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ORIGINAL CONTRIBUTION

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# A one-step method to prepare monodisperse polymer particles in the micron size range

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**Abstract** Micron-sized, monodisperse PMMA microspheres were produced in TEOS, under static condition by one step. The mechanism of this novel self-formation method was studied based on experiment results; it was found that the growth of PMMA microspheres was in two ways. The properties of the intermediate particles were studied by several methods. The size of finally obtained polymer particles could be controlled by adjusting the content of monomer in initial polymerization solution. The influence of the polymerization temperature on the preparation of polymer microspheres was also investigated.

**Keywords** Monodisperse · Polymer microsphere · One step · Static condition · Self-formation method

## Introduction

The preparation of polymer microspheres has drawn great interest because of their various applications [1, 2, 3, 4, 5, 6,7]. Furthermore, micron-sized, monodisperse polymer particles have been found many applications in the biomedical field, microelectronics, and etc. Many researchers studying polymer colloids are concentrating their attention on the production of such particles [8, 9, 10, 11,12]. So far, the seeding method is one of the most important ways to prepare monodisperse polymer particles with micron-sized diameter. Using this method and other related methods, the polymer particles were produced in size from several micronmeters to hundreds of micronmeters [13, 14, 15, 16, 17, 18,19]. However, preparing the seed particles with high monodispersity and controlling polymerization in this multistep experimental procedure are not so easy from the standpoint of process control to this method.

On the other hand, polymer microspheres prepared without any emulsifier are more advantageous owing to their clear surface. There have been several novel approaches to the preparation of polymer microspheres without addition of emulsifier or stabilizer [20, 21, 22,23]. As is well known, in the absence of emulsifier, it is difficult to design the polymerization recipes to finally obtain a stable microsphere dispersion, especially for the preparation of polymer microspheres with micrometer size range.

In this paper, we report a novel approach to prepare well-defined poly(methyl methacrylate) (PMMA) spheres with a narrow size distribution in static tetraethoxysilane (TEOS) medium by a stabilizer-free polymerization method. The formation mechanism discussed was based on the experiment results. It was found that there were two different ways in which polymer particles grew up. The size of the PMMA particles could be controlled in the micrometer range by varying the ratio of TEOS/MMA in initial polymerization solution. It is well known that TEOS is an important precursor in sol–gel method; therefore, if needed in sol–gel procedure, the product obtained can be directly applied without further purification or separation. Another interesting characteristic of this synthesis is that no mechanic stirring is needed in the formation of well-defined PMMA microspheres, i.e., a self-formation process is performed under static condition.

## Materials and methods

### Materials

Methyl methylacrylate was purified by washing with 5% NaOH solution, then with distilled water until neutral. The washed monomer was dried over anhydrous $Na_2SO_4$, and then distilled under reduced pressure. The initiator azobis(isobutyronitrile) (AIBN) was recrystallized from alcohol. Tetraethoxylisane (TEOS) was purified by distillation under reduced pressure. The distilled above all chemicals were purchased from Beijing Chemical Co. in reagent grade.

### Study of formation mechanism

In order to study the formation mechanism of PMMA microspheres, a polymerization solution of 15 ml MMA and 30 ml TEOS was prepared with AIBN initiator (1 wt% relative to MMA). A set of samples of 4 ml of the mixture were introduced into glass tubes, respectively. Each tube was sealed with a silicon rubber stopper. Free-radical polymerization of MMA were performed in static TEOS medium at 70 °C. At certain time intervals during the polymerization, a sample was taken out of the reactor and poured into 50 ml cold petroleum ether to stop the reaction. The as-made products were separated by centrifugal separation, then cleaned using six cycles of centrifugation (5,000 *g*), supernatant removal, and resuspension in 10 ml of petroleum ether. Finally, the PMMA microspheres obtained were dried in air.

### Preparation of PMMA microspheres

MMA, TEOS, and AIBN were weighed into 12-ml glass tube which sealed with a silicon rubber stopper. After mixing for 15 min with shaking, the mixture was then polymerized at a constant temperature for 12–48 h under static condition. The as-made PMMA particles were purified by following the same procedures as described in above section.

