

Gas permeability of mixed matrix membranes composed of poly(diphenylacetylene)s and dispersed metal chloride particles



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ARTICLE INFO

Article history:

Received 6 December 2017

Received in revised form

13 February 2018

Accepted 20 February 2018

Available online 23 February 2018

Keywords:

Mixed matrix membrane

Gas permeability

Polyacetylene

ABSTRACT

In this study, the effect of the addition of metal particles on the gelation properties of poly[1-(3,4-dimethoxyphenyl)-2-(4-trimethylsilylphenyl)acetylene] [poly(DMOTMSDPA)] and poly[1-phenyl-2-(4-trimethylsilylphenyl)acetylene] [poly(TMSDPA)] was examined. The addition of TaCl₅, NbCl₅, and MoCl₅ to poly(DMOTMSDPA) and poly(TMSDPA) solutions afforded gels. However, the addition of Ta(OCH₃)₅ and Mo(OCH₃)₅ did not induce gelation. Lewis acids such as TaCl₅, NbCl₅, and MoCl₅ can coordinate with the π -electrons from the polyacetylene backbone and lone pair of the methoxy groups. Mixed matrix membranes (MMMs) composed of poly(DMOTMSDPA) and these metal chlorides were fabricated by varying the amount of metal chloride. The metal chloride particles were uniformly dispersed in poly(DMOTMSDPA) because the polymer chains could interact with the metal chloride particles. The oxygen permeability of the MMMs composed of poly(DMOTMSDPA) was greater than that of pure poly(DMOTMSDPA). With the addition of 20 mol% of TaCl₅, the oxygen permeability increased. In addition, the gas permeability of poly(TMSDPA) was increased by the addition of TaCl₅. On the other hand, the gas selectivity values of MMMs were 1.8–3.1, suggesting that MMMs do not contain non-selective defects such as pinholes and interfacial voids in the matrix.

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1. Introduction

Gas separation membranes are attracting increasing attention because membrane separation exhibits advantages over conventional separation, such as low operation costs, low energy consumption, and facile operation [1–5]. Polymers with high gas permeability and selectivity have been developed previously; however, a general trade-off relationship between the permeability and selectivity has been noted [6]. To improve the permeation performance and to minimize the trade-off effect, mixed matrix membranes (MMMs) composed of organic polymers with inorganic particles have been prepared [7–9]. MMMs demonstrate the potential to achieve higher permeability, higher selectivity, or both as compared with existing polymer membranes. For example, Merkel et al. designed MMMs composed of poly(4-methyl-2-pentyne) and nanosized particles [10,11]. Poly(4-methyl-2-pentyne) is a glassy polymer, and the membrane thus formed exhibits a high free volume. Nanosized particles affect the packing of the polymer chains,

thereby enhancing their permeability and their selectivity for *n*-butane over methane. The free volume in the polymer matrix is expected to be increased by mixing of the nanosized particles with the polymer.

One important issue during MMM preparation is the aggregation of nanosized particles [7]. Because of their different physical properties, particularly, the difference in the density between inorganic particles and organic polymers, aggregation often occurs during MMM preparation. During the aggregation of these nanosized particles, pinholes form, resulting in non-selective defects in the MMM. Another issue is the detachment of the organic polymer from the inorganic particles, which also forms non-selective defects in the form of interfacial voids. A possible solution involves the use of a polymer that can interact with inorganic particles. Such an interaction would prevent not only the aggregation of particles but also the detachment of the polymer from the particles.

Previously, our group synthesized and investigated several substituted acetylene polymers, especially poly(diarylacetylene)s, for gas separation membranes [12–16]. These polymers are promising candidates for membranes with high gas permeability, which is due to the combination of their stiff main chains comprising alternating double bonds and the steric repulsion of the

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bulky side groups, both of which leading to the sparse structure of the polymer matrixes at the molecular level. Recently, our group reported the formation of a gel in a toluene solution of poly[1-(3,4-dimethoxy)phenyl-2-(4-trimethylsilyl)phenylacetylene] [poly(-DMOTMSDPA)] via coordination bonds upon the addition of TaCl₅ [17]. With the addition of a small amount of methanol to the gel, it reverted back into the solution. As a result, metal–polymer coordination bonds formed, inducing the formation of a supramolecular polyacetylene gel. This fact suggests that poly(DMOTMSDPA) interacts with TaCl₅; hence, MMM composed of poly(DMOTMSDPA) and TaCl₅ is predicted to be a defect-free, high-performance membrane.

In this study, the effect of the addition of various metal chlorides on the gelation properties of poly(DMOTMSDPA) was examined in detail. An MMM composed of poly(DMOTMSDPA) and metal chlorides was prepared, and its gas permeability was measured (Fig. 1). In addition, the MMMs of an analogous polymer without dimethoxy groups, i.e., poly[1-phenyl-2-(4-trimethylsilyl)phenylacetylene] [poly(TMSDPA)], were prepared and investigated. Contrary to our expectation, not only poly(DMOTMSDPA) but also poly(TMSDPA) formed supramolecular gels upon the addition of TaCl₅; this is probably occurred via the coordination between TaCl₅ and the π -electrons of the conjugated backbone. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images reveal the uniform dispersion of metal chloride particles in a polymer matrix. Upon the addition of metal chlorides, the gas permeability increased without a decrease in permselectivity.

