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Mathematical Model of Charge and Density Distributions in Interfacial Polymerization of Thin Films

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ABSTRACT: A general model for interfacial polymerization is proposed and solved numerically. The model takes into account diffusion and reaction of monomers, presence of unreacted functional groups on the growing polymer, and solubility effects. The formation of a polyamide film in composite separation membranes is taken as an example. The evolution of the concentrations of the polymer and unreacted moieties are followed explicitly, thus enabling the calculations of the limiting thickness and the asymmetric

distribution of density and charge in the resulting film. Such knowledge is important for the prediction of rejection and transport properties of the film. The effects of reaction kinetics, monomer concentrations, and hydrodynamic conditions on the properties of the film are analyzed, and a number of analytical correlations are developed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1162–1169, 2003

Key words: membranes; morphology; polyamides; films

INTRODUCTION

Interfacial polymerization (IP) as a method of preparation of thin film composite (TFC) membranes has been widely used and studied since Cadotte first introduced the method.^{1, 2} Applications of the TFC membranes include desalination and purification of water, separation of industrial effluents, and waste treatment. IP is also highly suitable for manufacturing polymeric films, such as polyamides for packaging or encapsulation.^{3–7} The general IP procedure used to fabricate TFC membranes is as follows.^{1, 2} Difunctional amines in a support membrane are brought in contact with an organic phase containing trifunctional acid chlorides. Subsequent fast polymerization results in the formation of a rejection layer. With a proper choice of monomers [such as piperazine or *m*-phenylenediamine (MPD) and trimesoylchloride (TMC)] and reaction conditions, a thin and dense layer is quickly formed that creates a barrier to further polymerization.

It has been shown that the formation of a thin film occurs very quickly and often results in an asymmetric density distribution. Based on small-angle X-ray scattering (SAXS) results, Sundet⁸ suggested the following scheme. An extremely fast reaction between amines and trifunctional acid chlorides occurs just within the organic phase and forms a highly branched network.

Polymerization proceeds to high molecular weights at a thin reaction zone where the amines interact with the acids. It is further believed that the reaction is likely to resemble the diffusion-limited aggregation (DLA) process,⁹ and first proceeds through the formation of functional colloidal particles that subsequently aggregate to a lower density structure.⁸

An important feature of the polyamide films is the presence of unreacted charged moieties (carboxylic and amine groups), which are believed to play a crucial role in the rejection and resistance to fouling. However, little is known about the actual content and distribution of these groups across the film, or the mechanism that leads to the asymmetric morphology of the thin film. It would be informative to know the effects of variables such as reactant concentration, diffusion, and reaction rates on the final film morphology.

Several efforts have focused on modeling the kinetics of film growth. Enkelman and Wegner^{10, 11} considered the effects of diffusion of amine and water through the film and the competition between the amidation and hydrolysis reactions. This model, unlike the later models, was capable of predicting the limiting thickness due to the hydrolysis reaction and explicitly introduced asymmetry to the film. However, the kinetic equation for this model poorly predicted the film growth, particularly at initial stages of the process. Janssen and te Nijenhuis^{5, 6} modeled the growth of a thin encapsulating film assuming that the amines diffuse through the film and then react instantaneously with the acid chloride. This model predicted an unlimited growth of the film thickness scaling as

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square root of time. Ji et al.¹² generalized this approach by introducing a finite reaction zone near the organic face of the growing film and limiting the amount of amine in the aqueous phase, which resulted in a finite film thickness at infinite time. However, this approach also implies that an isotropic film forms and does not account for the concentration distributions of the polymer and unreacted functional groups within the film that lead to pore and charge asymmetries. Thus, the information obtained through this model is clearly insufficient for characterizing and quantifying the rejection properties of the film.

Another common drawback of the models just described is the questionable assumption that the film (of zero thickness) already exists at the interface separating the phases where the respective monomers are uniformly distributed. In this respect, the model of Mikos and Kiparissides¹³ offered a significant improvement by considering the reaction, diffusion, and solution thermodynamics explicitly from the very first moment. However, the system and reactions considered by Mikos and Kiparissides were very different from our system, so their conclusions cannot fully apply to our system.

We developed a simple model for the formation of asymmetric thin films that explicitly considers the reaction and diffusion throughout the IP process. Its essential feature is the explicit account of the concentration of unreacted functional groups within the film. Comparison of our results with experimental observations and conjectures show qualitative agreement.

