

# Highly Crosslinked Polymer Particles by Dispersion Polymerization

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## SYNOPSIS

Monodisperse poly(divinylbenzene) and poly(styrene-co-divinylbenzene) particles were prepared in the 0.4–3  $\mu\text{m}$  size range by dispersion polymerization in methanol and methanol/co-solvent mixtures. The effects of polymerization parameters, such as the crosslinking monomer concentration, the co-solvent, and the presence of oxygen were studied. For good colloidal stability, it was necessary to use a relatively large fraction of crosslinking monomer. The initial presence of oxygen was also found to play an important role in determining the colloidal stability during the polymerization. Although the exact mechanism is not certain, it is considered likely that the oxygen promotes the grafting of poly(divinylbenzene) to the polyvinylpyrrolidone (PVP) stabilizer molecules. The growing particles were investigated by electron microscopy. Precipitation of small particles onto the nucleated particles was determined to be the primary mechanism of particle growth. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

There have been strong demands for highly crosslinked fine polymer particles with superior heat resistance and solvent resistance to serve as various spacers, slip property improvers for plastic films, etc. None of the currently available polymer particles are able to satisfactorily fulfill all of the following requirements: strength, heat resistance, solvent resistance, particle size, particle size distribution, surface properties, and productivity.

Extensive research efforts have been devoted to the development of uniform polymer particles by dispersion polymerization.<sup>1–4</sup> But it has been the common result that highly crosslinked polymer particles are difficult to prepare directly because of instability during the dispersion polymerization.<sup>5,6</sup> Recently, we found that highly crosslinked polymer particles can indeed be prepared by dispersion polymerization of polymerizable vinyl monomers in the presence of a dispersion stabilizer and radical po-

lymerization initiator provided that a specific amount of crosslinking vinyl monomer is employed and the reaction is carried out in a particular organic solvent. In this work, we discuss the synthesis of poly(divinylbenzene) particles and copolymer particles of divinylbenzene and styrene by dispersion polymerization using polyvinylpyrrolidone (PVP) as stabilizer with an oil-soluble azo initiator.

## EXPERIMENTAL

Divinylbenzene 55, divinylbenzene HP (Dow Chemical Co.), and styrene (Aldrich) each were washed with 10% sodium hydroxide solution and passed through an activated aluminum oxide column to remove inhibitor before use. The reported compositions of divinylbenzene 55 and divinylbenzene HP are given in Table I. All other materials were used without further purification, including polyvinylpyrrolidone (PVP K-30, MW = 40,000, GAF), 2,2'-azobis(isobutyronitrile) (AIBN, Kodak), and methanol (Purified, J. T. Baker).

All materials used in the standard recipe for the dispersion polymerization of divinylbenzene in methanol are listed in Table II. The amount of each

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**Table I** Composition of Divinylbenzene 55 and Divinylbenzene HP<sup>a</sup>

Component	Divinylbenzene 55	Divinylbenzene HP
Divinylbenzene (meta plus para)	55.5	80.0
Ethylvinylbenzene (meta plus para)	42.0	17.5

<sup>a</sup> Remaining components unreactive.

ingredient was kept constant in all experiments except where indicated. All polymerizations were carried out in 1-oz glass bottles. The ingredients were weighed into bottles and tumbled end-over-end at 40 rpm in a thermostatted bottle polymerizer unit maintained at 70°C. Following polymerization, the polymer particles were examined by scanning electron microscopy (SEM-ETEC Autoscan).

