

Reviews

Synthesis and Processing of Improved Organic Second-Order Nonlinear Optical Materials for Applications in Photonics

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The synthesis and processing steps required to fabricate prototype electrooptic modulators from poled polymeric materials containing nonlinear optical chromophores are reviewed. These include (1) synthesis of chromophores with large first hyperpolarizabilities, (2) covalent incorporation of these chromophores into polymer lattices which can be processed into optical-quality thin films and poled by application of electric fields, (3) induction of lattice-hardening reactions which lock-in poling-induced noncentrosymmetric order, (4) creation of buried channel, nonlinear optical waveguides by reactive ion etching, by electron cyclotron resonance etching, and/or by photochemical processing, (5) coupling of buried channel electrooptic modulators to fiber optic transmission lines by photochemical processing and silicon V-groove pigtailling, (6) deposition of metal drive electrodes and evaluation of resulting prototype modulators. While the focus of this article is upon the synthesis and processing of materials, some consideration is given to device concepts including various Mach–Zehnder modulators, birefringence modulators, directional couplers, photonic voltage sensors, and photonic detection of electromagnetic radiation. Although poled polymers are of primary interest, other techniques for ultrastructure synthesis of noncentrosymmetric lattices are reviewed, including molecular self-assembly, sequential synthesis, and laser-assisted poling.

1. Introduction

Rapid developments in the telecommunications field are pressing the need for improved photonic compo-

nents. The high expectations for optical communication technologies are fueled by advances in high-speed digital switching, improved networking software and cellular networks, direct broadcast systems, and fiber optics. Government needs include global telecommunications, remote fiber links, and optically controlled antenna

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arrays. On the commercial side, regional telephone companies expect to soon provide video and expanded computer services using more fiber optics, while the cable TV industry is seeking to expand services as well. The use of fiber optics permits transmission of data without repeaters and affords enormous bandwidth potential. The bulk of the devices in these systems will be fabricated from semiconductors, but organic materials are expected to find application in selected key roles. Low-loss, inexpensive optical waveguides and very high bandwidth, integrated optical modulators are two of the major areas where polymer materials will be used.

Electrooptic polymers for optical modulation and switching is a research area that requires not only that the frontiers of scientific knowledge be advanced but also that technologies are created which are competitive or superior to existing technologies (e.g., directly modulated lasers and inorganic electrooptic modulators). Polymer modulators have inherent advantages which make their applications in two areas particularly promising. The first is in very high frequency (>30 GHz) optical modulators where the fact that the velocity of optical waves is very near that of the modulating radio frequency (rf) wave makes traveling wave modulators with interaction lengths near 1 cm practical. The second area is in integrated semiconductor-polymer optical circuits wherein the rf signals are processed in silicon integrated circuitry and then applied directly onto the polymer modulator which has been fabricated on the silicon chip. This integration is possible because the polymers can be easily spin coated and waveguides and modulator structures can be fabricated using standard photolithography techniques developed by the semiconductor industry. For both of these applications, the key materials issue is whether the polymer electrooptic materials can be developed with sufficiently large EO effects, low optical loss, and good long-term stability. Certainly, the inorganic materials, such as semiconductors and oxide crystals (e.g., LiNbO₃), have the historical advantage as photonic materials and, to date, have dominated optical technology.

2. Chromophore Design and Synthesis

Molecular level polarization (induced dipole moment) can be represented by the following series expansion in the applied electric field, \mathbf{E} ,¹⁻³ (neglecting quadrupolar terms):

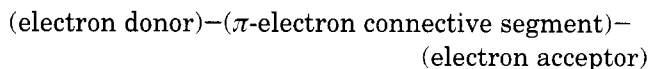
$$\mathbf{p} = \alpha\mathbf{E} + \beta\mathbf{E}\mathbf{E} + \gamma\mathbf{E}\mathbf{E}\mathbf{E} + \dots \quad (1)$$

α is the polarizability. β and γ are the first and second hyperpolarizabilities, respectively. On a macroscopic scale, the polarization can be expressed as

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

By symmetry, $\chi^{(2)} = 0$ for centrosymmetric lattices. Although Zyss and co-workers^{4,5} have proposed the development and exploitation of octupolar chromophores,

device development exploiting second-order, $\chi^{(2)}$, optical nonlinearities has largely focused upon dipolar chromophores of the form



