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SHORT COMMUNICATION

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On the copolymerization of acrylates in the modified microemulsion process

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Abstract Copolymerization of methyl methacrylate, methyl acrylate, butyl methacrylate, and butyl acrylate in turn was performed in the modified microemulsion polymerization process, i.e., continuous addition of monomer to a pre-emulsified system. It was found that the particle size of the copolymer microlatex did not change distinctly with the monomer composition. The estimation of emulsifier coverage on the microlatex particles indicated that the process switched from a traditional microemulsion to a normal seeded emulsion polymerization very soon after monomer dropping began. Therefore, a longer dropping time is needed to produce a microlatex with narrow dispersed particle size. Besides, in the modified microemulsion polymerization less emulsifier is needed to produce a stable microlatex. This behavior is related to the mechanism of normal seeded emulsion polymerization during monomer dropping.

Keywords Microemulsion · Acrylates · Copolymerization · Emulsifier

Introduction

Microemulsions are transparent, isotropic, and thermodynamically stable mixtures of oil and water stabilized by emulsifier, usually together with a coemulsifier. Microemulsion polymerization has been widely researched [1–16] since the first studies by Stoffer et al.[1, 2] and Atik et al. [3] in the early 1980s. It is well known that some monomers can act as coemulsifier and stabilize the microemulsion. In microemulsion polymerization, the coemulsifier activity of alkyl acrylate, which increases with the alkyl chain length for short and medium-length acrylates, can affect the particle size and stability of the microlatex [17].

On the other hand, it is difficult for conventional microemulsion polymerization to be used in industry because of the lower solid content and higher surfactant level. Many ways of modification [18–24], such as seed polymerization and semicontinuous polymerization, have been developed. In recent years, it was found that a microemulsion with high polymer content could be prepared through continuous addition of monomer to the polymerizing microemulsion [25, 26]. For example, Puig et al. [27] showed the preparation of polystyrene latex with a solid content as high as 40% by semicontinuous addition of monomer. However, whether the coemulsifier activity of monomers in the modified microemulsion polymerization is as important as that in the conventional procedure is still unknown.

In this paper we use Ming's modified microemulsion polymerization process [26], in which a monomer emulsion or microemulsion of low concentration was initiated and then monomers were continuously and slowly added to the polymerizing system with mild stirring. The monomers were selected from acrylates and methacrylates, which have different water solubility and were reported to have different coemulsifier activity in conventional microemulsion polymerization [17]. The aim of this article is to observe the effect of "coemulsifier activity of monomer" and the "dropping" time on the particle size of the microlatex in the modified microemulsion polymerization process. It is expected that the size of the microlatex particles could be well controlled without the influence of the nature of the monomers. The mechanisms of how the emulsifier stabilizes the microemulsion are also discussed.

Experimental

Materials

AR grade methyl methacrylate (MMA), methyl acrylate (MA), butyl methacrylate (MBA), and butyl acrylate (BA), purchased from Shanghai Reagent Co., Shanghai, China, were distilled under reduced pressure before polymerization. Octadecyltrimethylammonium bromide (OTAB) of AR grade with a purity of 99%, purchased from Shanghai Jingwei Co., was used as received. Potassium persulfate (KPS) from Shanghai Reagent Co. was purified by recrystallization from water. Deionized water was used for all experiments.

Modified microemulsion polymerization process

The preemulsion was prepared with 3.0 g of OTAB, 80 g of water, and 5 g of monomers in a 250-mL four-neck flask equipped with a reflux condenser, a thermometer, an addition funnel, a small-sized stir bar driven by an electric stirrer, N_2 inlet and outlet, and heated to 75 °C. A solution of 90 mg of KPS in 5 g of water was added and N_2 bubbled though the flask. The polymerization was then carried out under mild stirring and lasted for 0.5 h. After that, the remaining 25 g of monomers was continuously and slowly added to the polymerizing microemulsion within different dropping times. When the addition was complete, the flask was kept at 75 °C for another hour.

