Chinese Chemical Letters Vol. 14, No. 8, pp 863 – 865, 2003
http://www.imm.ac.cn/journal/ccl.html

Preparation of MMA-BA-DMAEMA Nanosized Latex

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Abstract: The terpolymer latex of methyl methacrylate (MMA)/butyl acrylate (BA)/ dimethyl aminoethyl methacrylate (DMAEMA) with diameter of less than 100 nm was prepared by seeding semi-continuous emulsion copolymerization using APS (ammonium persulfate) / TMEDA (N,N,N, N-tetramethylethylenediamine) as the redox initiators and SDS (sodium dodecylsulfate) and OP (P-octylpolyethylene glycol phenylether) as co-emulsifiers. The factors that influenced the process stability of the copolymerization and the particle size of the latex were investigated. The addition of aqueous ammonia as coagulation inhibitor provided better process stability of the copoly- merization. The addition of acetic acid as the acidification agent caused a remarkable reduction of the latex particle size.

Keywords: Emulsion copolymerization, dimethylaminoethyl methacrylate, stablity, nanosize.

Recently, the coatings industry has been forced to develop environmentally friendly coatings with less or ultimately zero VOCs (volatile organic compounds)[1]. Water-borne coatings have been promised to reduce the VOCs emitted from the coatings. Latex coatings and water-reducible coatings are the two major types of water-borne coatings approaches. One of the two dominant types of water-borne coating technology is latex. To improve the performance, cross-linking technology has been incorporated into latex coatings. The acrylate latex containing amine groups has been taken as a polymeric cross-linking agent of the latices with epoxy groups, to enhance the properties of anti-water, anti-solvent, rapid drying and mechanical strength of the film formed from the latices.

However, it is difficult to carry out the emulsion polymerization of hydrophilic monomer-containing system. Z. Yu *et al*. studied the emulsion copolymerization of MMA/BA/DMAEMA[2]. In their opinion, the hydrophilic homopolymer, which may flocculate the particles and make the latex coagulated, is likely to be formed. On the other hand, the monomer containing amine groups, such as DMAEMA, could feasibly constitute a redox initiation system with persulfate in the aqueous phase which makes the polymerization process more sophisticated at high polymerization temperature. In our opinion, the amine group of DMAEMA unit, which is electrolyte, can hydrolyze and produce cationic $\text{-}N^{+}Me_2OH^{-}$ in the aqueous phase, will likely make the anionic emulsion break and lead to coagulation.

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It is well known that nanosized latex is an essential premise for the formation of high quality films. Polymer latex particles with diameters less than 100 nm have been prepared through micro-emulsion[3]. Few workers have studied emulsion copolymerization containing the functional co-monomer DMAEMA with particle diameters less than 100 nm. As a part of systematic study, we aim to improve the process stability of the polymerization and reduce the particle size of the polymeric latex.

The polymer latex was produced by seeded semi-continuous emulsion polymerization in a 500 mL jacked glass reactor under argon. The deionized water, co-emulsifiers and 10% of the monomer mixture were sequentially added into the reactor and were emulsified by agitation. Aqueous ammonia (25%) was added into the reactor to keep pH>10. When the reactor was heated to 45°C the initiator solutions were introduced. 5 minutes later, the co-monomers were dropped at the speed about 0.4 mL/min into the reactor. After the monomer addition, the reaction was continued for 2 hours. Then the reactor was heated to 50°C. Acetic acid solution (35%) was dropped into the latex under violent stirring to adjust the final pH=7.5. The total solid content of the latex product is about 40%. The total emulsifier content of the latex product is about 2%.

The coagula on the wall and in the agitator of the polymerization reactor were collected, dried and weighed. The ratio of the coagula to total monomer was calculated and used to characterize the process stability of the emulsion polymerization process. The lower the coagulum ratio is, the more stable the emulsion polymerization process. Particle size of the latex was determined using a Particle Analyzer (Coulter, LS-230).

Figure 1 shows the effect of DMAEMA amount on the process stability of co-polymerization. It also shows the effect of the pH value of the reaction system on the process stability of copolymerization. It has been found that the process stability of copolymerization becomes better when the pH value of the reaction system is increased through the addition of the concentrated ammonia. With the addition of the concentrated ammonia, the hydrolysis degree and solubility of amine group are reduced and the flocculation of amine group would be decreased.

Figure 2 shows the effect of DMAEMA amount on the particle size of the latex. It also shows the effect of the addition of acetic acid on the particle size of the latex. We found that the addition of acetic acid as acidification agent caused a remarkable reduction of the latex particle size. It was considered that the water solubility of DMAEMA unit on the surface of the terpolymer would be increased after acidification and hence, the surface water solubility of the particle would be enhanced under violent stirring and the particle size would be reduced.

When the fraction of DMAEMA in the co-monomer mixture exceeds 10% the process stability of the copolymerization becomes better and there is a trend in the reduction of the latex size. This result may attribute to the assistant-emulsion effect of DMAEMA unit and the increased water solubility of the polymeric particles.

The effect of emulsifier type and concentration and polymerization temperature on the process stability of the copolymerization and properties of the latex are in close agreement with the results described in reference[2].

Figure 1 Effect of the amount of DMAEMA on the process stability of the copolymerization

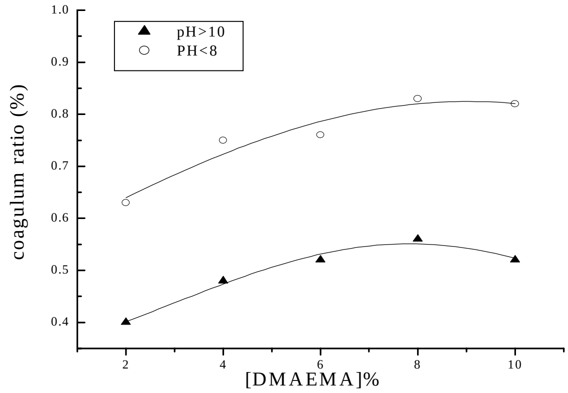
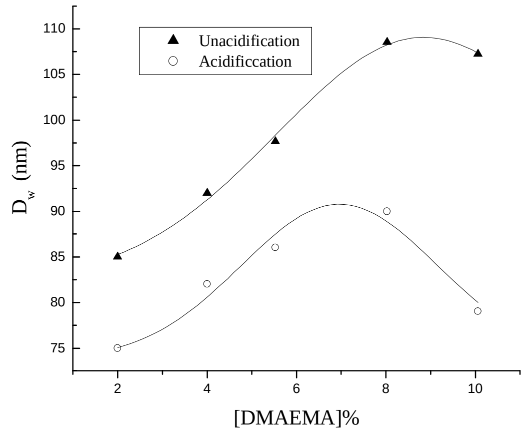


Figure 2 Effect of the amount of DMAEMA on the particle size of the terpolymer attices



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Received 8 October, 2002