

Seeding as a Means of Controlling Particle Size in Dispersion Polymerization

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ABSTRACT: Two distinctively different seeded dispersion polymerization processes employing micron and submicron size seed particles, respectively, have been used to gain a better mechanistic understanding of the dispersion polymerization process. Using monodisperse micron-size PMMA particles as seed, it was found that when low monomer/polymer ratios ($M/P < 2.50$) were used in methyl methacrylate (MMA) seeded dispersion polymerizations, particle growth dominates and the number of particles remains unchanged (i.e., narrow distributions are preserved). However, when higher M/P ratios (>2.50) were applied, bimodal or trimodal particle size distributions were produced, which is considered to result from the competition between particle growth and secondary nucleation. When small amounts of submicron seeds were used with the initial intention of gaining a better under-

standing of the nucleation process, it was surprisingly found that the final number of micron size particles was nearly the same as the initial number of submicron seed particles over a relatively wide range of reaction conditions, including seed, initiator, stabilizer, and monomer concentrations, and the medium composition. These results indicate that within certain limits seeded dispersion polymerization can be a more robust means of controlling particle size than *ab initio* dispersion polymerization in terms of reproducibly producing a target particle size. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 4096–4107, 2008

Key words: dispersion polymerization; radical polymerization; particle nucleation; stabilization; grafting; particle size distribution; molecular weight distribution

INTRODUCTION

Monodisperse polymer particles with micron size have received much attention because of their applications in various fields, such as HPLC and size-exclusion chromatography,^{1,2} medical research,^{3–5} DNA immobilization,⁶ size standards for microscopy,⁷ etc. To produce monodisperse particles with diameters above 1 μm , different techniques have been developed. Emulsifier-free emulsion polymerization can produce both submicron and micron size particles with narrow size distributions, with the particle size being controlled by the ionic strength of the aqueous phase and the initiator concentration.⁸ Seeded batch processes have been used by Vanderhoff et al.⁹ and Ugelstad et al.¹⁰ although these are often characterized as being tedious and hard to reproduce. Semicontinuous emulsion polymerization has subsequently been shown to be an efficient way to produce larger particle sizes, as described in patents by Paine et al.^{11–13}

Dispersion polymerization is a relatively simple process for preparing stable, micron size particles

with a narrow size distribution by polymerization in a system initially comprising a homogeneous solution of monomer, solvent, initiator, and stabilizer. A wide variety of polymer particles, including polystyrene,¹⁴ poly(methyl methacrylate),¹⁵ and poly(butyl acrylate)¹⁶ etc., have been prepared by this technique. Crosslinked polymer particles have also been obtained from dispersion polymerizations as demonstrated by Ober and Lok¹⁷ and Hattori et al.¹⁸ Siol et al.¹⁹ disclosed a dispersion polymerization process for the preparation of poly(methyl methacrylate) particles in the range of 2 to 20 μm , using percarbonic acid ester as initiator, a block copolymer stabilizer containing a polystyrene component, and a halogen-free solvent as medium. In general, repeatedly producing a target final size based on any given recipe can be difficult; reproducibility can be a problem requiring continuous adjustment of conditions and ingredients since impurities such as inhibitors in the monomer can greatly affect the results.

Seeded emulsion polymerization is often employed for better control of latex particle size. To obtain large particles ($>1 \mu\text{m}$), almost all of the related literature focuses on improving the swelling ability of the seed particles utilizing different strategies and techniques. One disadvantage of swelling is that the process is generally time-consuming and/or

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results in poor reproducibility. For example, sequential seeded emulsion polymerization requires many steps and an initial seed with a narrow particle size distribution.⁹ The monomer should be the same in each step as well. Reproducing Ugelstad's process¹⁰ has proven difficult by others. This is attributed to the difficulty in stabilizing the particles often leading to particles outside the main distribution (large particles from aggregation/coalescence and small particles from secondary nucleation). Purification may therefore be necessary. In some cases,²⁰ coagulation of seed particles might occur during the swelling step, which may not significantly affect the monodispersity of the final product if the increase in particle size (volume) is relatively large but can make it difficult to predict the final particle size for a given recipe.

Compared to numerous studies in *ab initio* dispersion polymerization, only a few investigations have been carried out in seeded dispersion polymerization.²¹ Structured micron-size polymer particles have been successfully prepared by seeded dispersion polymerization of styrene using a micron-size PBA seed, which was also prepared by dispersion polymerization.²² Polymer particles with different morphologies (core-shell, half-moon) have also been produced by seeded emulsion polymerization with seeds prepared via dispersion polymerization.²³

To our knowledge, seeded dispersion polymerization has not been applied as a useful tool to control particle size. In this paper, seeded dispersion polymerizations of MMA are described and the effects of reaction parameters, such as the properties of the polymer seeds (polymer type, size, and amount) and the secondary reaction components (initiator, stabilizer, crosslinker, and medium), on the final particle size and size distribution are investigated. Mechanistic aspects of dispersion polymerization are discussed based on these findings.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) (Fisher Scientific) monomer was purified via distillation under reduced pressure. Crosslinkers, including ethylene glycol dimethacrylate (EGDMA) (98%, 100 ppm monomethyl etherhydroquinone (MEHQ); Aldrich), divinylbenzene (DVB) (80%, 1000 ppm *p*-tert-butyl catechol; Aldrich), and allyl methacrylate (AMA) (200 ppm MEHQ inhibitor, Polysciences Inc.), were used as received. 2,2'-azobis(isobutyronitrile) (AIBN) (98%, Aldrich), ammonium persulfate (APS) ($\geq 98.0\%$, Aldrich), potassium persulfate (KPS) ($\geq 99.0\%$, Fisher), benzoyl peroxide (BPO) ($\geq 98.0\%$, Aldrich), 2,2'-azobis(2,4-dimethylvaleronitrile) (ADVN,) (Vazo 52,

DuPont), and 4,4'-azobis(4-cyanovaleric acid) (ACPA) (75%, Aldrich) initiators were used without further purification.

All other materials were used without further purification, including methanol (99.8%, VWR Scientific Products), and poly(vinylpyrrolidone) (PVP-K30, MW = 40,000 g/mol) (Aldrich). Reverse osmosis, deionized (DI) water was used in all experiments.

Polymerization and characterization

Seed latices

Two kinds of PMMA particles were utilized as seeds in seeded dispersion polymerization: micron and submicron size. The micron size seed latex ($D_n = 2.65 \mu\text{m}$, PDI = 1.01)²⁴ was prepared by dispersion polymerization. Two submicron PMMA particles were prepared by conventional emulsion polymerization²⁵: 194 and 317 nm, both having narrow particle size distributions as measured by dynamic light scattering (DLS, Nicomp 370).