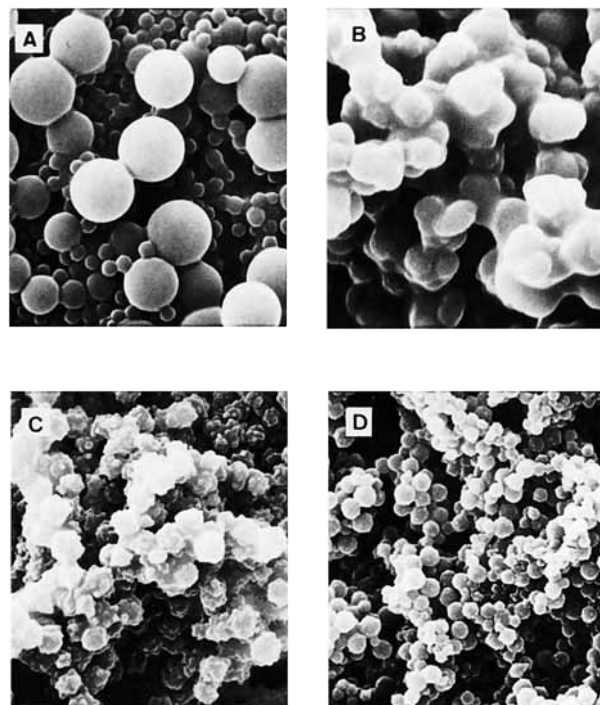
## RESULTS

### Effect of Crosslinking Monomer Concentration

Figures 1 and 2 compare SEM micrographs of eight poly(styrene-co-divinylbenzene) samples prepared in methanol with different amounts of crosslinking monomer, divinylbenzene (DVB). The amounts of DVB herein referred to are the amounts of pure divinylbenzene. DVB concentrations up to 0.55% (based on total monomer weight) produced stable particles with sizes ranging from 1 to 7  $\mu\text{m}$ . When 2 to 11% DVB was used, coagulation of the dispersion resulted. When 22% DVB was used, spherical particles were obtained, but these were flocculated with each other. Further increases in the DVB concentration resulted in the formation of stable dispersions with sizes ranging from 0.4 to 1.2  $\mu\text{m}$ .

**Table II** Standard Recipe for Dispersion Polymerization of Divinylbenzene 55

Ingredient	Weight (gm)
DOW Divinylbenzene 55	1.0
PVP K-30	0.2
AIBN	0.1
Methanol	10.0



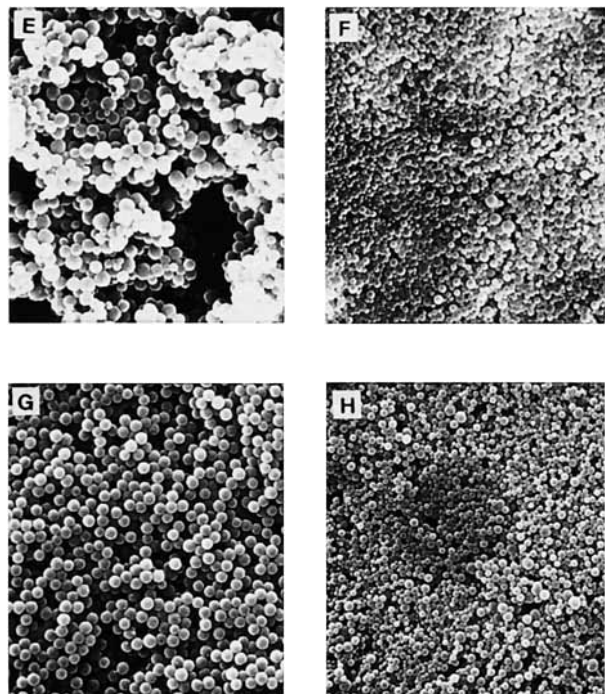
**Figure 1** SEMs of poly(styrene-co-divinylbenzene) particles prepared by dispersion polymerization with various divinylbenzene concentrations: (A) 0.55%; (B) 2%; (C) 5.5%; (D) 11% (based on total monomer weight).

### Effect of Dispersion Medium

In order to control the particle size, the effects of the addition of a good solvent (xylene) and a poor solvent ( $\text{H}_2\text{O}$ ) were investigated. As shown in Figures 3 and 4, the particle size increased with increasing xylene content up to 15% (by weight) followed by a broadening of the particle size distribution. In contrast, the particle size decreased with increasing water content in the recipe, as shown in Figures 5 and 6. Similar trends were noted in the dispersion polymerizations of styrene<sup>5</sup> and methyl methacrylate.<sup>7</sup> These were explained by the effect of the solvency of the media on the critical chain length for precipitation; better solvency led to longer chain lengths and larger particles while shorter critical chain lengths and smaller particles were favored for poorer solvents.

