Synthesis of Fluorescent Polymers by ATRP

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Introduction

Atom Transfer Radical Polymerization (ATRP) is a powerful polymerization technique capable of catalytically polymerizing structurally and functionally unique monomeric compounds.[1] The purpose of this project was to successfully synthesize a functionalized, fluorescent polymer from a reactive parent homopolymer. The target polymer exhibits limited functionality to minimize interactions as well as fluorescent activity, giving it ideal use for bioimaging.[2,3]

Experimental Design: Synthesis and Spectroscopy

A two step synthetic scheme was adopted to synthesize the target polymer under mild reaction conditions with reasonable yields. The first step is polymerizing the ATRP active monomer followed by a functionalization with nicotinamide:

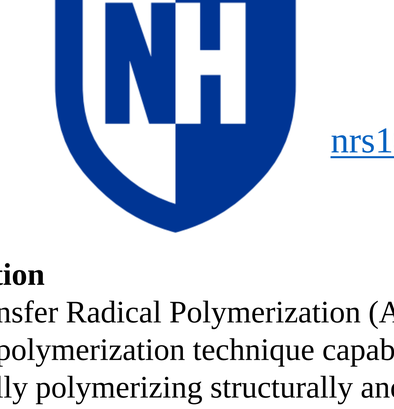

Figure 1: Synthesis of Functionalized Product from a Reactive Homopolymer

Size exclusion chromatography (SEC) provided molecular weight distribution. ^{1}HNMR of products and intermediates provided spectra which were used to assess reaction completeness and kinetics.

Results and Discussion:

^{1}HNMR spectroscopy, SEC, and fluorimetry were used to assess the reaction for completeness, kinetics, and fluorescent activity.

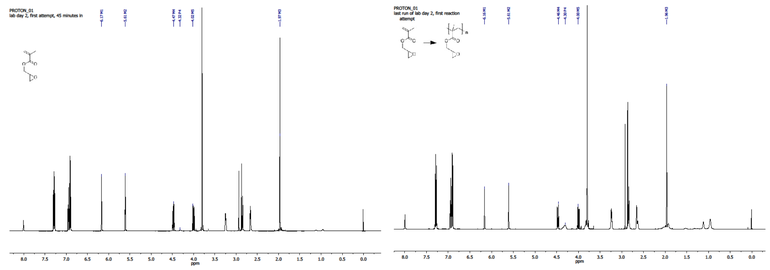

Figure 2: ^{1}HNMR Spectra of Polymerization at Times 0 min and 210 min

Indicated peaks represent polymerization completion over time.

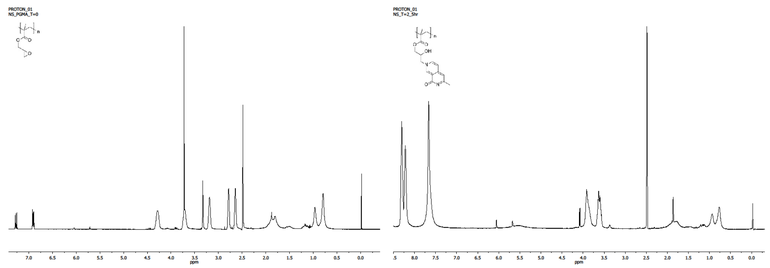

Figure 4: ^{1}HNMR Spectra of the Funcitonalization of the Homopolymer at Times 0 min and 150 min

Functionalization is evident by the disappearance of epoxide peaks between 2.5 and 3.25 ppm. Polymerization kinetics and fluorescent activity were discovered using the ^{1}HNMR spectra and fluorimetry, respectively:

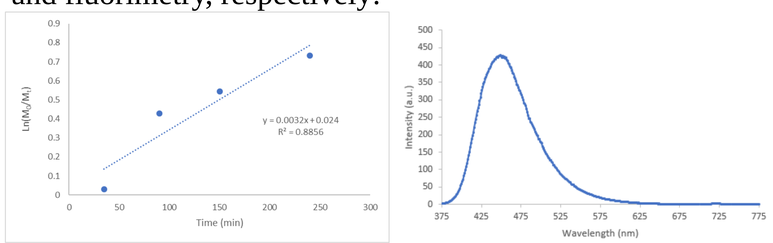

Figure 3: Reaction Kinetics of GMA Polymerization (Left) and Fluorescent Emission (Right)

The polymerization followed first order kinetics, with an uncharacteristic first point being attributed to inadequate temperature during the beginning of the reaction. Overall conversion at 3.5 h was calculated at 52%. Evidence of functionalization was confirmed through the use of ^{1}HNMR spectroscopy and fluorimetry, with experimental emission corresponding with literature findings.[1]

SEC data indicates successful ATRP polymerization over time. PDI values are extremely inconsistent, ranging from 1.7 to 7.

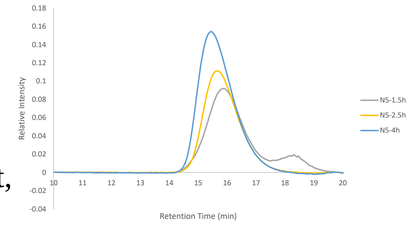

Figure 4: SEC Spectra

Future Work

A repeat polymerization would be beneficial to obtain more ideal kinetic data. While this specific polymerization is plentiful in the literature, experimental results are not entirely conclusive. Identification of a viscous biproduct after polymerization would also be useful, since it contributes to a significant proportion of lost yield of pure polymer.

Conclusions

An ATRP polymerization was carried out on a monomer, glycidyl methacrylate, to synthesize polyglycidyl methacrylate in 5.3% yield followed by a functionalization with nicotinamide in order to form a fluorescent active polymer in quantitative yields. Kinetics data for the polymerization were not conclusive. ^{1}HNMR and fluorimetry spectra strongly support the completion of the polymerization and subsequent functionalization.

Acknowledgements

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References

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2) Uthirakumar, P.; Hong, C.; Suh, E.' Lee, Y. *Journal of Applied Polymer Science*, **2006**, 102 (6), 5344-5350
3) Hou, M.; Lu, X.; Zhang, Z.; Xia, Q.; Yan, C.; Yu, Z.; Xu, Y.; Liu, R. ACS Applied Materials & Interfaces, 2017, 9 (51), 44316-44323