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Study on Controlling Particle Growth in Seeded Emulsion Polymerization with Regulated Coagulation Based on the Electrostatic Interactions

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Summary: 30wt% solid content, anionic seed copolymer latex P(methyl acrylate-co-methyl methacrylate) was prepared by conventional emulsion polymerization, and then the seeded emulsion polymerization was carried out accompanied with the electrostatic coagulation during the reaction in the presence of counter-ion species, such as cationic monomer and initiator. In this article, effects of cationic monomer (dimethyl aminoethyl methacrylate, DM) content, secondary monomer to seed polymer weight ratio, M/P and amount of emulsifier (polyoxyethylene nonylphenylether with 23 units of ethylene oxide, PEO23) were investigated on the effective particle growth and the stability of final latex. With 10wt% DM in monomer, M/P ratio at 2.0 were recommended. An optimal policy for handling the emulsifier content without the nucleation of secondary particles while achieving the controlled coagulative growth was proposed from the observations of polymer yield and particle size during the polymerization.

Introduction

Synthetic polymer latices and polymer particles have been prepared by several polymerization method, such as microemulsion, emulsion, emulsifier-free, miniemulsion, dispersion, seeded emulsion, suspension, and precipitation polymerization. The latices are normally utilized as emulsions in the industries of adhesives, synthetic paints, paper-coatings, and floor waxes. Plastisols, synthetic rubbers and some plastics such as ABS and AS are also produced by these

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heterogeneous systems. Applications utilizing individual polymer particles have also increased as specialty products in many fields, for example, for anti-body-enzyme diagnostic tests, conductive paints, spacers for display device, and so forth.[1] Advantages of seeded emulsion polymerization are well known its ability to prepare latex particles having large size and sharp distribution.[2] The composite polymer particles, such as those including various functional materials and those having unique structures of core-shell, [3-4] snowman [5] and dumbbell /egg [6] were also actually prepared by the seeded and multi-stage emulsion polymerizations. Such composite polymer particles have been applied in more sophisticated industry fields. The seeded emulsion polymerization is, therefore, recommended for preparing the functional polymer particles. The disadvantage of conventional seeded polymerization is, however, difficult to obtain large particles in one step due to the limited monomer-swelling of seed particle as proved by Morton et al. [7] The polymerization, therefore, need to be repeated several times to attain the desired particle size. Indeed, Vanderhoff et al. and NASA group[8] carried out successive seeded emulsion polymerizations in the non-gravitational field, and prepared extremely uniform and large particles of more than 30μm. On the other hand, a unique method for swelling seed particles based on the thermodynamical theory was reported in order to overcome the swelling limitation problem. They were the two-step swelling method by Ugelstad et al.[9-10] and the dynamic swelling method by Okubo et al.[11]

Coagulation of particles may be also efficient procedure for preparing large particles in one step, although it is difficult to improve the size distribution of seed particles further. Agitation, addition of electrolytes and flocculant, and in particular, interaction between counter-ions are key factors for the controlled coagulation of colloidal particles. Among these, the controlled coagulation between the two oppositely charged particles (a typical hetero-coagulation process) has been employed in the studies for preparing composite particles including inorganic silica powder[12] and magnetite[13]. These composite particles reveal a layer of small particles packed on the surface of a larger one. Okubo et al.[14] obtained core-shell composite particles by using stepwise heterocoagulation in which two different latices counter-charged with each other were blended.

As an advanced utilization of heterocoagulation, if the controlled coagulation is carried out successfully during the seeded emulsion polymerization, not only the efficient growth of particle size but also the formation of composite particles will be accomplished. The authors [15-16] have been working with this possibility. At first an anionic seed polymer particles, P(methyl acrylate-co-methyl methacrylate) P(MA-co-MMA) was synthesized with anionic initiator (ammonium persulfate. APS) and emulsifier (sodium lauryl sulfate, SLS), and then, using this anionic seed, seeded emulsion polymerization with cationic monomer (dimethyl aminoethyl methacrylate, DM) and initiator (2,2'-azobis-(2-amidinopropane)・2HCl, V-50) were carried out. It was confirmed that the final particles grew effectively via the parallel processes of the coagulation between the seed particles swollen with the secondary monomer and the electrostatic interactions between the anionic seeds and cationic secondary copolymers. New polymer particles dominant with hydrophilic DM was nucleated in the aqueous phase and incorporated inside the growing particle, while a layer of these particles was located on the surface.[17-18] Composite polymer particles of P(styrene-co-DM)/P(MA-co-MMA) were produced with hydrophilic domains being located on the surface and the inside as well. We have reported the effects of agitation rate, seed particle size and adjustment of pH before conducting the seeded polymerization in order to control the final particle size.[16] In this article, the effects of DM monomer content, M/P and emulsifier content will be reported as a continuation from the previous work, and also the growth of polymer particles was monitored along with the progress of the seeded polymerization.

