

# Kinetics and Mechanism of Seeded Dispersion Polymerization

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**ABSTRACT:** The kinetics and mechanism of seeded dispersion polymerization of methyl methacrylate (MMA) was studied by applying both micron and submicron PMMA seeds. Using a 1.7  $\mu\text{m}$  PMMA seed ( $N_p = 1 \times 10^{12}/\text{L}$ ) and a monomer polymer ratio (M/P) of 28/1, secondary nucleation was found to occur and the number of new particles exceeded that produced in a parallel *ab initio* dispersion polymerization. This was explained by the paradoxical initiator concentration effect seen in dispersion polymerizations where the number of particles decreases with increasing initiator concentration. In contrast, using 194 nm ( $N_p = 26 \times 10^{12}/\text{L}$ ; M/P = 833/1) and 317 nm ( $N_p = 5.6 \times 10^{12}/\text{L}$ ; M/P = 714/1) submicron seeds, it was found that the final

particle number was similar to (or less in a few cases) the initial seed number over a relatively wide range of initiator concentrations. With increasing initiator concentration, the initial reaction rate increased but the maximum reaction rate decreased slightly. This was explained by increased radical termination particularly in unstable nuclei, leading to a reduced radical entry rate. The reaction rate was found to be moderately dependent on the number of seed particles, but was independent of the seed surface area. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2979–2987, 2008

**Key words:** seeded dispersion polymerization; radical polymerization; particle nucleation; mechanism

## INTRODUCTION

In dispersion polymerization, a precondition to obtain a narrow particle size distribution is that the number of particles should remain constant after a relatively short nucleation period.<sup>1</sup> However, precise control of particle nucleation to produce a specific particle size has often proven difficult and reproducibility can sometimes be poor. Figure 1 shows SEM images of PMMA particles obtained in the first 1% conversion of a dispersion polymerization that would eventually produce monodisperse micron size particles. It can be seen that relatively large PMMA particles (up to 1  $\mu\text{m}$ ) were produced as well as numerous small particles less than 100 nm, particularly at the lowest conversion. Although some of the observed particles might result from the sample preparation (aggregation of unstable particles during the drying process), the larger particles in Figure 1 are likely to be relatively stable compared to the smaller ones (less than 100 nm) since the larger particles in these images all have similar sizes. Another interesting finding is that coagulation and coales-

cence can take place between relatively large particles and lead to nonspherical particles [see Fig. 1(b)]. One can argue that these doublets were formed during the sample preparation; however, if aggregation can take place at room temperature, it is more likely to occur at the reaction temperature (70°C).

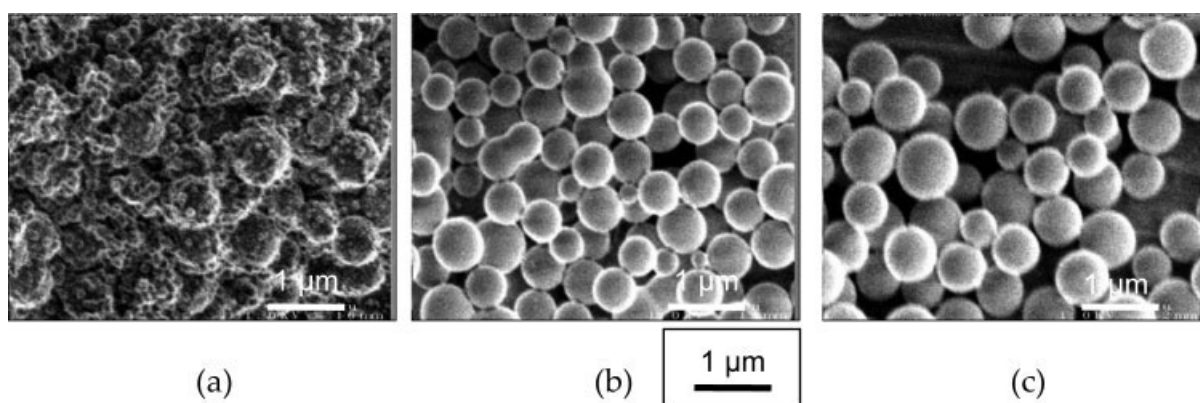
From Figure 1, one can also find that the particle size distribution near the end of the nucleation stage is not necessarily narrow. In fact, it is not likely or expected that the distribution is narrow by the end of nucleation. Monodispersity obtained in the final latex is achieved by competitive growth of the initially different size particles to finally form relatively large and uniform particles after a relatively long growth stage.

Difficulties in studying particle growth in conventional dispersion polymerization caused by the nucleation stage can be obviated by carrying out seeded studies, as is often done to study emulsion polymerization mechanisms. As part of this growth process, it is believed that unstable nuclei are formed throughout much of the reaction and these are captured by the much larger mature particles.<sup>2</sup> Therefore, it is also of importance to study conditions under which polydisperse particles are produced so that the conditions under which the nuclei are captured by mature particles can be understood.

