

Encapsulation of Titanium Dioxide in Styrene/*n*-Butyl Acrylate Copolymer by Miniemulsion Polymerization

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ABSTRACT: Miniemulsion copolymerization of styrene/*n*-butyl acrylate was investigated as a means of encapsulating hydrophilic titanium dioxide (TiO₂) in a film-forming polymer. Dispersion studies of the TiO₂ were first carried out to determine the choice of stabilizer, its concentration, and the dispersion process conditions for obtaining stable TiO₂ particles with minimum particle size. Through screening studies of various functional stabilizers and shelf-life stability studies at both room and polymerization temperatures, Solsperse 32,000 was selected to give relatively small and stable TiO₂ particles at 1 wt % stabilizer and with 20–25 min sonification. The subsequent encapsulation of the dispersed TiO₂ particles in styrene/*n*-butyl acrylate copolymer (St/BA) via miniemulsion polymerization was carried out and compared with a control study using styrene monomer alone. The lattices resulting from the miniemulsion encapsulation

polymerizations were characterized in terms of the encapsulation efficiencies (via density gradient column separations; DGC) and particle size (via dynamic light scattering). Encapsulation efficiencies revealed that complete encapsulation of all of the TiO₂ by all of the polymer was not achieved. The maximum encapsulation efficiencies were 79.1% TiO₂ inside 61.7% polystyrene and 63.6% TiO₂ inside 38.5% St/BA copolymer. As the density of the particles collected from the DGC increased from one layer to another, both the average particle size and the number of the TiO₂ particles contained in each latex particle increased. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3479–3486, 2006

Key words: encapsulation; titanium dioxide nanoparticles; Solsperse 32,000; dispersion; miniemulsion polymerization; density gradient column separation

INTRODUCTION

Encapsulation of pigments by film-forming polymer in the form of submicron particles is a process of special interest in both academia and in industry owing to the expected benefits, which include better pigment particle dispersion in a polymer matrix, improved effectiveness in light scattering in a paint film, and improved mechanical properties.¹ One of the most important applications of encapsulated pigment and filler particles is in latex paints. White pigment, usually TiO₂ (rutile), which is added to obtain hiding power, is one of the more expensive components of water-borne paints.² The light scattering produced when light falls on a film containing a white pigment (e.g., TiO₂) results in hiding power, brightness, and opacity of the film. TiO₂ has become the only white pigment of commercial significance because of its optical performance, safety, and cost. It has one of the highest refractive indexes of all materials. Thus, it is a very effective scatterer of visible light, and therefore,

provides good hiding power.^{3–5} In a film cast from a blend of polymer particles and pigment particles, a loss in scattering would be expected from any pigment–pigment contact. Ideally, all the pigment particles would have only polymer particles as near neighbors. Thus, any agglomerates of pigments present in the paint film will result in reduced scattering by the pigment particles. These problems can be eliminated or reduced by either complete or partial encapsulation of the pigment within either film-forming or non-film-forming polymer.^{2,6}

The encapsulation of inorganic particles of submicron size has been investigated using a number of different polymerization methods, including emulsion polymerization,^{7–22} interfacial polymerization,^{23–25} suspension polymerization,^{26–28} and more recently, miniemulsion polymerization.²⁹ Inorganic particles have included TiO₂, carbon black, magnetite, quartz powder, SiO₂, CdS, BaSO₄, and CaCO₃, while polymers have included polystyrene, poly(vinyl acetate), poly(butyl acrylate), and poly(methyl methacrylate). Both conventional and emulsifier-free emulsion polymerizations^{13–22} have been carried out. The major obstacles in successfully applying emulsion polymerization as an encapsulation method are attributed to the complexity of the particle nucleation mechanism (micellar, homogeneous) and the difficulties in control-

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ling the dispersion stability of the inorganic particles in the aqueous phase prior to and during polymerization. Moreover, in most of the encapsulation studies reported in the literature, neither the dispersion state of the inorganic particles nor the encapsulation efficiency was reported.

