Modeling of Diffusion Effects on Step-Growth Polymerizations

Job D. Guzmán,*,† Richard Pollard,‡ and Jay D. Schieber§

The Dow Chemical Company, 2301 N. Brazosport, Freeport, Texas 77004, Plug Power, Latham, New York 12110, and Illinois Institute of Technology, Chicago, Illinois 60616

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ABSTRACT: The effect of diffusion on linear, step-growth polymerizations has been quantified via "chain-by-chain" simulations of the polymerization process and a diffusion model consistent with reptation theories. The results show that diffusion limitations can narrow the molecular weight distribution and alter the way it evolves during polymerization; e.g., when diffusion is the limiting step, the polydispersity index ($PDI_1 = M_w/M_n$) converges to a value of ~1.3 at complete conversion. Nevertheless, diffusion limitations have little effect on the time dependence of conversion. Consequently (for this type of polymerization), modeling of diffusion phenomena is important only when an accurate calculation of the MWD is needed. We also show that the numerical value of the Hatta number, at the point of entanglement (φ), can be used to determine whether diffusion limitations are likely to be important in a given system. Guidelines for the estimation of φ are given.

Introduction

Several methods for the calculation of molecular weight distributions (MWDs) have been developed for step-growth polymerizations.[1−4] Most of these methods rely on the so-called "equal reactivity assumption", which states that all polymer chains of the same functional group are equally reactive, regardless of their molecular weight or any diffusion limitations that might exist in their environment. The basis for this assumption lies in the notion that collision (and consequently diffusion) of reactive chain ends, and not of the whole chain per se, is necessary for reaction to occur. Indeed, for flexible polymers, the diffusion of chain ends is faster than most chemical reactions. For a typical step-growth polymerization, it is estimated that only one chain-end collision out of 10^{13} is fruitful.[1]

There are, however, several situations where the equal reactivity assumption fails. For example, if reactive chain ends are far apart, they may explore their own neighborhoods rapidly, but collisions among reactive ends will not begin to occur until the chains (they are attached to) diffuse to each other. Chain ends become isolated not only in dilute solution but also in a concentrated, high-molecular-weight polymer, where reactive chain ends are surrounded by inert polymeric material. As the reaction progresses, the concentration of chain ends decreases and diffusion limitations become more important. Eventually, the overall polymerization rate is likely to be affected by diffusion.[5] Moreover, because larger polymer chains have longer diffusion times than their smaller counterparts, chain-length dependence of the overall kinetic parameters can be anticipated.

Evidence of diffusion effects on reactivity and polymerization mechanism has been apparent since early experimental studies.[6] In free-radical polymerization, the presence of diffusion limitations is so well documented that different manifestations have been given particular names. The impact of diffusion on the termination step is labeled as the Trommsdorff or gel effect, while the effects on propagation and initiation are known as the glass and the cage effect, respectively. Different theories for the modeling of such effects have been proposed.[7−9]

Diffusion effects on step-growth polymerizations are understood somewhat less. Most experimental studies have focused on rigid-rod-like molecules. For these systems, segmental diffusion is no longer rapid, and diffusion effects are magnified. Agarwal and Khakhar[10] have shown that shearing can increase the polymerization rate of rigid molecules. Theoretical studies[11] suggest that flow-induced orientation can also increase the polymerization rate of flexible molecules, when the polymerization is controlled by diffusion. In addition to changing the polymerization rate, diffusion limitations have been shown to alter the MWD. Distributions resulting from "flow-enhanced" polymerizations are broader than those predicted using the equal reactivity assumption,[10] i.e., the polydispersity index (PDI_1) is greater than 2. In the absence of significant flow-induced orientation, however, the resulting MWDs are narrower than what equal reactivity would indicate,[12,13] i.e., $PDI_1 < 2$. Attempts have been made to eliminate flow effects completely. In quiescent conditions, Gupta and co-workers[13] observed a final polydispersity index of approximately 1.3 for diffusion-controlled step-growth polymerizations. Diffusion limitations also seem to affect the evolution of polydispersity during polymerization. In a biocatalyzed polytransesterification, Kline et al.[14] observed a maximum in the polydispersity index at intermediate conversions. This phenomenon was attributed to diffusion limitations.

Models to account for diffusion effects on step-growth polymerizations have been developed previously. For example, Beers[15] modeled rigid chains, Gupta el al.[16] studied a nonlinear step growth homopolymerization, and Oshanin and Moreau[17] obtained an analytic solution for linear homopolymerization. However, modeling of diffusion in reactive systems faces both theoretical and numerical challenges, and different authors have used different approximations to overcome these obstacles.

In the work of Beers,[15] chain-length distributions are approximated by Lagrange polynomials to reduce computational burden in the integration of the population

* Author to whom correspondence should be addressed.
† The Dow Chemical Company.
‡ Plug Power.
§ Illinois Institute of Technology.

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balances. In the case of Gupta et al.,[16] the diffusion process is represented "in a simplistic but effective fashion" by a step function; i.e., it is assumed that chains can only react if they are less than a specified distance apart. Their approach is used to describe changes in the weight-average molecular weight, but no information on polydispersity is reported. The work of Oshanin and Moreau[17] assumes that the influence of chain length i on the effective rate constant K_i is dramatic ($K_i \gg K_{i+1}$) in order to obtain an analytic solution.

