Effect of Reaction Parameters on the Dispersion Copolymerization of Styrene and Methyl Acrylate

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Abstract: Dispersion copolymerizations of styrene (St) and methyl acrylate (MA) (100/0~0/100 wt%) in isopropanol/water media were carried out. The poly(St/MA) latexes, containing 100/0~50/50 wt%, had a narrow size distribution in the size range of 1.3~2.0 μm. The particle size of the poly(St/MA) latexes increased, and the molecular weight of the latex polymers decreased, upon increasing the MA content. Dispersion copolymerization of St/MA (75/25 in wt%) was also carried out to investigate the effects of various polymerization parameters on the particle size and the molecular weight of the resulting poly(St/MA) latexes. The number-average particle diameter increased upon increasing the reaction temperature and the concentrations of the monomer and AIBN initiator, and upon decreasing the concentration of PVP stabilizer and the water content in the isopropanol/H₂O media. The weight-average molecular weight increased upon increasing the concentrations of monomer and steric stabilizer and the water content in the isopropanol/H₂O media, but it decreased with the initiator concentration and polymerization temperature. The preferred polymerization recipes for making uniform poly(styrene-co-methylacrylate, 75/25 wt%) microparticles in size range 1.3~3.4 μm is established.

Keywords: dispersion copolymerization, styrene, methylacrylate, steric stabilizer, isopropanol/H₂O media, average particle size, average molecular weight

Introduction

Micron-size monodisperse polymer particles are used in a wide variety of scientific and technological applications [1-5]. These polymeric microparticles are difficult to obtain because their size lies between the size of the particles produced by conventional emulsion polymerization (0.05~0.3 μm) [6] and by suspension polymerization (50~1000 μm). Although several techniques [7,8] for the preparation of such micron-size monodisperse particles have been proposed, dispersion polymerization in polar media is known to be advantageous because micron-size monodisperse polymer particles can be prepared in a single-step. Almog and coworkers [9], Ober and coworkers [10], and many others [11-16] have studied dispersion homopolymerizations of styrene and methyl methacrylate in order to control particle size and achieve a narrow particle size distribution. The technological applications of monodisperse microsphere particles have been greatly increased by the use of copolymers. Typical combinations of monomers used to obtain these particles are styrene-butylmethacrylate [17], styrene-acrylonitrile [18], styrene-glycidyl methacrylate [19], styrene-acrylamide [20], styrene-butyl acrylate [21,22], styrene-divinylbenzene [23], and 2-hydroxyethylmethacrylate-N,N,N,N-dimethacryloylhydroxylamine [24]. However, up to now, few studies of single-step dispersion copolymerizations have been reported. This situation is probably due to the complex nature of comonomer mixtures, in which each new comonomer ratio must be treated as a new polymerization system. These comonomer systems are even more complicated if the comonomers polymerize at different rates or if they partition differently in the system once nucleation has taken place. In previous publications [18,21], we reported the synthesis of monodisperse styrene-acrylonitrile and styrene-butyl acrylate copolymer microparticles through single-step dispersion polymeri-
Table 1. Standard Recipe Used in Styrene/Methyl Acrylate Dispersion Copolymerization

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>wt%</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST/MA (75/25 wt%)</td>
<td>13.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Isopropanol/HO (70/30 wt%)</td>
<td>85.7</td>
<td>19.8</td>
</tr>
<tr>
<td>AIBN</td>
<td>0.2</td>
<td>0.05</td>
</tr>
<tr>
<td>PVP K-30</td>
<td>1.2</td>
<td>0.27</td>
</tr>
</tbody>
</table>

* Based on total weight (23.12 g). Polymerization conditions: 75 °C (polymerization temperature), 140 cycles/min at 24 hr.

ization and studied the effect of the polymerization parameters.

In this present study, we copolymerized styrene with methyl acrylate to investigate the effects of various polymerization parameters, such as the St/MA ratio, the concentrations of monomer, stabilizer, and initiator, the water/isopropanol ratio in the medium, and the polymerization temperature, on the particle size and on the molecular weight of the resulting poly(St/MA) product.

**Experimental**

**Materials**

Styrene (St) and methyl acrylate (MA), purchased from Junse, were vacuum distilled under nitrogen and stored at -10 °C before use. 2,2'-Azobisisobutyronitrile (AIBN, Junse) was used after recrystallization twice from methanol. All other materials were used without further purification. As the polymerization medium, isopropanol (Wako Chemicals)/distilled deionized-water mixtures were used. Poly(N-vinyl pyrrolidone) (PVP K-30, Junse) was used as a steric stabilizer.

