UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

(2)

DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

AD-A200 075

1b. RESTRICTIVE MARKINGS

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release;
Distribution unlimited

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S)
AFOSR-TR- 88-1068

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
University of Southern Mississippi		AFOSR/NC

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
Hattiesburg, MS 39406	Bldg. 410 Bolling AFB, DC 20332-6448

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
AFOSR	NC	AFOSR-84-0249

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
Bldg. 410 Bolling AFB, DC 20332-6448	61102F	2303	A3	

11. TITLE (Include Security Classification)
Novel Liquid Crystals - Polymers and Monomers - as Nonlinear Optical Materials

12. PERSONAL AUTHOR(S)
Anselm C. Griffin, III

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final	FROM 9/84 TO 12/87		7

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Nonlinear Optical Materials, Liquid Crystals, Polymers.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

18. Progress is reviewed on research into the design, synthesis and characterization of, primarily, side chain liquid crystalline polymers for nonlinear optics. Materials described are polyesters and vinyl polymers and copolymers having push-pull pi-electronic nlo structures as pendant groups. Chiral derivatives have also been prepared. The nlo species employed have been nitroaromatics and pyridine N-oxides. Results of collaborative efforts in further characterization (electrooptic, dielectric, Langmuir-Blodgett films) are described.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS	UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
Dr. Donald R. Ulrich	(202) 767-4963	AFOSR/NC

DD Form 1473, JUN 86 — Previous editions are obsolete. — SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

COMPLETED PROJECT SUMMARY

TITLE: Novel Liquid Crystals-Polymers and Monomers - As Nonlinear Optical Materials

PRINCIPAL INVESTIGATOR: Dr. Anselm C. Griffin
Chemistry and Polymer Science
University of Southern Mississippi
Hattiesburg, MS 39406

INCLUSIVE DATES: 1 September 1984 - 31 December 1987

GRANT NUMBER: AFOSR-84-0249

COST AND FY SOURCE: $84,602, FY 84; $84,700, FY 86; $90,063, FY 87

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JUNIOR RESEARCH PERSONNEL: R. S. L. Hung
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G. A. Howell

PUBLICATIONS:

"Synthesis of Side Chain Liquid Crystal Polymers for Nonlinear Optics", A. C. Griffin, A. M. Bhatti and R. S. L. Hung, Proc SPIE, 682, 65 (1987).

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"Liquid Crystal Polymers", Chemistry Department, Queen Mary College, University of London, London, England (July, 1987).

"Liquid Crystalline Side Chain Polymers as Nonlinear Optical Materials", American Chemical Society National Meeting, New Orleans, LA (September, 1987).

"Polyester Side Chain Liquid Crystalline Materials for Nonlinear Optics", Materials Research Society National Meeting, Boston, MA (December, 1987).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This project involved the design, synthesis and characterization of liquid crystalline materials having a potentially nonlinear optically active (nlo) species as a fundamental constituent of the liquid crystalline structure. Compounds of interest were usually polymeric and, in particular, side chain liquid crystalline polymers were primary target materials. The design concept was to use a pi donor-pi acceptor linearly conjugated system as simultaneously both the nlo species and the liquid crystalline (mesogenic) moiety. Second order nlo properties were design goals. Specific results included (a) use of polycondensation reactions to synthesize polyester side chain liquid crystals containing nitroaromatic nlo active species, (b) use of chiral diols in the above reactions to generate chiral nlo polymers, (c) preparation of pyridine N-oxide based side chain polymers having a push-pull pi electronic structure, (d) generation of a series of copolymers involving both an nlo component and a chiral non-nlo component to obtain a pi-transfer of chirality to the nlo species and to obtain a smectic A material, and (e) the fine tuning of specific reaction conditions to produce nitroaromatic based nlo side chain liquid crystalline polymers of the methacrylate type without crosslinking or significantly adverse side reactions.

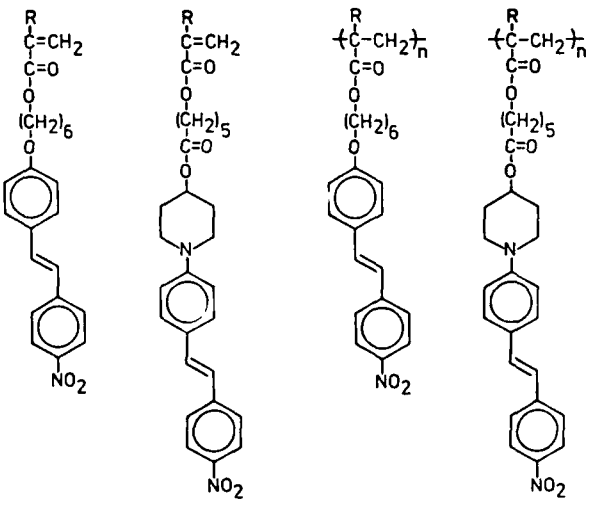
Materials described above were prepared and characterized chemically and both as polymers and as liquid crystals and were also made available to other laboratories for evaluation of optical and related properties. Particularly fruitful collaborations have resulted in the finding of unusual and interesting electric field alignment behavior of a nitroaromatic polyester liquid crystal by Professor Graham Williams (University College of Wales, Aberystwyth) and in the examination of film properties and nlo behavior of a Langmuir-Blodgett monolayer film from a nitroaromatic containing copolymer side chain liquid crystal by Professor Paras Prasad (SUNY-Buffalo).