### Gravimetrical determination of TEOS in PMMA particles

After purification following the above procedures, the particles obtained (5 g) were dispersed in the mixture of ammonia (25 wt%)–methanol with a volume ratio of 1:2 (200 ml). The hydrolysis of TEOS existing in the inner part of the prepared particles was performed in this medium at ambient temperature for 5 weeks. The amount of TEOS was determined gravimetrically by measuring the solid $SiO_2$ content after removal of PMMA and other organic compounds by calcination at 500 °C for 5 h.

### Analyses

TGA was performed with a PerkinElmer 7 Series thermal analyzer at a heating rate of 20 °C $min^{-1}$. The average size, size distribution, and surface morphology of as-made specimens were examined using a JSM35CF SEM instrument.

## Results and discussion

### Mechanism of formation

#### *The change tendency of size and weight*

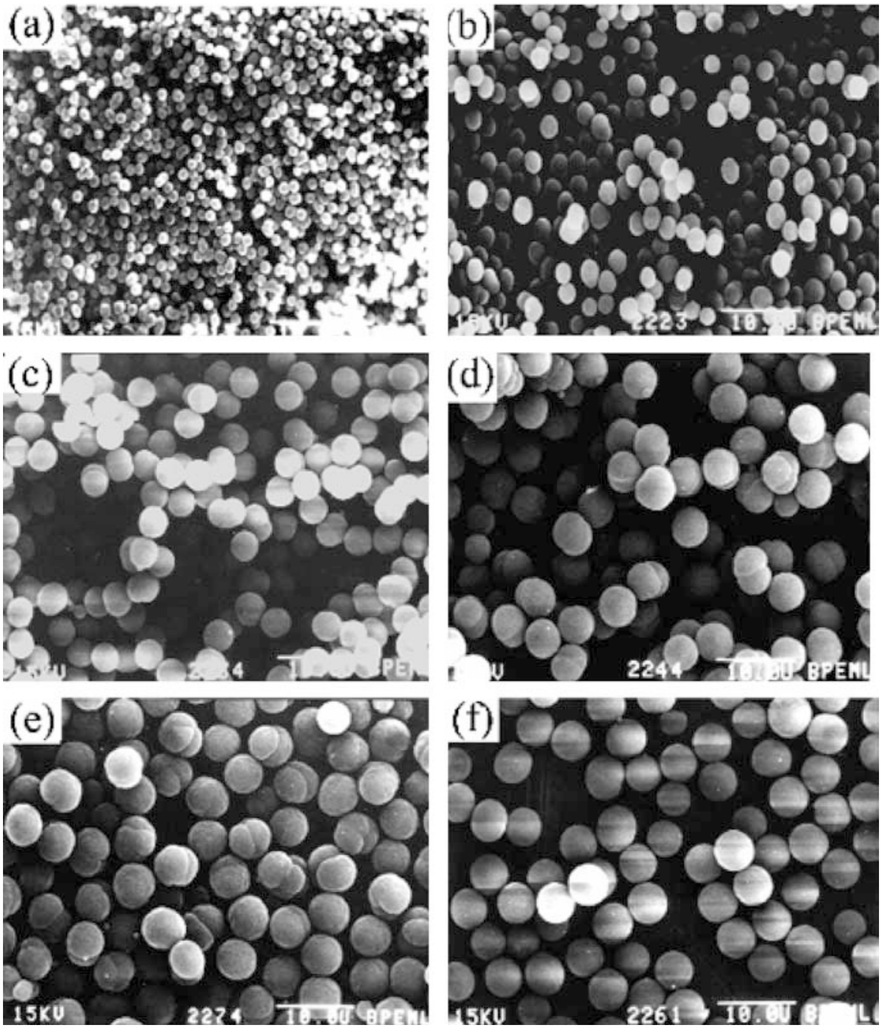
SEM photomicrographs of PMMA particles obtained at certain time intervals during the polymerization are shown in Fig. 1. It is obvious that, at earlier stage, as the time allowed for polymerization is increased, larger PMMA microspheres are formed. In other words, PMMA particles grow gradually from small spheres to larger one in the process of polymerization. In the meantime, the rate of change in the weight of the PMMA particles obtained increased during the process. The size and weight of obtained microspheres were plotted as a function of polymerization time in Fig. 2 to show this tendency; it is noticeable that there are abrupt increases in both size and weight at earlier stages of synthesis.

