Fundamental Studies on Morphology Control For Latex Systems with Application to Waterborne Coatings: The Effect of Polymer Radical Mobility In Latex Particles During Polymerization

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This work reports on the development of composite latex particle morphology in seeded, semicontinuous emulsion polymerization. Previous work has explained particle morphology development in terms of the ability of second stage polymer radicals to diffuse into, or "penetrate," the seed particles. This article investigates two separate effects that essentially alter the mobility of the second stage polymer radicals. The first is the initiator type, specifically nonionic versus ionic initiators, and the second is the use of chain transfer agent (CTA). It is shown that ionic initiators make it more likely to obtain core shell morphologies by decreasing the penetration of radicals, but only under a narrow set of conditions. Chain transfer agents, on the other hand, allow for more deviation from core shell morphologies by increasing the penetration of radicals, but significant changes were only observed at the highest concentration of CTA studied. Therefore, both factors are fairly subtle and effects are only observed under specific conditions.

INTRODUCTION

Polymer latices containing structured latex particles having two distinct polymer phases (composite particles) have many applications including widespread use as waterborne paints and coatings, adhesives, and impact modifiers. These latices are produced by starting with a "seed" latex, in which the seed particles are composed of one type of polymer, and polymerizing a different monomer within the existing seed particles during a second stage, usually by a free radical polymerization mechanism. In almost all cases the second stage polymer will phase separate within the seed particles and produce a structured particle. The properties of the final products depend largely on the particle morphology (the spatial arrangement of the two polymer phases within the particles). Therefore, there is much incentive to understand the factors that control particle morphology.

It is well known that particle morphology can be controlled by either thermodynamic or kinetic factors.[1-4] Morphology development under thermodynamically controlled conditions has been more thoroughly studied and the current level of understanding is much greater than in the case of kinetic control. Under thermodynamic control, the particle morphology development is driven by a minimization of the interfacial free energy of the system, resulting in what is called the equilibrium morphology.[1,4-10] However, in many cases the highly viscous conditions within the polymer particles limits the rearrangement of the two polymer phases and prevents the equilibrium morphology from being formed. In such cases the morphology is considered as being kinetically controlled.

Recently, it has been shown that kinetic control of particle morphology can be understood in terms of the ability (or inability) of second stage polymer radicals to penetrate into the interior of the seed particles.[3,11,12] Water soluble initiators are most commonly used in emulsion polymerization, so radicals are formed in the aqueous phase and then enter into particles where they

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Table 1—Characteristics of Seed Latices

Series	Monomer Ratio (by weight)	Solid Content (%)	T_g of Copolymer (°C)	Particle Size (nm)
Initiator type	50MMA/50MA	16.6	54	188 (QUELS)
CTA	50MMA/50MA	17.6	51	188 (CHDF)

continue to propagate. In many cases very slow diffusion rates can prevent the radicals from reaching the interior of the particles and this will confine the second stage polymerization to the outer shell areas. This situation will result in a core shell morphology even in cases where the equilibrium morphology is not core-shell. Quantification of the extent of penetration of second stage radicals has led to the calculation of so called "fractional penetration" values, which have proven to correlate very well to actual morphologies obtained in experiments.[3] Previous studies have altered the ability of radicals to penetrate by changing the nature of the seed polymer phase, for instance by changing the T_g of the seed polymer.[11-12] In the present work, the ability of the radicals to penetrate the seed particles, and thus the development of kinetically controlled morphologies, is studied by altering the mobility of the second stage radicals through changes to the nature of the radicals themselves. In particular, the effect of second stage initiator type and the effect of chain transfer agent on particle morphology are investigated.

One way to alter the mobility of second stage radicals within seed particles is to anchor them to the particle surface. There is an ongoing discussion in the literature about the extent to which ionic end groups on polymer chains resulting from ionic initiators can anchor to the particle surface. It is known that some portion of the initiator end groups will be present on the particle surface as this is commonly understood as being responsible for the colloidal stability of latices that are produced by surfactant free emulsion polymerization.[13,14] Numerous studies have described the measurement of charge density on particle surfaces,[14,16-19] thus confirming the presence of charged end groups. Various researchers have either used surface anchoring to help explain experimental results, or used the assumption that radicals are indeed surface anchored.[19-24]

One previous study by Jönsson et al. investigated the effect of charged vs. uncharged initiators on particle morphology.[25] However, this study used PMMA as the seed polymer, which has a very high T_g and was in the glassy state under the reaction conditions. Diffusion is very slow in these particles and the penetration concepts described previously suggest that penetration of radicals would be relatively limited whether or not the radicals were anchored. Therefore, it seems that these experiments did not fully answer the question of whether radical anchoring can have a significant effect on particle morphology.

