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Final Technical Report

N00014-86-K-0514

Nonlinear Optical Properties of Semiconducting Polymers

Institute for Polymers and Organic Solids
University of California, Santa Barbara
Santa Barbara, CA 93106

Principal Investigators:

Professor Alan J. Heeger
Department of Physics and MAterials Department (joint)

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I. Summary of Research Results:

This program focused on the nonlinear optical properties of semiconducting conjugated polymers. Specific emphasis was on fast time (picosecond regime) measurements of the photoconductivity of semiconducting polymers and on NLO measurements related to the mechanism and origin of the nonlinearity, on attempts to optimize the magnitude of the nonlinear response, and on developing novel methods for measurment of the

Substantial progress was made during the course of N00014-86-K-0514. This progress is documented in the eight (8) publications which resulted from the research. In the transient photoconductivity area, these publications focused on the carrier generation, mobility and carrier recombination processes. The reults are of particular importance; by implementing the Auston swith technique (to enable fast transient photoconductivity measurements with temporal resolution <100 ps), we were able to explore the photogeneration process early times. The results have caused a re-evaluation of the previously accepted Onsager geminate recombination process.

In the NLO area, we succeeded in demonstrating that for conjugated polymers the nonlinear response is highly anisotropic with subtantial nonlinearity only when the pump is polarized along the direction parallel to the polymer backbone. In attempting tio sort out the NLO mechanism we carried out comparative studies on cis and trans-polyacetylene. The larger NLO response from the trans-isomer (larger by at least a factor of 20) shows the importance of the degerate ground state.

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II. Technical Reports Submitted from N00014-86-K-0514

The technical reports are listed below; copies are attached for detailed information.

October 1, 1987 - End of the Year Report

1987 - Final Technical Report

October 1, 1987-September 30, 1988 - End of the Year Report

July 15, 1988 - End of the Year Report

November 21, 1988 - Progress Report

October 1, 1989 - End of the Year Report

October 1, 1989 - September 30, 1990 - End of the Year Report

III. Publications

The following publications credited ONR N00014-86-K-0514 for support:

1. Picosecond Photoconductivity in Trans-Polyacetylene (Solid State Commun.).
2. Carrier Photogeneration and Mobility in Polydiacetylene: Fast Transient Photoconductivity (Phys. Rev. Lett.).
3. Time Resolved Waveguide Modulation of a Conjugated Polymer (Applied Physics Lett.).
4. Mechanism for Photogeneration of Metastable Charged Solitons in Polyacetylene. (Phys. Rev. B).
5. Photoexcitation and Doping Studies of Poly(3-hexylthienylene) (Phys. Rev. B).
6. Anisotropy of the Third Order Nonlinear-Optical Susceptibility in a Degenerate-Ground-State Conjugated Polymer: Trans $(CH)_x$. (Phys. Rev. B).
7. Spectroscopy and Transient Photoconductivity of Partially Crystalline Polyaniline (Phys. Rev. B).
8. Transient Photoinduced Conductivity in Semiconducting Single Crystals of $YBa_2Cu_3O_{6.3}$: Search for Photoinduced Metallic State and for Photoinduced Superconductivity (Solid State Commun.)

to ONR
10/26/90

OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT
1 Oct 89 through 30 Sept 90

R&T Number: 4122017--04

Contract/Grant Number: N00014-86-K-0514

Contract/Grant Title: "Nonlinear Optical Properties of Semiconducting Polymers"

Principal Investigator: Drs. Alan J. Heeger and Daniel Moses

Mailing Address: Institute for Polymers and Organic Solids
University of California, Santa Barbara
Santa Barbara, CA 93106

Phone Number: (with Area Code) (805) 893-3184

E-Mail Address:

a. Number of Papers Submitted to Refereed Journal but not yet published: 0

b. Number of Papers Published in Refereed Journals: 7
(list attached)

c. Number of Books or Chapters Submitted but not yet Published: 0

d. Number of Books or Chapters Published: 0 (list attached)

e. Number of Printed Technical Reports & Non-Refereed Papers: 1
(list attached)

f. Number of Patents Filed: 0

g. Number of Patents Granted: 0 (list attached)

h. Number of Invited Presentations at Workshops or Prof. Society Meetings: 10

i. Number of Presentations at Workshops or Prof. Society Meetings: 1

j. Honors/Awards/Prizes for Contract/Grant Employees:
(list attached, this might include Scientific Soc Awards/Offices, Promotions, Faculty Awards/Offices etc)

k. Total number of Graduate Students and Post-Docs Supported at least 25% this year on this contract/grant:

Grad Students 3 and Post-Docs 0 including

Grad Student Female 0 and Post-Docs Female 0

Grad Student Minority 0 and Post-Doc Minority 0

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

d. Number of Papers Published in Refereed Journals: 7 List attached:

Anisotropy of the third-order nonlinear-optical susceptibility in a degenerate -ground-state conjugated polymer: *trans*-$(CH)_x$, M. Sinclair, D. Moses, K. Akagi and A. J. Heeger, Phys. Rev. B 38, 10 724 (1988).

Time-Resolved Waveguide Modulation of a Conjugated Polymer, M. Sinclair, D. McBranch, D. Moses and A. J. Heeger, Appl. Phys. Lett. 53, 2374 (1988).

Spectroscopy and Transient Photoconductivity of Partially Crystalline Polyaniline, S. D. Phillips, G. Yu, Y. Cao and A. J. Heeger, Phys. Rev. B 39, 10 702 (1989).

Fast Transient Photoconductivity in Polydiacetylene: Carrier Photogeneration, Carrier Mobility and Carrier Recombination, D. Moses and A. J. Heeger, J. Phys.: Condens. Matter 1, 7395 (1989).

Transient Photoinduced Conductivity in Semiconducting Single Crystals of YBa2Cu3O6.3: Search for Photoinduced Metallic State and for Photoinduced Superconductivity, G. Yu, A. J. Heeger, G. Stucky, N. Herron and E. M. McCarron, Solid State Commun. 72 4, 345 (1989).

Photogenerated Carriers in La2CuO4, YBa2O7-δ, and Tl2Ba2Ca(1-x)GdxCu2O8: Polarizability-Induced Pairing of Polarons, C. M. Foster, A. J. Heeger, Y. H. Kim and G. Stucky, Physica C 162-164 (1989) 1107 North Holland.

Photoexcited Polarons in High Temperature Superconducting Oxides: Structural Distortion and Low Frequency Polarizability, C. M. Foster, A. J. Heeger, Y. H. Kim, G. Stucky and N. Herron, Reviews of Solid State Science 4 (2 & 3) 601 (1990).

e. Number of Printed Technical Reports & Non-Refereed Papers: 1
List attached:

"Instantons" as the Origin of the Nonlinear Optical Properties of Polyacetylene, M. Sinclair, D. Moses, D. McBranch and A. J. Heeger (Nobel Symposium 73, Gräftåvallen, Sweden, June 1988.)

J. Honors/Awards/Prizes for Contract Grant Employees: Alan J. Heeger:

John Scott Award for 1989
"The 64th most cited scientist" in any discipline during the period 1973-84, according to "The Scientist"

mailed
9/25/89

OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/STUDENTS REPORT

for
Contract No. N00014-86-K-0514
(due date - October 1, 1989)

Title of Contract: Nonlinear Optical Properties of Semiconducting Polymers

Principal Investigators:
Alan J. Heeger (Dept. of Physics and Materials Dept., UCSB)
Paul Smith (Materials Dept., UCSB)
Fred Wudl (Dept. of Physics and Dept. of Chemistry, UCSB)

Institute for Polymers and Organic Solids
University of California, Santa Barbara
Santa Barbara, CA 93106

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Part I

a. Papers Submitted to Refereed Journals (and not yet published)

G. Yu, A.J. Heeger, G. Stucky, N. Herron and E.M. McCarron, Transient Photoinduced Conductivity in Semiconducting Single Crystals of $YBa_2Cu_3O_{6.3}$: Search for Photoinduced Metallic State and for Photoinduced Superconductivity, Solid State Communications (in press).

b. Papers published in Refereed Journals

M. Sinclair, D. McBranch, D. Moses and A.J. Heeger, Time-Resolved Waveguide Modulation of a Conjugated Polymer, Applied Physics Lett., 53, 2374 (1988)

M. Sinclair, D. Moses, K. Akagi and A.J. Heeger, Anisotropy of the Third-Order Nonlinear-Optical Susceptibility in a Degenerate-Ground-State Conjugated Polymer: trans-$(CH)_x$, Phys. Rev. B38, 10726 (1988)

S.D. Phillips and A. J. Heeger, Transient Photoconductivity in Oriented trans-Polyacetylene Prepared by the Naarman-Theophilou Method, Phys. Rev. B38, 6211 (1988)

Z. Vardeny, H.T. Grahn, A.J. Heeger and F. Wudl, Picosecond Dynamics in Polythiophene, Synth. Met. 28, C299 (1989); other support-NSF

M. Sinclair, D. McBranch, D. Moses and A.J. Heeger, Nonlinear Optical Properties of Conjugated Polymers, Synth. Met. 28, D645 (1989)

M. Sinclair, D. Moses, D. McBranch and A.J. Heeger, Nonlinear Ground State Fluctuations (Zero Point Motion) as the Source of the Nonlinear Optical Properties of Polyacetylene, Synth. Met. 28, D655 (1989)

D. McBranch, M. Sinclair, A.J. Heeger, A. O. Patil, S. Shi, S. Askari and F. Wudl, Linear and Nonlinear Optical Studies of Poly(p-phenylene-vinylene) Derivatives and Polydiacetylene 4BCMU, Synth. Met. 28, E85 (1989)

M. Sinclair, D. Moses, D. McBranch and A.J. Heeger, "Instantons" as the Origin of the Nonlinear Optical Properties of Polyacetylene, Proceedings of Nobel Symposium 73, "Physics of Low-Dimensional Systems, Physica Scripta, T27, 144 (1989).

c. Books (and sections thereof) submitted for Publication

None

d. Books (and sections thereof) Published

None

e. Technical Reports Published (including ONR Technical Reports) and Papers Published in Non-Refereed Journals

Time-Resolved Waveguide Modulation of a Conjugated Polymer, Sinclair et al. (23-3-1988)

Mechanism for Photogeneration of Metastable Charged Solitons in Polyacetylene, Colaneri, et al. (23-4-1988)

Photoexcitation and Doping Studies of Poly(3-hexylthienylene), Kim et al. (23-5-1988).

Anisotropy of the Third-Order Nonlinear-Optical Susceptibility in a Degenerate-Ground-State Conjugated Polymer: Trans-$(CH)_x$.(23-6)

f. Patents Filed

A patent disclosure has been submitted to the University titled "Photoinduced Superconducting Switch". The patent is based on the manuscript listed under Part 1, Section a, above. The University has made a positive decision to proceed with filing. The patent will be filed within the month of October, 1989.

g. Patents Granted

None

h. Invited Presentations at Topical or Scientific Society Conferences

P. Smith, ICSM '88, Santa Fe, NM (June 1988)
P. Smith, Organized ACS Symposium on Processing of Conducting Polymers, ACS Meeting, Dallas (April, 1989)
P. Smith, NATO ASI on "Soft Condensed Matter", Gielo, Norway (April, 1989)
F. Wudl, Symposium on Processing of Conducting Polymers, ACS Meeting, Dallas (1989).
F. Wudl, Symposium on Conducting Polymers, ACS Meeting, Los Angeles (October 1988)

A.J. Heeger, Symposium on the Chemistry of High T_c Superconductivity, ACS Meeting, Los Angeles (October 1988)

A.J. Heeger, Symposium on Molecular Electronics, APS Meeting, St. Louis (March, 1989)

A.J. Heeger, NATO Advanced Research Workshop on Conducting Polymers, Mons, Belgium, September 3-8, 1989.

i. Contributed Presentations at Topical or Scientific/Technical Society Conferences

S.D. Phillips, G. Yu Y. Cao, and A.J. Heeger, APS Meeting, St. Louis (March 1989)

j. Honors/Awards/ Prizes

A. J. Heeger, John Scott Award for 1989 (shared with Prof. A. G. MacDiarmid), $10,000 plus John Scott medal, awarded by John Scott Award Advisory Committee (via Board of Directors of City Trusts, Philadelphia)

k. Number of Graduate Students Receiving Full or Partial Support on this ONR Contract

Two (2)

l. Number of Postdoctoral Fellows Receiving Full or Partial Support on this ONR Contract

One (1)

Part II.

a. Principal Investigator

Alan J. Heeger

b. Dr. Peter Reynolds (ONR- Electronics)

c. Current Telephone Number
(805) 961-3184
FAX: (805) 961-4755

d. Brief (100-200 words) description of project

e. Significant Results During Past Year

We presented the first measurement of the NLO coefficient in a nonlinear waveguide made from a conjugated polymer. This novel technique was used to measure (and to time resolve on the picosecond time scale) the intensity-dependent refractive index of polydiacetylene 4BCMU. We developed a therory for thrid order NLO based on nonlinear zero-point motion in a conjugated polymer, and we presented experimental evidence that this novel mechanism played an important role in polyacetylene. We demonstrated evidence of intrinsic transport in conjugated polymers on the picosecond time scale through fast transient photoconductivity measurements.

f. Brief (100-200 words) summary of plans for next years work
We have recently shifted emphasis from polyacetylene to other semiconducting polymers that are stable and that can be processed by spin coating from solution into optical quality thin films. During the next year we will focus on these materials. In particular, we will carry out fast transient photoconductivity measurements on oriented and random films of poly(3-alkythiophene), poly(thienylenevinylene), dimethoxy-PPV, and dihexyloxy-PPV (PPV = polyphenylenevinylene). These materials will also be at the focus of our NLO measurements: specifically we plan to extend the nonlinear waveguide measurements and to carry out four-wave mixing measurements. We also intend to initiate measurements on the various semiconducting forms of polyaniline using novel orientation-inducing substrates to obtain the orientation. Finally, we are completing the construction of a Third Harmonic Soectroscopy Facility with capability of pumping from 0.25 eV to 2 eV. This will be used on the l polymers isted above to investigate two- and three-photon resonances as a means of investigating the fundamental origin of the NLO response

g. List of names of graduate students and post-doctorals currently working on project

Graduate student
D. McBranch

Postdotoral Researcher
D. Moses

Progress Report
ONR N00014-86-K-0514
November 21, 1988

Submitted to
Dr. Peter Reynolds
Physics Division
Office of Naval Research
800 No. Quincy
Arlington, Virginia

Nonlinear Optical Properties of Semiconducting Polymers

Institute for Polymers and Organic Solids
University of California, Santa Barbara
Santa Barbara, CA 93106

Principal Investigator:

Professor Alan J. Heeger
Soc. Sec. Number 508-34-6588
Tel. # (805) 961-3184

This has been an exciting and productive year, with important progress in both the study of the nonlinear optical properties of conjugated polymers and inthe study of the fast transient photoconductivity of these systems.

Highlights include the following:

1) The development of e new and important mechanism for third order nonlinear response. The paper describing this ("Instantons --- ") will appear in the Proceedings of the NOBEL SYMPOSIUM to be published in Physica Scripta (in press).

2) We succeeded in demonstrating nonlionear waveguiding for a spin-coated polymer. The response was shown to be on the picosecond time scale. The paper ("Time-Resolved---") is in press in APPLIED PHYSICS LETTERS.

3) We demonstrated the full anisotropy in the third order nonlinear response through third harmonic generation on oriented polymers. The paper ("Anisotropy ---") is in press in Physical Review B.

4) Transient photoconductivity was used to probe the intrinsic transport in improved polyacetylene. This same material when doped yields an electrical conductivity comparable to that of copper. The paper ("Transient Photoconductivity---") recently appeared in Physical Review B.

5) We have completed a study of the spectroscopy and transient photoconductivity of polyaniline which has been processed from solution in sulfuric acid. This is particularly important for the material in this form is crystalline with a relatively high degree of order.

I have enclosed copies of each of these manuscripts for your use and for your information.

"Instantons" as the Origin of the Nonlinear Optical Properties of Polyacetylene

M. Sinclair, D. Moses, D. McBranch and A. J. Heeger
Institute for Polymers and Organic Solids
University of California, Santa Barbara, CA 93106

and

J. Yu and W.P. Su
Department of Physics
University of Houston
Houston, TX 77004

Abstract

Third harmonic generation (THG) is used to probe the nonlinear susceptibility ($\chi^{(3)}$) of polyacetylene. The magnitude of $\chi_{\parallel}^{(3)}(3\omega;\omega,\omega,\omega)$ is $(4\pm2)\times10^{-10}$ esu with $\hbar\omega=1.17$eV; the only important component is that associated with π-electron motion along the backbone. Comparison of THG in cis- and trans-$(CH)_x$ shows that $\chi_{\parallel}^{(3)}|_{trans}$ is 15-20 times larger, implying a mechanism sensitive to the existence of a degenerate ground state. The results are consistent with calculations of $\chi_{\parallel}^{(3)}$ based on virtual generation of solitons enabled by nonlinear zero point fluctuations (instantons).

TIME-RESOLVED WAVEGUIDE MODULATION OF A CONJUGATED POLYMER

M. Sinclair[a], D. McBranch, D. Moses and A.J. Heeger
Institute for Polymers and Organic Solids and Department of Physics
University of California, Santa Barbara, CA 93106

ABSTRACT

We present a new pump and probe technique for measuring intensity-dependent refractive indices (n_2) of waveguide quality thin films, and we apply it to films of polydiacetylene-$(CH_2)_4OCONHOCOC_4H_9$ (PDA-4BCMU). Just below the exciton absorption band, the real part of n_2 is negative with magnitude $\approx 10^{-7}$ $(MW/cm^2)^{-1}$. The initial fast response of n_2 is followed by a slower (~2.5 ps) decay, in close agreement with the decay of the bleaching of the exciton absorption following resonant excitation. These results are consistent with phase space filling by excitons as the mechanism for the nonlinear index.

a) Permanent Address: Sandia National Laboratory, Albuquerque, NM, 87185

PHYSICAL REVIEW B VOLUME 38, NUMBER 0 15 NOVEMBER 1988

Anisotropy of the third-order nonlinear-optical susceptibility in a degenerate-ground-state conjugated polymer: *trans*-$(CH)_x$

M. Sinclair, D. Moses, K. Akagi,* and A. J. Heeger†

Department of Physics and Institute for Polymers and Organic Solids, University of California, Santa Barbara, California 93106

(Received 14 December 1987)

We present the results of a series of third-harmonic-generation (THG) measurements on the conjugated polymer polyacetylene which probe the magnitude and the origin of the third-order nonlinear-optical susceptibility of this material. By performing reflection THG measurements relative to a silicon standard, we have unambiguously determined the magnitude of the third-order susceptibility associated with tripling the fundamental of the Nd:YAG laser to be $\chi_{\parallel}^{(3)}(3\omega;\omega,\omega,\omega)=(4\pm2)\times10^{-10}$ esu, where $\chi_{\parallel}^{(3)}$ refers to that component of the third-order susceptibility tensor with all indices parallel to the chain direction. By measuring anisotropic THG in oriented films, we have shown that this component dominates. The magntiude and anisotropy are directly compared with results obtained from single crystals of polydiacetylene-(toluene-sulfonate) measured in the same apparatus. Finally, we have measured THG in both *cis*-rich and *trans* isomers of the same sample. We found that the measured response of the *cis*-rich samples scales with the residual *trans* content of the sample; $\chi_{\parallel}^{(3)}$ of the *trans* isomer is 15–20 times larger than that of the *cis* isomer. This symmetry-specific aspect of $\chi^{(3)}$ implies a mechanism which is sensitive to the existence of a degenerate ground state, as in *trans*-$(CH)_x$; it is consistent with the virtual generation of nonlinear solitons as a mechanism for the large measured third-order nonlinear-optical susceptibility of polyacetylene.

