

DOE/PC/94222-4

**TUNABLE COMPOSITE MEMBRANES  
FOR GAS SEPARATIONS**

**Progress Report**

**August 1, 1995 - October 31, 1995**

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

**Department of Chemistry  
The University of Texas (Dallas)  
Richardson, Texas 75083**

**October 1995**

**PREPARED FOR THE U. S. DEPARTMENT OF ENERGY  
UNDER GRANT NUMBER DE-FG22-94PC94222**

**US DOE PATENT CLEARANCE NOT REQUIRED PRIOR TO  
PUBLICATION OF THIS REPORT**

**MASTER**  
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED  
DLC

The fourth quarter of Grant DE-FG22-94PC94222 continued to see progress on five fronts: (a) instrument development, (2) polymer synthesis, (3) membrane fabrication and microscopy, (4) composite membrane fabrication and (5) permeability measurements.

- The membrane holder has been slightly modified to reduce the time required to attain an acceptable leak rate ( $\leq 10$  mTorr hr<sup>-1</sup>). The system was recalibrated using 0.92 mil polyethyleneterephthalate (Mylar™) and literature values for permeability were reproduced. The electrochemical permeation cell design has been modified to incorporate the above changes. The control program has also been modified to include corrected calculations for permeation, flux, solubility and diffusion. Programs to rapidly test for pin-holes in the membrane and to control the upstream gas pressure *via* the MKS 147 mass flow controller have been developed. An operators' manual for the instrument is being assembled.
- We have increased our stocks of monomers in the 3-alkylthiophene and the 3-methoxyethoxyethoxy series and have produced regiorandom and regioregular polymers of 3-octyl (POT) and 3-dodecylthiophene (PDDT). The regioregular materials are being synthesized *via* two routes: McCullough's method and Rieke's method. In the past the latter has suffered from low yields due to difficulties associated in making the active Zn catalyst. We now purchase this catalyst directly from Rieke Metals Inc. and the yields have increased up to the reported literature values. We have also purchased a sample of PDDT to compare its performance with material prepared in house.
- We have examined zeolite-polymer composite membranes with different zeolite loadings (10%, 25% and 50% by weight) using light and scanning electron microscopies in order to determine particle size distribution and homogeneity of dispersion. The distribution of zeolite (NaX) particles was fairly uniform across the length and width and excellent across the thickness of the film. The NaX crystallites displayed a reasonably uniform size distribution ranging between 2 - 5  $\mu$ m and this was carried over into the composite films made with the lower loading levels indicating that aggregation during the casting process was not occurring. At the highest loadings some clustering of the zeolites was observed.

- The accurate and reliable measurement of the permeability of a polymer membrane depends on 1) knowing the thickness of the membrane and 2) being able to reproducibly cast membranes so that multiple measurements can be made. To this end, a reliable method for solution casting poly(3-octylthiophene) (POT) and poly(3-dodecylthiophene) (PDDT) membranes was developed. To assess the reproducibility of the casting technique, the membrane thickness and surface roughness were measured by light microscopy (LM) and TappingMode™ atomic force microscopy (TMAFM), respectively. POT membranes were found to be of uniform thickness,  $21.7 \pm 0.7 \mu\text{m}$ , in the center 3.5 cm of the membrane. See Figure 1. This extent of uniformity exceeded the 2.5 cm diameter membrane requirement of the permeation cell. A similar measure of thickness uniformity was demonstrated for PDDT. The average root-mean-square roughness ( $R_{\text{rms}}$ ) value, measured from 4 samples taken from the center portion of 5 identically prepared POT membranes, was  $0.7 \pm 0.1 \text{ nm}$ . Based on these results, the casting technique was determined to be reliable and reproducible.

