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# γ-Ray-initiated dispersion polymerization of PMA in microreactor

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## Abstract

Micron size uniform poly(methyl acrylate) particles are synthesized by γ-ray-initiated dispersion polymerization in microreactor with ethanol–water media using poly(vinyl pyrrolidone) as stabilizer at room temperature. The microreaction technologies can strongly improve polymer particle size distribution. The effects of polymerization parameters, such as temperature, radiation time, radiation dose rate, media and the concentration of the stabilizer, on particle size and size distribution, are studied in detail.

*Keywords:* PMA; Particle size and size distribution; Radiation dispersion polymerization; Microreactor

## 1. Introduction

Micron size uniform polymer particles have received great attention in recent years because of extensive application in a lot of new technical fields [1–3], including instrument calibration standards, column packing material for chromatographic separation [4], support materials for biochemicals [5], clinical examination [6], 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. Micron-grade monodisperse polymer particles have been prepared by complicated emulsion polymerization e.g., in microgravity [7], successive seed [8,9] or multi-stage swollen method [10–12], and modified suspension polymerization [13–15]. Dispersion polymerization is a very attractive method due to its inherent simplicity of the single-step process, which suits not only a wide variety of monomers but also easy functionalization. Generally, dispersion polymerization is initiated with chemical initiator at a definite temperature. The reaction medium should dissolve both monomer and stabilizer. Radiation polymerization is one of the most convenient methods because of its nontemperature-dependent initiation and preparation of polymer particles without pollution of chemical initiators. Especially, it can shorten the nucleation period of polymer in dispersion polymerization, which is beneficial for the preparation of monodisperse polymer particles [16]. The size and size distribution of polymer particles in radiation dispersion polymerization are influenced not only by the monomer, dispersion media and stabilizer but also by the reaction temperature, irradiation fields, etc. Miniaturization of chemical reactors has demonstrated numerous benefits for synthesis, including the control of free-radical branching reaction, improved process conditions, improved conversion and selectivity [17]. Microreactor with a small volume of the reaction zone allows an application of high temperature or reactant concentration gradients, as well as significantly enhanced process control and heat management. Thereby, the unique advantages of microreaction systems are applied to carry out chemical reactions in unusual process regimes or under isothermal conditions [18]. The microreactor used in dispersion polymerization enables optimum reaction conditions to be established to prepare monodisperse polymer microspheres. In our research work, the micron-grade size and monodispersivity of PMA (poly(methyl acrylate)) microspheres were prepared by γ-ray-initiated dispersion polymerization in microreactor. The experiments were carried out in microreactor with ethanol–water media using PVP (poly(vinyl pyrrolidone)) as a typical stabilizer. The effect of temperature, media, monomer concentration, stabilizer concentration and dose rate on the morphology of PMA particles has been studied in detail.

## 2. Experimental

### 2.1. Materials

Methyl acrylate (MA) (Shanghai Chemical Reagent Co.) was purified by distillation to remove inhibitor and stored

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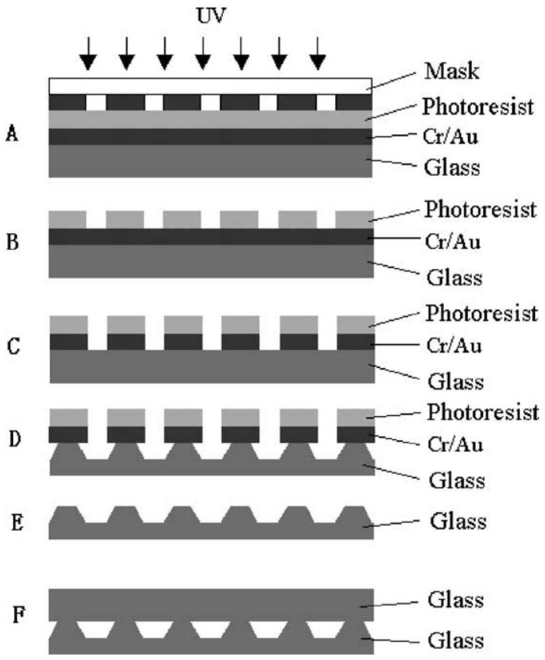

Fig. 1. The scheme of the fabrication of the microreactor.

at −10 °C before polymerization. PVP (Mw $4 \times 10^4$, K-30) was supplied by Shanghai Chemical Reagent Co. Ethanol of chemically pure grade was used without further purification. Deionized water was used throughout this work. Other reagents were of GR grade and used without further treatment.

