



Gas separation in polyimide membranes with molecular sieve-like chemical/physical dual crosslink elements onto the top of surface



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ARTICLE INFO

Keywords:

Polyimides
Gas separation
Surface modification
VUV excimer lamp
Silane coupling agent

ABSTRACT

The gas separation properties of vacuum ultra violet (VUV) irradiated polyimide membranes and surface-crosslinking polyimide membranes after VUV irradiation were investigated. The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy and the X-ray photoelectron spectroscopy (XPS) measurements of the membrane showed the increase in the number of hydroxyl groups after VUV irradiation and the formation of hydrogen bonds from the hydroxyl groups. The gas permeability of the surface-modified polyimide membrane decreased with increasing gas molecular size. Moreover, the permselectivity to H_2/CO_2 , H_2/N_2 , and H_2/CH_4 of the polyimide membranes irradiated with VUV and treated with 3-aminopropyltriethoxysilane (APTES) increased from 0.74 to 17, 13 to 230, and 14 to 600, respectively. Therefore, we successfully established a network structure by using hydroxyl groups formed by VUV irradiation and improved the hydrogen separation performance of the polyimide membranes.

1. Introduction

Sustainable Development Goals (SDGs) were adopted at the United Nations Summit in September 2015 to solve global problems, such as depletion of fossil resources and environmental alterations with climate change. Concurrently, many national governments, companies, and the civil society have promoted and applied SDGs. In this research, basing on SDGs, we focused on using hydrogen as a next-generation energy source to satisfy future energy demands and reduce climate change. Hydrogen can be generated from various energy sources and impose small burden on the environment during its use. As such, hydrogen is predicted to be a next-generation clean energy reserve that would replace conventional fossil resources [1,2]. However, prior to utilizing hydrogen energy, a simple hydrogen-refining method must be established for hydrogen supply facilities, such as a hydrogen station. In this regard, hydrogen purification by a polymer membrane separation method has gained increasing attention. This method can reduce the costs, and the polymer membrane is highly productive and processable [3,4]. Thus, polymer membrane separation can be used to establish a low-cost and highly efficient hydrogen supply facility that provides cheap hydrogen. Nevertheless, the hydrogen permeation and separation performance and the heat resistance and mechanical strength of the polymer membranes must be enhanced for practical applications.

Polyimide is a membrane material widely used in gas separation. Polyimide possesses a rigid backbone chain and is an excellent polymer

material with high heat resistance, chemical resistance, and mechanical strength. Among polyimide membranes, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride-based (6FDA-based) polyimides, which are fluorine-containing aromatic polyimides, exhibit excellent gas permeability because of their bulky CF_3 group [5].

To date, a crosslinking structure has been introduced into the polymer chain by ultraviolet (UV) irradiation, heat treatment, or using a crosslinking agent (such as diamine) to enhance the hydrogen gas separation performance of 6FDA-based polyimides [6]. UV irradiation is an excellent method increasing hydrogen permselectivity by forming a layer having high hydrogen selectivity with a small thickness ($< 1 \mu m$) [7]. Given that the UV irradiation reaction reaches a steady state as irradiation time progresses, the hydrogen separation performance of the polyimide membrane is only improved up to a certain point. To address this limitation, we focused on utilizing the hydroxyl group formed on the UV-irradiated membrane surface as a reaction point. Liu et al. reported that selectivity based on gas molecule size increased by introducing a cross-linked structure between polymer chains with the hydroxyl group of the polymer chain as a reaction point [8]. Therefore, Hydroxyl group-reactive materials, such as glutaraldehyde (GA) and 3-aminopropyltriethoxysilane (APTES), will react with the hydroxyl groups in the UV-modified layer. The hydrogen separation performance is improved by densifying the modified layer through the crosslinking structure formed by GA and APTES and the hydrogen bonding by hydroxyl groups of the materials.

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The thickness of the modified layer should be minimized to increase hydrogen permeance of polyimides. In this research, we focused on using vacuum ultra violet (VUV) irradiation. VUV has a shorter wavelength than UV and is absorbed by oxygen and nitrogen in the atmosphere. VUV does not enter into the membrane and can only be modified on the top membrane surface. Previous studies reported the influence of VUV irradiation on the surface characteristics and high-order structure of poly(lactic)acid (PLA) and poly(1-trimethylsilyl-1-propyne) (PTMSP) [9,10]. The reactive hydroxyl groups are thus predicted to form on the top membrane surface by VUV irradiation. However, the effect of VUV irradiation on the gas permeability of polyimide has not been reported yet.

In this study, VUV irradiation was performed on 6FDA–2,3,5,6-tetramethylethylenediamine (TeMPD) (PI), which consists of 6FDA and TeMPD. The structure and gas permeability of the VUV-irradiated PI membranes were investigated. GA and APTES were reacted with the VUV-irradiated PI membrane to form a crosslinking structure on the top

surface. The physical properties and gas separation performance of the surface-modified membranes were investigated.

