

Note

PREPARATION OF CAULIFLOWER-LIKE PMMA PARTICLES AND THEIR FORMATION MECHANISM^{*}

Dong-jun Wang^{a,b}, Xin-qiu Wang^a, Dan-dan Jia^b, Qun Luo^a, Zhen Zhen^a and Xin-hou Liu^{a**}

^aTechnical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100101, China

^bDepartment of Chemistry, Hebei Vocation-technical Teacher's College, Qinhuangdao 066600, China

Abstract A simple technique for preparing cauliflower-like PMMA particles by a self-formation method is proposed. PMMA particles can be obtained with tunable surface morphology by varying the polymerization time. Experimental results show that the formation of these cauliflower-like particles can be attributed to the special particle growth mechanism in the self-formation method.

Keywords PMMA, Particle, Preparation, Self-formation method

Polymer microspheres are now widely used in the fields of biomedical engineering, coatings, microelectronics, cosmetics, *etc.* Their uses in these areas not only require that the polymer particles have controlled size and state, but also that the particles must have designed morphologies. Several methods have been commonly used for the synthesis of micron-sized polymer particles, including suspension polymerization, mechanical comminution, and solution precipitation^[1, 2], but their particle morphology cannot be easily controlled by any of these methods. An activated swelling method was proposed to produce polymer particles with topological morphology^[3], rugby-ball-like polymer particles were prepared by utilizing the dynamic swelling method^[4]. Polymethyl methacrylate (PMMA) particles with several different morphologies were also produced by the spray drying technique^[5].

As is well known, polymer particles are prepared under the protection of stirring and addition of stabilizer in conventional fabrication techniques, such as dispersion polymerization and emulsification polymerization. We have previously proposed an novel method to prepare micron-sized polymer microspheres and monodispersed PMMA particles were obtained in static tetraethoxysilane (TEOS) medium without stabilizer^[6]. In this method, no exterior influence was imposed on the reaction system. Therefore, we called this technique the self-formation method, which is another special type of deposition polymerization.

The possibility of employing the above technique to fabricate PMMA particles with cauliflower-like morphology is reported in this paper. It was found that PMMA particles with tunable surface morphology could be obtained by varying the polymerization time of MMA. The formation of this morphology could be attributed to the special growth mechanism and the shrinkage of these polymer particles. This attempt was motivated by the fact that cauliflower-like PMMA particles can be used more efficiently in some applications, *e.g.* as catalytic substrates and in biomedical engineering.

The cauliflower-like PMMA particles were prepared as follows: a polymerization solution of 5 mL MMA and 15 mL TEOS was prepared with AIBN as initiator (1 wt% relative to MMA). After shaking the mixture for

^{*} This project was supported by the National Nature Science Foundation of China (Nos. 20204018 and 20374058).

^{**} Corresponding author: Xin-hou Liu (刘新厚), E-mail: wddj9999@263.net

15 min, the solution was then polymerized at 70°C for 4–48 h under static condition. The obtained product was separated by centrifugal separation, then redispersed in 20 mL petroleum ether and centrifuged (5000 r/min) to purify the product. Finally, the obtained PMMA microspheres were dried under vacuum at 50°C for 8 h.

Figure 1 shows the morphologies of PMMA particles prepared at different polymerization time. These SEM pictures reveal that cauliflower-like particles were achieved after drying at 50°C under vacuum; furthermore, the surface morphologies of these particles changed gradually with the polymerization time of MMA. Finally, smooth surface microspheres were obtained with long polymerization time after the same drying procedure. It should be noted that the surface of the microspheres obtained at the earlier polymerization stage was smooth before the drying procedure, as shown in the inset of Fig. 1(a) (particle was deformed in this picture under the SEM electron beam). These results indicated that the formation of cauliflower-like particles resulted from the shrinkage of particles with smooth surface.