Not all of the second stage polymer chains are expected to be anchored to the particle surface by ionic end groups. The fact that it is possible to produce inverted core shell morphologies even in cases where charged initiators are used in the second stage suggests that some end groups can be buried.[3] Furthermore, in cases using the common ionic persulfate initiators, not all of the end groups will be charged due to the possibility of side reactions (hydrolysis, etc.) giving rise to several possible end groups, some of which are uncharged.[15,26,27] This may decrease the effect that ionic initiators might have on particle morphology development. Another route to forming polymer chains that do not have ionic end groups, even when using ionic initiators, is chain transfer to monomer reactions. These reactions occur when the radical activity is transferred to a monomer molecule rather than incorporating the monomer molecule into the chain by propagation. This results in an uncharged radical that is small and mobile (compared to the original polymeric radical) and can continue to penetrate into the particles without any restrictions that may arise from end group anchoring.

This last point directs this discussion to a second approach that can be used to alter radical mobility, the chain transfer reaction. Chain transfer to monomer reactions occur very infrequently in a free radical polymerization, and can therefore be assumed to only play a minor role in the penetration of radicals under most conditions. However, many industrial recipes often make use of chain transfer agents (CTAs) to lower the molecular weight of the polymer produced. In a reaction with CTA, the radical activity is transferred to a CTA molecule, which again is much smaller than the original radical chain, and therefore can diffuse much faster. Fractional penetration calculations have shown

Table 2—Recipes for Representative Second Stage Experiments

Series	Initiator Type	Initiator Type	CTA
Seed latex (g)	72.4942	72.4705	79.7356
Water (g)	120.3255	120.2923	116.5857
SDS (g)	0.1131	0.1118	0.0724
$NaHCO_3$ (g)	0.0938	0.0939	0.0573
Initiator type	KPS	VA-086	KPS
Initiator solution (g)	7.6128	7.3361	3.3837
Initiator solution conc. (mol/L)	0.01	0.06	0.01
Initiator solution feed rate (ml/hr)	0.6	—	0.8
Styrene feed time (min)	60	60	120
Styrene feed rate (ml/hr)	13.2	13.2	7.7
Total styrene fed (g)	12.0	12.0	14
n-DM fed (g) (solution with monomer)	—	—	0.0350

that the majority of the distance that radicals penetrate into particles occurs while they are very short.[3] This is true because as they grow to significant lengths by propagation, their diffusion coefficients decrease drastically. Thus, it is possible that the use of chain transfer agents can increase penetration of second stage radicals by increasing the frequency at which short, mobile radicals are produced within the particles.

The above arguments have provided the motivation for the studies described in this article. These factors have been investigated by conducting a series of experiments using seed latices with particles composed of poly(methyl acrylate-co-methyl methacrylate), (P(MA-co-MMA), and polymerizing styrene in the second stage at a reaction temperature of 70°C. The equilibrium morphology for this system is an inverted core shell, where formation of a core of the second stage polystyrene is thermodynamically favored.[12] The glass transition temperatures (T_g) of the seed copolymers are in the range of 50-55°C. This condition of reaction temperature and T_g was chosen based on results of previous experiments that showed that a significant level of penetration, but not full penetration, is possible under these conditions.[11,12] Thus, the conditions are in the range where slight changes in the radical mobility should have an observable effect on the level of penetration, and hence the particle morphology. To study the effect of initiator type, experiments were performed at various styrene feed rates. At each feed rate one reaction was conducted using potassium persulfate (KPS) as the initiator, which produces charged end groups, and another using VA-086 initiator, which produces uncharged end groups. To study the effect of chain transfer, the styrene feed rate was fixed and various levels of n-dodecyl mercaptan (n-DM), a commonly used CTA, were added to the monomer feed stream. The resulting particle morphologies were observed using transmission electron microscopy (TEM). In the case of the CTA experiments, surfactant titrations were also performed to probe the composition of the particle surfaces.

