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ORIGINAL CONTRIBUTION

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Formation of monodisperse poly(methyl methacrylate) particles by radiation-induced dispersion polymerization. II. Particle size and size distribution

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Abstract Micron-sized poly(methyl methacrylate) particles were produced directly by radiation-induced dispersion polymerization in aqueous alcohol media using poly(*N*-vinylpyrrolidone) as a steric stabilizer at room temperature(10–35 °C). This method takes advantages of the specialities of radiation induction, and highly uniform polymer microspheres were obtained with high conversion. The gel effect was found from the polymerization kinetics curves. The number of nuclei produced in the early stage of the polymerization was found to be constant during the remainder of the polymerization. The effects of various polymerization parameters, such as irradiation dose rate, monomer concentration, stabilizer content, medium polarity, and polymerization temperature, on the particle size and the size distribution were investigated systematically.

Keywords Radiation-induced dispersion polymerization · Poly(methyl methacrylate) · Monodisperse particles · Particle size and its distribution

Introduction

There has been substantial interest in monodisperse polymer particles since Vanderhoff and Bradford [1] announced their preparation of polystyrene particles with highly uniform particle size in 1955. Monodisperse particles are finding a wide variety of applications, including instrument calibration standards, column packing material for chromatographic separation [2, 3], support materials for biochemicals [4], clinical examination [5], catalyst carriers, coating and ink additives, information storage materials, and so on. All these successful applications are ultimately dependent upon the particle size and its distribution, the morphology of the particles, and the surface characteristics. Therefore, the control of particle size and its uniformity has been focused on.

Various types of preparation methods producing monodispersed beads have been developed, such as suspension polymerization, emulsion polymerization and dispersion polymerization. Dispersion polymerization is a very attractive method owing to the inherent simplicity of the single-step process [6]. A typical example of this method is the dispersion polymerization of styrene in hydrocarbons, alcohols and various alcohol–ether or alcohol–water mixtures. Oil-soluble initiators such as 2,2′-azobis(isobutyronitrile) and benzoyl peroxide are extensively used in dispersion polymerization. In this work, γ-rays from ^{60}Co were used to initiate the dispersion polymerization. Such work has scarcely been reported before [7, 8]. Generally, radiation polymerization is one of the most convenient methods because of its nontemperature-dependent initiation and extremely large yield of radiation chemistry. Also, the radiation process can easily prepare a monodisperse polymer without the pollution of chemical initiators. In the present study, the dispersion polymerization of methyl methacrylate (MMA) with γ-ray from ^{60}Co was studied, and the influences of the dose rate, the monomer concentration, the stabilizer content, the medium polarity, the temperature, etc., on the particle size and its size distribution were determined.

Experimental

Materials

MMA was purified at 10 mmHg to remove inhibitor and was stored at –10 °C before polymerization. Poly(*N*-vinylpyrrolidone) (PVP) ($M_w = 4 \times 10^4$, K-30) was supplied by Shanghai Chemical Reagent Co. Deionized water was used throughout this work. Other reagents were of general reagent grade and wereused as received.

Preparation of poly(MMA) microspheres by dispersion polymerization

The syntheses of polymer particles were performed by γ-ray induced dispersion polymerization in different methanol/water mixtures, in which the monomer is easily soluble. Purified nitrogen was bubbled through the monomer solution at room temperature for about 15 min to get rid of oxygen. After that, the solution was directly fed into a special dilatometer [9] or a sealed glass ampoule, and held in a bath whose temperature was accurately controlled by a regulator. The polymerization was carried out at 19 °C at a fixed dose rate with γ-rays. The resulting polymers were centrifuged at 7,000 rpm and then washed with fresh methanol. This operation was repeated several times.

Characterization of the particles

The molecular weight of the polymer was determined in chloroform solution with a Ubbelode capillary viscometer at 20 °C. The average molecular weight can be calculated with the Mark–Houwink relation [10]: $[\eta] = 9.6 \times 10^{-3} M_n^{0.78}$ ml/g.

