

REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-00-

Public reporting burden for this collection of information is estimated to average 1 hour per response, gathering and maintaining the data needed, and completing and reviewing the collection of information, collection of information, including suggestions for reducing this burden, to Washington Headquarters, Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget,

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE		3. F. DATES COVERED Final - 1 September 1997 - 31 August 2000	
4. TITLE AND SUBTITLE Student Research Training in Materials for Nonlinear Optical Devices				5. FUNDING NUMBERS F49620-97-1-0391	
6. AUTHOR(S) Dr. Daniel J. Sandman Department of Chemistry					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Massachusetts One University Avenue Lowell, MA 01854				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 801 North Randolph Street, Room 732 Arlington, VA 22203-1977				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) A new thermally reactive diacetylene monomer 1,6-bis-(N-n-propyl-N-[p-tricyano- vinylphenyl]amino-2,4-hexadiyne has been synthesized and characterized. Crystal growth experiments are in progress.					
14. SUBJECT TERMS Monomer, diacerylene				15. NUMBER OF PAGES 8	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclas		18. SECURITY CLASSIFICATION OF THIS PAGE Unclas		19. SECURITY CLASSIFICATION OF ABSTRACT Unclas	
20. LIMITATION OF ABSTRACT					

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AUGMENTATION AWARDS FOR SCIENCE & ENGINEERING
RESEARCH TRAINING

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Grant Number: F49620-97-1-0391

Period: September 1, 1997-August 31, 2000

Objectives

The objective of this program is the training of students in research in advanced organic and polymeric materials for optical devices based on both linear and nonlinear processes. Nonlinear processes might be useful in technologies such as optical limiting and relevant materials would include polydiacetylenes and other conjugated polymers. The abstract of our proposal for grant F49620-97-1-0391 is given below along with rationales for shifting emphasis.

STUDENT RESEARCH TRAINING IN MATERIALS FOR NONLINEAR OPTICAL DEVICES

Abstract.

This proposal requests funding from the Ballistic Missile Defense Organization for two graduate students, two undergraduates, and a precollege student to participate in our program "Optical Processes and Devices Using Hydrogen Bonded Polydiacetylenes". With reference to our grant, the activities that these students would participate in are detailed. The undergraduate and precollege students would be involved in aspects of our work on urethane- and mixed urethane substituted polydiacetylenes and their chromic phase transitions. The graduate students would be involved in work related to polydiacetylenes with urethane groups isomeric to those discussed above, amide, and urea substituents and new work related to novel materials for optical limiting technologies. The resumes of two graduate students eligible for this program are included.

The experience of the principal and co-principal investigator in the supervision of both undergraduate and precollege students is summarized with particular emphasis on interaction with ethnic minorities.

New Objectives: We will also synthesize new conjugated polymers that would be of interest for optical and electronic properties. The optical properties would include light emission as photoluminescence or electroluminescence and a nonlinear process such as optical limiting. Objectives changed because our original material for chromic phase transitions was redirected because of irreproducible surfaces in these materials. We had begun work previously as noted above for optical limiting.

Status of effort

A new thermally reactive diacetylene monomer, 1,6-bis-(N-n-propyl-N-[p-tricyano-vinylphenyl]amino)-2,4-hexadiyne has been

synthesized and characterized. Crystal growth experiments are in progress.

The monomer 2-benzylidene-4,5-dicyano-1,3-dithiole(1) is polymerized by butoxide in butanol to a conjugated polymer with a weight average molecular weight(M_w) in the range 14000-60000 with a polydispersity of 2.1. Dimethylamino-2-propanol and sodium pentoxide in pentanol also bring about this polymerization. The polymer is assigned the cyclopolymerization structure given in Figure 1 based on ^1H and ^{13}C NMR spectra, IR spectra, and elemental analysis. The new samples of this polymer have better defined

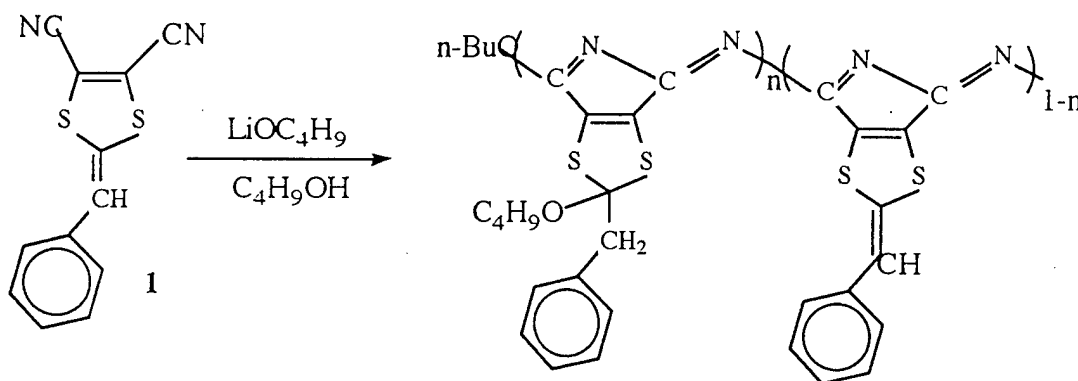


Figure 1. Polymerization of 2-benzylidene-4,5-dicyano-1,3-dithiole to a conjugated polymer; proposed structure.

