SLATT UNDERGRADUATE STUDENT FELLOWSHIP
FINAL REPORT

SLATT SCHOLAR:	Hannah Naguib
FACULTY ADVISOR:	Dr. Haifeng Gao
REPORT PERIOD:	Fall 2017-Spring 2018
PROJECT TITLE:	Synthesis of Hyperbranched Polymers with Post-functionalization Specificity
CONNECTION TO ND ENERGY'S RESEARCH AREAS (CHECK ALL THAT APPLY):	**(X) Energy Conversion and Efficiency** **( ) Sustainable and Secure Nuclear** **(X) Smart Storage and Distribution** **( ) Transformation Solar** **( ) Sustainable Bio/Fossil Fuels** **( ) Transformative Wind**

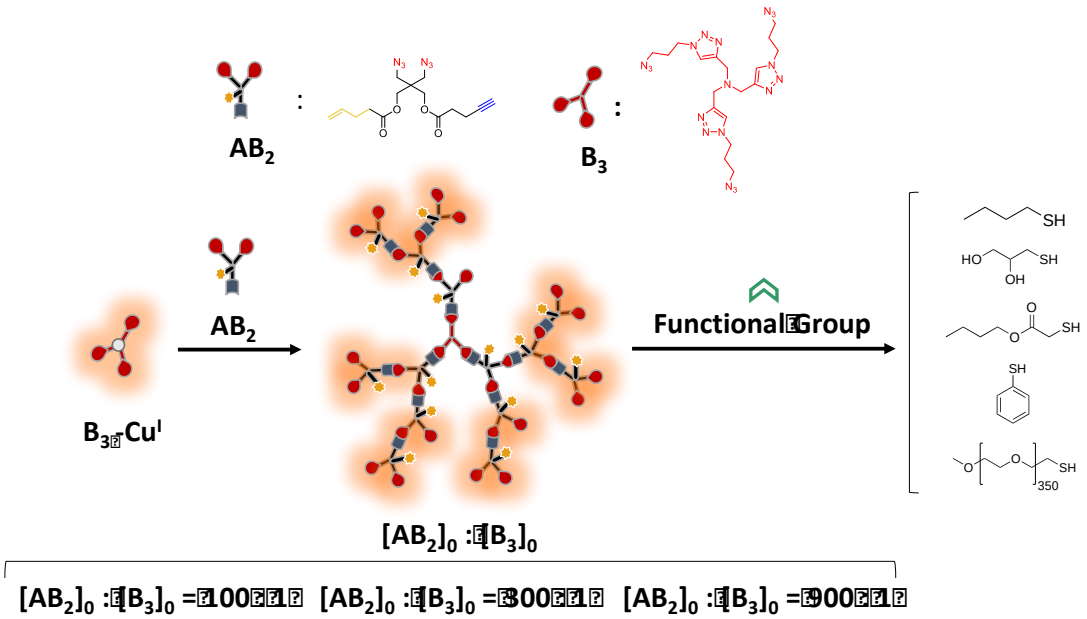
MAJOR GOALS AND ACCOMPLISHMENTS:
List your major research goals and provide a brief description of your accomplishments (1-2 sentences). Indicate the percentage completed for each goal. Please use a separate sheet to share additional details, technical results, charts, and graphics.

MAJOR RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Introduce size tunability to hyperbranched polymers	By using the CuAAC click reaction mechanism, size tunable hyperbranched polymers were synthesized in ratios of 100, 300, and 900 : 1 between the monomer and core molecules.	100
Introduce an adaptable polymer platform	By incorporating terminal dangling alkene groups on the monomers, thiol-ene reactions were able to easily introduce various functionalities.	100
Introduce water solubility to hyperbranched polymers	By reacting PEG thiols or the amino acid cysteine with the polymer in a thiol-ene reaction, water solubility is likely attainable.	75

RESEARCH OUTPUT:
Please provide detailed information below regarding any output resulting from your research project.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS	(Sponsor, Project Title, PIs, Submission Date, Proposal Amount) N/A
EXTERNAL AWARDS	(Sponsor, Project Title, PIs, Award Date, Award Amount) N/A
JOURNAL ARTICLES	(Journal Name, Title, Authors, Submission Date, Publication Date, Volume #, Page #s) In progress –no details concerning journal are known at this time. Synthesis of Hyperbranched Polymers with Post-functionalization Specificity, Chemistry Honors Thesis – University of Notre Dame Dept. of Chemistry and Biochemistry, 25 April 2018.
BOOKS AND CHAPTERS	(Book Title, Chapter Title, Authors, Submission Date, Publication Date, Volume #, Page #s) N/A
PUBLIC PRESENTATIONS, SEMINARS, LECTURES	(Event, Presentation Title, Presentation Date, Location) Notre Dame–Purdue Symposium on Soft Matter & Polymers, Synthesis of Hyperbranched Polymers with Post-functionalization Specificity, 16 Sept. 2017, Purdue University. ACS National Conference, Synthesis of Hyperbranched Polymers with Post-functionalization Specificity, 20 March 2018, New Orleans, LA.
AWARDS, PRIZES, RECOGNITIONS	(Purpose, Title, Date Received) N/A
INTERNAL COLLABORATIONS FOSTERED	(Collaborator Name, Organization, Purpose of Affiliation) N/A
EXTERNAL COLLABORATIONS FOSTERED	(Collaborator Name, Organization, Purpose of Affiliation) N/A
WEBSITE(S) FEATURING RESEARCH PROJECT	(URL) https://www3.nd.edu/~hgao/#rsh
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	(Please describe each item in detail) N/A

