

# Preparation of ABS (Acrylonitrile/Butadiene/Styrene) Latexes Using Hydroperoxide Redox Initiators

E. S. DANIELS, V. L. DIMONIE, M. S. EL-AASSER, and J. W. VANDERHOFF, *Emulsion Polymers Institute and Departments of Chemical Engineering and Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015*

## Synopsis

The 80/20 (w/w) azeotropic styrene/acrylonitrile mixture was copolymerized at 35, 50, and 70°C in crosslinked polybutadiene seed latexes of varying particle size (range 113–242 nm) using the *t*-butyl or cumene hydroperoxide/sodium formaldehyde sulfoxylate dihydrate/EDTA-chelated Fe<sup>+2</sup> redox initiator. Other initiators used for comparison were: (1) ammonium persulfate at 70°C; (2) ammonium persulfate/sodium bisulfite redox initiator at 35 and 50°C; (3) oil-soluble 2,2'-azobis(2,4-dimethylvaleronitrile) at 50°C. The following polymerization parameters were varied systematically: (1) polybutadiene seed latex particle size; (2) monomer/polymer swelling ratio; (3) polymerization temperature; (4) type and concentration of initiator; and (5) mode (and duration) of initiator addition. The following parameters were determined: (1) polymer yield (final conversion); (2) variation of conversion with time; (3) morphology of the latex particles; (4) amount of coagulum; and (5) fraction of styrene/acrylonitrile monomer mixture grafted to the polybutadiene seed latex (defined here as grafting efficiency). For polymerizations using the *t*-butyl or cumene hydroperoxide/sodium formaldehyde sulfoxylate dihydrate/EDTA-chelated Fe<sup>+2</sup> redox initiator, the rates of polymerization were faster, the grafting efficiencies were greater, and the amounts of coagulum were greater at 70°C than at 50 or 35°C. The rates of polymerization were decreased by decreasing the concentration of redox initiator or adding it incrementally. A 1.00/1.00/0.08 (w/w) *t*-butyl or cumene hydroperoxide/sodium formaldehyde sulfoxylate dihydrate/EDTA-chelated Fe<sup>+2</sup> ratio gave reasonable polymerization rates at 35 and 50°C, and a 0.48/1.00/0.07 ratio, at 70°C. The latexes were stabilized during polymerization with 3% (based on seed solids) nonionic Igepal CO-990 at 35°C, and 6% at 50 and 70°C. The grafting efficiency increased with decreasing particle size of the polybutadiene seed latex and decreasing monomer/polymer ratio. The rate of polymerization increased with decreasing monomer/polymer ratio. The monomer/polymer ratio also affected the morphology of the particles; higher values gave inclusions of poly(styrene-*co*-acrylonitrile) in the polybutadiene particles. There were no significant differences in polymerization kinetics or grafting efficiency between the *t*-butyl and cumene hydroperoxides.

## INTRODUCTION

In many processes, ABS (acrylonitrile/butadiene/styrene) resins are prepared by seeded emulsion polymerization of a styrene/acrylonitrile mixture in a polybutadiene seed latex. The poly(styrene-*co*-acrylonitrile) chains are grafted onto the rubber particles by addition across the residual double bonds of the polybutadiene or hydrogen abstraction from the polybutadiene, to give a radical which adds monomer units to form a grafted branch. The grafted poly(styrene-*co*-acrylonitrile) chains act as a steric stabilizer when the rubber particles are dispersed in a poly(styrene-*co*-acrylonitrile) matrix. The grafting efficiency and the resulting latex particle morphology strongly affect such mechanical

properties as melt flow behavior and impact strength, and the initiator system strongly affects the grafting efficiency and the particle morphology. This paper describes the copolymerization of the 80/20 (w/w) azeotropic styrene/acrylonitrile mixture in crosslinked polybutadiene seed latexes of different particle size using the *t*-butyl or cumene hydroperoxide/sodium formaldehyde sulfoxylate dihydrate/EDTA-chelated  $\text{Fe}^{+2}$  redox initiator at 35, 50, and 70°C.

Combinations of organic hydroperoxides with reducing agents and ferrous iron have been used in the emulsion polymerization of cold GR-S rubber.<sup>1</sup> Traditionally, ferrous pyrophosphate has been used as the source of  $\text{Fe}^{+2}$  and various sugars as the reducing agents; however, it was found that  $\text{Fe}^{+2}$  chelated by ethylenediaminetetraacetic acid (EDTA) activated the hydroperoxide-initiated emulsion polymerization of butadiene/styrene mixtures<sup>2</sup> when combined with sulfoxylate reducing agents such as sodium formaldehyde sulfoxylate dihydrate.<sup>1,3</sup> The EDTA- $\text{Fe}^{+2}$  chelate acted as a reservoir which regulated the  $\text{Fe}^{+2}$  concentration in the polymerization system and prevented premature precipitation of the iron.<sup>4</sup> This organic hydroperoxide/sodium formaldehyde sulfoxylate dihydrate/EDTA-chelated  $\text{Fe}^{+2}$  redox initiator gave high conversions and significant degrees of grafting in the emulsion copolymerization of styrene/acrylonitrile mixtures in polybutadiene seed latexes.<sup>4</sup> Traditionally, cumene hydroperoxide has been used as the oxidizing agent in these systems. Warson<sup>5</sup> suggested that the hydroperoxides which were the most effective in grafting reactions were those with the lowest solubility in water. Since *t*-butyl hydroperoxide has a higher solubility in water than cumene hydroperoxide, the purpose of this study was to compare the grafting efficiency, particle morphology, and degree of conversion of *t*-butyl and cumene hydroperoxides in the copolymerization of styrene/acrylonitrile mixtures in polybutadiene seed latexes.

## EXPERIMENTAL

### Materials: Crosslinked Polybutadiene Seed Latexes

The butadiene (Air Products & Chemicals) and divinylbenzene (Dow Chemical) monomers were used as received. The 2,2'-azobis(2,4-dimethylvaleronitrile) (Vazo 52; E. I. du Pont de Nemours) initiator, Igepal CO-730 and Igepal CO-850 (nonylphenol-ethylene oxide adducts of 15 and 20 mol ethylene oxide, respectively; GAF) emulsifiers, and *t*-dodecyl mercaptan (commercial grade; Pennwalt) chain transfer agent were used as received. Distilled-deionized water was used in all polymerizations.

