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Modified microemulsion polymerization is a useful method to prepare nanoscale poly(methyl methacrylate) (PMMA) latex with a high solid content (10–30 wt%) and nanoscale (20–40 nm) particles by only using 1–2 wt% surfactant. The main feature of modified microemulsion polymerization is that most of the monomer is post-added gradually into the initiated pre-microemulsion, and the surfactant can be utilized adequately. We find that the polymerization rate increases with the increasing of the post-addition rates, using the Mettler Toledo Reaction Calorimeter to accurately record the heat of reactions and calculate data. Furthermore, after analyzing the products in GPC, the post-addition rate is found to significantly influence the molecular weight of polymer: the molecular weight also increases with the increasing of the post-addition rate.

Keywords modified microemulsion polymerization, poly(methyl methacrylate) latex, post-addition rate, polymerization rate, molecular weight

Introduction

Since microemulsion polymerization was first reported by Stoffer and Bone in the early 1980's (1, 2), it has been widely studied because of its efficiency in producing polymer latices of 10–100 nm (3, 4). However, there are two major drawbacks in the conventional microemulsion polymerization: (1) low polymer contents, usually less than 10 wt%, and (2) low monomer/surfactant weight ratio, which raises concerns with cost required for materials and post-treatment to remove the surfactants after polymerization. A number of groups have tried to overcome these drawbacks to make microemulsion polymerization more practical (5–9). Gan et al. reported the polymerization of styrene (St) and methyl

methacrylate (MMA) in ternary Winsor I-like system, in which cationic surfactants were used. Although relatively high weight ratios of polymer to surfactant (around 8 : 1) were achieved in their systems, particle sizes of produced latices were still large, i.e., 30–100 nm (5, 6). Xu et al. polymerized St, butyl methacrylate (BMA), and MMA in nanosized microlatices ranging from 15 to 65 nm via hollow-fiber feeding of monomers, with the monomer/surfactant ratio up to 15 (9). Our laboratory also developed a modified microemulsion polymerization procedure to prepare high-solid-content (10–30 wt%) nanosized polymer latex (20–40 nm), in which the monomer was gradually added into the polymerizing microemulsion system without disturbing its stability, and a small quantity of surfactant (only 1–2 wt%) was utilized adequately (10, 11).

Recently, we were devoted to the progress of the modified microemulsion polymerization, especially the polymerization progress in the post-addition. We found that the post-addition rate of the monomer has significant influences on the polymerization rate and the molecular weight of the product. Here, we also report the controllability of the modified microemulsion polymerization.

Experimental

Materials

MMA from Shanghai Chemical Reagent Co. was distilled under reduced pressure before polymerization. Sodium dodecyl sulfate (SDS) was purchased from Shanghai Shengong Bioengineering Corp. and used as received. Ammonium persulfate (APS) and potassium persulfate (KPS), were purchased from Shanghai Aijian Reagent Factory and purified by re-crystallization in water. Ascorbic acid from Shanghai Xingxing Medicine Developing Center and a 30% hydrogen peroxide solution from Shanghai Taopu Chemical Factory were used as received. N,N,N,N-Tetramethylethylenediamine (TMEDA) was purchased from Ajax Chemicals (Australia) and purified by re-crystallization. 1-Pentanol (n-Pt), methanol, and chloroform from Shanghai Chemical Reagent were also used as received. Deionized water was used for all the polymerization experiments.

Instrument

The Mettler Toledo Reaction Calorimeter (RC1) (Key Center for Polymer Colloids, University of Sydney) is a computer-controlled, electronically safeguarded lab reactor, a useful device, for the performance of isothermal and adiabatic reactions, the determination of thermal data and constants, and their recording and mathematical evaluation.