Experimental

Materials

Commercial grade, methyl acrylate (MA), methyl methacrylate (MMA), styrene (ST) (Kishida Chemical Co.), and reagent grade, dimethyl aminoethyl methacrylate (DM, Tokyo Chemical Co.) were distilled under reduced pressure, and stored in a refrigerator. Ammonium persulfate (APS, Wako Pure Chemical Co.) was used as initiator for preparing the anionic seed latex, and 2,2'-azobis -(2-amidinopropane)·2HCl (V-50, Wako Pure Chemical Co.) was used as initiator for the seeded emulsion polymerization. Sodium lauryl sulfate of biochemistry grade (SLS, Merck) was used as emulsifier to prepare the anionic seed latex, and polyoxyethylene nonylphenylether with 23 units of ethylene oxide (PEO23, Kao Co) was used to stabilize the polymer particles in the seeded emulsion polymerization. To control the molecular weight of polymers, t-dodecyl mercaptan (TDM, Tokyo Chemical Co) was used as chain transfer agent. Distilled and deionized (DDI) water was used.

Apparatus

For preparing the seed latex, a 1000ml, 5-necked grass separator flask equipped with a nitrogen inlet, a condenser, a thermocouple and a dropping funnel for initiator solution was used. A 500ml, 4-necked flat-bottom flask equipped with the same set as above was used for seeded emulsion polymerization. A half-moon blade type impeller was used as a stirrer.

Analyses

Withdrawn latex sample was put in a small bottle with a screw cap, and then the polymer was precipitated with a few drops of 2N HCl, alum solution and excess methanol. The precipitated polymer was centrifuged, washed three times with methanol, and dried in vacuum oven at room temperature over 2 days. The dried polymer weight was measured to calculate the monomer conversion. From the photographs taken with SEM (JSM-5310, JEOL), the diameters of more than 200 polymer particles were measured to obtain the average particle diameter. One drop of the diluted latex (10000~20000 times) was dropped on a sample stub covered with an aluminum film and dried. Gold was spattered with a film coater (JFC-1200, JEOL). The average molecular weight of polymer soluble in tetrahydrofuran (THF) was determined with gel permeation chromatography, GPC (H810, Tosoh). The ζ-potential of polymer particles diluted 10000 times with DDI water was measured with ζ-potential analyzer (Zeecom, Microtech Nition).

Preparation of anionic seed latex

Typical recipe for preparing anionic seed latex is listed in the foot note of Table 1. A fixed content of SLS dissolved in DDI water, MMA, MA, and TDM was added in a 1000ml glass beaker, and mixed with a magnetic stirrer for 30 min.

Table 1. Characterization of anionic seed latex prepared with conventional emulsion polymerization and their typical recipe.

Run	Monomer conversion (%)	Average diameter (μm)	CV (%)	Number of seed particles ($\times 10^{-17}$/dm^3)	Mn ($\times 10^{-5}$)	ζ-potential (mV)
1406	96.7	0.12	27.6	3.21	0.99	-89.6
1408	99.9	0.11	17.8	4.29	1.45	-60.6
1409	100	0.10	15.7	5.74	0.99	-78.0

a) Recipe: DDI water 700g, MMA 150g, MA 150g, TDM 0.5g, SLS 8.0g, initiator (APS) 0.2g, Total 1000g.

b) Agitation rate during polymerization was maintained at 260rpm.

c) Polymerization was carried out at 333K for 3hr.