Particle size and conversion determination

Particle size was determined by dynamic light scattering on an L&G Microtrac Particle Analyzer 9200 series from Leeds & Northrup Co. Microlatex samples were diluted with deionized water to about 0.1 wt% of polymer concentration. The *Z*-average diameters were obtained by the instrument. The conversion was determined by gravimetry.

Results and discussion

Effect of the monomer dropping time on the particle size of the microlatexes

The characteristic of the modified microemulsion polymerization process is that the polymerization is performed in "starved" conditions. Therefore, the monomer must be added slowly and continuously. Table 1 shows the effect of monomer dropping time on the average size of particles in the microemulsion polymerization of MA. It can be seen that the particle size of the emulsion increased with increasing dropping speed. The average size of particles of the polymer emulsion became as high as 200 nm when the monomer was added within 30 min. For the fast dropping, in fact, at the end of dropping a lot of monomer had not polymerized (see the conversion data in Table 1). Thus, the polymerization was not in starved conditions and the remaining monomer would polymerize according to the mechanism of conventional emulsion polymerization. The particle size measurement also showed that the particle size was polydispersed for the fast dropping (see Fig. 1). This was attributed to the agglomeration of some particles due to the lower coverage by emulsifier. In order to obtain a monodispersed microlatex, the dropping time for the copolymerizations was kept at 120 min. The results show that at this dropping speed, the conversions at the end of dropping were all higher than 85%.

Particle sizes of the microlatexes obtained by copolymerization

The monomers used here are methyl methacrylate (MMA), methyl acrylate (MA), butyl methacrylate (BMA), and butyl acrylate (BA). It was reported that their coemulsifier activity in conventional microemulsion polymerization is quite different. The sequence of coemulsifier activity is BMA > BA and MMA > MA [17], which corresponds with their hydrophobic sequence [28].

The copolymerization of one monomer with another in turn was performed. The change of particle size of the microlatex with the monomer composition is shown in

Table 1 Effect of dropping time on the average size of particles in the polymerization of MA

Dropping time (min)	Conversion at the end of dropping (%)	Final conversion (%)	Particle size of polymer emulsion (nm)
30	40.7	94.5	207.2
80	79.2	91.3	68.3
120	86.0	94.5	60.4

Fig. 1a–c Effect of dropping time on the particle size distribution in the modified microemulsion polymerization of MA: **a** 120 min; **b** 80 min; **c** 30 min