The 2.65 μm PMMA seed was cleaned by replacing the serum of the latex with a methanol/water (70/30 wt/wt) mixture several times following sedimentation until no measurable solids could be detected in the serum. The 194 and 317 nm PMMA seed latices were cleaned by serum replacement to remove the surfactants and other residual ingredients.²⁶

Bottle polymerization

The ingredients were weighed and mixed in 2-oz glass bottles, purged with nitrogen, capped, and sealed. The bottles were then placed in safety baskets supported on a rotor and were rotated end-over-end at 45 rpm in a constant temperature water bath at 70°C for 24 h. Based on the weight of the seed added and its solids content, the number of particles per liter ($N_{p, ini}$) and their area ($A_{p, ini}$) were calculated.

Latex characterization

Scanning electron microscopy (SEM, Jeol 6300F) was used to determine the particle size and particle size distribution (PSD) of the particles. The latex was diluted to about 1 wt % solids with a methanol/water mixture (weight ratio = 70/30). 1 drop of the diluted latex was put on an aluminum stub, and dried in a hood at room temperature. The accelerating voltage was 1 kV and no coating was applied. Generally, at least 1000 particles were counted to obtain the particle size statistics. When a 'narrow' PSD is reported in the results, the PDI (polydispersity index; D_w/D_n) is in the range of 1.002–1.04.

TABLE I
Standard Recipe for Seeded Dispersion Polymerizations
using Micron-Size or Submicron Polymer Particles as
Seeds (70°C, 24 h)

Ingredient	Weight (g)	Comment
MMA + Polymer seed	3.0	9.80 wt % (M/P ratio varied)
AIBN	0.01–0.06	1.60–10.0 mM based on total volume
PVP K30	0.60	20.0 wt % (based on M+P)
MeOH/water (70/30 wt/wt)	27.0	–

RESULTS AND DISCUSSION

Seeded dispersion polymerization using micron-size seed

Seeded dispersion polymerizations were carried out with 2.65 μm PMMA particles as seed according to the recipes given in Table I.

Effect of initiator concentration

With a monomer/polymer (M/P) weight ratio of 1.16/1, seeded dispersion polymerizations of MMA were carried out using initiator (AIBN) concentrations varying from 1.60 to 10.0 mM (based on total volume). Monodisperse particles were obtained in all cases, while the measured particle sizes, presented in Figure 1, are slightly larger than the expected value calculated from the M/P weight ratio assuming that no new nucleation occurs and the final number of particles equals the initial number of seed particles. With different initiator concentrations, it is expected that the PMMA produced in the seeded dispersion polymerizations would have differing molecular weights. Figure 2 shows the molecular weight distributions of the PMMA formed in

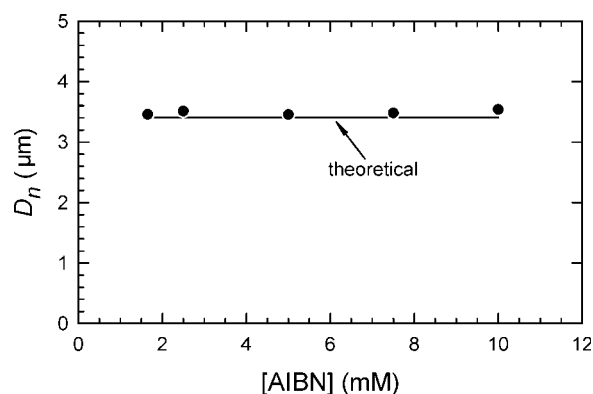


Figure 1 Particle size of PMMA particles prepared by seeded dispersion polymerization of MMA using 2.65 μm PMMA particles as seed with different initiator concentrations.

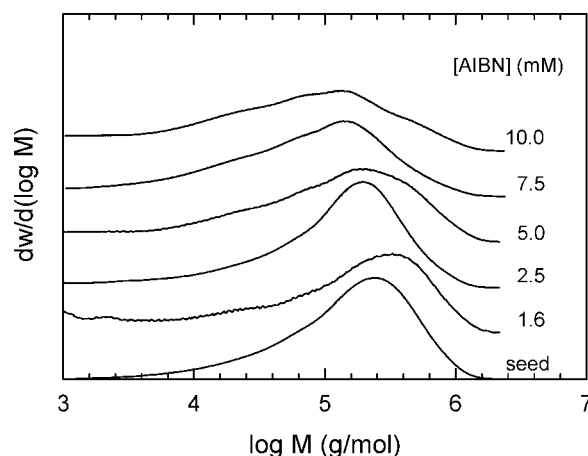


Figure 2 Molecular weight distributions of newly formed PMMA polymer prepared by seeded dispersion polymerization with different initiator concentrations.

the second stage. These were obtained by subtracting the molecular weight distribution of the seed polymer from the molecular weight distributions of the final polymers. It is clear that with higher initiator concentrations, lower molecular weight polymers were produced in the seed stage as would be expected by increased termination rates with increased radical concentrations.

Effect of monomer/polymer ratio

Figure 3 shows SEM images of the PMMA particles obtained from seeded dispersion polymerizations varying the weight ratio between monomer and seed polymer while maintaining the initiator concentration at 2.5 mM (Table I). When the M/P ratio was 2.5/1 or less, particles with narrow size distributions were obtained. At an M/P ratio of 3.0/1, a small amount of smaller particles appeared, while at even higher M/P ratios, polydisperse latices were produced.

The particle sizes are shown in Figure 4 where the sizes of the polydisperse latices are shown as distinct populations (bimodal at M/P = 3.0/1 and trimodal at all higher M/P ratios). The solid line represents the expected final particle size assuming no secondary nucleation or aggregation. It can be seen that at low M/P ratios ($\leq 2.5/1$) the particle size increases with increasing M/P ratio and agrees with the expected behavior, indicating that secondary nucleation was prevented with all of the additional monomer ending up as polymer in the original seed particles. For M/P ratios greater than 12/1, the particles have sizes in three distinct and curiously unvarying populations of sizes of about 1 μm , 2.5 μm , and 5 μm . The latter population is believed to result from the growth of the original polymer seed particles, while the other two populations are produced via secondary nucleation. It should be noted that the intermediate size population of particles happens to