MODEL DEVELOPMENT

We present a mathematical model for the formation of a thin-film membrane under nonsteady-state conditions. The two-dimensional surface of the film is assumed infinite (practically, it is determined by the available surface of the amine phase). Thus, we are only concerned with the profiles within the thickness of the thin film. The model is general and can be applied to many interfacial polymerization reactions that conform to the model formulation described later. However, it is especially relevant to the formation of polyamide desalination and separation membranes where the presence of functional groups within the membrane plays an important role in the separation process.² A schematic of the problem is shown in Figure 1.

We assume a constant concentration for the bifunctional reactant *A* (amines in support material) at the boundary of $x = 0$. This concentration is, in effect, the ratio of the concentration of amine in the aqueous phase and its partition coefficient. The data presented by Morgan³ suggest that for the pertinent diamines and solvents, the latter should be significantly >1 , allowing us to disregard the amine diffusion in the

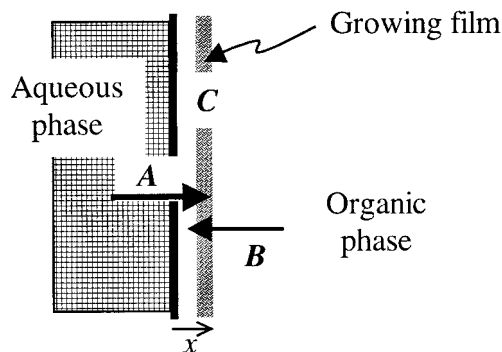


Figure 1 Schematic depiction of thin film growth by interfacial polymerization. Reactants *A* (aqueous phase) and *B* (organic phase) react to form a polymer film *C*.

aqueous phase. By disregarding the amine diffusion, we can justify the assumption of a constant N_A at $x = 0$, where N_A is the local amine concentration in the organic phase.

Initially, the concentration N_B of the trifunctional reactant *B* (acid chloride) is assumed to be uniform throughout the organic phase. It is known that the forming polyamide in its pure state is almost impermeable to the acids because of the large difference in polarity and thus very low solubility. Furthermore, once the polymer has been formed, the reaction is limited by diffusion of the amines through the polymer.^{3-5, 10} Therefore, we approximate the activity coefficient of *B* in the polymer-containing organic solvent as $\gamma_B = (1 - N_C)^{-1}$, where N_C is the volume fraction occupied by the polymer and is inaccessible for *B*. We assume the activity coefficient of amine (equal to unity) to be unaffected by the polymer. This simplification is likely to incorrectly predict the permeability of the developed film to amine, which will affect the rate of growth of the film at late stages, but should not change any of our principal conclusions about the resulting film structure.

Several works have considered the competing reaction of the amines with acid (HCl) resulting from amidation and hydrolysis of *B* with water carried by amines.^{6,11,12} However, the heterogeneous hydrolysis of the relevant acid chlorides appears to be very slow due to their low solubility in water.³ The presence of significant amounts of water in the organic phase is possible only after accumulation of rather large quantities of polymer. As our interest is mostly directed to the stages of incipience and early growth of the film, it is reasonable to neglect these additional reactions and assume the effective amine concentration in the absence of the acid acceptor to be reduced accordingly.

Finally, we assume that the polymer and aggregates of all sizes (included in the polymer concentration N_C) are immobile; that is, have zero diffusivity. This assumption is certainly unrealistic for small oligomers, yet the error should be significant only at the very

early stages of film growth because the relative fraction of the oligomer population rapidly decreases with increasing polymerization.

We follow the volume fraction profiles of five variables within the film: N_A , N_B , N_C , n_A , and n_B . The latter two are unreacted end groups of the growing polymer having amine (*A*) and acid chloride (*B*) functions, respectively. For consistency, all five variables are expressed as molar concentrations (mol/m³) multiplied by the molar volume $M = 10^{-4}$ m³/mol, which is assumed to be the same for the amine, acid chloride, and their respective monomer units. This approximation is well justified for MPD/TMC and piperazine/TMC pairs. For N_A , N_B , and N_C , these units are equivalent to volume fractions. The appearance and disappearance of these variables within the thin film as the polymerization reaction proceeds obey the following general equations:

$$\frac{\partial N_A}{\partial t} = \frac{\partial}{\partial x} \left(D_A \frac{\partial N_A}{\partial x} \right) - 2kN_A(n_B + 3N_B) \quad (1)$$

