Diffusion of Additives During *In-Situ* Suspension Polymerization

M. F. Cunningham
Xerox Research Centre of Canada, Mississauga, Ontario, Canada L5K 2L1

High value-added specialty composite materials can now be made by in-situ suspension polymerization of monomers with additives incorporated to impart a specific property. In these composite particles, the nature of the additive dispersion is often of critical importance in determining final product properties. During polymerization, viscosities in the droplets are sufficiently low that significant diffusion can occur, resulting in dramatic changes to the additive dispersion quality. This article examines the importance of process parameters controlling diffusion lengths of small particle additives during in-situ polymerizations. A model was developed to provide a basis for devising polymer reactor operating strategies that minimize small-particle diffusion. Effects of varying polymerization rate, molecular weight and initial conversion were investigated. Model results were validated by comparing to experimental data. Increasing the initial conversion is shown to be highly effective in reducing diffusion of additive particles.

Introduction

Suspension polymerization is a technology possessing several advantageous characteristics, both technical and economical. The presence of the aqueous phase provides a heat sink and maintains low suspension viscosity, thereby ensuring good heat transfer, simple temperature control, and ease of mixing. Suspension polymerization is also of significant industrial importance, being widely used to make a variety of resins. A thorough review has been published by Yuan et al. (1991). While suspension polymerizations are traditionally used to make resins, increasing research efforts are now being directed toward the preparation of high value-added composite materials by *in-situ* suspension polymerization of monomers with small particle additives incorporated to impart a specific property. For example, colored particles can be prepared by adding pigments (e.g., xerographic toners). The nature of the additive dispersion is often of critical importance in determining final product properties. Composite polymeric materials have traditionally been made by melt blending additives into a host resin. The product is usually in the form of pellets and can be pulverized if size reduction is desirable. However, there is commercial potential for very small composite particles, below the size range that can be efficiently achieved by mechanical grinding (approximately 10–15 μm). Suspension polymerizations can be designed to produce particles in this size range, but successfully designing a process that allows incorporation of additives presents complex engineering challenges. How well the additives are dispersed in the final particles is often critical to the end-use properties. During *in-situ* suspension polymerizations, the viscosity is sufficiently low during the early stages of the polymerization that significant diffusion will occur. If a uniform dispersion of additive particles within the droplet exists prior to starting the polymerization, diffusion can significantly alter the quality of the dispersion in the time it takes for the particles to polymerize and consequently the final properties can deteriorate. The design challenge in making small composite particles with good additive dispersion by suspension polymerization lies in determining reactor operating conditions that minimize the intraparticle mass transfer (diffusion) that inevitably occurs during polymerization.

An experimental research program was undertaken to design small composite polymeric particles by suspension polymerization. Conducting suspension polymerizations without

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Current address of M. F. Cunningham: Dept. of Chemical Engineering, Queen's University, Kingston, Ontario, Canada K7L 3N6.

additives for very small particles (less than 15–20 μm diameter) is a developed technology, but early attempts to incorporate additives led to serious problems related to poor additive dispersion in the final particles. The reason for the poor dispersion was identified as diffusion during polymerization. Typically the additive would diffuse out of the polymerizing particle and into the aqueous phase. In response to this problem, a modeling study was initiated to provide a design tool for selecting optimal conditions for operating the polymerization reactor. The model, which assumes Brownian diffusion and incorporates the polymerization kinetics, was subsequently used to guide the development of the process. During this period the modeling and experimental aspects of the project developed concurrently. The model was developed and refined in conjunction with ongoing process development. The effects of polymerization rate, initial molecular weight, and initial conversion have been studied, and the relative importance of these factors has been determined. The specific objective in this work was not to predict the final spatial distribution or morphology of the additive particles within the polymerized droplet, but rather to investigate and develop reactor operating strategies for minimizing diffusion of these particles and thus attempt to maintain the initial spatial distribution. To achieve this, established principles of polymerization kinetics and diffusion were employed to develop a model that provides fundamental new insight, not into polymerization or diffusion phenomena, but into the *operation* of polymerization reactors.

Interactions of additive particles with other additive particles are potentially of importance for concentrated dispersions, but in dilute systems such as those under consideration (volume loading is usually less than 2%), these interactions may be neglected. The calculations done in this work are valid for low solids systems (< 4 vol. %). For high solids systems, it is necessary to account for these interactions. The modeling shown below is designed for additive particles up to 500 nm in diameter.

The mean-square diffusion length resulting from Brownian motion is

$$\langle L^2 \rangle = D \times t, \tag{1}$$

where D is the diffusivity and t is diffusing time. The Stokes–Einstein (S–E) equation for noninteracting, spherical particles is

$$D = \frac{kT(t)}{3\pi\eta(t)d}, \tag{2}$$

where k is the Boltzmann constant, T is absolute temperature, $\eta(t)$ is the zero-shear viscosity, d is the diameter of the additive particle, and t is time. Accounting for variable viscosity and temperature,

$$\langle L^2 \rangle = \int_0^t D(t)\,dt = \frac{k}{3\pi d}\int_0^t \frac{T\,dt}{\eta(t)} \tag{3}$$

$$\langle L^2 \rangle^{1/2} = \left[\int_0^t D(t)\,dt\right]^{1/2} = \left[\frac{k}{3\pi d}\int_0^t \frac{T\,dt}{\eta(t)}\right]^{1/2}. \tag{4}$$

The S–E equation assumes the solvent medium acts as a continuum with respect to the length scale of the particle radius. Won et al. (1994) have discussed the validity of the S–E equation for polymer solutions. Both positive and negative deviations form S–E behavior have been reported. The authors note that ionic systems are more likely to show deviations than neutral systems, and the magnitude of the deviations is likely to be greater. In organic solutions of flexible polymers, adherence to S–E behavior is more common. The systems under consideration in this work belong to the latter category and therefore the S–E relationship has been used. The reader should, however, be aware of the possibility of deviations in certain systems. Using Eq. 4, mean diffusion lengths can be calculated if the viscosity inside the polymerization droplet is known as a function of time. This requires that conversion, molecular weight, and temperature be known as functions of time, and that a correlation relating them to viscosity be available.

Equation 2 represents a well-established expression relating temperature, particle diameter, and most importantly viscosity, to the diffusivity at any instant. The unique aspect of the current work is the challenge of designing process conditions so as to minimize, not the diffusivity itself as represented by Eq. 2, which would be a trivial task, but rather the integral of the mean diffusion length over the course of polymerization (Eq. 4) employing key reaction variables. The temporal evolution of the diffusivity, which in turn is determined primarily by the viscosity profile, is controllable through the choice of reaction conditions. In designing a process to minimize additive diffusion, the specific objective becomes determination of reactor operating strategies that minimize the integral of diffusivity.

Simulation of Polymerization Kinetics

Important mechanistic steps in the free-radical bulk-polymerization kinetics of methyl methacrylate and styrene include generation of free radicals by thermal decomposition of initiator, chain initiation, propagation, chain transfer (to monomer and/or chain transfer agent), and chain termination. These two monomers were selected because they approximately represent extremes of kinetic behavior and properties. Methyl methacrylate (MMA) has a pronounced gel-effect while that of styrene is relatively mild. Furthermore MMA polymerizations yield higher molecular-weight polymer at equivalent temperatures and initiator concentrations. The following steps are well known but are shown below for reference.

