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High-content polystyrene latex by microemulsion polymerization

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Summary

The semicontinuous addition of styrene to a low solid-content (6 wt%) polystyrene latex obtained by polymerization of a three-component microemulsion, allows the production of a high solid-content latex (ca. 40 wt%) containing small particles (< 40 nm) of high molecular weight (> 10^6 g/mol). The method can be extended to latex made from microemulsions containing other water-insoluble monomers.

Introduction

Emulsion and microemulsion polymerization are the only processes that allow the synthesis of colloidal particles of high molecular weight dispersed in an aqueous (or organic) medium with fast reaction rates.(1-6) However, microemulsion polymerization can yield particles smaller than 50 nm in routinely fashion, although it requires a much larger amount of surfactant. Typically, surfactant concentrations larger than 5 wt% are needed to produce 2 to 5 wt% polymer by microemulsion polymerization.(7-16) Hence, to make microemulsion polymerization an attractive and profitable process, it is important to minimize the amount of surfactant required or to reduce the ratio of surfactant to polymer produced. Recently, Gan et al.(17) were able to produce latex with 15% solids by polymerization of styrene in Winsor I-like microemulsions stabilized with only 1 wt% DTAB (dodecyltrimethylammonium bromide).

Here we present a method that involves the semicontinuous addition of styrene to a polystyrene latex produced by batch microemulsion polymerization to yield a high solid-content stable latex with similar characteristics to that of the parent microemulsion-made latex, i.e., nanosize particles and high molecular weight polymer.

Experimental

Reagent-grade styrene (Scientific Polymer Products) was passed through a DTR-7 column (SPP) to remove the inhibitor. DTAB (99% from Tokyo Kasei) was further purified by recrystallization from a 50:50 acetone-ethanol mixture. 2,2'-Azobis(2-amidinopropane) hydrochloride or V-50 (Wako Chem.) was recrystallized from methanol. HPLC-grade tetrahydrofuran (Merck) was used as the mobile phase for molecular weight determinations. Water was distilled and deionized.

Polymerization was carried out at 60°C in a 100 mL glass reactor. The microemulsion (6 wt% styrene, 14.1 wt% DTAB and 79.9 wt% water) was loaded in the reactor, heated to 60°C and sparged with argon for 30 min, before adding a concentrated aqueous solution of V-50 to give a concentration of 1 wt% with respect to monomer. During the whole microemulsion polymerization reaction and the semicontinuous addition of monomer, the system was continu-

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ously stirred and sparged with argon. Polymer was isolated by filtration after precipitation with methanol. Conversion was estimated by gravimetry.

Particle size was determined at 25°C with a Malvern 4700 QLS quasielastic light scattering apparatus equipped with a He-Ne ion laser (λ = 644 nm). Before QLS measurements, latexes were diluted up to 1000 times to minimize particle-particle interactions and filtered through 0.2 μm Millipore filters to remove dust particles. Particle size distributions were measured directly with a JEOL 100 CX transmission electron microscope (TEM). At least 400 particles were counted. To enhance the contrast, latex particles were stained with phosphotungstic acid (PTA). Average molecular weights and molecular weight distributions were measured with a Perkin Elmer LC30 gel permeation chromatograph equipped with a LC30 refractive index (Perkin Elmer) and a Dawn multiangle light scattering (Wyatt Technology) detectors. Columns with molecular weight range from 10^5 to 10^7 were employed.

Results and Discussion

Polymerization of styrene in three-component DTAB microemulsions initiated with V-50 at 60°C is fast, i.e., more than 90% conversion is achieved in less than one hour (Fig. 1). The initially transparent microemulsion becomes increasingly turbid as the reaction proceeds due to particle growth and the refractive index difference between the polymer particles and the dispersing medium. At the end of the reaction, a bluish and slightly opaque stable latex is obtained.

