

Film Diffusion Effects in Nylon 6,6 Polymerization

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Synopsis

An unsteady reaction-diffusion model has been developed to represent the polymerization of a nylon 6,6 prepolymer in a stationary film. A realistic kinetic and equilibrium description is incorporated by the use of apparent rate and equilibrium constants that are composition dependent. The model is suitable for evaluating the effect(s) of changes in throughput (film thickness), temperature, and catalyst activity on the performance of an idealized film reactor. The model is characterized by a single dimensionless parameter, the Thiele modulus. The composition-dependent kinetic constants are important for accurate prediction of molecular weight evolution in the film. Below a threshold value of the Thiele modulus, molecular weight generation is reaction-controlled, while above another threshold value it is diffusion-controlled.

INTRODUCTION

Most esterifications and amidations are reversible and the commercial production of polyesters and nylons requires significant condensate removal in order to reach a useful molecular weight ($M_n \approx 20,000$ g/mol). Therefore, proper understanding of the simultaneous reaction-diffusion problem is necessary as a fundamental basis for process models that incorporate mass transfer effects in polycondensation reactors.

Other studies have examined the problem of simultaneous reaction and diffusion in reversible polycondensations. Secor¹ analyzed the problem by numerically solving the penetration theory equations but did not investigate the effect of film thickness on the reaction. Hoftyzer and van Krevelen² also used a penetration theory model and linearized the second-order polymerization rate expression; their results are limited to small changes in bulk concentration. Gupta, Agarwalla, and Kumar³ studied the effect of mass transfer on polycondensations in simple geometries (film, solid, and hollow spheres) at very low molecular weights. Ault and Mellichamp⁴ and Amon and Denson⁵ have also formulated diffusion models for wiped-film reactors for polycondensations. In all of these studies, the effect of mass transfer was analyzed for systems with composition independent reaction rate and equilibrium constants and no gas-phase diffusional resistance to mass transfer.

It is well known that many polyamidations and polyesterifications appear to change reaction order with conversion. This apparent change has been quantified for nylon 6,6 with an activity-based kinetic model.⁶ In this paper, we will investigate the effect of these nonideal kinetics on a polymerization in a stagnant, stationary liquid film. In the vapor space above the film, there is a

large volume of steam vapor. Mass transport is assumed to take place between the film and the vapor in a direction perpendicular to the film. Initially, the film contains a nylon 6,6 prepolymer at equilibrium. In contrast to previous studies, the water transport is described by a constitutive relation that uses the gradient of the mole fraction of water as the driving force for diffusion, thereby leading to a model that requires only a single mutual diffusivity.

One of the goals of this study is to describe the time evolution of the molecular weight and the polydispersity (averaged across the film) for a range of representative film thicknesses and reaction conditions. Although we will assume that a Flory distribution exists locally throughout the film, the polydispersity of the entire film may deviate from 2. (This always happens when two or more fractions of the same polydispersity but different number average molecular weights are mixed.) A dimensionless group, the Thiele modulus, which is the ratio of a characteristic diffusion to a characteristic reaction time, will be important for our modeling and for interpreting the model results. For example, it is expected that, at low Thiele moduli, the molecular weight growth will proceed under reaction control, while at high Thiele moduli it will proceed under diffusion control. By simulation we will determine the range of values of the Thiele modulus that lead to diffusion control, or to reaction control along with the range of values where both are important.

PRELIMINARIES

The conservation of species mass in an n component mixture can be expressed by⁷

$$\frac{\partial C_i}{\partial t} + \vec{\nabla} \cdot \vec{N}_i = r_i \quad (1)$$

where \vec{N}_i is the flux of component i relative to fixed spatial coordinates. This flux is defined as

$$\vec{N}_i = C_i \vec{v}_i \quad (2)$$

where C_i is the molar concentration and \vec{v}_i is the velocity of component i relative to fixed spatial coordinates. Most constitutive relationships for diffusion are written, not in terms of \vec{N}_i , but in terms of fluxes relative to some average velocity. The molar average flux of component i relative to the molar average velocity, \vec{J}_i , is defined as

$$\vec{J}_i = C_i(\vec{v}_i - \vec{v}^*) \quad (3)$$

where the molar average velocity \vec{v}^* is defined as

$$\vec{v}^* = \frac{\sum_{i=1}^n C_i \vec{v}_i}{\sum_{i=1}^n C_i} = \sum_{i=1}^n x_i \vec{v}_i \quad (4)$$

The relative molar fluxes of the species obey the relation [see eqs. (3) and (4)]

$$\sum_{i=1}^n \vec{J}_i = \vec{0} \quad (5)$$

It is important to relate the two fluxes in order to incorporate an appropriate constitutive relation into the mass balance. The necessary relationship is

$$\vec{N}_i = \vec{J}_i + x_i \sum_{j=1}^n \vec{N}_j \quad (6)$$

where x_i is the mole fraction of component i which is given by $x_i = C_i/\hat{C}$. The total molar density, $\hat{C} = \sum_{i=1}^n C_i$ is related to the sum of the fluxes by the following identity that is used in deriving eq. (6):

$$\sum_{i=1}^n \vec{N}_i = \hat{C} \vec{v}^* = \sum_{i=1}^n C_i \vec{v}_i \quad (7)$$

CONSTITUTIVE RELATIONS

For multicomponent diffusion, a common generalization of Fick's law is

$$-\vec{J}_i = \sum_{j=1}^{n-1} d_{ij} \vec{\nabla} C_j, \quad i = 1, \dots, n-1 \quad (8)$$

In this relation, the driving force for diffusion is taken to be the gradient of molar concentration, $\vec{\nabla} C_j$. Another class of constitutive relations may be obtained by using the gradient of mole fraction, $\vec{\nabla} x_j$, as the driving force⁷⁻⁹:

$$-\vec{J}_i = \sum_{j=1}^{n-1} \hat{C} D_{ij} \vec{\nabla} x_j, \quad i = 1, \dots, n-1 \quad (9)$$