The mechanism of above phenomena is tentatively proposed as follows. In this system, it is well known that MMA and TEOS are miscible with each other; PMMA can be dissolved in MMA, but not in TEOS. Hence, at the beginning of this synthesis, the polymerization solution was transparent. However, with the proceeding of polymerization of MMA, the ratio of PMMA in polymerization solution increased with the consuming of MMA; therefore, PMMA began to separate from solution at a certain stage of the polymerization because of its insolubility in TEOS, and small PMMA particles naturally formed. These small particles created seeds on which further polymerization took place, because monomer polymerized much faster on the seeds than in solution due to gel effect. The gel effect results in the abrupt increase in size and weight of obtained PMMA microspheres, as shown in Fig. 1. We can also observe that there was no significant growth in both size and weight at final stages.

#### *Change from multicore particles to spherical particles*

Figure 1 also shows that a large number of particles apparently constituted by two or more sections, which indicates that the size of PMMA spheres can also increase by an unusual route, besides the gradual polymerization of MMA on seeds as discussed above. In the process of polymerization, two or more small particles could meet and adhere to each other because they were swollen by MMA at earlier stages. These multicore particles merged into a larger one and gradually transformed to spherical shape also because of their elastic property in swollen state. At earlier stages, as shown in Fig. 1a–e, it is easier for polymer particles to coagulate one another, owing to the high content of MMA in the polymerization solution; therefore, many multicore particles were found. Furthermore, the shape

**Fig. 1a–f** *SEM* images of *PMMA* particles obtained at certain time intervals during the polymerization at 70 °C: **a** 45 min; **b** 75 min; **c** 120 min; **d** 165 min; **e** 210 min; **f** 255 min



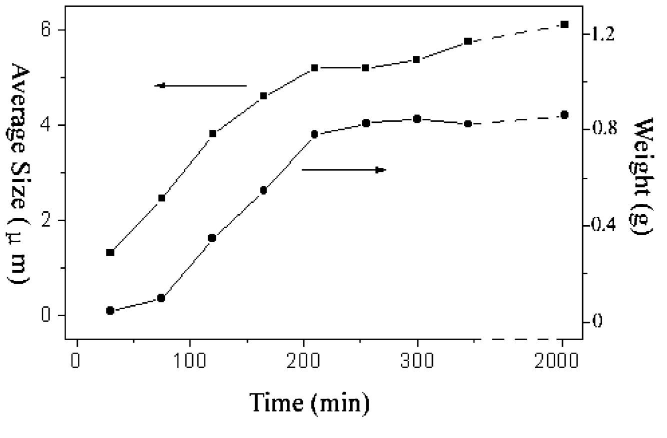


**Fig. 2** Changes in (**a**) average diameter of the PMMA particles, (**b**) weights of the corresponding polymer product during the preparation process

of these particles could change easily at these stages; we can observe that the different intermediate fashions, from peanut-shaped through ellipsoid to well-defined sphere. On the contrary, at final stages, as shown in Fig. 1f, the multicore particles seldom appeared in obtained samples as a result of the consuming of MMA. Meanwhile, it should be noted that there were grooves appeared on the surface of particles, as shown in Fig. 1c–e, which were significant evidences to indicate the merger of two or more small particles into a larger one. Finally, the grooves disappeared because the faster polymerization of MMA in these grooves than on the particle surface.

## Characterization of the intermediate particles

### *TGA study*

The characterization of the intermediate particles were studied by analyzing the particles obtained at different intervals in the process of polymerization. All samples were thoroughly washed as described in the Experimental part. Typical thermogravimetric analysis (TGA) curve of intermediate particle is given in Fig. 3. The TGA curve in Fig. 3a reveals three distinct weight losses occurring in the following temperature ranges: 30–100, 100–200, and 320–400 °C. The first zone can be attributed to desorption of water and MMA, while the second weight loss corresponds to TEOS desorption. The third weight loss is obviously due to PMMA decomposition in the temperature range 320–400°C. The weight losses in these temperature intervals are 9.39, 10.5, and 80.11 wt%, respectively; however, as shown in Fig. 3b, there are no distinct weight losses in the range 30–200 °C in the TGA curve of sample obtained with longer polymerization time. The above phenomena indicated that certain amounts of TEOS and MMA coexisted in the inner parts of intermediate particles at earlier stages.

