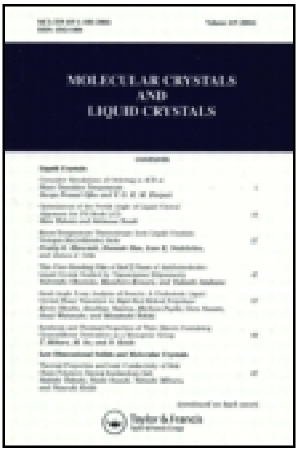

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Nonlinear Optical Polymer Systems and Devices

Donald R. Ulrich [a]

[a] Directorate of Chemical and Atmospheric Sciences, Air Force Office of Scientific Research, Bolling Air Force Base, Washington, D.C., 20332

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Nonlinear Optical Polymer Systems and Devices

DONALD R. ULRICH

Directorate of Chemical and Atmospheric Sciences, Air Force Office of Scientific Research, Bolling Air Force Base, Washington, D.C. 20332

Commercial and military interest in nonlinear optical (NLO) materials is being driven by the development of fiber optics, laser diodes, optical signal processing and optical computing. Active materials for optical modulation, routing and amplification are in high demand for optical communication and information processing technologies. Currently available materials, which include inorganic oxide crystals such as Lithium Niobate, $LiNbO_3$, bulk semiconductors, multiple quantum wells, and photorefractive and liquid crystal materials, lack several of the critical requirements for the implementation of practical, working systems.

The use of polymers for nonlinear optical processes is gaining increased attention, particularly over the past year, because of the ability to tailor molecular structures which have inherently fast response times and large second and third order molecular susceptibilities. Polymers provide synthetic and processing options that are not available with the other classes of NLO materials as well as excellent mechanical properties, environmental resistance and high laser damage thresholds.

This paper reviews the status of polymers for nonlinear optical applications. In essence it reviews in part the Air Force Office of Scientific Research program in NLO Polymers, initiated in 1982, and draws upon some of the most recent work impacting this area. Although the dominant work has been carried out in organic polymers, inorganic polymers have also been shown to possess interesting NLO responses.

ORIGIN OF NLO RESPONSE IN POLYMERS

Figure 1 shows the fundamental relationships for the molecular and macroscopic nonlinear optical response in polymers. Nonlinear optics is primarily concerned with response of a dielectric material to a strong electromagnetic field. Macroscopic nonlinear optical responses are expressed through the constitutive relation for the dielectric polarization $P(E)$ of a nonlinear medium in an intense optical field, E.

The macroscopic NLO behavior of organic NLO materials originates from the polarization response of molecular electrons. Similar to the macroscopic response, the microscopic polarization $p(E)$ is related to the applied field by the polarizability alpha (α), and the second and third order hyperpolarizabilities, beta (β) and gamma (γ), respectively. When molecules are immobile in the applied electrical or optical field, $\chi^{(2)}$, the second order susceptibility, results directly from the molecular β, and $\chi^{(3)}$, the third order susceptibility, from the molecular γ.

The first and third order terms in odd powers of E are common for all materials. The coefficient $\chi^{(1)}$, the linear electronic susceptibility, represents linear optics. The third order susceptibility $\chi^{(3)}$ represents third order nonlinear processes. Important examples include third harmonic generation and self-focusing.

The second order response $\chi^{(2)}$, occurs only in noncentrosymmetric

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

FIGURE 1 Fundamental relationships for the molecular and macroscopic nonlinear optical response in polymers.

media; that is, those lacking a natural center of inversion symmetry. Because of their odd ordered tensorial character, both $\chi^{(2)}$ and β automatically vanish in a centrosymmetric material system. Second order processes include harmonic generation (SHG) and optical rectification. The presence of a nonlinear optical response in a medium leads to a large number of technologically important processes and phenomena over the entire frequency range and, correspondingly, the frequency dependences, or dispersions, of $\chi^{(2)}$ and $\chi^{(3)}$ are fundamentally important properties of the nonlinear medium.

NLO POLYMERS IN OPTICAL APPLICATIONS

Figure 2 answers the question, "Where will NLO polymers fit in?" The opinion of several optical device designers, engineers and physicists, who were queried by the writer last February, are summarized here. At that time second order polymers were viewed as playing a major role in optical signal processing in such areas as spatial light modulators and neural networks. Optical communications were thought to be the domain of inorganic crystals, particularly lithium niobate or potassium dihydrogen phosphate.

Third order polymers were going to play a major role in all-optical signal processing as well as tuneable filters, degenerate four wave

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**

FIGURE 2 The role of NLO polymers in optical applications.

mixing, phase conjugation and sensor protection. While it was accepted that polymers would find a role in all-optical signal processing, there was a majority position that predicted use in parallel processing in polymer plane wave devices. A minority opinion stressed their role in serial processing in guided wave devices.

Little role was seen for polymers in digital (optical) computing for optical computing or optical switches. While multiquantum well devices were thought to be the material of choice, it was stressed that this application is strongly dominated by electronics.

ADVANTAGES OF NLO POLYMERS

Figure 3 summarizes the many important attributes which make polymer attractive for NLO consideration. They have emerged as a promising class of nonlinear optical materials due primarily to the electronic origin of the nonlinear polarization; they possess large,

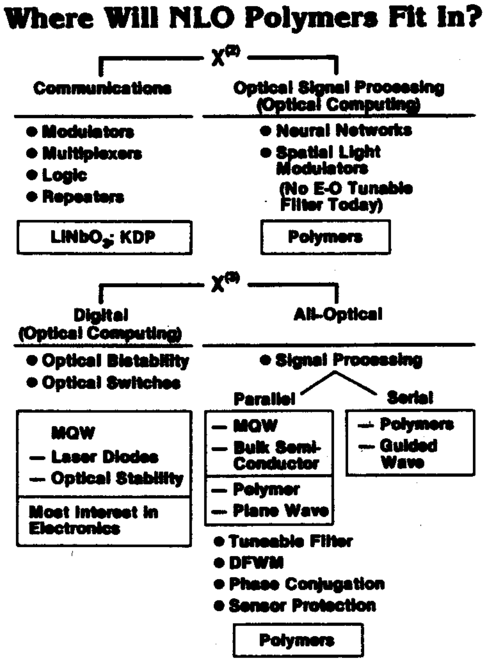


FIGURE 3 The advantages of NLO polymers.

nonresonant optical susceptibilities whose origin lies in ultrafast lossless excitations of highly charged correlated pi-electron states. Nonlinear optical polymers are nonresonant since the nonlinear optical polarization is electronic with little or no lattice phonon contribution.

A major advantage of polymers is their low dc dielectric constants, being of the order of 3 as compared to 28 in the inorganic single crystal lithium niobate for example. In polymer waveguiding films the low dc dielectric constant means shorter time constants and small velocity mismatch. That is, the travelling wave device may be designed to achieve precise matching of optical and microwave velocities. The much larger dielectric constant in lithium niobate results in a loss of phase matching over shorter waveguide lengths, which results in higher drive voltages and power requirements, limiting frequencies accessible.

