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TUNABLE COMPOSITE MEMBRANES
FOR GAS SEPARATIONS

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J. P. Ferraris, K. J. Balkus, Jr. and I. H. Musselman

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Department of Chemistry
The University of Texas (Dallas)
P. O. Box 830688
Richardson, Texas 75083-0688

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Abstract:

Poly 2-(3-thienyl)ethylacetate (PAET) was synthesized and solution cast as thin films to form dense membranes. These membranes are mechanically robust and are redox active, holding out promise as gas separation materials. The permeability properties of PAET membranes were evaluated for N₂ (0.048 ± 0.008 Barrers), O₂ (0.24 ± 0.02 Barrers), CH₄ (0.081 ± 0.005 Barrers), and CO₂ (1.4 ± 0.1 Barrers). The corresponding selectivity values () were: O₂/N₂ = 5.1, CO₂/N₂ = 29, and CO₂/CH₄ = 18.

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Executive Summary:

Poly 2-(3-thienyl)ethylacetate (PAET) was solution cast into mechanically strong, defect-free dense membranes which were evaluated in gas separation applications. The permeability properties of PAET membranes for N₂ (0.048 ± 0.008 Barrers), O₂ (0.24 ± 0.02 Barrers), CH₄ (0.081 ± 0.005 Barrers), and CO₂ (1.4 ± 0.1 Barrers) with the corresponding selectivity values () were: O₂/N₂ = 5.1, CO₂/N₂ = 29, and CO₂/CH₄ = 18 make it superior to poly(3-octylthiophene), POT, and poly(3-dodecylthiophene), PDDT, for separations of these gases.

Introduction

The use of membrane technology for gas separations offers significant thermodynamic and economic advantages over distillation processes. Target separations of importance to the coal and energy fields include N_2/O_2 , $\text{H}_2\text{S}/\text{syngas}$ and CO_2/CH_4 . Current strategies for improving these separations are largely directed towards processable polymers with thin ($<500 \text{ \AA}$) skins. Unfortunately most polymeric materials that provide commercially viable permeation rates exhibit poor selectivities and *vice versa* and there are inherent limitations in gas permeability/permselectivity for pure polymers. Our strategy relies on modification of composite membranes, preferably *in situ*, to enhance the permselectivity while maintaining acceptable permeabilities. The composites consist of electroactive (i.e., conducting) polymers, (which can be switched from rubbery to glassy), filled with selective absorbents (zeolites) which are impregnated with metals or catalysts to effect facilitated transport. The project is multifaceted and involves the efforts of a polymer synthesis group, a microporous materials group, a microscopy group and a permeability measurements group, all working in concert. This report summarizes the results of our efforts for last quarter.

The gas permeability properties of CPs can be tuned systematically by modifying the morphology and/or polarity of the polymer, for example, through redox chemistry. We have previously reported our results using this approach. The development of asymmetric membranes, consisting of a thin, dense, selective homogeneous skin layer supported by a thick, porous substrate, provides another strategy for enhancing permselectivity.

Gas separation properties of asymmetric membranes are generally determined by the thickness and microscopic structure of the skin layer. Optimum membrane properties of membranes are obtained if the thickness is minimized and the skin layer is defect-free. In this project, poly 2-(3-thienyl)ethylacetate (PAET), a polymer that can be surface-modified, was synthesized, characterized, and fabricated into membranes. Gas permeability properties of unmodified PAET were measured for N_2 , O_2 , CH_4 , and CO_2 and the permselectivity values for the gas pairs O_2/N_2 , CO_2/N_2 and CO_2/CH_4 were calculated.

Experimental

The monomer, 2-(3-thienyl)ethylacetate **3**, was synthesized according to (Scheme 1). In a 3-neck flask, a mixture of 2-(3-thienyl)ethanol **1** (50 mmole) (Aldrich Chem. Co. Inc.), triethylamine (75 mmole) (Aldrich), acetic anhydride **2** (75 mmole), and 4-dimethylaminopyridine (DMAP) (4 mmole) (Aldrich) was stirred under N₂ for 14 hr at room temperature. The reaction was followed by thin-layer chromatography (TLC) using a 90:10 hexane:ethylacetate solvent system. Following completion of the reaction, the solution was partitioned between ether and 2 N HCl. The organic layer was washed with saturated NaHCO₃ and dried over MgSO₄. The product **3** was recovered by evaporating the ether at reduced pressure. It was then purified by column chromatography using a 97:3 hexane:ethylacetate solvent system (93% yield) and characterized by FT-IR (Nicolet Avatar 360 FT-IR) and ¹H NMR (Eclipse 270). The purity (99%) was determined by GC-FID (Shimadzu GC-8A, Supelco DC-200 column).

