P-12

Separation of Hydrogen-Nitrogen Gas Mixture by PTMSP/PDMS-PEI Composite Membrane

Hyun-Kyung Lee and Tae-Beom Kang *

Department of Industrial Chemistry, Sang Myung University, Seoul 110-743, Korea

** Department of Chemistry, Sang Myung University, Seoul 110-743, Korea*

1. Introduction

The development of the gas separation processes using polymeric membranes has attracted a great deal of interest during the last two decades. Membrane in this application has to offer an excellent thermal stability, chemical/solvent resistance, and mechanical strength under operating conditions. Therefore, the research efforts have been focused on the modification of the membranes structure and composition in order to improve their selectivity as well as permeability [1-4]. In this work, the separation properties of the gas mixture (H_2/N_2) through poly[1-trimethylsilyl-1-propyne]/poly[dimethylsiloxane]-polyetherimide composite membrane were evaluated as a function of pressure.

2. Experimental

2.1. Polymer Synthesis

PTMSP sample was synthesized by using $TaCl_5$ catalyst as described previously [5]. PTMSP/PDMS graft copolymer was synthesized by method of metallization of PTMSP with *n*-butyllithium, as described elsewhere [6]. The graft copolymer was carried out in the glass reactor under argon atmosphere with the following condition. A solution of 2.0g of PTMSP (17.8 mmol) in 200ml of tetrahydrofuran was prepared at room temperature. Thereafter, 11.2ml of *n*-butyllithium (17.8 mmol) was added to this solution, and the mixture was reacted for 5h at -10℃. After stirring for 5h, 3.1g of hydroxy-terminated PDMS (Aldrich Chemicals) was added. Then, the reaction mixture was stirred for 10h at room temperature. The graft copolymer formed was precipitated several times in excess methanol. After filtration the polymer flakes were dried in vacuum for 24h at 60 ℃.

2.2. Polymer membrane preparation

The PTMSP/PDMS-PEI composite membrane consists of a porous polyetherimide (Aldrich Chemicals) support and a thin PTMSP/PDMS layer. The polyetherimide support was made by casting from a NMP solution (20 wt% PEI) on non-woven fabric at 25℃, followed by coagulating in ice-cold water and drying for 24 h in a vacuum oven. After drying at 60 ℃, the PEI support was wetted in toluene for 1 h. The PTMSP/PDMS copolymer was dissolved in toluene (3 wt% copolymer) and cast on the wet PEI support. Then, the composite membrane was dried in vacuum for 24h at 60 ℃.

2.3. Gas permeation measurements

The mixed-gas permeation properties of PTMSP/PDMS-PEI composite membrane were determined with a gas mixture containing 39mol% H_2/61mol% N_2. The experiments were measured at different pressures ($\triangle P$= 5-50 psi) and constant temperature (25℃).

3. Result and discussion

3.1. Characterization of membrane

FT-IR, SEM, ^{1}H-NMR, TGA and DSC measurements characterized the polymer membrane. The number-average and weight-average molecular weight of PTMSP/PDMS graft

copolymer were 5.02×10^5 and 6.76×10^5, respectively. Fig. 1 shows ^{1}H-NMR spectrum of PTMSP/PDMS graft copolymer. In the ^{1}H-NMR spectrum, the signals of methyl protons of PTMSP unit and PDMS unit were observed at 0.1 ppm. The IR spectrum of the membrane is shown in Fig. 2. In the IR spectrum, the absorption peaks derived from Si-C bond of PTMSP and PDMS were observed at 1244 and 1260 cm^{-1}, respectively, and the peaks derived from siloxane bond were found at 1100, 1020, and 800 cm^{-1}. The other absorption peaks agreed with IR spectrum of PTMSP/PDMS graft copolymer, reported by Nagase et al [6]. SEM picture taken from the cross section of the membrane is depicted in Fig. 3. The PTMSP/PDMS graft copolymer layer that was observed on the cross sections of the membranes at about 23 μ m thick layer. The total thickness of PTMSP/PDMS-PEI composite membrane was determined with a precision micrometer. The composite membrane with thickness of ~140 μ m was used for the permeation measurement. The glass transition temperature of PTMSP/PDMS graft copolymer was not detected by the DSC measurement in the temperature range between 100 and 300℃.

3.2. Gas separation results

Gas separation results for the PTMSP/PDMS-PEI composite membrane are given in Fig. 5. The data show that the real separation factors of H_2/N_2 increased as the pressure of permeation cell increased. PTMSP/PDMS-PEI composite membrane was shown to have the real separation factor (α =10.2) of H_2/N_2 which is about 2.3 times larger than that of PTMSP-PEI composite membrane at Δ P 30psi and 25℃.

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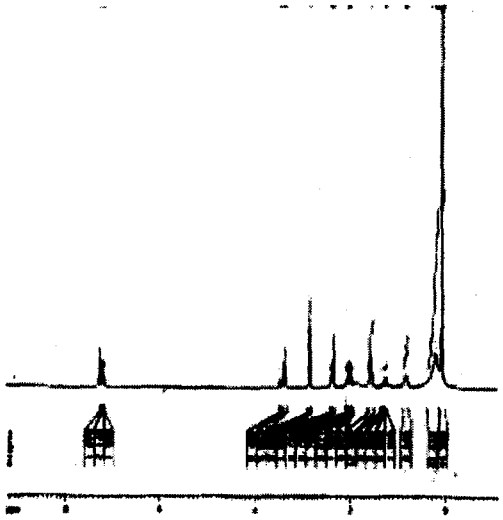

Fig. 1. ^{1}H-NMR spectrum of PTMSP/PDMS graft copolymer.