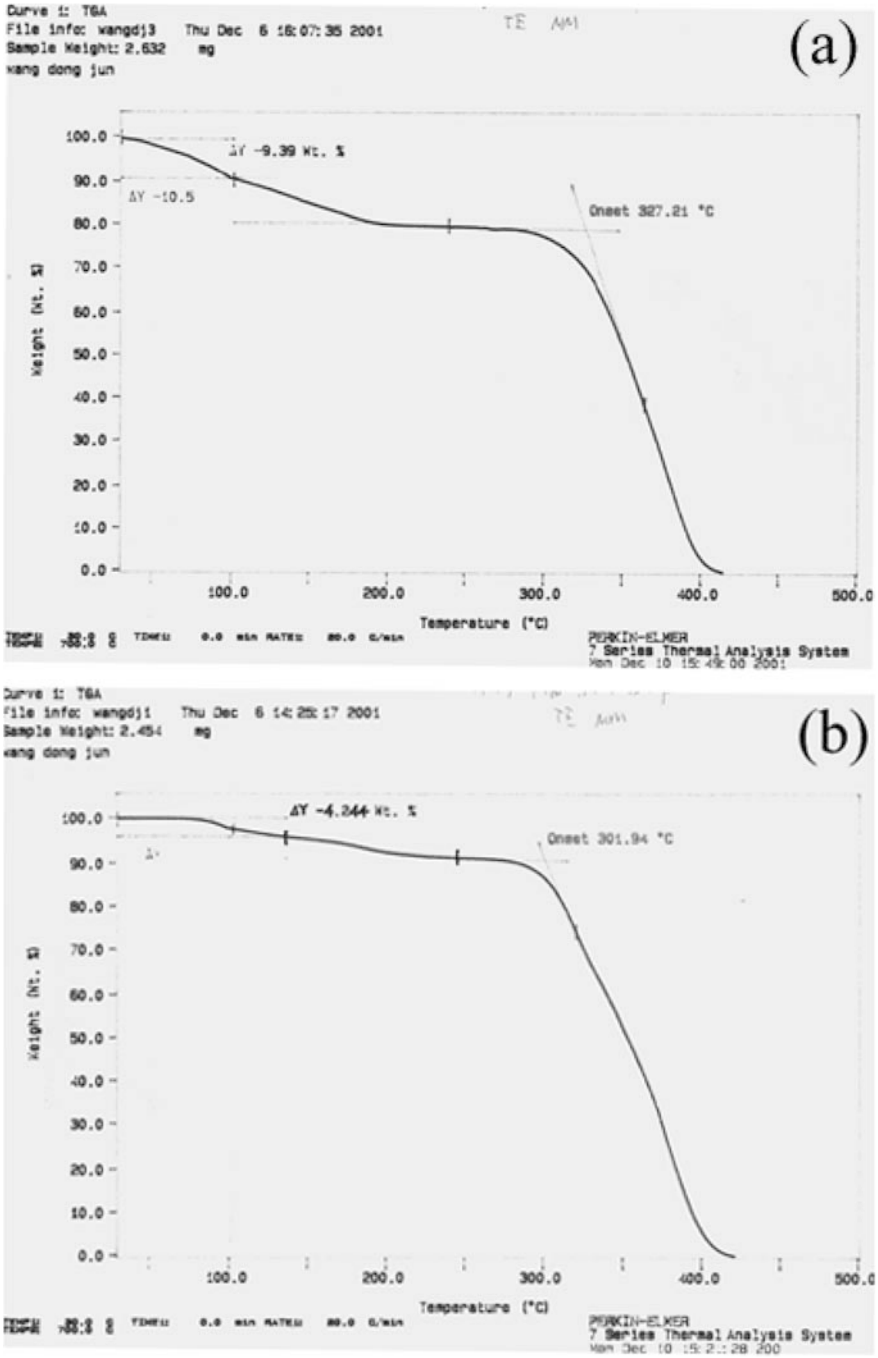


**Fig. 3** TGA curves of the intermediate particles obtained at different times during the polymerization at 70 °C: **a** 75 min; **b** 255 min. The volume ratio of MMA/TEOS in polymerization solution is 1:2

