OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

for

GRANT or CONTRACT: N0014-91-3-1643

R&T Code 4132049

MOLECULAR CONTROL OF LIQUID CRYSTALLINE ORIENTATION OF PBO AND PBT

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ATLANTA, GA 30332-0420

MAY 27, 1992

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OFFICE OF NAVAL RESEARCH

CHEMISTRY DIVISION

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RENEWAL PROPOSAL

Date Submitted: May 27, 1992 Date Received:

TITLE: Molecular Control of Liquid Crystalline Orientation of PBO and PBT

PRINCIPAL INVESTIGATOR: Issifu I. Harruna
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Native American

CONTRACTS & GRANTS OFFICIAL: Mr. Gary Richey
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Requested Funds: FY93 $90,000 FY94 _____ FY95 _____

TOTAL $90,000

Instrument Funds: FY93 _____ FY94 _____ FY95 _____

TOTAL _____

CONTRACT #: N00014-91-3-1643 R&T PROJECT CODE: 4132049

End date of current contract: April 30, 1992

Responsible Chemistry Division Scientific Officer: Dr. K. Wynn

Title of Last Technical Progress Report:

Authors: Dr. Harruna and Dr. Polk

ENCLOSURE(2)

OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R&T Number: 4132049
Contract/Grant Number: N00014-91-3-1643
Contract/Grant Title: Molecular Control of Liquid Crystalline Orientation of PBO & PBT
Principal Investigator: Issifu I. Harruna
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a. Number of papers submitted to refereed journals, but not published: 0
b. * Number of papers published in refereed journals (list attached): 0
c. Number of books or chapters submitted, but not yet published: 0
d. * Number of books or chapters published (list attached): 0
e. * Number of printed technical reports & non-refereed papers (list attached): 1
f. Number of patents filed: 0
g. * Number of patents granted (list attached): 0
h. Number of invited presentations at workshops or professional society meetings: 1
i. Number of presentations at workshops or professional society meetings: _____
j. * Honors/Awards/Prizes for contract/grant employees (list attached): 0
(This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.
k. Total number of Graduate Students and Post-Doctoral associates supported by at least 25% during this period, under this R&T project number:
Graduate Students: 5
Post-Doctoral Associates: 0
including the number of,
Female Graduate Students: 3
Female Post-Doctoral Associates: N/A
the number of
Minority* Graduate Students: 2
Minority* Post-Doctoral Associates: _____
and, the number of
Asian Graduate Students: 2
Asian Post-Doctoral Associates: _____
l. * Other funding (list agency, grant title, amount received this year, total amount, period of performance and relationship of that research to your ONR grant) None

* Use the letter and an appropriate title as a heading for your list, e.g.:
b. Published Papers in Refereed Journals, or, d. Books and Chapters published
Also submit these lists as ASCII files, preferably on a 3" or 5" PC-compatible floppy disks

* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

PART II

a. Principal Investigator: Dr. Issifu I. Harruna

b. Current telephone number: (404) 220-0175

c. Cognizant ONR Scientific Officer: Dr. Kenneth Wynn

d. Fibers which are spun from lyotropic solutions of extended chain polymers exhibit high strength and modulus in the direction of the fiber axis, however, the strength and modulus are poor in the direction perpendicular to the fiber axis. This leads to poor compressive properties and delamination problems for biaxially oriented films obtained by the processing of liquid crystalline solutions. We propose to improve the solubility and transverse mechanical properties of PBO and PBT by using a combination of block copolymerization and molecular orientation.

We propose to prepare block copolymers containing PBO and PBT segments and ABPBO segments radially oriented with respect to the anthrone nucleus and thereby prepare materials with improved solubility and transverse mechanical properties. Therefore we propose to improve the directional mechanical and solubility properties of PBO and PBT materials by controlling the geometries of block copolymer systems.

e. Preparation of 2,6-diamino-9,9-bis(4-aminophenyl)anthrone.

2,6-Diaminoanthraquinone was reacted with benzoyl chloride to protect the 2,6-diamino groups as the 2,6-diamide I. The anthraquinone-2,6-dibenzamide I was reacted with excess aniline and aniline hydrochloride at reflux to yield 9,9-bis(4-aminophenyl)-
anthrone-2,6-dibenzamide II. II was hydrolyzed in 70% sulfuric acid at 150 C for 10 min. to yield 2,6-diamino-9,9-bis(4-aminophenyl)-anthrone dihydrosulfate or in KOH solution to yield 2,6-diamino-9,9-bis(4-aminophenyl)anthrone III.

