Dispersion Polymerization of Styrene in Polar Solvents. 6. Influence of Reaction Parameters on Particle Size and Molecular Weight in Poly(*N*-vinylpyrrolidone)-Stabilized Reactions

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ABSTRACT: Polymerization of styrene in alcoholic media in the presence of poly(*N*-vinylpyrrolidone) (PVP) produces monodisperse latex particles from 1 to 18 μm in size. The results are rationalized in the context of a mechanism involving grafting of polystyrene chains to PVP steric stabilizer. Increasing the initial styrene concentration from 5 to 40% by volume increases the particle size obtained. Comparison of this effect to that of added toluene suggests that the primary effect of monomer concentration is a solvent effect: the more soluble the polystyrene is in the reaction medium, the larger the particles. The influence of PVP concentration and molecular weight was found to obey the approximate relationship $d_{50} = 90.4[\mathrm{PVP}]^{-0.31}\mathrm{MW}^{-0.18}$. The power law dependence of diameter on initiator concentration was found to be 0.39, in good agreement with prior work. The addition of a chain-transfer agent produced polydisperse particles with molecular weight dispersities (M_w/M_n) of ca. 100, modifying the power law dependence of size on initiator concentration to a slope of 0.19. A maximum in particle size was found in a series of solvents varying from 80% ethanol/water to ethanol and from methanol to decanol, with 4-μm particles obtained in butanol and pentanol, 1.2-μm particles in 80% ethanol/water, and 1.6-μm particles in decanol. The molecular weights correlated inversely with particle size and could be semiquantitatively rationalized on the basis of the locus of polymerization shifting from particle capture of growing oligomers from the continuous phase in the case of smaller particles to particle capture of dead polymer in the case of large particles.

Polymerization of styrene in polar solvents in the presence of a suitable steric stabilizer such as (hydroxypropyl)cellulose (HPC), poly(acrylic acid), or poly(*N*-vinylpyrrolidone) (PVP) generates latex particles in the 1–18-μm size range.[1–12] Under favorable circumstances, monodisperse particles can be obtained.

The mechanism of dispersion polymerization is complex and poorly understood. Stabilizer, stabilizer concentration, monomer concentration, initiator, and solvent all play important roles in determining the ultimate size and molecular weight of the particles formed. There have been few systematic examinations of the power law dependence of particle size on the reaction parameters. Most of the comprehensive data on the influence of stabilizer concentration and molecular weight on dispersion polymerizations were obtained for systems generating particles of <1 μm in hydrocarbon solvents.[6,13] The most comprehensive study of the PVP-stabilized styrene system to date has been the work of Vanderhoff, El-Aaser, et al.; however, molecular weight data were not reported.[12,14] While we and others have previously studied (hydroxypropyl)cellulose-stabilized polymerization of styrene in alcohols, that system generates monodisperse particles less frequently than the well-behaved PVP-stabilized system.[1–5,8–10]

The objective of the present work is to address the need for a quantitative data base describing the relationships among molecular weight, particle size, and size distribution and their dependence upon reaction parameters for the PVP-stabilized polymerizations of styrene in ethanol. These results will be compared to the predictions of a mechanistic model developed in the accompanying paper.[15]

Experimental Section

Reagents. Poly(*N*-vinylpyrrolidone) (PVP) was obtained in several molecular weights from Polysciences Inc. Except where noted, the 40 000 nominal molecular weight material was employed. Methanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, and decanol were obtained from Aldrich and used as received. Absolute ethanol was obtained from the Liquor Control Board of Ontario. Use of denatured ethanols gave slightly different results. Water was deionized with a Millipore Milli-Q water purification system. Styrene (Aldrich) and AIBN (Polysciences) were used without purification after it was established that purification had no impact on the particle size or molecular weight.[5] Aerosol OT-100 (AOT: bis(2-ethylhexyl) ester of sodium sulfosuccinic acid) was obtained from American Cyanamid, Triton N-57 (nonylphenyl polyether alcohol) was obtained from Rohm and Haas, and both were used as received.

Particle Syntheses. The reactions were conducted in groups of 6–12 sealed 125-mL bottles in a temperature-controlled shaker bath at 70.0 °C as described previously.[5] In this paper, initial concentrations of PVP and optional cosurfactant are reported in units of g L^{-1}, AIBN concentrations in terms of weight percent to monomer, and styrene concentrations as volume percent.