optical properties in the near infrared region than our previous samples. Photoluminescence has been observed in this polymer in both solution and thin film, and films of this polymer have semiconducting electrical properties in both undoped and iodine-doped forms with resistivities of 10^6 - 10^7 ohm-cm and 10^3 - 10^4 ohm-cm, respectively.

Using unprotected carbohydrates, electroactive polymers have been synthesized for the first time. All previous polymerizations initiated by carbohydrate reagents have used protected sugar derivatives. The polymer from 2-benzylidene-4,5-dicyano-1,3-dithiole is synthesized in yields up to 75% from the sugars sucrose and lactose in aqueous solution; this polymer has electronic spectral properties indistinguishable from that prepared as described above and a higher thermal decomposition temperature than that from butoxide in butanol. Moreover, determination of molecular weight using gel permeation chromatography(GPC) gave M_w values 263,000 and 232,000 for the polymers from sucrose and lactose, respectively. The respective polydispersities are 1.28 and 1.56. It is apparent that

there are significant advantages in the use of the sugar reagents for the polymerization of 1.

The reaction of sugar reagents with dicyanoalkenes and -arenes can be complex. A range of complexity is illustrated in Figure 2 for phthalonitrile. For the case of amino-substituted

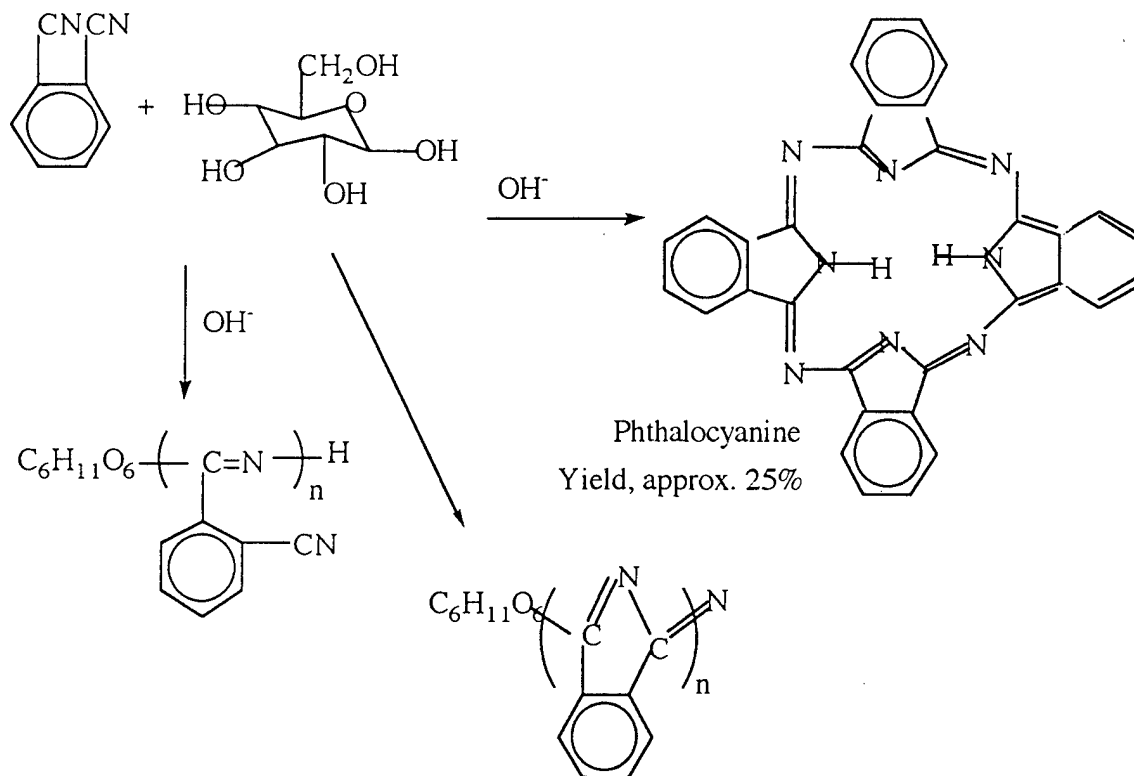


Figure 2. Range of reactivity of dicyanoalkenes and -arenes with alkaline sugars illustrated for the case of phthalonitrile and glucose.

phthalonitriles, polymerization at only one cyano group is observed. For the case of the insoluble amino material, the structure proof involved the use of solid state ^{13}C NMR using cross polarization and magic angle spinning methods. The polymerization of 4-amino-phthalonitriles is illustrated in Figure 3.

