

Influence of Poly(methyl methacrylate) Particles with Different Initial Temperature Rising Ramps on Size Distribution in Dispersion Polymerization

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Received 23 January 2008; accepted 7 October 2008

DOI 10.1002/app.29461

Published online 23 January 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The initial heating velocity was surprisingly found to play a key role in the size distribution of the resulting polymer particles in the dispersion polymerization of methyl methacrylate. Monodisperse poly(methyl methacrylate) particles had to be prepared by the mild and gradual increase of the reaction temperature. A universal conclusion was drawn from a series of experiments: the more slowly the initial temperature rose, the more the dispersity of the poly(methyl methacrylate) particles improved with a monomer concentration of 5–20 wt %, a 2,2-azobisisobutyronitrile concentration of 0.5–3 wt %, and a polyvinylpyrrolidone K-30 concentration of 20–60 wt %. The optimal heating velocity was 10–15°C/h. A heating ramp faster than 15°C/h led to polydisperse polymer particles or a poor dispersity. These interesting phenomena might be explained as a delicate bal-

ance between the formation rate of radicals and the capture of oligomer chains in the continuous phase when a slow heating strategy was used. For comparison, the dispersion polymerization of styrene and glycidyl methacrylate in an alcoholic medium was also investigated. Slow heating was slightly disadvantageous for the dispersity of polystyrene and poly(glycidyl methacrylate). Presetting at the polymerization temperature was practical for the production of monodisperse polystyrene and poly(glycidyl methacrylate). Furthermore, either a low reaction temperature or a long heating time caused the coagulation of poly(glycidyl methacrylate) or polydisperse particles. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 917–925, 2009

Key words: particle size distribution; polystyrene

INTRODUCTION

Polymer particles with diameters ranging from 1 μm to several micrometers have found a variety of technological applications as standard particles for the calibration of electron microscopes; original particles for further swelling to synthesize larger functional polymer particles, which are frequently used in biological separation techniques; medical and clinical diagnoses; chromatography; catalyst carriers, and so on.^{1–4}

Polymer particles with good dispersity, especially monodisperse polymer particles, have been found to be essential in some applications, for example, magnetic biological separation and immunoassays.^{2,5} Although monodisperse polymer particles can be obtained by emulsion polymerization, the size of polymer particles is often smaller than 1 μm and the particles often need further treatment, either by Vanderhoff's successive seeded emulsion polymerization⁶ or by Ugelstad's two-stage swelling processes,⁷ which are difficult and tedious in most cases. In Vanderhoff's method, latex particles prepared by

emulsion polymerization are subjected to a second emulsion polymerization step. Because the seed particles are already of submicrometer size, there is a greater probability of aggregation and subsequent phase separation.

Dispersion polymerization has recently received great attention for the preparation of polymer particles on a micrometer scope because of its simplicity and flexibility since the polymerization method was invented over 2 decades ago.^{8,9} It is an attractive and promising alternative to other polymerization methods, which affords micrometer-size monodisperse particles in a single-batch process. It is also a newly emerging technique for the preparation of monodisperse polymer particles of different sizes (1–10 μm) in very good yield and is suitable for a variety of monomers. Close control of the reaction conditions is essential to achieve the monodispersity of the prepared microspheres.

With regard to the polymerization seeds, people often chose polystyrene (PST) particles as the original particles for seed emulsion polymerization or the multiple-stage swelling reaction because of their excellent uniformity and simplicity of preparation. A number of reports in the literature have been related to the application of PST seed.^{10–12} Thus, most studies have focused on the reaction process, mechanism

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of styrene (ST), and PST particle size control. Anyway, PST is a kind of weak polar polymer; its main disadvantages include long playing for swelling processes¹² and difficult surface chemistry modification because of its lack of active groups. Polar polymer particles have obvious merits in seeded swelling polymerization.¹³ The use of polar seeds sharply shortens the swelling time and widens the scope of swellable monomers. In our previous research,¹⁴ we noticed that poly(alkyl methacrylate) was able to shorten the swelling time when poly (methyl methacrylate) (PMMA) microspheres several micrometers in size were used as a substitute for PST.