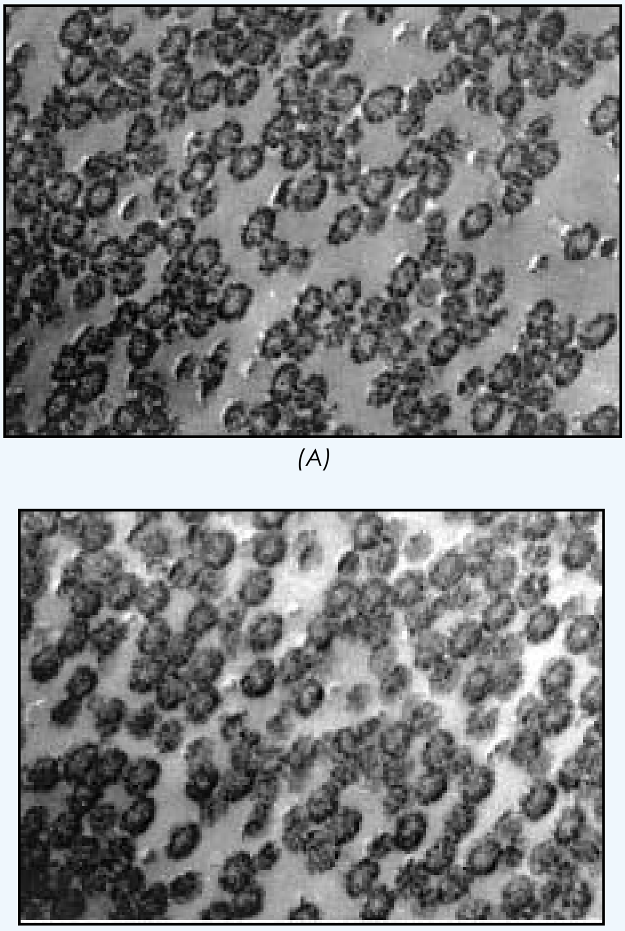
EXPERIMENTAL

Chemicals

Styrene, methyl acrylate and methyl methacrylate monomers (Acros Organics) were passed through a column of alumina adsorption powder (80-200 mesh, Fisher Scientific) to remove inhibitors and stored at –10°C. Potassium persulfate, (analytical grade, Acros Organics) VA-086 (2,2-Azobis[2-methyl-N-(2-hydroxyethyl) propionamide], Wako Chemical, Inc.), analytical grade sodium bicarbonate (EM Science), sodium dodecyl sulfate (99%, Acros Organics) and n-dodecyl mercaptan (Acros) were used as received. Deionized water from a Corning Mega Pureä D2 water purification system was used in all experiments.

Transmission Electron Microscopy

Samples of the final latices were dried at room temperature to remove water, and then ground into a powder. A small amount of the powder was then embedded in EPON 812 epoxy (Fluka Chemical Corp.) and cured at 60°C for eight hours. Microtomed sections of approximately 90 nm thickness were observed in a Hitachi H600 transmission electron microscope. It was not necessary to stain the samples, as there is already adequate contrast between polystyrene and the p(MA-co-MMA) phases in the microscope. However, for the CTA series experiments the particles were stained with Ruthenium oxide vapor before viewing in the TEM.



(A)

(B)

Figure 1—Microtomed TEM images of particles from initiator-type experiments with a two-hour styrene feed time. (A) KPS initiator, (B) VA-086 initiator.

Seed Latex Preparation

All seed latex polymerizations were conducted in a 1 L jacketed glass reactor at 70°C under a nitrogen atmosphere. Compositional drift during the copolymerization of MA and MMA was a concern. In order to obtain a seed polymer with uniform composition and a narrow T_g range, the seed latex was produced in a controlled manner by growing the particles starting from a previously formed preseed latex. The preseed latex was made by batch emulsion polymerization using the same monomers and ratios and had a particle size of approximately 70 nm. These particles were then grown to

Table 3—Conversion Averaged Monomer Concentrations (mol/L) in the Particles for the Initiator-Type Series

Styrene Feed Time (hr)	KPS Initiator	VA-086 Initiator
0.5	0.82	1.71
1	0.71	0.68
1	0.81	0.79
2	0.46	0.49
4	0.47	0.53
8	0.29	0.39

approximately 200 nm by semicontinuous emulsion polymerization with a slow monomer feed rate. In this way, the monomer concentration in the reactor is maintained at low levels so that compositional drift is avoided, producing a uniform, random copolymer.

For the seed latex used in the initiator type experiments, the latex was repeatedly passed through a column of ionic exchange resins (Barnstead/Thermolyne) to remove residual initiator (the surfactant and buffer will also be removed in this case). This step was necessary to allow the initiator type and concentration to be carefully controlled during the second stage polymerizations. In the CTA experiments this step was not necessary as KPS was used in all of these cases and the amount remaining in the seed latex was accounted for in the second stage recipes. The characteristics of the final seed latices are shown in *Table* 1.

In all polymerizations (both seed and second stage), samples were withdrawn from the reactor throughout the polymerization and the monomer conversion in each was determined gravimetrically. Particle sizes of the final latices and of intermediate samples were measured by quasi-elastic light scattering (QUELS) using a Coulterâ Nanosizerä or CHDF using a Matec Applied Sciences CHDF 2000. The glass transition temperatures of the seed latex polymers were determined using a Perkin-Elmer Pyris 1 differential scanning calorimeter.

Second Stage Polymerizations

The second stage polymerizations were conducted in a 250 ml glass reaction flask equipped with a water jacket and the temperature was regulated at 70°C under a nitrogen atmosphere. Stirring was performed using a magnetic stirrer at a rate fast enough to prevent the monomer from pooling as it was added to the reactor. All ingredients except the monomer and initiator were added to the reactor. Once the contents of the reactor reached 70°C, the initiator solution was added and the monomer and initiator (if necessary) feeds were started using a motor driven syringe pump. In all cases, the total amount of styrene added during the reaction was determined in order to give a stage ratio (mass of second stage monomer to mass of seed polymer) of 1:1.

