Synthesis of Highly Crosslinked Monodisperse Polymer Particles: Effect of Reaction Parameters on the Size and Size Distribution

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ABSTRACT: Monodisperse polystyrene particles crosslinked with different concentrations of divinylbenzene were synthesized in the 3.2–9.1 μm size range by dispersion polymerization in an isopropyl alcohol/toluene mixed-dispersion medium with poly(N-vinylpyrrolidone) as a steric stabilizer and 2,2'-azobisobutyronitrile as a radical initiator. The effects of the reaction parameters such as the crosslinking agent concentration, media solvency (controlled by varying the amount of toluene addition), the initiator concentration, and the stabilizer concentration on the particle size and size distribution were investigated with reference particles with a monodisperse size distribution and crosslinked by 1.5 wt % divinylbenzene. The appropriate increase in media solvency was a prerequisite for preparing crosslinked particles without coagulated and/or odd-shaped particles. The investigation of the effects of the polymerization parameters also shows that only specific sets of conditions produce particles with a monodisperse size distribution. The glass-transition temperatures of the particles increased with increasing divinylbenzene concentration. © 2002 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 40: 4368–4377, 2002

Keywords: dispersion polymerization; polystyrene; crosslinking; particle size distribution; polymerization parameter effect

INTRODUCTION

Monodisperse polymer particles have attracted much attention in many areas such as biomedical science and chemistry, catalyst supports, and packing materials.1–3 Furthermore, highly crosslinked monodisperse polymer particles are in greater demand for use as various spacers, slip-property improvers for plastic films, for solid-state peptide synthesis, and so forth in which good heat and solvent resistance are critical.4,5 Polymeric microspheres in the size range from 50 nm to 2 mm can be obtained via heterogeneous polymerization processes that are usually classified into suspension, emulsion, and dispersion polymerization.6,7 Suspension polymerization is suitable for polymer particles with a size range from 20 μm to 2 mm, but the resulting particles usually lack uniformity.6–8 The size of the latex particles prepared by emulsion polymerization is usually between 50 and 300 nm, and the latex has colloidal stability because of ionic or nonionic surfactants.6,9 Particles ranging from 1 to 10 μm...
with a narrow size distribution were prepared, either by Vanderhoff’s successive seeding method or by Ugelstad’s two-stage swelling method. However, both approaches are rather complicated and time-consuming.\textsuperscript{10,11} Dispersion polymerization is an interesting alternative to preparing micron-size monodisperse polymer particles in a single step. There are some examples of dispersion polymerization such as the polymerization of methyl methacrylate in hydrocarbons with poly(isobutylene),\textsuperscript{12} poly(12-hydroxystearic acid),\textsuperscript{1} or poly(2-ethylhexyl methacrylate)\textsuperscript{13} as a steric stabilizer and the polymerization of styrene in various alcohols with poly(acrylic acid),\textsuperscript{14,15} (hyhilizer and the polymerization of styrene in various hydroxypropyl cellulose,\textsuperscript{16,17} or poly(isobutylene),\textsuperscript{12} poly(12-hydroxystearic acid),\textsuperscript{1} or methyl methacrylate in hydrocarbons with polymerization such as the polymerization of styrene (remaining 30%) and the dispersion media (remaining 5%) were added slowly to the reaction mixture. The reaction mixture was then allowed to polymerize for 24 h under a constant agitation rate and temperature. The polymerization was quenched by pouring the reaction mixture into methyl alcohol (MeOH) at room temperature. The polymer was isolated by filtration. The isolated particles were washed with MeOH, MeOH/distilled water (50/50) and distilled water, and dried in a vacuum-freeze dryer. The standard method and the fixed or varied parameters in the dispersion polymerization of this study are listed in Table 1. The solubility parameter of the dispersion media, $\delta$ was calculated from the solubility parameters of component $\delta_i$ according to the equation, $\delta = (\Sigma \Phi_i \delta_i^{2})^{1/2}$, where $\Phi_i$ is the volume fraction of the $i$th component, $\delta$ (IPA) = 23.5 MPa$^{1/2}$, $\delta$ (toluene) = 18.2 MPa$^{1/2}$, and $\delta$(ethyl alcohol) = 26.0 MPa$^{1/2}$.\textsuperscript{15,21} The solubility parameter of styrene ($\delta = 19.0$ MPa$^{1/2}$) was excluded from the calculation because the styrene concentration was kept constant for all experiments.

