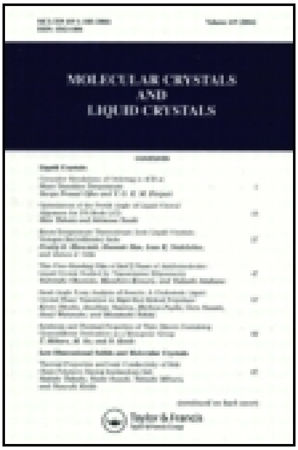

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Polymers for Nonlinear Optical Applications

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Polymers for Nonlinear Optical Applications

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Since the 1987 Brookhaven Symposium on Electroresponsive Molecular and Polymer Systems, the materials research targets that electro-optical and nonlinear optical (NLO) polymers must achieve for device and systems application have become better defined. The progress of second and third order NLO polymer development toward achieving these goals is reviewed. In particular polymer design is being guided by new concepts which have been predicted from theory and validated by experiment.

INTRODUCTION

At the 1987 Brookhaven Symposium on Electroresponsive Molecular and Polymer Systems, nonlinear (NLO) optical polymers were still in their infancy. Several polymer classes were identified for the development of $\chi^{(2)}$ and $\chi^{(3)}$ materials with device potential.[1] At that time polymers had been developed with electro-optic and second harmonic generation (SHG) coefficients equal to those of the inorganic crystal lithium niobate. However, major problems remained to develop films with high optical transparency and retention of alignment after electric field poling. The promise for polymers with nonresonant $\chi^{(3)}$ for all-optical signal processing and other applications had been shown with the picosecond nonlinear optical response of polydiacetylene and ladder polymers such as PBT, or poly (p-phenylene-2, 6-benzobisthiazole). However, at least three orders of magnitude improvement in the nonresonant third order nonlinear macroscopic susceptibility was considered necessary for marginal device operation.

The progress made in major directions since 1987 is reported in this paper. The materials research targets that electro-optic and nonlinear optical polymers must achieve for device and system applications have become better defined. This has accelerated efforts to develop new concepts and approaches for achieving second and third order materials with enhanced nonlinearities and low absorption coefficients.

WHERE *DO* NLO POLYMERS FIT IN?

Figure 1 summarizes the results of polling optical device designers in 1987, who were asked "where will NLO polymers fit in?" At that time the majority felt that

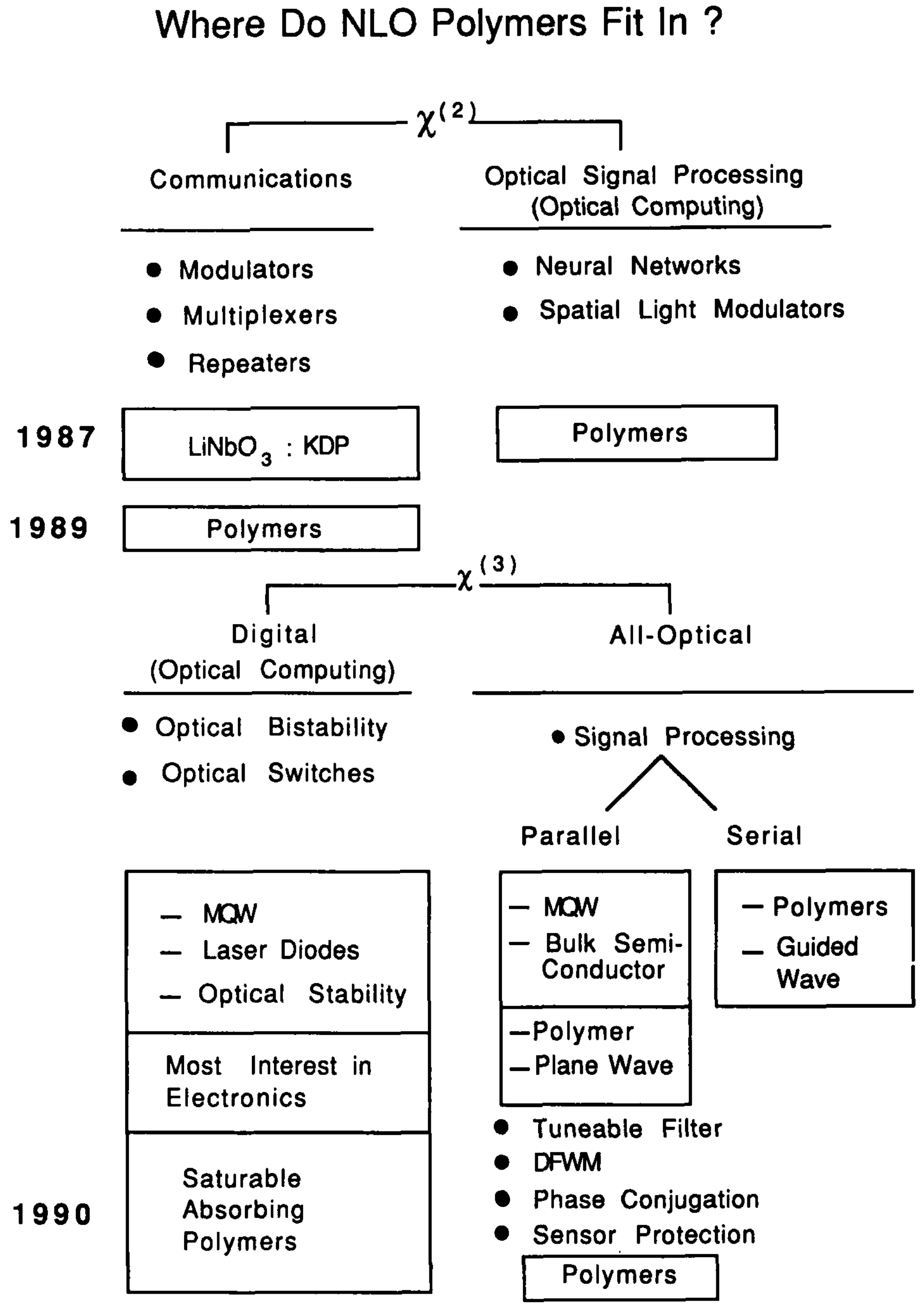


FIGURE 1 The device designers perception (1987) where NLO polymers would be used. Advances in $\chi^{(2)}$ polymers in 1989 and the discovery of saturable absorbing polymers in 1990 make polymers a potential competitor in each major $\chi^{(2)}$ and $\chi^{(3)}$ application.

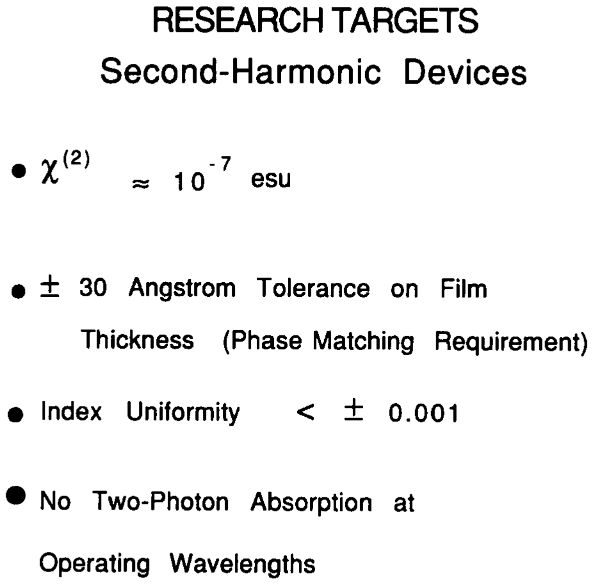
polymers would play an important role in electro-optic and all-optical signal processing and sensor protection applications. This prediction is proving to be correct as the device-impacted materials properties of polymers are improving.

However, the major advances have been in $\chi^{(2)}$ polymers for optoelectronic and telecommunication applications, which were thought to have been won by lithium niobate, potassium dihydrogen phosphate, and other crystals by default in 1987, and in saturable absorbing resonant $\chi^{(3)}$ polymers. While GaAs/GaAlAs multiple quantum wells were considered to dominate optical computing in 1987, provided that they could overcome the strong interest in digital electronics, these new resonant polymers have dramatically changed the scenario for all-optical computing and sensor protection.

POLYMER REQUIREMENTS FOR DEVICE APPLICATIONS

The device-driven materials requirements were examined quantitatively in 1988 at the NATO Advanced Study Workshop on Nonlinear Optical Effects in Organic Polymers.[2] The research targets identified for electro-optic and second harmonic devices, for all-optical serial and parallel signal processing, and for nonlinear filters for intense short-pulse lasers are summarized in Figures 2–5.

Device-driven materials requirements are well defined for second-order devices. Requirements on electro-optic activity and optical loss are most critical, and must be achieved simultaneously. Fast, i.e., greater than 10 GHz, and inexpensive phase and amplitude modulators are expected in the near term of 3–5 years. Likewise second-order polymers would enhance the application of frequency doubling of



RESEARCH TARGETS

Second-Harmonic Devices

- $\chi^{(2)} \approx 10^{-7}$ esu
- ± 30 Angstrom Tolerance on Film Thickness (Phase Matching Requirement)
- Index Uniformity < ± 0.001
- No Two-Photon Absorption at Operating Wavelengths

FIGURE 2 Polymer research targets for second harmonic devices.

RESEARCH TARGETS

Electro-Optic Devices

- Electro-optic Coefficient $r > 30$ pm/V
- Loss $\alpha < 0.1$ dB/cm
- Good Performance at 0.85 μm, 1.3 μm, 1.55 μm
- ± 50 Angstrom Dimensional Stability and Control
- 5 - 10 Year Stability

FIGURE 3 Polymer research targets for electro-optic devices.

RESEARCH TARGETS

All-Optical Serial Signal Processing

- $n_2 \gg 10^{-14}$ to 10^{-16} m^2/W
  $\alpha < 0.1$ cm^{-1}
- Picosecond Rates
- Optimum Performance Preferred for 1.3 μm and 1.55 μm
- Waveguide Processable Materials with ± 100 Angstrom Dimensional Stability and Control
- Thermal Nonlinearities, Relative to the Electronic, Are Too Large
- Smaller dn/dT
- No Hydrogen-Eliminate Vibrational Overtones

FIGURE 4 Polymer research targets for all-optical serial signal processing.

RESEARCH TARGETS

All-Optical Parrallel Signal Processing

- $n_2 = 10^{-7}\ m^2/W$
- Relaxation Times Shorter Than 1 Microsecond

Nonlinear Filter for Intense Short-Pulse Lasers

- $n_2 = 10^{-14}$ to $10^{-16}\ m^2/W$
- $\alpha < 1.0\ cm^{-1}$
- Relaxation Times Less Than 1 Picosecond

FIGURE 5 Polymer research targets for all-optical parallel signal processing and nonlinear filters for intense short pulse lasers.

semiconductor diode lasers to optical data storage and xerography. This could enable supplanting other approaches to generating blue light. Applications to communications, such as parametric amplifiers, are awaiting the next generation of $\chi^{(2)}$ polymers.

The device implications for third-order materials are still being formulated. In 1988 time scales longer than 10 years were implied for useful devices. This is still generally true although the prediction and discovery of saturable absorbing resonant polymers may accelerate use in some device designs.[3] As indicated by the research targets in Figure 4, the most promising applications at this time are all-optical serial information processing at terahertz and larger data rates. Figure 5 shows that all-optical parallel processing of optical information and dynamic holography require many orders of magnitude improvement in third-order optical nonlinearities. A critical requirement is to achieve nonlinear optical activity concurrently with low loss in waveguide processable materials.

At the same time that the primary critical requirements are being achieved, secondary requirements such as thermal and environmental stability must continue to be developed.