MS code no. BM3690 1988 PACS number(s): 42.65.Ky, 42.65.Bp, 42.50.Kb, 78.47.+p

I. INTRODUCTION

Although organic polymers have great potential for eventual application in nonlinear-optical elements, an understanding of the mechanism (or mechanisms) underlying their nonlinear susceptibilities is necessary before the design and synthesis flexibility afforded by organic chemistry can be applied to the development of new and better materials. Detailed experimental studies of prototype systems must therefore be performed in order to guide a parallel theory effort aimed at a general understanding of the nonlinear-optical properties of organic polymer materials.

The promise of conducting polymers as fast-response nonlinear-optical materials has been recently emphasized.[1-3] Polymers such as polyacetylene, polythiophene, and the soluble and processible poly(3-alkylthienylenes) contain a high density of π electrons, and they are known to exhibit photoinduced absorption and photoinduced bleaching, indicating major shifts of oscillator strength upon photoexcitation.[2,4] For polyacetylene, these nonlinear effects have been studied in detail in the picosecond[5(a),5(b)] and subpicosecond[5(c)] time regimes and have been correlated with the photoproduction of charge carriers through fast-photoconductivity measurements.[6] The data have demonstrated ultrafast response with nonlinear shifts in oscillator strength occurring at times of the order of 10^{-13} s. These *resonant* nonlinear-optical properties are intrinsic; they originate from the nonlinearity of the self-localized photoexcitations[7] which characterize this class of polymers: solitons, polarons, and bipolarons.[4]

In any material where photoexcitation results in shifts of oscillator strength (as is the case in conducting polymers), the optical properties will be highly nonlinear. The magnitude of the *resonant* $\chi^{(3)}$ can be estimated from the magnitude and frequency dependence of the photoinduced absorption and bleaching. For example, as a result of the shift in oscillator strength subsequent to photoexcitation, the complex index of refraction is intensity dependent, n_2 I

$$n(\omega)=n_0(\omega)+\Delta n(\omega,\omega_p)I(\omega_p)\,, \tag{1}$$

where the second term describes the nonlinear response at frequency ω due to an intense pump at pump frequency ω_p. Under pumping conditions which are resonant with the π-π^* transition of polyacetylene ($\hbar\omega_p=2.0$ eV), n_2 the existing data yield an estimate[2,7] for Δn(1.4 eV, 2.0 n_2 eV) $\approx10^{-4}$ $(\mathrm{MW/cm^2})^{-1}$. This large value for Δn implies a correspondingly large value for $\mathrm{Im}\chi^{(3)}$ through the relation n_2

$$\Delta n=4\pi^2/c\epsilon\chi^{(3)}\,, \tag{2}$$

where ϵ is the dielectric constant at the probe frequency n_2 (ω). Using the above value for Δn, we obtain $\mathrm{Im}\chi^{(3)}(-\omega_2=\omega_1-\omega_1-\omega_2)=5\times10^{-8}$ esu, an impressive value even under resonant conditions. From a Kramers-Kronig analysis of the photoinduced absorption data, one n_2 concludes that the real parts of Δn and $\chi^{(3)}$ are correspondingly large. Based on these observations, experimental studies of third-harmonic generation in polyacetylene and related conducting polymers were initiated in order to explore directly the third-order susceptibility as

Transient photoconductivity in oriented *trans*-polyacetylene prepared by the Naarmann-Theophilou method

S. D. Phillips and A. J. Heeger
Institute for Polymers and Organic Solids and Department of Physics, University of California, Santa Barbara, California 93106
(Received 20 January 1988)

We present transient-photoconductivity results of oriented *trans*-polyacetylene prepared by the Naarmann-Theophilou method. In addition to the u al fast-decaying photocurrent peak, we report a large long-lived, temperature-dependent tail not previously seen in other forms of polyacetylene. By comparison of the data to that obtained from high-quality single crystals of polydiacetylene, we conclude that the magnitude of this tail implies higher-quality polyacetylene. The anisotropic behavior for different polarizations of the incident light is presented together with the effect of light intensity, temperature, and external field strength.

INTRODUCTION

The role of nonlinear localized excitations such as solitons and polarons in the conducting polymer *trans*-polyacetylene have received considerable theoretical and experimental attention. Nevertheless, the dynamics of charge transport is not fully understood, particularly in the subnanosecond domain. Numerous experiments have probed this short-time domain through photoinduced bleaching,[1] photoinduced absorption,[2-5] and photoconductivity.[6-8] Photoinduced bleaching demonstrates that oscillator strength is rapidly (subpicosecond) removed from the interband transition upon sample illumination with light of energy greater than the band gap. Photoinduced absorption demonstrates that the oscillator strength is deposited in a low-energy peak (0.45 eV) and a high-energy peak (1.35 eV) on a similar time scale. Both photoinduced excitations decay rapidly, within tens of picoseconds. Transient-photoconductivity measurements, which measure the product of the number of charge carriers and their mobility, include contributions from all mobile charged species. Results from photoconductivity experiments also indicate a fast decay followed by a small, long-lived component. Sinclair and co-workers[6] reported transient photoconductivity in unoriented Shirakawa polyacetylene to have a roughly exponential initial decay of lifetime 300 ps. Stretch-oriented polyacetylene samples prepared by the Durham procedure have been measured by Bleier *et al.*,[8] who found a somewhat shorter initial photoconductivity decay time of 100–150 ps.

Recently, Naarmann and Theophilou[9,10] have developed an improved method of synthesizing polyacetylene which yields fewer sp^3 defects and significantly higher electrical conductivity subsequent to doping. In order to characterize the intrinsic properties of polyacetylene, it is necessary to probe the transport during the subnanosecond time domain, i.e., before the transport is dominated by the sample morphology. With this as motivation, we present in this paper the results of transient photoconductivity measurements on stretch-oriented Naarmann-Theophilou polyacetylene.

EXPERIMENTAL RESULTS

Details of the photoconductivity apparatus have been previously reported.[6] The incident laser beam was linearly polarized with a dichroic polarizer and subsequently rotated via a half-wave plate. Photon fluxes were in the range of 10^{14}–10^{15} cm^{-2} per pulse with energy of 2.2 eV (566 nm) and a pulse duration of 20 ps. The polyacetylene samples were free-standing stretch-oriented (6×) films with 200-μm-gap gold electrodes evaporated on it and attached with silver paint to the substrate. The time resolution of the data-acquisition system is approximately 40 ps.

Conductivity measurements performed with an electrometer yield a dark conductivity of 10^{-6} S/cm and a linear (Ohmic) current-to-voltage relationship over all voltages of interest. The samples were of the same batch tested by Basescu *et al.*[10] and found to have a doped (6 mol % of I_3^-) conductivity of 20000 S/cm, nearly 2 orders of magnitude larger than similarly doped polyacetylene samples obtained by the conventional Shirakawa method. All samples were mounted with the chain-orientation direction parallel to the biasing electric field. Sample preparation was performed in an inert atmosphere, and the photoconductivity experiments carried out under vacuum of 10^{-4} torr or less.

Figure 1 shows the transient photoconductivity at room temperature and at 80 K due to a 0.25-μJ pulse of 2.2 eV polarized perpendicular to the chains with a bias field of 1.5×10^4 V/cm. By careful waveform averaging with regard to trigger jitter, we are able to resolve an intense and sharp peak at short times (< 100 ps), which we believe was averaged out in previous studies.[6-8] In the room-temperature curve, a long-lived tail is clearly present, considerably longer and more intense than previously reported for aligned Durham[8] or for unoriented Shirakawa material.[6] Assuming an effective quantum efficiency at 50 ps of 0.01 (Refs. 3 and 4) (which includes the probability of escaping early recombination), this yields a mobility of 2 cm^2/V s, similar to that obtained for other forms of polyacetylene[6,8] and inferred from photoinduced dichroism.[1] Both peak and long-lived pho-

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Spectroscopy and Transient Photoconductivity of Crystalline Polyaniline

S.D. Phillips†, G. Yu†, Y. Cao and A.J. Heeger*

Institute for Polymers and Organic Solids

University of California, Santa Barbara

Santa Barbara, CA 93106

Abstract

The results of spectroscopy and transient photoconductivity measurements are presented for polyaniline in the fully reduced form (leucoemeraldine) and in the emeraldine base form. Results from partially crystalline films (cast from solution in sulfuric acid) and from amorphous films (cast from dimethylforamide) are compared. We observed a relatively strong photoconductive response from pumping at 3.7 eV into the π-π^* absorption of leucoemeraldine and a smaller photocurrent from pumping (at 1.9 eV and 3.7 eV) into the two absorptions which characterize the emeraldine base. The 3.7 eV photocurrent in leucoemeraldine is a factor of 4-8 larger than that from the similar ultraviolet absorption in the emeraldine base, and the two photocurrents show a similar dependence on biasing field (linear at low light levels and more complex at high light levels). The photocurrent in the emeraldine base from 3.7 eV pumping is a factor of 3-4 larger (per photon) than that from 1.9 eV pumping. The results are interpreted in terms of the one-dimensional band structures calculated for the two forms of polyaniline.

† Department of Physics, UCSB

*Department of Physics and Materials Department, UCSB

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OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS

REPORT

(July 15, 1988)

for

Contract # N00014-86-K-0514

"Nonlinear Optical Properties of Semiconducting Polymers"

Principal Investigator: Alan J. Heeger (508-34-6588)

Co-Investigator: Daniel Moses

Institute for Polymers and Organic Solids
University of California, Santa Barbara
Santa Barbara, CA 93106

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PART 1

a. Papers Submitted Refereed Journals (and not yet published)

Transient photoconductivity in oriented trans-polyacetylene prepared by the Naarmann/Theophilou method, S.D. Phillips and A.J. Heeger (Submitted to Physical Review B)

"Instantons" as the source of the nonlinear optical properties of polyacetylene, M. Sinclair, D. Moses, D. McBranch and A.J. Heeger (submitted to Physica Scripta and to be included in the Proceedings of the Nobel Symposium, 1988)

Anisotropy of the third order nonlinear optical susceptibility in a conjugated polymer; trans-$(CH)_x$, M. Sinclair, D. Moses, K. Akagi, and A.J. Heeger (submitted to Phys. Rev. B)

Nonlinear Optics of Conjugated Polymers, M. Sinclair, D. McBranch and A.J. Heeger (submitted to Synth. Met.)

Nonlinear Ground State Fluctuations (zero point motion) as the Source of the Nonlinear Optical Properties of Polyacetylene, M. Sinclair, D. Moses, D. McBranch and A.J. Heeger (submitted to Synth. Met.)

Linear and Nonlinear Optical Studies of Poly(p-phenylenevinylene) Derivatives and Polydiacetylene-4BCMU (Submitted to Synth. Met.)

b. Papers Published in Refereed Journals

Polarization dependence of transient photoconductivity in trans-polyacetylene, M. Sinclair, D. Moses, R.H. Friend and A. J. Heeger Phys. Rev. B36, 4296, (1987)

c. Books (and sections thereof) Submitted for Publication

Structural Relaxation and Nonlinear Zero-Point Fluctuations as the Origin of the Anisotropic Third-order Nonlinear Optical Susceptibiliy in trans-$(CH)_x$, M. Sinclair, D. Moses, K. Akagi and A.J. Heeger, "Polymers for Nonlinear Optics" (NATO ASI Series, to be published)

d. Books (and sections thereof) Published

Third order nonlinear optical susceptibility of trans-$(CH)_x$: A degenerate ground state conjugated polymer, M. Sinclair, D. Moses and A.J. Heeger Nonlinear Optical Properties of Polymers, Ed. by A.J. Heeger, J. Orenstein and D. Ulrich (Volume 109 of theSymposium Proceedings of the Materials Res. Soc. Pittsburgh, 1988)

Transient photoconductivity in polyacetylene and polydiacetlyene, D. Moses, M. Sinclair and A.J. Heeger , Nonlinear Optical Properties of Polymers, Ed. by A.J. Heeger, J. Orenstein and D. Ulrich (Volume 109 of theSymposium Proceedings of the Materials Res. Soc. Pittsburgh, 1988)

e. Technical Reports Published and Papers Published in Non-refereed Journals

None

f. Patents Filed

None

g. Patents Granted

None

h. Invited Presentations at Topical or Scientific/Technical Society Conferences

A.J. Heeger (Invited talks specifically focused on research carried out under this ONR Contract)

Symposium on "Nonlinear Optical Properties of Polymers", Materials Research Society (Boston) December, 1987

NATO Workshop on "Polymers for Nonlinear Optics", Sophia-Antipolis (France) July 1988

Nobel Symposium on "Physics of Low-Dimensional Systems", Graftavallen (Sweden), June, 1988

D. Moses (Invited talks specifically focused on research carried out under this ONR Contract)

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M. Sinclair (Invited talks specifically focused on research carried out under this ONR Contract)

Brookhaven Symposium on Conducting Polymers, Brookhaven National Laboratory, October, 1987

International Conference on Synthetic Metals (ICSM '88), Santa Fe, NM, June, 1988

F. Wudl (Invited talks specifically focused on research carried out under this ONR Contract)

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International Conference on Synthetic Metals (ICSM '88), Santa Fe, NM, June, 1988

i. <u>Contributed Presentations at Topical or Scientific/Technical Society Conferences</u>

A. American Physical Society Meeting, New Orleans, March 21-25, 1988

Transient Photoconductivity in trans-polyacetylene, S.D. Phillips and A.J. Heeger

"Instantons" as the Origin of the Nonlinear Optical Properties of Polyacetylene, M. Sinclair, D. Moses, and A.J. Heeger

B. International Conference on Synthetic Metals (ICSM '88), Santa Fe, NM, June 26-July 1, 1988

Linear and Nonlinear Optical Studies of Poly(p-phenylenevinylene(derivatives and Polydiacetylene-4BCMU, D. McBranch, M. Sinclair, A.J. Heeger, A.O. Patil, S. Shi, S. Askari and F. Wudl

Transient Photoconductivity in Conjugated Polymers, S.D. Phillips, G. Yu and A.J. Heeger

j. <u>Honors/Awards/Prizes</u>

NONE

k. <u>Number of Graduate Students Receiving Full or Partial Support on ONR Contract</u>

Two (2)

l. <u>Number of Postdoctoral Fellows Receiving Full or Partial Support on ONR Contract</u>

Two (2)

PART II

a. Principal Investigator
Professor Alan J. Heeger

b. Cognizent ONR Scientific Officer
Dr. Robert Junker

c. Current Telephone Number
(805) 961-3184

d. Brief (100-200) description of project

This program is directed toward the development of the fast photoconductive response and th enonlinear optical properties of semiconducting polymers. The research program is focussed on the fabrication of polymer films of optical quality, and the quantitative characterization of these polymers as optical materials with unusually fast photoconductive response and decay, and as nonlinear optical materials with remarkably large and anisotropic resonant and nonresonant values of $\chi^{(3)}$.

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a. Third harmonic generation was used to probe the nonlinear susceptibility ($\chi^{(3)}$) of polyacetylene. The magnitude (ppump polarization along the chain axis) is $(4\pm2) \times 10^{-10}$ esu with $\hbar\omega$=1.17 eV; the only important component is that associated with π-electron motion along th ebackbone. Comparison of THG in cis- and trans-polyacetylene shows that for the trans-isomer, $\chi^{(3)}$ is 15-20 times larger, implying a mechanism sensitive to the existence of a degenerate ground state. The results are consistent with calculations of the nonlinear response based on virtual generation of solitons by nonlinear zero point fluctuations (instantons).

b. We have developed a time-resolved waveguide modulation method to measure the magnitude and sign of the nonlinear refractive index (n_2) in films of conjugated polymers. We have successfully applied this technique to polydiacetylene-4BCMU; we find that n_2 is negative, with magnitude of approximately 10^{-7} $(MW/cm^2)^{-1}$. The response time of this nonlinearity is resolution limited (< 1 picosecond); the decay tiem was measured to be about 2.5 picoseconds. The technique is applicable to a wide variety of other conjugated polymers.

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We have recently developed a new pump/probe technique for measuring nonlinear refractive indices of waveguide quality thin films, and we have applied it successfully to films of polydiacetylene-4BCMU. Just below the exciton absorption band, the real part of the nonlinear refractive index (n_2) is negative with magnitude $\approx 10^{-7}$ $(MW/cm^2)^{-1}$. The decay of n_2 shows a fast initial component followed by a slower (~2.5 ps) decay, in close agreement with the decay of the bleaching of the exciton absorption following resonant excitation. These results are consistent with phase space filling by excitons as the mechanism of the nonlinear refractive index. We plan to extend the application of this technique to a number of soluble cojugated polymers now available in our laboratory. In addition, we plan to carry out a full spectroscopy (ir through visible) of third harmonic geberation in both cis and trans-polyacetylene. In the fast transient photoconductivity area, we will attempt to move into the sub-picosecond regime through implementation of electroOoptic sampling.

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D. McBranch

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D. Moses

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1. Carrier Generation and Mobility in Polydiacetylene: Fast Transient Photoconductivity, D. Moses, M.Sinclair and A.J. Heeger

2. Picosecond Photoconductivity in trans-Polyacetylene, M. Sinclair,D. Moses, A.J. Heeger

Reports on the rest of the publications are in preparation.