After the mixture was poured in the reactor, the temperature was raised to 333K in a water bath, and at the same time, the nitrogen was gently bubbled in the reaction mixture to displace the dissolved oxygen. After 1h, the initiator, APS solution was added in the reactor, and the polymerization was started under the nitrogen blanket. The characteristics of the resulting latex are given in Table 1. The particle sizes of resulting anionic seed latices were small, around 0.10～0.12 μ m, because a high concentration of SLS (8.0g/dm^3) was employed. It was shown in our previous work[15-16] that the smaller seeds yielded higher number of coagulation between them without deteriorating the stability of latex.

Seeded emulsion polymerization

The resulting anionic seed latex was dialyzed using cellulose membrane (UC 27-32-100, Sankou) for 24hr under the continuous flow of tap water, and then it was soaked in DDI water for another 24hr. After the characterization listed in Table 1, the required amount of seed latex (typical initial solid content in the seeded polymerization, 40g) was measured, and PEO23 and TDM were added. The desired amount of styrene, DM and DDI water were added in a stainless steel beaker, and the mixture was homogenized with an Ace Homogenizer (HF 93, SMT Co.) at 4000～5000rpm for 15min. The mixture was added in the seed latex, mixed, and the seed particles were swollen with the monomers, while being stirred with a magnetic stirrer at 700～800rpm for 1hr. The total weight of the mixture was 400g. Controlling of pH before the seeded emulsion polymerization was conducted using 2.0N HCl or 0.5N KOH, and then introduced in the reactor. The seeded emulsion polymerization was carried out after the same procedures as the preparation of anionic seeds. The temperature was 333K and the polymerization time was 20hr.

Result and discussion

Effect of DM monomer content

The advantage of adding DM monomer in the second stage polymerization is, for example, to prepare composite particles including hydrophilic polymer, and to provide cationic charge (together with V50) against the anionic seed particle.[17-18] In addition to the particle growth during the conventional seeded polymerization, in this particular system, more intensive particle growth can be expected because of the high viscosity of the seed particles swollen with styrene and the presence of cationic counter-ion against the anionic seeds.[15-18] In order to control the amount of cationic charge, the adjustment of pH before the seeded polymerization was conducted.[16] Increasing pH (9.5 and 10.0) reduced the particle growth due to the suppression of the cationic charge induced from the pendant, dimethylamino group in DM, while at the lower pH (8.0 and 8.5), the coagulums were formed in the final latex due to the excess amount of the counter-ion which also accelerated the nucleation of DM-rich secondary particles. The optimal selection of pH under the consideration of particle growth with controlled coagulation was found at 8.75-9.0. As a continuation of this result, the effect of DM monomer content (2.0, 4.0, 6.0, 8.0, 10.0 and 12.0g) in the seeded emulsion polymerization was conducted. In each experiment, styrene monomer was adjusted so that the total comonomer content can be fixed at 80g. The reaction mixture consisted of DDI water (187g), Run1409 seed anionic latex (133g; solid content in latex is 40g), TDM (0.24g), V-50 (0.24g) and PEO23 (2.0g). The characteristics of the latex after the seeded emulsion polymerization are shown in Table 2, in which the average number of coagulation of seed particles was calculated from the following expression.[16]

$$\frac{N_{sp}}{N_p} = \frac{w_s}{w_p}\left(\frac{d_p}{d_{sp}}\right)^3 \tag{1}$$

N_{sp} and N_p denote the number of seed polymer particles and the number of final polymer particles, w_s and w_p denote the solid content in the seed and the final latex, and d_{sp} and d_p denote the average diameter of the seed polymer particles and the final polymer particles, respectively. The experimental data for the case of DM, 10g was not listed because the reaction was forced to stop by the accumulation of extensive coagulums during the polymerization. It seems from Table 2 that the average particle size in the final latex increased until the 8.0g of DM, implying that the amount of cationic charge favored the coagulation under control, however, the highest DM monomer, 12g, the average number of coagulation decreased. In fact, the final size distribution was bimodal due to the generation of secondary small particles. The cationic, hydrophilic polymer did not precipitate nor was adsorbed on the surface of anionic growing particle, but grew by itself to form the secondary particles. Such similar scenario may arise with other factors, for example, high content of emulsifier (PEO23) and cationic initiator (V50).