Initiator decomposition

$$I \xrightarrow{k_d} 2R_0\cdot \tag{5}$$

Chain initiation

$$R_0\cdot + M \xrightarrow{k_i} R_1\cdot \tag{6}$$

Propagation

$$R_n\cdot + M \xrightarrow{k_p} R_{n+1}\cdot \tag{7}$$

Termination by combination

$$R_s\cdot + R_t\cdot \xrightarrow{k_{tc}} P_{s+t} \tag{8}$$

Termination by disproportionation

$$R_s\cdot + R_t\cdot \xrightarrow{k_{td}} P_s + P_t \tag{9}$$

Transfer to chain transfer agent z

$$R_n\cdot + z \xrightarrow{k_{fz}} P_n + R_z\cdot \tag{10}$$

Transfer to monomer

$$R_n\cdot + M \xrightarrow{k_{fm}} P_n + R_1\cdot \tag{11}$$

Inhibition (by species X)

$$R_n\cdot + X \xrightarrow{k_{tx}} P_n\cdot \tag{12}$$

Some solid additives will act as inhibitors in free-radical polymerizations. If such materials are used, the effect can be accounted for using Eq. 12. For the cases studied in this work, inhibition was not considered because for the additives used inhibition was not significant. It should be noted, however, that if inhibition does occur, it can be particularly damaging in the effort to minimize diffusion because it prolongs the time when viscosity is lowest.

The number- and weight-average molecular weights are calculated using moments of the chain-length distribution.

$$\overline{M_n} = M_0 \frac{\sum_{n=1}^{\infty} nP_n}{\sum_{n=1}^{\infty} P_n} \tag{13}$$

$$\overline{M_w} = M_0 \frac{\sum_{n=1}^{\infty} n^2P_n}{\sum_{n=1}^{\infty} nP_n} \tag{14}$$

In this study the polymerization simulation software POLYRED (Ray, 1990) was used to create and solve a system of dynamic material-balance equations that result from the reaction kinetics. Simulations were performed for a batch reactor. The kinetic model used in POLYRED is based on a model developed by Arriola (1989). Diffusion-limited termination and propagation are accounted for in the model. Although bulk polymerization kinetics have often been assumed to be applicable to suspension polymerization systems, Kalfas and Ray (1993) have recently shown that some differences can be expected due to mutual solubility of the monomer and aqueous phases. Accordingly a model accounting for mass transfer of monomer between phases due to the mutual solubility of the two phases was used. Modeling the interphase transport of monomer requires specification of total droplet surface area, therefore calculations were done for suspension droplets of 20 μm diameter, and with a 3:1 ratio of aqueous phase to organic phase, which represent typical operating conditions. The simulation results are insensitive to this ratio over a wide range of operating conditions (10:1 to 1:1). Tables 1 and 2 show the kinetic parameters used in the simulations. The polymerization conditions simulated (temperature, initiator concentrations) are typical of those used in preparation of composite suspension polymer particles.

Calculation of Viscosity Profiles During Polymerization

Viscosity of the polymerizing reaction mixture as a function of time was determined by (1) simulating the polymerization kinetics, thus providing conversion, molecular weight, and temperature as a function of time; and then (2) using viscosity correlations found in the literature to relate conversion,

Table 1. Parameters Used in Simulation of MMA and Styrene Suspension Polymerizations

Parameter	MMA	Styrene
k_p^o (L/mol/s)	$4.92E-5\cdot\exp[-4{,}353/RT]$ (Mahabadi and O'Driscoll, 1977)	$1.09E-7\cdot\exp[-7{,}050/RT]$ (Mahabadi and O'Driscoll, 1977)
k_t^o (L/mol/s)	$9.80E-7\cdot\exp[-701/RT]$ (Mahabadi and O'Driscoll, 1977)	$1.70E-9\cdot\exp[-2{,}268/RT]$ (Mahabadi and O'Driscoll, 1977)
k_{td}^o/k_{tc}^o	$2{,}483\cdot\exp[-4{,}073/RT]$ (Kalfas and Ray, 1993)	0 (Kalfas and Ray, 1993)
k_{fm} (L/mol/s)	$0.893E-3\cdot\exp[2{,}240/RT]$ (Kalfas and Ray, 1993)	$1E-3\cdot k_p$ (Kalfas and Ray, 1993)
k_{fz} (L/mol/s) [dodecanethiol]	$0.67\cdot k_p$ (Hutchinson, 1994)	$20\cdot k_p$ (Berger and Brandup, 1989)
f (ADVN)	0.6	—
k_d (ADVN) (s^{-1})	$1.258E-16\cdot\exp[-30{,}960/RT]$ (Ref. 15 in Meister and Malanga, 1989)	—
f (BPO)	—	1.0
k_d (BPO) (s^{-1})	—	$1.7E-14\cdot\exp[-30{,}000/RT]$ (Kalfas and Ray, 1993)
Monomer solubility in water	1.49% @ 60°C (Luskin, 1970)	0.062% @ 80°C (Boundy and Boyer, 1952)
Water solubility in monomer	2.07% @ 60°C (Luskin, 1970)	0.180% @ 80°C (Boundy and Boyer, 1952)

Table 2. Gel-effect Parameters Used in Simulation of MMA and Styrene Suspension Polymerizations

Gel-Effect Parameter	MMA (Schmidt and Ray, 1981)	Styrene (Hamer, 1983)
g_p $(k_p = k_p^o \cdot g_p)$	$V_f > V_{fpc}$: 1.0 $V_f \leq V_{fpc}$: $0.71E-4 \cdot \exp[171.53V_f]$, where $V_f = \phi_M V_{fM} + \phi_P V_{fP}$ $V_{fM} = 0.025 + 0.001 \cdot [T(°C) + 106.0]$ $V_{fP} = 0.025 + 0.48E-3 \cdot [T(°C) - 114.0]$ $V_{fpc} = 0.05$	1.0
g_t $(k_t = k_t^o \cdot g_t)$	$V_f > V_{ftc}$: $0.10575 \exp[17.15V_f - 0.01715T(°C)]$ $V_f \leq V_{ftc}$: $0.23E-5 \cdot \exp[75V_f]$, where $V_{ftc} = 0.1856 - 0.2965E-3 \cdot T(°C)$	$\exp[-0.4404X - 6.363X^2 - 0.1704X^3]$ (X = fractional conversion)

molecular weight, and temperature to the zero-shear viscosity at any time t. Because kinetic parameters and mechanistic models for free-radical polymerization are well developed, simulation of the kinetics can be done reasonably accurately. Agreement with experimental data was typically within 10% on rate and 15–20% on molecular weight. Stuber's (1986) correlation was used for the methyl methacrylate runs, while Chen's (1986) equation was used for styrene. Stuber's correlation is shown in Eq. 15, and Chen's is shown in Eq. 16.

$$\eta_0(c,M,T) = F\zeta$$

$$F = 0.00216[1 + 0.125(cM)^{0.5} + 3.75E-11(cM)^{3.4}]$$

$$\zeta = \exp[(600 + 80c + c^2)(1/T - 1/465.15) + 1.2E-5(c)^3], \qquad (15)$$

where c is polymer concentration (weight percent), M is polymer weight-average molecular weight (thousands), T is temperature (K), and the zero shear viscosity is in poise.

$$\ln[\eta_0] = -13.04 + 2{,}013/T + M^{0.18}\big[3.91w_p - 51.3w_p^2 + (5.88 + 13{,}085/T)w_p^3\big], \qquad (16)$$

where T is temperature (C), w is weight fraction polymer, and the viscosity is in Pa·s.