SECOND-ORDER POLYMER DEVELOPMENT

Figure 6 summarizes the state-of-the-art development in second-order polymers.[4] The approach commonly being pursued is to covalently bond a nonlinear active

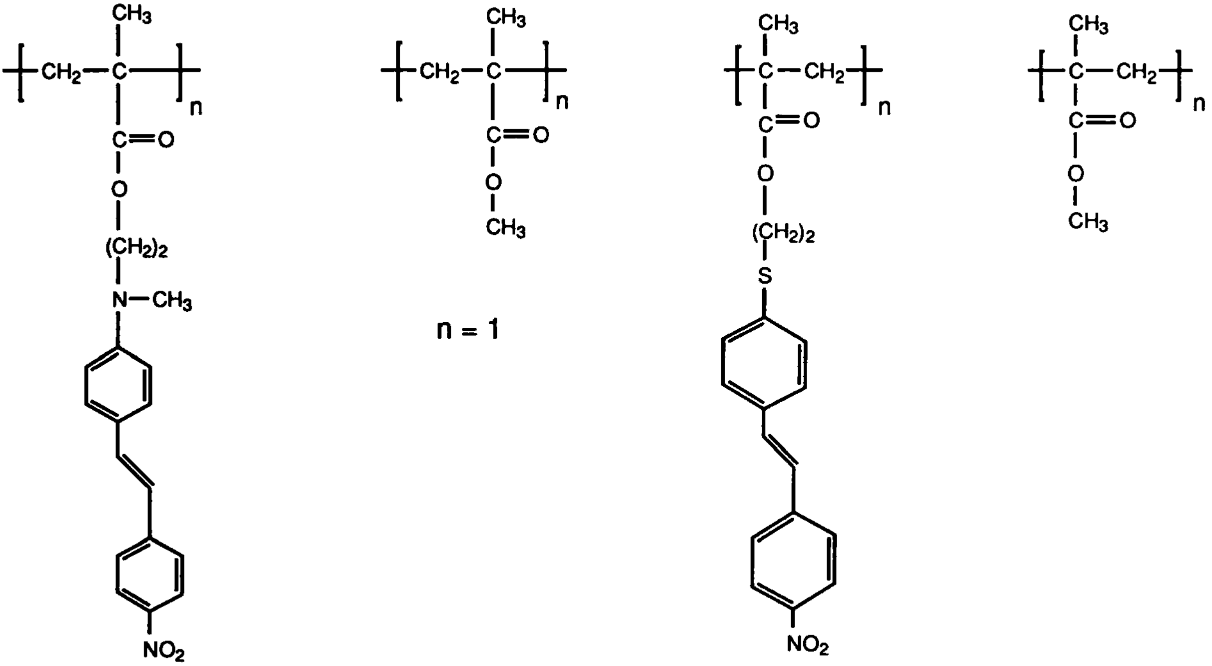


FIGURE 6 State-of-the-art second order polymers. Those in today's devices are on the left. Those on the right are candidates for second generation device materials.

segment such as 4-dimethyl-amino-4'-nitrostilbene (DANS) or para-methoxy-nitrostilbene (MONS) to a glassy polymer backbone as a side chain which is electrically aligned.[5] The backbone is usually poly(methylmethacrylate), polysiloxane, or polystyrene.

Electro-optic coefficients r_{33} (proportional to $\chi^{(2)}$) of up to 90 pm/V at 633 nm have been reported with DANS nonlinear active units. This compares favorably with $LiNbO_3$ whose r_{33} is 31 pm/V. Values of 40 to 50 pm/V have been measured at 1.3 and 1.55 μm. Sulfur substitution for the nitrogen in DANS enhances film processibility and transparency at 830 nm, an important wavelength for semiconductor diode lasers.

ELECTRICAL POLING AT GLASS TRANSITION TEMPERATURE

The electrical alignment of the optically-active component is receiving increased attention. This important process, which removes centrosymmetry in amorphous polymers, is essential to successful waveguide structure operation, and must be considered in any successful chemical synthesis strategy.

The polymers shown in Figure 6, also referred to as glassy poled polymers, utilize the transparent backbone polymer to maintain the electrically induced alignment of the molecules of the active compound. Current methodology involves heating the polymer to a viscous state, and applying an electric field. Taking place near the glass transition temperature of the polymer, the active side chains align via the electronic interaction between the dipoles of the nonlinear optical segments and the electrical field. After equilibrium is reached, the polymer is cooled to ambient temperature before the electrical field is removed. The alignment is frozen in with typical poling efficiencies of 10 to 20 percent.

A problem with the aforementioned approach to poling is that alignment is usually counteracted by thermal disordering effects. Raising the T_g achieves better stability. The effect of T_g on poling and alignment of the normalized second harmonic generation coefficient $\chi^{(2)}$ of the current glassy poled copolymers is shown in Figure 7.[6]

ELECTRIC FIELD POLING OF CHROMOPHORE-FUNCTIONALIZED POLYMERS

Another strategy being investigated to maintain long-term stability of $\chi^{(2)}$ after poling is chromophore-functionalized polymers. Marks and coworkers have demonstrated multiple chromophore functionalization of a high-T_g polymer with greater than one chromophore substituent per monomer subunit, as in Figure 8.[7] In this case poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was functionalized with chromophore substituent N-(4-nitrophenyl)-S-prolinoxy (NPPO) with chromophore densities as high as 25×10^{20} cm^{-3}. This system had corona-poled second harmonic coefficients d_{33}) (proportional to $\chi^{(2)}$) as high as 65×10^{-9} esu ($\lambda = 1.064$ μm),

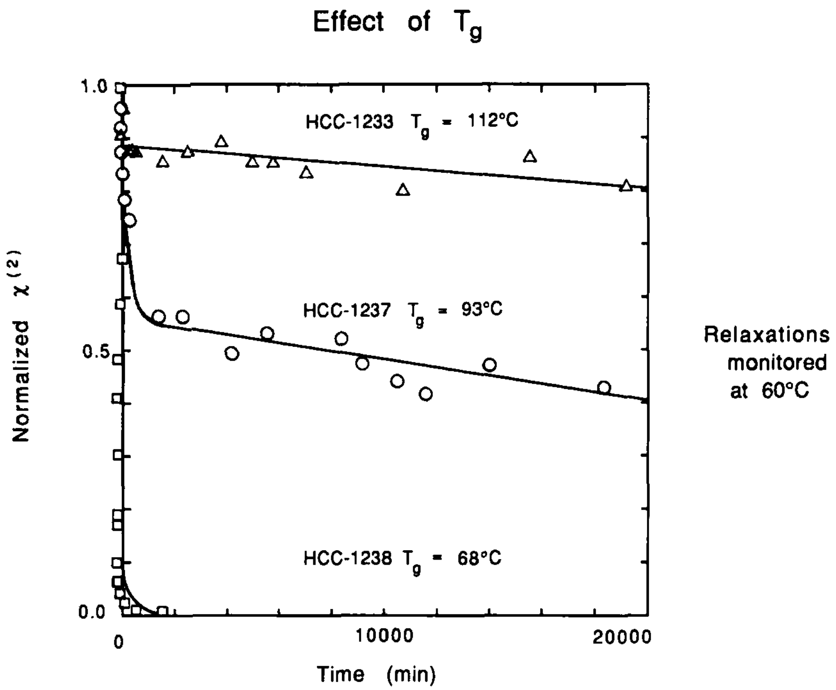


FIGURE 7 The effect of glass transition temperature T_g on poling and electrical alignment of current glassy poled copolymers shown in Figure 6.

and T_g = 173°C. During preliminary waveguiding experiments, a loss coefficient less than 1 dB/cm was estimated.

Figure 8 shows the temporal characteristics of corona-poled PPO-NPP films. Contact poling was carried out at 160–170°C with 1.2 MV/cm fields, and corona poling at 180–190°C for 30 minutes using a needle-to-film distance of 1.0 cm and a +4 kV potential. A superior temporal stability was demonstrated with the corona-poling induced chromophore orientation.

In another study Singer and colleagues investigated a corona-poled random copolymer consisting of a 4-dicyanovinyl-4′-(dialkylamino)azobenzene-substituted methacrylate dye side chain covalently attached to a methyl methacrylate polymer backbone.[8] The copolymer alignment decays to approximately 90% of the original value, a d_{33} decrease from 51 to 46 $\times 10^{-9}$ esu. In comparison the decay of a guest-host system of an analogous dicyanovinylazo dye dissolved in poly(methylmethacrylate decays to 25% of the original value. The r_{33} coefficient of the copolymer was 15 $\times 10^{-12}$ m/V (or 15 pm/V). The investigators reported that since at the low modulating frequency of 5 kHz the electro-optic effect is dominated by the electronic contribution, r_{33} should exhibit little dispersion up to high modulating frequencies.

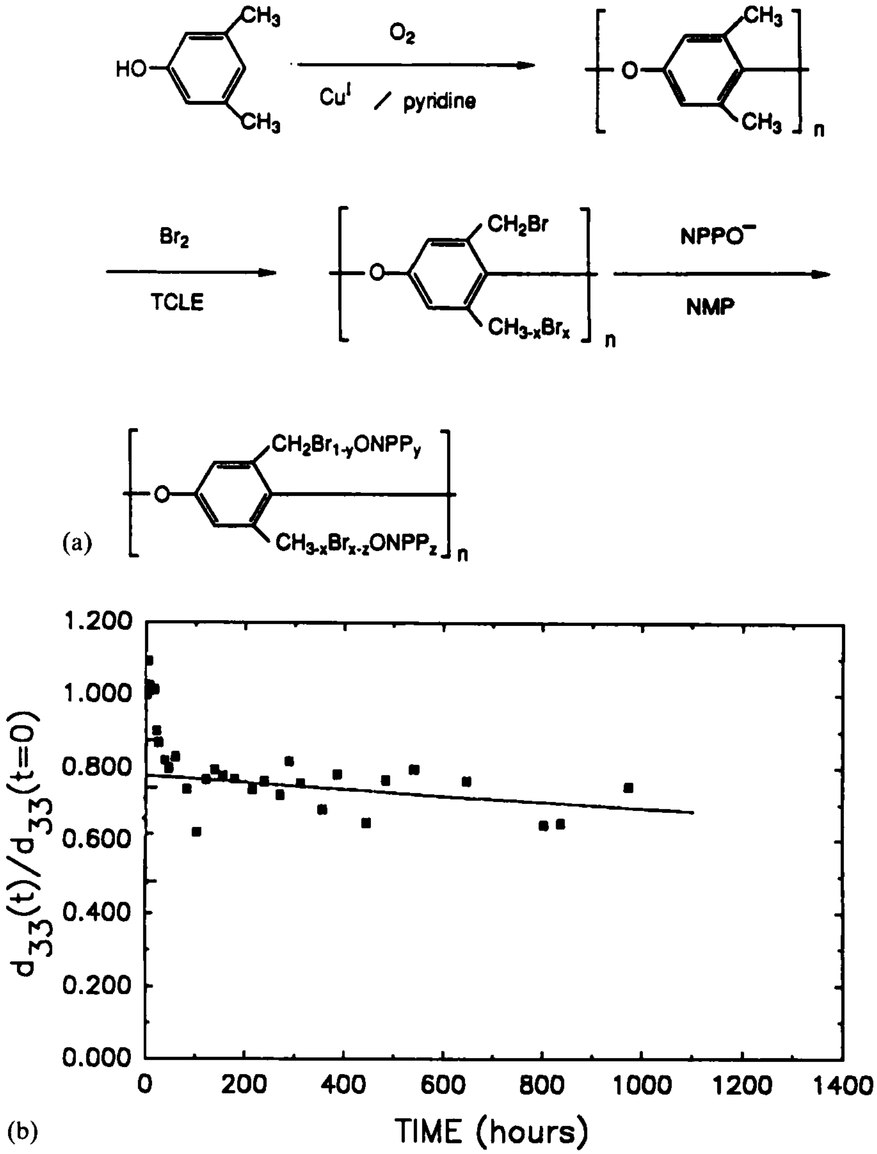


FIGURE 8 Chromophore-functionalized polymers. (A) Multiple-chromophore functionalization of PPO. (B) Temporal characteristics of corona-poled films.