The absorption coefficient of NLO polymers is about 1/10,000 that of inorganic crystals and compound semiconductors such as gallium arsenide. The absorptive losses relative to semiconductors reduce the heat load factor as well as increase the fan-out capability, making these materials potential fast logic arrays for optical computing. Since the nonlinearity is local and Kerr law type, there are no diffusion problems similar to that of carrier diffusion found in semiconductors. Interpixel spacings can be reduced to a few wavelengths of light. As will be discussed later in this paper, recent research results are demonstrating the potential for resonance enhancement, especially for third-order nonlinearities.

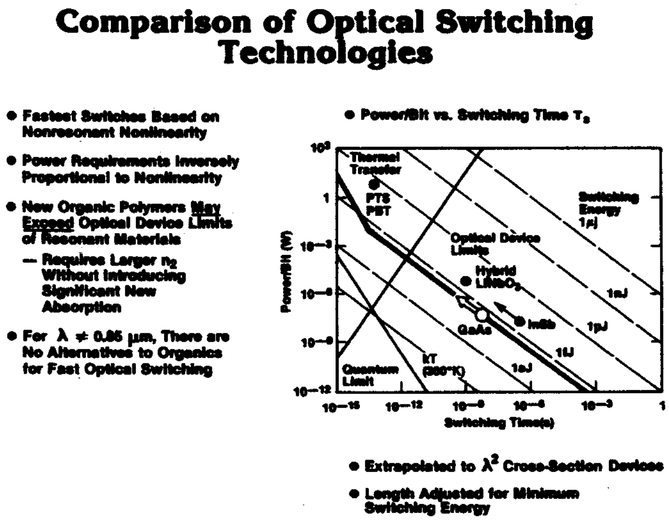
Polymers show excellent chemical and structural stability, and systems will not require the environmental protection or cryogenic hardware required with inorganic crystals. Because of the nonresonant nonlinearities, polymers can be used at room temperature operation in the ambient. Laser damage thresholds as high as GW/cm^2 have been achieved.

Polymers can be fabricated in many useful forms with flexible dimensions and controllable birefringence. These include self-supporting conformable films, liquid crystalline polymers, polymer blends and alloys, molecular composites, fibers, bulk materials, nonolayers, and guest-host structures. The molecular architectural flexibility through chemical synthesis and processing presents many new opportunities to achieve the essential macroscopic properties, and to alter linear and nonlinear optical properties in dimensions approaching visible optical wavelengths. Finally, there is the very high potential for mass production because of the compatibility with in-place polymer manufacturing processes.

POLYMERS AS AN OPTICAL SWITCHING TECHNOLOGY

Figure 4 compares power per bit versus switching time for semiconductors, inorganic crystals and conjugated polymers. New organic polymers, as exemplified by PTS diacetylene and the ordered polymer, poly(*p*-phenylene-2, 6-benzobisthiazole), or PBT, may exceed optical device limits of resonant materials. This requires a larger n_2 without introducing significant new absorption. As shown, the switching time of the conjugated polymers is several orders faster than hybrid lithium niobate and semiconductors. However, the power per bit is in the range of 1 watt, considerably higher than the other optical switching technologies. One focus of current research is to reduce the switching element power requirement. According to the device design relationships, power requirements are inversely proportional to achieving a large intensity dependent index of refraction, n_2.

This requirement is reflected in the optical performance comparison of polymers to gallium arsenide/gallium aluminum arsenide multiple quantum wells (Figure 5). The Figure of Merit for relative comparison is the ratio of the energy required to induce switching, given by n_2, to the product of switching time and the absorption coefficient associated with switching. The nonresonant polymer case is high compared to the resonance enhanced MQW case. An important observation is that NLO polymers show all NLO processes, while MQWs



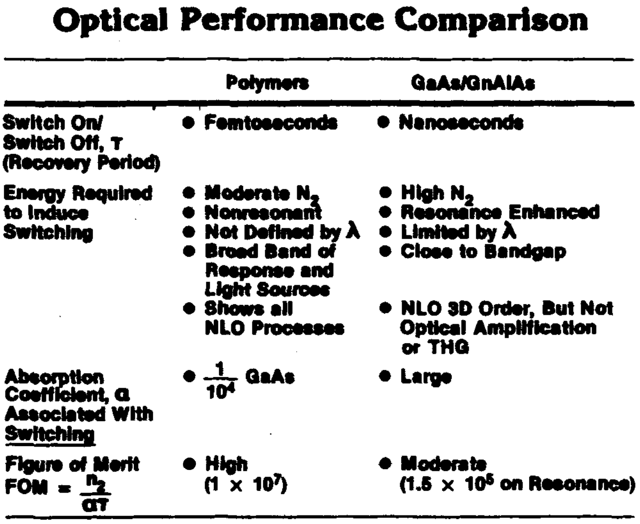
Comparison of Optical Switching Technologies

- 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 $\lambda \neq 0.85\ \mu m$, There are No Alternatives to Organics for Fast Optical Switching

- Power/Bit vs. Switching Time τ_s

- Extrapolated to λ^2 Cross-Section Devices
- Length Adjusted for Minimum Switching Energy

FIGURE 4 Comparison of NLO polymers with other optical switching technologies.



Optical Performance Comparison

	Polymers	GaAs/GnAlAs
Switch On/ Switch Off, τ (Recovery Period)	● Femtoseconds	● Nanoseconds
Energy Required to Induce Switching	● Moderate N_2 ● Nonresonant ● Not Defined by λ ● Broad Band of Response and Light Sources ● Shows all NLO Processes	● High N_2 ● Resonance Enhanced ● Limited by λ ● Close to Bandgap ● 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 × 10^7)	● Moderate (1.5 × 10^5 on Resonance)

FIGURE 5 Optical performance comparison of NLO polymers and multiple quantum wells.

show NLO third order, but no optical amplification or third harmonic generation.

TEMPORAL RESPONSES OF NLO POLYMERS

Polymers offer time responses ranging over fifteen orders of magnitude, including the large nonresonant electronic nonlinearities (fsespsec), thermal and motional nonlinearities (nsec-msec), configurational and orientational nonlinearities (usec-sec), and photochemical nonlinearities. The contribution of each of these to nonlinear optical processes needs to be understood in order to design polymers with ultrafast response times. Measurement then becomes a critical issue: the method and understanding what is being measured.

The characterization methods employed are third harmonic generation (THG), degenerate four wave mixing (DFWM), and intensity dependent refractive index n_2. The THG method of determining $\chi^{(3)}$ has the advantage that the measurement is not complicated by other effects. In contrast, $\chi^{(3)}$ measurement by DFWM or nonlinear refractive index determination can be complicated by contributions due to resonant excitations which can create excited state species, thermal effects and density changes. However, the advantage of DFWM is that the time response of the optical nonlinearity can be readily obtained, and from that the different contributions resolved.