Lu<sup>3</sup> studied the kinetics of seeded dispersion polymerization of styrene (St) using micron-size polystyrene (PSt) as seed. He found that, with the same

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**Figure 1** SEM images of PMMA particles at low conversions in MMA dispersion polymerization (left to right increasing conversion: Sample (c)  $\sim$  1.0% conversion). [AIBN] = 5.0 mM, [PVP K-30] = 20.0 wt % based on monomer, methanol/water = 70/30,  $T_r$  = 70°C, 400 rpm in the RC1 reactor.

monomer-to-polymer seed ratio (50/50 wt/wt), the reaction rate increased with decreasing PSt seed size (increasing number of particles) and increasing initiator concentration. In addition, the dependence of the reaction rate on initiator concentration was not found to be linear but decreased at higher initiator concentrations. Lu concluded that a heterogeneous polymerization mechanism can quantitatively describe the reaction rate at high conversions, although the radical entry mechanism could either be diffusive or colloidal.<sup>3</sup>

In Lu's work,<sup>3</sup> the kinetics of seeded dispersion polymerization was studied at only a single and relatively low monomer-to-polymer ratio ( $M/P = 1/1$ ), equivalent to starting at 50% conversion in an *ab initio* dispersion polymerization. However, by using higher  $M/P$  ratios, seeded reactions could be started at a much lower equivalent conversion approaching the end of particle nucleation in the *ab initio* polymerization. In this study, the kinetics of seeded dispersion polymerization with both micron and submicron seeds are investigated.

## EXPERIMENTAL

### Materials

Methyl methacrylate (MMA) (Fisher Scientific) was purified via vacuum distillation. All other materials were used without further purification, including methanol (VWR Scientific Products), 2,2'-azobis(isobutyronitrile) (AIBN) (Aldrich), and poly(vinylpyrrolidone) (PVP K-30) (Aldrich). Deionized (DI) water was used in all experiments.

### PMMA seed preparation

Micron-size PMMA seeds (1.7  $\mu\text{m}$ ) were prepared by seeded dispersion polymerization.<sup>4</sup> The particles were cleaned by repeated sedimentation and replace-

ment of the medium to remove the stabilizer (PVP K-30) and other soluble materials.

Conventional and emulsifier-free emulsion polymerizations<sup>5</sup> were applied to prepare submicron PMMA seed latices. The recipes are shown in Table I. The seed latices prepared by conventional emulsion polymerization were cleaned using the serum replacement technique<sup>6</sup> to remove the surfactants and other solubles from the latices.

### Polymerization using the RC1 calorimeter

Kinetics studies were carried out in a 1-L reactor (Mettler MP10) using the Mettler RC1 reaction calorimeter. All ingredients were initially charged into the reactor except the initiator (recipe given in Table II). The reactor was purged with nitrogen for about 15 min and checked for leaks. It was then sealed, followed by ramping the temperature to the reaction temperature (70°C) over 10 min. The calorimeter was calibrated to determine its operating parameters. A preheated (70°C) initiator solution (AIBN in methanol, 6 mL) was then injected after a stable reaction temperature was reached. During the reaction, tem-

**TABLE I**  
Recipes to Prepare Submicron PMMA Particles via Conventional (nos. 1 and 2) and Emulsifier-Free (no. 3) Emulsion Polymerization

Ingredient	Amount		
	No. 1	No. 2	No. 3
MMA	40 (mL)	40 (mL)	19.67 (g)
KPS (g)	0.16	0.16	0.142
NaHCO <sub>3</sub> (g)	0.16	0.16	–
Aerosol MA (5% aqueous solution) (g)	4.8	19.2	–
DI water (mL)	160	160	180.33
Characterization			
$D_v$ (nm)	317	194	422
PDI	1.006	1.026	1.007

**TABLE II**  
**Recipe for Seeded Dispersion Polymerizations**  
**in the RC1<sup>a</sup>**

Ingredient	Weight/g
MMA	50.54 minus weight of PMMA
PMMA seed	seed <sup>a</sup> (M/P ratio varied)
AIBN	0.2527 (~ 2.5 mM) or varied
PVP K-30	10.11
MeOH/water (70/30 wt/wt)	449.38

<sup>a</sup> If no seed was added, the reaction was carried out as an *ab initio* dispersion polymerization.

perature data (jacket,  $T_j$ , and reaction fluid,  $T_r$ ) were recorded from which the heat of reaction,  $Q_r$ , was obtained by postreaction evaluation. Samples were periodically withdrawn from the reactor for particle size analysis. The fractional conversion obtained via the evaluated data was scaled by the gravimetric final conversion. The polymerization rate was calculated from the heat of reaction:

$$R_p = \frac{Q_r}{(-\Delta H) \cdot V} \quad (1)$$

where  $R_p$  is the reaction rate (mol/L/s),  $Q_r$  is the rate of heat generation (J/s),  $(-\Delta H)$  is the molar heat of polymerization of the monomer (J/mol), and  $V$  is the total volume of the system (L). The molar heat of polymerization of methyl methacrylate is  $-57.8$  kJ/mol.<sup>7</sup>

### Latex characterization

#### Particle size

Scanning electron microscopy (SEM, Jeol 6300F) was used to determine the particle size and distribution. The latex was diluted to about 1 wt % with a methanol/water mixture (weight ratio = 70/30). One drop of the diluted latex was placed on an aluminum stub, and dried in a hood at room temperature. The accelerating voltage was 1 kV and no coating was applied.