ELECTRIC FIELD POLING WITH CROSSLINKING OF POLYMERS

In a third strategy, chromophore-functionalized polymers are simultaneously poled and crosslinked to significantly retard the rate of chromophore disorientation following field poling. Eich and colleagues have investigated a concept wherein nonlinear donor-π system acceptor molecules are incorporated in a rigid three-dimensional polymeric network with more than one chemical linkage between each NLO moiety and the network.[9]

Detailed studies were performed on tetrafunctional 4-nitro 1,2-phenylenediamine and bifunctional Bisphenol-a diglycidyether as the starting monomers. A precursor polymer, containing crosslinked sites attached to the NLO-active sites, is heated above its T_g, and a high electric field applied. Subsequent chemical crosslinking under the electric field advances the T_g, leading to in situ vitrification of the polymer. This stabilizes the electric-field induced orientation of the NLO moieties. A d_{33} = 13.5 pm/V, obtained from SHG experiments after simultaneous corona poling and curing at 140°C, remained stable over 500 hours at ambient.

Marks and coworkers have shown that a high β-guest chromophore can be dispersed in an optically transparent host matrix and simultaneously poled and chemically crosslinked.[7,10] Dry acetone or dichloromethane solutions of the high β-molecules DANS and Disperse Orange 1 were stirred with a thermosetting epoxy, EPO-TEK 301-2 (most likely a diglycidyl ether of bisphenol A according to Marks). Partial crosslinking of the matrix at 80°C prior to poling was necessary to avoid dielectric breakdown. Poling fields of $2 \times 10^4 - 6 \times 10^5$ V/cm were then gradually applied and maintained for measured periods of time at 80°C. The enhancement in overall SHG temporal stability compared to non-crosslinked guest-host systems is striking, as shown in Figure 9.

Marks and coworkers have investigated the SHG temporal characteristics of diepoxide crosslinked poly (p-hydrostyrene) functionalized with NPP.[7] Crosslinking agents were 1,2,7,8-diepoxyoctane or 1,4-butanediol diglycidyl ether. Films were corona-poled at 180°C for one hour, which induced high degrees of crosslinking and provided high electric fields without dielectric breakdown. The temporal characteristics of d_{33} for the corona-poled diepoxide cross-linked PHS-NPP films are more stable as a function of time than without the crosslinking agent.

ELECTRIC FIELD POLING OF LIQUID CRYSTALLINE POLYMERS

Figure 10 shows side chain liquid crystalline polymers developed by Griffin and coworkers in collaboration with Marks and colleagues, which demonstrate some very interesting SHG phenomena.[11] They are easily poled at room temperature, having a significant $\chi^{(2)}$ in the mesophase. With the field continuously applied, the $\chi^{(2)}$ diminishes as the temperature increases, going to zero at the mesophase-isotropic transition (125–145°C). Upon cooling back into the mesophase, the $\chi^{(2)}$ reappears and grows larger as the temperature decreases. That is, the $\chi^{(2)}$ tracks with the orientational order parameter of the liquid crystalline phase. A maximum value of d_{33} of 35×10^{-9} esu is reached at room temperature in Polymer 1, which also shows excellent temporal stability of SHG.

The preliminary interpretation of this observation is that dipoles in the nitroaromatic pendant groups which are aligned by the electric field can relax back easily in the isotropic phase where the pendant rods are "loosely" organized. However, they cannot relax back in the mesophase with its "closely packed" parallel ori-

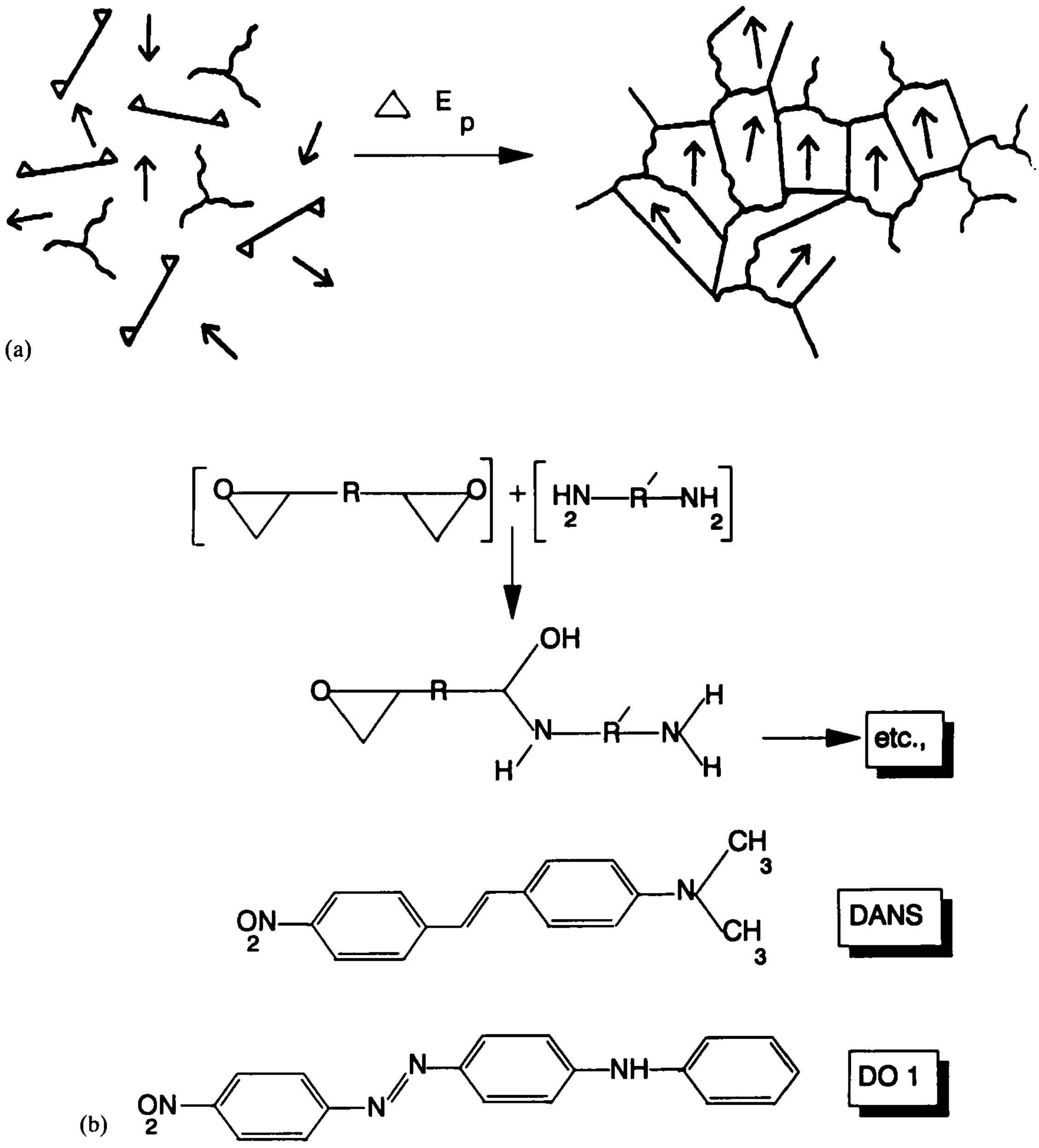


FIGURE 9 Simultaneous poling and crosslinking of chromophore-functionalized polymer. (A) The concept for doping an uncured epoxy. (B) The crosslinking chemistry and the NLO guest chromophores DANS and Disperse Orange 1 (DO 1). (C) The temporal stability of chromophore orientation in corona-poled, crosslinked films.

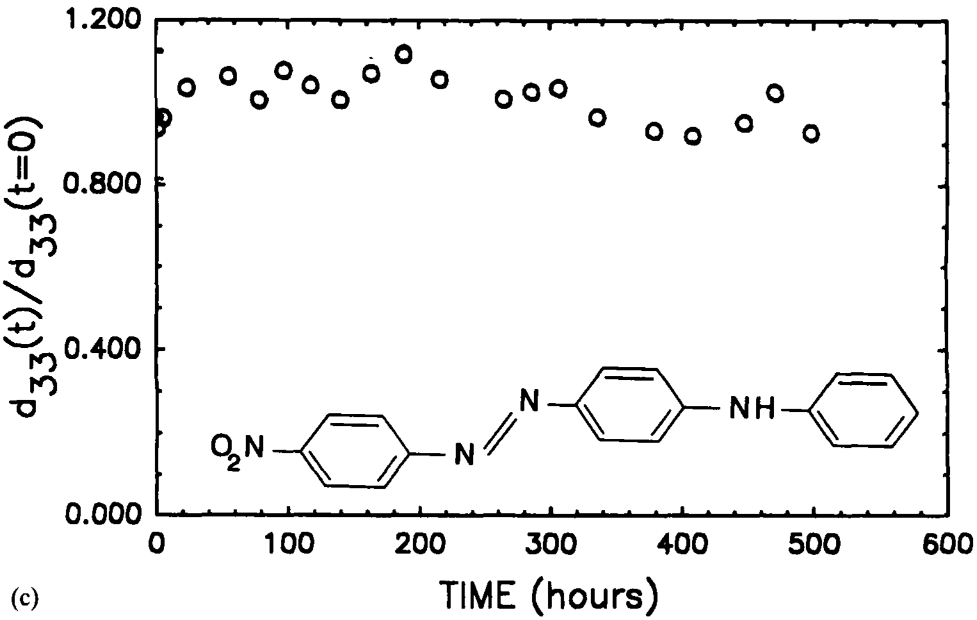


FIGURE 9 (*continued*)

entation of neighboring rods. That is, the motions of the pendant NLO dipoles are retarded and $\chi^{(2)}$ is enhanced significantly.

These polymer systems undergo a photoreaction for which, according to Griffin and Marks, there is preliminary evidence for a crosslinking reaction during poling. It is hypothesized that the stilbene C=C double bond participates in a photocrosslinking reaction leading to "freezing in" the dipolar order induced by the poling field. This sacrificial reaction of a small number of NLO units stabilizes the polar order of the others. This would permit a simple, yet effective means of providing temporal stability for the SHG in these types of polymers.

SECOND HARMONIC GENERATION IN ORGANOMETALLIC SALTS

Investigations have shown that organometallic salts can have a large powder SHG efficiency. Meredith reported in 1984 that $(CH_3)_2NC_6H_4$—CH=CH—$C_5H_4N(CH_3)$ $^+CH_3SO_4^-$ had a powder SHG efficiency approximately 220 times that of urea.[12] Dipolar interactions, which promote centrosymmetric crystallization by neutral dipolar compounds, could be negated by Coulombic interactions.

Green and coworkers in 1987 observed that a ferrocene complex (Z)-{1-ferrocenyl-2-(4-nitrophenyl) ethylene} has a powder SHG efficiency 62 times urea.[13] Marder and colleagues reported that the compound $(C_5H_5)Fe(C_5H_4)$—CH=CH—(4)—$C_5H_4N(CH_3)^+I^-$ at 1.907 μm fundamental radiation (to avoid absorption of the second harmonic by dark colored salts) had a powder SHG efficiency of 220 times that of urea.[14] Marder also reported that salts of the form

