

Supramicron Poly(butyl Acrylate)/Polystyrene Core-Shell Latexes

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SYNOPSIS

Latex particles of up to 2 μm can be made by standard emulsion polymerization methods, but attempts at larger sizes usually results in a crop of smaller particles or coagulation of the latex. In this work, it is shown that use of an oil-soluble initiator (2,2' azodiisobutyronitrile [AIBN]) provides a means by which large (6 μm diameter) polybutyl acrylate latex particles can be made by sequential core-shell polymerizations. It is suggested that the limited water solubility of AIBN decreases the formation of secondary particles and that the lower ionic strength of the water phase enhances stability of the latex compared to a conventional persulfate initiator. To further minimize formation of secondary particles, long reaction times and progressively larger proportions of seed latex are used in successive reactions. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Emulsion polymerization is a very useful technique to make polymer latexes of up to 2 μm in diameter. Unfortunately, extending the process to larger sizes results in either a coagulated latex or formation of secondary particles.¹ Although either suspension polymerization or nonaqueous dispersion polymerization may be used to make larger particles, emulsion polymerization has several advantages over these methods, including the ability to make monodisperse or controlled morphology (core-shell) particles.

Several approaches have been employed to increase the size of emulsion-polymerized particles. Ugelstad and co-workers used the concept of swelling to produce particles of large size.²⁻⁴ More recently, Okubo and Tsujihiro⁵ described a dispersion polymerization technique to make particles up to 100 μm . In a more novel approach, Vanderhoff et al.¹ exploited low gravity in a space-borne emulsion reaction to produce 5 μm monodisperse polystyrene latexes. All these techniques use involved procedures

and produce low-solids-content latexes. A standard emulsion method to make large particles at higher solids levels would be preferable.

Current work in our laboratory has focused on producing a poly(butyl acrylate) core-polystyrene shell composite particle that would be suitable for incorporation into polystyrene as a model toughening agent. Optimal toughening of polystyrene requires rubber particles of 2 μm or larger.⁶ Moreover, there are problems in obtaining true core-shell morphology in the poly(butyl acrylate) core-polystyrene shell system.^{7,8} However, we have found that when 2,2'-azodiisobutyronitrile (AIBN) initiator was used, along with other specific reaction conditions, the desired morphology could be obtained and latex particles of up to 6 μm diameter could be made.

Relatively little work has been published on the use of AIBN as an emulsion polymerization initiator. Initiation was thought to proceed in the oil (monomer) phase, but Al-Shahib and Dunn⁹ assumed that since the decomposition of AIBN produces two radicals, polymerization depends on the loss of one radical to the water phase. The efficiency of the radical was quite limited (4%) compared to the normal 50% in bulk polymerization because of cage effects. Work by Barton et al.^{10,11} on AIBN polymerization of butyl methacrylate has shown that the classic Smith-Ewart model is followed with some modifications.

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In this paper, the reaction conditions necessary for making large monodisperse poly(butyl acrylate)/polystyrene core-shell particles are detailed and possible reasons for the success of the technique are given.

EXPERIMENTAL

Materials

Butyl acrylate (Aldrich, reagent grade), allyl methacrylate (Aldrich, reagent grade), divinylbenzene (Aldrich, technical grade), ammonium persulfate (J. T. Baker), AIBN (Polysciences), and sodium dodecyl benzene sulfonate (Alcolac Siponate DS-10) were used as received. Styrene (Aldrich, reagent grade) was washed with successive portions of caustic solution and deionized water to remove polymerization inhibitors before use. Deionized water was used for all reactions.

Equipment

Latex particle sizes were measured by a modified Joyce-Loebl Mark III disk centrifuge using water as spin fluid with a methanol buffer layer.¹² The centrifuge was interfaced to a microcomputer and raw data were analyzed using a Brookhaven Instruments DCP disk centrifuge particle-size program. Residual latex monomer was determined using a Hewlett Packard 5880 gas chromatograph with a Carbowax packed column. Scanning electron microscopy was carried out using a Joel SEM at 15 kV. For transmission electron micrography, particles were cryosectioned using a Reichert-Jung microtome (Ultra-cut E) at -50°C . The $0.2\ \mu\text{m}$ sections were RuO_4

stained for 60 min and examined in a Phillips EM-400 at 120 kV.