### Effect of Added Air (Oxygen)

Figure 7 compares scanning electron micrographs of the particles resulting from the polymerizations conducted with various amounts of added air. These

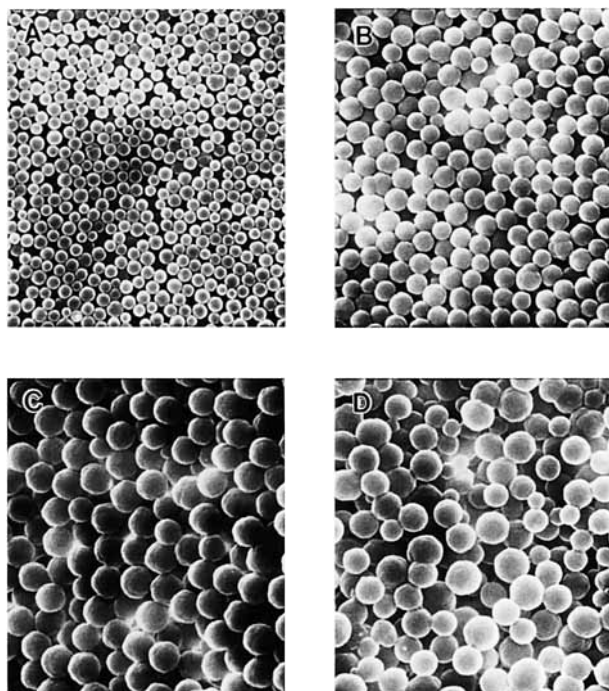


**Figure 2** SEMs of poly(styrene-co-divinylbenzene) particles prepared by dispersion polymerization with various divinylbenzene concentrations: (E) 22%, (F) 33%, (G) 55%; 100% of DOW divinylbenzene 55 (DVB 55%), (H) 80%; 100% of DOW divinylbenzene HP (DVB 80%) (based on total monomer weight).

samples were prepared by first purging the bottles with zero-grade nitrogen (Union Carbide Co.) for 3 min followed by injection of air via syringe through the rubber gasket at room temperature. The polymerization was begun by placing the bottles in the 70°C water bath. When no air was added, coagulation of the dispersion resulted. When 1 mL of air was added, spherical particles were obtained, but these were flocculated with each other. When 4 mL of air was added, a stable dispersion was obtained. The introduction of too much air, for example, 20 mL, resulted in a decrease in particle size and broader particle size distribution. These results will be discussed later.

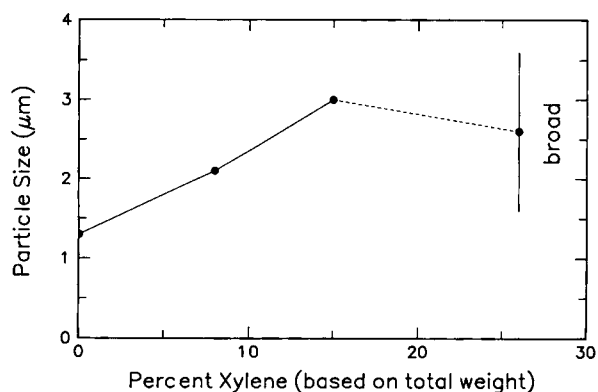
### Observation of Particle Growth

In order to investigate the mechanism of particle formation in the dispersion polymerization of DVB 55, the growing particles were observed at various reaction times by scanning electron microscopy (Fig. 8) and transmission electron microscopy (Fig. 9).

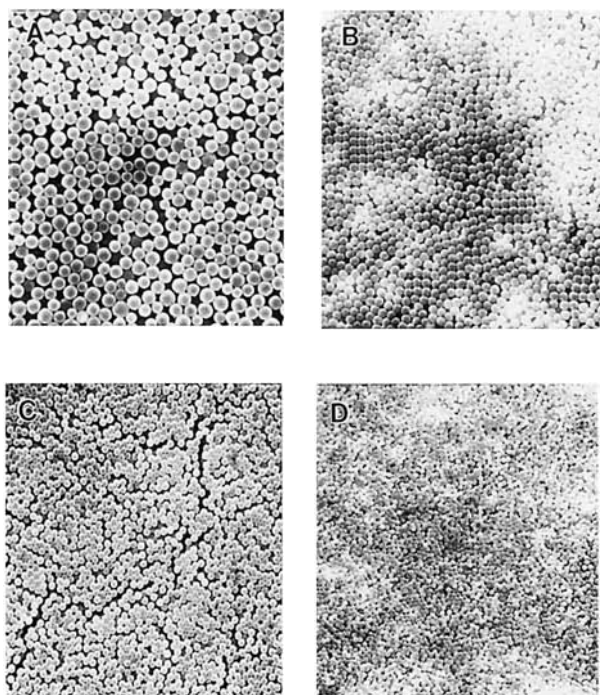


**Figure 3** SEMs of poly(divinylbenzene 55) particles prepared with various amounts of added xylene: (A) 0%; (B) 8%; (C) 15%; and (D) 26%.

