Colloid Polym Sci 274:1129–1136 (1996)

ORIGINAL CONTRIBUTION

P. Lacroix-Desmazes
A. Guyot

Reactive surfactants in heterophase polymerization

Part IV: Dispersion polymerization of styrene and methyl methacrylate: particle formation and prediction of final size

Received: 15 March 1996
Accepted: 3 June 1996

A series of publication from the EU program "Human Capital and Mobility (CHRX CT 93-0159)

P. Lacroix-Desmazes · Dr. A. Guyot (✉)
LCPP/CNRS-CPE Lyon
BP 2077
69616 Villeurbanne Cedex, France

Abstract The mechanism for the formation of polymer particles in the dispersion polymerization of methyl methacrylate and styrene in alcohol–water mixtures has been investigated. Methacrylic based poly(ethylene oxide) macromonomers and poly(vinylpyrrolidone) have been used as steric stabilizers. Dynamic light scattering as well as transmission electron microscopy have been applied to determine the evolution of the average particle size at the beginning of the polymerization. Stable nuclei from 80 to 400 nm in diameter size were detected. The nucleation process was quite rapid and completed within less than *ca.* 0.1% monomer conversion. The experimental results are compared with those predicted by the multibin kinetics model for coalescence developed by Paine [(1990) Macromolecules 23: 3109].

Key words Dispersion polymerization – steric stabilization – polystyrene – poly(methylmethacrylate) – nonionic macromonomers

Introduction

Dispersion polymerization in polar media is an attractive route to prepare monodisperse polymer particles in the 1–20 μm size range [1–4]. In the early stages of the polymerization, the polymer precipitates from an initially homogeneous reaction mixture containing monomer, initiator, steric stabilizer, and solvents. The particle formation stage is a very important period because it conditions the final particle size as well as the particle size distribution. In dispersion polymerization, the nuclei are thought to be formed by self or aggregative nucleation mechanism [5]. These nuclei aggregate with each other unless a sufficient amount of steric stabilizer is present on their surface. Paine has developed a multibin kinetics model for coalescence among unstabilized particles [6]. This model was used in dispersion polymerization to predict the size of polymer particles stabilized through grafting on hydrophilic polymers such as poly(vinylpyrrolidone) (PVP) [6] as well as through copolymerization with macromonomers such as poly(ethylene oxide) macromonomers [7].

Recent studies have demonstrated the usefulness of macromonomers in dispersion polymerization [8–11]. Indeed, much less macromonomer stabilizer is needed compared to more conventional stabilizers such as PVP. This is due to the fact that most of the macromonomers can be anchored to the surface while only a minor part of the total amount of PVP actually takes part in the stabilization of the particles.

In this paper, we look at the mechanism of formation of poly(methyl methacrylate) and polystyrene particles in dispersion polymerization in polar media. Dynamic Light Scattering (DLS) is a very useful technique because it allows to measure "instantly" colloidal particle sizes. Some attempts for applying this technique in dispersion polymerization were recently made by Shen et al. and it allowed them to detect 20 nanometers unstable nuclei and to follow their aggregation, but they were unable to detect mature particles [12]. Thus, DLS has been used in this study to determine *on line* the evolution of the average particle size at the very beginning of the polymerization. Moreover, Transmission Electron Microscopy (TEM) has been applied in the early stages of the polymerization as well as at the end of the polymerization in order to reinforce the reliability of the data obtained by DLS. These experimental results provide an interesting comparison with the theoretical models developed by Paine [6] and Kawaguchi et al. [7] and contribute to a better understanding of the nucleation process in dispersion polymerization.

Experimental

Materials

Methyl methacrylate (MMA) (Aldrich, 99%) and styrene (S) (Aldrich, 99%) were purified by distillation under reduced pressure. Polyvinylpyrrolidone (PVP-K30) (Aldrich, $M_w = 40\,000$ g/mol), 2,2′-azobis isobutyronitrile (AIBN) (Janssen Chimica, 98%), ethanol–water (95/5 v/v) (EtOH 95°), absolute ethanol (EtOH) and absolute methanol (MeOH) (Docks des alcools) were used as received. A commercially available methoxy poly(ethylene glycol) methacrylate MPEG 2000 ($M_w = 2000$ g/mol) was obtained from BP Chemicals. It was stabilized with hydroquinone monomethyl ether, and was thus purified by precipitation from chloroform in diethyl ether.

