Macromol. Symp. ***150****, 187–194 (2000)*

Mechanism and Model of Dispersion Polymerization Using Homopolymer as Dispersant in Polar Media

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SUMMARY: The mechanism of dispersion polymerization is described. The model is developed to predict the number of particles, the critical smallest size of the stable particles and the duration of the nucleation and particle formation stage. The key components of this model are a multibin coagulative nucleation theory for unstable nuclei coalescence through homogeneous nucleation and the grafting mechanism of stabilization. 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.

Introduction

Dispersion polymerization is an attractive alternative to other polymerization methods to prepare micron-size monodisperse polymer particles in a single step, which not only suits a wide variety of monomers but also permits easy functionalization. The mechanism of dispersion polymerization is complex and poorly understood. A few reports put the stress on the nucleation and stabilization mechanism. Paine[1] found and has claimed the exclusive effect of grafted-copolymer stabilizer in particle nucleation, which can be produced in situ and ends up on the particle surface when the steric dispersant (precursor homopolymer) contains active sites for chain transfer of radicals, while El-Aasser et al.[2] report that the steric dispersant itself would be adsorbed onto the surface of the particles and stabilize the particles in addition to the grafted-copolymer stabilizer, so a competition would exist between the adsorption of the grafted-copolymer stabilizer and the precursor homopolymer. Which one of these mechanisms is dominant is still subject to speculation. What is important is that the graft copolymer is necessary for the system stability and particle formation. Kawaguchi and Winnik[3] and Paine[4] have reported useful theoretical models for predicting particle number and size with and without macromonomer, respectively. Recently, major contributions have been made by Ahmed and Poehlein[5] and Soini et al.[6] in terms of kinetic models of dispersion polymerization. The objective of this paper is to develop a integrated model to predict the critical smallest size of the stable particles, the number of particles and the duration before the particle growth stage. Predictions of polymerization rate, evolution of

CCC 1022-1360/00/$ 17.50+.50/0

particle size and its distribution obtained from the simulation will be compared to experimental results in a future paper.

Mechanism of Dispersion Polymerization

Particle formation and growth stages in dispersion polymerization belong to a special case of the precipitation polymerization. Combined with the number of total particles and further study of the kinetics, dispersion polymerization may be divided into four stages as follows.

First, the pre-polymerization stage: the monomer, dispersant, and initiator are all dissolved in the dispersed media, and the reaction system is homogeneous prior to polymerization. Second, the nucleation stage: oligo-radicals, polymers and grafted-copolymer stabilizers are produced in the solution phase by solution polymerization. The key feature is the formation of grafted-copolymer stabilizer, which occurs in the continuous phase by chain transfer to the steric dispersant in situ. These precipitate from the homogeneous system to form unstable nuclei when they reach their critical chain length. A new phase thus appears. But the solution polymerization occurring in the continuous phase dominates the reaction. Third, the particle stabilization stage: the nuclei coalesce, which may be hindered by grafted-copolymer stabilizer till the particles are stabilized. In this stage, the polymerization in the particle phase gradually increases with more and more nuclei becoming "mature" particles. Finally, the particle growth stage: all particles have enough stabilizer and dispersant to be stabilized, and the number of stable particles become constant. The particles grow with absorption of monomer, initiator, oligo-radicals, grafted-copolymer stabilizer, the precursor dispersant from the continuous phase and capture of unstable nuclei before they mature in the continuous phase directly. Therefore, the smaller the particle size is, the more rapidly it grows (in diameter). So the size distribution of the final particles is relatively narrow, even monodisperse. In this stage, there are two polymerization loci, namely the monomer-swollen polymer particles and the continuous phase[7, 8].