In this work, we focus on flexible linear chains. The diffusion process is represented according to the theory of de Gennes.[18,19] We perform "chain-by-chain" simulations; i.e., we keep track of the concentration of every chain length so that additional approximations are not necessary to integrate the population balances. Also, modeling is extended beyond homopolymerization to include $A_2 + B_2$ step-growth polymerization (with the corresponding interplay between stoichiometric imbalance and diffusion effects).

Basic Equations

Homopolymerization. As an example of step-growth homopolymerization, consider the synthesis of Nylon via self-condensation of an amino acid

$$i\mathrm{H_2N{-}R{-}COOH} \rightarrow \mathrm{H{-}[NH{-}R{-}CO]}_i\mathrm{{-}OH} + (i-1)\mathrm{H_2O} \quad (1)$$

The reaction can be written as

$$(\mathrm{AB})_i + (\mathrm{AB})_j \xrightarrow{K_{i,j}} (\mathrm{AB})_{i+j} + \mathrm{H_2O} \quad (2)$$

where A and B represent the reactive functional groups (H_2N and COOH), and $K_{i,j}$ is the effective polymerization rate "constant" which, in the presence of diffusion limitations, depends on the lengths i and j of the two chains involved in the reaction. For an irreversible polymerization, the formation of a condensate (H_2O in the case of Nylon) does not affect the population balances of polymer chains. If one lets P_i denote the concentration of polymer chains with i repeat units, then in accordance with eq 2

$$\frac{\mathrm{d}P_i}{\mathrm{d}t} = \sum_{j=1}^{i-1} K_{i-j,j} P_{i-j} P_j - 2P_i \sum_{j=1}^{\infty} K_{i,j} P_j \quad (3)$$

where the factor of 2 appears because of the two reactions $(\mathrm{AB})_i + (\mathrm{AB})_j \rightarrow (\mathrm{AB})_{i+j}$ and $(\mathrm{AB})_j + (\mathrm{AB})_i \rightarrow (\mathrm{AB})_{j+i}$. Details concerning the derivation of eq 3 can be found elsewhere.[2] Also, note that eq 3 is a special case of Smoluchowski's coagulation equation.[20]

Typically, the initial condition for eq 3 is that only monomer is present at $t = 0$, i.e., if the initial monomer concentration is C_0, then

$$P_i = \begin{cases} C_0 & i = 1 \\ 0 & i > 1 \end{cases} \quad (4)$$

In the absence of diffusion limitations, the effective rate constant $K_{i,j}$ ought to reduce to the intrinsic reaction rate constant (k_{int}) which is given by the chemistry of the system and is independent of the chain lengths involved in the reaction. An expression consistent with this picture is

$$\frac{1}{K_{i,j}} = \frac{1}{k_{\mathrm{int}}} + \frac{1}{\mathring{k}_{i,j}} \quad (5)$$

In eq 5, $\mathring{k}_{i,j}$ is a "diffusional" rate constant, i.e., the polymerization rate for a system with no chemical barriers where reactions occur upon collision of functional groups. Collins and Kimball[21] appear to be the first to give a theoretical justification for eq 5. More recent theoretical studies supporting eq 5 also exist.[7,22]

For a bimolecular reaction, $\mathring{k}_{i,j}$ can be expressed in terms of the diffusivities $\mathscr{D}$ and trapping radii $\mathscr{R}$ of the reactants[20]

$$\mathring{k}_{i,j} \propto (\mathscr{R}_i + \mathscr{R}_j)(\mathscr{D}_i + \mathscr{D}_j) \quad (6)$$

Equation 6 is used here as a first approximation. For linear polymer systems, the implicit assumption is that the overall reaction time is greater than the time required for one chain to disengage from its original tube. Without this simplifying assumption, $\mathring{k}_{i,j}$ would be a function of the reaction time.[18,19] In eq 6, the trapping radius $\mathscr{R}_i$ is equal to the radius of gyration of a polymer chain with i repeat units.[18,19] Thus, for an ideal coil[23]

$$\mathscr{R}_i \propto \sqrt{i} \quad (7)$$

The relation between diffusivity and number of repeat units varies depending on whether the system is entangled or not[18,19]

$$\mathscr{D}_i \propto \begin{cases} i^{-1} & \text{nonentangled} \\ i^{-2} & \text{entangled} \end{cases} \quad (8)$$

In 1984, Tirrell[24] showed that available diffusion data were consistent with the "inverse square law" indicated by eq 8 for entangled, flexible, linear systems. More recent studies[25] suggest a slightly different exponent (-2.3 instead of -2). A value of two is used here, unless otherwise indicated. The sensitivity of the results to the value of this exponent is discussed in the results section.

The proportionality constants in eqs 6–8 can be lumped together. Consider the Hatta number (Ha)

$$\mathrm{Ha}(i,j) = \frac{k_{\mathrm{int}}}{\mathring{k}_{i,j}} = \frac{\phi}{(\sqrt{i} + \sqrt{j})(i^{-l} + j^{-l})} \quad (9)$$

where $l = 1$ below entanglement and $l = 2$ otherwise. Note that if $i < N_{\mathrm{ent}}$ and $j > N_{\mathrm{ent}}$, two different values of l will appear in eq 9. The larger the value of the constant ϕ, the more important diffusion is in the polymerization process. Conversely, $\phi = 0$ corresponds to the case of no diffusion limitations. In terms of the Hatta number the effective polymerization rate constant is given by

$$K_{i,j} = \frac{k_{\mathrm{int}}}{1 + \mathrm{Ha}(i,j)} \quad (10)$$

With $K_{i,j}$ defined by eqs 9 and 10, and given an initial condition (eq 4), eq 3 can be integrated to obtain the chain-length distribution P_i ($i = 1, 2, \ldots, \infty$). Knowledge of P_i permits the characterization of the polymer product.

