Production of Polymethylmethacrylate Particles by Dispersion Polymerization in Aqueous Media with Ceric Ammonium Nitrate

VOLGA BULMUŞ, ALI TUNCEL, and ERHAN PIŞKIN*

Hacettepe University, Chemical Engineering Department, 065323 Beytepe, Ankara, Turkey

SYNOPSIS

Polymethylmethacrylate particles with narrow size distributions with different sizes in the range of 1.25–4.58 μm were produced by dispersion polymerization of methylmethacrylate (MMA) in ethanol/water media, by using 2,2′-azobisisobutyronitrile (AIBN) (as an initiator), (PVP) poly(vinyl pyrrolidone) (as a stabilizer), and ceric ammonium nitrate (CAN) (as a coinitiator and also as a costabilizer). Particle size was increased by increasing the initiator concentration and the ethanol : water ratio, and by decreasing the monomer : dispersion medium ratio and the PVP and CAN concentrations. The addition of CAN in the recipe of the MMA polymerization improved the monodispersity, and also increased the monomer conversion rate. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Dispersion polymerization of methylmethacrylate (MMA), in organic media, was first introduced by Barret, who has extensively reviewed the general features of this process.[1,2] A number of other investigators have also studied production of PMMA lattices, containing monodisperse polymeric particles usually in the submicron size range, by dispersion polymerization in nonpolar media.[3-7] Polymerization mechanisms and the effects of polymerization parameters both on the size and monodispersity of the PMMA particles have been investigated, in which different stabilizers, usually block or graft copolymers, such as polystyrene-*block*-poly(ethylene-*co*-propylene) or polymethylmethacrylate grafted-poly(12-hydroxy stearic acid) have been used.

Preparation of micron-size monodisperse PMMA particles (1–6 μm), in polar media, was first demonstrated by Almog et al.[8] They polymerized MMA in a series of alcohols (i.e., methanol, ethanol, isopropanol, and butanol) in the presence of poly(vinyl pyrrolidone) (PVP) and 2,2′-azobis(isobutyronitrile) (AIBN) as a steric stabilizer, and the initiator, respectively. By using a cosurfactant, i.e., a quaternary ammonium salt (Aliquat 336, Henkel) they were able to increase the size of the particles without loosing the monodispersity.

Recently, dispersion polymerization of MMA in aqueous media (i.e., methanol/water mixtures) have extensively studied by Shen et al.[9-11] They used PVP with different molecular weights and Aliquat 336 as the steric stabilizer and costabilizer, respectively, with a series of initiators (AIBN, ABMN, and ADVN). Different crosslinkers (EGDMA, TMPTA, and DVB) were included in their polymerization recipe. They produced PMMA particles ranging in diameter from 2 to 10 μm, and discussed the effect of various polymerization parameters on the size and monodispersity.

In our previous reports we presented preparation of monosize polystyrene (PS) particles by dispersion polymerization,[13,14] and demonstrated incorporation of various functional groups (i.e., hydroxyl, carboxyl, dimethylamino) on these seed particles by coaxial polymerization,[15,16] and utilized these particles in diverse biomedical applications.[17-21] In our recent studies, we have aimed to prepare MMA and hydroxyethylmethacrylate (HEMA)-based homo- and copolymeric particles with narrow size distributions as support matrices for immobilization of various ligands (e.g., affinity-dyes, Protein A). This article

---

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 60, 697–704 (1996)
CCC 0021-8995/96/050697-08

reports the results of homopolymerization of MMA by dispersion process similar to that of Almog et al.,[8] and of Shen et al.,[11] with the difference that monosize particles were prepared by including ceric ammonium nitrate (CAN) in the polymerization recipe. This article presents the effects of polymerization parameters on the size, monodispersity, and yield of the PMMA particles, and also the role of CAN in the polymerization.

EXPERIMENTAL

Materials

The monomer, i.e., methylmethacrylate (MMA) (Rohm and Haas Ltd, Germany) was washed with 10 wt % aqueous sodium hydroxide solution NaOH to remove the inhibitor, and stored in a refrigerator until used. The initiator was 2,2′-azobis(isobutyronitrile) (AIBN) (BDH Chemicals Ltd., UK). The dispersion medium was prepared by mixing proper amounts of ethanol (Merck A.G., Germany) and distilled water. Poly(vinyl pyrrolidone) (PVP) (K-30, MW: 40,000) was obtained from Fluka Chemika (Switzerland) and was used as a steric stabilizer. Ceric ammonium nitrate (CAN) (BDH Chemicals, UK) was also included in the recipe.