### 2.2. Fabrication of microreactor

The microreactor is made of glass and was fabricated as follows: as shown in Fig. 1A, the 1 mm thick quartz glass used as substrate is rinsed with organic solvent and deionized water and heated at 200 °C for 30 min. The Cr/Au layer is sputtered on the glass. The 2 μm thick photoresist AZ4620 (Clariant Corp., Japan) is coated on the Cr/Au layer. The mask that had a pattern of the microchannel is laid on the photoresist AZ4620 film, and the microchannel in the photoresist AZ4620 film is made by UV exposure (Fig. 1B). After the hardbaking step of photoresist, the Cr/Au layer is etched by ion-beam etching (Fig. 1C). Then, as shown in Fig. 1D, the glass is etched by using buffered HF at room temperature. The photoresist and the Cr/Au layer are removed with acetone and the scavenger (10 g $Cs(SO_4)_2$ + 10 ml $HNO_3$ + 100 ml $H_2O$) (Fig. 1E). Next, two holes are etched in another piece of glass as the inlet/outlet of microreactor. Finally, as shown in Fig. 1F, two pieces of glass are bonded in an oven at 640 °C for 6 h. The finished microreactor is rinsed with distilled water. The overall dimensions of the microreactor are 40 mm long, 30 mm wide and 2 mm high. The microreactor contains 120 reaction channels. Each microchannel is 50 um wide, 50 um deep and 35 mm long.

### 2.3. Radiation source

$2.22 \times 10^{15}$ Bq $^{60}$Co γ-rays source was used throughout this work. Dose rate used in this work ranges between 30 and 150 Gy/min.

### 2.4. Polymerization

The standard recipe used in this study is as follows: MA 17 wt.%; PVP 5 wt.%; ethanol 71 wt.%; deionized water 9 wt.%; dose rate 68 Gy/min; polymerization time 360 min and temperature 20 °C. The amount of each ingredient was kept constant in all experiments except where indicated. Radiation dispersion polymerization was carried out in the microreactor. The mixtures were filled in the microreactor by pump. Then, the microreactor was irradiated by γ-rays for anticipating time. The γ-rays-initiated dispersion polymerization in a conventional vessel (50 $cm^3$) is carried out under the same reaction conditions (reactant concentration, medium, reaction temperature, irradiation dose rate).

### 2.5. Characterization

The irradiated reaction mixture is diluted with ethanol for getting the desired particle size (PS) and particle size distribution (PSD). The morphology of the resulting PMA particles was determined directly by Nikon OPTOPHOT-100 optical microscope and KYKY-1010B SEM. PS and PSD were measured with JL-9200 High Resolution Laser Particle Size Analyser (Jinan Micro-Nano Instrument Company, China). $D_w$ 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

The principal requirement for the dispersion polymerization process to take place is that the monomer and initiator are dissolved in a liquid that is a nonsolvent for the polymer. The formation of polymer particles in media involves the polymerization reaction of a monomer in an appropriate solvent initiated by a radical and the presence of a stabilizer. Initially, the mixture is clear and transparent but after a short induction period an opaque colloidal dispersion is formed. In this medium, the oligomers grow until a critical chain length is attained. When the phase inversion point is reached, the polymer chains start being insoluble in the medium and aggregate as spherical particles leading to white latexes [19]. Monodisperse polymer particles are only obtained when the initiation is rapid and the periods of repetitive nucleation are short [20]. The γ-ray-initiated polymerization produces free radicals at [21]. The formation of nuclei is completed in a short time after irradiation (about $10^{-6}$ s). Generally, dispersion polymerization is an exothermic reaction. The dissipation of heat will lead to locally overheated areas,