Miniemulsion polymerization has recently been applied as an alternative encapsulation process.^{29–31} This process was considered attractive based on the droplet size and stability, the polymerization mechanism inherent to miniemulsions,³² and the prospect of being able to create submicron droplets (50–500 nm) containing the inorganic pigment particles. Erdem et al.^{29,33,34} employed the miniemulsion polymerization approach to encapsulate TiO₂ particles (hydrophilic and hydrophobic) inside a non-film-forming polymer, polystyrene (PS). This study showed that the encapsulation of TiO₂ particles depends on the inorganic pigment particle size and its dispersibility and stability in the monomer medium. Moreover, complete encapsulation, which means the entire polymer (PS) encapsulating all of the TiO₂ particles, was not achieved. The maximum encapsulation efficiencies (83% TiO₂ inside 73% PS) were achieved using hydrophilic TiO₂ particles stabilized with 1 wt % OLOA 370 (polybutene-succinimide diethyl triamine, Chevron).³⁵ In that study, OLOA 370 was chosen as the dispersing agent and stabilizer for the pigment particles in styrene monomer, as it had been previously found to be an effective stabilizer for dispersing the TiO₂ particles, resulting in the highest encapsulation efficiencies. However, OLOA 370 has some disadvantages in that it first needs to be separated from its mineral oil diluent (50:50 w/w), requiring processing through a separation column followed by extensive washing.³³ Difficulties in this process also led to some irreproducibilities in the encapsulation. In this extension of our prior work, we sought to use a 100% active dispersing agent to avoid the time and effort of cleaning and also to eliminate the reproducibility issues. In addition, further encapsulation in a film-forming polymer, namely poly(styrene-*co*-*n*-butyl acrylate), was considered the logical next step with a major goal of determining how the encapsulation influences the final film properties, like contrast ratio and gloss, compared to physical pigment/latex blends.

The aims of this research are twofold. The first goal is to investigate the conditions required to obtain a good dispersion of TiO₂ particles (hydrophilic) in monomer as a prerequisite for any encapsulation via miniemulsion polymerization. The screening results using five different stabilizers are reported. Second, the application of the miniemulsion polymerization technique to the encapsulation of titanium dioxide (TiO₂) inside both a non-film-forming material (PS as reference) and a film-forming material (St/BA copolymer) will be investigated. The encapsulation efficien-

cies will be determined by the density gradient column (DGC) method. Also, the encapsulated polymer/copolymer particle size from each layer of the DGC will be determined by dynamic light scattering (DLS).

EXPERIMENTAL

Materials

Styrene (>99%, Sigma-Aldrich, St. Louis, MO) and *n*-butyl acrylate (>99%, Sigma-Aldrich) monomers were purified of inhibitors by passing them through columns filled with an appropriate inhibitor-removal packing material (Sigma-Aldrich). The monomers were kept refrigerated until use. Sodium lauryl sulfate (SLS; Fisher, Pittsburgh, PA), sodium bicarbonate (NaHCO₃; Sigma-Aldrich), and hexadecane (HD; Sigma-Aldrich) were used as received as surfactant, buffer, and costabilizer, respectively. Polystyrene homopolymer was obtained from a PS latex (100 nm) after first cleaning the latex via serum replacement³⁶ and then recovering the polymer ($M_n = 102,000$ g/mol) by drying. This PS homopolymer was dissolved in the monomer phase to improve the monomer droplet nucleation efficiency via the “enhanced nucleation” mechanism.³⁷ All other reagents were used as received. The solid to be encapsulated in this work was TiO₂ (hydrophilic, 30 nm, Degussa, Parsippany, NJ) under the brand name P-25. The TiO₂ sample was dried in a vacuum oven overnight at 110–130°C to remove all the moisture adsorbed on the surface and left to cool in a desiccator for further use. Solsperse^{38–40} 24,000 and 32,000 (100% active, Avecia, Wilmington, DE) were used as received. Solsperse 32,000 is basically a comb polymer with several anchors and several tails connected together in one molecule. Solsperse 32,000 is chemically a polyamine/polyester.⁴¹ Chloroform (Sigma-Aldrich), used in the determination of the amount of polymer associated with the TiO₂ in the bottom layer of the DGC, was used as received. Toluene (VWR, Bridgeport, NJ) was used as received to study the stability of Solsperse 32,000 at the polymerization temperature (i.e., 70°C) and also for determining the stabilizer molecular weight by vapor pressure osmometry (VPO). Benzil (MW = 210 g/mol, Sigma-Aldrich) was used as standard compound for VPO calibration. Deionized (DI) water was used for all experiments.