In several reports,^{15–17} researchers have discussed the preparation of monodisperse PMMA particles in the micrometer size range. Reaction parameters that may affect the size and size distribution, including reaction temperature, monomer concentration, decomposition rate, concentration of initiator, steric stabilizer concentration, and solvency of medium have been systematically investigated. Among these studies, only description of the monodispersity of PMMA particles has been given. Unfortunately, PMMA particles with poor dispersity were prepared, even under the optimal conditions published in previous studies. Amazingly, the initial temperature control played an important role in the size distribution of PMMA microspheres, which was often overlooked in former works. The dispersion polymerization of ST and glycidyl methacrylate (GMA) was comparatively examined in this study.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), ST (Tianjin Kermel Chemical Reagents Development Centre, China), and GMA (Beijing Ouhe Technology Co. Ltd., China) monomers were washed with a 1M aqueous sodium hydroxide solution to remove inhibitor, then washed with deionized water until they were neutral, and finally purified by vacuum distillation before use. 2,2-Azobisisobutyronitrile (AIBN) was purified by recrystallization in analytical-grade methanol. Benzoyl peroxide (BPO) was purified by recrystallization in chloroform and methanol. Polyvinylpyrrolidone (PVP) K-30 (weight-average molecular weight = 40,000) was supplied by Sigma–Aldrich (St. Louis, MO) and was used without additional purification. Di-2-ethylhexyl ester of sodium sulfosuccinic acid [Aerosol OT-100 (AOT-100), Sigma–Aldrich], methanol, ethanol, 2-methoxy ethanol, and all other solvents were supplied from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and were also used as received. Deionized water was used throughout the study.

TABLE I
Standard Recipe for the Dispersion Polymerization of MMA

Reagent	Weight (g)	Relative wt %
Methanol	25	87.64
MMA	2.5 ^a	8.76
PVP K-30	1.0 ^b	3.51
AIBN	0.025 ^c	0.09
Total	28.525	100

The final temperature was 55°C, the overall reaction time was 24 h, and the stirring rate was 120 rpm.

^a The monomer concentration was 10 wt % with respect to the solvent weight.

^b The PVP K-30 (weight-average molecular weight = 4.0×10^4 g/mol) concentration was 40 wt % with respect to the monomer weight.

^c The AIBN concentration was 1 wt % with respect to the monomer weight.

Preparation of PMMA microspheres

The standard recipe for MMA dispersion polymerization is given in Table I. MMA was polymerized in methanol under different conditions. In a typical example, 1.0 g of PVP was dissolved in 27.15 mL of methanol in a 100-mL glass bottle with a rubber cap and a magnetic stirrer; then, a solution of 25 mg of AIBN in 2.5 g of MMA was added. The polymerization vessel was purged with high-purity nitrogen for 10 min to remove oxygen. The glass bottle was then capped and sealed with a rubber cap. This bottle was placed in an oil bath, along with a magnetic stirring machine until dispersion polymerization continued to the preset time. The heating procedure was conducted in a specially designed way. The resulting product was purified with centrifugation/redispersion in methanol 10 times.

Preparation of poly(glycidyl methacrylate) (PGMA) microspheres

The standard amount of reactants for PGMA is illustrated later in Table V. In a typical example, 0.5 g of PVP was dissolved in 27.15 mL of methanol in a 100-mL glass bottle with a rubber cap and a magnetic stirrer, and then, a solution of 25 mg of AIBN in 2.5 g of GMA was added. The polymerization vessel was purged with high-purity nitrogen for 10 min to remove oxygen. The bottle was capped and sealed with a rubber cap. The well-sealed bottle was then placed in an oil bath until dispersion polymerization continued for the arranged period. The heating procedure was conducted in a specially designed way. The polymerization product was purified with centrifugation/redispersion in methanol 10 times.

Preparation of PST microspheres

The dispersion polymerization of ST was carried out in a mixture medium of methanol and 2-methoxy ethanol with the same procedure used for the preparation of PMMA. The general amount of each ingredient is listed later in Table VII. For example, 2.2 g of polymeric stabilizers were dissolved in an 85-g mixture solvent in a 250-mL glass bottle with a rubber cap and a magnetic stirrer, and then, a solution of 125 mg of AIBN in 12.5 g of ST was added. The polymerization vessel was purged with high-purity nitrogen for 10 min to remove oxygen. The bottle was capped and sealed with a rubber cap and then placed in an oil bath until dispersion polymerization continued for the arranged period. The polymerization product was purified with centrifugation/redispersion in methanol 10 times.

Particle characterization

Scanning electron microscopy (SEM) photographs were taken on a Hitachi S-4800 microscope. A drop of the methanol dispersion of the polymer was spread onto aluminum foil; the particles were then coated with gold *in vacuo*. In each example, 100 of the previous particles were measured to calculate the number-average diameter and size distribution. The number-average diameter was defined as $\sum d_i/N$, where d_i is the diameter of particle i , and N is the total number counted. The particle size distribution was expressed as the relative standard deviation [or coefficient of variation of the particles (%)]:

$$\varepsilon = \sqrt{\frac{\sum (d_i - \bar{d})^2}{n - 1}} / \bar{d}$$

where ε is the relative standard deviation, n is the total number counted, and \bar{d} is the number-average diameter.