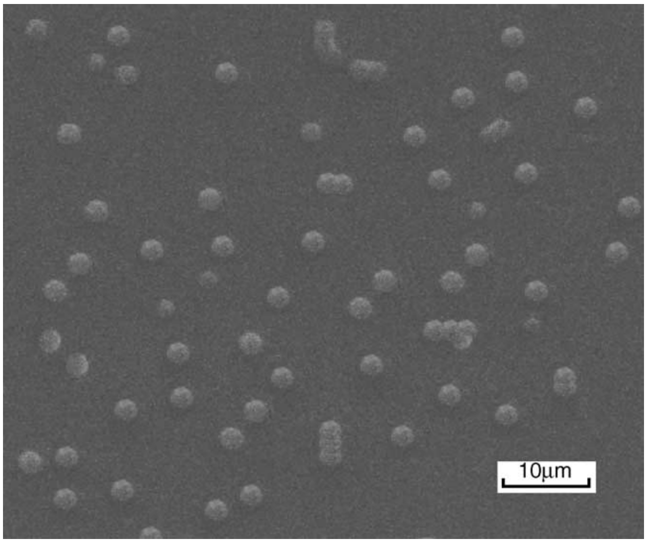

Fig. 2. SEM photographs of PMA microspheres polymerized in the microreactor: dose rate 68 Gy/min; MA 17 wt.%; alcohol 71 wt.%; water 9 wt.%; PVP 5 wt.%; temperature 20 °C; polymerization time 360 min.

which induces nonuniform particle growth in a conventional reactor. Also, the unevenness of dose rate in a conventional usual reactor produces nonuniform particle growth. Compared to a conventional reactor, the microreactor with a very small volume of reaction region allows polymerization to proceed under uniform and constant temperature and dose rate. From Figs. 2 and 3, we can see that the PMA particles prepared by γ-rays-initiated dispersion polymerization in microreactor are of narrower size distribution than those in a conventional reactor. The monodispersivity of PMA particles is improved by using microreaction technology.

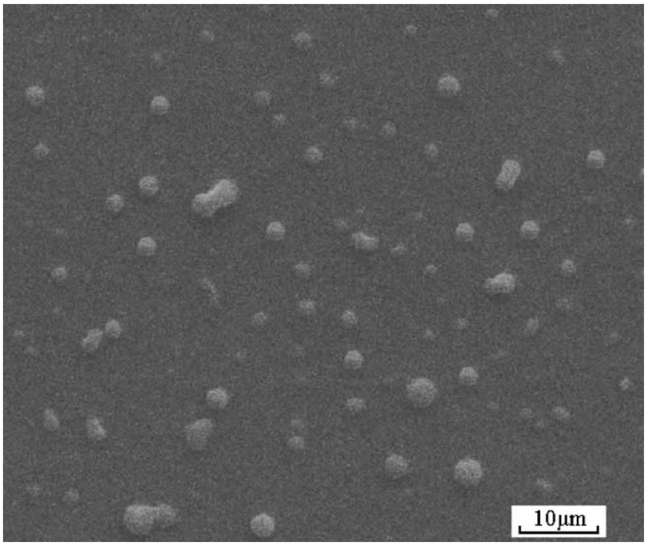

Fig. 3. SEM photographs of PVAc microspheres polymerized in usual vessel: dose rate 68 Gy/min; MA 17 wt.%; alcohol 71 wt.%; water 9 wt.%; PVP 5 wt.%; temperature 20 °C; polymerization time 360 min.

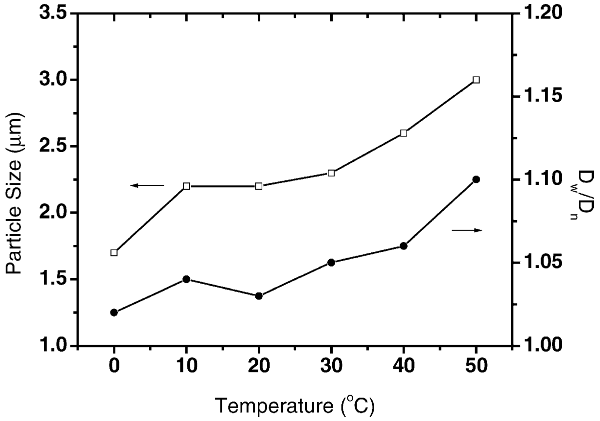

Fig. 4. Effect of temperature on the particle size and particle size distribution: dose rate 68 Gy/min; MA 17 wt.%; alcohol 71 wt.%; water 9 wt.%; PVP 5 wt.%; polymerization time 360 min.