The mth moment of the chain-length distribution is defined as

$$\lambda_m = \sum_{i=1}^{\infty} i^m P_i \tag{11}$$

The moments of the distribution can be used to calculate the number-average (DP_n) and weight-average (DP_w) degrees of polymerization

$$DP_n = \frac{\lambda_1}{\lambda_0} \tag{12}$$

$$DP_w = \frac{\lambda_2}{\lambda_1} \tag{13}$$

The polydispersity index PDI_1 is given by

$$PDI_1 = \frac{DP_w}{DP_n} = \frac{M_w}{M_n} \tag{14}$$

where M_n and M_w are respectively the number- and weight-average molecular weights, i.e., $M_n = M_0 DP_n$, $M_w = M_0 DP_w$, and M_0 is the molecular weight of the monomer.

Finally, the molecular weight distribution, i.e., the weight fraction W of chains of length i, is

$$W_i = \frac{iP_i}{C_0} \tag{15}$$

Since $\sum_{i=1}^{\infty} iP_i = C_0$ (at all times for the initial condition given), W_i in eq 15 is normalized according to $\sum_{i=1}^{\infty} W_i = 1$.

$A_2 + B_2$ Polymerization. Often, polymers are synthesized by reaction of not one but two bifunctional monomers. This leads to a more complicated reaction scheme than the one discussed in the previous section, and eq 3 needs to be modified. Consider, for example, the production of polyurethanes by reaction of diisocyanates and diols

$$O{=}C{=}N{-}R_{(1)}{-}N{=}C{=}O + HO{-}R_{(2)}{-}OH \rightarrow OCN{-}R_{(1)}{-}NH{-}COO{-}R_{(2)}{-}OH \tag{16}$$

If $(AB)_i$ represents a polymer chain of length i, with reactive end groups A and B, the chemical reactions are

$$(AA)_i + (BB)_j \xrightarrow{K_{i,j}} (AB)_{i+j} \qquad (BB)_i + (AB)_j \xrightarrow{K_{i,j}} (BB)_{i+j}$$
$$(AA)_i + (AB)_j \xrightarrow{K_{i,j}} (AA)_{i+j} \qquad (AB)_i + (AB)_j \xrightarrow{K_{i,j}} (AB)_{i+j} \tag{17}$$

To simplify the notation, let A_i be the concentration of chains of length i where both ends groups are of type A. In other words, $A_i \equiv (AA)_i$, and similarly, $B_i \equiv (BB)_i$ and $M_i \equiv (AB)_i$. With that notation, the population balances for the chemical reactions written above are

$$\frac{dA_i}{dt} = 2\sum_{j=1}^{i-1} K_{i-j,j} M_{i-j} A_j - 2A_i \sum_{j=1}^{\infty} K_{i,j}(M_j + 2B_j)$$
$$\frac{dB_i}{dt} = 2\sum_{j=1}^{i-1} K_{i-j,j} M_{i-j} B_j - 2B_i \sum_{j=1}^{\infty} K_{i,j}(M_j + 2A_j)$$
$$\frac{dM_i}{dt} = \sum_{j=1}^{i-1} K_{i-j,j}(4B_{i-j}A_j + M_{i-j}M_j) - 2M_i \sum_{j=1}^{\infty} K_{i,j}(M_j + A_j + B_j) \tag{18}$$

One peculiarity of $A_2 + B_2$ polymerizations, not present in homopolymerizations, is the possibility of stoichiometric imbalance. When the value of the initial index ratio $r = (A_1/B_1)|_{t=0}$ is different from 1, the attainable molecular weight of the polymer is severely limited.[2] Thus, $r \neq 1$ could delay or prevent the onset of diffusion effects.

Integration of eq 18 yields three chain-length distributions (A_i, B_i, and M_i). When moments are redefined as

$$\lambda_m = \sum_{j=1}^{\infty} i^m (A_i + B_i + M_i) \tag{19}$$

eqs 12−14 still apply. Similarly, the MWD (W_i) is given by

$$W_i = i(A_i + B_i + M_i)/\lambda_1 \tag{20}$$

The conversion p is defined in terms of the limiting reactant. For $r < 1$ with $C_0 = B_1|_{t=0}$

$$p = \frac{(1 + r)C_0 - \lambda_0}{2rC_0} \tag{21}$$

Note that λ_0 is proportional to the number of chains present in the reactive system. At $t = 0$, $\lambda_0 = A_1 + B_1 = (1 + r)C_0$. At $t = \infty$, $\lambda_0 = B_1 - A_1 = (1 - r)C_0$.

"Chain-by-chain" simulations of the polymerization process have been performed to quantify diffusion phenomena. This involves solving the population balances for all polymer chains with no averaging. In theory, the solution of an infinite set of ordinary differential equations (ODE) would be required, but in practice, accurate results can be obtained by solving a large but finite set of equations. An estimate for the number Inf of equations required is obtained from the analytic solution of the equal reactivity case. For most simulations it is satisfactory to use[26] Inf $\approx 10 \times DP_n$.