Dispersion polymerization in reactor and TEM measurements

Dispersion polymerization was carried out in a double-walled glass reactor (250 mL) fitted with a gas supply (N_2), a condenser and a glass stirrer. In a typical batch process, 36 g of water and 114 g of EtOH were purged with nitrogen during at least 1 h. The mixture was heated at 55 °C at 250 rpm, and 2.359 g of stabilizer was added to the reactor. The polymerization starts with the addition of a solution of 0.337 g of AIBN dissolved in 16.854 g of monomer.

During the polymerization, some samples were taken from the reaction medium. The polymerization was stopped by adding hydroquinone monomethyl ether and the sample was cooled in ice. The monomer conversion was determined from the respective solid contents. In addition, the latices were diluted with EtOH95° and a drop of this dispersion was placed on a Formvar coated electron microscope grid. The grids were placed under vacuum at ambient temperature in order to quickly evaporate the solvents and the unreacted monomer. They were then examined on a Hitashi HU12 Electron Microscope.

Dispersion polymerization and DLS measurements

In a typical run, a solution of 0.786 g of PVP-K30 and 0.112 g of AIBN dissolved in 12 g of water, 38 g of absolute ethanol and 5.618 g of styrene was prepared in a glass bottle which was cooled in ice. About 10 mL of this solution was passed through a 0.2 μm filter into a capped quartz cell which was subsequently used as the reactor for the dispersion polymerization. The solution was purged for a few minutes with nitrogen before being placed in the DLS equipment which was kept at a constant temperature of 55 °C.

The DLS measurements were performed on a Brookhaven Instruments BI8000, with an argon laser source (514 nm) at a fixed angle of 90°, at a power of 2 W. Individual measurements were made every 30 s. The refractive index as well as the viscosity of the medium at 55 °C, needed for the investigation of the DLS data, were measured on an Atago-3T refractometer and an Ubbelohde viscometer, respectively. The density of the medium at 55 °C was measured on a Yokogawa DM61 density meter.

Results and discussion

DLS and TEM measurements

The objective of this section is to correlate the experimental data with the aggregative nucleation model proposed by Paine [6].

The applied conditions for the dispersion polymerization of methyl methacrylate and styrene are summarized in Table 1.

Concerning the DLS measurements, the initial reaction mixture was homogeneous and colloidal species were detected only after a few minutes of reaction. The data

Table 1 Recipes for the dispersion polymerization of methyl methacrylate and styrene[a]

	A	B	C
MMA	5	–	–
Styrene	–	9.94	9.98
PVP-K30	4	1.39	–
MPEG2000	–	–	0.15
Water	–	21.23	16.85
EtOH 95°	–	–	72.82
Absolute EtOH	–	67.24	–
MeOH	90.9	–	–
AIBN	0.1	0.2	0.20
medium refractive index	1.326	1.369	1.366
medium density (g/cm^3)	0.776	0.8297	0.8235
medium viscosity (cP)	0.7527	1.0895	0.8386

[a] $T = 55$ °C; amounts are given in wt %.

after 4 min of analysis were not taken into account due to the occurrence of multiple scattering, which can artificially decrease the measured particle size.

At first, the dispersion polymerization of methyl methacrylate in methanol using PVP-K30 as steric stabilizer has been studied. The conditions were chosen in order to compare our results with those of Shen et al. [12], and the experiment was repeated three times. The evolution of the measured average particle size with time is seen on Fig. 1. A population of very small particles, from 12 to 35 nm in diameter size, was seen throughout the analysis. The other population concerned bigger particles whose average diameter size was roughly stabilized at *ca.* 345 nm. Although the estimation of bimodal particle size distribution from DLS data may be arguable, it has been found that this can be done in favorable conditions. For example, a blend of two model latices (75 nm and 340 nm, with a ratio 1/4 by weight for the small particles to the large particles) has been successfully analyzed with our DLS equipment, giving two peaks at 68 nm and 334 nm [13]. Our results differ from those of Shen et al. who observed an increase in the average diameter of the precipitated species, related to the aggregative mechanism, but did not observe the stabilization of the particle size. Possible differences may come from the induction period and the sensitivity of the apparatus, because the recipe and the experimental conditions were kept similar.

Such experiments were also conducted with styrene in ethanol–water (80/20 v/v) using PVP-K30 or macromonomers as steric stabilizers.

As seen on Fig. 2, in the case of PVP-K30, the experiment was repeated two times with a good reproducibility. Particles as small as 12 nm in diameter were sparingly detected, and the average particle size of the bigger population was stabilized at *ca.* 92 nm, which is a lower value than for the poly(methylmethacrylate) particles using the same stabilizer. When the small particles were not detected, the average value of the particle size distribution was close to the average particle size of the bigger population.

