

Dispersion Copolymerization of Styrene and Divinylbenzene. II. Effect of Crosslinker on Particle Morphology

B. THOMSON, A. RUDIN,* and G. LAJOIE

Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

SYNOPSIS

The amount of divinylbenzene (DVB) that can be incorporated in a one-shot dispersion copolymerization with styrene to form a coagulum-free latex is low (<0.5%), a consequence of steric stabilizer immobilization and the inability of the system to provide sufficient quantities of new stabilization materials. Inclusion of a polystyrene solvent in the charge and/or addition of excess stabilizer shortly after the nucleation period enables 0.7% to be inserted, and up to 1% DVB can be copolymerized successfully by linear addition over the major particle growth period. Immobilization of some adsorbed stabilizer chains results in deviations from sphericity. Microparticles ranging from classic smooth-surfaced spheres at low DVB concentrations to node covered cups and heavily dented spheres at higher levels, can be synthesized. Furthermore, batch addition of 1–6% DVB at least 7 h after nucleation produces monodisperse, stable latexes comprising particles bearing deformities due, not to graft immobilization, but to phase separation within the crosslinked particle skin that forms after DVB absorption. Lower amounts of divinyl monomer batch added before the 7-h mark permits synthesis of a variety of spheroidal and pod-shaped microparticles. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The goal of our present research is the development of new routes for the synthesis of polystyrene (PS) based materials for biochemical separations and solid phase peptide synthesis. To this end, the relatively little used technique of dispersion polymerization was selected, primarily because it allows the production, in a single reaction, of monodisperse latexes with diameters in the desired 5–10 μm range. The mechanism of the dispersion polymerization of styrene in ethanol with poly(vinyl pyrrolidone) (PVP) as steric stabilizer was detailed elsewhere,^{1–7} but the factors relevant to this discussion are that particle growth is radial and that stabilization occurs via adsorption of graft PVP–PS copolymer. There are two problems with the dispersion process germane to the production of materials for use as separation/support

media. First, until recently, only a very small amount of the crosslinker divinylbenzene (DVB) could be incorporated to form a stable latex, and second, the radial mode of particle growth precludes, for the moment, the direct synthesis of macroporous particles. It does, however, provide an opportunity to control the integration of comonomer during the synthesis. The problems concerning inadequate crosslinking were addressed and overcome in this laboratory, opening up the possibility of easily synthesizing a range of latexes in which control can be exercised over particle crosslink density. For insoluble beads it is clear that a uniform distribution of crosslinks is a desirable trait, translating to improved mechanical strength and consistent swelling properties. Moreover, once stability is assured, the dispersion method enables latexes composed of uniquely shaped particles to be made. Morphology is sensitive not only to the absolute level of DVB, but also to the time and duration of its delivery. Accordingly, the morphologies resulting from polymerizations in which the crosslinker is all present in the charge, added linearly over a long period, and batch

* To whom correspondence should be addressed.

Table I One-Shot Dispersion Copolymerizations of Styrene and DVB

Reaction	Charge ^a		Postnucleation Addition ^b (g PVP/g EtOH/g Solvent)	Product		Coagulum	Particle Shape ^c
	DVB	Solvent		d50	GSD		
DISP683	0.3	—	—	4.88	1.02	None	Sphere
DISP657	0.4	—	—	5.18	1.02	Tiny	Knobbly sphere
DISP636	—	—	(10/30/0) at 30 min	4.82	1.02	None	Sphere
DISP661	0.5	—	(5/15/0) at 30 min	5.19	1.02	Med-large	Cup (lava surface)
DISP668	0.5	—	(10/30/0) at 15 min				
180 min				3.22	1.02		Apple
420 min				4.45	1.02		Cup (flowerlike)
600 min				4.64	1.02		Cup (lava surface)
Product				4.78	1.02	Tiny	Cup (lava surface)
DISP449	0.5	20 (DMF)	—	8.63	1.03	None	Sphere
DISP630	0.6	20 (DMF)	(10/30/2.22) at 30 min	7.61	1.03	None	Cup (small nodes)
DISP391	0.6	20 (toluene)	—	7.89	1.03	None	Sphere
DISP676	0.7	20 (toluene)	(10/30/2.22) at 30 min				
120 min				4.24	1.03		Sphere
300 min				5.81	1.03		Smooth cup
600 min				7.15	1.03		Cup (small nodes)
Product				7.82	1.03	None	Cup (large nodes)

^a 25% styrene, 7.2% PVP, 2.5% AIBN, remainder ethanol.

^b Time zero corresponds to point of initiator solution addition; solutions warmed to 70°C before addition.

^c From SEM examination.

added several hours after nucleation, are presented and discussed with specific regard to the role played in their formation by the adsorbed steric stabilizer.

EXPERIMENTAL

Reagents

Styrene, DVB (55% mixture of meta and para isomers), and PVP (MW 40,000) were obtained from Aldrich, 2,2'-azobisisobutyronitrile (AIBN) was from Pfaltz & Bauer, ethyl alcohol was from Commercial Alcohols Ltd., and all were used as received. In the upcoming text, styrene concentration is expressed as weight percent of total charge, and AIBN, PVP, DVB, and PS solvent levels as weight percent of styrene.

Synthesis

Polymerizations were carried out in a 1-L glass kettle equipped with a nitrogen inlet, a stirrer (four-bladed, metal), and "sealed" with a Teflon gasket. In all reactions, the total charge weight, including initiator solution, was 400 g. The kettle was suspended in a water bath maintained at 70°C by an immersion circulator. In a typical procedure, the charge was

stirred (85 rpm) under nitrogen for 30 min before batch adding the initiator solution. Stirring was reduced to 60 rpm a few minutes after nucleation and maintained at that level for the remainder of the reaction; the rate was raised briefly for DVB batch additions. Polymerizations were run for about 22 h before cooling; latexes containing coagulum were filtered through cheesecloth. In syntheses requiring the slow (i.e., rates ≤ 1 mL/min) delivery of DVB solutions, a syringe pump (Sage Instruments) was employed. Each crude product latex was dried and stored as a fine white powder after the supernatant was changed twice by settling.

The recipe used to synthesize the lightly cross-linked latex DISP669 is as follows. Charge: 75 g styrene, 6.7 g PVP, 270.8 g ethanol. Initiator solution: 25 g styrene, 20 g ethanol, 2.5 g AIBN. DVB solution: 1.82 g DVB (1%), 41.61 g ethanol (55 mL), pumped in over 615 min. Details of reagent levels for all latexes are listed in Tables I, II, and III.

Particle Size Measurement

Diameters were measured using a 256-channel Coulter Counter Multisizer (Coulter Electronics), fitted with a tube containing a 30- μ m diameter orifice and calibrated with standard 5.11- μ m particles

Table II Dispersion Copolymerizations of Styrene and DVB in Which Crosslinker Is Added Slowly

Reaction	Charge ^a		Postnucleation DVB addition ^b	Product ^c		
	PVP	DVB		d50	GSD	Particle Shape
DISP642	6.7	—	0.5% over 615 min (55 mL), from 0 min	4.88	1.02	Sphere
DISP660	6.7	—	0.6% over 615 min (55 mL), from 0 min	4.84	1.02	Sphere
DISP578	6.7	—	0.68% over 615 min (55 mL), from 0 min	4.96	1.02	Slightly dented sphere
DISP658	6.7	—	0.9% over 615 min (55 mL), from 0 min	4.89	1.02	Sharply dented sphere
DISP669	6.7	—	1.0% over 615 min (55 mL), from 0 min	4.95	1.02	Heavily dented sphere
DISP384	7.2	0.2	0.3% over 506 min (60 mL), from 60 min	4.98	1.02	Sphere
DISP385	7.2	0.2	0.45% over 506 min (60 mL), from 60 min	4.94	1.02	Sphere
DISP386	7.2	0.2	0.6% over 507 min (60 mL), from 60 min	4.98	1.02	Slightly dented sphere
DISP405	7.2	0.2	0.8% over 513 min (60 mL), from 60 min	4.97	1.02	Heavily dented sphere

^a 25% styrene, 2.5% AIBN, remainder ethanol.

^b Time zero corresponds to point of initiator solution addition.

^c All products are coagulum free, except DISP405, where the amount is tiny.

provided by Coulter. The instrument was connected to a personal computer and analysis of the distributions employed software written by the authors. Many of the particles synthesized in this project are nonspherical, and the listed diameter should be considered as a gross size indicator, rather than an exact measurement. The Coulter Counter operates on the principal of volume displacement, that is, the volume of electrolyte shifted as a particle passes through the orifice is electronically sensed and assumed in the subsequent calculation that results in a diameter, to represent a spherical object.⁸

Scanning Electron Microscopy (SEM)

Two drops of 5 wt % ethanol dispersions were applied to clean aluminum stub surfaces, dried in under vacuum at ambient temperature overnight, then sputter coated with gold. The instrument used was a Hitachi S-570 SEM.

Extraction

Between 4 and 5 g of dry latex powder was weighted into a cellulose thimble. The sample was then extracted with toluene in a Soxhlet apparatus for 22–24 h. The gel remaining in the thimble was added to 200 mL of ethanol, then filtered, washed with ethanol, dried, and weighed.

RESULTS AND DISCUSSION

One-Shot Copolymerizations

In a one-shot dispersion copolymerization (i.e., with all reagents present in the homogeneous reaction mixture at the point of initiation), the level of DVB that can be incorporated to produce a stable latex is limited, under our conditions, to 0.4%. The reason for this lies in the nature of the stabilization mechanism. PVP–PS graft copolymer forms in the continuous phase of the reaction mixture and is subsequently adsorbed by particle surfaces, forming an antioalescence barrier. Incorporation of DVB, as a pendant vinyl group (PVG), in the hydrophobic PS arms of some of the new chains is an event that cannot be avoided if particle cores are to be rendered at least partially insoluble. This dangling vinyl unit remains at large until further reaction with a growing chain in the region of the particle subsurface. When this occurs, the ability of the adsorbed chain to act as an effective steric stabilizer is eventually compromised, because the reaction irreversibly links the PVP–PS chain to the bulk particle PS–DVB phase. Once freedom of movement has been restricted in this way and graft can no longer migrate with the advancing surface, it becomes redundant and unless it is replaced by fresh material from the continuous phase, the particle becomes unstable. Furthermore, graft production decreases with reaction time as (1) styrene and PVP levels fall and (2) rising medium polarity increasingly directs both monomer and any

Table III Dispersion Copolymerizations of Styrene and DVB in Which DVB Is Batch Added after Nucleation