Procedure

Polymerizations were carried out in a 4 L resin kettle with a glass cover having ports for stirring, N_2 purging, condenser, and monomer addition. The stirring was effected by a dual four-bladed marine-type propeller with downward flow at 150 rpm. All reactions were carried out in a constant temperature water bath at 80°C .

The makeup of a typical butyl acrylate reaction series is shown in Table I. For the seed reaction (#1), water was first charged to the reactor and stirred continuously while the reactor headspace was purged with N_2 . Ammonium persulfate was then added and the preemulsion fed in over an 8 h period. (Ammonium persulfate gives a more monodisperse latex compared to AIBN in the first reaction.) The upper stirrer blade was positioned near the top of the reactor solution to provide optimal mixing in the monomer addition region. After all the preemulsion was added, the latex was reacted for 1 h followed by addition of 5 mL of tertiary butyl peroxide (70% solution) and further postreaction for another hour. Finally, the latex was cooled and filtered through a fine mesh screen to remove residual coagulum.

For subsequent butyl acrylate shell addition reactions (#2-#5), water and seed latex from the previous reaction were charged to the reactor and the reactor was purged with N_2 . Note that the seed was diluted to insure that the surfactant concentration was well below the CMC so as to avoid second-generation particles. The preemulsion was pumped into the reactor over a 12-18 h period. These were

Table I Butyl Acrylate Core Latex Recipes

Component	Reaction Makeup (g)					
	#1	#2	#3	#4	#5	
Reactor charge	Water	1500	300	100	200	200
	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	5.4	—	—	—	—
	Seed latex	—	150	300	700	600
Preemulsion charge	Butyl acrylate	1080	1250	975	1000	1100
	Allyl methacrylate	10.8	12.5	12.0	10.0	11.0
	Water	540	1500	1300	1300	1200
	AIBN	—	14.0	13.0	12.0	13.0
	SDBS	10.8	12.5	12.0	12.0	11.0

SDBS = sodium dodecyl benzene sulfonate.

“starved-feed” reactions, and the residual monomer was less than 0.1% by weight at any time. The stirrer speed was kept at 150 rpm and the stirrer shaft raised as the reaction proceeded to insure good mixing in the monomer addition region. The latexes were approximately 42 wt % in solids content except for reaction #1, which was 32%.

When ammonium persulfate was used as an initiator in place of AIBN, the latex coagulated completely for particle sizes over 2 μm . Addition of larger amounts of SDBS surfactant for stabilization resulted in massive secondary particle generation.

Finally, a 0.1 μm -thick polystyrene shell was added to the polybutyl acrylate core:

Reactor charge: 2000 g reaction #5 seed
 Preemulsion: 100 g styrene
 150 g water
 0.5 g divinylbenzene
 0.5 g SDSBS
 2.0 g AIBN

After N_2 purging, the styrene preemulsion was pumped into the reactor over a 4–5 h period. In the final stages of the polymerization, the reaction latex coagulated, as insufficient surfactant was added to keep the reaction stable. This was intentional, since it was desired to isolate the latex with this procedure and to keep residual soap to a minimum to facilitate latex cleanup. However, even with adequate surfactant, the polystyrene-coated latex had low stability and tended to coagulate on prolonged stirring.

Note that five stages are used in the making of the 6 μm butyl acrylate core, not because of equilibrium swelling effects as detailed by Morton et al.¹³ but rather because the total number of latex particles must be decreased. For example, if all the latex in reaction #1 were converted into 6 μm particles, the total quantity of latex solids would be

$$1.08 \text{ kG} \times \frac{4/3\pi r_2^3}{4/3\pi r_1^3} = 1.08 \text{ kG} \times \frac{(3.00)^3}{(0.22)^3} = 2,738 \text{ kG}$$

(where r_2 = the radius of the final particle and r_1 = the radius of the seed particle) or about 3 tonnes. However, to maintain the necessary seed latex surface area (see below) for each step, the amount of seed latex must be lowered in steps in the particle buildup sequence.

RESULTS

The measured particle sizes for the above reactions are shown in Table II. It can be seen that the latexes are quite monodisperse with $D_w/D_n < 1.01$. The theoretical size of the latex particles can be calculated based on the size and amount of the seed latex and the amount of added monomer; these calculated values are also shown in Table II and are in good agreement with the observed particle sizes.

