AD-A198 305

A TOPICAL WORKSHOP

# ORGANIC AND POLYMERIC NONLINEAR OPTICAL MATERIALS

sponsored by

THE DIVISION OF POLYMER CHEMISTRY

AMERICAN CHEMICAL SOCIETY

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AUG 1 6 1988
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**MAY 16 - 19, 1988**

**VIRGINIA BEACH, VIRGINIA**

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

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Organic and Polymeric Nonlinear Optical Materials

12. PERSONAL AUTHOR(S)
Gerbi, D. J. and Tripathy, S. K.

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Workshop on Organic and Polymeric Nonlinear Optical Materials, May 16-19, 1988 at Virginia Beach, VA.

| 17. COSATI CODES | | | 18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) |
|---|---|---|---|
| FIELD | GROUP | SUB-GROUP | nonlinear optical materials, second order nonlinear optical susceptibility, third order nonlinear optical susceptibility, electro-optic, nonlinear optical devices |
| | | | |
| | | | |

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

At this Workshop on Organic and Polymeric Nonlinear Optical Materials, the latest developments in the areas of theory, characterization, synthesis, molecular assemblies, and potential device applications for organic and polymeric materials exhibiting nonlinear optical behavior are discussed. Topics discussed [illegible]

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| 22a. NAME OF RESPONSIBLE INDIVIDUAL<br>Dr. Donald Ulrich | 22b. TELEPHONE (Include Area Code) (202) 767-4960 / 22c. OFFICE SYMBOL NC |

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## INTRODUCTION

The objective if the workshop was to provide a forum for the sharing of information and the discussion of device applications in the area of organic and polymeric nonlinear optical materials. The workshop addressed the issues of theory, characterization, synthesis, molecular assemblies, and potential device applications. Multidisciplinary interactions are vital to the addvancement of research in this field, and the seventy-six participants included scientists from the USA, Japan, UK, France, Germany, and Canada and represented academic, industrial and government laboratories.

## WORKSHOP FOCUS

The workshop focus was divided into five half-day sessions and addressed the following topics.

Theory: Current theoretical work on nonlinear optical interactions in organic and polymeric materials was reviewed, with a focus on understanding the microscopic properties of these systems and their correspondence to the macroscopic properties. The value of modelling these systems and the usefulness of the theoretical projections for determining structural requirements for enhanced nonlinear optical activity was discussed.

Characterization: Experimental studies to determine the second and third order nonlinear optical susceptibilities of organic and polymeric systems was discussed. Limiting values

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for device applications derived from characterization studies were presented.

Molecular Assemblies: Characterization measurements have been carried out on many materials in a variety of forms to provide information on structure-property releationships. Molecular order is essential for second order nonlinear optical effects and may enhance third order effects. Therefore, control of molecular orientation in these systems is important. Useful molecular assemblies, including Langmuir-Blodgett films and electrically poled polymer systems were discussed.

Synthesis: The synthesis of organic and polymeric systems is most effective when carried out in conjunction with theoretical development and characterization efforts. Examples of how synthetic efforts can be used to enhance nonlinear optical activity and to improve the physical properties of materials under consideration for use in devices were presented.

Device Applications: Discussions addressed the current status and the future potential of devices utilizing organic and polymeric nonlinear optical materials.

## SUMMARY

The Workshop on Organic and Polymeric Nonlinear Optical Materials was very successful. The informal atmosphere encouraged informal discussions, of particular importance in this interdisciplinary field.

A Topical Workshop

# ORGANIC AND POLYMERIC NONLINEAR OPTICAL MATERIALS

*sponsored by*

**The Division of Polymer Chemistry**

**AMERICAN CHEMICAL SOCIETY**

May 16-19, 1988

Virginia Beach, VA

*Co-Chairmen*

*Diana Gerbi* *Sukant Tripathy*

The generous support of the contributors is gratefully acknowledged: Air Force Office of Scientific Research, Office of Naval Research, Du Pont Company, Hoechst-Celanese and 3M Company.

Monday Evening, May 16, 1988

| | |
|---|---|
| 3:00-9:00 p.m. | REGISTRATION |
| 6:30-9:30 p.m. | WELCOMING RECEPTION |

**PROGRAM:**

**Tuesday Morning, May 17, 1988**

| | | |
|---|---|---|
| 8:15 A.M. | | **Opening Remarks** |
| 8:20-9:10 | A. | *"An Overview on Nonlinear Optical Polymer Systems and Devices"* by D.R. Ulrich (Air Force Office of Scientific Research) |
| 9:10-10:00 | B. | *"Nonlinear Optical Effects in Polymeric Films"* by P.N. Prasad (State University of New York at Buffalo) |
| 10:00-10:30 | | **Break** |
| 10:30-11:20 | C. | *"Recent Advances in Nonlinear Optical Properties of Organic and Polymer Systems"* by A.F. Garito (University of Pennsylvania) |
| 11:20-12:10 | D. | *"Conjugated Polymers and Nonlinear Optics"* by S. Etemad (Bell Communications) |
| | | **Lunch** |

**Tuesday Afternoon, May 17, 1988**

| | | |
|---|---|---|
| 1:30-2:20 | E. | *"Anisotropy of the Third Order Nonlinear Optical Susceptibility in Conjugated Polymers"* by A.J. Heeger (University of California at Santa Barbara) |
| 2:20-3:10 | F. | *"Nonlinear Optics in Ordered Molecular Systems"* by K.D. Singer (AT&T) |
| 3:10-3:40 | | **Break** |

| | | |
|---|---|---|
| 3:40-4:30 | G. | *"Several Series of Novel Polydiacetylenes for Nonlinear Optics"* by H. Nakanishi (Research Institute for Polymers and Textiles, Japan) |
| 4:30-5:20 | H. | *"Resonance Effects in Cubic Hyperpolarisabilities of Conjugated Polymers,* by F. Kajzar (CEN Saclay, France) |

**Wednesday Morning, May 18, 1988**

| | | |
|---|---|---|
| 8:30-9:20 | I. | *"Nonlinear Optical Measurements on Liquid Crystals and Quasi-Liquid Crystals"* by Y.R. Shen (University of California at Berkeley) |
| 9:20-10:10 | J. | *"Nonlinear Optical Effects in Conjugated Systems"* by D. J. Gerbi (3M Co.) |
| 10:10-10:40 | | **Break** |
| 10:40-11:30 | K. | *"Optical Nonlinearity: Molecules, Assemblies and Wave Phenomena"* by G. R. Meredith (E.I. DuPont DeNemours and Co.) |
| 10:30-12:20 | L. | *"Characterization of Polymeric Nonlinear Optical Materials"* by G. Khanarian (Hoechst-Celanese) |
| | | **LUNCH** |

**Wednesday Afternoon, May 18, 1988**

| | | |
|---|---|---|
| 1:30-2:20 | M. | *"Preparation and Characterization of Organo-Transition Metal Langmuir-Blodgett Films"* by T. Richardson (University of Oxford, U.K.) |
| 2:20-3:10 | N. | *"Optical Properties of Organized Assemblies"* by S.K. Tripathy (University of Lowell) |
| 3:10-3:40 | | **Break** |
| 3:40-4:30 | O. | *"The Nonlinear Optics of Langmiur-Blodgett Films" by I. Peterson (GEC Research, Ltd., Great Britain)* |

**Wednesday Evening, May 18, 1988**

| | | |
|---|---|---|
| 6:00 p.m. | | POSTER SESSION<br>Wine & Cheese |
| 8:00 p.m. | | BANQUET |

**Thursday Morning, May 19, 1988**

| | | |
|---|---|---|
| 8:30-9:20 | P. | *"Advances in Organic Electro-Optic Devices"* by R.S. Lytel (Lockheed Research and Development) |
| 9:20-10:10 | Q. | *"Organic Nonlinear Optical Devices and Material Considerations"* by B.K. Nayar (British Telecom Research Laboratories, U.K.) |
| 10:10-10:40 | | **Break** |
| 10:40-11:30 | R. | *"Towards Nonlinear Optical Applications of Polydiacetylenes"* by M. Thakur (AT&T) |
| 11:30-12:20 | S. | *"High Resolution Laser Spectroscopy in Polymers" by D. Haarer (Universitat Bayreuth, West Germany)* |
| *12:20* | | *"Closing Remarks"* byK.J. Wynne(Office of Naval Research) |

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Mrs. G. Meredith (Leslie)
Mrs. S. Thakur

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"ORGANIC AND POLYMERIC NONLINEAR OPTICAL MATERIALS"

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A Topical Workshop

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| | | **Lunch** |

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| 10:40-11:30 | K. | *"Optical Nonlinearity: Molecules, Assemblies and Wave Phenomena"* by G. R. Meredith (E.I. DuPont DeNemours and Co.) |
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| | | **LUNCH** |

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| 2:20-3:10 | N. | *"Optical Properties of Organized Assemblies"* by S.K. Tripathy (University of Lowell) |
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| 8:00 p.m. | | BANQUET |

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| *12:20* | | *"Closing Remarks"* byK.J. Wynne(Office of Naval Research) |

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D. R. Ulrich
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# AN OVERVIEW ON NONLINEAR OPTICAL POLYMER SYSTEMS AND DEVICES

Accession For
NTIS GRA&I ☒
DTIC TAB ☐
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A-1

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## NLO Response in Polymers

Molecular Level — Microscopic Polarization Related to Applied Electric Field

$$p(E) = \alpha E + \beta E^2 + \gamma E^3 \ldots$$

Macroscopic NLO — Originates From Polarization Response of Molecular Electrons

$$P(E) = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \ldots$$

- $\chi^{(1)}$ — Represents Linear Optics
- $\chi^{(3)}$ — Represents Third Order Nonlinear Process i.e., Third Harmonic Generation, Self-Focusing

First and Third Order Terms of Odd Power of E Common to All Materials — Centrosymmetric

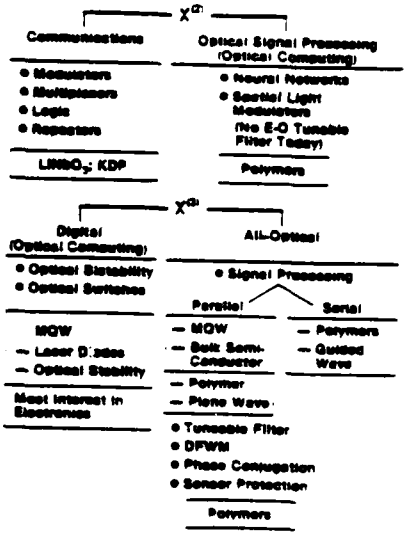
- $\chi^{(2)}$ — Second Order Response i.e., Second Harmonic Generation, Optical Rectification

Only in Noncentrosymmetric Medium — Lacks Center of Inversion Symmetry

## Why NLO Polymers?

- Subpicosecond Response Times
- Large, Nonresonant Nonlinearities
- Low DC Dielectric Constants
- Low Switching Energy
- Broadband
- Low Absorption
- Absence of Diffusion Problems
- Potential for Resonant Enhancement
- Ease of Processing and Synthesis Modification
- Room Temperature Operation
- Environmental Stability
- Mechanical and Structural Integrity

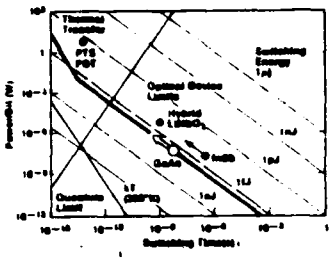
## Where Will NLO Polymers Fit In?



## Comparison of Optical Switching Technologies

- Fastest Switches Based on Nonresonant Nonlinearity
- Power Requirements Inversely Proportional to Nonlinearity
- New Organic Polymers May Exceed Optical Device Limits of Resonant Materials
  - Requires Larger $n_2$ Without Introducing Significant New Absorption
- For $\lambda \geq 0.85$ μm, There are No Alternatives to Organics for Fast Optical Switching

- Power/Bit vs. Switching Time $T_s$

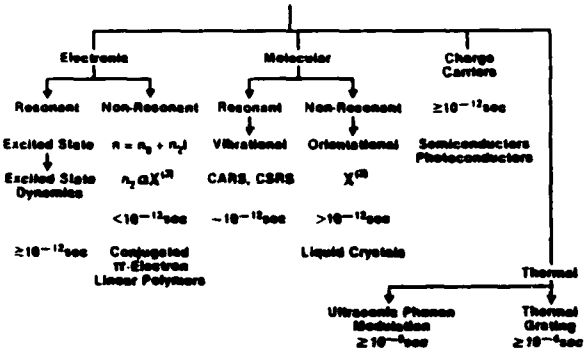



- Corresponds to $\lambda^2$ Cross-Section Devices
- Length Adjusted for Minimum Switching Energy

## Optical Performance Comparison

| | Polymers | GaAs/GaAlAs |
|---|---|---|
| Switch On/ Switch Off, τ (Recovery Period) | • Femtoseconds | • Nanoseconds |
| Energy Required to Induce Switching | • Moderate $N_2$<br>• Nonresonant<br>• Not Defined by λ<br>• Broad Band of Response and Light Sources<br>• Shows all NLO Processes | • High $N_2$<br>• Resonance Enhanced<br>• Limited by λ<br>• Close to Bandgap<br>• NLO 3D Order, But Not Optical Amplification or THG |
| Absorption Coefficient, α Associated With Switching | • $\frac{1}{10^4}$ GaAs | • Large |
| Figure of Merit FOM = $\frac{n_2}{\alpha\tau}$ | • High ($1 \times 10^7$) | • Moderate ($1.5 \times 10^6$ on Resonance) |

## Mechanisms of Four Wave Mixing




## Research Directions
## NLO Polymer Requirements

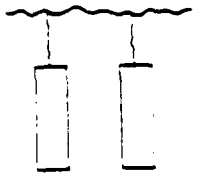
- Nonlinear Susceptibilities $\geq 10^{-6}$ esu
  - *Resonant vs Nonresonant*
- Ease of Processing
  - Solubility
- Thin Films of Reasonable Optical Quality
  - Transparency
  - Surface Smoothness
- Environmental Stability
- Low Switching Energy (PJ, Diode Lasers)
- Characterization and Separation of Electronic, Molecular, Thermal and Charge Carrier Contribution Mechanisms to Response Time

## Status NLO Polymer Classes

| Class | Examples | NLO Function |
|---|---|---|
| ISO Tropic | Glasses<br>Alloys<br>Composites | $\chi^{(2)}$, $\chi^{(3)}$ |
| Bond Alternation | Ladder Polymers<br>PTL, PQL<br>Polyacetylene<br>Polythiophene | $\chi^{(3)}$ |
| Liquid Crystalline Polymers (LCP) | Side Chain<br>LCPs | $\chi^{(2)}$ |
| Rigid Rod<br>Aromatic<br>Heterocyclics | PBT LCPs<br>PBO<br>BBL | $\chi^{(3)}$ |
| Polydiacetylenes | | Mostly $\chi^{(3)}$<br>Some $\chi^{(2)}$ |

## Second Order Polymers for Electrooptical Devices

- Pendant Side Chain Structure



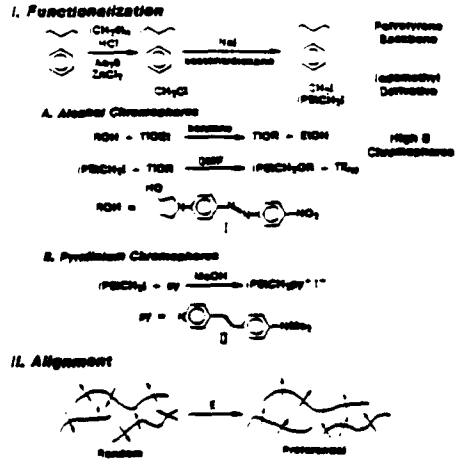
- High Activity

| | Polymer | $LiNbO_3$ |
|---|---|---|
| For SHG | $\chi^{(2)}$ = 120 pm/V | 10 pm/V |
| For Electrooptics | r = 35 pm/V | 30 pm/V |
| FOM = $\frac{r}{\varepsilon}$ | 10 | 1 |

- Excellent Secondary Properties
  - Spin Castable for Thin Film Waveguides, 2-4 Micron
  - Low Dielectric Constant ( $\varepsilon_{polymer}$ = 3; $\varepsilon_{LiNbO_3}$ = 30)
  - Low Loss (< 1 db/cm at 830 nm)
  - Melt Processable for Optics
  - Tg ~ 120 °C

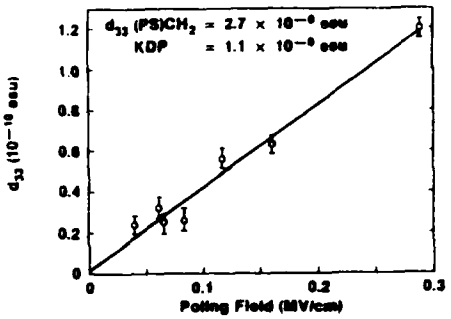
## Nonlinear Chromophores Covalently Linked to Glassy Polymer Constructs Noncentrosymmetric Assembly

Synthesis and Poling of Covalently-Functionalized Polymers for Frequency Doubling

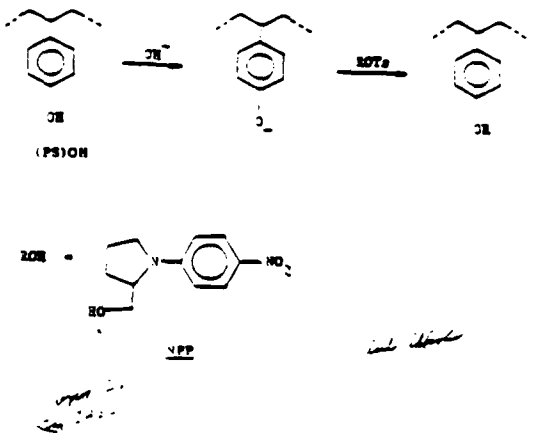


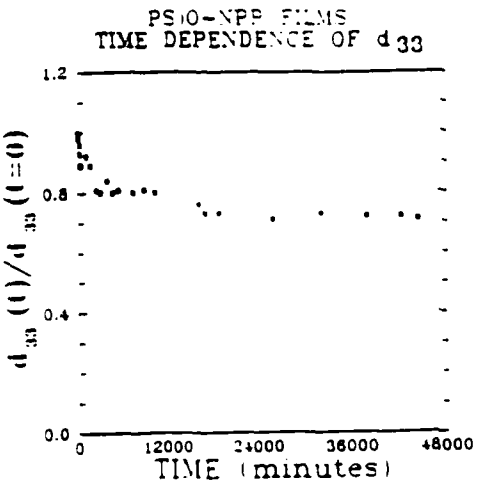

## Dependence of SHG On Poling Field

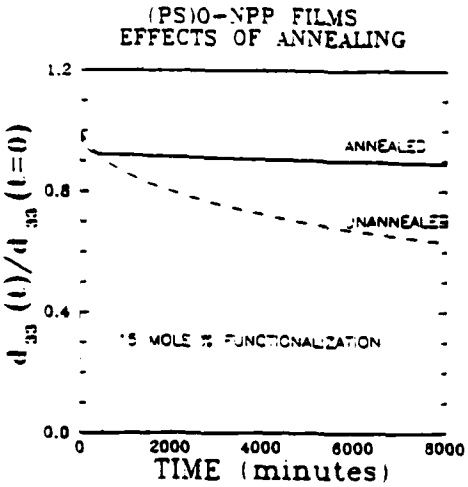
- Significant Non-Random Chromophore Alignment



## FUNCTIONALIZATION OF POLY(p-HYDROXY-STYRENE) WITH NLO CHROMOPHORES




**Values for $\chi^{(3)}$, Eg, W From Semiempirical Calculations and Experimentally Determined $\gamma$(HOMO)$^2$ Delocalization Length for Prototype Ladder Polymers and Polyacetylene**

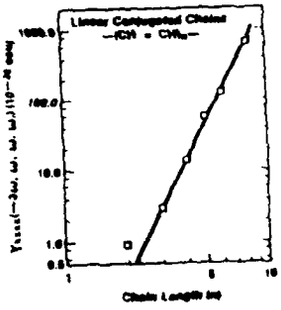
| Polymer | Band Gap Eg(eV) | Band Width W(ev) | $\chi^{(3)}$ (esu) | $N_d^*$ |
|---|---|---|---|---|
| Pristine Trans-PA | 1.8 | 10 | $6.5 \times 10^{-10}$ | 29 |
| Pristine PXL X = CH Ladder (Chance) | 0.7 | 1.5 | $5 \times 10^{-10}$ | 26-28 |
| Bipolaron State of PXL X = CH Ladder (Dalton) | 0.3 | 2 | $10^{-7}$ | |
| Protonated PXL | 3.8 | 3 | $2 \times 10^{-10}$ | |

## Implications of $\gamma(\text{HOMO})^2$ Delocalization Experiments For NLO Polymen Synthesis

- Negative Spin Density Confirms Electronic Excitation (Electron Correlation)
- Delocalization Length in Ladder Polymers and Polyacetylene the Same — 26 to 29 Atoms
- Indicates $\chi^{(3)}$ Will Not Increase Beyond 25 Repeat Units (60 Å)
- Ladder Polymers May be Superior to Open Chain Polyenilenes Because Improved $\pi$-Orbital Overlap Will Lead to Enhanced Delocalization and Reduced Optical Gap

## Dependence of $\gamma(-3\omega, \omega, \omega, \omega)$ On Chain Length

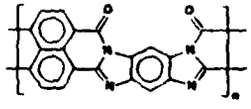
- Finite Chain Limit: $\gamma \propto n^{5.5}$
  - *Decreasing Excitation Energy*
  - Increasing Number of Spin Correlated States
- Polymer Chains: $\chi^{(3)} \sim 10^{-9}$ esu
  - 25 Repeat Units (60 Å)



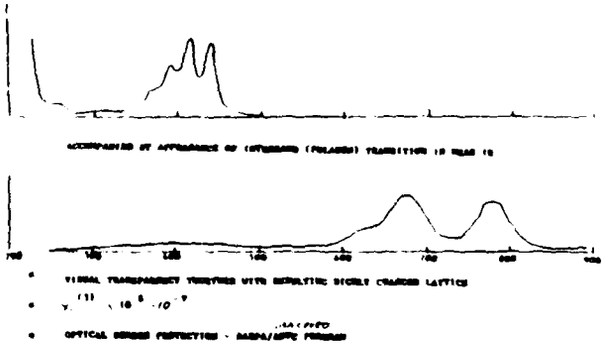

## Application of Dalton's Results

- Solubilized Ladder Polymers by Lewis Acid Charge Transfer Complex Forming Agents

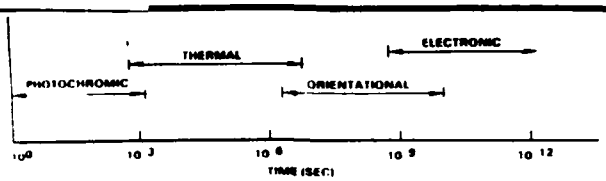
*Soluble Benzimidazophenanthroline (BBL)*



- Soluble in Organic Acids
- Reduces Intermolecular Attractive Forces and Allows Solubilization of Rigid Macromolecules



## NONLINEAR OPTICAL AND PHOTOCHROMIC POLYMERS




| PHOTO-CHROMIC | THERMAL NONLINEARITY | ORIENTATIONAL KERR NONLINEARITY | ELECTRONIC KERR NONLINEARITY |
|---|---|---|---|
| – OPTICAL FUSE | – DYE SENSITIZED THERMAL EFFECT | – LIQUID CRYSTAL POLYMERS | – ELECTRONIC $\chi(3)$ POLYMERS |
| – $10^{-3}$ D.C. | – $10^{-3}$ - $10^{-7}$ SEC | – $10^{-7}$ - $10^{-10}$ SEC | – $10^{-9}$ - $10^{-12}$ SEC |
| **THREAT** | **THREAT** | **THREAT** | **THREAT** |
| – GAS LASERS | – PULSED FLASH LAMP PUMPED LASERS | – Q-SWITCHED SOLID STATE LASERS | – Q-SWITCHED SOLID STATE LASERS |
| – CW SOLID STATE LASERS | – GAS LASERS | – PULSED FLASH LAMP PUMPED LASERS | – MODE LOCKED LASERS |
| | – CW SOLID STATE LASERS | | |

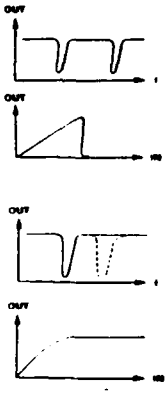
## HARDENING TECHNIQUES

FIXED NOTCH FILTERS

OPTICAL SWITCH

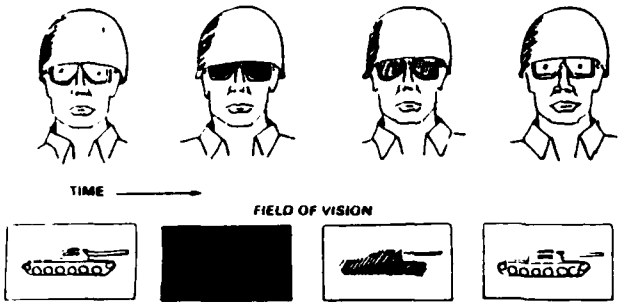
TUNABLE FILTERS

OPTICAL LIMITER




- SUB NANOSECOND RESPONSE TIMES
- MILLISECOND RECOVERY SPEEDS (AT LEAST)
- BROADBAND WAVELENGTH RESPONSE (OVER VISIBLE AND NEAR IR)
- REJECTION EFFICIENCY >99% BEFORE AND AFTER SWITCHING
- HIGH DAMAGE THRESHOLDS (~MW/cm²)
- LOW INSERTION LOSSES AND MINIMAL RETROFIT COMPLEXITIES

## SENSOR PROTECTION




FOCUS IS ON CONCEPTS WHICH CAN:

- PROTECT AGAINST RAPIDLY TUNABLE, PULSED, VISIBLE AND NEAR IR LASER THREATS TO HIGH GAIN OPTICAL SYSTEMS
- USEFUL FOR RANGEFINDERS, VISUAL SENSORS, CAMERAS, AND MOST IMPORTANTLY, THE EYE

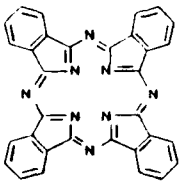
## Third Order Polymers for Optical Devices

- Planar Structure With Extended π Orbitals

M = Metal Atom

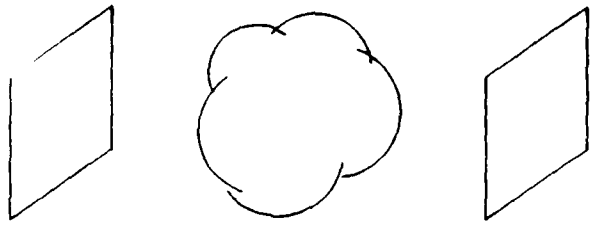
- Shift In Focus From Conjugated Off-Resonance to Systems on Resonance With Narrow Molecular Extinction Coefficients
- High Activity Through Saturable Absorption
  - Effective $N_2$ Equals AlGaAs MQW Structures
- Excellent Secondary Properties
  - Spin Castable For Thin Film Structure Applications
    - Optical Bistability
    - Parallel Processing

## Phthalocyanines



- Large NLO response discovered by A. Garito
- Numerous variants synthesized to tailor
  - NLO activity
  - Fabrication properties

## Basic Structure of an Optical Neural Network



**Input Plane of Neurons**

N, X (i)'s

**Optically Implemented Interconnections**

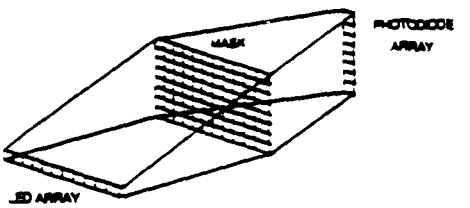
W (i,j)'s

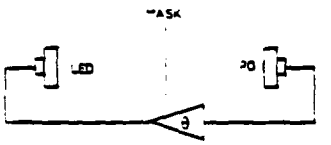
$N^2 \rightarrow N^{3/2}$

**Output Plane of Neurons**

N, X (j)'s

## OPTOELECTRONIC IMPLEMENTATION OF A NEURAL NETWORK

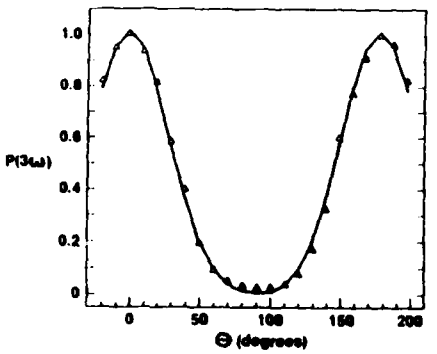



ELECTRONIC FEEDBACK

- DEMONSTRATED STEADY - STATE OPTICAL BISTABILITY COMPARABLE TO GAAS IN FAST - FRONT STALON OF 1000Å POLYMER FILM
- LINEAR ARRAY OF OPTICAL BISTABLE ELEMENTS THAT COULD REPLACE PHOTODIODES

## Angular Dependence of Reflected $\chi^{(3)}$ for Oriented Trans-Polyacetylene by Third Harmonic Generation




## Third Order Response in Polyacetylene

- **Resonant Process**
  - Photoexcited Nonlinear Excitations
  - Associated Structural Distortions (Solitions, Bipolarons, Polarons) Responsible for Large Shifts of Oscillator Strength Observed With Resonant Pumping Consequence of Electron-Phonon Interaction
  - Electronic Resonant Enhancement
    - Nonradiative Dissipation Produces Slower Responses
- **Reflected $\chi^{(3)}$**
  - $9 \times 10^{-10}$ esu Parallel to Polymer Chain
  - For Devices Polymer Must Be Able to Inherently Transmit or Guide Light

## Third Order NLO Response of Ordered Polymers

- Collinear Rigid Rod
- Planar Rigid Rod

Polybenzobisthiazole (PBT) — Polybenzobisoxazole (PBO)

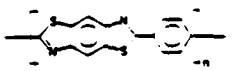
COMPARISON

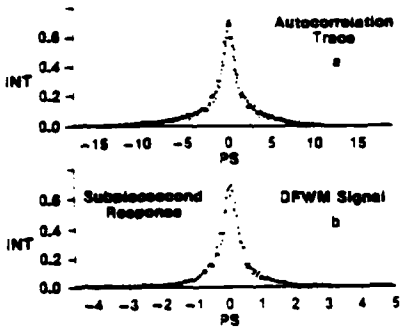
| | | | |
|---|---|---|---|
| Uniaxial PBT | — | Third Harmonic Generation | — $X^{(3)} \simeq 10^{-10}$ esu |
| Biaxial PBT | — | Degenerate Four Wave Mixing (DFWM) | — $X^{(3)} \simeq 10^{-11}$ esu |
| Uniaxial PBO | — | Degenerate Four Wave Mixing | — $X^{(3)} \simeq 2.5 \times 10^{-11}$ esu |

- Requirement for Film Quality — Avoid Inherently Grain or Fibrous Components Which Scatter Light

## Degenerate Four Wave Mixing of Biaxial PBT Ordered Polymer Films

Poly (p-phenylenebenzobisthiazole) (PBT)

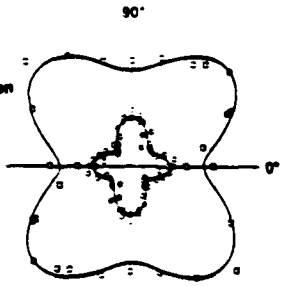





## Nonresonant Third Order Susceptibility $X^{(3)}$ in Biaxial PBT

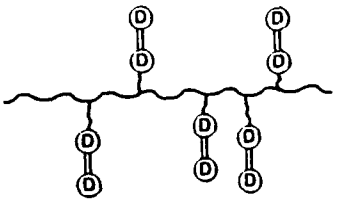
- Degenerate Four Wave Mixing

Polar Plot: $X^{(3)}$ As a Function of Film Rotation Angle




- New Feature for Third Order Devices
- Anisotropic $X^{(3)}$ Materials for Optically-Activated Birefringent Film Applications

## $X^{(3)}$ Polymers for Fibers



- $X^{(3)}$ units have modest activity but very low absorption
- Polymer backbone confers secondary properties
  - Spinability
- Shear and elongational flow yield alignment

# $\chi^{(3)}$ Materials

**Thin Limit**

**Properties**
- Near reasonance
- High $n_2$
- High absorption ($\alpha$)

**Material**
- Phthalocyanines

**Application**
- Etalons
- All optical SLM's

**Advantages**
- Fabrication ease
- Room temperature operation
- Potentially highest $n_2$ materials

**Thick Limit**

**Properties**
- Non resonant
- Lower $n_2$
- Very low absorption

**Material**
- Side chain polymer

**Application**
- NLO fibers
- All optical switching

**Advantages**
- Fiber spinning ease
- Potentially highest $n_2/\alpha$ materials

POLYALKYLTHIOPHENE

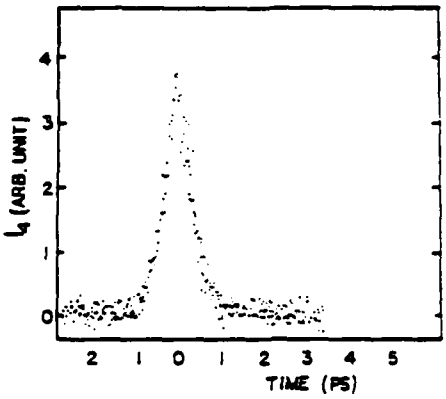
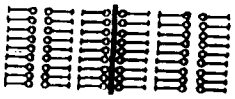



Fig. The degenerate four wave mixing signal obtained for a 20 layer thick Langmuir-Blodgett film of polyalkylthiophenes shown as a function of the delay of the backward beam; the wavelength is 602 nm and the excitation pulsewidth is 340 fs.

$\chi^{(3)} \sim 10^{-9}$ esu

POLYMER MULTIPLE QUANTUM WELLS



MOLECULAR ARCHITECTURE TAILORING

- o LIQUID CRYSTALLINITY
- o GUEST-HOST BLENDS
- o IN-SITU POLYMERIZATION AND ORDERING
- o RIGID/FLEXIBLE CHAIN CONFORMATIONS

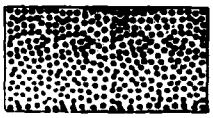
- o NEW HETEROSTRUCTURE ASSEMBLIES
  - GAAS ANALOGS
  - NON GAAS ANALOGS
- o QUANTUM DOT DOMAIN STRUCTURES

CHARGE CARRIER DYNAMICS

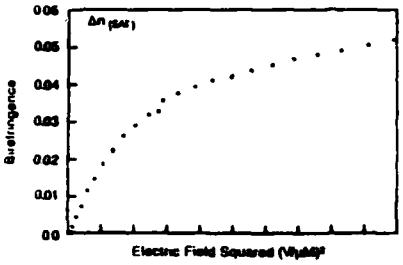
- o CHARGE TRANSFER INTERACTIONS
- o REDUCE DIMENSIONALITY OF CHARGE CARRIERS
- o INTERFACE SHG
- o PICOSECOND TRANSIENT ABSORPTION/GRATING
- o TRANSIENT ETALON EFFECTS/PHONON INDUCED PROCESSES

## LCC Composite

**New LCC's**



- $d << \lambda$ (Rayleigh scattering regime)
- Randomly oriented LC microdroplets
- Low scattering - hazy blue to transparent
- Kerr material with positive $n_2$



ADVANCED POLYMER BLENDS AND OPTICS

NLO POLYMERS

| GENERATION | SECOND ORDER NLO, $\chi^{(2)}$ | | INTER ORDER NLO, $\chi^{(3)}$ | |
|---|---|---|---|---|
| | HOMOPOLYMERS | | | |
| I (1985 - 1989) | o | ISOTROPIC | o | BOND ALTERNATION |
| | o | POLED | o | LADDER |
| | o | ORIENTED | o | ORDERED |
| | POLYMER - POLYMER INTERACTIONS { BLENDS - ALLOYS, MOLECULAR COMPOSITES } | | | |
| II (1990 - ?) | o | SELF-INDUCED POLARIZATION | o | NEAR-OFF RESONANCE |
| | o | SELF-ORGANIZING | o | PLANAR |

IMPROVEMENTS IN CALCULATION OF NLO SINGLE-MOLECULE PROPERTIES

- PARALLEL COMPUTING
- ABSORPTION LINEWIDTHS
- MOLECULAR CONFORMATIONS AND DEFECTS
- DEVELOPMENT OF ALTERNATIVE METHODOLOGIES, SUCH AS FINITE FIELD APPROACHES

GENERALIZATION OF SINGLE-MOLECULE TO BULK NLO PROPERTIES

- STATISTICAL AVERAGING OF ORIENTATION (FROZEN GAS MODEL)
- STATISTICAL AVERAGING OF CHAIN LENGTHS
- EFFECTS OF INTERMOLECULAR INTERACTIONS ON SINGLE MOLECULE NLO PROPERTIES
- EFFECTS OF INTERMOLECULAR INTERACTIONS ON MOLECULAR CONFORMATION AND STRUCTURE
- EFFECT OF INTERMOLECULAR INTERACTIONS ON MATERIAL ULTRASTRUCTURE

***THE KEY: INTERMOLECULAR INTERACTIONS!***

## Status of Understanding for Polymer Design

**Detailed Mechanism(s) of Nonlinear Optical Activity in Delocalized Electron Polymers Have Yet to Be Defined**

- Nonlinear Optical Activity May Not Be Simply Related to Bandgap
- Potential Contributions of D Orbitals to NLO (S-D Cross-Terms)
- Role of Electron-Phonon Interactions
- A Qualitative Correlation Between $\chi^{(3)}$ and Electron Delocalization Length
- Effect of Doping and Intermolecular Charge Transfer Needs to Be Clarified
- Quantitative Theory Lacking to Predict Macromolecules With Large Second Order (Beta) and Third Order (Gamma) Molecular Susceptibilities

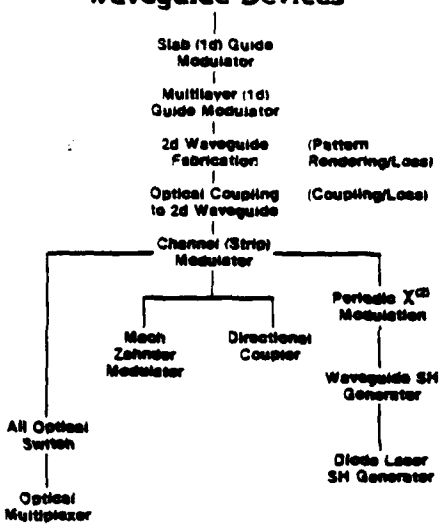
## State-of-Art $\chi^{(2)}$ Devices

- Traveling-Wave Electrode Mach-Zehnder Electrooptic Modulator

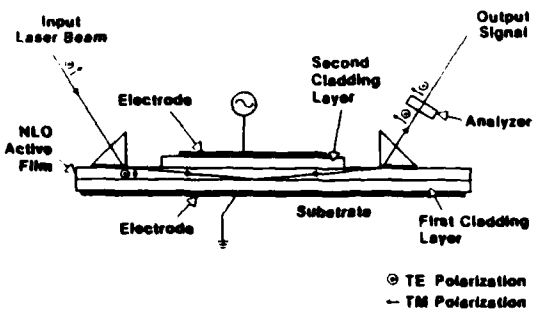
| | $LiNbO_3$ Modulator | Polymer Modulator |
|---|---|---|
| Switching Voltage (V) | 3 1/2 – 10 1/2 | 1.3 (0.7 With Higher $\chi^{(2)}$) |
| Power Requirement (W) | 0.6 – 5 | 0.03 |
| Maximum Frequency (GHz) | 8 – 24 | > 50 |

  — No Expected Velocity Mismatch Implies Higher Frequency Devices are Possible With Polymers
- Electrooptic Bragg Cell
  — High Speed Radar Signal Processing
  — 20 GHz as a Target
- Second Harmonic Generation
  — High Efficiency Doubling of a Diode Laser

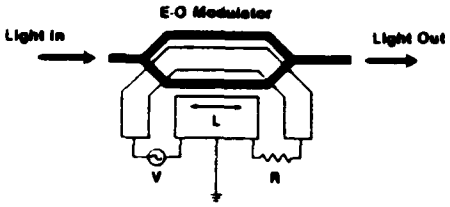
## Waveguide Devices




## Polymeric Electrooptic Modulator



## Traveling-Wave Waveguide

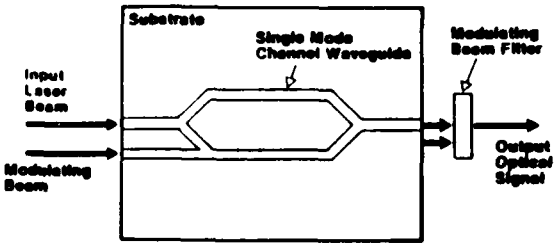



- Voltage Varies Along the Length ($L \geq \lambda$ Electrical)
- Important Device Parameters:
  - Voltage
  - Optical Mode Size
  - Drive Power
  - Speed
  - Length
  - Impedance

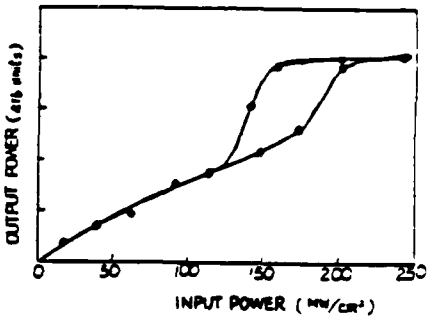
## State-of-Art $X^{(3)}$ Devices

- Far Less Progress Than $X^{(2)}$
- Large Payoff in Multiplexing and Demultiplexing
  - High Speed
  - Handle Many Inputs
  - Very High $X^{(3)}$
- Can Lead to:
  - All Optical Interferometer and Optical Switch
  - Optical Bistability and Digital Optical Information Processing
  - Optically Induced Dynamic Grating and Real-Time Holography
- Device Performance Depends on Material Properties in a Complicated Way
  - Determined by Device Architecture
  - Parallel/Analog Processing of 2D Image
  - Phase Conjugate Optics and Image Processing
  - Self Focusing/Defocusing Applications

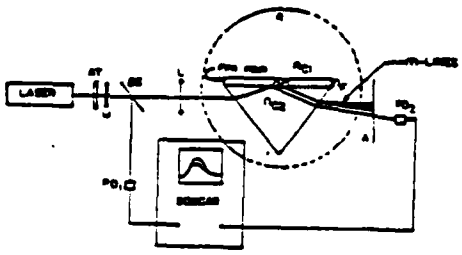
## Mach-Zehnder All Optical Modulator




OPTICAL BISTABILITY IN A NONLINEAR POLYMER FABRY-PEROT ETALON



OPTICAL BISTABILITY IN A POLYMER
QUASI WAVE GUIDE INTERFEROMETER




MERITS:

(i) Obtain Linear Refractive Index and Film Thickness

(ii) Obtain Both Magnitude and Sign of $\chi^{(3)}$

Ref 28

OPTICAL BISTABILITY IN A
NONLINEAR POLYMER
QUASI-WAVEGUIDE INTERFEROMETER

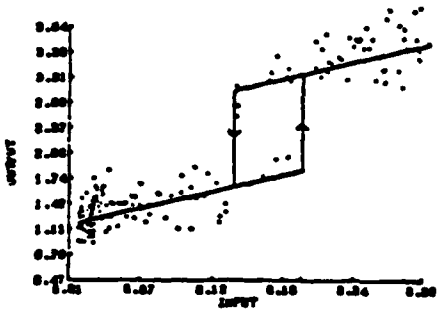



Figure 1. The observed optical bistability behavior in the poly-[illegible] polymer quasi-waveguide interferometer. The incoming angle is 45°.

## Summary

*Second Order*

- Poled Polymer Films
  - Close to Achieving Levels of Response for Electrooptic Device Application
- First Polymers Comparable to Lithium Niobate Reported
- Focus for Research to Achieve Optimum Electrooptic Modulation
  - $\chi^{(2)}$ Parallel to Film Surface

*Third Order*

- Nonlinearities of $10^{-8}$ esu Large for Nonresonance but Still Needs to be Larger ($\approx 10^{-7}$ esu) for Broad Device Application
- State-of-Art of $10^{-8}$ esu Will Find Applications in Optical Wave Guide Devices Such as Optical Switches and Optically Controlled Modulators
- Thin Film Applications Such as Etalons Unlikely Unless Significant Advances in Larger Nonlinearities, Optical Flatness and Optical Clarity

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# NONLINEAR OPTICAL EFFECTS IN POLYMERIC FILMS

NONLINEAR OPTICAL EFFECTS

IN

POLYMERIC FILMS

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SECOND ORDER NONLINEAR OPTICAL PROCESSES

CURRENT STATUS

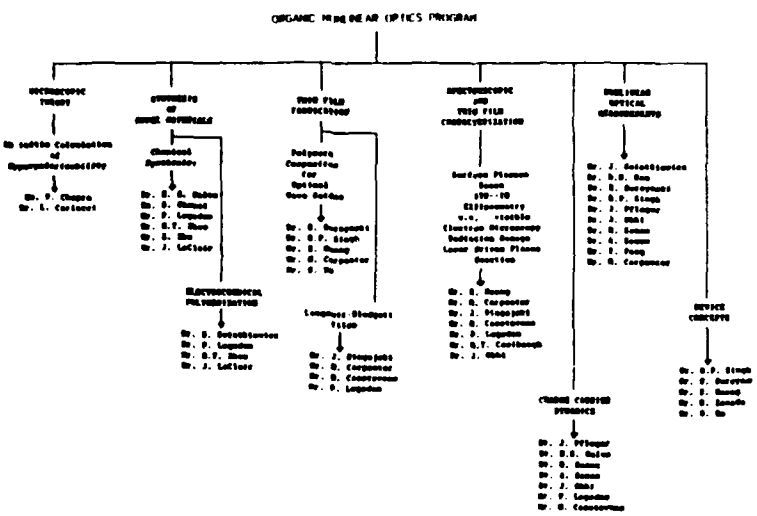
1. PREDICTABILITY OF STRUCTURE
   FOR MOLECULAR ENGINEERING
   ⟶ REASONABLE

2. LARGE $\chi^{(2)}$
   FAST RESPONSE TIME ⟶ ALREADY ACHIEVED
   LOW DC DIELECTRIC CONSTANT

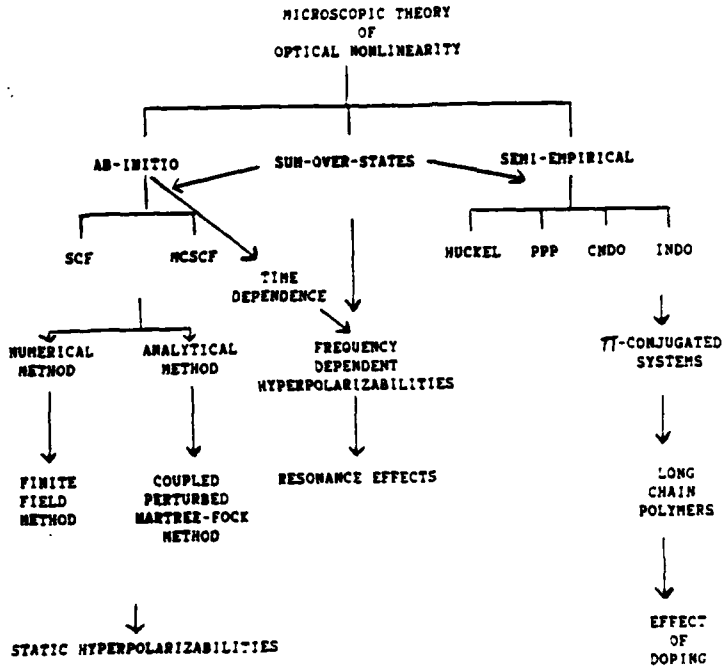
3. GUIDED WAVE PROCESSES - ALREADY DEMONSTRATED

4. POLYMERIC STRUCTURES
   NOT REQUIRED, BUT MAY BE DESIRABLE FOR MATERIALS
   PROCESSING AND DEVICE APPLICATIONS
   DOPED POLYMERS, LIQUID CRYSTALLINE POLYMERS, ETC.

5. DEVICES (?) : RESTRICTED BY MATERIALS LIMITATION



# B-3




Ab-initio Calculations of Second Hyperpolarizabilities (γ)

OBJECTIVE: Relative importance of σ and π contributions

Comparison of various π electron structures

π-electron conjugation effect

Sign of γ

Anisotropy of γ tensor

Effect of substituents

Conformational effect

Effect of Structural (conformational) defects such as solitons, polarons and bipolarons

⇩

Identify Structural Parameters for enchancing $\chi^{(3)}$

AB-INITIO APPROACH

DEFINE MOLECULAR HAMILTONIAN INCLUDING FIELD DEPENDENT STARK TERM

CONSTRUCT LCAO - MO - SLATER DETERMINANTS WITH A CHOICE OF AO BASIS SET

↓

OPTIMIZE THE GEOMETRY USING SCF

↓

CALCULATE DIPOLE MOMENT AS A FUNCTION OF FIELD

↓

POLYNOMIAL FIT TO GET γ

↓

CHANGE FIELD DIRECTIONS TO CALCULATE DIFFERENT COMPONENTS OF γ

↓

ORBITAL TRANSFORMATION TO SEPARATE σ AND π-CONTRIBUTIONS

↓

CONTOUR PLOTS TO OBTAIN FIELD INDUCED CHARGE REDISTRIBUTION

STATIC SECOND HYPERPOLARIZABILITIES (γ)

↓

NONRESONANT VALUE

MERITS OF THIS APPROACH:

ONLY GROUND STATE PROPERTIES NEED TO BE DEFINED

IN PERTURBATIVE CALCULATIONS INVOLVING EXCITED STATES EXPRESSION, EXCITED STATE PROPERTIES NEED TO BE CALCULATED

# B-4

SOME CONCLUSIONS OF THEORETICAL STUDIES OF MICROSCOPIC NONLINEARITY

1. THE CHOICE OF BASIS, PARTICULARLY THE INCLUSION OF DIFFUSE POLARIZATION FUNCTIONS, IS IMPORTANT IN DESCRIBING THE HYPERPOLARIZABILITIES OF CONJUGATED SMALL MOLECULES.

2. $\gamma$ IS ANISOTROPIC, WITH THE COMPONENT $\gamma_{ZZZZ}$ ALONG CHAIN GROWING RAPIDLY FOR THE CONJUGATED HYDROCARBONS SERIES POLYENES, POLYYNES AND CUMULENES AS THE CHAIN LENGTH GROWS.

3. FOR POLYENES, CHAIN LENGTH DEPENDENCE OF $N^{3.2}$ IS FOUND. FREE ELECTRON MODEL AND HUCKEL MODEL PREDICT $N^5$ AND $N^{5.3}$ RESPECTIVELY.

4. THE CORRESPONDING ORBITAL ANALYSIS SHOWS THAT THE SIGMA AND $\pi$-ELECTRON CONTRIBUTIONS TO $\gamma$ ARE OF OPPOSITE SIGNS.

5. CONTOUR MAP OF THIRD DERIVATIVE OF CHARGE DENSITY WITH RESPECT TO FIELD (REGIONAL CONTRIBUTION ANALYSIS OF $\gamma$) CONDUCTED FOR POLYYNES, INDICATES THAT THE NONLINEAR ELECTRONIC DISTORTION IS A CO-OPERATIVE EFFECT WITH A SUBSTANTIAL CHARGE TRANSFER ALONG THE ENTIRE LENGTH OF THE CHAIN.

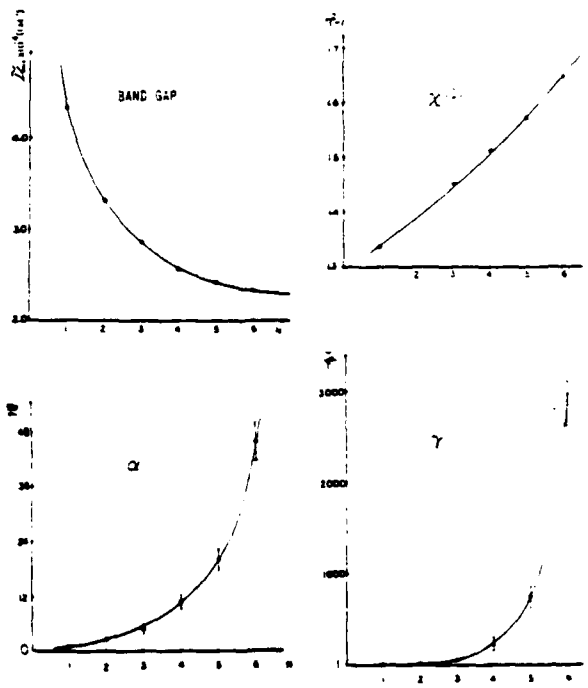
6. OUR SCF CALCULATION RESULTS FOR $\alpha$ COMPARE WELL WITH THOSE OF THE SOS METHOD, BUT $\gamma$ VALUES DO NOT AGREE.

7. IN THE SERIES R1 - C≡C - R2, THE LONGITUDINAL COMPONENT $\gamma_{ZZZZ}$ INCREASES AS THE ELECTRON WITHDRAWS GROUPS AT R1 OR R2 ARE SUBSTITUTED.

8. A COMPARISON OF $\gamma$ FOR CIS-BUTADIENE, TRANS-BUTADIENE AND THIOPHENE REVEALS THE FOLLOWING ORDER:

   TRANS-BUTADIENE) THIOPHENE) CIS-BUTADIENE

THIOPHENE OLIGOMERS
REPEAT UNIT DEPENDENCE



# B-5

THIOPHENE OLIGOMERS

DEPENDENCE OF $\alpha$ AND $\gamma$ ON NUMBER OF REPEAT UNITS (N)

$F = A \times BIN - \delta^{C}$ $\qquad$ $F = \alpha$ OR $\gamma$

| | | | |
|---|---|---|---|
| EXPT | FOR $\langle\alpha\rangle$ | C = 1.69 | FOR $\gamma$ C = 4.05 |
| OUR AB-INITIO CALCULATION ON POLYENES | FOR $\alpha$ | C = 1.3 - 1.5 | FOR $\gamma$ C = 3.2 - 3.4 |
| FREE ELECTRON MODEL | FOR $\alpha$ | C = 3 | FOR $\gamma$ C = 5 |
| PPP MODEL | $\alpha$ | C = 2.3 | $\gamma$ C = 5.3 |

FOR THIOPHENE

| | $\langle\alpha\rangle$ | $\langle\gamma\rangle$ |
|---|---|---|
| AB-INITIO CALCULATION | $8.21 \times 10^{-24}$ $(cm^3)$ | $1 \times 10^{-36}$ $(esu)$ |
| EXPT VALUE | $9.8 \times 10^{-24}$ | $3.5 \times 10^{-36}$ |

FOR BITHIOPHENE

| | $\langle\alpha\rangle$ |
|---|---|
| AB-INITIO CALCULATION | $1.45 \times 10^{-23}$ |
| EXPT VALUE | $2.5 \times 10^{-23}$ |

MEASUREMENTS OF $\chi^{(3)}$

RELEVANT PARAMETERS

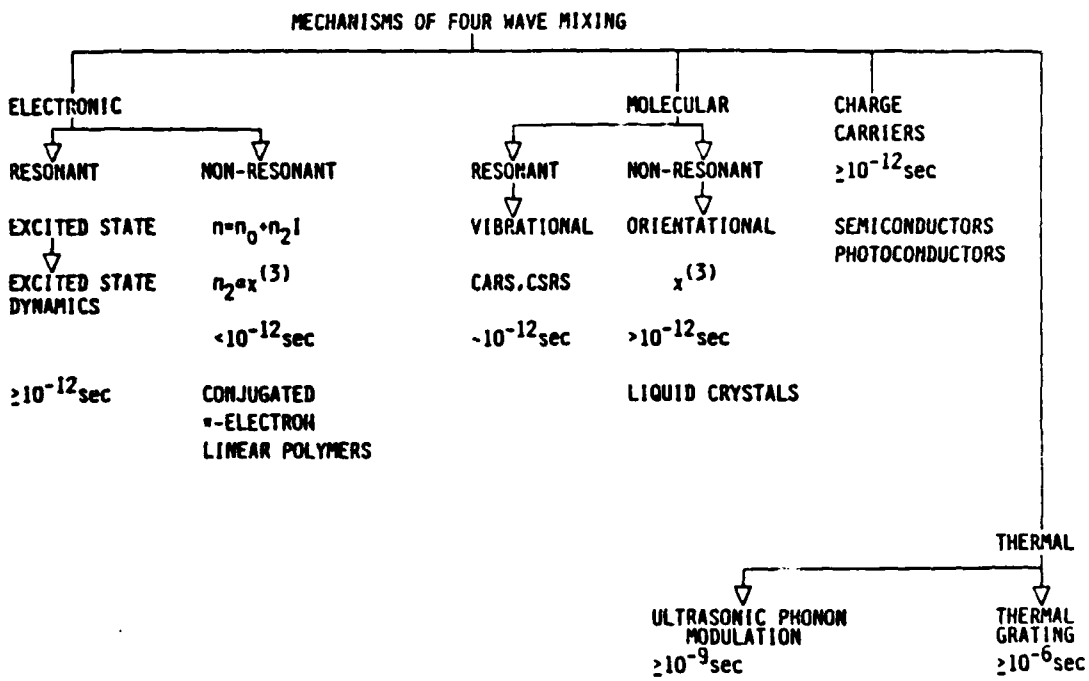
1. MAGNITUDE OF $\chi^{(3)}$
2. RESPONSE TIME
3. ANISOTROPY OF $\chi^{(3)}$
   FOURTH RANK TENSOR
4. SIGN OF $\chi^{(3)}$
5. REAL OR COMPLEX
6. LOCAL FIELD EFFECT
7. ELECTRONIC RESONANCE ENHANCEMENT
8. VIBRATIONAL RESONANCE ENHANCEMENT

TECHNIQUES USED

FEMTOSECOND DEGENERATE FOUR WAVE MIXING
OPTICAL WAVEGUIDE
NON-LINEAR FABRY PEROT
SURFACE PLASMON
THIRD HARMONIC GENERATION
KERR GATE EXPERIMENT

## MECHANISMS OF FOUR WAVE MIXING

- **ELECTRONIC**
  - **RESONANT**
    - EXCITED STATE
      - EXCITED STATE DYNAMICS
    - $\geq 10^{-12}$sec
  - **NON-RESONANT**
    - $n = n_0 + n_2 I$
    - $n_2 \propto \chi^{(3)}$
    - $< 10^{-12}$sec
    - CONJUGATED $\pi$-ELECTRON LINEAR POLYMERS
- **MOLECULAR**
  - **RESONANT**
    - VIBRATIONAL
    - CARS, CSRS
    - $\sim 10^{-12}$sec
  - **NON-RESONANT**
    - ORIENTATIONAL
    - $\chi^{(3)}$
    - $> 10^{-12}$sec
    - LIQUID CRYSTALS
- **CHARGE CARRIERS**
  - $\geq 10^{-12}$sec
  - SEMICONDUCTORS
  - PHOTOCONDUCTORS
- **THERMAL**
  - ULTRASONIC PHONON MODULATION
    - $\geq 10^{-9}$sec
  - THERMAL GRATING
    - $\geq 10^{-6}$sec



## MEASUREMENTS OF $\chi^{(3)}$

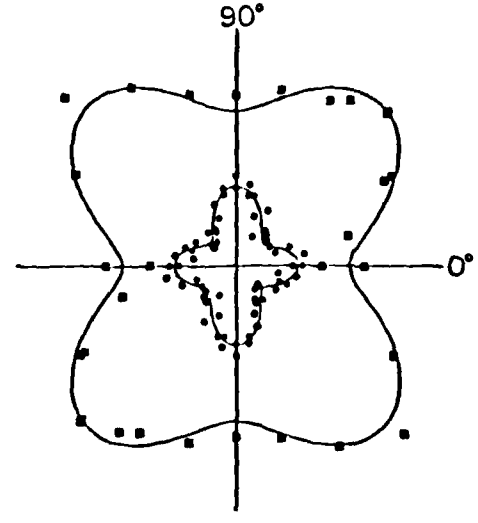
RELEVANT PARAMETERS:

1. MAGNITUDE OF $\chi^{(3)}$
2. RESPONSE TIME
3. ANISOTROPY OF $\chi^{(3)}$
   FOURTH RANK TENSOR
4. SIGN OF $\chi^{(3)}$
5. REAL OR COMPLEX (?)
6. LOCAL FIELD EFFECT
7. ELECTRONIC RESONANCE ENHANCEMENT
8. VIBRATIONAL RESONANCE ENHANCEMENT

TECNNIQUES USED:

FEMTOSECOND DEGENERATE FOUR WAVE MIXING
OPTICAL WAVEGUIDE
NON-LINEAR FABRY PEROT
SURFACE PLASMON
THIRD HARMONIC GENERATION
KERR GATE EXPERIMENT

POLAR PLOT: $\chi^{(3)}$ AS A FUNCTION OF FILM ROTATION ANGLE




RESONANT $\chi^{3}$ BY FOUR WAVE MIXING

ELECTRONIC RESONANCES

| SYSTEMS | MECHANISM | RESPONSE TIME | $\chi^{(3)}$ |
|---|---|---|---|
| PVK TNF | CORRELATED ELECTRON-HOLE PAIRS | >100 ps | $10^{-11}$ esu |
| POLYACETYLENE PMMA | SOLITON POLARON DYNAMICS | fs | $10^{-9}$ esu |
| PHTHALOCYANINES (LB FILMS) | EXCITON DYNAMICS | ps | $10^{-8}$ esu |
| POLYTHIOPHENE (ELECTROCHEMICALLY DEPOSITED) | POLARON DYNAMICS | fs | $10^{-9}$ esu |
| POLYALKYLTHIOPHENE (SOLUTION CAST FILMS LB FILMS | POLARON DYNAMICS | fs | $10^{-9}$ esu |

CAUTION:

$\chi^{(3)}_{3}$ DEPENDENT ON PULSE WIDTH GOING FROM 400fs TO 2 ps INCREASES $\chi^{3}$ BY A FACTOR OF 5 IN PHTHALOCYANINES

# B-7

NONLINEAR OPTICAL EFFECTS
IN
CONJUGATED POLYMERS
WITH
CONFORMATIONAL DEFECTS
(Bond Alternation)

NONRESONANT CASE: Change on Polymer Backbone can be Varied in a Controlled way - Tune $\chi^{(3)}$

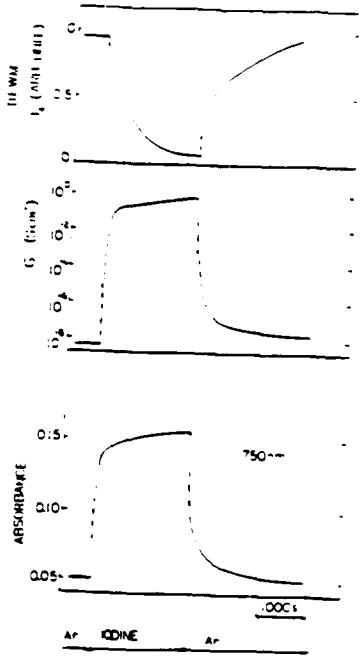
RESONANT CASE: Photoinduced Solitons and Bipolarons create Mid Gap States

Redistribution of Oscillator Strength

Large $\chi^{(3)}$ with Fast Response

A NEW PHENOMENON

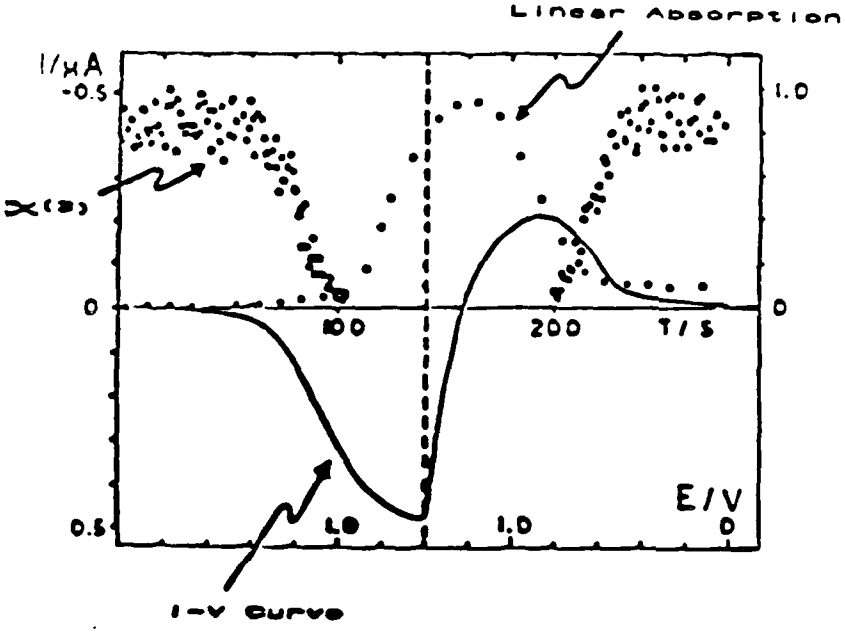
Chemical or Electrochemical Switching of $\chi^{(3)}$ Between High and Low States




POLYALKYLTHIOPHENE - LB FILMS
IODINE DOPING

IN-SITU ELECTROCHEMICAL STUDY OF
$\chi^{(3)}$ IN POLYTHIOPHENE

REDUCED FORM <-> OXIDIZED FORM <-> REDUCED FORM

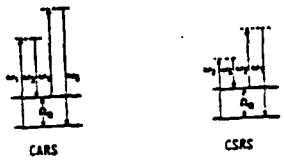



SWIATKIEWICZ, JANISZEWSKA AND PRASAD

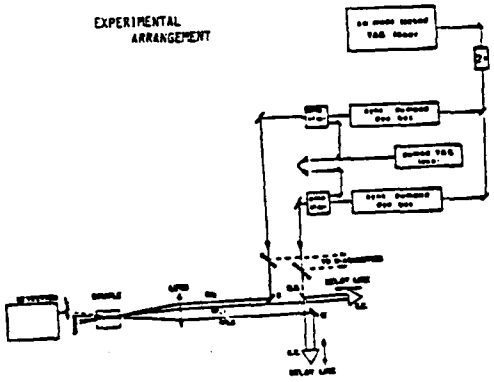
# B-8

PICOSECOND TIME-RESOLVED COHERENT
RAMAN SCATTERING

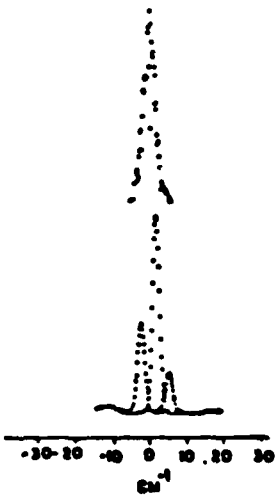
$\chi^{(3)}$

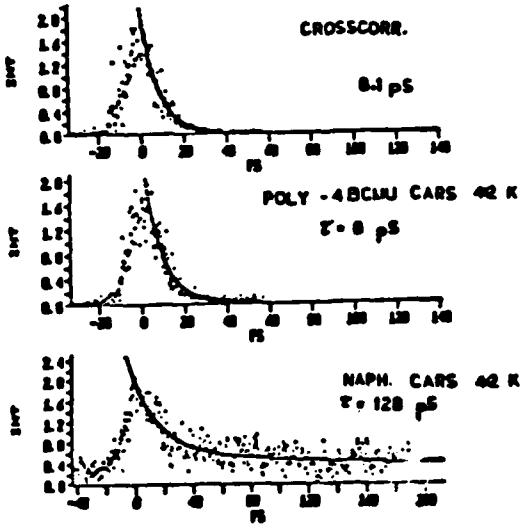



EXPERIMENTAL
ARRANGEMENT



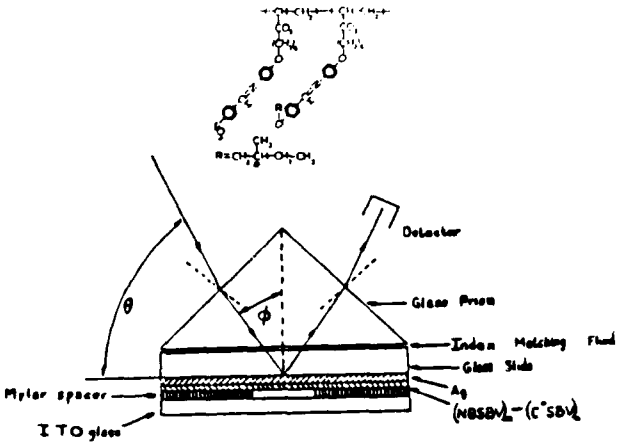
POLY - 4BCMU (LOW MOL. WT), 42 K

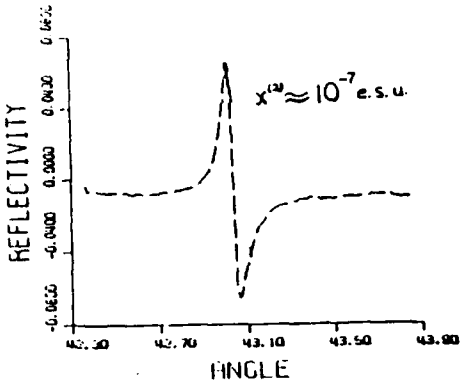


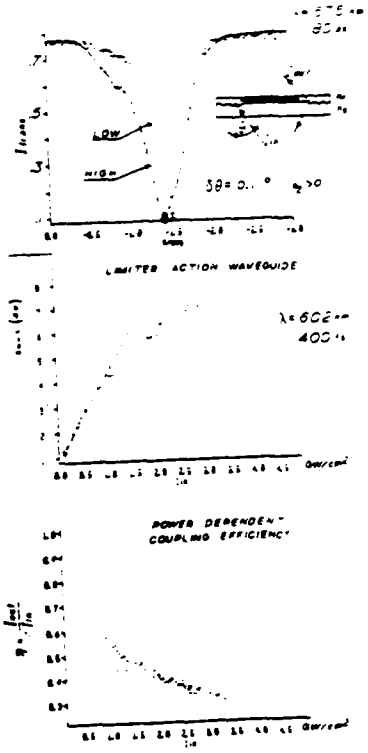
OPTICAL SWITCHING
OPTICAL BISTABILITY
OPTICAL LIMITER ACTION
LIGHT MODULATION

| | | |
|---|---|---|
| 1 | SURFACE PLASMON | ELECTRO-OPTIC MODULATION IN THE ELECTRICALLY POLED MONOLAYER LANGMUIR-BLODGETT FILMS OF A LIQUID CRYSTALLINE POLYMER |
| 2 | FABRY-PEROT ETALON | OPTICAL SWITCHING AND OPTICAL BISTABILITY<br>BOTH ABSORPTIVE AND DISPERSIVE |
| 3 | QUASI-WAVEGUIDE INTERFEROMETER | OPTICAL BISTABILITY |
| 4 | WAVEGUIDE | MAY BE ONLY EXAMPLE OF $\chi^{(3)}$ POLYMER WAVEGUIDE<br>LIMITER ACTION (INTENSITY DEPENDENT PHASE SHIFT)<br>INTENSITY DEPENDENT COUPLING ANGLE<br>FREQUENCY SPECTRUM SHAPING IN WAVEGUIDE PROPAGATION |
| 5 | HOLLOW FIBERS FILLED WITH NONLINEAR MATERIALS | LOW SCATTERING, GAIN AND AMPLIFICATION |




R. M. CARPENTER AND P. N. PRASAD



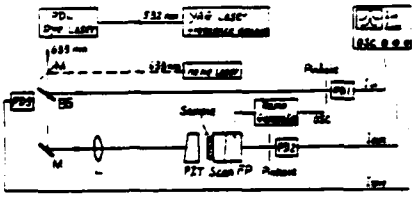


FIG. Experimental setup for the observation of optical instability.