2. Experimental

2.1. Materials

TaCl₅ (99.999%), NbCl₅ (99.995%), and MoCl₅ (99.99%) were purchased from Sigma-Aldrich Co. LLC. Other chemical reagents and organic solvents were purchased from Wako Pure Chemical Industries, Ltd. Ta(OCH₃)₅ and Mo(OCH₃)₅ were synthesized by the treatment of TaCl₅ and MoCl₅ with a large excess of methanol and purified by recrystallization. The polymerization solvent toluene was purified by distillation over calcium hydride. TaCl₅, which served as the main catalyst for polymerization, was used without further purification, while *n*-Bu₄Sn, which served as a co-catalyst, was purified by distillation under reduced pressure. Poly(-DMOTMSDPA) and poly(TMSDPA) were synthesized according to previously reported studies [17,18]. The molecular weights of the polymers used herein are as follows. Weight-average molecular weight (M_w) and number-average molecular weight (M_n) of poly(DMOTMSDPA) were 1.95×10^6 g/mol and 2.12×10^5 g/mol, respectively. Those of poly(TMSDPA) were 7.10×10^6 g/mol and 5.46×10^6 g/mol, respectively.

2.2. Measurements

Gel permeation chromatography using CHCl₃ as the eluent and polystyrene for calibration was carried out at 40 °C to estimate the molecular weights and polydispersity indices of the polymers on a Shimadzu LC-10AD chromatography system equipped with three polystyrene gel columns (Shodex K-804 L, K-805 L, and K-807 L) and a Shimadzu RID-6A refractive index detector. IR spectra were recorded on a Nicolet iS5 spectrometer (Thermo Fisher Scientific Inc.) using KBr pellets. Field-emission scanning electron microscopy (FE-SEM) was performed using a Seiko Instrument/Zeiss Ultra plus system (Seiko Instruments Co. Ltd., Chiba, Japan; Zeiss Co. Ltd., Oberkochen, Germany) to record cross-sectional images of the MMMs. For the images, the sample piece was covered with aluminum foil to prevent static charge during measurements. A 1 mm² piece of foil was cut from the cover on the sample, and then the exposed contact surface was examined at accelerating voltages of 5–15 kV. The Mo composition was determined by the ZAF correction method using an energy-dispersive X-ray spectrometer (Bruker AXS Co. Ltd., Kanagawa, Japan) in the FE-SEM analysis. TEM images were recorded on a JEOL JEM-2100 transmission electron microscope operated at an accelerating voltage of 200 kV. The membranes were cut to a thickness of 150 nm and then placed on TEM Formvar/carbon-coated copper grids. The images of the membranes were recorded on a Gatan Orius 200D CCD camera.

Gas permeability coefficients of the polymer membranes at 25 °C under an upstream pressure of 1 atm were recorded on a Tsukubarikaseiki K-315-N gas permeability apparatus. The permeability coefficient, P , which is expressed in barrer (1 barrer = 10^{-10} cm³ (STP) cm cm⁻² s⁻¹ cm Hg⁻¹), was measured from the slope of the steady-state line.

2.3. Gelation test

Gel formation studies were carried out by the addition of metal chlorides such as TaCl₅, NbCl₅, and MoCl₅ to the polymer solution. The test was carried out at room temperature under air. The concentrations of poly(DMOTMSDPA) and poly(TMSDPA) were 0.05 and 0.025 mol/L, respectively, because of the high M_w (7.1×10^6) for poly(TMSDPA). The detailed procedure is as follows: First, poly(-DMOTMSDPA) (0.047 g, 15×10^{-5} mol in terms of the repeating unit) was transferred into a glass tube and completely dissolved in toluene (2.5 mL). Second, TaCl₅ (0.027 g, 7.5×10^{-5} mol) in toluene (0.5 mL) was added to the solution. Gel formation was evaluated by inverting the test tube. The mixture remaining at the top of the inverted tube was defined as the gel.

2.4. Fabrication of MMMs

MMMs (thickness of 80–120 μ m) were fabricated by the

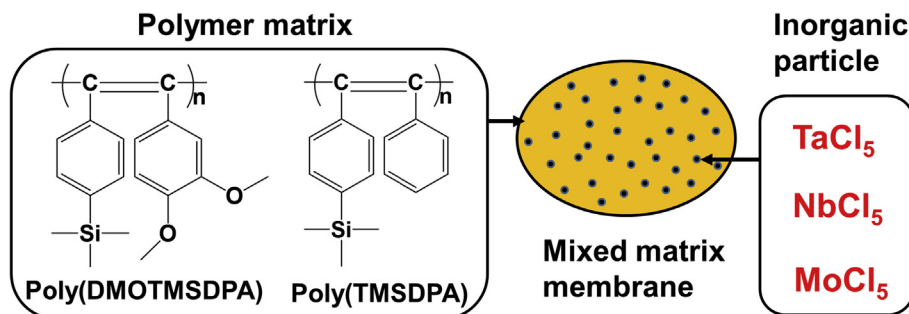


Fig. 1. MMMs of poly(DMOTMSDPA) and poly(TMSDPA) with metal chlorides.

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