### Materials: Styrene/Acrylonitrile Seeded Emulsion Copolymerization

The styrene (Fisher Scientific) and acrylonitrile (Monsanto) monomers were freshly distilled prior to use. The Igepal CO-990 (nonyl-ethylene oxide adduct of 100 moles ethylene oxide; GAF) and sodium lauryl sulfate (Onyx Chemical) emulsifiers were used as received. The redox initiator components, cumene hydroperoxide (Pennwalt), *t*-butyl hydroperoxide 90 (Pennwalt) or 70 (Arco Chemical), sodium formaldehyde sulfoxylate dihydrate (Polysciences), and EDTA-chelated  $\text{Fe}^{+2}$  (HAMP-ENE NaFe; W. R. Grace), were used as received.

### Polymerization: Polybutadiene Seed Latexes

A series of crosslinked polybutadiene seed latexes with average particle sizes in the range of 113–242 nm were prepared by emulsion polymerization in 12-oz capped pressure bottles at 50°C. Table I gives the polymerization recipes for these latexes. The average particle size was varied systematically by varying the concentration of nonionic Igepal CO-730 or Igepal CO-850 emulsifier. The Igepal CO-730 or Igepal CO-850 emulsifier was dissolved in the distilled-deionized water and charged to the bottles. The divinylbenzene, Vazo 52, and *t*-dodecyl mercaptan were mixed and charged to the bottles, which were then sparged with nitrogen and stoppered with a cork. The butadiene was condensed and weighed into the bottles, which were chilled in an ice-salt mixture to prevent vaporization of the butadiene. The bottles were then capped with a crown cap and rubber gasket, placed in a thermostated bath at 50°C, and tumbled end over end for 24 or 48 h. The resulting latexes were cooled and filtered through glass wool. The average particle sizes and particle size distributions were determined by transmission electron microscopy (see Particle Size and Morphology).

### Styrene-Acrylonitrile Mixtures

The azeotropic 80/20 (w/w) styrene/acrylonitrile mixture was copolymerized in the polybutadiene seed latexes of varying particle size using a 50/50 (w/w) monomer/polymer ratio and the *t*-butyl or cumene hydroperoxide/sodium formaldehyde sulfoxylate dihydrate/EDTA-chelated Fe<sup>+2</sup> redox initiator. Table II gives a typical polymerization recipe. The latexes were prepared by batch or semicontinuous polymerization in 50 mL Erlenmeyer flasks stirred with a magnetic stirrer and sealed with a Neoprene stopper pierced with two hypodermic needles to admit and release nitrogen. The seed latex and the deionized-distilled water were charged to the flask, followed by the emulsifier (10% solution) and EDTA-chelated Fe<sup>+2</sup> solution. For the batch polymerizations, the monomer mixture was added all at once and allowed to swell the seed particles for 30 min before polymerization; for the semicontinuous polymerizations, the monomer mixture was added continuously at a constant rate over a 30 min period using a syringe pump. The sodium formaldehyde sulfoxylate

TABLE I  
Polymerization Recipes for Crosslinked Polybutadiene Seed Latexes (50°C)

Sample	PBU-730	-730-1	-730-2	-850-1 (or -850)	-850-2
Ingredients (g)					
Butadiene	40.0	40.0	40.0	40.0	40.0
Divinylbenzene	0.80	0.80	0.80	0.80	0.80
Distilled-deionized water	120.0	120.0	120.0	120.0	120.0
<i>t</i> -Dodecyl mercaptan	0.08	0.08	0.08	0.08	0.08
Igepal CO-850	—	—	—	2.0	3.2
Igepal CO-730	2.00	2.00	3.20	—	—
Vazo 52	0.32	0.32	0.32	0.32	0.32
Reaction Time (h):	48	24	24	24	24

TABLE II  
Typical Recipe For a Composite Latex (50/50 M/P Ratio; 35°C)

Ingredients (g)	
Seed latex P Bu-850-1	23.36 (5.63 g polymer)
80/20 Styrene/acrylonitrile mixture	5.63
<i>t</i> -Dodecyl mercaptan	0.0024
10% Igepal CO-990 solution	1.70
Sodium formaldehyde sulfoxylate dihydrate	0.034
<i>t</i> -Butyl hydroperoxide	0.034
EDTA-chelated Fe <sup>+2</sup>	0.0028
Distilled-deionized water	6.51

dihydrate was added as an aqueous solution; the *t*-butyl or cumene hydroperoxides were added as an aqueous solution for the batch polymerizations and as a solution in the monomer mixture for the semicontinuous polymerizations; the aqueous initiator solution was added in increments at predetermined time intervals for the batch polymerizations or continuously for the semicontinuous polymerizations. The *t*-dodecyl mercaptan chain transfer agent was dissolved in the monomer mixture. The polymerization temperatures were 35, 50, and 70°C.

To determine the percent conversion, latex samples (ca. 0.5 g) were pipetted from the polymerization vessel into tared weighing vials at predetermined times during the polymerization, and three drops of 1% hydroquinone solution were added to each vial to stop the polymerization. The vials were dried in an air oven for 2 h at 105°C, placed in a desiccator to cool, and weighed to determine the percent solids. The percent conversion was calculated from the percent solids. The final latexes were cooled and filtered through glass wool to remove any coagulum; samples were freeze-dried and used to determine the grafting efficiency.

