Molecular simulation of polyamide synthesis by interfacial polymerization

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A molecular simulation is introduced for studying polyamide film formation by interfacial polymerization (IP), a highly used method for the synthesis of separation membranes. The simulation uses a modified cluster–cluster aggregation (CCA) model to simulate polymerization of functional monomers (e.g., trymesol chloride and phenylene diamine) at an interface between two liquid phases. By controlling the partition coefficient of each monomer in the opposite phase, the film is driven to form in the organic phase, as observed experimentally. The polymer film shows a dense core with looser ends, and an inhomogeneous charge distribution. The dense core of the membrane forms quickly, followed by slow polymerization reaction that leads to further densification of the membrane core. The simulation provides a basis for studying the IP process and can be used to carry out membrane performance studies on the molecular level.

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1. Introduction

Interfacial polymerization (IP), developed by Morgan et al. [1] is used to produce thin films, such as polyamides. The IP process is based on the reaction of two monomers in a two phase system, where the polymerization takes place in the interface between the two phases. In many cases the two monomers consist of a polyfunctional amine and an acid chloride, dissolved in an aqueous and an organic phase, respectively. IP is widely used and researched, especially regarding the production of thin film composite (TFC) membranes. The TFC membrane is composed of a thin polymer film mounted on a porous support layer, usually made of polysulfone [2]. These membranes are commonly used for desalination and liquid purification as reverse osmosis (RO) and nanofltration (NF) membranes.

It is believed that polymerization proceeds in the organic phase near the interface, due to the low solubility of acid chloride in water and relatively good solubility of amines in the organic phase. The film forms very quickly and continues to grow for several seconds. The film thickness may be of the order of tens of nanometers up to several microns, and is affected by the monomer concentration as well as the ratio between reactant concentration [5,6]. The film growth rate increases until diffusion of monomers through the film starts to be limited [3]. The termination of the reaction is explained by slower diffusion of diamines through the film as well as by hydrolysis of the acid chlorides that blocks the diamines and competes with the polymerization [3]. The rate of polymer production depends mainly on the solvent, monomer concentration and interfacial area available for reaction [1,4].

The major characteristics that determine membrane performance are set in the first few seconds of reaction [7]. Hence, understanding the relation between the polymerization conditions and the structure of the resulting thin film during incipient period of film formation is important since the degree of cross-linking [8,9], the porous structure [10] and chemical makeup of the film influence membrane performance.

With IP, it is possible to produce membranes with fixed charges that are formed from unreacted functional groups. Ion selectivity is determined by the presence of functional groups on the film surface and is apparently independent of film thickness [11]. In addition, these charges are believed to be helpful in reducing adhesion of foulants to the surface of the membrane, and effect retention of molecules in the membrane [12–15]. Experimental observations show a negatively charged layer on top of a positively charged layer in the porous support layer [16]. Frega and Srebnik [5] developed a mathematical model that showed an asymmetric distribution of charges within the film where the unreacted functional groups are found to separate in their respective phases around the interface. Indeed, their results showed a negatively charged thin layer facing the organic phase and a positively charged layer facing the aqueous phase.

The kinetics of film formation are difficult to observe experimentally due to the fast reaction. Using X-ray scattering and electron microscopy, Sundet [7] suggested that a highly branched low density polyamide film results from aggregation of colloidal particles. After the initial fast reaction of functional monomers, the increase in polymer weight, and thus membrane thickness, proceeds through relatively slow colloidal aggregation that forms a
fractal-like low density structure. Early theoretical models suggested an increase in film thickness with square-root of time, as in diffusion limited growth [6,17], which did not agree with experiments and later theoretical models that showed several stages of formations [18–20]. Freger [21] suggested an incipient film formation followed by a slow down due to film resistance to monomers diffusion through the film. Growth of the film becomes diffusion limited and continues until termination of the reaction.

Surprisingly, molecular models of IP film formation have not been developed. Such simulations can in principle be used to characterize membrane structure and performance for a large number of systems at very low cost. In this manuscript, we introduce a molecular simulation for IP film formation. We compare our resulting film to experimental and theoretical observations, in order to test the simulation as a tool for studying the IP process. While our current simulation relies on several simplifying assumptions (discussed below), it nonetheless captures important aspects of IP films.