Using MPEG2000 macromonomer as the steric stabilizer precursor, the DLS measurements were conducted three times with a poorer reproducibility than for the PVP experiment (Fig. 3). Small particles of about 11 nm were sparingly detected, and the average diameter size of the bigger population was stabilized at *ca.* 88 nm, which is in the same range as for the polystyrene particles using PVP-K30 as stabilizer.

These results revealed some important information. The colloidal species appeared suddenly and their size is as small as about 10–20 nm. The aggregation of these unstable nuclei is very fast, leading to particles greater than 300 nm and 80 nm for poly(methyl methacrylate) and polystyrene respectively within a few seconds. The

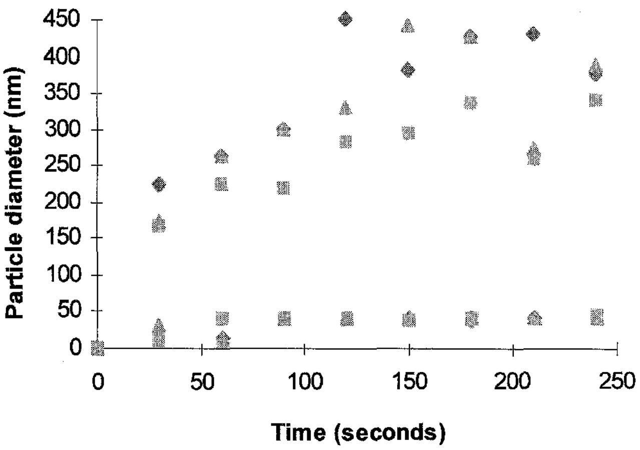

Fig. 1 DLS measurements for the dispersion polymerization of methyl methacrylate (type A); ■: run 1; ▲: run 2; ◆: run 3

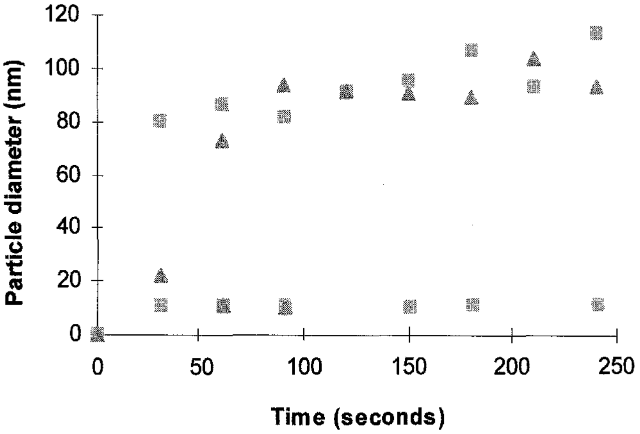

Fig. 2 DLS measurements for the dispersion polymerization of styrene (type B); ■: run 1; ▲: run 2

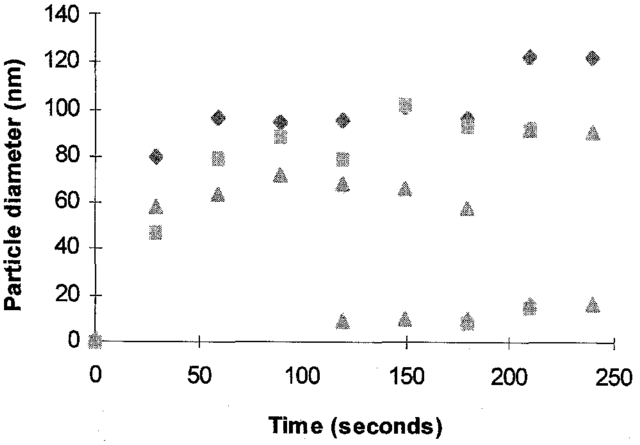

Fig. 3 DLS measurements for the dispersion polymerization of styrene (type C); ■: run 1; ▲: run 2; ◆: run 3

measured average particle size is quickly stabilized at a value which would correspond to the diameter size of the primary mature particles.

An experiment, which was conducted in a glass reactor, has been followed by TEM analysis in order to reinforce the previous results obtained by DLS. The preparation of the grids was very difficult, especially for those at the very beginning of the polymerization, due to the low conversion of monomer and the relative high poly(ethylene oxide) content of the samples. Although the grids were placed under vacuum to quickly evaporate the solvents and the unreacted monomer, we have not been able to prevent the particles from partially coalescing. Nevertheless, the obtained photographs of the samples are of great interest (Fig. 4). Indeed, attributing the smallest particle size observed on these photographs to the primary mature particles, it leads to an estimation of the critical particle size. Here, the critical particle size is defined, according to the mechanistic model of Paine, as the average diameter size of the particles when sufficient stabilizer is produced so that homocoagulation (coagulation of same-size particles) is inhibited and only heterocoagulation (coagulation of small particles with larger mature particles) can continue [6].

