TUNABLE COMPOSITE MEMBRANES

FOR GAS SEPARATIONS

Quarterly Progress Report

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Abstract:

Poly(3-dodecylthiophene) films were solution cast and subsequently subjected to chemical oxidation (doping), followed by chemical undoping. The microstructure of each form of the membrane was determined by optical microscopy (OM), scanning electron microscopy (SEM) and TappingMode Atomic Force Microscopy (TMAFM). Energy dispersive x-ray spectrometry (EDS) was used to elucidate the chemical composition of the membranes. Changes in microstructure after exposure to or protection from the laboratory atmosphere, and after permeability measurements, were assessed by these same techniques to estimate the environmental stability of the membranes. Although dramatic changes in topology occur for films exposed to the laboratory atmosphere, these are greatly reduced when the films are stored in containers that limit the access of moisture. Films exposed to dry gases in the permeameter exhibit essentially no change to their original microstructures. A revised manuscript entitled "Poly(3-dodecylthiophene) Membranes for Gas Separations" by I. H. Musselman, L. Li, L. Washmon, D. Varadarajan, S. J. Riley, M. Hmyene, J. P. Ferraris and K. J. Balkus, Jr., has been submitted to *J. Membrane Sci.*

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Executive Summary:

During this past quarter of project DE-FG22-94PC94222, continued significant progress was made in the synthesis and characterization of conducting polymer composite membranes for gas separations. Highlights from this funding period include:

- Poly(3-dodecylthiophene) films were solution cast and subsequently subjected to chemical oxidation (doping), followed by chemical undoping. The microstructure of each form of the membrane was determined by optical microscopy (OM), scanning electron microscopy (SEM) and TappingMode Atomic Force Microscopy (TMAFM). Energy dispersive x-ray spectrometry (EDS) was used to elucidate the chemical composition of the membranes.

- A systematic microscopy study of the changes in microstructure after exposure to or protection from the laboratory atmosphere, and after permeability measurements, was conducted to estimate the environmental stability of the membranes. Unprotected films were reactive to moisture, exhibiting dramatic changes in topology. These changes were greatly reduced when the films are stored in containers that limit the access of moisture. Films exposed to dry gases in the permeameter exhibit essentially no change to their original microstructures.

- A revised manuscript entitled "Poly(3-dodecylthiophene) Membranes for Gas Separations" by I. H. Musselman, L. Li, L. Washmon, D. Varadarajan, S. J. Riley, M. Hmyene, J. P. Ferraris and K. J. Balkus, Jr., has been submitted to *J. Membrane Sci.*

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, H_2S/syngas and CO_2/CH_4. Current strategies for improving these separations are largely directed towards processable polymers with thin (<500 Å) 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 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.

Experimental

Polymer synthesis and characterization

Random poly(3-dodecylthiophene) (PDDT) was synthesized using the method described by Tamao et al. Molecular weights of the PDDT (Mw = 249,100, Mn = 96,300) were determined by gel permeation chromatography (GPC) (CHCl$_3$, 5 mg/ml) using a Viscotek Model LR 40 calibrated with polystyrene standards. Ultraviolet/visible spectroscopy (Hitachi U2000) of PDDT in chloroform revealed a $_{max}$ of 433 nm confirming the regiorandom backbone coupling of the polythiophene.

Membrane fabrication

Small insoluble particulate matter was removed from the polymer by stirring the PDDT at room temperature overnight in HPLC grade chloroform followed by sequential filtration using a stainless steel syringe holder containing Millipore filters of decreasing pore size (8.0, 5.0, 3.0, 1.2 and 0.45 µm). The solution was then evaporated to dryness and the red polymer was transferred to an evaporation dish and placed in the dark at room temperature to evaporate the residual solvent. The purified PDDT was stored under nitrogen in the dark to minimize chemical and photooxidation.

For casting membranes, a 10% w/w solution of the dry, filtered polymer in tetrachloroethylene (99%) was prepared. The solution was stirred overnight and sonicated for 40 min to ensure complete dissolution. In a laminar flow hood (PureAire), membranes were cast on glass using an AccuLab Jr. Drawdown casting table equipped with a wire wound rod (AccuLab Jr. 48-76). A 0.85 mL aliquot of the polymer solution was transferred by pipet onto the clean glass substrate and then spread using the casting rod. The membrane was partially covered to slow solvent evaporation and to minimize photooxidation. Upon drying, a deep green membrane approximately 35 µm thick was formed. The membrane appeared translucent red by transmission.

