

REPORT DOCUMENTATION PAGE

REPORT SECURITY CLASSIFICATION none	1b. RESTRICTIVE MARKINGS none
SECURITY CLASSIFICATION AUTHORITY: has been declassified none	3. DISTRIBUTION / AVAILABILITY OF REPORT unlimited
DECLASSIFICATION / DOWNGRADING / DECONTROL none	

PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report # 65	5. MONITORING ORGANIZATION REPORT NUMBER(S) ONR N00014-89-J-1225
---	---

NAME OF PERFORMING ORGANIZATION University of Southern Mississippi	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research
---	-----------------------------------	---

ADDRESS (City, State, and ZIP Code) University of Southern Mississippi Department of Polymer Science Hattiesburg, MS 39406-0076	7b. ADDRESS (City, State, and ZIP Code) Chemistry Division 800 North Quincy Street Arlington, VA 22217-5000
--	--

1. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
--	-----------------------------------	---

2. ADDRESS (City, State, and ZIP Code) Chemistry Division 800 North Quincy Street Arlington, VA 22217-5000	10. SOURCE OF FUNDING NUMBERS
	PROGRAM ELEMENT NO. PROJECT NO. TASK NO. WORK ACCESSION NO.

1. TITLE (Include Security Classification)
Thianthrene-Based Poly(benzoxazole)s

2. PERSONAL AUTHOR(S)
R. A. Johnson, L. J. Mathias

3a. TYPE OF REPORT Technical	13b. TIME COVERED FROM 6/1/93 to 5/31/94	14. DATE OF REPORT (Year, Month, Day) 7/15/94	15. PAGE COUNT
---------------------------------	---	--	----------------

16. SUPPLEMENTARY NOTATION

17. COSATI CODES	18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD GROUP SUB-GROUP	

DTIC
ELECTE
S JUL 25 1994
F

See attached.

34-23191



20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED / UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION
--	--------------------------------------

22a. NAME OF RESPONSIBLE INDIVIDUAL Lon J Mathias	22b. TELEPHONE (Include Area Code) 601-266-4871	22c. OFFICE SYMBOL
--	--	--------------------

AD-A282 326

1994

THIANTHRENE-BASED POLY(BENZOXAZOLE)S

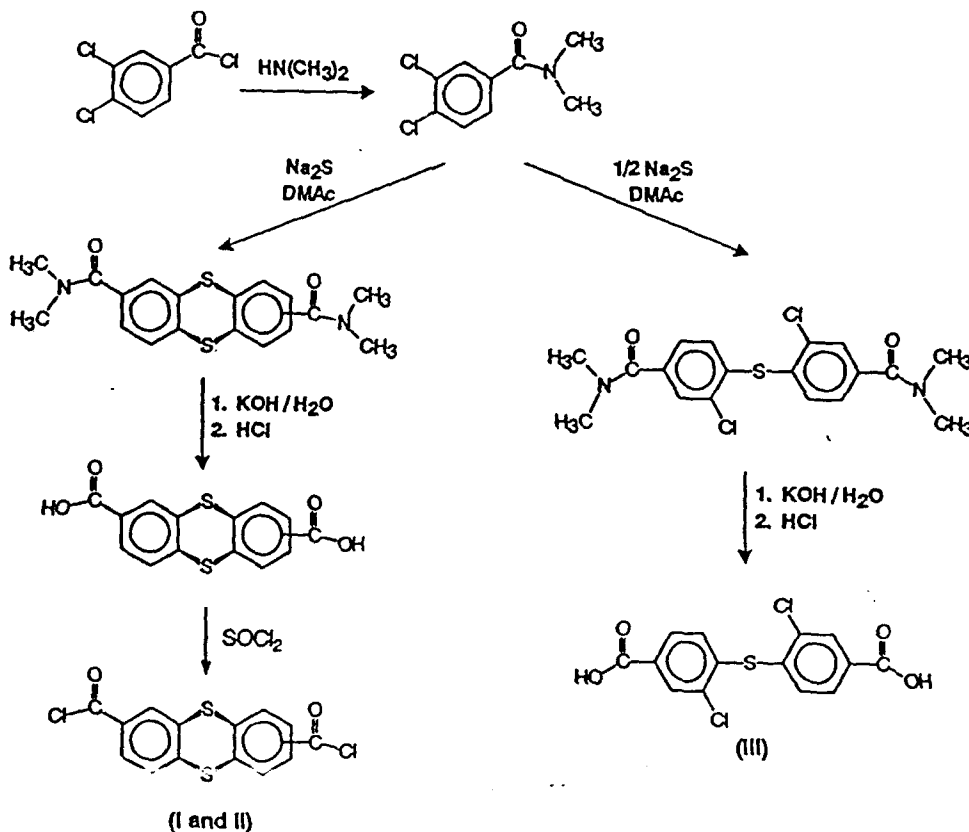
Randy A. Johnson and Lon J. Manias*
 Department of Polymer Science
 University of Southern Mississippi
 Hattiesburg, MS 39406-0076