The results are in relatively good agreement with the DLS measurements (Table 2). At the critical point, the particle size distribution is thought to be quite large (the geometric standard deviation = GSD = $(d_{84}/d_{16})^{1/2}$ is about 1.5); but after the critical point, the particle number should remain constant and the simulation developed by Paine showed that a monodisperse size distribution should evolve (GSD < 1.1) [6]. This was confirmed by TEM analysis of samples at higher conversion which indicates that the total particle number remained nearly constant and that monodisperse particles were produced (Table 2 and Fig. 5).

Fig. 4 TEM photographs of polystyrene particles prepared by dispersion polymerization (type C): sample n°1, $t = 4$ mn of polymerization (see Table 2)

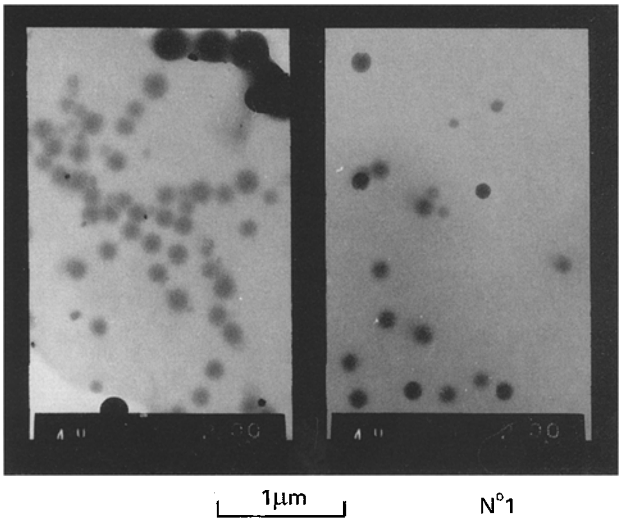

Table 2 DLS and TEM measurements of particle size

Sample N°	Styrene conversion[a] (%)	D_n (nm) (TEM) [D_{DLS}]	Number of Particles (per mL)
1	< 0.15	123 [70–120]	–
2	< 0.15	128	–
3	0.15	151	6.86×10^{10}
4	0.50	222	7.03×10^{10}
5	1.59	314	7.91×10^{10}
6	98	1333	6.38×10^{10}

[a] by gravimetry.

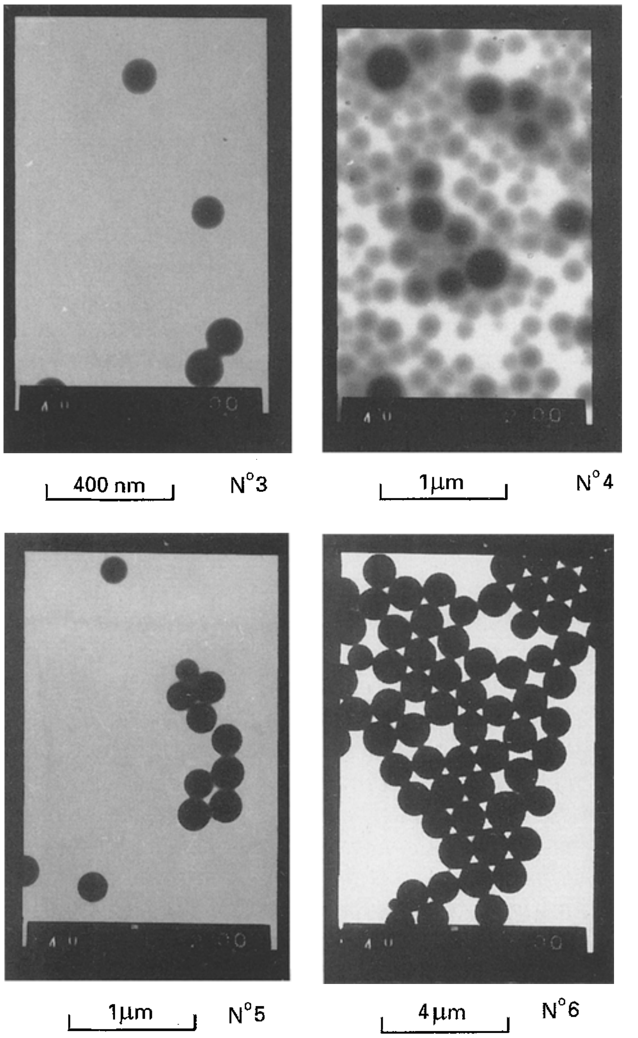

Fig. 5 TEM photographs of polystyrene particles prepared by dispersion polymerization (type C): samples n°3, 4, 5 and 6 (see Table 2)

