



Kinetics of interfacial polycondensation reactions – Development of a new method and its validation



Subhalaxmi Behera, Akkihebbal K. Suresh*

Department of Chemical Engineering, Indian Institute of Technology Bombay, Mumbai 400076, India

ARTICLE INFO

Article history:

Received 23 May 2017

Received in revised form

8 August 2017

Accepted 12 August 2017

Available online 23 August 2017

Keywords:

Reverse osmosis membranes

Polyamide

Interfacial polycondensation

Kinetics

ABSTRACT

The structure and function of the thin polymeric functional layer in reverse osmosis membranes depend on the kinetics of the interfacial polycondensation (IP) reaction by which the film is formed. It has been a challenge to achieve a quantitative understanding of these kinetics because of the high velocity of the reactions and the complex geometry of the support membrane in which the reaction takes place. In this work, we describe a novel and convenient technique for studying such kinetics, and demonstrate the method on the IP reaction between *meta*-phenylene diamine and trimesoyl chloride. The method involves studying the reaction in a simple geometry of a drop-continuous phase interface in an emulsion, under such conditions that all transport resistances are eliminated. The reaction course is followed through an on-line pH measurement using a fast probe. Interfacial areas available for reaction are measured by an encapsulation technique, under the conditions of reaction. The methods developed have been used to study the kinetics of the *m*-PDA-TMC reaction as a function of *m*-PDA concentration and surfactant (tween-85) concentration, and a surface-area based rate function has been shown to fit the data adequately.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Interfacial polycondensation (IP) is a step growth polymerization of two monomers dissolved in two immiscible phases. It is widely used in the synthesis of membranes or films for applications such as reverse osmosis [1], micro/nano encapsulation [2,3], and in the synthesis of thermo-labile polymers [4,5]. In particular, membrane-based desalination (reverse osmosis) is dominated by aromatic polyamide-based thin film composite membranes, in which the functional (polyamide) layer is produced by the interfacial polycondensation reaction between an amine monomer and an acid chloride monomer. In a typical procedure used to fabricate a TFC membrane, a macroporous support membrane (usually polysulfone on a nonwoven polyester fabric) is first dipped in an aqueous solution of *m*-Phenylene diamine (*m*-PDA), and then in an organic solution of trimesoyl chloride (TMC). A fast interfacial polycondensation reaction results in the formation of a very thin (100–200 nm) and dense skin layer of polyamide on top of the polysulfone membrane [1,6]. This thin layer, known as rejection

layer, is responsible for salt rejection in the desalination application. The performance of the rejection layer, in turn, is determined by the conditions under which the layer is produced, i.e., the conditions under which the IP reaction is carried out. Previous studies [2,3,7–9], have shown that important characteristics of the membrane, such as polymer crystallinity, molecular weight and MWD, depend on a competition between the kinetics of the reaction and the other rate processes involved. It is therefore essential to know the kinetics and understand the influence of various parameters on it. However, the kinetics of this process has proved difficult to study, firstly because it occurs in a very thin region on the support membrane (and possibly also inside its pores), and secondly because it is a very fast reaction with a timescale of the order of seconds. A method to study the kinetics of the reaction, and hence understand the effect of preparation parameters on the rate and evolution of structure, would thus be of a great value, not only for the membrane application, but also in other areas such as micro-encapsulation where such reactions are used.

Because of the difficulties mentioned in the previous paragraph, a qualitative approach to follow the kinetics is often the best that is possible. Such approaches usually involve the measurement of morphological changes in the formed polymer film [10].

* Corresponding author.

E-mail address: aksuresh@iitb.ac.in (A.K. Suresh).

Quantitative measurements, in which either a reactant concentration (using techniques such as UV-visible spectrophotometry [11–13], gas chromatography [14], high performance liquid chromatography, pH metry [2,3,15], FTIR [16] etc.) or some characteristic of the polymer film (e.g. thickness of polymer film, by techniques such as X-ray scattering, electron microscopy and light reflectometry [10,17–19], or film rigidity, say by pendant drop tensiometry [20]) is followed as a function of time, have been attempted. In either case, because of the speed of reaction, only on-line techniques with a fast response are useful, and even they can usually be applied only for applications such as micro-encapsulation, in which the reacting medium is accessible to the probe. Thus, the interfacial reaction between amines and isocyanates has been successfully studied using the pH of the aqueous medium to track the extent of reaction with time [2,3]. Bradbury and Crawford [12] studied the IP kinetics of the reaction between piperazine and terephthaloyl chloride in a two phase reaction mixture by measuring the concentration of terephthaloyl chloride at different time intervals through UV-visible spectroscopy. Enkelmann and Wegner [17] studied the IP reaction between sebacyl chloride and hexamethylene diamine leading to formation of linear polyamide. They established the conversion-time curve and derived a rate equation by measuring the rate of increase in membrane thickness with time using a light microscope. Tsai and Lee [13] and Wang et al. [21] studied the kinetics of the reaction between bisphenol-A and isophthaloyl chloride by monitoring the aqueous phase monomer concentration at different times, by separating the two-phase reaction mixture. A point to be aware of in such methods in which a reactant concentration is followed, is the possibility of the side reaction of hydrolysis of the organic phase monomer. Available studies [2,12,22–24] however, indicate that this side reaction is often of negligible importance in the presence of a monomer (such as an amine) of high reactivity towards the organic phase reactant (usually an acid chloride or an isocyanate). In all the above cases, the monomers are bifunctional and a linear polymer results.