Particle Size. Particle size and size distributions were measured with a 256-channel Coulter Multisizer. This instrument measures the number and individual volume of particles suspended in a mild electrolyte (solid by Coulter as Isoton II) by monitoring the current between two electrodes on either side of a small aperture through which the suspension is forced to flow. Electrical pulses induced by the impedance change as a particle passes through the aperture have an amplitude that is proportional to the particle volume. The pulses are counted and accumulated in 256 size-related channels assigned to some subset of diameters within the 30:1 dynamic range accessible from any one aperture.[16] In the case of monodisperse samples, 50 000–200 000 particles were counted at rates from 200 to 1000 counts per second, with <1% coincidence. A Hewlett-Packard HP 9836A computer interfaced to the Coulter Multisizer was employed to calculate and plot the number, area, and volume distributions and their parameters.

For a consistent set of parameters that describe both monodisperse and polydisperse samples, we define particle size as the d_{50} from the cumulative volume distribution (i.e., half of the mass is in particles smaller than the d_{50}). In a like manner

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the diameters d_{16} and d_{84} can be employed to define a geometric standard deviation (GSD = $(d_{84}/d_{16})^{1/2}$). For a log normal distribution, this would be the true geometric standard deviation (and $d_{50}/d_{16} = d_{84}/d_{50}$ = GSD). In many of our graphical representations of size data, we plot d_{50} in the center of a range from d_{16} to d_{84}. For monodisperse particles (say, GSD < 1.1), the GSD is approximately equal to 1 plus the coefficient of variation (CV). We prefer the GSD over the CV as a measure of dispersity because the GSD is relatively insensitive to the size range selected for the calculation, whereas the CV usually is not.

Several years of experience with the Coulter Multisizer has taught us that (1) the determination of particle size and GSD with this instrument is quite reproducible, (2) the measured particle size agrees well with independent measurement by electron microscopy, and (3) bimodal and multimodal distributions arising from secondary particle formation and large particle coalescence can be readily characterized. However, the noise inherent in the measurement of the electrical pulse amplitude and assignment of the particle to a given channel is ca. 2–4% in diameter, so that for monodisperse particles with GSDs <1.05, the calculated GSD overestimates the true width of the distribution. For purposes of exploring trends in particle size as reaction parameters are varied, this uncertainty in GSD is quite acceptable.

Molecular Weights. Molecular weights were measured with a Hewlett-Packard 1090 GPC using THF as solvent (1.0 mL min^{-1}) and HP PLgel columns. An HP 1037A refractive index detector was calibrated with monodisperse polystyrene standards from Pressure Chemical.

Results and Discussion

Evidence from our previous study of HPC-stabilized dispersion polymerization suggests the following qualitative mechanism.[1,4] The reaction begins as a homogeneous solution process that nucleates quickly. Grafted steric stabilizer is formed and adsorbed onto the growing particles until there is sufficient graft to stabilize them against coalescence. During the balance of the reaction, particles grow by absorption of monomer and subsequent particle phase polymerization, as well as by accretion of dead polymer formed by termination in the continuous phase.

There is no reason to believed the PVP-stabilized reactions behave significantly differently from the aforementioned model for HPC-stabilized reactions. Indeed, we have already shown by transmission electron microscopy that HPC, PVP, and PAA stabilizers all end up on the particle surface in 10–20-nm-thick layers—most probably grafted to the surface.[2] Furthermore, both PVP- and HPC-stabilized dispersion polymerized particles may be dissolved in dioxane and precipitated with methanol to generate new latex particles, stabilized by the graft present on the original particles.[2]

The following discussion rationalizes the observed results in the qualitative context of the foregoing mechanism. A more quantitative approach is advanced in the accompanying paper.[15]

Effect of Initial Styrene Concentration. Figure 1 shows the effect of initial styrene concentration on particle size, size distribution, and molecular weight. The initial styrene concentration is important because the particle count is determined very early in the reaction.[15] For this series of experiments, the PVP concentration was constant at 15.6 g L^{-1}. Monodisperse particles were obtained between 5 and 35% styrene, with size increasing monotonically from 2 to ca. 8 μm. Higher initial styrene concentrations generated polydisperse particles. A bimodal distribution was obtained at 2.5% styrene (potential causes for multimodal size distributions are discussed in the accompanying paper[15]). The molecular weight was roughly constant (except below 5% styrene), with M_w in the long plateau region averaging 123 000 (M_w/M_n was 4 in most cases). The data in Figure 1 show little difference in size, size distribution, or molecular weight of particles made with AOT or Triton N-57 at several concentrations. We conclude that these costabilizers have no effect on the reaction, as discussed in a previous report.[5]