The Hatta number for two chains of lengths i and j can be expressed as a function of the smallest chain only, i.e.

$$Ha(i,j) \approx Ha(\min(i,j), \min(i,j)) = \varphi\left(\frac{\min(i,j)}{N_{ent}}\right)^{l-1/2} \tag{22}$$

where $\min(i,j)$ is the minimum of i and j and φ is a proportionality constant given by $\varphi = (\phi/4)(N_{ent})^{l-1/2}$. The constant φ is also the value of the Hatta number at the entanglement point (where $\min(i,j) = N_{ent}$). The larger the value of φ, the more important diffusion limitations. The basis for eq 22 is that large chains with limited or no mobility can still react if smaller, faster chains reach

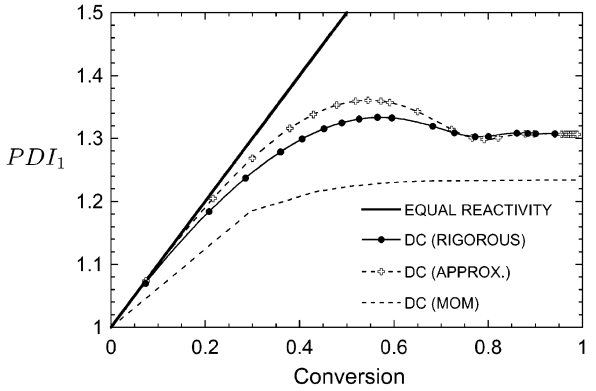

Figure 1. Evolution of PDI_1 for a step-growth homopolymerization. Equal reactivity: constant $K_{i,j}$. DC (rigorous): diffusion-controlled asymptote, $K_{i,j} = (\sqrt{i} + \sqrt{j})(i^{-2} + j^{-2})$. DC (approximation): diffusion-controlled asymptote calculated with $K_{i,j} = K_{\min(i,j),\min(i,j)} = 4 \times \min(i,j)^{-3/2}$. DC (MOM): diffusion-controlled asymptote calculated via the method of moments (MOM) and a closure approximation.[26]

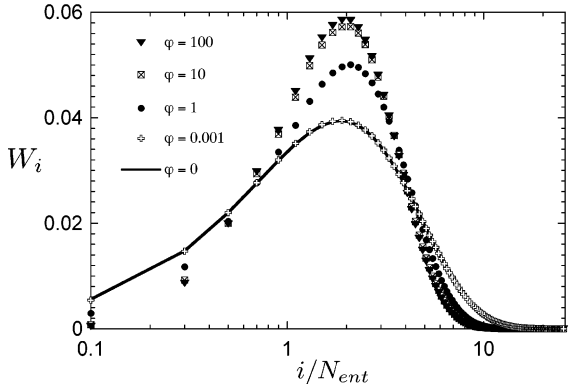

Figure 2. Effect of diffusion limitations on MWD. The results are for an irreversible, isothermal, $A_2 + B_2$ polymerization with $p = 0.999$, $r = 0.9$, and $N_{ent} = 10$. The larger φ, the more important diffusion is in the polymerization process. Only "oddmers" are plotted; the number of chains with an even number of repeat units is negligible due to the stoichiometric imbalance.

them. Therefore, it is assumed that polymerization of two chains is controlled by the diffusion of the smallest one. The Hatta number in eq 22 scales with chain length according to $l - 1/2 = 3/2$ for $\min(i,j) > N_{ent}$ and $l - 1/2 = 1/2$ otherwise. This is consistent with other theoretical studies.[18,19] The implementation of eq 22 can reduce memory requirements. In the codes developed here, memory requirements scale linearly with Inf when eq 22 is used. For eq 9, the scaling is quadratic. Additional information on the numerical technique is presented elsewhere.[26]

Results and Discussion

Homopolymerization. For a constant value of $K_{i,j}$ ($K_{i,j} = k_{int}$), the polydispersity index PDI_1 increases linearly with conversion. By contrast, in the diffusion-controlled regime ($K_{i,j} = \mathring{k}_{i,j}$), PDI_1 goes through a maximum at intermediate conversions and reaches a final value of approximately 1.3 (see Figure 1).

Two approximate calculations for the diffusion asymptote are also shown in Figure 1. One calculation is based on the method of moments and a closure assumption.[26] Computationally, this is the simplest way to estimate the diffusion-limited asymptote, but the estimate is not very good; viz., no maximum on the evolution of PDI_1 is observed, and the final PDI_1 value is below 1.3. The second approximate calculation is based on eq 22; i.e., the polymerization rate is expressed in terms of the smallest chain: $K_{i,j} \approx \mathring{k}_{(\min(i,j),\min(i,j))}$. This approximation improves computational efficiency without significant loss of detail. The maximum on the evolution of PDI_1 is retained, and results converge to the same final PDI_1 value observed for "rigorous" calculations.