AFOSR Program Manager: Dr. Donald R. Ulrich

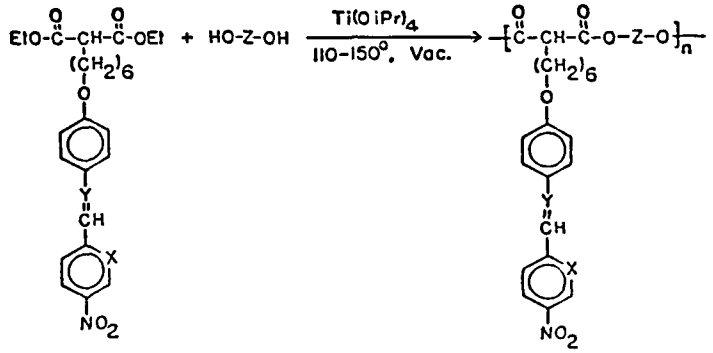
Final Report AFOSR-84-0249
A. C. Griffin

The early stages of this research involved considerable synthetic efforts to produce intermediates and ultimately side chain liquid crystalline polymers containing nonlinear optical (nlo) push-pull pi-electronic systems as pendant moieties. Work was directed both toward polymerization reactions and toward grafting reactions on preformed polymers. Grafting reactions, for example using poly(acryloyl chloride), were not initially as successful as desired and other grafting reactions were tried. At the end of the project period this generic approach was still being examined with very encouraging results attained recently. Advantages of this approach include initially defined polymer molecular weights and the use of non free radical coupling reactions. Disadvantages include incomplete reaction of functional groups on the polymer.

Polymerization reactions, however, offer the opportunity for a high density of nlo species along the polymer chain and primary effort was directed along these lines. Vinyl polymerization of acrylate or methacrylate monomers containing nlo groups as the pendant liquid crystalline moieties were examined first being of the 'classical' vinyl monomer type suited for free radical polymerization. The nitroaromatic group employed for nlo activity is, however, a retarder of free radical polymerization and ordinary, traditional polymerization conditions do not suffice to form polymer from acrylate monomer. Very recently, however, conditions have been discovered[1] for excellent free radical polymerization of methacrylate monomers of this type without undesirable crosslinking reactions. Structures of these polymers are shown below where R = methyl.



Condensation polymerization offers a most desirable route to nitroaromatic containing nlo side chain polymers and a synthetic sequence employing transesterification was used to produce several series of polyesters. As the titanium alkoxide catalyzed esterification reaction does not involve free radicals it is well suited for incorporation of nitroaromatic pendant groups into the polyme.. The polymerization route and polymer structures are shown below.

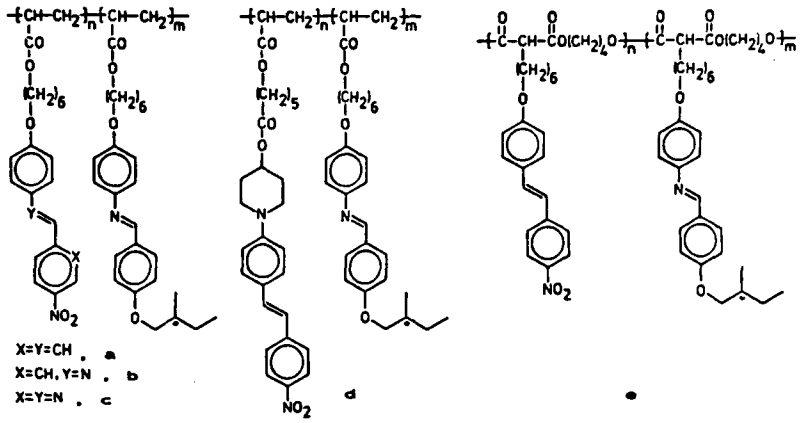


(1) X = CH, Y = CH, Z = $-CH_2CH_2CH_2CH_2-$
(2) X = CH, Y = CH, Z = $-CH_2CH_2CH(CH_3)-$
(3) X = CH, Y = CH, Z = $-CH_2CH_2CH(CH_3)CH_2CH_2CH_2-$
(4) X = CH, Y = N, Z = $-CH_2CH_2CH_2CH_2-$
(5) X = CH, Y = N, Z = $-CH_2CH_2CH(CH_3)-$
(6) X = CH, Y = N, Z = $-CH_2CH_2CH(CH_3)CH_2CH_2CH_2-$
(7) X = N, Y = N, Z = $-CH_2CH_2CH_2CH_2-$
(8) X = N, Y = N, Z = $-CH_2CH_2CH(CH_3)-$
(9) X = N, Y = N, Z = $-CH_2CH_2CH(CH_3)CH_2CH_2CH_2-$