Experiments in the initiator type series were conducted at various monomer feed rates, with the total styrene being fed over one-half, one, two, four, and eight hours. For the polymerizations with the one-hour feed time, repeat experiments were performed to check the reproducibility of both reaction kinetics and particle morphology. For each monomer feed rate two experiments were performed, one using KPS as the initiator, and the other using VA-086. The initiator concentrations were calculated in order to give the same rate of radical production for each initiator. This is an important issue as it provides the highest potential of observing changes in particle structure due exclusively to the variable under investigation. The value of the dissociation rate coefficient, k_d, at 70°C for KPS[13] (2.2×10^{-5} s^{-1}) is greater than that for VA-086[28] (3.83×10^{-6} s^{-1}). Therefore, a higher molar concentration of VA-086 was required in those reactions. When using KPS initiator, additional KPS solution was added continuously to account for the KPS dissociating to form radicals and maintain a constant KPS concentration in the reactor. This was not necessary when using VA-086 because its decomposition rate is slow enough that the change in concentration over the course of the reaction is negligible.

For the experiments in the CTA series, the total styrene was always fed over a period of two hours and KPS was always used as the initiator. The CTA, n-dodecyl mercaptan (n-DM), was added to the styrene monomer at various concentrations of 0, 0.11, 0.25, 0.59, and 1.25% (by weight). Representative recipes for the second stage polymerizations are given in *Table* 2, for both experiments in the initiator series at the one-hour feed rate, and for the experiment in the CTA series with 0.25% n-dodecyl mercaptan. In the initiator type series, the only variables to change between experiments were the initiator type and the monomer feed rate. In the CTA series, only the n-dodecyl mercaptan concentration in the monomer was varied.

RESULTS AND DISCUSSION

The conversion of monomer to polymer and the monomer concentration within the particles during the reaction are easily calculated by combining the solid content data obtained from gravimetric analysis of samples removed during the reaction with a mass balance calculation. In all experiments except for one, the conversion vs. time line was essentially parallel and close to the line representing the amount of monomer that had been fed vs. time. This indicates that the reaction is essentially at steady state during the majority of the reaction (rate of conversion of monomer to polymer equal to rate that monomer is fed to reactor) and that the monomer concentrations in the particles at any time are fairly low. Polymerizations conducted in this manner are commonly referred to as “starve fed” or “monomer starved.” Deviation from this behavior occurred in only one experiment, the experiment with VA-086 initiator when the monomer was fed over only 30 min. In this case, the conversion line did not follow the feed line, and resulted in an accumulation of monomer in the particles and a higher effective monomer concentration in this experiment.

Effect of Initiator Type

In the series of experiments studying initiator type, experiments were conducted at various monomer feed rates because this results in different monomer concentrations within the particles during the reactions. At faster monomer feed rates the monomer concentration tends to increase. This is important because the diffusion rates in the particles are a function of the monomer concentration.[29-34] Estimation of the diffusion coefficients of small molecules in the seed polymer using an empirical method[29] suggests that for the present system the values change very rapidly with monomer concentrations below about 10% (by weight) monomer. Since the experiments were largely starve fed and in this region of low monomer concentration during the reactions, slight changes in the monomer concentration of only a few percent can result in significantly different diffusion conditions in the particles and may result in significant changes in particle morphology. In fact this result was observed by Karlsson[12] using a very similar system and was the reason for choosing this type of system in the current study.

The monomer concentrations within the particles for the experiments in the initiator type series, averaged over conversion from the various samples withdrawn from the reactor, are shown in *Table* 3 for the various monomer feed rates. The first thing to note is that as the feed rate of monomer was increased (shorter feed times), the monomer concentrations within the particles also increased. Therefore, at faster feed rates the diffusion rates of radicals within the particles will be greater. It is also clear that for the slower feed rates (feed times of two, four, and eight hours) the monomer concentrations did not vary greatly, so for these polymerizations the diffusion rates of radicals will also be very similar.

The most important point to note from *Table* 3 is that for a given feed rate, the monomer concentrations are almost always the same whether KPS or VA-086 was used as the initiator. This is a very important point because it suggests that, for a given monomer feed rate, the diffusion rates of radicals within the particles are the same regardless of initiator type, unless differences result from radical anchoring when using KPS. For the repeat experiments at the one-hour feed time the monomer concentrations are fairly similar, confirming that the results are in fact reproducible. It is also seen that for the 30 min feed time the monomer concentrations are not the same. This is because for the experiment at this feed rate using VA-086 the reaction was not monomer starved, as discussed previously.

In all of the TEM images that follow, the darker areas represent the polystyrene phase. The images are of microtomed sections of the particles so that one is viewing cross sections of slices cut through the particles. It must be kept in mind that not all of the particles are cut directly through the center, but in many cases just the edges (tops or bottoms) of particles are included in the microtomed section. Therefore, to get an accurate representation of the internal structure of the particles, one should focus on the particles that appear largest in the TEM image, because these are the ones that were sliced more through the center of the particles.