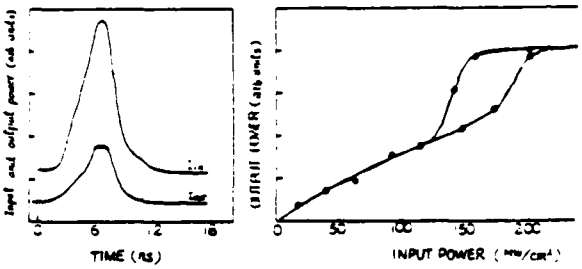



FIG 2 LEFT INPUT AND OUTPUT PULSES
RIGHT INPUT-OUTPUT CHARACTERISTICS

WHERE DO WE GO NOW?

1 ENHANCEMENT OF $\chi^{(3)}$

(A) DO WE NEED EXTENSIVE $\pi$ - ELECTRON DELOCALIZATION?

BAND GAP REDUCES. PROBLEM WITH NONRESONANT WINDOW

PROBLEM WITH DISTRIBUTION OF CONJUGATION LENGTH

A BROAD DISTRIBUTION OF BAND GAPS.

(B) DO WE NEED A HIGH MOLECULAR WEIGHT POLYMER?

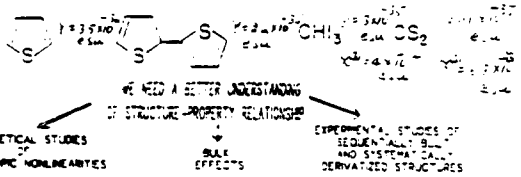
PROBLEM WITH SOLUBILITY

DERIVATIZE WITH LONG ALKYL CHAIN, REDUCES PACKING DENSITY

PROBLEM WITH DISTRIBUTION OF MOLECULAR WEIGHT

REFRACTIVE INDEX INHOMOGENEITIES

(C) DO WE NEED $\pi$ ELECTRONS?




WE NEED A BETTER UNDERSTANDING OF STRUCTURE-PROPERTY RELATIONSHIP

THEORETICAL STUDIES OF MICROSCOPIC NONLINEARITIES

BULK EFFECTS

EXPERIMENTAL STUDIES OF SEQUENTIALLY BUILT AND SYSTEMATICALLY DERIVATIZED STRUCTURES

2 OPTICAL QUALITY MATERIALS

PROCESSABLE MATERIALS

STRUCTURAL CONTROL, CHARACTERIZATION AND MATERIALS PROCESSING FOR LOW OPTICAL LOSS SYSTEMS

3 DEVICE PHYSICS AND DEVICE STRUCTURES

EXPERIMENTS WITH CHANNELED WAVEGUIDES, ETALONS, FIBERS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MS. S. GHOSAL
MR. J. SIEGAJSKI
MR. H.T. COOLBAUGH
MR. R. ZAWADA
DR. D.N. RAO
DR. S.P. SINGH
DR. J. PFLEGER
DR. L. JANISZEWSKA
MR. X. HUANG
MR. Y. PANG
MR. M. CARPENTER
MR. P. LOGSDON
MR. M. CASSTEVENS
MR. H.T. ZHAO

DR. DONALD R. ULRICH (AFOSR)

SUPPORT

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

A. F. Garito
University of Pennsylvania

# RECENT ADVANCES IN NONLINEAR OPTICAL PROPERTIES OF ORGANIC AND POLYMER SYSTEMS

C-2

# RECENT ADVANCES IN NONLINEAR OPTICAL PROPERTIES OF ORGANIC AND POLYMER SYSTEMS

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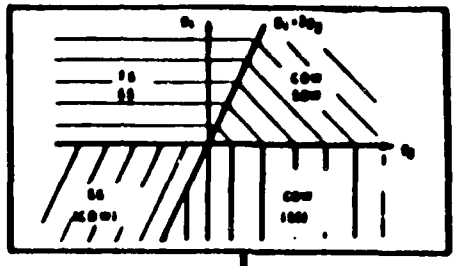
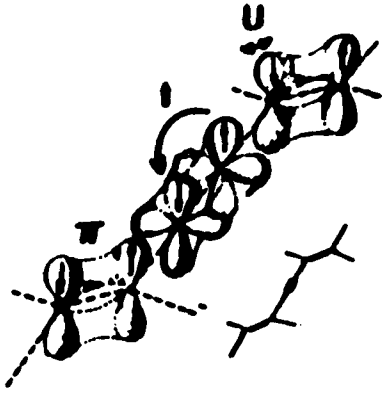
## ELECTRON CORRELATED STATES: ORIGIN OF THIRD ORDER NONLINEAR OPTICAL SUSCEPTIBILITY OF CONJUGATED LINEAR CHAINS

## FERMI GAS WITH ELECTRON-ELECTRON INTERACTIONS

QFT






$\theta_i = \theta_j$

**TIGHT BINDING : HUCKEL**

$H = \sum t_{ij} c^{\dagger}_{i\sigma} c_{j\sigma}$

$E = \alpha + 2t \cos ka$

- INDEPENDENT ELECTRONS
- EXCITONS

$U/t \to 0$

**HUBBARD**

$H = t \sum c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum n_{i\uparrow} n_{i\downarrow}$

- ELECTRON CORRELATION
- 2 PHOTON STATES
- SDWs
- CDWs

$U_{ij}$

**SCF - MO - MCI**

$H = \sum t_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} + \sum U_{ij} c^{\dagger}_{i\sigma} c_{i\sigma} c^{\dagger}_{j\rho} c_{j\rho} + \sum (-1 - \sum U_{ij}) c^{\dagger}_{i\sigma} c_{i\sigma} + \sum U_{ij}$

- ALL VALENCE ELECTRONS
- S, D, T, Q, ---- CI
- 2 PHOTON STATES

$U/t \to \infty$

**HEISENBERG**

$H = \sum J_{ij} \cdot \vec{S}_i \cdot \vec{S}_j$

$J_{ij} = -2 t_{ij}^2 / U$

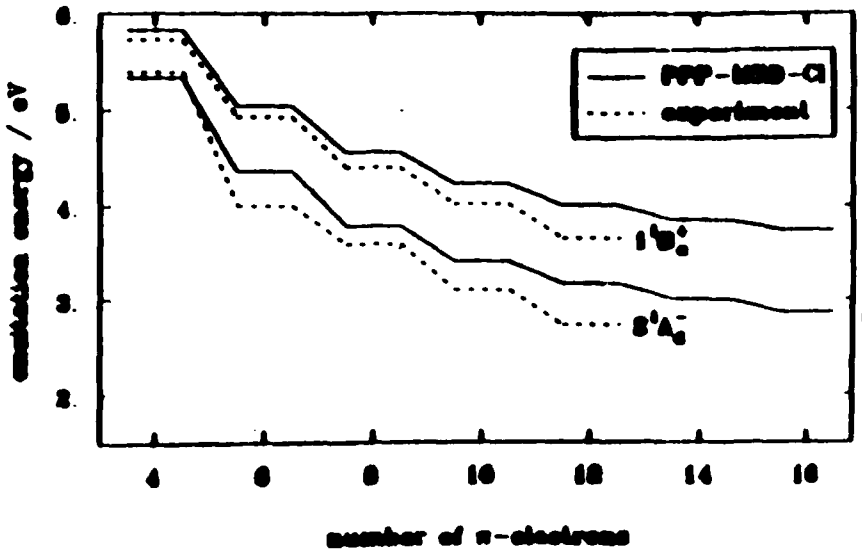
- 1D MAGNETIC CHAINS
- SDWs

ELECTRON DELOCALIZATION

COMPUTATION

# ELECTRON CORRELATION AND RESONANT PROCESSES

- $\pi$-ELECTRON STATES DOMINATED BY ELECTRON CORRELATIONS
- TWO PHOTON $2^1A_g$ STATE EXISTS BELOW FIRST OPTICALLY ALLOWED $1^1B_u$ STATE
- PPP AND HUBBARD MODELS OBTAIN CORRECT STATE ORDERING WITH INCLUSION OF AT LEAST DOUBLY EXCITED CONFIGURATIONS (DCI)

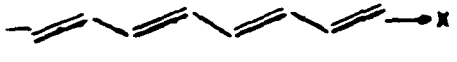



FROM TAVAN AND SCHULTEN, J. CHEM. PHYS. 85, 6602 (1986)

C-4

## ELECTRONIC STATES OF OT

| SYMMETRY | ENERGY (eV) | $\mu_{ag}$(D) | $\mu_{1^1B_u,n}$(D) |
|---|---|---|---|
| $5\,^1B_u$ | 7.30 | 1.14 | 0.00 |
| • $6\,^1A_g$ | 7.16 | 0.00 | • 13.24 |
| $4\,^1B_u$ | 7.01 | 1.11 | 0.00 |
| $3\,^1B_u$ | 6.47 | 0.01 | 0.00 |
| $5\,^1A_g$ | 6.07 | 0.00 | 1.11 |
| $4\,^1A_g$ | 6.00 | 0.00 | 2.84 |
| $3\,^1A_g$ | 5.19 | 0.00 | 0.07 |
| $2\,^1B_u$ | 4.79 | 0.88 | 0.00 |
| • $1\,^1B_u$ | 4.42 | • 7.81 | 0.00 |
| • $2\,^1A_g$ | 4.15 | 0.00 | • 2.82 |
| $1\,^1A_g$ | | | |




OT (octatetraene)

## VERTICAL EXCITATION ENERGIES: CHAIN LENGTH

| | $1\,^1B_u$ (eV) | | $2\,^1A_g$ (eV) | |
|---|---|---|---|---|
| N (sites) | Exp. | Theo. | Exp. | Theo. |
| 4 | 5.91 | 5.77 | 5.4(0-0) | 5.31 |
| 6 | 4.93 | 4.94 | 4.0(0-0) | 4.59 |
| • 8 | 4.40 | 4.42 | 3.97 | 4.15 |
| 10 | 4.02 | 4.07 | 3.48 | 3.90 |
| 12 | 3.65 | 3.83 | 2.91 | 3.74 |

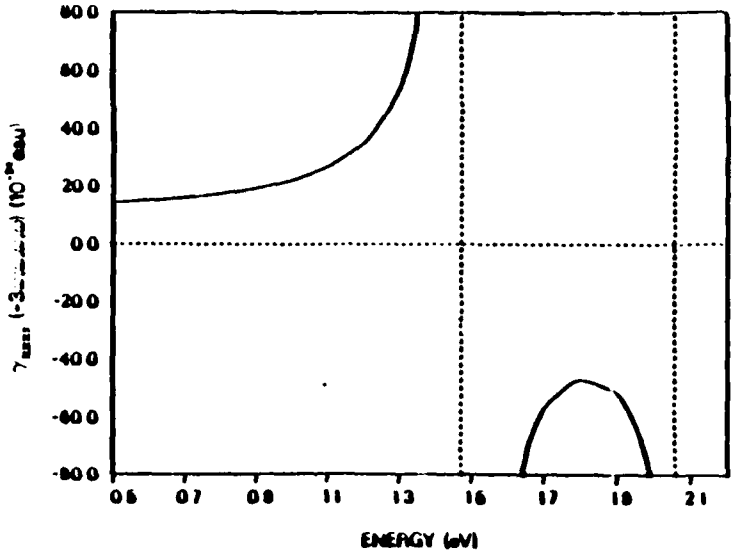
- DOMINANT 1 PHOTON STATE: $^1B_u$
- LOW-LYING $2\,^1A_g$ EXCITED STATE: ELECTRON CORRELATION

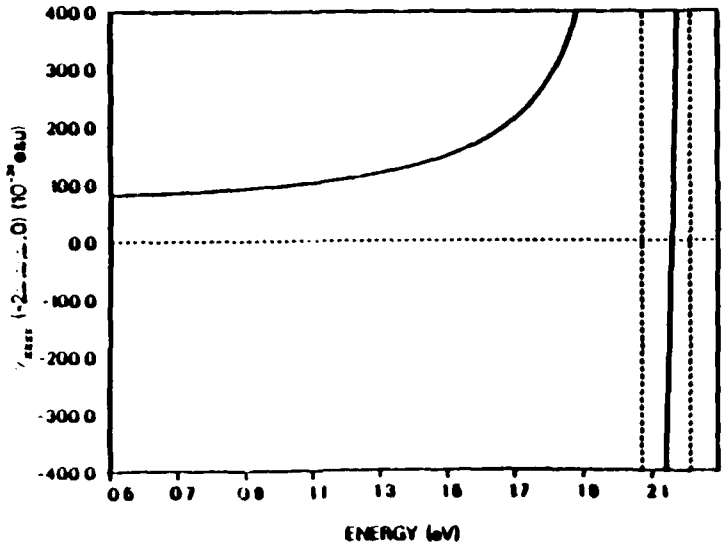
## MICROSCOPIC ORIGIN OF $\gamma(-3\omega;\omega,\omega,\omega)$ FOR LINEAR CONJUGATED CHAINS

| SYMMETRY | ENERGY (eV) | $\mu_{nn'}$(D) |
|---|---|---|
| $6\,^1A_g$ | 7.16 | (13.2) |
| $1\,^1B_u$ | 4.42 | 7.8 |
| $2\,^1A_g$ | 4.15 | (2.8) |
| $1\,^1A_g$ | | |

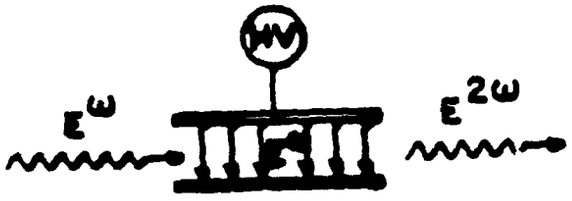
OT

- $\gamma_{xxxx}(-3\omega;\omega,\omega,\omega)$: $15.5 \times 10^{-36}$ esu ($\omega$: 0.65 eV/$\hbar$)
  $\gamma_g(-3\omega;\omega,\omega,\omega) = 3.4 \times 10^{-36}$ esu
- ONLY CONTRIBUTIONS: $g \rightarrow {}^1B_u \rightarrow {}^1A_g \rightarrow {}^1B_u \rightarrow g$
- $^1A_g$ STATES: THOSE WITH LARGEST $\mu_{nn'}$ WITH DOMINANT $^1B_u$ STATE
- 2 PHOTON $^1A_g$ STATES CRITICAL IN THIRD ORDER PROCESSES



# DC INDUCED SECOND HARMONIC GENERATION AND $\gamma_g$




$$P^{2\omega} = \gamma_g(-2\omega,\omega,\omega,0)\, E^{\omega} E^{\omega} E^{0}$$

$$\gamma_g(-2\omega;\omega,\omega,0) = \frac{1}{5}\left[\sum_i \gamma_{iiii} + \frac{1}{3}\sum_{i\neq j}\left(\gamma_{iijj} + \gamma_{ijij} + \gamma_{ijji}\right)\right] + \frac{1}{5}\frac{\mu}{kT}\beta_x(-2\omega;\omega,\omega)$$

- SECOND ORDER CONTRIBUTION $\beta_x$ VANISHES BY SYMMETRY

$\gamma_g$ VALUES (IN UNIT OF $10^{-36}$ esu) AT 1.787 eV:

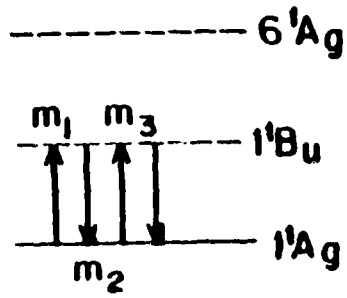
| | $\gamma_g$ (THEORY) | $\gamma_g$ (EXPERIMENT) |
|---|---|---|
| BUTADIENE (N=4) | 3.6 | 3.45 ± 0.2 |
| HEXATRIENE (N=6) (60% t -40% c) | 13.9 (12.9) | 11.3 ± 1.05 |

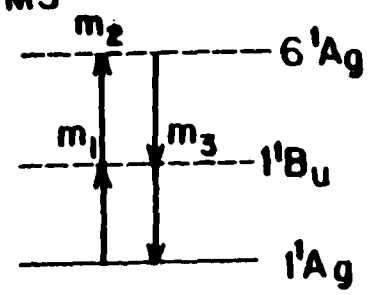
- CALCULATED $\gamma_g$ AGREES WITH EXPERIMENT BOTH FOR THE MAGNITUDE AND SIGN

## MICROSCOPIC ELECTRONIC ORIGIN OF $\gamma(-3\omega;\omega,\omega,\omega)$

$$\gamma_{ijkl}(-3\omega;\omega,\omega,\omega) = \frac{e^4}{4\hbar^3} \sum_{m_1 m_2 m_3} \frac{\langle g|r_i|m_3\rangle\langle m_3|r_j|m_2\rangle\langle m_2|r_k|m_1\rangle\langle m_1|r_l|g\rangle}{(\omega_{m_1 g}-\omega)(\omega_{m_2 g}-2\omega)(\omega_{m_3 g}-3\omega)} + \cdots$$

- TWO IMPORTANT TYPES OF CONTRIBUTING TERMS

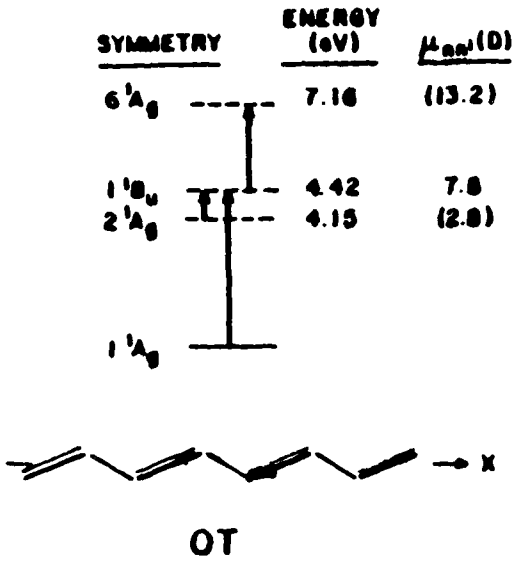


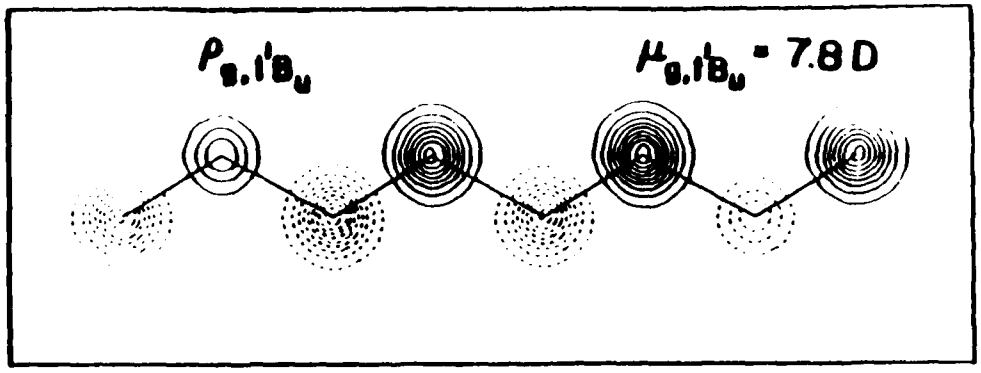



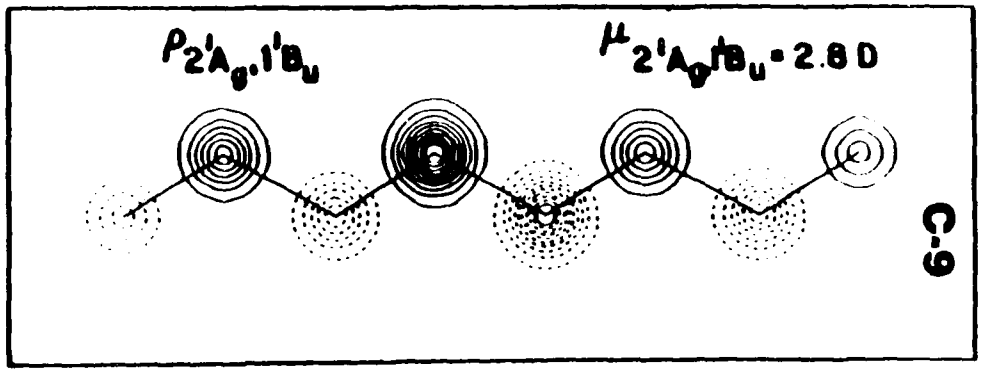

- INTERMEDIATE STATE $m_2$ IS THE GROUND STATE ITSELF
- NUMERATOR IS POSITIVE
- $(\omega_{gg}-2\omega)$ TERM IN DENOMINATOR IS NEGATIVE
- NEGATIVE CONTRIBUTION TO $\gamma$

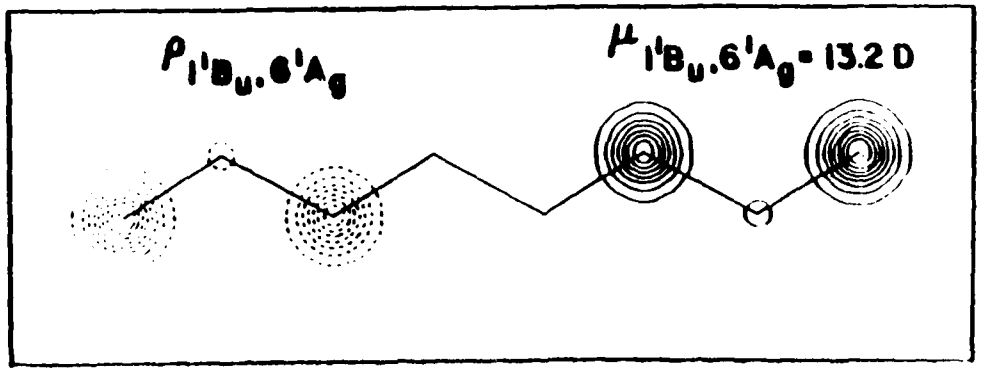
- INTERMEDIATE STATE $m_2$ IS THE UPPER $6^1A_g$ STATE
- NUMERATOR IS POSITIVE
- $(\omega_{m_2 g}-2\omega)$ TERM IN DENOMINATOR IS POSITIVE
- POSITIVE CONTRIBUTION TO $\gamma$

# TRANSITION DENSITY MATRIX DIAGRAMS




- $\langle \mu_{nn'} \rangle = -e \int r\, \rho_{nn'}(r)\, dr$
- CORRELATION OCCURS ACROSS ENTIRE CHAIN LENGTH
- $\mu_{1^1B_u,6^1A_g} \gg \mu_{2^1A_g,1^1B_u}$ : CHARGE SEPARATION IS LARGEST IN $\rho_{1^1B_u,6^1A_g}$

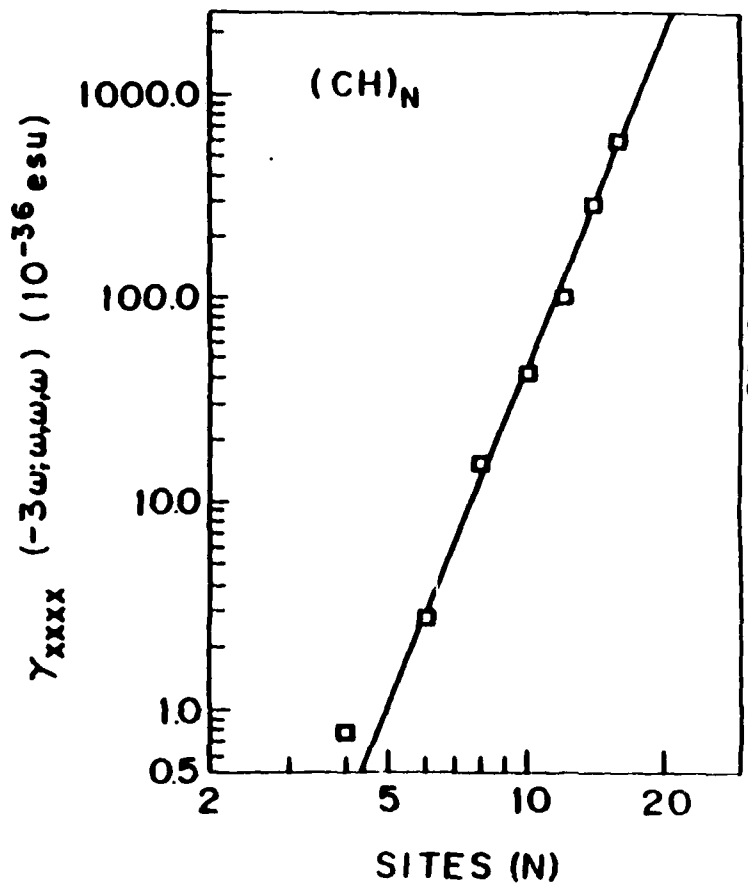
DEPENDENCE OF $\gamma(-3\omega;\omega,\omega,\omega)$ ON NUMBER OF SITES

- FINITE CHAIN LIMIT: POWER LAW DEPENDENCE

$$\gamma_{xxxx} \propto N^{5.4}$$

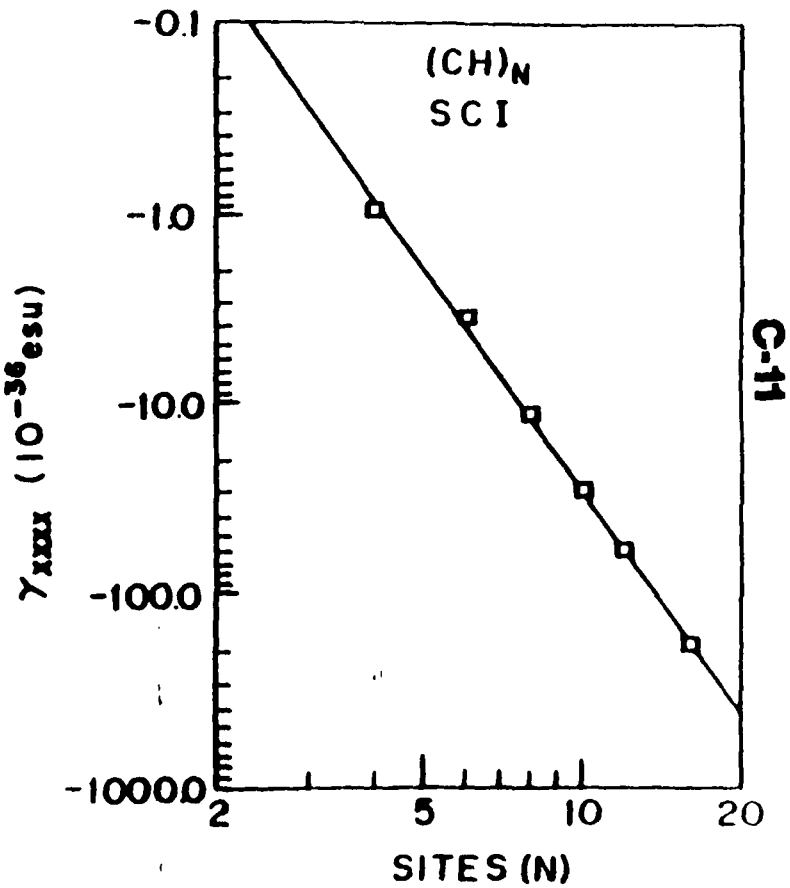
  - DECREASED EXCITATION ENERGY
  - INCREASED TRANSITION MOMENTS
  - INCREASED NUMBER OF CONTRIBUTING EXCITED STATE TERMS

- POLYMER CHAINS: $\chi^{(3)} \sim 10^{-9}$ esu
  - 50 SITES (60Å)

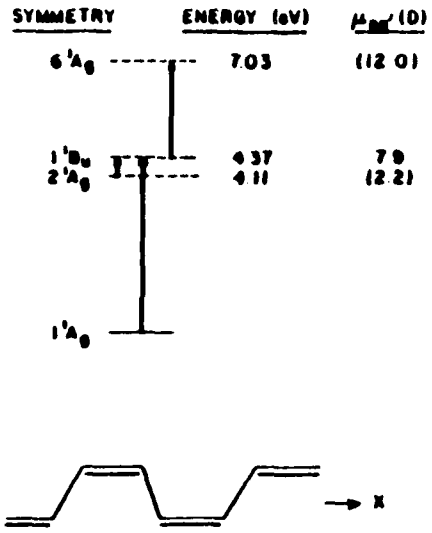


INCOMPLETE DESCRIPTION OF ELECTRON CORRELATION

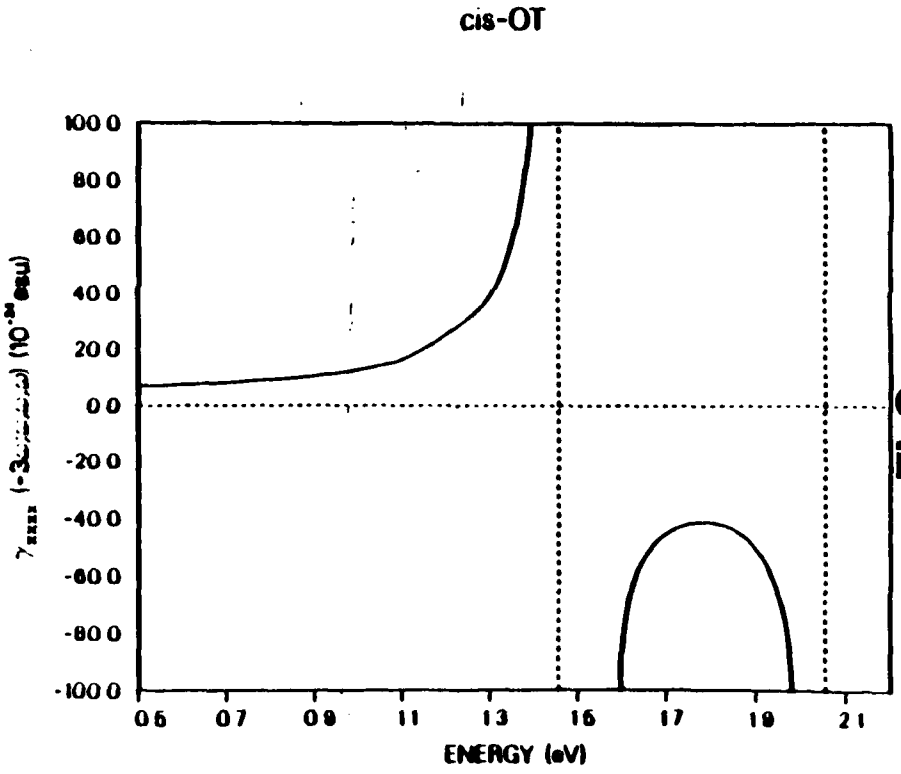
- SCI ONLY; OTHERWISE IDENTICAL TO FULL SDCI
- NEGATIVE SIGN FOR $\gamma_{xxxx}$ FOR ALL CHAIN LENGTHS
- SCI POWER LAW EXPONENT IS 3.9 AS COMPARED TO 5.4 OF SDCI



# MICROSCOPIC ORIGIN OF $\gamma(-3\omega;\omega,\omega,\omega)$ FOR cis - POLYENES




cis - OCTATETRAENE (cis - OT)



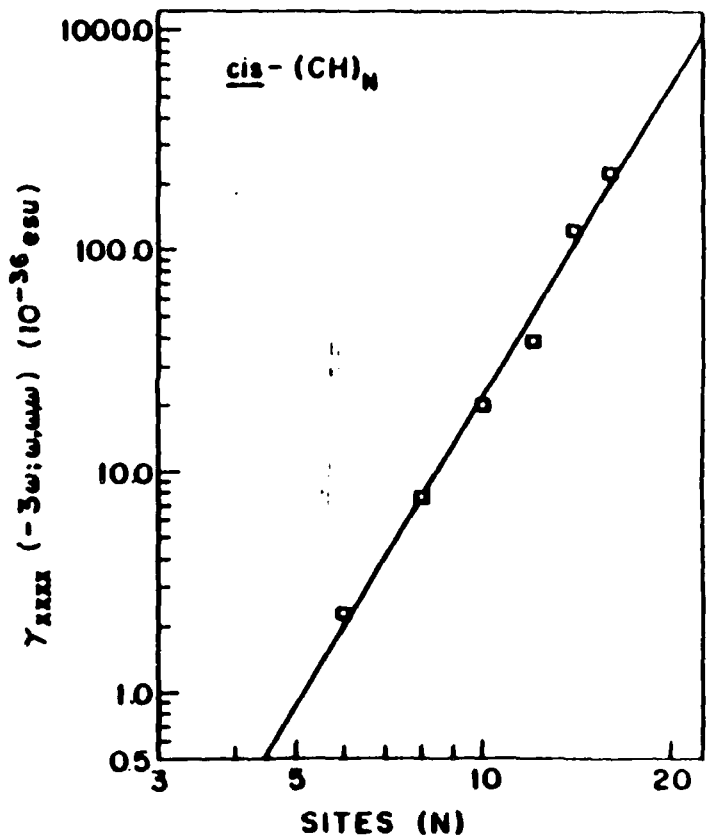

- $\gamma_{xxxx}(-3\omega;\omega,\omega,\omega) = 7.7 \times 10^{-36}$ esu
  $\gamma_g(-3\omega;\omega,\omega,\omega) = 1.8 \times 10^{-36}$ esu
  ($\omega$: 0.65 eV/Å)
- ONLY CONTRIBUTIONS: $g \to {}^1B_u \to {}^1A_g \to {}^1B_u \to g$
- $^1A_g$ STATES: THOSE WITH LARGEST $\mu_{nn'}$ WITH DOMINANT $^1B_u$ STATE
- 2 PHOTON $^1A_g$ STATES CRITICAL IN THIRD ORDER PROCESSES

DEPENDENCE OF $\gamma(-3\omega;\omega,\omega,\omega)$ ON NUMBER OF SITES

- FINITE CHAIN LIMIT: POWER LAW DEPENDENCE

$$\gamma_{xxxx} \propto N^{4.7}$$

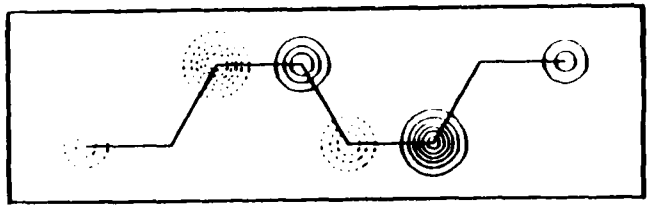
  - DECREASED EXCITATION ENERGY
  - INCREASED TRANSITION MOMENTS
  - INCREASED NUMBER OF CONTRIBUTING EXCITED STATE TERMS



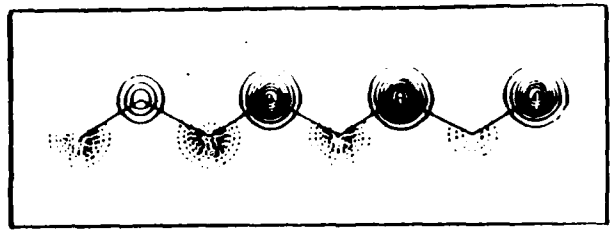
TRANSITION DENSITY MATRIX DIAGRAMS

$\rho_{g,1^1B_u}$

$\mu_{g,1^1B_u} = 7.9D$

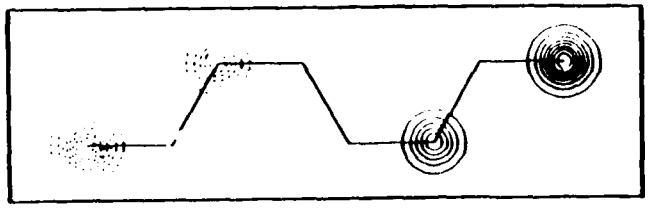


$\mu_{g,1^1B_u} = 7.8D$

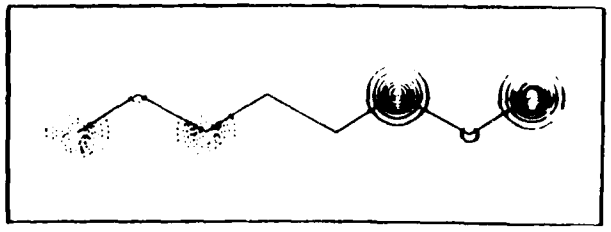


$\rho_{1^1B_u,6^1A_g}$

$\mu_{1^1B_u,6^1A_g} = 12.0D$



$\mu_{1^1B_u,6^1A_g} = 13.2D$



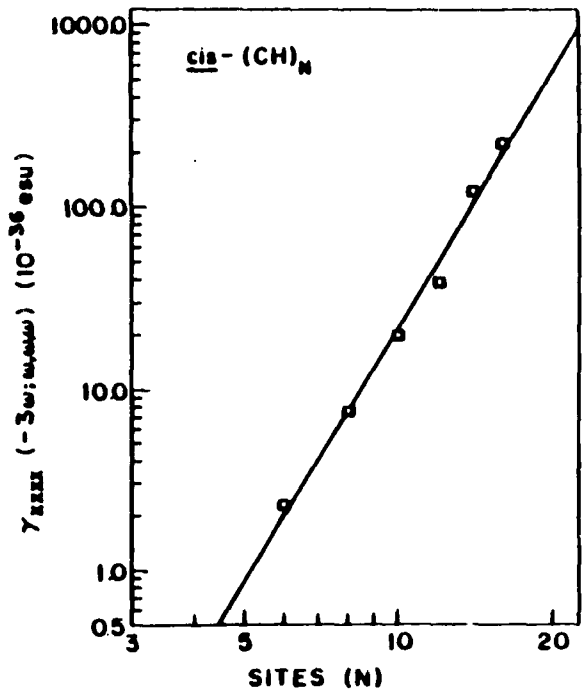
- CHARGE REDISTRIBUTION ESSENTIALLY THE SAME FOR <u>cis</u> AND <u>trans</u> CONFORMATIONS

DEPENDENCE OF $\gamma(-3\omega;\omega,\omega,\omega)$ ON NUMBER OF SITES

- FINITE CHAIN LIMIT: POWER LAW DEPENDENCE

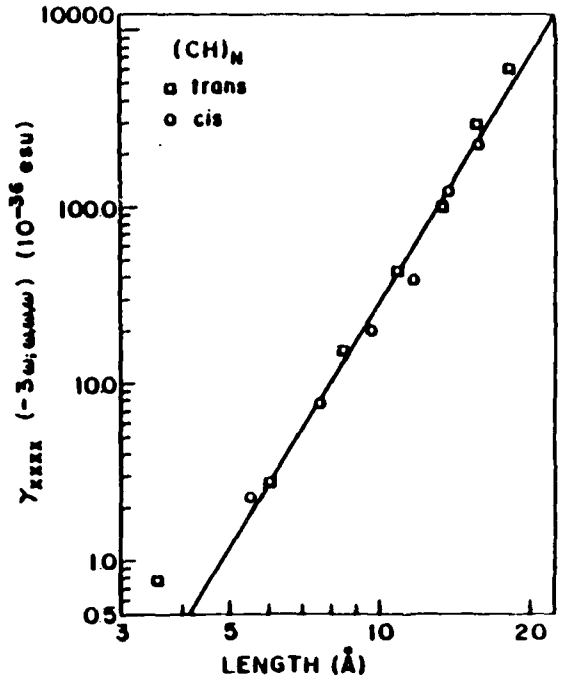
$$\gamma_{xxxx} \propto N^{4.7}$$

  - DECREASED EXCITATION ENERGY
  - INCREASED TRANSITION MOMENTS
  - INCREASED NUMBER OF CONTRIBUTING EXCITED STATE TERMS



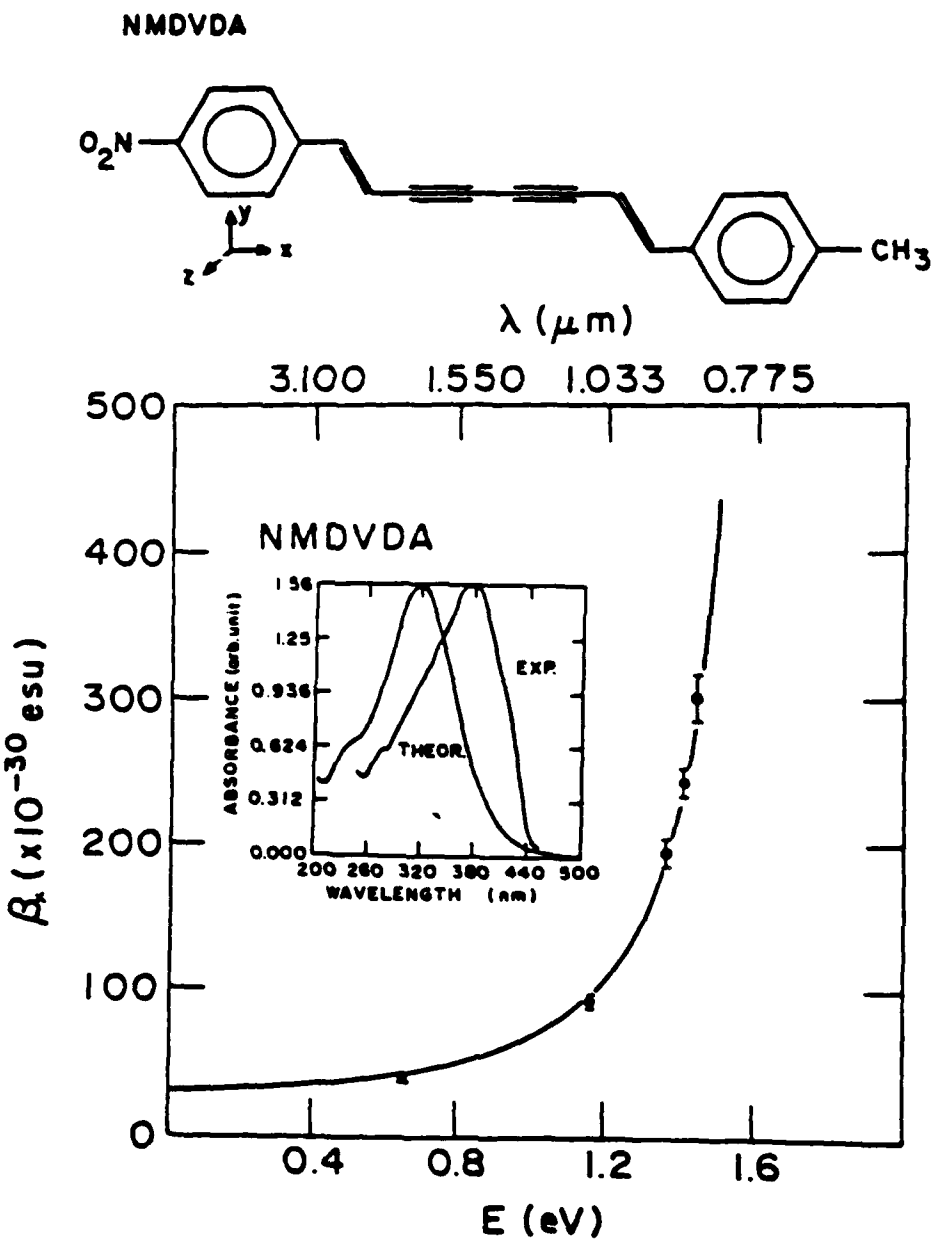
DEPENDENCE OF $\gamma(-3\omega;\omega,\omega,\omega)$ ON CHAIN LENGTH

- FINITE CHAIN LIMIT : $\gamma_{xxxx} \propto L^{4.6}$
- $\gamma_{xxxx}(-3\omega;\omega,\omega,\omega)$ FOR <u>cis</u> IS SMALLER THAN THAT FOR <u>trans</u> OF SAME NUMBER OF SITES
- DIFFERENCE IN $\gamma_{xxxx}(-3\omega;\omega,\omega,\omega)$ IS ACCOUNTED FOR BY DIFFERENCE IN LENGTH IN X-DIRECTION
- $\gamma_{xxxx}(-3\omega;\omega,\omega,\omega)$ MUCH MORE SENSITIVE TO CHAIN LENGTH THAN CONFORMATION

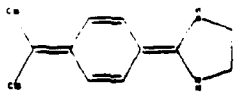


# C-17

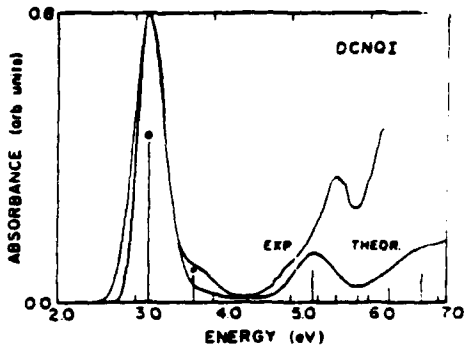
ELECTRON CORRELATED STATES: ORIGIN OF SECOND ORDER NONLINEAR OPTICAL SUSCEPTIBILITY OF CONJUGATED CYCLIC CHAINS

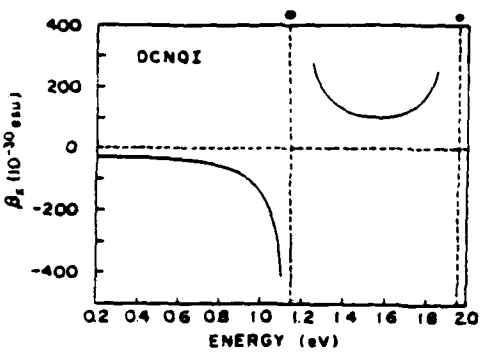


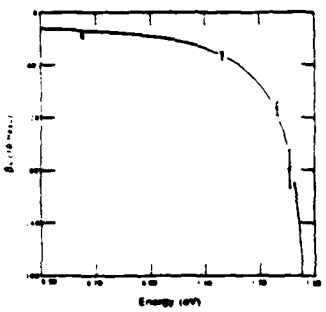
# DCNQI



| SYMMETRY $C_{2v}$ | ENERGY (eV) | $\mu^x_{nq}$ (D) | $\Delta\mu^x_n$ (D) |
|---|---|---|---|
| • $3A_1$ | 3.92 | 3.1 | -6.8 |
| $1B_2$ | 3.78 | 0.0 | -3.1 |
| • $2A_1$ | 2.31 | 9.0 | -4.1 |
| $1A_1$ | | | |



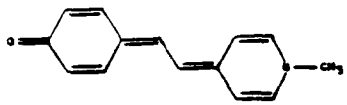
| DCNQI | Experimental | SDCI | SCI |
|---|---|---|---|
| $\mu_x$ (Debye) | 17.5 ±0.8 | 17 | 18.4 |
| $\beta_x$ ($10^{-30}$ esu) | -27 ±3 | -19.7 | -73.2 |
| $\mu_x\beta_x$ ($10^{-48}$ esu) | -474 ± 52 | -335 | -1347 |

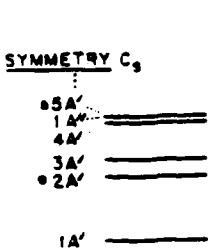
Comparison of Experimental and SDCI,SCI Values of Dipole Moment and the Second Order Microscopic Susceptibility at 0.65 eV.

| | SDCI | SCI |
|---|---|---|
| $\beta^{nn}_{xxx}$ | 44% | 85% |
| $\beta^{nn}_{xxx}$ | 56% | 15% |

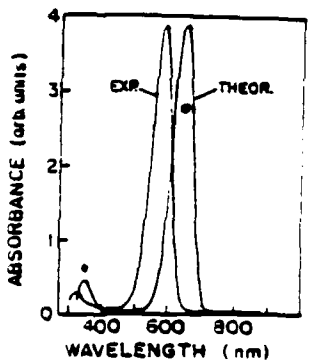
The percentage Contributions of Diagonal Term and Off-diagonal Term.

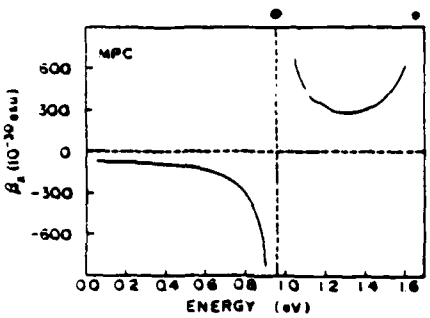
# MPC

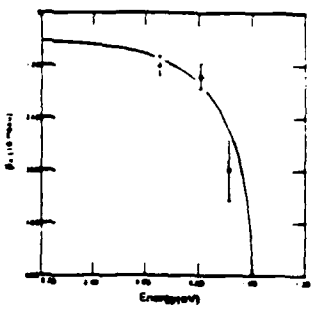





| ENERGY (eV) | $\mu^x_{ng}$ (D) | $\Delta\mu^x_n$ (D) |
|---|---|---|
| 3.69 | 4.7 | -8.3 |
| 3.69 | 0 | -20.0 |
| 3.54 | 0.4 | -13.8 |
| 2.42 | 0.1 | -14.1 |
| 1.92 | 12.0 | -4.4 |



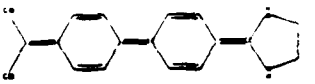
| MPC | Experimental | SDCI | SCI |
|---|---|---|---|
| $\mu_x$ (Debye) | 17.4 ±2.5 | 21.4 | 25.1 |
| $\beta_x$ ($10^{-30}$ esu) | -123 ± 22 | -104.7 | -236.4 |
| $\mu_x \beta_x$ ($10^{-48}$ esu) | -2140 ± 390 | -2240 | -5933 |

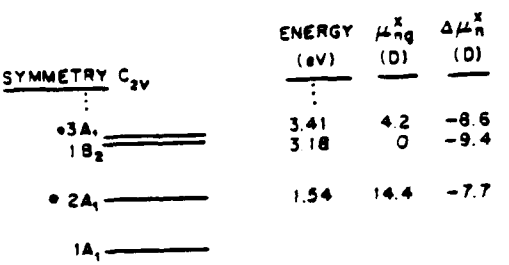
Comparison of Experimental and SDCI,SCI Values of Dipole Moment and the Second Order Microscopic Susceptibility at 0.65 eV.

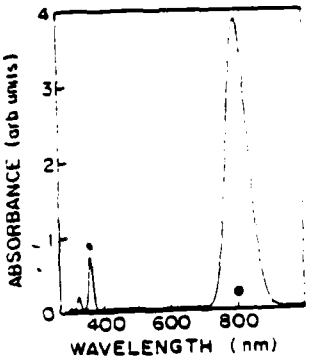
| | SDCI | SCI |
|---|---|---|
| $\beta^{w}_{xxx}$ | 55.5% | 86.4% |
| $\beta^{w}_{xxx}$ | 44.5% | 13.6% |

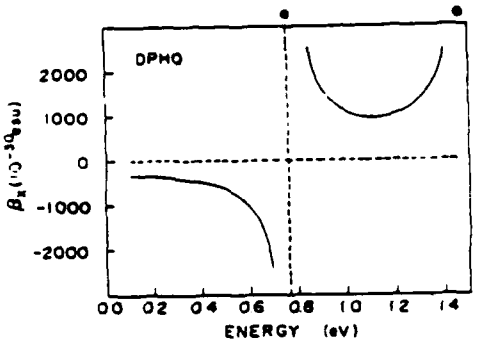
The percentage Contributions of Diagonal Term and Off-diagonal Term.

# DPHQ






| DPHQ | SDCI | SCI |
|---|---|---|
| $\mu_x$ (Debye) | 25.4 | 30.5 |
| $\beta_x$ ($10^{-30}$ esu) | -1410 | -626 |
| $\mu_x\ \beta_x$ ($10^{-48}$ esu) | -35800 | -19100 |

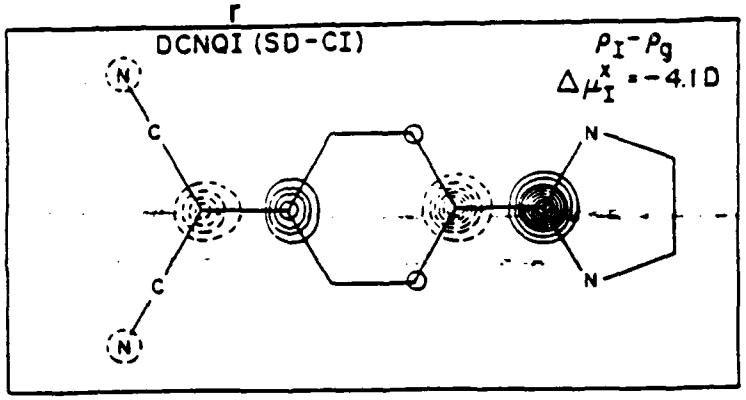
Comparison of Experimental and SDCI,SCI Values of Dipole Moment and the Second Order Microscopic Susceptibility at 0.65 eV.

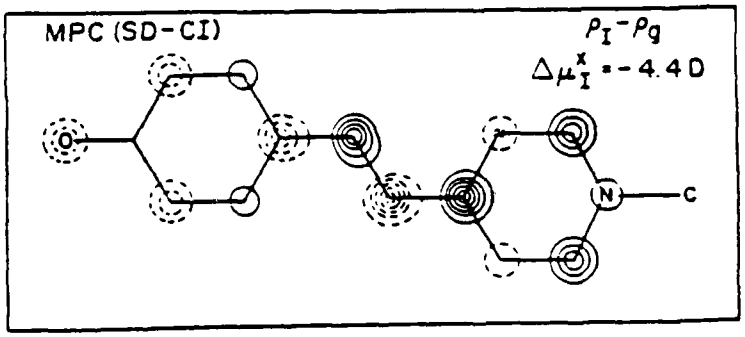
| | SDCI | SCI |
|---|---|---|
| $\beta^{NI}_{xxx}$ | 72% | 85% |
| $\beta^{NI}_{xxx}$ | 28% | 15% |

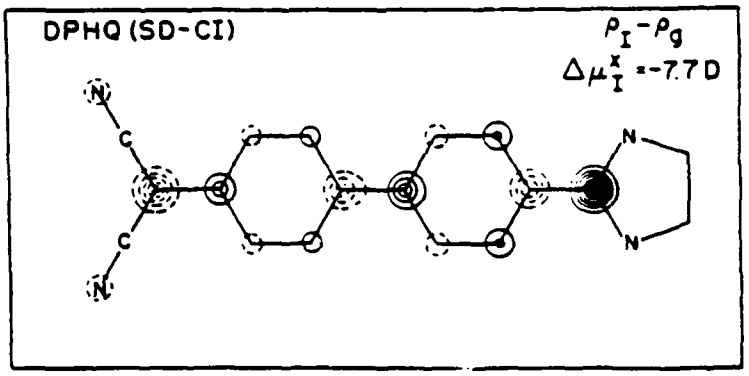
The percentac . Contributions of Diagonal Term and Off-diagonal Term.

ELECTRON DENSITY CORRELATION DIAGRAMS

$$\langle \Delta\mu_n \rangle = e \int_r r\,(\rho_n - \rho_g)\,dr$$

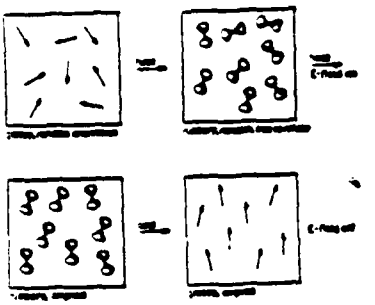


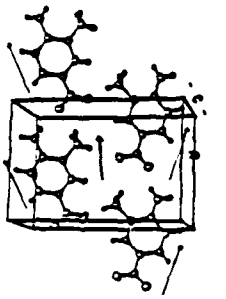



POLED POLYMER GLASSES

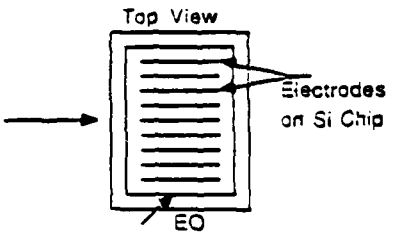
# C-22





MNA SINGLE CRYSTAL

TIR SLM DEVICES




Orientational Order

$$\chi^{(2)}_{111} = N \frac{\beta_{xxx}\mu_x E_x}{k_B T} f^{2\omega} (f^{\omega})^2 \left( \frac{1}{5} + \frac{4}{7}\langle P_2\rangle + \frac{8}{35}\langle P_4\rangle \right)$$

| CLASS | SYSTEM | $\mu_x\beta_x$ ($10^{-30}$cm$^5$Desu$^{-1}$) | $d_{11}$($10^{-9}$esu) ($\lambda$=1.907$\mu$m) | $r_{11}$($10^{-12}$m/V) ($\lambda$=0.633$\mu$m) |
|---|---|---|---|---|
| RESONANT RING | MNA | 66 | 0.8 | 0.3 |
| | AZO DYE | 530* | 6* | 2.5 |
| | MNA SINGLE CRYSTAL | | 230 | 67 |
| LINEAR CHAIN | NMDVDA | 200 | 2.3 | 0.9 |
| CYCLIC CHAIN | MPC | 2100 | 24 | 10 |
| | DCNQI | 470 | 5.3 | 2.2 |
| | DPHQ | 36000 | 410 | 170 |

*Measured at $\lambda$=1.58$\mu$m

RELATED REFERENCES


1. Third harmonic generation study of orientational order in nematic liquid crystals, Phys. Rev. A34, 5051 (1986).

2. Microscopic origin of second order nonlinear optical properties of organic structures, in Nonlinear Optical and Electroactive Polymers (Plenum, New York, 1988).

3. Recent developments in microscopic descriptions of the nonlinear optical properties of organic and polymer structures, in Proceedings SPIE 825 (1988).

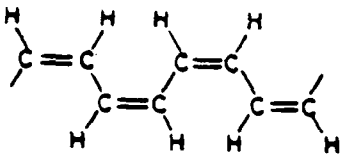
4. Nonlinear optical properties of linear chains and electron correlation effects, Phys. Rev. B - Rapid Communications (in press).

5. Symmetry controlled electron correlation mechanism for third order nonlinear optical properties of conjugated linear chains, in Electroresponsive Polymers, Special Issue, Mol. Cryst. Liq. Cryst. (1988).

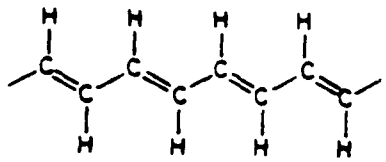
6. Nonlinear optical properties of polyenes: Electron correlation and chain conformation, in Nonlinear Optical Properties of Polymers (Materials Research Society, Boston, 1988) 109, p. 91.

S. Etemad
Bell Communications

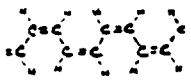
# CONJUGATED POLYMERS AND NONLINEAR OPTICS



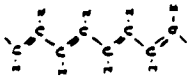
(a)



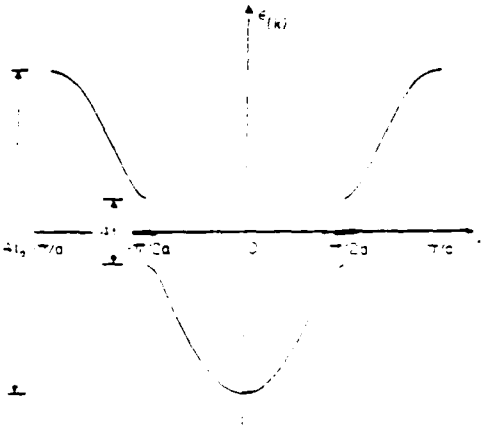
(b)



cis-



trans-

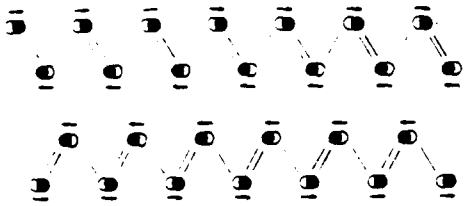



trans - $(CH)_x$

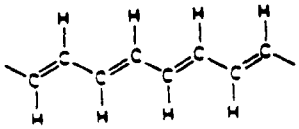
$t_0 = 2.5 - 3.0$ eV

$2\Delta = 4t_1 \approx \underline{1.5\ eV}$ c.f. a-Si

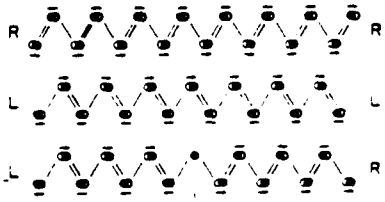
$t_2 \approx .05$ eV



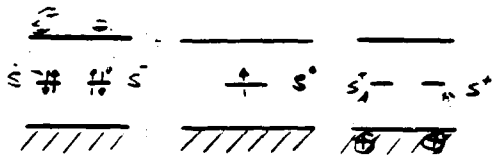
trans - $(CH)_x$



REVERSED CHARGE & SPIN




TRANS - $(CH)_x$

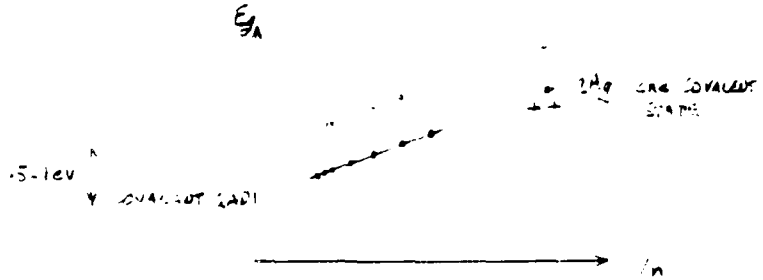


## CHEMISTRY VIEW

HIGHLY CORRELATED STATES

MANY BODY !

