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# Preparation of Monodisperse Melamine-Formaldehyde Microspheres via Dispersed Polycondensation

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**Abstract:** We have successfully synthesized relatively monodisperse and cross-linked melamine-formaldehyde (M-F) microspheres by dispersed polycondensation and subsequent pH adjustment with serum replacement cleaning. The average particle sizes ($\overline{D_w}$ : weight-average and $\overline{D_n}$ : number-average), the polydispersity index ($\overline{D_w}/\overline{D_n}$ ), the number of particles $N_p$, and the gel content of the M-F microspheres were observed by varying the pH, the surfactant concentration, and the polymerization temperature. We observed that both the pH and the polymerization temperature were predominant factors in determining $\overline{D_n}$ and $N_p$, but the effect that the temperature and pH had on the gel content ( > 94% for all samples) was negligible. The exponents of the slopes of plots of $N_p$ versus pH and surfactant concentration were -10 and 0.6, respectively. Particle nucleation and growth were achieved within short periods; the incessant coagulation occurred even in the presence of surfactants.

*Keywords:* dispersed polycondensation, melamine-formaldehyde, microsphere, monodisperse, nucleation, particle growth.

## Introduction

For many decades, the suspension and dispersion methods for polycondensates like amino resins, phenolic resins, polyesters, polyamide, polycarbonates, and polyurethanes, have gained increasing importance from the industrial point of view.[1-6] The dispersed polycondensation in aqueous media can be described as follows: (a) the largest oligomer/polymer chains coil up during an early stage of the polycondensation and form macromolecular aggregates; (b) the aggregates are poorly solvated (swollen) in the continuous medium; (c) as the concentration of these aggregates increases, they flocculate and form larger aggregates, i.e. nuclei; (d) polycondensation of the nuclei continues to grow by adsorbing small aggregates or prepolymer molecules from the homogeneous solution.

Among the heterogeneous polycondensates, some publications on phenolic-formaldehyde and melamine-formaldehyde (M-F) suspension can readily be encountered. Renner studied the M-F particle using several surfactants, which can be used as reinforcing materials for natural rubber.[7] Zubov and Hulewicz prepared monodispersed M-F microspheres in the aqueous phase having 1-7 $\mu$m diameters without surfactants.[8,9] Milotskii prepared 30-40 wt% solid phenol-formaldehyde microspheres using mixed surfactant system.[10] However, the particle nucleation and growth mechanism of polycondensate have not been established yet, which is important in the average particle size and size distribution control.

There are several techniques concerning the preparation of monodispersed latex microspheres with narrow particle size distribution and sub-micron or micron size. Among these, the emulsion and dispersion polymerizations are long-established techniques widely adopted in industry.[11-19] However, usually it has apparent drawbacks of limitation of monomers (usually vinyl monomers) and long reaction time. The dynamic swelling and membrane-emulsification methods seem to be the most probable techniques that can make large and monodispersed latex microspheres with high efficiency.[18,20-23] Monodispersed M-F microspheres can be utilized in electronic applications, such as liquid crystal display and anisotropic conductive films. In the application, monodispersity is highly required and should be accurately controlled. There have been, however, a few publications

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concerning monodispersed polycondensate microspheres and particle growth.[7,24,25]

In this work, relatively monodispersed and highly crosslinked M-F microspheres are prepared using sodium lauryl sulfate (SLS) and gum Arabic in the dispersed polycondensation method. The influences of the polymerization temperature, surfactant concentration, and the pH on the particle nucleation and growth will be discussed.

## Experimental

**Materials.** Melamine (Lancaster, England) and formalin (37% formaldehyde solution, Yakuri Pure Chemical, Japan) were used without purification. Gum Arabic (Daejung Chemical, Korea) and sodium lauryl sulfate (SLS, Duksan Chemical, Korea) were used as surfactants or/and stabilizers. For pH control, sodium hydroxide (NaOH, Duksan Chemical, Korea) and citric acid (Duksan Chemical, Korea) were used. DI (distilled and deionized, $>18.2\ \mathrm{M\Omega}$) water was used throughout all experiments. Basic recipe for the synthesis of monodispersed M-F microsphere is shown in Table I.