**Dispersion Polymerization**

The dispersion polymerizations were carried out according to the standard recipe given in Table 1. The ingredients were weighed and mixed in 2-oz glass bottles that were purged with nitrogen, capped, and sealed. The bottles were then placed in a shaker operating at 140 cycles/min in a constant temperature water bath at 75 °C for 24 hr. The conversion and solid content of these latexes were determined gravimetrically. Most of the polymerizations carried out in this study showed greater than 97 ~ 98 % conversion with negligible coagulum.

**Particle-Size Analysis**

Particle sizes of resulting dispersions were determined using scanning electron microscopy (SEM, Jeol Jsm 6400). For the SEM, one drop of the final dispersion was diluted in about 2 ~ 3 mL of methanol and one drop of the diluted dispersion was coated on the aluminum stub and dried at room temperature overnight. The samples were sputter-coated with gold, and examined at 15 kV.

The particle size of the latexes was measured from photographs and the particle size distributions (PSD) were determined from the ratio of the Number (\( D_n \)) and Weight (\( D_w \))-average diameters as follows:

\[
D_n = \frac{\sum d_i n_i}{N}
\]

\[
D_w = \frac{\sum d_i^2 n_i}{\sum n_i}
\]

where \( N \) is the total number of particles counted and \( d_i \) is the diameter of particle i.

\[PDI = \frac{D_w}{D_n}\]

**Molecular Weight Determination**

The molecular weights of latex polymers were measured using a GPC system (Waters 510) equipped with a differential refractometer detector and a Waters Styragel HR column (100, 500, and 10000 pore sizes).

**Results and Discussion**

**Effect of Styrene/Methyl Acrylate Ratio**

Figure 1 shows SEM micrographs of four poly(St/MA) dispersions prepared according to the recipe shown in Table 1. The particle size of the poly(St/MA) latexes increased upon increasing the MA content in the monomer mixture. The resulting poly(St/MA) latexes, containing 100/0 ~ 50/50 wt% St/MA monomer compositions, were found to be monodisperse particles with sizes in the range 1.3 ~ 2.0 µm. However, the poly(St/MA) latex at 25/75 wt% had a broad size distribution and the dispersion homopolymerization of methyl acrylate did not show any particles; it occurred in a clear-solution state throughout the polymerization.

Table 2 also shows the average particle sizes and average molecular weights for the five different St/MA dispersion polymerizations. Dispersion polymerization usually involves the polymerization of a monomer dissolved in a medium in the presence of a steric stabilizer to produce insoluble polymer particles dispersed in the continuous phase. Solution polymerization preferentially proceeds at the beginning of the polymerization, resulting in the formation of oligomer radicals. These oligomer radicals are stabilized by the adsorption of the steric stabilizer, and they become colloidal stable polymer particles. The particle nucleation stage in the
dispersion polymerization is closely related to the polarity of the reaction medium. For the polymerization of non-polar monomers in a polar medium, the increase in the polarity of the reaction medium in general generates a large number of nuclei, resulting in a decrease in the particle diameter of the latex. An increase of the methyl acrylate content in a St/MA monomer mixture leads to a decrease in polarity of the reaction medium (δ_r: 9.3; δ MA: 8.9) [25], leading to the formation of longer oligomer chains at the beginning of the copolymerization. Therefore, particle nucleation for MA-rich copolymerization would mainly occur at higher molecular weights because of the higher solubility of growing oligomers in the reaction medium. Thus, fewer nuclei are produced, which finally leads to fewer polymeric particles, but in larger sizes. For the homopolymerization of methyl acrylate in particular, homogeneous polymerization occurred throughout the polymerization. The average molecular weight of the poly(St/MA) latex polymers decreased upon increasing the MA content. Polystyrene latex polymer showed the highest molecular weight and the most broad size distribution. However, poly(methyl acrylate) latex polymer showed the lowest molecular weight. Upon increasing the styrene content in the St/MA monomer mixture, both the rate of nuclei formation and the rate of adsorption of the stabilizer would increase because of the increased polarity of the reaction medium, which would result in smaller, uniform particles, as shown in Figure 1. Once particles have been formed, they absorb the monomer and initiator from the continuous phase and polymerize to form mature particles mainly within the monomer-swollen particles until all of the monomer is consumed. Therefore, polystyrene latex polymers would have broader size distributions because they contain both high-molecular-weight species and low-molecular-weight species, originated from the polymerizations in particles and in solution, respectively. In general, from the viewpoint of the viscosity in the growing particles, the increased viscosity inside the growing particles for a styrene-rich (relatively hydrophobic monomer) composition would result in reduced termination rates and enhanced propagation rates. Typically, heterogeneous polymerizations lead to greater molecular weights than homogeneous polymerization does because of the increased viscosity in the growing particles. On the other hand, the poly(methyl acrylate) product showed the lowest molec-