Reaction	Charge ^a		Postnucleation DVB Addition ^b	Product		Particle Shape
	PVP	Other		d50	GSD	
DISP700	6.7	—	0.2% at 300 min	4.89	1.02	Sphere
DISP694	6.7	—	0.4% at 200 min	4.89	1.02	Spheroid
DISP690	6.7	—	0.4% at 300 min	4.71	1.02	Spheroid
DISP670	6.7	—	0.4% at 420 min	4.87	1.02	Sphere
DISP684	6.7	—	0.5% at 420 min	4.86	1.02	Sphere pod
DISP691	6.7	—	0.6% at 300 min	4.80	1.02	Deformed pod
DISP656	6.7	—	0.6% at 420 min	5.11	1.02	Pod
DISP687	6.7	—	0.6% at 420 min	4.78	1.02	Pod
DISP688	6.7	—	0.7% at 420 min	4.74	1.02	Pod
DISP705	6.7	—	0.7% at 420 min			
420 min				4.34	1.02	Sphere
480 min				4.49	1.02	Sphere
540 min				4.57	1.02	Sphere
600 min				4.61	1.02	Sphere
660 min				4.63	1.02	Sphere (wrinkled surface)
Product				4.66	1.02	Pod
DISP706	6.7	^c	0.7% at 420 min	5.39	1.03	Heavily dented spheres
DISP689	6.7	—	0.8% at 420 min	4.81	1.02	Pod
DISP693	6.7	—	0.9% at 420 min	4.75	1.04	Pods/deformed pods/severely deformed spheres
DISP697	6.7	—	1% at 200 min	Reaction failed		
DISP699	6.7	—	1% at 300 min	Reaction failed		
DISP675	6.7	—	1% at 420 min			
420 min				4.39	1.02	Sphere
480 min				4.55	1.02	Sphere
600 min				4.69	1.02	Slightly dented sphere
Product				4.98	1.02	Severely deformed sphere
DISP710	10.05	—	1% at 420 min	4.59	1.02	Deformed sphere
DISP698	13.4	—	1% at 420 min	4.07	1.02	Sphere
DISP693	6.7	20 (toluene)	1% at 420 min	Reaction failed		
DISP695	6.7	20 (water)	1% at 240 min	3.35	1.04	Deformed sphere
DISP702	6.7	^c	1% at 420 min	5.01	1.02	Severely deformed sphere
DISP707	6.7	0.3% DVB	1% at 420 min	4.90	1.02	Deformed sphere
DISP663	6.7	—	1% at 540 min	5.32	1.02	Sphere
DISP611	6.7	—	1% at 615 min	5.02	1.02	Sphere
DISP701	6.7	—	2% at 420 min	4.89	1.02	Sphere with large dimples
DISP709	13.4	—	2% at 420 min	4.13	1.02	Sphere with a few large dimples
DISP673	6.7	—	2% at 540 min	4.87	1.02	Sphere with large dimples
DISP703	6.7	—	6% at 420 min	5.05	1.10	Sphere with many small dimples
DISP674	6.7	—	6% at 540 min	5.25	1.02	Sphere with many small dimples

^a 25% styrene, 2.5% AIBN, remainder ethanol.

^b Time zero corresponds to point of initiator solution addition; DVB mixed with 10 g EtOH.

^c 0.41% DVB slow added over first 420 min of polymerization.

solution generated PS oligoradicals toward the particle phase. These trends hinder the replacement of ineffective adsorbed PVP-PS and, unless decisive action is taken to raise graft levels (e.g., by adding excess PVP soon after nucleation), existing particles begin to destabilize. The more DVB present initially, the more likely it is that graft is “contaminated” with copolymerized DVB, and the sooner coagulation commences. Finally, it should be evident that the consequences of DVB incorporation in the graft become critical over a relatively short time interval as a portion of the chains protecting a stable particle are immobilized, thus placing a “sudden” demand for additional stabilizer that outstrips the capacity of the system to supply it. With $\leq 0.3\%$ DVB in the charge, spherical particles result; at levels $\geq 0.5\%$, one can expect massive coagulation within a few hours. A scanning electron micrograph of a latex made with 0.4% DVB in the charge is shown in Figure 1(a), revealing the particle shape to be that of a knobbly sphere.

The absolute quantity of DVB tolerated in a one-shot copolymerization can be increased in two ways. In the first, the number of PS chains in the system is increased by addition of a chain transfer agent or by inclusion of a solvent for PS in the charge. The latter operates by raising continuous phase solvency for PS, shifting the polymerization locus away from the particle phase and into solution, where the average length of chains is decreased, which is a result of increased termination probability. Clearly, these are unsatisfactory remedies, as the increased amount of DVB incorporated is simply distributed over a greater number of chains: this is equivalent to raising the initiator concentration.

The alternative route involves adding excess PVP to the reaction mixture shortly after the nucleation period, which raises the supply of graft copolymer, permitting particles that would otherwise coagulate to remain stable. This option allows only a slight increase in added DVB (to 0.5%, see Table I), but endows the particles with an unusual morphology. For example, a routine polymerization with 0.5% DVB in the charge will fail completely; but by adding 10 g PVP 15 min after initiation, a stable latex is obtained. Figure 1(d) illustrates the shape of the particles from such a polymerization, perhaps best described as possessing a lavalike surface texture. The remaining two micrographs in Figure 1 document the formation of this shape, showing samples taken from the pot after 3 and 7 h of reaction. At the 3-h mark, particles look like apples, being smooth-surfaced and spherical, except for a single small dimple [Fig. 1(b)]. Four hours later [Fig. 1(c)],

this lone indentation is still visible but the entire surface has now been distorted to leave particles with an uneven, lumpy aspect; when viewed down the cup axis, they resemble flowers in bloom. Continued reaction sees the underlying cup shape partially engulfed and the surface becoming slightly smoother, giving the final lava texture. In polymerization DISP661, only 5 g of PVP was added to the reaction mixture after nucleation—not sufficient to prevent formation of a significant amount of coagulum—but the product is monodisperse and composed of lava coated cups. The control reaction (DISP636), in which 10 g of steric stabilizer was added to a styrene homopolymerization, yielded a monodisperse distribution of microspheres, conclusive proof that the excess stabilizer is not itself responsible for the surface distortions, but merely allows particles to remain dispersed.

Particle diameter increases markedly with the inclusion of a PS solvent in the charge.⁷ Otherwise, the beads produced are normal smooth-surfaced spheres as illustrated in Figure 2(a) for a latex synthesized with 0.5% DVB and 20% DMF in the initial reagent mixture. With 20% toluene present, polymerizations with both 0.5 and 0.6% DVB succeed, giving spherical particles, but the reaction fails with 0.7%. However, by adding 10 g of PVP after 30 min, the 0.7% product is coagulum free (DISP676), and consists of nonspherical microparticles [Fig. 2(d)]. The underlying cup configuration is very clear here, but this time the secondary structure comprises distinct bumps of uneven dimension dotted over the entire surface, with the exception of the inner cup walls; a very small number of spheres (3–4 μm) are also present. The development of this strange morphology was tracked by sampling the reaction mixture 2, 5, and 10 h after initiation. Electron micrographs of the latter two samples are shown in Figure 2(b) and (c); particles are spherical and monodisperse after 2 h (Table I).

The nonspherical particles typifying dispersion latexes with a high charge DVB content were observed previously. Tseng et al.² described them as “mortarlike,” but advanced no ideas on their formulation; Ober⁹ thought the shape to be indicative of deswelling, suggesting to him that “only surface crosslinking is taking place in the particles.” We believe this notion to be irreconcilable with dispersion kinetics and growth mechanisms; the beads are not deswollen, but deformed. With reference to polymerizations DISP668 and DISP676, we now present our view of the processes responsible for cup creation. The key factor is the level of DVB in the charge; above 0.5%, under our conditions, cups can

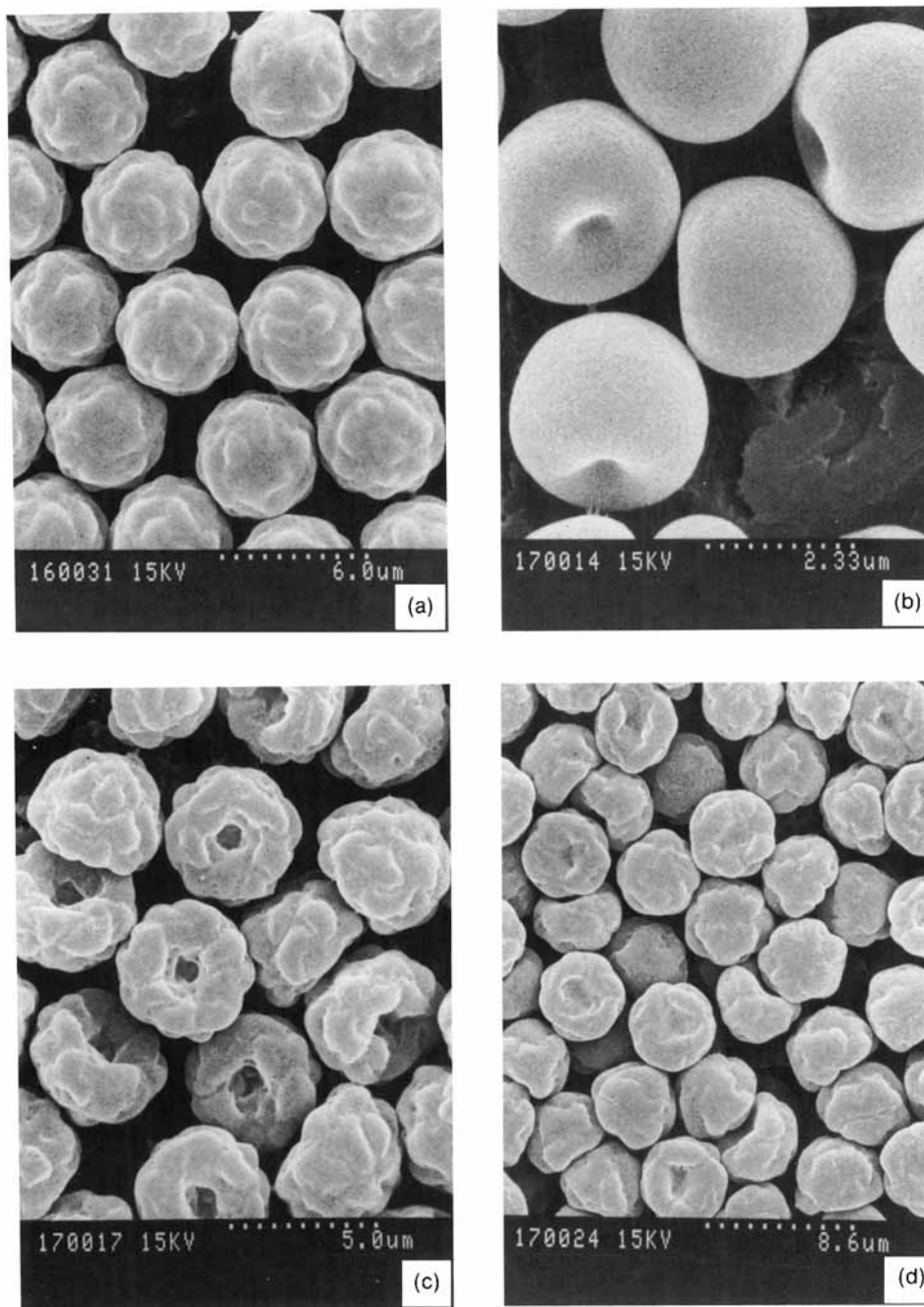


Figure 1 Scanning electron micrographs of dispersion polymerized latexes. Clockwise from top left: (a) DISP657, 0.4% DVB in the charge; (b) DISP668 (180 min); (c) DISP668 (420 min); (d) DISP668, 0.5% DVB in charge, 10 g PVP at 15 min.