Polymerization

Modified Microemulsion Polymerization of Methyl Methacrylate in RC1. The recipes of modified microemulsion polymerizations under varied conditions are shown in Table 1. The general procedure of modified microemulsion polymerization with SDS/n-Pt as surfactant/co-surfactant can be described as follows (10). The pre-microemulsion, composed of the entire amount of the surfactant, the co-surfactant, water, and an amount of the monomer that was a little higher than its solubility in water, was added into the reactor. The pre-microemulsion was heated to the reaction temperature and was stirred under a nitrogen atmosphere. Then, the requisite amount of the initiator, which was dissolved in

Table 1
The recipes of modified microemulsion polymerization in RC1

Sample	Surfactant (g)[a]	Initiator (g)	Reaction temperature (°C)	H$_2$O (g)[b]	MMA (g)[c]	Post-addition rate
A1	SDS/n-Pt 8.4/1.2	TMEDA/APS 0.1394/0.2736	40	446.4/30	12/72	72 g/150 min
A2	SDS/n-Pt 8.4/1.2	KPS 0.3244	50	496.4/10	12/72	72 g/150 min
A3	SDS/n-Pt 8.4/1.2	TMEDA/APS 0.1394/0.2736	40	446.4/30	12/72[d]	1. 15 g/40 min 2. 42 g/70 min 3. 15 g/40 min

[a]n-Pt was used as a co-surfactant.
[b]The first part of H$_2$O was added into pre-microemulsion and the second part was used to dissolve the initiator.
[c]The first part of the monomer was in the initial microemulsion, and the second part was post-added.
[d]The monomer was post-added in three periods of time with different rates.

a minimum quantity of water, was added. When the calibration of device (RC1) finished, meanwhile the polymerization had been initiated, the rest of the monomer in the addition bottle was added into the reactor at controlled rate. The heat flow was accurately recorded in the whole polymerization process.

Typical Modified Microemulsion Polymerization of Methyl Methacrylate. The general procedure of a typical modified microemulsion polymerization is the same as that in RC1, and the only difference is that an adaptable three-neck flask, equipped with a reflux condenser, an addition funnel, a nitrogen gas inlet and outlet, and a magnetic stirring bar, was used as a reactor. The recipes of modified microemulsion polymerizations under varied post-addition rates are shown in Table 2.

Post-Treatment and Characterizations of the Nanoparticles. The particle size and the polydispersity of the size distribution (PDI (12)) of the polymer latex were measured by dynamic light scattering on a Malvern 4700 from Malvern Instruments, Ltd.

The polymer particles were precipitated in methanol and vacuum-filtered, and the precipitate was dried in a vacuum oven overnight, then, re-dissolved in chloroform and precipitated again in methanol. The precipitated polymer was vacuum-filtered, washed successively with methanol and water to ensure the thorough removal of the surfactant, and dried in vacuum oven for 24. Gel permeation chromatography (GPC) measurements were carried out to measure the molecular weights of purified samples, with an HP series 1100 chromatograph equipped with Zorbax columns and refractive-index/ultraviolet dual-mode detectors. The elution rate of tetrahydrofuran (THF) was 1 mL/min, and standard PS was used for calibration.

Some Parameters in the Polymerization Process. In the whole polymerization process, RC1 recorded accurately the quantity of heat that the system emitted and the conversion

Table 2
The recipes of typical modified microemulsion polymerization

Sample[a]	Surfactant (g)[b]	Initiator (g)	Reaction temperature (°C)	H_2O (g)[c]	MMA (g)[d]	Post-addition rate (g/min)
B1	SDS/n-Pt 7/1	APS 1.14	70	400/10	10/51	0.17
B2	SDS/n-Pt 7/1	APS 1.14	70	400/10	10/51	0.26
B3	SDS/n-Pt 7/1	APS 1.14	70	400/10	10/51	0.60
B4	SDS/n-Pt 7/1	APS 1.14	70	400/10	10/51	1.02
B5	SDS/n-Pt 7/1	APS 1.14	70	400/10	10/51	2.04
C1	SDS/n-Pt 0.7/0.1	Vc/H_2O_2 0.09/0.06	30	40/3	1/5.1	0.06
C2	SDS/n-Pt 0.7/0.1	Vc/H_2O_2 0.09/0.06	30	40/3	1/5.1	0.13
C3	SDS/n-Pt 0.7/0.1	Vc/H_2O_2 0.09/0.06	30	40/3	1/5.1	0.26
C4	SDS/n-Pt 0.7/0.1	Vc/H_2O_2 0.09/0.06	30	40/3	1/5.1	0.51