It is interesting to pursue the implications of the grafting mechanism of particle stabilization. Grafting occurs in the continuous phase by chain transfer to the steric dispersant and usually obeys the standard kinetic expression, which is related to the lower molecular weight of the polymer (30,000 - 40,000) that was obtained at the beginning of the dispersion polymerization[8]. El-Aasser et al.[2] found by DLS that the nuclei appeared suddenly having diameters of about 15 - 20 nm in particles formation and these nuclei were unstable and quickly aggregated with each other. Comparison with experiment[2, 8] implies that smallest nuclei only have one grafted-copolymer stabilizer. Moreover, it is important to indicate that there would not be any adsorption of the precursor dispersant and monomer swollen in the particle phase before the particle growth stage because the nucleation and particle formation stages are finished in such a short time.

Multibin Particle Aggregation Model

Populations of the unstable nuclei are divided in accordance with the number of grafted copolymer stabilizers. With this concept, it is a simple matter to generate the rules governing nuclei coalescence until particles stabilize. In this case, bin j is assigned to the nuclei having j grafted copolymer chains and the nuclei in bin j only aggregate irreversibly at a diffusion-controlled rate with the nuclei below bin n, if n is minimum number of grafted copolymer chains for the stable particles. These rules can be expressed more explicitly by the following differential equations. The three terms in equations 1~4 correspond to (a) output of nuclei in bin i by coalescence in the preceding bin, (b) loss of nuclei in bin i by coalescence with another unstable nuclei bin j, (c) capture of nuclei in bin i by the stable particles.

$$\frac{d[R]}{dt} = 2fk_d[I]_0 - 2k_t[R]^2 - k_2[R]N_p \tag{1}$$

$$\frac{dN_1}{dt} = \frac{d[R]}{dt}B - N_1\sum_{j=1}^{n-1}(1-\frac{1+j}{2n})k_{1,j}N_j - (1-\frac{1+n}{2n})k_{1,n}N_1N_n \tag{2}$$

$$\frac{dN_i}{dt} = \frac{1}{2}(1-\frac{i}{2n})\sum_{j=1}^{i-1}k_{i-j,j}N_jN_{i-j} - (1-\frac{i+j}{2n})N_i\sum_{j=1}^{n-1}k_{i,j}N_iN_j - (1-\frac{i+n}{2n})k_{i,n}N_iN_n \tag{3}$$

$$i = 2,3,4,\cdots n-1$$

$$\frac{dN_n}{dt} = \frac{1}{2}\sum_{\substack{i=1\\ j=n-i}}^{n-1}(1-\frac{i+j}{2n})k_{i,j}N_iN_j \tag{4}$$

where B is the probability of grafting given by $C_{pvp}[PVP](X_n)/[M]$. k_{ij} is the rate constant for coagulation and is used as an adjustable parameter(reasonable values for k_2 are 10^9 $mol.L^{-1}.s^{-1}$), which depends only on the diameters of the coalescing particles as follows:

$$k_{ij} = k_2\left(\frac{1}{d_i} + \frac{1}{d_j}\right)(d_i + d_j)/4 \qquad (5)$$

The critical point defined by the appearance of the smallest stable particles occurs when the graft available equals the minimum graft required (labeled $Q_{\min}$), as shown in equations 6 and 7, respectively.

$$graft \quad available = 2fk_d[I]_0 t \frac{C_{pvp}[PVP](\overline{X}_n)}{[M]} = C_{PVP}[PVP]N_A X \qquad (6)$$

The graft required is given by the total surface area times $Q_{\min}$.

$$graft \quad required = N_p \pi d^2 Q_{\min} = \frac{6[M]MW_{MMA}Q_{\min}X}{\rho d} \qquad (7)$$

$$d_{crit} = \frac{6[M]MW_{MMA}Q_{\min}}{\rho C_{pvp}[PVP]N_A} \qquad (8)$$

$$n = \pi \times d_{crit}^2 \times Q_{\min} \qquad (9)$$

where, $Q_{\min}$ and $Q_{\max}$ (maximum grafted required) are shown in Figure 1, respectively. Other kinetics parameters have been reported in the preceding paper[8].