**Characterization**

The size and size distributions of the product particles were measured with a polarization intensity diffraction system (Coulter LS 230) in which a total of 42 measurements were made at 6 scattering angles and three wavelengths, each at two polarizations.\textsuperscript{22} A combination of the multiple wavelengths and the two polarizations provided information about the differences between the particle sizes. With this instrument, the geometric standard deviation was directly defined with $d_{16}$ and $d_{84}$ from the cumulative volume distribution, which is used by many researchers because of the insensitivity to the size range selected for the calculation.\textsuperscript{5,23–27}

The size, shape, and size distributions of the polystyrene particles were also characterized by a Hitachi S-2500 C scanning electron microscope (SEM) operated at 10 kV. The glass-transition temperatures ($T_g$) of the noncrosslinked and crosslinked monodisperse polystyrene particles

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**EXPERIMENTAL**

**Materials**

Styrene (Kanto) and divinylbenzene (DVB, Fluka) were treated with aqueous sodium hydroxide, washed with distilled water, vacuum-distilled in the presence of cuprous chloride, and stored at 4 °C until use. 2,2’-azobisisobutyronitrile (AIBN, Junsei) was purified by recrystallization in anhydrous ethanol. Poly(N-vinylpyrrolidone) (PVP, Aldrich; molecular weight: 40,000 g mol$^{-1}$), and all other reagents were used without further purification.

**Dispersion Polymerization**

In a typical experiment, a four-necked 1-L reaction vessel equipped with a thermostat, a stirrer (four-bladed, metal), a water condenser, and a nitrogen inlet was used. PVP, styrene (70% of total amount), DVB, and the dispersion media (isopropyl alcohol (IPA)/toluene mixture, 95% of total amount) were introduced into the reaction vessel, heated to 70 °C, and stirred at 120 rpm. Nitrogen gas was bubbled through the solution for deoxygenation. After 1 h, AIBN dissolved in styrene (remaining 30%) and the dispersion media (remaining 5%) were added slowly to the reaction mixture. The reaction mixture was then allowed to polymerize for 24 h under a constant agitation rate and temperature. The polymerization was quenched by pouring the reaction mixture into methyl alcohol (MeOH) at room temperature. The polymer was isolated by filtration. The isolated particles were washed with MeOH, MeOH/distilled water (50/50) and distilled water, and dried in a vacuum-freeze dryer. The standard method and the fixed or varied parameters in the dispersion polymerization of this study are listed in Table 1. The solubility parameter of the dispersion media, $\delta$ was calculated from the solubility parameters of component $\delta_i$ according to the equation, $\delta = (\Sigma \Phi_i \delta_i^{2})^{1/2}$, where $\Phi_i$ is the volume fraction of the $i$th component, $\delta$ (IPA) = 23.5 MPa$^{1/2}$, $\delta$ (toluene) = 18.2 MPa$^{1/2}$, and $\delta$(ethyl alcohol) = 26.0 MPa$^{1/2}$.\textsuperscript{15,21} The solubility parameter of styrene ($\delta = 19.0$ MPa$^{1/2}$) was excluded from the calculation because the styrene concentration was kept constant for all experiments.

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The size, shape, and size distributions of the polystyrene particles were also characterized by a Hitachi S-2500 C scanning electron microscope (SEM) operated at 10 kV. The glass-transition temperatures ($T_g$) of the noncrosslinked and crosslinked monodisperse polystyrene particles
were measured with a differential scanning calorimeter (DSC, PerkinElmer DSC7) at a heating rate of 10 °C/min. The Fourier transform-Raman (FT-Raman) spectra were obtained from a PerkinElmer 2000 NIR FT-Raman spectrometer. The samples were taken from the reaction mixture at set intervals, cooled to room temperature, and introduced to the spectrometer. From the decrease in the characteristic peak intensity of the styrene monomer, the extent of polymerization could be estimated as a function of time.

