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The Growth of Polystyrene Latex Particles*

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ABSTRACT

Our understanding of the factors controlling the growth of polystyrene latex particles has recently undergone extensive revision. For this compatible monomer-polymer system, it was generally presumed that monomer and polymer were uniformly distributed throughout the particles, whereas we have found quite the contrary. Under a wide range of conditions, growing latex particles actually exhibit a distributed structure in which a monomer-rich shell encapsulates a polymer-rich core. First elucidated in kinetic studies of styrene emulsion polymerization, this behavior has also been observed in particles which reside in a state of equilibrium saturation with monomer. The encapsulation phenomenon is governed by the microscopic thermodynamic environment of the latex particles which has, in turn, a profound effect upon the conformational behavior of the long-chain polymer molecules as they interact with the particle-water interface. The control of latex particle properties by the staged addition of several monomers (overcoating) has been part of the industrial lore for many years. The successful execution of

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this technique has been attributed to either a slow monomer addition technique or to the inherent incompatibilities of the successive generations of polymer. In situations involving the addition of a monomer which is compatible with the seed polymer, the encapsulation phenomenon is probably the controlling factor in the overcoating process.

INTRODUCTION

Recent advances on the mechanisms controlling the growth of polystyrene latex particles have provided new opportunities for research and technology. Based on the results of kinetic studies of ideal styrene emulsion polymerization, we postulated that growing latex particles possessed a core-shell structure in which a monomer-rich shell surrounds a polymer-rich core [1]. We have recently shown that the essential features of this morphology prevail under conditions of latex particle saturation [2]. That is, under a wide range of conditions, the monomer associated with an individual latex particle tends to overcoat the polymer rather than swelling it uniformly. This observation is remarkable inasmuch as styrene and polystyrene ordinarily form homogeneous solutions.

One can consider the implications of our findings from several related points of view—all of which are under active investigation in our laboratories—kinetics and mechanisms of emulsion polymerization, latex particle technology, and the fundamental molecular explanation for the observed behavior. In this paper we wish to relate our work to practices in latex particle technology. We first review the essential features of our published work.

BACKGROUND

Kinetics of Emulsion Polymerization

The kinetic studies [1] which led to the initial postulation of a definite morphology for growing polystyrene latex particles were based on formulations which exhibited continuous particle uniformity as well as Smith-Ewart, Case 2 kinetics from zero to about 60% conversion. Typical conversion-time curves are shown in Fig. 1. Two different amounts of anionic soap resulted in the two sets of rate data (13 ± 2 and $21 \pm 2\%$ /hr) shown.

Constant-rate growth can be described in terms of the Smith-Ewart theory, Case 2 [3], in which the rate of polymerization per particle, R_{pp} , is expressed as

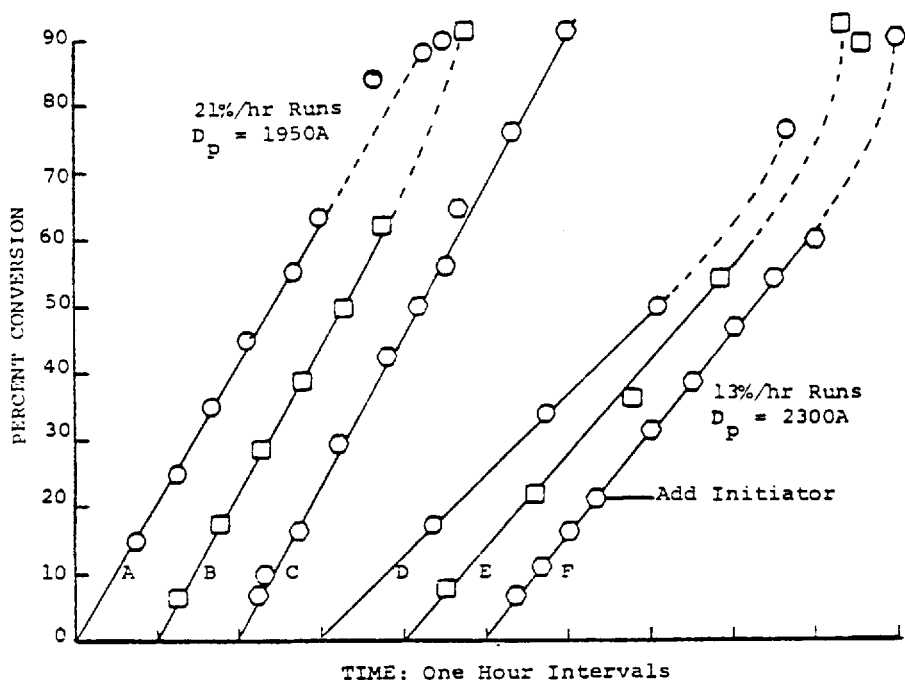


FIG. 1. Per cent conversion vs time for 13 and 21%/hr runs. Each curve is plotted on a time scale of 1-hr intervals so that it can be displayed separately in a concise fashion.

$$R_{pp} = k_p \bar{n} [M] \quad (1)$$

where k_p is the propagation constant, $[M]$ is the monomer concentration within the particle, and \bar{n} is the time-average, number of free radicals per particle. With $\bar{n} = \frac{1}{2}$, the rate of polymerization per particle is constant and independent of particle size, provided $[M]$ is constant.