Polymer membranes were annealed in a vacuum oven for 3 h at 393 K and subsequently allowed to cool under vacuum. Annealing serves to drive off residual solvent and to promote viscous flow, thus minimizing holes and defects in the membrane.

Establishing redox protocols

SEM/EDS was particularly valuable in establishing experimental procedures to oxidize and reduce PDDT membranes. SEM images were acquired from cross sections of as-cast, doped and undoped membranes to reveal their internal microstructures. When establishing the reduction protocol, a sandwich structure was initially observed for a membrane that was immersed in 10% hydrazine for 0.5 h. The inner (~20 µm) and outer (~10 µm) microstructures of this sandwich resembled those of the as-cast and doped

membranes, respectively. High and low antimony-to-sulfur (Sb/S) ratios were found to correlate with the outer and inner microstructures, respectively. Subsequent immersion of a doped membrane in 10% hydrazine for 3 h resulted in the formation of a uniform internal microstructure similar to that observed for the as-cast membrane for which the Sb/S ratio was smaller and constant throughout its thickness. These results suggest that the Sb anion partially diffused out of the membrane during reduction. Reduction for 2 h in a 15% aqueous hydrazine solution, as implemented for the combined permeability/microscopy studies, yielded similar results.

Membrane doping/undoping

Membrane doping was accomplished using two methods. In the first method, a membrane was oxidized for 45 min under N_2 in a Vacuum Atmosphere Co. glove box using a 3% w/w solution of antimony pentachloride ($SbCl_5$) in dry acetonitrile. The p-doped membrane was rinsed with dry acetonitrile and the rinse solvent was tested with ferrocene to insure complete removal of residual oxidant. In the second method, the oxidation process was conducted in a glove bag (I^2R, Inc.) under N_2. In the glove bag, a membrane was immersed for 3 h in a 15% w/w solution of $SbCl_5$ in dry acetonitrile. The doped membrane was then rinsed and tested as described above. The p-doped membranes were slightly brittle and dark blue in color. PDDT membranes were chemically undoped by immersing them for 2 h in a 15% w/w aqueous solution of hydrazine followed by rinsing with NANOpure (Barnstead) water. The undoped membrane was flexible and red in color.

Membrane characterization

Membrane morphology

Membrane surface morphology was investigated using optical microscopy (OM) (Wild-Leitz Ergolux Microscope), scanning electron microscopy (SEM) (Phillips XL 30) and TappingMode atomic force microscopy (TMAFM) (Nanoscope III Multimode

Scanning Probe Microscope, Digital Instruments, Inc.). The internal microstructure of the membrane was revealed through SEM of sample cross sections. Samples for OM and AFM were secured to steel pucks (Digital Instruments, Inc.) with double-stick conductive carbon tabs (Ted Pella). Samples for SEM surface imaging were attached similarly to aluminum SEM stubs (Ted Pella). Membrane cross sections, prepared by freeze fracture, were mounted in a cross section holder. All SEM samples were carbon-coated (Denton Vacuum DESK II Cold Sputter/Etch Unit with Carbon Evaporation Accessory) to eliminate sample charging. The OM reticle was calibrated (1.6 µm/div) at 1000x using a stage micrometer (Ronchi). The AFM J scanner was calibrated using a 10 µm pitch grating with a step height of 180 nm (Digital Instruments, Inc.). Values of root-mean-square roughness, R_{rms}, i.e. the standard deviation of the height values, were determined for each TMAFM image.

Membrane chemistry

Membrane composition was determined by elemental analysis (Galbraith Laboratories, Inc.), scanning electron microscopy/energy dispersive x-ray spectrometry (SEM/EDS) (Phillips XL 30, EDAX PV9800) and x-ray photoelectron spectroscopy (Kratos AXIS HS, Al K x-ray source, 40 eV pass energy, 90° take-off angle). Uniformity of doping/undoping across the thickness of the membrane cross section was evaluated using SEM/EDS by measuring the Sb L / S K intensity ratio for adjacent areas.

Results and Discussion

For as-cast PDDT membranes, optical microscopy (OM) reveals a smooth and featureless surface on the 200 µm scale. OM and scanning electron microscopy (SEM) demonstrate that these membranes are dense and uniformly thick, an important quality for the accurate measure of gas permeability. By TappingMode atomic force

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microscopy (TMAFM), the as-cast membranes appear extremely smooth, exhibiting a root-mean-square surface roughness, R_{rms}, of approximately 3 nm over a 100 μm^2 area. With chemical doping (R_{rms} = 21 nm) and undoping (R_{rms} = 110 nm), the PDDT surface becomes more rough. The internal membrane microstructure, which appears more coarse following oxidation, partially returns to its dense structure following undoping.

