AD-A142 148 PROGRAM FOR RESEARCH ON CONDUCTING POLYMERS(U) 1/1
CALIFORNIA UNIV SANTA BARBARA DEPT OF PHYSICS
A J HEEGER ET AL. 30 APR 84 N00014-83-K-0450
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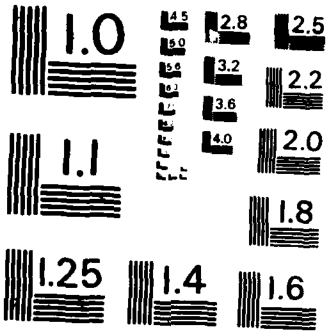
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(2)

"Program for Research on Conducting Polymers"
End-of-Year Report

(May 1, 1983 to April 30, 1984)

N00014-83-K-0450
Office of Naval Research

Principal Investigators: Drs. A. J. Heeger and Fred Wudl
Department of Physics
University of California, Santa Barbara
Santa Barbara, California 93106
Telephone: (805) 961-2001

Effective Dates of Contract: May 1, 1983 through April 30, 1984: $94,000

Description of Project

This research program consists of a parallel effort directe oward the synthesis of conjugated polymers and the haracterization of these polymers through a broad base of hysical measurements. The approach involves step-by-step ynthesis of new polymer systems using specific synthetic echniques; i.e. the design and synthesis of new conducting olymers. This involves close interaction between chemists and hysicists and a constant back-and-forth interplay to haracterize new materials and stimulate ideas on new systems. Continuing studies of the chemistry and physics of known onducting polymers is a critical part of the program, since uture progress is limited by an in-depth understanding of uccessful known systems. Recent efforts in the latter area ocused on the polyheterocycle, poly(thiophene).

Letter on file

A-1

Significant Results During the Period May 1, 1983 - April 30, 1984

A. Studies of the Chemistry and Physics of Poly(thiophene)

Using a new method of electrochemical polymerization of poly(thiophene) from dithiophene as the starting material, we obtain a high quality film with a sharp interband absorption edge. An *in situ* study of the absorption spectrum during the electrochemical doping process has been carried out. In the dilute regime, the results are in detailed agreement with charge storage via bipolarons; weakly confined soliton pairs with confinement parameter $\gamma \sim 0.1-0.2$. At the highest doping levels, the data are characteristic of the free carrier absorption expected for a metal. From a parallel electrochemical voltage spectroscopy (EVS) study, we find evidence of charge injection near the band edge and charge removal from the bipolaron gap states. In the dilute regime, the position of the chemical potential is consistent with charge storage in weakly confined bipolarons.

Extensive earlier studies of polyacetylene have demonstrated that the coupling of electronic excitations to nonlinear conformational changes is an intrinsic and important feature of conducting polymers. Although this coupling and the degenerate ground state lead to the novel soliton excitations in trans-$(CH)_x$, generalization of these concepts and application to the larger class of conjugated polymers has been an obvious goal of the field. The experimental evidence of electron-hole symmetry and weak confinement in polythiophene (carried out in this grant period) makes this polymer a nearly ideal example of a model system in which the ground state degeneracy has been lifted. The study of bipolarons (or confined charged solitons) in poly(thiophene) has now demonstrated that the concepts carry over in detail and that a quantitative understanding of the resulting phenomena is possible even for relatively complex systems.

B. Synthesis of New Conducting Polymers

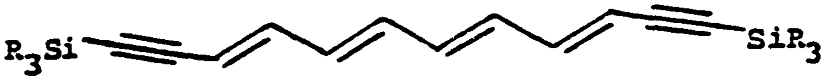
a. Poly-ynes

We prepared a number of precursors for the preparation of poly-ynes. These are $(CH_3)_3SiC{\equiv}CC{\equiv}CSi(CH_3)_3$ (1), $(CH_3)_3SiC{\equiv}CC{\equiv}CH$ (2), 1,6-bistrimethylsilylhex-1,5-diyne-3-ene(3) and hex-1,5-diyne-3-ene (4).