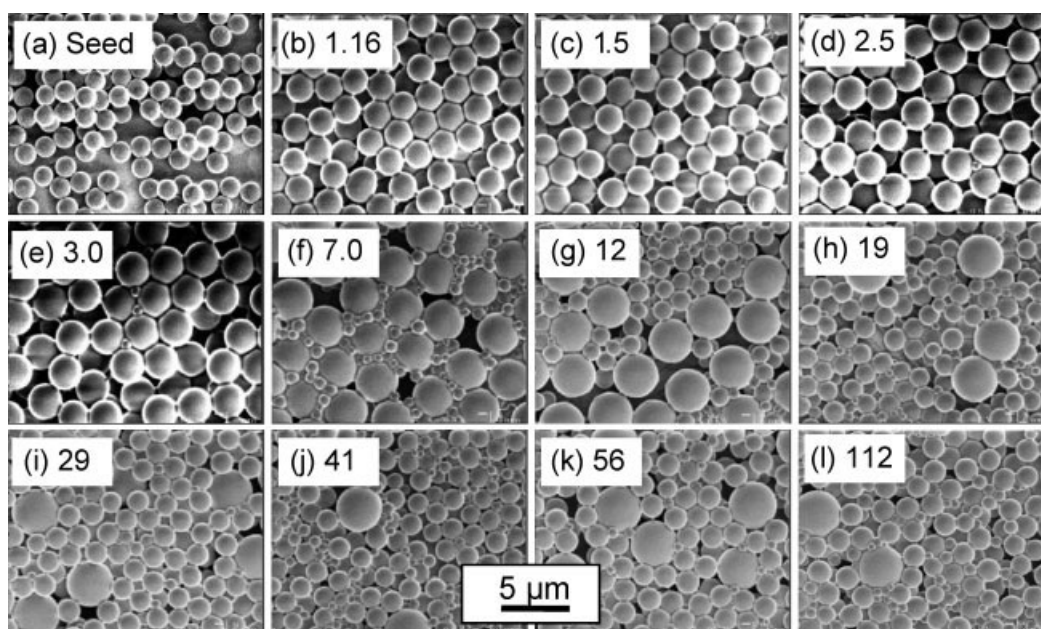


Figure 3 SEM images of PMMA particles prepared by seeded dispersion polymerizations with $[I] = 2.5$ mM, and different M/P ratios as indicated.

have a size similar to the original seed particles ($2.65 \mu\text{m}$), which were prepared by *ab initio* dispersion polymerization under similar reaction conditions (initiator and stabilizer concentrations, medium, and temperature). When M/P approaches infinity, the reaction will be an *ab initio* dispersion polymerization and produce $2.65 \mu\text{m}$ size particles. Therefore, with M/P ratios higher than tried here, it is expected that the seed particles will still grow, but the majority of the particles will be produced by new nucleation thereby creating a main population at a size of around $2.65 \mu\text{m}$.

A number of reaction conditions vary with increasing M/P ratio and constant final solids: (1)

increasing monomer concentration in the medium; (2) increasing solvency of the medium for the produced polymer; and (3) reduced number concentration, surface area, and volume of the seed particles. Table II and Figure 5 show the relationship between the M/P ratio and the initial seed number concentration and surface area (unswollen) for the reactions of Figure 3. Their exponential decrease with M/P provides some understanding as to why only low M/P ratios are successful in producing monodisperse particles. The rapid reduction in $N_{p,ini}$ and $A_{p,ini}$ with M/P creates conditions that generally promote secondary particle formation. The decreasing surface area of the seed particles provided by fewer seed particles can not capture all the unstable nuclei produced in the system and thus some stable particles are finally formed.

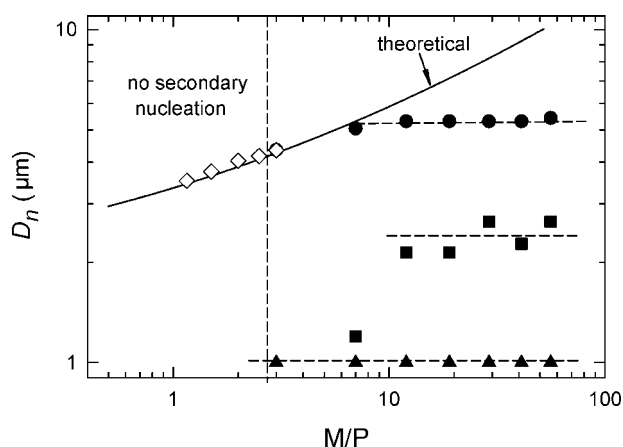


Figure 4 Particle sizes of different populations of PMMA particles prepared in seeded dispersion polymerizations using a $2.65 \mu\text{m}$ PMMA seed and different M/P ratios (~ 9.80 wt % total solids).

TABLE II
Characteristics of Seeded Dispersion Polymerization Using Micron-Size PMMA Seed

M/P	$N_{p,ini}$ (/L)	$A_{p,ini}$ (m^2/L)
1.157	3.08×10^{12}	67.98
1.5	2.66×10^{12}	58.66
2.5	1.90×10^{12}	41.90
3	1.66×10^{12}	36.66
7	8.31×10^{11}	18.33
12	5.11×10^{11}	11.28
19	3.32×10^{11}	7.33
29	2.22×10^{11}	4.89
41	1.58×10^{11}	3.49
56	1.17×10^{11}	2.57
112	5.88×10^{10}	1.30

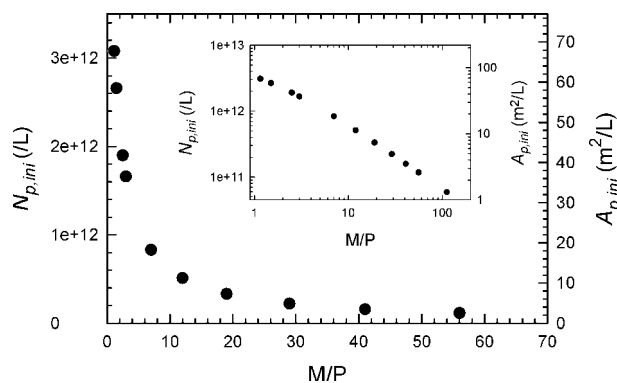


Figure 5 Relationship between the initial number of particles (and area) and the M/P ratio in seeded dispersion polymerizations using a 2.65 μm seed and 9.8 wt % final solids content. Inset shows the log-log relationship.

Besides the question as to why nucleation occurs beyond a certain low value of M/P, there are a number of other questions regarding these results. How does more than one population appear? And why do similarly sized populations appear beyond a 10/1 M/P ratio? What determines these sizes, and why is there little variation as M/P continues to increase? The answers to these should be important to our understanding of nucleation and growth in both seeded and *ab initio* dispersion polymerizations.

In seeded dispersion polymerization, the growth of the seed particles and new nucleation are two competitive processes consuming monomer. By increasing the M/P ratio, there is an increasing amount of monomer in the continuous phase, which can increase the likelihood of secondary nucleation as it promotes faster propagation. Meanwhile, the monomer concentration in the particles ($[M]_p$) will also increase, which can be expected to result in more monomer being polymerized in the seed particles leading to larger particles with increasing M/P.

This does not seem to be the case here. The partition ratio ($[M]_p/[M]_c$) has been shown through thermodynamic calculations to be relatively constant during a dispersion polymerization.²⁷ Values from 0.5 to 1.2 have been reported depending on the specific system. Therefore, given the similarities of two reactions where the only difference is M/P, $[M]_p$ is expected to vary in proportion to $[M]_c$. It turns out that only a modest difference in $[M]_c$ at the beginning of a reaction exists for large differences in the M/P ratio. For example, $[M]_{c,ini}$ for a value of M/P of 112 is only 1.13 times that at a value of M/P equal to 7.0. And the difference in $[M]_p$ is expected to be similar. Therefore, any difference in size based simply on the monomer concentration would likely be small. So why then do the seed particles all grow to a specific size, that is, 5 μm ? So far, we have no explanation for this phenomenon.