INTRODUCTION

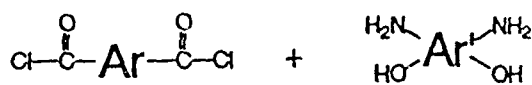
Poly(benzoxazole)s (PBOs) are a class of rigid-rod polymers that are known to have good thermal stability, high mechanical properties, and environmental resistance. Processing of PBOs is difficult since they have low solubility, high glass transition temperatures, and decompose before their melting points.

This study is focused on improving the processibility of poly(benzoxazole)s by increasing their solubility while maintaining good thermal stability. With this goal in mind, we synthesized thianthrene-based PBOs from thianthrene-2,7- and -2,8-dicarbonyl chlorides with commercially available bis-o-aminophenols. Polymers were prepared in poly(phosphoric acid) at 90-200 °C. Transparent PBO films were casted from polymerization solutions and m-cresol depending on solubility. Thermal analysis has shown 10% weight loss in air at > 500 °C. DMA has shown good mechanical properties with a transition > 400 °C for polymer I-HAB.

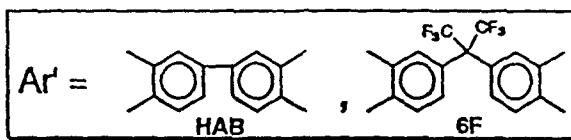
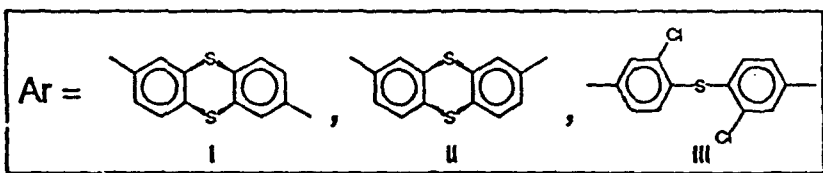
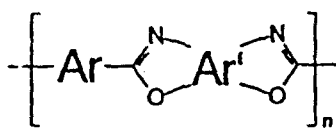
Synthesis of Thianthrene-2,7- and -2,8-dicarbonyl chlorides