There are very few good correlations available that span wide ranges of temperature, molecular weight, and polymer concentration (conversion). The correlations cited earlier are much more complete than most published correlations. Details of how these correlations were derived can be found in the references. Volume loading of additive was assumed to be sufficiently low that viscosity would not be significantly affected by the presence of the additive. Typical volume loadings for this type of application are less than 2%. Using the Einstein equation (Eq. 17), a 2% loading is predicted to increase the viscosity by only 5%. In many cases this exceeds the reliability of the actual viscosity measurement:

$$\eta = \eta_0(1 + 2.5\phi). \qquad (17)$$

For applications where the additive loading is high or when particle interactions are strong, correlations are available in the literature for estimating viscosities (e.g., Sudduth, 1993). Correction for viscosity is recommended when the volume loading of the droplets by additive particles exceeds about 5% or when the particles being used are strongly interacting. Calculation of cumulative mean diffusion distances at various times during the polymerization was done by simulating the polymerization kinetics for a given set of conditions, evaluating the viscosity during the polymerization by applying the correlations cited earlier (Eqs. 15 and 16), and finally by numerically integrating Eq. 4 over the reaction time. Cumulative mean diffusion length (CDL), which is shown in the figures discussed in the Results section, represents the total linear distance from its point of origin. An additive particle is predicted to diffuse during the polymerization, assuming its diffusional path was not restricted in any way.

In this modeling the objective is to develop reaction engineering strategies to minimize diffusion within polymerizing droplets, and not to attempt to predict the final spatial distribution of particles in the polymerized droplet. It was for this reason that the cumulative mean diffusion lengths were calculated, assuming there were no limits or boundaries to the distances they could diffuse. In actuality, a particle diffusing a large enough distance to meet the droplet boundary would experience one of three fates. It could diffuse out of the droplet into the aqueous phase (most common), or it could remain at the boundary indefinitely, or it could be repelled by the boundary and return to the droplet interior. The fate it experiences is determined by a complex set of forces, including the interactions between (1) the additive particle and the monomer/polymer matrix in the droplet; (2) the additive and the droplet boundary, which includes surfactant; and (3) the additive and the aqueous phase. Unfortunately, these interactions are highly specific to the system in question (monomer, polymer, additive, surfactant), and therefore results determined for a given system would not be generally applicable. (The question of whether or not sufficient data are available to even perform the calculations for a given system is another issue.) Further, over a long diffusion distance particle–particle collisions will occur, and therefore particle aggregation could also become an issue. However, if the objective is to minimize diffusion (so that particle interactions with each other and the droplet boundary do not occur), the fate of a particle that diffuses a long distance is of little consequence, since the reaction conditions used are already known to be undesirable.

Results

The effects of several factors on additive diffusion were investigated, including rate of polymerization, molecular weight of polymer formed during the polymerization, and the initial monomer conversion within the polymerizing droplets (i.e., at the beginning of the suspension polymerization). In practice, rate and molecular weight can be varied most easily, while varying the initial conversion is much more complex and will be discussed later. Examination of Eq. 4 reveals that variations in viscosity will be most important in determining the extent of diffusion, given that viscosity will increase by several orders of magnitude during polymerization, much greater than any other variable. The results of the simulations will depend quantitatively on the particular correlation used. However, the relative importance of various factors is insensitive to the correlation. Because most of the diffusion occurs early in the polymerization, establishing accurate viscosity correlations at low polymer concentrations is more critical than having very accurate models at higher polymer concentrations (> 50%). In these simulations an additive particle diameter of 100 nm was used; this is typical of the size used in practice. The mean diffusion lengths shown are inversely proportional to the particle diameter. Therefore the results calculated here can be easily scaled for additives with different diameters. It was assumed additive particle aggregation does not occur. (Particle aggregation would lead to increased mean diameters and therefore reduced diffusivities. As discussed in the previous section, given the objective of devising strategies to minimize diffusion, there is no reason to quantify the effects of aggregation since under conditions leading to aggregation, diffusion distances are too large to be of interest.) Typical profiles for mean diffusion distances as a function of time and conversion for methyl methacrylate (MMA) and styrene polymerizations are shown in Figures 1 and 2. The polymerization conditions are given in the figure captions. The figures show cumulative diffusion length, which is the total mean diffusion distance that has occurred up until time *t*. The slope of this curve represents the diffusion rate at time *t*.

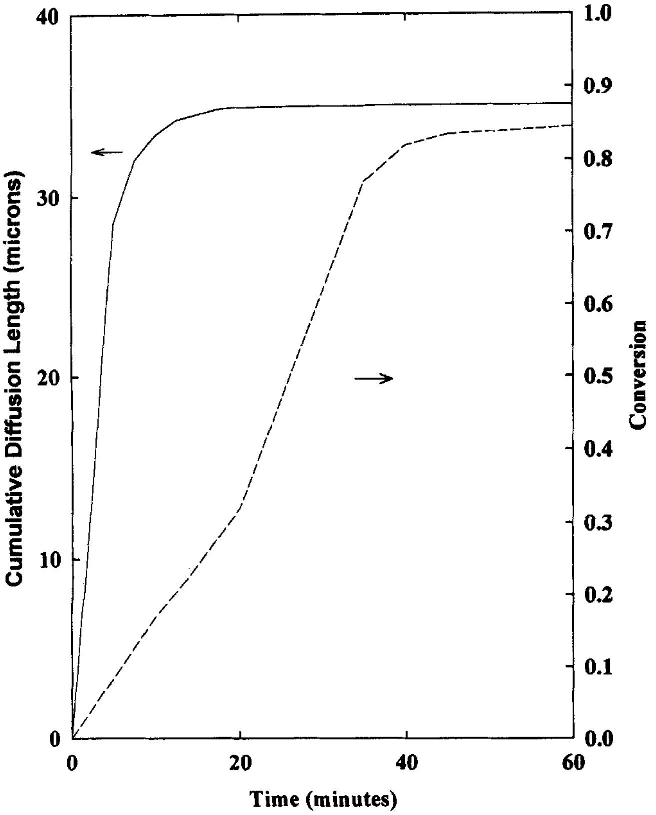


Figure 1. Cumulative diffusion length (solid line) and conversion (dotted line) as a function of time for MMA polymerization.

Polymerization conditions: $T = 60°C$; 3.0 wt. % ADVN.

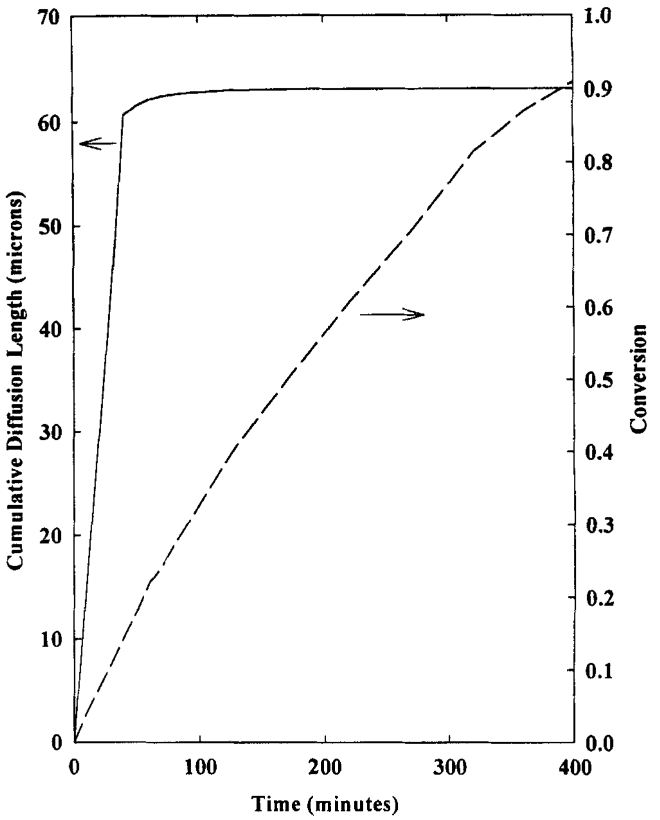


Figure 2. Cumulative diffusion length (solid line) and conversion (dotted line) as a function of time for styrene polymerization.