Analytical methods

For all miniemulsion experiments, a sonifier (Branson, Model 450; Ultrasonics, Danbury, CT) with 3/4” horn diameter and Microfluidizer (Model 110T, Microfluidics, Newton, MA) were used for homogenization. The sonifier was used in the pulsed mode (1 s per pulse cycle). The pulse duration was adjustable from 0.1 to

TABLE I
Properties of the TiO₂ Particles Used in the Dispersion and Encapsulation Studies⁴¹

Trade name	Surface area (m ² /g) ^a	Nature of surface ^{b,c}	Density (g/cm ³)	pH ^d (4% aqueous)	Particle size (nm) ^e
TiO ₂ -P25 (Degussa)	35–65	Hydroxyl groups	~4.1	3.5–4.5	~30

^a Determined by nitrogen adsorption (BET).

^b 20% Rutile, 80% Anatase (hydrophilic).

^c Aerosil process of the hydrolysis of gaseous titanium tetrachloride: $\text{TiCl}_4 + 2 \text{H}_2 + \text{O}_2 \rightarrow \text{TiO}_2 + 4 \text{HCl}$.

^d In aqueous dispersion of the powder.

^e Average primary particle size determined by TEM.

0.9 s. Dynamic light scattering (Nicomp, Model 370; Particle Sizing Systems, Santa Barbara, CA) was used to measure the TiO₂ particle size and the resulting polymer particle size. A LB-70M Beckman ultracentrifuge (Beckman Coulter, Fullerton, CA) equipped with a 6-tube swinging-bucket rotor (SW-41) was used to separate the encapsulated particles in the DGC. The amount of polymer associated with the TiO₂ in the bottom layer of the DGC was measured using a UV/Vis spectrophotometer (SPECTRONIC[®] GENESYS[™]; Thermo Electron, Waltham, MA). Vapor pressure osmometry (Knauer, Berlin, Germany) was used to determine the stabilizer's molecular weight.

Procedure

Dispersion of inorganic particles in nonaqueous medium

The characteristics of the TiO₂ used in this work are reported in Table I. The primary particle diameter is given as ~30 nm. However, the actual particle size is typically larger than this because of agglomeration. TiO₂-P25 is produced by the AEROSIL[®] process, which involves the hydrolysis of gaseous titanium tetrachloride.⁴²

For the preparation of pigment dispersion in monomer, the dried TiO₂ particles were slowly added to the oil phase containing stabilizer, which was stirred for ~20 min and then sonified for 1 h at an output power of 10 and duty cycle of 70% (Branson, Model 450). Samples were withdrawn during the sonification process for the determination of the particle size as a function of sonification time, as well as for the shelf-life stability as function of time. The particle sizes were determined by DLS.

Miniemulsion encapsulation polymerizations

The typical recipe used for miniemulsion polymerizations is shown in Table II. The experimental procedure was as follows. Each ingredient was dissolved in either the oil phase or aqueous phase, depending on its solubility. The SLS and sodium bicarbonate (NaHCO₃)

were dissolved in DI water, while the HD and PS homopolymers were dissolved in the monomer. The oil phase containing 3 wt % TiO₂ stabilized with 1 wt % Solsperser 32,000 was first stirred for 20 min and then sonified for 20 min at 10 output power and 70% duty cycle to obtain the best dispersion of TiO₂ with the minimum particle size. Then the aqueous and oil phases were mixed by magnetic stirring and sonified for 1 min at 7 output power and 60% duty cycle. The emulsion was then homogenized by cycling it through the Microfluidizer (80 psig pump pressure) for six passes to create the miniemulsion. The interaction chamber and receiving flask were cooled by ice baths to minimize any temperature rise. After the emulsification step, a potassium persulfate (KPS) initiator solution was added to the flask containing the emulsion. The polymerization was carried out with stirring (100 rpm) under an inert nitrogen atmosphere in a three-neck round-bottom reactor at 70°C for 4 h. The monomer conversion was determined gravimetrically.

Preparation of density gradient column

In the DGC separation method, the density of the medium increases in steps down the centrifuge tube.

TABLE II
Typical Recipe Used in Miniemulsion Encapsulation Polymerization

Ingredient	Amount (g)	Concentration
Styrene		
<i>n</i> -Butyl acrylate	35	
Styrene/BA (50 : 50 wt %)		
PS ^a	0.35	1 wt % ^b
Hexadecane	1.2681	3.62 wt % ^b
Solsperser 32,000	0.35	1 wt % ^b
TiO ₂	1.05	3 wt % ^b
Deionized water	140	
SLS	0.4036	10 mM ^c
NaHCO ₃	0.0158	1.34 mM ^c
KPS	0.0506	1.34 mM ^c

^a $M_n = 102,000$ g/mole.

