

# Preparation of Monodisperse Polystyrene Spheres Incorporating Polyimide Prepolymer by Dispersion Polymerization in the Presence of L-Ascorbic Acid

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**ABSTRACT:** Addition of a small amount of L-ascorbic acid (AA) unexpectedly provided uniform-sized polystyrene (PS) spheres in an ordinary dispersion polymerization process. PS spheres incorporated with polyimide prepolymer (BANI-M), designed as possible spacers for liquid crystal displays, were prepared from formulations containing a mixed solvent of isopropanol/2-methoxyethanol, 2,2'-azobisisobutyronitrile, and poly-N-vinylpyrrolidone (PVP) at 343 K. The average particle size decreased by the addition of AA; however, dramatic improvements of monodispersity were observed with various formulations. The best coefficient of variation was 1.37%, compared to 7.03% obtained without the presence of AA. Addition of AA was originally intended to scavenge a trace amount of oxygen remaining in the reactor system, promoting a rapid and short particle nucleation period, and thereby resulting in improved monodispersity. However, there was no difference in the initial reaction rate between the runs with and without AA; no noticeable induction period was observed even without AA provided that an ordinary procedure was employed to eliminate the dissolved oxygen through a nitrogen bubbling, and the nitrogen atmosphere was maintained during the reaction. It was proposed from <sup>1</sup>H-NMR analysis that the abstraction of hydrogen atom from the PVP chain by the oxidized form of AA promoted the formation of graft copolymer PVP-PS, which stabilizes precipitating chains in the nucleation period. Approximately 40% of BANI-M present initially was incorporated in the PS particles, which occupied 4–9% of the weight of polymer particles, well below the target value of 20%. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 897–907, 1998

**Key words:** dispersion polymerization; styrene; L-ascorbic acid; polyimide prepolymer; monodispersity

## INTRODUCTION

Nonaqueous phase dispersion (NAD) polymerization is well known for its ability to provide monodisperse polymeric spheres ranging from submicron to 15  $\mu\text{m}$ .<sup>1–3</sup> Its reaction mechanism, although still limited to a qualitative basis, has

been well established; nucleation of primary particles by the precipitation of oligomeric chains from an unfriendly solvent, and rapid growth via successive coagulations while being stabilized by the adsorption of amphiphilic stabilizers (normally polymers), which are composed of moieties soluble in the solvent and anchoring blocks on the surface of the growing polymer particles. The stability of the particles is secured by the soluble moieties that extend steric barriers around the particles and prevent them from approaching closely leading to the eventual coagulation. Once

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these polymer particles gain sufficient stability, the precipitating chains will be captured by the growing particles so that no further generation of stable particles will occur, and the polymerization will progress, somewhat analogous to the mechanism of emulsion polymerization.

In general, the studies have been conducted on polymers like polystyrene (PS) or polymethylmethacrylate (PMMA). However, recently more polar monomers such as hydroxyethylmethacrylate (HEMA) and acrylonitrile (AN) were successfully polymerized to yield uniform spheres or porous spheroids, an encouraging trend indicating that varieties of functional spheres can be obtained by dispersion polymerization.

Tseng et al.<sup>4</sup> conducted the NAD polymerization of styrene systematically, covering a wide range of monomer concentration, and varieties of small amounts of functional comonomers. Combinations of poly-*N*-vinylpyrrolidone (PVP) and several surface active agents such as Aerosol-OT, Triton N-57, and cetyl alcohol were used as the essential combinations of stabilizers. However, Paine and McNulty<sup>5</sup> proved experimentally that PVP alone was enough to produce monodisperse PS spheres, almost of the same size and CV as those prepared with the costabilizers. Ober and Lok<sup>6</sup> showed that the size and monodispersity of P(styrene-*co*-butylmethacrylate) spheres can be controlled by the amount of water added in ethanol. The importance of the polarity of the initial homogeneous solution, and its change during the polymerization, became recognized as one of the potentially influential factors with respect to the size and monodispersity. Tuncel et al.<sup>7</sup> correlated the average size of PS particles with the solubility parameter of the medium, and found that the maximum size was attained at a solubility parameter of 12.5 in mixed solvents of isopropanol, 1-butanol, 2-butanol, and water. Later, Paine<sup>8</sup> replaced Hildebrand's solubility parameter with that of Hansen's three-dimensional parameter, and correlated the size of PS particles with the polarity of the solvent by plotting the diameter in a coordinate composed of the hydrogen bonding component vs. the polar component of Hansen's parameter for the solvent.

PMMA spheres can be polymerized in mixed solvents of alkanes, including those of higher boiling point, with stabilizers such as P(12-hydroxy stearic acid).<sup>1</sup> Antl et al.,<sup>9</sup> as Tseng et al. had done with ST, investigated the MMA dispersion polymerization over a wide range of monomer concentration; the average diameter shifted more

than one order, from 0.18 to 2.6  $\mu\text{m}$ . Recently, Takahashi et al.<sup>10</sup> successfully prepared monodisperse spheres of hydrophilic polyhydroxyethylmethacrylate (PHEMA), and also polyacrylonitrile (PAN).<sup>11</sup> Using PVP in the mixed solvent of dimethyl formamide (DMF)/methanol (70 : 30), hollow spheres, more like entangled wool yarns, were obtained. With increasing amounts of DMF, coarse and gradually fine porous PAN spheres were obtained. Other functional and morphologically specific spheres are being prepared by dispersion polymerization to take advantage of the uniform spheres that can be obtained.

In the case of ST dispersion polymerization, the composition of good solvent (methoxy ethanol) and polar solvent (normally short-chain alcohol), selection of stabilizing polymer, amount of initiator, and the polymerization temperature are regarded to be controlling factors for the average diameter and monodispersity.

