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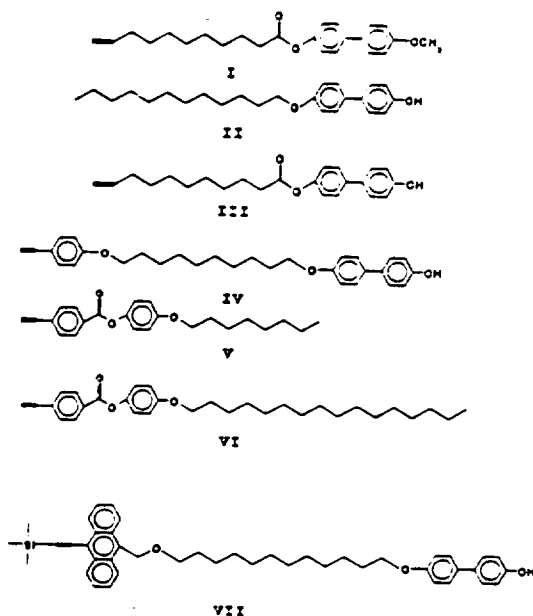
Final NLO 005

	New Technology Report	Form Approved O.M.B. No. 2700-0009	NT CONTROL NO. (Official use only)
<p style="text-align: right;">6 p. 1N-27-CR 14 CIT. 094472</p> INSTRUCTIONS			
<p>This form may be used when reporting inventions, discoveries, improvements or innovations to NASA. Use of this report form is optional; provided, however, that whatever report format is used contain the essential information requested herein.</p>		<p>the New Technology or Property Rights in Inventions clause. For further guidance as to what constitutes a satisfactory report, please refer to NHB 2170.3, Documentation Guidelines for New Technology Reporting.</p>	
<p>In completing each section, use whatever detail deemed appropriate for a "full and complete disclosure," as required by</p>		<p>Available additional documentation which provides a full, detailed description should be attached, as well as any additional explanatory sheets where necessary.</p>	
1. TITLE			
<p>Electro-Optically Active Monomers: Synthesis and Characterization of Thin Films of Liquid Crystalline Substituted Polyacetylenes</p>			
2. INNOVATOR(S) (Name and Social Security No.)*			
<p>R. S. Duran [REDACTED]</p>			
3. EMPLOYER (Organization and division)		4. ADDRESS (Place of Performance)	
<p>University of Florida Department of Chemistry</p>		<p>P. O. Box 117200 (318 Leigh Hall) Gainesville, FL 32611-7200</p>	
<p>SECTION I - DESCRIPTION OF THE PROBLEM THAT MOTIVATED THE TECHNOLOGY DEVELOPMENT (Enter A.-General Description of Problem Objective; B.-Key or Unique Problem Characteristics; C.-Past History/Prior Techniques; D.-Limitations of Prior Techniques)</p>			
<p>The overall objective of this study was the description of the behavior of mesogen substituted acetylene monomers and polymers in monolayer films at the air/water interface and as multilayer films including the formation of such films. Fundamental knowledge to be gained would include the effect of balancing hydrophilic and hydrophobic tendencies in a molecule more complex than the classical fatty acids or lipids. The effect of molecular shape on the packing and thus the ultimate stability of monolayers formed from these new molecules was explored. The work takes on the challenge of preorienting monomers in well-ordered arrays prior to attempting polymerization with the hope that order would be preserved in any resulting polymer. New knowledge gained with regard to the acetylenic monomers includes processing of the acetylene monomer into multilayer films, followed by the design and synthesis of a second generation of improved monomer structure for superior LBK film transfer properties. A third generation of acetylenic monomer was synthesized which approaches more closely the goal of solid state polymerization of these materials.</p>			
<p>A parallel study took a different approach. The materials are pre-formed poly(phenylene-acetylene) polymers so questions about reactivity are mute. The materials are a variation on the well-known hairy-rod polymers with regard to their Langmuir film-forming properties.</p>			
<p>Overall, the goal was to demonstrate that these polymers could be processed into NLO materials with novel polar order.</p>			
<p>* Supplying this information is voluntary, in accordance with Public Law 93-579 (Privacy Act of 1974). However, it is required for eligibility in the establishment of Space Act monetary awards.</p>			

SECTION II - TECHNICALLY COMPLETE AND EASILY UNDERSTANDABLE DESCRIPTION - NEW TECHNOLOGY THAT WAS DEVELOPED TO SOLVE THE PROBLEM OR MEET THE OBJECTIVE (Enter as appropriate A. - Specific description of item; B. - State of development; C. - Operation as a unit; D. - Functional operation; E. - Supportive theory; F. - Engineering specifications; G. - Peripheral equipment; H. - Drawings, graphs, etc.; I. - Parts or ingredients lists; and J. - Maintenance, reliability, safety factors)

A series of amphiphilic acetylenic monomer compounds was synthesized and investigated. A series of phenylene acetylene based polymers was also investigated. The goal of these studies was to improve the knowledge of the properties of these non-classical amphiphiles and indicate how the class of materials might effectively be incorporated in thin film form on solids for non-linear optical and electrically conducting applications.

