Mechanism of Seeded Dispersion Polymerization of Methyl Methacrylate Using Submicron Polystyrene Seed Particles

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ABSTRACT: Submicron polystyrene (PS) latex particles were used as seed in seeded dispersion polymerization of methyl methacrylate (MMA) to investigate the particle nucleation and aggregation behavior in this type of polymerization. The PS seed particles were located and tracked during the reaction using a refractive index matching technique. The number of PS seed particles present in the poly(methyl methacrylate) (PMMA) particles was investigated in detail throughout the reaction. The change in the distribution of PMMA particle populations containing different numbers of seed particles indicated that intensive nucleation and aggregation occurred during the early stage of the reaction until a transition point of 8.7% conversion was attained under the reaction conditions studied. The size of the large particles at this point was around 1 μm. These particles were regarded as mature particles that did not aggregate with other mature particles. Meanwhile, immature particle were still generated continuously from the continuous phase. These immature particles could not survive the aggregation process to grow to become mature particle, but instead, were captured by the mature particles. Therefore, the total number of the mature particles remained constant from this point until the end of the reaction. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 203–209, 2011

Key words: seeded dispersion polymerization; refractive index; nanoparticle; particle nucleation; particle aggregation

INTRODUCTION

The preparation of monodisperse polymer particles has received a great deal of attention because of the commercial and scientific interest in such particles.[1–5] Dispersion polymerization is an attractive method to produce micron-size polymer particles with a narrow size distribution in a single step and is suitable for a variety of monomers.[6] It has been defined as "a process by which stable colloidal polymer particles are formed in a continuous liquid medium through polymerization of a monomer which is completely miscible with this medium and in which a stabilizer has been initially dissolved."[7] Despite its simplistic description, dispersion polymerization is a complex heterogeneous polymerization process whose mechanism is not fully understood. It is believed that nucleation of stable particles in dispersion polymerization only occurs at the early stage of the reaction.[6,7] When the nucleation stage is completed, the polymerization conversion can be so low that is undetectable. After this nucleation stage, the particle number will remain constant toward the end of the reaction. Particle nucleation is the key process in dispersion polymerization that will determine the final particle size and number. Because of its transient behavior, it is difficult to investigate the particle nucleation in dispersion polymerization directly. Some investigators have studied dispersion polymerization by seeded techniques. Jiang et al.[8] utilized seeded techniques as a means to control the particle size in dispersion polymerizations. Several kinetic studies have also been carried out on dispersion polymerizations using micron and submicron size seed particles.[9–11]

In seeded dispersion polymerizations of MMA using submicron size latex particles as seed, it was found that the final particle concentration [*N*(final)] was not usually equal to the initial seed concentration [*N*(initial)], except under some specific conditions.[12] The difference between *N*(initial) and *N*(final) can be related directly to the particle nucleation and aggregation behavior during the reaction. To understand the mechanism of seeded dispersion polymerization, it is of great importance to be able to follow the location of the seed particles during the seeded dispersion polymerization process.

The refractive index matching technique has been demonstrated to make a solid material appear to

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disappear when placed in a liquid.[13–15] If two polymeric materials with different refractive indices were mixed together and immersed in a surrounding environment with a refractive index matching one of the polymeric materials, the matching polymer will become invisible and the other polymer will remain visible to the naked eyes or in an optical microscope. It can be found that the refractive index of glycerol is quite close to that of PMMA, whereas PS has a much higher refractive index, as listed in Table I.[16,17] So, if PS particles are used as seed in the seeded dispersion polymerization of MMA, and the particles are imaged in glycerol under an optical microscope, the PMMA will become transparent, whereas the PS will remain visible. Thus, the seed can be located and tracked during the seeded dispersion polymerization process.

In this study, PS latex particles were utilized as seed in seeded dispersion polymerizations of MMA. The PS seed particles were located and tracked during the reaction by means of the refractive index matching technique. The particle nucleation and aggregation behaviors were thus revealed, thereby clarifying the mechanism of dispersion polymerization.

EXPERIMENTAL

Materials

MMA (Aldrich) monomer was purified by vacuum distillation at about 50°C to remove inhibitor before use. Purified MMA was stored at 5°C until needed. All other materials were used as received without further purification, including the stabilizer, poly(vinylpyrrolidone) (PVP) K30 (TCI America), the alcohol, methanol (VWR), the initiator, 2,2′-azobis (isobutyronitrile) (AIBN) (Aldrich), and the glycerol (Aldrich). Deionized water was used in all experiments. The polystyrene seed latex particles, with a diameter of 303 nm, were obtained from the Dow Chemical Company (LS-1221B). The latex was cleaned by serum replacement[18] to wash out the surfactant and other water-soluble materials before use.