Preparation and Characterization

To prepare the polymerization medium, PVP and CAN were dissolved in the dispersion medium containing ethanol and water in a proper ratio, then the monomer phase, prepared by dissolving AIBN in MMA monomer, was mixed with the dispersion medium. The polymerization media were placed in glass bottles (200 mL), which were purged with nitrogen, capped, and sealed. The bottles were then placed in a temperature-controlled water bath at 65°C and shaken horizontally at 100 cycles/min for 24 h. The AIBN, PVP, and CAN concentrations, the ethanol : water ratio, and the MMA : dispersion medium ratio were changed to obtain the effects of these parameters on the size, size distribution, and yield of the PMMA particles. The experimental conditions are given in Table I.

The PMMA latex was cleaned first using a serum replacement technique. The latex from the polymerization bottle was centrifuged and the supernatant was removed. Distilled water (100 mL) was added and a new dispersion was stirred for 24 h at room temperature to remove any stabilizer remaining on the surface of the polymeric particles. This procedure was repeated three times. The PMMA latex solution was treated with a mixed bed of anion- and cation-exchange resins (H^+ and OH^- type, Amberlite, BDH) at the last step.

The dried microspheres were first sieved and the polymer aggregates were removed, and then the spherical polymeric particles were weighed in an electronic balance, and the particle yield was calculated by the following expression.

$$\%\ \text{Particle Yield} = (\text{wt of the dry polymeric particles}/\text{wt of the monomer}) \times 100$$

The average size and size distributions of the PMMA particles were evaluated using a scanning electron microscope (SEM, Model Leitz-AMR 1000 Raster Electronen Microscope, Frankfurt, Germany). The latex solution containing the particles was spread onto a metal disk and the solvent evaporated at room temperature. The dried particles were coated with a thin layer of (about 100 Å) of gold in vacuum. Three separate photographs (each containing 50–300 particles) were taken for each latex sample with 2000–4000 magnification. The size of the particles was measured on the photographs.

In order to study the kinetics of MMA dispersion polymerization and the effects of CAN on the monomer conversion, we conducted two sets of the experiments (Experiments 14 and 15, see Table I). In a typical experiment, polymerizations in a series of polymerization reactors containing the same amount of ingredients were started at the same time, and reactions were conducted at the same conditions. At selected time values, one of the reactors was processed to stop the reaction by adding excess amounts of ferrous sulfate solution (for quenching ceric ions) and hidroquinone (for inhibition of AIBN). The polymer phase (containing the polymer aggregates, not only the spherical particles) formed was removed, and was washed repeatedly with water, and then was dried to constant weight. The percentage conversion were calculated by using the following formula:

$$\%\ \text{Conversion} = (\text{wt of the dry polymer phase}/\text{wt of the monomer}) \times 100$$

Table I Polymerization Conditions

Experiment No.	AIBN Conc.[a] (mol %)	PVP Conc. (g/dL)	CAN Conc. (g/dL)	Ethanol/Water (mL/mL)	MMA/Dispersion Medium Ratio (mL/mL)
1	0.65	1.00	0.10	50/50	1.0/20.0
2	1.30	1.00	0.10	50/50	1.0/20.0
3	5.20	1.00	0.10	50/50	1.0/20.0
4	0.65	0.10	0.10	50/50	1.0/20.0
5	0.65	0.25	0.10	50/50	1.0/20.0
6	0.65	3.00	0.10	50/50	1.0/20.0
7	0.65	1.00	0.10	40/60	1.0/20.0
8	0.65	1.00	0.10	60/40	1.0/20.0
9	0.65	1.00	0.10	50/50	2.0/20.0
10	0.65	1.00	0.10	50/50	2.5/20.0
11	0.65	1.00	0.05	50/50	1.0/20.0
12	0.65	1.00	0.20	50/50	1.0/20.0
13	0.65	1.00	0.40	50/50	1.0/20.0
14	2.60	1.00	0.10	50/50	1.0/20.0
15	2.60	1.00	0.00	50/50	1.0/20.0

[a] Given on the basis of monomer content.