OFFICE OF NAVAL RESEARCH

END-OF-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS

October 1, 1987-September 30, 1988
for
Contract No. NOOO14-86-K-0514

Principal Investigator: Alan J. Heeger (508-34-6588)
Co-Investigator: Daniel Moses

Institute for Polymers and Organic Solids
University of California, Santa Barbara
Santa Barbara, CA 93106

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Part 1

a. Papers Submitted to Refereed Journals (and not yet published)

"Instantons" as the Origin of the Nonlinear Optical Properties of Polyacetylene, M. Sinclair, D. Moses, D. McBranch, A. J. Heeger, J. Yu and W.P. Su, Phys. Rev. B Rapid Commun. (in press).

Spectroscopy and Transient Photoconductivity of Crystalline Polyaniline, S. D. Phillips, G. Yu, Y. Cao and A. J. Heeger, submitted to Phys. Rev. B.

Nonlinear Optics of Conjugated Polymers, M. Sinclair, D. McBranch and A. J. Heeger, submitted to Syn. Mtls.

Nonlinear Ground State Fluctuations (zero point motion) as the Source of the Nonlinear Optical Properties of Polyacetylene, M. Sinclair, D. Moses, D. McBranch and A. J. Heeger, submitted to Syn. Mtls.

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Time-Resolved Waveguide Modulation of a Conjugated Polymer, M. Sinclair, D. McBranch, D. Moses and A. J. Heeger , Appl. Phys. Lett. 53 (24), 2374 (1988).

Anisotropy of the Third-Order Nonlinear-Optical Susceptibility in a Degenerate-Ground State Conjugated Polymer: Trans-$(CH)_x$, M. Sinclair, D. Moses, K. Akagi and A. J. Heeger, Phys. Rev. B 38 (15), 10 725 (1988).

Transient Photoconductivity in Oriented Trans-Polyacetylene Prepared by the Naarmann-Theophilou Method, S. D. Phillips and A. J. Heeger, Phys. Rev. B 38 (9), 6211 (1988).

Photoexcitation and Doping Studies of Poly(3-hexylthienylene), Y. H. Kim, D. Spiegel, S. Hotta and A. J. Heeger, Phys. Rev. B 38 (8), 5490 (1988).

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Optical Society of America, Topical Meeting on Nonlinear Optical Properties of Materials, Rensselaer Polytechnic Institute, Troy, New York, August 1988

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FINAL TECHNICAL REPORT

Office of Naval Research

N00014-86-K-0514

1987

Nonlinear Optical Properties of Semiconducting Polymers

Principal Investigator:

Professor Alan J. Heeger
Institute for Polymers and Organic Solids
University of California
Santa Barbara, CA 93106

We have made excellent progress in the first year of our program on the **"Nonlinear Optical Properties of Semiconducting Polymers"**. Specific accomplishments during this period include the following:

A. Instrumentation

Our picosecond transient spectrosocopy facility is in full operation with sub-picosecond pulses (autocorrelation pulses yield about 300 femtosecond pulse width). Pump/probe measurements of photoinduced bleaching, four-wave mixing experiments and third-harmonic generation experiments are underway.

B. Materials

We have put considerable effort into materials development directed toward oriented films of semiconducting polymers. We have succeeded in achieving both oriented films of polyacetylene on glass substrates and oriented fibers of 50/50 blends of poly(3-hexylthiophene) in polystyrene or polyethyleneoxide. The availability of these oriented materials has made possible, for the first time, measurements of the anisotropy in $\chi^{(3)}$ in conducting polymers (see below).

C. Specific Results and Publications (NOTE: preprings or reprints of these publications are attached as Appendices)

1. MEASUREMENT OF THE THIRD ORDER SUSCEPTIBILITY OF TRANS-POLYACETYLENE BY THIRD HARMONIC GENERATION. M. Sinclair, D. Moses, A. J. Heeger, K. Vilhelmsson, B. Valk and M. Salour (Solid State Commun. 61, 221, 1987).

An initial measurement of the third order nonlinear optical susceptiblity of trans-polyacetylene was carried out by use of third harmonic generation in non-oriented (isotropic) thin films. The measured susceptibility was $\chi^{(3)}(3\omega = \omega+\omega+\omega) = 5 \times 10^{-10}$ esu which is comparable to the magnitude of the large nonlinear susceptibilities measured in polydiacetylenes.

2. CARRIER PHOTOGENERATION AND MOBILITY IN POLYDIACETYLENE: FAST TRANSIENT PHOTOCONDUCTIVITY, D. Moses, M. Sinclair and A. J. Heeger, Phys. Rev. Lett. 58, 2710 (1987).

Transient photoconductivity experiments have been carried out on single crystals of polydiacetylene-(bis p-toluene sulfonate), PDA-TS. The low electric field photocurrent decay consists of a temperature independent fast (picosecond) initial component and a longer time (nanosecond) component with magnitude that is strongly temperature dependent. Using very small spacings between electrodes on the sample, we have succeeded in achieving sweep-out for the longer lived carriers; the data yield a mobility of ≈ 5 cm^2/Vs at room temperature in the ns regime. These results dmeonstrate that the Onsager geminate recombination model, previously used extensively for the polydiacetylenes, is not applicable to PDA-TS.

3. POLARIZATION DEPENDENCE OF TRANSIENT PHOTOCONDUCTIVITY IN TRANS-POLYACEYTLENE, M. Sinclair, D. Moses, R. H. Friend and A. J. Heeger, Phys. Rev. B (in press).

The results of a series of measurements of the polarization dependence of the transient photoconductive response in both oriented and non-oriented trans-polyacetylene were reported. Our data indicate that in non-oriented samples the short time photoconductivity is dominated by intrachain absorption and intrachain transport, while in oriented samples both interchain and intrachain photogeneration (with different absorption depths) of charge carriers are important. In oriented samples, the photoconduction due to interchain excitation is slightly larger than that due to intrachain excitation.

4. ANISOTROPY OF THE THIRD ORDER NONLINEAR OPTICAL SUSCEPTIBILITY IN A DEGENERATE GROUND STATE CONJUGATED POLYMER: TRANS-$(CH)_x$, M. Sinclair, D. Moses, K. Akagi and A. J. Heeger, Phys. Rev. B (submitted)

We present the results of a series of third harmonic generation (THG) measurements on the conjugated polymer polyacetylene which probe the magnitude and the origin of the third order nonlinear optical susceptibility of this material. By performing reflection THG measurements relative to a silicon standard, we have unambiguously determined the magnitude of the third order susceptibility associated with tripling the fundamental of the Nd:YAG laser to be $\chi_{\parallel}^{(3)}(3\omega;\omega,\omega,\omega) = (4\pm2) \times 10^{-10}$ esu, where $\chi_{\parallel}^{(3)}$ refers to that component of the third order susceptibility tensor with all indices parallel to the chain direction. By measuring anisotropic THG in oriented films, we have shown that this component dominates. The magnitude and anisotropy are directly compared with results obtained from single crystals of polydiacetylene-(toluene-sulfonate) measured in the same apparatus. Finally, we have measured THG in both cis-rich and trans isomers of the same sample. We found that the measured response of the cis-rich samples scales with the residual trans content of the sample, indicating that $\chi_{\parallel}^{(3)}$ of the trans isomer is at least an order of magnitude larger than that of the cis isomer. This symmetry specific aspect of $\chi_{\parallel}^{(3)}$ implies a mechanism which is sensitive to the existence of a degenerate ground state, as in trans-$(CH)_x$; it is consistent with the virtual generation of nonlinear solitons as a mechanism for the large measured third order nonlinear optical susceptibility of polyacetylene. A detailed theory of instantons as the origin of the nonlinear optical properties of polyacetylene is presented.

5. "INSTANTONS" AS THE ORIGIN OF THE NONLINEAR OPTICAL PROPERTIES OF POLYACETYLENE, M. Sinclair, D. Moses, D. McBranch, A. J. Heeger, J. Yu and W.-P. Su, Phys. Rev. Lett. (submitted).

Third harmonic generation (THG) is used to probe the nonlinear susceptibility ($\chi^{(3)}$) of polyacetylene. The magnitude of $\chi_{\parallel}^{(3)}(3\omega;\omega,\omega,\omega)$ is $(4\pm2) \times 10^{-10}$ esu with $\hbar\omega = 1.17$ eV; the only important component of $\chi^{(3)}$ is that associated with π-electron motion along the polymer backbone. Comparison of THG in cis- and trans-$(CH)_x$ shows that $\chi_{\parallel}^{(3)}|_{trans}$ is 15-20 times larger than $\chi_{\parallel}^{(3)}|_{cis}$. The symmetry specific $\chi_{\parallel}^{(3)}$ implies a mechanism sensitive to the existence of a degenerate ground state, consistent with nonlinear zero-point fluctuations ("instantons") as the origin of $\chi_{\parallel}^{(3)}$. We show that the results are consistent with theory based on virtual generation of solitons enabled by instantons.

6. TRANSIENT PHOTOCONDUCTIVITY IN ORIENTED TRANS-POLYACETYLENE PREPARED BY THE NAARMANN METHOD, S. D. Phillips and A. J. Heeger, Phys. Rev. (submitted).

We present transient photoconductivity results of oriented trans-polyacetylene prepared by the Naarmann method. In addition to the usual fast decaying photocurrent peak, we report a large long lived, temperature dependent tail not previously seen in other forms of polyacetylene. By comparison of the data to that obtained from high quality single-crystals of polydiacetylene, we conclude that the magnitude of this tail implies higher quality polyacetylene. The anisotropic behavior for different polarizations of the incident light is presented together with the effect of light intensity, temperature and external field strength.

Solid State Communications, Vol.61, No.4, pp.221-225, 1987.
Printed in Great Britain.
0038-1098/87 $3.00 + .00
Pergamon Journals Ltd.

Measurement of the Third Order Susceptibility of *Trans*-Polyacetylene by Third Harmonic Generation

M. Sinclair, D. Moses and A. J. Heeger
Department of Physic and Institute for Polymers and Organic Solids
University of California
Santa Barbara, CA 93106
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K. Vilhelmsson, B. Valk and M. Salour
TACAN Aerospace Corporation
Carlsbad, CA 92008

(Received 3 October 1986 by A. A. Maradudin)

Abstract

We report a measurement of the third order nonlinear optical susceptibility of *trans*-polyacetylene by third harmonic generation in thin films. The measured susceptibility is $\chi^{(3)}(3\omega = \omega + \omega + \omega) = 5 \times 10^{-10}$ esu, which is comparable to the magnitude of the large nonlinear susceptibilities measured in the polydiacetylenes.

We report the demonstration of third harmonic generation using thin films of polyacetylene, $(CH)_x$, as the nonlinear optical medium. With 100 ps pulses at 1.06 μ (1-100 MW/cm^2 peak power) incident on a 1000 Å non-oriented film, the conversion into 3ω was proportional to the cube of the incident power. The measured value for the third order susceptibility is $\chi^{(3)}(3\omega) = 5 \times 10^{-10}$ esu. Since the *trans*-$(CH)_x$ films used in this experiment were non-oriented, the value for $\chi^{(3)}$ parallel to the polyene chain ($\chi_\parallel^{(3)}$) is comparable to the corresponding value for polydiacetylene.

It is well known that organic materials with delocalized π-electron systems exhibit large nonlinear optical coefficients[1]. The large values of the higher order susceptibilities in conjugated polymers have been attributed to nonlinear response arising from the π-electron band structure and enhanced by electron-electron correlations. Although conducting polymers (e.g., polyacetylene, polythiophene, etc.) have received considerable attention because of their novel electrical and electrochemical properties[2], their potential as nonlinear optical materials has been realized only recently[3].

Polymers such as polyacetylene and polythiophene are known to exhibit photoinduced absorption and photoinduced bleaching, indicating major shifts of oscillator strength upon photoexcitation[4-6]. For polyacetylene, these phenomena have been studied in detail in the picosecond and sub-picosecond time regime[7-9] and correlated with the photoproduction of charge carriers through fast photoconductivity measurements[10]. As predicted by Su and Schrieffer[11], these data have demonstrated fast response with nonlinear shifts in oscillator strength occurring at times of the order of 10^{-13} seconds. These phenomena are experiment were not one photon resonant, the degree of two photon and three photon resonance can only be determined through studies in which the fundamental wavelength is tuned.

Figure 1 is a log-log plot of the third harmonic intensity (in W/cm^2) as a function of fundamental intensity (in MW/cm^2). The solid line is a best fit to the data assuming a cubic dependence of the third harmonic intensity on the fundamental intensity. The constant of proportionality is 4.3×10^{-6}. The inset shows the spectral content of the third harmonic intensity showing a resolution limited peak at 355 nm. Using Q-switched, modelocked pulses, we have extended the measurement to peak pump powers in excess of 10 GW/cm^2 without damage to the sample.

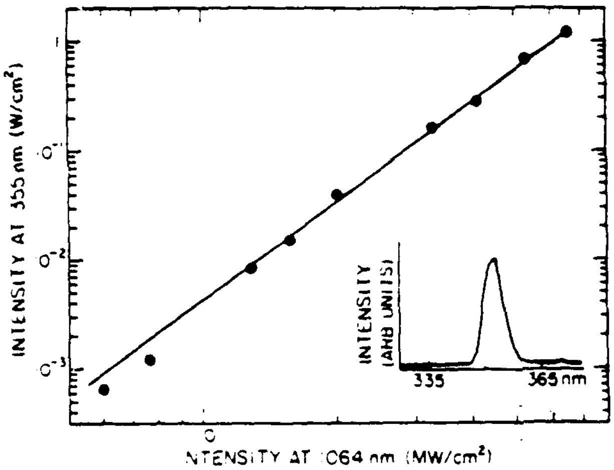

Fig. 1 Log-log plot of the third harmonic intensity (W/cm^2) as a function of the fundamental intensity (MW/cm^2). The solid line indicates a cubic dependence of the third harmonic intensities on the fundamental intensity. The inset shows that the spectral content of the third harmonic is resolution limited at 355 nm.

In the presence of strong absorption at ω and 3ω, the intensity of the third harmonic can be written in terms of the third order polarization as[21]

$$I(3\omega) = \frac{K|P^{(3)}(3\omega)|^2}{[(\Delta k)^2 + \frac{(\alpha_3 - 3\alpha_1)^2}{4}]} \qquad (2)$$

with

$$K = \frac{2\pi(3\omega)^2}{c\sqrt{\varepsilon_3}}[\exp(-3\alpha_1 L) + \exp(-\alpha_3 L) - 2\cos(\Delta kL)\exp-(3\alpha_1+\alpha_3)L/2] \qquad (3)$$

and

$$|P^{(3)}(3\omega)|^2 = \left(\frac{2\pi}{c\sqrt{\varepsilon_3}}\right)^3 |\chi^{(3)}(3\omega)|^2\, I^3(\omega) \qquad (4)$$

where $P(3\omega) = \chi^{(3)}(3\omega = \omega+\omega+\omega)E(\omega)E(\omega)E(\omega)$, α_1 and α_3 are the absorption coefficient at ω and 3ω, Δk is the phase mismatch and ε_3 is the dielectric constant at 3ω. This equation is a plane wave result which is valid when the sample thickness (0.1 μ) is much less than the confocal beam parameter of the focused gaussian beam (300 μ). Since $\alpha_3 \gg \alpha_1$ and $\alpha_1 L < 1$, we can rewrite eqn. 2 in the simplified form

$$I(3\alpha) = \frac{2\pi(3\omega)^2}{c\sqrt{\varepsilon_3}} \frac{|P^{(3)}(3\omega)|^2}{[(\Delta k)^2 + 1/4(\alpha_3)^2]} \qquad (5)$$

Using Eqns. 3, 4 and 5, one can relate the experimentally measured intensity at 3ω to the third order susceptibility:

$$\chi^{(3)}(3\omega) = \frac{c^2}{12\pi^2\omega}\{\sqrt{\varepsilon_1^3\varepsilon_3}\,[(\Delta k)^2 + \frac{(\alpha_3)^2}{4}]\,\frac{I(3\omega)}{I^3(\omega)}\}^{1/2} \qquad (6)$$

Materials, Ed D J Williams, American Chemical Society Symposium Series 233, (American Chemical Society, Washington, DC, 1983) Ch 8.
(b) A. J. Heeger, D Moses and M Sinclair, Synth. Met. 15, 95 (1986)

4 G. B. Blanchet, C R Fincher, T -C Chung and A J Heeger, Phys Rev Lett. 50, 1938 (1983)

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Carrier Photogeneration and Mobility in Polydiacetylene: Fast Transient Photoconductivity

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Transient-photoconductivity experiments have been carried out on single crystals of polydiacetylene-(*bis p*-toluene sulfonate), PDA-TS. The low-electric-field photocurrent decay consists of a temperature-independent fast (picosecond) initial component and a longer-time (nanosecond) component with magnitude that is strongly temperature dependent. Using small spacings between electrodes, we have succeeded in achieving sweepout for the longer-lived carriers; the data yield a mobility of ≈5 cm²/V·s at room temperature in the nanosecond regime. These results demonstrate that the Onsager geminate-recombination model, used extensively for the polydiacetylenes, is not applicable to PDA-TS.

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A prediction of remarkably high mobility,[1,2] of the order of 2×10^5 cm²/V·s, has been advanced by the analysis of transient transport experiments with the assumption that the quantum efficiency for electric-field-dependent carrier creation could be derived from the Onsager theory of geminate recombination.

In this Letter, we report fast-transient-photoconductivity measurements on polydiacetylene-(*bis p*-toluene sulfonate), PDA-TS, which enable us to address both the photogeneration mechanism—Is it limited by the geminate recombination processes usually described by the Onsager theory for localized states?—and the magnitude of the carrier mobility. We find that the photocurrent decay consists of a *temperature-independent* fast (picosecond) initial component and a longer-time (nanosecond) component with magnitude that is strongly temperature dependent. Using very small spacings between electrodes on the samples, we have succeeded in achieving sweepout of the of the longer lived carriers in relatively high electric fields ($>3\times10^4$ V/cm); the data yield a field-independent mobility of ≈5 cm²/V·s at room temperature in the nanosecond regime, far below the previously inferred value. The temperature independence of the initial photocurrent is interpreted as evidence for "hot" carriers.

The transient photoconductivity was measured with the Auston microstrip transmission line switch technique.[3,4] A dye-laser system was used to produce 20-ps pulses; detailed experiments were carried out at photon energies of 2.9 and 2.58 eV. The laser pulse energy was kept constant at 0.5 μJ/pulse. The transient signals were amplified and detected with overall time resolution limited by the preamplifier. Single-crystal samples used in these experiments were grown at Queen Mary College, cleaved to an approximate thickness of 100 μm, and mounted on the alumina substrate. The crystals were oriented with the PDA chains parallel to the electric field within the gap. The gold microstrip was evaporated directly onto the single crystal with gaps of $L=200$, 10, and 2.5 μm. The observation of carrier sweepout (see below) implies that the contacts are collecting (rather than Ohmic) at the short times relevant to this experiment. Since the transient signal amplitude is reproducible over long times, carrier injection is sufficient to eliminate any surface charging effects.