Seeded dispersion polymerization using submicron seed

194 nm PMMA latex as seed

Table III shows the results of seeded dispersion polymerizations using the 194 nm PMMA seed. The seed number concentration ($N_{p,ini}$) was varied over one order of magnitude from 4.84×10^{12} to 5.03×10^{13} L^{-1} , while the monomer to polymer seed ratio (M/P) was varied from 356 to 3740 [corresponding to surface areas ($A_{p,ini}$) of 0.56 to 5.95 $\text{m}^2 \text{L}^{-1}$]. Compared to the preceding study using the micron size seed (Table II), it can be seen that higher M/P and $N_{p,ini}$ values were used here, although the $A_{p,ini}$ values are substantially lower than the minimum value found to be successful using the large seed (41.9 $\text{m}^2 \text{L}^{-1}$) owing to the small volume of seed latex used. SEM images of the resulting PMMA particles are shown Figure 6. Unexpectedly

TABLE III
Results of Seeded Dispersion Polymerization Using 194 nm PMMA Seed Latex^a

	M/P	$N_{p,ini}$ (/L)	$A_{p,ini}$ (m^2/L)	Final Latex		$N_{p,final}$ (/L)
				D_n (μm)	PDI	
a		<i>Ab initio</i> polymerization		3.19	1.010	4.01×10^{12}
b	3740	4.84×10^{12}	0.57	2.93	1.011	5.18×10^{12}
c	2551	7.12×10^{12}	0.84	2.58	1.011	7.54×10^{12}
d	2593	1.46×10^{13}	1.72	2.12	1.008	1.37×10^{13}
e	1010	1.79×10^{13}	2.12	1.97	1.009	1.70×10^{13}
f	785	2.29×10^{13}	2.71	1.85	1.006	2.04×10^{13}
g	573	3.14×10^{13}	3.72	1.62	1.009	3.04×10^{13}
h	468	3.84×10^{13}	4.54	1.55	1.015	3.50×10^{13}
i	446	4.04×10^{13}	4.78	1.53	1.007	3.61×10^{13}
j	379	4.75×10^{13}	5.61	1.44	1.019	4.37×10^{13}
k	356	5.03×10^{13}	5.95	1.38	1.019	4.86×10^{13}

^a [AIBN] = 2.5 mM.

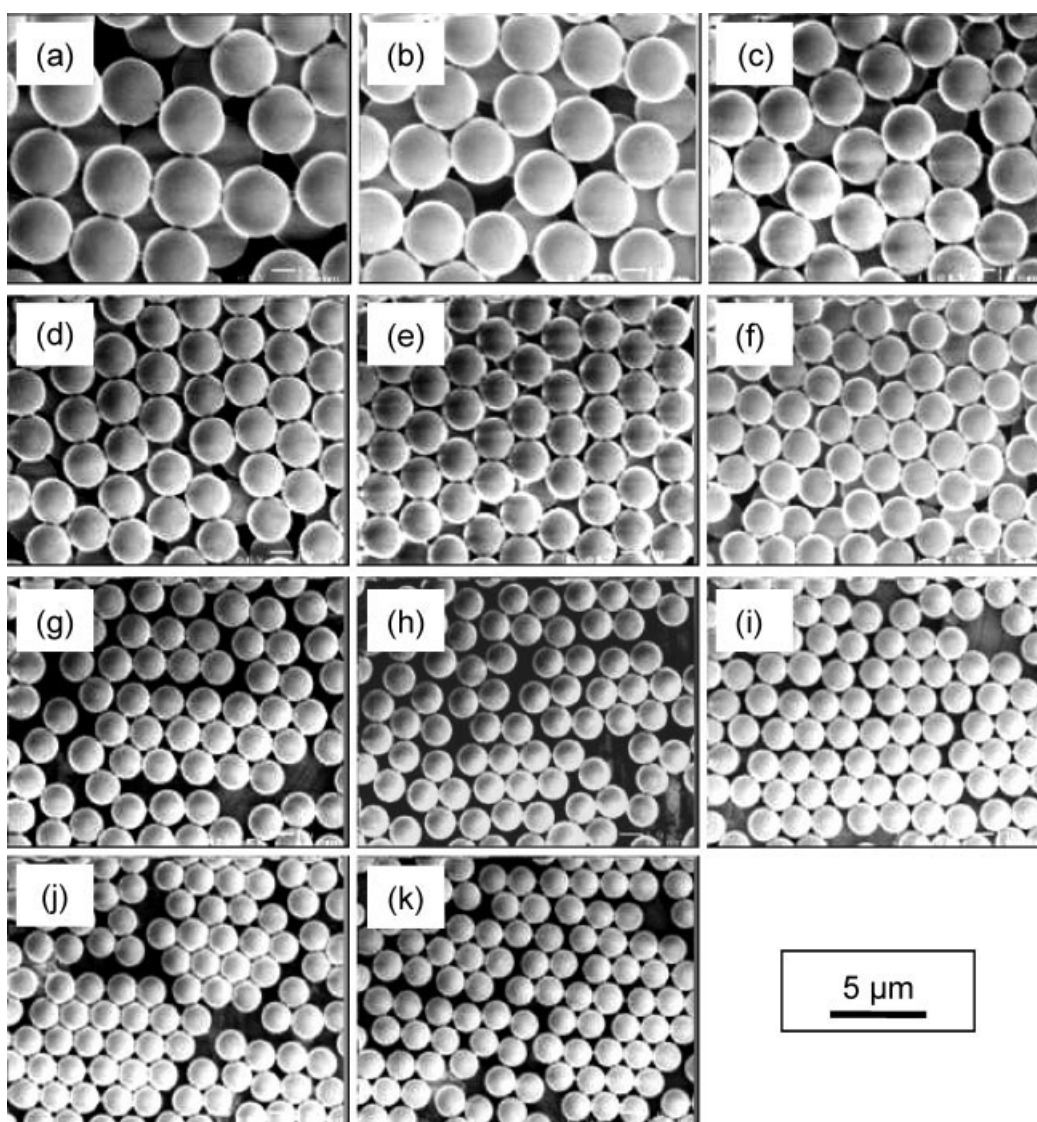


Figure 6 SEM images of PMMA particles obtained from *ab initio* (a) and seeded dispersion polymerizations (b–k) using 194 nm PMMA seed latex. Details of each sample are shown in Table III.

in all cases, micron-size PMMA particles with narrow size distributions were obtained.

