

혼합 소프트세그먼트를 포함한 폴리우레탄막을 사용한 VOCs/N₂ 혼합물의 분리

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Separation of VOCs/N₂ mixtures using polyurethane membranes containing mixed soft segments

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1. Introduction

Removal of volatile organic compounds (VOCs) from a waste gas stream in industry to be emitted into the atmosphere is urgently needed to prevent pollution. Polymeric membrane-based vapor permeation processes have demonstrated superior performance in treating such effluents for the removal of VOCs[1-3]. For VOCs removal from gas streams, the coating is usually made of silicone rubbers(PDMS), which provides a selectivity of several hundred toward some VOCs. Pure, single component, vapor-phase transport studies with these membranes were encouraging and showed that the ratio of permeabilities of selected organics (e.g., acetone, toluene, and trichloroethane) to nitrogen was in the range of 300-700[4]. The measured organic selectivities for actual organic/nitrogen feed mixtures, however, were only 15-60 for acetone, toluene and in the range of 10-12 for chlorinated compounds such as tetrachloroethylene, due to the combined effects of concentration polarization and a decrease in the permeability of the organic at low vapor partial pressures in the feed. In an attempt to improve upon these selectivities and also to address the problem of silicone rubber degradation by some organic vapors, Matsuura and co-workers

examined asymmetric aromatic polyetherimide membranes. Selectivities for carbon tetrachloride, benzene, and toluene were found to be high (20-80), but the organic fluxes were low. In our previous study[5], polyurethane membrane containing siloxane group was used for the separation of toluene/N₂ mixture and resulted in highly good performance about the permselectivity. In this paper, we report on the use of mixed soft segment-polyurethaneurea membrane containing ether and siloxane group for the separation of selected vapor-phase chlorine-containing compounds from nitrogen stream. Our rationale for choosing polyurethane was based on the following: (1) polyurethane membranes exhibited good thermal and chemical stability and high transmembrane fluxes during organic/organic pervaporation, (2) the permeability of pure nitrogen in polyurethane membranes films was found to be at least 2 orders of magnitude lower than that in silicone rubber[6], and (3) a variety of inexpensive polyurethane polymers with good mechanical properties are available.

2. Experimental and Results

2.1 Materials

Primary amine terminated poly(dimethyl siloxane) (PDMS) ($M_n = 900$) was kindly donated by Shinetsu Co. (Tokyo, Japan) and was normally used after completely drying in vacuum oven at 110°C. Hydroxyl terminated Pluronic L-31 was supplied by Aldrich Chemical Co. (Milwaukee, WI) and used as received. Poly(ethylene glycol) (PEG) ($M_n = 1,100$) and poly(propylene glycol) was supplied by Aldrich Chemical Co. (Milwaukee, WI) and used as received. 4,4'-methylene diphenyl diisocyanate (MDI), (Aldrich Chemical Co., Milwaukee, WI) and 1,6-hexanediol (Junsei Chemical Co., Ltd., Tokyo, Japan) were vacuum distilled before use. Dibutyltin dilaurate (Aldrich Chemical Co., Milwaukee, WI) was used as a catalyst. N, N-dimethyl acetamide (DMAc) and tetrahydrofuran (THF) were dried over calcium hydride and then conducted fractional distillation under vacuum.

2.2. Polymer synthesis

The segmented urethane block copolymers containing mixed soft segments such as Pluronic, PDMS, PPG, and PEG were prepared *via* the two-step condensation reaction. Solutions of Poloxamer, PDMS, PEG, PPG and MDI were prepared in a mixed solvent system of 1:3 (v/v) of DMAc to THF. The Pluronic, PEG, PPG, and PDMS solution, containing 0.1% dibutyltin dilaurate as catalyst, were added to the stirred MDI solution in several parts at 50-60°C under dry nitrogen atmosphere. The resultant mixture was extended with 1,6-hexanediol (HD) to form products of desired molecular weight.

2.3. Organic/N₂ separation experiments

Different VOCs/N₂ vapor feeds were examined in the present study, where VOCs concentration was varied up to its saturation at constant temperature. The compositions of these feed streams are 0.2-3 vol % (VOCs/dry N₂).

The experimental apparatus employed in the vapor-phase separation experiments is depicted schematically in Fig. 1. Vapor feed mixtures were prepared from ultra pure dry N₂ gas and reagent-grade VOCs. Separation experiments were carried out using a single vapor permeation cell that was housed in a constant-temperature chamber. The membrane area exposed to feed vapor was 11 cm². In all separation experiments, the permeation cell temperature was fixed at constant temperature, the feed stream pressure was 830 mmHg, and the permeate-side pressure was 0.01 atm. Feed- and permeate-side vapor phase organic concentrations were measured directly using online gas chromatography (a Shimadzu Model GC-14B chromatograph equipped with six channels-gas sampling valves and thermal conductivity and flame ionization detectors). The total mass flux of condensable feed components was determined by weighing samples of the permeate vapor that was collected in a liquid nitrogen cold trap over a known period of time. In the case of polyurethaneurea membrane containing PEG and PDMS, the selectivity of CCl₄/N₂ mixture in the feed mole fraction 0.0032 was 130 at 25°C, and generally the permselectivities of almost all the polyurethaneurea membranes used in present study showed good performance for the separation of VOCs/N₂ mixtures

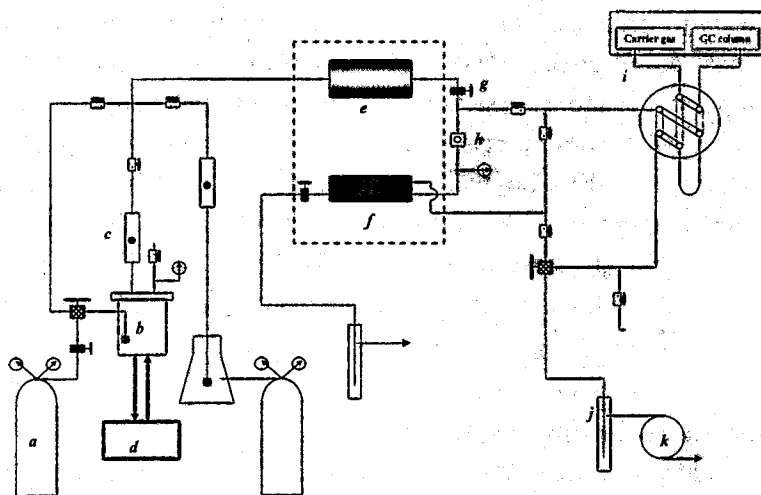


Figure 1. Vapor permeation apparatus

(a: N₂ cylinder, b: vapor generator, c: mass flow controller, d: circulation bath, e: buffer tank, f: membrane cell, g: pressure controller, h: solenoid valve, i: GC, j: cold trap, k: vacuum pump)

3. References

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