RESULTS AND DISCUSSION

Dispersion Polymerization

Extensive literature demonstrating that non-crosslinked and moderately crosslinked (below 0.5% on the basis of monomer) monodisperse polymer particles ranging from 1 to 10 μm can be synthesized via simple dispersion polymerization by varying the polymerization parameters such as the feed rate of the ingredients and/or polymerization conditions has been reported. However, in highly crosslinked systems (above 0.5%), monodisperse particles are difficult to prepare because of the resulting confined network structure of primary particles that make the nucleation and growth mechanism much more sophisticated. These primary particles are hard and glassy, making them difficult to be expanded by vinyl monomers and/or divinyl crosslinkers. In a recent study, the successful synthesis of monodisperse polystyrene particles crosslinked by over 10% of carboxyl group-contained urethane acrylate (CUA) has been reported. The CUA molecular weights are more than 10× larger than a simple divinyl crosslinker such as DVB. This means that the net number of potential crosslinking sites of CUA is the same level of one-tenth of the DVB used in this system. More recently, the precipitation polymerization of poly(divinylbenzene) and its copolymer was thoroughly investigated by the Stöver group. The precipitation polymerization method is different from the dispersion polymerization method in that the sizes of the resulting particles are relatively small, and coagulated particles are usually obtained in many cases.

Hattori et al. suggested that during the dispersion polymerization, the highly crosslinked particles (above 22 wt % on the basis of monomer) were not swollen by the DVB and styrene monomers. However, from the swelling-capacity experiments, it was shown that particles highly crosslinked by DVB (up to 20 wt %) were swollen by toluene. This suggests that in the case of appropriate use of toluene, highly crosslinked particles can be expanded not only by DVB and/or styrene but also by toluene. This implies that particle growth occurs both by precipitation of the polymer chain from the media phase onto the nucleated particles and by polymerization of the swollen DVB and/or monomer.

Figure 1 displays SEM micrographs of the particles prepared by dispersion polymerization with varying amounts of the crosslinker DVB. In this study, the noncrosslinked polystyrene particles were obtained in ethyl alcohol medium with AIBN as the initiator and PVP as the steric sta-

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Standard Method</th>
<th>Variation Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>DVB concentration (wt %)(^a)</td>
<td>1.5</td>
<td>0–3</td>
</tr>
<tr>
<td>Polymerization media</td>
<td>IPA/toluene = 93/7</td>
<td>100/0–79/21</td>
</tr>
<tr>
<td>AIBN concentration (wt %)(^a)</td>
<td>2.6</td>
<td>1–6</td>
</tr>
<tr>
<td>PVP concentration (wt %)(^a)</td>
<td>13</td>
<td>3–26</td>
</tr>
<tr>
<td>Initiator type</td>
<td>AIBN</td>
<td>Fixed</td>
</tr>
<tr>
<td>Polymerization temperature (°C)</td>
<td>70</td>
<td>Fixed</td>
</tr>
<tr>
<td>Styrene concentration (wt %)(^b)</td>
<td>15</td>
<td>Fixed</td>
</tr>
<tr>
<td>Stabilizer type</td>
<td>PVP (MW 40,000 g mol(^{-1}))</td>
<td>Fixed</td>
</tr>
<tr>
<td>Polymerization time (h)</td>
<td>24</td>
<td>Fixed</td>
</tr>
<tr>
<td>Agitation rate (rpm)</td>
<td>120</td>
<td>Fixed</td>
</tr>
</tbody>
</table>

