

Communication

Preparation and Stabilization of Emulsifier-free Macromolecule Nanoparticle Latex Particles

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By using acetone-water as the medium and potassium persulfate (KPS) as the initiator, emulsifier-free emulsion co-polymerization of styrene with co-monomers: MMA, BMA, EA and BDA under microwave irradiation has been investigated. The influence of the each co-monomer content and hydrophilicity on the hydrodynamic radius R_h of the synthesized copolymer nanoparticles is discussed in detail. The results show that the increase in ratio of hydrophilic copolymer causes an increase in consumption of the initiator in the initiation reaction, so an increase in the concentration of the surface $-\text{OSO}_3$ groups which cause the increase in the stability of the latex and gives rise to the formation of smaller micelles. The nano-particle radius will increase again when the co-monomer content increases to a certain degree. The curve of the particle hydrodynamic radius vs the co-monomer content has a minimum point.

Keywords Emulsifier-free emulsion polymerization, latex, microwave irradiation, nanoparticles

The latexes obtained by emulsifier-free emulsion polymerization show good adhesion and water-resistant properties and are characterized by having a narrow size distribution and 'clear' surface. They have been widely applied in biological systems.¹ In our previous work,² polystyrene latex particles with average hydrodynamic radius R_h of 72.4 nm were obtained under microwave irradiation. By adding a little methyl methacrylate (MMA) and using acetone-water as the medium, the copolymer nano-particles with average particle hydrodynamic radius of 16 nm were obtained.³ Because the applications of latex particles are influenced directly by their size and dis-

tribution, it is very important to control the particle size and distribution in the polymerization. On the other hand, the size and distribution of nano-particles could reflect the process and mechanism of the polymerization to a certain extent. In this work, using acetone-water as the medium and potassium persulfate (KPS) as the initiator, emulsifier-free emulsion co-polymerization of styrene with co-monomers: methyl methacrylate (MMA), butyl methacrylate (BMA), ethyl acrylate (EA) and maleic anhydride (BDA) has been conducted under microwave irradiation. The influence of each co-monomer content and hydrophilicity on the hydrodynamic radius R_h of the synthesized copolymer nano-particles is investigated. The stabilization of emulsifier-free latex is discussed in detail, too.

The microwave reactor with a frequency of 2450 MHz and a maximal output power of 650 W was used in this study. The co-polymerization was carried out in a three-necked flask equipped with a high-speed stirrer. Freshly distilled styrene, co-monomer, dissolved initiator potassium persulfate (KPS), acetone and de-ionized water were added into the flask and were stirred under microwave irradiation and nitrogen atmosphere for 8 h. The particle hydrodynamic radius (R_h) of the latex was determined by using a modified commercial laser light scattering (LLS) spectrometer (ALV/SP-125) equipped with a multi-digital correlator (ADLAS SPY 425 II; output power ~ 400 mW at $\lambda = 532$ nm). The details about LLS instrumentation can be found elsewhere.^{4,5} All the LLS measurements were conducted at 25.0 +

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0.1°C. The surface tension was measured by the biggest bubble method.

As shown in Fig. 1, when the ratio of acetone to water is 1:1, the particle hydrodynamic radii are around 16 nm and their distribution is quite narrow. Moreover, it should be pointed out that the size and distribution of the nano-particle latex are the same before and after the vacuum distillation of the acetone from the dispersion. This means that the system is very stable.

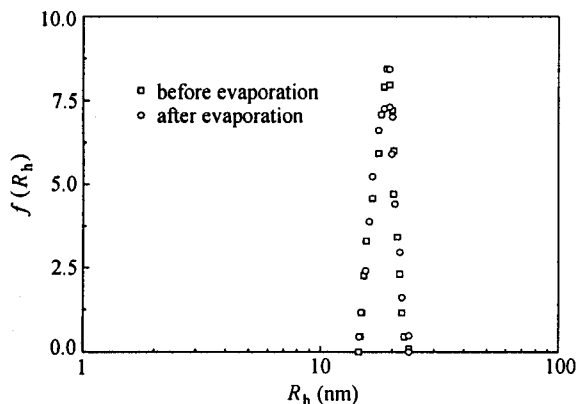


Fig. 1 Hydrodynamic radius distribution $f(R_h)$ of the copolymerized nano-particles of MMA and ST before and after the evaporation of acetone in the latex. Acetone: 69.37 g; H₂O: 69.37 g; St: 5.43 g; MMA: 5.43 g; KPS: 0.4280 g.

Fig. 2 shows the influence of the weight ratio of acetone to water on the average hydrodynamic radius of copolymer latex particle and interfacial tension of acetone-water solution. The increase of acetone in the system will decrease the interfacial tension. Furthermore, microwave radiation imposed the microstirring effect in the system. All these make the aggregation between the particles very difficult and prefer the smaller nano-particles to be formed. So the hydrodynamic radii of the particles will decrease when the acetone content increases.