These two constitutive relations are identical if and only if the total molar density (\hat{C}) is constant. In general, the elements of the two matrices of diffusion coefficients D_{ij} and d_{ij} will not be equal, although they are interrelated. In addition, these matrices are often composition dependent. If the Onsager reciprocity relations are valid,¹⁰ then these matrices possess certain strong "positiveness" properties.¹¹ However, the validity of the Onsager relations has been challenged in numerous publications.¹²

For a binary mixture of polymer molecules (P) and water (W) the diffusivity matrix reduces to a scalar. This diffusivity describes the relative mobility of the two species and may be composition dependent. From eqs. (5) and (9) and the definition of mole fractions ($x_P + x_W = 1$), we see that⁹

$$D_P = D_W = D \quad (10)$$

Therefore, if eq. (9) is used as a constitutive relation, it is inconsistent (and, in fact, unnecessary) to assume anything but a single diffusivity for a binary system. This is true even if one of the two components is completely stationary relative to fixed laboratory coordinates (e.g., an entangled polymer in a solvent). This further emphasizes the fact that the single diffusivity describes only the *relative motion* of the two components.

From eq. (8) and the definition of the total molar density ($\hat{C} = C_p + C_w$) it follows that

$$\vec{0} = (d_w - d_p) \vec{\nabla} C_w + d_p \vec{\nabla} \hat{C} \quad (11)$$

This relation shows that the diffusivity of the polymer and the water are equal only when $\vec{\nabla} \hat{C} = \vec{0}$, a very unlikely occurrence for two species of very different sizes.

If the composition dependence of the diffusivity for the nylon 6,6-water system were known for each constitutive law, there would be no difference in using either of them. Since we do not have any data on the composition dependence, and do not know the relative sensitivity of the diffusivities in the two constitutive relations, the choice becomes one of convenience and we use eq. (9) since it leads to a single diffusivity for a binary system. In addition, the Vrentas and Duda free volume theory¹³⁻¹⁵ predicts that the diffusivity that appears in eq. (9) should have a weak dependence on molecular weight and on solvent concentration under the conditions being studied ($T > T_g + 200^\circ\text{C}$ and less than 10 wt % solvent), especially for a solvent molecule as small as water. Limited experimental evidence on a crystalline polymer in a solvent (polyethylene in *o*-xylene) is in agreement with this prediction.¹⁶ This is important since we will treat the diffusivity as independent of concentration in our model.

NYLON 6,6 POLYMERIZATION

The polyamidation reaction may be represented as



where an amine (A) and carboxyl (C) end group react to form an amide linkage (L) and a water molecule (W). The reaction rates for the individual species are related by

$$r = r_w = r_L = -r_A = -r_C \quad (13)$$

The reaction rate is given by

$$r = k_{app} C_T [X_A X_C - (1/K_{app}) X_L X_W] \quad (14)$$

where $X_i = C_i/C_T$ and $C_T = C_A + C_C + C_L + C_W$ are the mole fractions and total molar concentration for the reacting mixture. The apparent rate and equilibrium constants in eq. (14) are complicated but known functions of temperature and composition.⁶

There are two sets of molar concentration (\hat{C} and C_T) and two corresponding sets of mole fractions (x_i, X_i) for the reacting mixture. For diffusion, the mixture is treated as a binary mixture of polymer and water since the end groups of a polymer molecule cannot diffuse independently from its amide linkages. Therefore, the binary total molar density and mole fractions are $\hat{C} = C_p + C_w$, $x_w = C_w/\hat{C}$, and $x_p = C_p/\hat{C}$. This implies that the polymer concentration is equal to the concentration of either end group for a stoichio-

metrically balanced feed (i.e., $C_P = C_A = C_C$). However, to describe the reaction, the mixture is treated as one containing four components—amine and carboxyl end groups, water and amide linkages—since the reactivity of these species depends only on the local environment. The total molar concentration for the quaternary mixture and the mole fractions are $C_T = C_A + C_C + C_L + C_W$ and $X_i = C_i/C_T$. It should be noted that for a polymer-solvent system the approximation that the total binary molar concentration (\hat{C}) is constant is a poor one.

STATIONARY FILM MODEL

The motion of all the chains of various lengths in the reacting prepolymer is described by a single diffusivity. Otherwise one would be forced to treat every species of differing chain length as an independent component giving rise to many additional diffusivities and conservation equations. We will treat the diffusivity as composition independent and the polymer will be assumed to be immobile with respect to fixed coordinates ($\vec{N}_P = \vec{0}$). Then, from eqs. (7) and (9)

$$\vec{N}_W = -\frac{\hat{C}D}{1-x_W} \vec{\nabla}x_W \quad (15)$$

where mole fractions denoted by lower case x are based on the pseudobinary representation of the liquid solution, i.e., $x_W = C_W/\hat{C}$ and $x_P = C_P/\hat{C}$. The assumption that the polymer does not move is frequently employed^{4,5} and is a good approximation when the polymer chains are entangled, but may be less accurate in the early stages of the polymerization.

Combining eq. (15) with the continuity eq. (1) leads to the following evolution equation for the water concentration:

$$\frac{\partial C_W}{\partial t} = \frac{\partial}{\partial Z} \left(\frac{\hat{C}}{1-x_W} \frac{\partial x_W}{\partial Z} \right) + \phi^2 r \quad (16)$$

Similarly for the polymer,

$$\frac{\partial C_P}{\partial t} = -\phi^2 r \quad (17)$$

The variables in the model have been scaled with respect to a characteristic time, length, concentration, and reaction rate constant. All further references to quantities appearing in eqs. (16) and (17) are dimensionless. We have chosen the characteristic time as (H^2/D) , where the diffusivity is taken at the temperature of the system. The length was chosen as the film height (H) and the concentration as the initial value for water (C_W^0). For the characteristic reaction rate constant we use the value at 200°C as both the water and the carboxyl end group mole fractions approach zero ($k_{app}^0 = 2.926/h$). In chemical reactor engineering, the dimensionless group that appears in eqs. (16) and (17) is the Thiele modulus,¹⁷ which may be thought of as the ratio of a

characteristic diffusion time to a characteristic reaction time.

$$\phi^2 = \frac{H^2/D}{1/k_{\text{app}}^0} = \frac{t_{\text{diffusion}}}{t_{\text{reaction}}} \quad (18)$$

The Thiele modulus will be important in interpreting the simulation results.