Polymerization

Seeded dispersion polymerization of MMA was carried out using the recipe listed in Table II. All ingredients were weighed into a 4 oz glass bottle except the AIBN initiator and part of the methanol that was used to dissolve the AIBN. The contents were stirred at room temperature with a magnetic bar and the bottle was purged with nitrogen for 20–30 s and capped with a rubber septum after all the PVP K30 was dissolved. Then bottle was then immersed in a 70°C water bath with continued magnetic bar stirring. The polymerization was started by injecting the AIBN solution into the bottle. Samples were taken from the reaction mixture at specific times using a syringe and needle. The samples were immediately placed in an ice bath to stop the polymerization reaction.

TABLE I
Refractive Index Values

Material	R.I.
Glycerol	1.475
PMMA	1.492
PS	1.589

TABLE II
Recipe for Seeded Dispersion Polymerization of MMA Using PS Particles as Seed

Ingredient	Amount
MMA	9.8 wt % on total
Solvent	Methanol/Water = 7/3(wt/wt)
PVP K30	20 wt % on monomer
AIBN	0.52 wt % on monomer
Seed (PS, LS-1221B)	13.94×10^{12} L^{-1}

Reaction temperature = 70°C.

Characterization

The polymerization conversion (x) was determined by gravimetric analysis on the samples taken from the reaction mixture. Samples were weighed in aluminum pans and a drop of aqueous hydroquinone solution was added to each pan to prevent further polymerization. The latex was dried in an oven at 70°C overnight and the remaining solids weighed. The solids content (X) and the conversion (x) was calculated using eqs. (1) and (2).

$$X = \frac{m_2 - m_0}{m_1 - m_0} \quad (1)$$

$$x = \frac{X \times (m_S + m_{PVP} + m_{AIBN} + m_{MMA} + m_{PS}) - (m_{PVP} + m_{AIBN} + m_{PS})}{m_{MMA}} \quad (2)$$

where m_0 is the mass of the empty aluminum pan, m_1 is the mass of the aluminum pan with the added latex, and m_2 is the mass of the aluminum pan after drying. m_S, m_{PVP}, m_{AIBN}, m_{MMA}, and m_{PS} are the masses of solvents, PVP, AIBN, MMA, and PS seed, respectively, before the reaction.

The polymerization reaction rate (R_p) was calculated using eq. (3):

$$R_p = \frac{\Delta x}{\Delta t}[M]_0 \quad (3)$$

where $[M]_0$ is the total monomer molar concentration before the polymerization.

The samples taken from the reaction mixture were centrifuged at 4500 rpm for 20 min, the supernatant was removed, and the particles were redispersed in water. This process was repeated 3–4 times to remove any water-soluble materials. The particles were then imaged by scanning electronic microscopy (SEM, HITACHI 4300). Particle size and size distribution were analyzed by measuring the size of the particles from the SEM images. About 500 particles were measured for each sample. The volume-average diameter (D_v) is reported as the size of the particles, as calculated from eq. (4):

$$D_v = \left[\frac{\sum n_i D_i^3}{\sum n_i}\right]^{1/3} \quad (4)$$

where n_i is the number of particles with diameter D_i. The number of particles, N (on a per unit volume basis), was calculated using eq. (5):

$$N = \frac{6mx}{\rho \pi D_v^3 V} \quad (5)$$

where m is the mass of the initial MMA, ρ is the density of the polymer (PMMA: 1.19×10^3 kg/m^3, PS: 1.05×10^3 kg/m^3), and V is the volume of the latex.

The PS seed particles were located in the PMMA particles by the refractive index matching technique. A drop of latex was dried on a cover slip and imaged using an optical microscope (Nikon ECLIPSE TE 300) at 1000× magnification. Then a drop of glycerol was placed on the dried particles and they were again imaged under the optical microscope at the same location. The PMMA became transparent and the PS seed particles were revealed at this point. To obtain a profile of the inside of the PMMA particles, a movie was taken while the focal plane was moved from the bottom to the top of the particles. Then, the number of the PS seeds inside each of the PMMA particles could be counted. 300–500 PMMA particles were analyzed by this method and the seed particles population distribution in the PMMA particles was obtained.