Figure 6 summarizes various resonant and nonresonant processes which give rise to four wave mixing. Also listed are the time-response of these processes. In order to separate these contributions, ultrashort pulses of several picoseconds or less are required. If there is a sufficient dispersion induced in $\chi^{(3)}$ due to resonances, the $\chi^{(3)}$ obtained by THG and that measured by DFWM may not be the same.

RESEARCH DIRECTIONS—NLO POLYMER REQUIREMENTS

Figure 7 summarizes the current priority research directions in NLO polymer development. The discussion in the aforementioned sections have cited the problems which are driving these requirements.

In devices based on third order response, nonlinearities of 10^{-8} esu or larger are required. While nonlinearities of 10^{-10} to 10^{-11} esu have been reported for off-resonance mainchain and side-chain polymers, they are large for a nonresonant material but still imply devices with large operating intensities. Such materials could be useful in degenerate four wave mixing for optical phase conjugation or as self-focusing for optical shutters; however it is still necessary to achieve larger susceptibilities for most applications. Values of resonant $\chi^{(3)}$ of 10^{-10} esu will be discussed in a later section, but there are performance tradeoffs in transmission, absorption and speed of response which need to be investigated.

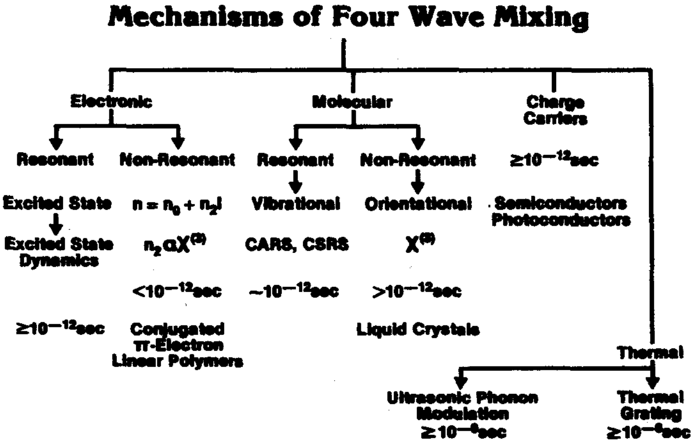
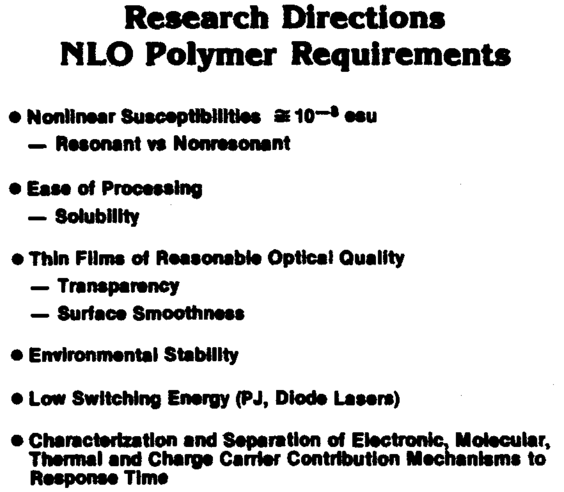


FIGURE 6 Processes contributing to four wave mixing in polymers.



Research Directions
NLO Polymer Requirements

- Nonlinear Susceptibilities $\gtrsim 10^{-8}$ 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

FIGURE 7 NLO polymer research requirements for device development.

Ease of processing is another requirement, particularly for both polymer processing and the deposition of optically clear films by nonvacuum techniques. Solubility is a key issue here. For example, the ladder polymers and ordered polymers, which have shown high nonresonant $\chi^{(3)}$ values, require strong acids as solvents.

The films must be able to transmit or guide light in addition to having reasonably large nonlinearities. Absorption and scattering losses need to be minimized; techniques for the fabrication of optically flat surfaces need to be refined.

The switching energy for NLO polymers is currently a picojoule. For nonresonant nonlinearities, operating intensities must be reasonable, and should be obtainable from diode laser sources. For promising materials, characterization and separation of electronic, molecular, thermal and charge carrier contribution mechanisms to response time are essential to further materials development and device application.

STATUS—NLO POLYMER CLASSES

The current classes of NLO polymers under investigation are listed in Figure 8. Considerable advances have been made in the past year in isotropic polymers, which include glasses, alloys and composites for $\chi^{(2)}$ and $\chi^{(3)}$ functions. The first organic guided wave device was

Status NLO Polymer Classes

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

FIGURE 8 Status of classes of NLO polymers.

fabricated as a Kerr effect modulator based on a MNA (2-methyl-4-nitroaniline)-PMMA polymer alloy structure. This demonstrated electrooptic modulation at 10 MHZ.[1]

The second class are polymers with bond alternations. These are third order NLO polymers, consisting of the ladder polymers such as PTL and PQL and polyacetylene and polythiophene in the conducting doped state.

There is some overlap with the rigid chain aromatic heterocyclics such as PBT, poly(*p*-phenylene-2, 6-benzobisoxazole), or PBO, and benzimidazoisoquinoline, or BBL. These are third order polymers which are structurally more durable. These are liquid crystalline polymers with extensive electron delocalization, but the intermediate length scale or oligomer scale was recently shown to be important.

The side chain liquid crystalline polymers are second order polymers, where the NLO polar group is the side chain mesogen. Polydiacetylenes are mostly third order with assymetric diacetylenes showing second order responses. Nonresonant $\chi^{(3)}$s of 10^{-9} to 10^{-10} esu have been reported in diacetylene single crystals; however, devices will require thin films which can be easily fabricated into layered structures and the molecular architecture tailored through chemical synthesis.

Recent significant results in the isotropic, bond alternation and rigid rod aromatic heterocyclic classes will be discussed in the following sections.

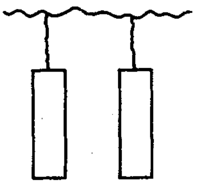
ISOTROPIC POLYMERS

Figure 9 shows nonlinear optical polymers which have been synthesized for which the active NLO unit is attached to the polymer backbone as a pendant side chain. Control of orientation and symmetry is achieved by poling in an external electric field at elevated temperatures resulting in second order susceptibilities larger than inorganic crystals.[2]

The polymer had a second harmonic generation (SHG) after poling that is several times higher than lithium niobate. In addition, for the first time in an NLO polymer the electrooptic coefficient is equal to that of an inorganic crystal. This is a major achievement since it was thought that an organic polymer with the same $\chi^{(2)}$ as an inorganic material would probably have a much smaller electrooptic coefficient *r*. The *r* in lithium niobate comes from lattice phonons and the contribution to *r* in organic polymers was essentially electronic. These polymers had a glass transition temperature of 120 C. Accelerated

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 Coatable 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

FIGURE 9 Comparison of poled second order polymers with lithium niobate.

life tests indicate that the second order activity should stay within 90% of the original value for five years.