^b Based on the oil phase.

^c Based on the aqueous phase.

The column is prepared as follows: sucrose solutions of decreasing concentration are carefully layered one on top of the other in a centrifuge tube. The solutions are drained down the side of the tube to minimize any mixing between layers. It was reported²⁹ that centrifugation at 37,000 rpm and 4°C for 2 h is sufficient to produce an equilibrium separation in the DGC. After placing all the layers in the DGC tubes, a small latex sample was layered on top of the column after first subjecting it to sonification for 30–60 s to remove any TiO₂ that could be physically attached to the polymer particles. In DGC, the particles separate according to their density, moving to positions in the gradient where the density of the medium (ρ_m) just below the particles is greater than the particle density (ρ_p) while the density of the fluid surrounding the particles is less than or equal to their density. Thus, the particles accumulate in an obvious band in the tube.

Determination of encapsulation efficiencies

The DGC was used to determine the encapsulation efficiencies of TiO₂ in the polystyrene and St/BA copolymer latex particles. After 2-h centrifugation at 37,000 rpm, each layer was removed and placed in a separate vial. The encapsulated polymer/copolymer was dried overnight in a crucible at 75°C to evaporate all of the water; the crucible was weighed periodically until a constant weight was achieved. Then each layer was burned and the TiO₂ (residue) weighed. Material balances were performed to estimate the amount of polymer encapsulating the total amount of TiO₂ measured.

The average particle size of the encapsulated particles for each DGC layer was determined by DLS and used in conjunction with the density of the layer to estimate the number of TiO₂ particles per encapsulated particle according to eq. (1):

$$N_{\text{TiO}_2} = \left(\frac{d}{d_{30}}\right)^3 \left(\frac{\rho_{\text{particle}} - \rho_{\text{polymer}}}{\rho_{\text{TiO}_2} - \rho_{\text{polymer}}}\right) \quad (1)$$

where d is the average diameter of the encapsulated particles, d_{30} is the average diameter of the primary TiO₂ particles (30 nm), ρ is the density of the i th species, namely the particle, polymer, and TiO₂. The density of the particles is treated as a range based on the density of adjacent layers in the column.

Determination of the polymer/copolymer associated with TiO₂ in the bottom layer of the DGC

As mentioned earlier, owing to the large density difference between the polymer shell (~1.05 g/mL) and the TiO₂ inorganic particles (4.1 g/mL) and the fact

TABLE III
Different Types of Stabilizers, Their Suppliers and the Anchoring End Group

Chemical name	Supplier	Reactive (anchoring) end group
Solsperse 32,000	Avecia	Amine (NH ₂)
Solsperse 24,000	Avecia	Amine (NH ₂)
PS-PEO (30 : 30)	Goldschmidt chemical	Hydroxyl (OH)
PS-PEO (7 : 20)	Goldschmidt chemical	Hydroxyl (OH)
PEG 600	Henkel	Ester backbone

that the maximum density that can be prepared in the DGC is only 1.339 g/mL, this layer may contain some encapsulated TiO₂. In general, it is expected that there will be some encapsulated TiO₂ in this layer. Thus, it is the objective of this experiment to reveal whether or not there is polymer/copolymer in this layer, and if so, determine the amount.

The experiment begins with the standard procedure for DGC separation as explained in the previous section. Upon finishing the centrifugation, the bottom layer, which usually contains a white solid, is collected separately from each column and transferred to a glass bottle. Before extracting any polymer from the TiO₂ particles, the sucrose was first removed from the solids. This cleaning step was performed by adding DI water to the bottles, which were placed in a water bath at 50°C overnight. The contents were centrifuged at 37,000 rpm for 1 h at 25°C and the solids were recovered after discarding the supernatant. The process of cleaning the solids with DI water followed by centrifugation was repeated several times to ensure that no sucrose remained. The recovered solids were dried in an oven at 75°C overnight before adding a specific amount of chloroform to extract any polymer from the solids. The final step was centrifugation of this mixture at 37,000 rpm for 1 h followed by collection of the supernatant. To determine the amount of polymer in the supernatant, a calibration curve for the polymer (polystyrene or styrene-butyl acrylate copolymer (50 : 50 wt %)) was established using a UV spectrophotometer.