Evidence for $\bar{n} = \frac{1}{2}$ and constant is provided by initiator perturbation studies [1, 4]. As shown in Fig. 1, for Curve F, the initiator concentration of a run in progress was suddenly doubled during its constant rate period. The observed invariance in the rate is evidence of $\bar{n} = \frac{1}{2}$ and constant. Shown in Fig. 2 are dynamic measurements of the particle weight fraction monomer $[M]_w$ vs per cent conversion [1]. The variable

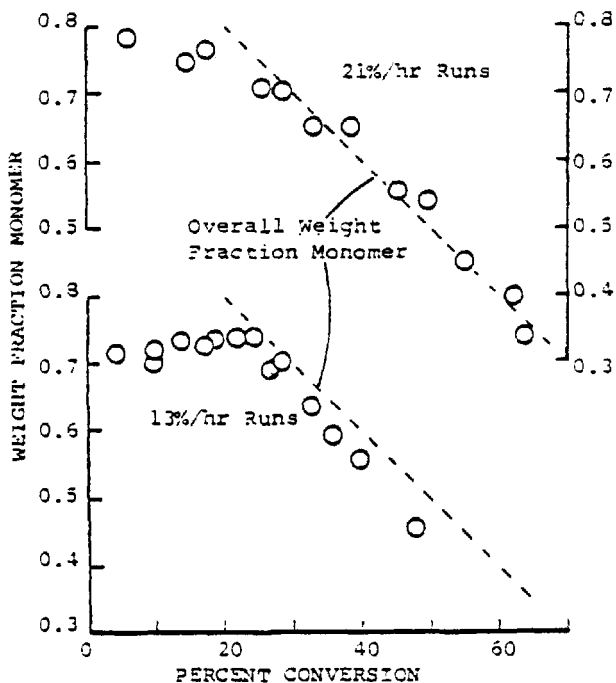


FIG. 2. Weight fraction monomer in latex particles vs per cent conversion for 13 and 21%/hr runs. Samples obtained during the progress of a run.

nature of $[M]_w$ stands in striking contrast to the extended constant rate period (0 to 60%) exhibited by these formulations and to the requirements of Eq. (1). It follows that a zone of essentially constant monomer concentration exists within the particle during the constant rate polymerization, and that this zone serves as the major locus of polymerization. Such a requirement is satisfied by a core-shell model, consisting of a polymer-rich core surrounded by a monomer-rich shell which serves as the major locus of polymerization.

The following experiment provided physical evidence for the core-shell model [1]. To a 13%/hr styrene run at 20% conversion a portion of butadiene was charged. We expected that copolymerization would result, and if the model were correct, that the final latex particle should consist of a mostly polystyrene core—corresponding to the core which

existed when the butadiene was charged—surrounded by a spherical styrene-butadiene copolymer shell. Since the unsaturated butadiene repeat unit could be stained with osmium tetroxide, an ultrathin cross-section taken through the center of the particle should appear as a doughnut shape under electron microscope observation. Figure 3

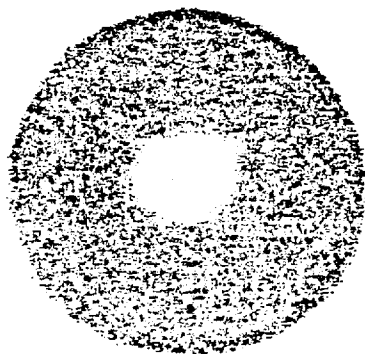


FIG. 3. Ultrathin cross section of a latex particle spiked with butadiene at 20% conversion and carried to 100% conversion. 250,000 \times .

shows a thin section taken from such a particle; it clearly shows the expected core and the stained ring.

(The appellation "core-shell model," which we first adopted to describe the observed morphology, ought not to be interpreted too literally as it implies two-phase behavior with pure polymer in the core and pure monomer in the shell. We attempted to avoid this implication by using the terms "monomer-rich shell" and "polymer-rich core." They imply a two-phase behavior where the polymer segment density is high in the central region of the particle and low in the peripheral region, and where the gradients are modest within the interior and near the periphery but steep at their interface. As the level of our understanding of the molecular phenomenon controlling the morphology advances, we find that the term "core-shell" might be

too restrictive. We now prefer "encapsulation" which connotes the possible existence of a more diffuse polymer segment density distribution—still high in the center and approaching zero at the particle water interface—in a particle which is overcoated with a sheath of nearly pure monomer.)

Equilibrium Encapsulation

To ascertain whether the encapsulation phenomenon was governed by kinetic or thermodynamic factors, we performed experiments of the following kind: Fresh monomer with a trace of butadiene was charged to a seed until the particles were saturated. Polymerization was carried to completion. In order to suppress any artifacts which might develop because of the incompatibility between polystyrene and poly(styrene-co-butadiene), the butadiene level was maintained at less than 0.7 wt%. Structures similar to that shown in Fig. 3 were obtained [2]. Figure 4 shows the expected morphology in a 3-stage polymerization. In line with our previous rationale, these results

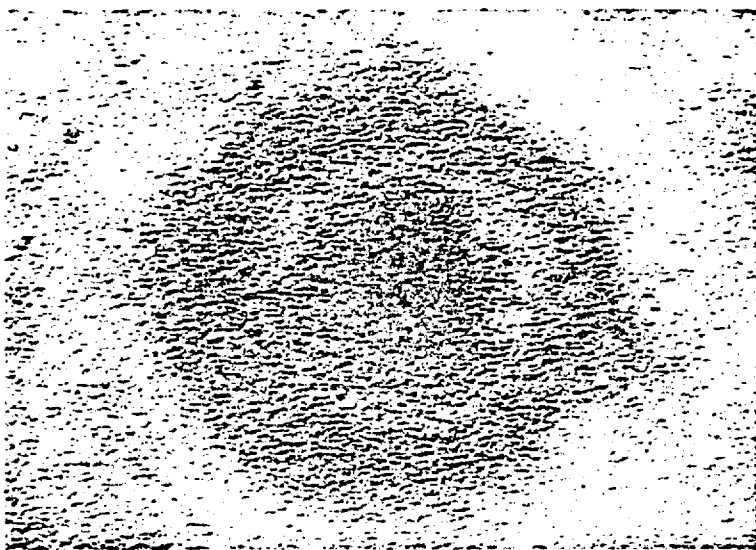


FIG. 4. Ultrathin cross section of a latex particle prepared in a three-stage emulsion polymerization. Stages 2 and 3 were initiated under conditions of equilibrium saturation. Trace amounts of butadiene were charged in Stages 1 and 3. 292,150 \times .

indicated that the primary mode of fresh monomer addition is encapsulation rather than uniform swelling and that the morphology is controlled by thermodynamic factors. These findings rule out kinetic control based on a rate of polymerization very much faster than the rate of monomer diffusion within the particles. So far, we find encapsulation to prevail in particles ranging from 500 Å to about 6000 Å in diameter.