#### Molecular weight analysis

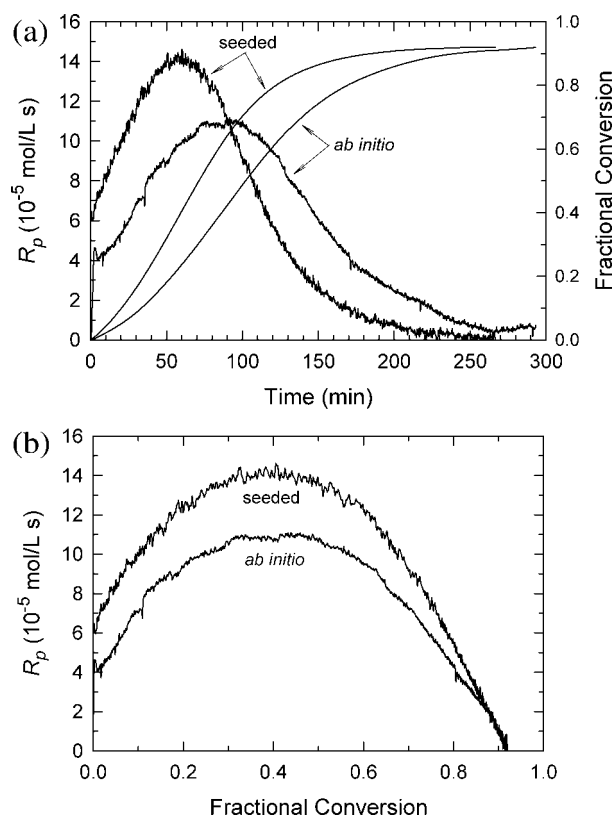
The molecular weight distributions of the PMMA were measured by gel permeation chromatography (GPC, Waters 2487 dual absorbance detector and/or Waters 410 differential refractometer detector). THF was used as the mobile phase. When using the UV detector, a wavelength of 235 nm was used. The THF flow rate was 1.0 mL/min. Waters HR3, HR4, and HR6 Styragel columns were used. Samples were filtered through a 0.45- $\mu$ m filter before injection. Polystyrene molecular weight standards with narrow

distributions were used for calibration. The following Mark-Houwink constants were used to obtain the molecular weights:  $K = 14.1$ ,  $\alpha = 0.70$  for PSt, and  $K = 7.5$ ,  $\alpha = 0.72$  for PMMA,<sup>7</sup> both in THF.

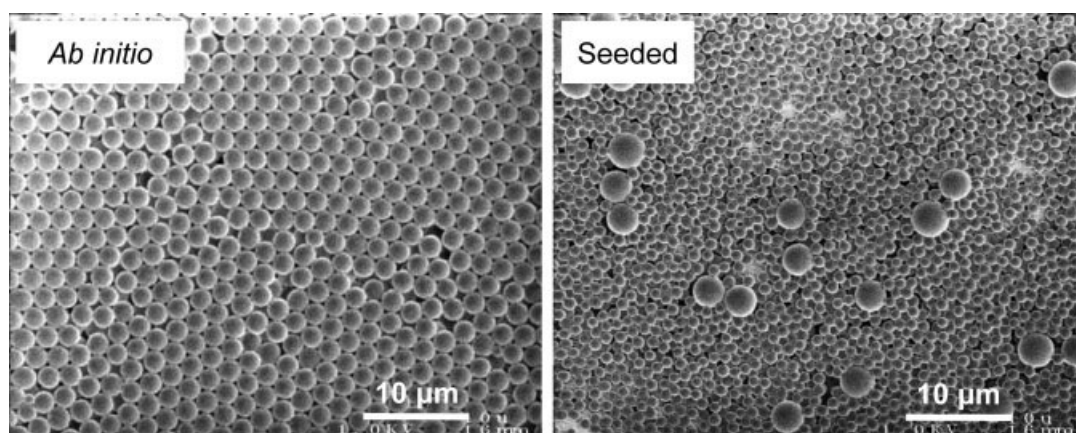
## RESULTS AND DISCUSSION

### Kinetics of seeded dispersion polymerization using micron-size seed

A seeded dispersion polymerization using a 1.7  $\mu$ m PMMA seed and a 28/1 M/P ratio was carried out in the RC1 with the results shown in Figures 2 and 3 along with the corresponding *ab initio* polymerization. Note that the amounts of AIBN and PVP were the same in both reactions. The initial number of particles ( $N_{p,ini}$ ) was  $1.0 \times 10^{12}$ /L corresponding to a surface area ( $A_{p,ini}$ ) of 8.7 m<sup>2</sup>/L. Faster reaction rates ( $R_{p,ini}$  and  $R_{p,max}$ ) were obtained in the seeded dispersion polymerization compared to the corresponding *ab initio* polymerization. However, the conversions at which  $R_{p,max}$  were achieved are about the same (~ 40%), as seen in Figure 2 (bottom). As can be seen by the micrographs in Figure 3, a bimodal distribution of particles was obtained in the seeded



**Figure 2** Kinetics of seeded dispersion polymerization of MMA using 1.7  $\mu$ m PMMA seed and corresponding *ab initio* polymerization: (a) reaction rate and fractional conversion as a function of time; (b) reaction rate as a function of fractional conversion.