### Characterization of Latex Copolymers

The grafting efficiency of the poly(styrene-*co*-acrylonitrile) was determined by solvent extraction with acetone [a solvent for the poly(styrene-*co*-acrylonitrile) but not for the polybutadiene]. To freeze-dry the latex, 3 mL latex samples were pipetted into a 50 mL round-bottom flask, which was attached to a vacuum pump through a cold trap; the flask was immersed in liquid nitrogen and swirled to deposit a thin coating of frozen latex on the wall, which was then dried for 3 h under vacuum at room temperature to remove the water; the flask was immersed in liquid nitrogen periodically during the freeze-drying process. Acetone solutions of the freeze-dried polymers (2% by volume) were prepared in 2-oz bottles, which were capped and shaken for 48 h at room temperature; the solutions were centrifuged at 20,000 rpm in a IEC Model B-35 Preparative Ultracentrifuge for 30 min at 5°C; then, 7.5 mL of the supernatant layer were pipetted into a tared aluminum pan and dried, first at room temperature and then for 1 h at 105°C, to evaporate the acetone; the samples were then cooled in a desiccator for several hours and weighed. The fraction of soluble poly(styrene-*co*-acrylonitrile) was determined from the percent solids corrected for the soluble fraction of the polybutadiene and the emulsifier, as well as the final percent conversion. The grafting efficiency was calculated from a material

balance between the soluble and insoluble poly(styrene-*co*-acrylonitrile). Replicate determinations were carried out for each latex recipe, and the grafting efficiencies were averaged. A variation of this method was used earlier to determine the grafting efficiency in similar latexes by extraction with methyl ethyl ketone in an analytical ultracentrifuge.<sup>6</sup>

### Particle Size and Morphology

The latexes were diluted to ca. 0.01% concentration in distilled-deionized water to a total volume of 10 mL, and two drops of 2% aqueous osmium tetroxide were added [osmium tetroxide adds to the residual bonds of the polybutadiene rendering the core more dense in the electron beam than the poly(styrene-*co*-acrylonitrile) shell]. One drop of the stained latex was placed on a carbon-coated Formvar film on a 200 mesh stainless steel grid and allowed to dry overnight in a dust-free environment. The sample was examined in the Phillips 300 transmission electron microscope. The particle sizes were measured from the electron micrographs using the Zeiss MOP-4 particle size analyzer.

The grafting efficiency of the poly(styrene-*co*-acrylonitrile) was determined by dispersing the freeze-dried polymer powder in acetone. The poly(styrene-*co*-acrylonitrile) was soluble in acetone but the polybutadiene was not. Therefore, the formation of a stable colloidal dispersion in acetone was taken as a demonstration of the presence of a grafted poly(styrene-*co*-acrylonitrile) shell of given thickness.<sup>7</sup> The grafted poly(styrene-*co*-acrylonitrile) chains would be solubilized but not dissolved by the acetone, and, in sufficient length and concentration, would give steric stabilization; too low a degree of grafting or too thin a grafted layer would give a coagulated mass rather than a colloidal dispersion.

## RESULTS AND DISCUSSION

### Screening Study

A screening study was carried out to prepare core-shell latexes by batch polymerization with minimal coagulum and without generating a new crop of poly(styrene-*co*-acrylonitrile) particles: a series of 15 g seeded polymerizations using a 50/50 monomer/polymer ratio was carried out at 35 and 70°C using the same polybutadiene seed latex with different emulsifiers. Anionic sodium lauryl sulfate in 0.0–1.6% concentration (based on seed latex) gave particle agglomeration at the lower concentrations and secondary particle generation at the higher concentrations [Fig. 1(A)]. Nonionic Igepal CO-990 in 2.0–3.0% concentration gave a uniform core-shell morphology without a new crop of particles at 35°C [Fig. 1(B)]; however, at 70°C, the polybutadiene seed latex agglomerated, even at 3.0% Igepal CO-990 [Fig. 1(C)]; 5.0–6.0% concentrations gave stable latexes of uniform core-shell morphology without a new crop of particles [Fig. 1(D)].

This screening study used both cumene and *t*-butyl hydroperoxides in 1.00/1.00/0.08 hydroperoxide/sodium formaldehyde sulfoxylate dihydrate/EDTA-chelated Fe<sup>+2</sup> weight ratio. The addition of the hydroperoxide (and the other redox initiators) at the beginning of the batch polymerization gave very fast polymerization rates and large amounts of coagulum. Addition of the hydro-

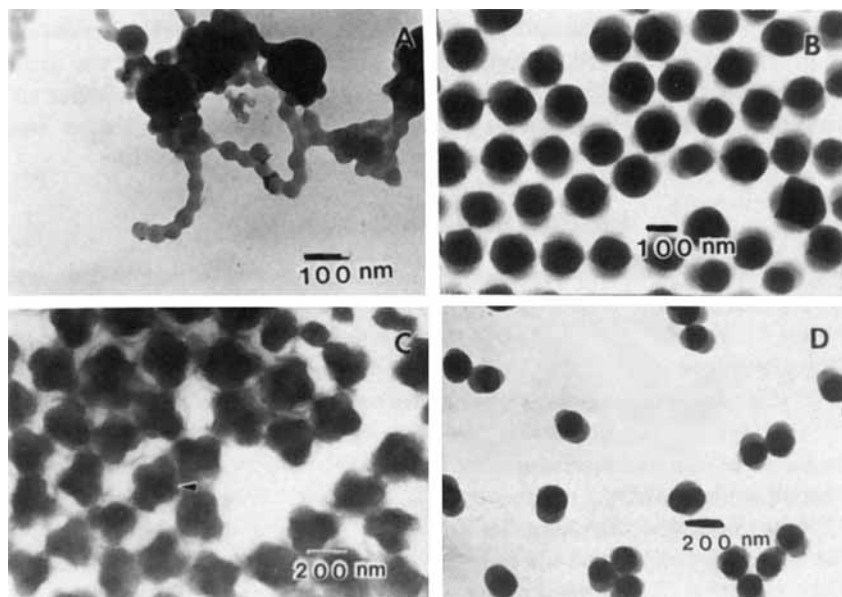


Fig. 1. Transmission electron micrographs of two-stage poly(styrene-co-acrylonitrile)/polybutadiene core-shell latex particles prepared using the same PBU-850 polybutadiene seed latex and cumene hydroperoxide initiator but different emulsifiers and polymerization temperatures: (A) 0.4% sodium lauryl sulfate, 35°C; (B) 2% Igepal CO-990, 35°C; (C) 3% Igepal CO-990, 70°C; (D) 5% Igepal CO-990, 70°C.

peroxide or sodium formaldehyde sulfoxylate dihydrate in several increments gave better control of the polymerization rate, as well as less coagulum and a more uniform core-shell morphology. Warson<sup>5</sup> also found that redox emulsion polymerizations were best carried out by adding one or more of the initiator components in increments. The results of this study were used to scale up the polymerizations from 15 to 37 g.

