Preparation of Polymer Micropheres in TEOS under Static Condition

Dongjun Wang,[†,††] Chenbin Gu,[†] Yongguo Zhou,[††] Xinqiu Wang,[†] Zhen Zhen,[†] Fangqiong Tang,[†] and Xinhou Liu*[†]
[†]*Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, 100101, P. R. China*
[††]*Heibei Vocation-technical Teacher' college, Changli, 066600, P. R. China*

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Well-defined PMMA microspheres have been synthesized in TEOS under static condition by one step, the formation and size control of the microspheres are discussed.

The synthesis of polymer microspheres has been of great interest, because of their applications in catalysis, separations, photonics, etc.[1–4] So far, there have been some novel approaches to the preparation of polymer microspheres. The seeding method is one of the most important ways to prepare micron-sized polymer particles.[5–7] Polymer microspheres prepared without any emulsifier are more advantageous on account of their clear surface; therefore, many researchers are concentrating their attention on this preparation.[8–10] In this paper, we describe a successful approach to prepare micron-sized ploy(methylmethacrylate) (PMMA) spheres with a narrow size distribution in tetraethoxysilane (TEOS) by a stabilizer-free polymerization method. It is well known that TEOS is an important precursor in sol-gel method, therefore, if needed in sol-gel procedure, the obtained product can be directly applied without further purification or separation. An interesting characteristic of this synthesis is that no mechanic stirring is needed in the formation of well-defined PMMA microspheres, that is, a self-formation process is performed under static condition.

In a typical preparation, a polymerization solution of MMA and TEOS was prepared with AIBN initiator (1 wt% relative to MMA). Radical polymerization of MMA was performed in static TEOS medium at 70 °C. The samples were dispersed into cold 100 ml methanol after polymerization for certain time. The obtained products were separated by centrifugal separation, and then washed five times with petroleum ether.

As shown in Figure 1, at early stage PMMA microspheres grow with reaction time. In the meantime, the product weight had a tendency to increase. It is noticeable that there are abrupt increases for both size and weight at the earlier stages. The mechanism of above phenomena is tentatively proposed as follows. 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 create seeds on which further polymerization took place, because monomer reacts much faster on the seeds than in solution owing to gel effect. The gel effect also results in the sudden increase of size and weight of obtained product. There is no significant growth in both size and weight at final stages. The reason why these particles in polymerization solution can keep individual and do not aggregate to large deposition may be attributed to the optimal interfacial tension between solid PMMA particles and TEOS medium in this TEOS-MMA-PMMA system.

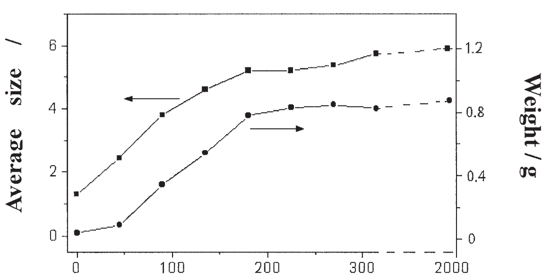

Figure 1. Changes in (a) average diameter of the PMMA particles, (b) weights of the corresponding polymer product during the preparation process. The volume ratio of MMA/TEOS in polymerization solution is 1/2, 4 ml of this solution for each sample.

Figure 2 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, that is, two or more small particles merged into a larger one in the process of polymerization. In this process, polymer spheres were swollen by MMA, they can adhesive to each other, and then these multi-core particles may gradually transform to spherical particles because of their elastic property. At earlier stages, as shown in Figure 1(A), it is easier for polymer particles to connect each other, owing to the high content of MMA in the polymerization solution. Furthermore, the shape of these particles is readily change at these stages, we can observe the different intermediate fashions, from peanut-shaped, through ellipsoid, to well-defined sphere. On the contrary, at final stages, the above phenomena cannot be observed as a result of the consuming of MMA.

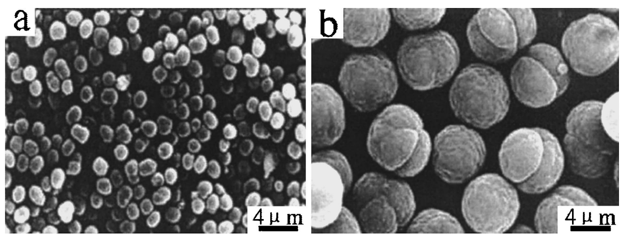

Figure 2. SEM pictures of multi-core particles in the process of preparation. (a) 30 min (b) 300 min. The volume ratio of MMA/TEOS in polymerization solution is 1/2.

As shown in Figure 3, the size of final obtained PMMA particles can be controlled, in the range from 1 μm to 8 μm, by adjusting the volume ratio of MMA/TEOS in the initial polymerization solution. For lower MMA/TEOS ratio, less monomer is available for the polymerization on each seed particle, meanwhile, the probability of small particles connecting to each other is lower, therefore, smaller particles is formed. However, it should be pointed that the diameter of the largest

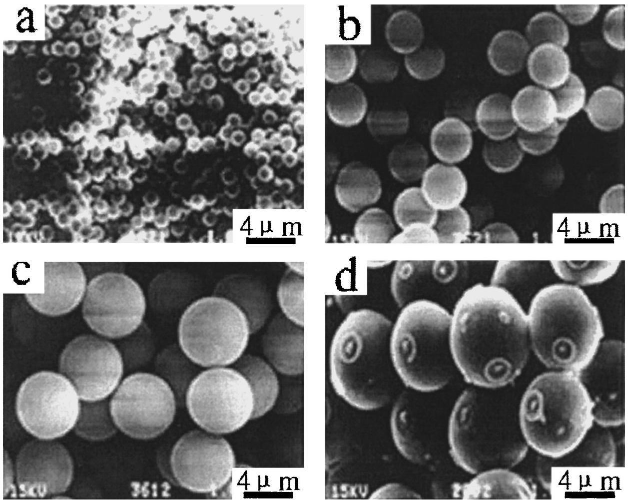

Figure 3. SEM pictures of PMMA microspheres prepared with different MMA/TEOS volume ratio in polymerization solution for 36 h: (a) 1/14 (b) 1/8 (c) 1/4 (d) 3/4.

particles prepared is limited below ca. 8 μm, because large aggregation of solid polymer was found in samples with TEOS/MMA ratio more than 3/4.

Figure 3(d) also shows that eye-like areas appeared on the surface of PMMA spheres; the number and position of the eye-like areas are irregular. Lower TEOS/MMA ratio leads to smaller size of eye-like area, and finally smooth surface was observed with MMA/TEOS ratio lower than 1/2 in initial solution, as shown in Figure 1(a, b, c). This happens because bigger microshperes tend to sink to the bottom of reaction vehicle as PMMA has higher density than TEOS, therefore, microspheres contact each other. For lower MMA/TEOS ratio, the smaller PMMA spheres disperse well in TEOS throughout the preparation.

It is obvious that further work should be done to clarify the mechanism leading to the formation of stable microspheres in the special example of dispersion polymerization. The application of this method in sol-gel procedure is still under investigation.

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