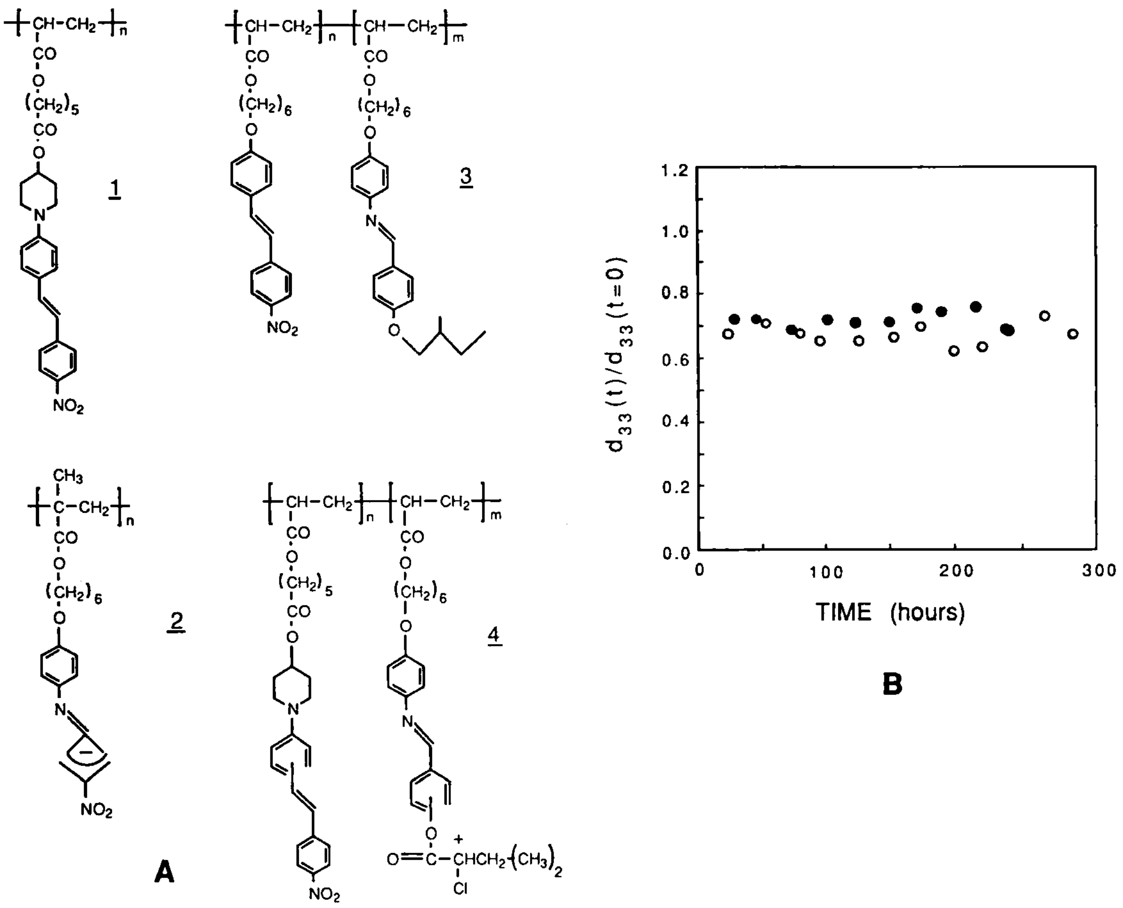


FIGURE 10 Room temperature poled side chain liquid crystalline polymers. (A) Structures. (B) Temporal stability of Polymer 1 after room temperature poling.

R—CH=CH—CH—$C_5H_4NCH_3^+X$— where R=4—$(CH_3)_2NC_6H_4$- and X=$CH_3C_6H_4SO_3$ showed a powder SHG efficiency of 1000 at 1.907 μm but 15 at 1.064 μm.[15] If R=4—$(CH_3)_2NC_6H_4$—CH=CH— and X=CF_3SO_3, an efficiency 500 times the urea standard was reported.

LADDER POLYMERS AS MODELS FOR SECOND ORDER MOLECULES

While organic and organometallic materials have been synthesized which demonstrate large values of the molecular second order hyperpolarizability, the successful exploitation of these high β-values as a bulk material $\chi^{(2)}$ is often limited by problems of processibility and thermal and photochemical stability. In addition there are problems of obtaining non-centrosymmetric crystalline structures and, as discussed earlier, relaxation of the molecular orientation. If useful intensities of the second harmonic are to be obtained, the material must be phase-matchable.

Dalton and coworkers in collaboration with Devine and Steier addressed these problems by using ladder polymers as models to design molecules with dye-type characteristics and thermal and photochemical stability.[16] On this premise they derived the three ring donor-acceptor compounds series in Figure 11. The $\mu\beta_o$ values were comparable to or better than MNA, but with improved thermal and photochemical stability.

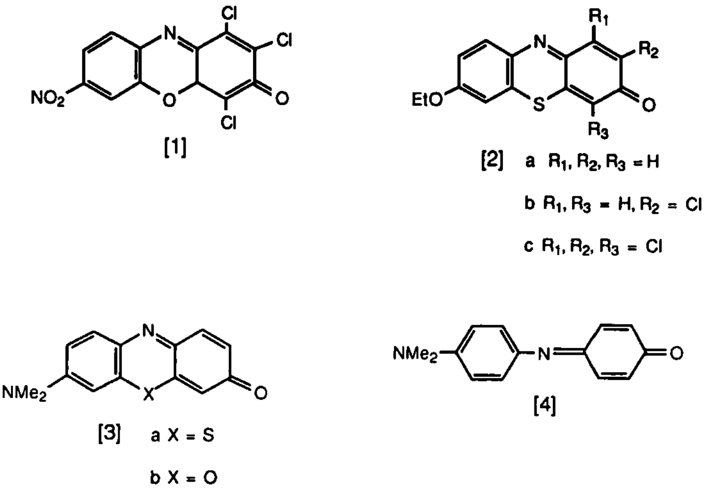
The trends for $\mu\beta_o$ values were obtained with the solvatochromatic technique, a method of limited accuracy, but suitable for establishing trends. The observed trends were confirmed by SHG measurements on corona-poled, dye-doped poly(vinyl acetate) films.

While the compound 2b gave the highest $\mu\beta_o$ value, the substituents of the stronger electron donating group, dimethylamino for ethoxy resulted in an increase of $\mu\beta_o$ from 105 to 250 × 10^{-30} D-esu (Debye-esu) (compound 3a).

PHASE-MATCHABLE SECOND ORDER COMPOSITES

The organic materials used for both frequency doubling and electrooptical effects are based on molecular structural design where a π-electron structure separates an electron donor group from an acceptor group, an example being 2-methyl-4-nitroaniline with a large second-order coefficient. However, this material is not phase-matchable for the largest component $\chi^{(2)}$ to produce efficient second harmonic generation.

Prasad has reported preliminary work on a class of materials which have the second order nonlinear coefficient comparable to and in some cases larger than MNA, but which also show phase matchability.[17] These are composites of iodoform complexes, such as $CHI_33C_9H_7N$ or $CHI_3 \cdot 3S_8$, and antimony triodide complexes like $SbI_3 \cdot 3S_8$.



A

Cpd.	Donor	X	Cl's	λmax (nm)	$\mu\beta_0$ (x 10^{-30} D-esu)
[2a]	EtO	S	0	483	85
[2b]	EtO	S	1	496	105
[2c]	EtO	S	3	519	50
[3a]	NMe_2	S	0	533	250
[3b]	NMe_2	O	0	508	75
[4]	NMe_2	none	0	567	200

B

FIGURE 11 Ladder polymers as models for second-order molecules. (A) The three ring donor-acceptor compound series. (B) The trends in second order molecular susceptibility (expressed as $\mu\beta_o$) for different bridging and donor atoms.

THIRD ORDER POLYMER DEVELOPMENT

The polymer ultrastructural design for $\chi^{(3)}$ has progressed as has the synthesis and processing for achieving these structures. In comparison to second-order polymers, substantial improvement is required in polymer properties such as optical nonlinearity, optical transparency, and processibility before serious device development can occur. Laser damage resistance for some third order polymers has been reported to be in the range of 4 GW/cm^2 and higher, which is a major advantage for device operation.

Comparison of data from different characterization techniques for $\chi^{(3)}$ such as degenerate four wave mixing (DFWM) and third harmonic generation (THG) is difficult. Each measures different components of $\chi^{(3)}$. One mechanism may be more manifested in THG measurements and another in DFWM. Data sets as a function of frequency or pulse conditions are very limited. As a result when $\chi^{(3)}$ values for new polymers are quoted, the operative mechanisms, the relative contributions of resonant and nonresonant processes, and the real and imaginary contributions to optical nonlinearity are not defined.

On the molecular level an effort must be made to separate intra- and intermolecular contributions to optical nonlinearity and to define structural disorder effects, particularly for measurements made near the bandedge where electronic, π-π^*, N-π^*, and charge transfer contributions may overlap. Further, for delocalized π-electron polymers to show good solubility, it is necessary to destabilize polymer-polymer interactions, and/or to enhance polymer-solvent interactions. Derivatization of polymer backbones and soluble precursor routes have been utilized.

COPOLYMERS WITH DEFINED π-ELECTRON CONJUGATION LENGTHS

Yu and Dalton have used these routes to control optical bandgap by synthesizing copolymer systems of rigid-rod electroactive and flexible chain segments.[18] The latter controls solubility and solid state morphology. Delocalized polymer segments of defined length control the NLO properties. A distribution of bandgaps associated with different polymer lengths can be avoided, and tailing of the optical spectra toward the infrared is prevented. For measurements made within the bandgap, the resonant contribution can be avoided.

Two examples of this class of copolymers are shown in Figure 12. Over the wavelength range of incident laser energy of 574 to 596 nm, the $\chi^{(3)}/\alpha$ value, the ratio of third order susceptibility to optical loss, falls into the range of 10^{-12} to 10^{-13} esu cm. This ratio is a figure of merit for device operation.

The copolymer triphenodioxazine (polymer a), a five-fused-ring unit, with an aliphatic flexible-chain spacer has a clearly defined optical bandgap, good processability, and high thermal stability (480°C). An extremely fast NLO process was demonstrated by DFWM at zero delay time, arising from the contribution of virtual electronic excitations, and a slower resonant electronic contribution.

This work suggests that the π-electron portion of a copolymer need only exceed the self-localization field length to yield optimum nonlinearity.[19] Garito and colleagues predicted that the hyperpolarizability tensor γ_{xxxx} exhibited a polymer chain dependence of $L^{4.6}$ for both cis and trans conformations, being much more sensitive to the physical length than the conformation. This prediction was in reasonable agreement with experimental values for short chain polyene, suggesting an effective π-electron delocalization length of 60 Angstroms. This result was also suggested by electron nuclear double resonance (ENDOR) magnetic resonance spectroscopic

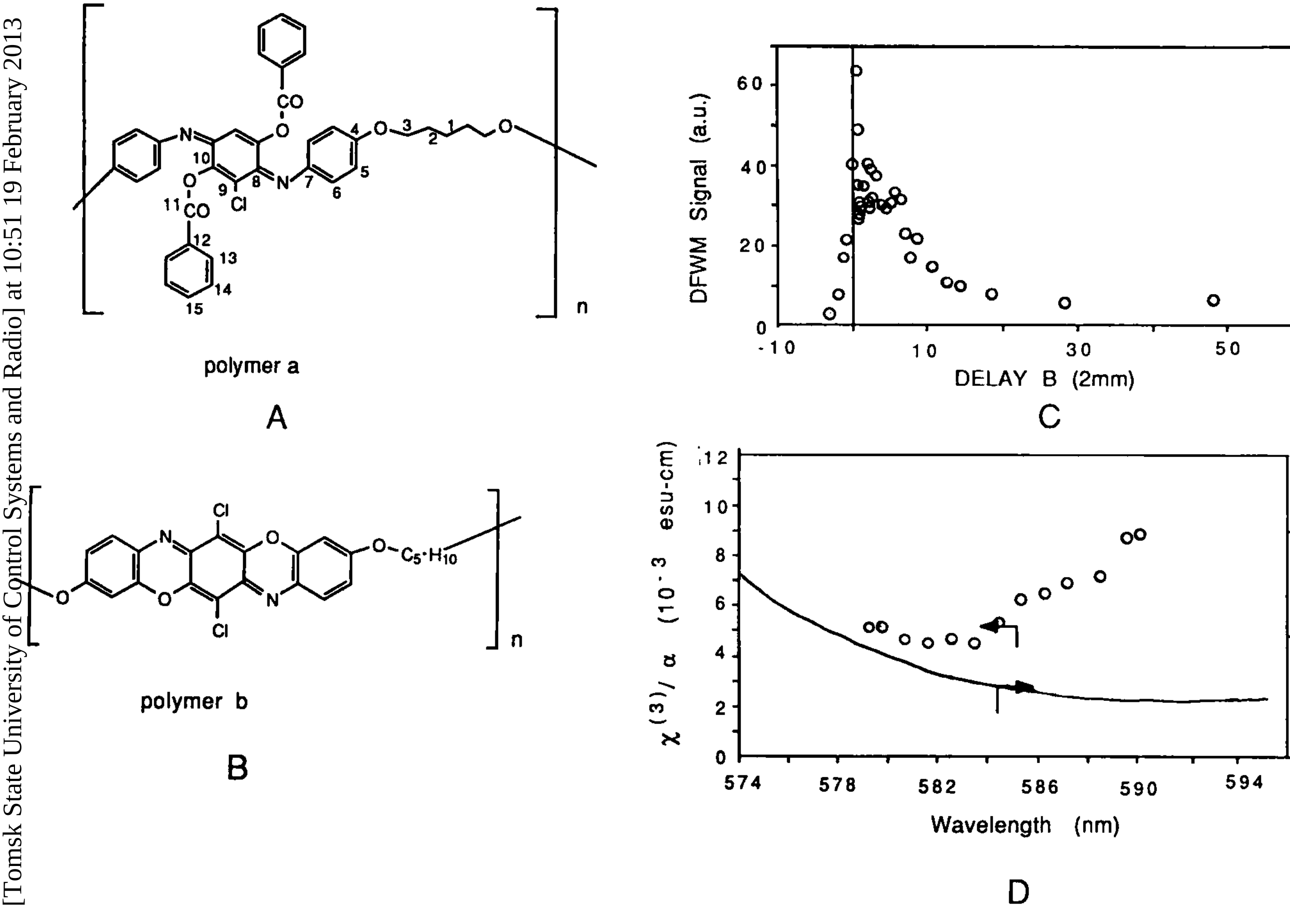


FIGURE 12 Rigid rod/flexible chain copolymers with defined conjugation length. (A) Open chain copolymer of triphenodioxazine and a flexible spacer. (B) An experimental copolymer system containing defined lengths capable of electron delocalization separated by saturated elements which can improve solubility. (C) DFWM signal pulse energy versus delay time for Polymer A. Note an extremely fast NLO process at zero delay time and a slower NLO process. (D) $\chi^{(3)}/\alpha$ and linear absorption as a function of wavelength for polymer A.

experiments.[20] Thus the elimination of the need for extended and highly conjugated segments enhances processability.