The size of the resulting polyMMA (PMMA) particles was examined using a Nicolet SEM X-65 scanning electron microscope. At least 300 individual particle diameters were measured from the photographs and the average was taken. The number- and weight-average particle diameters, d_n and d_w, were calculated from the equations $d_n = \Sigma d_i / N$ and $d_w = \Sigma d_i^4 / \Sigma d_i^3$, N being the number of particles. The particle size distribution was determined from d_w/d_n.

Results and discussion

Variation of polymerization conversion and polymer molecular weight with irradiation time

In the initial stage, the turbidity of the reaction mixtures was near zero; however, after a certain irradiation time, the turbidity started to increase. Typical conversion–time curves, generally S-shaped, are shown in Fig. 1. In general, the curve can be reproduced with a measurement error below 3%. The influence of the gel effect is observed in the conversion–time curve. The linear portion of the curve extends to quite high conversion levels (about 40–55%). It is pointed out that the polymerization conversion easily reaches higher values than that of the same system using chemical radical initiators at high temperature. The reason may be the higher activity and efficiency of free radicals which are produced by irradiation with γ-rays. The variation of the molecular weight with irradiation time is also shown in Fig. 1. The increase in the molecular weight with conversion is also an indication of the existence of the gel effect. The gel effect is more obvious [11] in this system when the molecular weight increases from 6,000 to 15,000 (about 2.5 times), i.e. the conversion increases from 8 to 50%.

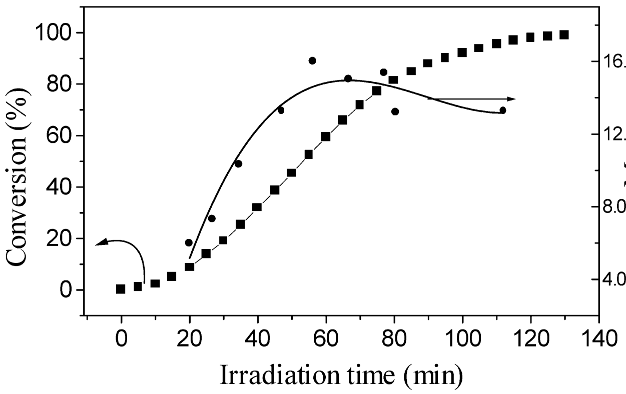

Fig. 1 Conversion versus time curve and polymer molecular weight versus time curve. Dose rate 40.6 Gy/min; methyl methacrylate (*MMA*) 15 wt%; MeOH/H_2O 75/5; poly(*N*-vinylpyrrolidone) (*PVP*) 5 wt%; 292 K

Particle growth

The relationship between the polymer conversion and the volume of the particles in the dispersion polymerization in aqueous methanol solution is shown in Fig. 2. The volume was found to increase linearly with the particle conversion. These data indicate that the number

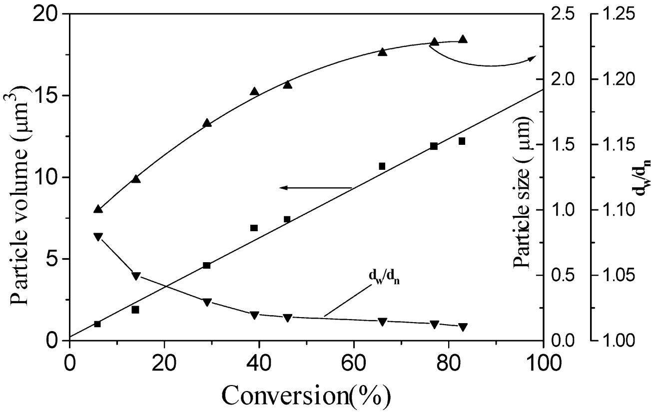

Fig. 2 Relationship between conversion and the average volume per particle, particle size and particle size distribution. Dose rate 73.1 Gy/min; MMA 15 wt%; MeOH/H_2O 75/5; PVP 5 wt%; 292 K

of particles is constant from an early stage of the polymerization, and therefore nucleation takes place in this early stage, followed by growth of the nuclei without formation of new particles. Figure 2 also shows that the resulting particle size increases gradually, and the 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.