### *Determination of TEOS by gravimetrical method*

The amount of TEOS in the inner parts of these particles was also determined by gravimetrical method, following the procedures described in the Experimental section. PMMA particles could be swollen by methanol; hence, hydrolysis reaction of TEOS to yield $SiO_2$ occurred simultaneously with the proceeding of swell in the inner parts of these particles. The silica contents in the same two samples as in Fig. 3a and b were determined gravimetrically after calcination of PMMA and other organic compounds. From these data, the quantities of TEOS in the two samples could be calculated, 8 and 1 wt%, respectively. Compared with the results of TGA, the data obtained by the above two methods are in agreement under our experimental conditions.

### *Surface morphology change as the result of volatilization of MMA and TEOS*

Another interesting phenomenon is that the same intermediate particles as in Fig. 3a shrunk into cauliflower-like particles after dried at 50 °C under vacuum for 8 h. This phenomenon contributes to the volatilization of small molecule, namely MMA and TEOS, from the inner parts of these particles. The SEM image showing the detailed surface morphology of these cauliflower-like particles is given in Fig. 4. However, there was no obvious change on the surface of the sample with long polymerization time after the same drying procedure.

The above several results clearly indicate that the intermediate particles contain certain amount of TEOS and unpolymerized MMA in their inner parts. At earlier stages, both MMA and TEOS existed in the intermediate particles because of their miscible property. With the consuming of MMA in the polymerization process, TEOS had to diffuse from the core of PMMA particles to the surfaces. Therefore, we could find above evidences that TEOS and MMA coexisted in the intermediate particles; however, little amounts of them were found in the sample with a long polymerization time.

**Fig. 4** Morphology of the same intermediate particles as shown in Fig. 3a after drying at 50 °C under reduced pressure for 24 h

## Properties of the final microspheres obtained

### *Size control by adjusting the ratio of MMA/TEOS*

Apart from the time dependence of the sphere size, as discussed in previous section, the dependence of the microsphere size on MMA/TEOS ratio in the initial polymerization solution was also observed. Another set of polymerizations was performed by changing the MMA-to-TEOS volume ratios between 1:14 and 3:4. As shown in Fig. 5, the size of the as-made microspheres clearly decreases with decreasing the volume ratio of MMA to TEOS in the initial polymerization solution; which average sphere diameter in the range from 1.2 to 7 μm. This case is an expected result because less monomer is available for the polymerization on each seed particle in the presence of lower monomer/TEOS ratio. Furthermore, the chance that the particles meet each other is also lower compared with higher corresponding ratio under identical reaction conditions. From the results presented here, it is clarified that the size of microspheres prepared by this method can be easily controlled, with a micrometer size range, by adjustment of the ratio of MMA to TEOS in initial solution. We have found that if the ratio of MMA/TEOS lower than 1:14 was used, smaller PMMA particles were achieved; however, the yield of PMMA particles was too low. On the other hand, it should be pointed that the diameter of the largest particles prepared under the present experimental conditions was limited below about 8 μm, because large aggregation of solid polymer appeared in samples with TEOS/MMA ratio more than 3:4.

### *Linkage of microspheres*

Figure 5d also shows that eyelike areas appeared on the surface of PMMA spheres; the number and position of the eyelike areas are irregular. The decrease in TEOS/MMA ratio led to smaller size of eyelike area, and smooth surface was observed when the samples prepared with MMA/TEOS ratio lower than 1:2 in initial solution, as shown in Fig. 5a–c. This phenomenon is related to the linkage of PMMA spheres for the samples prepared with higher MMA/TEOS ratios. This happens because there is not enough medium at TEOS to cover the surface of the solid spheres during the final stage for