$$\frac{\partial N_B}{\partial t} = \frac{\partial}{\partial x} \left(D_B \left(\frac{\partial N_B}{\partial x} + \frac{N_B}{1 - N_C} \frac{\partial N_C}{\partial x} \right) \right) - 3kN_B(n_A + 2N_A) \quad (2)$$

$$\frac{\partial N_C}{\partial t} = 2kN_A(n_B + 3N_B) + 3k(n_A + 2N_A)N_B \quad (3)$$

$$\frac{\partial n_A}{\partial t} = 2kN_A(n_B + 3N_B) - 3kn_AN_B - k'n_An_B \quad (4)$$

$$\frac{\partial n_B}{\partial t} = 6k(n_A + 2N_A)N_B - 2kN_An_B - k'n_An_B \quad (5)$$

where D_A and D_B are the diffusion coefficients of reactants *A* and *B*, respectively, which depend on polymer concentration. Their functional form is discussed below. The parameter k is the reaction rate constant of all amine-chloride group-group reactions. The intrapolymer (cross-linking) reaction rate constant is k' . For the concentrations to be expressed as volume fractions, the values of k and k' in m³/(mol · s) should be divided by M to be used in eqs. 1–5. Equations 1 and 2 describe the diffusion of *A* and *B* through the membrane and subsequent reaction with *B* and *A* functional groups. Equation 3 describes the formation of the polyamide film. Equations 4 and 5 describe the kinetic appearance and disappearance of functional groups on the formed aggregates. The integer coefficients preceding the kinetic terms correspond to the number of functional groups per reactant (2 for *A* and 3 for *B*). For instance, the coefficient “6” in eq. 5 is the product of $f_B = 3$ (the number of reacting groups in *B*) and $f_B - 1 = 2$ (the number of fixed acid groups added

upon reaction). Equations 1–5 are subject to the following boundary conditions:

$$N_A|_{x=0} = N_{A0} \quad (6a)$$

$$N_B|_{x=L} = N_{B0} \quad (6b)$$

and the following initial conditions:

$$0 \leq x \leq L: \quad N_C|_{t=0} = n_A|_{t=0} = n_B|_{t=0} = 0 \quad (7a)$$

$$0 < x \leq L: \quad N_A|_{t=0} = 0 \quad (7b)$$

$$0 < x \leq L: \quad N_B|_{t=0} = N_{B0} \quad (7c)$$

Equations 6 and 7 amount to assuming that the reaction takes place inside a unidimensional “box” of finite thickness L attached to the interface at the organic side, with concentrations of the monomers fixed at the boundaries. The validity of this assumption is discussed later.

Naturally, diffusion of the reactants will decrease as the volume fraction occupied by the formed polymer increases because of the geometric constraints imposed by the polymer. The “effective” diffusion coefficients of low molecular species in polymer gels and solutions have been shown to be satisfactorily described by the following relation:^{6,14,15}

$$D(N_C) = D_0(1 - \varepsilon N_C)^\alpha \quad (8)$$

where D_0 is the effective diffusion coefficient of the reactant in the pure solvent. Because the molecular sizes of the monomers under consideration (MPD or piperazine and TMC) are similar, we assumed equal D_0 values for both monomers ($\sim 10^{-5}$ cm²/s). Various works have suggested that the exponent α is between 1 and 3, depending on the polymer and solute.^{6, 14} The parameter ε , introduced here, is slightly smaller than unity and allows for finite solute diffusivity in the polymer.¹⁵ The value $\varepsilon = 0.99$ used in the present work gives an amine diffusivity in the polyamide close to that reported by Ji et al.¹²

The diffusivities in eq. 8 are, in effect, self-diffusivities. These values replace regular diffusivities if the chemical potential gradient, $\Delta\mu = RT \Delta \ln(\gamma N)$, rather than the concentration gradient, ΔN , is to be used as the driving force.¹⁶ This approach is essential for the *B* monomer, which, as a result of the effect of γ_B discussed earlier, can move against its own concentration gradient while being excluded from the film.

The rate constant k is known to be between 10² and 10⁶ L/(mol·s) for the reactions between acid chlorides and amines employed in IP synthesis,^{3, 17} and should not be lower for monomers of higher functionality. We therefore primarily used a relatively high value

[10^5 L/(mol · s), divided by M if volume fractions are to be used for concentrations]. In general, a number of different rate constants should be considered as the reaction proceeds because the reactivity of the groups in multifunctional monomers is known to decrease (typically by factors of 1.5–5)^{17, 18} after some groups have reacted. Nevertheless, the difference is only moderate, and we therefore neglect this complication by assuming that the reaction is significantly suppressed only when both reacting groups belong to a polymer moiety. In the latter case, the mobility and, thus, the probability of contact is severely restricted for both reacting species; that is, for the cross-linking reaction, the reaction rate constant k' was generally taken to be 10–100 times lower than k .