Since larger PMMA particles [3.19 μm , Table III (a)] were obtained by the parallel *ab initio* polymerization, the smaller particles produced in the seeded runs must result from the addition of a given amount of seed latex. Table III also shows the final particle sizes (D_n) and polydispersity indexes. The relationship between the final particle number concentration and the initial particle number concentration is plotted in Figure 7; the solid square symbols represent the data from Table III. The “theoretical” line (diagonal) represents the case where each seed particle grows to become a final particle without any secondary nucleation or aggregation. It can be seen that the experimental data roughly agrees with the theoretical, which indicates that in this set of experiments, secondary nucleation and aggregation were

suppressed or prevented and particle growth dominated the polymerizations. Similar results were obtained using the 314 nm monodisperse PMMA seed particles (circles in Fig. 7) when the initial number of seed particles were greater than the number produced in the parallel *ab initio* dispersion polymerization (in this case, $N_{p,ab\ initio} = 4.0 \times 10^{12} \text{ L}^{-1}$). When $N_{p,ini}$ is smaller than $N_{p,ab\ initio}$, the final particle size and number are roughly equal to those produced in the *ab initio* reaction.

Mixtures of 194 and 317 nm PMMA latices as seed

Various bimodal distributions of seed particles were prepared by mixing different ratios of the 194 and 317 nm PMMA latices [mixing ratios: $\text{Wt}(194\text{nm})/\text{Wt}(317\text{nm}) = 1/9, 3/7, 5/5, 7/3, \text{ and } 9/1$]; this was initially thought to be a means of tracking the

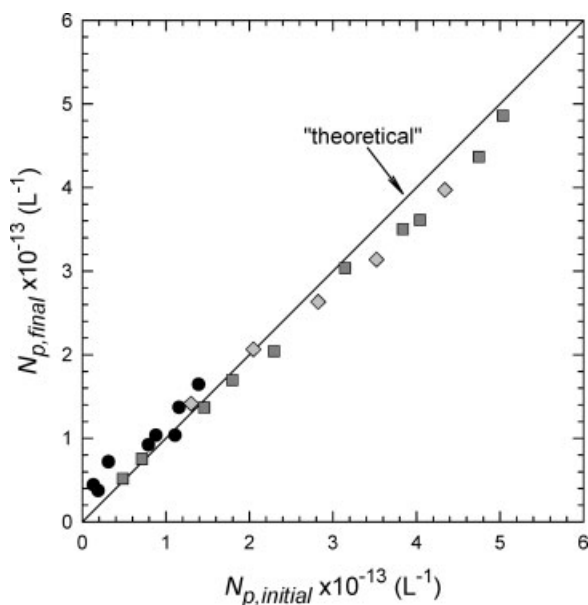


Figure 7 Relationship between final latex particle number concentration and initial seed number concentration in seeded dispersion polymerizations of MMA using 194 nm PMMA particles (squares), 317 nm PMMA particles (circles), and blends of 194 nm and 317 nm PMMA particles (diamonds) as seed latex.

growth of the particles with the expectation that a bimodal distribution would be the end result. Surprisingly, in spite of the bimodal seed, the final latex particles were unimodal with narrow size distributions. As shown in Figure 7 by the diamonds, the final number of particles appears to be determined by the initial number of particles in the seed mixture. Because the initial M/P is large and the seed particles grow hundreds of times in volume, the particle size distribution apparently “self-sharpens,” basically eliminating the 123 nm difference in initial seed diameters.

Figure 7 shows that, in spite of the PMMA seed particle size and size distribution, the final particle size is only dependent on the initial number of PMMA seed particles provided the seed number is greater than or equal to that produced in the parallel *ab initio* reaction. This opens a new window for producing micron-size polymer particles with better control of particle size and size distribution. These findings indicate that this seeded process is an attractive method to prepare polymer particles with a desired particle size without the numerous “trial and error” experiments normally required in *ab initio* dispersion polymerizations. The only crucial parameters found in seeded dispersion polymerizations are the initial seed number concentration ($N_{p,initial}$) and the initial *ab initio* recipe. Based on $N_{p,initial}$ and the amount of second stage monomer added, one can easily determine the final particle size. To expand

the possibilities of this process, the variation in a number of process variables was investigated. This was not an exhaustive study but rather a limited survey, as seen in the following.

Effect of initiator concentration

The AIBN initiator concentration was successfully varied from 1.65 to 6.67 mM in seeded dispersion polymerization of MMA using both the 194 nm ($N_{p,ini} = 2.6 \times 10^{13} \text{ L}^{-1}$) and 317 nm ($N_{p,ini} = 5.6 \times 10^{12} \text{ L}^{-1}$) PMMA seeds.²⁸ It was found that within this initiator range, the particle number is independent of the initiator concentration; the final particle size was determined solely by the initial number of seed particles. However, a 10 mM or greater AIBN concentration was found to produce polydisperse particles or coagulum in this system.

Effect of stabilizer concentration

Using a fixed number of seed particles ($2.60 \times 10^{13} \text{ L}^{-1}$ 194 nm PMMA), the stabilizer concentration was varied over the range of 1 to 20 wt % (based on monomer). The other ingredients were maintained constant. Results reported in Table IV show that stabilizer concentrations of 1 to 5 wt % were unable to provide sufficient stabilization and coagulum appeared. At 7.5 wt % and higher, particles with fairly narrow size distributions and similar particle size (1.7 μm) were obtained. This indicates that provided there is a minimum amount of stabilizer present in a seeded dispersion polymerization, the final particle size is independent of its concentration and is determined solely by the initial seed concentration.

Effect of monomer concentration

A single seeded dispersion polymerization recipe was modified solely by increasing the amount of MMA added up to an amount producing 26% solids. The initial 194 nm PMMA seed number concentration for all experiments was $2.60 \times 10^{13} \text{ L}^{-1}$. The results, reported in Table IV, indicate that concentrations of monomer beyond the standard recipe (≥ 13.1 wt %) produced broad or polydisperse distributions. The large particles appearing in the distributions were substantially larger than the theoretical size assuming all monomer polymerized in the existing seed; aggregation is the obvious cause. It should be noted that increasing the monomer concentration changes the solvency of the medium affecting most aspects of a dispersion polymerization system including the stabilizer, the oligomer chains produced in the continuous phase, and the partitioning of all species between the particles and the continuous phase.²⁷

TABLE IV
Effect of Other Variables in Seeded Dispersion Polymerizations

Effect of stabilizer						
[PVP K-30] /wt % ^a	1.0–5.0	7.5–20.0				
Latex	coagulum	1.6–1.7 μm				
<i>D</i> (theo.)	1.67 μm					
Effect of monomer concentration						
<i>M/P</i>	778	1037	1297	1556	2075	
Final PMMA Solids /wt%	9.8	13.1	16.3	19.6	26.1	
Latex	1.63 μm	1.9–2.5 μm broad		3.7–4.5 μm polydisp.		1.0–6.9 μm polydisp. 1.6–7.7 μm polydisp.
<i>D</i> (theo.)	1.67 μm	1.84 μm	1.98 μm	2.10 μm	2.31 μm	
Effect of medium composition						
Methanol/water wt/wt	50/50	60/40	70/30	80/20	90/10	100/0
Latex	coagulum	1.60 μm	1.63 μm	8.0 μm, polydisp.	coagulum	coagulum
<i>D</i> (theo.)	1.67 μm					

^a Based on monomer.