Temperature: 65°C; Shaking rate: 100 cpm; Total reaction volume: 105 mL; Dispersion medium: ethanol + water

RESULTS AND DISCUSSION

Dispersion polymerization process is usually used for the production of monosize polymeric particles in the micron-size range. Both the size and monodispersity can be controlled by changing the polymerization parameters. In dispersion polymerization the system is homogeneous prior to the polymerization. As it was proposed, when the polymerization is initiated by decomposition of the initiator molecules, oligomer chains grow in the continuous phase until they reach their critical size, at which time they were phase separated to form nuclei.[2,11,12] These nuclei are unstable and aggregate to form the polymeric particles, which absorb stabilizer molecules and oligomers from the dispersion medium and become mature (stable).[12] After this particle formation step, particles grow until they reach their final size by capturing nuclei or oligomers from the medium. This mechanism has not been fully established yet, but it is believed that the chain length of the precipitating oligomers and their number in each mature particle determines the final size while the kinetics (e.g., nucleation, aggregation, and adsorption rates) determine the monodispersity (uniformity in size) of the particles, which are affected by the various polymerization parameters as discussed in the following sections and also in the related literature.[1,2,10-12,22-26]

AIBN Concentration

In this group of experiments, effects of the initiator (i.e., AIBN) concentration on the dispersion polymerization of methylmethacrylate was investigated. Polymerizations were performed with three different AIBN concentrations (i.e., 0.65, 1.30, 5.20 mol %); within an ethanol : water (50 : 50) mixture; and at a constant MMA : dispersion medium ratio of 1 : 20 (Experiments 1–3, see Table I). The PVP and CAN concentrations were 1.0 g/dL and 0.1 g/dL, respectively. The polymerization temperature was 65°C. Figure 1 gives a representative photograph of PMMA particles obtained in this study.

Narrow particle size distributions were obtained for the PMMA particles prepared with AIBN initiator concentrations ranging 0.65–5.20 mol %. The increase in the initiator concentration led to larger particles with wider size distributions (Fig. 2). The average diameter increased from 2.5 to 3.12 μm as the initiator concentration was increased over this range.

Similar results were reported in the related literature,[11,14,22,27] which may be explained as follows: an increase in the initiator concentration causes an increase in the number of free radicals and, thus, the concentration of growing oligomer chains. Therefore, the time to reach the critical chain length at which the oligomers nucleate, by self or aggregative nucleations, is extended, which leads to a

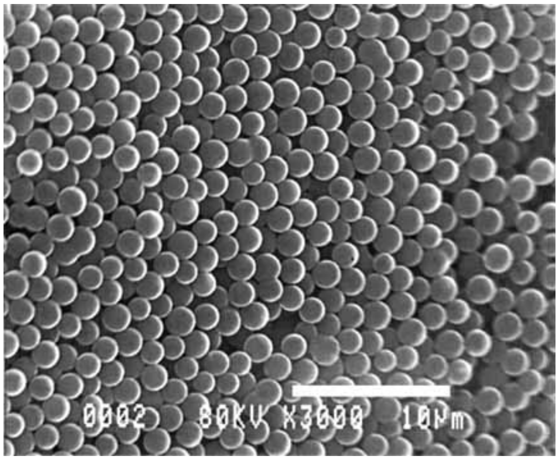
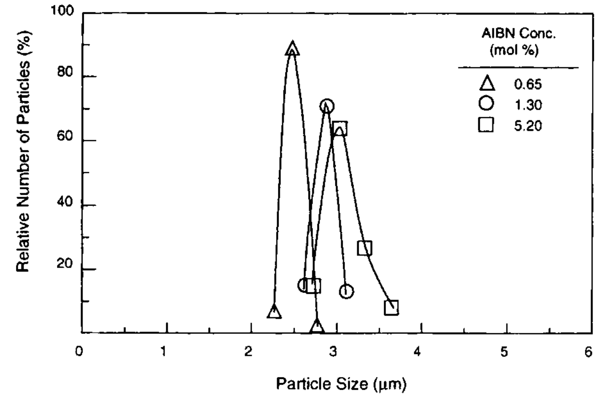


Figure 1 A representative SEM photograph of PMMA particles.



AIBN Concentration (mol%)	0.65	1.30	5.20
Average Particle Size (μm)	2.50	2.88	3.12
Particle Yield (%)	79.0	64.2	69.0

Figure 2 Effect of AIBN concentration on PMMA particle size, size distribution, and particle yield (Experiments 1-3, see Table I).

lower number of particles but with larger size. Moreover, the larger particles are less likely to capture nuclei or oligo-radicals from the continuous phase (due to lower surface area), which also results in retardation of the particle formation stage leading broaden particle size distribution.