Polymerization conditions: $T = 80°C$; 2.5 wt. % BPO.

The MMA polymerizations were simulated at 60°C using azobisdimethylvaleronitrile initiator (ADVN), while the styrene reactions were simulated at 80°C using benzoyl peroxide (BPO). Conditions were selected to ensure a reasonable reaction time suitable for a manufacturing process. The temperature selected for the styrene polymerizations is higher because styrene polymerizes more slowly than MMA. Figures 1 and 2 clearly show that most of the diffusion occurs very early in the polymerization. These results are more easily appreciated by examining Figure 3, which shows the dependence of viscosity on conversion for the polymerization conditions of Figures 1 and 2. The magnitude of the viscosity increase illustrates how much greater diffusion rates are early in the polymerization, and suggests design strategies should focus on controlling reaction conditions in the initial stages of polymerization.

Effect of polymerization rate

Results presented in Figures 1–3 suggest variation of the

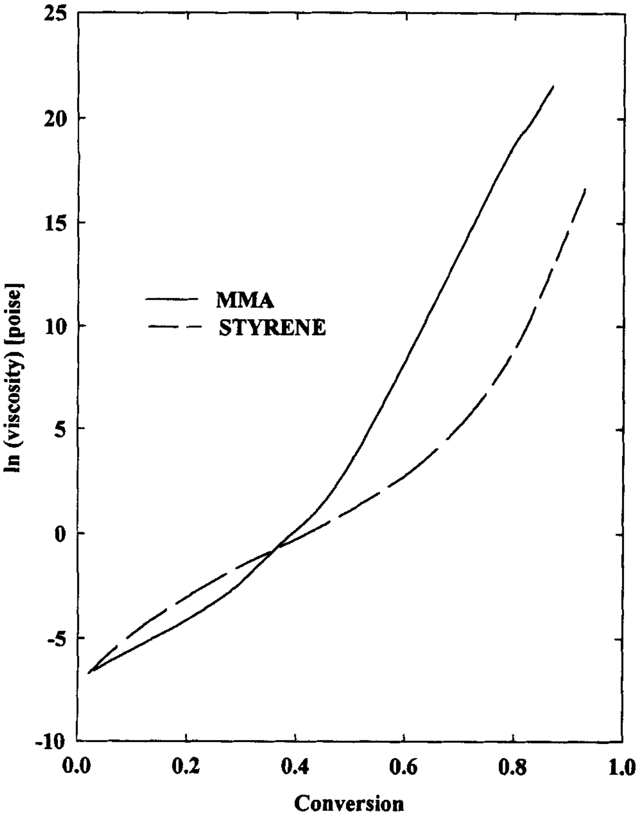


Figure 3. Dependence of viscosity on conversion for the polymerization conditions shown in Figures 1 and 2 (MMA; 60°C; 3.0 wt. % ADVN; styrene: 80°C, 2.5 wt. % BPO).

polymerization rate could be an effective method for controlling the extent of diffusion by controlling the time period in which polymer concentration and therefore viscosity are low. Studying the effects of varying the rate is not trivial, however, as increasing the rate simultaneously results in polymer with lower molecular weight being produced in the polymerization. The most straightforward approach to varying rate is to increase the temperature and/or the initiator concentration, but both approaches also affect molecular weight and therefore the diffusivity. (Temperature itself also directly affects diffusion rate.) Therefore a strategy was developed to study polymerizations where only the rate was varied. This was accomplished by employing a chain-transfer agent, so that a greater proportion of chain-termination events were due to chain transfer and not bimolecular termination. Under these conditions, rate and molecular weight can be varied independently. As the initiator concentration was decreased, the amount of chain-transfer agent (dodecanethiol) was increased such that the initial molecular weight remained constant. The effects of varying the initial polymerization rate are shown in Figure 4. Each curve in Figures 4–9 represents a *series* of polymerization simulated at different conditions. The reader will note that the rates simulated for the MMA and styrene polymerizations are much different. While it may seem to be a worthwhile exercise to simulate these reactions at the same rates to compare them directly, this is not realistic, as the MMA polymerizations are much faster than styrene due to the differences in the respective k_p^2/k_t ratios. In this case, as in all other cases, the cumulative diffusion length of MMA (a "fast" monomer) is considerably less than that of styrene (a "slow" monomer). Figure 4 shows that as polymerization rate is increased, mean diffusion distances do decrease somewhat (by about a factor of 2) but remain significant. Remembering the range of interest for particle diameter is less than about 15 μm, mean diffusion distances on the order of 50 μm are large relative to the suspension particle diameter and indicate that there would be significant additive diffusion to the droplet boundary and then into the aqueous phase.

Effect of varying molecular weight

A strategy of reducing diffusion lengths by increasing molecular weight was also examined. The effect of varying initial molecular weight can be determined provided the initial polymerization rate and the temperature remain constant. Molecular weights were varied by incorporating small quantities of the chain-transfer agent dodecanethiol into the simulations while maintaining a constant initiator concentration. Adding chain-transfer agents to reduce molecular weight has two important effects relevant to diffusion of additives. The first effect is reduction of the molecular weight, thereby altering the viscosity profile during the polymerization. The

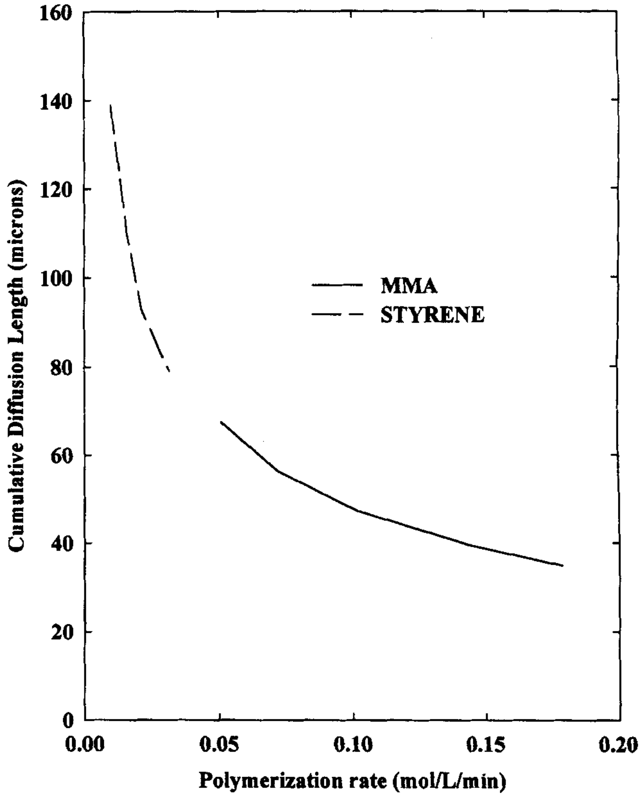


Figure 4. Effect of polymerization rate on cumulative diffusion length for MMA (solid line) and styrene (dotted line) polymerizations.