Thus, all these results are consistent with the model of particle formation proposed by Paine [6] and originally derived from the homogeneous nucleation theory of Fitch and Tsai [14]. It can be summarized as follows: 1) Polymers and graft stabilizer are formed from an initial reaction mixture; 2) Polymers and graft stabilizer with a molecular weight larger than a certain critical value precipitate and coagulate to form nuclei; 3) These nuclei aggregate until enough stabilizer is present at the surface of the particles; 4) This point is designed as the critical point after which the particle number remains constant (in favorable conditions, i.e., neither lack or excess of stabilizer produced during the entire polymerization) and the particle size distribution sharpens to produce monodisperse particles.

Comparison with the predictive models

In the preceding section, we have checked the reliability of the aggregative model in a qualitative way. Now, we will try to test this model in a more quantitative way, comparing the values of the critical and final particle size predicted by the model to those obtained in our experiments.

Theoretical background

The fundamental relation for the model of Paine [6] is expressed in the following equation

$$d_{50}^3 = 0.386 \frac{6\, MW_s (CL)}{\pi \rho N_A} k_1 k_2 t^2 , \tag{1}$$

where d_{50} is the volume median diameter (in cm^3), MW_s is the molar weight of the monomer (in g · mol^{-1}), (CL) is the chain length, ρ is the density of the polymer (in g · cm^{-3}), N_A is Avogadro's number, k_1 is a pseudo-zero-order rate of dead chain generation (in mol · L^{-1} · s^{-1}), and k_2 is a diffusion-controlled rate constant for coalescence of similar-sized particles (in L · mol^{-1} · s^{-1}).

Paine and Kawaguchi did not take into account the effect of transfer to solvent in their calculation, assuming negligible chain transfer [6, 7]. This is arguable because methanol, and to a greater extent ethanol, are known to have non negligible transfer constants. The usual relations for the rate of dead chain generation (Eq. (2)) and chain length (Eq. (3)) show that both k_1 and (CL) are sensitive to chain transfer (see the Glossary Notation at the end of this paper).

$$k_1 = \frac{2fk_d[I]}{(1+a)} + C_{SS} k_p [S] \left(\frac{2fk_d[I]}{k_t}\right)^{1/2} \tag{2}$$

$$CL = \left[\frac{(2fk_d[I]\,k_t)^{1/2}}{(1+a)\,k_p[M]} + \frac{C_{SS}[S]}{[M]}\right]^{-1} . \tag{3}$$

However, one can see that the mean volume diameter of the particles given by Eq. (1) is actually independent of chain transfer as well as of the termination mode because the product (CL) · k_1 *remains unchanged* (Eq. (4)).

$$(\mathrm{CL}) \cdot k_1 = k_p [M] \left(\frac{2fk_d[I]}{k_t}\right)^{1/2} . \tag{4}$$

Converting Eq. (1) from time base to conversion base by using Eq. (5), one can obtain Eq. (6):

$$\theta = k_p t \left(\frac{2fk_d[I]}{k_t}\right)^{1/2} \quad (\theta \ll 1) \tag{5}$$

$$d_{50}^3 = \frac{0.386 (CL)\, 3\, MW_s k_1 k_2 \theta^2 k_t}{\pi \rho N_A k_p^2 f k_d [I]} . \tag{6}$$

Then, we can determine the number of particles at any conversion (Eq. (8)) by substitution from Eq. (7):

$$N_p \frac{\pi d_{50}^3}{6} = \frac{\theta [M]\, MW_S}{\rho} \tag{7}$$

$$N_p = \frac{2 N_A k_p^2 [M] f k_d [I]}{0.386 (CL)\, \theta k_1 k_2 k_t} . \tag{8}$$

Grafting through chain transfer to polymer (model I)

As detailed by Paine [6], the graft available and the graft required are given by Eq. (9a) and Eq. (10) respectively:

$$\text{graft available} = C_{SP} [P]\, \theta N_A \tag{9a}$$

$$\text{graft required} = N_p \pi d_{50}^2 Q_{\min} = \frac{6\theta [M]\, MW_s Q_{\min}}{\rho d_{50}} . \tag{10}$$