$$Q_{\min} = \frac{1}{\left(3R_g\right)^2} \qquad (10)$$

$$R_g = A(0.75MW_{PVP})^b, \qquad A = 5.3\times10^{-4} \qquad and \qquad b = 0.32^{[1]}$$

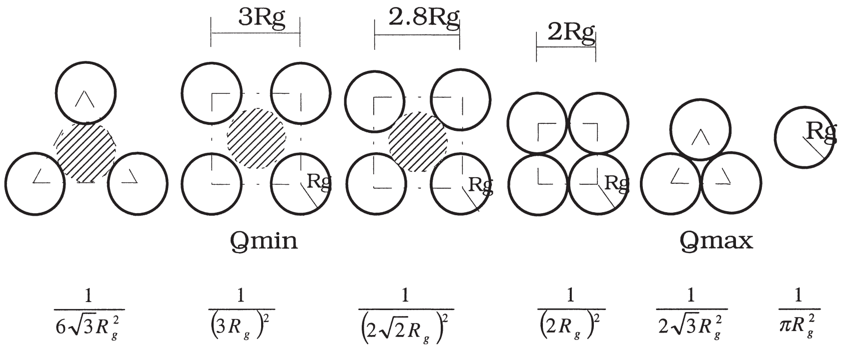

Figure 1 Qualitative vertical view of the particle's surface for the grafted-copolymer stabilizer coverage represented by Q_{min} and Q_{max}

Results and Discussion

The standard recipe used in this study is given by the following values: Temperature=60 °C, $CH_3OH:H_2O$=7:3 by wt, MMA=10wt% of total, AIBN=1 wt% of MMA, PVP-K30=10 wt% of MMA. The amount of each ingredient was kept constant in all experiments except as indicated.

Table 1 shows the relationship between the required minimum number of grafted PVPs per critical smallest stable particle and the molecular weight of PVP. The results indicate that the moderate molecular weight range of PVP will be required for the system stability. In contrast, the flocculation of the particles by "bridging" occurs if the molecular weight of PVP tends to very high, such as PVP-K90. On the other hand, the radius of gyration of the grafted-copolymer stabilizer chains may be too small to prevent coagulation by steric forces, such as PVP-K15.

Table 1 Relationship between Required Minimum Number of Grafted PVPs on the Surface of the Critical Smallest Stable Particle and Molecular Weight of PVP

PVP series	MW	R_g /nm	d_{cir} /nm	n	Experimental
K-15	8000	8.58	199	268	unstable
K-30	40000	14.4	75	14	stable
K-60	200000	24.0	52	5	stable
K-90	700000	35.9	24	0.2	unstable

The Gear method for integrating a stiff set of differential equations describing the various bins was used, leading to the qualitative and quantitative agreement with the results of the experiments. The number of stable particles is fixed very early in the polymerization, before 10 min. With increasing polymerization temperature, concentration of initiator and dispersant, the duration of the nucleation and particle formation stages will be shortened as shown in Figures 2, 4 and 6. Figure 8 shows that the nucleation and particle formation stages are almost the same if only the monomer concentration is varied. As illustrated in Figures 3, 5 and 7, the particle number increases with increasing polymerization temperature, concentration of initiator and dispersant. In addition, the change of particle number is not obvious if only the monomer concentration is varied shown in Figure 9.

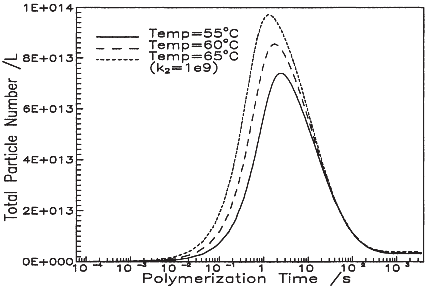

Figure 2 Relationship between all particle number and reaction time for different polymerization temperatures.