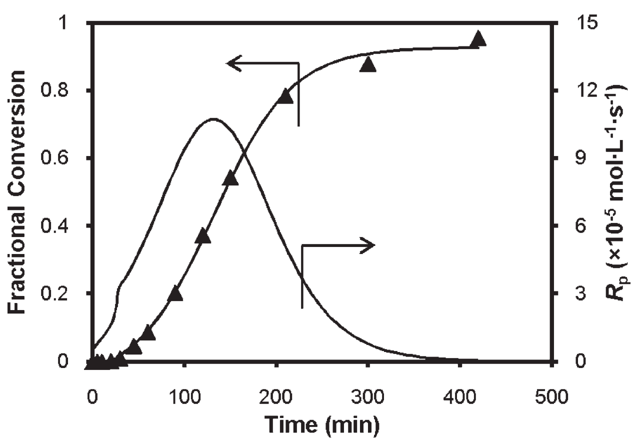

Figure 1 Time evolution of the conversion and rate of polymerization during the seeded dispersion polymerization of MMA.

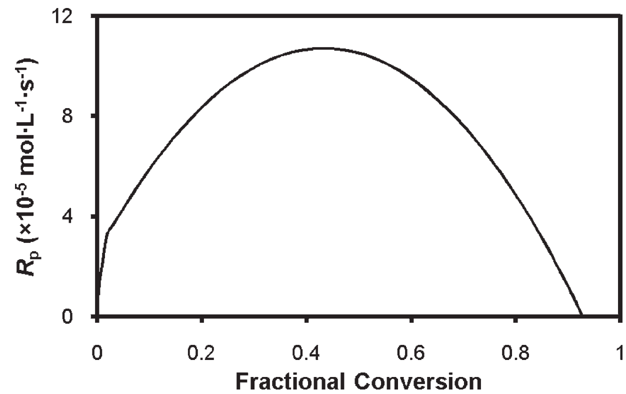

Figure 2 Evolution of reaction rate as a function of polymerization conversion during the seeded dispersion polymerization of MMA.

RESULTS AND DISCUSSION

Reaction kinetics and particle size and distribution

Figure 1 shows the time evolution of the conversion and rate of polymerization during the seeded dispersion polymerization of MMA using PS particles as seed. After an induction period of about 30 min, the polymerization began and reached about 95% conversion after 7 h. Figure 2 shows the evolution of reaction rate as a function of polymerization conversion. The rate increased to a maximum at about 45% conversion, and then decreased, because of the depletion of monomer. Figure 3 shows the evolution of the volume-average particle diameter and number of particles (on a unit volume basis) with conversion. The particle size increased continuously during the reaction. However, the particle number (on a unit volume basis) initially fluctuated and then became roughly constant for the rest of the reaction. Most of the monomer conversion took place, whereas the particle number (on a unit volume basis) remained constant, which is considered to be a precondition for achieving monodispersity of the final particles.

Figure 4 shows the evolution of the particle size distribution during the reaction. The size of the main population of particles increased continuously from the 303 nm seed particles to the 2.48 μm final particles. However, it was found that during the reaction, a minor population of small particles with size less than 200 nm was always detected. Evidence of the volume growth of these small particles was

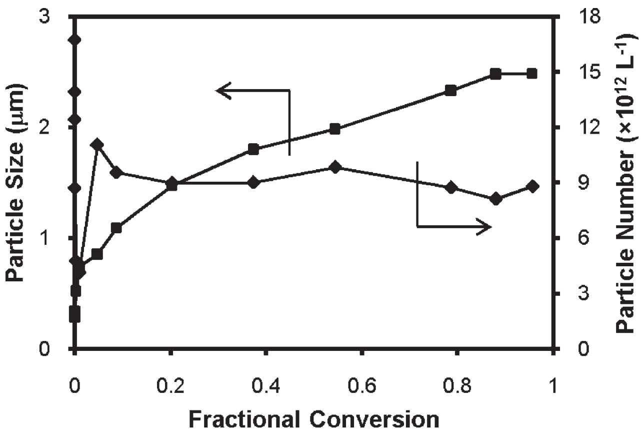

Figure 3 Evolution of the particle size and number during the seeded dispersion polymerization of MMA.

not found from the distribution evolution. These small particles were generated continuously during the reaction. They were not able to grow to become stable particles, but were captured by the larger particles, thereby contributing to their growth. Such suppression of the formation of new stable particles by the already stable particles helps to produce a narrow particle size distribution of the final particles.