form. As a crosslinked network begins to develop within each growing microsphere, the opportunity exists for some of the adsorbed stabilizer chains to join this structure, provided they have a PVG in their PS arm. In other words, some of the graft chains become physically linked to one another via

the bulk particle PS-DVB phase. In this situation, radial growth cannot be sustained indefinitely and the particle must either distort in some way to counter the effect of the linked PVP chains, or begin to destabilize. Deformation commences with the appearance of a small dimple on the surface, repre-

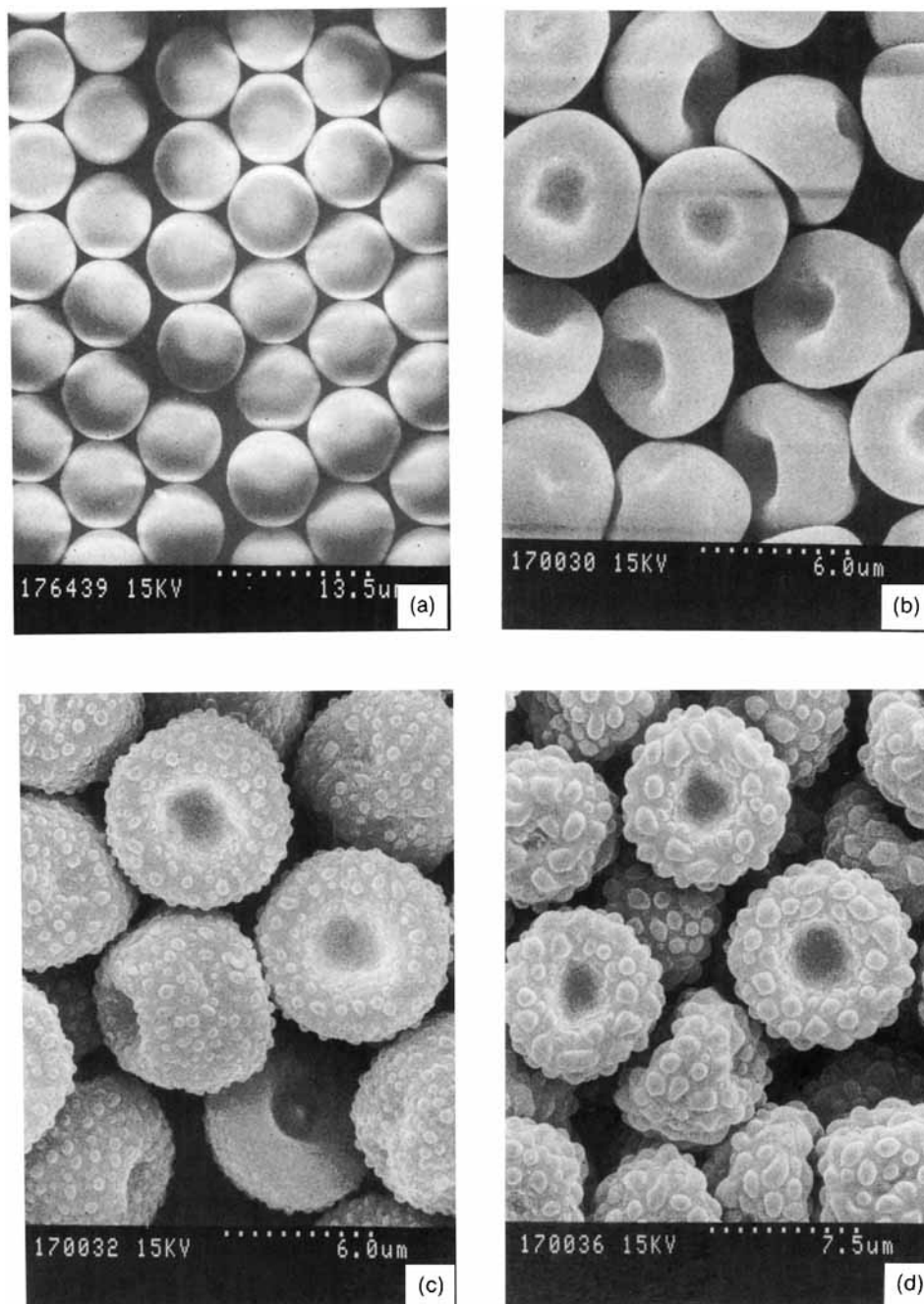


Figure 2 Scanning electron micrographs of dispersion polymerized latexes. Clockwise from top left: (a) DISP456, 0.5% DVB and 20% DMF in charge; (b) DISP676 (300 min); (c) DISP676 (600 min); (d) DISP676, 0.7% DVB and 20% toluene in the charge, 10 g PVP added at 30 min.

senting the location of an immobilized graft chain that finds itself at a “fixed” distance from a similar chain on the opposite, curved surface of the particle, courtesy of the now “inflexible” portion of the bulk particle network that unites them. The observation

of a single morphology at this stage, coupled with the improbability that the first graft chains to be immobilized in each microparticle are diametrically opposed to one another, leads to the hypothesis that both adsorbed steric stabilizer and bulk polymer are

capable of undergoing considerable reorganization to maintain a symmetrical profile, which minimizes surface exposure to the continuous phase, and to ensure that the direct line between the two locked sites forms the principal axis of the new, balanced particle shape. If this were not the case, then identical particles would not be observed at any stage of the polymerization, and rather than witness the quite remarkable morphological uniformity on display in Figures 1(b) and 2(b), a collection of asymmetric apples and cups would be the likely outcome if particles had no capacity to reshape in response to the constraints imposed by the crippled graft. In both DISP668 and DISP676, this intraparticle redistribution would not on its own be sufficient to uphold colloidal stability, hence the addition of excess PVP soon after nucleation to raise graft production and guarantee bead independence. The occasional smaller indentation also marks the outer surface of some cups [see Fig. 2(a)], and epitomizes graft chains immobilized after the initial redistribution. Growth is heavily restricted along the axial direction of the cup, but continues at angles to it, enhancing the overall contour. After 10 h of reaction [Fig. 2(c)], the cup surface is covered with small nodes of approximately 0.5- μm diameter. These denote regions on the surface protected by the mobile graft, where outward growth is still viable. In the product [Fig. 2(d)], their number is reduced and their shape less regular, indications that some merging has occurred. It should be noted that nodes of DISP676 do not appear on the inner walls of the cup, confirming that this is a region of little or no growth.

Both of these one-shot examples possess the basic cup morphology, but differ in their outer features, presumably a reflection of the different growth mechanisms operating in each case. Medium polarity is higher in DISP668, and the bulk of the propagation reaction takes place within the particle phase, unlike DISP676 where increased medium solvency due to the added toluene dictates displacement of the polymerization locus to the continuous phase. The average number of chains decreases with increasing polarity, limiting the options for mobility as crosslinking occurs. In the less polar instance, growth occurs as existing particles absorb polymeric material produced in the continuous phase, and opportunities for shape preservation rise as the material assimilated can be directed to those regions where expansion is still permitted; the result is a more clearly defined primary structure. The use of dimethylformamide, a more polar PS solvent than toluene, yields cups with smaller surface protuber-

ances, very similar to those pictured in Figure 2(c). By changing experimental conditions slightly, it should be possible to obtain smooth cups as a crude product, that bear a striking resemblance, in gross shape and dimension, to red blood cells.

The knobby sphere morphology (DISP657) lies between that of the lava cup (DISP668) and the common sphere (DISP683). There is insufficient DVB present at the 0.4% level to form cups, so particle sphericity is retained. There is, however, enough crosslinking and immobilization of PVP-PS chains to instigate surface deformation. When graft becomes paralyzed, growth advances around the anchored chains, which then define the boundary of a surface irregularity. One-shot copolymerizations yielding spherical latex particles undoubtedly contain adsorbed PVP-PS that is tied to the bulk particle phase, but deformation does not occur because the gel is insufficiently crosslinked to render it rigid enough to paralyze the graft; it has an elasticity that permits bound chains of the graft enough freedom of movement to maintain their favorable interfacial position delineating a sphere. Note that the large PVP surplus does not induce renucleation in any of the above reactions.

Removal of soluble material from latexes DISP657, 668, and 676 by toluene extraction causes their surface features to disappear, leaving, respectively, relatively smooth-surfaced spheres, relatively smooth-surfaced cups, and smooth cups. Gel contents of one-shot polymerizations containing between 0.5 and 0.7% DVB lie in the 50–60 wt % range. The fact that secondary structural features vanish as a result of this process implies that they are composed of loosely (or even non-) crosslinked PS. This makes qualitative sense; DVB is more reactive than styrene and will tend to be consumed earlier, during the formation of the primary morphology. Secondary features form later, when less crosslinker is available, and therefore should be largely composed of linear polymer. Withdrawal of this component causes the bead contour to retreat to that of the underlying primary morphology.

Slow Addition of DVB

Earlier work from this laboratory⁷ demonstrated that the total amount of DVB that could be successfully dispersion copolymerized with styrene was 1%. This was accomplished by starting the polymerization with 0.2% DVB in the charge and adding the remainder over 510 min, beginning 1 h after initiation; such latexes are denoted 0.2/ x %, where x lies between 0.3 and 0.8%. In a recent modification

of this procedure, we now commence the DVB solution addition at the point of initiation, with no crosslinker present in the charge, and continue pumping for 615 min; at the end of this period, particles have reached approximately 88% of their final volume (Table II). The division between stable (i.e., coagulum free) and unstable latexes for such linear additions occurs at around 1% DVB (Fig. 3). With < 0.65% DVB in the added solution, the synthesized particles are smooth-surfaced spheres, but above this level deviations from sphericity become apparent. Figure 4(a–c) shows SEM images of three latexes made in this way with, respectively, 0.68, 0.9, and 1% DVB. The shallow depressions characterizing the 0.68% sample indicate sites where an adsorbed PVP–PS chain has been immobilized. As already intimated, growth is restricted, or even eliminated altogether, at such locations, but can proceed around them, leaving the mature particle with the observed slightly dented appearance. At 0.9% DVB, particles are marked with noticeably deeper indentations and with 1% added, most possess a single major depression and several smaller ones; morphology is now approaching that of the cup. Lee and coworkers¹⁰ observed a similar morphology after applying a shell, containing a divinyl monomer, to butyl rubber stabilized PMMA particles dispersed in heptane, and speculated that deformation was the result of phase separation (undefined) within the particles. The trend in Figure 4 is clear: as the DVB addition rate is increased, larger deformities result. The deepest indentations develop early in the polymerization; the shallowest features form later. For comparison, a photomicrograph of the 0.2/0.8% latex, DISP405, synthesized during earlier work,⁷ is shown in Figure 4(d). Morphology is essentially the same as the 1% slow-add product, DISP669.