Preparation of star-like ABPBO, poly(2,4-benzoxazole)

2,6-Diamino-9,9-bis(4-aminophenyl)anthrone dihydrosulfate(0.00048 mole) was reacted with 2-amino-3-hydroxybenzoic acid(0.033 mole) in PPA to form a polymer with an inherent viscosity of 0.199 dL/g. The presence of amide groups and the anthrone carbonyl in the FTIR and C-13 FTNMR spectra of the polymer demonstrate the formation of the star-like polymer system. The DSC of the polymer showed a crystalline melting point of 305.6 C.

Miscellaneous

Also we have synthesized 2-chloro-4,6-dinitro-1,3-benzenediol for conversion to 4,6-diamino-1,3-benzenediol dihydrochloride (the precursor to PBO). We have synthesized 2,6-diaminobenzobisthiazole for conversion to 2,5-diamino-1,4-benzenedithiol dihydrochloride (the precursor to PBT). We also synthesized the ABPBO polymer using 9,9-bis(4-aminophenyl)anthrone-2,6-dibenzamide as the template.

f. Our plans for next year include preparation of the following: (1) the star-like homopolymer formed by the reaction of 2,6-diamino-9,9-bis(4-aminophenyl)anthrone III with dicarboxy-terminated PBO; (2) the star-like homopolymer formed by the reaction of III with dicarboxy-terminated PBT; (3) the ABPBO homopolymer formed by the reaction of III with 3-amino-4-hydroxybenzoic acid; (4) the ABPBO homopolymer formed by the reaction of III with 4-amino-3-hydroxybenzoic acid; (5) the star-like block copolymer formed by the reaction of III with 3-amino-4-hydroxybenzoic acid followed by reaction with a freshly polymerized PBO-PPA mixture; (6) the star-like block copolymer formed by the reaction of III with 3-amino-4-hydroxybenzoic acid followed by a freshly polymerized PBT-PPA mixture; (7) the star-like block copolymer formed by the reaction of III with first with a polymerized mixture of 4,6- diamino-1,3-benzenediol and excess isophthalic acid in PPA followed by reaction with a freshly polymerized PBO-PPA mixture; and (8) the star-like block copolymer formed by the reaction of III first with a polymerized mixture of 2,5-diamino-1,4-benzenedithiol and excess isophthalic acid in PPA followed by reaction with a freshly polymerized PBT-PPA mixture.

g. Graduate students: Laverne Avant (Ph.D. student, B.S. Jackson State U.); Joonwon Park (M.S.); Veronica Monares (M.S.); and Brian Khamvongsa (M.S.): and Agnes Thuo (Ph.D. student, Clark-Atlanta University).

PART III

MOLECULAR CONTROL OF LIQUID CRYSTALLINE ORIENTATION OF PBO AND PBT

PRINCIPAL INVESTIGATORS:

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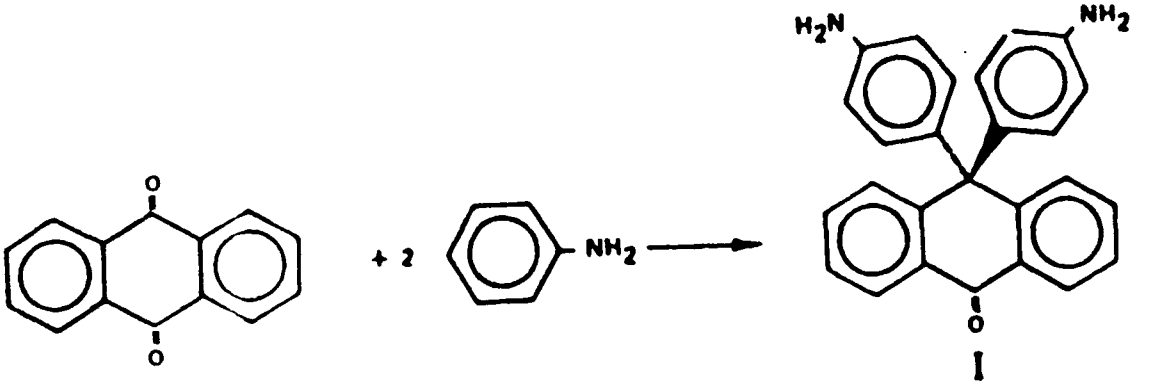

