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Effect of AA on Properties of St-MMA-AA Emulsifier-Free Latex Particles

Shiyuan Cheng, Cui'e Yan*
School of Chemistry and Material Science, Hubei University, Wuhan, 430062, P.R.China
Email : wuhy@public.wh.hb.cn

Linxian Feng
Dept.of Polymer Science, Zhejiang University, Hangzhou, 310027, P.R. China

SUMMARY: In order to obtain clean and monodisperse microspheres for diagnostic use, emulsifier-free emulsion copolymerization of styrene (St) and methyl methacrylate (MMA) was carried out in the presence of the functional monomer acrylic acid (AA). The morphology, size and size distribution of the latex particles were observed by TEM, and the distribution of --COOH in the latex was determined by conductimetric titration and the density of surface --COOH was computed. Effects of concentration of AA and its feeding process at different polymerization stages on the size and size distribution, density of surface --COOH of the latex particles (Dc) were investigated. The results show that the average diameter (D_w) decreases and its dispersion parameter (D_p) increases with increasing [AA] except if AA was added dropwise after the steady stage. The density of surface --COOH (Dc) increases with increasing [AA] no matter how AA was added. Dc is the largest when AA was added dropwise after the steady stage and Dc is the least when AA is added in one batch before polymerization.

Introduction

Emulsifier-free emulsion polymerization, mainly with styrene, has appeared to be a quite convenient and versatile method for producing monodisperse and well-characterized particles for biomedical and catalytic support applications. The controls of particle size, size distribution and reactive groups on the surface are very important requirements1). When used in the diagnostic field, it was shown that the hydrophobic-hydrophilic balance at the water-polymer interface is the key point2).

In our work, we use AA as the hydrophilic comonomer and ammonium persulfate (APS) as the initiator for the ternary emulsifier-free emulsion copolymerization of St and MMA. The hydrophilicity of the monomers increases successively from St, MMA to AA. Clinical

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diagnosis confirmed that some of the latex particles prepared in proper conditions show high sensitivity and specific activity after immobilizing Sj-SEA.

Effects of concentration of AA and its neutralization ratio on the distribution of --COOH were investigated by Sakota$^{3)}$ and Guillaume$^{4)}$. The present work focused on the effects at different polymerization stages of concentration and feed process of AA on the size, size distribution and density of surface --COOH of the latex particles. A kinetic model, Gamma Function, was proposed and the three stages were determined by fitting the conversion curves using the kinetic model$^{5)}$.

Experimental

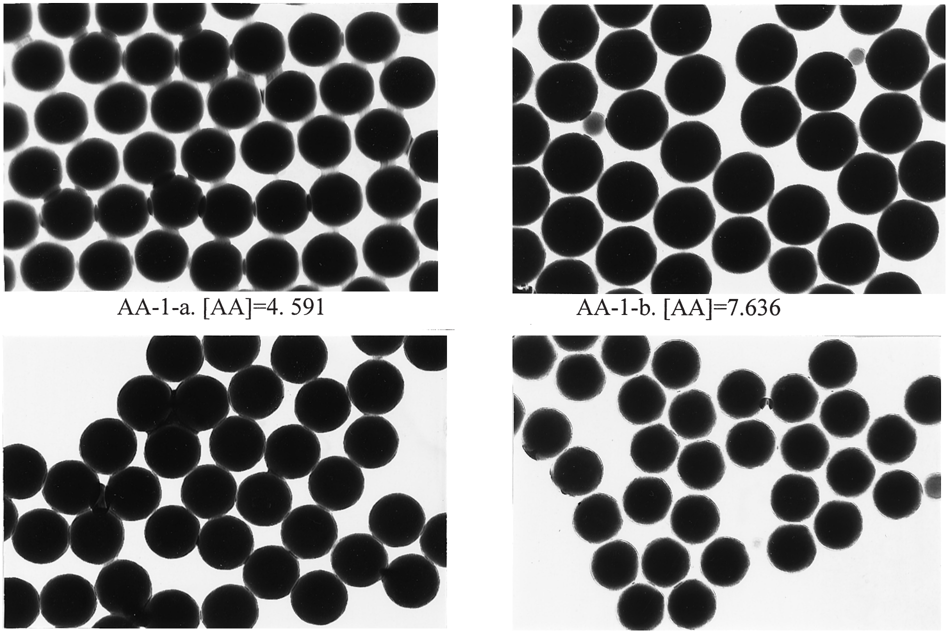
Materials. St, MMA and AA were distilled under reduced pressure and stored under nitrogen at 4 ^{0}C. Water was freshly deionized. APS was recrystallized from deionized water.