Rate was varied by varying initiator concentration; initial molecular weight was kept constant by addition of chain transfer agent (dodecanethiol). MMA: 60°C, $M_{w0} = 79$ K; styrene: 80°C, $M_{w0} = 34$ K.

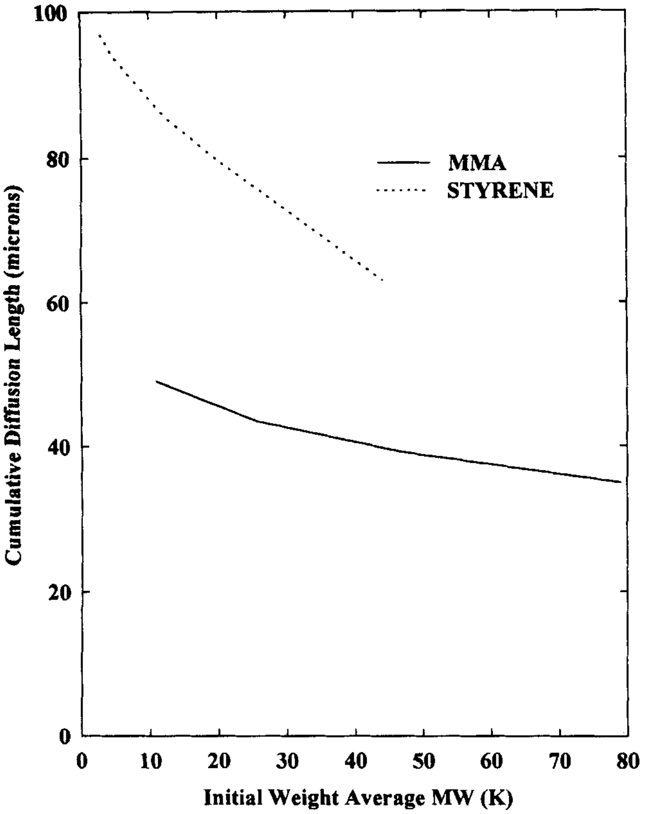


Figure 5. Weight average molecular weight (initial) dependence of cumulative diffusion length for MMA (solid line) and styrene (dotted line) polymerizations.

Molecular weight was varied by dodecanethiol addition. MMA: 60°C, 3.0 wt. % ADVN, $R_{p0} = 0.18$ mol/L/min; styrene: 80°C, 2.5 wt. % BPO; $R_{p0} = 0.025$ mol/L/min.

second effect is reduction of the severity of the gel-effect, which leads to an increase in the time required to reach the high conversion regime where diffusion becomes negligible. Results from a series of simulations with varying molecular weight are shown in Figure 5. Note that it is the *initial* weight-average molecular weight that is shown. This is a more representative measure than the final molecular weight (which is significantly higher because of the gel effect) since most of the diffusion occurs prior to the increase in molecular weight accompanying the gel effect. It is seen that diffusion distances do decrease somewhat as molecular weight increases, indicating that such a strategy is moderately successful. However, because molecular weight is often a critical parameter in determining final product properties, it would usually be unwise or impractical to devise a strategy around its variation.

Results presented thus far indicate that control of polymerization rate and molecular weight are only moderately effective strategies for control of additive diffusion, and that in the range of polymerization conditions used for *in-situ* suspension polymerizations, the predicted mean diffusion lengths remain unacceptably large (i.e., on the order of the droplet diameter). However, examination of the dependence of viscosity on polymer molecular weight and polymer concentration offers an alternative strategy. The dependence of viscosity on polymer concentration and molecular weight for dilute solutions can be approximately expressed as (Porter and Johnson, 1966)

$$\eta \propto \overline{M_w} c_p, \tag{18}$$

and for concentrated solutions as

$$\eta \propto \overline{M}_w^{3.4} c_p^5. \tag{19}$$

In the low conversion regime, viscosity (and therefore diffusion rate) is not nearly as sensitive to increases in polymer concentration and molecular weight as at higher conversion. This suggests that a better strategy for controlling diffusion would be to bypass the low conversion regime entirely and begin the polymerization with polymer already present. This is a less desirable option than controlling rate or molecular weight because of the additional process complexity it introduces. One of two approaches could be used. The first option would be to conduct a bulk prepolymerization of the monomer without the additives present, and then blend in the additives once the desired conversion had been reached. The partially polymerized mixture is then dispersed into an aqueous phase and heated to complete the polymerization in suspension. (Alternatively but equivalently a known weight of polymer can be dissolved in monomer to give the desired polymer concentration, and then initiators and additive particles can be blended in.) A potential problem with this approach lies in blending additive into a viscous mixture, particularly for additives that are difficult to disperse. A second option is to first blend the additive into the monomer, conduct a bulk polymerization to the desired conversion, disperse the partially polymerized mixture into aqueous phase, and then complete the reaction in suspension.

There is an additional process advantage to this type of approach; reactants can be added partway through the polymerization. This cannot be done in conventional suspension polymerization.

Effect of varying initial conversion

Figure 6 shows the results of simulated polymerizations in which particle formation occurred with partially polymerized monomer. Under these conditions, diffusion within the droplets commences only after a certain conversion has been attained. In terms of Eq. 4, the "viscosity history" the additive particles experience during the polymerization changes dramatically. For the styrene reactions the cumulative diffusion length is reduced to under 5 μm, and for MMA to under 1 μm. These lengths do represent a range where significant control of additive diffusion is achieved. The results clearly indicate that manipulating the initial viscosity via the monomer conversion is a far more effective route to controlling Brownian diffusion than control of either rate or molecular weight. The magnitude of the reduction in diffusion distances can be understood in terms of two primary factors: the importance of initial viscosity as discussed before, and the earlier commencement of the gel effect that leads to a rapid increase in conversion and molecular weight, and therefore viscosity. In fact if the initial conversion is at or near the

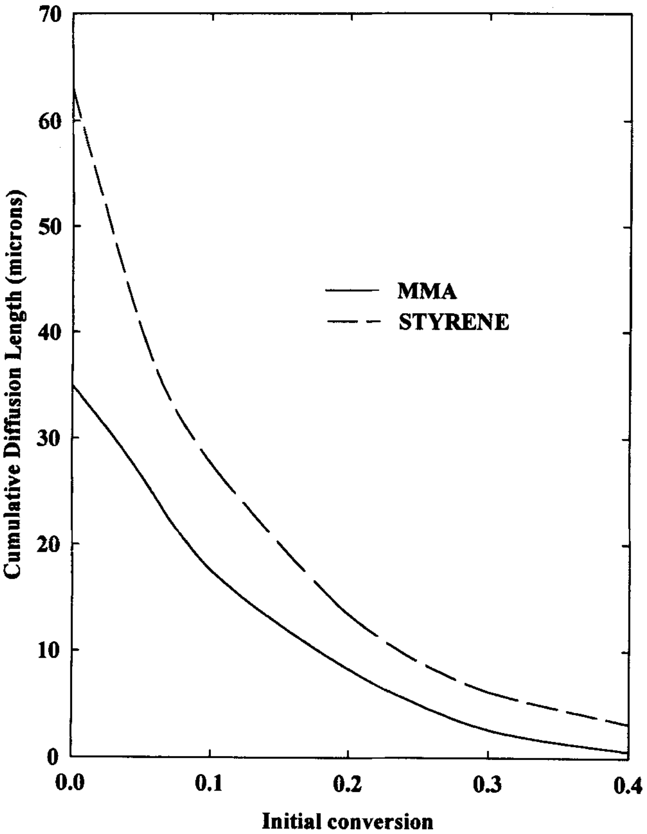


Figure 6. Effect of initial conversion for MMA (solid line) and styrene polymerizations (dotted line).

