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Micron-size Functional Uniform PMMA Particles by Dispersion Copolymerization in Polar Media

Kun Cao*, Bo-Geng Li, Zu-Ren Pan

State Key Laboratory of Chemical Engineering, Polymer Reaction Engineering Branch
Department of Chemical Engineering, Zhejiang University, Hangzhou 310027, CHINA

SUMMARY : A series of monodisperse copolymer particles in the size range of 1-5 μm are prepared by unseeded batch dispersion copolymerization of methyl methacrylate as major monomer in methanol-water medium using an azo-type initiator and poly(vinyl pyrrolidone) as steric dispersant. The effects of type and concentration of comonomer on the latex stability, the particle size and monodispersity of the copolymer particles are investigated. Moreover, the partitioning of the functional group dissolved in the supernatant, physically adsorbed and chemically anchored on the surface of the copolymer particles, and buried within the copolymer particles determined directly by conductometric titration are tentatively discussed.

Introduction

Dispersion polymerization is an attractive route to prepare micron-size uniform polymer particles in a single step. Most works focused on monodispersity of the polymer particles by dispersion homopolymerization using homopolymer as a dispersant since 80's(1-2), only a few articles(3-4) dealt with the preparation of uniform particles using special macromonomer as both a dispersant and a comonomer. Morever, very few papers(5-6) touched the unseeded dispersion copolymerization. This is probably due to the complex nature of the partitioning of the comonomer as it has different solubilities between monomer-swollen particles phase and continuous phase(7).

This article describes our research work done on the unseeded dispersion copolymerization of methyl methacrylate as major monomer with acrylic comonomer having different functional group in methanol-water media using poly(vinyl pyrrolidone) as steric dispersant related to the partitioning of the functional group, the particle size and its distribution.

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Experimental

Methyl methacrylate (MMA) was chemically pure grade and purified by reduced pressure distillation. All other monomers, including acrylic acid (AA), methacrylic acid(MAA), glycol methacrylate(GMA), 2-hydroxyethyl methacrylate (HEMA), 2-(dimethylamino) ethylmethacrylate (DMAEMA), ethylene glycol dimethacrylate (EGDMA) were used as shipped. Azo-bis-isobutyronitrile (AIBN) was purified by recrystallization. Poly(vinyl pyrrolidone)(PVP-K30, MW=40000) of commercial product and methanol of chemically pure grade were used without further purification. Water was deionized. The standard recipe used in this study was temperature = 60°C, $CH_3OH:H_2O$= 7:3 wt, monomer = 10 wt% of total, AIBN=1 wt% of Monomer, PVP-K30 = 10 wt% of monomer. The amount of each ingredient was kept constant in all experiments except indicated.

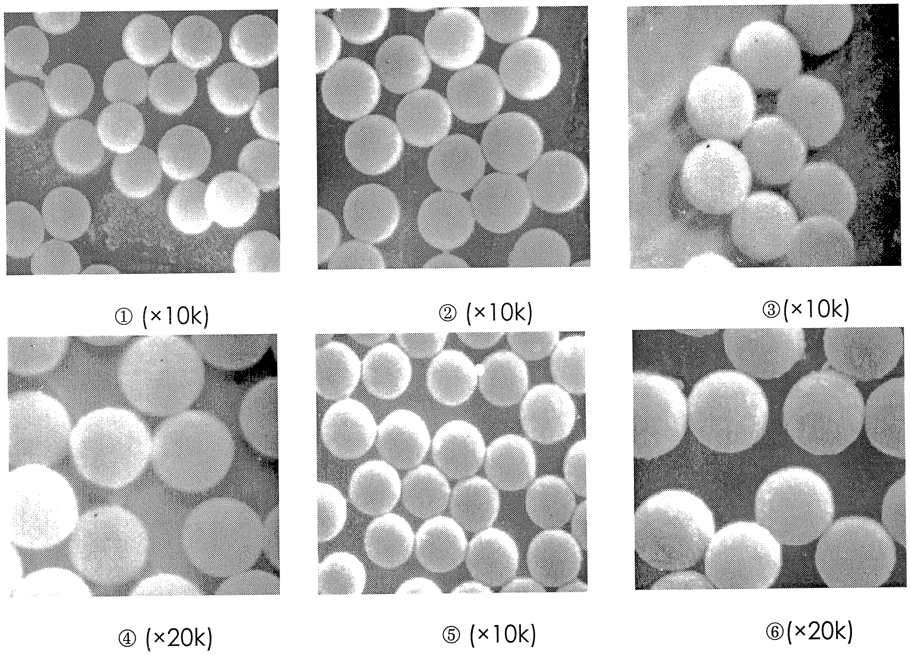
Dispersion polymerization was carried out in 500-ml jacketed glass reactor at a given temperature under nitrogen with an agitation speed of 50-120 rpm. To the resulting particles were added hydroquinone (inhibitor) solution as short-stop.