Gel contents of the slow-add latexes made with 0.68–1% DVB added over 615 min lie in the range 60–70 wt %. DISP578 survives the extraction procedure with most particles as either smooth-surfaced spheres or apples; a few have fissures or are otherwise deformed. With more DVB added (DISP669), the particles retain their as-polymerized morphology. The presence of submicron debris is a general feature of extracted one-shot and slow-add latexes synthesized with $\leq 1\%$ DVB; the exceptions are dispersions of the DISP676 type, which are comparatively free of such rubbish. Although the crosslinker was added uniformly during the major growth period of the microspheres, the high initiator level employed means that the huge number of chains generated are not efficiently joined. The relatively low gel fraction problem was overcome by design of a

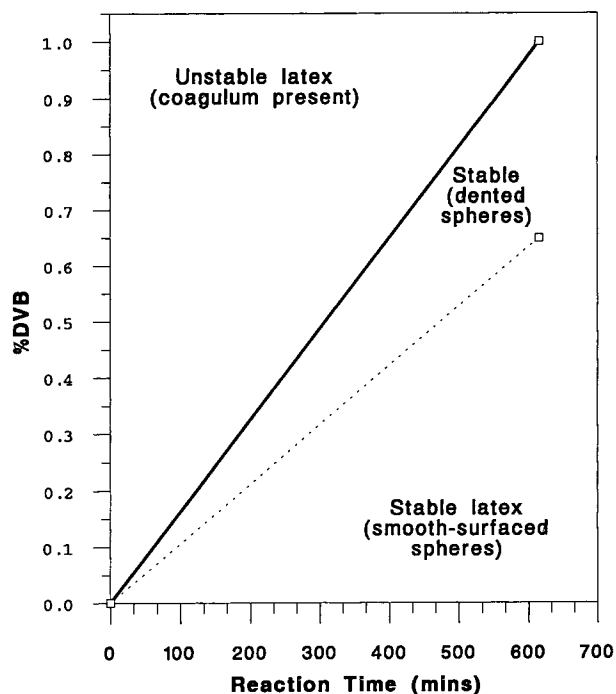


Figure 3 DVB vs. reaction time for slow addition dispersion copolymerizations.

synthetic procedure for production of true core-shell latexes by the dispersion technique, work that will be detailed in the final article of this series.

Comments on Emulsion and Suspension Polymerization Techniques

Before discussing batch addition of DVB, it is beneficial to briefly mention a few of the large number of articles that have appeared in the literature concerned, either directly or indirectly, with the synthesis of nonspherical latex particles. The strategies employed can be grouped under the headings of emulsion and suspension polymerization, with the latter encompassing swelling techniques, such as seeded polymerization, dynamic swelling,¹¹ and two-step swelling.¹²

In surfactant-free emulsion copolymerizations of styrene and DVB, two research groups were able to include up to 10% of the latter by batch¹³ and semicontinuous¹⁴ processes, both of which yielded monodisperse distributions of smooth-surfaced, spherical particles. Synthesis of core-shell latexes by emulsion can lead to distinct morphologies, depending upon several interrelated experimental factors recently reviewed by Rudin.¹⁵ For instance, Matsumoto and colleagues¹⁶ produced particles with a similar outline to the above knobby spheres

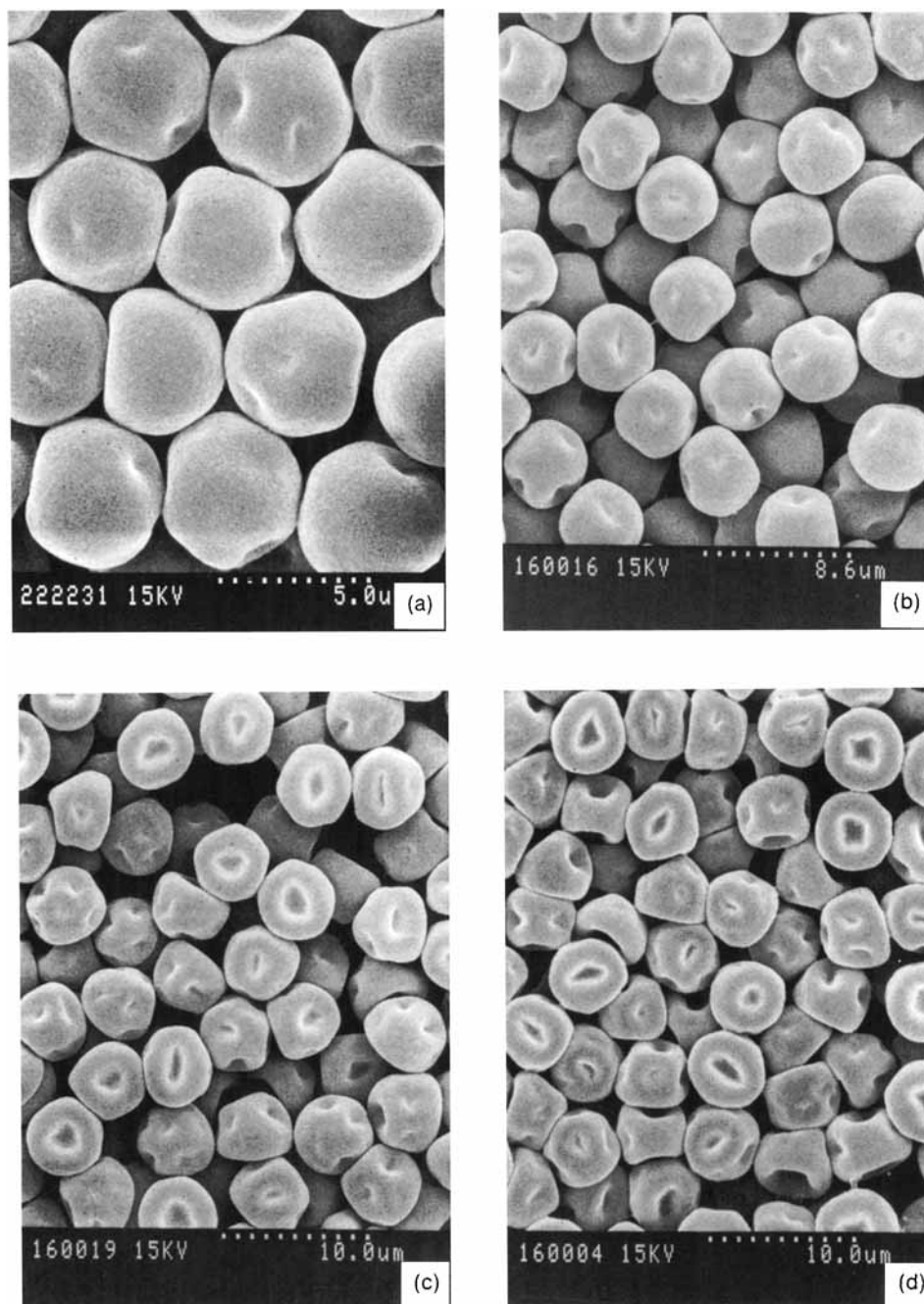


Figure 4 Scanning electron micrographs of dispersion polymerized latexes. Clockwise from top left: (a) DISP578, 0.68% DVB added over 615 min, (b) DISP658, 0.9% DVB added over 615 min; (c) DISP669, 1% DVB added over 615 min; (d) DISP405, 0.2% DVB in the charge, 0.8% added over 513 min, from 60-min mark.

(which they described as “confetti-like”), by seeded emulsion polymerization of styrene in the presence of a poly(ethyl acrylate) seed latex. These particular surface irregularities were proposed to arise from the polymerization of phase separated spherical do-

main of styrene that form near the surface of the seed particles. Emulsion stabilizers tend to be short chain surfactants (added and/or generated *in situ*) that impart stability by orienting appropriately across the polymer/water interface; in “surfactant-

free" reactions utilizing persulfate initiators, stabilization is provided by the ionic chain ends that take up station at this extremity.

Numerous variations on the suspension theme have been implemented to obtain highly crosslinked latexes, macroporous resins, and unusually shaped particles. Here, monomer droplets or monomer-swollen seeds exist as discrete entities prior to polymerization, with stabilization provided by a mixture of conventional surfactants and polymers [e.g., poly(vinyl alcohol) or PVP], the latter operating without grafting *in situ*. In particular, there has been relentless interest¹⁷⁻²¹ in the exploitation of such techniques for the production of macroreticular beads with a narrow size distribution and specific pore size characteristics. The heterogeneous interior native to these particles originates from the aggregation of a huge number of smaller spheres that form early in the polymerization when the lightly crosslinked polymer phase mutates to a lower energy physical state by division.^{22,23} Final surface texture depends on the extent of phase separation occurring during polymerization, which in turn is contingent on the level of crosslinker and diluent present, and can be either smooth or slightly bumpy.²⁴⁻²⁶ However, after the extraction of the soluble material to unplug the pores (those gaps between the multitude of joined microspheres), the fundamental spherical shape remains intact.

Li et al.²⁷ recently reported the suspension copolymerization of *p*-methylstyrene with 1,2-bis(*p*-vinylphenyl) ethane (and its *m* isomer); the vinyl sites of this crosslinker are deconjugated, unlike those of DVB. Spherical macroporous beads with a distinctive cauliflower surface texture were prepared, which compared very favorably with equivalent DVB-based resins as a packing material for size exclusion chromatography. Li and Stöver²⁸ and Hattori et al.²⁹ published article concerning the dispersion polymerization of DVB to obtain relatively uniform distributions of grossly spherical particles. The uneven surfaces peculiar to these insoluble microparticles are a consequence of the proposed growth mechanism involving precipitation of minute scraps of (essentially) poly(DVB) onto existing large particle surfaces. Li and Stöver³⁰ extended this work with their (stabilizer-free) precipitation polymerization of DVB, in which coalescence is thwarted by the inflexibility of particle surfaces. The two-step swelling strategy developed by Ugelstad¹² was employed to produce a variety of pear-shaped microspheres³¹ and particles with a single surface cavity.³² For example, in a PS seed greatly swollen with a hydrophilic monomer, during the subsequent

polymerization the seed polymer is partly excluded from the hydrophilic domain, thus skewing particle shape. In extreme cases, the seed is ejected entirely from the bead, leaving a surface discontinuity. Beautifully shaped symmetric and asymmetric particles (dumbbells, ice-cream cones, eggs, pears) were synthesized by Sheu et al.^{33,34} via seeded copolymerization of supermicron, monodisperse, crosslinked seeds. Heating these distended seeds to the polymerization temperature relaxes polymer chains, bringing about network contraction that causes absorbed material to be displaced, forming an appendage on the original particle. Several experimental parameters were determined to influence the number and size of these new domains, among them, the degree of seed crosslinking, seed diameter, monomer/polymer swelling ratio, polymerization temperature, and the level of DVB in the swelling mixture. Thermodynamically, the relationship between three variables was identified as crucial: the monomer-polymer mixing force, the elastic-retractile force, and the interfacial pressure. The mixing contribution arises from monomer absorption and favors particle expansion; the other components act to limit enlargement. For example, the size of the phase separated region was observed to increase with increasing seed crosslinking (over the 0.2–1.5% DVB range), a trend attributed to earlier network contraction due to shorter relaxation times associated with decreasing seed sol content. In other words, absorbed monomer (and possibly some linear PS) is excluded earlier from the swollen seed, thus allowing a larger phase separated region to form. With very lightly crosslinked seeds (e.g., 0.06% DVB) on the other hand, the unfavorable energy component originating from shrinkage of the network is insufficient to overcome the enhanced mixing contribution, and the particles remain spherical.