The context for the present work is our ongoing studies on the kinetics-structure-property relations in aromatic polyamide-based RO membranes, in which the reaction of interest is the one between *m*-phenylene diamine (*m*-PDA) and tri-mesoyl chloride, (TMC). Because of the tri-functionality of the acid chloride monomer in this case, the polymer is crosslinked; in fact, the degree of cross-linking affects the membrane structure and function in significant ways. While most studies in the literature are on linear systems, there are a few studies on this crosslinking/branching reaction, in which it is usually some film characteristic that is followed with time [8,16,25,26]. Chai and Krantz [27] and Khare et al. [10,28] have studied this reaction at a liquid-liquid (water-oil) interface using optical light reflectometry, pendant drop tensiometry and pendant drop mechanical analysis. In reflectometry measurement, the refractive indices were measured continuously to characterize the solidification of the polymer solution, under conditions that ensured a slow growth of the IP film. In the pendant drop technique, a drop of aqueous phase was rapidly lowered into organic phase and the drop shape monitored with time. The shape was related to the modulus of the film through a model. The viscoelastic and transport properties of the unsupported aromatic polyamide layer were used to determine the relative degree of cross-linking and branching that occurs simultaneously with the formation of linear polymer chains [10,28]. These authors concluded from their studies that, at low TMC concentrations, the reaction was limited by mass transfer of the TMC monomer in the organic solvent; while at high TMC concentrations, diffusion of *m*-PDA through the polyamide layer was limiting. Surprisingly, these authors found the reaction to occur towards the aqueous side of the interface at low

m-PDA concentrations. The degree of cross-linking reached a maximum for an intermediate TMC concentration (0.1 wt%), whereas the degree of branching and polydispersity increase monotonically with increasing TMC concentration. At high TMC concentrations, branching predominates over crosslinking. They also observed that the properties of the polyamide layer continued to change for more than 300 s after reaching maximum thickness, and attributed this behaviour to further cross-linking, i.e., the formation of linkages between linear macro-molecules, in the polyamide layer. However, no quantification of intrinsic kinetics could be obtained from their analysis.

Jin and Su [16] used a FTIR-based method to quantify the carboxylic acid content as a function of monomer concentrations, reaction time and temperature in the un-supported polyamide film prepared via IP polymerization of *m*-PDA in water and TMC in hexane. Their results show that the variations in the TMC and *m*-PDA concentrations have pronounced effects on the hydrophilicity (–COOH content) of the PA thin film, and the structure of the PA films changes with reaction time in ways that agree with the observations of Khare et al. [10,28]. Temperature increases the diffusion rate of *m*-PDA monomer through the interface and has a great effect on the IP reaction.

In an attempt to gain further insights on interfacially polymerized aromatic polyamide growth kinetics and improve on the time resolution of prior studies, Matthews et al. [29], used an *in-situ* diffuse reflectance spectroscopy (Rutherford backscattering spectrometry, RBS) to monitor the growth of the polyamide layer in real time, when the reaction takes place on a polysulfone support. For all TMC concentrations studied by them and for *m*-PDA concentrations above 2 g/l, about 50% of the total polyamide thickness forms in approximately two seconds of polymerization time. The polyamide growth rate slows substantially at larger times. They concluded from their studies that the polyamide forms predominantly within the pores of polysulfone support when the *m*-PDA concentration is < 0.5 g/L.

A survey of the literature thus shows only a few studies on the kinetics of the IP reaction; studies in crosslinking systems are even fewer. There are virtually no studies that report kinetic expressions which can be used in design or in understanding how kinetics affect the film structure. Virtually all such studies involve a liquid-liquid interface, either in a dispersed biphasic configuration or with one phase layered on top of the other. The methods in which a reactant concentration is followed with time seem to be the more convenient and promising (since they can be directly related to the rate of the reaction), but need to be fast relative to the kinetics of the reaction; also conditions need to be chosen such that side reactions are either suppressed or unimportant. Polymer film characteristics such as thickness or rigidity are difficult to relate directly to kinetics, especially with multifunctional monomers, since these characteristics depend on factors such as the extent of crosslinking and branching, in addition to the main reaction.

In this paper, an adaptation of the pH-based technique [2,3] is developed for studying interfacial polycondensation kinetics. The method has been used to study the kinetics of the reaction between *m*-PDA and TMC, and in particular, to determine the dependence of the reaction rate on the concentration of the amine monomer in the presence and absence of a surfactant. Although, as mentioned above, the interest here is in TFCMs for RO application, in order to facilitate the kinetic study, the reaction is carried out in a liquid-liquid dispersion. The method is based on the fact that, in a batch reaction, the pH of the continuous phase falls as the reaction proceeds, due to (i) the consumption of the (alkaline) monomer, and/or (ii) the accumulation of an acidic (usually HCl) byproduct. While this fall in pH, in principle, can be used to determine the intrinsic kinetics, it has to be ensured that the polymer film that forms does

Download English Version:

<https://daneshyari.com/en/article/5177623>

Download Persian Version:

<https://daneshyari.com/article/5177623>

[Daneshyari.com](https://daneshyari.com)