We have been trying to prepare monodisperse PS spheres incorporated with polyimide prepolymer based upon the concept that these spheres may be used as spacers for liquid crystal displays (LCD) because the prepolymer crosslinks when treated above 473 K, and contributes to the mechanical strength as well as excellent adhesion. That the spacer particles can be crosslinked, and adhere to the glass panels by the heat treatment, are potentially important requirements to commercialize thinner and, therefore, light-weight LCD panels. Crosslinking and adhesion between the panels will provide structural strength, and also prevent the movement of slightly off-sized spacer particles.

Intensive experiments revealed that the desired monodispersity for the spacers, less than 4% coefficient of variation (CV), was never achieved no matter how the compositions of polymerization recipe were changed on the basis of solvent-cosolvent ratio, initiator, and stabilizer concentrations. We shifted our strategy to shorten the nucleation period, as the La Mer diagram tells us that an instantaneous nucleation followed by a slow growth will favor monodispersity. We figured out that addition of an antioxidant might help decrease the induction period even though we were employing a nitrogen bubbling procedure in our stirred tank reactor before heating the system.

L-Ascorbic acid (AA), a well known antioxidant, was chosen for this purpose. The results exceeded our expectation overwhelmingly; very narrow-sized distributions with CV as low as 1.4% were obtained, although the size of the particles

became smaller than those obtained from the recipe without AA. This experience will be reported briefly in the following.

## EXPERIMENTAL

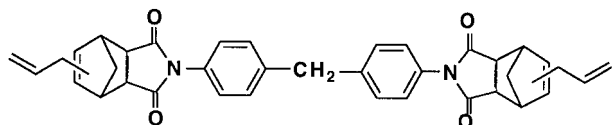
### Materials

All the reagents, unless stated otherwise, were purchased from Kishida Chemical Co. Styrene was a commercial grade, distilled under reduced pressure, and stored in a refrigerator. L-Ascorbic acid (AA, reduced form, biochemistry grade), 2,2'-azobisisobutyronitrile (AIBN, reagent grade), and polyvinylpyrrolidone (PVP-K30,  $M_w = 40,000$ , Tokyo Chemical Co.) were all used as received.

Isopropanol (IPA) and ethanol (EA) were reagent grade and used after distillation under the normal atmospheric pressure. 2-Methoxy ethanol (MeCell, reagent grade) and methanol (commercial grade) were used as received.

*d*-Chloroform and *d*<sup>6</sup>-acetone were used as the solvents for <sup>1</sup>H-NMR and <sup>13</sup>C-NMR measurements. Tetrahydrofuran (THF, commercial grade) was used as a carrier solvent for GPC.

The chemical structure of diphenylmethane-4,4'-bisallylnadiimide (BANI-M, Maruzen Petrochemical Co. Ltd.), one of the prepolymers of polyimide, is shown below.



BANI-M is miscible with styrene and MeCell, but insoluble in IPA. MeCell is the only solvent for AA existing in the polymerization recipe.

These reagents and prepolymers were used as received.

### Polymerization

A 300 cm<sup>3</sup> glass flat bottom flask, equipped with a condenser, a nitrogen inlet, and a 39/42 tapered glass stopper, was immersed in a thermostat, and placed on a magnetic stirrer. The nitrogen introduced in the flask was released from the top of the condenser. A clear IPA solution dissolving PVP K-30 was fed in the flask, and mixed with another clear solution of ST and MeCell dissolving AIBN and BANI-M. Granular AA crystals were added so that the contact with oxygen in the atmosphere

may be limited. Because IPA is neither a good solvent for BANI-M nor AA, the mixed solution became slightly opaque when the volumetric ratio (IPA/MeCell) was 155/20 or no MeCell was present. A gentle bubbling of nitrogen continued for 2 h under minimal agitation by a magnet bar. Agitation was controlled in this mild mode throughout the reaction. After 2 h elapsed, the nozzle of the nitrogen inlet was lifted from the solution and kept in the free space in the flask. Then the thermostat was heated to the reaction temperature, 343 K, and the polymerization was carried out for 16 h. After the heating was started, the haze observed in the mixture of IPA/MeCell 155/20 became clear and remained transparent until the nucleation was initiated, while the mixture remained opaque when no MeCell was present.

Monomer conversion was measured gravimetrically, and dried particles were provided for the observation by a SEM. After all the solids were separated from the continuous phase by a centrifuge, the clear supernatant was dried in an oven to remove solvents, and the glassy hard residue was saved for GPC measurement to estimate the amount of BANI-M not incorporated in the particles.

### Analysis

Average particle size and CV were determined from the photographs taken with a SEM (JSM-35CFII, JEOL). Average molecular weight of PS and the content of BANI-M remaining in the continuous phase were determined with a GPC (HLC-801, Tosoh, THF as a carrier solvent). In the latter measurement, after the evaporation of the solvents, IPA/MeCell, 10 mg of the residual

**Table I** General Recipe for NAD Polymerization of Styrene

Styrene (g)	50
BANI-M (g)	<b>5</b> , 10
AIBN (g)	<b>0.5</b> , 1.25
MeCell (mL)	0, <b>20</b> , 25, 35, 50
AA (g)	0, 0.2, 0.5, <b>1.0</b> , 1.5, 2.0
IPA (mL)	175, 150, <b>155</b> , 140, 125
PVP K-30 (g)	3, <b>6</b> , 9
Total (g)	ca. 240

BANI-M = polyimide prepolymer, AIBN = 2,2'-azobisisobutyronitrile, MeCell = 2-methoxyethanol, AA = L-ascorbic acid, IPA = isopropanol, PVP = polyvinylpyrrolidone. Polymerization temperature 343 K, 16 h.