Effect of methanol/water ratio

The solvency of the medium was varied more directly by using different methanol/water ratios (50/50–100/0) as reported in Table IV. As before, the 194 nm PMMA seed was added in a concentration of $2.60 \times 10^{13} \text{ L}^{-1}$. It was found that methanol/water ratios of 60/40 and 70/30 produced fairly narrow distributions of the PMMA particles while ratios above or below these produced polydisperse particles or coagulum. Increasing the methanol/water ratio results in a stronger solvency of the medium for the PMMA chains. In a normal dispersion polymerization this usually results in an increase in the particle size. In these seeded dispersion polymerizations, higher methanol/water ratios also led to large and polydisperse particles (i.e., at 80/20 methanol/water).

Effect of initiator type

It has been reported that other initiators such as persulfates are not as successful (particles often having rough surfaces) in dispersion polymerizations as

AIBN (or other azo initiators like AMBN (2,2'-azobis(2-methylbutyronitrile)) and ADVN).¹⁵ Here, experiments were carried out to see if a wider range of initiators could be applied in seeded dispersion polymerizations. The 194 nm PMMA latex was used as seed in all experiments. Both water-soluble and oil-soluble initiators were chosen. The molar concentration used for each initiator was kept the same as the AIBN in previous experiments (i.e., 5.0 mM). The results are summarized in Table V. It can be found that use of water-soluble initiators (APS, and KPS) was not successful with polydisperse submicron particles being obtained in all cases, both seeded and *ab initio*. For benzoyl peroxide (BPO) initiator, monodisperse particles were found in only one case where the highest number of seed particles was used ($N_{p,ini} = 1 \times 10^{14} \text{ L}^{-1}$); all others gave two populations of particles, micron and submicron in size. ADVN failed to produce particles with narrow distributions in all cases tried here; polydisperse distributions containing large particles ranging from several microns to above 30 microns were found despite the fact that this initiator has been successfully applied in MMA dispersion polymerizations in pure

TABLE V
Particle Size and Size Distribution of PMMA Particles Prepared by *Ab Initio* and Seeded Dispersion Polymerization Using Different Types of Initiators^a

N_{seed}	APS	KPS	BPO	ADV N	ACPA
<i>Ab initio</i>	submicron, polydisperse	submicron, polydisperse	two populations, submicron and micron	micron-size, polydisperse	micron-size, monodisperse
$2.0 \times 10^{12}/\text{L}$	submicron, polydisperse	submicron, polydisperse	two populations, submicron and micron	micron-size, polydisperse	micron-size, monodisperse
$5.0 \times 10^{12}/\text{L}$	"	"	"	"	"
$2.0 \times 10^{13}/\text{L}$	"	"	"	"	micron-size, polydisperse
$1.0 \times 10^{14}/\text{L}$	"	"	1.10 μm monodisperse	"	"

^a [Initiator] = 5.0 mM, [PVP K-30] = 20.0 wt % based on MMA, 70°C, polymerized in bottle polymerizer for 24 h.

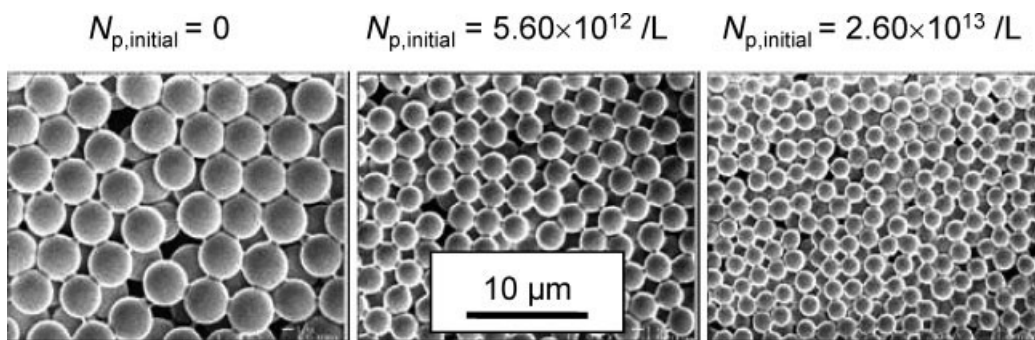


Figure 8 SEM images of PMMA particles obtained from dispersion polymerization (left) and seeded dispersion polymerizations (middle and right) without the addition of crosslinker.

methanol to produce 10 μm PMMA particles having a narrow distribution.¹⁵ With ACPA as initiator, PMMA particles with narrow size distributions were

produced in both the *ab initio* and the two lower $N_{p,ini}$ cases; polydisperse particles resulted for the two higher seed concentrations.