BOUNDARY CONDITIONS

From eqs. (16) and (17) we can see that two boundary conditions on the water concentration together with initial conditions for both polymer and water are required. The initial concentrations ($t \leq 0$) of amide linkages, amine and carboxyl ends, and water molecules is assumed to be uniform throughout the film. For $t > 0$ the water mole fraction at the gas-film interface is set to a fixed value depending on the ambient steam temperature and the pressure; Henry's law can be used to determine this constant

$$X_w = y_w P / \gamma_w P_w^0 \quad (19)$$

where y_w is the water mole fraction in the gas phase, γ_w the activity coefficient of water in the liquid phase, P_w^0 the vapor pressure of water, and P is the total pressure. Note that the mole fraction of water in the liquid phase in eq. (19) is a quaternary mole fraction, which is consistent with the fact that the activities of the solution should be described by these mole fractions.⁶ Since the incoming feed is about 90 mol %, amide linkages one may easily show that the concentration of water ($C_w = X_w \hat{C}$) can only change by about 3% at the interface ($Z = 1$) even if the reaction proceeds to completion. Thus, C_w can safely be taken as a constant at the gas-film interface.

At the wall ($Z = 0$) we assume that the flux of water is zero ($\vec{N}_w = \vec{0}$) or equivalently $\partial x_w / \partial Z = 0$ from eq. (9).

RESULTS AND DISCUSSION

The method of lines¹⁸ was used to integrate partial differential equations (16) and (17). Since we are assuming that no side reactions occur, that the polymer does not diffuse, and that an equimolar feed is used, the amine and carboxyl end group concentrations are equal to each other and to the concentration of polymer molecules. From the change in the amine end-group concentration and the initial condition, the amide linkage concentration was calculated.

A comprehensive picture of the relative importance of reaction and diffusion can be found by examining values of the Thiele modulus range from 0.1 to 100 (see Table I), which correspond to film thicknesses of 0.2–5.5 cm and a value for the diffusivity of water in a nylon 6 melt¹⁹ at 265°C of 2.5×10^{-4} cm²/s. The values of the characteristic diffusion time (H^2/D) are also shown in Table I. The characteristic reaction time ($1/k_{\text{app}}^0$) is 0.34 h.

The value of the Thiele modulus depends directly on the value of the reference reaction rate constant (characteristic reaction time) and on the system temperature through the temperature dependence of the diffusivity.

TABLE I
Typical Values of the Thiele Modulus at 265°C

H (cm)	H^2/D (min)	ϕ^2
0.2	2	0.1
0.4	10	0.5
1.2	100	5.0
1.7	200	10.
5.5	2000	100.

We have chosen k_{app}^0 to be 2.926/h, the value of the rate to be constant as the water, and amine end-group concentrations to approach zero at 200°C. If we had chosen 240°C as our reference temperature, the Thiele modulus would range from 0.6 to 600 for the same values of H^2/D in Table I.

Initially, the film contains a nylon 6,6 prepolymer ($M_n \approx 3500$ g/mol) at equilibrium containing 7.5% (wt) water. All model results are for the isothermal case (250°C). This is below the melting temperature of nylon 6,6²⁰ (265°C), although it is a typical low molecular weight processing temperature.²¹ However, we have estimated the melting point of the stationary film at equilibrium (infinite time) to be approximately 251°C with Flory's²² theory for melting point depression of polymers by solvent.

The water concentration profile for Thiele modulus approaching zero is shown in Figure 1. The base of the film is at $Z = 0$ and the gas-film interface is at $Z = 1$. At $\phi^2 = 0$, the reaction does not occur and the usual solution to the diffusion equation is obtained. The simulation results for a Thiele modu-

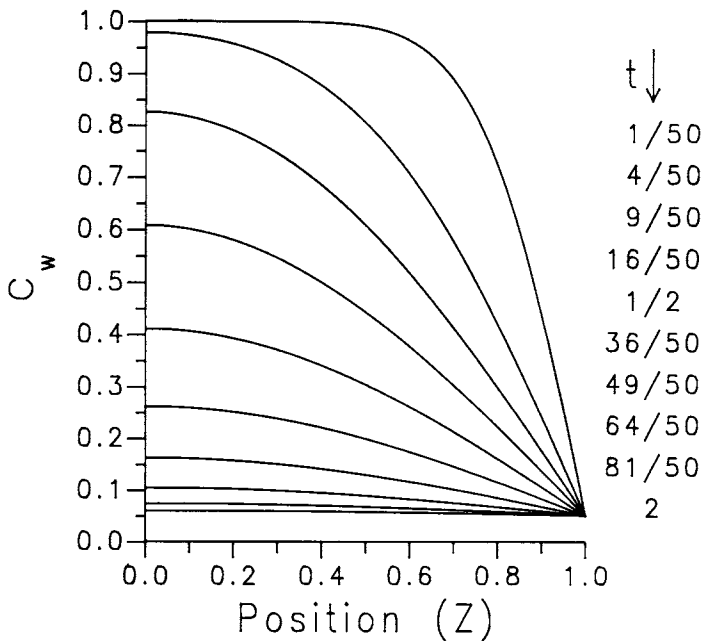


Fig. 1. Water concentration profiles for nylon 6,6 stationary film model ($\phi^2 = 0$).