Table 2. Result of seeded emulsion copolymerization (I). Effect of DM monomer content.

DM (g)	Average particle size (μm)	CV (%)	ζ-potential (mV)	Solid content in the final latex (g/g-lx)	Average number of coagulation
2.0	0.21	21.8	-32.1	0.291	3.18
4.0	0.27	19.5	-20.0	0.270	7.30
6.0	0.28	11.1	-25.4	0.276	8.00
8.0	0.50	24.5	-48.0	0.230	54.6
10.0	-	-	-	-	-
12.0	0.29	30.8	-36.8	0.246	9.90

a) Initial pH was adjusted at 9.0 and secondary monomer to seed polymer weight ratio, M/P was 2.0.

b) Agitation rate was maintained at 200rpm.

c) Polymerization was carried out at 333K for 20hr.

The addition of 12g DM monomer formed roughly 22.3g of coagulum in 400g of the final latex, while DM-rich, hydrophilic polymers acting as binders between growing particles. It can be said from this result that the threshold value for producing composite polymer particles including hydrophilic polymer in the stabilized latex is 8g of DM monomer. Probably the DM monomer content from 10.0g to 12.0g implies the boundary where the DM-rich, hydrophilic copolymers could form secondary, stable particles. Once the secondary polymer particles are stabilized, they may not so easily adsorb on the growing, anionic particles even though they are cationic because they are surrounded by their own electric double layers. In considering the dispersion stability of the particles after the polymerization, the addition of 8.0g DM seemed to be best. Besides no coagulums were found in the final latex, the absolute value of ζ -potential was higher than any other experiments. In this case, considerable amount of hydrophilic, cationic copolymers (and some particles) were incorporated in the growing particles during the controlled coagulation between the particles. The remaining source of counter-ion for anionic seed particles is the cationic initiator, V-50, and the effect of V-50 to the controlled coagulation and particle growth is now under investigation.

Effect of secondary monomer to seed polymer weight ratio, M/P

The effect of M/P, varied as 0.5, 1.0, 1.5, 2.0 and 2.5, to the behavior of seeded emulsion polymerization was examined. The basic recipe included 134g seed anionic latex of Run1408 (solid content in seed latex is 40g) as well as TDM (0.24g), V-50 (0.24g), PEO23 (2.0g), and the composition of comonomer, ST:DM, was fixed at 9:1. DDI water was added up to the total weight of 400g. The characteristics of resulting polymer particles are listed in Table 3. The polymer yield is plotted in Figure 1 as a function of the reaction time. The average particle diameter in the final latex and the average number of coagulation calculated from the equation (1) increased with higher M/P. It seems that the controlled coagulation by the electrostatic interaction and the swelling of comonomer proceeded well over the whole range of M/P, from 0.5 to 2.5. However, as shown in Figure 1, apparently the polymer yield for the highest M/P, 2.5 stalled in the later stage of the polymerization as the formation of uncontrolled coagulum became noticeable. Around 50g of coagulum was formed in 400g of the final latex. The failure of controlled growth may be due to the increase of viscosity in the growing particles by excess swelling of styrene in the comonomer. In the case of M/P 2.0, although the monomer conversion leveled off at around 70%, there was no uncontrolled coagulum formation in the final latex and the CV was the lowest 17.6%. The leveling off of polymer yield in the later stage of polymerization may be based on the decrease of number of polymer particles by controlled coagulation. As for the runs with lower M/P ratio, 0.5, 1.0 and 1.5, the polymerization progressed readily without the formation of uncontrolled coagulum, however, the growth of seed particles was disappointingly mediocre. The number of coagulation stayed around 4.