The influence of co-monomer concentration on the hydrodynamic radii of the synthesized copolymer nano-particles is shown in Fig. 3. Adding hydrophilic co-monomer continually into the system decreased the hydrodynamic radii of nano-particles remarkably and still to a certain stage. If still adding hydrophilic co-monomer into the system, the hydrodynamic radii of the particles will increase. All curves have their minima.

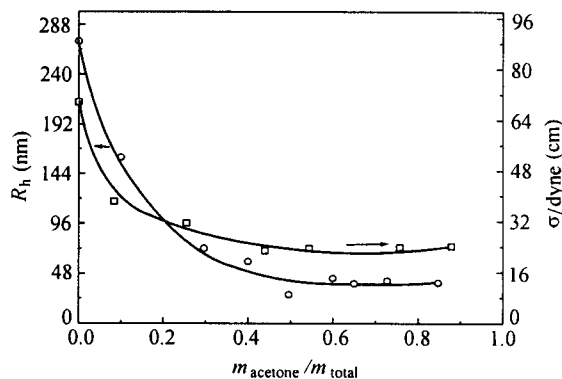


Fig. 2 Influence of the acetone content in the system on the hydrodynamic radius of PSt latex particle and surface tension of acetone-water solution.

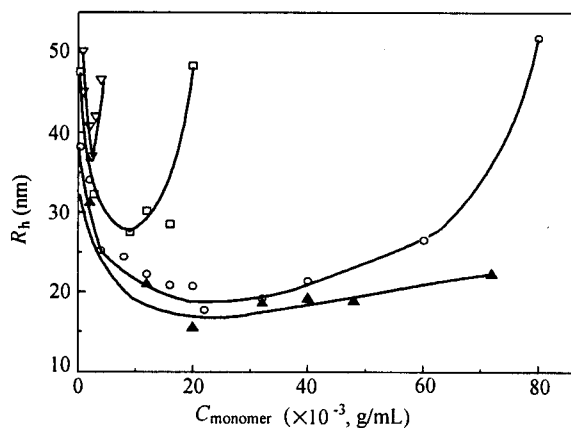


Fig. 3 Influence of co-monomer concentration on the hydrodynamic radius R_h of the synthesized copolymer nano-particles. KPS = 0.6 g; $m_{\text{styrene}} = 9.05$ g; $m_{\text{acetone}} = 115$ g; $m_{\text{H}_2\text{O}} = 115$ g; ∇ : BDA; \square : BMA; \circ : EA; \blacktriangle : MMA.

It is well known that water, ST, MMA, BMA and EA can be dissolved in acetone with no limit of their content. The solubility of the monomer in water will increase when both acetone and hydrophilic co-monomer are added into the system. This will cause the increase of the initiator consumption and the initiating reaction will be accelerated. So more nucleus were formed, and simultaneously the concentration of $-\text{OSO}_3$ on the surface of the particles was increased which makes the hydrophilicity of the particle surface increase. All these make the latex stable. And smaller micelles were obtained.⁶ When the co-monomer content reaches a certain extent, the particles will tend to aggregate, so that larger

particles will be formed. In this way the nano-particle radius will increase when the co-monomer content increases to a certain degree.

It can also be found in Fig. 3 that when the co-monomer is MMA, the size of the particle is the smallest one. When the co-monomer is EA, the number of the nucleus becomes smaller than that of MMA, because the solubility of EA in water is smaller than that of MMA. So the final particles with EA become bigger. when the co-monomer is BMA, the particles are further bigger due to the solubility of BMA is further smaller. Moreover, when the co-monomer is MMA and EA, the particle radius keeps constant for a relatively wide range of MMA and EA content. It means that the increase of MMA and EA content does not cause the increase of the particle volume. The reason for it is MMA and EA dissolve well in the water-acetone medium which cause the rate of nucleation bigger than the particle growing rate. So the number of the particles increases. Such phenomenon can also be found in the previous studies.^{3,7}

From Fig. 3 it can be found that the particle radius decreases when BDA is added, but it increases again once BDA content is larger than 0.4%. The BDA molecule can be hydrolyzed to form maleic acid and ionize H^+ and COO^- during the process of the reaction. So the surface charge will increase. Once the BDA content is superfluous, the surface charge will be saturated which will increase the repulsion among the particles to

make the macromolecule chains unwind. The ionic strength of the system increases simultaneously. All of the former factors make the latex unstable and aggregate to form larger particles. It can be deduced easily from the comparison of the two curves in Fig. 3 that the ionic co-monomer has little influence on the stability of the latex.

All of the above experiments are carried out under microwave irradiation. Nano-particle latex can also be obtained through conventional heating method but the reaction takes more time and the particle size distribution is wider. In addition, using the conventional heating method, the repeatability of the experiment is not good.

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