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Micron-size uniform poly(methyl methacrylate) particles by dispersion polymerization in polar media

1. Particle size and particle size distribution

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Abstract

Monodisperse poly(methyl methacrylate) (PMMA) particles in the size range of 1–5 μm were prepared by unseeded dispersion polymerization in methanol–water media using azo-type initiator and poly(acrylic acid) (PAA) or poly(vinyl pyrrolidone) (PVP) as a steric dispersant. The influences of various polymerization parameters, such as polymerization temperature and time, concentration and type of initiator, concentration, type and molecular weight of dispersant, composition of the reaction media including dispersed medium and monomer, content of electrolyte and crosslinking agent on the particle size and particle size distribution were systematically investigated.

Keywords: Dispersion polymerization; Poly(methyl methacrylate); Monodisperse polymer particles; Particle size and its distribution

1. Introduction

The production of uniform polymer particles in the 1–5 μm range has received a great deal of attention in recent years because of its many applications in new technical fields [1–3]. Micron-grade monodisperse polymer particles have been prepared by complicated emulsion polymerization including the space shuttle in microgravity [4], successive seed [5,6] or multi-stage swollen [7–9] method and modified suspension polymerization [10–12]. All of these methods are rather tedious and time-consuming. Dispersion polymerization is an effective simple method [13], which suits not only a wide variety of monomers but also permits easy functionalization.

In general, the reaction system is homogeneous prior to dispersion polymerization. The particle formation stage belongs to a special case of the precipitation polymerization, but particle growth takes place both during emulsion polymerization in the monomer-swollen particles phase and solution polymerization in the continuous phase [14,15].

Most works [16–25] focused on the monodisperse polystyrene microspheres, and only a few articles [26–28] dealt with the preparation of uniform poly(methyl methacrylate) (PMMA) particles in the micron size using special macromonomer or poly(vinyl pyrrolidone) (PVP) as a dispersant. Moreover, very few [29–31] studies have touched on dispersion copolymerization except in the patent literature.

In our research work, the dispersion polymerization of methyl methacrylate (MMA) was carried out in methanol–water media using poly(acrylic acid) (PAA), PVP or poly(vinyl alcohol) (PVA) as a dispersant. The influence of various polymerization parameters on the particle size (PS) and particle size distribution (PSD) were examined.

2. Experimental

2.1. Materials

2.1.1. Monomers

Methyl methacrylate (MMA) was chemically pure grade and purified by reduced pressure distillation. Ethylene glycol dimethacrylate (EGDM) were commerical grades and used without purification.

2.1.2. Initiators

Azo-bis-isobutyronitrile (AIBN), 2,2′-azobis-2,4-dimethylvaleronitrile (ADVN), benzoyl peroxide (BPO), potassium persulfate (KPS) were purified by recrystallization.

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Table 1
Standard recipe for dispersion polymerization of MMA

	Material	Weight (g)	Part
Monomer	MMA	30	100
Stabilizer	PAA or PVP	3	10
Initiator	AIBN	0.3	1
Dispersed medium	CH_3OH	189	630
Dispersed medium	H_2O	81	270

2.1.3. Dispersed media

Water was deionized and methanol of chemically pure grade was used without further purification.

2.1.4. Dispersants

PAA with viscosity-average molecular weight of 4.83×10^5 was prepared in our laboratory by aqueous solution polymerization at 80°C using KPS as initiator. PVA (KH-20), PVP (K-15,K-30,K-60,K-90), and PVPQ-100 (CTFA name is polyquaternium having quaternary ammonium group) were commercial products and used without further purification.

2.2. Preparation

The standard recipe used in this study is given in Table 1. The amount of each ingredient was kept constant in all experiments except where indicated. Dispersion polymerization was carried out in 500 ml jacketed glass reactor at given temperature for 6 h under nitrogen with an agitation speed of 100–120 rpm, the resulting PMMA particles was added to hydroquinone (inhibitor) solution for termination.