Normally, the film formation is considered an IP process without stirring.^{1–3, 19} For such conditions, the concentration of B in the organic phase in our model should be fixed at infinite distance. As will be shown later, the dense film emerges when the reaction zone reaches the location where the amine and acid chloride flows become stoichiometrically equal. It may be shown^{16, 20} that in the case of an infinite box, this condition can never be met. Indeed, assuming the reaction zone to be sufficiently narrow, which is the case for the fast reactions considered here, the amine and chloride fluxes will both decrease as $(\text{time})^{-1/2}$ or $1/X$, where X is the distance from the interface to the reaction zone, and we arrive at the paradoxical conclusion that the fluxes will never equalize and the film will never form.

In contrast, in a finite box, such a location always exists. When a dense film emerges, uniform profiles of the monomers are quickly established, with most of the resistance falling inside the film and further reaction proceeding independent of the box size. When the system is stirred, the boundary layer constitutes a finite box. During the formation of a membrane on an amine-soaked porous support, relative motion between the organic and aqueous phases is inevitably created for a time that might be long enough to initiate the irreversible film formation. The boundary layer thickness is roughly given by $L \sim (\nu y/U)^{1/2} \text{Pr}^{-1/3}$, where ν is the kinematic viscosity of the organic phase, y is the distance from the leading edge of the sample, U is the relative velocity, and $\text{Pr} = \nu/D_0$.²¹ Taking $\nu = 10^{-6}$ m²/s, $\text{Pr} = 10^3$ and $y_{\text{max}}/U = 1$ s (this is approximately the time taken to fully immerse the support) and averaging over y , we estimate the box size to be of the order of 50 μm . Moreover, as is well known by electrochemists,²² experiments on solid electrodes in quiescent solutions cannot last more than 10–50 s because of weak natural convection. Therefore, even in an “unstirred” solution adjacent to a flat solid surface there exists a “boundary layer” that is $\sim (10 \cdot 10^{-9})^{0.5}$ m ~ 100 μm thick. Obviously, this number should be substantially lower for a liquid–

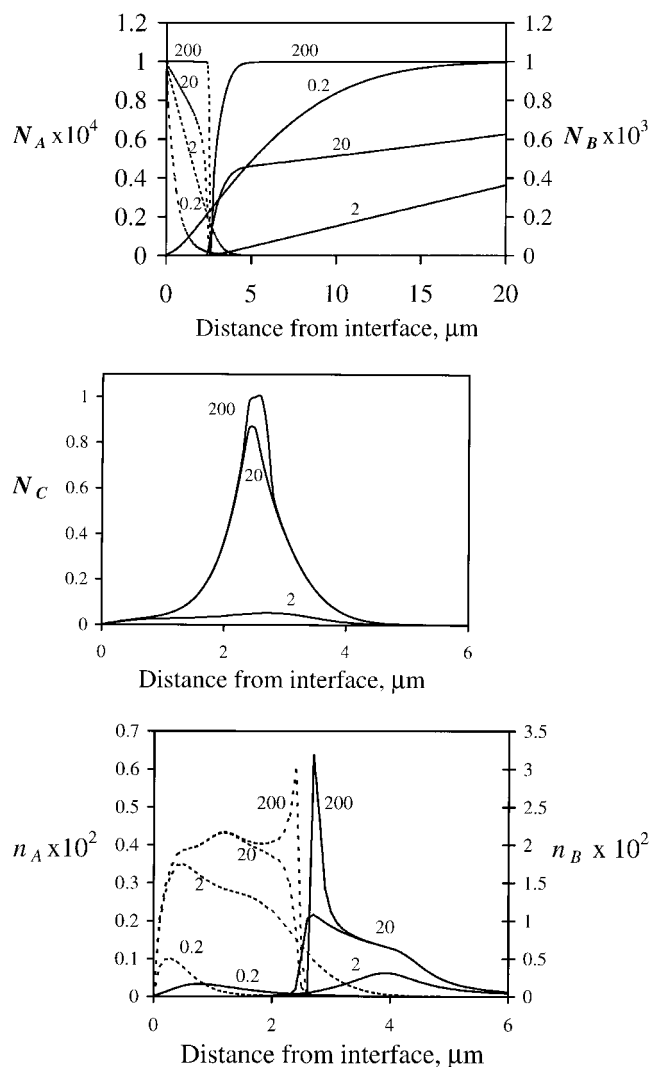


Figure 2 Concentration profiles of (a) monomers (amine, dashed line; acid, solid line), (b) polymer, and (c) uncharged groups (amine, dashed line; acid, solid line). The numbers denote the reaction time in seconds. [$k = 100$ m³/(mol^{-s}), $k'/k = 0.01$, $N_{A0} = 10^{-4}$, $N_{B0} = 10^{-3}$, $L = 50$ μm].

