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Molecular simulation of polyamide synthesis by interfacial polymerization

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ABSTRACT

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.

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 nanofiltration (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 apperantly 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]. Freger 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

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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., trymesol 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 depended on cluster size, i.e., $l_{max} \sim \sigma/N_M$ where l_{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_{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 for 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 10^6 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 $\sigma \cong 0.5$ 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 $L = 18.7\sigma$ along the y- and z-axes parallel to the interface and $L_x = 56.1\sigma$ 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 $x = L_x$). 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.