The sizes of the secondary particles were also determined. These smaller particles are fairly polydisperse ($D_w/D_n > 1.1$) and were not detectable until the third reaction stage. The size of the secondary particles increased with each additional shell, but the total mass of the second-generation particles was not significant as determined from SEM photographs.

A scanning electron micrograph is shown in Figure 1 for the PS/PBA composite latex particles. The particles show a regular spherical morphology and are slightly fused from the final coagulation step. Some off-sized particles are also seen. A transmission electron micrograph of a composite particle made using this process is seen in Figure 2. The polystyrene layer on the outside of the particle is highlighted by ruthenium tetroxide staining¹⁴ and an interior structure in the particle can also be seen.

Table II Particle Sizes of Latexes from Disk Centrifuge Analysis^a

Reaction	D_n (μm)	D_w/D_n	Calculated D_n (μm)	Secondary Particles (μm)
#1	0.44	1.007	—	—
#2	1.22	1.004	1.32	None
#3	2.38	1.008	2.47	< 0.1
#4	3.72	1.004	3.87	0.30
#5	(6.5) ^b	—	6.60	0.48

^a It was not possible to characterize the final butyl acrylate/polystyrene shell particle since it had coagulated.

^b The disk centrifuge analysis becomes unreliable for very large particles sizes. This value is an estimate.

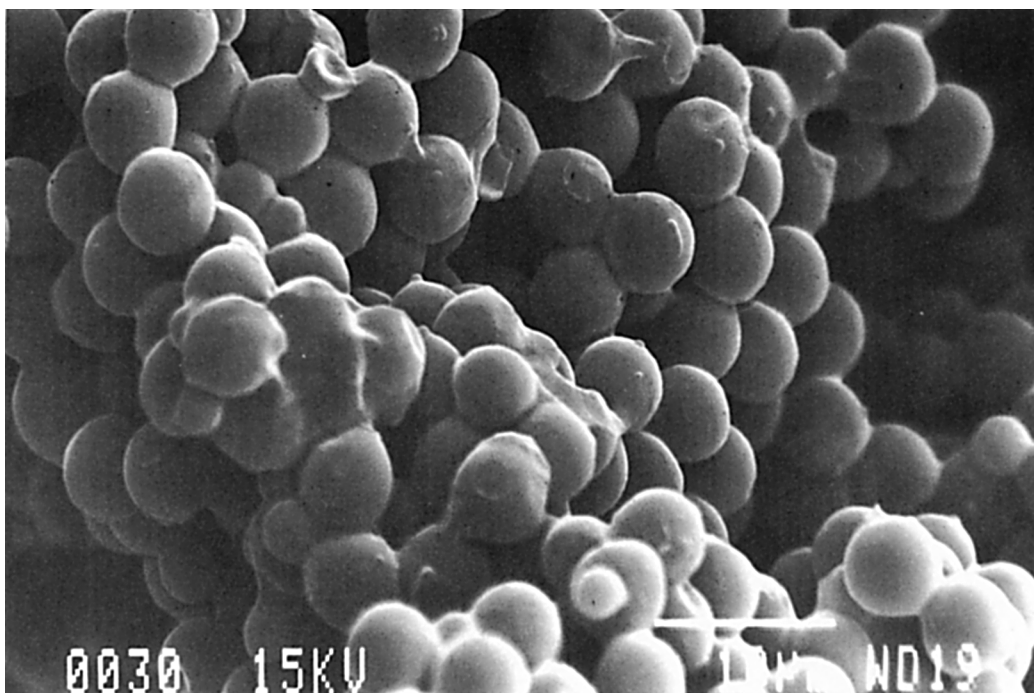


Figure 1 Scanning electron micrograph of composite latex particles. The scale (white bar) at the bottom of the micrograph is 10 μm in length.

However, the observed layered interior features do not correspond to the successive poly(butyl acrylate) shell thickness. It is surmised that the TEM section of the particle varies in thickness due to some unknown factor in the sectioning operation. Smaller secondary particles (0.4–0.5 μm) are also seen in the micrograph.