### 3.1. Effect of temperature

As shown in Fig. 4, with increasing polymerization temperature, the PMA particle size becomes large and the PMA particle size distribution broadens. The reasons can be, on the one hand the increase in temperature causes the increase of the oligomer solubility and thus increases critical chain length of the oligomers, resulting in larger size nucleus formation. On the other hand, higher temperature induces reduction of the adsorption rate of PVP, and the coagulation of the nuclei is increased, which results in larger size particles. Particle size distribution tends to broaden due to longer particle formation stage at higher temperature.

### 3.2. Effect of irradiation dose rate

Higher dose rate induces the increase of the concentration of the precipitated oligomeric chains. The aggregation process is enhanced and thus the larger size particles are formed. As shown in Fig. 5, the particle size becomes large

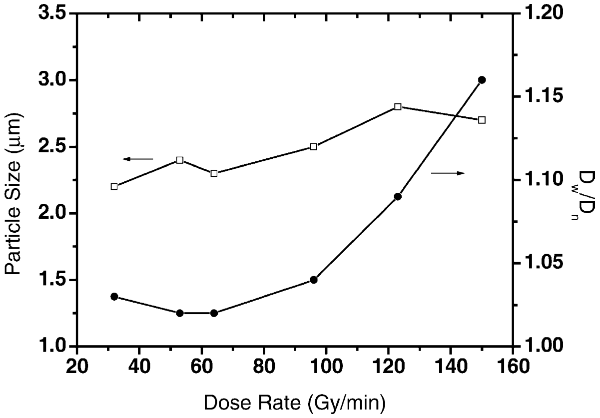

Fig. 5. Effect of radiation dose rate on the particle size and particle size distribution: MA 17 wt.%; alcohol 71 wt.%; water 9 wt.%; PVP 5 wt.%; temperature 20 °C; polymerization time 360 min.

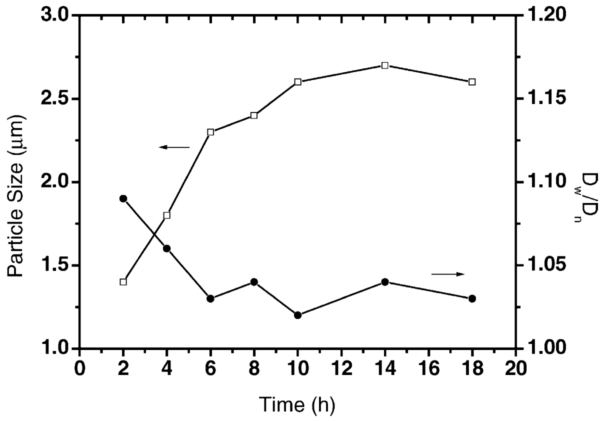

Fig. 6. Effect of polymerization time on the particle size and particle size disribution: MA 17 wt.%; alcohol 71 wt.%; water 9 wt.%; PVP 5 wt.%; temperature 20 °C.

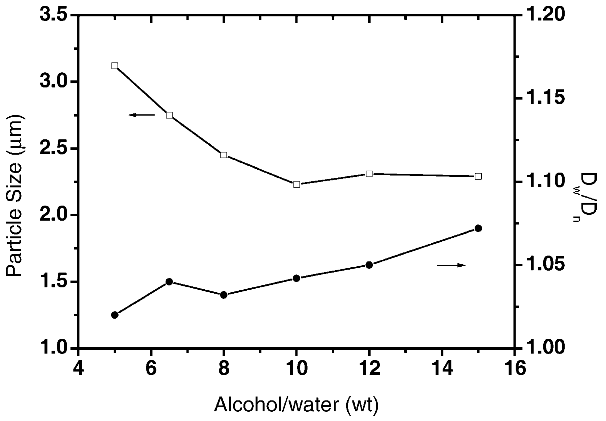

Fig. 7. Effect of alcohol–water ratio on the particle size and particle size distribution: dose rate 68 Gy/min; MA 17 wt.%; PVP 5 wt.%; temperature 20 °C; polymerization time 360 min.

with increasing dose rate. In addition, in the suitable range of dose rate, the dose rate has little effect on resulting particle size distribution. But the very high dose rate results in the broadening of the particle size distribution probably because the rate of oligomer free-radical formation is much larger than that of the adsorption rate of the stabilizer resulting in second nucleation.