Polymerization conditions are those used in Figures 1 and 2. MMA: 60°C, 3.0 wt. % ADVN; styrene: 80°C, 2.5 wt. % BPO.

onset of the gel-effect, autoacceleration will begin almost immediately. This principle has been recently recognized (Mahabadi, 1991) in the "semi-suspension polymerization" process in which monomer is partially polymerized to low polymer concentration (by, for example, bulk polymerization) and the second stage of the polymerization is then completed in suspension. This process has been shown to enable preparation of particles with smaller particle size than can be achieved with conventional suspension polymerization because interparticle diffusion or mass transfer (coalescence) is reduced. Kalfas (1992) also recognized the importance of initial viscosity in attempts to develop a continuous suspension polymerization process. A bulk prepolymerization reactor was used to raise the initial organic phase viscosity prior to creating a suspension of droplets in order to minimize reactor fouling and plugging of outlet lines. The governing principle was analogous to the approach discussed here, that is, the minimization of mass transfer through manipulation of the initial viscosity in the polymerization droplets.

It is interesting to next consider how much improvement can be obtained by combining increases in the polymerization rate with increasing initial conversion. Figure 7 shows that increasing the rate when polymer is already present does further reduce diffusion, although the incremental benefit is significantly reduced as initial conversion increases. Similarly, the marginal benefits of higher molecular weight decrease somewhat as initial conversion increases, as shown in Figure 8. These results provide evidence that the most influential factor in determining diffusion rates is the initial viscosity, which is most practically controlled by varying initial conversion.

Temperature profiles and preparation time

The polymerizations simulated thus far have assumed isothermal temperature profiles, which is a reasonable assumption for small-scale laboratory reactors that can be heated from ambient temperature (where particle formation is done) to the reaction temperature in 1–2 min. However, in larger scale reactors dynamics are much slower. Consequently a finite time is required to heat a reactor's contents from ambient temperature to the desired reaction temperature. Heating rates on the order of 1°C/min are reasonable for 1,000–5,000 gal (6.9–34.4 MPa) reactors. During this heating period, additives will continue to diffuse under Brownian motion inside the polymerizing droplets. The lower the initial viscosity, the faster diffusion will be during the heating period. Another issue is that there may be additional preparation time required in the process between the time particle formation occurs and the time the polymerization reactor begins heating. For example, if different vessels are used for particle formation and polymerization, the suspension will have to be transferred between vessels. To investigate the effects of (1) finite heating and (2) preparation times, simula-

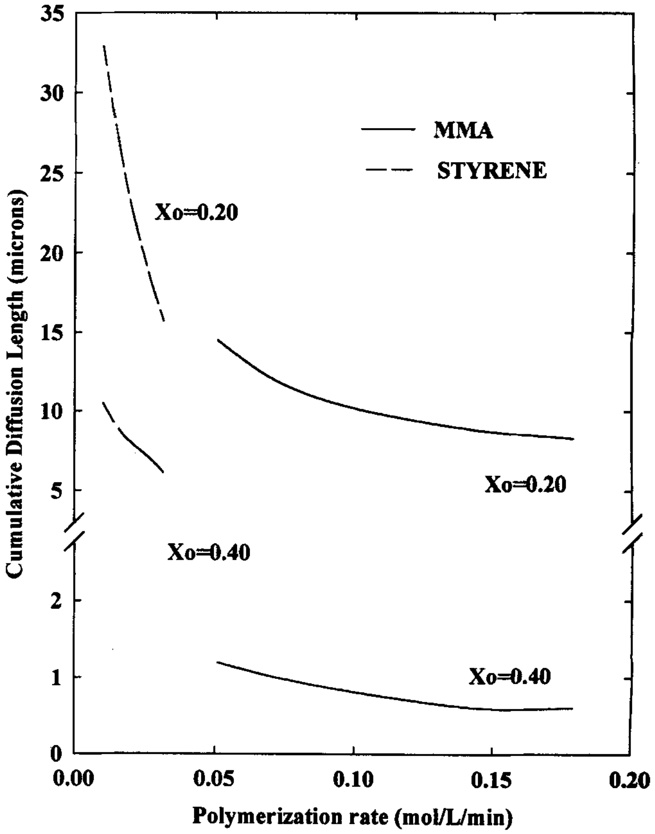


Figure 7. Effect of polymerization rate on cumulative diffusion length for MMA (solid line) and styrene (dotted line) polymerizations at 20% and 40% initial conversion.

MMA: 60°C, M_{w0} = 79 K; styrene: 80°C, M_{w0} = 34 K.

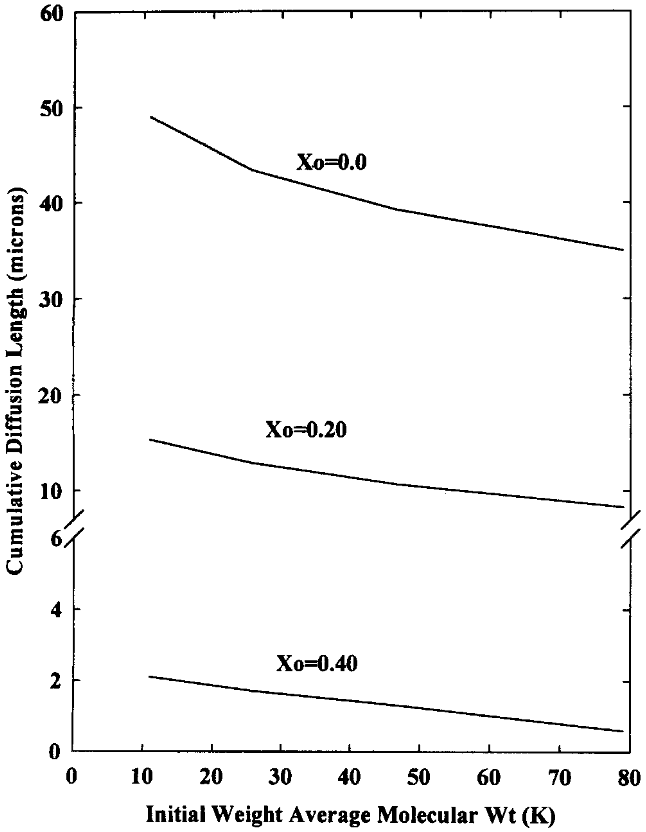


Figure 8. Weight average MW (initial) dependence of cumulative diffusion length for MMA at various initial conversions.