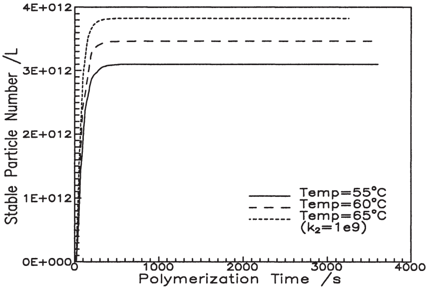

Figure 3 Relationship between stable particle number and reaction time for different polymerization temperatures.

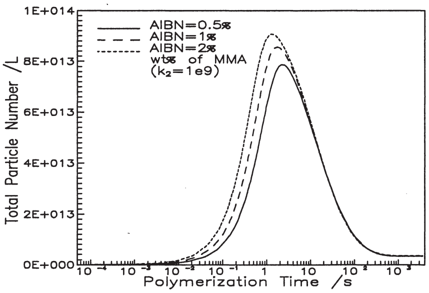

Figure 4 Relationship between all particle number and reaction time for different initiator concentrations.

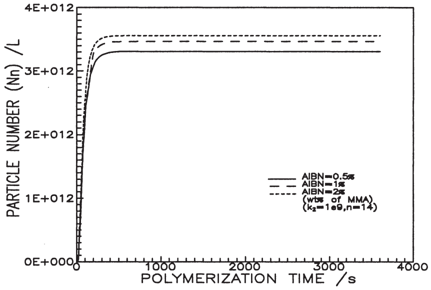

Figure 5 Relationship between stable particle number and reaction time for different initiator concentrations.

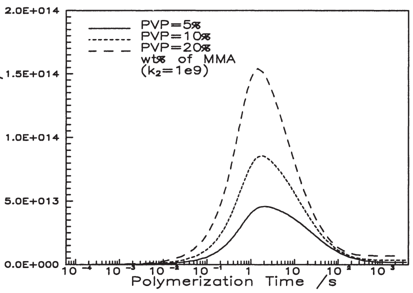

Figure 6 Relationship between all particle number and reaction time for different dispersant concentrations.

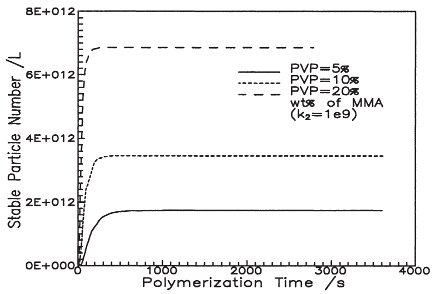

Figure 7 Relationship between stable particle number and reaction time for different dispersant concentrations.

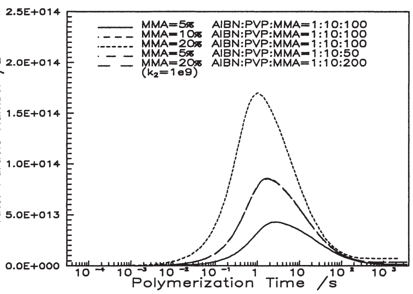

Figure 8 Relationship between all particle number and reaction time for different monomer concentrations.

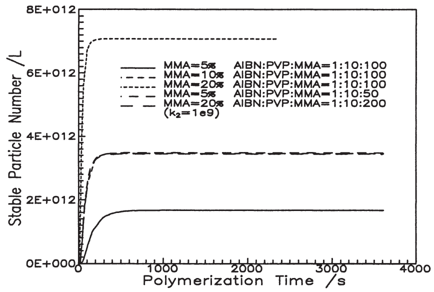

Figure 9 Relationship between stable particle number and reaction time for different monomer concentrations.

Conclusions

On the basis of the described mechanism, an integrated model for multibin coagulative nucleation theory and the grafting mechanism of stabilization is developed to predict the time evolution of particle number and the duration before the particle growth stage. The model as implemented here indicates that the stability of polymerization system becomes poor if the molecular weight of dispersant is too low or too high. The particle number increases and the duration before the particle growth stage tends to be shortened with increasing polymerization temperature, concentration of initiator and dispersant but not the concentration of monomer.

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