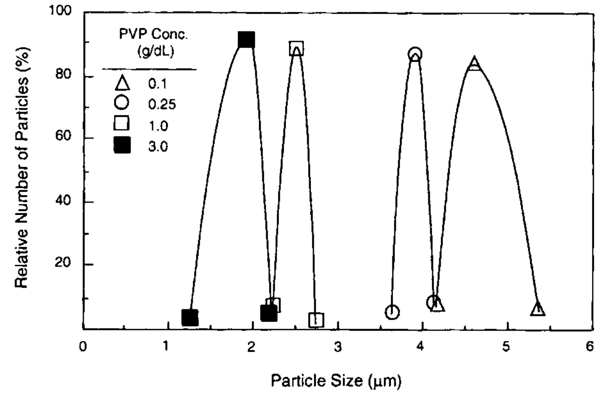
The particle yield values were in the range of 64.2–79.0% (Fig. 2). Note that these values are not equal to the monomer conversion values, which were usually higher than 90%.[28] As mentioned before, a part of the polymer phase was as polymer aggregates (not as spherical particles) that were removed by sieving; therefore, particle yields were lower than monomer conversions.

PVP Concentration

In this study, the stabilizer was poly(vinyl pyrrolidone) (molecular weight: 40,000), which was also utilized by other groups.[8,11,22,25] Polymerizations were performed with four different PVP concentrations (i.e., 0.10, 0.25, 1.0, and 3.0 g/dL); within an ethanol : water (50 : 50) mixture; and at a constant MMA : dispersion medium ratio of 1 : 20 (Experiments 1, 4–6, see Table I). The AIBN and CAN concentrations were 0.65 mol % and 0.1 g/dL, respectively. The polymerization temperature was 65°C.

In this group of experiments, PMMA particles with narrow size distribution were obtained, and the particle size was found to increase with decreasing concentration of PVP, over the studied range, as illustrated in Figure 3. Similar results were reported for dispersion polymerization of both styrene and MMA.[11,14,22,26] It is assumed that an important role of the stabilizer is in the particle formation step, when its concentration is increased in the viscosity of the medium,[11] the rate of adsorption of stabilizer molecules, and the number of nuclei increase, which reduce the extent of aggregation and, thus, result smaller particles.

As seen in Figure 3, particle yield values were in the range of 66.4–79.0%, except in the experiment (Experiment 4) in which the PVP concentration was 0.1 g/dL. Note that in this case the largest particles with the broadest size distribution, but with



PVP Concentration (g/dL)	0.10	0.25	1.00	3.00
Average Particle Size (μm)	4.58	3.89	2.50	1.94
Particle Yield (%)	20.4	66.4	79.0	78.6

Figure 3 Effect of PVP concentration on PMMA particle size, size distribution, and particle yield (Experiments 1, 4–6, see Table I).

very low particle yield, were obtained. Most probably, there were not enough stabilizer molecules to stabilize the forming polymeric spheres; therefore, they have aggregated, which were removed and then the particle yield was determined.

Ethanol : Water Ratio

One of the important parameters in dispersion polymerization is the nature of the solvent used in the polymerization medium.[8,11,14,22-27] A series of alcohols was studied by Almog et al., showing a constant increase in the diameter of the resulting PMMA particles (from 1.8 to 5.2 μm) when changing from methanol to ethanol, isopropanol, and *t*-butanol.[8] Shen et al. have used water : methanol mixtures to demonstrate the effect of the solvency of the medium on particle size. They have reported that the PMMA particle size decreased (from 3.2 to about 0.5 μm) with increasing water content, and the size distribution remained narrow until a water content of 40 wt % was reached.

We have used ethanol : water mixtures in our studies. Polymerizations were performed with three different ethanol : water ratios (i.e., 40 : 60, 50 : 50, 60 : 40), at a constant MMA : dispersion medium ratio of 1 : 20 (Experiments 1, 7, and 8, see Table I). The AIBN, PVP, and CAN concentrations were 0.65 mol %, 1.0 g/dL, and 0.1 g/dL, respectively. The polymerization temperature was 65°C.