[a]The series B is thermal initiation system, and the series C is redox initiation system.
[b]n-Pt was used as a co-surfactant.
[c]The first part of H_2O was added into pre-microemulsion and the second part was used to dissolve the initiator.
[d]The first part of the monomer was in the initial microemulsion, and the second part was post-added.

(α(t)), polymerization rate (R_p), post-addition rate (R_{feed}) can be estimated as follows:

$$\alpha(t) = \frac{H_t^r}{H_{tend}^r} = \frac{\int_0^t (Q - Q_b)dt}{\int_0^{tend}(Q - Q_b)dt} \tag{1}$$

where H_t^r is heat of reaction from start to time t, H_{tend}^r is heat of whole reaction, Q is the sum of heat flow and Q_b is the baseline for Q.

$$Rp = \frac{Q - Q_b}{V_{aq}\Delta H_{polym}} \tag{2}$$

where V_{aq} is the volume of aqueous phase and ΔH_{polym} is the enthalpy difference of the polymerization, which in the polymerization of MMA is $-57.8\,KJ/mol$ (13).

$$R_{feed} = \frac{m_{feed}}{V_{aq}\Delta t M_m} \tag{3}$$

where m_{feed} is the mass of monomer post-added, V_{aq} is the volume of aqueous phase, Δt is the time of post-addition and M_m is the molecular weight of monomer.

Results and Discussion

The Effect of the Post-Addition Rate on the Process of Polymerization

The data got from RC1 was calculated in the Equations. (1, 2, 3), and the results were shown in Figures 1, 2, and 3. Since the calibration of the device and heating-up were necessary, which lasted about 40 min, there is one stage of blank before post-addition, and the pre-microemulsion had polymerized completely during this stage. Figures 1 and 2 show the similar results: in a constant R_{feed}, the R_p didn't vary, but kept relatively steady in the entire post-addition process. However, in Figure 3, it is clear that the R_p is significantly correlated with the R_{feed}: when MMA was post-added at three different rates of 0.375 g/min, 0.6 g/min, 0.375 g/min, the R_p curve also showed three stages of different slope coefficients correspondingly, and the tendency agreed well with the change of the R_{feed}. After the post-addition stopped, the R_p fell rapidly and immediately, and the conversion had been more than 90%. These results indicated that in our modified microemulsion polymerization, the post-addition rate is very important, and it is feasible to control the polymerization via controlling the post-addition rate.

As we know, one advantage of emulsion polymerization is that it can achieve both high molecular weights and high polymerization rates simultaneously because of the
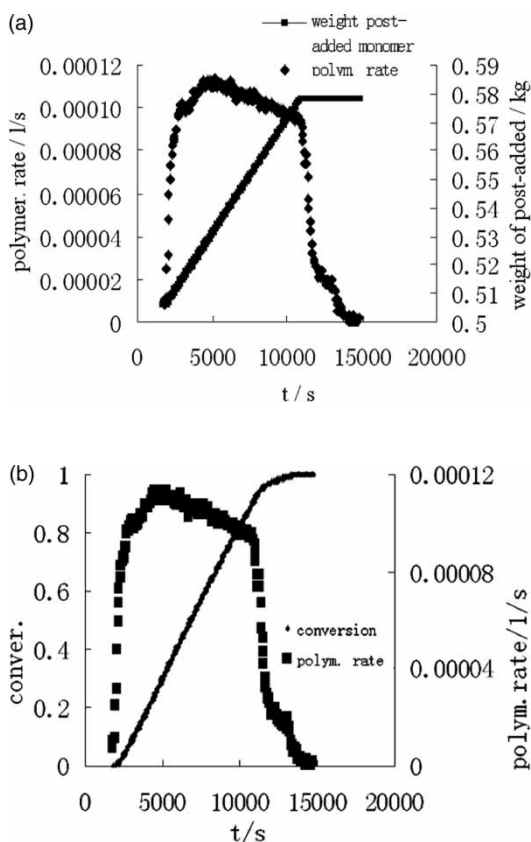