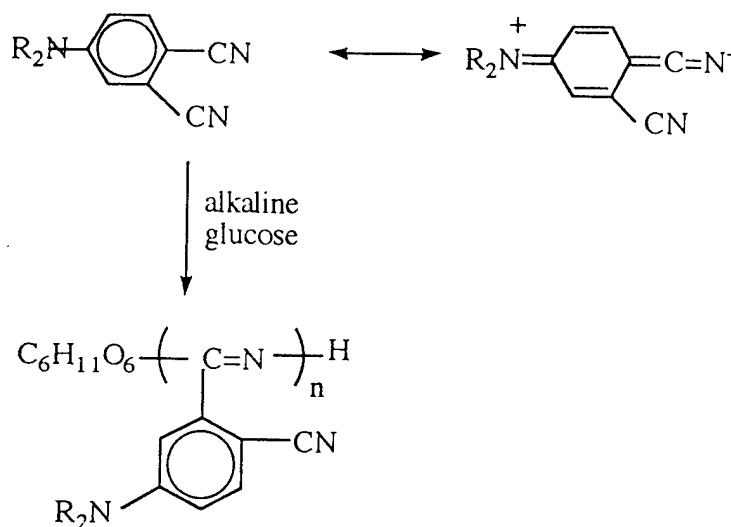


Figure 3. The observed polymerization of 4-aminophthalonitriles. The resonance structures of the monomer illustrate a buildup of electron density at the cyano group *para* to the amino group and hence offer a rationalization for the observed product.

Diiminoisoindoline may be doped into phthalonitrile or its 4-methoxy derivative, and the doped solid undergoes thermal reaction to give a phthalocyanine. These experiments provide examples of the rendering of an unreactive solid chemically reactive by doping. The thermal decomposition products of phenyliminoisoindoline include ammonia, phthalonitrile, 1,3-bis-phenyliminoisoindoline and phthalocyanine.

Accomplishments

The synthesis of electroactive polymers using "reagents" from natural sources such as sugars or enzymes is a significant advance in the methodologies used to make such materials. These processes have no environmentally "hostile" substances to dispose. These new processes represent important alternative methods to make materials that we were already making. In recent years, there has been considerable effort devoted to the development and implementation of procedures for chemical synthesis that do not involve large quantities of hazardous materials that must be disposed. Reactions that take place in the solid state also have no solvent to discard. These activities are often termed "green chemistry" and are being implemented rapidly in both civilian and military technologies.

Personnel Supported

Graduate students: Naja A. Ellis, Christopher Drew, Jeffrey Njus, Althea Anagnostopoulos, Mark S. Frahn

Undergraduate students: Christine Daudelin, Nandell F. Keene, Monica A. Rixman, Dorothy Wu, Joshua Roth, Paul Gauthier, Jessica Pirog, Jennifer Hankins, Bradford Sullivan, Jonathan Fischer, Stephen Emelett.

6. Publications

1. A. Anagnostopoulos, L.A. Samuelson, K.S. Alva, A.L. Cholli,, J. Kumar, and S.K. Tripathy, "Template-Guided Enzymatic Polymerization of Aniline", Proc. ACS Div. Polym. Materials: Science and Eng., 78, 197-198(1998).
2. M.A. Rixman and D.J. Sandman, "Synthesis and Unexpected Reactivity of 2-Benzylidene-4,5-dicyano-1,3-dithiole Polymer Preprints, 39(2), 558-559(1998).
3. L.A. Samuelson, A. Anagnostopoulos, K.S. Alva, A.L. Cholli,, J. Kumar, and S.K. Tripathy, Macromolecules, 31, 4376-4378(1998).
4. D.J. Sandman, M.A. Rixman, Z.-H. Tsai, "Approaches to New Conjugated Polymers from Dicyanoalkenes and -Arenes", Proc. ACS Div. Polym. Materials: Science and Engineering, 80, 112-113(1999).
5. D.J. Sandman, M.A. Rixman, C. Daudelin, S. Shah, Z. Zhang, and N.A. Ellis, Mol. Cryst. Liq. Cryst., "Solid State Reactions of Phthalonitrile and Related Compounds" in press.
6. M.A. Rixman and D.J. Sandman, "A Conjugated Polymer from 2-Benzylidene-4,5-dicyano-1,3-dithiole", Macromolecules, 33, 248-249 (2000).
7. C. Drew, X. Wang, K. Senecal, H. Schreuder-Gibson, J. He, S. Tripathy, and L. Samuelson, "Electrospun Nanofibers of Electronic and Photonic Polymer Systems", Proc. SPE 58th Annual Technical Conference and Exhibits(ANTEC 2000), 1477-1481.
8. D.J. Sandman, M.A. Rixman, Z.H. Tsai, D. Wu, and I-B. Kim, "Use of Carbohydrate Reagents for the Polymerization and Oligomerization of Dicyanoalkenes and -arenes", Polymer Preprints, 41(2), 1215-1216 (2000).