liquid interface. Therefore, most of the simulations were performed using a 50- μm box, but in an additional series of simulations, the box size was taken as a parameter and varied to assess the possible effect of hydrodynamics on the resulting film.

RESULTS AND DISCUSSION

In Figure 2 we present numerical results from eqs. 1–8 for the progression in time of the concentration profiles of the reactants (Figure 2a), total polymer (Figure 2b), and unreacted functional groups in the polymer (Figure 2c) obtained numerically for box size $L = 50$ μm . Within seconds, n_A , n_B , and N_C emerge. A thin film develops quickly ~ 2.5 μm within the organic phase. For the particular set of parameters shown, the final polymer concentration profile, which nearly fully

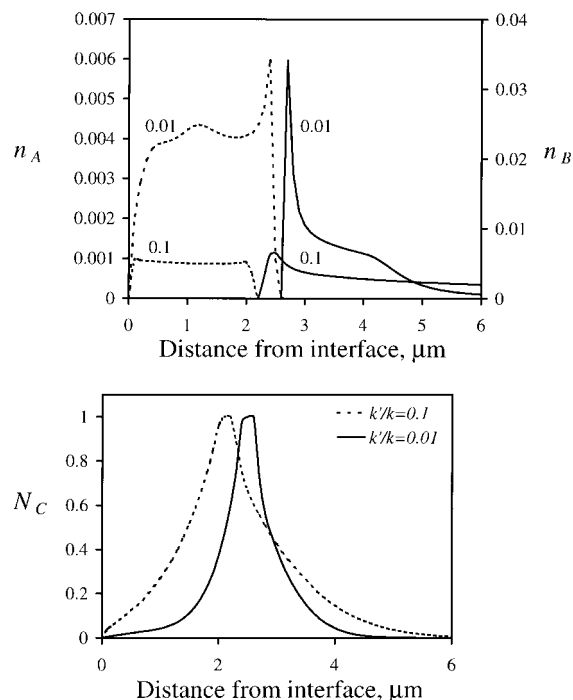


Figure 3 Concentration profiles of (a) unreacted groups (amine, dashed line; acid, solid line) and (b) polymer for $k'/k = 0.01$ and 0.1 , for reaction time 200 s [$k = 100 \text{ m}^3/(\text{mol}^{-1}\text{s})$, $N_{A0} = 10^{-4}$, $N_{B0} = 10^{-3}$].

develops in ~ 20 s, has an asymmetric unimodal curve with a tail that extends towards the organic phase. This tail is likely to cause the well-known rough morphology of the surface of the TFC composites.²³

We can see from Figure 2c that an even more prominent asymmetry develops in the distribution of the charged groups. The minor peculiar features (e.g., small local maxima in the profiles) apparently reflect some narrowing of the reaction zone as a result of the polymer formation so that unreacted groups formed at the earliest stage could not be later reached by the opposite monomer. As mentioned earlier, information on the fixed charges is highly important in connection to the ion rejection by the membrane. Due to the different solubility of the monomers in the polymer-rich solvent, the acid groups occupy a relatively thin layer at the organic face of the film, whereas the amino groups dominate throughout the rest of the film.

This qualitative behavior of the charge distribution is preserved for larger ratios of the rate constants, k'/k , as seen from Figure 3a. However, as expected, higher crosslinking reaction rates decrease the content of the charged groups in the membrane. On the other hand, Figure 3b shows that the thickness in this case is larger because the monomer addition is slower due to the competing crosslinking reaction, which is equivalent to effective reduction of k and widening of the reaction zone (vide infra). Recently, Schaep and Vandecasteele²³ determined the fixed charge content of some

nanofiltration TFC membranes. For the NF-40 polyamide composite, they obtained surface charges of the order 10^{-6} and 10^{-5} mol/m^2 for positive and negative groups, respectively. For the thickness of the skin of the order 10^{-7} m , these concentrations corresponds to $n_A \sim 10^{-3}$ and $n_B \sim 10^{-2}$ in the units of Figures 2c and 3a, which provides some justification for the choice of k/k' between 10 and 100.