### 3.3. *Effect of polymerization time*

The results are shown in Fig. 6. The particle size increases with the increase of the polymerization time, and the particle size distribution becomes narrow. In a typical dispersion polymerization, the stage of primary particle formation is normally completed very quickly, in a few seconds after the start of the reaction [22]. Particle formation in dispersion polymerization must be considered as an irreversible process, i.e. when the particles are formed they are thermodynamically stable. Once the stabilized polymer particles were formed, they were swollen by monomer because of the monomer partition in both continuous and particle phases [23,24]. The polymerization continued to occur in the particles as long as they could continuously capture radicals formed in the continuous phase. New particles are not produced and the number of the particles is constant in the particle growth stage. So the polymer particles become large with the prolongation of the polymerization time. The particles size becomes uniform because little particles grow faster than large particles during polymerizing processes.

### 3.4. *Effect of media*

The ratio of ethanol to water as a function of particle size and particle size distribution of PMA is shown in Fig. 7. The lower ratio of ethanol to water causes the larger size PMA particle formation as polymerization is performed in the microreactor. The result is inconsistent with the result of polymerizing in a conventional reactor. The authors suppose that the process of formation and growth of the particles is strongly dependent on the solubility parameters of the resulting polymer in the dispersion medium. Ethanol is a better solvent for PMA than water. Generally, with increasing ethanol content in the media, the resulting particle size increases due to increasing solubility of oligomers and therefore increasing critical oligomer chain length. PVP as a stabilizer has the tendency of being absorbed on the body surface. In microreaction systems, before the primary particle formation, a large part of PVP is absorbed on the surface of the microreactor's inner walls because of very large surface-to-volume ratio of the microreactor, which induces the decrease of "free" PVP in the solution. In the nuclei formation step, the critical chain length in the media of lower ratio of ethanol to water is shorter than that in the media of higher ratio of alcohol to water and thus lower size nuclei are produced. The smaller nuclei easily coagulate to form larger size nuclei under the relative low "free" PVP conditions and the number of stabilized nuclei decreases, which results in the larger particle formation [25]. The increase in ratio of ethanol to water causes broad particles size distribution because of the long duration nucleation.

### 3.5. *Effect of PVP content*

The data in Fig. 8 shows that the particle size decreases with increasing concentration of PVP (3–9%). At the concentration of PVP above 9%, the particle size is constant. A higher PVP concentration produces faster stabilizer adsorption, and hence a greater number of particles are stabilized during the primary stabilization processes, which causes the formation of smaller size particles. As PVP content outreaches the saturation adsorption of the particles, the superfluous PVP play little role in preventing the particles from aggregation. So the particle size is not influenced by further increase of PVP concentration. From Fig. 8, one can find the optimum PVP concentration to prepare the desired size of the PMA particles.

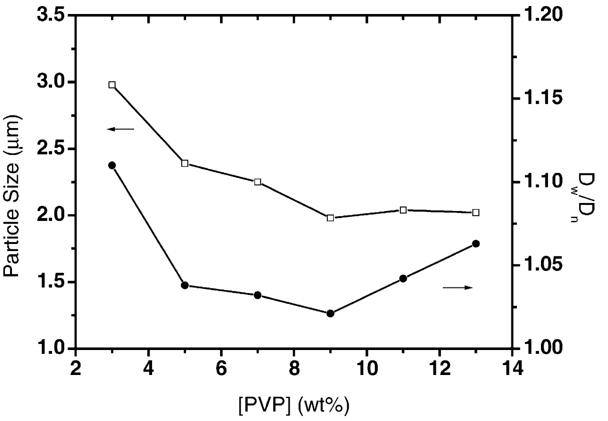

Fig. 8. Effect of PVP concentration on the particle size and particle size distribution: dose rate 68 Gy/min; MA 17 wt.%; alcohol 71 wt.%; water 9 wt.%; temperature 20 °C; polymerization time 360 min.

## 4. Conclusions

Uniform size particles of PMA can be prepared by radiation-initiated dispersion polymerization in microreactor using PVP as a stabilizer with alcohol–water media at room temperature. The increase of the reaction temperature, radiation dose rate and polymerization time, respectively, causes the larger size particle formation. But the particle size decreases with the increase of the ratio of alcohol to water and the PVP content. Generally, narrow size distribution particles are produced with lower temperature, longer polymerization time, suitable radiation dose rate, ratio of alcohol to water and PVP content.

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