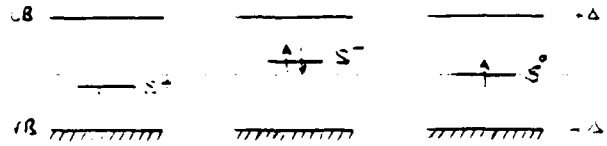
CASE STUDY : FINITE POLYENES




n = CONJUGATION LENGTH

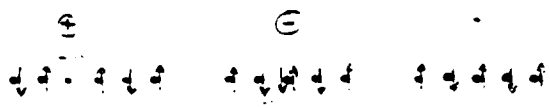
## COULOMB INTERACTIONS

### PERTURBATION APPROACH



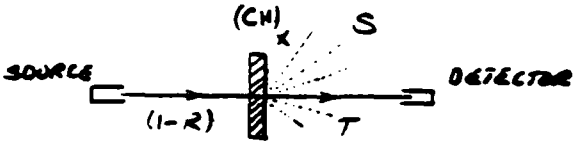

"MID-GAP" TRANSITIONS

### HIGHLY CORRELATED STATES



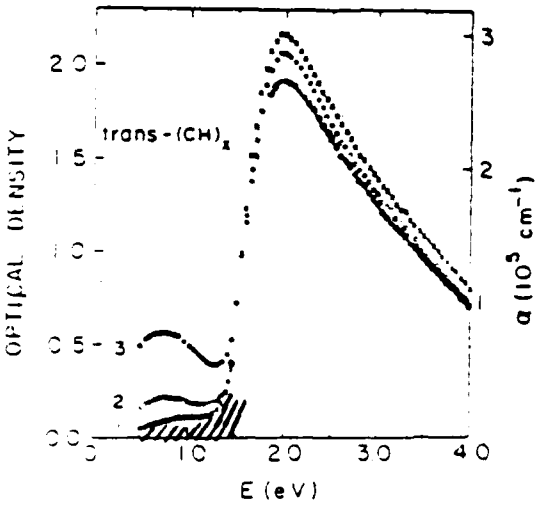
LOWEST ENERGY TRANSITIONS

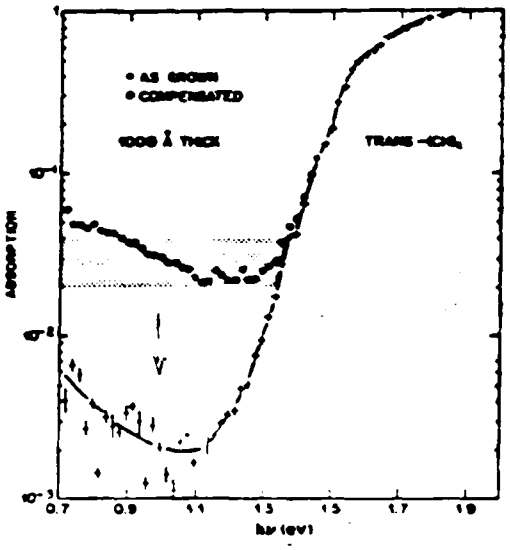
- $S^0$ ABSORPTION AT BAND GAP




$$1 - R = T + S + A$$

EFFECT OF COMPENSATION WITH $NH_3$

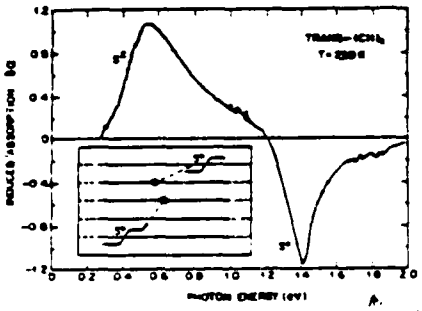



SCATTERING

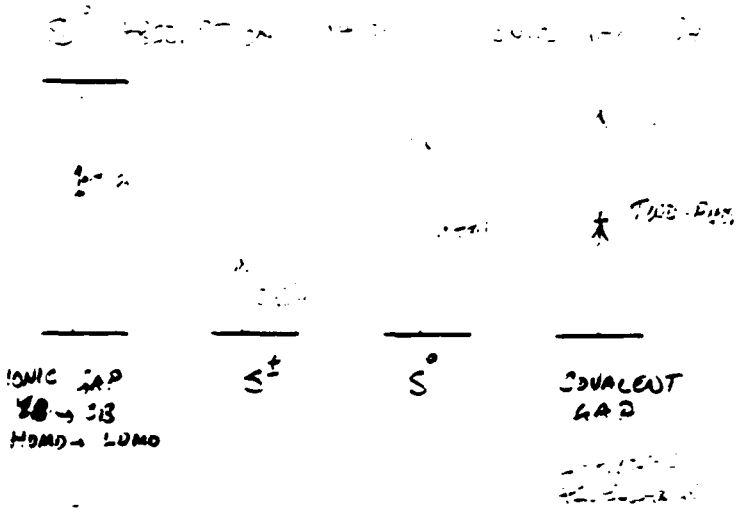
LONG TIME BEHAVIOR

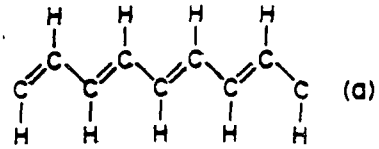
MOL. CRYST. LIQ. CRYST. 117, 275.

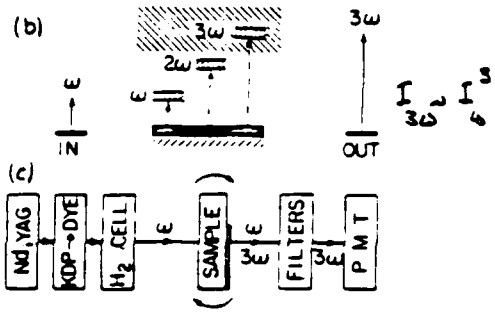



$e/h + 2S^0 \rightarrow 2S^{\pm}$

PRB 30, 786 (84)




FILM: COMPENSATED $(CH)_x$ Fig.
700 Å THICK ; UNIFORM

WHERE IS THE $2^1A_g$ (COVALENT GAP)
WITH RESPECT TO $1^1B_u$ (IONIC GAP)

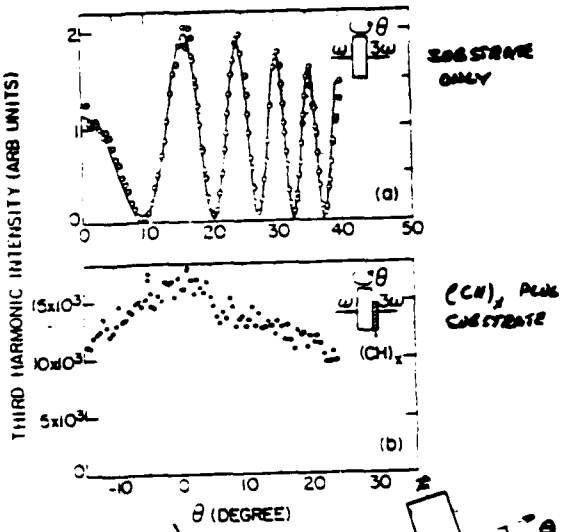
## THIRD HARMONIC GENERATION

$$\chi^{(3)}(3\omega;\omega,\omega,\omega) = \sum_{nmn} \Omega_{gn}\Omega_{nm}\Omega_{mn}\Omega_{n'g}$$

$$\left[ \frac{1}{(E_{ng}-3\omega)(E_{mg}-2\omega)(E_{n'g}-\omega)} + \frac{1}{(E_{ng}+\omega)(E_{mg}-2\omega)(E_{n'g}-\omega)} + \frac{1}{(E_{ng}+\omega)(E_{mg}+2\omega)(E_{n'g}-\omega)} + \frac{1}{(E_{ng}+3\omega)(E_{mg}+2\omega)(E_{n'g}+\omega)} \right]$$

TRANSITIONS BETWEEN ALL STATES
IRRESPECTIVE OF SYMMETRY

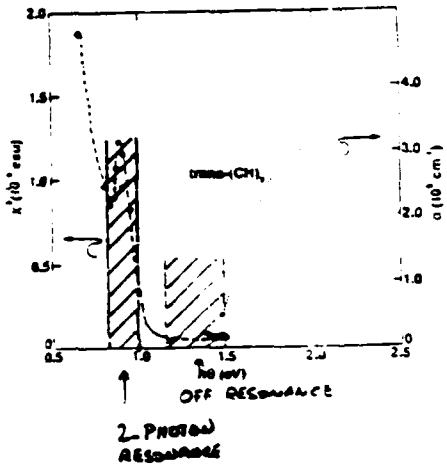
$\chi^3$ OF $(CH)_x$ : CALIBRATION



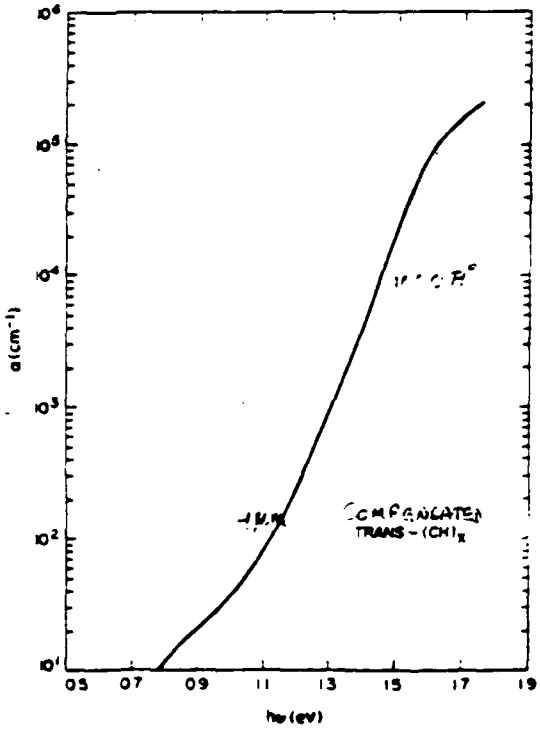

$$\ell_c = \frac{\lambda_\omega}{6(n_\omega - n_{3\omega})}$$

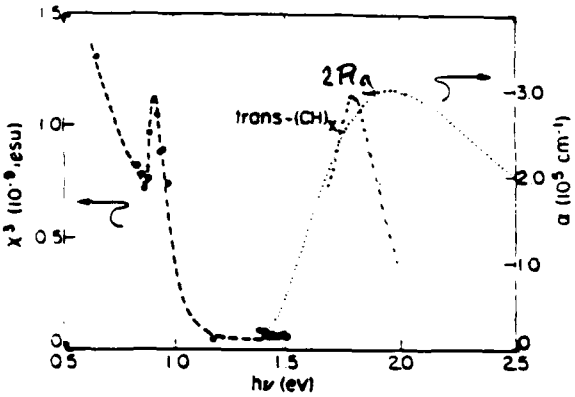
$$I_{3\omega} \sim I_\omega^3 \cdot |\chi^3|^2 \cdot \sin^2\left(\frac{L\cos\theta}{2\ell_c}\right)$$

$\chi^{(3)}_{NAG}$ : VERY LARGE




$\chi^{(3)}$ LARGE




$2A_g$ STATE IS CLOSE TO $1B_u$ STATE ?!

# FREE ELECTRON LASER
## (FEL)

INTENSE TUNABLE IR RADIATION

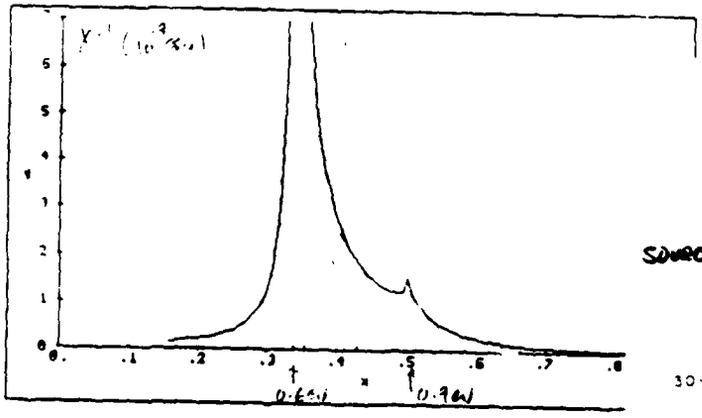
1 → 100 KW IN 2-10 μm RANGE

STANFORD → DUKE

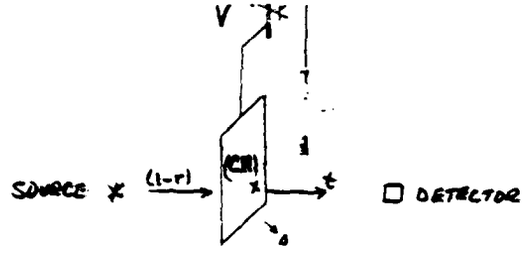
< PARTICLE IN A BOX

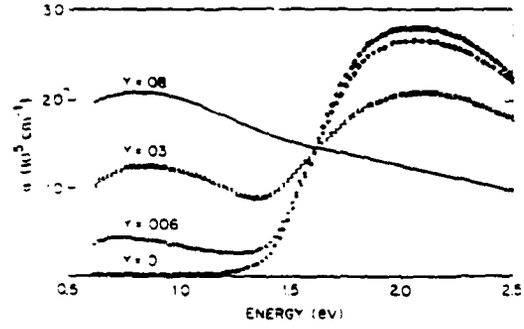
< DIMERIZATION

< IONIC & COVALENT STATES




U=0 CALCULATION  W K Wu

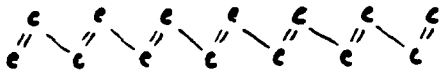



$\xi \chi_{EL} = 1.1 \times 10^{-17}$ cm$^{-1}$ eV / injected charge

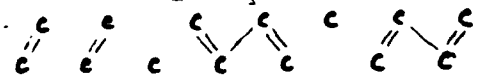
ENHANCED BY ~ $\xi/a$

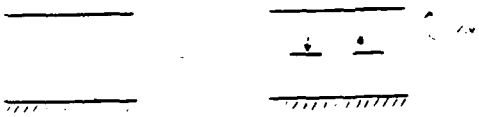
## DOPING & SOLITON FORMATION



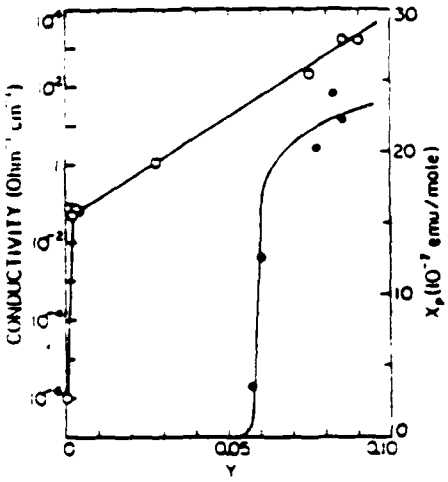
$\xi = ?\Delta$

$\xi = 2\xi_s = 2 \times 2\Delta/\pi$





NO SPIN.




Murayama et al PRB 29, 2341 (1984)

## SIGNATURES OF SOLITON DOPING

APPEARANCE OF ABSORPTION BAND NEAR MIDGAP

APPEARANCE OF ENHANCED IR ACTIVE LOCAL MODES

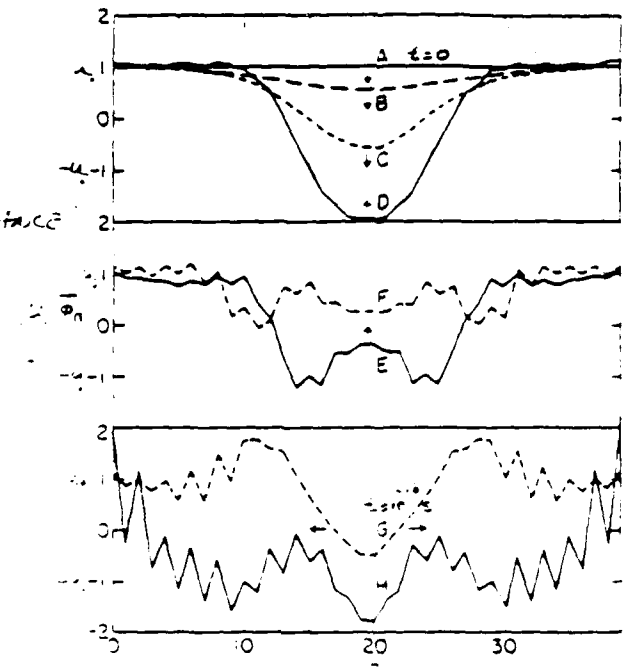
NO INCREASE IN $\chi$

PHOTOEXCITATION

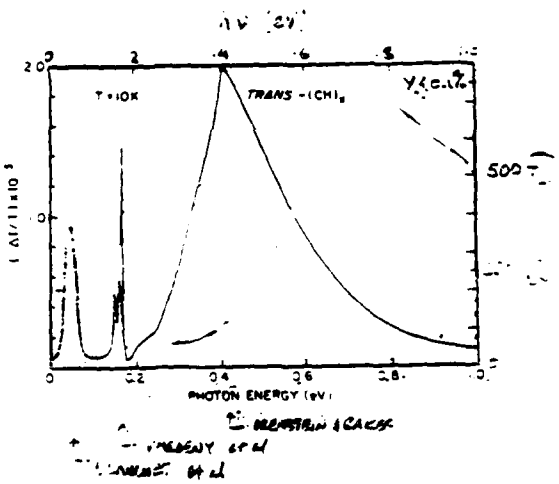
IN POLYACETYLENE

Su & Schrieffer Proc. Nat. Acad. Sci. USA

SPEED OF RESPONSE (RESONANCE)

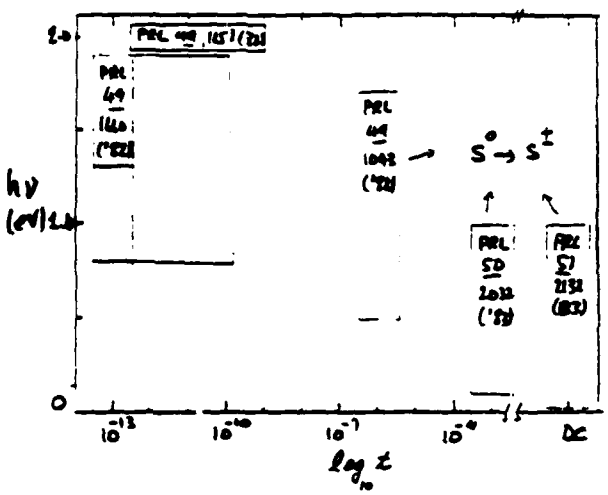


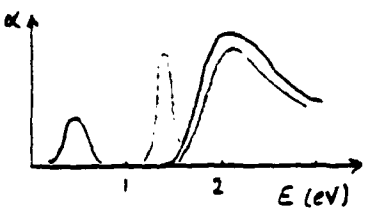

$t > 10^{-2}$ sec.




ELECTRONICALLY ENHANCED IR MODES

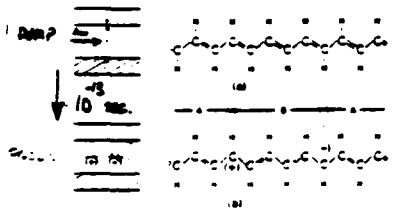
↳ SELF TRAPPED CHARGE IN CDW

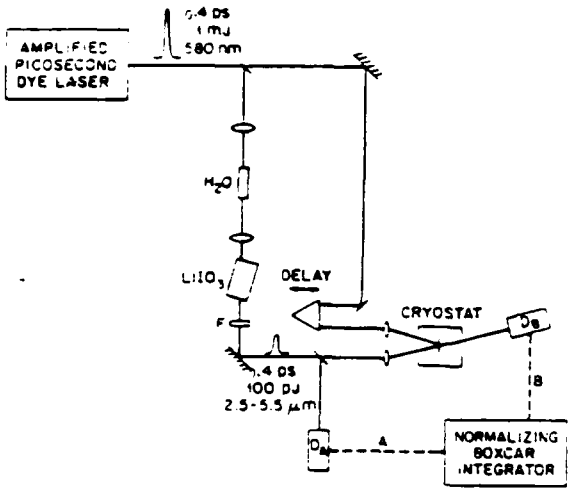


# D-10

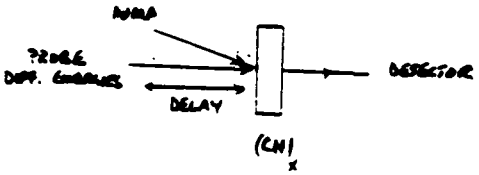
Su & Schrieffer, Proc. Nat. Acad. Sci 77, 5626 (80)

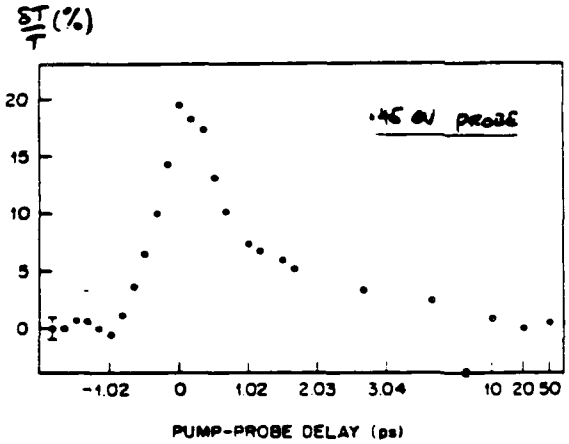


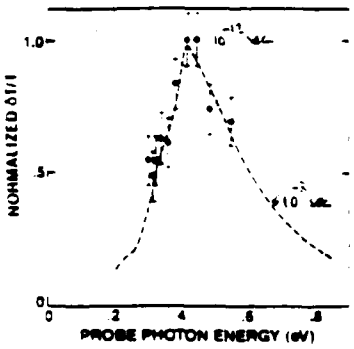



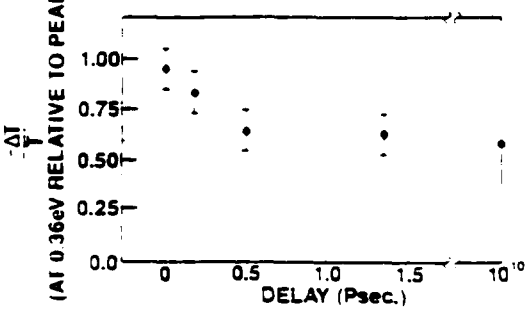

$E_{e/h} > E_{2S^{\pm}}$ $\quad (E_s = \frac{2\Delta}{\pi})$

$\tau \sim 1/\omega_{ph}$ $(10^{-13}$ sec$)$




< 0.1 ps RISETIME

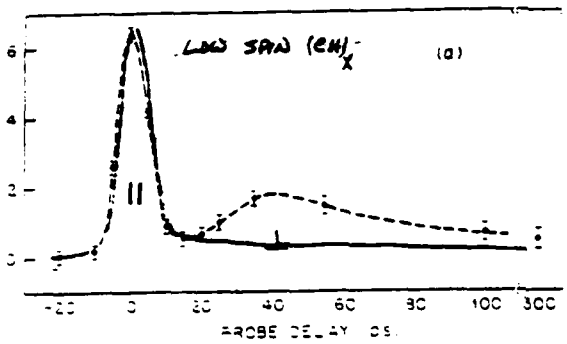
~ 0.5 ps LIFETIME

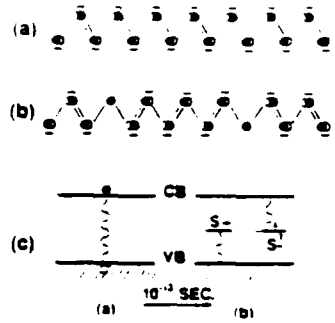
POWER DECAY (1D DIFF. ?)

# D-11

$h\nu \rightarrow 2S^{\pm}$

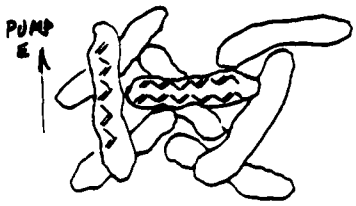
$h\nu \rightarrow e/h$
$e/h + 2S^{0} \rightarrow 2S^{\pm}$

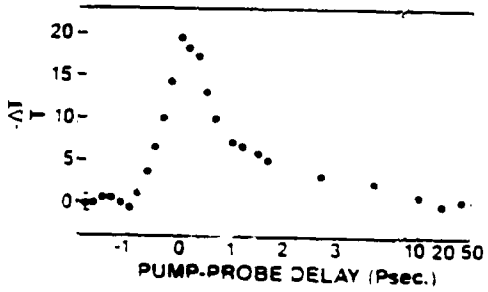


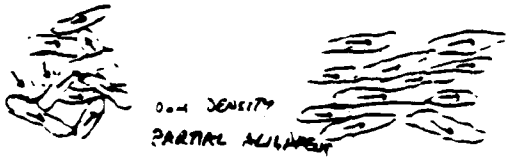

PUMP ∥ PROBE

PUMP ⊥ PROBE



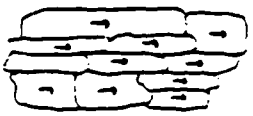




SHIRAKAWA $(CH)_x$



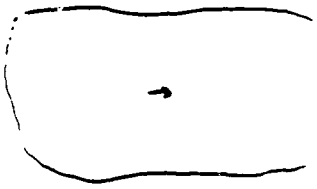

MAGNITUDE OF $\chi^{(3)}$

* OFF RESONANCE TRANSPARENT GAP



DURHAM $(CH)_x$
100% ALIGNMENT
100% SPACE FILLING
MACROSCOPIC DOMAINS

* POTENTIAL APPLICATIONS



WINNER'S $(CH)_x$

* INTRINSIC ABSORPTION IS SMALL 1-3μ
* SCATTERING LOSS IS MORPHOLOGY DEPENDENT

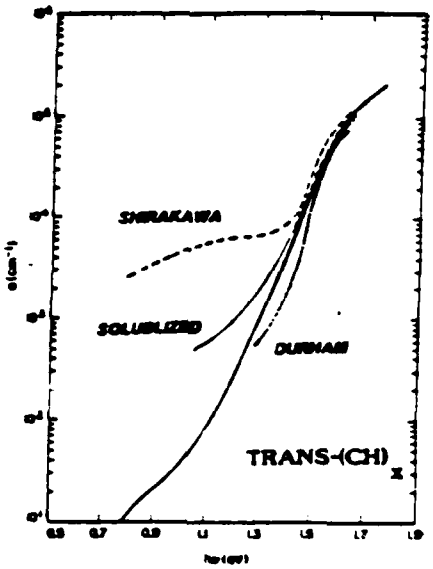
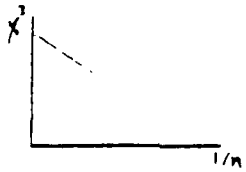



FIGURE OF MERIT

* $\chi^{(3)}/\alpha_{Total}$




FOR n LARGE DIFFERENTIAL GAIN IS NOT LARGE

* $\alpha_{TOTAL} = \alpha_{abs} + \alpha_{SCATTERING}$

→ PROCESSABILITY ( [illegible] )
EASE OF FABRICATION

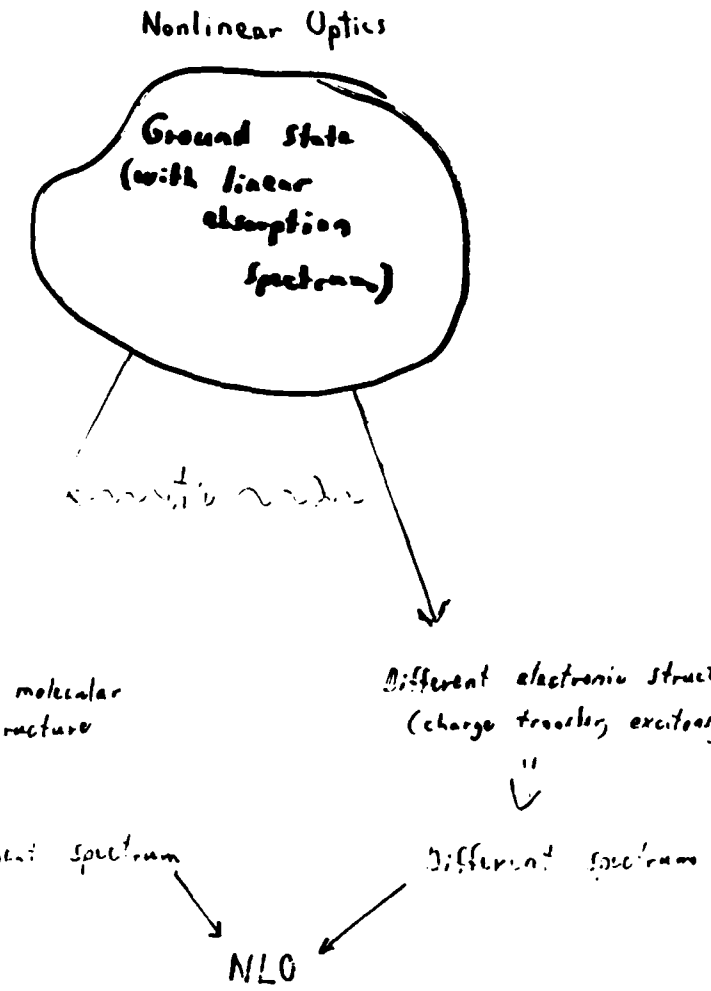
A. J. Heeger
University of California at Santa Barbara

# ANISOTROPY OF THE THIRD ORDER NONLINEAR OPTICAL SUSCEPTIBILITY IN CONJUGATED POLYMERS

"Instantons" as the source of

Nonlinear Optical Properties

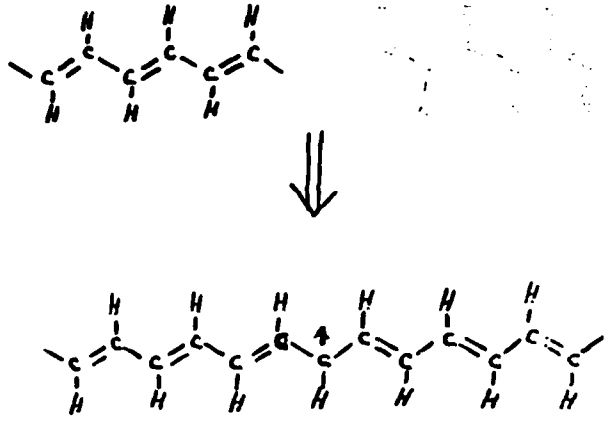
of Polyacetylene




Acknowledgement:
M. Sinclair
D. Moses
W.-P. Su

trans - $(CH)_x$

Broken symmetry with 2-fold degenerate ground state



**Bond-alternation domain wall or "Soliton"**

? "particle" consisting of structural alternation

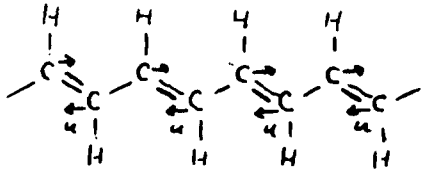
p'si

localized non-bonding electronic state

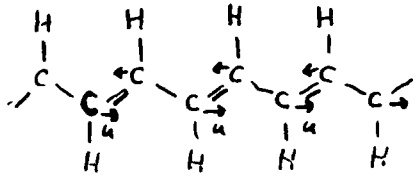
$m_s \sim 5\, m_e$

trans - $(CH)_x$ : two-fold degenerate ground state

$+u_0$

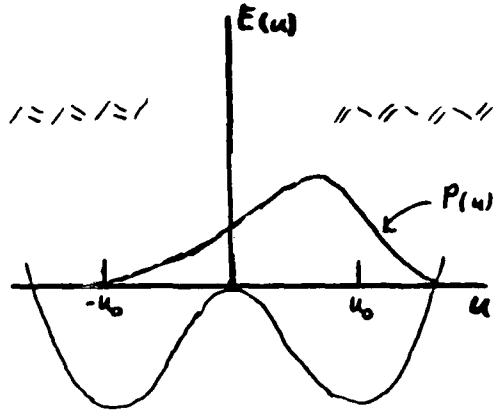


$-u_0$



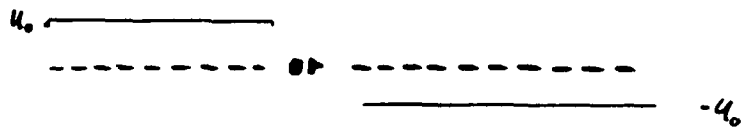
Quantum (zero point) fluctuations are important!

## "Instantons" as the Source of $\chi^{(3)}_{\parallel}$ in Trans-$(CH)_x$

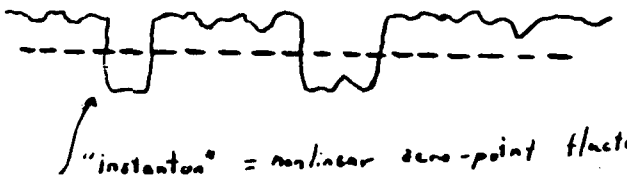



Order parameter $\varphi = \pm(-1)^n u_n \overset{\text{(classical)}}{=} \pm u_0$

Classical:




Quantum:



"instanton" = nonlinear zero-point fluctuation

## Instantons in polyacetylene

The effect of nonlinear ground state fluctuations on the photoproduction of charged solitons

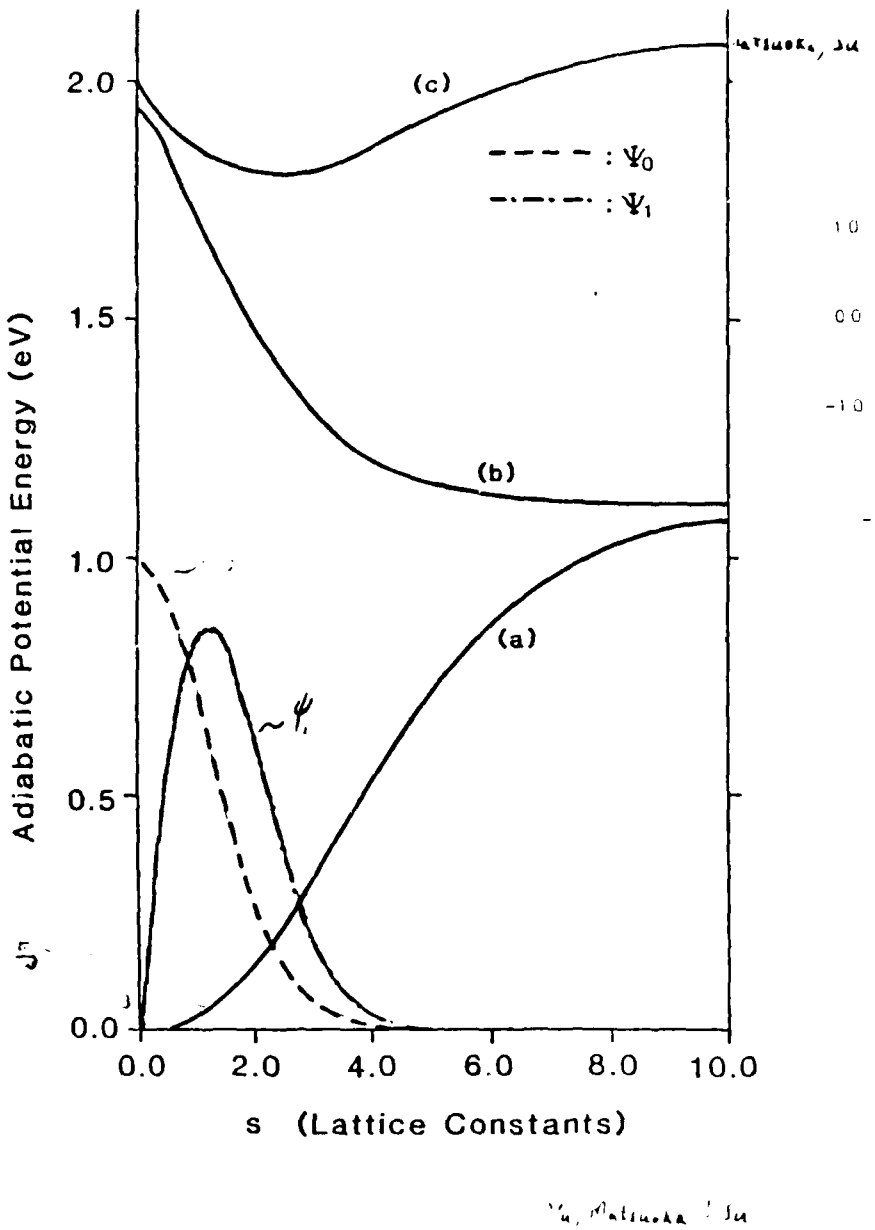
Creation energy for soliton-antisoliton pair

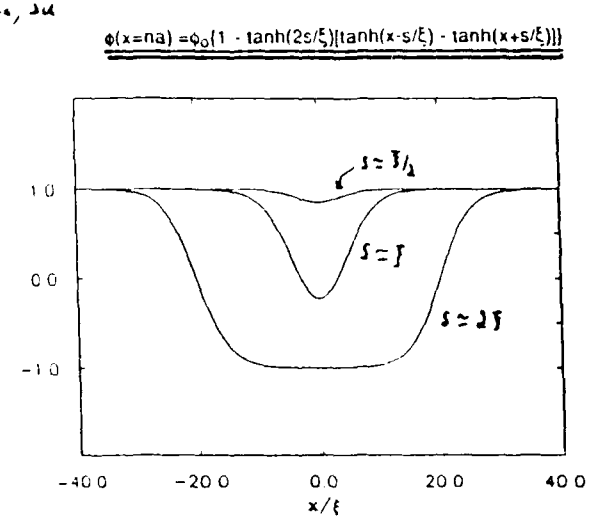
$$2E_s = \frac{2}{\pi} E_g < E_g$$

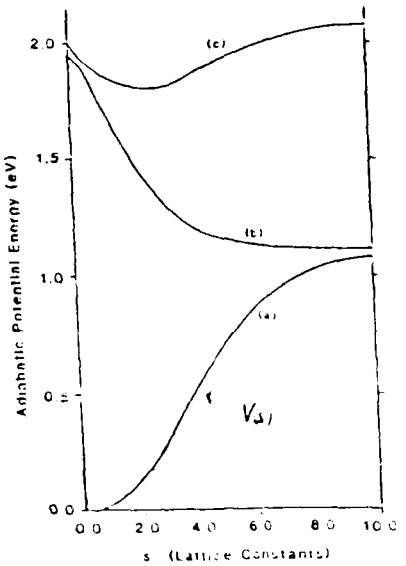
Can one get direct photogeneration of solitons for $\hbar\omega < E_g$ ?

Yes --- with help from ground state fluctuations !!

E-4



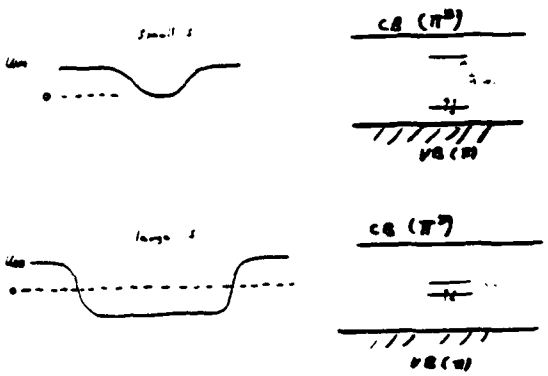

$U_{s1} = \frac{1}{2} m (\dot{s})^2 - V_{s1}$

& solve

$\Psi_0 = \xi \psi$

straightforward QM problem

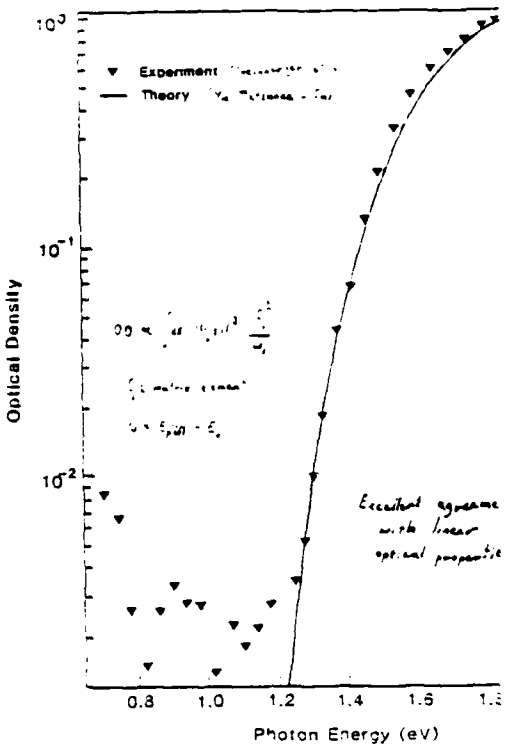
For each s ---- gap states appear




$$\Delta E = \frac{4}{\pi}\Delta + \hbar\omega_0(s)$$

$$E_g = 2\Delta = 1.8 - 1.9\,eV$$

$$\frac{4}{\pi}\Delta \simeq 1.15\,eV \quad \text{(threshold)}$$



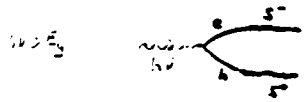

The connection to resonant

nonlinear optical properties

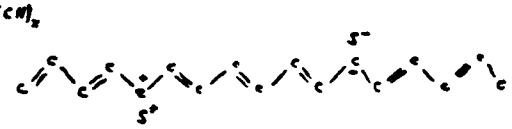
# E-7

## Soliton Photogeneration & Confinement in $(CH)_x$

Dynamical calculations (Su & Schrieffer) show that after photogeneration of e-h pair, lattice distortion forms in very short time ($\sim 10^{-13}$ sec) leading to photogenerated $S^+$ and $S^-$ pairs



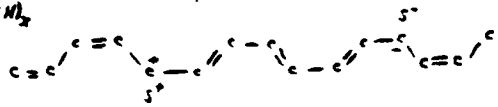

Trans-$(CH)_x$




Two states are equivalent --- $S^+$ and $S^-$ "free"

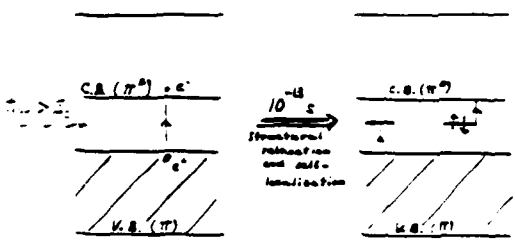
Higher energy region

cis-$(CH)_x$



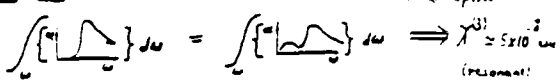

$S^+$ and $S^-$ are "confined"

Photogeneration of Solitons




Sum Rule

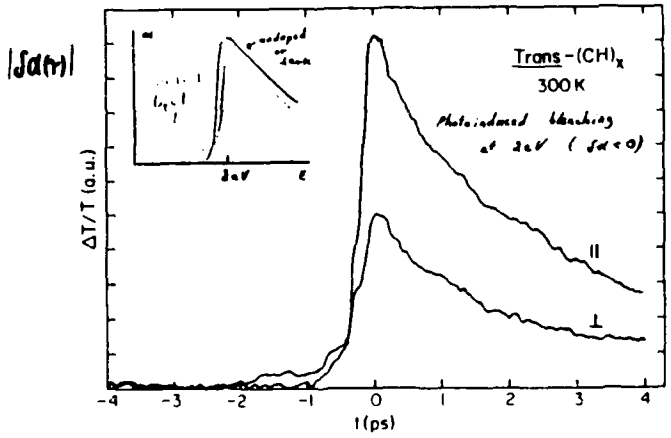
Nonlinear Optics!



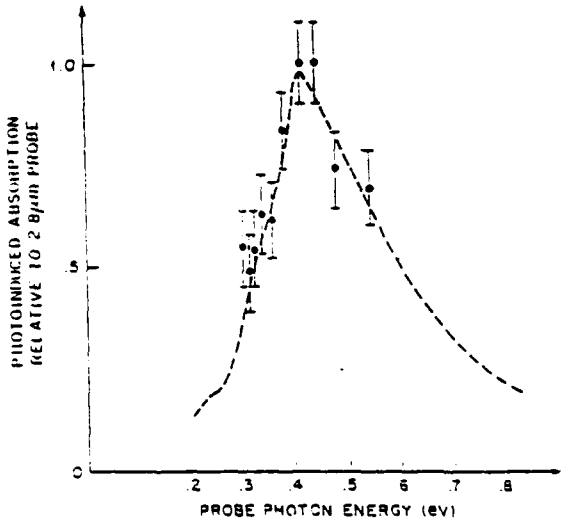

Index of refraction is different after absorption of 1st photon

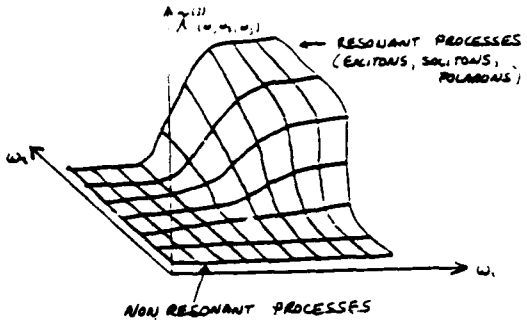
Resonant NLO process

Vardeny, Strait, Moses, Chung & AJH
PRL (1982)



Rubloff, Etemad et al



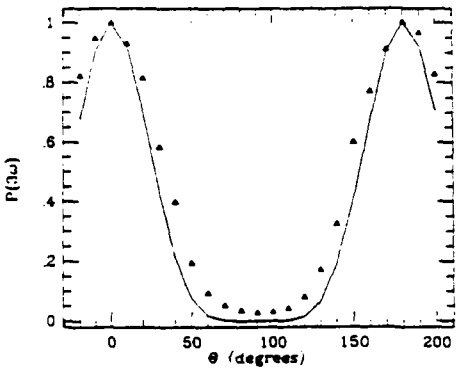

We have seen how solitons lead directly to resonant NLO

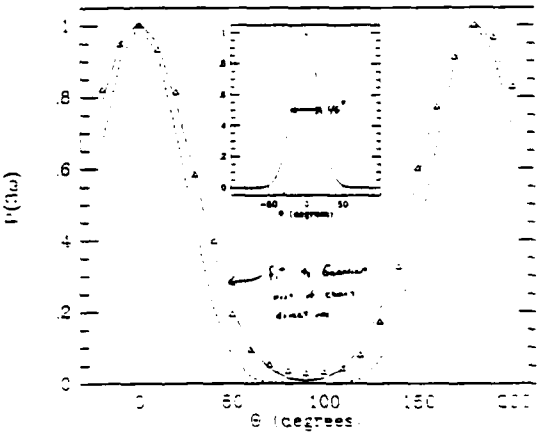
What about non-resonant NLO ?

Yes ---- Instantons

THIRD HARMONIC GENERATION IN ORIENTED $\Sigma^{-}(CH)_x$

$$P(3\omega) \propto \chi^{(3)}_{\parallel} E^6_{\parallel} = \chi^{(3)}_{\parallel} E^6 \cos^6\theta$$




Alignment Direction

Polarization direction

$\chi^{(3)}_{\parallel}(3\omega;\omega,\omega,\omega) = (4 \pm 2) \times 10^{-10}$ e.s.u

All nonlinearity associated with [illegible]

Nonlinear $\chi^{(3)}(3\omega;\omega,\omega,\omega)$

Third order perturbation theory on the excited states of the s-configurations yields

$$\chi^{(3)} = N_s \Sigma_{nm} |\langle g|r|n\rangle|^2 |\langle n|r|m\rangle|^2 |\langle m|r|g\rangle|^2 \times$$
$$[(1/(E_{mg}-3\omega)(E_{mg}-2\omega)(E_{ng}-\omega) + 1/(E_{mg}-\omega)(E_{mg}-2\omega)(E_{ng}-\omega)$$
$$+ 1/(E_{mg}-\omega)(E_{mg}-2\omega)(E_{ng}-\omega) + 1/(E_{mg}-\omega)(E_{mg}-2\omega)(E_{ng}-3\omega)]$$

where $E_{mg} = E_{s,m} - E_{s,g}$,

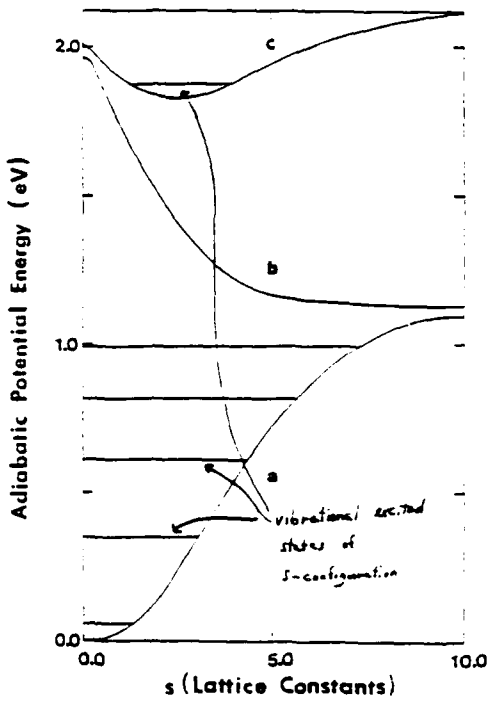
$E_{s,g}$ is the ground state energy

$E_{s,a}$ (den m) are the energies of excited states of the s-configurations

$|a\rangle$ are the dipole matrix elements

$N_s = n_s \rho_c$ where $n_s = (L/2)^3$ is the unitse space for solution pairs on a chain of s and $\rho_c$ is the density of chains per unit area.

The sum $n$ and $m$ denote excited states with symmetry opposite to $g$ and $m = s$ an excited state with the same symmetry as $g$.




To estimate the magnitude of $\chi_s^{(3)}$ we consider the term in the full sum where the matrix elements go from $g \to E_s(s) \to n \to E_s(s) \to g$. We ignore the various vibrational states of the s-configuration and consider only the single contribution ($\chi_s^{(3)}|_0$):

$$\chi_s^{(3)}|_0 = N_s \Sigma_{ss'} |\phi_0(s)|^2 \phi_0(s')|^2 (|f_s|^2 |f_{s'}|^2 / 2\omega) \times$$
$$[-(1/(E_s-3\omega)(E_s-\omega) + 1/(E_s-\omega)(E_s-3\omega)].$$

For $3\omega \approx E_s$

$$\chi_s^{(3)}|_0 = -4N_s \Sigma_{ss'} |\phi_0(s)|^2 \phi_0(s')|^2 (|f_s|^2 |f_s|^2 / E_s^2 E_s)$$

where $f_s$ is the matrix element between the ground state with wave function $\phi_0(s)$ and the excited state with energy $E_s$ relative to the ground state. Since

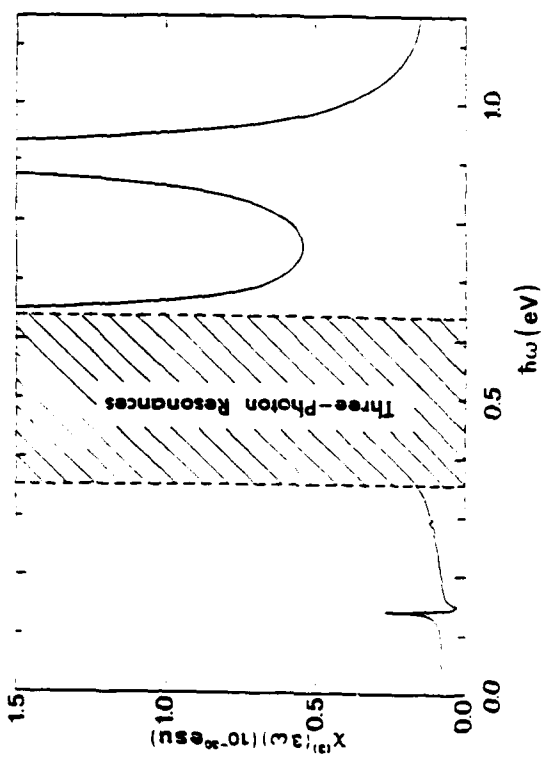
$$\alpha = N_s \Sigma_s |\phi_0(s)|^2 \alpha_0$$

is the linear term in the polarizability,

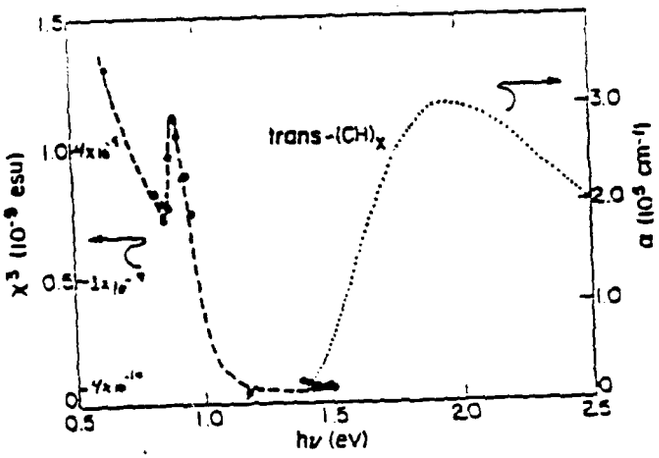
$$\chi_s^{(3)}|_0 = -(4\alpha) \Sigma_s |\phi_0(s)|^2 (\alpha_0 / E_s)$$

$$\chi_s^{(3)}|_0 = (8\pi/a)(N\rho_c)^{-1} \alpha^2 / E_0$$

$$\chi_s^{(3)}|_0 = 3 \times 10^{-10} \text{ esu}$$



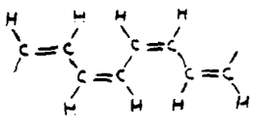
# E-10




Kajzar, Etemad, Messier & Baker
Synth. Met. 17, 563 (1987)

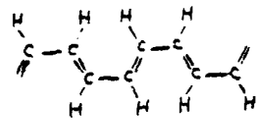
Symmetry Forcing Origin of $\chi^{(3)}$ Comparative Measurements of [illegible] and Trans-(CH)

[illegible] the ground-state degeneracy

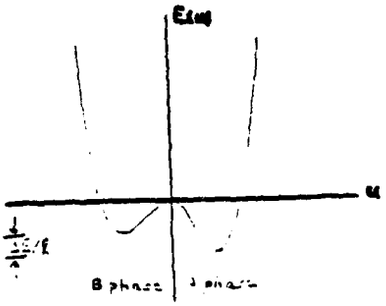


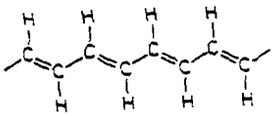
A phase

Not equivalent

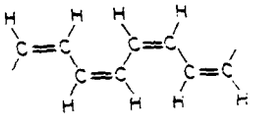


B phase



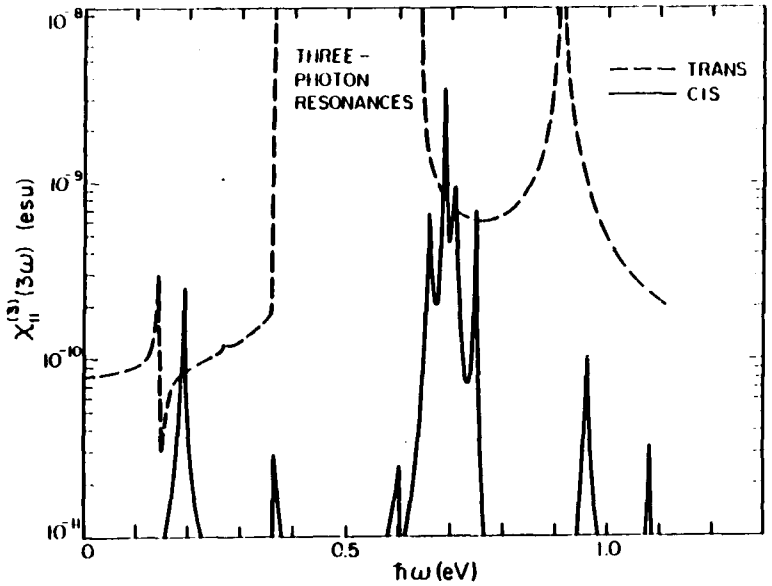
TRANS

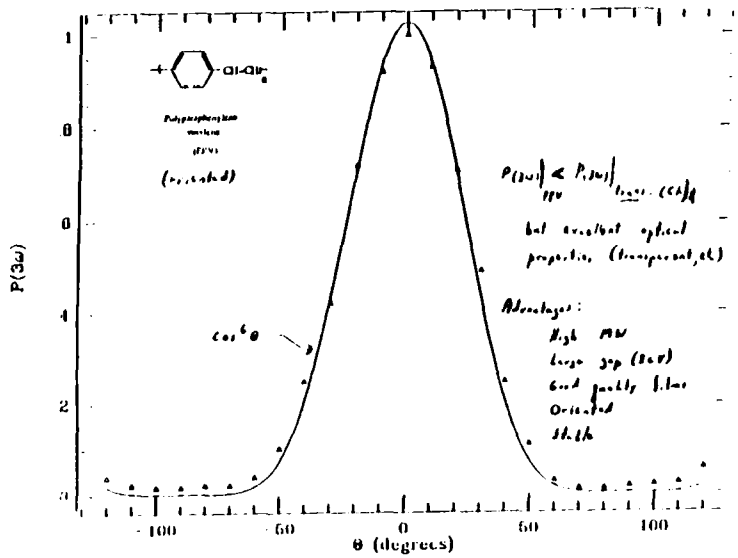


CIS

Result $\chi^{(3)}_{(3\omega)\,CIS} < \frac{1}{6}\,\chi^{(3)}_{(3\omega)\,trans}$

Best number $\chi^{(3)}_{trans} = (15-20)\,\chi^{(3)}_{CIS}$




Conclusions

1) Large $\chi^{(3)}$'s are a general feature of conjugated polymers

2) Nonlinearity is associated with the π-electrons

3) At 1.06 μm $\chi^{(3)}_{(3\omega)}|_{trans-(CH)_x} \simeq \chi^{(3)}_{(3\omega)}|_{PDA}$

At longer wavelengths $\chi^{(3)}_{(3\omega)}|_{trans-(CH)_x}$ is certainly larger by considerable factor

4) For polyacetylene $\chi^{(3)}|_{trans} > 10\ \chi^{(3)}_{cis}$

5) Nonlinearity from rigid bond structure is not dominant contribution [illegible] $trans-(CH)_x$ [illegible]

Questions:

1) Why is trans-$(CH)_x$ special?

2) How to correct measurement $\chi^{(3)}$'s to know resonant properties?

