Separation of VOCs from nitrogen stream using segmented urethane block copolymer membranes with different soft segments

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ABSTRACT

Urethane block copolymers, containing soft segments such as polydimethylsiloxane (PDMS), polytetramethylene glycol (PTMG) and PEO-PPO-PEO (Poloxamer) block copolymer, were synthesized and examined for the vapor-phase separation of toluene from nitrogen stream by using vapor permeation equipment. Generally permeabilities of PTMG and PDMS based urethane membranes were higher than those of Poloxamer based urethane membranes. Organic vapor permeability in the PDMS and PTMG soft segment urethane membranes were greater than those measured in the Poloxamer films, due to more polymer swelling. The membranes performed best with toluene, with toluene/dry N_2 selectivities ranging from 120~200 and permeabilities as high as 23×10^{-9} mol/m^{2}sPa for saturated toluene feeds at 23°C.

INTRODUCTION

Since the last years, the industries generating volatile organic compounds (VOCs)-containing waste air streams have been increasing economic and regulatory pressure. Particularly various industrial processes such as painting, solvent degreasing, printing, dry-cleaning, polymer synthesis involve the use of large amounts of solvents such as aromatic (toluene, xylene, benzene) and chlorine-containing organic compounds (dichloroethane, trichloroethane, carbon tetrachloride) [1].

In the last decade, remarkable progress in the field of membrane separation technology has made vapor permeation an interesting alternative to the conventional methods such as incineration, carbon adsorption and compressible condensation [2].

The conventional processes, namely, thermal, catalytic or biological oxidation procedures that eliminate organic solvents ought to only be utilized in cases where recovery is not reasonably possible. This is usually the case with very large waste air streams with low concentrations of organic solvents and with mixtures composed of several components that result in a condensate for which no suitable utilization can be found. From economic viewpoint, the procedures of desirable choice are those that enable the solvent to be recovered and recycled. Presently, research has spurred more interest in these fields due to potentially practical applications using more novel methods of membrane separation such as the recovery of volatile organic vapors from air or nitrogen streams and the separation of aqueous-organic or organic-organic mixtures via pervaporation. Especially from the past decades to present, the investigation on diffusion and permeation of organic compounds in polydimethylsiloxane or composite-thin coated silicone rubber membranes was in a great interest [3-6].

The aim of this study is to examine organic solvents in their permeation and swelling behavior through segmented urethane block copolymer membranes with different soft segments. In this study, we will report the toluene/dry N_2 separation through urethane membranes with single and mixed soft segments.

EXPERIMENTAL

Materials

Primary amine terminted poly(dimethyl siloxane) (M_n = 900) was supplied by Shinetsu Co. and normally used after dried in vacuum oven at 110°C. Hydroxy terminated tradename Poloxamer (Pluronic L-31) was supplied by Aldrich Co. and used as received. Poly(tetramethylene glycol) (PTMG) (Mn = 1,100) was supplied by BASF and used as received; 4,4'-methylene diphenyl diisocyanate (MDI) (Aldrich) and 1,4-butandiol (Arco) were vacuum distilled before use. Dimethyl acetamide (DMAc) and tetrahydrofuran (THF) were dried over calcium hydride and then fractional distilled under vacuum.

Synthesis

The segmented urethane block copolymers containing soft segments such as Poloxamer, PDMS, and PTMG were made from the two-step condensation reaction. Solutions of Poloxamer or PTMG and PDMS and MDI were prepared in a mixed solvent system of 1:3 (v/v) of N,N'-dimethlyacetamide to tetrahydrofuran. The Poloxamer or PTMG and PDMS solution, containing 0.1% dibutyltin dilaurate as

catalysts, was added to the stirred MDI solution in several parts at 50~60°C under nitrogen atmosphere.

Vapor permeation experiments

Different N_2/organic vapor feeds were examined in the present study, where each organic species concentration was varied up to its saturation at 23°C. The compositions of these feed streams are 0.2~3 vol% (toluene/dry N_2). Vapors feed mixtures were made from ultra pure dry nitrogen gas and reagent-grade toluene. 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 0.0013 m^2. In all separation experiments, the permeation cell temperature was fixed at 23oC, the feed stream pressure was 800 mmHg, and the permeate side pressure was 0.01 atm. Feed- and retentate-side vapor-phase organic concentrations were measured directly using online gas chromatography (a Shimadzu Model GC-14B chromatograph equipped with 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 collected in a liquid nitrogen cold trap over a known period of time.

RESULTS AND DISCUSSION

Solution-cast homogeneous dense membranes prepared from urethane block copolymers with PTMG, PDMS and Poloxamer soft segments were investigated for the vapor-phase separation of toluene from dry nitrogen stream. In this study, although the effect of presence of water vapor (humidity) was not taken into account, these membranes were found to be alternatives to pure polydimethylsiloxane for toluene/N_2 separation. Measurements of swelling equilibrium behavior and toluene/N_2 separation experiments using vapor permeation apparatus were used to expect and evaluate membrane for organic vapor separation. As a rule, permeabilities of PTMG and PDMS based urethane membranes were higher than those of Poloxamer based urethane membranes. Toluene vapor permeability in the PDMS and PTMG soft segment urethane membranes were greater than those measured in the Poloxamer films, due to more polymer swelling. The greater swelling of the PDMS and PTMG based membranes increased the nitrogen permeabilities and lowered the toluene/N_2 selectivities relative to those for Poloxamer based membranes. Up to feed-flow rate 100 cc/min, all of those showed a linear dependence on saturated feed concentration. The membranes performed best with toluene, with toluene/dry N_2 selectivities ranging from 120~200 and pressure-normalized permeabilities as high as 23×10^{-9} mol/m^2sPa for saturated toluene feeds at

23°C and a downstream pressure of 0.005-0.01 atm.

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