Attempts to prepare polyynes using traditional chemistry (Ullman coupling) on either acetylene, butadiyne, or 3 and 4, above, have produced polymers which are heavily contaminated with copper. These polymers are blue-black and exhibit infrared spectroscopy commensurate with a structure containing C=C (for material derived from 3 and 4, above) and C≡C bonds (for material derived from all monomers). Unfortunately the copper is tenaciously entrained in these materials so that new approaches to couple sp hybridized carbons are currently being explored (see below).

b. Mixed Polyenes.

We have succeeded in the preparation of $(CH_3)_3SiC\equiv C(CH=CH)_4C\equiv CSi(CH_3)_3$ (5) and found that the yields reported in the literature are not reproducible; it has therefore been taking us longer to build up enough of this compound to submit it to further reactions. This compound is an important step in our program. In connection with designing alternate methods for the preparation of all trans polyacetylene, we found that the tetraenediyne 6 could be made in one step by an existing literature procedure.



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While interesting polyene-polydiynes could be prepared by removing the silyl groups and Ullman coupling, the resulting tetraenediyne, a much more interesting polymer , would result if one only mono-deprotected 6 and prepared the Ullman coupling product 7.

$$R_3Si-C\equiv C\leftarrow CH=CH\rightarrow_4 C\equiv C-C\equiv C\leftarrow CH=CH\rightarrow_4 C\equiv C-Sir_3 \begin{array}{c}\rightarrow\\\rightarrow\\\rightarrow\\\rightarrow\end{array} [CH_2=CH(CH=CH)_nC\equiv C]_2$$

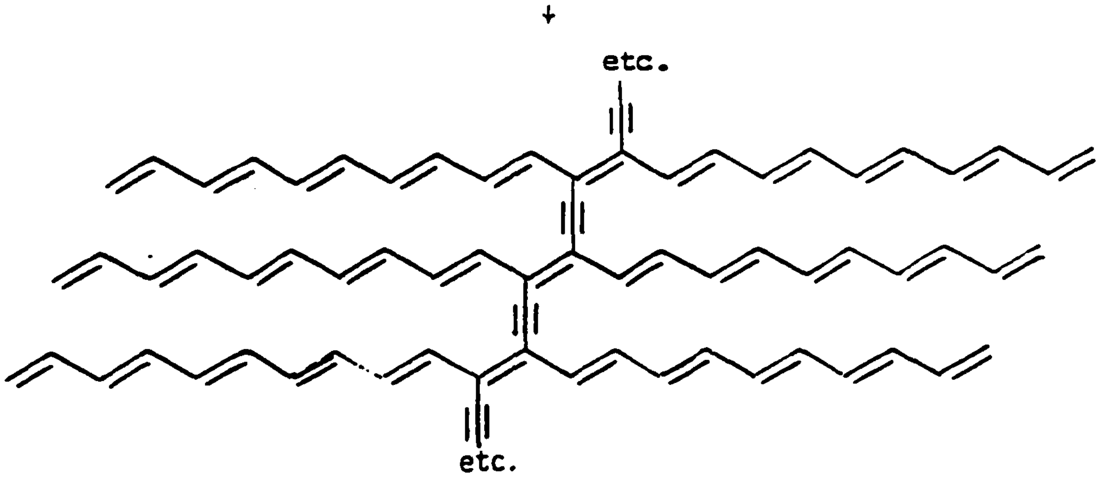
7

The polyene units could be extended with a little extra work on the end groups (hydrolysis, hydroboration, mercuration, lithiation and coupling with an alkene iodine via a cuprate).

Since diacetylenes polymerize in the solid state to form crystalline polymers, monomer 7, its elongated derivative, or its deprotected, reduced product 8 would produce a polydiacetylene:

$$CH_2=CH(CH=CH)_4C\equiv C-C\equiv C-(CH=CH)_4CH=CH_2$$

8



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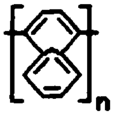
Recently, Planchetta et al. [Makromol. Chem., Rapid Commun. 3, 249 (1982)] have shown that RO $C(O)-(CH_2)_9C\equiv C-C\equiv C-(CH_2)_9-OC(O)R$ polymerize under the usual conditions to form unusual polydiacetylenes of weight-average molecular weights from 8 X 10^5 to 1.3 X 10^6. Therefore, long chain appendages do not appear to interfere with the well-known Wegner-Baughman solid state polymerization reaction.