Microstructure

       As-cast membrane

The as-cast PDDT membrane microstructure was investigated by OM, SEM and TMAFM. Optical microscopy revealed a surface with few features on the 200 μm scale (Fig. 1a). Since these membranes are nonporous, smooth and of uniform chemical composition, there is no mechanism for contrast (e.g. topographic or atomic number) in the scanning electron microscope (Fig. 1b). TMAFM proved to be a valuable technique for the 3-dimensional evaluation of the smooth PDDT membrane surface. The root-mean-square surface roughness, R_{rms}, for a 10 x 10 μm TMAFM image was 3 nm (Fig. 1c). An SEM image (Fig. 5d) of an as-cast PDDT membrane cross-section revealed a dense and featureless structure similar to that observed for the surface (Fig. 1b). A similar microstructure was observed for as-cast PDDT membranes following permeability measurements.

       Doped membrane

Within several hours of oxidation (15% $SbCl_5$, 3 h), microscopy images were acquired from doped PDDT membranes so that the observed microstructure could be correlated with permeability measurements, reported last quarter. OM, SEM and TMAFM (Fig. 2a, 2b, 2c) images showed the presence of shallow depressions at the membrane surface suggesting that it had been etched. Consequently, TMAFM revealed an increased surface roughness (R_{rms} = 16 nm). SEM/EDS of a membrane cross section revealed a coarse microstructure (Fig. 2d) and a Sb/S ratio which ranged from 0.4 to 0.5

across the membrane thickness demonstrating a uniform Sb distribution. A similar microstructure was observed following permeability measurements providing evidence that the membrane was stable in the vacuum environment of the permeameter (Fig. 3).

The stability of the doped membrane microstructure outside the vacuum chamber was investigated by TMAFM and SEM/EDS. Following the oxidation of two membranes (6% $SbCl_5$, 3 h) and the acquisition of TMAFM images from each of their surfaces (Fig. 4a, 4b), one membrane was placed in a fluoroware container and the other was left in air. TMAFM images were then acquired from these membrane surfaces at 1-2 h intervals for 30 h, the approximate time required to obtain permeability measurements from a single membrane. The microstructure of the sample stored in fluoroware did not change significantly in 30 h (Fig. 4c), whereas the sample which remained in air developed small spherical features on its surface (Fig. 4d). These features may have been caused by the reaction of $SbCl_5$ with moisture and/or air which was less available in the closed fluoroware container.

A membrane was doped similarly for SEM/EDS analysis (Fig. 5). Following oxidation, a piece of the membrane was carbon-coated and investigated by SEM/EDS. No significant features were observed (Fig. 5a). The membrane was shielded from light and stored in air. On each of several subsequent days, additional pieces of the doped membrane were prepared for SEM/EDS. Spherical features were present 1 day after oxidation (Fig. 5b) and larger particles, rich in Sb and Cl, appeared 2 days following oxidation (Fig. 5c). In contrast, the piece of membrane carbon-coated immediately after oxidation (Fig. 5a) retained its featureless appearance after two days suggesting that the coating provided protection from air/moisture. The TMAFM and SEM/EDS results suggest that the *surface* microstructure of the doped PDDT membrane changes with time in an *ambient* environment. Therefore, when correlating membrane microstructure with gas transport properties, membranes should be characterized (permeability, microstructure) within several hours of oxidation.

Reduced membrane

Microscopy images were acquired from a membrane that was first doped (15% SbCl$_5$, 3 h) and then undoped (15% hydrazine, 2 h). OM (Fig. 6a) and TMAFM (Fig. 6c) (R_{rms} = 110 nm) showed that the surface of the undoped membrane was rougher than either the as-cast (Fig. 1a) or doped (Fig. 2a) membranes. A coarse structure with some pits was observed in the SEM image of an undoped cross section (Fig. 6d). These pits, if extensively distributed through the membrane thickness, could give rise to Knudsen flow and may account for the "failure" of some of these membranes during permeability measurements. Although EDS revealed a lower Sb/S ratio than was observed for the doped membrane, it was still as high as 0.3. Nevertheless, the red color and flexibility of the membrane indicate that it was undoubtedly reduced. No significant changes in membrane microstructure were observed in images acquired after permeability measurements.