RESULTS AND DISCUSSION

Dispersion polymerization of MMA

Although the dispersion polymerization technique has been, until now, the simplest method for the production of micrometer-sized polymer particles, the control of particle size and especially size distribution is complicated. The factors that may affect the particle size and size distribution include the temperature; initiator type; solvent system; concentration of monomer, initiator, and stabilizer; and even stirring speed for a specific reaction system. Some reports^{16,17} have discussed the control of the PMMA particle size and size distribution; the reaction parameters, such as temperature, initiator type

TABLE II
Influence of the Heating Velocity on the Particle Size and Particle Size Distribution of PMMA

Entry	1	2	3	4	5
Time to 55°C (h)	0	0.5	1.5	2	3
D_n (μm) ^a	4.55	4.07	3.97	3.72	3.64
CV (%) ^b	18.1	16.6	10.0	4.28	1.5

The polymerization conditions are the same as those listed in Table I, except for different intervals from room temperature to the preset reaction temperature.

^a Number-average diameter of microspheres: $D_n = \sum d_i / N$.

^b Coefficient of variation: CV (%) = Standard deviation / D_n .

and concentration, stirring speed, concentration and molecular weight of steric stabilizers, and monomer concentration, have systematically been investigated. However, the particle size distribution has only been simply described; detailed particle size distribution was not given in those studies. Moreover, no one paid much attention to the potential effect of the initial heating process on the polymerization. In our studies, we noticed that PMMA particles of poor dispersity were produced according to the published literature, but monodisperse PMMA particles were produced by slow heating.

The polymerization was at first carried out with PVP K-30 by an AIBN initiator at 55°C; the recipe is listed in Tables I and II (entry 1). The procedure was a little modification of Shen and coworkers's method^{16,17} for weight aim. The coefficient of variation of the particles or relative standard deviation (%) was used to evaluate the index of dispersity of the polymer microspheres. In previous studies, a universally accepted idea has been that proper temperature, initiator concentration, stabilizer concentration, and monomer concentration are necessary for the formation of monodisperse polymer particles. For MMA dispersion polymerization in methanol-containing solvent, monodisperse PMMA particles could be produced under the following conditions: 50–60°C for temperature, 0.5–3 wt % initiator on the basis of monomer weight, 5–20 wt % monomer on the basis of solvent weight, and 20–60 wt % stabilizer on the basis of monomer weight. Therefore, the reaction temperature 55°C, 1 wt % AIBN, 10 wt % MMA, and 40 wt % PVP K-30 were chosen for standard recipe for our study.

The samples in other entries in Table II were similar to that in entry 1 except for the heating procedure. In the sample in entry 1, the heating bath was preset at 55°C; the samples in entries 2–5 needed 0.5, 1.5, 2, and 3 h to reach 55°C from room temperature (25°C) and then were stabilized at 55°C throughout polymerization. Table II shows us the number-