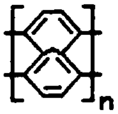
c. Polyannulenes.

This has been the most successful part of our new synthesis research so far. Through a collaboration with Professor Vogel (Koln) we have obtained 10g of methano[10]annulene and 500g of isotetraline, a precursor to substituted methano[10]annulenes. We prepared precursors to polymers 10 and 11 (below) and very recently made a small amount of polymer 9 as well as the important dimer (bis methanoperylene) 12.



10a

10b



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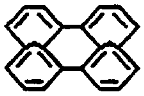

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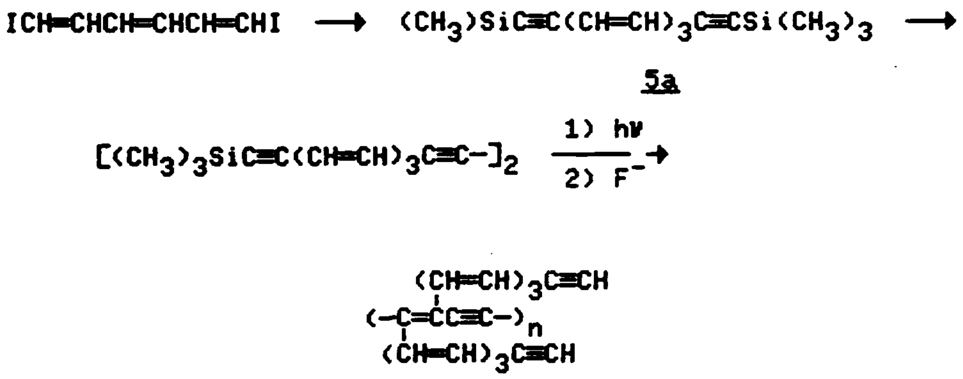
C. Plans for Next Year's Work

As implied above, there is a serious gap in synthetic organic chemical methodology for the formation of carbon-carbon bonds from sp hybridized precursors. We are, and will, study coupling reactions which are truly catalytic in added transition metal. The first attempts will involve Kumada-type chemistry using alkynyl Grignard reagents and iodoacetylenes. Preliminary results are encouraging. We have recently shown that alkynyl Grignard reagents can be coupled efficiently with alkenyl halides. This is an exciting result because it will allow us to prepare, for the first time the elusive "parent" (unsubstituted) polydiacetylene $[(-CH{=}CH-C{\equiv}C-)_n]$.

In Scheme I, below is shown a new approach to the trienediyne (5a), an analog of 5, above.

Scheme I



$$ICH{=}CHCH{=}CHCH{=}CHI \longrightarrow (CH_3)SiC{\equiv}C(CH{=}CH)_3C{\equiv}CSi(CH_3)_3 \longrightarrow$$

5a

$$[(CH_3)_3SiC{\equiv}C(CH{=}CH)_3C{\equiv}C-]_2 \xrightarrow[2)\ F^-]{1)\ h\nu}$$

$$(-\underset{(CH{=}CH)_3C\equiv CH}{\underset{|}{C}}{=}\overset{(CH{=}CH)_3C\equiv CH}{\overset{|}{C}}C{\equiv}C-)_n$$

13

This approach should allow us to pursue our attempts to prepare the intriguing crossconjugated polymer 13.

Physical measurements will support these synthetic efforts as well as continuing the current focus on the properties of carefully prepared poly(thiophene). High priority will be placed on an experimental attempt to detect photo-induced absorption in polythiophene in response to illumination by photons with $\hbar\omega > E_g$. If successful, this experiment should lead to the kind of definitive description of the photoexcitations that has been possible in polyacetylene using similar techniques (see Blanchet et al., Phys. Rev. Lett. 50, 1938 (1983); this paper was also supported by ONR during the previous grant period).