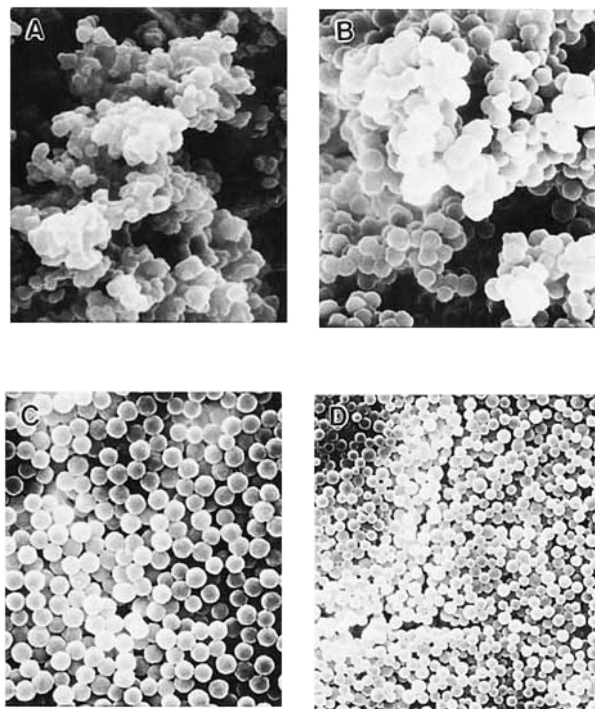
The relative number of particles versus time is shown in Figure 10. These numbers represent the number of particles at any given time divided by the final number of particles in the dispersion as determined by measuring the particle sizes in Figures 8 and 9 and comparing these to the conversions reported in Figure 11. The number of growing particles was constant after 3 h reaction time.



**Figure 4** Effect of the amount of added xylene on the particle size.



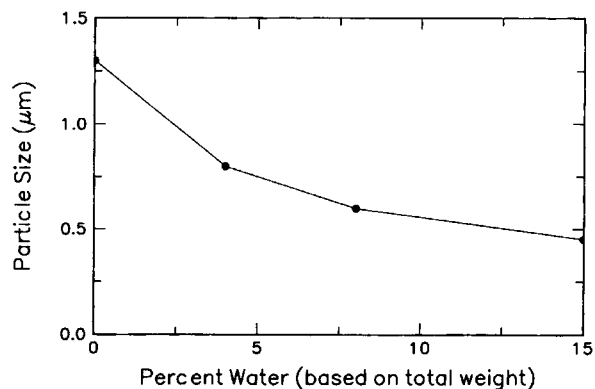
**Figure 5** SEMs of poly(divinylbenzene 55) particles prepared with various amounts of added water: (A) 0%; (B) 4%; (C) 8%; and (D) 15%.



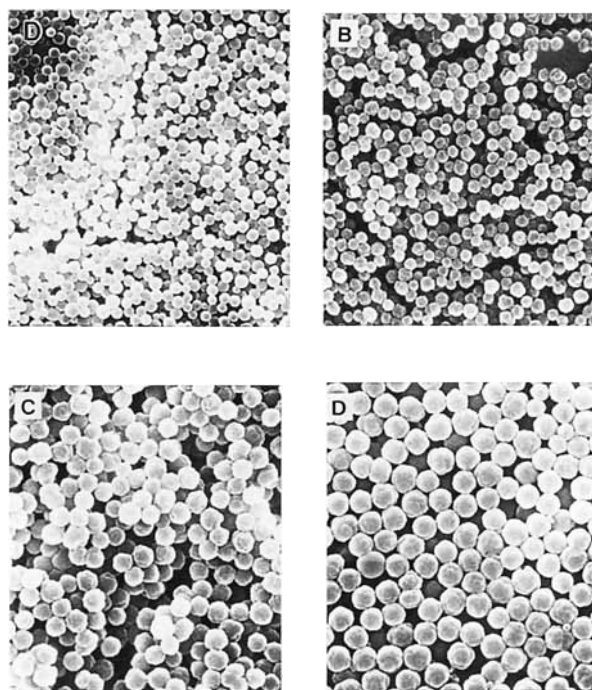
**Figure 7** SEMs of poly(divinylbenzene 55) particles prepared by dispersion polymerization with various amounts of added air: (A) 0 mL; (B) 1 mL; (C) 4 mL; (D) 20 mL (atmospheric pressure, room temperature).