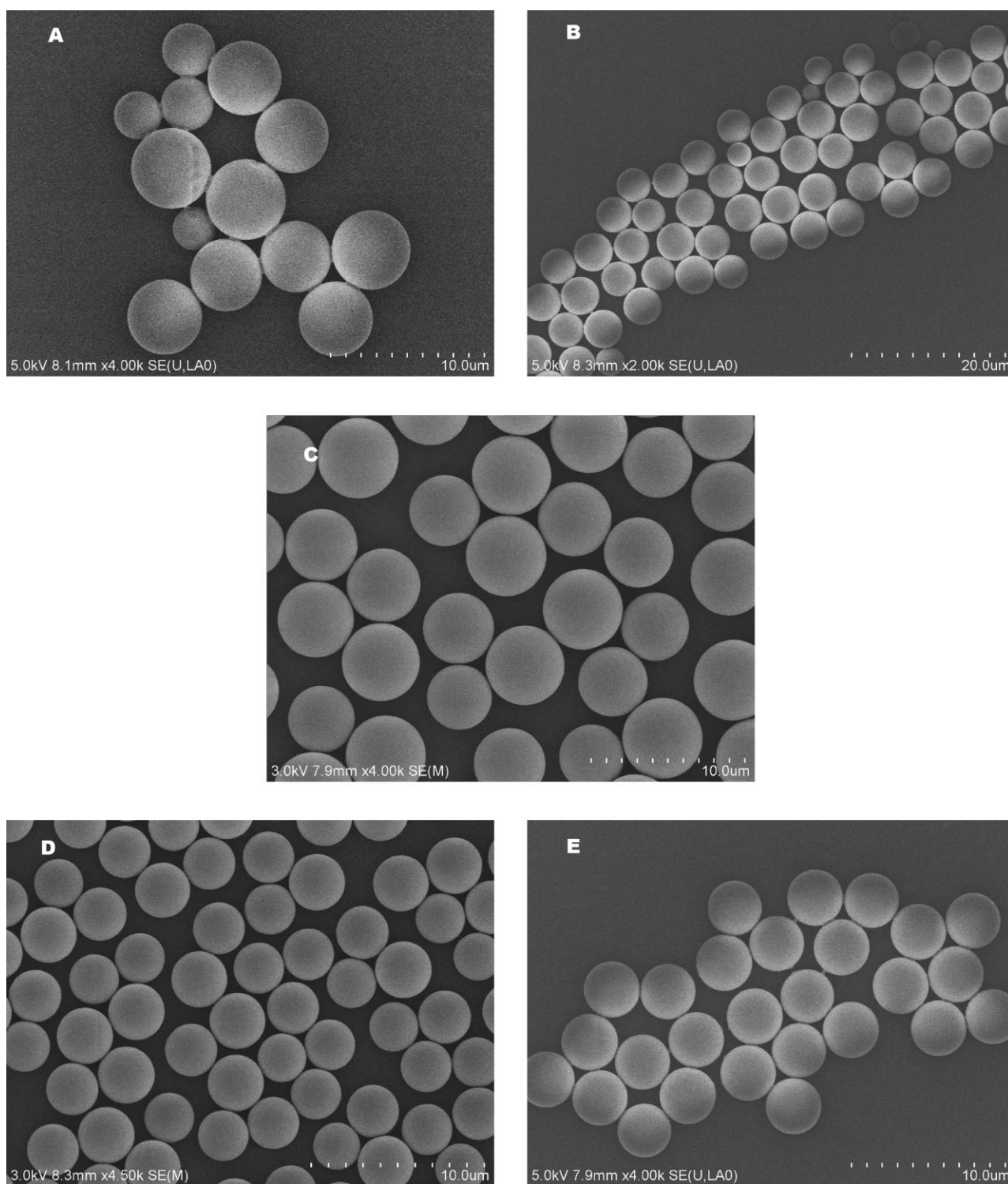


Figure 1 SEM photographs of PMMA microspheres produced by dispersion polymerization in methanol. The conditions were those listed in Table I, except for the initial time from room temperature to 55°C: (A) 0, (B) 0.5, (C) 1.5, (D) 2, and (E) 3 h.

average diameter and coefficient of variation of the PMMA microspheres with the five different initial heating ramps. An interesting phenomenon was observed: the more slowly temperature rose at the beginning, the much better the size distribution became. When the temperature was preset at 55°C,

monodisperse PMMA microspheres could not be obtained; the dispersity still remained poor when the temperature increasing time was shorter than 1.5 h from room temperature to the prearranged temperature. However, when the velocity of heating decreased, say to 2 h (15°C/h for heating velocity),

TABLE III
Influence of the Preset Temperature or Moderate Heating on the Particle Size and Particle Size Distribution of PMMA with Different Stabilizer Concentrations

PVP K-30 (wt %)	20	20	40	40	60	60
D_n (μm) ^a	5.54	4.85	4.55	3.64	3.15	1.66
CV (%) ^b	19.8	8.2	18.1	1.5	22.8	5.6
Time to the preset temperature (h)	0	3	0	3	0	3

The polymerization conditions are the same as those listed in Table I, except for different intervals from room temperature to the preset reaction temperature.

^a Number-average diameter of microspheres: $D_n = \sum d_i / N$.

^b Coefficient of variation: CV (%) = Standard deviation/ D_n .

the dispersity significantly improved to 4.28% (coefficient of variation). When the heating time was extended to 3 h (20°C/h for heating velocity), a considerable improvement was observed, and the index of dispersity was 1.5%, which was ideal for further swelling procedures. A more visual illustration is given in Figure 1.

Table III indicates the effect of the preset temperature and initial slow heating on the PMMA particle size and particle size distribution with 20, 40, and 60 wt % steric stabilizer concentration. Apparently, slow heating was unlimitedly helpful to the formation of monodisperse PMMA particles. A similar result is given in Table IV. With different monomer concentration, initiator concentration, type of initia-

TABLE IV
Influence of the Preset Temperature or Moderate Heating on the Particle Size and Particle Size Distribution of PMMA with Different Reaction Parameters

Initiator	Time to the preset temperature (h)	Initiator concentration (wt %) ^a	Monomer concentration (wt %) ^b	D_n (μm) ^c	CV (%) ^d
BPO	0	1	10	0.862	32.8
BPO	3	1	10	0.978	28.9
AIBN	0	1	10	4.55	18.1
AIBN	3	1	10	3.64	1.5
AIBN	0	2	10	5.79	8.8
AIBN	3	2	10	2.198	4.7
AIBN	0	3	10	7.593	10.9
AIBN	3	3	10	2.401	4.5
AIBN	0	0.5	20	4.472	7.8
AIBN	2	0.5	20	3.952	6.8
AIBN	3	0.5	20	3.685	5.6
AIBN	0	1	20	6.287	11
AIBN	3	1	20	3.107	4.9

The polymerization conditions are the same as those listed in Table I, except where indicated.

