During Summer Quarter, in addition to continuing my effort towards making PDI-bis(trguanidine) (1) that I began during the academic year, I pursued the syntheses of PDI-pyrrolidinyl-bis(norspermidine) (2) and PDI(C_{11}COOH)bis(norspermidine) (3) as novel small molecules. The objective with these new molecules will be to form membranes that are both more robust and have more desirable electronic properties when the PDI derivative is combined with a charged, conducting polymer. In parallel with making these compounds, I grew membranes with PDI-bis(norspermidine), which I had helped make earlier in the year, to test the effects of different polymer concentrations and stabilizing agents on membrane formation.

In attempting to make 1, I have successfully purified and characterized the fully protected triguanidine precursor (4). However, upon deprotecting the triflouroacetate group, I have not been able to confirm the product by LC/MS, and both attempts at coupling the deprotected product to PDI(C_{5}COOH) have been unsuccessfull. Thus, future attempts to make a guanidinium-substituted PDI end group will likely focus on norspermidine, which has fewer amines and may be easier to guanylate. While I was not able to reach the final target 1, I greatly improved my synthesis and purification abilities through my attempts to do so, and I learned how to optimize the process to get the purest product most efficiently.

As a separate direction, we identified molecule 2 to be an interesting target because of its altered redox properties. The pyrrolidine groups attached in the bay region of 2 make the PDI core more electron-rich, which could increase the driving force for reducing the catalyst. To make 2, I coupled the PDI-pyrrolidinyl(C_{5}COOH) carboxylic acid precursor that Adam Weingarten made to the norspermidine from Roman Kazantsev. After flash column purification, LC/MS, $^1$HNMR, $^{13}$CNMR, and HSQC spectra positively confirmed the formation of 2.

Additionally, 3 was chosen because the longer linker provides greater separation between the PDI core and the positively charged end groups. These positively charged groups are desirable for imparting water solubility and attracting the negatively charged polymer but are believed to hinder the pi-pi stacking interactions between the PDI cores. After attempting to couple the PDI(C_{11}COOH) that I made with Roman’s norspermidine, I purified the product, but neither the crude nor pure product was visible by MALDI or LC/MS. The $^1$HNMR spectra contains peaks that likely correspond to desired chemical shifts, so it is possible that the molecule was obtained yet does not fly by mass spectrometry.

Norspermidine was used as the end group in molecules 2 and 3, because at low pH norspermidine acquires four positive charges instead of six for spermine or triguanidine. We
thought that fewer positive charges on the small molecule would increase the osmotic pressure difference between the internal and external compartments of the sac, thus driving more outward polymer growth and increasing the order of the system. This hypothesis will be tested if Roman or Adam decide to grow membranes using molecules 2 and 3 in the coming weeks.

While membranes that Roman and I have made so far with PDI-bis(norspermidine) show evidence by SEM of fiber formation, no distinct diffusion barrier has been seen, and growth of fibers perpendicular to the membrane has been limited. Membrane trials conducted with PDI-bis(norspermidine) at different concentrations and time points show that the most stable membranes with 0.5 wt% PDI-bis(norspermidine) and 3.0 wt% P3HT-COOH polymer after 24 hours. However, at this concentration, the polymer solution is much more viscous than other polymer solutions (e.g., polystyrene sulfonate) that have been successfully used to make membranes. Given that the PDI/P3HT-COOH system seems to be producing a spherical mass of fibers instead of a more highly ordered membrane structure, it is possible that the high viscosity of the P3HT-COOH hinders the desired mechanism of membrane formation.

To further stabilize the membranes for ethanol exchange and critical point drying, we had the most success by soaking the membranes in a solution of 4 wt% gluteraldehyde and 3 wt% sucrose for 3 hours. Soaking in a solution of 20 wt% EDC for 20 minutes was also tested. While the EDC appeared to stabilize the sac, SEM with Roman showed the outer surface of the sacs had become flattened, mat-like, and apparently less ordered. To see if this effect is indeed a consequence of the type of cross-linking that occurs with EDC (i.e., between the amines of the PDI and the carboxylic acids of the polymer), the membranes should be soaked in different concentrations of EDC at different time intervals and the structures observed by SEM.

Based on our observations, it is likely that the formation of a distinct diffusion barrier and growth of perpendicular fibers would improve if the PDI molecules were more aggregated in solution before the droplet of polymer is introduced. Thus to achieve more highly ordered sacs going forward, it will be important to characterize the degree of self-assembly in solution of the small molecule PDI derivatives. Furthermore, these membranes will be used be used for H₂ production in an aqueous solution, which requires incorporation of a catalyst into the membrane. Roman’s preliminary tests with soaking the membrane in a Pt catalyst solution and shining light onto the light-absorbing membrane have showed H₂ production by GPC analysis, and he will be conducting further experiments to reproduce and confirm the validity of these results.

I hope to remain in touch with Roman and Adam over the coming months and stay updated with the progress of these efforts. Although I will be studying in London for Fall 2011 and will not be formally conducting research during the coming quarter, I look forward to continuing my involvement with the project as much as possible. During my time thus far in the Stupp Group, I have become used to addressing unexpected challenges that arise during research and working through these obstacles in a group environment with both one-on-one collaboration and group meetings. Therefore, I feel that this experience has been exceedingly valuable for me and will help me better carry out the graduate level research I intend to pursue in the future.
Appendix

1. PDI-bis(triguanidine)

2. PDI-pyrrolidinyl-bis(norspermidine)

3. PDI(C_{11}COOH)bis(norspermidine)

4. Protected triguanidine precursor