Polymer Journal, Vol. 22, No. 8, pp 759—761 (1990)

SHORT COMMUNICATION

Preparation of Monodispersed Poly(methyl methacrylate) Particle in the Size of Micron Range

Shiro KOBAYASHI,* Hiroshi UYAMA, Ikuo YAMAMOTO, and Yasuhiro MATSUMOTO

Department of Molecular Chemistry and Engineering, Faculty of Engineering, Tohoku University, Aoba, Sendai 980, Japan

(Received April 19, 1990)

KEY WORDS Dispersion Polymerization / Monodispersed Particle / Poly(methyl methacrylate) / Polymeric Stabilizer / Poly(2-ethyl-2-oxazoline) / Polyethylenimine /

Recently, preparation of monodispersed polymer particles in the size of a micron range has received much attention in biomedical and technological fields. A dispersion polymerization of styrene in an alcohol gave polymer particles with a narrow size distribution in the micron size range.[1-4] This system uses a highly polar polymer such as poly(*N*-vinylpyrrolidone) and hydroxypropyl cellulose as a polymeric steric stabilizer.

A dispersion polymerization of methyl methacrylate (MMA) in non-polar media has long been known.[5] Two papers have been reported in this framework for the preparation of micron-size monodispersed PMMA particles.[6,7] A dispersion polymerization of MMA in polar media, however, have been scarcely studied. Preparation of micron-size monodispersed particles of PMMA by dispersion polymerization in methanol was only once claimed by Almog *et al.*,[1] but no detail has been reported. In this communication we deal with a dispersion polymerization of MMA in an aqueous methanol solution giving monodispersed PMMA particles in the size of a micron range.

The dispersion polymerization of MMA was carried out in a mixture of methanol and water (70 : 30 wt%) by 2,2′-azobis(4,4-dimethylvaleronitrile) (ADVN) at 56°C for 6 h under argon to give a stable dispersion system. Polymeric stabilizers used were poly(2-ethyl-2-oxazoline) (PEtOZO) ($M_w = 500{,}000$) and branched polyethylenimine (PEI) ($M_w = 40{,}000$). The resulting particles were analyzed by scanning electron microscopy (SEM).

Table I shows particle size (D_n) and size distribution (D_w/D_n)[8] of PMMA with respect to the stabilizer concentration. In using PEtOZO as a stabilizer, the particle size decreased by increasing the concentration of the stabilizer (entry 1—5). A similar phenomenon has been observed in the dispersion polymerization of styrene in an alcohol.[1-4] When the concentration of PEtOZO based on MMA was more than 10%, particles with narrow size distribution were obtained (Figure 1(A)). Below this concentration, the size distribution was broader (entry 1). Monodispersed PMMA particles were also produced by using PEI as a stabilizer (entry 6—9) (Figure 1(B)). It is to be noted that the diameter of particles obtained by the PEI stabilizer was smaller than that by the PEtOZO stabilizer. This is probably because amino groups of PEI were partly ionized in aqueous methanol solution (pK_a of PEI ~ 8.5),[9] and hence, PEI acted not only as a steric stabilizer but also as

Table I. Effect of stabilizer concentration on particle size and size distribution of PMMA by dispersion polymerization[a]

Entry	Stabilizer	Stabilizer concentration[b]	D_n / μm	D_w/D_n
1	PEtOZO	5	4.6	1.08
2	PEtOZO	10	3.9	1.03
3	PEtOZO	20	2.8	1.02
4	PEtOZO	30	2.6	1.02
5	PEtOZO	50	2.0	1.01
6	PEI	10	1.4	1.02
7	PEI	20	1.3	1.01
8	PEI	30	1.3	1.01
9	PEI	50	1.1	1.01

[a] Polymerization of MMA (10 wt% based on total) was carried out in a mixture of methanol and water (70 : 30 wt%) by ADVN initiator (1 wt% based on MMA) at 56°C for 6 h.
[b] Weight % for MMA.