2.3. Characterization

The morphology of produced PMMA particles was observed directly by Nikon PFX optical microscope and scanning electron microscopy (SEM). PS and PSD of each sample without any washing were obtained from measurements using a 256 Coulter counter LS230. D_w and D_n are defined as weight and number average diameters, respectively. PSD is expressed as polydispersity index (D_w/D_n).

3. Results and discussion

3.1. Effect of polymerization temperature

Table 2 shows that a larger particle size is formed at the higher temperature. The size distribution is not much affected by temperature. These results can be explained as follows. With increasing temperature, the critical oligomeric chain length increases and thus the concentration of the precipitated oligomeric chains. Along with this, the adsorption rate of the stabilizer and the viscosity of the continuous phase are reduced. All of these can contribute to an increase in particle size. However, the increase of the graft-stabilizer will lead to the formation of smaller particles. The size distribution tends to broaden if the particle formation stage is longer.

Table 2
Effect of temperature on PS and PSD[a]

Temperature (°C)	D_W/D_n	PS (μm)
55[b]	–	–
60[b]	1.04	2.24
65[b]	1.10	2.14
70[b]	1.02	3.40
50	1.01	1.85
55	1.03	1.19
60	1.01	2.14
65	1.01	2.81
50[c]	1.01	4.43
60[c]	1.12	7.42

[a] MMA=10 wt.% of total; PAA=10 wt.% of MMA; AIBN=1 wt.% of MMA; MeOH:H_2O=7:3 wt.; –: coagulation.
[b] PVP/MMA=10 wt.%.
[c] MeOH:H_2O=9:1 wt.

3.2. Effect of polymerization time

Fig. 1 shows that the resulting particle size increases gradually, and size distribution tends to become more monodisperse during the polymerization process. The reason is due to the higher adsorption ability of smaller particles in the particle growth stage. Here, the essential prerequisite is that new particles are not produced in the particle growth stage. It is clear that the particle number is constant after the particles formation stage due to the linear relationship of the average volume per particle versus conversion in Fig. 2.

We conclude that one of the basic requirements for the formation of monodisperse particles is that there should be no formation of new particles and no coalescence of the existing particles during the particle growth stage.

3.3. Effect of concentration and type of initiator

Fig. 3 shows the effect of AIBN concentration on the particle size. With increasing the initiator concentration, the particle size increases and the size distribution tend to broaden in general, though in detail the behaviour is complete. The following changes are caused by an increase of initiator concentration: (1) the number of free radicals and thus the concentration of the precipitated oligomeric chains increases; (2) the solubility of graft-stabilizer with shorter PMMA segment in media increases. Obviously, the aggregation process is enhanced, resulting in larger particles. However, the larger particles capture less nuclei or oligo-radicals from the continuous phase due to their lower total surface area. Therefore, the particle size distribution will be significantly broadened when particle formation continues beyond a certain period. Meanwhile, an increase of graft-stabilizer level will lead to the formation of smaller particles.

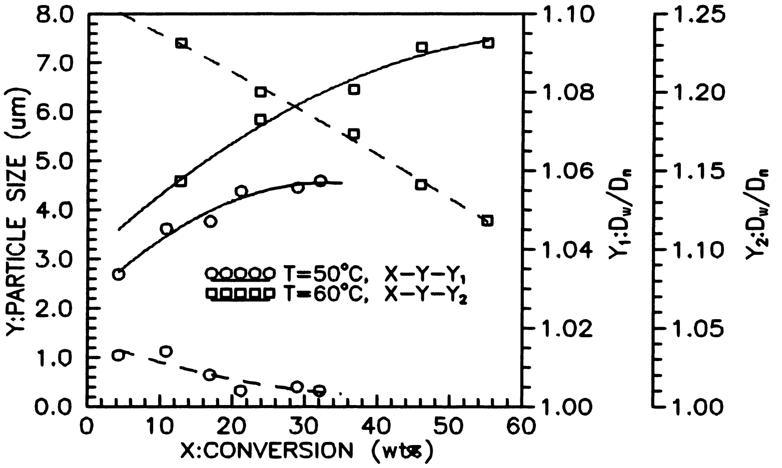

Fig. 1. Relationship between PS, PSD and reaction time: T=60°C; MMA=10 wt.% of total; PAA=10 wt.% of MMA; AIBN=1 wt.% of MMA; MeOH:H_2O=9:1.