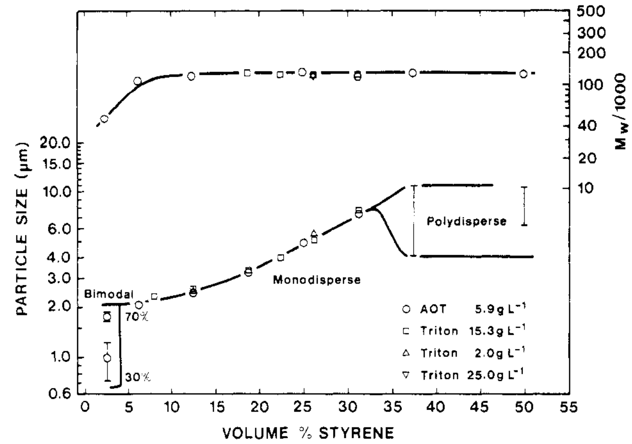

Figure 1. Effect of styrene concentration on size, size distribution, and molecular weight of particles formed in ethanol at constant PVP concentration, but with various amounts of AOT and Triton N-57 ([PVP] = 15.6 g L^{-1}; [AIBN] = 1 wt %). The cluster of data at 26.3% styrene includes Triton concentrations from 2 to 25 g L^{-1} and AOT at 5.9 g L^{-1}. Literature data at 11.3% styrene are from ref 12.

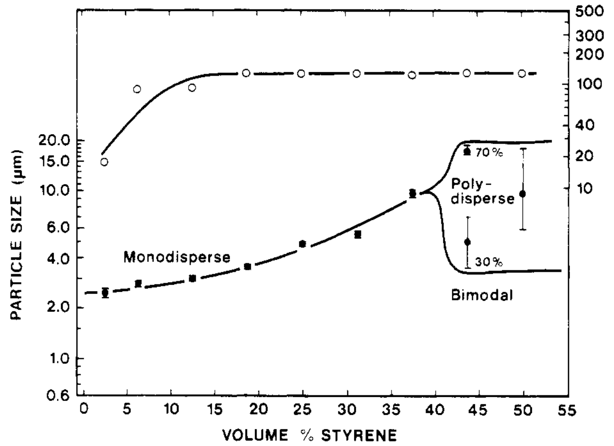

Figure 2. Effect of styrene concentration on size, size distribution, and molecular weight of particles formed in ethanol at a constant ratio of PVP to styrene ([PVP] = 6.6 wt % of styrene (60.0 g of PVP per L of styrene); [AIBN] = 1 wt %; [Triton N-57] = 15.0 g L^{-1}).

The range of styrene concentrations generating monodisperse particles can be extended somewhat by increasing the PVP concentration in proportion to the styrene concentration, as shown in Figure 2. The shapes of the curves are similar to those in Figure 1, but bimodality was avoided as low as 2% styrene. At 44% styrene, however, a bimodal product was obtained, comprised of 70 vol % of 17.4-μm monodisperse particles and 30 vol % of 5-μm polydisperse particles. The onset of secondary particle formation immediately precedes the broad polydisperse result obtained at 50% styrene, indicating that multiple particle populations may have been formed in the case of polydisperse particles.

The shape of the size curves in Figures 1 and 2 is similar to that for particle size as a function of toluene content in methanol/toluene mixtures (Figure 3), although the molecular weights are different in the latter case, decreasing as size increases. Indeed, if the 12.5% sty-

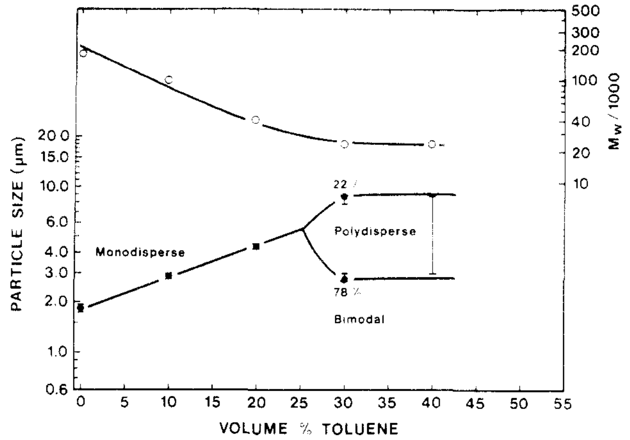

Figure 3. Effect of toluene concentration on size, size distribution, and molecular weight of particles formed in methanol ([PVP] = 15.6 g L^{-1}; [AIBN] = 1 wt %; [Triton N-57] = 15.0 g L^{-1}).