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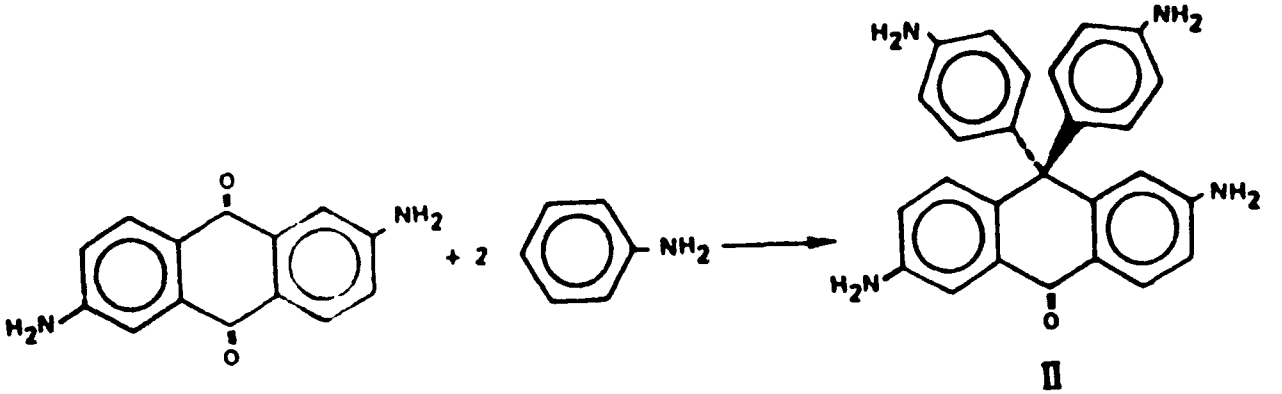

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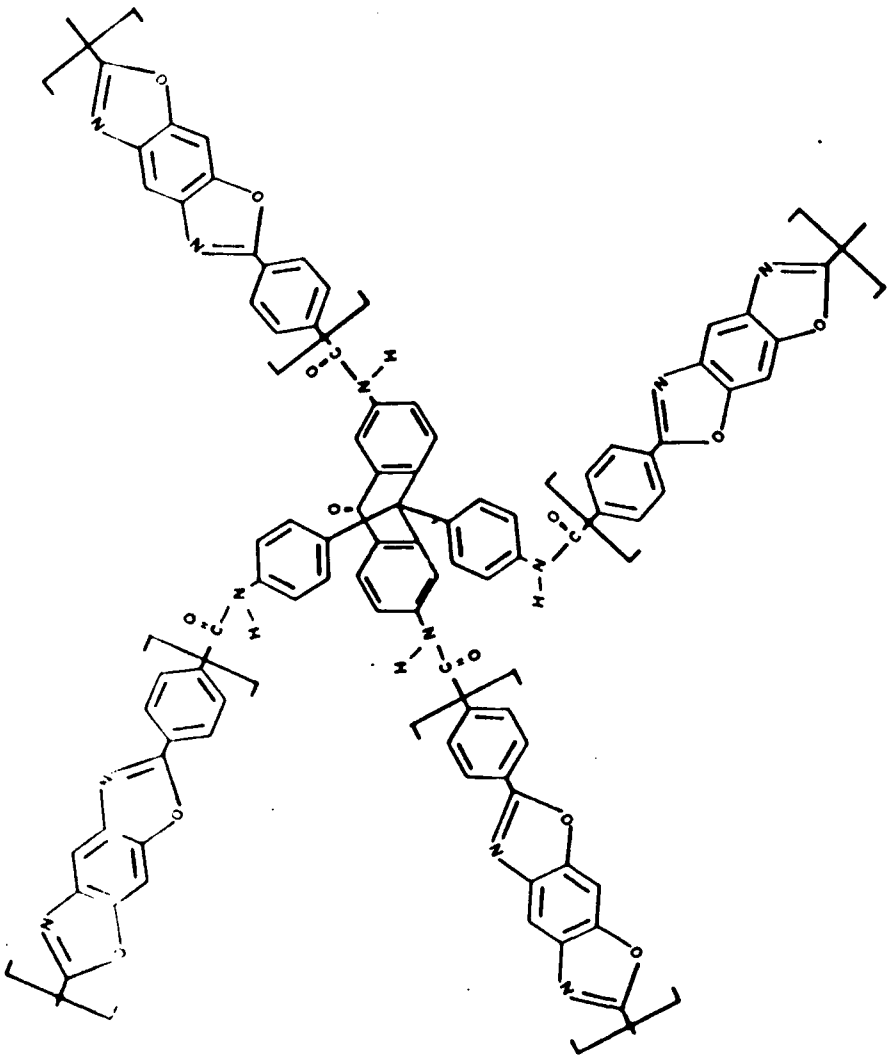