\(^a\) Based on monomer weight.
\(^b\) Based on total media weight.
bilizer (P1). Moderately crosslinked (0.75 wt % on the basis of styrene monomer) particles (P2) and highly crosslinked (1.5 wt %) particles (P3 and P4) were also obtained in IPA and an IPA/toluene mixed media, respectively, with the same initiator and stabilizer. The results of the P3 and P4 experiments showed that the size control of crosslinked particles without a breakdown in monodispersity was possible with an additional increase in the media solvency and a subsequent variation in the initiator concentration. All the resulting particles were in their respective monodisperse size distributions. The reaction parameters varied for the synthesis were media solvency, and the concentration of DVB and AIBN, whereas all other reaction parameters such as the polymerization temperature, agitation type, agitation rate, stabilizer type, and so forth were kept constant. The methods and results of the monodisperse polystyrene particles crosslinked with different DVB concentrations are summarized in Table 2. The $T_g$'s of the particles prepared with various amounts of DVB are also summarized in Table 2, which suggests that the $T_g$'s increased with increasing DVB concentration. These results infer that the higher DVB concentration, the better the thermal properties.

Polystyrene particles crosslinked with 1.5 wt % DVB (P3) were selected as a reference to investigate the effect of polymerization parameters on the polystyrene particles. All the methods used for the dispersion polymerization investigating the parameter effects were the same as the standard method shown in Table 1 except for one of the following parameters: the DVB concentration, the amount of toluene added, the AIBN concentration, and the PVP concentration.

**Fixed Variables**

The first objective of this study was the synthesis of highly crosslinked monodisperse polymer particles, and media solvency control was selected as the key factor. Because the effect of the polymerization parameters on the particles was not discussed in any of the cases, the dependence of the polymerization parameters on the particles was not considered in this study.

![Figure 1. SEM micrographs of highly monodisperse polystyrene particles crosslinked by 0 wt % (P1), 0.75 wt % (P2), and 1.5 wt % (P3 and P4) of DVB.](image)

**Table 2.** Methods and Results of Monodisperse Polystyrene Particles Crosslinked with Different DVB Concentrations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
</tr>
</thead>
<tbody>
<tr>
<td>DVB concentration (wt %)</td>
<td>0</td>
<td>0.75</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Solubility parameter (MPa$^{1/2}$)</td>
<td>26</td>
<td>23.5</td>
<td>23.2</td>
<td>22.8</td>
</tr>
<tr>
<td>AIBN concentration (wt %)</td>
<td>2.6</td>
<td>3.5</td>
<td>2.6</td>
<td>5.2</td>
</tr>
<tr>
<td>PVP concentration (wt %)</td>
<td>13</td>
<td>13</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>Mean size (μm)</td>
<td>4.5</td>
<td>3.5</td>
<td>5.2</td>
<td>9.1</td>
</tr>
<tr>
<td>GSD&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.01</td>
<td>1.01</td>
<td>1.01</td>
<td>1.02</td>
</tr>
<tr>
<td>$T_g$ (°C)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>96.6</td>
<td>99.8</td>
<td>101.2</td>
<td>101.2</td>
</tr>
</tbody>
</table>

<sup>a</sup> P1, EtOH 100%; P2, IPA 100%; P3, IPA/toluene = 93/7; P4, IPA/toluene = 86/14.

<sup>b</sup> GSD = $(d_{95}/d_{16})^{1/2}$.

<sup>c</sup> Observed on second heating.
ization media was not limited to a solubility change alone, not only were the polymerization media varied but so were some of the other parameters.\textsuperscript{4,17,23} To simplify the approaching method to the desired highly crosslinked monodisperse particles, the number of parameters varied was minimized.