**Preparation of Monodispersed Melamine-Formaldehyde Microspheres.** 0.3 L-rounded flask equipped with three inlets was used for the polycondensation. The unreacted formaldehyde was refluxed by condenser. In the preparation of methylolmelamine prepolymer, calculated amounts of melamine and formalin were added into the flask with surfactant mixture solution prepared prior to the prepolymer reaction. The polymerization temperature was 85 ℃ and stirring rate was 400 rpm. The initial pH of the aqueous phase was adjusted to 8.5 by adding 0.1 N NaOH solution. After 1.5 hr reaction, the temperature was adjusted to 50, 65, and/or 80 ℃ and then the pH was adjusted to acidic condition, from 4.0 to 6.0 by adding 0.1 N citric acid solution. During the formation of monodispersed M-F microsphere, 4-5 mL of the sample was taken from the reaction mixture with appropriate time intervals (depends on the pH and temp.). The sample was diluted with 20 mL of DI water and then quenched with ice. Finally, the pH of the sample was adjusted to 10 with 0.1 N NaOH solution and cleaned in the serum replacement cell equipped with 0.2 $\mu$m filter for 3 days. The overall reaction scheme is illustrated in Figure 1.

**Table I. Basic Recipe for Synthesis of the M-F Microspheres**

| Components | Amount (g) |
|---|---|
| Melamine | 5.79 |
| Formaldehyde<br>(37% aqueous solution) | 16.78 |
| Surfactant Mixture[a] | 0.30, 0.80, 1.30, 3.30, and 5.00 |
| DDI Water | 89.43 |
| Sodium Hydroxide (NaOH) | Variable[b] |
| Citric Acid | Variable[c] |

[a] Weight ratio of gum Arabic to sodium lauryl sulfate was fixed as 1.0.

[b] Appropriate amount of 0.1 N NaOH aq. solution was used for prepolymer (methylolmelamine) reactant solution.

[c] Appropriate amount of 0.1 N citric acid aq. solution was used for dispersed polycondensation.

**Characterization.** The average particle sizes ($\overline{D_w}$: weight-average and $\overline{D_n}$: number-average) and the polydispersity index (PDI, $\overline{D_w}/\overline{D_n}$) were obtained from scanning electron microscopy (SEM, JSM-5400, JEOL Co., Japan) equipped with image analysis software by counting over 500 microspheres. The $\overline{D_w}$ and $\overline{D_n}$ can be expressed as following equations.

$$\overline{D_w} = \frac{\sum n_i D_i^4}{\sum n_i D_i^3} \tag{1}$$

$$\overline{D_n} = \frac{\sum n_i D_i}{\sum n_i} \tag{2}$$

The number of particle per unit volume ($N_p$) can be calculated using the following equation:

$$N_p = \frac{6m}{\pi \overline{D_n}^3 \rho_{MF}} \tag{3}$$

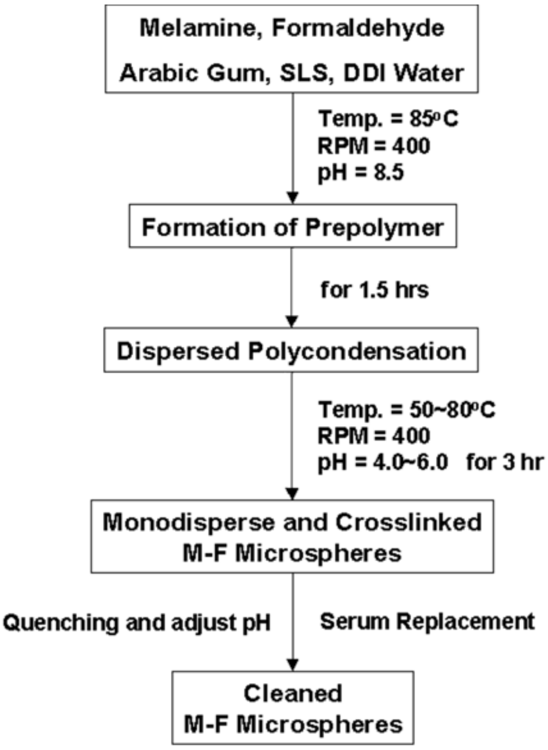


**Figure 1.** Synthetic procedure of the M-F microspheres via dispersed polycondensation.

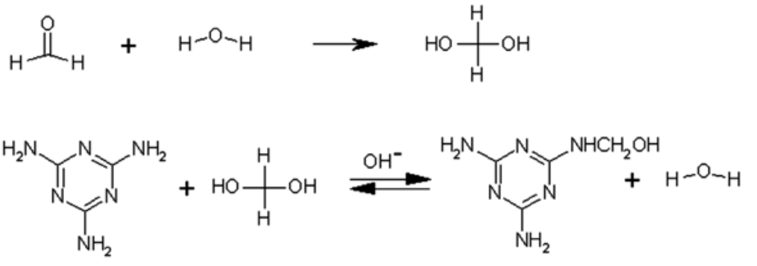
where, $m$ is the weight of unit volume of M-F latex, $\rho_{MF}$, the density of M-F particle, respectively. Particle size distribution of coagulating M-F microspheres was determined by using light scattering (DLS, BI-9000, Brookhaven Instrument, London, UK). Gel content was characterized by solvent extraction method. Dried M-F powder samples were obtained by centrifugation after the removal of surfactant by using a serum replacement as mentioned above. 0.1 g of the M-F powder was immersed in 10 g of cyclohexane solvent for 1 week and stirred mildly at room temperature to promote swelling and dissolution equilibrium. The cyclohexane swollen M-F sample was then carefully removed from the cyclohexane by using 10 $\mu$m membrane filter. The filtered cyclohexane solution from the M-F powder contains dissolved M-F, which could be determined gravimetrically. The gel content was determined from the weights of the dissolved M-F ($W_{sol}$) and dried M-F powder ($W_{tot}$) using the following equation:

$$\text{Gel}(\%) = \frac{W_{tot} - W_{sol}}{W_{tot}} \times 100(\%) \tag{4}$$

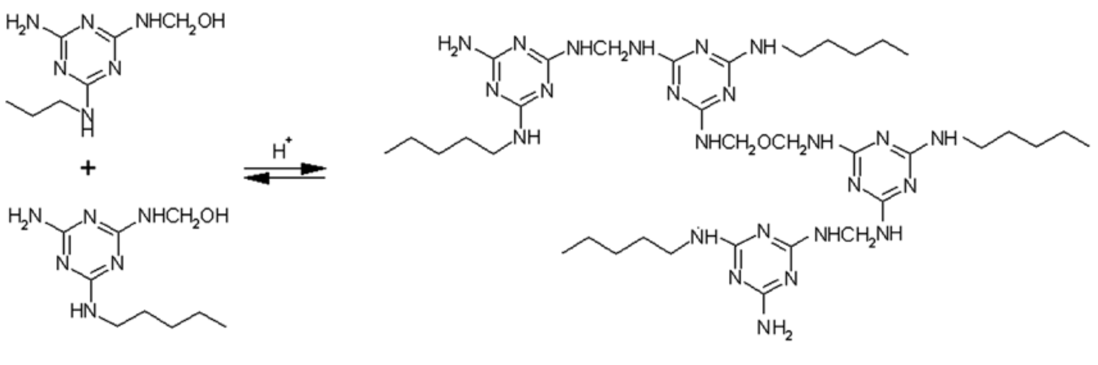
## Results and Discussion

**Melamine Formaldehyde Prepolymer.** The representative reaction scheme of the M-F prepolymer is illustrated in Figure 2. The M-F prepolymer is well known as methylolmelamine. Two main steps are involved in the preparation of the M-F precursor.[25] First, nucleophilic addition reactions of melamine to formaldehyde under basic conditions result in random substitution of the amino groups and then formation of methylolmelamine water-soluble mixtures (a). Next, two different types of linkage can be resulted from the oligomerization by the formation of bridges between triazine rings: either between two methylol groups producing a methylene other bridge or between a methylol group and an amino group producing a methylene bridge. Cross-linked networks are formed among a large number of oligomeric derivatives during polycondensation reaction (b).[26] These bridge formations can be affected by many reaction parameters, such as pH, molar ratio of melamine to formaldehyde, and reaction temperature. In fact, it is difficult to represent an M-F unit with a clear chemical structure and a well-defined repetition unit because of the wide variation in functionality, structure and reactivity of the intermediates involved in the reaction.