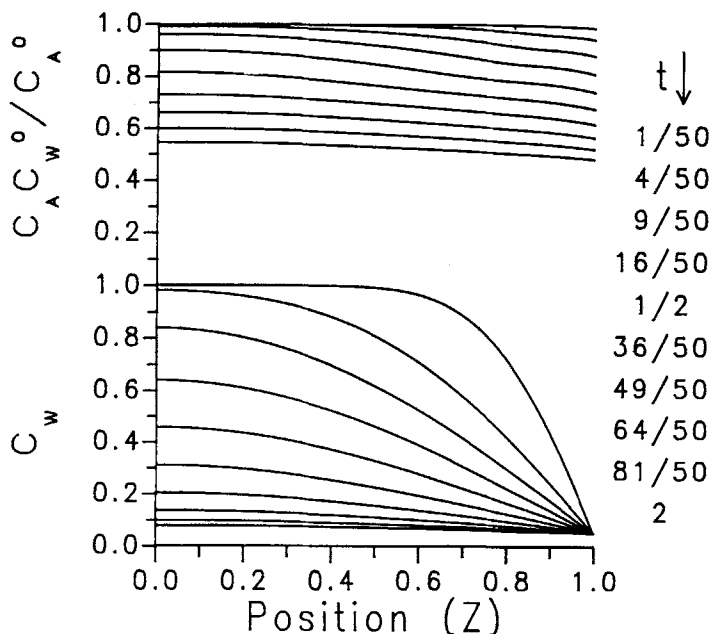


Fig. 2. Water and polymer concentration profiles for nylon 6,6 stationary film model ($\phi^2 = 0.5$).

lus of 0.5 are shown in Figure 2. In this case, the reaction proceeds at a fairly constant rate through the film as shown by the flat amine end-group concentration profile; however, the water profile varies significantly. This is because the reaction proceeds slowly enough so that the mixture remains far from equilibrium and nearly approximates an irreversible polymerization. An irreversible reaction would not be affected by the water concentration and would proceed with the same reaction velocity through the entire film, giving rise to a completely flat amine end-group profile. As expected, the water concentration profiles are similar to Figure 1.

The results for a Thiele modulus of 5 are shown in Figure 3 where the curvature of the water concentration profiles has changed. The amine end-group profiles also vary significantly through the film and reach equilibrium at the gas-film interface by $t = 2$, as indicated by the amine profiles merging into a single point at $Z = 1$. At long times the entire film will reach equilibrium. The kinks and bumps in the amine end-group profile are due to the fact that both the reaction rate constant and the equilibrium constant change significantly with composition across the film⁶; if these parameters are taken as constants, these features disappear.

Eventually, the entire film will reach equilibrium if $\phi^2 > 0$. For this example, the equilibrium molecular weight (number average) is 15,400 g/mol and the water concentration is 0.4 wt % ($X_w = 0.025$). The evolution of the number average molecular weight, averaged over the film thickness, is shown in Figure 4. At very high values of the Thiele modulus, the reaction time is much smaller than the diffusion time, local equilibrium is attained quickly throughout the film, and the process is diffusion-controlled. The upper limit is always set by reaction equilibrium, but it is diffusion that controls the rate of approach in this case.

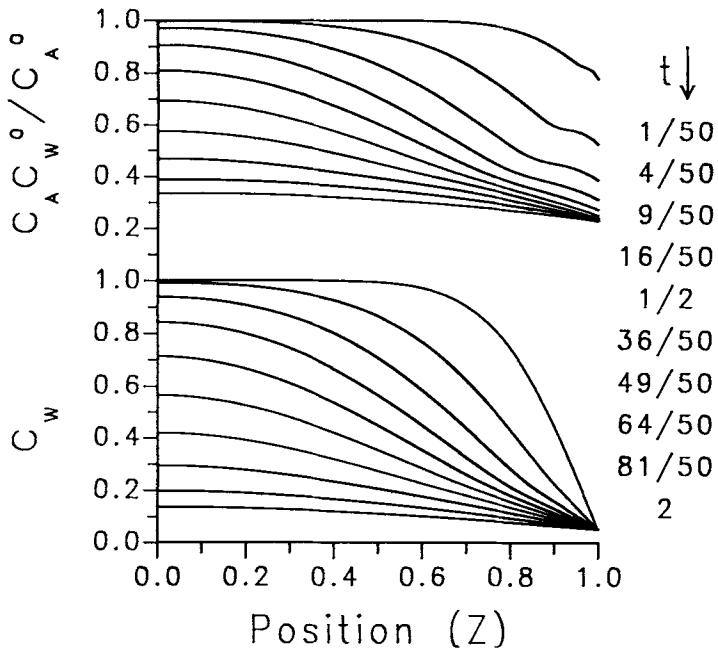


Fig. 3. Water and polymer concentration profiles for nylon 6,6 stationary film model ($\phi^2 = 5$).