Scheme 1. Monomer Synthesis

The monomer, 2-(3-thienyl)ethylacetate, was polymerized according to published literature methods. (Scheme 2). In a 3-neck round bottom flask, equipped with a reflux condenser, the 2-(3-thienyl)ethylacetate monomer (0.1 mole) was stirred in 1 L of chloroform (CHCl₃) under N₂. Ferric chloride (FeCl₃) (0.4 mole) (Aldrich) was added batchwise to the reaction mixture which was then stirred overnight at room temperature. The polymer, poly 2-(3-

thienyl)ethylacetate (PAET) **4**, was precipitated in methanol (1 hr with stirring). The mixture was vacuum filtered and the recovered polymer was stirred in water for one hr to remove the remaining FeCl_3 . Then, the polymer was dissolved in HPLC grade CHCl_3 and de-doped using 28% NH_4OH . The organic phase was washed with deionized water and then dried over MgSO_4 . The product was recovered by evaporating the CHCl_3 at reduced pressure. The polymer was removed from the flask using a small amount of methanol and dried in a vacuum oven at room temperature. The polymer was purified by Soxhlet extraction using a series of solvents including methanol first (1 day), followed by hexane (1-2 days), and then chloroform (3-5 days). The solvent was evaporated under reduced pressure and the polymer was dried in a vacuum oven at room temperature.

The polymer structure was characterized by FTIR-ATR (film), ^1H NMR, and UV-Vis. The molecular weight was determined using GPC. UV-Vis reflectance spectroscopy of PAET films showed an absorption maximum at (λ_{max}) 567 nm. GPC samples were prepared by dissolving ~3 mg of PAET in 1 ml CHCl_3 . The molecular weights (M_w) of the two different polymer batches used are 96,000 and 120,000. Yield: 70%.

Scheme 2. Polymer Synthesis

Membrane Fabrication

The dried PAET polymer was stirred in chloroform at room temperature until dissolved. The solution was sonicated for 20 min and was filtered through a series of Millipore filters (8, 5, 3, 1.2, and 0.45 μm). The solvent was evaporated at reduced pressure. The polymer was

removed from the flask by adding a small amount of methanol and was dried in a vacuum oven at room temperature. The dried, filtered polymer was dissolved in HPLC grade CHCl_3 to make an 8% w/w solution, which was stirred overnight at room temperature and sonicated for 30 min before casting. Also, prior to casting, an Acculab Jr. Drawdown machine, equipped with a glass plate and a wire wound rod (#48-76), was placed inside a glove bag saturated with chloroform. The glove bag assembly was set in a laminar flow hood (Pure Aire). A 0.8-1.0 ml aliquot of polymer solution was placed on the glass plate and then spread using the casting rod. The membrane was allowed to dry inside the glove bag uncovered. The membrane was removed from the glass plate using a sharp blade and placed on an adhesive aluminum tape (R. Hughes Co., Inc.) to hold the membrane. The membrane was annealed in a vacuum oven at increasing temperatures, 50 °C for 24 hr, 70 °C for 24 hr and 200 °C for 48 hr, cooled to room temperature, and stored under N_2 in a glove bag.

Gas Permeability Measurements

Gas permeability was measured using a custom permeameter and software as previously described.

Membrane Characterization

The morphology of PAET membrane surfaces and cross-sections was investigated using SEM (ISI WB-6 SEM, Everhart-Thornly secondary electron detector). The samples were coated with ~4-5 nm of gold-palladium using a Denton Vacuum Desk II Cold Sputter/Etch Unit (Denton Vacuum, Inc.) to make them conductive. The samples were imaged using a 15 kV accelerating voltage and a 10 mm working distance.

FTIR-ATR (Nicolet Avatar 360 FTIR – Avatar Single-Bounce HATR Smart accessory, ZnSe, DTGS) spectra of the unmodified and surface modified PAET membranes were acquired and compared to follow the progress of the hydrolysis reaction.

The topography of the unmodified and surface modified PAET membrane surfaces was investigated using TMAFM [Nanoscope III Multimode Scanning Probe Microscope, J scanner,

Etched Silicon Probe (TESP) tips, (Digital Instruments, Inc.)]. Images were acquired with a pixel density of 512 x 512, a scan rate of 2 Hz, a scan size of 20 μm , and a z-range (height) of 150 nm. The approximate pit surface area (%) and size (diameter and depth) in the asymmetric membranes were determined by bearing and section analysis, respectively.

UV-Visible reflectance spectra (Hewlett Packard 8453 – labsphere RSA-HP-8453 Reflectance Spectroscopy Accessory, Photodiode Array) of the unmodified and surface modified PAET membranes were acquired.