Number of seed particles incorporated in each PMMA particle

Figure 5 shows optical micrographs obtained by utilizing the refractive index matching technique to locate and count the PS seed particles inside the PMMA particles. Both images were taken of the same group of particles. The left one was taken under the dry stage. In this image, the PMMA particles are visible. The PS seed particles are not visible since they are buried inside the PMMA particles. The right one was taken after these PMMA particles were immersed in glycerol. In this image, the PMMA particles become nearly transparent, for the refractive index of PMMA is quite close to that of glycerol. The PS particles now become visible (black dots in the gray PMMA particles).

The right image of Figure 5 shows the PS particles in a given focal plane. However, the size of the PMMA particles is around 2.5 μm and the size of PS seed particles is about 300 nm. In this situation, there could be some PS particles that are not in focus (unseen) because they are located in the parts of the PMMA particles outside the focal region. To find every PS particle inside the PMMA particles, a video was recorded while the focal plane was moved from the bottom to the top of the PMMA particles. Then, the number of PS particles was counted for each PMMA particle in the video. The results are listed in Table III. It was found that about 60% of the PMMA particles contained one single PS particle, 24% contained two PS particles, 9% contained no PS particles, and there were a few that contained more than two PS particles, but these comprised a small population.

Figure 5 and Table III represent the results for the sample taken at a conversion of 95.6%. After analyzing all the samples taken at different conversions by this method, the evolution of the PMMA particle populations with different numbers of PS particles was obtained as plotted in Figure 6. It can be seen that during most of the reaction time (polymerization conversion from 8.7% to the end of the reaction), the population distribution remained essentially constant. Sixty percent of the PMMA particles contained one PS seed, 23% contained two seeds, and 9% had no seed present.

There is a significant transition point which is located at 8.7% conversion, as can be noted in Figure 6. From the beginning of the reaction to this point, the population of particles with one seed decreased from 100% as seed particles to about 60%,

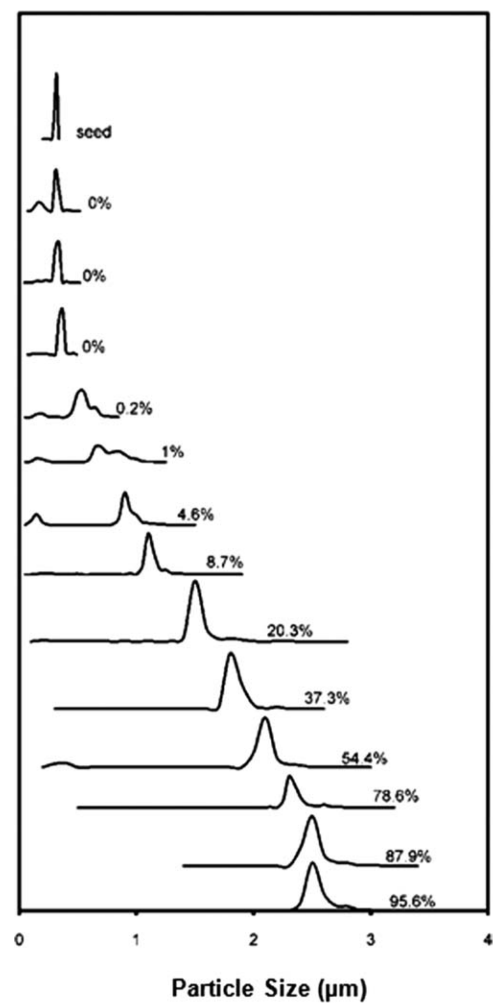

Figure 4 Evolution of the particle size distribution with conversion.