### Copolymerization Kinetics

Figure 2 shows the conversion-time curves for the seeded batch emulsion copolymerizations of styrene-acrylonitrile mixtures in the 160 nm diameter polybutadiene seed latex at 50/50 monomer/polymer ratio initiated by 14.5 and 7.26 *M* cumene and *t*-butyl hydroperoxides at 35 and 70°C, respectively. The cumene or *t*-butyl hydroperoxides and the sodium formaldehyde sulfoxylate dihydrate were added in four increments at 0, 30, 60, and 90 min for the polymerizations at 35°C and in 10 increments over a 100 min period for the polymerizations at 50°C; the EDTA-chelated Fe<sup>+2</sup> was added initially in both cases. For both polymerization temperatures, the polymerization rates were extremely rapid, and the conversion-time curves showed a pronounced autoacceleration; however, as expected, the rates at 50°C were faster than those at 35°C. There were no significant differences in polymerization rate between the cumene and *t*-butyl hydroperoxides. The autoacceleration was similar to that observed in acrylonitrile polymerizations at 10–30% conversion.<sup>8</sup> The final conversions and amounts of coagulum (0.3–1.0%) were about the same in all 4 polymerizations. Thus, the polymerization rates for equimolar concentrations

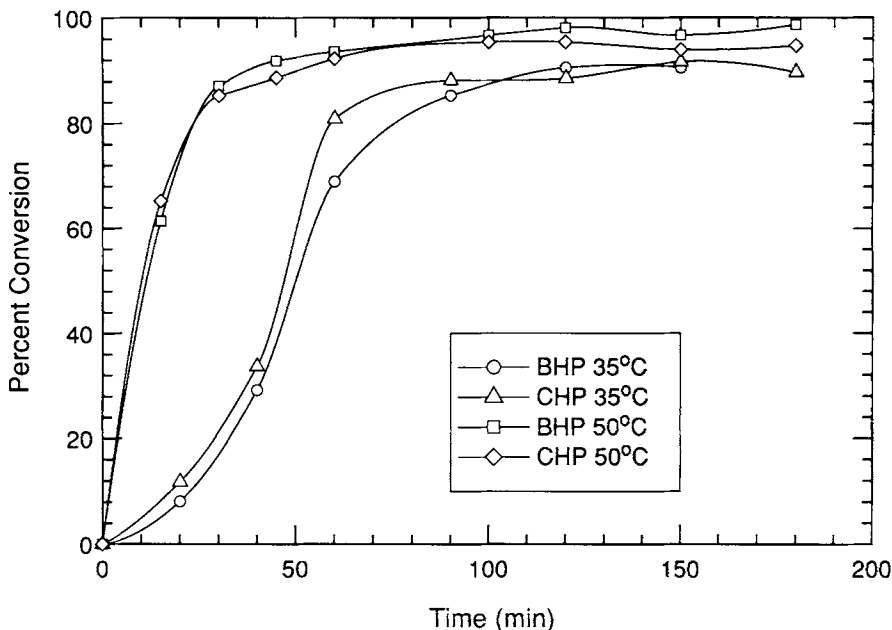


Fig. 2. Variation of percent conversion with time for seeded emulsion polymerization of 80/20 styrene/acrylonitrile mixture in polybutadiene seed latex PBu-850-1 using *t*-butyl hydroperoxide (BHP) or cumene hydroperoxide (CHP) initiator.

of cumene and *t*-butyl hydroperoxides in the redox initiator systems were essentially the same at both 35° and 50°C.

### Effect of Polybutadiene Seed Latex Particle Size

Five crosslinked polybutadiene latexes of 113–242 nm diameter were used as seed latexes for the copolymerization of the styrene/acrylonitrile mixtures. The polymerizations at 30% solids and 50/50 monomer/polymer ratio using *t*-butyl hydroperoxide initiator were run at 35°C. The final conversions were 91.9–98.5%, and the amounts of coagulum were 0.4–2.4%. Table III gives the average particle sizes of the polybutadiene seed latexes. These latexes comprised relatively narrow particle size distributions: the coefficients of variation were

TABLE III  
Particle Size of Polybutadiene Seed Latexes<sup>a</sup>

Seed latex	$D_n$ (nm)	$D_w$ (nm)	$\sigma/D_n$ (%)	PDI
PBu-730	242	247	8.0	1.020
PBu-730-1	192	202	13.0	1.053
PBu-850-1	160	164	8.6	1.022
PBu-730-2	141	149	12.8	1.052
PBu-850-2	113	120	14.6	1.064

<sup>a</sup>  $D_n$ : Number-average diameter;  $D_w$ : Weight-average diameter;  $\sigma/D_n$ : Coefficient of variation; and PDI: Polydispersity index ( $D_w/D_n$ ).

8–15%. These relatively narrow particle size distributions facilitated the interpretation of the core-shell particle morphology.

Figure 3 shows that the rate of polymerization/particle increased exponentially with surface area/particle (which varied with seed particle size). The rate of polymerization/particle was obtained by dividing the slope of the linear region of the conversion–time curve for each seeded emulsion polymerization by the total number of particles. Seed latex P Bu-730 (Table III), which had the largest surface area, showed the fastest rate of polymerization/particle. Table IV gives the results of fitting the curve of Figure 3 with the linear  $y = a + bx$ , power  $y = ax^b$ , and exponential  $y = ae^{bx}$  equations, where  $y$  is the rate of polymerization/particle and  $x$  is the surface area/particle. The exponential equation gave the best fit ( $a = 7.45 \times 10^{-17}$ ;  $b = 1.50 \times 10^9$ ; confidence  $R^2 = 1.00$ ). The exponential equation also gave the best fits with the variation of rate of polymerization/particle with average particle volume ( $a = 1.23 \times 10^{-16}$ ;  $b = 3.18 \times 10^{14}$ ; confidence  $R^2 = 1.00$ ) and average particle diameter ( $a = 1.78 \times 10^{-17}$ ;  $b = 0.020$ ; confidence  $R^2 = 0.98$ ). The power equation gave poorer fits, with the rate of polymerization/particle varying with the 1.47 power of the surface area/particle (confidence  $R^2 = 0.93$ ), the 0.97 power of the average particle volume (confidence  $R^2 = 0.93$ ), and the 2.90 power of the average particle volume (confidence  $R^2 = 0.93$ ), which suggests that the rate of polymerization was proportional to the average particle volume; however, the confidences  $R^2$  were lower than for the exponential fit. The classical Smith–Ewart theory<sup>9</sup> postulates that the rate of polymerization/particle is independent of particle size for case 2 (average number of radicals/particle = 0.5) and is proportional to the particle volume for case 3 (average number of radicals/particle