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**Table 2. Effect of Monomer Ratio in Five Different Styrene/Methyl Acrylate Dispersion Polymerizations**

<table>
<thead>
<tr>
<th>Samples</th>
<th>ST/MA (wt %)</th>
<th>$D_{p} (\mu m)$</th>
<th>PDI</th>
<th>$M_n \times 10^4$</th>
<th>MWD</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100 / 0</td>
<td>1.31</td>
<td>1.072</td>
<td>14.00</td>
<td>3.59</td>
</tr>
<tr>
<td>B</td>
<td>75 / 25</td>
<td>1.65</td>
<td>1.009</td>
<td>5.45</td>
<td>3.30</td>
</tr>
<tr>
<td>C</td>
<td>50 / 50</td>
<td>1.95</td>
<td>1.002</td>
<td>3.44</td>
<td>2.46</td>
</tr>
<tr>
<td>D</td>
<td>25 / 75</td>
<td>Broad</td>
<td></td>
<td>2.48</td>
<td>2.67</td>
</tr>
<tr>
<td>E</td>
<td>0 / 100</td>
<td>-----</td>
<td></td>
<td>1.11</td>
<td>2.37</td>
</tr>
</tbody>
</table>
Figure 2. SEM photographs of four different monomer concentrations in styrene/methyl acrylate (75/25 in wt%) dispersion copolymerization (A 6.9, B 13, C 18, D 23 wt%).

Table 3. Effect of Monomer Concentration in Styrene/Methyl Acrylate (75/25 in wt%) Dispersion Copolymerization

<table>
<thead>
<tr>
<th>Samples</th>
<th>Monomer (wt%)</th>
<th>(\bar{D}_p (\mu m))</th>
<th>PDI</th>
<th>(M_n \times 10^4)</th>
<th>MWD</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6.9</td>
<td>1.30</td>
<td>1.006</td>
<td>2.9</td>
<td>2.94</td>
</tr>
<tr>
<td>B</td>
<td>13</td>
<td>1.74</td>
<td>1.001</td>
<td>6.7</td>
<td>3.27</td>
</tr>
<tr>
<td>C</td>
<td>18</td>
<td>1.97</td>
<td>1.001</td>
<td>8.6</td>
<td>3.07</td>
</tr>
<tr>
<td>D</td>
<td>23</td>
<td>2.53</td>
<td>1.004</td>
<td>9.5</td>
<td>2.87</td>
</tr>
</tbody>
</table>

molecular weight and a narrower size distribution because the monomer was polymerized only in the solution state.

Dispersion Polymerization of Styrene/Methyl Acrylate (75/25 in wt%)

Effect of Monomer Concentration

In this set of experiments, the concentration of the monomer mixture was varied from 6.9 to 23 wt% and the amount of the other components were the same as those listed in Table 1. The SEM photographs and the average particle sizes and average molecular weights of the latexes are given in Figure 2 and Table 3, respectively. The average particle sizes and the average molecular weights generally increased upon increasing the monomer concentration. All the particles formed in this study had narrow size distributions in the range 1.3 to 2.5 \(\mu m\). Increasing the monomer concentration would increase the solvency of the medium for the polymer formed at the initial stage of the polymerization, resulting in an increase of the critical chain length of the growing oligomer molecules and, at the same time, decrease the adsorption rate of the PVP stabilizer. These features would lead to the formation of larger particles. The increase in molecular weight with respect to the monomer concentration would also be related to the increase of the monomer concentration present in the polymer particles.