2. Simulation model

We base our IP simulation model on the classical model of cluster–cluster aggregation (CCA), developed by Meakin [22]. The classical CCA model proceeds through Brownian movement of single particles and clusters. Aggregation occurs when a minimum distance between particles is reached. In general, aggregation can be classified as diffusion limited CCA (DLCA), where particles stick upon contact, or reaction limited CCA (RLCA) where aggregation depends on a pre-assigned sticking probability. Low density dendritic structures are observed for DLCA, while more compact structures are observed for RLCA with low sticking probability [23].

Since IP films in general have relatively loose structures, we consider DLCA as a compatible model to describe the IP process. DLCA has been used to describe polymerization processes. Among the findings of those models were dependence of mixture composition on the fractal dimensionality [24], a power-law dependency of molecular weight growth with time [24,25] and both reaction and diffusion limited behaviors at different stages of the reaction [26].

Our simulation model is based on the polymerization reaction of, e.g., trimesol chloride (TMC) and phenylene diamine (PD), where reaction between monomers of different types is limited by the number of available functional groups of each monomer. In this work, we assume no reaction byproducts, and thus polymerization occurs through aggregation of functional monomers and clusters. Thus, the competing hydrolysis reaction is neglected, which may lead to even faster termination of the reaction [3] than that observed in our simulation.

Our system consists of a three dimensional off-lattice asymmetric box with the x:y:z axis length ratio being 3:1:1, where the x-direction is perpendicular to the interface between the two phases. Periodic boundaries are taken in the y and z. The total volume of the box is determined by the average monomer density simulated. Initially, monomers of each type are randomly placed in two sections of the simulation box, separated by a fictitious interface. The solvent molecules are not explicitly simulated and implicitly affect the monomers through the diffusivity. The monomers are taken as soft spherical particles with maximum allowable overlap of 0.8σ, where σ is the monomer diameter. While the monomers are given a fixed functionality, a specific location of the functional groups on the particle surface is not assigned. Simulation proceeds by diffusion and aggregation of TMC monomers with up to three PD monomers, and similarly aggregation of PD monomers with up to two TMC monomers in accordance with the respective monomer functionalities. The mobility of the monomers is taken to be inversely dependent on cluster size, i.e., \( l_{\text{max}} = \frac{1}{N_M} \) where \( l_{\text{max}} \) is the maximum allowable step size and \( N_M \) is the number of monomers in the cluster. The actual step size, \( l \), may be lower to avoid overlap between monomers. \( l_{\text{max}} \) was chosen to be 2.4σ, which is the approximate mean free path of the particles under the concentrations studied, as specified below.

Apart from overlap, an attempted move may be also rejected due to miscibility considerations. The known low miscibility of the TMC monomers in the aqueous phase is simulated by giving TMC monomers a probability for displacement that depends on the composition of the surroundings of the diffusing monomer. That is, if a TMC monomer attempts to move into a location with high concentration of amines, the move will be accepted with a probability proportional to the ratio of TMC-to-amine monomers in that location, where the proportionality constant is the TMC partition coefficient in the aqueous phase, taken to be 0.01. Aggregation occurs between functional groups that come within a cut-off distance of 1.1σ. Once aggregated, the cluster is assumed to be rigid and the relative positions of the monomers in the cluster remain fixed throughout the remainder of the simulation. Simulation proceeds until a limiting rate of aggregation is reached, which required on the order of 10⁶ iterations. The simulation was made more efficient by using neighbor lists [27] for the aggregates and monomer environment.