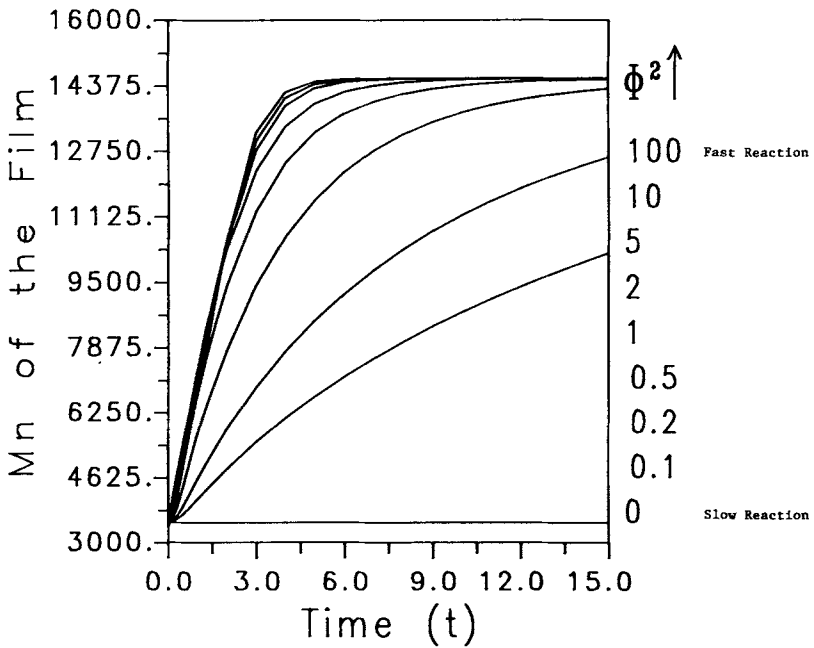


Fig. 4. Film average M_n evolution for nylon 6,6 stationary film model at various Thiele moduli.

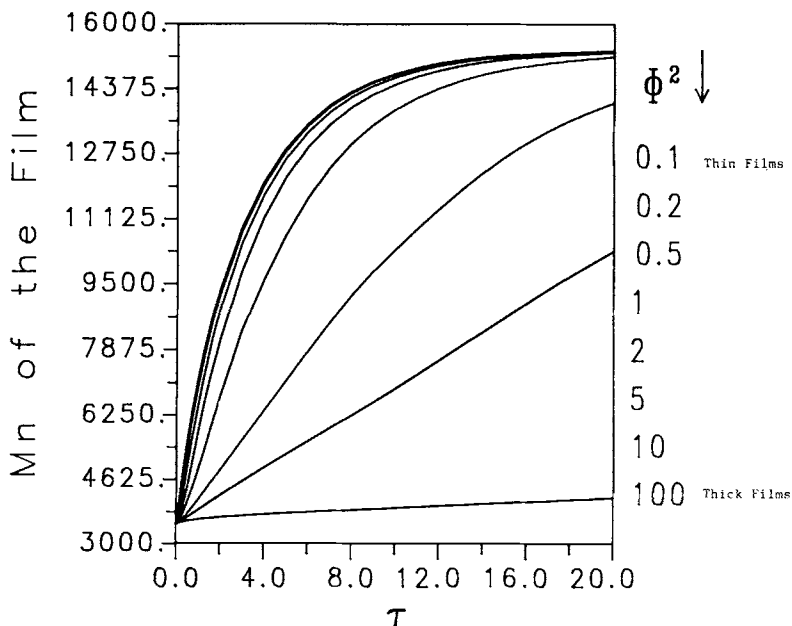


Fig. 5. Film average M_n evolution for nylon 6,6 stationary film model at various Thiele moduli.

Figure 4 is most useful when one wants to anticipate the benefits of changing the reaction rate (and hence the Thiele modulus) via a catalyst while maintaining a constant film height and temperature. This keeps the characteristic time the same for the various curves and allows direct comparison between them. At low Thiele moduli, it takes a long time to reach the equilibrium molecular weight, and there is a big incentive to increase the reaction rate (via a better catalyst), thereby increasing ϕ^2 and greatly reducing the transient time. However, at Thiele moduli greater than 5 very little enhancement is possible since diffusion of water out of the film controls the molecular weight growth. High reaction rates rapidly produce local equilibrium in the film and increasing the reaction rate does not speed the growth of molecular weight.

To analyze the benefits of decreasing the film thickness (decreasing Thiele modulus), Figure 5 is more useful because the abscissa scale, $\tau = t\phi^2$, is a new dimensionless time, scaled by the characteristic reaction time for reaction, which is independent of the film height [see eq. (18)]. Under fixed reaction conditions and for Thiele moduli greater than 2, Figure 5 shows that decreasing the film height always leads to significantly shorter transient times. However, very little benefit is realized below $\phi^2 = 1$; at low Thiele moduli, diffusion is fast and the molecular weight growth is reaction-controlled. Decreasing the film height further is not productive.

The film-average molecular weight for $\phi^2 = 5$ and 100 is shown in Figure 4 and in more detail in Figure 6. The two profiles cross twice. These curves can only be compared if one considers a system with a fixed film height (characteristic time) in which the Thiele modulus is changed via catalyst addition. The corresponding molecular weight profiles are shown in Figures 7 and 8. At short times, the higher Thiele modulus corresponds to a more rapid generation of

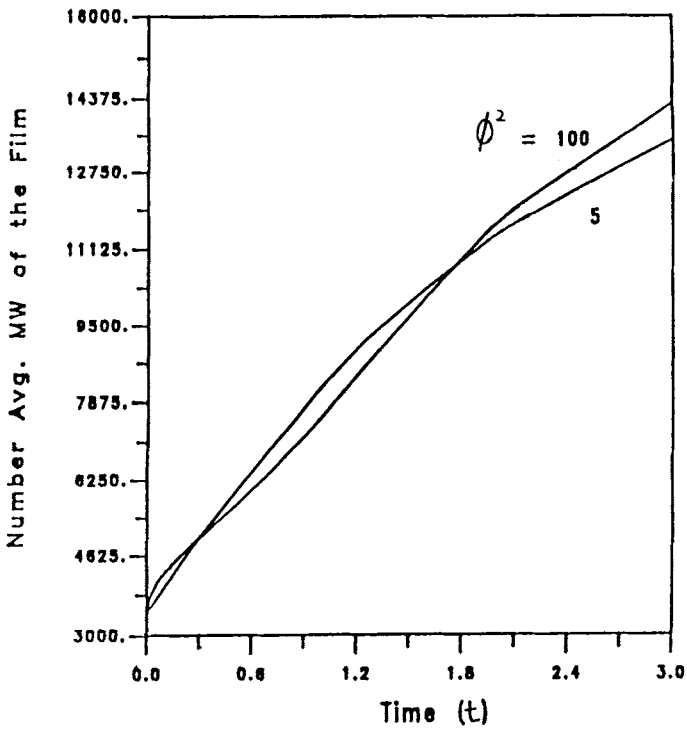


Fig. 6. Film average M_n evolution for nylon 6,6 stationary film model for $\phi^2 = 5$ and 100.