In Fig. 1, we show the transient photocurrent decay following a 2.9-eV photopulse at a series of temperatures (electric field of 2.5×10^4 V/cm across a gap of 200 μm). Experiments at a lower field, 1.5×10^3 V/cm, yield the same temperature dependence of the waveform. Each waveform is characterized by a fast initial response followed by a fast decay to a more slowly decreasing "tail." The rise time is limited by the temporal resolution of the measuring system, since the initial photogeneration process is instantaneous on this time scale. For the 2.9-eV pump, as the temperature is lowered, both the peak value

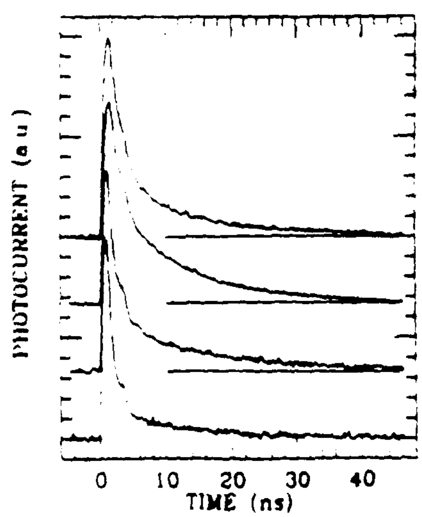

FIG. 1. Transient photocurrent wave forms (resolution 400 ps) for PDA-TS at various temperatures: from top to bottom: 300, 180, 60, and 15 K. The horizontal lines indicate the zero for the upper three wave forms.

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determined from the sweepout is in agreement with that inferred in the 200–400-ns time scale by Reimer and Bassler in their attempt to carry out time-of-flight measurements from contact injected carriers.[7]

Because of the sweepout, Q_{tail} saturates at fields above 3×10^4 V/cm; $Q_{initial}$, however, continues to increase even at the highest fields. Since the unresolved initial peak decays in less than 300 ps, there is not sufficient time to sweep out the charge before it is thermalized and trapped, etc., into the tail.

We have ruled out the possibility that this effect is due to a field-induced increase in the decay rate.[8] In that case, the decrease in relative photocurrent arises since at high fields the carriers reach recombination centers more rapidly, an effect which is particularly effective in 1D. In PDA-TS, however, the sweepout time (or equivalently, the sweepout field) depends on L as noted above. Moreover, the sweepout phenomenon is found *only* when the length of the sample is comparable to the distance that a carrier can travel during its average lifetime. Studies at the same electric field strengths on longer samples with $L=200$ μm do not indicate any change in shape of the waveforms (see Fig. 1).

Having determined the mobility in the tail, we can obtain the $\eta\phi$ product. The photocurrent measured at the beginning of the tail is 1.3×10^{-5} A, resulting from an absorbed photon density of $N=3\times10^{20}$ cm^{-3}. This leads to a value for the photoconductivity of 3×10^{-3} S/cm at ≈4 ns. Using $\sigma=(\eta\phi)\mu eN$, we find $\eta\phi\approx10^{-3}$ at the beginning of the tail. The sweepout experiments with $L=10$ and 2.5 μm indicate a field-independent mobility (within our experimental accuracy). This result and the linear dependence of the photocurrent on E for $L=200$ μm (in the field range of the sweepout measurements) imply a field-independent $\eta\phi$.

The field and temperature independence of $\eta\phi$ are in sharp disagreement with the Onsager theory of geminate recombination. The theory would predict that the quantum yield, which determines the initial photoconductive response, should be limited by the probability to escape geminate recombination: $\eta\phi$ should increase linearly in the applied electric field strength and should decrease exponentially as the temperature is lowered.[1,9] In addition, the carriers which undergo geminate recombination would produce zero net photocurrent (contributions from the geminate electron and hole would cancel). Thus, the rapid decay of the initial peak into the longer-lived tail is not due to geminate recombination. We conclude that, although early-time recombination is clearly important ($\eta\phi=10^{-3}$ at 4 ns), this is not properly described by the Onsager theory of geminate recombination.

Traditionally, the dominant mechanism for recombination (e.g., bimolecular versus monomolecular) has been studied by the measuring of the dependence of the photoconductive response on the illumination intensity. We have measured the intensity dependence of the peak photocurrent as well as $Q_{initial}$ and Q_{tail}. At relatively high intensity ($>10^5$ W/cm^2), the exponents for the peak photocurrent, $Q_{initial}$ and Q_{tail}, are 1.0, 1.1, and 0.74, respectively.[10] In PDA-TS, the precise determination of the recombination mechanisms is made difficult by the known existence of trap levels (significant photoconductivity has been observed for photon energies well below the single-particle energy gap[2]) which can drastically affect the illimination intensity dependence of the photocurrent.[11]

We suggest that the initial fast peak in the photocurrent is due to hot carriers in extended band states that have acquired excess energy due either to the difference in photon excitation energy and the minimum band-state energy at the bottom of the conduction band or to ballistic acceleration of the carriers by the external field prior to the first trapping (or scattering) event. Calculations of the latter effect for traditional semiconductors demonstrate[12] overshoot of the drift velocity in the subpicosecond regime. The larger initial photocurrent would, therefore, be due to a greater drift velocity than that inferred from μE (with $\mu\sim5$ cm^2/V·s) at longer times. If this excess energy is much greater than k_BT, then the lattice temperature is not important to the initial decay rate; rather, the decay comes from a decrease in drift velocity as the hot carriers thermalize. As the carriers thermalize (and recombine), a significant fraction fall into traps that govern their transport at longer times. It is this trap-dominated transport which we associate with the longer-time "tail" photoconductivity. At low temperatures, the probability of emission from traps is drastically reduced and, consequently, the tail should go to zero, in agreement with the experimental observations.

We note that since the sweepout drift velocity in the tail is $\sim2\times10^5$ cm/s, the much higher conductivity in the peak may result from a drift velocity greater than the sound velocity (consistent with hot carriers). This would imply that the time for thermalization to a polaron configuration is in the picosecond regime and may be resolvable with improved experimental techniques.

The inapplicability of Onsager geminate-recombination theory to PDA-TS is perhaps not surprising, since one expects such concepts to be accurate only when the photoexcited carriers are localized. Although localization is to be expected in amorphous materials or in very narrow-band molecular crystals, the broad π bands of conjugated polymers tend toward extensive delocalization.[13] Although a geminate pair can be self-localized by the Coulomb interaction, this effect can play no role if there are no bound excitons (as appears to be the case in polyacetylene[14]). Since bound excitons are known[2] to exist in PDA-TS, geminate recombination may be involved in the initial decay of photoexcitations. Our results on PDA-TS imply, however, that the role of geminate recombination as developed within the Onsager formulation[1,9] (which has been often invoked but seldom

POLARIZATION DEPENDENCE OF TRANSIENT PHOTOCONDUCTIVITY IN TRANS-POLYACETYLENE

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ABSTRACT: We present the results of a series of measurements of the polarization dependence of the transient photoconductive response in both oriented and non-oriented trans-polyacetylene. Our results indicate that in non-oriented samples the short time photoconductivity is dominated by intrachain absorption and intrachain transport, while in oriented samples both interchain and intrachain photogeneration (with different absorption depths) of charge carriers are important. In oriented samples the photoconduction due to interchain excitation is slightly larger than that due to intrachain excitation.

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samples at low temperature) another peak appears in the photoinduced absorption which is delayed by approximately 40 ps relative to the initial peak. This peak is larger when the pump and probe polarizations are orthogonal than when they are parallel. This has been interpreted as evidence for charged soliton formation by a secondary process[6] in which the initial excitations are polarons created through interchain absorption.

Both of these experiments take advantage of the fact that even though the samples are macroscopically isotropic, they are microscopically anisotropic. When an electron - hole pair is generated via photon absorption, the excitation rapidly self localizes (i.e. forms a soliton or polaron)[7]. Thus, for short times, the excitation retains a memory of the chain segment on which it was created.

This paper presents the results of a series of transient photoconductivity measurements which probe the anisotropy of photocarrier generation and transport in *trans*-$(CH)_x$. The first section will deal with experiments performed on non-oriented samples. The results of these measurements show that photogeneration proceeds primarily through intrachain processes and (at short times) transport is along the chain. The second section is devoted to oriented samples. Again, transport is along the chain; however, in this case it is possible to have interchain generation with relatively high quantum efficiency. The final section will address the origin of this apparent difference between the two types of samples.

2. PHOTOGENERATION AND TRANSPORT IN NON-ORIENTED SAMPLES

Polarized fast transient photoconductivity in non-oriented samples of *trans*-$(CH)_x$ can loosely be viewed as pump and probe experiments in which the probe is the dc bias field. This field defines a unique direction along the sample, and the direction of the polarization of the optical field can be varied with respect to this direction. The measured photocurrent and the component of this velocity along the bias field is

$$v_E \propto \cos^2(\Theta) \ . \tag{3}$$

Thus the photocurrent due to chains with this orientation may be written as

$$I_P \propto \left\{\alpha_{\|}\eta_{\|}\cos^2(\Theta-\Phi)+\alpha_{\perp}\eta_{\perp}\sin^2(\Theta-\Phi)\right\}\cos^2(\Theta) \ . \tag{4}$$

Note that those chains which are oriented parallel to the bias field will be the most effective for carrying current. If intrachain photogeneration dominates, then light polarized parallel to the static field will favor creation of carriers on these chains, and if interchain photogeneration dominates then light polarized perpendicular to the static field will dominate creation of carriers on these chains.

The above analysis is not expected to apply for all of the *trans*-$(CH)_x$ chains since structural studies indicate that approximately 80% of the material is crystalline and the remaining fraction is amorphous. The contribution of the amorphous regions to the photoconductivity is expected to be isotropic and will tend to decrease the overall anisotropy. Assuming the photoconductivity due to the amorphous regions is equivalent to that of the crystalline portions Eq. (4) becomes

$$I_p \propto (1-f)\left\{\alpha_{\|}\eta_{\|}\cos^2(\Theta-\Phi)+\alpha_{\perp}\eta_{\perp}\sin^2(\Theta-\Phi)\right\}\cos^2(\Theta)+f \tag{5}$$

where f is the amorphous fraction. Averaging over all orientations in the plane then yields

$$I_P(\Phi) \propto \frac{1}{8}(1-f)\left\{\alpha_{\|}\eta_{\|}[1+\cos^2(\Phi)]+\alpha_{\perp}\eta_{\perp}[1+\sin^2(\Phi)]\right\}+\mathrm{f} \tag{6}$$

and the ratio of the photocurrent for polarization parallel to the field to that for polarization perpendicular to the field is

$$\frac{I_P(0)}{I_P(90)} = \frac{(1-f)\left(3\alpha_{\|}\eta_{\|}+\alpha_{\perp}\eta_{\perp}\right)+8f}{(1-f)\left(\alpha_{\|}\eta_{\|}+3\alpha_{\perp}\eta_{\perp}\right)+8f} \ . \tag{7}$$

The dependence of the peak photocurrent on polarization direction for a typical sample is shown in Fig. 2. The angle between the bias field and the polarization of the optical field is Φ. The solid line is a fit to the functional form

$$I_P(\Phi) \propto A[1 + B\cos^2(\Phi + C)] \tag{9}$$

where the values of the coefficients A,B, and C are 0.5, 0.9, and -2° respectively. Using these values, the anisotropy ratio (defined as the ratio of the peak photocurrent with polarization parallel to the bias field, to that with polarization perpendicular to the bias field) for this sample is $\frac{I_P(0)}{I_P(90)} = 1.9$. This value varied slightly from sample to sample but (for all thin samples) was in the range $\frac{I_P(0)}{I_P(90)} = 1.8 \pm 0.1$. For samples which were obviously thicker this ratio was somewhat smaller.

Using a cw light source and a chopper, the cw photoconductive response was also measured on the same samples. In contrast to the transient response, the cw photocurrent was isotropic to within 5%. Thus at later times the excitations have "forgotten" their initial polarization. This is in agreement with the decay of photoinduced dichroism at times beyond a few nanoseconds.

The fact that the photocurrent is almost twice as large when the light is polarized parallel to the static field suggests two possibilities for the photoconduction. Either the photoexcitations are produced as a result of intrachain absorption and transport occurs primarily along the chain or they are produced as a result of interchain excitation and transport occurs primarily perpendicular to the chains. The second possibility is ruled out since the photoconductive response has been shown to be at least 50 times larger when the static field is parallel to the chain[10]. Further, the close agreement between the photoconductivity anisotropy ratio and the anisotropy ratio measured in the midgap photoinduced absorption experiments[5] indicates that both experiments are looking at the same excitation, the soliton. Thus, the origin of photoconduction in *trans*-$(CH)_x$ is function of the polarization direction[2]. With light polarized parallel to the chain direction the reflectivity is $R_{||} \sim 0.5$ while the reflectivity for light polarized perpendicular to the chain is approximately $R_{\perp} \sim 0.05$. Thus, corrections must be made for the number of absorbed photons. Since the sample is optically thick for both polarizations the correction factor is

$$\frac{(1 - R_{\perp})}{(1 - R_{||})} \approx 2 \; . \tag{10}$$

After these corrections are made there is very little anisotropy left in the transient photocurrent. The anisotropy which remains after correcting for reflectivity still favors perpendicular polarization. It must also be remembered that the absorption depths for the two different polarizations are very different. This means that (all other things being equal) the density of photoexcited carriers will be much greater within the optical absorption depth for the parallel polarization. Thus, any bimolecular recombination processes will be more important for the parallel case.

As in the non-oriented case, the shape of the waveforms was independent of the polarization direction. Also, both polarizations have the same intensity dependence (linear). We are left with the conclusion that there is very little difference between the photocurrents due to the two different polarization states.

It is reasonable to assume that parallel polarization favors intrachain excitation of electron-hole pairs (and subsequently soliton pairs), while perpendicular polarization leads to the generation of interchain electron - hole pairs (and subsequently polarons). If this assumption is correct, our results then indicate that one of two situations must be occurring: either the photoconductivity related properties (e.g. mobility along the chain) of solitons and polarons are similar, or one type of excitation is rapidly converted to the other (i.e. polarons rapidly recombine to form solitons). However, with these results alone it is not possible to determine which of these is more important.

anisotropy in the absorption coefficient and the high degree of alignment of the Durham samples.

The anisotropy ratio of the absorption coefficient in *trans*-$(CH)_x$ has been estimated[2] as $\frac{\alpha_{\parallel}}{\alpha_{\perp}} \approx 25$. Thus, while samples of thickness $\sim$ 1000 Å may be relatively thick for light polarized parallel to the chain they are still thin for light polarized perpendicular to the chain. When light propagates through such a sample of non-oriented polyacetylene, any chains which are oriented with an angle less than $\cos^{-1}(0.2) \approx 80°$ to the polarization direction will have a greater probability of absorbing a photon through intrachain absorption than interchain absorption. The result is that a very small fraction of the photons are absorbed due to interchain processes. In fact the ratio of the number of photons absorbed via intrachain processes to that for interchain processes is (assuming the chains orientations are randomly distributed in two dimensions) given by the ratio of the absorption coefficients. As a consequence, experiments on non-oriented *trans*-$(CH)_x$ are dominated by intrachain absorption consistent with the results obtained in the photoconductivity experiment.

In contrast, the high degree of alignment in stretch oriented Durham polyacetylene allows one to overcome the large anisotropy in the absorption coefficients and "force" the photons to be absorbed via interchain absorption. With these materials it should be possible to compare the behavior of solitons and polarons. The differences between these two excitations, as they relate to photoconductivity, appear to be very small. The slight anisotropy which exists indicates that interchain absorption is more efficient for producing photoconductivity.

5. CONCLUSIONS

In conclusion, we have measured the polarization dependence of the photoconductive

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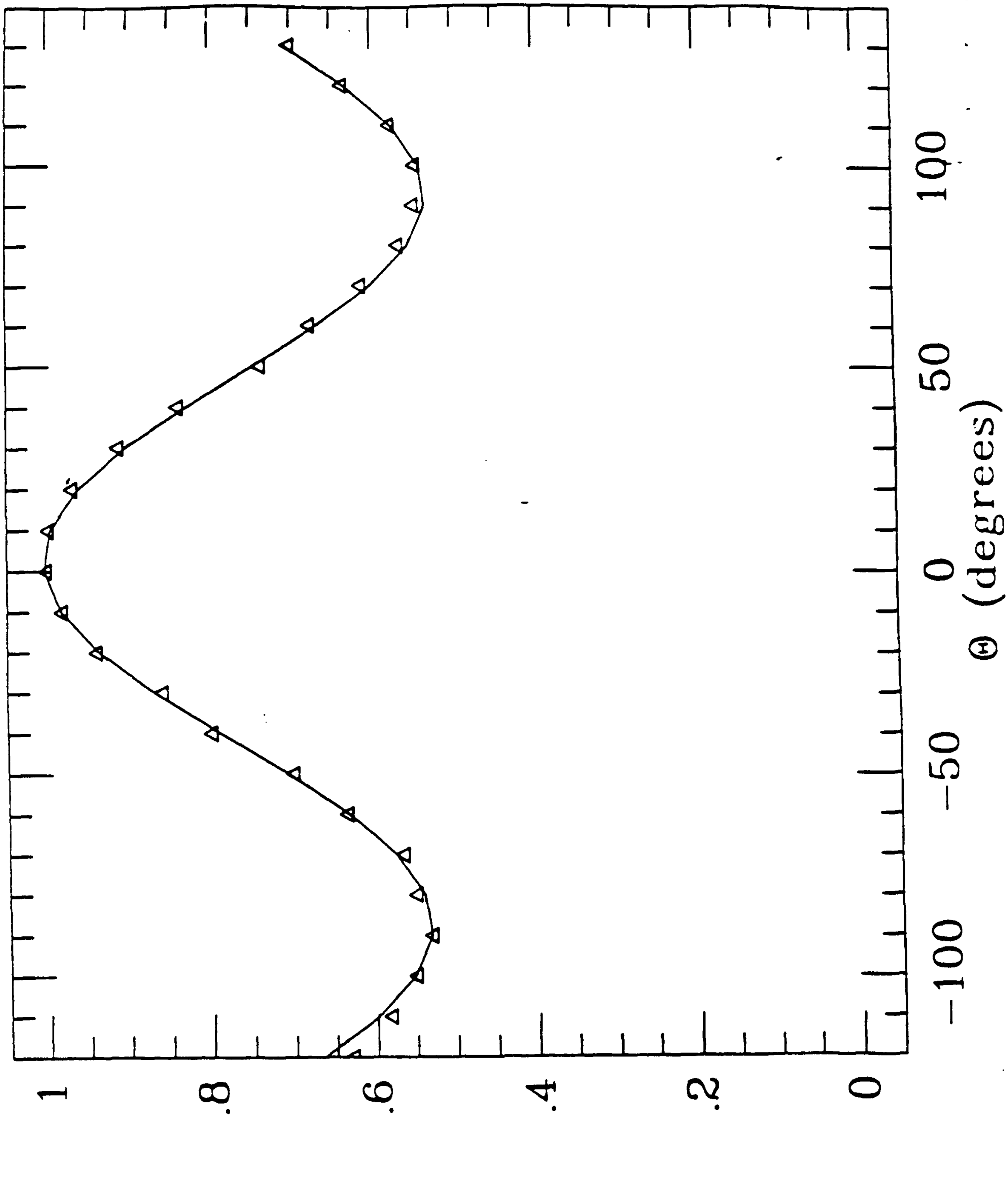
FIGURE CAPTIONS

Figure 1: Schematic diagram showing relative orientations of a typical *trans*-$(CH)_x$ chain, the polarization of the incident light, and the dc electric field.