Experimental Procedure. At 84 ^{0}C, in a 250-mL four-neck receptor continuously purged with nitrogen and equipped with a Teflon stirrer, condenser and thermocouple, emulsifier-free emulsion copolymerizations of St, MMA were carried out with different feeding processes of AA at different polymerization stage. Three cases were involved: AA was added in one batch before polymerization (denoted by AA-1), dropwise at the latter stages of the nucleation (denoted by AA-2) and dropwise after the steady stage (denoted by AA-3). The best volume ratio of St/MMA in the monomers in terms of the stability of the emulsions, was found to be 2 (value used for all runs in this paper). The agitation speed for all runs was 200 rpm and the reaction time was 12 h to assure a complete reaction. Latex stability was good as demonstrated from the fact that no coagulum adhered on the reactor and no separation or coagulation was observed on standing for four months.

The conversions were determined by use of gravimetric method. The morphology, average diameter (D_w) and its dispersion parameter ($D_p = \delta / D_w$,$\delta = \left[\sum_{i=1}^{n}(D_{wi} - D_w)^2/(n-1)\right]^{1/2}$) of the latex particles were determined from electron micrographs with a JEM-100SX TEM. Particle number (N_p) was estimated by use of the mass balance and the corresponding data of D_w and conversion. The distribution of --COOH in the latex was determined by Hen conductometric titration[6].

Results and discussion

Size and size distribution TEM photographs of latex particles with different concentration of AA at the three cases were shown in Figure 1, 2 and 3 respectively.



AA-1-a. [AA]=4. 591

AA-1-b. [AA]=7.636

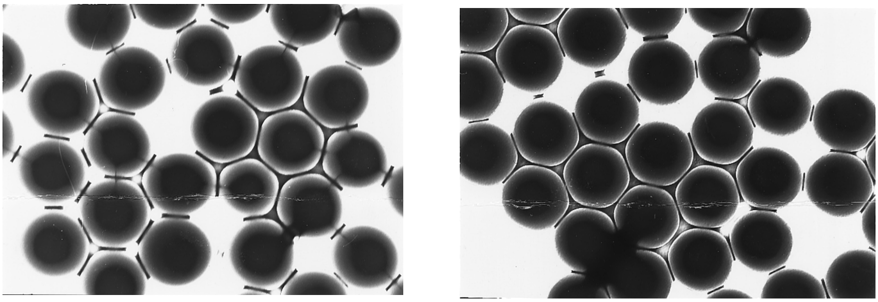
AA-1-c. [AA]=15.191

0.25 μm

AA-1-d. [AA]=22.668

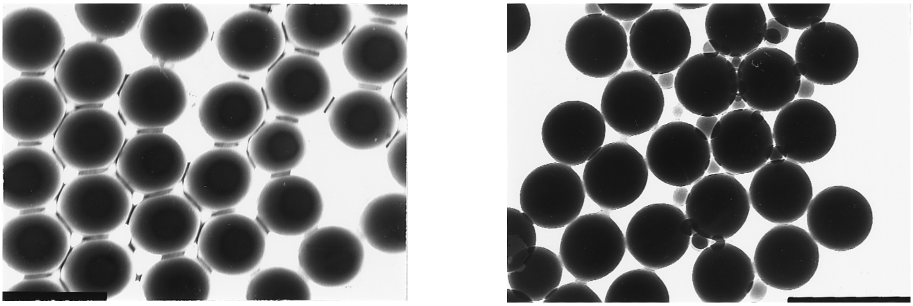
Fig1. TEM photographs of latex particles at different [AA] (10^{-2} mol/L) (AA added initially in one shot)

Figure 1 shows that the particles are spherical and uniform except for few small particles. Particle size decreases with increasing the concentration of functional monomer AA when AA is added in one shot before polymerization.