Numbers in bold letters are those selected as a standard recipe.

solid composed of PVP K-30 and BANI-M was soaked in 2 mL of THF. The supernatant was injected into the columns, and the amount of BANI-M not incorporated in the polymer particles was determined from the peak area of BANI-M. No noticeable peak of PS was observed because this analysis was only conducted for the runs that yielded a clear supernatant after the centrifugation, which separated the polymer particles from the continuous phase. Weight percentage of BANI-M incorporated in the polymer particles was also determined with an NMR (ALPHA-500, JEOL, 500 MHz, 200 scans).

## RESULTS AND DISCUSSION

### Polymerization Recipe

The general recipe for the NAD polymerization is shown in Table I. The content of styrene is 20 wt %, and fixed for all the experiments. For the other ingredients, numerals expressed in bold letters are selected as standards.

### Polymer Particles without the Addition of AA

The first part of the experimental results listing average diameter and the coefficient of variation

**Table II Average Diameter and Coefficient of Variation (CV) of Polymer Particles (No. 1)**

a) Effect of addition of BANI-M without L-ascorbic acid						
Run No.	IPA (mL)	MeCell (mL)	BANI-M (g)	Monomer Conversion (%)	Average Diameter ( $\mu\text{m}$ )	CV (%)
960	150	25	5	94.0	5.16	7.24
b) Effect of addition of L-ascorbic acid						
Run No.	IPA (mL)	MeCell (mL)	AA (g)	Monomer Conversion (g)	Average Diameter ( $\mu\text{m}$ )	CV (%)
962	140	35	0	69.4	4.38 (0.58–26.5) <sup>a</sup>	69.7
969	140	35	1	89.0	2.76	1.83
982 <sup>b</sup>	140	35	1	57.0	2.20	40.9
963	155	20	0	94.6	4.59 (2.40–6.04)	11.4
965	155	20	1	90.7	2.31	2.28
972	175	0	0	93.6	3.09	8.98
973	175	0	1	95.6	1.19	11.2
c) Effect of solvent composition in the presence of L-ascorbic acid						
Run No.	IPA (mL)	MeCell (mL)	AA (g)	Monomer Conversion (%)	Average Diameter ( $\mu\text{m}$ )	CV (%)
970	125	50	1	86.0	1.48 (0.84–3.51) <sup>a</sup>	16.6
969	140	35	1	89.0	2.76	1.83
965	155	20	1	90.7	2.31	2.28
973	175	0	1	95.6	1.19	11.2

Other ingredients are those of the standard recipe.

<sup>a</sup> Shows the range of the particle diameter observed.

<sup>b</sup> Without nitrogen bubbling before polymerization and no nitrogen sealing during the reaction.

Other ingredients are those of the standard recipe.

<sup>a</sup> Shows the range of the particle diameter observed.

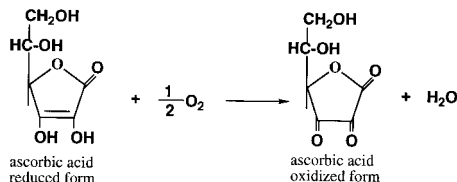
(CV) against the variation of the polymerization recipe, is shown in Table II. The CV of 7.24%, as shown in Table IIa), was the best of all runs obtained by changing the amount of each component. This result implies that the uniformity of the polymer particles, an advantage of the NAD polymerization, was lost to some extent due to the addition of BANI-M. Run 900 without BANI-M, not shown in Table II because of the larger scale polymerization (styrene 148.5 g, divinylbenzene 1.5 g, IPA 645 g, MeCell 105 g, PVP K-30 24 g, and AIBN 5 g), yielded a respectable CV of 4.80%. Increase of PVP K-30 was of no avail.

### Effect of the Addition of AA

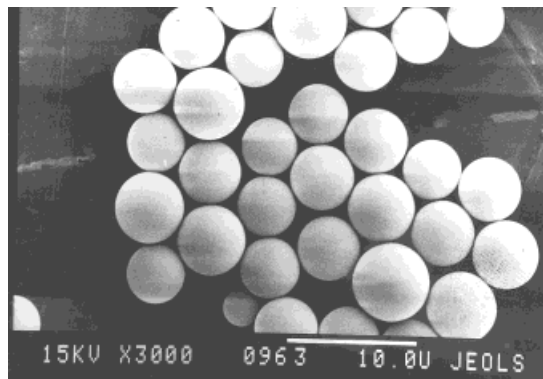
To improve the monodispersity of the particles, we shifted our efforts to eliminate the residual oxygen remained in the reaction mixture even after a lengthy bubbling of nitrogen. A 2-h gentle bubbling may not be sufficient, but vigorous bubbling will merely invite evaporation of the solvents and styrene. We screened chemicals commercially available as antioxidants, and L-ascorbic acid emerged as a probable candidate. AA, which traps  $O_2^-$  ions or  $\cdot OH$  radicals *in vivo*, has been used commercially as an antioxidant, and is believed to react with oxygen according to Scheme 1.

For example, 1 g of AA ( $M_w = 176$ ) is capable of consuming 90.9 mg of oxygen in the  $O_2$  form. Suppose the solubility of oxygen in 240 g of the reaction mixture is 10 ppm; then the weight of dissolved oxygen is 2.4 mg. Suppose also one atom of air occupies 300 mL of the free space in the reactor system at 298 K. The oxygen content is calculated to be 79 mg, pretty close to 90.9 mg. However, this air is rapidly swept away once the flow of nitrogen is started, allowing us to conclude that even 0.1 g of AA is sufficient for the consumption of oxygen present in the reaction system.