Results and Discussion

A. Membrane Fabrication

TMAFM analysis showed the presence of small bumps or mounds on the surface of the membrane after drying (Figure 1). These bubble-like features seemed to form when the solvent evaporated. The membrane was annealed at increasing temperatures (50 °C for 24 hr, 70 °C for 24 hr and 200 °C for 48 hr) to remove the bubble-like structures and minor defects (Figure 2). Annealing at high temperatures decreased the size of the mounds and created a smoother surface. The maximum effective annealing temperature was determined to be 230 °C. Annealing at higher temperatures caused the membrane to decompose and become brittle. SEM analysis of the membrane showed a smooth top surface (Figure 3a) and cross-section analysis revealed the presence of small holes in the membrane (Figure 3b). These holes did not extend through the entire thickness of the membrane.

B. Gas Permeability Measurements

Sequential gas permeability measurements of PAET were made for N₂, O₂, CH₄, and CO₂ and permselectivity values were calculated for the gas pairs O₂/N₂, CO₂/N₂, and CO₂/CH₄. Two batches of polymer with molecular weights (Mw) of 120,000 and 96,000 exhibited similar permeability properties for the gases analyzed. In Table 1, the permeability and permselectivity values for each of 5 membranes are reported as the average of the last 4 runs of each gas. The

grand average values are the averages of the 5 membranes (Figures 4 and 5). The evaluated values of gas permeability for PAET follow the trend P_{CO_2} (1.4 ± 0.1 Barrers) > P_{O_2} (0.24 ± 0.02 Barrers) > P_{CH_4} (0.081 ± 0.005 Barrers) > P_{N_2} (0.048 ± 0.008 Barrers). The permselectivity coefficients, $\alpha_{\text{O}_2/\text{N}_2} = 5.1 \pm 0.6$, $\alpha_{\text{CO}_2/\text{N}_2} = 29 \pm 4$ and $\alpha_{\text{CO}_2/\text{CH}_4} = 18 \pm 2$, indicate that the membranes are defect-free.

Table 1. Gas permeability and permselectivity of unmodified PAET membranes

Permeability $\times (10^{-10})$ Barrers (cc(STP)cm)/(cm ² s cm Hg)							
	Membrane						
Gas	1	2	3	4	5	Grand Ave.	Std. Dev.
N₂	0.039	0.042	0.055	0.056	0.050	0.048	0.008
O₂	0.22	0.24	0.27	0.24	0.24	0.24	0.02
CH₄	0.085	0.080	0.073	0.084	0.082	0.081	0.005
CO₂	1.3	1.4	1.5	1.4	1.4	1.4	0.1

Permeability is the product of the diffusivity (kinetic) and solubility (thermodynamic) coefficients of a gas in a polymer membrane. The diffusivity coefficient is dependent on the kinetic diameter (size and shape) of the penetrant gas and the free volume of the polymer. The solubility coefficient of a penetrant gas in a membrane is determined by its condensability as well as by polymer-penetrant interactions (i.e. polarity). The general trend in permeability observed for PAET suggests that the permeation rate is affected by both diffusivity and solubility. The higher permeability values observed for the smaller gas molecules (CO₂ and O₂) can be attributed to a significant diffusivity effect determined by the kinetic diameters of the gases. However, the non-linear dependence of PAET gas permeability on kinetic diameter shows that there is a considerable solubility effect on the permeability of the gases analyzed. Carbon dioxide, which is the smallest and most condensable among the gases analyzed, exhibits the highest diffusivity and solubility and, therefore, the highest permeability. Oxygen has a higher permeability than CH₄ and N₂ owing to its smaller kinetic diameter. Although CH₄ is a larger molecule than N₂, the

permeability of CH₄ exceeds that of N₂ owing to its higher solubility coefficient brought about by its higher critical temperature.

Conclusions

PAET membranes with excellent mechanical properties were fabricated and characterized using SEM, TMAFM, FTIR-ATR, and UV-Vis. TMAFM revealed mounds or bubble-like structures at the membrane surface, which appeared to form during the evaporation process following solution casting. These features do not extend through the bulk of the membrane, however, and the permeability and permselectivity properties for the gases analyzed follow the typical trend observed in rubbery polymers.

Figure 1. TMAFM image of as-cast PAET membrane surface after drying (cast inside a glove bag saturated with CHCl_3 vapor, uncovered, CHCl_3 – solvent)

**Figure 2. TMAFM image of unmodified PAET membrane after annealing
50 °C (24hr), 70 °C (24hr), 200 °C (48hr)**

(a)

(b)

Figure 3. SEM image of unmodified PAET membrane (a) surface (b) cross-section

Figure 4. Gas permeability of unmodified PAET membranes

Figure 5. Gas permselectivity of unmodified PAET membranes