**Swelling Capacity of Highly Crosslinked Polymers**

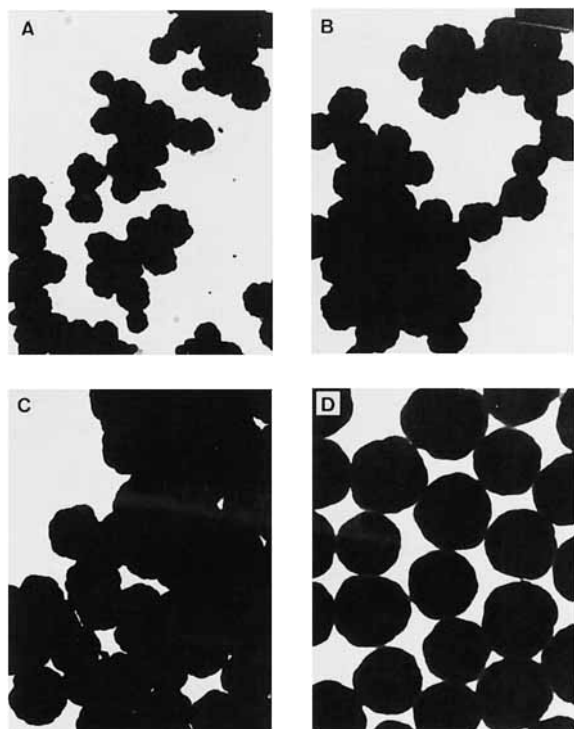
In order to better understand the polymerization mechanism (loci) in these dispersion polymerizations, the swellability of highly crosslinked polymers was measured. Model samples were prepared in glass tubes (diameter = 6 mm) by bulk polymerization at 75°C using the recipe given in Table III. Polymers of 10-mm lengths (removed from the tubes) were



**Figure 6** Effect of the amount of added water on the particle size.



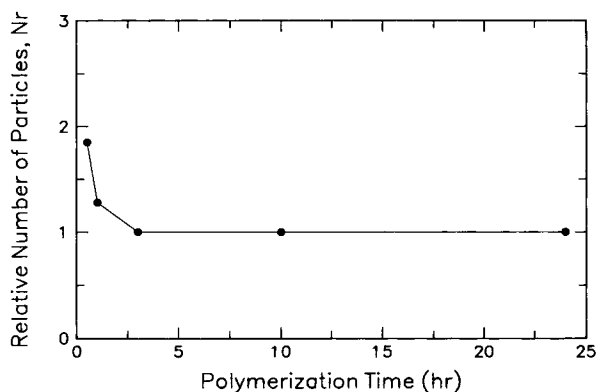
**Figure 8** SEMs of poly(divinylbenzene 55) particles prepared by dispersion polymerization at various reaction times: (A) 0.5 h; (B) 1 h; (C) 3 h; (D) 24 h.



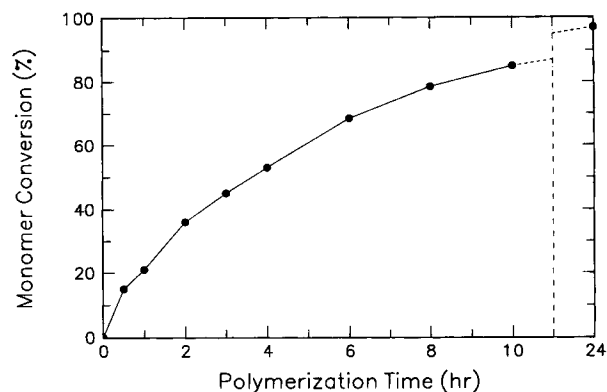
**Figure 9** Transmission electron micrographs of poly(divinylbenzene 55) particles prepared by dispersion polymerization at various reaction times: (A) 0.5 h; (B) 1 h; (C) 3 h; (D) 24 h.

dipped in toluene for 7 days at 23°C. From the change in the weights, the swelling capacities ( $V/V_0$ ) were calculated. The results are shown in Figure 12.

Using more than 22% DVB, the crosslinked polymers could not be swollen with toluene. These re-



**Figure 10** Relative number of particles vs. polymerization time for the dispersion polymerization of divinylbenzene 55.