DISCUSSION

Particle Morphology

The poly(butyl acrylate) core/polystyrene shell system is well known for its unusual morphology.^{7,8,15,16} Typical problems include “phase inversion” of the particle, wherein the second-stage polystyrene migrates to the center of the particle while displacing poly(butyl acrylate) to the outside, thus giving an inverted core/shell particle. The reason for this has been discussed extensively elsewhere,^{17,18} but simply stated, the particle changes to minimize surface energy at polymer/polymer and polymer/water interfaces. In this system, the more hydrophobic polystyrene preferentially diffuses to the interior of the particle, leaving the more hydrophilic poly(butyl acrylate) on the surface.

To obtain the desired poly(butyl acrylate) core/

polystyrene shell morphology, two variations on the normal emulsion techniques were employed:

1. AIBN initiation provides a more hydrophobic poly(butyl acrylate) surface compared to the sulfate-ended polymers resulting from $(\text{NH}_4)_2\text{S}_2\text{O}_8$ initiated reactions. Thus, the tendency to invert (or form other morphologies) is reduced.
2. Although minimization of free energy is the major factor in determining morphology, polymer chain mobility must also be considered.¹⁸ If the polymer chains are immobilized, then it is not possible for rearrangement to take place. This was accomplished by cross-linking of the poly(butyl acrylate) core with allyl methacrylate and of the styrene phase by divinylbenzene.

Using the above conditions in conjunction with a starved feed reaction, the proper core/shell morphology was obtained as evidenced by the TEM section in Figure 2.

Particle Size

In core-shell emulsion reactions, it is critical that during the shell polymerization step monomer adds

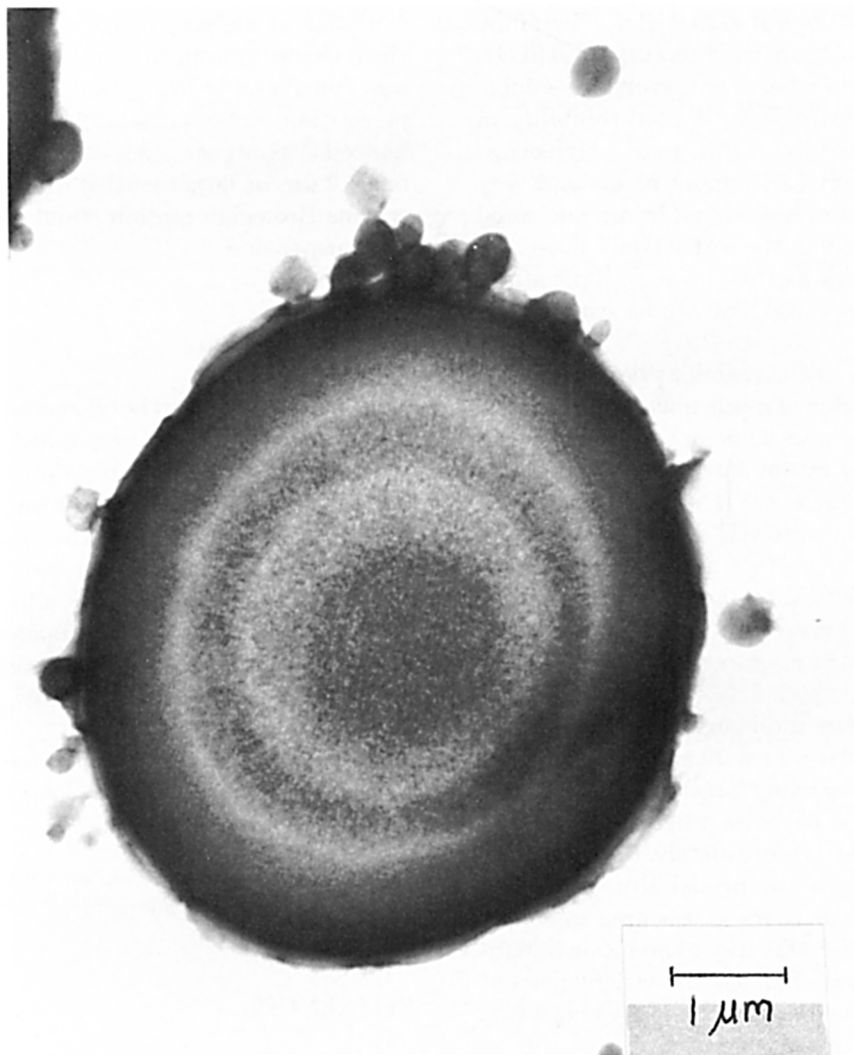


Figure 2 Transmission electron micrograph of latex particle. The polystyrene phase is rendered dark by RuO₄ staining.

to the seed latex and does not contribute to the formation of any new primary particles. To this end, the amount of surfactant added in the shell polymerization stage must be high enough to stabilize the latex yet be below the critical micelle concentration (CMC), where new particles may be nucleated.