**Particle Nucleation and Growth.** In Table II, $\overline{D_n}$, PDI ($\overline{D_w}/\overline{D_n}$), and other physical properties of the M-F microspheres prepared with varying process variables are listed. Sample ID, from T-1 to T-3, indicates the variation of the reaction temperature, S-1~S-5, the surfactant variation, and



(a) Formation of prepolymer (methylolmelamine) under the basic condition



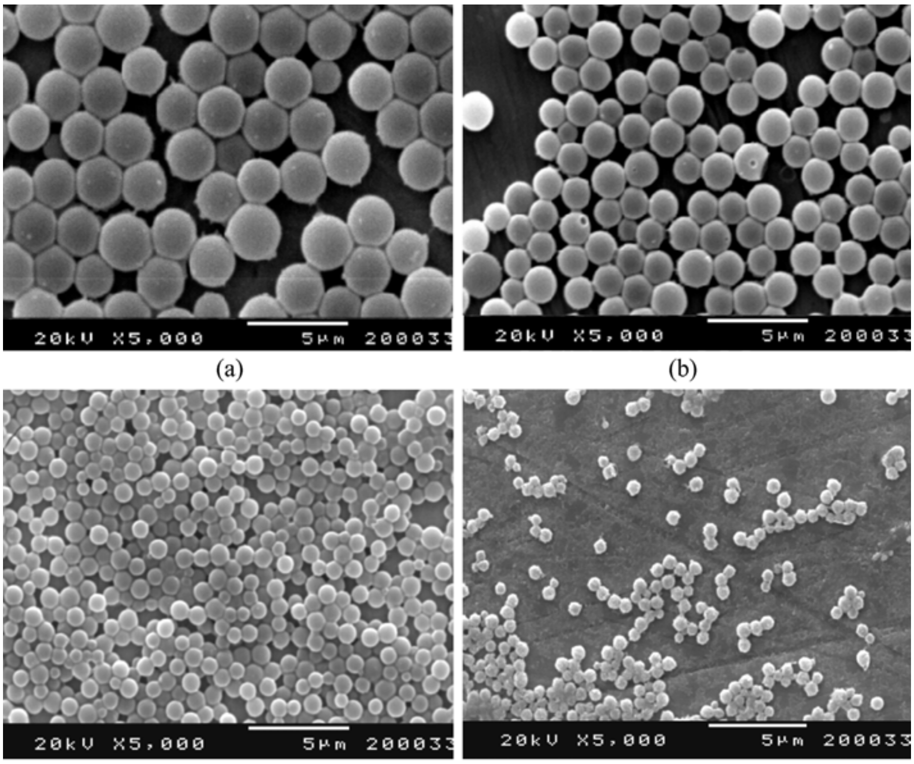
(b) Dispersed polycondensation reaction under the acidic condition

**Figure 2.** Reaction scheme of the M-F polycondensate; (a) formation of the methylolmelamine and (b) formation of the M-F microsphere via polycondensation.

**Table II. Average Particle Sizes and Polydispersity Indices of the M-F Particles Prepared with Varying Process Variables**

