



Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec



Enhancing the solvent-dendrimer miscibility at the interface and its impact on the thin film composite membrane

J.Y. Sum, J.J. Beh, A.L. Ahmad, B.S. Ooi*

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, Pulau Pinang, Malaysia

ARTICLE INFO

Article history:

Received 11 May 2017

Received in revised form 24 August 2017

Accepted 18 September 2017

Available online xxx

Keywords:

Interfacial polymerization

Thin film composite membrane

Co-solvent

Poly(amidoamine)

Dendrimer

ABSTRACT

Poly(amidoamine) (PAMAM) based thin film composite (TFC) membranes were prepared via interfacial polymerization with the aid of co-solvent. The addition of acetone promoted miscibility between the hexane and water phases, which enhanced the dissolution of the dendrimer and water into the reaction zone. By adding acetone, the membranes showed enhanced multivalent cation rejection. However, the presence of moisture promotes the hydrolysis of unreacted acyl chloride which lead to pore broadening effect. Pore enlargement was related to the presence of moisture in organic phase which was diffused from aqueous phase due to its affinity toward acetone–hexane solution.

© 2017 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

Introduction

Polyamide thin film composite (TFC) membrane which is typically used as nanofiltration (NF) or reverse osmosis (RO), consists of dense skin layer built on top of an ultrafiltration support layer [1]. The performances of the membrane depend on the skin layer properties which can be tailored during interfacial polymerization (IP). IP involves polycondensation reaction of amine and acyl chloride monomers, whereby an ultrathin polymer film is formed immediately at the interface of two immiscible solvent which carried the respective monomers [2]. It was commonly accepted that interfacial polymerization takes place in organic phase due to unfavorable dissolution of acyl chloride in aqueous phase [2,3]. The reaction is a diffusion-controlled process, thus the type of aqueous monomer used is critical as it will affect the physiochemical properties of membrane. In recent years, poly(amidoamine) (PAMAM) dendrimer has been widely used as monomer in membrane synthesis [4–6]. The PAMAM molecules contains numbers of amine terminal groups as reactive sites for polymerization. Our previous work reported on the synthesis of high flux TFC membranes by using PAMAM as monomer [7]. The membrane has exceptional water permeability, but perform poorly in salt removal. The membrane performance was marginally improved by increasing the PAMAM concentration, signified the poor partitioning and diffusion of such a big monomer into the organic phase.

The high hexane–water interface tension and poor dissolution of PAMAM in hexane limit the availability of PAMAM in the reaction zone. The extent of reaction was thus reduced and consequently a loose and defective membrane skin layer was obtained.

Various factors are contributing to the rate of amine monomers diffusion, includes the reactant concentration, the choice of solvent used and liquid interface miscibility [8,9]. The presence of phase transfer additives in either organic or aqueous phase could greatly enhance the IP process. Additive such as surfactant possess hydrophobic long alkyl chained to hydrophilic functional group, enable it to partition in both organic and aqueous phases [10,11]. The miscibility of both liquid phases was promoted and the amine monomers are free to diffuse across the interface. On the other hand, phase transfer catalyst (PTC) such as ammonium salt [12,13] and 4-dimethylaminopyridine (DMAP) [14] were also used to facilitate the transportation of aqueous amine monomers across the interface. A complex by the water-soluble PTC, water and the amine monomer through electron donor–accepter systems was formed. The formed complex is subsequently transported to the organic phase due to the presence of alkyl group in the PTC which enables the complex to be solubilized in organic phase.

The use of co-solvent in IP for monomer diffusion enhancement was demonstrated by Hirose et al. in which isopropyl alcohol was added into aqueous phase for the preparation of RO membrane [12]. Membrane permeability was enhanced while maintaining high salt removal rate. They claimed that it was due to the enhanced miscibility of hexane–water phases because of co-solvent addition. Similar observation was reported when different type of co-solvents such as acetone [13–15], dimethyl

* Corresponding author. Fax: +60 45941013.

E-mail addresses: chobs@usm.my, ooibse@gmail.com (B.S. Ooi).

<http://dx.doi.org/10.1016/j.jiec.2017.09.031>

1226-086X/© 2017 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

sulfoxide [16,17], hexamethyl phosphoramidate [18] and ethers [19–21] were used. Thorough investigations of co-solvent assisted interfacial polymerization and its influences on the physiochemical properties of membrane were reported by Tsuru and his group recently [14,15,22,23]. They demonstrated the precise control of skin layer thickness, pore size and membrane performances by varying the types and concentrations of co-solvent. A multi-layered structured polyamide skin layer was obtained, resulting from enhanced diffusivity of diamine monomers across the interface [22]. The multi-layered structure facilitated the water passage contributed by high effective surface area and less transport resistance in the film. Besides mass transfer enhancement, the co-solvent was also reported for the improved of bimolecular nucleophilic substitution (S_N2) reaction. The presence of polar aprotic solvent may greatly enhanced the reactivity of polymerization [18,24]. Co-solvent such as dioxane was capable to enhance the dispersion stability of inorganic filler in organic phase [20]. It may also granted an uniform and thorough wetting of the support by amine monomers [25].

