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TUNABLE COMPOSITE MEMBRANES
FOR GAS SEPARATIONS

Progress Report

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MASTER

During the fifth quarter of Grant DE-FG22-94PC94222 there has been significant progress on four fronts: (a) instrument development, (2) polymer synthesis and characterization, (3) membrane fabrication and microscopy, and (4) permeability measurements.

- The electrochemical permeation cell has been constructed and is undergoing calibration testing. An schematic view of this cell is shown in Figure 1:

Figure 1

In practice a membrane is sandwiched between frits (4) and (6) which serve as porous supports and electrodes. The membrane is electrically isolated from the cell via the two teflon holders. Electrical connection is made through the grounded single end connectors on each flange. This allows us to apply a potential across the membrane to maintain a particular oxidation level. A photograph of the actual cell in exploded view is shown in Figure 2.

The permeameter program has been modified to include control of the potential across the membrane and the monitoring of the current. An operators manual has been written.

- Recent permeability measurements suggest that in addition to the anticipated differences associated with stereoregularity and structure, there may also be a dependence on the molecular weight of the polymer used. This has prompted us to expand our synthesis effort to include a range of molecular weights for the polymers. These include the 3-alkylthiophene and the 3-methoxyethoxyethoxy series in both regiorandom and regioregular architectures. Preliminary studies on

moderate MW (>150K) regioregular poly-(3-dodecylthiophene), PDDT, suggest that lower molecular weight materials possess better membrane characteristics in terms of processability and flexibility.

- The microstructure and surface chemistry of poly(3-n-dodecylthiophene)(PDDT) membranes in the neutral, oxidized (1 hr in 1% w/w solution of NOBF₄ in dry acetonitrile) and reduced (0.5 hr in 10% w/w solution of hydrazine in water) states were investigated by atomic force microscopy (AFM) (Figure 3) and x-ray photoelectron spectroscopy (XPS), respectively.

By AFM, the surface of the neutral PDDT membrane appeared relatively smooth (Figure 3a). XPS revealed the presence of C, O, and S as well as small amounts of F, Cl and Si. The S binding energy is correct for a thiophene. The Cl is consistent with the presence of anhydrous ferric chloride (FeCl₃) used in the polymerization reaction. The F is difficult to identify based on a weak signal. The Si could be a siloxane or silicone (both popular contaminants) although a non-stoichiometric silicon oxide is also possible.

In contrast to the neutral membrane, AFM revealed raised features on the surface of the oxidized membrane (Figure 3b). A similar structure has been observed for vapor deposited polythiophene films subjected to alternate oxidation chemistry.¹ This result suggests that these features may result from a morphological change to the polymer which accompanies chemical oxidation. XPS showed the presence of N, B and F, in addition to the elements detected for the neutral membrane. This new chemistry is consistent with the oxidizing agent, however, it is expected that the oxidant is distributed uniformly through the membrane. Angle-dependent XPS is in progress to determine whether, in fact, the raised features are due to the presence of residual oxidant. We believe this to be improbable since, following oxidation, the film was rinsed extensively with acetonitrile until the oxidant in the washings was not be detected with ferrocene.

AFM revealed a smooth surface for the reduced PDDT membrane (Figure 3c). As expected, XPS spectra exhibited much lower levels of the oxidant.

Figure 3a Neutral PDDT

Figure 3b: PDDT Oxidized with NOBF_4 (top view)

Figure 3b: PDDT Oxidized with NOBF_4 (side view)

Figure 3c: Reduced PDDT Membrane

- The time investment we previously made in the construction of an automated permeameter is starting to pay dividends in terms of reliability of data. We have instituted a well-defined protocol for film casting and measurement that allows impressive results with respect to precision in our measurements. Recently

several interesting features of these poly(alkylthiophene) systems have emerged. For example, in our study of PDDT we note modest differences in permeability and permselectivity with method of preparation. In several cases both *simultaneously increase* in higher molecular weight preparations. This is analogous to what we observed previously when related polymers were chemically oxidized. In a typical experiment several membranes are cast and thickness verified by optical microscopy. The membranes are then subjected to permeability measurements at controlled temperature using a series of gases (N₂, O₂, CO₂, and He). The permeability for each respective gas is measured on average 5 times before proceeding to the next member of the series and the series is then repeated several times to ensure that the permeability characteristics of the membranes are reproducible over the many hours of testing for each experiment. Representative results for PDDT of lower (<50 K) and higher (>50K) MW are shown in the following table.

Membrane	P _{N2}	P _{O2}	$\alpha_{N2/O2}$
< 50K	3.77	7.05	1.87
> 50K	9.10	21.22	2.33

This greater than 20% difference in α warrants further investigation of the polymer microstructure and its relationship to permeability. This will require examining a range of different molecular weights as well as methods of preparation in order to better define the origin and mechanism of this behavior. However, we can speculate that we may be observing ultramicroporosity effects that could stem from backbone stiffening from oxidation and/or side-chain crystallization. We anticipate being able to provide a more exhaustive summary of permeability/permselectivity data as a function of polymer type, stereochemistry and oxidation level during the next quarter.

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