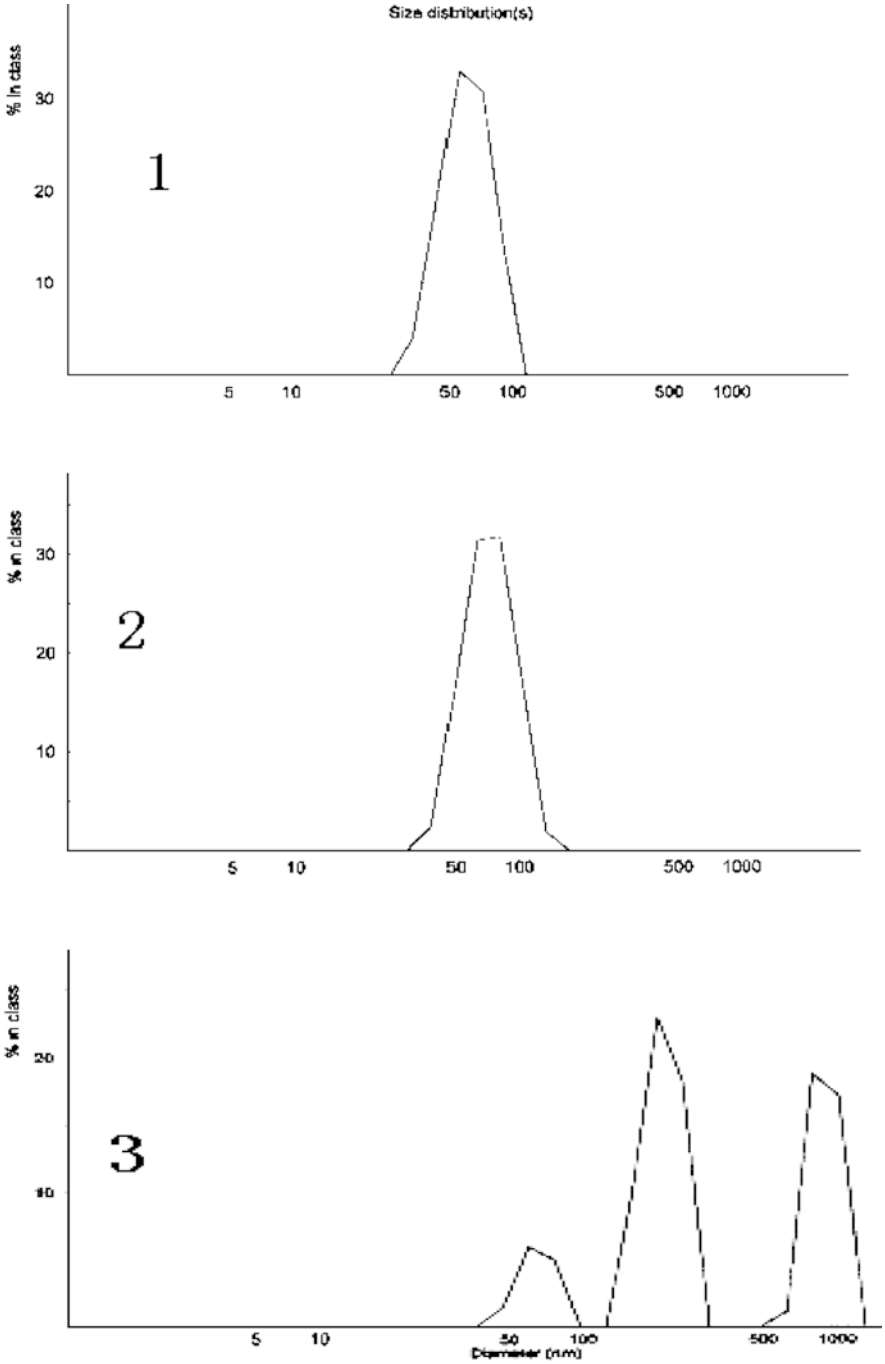

Fig. 2. It can be seen that the particle size of the copolymer microlatex did not change distinctly when one monomer was substituted gradually by another one having different coemulsifier activity, even in the copolymerization of MA and BMA whose difference of coemulsifier activity is reported to be the biggest among the monomers studied [17].

In previous studies [16, 19, 21, 22] on conventional microemulsion polymerization, the particle size and the particle number of the copolymer microemulsion changed as the composition of the monomer altered. In particular, in the ternary microemulsion polymerization of acrylate monomers, the coemulsifier activity of monomers increases with increasing number of carbon atoms in the alkyl side chain. The monomer having coemulsifier activity favors the formation of micelles with a monomer-saturated shell; therefore, it favors the stability of the microemulsion [17]. However, our

Fig. 2a–c Dependence of particle size and size dispersion D_v/D_n of the copolymer emulsion on the monomer composition: **a** BA/BMA; **b** MA/MMA; **c** MA/BMA