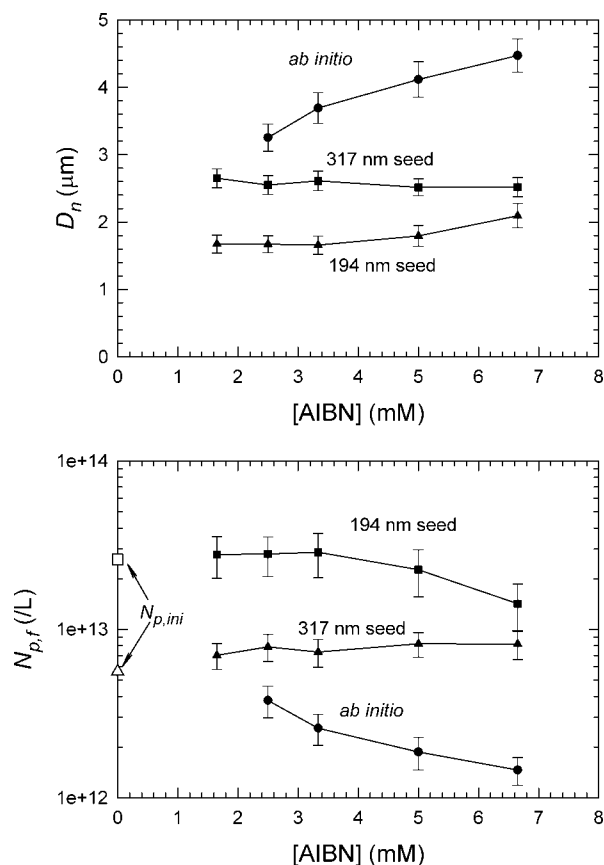
**Figure 3** SEM images of PMMA particles prepared via *ab initio* and seeded (1.7 µm PMMA seed) dispersion polymerization.

polymerization while the *ab initio* polymerization produced a narrow size distribution of 2.65-µm particles. The larger particle size population ( $\sim 4$  µm) found in the seeded polymerization is considered to result from the growth of the original seed particles, which should have grown to about 5.2 µm in the absence of secondary nucleation. The smaller particles ( $\sim 1$  µm) are the result of secondary nucleation. Since the population of 1-µm particles still has a narrow size distribution, their number should also have remained roughly unchanged after a short nucleation period. It is estimated that about  $6.6 \times 10^{13}/L$  of these particles were generated, which is one order of magnitude higher than in the corresponding *ab initio* dispersion polymerization.

How to explain these results? At first glance they seem counter intuitive. In the seeded reaction, the seed and its surface area should reduce the presence of initiator and radicals in the continuous phase, which would normally be expected to reduce the amount of secondary nucleation. The seed also occupies a certain fraction (albeit small) of the stabilizer on its surface and this too should lead to fewer new particles being stabilized. And yet the evidence is to the contrary. More new particles are formed in the presence of seed than in their absence. One way to explain this is by recalling the paradox of the initiator concentration effect found in dispersion polymerization systems such as styrene and MMA. In these systems, the particle size has been found to increase with increasing initiator concentration.<sup>1</sup> This too is counter intuitive; typically one would expect more particles to be formed with more initiator added, that is decreasing size with increasing initiator concentration. Nonetheless, this has been reported by many authors and has generated a number of explanations. The most reasonable of these is that there is a competition between the stabilization and limited aggregation of nuclei, which is dependent on

the rate of generation of unstable nuclei and the adsorption of the polymeric stabilizer.<sup>8</sup> More particles are favored by faster stabilizer adsorption and a slower rate of production of oligomers and unstable nuclei. The latter is favored by lower initiator concentrations. So how can this explain the seeded polymerization results? The presence of the seed reduces the rate of oligomer and nuclei formation by first, absorbing some of the initiator (partitioning into the seed particles) and second, adsorbing some oligomers and nuclei. In this way, these act in a manner analogous to decreasing the initiator concentration and this leads to an increasing number of smaller particles nucleated in the seeded reaction. Obviously, the seed is far from being sufficient to gather all oligomers and nuclei such that no new particles are formed. This explanation is necessarily qualitative as there is no quantitative theory available to our knowledge.