2. Experimental

2.1. Materials

6FDA (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) was used as acid anhydride monomer, and TeMPD (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) was used as diamine monomer. *N*-methyl-2-pyrrolidone (NMP; Junsei Chemical Co., Ltd., Tokyo, Japan; purity: 99.0%+) was utilized as polymerization solvent. Pyridine (Junsei Chemical Co., Ltd., Tokyo, Japan; purity: 99.5%+) and acetic anhydride (Ac₂O, Junsei Chemical Co., Ltd., Tokyo, Japan; purity: 97.0%+) were used as cyclodehydration catalyst and were dehydrated with well-dried 4A molecular sieves. Tetrahydrofuran (THF, Junsei Chemical. Co., Ltd., Tokyo, Japan, purity: 99.5%+) was employed as good purification

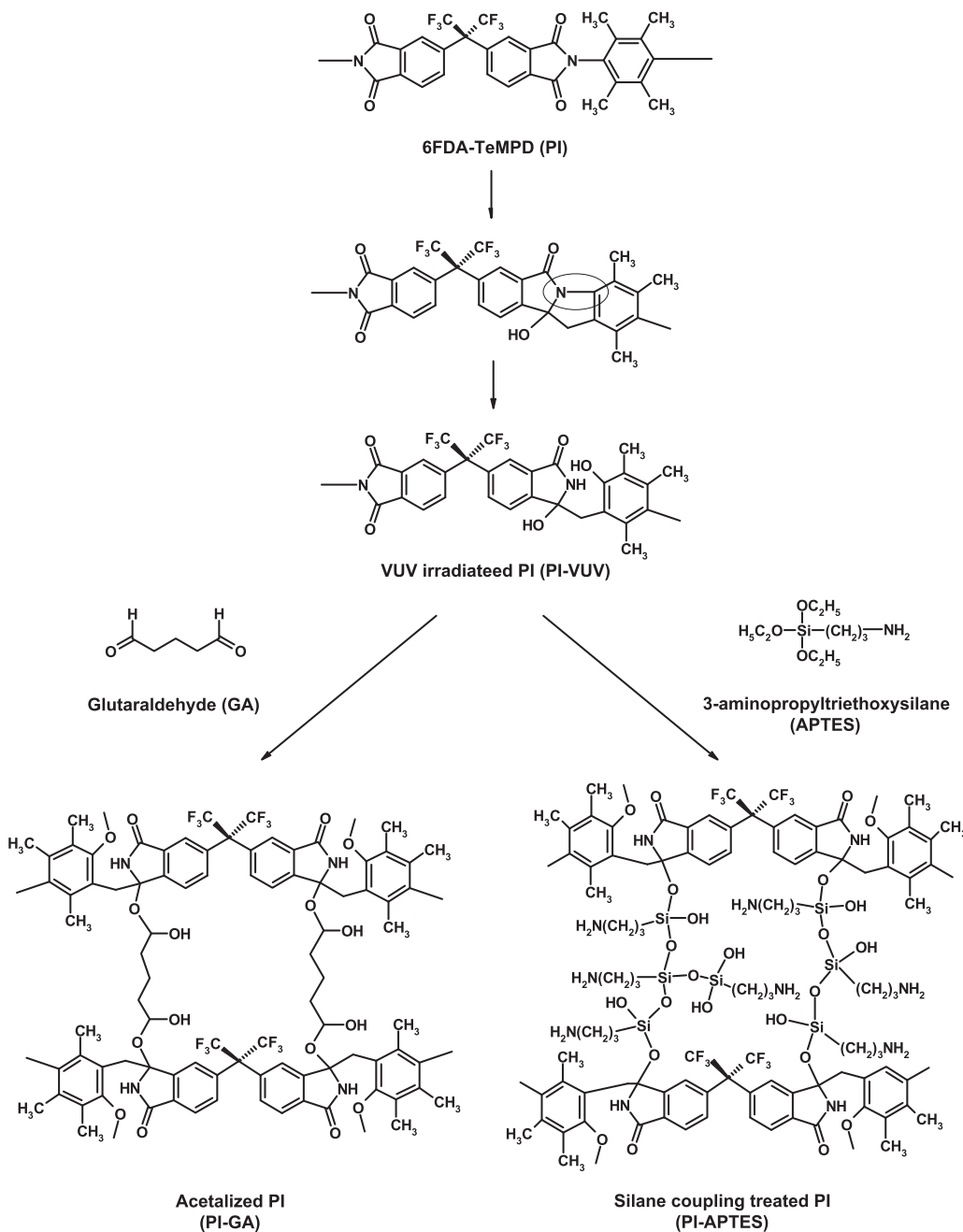


Fig. 1. Reaction mechanism of PI under VUV irradiation, acetalization, and silane coupling treatment.

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