For a lumped element waveguide, a low frequency device, the figure of merit is shown in Figure 9. Simply stated it consists of the ratio r to the dielectric constant. The polymer has a figure that is about ten times that of lithium niobate.

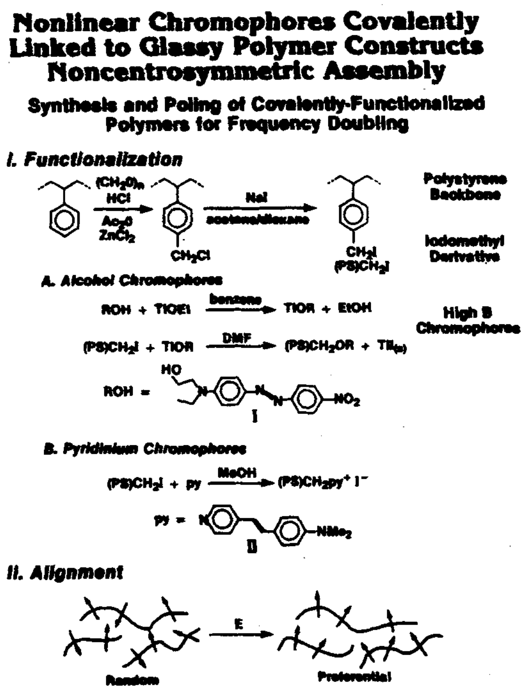
Figures 10 and 11 show the synthesis and poling of covalently functionalized glassy, high glass transition temperature polymers with chromophores having large quadratic hyperpolarizabilities.[3] Polystyrene was chloromethylated, converted to the iodemethyl derivative, and then covalently linked to the chromophores 4-(4-nitrophenylaza)(N-(ethyl)(2-hydroxy-ethyl))aniline (I) or 4-(4-N,N-dimethylaminostyryl) pyridine (II). At 1.064 micrometers, the measured second harmonic coefficients were more than twice those of potassium dihydrogen phosphate after poling (Figure 11). These results suggest a significant nonrandom chromophore alignment in this ionic polymer.

BOND-ALTERNATION POLYMERS

Advances are starting to be made in understanding the consequences of electron delocalization for synthesis of polymers with large $\chi^{(3)}$.

Electron nuclear double resonance (ENDOR) and electron spin echo (ESE) measurements reveal the very interesting discovery that the intrinsic pi-electron HOMO (highest occupied molecular orbital) delocalization lengths of the high symmetry heteroaromatic ladder polymers are comparable to that of polyacetylene.[4] The results of the polaron wavefunction are summarized in Figure 12 along with the values of third order susceptibility, band gap and band width from semiempirical calculations. The number of atoms over which the electron delocalization extends, N, is 26 to 28.

The magnitude of the nonresonant third order susceptibilities of 10^{-10} esu are comparable. Etemad, *etc.* have shown that the pi-only theory of Flytzanis can be used to estimate the $\chi^{(3)}$ for polyacetylene; Chance, *et al.* have shown that MNDO/VEH calculations can be used with Flytzanis theory to estimate the $\chi^{(3)}$ for heteroaromatic ladder polymers.[6] Dalton, Hellwarth and Feinberg have obtained order-of-magnitude agreement with preliminary experimental data.[7] In addition, theoretical calculations suggest that $\chi^{(3)}$ as high as 10^{-7} esu may be realizable by doping ladder polymers to their bipolaron state.[8] This assumes that the polymer lattice constants are not affected by



Nonlinear Chromophores Covalently Linked to Glassy Polymer Constructs Noncentrosymmetric Assembly

Synthesis and Poling of Covalently-Functionalized Polymers for Frequency Doubling

FIGURE 10 Covalently-functionalized glassy polymers for frequency doubling.

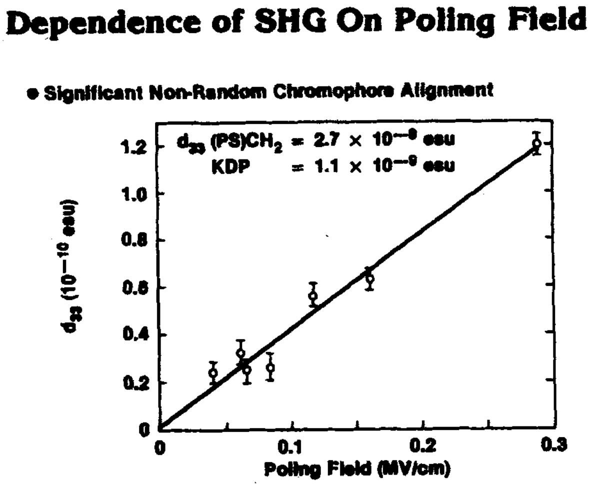
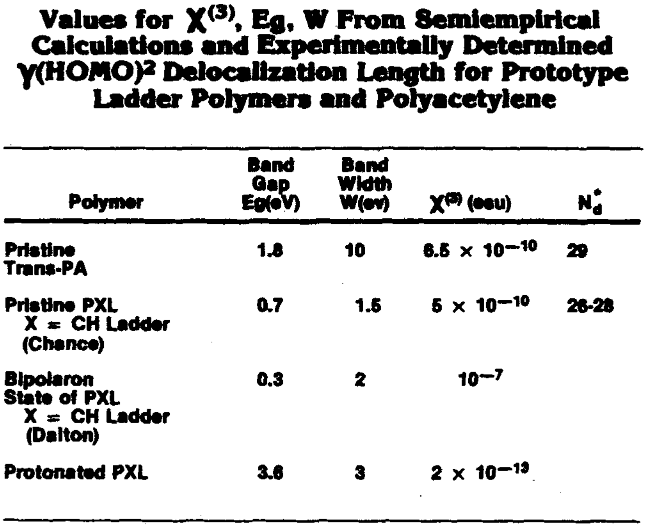


FIGURE 11 Second harmonic coefficients in poled glassy polymers.



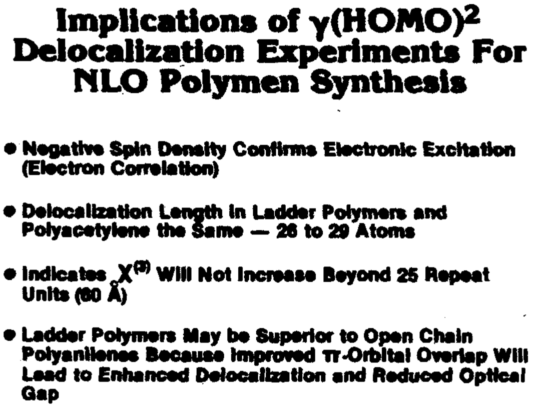
Values for $\chi^{(3)}$, Eg, W From Semiempirical Calculations and Experimentally Determined γ(HOMO)^2 Delocalization Length for Prototype Ladder Polymers and Polyacetylene

Polymer	Band Gap Eg(eV)	Band Width W(ev)	$\chi^{(3)}$ (esu)	N_d^*
Pristine Trans-PA	1.8	10	6.5×10^{-10}	29
Pristine PXL X = CH Ladder (Chance)	0.7	1.5	5×10^{-10}	26-28
Bipolaron State of PXL X = CH Ladder (Dalton)	0.3	2	10^{-7}	
Protonated PXL	3.6	3	2×10^{-13}	

FIGURE 12 Intrinsic pi-electron delocalization lengths of heteroaromatic ladder polymers and polyacetylene.

doping. The enhancement in NLO activity is accompanied by a reduction in the spectral region of optical transparency.