Composition by elemental analysis

As-cast membrane

The composition of an annealed as-cast PDDT membrane was investigated by EDS and by elemental analysis. In part, annealing the membrane served to drive off residual solvents. Although carbon and hydrogen cannot be measured by EDS, sulfur, iron and chlorine K lines were detected. The presence of sulfur is attributed to the thiophene ring whereas iron and chlorine are attributed to the FeCl$_3$ oxidant used in the polymerization reaction.

Elemental analysis of the as-cast PDDT membrane revealed the C, H, Cl and Fe content to be 74.34, 9.80, 1.63 and 0.57 percent by weight, respectively. By difference, the sulfur content is 13.66%. To within 7%, these experimental results corroborate the theoretical values of 76.73, 10.46 and 12.80 weight percent for C, H, and S, respectively, in PDDT. The C/S atomic ratio is low, 14.5 instead of the expected value of 16. The S/Fe atomic ratio of 42 translates to a 2.4% (maximum) oxidation level for the as-cast

PDDT membrane provided that the Fe species are associated with oxidized thiophene rings. The typical maximum level of doping in polythiophene materials is on the order of 25-33%. The oxidation level in the membrane could be even smaller if Fe is present not as a dopant but as a contaminant. Regardless, it remains important to measure the Fe concentration since it may impact the measured values of permeability.

Doped membrane

Elemental analysis results were obtained for PDDT membranes doped in a glove box and glove bag in order to derive a relationship between the gas transport properties and doping level (the molar ratio of dopant anion over monomer unit). The three elements of PDDT, C, H, and S, and the oxidant elements Sb and Cl were analyzed. The doping levels, ~9% (glove box) and ~23% (glove bag), were calculated based on the assumption that all the antimony in the polymer was associated with the sulfur of the thiophene rings i.e. all the antimony species acted as dopants. However, elemental analysis showed that the Cl/Sb molar ratio was 3.6 - 3.8 instead of the expected 5.0 suggesting that $SbCl_5$ underwent decomposition or other reactions during the doping process, e.g. adduct formation with water ($SbOCl_3$, $H_4Sb_2O_7$). High resolution XPS of the Sb 4d peak revealed a binding energy of 35.1 eV which is consistent with the +5 oxidation state of the $SbCl_6^-$ anion.

$$3\ SbCl_5\ +\ 2\ e^-\ \longrightarrow\ 2\ SbCl_6^-\ +\ SbCl_3$$
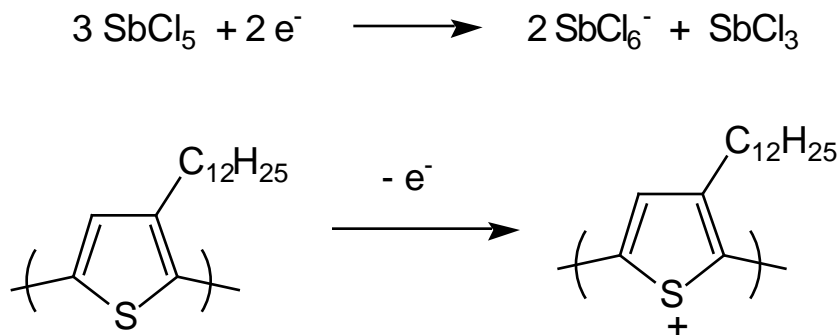
Conclusion

Poly(3-dodecylthiophene) films were solution cast and subsequently subjected to chemical oxidation (doping), followed by chemical undoping. The microstructure of each form of the membrane was determined by optical microscopy (OM), scanning electron microscopy (SEM) and TappingMode   Atomic Force Microscopy (TMAFM). Energy dispersive x-ray spectrometry (EDS) was used to elucidate the chemical composition of the membranes. Changes in microstructure after exposure to   or protection from the laboratory atmosphere, and after permeability measurements, were assessed by these same techniques to estimate the environmental stability of the membranes.   Although dramatic changes in topology occur for films exposed to the laboratory atmosphere, these are greatly reduced when the films are stored in containers that limit the access of moisture. Films exposed to dry gases in the permeameter exhibit essentially no change to their original microstructures.

B

5 μm

D

20 μm

A

20 μm

C

75.0 nm
37.5 nm
0.0 nm

10.0

7.5

5.0

2.5

0   2.5   5.0   7.5   10.0
μm

A

B

C

D

A

B

20 μm

5 μm

C

250.0 nm

125.0 nm

0.0 nm

10.0

7.5

5.0

2.5

0

2.5   5.0   7.5   10.0

μm

D

10 μm