We next considered two limitations in the use of butadiene tagging and subsequent particle slicing as a means of physically observing the particle morphology [2]. One could argue that the morphology so revealed was caused by the incompatibility between the polystyrene molecules of the seed particle and the poly(styrene-co-butadiene) molecules of the second generation of growth. Although we had reason to believe that incompatibility was not affecting our arguments, we felt it imperative to establish an insolubility-free test. A second limitation is imposed by the fact that finding the confirming structures in the electron microscope is akin to looking for the proverbial needle in the haystack. Consequently, this approach could never have a statistical basis. To eliminate these limitations, we undertook a series of experiments that utilized tritiated styrene as the tagging agent and autoradiography as the detecting method [2]. Tritiated styrene could never be argued to introduce compatibility problems, and the experiments were performed in such a way that thousands of particles could be observed.

A 1520-Å diameter, tagged-seed particle was twice overcoated under equilibrium saturation conditions with untagged styrene to produce a final untagged shell thickness of 1330 Å (calculated on the basis of a pure polymer core and a pure monomer shell at equilibrium saturation). Tritium as a low energy emitter (maximum of 18 keV) has a track length of only 500 to 800 Å in a material such as polystyrene. If the particles so constructed were core-shell in character, β -absorption should occur as depicted in Fig. 5A and the photographic emulsion coating the particles should not become exposed. In order to provide a basis for the comparison the 1520 Å particle, with tagging throughout, was also exposed. Such particles (Fig. 5B) should show numerous traces. It is impossible to uniformly coat the particles with a monolayer of photographic emulsion as depicted in Figs. 5A and 5B. In practice the particles are placed on a parlodion-coated microscope grid in the conventional manner, and then a film of the photographic emulsion is placed over them as depicted in Fig. 5C. Our results are shown in Figs. 6A and 6B. As predicted, innumerable traces are observed in the control (Fig. 6A) and none are observed in the tagged-seed-untagged-shell particle (Fig. 6B). These results constitute the most convincing evidence yet presented to support the encapsulation model for latex growth.

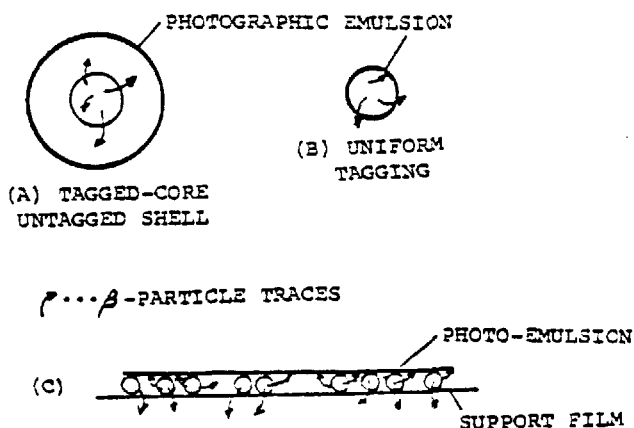


FIG. 5. Schematic showing the application of autoradiography for confirming the encapsulation model. (A) β -Particles are absorbed within the untagged shell, and the photoemulsion remains unexposed. (B) β -Particles activate the photoemulsion. (C) Latex particles sandwiched between the parlodion film and the photoemulsion.

Theoretical Considerations

At present we have more unanswered questions than answered ones. For instance, what are the fundamental factors accounting for the formation of the encapsulation morphology? What is the precise density distribution of polymer segments within the particle? What is the detailed mechanism for chain growth? Some insights have been gained and are described elsewhere [2, 5, 6]. First and foremost, a latex particle is a microscopic rather than a macroscopic thermodynamic system, and we cannot expect the laws or observations of macroscopic thermodynamic systems to apply without suitable modification.

Furthermore, we believe the encapsulation phenomenon to be controlled primarily by the long-chain conformational properties of the polystyrene molecules and their interaction with the latex particle-water interface, and we have based a heuristic argument upon this assertion [2, 5]. Briefly, in a uniformly distributed latex particle, only those molecules near the center of the particle will be able to occupy their favored random-coil conformations. On the other hand, a polymer molecule whose center of mass is located near the particle periphery cannot occupy its preferred conformation, but

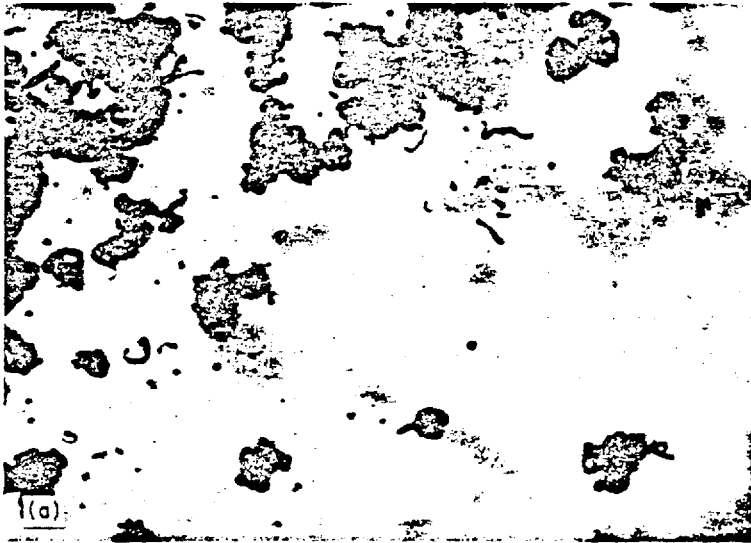


FIG. 6A. Autoradiograph of 1520 Å seeds with tagging throughout, showing large amounts of traces near the tritium-active latices. Exposure time: 1608 hr. The latex particles are observed as gray spheres in the background, while the traces appear as black irregular dots, strands, and clusters. 23,085 \times .