Latex particles of the polymer at 14% conversion and at almost 100% conversion photographed by scanning electron microscopy are shown in Fig. 3a and b, respectively. The particle diameters of the polymer latex were estimated to be around 1.1 ± 0.15 and 2.3 ± 0.1 μm, respectively. The size distribution of these particles is quite narrow. The monodispersity of a colloidal dispersion obtained from a synthetic process has been discussed by Lamer and Dineager [12], and the authors indicated that monodispersity is only obtained when the initiation and nucleation stage is very short compared with the overall time for condensation. The γ-rays produce a higher rate of free-radical formation and initiation in the radiation polymerization. The formation of nuclei is finished in a short time after irradiation (about 10^{-6} s) [13]. Insoluble polymer particles are formed as soon as the chain length has reached its solubility limit. After the nuclei formation step, the number of particles becomes constant at a polymerization conversion below 10% with an irradiation time of 5–30 min. The induction period and the nucleation period are both quite short, and the radicals produced after the nucleation period do not contribute to the formation of new nuclei [13]; thus this can easily lead to monodispersity.

Influence of various polymerization parameters on the particle size and its distribution

In this study, the influences of various polymerization parameters, including polymerization temperature, stabilizer concentration, irradiation dose rate, monomer concentration and solvency of the medium, were investigated systematically. The standard recipes and synthesis parameters used in this study are given in Table 1. The amount of each ingredient was kept constant in all the experiments except where indicated. Usually two sets of experimental data were obtained for each parameter.

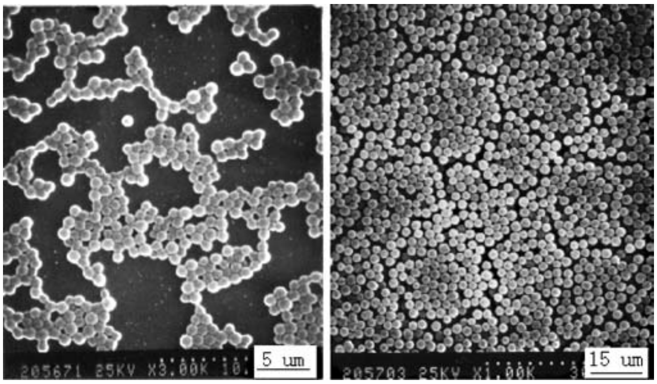

Fig. 3 Scanning electron microscope photographs of poly(MMA) microspheres: **a**14% conversion; **b** 96% conversion. Dose rate 73.1 Gy/min; MMA 15 wt%; MeOH/H_2O 75/5; PVP 5 wt%; 292 K

Table 1 Recipes and synthesis parameters for the dispersion polymerization of methyl methacrylate

	Standard recipe or parameter	Experimental variation
Initial monomer concentration (wt%)	15.0	10.0–21.0
Polarity of dispersion medium (MeOH/H_2O w/w)	15/1	7/1–26/1
Stabilizer content (wt%)	5.0	2.5–6.5
Dose rate (Gy/min)	73.1	40.6–92.2
Temperature (°C)	19	13–55

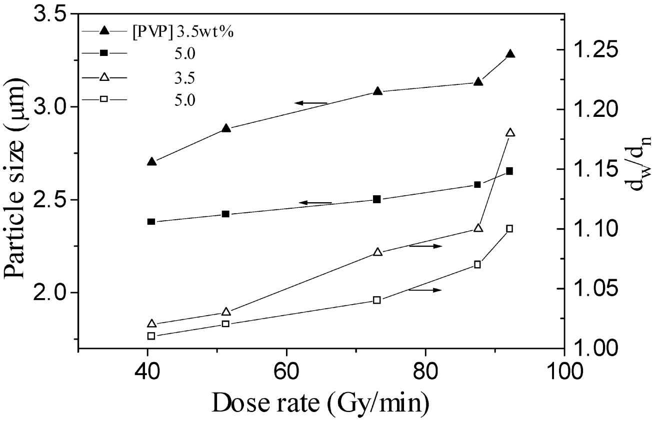

Fig. 4 Effect of irradiation dose rate on the particle size and the size distribution for two stabilizer contents. MMA 15 wt%; MeOH/H_2O 75/5; 292 K