The acetylenic monomer compounds were synthesized and characterized with a view towards polymerizing them in monolayers and subsequently depositing them on solids. First, several liquid crystalline monoacetylenes having the structures below were studied. While stable Langmuir monolayers could be obtained through mixing the compounds with other surfactants, satisfactory polymerization could not be obtained.



A second series of compounds containing phenyl acetylenic groups was then synthesized. These compounds formed better Langmuir monolayers. It was hoped that improved molecular design would improve the amphiphilic character while the phenyl acetylenic groups would allow initiation of polymerization by lower energy (visible light) radiation. These compounds formed stable Langmuir monolayers but were not significantly more polymerizable than the first materials.

Towards the end of the grant a third type of compound containing an anthracenal acetylenic group was synthesized. This material was motivated by the fact that it should be polymerizable at even lower energies, indeed literature claims indicated that this class of compounds were polymerizable in the bulk. By the end of the grant, this monomer had been prepared and characterization was started. Another potentially attractive feature of these anthracene derivatives is their ability to carry significant charge and thus their potential for photorefractive properties. The monomer was found to form stable monolayers consistent with close-packing of the anthracene units. Though insufficient time was left to complete characterization studies, this type of monomer should hold promise for continued work in this area.

The second approach taken was the study of monolayers of a series of preformed poly(phenylene-ynenes). These materials were prepared in collaboration with Dr. J. LeMoigne in Strasbourg, France. The materials, poly(2-(11-hydroxy undecanoxy)-5-methoxyphenylene-ethynolene), poly(2-(11-hydroxyundecanoxy)-5-methoxyphenylene-ethynolene-pyridine-ethynolene), and poly(2,5-di-(11-hydroxyundecanoxy)phenylene-ethynolene-pyridinium bromide-ethynolene) all spread to form monolayers. Two of the polymers were observed to form microscopic network morphologies after treatment by a simple processing procedure. The properties of one polymer's network was studied in detail including the network dynamics. A model for the nanoscale orientation of the polymer within its network was proposed. In addition, a new method for estimating the line tension between 2-D phases based on the observation of cell coalescence was developed. This class of materials may hold promise for nanopatterned thin film structures.

SECTION II (Con.)

SECTION III – UNIQUE OR NOVEL FEATURES OF THE TECHNOLOGY AND THE RESULTS (OR BENEFITS) OF ITS APPLICATION *(Enter as appropriate A. – Novel or unique features; B. – Development or conceptual problems; C. – Operating characteristics, test data; D. – Analysis of capabilities; E. – Source of error; and F. – Advantages/shortcomings)*

The materials synthesized in this study are a variation on the well-known hairy-rod polymers with regard to their Langmuir film-forming properties. The chemical nature of the polymer backbone puts the polymers synthesized into the class of NLO polymers which have promise for excellent optical properties. The shape of these rigid-rod molecules leads to comparisons with theoretical models of needles on a 2D plane. These polymers differ from previously studied rigid-rod polymers in that the alkyl side chains which give these polymers their solubility are terminated with a hydroxy group. Thus the Langmuir films gain stability not only from the packing of the polymers but also through strong adsorption to the water surface. This difference leads to non-classical 2D phase behavior. New knowledge gained with regard to the poly(phenylene-acetylene)s includes detailed description of the two-dimensional phase behavior of these materials. This description includes not only the microscale morphology of 2D phase separation but also a description of the nanoscale intra- and intermolecular arrangement.

Overall, the benefits of the approach taken are that the polymers produced are highly ordered and processable as thin film coatings. The disadvantage is the poor reactivity observed in many of the monomers and the difficulties associated with producing sizable quantities of material.

SECTION III (Con.)

SECTION IV - ADDITIONAL DOCUMENTATION (Include or list below any pertinent documentation which aids in the understanding or application of the new technology. IF NOT TOO BULKY OR DIFFICULT TO REPRODUCE, INCLUDE COPIES WITH THIS REPORT. For those references or additional documentation available but NOT included in this report (due to their being nonessential to a basic understanding of the new technology and which may be costly to reproduce or handle) complete item A, below)

A. AVAILABLE DOCUMENTS (Check and complete)	<input checked="" type="checkbox"/>	1. PAPERS, ARTICLES		4. ASSEMBLY/MFG. DRAWINGS		7. TEST DATA
		2. CONTRACTOR REPORTS		5. PARTS OR INGRED LIST		8. ASSEMBLY/MFG. PROCED.
		3. ENGINEERING SPECS.		6. OPERATING MANUALS		9. COMPUTER TAPES/CARDS
		10. OTHER (Specify)				

B. INDICATE THE DATES OR THE APPROXIMATE TIME PERIOD DURING WHICH THIS TECHNOLOGY WAS DEVELOPED (i.e. conceived, constructed, tested, etc.)