In this work, acetone was added as a co-solvent to enhance the partitioning of PAMAM into organic phase during interfacial polymerization. It was commonly reported for small and highly diffusive aqueous monomer such as MPD and piperazine in preparation of TFC membrane. The PAMAM-G0 dendrimer on the other hand is an organized branched structure with hydrophilic moieties. Due to its big molecular size and hydrophilic nature, the dendrimer will diffuse less efficiently across the nascent thin film that is formed during interfacial polymerization. Acetone has solubility parameter falls between water and hexane, enables it to partition into both aqueous and organic phases [26]. To our best knowledge, phase transfer of such a big and hydrophilic PAMAM monomer with profound diffusional resistance has never been reported. The prime objective of this work is to probe the interfacial miscibility of monomer and the subsequently carried over moisture on the membrane performances.

Material and methods

Chemicals and materials

Polysulfone resin in pellet form (Udel P-1700, Solvay Advanced Polymer), polyvinylpyrrolidone (Sigma–Aldrich), *N*-methylpyrrolidone (Merck) and polyester fabric (Texlon Corporation) were

used as material in synthesis of polysulfone substrate membrane. Ethylenediamine core poly(amidoamine) dendrimer 0 generation (G0) (PAMAM, 20 wt.% in methanol) and 1,3,5-benzenetricarbonyl trichloride (TMC, 98% assay) were obtained from Sigma–Aldrich. Solvent and reagent used during membrane synthesis and performance evaluation such as *n*-hexane, acetone and triethylamine (TEA), analytical grade sodium chloride (NaCl), sodium sulphate (Na_2SO_4), magnesium chloride ($MgCl_2$), magnesium sulphate ($MgSO_4$), glucose, potassium hydroxide (KOH), hydrochloric acid (HCl) and potassium chloride (KCl) were obtained from Merck. The Hydranal methanol and Composite-5 solution which were used in moisture content determination were obtained from Sigma–Aldrich. All chemicals were used without further purification.

Preparation of thin film composite membranes

Polysulfone (PSF) UF support was prepared by non-solvent induced phase inversion method as reported in our previous work [7]. The top active layer was formed by interfacial polymerizing 0.5% (w/v) PAMAM and 0.1% (w/v) TMC, with the addition of 2% (w/v) TEA as acid acceptor in aqueous solution. The aqueous phase contains 1.8% (w/v) of methanol contributed by the PAMAM feedstock solution which could play the role as co-solvent in promoting miscibility between the hexane and water. Acetone was used as co-solvent with concentration ranging from 0 to 8% (w/v) in hexane solution. The reaction scheme between PAMAM and TMC is illustrated in Fig. 1. The prepared PSF UF membrane was first wetted with 0.5% (w/v) PAMAM aqueous solution for 10 min. After that, the PAMAM solution was removed, followed by reaction with TMC in hexane/acetone solution for 30 s. Next, the membrane was heat treated at 60 °C for 15 min to promote further crosslinking and residual solvent removal.

Membrane characterization

Surface functional groups were characterized by Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) (Thermoscientific, Nicolet iS10). Each IR spectrum was obtained from the average of 32 scans with resolution of 4 cm^{-1} . Contact angle of the membrane was determined by using contact angle goniometer (Model 200-00, Ramè-hart Instrument Co.). $8\ \mu\text{L}$ of deionized water was dropped onto the membrane surface by

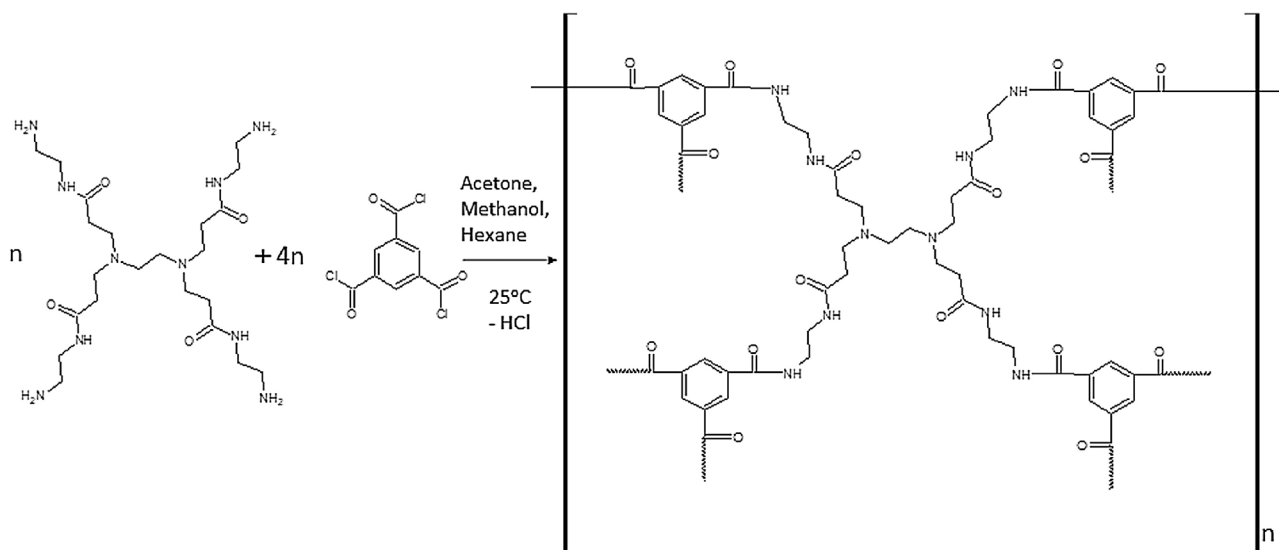


Fig. 1. Proposed reaction scheme of PAMAM with TMC.

Download English Version:

<https://daneshyari.com/en/article/6667159>

Download Persian Version:

<https://daneshyari.com/article/6667159>

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