The critical diameter is reached when graft available = graft required, leading to Eq. (11a):

$$d_{\mathrm{crit}} = d_{50} = \frac{6 [M]\, MW_s Q_{\min}}{\rho C_{SP} [P] N_A} . \tag{11a}$$

Applying Eq. (6) at the critical point in order to determine the critical conversion (Eq. (12)) and assuming that the number of particles remains constant after this point (Eq. (13)), one can predict the final particle size (Eq. (14a)):

$$\theta_{\mathrm{crit}} = d_{\mathrm{crit}}^{3/2} k_p \left(\frac{\pi \rho N_A f k_d [I]}{0.386 (CL)\, 3\, MW_s k_1 k_2 k_t}\right) \tag{12}$$

$$d_f^3 = \frac{d_{\mathrm{crit}}^3}{\theta_{\mathrm{crit}}} \tag{13}$$

$$d_f = \left(\frac{6\,MW_s}{\rho N_A}\right)^{2/3} \left(\frac{Q_{\min}[M]}{C_{SP}[P]}\right)^{1/2} \left(\frac{1}{k_p}\right)^{1/3} \times \left(\frac{0.386\,(CL)\,k_1 k_2 k_t}{2\pi f k_d [I]}\right)^{1/6}. \qquad (14a)$$

Moreover, an expression for $Q_{\min}$, which differs a little from the relation initially suggested by Paine, has been proposed by Kawaguchi, considering the critical surface S_{crit} as the surface covered by a random coil consisting in a stabilizer chain affixed on the surface of a particle [7]:

$$Q_{\min} = \frac{1}{S_{\text{crit}}} = \frac{3}{(5\pi R_g^2)} \qquad (15)$$

with,

$$R_g = A(0.75\,M_w)^b \qquad (16a)$$

where the coefficient 0.75 is to take into account the random point of grafting along the stabilizer chain [6].

Grafting through copolymerization with a macromonomer (model II)

Assuming that $[D] \ll r_1[M]$ and $r_2[D] \ll [M]$, and providing the copolymerization takes place mainly in solution in the early stages of the polymerization ($\theta \ll 1$), the usual equations of copolymerization lead to Eq. (17):

$$\theta_D = 1 - (1-\theta)^{1/r1} \cong \frac{\theta}{r_1}. \qquad (17)$$

The graft available is then determined by Eq. (9b):

$$\text{graft available} = \theta_D [D] N_A \cong \frac{[D] N_A \theta}{r_1}. \qquad (9b)$$

The equality between graft available (Eq. (9b)) and graft required (Eq. (10)), at the critical point, leads to Eq. (11b):

$$d_{\text{crit}} = d_{50} = \frac{6\,[M]\,MW_s\,Q_{\min}\,r_1}{\rho\,[D]\,N_A}. \qquad (11b)$$

Finally, one can also predict the final particle size (Eq. (14b)):

$$d_f = \left(\frac{6\,MW_s}{\rho N_A}\right)^{2/3} \left(\frac{Q_{\min}[M]\,r_1}{[D]}\right)^{1/2} \left(\frac{1}{k_p}\right)^{1/3} \times \left(\frac{0.386\,(CL)\,k_1 k_2 k_t}{2\pi f k_d [I]}\right)^{1/6}. \qquad (14b)$$

The radius of gyration of the stabilizing PEO chain being determined by:

$$R_g = A(M_w)^b. \qquad (16b)$$

Prediction of absolute particle size

The values used for the calculation at $T = 55\,^\circ\text{C}$ are the following:

Relative to styrene: $MW_s = 104.15$ g/mol, $\rho = 1.05$ g/cm^3, $k_t = 6.8 \times 10^7$ L/mol/s, $k_p = 286$ L/mol/s [15, 16]; methyl methacrylate: $MW_s = 100.12$ g/mol, $\rho = 1.19$ g/cm^3, $k_t = 2.47 \times 10^7$ L/mol/s, $k_p = 734$ L/mol/s [15, 16]; AIBN: $f = 1$, $k_d = 4.79 \times 10^{-6}\,\text{s}^{-1}$ [15]; PVP-K30: $M_w = 40\,000$ g/mol, $A = 5.3 \times 10^{-8}$, $b = 0.32$ [17]; MPEG2000: $M_w = 2344$ g/mol, $A = 1.6 \times 10^{-8}$, $b = 0.585$ [18], $r_1 = 1.1$ [19]; diffusion: $k_2 = 1 \times 10^9$ L/mol/s [6].