Table 3. Result of seeded emulsion copolymerization (Ⅱ) Effect of secondary monomer to seed polymer weight ratio, M/P

M/P	ST (g)	DM (g)	Average particle size (μm)	CV (%)	ζ-potential (mV)	Average number of coagulation
0.5	18.0	2.0	0.19	25.8	-25.2	3.70
1.0	36.0	4.0	0.21	22.7	-25.0	3.50
1.5	54.0	6.0	0.23	32.9	-47.5	4.00
2.0	72.0	8.0	0.30	17.6	-42.2	8.10
2.5	90.0	10.0	0.39	31.5	-23.2	19.3

a) Initial pH was adjusted at 9.0.

b) Agitation rate was maintained at 200rpm.

c) Polymerization was carried out at 333K for 20hr.

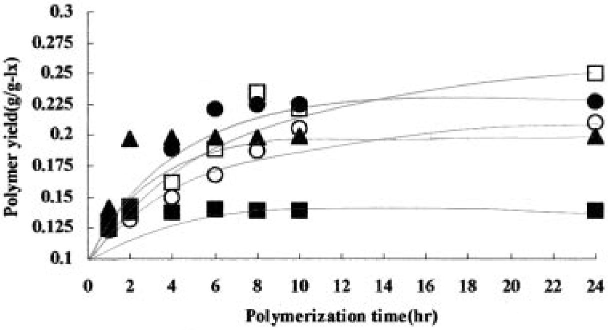

Figure 1. Polymer yield against polymerization time. I. Effect of M/P ratio

■=M/P:0.5, ▲= M/P:1.0, ●= M/P:1.5, □= M/P:2.0, ○= M/P:2.5.

By summarizing these results, it can be said that the M/P ratio of 2.0 is recommended for the controlled growth of seed particles without the formation of uncontrolled coagulums. There is no reasonable explanation against the difference between the number of coagulation as shown for the run with DM 8.0g in Table 2 (54.0) and for the run with M/P 2.0 in Table 3 (8.10). Only difference is the employment of different seed latex, 1409 and 1408. Only the ζ-potential is noticeably different (-78.0 and -66.6mV, respectively). Apparently, the higher density of negative (anionic) charges was favored for the effective coagulation. In the previous work, which reported the effect of seed particle size,[16] a great difference in the average number of coagulation was observed when the seed particle sizes of 0.08 and 0.11 μm were employed. The average number of coagulation significantly decreased from 179 to 69.4 with increasing the seed particle size. Probably the seed particle size around 0.10 μm may be pretty sensitive to the coagulation process.

Effect of emulsifier content

The primary role of emulsifier in emulsion polymerization is to supply the loci of reaction based on the micellar nucleation mechanism,[19-21] and for the homogeneous nucleation mechanism,[22] to stabilize the precipitating oligomers, promoting them to the growing polymer particles. An adequate amount of emulsifiers to be adsorbed on the surface of growing polymer particles is essential to carry on the emulsion polymerization in stable state. The effect of different amount of emulsifier is, therefore, worthwhile to investigate for the controlling of coagulation between the seeds and also undesirable generation of secondary particles. The selection of the emulsifier content was set at 1.00-2.00g as shown in Table 4 which also provides the characteristics of the obtained polymer particles after the polymerization. The standard recipe includes the anionic seed latex, Run1406 (138g, solid content in latex is 40g), DDI (185g), styrene (72g), DM (8g), TDM (0.24g) and V-50 (0.24g). Other conditions are listed in the lower part of Table 4. The average particle diameter and CV in the final latex are plotted in Figure 2 against the emulsifier concentration.

Table 4. Recipe and result of seeded emulsion copolymerization (III) Effect of emulsifier content.

Emulsifier contetnt (g)	ST (g)	DM (g)	ζ -potential (mV)	Solid content in the final latex (g/g-lx)	Average number of coagulation
1.00	72.0	8.0	-28.6	0.182	37.3
1.25	72.0	8.0	-31.0	0.240	23.3
1.50	72.0	8.0	-30.9	0.253	20.8
1.75	72.0	8.0	-33.1	0.254	15.6
2.00	72.0	8.0	-22.7	0.277	11.4

a) Initial pH was adjusted at 8.75 and secondary monomer to seed polymer weight ratio, M/P was 2.0.

b) Agitation rate was maintained at 180rpm.

c) Polymerization was carried out at 333K for 20hr.