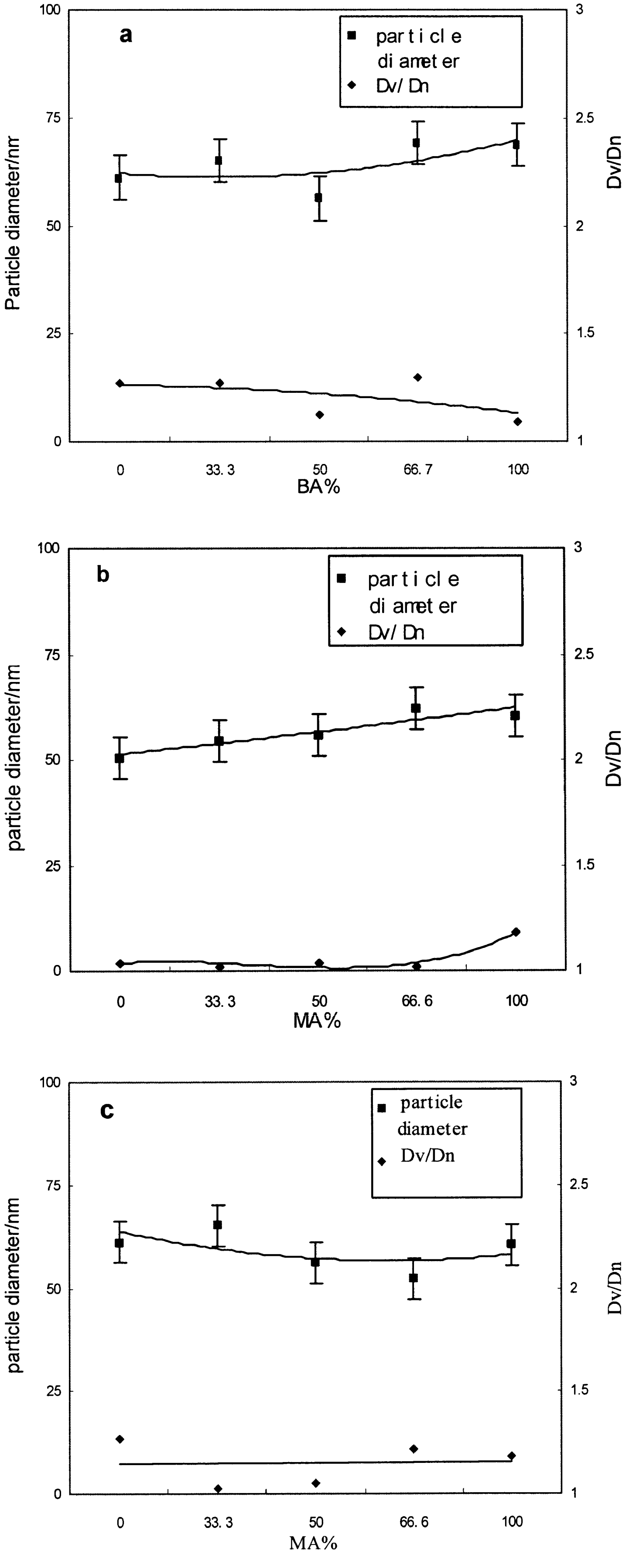

Table 2 The eEmulsifier coverage in the modified process of microemulsion polymerization of MA

Total time (min)	Dropping time (min)	Monomer added (g)	Particle size (nm)	Emulsifier coverage (%)	Instant conversion (%)
30	0	5	31.7	(120)	80.4
60	30	11.2	39.7	67	77.4
90	60	17.5	47.3	51	82.3
150	120	30	51.7	41	86.0
210	–	30	60.4	38	94.5

experimental results show that the coemulsifier activity of monomers seems unimportant in the modified microemulsion polymerization process. The different behavior should be attributed to the different polymerization process. In the conventional process all the monomers are added at the beginning of polymerization and consumed gradually, whereas during the modified microemulsion polymerization process monomers were added continuously and slowly into an initiated system. In order to explore the different mechanism, the emulsifier coverage of emulsion particles was monitored during the whole process of polymerization. The emulsifier coverage of particles (C_r) was estimated based on the particle size measurement of the microlatex using a simple geometrical model [29] as follows

$$S = \frac{3M_s}{R\,N_A} \cdot \frac{W_p}{W_s} \tag{1}$$

where M_s and N_A are the molar mass of the emulsifier and Avogadro's number, respectively, R is the particle radius of the microlatex, W_p/W_s is the weight ratio of polymer to emulsifier, and W_p can be calculated from the weight of the fed monomer and the monomer conversion. S is the value of the occupied surface area per emulsifier molecule, which was reported to be 0.18 nm^2 [29]. The experimental result for the modified microemulsion polymerization process of MA is shown in Table 2. In the preemulsion step, the polymerization followed the mechanism of the traditional microemulsion process because of the high weight ratio of emulsifier to monomer. It was found that at the end of preemulsion polymerization not all emulsifier was absorbed on the surface of polymer particles, and about 20% of the emulsifier amount was excess. However, the extra emulsifier was consumed very soon after monomer dropping began. In this case, the emulsifier coverage was insufficient, and the polymerization process switched from traditional microemulsion to a normal seeded emulsion polymerization. Therefore, the coemulsifier activity of the monomers was not important any more, whereas the starved conditions or dropping time became significant. In this case the monomer has to diffuse to the already formed particles and no new particles are nucleated.