Dalton and Yu have further examined other new polymers incorporating a variety of electroactive moieties with defined π-electron conjugation lengths.[21] They found that the largest values of $\chi^{(3)}/\alpha$ observed were 10^{-12} esu cm for triphenodioxazine, 6,6′-dimethoxy-quinolidine, metal phthalocyanine, and metal tetraazoannulene.

CONFINED DELOCALIZATION IN LADDER POLYMERS

Electron Paramagnetic Resonance measurements and ENDOR, shown in Figure 13, indicate HOMO (highest occupied molecular orbital) delocalization/localization phenomena in ladder polymers, such as BBL(poly[7-oxo-7,10-benz[de]imidazo[4′,5′:5, 6]-benzimidazo[2,1-a]isoquinoline-3,4: 10,11-tetrayl)-10-carbonyl]) similar to that observed for polyacetylene.[20] Thermally stable to 550°C in air, BBL showed DFWM $\chi^{(3)}$ of 2×10^{-9} esu at 532 nm ($\alpha = 18.3 \times 10^4$ cm^{-1}) and approximately 10^{-11} esu at 1.064 μm.[20,22] These represent current numbers being measured on ladder polymers, and as pointed out by these investigators, the separation of nonresonant from resonant contributions is important for device material design.

This has been demonstrated by Hellwarth and coworkers in a study of the picosecond nonlinear optical response of polyquinoxaline-based aromatic conjugated ladder thin films.[23] They reported a DFWM technique for measuring all the tensor components of $\chi^{(3)}$ which govern both the electronic and lattice-related nonlinear responses. Their analysis estimated the errors in the tensor component's values arising from uncertainties in both the spatial and temporal profiles of the optical pulses used for measurement.

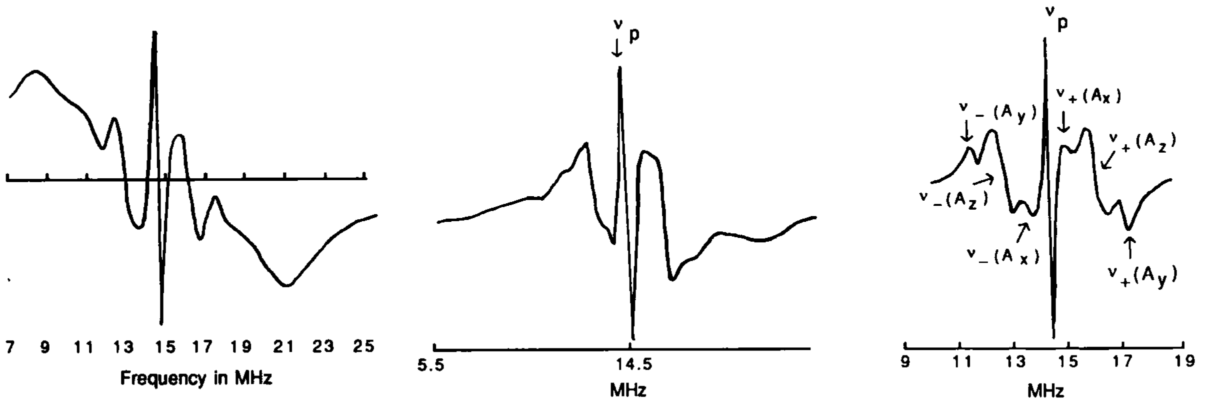
CHARGE-ENHANCED THIRD ORDER NONLINEARITY IN LADDER POLYMERS

Doping of ladder polymers may be another way to introduce optical windows and increasing $\chi^{(3)}$. The calculations of DeMelo and Silbey suggest that $\chi^{(3)}$ increases on going from the neutral to the polaronic lattice.[24] Dalton has demonstrated the effect of chemical doping on the linear optical spectrum of a delocalized phenylpolyene oligomer.[25] As shown in Figure 14, the neutral state spectra of delocalized phenypolyene oligomer is characterized by a strong absorption in the visible and transparency in the infrared. Chemical doping produces the polaron/bipolaron states which introduce the generation of a charged (polaron/bipolaron) lattice with transparency in the visible and absorption in the infrared. These spectra represent a fundamental mechanism of optical nonlinearity wherein excitation across the bandgap will produce electron-hole pairs. These can rapidly decay into polaronic species by structural relaxation.

Spangler and coworkers studied the ladder model systems triphenodithiazine and triphenodioxazine, which are related to PTL (poly[2H,11H-bis[1,4]triazino[3,2-b:3′2′-m]triphenodithiazine-3,12diyl-2,11-diylidene-11,12-bis(methylidine)]) and POL

ELECTRON DELOCALIZATION IN ELECTROACTIVE AND LADDER POLYMERS

- Development of Theory of Electron Nuclear Double Resonance (ENDOR)



Polyacetylene
Computer Simulation

Polyacetylene
ENDOR Spectrum

Aromatic Heterocyclic (BBL)
ENDOR Spectrum

- Electronic Spin Density Confirms Electronic Excitation (Electron Correlation)
- Highest Occupied Molecular Orbital (HOMO) Exhibits <u>Comparable</u> Finite Intrinsic Delocalization in Conducting and Ladder Polymers

FIGURE 13 Electron Nuclear Double Resonance (ENDOR) shows that there is comparable finite intrinsic delocalization in polyacetylene and the BBL ladder polymer.

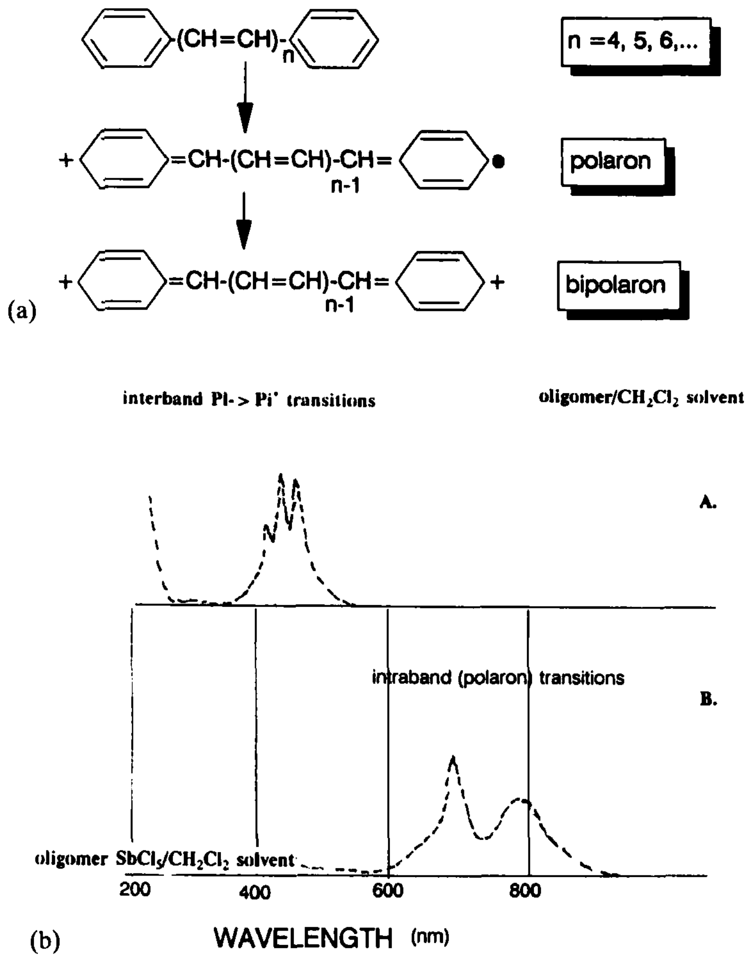


FIGURE 14 Effect of chemical doping on the linear optical spectrum of a delocalized electron ladder polymer. (A) Polaron and bipolaron formation in diphenylpolyenes. (B) The introduction of a visual transparency with the generation of a charged (polaron) lattice. This spectrum represents a fundamental mechanism of optical nonlinearity.

(poly[2H,11H-bis[1,4]oxazino[3,2-b:3′,2′-m]triphenodioxazine-3,12-diyl-2,11-diylidene-11,12-bis (methylidine)]), doped with solutions of $SbCl_5$ in CH_2Cl_2.[26] A new band structure, shifted far to the red as illustrated in Figure 15, replaces the original π-π^* band of the original compound. This shows that the wavelength of maximum absorption and the band edge of both the original π-π^* transition and eventual bipolaronic state can be manipulated by substituent choice and the nature of the unconjugated heteroatom in the ring system.

If the intrinsic delocalization in ladder polymers is confined as Garito and Dalton have pointed out, the NLO-active segments could contain oligomeric ladder segments. Choice of ladder heteroatom combination, substituent group identity and the length of each ladder segment is a way to design precise control over NLO