E-11

K. D. Singer

AT&T

# NONLINEAR OPTICS IN ORDERED MOLECULAR SYSTEMS

# F-2

## NONLINEAR OPTICS IN ORDERED MOLECULAR SYSTEMS

K.D. SINGER and M.G. KUZYK
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## OUTLINE

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- NONLINEAR OPTICS IN MOLECULAR ENSEMBLES
- FILMS POLED UNDER UNIAXIAL STRESS
- NEW POLYMERS
  - MATERIALS
  - CORONA POLING
  - NONLINEAR OPTICAL PROPERTIES
  - MOLECULAR ORIENTATION DISTRIBUTION

## MOLECULAR MATERIALS

- MACROSCOPIC POLARIZATION

$$P_i(t) = \chi_i^{(0)} + \chi_{ij}^{(1)}(t)E_j(t) + \chi_{ijk}^{(2)}(t)E_j(t)E_k(t) + \chi_{ijkl}^{(3)}(t)E_j(t)E_k(t)E_l(t) + \cdots$$

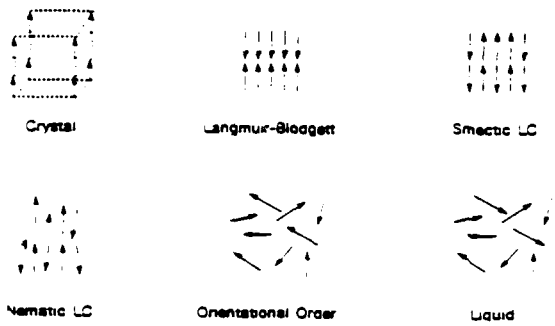
- MICROSCOPIC POLARIZATION

$$p_I(t) = \mu_I^{(0)} + \alpha_{IJ}(t)F_J(t) + \beta_{IJK}(t)F_J(t)F_K(t) + \gamma_{IJKL}(t)F_J(t)F_K(t)F_L(t) + \cdots$$

- VAN DER WAALS MATERIALS

$$P_i(t) = \frac{1}{V}\langle p_I(t)\rangle_i$$

## MATERIAL CLASSES




## MOLECULAR ORDER

- MOLECULES FIXED IN LATTICE

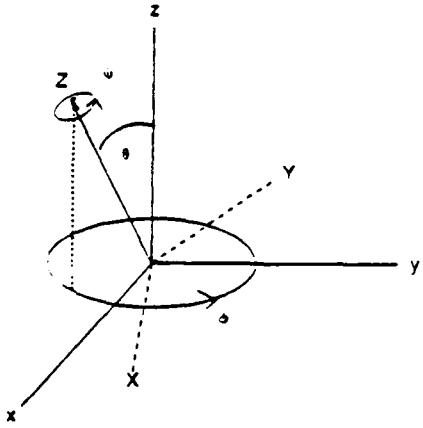
$$\chi^{(n)}_{ijkl\ldots} = N_u \sum_{I,J,K,L\ldots} \sum_{s=1}^{q} a_{iI(s)} a_{jJ(s)} a_{kK(s)} \cdots \xi^{*}_{IJKL\ldots}(s)$$

- THERMODYNAMIC ENSEMBLE

$$\chi^{(n)}_{ijkl\ldots} = N \langle \xi^{*}_{IJKL\ldots} \rangle_{ijkl\ldots}$$

$$\langle \xi^{*}_{IJKL\ldots} \rangle_{ijkl\ldots} = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta \int_0^{2\pi} d\psi \, \xi^{*}_{IJKL\ldots} a_{iI} a_{jJ} a_{kK} \cdots G(\phi, \theta, \psi)$$

## EULER ANGLES



## SYMMETRY CLASSES

$\chi^{(2)}$ components for point group $\infty mm$

| | 1 | 2 | 3 |
|---|---|---|---|
| 1 | 0 | 0 | $\chi^{(2)}_{311}$ |
| 2 | 0 | 0 | $\chi^{(2)}_{311}$ |
| 3 | 0 | 0 | $\chi^{(2)}_{333}$ |
| 4 | 0 | $\chi^{(2)}_{133}$ | 0 |
| 5 | $\chi^{(2)}_{133}$ | 0 | 0 |
| 6 | 0 | 0 | 0 |

$\chi^{(3)}$ components for point group $\infty/mmm$

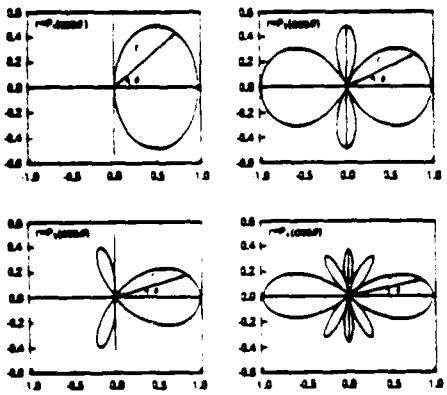
| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| 1 | $\chi^{(3)}_{1111}$ | $\chi^{(3)}_{1122}$ | $\chi^{(3)}_{1133}$ | 0 | 0 | 0 |
| 2 | $\chi^{(3)}_{2211}$ | $\chi^{(3)}_{2211}$ | $\chi^{(3)}_{2233}$ | 0 | 0 | 0 |
| 3 | $\chi^{(3)}_{3311}$ | $\chi^{(3)}_{3311}$ | $\chi^{(3)}_{3333}$ | 0 | 0 | 0 |
| 4 | 0 | 0 | 0 | $\chi^{(3)}_{2323}$ | 0 | 0 |
| 5 | 0 | 0 | 0 | 0 | $\chi^{(3)}_{3323}$ | 0 |
| 6 | 0 | 0 | 0 | 0 | 0 | $2(\chi^{(3)}_{1111} - \chi^{(3)}_{1122})$ |

Row and column labels: 1 = 11; 2 = 22; 3 = 33; 4 = 23,32; 5 = 31,13; 6 = 12,21

## DISTRIBUTION FUNCTION

$$G(\theta) = \sum_{l=0}^{\infty} \frac{(2l+1)}{2} A_l P_l(\cos\theta)$$

LEGENDRE POLYNOMIALS



## SUSCEPTIBILITIES

$$\chi^{(2n)}_{ijkl\ldots} = \sum_{m=0}^{n} u^{(2m-1)}_{ijkl\ldots} \langle P_{2m-1} \rangle$$

$$\chi^{(2n-1)}_{ijkl\ldots} = \sum_{m=0}^{n-1} u^{(2m)}_{ijkl\ldots} \langle P_{2m} \rangle$$

- SECOND ORDER

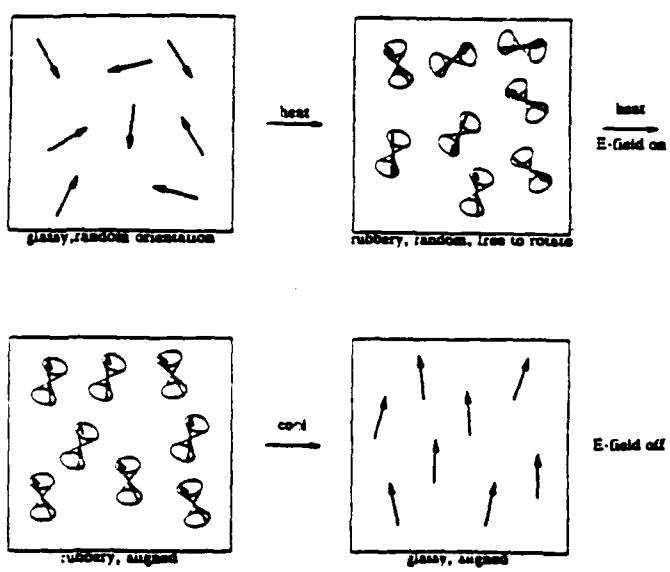
$$\chi^{(2)}_{3333} = NB^{*}_{zzz}\left(\frac{3}{5}\langle P_1 \rangle + \frac{2}{5}\langle P_3 \rangle\right)$$

$$\chi^{(2)}_{1113} = \chi^{(2)}_{1131} = \chi^{(2)}_{3111} = NB^{*}_{zzz}\left(\frac{1}{5}\langle P_1 \rangle - \frac{1}{5}\langle P_3 \rangle\right)$$

- THIRD ORDER

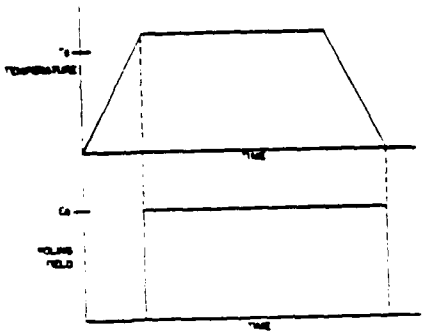
$$\chi^{(3)}_{3333} = N\gamma^{*}_{zzzz}\left(\frac{1}{5} + \frac{4}{7}\langle P_2 \rangle + \frac{8}{35}\langle P_4 \rangle\right)$$

## ELECTRIC FIELD POLING



# F-5

## POLED MATERIALS



$$G_u(\Omega, E_p) = \frac{\exp[-\frac{1}{kT}(\sum_v U_{uv} - \mathbf{m}_u^* \cdot \mathbf{E}_p)]}{\int d\Omega \exp[-\frac{1}{kT}(\sum_v U_{uv} - \mathbf{m}_u^* \cdot \mathbf{E}_p)]}$$

$$\chi_{ijk}^{(2)} = v_{ijk}^{(0)} < P_0 > + v_{ijk}^{(2)} < P_2 > + v_{ijk}^{(4)} < P_4 >$$

## POLING UNDER UNIAXIAL STRESS

- SECOND HARMONIC TENSOR PROPERTIES
- MOLECULAR DISTRIBUTION

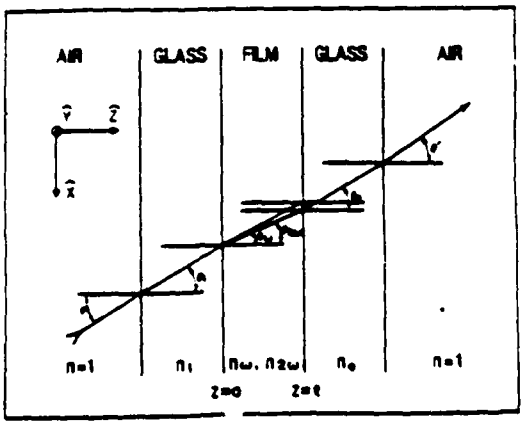
## SECOND HARMONIC GENERATION

$$P_1^{(2)}(2\omega) = 2d_{31}(-2\omega;\omega,\omega)E_1(\omega)E_3(\omega)$$

$$P_2^{(2)}(2\omega) = 2d_{31}(-2\omega;\omega,\omega)E_2(\omega)E_3(\omega)$$

$$P_3^{(2)}(2\omega) = d_{31}(-2\omega;\omega,\omega)\left[E_1^2(\omega) + E_2^2(\omega)\right] + d_{33}(-2\omega;\omega,\omega)E_3^2(\omega)$$

## EXPERIMENTAL GEOMETRY




## SECOND HARMONIC INTENSITY

$$P_T = \frac{512\pi^3}{A}|d_{33}|^2 t_1^4 t_\omega^4 T_{2\omega} t_0^2 p^2(\theta) I_\omega^2 \left[\frac{1}{n_\omega^2 - n_{2\omega}^2}\right]^2 \sin^2\psi$$

- P-POLARIZED INCIDENT LIGHT

$$p(\theta) = (a\cos^2\theta_\omega - \sin^2\theta_\omega)\sin\theta_{2\omega} + 2a\cos\theta_\omega \sin\theta_\omega \cos\theta_{2\omega}$$

- S-POLARIZED INCIDENT LIGHT

$$p(\theta) = a\sin(\theta_{2\omega})$$

$$\text{or} \quad a = \frac{d_{31}}{d_{33}}$$

## ORDERING ENERGY

$$G_u(\Omega) = \frac{\exp[-\frac{U}{kT}]}{\int d\Omega \exp[-\frac{U}{kT}]}$$

- ELECTRIC FIELD POLING

$$U_E = \mathbf{m}_u^* \cdot \mathbf{E}_p$$

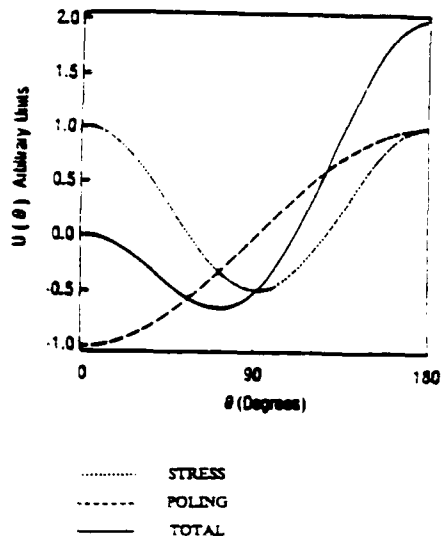
$$\chi^{(2)}_{333} = N\beta^*_{zzz}\frac{m_z^* E_p}{kT}\left(\frac{1}{5} + \frac{4}{7}\langle P_2\rangle + \frac{8}{35}\langle P_4\rangle\right)$$

$$\chi^{(2)}_{113} = \chi^{(2)}_{131} = \chi^{(2)}_{311} = N\beta^*_{zzz}\frac{m_z^* E_p}{kT}\left(\frac{1}{15} + \frac{1}{21}\langle P_2\rangle - \frac{4}{35}\langle P_4\rangle\right)$$

- UNIAXIAL STRESS

$$U_T = U_P + U_E = bP_2(\cos\theta) - m^* E_p P_1(\cos\theta)$$

## ORDERING ENERGY

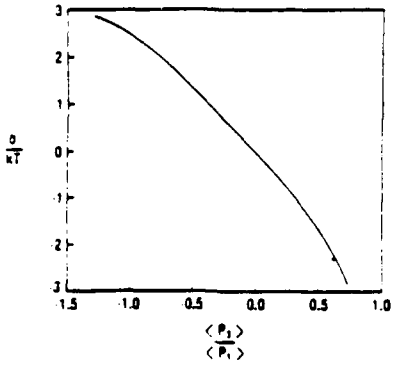



## STRESS POTENTIAL

$$\frac{\exp\left[-\frac{(U_P - U_E)}{kT}\right]}{\left(\frac{m^* E}{kT}\right)} = a_1\left(\frac{b}{kT}\right)P_1(\cos\theta) + a_3\left(\frac{b}{kT}\right)P_3(\cos\theta)$$

$$\frac{\langle P_3\rangle}{\langle P_1\rangle} = \frac{3}{5}\frac{a_3}{a_1}$$

$b$ = magnitude of stress potential




## DISTRIBUTION FUNCTION

$$\langle P_1\rangle = \frac{2}{3}\frac{m^* E_p}{kT}\frac{a_1}{A_n}$$

$$\frac{\langle P_3\rangle}{\langle P_1\rangle} = \frac{1-3a}{1+2a}$$

$$\langle P_2\rangle = \frac{1}{2}\left(\frac{\langle P_1\rangle}{\left[\frac{m^* E_p}{3kT}\right]} - 1\right)$$

$$\langle P_4\rangle = \frac{1}{4}\left(\frac{\langle P_3\rangle}{\left[\frac{m^* E_p}{7kT}\right]} - 3\langle P_2\rangle\right)$$

## FILMS POLED UNDER STRESS

- DISPERSE RED 1 DYE DISSOLVED IN PMMA

| Film # | Dye Number Density $N$ ($10^{20}/cm^3$) | Thickness $l$ ($\mu m$) | Poling Field $E_p$ ($MV/cm$) | Stress $\sigma$ ($dyne/cm^2 \times 10^7$) |
|---|---|---|---|---|
| 1 | 2.42 | 4.0 | 0.60 | 0.00 |
| 2 | 1.08 | 4.9 | 0.25 | 3.71 |

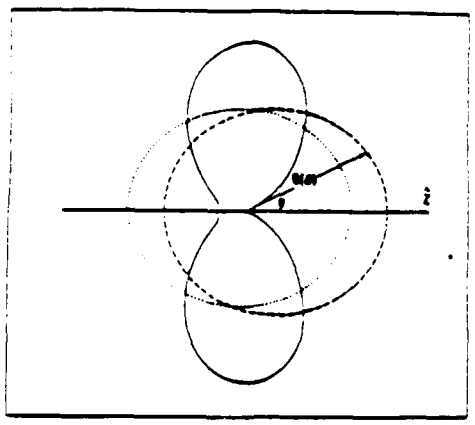
- RESULTS

| Film # | $a$ | $\frac{\mu^* E_p}{kT}$ | $\frac{b}{kT}$ | $\langle P_1 \rangle$ | $\langle P_2 \rangle$ | $\langle P_3 \rangle$ | $\langle P_4 \rangle$ | $\Delta n$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.33 | 0.50 | 0.00 | 0.16 | -0.020 | 0.00 | 0.015 | 0.0014 |
| 2 | 0.7 | 0.20 | 1.2 | 0.041 | -0.20 | -0.019 | -0.02 | -0.0043 |

## NEW MATERIALS

## DISTRIBUTION FUNCTION

$r \propto d \propto N \beta \mu E_p$




- MOLECULES
- CORONA POLING
- POLYMERS

..... ISOTROPIC
------- POLED
——— STRESS + POLED

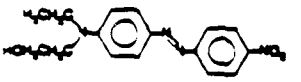
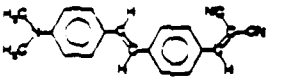
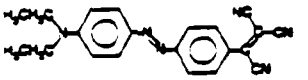
## MOLECULES

$\beta\mu$ MEASURED BY EFISH

- DIRECT MEASUREMENT IN DIPOLAR SOLVENT, DMSO
- INFINITE DILUTION TECHNIQUE

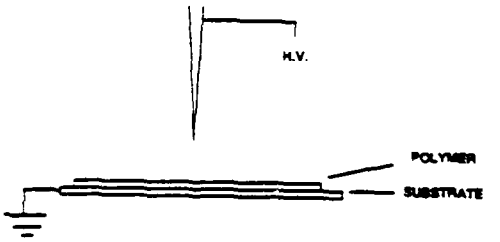
# F-8

## RESULTS

| Molecule | | $\beta\mu$* |
|---|---|---|
| DR1 |  | 1090† |
| DCV |  | 2850† |
| TCV |  | 4110# |

* $\beta\mu$ in $10^{-30} cm^5 D/esu$
† $\lambda = 1.356 \mu m$
\# $\lambda = 1.58 \mu m$

## CORONA POLING

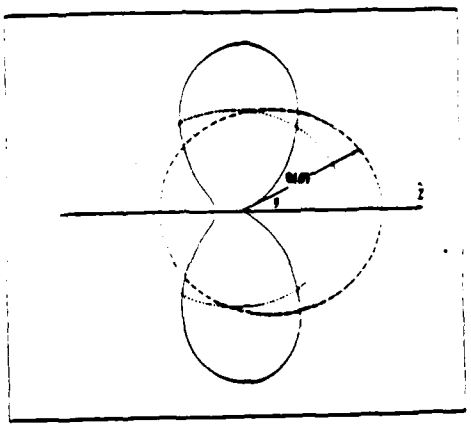



- NO ELECTRODE DEPOSITION
- HIGHER POLING FIELD

# F-9

- RESTRICTED MOTION
  - REDUCES POSSIBLE SUSCEPTIBILITY
  - REDUCES DECAY MECHANISM
- CORONA POLING ALTERS MOLECULAR DISTRIBUTION

## DISTRIBUTION FUNCTION



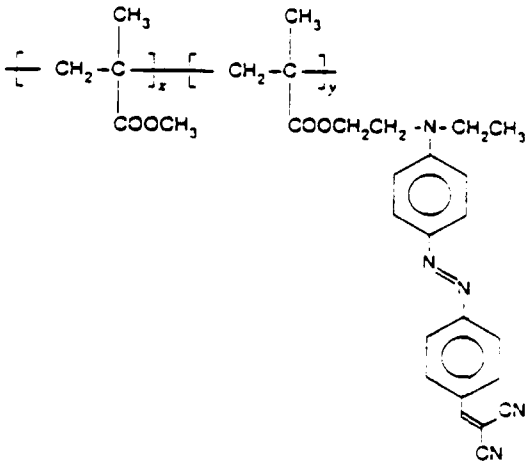
..... ISOTROPIC
------- ELECTRODE POLED
——— CORONA POLED

## SUMMARY

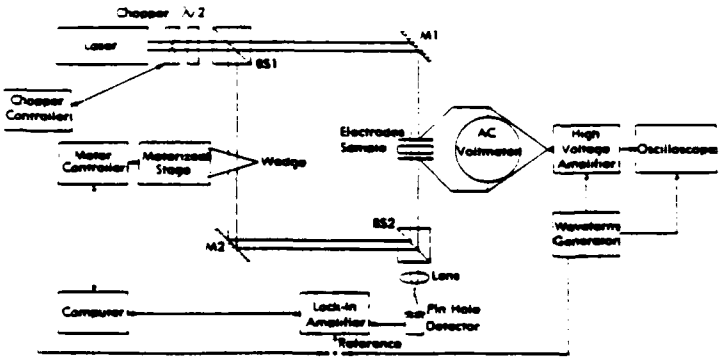
- NONLINEAR OPTICS CAN REVEAL MOLECULAR DISTRIBUTION
  - INTERNAL AND EXTERNAL FORCES
- CORONA POLING
- NEW MATERIALS

## SIDE-CHAIN POLYMERS

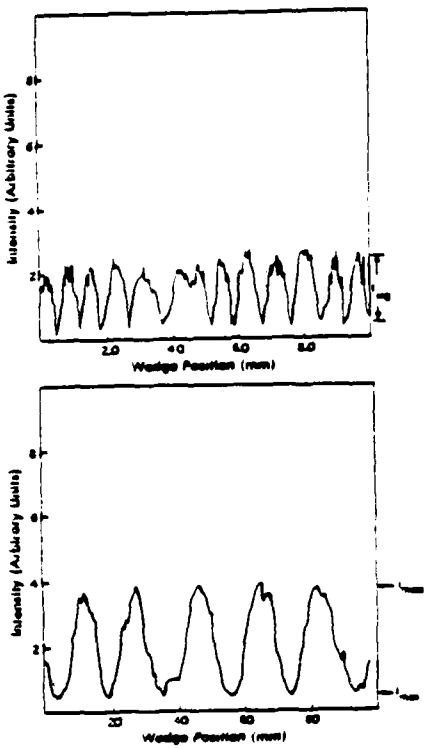
- HIGHER NUMBER DENSITY
- RESTRICTED MOTION
  - EFFECT ON POLING
  - EFFECT ON RELAXATION LIFETIME




## ELECTRO-OPTIC MEASUREMENT



## ELECTRO-OPTIC MEASUREMENT




## RESULTS

| MATERIAL | $N$ | $n$ | $d_0$ | $d_r$ | $r_{33}^0$ | $r_r$ |
|---|---|---|---|---|---|---|
| | ($10^{20}/cm^3$) | | ($10^{-8}$ esu) | ($10^{-8}$ esu) | ($10^{-12}$ m/V) | ($10^{-12}$ m/V) |
| DCV-MMA (corona) | ~6 | 1.58 ($\lambda = .8$) | $d_{33} = 29$ $d_{31} = 20$ | $d_{33} = 26$ $d_{31} = 18$ | $r_{33}^0 = 9$ $r_{31}^0 = 6$ | $r_{33} = 9$ $r_{31} = 6$ |
| DCV/PMMA (corona) | 2.3 | 1.53 ($\lambda = .8$) | $d_{33} = 34$ $d_{31} = 17$ | $d_{33} = 9$ $d_{31} = 4.5$ | | |
| DR1/PMMA (corona) | 2.3 | 1.52 ($\lambda = .8$) | $d_{33} = 13$ $d_{31} = 6$ | | | |
| DR1/PMMA (electrode) | 2.7 | 1.52 ($\lambda = .8$) | $d_{33} = 6$ $d_{31} = 2$ | | | |

G-1

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# SEVERAL SERIES OF NOVEL POLYDIACETYLENES FOR NONLINEAR OPTICS

# G-2

Several Series of Novel Polydiacetylenes

for Nonliner Optics

by

Hachiro NAKANISHI

(Res.Inst.for Polymers & Textiles)

1. Significance of Crystal Engineering for Aromatic Substituted Polydiacetylenes (APDA)
2. APDAs by a Hydrogen-Bonding Effect
3. APDAs by a Bending Effect (I)
4. APDAs by a Bending Effect (II)
5. APDAs by an Anchor-Void Effect
6. APDAs by a Fluorine-Subsitution Effect
7. APDAs by Complex Effects
8. Preliminary Evaluation of $X^{(3)}$ of APDAs
9. Conclusion

Coworkers : H. Matsuda
S. Okada
M. Kato
S. Takaragi
M. Ohtsuka

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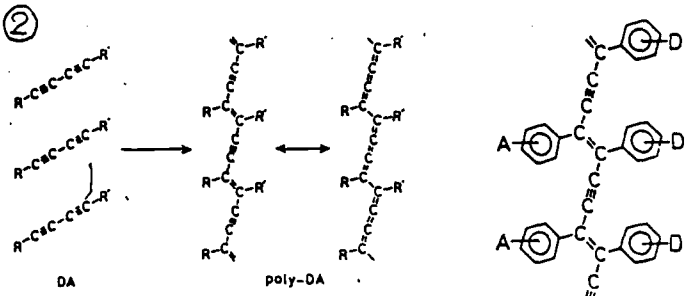
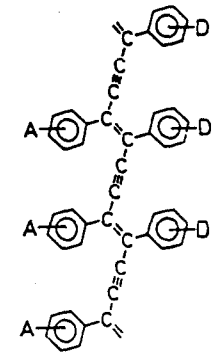
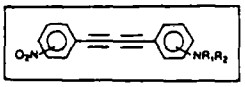



| 化合物 | 結晶方向 | $\chi^{(3)}$ ($10^{-12}$ esu) 2.53 μm | 1.90 μm |
|---|---|---|---|
| TCDUモノマー | //c | — | 1.2 ± 0.5 |
| | //[illegible] | — | 1.1 ± 0.5 |
| TCDUポリマー | //c (主結晶方向) | 270 ± 140 | 700 ± 300 |
| | ⊥c | < 4 | < 1 |
| PTSポリマー | //c (主結晶方向) | 1600 ± 1000 | 8000 ± 3000 |
| | ⊥c | < 20 | < 100 |
| ゲルマニウム | (100) | 4000 ± 2000 (10.6 μm) | |
| ガリウムヒ素 | (100) | 400 ± 200 (10.6 μm) | |

C. Sauteret et al. (1976)



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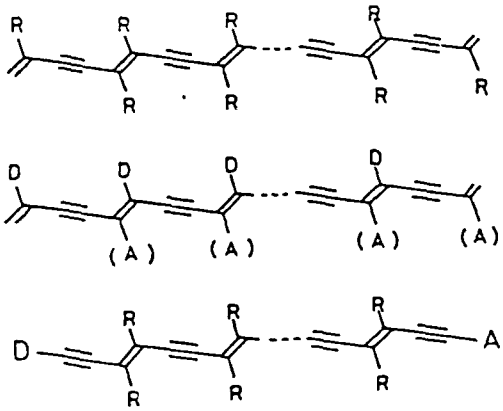



Fig. 1 Interesting polydiacetylene structures for NLO. ( R=Ar)

④

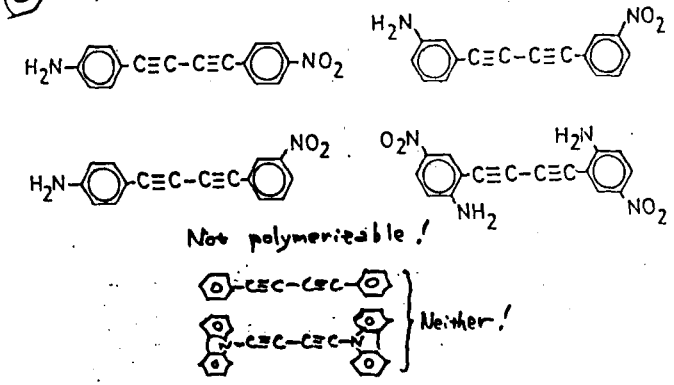
Bandwidths(BV), Bandgaps(Eg), and Ionization Potentials(IP) for Acetylenic(A) and Butatrienic(B) Polydiacetylenes By VEH Calculation.

| Substituents | | BV | Eg | IP |
|---|---|---|---|---|
| H | in A | 3.972 | 2.596 | 5.338 |
| $C_6H_5$ | in A | 1.116 | 1.769 | 4.903 |
| $CH_3$ | in A | 3.265 | 2.449 | 5.039 |
| H | in B | 4.816 | 0.154 | 4.277 |
| $C_6H_5$ | in B | 1.878 | 0.215 | 4.133 |
| $CH_3$ | in B | 4.136 | 0.435 | 4.032 |

B.J.Orchard & S.K.Tripathy, Macromol., 19, 1884 (1986).

G-3

⑤




⑥

表7 Solid-State Photo-Reactivity of Derivatives of Diphenyldiacetylene as Dependent from Nature and Position of the Substituents at the Phenyl Rings[a]

| | Substituents | Position | Reactivity[b] % Yield | color[c] | Crystal Shape[d] | Solubility in IDIPA[e] |
|---|---|---|---|---|---|---|
| I | H | ⊖ | no | – | needles | – |
| II | $-NO_2$ | • | 2.0 | red | needles | yes |
| III | $-NO_2$ | m | 3.5 | red | needles | yes |
| IV | $-NO_2$ | ⊕ | no | – | needles | – |
| V | $-NH_2$ | • | no | – | platelets | – |
| VI | $-NH_2$ | m | no | – | platelets | – |
| VII | $-NH_2$ | ⊕ | no | – | microcryst. | – |
| VIII | $-NH-C(=O)-CH_3$ | • | 19 | red-violet | needles | no[f] |
| IX | $-NH-C(=O)-CH_3$ | m | 35 | green-blue | needles | yes |
| X | $-NH-C(=O)-CH_3$ | ⊕ | no | – | needles | – |
| XI | $-NH-C(=O)-Ph$[f] | • | 0.2 | light purple | needles | yes |
| XII | $-NH-C(=O)-Ph$ | m | 3.0 | violet | needles | yes |
| XIII | $-NH-C(=O)-Ph$ | ⊕ | no | – | needles | – |
| XIV | $-NH-C(=O)-NH-Ph$ | • | 4.0 | light blue | elongated plates | yes |
| XV | $-NH-C(=O)-NH-Ph$ | m | 13 | green-blue | elongated plates | no[f] |
| XVI | $-NH-C(=O)-NH-Ph$ | ⊕ | no | – | elongated plates | – |

[a] General structure: R-⟨⟩-C≡C-C≡C-⟨⟩-R
[b] After 1 hour of uv-irradiation at 25 °C, crystals suspended in propanol-water 1:10 (v/v)
[c] Of the mixture of monomer and polymer as polymerized
[d] Of the monomeric and polymeric crystals
[e] Of the polymer in hexamethyl phosphoric trimmide at 100°C
[f] Ph = phenyl-
[g] Soluble in conc. $H_2SO_4$

G. Wegner (1971)

⑦

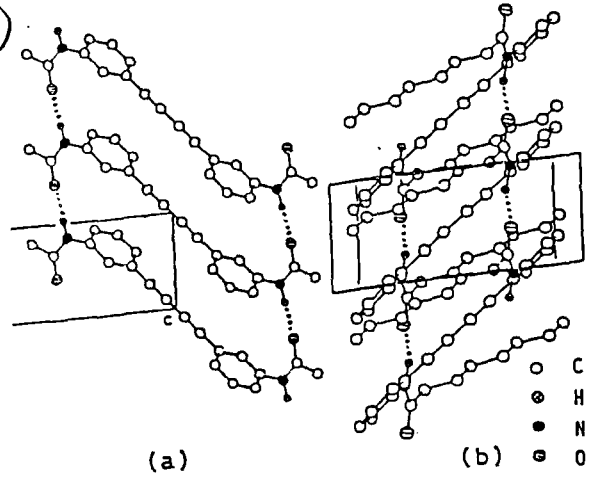
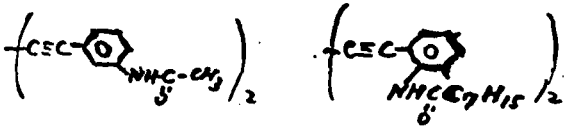



図2　2と3の結晶構造



⑧

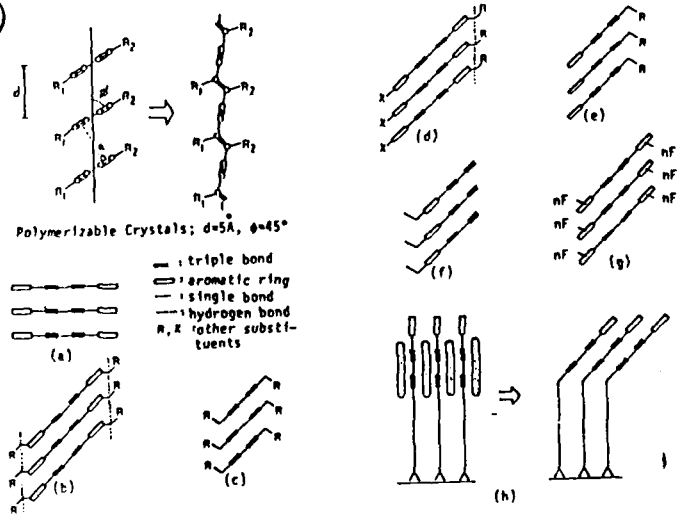


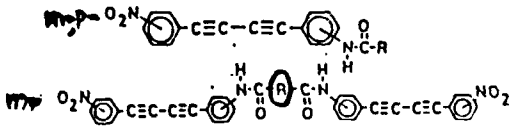

Fig. 2 Crystal engineering of polydiacetylenes with π-conjugation between main chain and

G-4

⑨ 表 2　アミド基を持つ新規ジアセチレンの固相重合性

| Structure | Substituent of -N-C-R position ( R ) (H, O) | | Reactivity | Polymer* Yield(%) |
|---|---|---|---|---|
| (3) | o | ($-C_{17}H_{35}$) | + | 13.4 |
| | m | ($-C_{17}H_{35}$) | + | 8.9 |
| | p | ($-C_{17}H_{35}$) | - | |
| | m | ($-C_7H_{14}COOH$) | + | 13.8 |
| | m | ($-C_{18}H_{36}COOH$) | + | |
| (4) | m | ( none ) | - | |
| | m | ($-C_4H_8-$) | + | |
| | m | ($-C_7H_{14}-$) | - | |
| | m | ($-C_8H_{16}-$) | + + | 58.8 |
| | m | ($-C_{18}H_{36}-$) | + + | 92.9 |

* $^{60}Co$ γ ray at the dose of ca. 100 MRad.
- stable, + reactive, + + highly reactive.

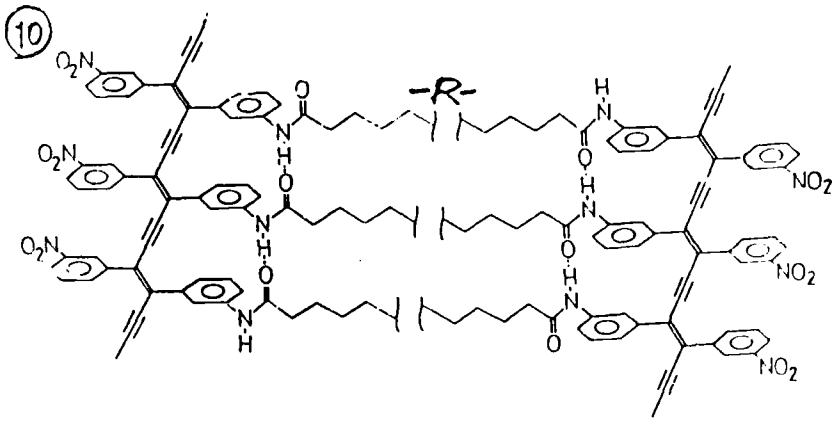


( 3 )



( 4 )

⑩



⑪

Table　Reactivity of 4-n

| n | Reactivity | IR $\nu_{C=O}$ ($cm^{-1}$) | mp (°C) |
|---|---|---|---|
| 7 | - | 1672 | 208 |
| 8 | ++ | 1656 | 189 |
| 9 | + | 1667 | 155 |
| 10 | ++ | 1647 | 194 |
| 11 | + | 1661 | 159 |
| 18 | +++ | 1658 | 175 |

⑫

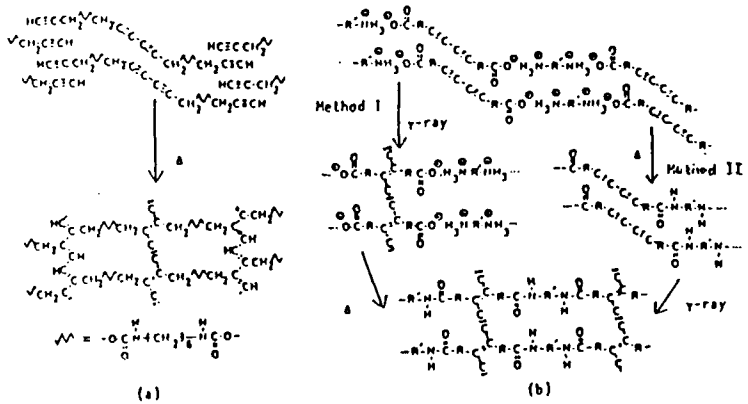
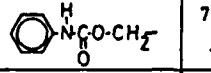
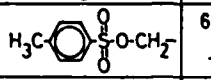



Figure 1. Schematic presentation of 2-D solid-state polymerization of diacetylene-acetylenes (a) and diacetylene nylon salts (b).

(13)

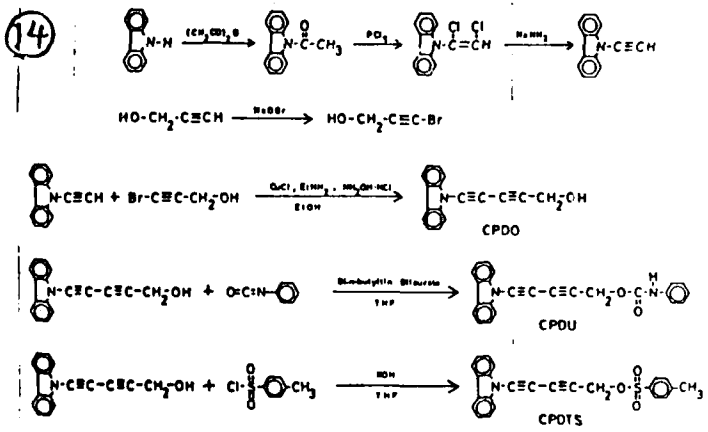
$R_1-C\equiv C-C\equiv C-R_2$

| $R_1$ \ $R_2$ | A | B | C | D | E | F |
|---|---|---|---|---|---|---|
| A | 86.0 – | | | | | |
| B | 129 – | >240 – | | | | |
| C HO-$CH_2$- | 68.3 + | 132 ++ | 113 + | | | |
| D  | 70.8 + | 160 ++ | 93.0 ++ | 145 + | | |
| E $H_3C$-  | 64.8 – | 111 ++ | 62.5 ++ | 114 + | 96.0 ++ | |
| F | 153 – | | 125 ++ | 112 ++ | 123 ++ | >220 ++ |

m.p./°C
reactivity

- stable, + reactive, ++ highly reactive

(14)




Scheme of synthetic procedures of CPDO and the derivatives.

(15)

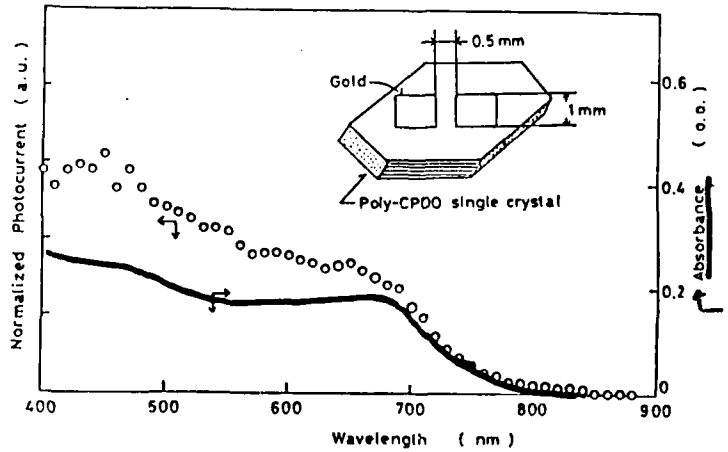



Fig. 7 Action spectrum of photocurrent (O) and absorption spectrum (——) of poly-CPDO.

(16)

Table 3 Band Gap Energies and Ionization Potentials of Polydiacetylenes

| Polydiacetylene | Eg( eV ) | I.P.( eV ) |
|---|---|---|
| poly-PTS | 2.1 | ( 5.3 )* |
| poly-DCHD | 2.3 | |
| poly-CPDO | 1.6 | 4.4 |

* Calculated

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(17)

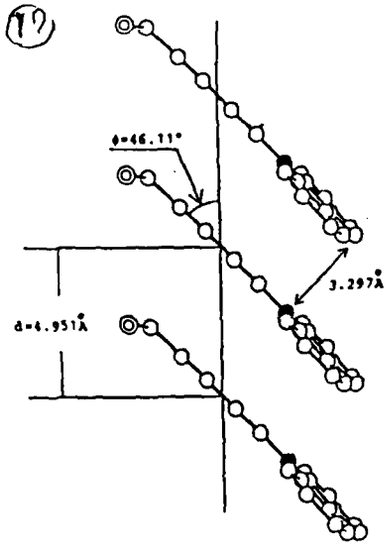



Table Crystallographic data of CPDO's.

| | Monomer | Polymer |
|---|---|---|
| Formular | $C_{17}H_{11}NO$ | $C_{17}H_{11}NO$ |
| Mr | 245.3 | 245.3 |
| Crystal System | Monoclinic | Monoclinic |
| Space Group | $P2_1/a$ | $P2_1/a$ |
| a (Å) | 16.249(3) | 16.494(6) |
| b (Å) | 4.951(1) | 4.873(3) |
| c (Å) | 17.360(4) | 19.513(8) |
| β (°) | 113.53(2) | 124.27(3) |
| V ($Å^3$) | 1280.4(5) | 1296 (1) |
| Z | 4 | 4 |
| Dx(Mg $m^{-3}$) | $1.27_8$ | $1.25_4$ |
| Dm(Mg $m^{-3}$) | 1.27 | 1.26 |

(18)

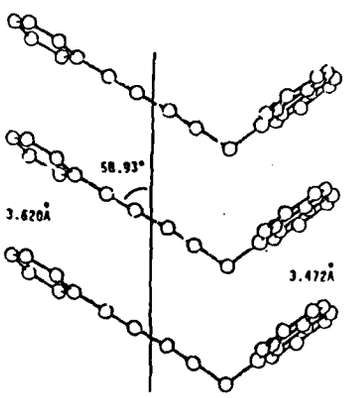
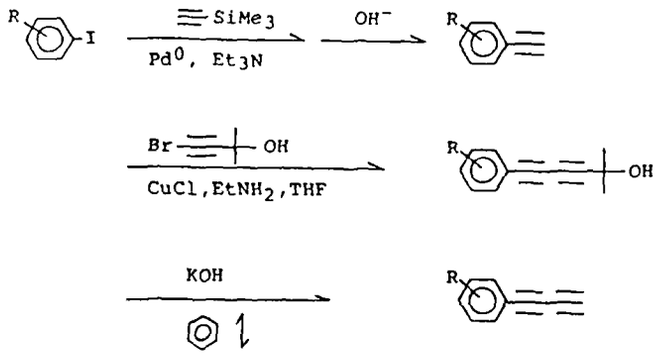



Table Crystallographic data

| | |
|---|---|
| Formular | $C_{23}H_{15}N$ |
| Mr | 305.4 |
| Crystal System | Monoclinic |
| Space Group | $P2_1/c$ |
| a (Å) | 13.180 (4) |
| b (Å) | 4.296 (1) |
| c (Å) | 28.776 (2) |
| β (°) | 91.71 (3) |
| V ($Å^3$) | 1628 (1) |
| Z | 4 |
| Dx(Mg $m^{-3}$) | 1.246 |
| Dm(Mg $M^{-3}$) | 1.244 |
| R | 0.077 |

(19)




(20)

Table Solid state polymerizability of Phenylbutadiyne derivatives.

| NO. | R | UV | γ | Δ | 重合収率 (%) | [γ線量 MRad] |
|---|---|---|---|---|---|---|
| 1 | 2-$NO_2$ | O | O | O | 95.6 | [70.0] |
| 2 | 3-$NO_2$ | O | O | O | 94.3 | [25.5] |
| 3 | 4-$NO_2$ | × | × | O | — | [50.0] |
| 4 | 2-$NH_2$ | O | O | O | 99.0 | [70.0] |
| 5 | 3-$NH_2$ | O | O | O | 100 | [27.0] |
| 7 | 2-$NH_2$ 5-$NO_2$ | O | O | O | 100 | [156.0] |

O : active
× : inactive

(21)

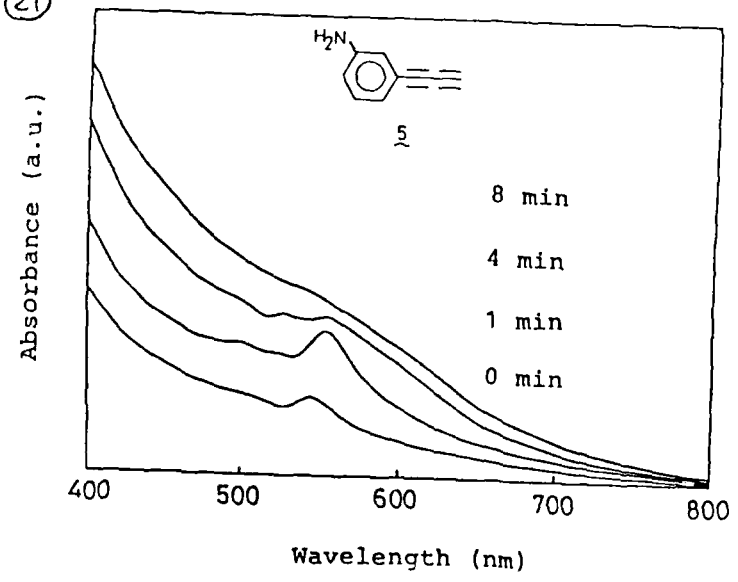
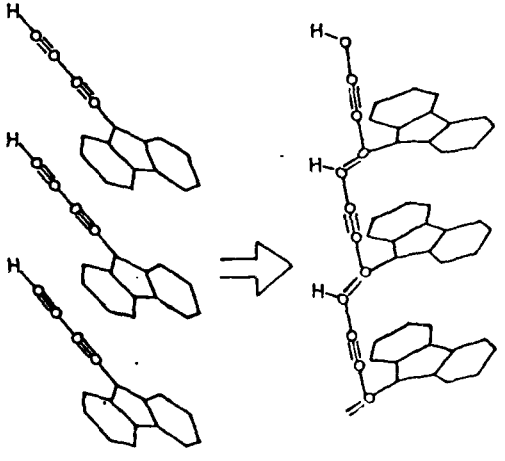



Fig. Absorption spectra of 5 with changing UV irradiation time.

(22)




(23)

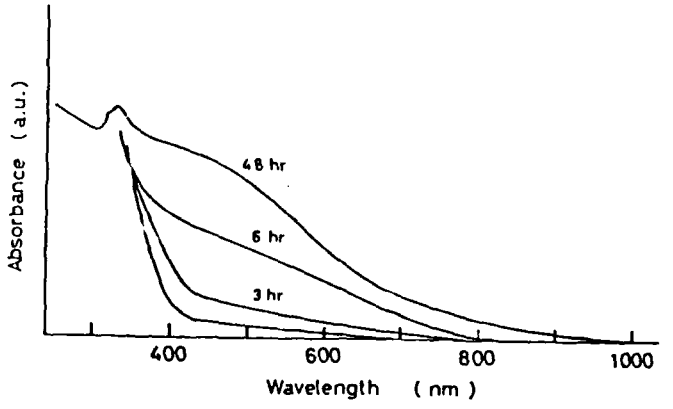



Figure Absorption spectra change of CBDy by heating at 50°C.

(24)

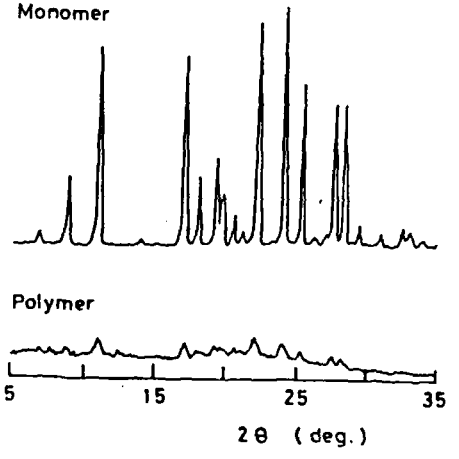
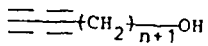
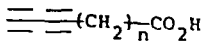



Figure X-ray powder diffraction patterns of CBDy.

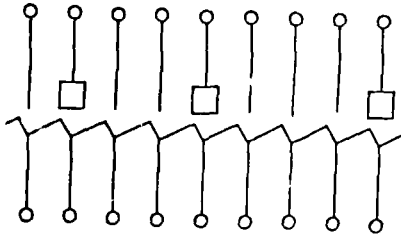
(25)



1-n (n=20,22)



2-n (n=20,22)



(26)

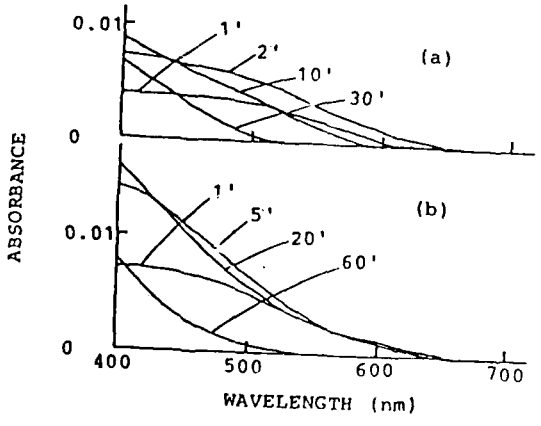
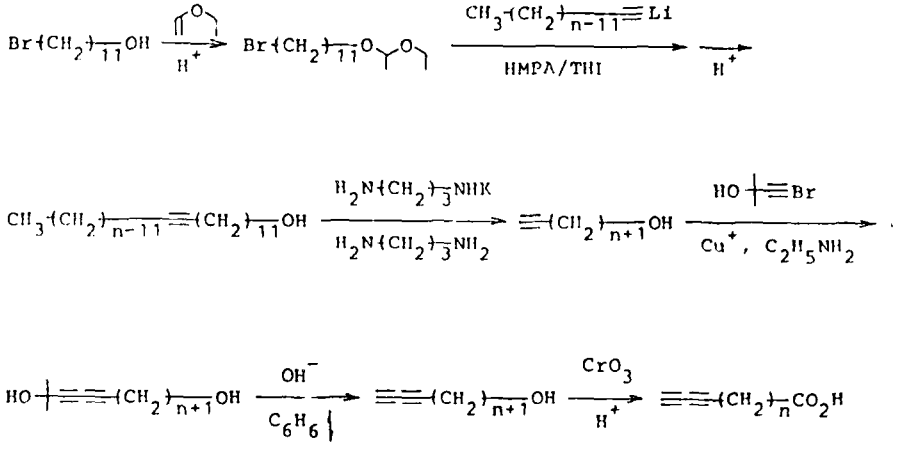
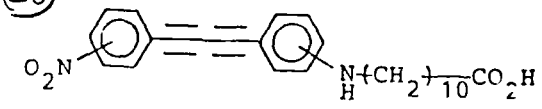



Fig. 4. Visible spectra of 20 layers of 1-20(a) and 2-20(b).

(27)

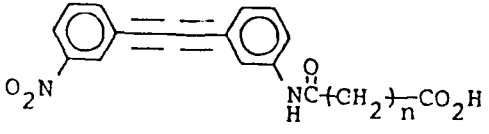



(28)



3-m (3,3'-substituted)

3-p (4,4'-substituted)



4-n (n=7,10)

(29)

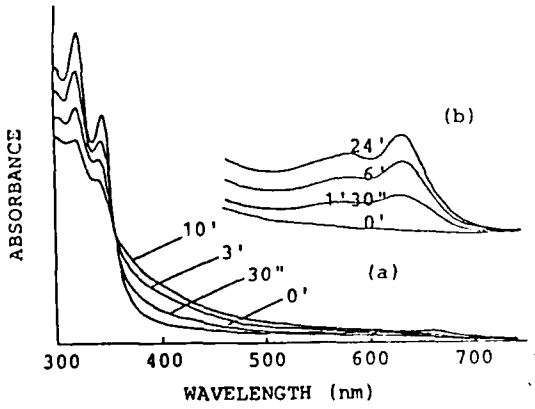
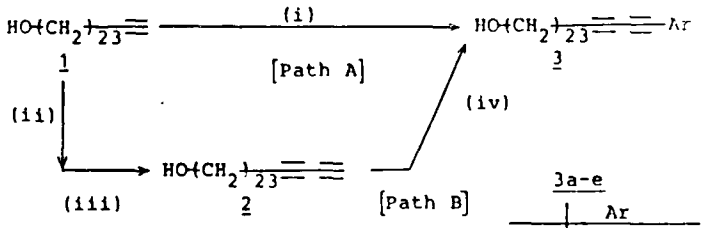



Fig. 8. UV-visible spectra of multilayers of 4-7(a) and 4-10(b).

(30)




(i) Br—≡—Ph, $Cu^+$, amine

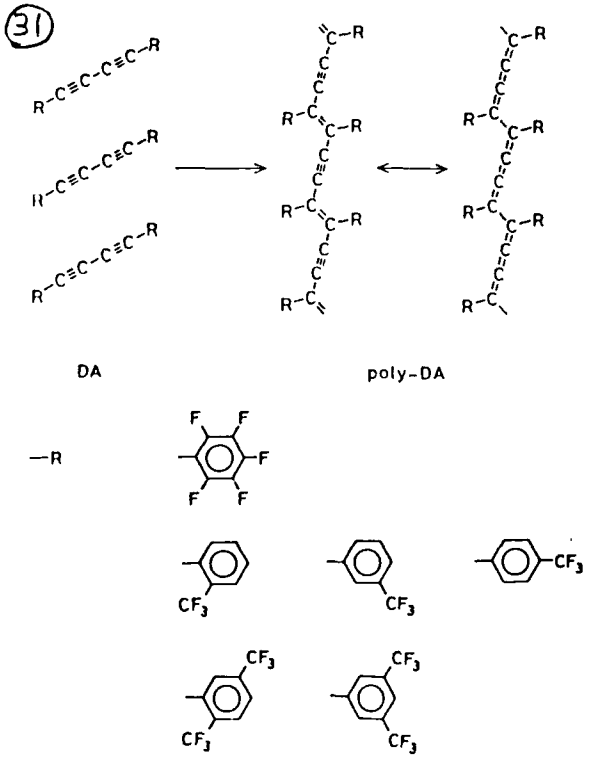
(ii) Br—≡—OH, $Cu^+$, amine (iii) $OH^-$

(iv) Ar-I, $(PPh_3)_2PdCl_2$, $Cu^+$, amine

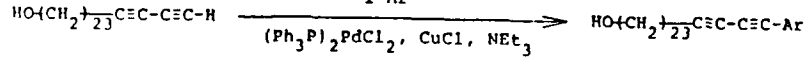
3a-e

| | Ar |
|---|---|
| 3a | phenyl |
| 3b | 2-tolyl |
| 3c | 3-tolyl |
| 3d | 4-tolyl |
| 3e | 9-anthryl |

(31)




(32)




3 : Ar

3a : phenyl
3b : 2-tolyl
3c : 3-tolyl
3d : 4-tolyl
3e : 9-anthryl
3f : pentafluorophenyl
3g : 2-(trifluoromethyl)phenyl
3h : 3-(trifluoromethyl)phenyl
3i : 4-(trifluoromethyl)phenyl
3j : 2,5-bis(trifluoromethyl)phenyl
3k : 3,5-bis(trifluoromethyl)phenyl

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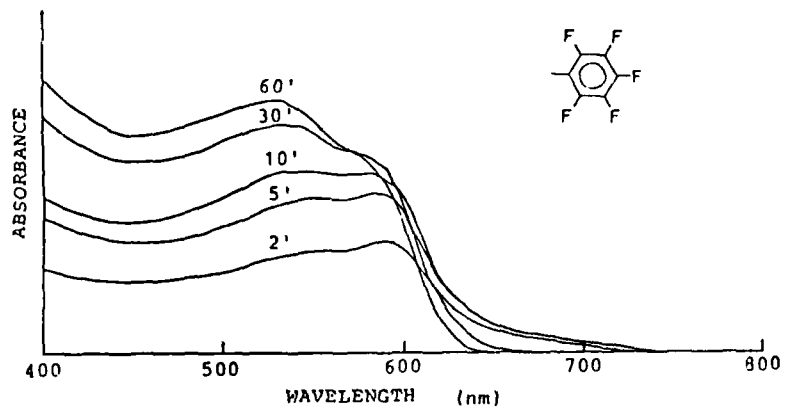


Fig. Absorption spectra of 3f dispersed in KBr with changing UV-irradiation time.

35

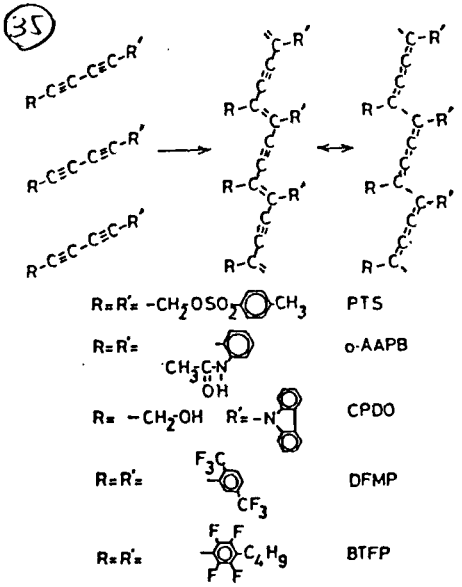


Fig. 1 Solid-state polymerization scheme and polydiacetylene derivatives.

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Table Polymer yield by γ-ray irradiation.

| Substituents of phenyl group | γ-ray dose (Mrad) | Polymer yield (%) |
|---|---|---|
| —— | 19.7 | 2 |
| pentafluoro | 19.7 | 82 |
| 2-(trifluoromethyl) | 100 | 11 |
| 3-(trifluoromethyl) | 100 | 1> |
| 4-(trifluoromethyl) | 100 | 18 |
| 2,5-bis(trifluoromethyl) | 50.3 | 98 |
| 3,5-bis(trifluoromethyl) | 50.3 | 1> |

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Table 1 $\chi^{(3)}$ values of polydiacetylene thin films

| Poly-DA | Thickness (μm) | $\chi^{(3)} \times 10^{11}$ (esu) Pumping Wavelength (μm) 1.83 | 1.88 | 1.94 |
|---|---|---|---|---|
| DFMP | 1.09 | 2.4 | 3.5 | 2.6 |
| | 0.98 | 3.7 | | 2.4 |
| BTFP | 0.070 | 28 | 32 | 13 |
| | 0.054 | 26 | | 15 |
| PTS | 1.35 | | | 1.1 |

Reference: fused quartz, $\chi^{(3)} = 3 \times 10^{-14}$ esu at 1.89μm

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# RESONANCE EFFECTS IN CUBIC HYPERPOLARISABILITIES OF CONJUGATED POLYMERS

RESONANCE EFFECTS IN CUBIC HYPERPOLARISABILITIES OF CONJUGATED POLYMERS

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Département d'Electronique et d'Instrumentation Nucléaire
Laboratoire de Physique Electronique des Matériaux
CEN Saclay, 91191 GIF SUR YVETTE, France

- THIN FILM PREPARATION TECHNIQUES (polydiacetylenes)
- THIRD ORDER OPTICAL HYPERPOLARISABILITY DETERMINATION TECHNIQUES
  - Third Harmonic Generation
  - Electric Field Induced Second Harmonic Generation
- NONLINEAR SPECTROSCOPY IN PDA THIN FILMS
  - Multiphoton resonances
  - Two photon resonance → Kerr susceptibility → intensity dependent index of refraction
  - Temperature variation of cubic susceptibility
  - Nonlinear Optical Dispersion
- POLARISATION EFFECTS IN PDA THIN FILMS

PDA THIN FILM PREPARATION TECHNIQUES

- Langmuir - Blodgett technique
- Solution casting
- Dipping technique (from a polymer solution)
- Evaporation technique (sublimation, epitaxy)
- Shear technique (thin monocrystalline films)

any thin films (0.001 μm up a few tens of microns)

- Nonlinear optical properties characterisation

$l \ll l_c$ $\qquad l_c = \lambda_p / 2(n_M - n_p)$

$\mu = \begin{cases} 2 & \text{EFISH} \\ 3 & \text{THG} \end{cases}$

$I_{2\omega} \sim I^2 l_c^2$
$I_{3\omega} \sim I^3 l_c^3$ $\qquad$ "phase matching"

- Nonlinear spectroscopy

  harmonic light within absorption range

- Integrated optics
- Thin film devices

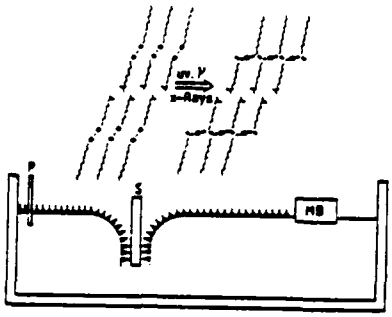
LANGMUIR- BLODGETT METHOD OF THIN FILM DEPOSITION

Diacetylene monomers :

$R_1 - C \equiv C - C \equiv C - R_2$

$R_1 = CH_2)_n COOH \qquad n=0, 9$

$R_2 = CH_2)_m CH_3 \qquad m=10, \ldots, 15$



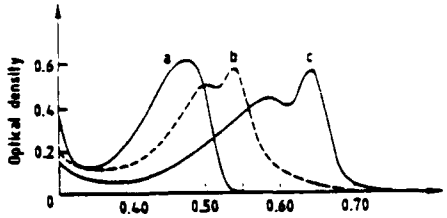

P-pressure sensor $\qquad$ MB - mobile barrier $\qquad$ S - substrat

Transfer layer by layer of monomer film

Polymerisation of monomer film by UV, γ, X-Ray radiation

Polymerisation of the monomer film on water subphase

Transfer of polymer monolayer ~30Å thick) on a substrat




Optical absorption spectra of different diacetylene polymers:

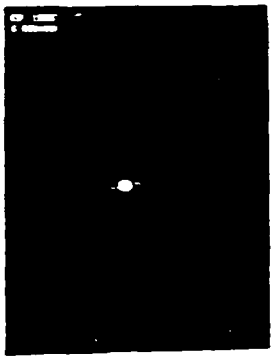
a - yellow form (polymer solution amorphous phase)

b - red form (stable)

c - blue form

# H-3

Electron micrograch of a poly-diacetylene monolayer



Electron diffraction patterns of a poly-diacetylene monolayer

PRINCIPAL PROPERTIES OF LB FILMS

- Centrosymetric thin films with controllable thickness (each layer ~ 30Å thick)
- Thickness limited to a few thousand of ängstroms
- Two-dimensional order
- Films exposed from polycrystallites
  large light scattering

SOLUTION CASTING

Soluble polymers

$$R_1 - \overset{*}{\underset{*}{C}} - C \equiv C - \overset{*}{C} - R_2$$

3-BCMU $R_1 = R_2 = (CH_2)_3OCONHCH_2COOC_4H_9$

4-BCMU $R_1 = R_2 = (CH_2)_4OCONHCH_2COOC_4H_9$

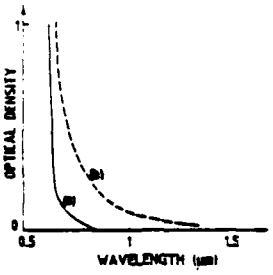
TS-12 $R_1 = R_2 = (CH_2)_4OSO_2C_6H_4CH_3$

Thin films with thickness varying from a few thousands ängstrom to a few tens of microns

Crystallites - large light scattering

Large surface roughness - light scattering by surface

Surface light scattering effects in solution cast 4-BCMU film (red form).

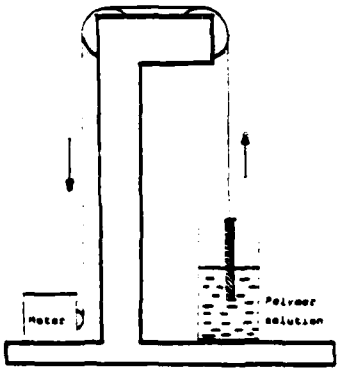


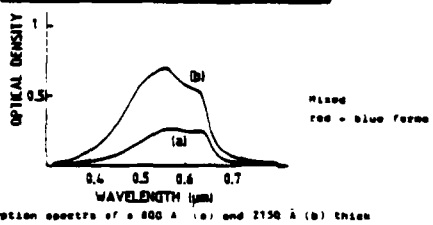

Tail of optical absorption spectrum of a 50 μm thick native 4-BCMU film (b) and after an annealing at 400° C under vacuum and a simultaneous sealing of a silica plate on free film face (a).

# H-4

DIPPING TECHNIQUE

from a polymer solution



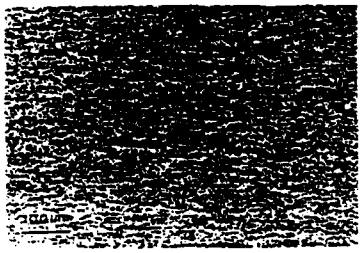




Absorption spectra of a 800 Å (a) and 2150 Å (b) thick polymer films obtained by dipping technique from 3-BCMU solution in $CHCl_3$.

MONOMER EVAPORATION TECHNIQUE SUBLIMATION

High vacuum $\sim 10^{-8}$ Torr

Works for practically all DA monomers. Delicate in the case of monomers polymerising thermally like TS-4 PTS. DCH yields homogeneous thin films with thickness varying from a few hundreds to a few tens of microns.

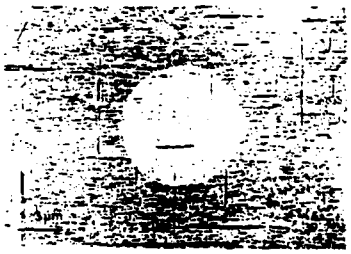


Electron micrograph of a poly-DCH $R_1 \equiv R_2 \equiv CH_2 \equiv C_{12}H_8$ thin film showing an isotropic orientation of crystallites.

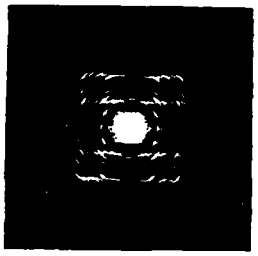
Light scattering by crystallites - this can be reduced by a cooling of substrate diminution of the crystallites size..

EPITAXY

KBr single crystal substrate



Electron micrograph of a bi-oriented pDCH film (250 Å) evaporated on KBr single crystal substrate



Electron diffraction of a central part of bi-oriented 250 Å thick p-DCH film

THIRD HARMONIC GENERATION EXPERIMENTS

In principle $E^R_{3\omega} = E^S_{3\omega} - E^P_{3\omega}$

Often $|E^P_{3\omega}| \gg |E^S_{3\omega}|$

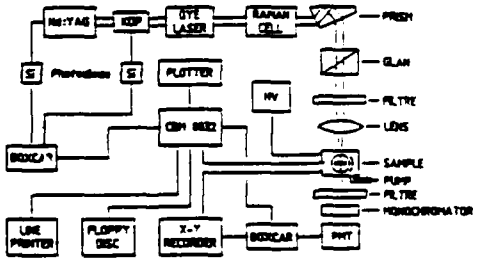
Harmonic intensity (for a transparent film)

$$J_{3\omega} = \frac{2304\pi^4}{C^2}\left(\frac{\chi_0^{(3)}}{(n_0^P - n_{3\omega}^P)}\right)^2\left(\frac{l}{\lambda_{3\omega}}\right)^2 |A|^2 J_\omega^3$$

does not depend on the refractive index dispersion "phase matching"

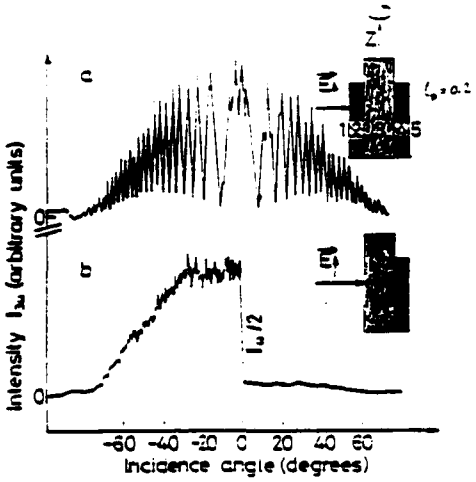
For an absorbing film at harmonic frequency

$$J_{3\omega} = \frac{2304\pi^4}{C^2}\left(\chi_0^{(3)}A\right)^2 J_\omega^3 f_a \qquad f_a = \frac{(1-\exp(-\alpha_{3\omega}l/2))^2 - (\Delta\psi)^2\exp(-\alpha_{3\omega}l/2)}{[(n_{3\omega}^P)^2 - (n_0^P)^2 - (\mathcal{K}_{3\omega}^P)^2]^2 + 4(n_{3\omega}^P)^2(\mathcal{K}_{3\omega}^P)^2}$$

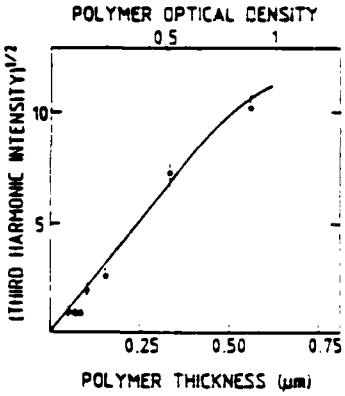



Experimental set-up for third harmonic generation measurements.

# H-5




Third harmonic intensity from an LB PUA film in function of rotation angle.




$\chi^{3)}(-3\omega;\omega,\omega,\omega)$ phase determination

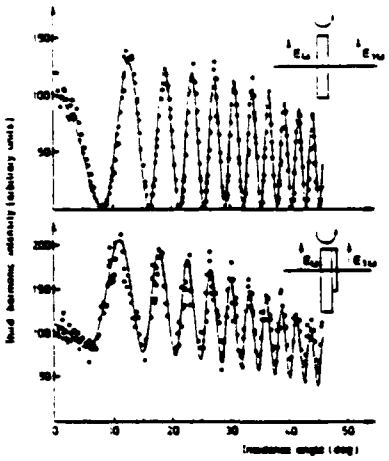



FIG. 4. Third harmonic intensity in function of incidence angle for (a) silica plate and (b) silica plate + polymer film in vacuum. Points represent measured values and solid lines the calculated ones with tabulated values of refractive indices for silica.[1]

Kaplan, Messier, and Rosina

J. Appl. Phys., Vol. 60, No. 9, 1 November 1986

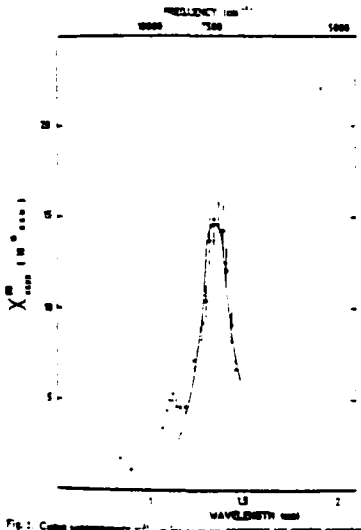



Fig. 1. Cubic susceptibility [illegible] corrected for crystal absorber, as a function of the laser fundamental wavelength. The [illegible] is a [illegible] as described in the text.

DIELECTRIC FIELD INDUCED OPTICAL SECOND HARMONIC GENERATION

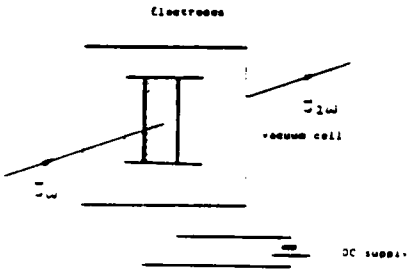
Dehydroabietylamine - centrosymmetric structure

no second harmonic generation

By applying an external DC field

centrosymmetry broken

second harmonic generation

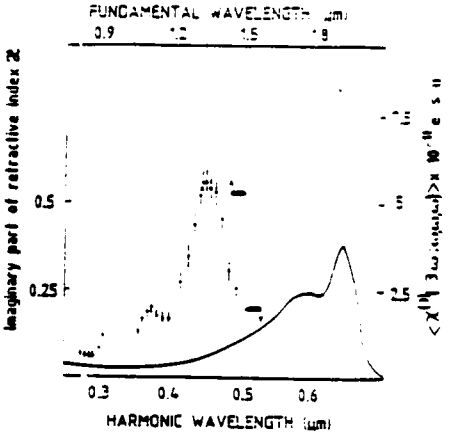



Comparison with a single crystal quartz standard (Q)

$$\langle \chi^{(3)}(-3\omega;\omega,\omega,0)\rangle = \frac{\Pi_{2\omega}}{3\omega\, E_{dc}} \times \frac{\chi^{(3)}(3\omega;\omega,\omega,0)\, \Pi_{2\omega}}{\chi^{(3)}(-3\omega;\omega,\omega,0)\, \Pi_{2\omega}} \cdot \frac{n_{\omega}}{n_{2\omega}} \cdot \frac{\overline{T_{2\omega}}\, T_{\omega}}{\overline{T_{\omega}}\, T_{2\omega}} \cdot \frac{\Pi_{\omega}}{\Pi_{2\omega}}\, \chi^{(3)}(3\omega;\omega,\omega,0)$$

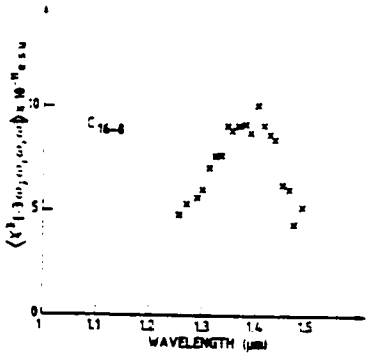
(e.s.u.)