Effect of emulsifier amount on particle size

Since the type of monomer did not affect the size of polymer particles in the modified microemulsion polymerization, the most efficient way to modulate the size of the microlatex is to change the amount of emulsifier in the system. The more the amount of emulsifier, the more places there are where nucleation occurs. The experimental results of the polymerization of MA are shown in Table 3, where the amount of OTAB varied from 1.0 to 4.0 g for the total 30 g of monomer with a dropping time of 120 min. It can be seen that the particle size decreases with increasing amount of emulsifier, and the microemulsion system becomes more stable. Table 3 also shows the dependence of emulsifier coverage on the amount of emulsifier before monomer dropping and at the end of the polymerization. With increasing amount of emulsifier, the coverage after preemulsion polymerization varied from insufficient to excessive. In the case of 3 and 4 g of emulsifier, the dispersion energy is not sufficient to break the monomer droplets further and the extra emulsifier formed additional micelles in water [29]. Thus, in the monomer dropping step the switch point from traditional microemulsion to a normal seeded emulsion polymerization must be delayed with increase of emulsifier.

Table 3 Effect of emulsifier amount on the particle size and the emulsifier coverage in the polymerization of MA

Emulsifier amount (g)	Particle size before monomer dropping (nm)	Emulsifier coverage before monomer dropping (%)	Particle size at the end of polymerization (nm)	Emulsifier coverage at the end of polymerization (%)
1	60.8	77	114	24
2	40.9	100 (104)	76.6	32
3	31.7	100 (120)	60.4	38
4	27.1	100 (137)	47.4	40

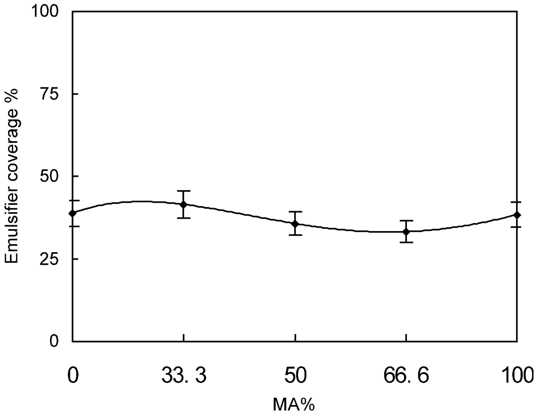

Fig. 3 Emulsifier coverage on the microlatex particles of MA/BMA copolymer

Emulsifier coverage

It was reported that in the modified process the lowest emulsifier coverage on the microlatex particles was about 35% [30], while using the conventional process it is impossible to produce a microlatex with such a low coverage. Figure 3 shows that, based on the measured data of the particle size, the estimated emulsifier coverage on the microlatex particles of MA/BMA copolymer was 35–45%. In this study, the final emulsifier coverage of the copolymer microlatex was proportional to the particle size measured, because of the same weight ratio of emulsifier to monomers (see Eq. 1). Thus, the copolymer microlatexes of BA/BMA and MA/MMA have a similar emulsifier coverage as the copolymer of MA/BMA since they have asimilar particle size. The lower emulsifier coverage can be attributed to the fact that in the modified process, most of the monomers were polymerized according to the mechanism of normal seeded emulsion polymerization.

Conclusion

In the modified microemulsion polymerization process, the particle size of the copolymer microlatex did not change distinctly with the monomer composition. The coemulsifier activity of monomers, which was often observed in the conventional microemulsion process, seems unimportant in the modified process. This behavior is attributed to the fact that the process switched from a traditional microemulsion to a normal seeded emulsion polymerization very soon after monomer dropping began. Besides, in the modified microemulsion polymerization less emulsifier is needed to produce a stable microlatex. This can also be explained by the mechanism of normal seeded emulsion polymerization during monomer dropping. In this case a longer dropping time is significant to produce a microlatex with narrow dispersed particle size.

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