**Figure 11** Conversion-time curve corresponding to the polymerization producing the particles shown in Figures 8 and 9.

sults suggest that during the dispersion polymerization, the highly crosslinked polymer particles were never swollen by the DVB and styrene monomers. These findings combined with the observation of particle growth, imply that the primary mechanism of particle growth is by the precipitation of polymer onto the nucleated particles. This is also consistent with the polymerization kinetics, which qualitatively follow what would be expected of solution polymerization kinetics (decreasing polymerization rate). These are in contrast to those found in the dispersion polymerization of styrene,<sup>8</sup> the latter showing a significant increase in the rate due to polymerization within the polymer particles.

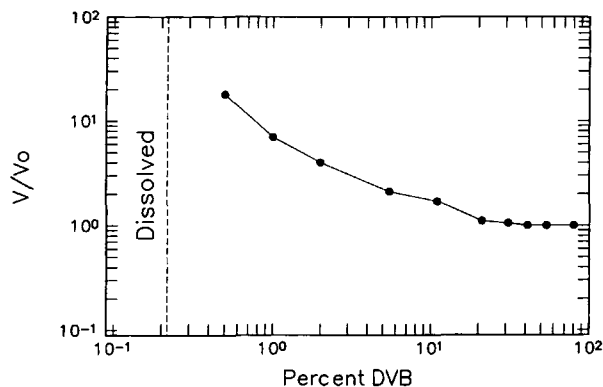
### Heat Resistance

The glass transition temperatures ( $T_g$ ) of the bulk polymer prepared with varying amounts of DVB were measured by differential scanning calorimetry (DSC). The results given in Figure 13 show an increase in  $T_g$  with DVB content in the copolymer. However, above 22% DVB, no  $T_g$  was detectable up

**Table III** Recipe for the Preparation of Highly Crosslinked Polymer Samples at 75°C

Ingredient	Amount (g)
DOW Divinylbenzene 55	0-6
Styrene	6-0
	Total = 6
BPO <sup>a</sup>	0.24

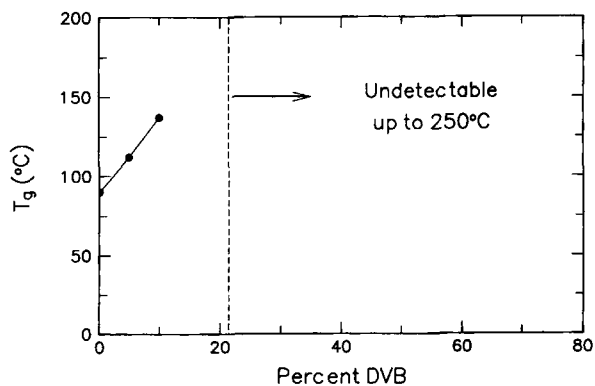
<sup>a</sup> Benzoyl peroxide.



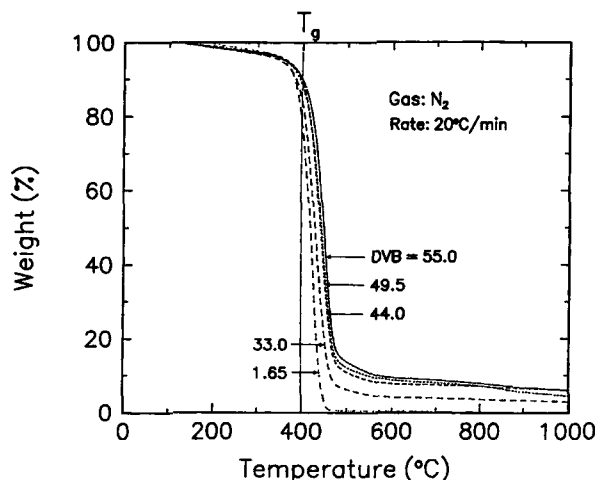
**Figure 12** Log-log plot showing the effect of the added amount of crosslinker (divinylbenzene; DVB) on the swelling capacity of divinylbenzene/styrene copolymers with toluene ( $V_0$  = initial volume,  $V$  = swollen volume).

to 250°C. These results suggest that the wriggling (segmental) motions of the polymer chains were prevented due to the high level of crosslinking even at these high temperatures.

The heat resistance of the polymers was measured by monitoring the weight loss either with increasing temperature or time (at a given temperature) using a thermobalance. Figure 14 shows the pyrolysis curves obtained for the polymers with varying DVB content. These indicate that the higher the DVB content, the better the heat resistance. These results are confirmed in Figure 15, which shows the weight loss obtained when the samples (0.2 g) were held at 300°C for 5 h (under N<sub>2</sub>). As might be expected, higher levels of crosslinking resulted in a better heat resistance.