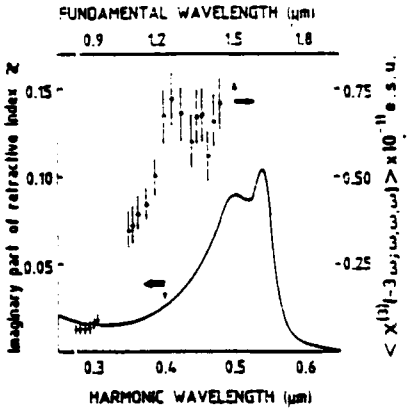
f - polymer film



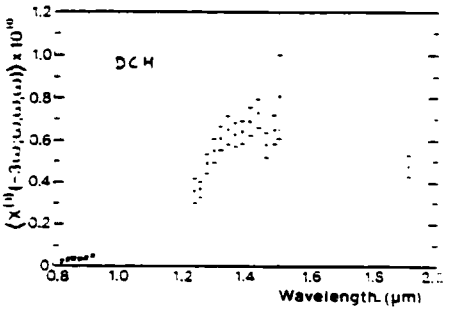

$C_{16-5}$ LB film - blue form

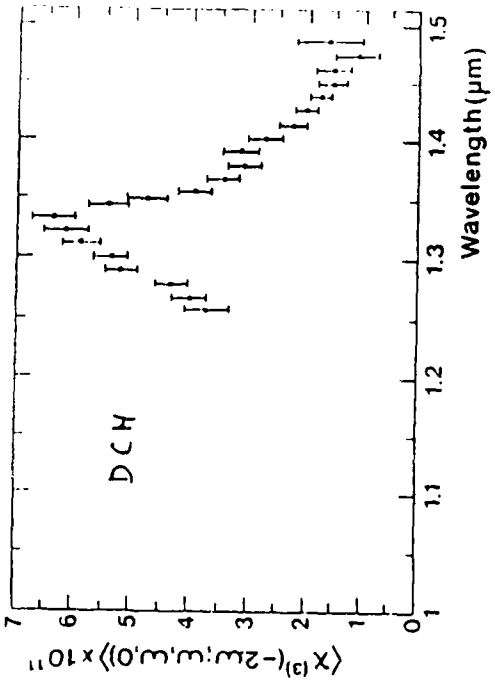
Evaporated under vacuum films

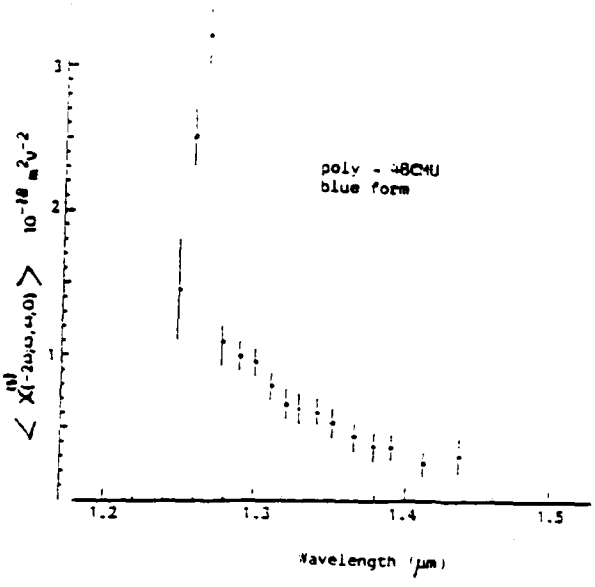


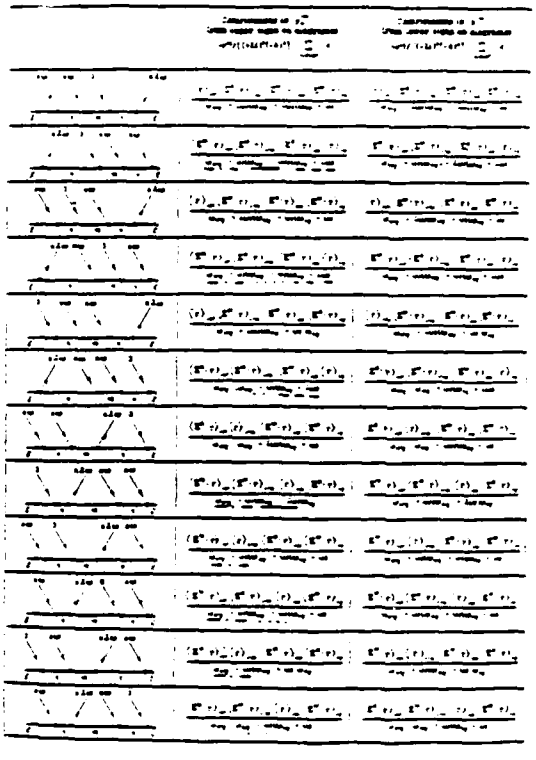

$C_{16-8}$ LB film - red form





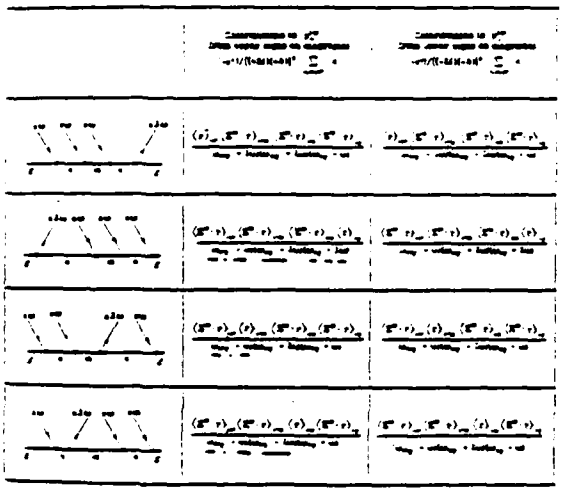

Tensor elements contributing to $\chi^{(3)}(-2\omega;\omega,\omega,0)$ (EFISHG)



J. F. Ward, Rev. Mod. Phys., 37, 1 (1965)

- two photon resonance with the same symmetry (as fundamental) level
- two photon resonance with opposite (to fundamental) symmetry level
- one photon resonance

Tensor elements contributing to $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ (THG)



J. F. Ward, Rev. Mod. Phys., 37, 1 (1965)

- two photon resonance with a (same symmetry as fundamental) level
- three photon resonance
- one photon resonance

Tensor elements contributing to optical Kerr susceptibility $\chi^{(3)}(-\omega;\omega,\omega,-\omega)$

| | | |
|---|---|---|
| | [illegible] | [illegible] |
| | [illegible] | [illegible] |
| | [illegible] | [illegible] |
| | [illegible] | [illegible] |
| | [illegible] | [illegible] |
| | [illegible] | [illegible] |
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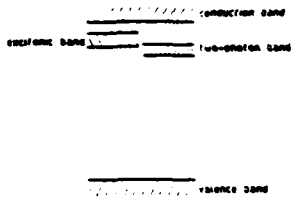
| | [illegible] | [illegible] |

J.F. Ward, Rev. Mod. Phys. 37, 1 (1965)




Band structure of the PDA monomers

—— - two photon resonance

- . - one photon resonance

Intensity dependent index of refraction

$$n = n_0 + n_2 I^{\omega}$$

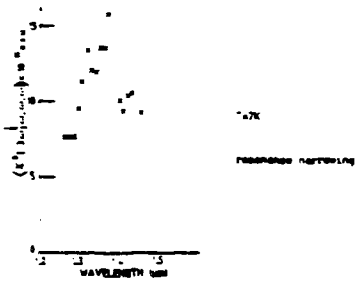
$$n_2 = 12\pi^2 \chi^{(3)}(-\omega;\omega,\omega,-\omega)/n_0^2 c$$

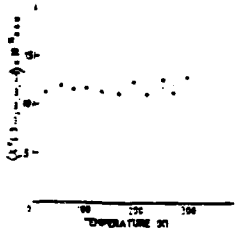
At two photon resonance - $\chi^{(3)}(-3\omega;\omega,\omega,-\omega)$ complex

↓

active optical bistability

Temperature variation of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$




Constancy of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ vs temperature - excitonic origin of cubic hyperpolarizability - phase space filling model (Schmitt-Rink et al. Phys. Rev. B32, 1985)

# H-9

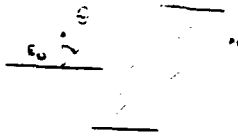
NONLINEAR OPTICAL DICHROISM

Enhanced $\chi^{(3)}$ along e.g. in direction of polymer chain

$\theta$ - angle between incident electric field and polymer chain

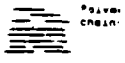
Harmonic intensity

$$I_{3\omega} \sim \cos^8\theta \, I_\omega^3$$




Exemplar: epitaxial DCH thin film

Bi-axial orientation of polymer chains mutually perpendicular




In linear optics crossed polarizers, linear optical dichroism

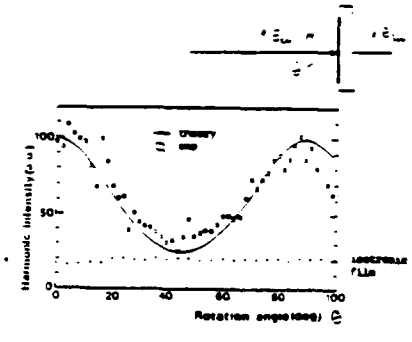
$$I_\omega = I_{\omega_0} \cos^2\theta + \cos^2(90^\circ - \theta) = I_{\omega_0}$$

In THG experiments

$$E_{3\omega} = A(\cos^2\theta - \sin^2\theta) E^3_\omega \quad \text{harmonic field}$$

$$I_{3\omega} = E_{3\omega}^2 = A^2 \cos^2\theta - \sin^2\theta)^2 I^3_\omega \quad \text{harmonic intensity}$$

$\theta$ - angle between incident electric field and polymer chain




Third harmonic intensity from a bi-oriented p-DCH thin film obtained by epitaxy on a KBr single crystal substrate.

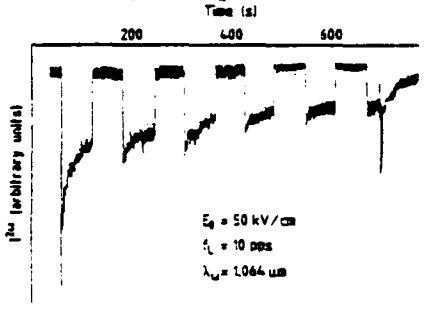
POLARIZATION EFFECTS

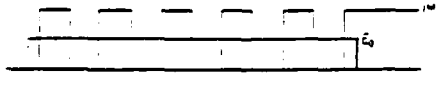
LB film

"Sliding layers" LB film

$Q = (CM_0)_g \cos Cd_{1/2}$

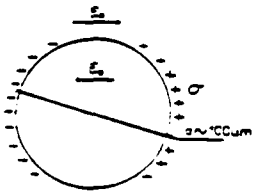
$Q' = (CM_0)_{or} C$




Decrease of SH intensity due to an internal polarization

creation of e-h pairs and their separation in external DC field




Setting of the internal polarization by charge drainage at the laser spot boundaries.

## CONCLUSIONS

### ADVANTAGES

Large $\chi^{(3)}$ with fast response time ps

Two photon resonance in telecommunications window 1.3 - 1.6 μm

active optical bistability

logic systems

Thin film feasibility by different techniques

organic thin films

epitaxy

Optical gap and physico-chemical properties can be modified by a choice of side groups

### PROBLEMS

Light scattering

amorphous thin films

Photodecomposition

Chemical stability - PTS

blue-red transformation in some cases

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Fabrice CHABRA - graduate student

Jacques BANIDE

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# NONLINEAR OPTICAL MEASUREMENTS ON LIQUID CRYSTALS AND QUASI-LIQUID CRYSTALS

# Optical Nonlinearities of Liquid Crystals and Quasi-Liquid Crystals

Motivation:

Liquid crystal molecules are highly nonlinear

Existence of many liquid crystals with different molecular structures

Dependence of nonlinearities on molecular structure

Gary Buskovic
Theo Rasing

Technique for measuring $\overleftrightarrow{\alpha}^{(2)}$

SHG from molecular monolayer spread on water

$$\chi^{(2)}_{ijk} = N L_{ii} L_{jj} L_{kk} \langle G^{\alpha\beta\gamma}_{ijk}(\Omega) \rangle \alpha^{(2)}_{\alpha\beta\gamma}$$

If $\Omega \equiv \theta$ and $L$'s are known, then the $n$ elements of $\overleftrightarrow{\alpha}^{(2)}$ can be deduced from measurements of $n+1$ independent components of $\overleftrightarrow{\chi}^{(2)}$.

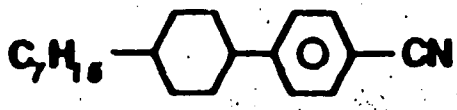
Advantages:

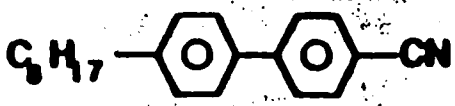
1. Molecular density can be a variable.
2. Local field effect could be less important.

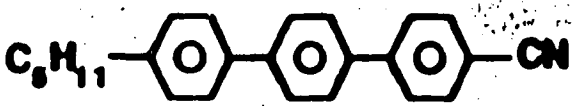
Disadvantages:

1. Not all molecules are spreadable on water.
2. Molecules could interact with water.

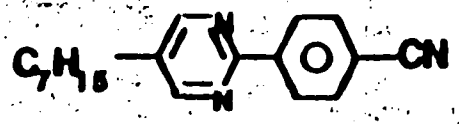
ALKYL-CYANO-(POLY)-PHENYLS

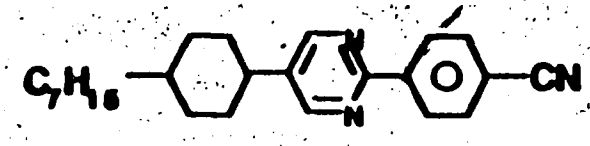
I 

II 

III 

ALKYL-CYANO-PHENYLPYRIMIDINES

IV 

V 

ALKOXY-CYANO-BIPHENYL

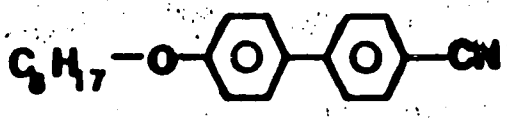
VI 

**TABLE 1** Second order polarizabilities, $\alpha_{zzz}^{(2)}$, for molecules I - VI. $\theta_0$ is the average orientation angle of the molecular long axis to the surface normal, as calculated from the SHG data.

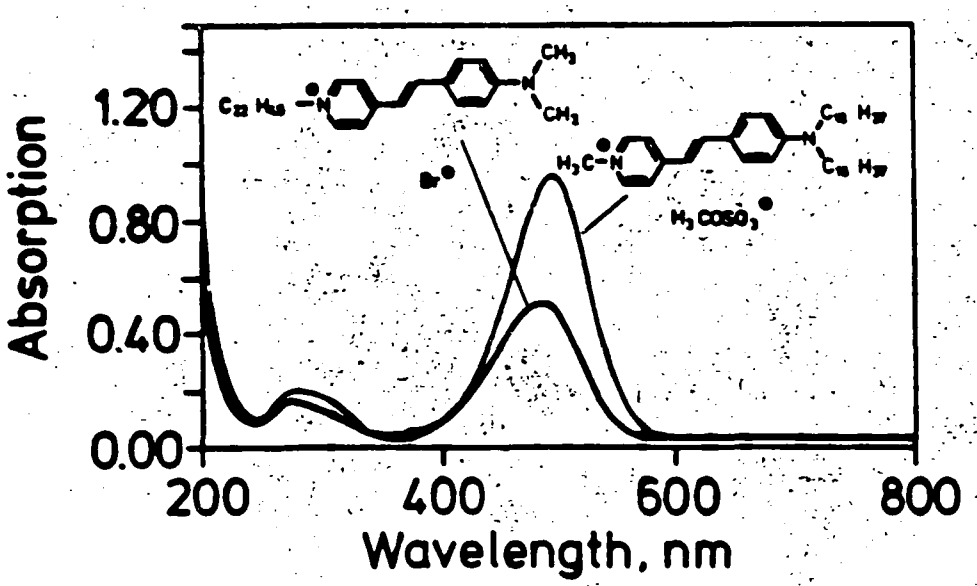
| | $\lvert\alpha_{zzz}^{(2)}\rvert$ ($10^{-30}$ esu) at 2ω resonance | $\lvert\alpha_{zzz}^{(2)}\rvert$ ($10^{-30}$ esu) at 1.06 μm | $\theta_0$ (°) |
|---|---|---|---|
| I | 4 | a | 80 ± 10 |
| II | 25 | 3 | 71 ± 2 |
| III | 13 | a | 60 ± 2 |
| IV | 8 | a | 79 ± 3 |
| V | 8 | a | 82 ± 4 |
| VI | 40 | 5 | 78 ± 2 |

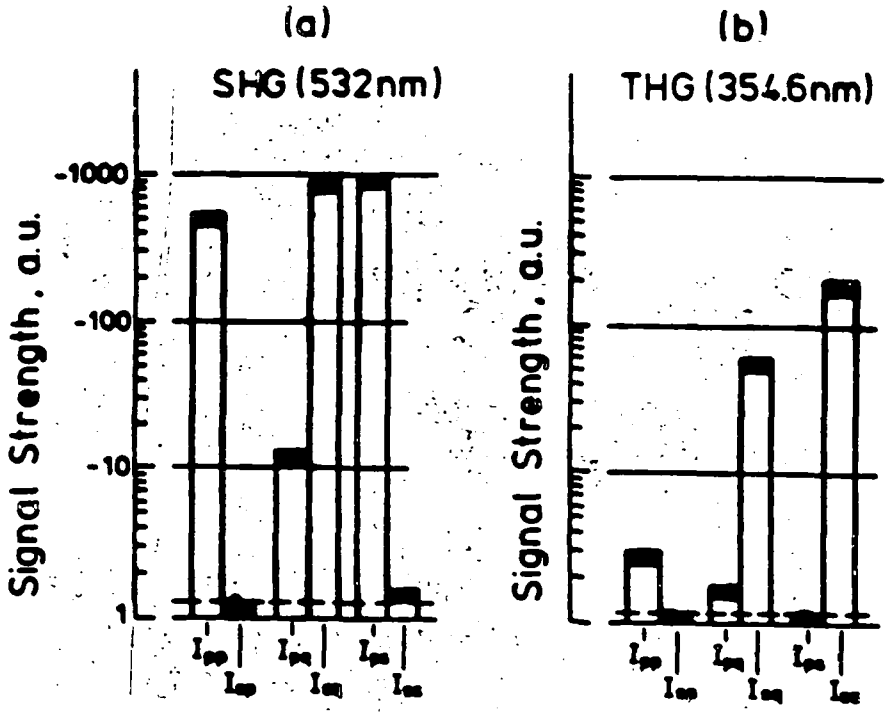
Results:

1. $\alpha^{(2)} \sim 10^{-29}$ esu
2. CN is a better electron donor than COOH.
3. Interruption of electron delocalization decreases $\alpha^{(2)}$
4. Triphenyl is worse than biphenyl presumably because of twist between phenyl rings.

# Nonlinearities of Hemicyanine Dyes and the Environmental Effect

G. Marowsky
L.F. Chi
D. Möbius
R. Steinhoff
D. Dorsch
B. Rieger



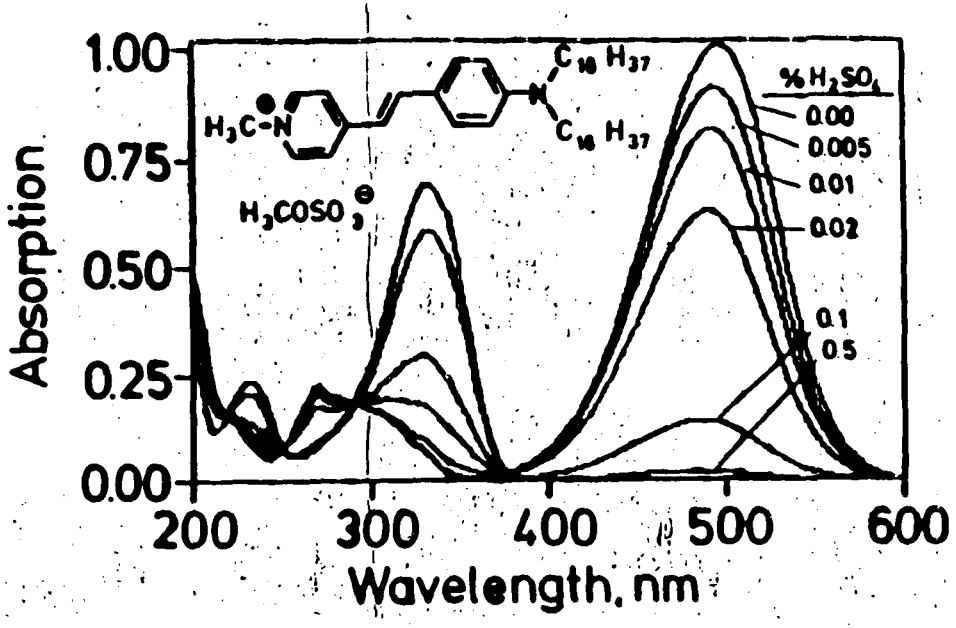


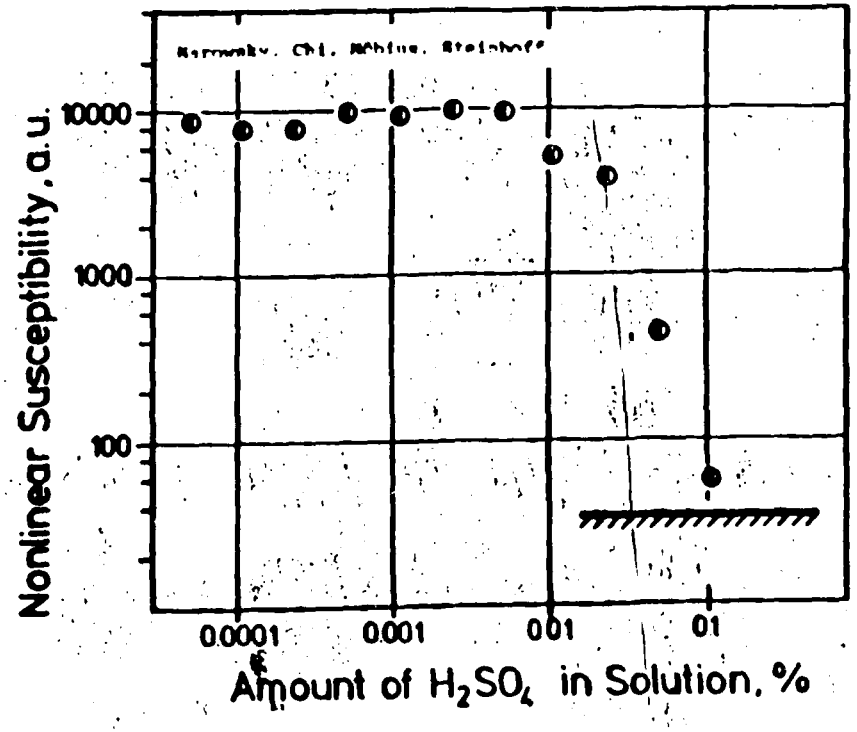

Marowsky, Chi, Möbius, Steinhoff, Shen, Dorsch, Rieger: Nonlinear Optical Properties ...
Fig. 2

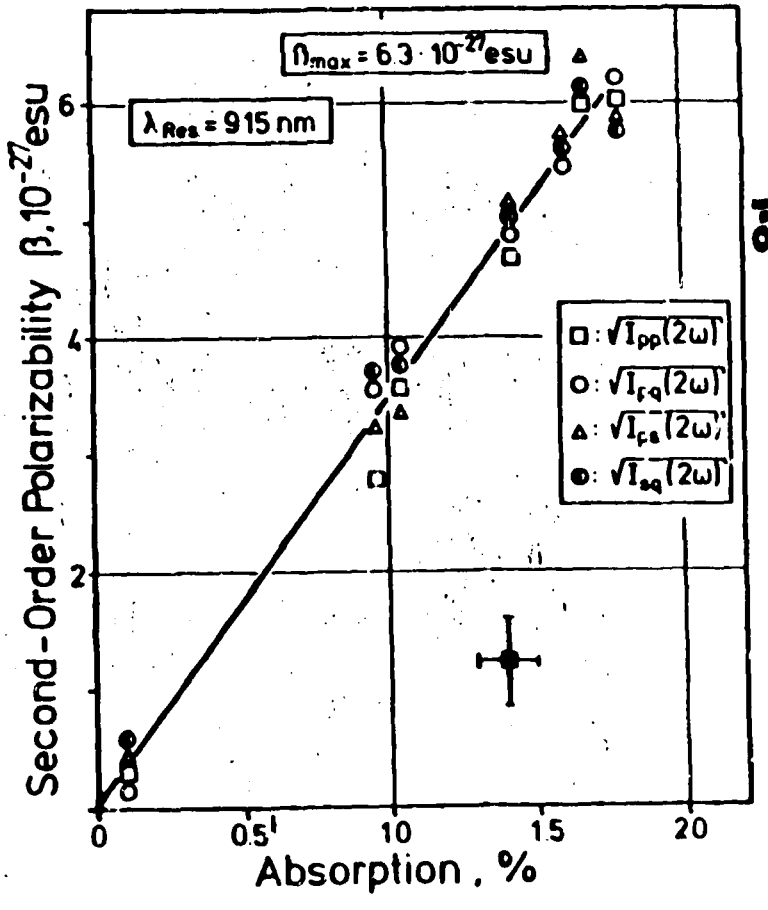
Effects of Protonation

1. Suppresses charge-transfer absorption
2. Drastically reduces $\chi^{(2)}$.
3. $\chi^{(2)} \propto$ charge-transfer absorption
   $\propto N_{\text{unprotonated}}$
4. UV absorption band has little effect on $\chi^{(2)}$.

Marowsky, Chi, Möbius, Steinhoff, Shen, Dorsch, Rieger: Nonlinear Optical Properties ..



# Poling

on

# Quasi Liquid Crystal Films

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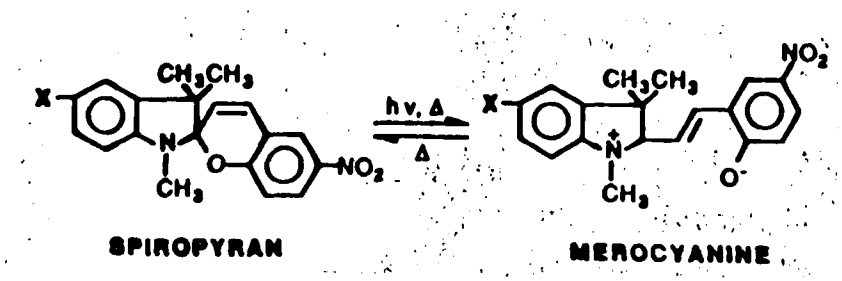
F.P. Shvartzman
I.R. Cabrera
V.A. Krongauz




## Theory of Poling

Assume $\overleftrightarrow{\alpha}^{(2)}$ and $\vec{p}$ dominated by $\alpha^{(2)}_{\xi\xi\xi}$ and $p_\xi$. $\vec{E}$ along $\hat{x}$

$$\chi^{(2)}_{xxx} \propto \alpha^{(2)}_{\xi\xi\xi} \langle \cos^3\theta \rangle$$

$$\chi^{(2)}_{yyx} \propto \alpha^{(2)}_{\xi\xi\xi} [\langle \cos\theta \rangle - \langle \cos^3\theta \rangle]$$

$$\langle \cos^n\theta \rangle = \int_{-1}^{1} \cos^n\theta \, e^{-V/kT} d(\cos\theta) / Z$$

$$V = V_N - u\cos\theta - pE\cos\theta$$

$$V_N = -U_2 P_2(\cos\theta) - U_4 P_4(\cos^4\theta) -$$

$$\langle \cos^n\theta \rangle \cong \int_{-1}^{1} \cos^n\theta \left(1 + \frac{u+pE}{kT}\cos\theta\right) e^{-V_N/kT} \times d(\cos\theta) / Z_N$$

$$= \langle \cos^n\theta \rangle_0 \qquad n \text{ even}$$

$$= \frac{u+pE}{kT} \langle \cos^{n+1}\theta \rangle_0 \qquad n \text{ odd}$$

$\langle \cos^2\theta \rangle = \langle \cos^2\theta \rangle_0$ indep of $E$

$$\langle P_2(\cos\theta) \rangle = \tfrac{1}{2}(3\langle \cos^2\theta \rangle - 1) = \langle P_2(\cos\theta) \rangle_0$$

$$\equiv S$$

obtained from birefringence

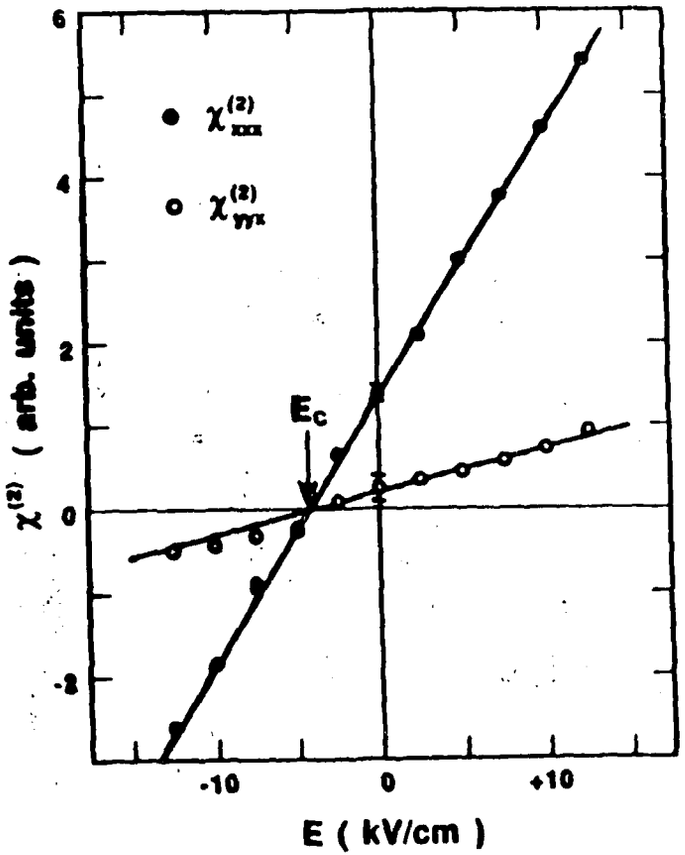
$$\langle \cos\theta \rangle = \langle \cos^2\theta \rangle_0 \left(\frac{u + pE}{kT}\right)$$

$$\langle \cos^3\theta \rangle = \langle \cos^4\theta \rangle_0 \left(\frac{u + pE}{kT}\right)$$

$$\chi^{(2)}_{xxx} \propto \langle \cos^4\theta \rangle_0 \left(\frac{u + pE}{kT}\right)$$

$$\chi^{(2)}_{yyx} \propto [\langle \cos^2\theta \rangle_0 - \langle \cos^4\theta \rangle_0] \left(\frac{u + pE}{kT}\right)$$

Measurements of $\chi^{(2)}_{xxx}$ and $\chi^{(2)}_{yyx}$ versus $E$ allow the determination of $\langle \cos^4\theta \rangle_0$, $u$, and $p$.



D. J. Gerbi

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# NONLINEAR OPTICAL EFFECTS IN CONJUGATED SYSTEMS

# SECOND ORDER NONLINEAR OPTICAL EFFECTS IN CONJUGATED SYSTEMS

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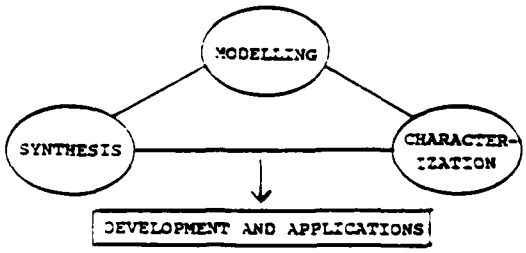
ADVANCED OPTICAL MATERIALS
SCIENCE RESEARCH LABORATORY
3M CORPORATE RESEARCH LABORATORIES

## ADVANCED OPTICAL MATERIALS PROGRAM (ORGANIC-BASED DEVICES)




- IDENTIFY CANDIDATE MATERIALS
- UNDERSTAND AND MAINTAIN MOLECULAR ORDER
- DETERMINE APPLICATIONS OF MATERIALS, FEASIBILITY IN DEVICES

$\underline{X^{(2)}}$

OPTICAL COMMUNICATIONS

**FIBER OPTICS LAB**
**TELCOMM**
**3M DORRAN**
**EOTEC**

SENSORS

**FIBER OPTICS LAB**

$\underline{X^{(3)}}$

OPTICAL SIGNAL PROCESSING

**INFORMATION AND IMAGING TECHNOLOGIES**

OPTICAL SIGNAL PROCESSING
OPTICAL SENSOR PROTECTION

**AFOSR**

## OUTLINE

I. REVIEW OF SECOND ORDER NONLINEAR OPTICS, CHARACTERIZATION METHODS AND DEVICE CONFIGURATIONS

II. ADVANTAGES OF ORGANIC NONLINEAR OPTICAL MATERIALS

III. MATERIALS PROCESSING/APPLICATIONS

IV. ELECTRO-OPTIC MATERIALS - CRYSTALS AND POLED POLYMER SYSTEMS

## REVIEW OF SECOND ORDER NONLINEAR OPTICAL EFFECTS

### MACROSCOPIC POLARIZATION:

$$P_i = P_{o_i} + X^{(1)}_{ij} E_j + X^{(2)}_{ijk} E_j E_k + X^{(3)}_{ijkl} E_j E_k E_l \cdots$$

### MICROSCOPIC POLARIZATION:

$$P_i = P_{o_i} + \alpha_{ij} E_j + \beta_{ijk} E_j E_k + \gamma_{ijkl} E_j E_k E_l \cdots$$

**ELECTRO-OPTIC EFFECT:**

**Index of refraction changes with applied voltage**

$$n = n_o + \Delta n(E)$$

$$\Delta n \propto X^{(2)}$$

**SUM FREQUENCY GENERATION:**

**Output frequency = sum of input frequencies**

$$w(out) = w_1 + w_2$$

**SHG:** $I(2w) \propto [X^{(2)}]^2 [I(w)]^2$

**DIFFERENCE FREQUENCY GENERATION:**

**Output frequency = difference of input frequencies**

$$w(out) = w_1 - w_2$$

CHARACTERIZATION METHODS
FOR
SECOND ORDER NONLINEAR OPTICAL MATERIALS

**POWDER SHG**

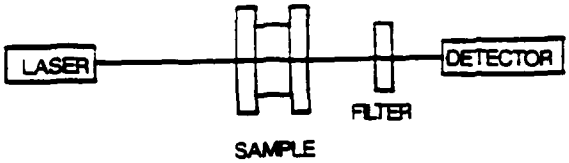
**SINGLE CRYSTAL SHG**

**EFISH**

**POLYMER POLING**

**ELECTRO-OPTIC EFFECT**

**POWDER SHG**



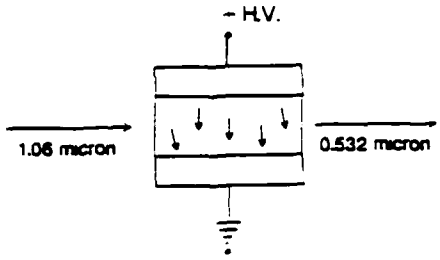

$$\eta = \frac{I(2w)sample}{I(2w)urea}$$

MATERIAL FORM: MICROCRYSTALLINE POWDER

ADVANTAGES: USEFUL FOR SCREENING

DISADVANTAGES: CANNOT RESOLVE MICRO- AND MACROSCOPIC CONTRIBUTIONS TO NONLINEARITY

**EFISH**

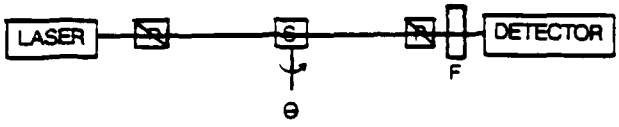



MATERIAL FORM: SOLUTION (LOW POLARITY SOLVENTS)

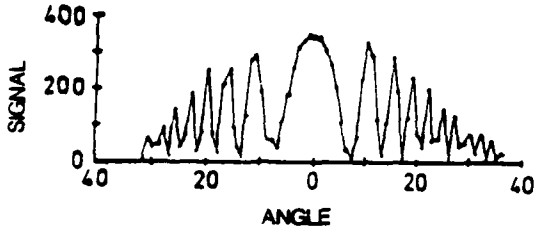
ADVANTAGES: OBTAIN MOLECULAR PROPERTIES. COMPARISONS

DISADVANTAGES: MOLECULAR PROPERTIES ARE SUBJECT TO ENVIRONMENT

**SINGLE CRYSTAL SHG**




MAKER FRINGE




MATERIAL FORM: LARGE SINGLE CRYSTAL (mm to cm)

ADVANTAGES: MEASURES TENSOR ELEMENTS $X^{(2)}_{ijk}$

DISADVANTAGES: REQUIRES CRYSTAL ORIENTATION, INDICES OF REFRACTION, POLISHING

**POLYMER POLING**

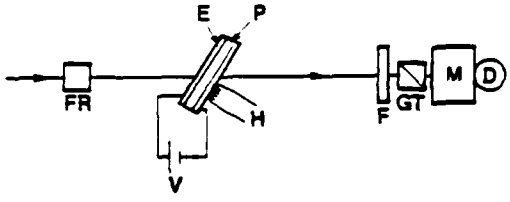



Figure 2. Experimental set-up for thin film SHG measurements using Fresnel rhomb FR, transparent electrodes E, polymer film P, poling voltage V, heater H, laser filter F, Glan-Thompson prism GT, monochromator M and detector D.

MATERIAL FORM: POLYMER SYSTEM

ADVANTAGES: REAL LIFE ENVIRONMENT, EASY SIGNAL DISCRIMINATION

DISADVANTAGE: NOT A DIRECT MEASUREMENT FOR E-O

**ELECTRO-OPTIC EFFECT**

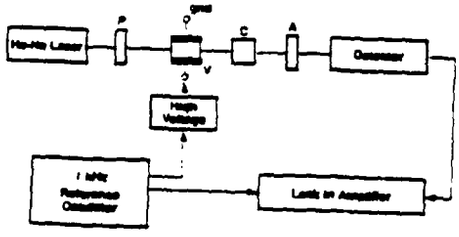



*Figure 1. Experimental set-up for electro-optic measurements using polarizer P, analyzer A, and Babinet-Soleil compensator C.*

MATERIAL FORM: POLYMER SYSTEMS, CRYSTALS

ADVANTAGES: DIRECT MEASUREMENT (DEVICE FORM)

DISADVANTAGES: LESS SENSITIVE THAN SHG
NOT AN IN-SITU TEST
CRYSTALLOGRAPHIC ORIENTATION
FOR CRYSTALS

## *ADVANTAGES OF ORGANIC MATERIALS*

- SYNTHETIC TAILORABILITY VIA DELOCALIZATION/SUBSTITUENTS
- SUBPICOSECOND RESPONSE TIMES
- TRANSPARENCY
- MECHANICAL AND STRUCTURAL STABILITY
- HIGH RADIATION DAMAGE THRESHOLD
- ENVIRONMENTAL STABILITY
- PROCESSABILITY
- ROOM TEMPERATURE OPERATION OF DEVICES

## *MATERIALS PROCESSING*

**SPIN-COATED POLYMERS**

e.g. CHANNEL WAVEGUIDES

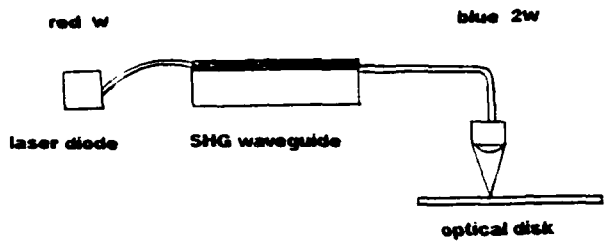
- REQUIRES LOW LOSS (<1 dB/cm)
- REPRODUCIBLE WELL-KNOWN TECHNIQUES AVAILABLE
- INDUCE ORDER RATHER THAN RELY ON CRYSTAL PACKING

**CRYSTALS**

e.g. BULK CRYSTALS
CHANNEL WAVEGUIDES
VAPOR DEPOSITED FILMS

- REQUIRES LOW LOSS (<1 dB/cm)
- BULK CRYSTALS MUST BE DURABLE ENOUGH FOR CUTTING AND POLISHING
- COMPLETE CRYSTALLOGRAPHIC ORIENTATION IS REQUIRED
- PRINCIPAL OPTIC INDICES AND AXES RELATIVE TO EXTERNAL MORPHOLOGY MUST BE DETERMINED

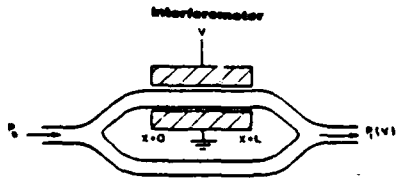
## SECOND HARMONIC GENERATION APPLICATIONS



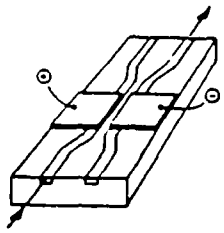

doubling optical frequency gives 4x storage density

## APPLICATIONS – ELECTRO-OPTIC EFFECT

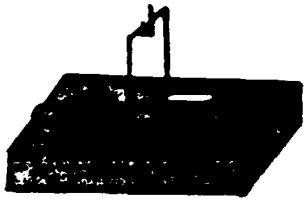
**modulator**




**directional coupler**



## ELECTRO-OPTIC PHASE SHIFTER



MODULATOR, GYRO

* COMPARE $LiNbO_3$

$\lambda$ = 850 nm

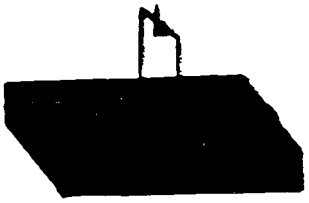
Insertion loss 6dB

BW = 3 GHz

$V_\pi$ = 5V (4 cm)

Room Temperature

## ELECTRO-OPTIC PHASE SHIFTER



NONLINEAR OPTICAL CRYSTAL

$$\chi^{(2)}_{33} = \frac{\lambda n_e d}{2V_\pi L}$$

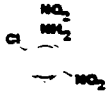
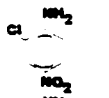
$$\chi^{(2)}_{33} \approx 3 \times 10^{-7} \text{ esu} \approx 30 \cdot \chi^{(2)} \text{ (urea)}$$

POLED POLYMER

$$\chi^{(2)} = c\, N \mu\beta E \qquad N = 1 \text{ Molar}$$
$$E = 0.4 \text{ MV/cm}$$

$$\Rightarrow \mu\beta \sim 50 \cdot \mu\beta \text{ (DNA)}$$

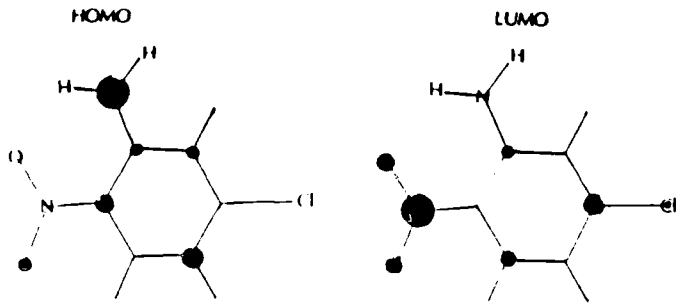
$$A < 0.1/\text{cm} \qquad (1 \text{ dB/cm})$$

| HALONITROANILINES | RELATIVE EFFICIENCY (UREA) | $\mu$ (DEBYE |
|---|---|---|
| | 20 | 4.471 |
| | ≤0.001 | — |
| | ≤0.001 | 9.460 |
|  | ≤0.001 | 4.433 |
|  | 2 | 7.722 |
| | 0.03 | 5.281 |
| | ≤0.001 | 8.023 |

| MATERIAL | SPACE GROUP | a | b | c | α | β | γ | Z |
|---|---|---|---|---|---|---|---|---|
| 5-chloro-2-nitroaniline (phase I) | $Pna2_1$ | 30.844 Å | 3.852 Å | 6.004 Å | 90° | 90° | 90° | 4 |
| 5-bromo-2-nitroaniline (5-chloro-2-nitroaniline) (phase II) | $P\bar{1}$ | 7.344 | 7.844 | 7.091 | 97.95 | 116.69 | 83.23 | 2 |
| 2-chloro-4-nitroaniline* | $Pna2_1$ | 11.25 | 16.85 | 3.87 | 90 | 90 | 90 | 4 |
| 3-chloro-4-nitroaniline | $P2_1/C$ | 3.813 | 12.531 | 14.467 | 90 | 91.20 | 90 | 4 |

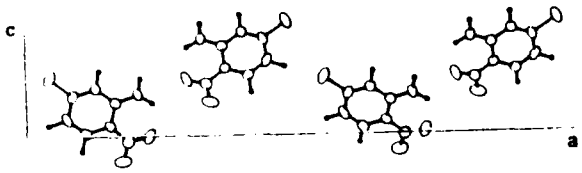
* A. T. McPhil and G. A. Sim, J. Chem. Soc., 227 (1965)

MOLECULAR MODELLING




$\beta \propto$ difference in ground state and excited state dipole moments

5-CHLORO-2-NITROANILINE



a = 30.844 Å
b = 3.852
c = 6.004

SPACE GROUP
$Pna2_1$

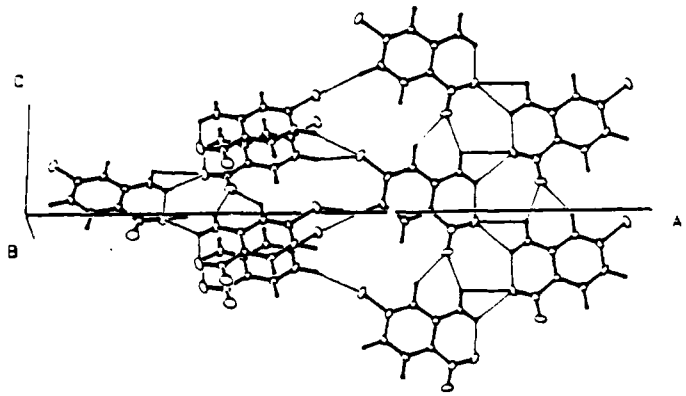


Figure 4. An illustration of the crystal structure of 5-chloro-2-nitroaniline. Significant intra- and intermolecular hydrogen bonding indicated by thin lines.

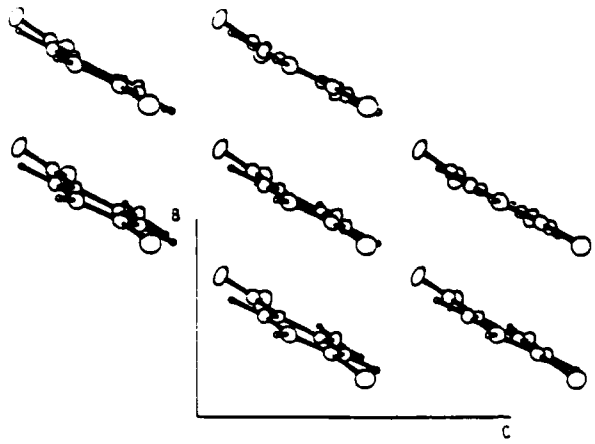


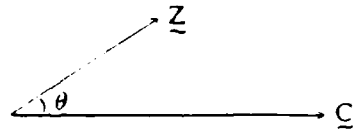

Figure 5. A projection of the ribbon-like packing structure of 5-chloro-2-nitroaniline. Molecules in each row are connected by significant intermolecular hydrogen bonding.

5-CHLORO-2-NITROANILINE

SPACE GROUP $Pna2_1$

polarization axis : C-axis

$P \propto \chi(333) \propto \beta(zzz)\cos^3\theta$



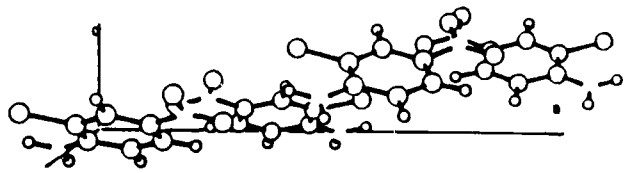

$\underset{\sim}{Z}$ : polarization axis of molecule

$\underset{\sim}{C}$ : polarization of crystal

$\underset{\sim}{Z} \cdot \underset{\sim}{C} = \cos\theta = 0.906$

SHG PACKING EFFICIENCY ≈ 0.74

2-CHLORO-4-NITROANILINE



ELECTRODE CONFIGURATION
FOR MEASURING E-O EFFECT

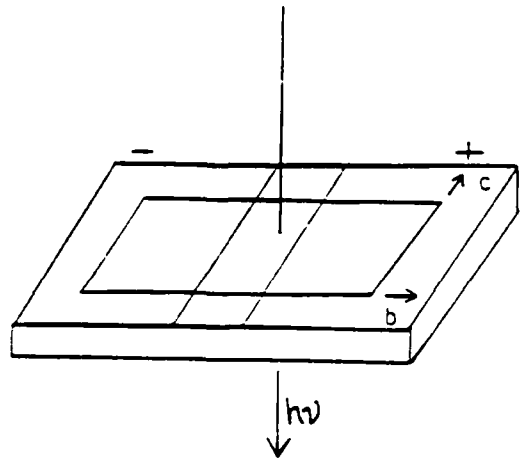
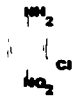
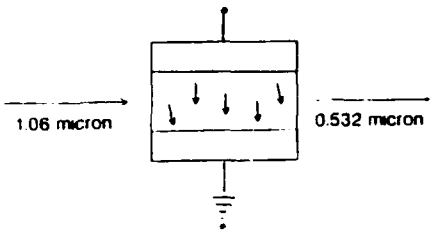



FIGURE OF MERIT = $\frac{1}{2}|n_1^3 r_{13} - n_2^3 r_{23}| = 18$ pm/v

$E^{DC} = \hat{y}$

## EFISH on 3-CHLORO-4-NITROANILINE

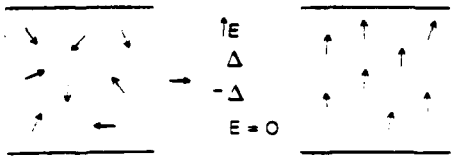



$\mu\beta = 6.9 \times 10^{-29}$ esu

## SHG STUDIES OF POLED POLYMERS

PRINCIPLE OF POLING GUEST/HOST SYSTEMS

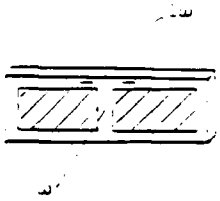



*INVESTIGATE:*

- Extent of ordering
- In-situ $\beta$
- Poling dynamics

## CONDITIONS FOR POLING

### 3-CHLORO-4-NITROANILINE IN PMMA



- 0.7 M in PMMA (10% by wt)
- $E = 6 \times 10^4$ V/cm
- $T = 110^\circ$ C

## RESULTS OF POLING EXPERIMENTS

- CALCULATED $\beta$ AGREES WITH MEASURED
- OBSERVED DECREASE OF $\chi^{(2)}$ WITH TIME

| CONDITIONS | $\chi^{(2)}$ (esu) |
|---|---|
| E, 110° C | $1 \times 10^{-10}$ |
| E, RT | $1 \times 10^{-10}$ |
| E = 0 (30 sec), RT | $0.5 \times 10^{-10}$ |
| E = 0 (65 hr), RT | $0.39 \times 10^{-10}$ |

*POLED POLYMER SYSTEMS FOR ELECTRO-OPTIC EFFECT*

| GUEST | $\mu \cdot \beta$ (x $10^{-28}$ D-esu) at 1.58 microns | A/molar 810 nm | 1000 nm | 1300 nm | 1500 nm |
|---|---|---|---|---|---|
| 3MX-40 | 37 | 84 | 51 | 30 | 27 |
| 3MX-3 | 19 | 1.5 | 0.13 | 0.09 | 0.1 |
| 3MX-36 | 18 | 0.6 | 0.3 | 0.3 | 0.3 |
| 3MX-2 | 15 | 0.5 | 0.6 | 0.6 | 0.6 |
| 3MX-1 | 11 | 0.07 | 0.06 | 0.05 | 0.07 |
| 3MX-8 | 10 | 0.03 | 0.04 | 0.04 | 0.04 |

K-1

G. R. Meredith
E. I. Dupont DeNemours and Co.

# OPTICAL NONLINEARITY: MOLECULES, ASSEMBLIES AND WAVE PHENOMENA

L-1

G. Khanarian
Hoechst-Celanese

# CHARACTERIZATION OF POLYMERIC NONLINEAR OPTICAL MATERIALS

Characterization of Nonlinear
Optical Organic Materials

G. Khananan
Hoechst Celanese Corporation
Summit, New Jersey 07901

ACS Workshop
Virginia Beach, May, 1988

T. CHE
R. DEMARTINO
D. HAAS
T. LESLIE
H. MAN
J. STAMATOFF
C. TENG
H. YOON

OUTLINE

- Molecular Miller's Rule
- Polymer Structure and
- Measurement of $\chi^{(2)}$ by Second Harmonic Generation
- Measurement of $\chi^{(2)}$ by the Pockels Effect
- Results for MNA/PMMA
- MNA/PMMA/Sol-Gel Glasses - Role of Molecul Motion
- Langmuir Blodgett Films - Role of Internal Optical Field
- Application to Devices

## Schematic

| | | |
|---|---|---|
| **Materials Development** | Design of organic molecules | (Intuition, computer modeling and quantum mechanics) |
| | ↓ Synthesis | |
| | ↓ Characterization | (Optical, electro-optical...) (Solvato-chromism) (Structure/property algorithm) |
| | ↓ Formulation of polymeric systems | (Guest-host, single component LCs) (Tractability, amphiphilicity) |
| | ↓ Fabrication | (Thin films, 3D articles) |
| | ↓ Fabrication to critical standards | (Dimensions & relation to activity, shape, size...) |
| **Device Design and Evaluation** | ↓ Conversion to device format | |
| | ↓ Evaluation of device | |

# L-3

## BASIC PHYSICS

MOLECULAR

$$p = \mu_0 + \alpha E + \beta E^2 + \gamma E^3$$

MATERIAL

$$P = \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3$$

$$\frac{d^2 r}{dt^2} + 2\gamma \frac{dr}{dt} + \omega_0^2 r - \xi r^2 = -\frac{e}{m} E$$

$$\chi^{(1)}(\omega_n) = \frac{Ne^2}{m} \frac{1}{\omega_0^2 - 2i\gamma\omega_n - \omega_n^2}$$

$$\chi^{(3)}(\omega_n, \omega_m) = -\frac{m\xi}{N^2 e^3} [\chi^{(1)}(\omega_n)][\chi^{(1)}(\omega_m)][\chi^{(1)}(\omega_n + \omega_m)]$$

## ANHARMONIC OSCILLATOR MODEL

$$\beta_{xxx} = \frac{-m\xi}{Ne^3} \alpha_{xx}^2$$

m mass of electron

e charge of electron

N oscillator strength

$\xi$ anharmonic constant

$$= \frac{\omega^2}{L}$$

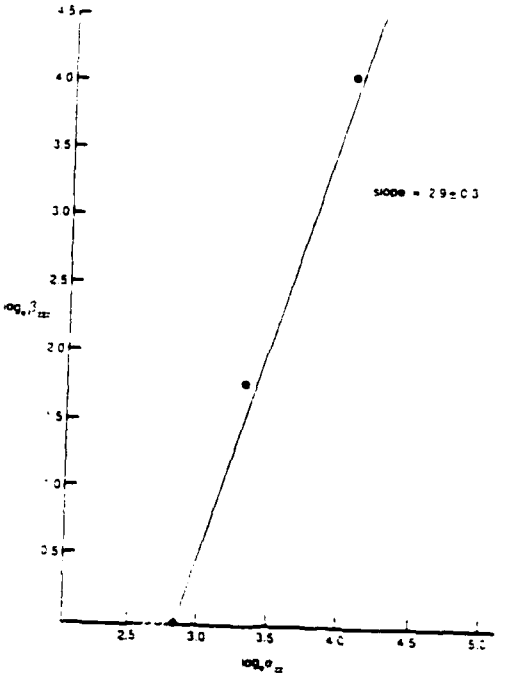
$\omega$ angular frequency

L length of molecule

| | Exp. ($10^{30}$ esu) | Theory ($10^{30}$ esu) |
|---|---|---|
| $\frac{m\xi}{Ne^3}$ | 1 | 3.0 |

$\log_e \beta_{zzz}$ versus $\log_e \alpha_{zz}$

Verification of molecular Miller's Rule



# L-4

$$\eta^K = \frac{[illegible]}{[illegible]}$$

- [illegible] - molecular weight
- [illegible] - refractive index
- [illegible] - wavelength of light
- [illegible] - dielectric constant
- [illegible] - density
- [illegible] - Kerr constant
- $\eta^K$ - molar Kerr constant

$$\eta^K = \frac{[illegible]}{310} \left[ \frac{[illegible]}{[illegible]} + \frac{3\,\mathrm{tr}([illegible])}{kT} + \frac{[illegible]}{3kT} + 10\nu \right]$$

$$\hat{\alpha}_{zz} = \alpha_{zz} - \bar{\alpha}$$

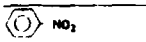
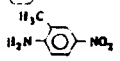
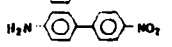
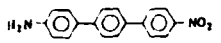
$$\mathrm{tr}([illegible]) = \hat{\alpha}_{zz}\hat{\alpha}_{zz} + \hat{\alpha}_{xx}\hat{\alpha}_{xx} + \hat{\alpha}_{yy}\hat{\alpha}_{yy}$$

$$\beta_z = \beta_{zzz} + \beta_{zxx} + \beta_{zyy} \quad \text{(1st hyperpolarizability)}$$

- $\nu$ = mean 2nd hyperpolarizability
- $N_0$ = Avogadro's number
- $k$ = Boltzmann's constant
- $T$ = temperature
- $\bar{\alpha}$ = mean polarizability
- $\mu_z$ = dipole moment

TABLE I

Molar Kerr constants $_mK$ ( x $10^{-9}$ esu), linear polarizability $\alpha_{zz}$ ( x $10^{-24}$ esu) and $\beta_{zzz}$ ( x $10^{-30}$ esu)

| Compound | $_mK$ | $\alpha_{zz}$ | $\beta_{zzz}$ |
|---|---|---|---|
|  | 0.985 | 13.2 | 1.0 |
|  | 6.850 | 18.7 | 5.7 |
|  | 14.5 | 29.5 | 20 |
|  | 16.9 | 39.6 | 51 |

$_mK$ values are at 0.633 μm. $\alpha_{zz}$ has been deduced from equation 3, and literature values for the dipole moment $\mu_z$ and the average polarizability. $\alpha_{zz}$ values reported above are at 1.9 μm. A dispersion formula has been used to go from 0.633 to 1.91 μm. $\beta_{zzz}$ are also at 1.91 μm.

## Types of Molecular Packing

| Packing | Type | Order | Magnitude |
|---|---|---|---|
| | Non-centric | Second | Moderate |
| | Non-centric | Second | Strong |
| | Centric | Third | Strong |
| | Centric | Third | Weak |

$\xrightarrow{-\quad +}$ Direction of dipole moment

$\chi^{(3)}$ OF POLED FLEXIBLE DIPOLAR POLYMERS

- Theory same as for efish
- Exact calculations can be done for single chains - Flory Theory

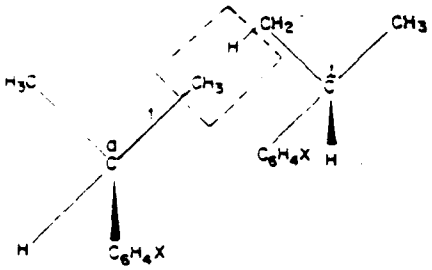



FIG. 2. Designation of bonds of PPNS, $X = NO_2$.

TABLE II. $(\mu \cdot \beta)/x$ ($\times 10^{-48}$ cm$^4$) and $\langle \mu^2 \rangle / x$ ($\times 10^{-36}$ SC$^2$ cm$^2$) of poly(p-nitrostyrene) vs tacticity $p_r$, $T = 298$ K, $x = 200$ repeat units.

| $P_r$ | $\frac{(\mu \cdot \beta)}{x}$ | $\langle \mu^2 \rangle / x$ |
|---|---|---|
| 0.0 (isotactic) | 21.5 | 10.7 |
| 0.2 | 16.6 | 8.27 |
| 0.4 | 16.3 | 8.12 |
| 0.6 | 16.8 | 8.36 |
| 0.8 | 16.4 | 8.17 |
| 1.0 (syndiotactic) | 12.5 | 6.23 |

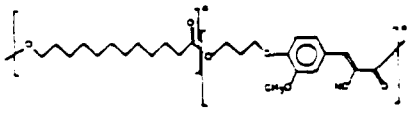


Table 2: Average Monomer Susceptibilities for Various Molecular Weight Copolymers.

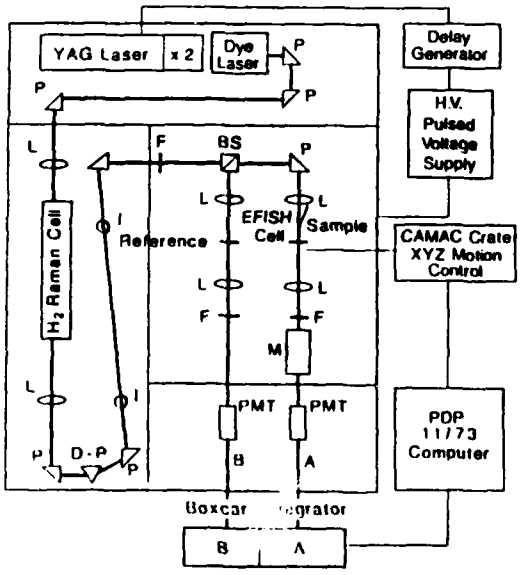
| Molecular Weight,[a] $\overline{M}_n$ | Calculated Number of Monomer Units, n | $M_z B_z / n$ ($10^{-48}$ esu) | Enhancement Factor, G |
|---|---|---|---|
| NLO chromophore[b] | — | 57 | — |
| 17,000 | 37 | 830 | 15 |
| 70,000 | 152 | 1140 | 20 |

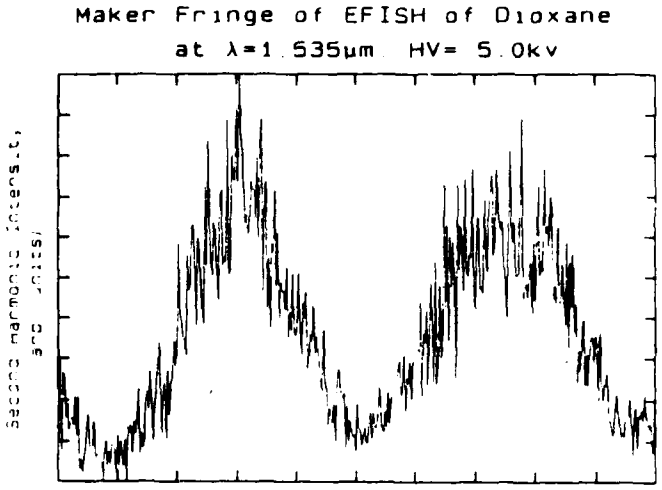
[a] Determined by GPC relative to polystyrene.

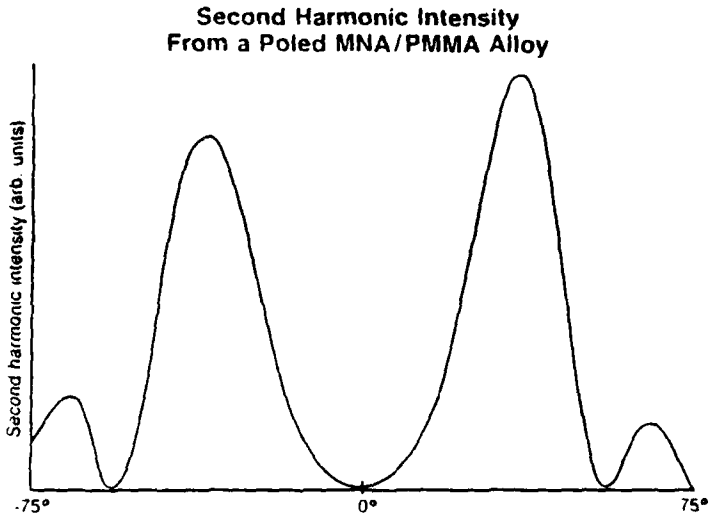
[b] Structure II from Table 1.

C. S. Willand, S. E. Feth, M. Scozzafava, and D. J. Williams
Corporate Research Laboratories, Eastman Kodak Company, Rochester, N. Y.

G. D. Green,* J. I. Weinschenk, III, H. K. Hall, Jr., and J. E. Mulvaney
C. S. Marvel Laboratories, Department of Chemistry, University of Arizona, Tucson, Az.