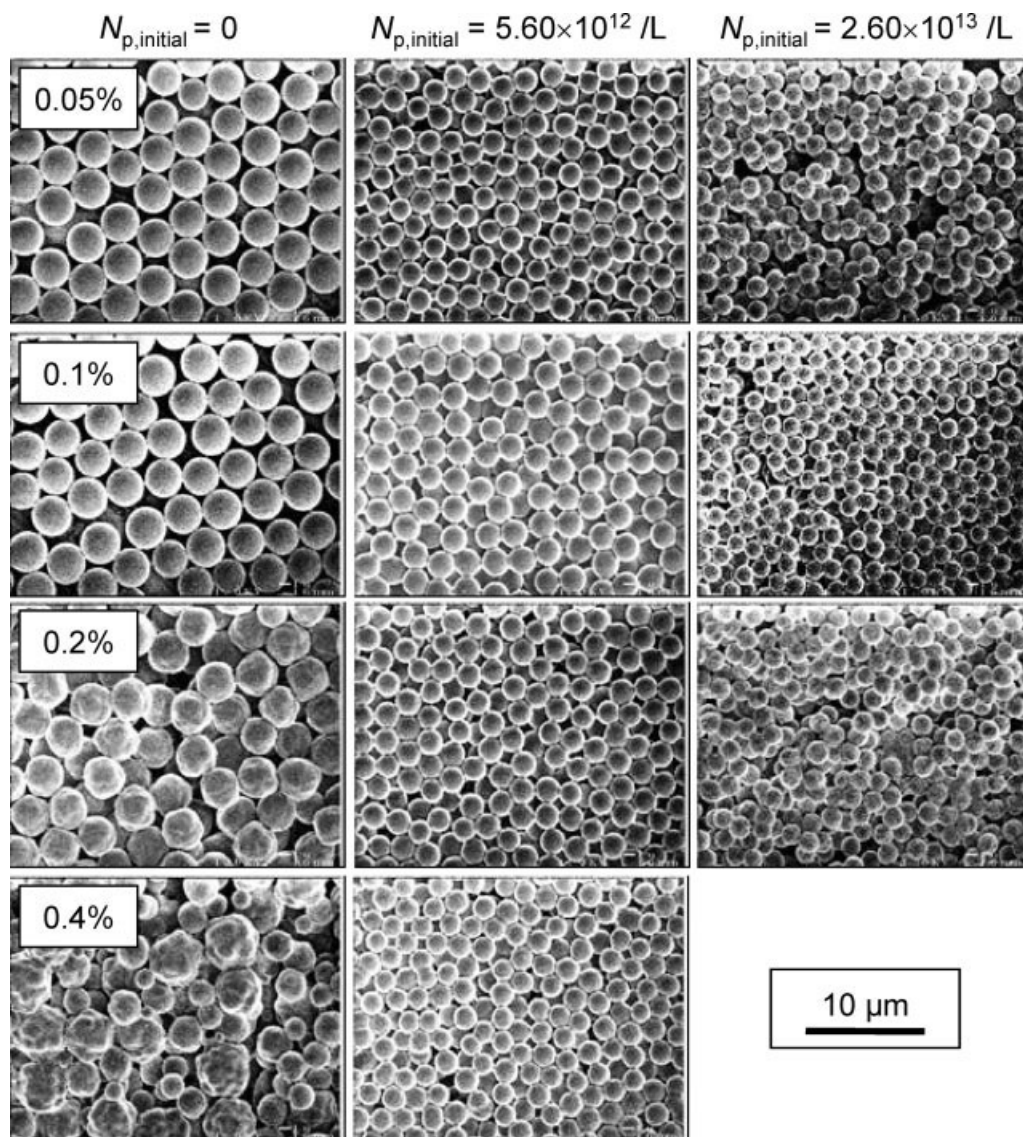


Figure 9 SEM images of PMMA particles prepared by dispersion polymerization and seeded dispersion polymerization with various EGDMA concentrations.

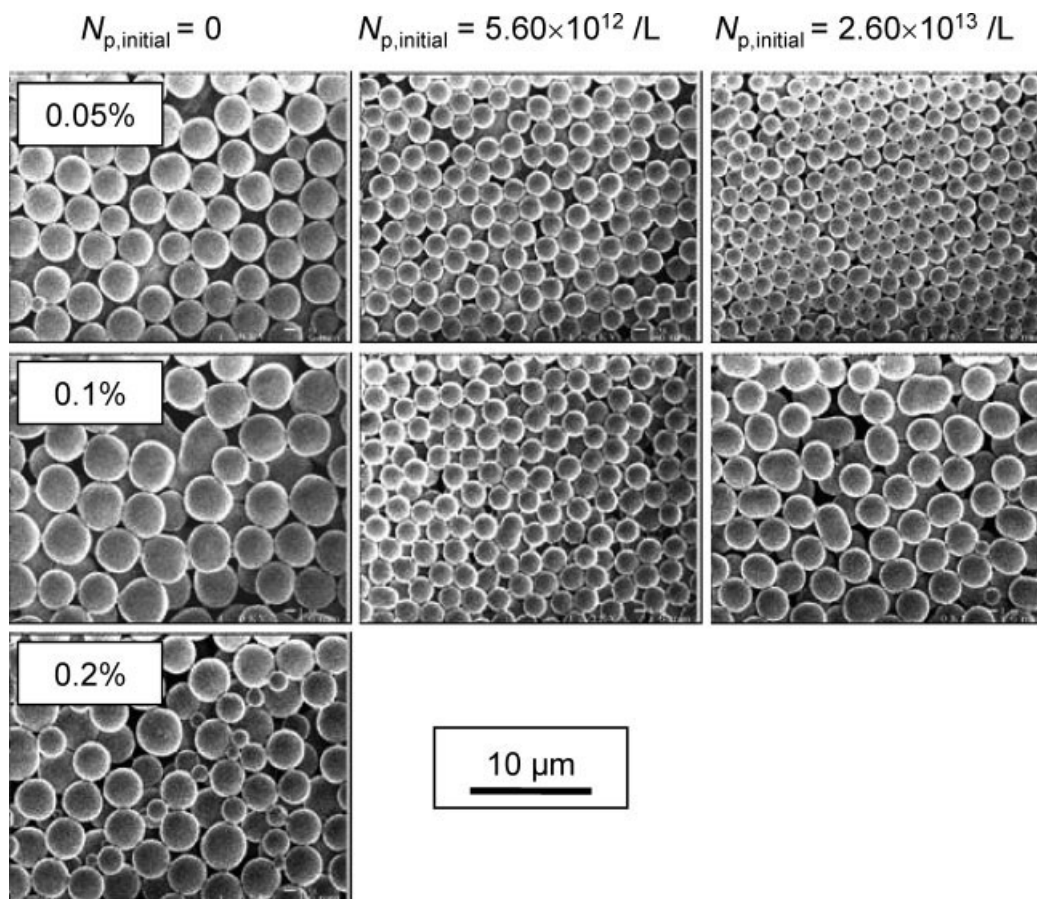


Figure 10 SEM images of PMMA particles prepared by dispersion polymerizations and seeded dispersion polymerizations with various DVB concentrations.

Addition of crosslinker in *ab initio* and seeded dispersion polymerizations

Because micron-size crosslinked particles have found application in various fields such as display technologies, we investigated three different crosslinkers in seeded dispersion polymerization: ethylene glycol dimethacrylate (EGDMA), divinylbenzene (DVB), and allyl methacrylate (AMA). The concentrations of these crosslinkers were 0.05, 0.10, 0.20, and 0.40 wt % based on monomer and were added as solutions in methanol. Polymerizations were carried out with and without PMMA seed (AIBN = 5.0 mM, PVP-K30 = 20.0 wt % based on MMA). The 194 nm PMMA seed latex was used at a concentration of $2.60 \times 10^{13} \text{ L}^{-1}$ and the 317 nm PMMA latex at $5.60 \times 10^{12} \text{ L}^{-1}$.

For comparison, *ab initio* and seeded dispersion polymerizations were carried out with SEM images of the resulting PMMA particles being shown in Figure 8. Micron-size PMMA particles were obtained, and in the seeded dispersion polymerizations, the final particle sizes were close to the value expected if all the second stage MMA was incorporated into the original seed particles.