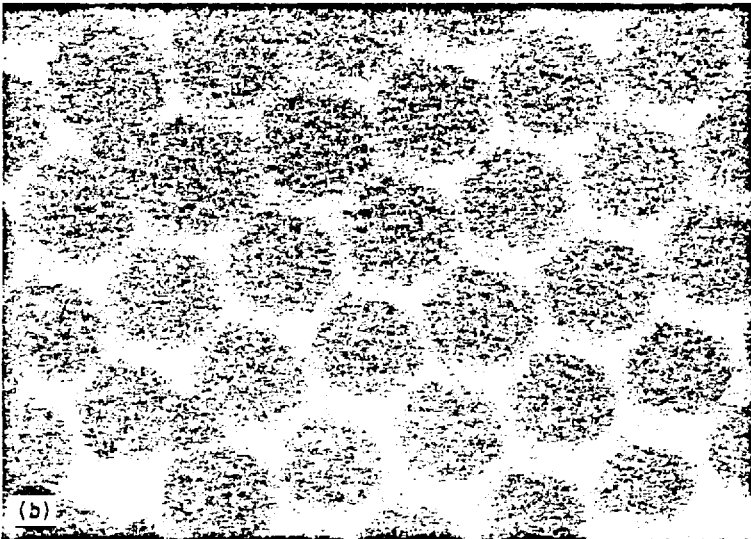


FIG. 6B. Autoradiograph of 1520 Å seed latex with tagging throughout, twice overcoated with pure polymer to 4180 Å. Essentially no traces were observed in such samples. The latices have distributed themselves in a hexagonal array. 46,170 \times .

it will be "compressed" against the particle-water interface. The net result would be an unusually low conformational degree of freedom and correspondingly low entropy for a polymer molecule near the particle periphery. A model more entropically favored would consist of a central region with a dense network of entangled, coiled polymer chains plus some monomer and a peripheral region with a dilute network of polymer chains which would occupy their most favored conformations. (The foregoing should not be construed as an argument "proving" the existence of the encapsulation morphology. It is offered to serve as a basis for further study and discussion. Evidence for encapsulation resides in the experimental observations just reviewed.)

TECHNOLOGICAL CONSIDERATIONS

Overcoating in Multistage Polymerizations

The control of latex particle properties by the staged addition of several monomers, in a process referred to as overcoating, has been part of the industrial lore for many years. Latex particle consistency can be varied in multistage emulsion polymerizations to improve mechanical properties and film-forming ability or to give regions of selective reactivity. Some simple examples are: 1) glassy-cores with rubbery shells for the manufacture of a reinforced rubber, 2) rubbery shells with a thin layer of glassy polymer for a tack-free latex product that can be readily handled, 3) rubber cores with glass exterior shells for improved impact resistance, and 4) cores formulated for superior mechanical properties (and/or low cost) coated with a thin-shell formulated for its film-forming ability. The patent literature describes many more sophisticated applications of the multilayering technique. See, for example, U.S. Patents issued to 1) Goodman et al. [7] on latex preparations for use as paper impregnators, 2) Hahn and Heaps [8] on latexes for gloss paints, 3) Pfleuger and Gebelein [9] on latex preparations for vapor resistant paper coatings, 4) Settlage [10] on latexes for the manufacture of solvent resistant and grease proof wrapping papers, plus 5) Ryan and Crochowski [11] who use latexes to prepare interpenetrating polymer networks.

Studies of latex polymers prepared by multistage addition methods as described in the open literature are also of interest. Hughes and Brown [12] discussed the properties of heterogeneous polymer systems prepared in "two-stage emulsion polymerizations." Several aspects of latex morphology were reviewed by Bradford and Vanderhoff [13]. Kato has presented an electron microscope study of ultrathin sections of ABS latex particles [14], prepared by layering a copolymer of acrylonitrile (A) and styrene (S) on a seed of polybutadiene (PB). Chujo et al. described

the effects of various monomer addition methods in the emulsion polymerization of vinyl acetate and butyl acrylate [15]. Huguet and Paxton have described the properties of a styrene-acrylonitrile copolymer grafted onto a polybutadiene latex seed [16]. Recently, Sperling et al. [17] reported on the mechanical properties of interpenetrating polymer networks prepared in seeded emulsion polymerizations.

In order to illustrate how the overcoating process is practiced, we cite extensively from the Hahn and Heaps patent [8] on the preparation of an approximately 45% solids latex containing 48.5% styrene, 39% 2-methyl hexyl acrylate, 6% acrylonitrile, and 6.5% methacrylic acid. The solutions given in Table 1 were prepared.

TABLE 1

Component	Parts
Kettle Charge	
Water (distilled)	402
Triton X-100 ^a	1.7
Triton X-770 ^b	1.2
Tetrasodium pyrophosphate	0.2
Catalyst and Emulsifier Premix	
Water (distilled)	132
Triton X-100 ^a	0.5
Triton X-770 ^b	10.7
Potassium persulfate	2.7
Monomer Charge I	
Acrylonitrile	24
Styrene	56
Monomer Charge II	
Styrene	138
2-Ethylexyl acrylate	125
Monomer Charge III	
2-Ethylexyl acrylate	31
Methacrylic acid	26

^aAn ethylene oxide condensate of nonylphenol.

^bSodium salt of an alkyl aryl polyether sulfate.

The kettle charge is added to a glass-lined reaction vessel that is fitted with a reflux condenser and a stirrer and is refluxed (at atmospheric pressure) for 15 min to deoxygenate the solution. Ten parts of the catalyst and emulsifier premix are then added to the reaction vessel. The balance of the catalyst and emulsifier premix is added to the reaction vessel at a uniform rate of 1.3 parts/min, the total time of addition being 100 min. As soon as the initial aliquot of the catalyst and emulsifier premix is added to the reaction vessel, Monomer Charge I is added to the reaction vessel at a uniform rate of 2 parts/min, the time of addition for this monomer charge being about 30 min. Immediately thereafter, Monomer Charge II is added to the reaction vessel at a uniform rate of 5.5 parts/min, the total time of addition of this monomer charge being about 50 min. Immediately thereafter, Monomer Charge III is added to the reaction vessel at a uniform rate of 5 parts/min, the addition of Monomer Charge III requiring approximately 10 min. Reflux is continued for an additional 15 min to polymerize the final traces of monomers. Reflux is then continued for an additional 15 min and 60 parts of distillate are removed so as to remove by steam distillation any residual monomers present in the latex. The catalyst concentration and monomer addition times are selected so that the monomers polymerize at substantially the rate they are added to the reaction vessel.

In the above procedure, overcoating is achieved by slow monomer addition. That is, an additional monomer charge is not added until the previous charge is nearly polymerized and then it is added at such a rate that polymerization will occur before the monomer has sufficient time to penetrate very far into the seed particles. Recall from Fig. 4, however, that overcoating can be achieved even when all monomer is added well beforehand in each of the second and third stages of polymerization.