Figure 2: Dependence of the peak photocurrent on polarization direction for a non-oriented (isotropic) sample.

Figure 3: Dependence of the peak photocurrent on the polarization for an oriented sample; for $\Theta = 0$, the polarization is parallel to the applied field (and parallel to the chain direction).

Figure 2: Dependence of the peak photocurrent on polarization direction for a non-oriented (isotropic) sample.



ANISOTROPY OF THE THIRD ORDER NONLINEAR OPTICAL SUSCEPTIBILITY IN A DEGENERATE GROUND STATE CONJUGATED POLYMER; TRANS-$(CH)_x$

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Abstract

We present the results of a series of third harmonic generation (THG) measurements on the conjugated polymer polyacetylene which probe the magnitude and the origin of the third order nonlinear optical susceptibility of this material. By performing reflection THG measurements relative to a silicon standard, we have unambiguously determined the magnitude of the third order susceptibility associated with tripling the fundamental of the Nd:YAG laser to be $\chi_{\parallel}^{(3)}(3\omega;\omega,\omega,\omega) = (4 \pm 2) \times 10^{-10}$ esu, where $\chi_{\parallel}^{(3)}$ refers to that component of the third order susceptibility tensor with all indices parallel to the chain direction. By measuring anisotropic THG in oriented films, we have shown that this component dominates. The magnitude and anisotropy are directly compared with results obtained from single crystals of polydiacetylene-(toluene-sulfonate) measured in the same apparatus. Finally, we have measured THG in both cis-rich and trans isomers of the same sample. We found that the measured response of the cis-rich samples scales with the residual trans content of the sample, indicating that $\chi_{\parallel}^{(3)}$ of the trans isomer is at least an order of magnitude larger than that of the cis isomer. This symmetry specific aspect of $\chi_{\parallel}^{(3)}$ implies a mechanism which is sensitive to the existence of a degenerate ground state, as in trans-$(CH)_x$; it is consistent with the virtual

I. INTRODUCTION

Although organic polymers have great potential for eventual application in nonlinear optical elements, an understanding of the mechanism (or mechanisms) underlying their nonlinear susceptibilities is necessary before the design and synthesis flexibility afforded by organic chemistry can be applied to the development of new and better materials. Detailed experimental studies of prototype systems must therefore be performed in order to guide a parallel theory effort aimed at a general understanding of the nonlinear optical properties of organic polymer materials.

The promise of conducting polymers as fast response nonlinear optical materials has been recently emphasized[1-3]. Polymers such as polyacetylene, polythiophene and the soluble (and processible) poly(3-alkylthienylenes) contain a high density of π-electrons, and they are known to exhibit photoinduced absorption and photoinduced bleaching, indicating major shifts of oscillator strength upon photoexcitation[2,4]. For polyacetylene, these nonlinear effects have been studied in detail in the picosecond[5a,b] and sub-picosecond[5c] time regime and correlated with the photoproduction of charge carriers through fast photoconductivity measurements[6]. The data have demonstrated ultra-fast response with nonlinear shifts in oscillator strength occurring at times of the order of 10^{-13} seconds. These resonant nonlinear optical properties are intrinsic; they originate from the nonlinearity of the self-localized photoexcitations[7] which characterize this class of polymers: solitons, polarons and bipolarons[4].

In any material where photoexcitation results in shifts of oscillator strength (as is the case in conducting polymers), the optical properties will be highly nonlinear. The magnitude of the resonant $\chi^{(3)}$ can be estimated from the magnitude and frequency dependence of the photoinduced absorption and reflection THG measurements relative to a silicon standard, we have unambiguously determined the magnitude of the third order susceptibility associated with tripling the fundamental of the Nd:YAG laser to be $\chi_{\parallel}^{(3)}(3\omega;\omega,\omega,\omega) = (4 \pm 2) \times 10^{-10}$ esu, where $\chi_{\parallel}^{(3)}$ indicates that component of the third order susceptibility tensor with all indices parallel to the chain direction. We have successfully measured the anisotropic THG in oriented thin films and demonstrated that all the nonlinearity is associated with the π-electron polarizability along the conjugated chain. The magnitude and anisotropy are directly compared with the results obtained from single crystals of polydiacetylene-(toluene-sulfonate), PDA-TS, measured simultaneously and in the same apparatus. When pumping at 1.06 μm (1.17 eV), the third harmonic power generated (on reflection) from a cleaved single crystal of PDA-TS is about a factor of two greater than that from an oriented film of trans-$(CH)_x$. Finally, we have measured THG in cis-rich and trans isomers of the same sample. The measured response the cis-rich samples scales with the residual trans content of the sample, indicating that $\chi_{\parallel}^{(3)}$ of the trans isomer is at least an order of magnitude larger than that of the cis isomer. This symmetry specific aspect of $\chi_{\parallel}^{(3)}$ implies an underlying mechanism which is sensitive to the existence of a degenerate ground state, as in trans-$(CH)_x$. The large $\chi_{\parallel}^{(3)}$ when pumped sub-gap is therefore consistent with the virtual generation of nonlinear solitons as a mechanism for the nonlinear optical susceptibility of polyacetylene. This mechanism is developed and discussed in detail; we conclude that the nonlinear zero point fluctuations of the ground state lead to an important mechanism for nonlinear optics, particularly in polymers with a degenerate ground state.

sample and the reference under identical conditions, then one can determine the unknown $\chi^{(3)}$ using the following relation

$$\frac{P_s}{P_r} = \frac{|\chi_s^{(3)}|^2 F_s}{|\chi_r^{(3)}|^2 F_r} \tag{5}$$

for the ratio.

The experimental arrangement used to measure the third harmonic intensity is shown in Fig. 1. It consists of a mode-locked Nd:YAG laser and fiber-grating pulse compressor which produce an 82 MHz train of pulses with autocorrelation FWHM of 4.5 ps and ~5 KW peak power. A half-wave plate and polarizing cube were used as a variable attenuator, and the beam was directed onto the sample by means of a dichroic filter which was chosen to have high reflectivity at λ = 1.06 µm and high transmissitivity at λ = 355 nm. The fundamental beam was focused to a spot size of ~ 30 µm at the sample by a converging lens which also served to recollimate the reflected third harmonic. After recollimation, the third harmonic passes through the dichroic filter and the notch filter to reach the photomultiplier tube. A recollimating lens and dichroic filter were also mounted after the sample so that third harmonic generation could also be measured in the transmission mode. The fundamental beam was chopped, and lock-in detection was used to measure the output of the photomultiplier tube. For the polarization dependence measurements, an additional half-wave plate was inserted between the dichroic filter and the focusing lens to allow the polarization of the fundamental beam to be rotated at the sample.

III. MAGNITUDE AND ANISOTROPY OF $\chi^{(3)}$ FOR TRANS-$(CH)_x$ AND FOR PDA-TS: A DIRECT COMPARISON

The third harmonic power reflected from the (glass side) surface of the oriented trans-$(CH)_x$ samples (when the polarization of the fundamental beam is parallel to the alignment direction of the sample) is approximately 2000 times larger than the power reflected from the surface of intrinsic silicon under identical conditions. Assuming that the optical properties of the oriented samples are those determined for oriented Durham trans-polyacetylene[11], the appropriate optical constants are as follows:

for silicon[12]

$$N_1 = \sqrt{\varepsilon_1} = 3.55 \text{ and } N_3 = \sqrt{\varepsilon_3} = 5.55 + i3.04;$$

for trans-$(CH)_x$ [13]

$$N_1 = \sqrt{\varepsilon_1} = 3.8 \text{ and } N_3 = \sqrt{\varepsilon_3} = 0.7 + i1.4.$$

Using these values and Eq. 4 yields $F_{(CH)x} = 3.4 \times 10^{-2}$ for trans-$(CH)_x$ and $F_{Si} = 2.4 \times 10^{-4}$ for silicon. Finally, with the help of Eq. 5 we calculate

$$\chi_{\parallel}^{(3)} = [P_{(CH)x}/P_{Si}]^{1/2}\,[F_{Si}/F_{(CH)x}]^{1/2}\chi_{Si}^{(3)} \tag{6}$$

or

$$\chi_{\parallel}^{(3)} \approx 4\chi_{Si}^{(3)} = (4 \pm 2) \times 10^{-10} \text{ esu} \tag{7}$$

where we have used $\chi_{Si}^{(3)} \approx 10^{-10}$ esu.

We have estimated the error bars in eqn. 7 based on the repeatability of the result from measurement to measurement. The main source of error in this determination of $\chi_{\parallel}^{(3)}$ is sample inhomogeneity (i.e., the magnitude of the

For comparison, we have measured the magnitude and the polarization dependence of the third harmonic power from a single crystal of PDA-TS. The magnitude was obtained in a relative measurement in which the polydiacetylene third harmonic power was directly compared to that from a trans-$(CH)_x$ samples (both oriented and non-oriented) which were in turn referenced to silicon.

The third harmonic power reflected from the PDA-TS sample varied considerably as a function of position on the sample surface. These variations were attributed to surface roughness of the PDA polymer crystal. Since the reflection technique depends critically on surface quality, the spots yielding the highest third harmonic (and hence the best surface quality) were used. The reflected third harmonic power was reproducible from "good" spot to "good" spot. For polyacetylene, the response was somewhat more uniform.

We found that the third harmonic power generated on reflection from single crystal PDA-TS was about a factor of two larger than that from oriented trans-polyacetylene. In order to complete the comparison between the nonlinear susceptibilities of these two materials, accurate values of their linear optical constants are required. If we take $N_1 \approx 2$ for PDA-TS and assume that the two materials have the same N_3, then $\chi_{\parallel}^{(3)}$ of trans-$(CH)_x$ is somewhat larger than that of PDA-TS. More precise measurements of these linear optical constants are currently under way.

In evaluating the comparison between these two conjugated polymers, one must note that this measurement tends to favor PDA-TS since the "good" spots on a cleaved single crystal surface should be of much higher surface quality than the surface of a (fibrillar) polyacetylene film. Moreover, with the incident beam at 1.06 μm (1.17 eV), the third harmonic response of trans-$(CH)_x$ is at a minimum between strong resonances[3] in $\chi^{(3)}$. As a result, $\chi_{\parallel}^{(3)}$

IV. SYMMETRY SPECIFIC ORIGIN OF $\chi^{(3)}$: COMPARATIVE MEASUREMENTS OF $\chi^{(3)}$ IN CIS AND TRANS-POLYACETYLENE

Polyacetylene is unique in that it can be prepared in two different forms: cis-polyacetylene and trans-polyacetylene; these two different isomers are shown in Fig. 4. The existence of these two different isomers with different symmetry allows one to explore the specific origin of observed phenomena. Trans-$(CH)_x$ has a two-fold degenerate ground state and can support solitons as the fundamental nonlinear excitations[15]. In cis-$(CH)_x$, this ground state degeneracy has been lifted so that for the cis isomer the important nonlinear excitations are polarons and bipolarons. Thus, for example, subsequent to resonant (interband) photoexcitation, the shifts in oscillator strength will be quite different in the two cases. Moreover, the implied changes in the nonlinear optical properties (bigger shifts in oscillator strength imply larger $\chi^{(3)}$) due to this fundamental change in polymer symmetry can be probed on the same physical sample; conversion from cis- to trans-$(CH)_x$ can be accomplished simply by heating the sample to ≈ 150° C for about 1/2 hour.

Films of cis-$(CH)_x$ were synthesized using the Shirakawa method. By carrying out the polymerization and subsequent washing etc. at - 78° C, nearly 100% cis-$(CH)_x$ can be obtained. The cis-$(CH)_x$ samples were prepared as thick films (several microns in thickness) on pre-cut glass substrates made to fit into the sample holder on the cold-finger of the cryostat used for the nonlinear optical measurements.

Unfortunately, the transfer of the sample from the synthesis reactor to the measurement cryostat required bringing the sample to room temperature. Since partial conversion to the trans-$(CH)_x$ isomer is unavoidable when the temperature of the polyacetylene film is raised, our initial experiments were designed to minimize the time period at room temperature. By coordinating the that of trans-$(CH)_x$ by a factor of approximately 40. The results are consistent with negligible contribution to $P(3\omega)$ from the cis-$(CH)_x$ portion of the sample. After including the measurement uncertainties in $P(3\omega)$ and in the determination of the cis-trans content, we conclude that $\chi^{(3)}(\omega,\omega,\omega)$ for cis-$(CH)_x$ is at most one-tenth of that of trans-$(CH)_x$. This upper limit can be improved in future experiments by further reduction of trans-content in the initial measurement (before isomerization). In order to accomplish this, we have initiated plans for the construction of a synthesis reactor cell which is compatible with in-situ measurement of $\chi^{(3)}$, thus avoiding the need to transfer the sample.

If the mechanism for the nonlinear optical response is related to virtual production of the nonlinear excitations of the polymer as argued in the Introduction, conversion from cis-$(CH)_x$ to trans-$(CH)_x$ should have a major effect. The experimental results presented in the preceding paragraphs are consistent with this hypothesis.

V. DISCUSSION OF THE MECHANISM: $\chi^{(3)}$ FROM VIRTUAL SOLITONS ENABLED BY QUANTUM ZERO-POINT FLUCTUATIONS OF THE POLYMER CHAIN

The anisotropy of the THG for both trans-$(CH)_x$ and PDA-TS demonstrates that the nonlinearity is entirely associated with the nonlinear polarizability of the π-electrons in the conjugated polymer backbone. The nearly identical magnitude of the third harmonic response in these two materials is quite remarkable in the context of traditional explanations[16] in which the mechanism for nonlinear optical response is nonlinear polarizability of the delocalized π-electrons within a rigid lattice (and a rigid band structure). In this point of view, the third order susceptibility would be strongly dependent

The data of Figs. 2 and 3 demonstrate that the nonlinear susceptibility is polarized entirely along the polymer backbone. Thus, in comparing $\chi_{\parallel}^{(3)}$ for cis- and trans-$(CH)_x$, one should consider the one-dimensional gaps for intrachain π-π^* excitation; for cis- and trans-$(CH)_x$, these are nearly equal. For trans -$(CH)_x$, $E_g(1d) \approx 1.7$ eV has been estimated from resonant Raman scattering[21] and 1.9 eV from a fit of the absorption tail arising from anharmonic quantum fluctuations of the lattice[20]. For *cis* -$(CH)_x$ the 1d gap is about 2 eV. Therefore, the major difference in $\chi^{(3)}$ for the two isomers of polyacetylene appears to be larger than can be accounted for in the context of rigid band theory, and it implies a mechanism which is sensitive to the existence of a degenerate ground state.

In attempts directed toward a deeper understanding of the mechanisms for nonlinear optical response of cojugated polymers, it is important to develop the connection between the **nonresonant** nonlinear response for pumping well below the absorption edge to the **resonant** nonlinear response for pumping directly into the principal absorption band. In the polydiacetylene case, Greene et al[22] have analyzed the resonant nonlinear response in terms of phase-space filling by one-dimensional excitons. In a beautiful argument, they showed how the concept of exciton-polaritons could be used to generalize this mechanism to the nonresonant regime well below the exciton absorption edge. For trans -$(CH)_x$, we have shown that for **resonant** pumping, the shifts in oscillator strength due to the photogeneration of charged solitons lead to relatively large changes in the optical constants. In the following paragraphs, we generalize this idea to the nonresonant regime where the nonlinear response is due to virtual soliton-antisoliton pairs.

We consider the effects of quantum lattice fluctuations on the optical properties. Following Yu, Matsuoka and Su[20a], we consider fluctuations in for ω_p above the gap, δn_s time evolves to $\delta n_\infty(\omega)$ which comes from the shift in oscillator strength from the interband transition into the mid-gap transition[2,4,5,23]. Since the time resolved spectroscopy has been thoroughly studied for pumping at $\hbar\omega_p > E_g$, one knows the complete time evolution of $\delta\alpha(\omega)$ and of $\delta n(\omega)$ subsequent to pumping into the interband transition.

If the pump frequency is in the region between 2Δ and $(4/\pi)\Delta$, then one pumps the specific nonlinear configuration s of equation (10) which is resonant with the pump; the excited s-configuration then evolves (in time) following down the excited state energy curve $E_{p'}(s)$ (see Figure 5) toward a well-separated charged soliton pair each with a state at mid-gap. Again, one expects a corresponding δn_s which also evolves with time after the photon is absorbed from that characteristic of the originally pumped $s(t=0)$ evolving to a charged soliton pair each with a state at mid-gap. Pumping at $\hbar\omega_p = 4\Delta/\pi$ directly generates a free soliton pair with a corresponding $\delta n_\infty(\omega)$; when pumping at the soliton pair creation energy, there is no time delay nor any time evolution since the free soliton pair is created directly (although with vanishingly small probability). The above are all resonant processes; they involve a real absorption of photons to form either electron-hole pairs ($\hbar\omega_p > E_g$) or excited s-configurations ($\hbar\omega_p < E_g$) which time-evolve to separated charged soliton pairs. Thus, these resonant processes lead to highly nonlinear optical phenomena with characteristic time evolution and with corresponding changes in the complex index of refraction.