The implications of the aforementioned results for NLO polymer synthesis are summarized in Figure 13. Using a microscopic many-electron description for linear conjugated polyene chains, Garito and coworkers have shown that there is a finite chain limit of 25 repeat



Implications of γ(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 Polyanilenes Because Improved π-Orbital Overlap Will Lead to Enhanced Delocalization and Reduced Optical Gap

FIGURE 13 Implications of ENDOR and ESE delocalization experiments for NLO polymer synthesis.

units (60 Angstroms) beyond which $\chi^{(3)}$ will not increase.[9] The dependence of γ on chain length exhibits a power law dependence of 5.5, decreasing excitation energy and increasing number of spin correlated states being major factors (Figure 14).

Two examples of the application of these results are shown in Figures 15 and 16, wherein heteroaromatic polymers have been synthesized by condensation reactions which permit sequential synthesis of polymers and oligomers of defined chain length, and which permit synthesis of fused heterocyclic polymers via open-chain intermediates.[10] Solubility in a variety of solvents is controlled by derivatization and in particular para substitution is employed to maintain symmetry and to prepare oligomers suitable for film formation. Figure 15 shows the synthesis of derivated quinones, and Figure 16 shows the potential for reducing intermolecular attractive forces and allowing the solubilization of rigid macromolecules by Lewis acid charge transfer complex forming agents.

The research of Professor Garito at the University of Pennsylvania has shifted from conjugated off-resonance to systems on resonance with narrow molecular extinction coefficients (Figure 17). Planar structures with extended pi-orbitals are predicted to have third order nonlinear activity comparable to AlGaAs multiquantum well structures on resonance but with higher speeds.[11]

Sinclair has presented data on the angular dependence of $\chi^{(3)}$ of trans-polyacetylene (Figure 18). The resonant reflected $\chi^{(3)}$ parallel

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)**

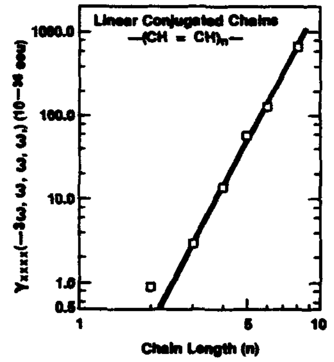
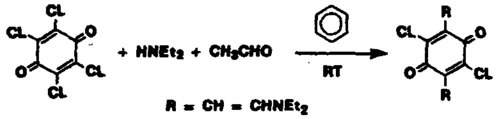


FIGURE 14 Dependence of $\chi^{(3)}$ conjugated polyene chain length.

Application of Dalton Results

- Solubilized Ladder Polymers by Derivatization
- Prevents Aggregation Due to Steric Forces
- Optical Quality Biaxial Films

Derivatized Quinones by Mannich Reaction



Polaron and Bipolaron Charged Species at Appropriate Stages of Oxidation and Reduction. Optical Gap ≈ 1.3 eV

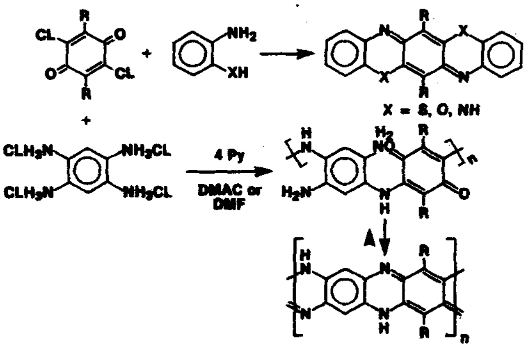
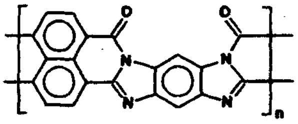


FIGURE 15 Solubilized quinone ladder polymers by derivatization.

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

FIGURE 16 Solubilized rigid macromolecules by charge transfer complex forming agents.

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 Coatable For Thin Film Structure Applications**
    - **Optical Bistability**
    - **Parallel Processing**

FIGURE 17 New third order saturable absorption polymers.

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

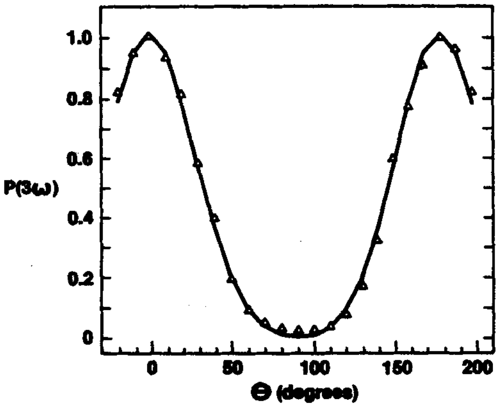


FIGURE 18 Reflected third order response in polyacetylene.

to the polymer chain was $9 \pm 5 \times 10^{-9}$ esu. The mechanism suggested is that the nonlinear excitations observed with resonant pumping affect nonresonant optical processes. Via the electron-phonon interaction, the light induced polarization causes a structural response—solitons, polarons, and bipolarons—and an associated third order susceptibility. A topic still to be addressed here is that for devices the polymer must be able to inherently transmit or guide light.[12]

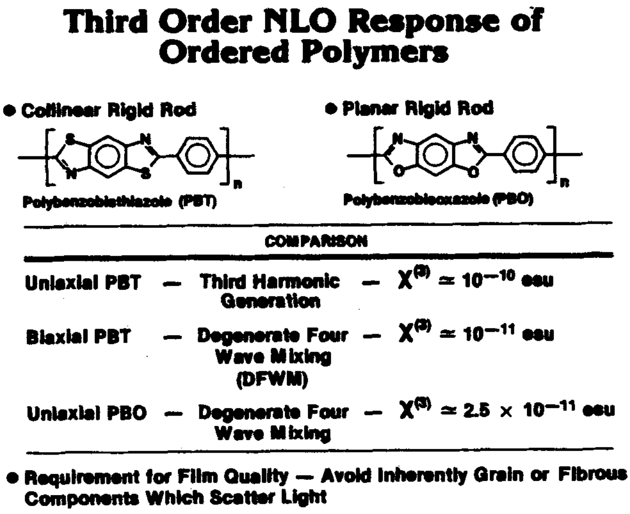
RIGID ROD AROMATIC HETEROCYCLICS

The rigid rod aromatic heterocyclics, or ordered polymers were initially designed as structural polymers with high strength, high modulus, excellent high temperature thermal-oxidative stability, and high laser damage thresholds. These polymers, poly(*p*-phenylene-2, 6-benzobisthiazole), or PBT, and poly(*p*-phenylene-2, 6-benzobisoxazole), or PBO, have a rigid chain structure which impacts liquid crystalline orderability. It was postulated that the natural cooperative alignment of the liquid crystalline rigid rod structure in cooperation with the highly charge-correlated pi-electron states would lead to large nonresonant nonlinearities.