3/1/92-6/21/95

C. LIST THE FIRST PUBLICATION OR PUBLIC DISCLOSURE OF THE NEW TECHNOLOGY, AND DATES

Advincula, R. C., Roberts, M. J., Zhang, X., Blumstein, A., Duran, R. S.,
 "Crystalline Acetylenic Compounds: Behavior at Air-Water Interfaces" in
 Macromolecular Assemblies in Polymeric Systems (ACS Symp. Series 493),
 edited by Stroeve, P. and Balazs, A. C., 10-19, 1992.

D. LIST THE DATES AND ANY PARTICULARLY PERTINENT PAGE NUMBERS OF OTHER PUBLICATIONS WHICH ARE AVAILABLE BUT NOT ATTACHED

E. DEGREE OF TECHNOLOGICAL SIGNIFICANCE (Check in your best judgment the statement which best expresses the degree of technological significance of this technology)

1. MODIFICATION TO EXISTING TECHNOLOGY
 2. SUBSTANTIAL ADVANCE IN THE ART
 3. MAJOR BREAKTHROUGH

COMMENTS

SIGNATURE(S) OF INNOVATOR(S) DATE

Randy Dawson 1 Dec 1996

PUBLICATIONS

The research resulted in five papers published or in process in peer-reviewed journals and one non-peer reviewed publication as noted below. During the course of the grant, Joe Roberts, the Ph.D. student supported by NASA, spent several months at the Lewis Research Center doing synthesis in support of the project. In addition, the research has been presented at eight meetings as noted below.

Peer-Reviewed Research Publications:

"Langmuir Film Properties of Derivatives of Poly(phenylene Ethynylene), in preparation for submission to *Journal of Physical Chemistry*.

"Dynamic Properties of a Two-Dimensional Cellular Network of Polymer", in preparation for submission to *Journal of Physical Chemistry*.

"Calculation of Line Energy from Cell Coalescence Events in a Langmuir Film", in preparation for submission to *Journal of Physical Chemistry*.

Roberts, M. J., Shen, W. W., Servay, T. J., Advincula, R. C., Awartani, R., Meador, M. A., Duran, R. S., "Langmuir and Langmuir-Blodgett-Kuhn Films of Mesogen Substituted Acetylene Monomers", submitted to *Thin Solid Films*, 1995.

Advincula, R. C., Roberts, M. J., Zhang, X., Blumstein, A., Duran, R. S., "Liquid-Crystalline Acetylenic Compounds: Behavior at Air-Water Interfaces", in *Macromolecular Assemblies in Polymeric Systems* (ACS Symp. Series #493), Ed., Stroeve, P. and Balazs, A. C., 10-19, 1992.

Non-Peer Reviewed Research Publications

Roberts, M. J., Advincula, R. C., Zhang, X., Blumstein, A., Duran, R. S., "Behavior of Liquid Crystalline Acetylene Compounds at the Air-Water Interface", *Polymer Preprints*, 32(1), 252 (1991).

Presentations at Peer Workshops/Conferences:

"Energetics of Cell Coalescence in a Langmuir Film", Roberts, M. J., Teer, E. J., Moroni, M., LeMoigne, J., Duran, R. S. (talk given at ACS Spring National Meeting, April 1995).

"Langmuir-Blodgett-Kuhn Films of a Liquid-Crystalline Phenylacetylene", Roberts, M. J., Meador, M. A., and Duran, R. S. (poster presentation at ACS Spring National Meeting, April 1995).

Roberts, M. J., Moroni, M., LeMoigne, J., Duran, R. S. (poster presentation at the Gordon Research Conference on Organic Thin Films, February 1994).

"Polymeric Two-Dimensional Foams as Investigated by Brewster Angle Microscopy", Roberts, M. J., Moroni, M., LeMoigne, J., Duran, R. S. (poster presentation at LB6 - Sixth International Conference on Organized Molecular Films, July 1993).

"Main-Chain Liquid Crystalline Alkynyl Polymers and Copolymers at the Air/Water Interface", Roberts, M. J., Duran, R. S., Moroni, M., LeMoigne, J. (poster presentation at Florida Advanced Materials Chemistry Conference, March 1993).

"Main-Chain Liquid Crystalline Alkynyl Polymers and Copolymers at the Air/Water Interface", Roberts, M. J., Duran, R. S., Moroni, M., LeMoigne (poster presentation at the Materials Research Society Meeting, December 1992).

"Behavior of Substituted Polyacetylenes at the Air-Water Interface", Roberts, M. J. Advincula, R. C., and Duran, R. S. (poster presentation at the Annual Research Highlights Meeting of the University of Florida Center for Surface Science and Engineering, March 1992).

"Langmuir-Blodgett Films of a Liquid Crystalline Alkyl-substituted Mono-acetylene", Roberts, M. J. and Duran, R. S. (poster presentation at the Materials Research Society Meeting, December 1991).