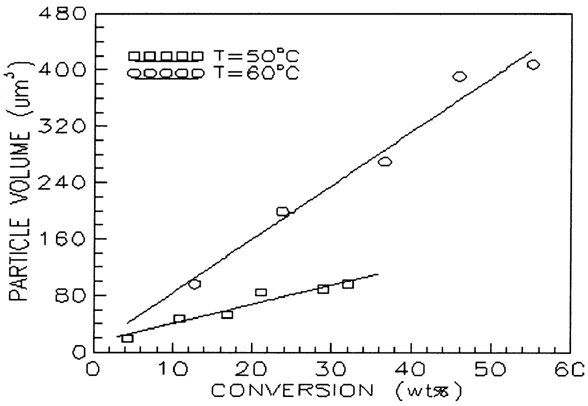

Fig. 2. Relationship between conversion and the average volume per particle: T=60°C; MMA=10 wt.% of total; PAA=10 wt.% of MMA; AIBN=1 wt.% of MMA; MeOH:H_2O=9:1.

Table 3
Effect of initiator type on PS and PSD[a]

Type	D_W/D_n	PS (μm)
ADVN	1.01 (1.03)	4.23 (3.35)
AIBN	1.04 (1.02)	2.24 (1.41)
BPO	1.18	1.02
KPS	–	–

[a] T=60°C; MMA=10 wt.% of total; PVP=10 wt.% of MMA; MeOH:H_2O=7:3 wt.; –: coagulation; Parenthesis denote PAA as a dispersant substituted for PVP.

The influence of initiator type is also shown in Table 3. The more active the initiator, the larger the particle size becomes and the narrower the size distribution tends to be. Hattori et al. [25] found that the surface of the particles was not smooth using ammonium persulfate as initiator and did not understood the reason for this. A reason can be shown that the initiator fragments including sulfate and hydroxy radical may be trapped within the graft-stabilizer chains, and hence, the head and the end of the graft-stabilizer chains may be hydrophilic PVP and sulfate radical or hydroxy, respectively. Thus, the graft-copolymer has weaker stabilization because of greater hydrophilicity. On the other hand, hydrogen bonds may be formed between chains of PVP and the hydroxy group, and a network structure (bridging) among the graft-stabilizers may be formed.

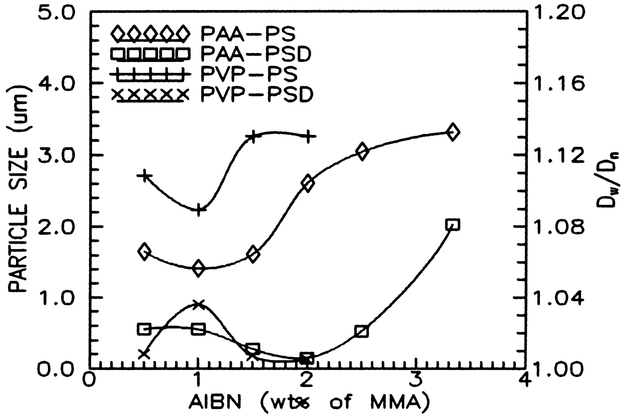

Fig. 3. Effect of AIBN concentration on PS and PSD: T=60°C; MMA=10 wt.% of total; Dispersant=10 wt.% of MMA; MeOH:H_2O=7:3.

3.4. Effect of concentration and type of dispersant

As illustrated in Fig. 4, the suitable concentration range of the dispersant for the preparation of uniform particles is limited. Moreover, this limited concentration range for PAA is broader than that of PVP because PAA acts as both a dispersant and a surfactant in situ and PVP only as a dispersant. It was observed that a broader size distribution is formed when increasing PVP concentration. The reason may be that graft rate between MMA oligomer chains and PVP is constant with further increasing PVP concentration, but the viscosity of the polymerization system will increase.