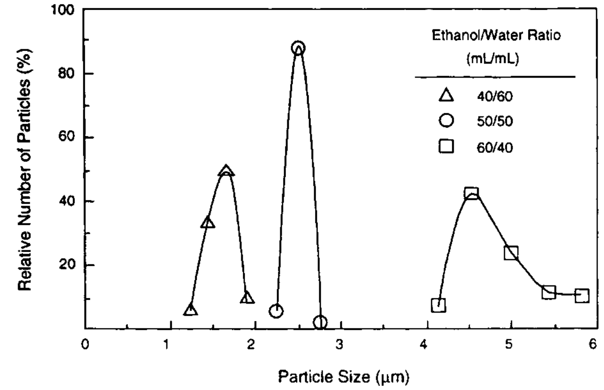
Figure 4 shows that ethanol : water ratio significantly affected both size and size distribution of the PMMA particles produced, as also reported by others.[8,11,14] The particle size increased from 1.67 to 4.58 μm, with the increase in the ethanol : water ratio from 40 : 60 to 60 : 40.

The initial solubility parameters of the polymerization media prepared with different ethanol : water ratios were calculated according to the following expression, and given in Table II.[25]

$$\delta_{\text{MED}} = (x_e\delta_e^2 + x_w\delta_w^2 + x_m\delta_m^2)^{1/2} \qquad (1)$$

where, x_e, x_w, and x_m are the volume fractions of ethanol, water, and methylmethacrylate; δ_{MED}, δ_e ($= 12.7\ (\text{cal/cm}^3)^{1/2}$), δ_w ($= 23.4\ (\text{cal/cm}^3)^{1/2}$), and δ_m ($= 8.8\ (\text{cal/cm}^3)^{1/2}$) are the solubility parameters of the medium, ethanol, water, and methylmethacrylate, respectively.[29]

Note that polarity of the medium decreases with an increase in the ethanol content, as shown in Table II. Because the oligomer chains formed during polymerization are relatively apolar, these chains can reach higher molecular weights by remaining in the dissolved form. Then nucleation occurs at a relatively higher molecular weight due to the higher solubility of polymer chains in relatively apolar medium. The narrowest size distribution was observed at an ethanol : water ratio of 50 : 50. The distribution curves were broader, especially at higher ratios, which may be due to the high adsorption rate of stabilizer, which would extend the particle formation stage, resulting in a broad distribution.



Ethanol/Water Ratio (mL/mL)	40/60	50/50	60/40
Average Particle Size (μm)	1.67	2.50	4.58
Particle Yield (%)	70.8	79.0	73.3

Figure 4 Effect of ethanol/water on PMMA particle size, size distribution, and particle yield (Experiments 1, 7, and 8, see Table I).

As seen in Figure 4, high particle yields (more than 70%) were observed over the experimental range, and did not change with the ethanol/water ratio.

MMA : Dispersion Medium Ratio

In this group of experiments, polymerizations were performed with three different monomer : dispersion medium ratios (i.e., 1.0 : 20, 2.0 : 20, and 2.5 : 20); within an ethanol : water (50 : 50) mixture (Experiments 1, 9, and 10, see Table I). The AIBN, PVP, and CAN concentrations were 0.65 mol %, 1.0 g/dL, and 0.1 g/dL, respectively. The polymerization temperature was 65°C.

It should be noted that concentration of the monomer should be lower than a certain limit, which depends on the medium, in order to prevent formation of a two-phase system prior to the polymerization. It is not possible to obtain uniform particles in heterogeneous media.[14,28] Therefore, the maximum MMA : dispersion medium ratio studied in this group of experiments was 2.5 : 20 mL/mL. As

Table II **Initial Solubility Parameters of the Polymerization Media Prepared with Different Ethanol/Water Ratios Including Metylmethacrylate**

Ethanol/Water (mL/mL)	Solubility Parameter, δ_{MED} (cal/cm^3)$^{1/2}$
40/60	19.44
50/50	18.47
60/40	17.45

seen in Figure 5, the increase in the monomer content resulted smaller particles. However, further increase in this ratio gave larger particles (4.17 μm) with broader size distribution. Shen et al. reported similar behavior in their studies.[11] Note that there was a slight decrease in the initial solubility parameter (therefore, in the initial polarity) of the polymerization medium with the increase in the monomer content. Therefore, the change in the polarity cannot be the main reason for the change in the particle size. This behavior may be explained by competitive effects of the changes of the polymerization rate and stabilizer adsorption rate, as also mentioned by them.