Effect of irradiation dose rate

The effect of the irradiation dose rate on the particle size and the size distribution was studied in the range 40–100 Gy/min. As seen from Fig. 4, the average particle size increases with increasing dose rate at two PVP concentrations, and the size distribution tends to broaden in general. This expected behavior is also discussed in the literature [14]. It is considered that the dose rate affects the number of nuclei, the growth of particles and the yield. Therefore the particle size and its distribution depend on the dose rate under the same conditions, and this is similar to the effect of a radical initiator in chemical dispersion polymerization. A greater initiator concentration would lead to grafts of shorter oligomer chain length which have greater solubility in the reaction medium. The adsorption of the grafted stabilizer on the particles would therefore be retarded, leading to larger size particle. The increased size distribution (d_w/d_n) with increasing dose rate can be explained by the smaller surface area of the large particles that adsorb oligomers in the solution less efficiently. Consequently, the oligomers (or PMMA) in solution can nucleate during the later stages of the reaction and hence the distribution of the particle size in the product is broader.

Effect of stabilizer concentration

In the present system, a water- and methanol-soluble polymer (PVP), which possesses active α-hydrogens as possible chain-transfer sites, was used as a steric stabilizer. The response of the particle size to PVP concentration at two different monomer concentrations is shown in Fig. 5. As the stabilizer concentration increased, the particle size decreased. A higher stabilizer concentration causes faster stabilizer adsorption, and hence for a given rate of nucleation a greater number of particles with smaller size will be stabilized during the primary stabilization process. As illustrated in Fig. 5, the suitable concentration range of the dispersant for the preparation of uniform particles is from 4 to 7 wt%. It was observed that a broad size distribution is formed when the PVP concentration is higher than 7 wt%. The reason may be that the graft rate between MMA oligomer chains and PVP is constant with further increasing PVP concentration, but the viscosity of the polymerization system increases.

Effect of medium polarity

In a series of articles which describe the synthesis and properties of polymer particles the important role of solvent has been discussed. The composition of the reaction medium (methanol/water) also affects the outcome of the reaction. The influence of the alcohol/water ratio on the particle size and the size distribution at two different temperatures is shown in Fig. 6. The more hydrophilic the medium is, the smaller the PMMA particles will be. Similar tendencies in the relationships between the polarity of the polymerization media and the size of the resulting polymer particles have been observed when nonpolar monomers are polymerized in polar media [15, 16]. With increasing methanol content in the media, the resulting particle size increases owing to the increasing solubility of the graft stabilizer and the critical oligomer chain length. Therefore, adding more methanol extends the particle formation stage, resulting in a broader distribution.

Effect of monomer concentration

The initial monomer concentration is important because the particle number is determined very early in the reaction [17]. The effect of the initial monomer concentration on the particle size and the size distribution is shown in Fig. 7 for two alcohol/water ratios. An increase in the initial monomer concentration leads to large PMMA particles. When the monomer concentration was between 10 and 15%, monodisperse particles were obtained. Larger particles, obtained at MMA concentrations higher than 18%, capture oligomers in solution less efficiently owing to the smaller total surface area. The oligomeric radicals in solution can continue to aggregate (nucleate) to generate new particles and result in a broader size distribution.