In addition, seven representative dispersants including changes of type and molecular weight are used in Table 4.

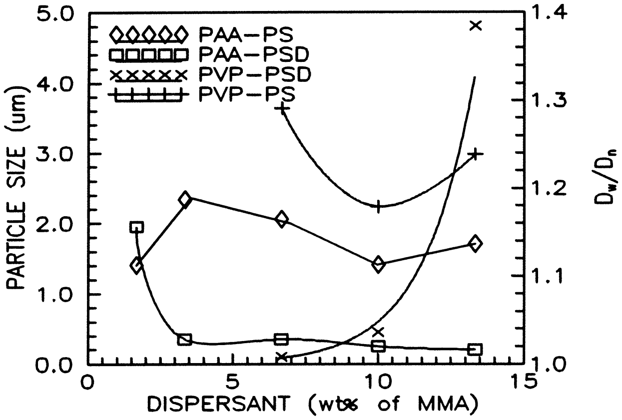

Fig. 4. Effect of dispersant concentration on PS and PSD: T=60°C; MMA=10 wt.% of total; AIBN=1 wt.% of MMA; MeOH:H_2O=7:3.

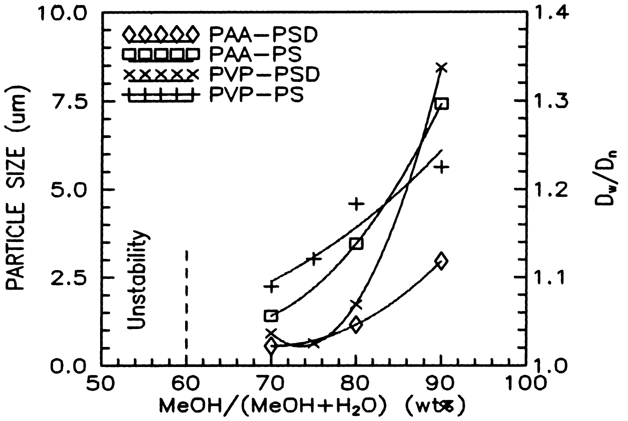

Fig. 5. Effect of dispersed medium on PS and PSD: T=60°C; MMA=10 wt.% of total; Dispersant=10 wt.% of MMA; AIBN=1 wt.% of MMA.

The results can be described as follows. The particle size decreases and the size distribution becomes more monodisperse with dispersant hydrophilicity increasing or if the dispersant has an ion-group. The dispersants, with the lower molecular weight cannot stabilize the particles sufficiently to prevent their agglomeration. PVP with the higher molecular weight stabilizes the particles more effectively but tends to produce polydisperse particles due to solution viscosity increasing and different graft-probability of dispersant. However, the higher the molecular weight of PVP gets, the lower the adsorption rate of stabilizer.

3.5. Effect of media

Varying the weight ratios of methanol–water mixtures as dispersed media demonstrates the relationship between the solvency of the media and the particle size (Fig. 5). With increasing methanol content in the media, the resulting particle size increases due to increasing solubility of graft-stabilizer and critical oligomer chain length. Therefore, adding more methanol extends the particle formation stage, resulting in a broader distribution. Since water is also a good solvent for PVP or PAA, the solubility of dispersant will not be affected significantly by the presence of water. On the other hand, water is a poor solvent for PMMA than methanol, so the lower the methanol content, the higher the generation rate of nuclei and the higher the adsorption rate of stabilizer. This makes it more difficult for the existing particles to capture all the nuclei and aggregates from the continuous phase before they become the stable particles. On the whole, monodisperse particles can be obtained in the ratio range of methanol to water from 7/3 to 8/2.

Table 4
Effect of dispersant type on PS and PSD[a]

Type	D_W/D_n	PS (μm)
PAA (Mη=4.83×10^5)	1.02	1.41
PVA-KH20	1.01	2.73
PVP-K15 (Mη=8000)	–	–
PVP-K30 (Mη=40,000)	1.04	2.24
PVP-K60 (Mη=200,000)	1.01	2.58
PVP-K90 (Mη=700,000)	1.10	0.74
PVP-Q100	1.01	1.98

[a] T=60°C; MMA=10 wt.% of total; AIBN=1 wt.% of MMA; MeOH:H_2O=7:3 wt.; –: coagulation.