As for the reaction kinetics, the results in Figures 2 and 3 imply that the number of particles plays a significant role. The maximum rate in the seeded reaction is about 1.3 times that in the *ab initio* reaction even though the number of particles is about an order of magnitude higher in the seeded reaction. Obviously, the rate of polymerization is a relatively weak function of the number of particles as compared to what is typically found in emulsion polymerization. Here the dependence of the rate on the number of particles is considered to decrease approaching zero as the size of the particles increases to the extent that pseudobulk kinetics prevail (high average number of radicals per particle where radical segregation no longer applies). However, this scenario is usually that described when employing oil soluble initiators in seeded emulsion polymerization whereby relatively large particles ( $>0.5$  µm) are being prepared.<sup>9</sup> There is some evidence that when a water soluble initiator is



**Figure 4** Particle size and particle number concentration as a function of initiator concentration in *ab initio* and seeded dispersion polymerizations.

employed, there remains a weak dependence on the number of particles even when pseudobulk kinetics should apply and this is caused by the dependency of the rate of adsorption of radicals from the continuous phase on the number of particles.<sup>10</sup> This scenario can also apply to these dispersion polymerizations where a significant fraction of the radicals are considered to originate in the continuous phase with some fraction of these being absorbed by the particles where they propagate. Higher absorption rates lead to higher numbers of radicals growing in the particles and thus higher polymerization rates. This is the likely explanation for the results presented here; the greater number of particles generated in the seeded polymerization lead to a larger total number of growing radicals in the particles by virtue of their ability to absorb a greater amount of radicals from the continuous phase.

#### Seeded dispersion polymerization using submicron seeds

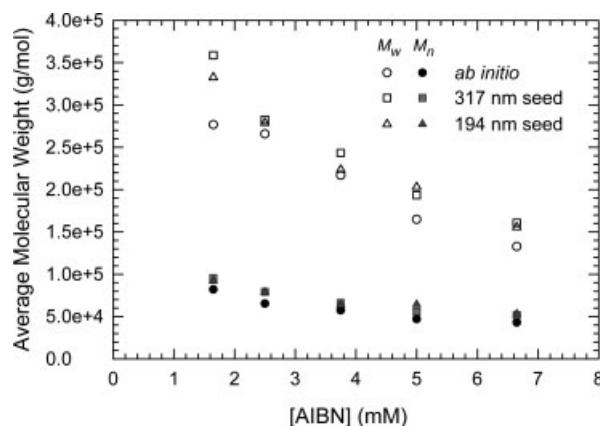
The original idea behind carrying out seeded dispersion polymerizations using submicron seeds was to attempt to begin polymerization under conditions

just beyond the nucleation stage in an *ab initio* reaction. This was expected to provide a new perspective in the study of the kinetics and mechanism of dispersion polymerization. The recipe would simply be an *ab initio* recipe to which varying amounts and sizes of submicron seed particles would be added. A screening study was first performed whereby the product latices were first checked for their particle size to determine if the seeding worked in the sense that each seed particle resulted in one final latex particle. If this was not the case and more particles were produced, then this would indicate that the conditions chosen were not past the nucleation stage in the *ab initio* reaction.

#### Screening study

PMMA latex particles with diameters of 194 and 317 nm were used in seeded dispersion polymerizations based on the recipe in Table II. The concentrations of the seeds were  $2.60 \times 10^{13}/\text{L}$  ( $3.07 \text{ m}^2/\text{L}$ ) and  $5.60 \times 10^{12}/\text{L}$  ( $1.78 \text{ m}^2/\text{L}$ ), respectively. These would represent conversions of  $\sim 0.12$  and  $0.14\%$  in the *ab initio* reaction (i.e., very low conversions) or M/P ratios of 833/1 and 714/1, respectively. These are much larger ratios than used in the preceding study with the  $1.7\text{-}\mu\text{m}$  seed. Parallel *ab initio* polymerizations were carried out for comparison. Five different AIBN initiator levels (1.65, 2.5, 3.35, 5.0, 6.67 mM) were employed. The reactions were carried out in a bottle polymerizer. The resulting particle sizes and corresponding numbers of particles are presented in Figure 4 as a function of the initial AIBN concentration. All of the particle sizes plotted represents narrow size distributions. The error bars reflect the standard deviation on the number-average diameter. Note that no data is presented for the *ab initio* reaction at 1.65-mM initiator concentration; polydisperse particles were obtained for this one sample. The remainder of the *ab initio* results show an increasing particle size with increasing AIBN, as reported for the paradoxical results discussed earlier. For the seeded reactions, most of the results show a constant number of final particles close to the original seed number implying that each seed particle grew to become a micron size particle. The two highest AIBN concentrations with the 194 nm seed show a decreasing number of particles indicative of some limited aggregation but no new particles are evident in any of the results confirming that these seeded polymerizations were begun past the point of nucleation in the *ab initio* system. This implies that the nucleation stage ends at a very low conversion ( $<1\%$ ) in this system.

The number and weight-average molecular weights are presented in Figure 5 as a function of the initial AIBN concentration. The molecular weights decreased



**Figure 5** Weight- and number-average molecular weights as a function of initiator concentration in *ab initio* and seeded dispersion polymerizations.

as expected, although the differences between the three polymerizations at a single initiator concentration are small despite the variation in particle size. These results indicate that the molecular weight can be varied independently of the particle size through seeded dispersion polymerization. The influence on the polymerization kinetics is described in the following.

### Kinetics of seeded dispersion polymerization

Based on the screening results, the 317 nm PMMA latex particles were chosen as the seed (0.3 wt % on monomer) to study the effect of initiator concentration in MMA seeded dispersion polymerizations. The recipe is again that given in Table II. Three AIBN initiator concentrations (2.5, 5.0, and 7.5 mM) were used resulting in the reaction kinetics shown in Figure 6. First, it can be seen that increasing the initiator concentration increases the initial rate ( $R_{p,ini}$ ) but decreases the maximum rate ( $R_{p,max}$ ), which at first glance would not be expected. The power dependencies of these rates on the AIBN initiator concentration are given by eqs. (2) and (3).