This has been shown by the work of Garito[13] and Prasad[14] in uniaxial and biaxial films which were actually fabricated for structural goals. The results are compared in Figure 19. With third harmonic measurements on 50 micron thick uniaxial films of PBT, which were light yellow in color and had a ribbon-like domain morphology, Garito measured χ^{-10} esu. He shows that for the PBT monomer repeat units, the pi-electron states of importance to the large third order response are highly charge correlated and consist of alternating single and double bonds. There is considerable overlap with the considerations for monomer, oligomer and polymer design presented in the previous section.

As-spun 10 micron thick biaxial films (by Foster-Miller, Inc) of PBT were studied by Prasad with degenerate four wave mixing (DFWM) at 585 and 605 nm with a measured value of $\chi^{(3)}$ of 10^{-11} esu at both wavelengths (Figure 20). Prasad also measured a $\chi^{(3)}$ of 10^{-11} for uniaxial PBO.[13] For PBT and PBO, a subpicosecond response time limited only by the laser pulse width and film optical quality was observed.

Biaxial films offer some very new features for third order devices if the $\chi^{(3)}$ values can be made larger. These would be the basis for optically-birefringent film applications. The value of $\chi^{(3)}$ depends on



Third Order NLO Response of Ordered Polymers

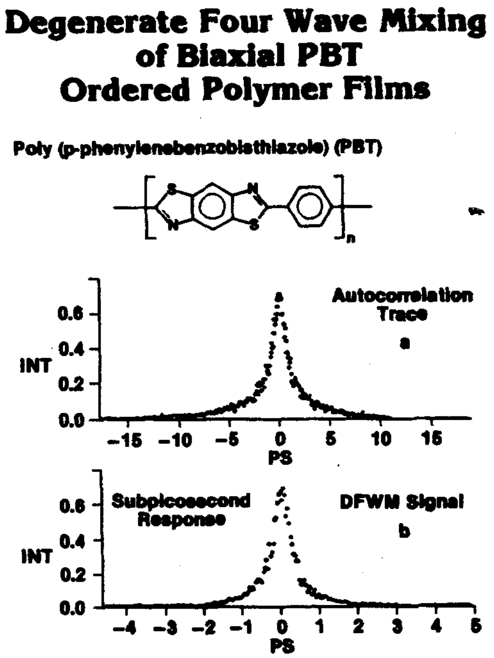
- **Collinear Rigid Rod**
- **Planar Rigid Rod**

COMPARISON

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

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

FIGURE 19 Comparison of third order response in ordered polymers.



Degenerate Four Wave Mixing of Biaxial PBT Ordered Polymer Films

Poly (p-phenylenebenzobisthiazole) (PBT)

FIGURE 20 Subpicosecond response of nonlinear optical processes in biaxial PBT films by degenerate four wave mixing.

the orientation of the biaxial PBT film. This can be explained by its tensor property in a biaxial symmetry. Figure 21 shows a polar plot of the relative values of $\chi^{(3)}$ as a function of the angle of rotation of the film. Squares represent the data points obtained for the vertical polarization of all the beams for degenerate four wave mixing and circles correspond to the data points obtained when the pump beams are vertically polarized but the probe beam and the signal are horizontally polarized. The solid curves represent the theoretical fits.

Synthesis research in the ordered polymers is being guided by the findings of Dalton and Garito discussed in the previous section. Synthesis is focusing on the intermediate scale regime of liquid crystalline polymers and oligomers (50 to 60 Angstroms) and materials design on the tradeoffs of NLO response, chain length, processibility, and film quality. The later requirement is necessary to avoid inherently grainy or fibrous components which scatter light.

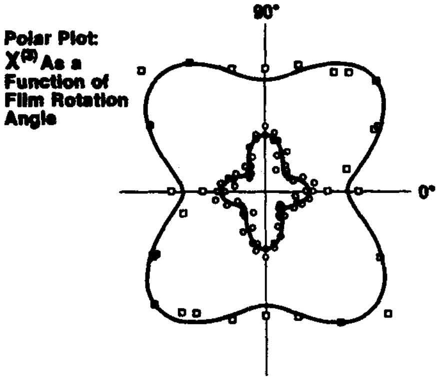
STATUS OF UNDERSTANDING FOR NLO POLYMER DESIGN

A conclusion derived from the discussion of the status of NLO polymers is that the detailed mechanism(s) of nonlinear optical activity in delocalized electron polymers have yet to be defined (Figure 22). The most critical limitation lies in the lack of quantitative theory to predict macromolecules with large second order (beta) and third order (gamma) molecular susceptibilities. There now exists an elegant set of second order semiempirical theory. However, while the beta can be calculated once the molecule is synthesized, the beta cannot be quantitatively predicted for another molecule. With regard to the status of third order theory, gamma can be predicted for small molecules, but not long macromolecules. There is a need to develop theory to predict structures with large gamma, and a more sophisticated theory to understand local field effects and the role of intermolecular charge transfer.

There have been three recent advances in theory. In second order theory the importance of electron correlation in determining linear and nonlinear optical properties of cyclic polyenes and quinoid structures has been shown.[16] There has also been success in predicting the NLO response for new, elaborate molecular chromophores for frequency doubling property, beta, based on an efficient Pariser, Parr, Pople pi-electron formalism.[17] In third order theory the microscopic origin of third order NLO properties for linear conjugated chain

Nonresonant Third Order Susceptibility $\chi^{(3)}$ in Biaxial PBT

- **Degenerate Four Wave Mixing**



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

FIGURE 21 Orientational dependence of nonresonant third order response in biaxial PBT.

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**

FIGURE 22 Status of nonlinear optical mechanisms understanding in NLO polymers.

polyenes and diacetylenes resides in the spin-correlated state, showing the importance of electron correlations. The ordered polymers cited in the previous section are considered to be a complex version of the linear chain problem. They are chemically different, but physically the same.[18]

On the theoretical front other important questions remain to be answered, including the potential contribution of d orbitals to nonlinear optical activity. It is well known that these are not important for linear polarizability but there is reason to believe that these, e.g., s-d cross terms may contribute to higher order terms. Also the role of electron-phonon interactions needs to be considered. New computational schemes suggest that it may now be reasonable to undertake such an investigation.