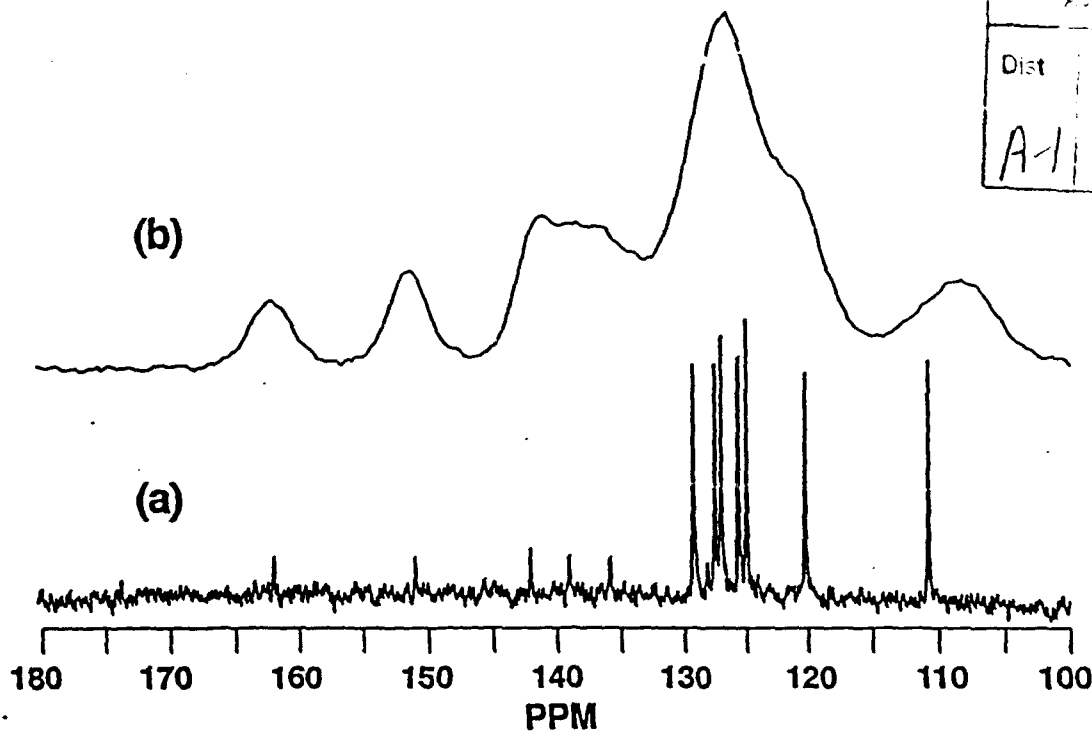
Poly(benzoxazole) synthesis



PPA
90-200 °C



Accession No.	
NTIS	
DTIC	
Unannounced	
Justification	
By	
Distribution	
Availability Codes	
Dist	
A-1	



¹³C NMR of (a) 2,7-bis(2-benzoxazolyl)thianthrene (model) and (b) thianthrene-biphenyl PBO (I - HAB) in CDCl₃ and solid state, respectively.

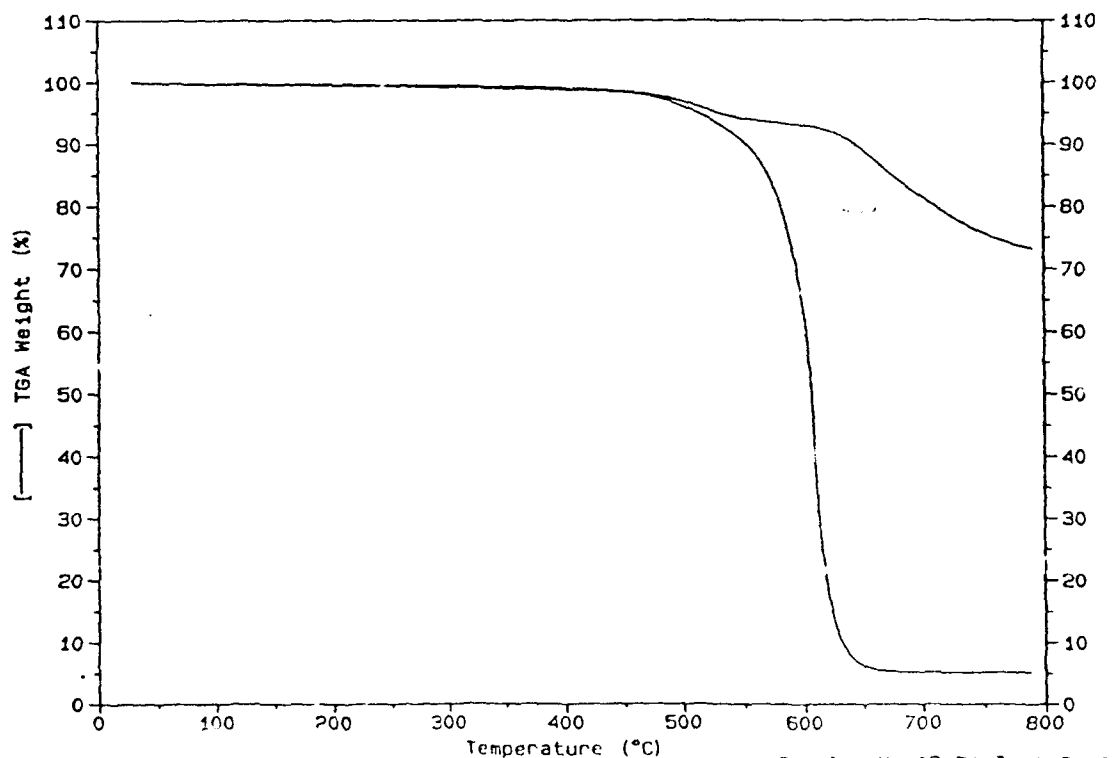
POLYMERS	H ₂ SO ₄	MeSO ₃ H	m-cresol	CHCl ₃	THF	dichloro- benzene	MeNO ₂ ^a AlCl ₃
I - HAB	b	b	-	-	-	-	→
I - 6F	++	++	++	-	-	→	++
II - HAB	b	++	-	-	-	-	++
II - 6F	++	++	++	-	-	→	++
III - HAB	++	++	-	-	-	-	++
III - 6F	++	++	++	→	-	++	++

- ^a 18 wt% AlCl₃.
 b Partially soluble.
 ++ Soluble at ambient temperature.
 → Soluble hot.
 - Insoluble.