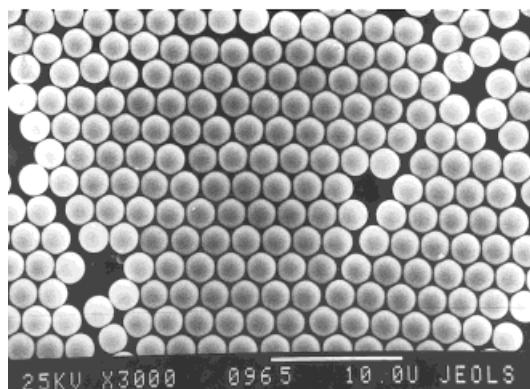
It is shown in Table IIb) that the addition of AA induced a dramatic effect on the average size and CV of the resultant polymer particles. The size of polymer particles significantly reduced. At first, we regarded this result as probably due to



Scheme 1



a) Run 963 without L-ascorbic acid.  
 $dp = 4.59 \mu m$ , CV = 11.4%



b) Run 965 L-ascorbic acid was added.  
 $dp = 2.31 \mu m$ , CV = 2.28%

**Figure 1** SEM photographs of polymer particles. Addition of L-ascorbic acid dramatically improved the monodispersity of spheres.

the reduction of the residual oxygen remaining in the reaction mixture according to the reaction shown in Scheme 1. However, the later experiments, conducted by adopting the same recipe as run 978 and the one without AA, revealed no noticeable difference in the initial reaction rate. Virtually no induction period was detected even in the run without AA.

In run 982, the capacity of AA for scavenging oxygen was examined without bubbling nitrogen in the reaction mixture before heating, or nitrogen sealing during the period of polymerization. The result was rather disappointing; only 57% monomer conversion with a wide size distribution. A proper procedure to remove oxygen was proved to be an absolute necessity even in the runs with AA.

Obviously, the reaction rate (Scheme 1) is not

sufficient to annihilate all the oxygen remaining in the reaction mixture. The contribution of AA to the improved monodispersity should be located elsewhere.

Another possibility is enhanced grafting of PVP K-30 with styrene monomer, which promotes the

stability of polymer particles in the nucleation-agglomeration stage. The enhanced stability will enable smaller particles to grow independently without further agglomeration with each other. This discussion will be resumed in the latter part of this article.

**Table III Average Diameter and Coefficient of Variation (CV) of Polymer Particles (No. 2)**

a) Effect of amount of L-ascorbic acid						
Run No.	IPA (mL)	MeCell (mL)	AA (g)	Monomer Conversion (%)	Average Diameter ( $\mu\text{m}$ )	CV (%)
962	140	35	0	69.4	4.38 (0.58–26.5) <sup>a</sup>	69.7
989	140	35	0.2	91.2	1.98	1.91
979	140	35	0.5	87.6	2.03	1.88
984 <sup>b</sup>	140	35	0.5	> 100 <sup>c</sup>	2.71	2.44
969	140	35	1	89.0	2.76	1.83
980	140	35	1.5	> 100 <sup>c</sup>	4.90	5.26
987	140	35	2	95.1	3.94 (1.21–8.91)	51.3
963	155	20	0	94.6	4.59 (2.40–6.04)	11.4
967	155	20	0.2	78.4	2.39	10.3
966	155	20	0.5	90.5	1.97	2.85
965	155	20	1	90.7	2.31	2.28
988	155	20	1.5	83.7	3.05	3.58
964	155	20	2	98.0	1.59	4.11

Other ingredients are those of the standard recipe.

<sup>a</sup> Shows the range of the particle diameter observed.

<sup>b</sup> The same recipe as run 979 except no addition of BANI-M.

<sup>c</sup> Due to an evaporation of the solvents.

b) Effect of PVP K-30 concentration in the presence of L-ascorbic acid

Run No.	PVP K-30 (g)	AA (g)	Monomer Conversion (%)	Average Diameter ( $\mu\text{m}$ )	CV (%)
985	3	1	80.9	6.67	17.5
965	6	1	90.7	2.31	2.28
978	9	1	80.0	3.08	1.37

Other ingredients are those of the standard recipe.

c) Effect of AIBN concentration in the presence of L-ascorbic acid

Run No.	AIBN (g)	AA (g)	Monomer Conversion (%)	Average Diameter ( $\mu\text{m}$ )	CV (%)
969	0.5	1	89.0	2.76	1.88
974	1.25	1	91.8	2.69	16.4

Other ingredients are those of the standard recipe except IPA 140 mL and MeCell 35 mL.

SEM photographs of run 963 without AA and run 965 with 1 g of AA are shown in Figure 1. The reduction of particle size and improved monodispersity of run 965 are quite evident.

#### Effect of Solvent Composition in the Presence of L-Ascorbic Acid

As IPA is neither a good solvent for BANI-M nor AA, the composition of the mixed solvent becomes an important issue for monodispersity of the resultant particles. In Table IIc), the solvent composition was changed for a fixed amount of AA (1 g). Experimentally, it is well known that the size of the particles increases with increasing the fraction of good solvents for the related polymer, 2-methoxy ethanol in this case. The average diameters shown in Table IIc) agreed with this tendency except run 970, which yielded a broader size distribution. This run was repeated, and a smaller average diameter of 1.22  $\mu\text{m}$  resulted. Because MeCell is a good solvent of AA, fully dissolved AA may offset the solvency of MeCell as the later data

in Table IIIa) imply. On the contrary, the large CV of run 973, even with the addition of AA, is attributed to the inhomogeneity of the reaction mixture because no good solvent for AA was present in this recipe. Reasonable monodispersity was obtained with the volumetric ratio (IPA/MeCell) of 155/20 or 140/35 provided that the weight of styrene was 50 g.