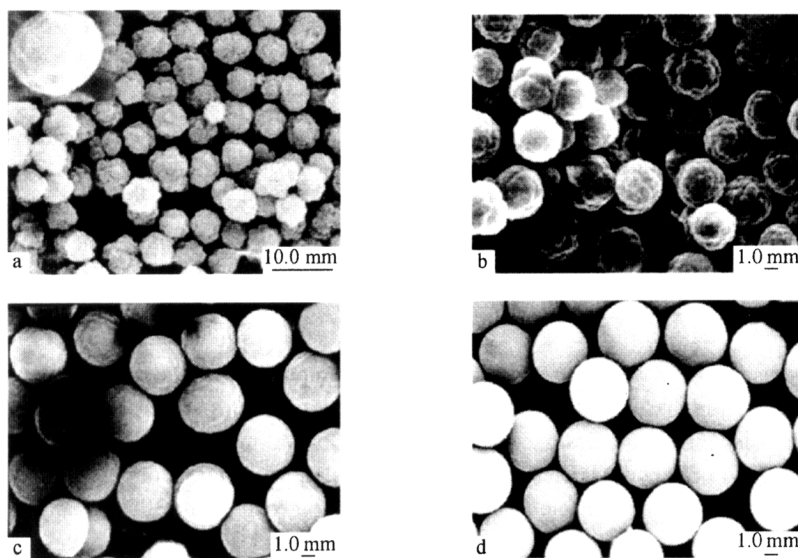


Fig. 1 Typical SEM microphotographs of PMMA particles prepared at different polymerization time a) 5 h; b) 10 h; c) 20 h; d) 48 h

The TGA curves in Fig. 2 reveal three distinct weight loss regions occurring in the following temperature ranges: 30–100, 100–200 and 320–400°C. The first region can be attributed to the desorption of MMA and other small molecules, 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. In these samples, weight losses decrease with increasing polymerization time in the range of 4–48 h.

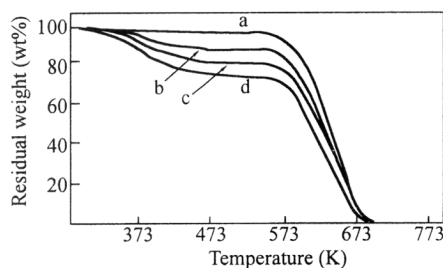


Fig. 2 TG curve of PMMA particles prepared at different polymerization times a) 48 h; b) 20 h; c) 10 h; d) 5 h

The above results clearly reveal that the particles have adsorbed certain amounts of TEOS and unpolymerized MMA in their inner parts before the drying procedure. At the earlier stage of polymerization, both MMA and TEOS coexist in the particles because of their miscibility property. With the consumption of MMA during the polymerization process, TEOS has to diffuse from the core of PMMA particles to the surfaces.

The achievement of cauliflower-like morphology is a consequence of the special formation mechanism of these PMMA particles in this method. As discussed previously^[6], the growth of PMMA spheres proceeded in an unusual way, that is, several small particles merged into a larger one in the process of polymerization. Multi-core PMMA was formed at the earlier stages of polymerization. Furthermore, the degree of polymerization is higher in these small cores than that in other parts. This results in different content of TEOS and MMA at different regions in one particle. Therefore, unequal shrinkage of these particles occurs in the drying process and cauliflower-like morphology is naturally formed. On the other hand, the above phenomenon can not be observed for the particles obtained at the final stage of reaction, because of uniform distribution of small molecule.

ACKNOWLEDGEMENT One of the authors (D. Wang) would like to express his appreciation to Hebei Scientific Research Fund for providing the Doctoral Fellowship (No. 2002128).

REFERENCES

- 1 Arshady, R., *Colloid Polym. Sci.*, 1992, 270: 717
- 2 Kim, J.W., Ryu, J.H. and Suh, K.D., *Colloid Polym. Sci.*, 2001, 279: 146
- 3 Noda, I., Kamoto, T., Sasaki, Y. and Yamada, M., *Chem. Mater*, 1999, 11: 3693
- 4 Okubo, M., Minami, H. and Morikawa, K., *Colloid Polym. Sci.*, 2001, 279: 931
- 5 Zhou, X.D., Zhang, S.C., Huebner, W. and Ownby, P.D., *J. Mater. Sci.*, 2001, 36: 3759
- 6 Wang, D.J., Gu, C.B., Zhou, Y.G., Wang, X., Zhen, Z., Tang, F.Q. and Liu, X.H., *Chem. Lett.*, 2003, 32: 36