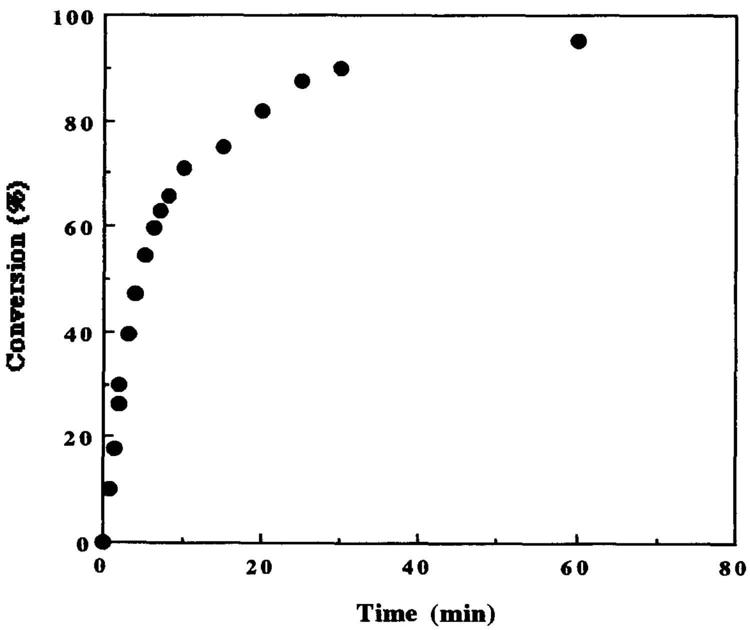

Figure 1. Conversion as a function of time for the polymerization initiated at 60°C with V-50 of a microemulsion containing 6 wt% styrene, 14.1 wt% DTAB and 79.9 wt% water.

The number average particle size (D_n) is about 20 nm and the weight-average molecular weight (M_w) is about 2.1 x 10^6. These values are typical of microemulsion polymerization of styrene.[12]

After one hour, when the reaction has slowed down considerably, the semicontinuous addition of monomer begins. The procedure consists in adding 5 mL of styrene to a 100 mL of latex produced by batch microemulsion polymerization; monomer addition is repeated every 20 minutes for over 4 hours. The solid content in the latex increases from 6 wt% to near 40 wt% (Fig. 2). Conversions of monomer to polymer are close to 90% after each addition (Fig. 2), which indicate that the intervals for the additions are well chosen. The addition procedure is stopped *only* because of the high viscosity of the concentrated latex which hinders the agitation of the system. The final latex is stable, opaque and highly viscous. In fact, all the latexes have remained stable against coagulation for months. Incidentally, repeated runs demonstrate that this procedure is very reproducible.[18]

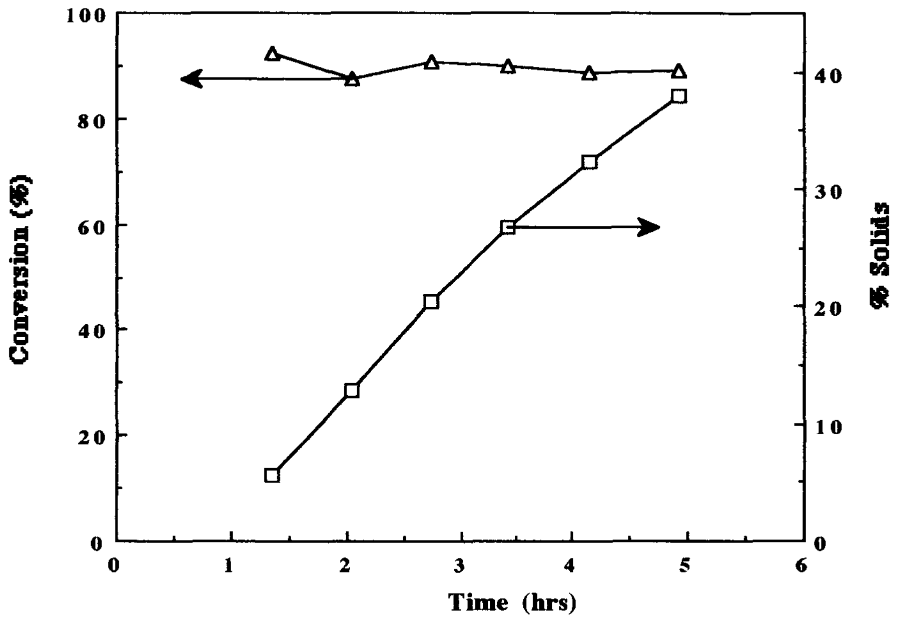

Figure 2. Conversion and solid content obtained during the semicontinuous addition of styrene to a latex produced by batch microemulsion polymerization.