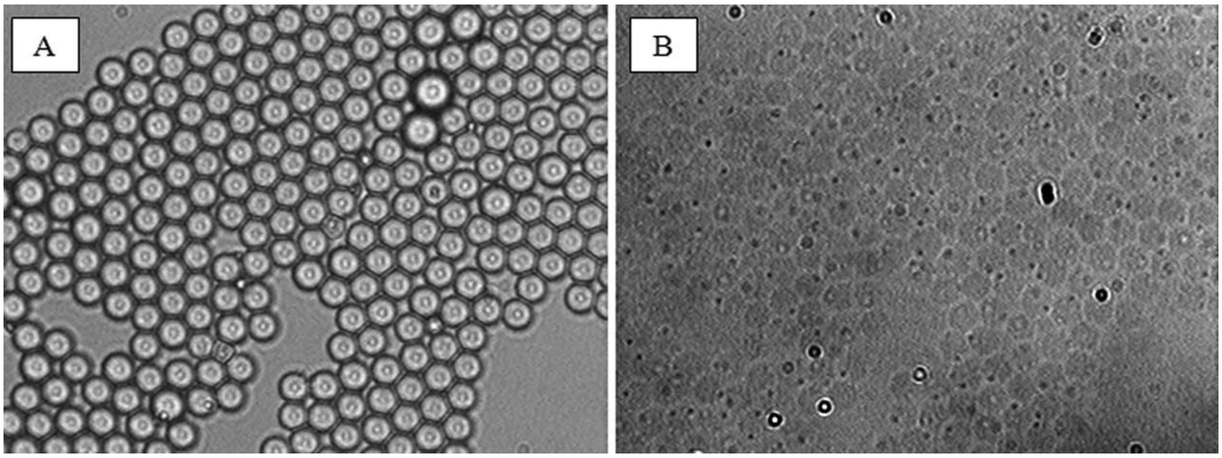

Figure 5 Optical microscope images of the final particles utilizing refractive index imaging. A: Dry stage; B: In glycerol.

whereas the population of particles with two seeds increased from zero to about 23%. This is a result of the aggregation of particles containing seeds. Also during this stage, the population of particles with no seed increased from zero to about 9%, which is due to the nucleation reaction. Aggregation and nucleation occurred dramatically at the very early time of the reaction (<1% conversion), then became less important after that, which can be seen as the change of the slope of the lines before and after 1% conversion. After the transition point of 8.7% conversion, the distribution of PMMA particle populations containing different numbers of seed particles remained constant toward the end of the reaction. The particle size of the large-particle population at the transition point was about 1 μm. A broad particle size distribution was detected during the early stages of the polymerization, even though the PS seed particles were uniform in size. This is the result of the nucleation and aggregation processes that produce different sized particles. Nonetheless, the size distribution of the final particles was still quite narrow, because most of the monomer was added to the particles when the particle number (on a unit volume basis) remained constant and these particles grew in parallel.

Figure 7 shows the evolution of the ratio of the total number of PMMA particles [*N*(particle)] to the number of PS seed particles [*N*(seed)] during the seeded dispersion polymerization. The reaction started with an *N*(particle)/*N*(seed) ratio of 1, owing to the presence of only the seed particles in the reaction mixture. A slight increase in the *N*(particle)/*N*(seed) ratio in the early stages of the reaction was detected. This is a consequence of the nucleation of new particles. This ratio then decreased as the polymerization proceeded to about 0.7 at about 10% conversion. After that, the *N*(particle)/*N*(seed) ratio remained roughly constant to the end of the reaction. The change in *N*(particle)/*N*(seed) with conversion is consistent with the transition point described in Figure 6.

The initial PS seed particle concentration [*N*(initial)] was 13.94×10^{12} L^{-1}, and the final particle concentration [*N*(final)] was 8.81×10^{12} L^{-1}. The *N*(final)/*N*(initial) ratio was 0.632, which is consistent with 0.7 obtained from the *N*(particle)/*N*(seed) ratio during the reaction. This indicated that all of the seed particles ended up inside the final particles.

Nucleation and aggregation processes take place simultaneously during dispersion polymerization. The nucleation of primary particles takes place continuously throughout the reaction. These primary particles can grow in volume by aggregating with other particles, as well as by growth through polymerization inside the particles. So, there could be

TABLE III
Analysis of PS Seed Particles Present in PMMA Particles

Number of PS particles in one PMMA particle	D_v (μm)	Number of final particles	Relative particle number	Total number of seed particles
0	2.17	21	9.05%	0
1	2.27	140	60.34%	140
2	2.37	56	24.14%	112
3	2.44	10	4.31%	30
4	2.59	3	1.29%	12
5	3.08	2	0.86%	10

populations of particles with different sizes in the system. Aggregation could take place among the small particles, or between small ones and large ones, or even among the large particles. However, when a particle grows to a certain size, it is considered to be a mature particle. Mature particles will aggregate with themselves at such a low rate that they can be regarded as stable particles. However, the aggregation between mature and small (immature) particles, also referred to as the capture of small particles, can still be fast. This capture of small particles, as well as the aggregation among the small particles, will consume most of the nucleated primary particles. Only a small number of these nucleated particles can survive these processes to become mature particles. When a certain number of mature particles are generated in the reaction system, the immature particles will not be able to grow to become mature particles before they aggregate with other particles (mature or immature). In this case, no new mature particles will be generated. Since the mature particles will not aggregate with other mature particles, the total number of mature particles will remain constant. These mature particles will grow in parallel and end up with a narrow particle size distribution.