### Uniformity in Membrane Thickness

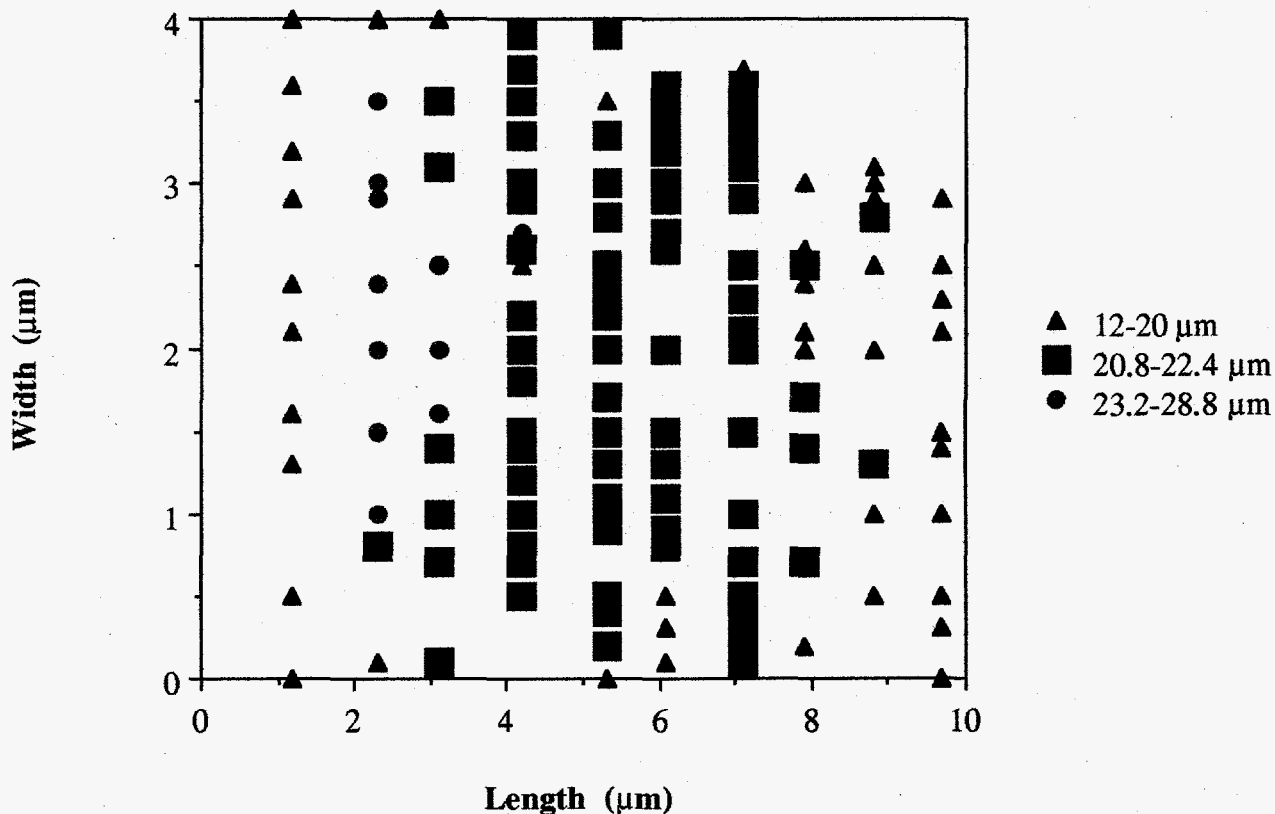


Figure 1

The microstructures of neutral, oxidized (by  $\text{NOBF}_4$ ) and reduced (by hydrazine) PDDT membranes were studied by LM, scanning electron microscopy (SEM) and TMAFM. By TMAFM, the first few neutral PDDT membranes exhibited round domains  $\sim 0.25 \mu\text{m}$  in diameter. These domains appeared to give way during oxidation leaving pits in the surface having approximately the same average diameter as the domains. The membrane fabrication procedure was then modified to include sonicating the solution prior to casting in an attempt to break up possible polymer aggregates. This process lead to the formation of apparently defect free neutral membrane surfaces (Figure 2) which were able to withstand the oxidation (Figure 3) and reduction (Figure 4) processes. All figures are images of a  $5 \mu\text{m} \times 5 \mu\text{m}$  area.