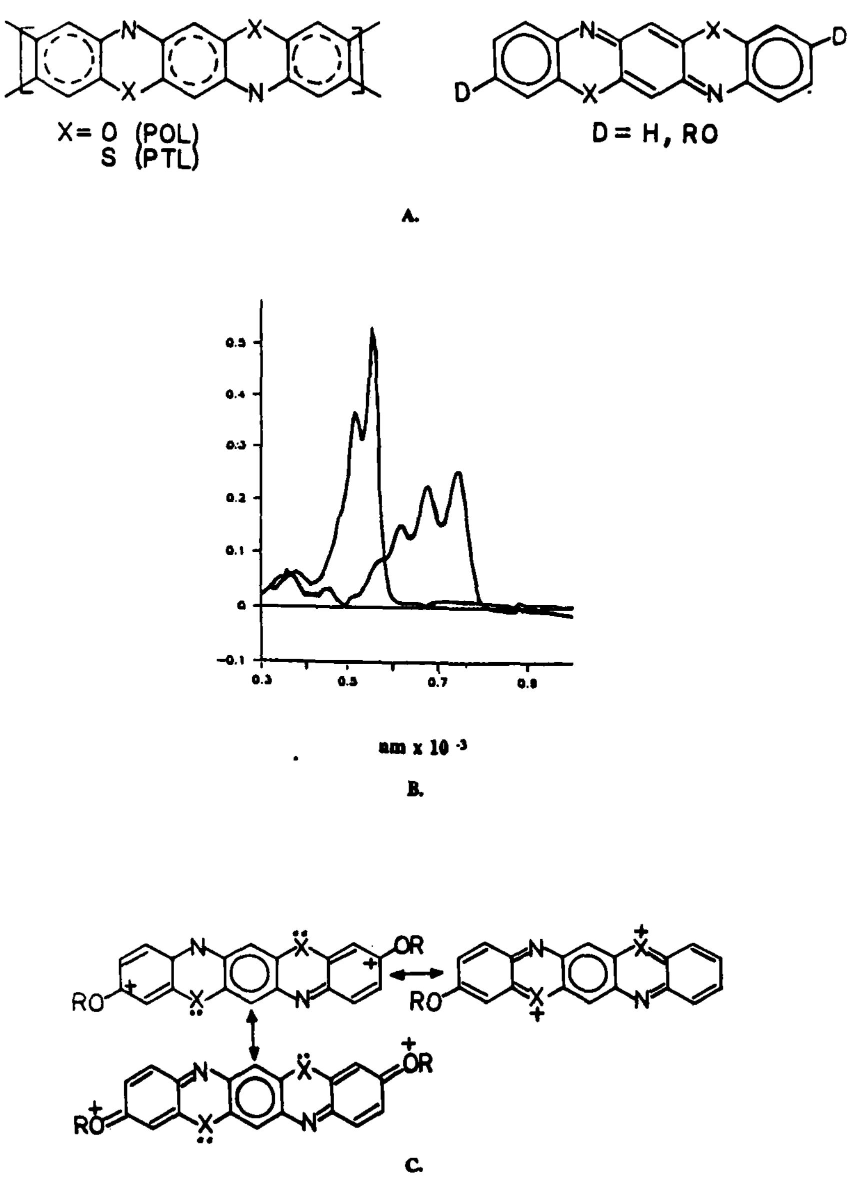


FIGURE 15 Stabilization of biopolaron states in model ladder systems for $\chi^{(3)}$ enhancement and visual transparency. (A) Schematic representation of hypothetical electron delocalization in PTL and POL and model compounds. (B) PTLM and PTLM bipolaron absorption spectra where M refers to the monomeric polymer model. The doping process produces a new band structure shifted far to the red, replacing the π-π* band of the original compound. (C) Stabilization can be achieved by mesomeric interaction with either substituent group or ring heteroatom lone pairs.

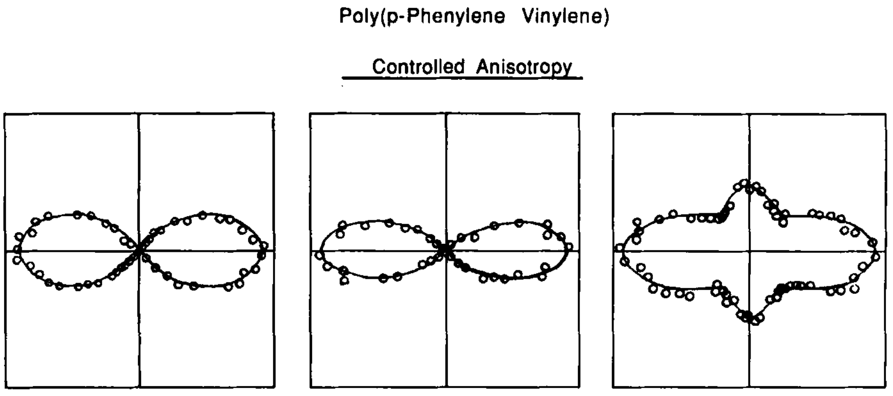
properties. Solubility and film processibility could be controlled by varying the size and nature of the spacer.

Recently, Hellwarth and colleagues observed bioloaronic enhanced third-order optical nonlinearity in POL ladder polymers.[27] The wavelength dependence of the bipolaronic enhanced nonlinearity is consistent with the change of absorption spectra due to the formation of bipolaronic state during electrochemical doping. Hellwarth reports that a large (5×10^{-9} esu) and fast (120 psec) nonresonant $\chi^{(3)}$ is found at 645 nm. In addition these ladder thin films possess excellent thermal and chemical stability with a laser damage threshold as high as 10 GW/cm^2.

PROCESSIBILITY FOR CHAIN ALIGNMENT ENHANCED $\chi^{(3)}$

Processibility to achieve ordered polymers with chain alignment is another approach for enhancing $\chi^{(3)}$ without introducing a new mechanism. This has been demonstrated with the poly-*p*-phenylene vinylenes (PPV) and their analogs, such as poly thienyl vinylene (PTV). Good optical quality films can be prepared through a soluble sulfonium salt precursor, some of which are water soluble. This enables the device structure to be made with the precursor polymer, and then converted to the PPV polymer by heat treatment.

PPV and its 2,5 methoxy derivatives have been processed as uniaxial and biaxial stretch-oriented free standing films.[28] The change in $\chi^{(3)}$ value (actually the square root of the DFWM signal) as a function of film rotation with respect to the incident electric field vector yields polar plots. The controlled anisotropy is illustrated for several polar plots in Figure 16.



Uniaxial Draw Ratio 6:1

$\chi^{(3)}_{1111}/\chi^{(3)}_{2222} = 18$

Uniaxial Draw Ratio 10:1

$\chi^{(3)}_{1111}/\chi^{(3)}_{2222} = 39$

Biaxial Draw Ratio 6:1 and 3.5:1

$\chi^{(3)}_{1111}/\chi^{(3)}_{2222} = 1.5$

FIGURE 16 Polar plots (orientational anisotropy) for uniaxially and biaxially stretched PPV films. The circular dots represent experimental data points; the solid lines are theoretical fits. They $\chi_{1111}^{(3)}$ value is $(\chi^{(3)})_{\parallel}$, which is the orientation parallel to the draw direction. The $\chi_{2222}^{(3)}$ value is $(\chi^{(3)})_{\perp}$ value, which is oriented perpendicular to the draw direction.

In the 6:1 uniaxially stretched PPV films the $\chi^{(3)}$ values parallel and perpendicular to the draw direction are 1.2×10^{-9} esu and 0.063×10^{-9} esu, respectively.[29] The refractive indices in the parallel and transverse directions are 2.89 and 1.63. This large birefringence with the femtosecond response time makes PPV a potential replacement for the slower responding liquid crystals in rapid optical beam steering applications. The liquid crystals have a large birefringence, but a microsecond response.

The highest $(\chi^{(3)})_{\parallel}$ values are obtained when the electric vectors are parallel to the draw direction. The minimum $(\chi^{(3)})_{\perp}$ value is for the orientation when all electrical vectors are perpendicular to the draw direction. A $(\chi^{(3)})_{\parallel}/(\chi^{(3)})_{\perp}$ ratio of 39 for the 10:1 uniaxial stretched PPV film indicates a very high degree of orientational anisotropy. X-ray shows a high degree of polymer chain alignment along the draw direction. The orientational anisotropy in PPV offers a route to polarization bistability in devices.

A subpicosecond response of $\chi^{(3)}$ is observed as expected under nonresonant conditions. However, in the 10:1 uniaxially stretched film a weak tail with a longer time constant indicates that even the apparent nonresonant regime (below the band gap) is not free of absorption. An unusual behavior was observed for uniaxial (2,5-dimethoxy paraphenylene vinylene). Along the draw direction $\chi^{(3)}$ is complex with a negative real part and has a response time that is longer than the optical pulse resolution. In contrast, $\chi^{(3)}$ along the transverse direction is largely real and positive, its response time being much faster. It is limited by the laser pulse width of about 400 femtoseconds.

Heeger and Smith have found that NLO polymers can be deposited as meso-epitaxial films by orientation-inducing substrates using Teflon films aligned by rubbing.[30] Patel and coworkers recently reported an epitaxial method for orienting thin films of polydiacetylenes (poly 4BCMU) on ordinary alignment polymers which have been stretched by rubbing.[31] Poly (1,4-butylene terephthalate) was the alignment polymer.

Polythiophene is air stable, unlike polyacetylene. When derivatized by long alkyl substitution, polythiophenes become soluble and can be processed in several ways, including forming Langmuir-Blodgett films.[32] The $\chi^{(3)}$ behavior has been measured in several forms. Values of 4×10^{-9} esu and 4×10^{-10} esu have been measured at 532 and 602 nm, respectively. The nonlinearity is resonant with a subpicosecond response time. Prasad and coworkers reported the femtosecond time-resolved DFWM in a 3-dodecyl polythiophene film shown in Figure 17. At 1.060 μm Yang and coworkers measured $\chi^{(3)}$ values of greater than 3×10^{-11} esu, which is about two orders of magnitude smaller than the values measured at resonance.

OPTICAL BISTABILITY IN RANDOM GLASSY POLYMERS

Garito and Wu discovered the first case of absorptive optical bistability occurring through the nonlinear electronic excitations of a random solid medium contained in a resonant Fabry-Perot cavity.[3,33] The medium is a glassy polymer ultrathin film consisting of quasi-two dimensional conjugated discs of silicon naphthalcyanine

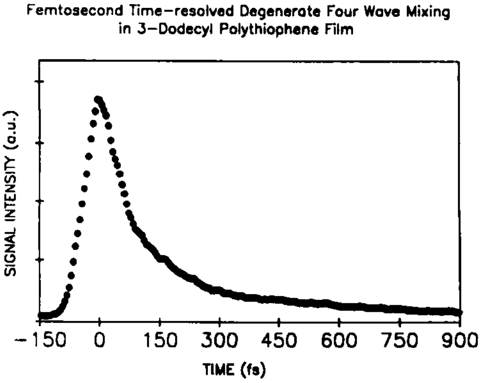


FIGURE 17 The femtosecond degenerate four wave mixing phase conjugate signal from a polythiophene monolayer (22 Angstrom) film. The value of $\chi^{(3)}$ is approximately 10^{-9} at 602 nm.

oligomers (SINC) randomly distributed in a glassy matrix shown in Figure 18. Both pure SINC and SINC polymer alloy ultrathin films, synthesized by Kalyanaruman and Sounik, were directly formed by spin coating techniques as homogeneous, high optical quality films (loss < 1 dB/cm) at 810 nm.

The linear absorption spectra of the pure SINC film and a solid solution film of SINC in PMMA each exhibit an intense electronic excitation centered in the near infrared region having an exceptionally large linear absorption coefficient of 1×10^5 cm^{-1}. The on-site electronic excitation of the quasi-2Ddiscs is easily saturable at fast timescales (10^{-9}–10^{-10} seconds). The nonlinear refractive index n_2 obtained from the saturable absorption results is 1×10^{-4} cm^2/kW which is comparable to GaAs and GaAs/GaAlAs multiple quantum wells.

Recently Garito and Wu discovered that the central frequency for nonlinear absorption and bistability is tunable in these systems over the near infrared-visible range (800-400 nm), demonstrating that the observed phenomena and microscopic description are general to entire classes of quasi-two dimensional structures. Nearly any laser source can be used in implementing these phenomena.