^a The AIBN concentration was based on the monomer weight.

^b The monomer concentration was based on the solvent weight.

^c Number-average diameter of microspheres: $D_n = \sum d_i / N$.

^d Coefficient of variation: CV (%) = Standard deviation/ D_n .

tor, and concentration of steric stabilizer, the slow heating process was inevitably in favor of the dispersity of PMMA particles. The initiator BPO has been considered poor for preparation of uniform polymer microspheres by dispersion polymerization.⁸

Dispersion polymerization starts in a homogeneous medium of monomers, free-radical initiator, and polymeric stabilizer dissolved in a suitable single solvent or solvent mixture. The initiator decomposes and generates free radicals in the continuous phase when the reaction mixture is heated. Free radicals that reach a critical chain length precipitate by either a self or aggregative nucleation process and form nuclei, and the stabilizers are then adsorbed on the surface of the resulting particles to form stable particles. Once stable particles are formed, they absorb the monomer from the continuous phase. After a sufficient number of particles, which can capture all free radicals and nuclei in the continuous phase, are formed, no more particles will be formed, and polymerization mainly takes place within the monomer-swollen particles, and the particle formation stage is completed. These particles grow by capturing small nuclei, oligomeric radicals from the continuous phase, and polymerizing the adsorbed monomer inside the particles. This continues until all of the oligomeric radicals and nuclei generated in the reaction medium are consumed.

So, it is convenient to divide the whole process into two major stages, that is, the particle formation stage, in which the formation of particles or nuclei

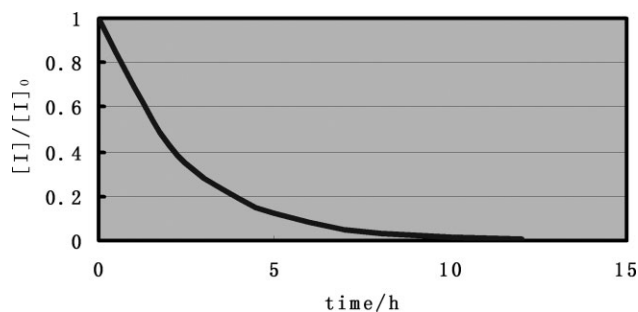


Figure 2 Relationship between the initiator residual percentage and time (decomposition dynamics).

TABLE V
Standard Recipe for the Dispersion Polymerization of GMA

Reagent	Weight	Relative wt %
Methanol	25 g	—
GMA	2.5 g	10 ^a
PVP K-30	0.5 g	20 ^b
AIBN	25 mg	1 ^c

The reaction temperature was 70°C, the overall reaction time was 24 h, and the stirring rate was 120 rpm.

^a The monomer concentration was 10 wt % with respect to the solvent weight.

^b The PVP K-30 (weight-average molecular weight = 4.0×10^4 g/mol) concentration was 20 wt % with respect to the monomer weight.

^c The AIBN concentration was 1 wt % with respect to the monomer weight.

and aggregation between them are predominant, and the particle growth stage, in which particle growth is predominant. The basic requirements for the formation of monodisperse particles include (1) a short particle formation stage (relative to the growth stage) and (2) a particle growth stage free from both the formation of new particles and the coalescence of existing particles. There is general agreement that nuclei are formed throughout the polymerization process, whereas the number of particles is decided in the early stages. After the particle formation stage is complete, the number of particles does not change, but the particles increase in size.

From the previous discussion, the balance between the consumption of radicals and the formation of new radicals is of importance for the formation of monodisperse polymer particles. The production rate of initial radicals ($d[R^\bullet]/dt$) is described as follows:

$$\frac{d[R^\bullet]}{dt} = 2fk_d[I] = 2fk_d[I]_0 e^{-k_d t}$$

where f is the initiator efficiency, $[I]_0$ is the initial concentration of the initiator, t is the polymerization time, and $[I]$ is the concentration of the initiator at t ;

where f and $[I]_0$ are constants for a specific reaction system. On the other hand, k_d , the rate constant of decomposition, is a function of temperature and follows an Arrhenius experimental equation:

$$k_d = A_d e^{-E_d/RT}$$

where A_d is frequency factor, E_d is the activation energy of decomposition, R is the gas constant, and T is the temperature (in Kelvin).

At any fixed temperature, k_d is a constant. $d[R^\bullet]/dt$ decreases exponentially (also see Fig. 2).

Thus, the formation rate of radicals is fastest at the beginning but decreases sharply as the reaction continues. That is, the concentration of formed oligomers is very high at the preliminary stage. It is difficult to capture all free radicals and nuclei in the continuous phase unless more stable particles are formed, so the particle formation stage extends, and polydisperse particles are probably produced.