Figures 1a and 1b show the morphology results for both the KPS and VA-086 polymerizations with a two-hour monomer feed time. It is clear that the resulting morphology in both cases consists of a shell of polystyrene domains around the seed polymer, but also with many occlusions of polystyrene within the seed polymer core. This suggests that some level of penetration is possible, but that penetration is restricted enough so that there is a larger concentration of second stage polystyrene domains at the particle surface. In these pictures there is no obvious difference between the morphologies obtained with either initiator. The TEM photos for the experiments with the four- and eight-hour feed times all showed the same "occluded core shell" morphologies as for the two-hour feed time in *Figure* 1, so they have not been included for the sake of brevity. There was still no observable difference in the morphologies obtained for the different initiators. The identical morphologies for the three slower feed rates are expected by the similarity in their effective monomer concentrations during the reaction (and thus similar diffusion rates), as shown in *Table* 3. The fact that essentially identical morphologies are obtained in all of these experiments irrespective of which initiator is used shows that radical anchoring due to charged end groups does not have a significant effect on particle morphology development under these conditions.

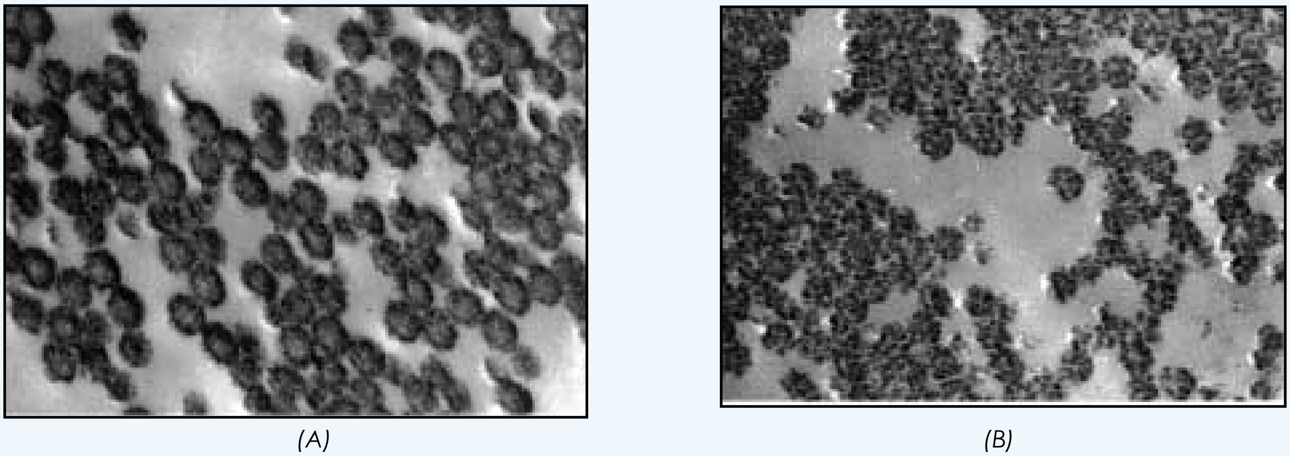
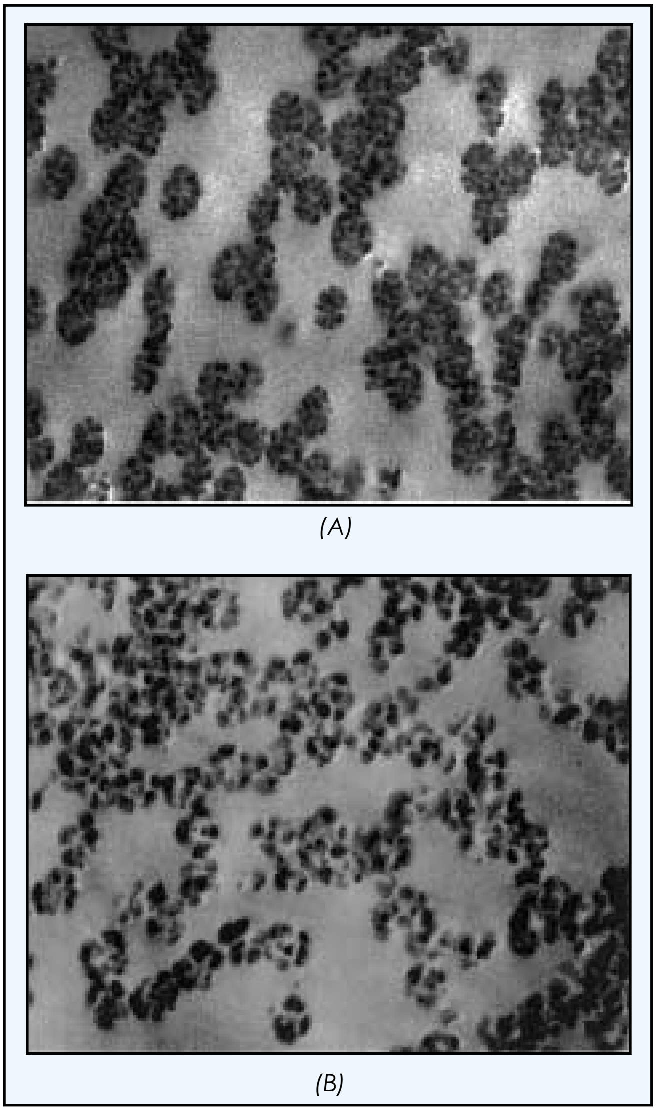