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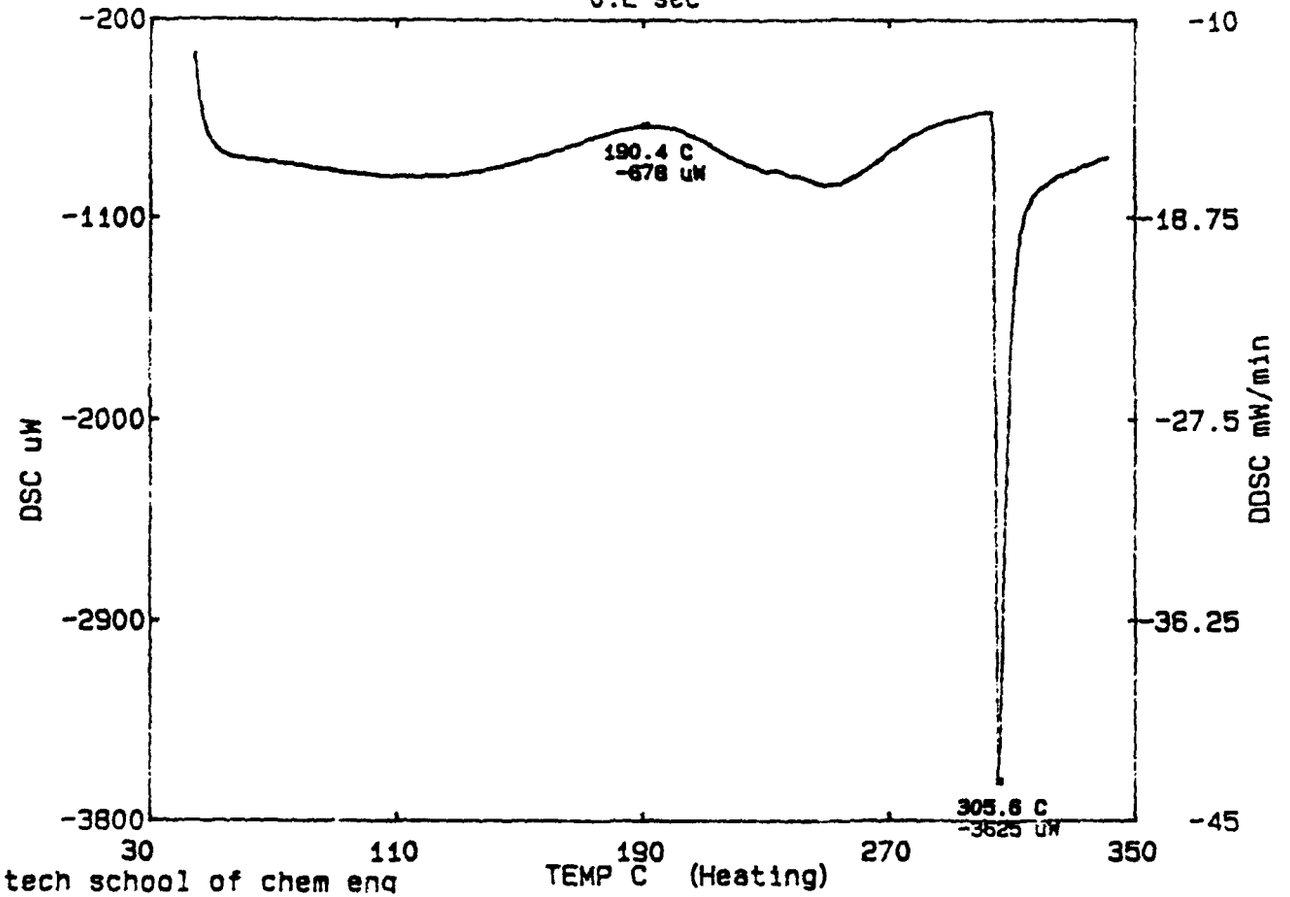

georgia tech school of chem eng

STAR-LIKE POLY(2,4-BENZOXAZOLE)

Star-like poly(2,4-benzoxazole) was synthesized by the reaction of 2,6- Diamino-9,9-bis(4-aminophenyl)anthrone dihydrosulfate with 2-amino-3-hydroxybenzoic acid in PPA. The polymer had an inherent viscosity of 0.199 dL/g in methanesulfonic acid and a crystalline melting point of 305.6 C. The FTIR and C-13 FTNMR spectra are consistent with the proposed structure.