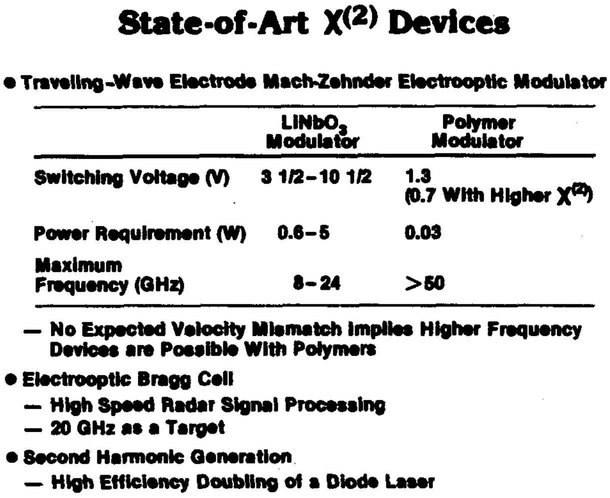
NONLINEAR OPTICAL POLYMERS IN SECOND ORDER DEVICES

The collective expert opinion of where NLO polymers will fit in devices was summarized in Figure 1. The emphasis of the industrial national effort has been on $\chi^{(2)}$ polymers for spatial light modulators, the fundamental unit for optical computing, and integrated optical devices. The Air Force and DARPA programs, with an interest in optical computing and signal processing, optical memories, and optical sensor protection, have addressed both $\chi^{(2)}$ and $\chi^{(3)}$ devices.

The state-of-the-art for second order devices is shown in Figure 23. The device development flow diagram for waveguide devices is shown in Figure 24. The most fundamental electrooptic device is the modulator. The first one-dimensional (1-D) slab organic guided wave device fabricated was based on MNA/PMMA and operated at 10 MHz. This was achieved in the Kerr effect modulator shown in Figure 25, and demonstrated the prototype of the multilayer (1-D) guide modulator.

In the 1-D modulator, the input beam is decomposed into TE and TM modes of equal intensity and the applied electrical signal selectively modulates the phase of the TE mode. When the modes are recombined at the exit prism, the polarization state of the combined output beam is modulated. The output beam, using an analyzer, is thus modulated between the off (no light) and the on (full light) state. A number of devices to 500 MHz have since been fabricated with recent demonstration in the GHz region.[20]

The advancements described earlier in isotropic polymers have



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

FIGURE 23 Device state-of-the-art with $\chi^{(2)}$ polymers.

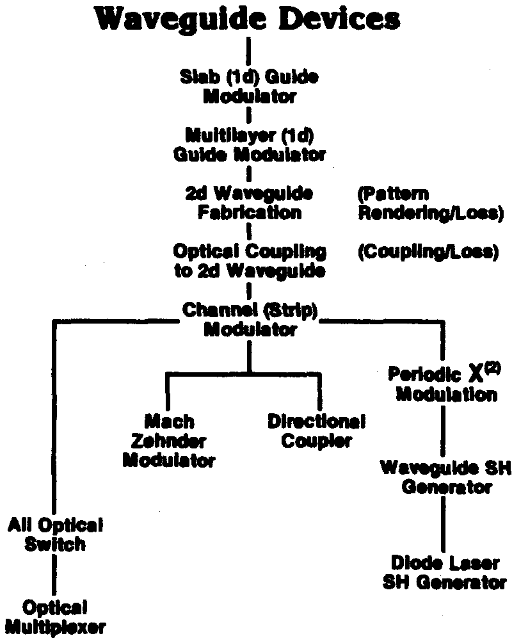


FIGURE 24 Flow diagram for waveguide device development.

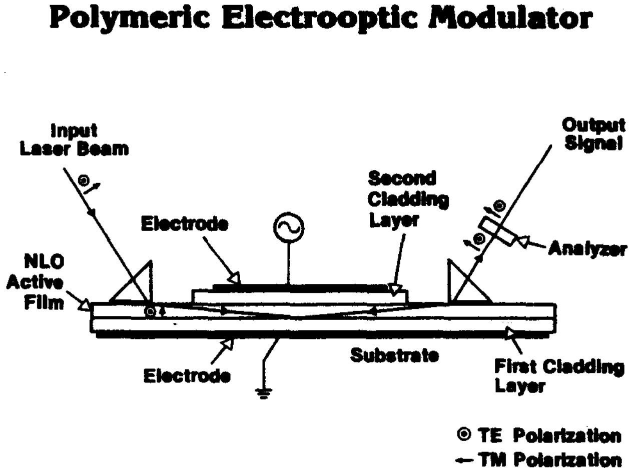


FIGURE 25 MNA/PMMA I-D slab guided wave device.

made it possible to investigate two-dimensional waveguide designs. Second-order poled polymer films now outperform the inorganic crystal lithium niobate ($LiNbO_3$).[21] Several designs exist among which the Mach Zehnder interferometer is the most common.

A thin film waveguide electrooptic modulator can operate employing one of three modulating systems: Mach-Zahnder interferometry, directional coupling or rotation of the optical polarization. The Mach-Zehnder interferometer is the most common design.[22] This high-frequency traveling wave device, shown in Figure 26, has been designed to provide a match in the optical and electron phase velocities.[23] Light is guided into the two-dimensional waveguide, divided into two legs, and recombined into a common output guide. Electrical modulating signals, operating at microwave frequencies, travel across electrodes at speeds which must be commensurate with the speed of light within the waveguide to achieve optimum performance.

Since the low dielectric constant of the NLO polymers is on the order of 3, the traveling wave device may be designed to achieve precise matching of optical and microwave velocities. The large dielectric constant of $LiNbO_3$ results in a rapid loss of phase matching over shorter waveguide lengths, resulting in higher drive voltages and power requirements and limiting the frequencies accessible to 8 to 24 GHz (Figure 23). Because phase matching is possible for polymeric materials, the maximum frequency of single mode devices is limited only by electrode losses, being in the vicinity of 50 GHz using conventional electrodes.

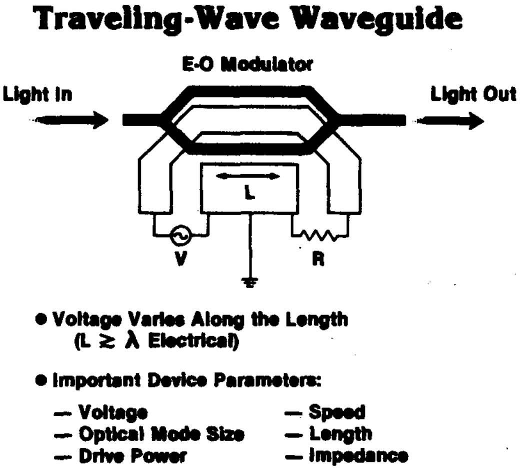


FIGURE 26 High frequency polymeric traveling wave waveguide.

Current Air Force interest is in using these materials and devices for electrooptical Bragg Cells for high speed radar signal processing and for high frequency doubling of a diode laser (Figure 23).