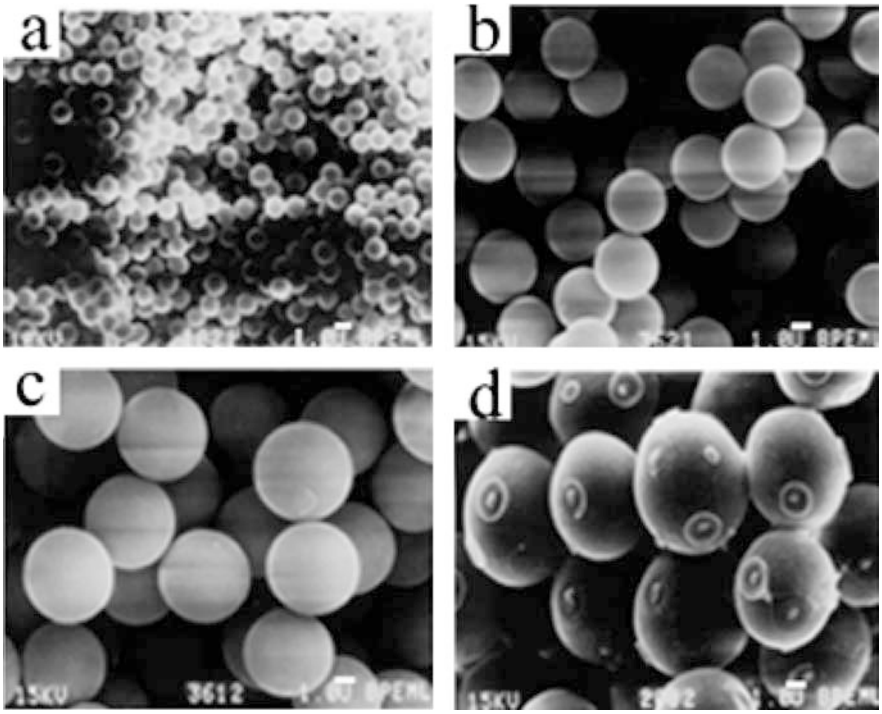


**Fig. 5** SEM pictures of PMMA microspheres prepared with different MMA/TEOS volume ratios in polymerization solution at 70 °C for 48 h: **a** 1:14; **b** 1:8; **c** 1:4; **d** 3:4

the samples with higher MMA/TEOS ratios. Furthermore, bigger microspheres tend to sink to the bottom of reaction vehicle due to PMMA to higher density than TEOS; therefore, microspheres contact each other. For lower MMA/TEOS ratio, TEOS can effectively prevent PMMA spheres to attach each other in the process of preparation.

### *Size distribution*

A representative SEM photograph of the final product prepared by the present method at 70 °C for 36 h with the TEOS/MMA volume ratio of 3:4 is shown in Fig. 6, which illustrates the copiousness in quantity and the uniformity in size distribution.

## The effect of polymerization temperature

The influence of polymerization temperature on the formation of PMMA microspheres was examined by changing the temperature in the range from 50 to 90 °C. There was no significant difference in the size of the obtained microspheres by changing the polymerization temperature in the studied range. However, preparation time of microsphere sample was shorter at higher temperature because of the faster reaction rate.

It should be noted here that the fraction of multicore particles in obtained samples increased with the increasing of polymerization temperature. A typical SEM photograph of sample produced at 90 °C is given in Fig. 7. As seen in Fig. 7, multicore particles with different shapes could be found easily throughout the sample. As we have discussed earlier, polymerization of MMA reacts faster at higher polymerization temperature. Consequently, the intermediate particles had not enough time in elastic state for the change from multicore particles to spherical particles under higher tem-