Batch Addition of DVB

The third method of introducing crosslinker is a simple batch addition long after the nucleation period. The need for stabilizer diminishes as particles approach maturity, making possible a large increase in the amount of DVB tolerated. The relevant experiments, ranked by DVB level, are listed in Table III. There are several noteworthy trends that emerge from these data and we now discuss these in detail. It is notable that there are no deformities characteristic of immobilized graft among this range of shapes. Such surface features depend on the presence of crosslinker during nucleation or very shortly thereafter. The addition of DVB long after this pe-

riod to a stable population of spheres would not be expected to paralyze graft copolymer because (1) much of the stabilizer required to steady the microspheres is already in place, and (2) even if a PVG-containing graft chain is adsorbed and undergoes further reaction, the odds are that it links to a core PS chain and thus remains mobile. In summary, graft immobilization cannot be implicated as the primary cause of deformation.

Clearly, the late addition of crosslinker is responsible for the listed particle shapes, and the results can be subdivided into two categories reflecting the amount of crosslinker and the time of its addition; we label these “high/late” and “low/early.” Into the first category fall latexes produced by addition of at least 1% DVB at any time from 420 min onward. These particles all possess a spherical outline but are marked by indentations that can leave them as almost smooth-surfaced spheres, with a dimpled texture, or very severely deformed. The second set embraces latexes made with less than 1% DVB added before the 420-min mark, but their constituent particles are inherently nonspherical, ranging from spheroids to deformed pods. The other possible combinations are “low/late” and “high/early,” but as these result, respectively, in microspheres and utter failure, they will not be discussed.

High/Late Latexes

It is known that the level of styrene residing in the particle phase remains low throughout a conventional dispersion polymerization, and it is helpful in contemplating the origin of these unusual forms to think of the growing microspheres as consisting of a hard PS core surrounded by a thin, viscous layer of monomer swollen polymer. As the reaction progresses, both conversion and surface area increase, and the thickness of this soft outer skin will therefore decrease. When the divinyl monomer is added to the pot, it partitions between the solid and continuous phases, the proportion going to each depending on medium polarity (i.e., time of addition). Medium polarity continuously increases with conversion, and it is reasonable to assume partitioning in favor of the particle phase; the exceptions are polymerizations carried out in the presence of PS solvents. Reactive divinyl monomer in a particle subsurface is rapidly converted to PVGs that, after further reaction, disturb the status quo with regard to monomer absorption, that is, a new variable (crosslinked PS) is introduced that can profoundly affect the existing radial growth mechanism.

The generation of a net around the core, and its subsequent tightening as PVGs are consumed, is a nonuniform process; if it were uniform, no deformation would be observed. Uneven crosslinking across the surface provokes phase separation of monomer (and possibly linear PS) from the densest parts of the network into regions where mixing is still thermodynamically favorable. Although monomer and polymer are shifting within the particle skin in response to irregular crosslinking, ejection of these materials into the solution phase does not occur. This sequence of events is loosely related to the experiments of Sheu et al.,^{33,34} but differs in one important respect. Rather than commence with a dead crosslinked seed swollen with monomer, whose subsequent phase separation into an entirely new domain is governed by a mix of factors, the formation of our crosslinked network occurs while the seed is still growing. In other words, the batch addition of DVB to an incomplete dispersion polymerization is a dynamic variation of the same theme and leaves the affected particles, not with clearly defined appendages, but with a unique dented morphology. Even after the core is surrounded by this patchy web of crosslinked PS, the beads are still capable of further outward growth, likely to be concentrated in regions of lowest viscosity (least crosslinked). This, in combination with the effect of external surface pressure and continued crosslinking, reinforces and smoothes the developing surface features.

Adding 1% DVB after 420, 540, and 615 min yields latexes ranging from severely deformed spheres at 420 min [DISP675, Fig. 5(a)] to perfectly smooth spheres at 615 min (DISP 611). In the 540-min product, the beads are spherical but with the merest hint of surface roughness [DISP663, Fig. 5(b)]. Deformation decreases with addition time because the added DVB is dispersed over a greater surface area and concentrated in a thinner surface layer. One hour after the 420-min addition, the latex particles are still round; and after a further 2 h the first surface irregularities appears [Fig. 5(c)]. The particles are still grossly spherical at this point, meaning that considerable deformation occurs over the remaining 12 h of reaction time, when growth is slow (approx. 17 vol % remaining).

At 540 min, particles have reached roughly 86% of their final volume, and batch adding 2–6% DVB increases the number of phase separated regions and decreases their size. At 2% [DISP673, Fig. 5(d)], beads are marked by a few fairly large, circular dents; but at 6% [DISP674, Fig. 6(a)], the dents are smaller and more numerous—the “golf ball” morphology. The more DVB added at a particular time, the

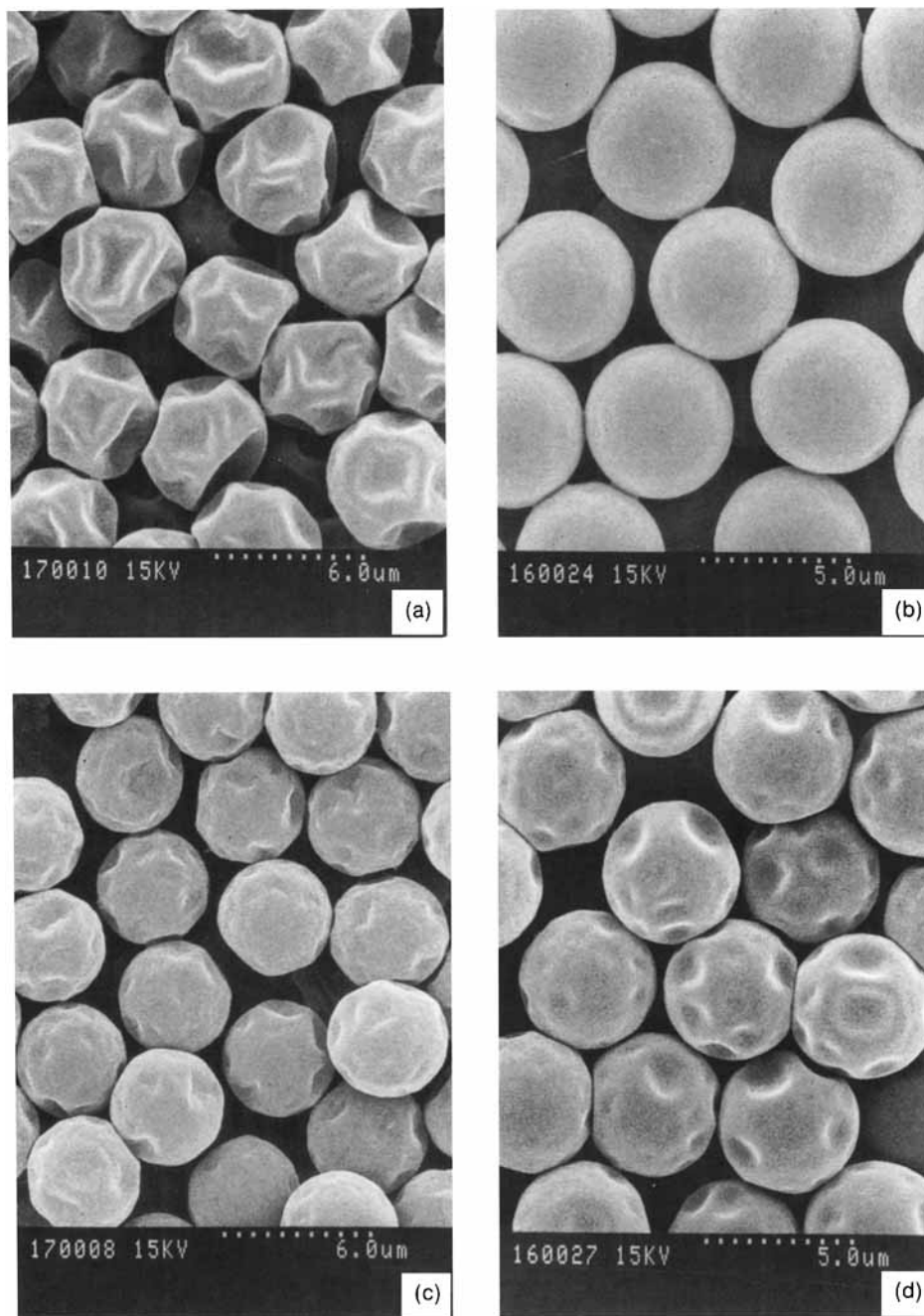


Figure 5 Scanning electron micrographs of dispersion polymerized latexes. Clockwise from top left: (a) DISP675, 1% DVB batch added at 420 min; (b) DISP663, 1% DVB batch added at 540 min; (c) DISP675 (600-min sample); (d) DISP673, 2% DVB batch added at 540 min.

greater the amount that partitions to the particle phase and the more rapid the subsequent crosslinking and phase separation processes within the surface skin of the particles. At 1%, there is just enough crosslinker present to very slightly distort the bead

surface. Repeating the same three experiments, but this time adding the DVB after 420 min, produces a similar trend. At 1%, there is insufficient crosslinker to effectively envelop the core in a network. Crosslinking is therefore very uneven, leading to