Figure 1. Sample A1: (a) weight of post-added MMA and polymerization rate vs. reaction time; (b) conversion and polymerization rate vs. reaction time.
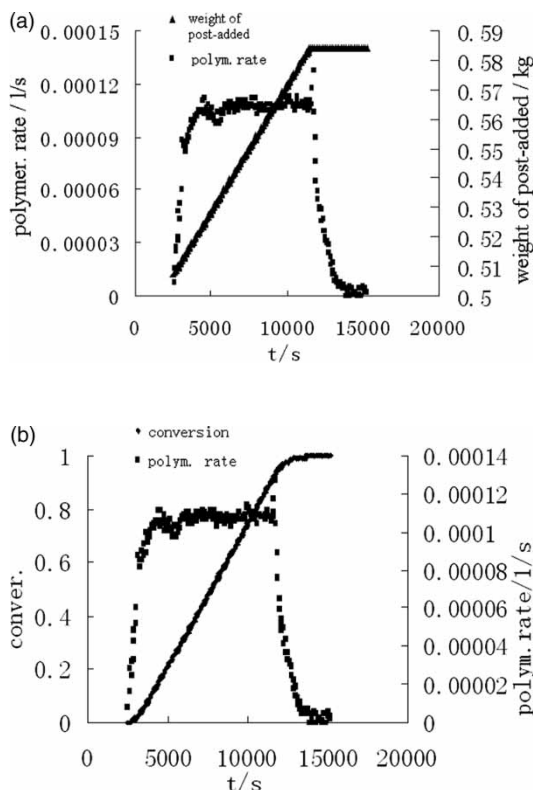
Figure 2. Sample A2: (a) weight of post-added MMA and polymerization rate vs. reaction time; (b) conversion and polymerization rate vs. reaction time.

compartmentalization effect. In the radical emulsion polymerization, $R_p = k_p N' \bar{n} [M] / N_A$, where N' is the number of latex particles per unit volume of aqueous phase, $\bar{n}$ is the average number of radicals per latex particle, $[M]$ is the concentration of monomer in latex particle, and N_A is the Avogadro number (13). The three figures all show that when the post-addition was completed, the conversion of the monomer had been up to more than 90%, which means that most of the monomer could polymerize in the active particles in a very short time after post-added, and if the R_{feed} kept constant, the concentration of monomer in the latex particle ($[M]$) was always low in the entire procedure and could be seen as constant.

Figure 1 was compared with Figure 2, although the R_p both kept steady in the entire post-addition process, it is clear that there was a tiny difference between them: in Figure 1, the R_p slightly declined with time passing, but in Figure 2, the R_p kept constant. It could be explained as below.

Based on the solid content (C_s) and the particle size (d), the number of particles (N_p) in the two samples can be estimated as follows:

$$\frac{1}{6} N_p \pi d^3 \rho = V \cdot C_s \tag{4}$$

where ρ is the density of the particles, V is the total volume of system. So, when V and C_s keep constant, the N_p is related to the particle size. As mentioned in Table 3, the particle
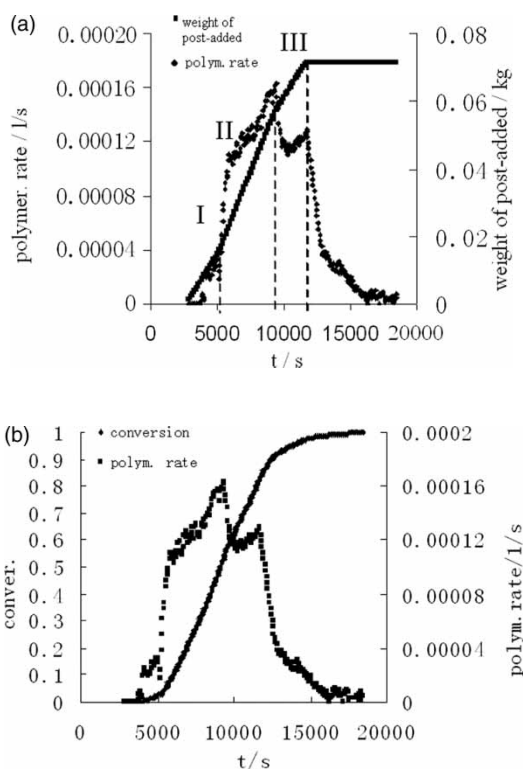
Figure 3. Sample A3: (a) weight of post-added MMA and polymerization rate vs. reaction time; (b) conversion and polymerization rate vs. reaction time.

size of sample A1 is 28.9 nm and that of sample A2 is 41.3 nm. Furthermore, the only difference between the two samples is that A1 was initiated by redox initiation, but A2 was by thermal initiation. The result indicated that the redox initiation system could generate more particles than the thermal initiation system. It is also found that after initiation, the R_p would be up to the maximum value soon, and the maximum R_p of Figure 1 is higher than that of Figure 2, which means that there were more active particles (the latex particles with radical) in the redox initiated microemulsion (A1). So,

Table 3

The particle size and molecular weight of the samples prepared in RC1

				Particle size[a]	
Sample	Mw($\times 10^5$)	Mn($\times 10^5$)	Mw/Mn	Dz(nm)	PDI
A1	3.7	2.2	1.7	28.6	0.1
A2	5.1	3.1	1.7	41.3	0.52
A3	6.0	2.4	2.5	33.8	0.44

[a]Dz is z-average diameter determined by dynamic light scattering, and PDI = μ_2/Γ^2 = polydispersity of the size distribution, see reference 12.

in the redox initiation system, the same amount of monomer post-added in unit time as the thermal initiation system could not maintain polymerization with more active particles, and quite a bit of active particles would lose their activity (the radicals ended). With the decrease of the number of active particles, the R_p was gradually declining after it reached maximum value, till the post-addition completed, then it declined sharply.

In Figure 3, the R_p kept rising on stage I and II: On stage I, when the system was just initiated, the number of active particles had not reached a high level and still increased, and the monomer post-added was sufficient to support the polymerization; on stage II, the higher R_{feed} maintained the polymerization, and the number of active particles kept increasing. Then the R_{feed} lowered on stage III, which made quite a few active particles unable to get enough monomer to keep growing. This is the main reason that why the R_p of sample A3 varied in the polymerization process as shown in Figure 3.

The Effect of the Post-Addition Rate on the Molecular Weight of Product

The results shown in Tables 2 and 4 and Figure 4 indicate that, in the thermal and redox initiation system, the molecular weights are always increasing with the increasing of post-addition rates (From B1 to B5, and from C1 to C4). In Figure 5, the elution volumes of the samples of series B, in refractive-index mode of GPC, are illustrated. It is clear that there are two separate peaks in the signals of B1, B2, which turn to a single peak for B3, B4, and a broadening peak with shoulder for B5.

As discussed above, in our modified microemulsion polymerization, the post-addition rate is a very important parameter to the polymerization rate, R_p. Here, we continue to discuss its effect on molecular weight. It has been reported that in emulsion polymerization, the concentration of radicals could be high because of the compartmentalization effect, then the R_p could be very high (13) and the radical chain transfer to monomer is the dominant termination of the growing polymer chains for most of oil-in-water (o/w) microemulsion polymerizations (14–16). In the process of chain transferring to

Table 4
The particle size and molecular weight of the samples prepared through typical modified microemulsion polymerization