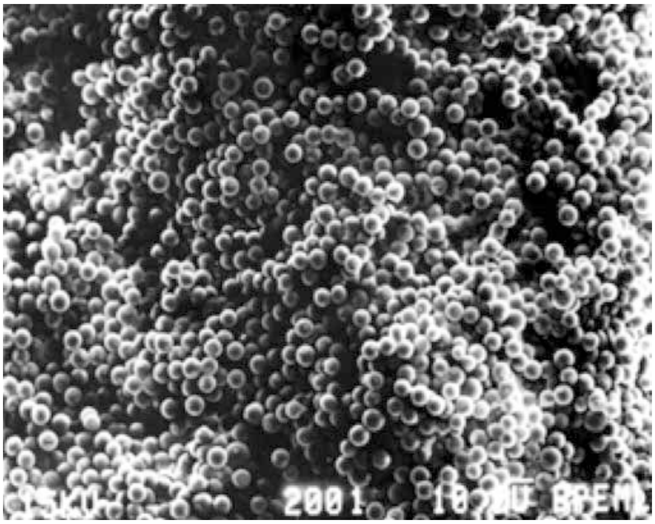


**Fig. 6** SEM image of a typical sample produced with an MMA/TEOS volume ratio of 3:4 in polymerization solution at 70 °C for 48 h

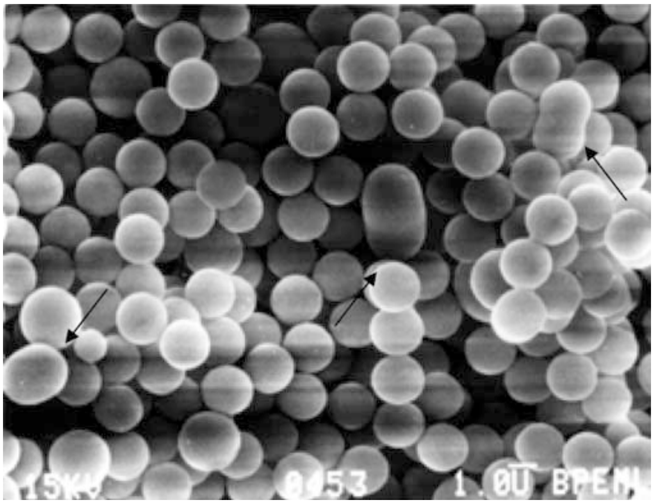


**Fig. 7** SEM picture of PMMA particles prepared with an MMA/TEOS volume ratio of 1:10 in polymerization solution at 90 °C for 24 h

perature condition. Namely, the rapid consuming ratio of MMA made the elastic intermediate particles exist in short time; the final obtained particles could keep in the shape of multicore or ellipsoid.

## Conclusion

This work introduced an novel technique, as called self-formation method, to prepare well-defined PMMA microspheres with a narrow size distribution. In the growth of these microspheres, an abrupt increase in microsphere size and weight at earlier stages of synthesis was observed due to the gel-effect. It was found that the intermediate particles contained certain amounts of TEOS and MMA, which resulted in the elastic property of the intermediate particles and cauliflower-like morphology after volatilization of MMA and TEOS. Using the present method, it is easy to control the PMMA particle size in the micrometer range. This simple, direct method may provide another example of preparing polymer microspheres.

In this paper, we have found that there were several characteristics of this self-formation method different from previously reported methods:

1. Monodisperse polymer particles in the micron-size range were easily prepared in one step in static condition.
2. Without the protection of stabilizer, the merger of two or more small particles into a bigger one was an important way for the particle growth.
3. The size of finally obtained polymer microspheres could be controlled by varying the formation of the initial polymerization solution.

The study of preparation of PMMA microspheres by using MMA–TEOS system has given an initial example for this novel preparation technique; it has theoretical significance for further investigation in other systems under static condition without stabilizer, other than MMA and TEOS. So far, it is not clear yet why the particles in polymerization solution can keep individual and do not aggregate to large deposition; this may be attributed to that there is an optimal interfacial tension between PMMA particles and TEOS medium. In other words, TEOS not only play the role of medium, but also play the role of stabilizer. We believe that this procedure can be extended to other systems having the same properties. It has been found that some kinds of comonomer, such as maleidide or N-substituted maleimide, can be added into this system to form copolymer microspheres with MMA. However, the presence of many other kinds of monomer will drastically impact the formation of polymer particles. It is obvious that further work should be done to clarify the mechanism leading to the self-formation of polymer or copolymer microspheres in proper medium. On the other hand, we have found that there is an easy way to prepare hollow or core–shell $SiO_2$ microspheres using this MMA–TEOS system, in which only two main procedures will be required; this research is still under investigation.

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