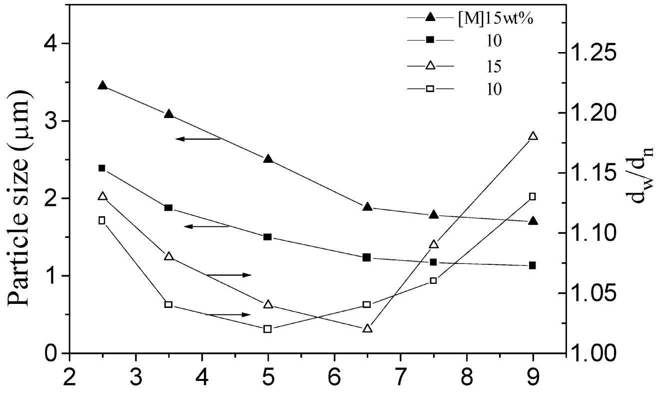

Fig. 5 Effect of stabilizer content on the particle size and the size distribution for two monomer contents. Dose rate 73.1 Gy/min; MeOH/H_2O 75/5; 292 K

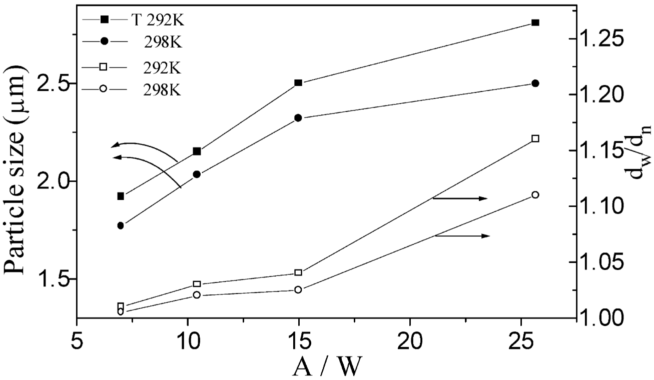

Fig. 6 Effect of alcohol/water ratio on the particle size and the size distribution at two polymerization temperatures. Dose rate 73.1 Gy/min; MMA 15 wt%; PVP 5 wt%

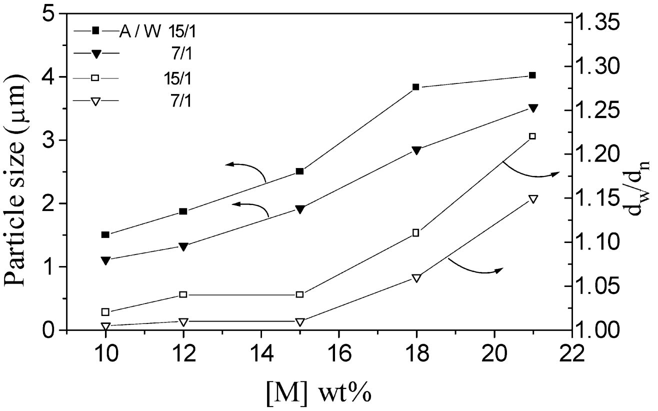

Fig. 7 The effect of monomer concentration on the particle size and the size distribution at two alcohol/water ratios. Dose rate 73.1 Gy/min; PVP 5 wt%; 292 K

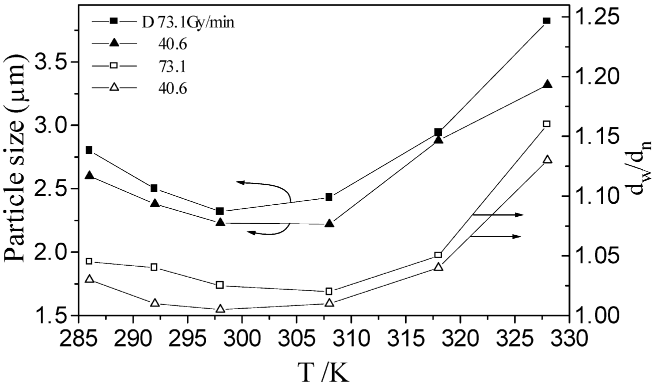

Fig. 8 The effect of polymerization temperature on the particle size and the size distribution at two dose rates. MMA 15 wt%; MeOH/H_2O 75/5; PVP 5 wt%

Effect of polymerization temperature

The curve in Fig. 8 tells us that the particle size decreases in general and that the size distribution remains monodisperse with increasing polymerization temperature if the temperature is lower than 35 °C. With further increase in the polymerization temperature the particle size increases very quickly and the size distribution tends to be broader. These results suggest that the mechanism for particle nucleation depends greatly on the molecular weight of the polymer produced by the polymerization before the initial precipitation. If a polymer of high molecular weight is formed, most of the polymer precipitates to form nuclei (either as individual chains or more probably as an aggregate). If a low-molecular-weight polymer is produced, fewer chains would precipitate. This would result in fewer nuclei being formed and, in the absence of coalescence, larger particles would eventually be formed, and these would be composed of polymer with lower molecular weight.