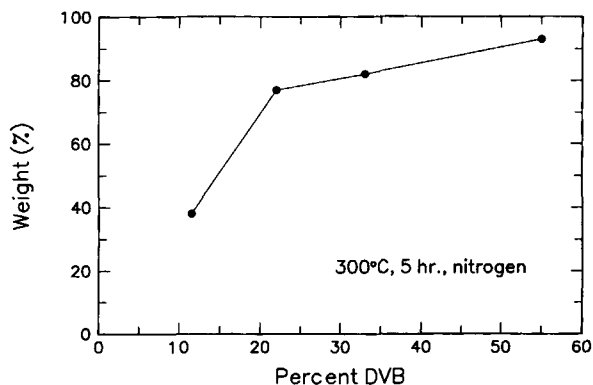
**Figure 13** Effect of DVB content on the glass transition temperature of divinylbenzene/styrene copolymers prepared by bulk polymerization.



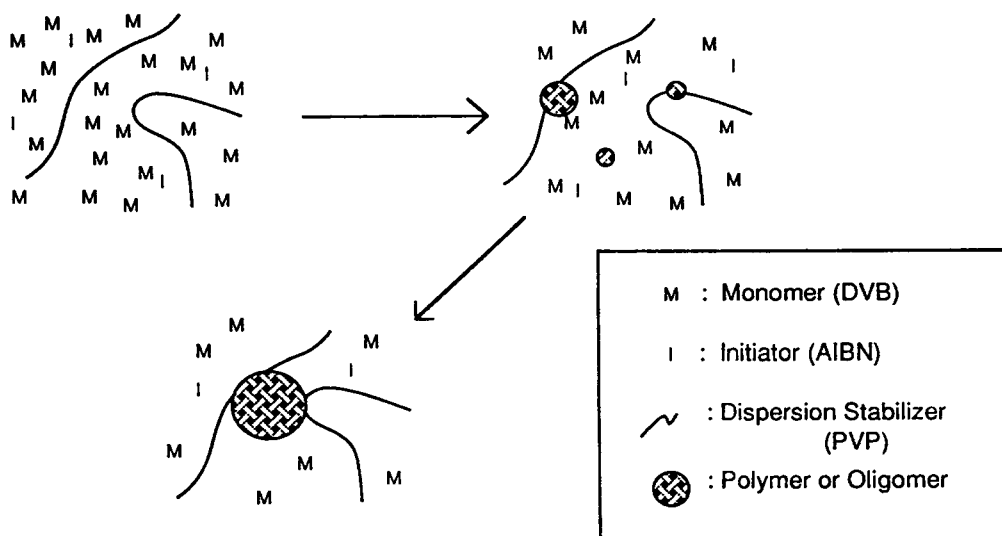
**Figure 14** Effect of DVB content of divinylbenzene/styrene copolymers prepared by bulk polymerization on the pyrolysis curves (changing temperature).

### DISCUSSION

The results obtained with the addition of controlled amounts of air to the reaction bottles suggest that the initial presence of oxygen plays an important role in determining the colloidal stability of the particles formed during the dispersion polymerization of DVB. One possible explanation for this behavior lies in the grafting reactions that can take place during the dispersion polymerization. These reactions are considered to be important in determining the stability, and thus, the particle size formed in these polymerizations. Grafting of DVB to the PVP



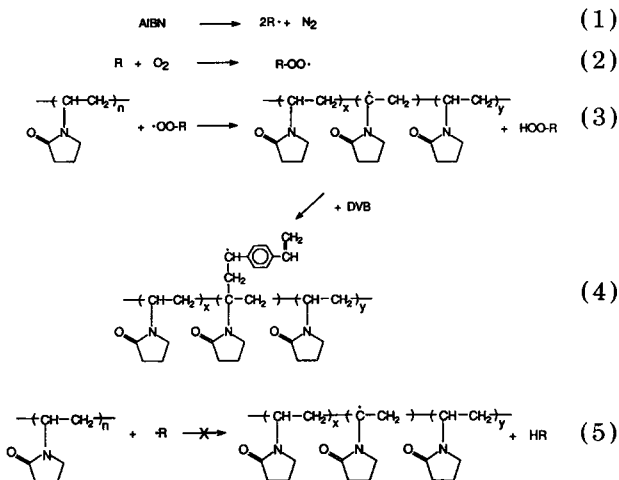
**Figure 15** Effect of DVB content of divinylbenzene/styrene copolymers prepared by bulk polymerization on the heat resistance (wt % of initial sample remaining) at 300°C.