(A) (B)

Figure 2—Microtomed TEM images of particles from initiator-type experiments with a one-hour styrene feed time. (A) KPS initiator, (B) VA-086 initiator.


(A)

(B)

Figure 3—Microtomed TEM images of particles from initiator-type experiments with a half-hour styrene feed time. (A) KPS initiator, (B) VA-086 initiator.

The morphology results for the reactions with a one-hour feed time are shown in *Figures* 2a and 2b. Here, the experiment with the KPS initiator shows a similar occluded core shell morphology as observed for the experiments with slower feed rates. However, for the experiment with the VA-086 initiator there is no shell of polystyrene domains around the particles. Instead, the morphology from this experiment is simply an occluded type with domains of polystyrene located uniformly throughout the particles. This clearly shows that the uncharged radicals from the VA-086 initiator were able to penetrate into the seed particles more easily than the charged radicals from the KPS initiator. The monomer concentrations are very close for the two experiments and result in very similar diffusion rates for the incoming radicals. Therefore, the differences in the morphologies are due to at least partial anchoring of the sulfate end group from the KPS at the particle surface, which prevents full penetration. TEM results for the repeat experiments at the one-hour feed time showed the same morphologies. Again, the experiment with KPS showed a polystyrene shell on the particles while the experiment with VA-086 was fully occluded with no shell, proving that this result is in fact real and reproducible. These photos have not been included here for the sake of brevity.

The morphology results for the experiments with the fastest feed rate, when the styrene was fed over one-half-hour, are shown in *Figures* 3a and 3b. In this figure, it is clear that neither reaction resulted in a morphology with a shell of polystyrene and in both cases strictly occluded morphologies were obtained. This shows that anchoring of radicals alone cannot cause core-shell morphologies to be obtained in all cases when ionic initiators are used in the second stage. In fact, this result is not surprising as morphologies deviating from core shell have been reported in previous studies that used KPS initiator.[3,12] In the present case, when the styrene was fed at a fast rate such as with the half-hour feed time, the monomer concentrations and thus the diffusion rates increased enough so that full penetration was possible and fully occluded morphologies resulted. Radical anchoring due to using KPS initiator was in itself not able to prevent this full penetration from occurring.

Another point that is clear from the morphology results for the half-hour experiments is that the sizes of the polystyrene domains in the experiment with VA-086 are much larger than those for the KPS experiment. This is surely due to the fact that the monomer concentration in the VA-086 experiment was significantly greater than in the experiment with KPS, as shown in *Table* 3 and discussed previously. This higher monomer concentration means that in the experiment with VA-086 the dead polymer chains will be able to diffuse more easily than in the KPS experiment. Increased diffusion of the polymer chains will allow more consolidation of the phases, resulting in larger polystyrene domains. The driving force for this consolidation (likely to occur via Ostwald ripening) is a lowering of the total interfacial free energy of the system.[1]

Effect of Chain Transfer Agent

This set of experiments used a different seed latex (although with essentially the same properties) than the one in the initiator type series, and this was the reason for repeating the experiment with pure styrene (0% n-DM). In all cases, the monomer concentrations during the reactions were in the range of 0.4 to 0.5 M in the particles, which is the same observed in the initiator type series for this feed rate. The molecular weight results for the polystyrene produced in the second stage, as determined by GPC (calibrated using polystyrene standards) are shown in *Table* 4. The polydispersity (weight average MW divided by number average) values range from 2-4 and are thus quite high. This is common for second stage emulsion polymerization reactions. The discussion that follows will focus on the number average molecular weight, since this gives the best indication of the conditions that exist for the diffusion of the majority of the chains that are formed.