If a mild and slow heating procedure is used, the temperature rises gradually. The initial k_d value for the initiator is lower than that at higher temperatures. k_d will gradually increase as the temperature rises; the two contrary factors cause the formation rate of radicals to decrease slowly, which maintains a relatively moderate decrease, instead of an exponential decrease. On the other hand, compared with static temperature, slow heating (called *dynamic temperature*) means that, at the beginning of the reaction, there are (1) a decrease in the critical chain length due to the decrease in the solvency of the continuous phase, (2) a decrease in the concentration of the precipitated oligomer chain due to decreases in both the decomposition rate of the initiator (fewer radicals) and the propagation rate of oligomer radicals (slower growth of the oligomer chains), (3) an increase in the adsorption rate for PVP due to the decrease in the solubility of PVP in methanol, and (4) an increase in the viscosity of the continuous phase. All of these can contribute to a decrease in the particle size and a relative shorter particle formation stage (relative to the growth stage). These

TABLE VI
Influence of the Preset Temperature or Slow Heating on the Particle Size and Particle Size Distribution of PGMA with Different Reaction Parameters

Final temperature	60°C	60°C	65°C	65°C	65°C	70°C	70°C	70°C
Time to the preset temperature	0 min	1 h	0 min	1 h	3 h	0 min	5 min	10 min
D_n (μm) ^a	Coagulated	Coagulated	Poor dispersity	Coagulated	Coagulated	1.58	1.41	Coagulated
CV (%) ^b	—	—	—	—	—	2.6	10.3	—

The polymerization conditions are the same as those listed in Table V, except for the intervals from room temperature to the preset reaction temperature and the final polymerization temperature.

^a Number-average diameter of microspheres: $D_n = \sum d_i/N$.

^b Coefficient of variation: CV (%) = Standard deviation/ D_n .

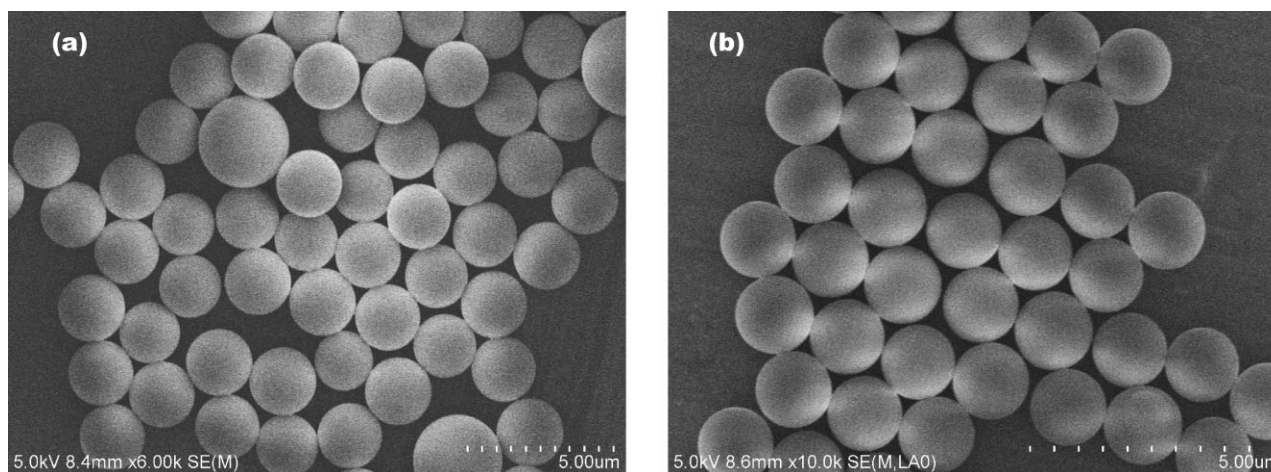


Figure 3 SEM photographs of PGMA microspheres produced by dispersion polymerization in methanol. The conditions were those listed in Table V, except for the initial time from room temperature to 70°C: (a) 5 and (b) 0 min.

factors will finally lead to good dispersity for the polymer particles.

Not only the temperature but also the heating velocity are polymerization parameters that may affect the dispersity index of polymer particles. Foregoing published studies did not consider the influence of temperature transfer velocity on the size distribution. The fact is that, when we put the polymerization bottle into the heating bath, the temperature of the monomer will reach the bath's temperature, but over a period of time. The time needed is different, depending on rotation speed, volume of medium, the coefficient of heat transfer, and so on.

This question should be examined extensively because the laboratory's conditions are different from industrial conditions, and the heat transfer and mass transfer are easy to control because of their smaller amounts, but it is necessary to consider the effect of heat and mass transfer on an industry scale. Uniform monodisperse polymer particles and consistent, stable production should be our aim in the choice of polymer microspheres.