#### Optimal Amount of AA

In Table IIIa), the amount of AA in the recipe was changed for the two compositions of the mixed solvent (IPA/MeCell = 140/35 and 155/20). For the runs with better solvency (140/35), the size distribution became slightly narrower when the weight of AA was raised from 0.2 to 1.0 g, and broader when raised from 1 to 2 g. For the runs with IPA/MeCell = 155/20, the tendency is similar to those with 140/35; however, the CV values are still respectable at the higher AA values (1.5 and 2 g) compared with runs 980 and 987. Because an increase of AA weight invites inhomoge-

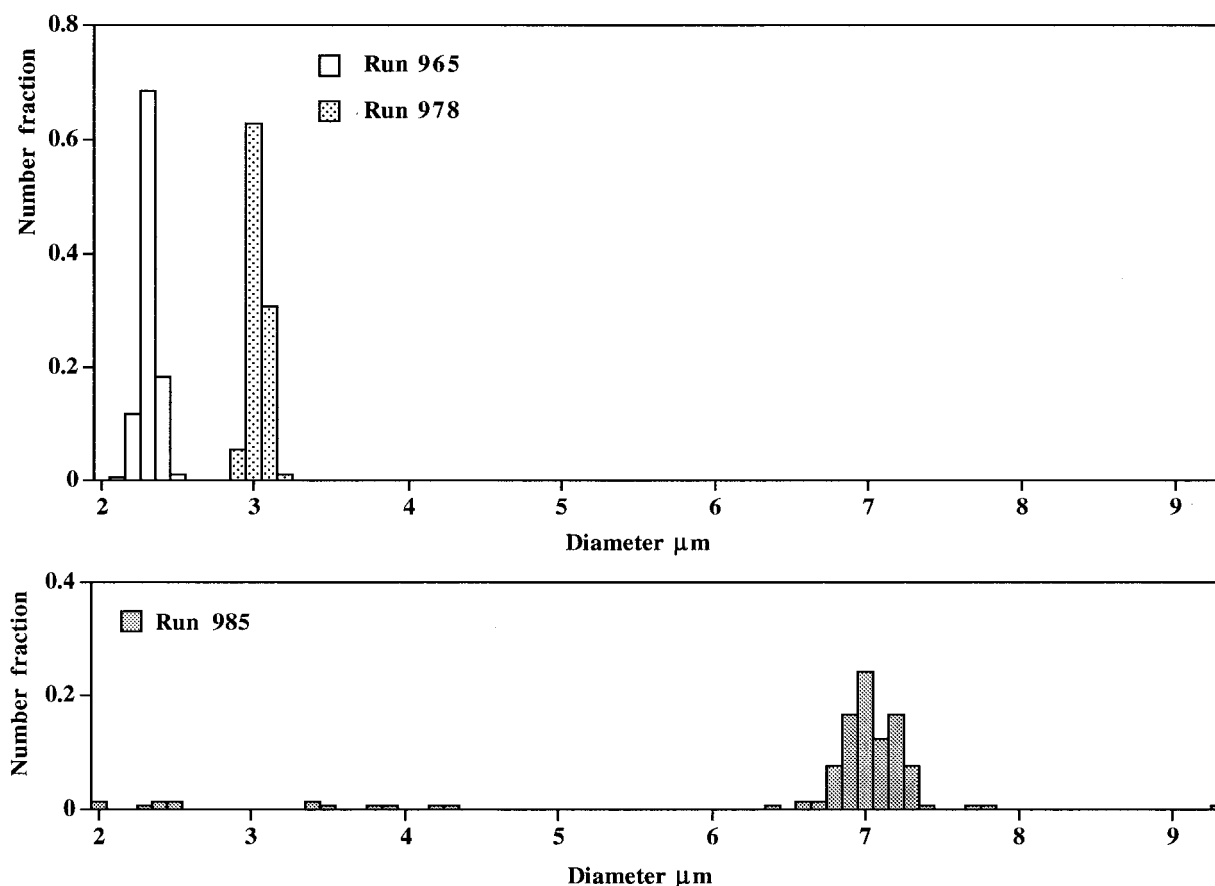
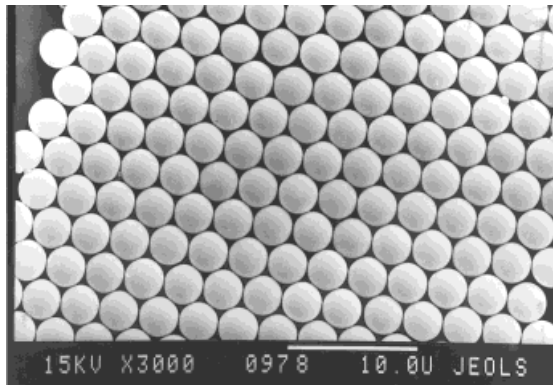


Figure 2 Histograms of particle diameter. Effect of PVP K-30 concentration.



**Run 978 The lowest CV was obtained.  
PVP K-30 9 g.  
dp = 3.08  $\mu\text{m}$ , CV = 1.37%**

**Figure 3** SEM photograph of monosized polymer particles.

neity of the reaction mixture before the nucleation, even though AA is eventually soluble during the heating of the mixture, this may be a probable explanation for the broadening of the size distribution (higher CV).

Comparison between the pairs with a same weight of AA, as discussed in the previous section, implies again that the addition of AA may have obscured the effect of the solvency on the particle size.

#### Effect of Amount of the Other Ingredients

The second part of Table III shows the experimental results with varied amounts of the ingredients other than AA.