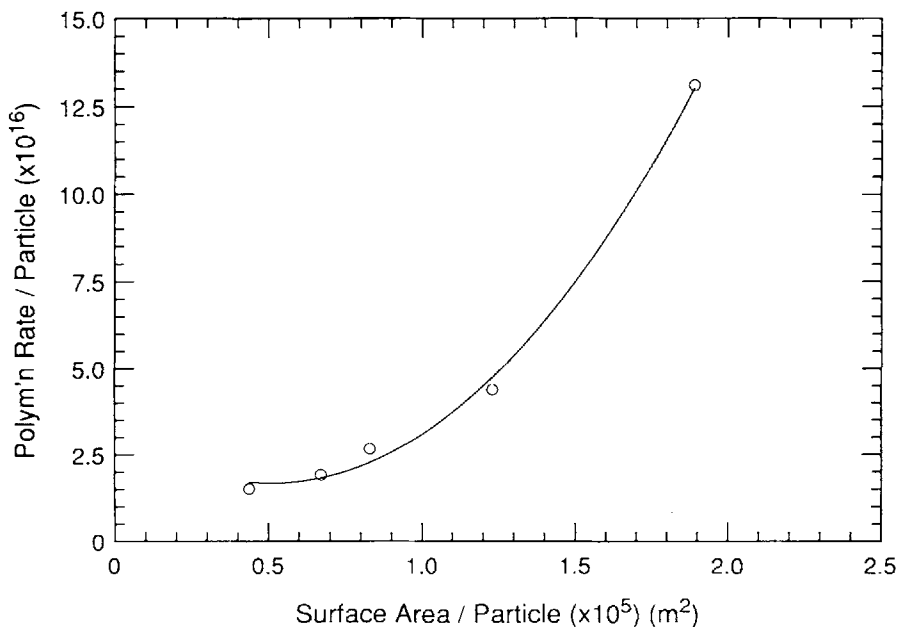


Fig. 3. Variation of polymerization rate/particle (in percent conversion/minute/particle) with surface area/particle for seeded emulsion polymerization of 80/20 styrene/acrylonitrile mixture in polybutadiene seed latexes of 113–242 nm diameter using *t*-butyl hydroperoxide initiator.



TABLE IV  
Rate of Polymerization/Particle and Kinetic Parameters  
(*t*-butyl hydroperoxide; 3% Igepal CO-990; 35°C)

Sample	$D_v$ (nm)	$R_p$ (%/min)	$N$ ( $\times 10^{-15}$ )	$R_p$ /particle (%/min) ( $\times 10^{-15}$ )	A/particle (nm <sup>2</sup> ) ( $\times 10^{-10}$ )	V (nm <sup>3</sup> ) ( $\times 10^{-15}$ )
BHP-B35-48	243	1.04	0.79	1.32	18.9	7.56
BHP-B35-41	194	0.68	1.55	0.439	12.3	3.82
BHP-B35-40	161	0.73	2.73	0.267	8.29	2.20
BHP-B35-43	144	0.74	3.85	0.192	6.71	1.56
BHP-B35-42	116	1.12	7.41	0.152	4.37	0.809
Equation			$a$		$b$	$R^2$
Rate of Polymerization/Particle with Surface Area/Particle						
Linear	$y = a + bx$		$-3.47 \times 10^{-16}$		$8.12 \times 10^{-7}$	0.91
Power	$y = ax^b$		0.010		1.47	0.93
Exponential	$y = ae^{bx}$		$7.45 \times 10^{-17}$		$1.50 \times 10^9$	1.00
Rate of Polymerization/Particle with Average Particle Volume						
Linear	$y = a + bx$		$7.17 \times 10^{-10}$		$-1.03 \times 10^5$	0.53
Power	$y = ax^b$		0.040		0.97	0.93
Exponential	$y = ae^{bx}$		$1.23 \times 10^{-16}$		$3.18 \times 10^{14}$	1.00
Rate of Polymerization/Particle with Average Particle Diameter						
Power	$y = ax^b$		$1.25 \times 10^{-22}$		2.90	0.93
Exponential	$y = ae^{bx}$		$1.78 \times 10^{-17}$		0.020	0.98

$\gg 0.5$ ). For polystyrene, Smith-Ewart case 2 is limited to particle sizes of 150 nm or smaller combined with low rates of radical generation (eg, persulfate ion at 50°C or lower). At larger particle sizes, or faster rates of radical generation, the average number of radicals/particle exceeds 0.5 and increases with increasing particle size and rates of radical generation, eventually approaching Smith-Ewart case 3, which corresponds to bulk polymerization. Although the present kinetic data are insufficient to give accurate values for the average number of radicals/particle, it is obvious that the values are greater than the 0.5 value for Smith-Ewart case 2 and may even approach the values for Smith-Ewart case 3. Moreover, the average number of radicals growing in the monomer-swollen seed particles increased with increasing seed latex particle size. There were no secondary poly(styrene-*co*-acrylonitrile) particles formed in these latexes, which suggested that, if small particles were formed by homogeneous nucleation in the aqueous phase, they were quickly captured by the seed particles.