MAJOR GOALS AND ACCOMPLISHMENTS
(Additional Details, Technical Results, Charts and Graphics)

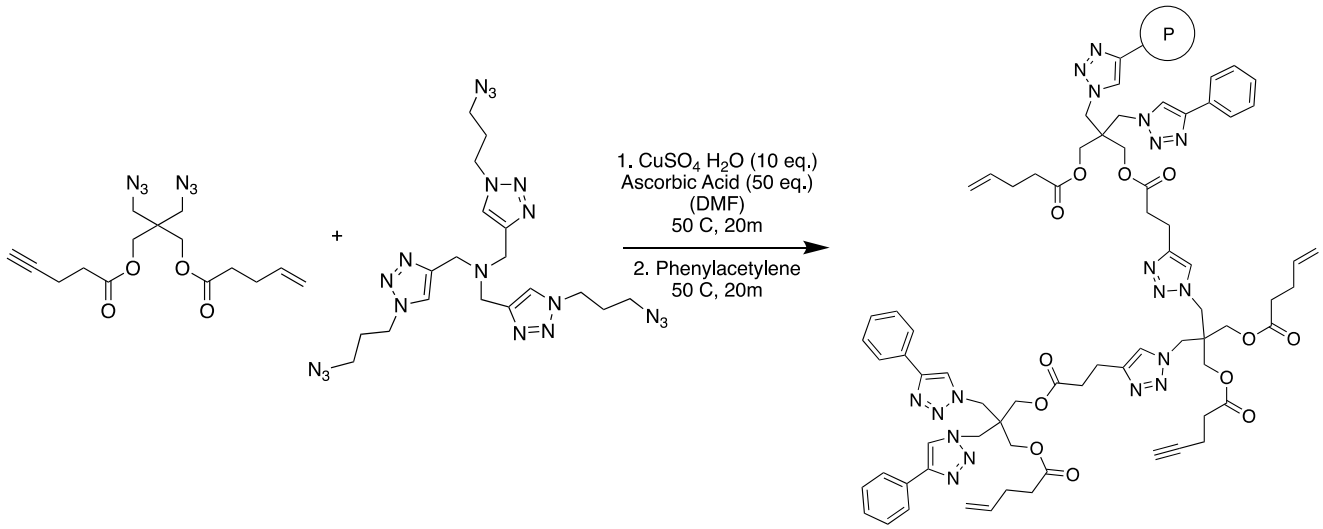


Scheme 1. Synthesis of hyperbranched copolymer with AB_2 monomer and B_3 core capable of post-functionalization reactions with thiols through thiol-ene chemistry due to dangling terminal alkene groups on the monomer.

Table 1. Comparison of copolymerization results of varying ratios of AB_2 monomer to B_3 core.

$[AB_2]_0 : [B_3]_0$	Conversion (%)[a]	MALLS (g mol^{-1})[a]	Theoretical MW (g mol^{-1})[b]	Dispersity (M_w/M_n)[a]
100 : 1	97	3.64 x 10^4	3.53 x 10^4	1.04
300 : 1	99	11.1 x 10^4	10.5 x 10^4	1.05
900 : 1	85	24.9 x 10^4	31.4 x 10^4	1.09

[a] Conversion percentage, MALLS, and dispersity (M_w/M_n) measured via THF SEC with RI detector based on linear PMMA standard. [b] Theoretical MW calculated based on $[AB_2]_0 : [B_3]_0$ ratio.