Semiempirical quantum mechanical calculations of first hyperpolarizabilities, β , for such dipolar chromophores have proven quite successful in predicting trends in structure/function relationships.⁶⁻¹⁶ Marder and Perry,¹¹⁻¹⁶ in particular, have been successful in using simple (two-level) calculations to guide synthetic efforts aimed at optimizing molecular hyperpolarizabilities. Within the framework of a two-state calculation, the hyperpolarizability, β , depends upon the transition dipole, μ_{ge} , the difference between the dipole moments of the ground and excited state, $\mu_{ee} - \mu_{gg}$, and the optical gap, E_{ge} . Explicitly

$$\beta \propto (\mu_{ee} - \mu_{gg})(\mu_{ge}^2)/E_{ge}^2 \quad (3)$$

The transition moment, the dipole difference, and the optical gap all exhibit different dependence upon the difference in donor and acceptor strengths and upon the coupling integral. This leads to a predictable but nontrivial dependence of β upon physical quantities such as bond length alternation. It is interesting to consider, from a historical perspective, the development of chromophores with improved β values. Throughout the 1980s, state-of-the-art organic second-order chromophores largely consisted of stilbene or azobenzene moieties end-capped with electron-donating groups such as *N,N*-dimethylamino and electron-withdrawing groups such as the nitro group. 4-(*N,N*-Dimethylamino)-4'-nitrostilbene (DANS), for which $\mu\beta = (446-580) \times 10^{-48}$ esu, continues to be a useful reference. During the 1980s, efforts to increase hyperpolarizability focused upon finding stronger donor and acceptor groups and upon increasing the length of the π -electron connective segment. In 1991, Marder and co-workers¹² demonstrated that there is an optimal combination of donor and acceptor strengths required to maximize $\mu\beta$ for a given connective segment and beyond that point, increasing the donor-acceptor strengths leads to a diminution of hyperpolarizability. In 1993, Gorman and Marder¹³ showed that hyperpolarizability could be correlated with bond length alternation. For donor-acceptor-substituted polyenes, bond length alternation is related to the relative contributions of neutral and charge-separated resonance structures which is, in turn, dependent upon donor-acceptor strength. Molecules with aromatic

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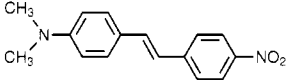
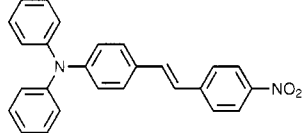
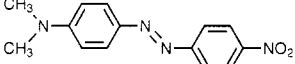
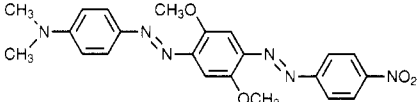
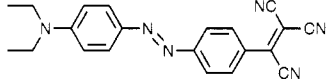
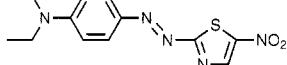
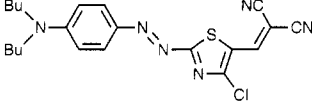
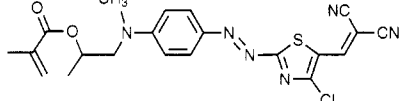
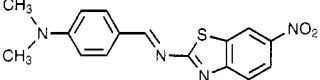
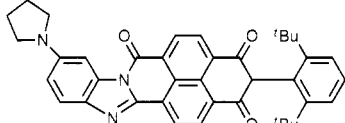
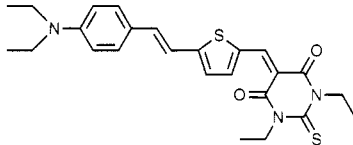
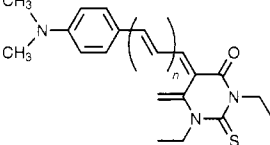
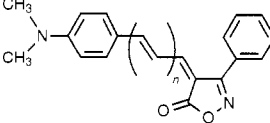
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Table 1. Representative NLO Chromophores and Their Corresponding $\mu\beta$ Values