Using the above equations, the predictive results concerning the final particle size, the critical particle diameter, the critical conversion, and the duration of the nucleation process are presented in Table 3. They can thus be compared to the experimental results.

It can be seen that the models provide predictive data which are in quite good agreement with the experimental results in the case of polystyrene but deviate strongly in the case of poly(methyl methacrylate). Some assumptions of the models can be discussed to explain such a deviation. The models do not take into account the fraction of stabilizer effectively present at the surface of the particles. Indeed, the graft stabilizer produced in situ can either remain soluble in the serum or buried in the particles. The efficiency of the graft stabilizer depends on several factors:

Table 3 Comparison between the predictive models and the experimental results

	MMA/PVP		S/PVP		S/MPEG2000	
	model I	experiment	model I	experiment	model II	experiment
d_f (nm)	770	6578[a]	1208	833[b]	1703	1352[c]
d_w/d_n		< 1.1		1.021		1.014
d_{crit} (nm)	54	345	70	92	139	88
θ_{crit} (%)	0.034	0.013[d]	0.019	0.126[d]	0.054	0.028[d]
t_{crit} (s)	11	4[e]	18	117[e]	50	26[e]

a: 75% monomer conversion; b: 88% monomer conversion; c: 98% monomer conversion; d: calculated with Eq. 7; e: calculated with Eq. 5.

1) the relative molecular weight of the graft: the higher the molecular weight of the graft, the higher the probability of adsorption on the particles (note that this factor is greatly dependent on the termination mode and on the occurrence of chain transfer to solvent (Eq. (3)); 2) the solubility parameter of the serum: the greater the difference of the solubility between the graft and the serum, the higher the probability of adsorption on the particle; 3) the compatibility between the stabilizing polymer and the core polymer: the lower compatibility between the stabilizing polymer and the core polymer, the lower the risk of burying the graft stabilizer; 4) the proximity of the polymerization temperature from the glass transition temperature T_g of the polymer particles: the higher the T_g of the polymer particles, the lower the possibility of the stabilizing polymer chains to reorient on the surface of the particles. In the case of the polymerization of methyl methacrylate in methanol, the swelling of the particles by monomer and solvent should be very limited, so that the T_g of the particles could be higher than the polymerization temperature. Moreover, the compatibility of PVP with PMMA is thought to be higher than that with polystyrene. It results that the efficiency of the graft-PVP stabilizer should be low in the polymerization of methyl methacrylate in methanol. We have introduced the efficiency of the graft-PMMA stabilizer in the model through a correcting factor f_s (Eq. (9′a)):

$$\text{graft available} = f_s\, C_{SP}\, [P]\, \theta\, N_A \qquad (9'a)$$

This allows us to match the critical diameter determined by DLS ($d_{crit} = 345$ nm), leading to $f_s = 0.15$ and to a critical diameter $d_{crit} = 359$ nm, a critical conversion $\theta_{crit} = 0.59\%$ and a critical time $t_{crit} = 183$ s. Moreover, as the recalculated final particle size $d_f = 1987$ nm (with $f_s = 0.15$) is much lower than the experimental final particle size $d_{f(exp.)} = 6578$ nm, it can be deduced that a controlled coalescence occurred even after the critical point probably due to the progressive burying of the graft-PVP stabilizer.

As a conclusion, the models give only a rough approximation of the absolute particle size. Moreover, as detailed by Paine and Kawaguchi et al. [6, 7], the predictive scaling of particle size for the model I leaves some discrepancies between prediction and experiment while the power law dependence of the predictive model II on the concentration of initiator and macromonomer is much more reliable. This illustrates the usefulness of macromonomers as prestabilizers in dispersion polymerization. Indeed, the mechanism of stabilization can be better-controlled when macromonomers are used. For the same reason, the use of well-defined thiol-ended low molecular weight polymers (ex: PEO chain) as steric stabilizer precursors could be of increasing interest in this field [20–22].

Conclusion

The main conclusion of this study is that DLS and TEM measurements are consistent with the basis of the multibin aggregation model developed by Paine [6]. Stable nuclei from 80 nm to 400 nm in diameter size were detected. They were attributed to the formation of primary mature particles. The nucleation process was quite rapid and completed within less than *ca.* 0.1% monomer conversion. Thus, the present work contributes to a better understanding of the nucleation process in dispersion polymerization in polar media. However, the predictive models give only a very rough approximation of the absolute particle size. Factors such as the polarity of the reaction medium, the composition of the graft and the T_g of the particles should be included in a more complex model in order to predict accurate particle size.