For linear, entangled, flexible chains, the final PDI_1 value is not sensitive to the diffusion scaling "law" used. If, following Lodge,[25] the exponent in eq 8 is changed from -2 to -2.3, the predicted final polydispersity changes from 1.3 to 1.27. Whether polymer chains are entangled or not plays a more significant role. For the calculations shown in Figure 1, it was assumed that polymer chains are entangled at all times during the polymerization. If chains stay unentangled throughout the polymerization, the model indicates a final polydispersity of approximately 1.5. Similarly, chain architecture and rigidity are expected to be important factors. For rigid or branched polymers, the diffusion coefficient depends more strongly on chain length than the inverse square law or the Lodge model indicates.[27–29] For these systems, final polydispersity indices lower than 1.27 are anticipated.

$A_2 + B_2$ Polymerization. Here, we discuss cases where reactivity and diffusion limitations are comparable and when both entangled and nonentangled polymer chains are present. For computational efficiency, however, eq 22 is used instead of eq 9. The specific values for k_{int} and C_0 are not important because results are presented in dimensionless form. Results are sensitive to the initial index ratio r, the attained conversion p, and the value of φ (the magnitude of the Hatta number at the entanglement point). A value of $N_{ent} = M_e/M_0 = 10$ has been used in all simulations (M_e is the molecular weight between entanglements).

For an irreversible, isothermal, batch, $A_2 + B_2$ polymerization, it is found that diffusion limitations narrow the MWD. At small molecular weights, this occurs because the disappearance of short chains is favored relative to long chains (short chains can move more quickly to a reaction site). At high molecular weights, diffusion limitations also narrow the MWD because the accessibility of large molecules to reaction sites, which would produce even larger chains, is hindered.

Figure 2 shows the MWD at 0.999 conversion for an initial index ratio of 0.9. Results are presented for different values of φ. For $0.001 < \varphi < 10$, the exact distribution is sensitive to this parameter; it becomes narrower when the value of φ increases. When $\varphi > 10$, the diffusion-limited asymptote (where $K \rightarrow \mathring{k}$) is approached. Conversely, when $\varphi < 0.001$, the behavior corresponds to the kinetically limited asymptote (where the equal reactivity assumption applies).

Figure 2 also indicates that, for the same conversion, the peak of the MWD (a rough estimate of the number-average molecular weight M_n) is not sensitive to diffusion effects. This is because conversion is defined in terms of the number of chains that have reacted. At the same conversion (and for the same r), M_n is expected to be the same regardless of diffusion limitations. The MWDs for other values of the index ratio are qualitatively similar, but the range where the distributions are sensitive to the value of φ can differ from the one observed in Figure 2.

Table 1. Diffusion Parameters for PE[a] and PS[b]

	PE (HPB)[31,32]	PS[24,34]	units
T	125	175	°C
DM^2	0.25	0.01	(cm g/mol)^2 s^{-1}
E_D/R	3127	9020	K^{-1}
R/M	0.27	0.43	Å mol/g
M_e	1250	18500	g/mol
$\mathring{k}_{Me}$	4.5×10^8	4.0×10^5	L/(mol s)

[a] Polyethylene. [b] Polystyrene.

Table 2. Reaction Parameters for Typical Polymers[35]

polymer	T [°C]	k_{int} [L/(mol s)]	E_a/R [K^{-1}]
PET[a]	275	1.0×10^{-2}	7048
PU[b]	60	2.3×10^{-4}	4210
PA[c]		1.0×10^5	
PE[d]	60	5.4×10^8	156
PS[d]	60	6.0×10^7	962
PMMA[d,e]	60	2.6×10^7	1431

[a] Poly(ethylene terephthalate), catalyzed with Sb_2O_3. [b] Polyurethane. [c] Polyamide (from piperazine and terephthaloyl chloride). [d] The indicated rate corresponds to the termination step in free radical polymerization. [e] Poly(methyl methacrylate).

Table 3. φ Values for Typical Polymers[a]

polymer	φ	$(E_a - E_D)/R$ [K^{-1}]
PET	3.5×10^{-9}	
PU	1.3×10^{-7}	
PA[b]	1.4×10^1	
PE	2.2×10^0	−2971
PS	1.2×10^4	−8058
PMMA	5.9×10^3	

[a] T = 100 °C for both k_{int} and $\mathring{k}_{Me}$. [b] k_{int} was assumed to be independent of T.

The value of φ for a particular polymer can be determined if the molecular weight between entanglements, the diffusion coefficient, the radius of gyration, and the intrinsic reaction rate constant are known. When the diffusion process is characterized by one chain length (as in eq 22), the value of the diffusional rate constant can be obtained from[30]

$$\mathring{k}_{i,i} = 8\pi N_A \mathscr{R}_i \mathscr{D}_i \tag{23}$$

where N_A is Avogadro's number. The research groups of Bartels and Tanzer et al.[31,32] have obtained relevant data for hydrogenated polybutadiene (HPB, a polyethylene-like polymer). Combination of their experimental results (Table 1) into eq 23 yields $\mathring{k}_{Me} = 4.5 \times 10^8$L/(mol s) at 125 °C for M_e = 1250 g/mol (polyethylene's M_e[33]). This value of $\mathring{k}$ is rather large. The diffusional rate constant for other polymers, however, is expected to be smaller than 10^8 because most polymers contain bulkier side groups than HPB or polyethylene (PE). The diffusional rate constant for polystyrene (PS) is given in Table 1.

Polymers resulting from step-growth polymerizations (e.g., polyesters, polyurethanes, polyamides) may have $\mathring{k}_{Me}$ values similar to those of PS. Unfortunately, this could not be verified because values of $\mathscr{D}_M$ for these polymers could not be found in the literature.