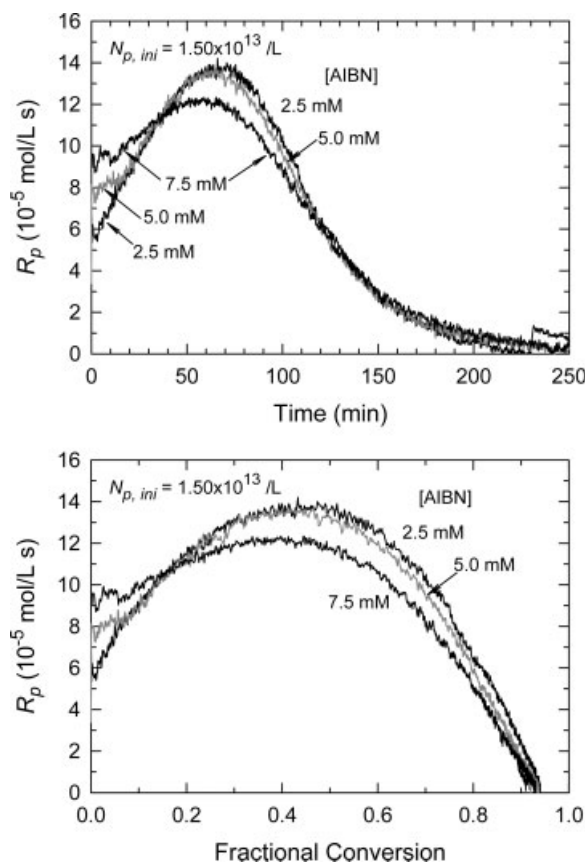
$$R_{p,ini} = 7 \times 10^{-4} [\text{AIBN}]^{0.42} \quad (2)$$

$$R_{p,max} = 7 \times 10^{-5} [\text{AIBN}]^{-0.12} \quad (3)$$

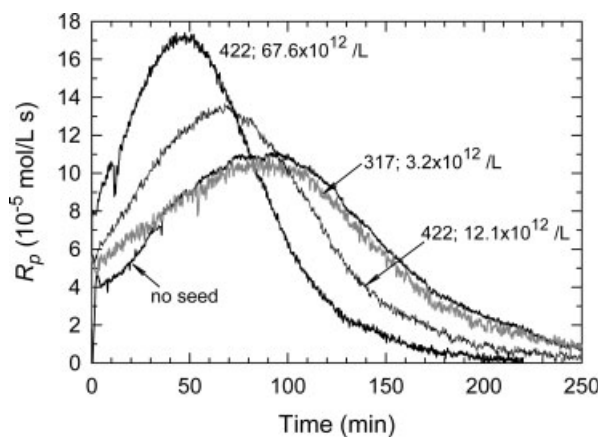
The exponent of 0.42 for the initial rate is not far from the 0.5 power expected for solution, bulk or pseudobulk reactions and may reflect the initial polymerization conditions in these seeded reactions. However, the divergence from these conditions begins immediately with the rate increasing the most for the lowest initiator concentration. At  $R_{p,max}$  which occurs at about the same conversion for all three initiator concentrations, the monomer concen-

tration inside the polymer particles, the volume of the polymer phase, the particle size and number of particles are all the same. The fact that increasing initiator concentration had a slightly negative effect on  $R_{p,max}$  indicates that increasing the initiator concentration did not lead to an increase in the radical concentration but instead a decrease must have occurred to account for the reduced rate. So how can these results be explained?

We propose that in these seeded reactions a similar explanation for the decreasing rate with increasing initiator concentration exists as for the particle size paradox where in *ab initio* dispersion polymerizations of MMA, the number of particles decreases with increasing initiator. The rate of seeded dispersion polymerization is the summation of a number of contributions. First and foremost is the polymerization within the swollen polymer particles. Here the initiator decomposes producing radicals that propagate as in a bulk polymerization; the large size of the particles ensures that many radicals can coexist (in the thousands for micron size particles) and no radical segregation effects exist. However, the radicals appearing there are not only those produced



**Figure 6** Rate of polymerization as a function of time (top) and conversion (bottom) for MMA seeded dispersion polymerizations using a 317 nm PMMA seed latex and varying initiator concentration.



**Figure 7** Rate of polymerization as a function of time for seeded dispersion polymerizations with different initial seed number concentrations (317 and 422 indicate the seed particle size (nm); initial seed number concentration also indicated).

by initiator decomposition within the particles; radicals entering from outside also make a contribution. These radicals can enter in any form, as primary radicals from freshly decomposed initiator, as oligomers, which have grown in the continuous phase (shorter than their critical chain length), and as colloidal particles (unstable nuclei). The latter are likely to contain zero or one radical as their small size (nm scale) does not allow two radicals to coexist without immediate mutual termination. These nuclei can be formed by collapse of an oligomer exceeding its critical chain length or by aggregation of oligomers. These unstable nuclei may also aggregate with themselves before finding a large mature particle.