Glossary notation

a	coefficient depending on the mode of termination $0 < a < 1$
A	proportionality constant for the relation $R_g = A \,.\, M_w^b$
b	exponent relating radius of gyration to molecular weight
CL	chain length (in monomer units)
C_{SP}	chain transfer constant for transfer to polymeric stabilizer (per monomer unit)
C_{SS}	chain transfer constant for transfer to solvent
$[D]$	macromonomer concentration (in mol/L)
d_{50}	volume median diameter
d_{crit}	critical diameter, above which same-size particle coalescence is inhibited
d_f	final particle size
f	fraction of initiator fragments initiating polymerization
f_s	factor of efficiency for the graft stabilizer
k_1	pseudo-zero-order rate of dead chain generation (in mol/L/s)
k_2	diffusion-controlled rate constant for coalescence of similar-sized particles (in L/mol/s)
k_d	rate constant for initiator decomposition (in s^{-1})
k_p	polymerization rate constant (in L/mol/s)
k_t	termination rate constant (in L/mol/s)
$[I]$	initiator concentration (in mol/L)
$[M]$	monomer concentration (in mol/L)
M_w	molecular weight of stabilizer chains (in g/mol)
MW_s	molecular weight of monomer (in g/mol)
N_A	number of Avogadro
N_P	number of particles per liter
$[P]$	concentration of polymeric stabilizer (in mol monomer unit/L)

Q_{min}	minimum graft coverage required to stabilize particles against same-size coalescene (in graft/cm^2)
r_1, r_2	reactivity ratios in copolymerization of monomer (1) with macromonomer (2)
R_g	radius of gyration of stabilizer chains in solution (in cm)
$[S]$	concentration of alcohol (solvent) (in mol/L)
ρ	density of polymer (in g/cm^3)
θ	monomer conversion
θ_D	macromonomer conversion
θ_{crit}	monomer conversion corresponding to d_{crit}
t_{crit}	time of polymerization corresponding to θ_{crit} (in s)

Acknowledgments The authors would like to thank ELF ATOCHEM for their support of this research.

References

1. Shen S, Sudol ED, El-Aasser MS (1993) J Polym Sci, Part A: Polym Chem 31: 1393
2. Ober CK, Lok KP (1987) Macromolecules 20:268
3. Okubo M, Shiozaki M, Tsujihiro M, Tsukuda Y (1991) Colloid Polym Sci 269:222
4. Paine AJ, Luymes W, Mc Nully J (1990) acromolecules 23:3104
5. Barrett KEJ (1974) In: Barrett KEJ (ed) Dispersion polymerization in organic media, Wiley Interscience, New York, pp 143–151
6. Paine AJ (1990) Macromolecules 23:3109
7. Kawaguchi S, Winnik MA, Ito K (1995) Macromolecules 28:1159
8. Palluel ALL, Westby MJ, Bromley CWA, Davies SP, Backhouse AJ (1990) Makromol Chem, Macromol Symp 35/36:509
9. Kobayashi S, Uyama H, Choi JH, Matsumoto Y (1993) Polym International 30:265
10. Kobayashi S, Uyama H, Lee SW, Matsumoto Y (1993) J Polym Sci, Part A: Polym Chem 31:3133
11. Lacroix-Desmazes P, Guyot A, two papers submitted to Macromolecules (Part II) and Polym Bull (Part III)
12. Shen S, Sudol ED, El-Aasser MS (1994) J Polym Sci, Part A: Polym Chem 32: 1087
13. Chu F, Graillat C, Guillot J, Guyot A, to be published
14. Fitch RM, Tsai CH (1971) In: Fitch RM (ed) Polymer Colloids. Plenum Press, New York
15. Brandup J, Immergut EH (eds) (1989) In: Polymer Handbook, 3rd ed. Wiley, New York
16. Gilbert RG (1995) In: Ottewill RH, Rowell RL (eds) Emulsion Polymerization: A Mechanistic Approach. Academic Press, London
17. Ali S, Ahmad N (1982) Br Polym 14:113
18. Zhou P, Brown W (1990) Macromolecules 23:827
19. Ito K, Tsuchida H, Hayashi A, Kitano T, Yamada E, Matsumoto T (1985) Polym J 17(7):827
20. Bourgeat-Lami E, Guyot A (1995) Polym Bull 35:691
21. Vidal F, Guyot A (1995) New J Chem 19: 1081
22. Yabuuchi N (1994) ACS Polymer Preprints 35(1):807