Interestingly, the observed charge distributions explain the contradiction encountered while trying to determine the charge of TFC polyamide membranes using various experimental methods. These membranes are often found to be negatively charged based on the results obtained using the streaming potential (SP) technique.²⁴ This finding is also supported by X-ray photoelectron spectroscopy (XPS or ESCA) data indicating that n_B for TMC/MPD composites is $\sim 13\%$ of N_C .²⁴ Both methods, however, reflect the very thin outermost layer of the skin ($<1 \text{ nm}$) and are in full agreement with our results that indicate a high negative charge for that layer of the skin. However, nuclear magnetic resonance (NMR)^{25, 26} or Fourier transform infrared (FTIR) spectra,²⁷ which give a picture averaged over the whole skin, show very few or no acid groups. More importantly, the selectivity of the membrane toward ions of various charge indicates that the membrane charge is very small.²⁸ It has been suggested recently that the actual selectivity mechanism in such membranes might be the dielectric exclusion and not the Donnan exclusion as has been long believed (most clearly it is seen for TFC nanofiltration membranes).²⁹ Our results show that the average charge of the skin that determines the selectivity towards ions of different charge can be quite low and, on average, the skin might indeed behave just as a dielectric medium, with the charge repulsion being of secondary importance.

We attempted to obtain direct visualization of the charge distribution in the polyamide layer of composite nanofiltration membranes using TEM combined with amine- and acid-selective staining. A cross-section of a membrane treated with uranyl salt (acid-selective stain) is shown in Figure 4.³⁰ In agreement with the calculated profiles, it clearly shows a thin and dark acid-rich layer separated from the dark support by a bright amine-dominated region.

The time evolution of the film thickness is shown in Figure 5. We define the thickness, δ , as the film width where N_C is >0.2 , which roughly corresponds to the percolation threshold for many continuous systems. Because δ cannot be determined for early times, in this particular plot we used the thickness δ_M , which was measured as the total volume of the polymer formed per unit interface area ($\delta_M = \int N_C dx$) and would be equivalent to the thickness of the polymer if it all precipitated onto the interface. For a developed film, δ_M is well correlated with δ but changes in a continu-

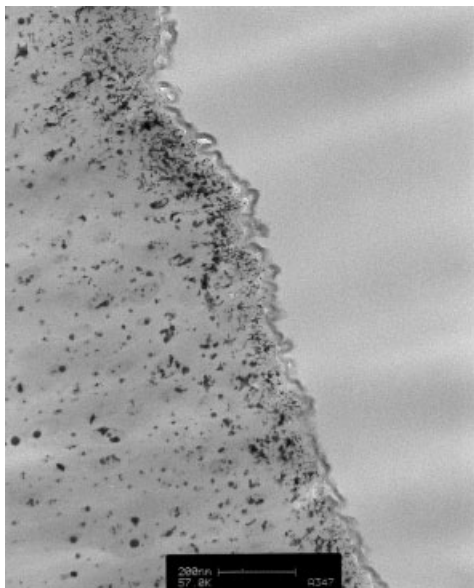


Figure 4 A TEM image of the cross-section of an uranyl-stained NF-270 membrane (Dow-Filmtec).

ous manner for all times. The thickness–time curve shown in Figure 5 differs significantly from the square root law derived in the earlier models. The initial increase is fast and linear and is followed by a slow growth phase (plateau). Only the latter, slow growth follows the mechanism proposed by earlier models.^{5,6,10,12} Inspection of the curves presented by Enkelman and Wegner^{10,11} and Ji et al.¹² and the light reflection data of Chai and Krantz¹⁹ shows that our results might provide a much better fit to the experimental results, particularly concerning the early stages of the process.

