



ELSEVIER

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Molecular dynamics simulation and positron annihilation lifetime spectroscopy: Pervaporation dehydration process using polyelectrolyte complex membranes

Yun-Hsuan Huang^b, Quan-Fu An^{a,*}, Tao Liu^a, Wei-Song Hung^b, Chi-Lan Li^c,
Shu-Hsien Huang^d, Chien-Chieh Hu^b, Kueir-Rarn Lee^{b,**}, Juin-Yih Lai^b

^a MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science & Engineering, Zhejiang University, Hangzhou 310027, China

^b R&D Center for Membrane Technology, Department of Chemical Engineering, Chung Yuan University, Chung-Li 32023, Taiwan

^c Department of Applied Cosmetology, Taoyuan Innovation Institute of Technology, Chung-Li 32091, Taiwan

^d Department of Chemical and Materials Engineering, National Ilan University, I-Lan 26047, Taiwan

ARTICLE INFO

Article history:

Received 3 June 2013

Received in revised form

23 September 2013

Accepted 25 September 2013

Available online 1 October 2013

Keywords:

Polyelectrolyte

Polyelectrolyte complex membrane

Pervaporation

Positron annihilation lifetime spectroscopy

(PALS)

Molecular dynamics (MD) simulation

ABSTRACT

The micro-structure of various novel polyelectrolyte complex membranes (PECMs) was investigated by means of molecular dynamics (MD) simulation and positron annihilation lifetime spectroscopy (PALS). These PECMs that differed in their chemical structure design were applied to dehydrate a 90 wt% ethanol aqueous solution by pervaporation, and their separation performance was correlated with their microstructure. Free-volume size and free-volume size distribution were determined both by the PALS and MD simulation techniques. To describe the free-volume shape and the polymer chain flexibility and stiffness, MD simulation analysis in terms of radial distribution function and mean square displacement was also conducted. Results obtained from PALS and those from MD simulation were in agreement with each other. These results were highly consistent with the chemical structure of the PECMs designed in this study and were demonstrated to correlate well with the membrane pervaporation separation performance.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Pervaporation separation processes are economical alternatives to conventional ones for difficult-to-separate mixtures such as azeotropes, isomers, and heat-sensitive mixtures [1–3]. The separation of aqueous–organic mixtures is common in industries. Among the many aqueous–organic mixtures that form azeotropes, ethanol–water systems have been widely investigated [4]. Recently, polyelectrolyte complex membranes (PECMs) have been receiving attention because of their ability to dehydrate aqueous–organic mixtures, which is ascribed to their high hydrophilicity and high ionic cross-linking properties.

PECMs are polymeric materials that contain two oppositely charged polyelectrolytes. They are commonly prepared by the following methods: bilayer casting [5–7], blending [8,9], and layer-by-layer assembly (LbL) [10–12]. A new method to prepare PECMs is called acid-protection alkali-de-protection, in which soluble

polyelectrolyte complexes are produced by pH adjustment with an acid and are then deprotonated with a base [13,14]. These PECMs show high permeability and selectivity in dehydrating aqueous organic mixtures by pervaporation [14–16].

To date, many researchers have been investigating on how to improve the separation performance of membranes for dehydrating aqueous–organic mixtures. In this regard, the chemical structure is an important factor that affects the performance of polymeric materials. Hence, to achieve improved or tailored separation performance, researches on chemical structure design and its correlation with pervaporation performance have been conducted [17,18]. Free-volume properties play a key role in pervaporation processes that are governed by the solution-diffusion mechanism. It is important to understand, therefore, the correlation between free-volume and the design of polymeric material chemical structure.

Two powerful techniques can give an understanding of the microstructure of polymeric materials: positron annihilation lifetime spectroscopy (PALS) and molecular dynamics (MD) simulation. PALS is an experimental technique for measuring free volume-properties such as free-volume size, free-volume intensity, and free-volume distribution [19–24]. MD simulation is a computational technique for gaining insight into polymeric membranes by giving prediction on

* Corresponding author. Tel./fax: +86 571 87953780.

** Corresponding author. Tel.: +886 3 2654190; fax: +886 3 2654198.

E-mail addresses: angf@zju.edu.cn (Q.-F. An), krlee@cycu.edu.tw (K.-R. Lee).

their microstructure at the molecular scale [25–28]. From past studies, PALS and MD simulation techniques have been successfully used in analyzing free-volume properties. A coincidence of results obtained from experimental and computational work has been reported [29–33].

In this study, we synthesized various polycations that differ in the length of their side chains, depending on the size of alkyl group. These new polycations were used to fabricate novel PECMs, which were applied to dehydrate ethanol–water mixtures. PALS and MD simulation techniques were adopted to analyze the microstructure of the PECMs.

2. Experimental section

2.1. Materials

Sodium carboxymethyl cellulose (CMCNa) with an intrinsic viscosity of 625.1 mL/g, dissolved in 0.1 M sodium hydroxide aqueous solution, was obtained from Sinapharm Chemical Reagent Co., Ltd., Shanghai, China. The polycation, poly(N-alkyl-4-vinylpyridinium) (PAVP), was synthesized according to the procedure described in our previous study [34]. In this study, the PAVP substituted with an alkyl halide was referred to as PAVPm, where m denoted the substitution degree with respect to the number of carbons in the alkyl halide. Thus, the value of m could be 0, 2, 4, 6, or 8; $m=0$ referred to the condition at which no alkyl halide was added. The chemical structure of the CMCNa polyanion and the PAVPm polycations is shown in Fig. 1. All other organic solvents and reagents, including ethanol, sodium hydroxide, and hydrochloric acid, were analytical reagent grade. The substrate polysulfone ultrafiltration membrane (MWCO=35,000 Da) was provided by the Development Centre of Water Treatment Technology, Hangzhou, China. Deionized water with a resistivity of 18 M Ω cm was used in all experiments.