This work focuses on the regime of incipient film formation [21]. We simulate gelation of a several thousands of monomers, which allows us to model the formation of a thin interfacial film approximately 10 nm thick. Most simulations consisted of a stoichiometric composition of 1200 TMC monomers and 1800 PD with total monomer volume fraction of 0.08, which corresponds to a concentration of 2–mol/L (assuming σ ≈ 0.5 nm). While this concentration is nearly 5-fold higher than practical experimental concentrations [1], we used this value due to the larger box dimensions and long simulation times necessary for practical experimental conditions. Nonetheless, we believe the trends reported below under these higher concentrations should indicate qualitative behavior at lower concentrations. Specification of the number of monomers and volume fraction dictates the simulation box dimensions, corresponding to box length \( L = 18.7σ \) along the y- and z-axes parallel to the interface and \( L_x = 56.1σ \) in the x-axis perpendicular to the interface. We chose asymmetric box dimensions so that film growth would not be limited by depletion of bulk monomers. In principle, a particle bath with constant bulk monomer concentration should be added at the box ends (x = 0 and x = Lₓ). This and other changes to the simulation are currently being implemented and their effect on simulation results will be reported elsewhere.

3. Results and discussion

In Fig. 1 we show simulation snapshots of film formation at different stages of the simulation. As time progresses, the formation of a thin film at the organic (left) side of the interface is clearly seen. Due to the restriction of a fixed number of monomers in the simulation box, a noticeable depletion in the concentration of bulk monomers is observed, especially at later stages of film growth. Two considerations led us to keep the simplified simulation of a fixed number of particles—a depletion zone in the vicinity of the reaction is expected, and more importantly, we chose an asymmetry between the x-dimension and other two box dimensions such that at higher box lengths the same results were essentially preserved, i.e., the reaction slows down because of the polymer barrier and not due to the lack of monomers.
3.1. Structure and chemistry

The thickness of the final film depends strongly on the initial monomer concentration at low concentrations. The dependence of film thickness ($\delta$) as a function of total monomer volume fraction ($\phi$) is shown in Fig. 2. The final film thickness decreases almost linearly with an increase in monomer volume fraction until a plateau is reached at $\phi \sim 0.1$. The plateau at high monomer concentrations can be explained by the fast formation of a dense impenetrable film at the interface between the large number of functional monomers initially present in the immediate vicinity of the interface. Hence, once the monomers near the interface have been consumed, the diffusion of monomers through the dense film is limited and further film growth proceeds at a very slow rate. The decrease with volume fraction appears to agree with theoretical results supported by experiments presented by Freger and coworkers [5,16]. However, our limited data cannot confirm their prediction of cubic root dependence of film thickness on monomer concentration, rather a stronger dependence is observed especially at low concentrations.

The film seen in Fig. 1 forms in the organic phase due to the lower miscibility of TMC in the aqueous phase. This is more clearly seen in a plot of the film density (Fig. 3a) and unreacted functional groups (Fig. 3b) relative to the initial density of monomers and each type of functional group, respectively. The bulk of the film at the final stages of its formation is located in the organic phase and shows a core that is nearly five times more dense than the initial bulk monomer concentration. Furthermore, the film displays a somewhat longer tail towards the aqueous phase than in the organic phase. The density of unreacted groups is also very high, indicating the formation of a highly charged film. Moreover, the unreacted groups are spread inhomogenously in the film, with a tendency towards each of the respective phases. The asymmetry of unreacted groups within the film at later stages of the reaction is expected [5] and implies the possible formation of negatively and positively charged layers in the film, as has been observed experimentally [17]. However, the distribution of unreacted functional groups in the simulated film is much more homogeneous than that predicted by the model of Freger and Srebnik [5]. This is due to the fast formation of an impenetrable film in the simulation that limits the consumption of unreacted groups in the film by diffusing monomers. Moreover, the assumption of rigid clusters does not allow for internal mobility of the clusters, which may lead to further cross-linking reactions and consumption of functional groups. Finally, curing of the formed polymer at
elevated temperatures brings the reaction closer to completion for manufactured membranes.

The resulting film is relatively dense and displays a void fraction, ε, of approximately 0.6 at its densest part, suggesting that the film does not display fractal behavior [28]. The surface area-to-volume ratio (S/V) of the film combined with its porosity provides an indication of film structure. For a random object, the expect average value for S/V is simply 6ε (in units of $\sigma^{-1}$) [29]. Higher values imply a disconnected structure where contacts between particles are minimized. Much lower values imply the formation of walls separated by large voids. Dense regions within the film are expected to be characterized by $S/V \sim \sigma^{-1}$, where $\sigma$ is the diameter of a monomer unit, while the very porous ends of the film by $S/V \sim 4\sigma^{-1}$ (assuming that on averages each monomer forms two bonds to ensure film connectivity). While the initial dispersion of monomers showed an average $S/V$ of 5.3 $\sigma^{-1}$, the final film has a lower average $S/V$ of 4.2 $\sigma^{-1}$, still indicating a relatively loose film structure.