The numbers of radicals entering from outside the particles is largely governed by events in the continuous phase since in these seeded polymerizations the only difference is the overall initiator concentration. The partitioning of the initiator favors the continuous phase in absolute amount since this phase constitutes about 90% of the system and partitioning does not strongly favor the particles as would be the case in an aqueous system. If the entering species were primary radicals or oligomers, the rate would be expected to increase with increasing initiator concentration. Since this is not the case, it points to colloidal (unstable nuclei) entry as the likely source of a reduced entry rate with increasing initiator concentration. This can be envisioned by the greater aggregation of radical oligomers and nuclei produced in the continuous phase, which leads to an increased termination of radicals. The unstable nuclei are likely to be larger in size prior to "entry" (aggregation with a mature particle) for higher initiator concentrations since this is considered the likely scenario explaining the particle size paradox. This loss of radicals through aggregation must occur to such an

extent that the effective entry rate of radicals (unstable nuclei containing a radical) is reduced with the increasing initiator concentration. This seems qualitatively plausible but may need some quantification through mathematical modeling to confirm this scenario.

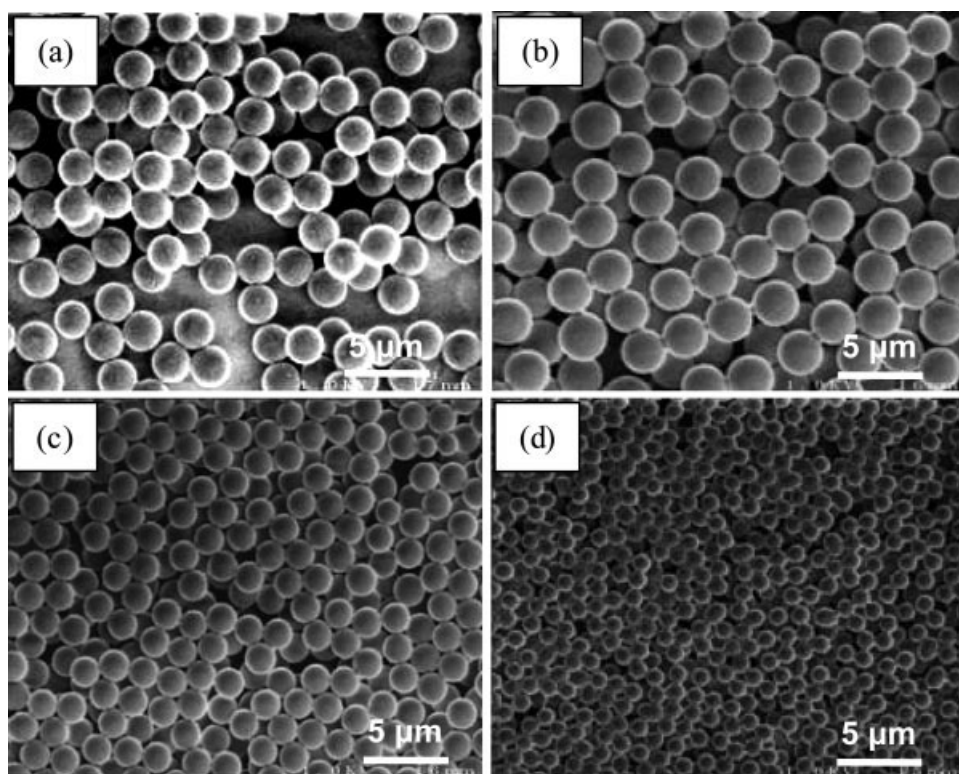
#### Effect of initial seed number concentration

Under certain reaction conditions, the final number of particles in MMA seeded dispersion polymerizations using submicron seeds equals the initial seed number. This provides an opportunity to study the effect of seed number concentration on the kinetics of MMA seeded dispersion polymerization using the RC1. Two seed sizes were employed: 317 and 422 nm PMMA. The results are presented in Figure 7. A parallel *ab initio* MMA dispersion polymerization is provided for reference. SEM images of the PMMA particles produced in the seeded polymerization along with the *ab initio* reaction are shown in Figure 8 where it can be seen that narrow particle size distributions were achieved in all reactions. However, for the lowest seed concentration, the final number of particles was about double the initial number and was nearly the same as the number produced in the parallel *ab initio* reaction ( $6.7 \times 10^{12}/L$ ). This is an interesting finding, which implies that the particle size cannot be increased to a size larger than produced in the *ab initio* reaction; new particles are formed instead.

The kinetics results in Figure 7 indicate that increasing the seed number concentration increases the reaction rate. However, the dependence is relatively weak as noted previously;  $R_{p,max}$  only increased 1.3–1.4 times, while the number of seed particles increased 5.6 times. The reaction rate profiles for the lowest initial seed number and the *ab initio* reaction are nearly the same as would be expected for two systems resulting in the same final number of particles.