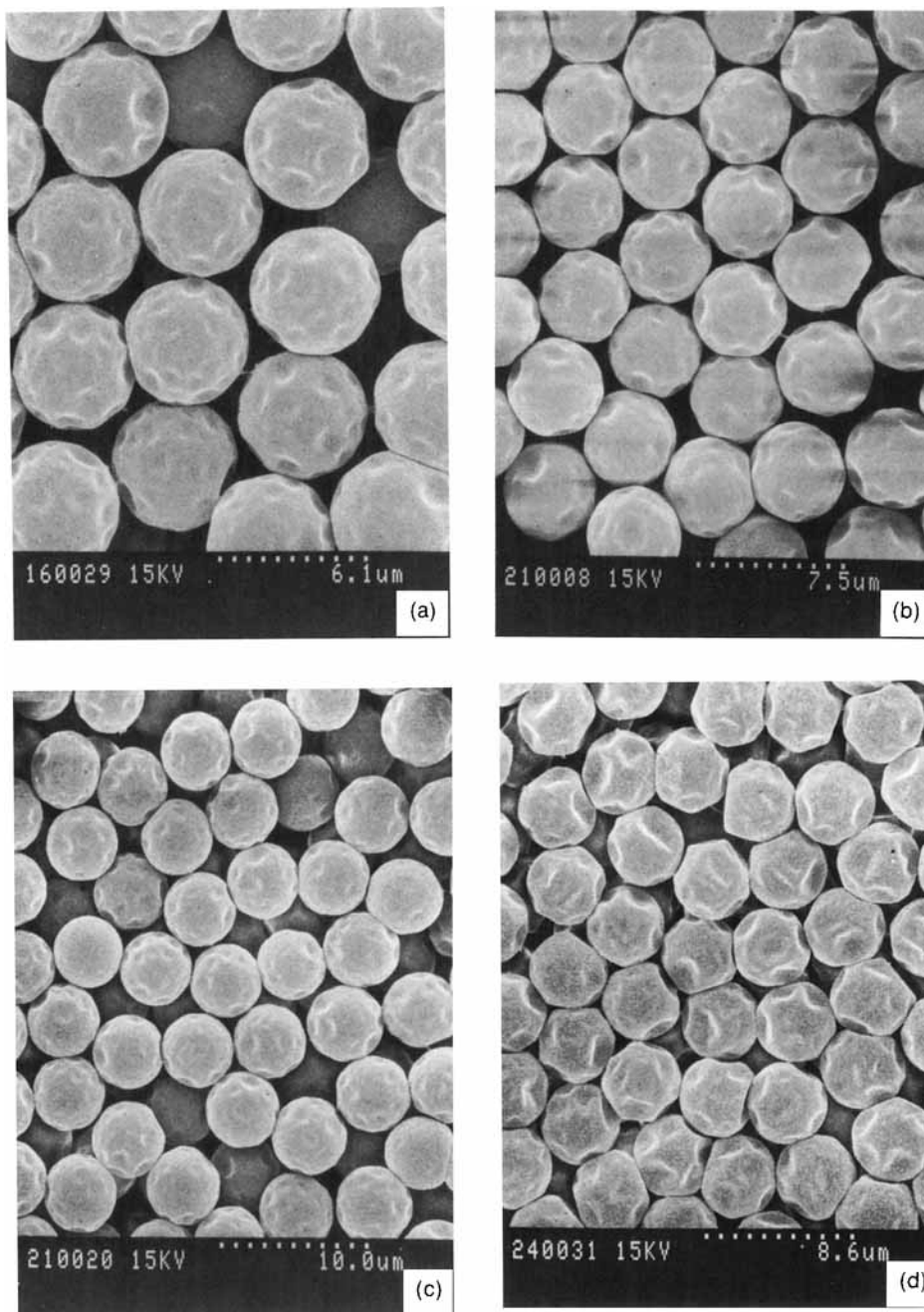


Figure 6 Scanning electron micrographs of dispersion polymerized latexes. Clockwise from top left: (a) DISP674, 6% DVB batch added at 540 min; (b) DISP701, 2% DVB batch added at 420 min; (c) DISP703, 6% DVB batch added at 420 min; (d) DISP710, 10.05% PVP in the charge, 1% DVB batch added at 420 min.

greater phase separation. In experiments where 2% [DISP701, Fig. 6(b)] and 6% [DISP703, Fig. 6(c)] DVB was added, final particles are spherical with numerous small, circular indentations covering their surfaces; the dents are slightly smaller and more abundant in the 6% product.

The effect on morphology of altering total surface area while maintaining the same continuous phase polarity profile was examined by varying the amount of PVP in the charge. In this series, particle number, total surface area, and surface pressure at the point of DVB addition all rise with stabilizer level, and a

clear trend of decreasing particle deformation emerges. At 6.7, 10.05, and 13.4% PVP, the shapes obtained are, in order, severely deformed spheres [DISP675, Fig. 5(a)], deformed spheres [DISP710, Fig. 6(d)], and perfectly smooth-surfaced spheres (DISP698). The smaller the microsphere size at the time of crosslinker addition, the higher the pressure exerted on their surfaces by the continuous phase. By doubling PVP content from our normal operating level of 6.7%, the pressure is high enough to inhibit demixing in the particle surface layer and the microspheres remain featureless. Raising DVB concentration to 2% at this PVP level (DISP709) gives slightly dented beads; the depressions are circular, but less widespread than those in DISP701. Again, the extra DVB speeds the crosslinking and phase separation processes, outweighing the demixing tendency of a high interfacial pressure: for another example, compare DISP663 and DISP673.

As medium polarity decreases, the extent of particle deformation increases, with complete failure occurring for the polymerization containing toluene (DISP693). With a PS solvent in the charge, much of the polymerization occurs in the continuous phase and particles grow by absorption of these chains. The majority of the batch-added DVB will therefore be rapidly consumed in solution, promoting renucleation that eventually causes destabilization of the existing large particles (which cannot compete effectively for available graft stabilizer). Operating at the other end of the polarity scale, with water rather than toluene in the charge, the situation is entirely different. Here, nucleation is more extensive,⁷ the bulk of the polymerization occurs within the particle phase, and bead growth is faster; a gel effect is in operation that raises average molecular weight (i.e., fewer chains exist). Because this highly polar medium produces small particles, it might seem reasonable to expect no change in morphology as a result of DVB addition. This would be wrong. Carrying out the polymerization in aqueous ethanol (DISP695) results in a stable latex comprised of deformed spheres [Fig. 7(a)]. In this experiment, the crosslinker was added after only 240 min to compensate for faster particle growth in this medium and to make the result comparable to DISP675; in both experiments then, the DVB was added with particles at approximately 68% of their final volume. Added divinyl monomer rapidly accumulates and reacts in the solid phase, but the higher interfacial pressure prevailing throughout bead growth in this very polar medium is not sufficient to counteract the swift phase separation

taking place at the particle surface. The outcome is a latex consisting of small (3.35 μm) deformed particles, but less so than in the equivalent all-ethanol reaction (DISP675).

The effect on final shape of crosslinking the core prior to the batch addition is tested in two different ways. The first is a one-shot experiment with 0.3% DVB [DISP707, Fig. 7(b)], the second a slow-add version in which 0.41% DVB was pumped in over 7 h [DISP702, Fig. 7(c)]. Note that in both cases, the level of DVB selected to crosslink the core is close to the allowable maximum for an undeformed product, that is, if the reactions were allowed to run their course without the addition of surplus divinyl monomer, spherical latex particles would be obtained. The slow-add attempt has no effect on final shape, the outcome being the same as batch addition to a homopolymeric core; but with 0.3% in the charge, the microparticles are globular and marked quite evenly with angular dents, far removed from the buckled appearance of DISP675 and DISP702. With DVB in the charge, a gradient copolymerization results and the outer reaches of each particle are only very lightly crosslinked relative to the central core. Also, because all crosslinker is present at initiation there is ample time before the batch addition for network formation to be well advanced. In other words, many of the PS chains at the surface are actually part of the bulk PS-DVB phase. When excess DVB is absorbed, soon after the 420-min mark, it enters a region that is already lightly and unevenly crosslinked, and its consumption in the surface layer results in more rapid phase separation than would otherwise be the case. Restricted maneuverability of the existing surface chains localizes their displacement in response to events following the batch addition. The outcome is equivalent to batch adding more than 1% DVB to a homopolymeric core, that is, smaller and more numerous deformities scar the final microspheres.

Slow addition of DVB prior to the batch addition evens out the distribution of crosslinker in the core but does not affect the processes arising from batch addition of a further 1% DVB at 420 min because insufficient time has passed for all of the slow-added DVB to be incorporated into a network within the particle; there is a time lag between DVB copolymerization and further reaction of the resulting PVGs to form network joints. The upshot is that PS chains residing in the outer layer of the core remain mobile and unable to modify the phase separation process activated by the batch addition of surplus DVB.