The morphology of the produced copolymer particles were observed directly by scanning electron microscopy (SEM). The particle size (PS) and particle size distribution (PSD) of each sample without any washing were obtained from measurements of a 256 Coulter LS230. The carboxyl and the amino group density on the surface of the PMMA particle, cleaned by multi-rinsing method, were determined directly by conductometric titration. In addition, the hydroxyl groups on the surface of the cleaned particles were oxidized to the carboxyl group in 10^{-5} N solution of silver nitrate and a known potassium persulfate solution at 60°C over 8 hr. As a prerequisite condition, we impose that there are no variations of PS and PSD for the different pretreatment methods.

Results and Discussion

For the purpose of the functionalization, a series of monodisperse copolymer particles in the size range of 1-5 μm are prepared by unseeded batch dispersion copolymerization of MMA as major monomer in a methanol-water medium using azo-type initiator and PVP as steric dispersant. Typical SEM micrographs of the copolymer particles are shown in Figure 1.

Tables 1 and 2 imply that the particle size becomes large with higher polarity and hydrophilicity of monomer, and the particle size tend to become large while the comonomer has the higher e value except HEMA, respectively. A reason can be that the comonomer with electron-releasing substituents tend to partition in particle phase due to solvability. Thus, the polarity of the continuous phase is similar to that in dispersion homopolymerization of MMA. Figures 2 and 3 show that the particle size increases and the size distribution tend to be more monodisperse when a small amount of AA or MAA is added. On the contrary, the particle size will decrease and its distribution tends to be broader owing to second particle formation stage if ratio of AA or MAA to MMA is more than certain value, leading to unstabilization. The influence of pH value is illustrated in Table 3. The results indicate that the particle size decreases and size distribution tend to be broader with increasing apparent neutralization degree of AA. Moreover, polymerization system becomes unstable in basic medium. In addition, Table 4 shows that the particle size decreases and size distribution are similar with adding a given electrolyte (sodium chloride).



① (×10k) ② (×10k) ③(×10k)

④ (×20k) ⑤ (×10k) ⑥(×20k)

Figure 1 SEM micrographs of micron-size functional uniform PMMA particles by unseeded batch dispersion copolymerization. ① Poly(MMA-co-AA) particles, ② Poly(MMA-co-MAA) particles, ③ Poly(MMA-co-HEMA) particles, ④ Poly(MMA-co-DMAEMA) particle, ⑤ Poly(MMA-co-GMA) particles, ⑥ Poly(MMA-co-EGDM) particles.

We found that the partitioning of the carboxyl group dissolved in the supernatant, physically adsorbed and chemically anchored on the surface of the copolymer particles, and buried

Tab.1 Effect of comonomer type on PS & PSD

Comonomer	D_w/D_n	PS /μm
AA	1.02	3.6
MAA	1.01	3.4
GMA	1.01	2.7
HEMA	1.02	2.7
DMAEMA	1.08	2.3
MMA	1.04	2.2

MMA:comonomer = 29:1

Tab. 2 Q and e values for monomer

Monomer	e[8]	Q[8]	e[9]	Q[9]
AA	0.88	0.83	0.77	1.15
MAA	0.62	0.98	0.65	2.34
GMA	0.20	0.96	0.57	1.03
HEMA	-0.39	1.78	0.20	0.80
DMAEMA	-----	-----	0.47	0.68
MMA	0.40	0.78	0.40	0.74

Tab. 3 Effect of pH value on PS and PSD

NaOH / %	pH	D_w/D_n	PS / μm
0.000	3.5	1.09	1.9
0.074	5.5	1.72	1.7
0.185	7.0	1.97	1.7
0.555	8.1	----	----
0.777	9.5	----	----

MMA:AA = 28:2, ----:coaglution

Tab. 4 Effect of electrolyte on PS and PSD

NaCl / wt% of total	D_w/D_n	PS / μm
0	1.09	1.9
1.0	1.10	1.8
1.67	1.08	1.4
2.33	1.12	0.87
3.33	1.10	0.91