The average diameter and the average number of coagulation decreased with the increasing emulsifier content which led to stabilize the seed particles. The ζ -potential of polymer particles in the final lattices were around -20~-30mV. Approximately 50g of uncontrolled coagulum was formed in 400g of the final latex in the run of emulsifier content, 1.0g which clearly indicated inadequate adsorption of soap molecules on the surface of growing particle.The solid content remained in the latex was, therefore, remarkably lower than those in the runs of emulsifier content, 1.25-2.0g. The average number of coagulation decreased with increasing amount of emulsifier, indicating that the controlled coagulation process slowed down by the stabilizing effect of PEO 23. In other words, the conditioning to promote the controlled coagulation and the stabilization of latex are in a trade-off relationship. It is interesting to note in Figure 2 that the CV, coefficient of variation, steadily decreased with the average diameter until the emulsifier content, 1.75g and increased again at 2.0g.

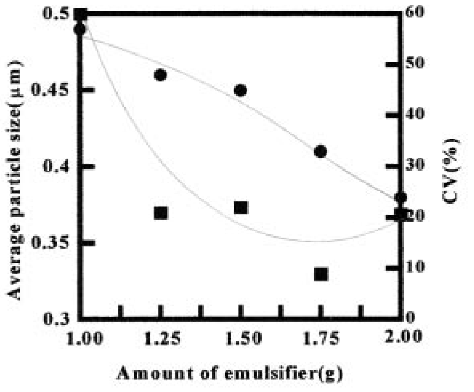

Figure 2. Average particle size and CV vs. amount of emulsifier. ●= Average particle size (μ m), ■= Coefficient of variation, CV (%).

This suggests that the secondary nucleation of polymer particles became noticeable to affect the over-all particle size distribution. Apparently excess PEO23 molecules promoted the stability of DM-rich, hydrophilic copolymers generated in the aqueous phase before they were adsorbed on the surface of anionic particles. In this series of experiments, the emulsifier content of 1.75g seemed to be the limit to suppress the secondary nucleation in a tolerable range. As mentioned above, the addition of emulsifier at the seeded polymerization stage results in the stabilization of the latex during the polymerization, while obstructing the controlled coagulation process. In order to control the particle size and size distribution of composite particles in the final latex, a policy of optimal addition of emulsifier, its concentration and the timing of addition, shpuld be established. In the next section, this possibility will be discussed by following the growth of polymer particles during the polymerization.

Growth of polymer particles during the seeded emulsion polymerization

Polymer yield is plotted against the polymerization time in Figure 3 with the amount of emulsifier changed. In Figure 4, the growth of polymer particles is shown as a plot of the average particle diameter against the polymerization time. From Figure 3, it is clear that the final polymer yield (solid content in the latex) decreased slightly for each run compared to the point before (18hr sample). This indicates that the uncontrolled coagulum more or less started to form towards the end of polymerization. Secondly, the polymerization rate (slope of the curve) depended on the number of polymer particles, in other words, as the particle size grew larger, the rate of polymerization leveled off. For example, the polymer yield for the run with lowest PEO content, 1.0g, the polymer yield stalled at around 0.18g/g-lx. This is partly due to the gradual build up of uncontrolled coagulum.

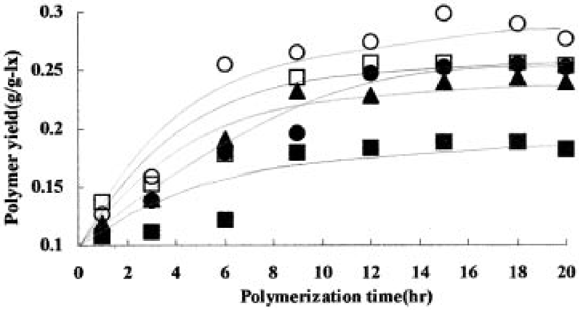

Figure 3. Polymer yield against polymerization time. Ⅱ. Effect of emulsifier content ■= PEO23:1.0g, ▲= PEO23:1.25g, ●= PEO23:1.50g, □= PEO23:1.75g, ○= PEO23:2.00g.