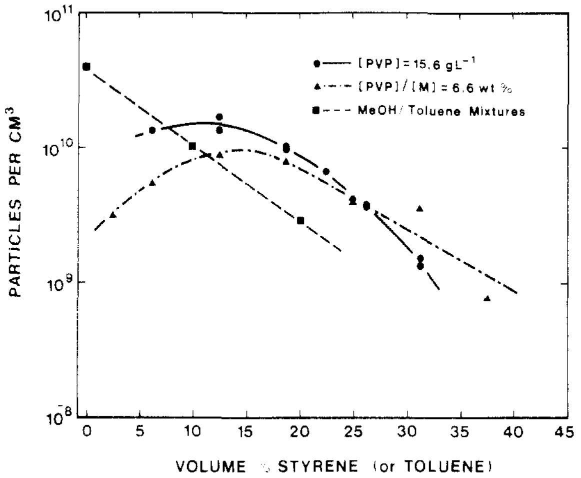

Figure 4. Particle concentrations corresponding to the monodisperse particles in Figures 1–3.

rene content were added to the toluene content, the breakdown from monodisperse to polydisperse particles in Figure 3 would have occurred around 40% aromatic content (60% alcohol)—very similar to Figures 1 and 2. *Therefore, it appears that the major effect of monomer concentration is due to changes in the initial solvency of the reaction medium.*

Further insight into the commonality of Figures 1–3 can be obtained by examining Figure 4, which shows how the particle concentration varies with initial styrene or toluene concentration. Particle counts of 10^9–10^{11} per milliliter were observed for the monodisperse particles. When initial styrene concentration was varied, there was a maximum in particle count between 10 and 15% styrene. At higher initial concentrations, increased solubility of polystyrene permits more coalescence, while at lower concentrations, lower molecular weight may have the same effect. No maximum in particles count was observed as toluene concentration was varied (Figure 4). However, if the 12.5% initial styrene concentration were added to the toluene concentration, the curve would shift to the right and lie almost on top of the solid line. Therefore, all the toluene data are to the right of the expected maximum, and they fit the general trend for the particle concentration to decrease as total styrene plus toluene concentration increases above 10–15%.

Effect of PVP Concentration and Molecular Weight. Figure 5 shows the response of particle size to PVP concentration for three different molecular weights of stabilizer. The slopes of these three lines are around −0.3 and not distinguishably dependent upon molecular weight (Table I). These slopes are substantially smaller than one would expect for the simplest adsorption mechanism of stabilization by PVP, where the amount of surface area stabilized would be proportional to the stabilizer concentration, predicting a slope of −1. Values of such slopes in the literature tend to vary between −0.3 and −1.0 in hydrocarbon solvents.[6,13] In the work most closely related to the present investigation, Almog et al. found almost no effect of PVP concentration on polystyrene particle size over the 15–30 g L^{-1} range in ethanol (a slope of ca. −0.07 can be computed from the three data points in Figure 3 of that paper[11]). However, the PVP molecular weight was not reported, and the reactions were conducted in the presence of a cationic surfactant added in 2/7 the amount of the PVP, so the cited work may not be directly comparable to the present work.

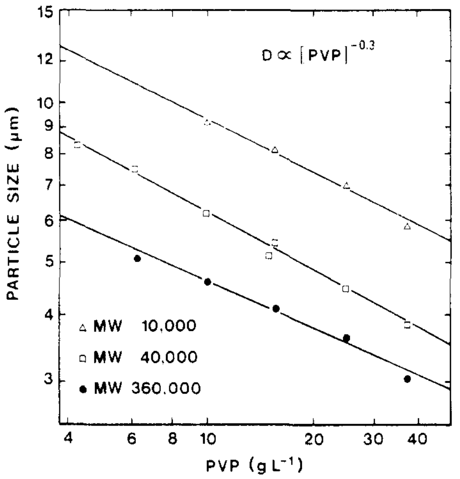

Figure 5. Effect of PVP concentration and molecular weight on particle size in ethanol (26.3% styrene; [Triton N-57] = 15.0 g L^{-1}; [AIBN] = 1 wt %). Results of least-squares analyses are summarized in Table I.

Table I
Results of Least-Squares Fits to d_{50} = exp(A ln [PVP] + B)

	PVP mol wt		
	10 000	40 000	360 000
slope (A)	−0.33 ± 0.03	−0.36 ± 0.01	−0.27 ± 0.02
intercept (B)	2.99 ± 0.07	2.65 ± 0.03	2.15 ± 0.05
r^2	0.99969	0.99964	0.99960
σ_d/μm	0.19	0.13	0.11