List of Reports, etc., for Period May 1, 1983 to April 30, 1984

Technical Report #1 "Charge Storage in Doped Poly(thiophene): Optical and Electrochemical Studies"

Dissertations: none

Publications: "Photoexcitations in trans-$(CH)_x$: A Fourier-Transform Infrared Study" by G. Blanchet, C. R. Fincher, T.-C. Chung and A. J. Heeger, Phys. Rev. Lett. 50, 1938 (1983)

Manuscripts submitted: "Charge Storage in Doped Poly(thiophene): Optical and Electrochemical Studies" by T.-C. Chung, J. H. Kaufman, A. J. Heeger and F. Wudl, accepted for publication in Phys. Rev. B.

Honors and Awards

Professor A. J. Heeger received the 1983 Oliver P. Buckley Prize in Solid State Physics. Much of the research recognized by this award was supported by ONR.

Personnel Supported on this Contract During May 1, 1983 - April 30, 1984

Graduate Students

J. Chen (partial)

H. Schaffer (partial)

Postdoctorals

D. Moses (partial)

M. Boysel (partial)

Principal Investigators

A. J. Heeger (1/2 summer month)

F. Wudl (1/2 summer month)

REPORT OF INVENTIONS AND SUBCONTRACTS

(Pursuant to "Patent Rights" Contract Clause) (See Instructions on Reverse Side.)

FORM APPROVED
OMB NO. 0704-0016

1a. NAME OF CONTRACTOR/SUBCONTRACTOR Regents of University of California

b. ADDRESS *(include Zip Code)* Santa Barbara, CA 93106

c. CONTRACT NUMBER N00014-83-K-0450

d. AWARD DATE *(YYMMDD)* 5/1/83 - 4/31/86

2a. NAME OF GOVERNMENT PRIME CONTRACTOR same as 1a.

b. ADDRESS *(include Zip Code)*

c. CONTRACT NUMBER

d. AWARD DATE *(YYMMDD)*

3. TYPE OF REPORT *(check one)* ☒ INTERIM ☐ FINAL

4. REPORTING PERIOD *(YYMMDD)*
FROM
TO 5/1/83 -5/1/84

SECTION I - SUBJECT INVENTIONS

5. "SUBJECT INVENTIONS" REQUIRED TO BE REPORTED BY CONTRACTOR/SUBCONTRACTOR *(If "None", so state)* NONE

a. NAME OF INVENTOR(S) *(Last, First, M.I.)*	b. TITLE OF INVENTION(S)	c. DISCLOSURE NO., PATENT APPLICATION SERIAL NO. OR PATENT NO.	d. ELECTION TO FILE PATENT APPLICATIONS				e. CONFIRMATORY INSTRUMENT OR ASSIGNMENT FORWARDED TO CONTRACTING OFFICER	
			UNITED STATES		FOREIGN			
			YES	NO	YES	NO	YES	NO
	Alan J. Heeger, Principal Investigator							

f. EMPLOYER OF INVENTOR(S) NOT EMPLOYED BY CONTRACTOR/SUBCONTRACTOR.

i. NAME OF INVENTOR *(Last, First, M.I.)*

ii. NAME OF EMPLOYER

iii. ADDRESS OF EMPLOYER *(include Zip Code)*

i. NAME OF INVENTOR *(Last, First, M.I.)*

ii. NAME OF EMPLOYER

iii. ADDRESS OF EMPLOYER *(include Zip Code)*

g. ELECTED FOREIGN COUNTRIES IN WHICH A PATENT APPLICATION WILL BE FILED.

i. TITLE OF INVENTION	ii. FOREIGN COUNTRIES OF PATENT APPLICATION

SECTION II – SUBCONTRACTS (Containing a "Patent Rights" clause)

6. SUBCONTRACTS AWARDED BY CONTRACTOR/SUBCONTRACTOR. *(If "None", so state)* NONE

a. NAME OF SUBCONTRACTOR(S)	b. ADDRESS *(include Zip Code)*	c. SUBCONTRACT NO.(S)	d. DAR "PATENT RIGHTS"		e. DESCRIPTION OF WORK TO BE PERFORMED UNDER SUBCONTRACT(S)	f. SUBCONTRACT DATES *(YYMMDD)*	
			CLAUSE NO.	DATE *(YYMM)*		AWARD	ESTIMATED COMPLETION