Effect of the weight of PVP K-30 on the average size and the distribution is shown in Table III b) and Figure 2. Increased amounts of PVP K-30 improved the monodispersity (smaller CV); however, the average size increased again at the highest concentration of PVP K-30 (9 g). This may be partly due to the presence of BANI-M and AA, their behaviors not being fully understood, and also due to the difficulty of the reproducibility of experiments. A SEM photograph of run 978 having the narrowest size distribution is shown in Figure 3. The coefficient of variation, 1.38%, is equivalent to those monosized spheres produced in the space shuttle by repeated seeded emulsion polymerizations.<sup>13</sup>

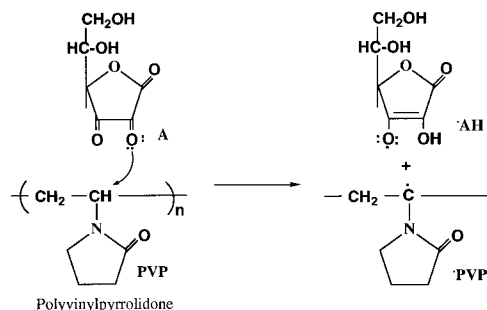
#### Role of AA in the Improvement of Monodispersity

A probable mechanism in which AA plays a vital role for the production of monodisperse spheres will be proposed in the following section.

Hattori et al. reported that the stability of dispersion polymerization of styrene-*co*-divinylbenzene (PS-DVB) improved substantially by sealing a trace amount of oxygen in polymerizing ampoules, and monosized PS-DVB spheres were obtained.<sup>14</sup> They proposed a mechanism that the peroxide formed by the presence of oxygen decomposed, and the radical abstraction of a hydrogen atom bonded to the tertiary carbon atom on the backbone of PVP. Then, the PVP radical initiates the polymerization to form graft copolymers that greatly contribute to the stability and eventual formation of PS-DVB spheres.

As Paine et al.<sup>15</sup> demonstrated by TEM photographs, the formation of graft copolymers between the stabilizer polymer and monomers has been believed to be a vital step to produce a stable dispersion with excellent monodispersity. In our study, we also tried to find out any possible route for a grafting process that involves AA and also BANI-M.

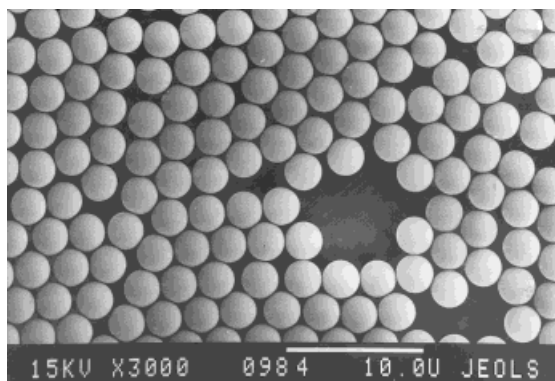
Assuming that the oxidized form of AA takes part in the abstraction of a hydrogen atom from PVP, Scheme 2 can be written,



**Scheme 2**

Experimental evidence of Scheme 2 can be obtained from a SEM photograph of run 984 as shown in Figure 4. No BANI-M was added in the reaction mixture of run 984 in order to investigate the role of AA under the circumstance without BANI-M. As shown in Figure 4, the polymer particles are quite monodisperse, with an average diameter of 2.71  $\mu\text{m}$ , and a respectable CV of 2.44%. It is clear that AA is, by itself, effective in yielding uniform spheres with very narrow size distributions, probably by promoting the grafting of the polymeric stabilizer, PVP, by Scheme 2. Notice





**Run 984 without polyimide prepolymer (BANI-M).**

**dp = 2.71  $\mu\text{m}$ , CV = 2.44%**

**Figure 4** SEM photograph of polymer particles. Absence of polyimide prepolymer (BANI-M) does not affect the monodispersity of spheres.

that the radical  $\cdot\text{AH}$  is still active for further abstraction of a hydrogen atom. However, another possibility, that AA acted as a chain transfer agent, is denied from the measurement of average molecular weight by GPC. A small and sharp peak of the incorporated BANI-M, which is detected at the end of the distribution curve, was excluded from the calculation. The number average molecular weight ( $M_n$ ) and the polydispersity ( $M_w/M_n$ ) of runs 962 and 963, without the addition of AA, were 16,800, 2.72 and 16,300, 3.27, respectively, whereas, runs 965 (1.0 g AA) and 966 (0.5 g AA) yielded 20,300, 3.57 and 19,300, 3.11, respectively.

### Measurement of BANI-M Incorporated in Polymer Particles

The amount of BANI-M, measured either from the peak in the GPC curve or from the spectra of  $^1\text{H-NMR}$ , is shown in Table IV. The values obtained from GPC measurement are larger than those from NMR analysis, probably because the indirect method measures the weight of BANI-M remaining in the mixed solvent. NMR analysis is regarded as being more reliable because the incorporated BANI-M can be measured directly. The theoretical percentage of incorporation is 20% for run 986, and 10% for all the other runs. The attained incorporation is by no means encouraging, only 40 to 45% of incorporation with respect to the theoretical values. Twenty percent of incorporation is desirable for BANI-M to exert adhesion and toughening by crosslinking at a higher temperature. When the composition of the mixed solvent becomes less favorable for BANI-M, it will prefer to be incorporated in the polymer particles as styrene, a good solvent, is converted to PS. If the phase separation between BANI-M and PS is adequately prevented, a higher percentage of the incorporation can be attained. For example, P(styrene-*co*-MMA) spheres crosslinked with ethyleneglycoldimethacrylate were prepared by using the SPG emulsification technique, which contained more than 20% of BANI-M.<sup>16</sup> Modification of the polymerization recipe, in particular combination of monomers as well as of the mixed solvent, is being investigated for further progress on this objective.