In spite of these precautions, in some cases, secondary particles form even at surfactant levels well below the CMC.¹⁹ The generation of these particles is thought to be due to water-phase polymerization of monomers by persulfate initiators to form ionic-ended macroradicals. As the macroradicals add more monomer units, the water solubility limit is reached and they collapse to form primary particles in which the ionic-ended polymer chains function as surfactants. Further growth of the primary particle occurs

by capture of newly nucleated particles and by transfer of monomer to the particle. This mechanism is in contrast to the Smith-Ewart theory²⁰ in which polymerization is assumed to occur only in the organic phase by "stung" particles. Indeed, in ordinary persulfate-initiated reactions, the formation of oligomeric radicals in the water phase can be a major contributor to the polymerization process²¹ and this has led to "soap-free" emulsion polymerization techniques.

Thus, in successful core-shell polymerizations, shell growth occurs by both polymerization within the shell and by capture of newly nucleated particles.²² At low surfactant levels, the latter predominates.²³ As the latex particles grow, however, the specific surface area (total surface area/mass polymer) decreases and it becomes more difficult to

sweep up any newly nucleated particles. Therefore, a second generation of particles becomes more likely.

In contrast to water-based initiators, oil-soluble initiators such as AIBN have limited solubility in the water phase. Because of this, most polymerization occurs in the oil (monomer) phase and very little within the water phase. In addition, nucleated particles that do form in the water phase have limited colloidal stability as they have no ionic stabilization and thus are more likely to be swept up by the latex particles.

Other conditions in the reactions described here facilitated the gathering of newly nucleated particles. Long reaction times give sufficient time for collection of the particles by the latex and starved feed conditions assure that there is no ready supply of monomer to promote growth of newly nucleated particles. As well, the surface area of the seed was kept as large as practical by increasing the volume of seed latex in reactions seeded with larger particles. The surface area of the seed in the various stages is shown in Table III.

As can be seen, the total surface area decreases sharply as particle size increases and this cannot be easily compensated by using larger amounts of seed, since the seed quickly becomes a significant portion of the reactor volume. Unfortunately, the lower seed area tends to increase the probability of second-generation particles as there is less area to collect the nucleated particles. One way to maintain a high-seed surface area is to increase the weight percent of solids, but this is not feasible at already high solids contents such as is the case here.

There were some problems of polymer formation at the top of the reactor because of AIBN initiator volatility. This was quite noticeable at longer reaction times, although the amount of overhead polymer never exceeded 10% of the added monomer. Although there was some formation of coagulum on the stirrer shaft, coagulation did not seem to be a major problem. This was in contrast to the case of persulfate initiation in which there was massive co-

agulation at higher particle sizes. It is possible that since the total ionic strength of the aqueous phase was considerably lower than in a persulfate polymerization, colloidal stability of the latex is enhanced.²⁴ However, once stirring was stopped, latexes 2 μm or larger settled over time due to their size, as Brownian motion is not sufficient to maintain suspension.

CONCLUSIONS

The well-known poly (butyl acrylate) core/polystyrene shell latex can be extended to large particle sizes when appropriate reaction conditions and a nonionic initiator (AIBN) are employed. Although not completely eliminated, the problems associated with formation of secondary formation of particles and coagulation are reduced sufficiently such that particles up to 6 μm could be made. In addition, the proper morphology for the particles was also retained by use of these conditions.

We would like to take this opportunity to thank Dow Chemical USA, Dow Chemical Canada, and the National Sciences and Engineering Research Council of Canada for financial support. Thanks also to A. Payne and P. Gerroir at the Xerox Research Center of Canada for transmission electron micrography of the latex particles.

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Table III Surface Area of Seed

Reaction	Seed (g)	Surface Area (m^2/L) ^a
#2	48.5	2120
#3	134	1472
#4	305	821
#5	241	466

^a Volume includes dilution water.

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Received September 30, 1991

Accepted January 21, 1992