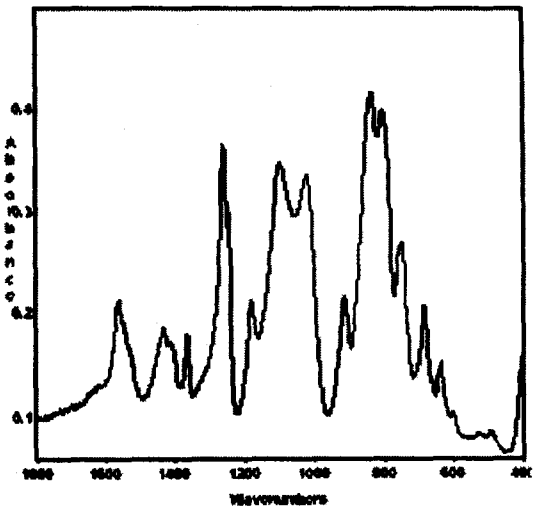

Fig.2. FT-IR spectrum of PTMSP/PDMS graft copolymer.

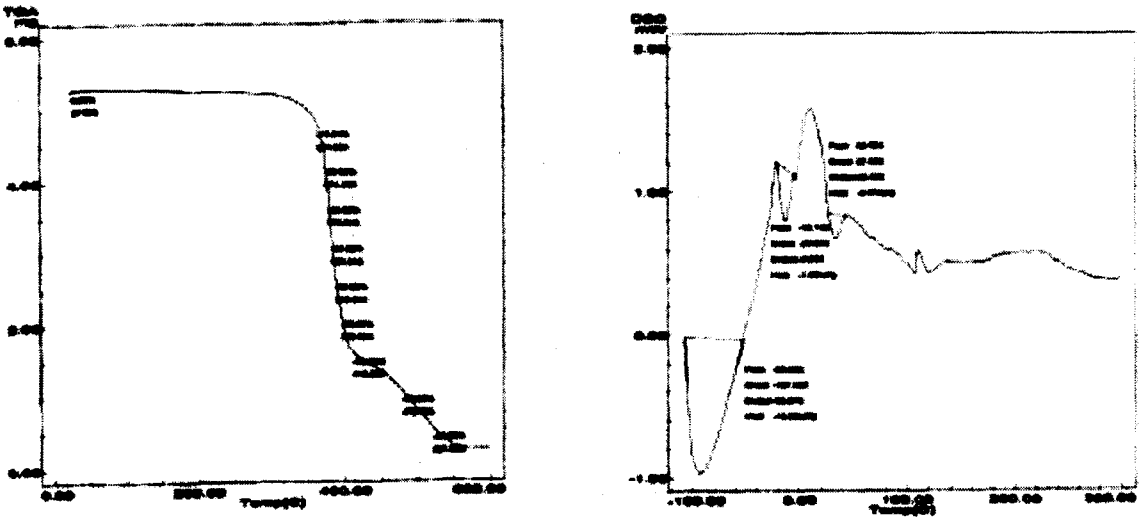

Fig. 4. TGA and DSC curves of PTMSP/PDMS graft copolymer.

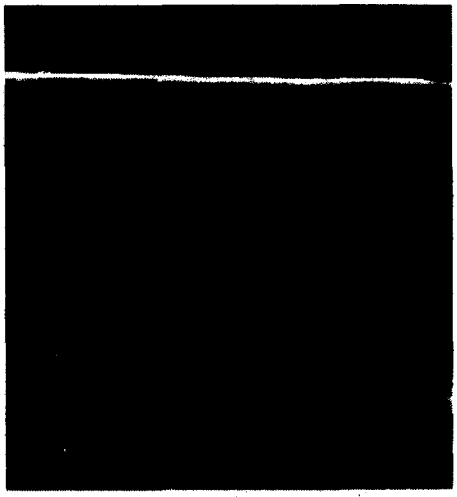

Fig. 3. SEM micrograph of the cross-section of PTMSP/PDMS-PEI composite membrane.

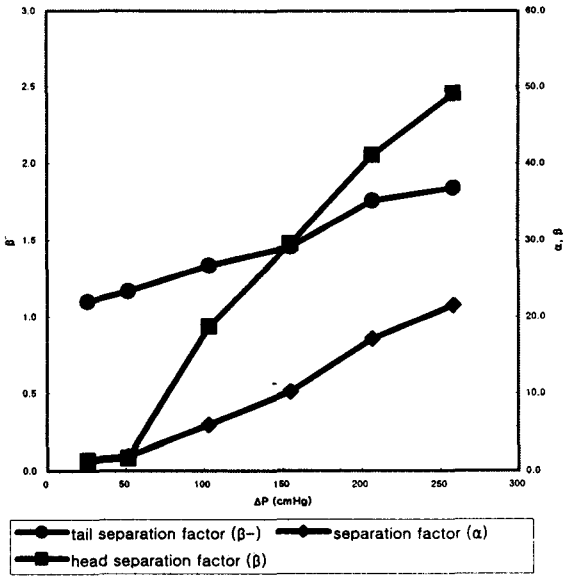

Fig. 5. Pressure effect with PTMSP/PDMS -PEI membrane on the real separation factor(α), head separation factor(β), and tail separation factor (β -), respectively.