2.2. Preparation of polyelectrolyte complex membranes

Soluble polyelectrolyte complexes (PECs), represented as PAVPm–CMCNa, were prepared according to the method described in detail in our previous study [14,34]. Fig. 1(c) shows the chemical structure of the PECs. Solutions of 0.01 M PAVPm and 0.01 M CMCNa were prepared. The HCl concentration in both solutions was 0.007 M. Then, a 200 mL PAVPm solution was added dropwise

into a 400 mL CMCNa solution while stirring the resulting mixture, which instantaneously became turbid. This turbidity indicated the occurrence of ionic complexation between CMCNa and PAVPm. At the complexation endpoint, insoluble PEC precipitates settled at the bottom of the flask. These PECs were separated by decantation, washed with deionized water several times, and then dried in an oven at 60 °C for 24 h.

PECs were dissolved in a 0.1 M NaOH aqueous solution. The pH of the solution was controlled at about 8, so as to completely dissolve the PECs. The result was a solution with a concentration of 2.5 wt% PECs. In preparing a PECM, a PEC solution with a volume of 8 mL was cast on an 8 cm \times 8 cm polysulfone membrane in a dust-free atmosphere at room temperature. The PEC coverage on the substrate surface was controlled with the use of a casting knife with a gap thickness of 440 μ m. All of the PEC membranes thickness was about 4.5 ± 0.5 μ m. The membrane was dried at 60 °C for 4 h, and it was then stored for further use. The conditions for preparing all the membranes were kept the same.

2.3. Membrane characterization

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were obtained with Perkin Elmer Spectrum One. For the polycation chemical characterization, a 1-D nuclear magnetic resonance (NMR) spectroscopy (¹H, ¹³C, and DEPT-135) was adopted. Furthermore, for the carbon and proton chemical structure assignment, a 2-D NMR (H–H COSY and C–H HSQC) was used. All NMR spectra were obtained at 400 MHz with Bruker AVANCE II system, using D₂O solvent.

2.4. Positron annihilation lifetime spectroscopy

Positron annihilation lifetime spectroscopic experiments were conducted to determine the free-volume in PECMs. A conventional fast-fast coincidence spectrometer with a time resolution of 250 ps was used. A radioactive source of ²²Na (0.74 MBq), sealed in between 12- μ m thick Kapton films, was sandwiched in two stacks of membrane samples that consisted of several layers of free-standing PECMs. Each stack of sample had a total thickness of 1 mm. Positron annihilation lifetimes were recorded using a fast-fast coincidence timing system. A time-to-amplitude converter was used to convert lifetimes and to store timing signals in a multi-channel analyzer (Ortec System). Two million counts were collected,

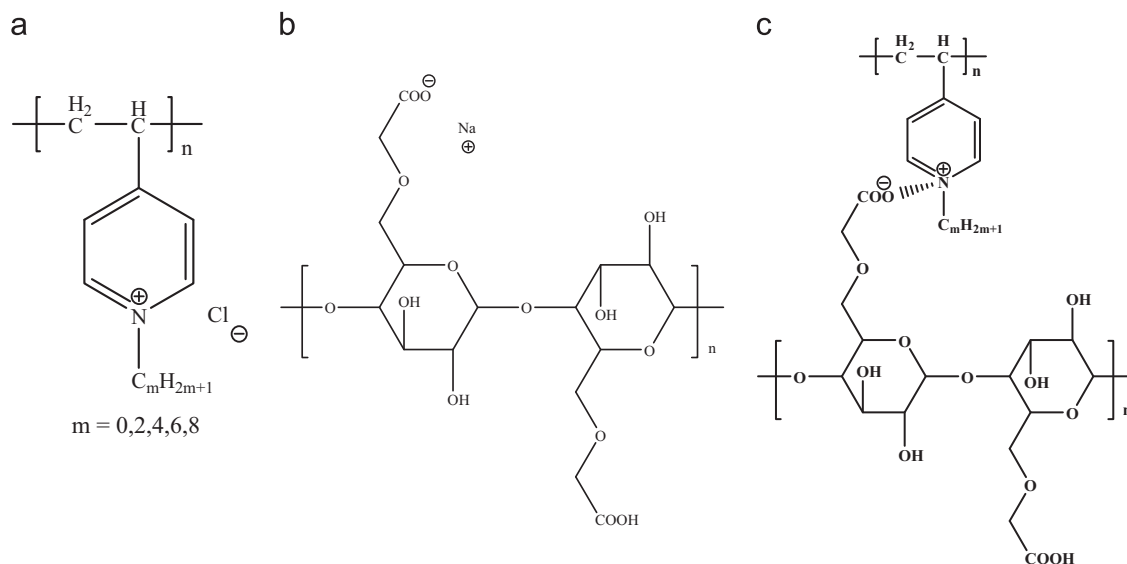


Fig. 1. Chemical structure of polyelectrolytes, (a) PAVPm polycation and (b) CMCNa polyanion, and of polyelectrolyte complexes, (c) PAVPm–CMCNa.

Download English Version:

<https://daneshyari.com/en/article/7022319>

Download Persian Version:

<https://daneshyari.com/article/7022319>

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