**Figure 16** Mechanism of particle nucleation in the dispersion polymerization of divinylbenzene 55.

(DVB-*g*-PVP) allows bonding of the PVP to the particles, thereby enhancing stability. Oxygen may promote the formation of the DVB-*g*-PVP. The greater the quantity of grafted stabilizer, the greater the number and thus smaller the particles should be as shown by the results in Figure 7 (C and D).

Grafting involves abstraction of hydrogen from the PVP molecule creating a radical site which can add DVB. The following reactions can occur:



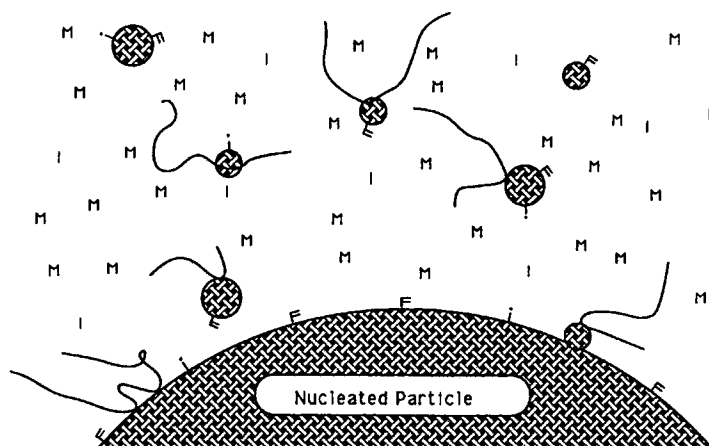
where  $\text{R}\cdot$  represents the free radical formed by initiator decomposition. First, the AIBN is decomposed by heating to yield two radicals and a nitrogen mol-

ecule [reaction (1)]. The oxygen reacts rapidly with a radical to form the peroxy radical [reaction (2)].<sup>9</sup> Reaction (5) is considered to be less likely than reaction (3) because the bond energy of  $\text{H}-\text{O}$  is larger than  $\text{H}-\text{C}$ , and thus,  $\text{ROOH}$  is more stable than  $\text{RH}$  ( $\text{H}-\text{O}$  bond = 110.6 Kcal/mol, calculated from  $\text{H}_2\text{O}$ ;  $\text{H}-\text{C}$  bond = 99.5 Kcal/mol, calculated from  $\text{CH}_4$ ).<sup>10</sup>

During particle nucleation, the precipitation of growing polymer chains occurs when the chain length exceeds some critical value, thereby forming nuclei (see Fig. 16), which can either continue to grow to become mature polymer particles or can aggregate with other nuclei, also forming mature particles.<sup>4</sup> Continued aggregative growth of these mature particles is proposed to occur as shown in Figure 17. This differs from previous models such as for polystyrene or poly(methyl methacrylate) in that growth in these systems is said to occur primarily by polymerization within the particles.<sup>8</sup> This is not likely in these polymerizations because of the nonswellability of the highly crosslinked poly(divinylbenzene 55) particles.

## CONCLUSIONS

Highly crosslinked polymer particles having a comparatively uniform particle size within the size range 0.4–3  $\mu\text{m}$  were prepared directly by dispersion polymerization of divinylbenzene without using seed



**Figure 17** Mechanism of particle growth in the dispersion polymerization of divinylbenzene 55.

particles. For good colloidal stability, it was necessary to use a relatively large amount of crosslinking monomer (> 11%). Precipitation onto the nucleated particles is considered to be the primary mechanism of particle growth. Oxygen plays an important role in determining the colloidal stability in the dispersion polymerization of divinylbenzene 55. It may promote the grafting of poly(divinylbenzene 55) onto the polyvinylpyrrolidone (PVP) stabilizer molecules. The  $T_g$  was increased by increasing the fraction of crosslinking monomer (DVB) in the DVB/styrene bulk polymerizations. No  $T_g$  was detectable up to a limit of 250°C when using more than 22% DVB. The heat resistance was improved by increasing the crosslinking monomer (DVB) to styrene ratio.

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