RESULTS AND DISCUSSION

Dispersion studies of TiO₂ in organic phase

In initial screening experiments, five different functional stabilizers (Table III) were selected for investigation of their ability to stabilize TiO₂ in nonaqueous media using the typical recipe shown in Table IV. All the dispersions were subjected to 1-h sonification and samples were withdrawn during sonification at specific time intervals. Photographs were taken to visually record the stability of 3 wt % TiO₂ particles stabi-

TABLE IV
Recipe Used in the Dispersion Study of TiO₂ with Different Stabilizer Concentrations

Styrene (g)	Stabilizer (g)	TiO ₂ (g)
35	0.175 (0.5 wt %) ^a	1.05 (3 wt %) ^a
	0.35 (1 wt %) ^a	
	0.7 (2 wt %) ^a	

^a Based on monomer.

lized with 1 wt % of the different stabilizers in styrene monomer after sonification at 10 output power and 70% duty cycle. It became obvious that three out of the selected five stabilizers did not provide sufficient stabilization of TiO₂ in styrene as noted by significant sedimentation in 24 h. These three represent PS-PEO block copolymers with different block lengths, namely 30:30 and 7:20 PS-PEO, and the PEG 600. On the other hand, Solsperse 32,000 and Solsperse 24,000 provided excellent stability and no TiO₂ sedimentation was visually observed. The particle size distributions of the TiO₂ dispersions obtained using these two dispersants were comparable, as well as their shelf-life stability. Figure 1 shows that for both Solsperse 24,000 and 32,000, as the sonification time increased, the particle size (reported as the averages) decreased up to 15–25 min and then leveled off. The dispersion of TiO₂ in styrene using Solsperse 32,000 resulted in particle sizes slightly smaller than the dispersions using Solsperse 24,000. In addition, the particle size was measured as a function of time (up to 48 h) for samples withdrawn at 15, 20, and 60 min sonification times, with the results shown in Figure 2. In all cases, the particle size did not change significantly for either Solsperse 24,000 or 32,000, indicating good stability. On the basis of these findings, the stability using Sol-

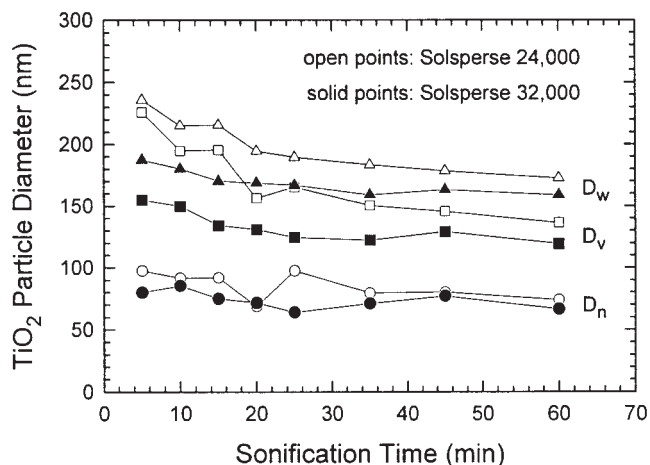


Figure 1 TiO₂ particle size in styrene as a function of sonification time using Solsperse 24,000 and 32,000 as stabilizers.