In general, the successful execution of the overcoating process has been attributed variously to monomer-polymer or polymer-polymer incompatibility and/or to slow monomer addition methods. Our work shows that quite another factor can enter the picture and actually control the situation: namely, the encapsulation phenomenon. Thus there is a continued need for systematic studies which explore the effect of particle composition on morphology and mechanical properties as well as for fundamental studies in controlling particle morphology through control of the polymerization process.

We have explored the effect of increasing the butadiene-to-styrene ratio in the overcoat charge for a polystyrene seed on the particle morphology. This situation falls into the general category of overcoating with a monomer system (Monomer II) which is substantially soluble in the polymer seed (Polymer I), but the second generation polymer (Polymer II) is incompatible with Polymer I. Note that in this series of our studies we are seeking to enhance

incompatibility between Polymers I and II rather than suppress it as we have in all our earlier studies. Thus we are seeking to ascertain the role of polymer-polymer compatibility in controlling latex particle morphology.

The only similar study we are aware of is reported by Kato [14] on the morphology of ABS latexes. In this case the order of the butadiene addition was reversed: i.e., A and S were layered on a seed of PB. According to Sperling et al. [17], reversing the order of monomer charging can substantially modify the morphology of materials containing butadiene. Unfortunately, Kato utilized a commercial resin, and he does not report extensively on the preparation procedures nor on the ratio of A to S in the Monomer II charge. Despite these difficulties we were able to draw some important parallels with his work.

SEED GROWTH EXPERIMENTS WITH INCREASING BUTADIENE CONTENT

Polymerizations

All latexes were prepared by following the formulations and procedures of Woods et al. [18] with some slight modifications. The formulations are given in Table 2. The polystyrene seed particles (as

TABLE 2

Formulations	Seed preparation (g)	Seeded polymerization (g)
Water	172.74	172.98
Monomer	122.52 (styrene)	62.33
Siponate ^a	0.219	None
Triton X-100 ^b	4.233	0.334
K ₂ S ₂ O ₈	0.225	0.037
NaOH	0.420	0.0051
Seed charge	None	64.29 ^c
Dodecyl mercaptan	None	3.0

^aSodium dodecyl benzene sulfonate.

^bA nonionic octylphenoxy ethyl surfactant, product of Rohm and Haas Co., Philadelphia, Pennsylvania.

^c40.8% polystyrene from seed preparation.

determined by electron microscopy) were 1840 Å in diameter. In the reseeded experiments the monomer-to-polymer ratio was 2.4 just below saturation, and 48 hr were allowed for equilibrium of monomer and polymer. The measured final particle diameter was 2740 Å vs a value of 2760 Å calculated from the formulation stoichiometry and the seed diameter of 1840 Å. The butadiene content in the overcoat was varied as 6, 10, 15, and 50 wt%—based on the Monomer II charge. For the charge containing 50% butadiene, the reaction time increased to 36 hr from the normal 10 to 12 hr for an all-styrene charge. The butadiene was obtained by distillation from a pressurized cylinder, with cooling coils immersed in an acetone-Dry Ice bath.

The electron microscope techniques for direct observation of latex particles are standard. The procedures for imbedding, slicing, and staining are described elsewhere [2]. The particles containing 50% butadiene in the Monomer II charge were fixed with osmium tetroxide prior to destabilizing and subsequent imbedding.

Observations

The essential features of the core-shell morphology first displayed in our work (Fig. 3) prevailed in all the micrographs observed. In all cases the core and shell dimensions correspond to the original seed and seeded diameters, respectively. Figures 7a to 7d show thin cross-sections obtained for increasing butadiene content. The most pronounced morphological changes which appear with increasing butadiene content are best displayed in Fig. 7b for the 10% butadiene formulation. Two features are noteworthy: 1) the occurrence of a dark ring around the core and 2) dark spots inside the core, both of which indicate a high concentration of butadiene. Under electron microscope observation the inclusions within the core were actually observed to move about in rather rapid random motion. This motion has been tentatively ascribed to differential heating of the sample area by the electron beam. Figure 8 shows a field of thin sections for the 10% butadiene specimen of Fig. 7b.

The observation of butadiene in the core is evidence that some polymerization occurs within the core—most likely a modest amount in light of our original arguments [1]. Some caution ought to be followed, however, in extrapolating an interpretation based on micrographs obtained from latexes at 100% conversion to a kinetic situation that prevails from zero to 60% conversion. [Shortstopping the reaction at lower conversions to obtain the requisite samples for microscopy does not offer an alternative solution because of the shrinkage (and therefore, changes in morphology) such particles would suffer when unreacted monomer was removed.] This indicates that the core has a composite structure, and, under conditions of