| Sample ID | Temp. (°C) | Surfactant (%)[a] | pH | Gel Content (%) | $\overline{D_n}$ ($\mu$m) | PDI ($\overline{D_w}/\overline{D_n}$) | $N_p$ ($10^{10}$cm$^{-3}$) |
|---|---|---|---|---|---|---|---|
| T-1 | 50 | 3.0 | 5.5 | 94.3 | 1.48 | 1.03 | 18.08 |
| T-2 | 65 | 3.0 | 5.5 | 94.5 | 2.69 | 1.05 | 3.01 |
| T-3 | 80 | 3.0 | 5.5 | 94.6 | 4.48 | 1.03 | 0.65 |
| S-1 | 60 | 0.5 | 5.0 | 95.2 | 2.76 | 1.05 | 2.78 |
| S-2 | 60 | 0.8 | 5.0 | 94.8 | 2.58 | 1.04 | 3.41 |
| S-3 | 60 | 1.3 | 5.0 | 95.1 | 2.35 | 1.05 | 4.52 |
| S-4 | 60 | 3.3 | 5.0 | 95.0 | 1.93 | 1.04 | 8.15 |
| S-5 | 60 | 5.0 | 5.0 | 95.2 | 1.75 | 1.07 | 10.93 |
| P-1 | 60 | 3.0 | 4.0 | 97.1 | 0.67 | 1.02 | 194.80 |
| P-2 | 60 | 3.0 | 4.5 | 96.6 | 0.94 | 1.04 | 70.55 |
| P-3 | 60 | 3.0 | 5.0 | 95.1 | 1.82 | 1.04 | 9.72 |
| P-4 | 60 | 3.0 | 6.0 | 94.5 | 2.73 | 1.06 | 2.88 |

[a] wt% based on the total reaction mixture except surfactant.



(a) (b) (c) (d)

**Figure 3.** SEM photos of the M-F microspheres prepared with varying the pH; (a) pH=6.0, (b) pH=5.0, (c) pH=4.5, and (d) pH=4.0.

P-1~P-4, the pH variation, respectively. From the time-evolution particle size data (Figures 4, 6, and 7), coagulation among the M-F microspheres was observed regardless of the process variables even though the coagulation rate could not be measured. The coagulation among the microspheres seemed to be accelerated by residual formaldehyde and water-soluble methylolmelamine in the reaction mixture, which could be prevented by using a serum replacement stirred cell after the formation of the M-F microspheres having narrow particle size distributions.

**The Effects of Aqueous pH.** SEM photos in Figure 3 show the M-F microspheres prepared with varying pH. The photos were captured from the samples with pH adjustment and serum replacement cleaning. The uniformity of the particle size seems not so good as radical polymerizations in dispersion or emulsion, because they are not prepared in optimal condition. As the pH decreased, the average particle sizes of the M-F microsphere significantly decreased. The PDI value decreased slightly as the pH decreased. It was found that the M-F particles were nucleated at a certain reaction time and grown up within very short time. The growth period mainly depends on the pH. As mentioned above, both rate and extent of the polycondensation increased as the concentration of $[H^+]$ increased.

In fact, it can be seen that the rate of the particle formation is drastically changed with varying the pH (Figure 4). In the case of the lowest pH (4.0), the turbid and milky-white latex was obtained within only a few minutes right after lowering the pH from 8.5 to 4.0. On the other hand, it took more than 60 min to obtain the milky-white one under the pH, 6.0. This result showed that the overall polycondensation and coagulation rates were predominantly governed by the aqueous pH. All the $\overline{D_n}$ curves in the Figure 4 seem to show so-called ‘induction’ period. Sizes of methylolmelamine aggregates at the early stage of the reaction were not determined by SEM, however, their sizes were found to be less than 50 nm (this may have uncertainty due to high reactivity of the sample) by light scattering method. In the case of the pH 6.0, the M-F microsphere grows gradually for relatively long period as compared with the pH 4.0.

Figure 5 shows the number of microspheres ($N_p$) produced varying the pH and surfactant concentration. The pH dependency of on the $N_p$ was linear within experimental range and its exponent value from the slope was -10 for the logarithmic pH variance.

**The Effects of Surfactant Concentration.** As described in Table I, gum Arabic and SLS were used as surfactants (and/or stabilizers) and the ratio of the mixture was fixed as 1.0 in all samples. The average particle size decreased as the surfactant concentration increased, however, the surfactant concentration apparently affected neither PDI nor gel contents. As shown in Figure 5, the $N_p$ against the surfactant concentration increased linearly and its slope was 0.6, which can be seen in classical nucleation theory of emulsion polymerization.$^{27}$ The relationship between the $N_p$ and surfactant concentration seems to be very complex and the effects of the surfactants were not investigated in this work. The role of the surfactant in the M-F system seems to be unclear due to the paucity of data. However, it is believed that the coagulation mechanism is predominant in the particle nucleation of the M-F particle and that the coagulation occurs among water-insoluble methylolmelamines before their concentration reaches supersaturation. From the relationship between the $N_p$ and surfactant concentration, it can be expected that the surfactants stabilize nucleated particles and that the stabilized particles capture the water-insoluble methylolmelamines.