It is possible to vary the rate of free-radical generation by changing either the reaction temperature, the initiator type, or the initiator concentration. According to Tseng et al.,\textsuperscript{18} the effects of initiator on the resulting particles in dispersion polymerization, initiators with moderate decomposition rates [AIBN, 4,4’-azobis(4-cyanopentanoic acid) and 2,2’-azobis(2-methylbutyronitrile)], and half-lives at 70 °C (300–500 min) produced stable dispersions with a narrow size distribution. In contrast, initiators with a rapid decomposition rate [2,2’-azobis(2,4-dimethyl valeronitrile), half-life: 70 °C, 58 min] and those with a slow decomposition rate (benzoyl peroxide, half-life: 70 °C, 1049 min) resulted in particles with a broad size distribution.\textsuperscript{18} In this study, the initiator concentration was varied to control the rate of free-radical generation, whereas the type of initiator and reaction temperature used for all experiments were AIBN and 70 °C, respectively. The total solubility parameters were influenced by not only the media composition but also the monomer concentration. The solubility parameter of the total reaction mixture changed during dispersion polymerization because of monomer consumption.\textsuperscript{26} The solubility parameter of the initial reaction mixture used here was controlled by varying the amount of toluene added. However, the solubility contribution of the styrene monomers remaining in the reaction mixture was not considered because the initial styrene concentration was kept constant for all experiments. Three important polymerization parameters are related to the stabilizer in dispersion polymerization—the stabilizer type, the concentration, and the molecular weight. Bamnolker and Margel\textsuperscript{36} reported the effects of stabilizers on the resulting particles in dispersion polymerization. They showed that PVP was the most effective stabilizer among the other stabilizers investigated when AIBN was used as the initiator.\textsuperscript{36} In addition, the PVP molecular weight is analogous to the effect of the stabilizer concentration. For example, the average particle size decreased with increasing PVP molecular weight, and a similar size decrease was observed with increasing PVP concentration in the dispersion polymerization of styrene.\textsuperscript{27,36} The type of stabilizer and stabilizer molecular weight used in this study were PVP and 40,000 g mol\textsuperscript{-1}, respectively. However, the stabilizer concentration was varied to investigate the effect of the stabilizer. Figure 2 portrays the intensity of the characteristic peaks for the styrene monomer (1630 cm\textsuperscript{-1}). The intensity decreased during dispersion polymerization with over 90% of styrene monomer being polymerized within 24 h after initiation. The reaction vessel (1-L based) was designed as mentioned in the experimental section, and all the related physical parameters such as the shape of the reaction vessel and the stirrer, the agitation rate, and so forth were kept constant for all experiments.

The fixed parameters and varied parameters used for the synthesis of highly crosslinked monodisperse polymer particles and for investigating the effects of the parameters on the highly crosslinked polystyrene particles are summarized in Table 1.

Effect of Crosslinking Agent Concentration

Figure 3 displays SEM micrographs of four polystyrene particles prepared in IPA/toluene mixed-dispersion media with different concentrations of

![Figure 2](https://via.placeholder.com/150)

**Figure 2.** FT-Raman spectra recorded in the 1540–1680 cm\textsuperscript{-1} region during dispersion polymerization (from the top, after initiation and 2, 4, 6, and 24 h after initiation).
the crosslinking agent, DVB. The amount of all other ingredients and polymerization conditions for the A1–A3 experiments were the same as that used in the standard method given in Table 1. As the DVB concentration increased from 0 to 3 wt% (on the basis of styrene), the average particle diameter decreased. However, the particle monodispersity had deteriorated with increasing DVB concentration. The results of the dispersion polymerization in the presence of various DVB concentrations are summarized in Table 3. The broad size distributions of the A1, A2, and A3 particles may have their origin in the different network structure, which may change the particle growth/precipitation mechanism. Increasing DVB concentration decreases the swelling capacity of the particles, which hinders the particles’ ability to grow by polymerization of a swollen monomer. An excessive monomer existing in the polymerization media forms a grafted oligomer, which has difficulty in adsorbing onto the existing particle but precipitates (secondary particle stabilization). This suggests that the only specific set of reaction conditions gives the monodispersity and other crosslinking agent concentrations with more or less DVB product particles with a broader size distribution.