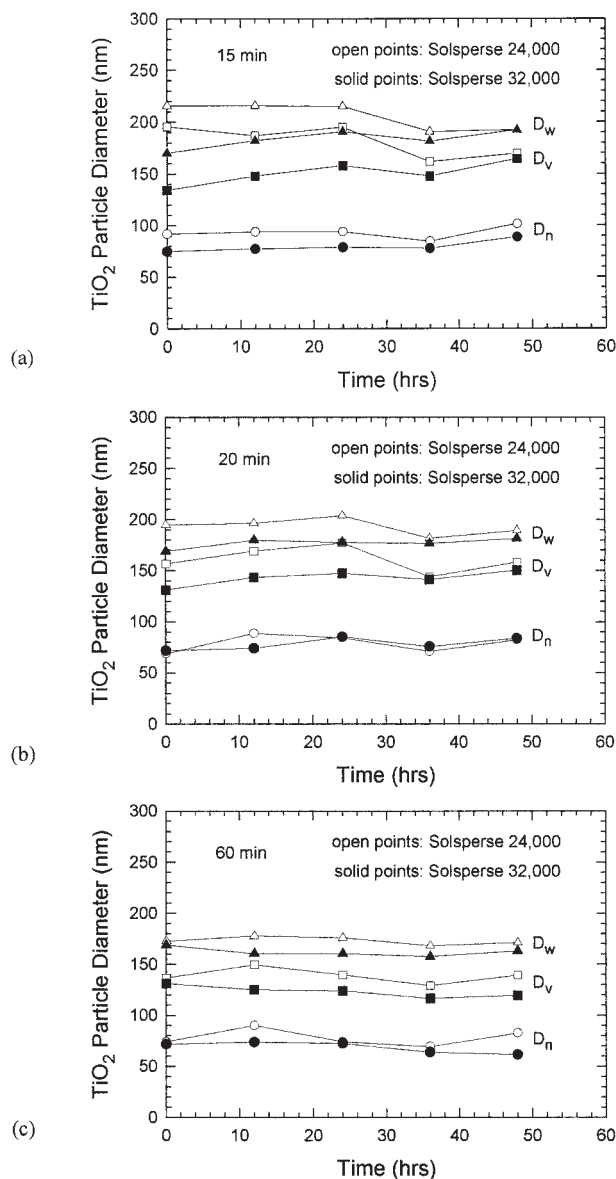


Figure 2 Shelf-life stability (particle size versus time) of TiO₂ dispersions in styrene at room temperature, prepared using Solsperse 24,000 and 32,000 at different sonification times and 10 output power and 70% duty cycle: (a) 15 min, (b) 20 min, and (c) 60 min sonification.

sperse 32,000 at polymerization temperature (70°C) was checked. This was done in toluene instead of styrene owing to the possibility of thermal polymerization. Samples were again taken for particle size measurements over a 48-h period. Almost no change in the particle size occurred (Fig. 3) over the entire course of the measurements, indicating a stable dispersion. No sedimentation was observed as well.

The effect of the Solsperse concentration on the evolution of particle size (D_v) with sonification time is illustrated in Figure 4 for three levels of stabilizer. The results do not indicate any consistency, with scatter of the data only generally indicating smaller particles

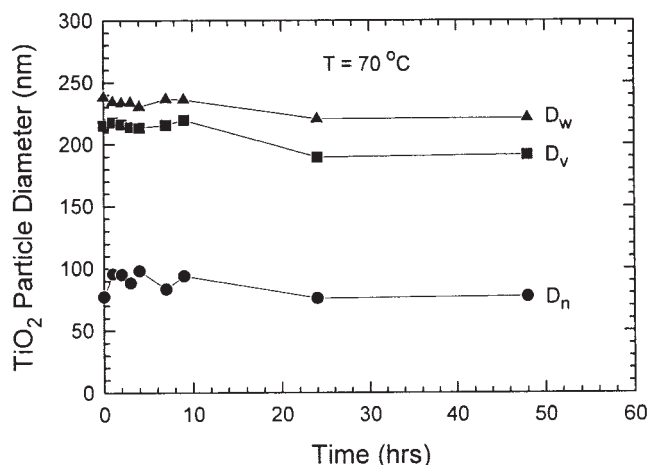


Figure 3 TiO₂ particle size as a function of time at 70°C for 3 wt % TiO₂ particles stabilized with 1 wt % Solsperse 32,000 in toluene after 20 min sonification at 10 output power and 70% duty cycle.

with increasing sonification time. 1 wt % Solsperse was chosen as the concentration for the remainder of the experiments.

Encapsulation efficiencies

Following polymerization of the miniemulsions, the DGC method was used to determine the encapsulation efficiencies of the TiO₂ in polystyrene and St/BA copolymer. The results are reported in Tables V and VI, respectively. The encapsulation efficiency of TiO₂ in PS was determined to be 79% of the TiO₂ encapsulated inside 62% of the PS, while for the St/BA copolymer latex, it was found to be 64% of the TiO₂ encapsulated inside 39% of the St/BA copolymer. For both PS and St/BA copolymer, the remaining TiO₂, (20.9%

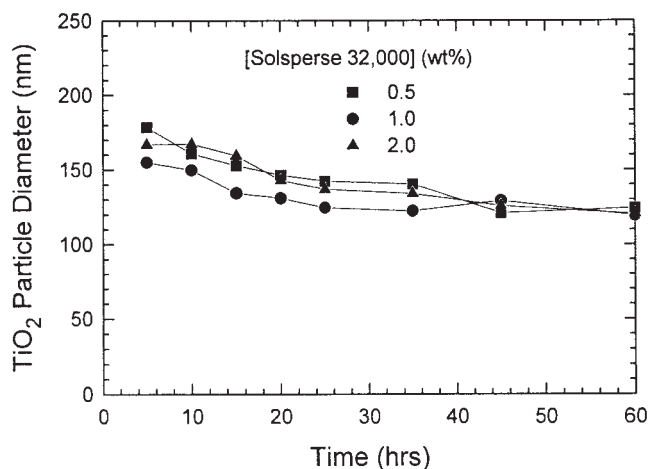


Figure 4 The effect of sonification time on TiO₂ particle size (D_v) (3 wt %) using different concentrations of Solsperse 32,000 at 10 output power and 70% duty cycle sonification.