chromophore	nonlinearity	ref
	$\mu\beta = 580 \times 10^{-48}$ esu (1.907 μm)	a
	$\mu\beta = 788 \times 10^{-48}$ esu (1.907 μm)	b
	$\mu\beta = 800 \times 10^{-48}$ esu (1.58 μm)	c
	$\mu\beta = 1040 \times 10^{-48}$ esu (1.064 μm)	d
	$\mu\beta = 4100 \times 10^{-48}$ esu (1.58 μm)	c
	$\mu\beta = 2190 \times 10^{-48}$ esu (1.58 μm)	c
	$\mu\beta = 5320 \times 10^{-48}$ esu (1.58 μm)	c
	$\mu\beta = 1658 \times 10^{-48}$ esu (1.907 μm)	e
	$\mu\beta = 640 \times 10^{-48}$ esu (1.064 μm)	d
	$\mu\beta = 1500 \times 10^{-48}$ esu (1.907 μm)	f
	$\mu\beta = 2400 \times 10^{-48}$ esu (1.907 μm)	g
	$n = 0$ $\mu\beta = 370 \times 10^{-48}$ esu (1.907 μm) $n = 1$ $\mu\beta = 1457 \times 10^{-48}$ esu (1.907 μm) $n = 2$ $\mu\beta = 3945 \times 10^{-48}$ esu (1.907 μm) $n = 3$ $\mu\beta = 9831 \times 10^{-48}$ esu (1.907 μm)	h
	$n = 0$ $\mu\beta = 312 \times 10^{-48}$ esu (1.907 μm) $n = 1$ $\mu\beta = 1202 \times 10^{-48}$ esu (1.907 μm) $n = 2$ $\mu\beta = 3156 \times 10^{-48}$ esu (1.907 μm) $n = 3$ $\mu\beta = 8171 \times 10^{-48}$ esu (1.907 μm)	h

^a Rao, V. P.; et al. in *Nonlinear Optical Properties of Organic Materials V*; Williams, D. J., Ed.; Proc. SPIE **1992**, 1775, 32. ^b Tweig, R. J.; et al. *Mater. Res. Soc. Symp. Proc.* **1994**, 328, 421. ^c Dirk, C. W.; et al. *Chem. Mater.* **1990**, 2, 700. ^d Xu, C. Ph.D. Thesis, University of Southern California, Los Angeles, 1993. ^e Ra, Y. S., personal communication. ^f Yamada, S.; et al. *Mater. Res. Soc. Symp. Proc.* **1994**, 328, 523. ^g Jen, A. K.; et al. *Mater. Res. Soc. Symp. Proc.* **1994**, 328, 413. ^h Marder, S. R.; et al. *Science* **1994**, 263, 511.

ground states tend to be more bond length alternated than a simple polyene of comparable length. This phenomena can be attributed to the high price in energy which must be paid for loss of aromaticity upon polarization. Marder and co-workers focused upon two design factors in optimizing hyperpolarizability: (1) For

a chromophore which has a connective segment (bridge) that loses aromaticity upon polarization but also has an acceptor that gains aromaticity upon polarization, bond length alternation of the bridge is reduced and a significant enhancement in $\mu\beta$ results. Such acceptors include 3-phenyl-5-isoxazolone and thiobarbituric acid

derivatives (see Table 1). (2) Optical nonlinearity can be improved by replacing benzene rings with heterocyclic rings such as thiazole or thiophene. Such structures have less aromatic stabilization energy and their use results in $\mu\beta$ values an order of magnitude greater than DANS (see Table 1). If chromophores noted in Table 1 could be incorporated in high number density and with a high degree of noncentrosymmetric order into macroscopic lattices, then electrooptic coefficients on the order of several hundred picometers per volt could be obtained. Note that electrooptic coefficients of approximately 400 pm/V at 820 nm have been measured for single crystals of the chromophore 4'-(dimethylamino)-N-methyl-4-stilbazolium tosylate.¹⁷ Of course, at 820 nm significant resonance enhancement exists; the values in Table 1 are measured at 1.9 μm (far off resonance) to minimize variations associated with resonance enhancement. A problem encountered in efforts at optimizing optical nonlinearity is the fact that chemical modification to effect improvement in $\mu\beta$ often results in decreasing the optical gap. Since electrooptic modulator applications require a high degree of transparency at the operating wavelength, such reduction in optical gap can limit the application of the modulator. This is particularly a problem for operation at diode laser wavelengths, e.g., 820 nm. Recently, various workers^{18,19} have pointed out the need to consider modification of chromophores by solvation when calculating hyperpolarizabilities.

A requirement for utilization of chromophores for device fabrication is that they be able to withstand temperatures and chemical reaction conditions encountered in processing operations required for producing devices (e.g., deposition of metal drive electrodes) and in long term operation with intense laser fields and temperatures generated by nearby electronic components. Garito and co-workers^{20,21} have pursued the development of chromophores with exceptional thermal stability by considering fused ring systems. Jen et al.²²⁻²⁴ have focused upon realizing improved thermal stability of chromophores by exploring the incorporation of heteroaromatic moieties. Wada et al.²⁵ discuss achieving thermal stability by synthesizing supramolecular chromophores based on acceptor substituted

carbazoles. Twieg and co-workers²⁶⁻²⁸ have carried out a very systematic evaluation of the thermal stability of chromophores by executing thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and cyclic voltammetry (CV) measurements. For lophine and azobenzene chromophores, they find strong correlation of thermal stability (as defined by TGA and DSC measurements) with the oxidation potential measured by CV. They also observe that the thermal stability of amine donor groups can be improved by switching from alkyl- to arylamines. An aspect of chromophore development is the characterization of hyperpolarizabilities; the two most popular methods for accomplishing characterization of chromophore second-order molecular optical nonlinearity are electric field induced second harmonic generation (EFISH)^{1,22,28-33} and hyper-Rayleigh scattering^{34,35} measurements. For chromophores to be of utility for nonlinear optical applications, they must be assembled into a noncentrosymmetric lattice; this assembly process places additional requirements on chromophore design.

