0	20	7.12
27	44.5	45.5	45.8	8.7	50.8	25	7.02
37[d]	46.0	46.8	47.2	9.0	54.4		7.04
23	58.3	65.9	68.0	21.7	81.4		7.38
21	53.8	63.1	65.0	14.5	68.6		7.68
22	39.5	40.6	40.9	9.4	47.0	21	7.45
25	33.3	33.8	34.0	7.7	46.6	12	7.08
30	41.4	42.0	42.2	8.6	49.6	14	7.23
26	48.7	49.8	50.1	9.2	55.0	20	7.12
22	39.5	40.6	40.9	9.4	47.0	21	7.45
28	45.2	46.1	46.3	8.4	53.8	19	6.96
24	51.5	52.8	53.2	9.7	57.4	24	7.14

[a]See Table 1
[b]pH was measured at room temperature after polymerization
[c]Number of dendrimer molecules per particle
[d]Duplicate preparation of the preceding sample

content of styrene (samples 22 and 25), indicate that the size of particles decreases with increasing concentration of emulsifier.

The particles had systematically smaller diameters with increasing dendrimer content by emulsion polymerization at a high content of styrene and SDS (samples 29, 26, and 27) or at a low content of styrene and SDS (samples 23, 21, and 22). At first the surfactant molecules surround the dendrimer molecules or clusters completely, and then the swollen micelles are formed. The number of swollen micelles increases with increasing the content of dendrimer PAMAM, so the content of styrene in each swollen micelle decreases. When the emulsion polymerization is carried out, the size of the particles is related to the content of the styrene in swollen micelle.

Though the particles are obtained by emulsion polymerization at a high content of SDS (samples 25, 30, and 26) or at a low content of SDS (samples 22, 28, and 24), the results show that the size of particles increases with increasing amount of styrene. All of the particles are low polydispersity, and the stability of emulsions is good. These phenomena are similar to conventional emulsion polymerization.

Polystyrene lattices of low polydispersity were obtained only in the presence of the dendrimer and a concentration of SDS no greater than 7 mM. These results suggest that the dendrimer and SDS form a seed emulsion having a narrow size distribution. Clear solutions were obtained from the mixtures of SDS and starburst dendrimer PAMAM in water. Addition of monomer to the clear solutions gave mixtures that had the same appearance as a mixture of styrene, SDS, and water at the start of seed emulsion polymerizations, where the styrene is present mainly in monomer droplets. Therefore, in interval I of the emulsion polymerization [1, 15], radicals from persulfate initiate styrene polymerization in the aqueous phase, and polymer

radicals are captured by styrene-swollen dendrimer-surfactant aggregates whose sizes may not differ greatly from the sizes of styrene-swollen SDS micelles above the critical micelle concentration. These first-formed polymer particles could continue growth by swelling with more styrene and capture of more polymer radicals. They could also grow by aggregation with other particles and with dendrimer-surfactant aggregates. During polymerization the small dodecyl sulfate anions are expected to equilibrate between the surfaces of growing particles, monomer droplets, and aqueous solution, but the larger dendrimers and the polystyrene must either remain in their original particles or combine with other particles by collisions. The small final particle sizes and low polydispersities indicate that growth by collision is not extensive, and that a large number of very small primary polymer particles remains at the end of interval I. Growth of particles during interval II then proceeds by transport of monomer from droplets to polymer particles, capture of polymer radicals, and polymerization, as in conventional emulsion polymerizations. Growth during interval II narrows the distribution of particle diameters.

The sizes and polydispersities of the polystyrene lattices produced from PAMAM and SDS are very similar to those reported before from the poly(propyleneimine) dendrimer DAB-*dendr*-$(NH_2)_{64}$ or dodecanamide-modified DAB-*dendr*-$(NH_2)_{64}$ and SDS in water [12, 13]. All of the dendrimers produce lattices in the range of 30–60 nm in diameter and $CV < 10\%$. TEM images of lattices exhibit single particles and some clusters of two or more particles. The particles are larger from DLS measurements than from TEM measurements because of the small clusters. All of these results show that aggregates of dendrimers and SDS act as templates in emulsion polymerization of styrene.

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