Effect of Stabilizer Concentration

To investigate the effect of the PVP K-30 stabilizer’s concentration, four different concentrations (i.e., 4.5, 9, 18, and 36 % based on monomer wt.) were used. Figure 3 shows the log-log plots of the particle diameter \(\bar{D}_p\) vs stabilizer concentration and of the weight-average molecular weight \(M_w\) vs stabilizer concentration, respectively. The number-average particle size decreased from 1.9 to 1.4 \(\mu m\) and the weight-average molecular weight increased from 47900 to 65000 upon increasing the stabilizer concentration, resulting in \(\bar{D}_p \propto [\text{PVP}]^{0.41}\) and \(M_w \propto [\text{PVP}]^{0.41}\) relationships. More stabilizer can stabilize a larger number of nuclei, which results in more particles, but with smaller size. In other words, a higher surface area would offer a greater monomer diffusion rate, which leads to a higher monomer concentration in the polymer.
particles during the polymerization and higher polymerization rates and higher molecular weights [12].

**Effect of Initiator Concentration**

The polymerizations were carried out with four different AIBN concentrations (i.e., 0.5, 1.67, 3.33, and 6.66 wt%) in a dispersion medium containing 70% isopropanol and 30% water at a constant PVP K-30 stabilizer concentration, as described in Table 1. Figures 4 and 5 show the SEM photographs of the latex particles and the log-log plots of the particle diameter (\(D_n\)) vs AIBN concentration and of the weight-average molecular weight (\(M_w\)) vs AIBN concentration, respectively. All of the particles formed in this study had a narrow size distri-

**Figure 3.** Plots of particle size and \(M_w\) as functions of the PVP concentration.

**Figure 5.** Plots of particle size and \(M_w\) as functions of the AIBN concentration.

bution. The number-average particle size increased from 1.5 to 3.1 \(\mu\)m and the weight-average molecular weight decreased from 128000 to 11000 upon increasing the AIBN concentration. The increase in the AIBN concentration caused an increase in the number of free radicals formed during the polymerization. This phenomenon leads to a large number of lower molecular weight polymer chains, which are more soluble in the medium. In dispersion polymerization, particle nucleation occurs when the polymer chains reach a certain molecular weight at which point they become insoluble in the dispersion medium. At a high initiator concentration, therefore, because of the low concentration of high-molecular-weight chains in the medium, fewer nuclei

**Figure 4.** SEM photographs of four different AIBN initiator concentrations in styrene/methyl acrylate (75/25 in wt%) dispersion copolymerization (A 0.5, B 1.67, C 3.33, D 6.66 wt%).
Table 4. Effect of Polymerization Temperature in Styrene/Methyl Acrylate (75/25 in wt%) Dispersion Copolymerization

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temp. (°C)</th>
<th>$\bar{D}_p (\mu m)$</th>
<th>PDI</th>
<th>$M_n \times 10^4$</th>
<th>MWD</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>65</td>
<td>1.23</td>
<td>1.027</td>
<td>6.49</td>
<td>3.93</td>
</tr>
<tr>
<td>B</td>
<td>70</td>
<td>1.48</td>
<td>1.004</td>
<td>5.93</td>
<td>3.95</td>
</tr>
<tr>
<td>C</td>
<td>75</td>
<td>1.58</td>
<td>1.031</td>
<td>5.45</td>
<td>3.30</td>
</tr>
<tr>
<td>D</td>
<td>80</td>
<td>1.89</td>
<td>1.004</td>
<td>4.94</td>
<td>2.86</td>
</tr>
</tbody>
</table>

Table 5. Effect of Isopropanol/Water Ratio in Styrene/Methyl Acrylate (75/25 in wt%) Dispersion Copolymerization

<table>
<thead>
<tr>
<th>Samples</th>
<th>IPA/H₂O (wt%)</th>
<th>$\delta^*$</th>
<th>$\bar{D}_p (\mu m)$</th>
<th>PDI</th>
<th>$M_n \times 10^4$</th>
<th>MWD</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100/0</td>
<td>11.5</td>
<td>0.65 – 11.74</td>
<td>Broad</td>
<td>2.21</td>
<td>2.40</td>
</tr>
<tr>
<td>B</td>
<td>90/10</td>
<td>12.7</td>
<td>0.45 – 7.63</td>
<td>Broad</td>
<td>3.01</td>
<td>2.35</td>
</tr>
<tr>
<td>C</td>
<td>85/15</td>
<td>13.3</td>
<td>3.36</td>
<td>1.002</td>
<td>3.45</td>
<td>2.57</td>
</tr>
<tr>
<td>D</td>
<td>70/30</td>
<td>15.1</td>
<td>1.54</td>
<td>1.001</td>
<td>5.71</td>
<td>3.24</td>
</tr>
<tr>
<td>E</td>
<td>55/45</td>
<td>16.9</td>
<td>0.07 – 1.15</td>
<td>Broad</td>
<td>8.59</td>
<td>3.84</td>
</tr>
</tbody>
</table>

$\delta^*$ values just before the beginning of the polymerization (including monomer) [17].