Values for intrinsic rate constants of some typical polymerizations are given in Table 2. Note that, in general, free radical polymerizations are faster than their step-growth counterparts. Estimated values for φ are given in Table 3. To estimate φ values, it has been assumed that the $\mathring{k}_{Me}$ value of PS is representative of the diffusional rate constants of polymers obtained via step-growth polymerization.

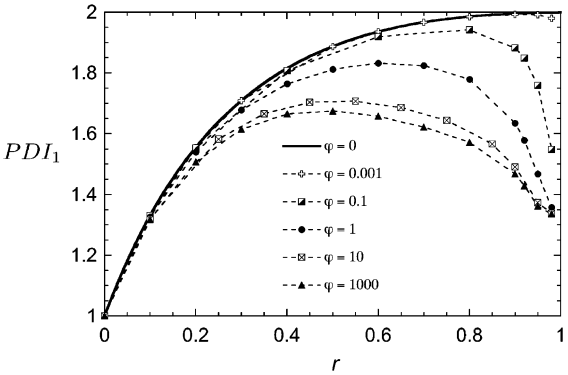

Figure 3. Effect of stoichiometric imbalance on PDI_1. The polydispersity index at 0.999 conversion is plotted against the value of r for different values of φ. Because of computer memory limitations, r = 0.98 is the highest index ratio simulated.

The results shown in Figure 2 indicate that the φ values for PET and PU (shown in Table 3) are too small for diffusion limitations to be significant. Diffusion limitation, however, can be important in other step-growth polymerizations. For example, in the formation of PA, the reaction of diacid chlorides and diamines is so fast (φ = 14) that the diffusion-controlled asymptote could be reached.

Figure 3 shows how the polydispersity index at 0.999 conversion depends on index ratios ranging from 0 to 0.98. When r = 0.6, the polydispersity index stays near the kinetically limited asymptote for values of φ as high as 0.1. On the other hand, for r = 0.98, the diffusion-limited asymptote can be reached with values of φ as low as 1. It appears that if one increases the value of r further, all MWDs with $\varphi > 0$ would eventually reach the diffusion-limited asymptote. This is because, in theory (neglecting cyclization reactions), chains can become arbitrarily large for this type of polymerization when r = 1. In that respect, results in Figure 3 for φ = 0.001 correspond to the kinetically limited asymptote only because, for r = 0.98, the molecular weight attained by the system is not high enough for diffusion to be important. For r = 0.98 and p = 0.999, polymer chains contain approximately 1000 repeat units as a maximum and only 100 on average. In this case, for φ = 0.001 and N_{ent} = 10, the Hatta number (eq 22) for the longest chain is 1, whereas the Hatta number for the average chain is only 0.032. That is not enough for diffusion limitations to affect the MWD.

Something analogous can occur in real polymers. Polymer chains cannot in general become arbitrarily large because of factors such as reversibility and side reactions. If the final molecular weight is not high enough and the value of φ is low, diffusion effects can be negligible. For $\varphi \geq 0.1$, however, diffusion limitations can affect the MWD significantly, even for moderate molecular weights (see Figure 3).

Predictions for $\varphi \geq 1$ appear to converge to a polydispersity index of ~1.3 at r = 0.98 and p = 0.999. Results were tested using different ODE solvers.[26] The convergence to 1.3 appears to be genuine. Recall that in the kinetically limited regime a final polydispersity index of 2 is reached at complete conversion. The model indicates an analogous 1.3 value for diffusion-controlled polymerizations (of linear, flexible chains).

Figure 4 shows the evolution of the polydispersity index (PDI_1) with increasing conversion p for various values of φ at r = 0.98. Without diffusion (φ = 0), PDI_1

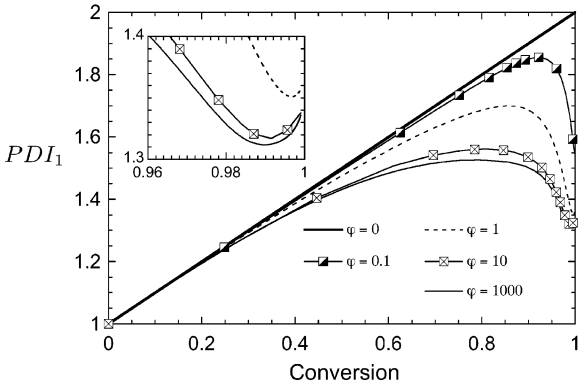

Figure 4. Evolution of PDI_1 for an $A_2 + B_2$ polymerization. $r = 0.98$ in all calculations. Values of φ indicate the importance of diffusion.

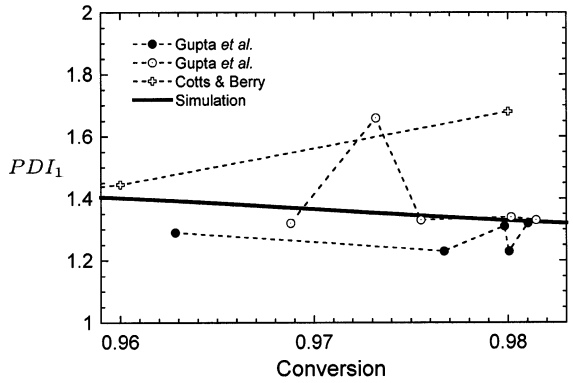

Figure 5. Chain-by-chain simulations and experimental data. Solid line: predictions for the diffusional asymptote of an $A_2 + B_2$ polymerization. Points: data for the step-growth polymerization of rodlike chains.[12,13] The two runs shown for Gupta et al.[13] differ in the initial concentration of monomer.