With respect to the effect of PVP molecular weight on the reaction, as illustrated in Figure 5, there is little difference in the slope among the molecular weights of PVP used. The full data set was fit to $d = K[\mathrm{PVP}]^a\mathrm{MW}^b$ with exponents a = −0.31 ± 0.03 and b = −0.18 ± 0.015 (K = 90.4; explained variance, r^2 = 0.939; standard deviation, s = 8.4%). This expands upon the preliminary investigation by Vanderhoff and El-Aasser, where it was qualitatively noted that an increase in PVP molecular weight decreased the particle size.[12] For comparison, in heptane polymerization of methyl methacrylate, Susoliak and Barton also found the PMMA particle size to decrease as the overall molecular weight of the triblock isoprene–styrene–isoprene stabilizer increased ($b < 0$).[13] Corner found no noticeable effect on polystyrene particle size as a function of poly(acrylic acid) molecular weight from 3500 to 10^6 ($b = 0$).[7] We also found little effect on PS particle size as HPC molecular weight was varied from 64 000 to 300 000, although slightly larger particles were formed at an intermediate MW of 100 000 ($b \approx 0$).[17]

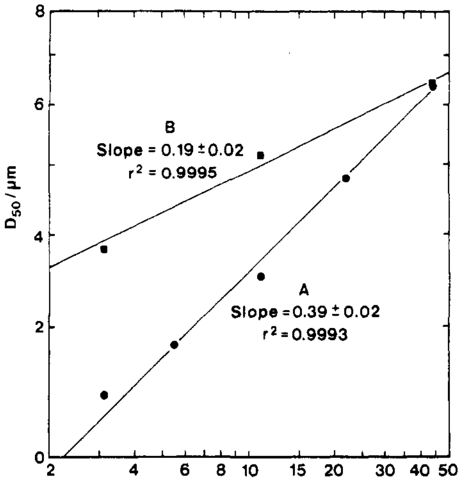

Figure 6. Effect of AIBN concentration on particle size without (line A) and with (line B) 0.36 wt % butanethiol chain-transfer agent (20% styrene with 1% AIBN; [Triton N-57] = 15.6 g L^{-1}; [PVP] = 15.6 g L^{-1}).

The small effect of PVP molecular weight observed here may represent a balance between improved stabilization by longer PVP chains (which might make the exponent b more negative) and poorer adsorption of graft containing longer PVP chains onto the particle surface (which should make the exponent b positive). One reason graft copolymer containing longer PVP chains could be less strongly adsorbed is that the PVP:PS ratio is greater, so it could be more soluble in the continuous phase, particularly at the beginning of the reaction, when a significant amount of styrene is present. If this rationalization were correct, one would not expect identical values of b for different conditions or for different systems. Indeed, examination of the fit residuals shows that log d_{50} is not exactly linear in log MW and that the value $b = -0.18$ cited above is only a first-order approximation.

Effect of Initiator and Chain-Transfer Agent. We found the particle size proportional to AIBN concentration to the 0.39 power (Figure 6). This is in excellent agreement with the earlier work of Vanderhoff and El-Aasser, who obtained an exponent of 0.4 under similar conditions.[12] We believe that larger particles are obtained at higher initiator concentrations because lower molecular weight polystyrene is formed, making the grafted PVP–PS more soluble and less effective as a stabilizer.

In the presence of 0.36 wt % butanethiol chain-transfer agent, polydisperse particles were obtained, and the slope in Figure 6 decreased to 0.19. The GPC chromatograms of these particles contained several broad peaks and the ratio M_w/M_n was around 100. Like the monomer and initiator, the chain-transfer agent may have distributed itself between the continuous and polymer phases, influencing the kinetics in both. Additionally, the lowest molecular weight polystyrene might have been formed at the beginning of the reaction, with the result that the initial PVP–PS graft could be a very poor stabilizer.

Solvent Effects. Figure 7 shows the particle size and molecular weight of a series of particles formed in straight-chain alcoholic solvents from methanol to decanol and in ethanol/water mixtures containing from 80 to 100% ethanol. The particle size increases from ca. 1.16 μm in 80% ethanol/water to 4–4.5 μm in butanol and then decreases to 1.64 μm in decanol. All these particles were monodisperse. This is very similar to data obtained for the HPC-stabilized polymerization of styrene in straight-chain alcohols[4] and indicates the best solubility parameter match to PVP stabilizer occurred in butanol solvent. Interestingly, the molecular weight curve was almost the mirror image of the particle size curve, with M_w = 100 000 from butanol and M_w = 390 000 from 80% ethanol/water. This increased molecular weight in smaller particles is a very common correlation (see below): in this case, $M_w \propto d^{-1.3}$.