Sample	Mw($\times 10^5$)	Mn($\times 10^5$)	Mw/Mn	Particle size[a]	
				Dz(nm)	PDI
B1	0.89	0.25	3.55	19.8	0.17
B2	1.25	0.27	4.66	20.2	0.14
B3	1.52	0.67	2.27	26.9	0.2
B4	1.93	1.02	1.89	22.5	0.11
B5	3.82	1.05	3.63	33.5	0.1
C1	1.53	0.52	2.97	18.7	0.36
C2	1.07	0.52	1.76	17.6	0.31
C3	2.51	1.19	2.12	15.9	0.25
C4	3.64	1.42	2.56	30.7	0.17

[a]Dz is z-average diameter determined by dynamic light scattering, and PDI = μ_2/Γ^2 = polydispersity of the size distribution, see reference 12.
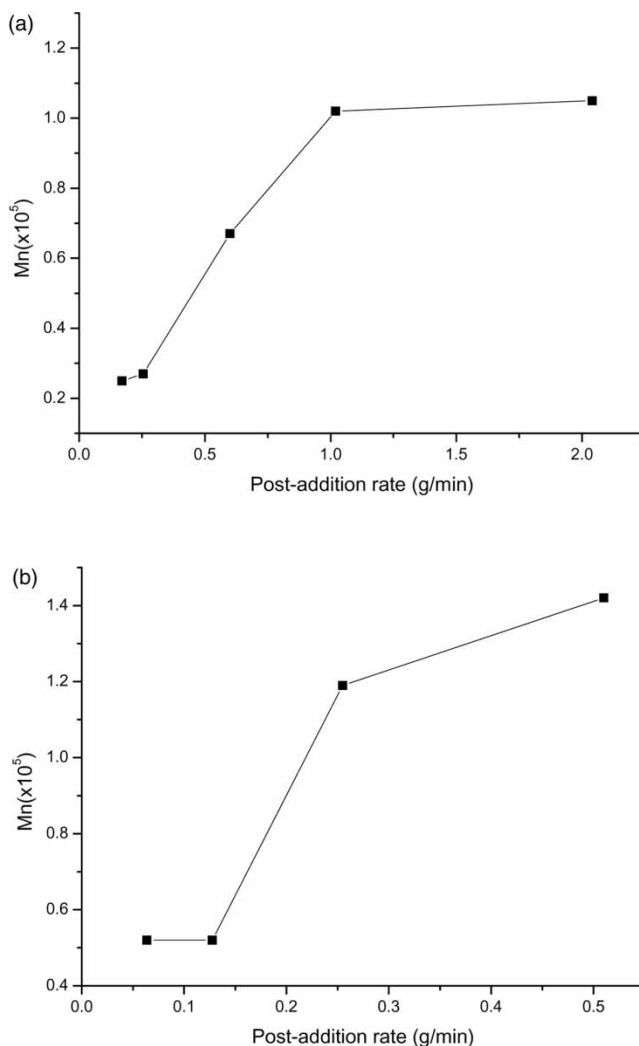
Figure 4. Mn vs. post-addition rate: (a) series B prepared in thermal initiation system; (b) series C prepared in redox initiation system