SECTION III – CERTIFICATION

7. CERTIFICATION OF REPORT BY CONTRACTOR/SUBCONTRACTOR. *(Not required if ☐ Small Business or ☒ Non-Profit organization.) (Check appropriate box)*

a. NAME OF AUTHORIZED CONTRACTOR/SUBCONTRACTOR OFFICIAL *(Last, First, M.I.)*

b. TITLE

c. I certify that the reporting party has procedures for prompt identification and timely disclosure of "Subject Inventions," that such procedures have been followed and that all "Subject Inventions" have been reported.

SIGNATURE OF AUTHORIZED CONTRACTOR/SUBCONTRACTOR OFFICIAL

DATE *(YYMMDD)*

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EDITION OF 1 OCT 75 IS OBSOLETE

INSTRUCTIONS

GENERAL

This form is for use in submitting INTERIM and FINAL invention reports to the Contracting Officer and for use in the prompt notification of the award of subcontracts containing a "Patent Rights" clause. If the form does not afford sufficient space, multiple forms may be used or plain sheets of paper with proper identification of information by Item No. may be attached.

An INTERIM report is due at least every 12 months from the date of contract award and shall include (a) a listing of "Subject Inventions" during the reporting period, (b) a certification of compliance with required invention identification and disclosure procedures together with a certification of reporting of all "Subject Inventions," and (c) any required information not previously reported on subcontracts awarded during the reporting period and containing a "Patent Rights" clause.

A FINAL report is due within 6 months if contractor is a small business firm or domestic nonprofit organization and within 3 months for all others after completion of the contract work and shall include (a) a listing of <u>all</u> "Subject Inventions" required by the contract to be reported, and (b) any required information not previously reported on subcontracts awarded during the course of or under the contract and containing a "Patent Rights" clause.

While the form may be used for simultaneously reporting inventions and subcontracts, it may also be used for reporting, promptly after award, subcontracts containing a "Patent Rights" clause.

Dates shall be entered where indicated in certain Items on this form and shall be entered in four or six digit numbers in the order of year and month (YYMM) or year, month and day (YYMMDD). Example: April 1981 should be entered as 8104 and April 15, 1981 should be entered as 810415.

Item 1a. Self-explanatory.

Item 1b. Self-explanatory.

Item 1c. If "same" as item 2c, so state.

Item 1d. Self-explanatory.

Item 2a. If "same" as item 1a, so state

Item 2b. Self explanatory

Item 2c. Procurement Instrument Identification (PII) number of contract (DAR 20 203).

Item 2d thru 5e. Self-explanatory.

Item 5f, ii and iii. The name and address of the employer of each inventor not employed by the contractor or subcontractor is needed inasmuch as the Government's rights in a reported invention may not be determined solely by the terms of the "Patent Rights" clause in the contract. Example (1): If an invention is made by a Government employee assigned to work with a contractor, the Government rights in such an invention will be determined under Executive Order 10096. Example (2): If an invention is made under a contract by joint inventors and one of the inventors is a Government employee, the Government's rights in such an inventor's interest in the invention will also be determined under Executive Order 10096, except where the contractor is a small business or nonprofit organization, in which case the provisions of Section 202(e) of P.L. 96-517 will apply.

Item 5g, i. Self-explanatory.

Item 5g, ii. Self-explanatory with the exception that the contractor or subcontractor shall indicate, if known at the time of this report, whether applications will be filed under either the Patent Cooperation Treaty (PCT) or the European Patent Convention (EPC). If such is known, the letters PCT or EPC shall be entered after each listed country.

Item 6a. Self-explanatory.

Item 6b. Self-explanatory.

Item 6c. Self-explanatory.

Item 6d. Patents Rights Clauses are located in DAR 7-302.23

Item 6e thru 7b. Self-explanatory.

Item 7c. Certification not required by small business firms and domestic nonprofit organizations.