AA-2-a. [AA]=7.636

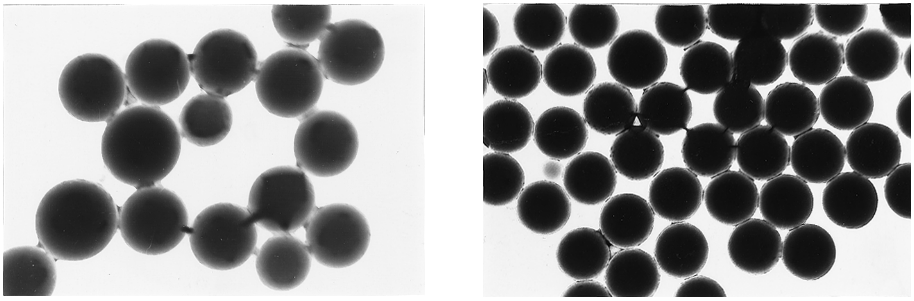
AA-2-b. [AA]=15.191



AA-2-c. [AA]=21.183 0.25 μm AA-2-d. [AA]=30.069

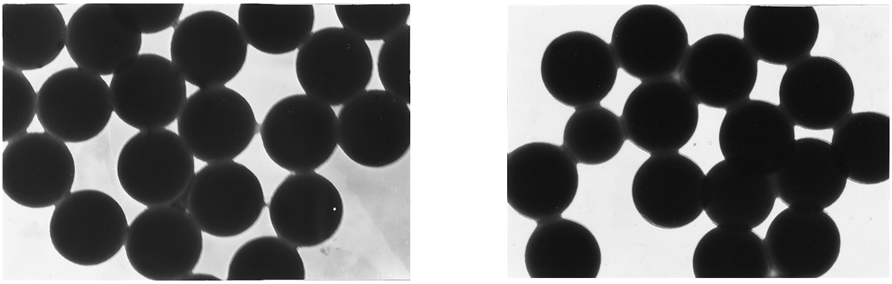
Fig. 2. TEM photographs of latex particles at different [AA] (10^{-2} mol/L). AA was added dropwise at the latter nucleation stage .

This is a general trend that has been observed in emulsifier-free emulsion polymerization in the presence of an ionic comonomer.



AA-3-a. [AA]=7. 636

AA-3-b. [AA]=15.191



AA-3-c. [AA]=21.183 0.25 μm AA-3-d. [AA]=30.069

Fig 3. TEM photographs of latex particles at different [AA] (10^{-2} mol/L). AA was added dropwise after the steady stage.

Figure 2 shows that the particles have not a distinct round shape. Particle size changes slightly and size distribution broadens with increasing concentrations of functional monomer when AA is added dropwise at the latter nucleation stage. Figure 3 shows that the particles are spherical but are not distinctly uniform. Particle size approximately increases with increasing the concentration of functional monomer AA when AA is added dropwise after the steady stage. For the three cases, changes in D_w and D_p of the latex particles for different [AA] are respectively shown in Fig 4 and 5. D_w decreases and D_p increases with increasing [AA] when AA was added in one batch before polymerization. D_w is larger and slightly decreases, and D_p increases significantly with increasing [AA] when AA was added dropwise at the latter nucleation stage. D_w and D_p show a minimum with increasing [AA] when AA was added dropwise after the steady stage.