7. Interactions/Transitions Papers presented at meetings:

Monica A. Rixman and Daniel J. Sandman, "Synthesis and Unexpected Reactivity of 2-Benzylidene-4,5-Dicyano-1,3-dithiole", presented at the 215th American Chemical Society National Meeting, Dallas, Texas, March 29-April 2, 1998; Abstract ORGN 326.

A. Anagnostopoulos, L.A. Samuelson, K.S. Alva, A.L. Cholli,, J. Kumar, and S.K. Tripathy, "Template-Guided Enzymatic Polymerization of Aniline", presented at the 215th American Chemical Society National Meeting, Dallas, Texas, March 29-April 2, 1998; Abstract PMSE 0138.

Monica A. Rixman and Daniel J. Sandman, "Synthesis and Unexpected Reactivity of 2-Benzylidene-4,5-Dicyano-1,3-dithiole", presented at the 216th American Chemical Society National Meeting, Boston, Massachusetts, August 23-27, 1998; Abstract POLY 150.

M.A. Rixman and D.J. Sandman, "Attempts on the Synthesis of Phthalocyanine Analogs. The Unusual Reactivity of 2-Benzylidene-4,5-dicyano-1,3-dithiole" presented at the American Chemical Society National Meeting, Anaheim, California, March 21-25, 1999, Abstracts of Papers CHED 261.

D.J. Sandman, M.A. Rixman, Z.-H. Tsai, "Approaches to New Conjugated Polymers from Dicyanoalkenes and -Arenes", Abstracts of Papers PMSE 165. at the American Chemical Society National Meeting, Anaheim, California, March 21-25, 1999.

D.J. Sandman, M.A. Rixman, C. Daudelin, S. Shah, and U. Drechsler, "Solid State Reactions of Phthalonitrile and Related Compounds" at the 14th International Conference on the Chemistry of the Organic Solid State, Cambridge, U.K., July 25-30, 1999.

D.J. Sandman, "Conjugated Polymers and Oligomers from Dicyanoalkenes and -Arenes", presented at the First International Conference on Porphyrins and Phthalocyanines", Dijon, France, June 25-30, 2000, Paper Oral 276.

D.J. Sandman, M.A. Rixman, Z.H. Tsai, D. Wu, and I-B. Kim, "Green Chemistry Approaches to Conjugated Materials" Abstracts of Papers I&EC 106, invited lecture presented at the American Chemical Society National Meeting, Washington, D.C., August 20-24, 2000:

D.J. Sandman, M.A. Rixman, Z.H. Tsai, D. Wu, and I-B. Kim, "Use of Carbohydrate Reagents for the Polymerization and Oligomerization of

Dicyanoalkenes and -arenes", Abstracts of Papers POLY112, presented at the American Chemical Society National Meeting, Washington, D.C., August 20-24, 2000:

Interactions:

Samples of the polymer from 2-benzylidene-4,5-dicyano-1,3-dithiole were supplied to Dr. Thomas Cooper, Wright-Patterson Air Force Base, for evaluation as an optical limiter in the near infrared spectral region.

Samples of 2-benzylidene-4,5-dicyano-1,3-dithiole were supplied to Dr. Thomas Cooper, Wright-Patterson Air Force Base, for a study of the fluorescence spectrum.

Samples of the new infrared absorbing polymers from 4-nitro-phthalonitrile and tricyanovinyl dimethylaniline were supplied to Dr. Thomas Cooper, Wright-Patterson Air Force Base, for evaluation as optical limiters in the near infrared spectral region.

9. Honors/Awards

American Chemical Society POLYED Award for Undergraduate Summer Research to Nandell F. Keene and Monica A. Rixman, Summer 1998.

Northeastern Section of the American Chemical Society Richards/Norris Award for Undergraduate Summer Research 1998, to Monica A. Rixman.

National Science Foundation Predoctoral Fellowship awarded to Monica A. Rixman(2000) for her graduate work at Massachusetts Institute of Technology.