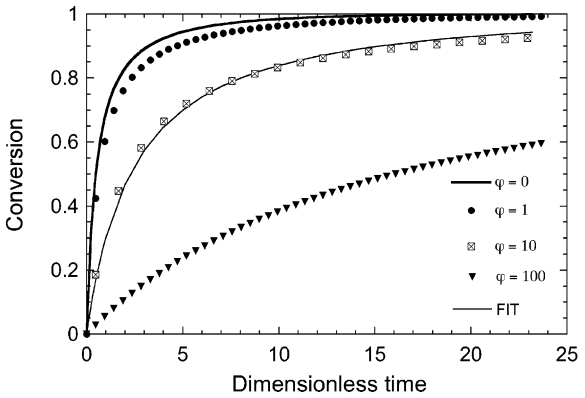

Figure 6. Effect of diffusion on reaction time. The dimensionless time, τ, is given by $\tau = C_0 k_{int} t$, where C_0 is the initial concentration of reactive groups and t is time. Different symbols in the figure represent the evolution of conversion for different values of φ. The thin line is the analytical result for an "ideal" polymerization (eq 24) where k_{int} was adjusted to fit the results for $\varphi = 10$.

increases monotonically as the polymerization proceeds since each reaction can create polymers chains of different lengths. In the presence of diffusion, however, the spread of the distribution reaches a maximum at $p < 1$. Beyond a certain p, PDI_1 decreases because the reaction of short chains is favored while the formation of long chains is hindered. Nevertheless, narrowing of the distribution does not continue indefinitely. A final upturn in the polydispersity index is observed for high values of φ (see inset in Figure 4). This upturn could explain why diffusion limitations do not generate a monodisperse polymer. As the MWD is narrowed, the concentration of chains of average length is maximized. There is a point where concentration effects outweigh diffusion phenomena. Then, chains of average length react preferentially to form larger chains, and the MWD continues its spread to higher molecular weights. Could this new spread of the distribution continue until the equal-reactivity MWD is recovered? It seems unlikely. At some point, diffusion-limitations should start dominating again, and the distribution would become narrower.

Nonmonotonic MWDs analogous to those presented in Figure 4 have also been found in the modeling work of Beers.[15] However, the nonmonotonic evolution of PDI_1 with increasing conversion is hard to confirm experimentally because diffusion-controlled reactions are normally very fast at early stages of the polymerization. In the few cases where the evolution of PDI_1 has been measured (for a diffusion-controlled, step-growth polymerization), data are available only at high conversions (where the variations in PDI_1 have already been damped).

Available experimental data and model predictions are presented in Figure 5. The experimental data correspond to step-growth polymerizations of rigid polymers. The data of Cotts and Berry[12] are probably affected by flow-induced orientation of the "rodlike" molecules because a conventional stirred tank was used to conduct the polymerization. To measure PDI_1 in "quiescent conditions", Gupta et al.[13] employed a customized dual-reactor system. It is not clear, however, why Gupta's data (for rigid polymers) converge to the same final polydispersity as our model for flexible chains. Factors other than flow could still be affecting the polymerization. Gupta et al.[13] proposed the presence of a slow side reaction.

Diffusion effects can retard the progress of a step-growth polymerization. However, whether a particular polymerization is hampered by reactivity or by diffusion limitations can be hard to discern. Consider the relationship[2]

$$p = \frac{1 - \exp[-2\tau(1-r)]}{1 - r\exp[-2\tau(1-r)]} \tag{24}$$

which is valid in the absence of diffusion effects. Equation 24 applies directly to the example with $\varphi = 0$ using $\tau = C_0 k_{int} t$. If τ is redefined as $\tau = C_0 k_{obs} t$, with k_{obs} as an adjustable parameter, eq 24 can also give results close to those of the diffusion model at other φ values. This is illustrated in Figure 6.

The proximity of eq 24 to the result with diffusion emphasizes that if one just needs to consider conversion rates, one can lump together the effects of diffusion and reaction and use an algebraic expression based on the equal reactivity assumption. In other words, the shape of experimentally obtained plots of conversion vs time is not affected by diffusion limitations. On the other hand, if intrinsic kinetics can be measured, e.g., by kinetic measurements in a dilute system, conversion vs time plots (in a concentrated system) can provide an estimate of the magnitude of diffusion limitations. Here, it has been found that the observed, lumped, reaction rate constant (k_{obs}) can be correlated with φ by

$$\varphi \approx 3\left(\frac{k_{\text{int}}}{k_{\text{obs}}} - 1\right) \tag{25}$$

To obtain eq 25, k_{obs} values (in eq 24) were fit to conversion plots (obtained via chain-by-chain simulations) for different values of φ and k_{int}. Since $\varphi = k_{\text{int}}/\mathring{k}_{\text{Me}}$, eq 25 provides an alternative to eq 23 for the estimation of $\mathring{k}$ values.