Table 4—Molecular Weights of Second Stage Polystyrene in CTA Experiments

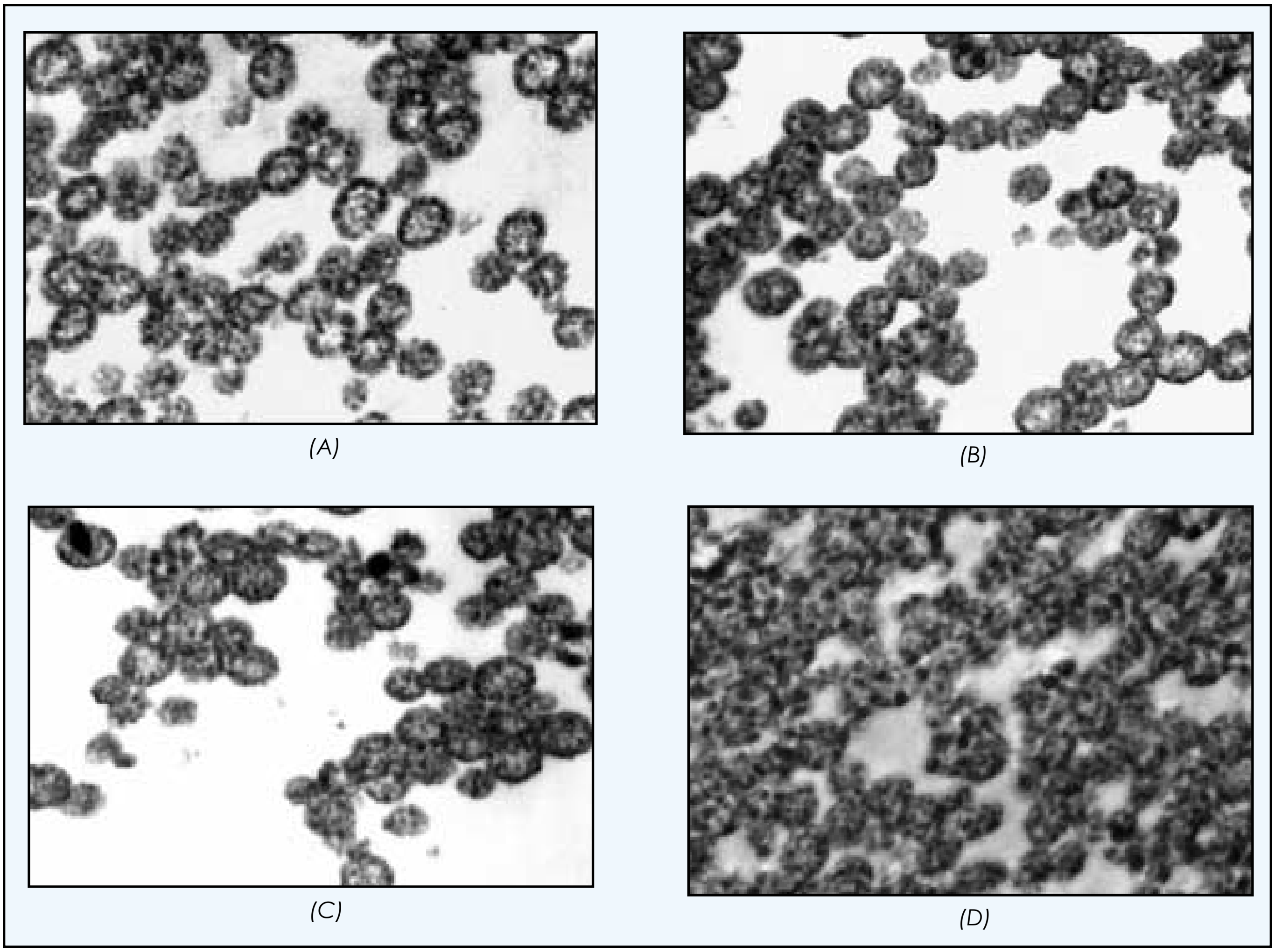
% n-DM	Wt. Ave., Mw (g/mol)	Num. Ave., Mn (g/mol)	Polydispersity, Mw/Mn	Transfers per Entered Radical
0	910,600	321,500	2.8	0
0.11	480,300	130,100	3.7	1.5
0.25	365,900	101,800	3.6	2.2
0.59	273,000	83,700	3.3	2.8
1.25	155,700	36,400	4.3	7.8

It is clear that the addition of n-DM was effective in decreasing the molecular weight of the polystyrene as more n-DM was added, as the weight average values decreased from 320,000 without n-DM to 36,000 with 1.25% n-DM. The last column gives an estimation of the number of transfer reactions that occurred per entered radical. This is determined by comparing the number average MW values for the experiments with added n-DM to the first experiment with no n-DM. It is assumed that with no n-DM, most radicals do not experience transfer reactions since the only possible reaction (other than transfer to polymer, which does not help penetration) is transfer to monomer. Since the molecular weight produced in this experiment is below 10^6 g/mol, it can be assumed that most chains are stopped by termination reactions rather than transfer to monomer. The number of transfer steps per entered radical gives an idea of the frequency at which short mobile radicals are formed in the experiments with added n-DM. At 0.11% n-DM, there are on average between one and two transfer reactions occurring per entered radical. At the highest concentration of 1.25% n-DM, the average is almost eight transfer reactions. Therefore, the frequency of transfer reactions varies greatly between the various experiments.