Figure 3 shows the z-average particle size (D_z), determined by QLS, and M_w of the polymer obtained during the semicontinuous addition procedure. Although particle size increases during the addition process, final particle size is still smaller than 50 nm, i.e., within the typical size of microemulsion polymerization.[6] Molecular weight, on the other hand, remains fairly constant throughout the process. This is because molecular weight in microemulsion polymerization is controlled mainly by chain transfer reactions to monomer.[6, 13, 16, 19]

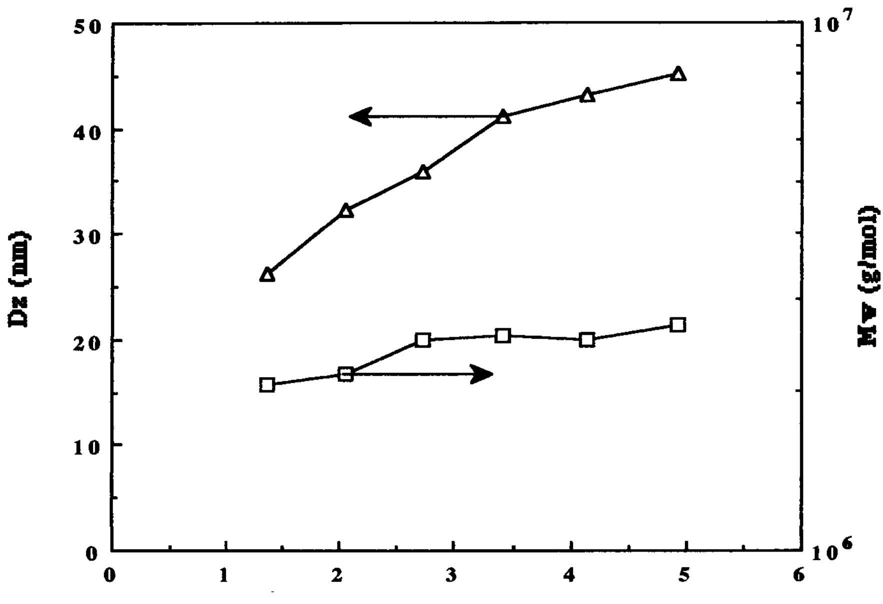

Figure 3. Weight-average molecular weight and z-average particle size, measured with QLS, obtained during the semicontinuous addition of styrene to a latex produced by batch microemulsion polymerization.

Table 1 reports particle size measured by TEM and by QLS, weight-average and number- average molecular weights and the average number of polymer chains per particle. The latter were calculated with the number-average molecular weight and the number-average particle size with the assumption that particle size distribution is monodispersed. The average number of polymer chains per particle is unusually low, which is typical of microemulsion polymerization,(6) and remains low during the whole addition procedure.

% solids	D_n [a] (nm)	D_w [a] (nm)	D_z [a] (nm)	D_z [b] (nm)	$M_n \times 10^6$ (g/mol)	$M_w \times 10^6$ (g/mol)	N_c
5.54	20.2	24.9	27.3	26.2	1.1	2.1	5.8
12.78	—	—	—	32.3	1.4	2.2	8.2
20.36	22.8	31.0	35.2	35.9	1.7	2.5	9.0
26.71	23.5	32.9	37.6	41.1	1.7	2.6	14.0
32.34	—	—	—	43.2	1.7	2.5	15.9
38.04	27.4	39.3	43.8	45.1	1.8	2.7	16.8

Table 1. Particle size, average molecular weights and average number of chains per particle in latexes obtained at different stages of the semicontinuous addition of monomer to a microemulsion-made polystyrene latex: a)TEM; b)QLS.

Conclusions

Microemulsion polymerization is a process that allows the synthesis of tiny particles containing high molecular weight polymer but it requires much larger amounts of surfactant than emulsion polymerization.[6] Since particles grow during the reaction at the expense of the smaller microemulsion droplets, there is always excess surfactant at the end of a microemulsion polymerization. Recently, Full et al.[19] found by small-angle neutron scattering (SANS) that the final latex from the polymerization of styrene in DTAB microemulsions contains polymer particles of about 20 nm and a large population of small micelles formed from the excess surfactant. Hence the excess surfactant can be used to promote further nucleation and to stabilize new particles if more monomer is added to this latex.

Here we have shown that stable latex of high solid content (ca. 40%) with particles having similar characteristics to those of the parent latex, can be produced by the semicontinuous addition of styrene to a latex produced by microemulsion polymerization -- without adding more initiator. The fact that the particles grow and that the particle size distribution skews slightly toward larger sizes,[18] indicates that new particles form and grow when there is enough surfactant; however, some of the added monomer can swell the existing particles and react there, causing an increase in the average particle size, particularly during the final stages of the semicontinuous addition. This technique has been extended successfully to latexes made with other monomers.[18]

Acknowledgments

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