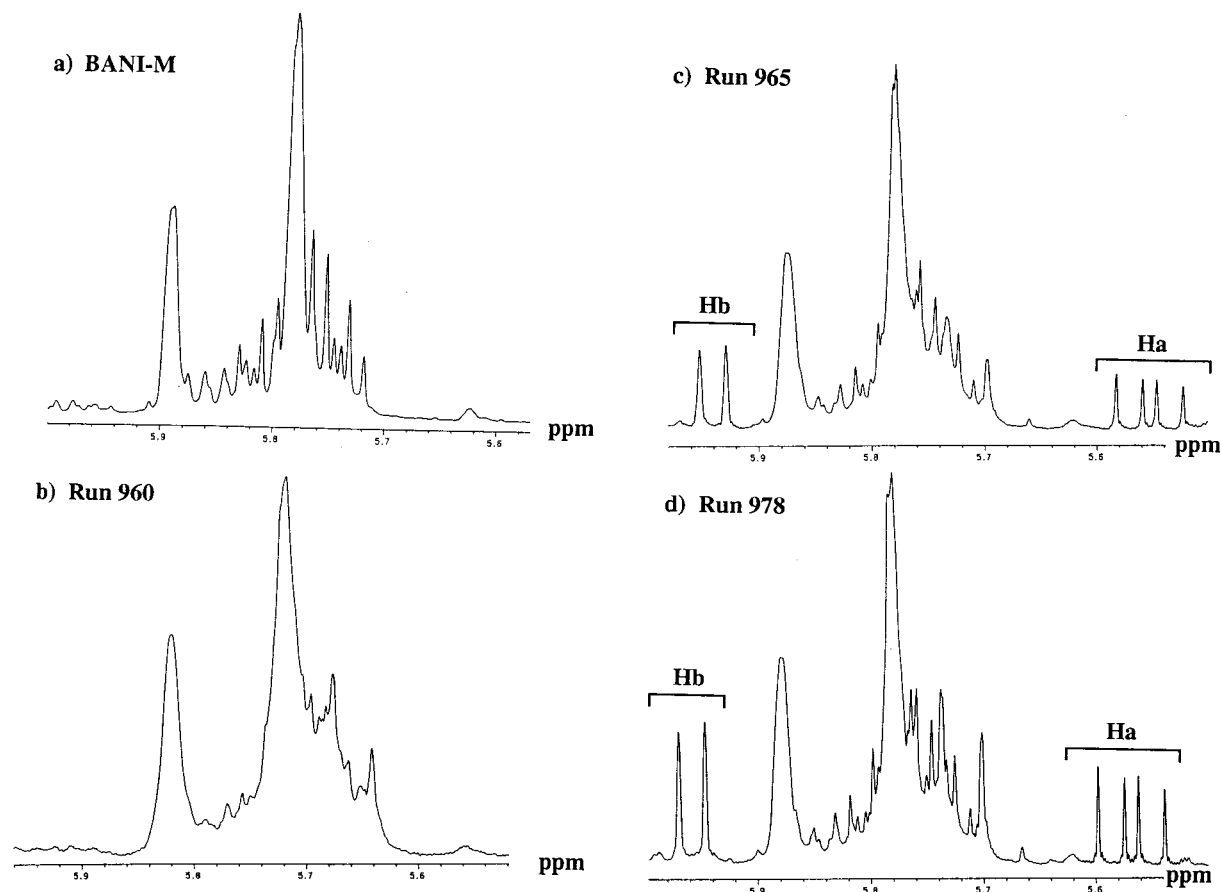
**Table IV Evaluation of BANI-M Incorporation in Polymer Particles**

Run No.	IPA (g)	MeCell (g)	AA (g)	BANI-M (g)	Monomer Conv. (%)	Average Diam. ( $\mu\text{m}$ )	CV (%)	% of BANI-M in Polymer Particles	
								by GPC	by NMR
979	140	35	0.5	5	87.6	2.03	1.88	—	3.87
969	140	35	1	5	89.0	2.76	1.83	4.8	4.26
974 <sup>a</sup>	140	35	1	5	91.8	2.69	16.4	4.9	—
986	140	35	1	10	67.6	4.77	19.0	12.1	9.13
960	150	25	0	5	94.0	5.16	7.24	—	3.80
967	155	20	0.2	5	78.4	2.39	10.3	5.5	—
966	155	20	0.5	5	90.5	1.97	2.85	—	3.20
965	155	20	1	5	90.7	2.31	2.28	—	3.54
985 <sup>b</sup>	155	20	1	5	80.9	6.67	17.5	4.7	—

Other ingredients are those of the standard recipe.

<sup>a</sup> AIBN 1.25 g.

<sup>b</sup> PVP K-30 3 g.



**Figure 5**  $^1\text{H-NMR}$  spectra of vinyl protons in BANI-M. (a) BANI-M, (b) run 960, without the addition of L-ascorbic acid, (c) run 965, (d) run 978. L-Ascorbic acid was added for run 965 and 978.

### Contribution of BANI-M to the Stability Theory

Additional substantial evidence was obtained from  $^1\text{H-NMR}$  spectra of dried polymer particles dissolved in *d*-chloroform, which implied a contribution of BANI-M to the stabilizing mechanism. As shown in Figure 5, new vinyl proton ( $-\text{CH}=\text{CH}-$ ) peaks emerged in those runs [965 and 978 in Fig. 5 (c) and (d)], which revealed a remarkable reduction in CV. New vinyl protons are only likely to be formed from an abstraction of allyl hydrogen from BANI-M, as shown in Scheme 3.