3.2. Reaction kinetics

We can estimate the time for the formation of the film in the simulated incipient stage of IP by comparing the calculated diffusivity to the diffusivity in liquids, according to

$$t_1 = \frac{D}{D_0} \quad (1)$$

where $t_1$ is the time for a single iteration of the simulation (trial move and/or aggregation), $D$ is the calculated diffusivity in units of $\text{cm}^2/\text{iteration}$ and $D_0$ is the average diffusivity coefficient in dilute liquid solutions, on the order of $10^{-5} \text{ cm}^2/\text{s}$ [30]. We calculated $\langle D \rangle \approx 0.001 \text{ nm}^2/\text{iteration}$, obtaining $t_1 = 10^{-12} \text{ s}$, or $t_{\text{run}} \approx 1 \mu\text{s}$ for a simulation run. Since our simulated system contains a relatively high initial concentration of monomers, the barrier to further polymerization is reached several orders of magnitude more quickly than observed by experimental studies. Our calculations indicate that monomer diffusivity is strongly dependent on the concentration, i.e., a 2-fold increase in concentration leads to more than an order of magnitude decrease in the diffusivity.

According to Freger [21], IP film formation can be divided into three regimes: incipient film formation, slow-down, and diffusion-limited growth. Each regime is characterized by different reaction kinetics. The initial step is characterized by a thin reaction zone, where polymer begins to grow. Once a polymer layer forms, the decreasing diffusivity of monomers within the film and increasing resistance of the film lead to shrinking of the reaction zone. Thus, the incipient film is characterized by a dense barrier layer and looser structure on either side, as seen in Fig. 3. Following this stage, film growth proceeds by diffusion of the monomers through the film until their consumption by other monomers or unreacted functional groups within the film.

Under the conditions simulated, we obtain an impenetrable dense film whose growth essentially terminates at the slow-down regime following the incipient stage of formation. Diffusion-limited growth is negligible for the timescales of our simulation. In Fig. 4 we plot the change in the number of clusters, number of monomers making up the film, and film thickness with simulation time. It is seen that clustering begins instantly and proceeds at an exponentially decreasing rate, leading to the formation of a finite film early on in the simulation. It is further observed that once final film thickness is reached, the film becomes somewhat more dense (i.e., the number of monomers making up the film increases while its thickness remains constant) until further aggregation between functional monomers eventually stops. We do not observe a definite scaling of the increase in film thickness with the square-root of time, as predicted by earlier models [6,17,21] at any stage of the simulation. That is, under the simulated conditions, the polymerization reaction terminates in a dense impenetrable film that does not allow for substantial diffusion limited growth. Furthermore, increase of the amount of polymer with time appears to initially follow $N_p \sim t^2$ (where $t$ is the simulation time) and does not agree with the prediction of a linear increase of the amount of polymer with time, predicted by Freger [21], but fortuitously agrees with his scaling predictions of the maximum polymer concentration ($N_{p,\text{max}}$) for the initial stages of film formation. On the other hand, a plot of the maximum polymer concentration as a function of reaction time as obtained from the simulation (Fig. 5) shows a rather logarithmic rate of increase, much slower than the trend predicted. Freger [21] argues that the increase of $N_{p,\text{max}}$ with $t^2$ is a result of accumulation of unreacted functional groups on the forming polymer film that leads to an apparent increased rate. According to Freger, the growth of $N_{p,\text{max}}$ discontinues abruptly when film growth becomes diffusion limited. However, we observe a decreasing rate of polymer formation in the central dense region of the film to an asymptotic value. Since we studied polymerization at high initial monomer concentrations, the initial film layer is quite dense, and diffusion of monomers from the other phase is limited early on in our simulation. The rate of polymer formation at lower densities that are closer to experimental set-ups will be addressed in a future study. However, preliminary results indicate that even at experimentally relevant monomer concentrations the increase in maximum amount of polymer in the film is gradual and levels off to an asymptotic value.