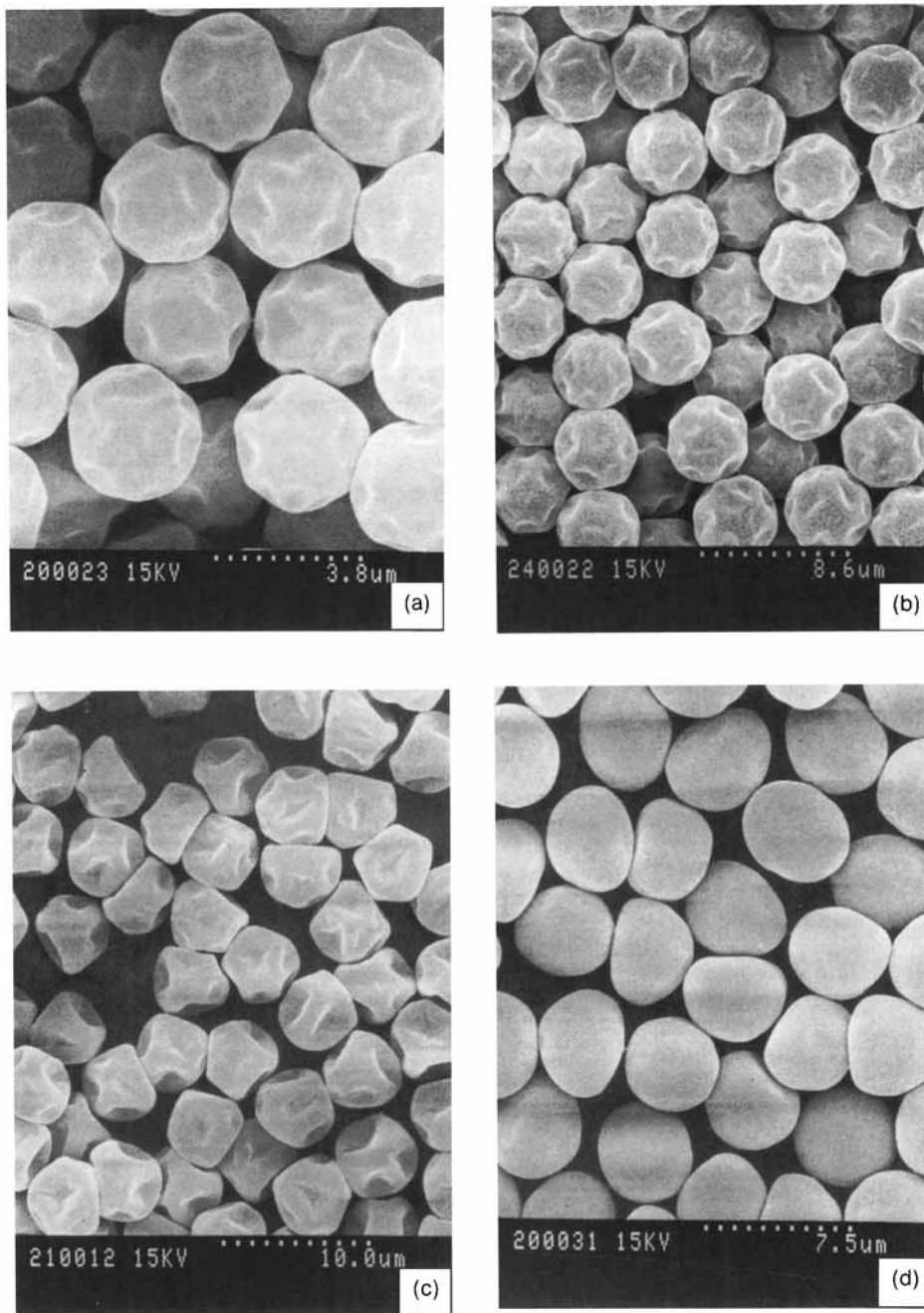


Figure 7 Scanning electron micrographs of dispersion polymerized latexes. Clockwise from top left: (a) DISP695, 20% water in the charge, 1% DVB batch added at 240 min; (b) DISP707, 0.3% DVB in the charge, 1% batch added at 420 min; (c) DISP702, 0.41% DVB added over 420 min; then 1% batch added; (d) DISP694, 0.4% DVB batch added at 200 min.

Low/Early Latexes

Microparticles synthesized by batch adding less than 1% DVB before 420 min of reaction are nonspherical. The exceptions are those in which only a very small amount of crosslinker is added (DISP700,

DISP670), insufficient to interrupt normal radial growth. The effect on morphology of adding 0.4% DVB at different stages of particle growth was examined. At 200 [DISP694, Fig. 7(d)], 300 [DISP690, Fig. 8(a)], and 420 (DISP670) min, stable dispersions

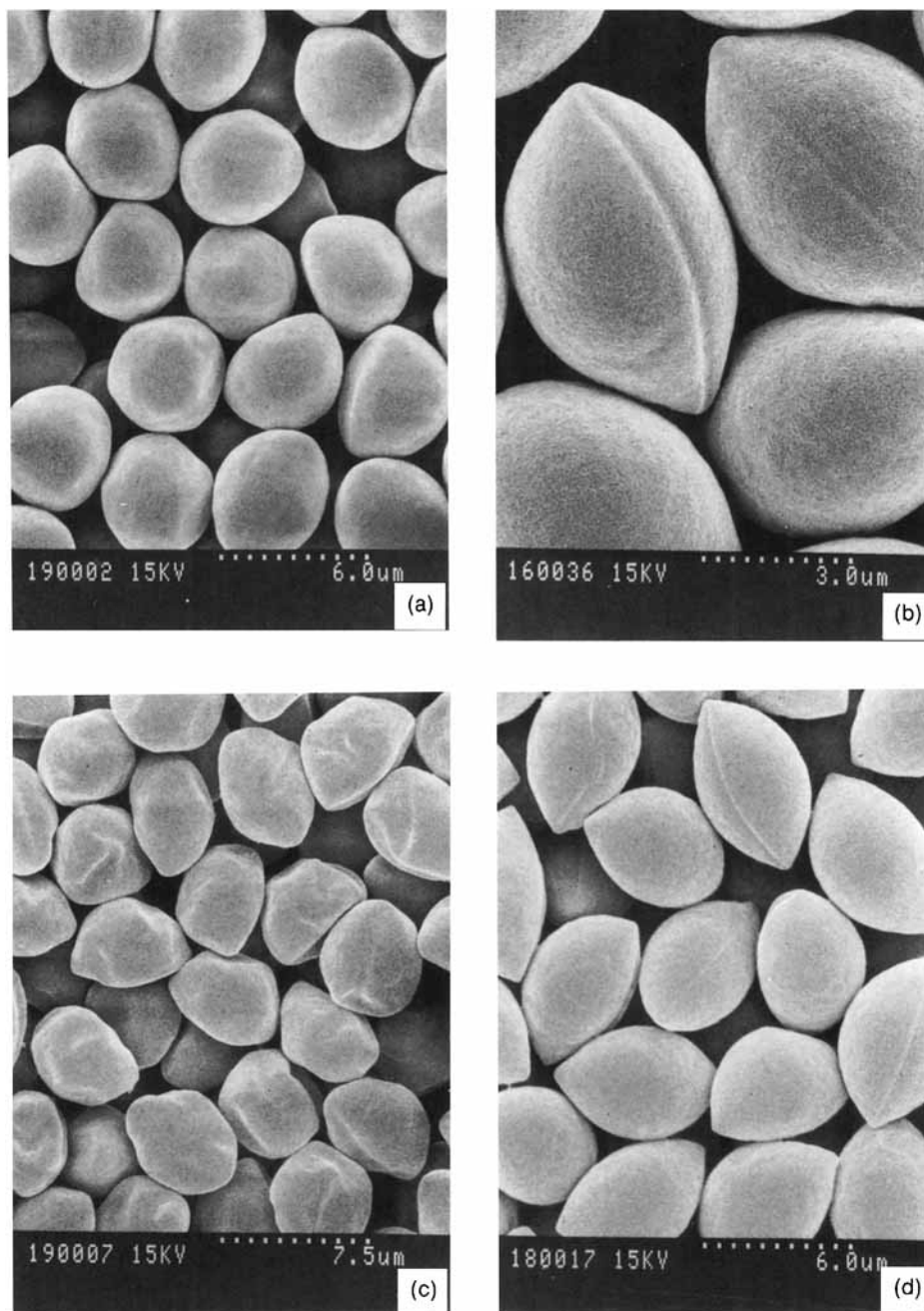


Figure 8 Scanning electron micrographs of dispersion polymerized latexes. Clockwise from top left: (a) DISP690, 0.4% DVB batch added at 300 min; (b) DISP656, 0.6% DVB batch added at 420 min; (c) DISP691, 0.6% DVB batch added at 300 min; (d) DISP689, 0.8% DVB batch added at 420 min.

are obtained, the latter consisting of smooth-surfaced spheres, the first two of smooth-surfaced spheroids. Increasing DVB level to 0.6% and adding at 420 min yields pod shaped particles, each with a characteristic indented “seam” running down its

length [DISP656, Fig. 8(b)]. Addition 2 h earlier of the same amount produces a morphology we describe as a deformed pod [DISP691, Fig. 8(c)]; many of the elongated particles have this seam still clearly visible. The change in shape with rising DVB is clear

in this category of latexes. For example, at 300 min, morphology ranges from the sphere (0.2%), to spheroid (0.4%), to deformed pod (0.6%), to utter failure when 1% is added: the latter is an example of a high/early latex. The 420-min point of addition is useful in that it allows access to the full range of batch addition morphologies: spheres at 0.4% (DISP670); sphere pods at 0.5% (DISP684), pods in the 0.6–0.8% range [e.g., DISP689, Fig. 8(d)]; a mixture of severely deformed spheres, deformed pods, and pods at 0.9% [DISP693, Fig. 9(a)]; severely deformed spheres at 1% [Fig. 5(a)]; and dimpled spheres between 2 and 6% [Fig. 6(b,c)].

The fact that low/early particles are nonspherical indicates that some phase separation does occur as a result of the batch addition; smooth surfaces, on the other hand, suggest that the process is slow. At low levels of DVB (DISP694, 690), crosslinking in the particle surface is limited to the formation of a very loose, patchy network. This takes some time to develop and affects the radial growth pattern; but when it does, growth still continues outward, but in a direction dictated by the least dense portion of the network. The outcome is a set of microparticles that deviate only slightly from sphericity. The next shape in the series is the sphere pod (DISP684), particles which are essentially “fat” spheres, but each has a very slight seam across one face; this form straddles the spheroid and pod types. True pods are accessible via batch addition of between 0.6 and 0.8% DVB at 420 min. They are symmetric, smooth-surfaced, and marked by an unbroken groove running across their surface from tip to tip, giving them an oysterlike appearance [Fig. 8(b)]; a few possess a nonlinear seam [see top left particle in Fig. 8(d)].

A polymerization was sampled several times after batch adding 0.7% DVB at 420 min (DISP705) in the hope that SEM analysis would shed light on pod evolution; but it was not until 660 min (4 h after the crosslinker addition) that a departure from sphericity was observed [Fig. 9(b)]. These microspheres have a slightly wrinkled surface texture, an indication that phase separation is underway; but somehow, over the remaining 12 h of the reaction, when total volume increases by less than 2%, the smooth-surfaced pod evolves. The task seems impossible, given that particle phase T_g is constantly rising, but must involve considerable elongation of the particle. One final experiment was undertaken in which the core was crosslinked by slow addition of 0.41% DVB prior to adding 0.7% at 420 min [DISP706, Fig. 9(c)]. The resulting particles are heavily dented spheres, much like those obtained by slow addition [Fig. 4(c,d)].

Recall that batch adding 1% DVB to a similar core did not affect final morphology, that is, the added crosslinker dominated shape development. With only 0.7% DVB added, graft immobilization appears to be the dominant phenomenon in determining final shape. The crosslinking process is slower with less DVB batch added; compare Figure 9(b) with DISP675 at 600 min [Fig. 5(c)]. In the meantime, core rigidity increases as more PVGs are consumed. However, as spheres would result in the absence of the extra DVB, the latter in some way exacerbates the immobilization of graft. Some adsorbed stabilizer chains will contain PVGs and, given sufficient time, the batch-added DVB may diffuse widely enough to encounter these vinyl units and restrict movement of their parent chain by further reaction. This is a curious morphology and one whose development we are unable to satisfactorily explain at present. All that can be said for certain is that a lightly crosslinked core inhibits pod formation, evidence that pod development does indeed involve a major reorganization of the particle phase.

The final low/early type, produced when a higher level of DVB is added at a particular time, is the deformed pod [e.g., 0.6% at 300 min, Fig. 8(c)]. Of particular interest is the addition of 0.9% DVB at 420 min, which produces a latex composed of a mixture of particle shapes—pods, deformed pods, severely deformed spheres [Fig. 9(a)]—and represents the “boundary” between the low/early and high/late classes. What is significant here is that the variety of final morphologies suggests nonuniform absorption of crosslinker. For example, the formation of a severely deformed sphere requires that the microsphere in question contain more DVB than a similar particle that ends up as a smooth-surfaced pod. The Coulter Counter measurement of DISP693 results in a peak with a distinct high micron shoulder, accounting for the higher geometric standard deviation (GSD) of the sample (Table III). In our experience, severely deformed microspheres such as DISP675 have slightly larger diameters than the corresponding PS spheres; whether this is due to a measurement limitation of deeply indented particles by electro-sensing, or whether such beads really do have a higher total volume than spheres, is not known at present. Either way, a mixture of smooth-surfaced and deformed microparticles (DISP693) is reflected in a broader overall size distribution.