Dispersion polymerization of GMA

Polymers derived from GMA are attractive as reactive starting materials for the design of a whole range of compounds with various functional groups. These functional groups can be used directly or via modification with cationic, anionic, chelate-forming, or fluorescent routes for the immobilization of biopolymers (enzymes, antibodies, cells) and other sensitive compounds. In the form of beads the size of hundreds of micrometers, they are used as reactive supports and carriers, fillings of chromatographic columns, and in diagnostics. Spherical GMA particles are typically produced in an aqueous medium by suspension radical polymerization (the main dis-

advantage of which is the formation of a broad size distribution) or by multistep seeded polymerization. The preparation of GMA particles in the micrometer size range is still problematic, and such particles are not readily available and have received much attention recently.

The standard recipe for GMA dispersion polymerization is given in Table V. The procedure was a little modification of Takahashi and coworkers's method.^{18,19} The results are indicated in Table VI. Three temperatures were tested: 60, 65, and 70°C. When the temperature was below 65°C, in case of prefixed or slow heating, monodisperse particles could not be prepared. Only when the temperature rose to 70°C at the same time and the heating time was shorter than 5 min, with the preferred preset at 70°C, were PGMA particles of good dispersity prepared. Figure 3 shows the different effects with a preset temperature and a 5-min period. Quick

TABLE VII
Standard Recipe for the Dispersion Polymerization of ST

Reagent	Weight (g)	Relative wt %	Note
Ethanol	59.7	59.8	
2-Methoxyethanol	25.3	25.3	
ST	12.5	12.5	14.7 wt % ^a
PVP K-30	1.8	1.8	17.6 wt % ^b
AOT-100	0.4	0.4	
AIBN	0.125	0.1	1 wt % ^c
Total	100	100	

The final temperature was 65°C, the overall reaction time was 12 h, and the stirring rate was 120 rpm.

^a The monomer concentration was based on the solvent weight.

^b The concentration of the steric stabilizer mixture [PVP K-30 (weight-average molecular weight = 4.0×10^4 g/mol) and AOT-100] was based on the monomer weight.

^c The AIBN concentration was 1 wt % with respect to the monomer weight.

TABLE VIII
Influence of the Preset Temperature or Slow Heating on the Particle Size and Particle Size Distribution of PST with Different Reaction Parameters

Initiator	Time to the preset temperature	Monomer concentration (wt %) ^a	Initiator concentration (wt %) ^b	D_n (μm) ^c	CV (%) ^d
BPO	0 h	12.5	1	1.078	25.5
BPO	3 h	12.5	1	0.938	18.0
AIBN	0 h	12.5	2	1.626	0.1
AIBN	3 h	12.5	2	1.400	5.5
AIBN	0 h	12.5	4	1.643	4.3
AIBN	3 h	12.5	4	1.459	3.1
AIBN	0 h	20	1	2.554	0.1
AIBN	3 h	20	1	1.709	9.5
AIBN	0 h	12.5	1	1.638	0.1
AIBN	3 h	12.5	1	1.392	4.2
AIBN	0 h	10	1	1.748	1.0
AIBN	3 h	10	1	1.136	4.0

The polymerization conditions are the same as those listed in Table VII, except where indicated.

^a The monomer concentration was based on the solvent weight.

^b The AIBN concentration was based on the monomer weight.

^c Number-average diameter of microspheres: $D_n = \sum d_i / N$.

^d Coefficient of variation: $CV (\%) = \text{Standard deviation} / D_n$.

heating had an advantage in the dispersion polymerization of GMA; for example, when the temperature rose to 70°C within 5 min, dispersion polymerization was smooth, but if the temperature increase took longer than 10 min, the reaction was unstable, aggregation existed, and no stable polymer particles were produced. In conclusion, it was necessary to shorten the heating interval to obtain a good size distribution in the PGMA particles. A preset at a high temperature was preferred. This was contrary to MMA.

The slower the temperature rise was, the worse the dispersity became. High temperatures were necessary to avoid coagulation.

Another amazing phenomenon was that when polymerized at lower temperatures, the polymer could not be washed with methanol alone but could be washed by a mixture of methanol and water. If methanol was used to wash the dispersion polymerization product, precipitation occurred, and the product coagulated so it could not be washed further. When GMA was polymerized at 70°C and the heating time was short at 5 min, the product could be washed by only methanol or a mixture of methanol and water. The reason is still not clear.

Dispersion polymerization of ST

ST is the monomer that has been most extensively investigated, but the effect of slow heating has not been mentioned. Table VII gives the normal recipe for preparation monodisperse PST. Further experimental results are given in Table VIII with different monomer concentrations, initiator concentrations, types of initiator, and steric stabilizer concentrations. The initiator BPO was also proven poor in the dispersion polymerization of ST; a similar conclusion was reached with GMA.