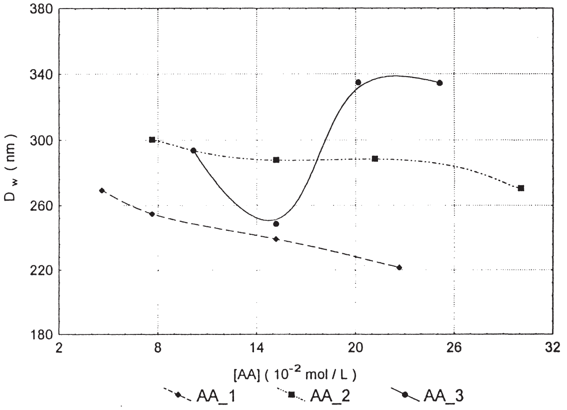


Fig. 4. Changes of D_w of the latex particles with different [AA] for the three cases

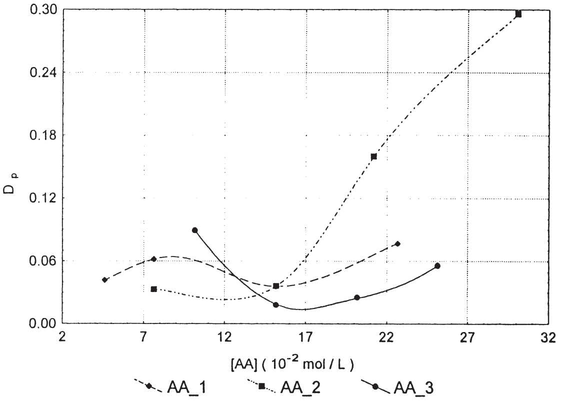


Fig. 5. Changes of D_p of the latex particles with different [AA] for the three cases

According to Fitch et al.[7] for emulsifier-free emulsion polymerization, the nucleation rate dN_p/dt can be expressed as in (a), where R_i, R_c and R_f are respectively the rates of initiation, capture and flocculation; and b is an efficiency factor:

$$dN_p/dt = bR_i - R_c - R_f \qquad (a)$$

$$R_i = k_{pw}[M]_w[O]_w \qquad (b)$$

Equation (b) represents the dependence of the initiation rate on the monomer $[M]_w$ and the oligoradical $[O]_w$ concentrations and k_{pw}, the propagation rate constant in water. In this system, owing to the homogeneous nucleation 5) and to the high solubility of AA in water, $[M]_w$ increases with increasing [AA] when AA is fed in one batch before polymerization, so R_i and dN_p/dt increases. It indicates that N_p increases, as a result, D_w decreases. There is no AA in the reaction at the early nucleation stage when AA is added at the latter nucleation stage. So a large amount of flocculation occurred between the primary particles at the beginning of the nucleation due to the absence of –COOH located at the surface. As a result, D_w of the AA-2 series is larger than for the AA–1 series. AA is mainly located at the surface of the latex particles when it is added at the end of polymerization, so D_w of the run of AA-3 series approximately increases with increasing [AA].

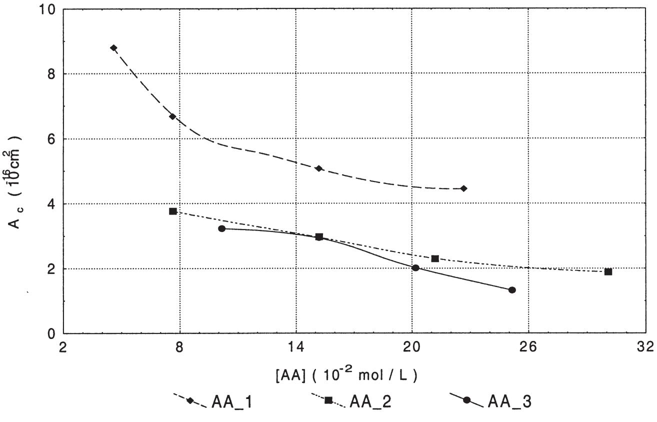


Fig. 6 Changes of A_c of the latex particles with different [AA] for the three cases

Density of surface –COOH

Changes of the average occupying surface area per surface --COOH group (A_c) of the latex particles with different concentration of AA in the three cases were respectively shown in

Figure 6. The density of surface --COOH (Dc) increases with increasing concentration of AA, no matter how AA was fed. Dc is the largest when AA was added dropwise after the steady stage and Dc is the least when AA was added in one batch before polymerization. This suggests that functional group anchoring at the particle surface can be improved if the functional monomer is added at the end of the nucleation stage and it can be further improved if the functional monomer is added at the end of polymerization.

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