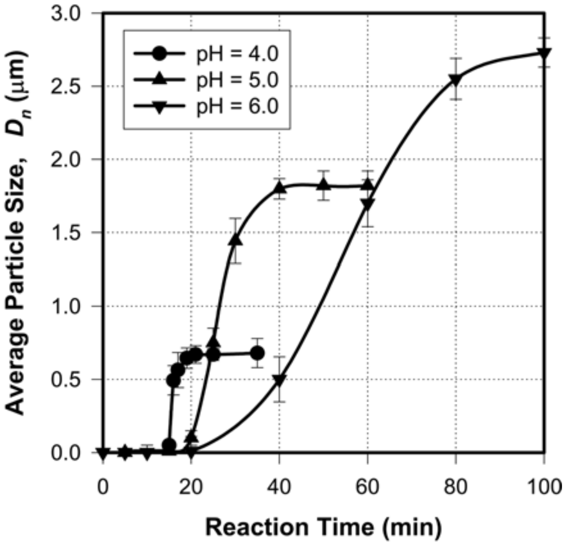


**Figure 4.** Average particle size of the M-F microsphere vs. reaction time with varying pH.

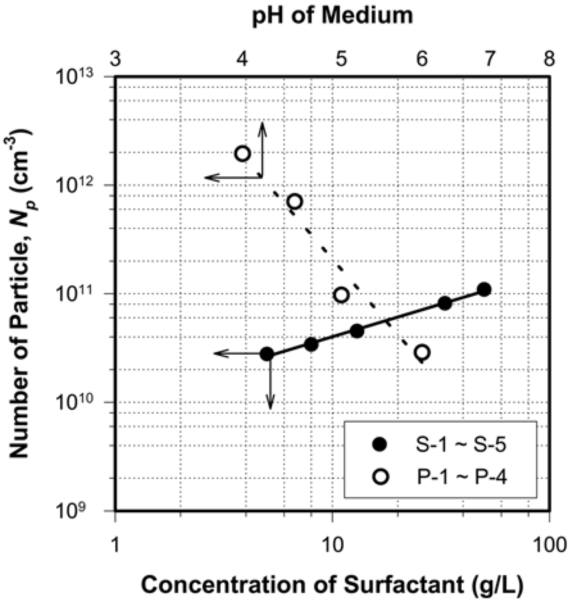


**Figure 5.** Calculated number of the particle ($N_p$) vs the surfactant concentration (S-1 ~ S-5) and pH (P-1 ~ P-4).

**The Effects of Reaction Temperature.** As shown in Table II, the average diameters of the microsphere increased as the reaction temperature increased. There were no significant changes in the gel contents and PDI values, however; time-evolution of the average particle size versus reaction temperature was not shown in this paper, but the similar reaction profiles were obtained as compared with the pH variation. The polycondensation rate among water-soluble M-F prepolymers is accelerated by elevated reaction temperature. In fact, the period of nucleation and particle growth was shortened