ELECTRO-OPTIC DEVICES

The synthesis of the aforementioned glass polymer films containing molecular units with large nonlinear polarizabilities has led to the rapid implementation of polymer integrated optics. Figure 19 compares the current state-of-the-art of physical and device properties of titanium-lithium niobate integrated optics with polymer integrated optics.[34]

Packaging is still an unknown and will be the determining factor for successful manufacturing and low cost.[34] One advantage is the potential level of integration into optical packages because of small single-mode waveguide dimensions, being approximately 3 to 5 μm, and high waveguide packing density (20 μm centers for less than 30 dB crosstalk over 10 cm). Another advantage is the potential for novel

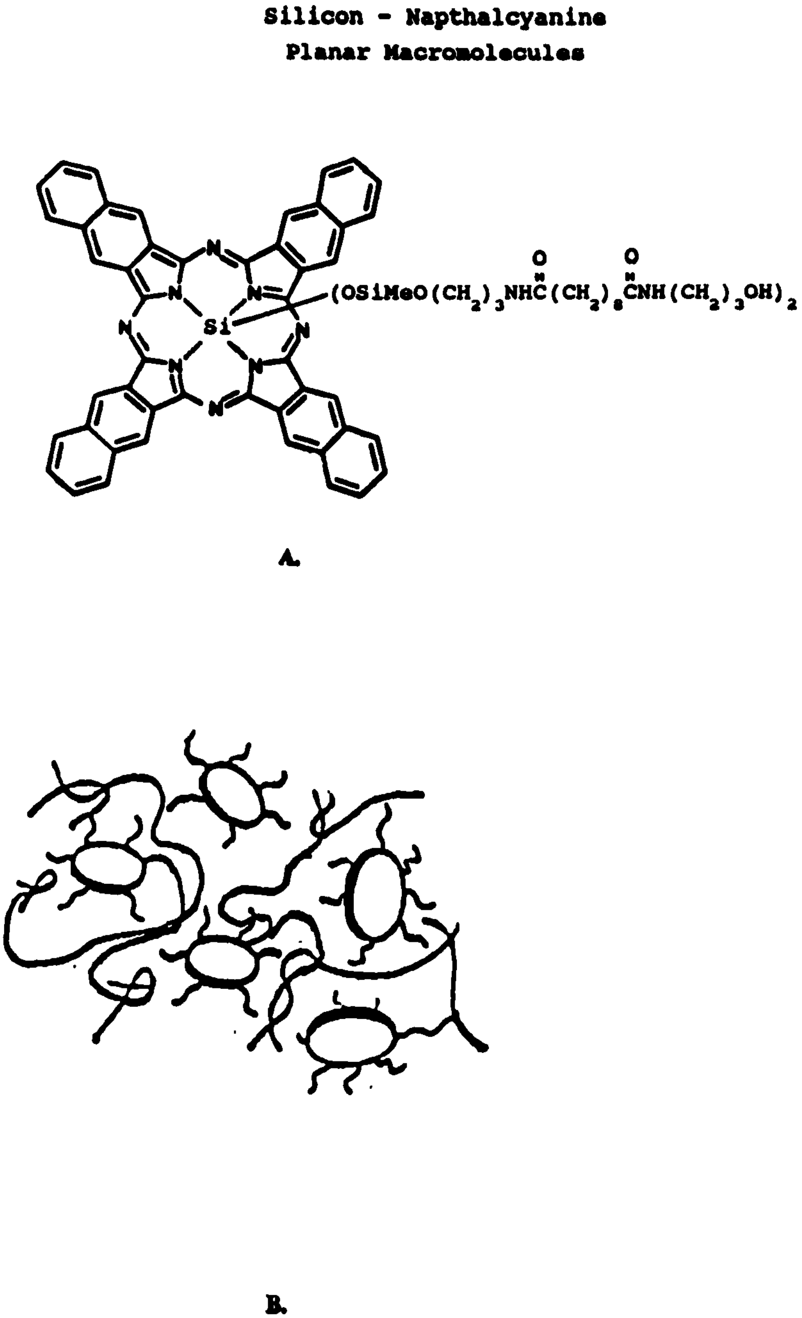


FIGURE 18 Saturable absorbing resonant polymers. (A) Molecular structure of silicon naphthalocyanine (SINC). (B) Schematic of quasi-two dimensional conjugated discs of SINC randomly distributed in a glassy polymer.

PHYSICAL AND DEVICE PROPERTIES	Ti-Lithium Niobate	Organic Polymers
Electro-optic coefficient (pm/V)	32	10 - 50
Dielectric constant	28	4
Loss (dB/cm @ $\lambda = 1.3$ μm)	0.1	0.2 - 0.5
Space-bandwidth product (GHz-cm)	10	120
Crystal growth temperature (°C)	1000	NA
Waveguide processing temperature (°C)	1000	150 - 200
Waveguide processing time	10 hr	10 min
Multiple layers possible	No	Yes
Fabrication and processing	difficult	simpler
Packaging	expensive	UNKNOWN
Maturity	30 years	10 years

FIGURE 19 Comparison of state-of-the-art physical and device properties of titanium-lithium niobate versus polymeric waveguides. Packaging is a major factor for economic success.

hybrid optoelectronic packages. These include multilevel polymer/metal interconnect packages; hybrid optical multichip modules; hybrid packaging and connection of sources detectors, and electronic components; and integrated silicon substrates containing detectors, amplifiers, and other circuitry.

With nonlinear optical active polymers, the materials are not yet nearly as mature as passive and photoresist polymers, and variations in all optical and electrical properties are expected and observed from one batch to another. Moreover, the requirement to pole a waveguide can add many mask steps to the process and introduces the need to be concerned with the electrical properties of the core and cladding materials, and their compatibility with electrode materials. As a consequence all reported device structures exhibit desired effects, but do not yet achieve the performance expected from these potentially important materials.

The earliest channel waveguide device work was reported by Lytel and coworkers, and demonstrated multimode switching, coupling, and modulation in channel waveguides.[35,36] These devices were based on organic polymers spun-coated into high quality thin films on optical substrates. As spun, the films are isotropic and thus exhibit no linear electro-optic effect, r. In addition to inducing a noncentrosymmetric structure to achieve a macroscopic electro-optic effect, electric field poling has been extensively studied as a means to partially align nonlinear optical molecules in an inert polymer matrix to induce a macroscopic r.

Lytel, *et al.*, developed a new method, selective poling, to define active channel waveguides for its first devices. An electrode pattern, defining the channel waveguides, is deposited on an optical substrate and covered with a buffer layer, to isolate the active waveguide from the electrode. This is shown in Figure 20.[34]

The buffer material must be chosen to have an index lower than the guiding layer and to be compatible with the required processing. The electro-optic polymer is spun directly onto the lower buffer layer, and different buffer layers must often be used with different nonlinear polymers. A metal ground plane is then deposited directly onto the nonlinear polymer for poling using standard photolithographic techniques. The nonlinear layer is then poled by applying the electric field above the polymer glass transition temperature and cooling the sample to room temperature under the influence of the field. The degree of alignment induced and the resultant electro-optic coefficient can be calculated based on a statistical average of the molecular susceptibilities. In this case only those regions of the material defined by the electrode pattern on the electro-optic material are poled.[34]

Since most organic nonlinear optical molecules also possess an anisotropic microscopic linear polarizability, the poled region becomes birefringent. The poled regions are uniaxial, with n_e oriented along the direction of the poling field. Consequently, TM waves propagating along the device structure will experience a greater refractive index in the poled regions than the unpoled regions, and so can be confined in the lateral dimension. Thus, by applying the poling fields using electrodes patterned to define the waveguide network, including both active and passive sections, no further patterning of the NLO organic layer is required to form the channel electro-optic waveguide structures. The devices are then completed by etching off the poling electrode, applying an upper buffer layer and depositing the

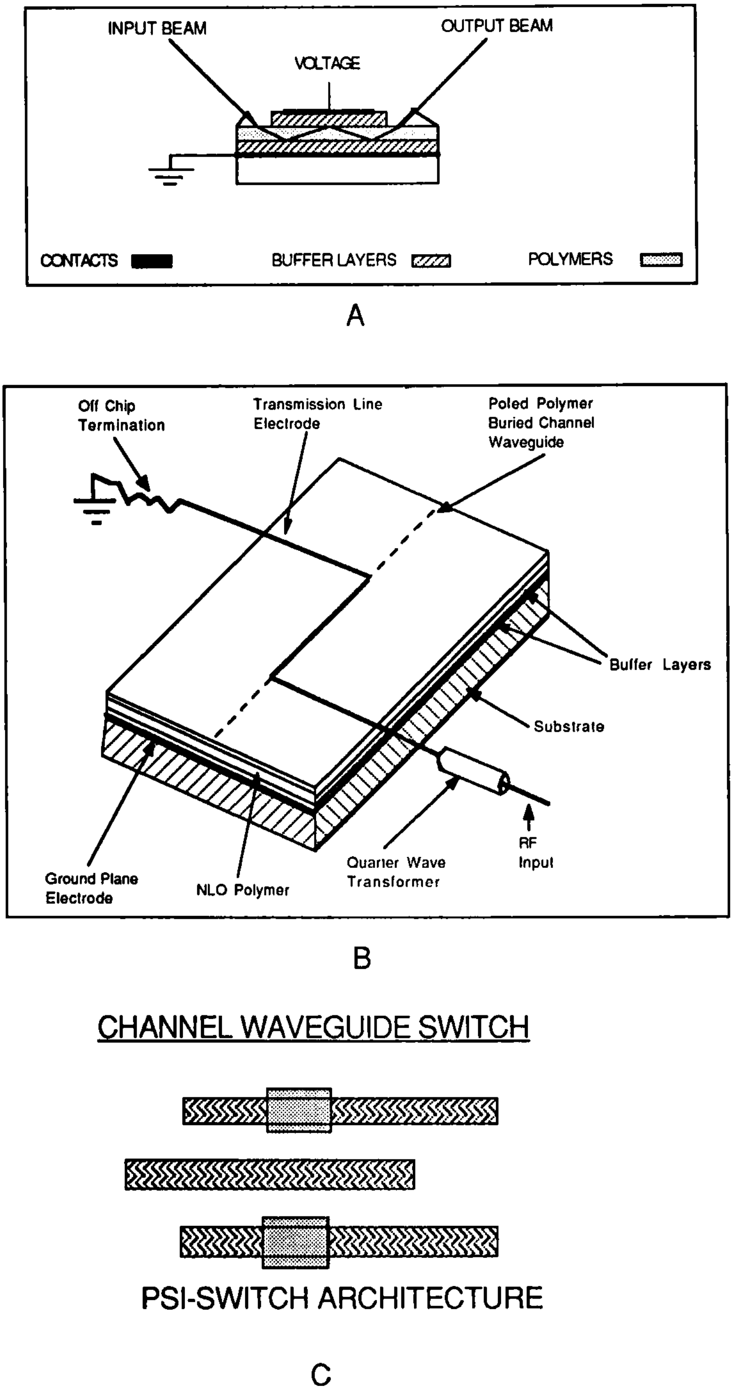


FIGURE 20 Second order polymer electrooptic devices. (A) Waveguide construction. (B) Schematic diagram of polymeric traveling wave phase modulator. (C) Schematic of evanescent waveguide switch.

patterned switching electrode. The switching electrodes are positioned to address only the sections of the guide desired to be active.[34]

To the author's knowledge, this technique represents the state-of-the-art for designing and constructing electro-optic devices. Using this technique, Lytel has fabricated poled polymer channel waveguides, and has demonstrated modulators, couplers, and bends in electro-optic polymer materials.

Using the poled polymer waveguide fabrication technique a 1.0 Ghz traveling wave phase modulator was constructed by Lytel's group and is shown schematically in Figure 20. This device was constructed to investigate the material response at RF frequencies and to verify theoretical performance predictions. It was not optimized for optical or electrical performance and was not packaged.[34]

Of note here is that the signal at 260 MHz for a drive voltage of 8.7 volts represented a phase modulation of 60% of full wave and yielded a value for the electro-optic coefficient, r, exactly the same as that measured at low frequency. Thus no dispersion is observed in r out to 260 Mhz.

Figure 20 illustrates a schematic of a new switching device, the psi switch.[37] This device is an evanescent, triple-coupler, providing in principle complete switching of light from a center guide to either of two outer guides. A prototype was fabricated in an oxynitrostilbene polymer material to demonstrate both single-mode operation and switching at moderate frequencies. This type of device has great potential for optical interconnection networks, but requires extraordinary control of the material properties to achieve both precise waveguide dimensions and effective indices.

Other new device prototypes including 2 × 2 switches, Mach-Zehnder modulators, and even tunable etalons have been reported.[38]

Lee and coworkers reported on a solution to minimize the lowering of frequency doubling conversion efficiency due to destructive interference.[39] While polymeric nonlinear optical materials were initially characterized by SHG of 1.3 μm or 1.9 μm light, they are investigating waveguide device design in polymer films for doubling 1.3 m to 0.83 m light and taking advantage of the requirement for polymers to be poled in order to generate a non-zero $\chi^{(2)}$. The second harmonic generation is limited by the same velocity mismatch that occurs in travelling-wave modulators. The fundamental and harmonic travel at different velocities. At 3 to 15 μm down he waveguide, the harmonic light being generated is 180° out of phase with and destructively interferes with the light being generated at the beginning of the device.