T = 60°C, 3.0 wt. % ADVN, R_{p0} = 0.18 mol/L/min.

tions were conducted assuming (a) a 30-min preparation time (i.e., a 30-min period between the time a particle is formed and when heating of that particle commences) and/or (b) a reactor heating rate of 1°C/min from 20°C to the desired reaction temperature. Figure 9 shows a comparison of results at various initial conversions during MMA polymerizations. When the initial conversion is low, considerable additional diffusion occurs during the preparation and heating times. In process scale-up this could present a major problem for which there is no simple remedy. However, as the initial conversion increases, the effects become significantly smaller, to the point where they virtually disappear beyond about 30% initial conversion. (Cumulative diffusion lengths are under 1 μm at higher conversions.) This type of process could be transferred from the laboratory to manufacturing scale with a much higher degree of confidence than a conventional *in situ* suspension polymerization. Two important observations are evident. The first is that initial conversion is by far the most powerful variable for controlling diffusion in polymerizing suspension particles. The second is that at sufficiently high initial conversion, the influence of other factors on diffusion becomes small or negligible.

The Model as a Process Design Tool

A model capable of describing both polymerization kinetics and the diffusional behavior can be of considerable value in designing a process to produce composite suspension polymerization particles. The unique feature of these polymerizations that distinguishes them from traditional suspension polymerizations is the presence of the additive that gives the product its real value. How well that additive is dispersed within the particle determines that value. The model presented calculates the cumulative diffusion length (CDL), but this is a quantity that cannot be directly measured experimentally. However, it is the most fundamental and most appropriate metric for designing a process and selecting reactor operating conditions. Although it cannot be directly measured, there are other means of assessing the CDL, both quantitative and qualitative. Many additives of interest will readily diffuse out of the polymerizing droplet into the aqueous phase once they diffuse to the droplet boundary. In this case determining the percentage of additive remaining within the particle (for example, by thermal gravimetric analysis (TGA)) provides a quantitative conservative estimate of the CDL (i.e., a lower limit). For example, if the particle diameter is 10 μm and all of the additive is retained, the mean CDL must be less than about 5 μm (particle radius). If a significant portion of the additive is lost to the aqueous phase, the mean CDL must be in excess of the radius. Because retention of all of the additive is essential to this type of process, those conditions that yield CDLs in excess of the particle

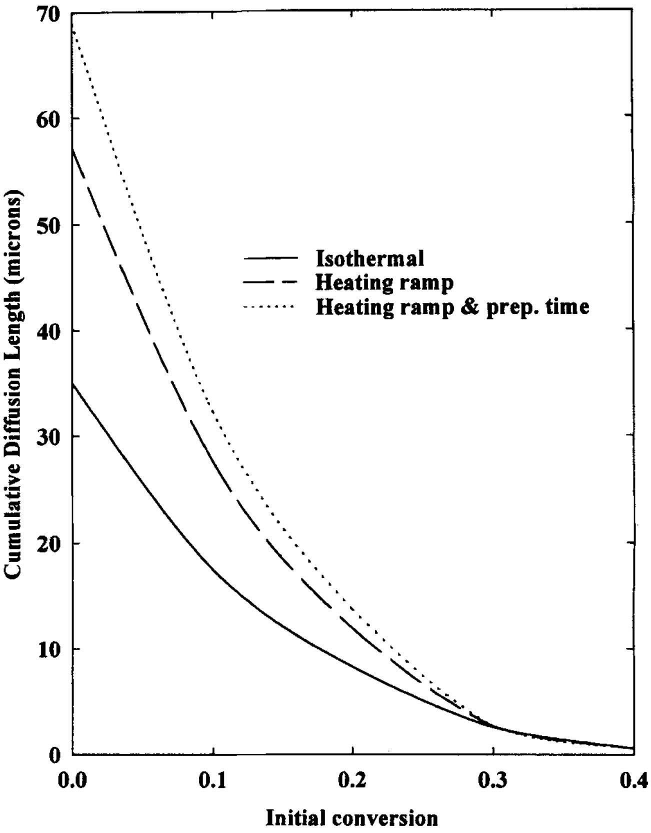


Figure 9. Cumulative diffusion length as a function of conversion during MMA polymerization, allowing for temperature ramping and preparation time (t = 60°C, 3.0 wt. % ADVN).

(i) isothermal, no preparation time; (ii) ramping rate of 1°C/min, no preparation time; (iii) 30 min preparation time followed by ramping rate of 1°C/min.

diameter are not of interest. Using the model, the process can be designed to ensure experiments are being conducted under conditions that will yield CDLs in the required range.

Designing a process using this model proceeds as follows. The first selection is the monomer. Although different monomers display a wide range of rates, and although the model has shown that faster polymerizing monomers will give lower CDLs, in most cases selection of the monomer will be dictated by end-use criteria, and hence there will be little flexibility. Similarly, additive selection will probably be confined. It would be preferable to use additives with larger diameters to minimize diffusion (see Eq. 2), but this may not be desirable for end-use properties. The next issue is the selection of the polymer particle size, which requires consideration of the intended application. This selection effectively determines the requirement for mean diffusion length; smaller particle sizes will require lower CDLs to prevent diffusion of the additives from the particle. The chosen particle size can be prepared by varying stabilizer type and concentration, and the agitation rate.

The remaining choices in designing the process are (1) initiator type and concentration, which affect the polymerization rate and molecular weight; (2) the reaction temperature profile, which also influences rate and molecular weight, as well as the diffusion coefficient (Eq. 2); and (3) the initial conversion. With the objective of minimizing the mean diffusion length, the design issue then becomes one of selecting the optimal combination of the conditions cited earlier for operating the reactor. It is at this stage that the model becomes a valuable design tool. With the polymer particle size specified, the requirement for the CDL is known. The model can then be used to guide the experimental program. Model development should not stop at this stage, but rather should be continuously refined as more experimental data becomes available.

Tables 3 and 4 present data showing the effects of varying initial conversion and initiator concentration, respectively, on the percentage of additive retained within the particles in MMA *in situ* suspension polymerizations. (This is the percentage of additive that does not diffuse out of the particle into the aqueous phase when it reaches the droplet surface, for an additive that readily diffuses into the aqueous phase.) The conditions are given in the table footnotes. As shown in Table 3, as the initial conversion increases from 0.0 to 0.30, the percentage of additive retained increases from 4.2% to 100%. When the initial conversion is at or near zero, the viscosity is sufficiently low that nearly all of the additive diffuses out of the polymerizing particle. Increasing the initial conversion reduces the cumulative diffusion length, and consequently a greater portion of the additive does not have the chance to diffuse as far as the particle boundary. When the initial conversion is 0.30, additive retention is 100%. For these conditions the model predictions of Figure 6 show the CDL decreasing from 34 μm to 3 μm as initial conversion is increased from 0.0 to 0.30. Given that the mean particle diameter is 13 μm in this data set, complete additive retention would require the CDL to be less than about 6.5 μm. The agreement between the experimental data (which represents a conservative estimate of the CDL) and the model predictions is quite good, and is sufficiently accurate to validate the model as a useful design tool. Table 4 shows experimental results of varying the initiator concentration and hence the polymerization rate when the initial conversion is 0.19. This situation illustrates a case where most of the additive is retained by virtue of having the initial conversion relatively high but the additive retention must be increased to 100%. Given this problem, the choice faced by the designer is one of trying to achieve 100% retention by further increasing initial conversion, which may pose experimental difficulties, or by increasing another variable such as the polymerization rate. As shown in Table 2 the percentage of additive retained shows little sensitivity to increases in the rate at this value of the initial conversion. There is a modest increase in additive retention, but it does not rise to the required 100%. The magnitude of the rate effect is in good agreement with the model predictions shown in Figure 7.