SECOND HARMONIC GENERATION FROM POLED POLYMERS

The second harmonic intensity is given by

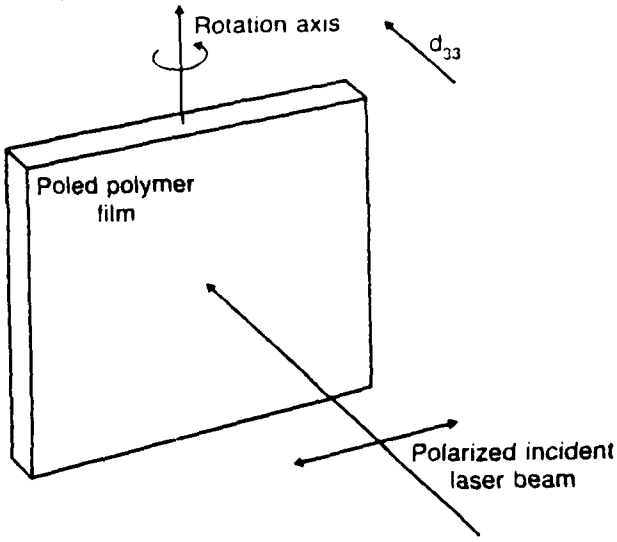
$$\frac{I(2\omega)}{I(\omega)} \sim t^4 T d_{ij}^2 p^2 l_c^2 \sin^2\left(\frac{\pi}{2}\frac{L}{l_c}\frac{n}{(n^2-\sin^2\theta)^{1/2}}\right)$$

| | |
|---|---|
| t, T | Fresnel transmission factors |
| d | Second harmonic coefficient |
| p | Projection factor of d tensor onto optical electric field |
| $l_c$ | Coherence length |
| n | Refractive index |
| L | Thickness of sample |
| θ | Angle of rotation |

$\chi^{(2)}(-2\omega, \omega, \omega) = 2d$

When θ = 0 , p = 0 and there is no component of d along E, and there is no second harmonic observed

The Maker fringe arises from an interference between the fundamental beam and generated harmonic wave



## THEORY OF MEASUREMENT FOR POCKELS AND KERR EFFECT

The birefringence $\Delta n$ induced in a Kerr cell is:

$$\Delta n = \lambda B E^2$$

and in a Pockel cell:

$$\Delta n = 1/2\ m^3 E$$

The birefringence results in a retardation $\Gamma$

$$\Gamma = \frac{2\pi \Delta n l}{\lambda}$$

in the small angle approximation. Equation 4 becomes:

$$\frac{I}{I_0} = \frac{1}{2}[1 + \Gamma]$$

A sinusoidal voltage is applied across the electro-optic cell

$$V = V_0 \sin wt$$

Substituting Equation 7 into Equation 5

$$\frac{I}{I_0} = \frac{1}{2} + \frac{\Gamma_{Kerr}}{2} + \frac{\Gamma_{Pockel} \sin wt}{2} - \frac{\Gamma_{Kerr} \cos 2wt}{2}$$

## POCKELS EFFECT

The optical retardation is

$$\Gamma = \frac{2\pi}{\lambda} l \Delta n$$

| | |
|---|---|
| $l$ | Optical path length |
| $\Delta n$ | Induced birefringence |
| $\lambda$ | Wavelength of light |

The induced birefringence

$$\Delta n = \frac{1}{2}(n_3^3 r_{33} - n_1^3 r_{31}) E$$

| | |
|---|---|
| $r$ | Pockels constant |
| $n$ | Refractive index |
| $E$ | Applied electric field |

For poled materials

$$r_{31} \cong \frac{r_{33}}{3}$$

This result is obtained from a thermodynamic model for poling

- Boltzmann statistics

The apparent angular dependence of the Pockels effect arises from change of optical path length

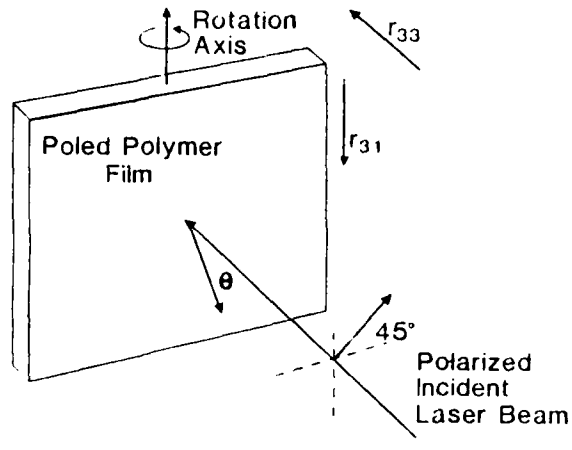
$$\frac{d}{\cos\theta}$$

where d is the thickness of the sample

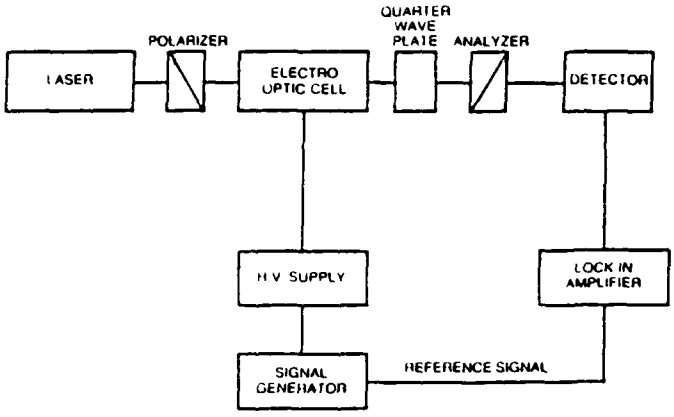
The analyzing light beam sees a different birefringence as a function of angle

$$\Delta n(\theta) = \Delta n(\theta = 90°) \sin^2\theta$$

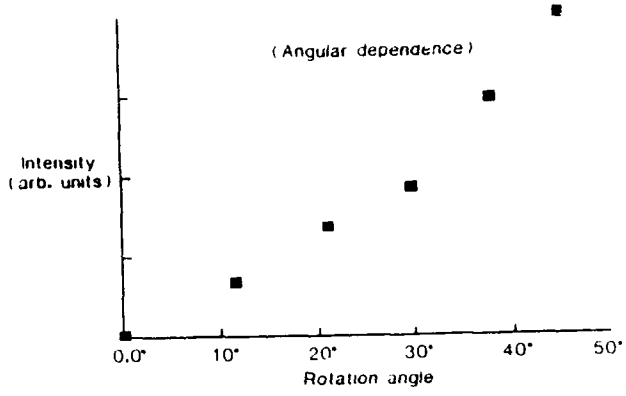
$\theta$ is the angle between the normal axis of sample and the light beam



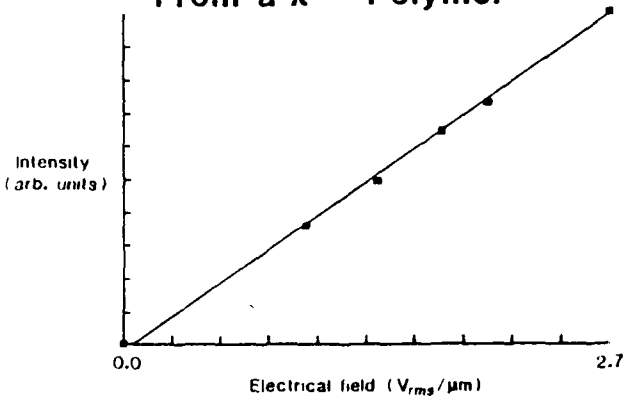
## SCHEMATIC OF ELECTROOPTIC APPARATUS



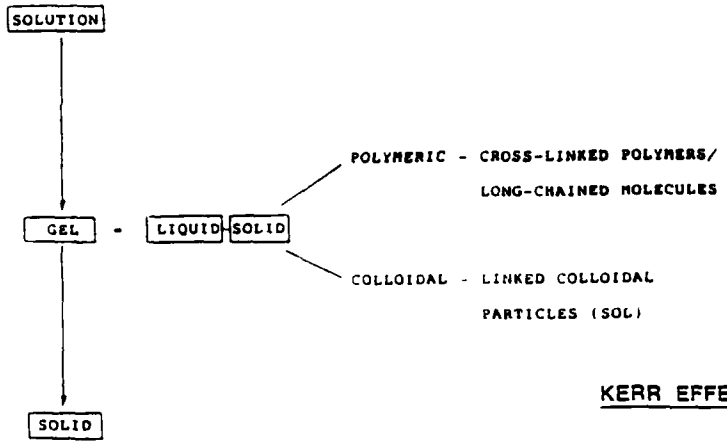

## Pockels Effect from Poled MNA / PMMA Sample




## Pockels Linear Electro-optic Effect From a $X^{(2)}$ Polymer



SOL-GEL TECHNOLOGY



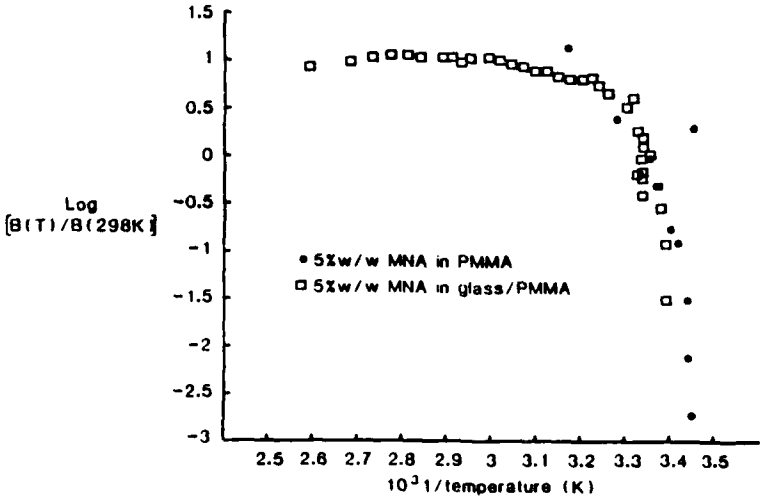

## KERR EFFECT OF SOL-GEL GLASS

MNA added to sol-gel glass

PMMA is added to sol gel glass to give mechanical strength

Slab was cut and polished for electro-optic measurement

**Arrhenius Plot of Kerr Constant for MNA Optical Composites**



## THERMODYNAMIC MODEL

Assume that nonlinear optical molecules are distributed orientationally according to Boltzmann statistics.

$$\chi^{(3)}(-2\omega,\omega,\omega) = Nf^4\beta \frac{\epsilon(n^2+2)}{n^2+2\epsilon}\frac{\mu E}{5kT}$$

| | |
|---|---|
| N | number density |
| f | internal field |
| $\beta$ | hyperpolarizability |
| $\mu$ | dipole moment |
| E | poling field |
| k | Boltzmann constant |
| T | temperature |
| $\epsilon$ | dielectric constant |
| n | refractive index |

## RESULTS

| Sample | $\chi^{(3)}(-2\omega,\omega,\omega)$ | $\chi^{(3)}(-\omega,\omega,0)$ | $\chi^{(3)}$(calc) |
|---|---|---|---|
| 10% MNA/PMMA | 1.6 | 1.5 | 0.6 |

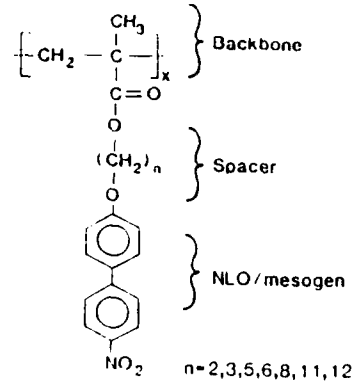
All $\chi^{(3)}$ values are $\times 10^{-9}$ esu and are at 1.06 $\mu$m

$\chi^{(3)}(-2\omega,\omega,\omega)$ measured at 1.06 $\mu$m

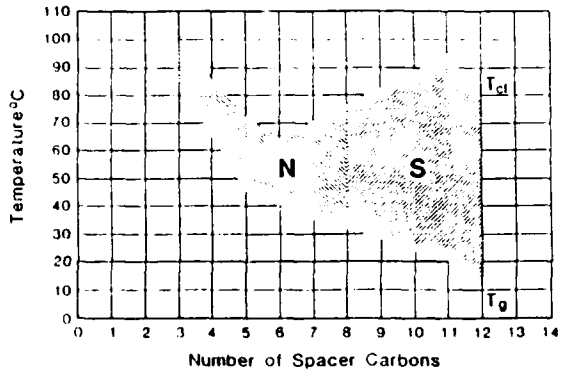
$\chi^{(3)}(-\omega,\omega,0)$ measured at 0.63 $\mu$m and a dispersion relation was used to obtain values at 1.06 $\mu$m

$\chi^{(3)}$(calc) used the thermodynamic model

### NLO Side Chain Polymers First Generation




### Dependence of Glass and Clearing Temperatures on Carbon Spacer Length



# NLO Polymer Properties

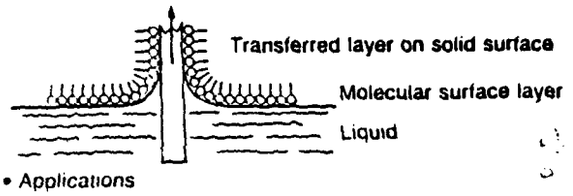
| | |
|---|---|
| $\chi^{(2)}$ at 1.3 μm | > 50 pm/V |
| r (calculated) | > 14 pm/V |
| n (1.3 μm) | 1.57 |
| ε (DC) | 3.5 |
| ε ($n^2$) | 2.6 |
| waveguide loss at 1.3 μm | 0.9 dB/cm |

Spin coatable from common solvents

Poled for application
Stable (< 10% loss) at > 50°C for 5 years

## Langmuir-Blodgett Film (LBF) Formation

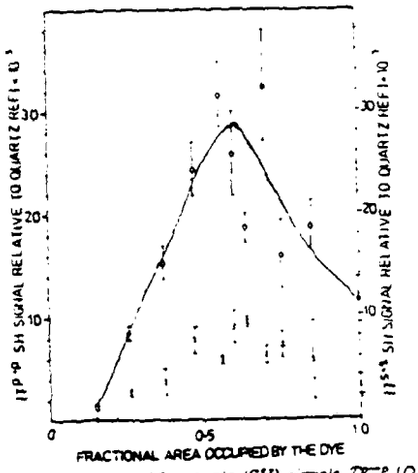
- Is the deposition on a surface of a single molecular layer at a highly ordered state
- Sequential deposition leads to periodically structured films
- It is done by transfer of a compressed molecular surface layer on a liquid onto a solid surface by dipping




- Applications
  - — Nonlinear optics: Bistable switches
    Thin film SH and TH generation
  - — Electro-optics: Thin film light modulator
  - — Integrated optics: Planar dielectric wave guides

LANGMUIR BLODGETT FILMS

- 2D Material
- Orientation of Molecules by Surface
- Useful for Fundamental Studies of:
  - Interaction of radiation with molecules (spectroscopy)
  - Tilt angles
  - Hyperpolarizability
  - Molecule/surface interactions
  - Interaction between layers
  - Local optical electric field effects




g. 5. Plot of the second-harmonic (SH) signals $T^{p-p}$ (O) and $T^{s-s}$ (X) relative to the quartz reference slab versus the area fraction cupied by the dye in the mixed monolayer.

I.R. GIRLING ET AL JOSA B, 1987, VOL. 4, P. 950

Local Optical Electric Field

$$p_z = \mu_z + (\alpha_{zz}) F_z + (\beta_{zzz}) F_z^2 + (\gamma_{zzzz}) F_z^3$$

$$F_z = E_z + \sum_i T_{zz}^{(i)} p_z$$

$$T_{zz}^{(i)} = \frac{-1}{r_{(i)}^3}$$

$\mu$, $\alpha$, $\beta$ and $\gamma$ are the dipole moments and polarizabilities

Z axis is normal to glass surface

Linear Mean Field Approximation

* Neglect fluctuation in dipole moment
* Assume that linear polarizability alone changes local dynamic optical field.

$$\sum_i T^{(i)} = \rho \int_0^a \frac{2\pi r dr}{r^3}$$

$$= \frac{2\pi\rho}{a}$$

$\rho$ = surface density of dipoles

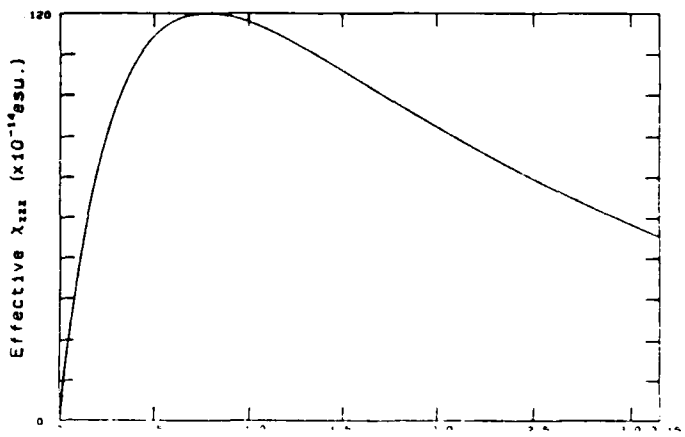
a = radius of nonlinear optical molecule

Results for the nonlinear susceptibility

$$\chi_{zzz} = \frac{3a}{2\pi\alpha_{zz}} \frac{x}{(1+x)^2} - \frac{3\gamma\mu a}{2\pi\alpha_{zz}^2} \frac{x^2}{(1+x)^2}$$

$$x = \frac{2\pi\alpha_{zz}\rho}{a}$$

Variation of effective $\chi_{zzz}$ of a Langmuir Blodgett Film versus normalized concentration of active nonlinear optical molecule

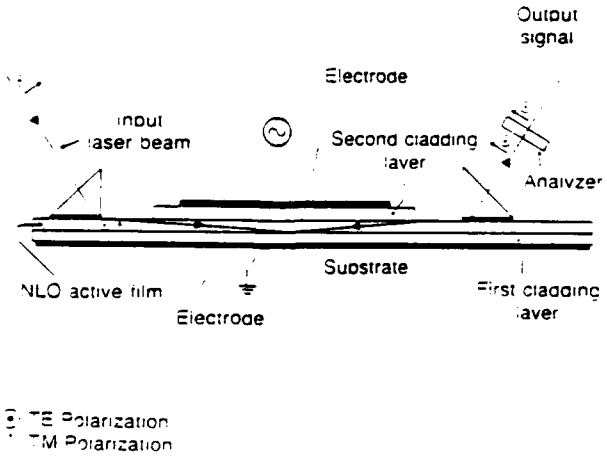


## CLASSES OF ORGANIC NLO DEVICES

- Electro-Optic Devices
  - Control of light with electronics
  - Based on the second order NLO susceptibility $\chi^{(2)}$
  - Applications: Hybrid optical processing and optical communications
- All Optical Devices
  - Control of light with light
  - Based on the third order NLO susceptibility $\chi^{(3)}$
  - Applications: All optical computing and ultra-fast optical communications

## POLYMER GUIDE FABRICATION PROCESS COMPONENTS

- Spin Coating (thin film formation)
- Buffer Layer and Substrate Materials
- Patterning
- Metallizing
- Beam Coupling



## MODULATOR RESULTS

| MATERIAL | LENGTH (CM.) | $V_\pi$ (V) | $\lambda$ (nm) | $F_{MAX}$ (MHz) | $r_{33}$ (pm/V) |
|---|---|---|---|---|---|
| PMMA: pNA | 1.0 | 450 | 633 | 30 | .5 |
| HCC #0520 | 1.0 | 45 | 633 | 0.5 | 3.5 |
| HCC #1622 | 2.0 | 30 | 830 | 10* | 3.75 |
| HCC #1238 | 1.5 | 4.0 | 830 | 1 | 20 |

$$r_{33} = \frac{3 \lambda G}{2n^3 L V_\pi \Gamma}$$

$\Gamma \approx .85$ to $.95$ for these structures

## OTHER MATERIAL PROPERTIES

> N FROM 1.51 TO 1.66

> ε (100 KHZ) ≈ 3.8

### SUMMARY

- Organic NLO research at HCC has developed outstanding NLO and EO polymers
- These materials, additionally, exhibit combination of excellent performance characteristics and fabrication properties for NLO and EO devices
- Initiative to develop a series of important NLO devices has been undertaken at HCC
- Fabrication science and technology for the materials is a key component of the initiative

M-1

T. Richardson

University of Oxford, U. K.

# PREPARATION AND CHARACTERIZATION OF ORGANO-TRANSITION METAL LANGMUIR-BLODGETT FILMS

# M-2

## THE PREPARATION AND CHARACTERISATION OF ORGANO-TRANSITION METAL LANGMUIR-BLODGETT FILMS

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A SERIES OF NOVEL RUTHENIUM COMPOUNDS HAVE BEEN DEVELOPED FOR USE WITH THE LANGMUIR-BLODGETT DEPOSITION TECHNIQUE. COMPLEXING OF A η- RUTHENIUM (CYCLOPENTADIENYL-BIS TRIPHENYLPHOSPHINE)) HEAD GROUP TO A CYANOTERPHENYL LIQUID CRYSTAL MOLECULE HAS BEEN SHOWN TO INCREASE THE SECOND-ORDER NON-LINEAR OPTICAL HYPERPOLARIZABILITY AND FURTHERMORE INDUCE MULTILAYER FORMATION. OPTICAL ABSORPTION DATA HAVE REVEALED THE EXCELLENT REPRODUCIBILITY OF SUCCESSIVE MONOLAYER TRANSFER. SECOND HARMONIC GENERATION HAS BEEN OBSERVED AND THE EFFECT HAS BEEN INCREASED BY INCORPORATING UNSUBSTITUTED LIQUID CRYSTAL MOLECULES INTO THE VOIDS BETWEEN THE TERPHENYL CHAINS OF ADJACENT RUTHENIUM SUBSTITUTED MOLECULES. WE HAVE FURTHER OPTIMISED THE NON-LINEAR RESPONSE BY SYSTEMATICALLY VARYING THE ELECTRON-RELEASING CHEMICAL GROUP AND THE CONJUGATION WITHIN THE MOLECULE.

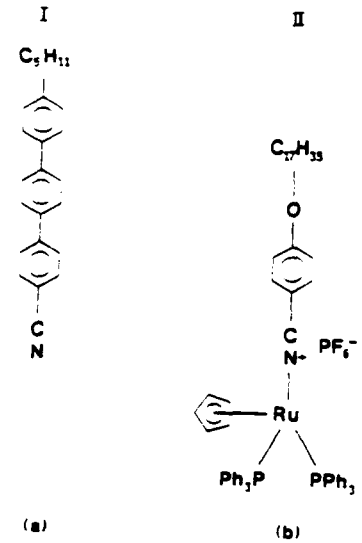



FIGURE 1

(A) A TYPICAL CYANO-TERPHENYL MOLECULE (I).

(B) THE $[(C_5H_5)\ Ru\ (PPh_3)_2]$ SUBSTITUTED MOLECULE POSSESSES A LARGER SECOND-ORDER NON-LINEAR OPTICAL HYPERPOLARIZABILITY THAN COMPOUND I.

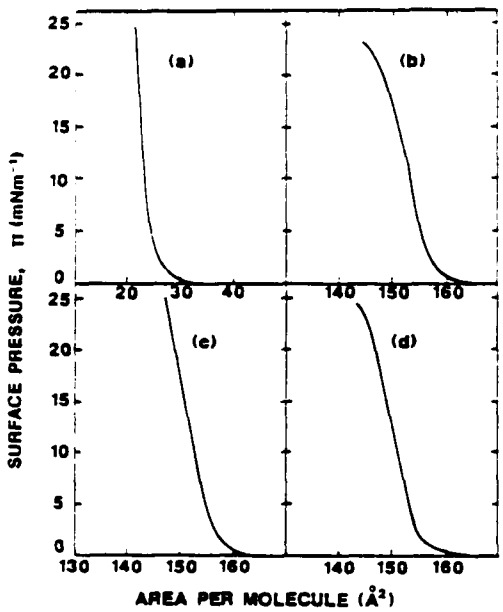



FIGURE 2

THE BEHAVIOUR OFMOLECULES OF COMPLEX I AND II UNDERGOING COMPRESSION ON THE WATER SURFACE. (A) COMPLEX I AT PH 5.8, (B, C AND D) COMPLEX II AT PH 3.8, 5.8 AND 8.7 RESPECTIVELY. THE MOLECULAR AREAS AT RELATIVELY HIGH SURFACE PRESSURE (20 MNM⁻¹) CORRESPOND ACCURATELY TO THE MEASURED CROSS-SECTIONAL AREA OF THE RUTHENIUM HEAD GROUP.

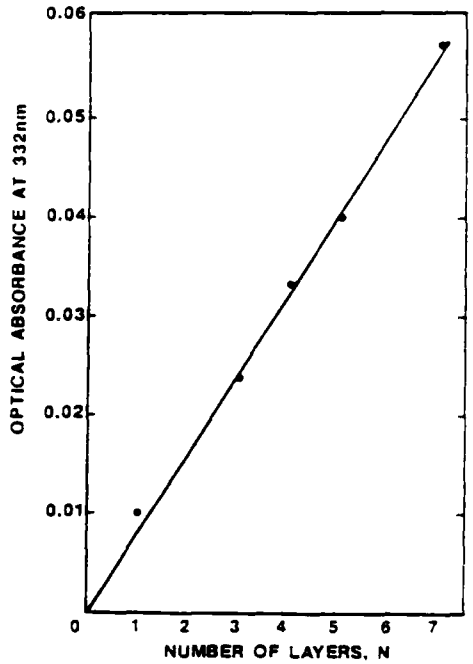



FIGURE 3

OPTICAL ABSORPTION VERSUS THE NUMBER OF TRANSFERRED MONOLAYERS. THE LINEAR RELATIONSHIP INDICATES THE REPRODUCIBILITY OF SUCCESSIVE MONOLAYER DEPOSITION.

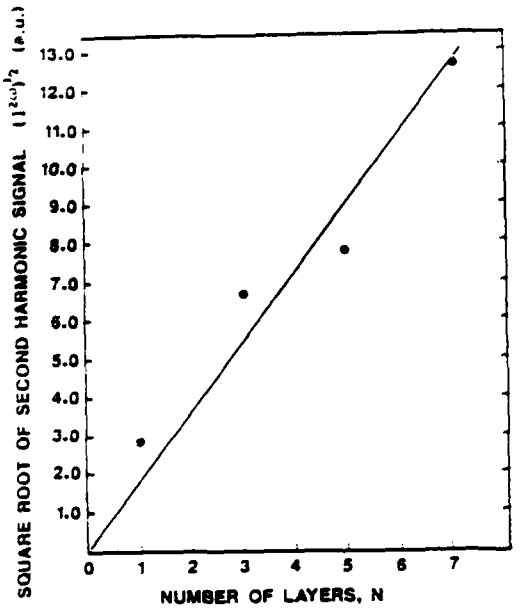
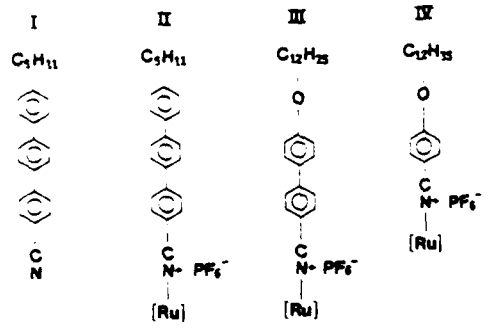



FIGURE 4

THE RELATIONSHIP BETWEEN THE SQUARE ROOT OF THE SECOND HARMONIC GENERATION SIGNAL AND STRENGTH THE THICKNESS OF THE FILM. THE APPROXIMATELY LINEAR RELATIONSHIP IMPLIES THE UNIDIRECTIONAL ALIGNMENT OF THE MOLECULES.




| COMPLEX | SHG SIGNAL NORMALIZED TO II |
|---|---|
| II | 1.0 |
| II/I | 1.5 |
| III | 11.0 |
| IV | 77.0 |

FIGURE 6

OPTIMISATION OF NON-LINEAR RESPONSE. THE SECOND HARMONIC SIGNAL IS HIGHLY DEPENDENT UPON THE ELECTRON DONOR AND THE DEGREE OF CONJUGATION.

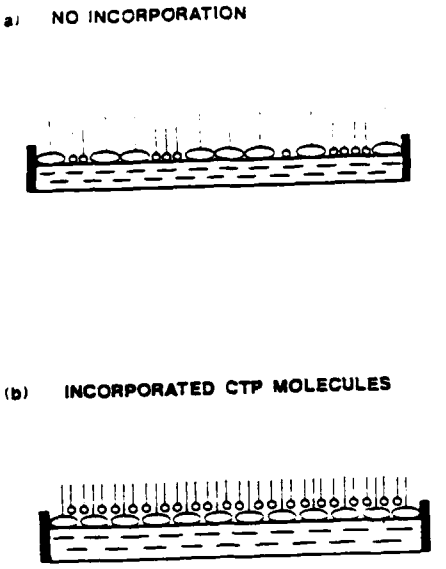



FIGURE 5

HIGH PACKING DENSITY STRUCTURES.

(A) THE LIQUID CRYSTAL MOLECULES MAY REMAIN ON THE WATER SURFACE.

OR

(B) THEY MAY BE INCORPORATED INTO THE MATRIX FORMED BY THE RUTHENIUM SUBSTITUTED MOLECULES.

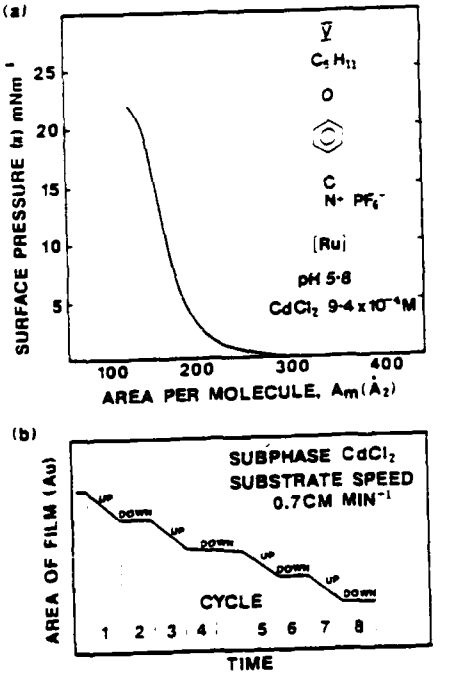



FIGURE 7

OPTIMISATION OF THE CARBON CHAIN LENGTH:-

(A) II VS. Am PLOT FOR COMPLEX V, SHOWN IN INSERT

(B) THE Z-TYPE DEPOSITION OF COMPLEX V. HIGHER RATES OF DEPOSITION ARE POSSIBLE WITH $CdCl_2$ IN THE SUBPHASE.

S. K. Tripathy
University of Lowell

# OPTICAL PROPERTIES OF ORGANIZED ASSEMBLIES

# OPTICAL PROPERTIES OF MOLECULAR ASSEMBLIES

SUKANT TRIPATHY
UNIVERSITY OF LOWELL
LOWELL, MA 01854

- Selected conjugated molecular and Macromolecular systems
- Organized mono and multilayer assemblies
- Characterization of microstructure and morphology
- Measurement and anticipation of electronic and optical properties

## Selection of materials

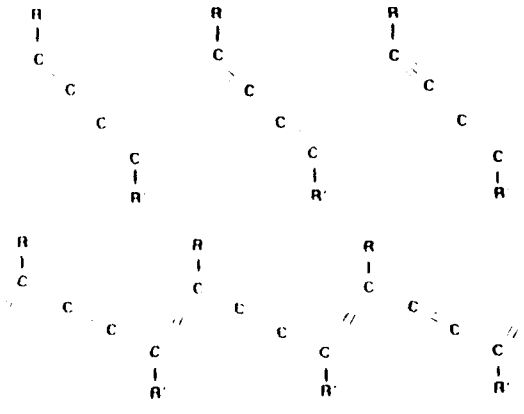
1. Linked donor-acceptor molecules.

   anticipated large 2nd order effects.
   example MNA

2. Polymers with delocalized backbone electronic structure.

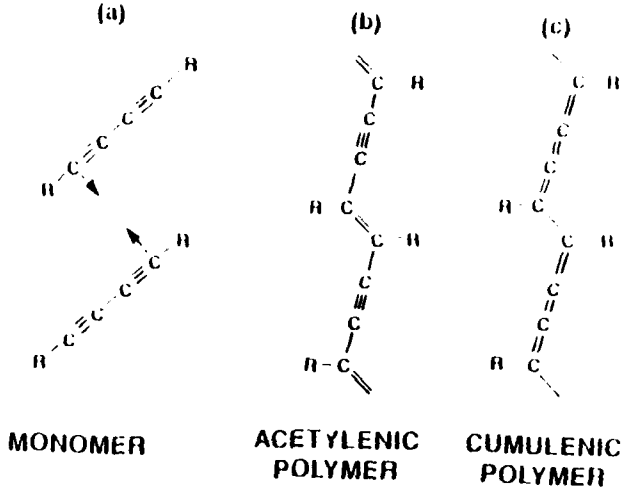
   anticipated large 3rd order susceptibilities.
   example Polydiacetylenes

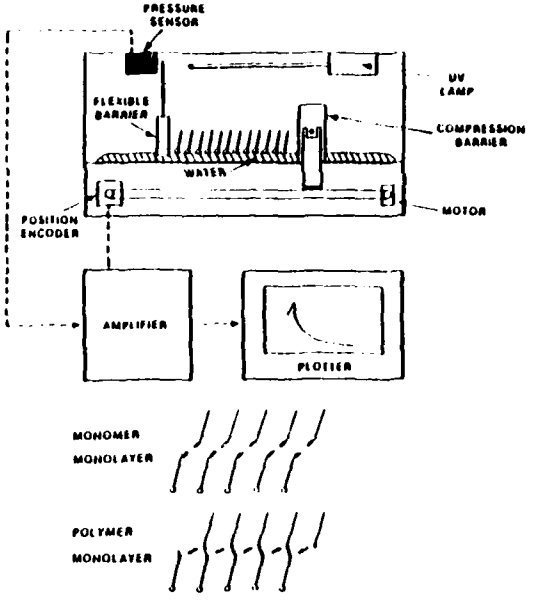
POLYDIACETYLENES

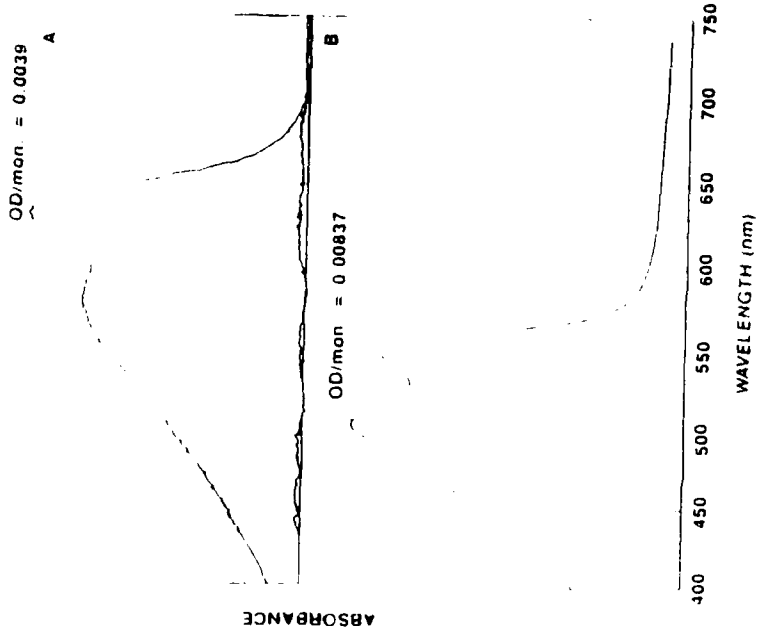


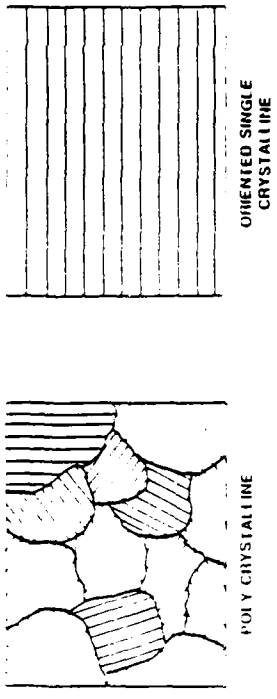
- Backbone Responsible for the Optical and the Nonlinear Optical Properties
- The Side Groups Provide a Handle for Fabrication and Structure Control

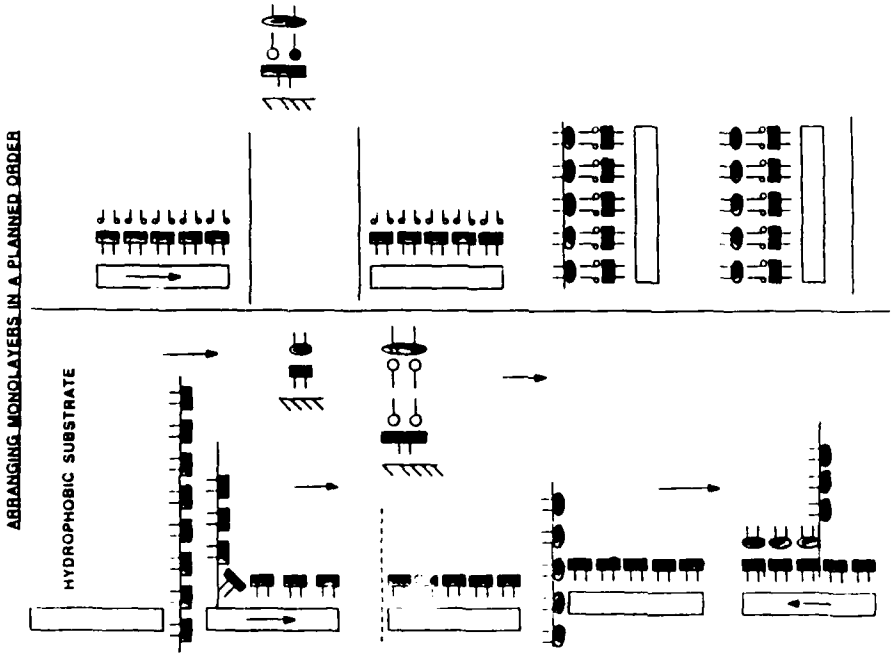
N-2

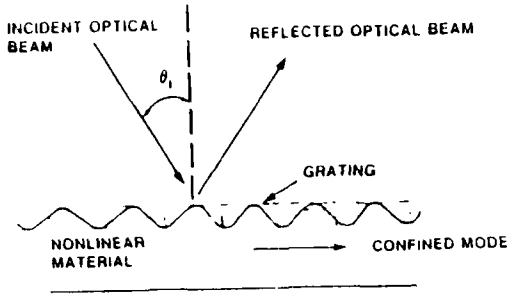

(a)
(b)
(c)
MONOMER
ACETYLENIC POLYMER
CUMULENIC POLYMER

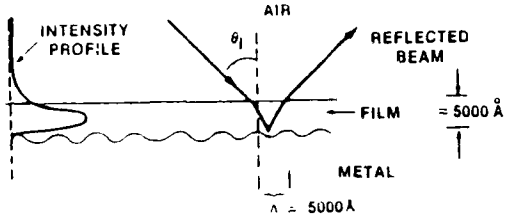

PRESSURE SENSOR
UV LAMP
FLEXIBLE BARRIER
COMPRESSION BARRIER
WATER
POSITION ENCODER
MOTOR
AMPLIFIER
PLOTTER
MONOMER MONOLAYER
POLYMER MONOLAYER

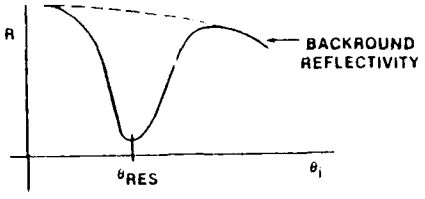

OD/mon = 0.0039
A
B
OD/mon = 0.00837
ABSORBANCE
400
450
500
550
600
650
700
750
WAVELENGTH (nm)


ORIENTED SINGLE CRYSTALLINE
POLY CRYSTALLINE


ARRANGING MONOLAYERS IN A PLANNED ORDER
HYDROPHOBIC SUBSTRATE

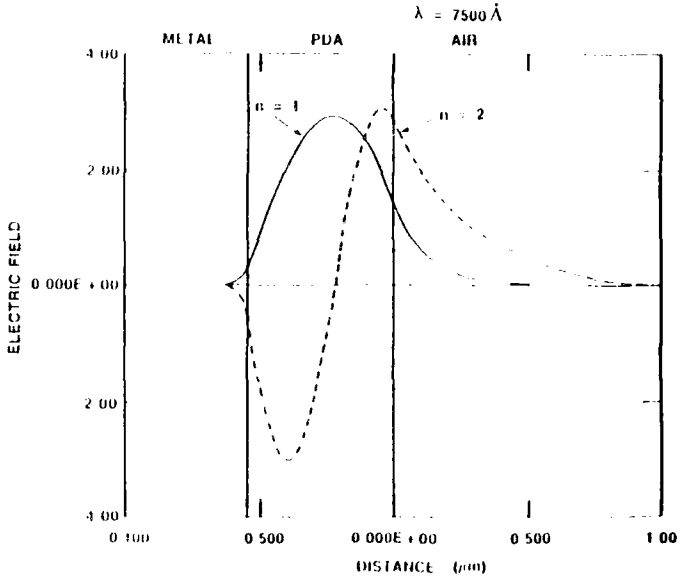


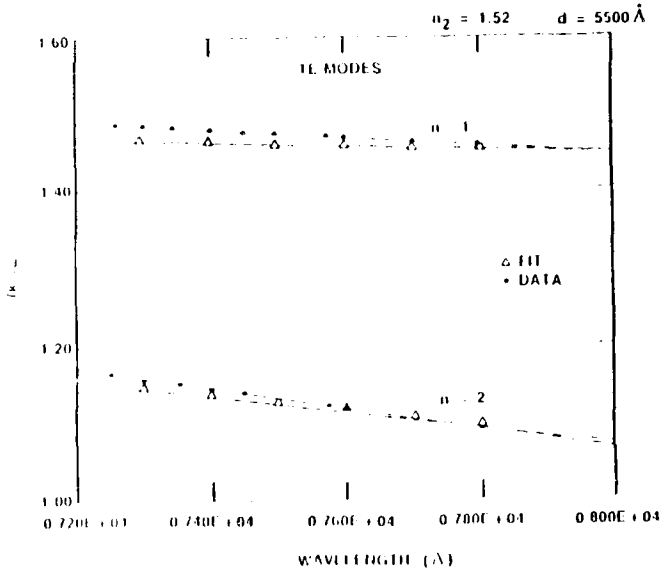



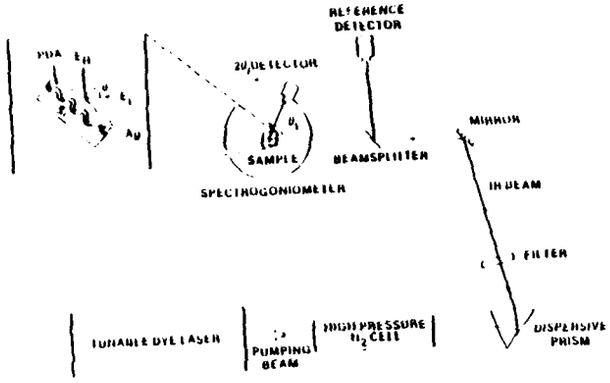



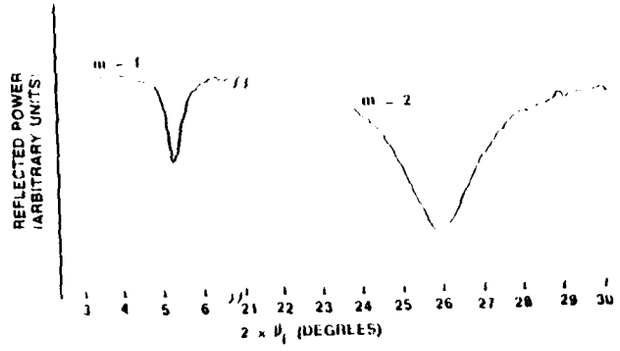

$n_g = \lambda_0/\Lambda \pm \sin(\theta_{RES})$

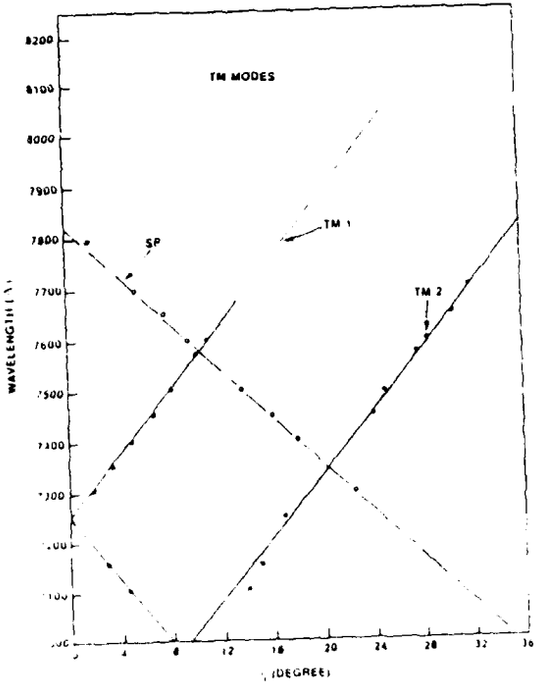
$(n_g = k_g/k_0)$

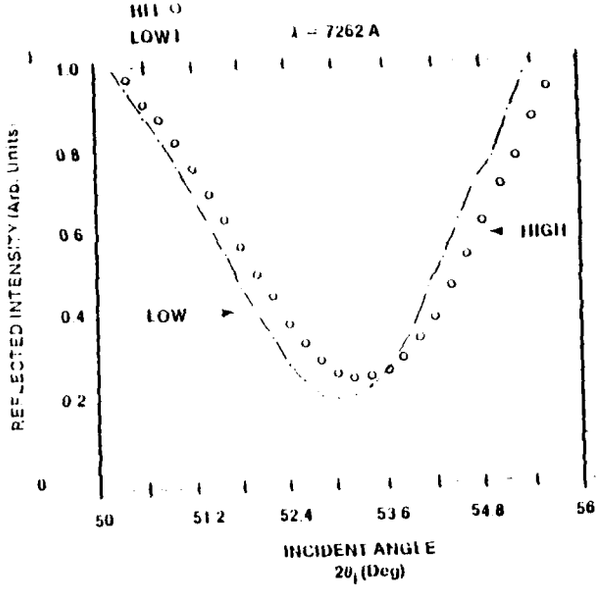


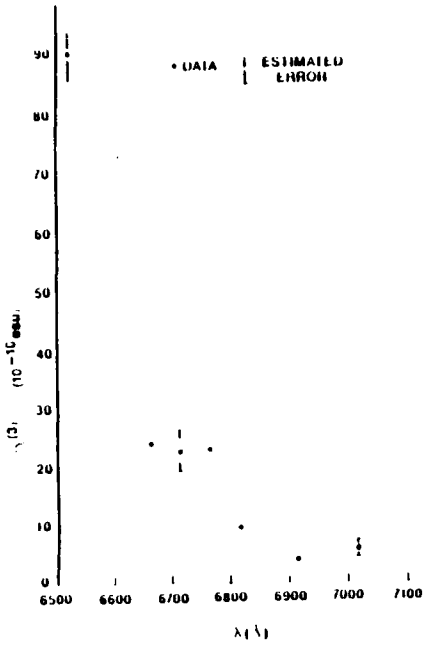



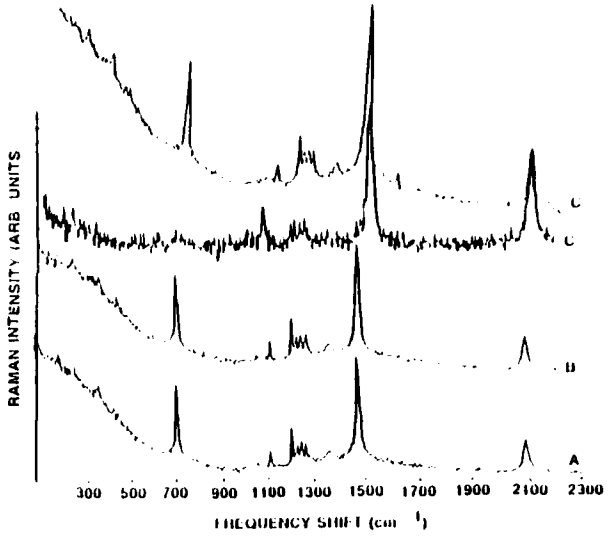

REFERENCE DETECTOR
2θ DETECTOR
SAMPLE
BEAMSPLITTER
SPECTROGONIOMETER
MIRROR
IR BEAM
FILTER
DISPERSIVE PRISM
TUNABLE DYE LASER
PUMPING BEAM
HIGH PRESSURE H2 CELL

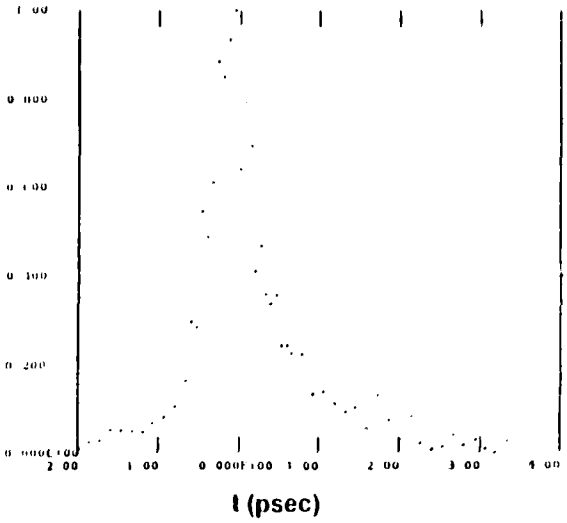

REFLECTED POWER (ARBITRARY UNITS)
m = 1
m = 2
3 4 5 6 21 22 23 24 25 26 27 28 29 30
2 × θi (DEGREES)

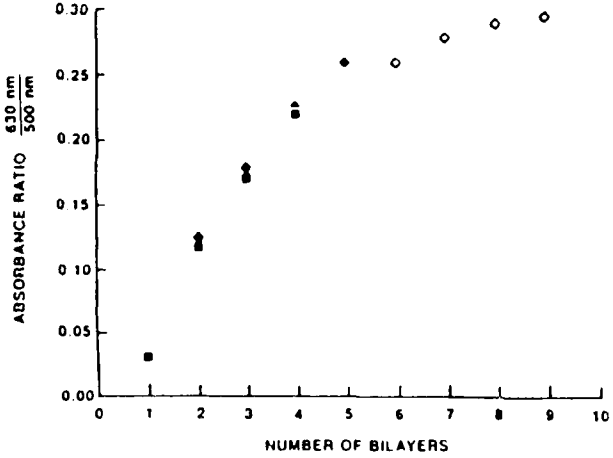

TM MODES
TM 1
TM 2
SP
WAVELENGTH (λ)
8200
8100
8000
7900
7800
7700
7600
7500
7400
4 8 12 16 20 24 28 32 36
(DEGREE)


HIT O
LOW I
λ = 7262 A
REFLECTED INTENSITY (Arb. Units)
1.0
0.8
0.6
0.4
0.2
0
HIGH
LOW
50 51.2 52.4 53.6 54.8 56
INCIDENT ANGLE
2θi (Deg)

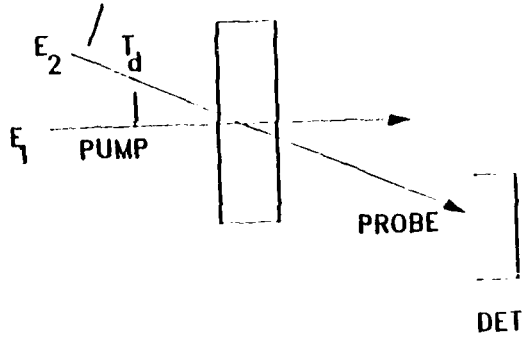

DATA
ESTIMATED ERROR
0
10
20
30
40
50
60
70
80
90
6500
6600
6700
6800
6900
7000
7100

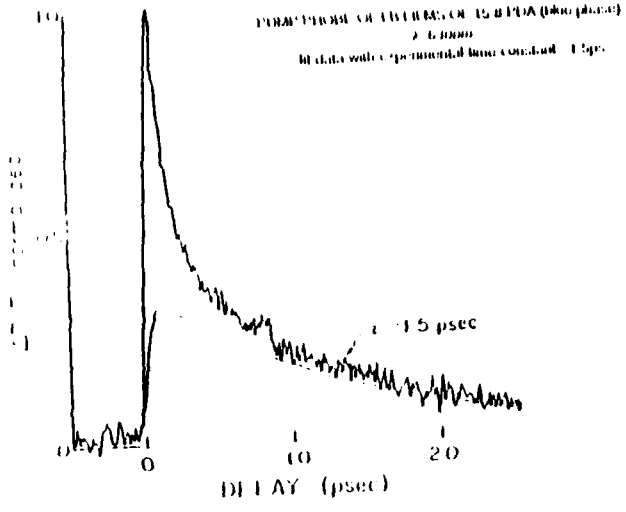

RAMAN INTENSITY (ARB UNITS)
C
C
B
A
300
500
700
900
1100
1300
1500
1700
1900
2100
2300
FREQUENCY SHIFT (cm⁻¹)


t (psec)

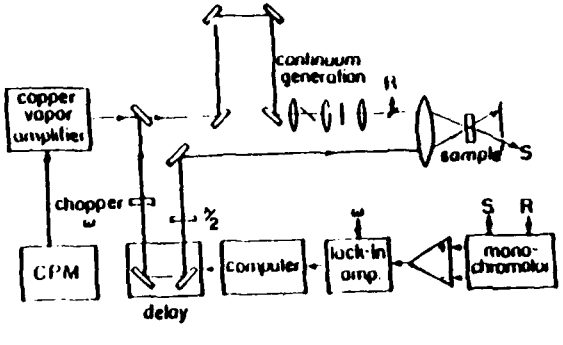

ABSORBANCE RATIO 630 nm / 500 nm
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0
1
2
3
4
5
6
7
8
9
10
NUMBER OF BILAYERS

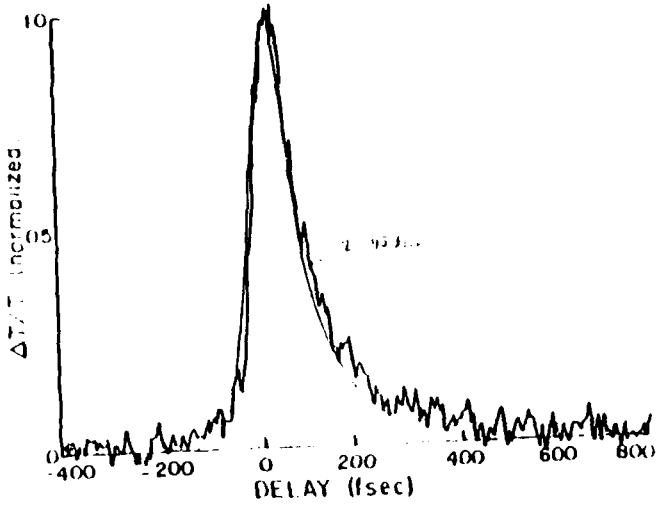
PUMP–PROBE: SATURATED ABSORPTION

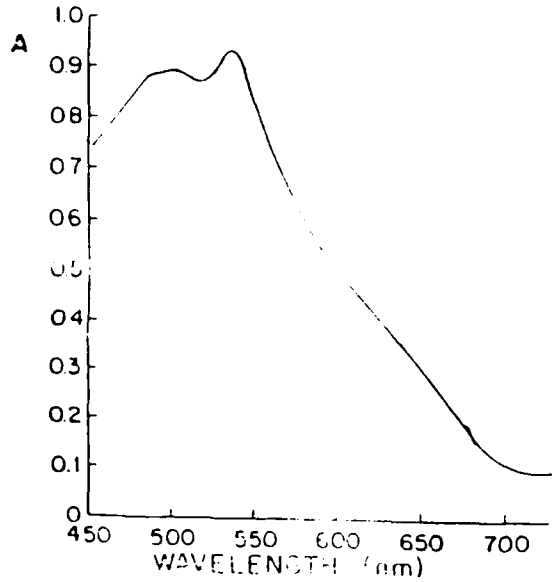



EXPERIMENTAL SCHEMATIC






LINEAR ABSORPTION SPECTRUM OF LASER-INDUCED RED PHASE LB FILMS OF PDA 15-8

SCF ab initio Hartree Rock

Semi empirical (EH)

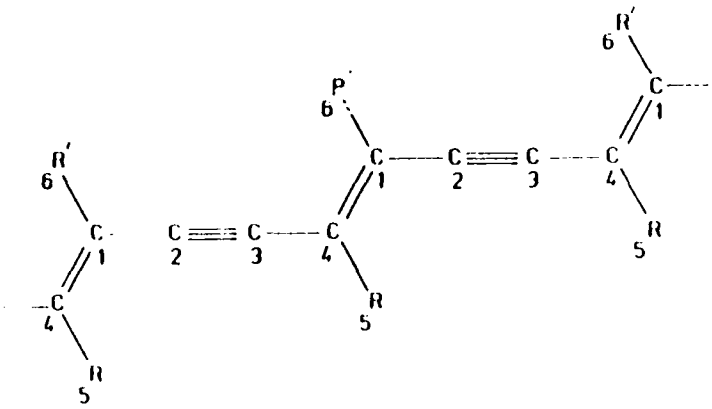
VEH gives ab initio quality results

σ and π bonds treated equally

MNDO - Excellent geometry all electrons.

| | $\Delta H_f$ | Etot |
|---|---|---|
| PDA | 498.6 | -106275.8 |
| PBT | | -106159.7 |

Δ/rep. = 14.5 Kcals/Mole



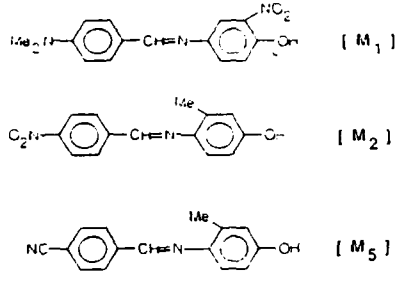

Structure of the polydiacetylene backbone. The numbers label the carbon atoms on the backbone and the single masses representing the sidegroups R and R' in the vibrational model

BANDGAP OF PDA AS A FUNCTION OF NONPLANARITY

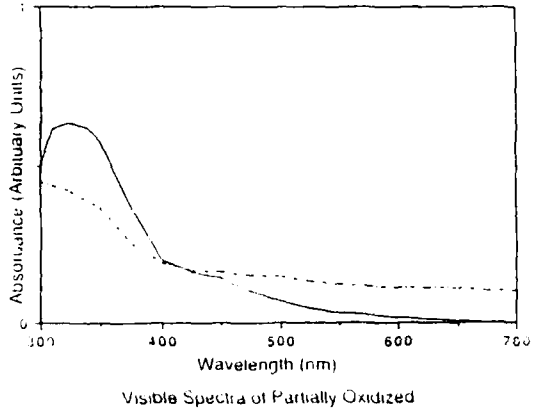
| | 0° | 5° | 10° | 15° | 20° |
|---|---|---|---|---|---|
| eV | 2.596 | 2.558 | 2.585 | 2.612 | 2.721 |
| $cm^{-1}$ | 20938 | 20631 | 20850 | 21070 | 21947 |
| nm | 478 | 485 | 480 | 475 | 458 |

**EFFECT OF SUBSTITUENTS ON PDA ELECTRONIC STRUCTURE**

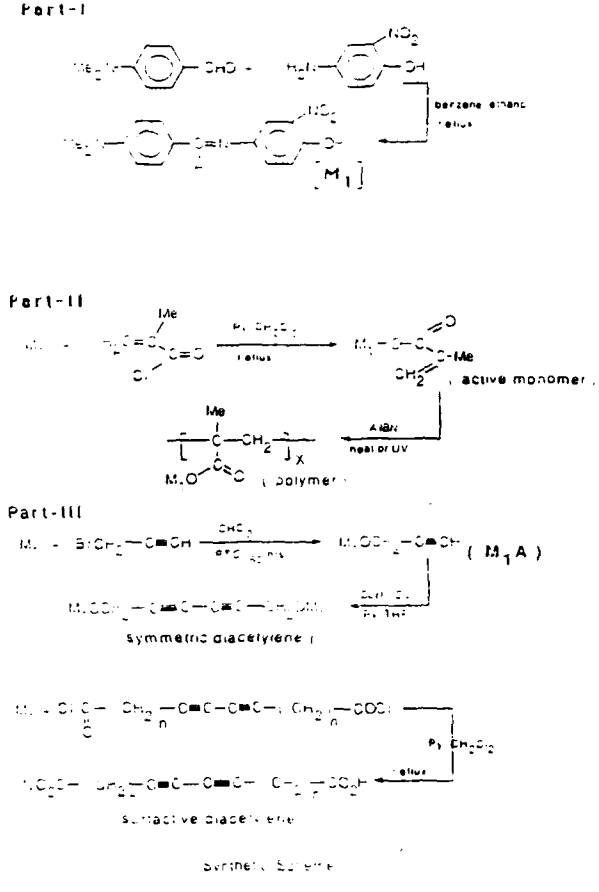
| | BW | $E_g$ | $E_{ip}$ |
|---|---|---|---|
| PDA | 3.972 (32043) | 2.596 (20938) | 5.338 (43056) |
| $r_2$- PDA | 1.115 (8998) | 1.769 (14266) | 4.903 (39544) |
| $(CH_3)_2$- PDA | 3.265 (26337) | 2.449 (19753) | 5.039 (40642) |




Molecular Structures of Some Representative Molecules

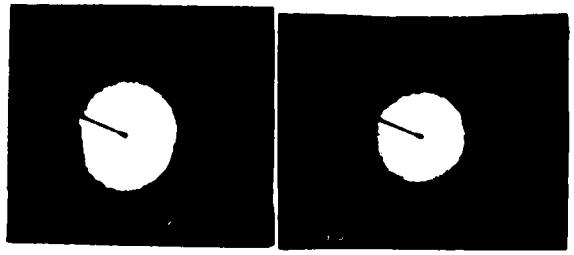



Visible Spectra of Partially Oxidized *Polypyrrole in Solution*

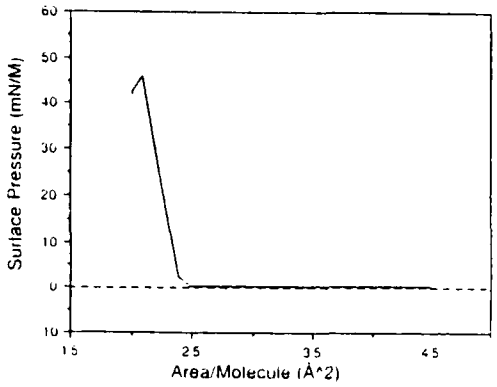



Synthetic Scheme

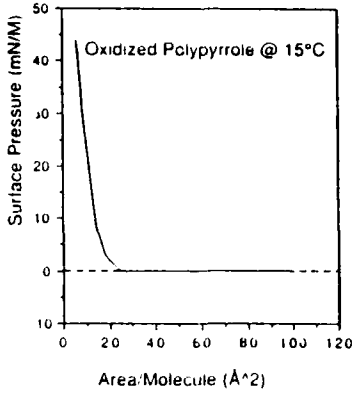
TEM MICROGRAPH OF A POLYPYRROLE MONOLAYER

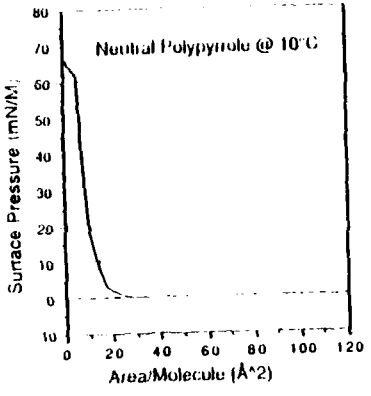


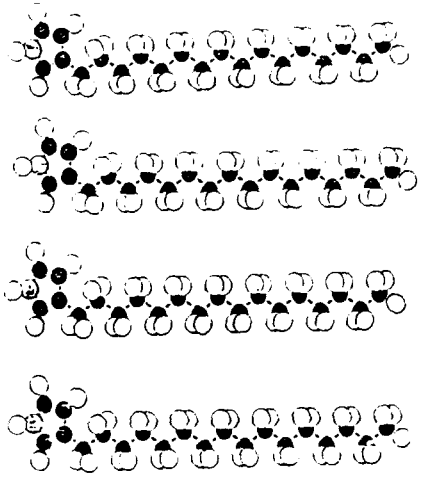
| PYRROLE: HDP=500: 1 | POLYPYRROLE |
|---|---|
| $d_1$=2.58A | $d_1$=2.54A |
| $d_2$=1.55A | $d_2$=1.55A |
| $d_3$=1.33A | |
| $d_4$=1.01A | |
| $d_5$=0.90A | |

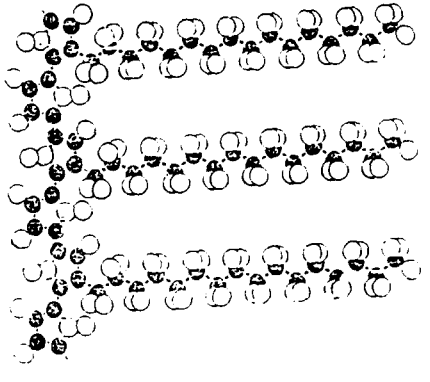


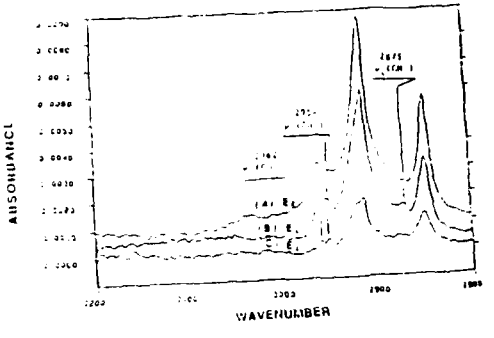

Isotherms of 3-Hexadecyl Pyrrole
(mixed monolayers with pyrrole monomer)










IR SPECTRA OF $C_{18}H_{33}$ PYRROLE LB FILMS IN THE C-H STRETCHING REGION

(A) TRANSMISSION OF 5 MONOLAYERS ON ZnSe

(B) GIR OF 5 MONOLAYERS ON Pt

(C) GIR OF 1 MONOLAYER ON Pt

N-12

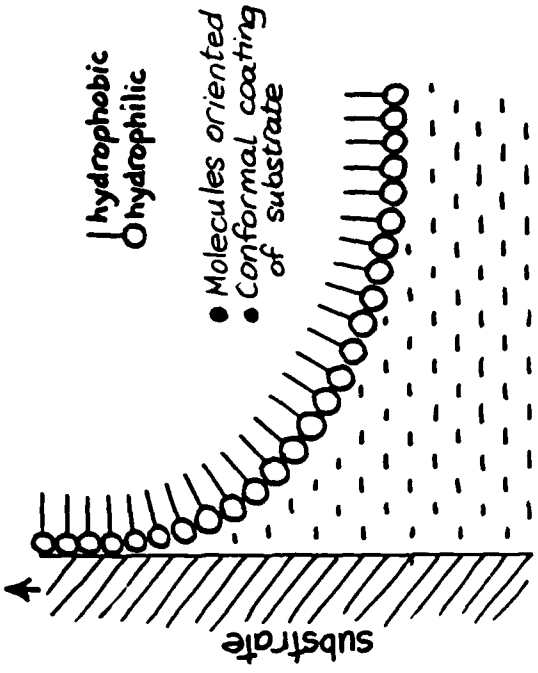
I. Peterson
GEC Research, Ltd., Great Britain

# THE NONLINEAR OPTICS OF LANGMUIR-BLODGETT FILMS

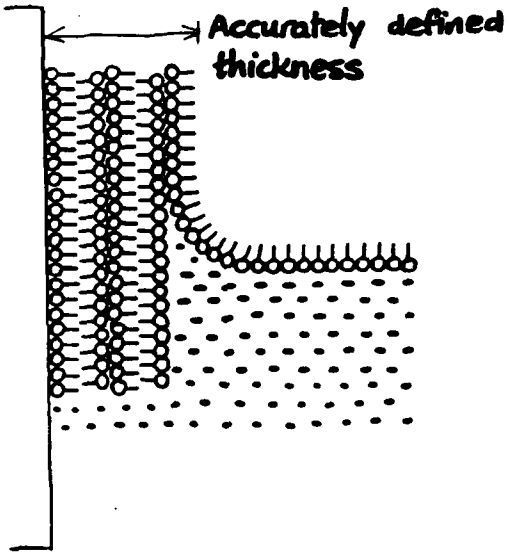
# THE NONLINEAR OPTICS OF LANGMUIR-BLODGETT FILMS

*Theoretical advantages:*

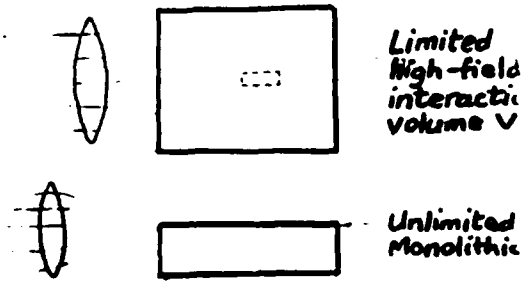
- Good geometry
- Chromophore alignment
- Dense packing



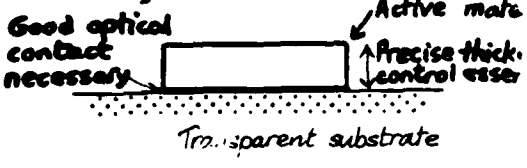

## Building up thick films




## Geometry




## Overlay structure



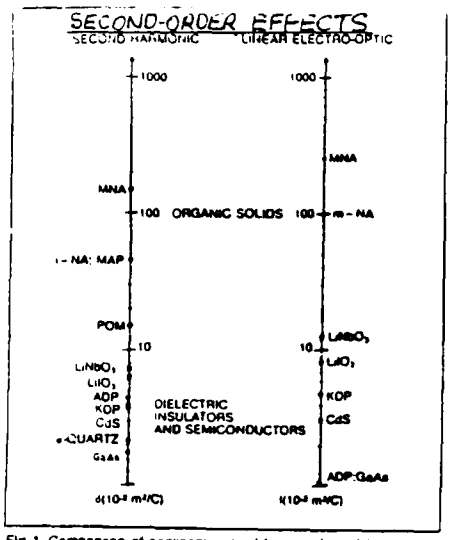
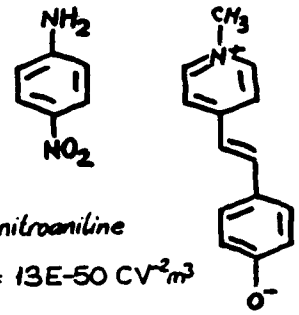



Fig 1 Comparison of nonlinear optical figures of merit for organic and inorganic solids. (d is measured at 1.05 μm; χ is the strain-free quantity measured at 0.633 μm, except for GaAs where it is measured at 0.9 μm)

F Garito & K D Singer
Laser Focus 80(1982) 59

WHAT MOLECULE?




p-nitroaniline
$\beta$ = 13E-50 $CV^{-2}m^3$

'Gedye'
merocyanine
$\beta$ = 370E-50 $CV^{-2}m^3$

| | | |
|---|---|---|
| $\frac{\beta}{\varepsilon_0 V}$ | 65 pm/V | 1100 pm/V |

cf $LiNbO_3$ $\chi^{(2)}_{SHG}$ = 10 pm/V

## Two-state Approximation

$$\beta = \frac{3e^2\hbar^2}{2m} \cdot \frac{W_0}{(W_0^2-4W^2)(W_0^2-W^2)} \cdot f\Delta\mu$$

| | |
|---|---|
| $W_0$ | State transition energy |
| $W$ | Photon energy $\hbar\omega$ |
| $f$ | Oscillator strength |
| $\Delta\mu$ | Dipole moment difference |

The best materials have

- Long-wavelength absorption
- Strong absorption
- Charge transfer

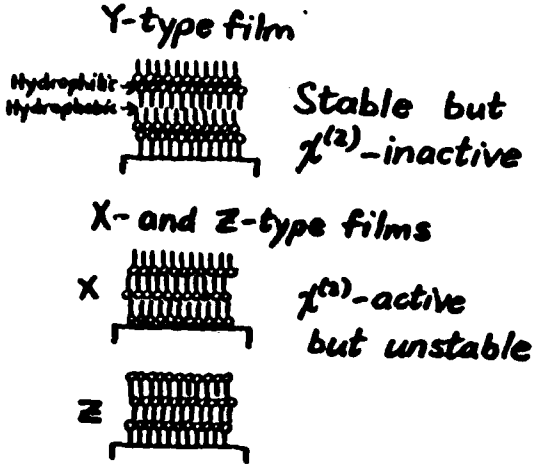
Ian Girling
Graham Cross
John Earls
} GEC Hirst Researc

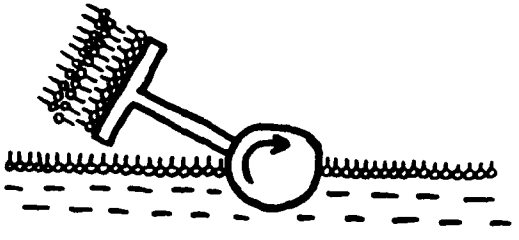
JOERS (LB nonlinear opt

| | |
|---|---|
| Durham | Mike Petty |
| Lancaster | Richard Tredgold |
| Hull | George Gray |
| Plessey | Jack Brettle |
| British Telecom | Roger Heckingbott |

My new address.....