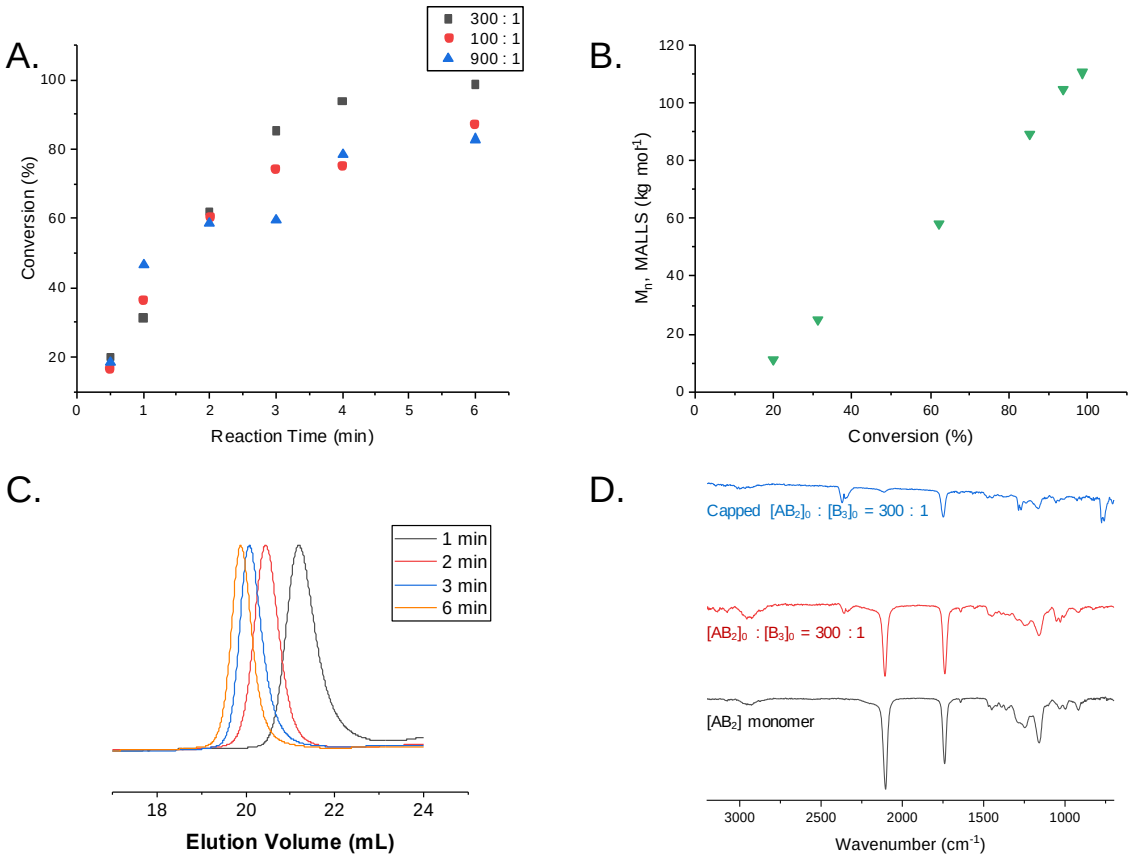


Figure 2. (**A**) Kinetics of copolymerization of $[AB_2]_0 : [B_3]_0 : [CuSO_4 \bullet 5H_2O]_0 : [\text{ascorbic acid}]_0 = m : 1 : 10 : 50$ in DMF at 50˚C (m = 100, 300, 900). (**B**) Progression of molecular weight (M_n) of $[AB_2]_0 : [B_3]_0 = 300 : 1$ determined by THF SEC (RI detector) with linear PMMA standard. (**C**) Overlay of kinetics aliquot SEC traces over the course of the copolymerization reaction of AB_2 with B_3 core in a 300 : 1 ratio. (**D**) FT-IR corresponding to AB_2 monomer, uncapped $[AB_2]_0 : [B_3]_0 = 300 : 1$ copolymer, and phenylacetylene-capped $[AB_2]_0 : [B_3]_0 = 300 : 1$. Strong peak at 2103 cm^{-1} indicative of azide vibrational stretching.

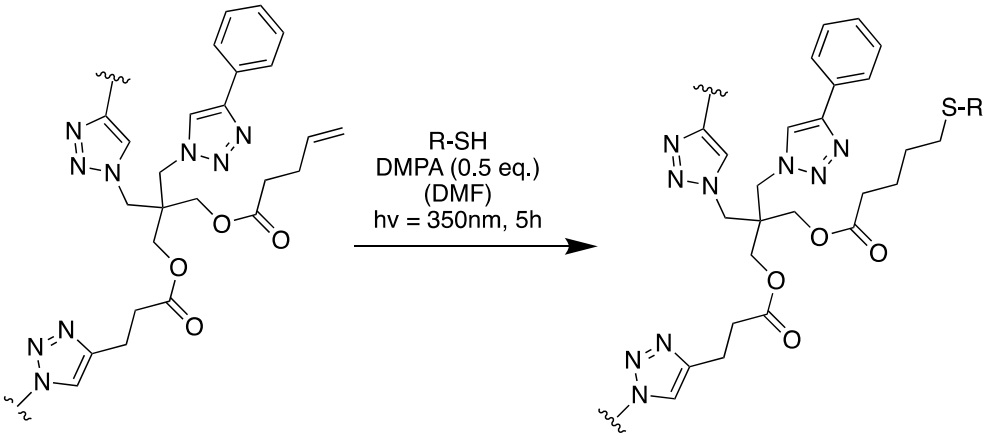
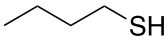
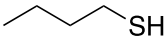
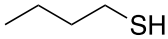
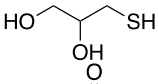
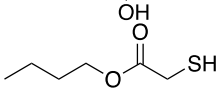
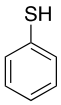
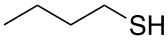
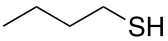


Table 2. Various thiol-ene reactions attempted for optimization and scope of study.