In the case of seeded dispersion polymerization, the seed particle size was small and comparable to the newly-formed particles at the beginning of the reaction. So aggregation could take place among all the particles. The aggregation between seed particles or particles containing a seed caused the number of particles containing one seed particle to decrease and the number of particles containing two or more seed particles to increase. The aggregation among the newly formed particles, as well as the polymerization inside these particles, resulted in the volume growth of these particles, thus representing the

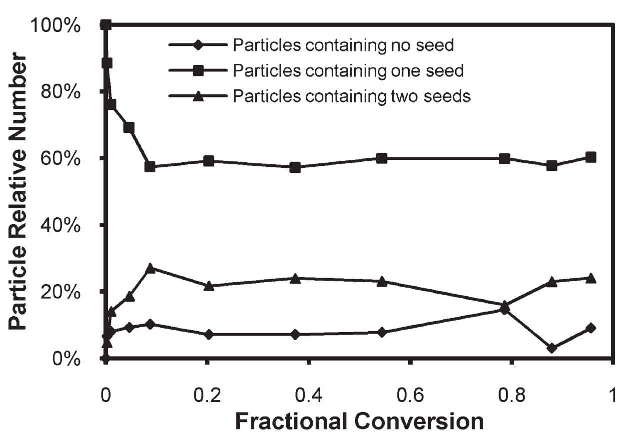

Figure 6 Populations of particles containing different numbers of seed particles. Small populations of particles containing more than two seed particles are not presented in this figure.

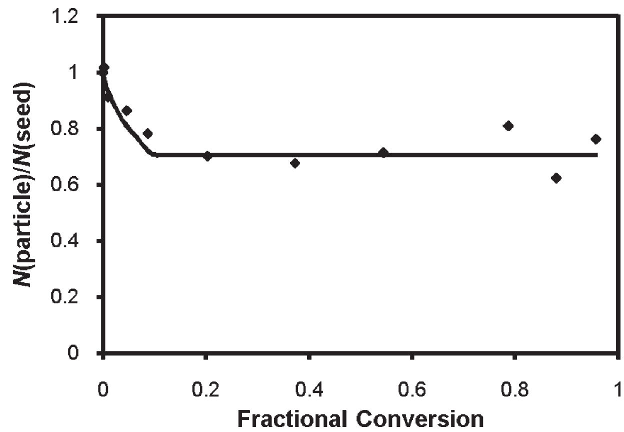

Figure 7 Evolution of the ratio of the particle number to the seed number during the seeded dispersion polymerization of MMA.

particles containing no seed. With the growth of particles, the nucleation was reduced because large particles capture more oligomers and unstable particles. Meanwhile, aggregation was also reduced when the particle size was larger. When the polymerization reached 8.7% conversion, the transition point, a certain number of mature particles were generated. These mature particles (larger than 1 μm) did not aggregate with each other, and so their population remained constant. However, the small immature particles were still continuously generated. These particles aggregated with other small particles, as well as being captured by the large mature particles. The capture of all the newly generated particles prevented any further nucleation of new mature particles, thereby keeping the number of large particles constant.

CONCLUSIONS

Seed particles were located and tracked in the seeded dispersion polymerization of MMA using PS latex particles as seed by means of a refractive index matching technique. After determining the number of seed particles in each PMMA particle during the reaction, the population distribution of PMMA particles containing different seed numbers was obtained as a function of the polymerization conversion. As a result of the competition between the nucleation and aggregation processes during the seeded dispersion polymerization, a significant transition point could be detected at a conversion of 8.7%. From the beginning of the reaction to this transition point, the number of PMMA particles containing no seed particle increased from zero to 9%; the number of PMMA particles containing one seed particle decreased from 100 to 60%; and the number of PMMA particles containing two seed particles increased from zero to 23%. Their numbers remained constant after the transition point to the end of the reaction. This phenomenon offers insights into particle nucleation and aggregation behavior which takes place throughout the entire dispersion polymerization process and represents the two competitive processes that control the final particle size and number. Particles are continuously generated and aggregate with each other until enough mature particles (i.e., larger than 1 μm) are formed at the transition point. These mature particles will not aggregate with each other, but will capture all the immature particles which are still generated from the continuous phase. Therefore, the number of the mature particles will remain constant to the end of the reaction.

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