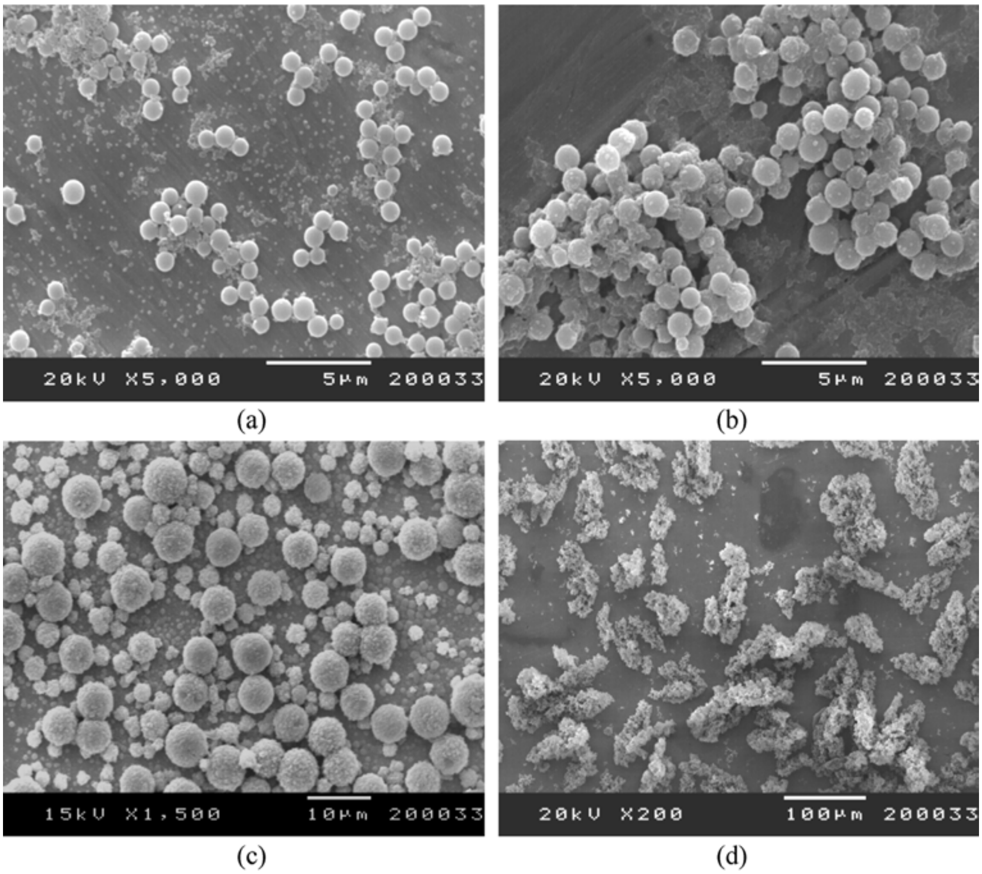


**Figure 6.** SEM photos of the coagulating M-F microspheres against reaction time (without serum replacement); (a) $\overline{D_n} = 1.2\ \mu$m at 120 min, (b) $\overline{D_n} = 1.5\ \mu$m at 150 min, (c) $\overline{D_n} = 6.3\ \mu$m at 180 min, and (d) $\overline{D_n} = 115.8\ \mu$m at 240 min.

at higher reaction temperature.

**Coagulation under Uncontrolled Condition.** Figure 6 shows the particle-evolution due to coagulation among the pre-existing microspheres. These microspheres were prepared under the same condition as the P-2 sample without pH adjustment and/or serum replacement. The M-F microspheres in Figure 6(a) were taken at 120 min, Figure 6(b), 150 min, Figure 6(c), 180 min, and Figure 6(d), 240 min, respectively. Numerous freshly nucleated small particles are seen in Figure 6(a). The photos, Figure 6(b) and (c), show larger aggregates and coagulated particles. The morphology of the hetero-coagulated particles seems like raspberry and these particles are growing continuously via the polycondensation and coagulation reaction all through the reaction time. In Figure 6(d), the coagulating M-F microspheres were obtained and their shapes became irregular. This coagulation was resulted from the bridging reaction among reactive methylol groups in the M-F prepolymers in the presence of remaining water-soluble methylolmelamines.

The particle size distributions of these coagulating microspheres were measured by dynamic light scattering and shown in Figure 7. Figure 7(a) shows the particle size distribution of M-F particles taken at 120 min. A lot of sub-micron sized particles were observed. This result means that the nucleation continues all through the reaction. 30 min later, small particles ranged below 100 nm were still observed and there are also bigger particles over 10 $\mu$m in Figure 7(b). Another 30 min later, the nano-sized particles disappeared and the particle size distribution became very broad (Figure 7(c)). At 240 min, a large number of coagulated aggregates around 100 $\mu$m were found (Figure 7(d)).