As seen in Figure 5, high particle yields (about 80%) were achieved when the MMA : dispersion ratio was low. However, a very low particle yield was observed in the experiment (Experiment 4) at which the MMA : dispersion ratio was 2.5 : 20 mL/mL. Note also that the largest particles with the broadest size distribution were obtained in this case.

CAN Concentration

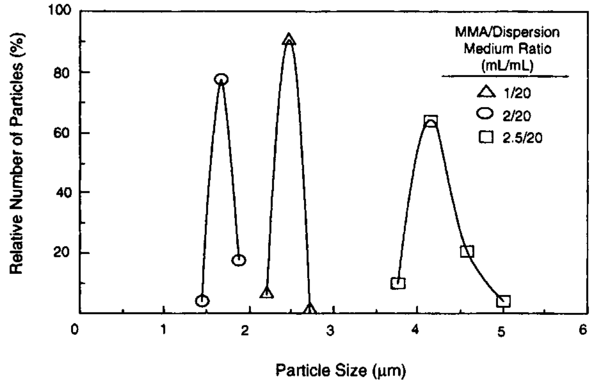
Almog et al. have included a cationic costabilizer, i.e., Aliquat 336 (methyl tricaprlyl ammonium chloride) in their recipe for MMA dispersion polymerization, and have found a significant improvement in the monodispersity.[8] They have attributed this improvement to the increase in electrostatic repulsion between the particles, which stabilizes the system, and the decrease in surface tension of the medium, which results a decrease in the free energy needed for particle formation, and probably shortens the nucleation time.

Recently, Shen et al. utilized Aliquat 336, and also an anionic surfactant Aerosol OT-100 (di-2ethylexyl ester of sodium sulfosuccinic acid) and a nonionic cethyl alcohol, and have reported that only Aliquat 336 is an effective costabilizer in the MMA dispersion polymerization.[11] They have found that the addition of Aliquat 336 not only decreased the particle size but also improved the monodispersity, especially when the stabilizer (i.e., PVP) concentration is less than 4 wt %.

In this study, instead of Aliquat 336, we have included ceric ammonium nitrate (CAN), $\mathrm{Ce^{IV}(NH_4)_2(NO_3)_6}$, in our MMA dispersion polymerization recipe, in order to shorten the nucleation time, thus improving the monodispersity of the resultant particles. Note that CAN is a versatile reagent for oxidation of numerous functional groups in organic synthesis at mild reaction conditions and fast conversions.[30] Radical polymerizations with redox systems containing ceric salts, and recently ceric-induced grafting of acrylates on to natural polymers, have attracted much interest.[31-33]

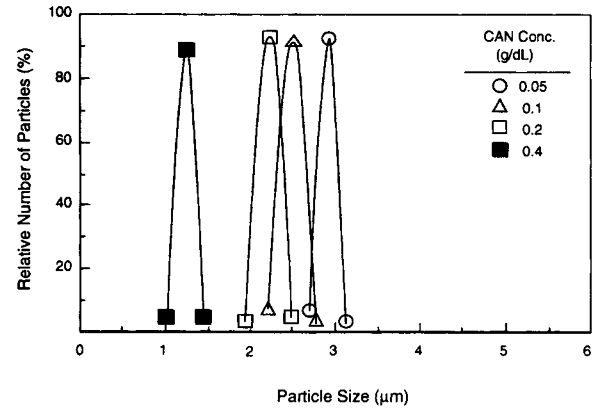
In this group of studies we first investigated the effect of CAN concentration on the PMMA particle size and size distribution. Polymerizations were performed with four different CAN concentrations (i.e., 0.05, 0.10, 0.20, and 0.40 g/dL); within an ethanol : water (50 : 50) mixture; and at a constant MMA : dispersion medium ratio of 1 : 20 (Experiments 1, 11–13, see Table I). The AIBN and PVP concentrations were 0.65 mol % and 1.0 g/dL, respectively. The polymerization temperature was 65°C.

Figure 6 shows that there is a significant effect of the CAN concentration on the size and size distribution of the PMMA particles. The PMMA particle size decreased from 2.92 to 1.25 μm when the CAN concentration was increased from 0.05 to 0.40 g/dL. The particle size distribution curves were



MMA/Dispersion Medium Ratio (mL/mL)	1/20	2/20	2.5/20
Average Particle Size (µm)	2.50	1.67	4.17
Particle Yield (%)	79.0	84.1	8.64

Figure 5 Effect of MMA : dispersion medium ratio on PMMA particle yield (Experiments 1, 9, and 10, see Table I).



