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14. ABSTRACT With the aim to achieve rapid and efficient topochemical polymerizations in the solid-state, via solution-based processing of thin-films, we report the integration of a diphenyldiacetylene monomer and a poly(styrene-b-acrylic acid) block copolymer template for the generation of supramolecular architectural photopolymerizable materials. This strategy takes advantage of non-covalent interactions to template a topochemical photopolymerization that yields a polydiphenyldiacetylene (PDPDA) derivative. In thin films, it was found that hierarchical self-assembly of the diacetylene monomers by microphase segregation of the block copolymer template enhances the topochemical					
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Report Title

Final Report: Highly Ordered Semiconducting Polymers for Sensing Applications

ABSTRACT

With the aim to achieve rapid and efficient topochemical polymerizations in the solid-state, via solution-based processing of thin-films, we report the integration of a diphenyldiacetylene monomer and a poly(styrene-b-acrylic acid) block copolymer template for the generation of supramolecular architectural photopolymerizable materials. This strategy takes advantage of non-covalent interactions to template a topochemical photopolymerization that yields a polydiphenyldiacetylene (PDPDA) derivative. In thin films, it was found that hierarchical self-assembly of the diacetylene monomers by microphase-segregation of the block copolymer template enhances the topochemical photopolymerization, which is complete within a 20 second exposure to UV-light. Moreover, UV-active cross-linkable groups were incorporated within the block copolymer template to create micropatterns of PDPDA by photolithography, in the same step as the polymerization reaction. The materials design and processing may find potential uses in the microfabrication of sensors and other important areas that benefit from solution-based processing of flexible conjugated materials.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

2013

September, Steven's Institute of Technology, Chemical Engineering and Materials Science Department Colloquium, Hoboken, NJ.

December, Materials Research Society, Point-and-Click Synthesis–Implementations of Click Chemistry in Polymers, Boston, MA.

2014

March, ACS National Meeting, PMSE Young Investigator Symposium, Dallas, TX

April, University of South Carolina, Department of Chemistry & Biochemistry, Columbia, SC

May, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, China.

June, Canadian Chemistry Conference, Pi-Conjugated Materials: From Design to Application, Vancouver, Canada

August, ACS National Meeting, Advancing Materials Synthesis and Assembly toward Technology Challenges. San Francisco, CA.

October, Society for the Advancement of Chicanos and Native Americans in Science National Meeting, Los Angeles, CA.

2015

August, Gordon Research Conference on Electron-Donor Acceptor Interactions, New Strategies for Solar Energy Conversion Session, Newport, RI.

July, Gordon Research Conference on Photochemistry, Easton, MA.

Number of Presentations: 6.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

2014	NSF CAREER Award
2014	3M Non-Tenured Faculty Award
2014	ACS PMSE Young Investigator

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Liangliang Zhu	1.00
FTE Equivalent:	1.00
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PhDs

NAME

Total Number:

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Statement of the Problem:

Most work on polydiacetylenes involves the use of the liposome form of the self-assembled aliphatic derivatives of 10,12-pentacosadiynoic acid. While these materials show good sensitivity to a range of analytes, their structure limits processability, and thus implementation in real-world devices. Other work using small molecules relies on short-range interactions, like van der Waals forces, so only short-range order is achieved. By tethering diacetylenes to a macromolecular structure capable of phase segregation, hierarchical self-assembly and long range order can be achieved, combined with facile polymer processing. Furthermore, the polymer backbone provides an opportunity for additional functionality such as targeting moieties.

Materials exhibiting a colorimetric response hold tremendous promise for wearable sensors. These sensors can be read on demand, without the need for additional equipment or instrumentation, which can prove advantageous in an environment where the Warfighter is exposed to toxic substances in the air or on surfaces. The use of polymers dramatically enhances processability of the material; thin films or fibers can be easily accessed. Additionally, this system provides the opportunity for more sensitive response from the inherent conductive and fluorescent properties of diacetylene materials.

Project execution:

To tackle the various challenges associated with obtaining solution-processable thin-films of polydiacetylene by conventional techniques, we employ a BCP template-based approach that drastically enhances the topochemical photopolymerization. Additionally, strongly phase segregating BCPs, such as polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) templates can be chemically modified in order to access micropatterns by photolithography, which may be beneficial for the fabrication of multiple devices on a single wafer. Figure 1 shows the supramolecular grafting strategy that exploits strong hydrogen-bonding interactions between the imidazolyl diphenyl-diacetylenemonomer (IDA) and PS-*b*-PAA. It must be noted that the Figure is a simplified representation for the templating strategy. It is not expected that single BCP chains will template single-chain polymerizations of IDA. The supramolecular complex of these two systems is termed PS-*b*-P(AA-*sg*-IDA), where *sg* stands for supramolecular graft of the IDA monomers to the PAA block. This approach takes advantage of the fact that: 1) the DPDA moiety has a larger molar extinction coefficient relative to a conventional DA; 2) non-covalent interactions provide modularity to tune the monomer loading ratios; 3) the complexes can be processed from solution by spin-coating, and 4) microphase segregation of the side-chain functional BCPs induces local order that enhances the topochemical polymerization.

Project outcomes:

The BCP-templated strategy developed in this project has enabled us to efficiently drive the topochemical polymerization of a diphenyl diacetylene derivative (IDA) in solution and thin films. It is important to note that common strategies rely on crystal engineering and/or stringent supramolecular recognition design, which can be challenging to control in a predictable fashion. The viability of our approach is not only rooted on processability and modularity, but also on the facile synthesis of the materials. Hydrogen-bonding interactions between imidazole on the IDA monomer and the acrylic acid on the BCP template provided effective molecular alignment that led to rapid photochemical polymerization to synthesize a supramolecularly grafted PDPDA. Moreover, the microphase-segregated structure arising from the BCP further improves the organization of the IDA monomers, which led to the solid-state, BCP-templated polymerization. Notably, the topochemical reaction can be completed within tens of seconds. Exploiting such rapid reactivity, we fabricated micropatterns by photolithography through the simultaneous cross-linking of 4-bromostyrene-functional BCP thin-films during photopolymerization. Future studies will be geared toward exploiting this templated supramolecular grafting strategy, which could be useful in other topochemical reactions that require highly uniform molecular alignment.

Technology Transfer