What about truly virtual processes for $\hbar\omega_p$ below the $(4/\pi)\Delta$ threshhold? We argue that

$$\langle \delta n(\omega, \omega_p) \rangle = \Sigma_s(\text{probability of finding a charged configuration s})\delta n_s(\omega).$$

$$[(1/(E_{ng}-3\omega)(E_{mg}-2\omega)(E_{lg}-\omega) + 1/(E_{ng}+\omega)(E_{mg}-2\omega)(E_{lg}-\omega)$$
$$+ 1/(E_{ng}+\omega)(E_{mg}+2\omega)(E_{lg}-\omega) + 1/(E_{ng}+\omega)(E_{mg}+2\omega)(E_{lg}+3\omega)] \quad (13)$$

where $E_{ng}=(E_{s,n} - E_{s,g})$, $E_{s,g}$ is the ground state energy, $E_{s,\alpha}$ (α=n,m,l) are the energies of excited states of the s-configurations, $f_{\alpha\beta}$ are the dipole matrix elements. In eqn. 13, $N_o=n_o\rho_c$ where $n_o=(L/2\xi)$ is the phase space for soliton pairs on a chain of length L, and ρ_c is the density of chains per unit area. In the sum, n and l denote excited states with symmetry opposite to g, and m is an excited state with the same symmetry as g. Yu, Matsuoka and Su[20a] have shown that there are ten vibrational excited states of the s-configuration with the same parity as the ground state which contribute to $\chi_{\parallel}^{(3)}$; one at $\approx$1.8eV and a series of nine others approximately equally spaced below 1 eV. As noted by Su[25], the energies of the two-photon resonances implicit in eqn 13 are in good agreement with the resonant THG response (at 0.9 eV and for $\hbar\omega$<0.5eV)[3].

To estimate the magnitude of $\chi_{\parallel}^{(3)}$ we consider the term in the full sum of eqn. 13 where the matrix elements go from $g \rightarrow E_{p'}(s) \rightarrow g \rightarrow E_{p'}(s) \rightarrow g$; i.e we ignore the various vibrational states of the s-configuration and consider only this single contribution ($\chi_{\parallel}^{(3)}|_0$):

$$\chi_{\parallel}^{(3)}|_0 = N_o\Sigma_{ss'}|\phi_o(s)|^2|\phi_o(s')|^2(|f_s|^2|f_{s'}|^2/2\omega) \times$$
$$[-(1/(E_s-3\omega)(E_{s'}-\omega) + 1/(E_s+\omega)(E_{s'}+3\omega)]. \quad (14)$$

For $3\omega<E_s$

$$\chi_{\parallel}^{(3)}|_0 \approx -!N_o\Sigma_{ss'}|\phi_o(s)|^2|\phi_o(s')|^2(|f_s|^2|f_{s'}|^2/E_s{}^2E_{s'} \quad (15)$$

are indeed in agreement with experiment. These calculations are underway, and the results will be reported separately.

VI. CONCLUSION

We have determined the magnitude of the third order susceptibility associated with tripling the fundamental of the Nd:YAG laser (1.06 μm, 1.17 eV) to be $\chi_{\parallel}^{(3)}(3\omega;\omega,\omega,\omega) = (4 \pm 2) \times 10^{-10}$ esu, where $\chi_{\parallel}^{(3)}$ refers to that component of the third order susceptibility tensor with all indices parallel to the chain direction. By measuring anisotropic third harmonic generation in oriented films, we have shown that this component dominates. The magnitude and anisotropy were directly compared with results obtained from single crystals of polydiacetylene-(toluene-sulfonate) measured in the same apparatus. The third harmonic power generated by PDA-TS was found to be about a factor of two greater than that of trans-$(CH)_x$ (for pumping at 1.06 μm). The anisotropy of the THG for both trans-$(CH)_x$ and PDA-TS demonstrates that the nonlinear optical properties are entirely associated with the nonlinear polarizability of the π-electrons in the conjugated polymer backbone.

The close agreement between the THG in trans-$(CH)_x$ and PDA-TS was inferred to be simply accidental; the nonlinear mechanisms in the two cases are different, and in neither case is the conceptually simple nonlinearity arising from the rigid band structure in third-order perturbation theory the dominant mechanism.

Third harmonic generation was measured in both cis-rich and trans isomers of the same sample (before and after thermal isomerization). The measured response of the cis-rich samples was found to scale with the residual trans content, indicating that $\chi_{\parallel}^{(3)}$ of the trans isomer is at least an order of magnitude larger than that of the cis isomer.

fluctuations of the ground state lead to an important mechanism for nonlinear optical properties, particularly in polymers with a degenerate ground state. Lifting the ground state degeneracy suppresses the nonlinear response, in agreement with our experimental results. In addition, the usual interband transitions (i.e. virtual electron-hole pairs) can be expected to contribute to $\chi_{\parallel}^{(3)}$. An important goal of future work will be to sort out the relative importance of the two processes in order to understand the large nonlinear susceptibility of trans-polyacetylene and in order to guide the development of new and better materials.

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FIGURE CAPTIONS:

Figure 1: Schematic diagram of the experimental arrangement used to measure the third harmonic intensity.

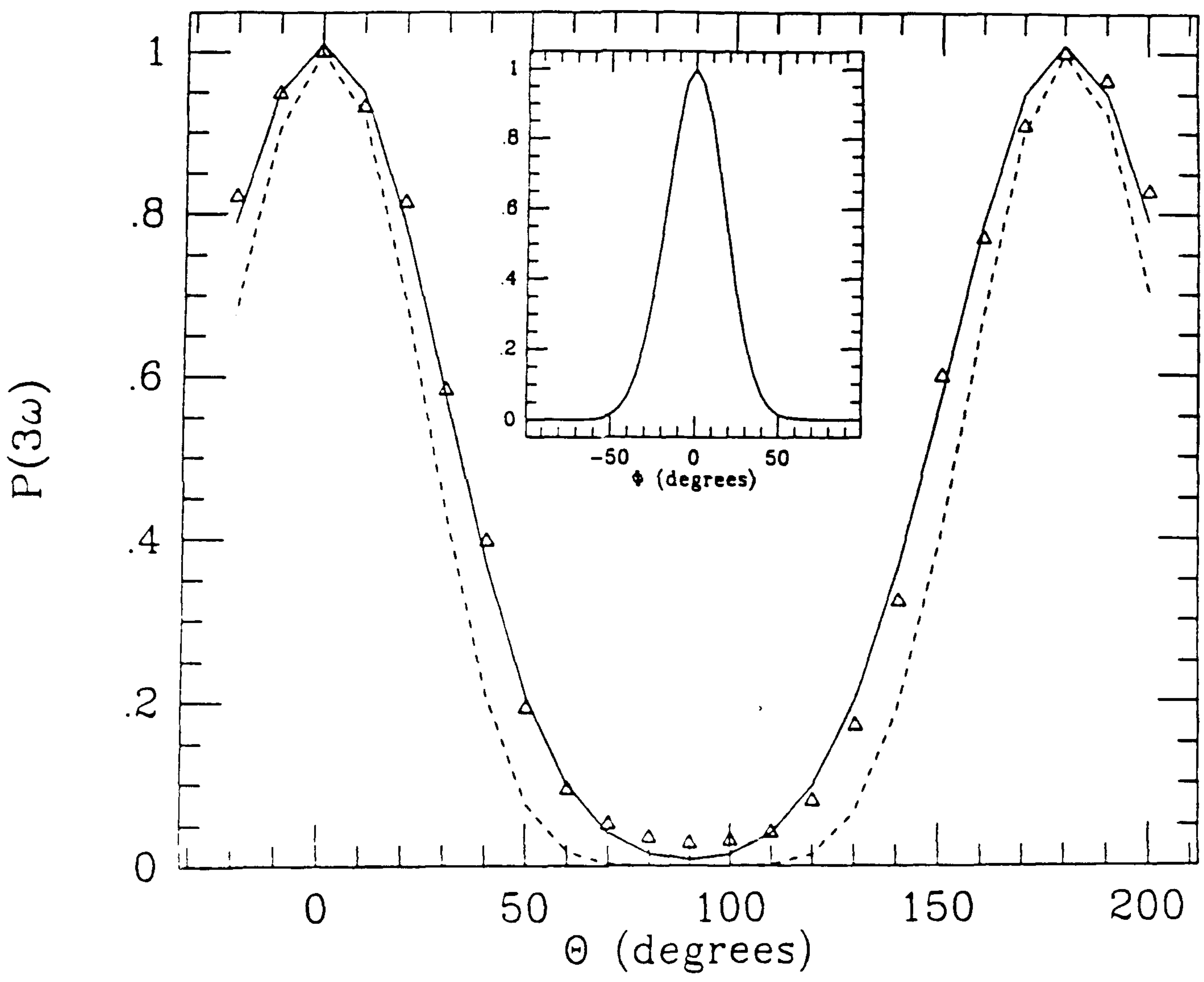
Figure 2: The polarization dependence of third harmonic generation from an aligned sample. The dashed curve shows the type of behavior expected for a perfectly aligned one-dimensional system ($\cos^6\Theta$); the solid line represents the best fit of the functional form of Eq. 9 to the data. The value of Φ_0 which achieves best fit corresponds to a chain orientation distribution (a gaussian as shown in the inset) with FWHM of 40°.

Figure 3: The polarization dependence of the THG from PDA-TS ; the third harmonic power from the polydiacetylene crystal accurately follows the $\cos^6\Theta$ relation.

Figure 4: Chemical structure diagrams of the two different isomers of polyacetylene.

Figure 5: a. Sketch of the fluctuations in the staggered order parameter described by the one-parameter family of configurations: $\phi(x=na) = \phi_0\{1 - \tanh(2s/\xi)[\tanh(x-s/\xi) - \tanh(x+s/\xi)]\}$

b. Adiabatic potential curves for the electronic ground state (a) and first excited state (b) as a function of s for the configuration of Fig. 5a (from ref. 20a)



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Θ (degrees)
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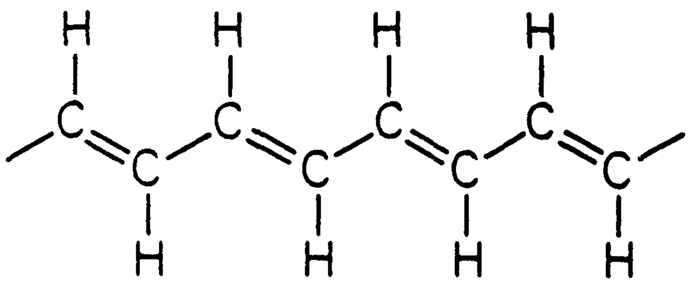
.6
.4
.2
0
50
100
150
200
-50



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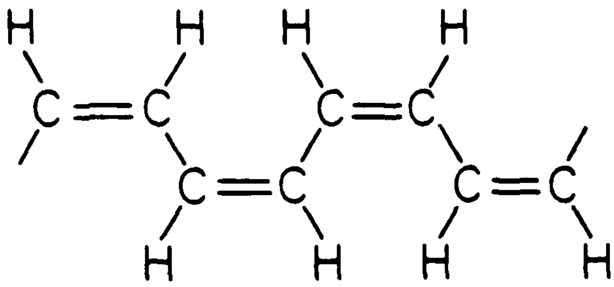

CIS

"Instantons" as the Origin of the Nonlinear Optical Properties of Polyacetylene

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Abstract

Third harmonic generation (THG) is used to probe the nonlinear susceptibility ($\chi^{(3)}$) of polyacetylene. The magnitude of $\chi^{(3)}(3\omega;\omega,\omega,\omega)$ is $(4\pm2)\times10^{-10}$ esu with $\hbar\omega=1.17$eV; the only important component of $\chi^{(3)}$ is that associated with π-electron motion along the polymer backbone. Comparison of THG in cis- and trans-$(CH)_x$ shows that $\chi_{\parallel}^{(3)}|_{trans}$ is 15-20 times larger than $\chi^{(3)}|_{cis}$. The symmetry specific $\chi_{\parallel}^{(3)}$ implies a mechanism sensitive to the existence of a degenerate ground state, consistent with nonlinear zero-point fluctuations ("instantons") as the origin of $\chi^{(3)}$. We show that the results are consistent with theory based on virtual generation of solitons enabled by instantons.

For anisotropy measurements, aligned films of trans-$(CH)_x$ were grown on glass by suspending the catalyst in a liquid crystal solvent[4]; the reaction was carried out with the liquid crystal oriented in the 1 tesla field of an electromagnet. The film thickness for reflection measurements was $\sim 1 \mu m$. The comparative cis-trans measurements used films prepared on glass by the standard Shirakawa method.

The third harmonic power, $P(3\omega)$, reflected from oriented trans-$(CH)_x$ (polarization at ω parallel to the alignment direction) is ≈ 2000 times larger than that from silicon under identical conditions. Using the optical constants of silicon[3] ($n_1=3.55$, $n_3=5.55+i3.04$) and oriented trans-$(CH)_x$[5], ($n_1=3.8$, $n_3=0.7+i1.4$), and assuming[3] $\chi^{(3)}|_{Si} \approx 10^{-10}$ esu, we obtained $\chi_{\parallel}^{(3)} = (4 \pm 2) \times 10^{-10}$ esu. The estimated error arises from sample inhomogeneity; $P(3\omega)$ varied somewhat from place to place on the sample.

Fig. 1 shows the polarization dependence of $P(3\omega)$. Assuming perfectly oriented $(CH)_x$ chains and that the only significant component of the tensor is $\chi_{\parallel}^{(3)}$, $P(3\omega)$ is expected to vary as $|\chi^{(3)}\cos^3\Theta|^2$ where Θ is the angle between the chain and polarization directions (dashed curve in Fig. 1). For comparison, we measured the magnitude and polarization dependence of $P(3\omega)$ from a single crystal of PDA-TS; $P(3\omega)$ was about a factor of two larger than that from oriented trans-$(CH)_x$, and varied[1,6] as $\cos^6\Theta$. Since the response of trans-$(CH)_x$ increases at lower frequencies[7], $\chi^{(3)}$ for trans-$(CH)_x$ is larger than that of PDA-TS for longer wavelengths. To our knowledge, this is the first direct comparison of $\chi_{\parallel}^{(3)}$ for the two materials.

Since the polarization dependence of the PDA-TS results accurately follows the $\cos^6\Theta$ relation, the deviations from the $\cos^6\Theta$ dependence in Fig. 1 are the result of imperfect chain alignment in partially oriented trans-$(CH)_x$ samples. To account for this, we have fit the data to a model which incorporates a gaussian distribution of chain orientations. Specifically, we assume that the total response can be written as a sum from chains which are oriented at an angle Φ with respect to the alignment direction;

two materials is remarkable in the context of traditional explanations in which the mechanism is nonlinear polarizability of the delocalized π-electrons within a rigid lattice (and a rigid band structure)[10]. For this mechanism, $\chi^{(3)}$ must be strongly dependent on the magnitude of the single particle energy gap (~ the sixth power). This is certainly not true for the results described above.

The onset of absorption in trans -$(CH)_x$ is well below that of PDA-TS. More importantly, the absorption edge at ~2eV in PDA-TS is due to a neutral exciton[11]; the interband transition is at 2.4 eV[12]. For trans -$(CH)_x$, the onset of absorption at ~1.5 eV is due to an interband transition broadened on the leading edge by dynamical effects and by disorder. In trans -$(CH)_x$, the onset of photoproduction of solitons coincides with the onset of photoconductivity[13] and absorption[14] demonstrating that there is no bound exciton. The sub-gap absorption below 2 eV in trans -$(CH)_x$ is consistent with the mechanism in which the absorption tail is caused by the anharmonic quantum fluctuations of the lattice[2,15]. We conclude that the comparable THG in trans -$(CH)_x$ and PDA-TS is accidental; the mechanisms in the two cases are different, and in neither case does the nonlinearity arise from nonlinear polarizability of the delocalized π-electrons in a rigid band structure.

The single particle energy gaps of cis - and trans -$(CH)_x$ are relatively close; for trans -$(CH)_x$, $E_g(1d) \approx 1.7$-1.9 eV, whereas for cis -$(CH)_x$ the 1d gap is ≈ 2.0-2.2 eV[9]. Thus, the major difference in $\chi^{(3)}$ for the two isomers implies a mechanism which is sensitive to the existence of a degenerate ground state. We, therefore, consider the effects of instantons (which are present only in the case of a degenerate ground state) on the optical properties. The fluctuations in the staggered order parameter $\phi_n = (-1)^n u_n$ are described by the one-parameter family of configurations[2] (see Fig. 2a):

$$\phi(x=na) = u_o\{1 - \tanh(2x_o/\xi)[\tanh(x-x_o/\xi) - \tanh(x+x_o/\xi)]\} \qquad (2)$$

where $E_{ng}=(E_n - E_o)$, and $f_{\alpha\beta}$ are the dipole matrix elements. In eqn 3, $N_o \approx n_o \rho_c$ where n_o is the average number of $S\bar{S}$ pairs on a chain of unit length, and ρ_c is the density of chains per unit area. Monte Carlo simulations[18] have shown that the reduction of the dimerization order parameter is about 15%. Since this is also approximately the reduction in average order parameter in a polyacetylene ring of size 4ξ (just large enough to contain an $S\bar{S}$ pair), we estimate $n_o=1/4\xi$. In the sum, n and l denote excited states with symmetry opposite to g, and m is an excited state with the same symmetry as g. The excited states are in product form, $\psi(s)\zeta(s)$ where $\psi(s)$ is a vibrational eigenstate and $\zeta(s)$ is the many-electron wave function associated with the classical lattice configuration s. Thus, the matrix elements factorize into an electronic dipole matrix element and an overlap integral, as in the usual Born-Oppenheimer approximation. <u>We emphasize that the lattice overlap integral would be zero, except for the instantons in the ground state</u>. Although interband transitions (virtual electron-hole pairs dressed with phonons)[19] are also expected to contribute to $\chi_{\parallel}^{(3)}$, we sum over the non-classical bound vibrational states only, since we find that this contribution is an order of magnitude larger than the contribution from the band states.