Chirality for noncentrosymmetry can be introduced in the aliphatic diol unit and thereby imparted to the polymer. Characterization of these materials as to their chemical structures, their polymeric nature and their liquid crystalline behavior has been completed and reported.[2,3] These materials are either nematic, chiral nematic or smectic A depending on details of their chemical structure. Pyridine imines show a strong tendency to form smectic A phases due to the strong lateral dipole of the pyridine ring. One of these materials, polymer 5, has been examined in detail by Professor G. Williams (University College of Wales, Aberystwyth) for its alignment in electric fields and its dielectric characteristics. An interesting effect of the helical nature of this chiral polymer on electro-optical properties was observed.[4] In addition this polymer is dual frequency addressable.[4]

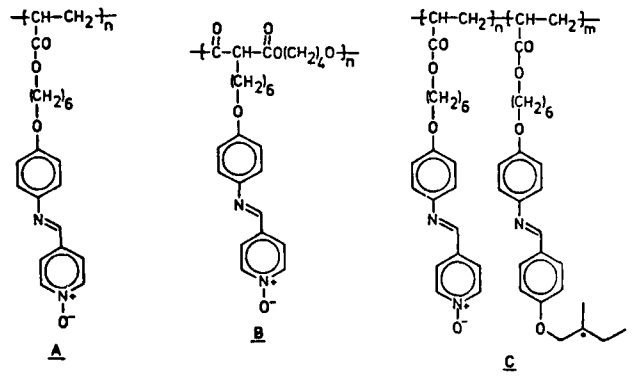
It seemed desirable to incorporate into the molecular design an intimate association of the nlo pi-electronic network and chirality. That is, the chirality should be proximal to the nlo species. Copolymers from vinyl monomers and, separately, from polycondensation monomers were designed and synthesized.[5] The aim was to take advantage of the intimate association of pi-electron rich and pi-electron poor pendant groups and to use this electrostatic attraction to transfer chirality from the electron rich aromatic rings of the chiral component to the electron poor aromatic ring of the nlo

species. Such copolymers should have, and did have, pronounced smectic A phases. Structures of these copolymers are shown below.



One of these copolymers has been examined by Professor P. N. Prasad (State University of New York at Buffalo). He has formed a monolayer film from this material using Langmuir-Blodgett techniques and has fully characterized the film.[6] In addition recent evaluations of χ^2 have been made by second harmonic generation and by electrooptical measurement. This is to our knowledge the first report of a L-B film from a thermotropic liquid crystalline polymer.

As an attractive push-pull pi-electronic system 4-substituted pyridine N-oxides were examined as pendant groups in a potentially side chain liquid crystalline polymeric structure.[7] Although the bulk of the polymer appeared to contain the pyridine N-oxide functionality intact, the chemical reactivity of this group led to difficulties (side reactions) during polymerization. A transparent isotropic glass was obtained - no liquid crystallinity was observed. As an isotropic, glassy nlo polymer these materials may have



promise, however. As mentioned earlier, considerable effort has been devoted to solving difficulties in the free radical polymerization of acrylate and methacrylate monomers containing nitroaromatic nlo pendant groups. It has been found[1] that acrylates do not homopolymerize without crosslinking but that

methacrylates can be polymerized quite nicely without crosslinking given the proper set of reaction conditions to give liquid crystalline materials. In summary several series of side chain liquid crystalline polymers having a wide variety in polymer structure and in nlo chemistry have been designed, synthesized and characterized. Optical evaluation and related examinations are underway at a number of laboratories with noteable success having been achieved in two such collaborations to date.

References

1. "Side Chain Liquid Crystalline Polymers for Nonlinear Optics", A. C. Griffin and A. M. Bhatti, Organic Materials for Nonlinear Optics, Royal Society of Chemistry, London, England, in preparation.

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Professional Personnel Associated With the Research

Senior Personnel: Dr. A. M. Bhatti
Dr. M. L. Steele (one summer only)

Junior Personnel: R. S. L. Hung
C. R. Walton
G. A. Howell (one summer only)

R. S. L. Hung received the Ph.D. in August, 1987. His Ph.D. dissertation title was "I. Novel Side Chain Liquid Crystalline Polymers as Nonlinear Optical Materials II. Main Chain Liquid Crystalline Polymers and Polymer Model Compounds".

Interactions

A listing of presentations resulting from this project is attached. Samples of our polymers have been sent (with AFOSR approval) to the following laboratories for further examination: Professor P. N. Prasad, SUNY-Buffalo; Professor G. Williams, Aberystwyth; Professor L. L. Hench, Florida; Dr. R. Lytel, Lockheed; Dr. D. Y. Yoon, IBM-San Jose; Professor T. J. Marks, Northwestern. Particularly fruitful interactions have been discussed in the body of the technical report.

New Discoveries, Inventions or Patent Disclosure

As reported to AFOSR by the University's Office of Research and Sponsored Programs, patent applications have been filed in the U.S. (U.S. patent Application Serial No. 917,710 "Side Chain Liquid Crystalline Polymers as Novel Nonlinear Optical Materials", filed October 10, 1986 - no response to date from the Patent Office) and in Canada by the same title (Application number 548,971, filed October 9, 1987 - no response to date).