MMA:AA = 28:2

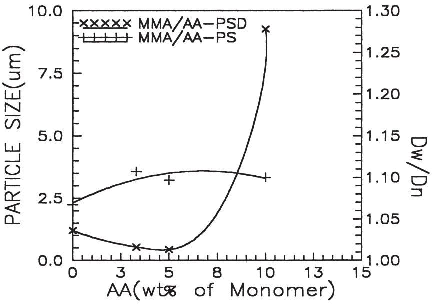


Fig. 2 Effect of ratio of MMA to AA on PS and PSD

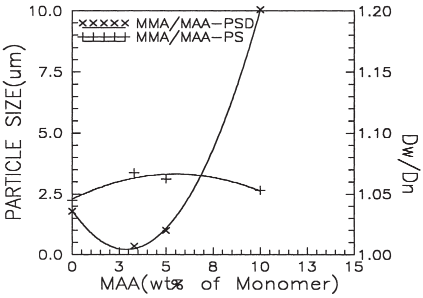


Fig.3 Effect of ratio of MMA to MAA on PS and PSD

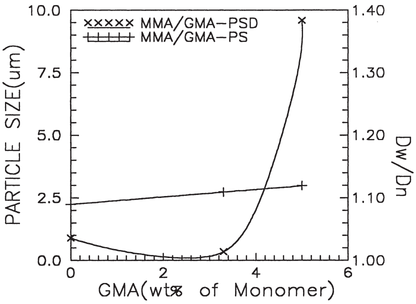


Fig. 4 Effect of ratio of MMA to GMA on PS and PSD

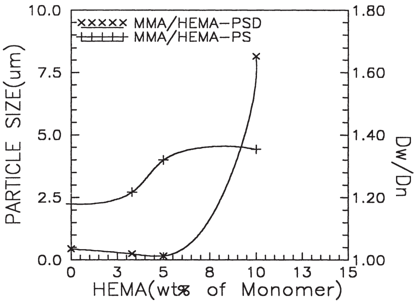


Fig. 5 Effect of ratio of MMA to HEMA on PS and PSD

within the copolymer particles is not constant. Table 5 shows that the partitioning of the carboxyl group in the supernatant and physically adsorbed on the surface of the particles increases with increasing ratio of AA to MMA. On the contrary, more carboxyl group will be buried within the copolymer particles if EGDMA is added, as shown in Table 6. Table 7 indicates that only the carboxyl group proportion in the supernatant increases if an electrolyte added. The copolymer particles have an actual parking area of 50 to 150 Å ^{2} per functional carboxyl group.

Tab. 5 Effect of MMA/AA ratio on the carboxyl group partitioning

MMA:AA	29:1	28:2	27:3
Supernatant (%)	4	6	9
Physically adsorbed on the surface (%)	11	32	42
Chemically anchored on the surface (%)	18	16	13
Buried within particles (%)	67	46	36
Area per functional group (Å^2)	93	56	78

Tab. 6 Effect of EGDMA concentration on the carboxyl group partitioning

EGDM % of Monomer	0	0.045	0.075	0.11
Supernatant (%)	6	6	6	6
Physically adsorbed on the surface (%)	32	25	17	15
Chemically anchored on the surface (%)	16	15	14	13
Buried within particles (%)	46	54	63	66
Area per functional group (Å^2)	56	70	76	103

MMA:AA = 28:2

Tab. 7 Effect of NaCl concentration on the carboxyl group partitioning

NaCl (%) of total	0	1	1.67
Supernatant (%)	6	28	46
Physically adsorbed on the surface (%)	32	24	20
Chemically anchored on the surface (%)	16	13	10
Buried within particles (%)	46	35	24
Area per functional group (Å^2)	56	79	153

MMA:AA = 28:2

The effect of GMA or HEMA concentration on PS and PSD are shown in Figure 4 and 5, respectively. Table 8 shows the relationship between ratio of DMAEMA to MMA and PS & PSD. In general, addition of comonomer will decrease flexibility of polymerization conditions for monodisperse particles. Table 9 is about the effect of crosslinking agent on the dispersion copolymerization of MMA and AA. The results indicate that the particle size increases and PSD distribution stays similar

Table 10 is about the amino group partitioning. Finally, the hydroxyl density on the surface of the MMA/HEMA copolymer particles is tentatively measured. The results indicate that the proportion of hydroxyl group chemically anchored on the surface is less than 5 percent.

Tab. 8 Effect of ratio of MMA to DMAEMA on PS and PSD

MMA:DMAEMA	D_w/D_n	PS / µm
29:1[a]	1.08	2.3
28:2[a]	1.03	3.3
27:3[a]	1.10	2.6
26:4[a]	1.34	3.2
29:1[b]	1.05	3.1
28:2[b]	1.06	3.6
27:3[b]	1.14	4.0
26:4[b]	1.26	3.6

a:AIBN = 1wt% of M, b:AIBN = 2wt% of M

Tab. 9 Effect of EGDMA concentration on PS and PSD

EGDM(wt% of M)	D_w/D_n	PS / µm
0.000	1.09	1.9
0.045	1.11	2.7
0.075	1.11	2.3
0.105	1.11	2.7
0.167	1.11	2.9
0.233	----	----
0.300	----	----

MMA:AA = 28:2, ----:coaglution

Tab. 10 Effect of AIBN concentration on the amino group partitioning

AIBN wt% of Monomer	1.0	2.0
Supernatant (%)	61	67
Physically adsorbed on the surface (%)	11	7
Chemically anchored on the surface (%)	8	3
Buried within particles (%)	20	23
Area per functional group (Å^2)	129	187

MMA:DMAEMA = 28:2

Conclusions

The effect of type and concentration of acrylic comonomer having different functional group monomer on the latex stability, the particle size and monodispersity of the copolymer particles are discussed, and related to the activity and hydrophilicity of the comonomers and the polarity of the continuous phase. In general, addition of comonomer will cause poor stability and decrease flexibility of polymerization conditions. Moreover, the partitioning of functional group chemically anchored on the surface of the copolymer particles is poorly controlled. This may be a fatal weakness for applications of unseeded batch dispersion copolymerization.

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