CAN Concentration (g/dL)	0.05	0.10	0.20	0.40
Average Particle Size (μm)	2.92	2.50	2.22	1.25
Particle Yield (%)	77.0	79.0	69.2	71.8

Figure 6 Effect of CAN concentration on PMMA particle size, size distribution, and particle yield (Experiments 1, 11–13, see Table I).

narrow over the studied range. However, a further increase in the CAN concentration led to unstability in the polymerization system.[28] Note also that CAN did not stabilized the system without PVP. The decrease in the average size and improvement in the monodispersity may be attributed to the possible increase in the initiation rate of the polymerization (means shortened the particle formation step) due to Ce^{IV} ions (i.e., a coinitiator effect), and also due to costabilization effect of CAN, which may be as a result of interaction with PVP or adsorption of the CAN on the forming particle (reducing aggregation of nuclei), similar to Aliquat 336, as proposed by others.[8,11] Note that it was possible to initiate MMA dispersion polymerization by using only CAN (without AIBN); however, both monomer conversion and particle yield were very small in that case.[28] In addition, we proposed that CAN is an inorganic salt, which may cause a salting out of the MMA oligomers forming in the medium, and thus leading a decrease in the nucleation time, which results in a decrease in the average size and an improvement in the monodispersity.

As seen in Figure 6, particle yield values were satisfactory and when between 69.2–79.0% were achieved in the experimental range.

In order to present the effects of CAN on the kinetics of polymerization we conducted two sets of experiments (Experiments 14 and 15, see Table I), which were performed with CAN (CAN concentration: 0.1 g/dL) and without CAN. Other conditions were exactly the same, which were as follows: temperature, 65°C; shaking rate, 100 cpm; total reaction volume, 105 mL; dispersion medium, ethanol + water; AIBN concentration: 2.60 mol %; ethanol : water ratio, 50 : 50; MMA : dispersion medium ratio, 1 : 20; and PVP concentration, 1.0 g/dL.

Figure 7 gives the change of monomer conversion with time in these experiments. Note that the "arrows" on the graph indicate the time when the phase separations occurred (a sudden change in turbidity in the medium was observed). As seen here, the presence of CAN significantly increased the rate of polymerization, as expected from the discussions above. In the literature related to dispersion polymerization of MMA there is no report on the polymerization reaction rate, which is, of course, an important consideration especially at industrial scale production. Therefore, the addition of CAN in the recipe of the MMA polymerization is not only important to improve the monodispersity, but also to achieve high conversions in short periods of time.

CONCLUSIONS

PMMA particles with narrow size distributions with different sizes in the range of 1.25–4.58 μm may be produced by dispersion polymerization of MMA in ethanol : water media, by using AIBN (as an initiator), PVP (as a stabilizer), and CAN (as a coinitiator and also as a costabilizer). Particle size may be increased by increasing the initiator concentration and the ethanol : water ratio, and by decreasing the monomer : dispersion medium ratio and the PVP and CAN concentrations. The addition of CAN in the recipe of the MMA dispersion polymerization is not only important to improve the monodispersity, but also to achieve high monomer conversion rates.

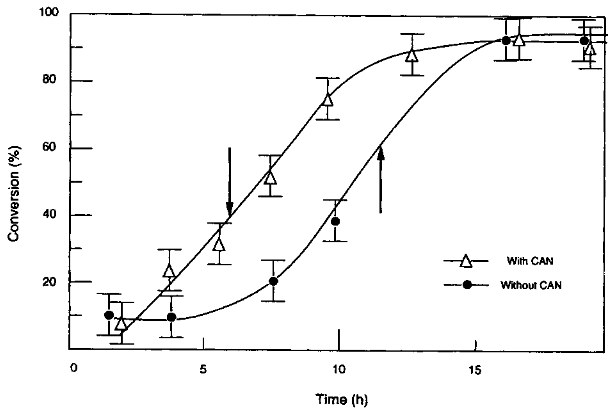


Figure 7 Effects of CAN concentration on kinetics of MMA dispersion polymerization (Experiments 14 and 15, see Table I).