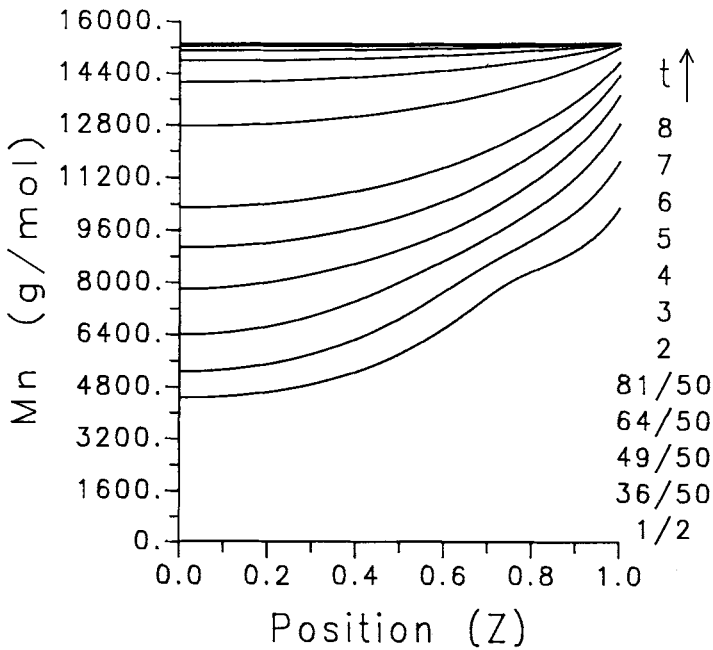


Fig. 7. Molecular weight profiles for nylon 6,6 stationary film model ($\phi^2 = 5$).

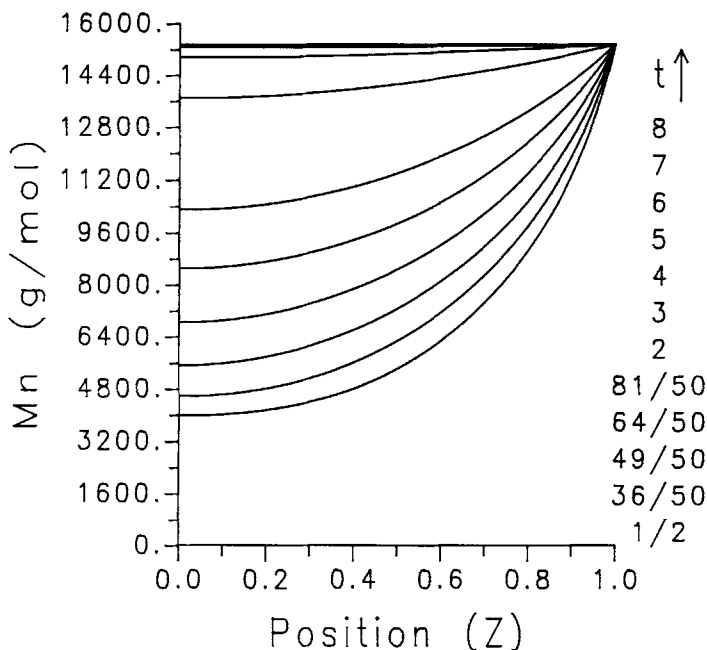


Fig. 8. Molecular weight profiles for nylon 6,6 stationary film model ($\phi^2 = 100$).

molecular weight at the gas-film interface. However, water is replenished more rapidly at the interface (due to the higher reaction rate), thus keeping the concentration of water in the interior of the film higher relative to the lower Thiele modulus film. Since the process is diffusion limited (high ϕ^2), and begins at equilibrium, a certain amount of water must diffuse out of the interior of the film before the reaction can proceed. Eventually, enough water diffuses out of the film so that the higher reaction rate does indeed increase the rate of molecular weight generation. This anomaly does not occur at low Thiele moduli as the diffusion is rapid relative to the reaction.

The predictions of this nylon 6,6 kinetic model were compared to those of an idealized model based on constant rate and equilibrium constants in the kinetic description; forward reaction rate constants of 177/h and 58/h were used. These correspond to the initial and the equilibrium ($t \rightarrow \infty$) values of k_{app} in the nylon 6,6 stationary film simulation. An equilibrium constant of 470 was used, which is the equilibrium value in the nylon 6,6 simulation. The results from the idealized model are compared to those of the nylon 6,6 model in Figure 9 for $\phi^2 = 5$ and $\phi^2 = 0.2$. At the larger Thiele modulus, the ideal model does not have much error because the effect of variations in the forward reaction rate constant with composition are diminished as equilibrium is reached in the film. The nonideal model predicts a faster molecular weight evolution because the equilibrium constant is greater than the final value of 470 (K_{app} increases with water content in this composition regime) during the course of the simulation.