The overall reaction scheme of the M-F polycondensation and particle formation can be summarized as follows: In first step, the water-soluble methylolmelamine is formed by the reaction between melamine and formaldehyde under the basic condition. In second step, the particle nucleation is achieved by the polycondensation and followed by the particle growth (third step), via coagulation among the water-insoluble polycondensates. During the third step, monodispersed M-F latex microspheres having various particle sizes and physical properties can be formed according to the reaction condition. The average particle sizes were maintained for the beginning of the fourth step, but all the growing microspheres are eventually aggregated due to the homo- and

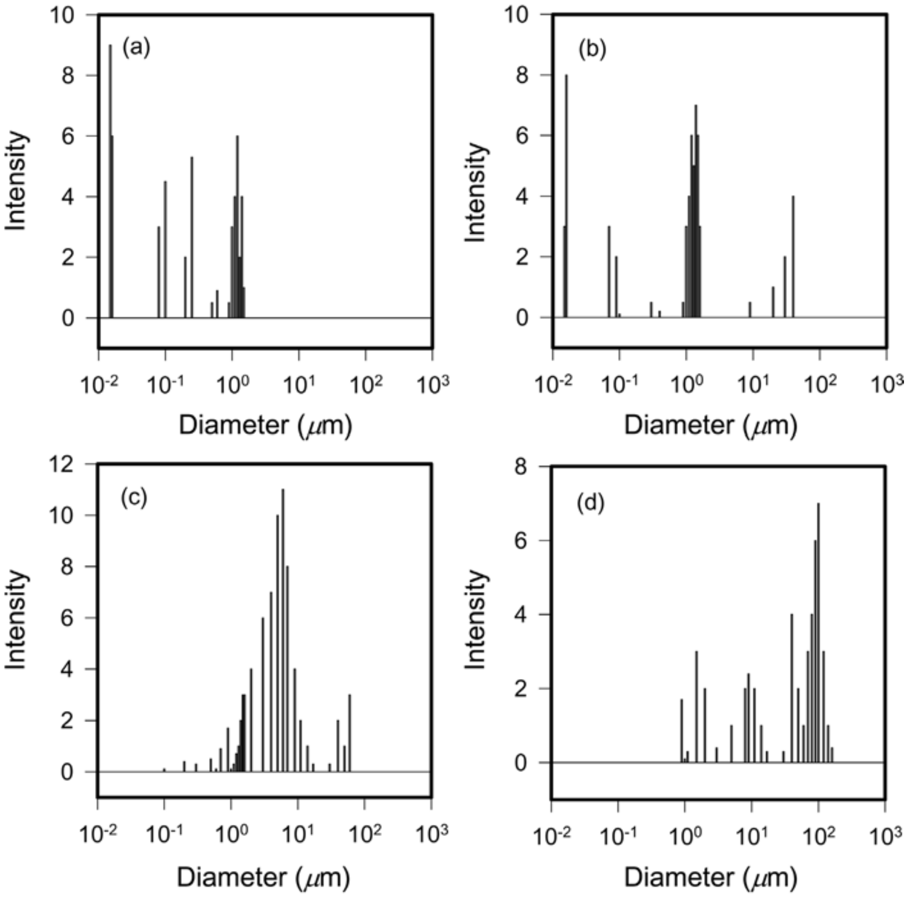


**Figure 7.** Particle size distributions of the M-F microspheres versus reaction time.

hetero-coagulation unless water-soluble methylolmelamines are cleaned. The pH adjustment itself without serum replacement could not prevent coagulation.

## Conclusions

As demonstrated by microscopic study, the pH of the reaction medium was the most critical factor governing the average particle size and PDI values. The water-soluble methylolmelamine prepolymers aggregate and form water-insoluble nuclei, which coagulate further to form cross-linked microspheres under the acidic condition. The acidic condition accelerates the formation of both the methylolmelamine prepolymers and M-F microspheres due to the bridging reaction among these reactive methylol groups. Concerning the nucleation, the water-insoluble M-F polycondensates act as nuclei and the microspheres can be formed by the coagulation among these polycondensates. It was observed that the nucleation and particle growth were achieved by the coagulation reaction among the M-F polycondensates within relatively short period. The effect of surfactant concentration on the particle stability seems unclear due to incessant coagulation; however, a linear relationship between the $N_p$ and surfactant concentration was observed. The serum replacement method could eliminate the coagulation among the monodispersed mature microspheres and maintain the colloidal stability regardless of the surfactant concentration.

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