REFERENCES

1. K. E. J. Barrett, *Br. Polym. J.*, **5,** 259 (1973).
2. K. E. J. Barrett, Ed., *Dispersion Polymerization in Organic Media,* John Wiley, London, 1975.
3. L. Antl, J. W. Goodwin, R. D. Hill, R. H. Ottewill, S. W. Owens, and S. Papworth, *Colloid Surf.*, **17,** 67 (1986).
4. C. Pathmamanoharan, C. Slob, and H. N. W. Lekkerkerker, *Colloid Polym. Sci.*, **267,** 448 (1989).
5. J. Stejkal, P. Kratochvil, P. Koubik, Z. Tuzar, J. Urban, M. Helmstedt, and A. D. Jenkin, *Polymer,* **31,** 1816, (1990)
6. K. Kargupta, P. Rai, and A. Kumar, *J. Appl. Polym. Sci.*, **49,** 1309 (1993).
7. M. Helmstedt and H. Schafer, *Polymer,* **35,** 3377 (1994).
8. Y. Almog, S. Reich, and M. Levy, *Br. Polym. J.*, **14,** 131 (1982).
9. S. Shen, Ph.D. dissertation, Lehigh University, Pennsylvania, 1991.
10. S. Shen, M. S. El-Aasser, V. L. Dimonie, J. W. Vanderhoff, E. D. Sudol, *J. Polym. Sci., Part A: Polym. Chem.*, **29,** 557 (1991).
11. S. Shen, E. D. Sudol, and M. S. El-Aasser, *J. Polym. Sci., Part A: Polym. Chem.*, **31,** 1393 (1993).
12. S. Shen, E. D. Sudol, and M. S. El-Aasser, *J. Polym. Sci., Part A: Polym. Chem.*, **32,** 1087 (1994).
13. A. Tuncel and E. Pişkin, Turkish Pat. 24125 (1991).
14. A. Tuncel, R. Kahraman, and E. Pişkin, *J. Appl. Polym. Sci.*, **50,** 303, (1993).
15. A. Tuncel and E. Pişkin, Turkish Pat. 24126 (1991).
16. A. Tuncel, R. Kahraman, and E. Pişkin, *J. Appl. Polym. Sci.*, **51,** 303, (1994).
17. M. T. Ercan, A. Tuncel, B. E. Ercan, M. Mutlu, and E. Pişkin, *Nucl. Med. Biol.*, **18,** 253 (1991).
18. M. T. Ercan, A. Tuncel, B. E. Ercan, and E. Pişkin, *J. Microencap.*, **18,** 253 (1993).
19. A. Tuncel, A. Denizli, D. Purvis, C. R. Lowe, E. Pişkin, *J. Chromatogr.*, **634,** 161 (1993).
20. E. Pişkin, A. Tuncel, A. Denizli, and H. Ayhan, *J. Biomater. Sci., Polym. Ed.*, **5,** 451, (1994).
21. H. Ayhan, A. Tuncel, N. Bor, and E. Pişkin, *J. Biomater. Sci., Polym. Ed.*, **7,** 329 (1995).
22. C. M. Tseng, Y. Y. Lu, M. S. El-Aasser, and J. W. Vanderhoff, *J. Polym. Sci., Polym., Chem. Ed.*, **24,** 2995 (1986).
23. K. P. Lok and C. K. Ober, *Can. J. Chem.*, **63,** 209 (1985).
24. C. K. Ober and K. P. Lok, *Macromolecules,* **120,** 2689 (1987).
25. A. J. Paine, *Macromolecules,* **23,** 3109 (1990).
26. A. J. Paine, w. Luymes, and J. NcNulty, *Macromolecules,* **23,** 3104 (1990).
27. C. K. Ober and M. L. Hair, *J. Polym. Sci.*, **25,** 1395 (1987).
28. V. Bulmuş, M.Sc. Thesis, Hacettepe University, Ankara, Turkey (1995).
29. J. Brandruip and E. H. Immergut, Eds., *Polymer Handbook,* 3rd ed., John Wiley & Sons, New York, 1989.
30. K. Rück and H. Kunz, *J. Prakt. Chem.*, **336,** 407 (1994).
31. Y. Sun, X. Chen, and X. Feng, *Makromol. Chem.*, **191,** 2093 (1990).
32. M. Liu, R. Cheng, J. Wu, and C. Ma, *J. Polym. Sci., Part A: Polym. Chem.*, **31,** 3181 (1993).
33. S. B. Shah, C. P. Patel, and H. C. Trivedi, *Angew. Makromol. Chem.*, **214,** 75 (1994).

Received May 15, 1995
Accepted October 15, 1995