The molecular weight evolution for $\phi^2 = 0.2$ is also shown in Figure 10. This Thiele modulus corresponds to a film thickness of about 0.25 cm. The ideal model has significant error because it does not properly reflect the changes in

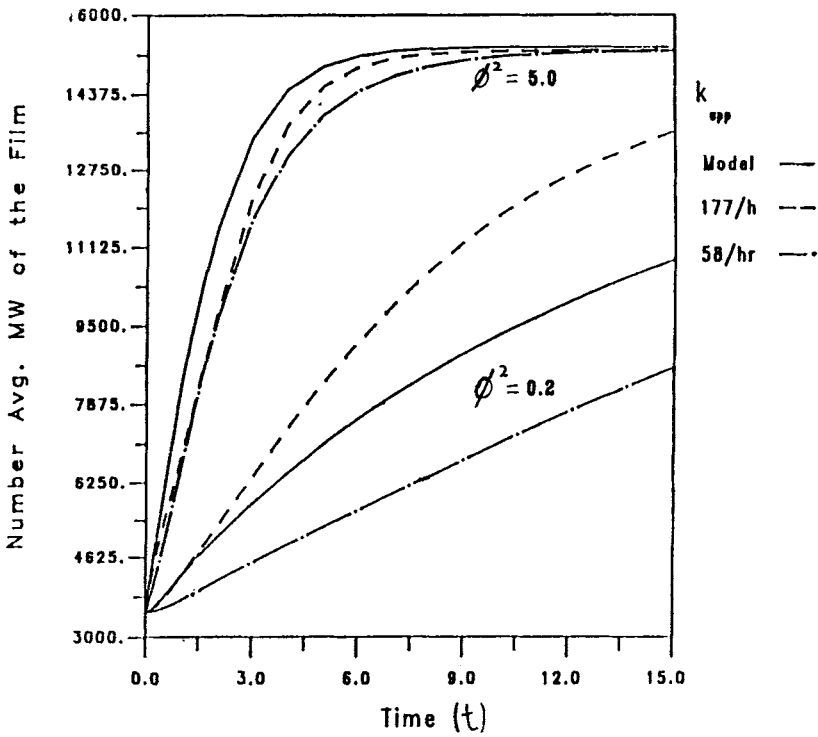


Fig. 9. Film average M_n evolution for nylon 6,6 and ideal stationary film models for $\phi^2 = 0.2$ and 5.

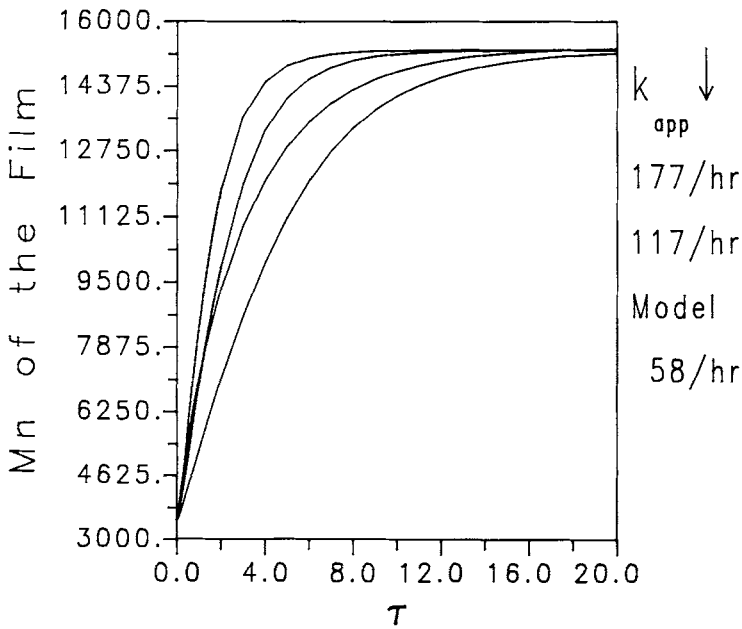


Fig. 10. Film average M_n evolution for nylon 6,6 and ideal stationary film models for $\phi^2 = 0.2$.

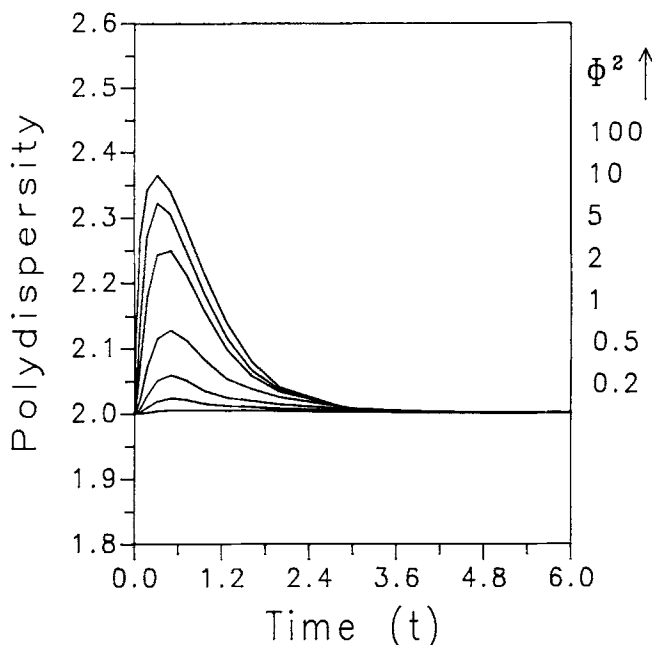


Fig. 11. Polydispersity evolution for nylon 6,6 stationary film model.

the reaction rate constant. If a mean value for the forward reaction rate constant of 117/h is used, the agreement is only slightly better. The characteristic reaction time is 0.34 h, and Figure 10 shows the prediction of the time required to reach a given molecular weight can easily be from 0.5 to 1 h in error. Similarly, the prediction of the molecular after a given reaction time can be 500–2000 g/mol in error. Thus, it is necessary to properly describe the composition dependence of both the rate and equilibrium constants for an accurate model. In addition, even if the composition dependence of the rate constants is known, there is no obvious way to choose an average value so that the ideal description may be used. For systems with a significant composition dependence the ideal model results will have large errors, especially at low values of the Thiele modulus (i.e., under reaction control).