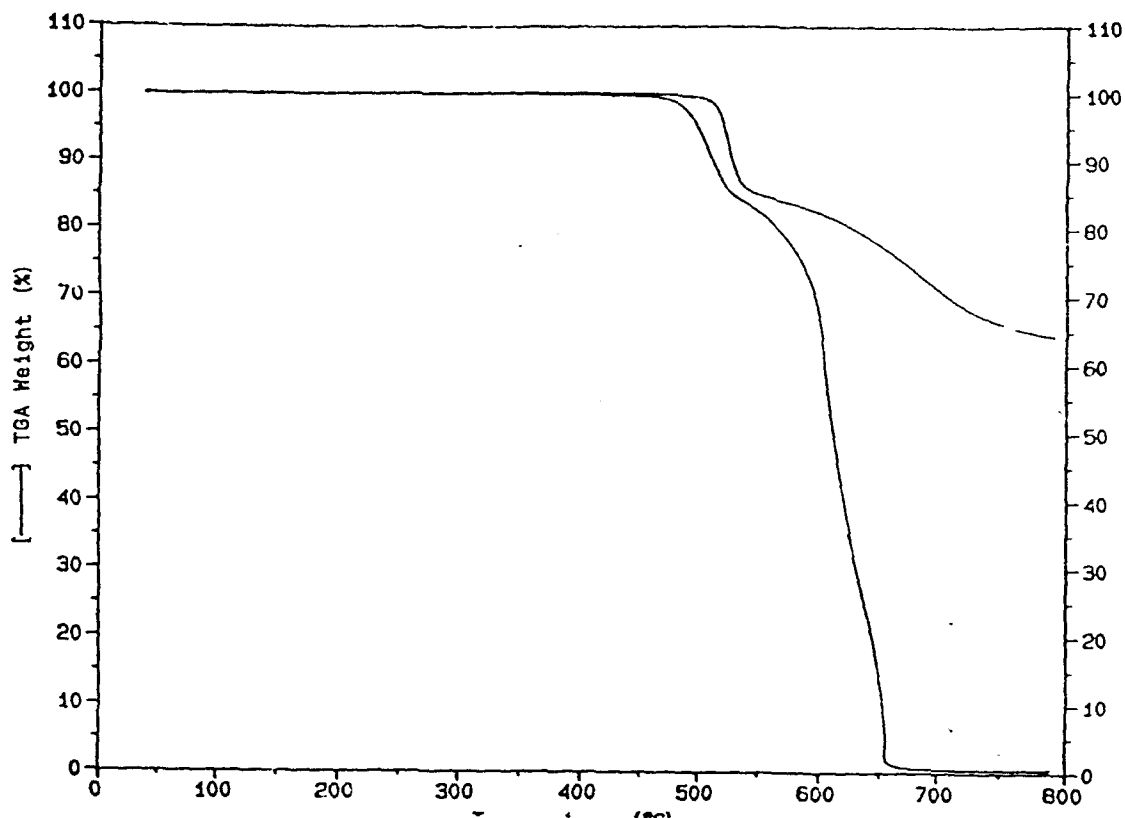
POLYMERS	n_m (dL/g)	TGA ^b (°C)	
		onset temp. (N ₂ / air atm.)	10% wt. loss (N ₂ / air atm.)
I - HAB	-	451 / 450	643 / 551
I - 6F	0.92 ^a	478 / 455	533 / 528
II - HAB	-	462 / 391	655 / 590
II - 6F	1.51 ^a	435 / 442	545 / 526
III - HAB	-	473 / 459	533 / 511
III - 6F	0.88 ^a	453 / 449	500 / 488

- ^a Measured in m-cresol at 30 °C.
^b Measured at heating rate of 10 °C/min.

TGA of PBO I-HAB in nitrogen (upper trace) and air (lower trace).



TGA of PBO III-HAB in nitrogen (upper trace) and air (lower trace).



DMA of PBO I-HAB.