Institut für phys. Chemie
Universität Mainz FRG



## Deposition of $\chi^{(2)}$-active

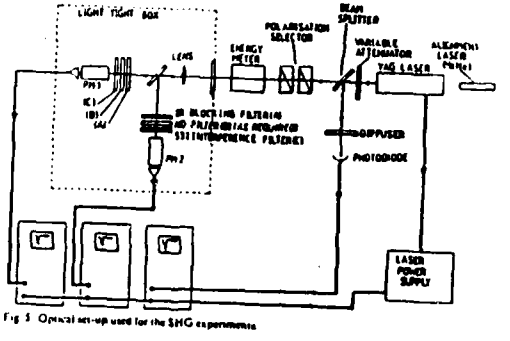
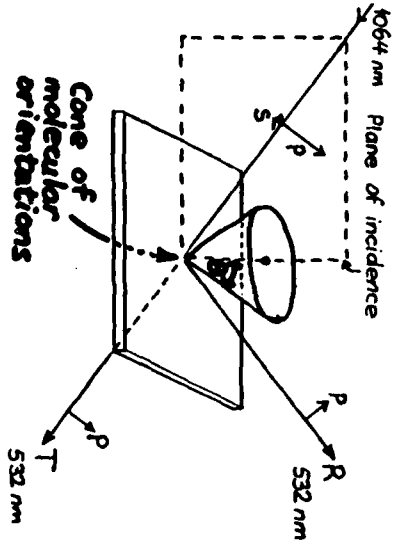


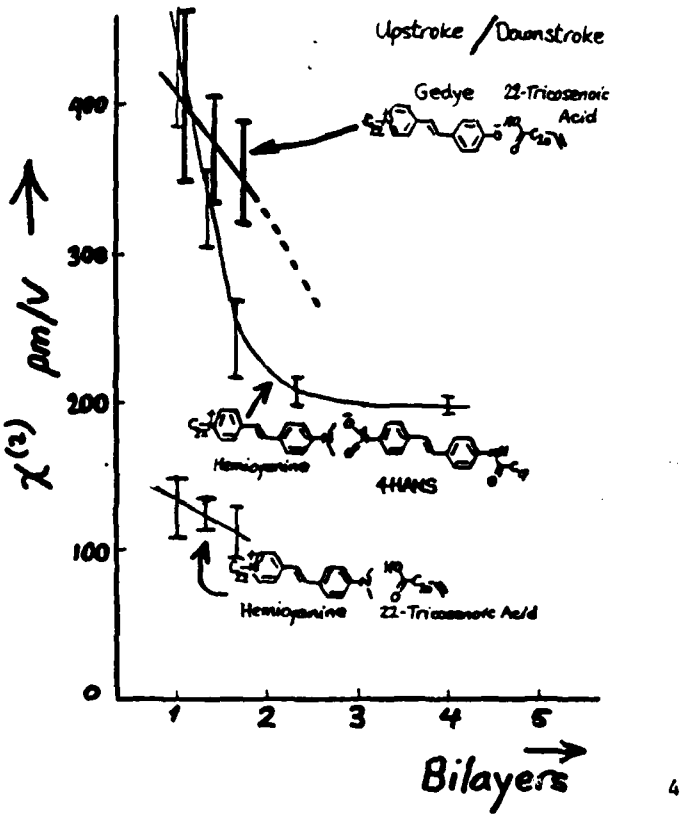

Fig 5 Optical set-up used for the SHG experiments

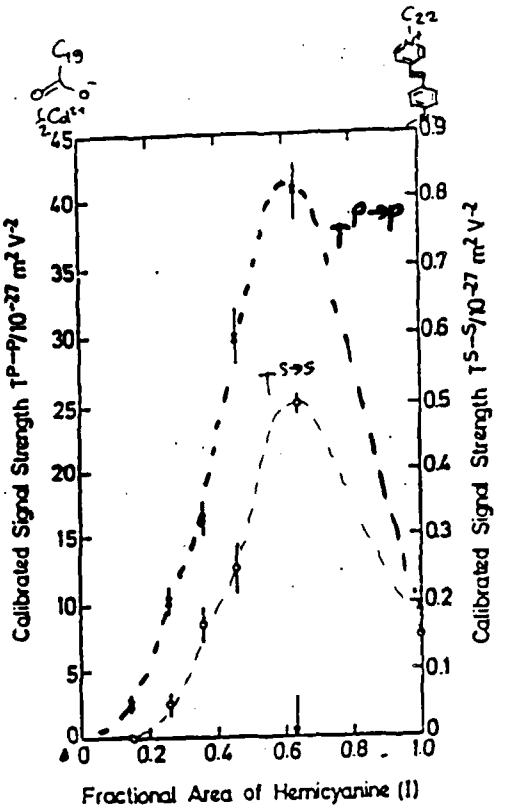
## Second Harmonic Generation




GEDYE MEROCYANINE MONOLAYERS

| | $\chi^{(2)}$(pm/v) $\theta^{\circ}$ | |
|---|---|---|
| Low $\pi$ | 250 | 15 |
| High $\pi$ | 1300 | 9 |

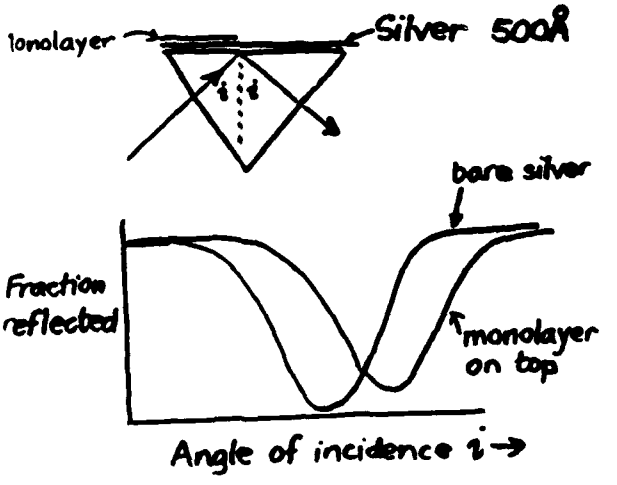


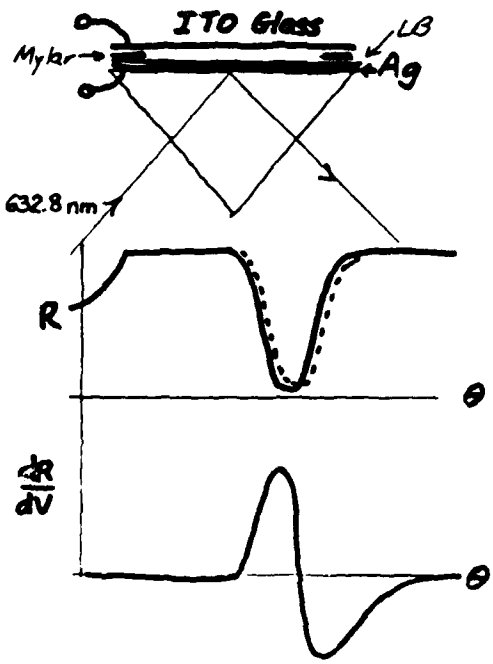

4 $T^{p\to p}$(x) and $T^{s\to s}$(o) second harmonic signal ($10^{-27}$ $m^2V^{-2}$) from mixed monolayer

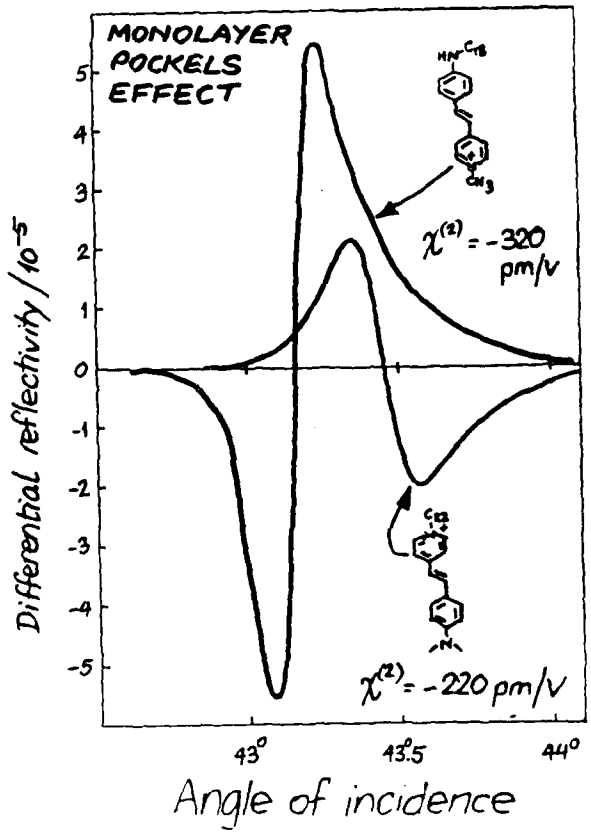
## Measurement of refractive index

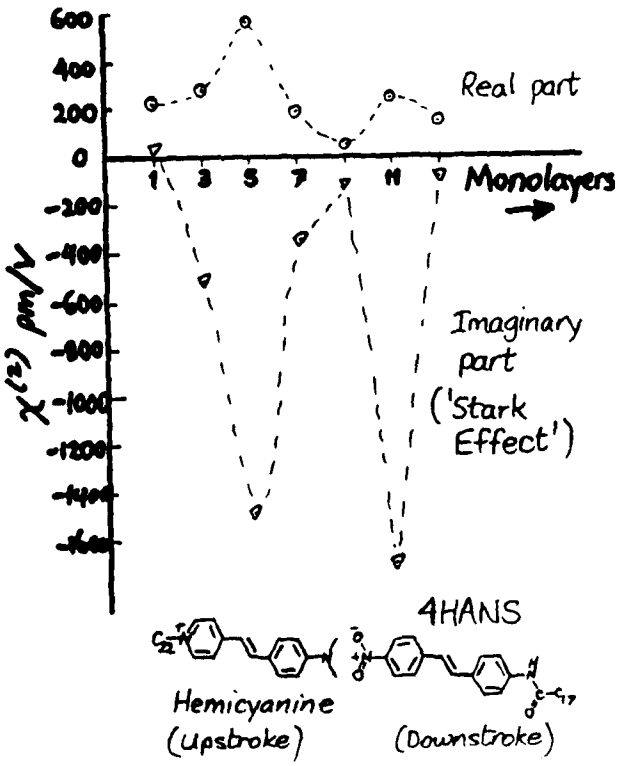
## Surface plasmon Attenuated Total Reflection

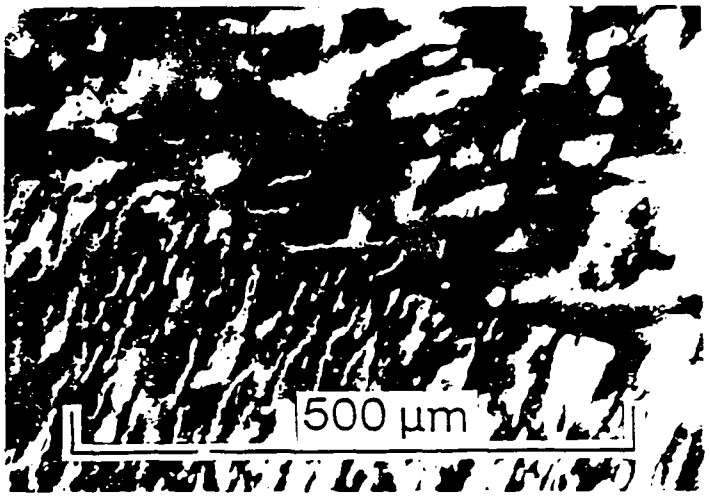


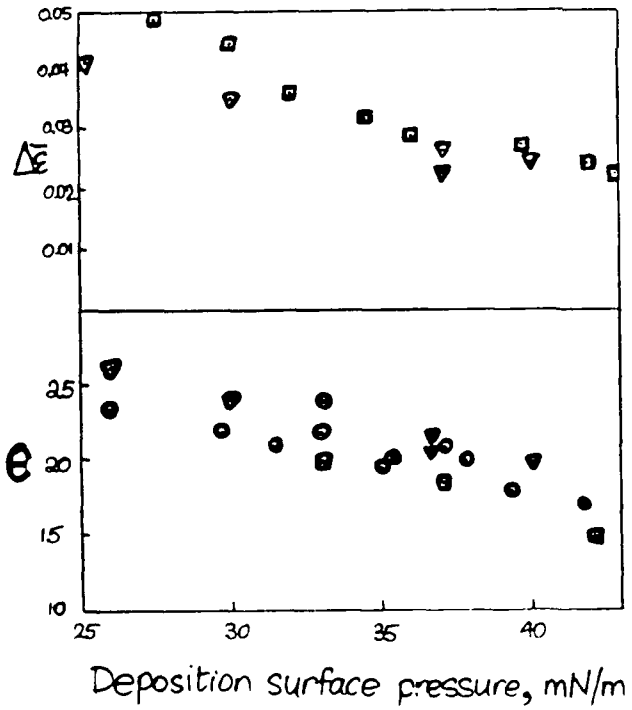
## Pockels-ATR Technique

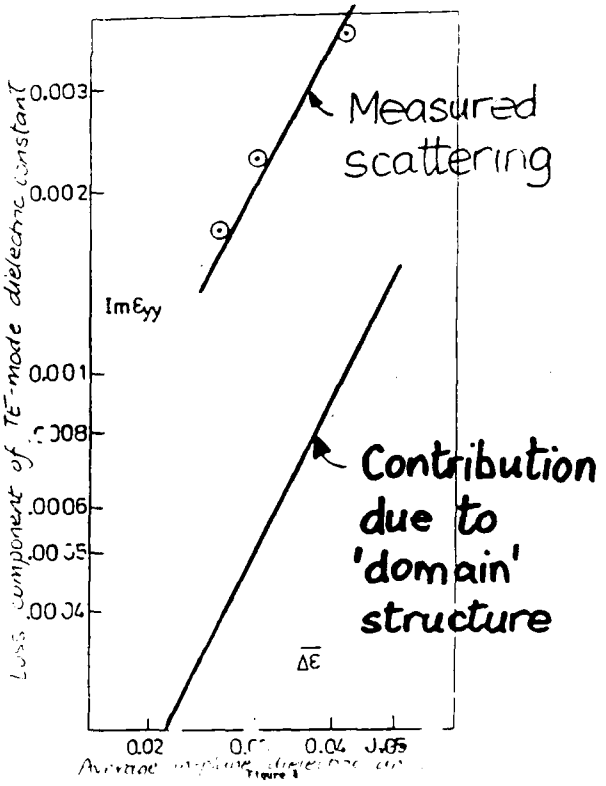



500 µm


0.05
0.04
0.03
0.02
0.01
$\overline{\Delta\varepsilon}$
2.5
2.0
1.5
1.0
$\varepsilon$
25
30
35
40
Deposition surface pressure, mN/m


0.003
0.002
0.001
0.0008
0.0006
0.0005
0.0004
Im$\varepsilon_{yy}$
$\overline{\Delta\varepsilon}$
0.02
0.04
Measured scattering
Contribution due to 'domain' structure

R. S. Lytel
Lockheed Research and Development

# ADVANCES IN ORGANIC ELECTRO-OPTIC DEVICES

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LOCKHEED

# ADVANCES IN ORGANIC ELECTRO-OPTIC DEVICES

MAY 19, 1988

R. LYTEL

Lockheed Research and Development Division
LOCKHEED MISSILES AND SPACE COMPANY INC
3251 Hanover St Palo Alto California 94304

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## ACKNOWLEDGEMENTS

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U.S. ARMY
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* W ELSER

U. PENN
* A.F. GARITO

HOECHST CELANESE
* J STAMATOFF
* R DEMARTINO
* H YOKIN

U.S. MISS
* A GRIFFIN

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## THE LOCKHEED ORGANIC DEVICES GROUP

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M. STILLER

**ANALYSIS**

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G.F LIPSCOMB
R LYTEL
D. SWANSON
A. TICKNOR

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R. STONE

**WAVEGUIDES**

G.F LIPSCOMB
R LYTEL
M STILLER
J THACKARA
A. TICKNOR

**SPATIAL LIGHT MODULATORS**

D ARMITAGE
W EADES
M. STILLER
J THACKARA

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## MAJOR BENEFITS OF NONLINEAR ORGANIC/POLYMERIC MATERIALS

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* ORGANIC/POLYMERIC MATERIALS OFFER UNIQUE OPTICAL AND STRUCTURAL FEATURES FOR DEVICE APPLICATIONS
* MOLECULAR PROPERTIES CAN BE ENGINEERED TO ACHIEVE DESIRED MACROSCOPIC PROPERTIES

| STRUCTURAL | OPTICAL |
|---|---|
| * MOLECULAR ENGINEERING | * LARGE, NONRESONANT RESPONSE |
| * THIN FILMS AND BULK CRYSTALS | * LOW DC DIELECTRIC CONSTANTS |
| * ROOM TEMPERATURE OPERATION | * FAST NLO RESPONSE |
| * CHEMICAL/STRUCTURAL STABILITY | * HIGH OPTICAL DAMAGE THRESHOLD |
| * INTERNAL GRATINGS/STRUCTURE | * BROADBAND |
| * ARCHITECTURAL FLEXIBILITY | * LOW ABSORPTION |

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## ORGANIC MATERIALS IN INTEGRATED OPTICS

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- CURRENT TECHNOLOGY: $TiLiNbO_3$
  - Materials Dev. Began in 1960s
- r = 32 pm/V
  - Larger Modulating Voltage
  - Little Improvement Expected
- LIMITED FABRICABILITY
  - 1000°C Processing
  - Depth Limited to 5 μm
  - Low Index Change Δn
  - Loss > 0.1 dB/cm
  - Optical Damage (Photorefractor)
- LARGE DIELECTRIC CONSTANT (28)
  - Longer Time Constants = RC
  - Large Velocity Mismatch in Traveling Wave Modulator
- MASS PRODUCTION DIFFICULT

- PROPERTIES OF POLYMERIC ORGANIC E-O MATERIALS
  - Materials Dev. Began 1975
- r = 14-53 pm/V (poled films*)
  - Lower Modulating Voltage
  - Potentially Much Larger r
- FLEXIBLE FABRICATION
  - Low Temperature Processing
  - Flexible Dimensions
  - Controllable Index Change Δn
  - Loss < 0.8 dB/cm**
  - High Optical Damage Threshold
- LOW DIELECTRIC CONSTANT (4)
  - Shorter Time Constants = RC
  - Smaller Velocity Mismatch
- POTENTIAL FOR MASS PRODUCTION

* See Proc. Materials Research Society, Boston, MA (12/87)
** Current Lockheed/Hoechst Celanese Result

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## ORGANIC MATERIALS IN OTHER DEVICES

LOCKHEED

| ELECTRO-OPTIC DEVICES | ALL-OPTICAL DEVICES |
|---|---|
| * SPATIAL LIGHT MODULATORS, TUNABLE FILTERS, SHUTTERS | * ETALON SWITCHES, ALL-OPTICAL FILTERS, NONLINEAR WAVEGUIDE DEVICES |
| * MATERIALS WITH LARGE r AND LOW DIELECTRIC CONSTANTS EXIST AND ARE AVAILABLE | * NONRESONANT NONLINEARITIES ARE STILL FAR TOO SMALL FOR MICRON SIZED DEVICES. RESONANT MATERIALS REQUIRED |
| * FABRICATION UNDERWAY IN THIS PROJECT | * NONRESONANT MATERIALS NEARLY ADEQUATE FOR GUIDED WAVE DEVICES |

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## ORGANIC E-O THIN-FILM WAVEGUIDE MODULATORS

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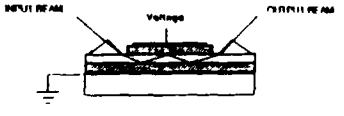


| CONTACTS | BUFFER LAYERS | POLYMERS |
|---|---|---|
| COPPER | POLYSILOXANE RESIN | MMA/PMMA |
| ALUMINUM | UV CURABLE COATINGS | PC69 |
| GOLD | SILICON DIOXIDE | C-22 |
| ITO | 2 COMPONENT EPOXY | HCC-1237 (new) |

* TYPICAL LAYER THICKNESS OF ORDER 2 MICRONS
* POLING ACCOMPLISHED PRIOR TO FINAL ASSEMBLY

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## POLED ORGANIC E-O LAYER PREPARATION

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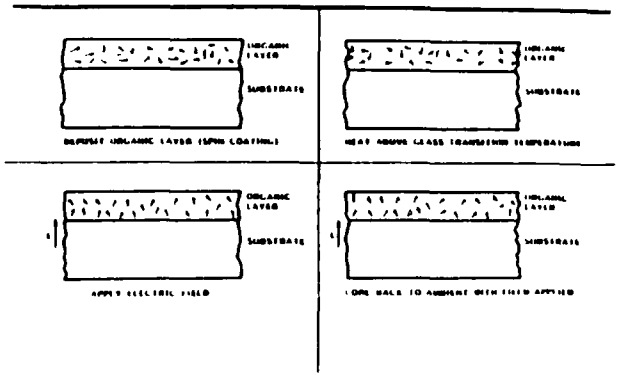


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## POLED POLYMER FILMS AND SLAB WAVEGUIDE MODULATORS

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| (wavelength = 0.83 μm) | PC6S | C-22 |
|---|---|---|
| E-O COEFFICIENT (pm/V) | 2.8 | 14.0 |
| TM REFRACTIVE INDEX (POLED) | 1.7 | 1.58 |
| TM INDEX DIFFERENCE (POLED-UNPOLED) | 0.06 | 0.005 |
| WG LENGTH (cm) | 1.8 | 2.5 |
| MEASURED LOSS (dB/cm) | 3.4 | 0.8 |
| HALF-WAVE VOLTAGE (volts) | 48 | 7 |

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## FABRICATION OF CHANNEL WAVEGUIDES BY SELECTIVE POLING

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- SINGLE POLARIZATION BURIED CHANNEL WAVEGUIDES CAN BE FABRICATED BY SELECTIVE ELECTRIC FIELD POLING IN THIN FILM POLYMERS USING VERTICAL OR TRANSVERSE ELECTRODES
- POLING PRODUCES HIGHER INDEX, E-O CHANNELS BURIED IN SURROUNDING, UNPOLED, LOWER INDEX POLYMER
- WAVEGUIDE PATTERN DEFINED BY PHOTOLITHOGRAPHY
- RELATIVELY LOW TEMPERATURE PROCESSING, 100-200 C
- FLEXIBLE DIMENSIONS IN HEIGHT AND WIDTH, 1-100 MICRONS
- VARIABLE INDEX DIFFERENCE $\Delta n = 0.001$-$0.05$
- CAN MODE MATCH TO STANDARD SINGLE MODE FIBER
- CONCEPT PROVED IN DEVICE STRUCTURES: MACH ZEHNDER INTERFEROMETER, COUPLER, TRAVELING WAVE MODULATOR

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## VERTICAL AND TRANSVERSE POLING OF GLASSY POLYMER FILMS/WAVEGUIDES

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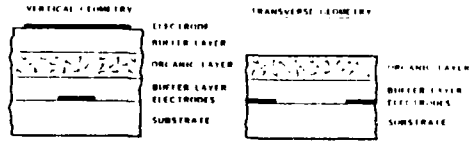
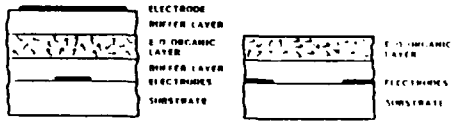



PRIOR TO POLING




AFTER POLING

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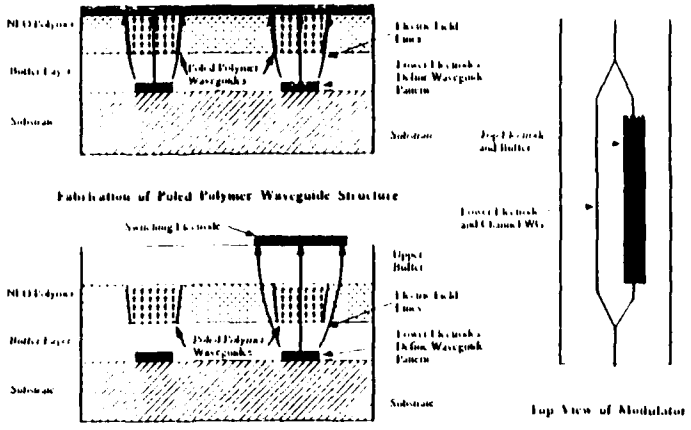
## INTEGRATED OPTIC MODULATOR FABRICATION




Fabrication of Poled Polymer Waveguide Structure

Optical Modulation By Electro-Optic Modulation

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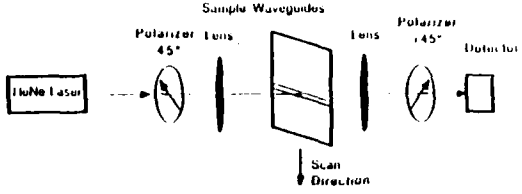
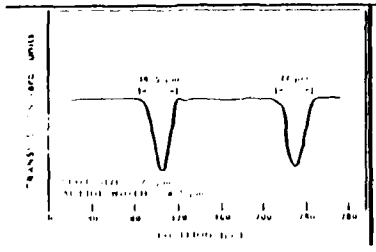
## CHANNEL BOUNDARY IN SELECTIVELY-POLED GUIDES



- Test of the Extent of Poling Beyond the Electrode Boundaries
- Sample Placed at 45° Between Crossed Polarizers
- Focused HeNe Spot Scanned Across Poled Waveguide Regions
- Poling Induced Birefringence at the Guide Boundary Would Cause Increased Signal
- Metallic Poling Electrode Blocks Beam and Causes a Dip in the Background Signal
- Poling Sharply Confined to the Electroded Region

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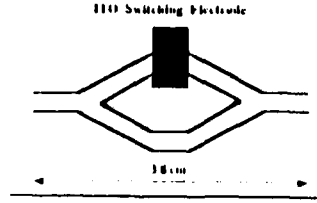
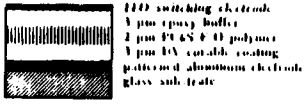
## FABRICATION AND OPERATION OF A SELECTIVELY-POLED M-Z INTERFEROMETER




- POLED PC6S, 90°C, 5 MIN, 100 V/μm
- GOLD POLING ELECTRODE ON PC6S, REMOVED AFTER POLING
- 3° BRANCH ANGLE
- 780 nm LIGHT, TM MODE CONFINED
- GUIDE DIMENSIONS 2 x 7 μm

Device Structure After Poling Completed




INPUT Y-BRANCH

P-5

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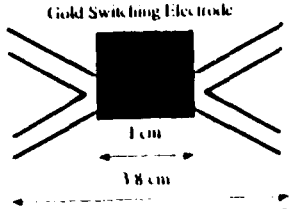
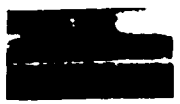
## FABRICATION AND OPERATION OF A SELECTIVELY-POLED DIRECTIONAL COUPLER




- POLED C 22, 105° C, 15 MIN, 90 V/μm
- 3° COUPLING ANGLE
- 830 nm LIGHT, TM MODE CONFINED
- INPUT/OUTPUT GUIDES 2 x 7 μm
- COMMON GUIDE 2 x 13 μm

Device Structure After Poling Completed



a) BAR STATE (120 V)

b) CROSS STATE (65 V)

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## TRAVELING WAVE INTEGRATED OPTIC PHASE MODULATOR

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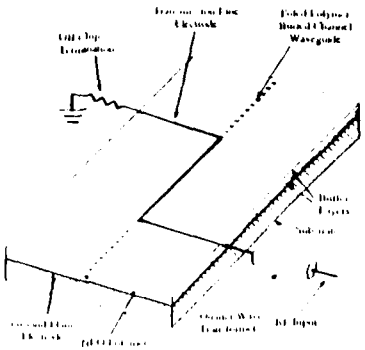
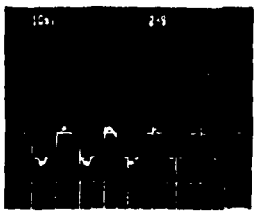


- POLED C 22 CHANNEL (100V/μm)
- ACTIVE PATH LENGTH 4 cm
- WAVELENGTH 830 nm
- DEVICE IMPEDANCE 9.5 ohms
- DRIVE SIGNAL 0.5 W (applied through transformer, 1/4 wave @250 Mhz)



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## TRAVELING WAVE MODULATORS

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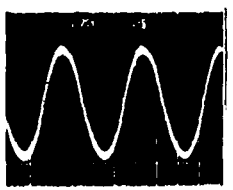
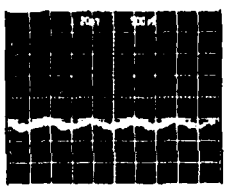
- PHASE MODULATOR IN ONE ARM OF A MACH ZEHNDER INTERFEROMETER
- CALCULATED MODULATION DEPTH USING MEASURED AT LOW FREQUENCY EQUALS MEASURED MODULATION DEPTH AT HIGH FREQUENCY
- IMPEDANCE MATCHED, 9.5 Ω



270 MHz

- PHASE MODULATOR IN ONE ARM OF A MACH ZEHNDER INTERFEROMETER
- RESPONSE SMALL DUE TO IMPEDANCE MISMATCH BUT
- CLEAR GHz MODULATION IS OBSERVABLE



1 GHz

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## SIGNIFICANCE OF ORGANIC E-O WAVEGUIDE RESEARCH

LOCKHEED

| CRITICAL RESULTS | IMPLICATIONS |
|---|---|
| • POLED POLYMER WAVEGUIDE FAB IS CHEAP, FAST, AND SIMPLE | • MASS PRODUCTION POSSIBLE |
| • PATTERNS DETERMINED BY ORDINARY PHOTOLITHOGRAPHY | • COMPLEX DEVICES ON A CHIP |
| • E O COEFFICIENTS NEARING LITHIUM NIOBATE LEVELS | • LOW DRIVING VOLTAGES COMPATIBLE WITH IC |
| • DIELECTRIC CONSTANTS ARE 7-10 TIMES SMALLER THAN INORGANICS | • FASTER RESPONSE TIMES AND HIGHER SENSITIVITY |
| • MODULATION TO 1.3 GHz SHOWN, TO >>GHz ACHIEVABLE | • HIGH SPEED SWITCHING AND INTERCONNECTION |
| • DEVICES BUILT AND OPERATED INTERFEROMETERS, COUPLERS, AND LW PHASE MODULATORS | • PROOF OF CONCEPT COMPLETE, CAN MOVE TO COMPLEX DEVICE FABRICATION |

Q-1

B. K. Nayar
British Telecom Research Laboratories, U. K.

# ORGANIC NONLINEAR OPTICAL DEVICES AND MATERIAL CONSIDERATIONS

# ORGANIC NONLINEAR OPTICAL DEVICES AND MATERIAL CONSIDERATIONS

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| J RUSH | B J McARDLE |
| P DUNN | H MORRISON |
| | E A SHEPHERD |
| | C S YOON |

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## OUTLINE

1. Review of device requirements for optical signal processing
2. Why organics?
3. Bulk devices
4. Guided wave devices
5. Crystal cored fibres
6. Material requirements dictated by the device design
7. Review of the present status

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## NON-LINEAR OPTICAL PROCESSES

$$P_i = \epsilon_0 \left[ \chi_{ij}^{(1)} E_j + \chi_{ijk}^{(2)} E_j E_k + \chi_{ijkl}^{(3)} E_j E_k E_l + \ldots \right]$$

- $\chi_{ij}^{(1)}$ — Linear susceptibility
- $\chi_{ijk}^{(2)}, \chi_{ijkl}^{(3)}, \ldots$ — Non-linear susceptibilities

$\chi_{ijk}^{(2)} = 0$ in centrosymmetric media

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## NONLINEAR OPTICAL DEVICES FOR SIGNAL PROCESSING

- Amplitude/Phase Modulators
- Switching Matrices
- Bistable Elements
- Frequency Convertors
- Tunable Sources
- Amplifiers
- Real-time phase conjugators

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## WHY ORGANIC MATERIALS?

- Large optical nolinearities
- Fast response times
- High optical damage thresholds
- Large birefringence
- Material optimisation using "Molecular Engineering"

Q-4

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## DISADVANTAGES OF ORGANIC MATERIALS

- Low melting points
- Mechanically weak
- Susceptible to chemical attack
- Complex transmission spectra
- Health hazards

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## MATERIAL SYSTEMS

**SINGLE CRYSTAL**

- Bulk
- Thin film
  - -planar
  - -overlays
- Confined growth
  - -channels
  - -fibres

**POLYMER FILMS**

- LC polymers
- Guest-host polymers
- LB films



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## BULK ORGANIC DEVICES

| DEVICE TYPE | MATERIALS |
|---|---|
| SHG | DAN, mNA, MBA-NP, MAP, NPP, POM, Urea |
| SFG | Urea |
| OPA | POM, NPP |
| OPE | POM |
| OPO | Urea |

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## BULK MBA-NP CRYSTAL GROWTH

- Material Purification
  - column chromatography
  - successive recrysatallisations
- Selection of perfect seeds
  - X-ray topography
- Solution growth by temperature lowering of a seeded saturated methanol solution

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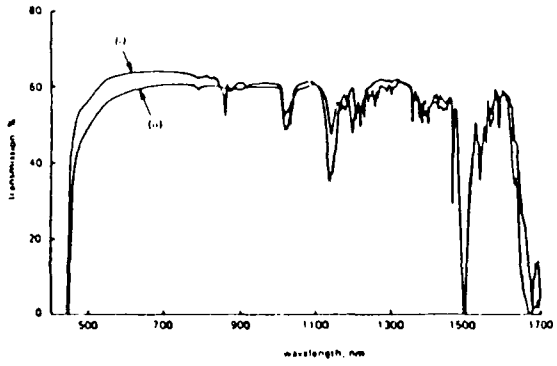
## MBA-NP CRYSTAL TRANSMISSION SPECTRA

Crystal Cut: (001); Propagation: [001]

Input Polarisation: (i) [100] and (ii) [010]

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## MBA-NP SHG RESULTS

- Large single crystal growth
  - $5x3x3\ cm^3$
- Type I Phase-Matched SHG
  - $d_{eff} = 3.4x10^{-12}$ m/V
- $d_{22} = 25x10^{-12}$ m/V

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## ADVANTAGES OF GUIDED WAVE NONLINEAR INTERACTIONS

- Semiconductor laser powers adequate
- Long interaction lengths
- Phase-matching using modal dispersion
- Ease of coupling to optical fibres

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## ACTIVE WAVEGUIDE TYPES

- PLANAR
  - — Two-dimensional eg slab
  - — Three-dimensional eg channel
- FIBRE
  - — Polished/D-shaped fibres with overlays
  - — Crystal cored fibres
  - — Doped fibres



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## ACTIVE WAVEGUIDE DEVICE TYPES

- Waveguide
- Directional Coupler
- Waveguide Interferometers
  - — Mach-Zehnder, Ring Resonator etc
- Waveguide Fabry-Perot

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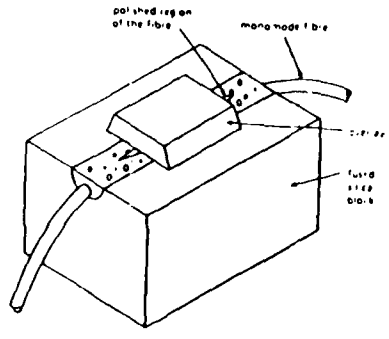
## POLISHED / D-SHAPED FIBRES WITH NONLINEAR OVERLAYS




- Evanescent mode field interacts with the Nonlinear Overlay eg
  - — Change in the overlay index can be used to modulate Amplitude or Phase of the fibre mode



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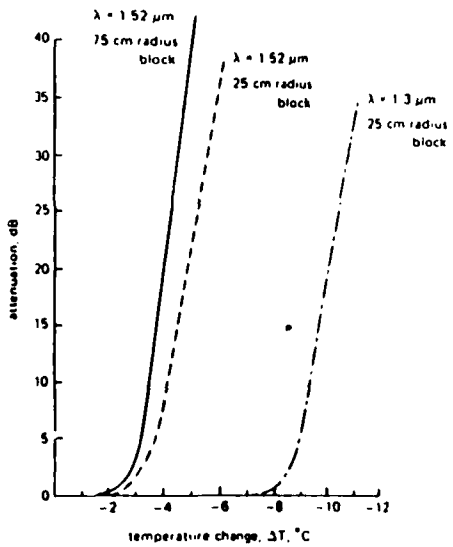
## ATTENUATION OF A POLISHED FIBRE WITH A REDUCTION IN THE OIL OVERLAY TEMPERATURE ie INCREASE IN INDEX

$$\frac{dn_D}{dT} = -3.7\times10^{-4}\ {}^{\circ}C$$

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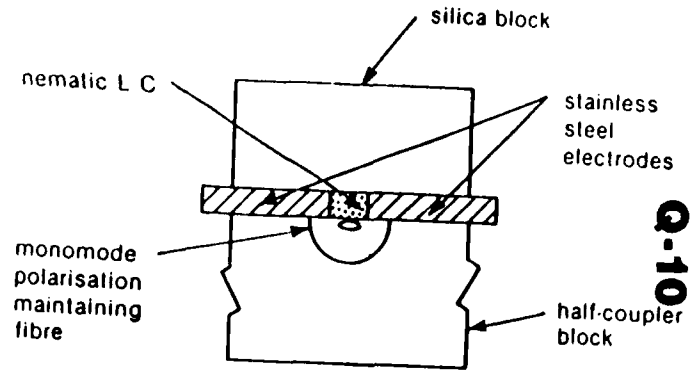
## SCHEMATIC OF A FIBRE E-O MODULATOR WITH A NEMATIC LC OVERLAY




Q-10

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## CHARACTERISTICS OF A FIBRE E-O AMPLITUDE MODULATOR WITH A NEMATIC LIQUID CRYSTAL OVERLAY

- Insertion Loss
  - — Horz Pol: 1.2dB and Vert Pol: 0.5dB
- Modulation Depth (Vert Pol): >30dB
- Switching Voltage: 5V
- Switching Field Strength: 0.2V/$\mu$m
- Response Times: $\tau_r = 2.5$ms and $\tau_f = 160$ms

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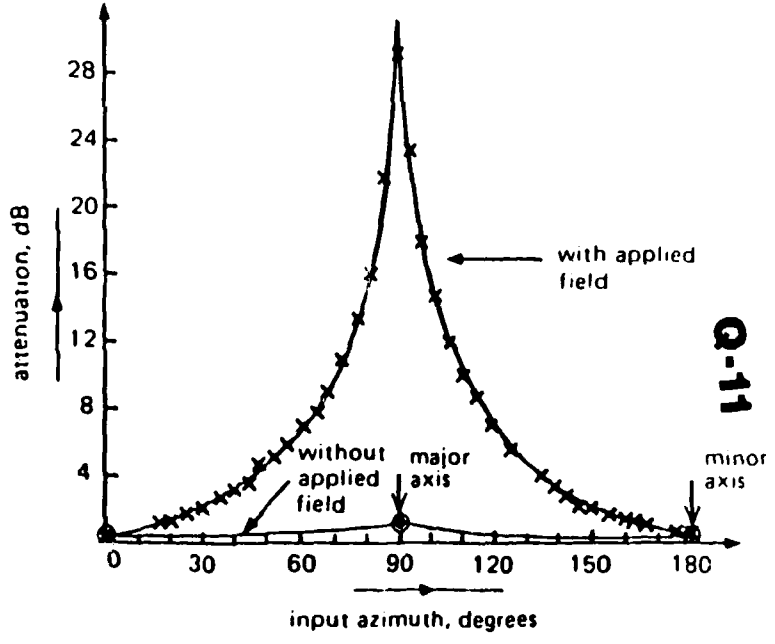
## EXTINCTION RATIO OF A LC FIBRE MODULATOR WITH INPUT AZIMUTH ANGLE




Q-11

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## WHY CRYSTAL CORED FIBRES?

- Peak intensity in the core
- Good geometrical uniformity
- Large choice of cladding glasses
- Encapsulation of crystal core
- In-line fibre device

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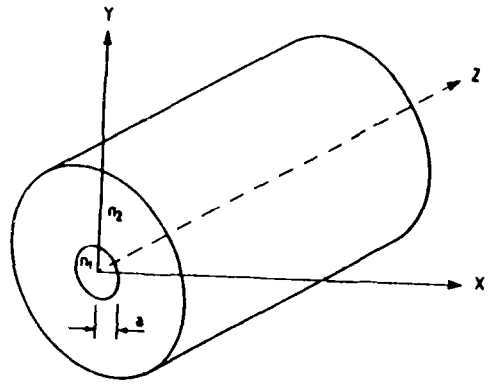
## CRYSTAL CORED FIBRES

- Cylindrical waveguiding structure




- For optical guidance $n_1 > n_2$
- Applications: Three-wave and Four-wave mixing processes

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## FABRICATION PROCESS

- Selection of suitable cladding glass
  - — $\Delta n = n_c - n_{cl} < 0.05$
- Drawing of small bore capillaries
  - — Bore diameter = 2 to 10$\mu$m
- Capillaries filled with the crystal melt
- Growth of single orientated crystal

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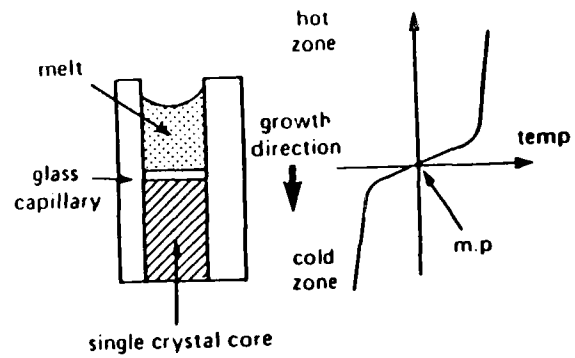
## CRYSTAL CORED FIBRE FABRICATION

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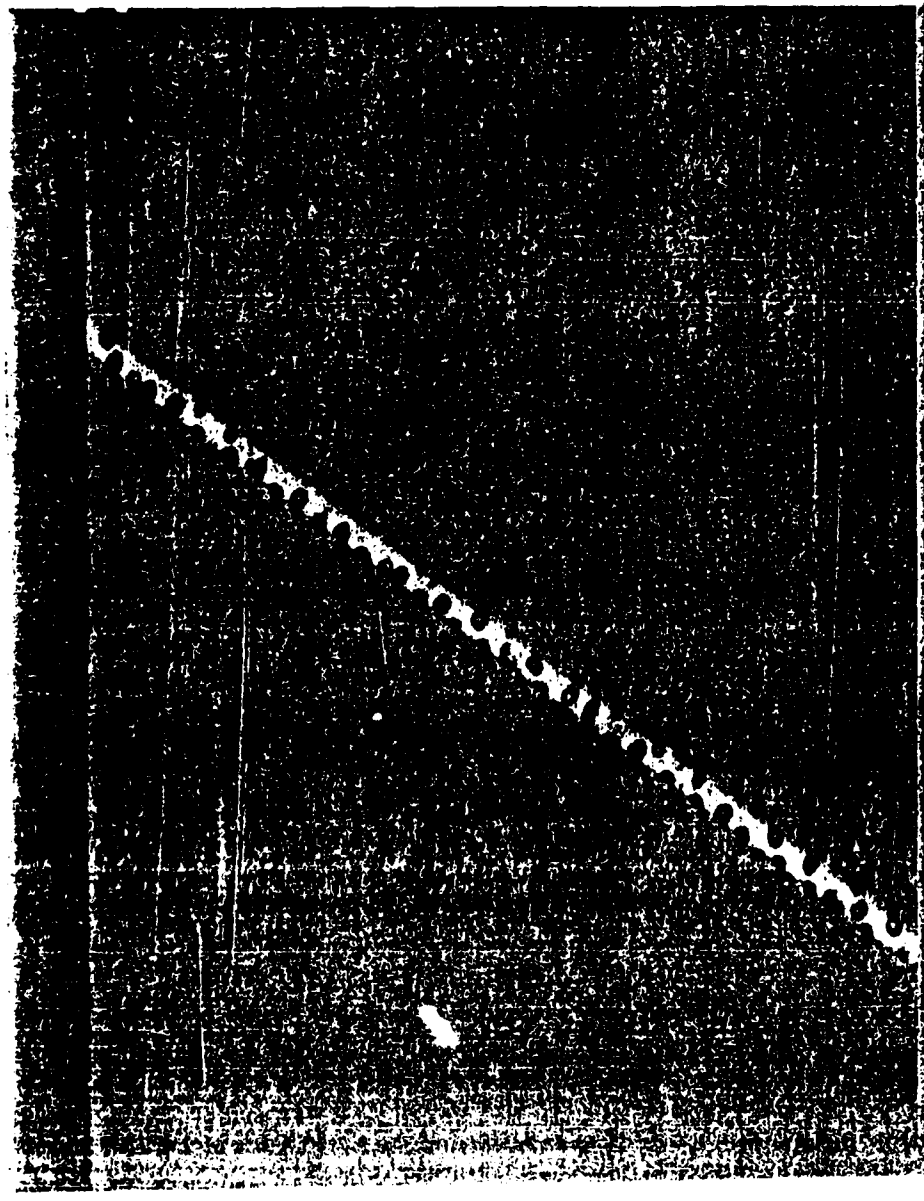
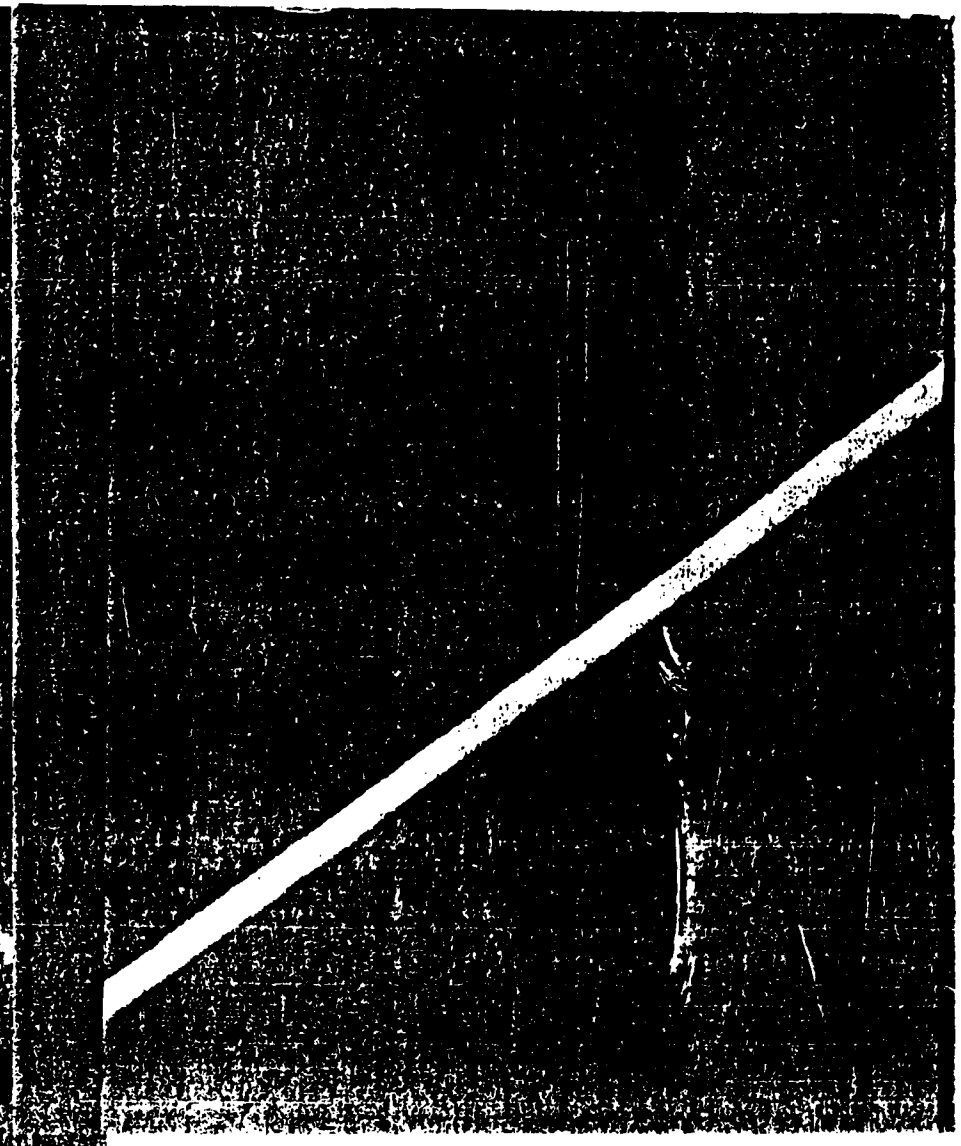
Defects in CCFs



SINGLE CRYSTAL CORE



## FACTORS INFLUENCING DEFECT FREE CRYSTAL GROWTH

- Material Purity
- Adsorbed Oxygen
- Bubbles
- Temperature Gradient
- Growth Rate
- Vibration

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## MATERIAL REQUIREMENTS FOR GROWTH IN GLASS CAPILLARIES

- Chemical stability
- Low melting point
- Optically transparent
- Refractive index < 2.0
- Non-centrosymmetric crystal
- Large transverse nonlinear coefficient

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## ASSESSMENT OF CCFs

- Polarising Microscope
  - — Crossed Polars
    - * Uniformity of orientation, defects/voids
  - — Parallel Polars
    - * Defects/Voids
- X-ray Diffraction
  - * Crystal Orientation
- Optical Transmission

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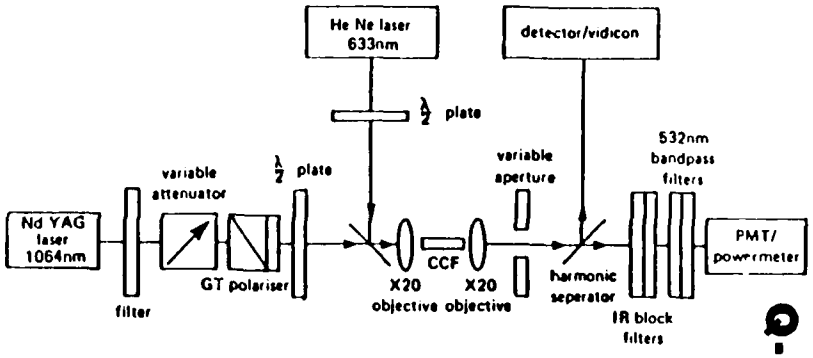
## EXPERIMENTAL SET-UP FOR OPTICAL CHARACTERISATION OF CCFs



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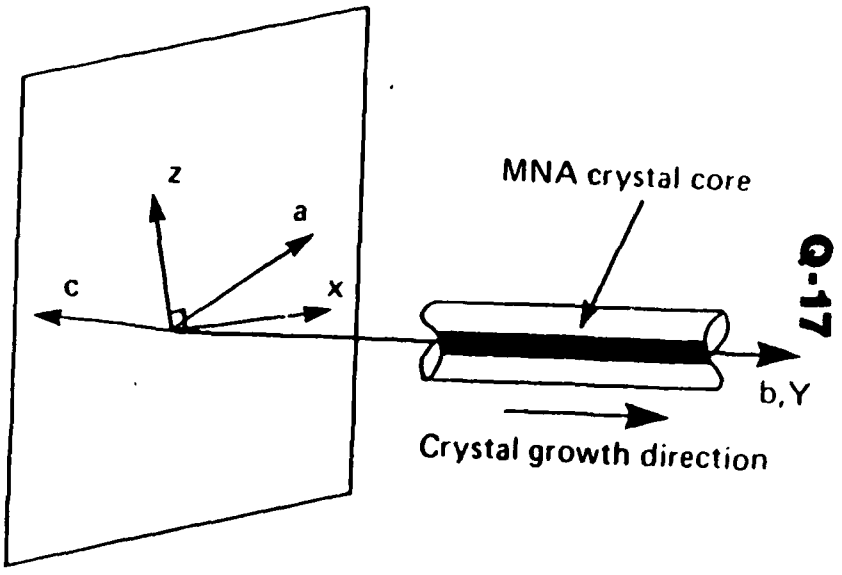
## SUMMARY OF SHG EXPERIMENTS IN CCFs

| Reference | Core |
|---|---|
| Nayar (1982&1983) | benzil |
| Vidakovic et al (1984) | NPP |
| Umegaki et al (1985) | MNA |
| Umegaki et al (1986) | MNA |
| Tomaru et al (1986) | DAN |
| Holdcroft et al (1987) | MNA |
| Nayar et al (1987) | acetamide, MNA |
| Vidakovic et al (1987) | NPAN |
| Holdcroft et al (1988) | DAN |
| Kerkoc et al (1988) | DAN |

## MNA CRYSTAL ORIENTATION IN CCFs



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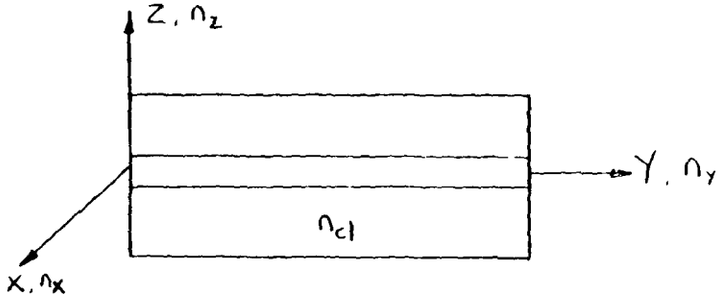
## MNA CORED SILICA FIBRE POLARISER




- Refractive Indices of MNA:
  $n_x$ (633nm) = 1.8 and $n_z$ (589nm) = 1.453

- Silica Cladding, $n_{cl}$ (589nm) = 1.458

- Hence transmission of *only x-polarised* light

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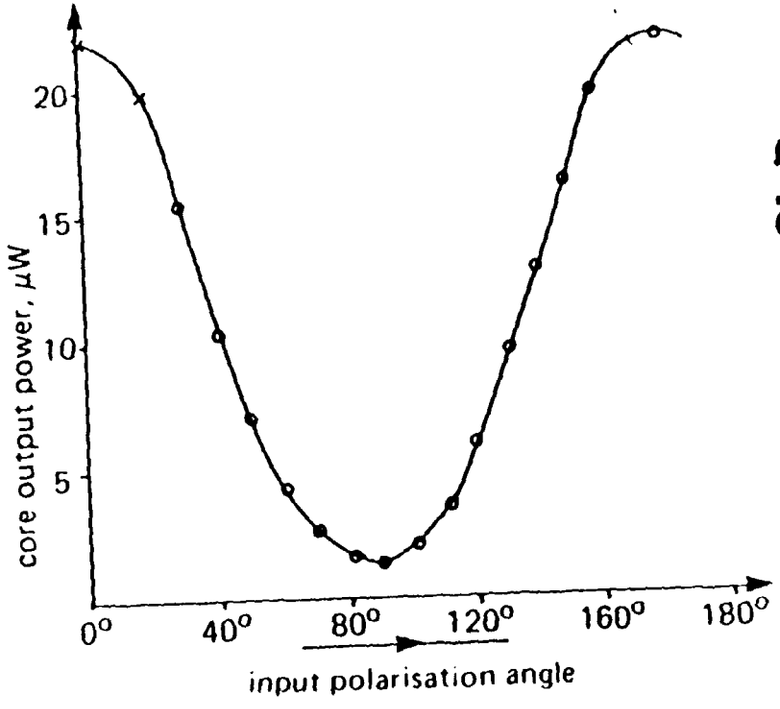
## POLARISATION TRANSMISSION CHARACTERISTIC OF A MNA CORED SILICA FIBRE

Wavelength: 633nm; Extinction Ratio: 12.8dB

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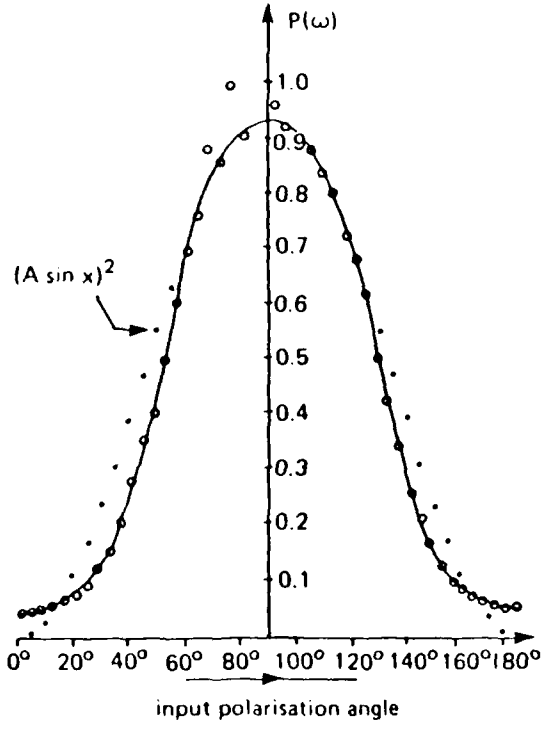
## SH POWER CHARACTERISTIC OF A MNA CCF AS A FUNCTION OF INPUT POLARISATION

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## CCF INSERTION LOSSES

| CRYSTAL CORE | LOSS, dB/cm |
|---|---|
| acetamide | 1.1 |
| benzil | <2.0 |
| DAN | 10 |
| MNA | 20 |
| NPP | High |

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## SUMMARY OF CCF SHG RESULTS

$\lambda_f = 1064nm$; Length $= 10\text{-}15mm$; Core dia. $= 6\text{-}10\mu m$

Average $P_f = 10mW$; Peak $P_f = 50W$

| Material | Transmission, % | Efficiency, % |
|---|---|---|
| Acetamide | 5 | $0.25\text{-}1 \times 10^{-6}$ |
| DAN | 0.5 | $2 \times 10^{-3}$ |
| MNA | 0.2-0.6 | $0.2\text{-}4 \times 10^{-5}$ |

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## LATEST BTRL SHG RESULTS FOR DAN IN SILICA CCFs

$\lambda_f = 1064nm$; $P_f$ (avg) $= 1mW$; $P_f$ (peak) $= 10W$

Pulse Width $= 200ns$; Rep Rate $= 500Hz$

Fibre length $= 10\text{-}15mm$; Core dia $= 6\mu m$

| Publication | Throughput,% | Efficiency,% |
|---|---|---|
| CLEO'88 | 5-15 | 1-1.5 |

Ref: G E Holdcroft et al, paper WM55



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## PRESENT STATUS OF SHG IN CCFs

- Typical conversion efficiencies < 0.1%

DUE TO

- Unsuitable crystal orientation
- Low transmission
  - — Poor crystal end quality
  - — Voids and defects
- Un-optimised waveguide design
  - — Lack of data on optical properties

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## DEVICE DESIGN REQUIREMENTS

- Bulk refractive indices
- Effective mode refractive indices
- Uniformity of guiding region dimensions and index difference
- Low waveguide attenuation
- Optical damage and intensity dependent index change