The polymer molecular weight occurs in the conventional free-radical polymerization as a result of the shorter chain length produced by a higher polymerization temperature. However, this trend is not a characteristic of the radiation polymerization process. According to the basic theory of radiation polymerization, the relationship between the average degree of polymerization (P_n) and temperature is expressed as follows:

$$\ln[P_n(T_2)/P_n(T_1)] = \left[\left(E_p - E_t/2\right) - E_i/2\right] (1/T_1 - 1/T_2)/R \quad T_2 > T_1 .$$

This is a simple kinetics model where E_p, E_t and E_i are the activation energies for the propagation, termination and initiation reactions, respectively. The activation energy of initiation is about zero because of radiation initiation, so (E_p–$E_t/2$) is greater than zero. Thus, at lower temperatures, the degree of polymerization increases with the increase in temperature. It can be seen from Fig. 8 that the particle size decreases with the increase in polymerization temperature when the temperature is lower than 35 °C. However, at higher temperatures, the chain transfer rate constant, k_{tr}, increases much faster than the chain propagation rate constant, k_p, which lowers the molecular weight. An inverse correlation between the particle size and the molecular weight [18] is typical of any dispersion polymerization product and can be accounted for by changes in the locus of polymerization.

Conclusion

In this study, highly uniform PMMA microbeads in the size range 1.0–5.0 μm were obtained by radiation-induced dispersion polymerization of MMA carried out in methanol/water media using PVP as the sole stabilizer. The gel effect is evident from the increase in the molecular weight and the polymerization conversion versus irradiation time curves. The number of microspheres is constant during the polymerization after the nucleation step. In general, the size of the resulting PMMA particles increases with increasing irradiation dose rate, monomer concentration and decreasing polarity of polymerized media, stabilizer concentration and polymerization temperature. Although the PMMA particles can also be prepared by chemical methods using chemical radical initiators, purified monodisperse microspheres can be obtained easily by radiation-induced polymerization.

References

1. Vanderhoff JW, Bradford EB (1971) Polymer colloid I. New York, Plenum
2. Ugelstad J (1985) J Polym Sci Polym Symp 72:225
3. Christpher KO (1985) J Polym Sci Polym Lett Ed 23:103
4. Lok KP, Ober CK (1985) Can J Chem 63:209
5. Okubo M (1987) Colloid Polym Sci 265:957
6. Barrett KEJ (1975) Dispersion polymerization in organic media. New York, Interscience
7. Xu ZL, Zhang ZC, Zhang MW (1999) J Dispersion Sci Technol 20:1647
8. Yoshida M, Kobota T, Asano M, Kumakura M (1986) Colloid Polym Sci 267:986
9. Zhang ZC, Jiang PY, Zhang MW (1990) J Radiat Res Radiat Process 8:100
10. Brandrup J, Immergnt EH (eds) (1989) Polymer handbook, 3rd edn. Wiley, New York
11. Ishige T, Hamielec AE (1973) J Appl Polym Sci 17:1479
12. Lamer VK, Dinegar RH (1975) J Am Chem Soc 72:4847
13. Naka Y, Kaetsu I, Yamamoto Y, Hayashi K (1992) J Polym Sci Part A Polym Chem 29:1197
14. Ober CK, Hair ML (1987) J Polym Sci 25:1395
15. Almong Y, Reich S, Levy M (1982) Br Polym J 14:131
16. Ober CK, Lok KP (1987) Macromolecules 20:268
17. Paine AJ (1990) Macromolecules 23:3109
18. Paine AJ (1990) Macromolecules 23:3104