We have assumed the polydispersity to be 2 at all points within the film, which is the classic result of Flory²² for the equal reactivity case. However, the film is really a mixture of many fractions with the same polydispersity (2) but with different number average molecular weights. Thus, the polydispersity of the entire film will deviate from 2 if the number average molecular weight varies from point to point. The film-averaged number average molecular weight, weight average molecular weight, and polydispersity can be calculated from the number average molecular weight profile. The time evolution of the film averaged polydispersity at various Thiele moduli is shown in Figure 11. The polydispersity deviates by as much as 20% from a value of 2 for Thiele moduli in the range of 0.2–100. All of the deviations due to mass transfer act to increase the polydispersity, particularly at short times. The deviations increase with Thiele modulus and a maximum is seen near a time of 0.5–1. As the film approaches equilibrium the polydispersity deviates negligibly from 2.

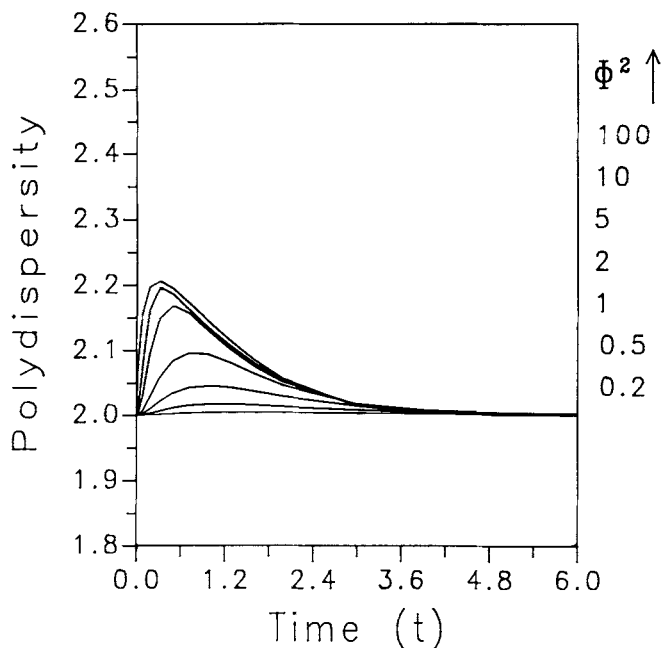


Fig. 12. Polydispersity evolution for ideal stationary film model.

If one considers the apparent rate and equilibrium constants to be composition-independent (Fig. 12), the polydispersity shows the same overall pattern but the variations are smaller in magnitude. The maxima also occur at longer times with decreasing Thiele modulus.

Mass transfer causes relatively small deviations in the polydispersity from a value of 2. Thus, if large deviations from 2 are observed, they can be attributed to changes in end-group reactivity with chain length (a failure of the equal reactivity hypothesis) and/or additional side reactions rather than to mass transfer effects.

CONCLUSIONS

It is necessary to have accurate rate and kinetic constants to accurately describe the molecular weight generation of nylon 6,6 in a film. At a fixed film thickness, it is beneficial to increase the reaction rate via catalyst addition until a Thiele modulus of 5, because molecular weight generation is diffusion-limited beyond this point. At fixed reaction conditions, it is beneficial to decrease the film thickness until a Thiele modulus of 1, since molecular weight generation is reaction limited below this value. Mass transfer causes the polydispersity averaged across the film to deviate somewhat from a value of 2 at short times.

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APPENDIX: NOMENCLATURE

A	amine end group
C	carboxyl end group
\hat{C}	total molar density ($\sum_{i=1}^n C_i$) (mol/L) after eq. (16), ($\sum_{i=1}^n C_i/C_W^0$), dimensionless
C_i	concentration of component i (mol/L) after eq. (16), (C_i/C_W^0), dimensionless
C_T	quaternary molar density for nylon 6,6 amidation ($C_T = C_A + C_C + C_L + C_W$) (mol/L) after eq. (16), (C_T/C_W^0), dimensionless
C_W^0	initial water concentration (mol/L)
d_{ij}	multicomponent diffusivity matrix (cm^2/s)
D	binary system diffusivity (cm^2/s)
D_{ij}	multicomponent diffusivity matrix (cm^2/s)
H	film height (cm)
\bar{J}_i	the molar flux of component i relative to the molar average velocity (mol/ cm^2 h)
k_{app}	apparent forward reaction rate constant (1/h)
K_{app}	apparent equilibrium constant ($X_L X_W/X_A X_C$), dimensionless
L	amide linkage
M_i	molecular weight of the i th species (g/mol)
M_n	number average molecular weight (g/mol)
\bar{N}_i	molar flux of water in a spatially fixed reference frame (Eulerian frame) (mol/ cm^2 h)
P	pressure in the gas phase (Pa)
P_W^0	vapor pressure of water (Pa)
r	forward amidation reaction rate per unit volume $\{r = k_{\text{app}} C_T [X_A X_C - (1/K_{\text{app}}) X_L X_W]\}$ (mol/L h) after eq. (16), $\{r = k_{\text{app}} C_T [X_A X_C - (1/K_{\text{app}}) X_L X_W]/k_{\text{app}}^0 C_W^0\}$, dimensionless
r_i	rate of production of component i (mol/l h)
t	time (h) after eq. (16), $[t/(H^2/D)]$, dimensionless
\bar{v}_i	the average velocity of component i relative to a spatially fixed reference frame (cm/h)
\bar{v}^*	the molar average velocity of all components relative to a spatially fixed reference frame (cm/h)
W	water molecule
x_i	mole fraction of component i (C_i/\hat{C}), dimensionless
X_i	quaternary mole fraction of component i for nylon 6,6 amidation (C_i/C_T), dimensionless
y_W	mole fraction of water in the gas phase, dimensionless
Z	length (cm) after eq. (16), (Z/H), dimensionless

Greek

γ_W	activity of water in the gas phase, dimensionless
ϕ^2	Thiele modulus ($H^2 k_{\text{app}}^0/D_W$), dimensionless time ($t\phi^2$), dimensionless

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