Figure 4 shows that the grafting efficiency of the poly(styrene-*co*-acrylonitrile) onto the polybutadiene particles varied linearly with the total surface area of the seed latex. The latex of smallest particle size (PBu-850-2), with a surface area of 821 m<sup>2</sup>/dL at 30% total solids, showed a higher efficiency of grafting than that of largest particle size (PBu-730), with a surface area of 400 m<sup>2</sup>/dL. The grafting efficiency of the poly(styrene-*co*-acrylonitrile) was 29–

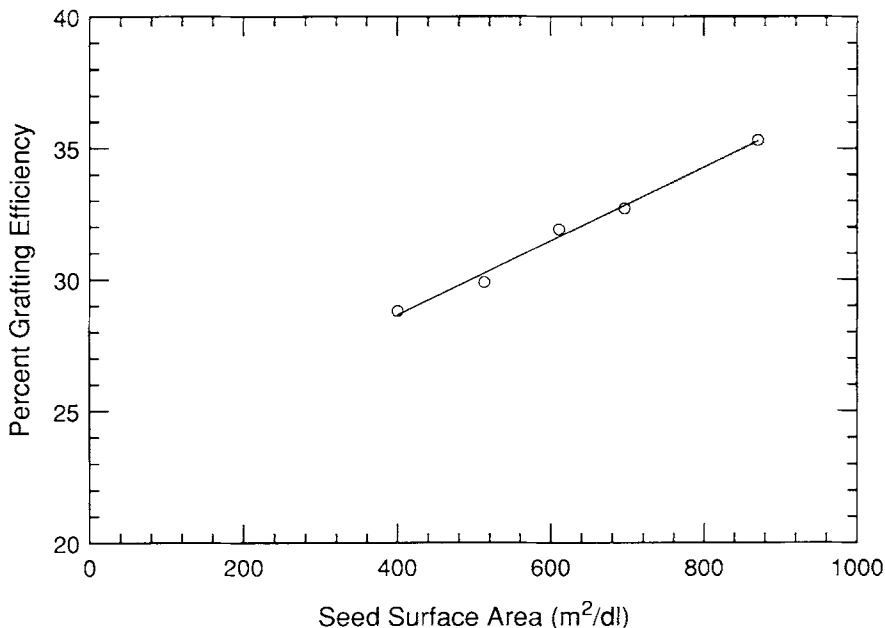


Fig. 4. Variation of grafting efficiency (percent of second-stage monomer grafted onto polybutadiene seed latex) with seed surface area.

35%, and the linear variation of the grafting efficiency with seed surface area showed that the grafting was an interfacial phenomenon. Similar results were reported for poly(methyl methacrylate) grafted onto polybutadiene seed latex using persulfate ion initiator,<sup>10</sup> poly(styrene-*co*-acrylonitrile) grafted onto poly(*n*-butyl acrylate) seed latex,<sup>11</sup> and poly(styrene-*co*-acrylonitrile) grafted onto polystyrene seed latex.<sup>12</sup> For this last case, the grafting efficiency increased exponentially with increasing seed surface area. No significant differences in morphology were observed among the latexes produced using the different-sized seed latexes.

#### Effect of Monomer/Polymer Ratio

Table V shows the effect of monomer/polymer phase ratio on the rates of polymerization and the amounts of coagulum of these composite latexes. The

TABLE V  
Effect of Monomer/Polymer Ratio (*t*-butyl hydroperoxide; 3% Igepal CO-990; 35°C)<sup>a</sup>

Sample	M/P	Coagulum (%)	$R_p$ (%/min)	$N$ ( $\times 10^{-16}$ )	$S$ (m <sup>2</sup> /dL)
BHP-B35-40	50/50	1.0	0.73	2.73	611
BIIP-B35-46	60/40	0.6	0.51	2.17	484
BHP-B35-44 <sup>b</sup>	70/30	1.3	0.40	1.63	363
BHP-B35-45 <sup>b</sup>	85/15	0.6	0.23	0.82	185

<sup>a</sup> Seed latex PBu-850-1 160 nm diameter.

<sup>b</sup> Acetone dispersible.

amounts of coagulum were about the same for all monomer/polymer ratios at 35°C. The rate of polymerization  $R_p$  corresponding to the linear region of the conversion time curves increased with increasing number of seed latex particles  $N$ , increasing seed surface area  $S$ , and decreasing monomer/polymer ratio. Table VI gives the results of fitting these data with the linear  $y = a + bx$ , power  $y = ax^b$ , and exponential  $y = ae^{bx}$  equations, where  $y$  is  $R_p$  in %/min and  $x$  is in N/dL latex. The rate of polymerization varied in proportion to the number of particles ( $a = 9.93 \times 10^{-4}$ ;  $b = 2.54 \times 10^{-16}$ ; confidence  $R^2 = 0.97$ ), which is in accord with Smith-Ewart case 2. However, the power equation ( $a = 4.17 \times 10^{-15}$ ;  $b = 0.92$ ; confidence  $R^2 = 0.98$ ) and the exponential equation ( $a = 0.14$ ;  $b = 5.95 \times 10^{-16}$ ; confidence  $R^2 = 0.99$ ) gave even better fits. The rate of polymerization varied in proportion to the total surface area of the particles ( $a = -7.11 \times 10^{-4}$ ;  $b = 1.14 \times 10^{-3}$ ; confidence  $R^2 = 0.97$ ). However, the power equation ( $a = 1.75 \times 10^{-3}$ ;  $b = 0.93$ ; confidence  $R^2 = 0.98$ ) and the exponential equation ( $a = 0.14$ ;  $b = 2.67 \times 10^{-3}$ ; confidence  $R^2 = 0.99$ ) gave even better fits. Thus, these data were insufficient to distinguish between the proportionality of the rate of polymerization to the number of particles or the overall particle surface area. Probably, the range of variation of the monomer/polymer ratio was insufficient to distinguish definitively between the two proportionalities. Therefore, it is concluded that the results are either in accord with Smith-Ewart case 2 or deviate positively from it.

Figure 5 shows the variation of grafting efficiency [ie, the fraction of the styrene/acrylonitrile mixture grafted to the polybutadiene seed particles; earlier designated as "maximum grafting efficiency"<sup>12</sup>] with monomer/polymer ratio (lower curve) as well as that of the "grafting density" (ie, the amount of poly(styrene-co-acrylonitrile) grafted to the polybutadiene seed particles based

TABLE VI  
Overall Rate of Polymerization and Kinetic Parameters  
(*t*-butyl hydroperoxide; 3% Igepal CO-990; 35°C)

Sample	M/P	$R_p$ (%/min)	$N$ ( $\times 10^{-15}$ )	$S$ ( $m^2/dL$ )
BHP-B35-40	50/50	0.73	2.73	611
BHP-B35-46	60/40	0.51	2.17	484
BHP-B35-44*	70/30	0.40	1.63	363
BHP-B35-45*	85/15	0.23	0.82	185

Equation		$a$	$b$	$R^2$
<u>Overall Rate of Polymerization with Number of Particles</u>				
Linear	$y = a + bx$	$9.93 \times 10^{-4}$	$2.54 \times 10^{-16}$	0.97
Power	$y = ax^b$	$4.17 \times 10^{-15}$	0.92	0.98
Exponential	$y = ae^{bx}$	0.14	$5.95 \times 10^{-16}$	0.99
<u>Overall Rate of Polymerization with Total Surface Area</u>				
Linear	$y = a + bx$	$-7.11 \times 10^{-4}$	$1.14 \times 10^{-3}$	0.97
Power	$y = ax^b$	$1.75 \times 10^{-3}$	0.93	0.98
Exponential	$y = ae^{bx}$	0.14	$2.67 \times 10^{-3}$	0.99

\* Acetone dispersible.