Since the monomer is another important part of the initial solvent system, initial monomer concentration has considerable effect on the resulting particles. The curve in Fig. 6 tells us that the particle size increases in general and the size distribution remains monodisperse with increasing monomer concentration if monomer concentration is less than 15 wt.%. With further increase in the monomer concentration the solution polymerization rate will be increased, and also solvency of the medium for the polymers being formed. It will also bring about increasing length of the PMMA segments in graft-copolymer stabilizer produced in situ during the polymerization, which will increase the adsorption rate of the stabilizer, favoring the formation of the smaller particles.

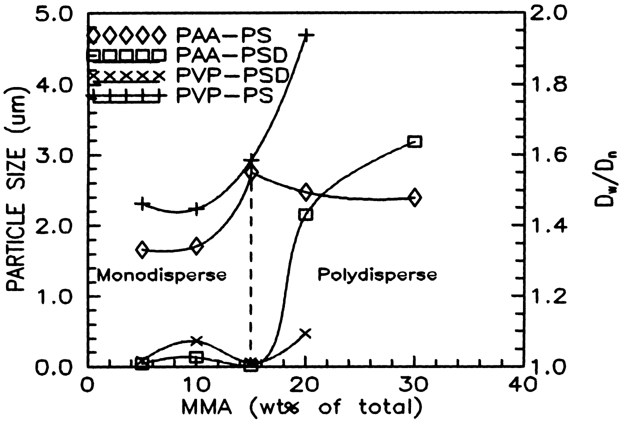

Fig. 6. Effect of MMA concentration on PS and PSD: T=60°C; Dispersant=10 wt.% of MMA; AIBN=1 wt.% of MMA; MeOH:H_2O=7:3.

Table 5
Effect of NaCl on PS, PSD and the stability of dispersion polymerization of MMA[a]

NaCl (wt.% of media)	D_W/D_n	PS (μm)
0	1.04 (1.03)	2.24 (2.05)
1.11	1.01 (1.02)	1.94 (1.09)
1.85	1.04 (1.03)	1.76 (1.20)
3.7	1.19 (–)	0.41 (–)

[a] T=60°C; MMA=10 wt.% of total; AIBN=1 wt.% of MMA; PVP=10 wt.% of MMA; MeOH:H_2O=7:3 wt.; Parenthesis denote EGDM=0.5 wt.% of MMA; –: coagulation.

When monomer concentration exceeds 20 wt.%, the particle size decreases and size distribution tends to be broader, suggesting a large change of the polarity of the solvent during the polymerization process at the higher monomer concentration.

3.6. *Effect of electrolyte and crosslinking agent*

Table 5 shows the influence of electrolyte with or without EGDM. The results indicate that the particle size decreases and the size distribution tends to be broader with increasing sodium chloride content due to the change of surface potentials. In addition, one can see that EGDM as crosslinking agent causes a smaller particle size due to the increase of the particle density. Flocculation was observed if the concentration of electrolyte is greater than the upper limit shown here.

4. Conculsions

Monodisperse PMMA particles in the size range of 1–5 μm were obtained by dispersion polymerization carried out in methanol–water media. AIBN or ADVN and PAA or PVP were utilized as initiator and steric dispersant, respectively.

In general, the size of the resulting PMMA particles will increase with increasing polymerization temperature, initiator concentration and activity, concentration of MMA and decreasing polarity of polymerized media and dispersant, molecular weight and concentration of PVP. Moreover, the shorter the particle formation stage is, the narrower the particle size distribution, provided that new particles are not produced and that flocculation and coagulation in the particle growth stage are excluded.

The addition of a small amount of crosslinking agent reduces the particle size but does not show any significant effect on the size distribution. However, there is a marked drop in the stability of the polymerization system. Addition of electrolyte reduced the particle size but had little effect on the PSD.

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