The effect of the reaction rate constant on the thickness of the film is shown Figure 6a. The simulations suggest that δ scales approximately as $k^{-1/3}$. A simple scaling analysis also predicts this behavior. Assuming that the film thickness is determined by the width of the reaction zone, δ (this width is determined by the

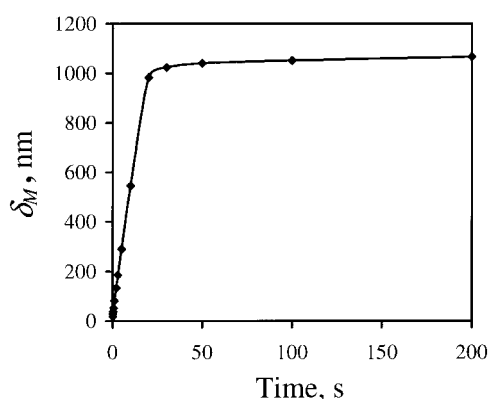


Figure 5 Film thickness (δ_M) as a function of time for $k = 100 \text{ m}^3/(\text{mol} \cdot \text{s})$, $k'/k = 0.01$, $N_{A0} = 10^{-4}$, $N_{B0} = 10^{-3}$.

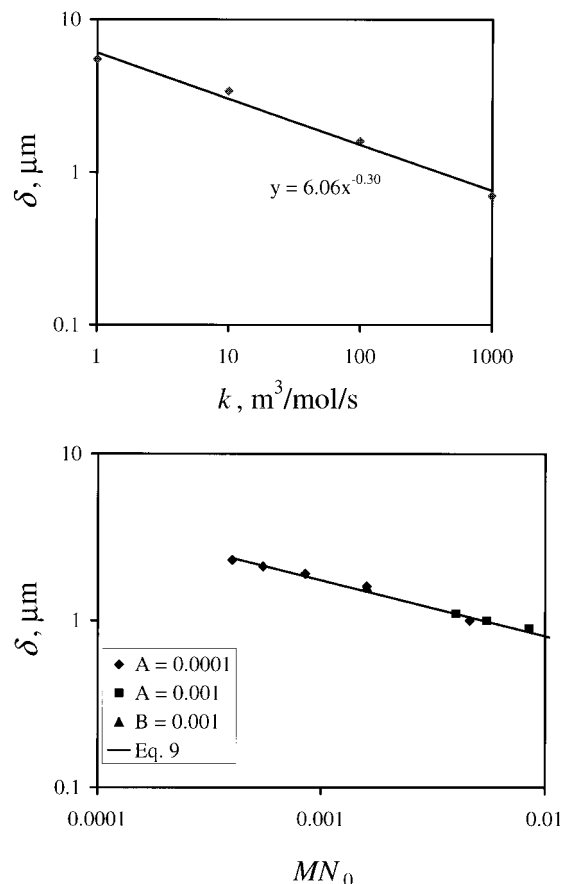


Figure 6 Film thickness (δ) at plateau onset as a function of (a) reaction rate constant k and (b) initial monomer concentrations in respective phases, one (A or B) fixed at the value shown in the legend and the other varied.

condition that the diffusion of A and B to the zone and the rate of disappearance due to reaction are stoichiometrically related when the polymer peak emerges), then the average concentration of the amine groups of A in the reaction zone is roughly $N_A^* \sim f_A$. Similarly, $N_B^* \sim f_B J_B \delta / D_0 \sim f_A J_A \delta / D_0$, where f_A and f_B are the functionalities of A and B , respectively. The rate of group consumption by the reaction per unit interface area may then be formulated as $f_A J_A \sim k N_A^* N_B^* \delta \sim k (f_A J_A \delta / D_0)^2 \delta$. By noting that $J_A \sim D_0 N_{A0} / X$ and $J_B \sim D_0 N_{B0} / (L - X)$, we find that, in agreement with simulations, $X \sim L N_{A0} f_A / (N_{A0} f_A + N_{B0} f_B)$, then $f_A J_A \sim D_0 (N_{A0} f_A + N_{B0} f_B) / L$ and, finally,

$$\delta \sim [D_0 L / k (f_A N_{A0} + f_B N_{B0})]^{1/3} \quad (9)$$

where L is the simulated box size or film thickness. The δ – k dependence predicted by our simulations is in agreement with eq. 9. Equation 9 also predicts the dependence of the final thickness on the concentration of monomers and on the box size (hydrodynamic conditions). The variation of the thickness with the monomer concentrations for $k = 10^2 \text{ m}^3/(\text{mol} \cdot \text{s})$, k'/k

= 0.01, and $L = 50 \mu\text{m}$ is shown in Figure 6b. The results are presented as δ at the plateau onset versus $N_0 = N_{A0} + 3/2N_{B0}$. The results are in excellent agreement with eq. 9, where the only degree of freedom is the proportionality constant (≈ 0.75).