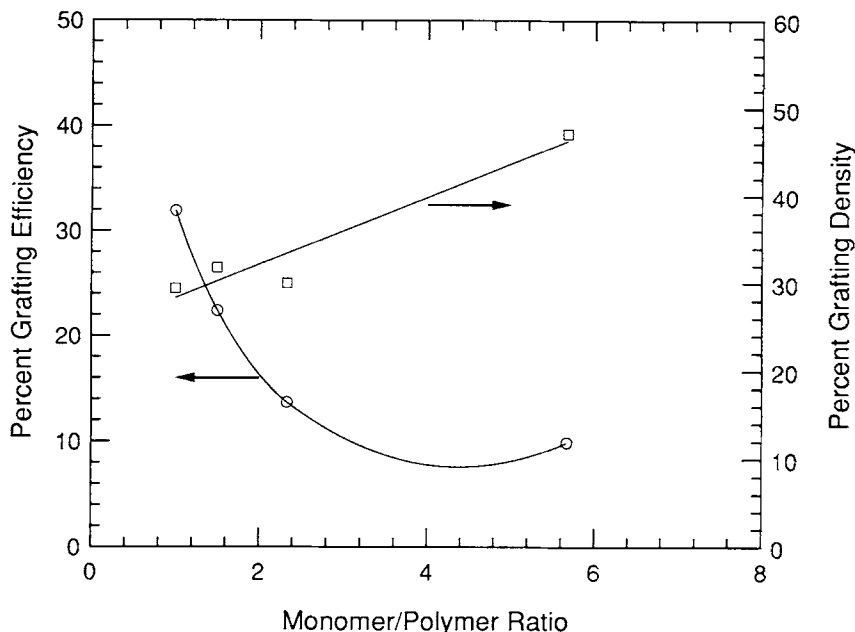


Fig. 5. Variation of grafting efficiency (percent of second-stage monomer grafted onto polybutadiene seed latex) and grafting density (percent of second-stage monomer grafted onto polybutadiene seed latex based on polybutadiene seed) with monomer/polymer ratio.

on polybutadiene seed) (upper curve). The grafting efficiency decreased with increasing monomer/polymer ratio because the lower the monomer concentration in the particles, the greater was the probability of hydrogen abstraction as opposed to propagation. In contrast, the grafting density increased with increasing monomer/polymer ratio because the proportion of polybutadiene seed decreased with increasing monomer/polymer ratio, resulting in a greater amount of grafted copolymer based on a smaller amount of polybutadiene seed. These results were consistent with the theoretical models of Rosen<sup>12</sup> and Brydon et al.<sup>13,14</sup> for the grafting of styrene onto polybutadiene in solution polymerization, and that of Sundberg et al.<sup>14</sup> for the grafting of styrene onto polybutadiene latex in emulsion polymerization.

Figure 6 shows that increasing the monomer/polymer ratio gave thicker poly(styrene-*co*-acrylonitrile) shells around the polybutadiene cores as well as spherical inclusions of poly(styrene-*co*-acrylonitrile) inside the particles. The thicker poly(styrene-*co*-acrylonitrile) shells formed at the higher monomer/polymer ratios would hinder the diffusion of the monomer out of the swollen seed latex particles, resulting in domain formation within the particles. The freeze-dried latex powders were dispersible in acetone for monomer/polymer ratios of 70/30 or greater, indicating that, in these samples, the poly(styrene-*co*-acrylonitrile) formed a continuous concentric high  $T_g$  shell around the low  $T_g$  polybutadiene core, which prevented the particles from coalescing during the freeze-drying process. Figure 6 confirmed this morphology. The grafted poly(styrene-*co*-acrylonitrile) chains which gave dispersibility in acetone would also disperse and stabilize the particles in a poly(styrene-*co*-acrylonitrile) matrix.

