PRF Grant #57814-UNI7

Title: Characterization of Methacrylate Porous Polymer Monoliths for Use as Oil Sorbers

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During the past academic year (2018-19), four NKU undergraduate students worked on this project in the Daniels lab. Three of them worked on the project during both the Fall and Spring semesters, two sophmores and a senior. The remaining student was a sophomore who joined the lab in the Spring semester. During the 2019 Summer semester, five undergraduate students worked in the Daniels lab. Four of them were NKU students: one rising senior (part time), three rising juniors (one part time and two full time). The rising juniors were continuing their studies from the academic year. The senior from the academic year did not conduct research during the summer. The rising senior was a new hire for the summer. The remaining student was an exchange student from Scotland, a rising senior at Glasgow Caledonian University. With the much appreciated help of the students, the awardee was able to advance this project in three ways: (1) synthesize pH responsive poly(2-(dimethylamino) ethyl-methacrylate (PDMAEMA) porous polymer monoliths (PPMs), (2) characterize the methacrylate PPMs via Scanning Electron Microscopy (SEM), and (3) to obtain and analyze the behaviors of 2 analytes in a selected solution via Capillary Electrochromatography (CEC).

The first prong of the project wielded three reliable fabrications of PDMAEMA (Figure 1). The previous year (Spring and Summer 2018) was spent experimenting with the synthesis of the pH-responsive polymer. was a wrought with hurdles. This year allowed for reliable fabrications that could be repeatedly exposed to extreme pHs, 2 and 12. Polymers 324, 326, and 329 were selected for their ideal features. These were all white, opaque, and near stiff, yet malleable solids. All three were made with propanol porogen in the casting solution, which also contained dibasic (324 & 326) or monobasic (329) sodium phosphate buffer. 324 was 75% DMAEMA while 326 and 329 85% DMAEMA. These polymerized in a 90 ^{o}C water bath for 48 hours. These samples were air dried and subsequently exposed to 0.1 M HCl and NaOH.

The second prong was characterization of the PPMs via SEM (Figure 2). The three fabrications of PDMAEMA were imaged. Also, once the polymers were exposed to acid and base, the polymers were imaged to show the visible responsive reaction. Literature has shown that PDMAEMA will expand in acidic environments and shrink in basic ones (Zhao 2015). However, that has only been shown in strand-like morohologies. The experiments from this summer shows that this behavior persists in a non-destructive manner in the monolithic morphology (Hayes).

The third prong of the project was to perform capillary electrochromatography experiments with the monoliths grown inside capillaries with an inner diameter of 75 microns. Experiments were performed at different temperatures in efforts to examine the dynamics of model molecules, aliphatic benzenes in this study, in the presence of the responsive monoliths (data not shown). This endeavor is still ongoing as the number of experiments to elicit reliable data is quite large.

The American Chemical Society Petroleum Research Fund was extremely helpful in allowing the awardee to focus on undergraduate research opportunities and furthering foundational scientific knowledge. Work on these projects continues with a total of three undergraduate NKU students. Dissemination of these accomplishments have already taken place (June 2019, “Northeastern Regional ACS Meeting”, Saratoga Springs, NY; August 2019, “Heather Bullen Research Celebration”, Northern Kentucky University, Highland Heights, KY; November 2019, “Kentucky Academy of Sciences”, Berea College, Berea, KY). Other regional opportunities in the Spring and Summer semesters will be taken advantage of. A manuscript is also under preparation, with plans of submission in January 2020.

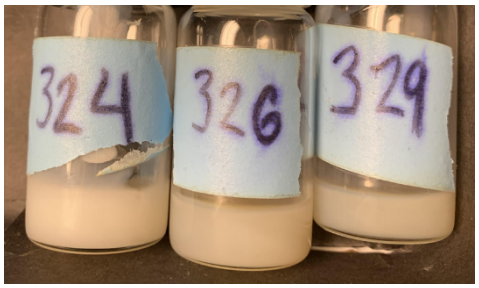


Figure 1: Polymer selected for further study.

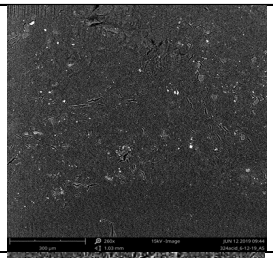
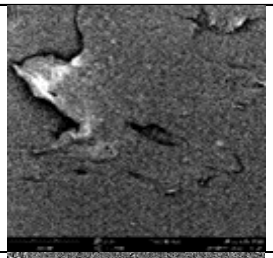
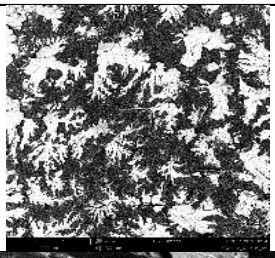
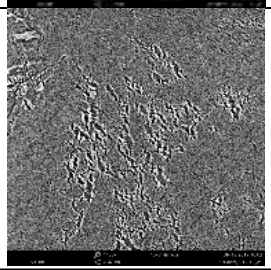
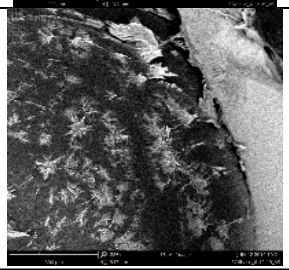
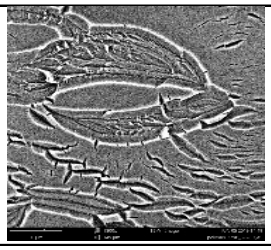
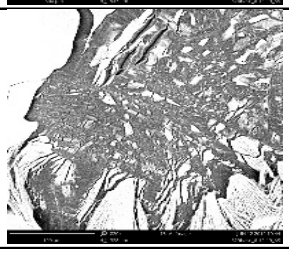
Air-Dried Polymers 324, 326, 329 SEM			Table 1: SEM images of air-dried DMAEMA polymers.
	Unexposed	0.1 M HCl	0.1M NaOH
324			
326			
329			

Figure 2: The diagram above is a collection of cast polymers. The top row is 75:25 DMAEMA:Styrene. The middle and bottom rows are 85:15 DMAEMA:Styrene. The columns depict the polymers unexposed (left), exposed to pH 2 (center) and exposed to pH 12 (right).

References

Zhao, L., Liu, M.,, Li, S., Li, A., An, H., Ye, H., Zhang, Y., Aggregation and supreamolecular chirality of 5,10,15,20-tetrakis-(4-sulfonatophenyl)-porphyrin on an achiral poly(2-(dimethylamino)ethyl methylacrylate)-grafted ethylene-vinyl alcohol membrane. 2015, Journal of Materials Chemistry C, 3, 3650-58.

Hayes, M., Smith, A., Arrasith, C., Davis, W., Daniels, C., Characterization of PDMAEMA:Styrene monolithic polymer morphologies. In preparation.