Fabrication of nanomembrane with self-organized molecular channels for preferential CO_2 separation

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There has been an increasing interest in CO_2 capture by membranes for significantly reducing greenhouse gas emissions. We developed a CO_2 separation membrane with highly uniform and vertically-aligned nanochannels across the membrane, by utilizing simultaneous microphase separation behavior of poly (styrene-*b*-ethylene oxide) (PS-PEO) block copolymer. The membrane shows high CO_2 selectivity, and it was revealed that the phase of PEO domains plays a vital role in the CO2 selectivity of the membrane.

Introduction

Membrane separation is considered as a next generation CO_2 capture technology. Poly(ethylene oxide) (PEO) has polar ether groups and shows high CO_2 affinity [1]. Although PEO has been considered as a suitable membrane material, solid PEO has considerable gas resistance because of its high crystallinity. Therefore, there have been many studies to utilize liquid-like PEO with low molecular weight for gas separation membrane [2, 3].

In this study, we employed block copolymer of poly (styrene-*b*-ethylene oxide) (PS-PEO) to prepare a nanometer-thick membrane and utilized its microphase separation phenomenon to construct vertically aligned PEO nanochannels across a nanomembrane [4]. We expected that PEO nanochannels act as a path of CO_2 permeation and that the thermal property of PEOs in nanochannels would be different from that of the bulk one because of the nanoconfined effect. Here, we report the development of PS-PEO nanomembrane and its gas permeation property

Experiments

A polydimethylsiloxane (PDMS) membrane on an anodized porous filter was treated with oxygen plasma for 5 sec to make its surface hydrophilic. PS-PEO (2 wt% in toluene) was then spin-coated onto it, and the membrane was exposed to toluene vapor for 10 min at room temperature and then dried under reduced pressure for 20 min (PS-PEO/PDMS). The thermal property of the PS-PEO powder was investigated by a differential scanning calorimeter (DSC). Scanning electron microscopy (SEM) and grazing incidence small angle X-ray scattering (GISAXS) was used to determine phase separation structures of the membrane. The CO_2 and N_2 permeance were measured at different temperatures with a pressure difference of 200 kPa between the feed and permeate sides of the membrane.

Results & Discussion

Figure 1 shows the surface image of PS-PEO on PDMS and hexagonally-aligned nanodots. These dots correspond to phase-separated PEO domains whose diameters and distances are approximately 20 nm. The thicknesses of the PS-PEO layers were about 80 nm. In the DSC measurement, endothermic and exothermic peaks of PEO alone and PS-PEO were observed at 51 °C and -26 °C, which corresponds to the phase transition of PEO moieties, respectively. From this result, PEO in nanochannels is a liquid-like phase at room temperature, even though the bulk PEO polymer with the same molecular weight is in solid state. In the gas permeation experiments, CO_2 selectivity over N_2 of PS-PEO/PDMS reached 32. In addition, the CO_2 selectivity of the PS-PEO membrane increased after annealing at above its melting point (51°C). We believe that the liquid-like phase of PS-PEO/PDMS (a) 2 surface of PEO in nanodomain persists

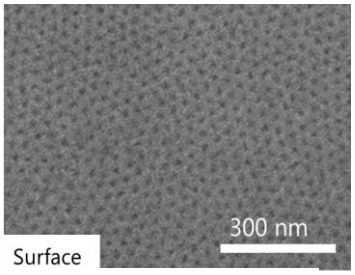

Figure 1: Surface SEM image of PS-PEO/PDMS

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