By using a finger electrode structure, the polymer can be poled periodically. The second harmonic builds up in the waveguide until the waves are just out of phase and enter an unpoled polymer region. No new harmonic light is generated, the fundamental and harmonic optical signals travelling in the unpoled polymer until they are again in phase. They then enter the next poled region, enhanced SHG being observed.

The application of electro-optic polymer materials to practical devices will require some significant advances in the development of the materials.[34] There are no intrinsic science limitations to prevent this. These required advances arise mainly from the required thermal stability of the polymer poled state and the stability and tolerances required to minimize or control device or package performance variations when operating over a desired environmental range. Lytel points out that the full assembly of a device, be it a fiber-pigtailed modulator or an integrated module, will require such processes as fiber attachment using established, standard industry processes, module packaging and final systems assembly. These need to be compatible with military end use requirements of 125°C continuous use and 200°C storage.

Most of the current research electro-optic polymers exhibit glass transition temperatures of order 130° to 150°C. This low T_g results in high polymer chain diffusion rates and a calculable variation of at least 10% in the optical properties of the poled state over 5 years operation at ambient temperature, according to Lytel.

The performance limitations of these materials are due to the fact that they have not yet been formulated for field use. Some of the aforementioned second-order polymer research shows that crosslinked systems and higher temperature host materials are approaches to better thermal and poling stability.

THIRD-ORDER NONLINEAR POLYMERIC DEVICES

The area of third-order nonlinear polymeric devices is still in its early stages. This reflects both the infancy of third-order nonlinear device concepts, as well as the developmental stage of third-order nonlinear polymeric materials and mechanisms.

Prasad and coworkers demonstrated the intensity dependent phase shift due to electronic nonlinearity in a polyamic acid waveguide (Figure 21).[40] Propagation distances over 5 cm were achieved with total attenuation of approximately 1.2 cm^{-1}. Intensity-dependent coupling efficiency, limiter action behavior and intensity dependent coupling angle have been observed using grating excitation with 400 fs, 80 ps, and 10 ns pulses.

The grating coupler used in this experiment was fabricated on a fused silica glass substrate by reactive ion-milling technique. With these gratings the coupling angles were all within a few degrees of normal incidence. A 1 μm thick film of polyamic acid was spin coated from N,N-diamethylacetamide solution and dried under ambient conditions for a few hours.

A nonlinear grating coupler analysis identifies the subpicosecond and picosecond processes in the waveguide with electronic nonlinearity. The intensity dependent refractive index (electronic nonlinearity) for thin polyamic acid film waveguide was determined to be 3×10^{-18} m^2/W.

Most of the third order devices constructed and tested have used polydiacetylene films and crystals. This is because of the availability of these materials in quantity. Many of the current research polymers are not available yet in the reproducible quantities required for device studies and evaluation.

As an extension of his work, Prasad performed measurements of the refractive indices of poly-4-BCMU, poly[5,7-dodecadiyne-1, 12-diol-bis(n-butoxycarbonylmethylurethane)] films, and the fabrication of an efficient integrated optical coupler.[41] The refractive index measurements were performed in the visible and near infrared using blazed grating couplers. The analysis led to the optimization of a blazed-grating input coupler with a coupling efficiency larger than 45% at 1.064 μm.

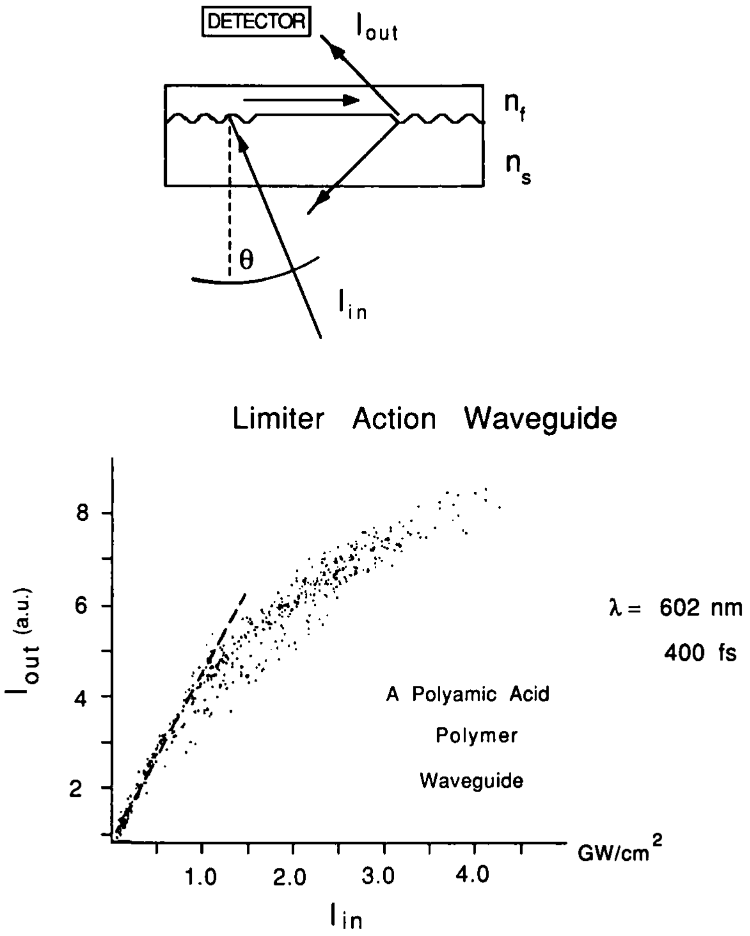


FIGURE 21 Third order nonlinear optical processes in a polyamic acid polymer waveguide. Intensity-dependent coupling efficiency, limiter action behavior, and intensity dependent coupling angle have been observed using grating excitation with 400 fs, 80 ps, and 10 ns pulses.

Stegeman and coworkers found that spin-coated and solution-cast films of poly-4BCMU irreversibly bleach when irradiated by light tuned within the absorption band of the polymer sample.[42] Verification of the mechanism is incomplete. Characteristic bleaching times have been measured at several wavelengths, and the refractive index measured at 1.064 μm for various photobleaching energies. Stegeman found that the loss at 1.064 μm to be 5 dB/cm for both unbleached and bleached films, indicating that the bleaching process does not degrade the optical quality of the films.

Refractive index changes as large as -0.08 have been measured. The decrease in refractive index has been used to define waveguide channels and gratings.

Stegeman used third-harmonic generation at a fundamental wavelength of 1.9 μm in vacuum to measure $\chi^{(3)}$ of spin-coated thin films. Calculations indicated that there was a two order of magnitude decrease in the $\chi^{(3)}$ of the bleached films. This observation is consistent with the model of Flytzanis that links optical nonlinearities with linear absorption by means of electron delocalization.[43]

Etemad and colleagues have reported waveguiding in poly(4BCMU) and poly(3BCMU) or poly[4,6-decadiyne-1,10dionbis(n-butoxycarbonyl-methylurethane)].[44] The guiding of 1.06 μm light over 3 cm pathlengths was demonstrated in spun films. The estimated transmission losses were as low as 1 dB/cm. Polymer chains were found to lie in the plane of the spun films in a random arrangement. This resulted in different refractive indices parallel and normal to the plane of the film.

The measured nonlinearity corresponded to a TE waveguide mode. From the third-harmonic intensity, $\chi^{(3)}$ was estimated to be approximately 7×10^{-11} esu at 1.06 μm.

An important observation to cite is that all $\chi^{(3)}$ measurements reported at 1.06 μm, whether for polydiacetylene or the aforementioned research ladder and electroactive polymers, are of the order of 10^{-10} esu.

Etemad and coworkers also observed nonlinear optical transmission and switching phenomena due to both picosecond electronic and slow thermal nonlinearities at 1.06 μm in directional coupler devices fabricated from the same polydiacetylenes.[45] The ultrafast electronic nonlinear phenomena originated from intensity-dependent changes in the imaginary part of the refractive index due to two-photon absorption effects.

Referring to the work of Stegeman,[46] Etemad cites that when a nonlinear optical device is operated at wavelengths close to a two-photon resonance, the intensity-dependent absorption can easily mask the effects of a change in the real part of the index. Thus the two-photon resonance sets important and fundamental limits on device operations. Etemad concludes that the results show specifically how the presence of two-photon absorption modifies the behavior of polydiacetylene-based directional couplers, and indicates the need to find true off-resonance wavelengths in these materials.

Thakur and Krol recently reported all-optical phase modulation in the waveguide of (poly{bis-(p-toluene sulfonate) of 2,4-hexadiyne-1, 6-diol]), a polydiacetylene single crystal.[47] The phase change was measured as a function of optical intensity by the Mach-Zehnder interferometric method. A π phase shift was observed for a 2-mm-long waveguide as the peak intensity was increased by about 7 MW/cm^2 for polarization parallel to the chain axis at 1.06 μm. The observed phase change was electronic in origin.

A major advance for the design of devices with $\chi^{(3)}$ polymers was the prediction and experimental verification that quasi two-dimensional conjugated disc-like structures of silicon naphthalocyanine behave as on optical Bloch system. They have an on-resonance intensity dependent refractive index n_2 of 1×10^{-4} cm^2/kW in the wavelength range of standard laser diodes.[3,33] Based on this result, electronic absorptive optical bistability is observed on a nonosecond time scale in a nonlinear Fabry-Perot interferometer employing the saturably absorbing naphthalocyanine film as the nonlinear optical medium.

Since these polymers demonstrate transparency at low laser power, they have become the basis for new devices for sensor and eye protection from incident laser energy.[48] All materials show transparency at high laser power due to a process called saturable absorption. This is always above the laser damage or burn-out intensity. However, these new disc-like oligomers and polymers show saturable absorption at laser powers far below burn-out. Thus, opaque polymers can become transparent at very low laser incident intensity. This phenomenon is the basis for the design of saturable optical reflector devices, which in principle are periscopes.

SUMMARY AND PROSPECTS

Device-driven polymer requirements are well defined for second order devices. The best waveguiding performance to date had been with films of glassy polymer backbones convalently bonded to a side chain containing a nonlinear active segment with a large polarizability which is electrically aligned. A 1.0 GHz travelling wave modulator constructed with poled polymer waveguide fabrication represents the state-of-the-art for electro-optic polymer devices.

The application of electro-optical polymers to practical higher performance devices is contingent upon advances arising mainly from the required thermal stability of the polymer poled state. In response research groups are addressing the synthesis of second order polymers with higher glass transition temperatures, i.e., 150–200°C, chromophore-functionalized polymers, electric field poling with crosslinking of polymers, room temperature poling and photocrosslinking of liquid crystalline polymers, and the use of ladder polymer models to design polymers with dye-type characteristics and excellent thermal and photochemical stability.

The device implications for third order materials are still being formulated. The critical issues still remain achieving nonlinear optical activity concurrently with low loss in waveguide processible materials, the figure of merit being expressed by the ratio of $\chi^{(3)}/\alpha$. This reflects both the infancy of third order nonlinear device concepts as well as the development stage of nonlinear polymer materials and mechanisms. Most of the third order devices constructed and tested have used polydiacetylene films and crystals because of their availability, the advanced research polymers not yet being available to device engineers in the reproducible quantities required.

Major directions for advanced third order polymer research include copolymers with defined π-electron conjugation length, confined delocalization in ladder and electroactive polymers, charge enhanced nonlinearity in polymers, and processing for chain alignment enhanced $\chi^{(3)}$. A general observation has been that while $\chi^{(3)}$ in the range of 10^{-9} to 10^{-10} esu and higher have been reported at 532 and 602 nm, the relative contributions of resonant and nonresonant processes have not been determined and defined. The largest values of $\chi^{(3)}/\alpha$ reported have been 10^{-12} esu cm. In the infrared at 1.06 μm nonresonant values of 10^{-11} esu have been reported in general for ladder and electroactive polymers.

A significant advance in third order polymer development since 1987 has been the prediction and experimental verification that quasi two-dimensional conjugated disc-like structures of silicon naphthalocyanine demonstrate an on-resonance intensity dependent refractive index which is comparable to GaAs/GaAlAs multiple quantum wells in the wavelength range of standard laser diodes. Electronic absorptive optical bistability is observed on a nanosecond time scale.

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