![Fig. 4. Number of clusters $N_c$ (triangles), number of monomers making up the polymer film $N_p$ (squares) and film thickness $\delta$ in units of $\sigma$ (circles) as a function of iteration time for a typical simulation run. Solid black curves shows scaling of $N_p$ with the square of time.](image1)

We estimate the thickness of the reaction zone from the location of aggregation reactions that occur along the x-axis perpendicular to the film as a function of simulation time, shown in Fig. 6. It can be visually seen that the reaction zone narrows and shifts to the organic phase as polymerization progress. By calculating the average distance from the mean location of the reactions at a given
where 

dr

grey curve shows average taken every 20,000 iterations.

function of CCA iteration. Black curve shows average taken every 200,000 iterations; Fig. 7.

Average thickness of the reaction zone (in units of monomer size, as polymerization reaction progresses, shown in Fig. 7. The reaction zone thickness shows significant fluctuations when plotted over 20,000 iteration interval due to the relatively small scale of the simulation. Nonetheless, \( \delta \) averaged over 200,000 iterations shows a gradual decrease to a very narrow thickness of approximately 3\( \sigma \), similar to Freger’s predictions for the incipient film formation regime [21]. In addition, we observe in Fig. 6 that the number of reactions per unit time decreases substantially towards the end of the simulation, indicating that we reached the slowdown regime under our simulated conditions. By comparison with Fig. 3, it can be observed that the reaction zone is centered about the diffusion-limiting dense region of the polymer.

Several factors lead to the observed narrowing of the reaction zone: (1) the quick formation of dense polymer film creates a barrier to diffusion, (2) the limited diffusion of the organic monomers within the film, which also leads to the shift of the reaction zone to the organic phase and (3) the consumption of the unreacted organic end groups by the amines that now have to diffuse through the length of the film to reach the organic monomers. This last factor also contributes to the shift of the reaction to the organic side. Furthermore, the narrowing of the reaction zone contributes to the increase of unreacted charged groups in the film (Fig. 3) since these groups cannot be reached at later stages of the reaction [5].

As the formation of the dense polymer film progresses, monomer diffusivity through the film becomes increasingly limited. The diffusion of monomers through the film is calculated from

\[
D = \frac{\sum_{i=1}^{n} (d_{r_i})^2}{n \Delta t}
\]

where \( dr \) is the distance a monomer passes in a given time period \( \Delta t \) and \( n \) is the number of monomers included in the average in that time period. In Fig. 8 we show a plot of the average monomer diffusivity through the polymer film, averaged over several independent simulation runs. Initially, we observe a drop in the diffusivity as the film begins to form. Once formed, the diffusivity through the film decreases gradually as the film thickens and becomes more dense. The finite diffusivity of the monomers observed in Fig. 8 is of the unreacted monomers diffusing in the looser ends of the film. That is, diffusion of monomers through the film is not observed under the simulated conditions and the diffusion-limited growth of the film is not reached.

4. Conclusions

We presented a molecular simulation model of interfacial polymerization that occurs at the interface of an organic and an aqueous phase. The partition coefficient of the organic species is taken to be low in the aqueous phase such that polymerization occurs primarily in the organic phase. As is known for such thin film membranes, the density and charge distributions are found to be nonhomogeneous, which may reflect on the separation properties of the membrane. Although our simulated model is much smaller than the experimental system, we observe the reaction regimes of incipient film formation and slowdown due to limited diffusion of unreacted monomers within the film. To our knowledge, this model provides the first reported simulation of the IP process, and upon improvement and scaling, can be used for further structural and kinetic studies for better understanding of the process. Furthermore, membrane performance can be evaluated on the formed membrane through simulated diffusion studies of ionic and other species through the obtained films. To achieve size of experimental set-up, the simulation box must be increased by an order of magnitude. In addition, the number of monomers must be allowed to increase in the course of the simulation in order to retain experimental conditions of a constant bulk concentration. These changes are currently being implemented and will be reported in future communications.

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References


