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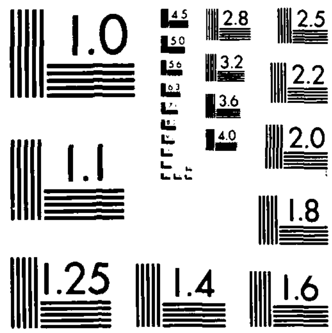
SCIENCE SECTION L F HANCOCK ET AL 01 AUG 87 TR-1
UNCLASSIFIED N00014-85-K-0899 F/G 7/6 NL



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R&T Code 1513A;DHP

Technical Report No. 1

Proton Abstraction As A Route To Conductive Polymers

by

Lawrence F. Hancock, Brian L. Hilker, William Chapman
and Bernard Gordon III

Prepared for Publication

in the

ACS Division of Polymer Chemistry, Polymer Preprints

Penn State University
Polymer Science Section
Materials Science and Engineering Department
University Park, PA 16802

August 1, 1987

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS NONE
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approach for public release; Distribution unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report Number: 1	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION The Pennsylvania State University 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION OFFICE OF NAVAL RESEARCH
6c. ADDRESS (City, State, and ZIP Code) University Park, PA 16802	7b. ADDRESS (City, State, and ZIP Code) Arlington, VA 22217
8a. NAME OF FUNDING/SPONSORING ORGANIZATION OFFICE OF NAVAL RESEARCH 8b. OFFICE SYMBOL (If applicable) ONR	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-85-K-0899
8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)

Proton Abstraction as a Route to Conductive Polymers(unclassified)

12. PERSONAL AUTHOR(S) L. F. Hancock, B. Hilker, W. Chapman and B. Gordon III

13a. TYPE OF REPORT	13b. TIME COVERED FROM ____ TO ____	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
		8/1/87	

16. SUPPLEMENTARY NOTATION

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

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

PROTON ABSTRACTION AS A ROUTE TO CONDUCTIVE POLYMERS

L. F. Hancock, B. Hilker, W. Chapman and B. Gordon III
Deaprtment of Materials Science and Engineering, Polymer Science Program
The Pennsylvania State University, University Park, PA 16802

Proton abstraction doping has been demonstrated as a viable alternate procedure for the synthesis of electrically conductive polymers through the preparation of poly(p-phenylene pentadienylene), which when doped displayed a conductivity of 10^{-1}S/cm. Additional procedures being used for the synthesis of proton abstraction doping precursors includes sulfur ylide and Grignard condensations, details will be presented. These systems offer tremendous advantages for the study of effects arising from dopant density and conjugation length in organic conductors. One interesting result involves the conductivity of 1,5-diphenylpentadiene, a low molecular weight model for poly(p-pheynlene pentadienylene). 1,5-Diphenylpentadienyl

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☑ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION (SEE ATTACHED) Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Kenneth J. Wynne	22b. TELEPHONE (Include Area Code) (202)696-4410 22c. OFFICE SYMBOL ONR

DD FORM 1473, 84 MAR   83 APR edition may be used until exhausted. All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE

anion displays a conductdivity of 8S/cm which supports the conclusion that polymeric delocalization of charge is not a necessity.

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L. F. Hancock, B. Hilker, W. Chapman and B. Gordon III
Department of Materials Science and Engineering
Polymer Science Program
The Pennsylvania State University
University Park, PA 16802

Although the structural, electrical, and solid-state properties of conducting polymers have received much attention from researchers[1], new "doping" methods have not been pursued. This work reports our ongoing research into an alternative synthetic procedure for the preparation of electrically conductive polymers, by proton abstraction "doping".

It can easily be seen that identical charge delocalized systems can be prepared through either reduction of an all-conjugated polymer or through *proton abstraction* from a polymer whose conjugated sequence lengths are interrupted by relatively acidic methylene moieties, figure 1.

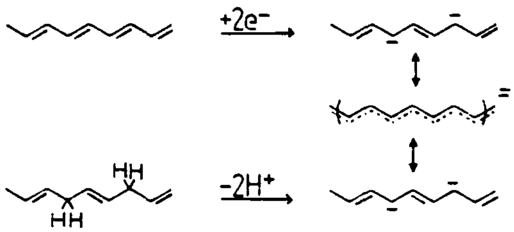

FIGURE 1

Proton abstraction has been confirmed as a viable technique through the synthesis of poly(p-phenylene pentadienylene) and its doping by treatment with n-BuLi.[2] Preliminary electrical measurements for the dark blue/black solid showed a conductivity of 5.0×10^{-1} S/cm.