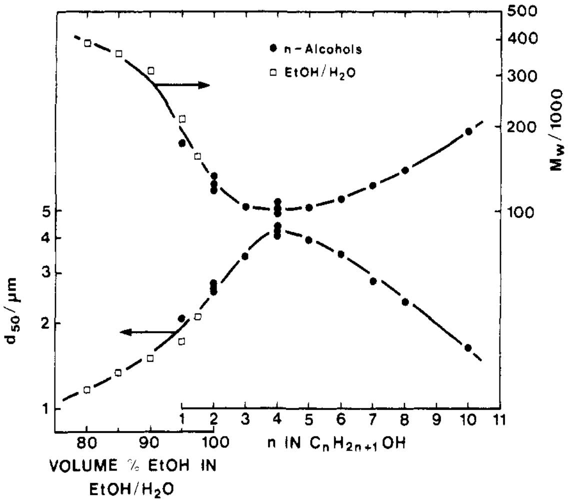

Figure 7. Effect of solvent on the particle size and molecular weight of polystyrene particles ([styrene] = 13.5%, [PVP] = 15.6 g L^{-1}; [AIBN] = 1 wt %; [AOT] = 4.3 g L^{-1}). Note that the solvency scale from methanol to decanol has been arbitrarily extended to the left by using ethanol/water mixtures.

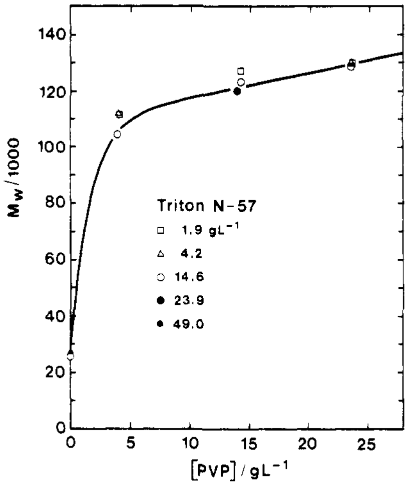

Figure 8. Effect of PVP concentration on particle molecular weight for various levels of added Triton N-57 (26.3% styrene; 1% AIBN). Coagulum was obtained at zero PVP; particle sizes for the other three levels of PVP were 4.4, 5.35, and 8.4 μm, respectively, as [PVP] decreased.

Particle Size/Molecular Weight Inverse Correlation. In most cases of dispersion polymerization, an inverse correlation between particle size and molecular weight is noted: the larger particles have the lowest molecular weights (see, for example, Figures 3, 7, and 8). When particle size is infinite (coagulum formed in the absence of stabilizer), the molecular weight is very close to that expected for solution polymerization (Figure 8). As the particle size decreases, M_w increases. The relative constancy of molecular weight in Figures 1 and 2 appears to represent a balance between this effect and the tendency for solution-based molecular weights to increase as [M] is increased.

The rationale for the higher molecular weight from smaller particles lies in the locus of polymerization, which is in both the solution (continuous) phase and the monomer swollen particle phase. The molecular weights from particle-phase polymerization are usually higher than those from solution polymerization because the termination rate is reduced by the viscosity of the monomer/polymer particle medium (the gel effect[18]). There are two contributors to particle-phase polymerization: that caused by initiation and polymerization inside the particles and that caused by the capture of solution-initiated oligomeric radicals. For the same volume fraction of polymer, the former is not particle size dependent, whereas the latter is very much dependent on particle size. In the case of small particles, a higher proportion of particle-phase polymerization occurs because solution-initiated oligomeric radicals (which might otherwise contribute to solution polymerization) are captured more efficiently by smaller particles because of their greater surface area.

The capture of oligomeric radicals, $\mathrm{R}^\bullet$, can be described by Smoluchowski diffusion kinetics,[19] where the rate of capture = $kN_\mathrm{p}[\mathrm{R}^\bullet]$ and the second-order rate constant, k, is proportional to the product of the sum of diffusion constants times the sum of radii of the particle and radical, respectively: $k \propto (D_\mathrm{p} + D_{\mathrm{R}^\bullet})(r_\mathrm{p} + r_{\mathrm{R}^\bullet})$. Since $D_{\mathrm{R}^\bullet} \gg D_\mathrm{p}$ and $r_\mathrm{p} \gg r_{\mathrm{R}^\bullet}$, $k \propto D_{\mathrm{R}^\bullet} r_\mathrm{p}$. When dispersion polymerizations generating large particles are compared to those generating small particles, the conservation of total mass requires that the number of particles, N_p, be inversely proportional to the particle volume: $N_\mathrm{p} \propto r_\mathrm{p}^{-3}$, with the result that the overall rate of capture becomes inversely proportional to the square of the particle size: rate $\propto r_\mathrm{p}^{-2}$. High capture efficiencies are well-known in the case of emulsion polymerization, where initiation occurs in the water phase and the submicron particles rapidly scavenge the oligomeric radicals before they can terminate in the aqueous phase, resulting in very high molecular weight.[20]