Other Factors Affecting Polymerization. The results presented here describe the effect of diffusion limitations in isolation from other factors such as volume and temperature changes, the presence of solvent, reversibility, and side reactions. However, the model can be modified to account for these factors without much difficulty. For example, eqs 3 and 18 apply to a batch reactor if either the volume V is constant or the concentrations are expressed per total mass. To consider volume changes explicitly, multiply the population balances by V, e.g., for homopolymerization

$$\frac{\mathrm{d}}{\mathrm{d}t}(VP_i) = V\left(\sum_{j=1}^{i-1} K_{i-j,j}P_{i-j}P_j - 2P_i\sum_{j=1}^{\infty} K_{i,j}P_j\right) \tag{26}$$

To integrate eq 26, an expression for the time dependence of V is needed. Often, a linear dependence with conversion is assumed, e.g.

$$V = V_0(1 + \epsilon p) \tag{27}$$

In the absence of cooling, the temperature usually increases with conversion during a polymerization. Since activation energies for diffusion in polymers can be larger than those for polymerization (see Table 3), one can expect φ to decrease with increasing temperature. Hence, if diffusion effects are not important under isothermal conditions, they will be even less important under, say, adiabatic conditions.

The presence of solvent not only enhances the mobility of chains but also reduces the dependence of $\mathring{k}_{i,j}$ on chain length.[22] In a dilute system, diffusion limitations are not likely to affect the MWD, but they could still decrease the polymerization rate. At infinite dilution, the diffusional rate constant for a second-order reaction where concentrations are expressed in mol/m^3 can be estimated using[22]

$$\mathring{k} = RT/\eta_{\text{s}} \tag{28}$$

where $\mathring{k}$ is assumed to be chain length independent and η_{s} and R correspond to solvent viscosity and universal gas constant (8.314 J/(mol K)), respectively. Note that eq 28 is consistent with the Stokes−Einstein relation ($\mathscr{D} = k_{\text{B}}T/(6\pi\eta_{\text{s}}\mathscr{R})$) and eq 23.[36]

Population balances for a reversible $A_2 + B_2$ polymerization are given elsewhere.[26] The presence of reversibility is expected to lessen diffusion-limitation effects because thermodynamic equilibrium is not affected by transport processes. At equilibrium, the equal-reactivity MWD should be recovered. Diffusion limitations, however, could delay the approach to equilibrium significantly. Equilibrium for a diffusion-limited system might not be attainable in typical polymerization processes. Moreover, reaching equilibrium in step-growth polymerizations is often unwanted. In cases where a condensate byproduct is formed during polymerization, the reaction is often forced to completion by removal of the condensate. If the condensate removal rate is very fast, the polymerization can be considered irreversible. Away from this limit, it would be necessary to describe the dynamics of condensate removal in the model.

Diffusion limitations are likely to favor cyclization reactions. The population balances given here can be modified to include these and, in principle, other side reactions. Population balances for cyclization reactions can be found elsewhere.[2]

Conclusions

A modeling framework for the analysis of diffusion effects on step-growth polymerizations has been developed. Modeling results indicate some characteristic features of diffusion-affected step-growth polymerizations, namely that (i) diffusion limitations narrow the MWD, (ii) the evolution of PDI_1 with conversion is not linear, and (iii) a final PDI_1 of ~1.3 is predicted.

If diffusion limitations are important, mathematical models of step-growth polymerization that use parameters where the effects of reaction and diffusion are lumped together are only satisfactory when interest is confined to the number-average molecular weight and the time dependence of the conversion. The results presented here show that if knowledge of the polydispersity index or the molecular weight distribution (MWD) is required, the models should represent diffusion as an independent physical process.

Diffusion phenomena can be described using the Hatta number Ha, a dimensionless ratio of reaction and diffusion rates. This parameter is a function of chain length but may be characterized uniquely by its value φ where the chains become entangled. There is a range of values for φ (approximately $0.001 < \varphi < 10$ for typical molecular weights) over which the behavior shifts from the asymptotes of kinetic control (the equal-reactivity MWD) to diffusion control. Guidelines for the estimation of φ have been presented. If the value of φ is low (i.e., $\varphi < 0.001$), diffusion limitations are unlikely to affect the polymerization process. Since the definition of φ is independent of the polymerization mechanism, the value of φ is also expected to be an indication of the importance of diffusion limitations in polymerization mechanisms other than linear step growth. The range for φ, however, depends on the final molecular weight reached by the system. If the molecular weight is exceptionally high, diffusion effects could be observed even for values of φ below 0.001.

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(5) The number of chain ends in the system λ_0 is inversely proportional to the average chain length DP_{n} (e.g., for homopolymerization, $\lambda_0 \propto (1 - p)$ and $\text{DP}_{\text{n}} = 1/(1 - p)$, thus $\lambda_0 \propto 1/\text{DP}_{\text{n}}$). For that reason, despite the fact that the overlap parameter $\mathscr{P}$(the number of chains partially contained inside the pervaded volume of a give chain) increases with the square root of chain length ($\mathscr{P} \propto \sqrt{N}$), the number of chain ends in the pervaded volume $\hat{\lambda}_0$ is still expected to decrease with chain length: $\hat{\lambda}_0 \sim 1/\sqrt{N}$. This indicates that segmental diffusion alone will have an ever-increasing difficulty to bring chain ends together. We hypothesize that at some point the diffusion of the whole chain becomes necessary.

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