Figure 10 shows two transmission electron micrographs of PMMA particles made with different initial conversions. Figures 10a and 10b are for initial conversions of 0.10 and 0.30, respectively. In Figure 10a it can be seen that the additive still remaining has diffused to the particle boundary. In fact, about half of the additive that was originally present has diffused out of the particle altogether. In this case the CDL of the additive during polymerization must have been significantly larger than the particle radius (6.5 μm). In Figure 10b, however, the additive remains well-dispersed throughout the particle, with only a small accumulation at the boundary, indicating the CDL during polymerization was considerably less than the particle radius (5.5 μm). The predicted CDLs for Figures 10a and 10b of 20 μm and 3 μm provide semiquantitative agreement with the photographs.

Table 3. Effect of Initial Conversion on Weight Percentage of Additive Retained within the Particle*

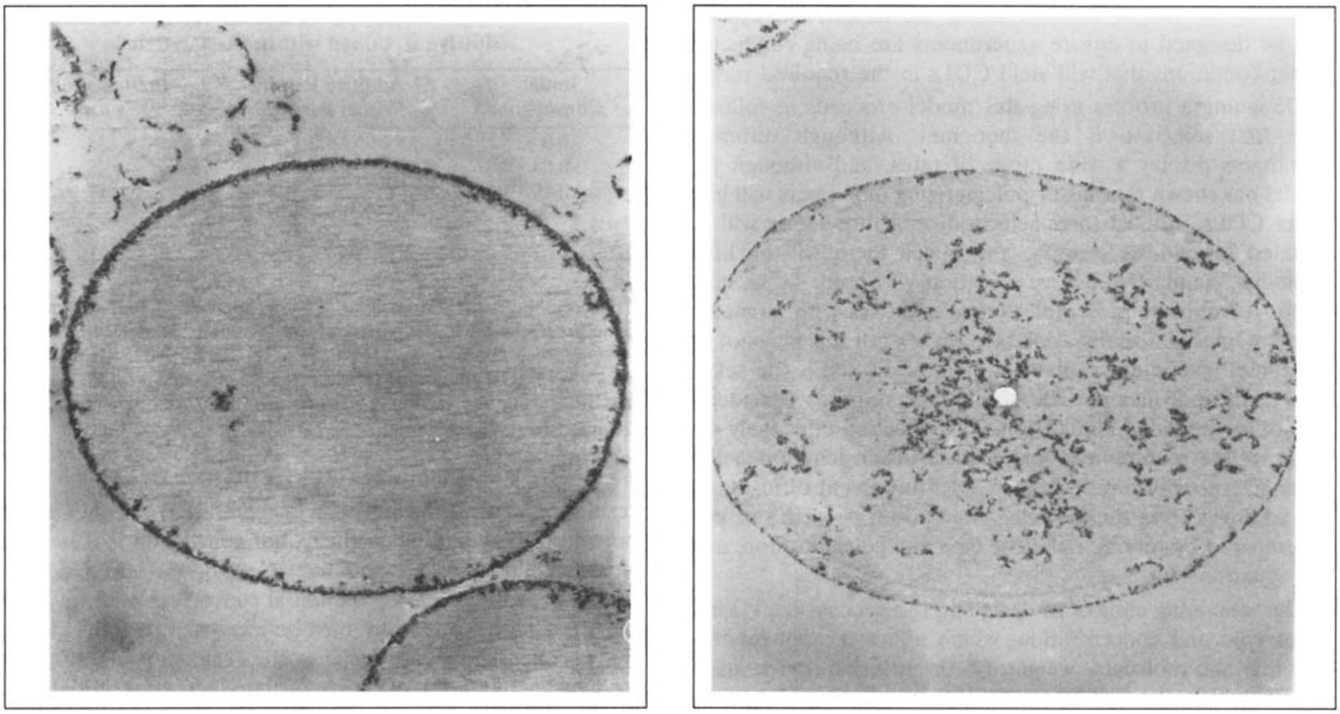
Initial Conversion	% Additive Retained Within Particle	Predicted CDL (μm)
0.0	4.2	34
0.04	16	28
0.10	51	17
0.19	86	8
0.30	100	3

*The remainder of the additive diffuses out of the particle into the aqueous phase during polymerization. Monomer is methyl methacrylate. Process conditions: 3.0 wt. % ADVN; $T = 60°C$ (isothermal). Mean volume diameter of final particles = 13 μm. Weight percentage filler retained within particles was measured by TGA. CDL (cumulative diffusion length) predictions are from Figure 6.

Table 4. Effect of Varying Initiator Concentration (ADVN) on the Weight Percentage of Filler Retained within the Particle*

Wt. Fraction ADVN	Polymerization Rate (Calc.) mol/L/min	% Additive Retained Within Particle	Pred. CDL μm
2.0	0.117	79	9.5
3.0	0.144	86	8.7
4.5	0.176	89	8.0

*Monomer is methyl methacrylate. Initial conversion 0.19; $T = 60°C$ (isothermal). Mean volume diameter of final particles = 13 μm. Weight percentage filler retained within particles was measured by TGA. CDL (cumulative diffusion length) predictions are from Figure 7.



(a)

(b)

Figure 10. Transmission electron micrographs of PMMA particles at different initial conversions.

(a) Initial conversion 0.10 (particle diameter 13 μm); (b) initial conversion 0.30 (particle diameter 11 μm).

Conclusions

A study of reactor operating strategies for minimizing the cumulative diffusion of additive particles during *in-situ* suspension polymerizations has been reported. Polymerization rate, initial molecular weight, and initial conversion were studied for MMA and styrene polymerizations. The most important factor in determining mean diffusion lengths is the initial conversion of the suspension droplets. Dispersion of the droplets should be done at the highest possible initial conversion (preferably 30% or greater) to minimize the cumulative diffusion that occurs during polymerization. Depending on the system in question, this may not be a trivial matter. It was shown, both computationally and experimentally, that at initial conversions of about 30%, mean diffusion lengths on the order of 1 μm are attainable. Diffusion lengths are further minimized, albeit moderately, by increases in polymerization rate and molecular weight. However, because rate and molecular weight cannot typically be adjusted independently, and since molecular weight is often a product specification, they may not be appropriate control factors. Another significant factor is the rate behavior of the monomer(s). In designing a process it should be remembered that a "fast" monomer is advantaged over a slower monomer. Preparation and reactor heating time, which represent unavoidable scale-up constraints, result in significant increases in diffusion distances at low initial conversions, but become negligible as the initial conversion increases beyond about 30%.

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Notation

g_p = gel-effect parameter for propagation
g_t = gel-effect parameter for termination
I = initiator
k_d = initiator-decomposition constant
k = chain-initiation constant
k_p = propagation-rate constant
k_t = overall termination-rate constant
k_{tc} = termination constant (combination)
k_{td} = termination constant (disproportionation)
k_{fz} = transfer constant to species z
k_{fm} = transfer constant to monomer
k_{tx} = rate constant for inhibition by species x
M = monomer
M_0 = molecular weight of repeating unit
P_i = polymer of chain length i
$R_0\cdot$ = primary radical
$R_i\cdot$ = radical of chain length i
$R_z\cdot$ = radical from transfer to species z
V_f = fraction-free volume
V_{fpc} = critical fraction-free volume for propagation
V_{ftc} = critical fraction-free volume for termination
x = conversion
x_o = initial conversion (at $t = 0$)
ϕ = volume fraction

Subscript and superscript

M = monomer

o = prior to onset of diffusion control

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