TABLE V
Encapsulation Efficiency Determination by Density Gradient Column Using Sucrose as the Medium for 3 wt % TiO₂ Hydrophilic Particles Encapsulated in Polystyrene

ρ (g/mL)	TiO ₂ D_v (nm) ^a	Polymer in each layer (wt %) ^b	TiO ₂ in each layer (wt %) ^c
1.0810	152	30.67	12.17
1.1270		13.59	24.34
1.1785		11.55	18.25
1.2297		5.93	24.34
Total (%)		61.74	79.10

^a TiO₂ particle size measured by DLS.

^b Based on the total amount of polymer in the sample (0.1063 g).

^c Percentage of TiO₂ in each layer, based on the total amount of TiO₂ in the loaded sample (0.0033g). Solids content = 21.57 wt %. Latex loaded = 0.508 g (0.1096 g solid).

and 36.4%, respectively) was found in the bottom layer of the DGC, while the remaining PS and St/BA copolymer (38.3%, and 61.5%, respectively) could be found in either the top layer of the DGC (i.e., 1.05 g/mL) or associated with the TiO₂ in the bottom layer. These results for PS show no improvement over those previously reported using OLOA 370 as stabilizer for the TiO₂ (83% of the TiO₂ encapsulated in 73% of the PS).³⁴ And clearly, the encapsulation efficiency was reduced in the copolymer system. This was not surprising in that the encapsulation experiments using *n*-BA alone as the monomer were unsuccessful, resulting in a significant amount of coagulum upon polymerization. The Solsperse 32,000 was clearly not as effective a stabilizer in the presence of the *n*-BA.

The average sizes (D_v) of the PS and p(St/BA) encapsulated particles were determined for each layer in the DGC by DLS and are reported in Tables VII and VIII, respectively. For the polystyrene latex, the aver-

TABLE VI
Encapsulation Efficiency Determination by Density Gradient Column Using Sucrose as the Medium for 3 wt % TiO₂ Hydrophilic Particles in St/BA Copolymer

ρ (g/mL)	TiO ₂ (D_v) (nm) ^a	Polymer in each layer (wt %) ^b	TiO ₂ in each layer (wt %) ^c
1.0810	151	16.27	15.15
1.1270		10.35	18.18
1.1785		7.53	15.15
1.2297		4.33	15.20
Total (%)		38.48	63.64

^a TiO₂ particle size measured by DLS.

^b Based on the total amount of copolymer in the sample (0.1060 g).

^c Percentage of TiO₂ in each layer, based on the total amount of TiO₂ in the loaded sample (0.0033 g). Solids content = 21.57 wt %. Latex loaded = 0.5081 g (0.1092 g solids).

TABLE VII
Estimated Average Number of TiO₂ Particles per PS Particle in Each DGC Layer

Density range (g/mL)	Encapsulated particles D_v (nm) ^a	Average $N_{\text{TiO}_2/\text{PS}}$ particle
1.06–1.08	121	~1
1.09–1.127	216	9
1.128–1.1785	279	34
1.179–1.2294	322	73

^a Measured by DLS.

age particle size of the unencapsulated particles in the upper layer of the DGC (i.e., 1.05 g/mL) was determined to be 97 nm and increased up to 322 nm in the 1.2297 g/mL density layer when TiO₂ was encapsulated. The average size of the unencapsulated St/BA copolymer particles in the upper layer of the DGC was determined to be 90 nm and also increased as the density increased, where the particle size at the highest density was 351 nm. These results are similar to those reported previously by Erdem et al.³⁴

The number of primary TiO₂ particles per encapsulated particle was estimated based on the average particle size and the upper limit of the density for the particles present in each layer and are reported in Tables VII and VIII for the PS and p(S/BA) systems, respectively. Of course, most of the TiO₂ particles are present as aggregates rather than primary particles. Since the average particle size increases with increasing density, the number of encapsulated TiO₂ particles must increase to accommodate both the size and density increase. These results are combined in Figure 5, where it can be seen that the encapsulated particle size is not only smaller for the PS system but also changes more significantly from one layer to the next. This is a consequence of the better stabilization provided by the Solsperse 32,000 in styrene alone; smaller aggregate sizes resulted in smaller encapsulated particles.