Copolymer $[AB_2]_0 : [B_3]_0$	Equivalents of Thiol [a]	Thiol	Molecular Weight (M_n) [b]	Dispersity (M_w/M_n) [b]	Conversion (%) [a]
300 : 1	2.5		5.02×10^4	1.06	100
300 : 1	1		4.21×10^4	1.08	100
300 : 1	0.5		4.83×10^4	1.11	48
300 : 1	1		5.38×10^4	1.05	100
300 : 1	1		3.26×10^4	1.13	91
300 : 1	1		4.47×10^4	1.04	2
100 : 1	1		5.11×10^4	1.30	89
900 : 1	1		5.66×10^4	1.77	93

[a] Stoichiometry in relation to equivalents of $[AB_2]_0 : [B_3]_0$. Conversion calculated according to ^{1}H NMR integration. [b] Molecular weight determined according to THF SEC with RI detector based on linear PMMA standard.

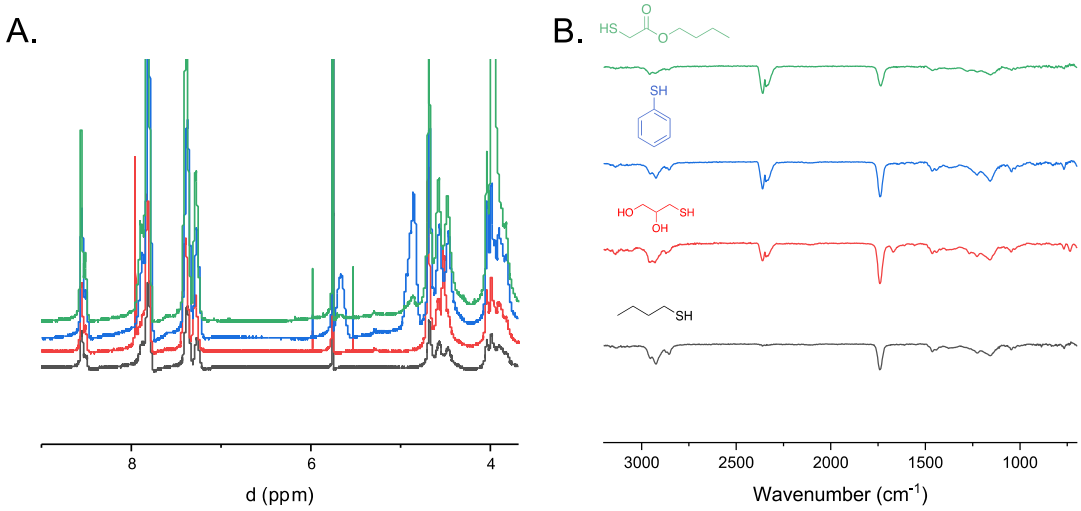


Figure 3. Thiolene post-functionalization results determined by ^{1}H NMR (**A**) and FT-IR (**B**). {$[AB_2]_0 : [B_3]_0$ = 300 : 1} : thiol = 1 : 1 (1-butanethiol, thioglycerol, thiophenol, thioester). Note the complete disappearance of the NMR peak at 5.7 in Figure 3A indicating the complete conversion of these reactions to final product in each of the thiol-ene reactions, excluding that which corresponds to thiophenol.

A tandem click chemistry synthetic pathway was developed for the production of hyperbranched polymers with tunable molecular weights, low polydispersities, and the ability for rapid surface functionalization with high yields. CuAAC click chemistry proved efficient for the pairing of a triazole B_3 core with AB_2 monomer in order to introduce elements typical of dendrimers to hyperbranched polymers, the other member of the dendritic polymer family. Thus, the key advantages of both dendrimers and hyperbranched polymers were combined through copolymerization reactions.

Furthermore, these highly specific hyperbranched polymers, following their facile syntheses, are ideal candidates for thiol-ene click chemistry post-functionalizations in order to introduce additional chemical moieties into the polymer structure. Reaching full conversion in less than 10 minutes, thiol-ene chemistry is an ideal method for attaining diverse libraries of post-functionalized hyperbranched polymers.

More details concerning this project can be found in my Honors Thesis for the Department of Chemistry and Biochemistry.