As shown in Table VIII, the size distribution was not much affected by the heating velocity. In the case of slow heating or prearranged temperature, little influence was noticed on the coefficient of variation (%) of PST. The ST dispersion polymerization was not influenced more, only slightly; the index of dispersity worsened, for example, when the time of temperature increase was longer than 3 h. The coefficient of variation (%) just changed slightly in high concentrations of monomer, high concentrations of

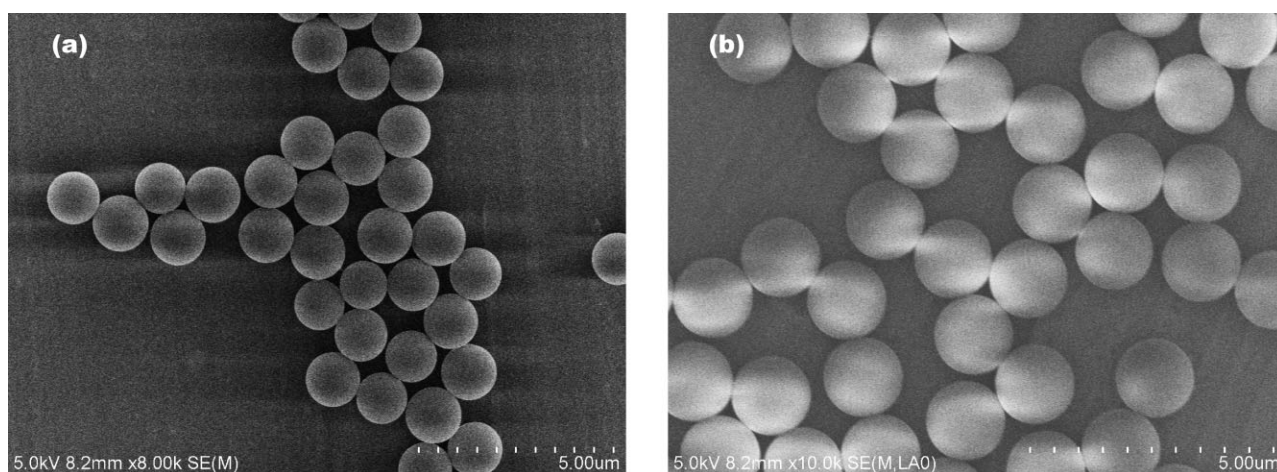


Figure 4 SEM photographs of PST microspheres produced by dispersion polymerization in ethanol/2-methoxyethanol. The conditions were those listed in Table VII, except for the time from room temperature to 65°C: (a) 3 and (b) 0 h.

initiator, or low concentrations of stabilizer, with a slow temperature rise having a mild influence on the coefficient of variation (%). A quick increase in temperature was good for the formation of monodisperse PST, but larger particles were formed with the short heating time. Figure 4 gives SEM photographs of PST microspheres produced by dispersion polymerization in ethanol/2-methoxyethanol. The times needed for the sample to go from room temperature to 65°C were 3 h [Fig. 4(a)] and 0 h [Fig. 4(b)], respectively.

CONCLUSIONS

Dispersion polymerization is a suitable technique for producing monodisperse spherical particles in the micrometer range, which are difficult to obtain by other single-step techniques. The basic requirements for the generation of monodisperse microspheres by this technique included a short particle formation stage and a particle growth stage free from both the formation of new microspheres and the coalescence of existing particles. Dispersion polymerization is highly sensitive to small changes in the numerous reaction parameters involved in the process; narrow-distribution PMMA particles were synthesized with excellent repetition by a slow temperature rise and not by the published procedure.

If a gradual heating procedure was carried out, the formation rate of free radicals initially decreased moderately during the nuclei formation stage. The formation rate of free radicals decreased sharply when a fixed temperature was chosen. The balance between the rate of radical formation with the rate of radical disappearance was considered to be established easily with slow heating at the original stage; in this way, the most uniform PMMA particles were obtained. Finally, PMMA particles ranging in diameter from 1 to 6 μm were prepared by dispersion polymerization.

However, this relationship did not apply to the dispersion polymerizations of ST and GMA. For the dispersion polymerization of ST, the temperature effect was weak. The preferred procedure included a fixed temperature. Slow heating was disadvantageous to the index of dispersity of the PST particles. On the other hand, the dispersion polymerization of

GMA was different from that of ST and MMA. The temperature had to be above 65°C, and the preferred temperature was 70°C. Slow heating did considerable harm to the dispersity of PGMA. When the time to reach the preset temperature from room temperature was longer than 30 min, nonuniform spheres were prepared. In 5 min at 70°C, uniform PGMA particles were prepared.

The heating methodology had different effects on the dispersion polymerizations of the three monomers, polar MMA, GMA, and nonpolar ST. Interestingly, different heating methods were needed to produce narrow-size-distribution PMMA, PGMA, and PST particles.

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