The TEM photos for the various CTA experiments are shown in *Figure* 4A-D. *Figure* 4A corresponds to the experiment without added n-DM and shows a morphology in which the polystyrene domains have penetrated to a significant extent but are still preferentially located towards the outer shell of the particles. This morphology is essentially the same as in the similar experiment in the initiator-type series in *Figure* 1A. In *Figure* 4B the particles for the experiment with 0.11% n-DM are shown. These indicate that the level of penetration may have increased slightly, but the morphology is largely similar to the experiment without n-DM. It is still possible to find particles (the ones cut more through the center during microtoming) that show less polystyrene domains within the center of the particles than towards the outside shell. The photos for the experiment with 0.25% n-DM have not been included because they are essentially the same as the experiment at 0.11% (which is not all that surprising given that the molecular weights produced are very similar). *Figure* 4C shows the particles for the experiment with 0.59% n-DM. This photo suggests a further increase in the level of penetration from *Figures* 4A and B. It is now more difficult to find particles that are largely free of polystyrene domains at the center, but it does appear that there is a slightly higher concentration of polystyrene domains towards the outside of the particles. The morphology has changed from the case without n-DM, but this change is not drastic.

The particles formed using 1.25% n-DM, the highest concentration studied, are shown in *Figure* 4D. Here it is very clear that the morphology has changed significantly from the previous experiments. Now there is no indication of a gradient in the density of polystyrene domains from the center towards the outside. The particles are fully occluded, with domains being located uniformly throughout the particles. In addition, the polystyrene domains are clearly larger than in the previous experiments. The larger domains indicate an increased level of consolidation of the two polymer phases. Consolidation of the polystyrene domains requires diffusion of the polymer chains. The molecular weight of the polystyrene formed in this experiment is significantly lower than in the other experiments, with the number average being only 36,000 g/mol. Lower molecular weight chains are able to diffuse far more easily than longer chains, and this allows for increased levels of consolidation giving rise to significant differences in the final morphologies produced. Therefore, there are two factors that affect the morphology when using CTA. The first is the increased frequency at which small, mobile radicals are formed which allows for increased levels of penetration. The second is the production of lower molecular weight polymer, which is able to diffuse more easily and form larger, more phase consolidated domains. The results of these experiments show that the second effect seems to result in more drastic changes in morphology, but is only realized at significantly higher levels of CTA where much lower molecular weights are produced.

The existence of the many separate polystyrene domains in all of the observed morphologies in this study means that the particles have not reached the equilibrium morphology. Therefore, the morphology is controlled by kinetic factors in these systems. The fact that the radicals are able to penetrate the seed particles simply means that the morphology will not be restricted to core-shell. It does not mean that the equilibrium inverted core shell morphology will be achieved. The penetration of polystyrene in this case occurs because when the short radicals enter the seed particles from the water phase, the diffusion rates within the particles are fast enough to allow them to penetrate significant distances before they get too long and their diffusion rate slows down. It has been shown that the use of ionic initiators tends to decrease this level of penetration, while the use of CTA tends to increase penetration. However, in order for full phase consolidation to occur, even the long radicals and dead polymer chains must be able to diffuse fast enough to allow the separate polystyrene domains to come together and consolidate the separate polymer phases. The extent to which this was able to occur increased at higher CTA levels due to lower



(A)

(B)

(C)

(D)

Figure 4—Microtomed TEM images of particles from CTA experiments. (A) 0% n-DM, (B) 0.11% n-DM, (C) 0.59% n-DM, and (D) 1.25% n-DM.

molecular weight chains being produced, but not enough to allow the fully equilibrium morphologies to be produced.

CONCLUSIONS

The experiments conducted in this study show that both the use of ionic initiators and the use of CTA can affect particle morphology development, but that the effects are fairly subtle. The use of ionic initiators tends to decrease the penetration of radicals and increase the likelihood of forming core shell morphologies due to possible chain anchoring, but significant differences were only observed under very specific conditions when the styrene was fed over one hour. At faster feed rates, similar occluded morphologies resulted for both initiators, and at slower feed rates similar occluded core shell morphologies resulted for both initiators. The use of CTA was shown to slightly increase the level of penetration of the second stage polymer into the seed particles. However, obvious changes in morphology were only observed at the highest CTA concentration when the molecular weight of the polystyrene was significantly decreased, which then resulted in larger domains and more phase consolidated structures.

It should be kept in mind that the experiments here were designed using a system in which significant levels of penetration, but not full penetration, of the second stage polymer into the seed was possible. This was done by controlling the T_g of the seed polymer relative to the reaction temperature, in order to increase the possibility of observing changes in the morphology due to radical anchoring and chain transfer. Even under these conditions the effects were subtle. It is likely that under most conditions the effects of these variables will not be significant. For instance, when using a seed polymer with a low T_g relative to the reaction temperature, full penetration is likely to be possible and should occur whether or not ionic initiators or chain transfer agents are used. On the other hand, when the seed T_g is high compared to the reaction temperature, penetration should be restricted regardless of whether nonionic initiators or CTA is used.

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