The simple kinetic analysis that follows demonstrates that the crossover from efficient capture of radicals to termination in the continuous phase may occur in the 1–10-μm size range. Ignoring escape of oligomer from the particles, the steady-state condition for oligomer concentration in the continuous phase, $[\mathrm{R}^\bullet]$, is given by eq 1, with terms for initiator decomposition, termination in the continuous phase, and capture by the growing particles, respectively.

$$\mathrm{d}[\mathrm{R}^\bullet]/\mathrm{d}t = 2fk_\mathrm{d}[\mathrm{I}] - 2k_\mathrm{t}[\mathrm{R}^\bullet]^2 - kN_\mathrm{p}[\mathrm{R}^\bullet] = 0 \qquad (1)$$

From eq 1, one can solve for the steady-state concentration of oligomeric radicals (eq 2) and identify the ratio of oligomer termination in the continuous phase to capture (eq 3).

$$[\mathrm{R}^\bullet] = \frac{kN_\mathrm{p}}{4k_\mathrm{t}}\left[\left(1 + \frac{16k_\mathrm{t} fk_\mathrm{d}[\mathrm{I}]}{k^2 N_\mathrm{p}^{\,2}}\right)^{1/2} - 1\right] \qquad (2)$$

$$\frac{\text{rate of termination}}{\text{rate of capture}} = \frac{2k_\mathrm{t}[\mathrm{R}^\bullet]^2}{kN_\mathrm{p}[\mathrm{R}^\bullet]} = \frac{1}{2}\left[\left(1 + \frac{16k_\mathrm{t} fk_\mathrm{d}[\mathrm{I}]}{k^2 N_\mathrm{p}^{\,2}}\right)^{1/2} - 1\right] \qquad (3)$$

Substituting reasonable values for the known parameters from the literature ($k_\mathrm{t} = 6.1 \times 10^7$, $f = 1.0$, $[\mathrm{I}] = 0.015$ mol L^{-1}, $k_\mathrm{d} = 3.2 \times 10^{-7}$),[1,15] the expression for N_p in eq 4 (where d_f is the final diameter and Φ_m is the initial volume fraction of monomer (0.15, for example)), and a reasonable expression for k ($10^9 d$ (in L mol^{-1} s^{-1}), where all diameters are in microns), one obtains eq 5 to relate the instantaneous ratio of continuous-phase termination to capture.

$$N_\mathrm{p} = \frac{6}{\pi d_\mathrm{f}^{\,3}} \times 1000\Phi_\mathrm{m} \times \frac{10^{12}}{6.023 \times 10^{23}} \approx \frac{5 \times 10^{-10}}{d_\mathrm{f}^{\,3}} \quad (\text{in mol L}^{-1}) \qquad (4)$$

$$\frac{\text{rate of termination}}{\text{rate of capture}} = \frac{1}{2}\left[\left(1 + \frac{1100[\mathrm{I}]d_\mathrm{f}^{\,6}}{d^2}\right)^{1/2} - 1\right] \qquad (5)$$

Numerical analysis of eq 5 shows that when 1-μm particles are formed, the vast majority of the oligomeric radicals are captured before terminating in the continuous phase; when 3–4-μm particles are formed, a majority of oligoradicals terminate in the continuous phase; and when 10-μm particles are formed, most of the radicals initiated in the continuous phase terminate there as well. Indeed, in the limit of unstabilized reactions, where one obtains a single polymer lump of essentially infinite particle size, the final molecular weight is often close to that expected for solution polymerization (Figure 8).[1]

In all cases, the partitioning of monomer and initiator permits concurrent particle-phase initiation and polymerization to compete with continuous-phase initiation,[9,14] but, in alcoholic media, there is little thermodynamic bias to drive the monomer or initiator into the particles, and this contribution, while sometimes significant, is not dominant. Thus, *the overall result is that small particles grow by capture of oligomeric radicals from solution (leading to high molecular weight), while large particles grow by capture of dead polymer from solution (of low molecular weight).*

Conclusions

We have examined the influence of the major reaction variables on the size, size distribution, and molecular weight of PVP-stabilized polystyrene particles prepared in alcoholic media. The major effect of monomer concentration appears to be due to changes in the solvency of the reaction medium, since toluene addition gives similar results. The dependence of particle size on PVP concentration and molecular weight was fit to $d = K[\mathrm{PVP}]^a \mathrm{MW}^b$ with exponents $a = -0.31$ and $b = -0.18$. The exponent a is much smaller in magnitude than the value of -1 expected for the simplest adsorption mechanism. The particle size depends on AIBN concentration to the 0.39 power, consistent with the notion that when lower molecular weight polystyrene is formed at higher AIBN concentrations, the grafted PVP–PS is more soluble and, therefore, less effective as a stabilizer. The effect of solvent on these reactions is significant: in a series of *n*-alcohols, the particle size increased from 1.16 μm in 80% ethanol/water to 4–4.5 μm in butanol and then decreased to 1.64 μm decanol, indicating an optimum match to PVP solubility parameters in the C_4–C_5 alcohols. The molecular weight correlated strongly inversely with particle size in these solvents, consistent with significant continuous-phase termination and capture of dead polymer by larger particles.