To estimate the magnitude of the instanton mechanism, we consider initially the single term with matrix elements f_s from $g \rightarrow E_{p'}(s) \rightarrow g \rightarrow E_{p'}(s) \rightarrow g$ $(\chi_{\parallel}^{(3)}|_0)$; for $3\omega < E_s$, $\chi_{\parallel}^{(3)}|_0 \approx -4N_o\Sigma_{ss'}|\psi_o(s)|^2|\psi_o(s')|^2(|f_s|^2|f_{s'}|^2/E_s^2E_{s'})$. Since $\alpha_s=|f_s|^2/E_s$ is the polarizability of the s-configuration, $\alpha = N_o\Sigma_s|\psi_o(s)|^2\alpha_s$ is the total (linear) contribution to the polarizability which is turned-on by the nonlinear zero-point fluctuations, and

$$\chi_{\parallel}^{(3)}|_0 \approx -(4\alpha)\Sigma_s|\psi_o(s)|^2(\alpha_s/E_s). \tag{4}$$

This term has a semi-classical origin; it arises from the modulation of the linear polarizability of the configuration s by the oscillating electric field well below resonance. The low frequency dielectric constant of <u>trans</u>-$(CH)_x$ is $\varepsilon_{\parallel} \approx 15$[5]. Since the fraction of the total oscillator strength in the sub-gap absorption tail is approximately 20% of the total, and

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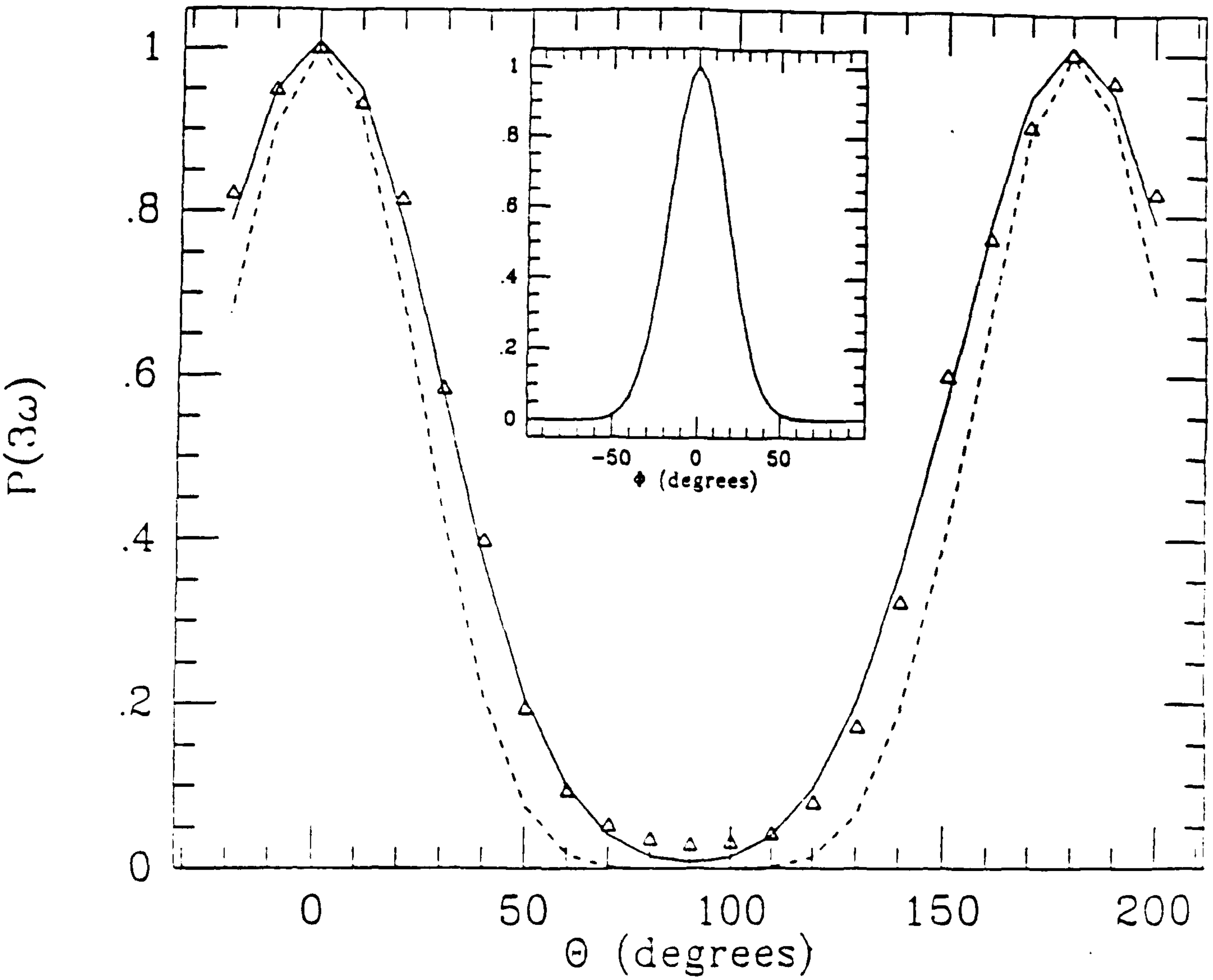

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.2
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-50
0
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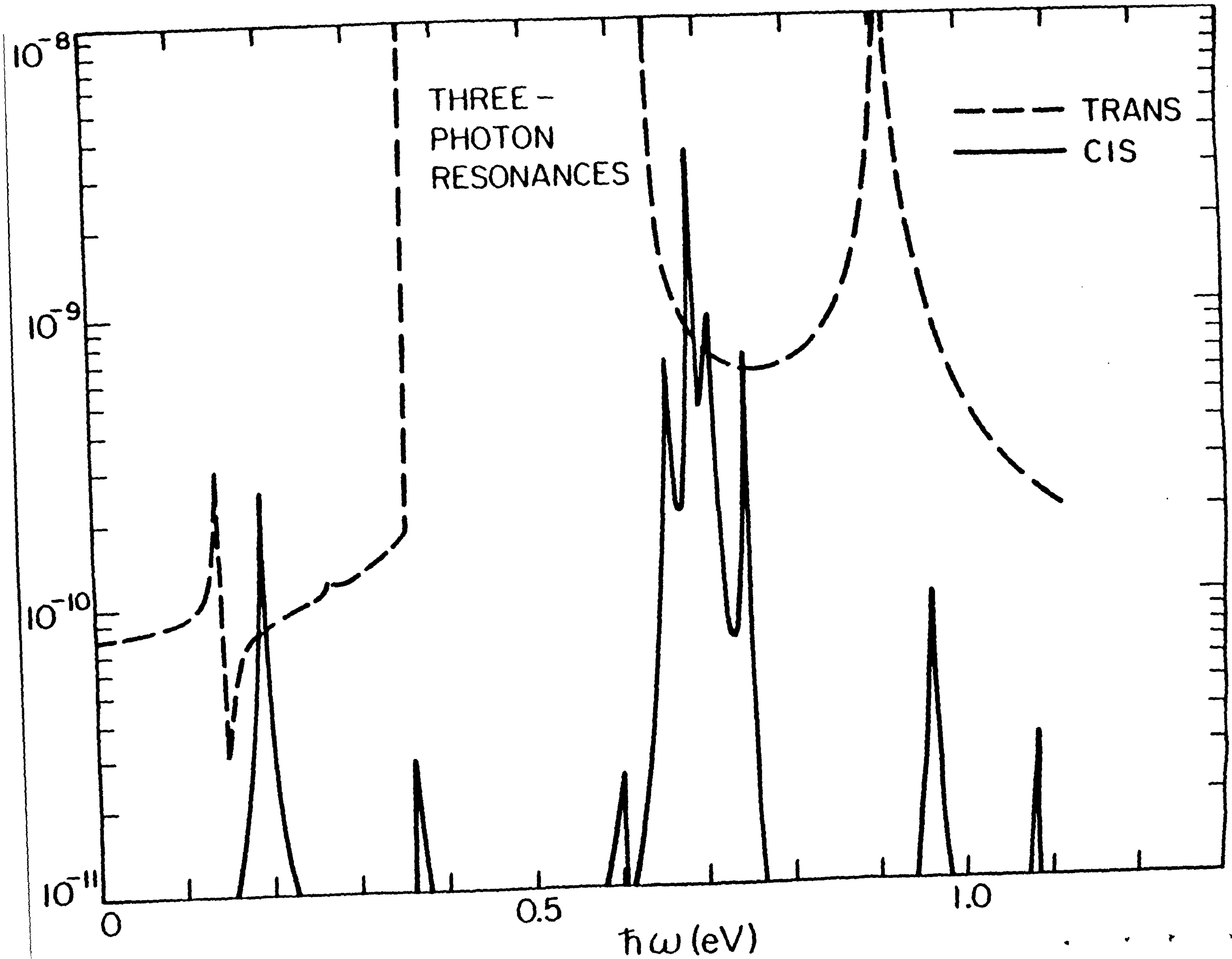
Φ (degrees)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TRANSIENT PHOTOCONDUCTIVITY IN ORIENTED TRANS-POLYACETYLENE PREPARED BY THE NAARMANN METHOD

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Abstract

We present transient photoconductivity results of oriented trans-polyacetylene prepared by the Naarmann method. In addition to the usual fast decaying photocurrent peak, we report a large long lived, temperature dependent tail not previously seen in other forms of polyacetylene. By comparison of the data to that obtained from high quality single-crystals of polydiacetylene, we conclude that the magnitude of this tail implies higher quality polyacetylene. The anisotropic behavior for different polarizations of the incident light is presented together with the effect of light intensity, temperature and external field strength.

is dominated by the sample morphology. With this as motivation, we present in this paper the results of transient photoconductivity measurements on stretch oriented Naarmann polyactylene.

Experimental Results

Details of the photoconductivity apparatus have been previously reported.[5] The incident laser beam was linearly polarized with a dichroic polarizer and subsequently rotated via a half-wave plate. Photon fluxes were in the range of 10^{14} - 10^{15} cm^{-2} per pulse with energy of 2.2 eV (566 nm) and a pulse duration of 20 ps. The polyactylene samples were free standing stretched oriented (6X) films with 200 μm gap gold electrodes evaporated upon it and attached with silver paint to the substrate. The time resolution of the data acquisition system is approximately 40 ps.

Conductivity measurements performed with an electrometer yield a dark conductivity of 10^{-6} S/cm and a linear (ohmic) current-to-voltage relationship over all voltages of interest. The samples were of the same batch tested by Basescu et al.[(9)] and found to have a doped (6 mole % of I_3^-) conductivity of 20,000 S/cm, nearly two orders of magnitude larger than similarly doped polyactylene samples obtained by the conventional Shirakawa method. All samples were mounted with the chain orientation direction parallel to the biasing electric field. Sample preparation was performed in an inert atmosphere, and the photoconductivity experiments carried out under vacuum of 10^{-4} torr or less.

Figure 1 shows the transient photoconductivity at room temperature and at 80K due to a 0.25 μj pulse of 2.2 eV polarized perpendicular to the chains with a bias field of 1.5×10^4 V/cm. By careful waveform averaging with regard to trigger jitter, we are able to resolve an intense and sharp peak at

Figure 3 displays the first 800 picoseconds of the 300 K data of Fig. 1 together with a convolution of $t^{-0.50}$ and a 36 ps rise time guassian. The gaussian represents the instrumental resolution and the time constant of 36 ps taken from the rise time of the data. The power law decay dependence is more clearly seen in Fig. 4. At early times (before 700 ps), the decay is $t^{-0.5}$, changing to t^{-1} at approximately 1 ns .

Figure 5 shows the anisotropy of the peak photocurrent for both the raw data and corrected for reflectance by the function, $(1-R_{\parallel})\cos^2(\theta) + (1-R_{\perp})\sin^2(\theta)$, where θ is the angle between the light polarization vector and the chain direction. The reflection coefficient for light polarized parallel ($R_{\parallel}$) and perpendicular ($R_{\perp}$) to the chain direction is 0.50 and 0.05, respectively.[17] Even after the reflection correction, there is still a net anisotropy which varies as $A(1 + 0.7 \sin^2\theta)$ favoring the perpendicular polarization.

Figure 6 shows the dependence of the photoconductivity as a function of light intensity at three separate delay times after the laser pulse. All three curves were taken with a 1.1 GHz amplifier with a rise time of several hundred picoseconds. The intensity dependence of the peak thus contains some averaging with longer times (which have a sublinear dependence); hence, the 0.92 exponent should be taken as a lower limit and the true peak dependence is probably linear, as reported by other authors.[5,7] At longer times (1.5 ns and 4.0 ns), the dependence becomes clearly sublinear.

Discussion

Naarmann polyacetylene has attracted considerable interest because of the remarkably high conductivity[8,9] of the doped material. This enhanced conductivity is believed to be related to the higher quality of the polymer as inferred from the low sp^3 defect content found in this material.[8] This motivated which, by our assumption, implies one half the charge carriers are trapped by 175 ps at 80 K. The distance traveled by these charge carriers can be estimated by assuming either a random walk[2] with a jump time of 0.1 ps and a thermal velocity of ~ 10^6 cm/s or a uniform motion with a drift velocity ($v = \mu E$) of 3 x 10^4 cm/s. Both lead to an average distance traveled before trapping of roughly 400 Å which corresponds to ~ 1 per 300 carbon atoms. These residual traps may be unrelated to sp^3 content, since they appear to be of the same energy (0.05 eV) and density (~ 1%) as oxygen induced traps which have been calculated[11] and measured.[12] Thus, the resemblance of the low temperature photoconductivity decay in Naarmann material to that of the room temperature Shirakawa and Durham material occurs because, in both cases, the trap depth is large relative to the thermal energies available to the charge carriers.

The temperature independence of the peak photocurrent has been previously explained by considering the charge carriers produced to be "hot"[5,7] and, thus, their mobilities are independent of the thermal energy of the lattice. However, calculations[13] suggest that thermalization should occur within 1 ps. In addition, Shank[14] has observed anomalous photoinduced absorption decay behavior in the subpicosecond domain and attributed this to thermalization of hot carriers with a thermalization time of 160 fs. This evidence has led to the suggestion[13] that the temperature independent photoconductivity results are due to heating of the sample by the laser pulse. Our data on Naarmann polacetylene demonstrate that it is possible to observe genuine temperature dependence when it is present, at least for times greater than 50 ps and temperatures above 80 K, providing evidence against the sample-heating hypothesis. Between 80 - 30 K, the decay curve is temperature independent. This is consistent with the temperature law beyond 1 ns. Bleier et al[7] has measured a t^{-1} dependence from 10 ns (the earliest time measured) to microseconds at which time the system reverts back to a $t^{-0.5}$ decay, which persists at least up to 100 ms. The transition at 700 ps to a more rapid photoconductivity decay while the photoinduced absorption decay slows can be explained by deep trapping. This would decrease the photoconductivity by reducing their average drift velocity but increase the photoinduced signal by preserving the number of excitations in traps, thus slowing recombination. The long lived (microsecond to second) photoconductivity has been extensively studied by Etemad and coworkers[16] who concluded it is a result of dispersive (hopping) transport from energetically equivalent sites.

Thus, there are three broad time regimes relative to photoconductivity:

(i) the subnanosecond domain which may provide information on intrinsic one dimensional transport;

(ii) the transitional regime from nanoseconds to microseconds where deep trapping is important; and, finally,

(iii) the microsecond to seconds domain where dispersive transport dominates.

The anistropy of the peak photocurrent is shown in Fig. 5; both the raw data and the data after correction for the polarization-dependent reflection are shown. The corrected data indicate a slight anisotropy, ≈1.7, in favor of the perpendicular polarization. The same value for the anisotropy was obtained in highly aligned Durham polyactylene.[7] Two independent factors favor the photoconductivity generated by light with perpendicular polarization. First, it is expected that polarons on different chains should have a greater probability of escaping geminate recombination than a S^+, S^- pair confined to the same chain. Secondly, the absorption depth for the perpendicular case is more than an order of magnitude greater than the parallel case (a factor of 25 for perfectly coefficients, $n_{s,p}$ is the probability of solitons or polarons to escape early time recombination, $\mu_{s,p}$ is the mobility for solitons and polarons and f is the fraction of solitons generated during perpendicular polarization illumination. This equation is of the form $A+B\sin^2\theta$, in agreement with the form of the anisotropy data.

Assuming all excitations created with the perpendicular polarization are polarons (f = 0), then the ratio $\mu_p n_p/\mu_s n_s$ is 1.7. Since the mobility of polarons is estimated to be somewhat larger than that of solitons[13], it is surprising that the observed ratio is so small. Either the probability to escape recombination for polarons and solitons are similar, or only a fraction f of the charge carriers generated with the perpendicular polarization are polarons and the remaining fraction (1 - f) are solitons. Recent calculations by Baeriswyl and Maki[25] imply that because of the zig-zag structure of the polyacetylene chain the intrachain absorption dominates, even for perpendicular polarization. Thus, for perpendicular polarization, such intrachain absorption will lead to soliton pairs on the same chain. Based on their estimates, we conclude that perpendicular polarization will yield f ~ 2/3 which results in the ratio $\mu_p n_p/\mu_s n_s = 3.1$. Thus, we attribute the observed intrinsic anisotropy to the enhanced creation of polarons for the perpendicular polarization. Similar conclusions have been reached in photoinduced absorption experiments.[17]

Finally, we discuss the intensity dependence of the photoconductivity for the perpendicular polarization, as shown in Fig. 6. As discussed in the experimental section, the peak is linear in intensity, as expected for this range of fluence from the excitation densities calculated above. The long lived tail present in the Naarmann material provides us with the opportunity to measure the intensity dependence at later times. One possible explanation of the data is to assume that the photocarriers tend to saturate the traps. This would lead

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Figure Captions

Fig. 1. Transient photovoltage across 50 ohms (see text). • - 300 K; Δ - 80 K.

Fig. 2. Temperature dependence of photovoltage (across 50 Ω) at 1.5 ns, 300 K.

Fig. 3. The first 800 ps of photovoltage in Fig. 1. • - subnanosecond photovoltage, 300 K; _____ - convolution of $t^{-0.5}$ and 36 ps gaussian.

Fig. 4. Power law decay of photovoltage from Fig. 1. _ _ _ _ - $t^{-0.55}$; _____ - $t^{-1.1}$.