Figure 6. SEM photographs of five different isopropanol/water ratios in styrene/methyl acrylate (75/25 in wt%) dispersion copolymerization (A 100/0, B 90/10, C 85/15, D 70/30, E 55/45 wt%).

were produced, which led to a lower number of particles, but with larger sizes. A lower surface area, due to larger particle size, would offer a lower monomer concentration in polymer particles during the polymerization, resulting in lower molecular weights.

Effect of Polymerization Temperature
The effect of the polymerization temperature on the average particle size and average molecular weight was studied. The polymerization recipe used was the same as that shown in Table 1, except that the polymerization temperature was varied from 65 to 80 °C. The SEM photographs, average particle sizes, and the average molecular weights of the latexes obtained at the four different polymerization temperatures are given in Table 4. The number-average particle size increased from 1.2 to 1.9 μm and the weight-average molecular weight decreased from 65000 to 49000 upon increasing the polymerization temperature. The reasons for that may be explained similarly to those adopted in the section describing the effect of the initiator concentration. A higher polymerization temperature generates more free radicals, resulting in few larger-size particles and lower molecular weights.

Effect of Isopropanol/Water Ratio
The effect of the isopropanol/water ratio on the dis-
persion copolymerization of St/MA (75:25 wt%) was
studied in terms of the particle size and the molecular
weight. The isopropanol/water medium ratio was varied
from 100/0 to 55/45 in wt%, a range in which all of the
ingredients are soluble and become homogeneous. The
SEM photographs and the number-average particle sizes
and weight-average molecular weights obtained using
five different isopropanol/water media are given in Table
5 and Figure 6. The number-average particle diameter
decreased and the weight-average molecular weight in-
creased upon increasing the water content; in other words,
the polarity of the dispersion medium. The solubility of
the St/MA (75:25 wt%) monomer mixture decreased
upon increasing the water content in the dispersion
medium. When the water content of the medium was
high, more monomer may transfer to the growing par-
ticles, which leads to a higher monomer concentration
inside the particles during the polymerization. Therefore,
a high molecular weight was observed upon increasing
the water content in the dispersion medium. The polymer
particles obtained from pure isopropanol as the disper-
sion medium were larger, but not uniform. However,
more-uniform latexes, but smaller in size, were produced
at a 15 ~ 30 % water content. The general trend is that
increasing the water content of the dispersion medium
results in latexes of smaller size and with more-uniform
distribution. Increasing the water content decreases the
solventy of the medium for the polymer formed at the
initial stage of the polymerization, resulting in an increase
in the number of precipitated oligomer molecules in the
medium and, at the same time, an increase in the
adsorption rate of the PVP stabilizer. Therefore, smaller
particles were formed upon increasing the water content
of the medium. In dispersion polymerization, uniform
particles can be obtained when there is no secondary par-
ticle nucleation after the primary particle nucleation within
a short time [26]. The polymer particles obtained at 15 ~
30 % water content are very likely to arise by this way.

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**Conclusion**

In this study, poly(styrene-co-methyl acrylate) micro-
particles with a narrow size distribution and having sizes
in the range 1.2 ~ 3.4 μm were prepared by dispersion
copolymerization. The poly(St/MA) latexes, containing
100/0 ~ 50/50 wt%, also had narrow size distributions in
the size range 1.3 ~ 2.0 μm. The particle size increased and
the molecular weight decreased upon increasing the
MA content. Especially, the polymerization of pure
methyl acrylate occurred in a clear-solution state and the
product showed the lowest molecular weight. Dispersion
copolymerization of St/MA (75/25 in wt%) was also
carried out to investigate the effects that various poly-
merization parameters have on the particle size and the
molecular weight of the resulting poly(St/MA) latexes.
The number-average particle diameter increased upon
increasing the reaction temperature and the concentra-
tions of monomer and AIBN initiator, and upon dec-
creasing the concentration of the PVP K-30 stabilizer and
the water content in the isopropanol/H2O media. The
weight-average molecular weight increased upon in-
creasing the concentrations of monomer and steric stab-
ilizer and the water content in the isopropanol/H2O media,
but decreased with the initiator concentration and poly-
merization temperature.