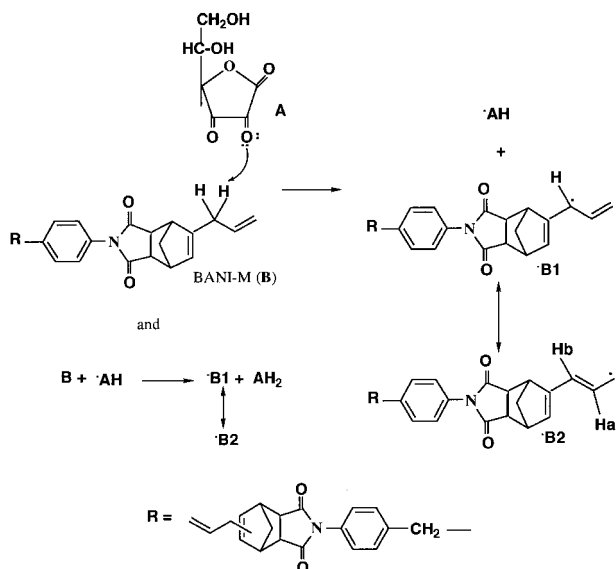
The formation of  $\cdot\text{B2}$  radical leads to two new vinyl protons, and this is reflected in the appearance of four sharp signals in 5.5–5.6 ppm (Ha), and double peaks near to 5.9 ppm (Hb) in the spectra of run 965 and 978. On the contrary, the spectrum of run 960 [Fig. 5 (b)], polymerized without the addition of AA, showed no noticeable peaks in those locations.  $\cdot\text{B2}$  may also abstract a hydrogen atom from PVP, or initiate new chains

or terminate polymeric radicals. Either way, BANI-M can be regarded as cooperating with ascorbic acid to promote Scheme 2 for the improved stabilization of polymer particles.

As the data indicate, all these reactions (Schemes 1 to 3) predominantly take place in the nucleation stage. Notice that even though 1 g of AA was added, run 973 in Table IIa) shows a poor CV of 11.2%. No MeCell was present in this recipe, and while a part of the AA crystals was still undissolved during the heating period, the nucleation started gradually. These overlapping incidents canceled the advantage created by the addition of AA.

### CONCLUSION

Addition of a small amount of L-ascorbic acid in the nonaqueous phase dispersion polymeriza-



tion of styrene yielded remarkably monodisperse polymer particles, the coefficient of variation attained a minimum of 1.38%. Polyimide prepolymer (BANI-M) was incorporated in the polymer particles to utilize them as a potential spacer for liquid crystal displays. In addition to the uniform size, adhesion and crosslinking by heat treatment will provide a strong resilience to the LCD boards. The percentage of the incorporated BANI-M remained 4 to 9% of the particle weight in the present stage. Further improvement of the incorporation can be expected by the modification of polymerization recipe. New experiments will be conducted by reselecting the components and compositions of solvents and monomers.

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## REFERENCES

1. K. E. J. Barrett, Ed., *Dispersion Polymerization in Organic Media*, J. Wiley, New York, 1974.
2. M. D. Croucher and M. A. Winnik, *An Introduction to Polymer Colloids*, F. Candau and R. H. Ottewill, Eds., Kluwer Academic Publishers, Dordrecht, 1990, p. 35.
3. E. D. Sudol, *Polymeric Dispersions: Principles and Applications*, J. M. Asua, Ed., Kluwer Academic Publishers, Dordrecht, 1997, p. 141.
4. C. M. Tseng, Y. Y. Lu, M. S. El-Aasser, and J. W. Vanderhoff, *J. Polym. Sci., Part A: Polym. Chem.*, **24**, 2995 (1986).
5. A. J. Paine and J. McNulty, *J. Polym. Sci., Part A: Polym. Chem.*, **28**, 2569 (1990).
6. C. K. Ober and K. P. Lok, *Macromolecules*, **20**, 268 (1987).
7. A. Tuncell, R. Kahraman, and E. Piskin, *J. Appl. Polym. Sci.*, **50**, 303 (1993).
8. A. J. Paine, *J. Polym. Sci., Part A: Polym. Chem.*, **28**, 2485 (1990).
9. L. Antl, J. W. Goodwin, R. D. Hill, R. H. Ottewill, S. M. Owens, S. Papworth, and J. A. Waters, *Colloid Surf.*, **17**, 67 (1986).
10. K. Takahashi, S. Miyamori, H. Uyama, and H. Kobayashi, *J. Polym. Sci., Part A: Polym. Chem.*, **34**, 175 (1996).
11. K. Takahashi, H. Uyama, and H. Kobayashi, *Preprint of 9th Polymeric Microspheres Symposium*, p. 31, 11/11–13, 1996, Tsukuba University, Tsukuba, Japan.
12. A. Mochizuki, *Preprints of 4th Forum of Polymeric Materials*, p. 125, Tokyo, Japan (1995).
13. J. W. Vanderhoff, M. S. El-Aasser, F. J. Micale, E. D. Sudol, C. M. Tseng, H. R. Sheu, and D. M. Kornfeld, *ACS Polym. Preprint*, **28**, 455 (1986).
14. M. Hattori, E. D. Sudol, and M. S. El-Aasser, *J. Appl. Polym. Sci.*, **50**, 2027 (1993).
15. A. J. Paine, Y. Deslandes, P. Gerroir, and B. Henrissat, *J. Colloid Interface Sci.*, **138**, 170 (1990).
16. A. Matsuda, M. Nagai, G.-H. Ma, and S. Omi, *Preprint of 9th Polymeric Microspheres Symposium*, p. 29, 11/11–13, 1996, Tsukuba University, Tsukuba, Japan.