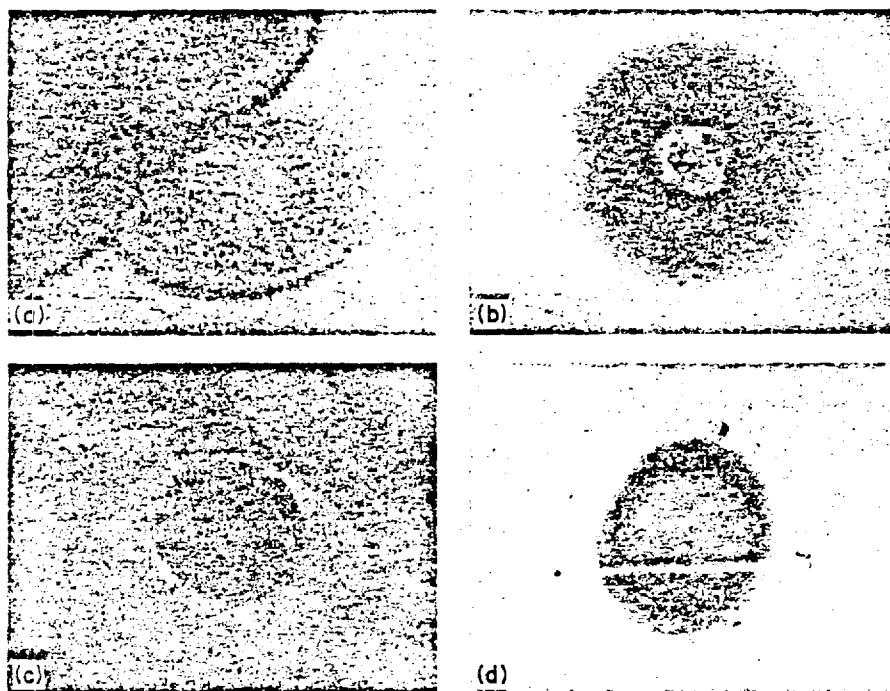


FIG. 7. Ultrathin cross sections of latex particles prepared in two-stage emulsion polymerizations. Seed growths were conducted under conditions of equilibrium saturation with varying amounts of butadiene in the Monomer II charge. (a) 6% butadiene in Monomer II charge, 249,230 \times . (b) 10% butadiene in Monomer II charge, 205,200 \times . (c) 15% butadiene in Monomer II charge, 213,360 \times . (d) 50% butadiene in Monomer II charge, 139,650 \times .

industrial practice, latex particles have perhaps a more complex morphology than heretofore appreciated.

Figure 9 is a micrograph of a platinum shadowed 50% butadiene latex particle (not sliced but deposited on a collodion film in the normal manner). The core-shell morphology can be clearly discerned because of the difference in electron opacity between the rigid polystyrene core and the flattened copolymer shell. Curiously, as shown in Fig. 7d, the 50% butadiene thin section does not show the core inclusions as observed in Fig. 7b for the 10% butadiene specimen.

The only analogous studies of ultrathin sections we know of are

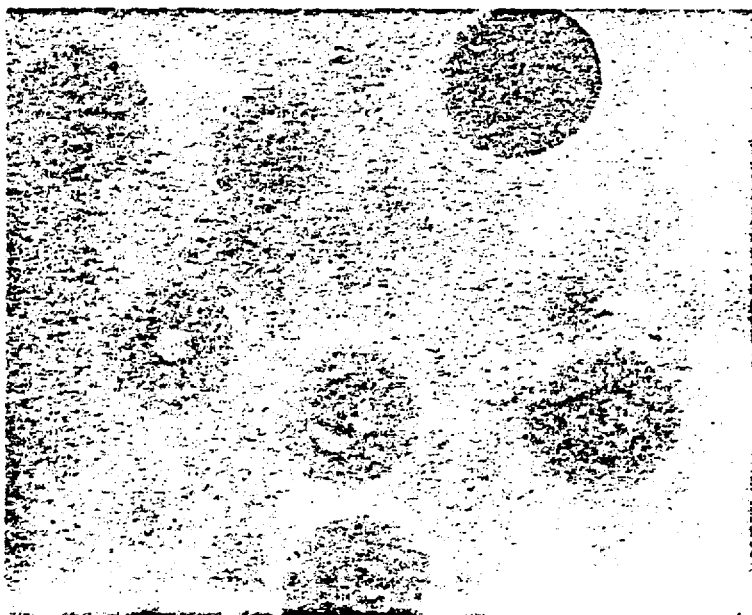


FIG. 8. A field of cross sections obtained from the latex sample containing 10% butadiene in the Monomer II charge. 129,675 \times .

reported by Kato [14] for ABS particles. He varied the ratio of rubber seed (PB) to glassy-shell (AS) from 80/20 to 20/80. (He did not specify the A/S ratio.) He also varied the rubber seed size. It is difficult to compare our results with his because he does not adequately describe the preparation procedures in the seeded polymerization, and the experimental variables in the seeded polymerizations are not the same. One of Kato's primary objectives was to demonstrate that the AS monomer charge actually grafted in such a way to form a core-shell structure. He was evidently concerned with the effect incompatibility would have on the bonding between the PB and the newly formed AS copolymer.

Kato found the core-shell morphology to prevail over a Monomer II to seed weight ratio range of 0.25 to 4.0, the shell thickness increasing with increasing Monomer II content. He also found that, when large and small seed particles were used together, the simple core-shell morphology prevailed only in the small particles. With the large particles (approaching 1μ in diameter after seeded polymerizations) the

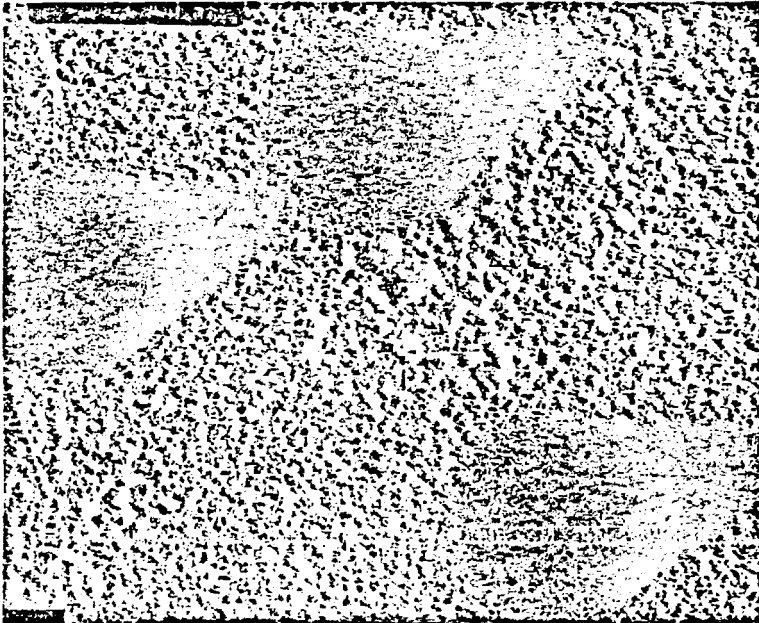


FIG. 9. Micrograph of a platinum-shadowed sample of the latex containing 50% butadiene in the Monomer II charge. 57,710 \times .