Polymer/copolymer associated with TiO₂ in the bottom layer of the DGC

The analysis of the bottom layer of the DGC proved that indeed there was some polymer/copolymer

TABLE VIII
Estimated Average Number of TiO₂ Particles per St/BA Copolymer Particle in Each DGC Layer

Density range (g/mL)	Encapsulated particles D_v (nm) ^a	Average $N_{\text{TiO}_2/\text{P(S/BA)}}$ particle
1.06–1.08	310	9
1.09–1.127	329	31
1.128–1.1785	336	57
1.179–1.2294	351	92

^a Measured by DLS.

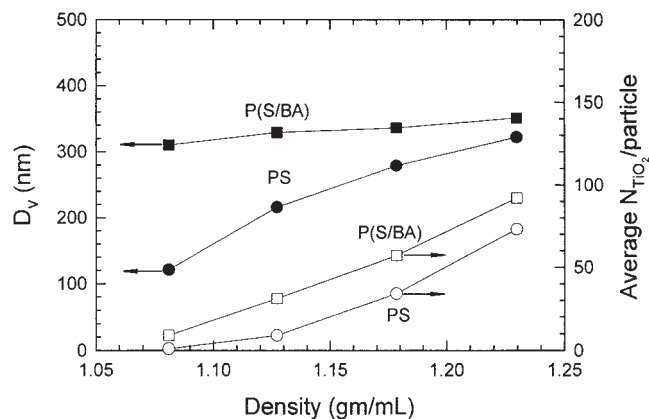


Figure 5 Average encapsulated particle size and number of primary TiO₂ particles per encapsulated particle as a function of density in the DGC for the PS and P(S/BA) systems.

present along with the TiO₂. The weight percent of the polystyrene found there constituted about 11 wt % of the polymer in the charged latex. This amount of polymer is likely to be in the form of polystyrene-encapsulated TiO₂ particles having a density greater than 1.2297 g/mL. The TiO₂ encapsulation efficiency in the polystyrene miniemulsion latex was determined to be ~80% while the remaining TiO₂ (20%) was assumed to be unencapsulated and at the bottom layer of the DGC. However, only 18.5 wt % of the TiO₂ was located in the bottom layer, which means that 1.5 wt % of the TiO₂ was lost during the cleaning and recovery process after centrifugation. On the other hand, the amount of copolymer associated with the TiO₂ constituted 12 wt % of the copolymer latex charged into the DGC. This percentage should be higher than that for the polystyrene because the TiO₂ encapsulation efficiency in this batch was determined to be ~64%. The rest of the TiO₂ (36%) should be found in the bottom layer of the DGC. However, results showed that only 21 wt % of the TiO₂ in the latex was in the bottom layer.

CONCLUSIONS

Dispersion and shelf-life stability studies of 3 wt % TiO₂ dispersions in monomer using different types of stabilizers indicated that Solsperse 32,000 was the best of the stabilizers tested, where 15–25 min sonification was sufficient to produce the smallest TiO₂ particle size. Increasing the sonification time up to 1 h at 10 output power and 70% duty cycle did not help achieving a narrower TiO₂ size distribution. The Solsperse 32,000 stabilizer concentration over the range tested did not have a significant effect on the TiO₂ particle size; 1 wt % Solsperse 32,000 was chosen for the remaining studies.

The encapsulation of 3 wt % TiO₂ in PS and 50/50 wt/wt St/BA copolymer via miniemulsion polymerization was investigated. The encapsulation efficiencies, determined by DGC, were 79 wt % of the TiO₂ encapsulated by 62% of the PS and 64% encapsulated in 39% of the St/BA copolymer. Also, the encapsulated particle size was determined for each layer in the DGC. For the polystyrene latex, the average particle size of the unencapsulated PS particles was determined to be 97 nm (D_v) and increased up to 322 nm when TiO₂ was encapsulated. In the S/BA copolymer system, the average unencapsulated particle size was determined to be 90 nm and also increased up to 351 nm as the density increased. This increase was attributed to the increasing number and size of the TiO₂ particles (or aggregates) encapsulated in each particle. A significant amount of polymer/copolymer (11%/12%) was also found in the bottom layer of the DGC.

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