Many polymeric structures applicable to proton abstraction doping may be proposed. Synthetic routes being pursued in our laboratory include Wittig, sulfur ylide and Grignard condensations. A Wittig procedure was used for the synthesis of poly(p-phenylene pentadienylene) (3), figure 2.

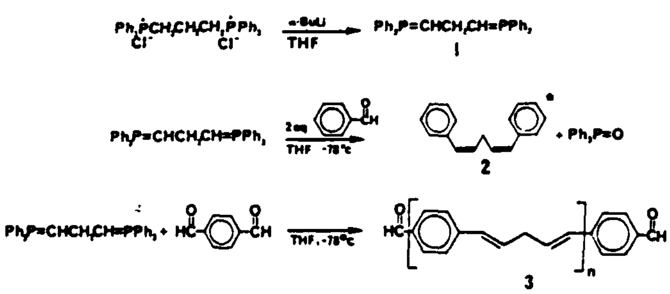

FIGURE 2

Sulfur ylide chemistry has previously been used for the synthesis of poly(phenylene vinylene).[3] A similar procedure is being used for the preparation of poly(methylene-p,p'-stilbenylene) (7), figure 3.

Compound 4, which is prepared through the chloromethylation of diphenylmethane, has also been employed in a bis-Grignard condensation with terephthalaldehyde for the preparation of 10, figure 4. Detailed results will be presented.

These systems offer tremendous advantages for the study of effects arising from dopant density and conjugation length in organic conductors. Interesting results with regard to conjugation length have been obtained for the poly(p-phenylene pentadienylene) system.

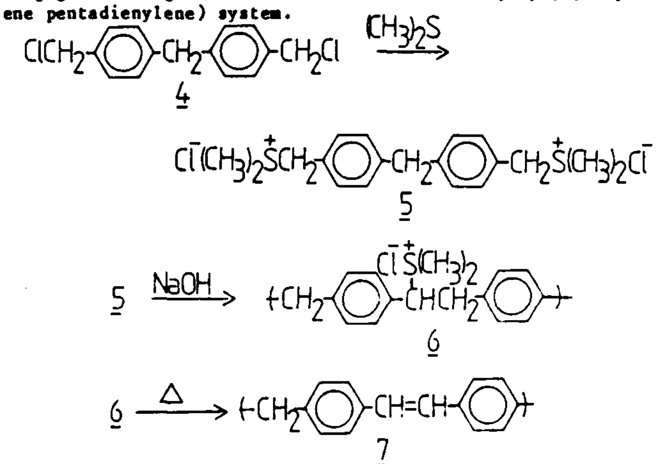

FIGURE 3

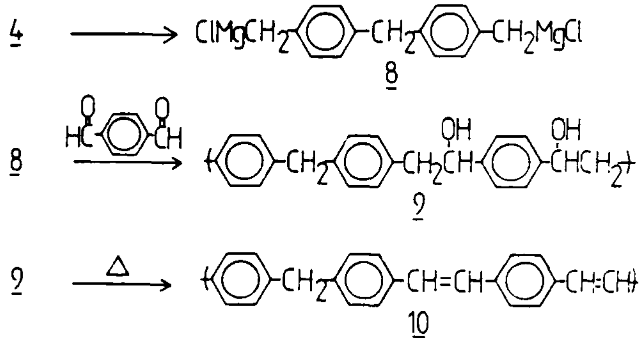

FIGURE 4

1,5-Diphenylpentadiene (2), an analogous low molecular weight model, *displays a conductivity of 8S/cm* upon proton abstraction doping to form the 1,5-diphenylpentadienyl anion. This is comparable to conductivity measurements on arene radical cation salts normal to the stack direction of the aromatic rings (1-10S/cm).[4] Enhanced conductivities parallel to the stack direction (10^3 S/cm) suggest that orientation of the most probably amorphous 1,5-diphenylpentadienyl anion should lead to enhanced conductivities.

In conclusion, additional synthetic schemes for the preparation of proton abstraction doping precursors are being developed as supplements to the previously developed Wittig procedure. The ability to control the nature and location of the dopant site makes these systems versatile subjects for future studies.

ACKNOWLEDGEMENT: The support of the Office of Naval Research is gratefully acknowledged.

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