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A Novel Method for Preparing Approximately Micron-sized Polymethyl Methacrylate Microspheres with Clear Surface

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Abstract: Polymethyl methacrylate (PMMA) microspheres with clear surface and diameter close to 1 μm were synthesized by newly soap-free emulsion polymerization. The results showed that the presence of ethanol and NaCl made the increase of diameter and distribution, while the presence of toluene could avoid the problem of the increase of distribution, resulting a harvest of PMMA microspheres with a diameter close to 1 μm.

Keywords: Soap-free emulsion polymerization, polymethyl methacrylate microspheres, competition solvent, cosolvent, electrolyte, diameter and distribution.

Micron-size monodispersed microspheres can be used in immunoassay, cell separation, drug screening and chromatography[1], *etc*. All these fields need functional microspheres with clear surface. There are some methods for preparing these microspheres, such as dispersion polymerization, seed polymerization and micro-suspension polymerization, but these methods need surfactants or other stabilizers, which can contaminate the products, and difficult to clean from the surface of microspheres, so that their application is limited.

By using soap-free emulsion polymerization, monodispersed microspheres with a clear surface can be prepared, but the average diameter is usually less than 500 nm[2], so the method needed to be improved.

According to the nucleation theory of soap-free latex, PMMA microspheres are homogeneous phase nucleation, and are stablized by the initiator moiety in water[2]. If cosolvent ethanol is added into the system, the solubility of methyl methacrylate (MMA) and oligo-PMMA chain will increase; on the other hand, the introduction of NaCl to the system will decrease the stability of latex to make the latex accumulate. All these factors will lead to increase of the average diameter of microspheres. However, increase of the solubility of MMA and oligo-PMMA induced the inhencement of the accumulating speed and the high reaction heat, the second-nucleation will increase, in the result the distribution of microspheres was widened. For solving these problems caused by ethanol and NaCl, toluene，as a competition solvent of MMA and a heat-emission agent in the middle and later period of reaction, was added to the reaction system. As a

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result, the PMMA microspheres closed to micron-size with clear surface were obtained successfully as expected.

PMMA microspheres were synthesized in batch process at 70°C for 6~8 h under nitrogen atmosphere. Water (60 mL), MMA (9 g), potassium persulfate (0.09 g), sodium chloride (0.1 g) and ethanol (0~6 mL) were added to the reaction system at the beginning, and toluene (0~4 g) was added at different reaction stage. The average diameter and distribution of product were determined by Mastersizer 2000 particle sizer (Malvern Instruments Ltd.).

Figure 1 and **Figure 2** were the diameter, distribution graphs of PMMA microspheres without toluene and with toluene in the reaction system, respectively. As shown in **Figure 1**, only in the presence of ethanol without toluene in the reaction system, the diameter of PMMA microspheres increased limitedly, its distribution changed no obviously on certain condition. In the presence of ethanol and NaCl, the diameter and distribution of PMMA microspheres increased, and the second-nucleation of PMMA could be observed obviously. As shown in **Figure 2**, addition of toluene could eliminate the second nucleation of PMMA and avoid the increase of the distribution caused by ethanol and NaCl. The diameter of PMMA microspheres closed to 1 μm in this condition.

Table 1 and **Table 2** presented the influence of amount of toluene and its adding period on the diameter and distribution of PMMA microspheres, respectively. As shown in **Table 1**, when the amount of toluene was in the range of 4~2 g, the diameter of microspheres were closed to 1 μm, and the distribution was approximately uniform. However, when the amount of toluene decreased to 1~0 g, the diameter and the distribution of microspheres increased obviously.

Table 2 showed that in the first 90 min of addition of toluene, the diameter and distribution had no obvious change, but after 120 min of addition of toluene, the diameter and distribution of microspheres increased markedly. Because toluene is a good solvent for MMA, so it will contest MMA with ethanol in water. At the beginning of the reaction, great amount of MMA existed, the solubility of MMA had no obvious change, therefore the reaction rate and nucleation would hardly be affected. However, at the middle and later period of reaction, the exhaustion of MMA led to the ratio of toluene to be increased, and made the solubility of MMA in water to be decreased, so the self-acceleration of the reaction would be avoided. In other way, at the middle and later period of the reaction, the volatility of toluene would take off the large reaction heat to avoid the second-nucleation in some degree.