monomer, the amount of radicals will not change, but if the concentration of monomer is always very low, the radicals may lose their activity in other termination modes such as combination and disproportionation, which will decrease the amount of radicals in microemulsion. When the monomer was post-added slowly, as discussed above, it was consumed rapidly and could not afford to maintain polymerizing a lot of radicals. So, only a part of the radicals could keep polymerizing, and the other may terminate in various termination modes. In the signals of GPC of B1 and B2 (Figure 5), the first peak, which is small elution volume (higher molecular weight), maybe attributed to the part of keeping polymerizing, and the second peak of large elution volume (lower molecular weight) maybe attributed to the part terminated in various modes. The curve of B1 clearly illustrates that a large number of active chains terminated when the post-addition rate was low, and the total amount of active chains kept decreasing.
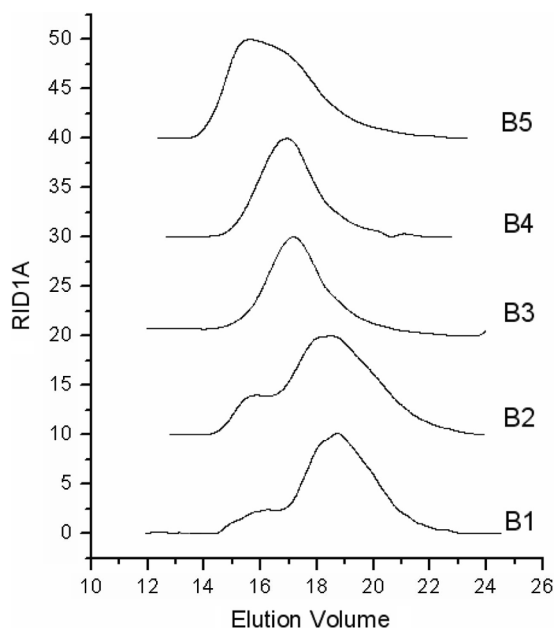
Figure 5. The elution volumes of sample of series B in refractive-index mode of GPC.

Meanwhile, only a small part of active chains could keep growing till the theoretic molecular weight, which is defined by both propagation rate constant and monomer transfer constant, was reached. With the R_{feed} increasing, the first peak became higher and the second one became lower, which means more active chains can get sufficient monomer to keep activity. The result is that the molecular weights became larger and the distribution became narrower (From B1 to B4 in Table 4).

B5 is a special sample because of its wide molecular weight distribution, which is illustrated by the broadening peak with shoulder. It is assumed that the monomer was post-added too fast for diffusing and polymerizing simultaneously, then maybe, a few residue monomer droplets left and a part of the surfactant might leave the surface of latex particles to stabilize the residue monomer droplets. More importantly, the polymerizing particles whose surfaces were not covered by adequate surfactant might attract each other, even aggregate together in a small quantity, and the probability for bigger particles to arrest radicals in aqueous was more than that for smaller ones. So, the growing chains would terminate in two different termination modes: a part of growing chains kept growing till terminated by transfer to monomer, which produced the polymer with higher molecular weight, and the other growing chains would be terminated by the new-entry radicals instantaneously as they entered the particles, seemed as zero-one system (13), which produced the polymer with lower molecular weight. That is why the B5 signal is a peak for higher molecular weight with a shoulder of lower molecular weight.

The serial C samples (Figure 4b), which were prepared in the redox system, showed similar tendency to that initiated in the thermal system: the molecular weight increased with the increasing of R_{feed}. As discussed above, the redox initiation system can generate more particles than the thermal initiation system, which can be estimated from the smaller particle size. When MMA was post-added slowly (C1, C2), the molecular

weights were relatively lower than that of samples synthesized at high post-addition rate (C3, C4).

In Figure 4, it is also shown that the molecular weight of the polymer could not increase infinitely with the increasing of R_{feed}, and in high R_{feed}, the increase of molecular weight became obviously slower. When the R_{feed} reached a proper critical value, the monomer post-added would be sufficient for supporting the need of radicals, and radicals termination will be dominated by the mode of chain transfer to monomer. But when the R_{feed} is above the critical value, the combination termination of radicals, as that in conventional emulsion polymerization, would also happen, so the molecular weight will not increase markedly.

Conclusion

PMMA nanoparticles were prepared by a modified microemulsion polymerization. In this method, the post-addition rate is a very important parameter, which can influence the polymerization rate and obviously, the molecular weight of the product. Whether in the thermal initiation system or redox initiation system, both R_p and molecular weight increased with the increasing of R_{feed}, till the critical value was reached. If R_{feed} exceeded the critical rate, it is predicted that the molecular weight would not increase significantly and the molecular weight distribution would become wider, because the radicals would terminate in two different modes. The serial of experiments showed that it was possible to control both the process of polymerization and the characterization of product simultaneously via controlling post-addition, which makes the large-scale preparation of high-quality nanoscale polymer latices practicable.

Acknowledgements

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