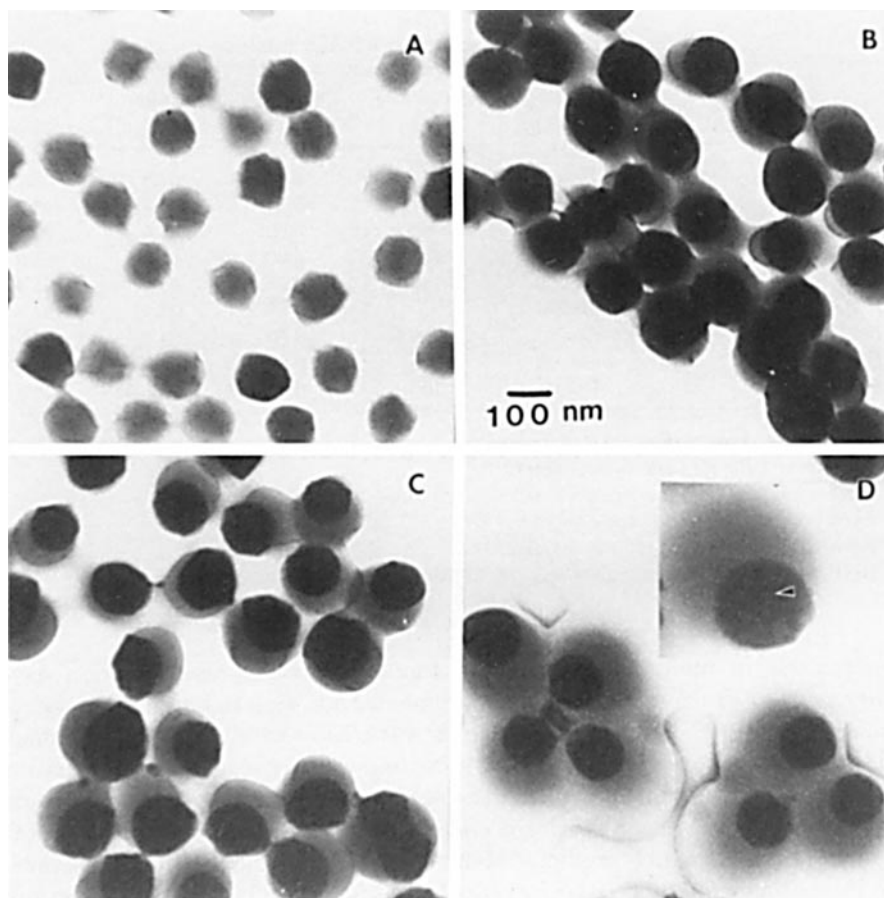


Fig. 6. Transmission electron micrographs showing the effect of increasing monomer/polymer ratio on the morphology of two-stage poly(styrene-co-acrylonitrile)-polybutadiene core-shell latex particles stained with osmium tetroxide: (A) 50/50; (B) 60/40; (C) 70/30; (D) 85/15.

### Effect of Mode of Addition of Monomer and Initiator

Two modes of initiator addition were used: (1) in the batch polymerizations, increments of the cumene or *t*-butyl hydroperoxide and sodium formaldehyde sulfoxylate dihydrate were added at predetermined intervals during the polymerization, which simulated continuous initiator addition; (2) in the semicontinuous polymerizations, the cumene or *t*-butyl hydroperoxide was added continuously in monomer solution, and the sodium formaldehyde sulfoxylate dihydrate was added at the beginning of the polymerization and at the end of the monomer addition period. Table VII shows the results of these different modes of addition at polymerization temperatures of 35, 50, and 70°C. The continuous addition of the cumene or *t*-butyl hydroperoxides in monomer solution in the semicontinuous polymerizations gave a slower initial polymerization rate than the incremental addition in the batch polymerizations because the monomer concentration in the particles at any given time was lower in the semicontinuous polymerizations; however, the final conversions after about 5 h were about the same. At 50 and 70°C, the continuous addition of the cumene or *t*-butyl hy-

TABLE VII  
Effect of Mode of Monomer and Initiator Addition

Sample	<i>T</i> (°C)	Mode of addition	Duration (min)	[BHP] <sup>a</sup> (%)	Conv (%)	Grafting (%)
BHP-B70-10 <sup>b</sup>	70	Batch	<sup>c</sup>	0.17	93.8	38.2
BHP-C70-2 <sup>b</sup>	70	Cont.	100	0.17	94.3	45.0
BHP-C50-2 <sup>d</sup>	50	Cont.	80	0.60	97.0	21.6
BHP-C50-3 <sup>d</sup>	50	Cont.	100	0.60	92.0	21.3
BHP-C50-4 <sup>d</sup>	50	Cont.	135	0.60	95.0	33.6
BHP-B50-62 <sup>e</sup>	50	Batch	<sup>f</sup>	0.60	96.7	54.5
BHP-C50-50 <sup>e</sup>	50	Cont.	100	0.60	94.0	46.5
BHP-C35-2R <sup>d</sup>	35	Cont.	70	0.60	94.6	21.8
BHP-C35-2 <sup>d</sup>	35	Cont.	100	0.60	95.6	27.7

<sup>a</sup> *t*-Butyl hydroperoxide based on monomer.

<sup>b</sup> Seed latex PBu-850; 160 nm diameter.

<sup>c</sup> BHP added in equal increments at 0, 30, 60, 90 min.

<sup>d</sup> Seed latex PBu-730; 242 nm diameter.

<sup>e</sup> Seed latex PBu-850-1; 160 nm diameter.

<sup>f</sup> BHP added in equal increments at 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 min.

droperoxides in monomer solution in semicontinuous polymerization gave higher grafting efficiencies than the incremental addition in batch polymerization; at 35 and 50°C, the grafting efficiency was greater with the longer monomer addition times. The grafting efficiency increased with increasing polymerization temperature for the same polybutadiene seed latex and initiator concentration. These results are in accord with the earlier models of grafting of monomers to polybutadiene,<sup>13,14</sup> which predicted that the grafting efficiency should decrease with increasing monomer/polymer ratio. In this work, the batch polymerizations would have a higher monomer/polymer ratio than the semicontinuous polymerizations at most conversions, and the grafting efficiency would be lower. The semicontinuous polymerizations would have a lower monomer/polymer ratio at most conversions, and the grafting efficiency would be higher; moreover, a slower rate of monomer addition would give a lower monomer/polymer ratio at any given conversion and thus a higher grafting efficiency. This was confirmed experimentally by the results given in Table VII.

## CONCLUSIONS

In the batch or semicontinuous polymerization of 80/20 (w/w) styrene/acrylonitrile mixtures in polybutadiene seed latexes using the cumene or *t*-butyl hydroperoxide/sodium formaldehyde sulfoxylate dihydrate/EDTA-chelated Fe<sup>+2</sup> redox initiator, the rate of polymerization was controlled by the incremental or continuous addition of the hydroperoxide. The use of 3% Igepal CO-990 emulsifier at 35°C, or 6% at 50 or 70°C, gave stable latexes with low levels of coagulum and no secondary particle generation. There were no significant differences between the cumene and *t*-butyl hydroperoxides in terms of the rate of polymerization, particle morphology, and grafting efficiency of the styrene/acrylonitrile mixture on the polybutadiene core. However, *t*-butyl hydroperoxide showed 2 qualitative advantages over cumene hydroperoxide:

(1) it had a higher solubility in water, making it more convenient to add in aqueous solution; (2) it gave a lower residual odor in the final latex. The mode and rate of monomer and initiator addition determined the rate of polymerization, the amount of coagulum, and the grafting efficiency. Slower monomer addition rates gave higher grafting efficiencies. Higher polymerization temperatures gave higher grafting efficiencies, but also increased amounts of coagulum. The grafting was an interfacial process: the grafting efficiency increased with decreasing particle size of the polybutadiene seed latex and decreasing monomer/polymer ratio. Poly(styrene-co-acrylonitrile) inclusions were formed inside the polybutadiene core at higher monomer/polymer ratios. The freeze-dried latexes prepared with monomer/polymer ratios of 70/30 or higher were dispersible in acetone.

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