Table II. Effect of monomer concentration on particle size and size distribution of PMMA by dispersion polymerization[a]

Entry	Monomer concentration[b]	D_n / μm	D_w/D_n
10	5	2.3	1.02
3	10	2.8	1.02
11	15	3.4	1.04
12	20	3.1 (1.2—5.5)[c]	1.32
13	30	2.4 (0.8—9.0)[c]	2.26

[a] Polymerization was carried out using PEtOZO (20 wt% based on MMA) in a mixture of methanol and water (70 : 30 wt%) by ADVN initiator (1 wt% based on MMA) at 56°C for 6 h.
[b] Weight % for total.
[c] The value in the parenthesis is the range of particle size.

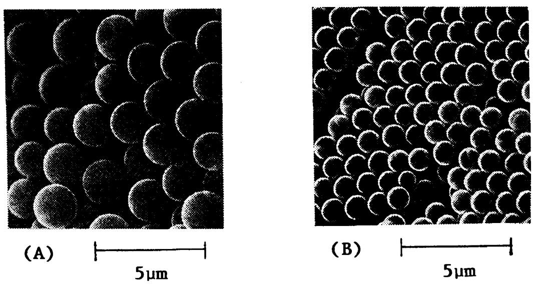

Figure 1. SEM photographs of PMMA particles prepared in aqueous methanol solution: (A) entry 5; (B) entry 9.

Table III. Effect of initiator concentration on particle size and size distribution of PMMA by dispersion polymerization[a]

Entry	Initiator concentration[b]	D_n / μm	D_w/D_n
14	0.5	2.5	1.01
3	1	2.8	1.02
15	2	3.1	1.02
16	4	4.2	1.07

[a] Polymerization of MMA (10 wt% based on total) was carried out using PEtOZO (20 wt% based on MMA) in a mixture of methanol and water (70 : 30 wt%) by ADVN initiator at 56°C for 6 h.
[b] Weight % for MMA.

an electrostatic one.

With different monomer concentrations the dispersion polymerization of MMA using PEtOZO as a stabilizer was carried out (Table II). As the monomer concentration increased from 5% to 15% (entry 10, 3, and 11), the average particle diameter increased from 2.3 to 3.4 μm. In this range, relatively monodispersed PMMA particles were produced. When the monomer concentration further increased, the resulting polymer particles possessed broader size distribution (entry 12 and 13).

Table III shows the effect of initiator concentration on the particle size and size distribution. The particle size increased by increasing the concentration of ADVN. This is probably because at a higher initiator concentration, the larger chain termination by the initiator makes the production of nuclei decrease, and hence, the final particles become larger.[10] When the concentration of ADVN was less than 2%, particles with narrow size distribution were obtained.

In summary, monodispersed PMMA particles in the size of a micron range were obtained by dispersion polymerization of MMA in aqueous methanol solution. The more detail studies including the size control of particles in the present polymerization system are now in progress.

REFERENCES AND NOTES

1. Y. Almog, S. Reich, and M. Levy, *Br. Polym. J.*, **14**, 131 (1982).
2. K. P. Lok and C. K. Ober, *Can. J. Chem.*, **63**, 209 (1985).
3. C. M. Tseng, Y. Y. Lu, M. S. El-Aasser, and J. W. Vanderhoff, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 2995 (1986).
4. M. Okubo, K. Ikegami, Y. Yamamoto, *Colloid Polym. Sci.*, **267**, 193 (1989).
5. K. E. J. Barrett (Ed.), "Dispersion Polymerization in Organic Media," Wiley, London, 1975.
6. B. Williamson, R. Lukas, M. A. Winnik, and M. D. Croucher, *J. Colloid Interface Sci.*, **119**, 559 (1987).
7. L. Antl, J. W. Goodwin, R. D. Hill, R. H. Ottewill, S. M. Owens, and S. Papworth, *Colloids Surfaces*, **17**, 67 (1986).
8. The definition of two kinds of average diameter, D_n and D_w, are defined as follows;

$$D_n = \frac{\Sigma N_i D_i}{\Sigma N_i}, \quad D_w = \frac{\Sigma N_i D_i^4}{\Sigma N_i D_i^3}$$

where N_i is the number of particles with diameter D_i.
9. S. Kobayashi, K. Hiroishi, M. Tokunoh, and S. Saegusa, *Macromolecules*, **20**, 1496 (1987).
10. C. K. Ober and M. L. Hair, *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 1395 (1987).