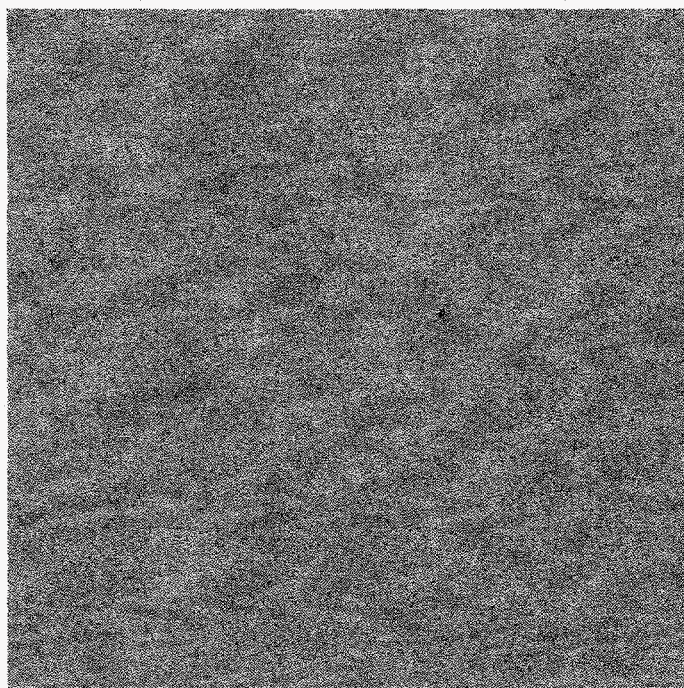
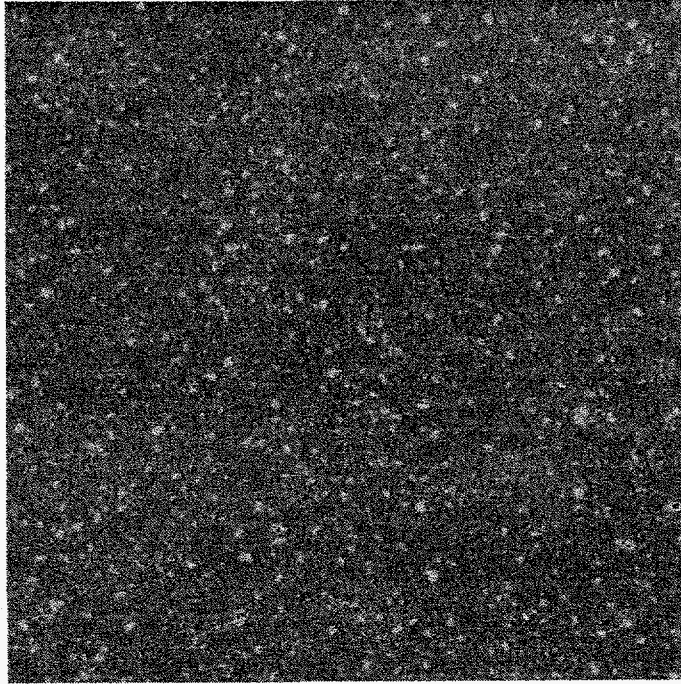
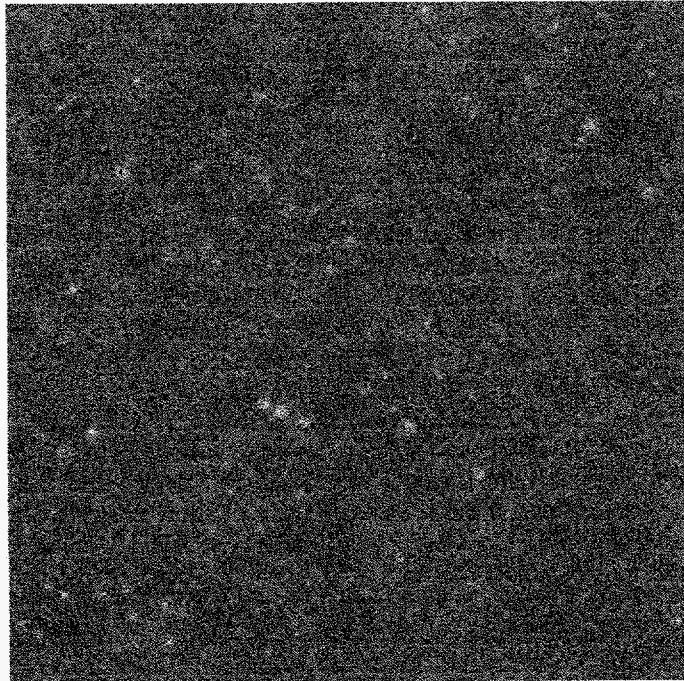


Figure 2



**Figure 3**



**Figure 4**

**DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.