CONCLUSIONS

The polymerization of styrene with DVB, in which the latter is added in a deliberate manner, allows

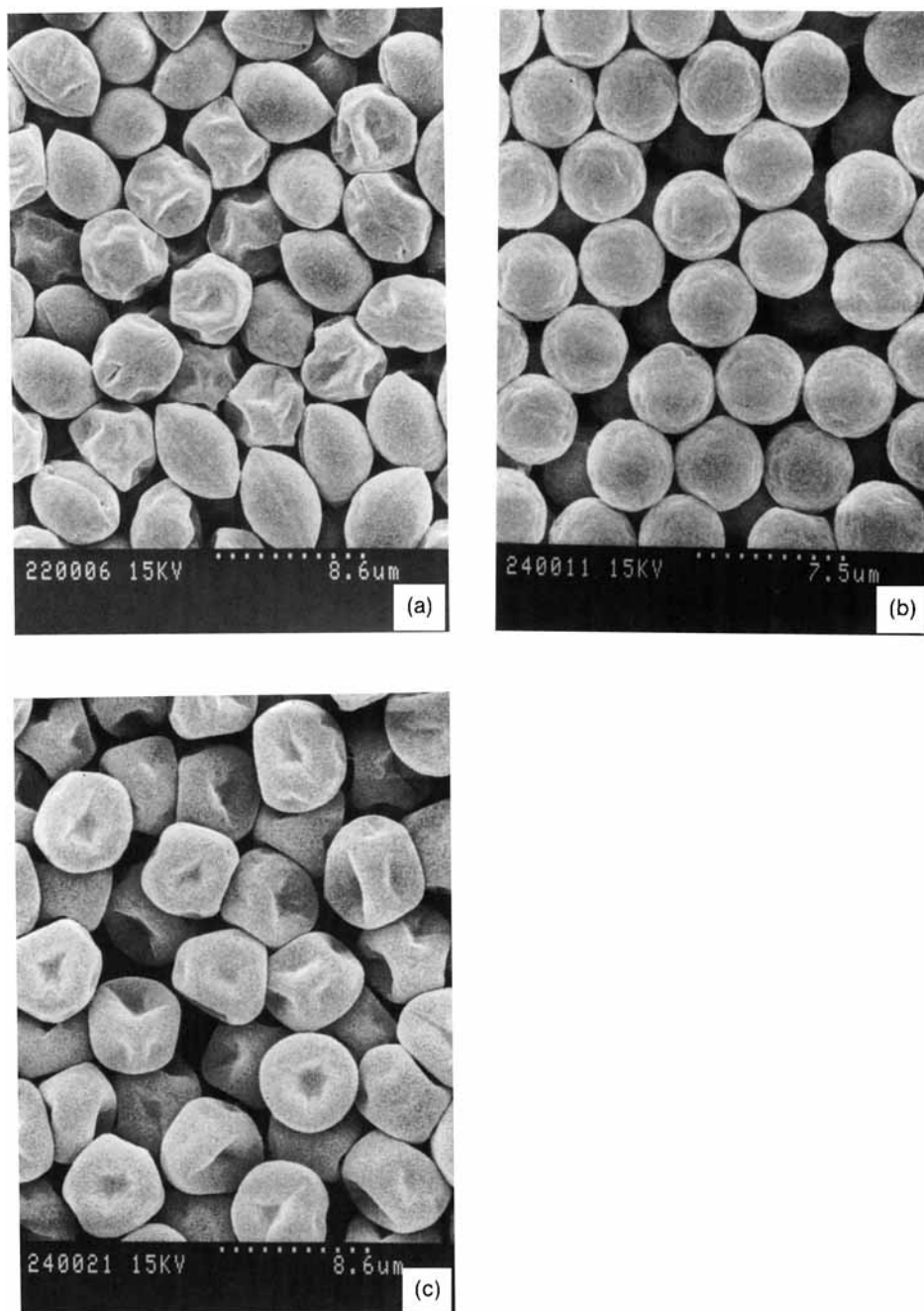


Figure 9 Scanning electron micrographs of dispersion polymerized latexes. Clockwise from top left: (a) DISP693, 0.9% DVB batch added at 420 min; (b) DISP705, 0.7% DVB batch added at 420 min (660-min sample); (c) DISP706, 0.41% DVB added over 420 min, then 0.7% batch added.

the production of several new classes of monodisperse latexes; and methods, based on the dispersion copolymerization of these monomers in ethanol, for their synthesis were described. The protocols developed extend the range of parameters that can be manipulated to build specific properties (crosslink

uniformity, shape) into a latex. Morphological observations offer compelling evidence for our view that the stability of one-shot and slow-add latexes is intimately related to the mobility of the adsorbed steric stabilizer, and that the amount and time span of added DVB are the crucial factors in determining

final shape. The process responsible for particle deformation in batch-add copolymerizations is different. Distinctive particle forms result, a consequence of the uneven crosslinking that occurs when the DVB partitions into the solid phase. Overall sphericity is retained in high/late latexes because there is sufficient DVB to ensure network formation over the entire particle surface, but phase separation in the surface layer is the inevitable consequence of nonuniform crosslinking, and prompts a redistribution of mobile surface material, which leaves final microparticles with a characteristic dimpled form. With low/early polymerizations, nonspherical shapes are obtainable because less extensive and slower surface crosslinking allows particles time to respond and reorganize. Most of the shapes discussed are not accessible by emulsion or suspension polymerization because in these methods there is normally little bond formation between stabilizer and the bulk phase polymer. The syntheses described herein add to the number of distinct particle types available. Such products could find application as models in nonspherical packing studies, and as standard colloids in the analytical sizing field.

This research was supported by the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

1. K. Barrett, Ed., *Dispersion Polymerization in Organic Media*, Wiley, London, 1975.
2. C. Tseng, Y. Lu, M. El-Asser, and J. Vanderhoff, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 2995 (1986).
3. M. Croucher and M. Winnik, *NATO ASI Appl. Sci.*, **138**, 209 (1988).
4. A. Paine, W. Luynes, and J. McNulty, *Macromolecules*, **23**, 3104 (1990).
5. A. Paine, *Macromolecules*, **23**, 3109 (1990).
6. M. Croucher and M. Winnik, *NATO ASDI Series C*, **303**, (1990).
7. B. Thomson, A. Rudin, and G. Lajoie, *J. Polym. Sci., Polym. Chem. Ed.*, **33**, 345 (1995).
8. A. Palmer, P. Logiudice, and J. Cowley, *Am. Lab.*, **26**(11), 17 (1994).
9. C. Ober, *Makromol. Chem., Macromol. Symp.*, **35/36**, 87 (1990).
10. K. Lee, M. Winnik, and T. Jao, *J. Polym. Sci., Polym. Chem. Ed.*, **32**, 2333 (1994).
11. M. Okubo and M. Tsujihira, U.S. Pat. 4,996,265 (1991).
12. J. Ugelstad, U.S. Pats. 4,336,173 (1982) and 4,459,378 (1984).
13. D. Zou, V. Derlich, K. Gandhi, M. Park, L. Sun, D. Kriz, Y. Lee, G. Kim, J. Aklonis, and R. Salovey, *J. Polym. Sci., Polym. Chem. Ed.*, **28**, 1909 (1990).
14. Z. Ding, S. Ma, D. Kriz, J. Aklonis, and R. Salovey, *J. Polym. Sci., Polym. Phys. Ed.*, **30**, 1189 (1992).
15. A. Rudin, 3rd Int. Symp. Radical Copolym. Dispersed Media, Lyon, 1989.
16. T. Matsumoto, M. Okubo, and S. Shibao, *Kobunshi Ronbunshu*, **33**, 575 (1976).
17. L. Kulin, P. Flodin, T. Ellingsen, and J. Ugelstad, *J. Chromatogr.*, **514**, 1 (1990).
18. T. Ellingsen, O. Aune, J. Ugelstad, and S. Hagen, *J. Chromatogr.*, **535**, 147 (1990).
19. V. Smigol and F. Svec, *J. Appl. Polym. Sci.*, **46**, 1439 (1992).
20. S. Omi, K. Katami, A. Yamamoto, and M. Iso, *J. Appl. Polym. Sci.*, **51**, 1 (1994).
21. C. Cheng, J. Vanderhoff, and M. El-Asser, *J. Polym. Sci., Polym. Chem. Ed.*, **30**, 245 (1992).
22. K. Kun and R. Kunin, *J. Polym. Sci.*, **6**, 2689 (1968).
23. O. Okay, *J. Appl. Polym. Sci.*, **32**, 5533 (1986).
24. J. Ugelstad, H. Mfutakamba, P. Mørk, T. Ellingsen, A. Berge, R. Schmid, L. Holm, A. Jørgedal, F. Hansen, and K. Nustad, *J. Polym. Sci., Polym. Symp.*, **72**, 225 (1985).
25. K. Kobayashi and M. Senna, *J. Appl. Polym. Sci.*, **46**, 27 (1992).
26. M. Okubo, Y. Katayama, and Y. Yamamoto, *Colloid Polym. Sci.*, **269**, 217 (1991).
27. W. Li, H. Stöver, and A. Hamielec, *J. Polym. Sci., Polym. Chem. Ed.*, **32**, 2029 (1994).
28. K. Li and H. Stöver, *J. Polym. Sci., Polym. Chem. Ed.*, **31**, 2473 (1993).
29. M. Hattori, E. Sudol, and M. El-Asser, *J. Appl. Polym. Sci.*, **50**, 2027 (1993).
30. K. Li and H. Stöver, *J. Polym. Sci., Polym. Chem. Ed.*, **31**, 3257 (1993).
31. A. Skjeltop, J. Ugelstad, and T. Ellingsen, *J. Colloid Interface Sci.*, **113**, 577 (1986).
32. J. Ugelstad, P. C. Mørk, H. R. Mfutakamba, E. Soleimany, I. Nordhuus, R. Schmid, A. Berge, T. Ellingsen, O. Aune, and K. Nustad, *NATO ASI Series E*, **67**, 51 (1983).
33. H. Sheu, M. El-Asser, and J. Vanderhoff, *J. Polym. Sci., Polym. Chem. Ed.*, **28**, 629 (1990).
34. H. Sheu, M. El-Asser, and J. Vanderhoff, *J. Polym. Sci., Polym. Chem. Ed.*, **28**, 653 (1990).

Received May 12, 1995

Accepted September 12, 1995