However from the kinetic point of view, the initiator radicals generated in the aqueous phase are unlikely to diffuse into the core of larger particles where the viscosity is high by the swollen monomer. The growth of polymer chains are limited at the surface, and eventually the uncontrolled coagulation becomes dominant due to the deficient stabilizer on the surface. This mechanism appeared to be seen in the other runs. Regardless the PEO23 content and the level of polymer yield, the polymerization slowed down at around 10hr. This tendency is also detected in Figure 1. From Figure 4, this corresponds to the average particle diameter, 0.33-0.4μm. On the other hand, in the run of highest PEO23, an acceleration of polymerization rate can be detected from 3 to 5hr which implies it is due to the secondary nucleation of polymer particles. In Figure 4, it is also interesting to note that in the run with lowest PEO23 content, 1.0g, the average particle diameter increased efficiently to more than 0.4μm at 3hr, stayed almost constant until 18hr, and then increased again at 20hr.

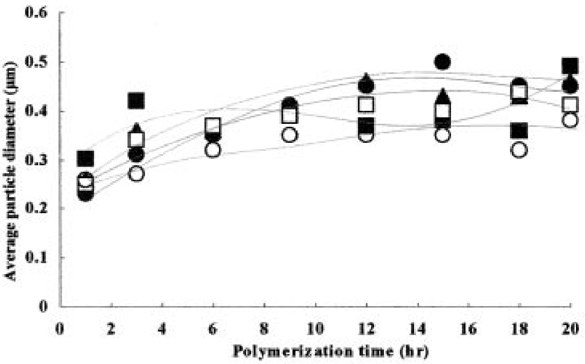

Figure 4. Average particle size against polymerization time. Effect of emulsifier content. ■= PEO23:1.0g, ▲= PEO23:1.25g, ●= PEO23:1.50g, □= PEO23:1.75g, ○= PEO23:2.00g.

The initial growth probably progressed by the electrostatic interaction between the counter charges (controlled coagulation), while the stability of latex was still maintained. As the polymerization progressed further, gradually the stability of particles was deteriorated, and uncontrolled coagulum started to form by the coagulation between the growing particles. Eventually the amount of uncontrolled coagulum reached to around 50g/dm^3 latex. From these results, an optimal policy concerned with the control of emulsifier content can be proposed. The seeded emulsion polymerization can be started with a minimum addition of emulsifier barely enough to stabilize the polymer particles. After the controlled growth of polymer particles progressed, extra amount of emulsifier should be added either continuously or intermittently to prevent the formation of uncontrolled coagulum between the growing particles. In this way, undesirable nucleation of secondary particles can be prevented without seriously deteriorating the stability of latex. As for the leveling off of monomer conversion, supplementary addition of oil-soluble initiator may promote the polymerization inside the large particles swollen with unreacted monomer. Further experimental evidences such as the variations of ζ -potential, TEM observation of ultra-thin cross-section of growing particles with DM domains stained with methyl iodide, and Tg of polymers during the polymerization will promote a better understanding of the controlled growth of seed particles.

Conclusion

Anionic seed copolymer latex P(MA-co-MMA) was prepared by conventional emulsion polymerization, and then the seeded emulsion polymerization accompanied with the electrostatic coagulation between opposite-charged ions was carried out using the secondary monomers of ST and DM. The effect of DM monomer content, secondary monomer to seed polymer weight ratio, M/P and amount of emulsifier added in the seeded polymerization were examined in order to control the coagulation between the seeds to obtain particles of large size. For the preparation of ideal latex product, such as higher monomer-conversion, lower CV, less amount of uncontrolled coagulum and higher stability, the optimal conditions were found for the DM monomer content and M/P. The addition of DM monomer increased the particle size until 8g to the 400g total latex, and highest content of DM, 12g nucleated the secondary particles, although the larger particles were also obtained. The increasing of M/P promoted the growth of particles, however, the highest M/P (2.5) formed untolerable amount of coagulum in the final latex. The optimal M/P was 2.0. The stability of latex gained by increasing amount of emulsifier is a trade-off to the progress of controlled coagulation between the seed polymer particles. Excess addition of emulsifier led to the nucleation of the secondary polymer particles, while suppressing the controlled coagulation process. From the observations of polymer yield and average particle size during the polymerization, an optimal policy to control the emulsifier content was proposed including a probable addition during the polymerization.

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