Equation 9 suggests that the film thickness should decrease with monomer concentration. This conclusion contradicts the results of Enkelman and Wegner^{10, 11} and of Janssen and te Nijenhuis⁶ who, in agreement with their models, observed a square root dependence of the thickness on concentration. Apparently, the film growth in those cases was determined by the slow stage following the plateau formation, presumably due to the higher permeability of the film to amine and/or higher hydrophobicity of the aliphatic monomers used that could effectively prevent hydrolysis. In contrast, the tendency observed by Chai and Krantz¹⁹ for the MPD/TMC system is in qualitative agreement with eq. 9. In this case, the thickness of the denser and more hydrophilic MPD/TMC films is probably governed primarily by the earlier stages of the IP process described by the present model, after which the reaction is effectively terminated by hydrolysis and/or very slow diffusion of amine in the film.

Finally, in Figure 7 we present the effect of the hydrodynamic conditions (i.e., box size) on the film thickness and charge distribution. Clearly, a larger reaction zone allows for a thicker film to form, as is seen in Figure 7a. This process, however, requires a longer time period to reach the plateau region. The simulation results seem to predict a somewhat stronger dependence of δ on box size (Figure 7b) than eq. 9 at short time periods (< 200 s), which decreases, however, at longer periods of time. It is worth noting that, despite our *a priori* assumption that $50 \mu\text{m}$ seems to be a plausible value for the box size, the time and thickness in the actual IP process employed in fabricating the TFC membranes^{1, 2} corresponds much closer to a $5\text{-}\mu\text{m}$ box. Whether such a small box is indeed created by the hydrodynamic conditions in the process or there are other effects present is still a question to be answered.

CONCLUSIONS

We present a mathematical model for interfacial polymerization that explains phenomena observed in polyamide membranes. Our model accounts for the charge and density distributions within the film, which agree with and clarify experimental observations. Film growth is predicted using independently measurable quantities, such as reactant diffusivities and reaction rate constants. Parameters that cannot be measured directly (such as permeability) are more important for late stages of film growth and have minor impact on our results. Our model better describes the kinetics of early stages of film growth than

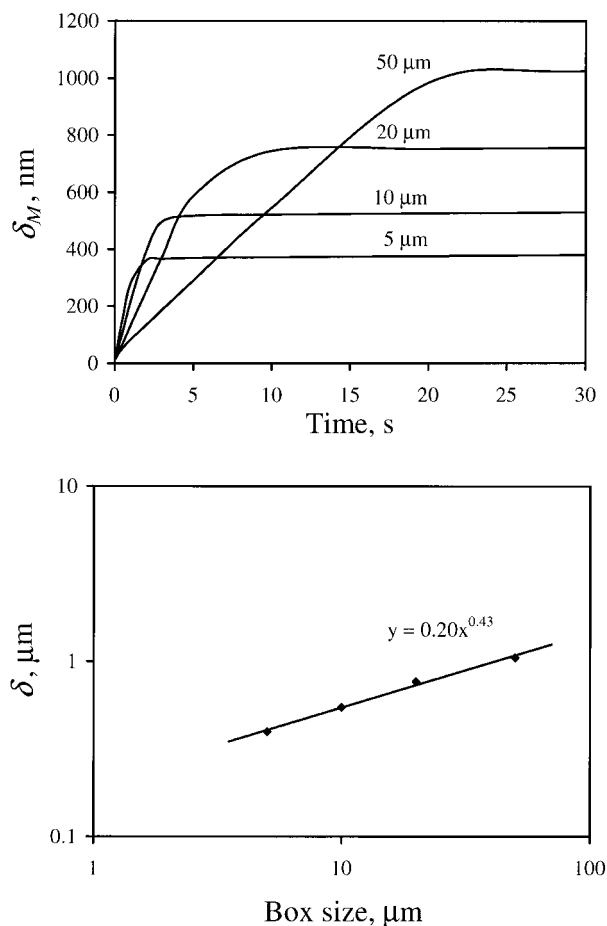


Figure 7 Effect of hydrodynamic conditions (box size L) on (a) the kinetics of film growth and (b) the thickness of the film at plateau onset.

the other models previously proposed. However, two shortcomings of our model are its strong dependence on box size and the unlimited growth with time of the film. The latter could probably be controlled through inclusion of a competing hydrolysis reaction of the amines.^{10, 11} Finally, a more quantitative model should include the diffusion of oligomers, which might lead to their adsorption onto the interface, thus reducing the dependence of the model on box size and resulting in faster termination of the reaction, thinner film, and a shift of its position closer to the interface.

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