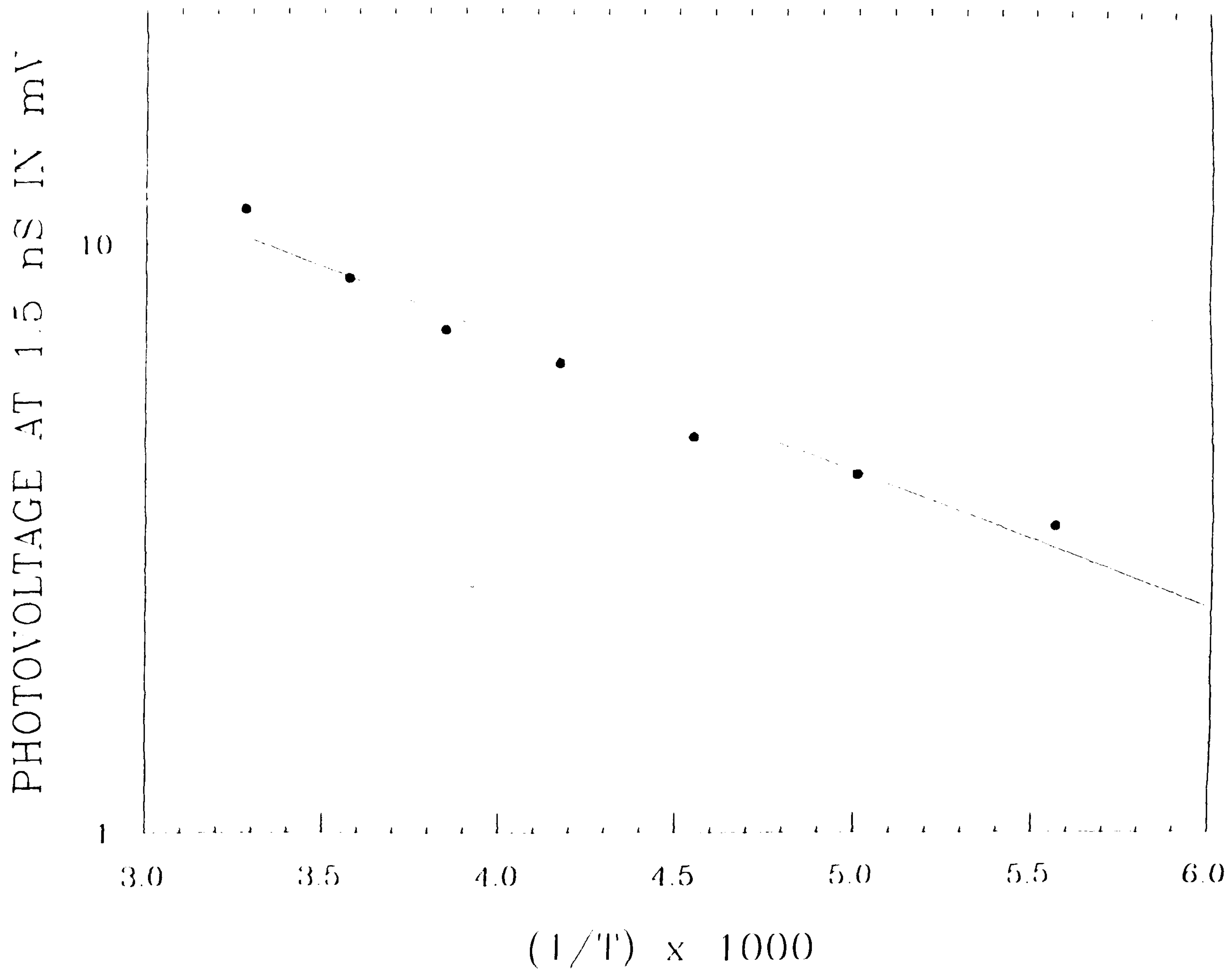
Fig. 5. Anisotropy of the peak photovoltage, $\theta = 0$, corresponds to optical polarization parallel to chain direction; • - raw data; Δ - corrected for reflection dependence; _____ fit to data (corrected for reflectance, triangles) of form - $A(1 + B \sin^2 \theta)$. $B = 0.7$.

Fig. 6. Intensity dependence of photovoltage at three different times.

• - peak, $i_{ph} \sim I^{0.92}$;

o - 1.5 ns, $i_{ph} \sim I^{0.75}$;

Δ - 4 ns, $i_{ph} \sim I^{0.50}$.


PHOTOVOLTAGE AT 1.5 nS IN mV
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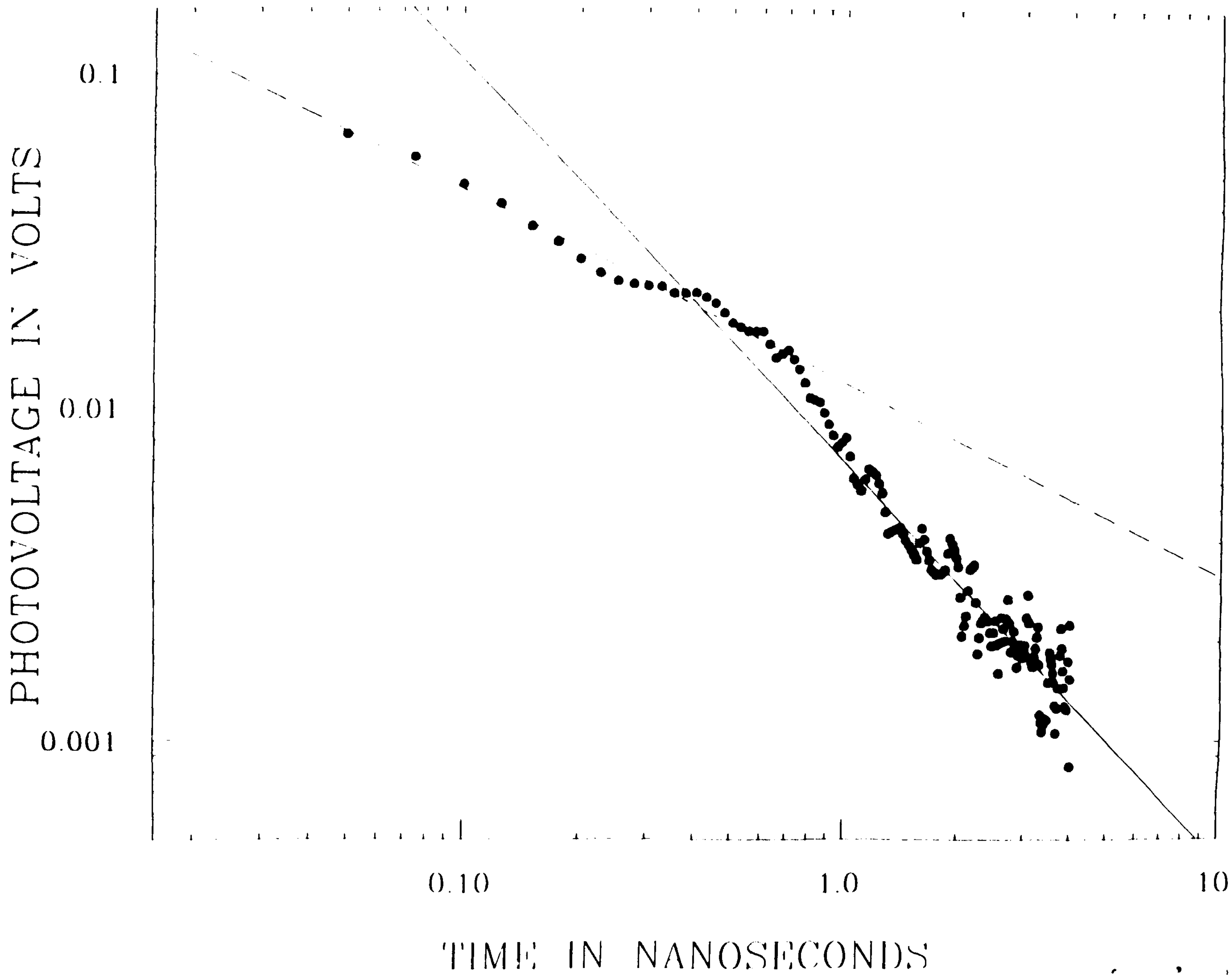
3.5
4.0
4.5
5.0
5.5
6.0
(1/T) x 1000


PHOTOVOLTAGE IN VOLTS
0.1
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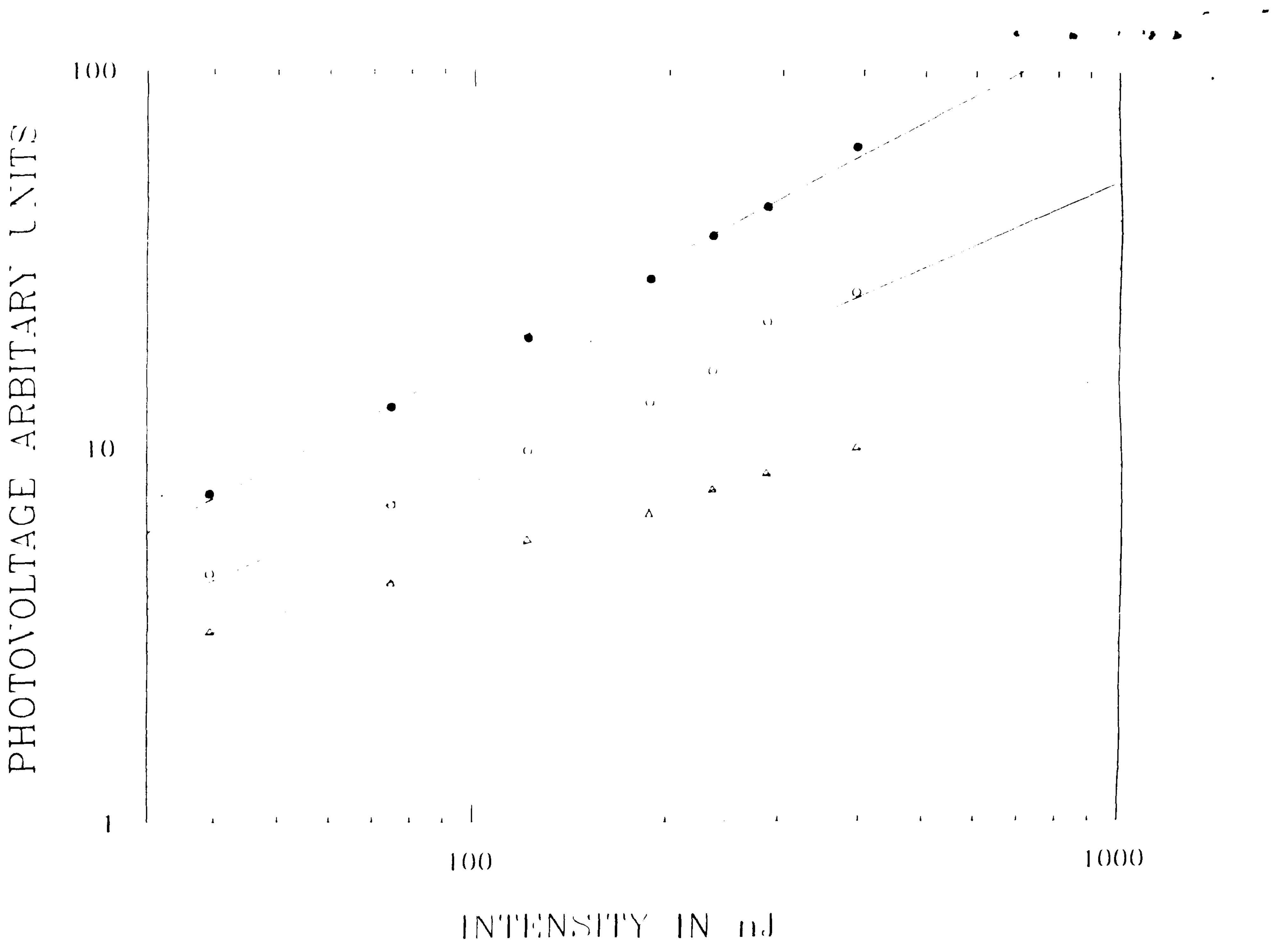
0.001
0.10
1.0
10
TIME IN NANOSECONDS



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Office of Naval Research
End-Of-The-Year Report
October I, 1987

Publications/Patents/Presentations/Honors/Students Report

for

Contract N00014-86-K-0514

"Nonlinear Optical Properties of Semiconducting Polymers"

Principal Investigators
Alan J. Heeger
Daniel Moses

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Santa Barbara, CA 93106

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ONR N00014-86-K-0514

a. Papers Submitted to Refereed Journals (not yet published)

"Carrier Photogeneration and Mobility in Polydiacetylene: Fast Transient Photoconductivity", D. Moses, M. Sinclair and A. J. Heeger (submitted to Phys. Rev. Letters).

"Nonlinear Excitations and Nonlinear Phenomena in Conductive Polymers", A. J. Heeger, D. Moses and M. Sinclair (to be published in ACS Symposium Series).

"Photogeneration of Nonlinear Excitations in Semiconducting Polymers: Fast Response Nonlinear Optical Phenomena", A. J. Heeger, D. Moses and M. Sinclair (to be published in Springer-Verlag "Solid-State Sciences" series).

"Polarization Dependence of Transient Photoconductivity in Trans-Polyacetylene", M. Sinclair, D. Moses, R. H. Friend and A. J. Heeger (submitted to Phys. Rev. B).

b. Papers Published in Refereed Journals

"Carrier Photogeneration and Mobility in Polyadiacetylene: Fast Transient Photoconductivity", D. Moses, M. Sinclair and A. J. Heeger, Phys. Rev. Letters

"Picosecond Photoconductivity in Trans-Polyacetylene", M. Sinclair, D. Moses and A. J. Heeger, Solid State Commun., Vol. 59, No. 6, 343 (1986).

c. Books (and sections thereof Submitted for Publication

None

d. Books (and sections thereof) Published

"Polyacetylene, $(CH)_x$: New Concepts and New Phenomena, A. J. Heeger, Handbook of Conducting Polymers, Vol. 2, ed. T. Shotheim (Marcel-Dekker, N.Y., 1986), p. 729.Q.

"Electrically Conducting Polymers, A. J. Heeger and A. G. MacDiarmid, in Encyclopedia of Materials Science and Engineering, Ed. Michael B. Bever (Pergamon Press, Oxford, 1986), p. 1399.

"Nonlinear Excitations and Nonlinear Phenomena in Conductive Polymers, A. J. Heeger, D. Moses and M. Sinclair, in Polymers for High Technology - Electronics and Photonics, ACS Symposium Series 346, ed. M. J. Bowden and S. R. Turner, (Amer. Chem. Soc., Washington, D.C., 1986), p. 372.

e. Technical Reports Published & Papers Published in Non-Refereed

None

f. Patents Filed

"Fibers and Tapes of 'Intractable' Conducting Polymers"

g. Patents Granted

None

h. Invited Presentation at Topical or Scientific/Technical Society

A. J. Heeger

International Workshop, "Electrochemistry of Polymer Layers, Duisberg, Germany (September 1986)

Novel Microstructures Program Annual Review, Naval Research Laboratory, Arlington, Virginia (October 1986)

Seminar, University of Houston, Houston, Texas (November 1986)

Seminar, University of California, Riverside (November 1986)

Materials Research Society, Boston (December 1986)

Seminar, IBM Almaden Research Laboratory, San Jose, California (January 1987)

American Chemical Society meeting, Denver, Colorado (April 1987)

International Symposium of Electrical Interactions in Complex Fluids, Colmar, France (June 1987)

Adriatico Research Conference on "One-Dimensional Organic Conductors: Chemistry, Physics and Applications" (June 1987)

Adriatico Research Conference on "High Temperature Superconductors" (July 1987)

Novel Microstructures Program Annual Review, Naval Research Laboratory, Arlington, Virginia (October 1986)

Seminar, University of California, Berkeley (October 1986)

American Chemical Society meeting, Louisville, Kentucky (November 1986)

Seminar, University of California, Los Angeles (February 1987)

Seminar, University of Minnesota, (March 1987)

Seminar, University of North Dakota (March 1987)

Invited Talk, American Chemical Society meeting, Denver, Colorado (April 1987)

Seminar, University of Wyoming (April 1987)

Seminar, University of Idaho (April 1987)

Seminar, Exxon Research and Engineering Co., Annandale, New Jersey (June 1987)

Invited Talk, First International Conference on Heteroatom Chemistry, Kobe, Japan

D. Moses

International Winter School for Electronic Properties of Polymers, "Electrical Conductivity of Polyacetylene: σ > X 10^4 σ/cm" and "Picosecond Photoconductivity in Polyacetylene: Carrier Sweepout and the Inadequacy of the Geminate Recombination Model," Kirchberg, Austria (March 1987).

i. Contributed Presentations at Topical or Scientific/Technical Society Meetings

A. J. Heeger

American Physical Society meeting, New York (March 1987)

American Chemical Society meeting, Denver, Colorado (March 1987)

F. Wudl

American Physical Society meeting, New York, N.Y. (March 1987)

American Chemical Society meeting, Denver, Colorado (April 1987)

j. Honors/Awards/Prizes

None

k. Number of Graduate Students Receiving Full or Partial Support on ONR Contract

None

l. Number of Postdoctoral Fellows Receiving Full or Partial Support on ONR Contract: 2

M. Sinclair
K. Akagi

Part II

a. Principal Investigator: Alan J. Heeger
Co-Investigator: D. Moses

b. Cognizant ONR Scientific Officer: Dr. B. R. Junker

c. Current Telephone Number: (805) 961-2001

d. Brief (100-200 words) Description of Project

Semiconductor polymers such as polyacetylene and polythiophene ha experimentally demonstrated nonlinear optical properties (photc uced absorption, photoinduced bleaching and photo-luminescenc with characteristic time scales in the sub-picosecond time scale. These phenomena are intrinsic and arise from the unique features of this novel class of materials. As demonstrated through studies of photoinduced absorption, photoinduced bleaching, and fast transient (picosecond) photoconductiviet,the origin of the remarkably large resonant nonlinear response is the photogeneration of nonlinear excitations (solitons and polarons). Nonresonant (sub-gap) pumping leads to values of $\chi^{(3)}$ from third harmonic generation of $\chi^{(3)} \approx 9\times10^{-9}$ esu, the largest nonresonant value ever measured. As a growing class of electronic materials, these polymers must be evaluated as fast response optical materials for use in a variety of applications.

e. Significant Results During Last Year (50-100 words)

Our picosecond transient spectroscopy facility is in full operation with sub-picosecond pulses (autocorrelation pulses yield about 300 femtosecond pulse width). Pump/probe measurements of photoinduced bleaching, four-wave mixing experiments, and third-harmonic generation experiments are underway. We have put considerable effort into materials development directed toward oriented films of semiconducting polymers. We have succeeded in achieving both oriented films of polyacetylene on glass substrates and oriented fibres of 50/50 blends of poly(3-hexylthiophene) in polystyrene or polyethyleneoxide. The availability of these oriented materials has made possible, for the first time, measurements of the anisotropy in $\chi^{(3)}$ in conducting polymers.

f. Brief (100-200 words) Summary of Plans for Next Year's Work

Research planned for the coming year will focus in the following three areas:

A. Picosecond photoconductivity of polymer semiconductors

B. Fabrication and Experimental Study of Polymer Fast Photodiodes

C. Time-resolved spectroscopy of polymer semiconductors

g. List of Names of Graduate Students and Postdoctorals Currently Working on Project: 2

D. Moses
M. Sinclair

h. Technical Reports Submitted to ONR During The Past Year: 2