AS copolymer adhered to the surface in hemispherical, wartlike appendages, whereas we find the completely spherical core-shell morphology to prevail in particles up to at least 6000 Å in diameter. It is impossible to explain the latter results with the scant polymerization procedures given by Kato; it might have resulted from a failure to allow sufficient time for latex saturation (see Bradford and Vanderhoff [13]). Kato's micrographs also show inclusions in the core, indicating the presence of the second monomer as we have also noted. In the ABS system, the inclusions are more clearly defined than they are in our work. It is impossible to unambiguously state the reasons for this without having more knowledge of Kato's formulations. It might possibly be ascribed to the different order of butadiene addition or to the fact that the seeds in Kato's work might be lightly cross-linked, thereby enhancing phase separation of the included material. The role of these core inclusions in establishing a polymer's mechanical properties remains to be elucidated.

FACTORS CONTROLLING LATEX
PARTICLE MORPHOLOGYOvercoating

We now wish to discuss the implications of our findings with regard to the factors controlling the morphology of latex particles prepared in multistaged monomer additions. In macroscopic multicomponent polymer blend systems, several factors control the morphology. Among these are the organochemical structure, the macromolecular structure, mixing (especially if the specimens are prepared from the melt), and orientation. In latex systems the morphology is controlled by the organochemical structure, the macromolecular structure and, most importantly, by the mode of monomer addition. Bradford and Vanderhoff [13] have shown that the exterior morphology can be distorted from spherical in seeded polymerizations by not allowing sufficient time for the second stage monomer to saturate the seed particles. Similar effects were observed in competitive growth polymerizations where the monomer is a poor solvent for the seed polymer. We are concerned with situations in which a spherical particle shape is maintained.

In practice, execution of the overcoating process is accomplished by adding the monomers in such a manner that they do not have sufficient time to completely "swell" the particle, and they tend to layer around the original seed particle to form a core-shell structure. Polymer-polymer incompatibility is thought to aid this layering process. Our work suggests that one need not worry about diffusion or even incompatibility in compatible monomer-polymer systems; for, even under conditions of equilibrium saturation, core-shell structures can be obtained. This observation should ease the rigor of scheduled monomer additions in multistage latex synthesis.

This last contention is supported by the results obtained by Sperling et al. [19] who studied the dynamic mechanical properties of two-stage latex polymers prepared both by dropwise addition of Monomer II to Polymer I and by charging the total amount of Monomer II all at once to Polymer I. The polymer composition in both cases was 1:3 ethyl methacrylate to *n*-butyl methacrylate, each cross-linked with 0.4 wt% tetraethyleneglycol dimethacrylate, corresponding to core and shell, respectively. Their data, summarized in Fig. 10, are nearly identical for both specimens, thereby indicating that there are no important differences in the morphology of the two specimens. (Slow monomer addition may still be required in order to maintain adequate temperature control.)

In order to ascertain how the inherent incompatibility of the component polymers might affect particle morphology, we prepared

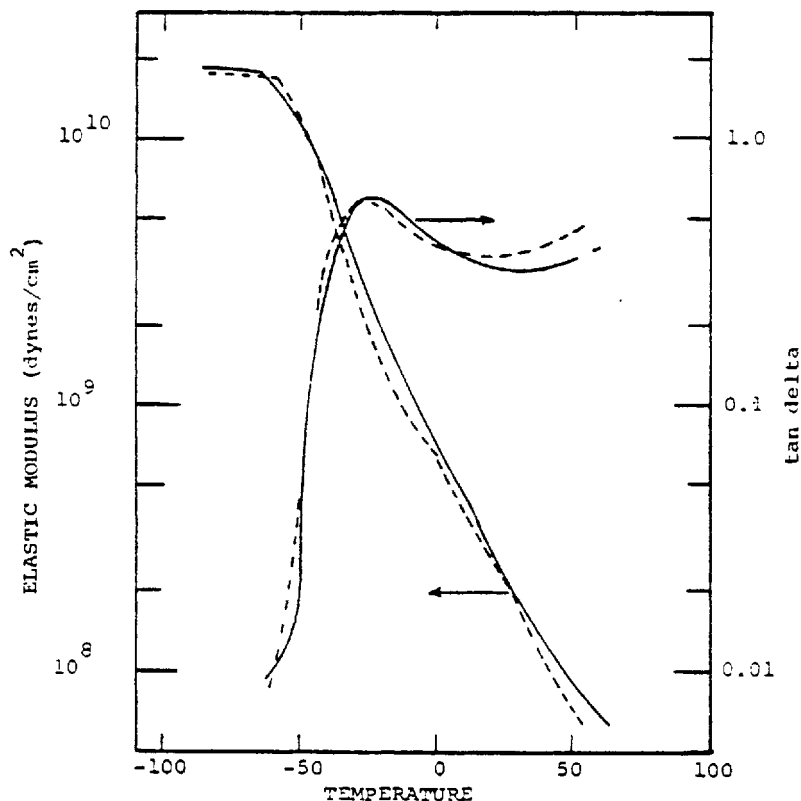


FIG. 10. Dynamic mechanical behavior of latex prepared in a two-stage emulsion polymerization. Seed: 1 part PEMA. Overcoat: 3 parts PnBA. Polymerization temperature: 60°C. Monomer II addition: (--) Dropwise and (—) all at once. After Ref. 19.

thin films of latex polymer for electron microscope observation. A thin film of the 10% butadiene latex polymer (Fig. 11) was prepared by casting over water from a 1% amyl acetate solution. Grids were placed on the floating film and then picked up in such a way as to carry off the cast film. The specimens were dried and exposed to osmium tetroxide. The important point in this experiment is that we prepared this film from macroscopic homogeneous solution under conditions where the components were mobile and well mixed. The film observed should then pertain to a state of thermodynamic equilibrium, and the structures

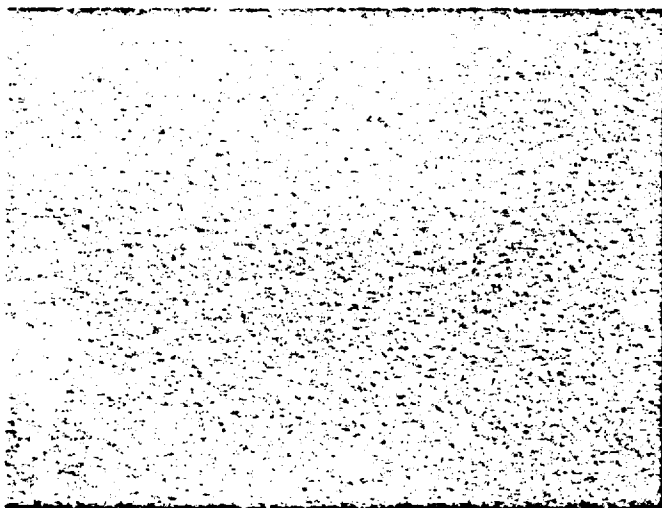


FIG. 11. A thin film case from a homogeneous solution of the latex polymer containing 10% butadiene in the Monomer II charge. 282,150 \times .