**Effect of Media Solvency**

SEM micrographs of four polystyrene particles crosslinked by 1.5 wt% of DVB with four different dispersion media solvencies are illustrated in Figure 4. Varying the amount of added toluene to the dispersion media was used to control the media solvency. According to the standard method given in Table 1, the amount of all the other ingredients and polymerization conditions were kept constant for the B1–B3 experiments. As the amount of toluene added increased from 7 to 28% (w/w on the basis of IPA), which means the total dispersion media solubility parameter changed from 23.5 to 22.5 MPa$^{1/2}$, the average particle diameter

<table>
<thead>
<tr>
<th>Parameter</th>
<th>DVB Concentration (wt %)</th>
<th>Media Solvency Effect</th>
<th>AIBN Concentration Effect</th>
<th>PVP Concentration Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>DVB concentration (wt %)</td>
<td>1.5</td>
<td>0</td>
<td>0.75</td>
<td>3</td>
</tr>
<tr>
<td>Solubility parameter (MPa$^{1/2}$)</td>
<td>23.2</td>
<td>—</td>
<td>23.5</td>
<td>22.8</td>
</tr>
<tr>
<td>AIBN concentration (wt %)</td>
<td>2.6</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PVP concentration (wt %)</td>
<td>13</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Mean size (µm)</td>
<td>5.2</td>
<td>7.2</td>
<td>5.7</td>
<td>2.0</td>
</tr>
<tr>
<td>GSD$^b$</td>
<td>1.01</td>
<td>1.42</td>
<td>1.15</td>
<td>1.10</td>
</tr>
</tbody>
</table>
increased. This can be simply explained by the effect of media solvency on the critical chain length for precipitation in the early stage of polymerization. In other words, better solvency led to longer chain lengths and larger particles, whereas a shorter critical chain length and smaller particles were favored for poorer solvents. The result of the dispersion polymerization in the presence of various amounts of toluene is summarized in Table 3. The average particle diameter and the size distribution of the resulting particles as a function of the amount of added toluene in Table 3 suggest that the sole media solvency change with more or less added toluene produced particles with a broader distribution. This suggests that only specific sets of reaction conditions can yield monodispersity for a specific crosslinking agent concentration.

**Effect of Initiator Concentration**

Figure 5 compares the SEM micrographs of four polystyrene particles crosslinked with 1.5 wt % DVB prepared in an IPA/toluene mixed-dispersion medium with different initiator (AIBN) concentrations. The amount of all the other ingredients and polymerization conditions for the C1–C3 experiments were kept the same as the standard method given in Table 1. The size of the resulting particles increased from 2.2 to 7.4 μm as the AIBN concentration increased from 1 to 6 wt % (on the basis of styrene). This behavior has also been discussed extensively in the literature. The increase in the initiator concentration caused an increase in the number of free radicals, meaning that polymerization begins with more radicals per unit volume. This leads to a shorter polymeric chain that is more soluble in the polymerization media. Consequently, there are fewer chains long enough to precipitate from the media. Therefore, fewer primary particles are produced that lead to a lower number of particles but with larger size. The result of the dispersion polymerization in the presence of various AIBN concentrations is summarized in Table 3. As shown in Figure 5 and
Table 3, a variation in the AIBN concentration, except for experiment C1, produced good-shaped polystyrene particles with a relatively narrow size distribution that is not in accordance with the other polymerization parameters discussed in this article. This trend is similar to the previous work reported by Tseng et al.\(^{18}\) who found that initiators with moderate decomposition rates such as AIBN (half-life: 70 °C, 289 min) produced stable dispersions with a narrow size distribution. The experimentally determined explanation of the flocculated small particles in a highly crosslinked system prepared at a low initiator concentration in experiment C1 may result from the role played by the oligomeric free radicals during the nucleation stage. The lower initiator concentration caused a decrease in the instantaneous concentration of oligomeric radicals, which in turn decreased the rate of flocculated small-particle formation.