Table 1 Influence of addition of toluene on PMMA microspheres

Toluene(g)	4	3	2	1	0
Diameter(μm)	0.966	0.911	0.899	5.582	27.067
Uniformity	0.188	0.177	0.174	7.005	0.326

Figure 1 Diameter and distribution of PMMA microspheres without toluene in the reaction system

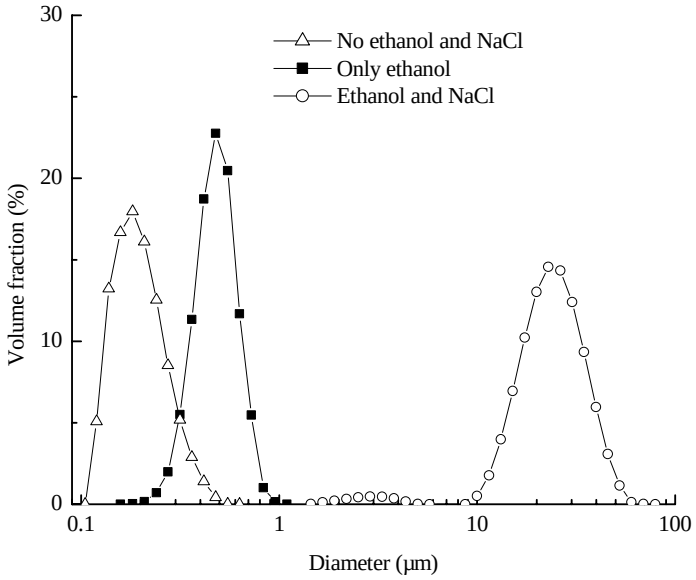

Figure 2 Diameter and distribution of PMMA microspheres with toluene in the reaction system

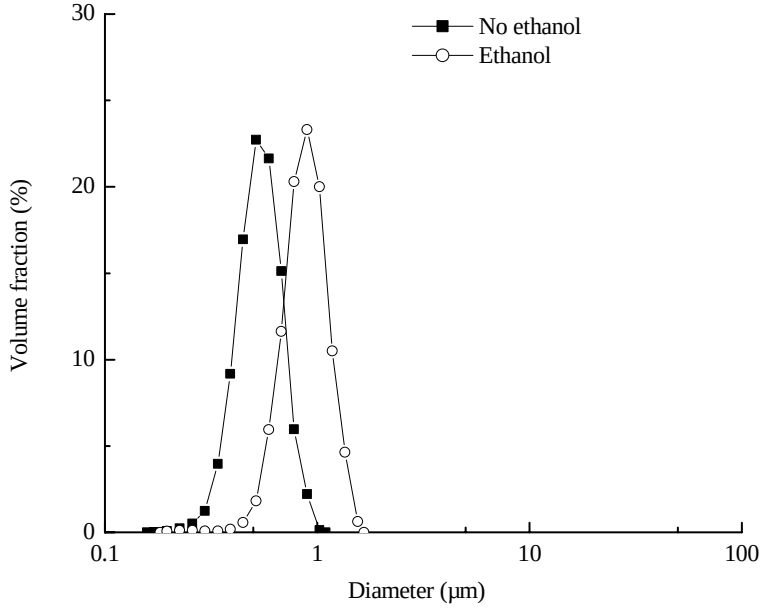

Table 2 Influence of the adding period of toluene on PMMA microspheres

Adding period (min)	0	10	60	90	120
Diameter (μm)	0.990	0.899	0.966	0.907	22.614
Uniformity	0.180	0.174	0.167	0.204	1.123

Conclusion

Approximately micron-sized PMMA microspheres with clear surface could be prepared by the modified soap-free emulsion polymerization. The presence of ethanol and NaCl could increase the diameter of the microspheres, and toluene could control the reaction rate and reaction heat, therefore it could stablize the monodispersion of the soap-free microspheres.

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