observed in Fig. 11 should also be independent of any mixing considerations as they are in incompatible styrene-butadiene systems prepared from the melt. Thus in seeded polymerizations where Monomer II and Polymer I are compatible, if the monomer actually swelled the seed particles and if incompatibility controlled the particle morphology, then structures similar to that shown in Fig. 11 should be observed rather than the core-shell structure. In conclusion, for seeded polymerizations with compatible monomer-polymer systems, the incompatibility of Polymer I with Polymer II is probably not a factor in controlling the primary features of particle morphology, and the dominating factor is the encapsulation phenomenon. Polymer-polymer incompatibility might very well be a controlling factor in establishing such secondary morphological features of the high butadiene content latexes as the butadiene inclusions in the core and the high concentration of butadiene in the dark ring surrounding the core.

The case against polymer-polymer incompatibility as a controlling factor for the primary morphological features is reinforced by considering an alternate explanation for the appearance of the core-shell structure. One might be tempted to argue that at equilibrium saturation the particles are actually homogeneously distributed and that during re-polymerization the formation of Polymer II, which is incompatible with

Polymer I, causes Polymer I to selectively migrate to the core and Polymer II to the periphery—all en masse—even though the second generation polymer in the initial stages of the reseeded polymerization is present in minor portion. Such mass migration would also be precluded as polymerization proceeded (within the time-scale of the repolymerization) because of the high viscosity that would prevail in a homogeneously distributed particle. Because of the lack of a driving force for polymer migration in the early stages of reseeded and the limited mobility of the polymeric species in the later stages, polymer-polymer incompatibility should be manifested more as shown in Fig. 11 and not in a core-shell morphology. Selective migration of the tagged molecular species in the autoradiography experiments would be an equally preposterous explanation, and this fact also argues in favor of morphology control by the encapsulation phenomenon.

Latex Interpenetrating Polymer Networks

The synthesis of a (cross-linked) polymer Network II within a pre-existing (cross-linked) polymer Network I results in a class of polymer blends known as interpenetrating polymer networks (IPN's) [20]. These double network structures display most of the properties of polymer blends, but in addition they provide a way of controlling phase domain size as well as the extent of molecular mixing. The original IPN's were prepared in (bulk) macroscopic systems, but recent efforts have been made to extend the same principles to preparing latex-based IPN's [17, 19]. It must be recognized at this juncture, however, that because of the encapsulation phenomenon, completely analogous systems cannot be prepared. Some interpenetration will occur when Monomer II is added to latex Polymer I, but uniform swelling of Network I is, of course, ruled out.

Plasticization of Latexes

Bradford et al. [13, 21] have reported attempts to plasticize latex particles by adding plasticizer directly to aqueous suspensions. This was done in order to obtain film-forming latexes from those polymers which were not ordinarily film-formers at room temperature. Some of the plasticizer-latex combinations they studied did not form continuous films as readily as normal film-formers do. In particular, considerable aging of the plasticizer-latex combination was required before films could be formed. The peculiar effects observed with latex plasticization was attributed to a slow diffusion of plasticizer into the latex particles, whereas the encapsulation phenomenon dictates that complete homogeneous plasticization of the latex particles cannot be achieved

PLASTICIZATION of LATTICES to OBTAIN
FILM FORMING POLYMERS

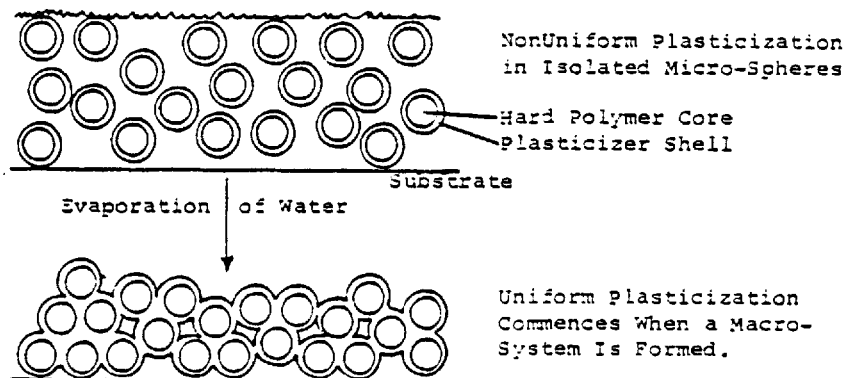


FIG. 12. A schematic drawing showing, according to the encapsulation phenomenon, how the process of latex plasticization might actually occur. For illustrative purposes the particles are shown as "pure" core-shell.

while the particles are in aqueous suspension. Although Bradford et al. considered aging times of the latex-plasticizer mixtures, they did not consider or state the aging times of the films prior to electron microscopy. This circumstance is unfortunate, since according to our work the age of the film prior to microscopy is an important parameter in assessing their results. As we have attempted to depict in Fig. 12, for the extreme case of complete core-shell separation, only in the process of forming the film with removal of the water as the particles come into contact can the plasticizer begin to distribute uniformly. This occurs because of removal of the aqueous interface and formation of an "oil-oil" interface between the newly contacted particles. The polymer molecules are now free to mix, and uniform distribution of polymer and plasticizer can thereby be achieved.

SUMMARY

We have been primarily concerned with the factors that control the latex overcoating process in systems where Monomer II is compatible with Polymer I but Polymers I and II are incompatible. The core-shell

morphology that results is probably controlled by the same factors that control the encapsulation phenomenon in compatible, homopolymer processes—such as styrene emulsion polymerization. Polymer-polymer incompatibility might result in such secondary morphological features as core inclusions. Further research in this important area of industrial polymer engineering is warranted.

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