**Effect of Stabilizer Concentration**

Figure 6 portrays SEM micrographs of four polystyrene particles crosslinked by 1.5 wt % DVB prepared in IPA/toluene mixed-dispersion media with different stabilizer (PVP) concentrations. All the other methods used for the D1–D3 experiments were the same as the standard method given in Table 1. According to the methods used for producing the P1–P4 particles summarized in Table 2, the stabilizer concentration was not varied for the synthesis of the crosslinked monodisperse particles, whereas the other three parameters mentioned previously, that is, the DVB concentration, the media solvency, and the AIBN concentration, were varied. However, as pointed out by Bamnolker and Margel,\(^{36}\) not only is the size highly dependent on the type and concentration of stabilizer used in dispersion polymerization but so is the monodispersity of the resulting particles. In the series of experiments with increasing PVP concentration from 3 to 26 wt % (on the basis of monomer), the average particle diameter decreased from 9.2 to 3.2 μm. In this PVP concentration interval, the particle size distribution was relatively narrow but broader than P3 suggesting that specific sets of reaction conditions yield monodispersity, and any deviation in the concentration of any ingredient produces particles with a broader distribution. The result of the dispersion polymerization in the presence of various PVP concentrations is summarized in Table 3.

**Effect of the Polymerization Variables on the Broadness of the Size Distribution**

The following nucleation/growth mechanism suggested by Paine\(^{27}\) has been widely accepted for fitting many cases of dispersion polymerization (see Fig. 7): The initial reaction mixture was a homogeneous solution of polymerization ingredients (initiator, stabilizer, monomer, and crosslinking agent) in the media (1). Insufficiently stabilized small nuclei were formed by hydrogen abstraction and grafting (2). These small nuclei aggregated until the particle surfaces were stabilized sufficiently by the grafted stabilizers. The primary stabilized particles were then formed (3). These primary particles grew to the final monodisperse particles when they were inside the polymerization of the swollen monomer (particle growing part), and the grafted oligomeric stabilizer adsorbed simultaneously to the growing particle surface (particle stabilizing part) (4-a). The breakdown of the monodispersity of the particles size distribution might have occurred by either
secondary stabilization (4-b) or large particle agglomeration (4-c). Secondary nucleation occurs when the primary particles are no longer monomer-swellable and the growing oligomeric chains in the media phase become insoluble in the media (B1). Large particle agglomeration also occurs when the surface of the primary particles becomes unstable because of excess interior polymerization, which is mainly observed in a higher media-solvency system (B2, B3). The broader size distribution, which occurred in the A, C, and D series of the experiments, can also be explained by the breakdown of the monodispersity during particle growth. The decrease in the DVB concentration from the standard method (A1, A2) enhanced the monomer-swelling capacity of the particles to grow by the excess inside polymerization reaction that resulted in precipitation from the media (secondary nucleation). The increase in the PVP concentration from the standard method (C1) led to a larger number of grafted stabilizers that resulted in precipitation from the media (secondary nucleation). However, a decrease in the PVP concentration (D3) led to a smaller number of grafted stabilizers, resulting in insufficiently stabilized growing particles that agglomerated (large-particle agglomeration).

**CONCLUSIONS**

Monodisperse polystyrene particles crosslinked by 0–1.5 wt % (on the basis of monomer) of DVB in the size range of 3.5–9.1 μm successfully completed dispersion polymerization. The $T_g$ of the prepared particles increased with increasing DVB concentration. The effects of the polymerization parameters that play key roles in the synthesis of crosslinked monodisperse particles were investigated. The average particle sizes generally increased with increasing media solvency (by increasing amount of added toluene) and increasing AIBN concentration, whereas the average particle sizes decreased with increasing DVB concentration and increasing PVP concentration. There are only specific sets of conditions that produce crosslinked particles with a monodisperse size distribution. Therefore, crosslinked monodisperse particles can be obtained with the following synthetic strategy. For a given specific DVB concentration, an appropriate increase in media solvency is essential for obtaining a stable dispersion without coagulated and/or odd-shaped particles. Variations in the initiator and/or stabilizer concentration should be followed to produce particles with a monodisperse size distribution.

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REFERENCES AND NOTES