In the accompanying paper, we propose an integrated model for dispersion polymerization and compare the predicted scaling exponents with those reported herein and in the literature.[15]

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Registry No. PVP, 9003-39-8; polystyrene, 9003-53-6.

Dispersion Polymerization of Styrene in Polar Solvents. 7. A Simple Mechanistic Model To Predict Particle Size

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ABSTRACT: An integrated model for dispersion polymerization is developed to predict particle size from first principles. The key components of this model are a multibin kinetic model for unstabilized particle coalescence, the grafting mechanism of stabilization, and the radius of gyration of the grafted stabilizer chains. A critical point is defined where similar-sized particles stop coalescing with one another because the graft available equals the minimum graft required to stabilize the particles. Examples indicate that the particle count is determined within the first 1% of conversion, in agreement with experiment, and that the critical size particles are larger than 0.1 μm—significantly bigger than nuclei. In cases where full adsorption of graft is likely, absolute prediction of particle size is remarkably consistent with experiment. More generally, however, partial adsorption of graft is likely to affect the predicted scaling of diameter with stabilizer, initiator and monomer concentrations, and stabilizer molecular weight. Above the critical size, the size distribution narrows because the growing particles continue to capture dead polymer formed in solution. Observed loss of monodispersity by stabilization of secondary particles or coalescence of large particles is readily explained with this model. A critical factor influencing the final size distribution is the locus of polymerization and how it changes during the reaction.

During dispersion polymerizations latex particles are formed from an initially homogeneous reaction mixture by polymerization in the presence of a suitable steric stabilizer polymer.[1-17] In hydrocarbon solvents, poly(dimethylsiloxane), poly(isobutylene), poly(12-hydroxystearic acid), and poly(2-ethylhexyl methacrylate) have been employed as stabilizers for polymerization of methyl methacrylate.[7-11] Styrene monomer has been polymerized in alcohols with steric stabilizers such as (hydroxypropyl)cellulose (HPC), poly(acrylic acid) (PAA), or poly(*N*-vinylpyrrolidone) (PVP).[1,4,6,12-17] In favorable circumstances, these particles can have a very narrow, or even monodisperse, size distribution.

Our previous work on the dispersion polymerization of styrene in alcohols had focused primarily on HPC and, more recently, on PVP as steric stabilizer.[1-6] These efforts continued work initiated by Ober, Lok, and Hair (HPC and PAA),[13-15] Almog et al. (PVP and others),[17] and Vanderhoff and El-Aasser et al. (PVP).[16] Although a costabilizer (anionic or nonionic surfactant) was employed with PVP in the investigations by Vanderhoff and El-Aasser, recent evidence suggests that this additive has no influence on the outcome of the reaction in most of the parameter space investigated.[5] The gross features of the HPC- and PVP-stabilized reactions are substantially similar and are comparable to reactions stabilized by PAA, poly(vinyl butyral), and poly(*N*-vinylpyridine).[18]

The preceding work by us and others has shown the mechanism of dispersion polymerization to be complex and poorly understood. It is known that the particle count is fixed very early in the reaction, before 2-5% conversion, and that, at this point, the particles are already monodisperse. Stabilizer, stabilizer concentration, monomer concentration, initiator, and solvent all play important roles in determining the ultimate particle size and molecular weight of the product. To date, mechanistic models of the process are qualitative in nature. Some are sensible on an intuitive basis, but none are quantitatively useful for predicting the particle size and size distribution—properties of the greatest interest.

Three key aspects of any mechanistic model are (1) the mechanism of stabilization, (2) the role of solvent, and (3) the locus of polymerization.

1. For polymerization of styrene in polar solvents stabilized by HPC, we found that the steric stabilizer becomes grafted and ends up on the particle surface.[1-3] Dispersion-polymerized particles may be dissolved in a good solvent such as dioxane and precipitated with a solvent that is poor for polystyrene but good for the steric stabilizer to generate new particles with similar surface-bound HPC.[1-3]

2. The effects of solvent seem to be related to the solubility properties of the grafted stabilizer—the greater its solubility, the larger the particle size.[4] Indeed, the