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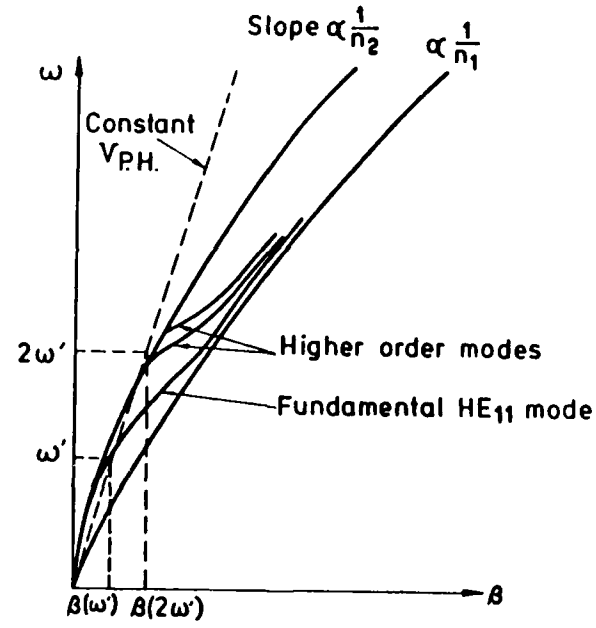
## PHASE-MATCHING IN WAVEGUIDES

- Different mode orders
  - same or orthogonal polarisations
- Same order mode (orthogonal polarisations)
  - birefringent core material
  - elliptical core shape
- Hence require cladding glass of appropriate index and dispersion

## PHASE-MATCHING FOR RADIATION SHG



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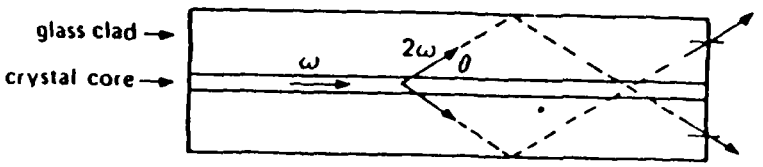
## RADIATION SHG IN CCFs

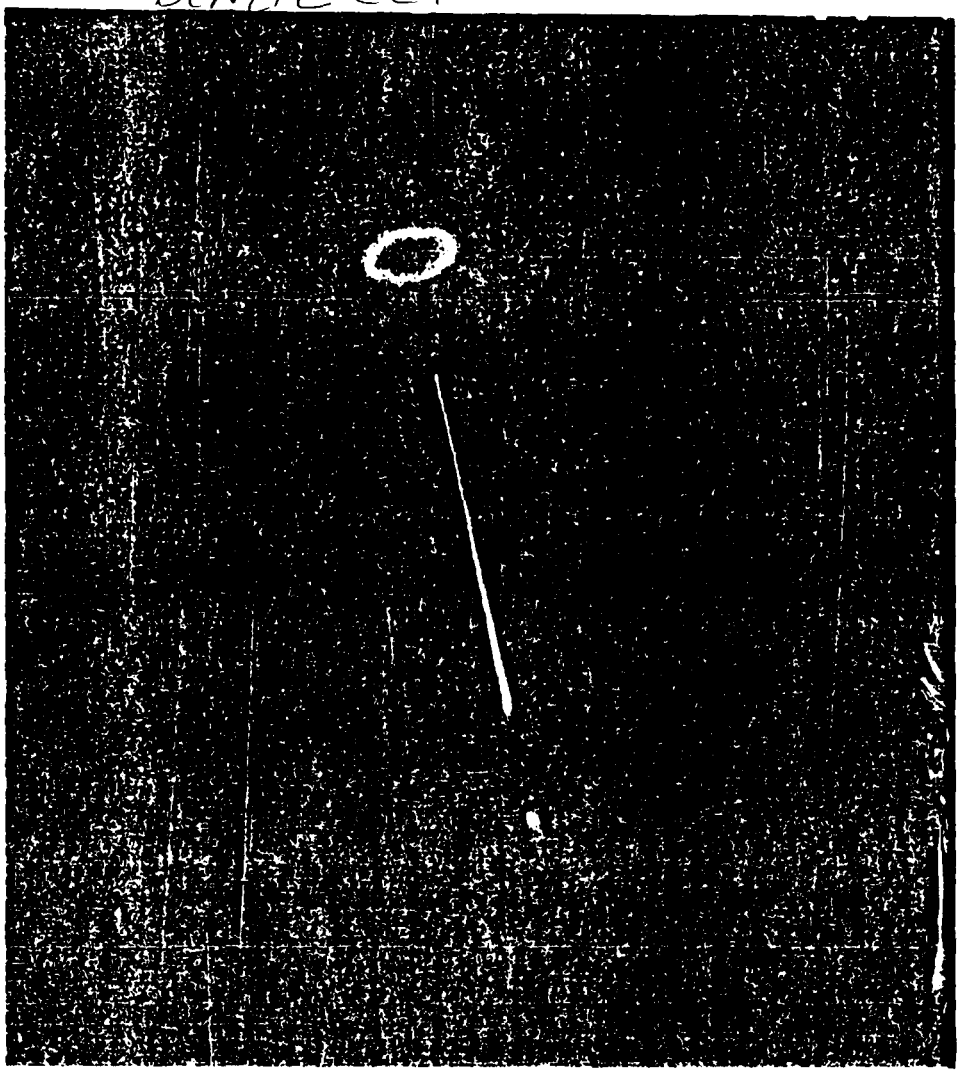



$$\cos\theta = \frac{n_e^{(\omega)}}{n_{cl}^{(2\omega)}}$$

$$\delta n = n_{cl}^{2\omega} - n_{cl}^{\omega} \geq \left[ n_e^{\omega} - n_{cl}^{\omega} \right]$$

- **Advantage: Relaxed phase-matching constraints on guide dimensions and dispersion**
- **Disadvantage: Efficiency $\alpha$ Fibre length**

RADIATION FILED SHG IN A BENZIL CCF



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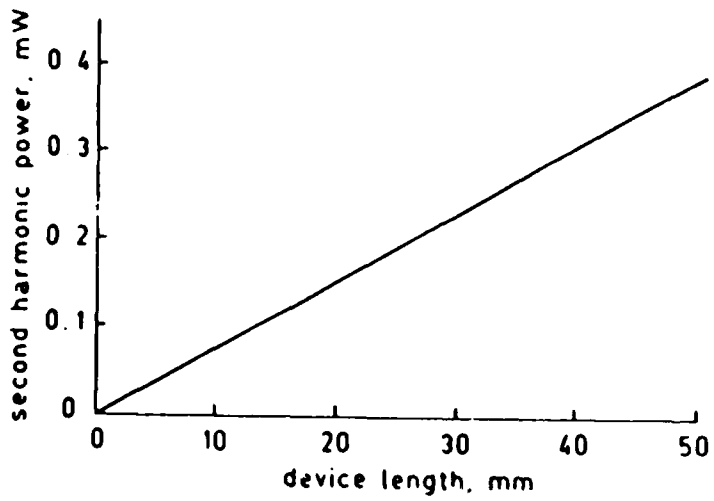
## EFFICIENCY OF RADIATION SHG

$P_f = 10mW$; $\lambda_f = 1.5\mu m$; $d = 250pm/V$; $n = 1.65$

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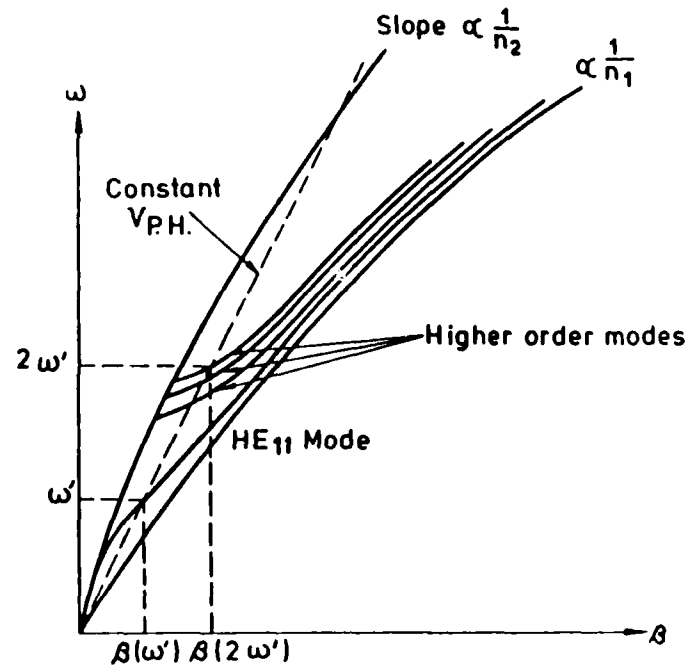
## PHASE-MATCHING FOR GUIDED WAVE SHG

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## PHASE-MATCHED SHG IN WAVEGUIDES

- **PUMP DEPLETION**

$$\eta = \tanh^2 \left[ \kappa \sqrt{P_{in}^{(\omega)}}\, L \right]$$

where

$$\kappa = \frac{\omega}{2} \epsilon_0 d_{im} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} E_{\nu}^{(\omega)} E_{\mu}^{(\omega)} . E_{\mu}^{(2\omega)} \, dx \, dy$$

- **For efficient SHG require optimistation of the "overlap integral".**

  - **Hence waveguide design**

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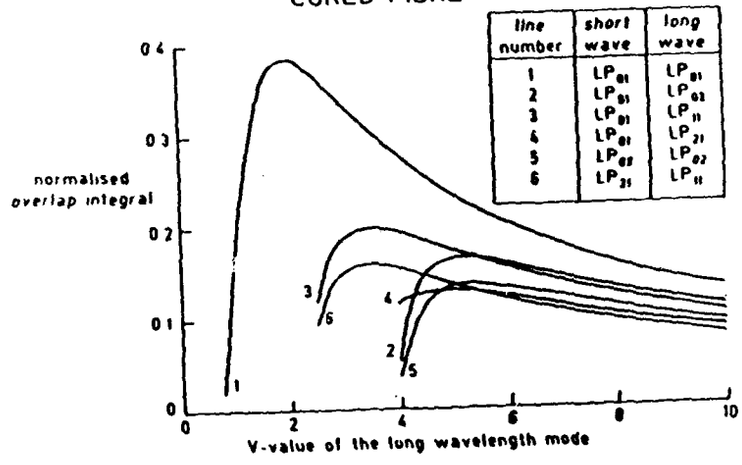
NORMALISED FIELD OVERLAP INTEGRAL IN A CRYSTAL CORED FIBRE




| line number | short wave | long wave |
|---|---|---|
| 1 | $LP_{01}$ | $LP_{01}$ |
| 2 | $LP_{01}$ | $LP_{02}$ |
| 3 | $LP_{01}$ | $LP_{11}$ |
| 4 | $LP_{01}$ | $LP_{21}$ |
| 5 | $LP_{02}$ | $LP_{02}$ |
| 6 | $LP_{21}$ | $LP_{11}$ |

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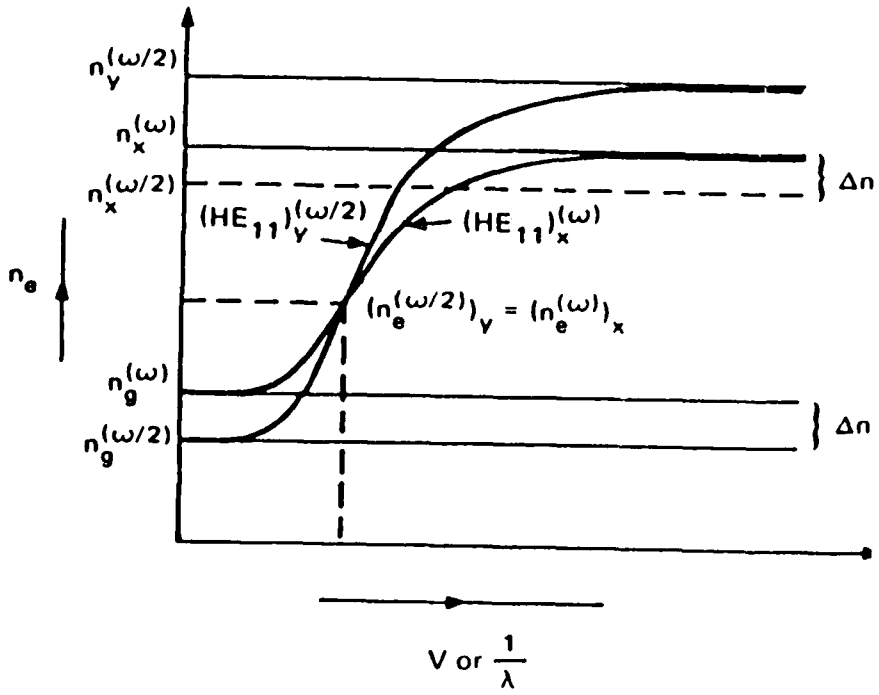
## SH PHASE-MATCHING BETWEEN THE LOWEST ORDER ORTHOGONAL MODES




## SH POLARISATION

$$\begin{bmatrix} P_x \\ P_y \\ P_z \end{bmatrix}_{2\omega} = \epsilon_0 \begin{bmatrix} d_{11} & \underline{d_{12}} & \underline{d_{13}} & d_{14} & d_{15} & d_{16} \\ \underline{d_{21}} & d_{22} & \underline{d_{23}} & d_{24} & d_{25} & d_{26} \\ \underline{d_{31}} & \underline{d_{32}} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \begin{bmatrix} E_x^2 \\ E_y^2 \\ E_z^2 \\ 2E_yE_z \\ 2E_zE_x \\ 2E_xE_y \end{bmatrix}_{\omega}$$

Q-26

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## USEFUL CRYSTAL CLASSES FOR PM-SHG BETWEEN LOWEST ORDER ORTHOGONAL MODES

| CRYSTAL SYSTEM | CLASS | COMMENTS |
|---|---|---|
| Triclinic | 1 | Any orientation |
| Monoclinic | m, 2 | Specific orientation & index requirements |
| Orthorhombic | mm2 | As above |
| Tetragonal | 4, 4 | z-axis transverse & -ve uniaxial |
| Trigonal | 3, 3m | As above |
| Hexagonal | 6, 6mm | As above |

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## GUIDED WAVE SHG IN A SUITABLY ORIENTATED mNA CCF

- Require: Y-axis parallel to the fibre axis

| Wavelength, nm | Refractive Index |
|---|---|
| 532 | $n_z = 1.7006$ |
| 1064 | $n_z = 1.6320$ |
| 1064 | $n_x = 1.7196$ |

- PM between lowest order orthogonal modes with $n_g = 1.66$ and $\Delta n_g = 0.0245$

Calculated 10% SHG efficiency with

$P_{in} = 1mW$; $L = 25mm$; Core dia $= 1.1\mu m$

Q-27

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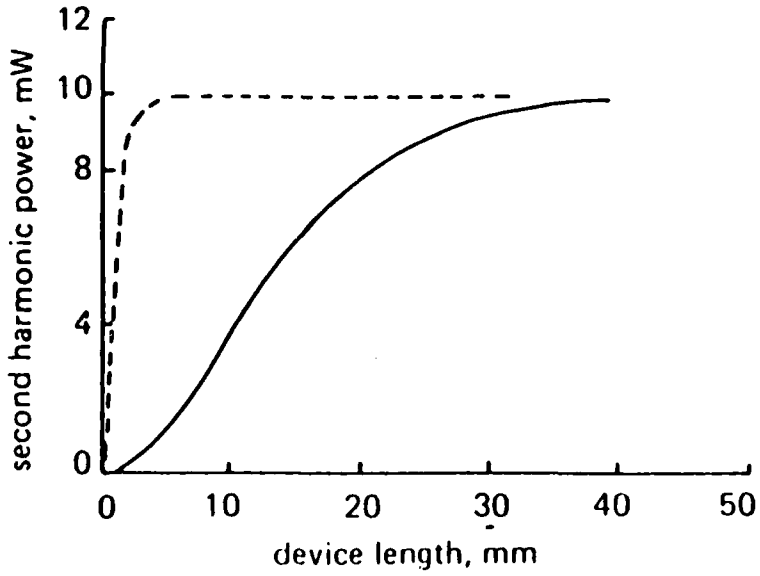
## SHG OUTPUT FOR THE $LP_{01}$ MODE IN A CRYSTAL CORED FIBRE

Fundamental Power: 10mW

$V = 2.0$; $\lambda_f = 1500$nm; $\Delta = 0.1$; $n = 1.65$

d(------) = 250pm/V; d(——) = 20pm/V

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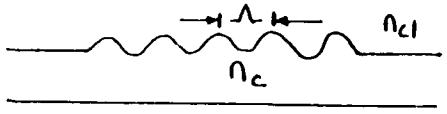
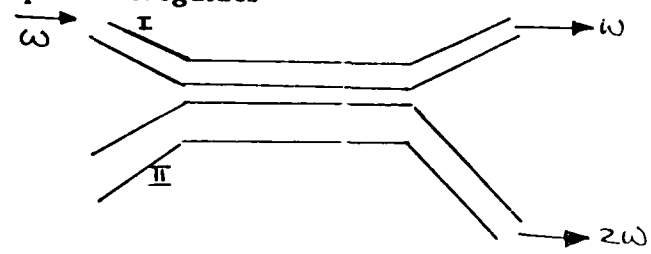
## PHASE-MATCHING SCHEMES FOR GUIDED WAVE INTERACTIONS

- Electro-optic/Temperature tuning
- Grating structures




$$\Delta\beta = \beta^{(2\omega)} - 2\beta^{(\omega)} = \frac{2\pi}{\Lambda}$$

- Coupled waveguides

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## ADVANTAGES OF CCF OPTICAL PARAMETRIC AMPLIFIER

- Independent of modulation format
- Independent of data bit rate
- Redundancy in pump lasers
- In-line device

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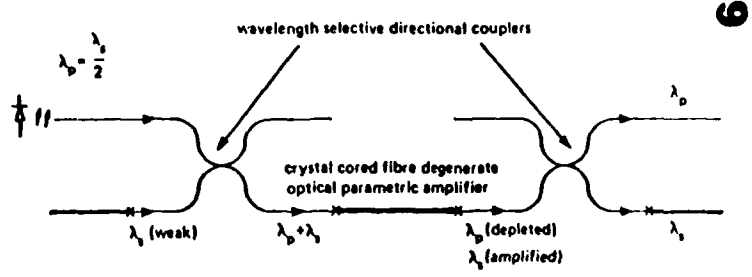
## A CCF ALL OPTICAL AMPLIFIER

GAIN = 40dB

With

$P_p = 10mW$; $d_{eff} = 250 \times 10^{-12} m/V$

V-value = 2.0; $\Delta = 0.1$; L=10mm

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## CONCLUSIONS

Semiconductor diode pumped nonlinear devices are feasible

CCF DEVICE REQUIREMENTS

- Higher transmission
  - — Defect/void free crystal growth
  - — Better end preparation
- Efficient device designs
- New materials

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R-1

M. Thakur

AT&T

# TOWARDS NONLINEAR OPTICAL APPLICATIONS OF POLYDIACETYLENES

# R-2

## TOWARD NONLINEAR OPTICAL APPLICATIONS OF POLYDIACETYLENES


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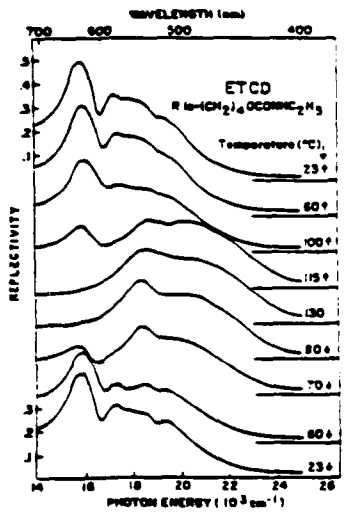
M. GOMEZ
H. TANAKA
A. TONELLI


## TOPICS

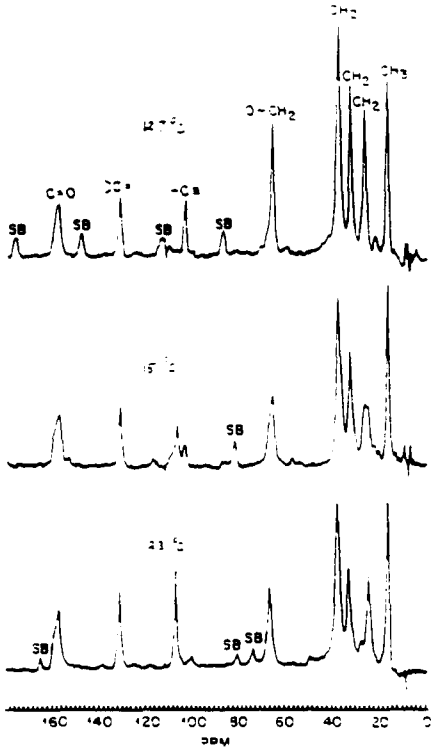
- MATERIALS ASSESSMENT
- GROWTH OF THIN SINGLE CRYSTAL FILMS
- FABRICATION OF DEVICE STRUCTURES
- DEMONSTRATION OF CHANNEL WAVEGUIDING
- INTENSITY DEPENDENT PHASE-MODULATION

## IMPORTANT PARAMETERS FOR MATERIALS SELECTION

- EXTENT OF CONVERSION (MONOMER → POLYMER)
- EXTENT OF CONJUGATION (PLANARITY)
- THERMAL STABILITY (THERMOCHROMISM)
- SOLUBILITY
- EASE OF CRYSTALLIZATION



# R-3




**$^{13}C$ Chemical Shifts of Polydiacetylenes**

$^{13}C$, ppm vs. TMS

| | C=O | >C= | -C≡ | α-$CH_2$ | β-$CH_2$, γ-$CH_2$ |
|---|---|---|---|---|---|
| ETCD (blue) | 157.5 | 131.6 | 107.4 | 37.3 | 24.5 |
| PTS-6 (blue) | — | 131.3 | 107.1 | — | — |
| PTS-12 (blue) | — | 131.0 | 106 | — | — |
| TCDU (blue) | — | — | 107.3 | — | — |
| ETCD (red) | 158.3 | 132.0 | 103.6 | 37.8 | 26.4 |
| TCDU (red) | 155.8 | 131.5 | 102.9 | 37.9, 32.3 | 25.9, 21.8, 28.0, 30.8 |
| ETCD (melt) | 158.1 | 130.8 | 102.5 | 37.3 | 27.2 |

## CONCLUSIONS FROM NMR STUDIES

- **THE CONJUGATION LENGTH IS DETERMINED BY THE EXTENT OF PLANARITY OF THE CHAIN-BACKBONE.**
- **INCREASE OF CHAIN LENGTH DOES NOT GUARANTEE INCREASE OF CONJUGATION LENGTH.**
- **THE ACETYLENIC FORM IS PREDOMINANT IN POLYDIACETYLENES INDEPENDENT OF PHASES.**

# R-4

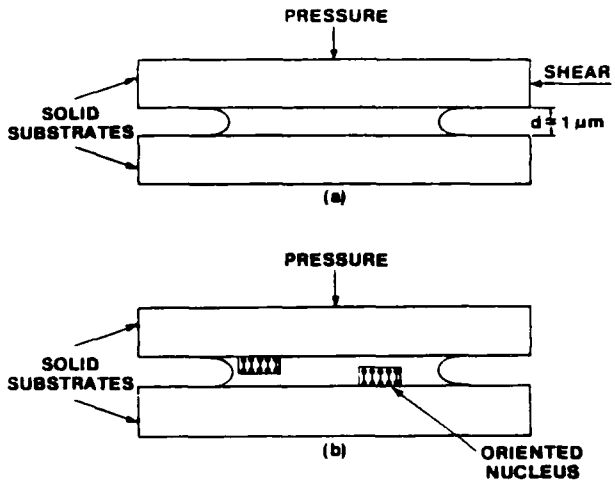
## GROWTH OF SINGLE THIN FILM CRYSTALS

- THE SHEAR METHOD

  ORIENTATIONAL PRINCIPLES
  REQUIREMENTS ON MOLECULAR SHAPE
  GROWTH PARAMETERS
  CONTROL OF THICKNESS
  OPTICAL QUALITY OF FILMS

- COMPARISON WITH THE L-B METHOD

- ASSESSMENT OF APPLICABILITY



SPREADING COEFFICIENT

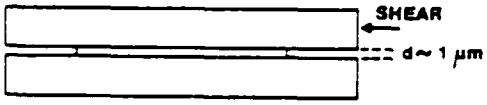
$$S_{B/A} = \gamma_A - \gamma_B - \gamma_{AB}$$

$$= W_{AB} - W_{BB}$$

$\gamma$ = SURFACE TENSION
$W_{AB}$ = WORK OF ADHESION
$W_{BB}$ = WORK OF COHESION

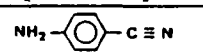
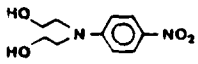
FOR SPONTANEOUS SPREADING

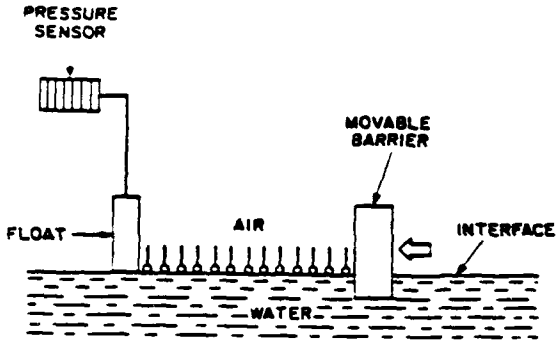
$$S_{B/A} > 0$$

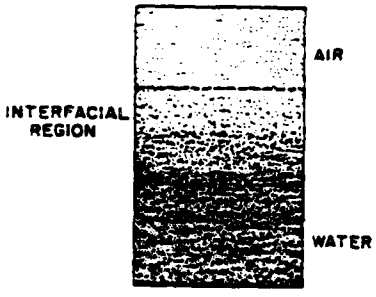



TOTAL SHEAR $T = T_{cap} + T_{ext}$
LATERAL PRESSURE $P \sim 10^7$ DYNES/cm$^2$
EQUILIBRIUM SPREADING PRESSURE OF A MONOLAYER
$P_{mono} \sim 10^7$ DYNES/cm$^2$

## COMPARISON OF THE CALCULATED MOLECULAR LENGTHS WITH THE OBSERVED d-SPACINGS

| MATERIALS | CALCULATED LENGTH L (Å) | COMPENSATED LENGTH L sinφ (Å) | d-SPACINGS OF 1ST ORDER REFLECTIONS (Å) |
|---|---|---|---|
| RC ≡ C — C ≡ CR WITH R | | | |
| 1. — $CH_2$ OH | ~8.1 | 8.1 | 8.05 |
| 2. — $(CH_2)_4$ OCONH $C_2H_5$ | ~17.9 | 17.9 | 17.87 |
| 3. — $(CH_2)_4$ OCO NH $C_6H_5$ | ~19.5 | 19.5 | 18.94 |
| 4. — $CH_2$ $OSO_2$ $C_6$ $H_4$ $CH_3$ | ~14.8 | 12.9 | 12.87 |
| 5. — $(CH_2)$ OCO NH $CH_2COOC_4H_9$ | ~26.9 | 26.9 | 26.80 |
|  | ~8.0 | 8.0 | 8.40 |
|  | ~10.5 | 10.5 | 10.05 |




## COMPARISON OF THE L-B AND THE SHEAR METHOD

- POLAR INTERACTIONS HAVE IMPORTANT ROLES IN BOTH THE METHODS.
- IN THE L-B TECHNIQUE A LIQUID IS USED AS THE SUBSTRATE. IN THE SHEAR METHOD SOLID SUBSTRATES ARE UTILIZED.
- THE L-B METHOD APPLIES TO AMPHIPHILIC MOLECULES ONLY. THE SHEAR METHOD IS APPLICABLE TO A BROADER RANGE OF MOLECULES.
- THE L-B METHOD PROVIDES ORDER ALONG ONE DIRECTION ONLY. THE SHEAR METHOD LEADS TO 3-D ORGANIZATION.
- THE L-B FILMS HAVE MICRO-DOMAIN MORPHOLOGY (POOR OPTICAL QUALITY).
  THE SHEAR-GROWN FILMS ARE UNIFORM SINGLE CRYSTALS (EXCELLENT OPTICAL QUALITY).

## INTENSITY DEPENDENT PHASE MODULATION

$$n = n_0 + n_2 I$$

$$\Delta\phi = \frac{2\pi}{\lambda} n_2 I L \,, \quad L = \text{LENGTH OF PROPAGATION}$$

$\Delta\phi$ = PHASE SHIFT

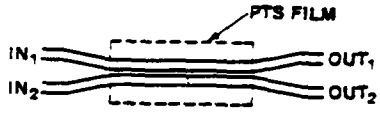
FOR $\lambda \sim 0.8$ TO $2.0\,\mu$

$n_2$ OF PTS $\sim 7 \times 10^{-6}$ cm$^2$/MW (HERMANN AND SMITH, 1980)

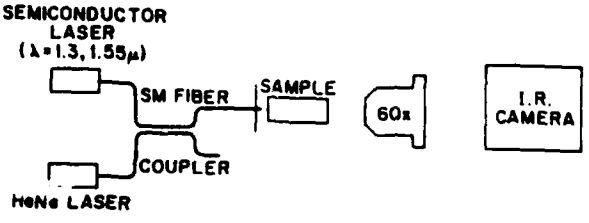
IF OPTICAL PULSES ($\lambda \sim 1\,\mu$) OF PEAK POWER $\sim$ 500 mW ARE FOCUSSED ON A CROSS-SECTION $\sim 1\,\mu m^2$

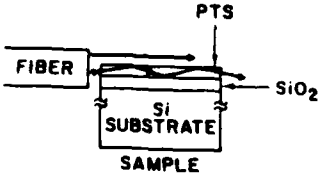
$\Delta\phi \longrightarrow \pi$

FOR L $\sim$ 1.4 mm.

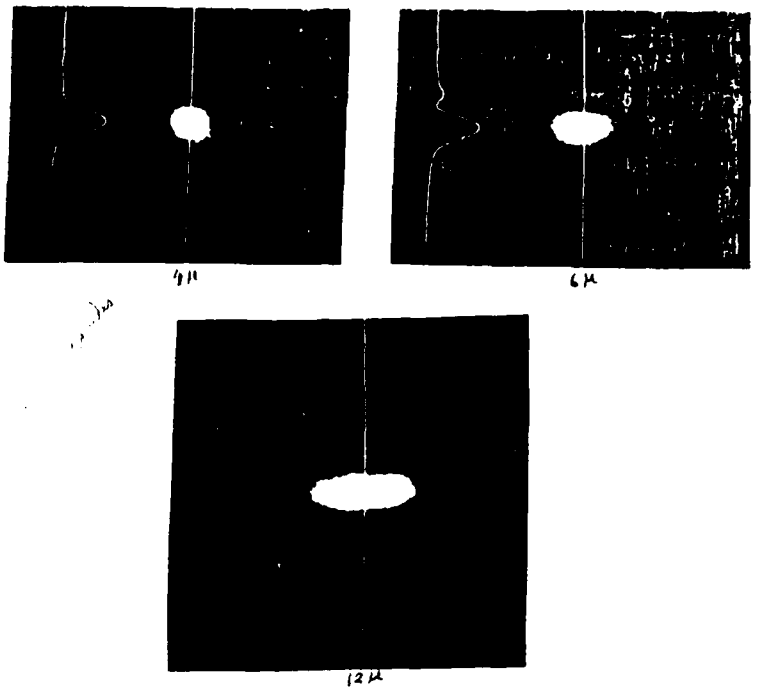



WITH SUBPICOSECOND PULSES
ENERGY REQUIREMENT < 1 pj/bit.
THE DATA-RATE THAT THE DEVICE COULD HANDLE $\sim$ 1 THz
NONABSORPTIVE $\longrightarrow$ NO THERMAL DAMAGE.



# R-6




## SUMMARY

- A COMPARATIVE EVALUATION IS MADE FOR DIFFERENT POLYDIACETYLENES IN RELATION TO NLO DEVICE APPLICATIONS.
- $C^{13}$ – NMR RESULTS SHOW THAT THE CONJUGATION LENGTH IS DETERMINED BY THE EXTENT OF PLANARITY OF THE CHAIN BACKBONE AND NOT BY THE CHAIN LENGTH.
- THE ORIENTATIONAL PRINCIPLES OF THE SHEAR METHOD ARE DISCUSSED IN COMPARISON WITH THE L-B TECHNIQUE.

## SUMMARY (Cont.)

- THE SUPERIORITY OF THE SHEAR METHOD IN PROVIDING GOOD OPTICAL QUALITY SINGLE CRYSTAL FILMS OF CONTROLLED THICKNESS AND ORIENTATION IS DEMONSTRATED WITH MANY EXAMPLES.
- CHANNEL WAVEGUIDING IS DEMONSTRATED (PROPAGATION > 5 mm) FOR SHEAR-GROWN PTS FILMS.
- PRELIMINARY RESULTS OF INTENSITY DEPENDENT PHASE CHANGE IN PTS WAVEGUIDES ARE DISCUSSED.

D. Haarer
Universitat Bayreuth, West Germany

# HIGH RESOLUTION LASER SPECTROSCOPY IN POLYMERS

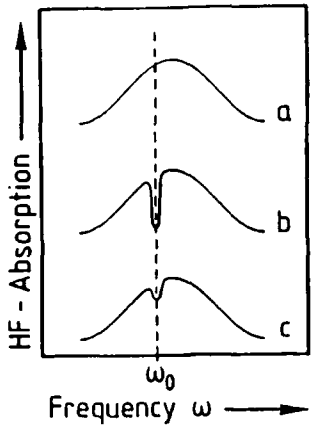



**Fig.3.1.** Local saturation of an NMR line at the frequency $\omega_0$ (a) before, (b) during, and (c) after irradiation at $\omega_0$ [3.1]

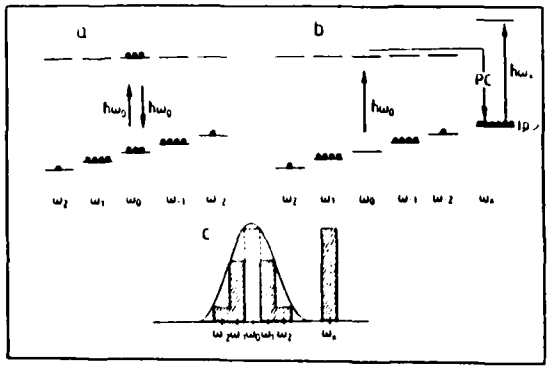



**Fig.3.2.** (a)Radiation saturation of an ensemble of five optical two-level systems at the center frequency $\omega_0$. (b) *Photochemical bleaching of an ensemble of five two-level* systems at the center frequency $\omega_0$. Creation of a photoproduct state absorbing at the frequency $\omega_L$. (c) Absorption after photochemical bleaching as described in Fig 3.2b. The photoproduct shows up at the frequency $\omega_L$

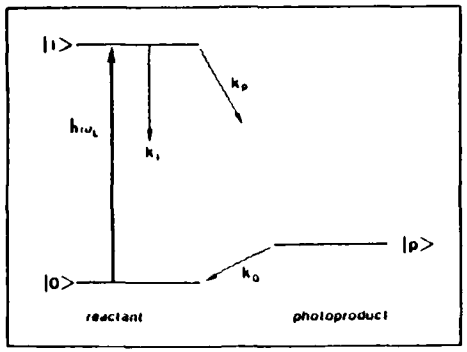



**Fig.3.3.** Three-level system with the reactant levels $|0\rangle$ and $|1\rangle$ and the photoproduct level $|p\rangle$. $K_1$, $K_p$ and $K_0$ are the decay rate constants of the various states. $\omega_L$ is the hole-burning frequency

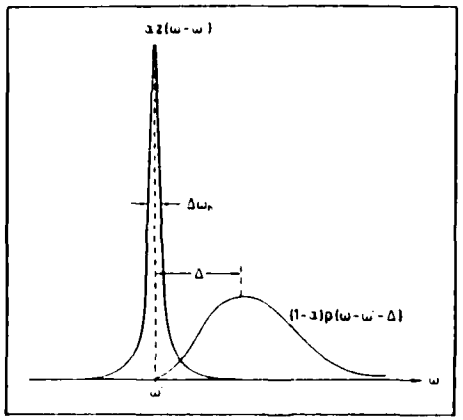



**Fig.3.4.** General lineshape function of an electronic excitation of a guest molecule in a solid host matrix: Schematic view of a zero-phonon line and its phonon sideband. The phonon sideband has an intensity of $(1-\alpha)$ and is displaced by the lineshift parameter $\Delta$. The latter corresponds to half the "Stokes shift"

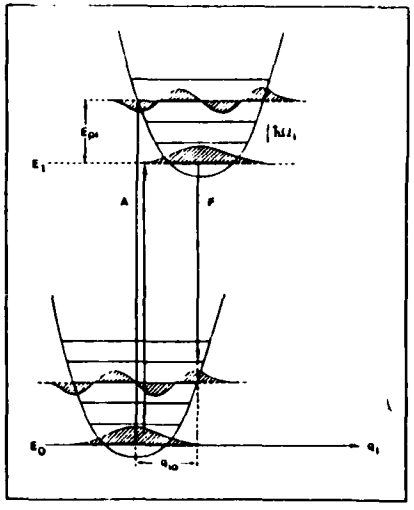



Fig.3.5. Energy diagram for interpreting phonon side-band spectra in terms of the excited state displacement $q_{10}$. The phonon frequency is $\Omega_1$. The figure shows a zero-phonon and a three-phonon transition in absorption (A) and emission (F), respectively

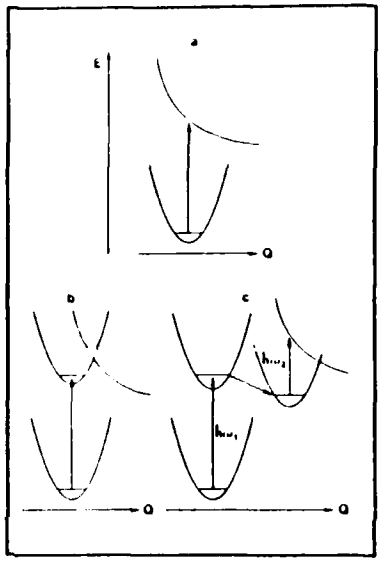



Fig.3.6a-c. Photochemical reaction schemes plotted as a function of one configurational coordinate Q. (a) Repulsive exciplex-like state. (b) Level-crossing from a "quasi-stable" excited state. (c) Two-photon reaction with photon energies $\hbar\omega_1$ and $\hbar\omega_2$. The level which absorbs the photon $\hbar\omega_2$ is a long-lived intermediate state

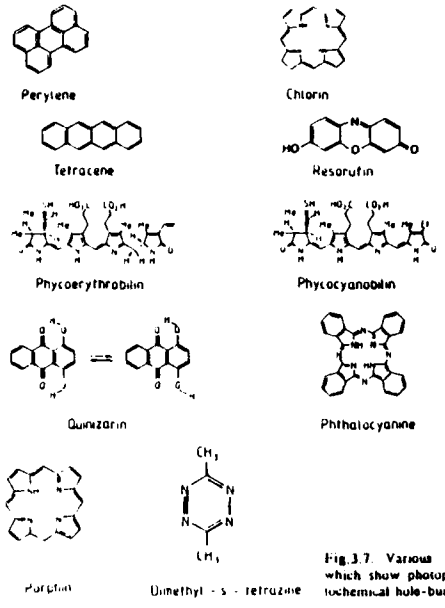



Fig.3.7. Various dye molecules which show photophysical and photochemical hole-burning

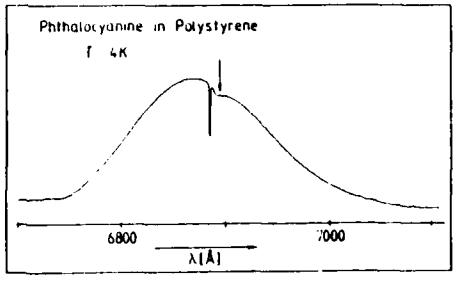



Fig.3.8. Experimental hole spectrum of phthalocyanine in polystyrene at 4 K. The pseudo-phonon wing is marked by the wavy arrow

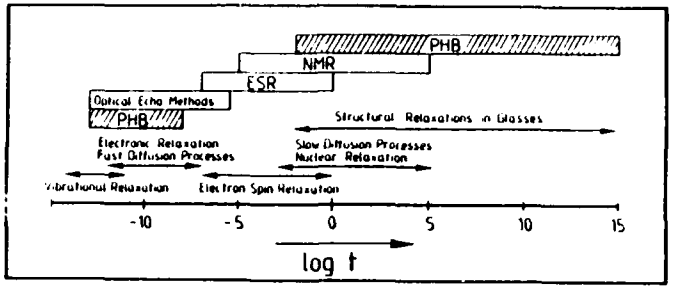



Fig.3.9. Logarithmic scale of relaxation times and of methods of measuring characteristic time constants. Hole-burning is especially well suited for very short and very long relaxation times (see text)

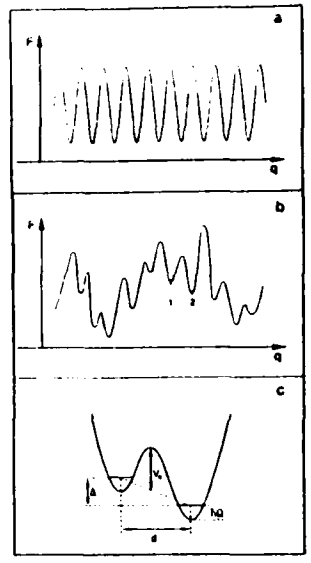



Fig.3.10. (a) Periodic potential of a crystalline solid. (b) Potential along a fictitious coordinate q of a glass: Note the lack of periodicity. (c) Idealized two level scheme with the two parameters $\Delta$ and $V_0$ (see text). The oscillators in the two wells are separated by the distance d and have a zero-point frequency on the order of $\Omega$

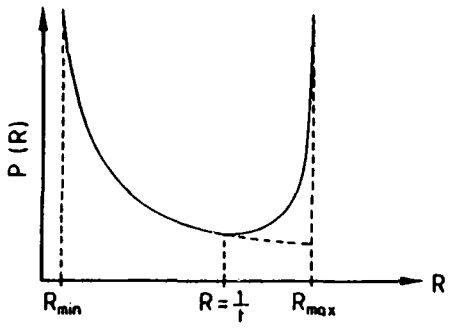



Fig.3.11. Rate distribution as calculated by *Jäckle* [3.98]. For the definition of the two limiting rates $R_{min}$ and $R_{max}$ see text

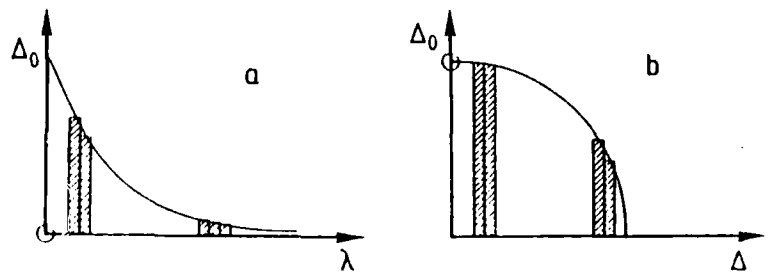



Fig.3.12. Functional dependence of the tunnelling matrix element $\Delta_0$ on the TLS-parameters $\lambda$ (Fig.3.12a) and $\Delta$ (Fig.3.12b) (see text)

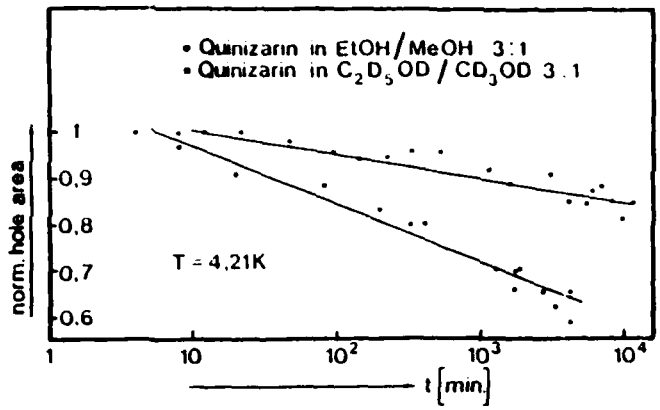



Fig.3.13. The decay of the area of photochemical holes of quinizarin in alcohol glass for deuterated (*squares*) and protonated systems (*dots*)

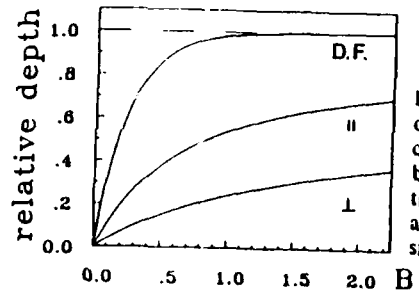



Fig.3.15. Dependence of the relative depth of a photochemical hole on the irradiated light dose B. The upper curve shows the maximally bleached distribution function with a polarization factor of unity. The two curves with parallel and perpendicular polarization are also shown [3.40]

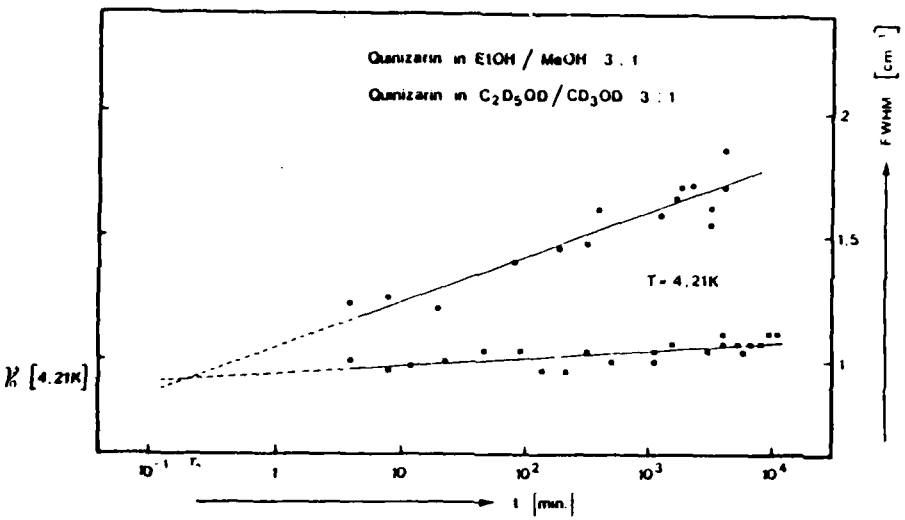



Fig.3.14. Line broadening of the photochemical holes of quinizarin in alcohol glass for deuterated (*squares*) and protonated systems (*dots*)

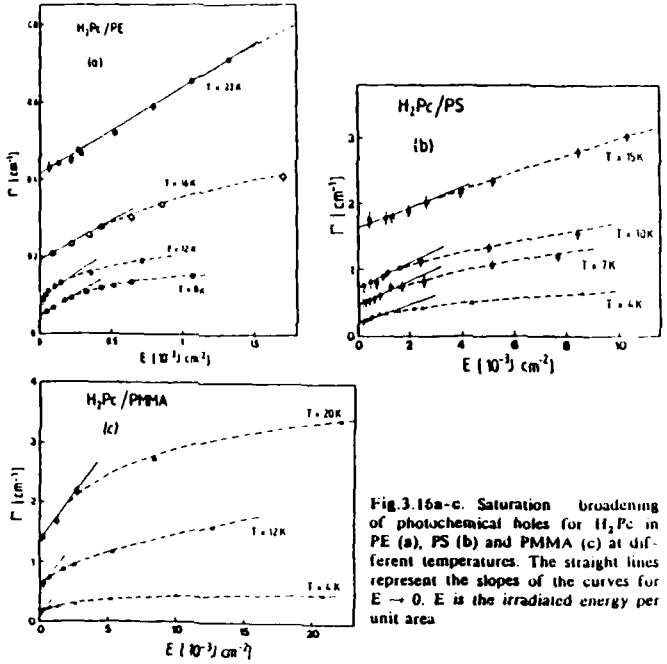



Fig.3.16a-c. Saturation broadening of photochemical holes for $H_2Pc$ in PE (a), PS (b) and PMMA (c) at different temperatures. The straight lines represent the slopes of the curves for $E \to 0$. E is the irradiated energy per unit area

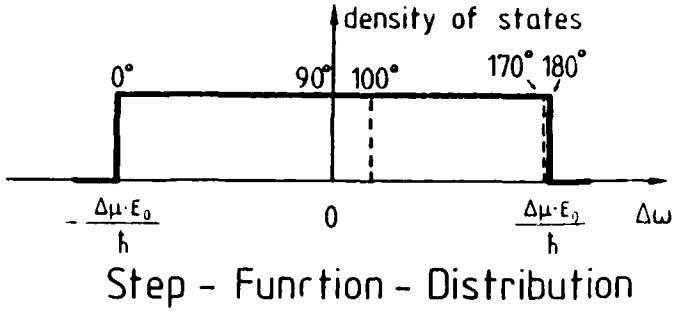



**Fig.3.17.** Distribution function of the absorption frequencies of guest molecules in an electric field $E_0$. All molecules absorb at the 0-frequency for $E = 0$; they have identical dipole moment changes $\Delta\mu$ but are oriented randomly with respect to the external E-field. The numbers indicate the orientation angles for some representative frequency shifts

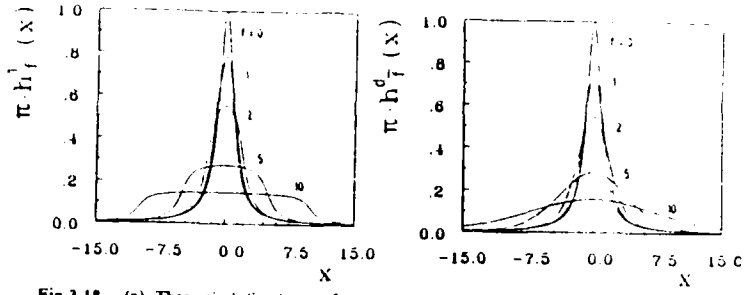
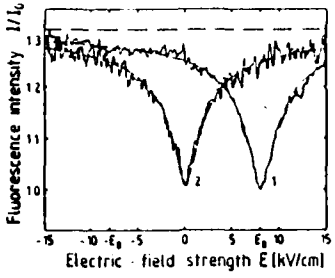



**Fig.3.18.** (a) Theoretical lineshape of a spectral hole for different external field strengths f. All absorbers have the same $\Delta\mu$ value. For a field value of $f = 1$, the Stark broadening equals the linewidth. (b) The same calculations as a) with a Gaussian distribution of $\Delta\mu$ values



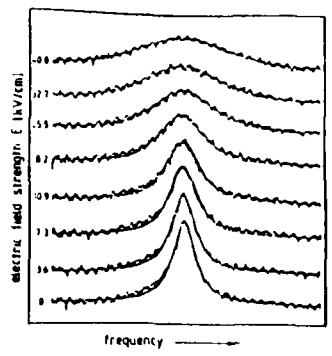




**Fig.3.19.** Fluorescence excitation spectra of two holes. One spectrum was burned at E = 0 and one was burned at the field $E_B$ [3.123]

**Fig.3.20.** Measured and calculated hole profiles for the system Zn-TBP $(C_6H_4CH_3)_4$ in polyvinylbutyral (see [3.124]). Here the average change in dipole moment is $\Delta\mu = 0.174$ Debye units

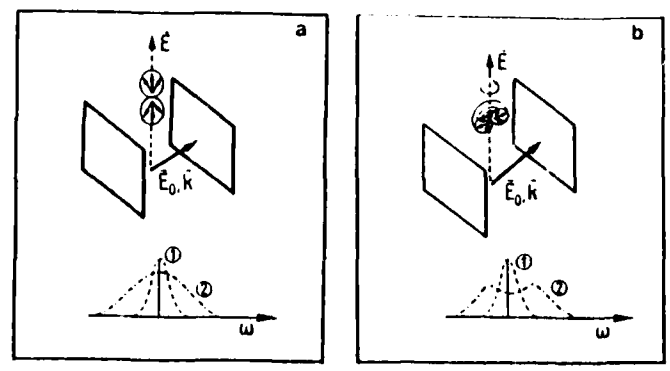



**Fig.3.21.** Dipolar $\Delta\mu$ configurations for $\Delta\mu$ parallel (a) and perpendicular (b) to the transition dipole moment. $E_0$ is the electric field strength and k is the wave vector of the incident light

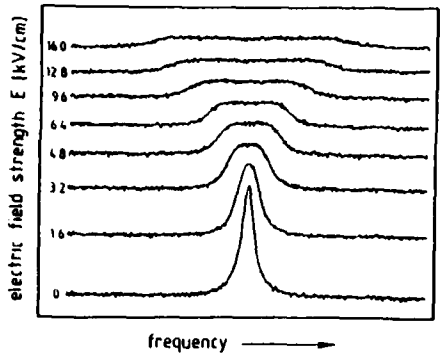
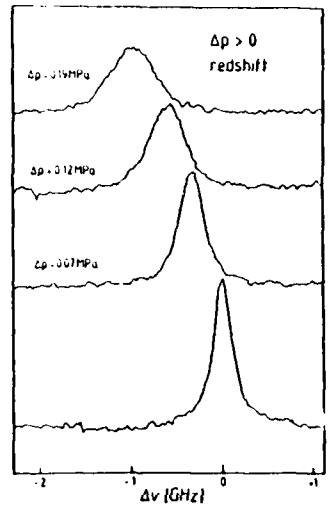



Fig.3.22. Measured and calculated hole profiles for $H_2Ch$ in polyvinylbutyral [3.124]. Here the calculated $\Delta\mu$ value is $\Delta\mu = 0.214$ Debye units



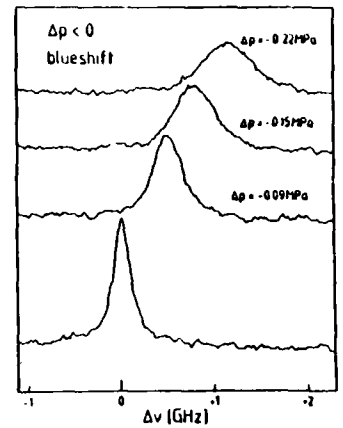




Fig.3.23a,b. Line shift of the molecule $H_2Pc$ in polyethylene for positive (a) and negative (b) pressures

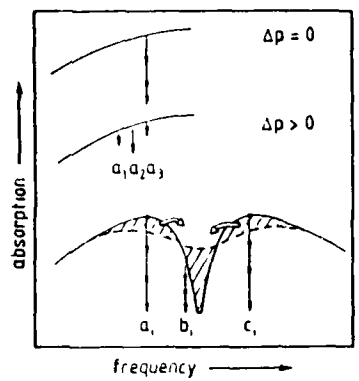



Fig.3.25. Line broadening of sites which had been site-selected at $\Delta p = 0$ and which drift apart at higher pressures $\Delta p \neq 0$. At higher pressures the frequency range of the absorbers extends from $a_1$ to $a_2$. The lower part of the figure shows the line broadening for various sets of molecules $a_i$, $b_i$ and $c_i$

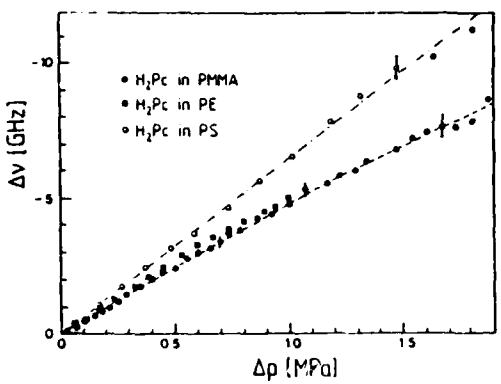



Fig.3.24. Line shifts of $H_2Pc$ in PS, PE and PMMA in the low pressure regime

# POSTER SESSION ABSTRACTS

**Optical Kerr Measurements on some Ferrocene Derivatives.**

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We report here preliminary results from a study of the third order non-linearities in a range of organo-metallic compounds. These initial measurements have been carried out carried using the optical power limiter technique developed by Soileau *et al* [1], where the critical power for self-focusing is measured and used to calculate $n_2$. The materials measured were solutions of ferrocene in ethanol, varying from $10^{18}$ to $10^{19}$ molecules/cc and a liquid ferrocene derivative, bis(trimethylsilyl)ferrocene. A value of $\gamma$ for ferrocene of $4.1 \times 10^{-34}$ esu was found for the solution studies, in good agreement with that measured for the liquid derivative of $4.6 \times 10^{-34}$ esu . The experiments were carried out at 1.06 $\mu$m with 10 ns pulses. We are currently repeating the measurements using other techniques and shorter pulses to distinguish the various possible contributions to the observed $n_2$.

(1) M.J.Soileau, W.E.Williams and E.W.Van Stryland;IEEE J Quant Elect.,QE-19,(1983),731.

# Theoretical models for the second hyperpolarizability of novel conjugated polymers

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Theoretical models will be presented for the chain length dependence of the second electronic hyperpolarizability of simple polyenes, simple polyynes, and more complicated unsaturated organic materials. The hyperpolarizability of conjugated polymers which incorporate novel localized electronic states will be described as well. These materials present the possibility of achieving enhanced hyperpolarizabilities due to mixing of appropriate "gap states" with the delocalized states of the conjugated polymer. They also present the possibility of designing materials with "switchable" hyperpolarizabilities.

# NONLINEAR OPTICAL PROPERTIES OF TRANSITION METAL POLY-YNES

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Data from third harmonic generation (with a 1.06-μm fundamental), power limiting and four-wave mixing measurements of solutions and films of transition metal poly-ynes were used to verify that these compounds have large third-order optical susceptibilities. The large third-order nonlinearities observed in four-wave mixing studies of metal poly-yne solutions may originate, in part, from contributions from the real and imaginary components of intense two-photon absorptions associated with the metal-organic compounds. We will discuss our latest four wave mixing experiments and the direct observation of two-photon absorption in metal poly-ynes.

We will also discuss the correlation of polymer chain length and structure with third-order hyperpolarizability per repeat unit for several metal polymers and oligomers.

# REVERSE SATURABLE ABSORBERS: INDANTHRONE AND ITS DERIVATIVES

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Indanthrone has been shown to exhibit the phenomenon of reverse saturable absorption.[1] The wavelengths at which indanthrone behaves in this fashion can be changed by structural modification of the indanthrone chromophore. The derivatives which have been synthesized have been shown to be more efficient reverse saturable absorbers than the parent chromophore.

It is advantageous to extend the range of nonlinear behavior to any desired portion of the spectrum, and this is best accomplished by substitution on the aromatic portion of the indanthrone molecule. We have demonstrated that oxidized indanthrone, monochloroindanthrone and an oligomer of indanthrone are more efficient saturable absorbers than the parent. Oxidized and monochloro-indanthrone exhibit reverse saturable absorption at both 1064 nm and 532 nm, whereas indanthrone itself exhibits the phenomenon at 532 nm only. The oligomer, which consists of three anthraquinone units, has proved to be an efficient reverse saturable absorber at 1064 nm as well as at 532 nm.

[1]C. R. Giuliano and L. D. Hess, IEEE J. Quantum Elec. QE-3, 338 (1966).

This work was supported in part by the Dept. of the Navy under Contract No. N00039-87-C-5301.

THE PREPARATION AND CHARACTERIZATION OF POLYMERIC MATERIALS WITH ENHANCED SECOND ORDER NONLINEARITIES. M.L. Schilling, H.E. Katz, D.I. Cox, AT&T Bell Laboratories, Murray Hill, NJ 07920.

We have recently introduced a new class of organic materials for second order nonlinear optics, consisting of poled films of dye-containing polymers. In the past year, some uncommon functional groups (di- and tricyanovinyl) have been shown to enhance the molecular susceptibilities of the nonlinear moieties when used instead of their more usual counterparts. Dyes with enhanced nonlinearities by virtue of the cyanovinyl substituents have been exploited in the preparation of bulk materials with some of the highest second order susceptibilities yet reported.

The synthesis of conformationally defined dye aggregates, whose subunit dipoles are constrained to be additive, is in progress. These dyes can then be incorporated into polymeric materials, taking advantage of their enhanced effective dipole moments for increased orientation in poling experiments. We will report some of the new synthetic organic chemistry that has been utilized in preparing our latest electro-optical materials.

# Second Harmonic Generation in Doped Glassy Polymer Films as a Function of Physical Aging

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Northwestern University

Evanston, Illinois

March 31, 1988

## ABSTRACT

The temporal stability of second harmonic generation (SHG) intensity is measured in poly(methyl methacrylate) (PMMA) and bisphenol-A-polycarbonate (PC) doped with nonlinear optical dyes in electric field poled films. Doped PC films show slower SHG decay than doped PMMA films at times less than 8 hours. In PC+DANS films aged 10 hours at 25°C, there is no SHG decay over the first 8 hours, whereas in PMMA+DANS aged at 25°C and at 60°C the effect is much smaller. Two dopants show the effect of size on SHG decay, with the larger dopant showing increased temporal stability. Good agreement is obtained when decay curves are fit using a Williams-Watts stretched exponential.

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# ELECTRO-OPTIC, POLYMER CLAD, E-FIELD SENSOR

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**Abstract**

There is a military need for sensor systems that combine high sensitivity, immunity to EMI/RFI, large bandwidth, and low power and cost. The hybridization of present day electronic components with optical components offers the promise of sensor systems that meet these requirements.

Unisys has been developing a PVDF-coated fiber optic, electric field sensor and now has expanded its program to include nonlinear organic polymers as cladding and waveguide material. This paper will report on progress using Guest/Host (GH) polymers as cladding material.

The concept of an all dielectric high frequency sensor is demonstrated. The sensor consists of a $Ag^{+}$ exchange waveguide coated with a GH nonlinear polymer glass. The sensor is incorporated into one arm of a Mach-Zender interferometer and exhibits a figure of merit of 4 microradians/volt/meter/meter. The frequency response is flat from DC to our current instrumentation limit of 5 MHz.

This sensor design was chosen primarily as a vehicle that would allow an easy method to test and verify design parameters for fiber sensor systems. These parameters include index and depth of guide vs. index, thickness and E-O coefficients of the cladding. We will present a comparison of the results of this sensor with those from the PVDF sensor program.

# MOLECULAR CONFORMATION AND THE STABILITY OF TICT STATE IN P,P'-DISUBSTITUTE-1,6-DIPHENYL-1,3,5-HEXATRIENES

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## ABSTRACT

The p,p'-disubstituted linear diphenyl polyenes are expected to have a high optical nonlinear susceptibility because of its large permanent dipole moment induced by the substituents. The photophysical properties for a series of p,p'-disubstituted-1,6-diphenyl-1,3,5-hexatrienes (referred as D,A-DPH) are investigated, where D and A are the electron-donating and - accepting groups of $-OCH_3$, $-N(CH_3)_2$ and $-NO_2$. In all solvents used, a dual fluorescence is observed for D,A-DPH containing the internal rotation groups of $-N(CH_3)_2$ and/or $-NO_2$, suggesting that the "a*" fluorescence (the locally excited state gives the normal "b*" fluorescence) is originated from a twisted intramolecular change transfer (TICT) state. The stability of TICT state is sensitive to the D and A substituents and their relative twisting angles. The observed results provide the evidence of the $\pi$-electron distortion and thus the enhancement of optical nonlinearity in this class of molecules.

# Second and Third – Order Nonlinear Optical Properties of End – Capped Acetylenic Oligomers

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We have been investigating the second and third – order nonlinear optical properties of a variety of acetylenic oligomers. A series of symmetric acetylenic oligomers of the form

$$R-(C\equiv C)_n-R \qquad \text{I}$$

have been investigated for third – order nonlinear susceptibility. A series of new compounds of the form

$$D-(C\equiv C)_n-A \qquad \text{II}$$

where D and A are electron donor and acceptor groups, respectively, have been synthesized and investigated for second – order nonlinearity. Third – order nonlinear susceptibilities of series I molecules in solution have been measured using third harmonic generation (THG). THG susceptibilities at 1064 nm have been determined for various oligomer lengths and end – capping groups. X(3) increases with length and varies with the nature of the end – group. Series II compounds have been screened for second harmonic generation by using the Kurtz powder method. Several samples show SHG efficiencies comparable to urea. Characterization of molecular hyperpolarizabilities for the series is in progress.

# Optical Field Induced Scattering in Polymer Dispersed Liquid Crystal Films

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Kent State University
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## ABSTRACT

We report observations of optical field induced scattering in polymer dispersed liquid crystal films due to reorientation of the liquid crystal molecules by the optical field of a CW argon ion laser. These composite materials consist of nearly spherical liquid crystal droplets dispersed in a polymer binder. As previously reported [1,2,3], films of these materials may be switched from an opaque scattering state to a clear transparent state by application of a d.c. or low frequency a.c. electric field. An applied low frequency electric field is used to align the liquid crystal in an orientation such that the refractive index of the liquid crystal within the droplet is matched with that of the polymer binder. If a sufficiently intense optical field is applied to the transparent film, it will reorient the liquid crystal director, and give rise to a refractive index mismatch and hence scattering.

1. J.W. Doane, N.A. Vaz, B.-G. Wu and S. Zumer, App. Phys. Lett. 48, 269 (1986).

2. J.L West, Mol. Cryst. Liq. Cryst. (in press).

3. S. Zumer and J.W. Doane, Phys. Rev. A 34, 3373 (1986).

**FABRICATION OF WAVEGUIDE STRUCTURES FROM SOLUBLE POLYDIACETYLENES.** **G.L. Baker, N.E. Schlotter, J.L. Jackel, P. Townsend, S.Etemad, Bell Communications Research, Red Bank NJ 07701.**

Thin waveguide structures were fabricated from spun films of poly(3-BCMU) and poly(4-BCMU) by two separate processes. In the first, micron-sized features were patterned in polydiacetylene films using deep-UV lithography. This multilayer process utilizes a novel silicon-substituted polyacetylene as the resist layer, and can be used to generate sub-micron sized features in thick (>1$\mu$m) polydiacetylene films.

In the second method, composite waveguides were fabricated from a patterned glass substrate and an overlayer of the polydiacetylene. These composite structures are relatively simple to prepare and are mechanically robust. Guides constructed as described above performed well with minimal losses and single-moded behavior at laser wavelengths of 1-1.5 $\mu$m.

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