NONLINEAR OPTICAL POLYMERS IN THIRD ORDER DEVICES

Nationally and internationally there has been far less progress in $\chi^{(3)}$ devices because most of the effort has been on $\chi^{(2)}$ devices (Figure 27). This is a new area where considerable progress has been made in the development of new materials with high nonresonant nonlinearities. While nonlinearities of 10^{-10} to 10^{-11} esu have been achieved, which are very high in nonresonant materials, two orders of magnitude higher need to be achieved for practical device application. This is because large operating intensities are still required; lower intensities which should be obtained from diode laser sources are required.

At the current state-of-the-art $\chi^{(3)}$ polymers will find use in optical waveguide devices as illustrated by bistable optical switches and optically-controlled modulators and switches. Third-order integrated optics devices will include distributed couplers, directional couplers, Mach Zehnder interferometers and Bragg reflectors. The optical Mach-Zehnder modulator will utilize $\chi^{(3)}$ polymers which exhibit intensity dependent refractive indices (Figure 28).[24] In a typical Mach-Zehnder switch, the input beam is divided into two channels. When a high

State-of-Art $\chi^{(3)}$ Devices

- **Far Less Progress Than $\chi^{(2)}$**
- **Large Payoff in Multiplexing and Demultiplexing**
  - — **High Speed**
  - — **Handle Many Inputs**
  - — **Very High $\chi^{(3)}$**
- **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**

FIGURE 27 Device state-of-the-art with $\chi^{(3)}$ polymers.

intensity modulating beam is introduced into a channel, the refractive index of the channel changes and it creates a phase difference of the input beam in the channel relative to the beam in the other channel. If the phase difference is equal to pi, the two cancel each other when they are recombined. A fast optical Mach-Zehnder switch may be used for digital signal processing.

Optical bistability has been observed in a poly-4-BCMU polydiacetylene polymer quasi-wavelength interferometer by Singh and Pra-

Mach-Zehnder All Optical Modulator

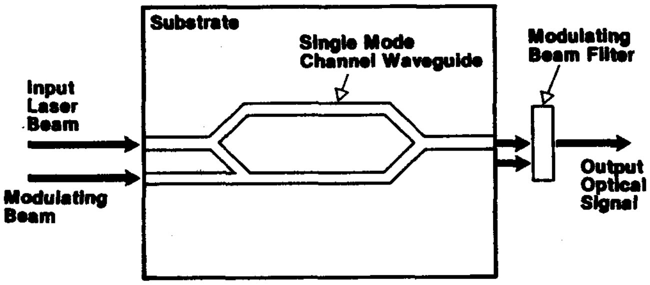


FIGURE 28 Schematic for $\chi^{(3)}$ polymer Mach Zehnder modulator.

sad.[25] Biaxial NLO polymers as demonstrated with the rigid rod ordered polymer PBT offer additional device design options based on polarization bistability.[26]

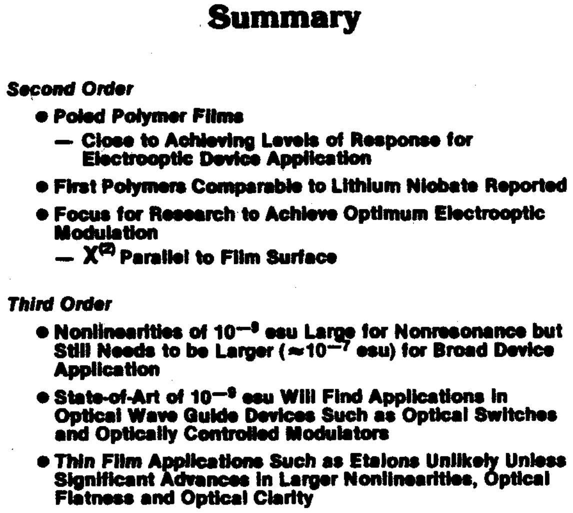
Thin film devices such as etalons will require the improved $\chi^{(3)}$ polymers.[27] Currently nonresonant polymers do not have the large nonlinearities for the low switching intensities which are required. New approaches as discussed earlier are being investigated.

There will be large payoff in fast optical multiplex switching, based on high n_2 polymers, which combines optical signals from many channels converted to a single temporal signal for easy transmission.[28] As a high intensity pulse from a picosecond mode-locked laser transverses through a high n_2 medium, it sequentially opens the channels and thus creates a temporal signal. A similar design is used to demultiplex the transmitted signal to retrieve the individual signals. This can lead to digital optical information processing and other applications cited in Figure 27.

Device design with $\chi^{(3)}$ materials is often guided by the architecture or electrical parameters. Thus careful investigation of polymer properties concurrent with their operational performance in device prototypes should lead to parallel/analog processing of 2-D images and other applications cited in Figure 27. For example the optical Kerr cell design can be used also for analog optical signal processing such as optical scanning.

NONLINEAR OPTICAL POLYMERS IN OPTICAL NEURAL NETS

In an interdisciplinary collaboration with Drs. Lee Giles and Kevin Malloy at AFOSR, we plan to examine the feasibility of using $\chi^{(3)}$ polymers as multifunctional materials for optical neural computing.[29] Brain-like computations are characterized by parallel processing, system modularity and dense interconnectivity of neurons (computational units). The advantages for the optical approach are interconnectivity and parallelism, but the restrictions for the optical implications of neutral nets have yet to be defined. Architectures, dynamics and representation of information have to be expressed optically; models are starting to emerge. The architecture-imposed requirements on device design is an unknown which impacts the material properties requirement. The materials problem is to determine how $\chi^{(3)}$ polymers could: (1) mimic neuron slabs and arrays; and (2) optically implement interconnects in optical and hybrid optical/electrical architectures.



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**
  - **$X^{(2)}$ Parallel to Film Surface**

Third Order

- **Nonlinearities of 10^{-9} esu Large for Nonresonance but Still Needs to be Larger ($\approx 10^{-7}$ esu) for Broad Device Application**
- **State-of-Art of 10^{-9} 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**

FIGURE 29 Summary of status of second and third order materials and devices.

SUMMARY

The status of polymers for nonlinear optical applications has been reviewed (Figure 29). Significant advances have been made in the past year in the isotropic, bond alternation and rigid rod aromatic heterocyclic classes of NLO polymers. The first second order polymers with second harmonic generation and electrooptic coefficients comparable to lithium niobate have been achieved. These poled polymer films are close to achieving levels of response for electrooptic device application. The focus for future research to achieve optimum electrooptic modulation will include the difficult problem of poled $\chi^{(2)}$ parallel to the film surface.

Nonlinearities of 10^{-10} esu have been reported in third order polymers. These are large for nonresonance, but still need to be of the order of 10^{-7} esu for broad device applications. State-of-the-art NLO polymers will find applications in optical waveguide devices such as optical switches and optically controlled modulators. Thin film applications such as etalons will be unlikely unless significant advances are made in larger nonlinearities, optical flatness, and optical clarity. The feasibility of using $\chi^{(3)}$ polymers for optical neural computing in optical or hybrid optical/electrical configurations is being considered.

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