#### Seed number versus seed surface area

Several seeded dispersion polymerizations were carried out to try to understand whether the effect of seed number on the kinetics was related to their total area rather than their number. Figure 9 shows the kinetics obtained using two different seed sizes (194 and 317 nm PMMA) at the same initial number concentration ( $8.0 \times 10^{12}/L$ ) but differing initial seed surface area. It can be seen that the two reactions have nearly the same kinetics and both have higher reaction rates than the corresponding *ab initio* dispersion polymerization. To extend this, the results of seeded dispersion polymerization using seeds differing in size and  $N_{p,ini}$  but having the same total sur-

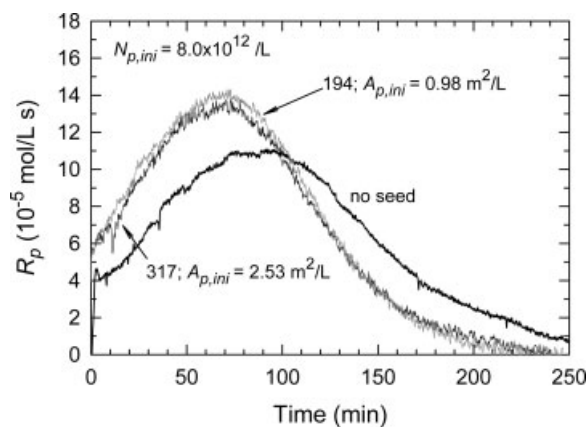


**Figure 8** SEM images of particles produced by MMA seeded dispersion polymerization with different initial seed number concentrations: (a) *ab initio* reaction; (b) 317 nm seed,  $3.2 \times 10^{12}/L$ ; (c) 422 nm seed,  $12.1 \times 10^{12}/L$ ; (d) 422 nm seed,  $67.6 \times 10^{12}/L$ .

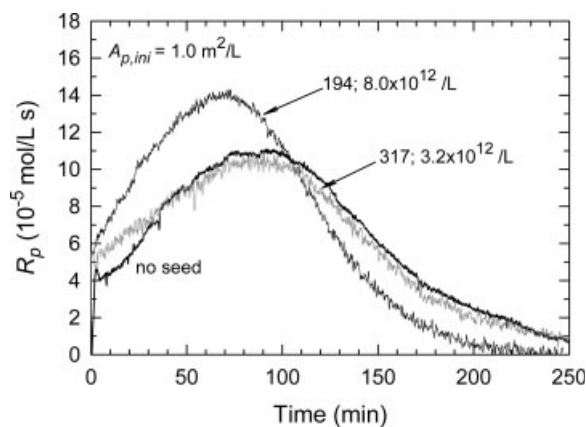
face area ( $A_{p,ini}$ ) are shown in Figure 10. It can be seen that different kinetics were observed for the same initial surface area, which confirms that it is not the surface area that governs the kinetics. From these results, it is clear that the seed number concentration has a significant albeit relatively modest effect on the kinetics of seeded dispersion polymerization.

## CONCLUSIONS

Seeded dispersion polymerization of MMA using a  $1.7 \mu\text{m}$  PMMA seed and a relatively high M/P ratio (28/1) failed to produce a monodisperse particle population grown from the seed. Secondary nucleation occurred along with growth of the original seed particles and the number of new particles exceeded



**Figure 9** Rate of polymerization as a function of time for seeded dispersion polymerizations using the same seed number concentration of two different size seeds.  $N_{p,ini} = 8 \times 10^{12}/L$  (317 and 194 seed particle sizes (nm);  $A_{p,ini}$  is the initial seed surface area).  $N_{p,f}$  *ab initio* =  $6.7 \times 10^{12}/L$ .



**Figure 10** Rate of polymerization as a function of time for seeded dispersion polymerizations using different seeds with the same surface area.  $A_{p,ini} = 1.0 \text{ m}^2/L$  (317 and 194 seed particle sizes (nm); initial number concentration also indicated).



that produced in a parallel *ab initio* dispersion polymerization carried out under the same conditions but with no seed added. It is apparent that all of the growing oligomeric polymer chains and nuclei formed in the continuous phase could not be captured by the existing seed particles owing to the small seed number concentration and thus, secondary nucleation occurred. The reaction rate was higher than the corresponding *ab initio* reaction owing to the significantly large number of newly formed particles. The larger number of nucleated particles produced compared to the *ab initio* reaction is attributed to the same mechanism whereby the number of particles in dispersion polymerizations of MMA increases with decreasing initiator concentration.

In screening studies using 194 and 317 nm PMMA seeds added in small quantities to an *ab initio* dispersion polymerization recipe (equivalent to conversions of 0.12 and 0.14%) to simulate the end of the nucleation stage, the final number of particles was in most cases about the same as the initial number added, implying growth of the seed only. Kinetics studies with the 317 nm seed showed an increasing initial rate of reaction with increasing initiator but a decreasing rate maximum. The latter was attributed to decreased radical entry from the continuous phase owing to an increased termination in the unstable nuclei.

Further seeding studies using 317 and 422 nm PMMA seeds showed that seed growth alone

occurred only when the number of initial seed particles equaled or exceeded the number of particles produced in the parallel *ab initio* reaction. The kinetics showed a weak dependence of the rate on the number of particles. The seed number rather than the seed area was the parameter determining the rate of polymerization.

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