Ethylene glycol dimethacrylate as crosslinker. Both *ab initio* and seeded dispersion polymerizations were carried out for all crosslinkers with the results presented in a series of SEM images. The left column in Figure 9 shows the PMMA particles prepared by *ab initio* dispersion polymerizations with EGDMA; the other two columns show the PMMA particles obtained from the corresponding seeded dispersion polymerizations. Without seed, smooth spherical particles were obtained at 0.05 and 0.1% EGDMA. Compared with the run where no crosslinker was added (Fig. 8, left micrograph), the particle sizes were about the same and the distributions were narrow. At 0.2% EGDMA, the resulting particles had a rough (bumpy) surface, but still a fairly narrow size distribution. When the EGDMA concentration was increased further to 0.4%, a lot of nonspherical particles were produced together with smaller particles. However, in the seeded dispersion polymerizations, smooth spherical particles with narrow size distributions were obtained in most cases. Nearly complete coagulation occurred at 0.4% EGDMA and the highest $N_{p,initial}$ (no micrograph taken). These results indicate

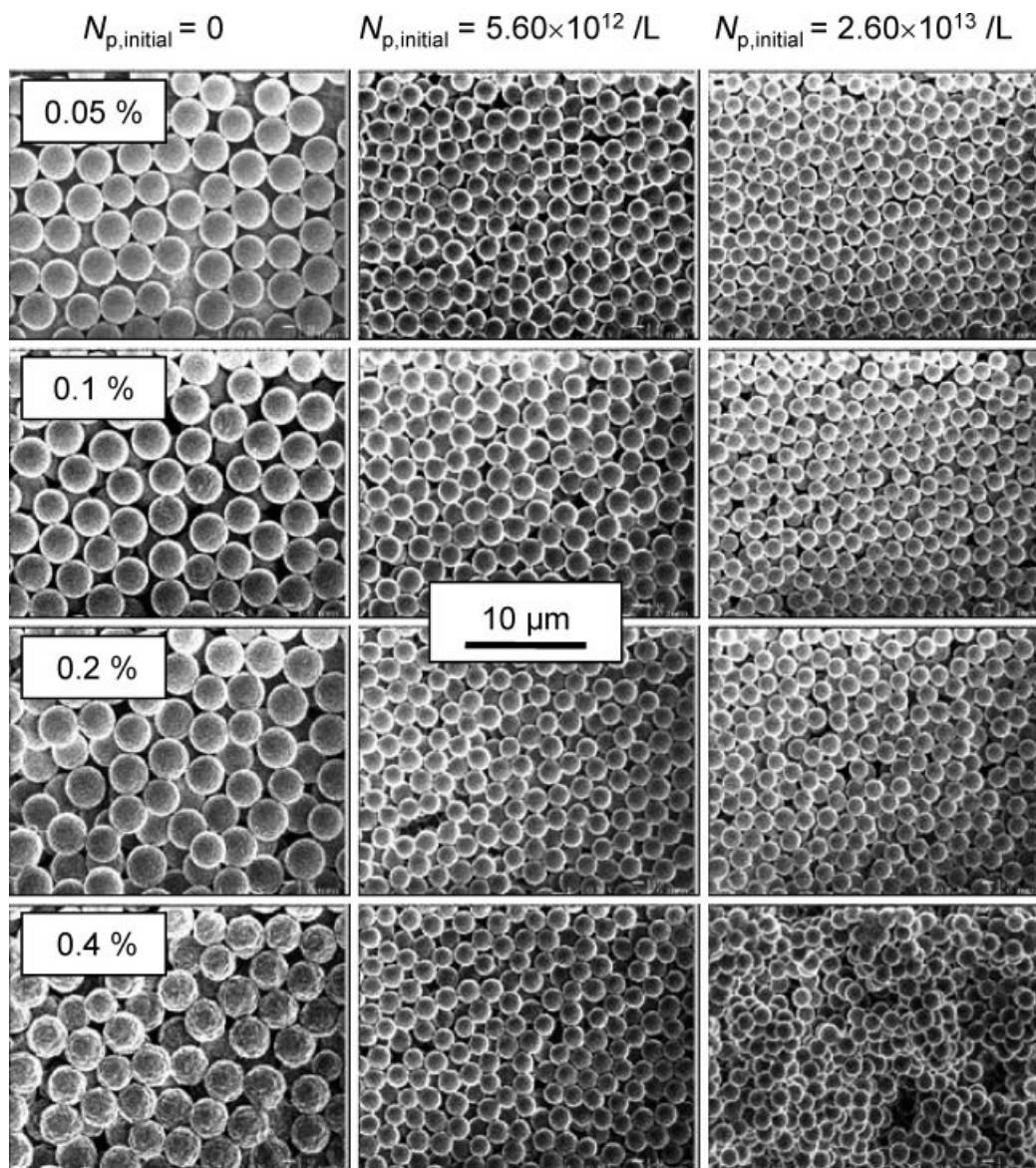


Figure 11 SEM images of PMMA particles prepared by dispersion polymerizations and seeded dispersion polymerizations with various AMA concentrations.

a distinct advantage of seeded dispersion polymerization in preparing crosslinked polymer particles.

Divinylbenzene as crosslinker. As shown in Figure 10, nonspherical particles were obtained in *ab initio* dispersion polymerizations containing DVB, even at a concentration as low as 0.05%; at higher DVB concentrations (>0.2%), coagulation occurred. In the seeded dispersion polymerizations with the lower $N_{p,ini}$, better control of the particle size and size distribution was achieved for DVB concentrations of 0.05 and 0.1%. For the higher $N_{p,ini}$, only the 0.05% DVB concentration gave better control; higher DVB concentrations resulted in nonspherical particles and coagulum.

Allyl methacrylate as crosslinker. Increasing amounts of AMA in *ab initio* dispersion polymerizations (left

column in Fig. 11) had little effect on the particle size but lead to somewhat broader particle size distributions. Rough particle surfaces can also be seen at the highest AMA level. In the seeded dispersion polymerizations, better control of the particle size and size distribution was achieved and the expected particle sizes (smaller than the *ab initio* size) were obtained for both initial seed particle concentrations.

CONCLUSIONS

In seeded dispersion polymerizations using 2.65 micron seed particles, the weight ratio of second stage monomer to seed polymer (M/P) has to be relatively low ($\leq 2.5/1$) to prevent the formation of new particles via secondary nucleation; this allows only

modest increases in the particle size. The supposition is that when M/P is sufficiently low, the total surface area present in the system is enough to capture all the newly formed unstable nuclei in the continuous phase, preventing secondary nucleation.

However, it has also been shown in seeded dispersion polymerizations using submicron seed particles that secondary nucleation can be prevented even when the surface area of the seed was relatively small (smaller than the minimum required for the micron-size seed). By using submicron polymer particles as seed, seeded dispersion polymerization shows a number of advantages compared to *ab initio* dispersion polymerization. First, under certain conditions, the final number of particles equals the initial number of seed particles. This provides a feasible means of reproducibly producing micron-size polymer particles with narrow size distributions. Second, the particle size distribution of the polymer seed does not need to be monodisperse provided they are relatively small in size compared to the final particles. This was shown by using a mixture of two different particle size seeds. And third, the control of particle size, distribution, and morphology in dispersion polymerizations employing crosslinking agents (EGDMA, DVB, and AMA) is generally improved over *ab initio* polymerizations by applying the seeded process.

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