3. Preparation of Noncentrosymmetric Lattices

We can define three general approaches to achieving noncentrosymmetric lattices of nonlinear optical chromophores: (1) exploitation of molecular self-assembly—most notably, crystal growth, incorporation into inclusion compounds, or formation of liquid-crystalline (ordered) domains in bulk materials; (2) sequential synthesis exploiting van der Waals, ionic, or covalent interactions; and (3) utilization of external forces, e.g., induction of molecular order by electric field poling. All techniques are hindered by the repulsion of closely packed dipolar chromophores. The precise effects of dipolar repulsion and various ordering forces can be understood within the framework of London theory.³⁶

3.1. Molecular Self-Assembly. Of course, when ordering forces are weak and numerous, such as for van der Waals interactions, it is not a simple matter to predict the formation of noncentrosymmetric lattices. For example, the development of single-crystal, second-order materials is hampered by the absence of general rules for predicting crystal structure from molecular structure.³⁷ Some progress has been made in this arena exploiting molecular asymmetry, chirality, hydrogen

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bonding, dipole reduction, changing counterions in organic or organometallic salts, and making use of noncentrosymmetric rearrangements in centrosymmetric organic crystals.^{17,33,37-47} Unfortunately, even when noncentrosymmetric crystal lattices are realized, crystals appear to be plagued by growth anisotropy, that is, crystals tend to grow as long needles unsuitable for preparation of optical samples.⁴⁰

Another approach to the realization of macroscopic noncentrosymmetric order is to incorporate polar chromophores into host materials with appropriate cavities. This approach was first demonstrated by Tomaru and co-workers⁴⁸ using β -cyclodextrin (β -CD) as a host material for a variety of nitroaniline chromophores. Additional samples of NLO chromophores incorporated into β -CD have been reported by Eaton and co-workers⁴⁹⁻⁵¹ who also expanded consideration to other hosts (including thiourea, tris-*o*-thymotide, and deoxycholic acid) and organometallic guests (mainly of the arylmetal tricarbonyl type). These workers concluded that of the possible types of inclusion hosts, the ones with channels rather than cages, were likely to yield preferential interactions leading to noncentrosymmetric organization of guest molecules. More recently, Cox and co-workers⁵² have investigated polar molecules incorporated into inorganic molecular sieve hosts. The wide variety of pore structures, sizes, shapes, and framework charge densities available in molecular sieves makes them attractive, as this size and shape variability permits the host to be matched to the guest so that a preferred orientation can be realized. Variation in host framework charge density or dielectric constant, via variation of the Si/Al ratio, or the use of other framework atoms can be used to define guest-host and guest-guest electrostatic interactions. Inorganic hosts have the advantage, relative to organic hosts, of improved rigidity and improved thermal stability. Cox et al. investigated a number of centrosymmetric and noncentrosymmetric molecular sieve hosts employing *p*-nitroaniline type guest molecules. They systematically varied guest concentration, guest structure, and the charge density of the host framework. The major disadvantage of their materials was their inability to

obtain single crystals of adequate dimensions. Ogawa et al.⁵³ have recently investigated second harmonic generation from *p*-nitroaniline intercalated into tetramethylammonium saponite films under the influence of an electric field. Lacroix and co-workers^{54,55} have investigated incorporation of cationic chromophores into optically transparent MPS₃ (M = Mn, Cd) phases.

Numerous attempts have been made to obtain macroscopic noncentrosymmetric order by incorporating NLO chromophores into ordered phases, e.g., liquid-crystalline materials.⁵⁶⁻⁶² These efforts extend from the early work of Meredith et al.⁵⁶ doping DANS into a thermotropic nematic liquid crystalline polymer to the recent work of Wegner and co-workers⁵⁸⁻⁶⁰ incorporating NLO chromophores into polymers which form two-dimensional layered structures. Swager and co-workers have discussed designing thermodynamically stable polar assemblies based on columnar liquid crystals.^{61,62}

3.2. Sequential Synthesis Methods. We divide sequential synthesis methods into the four categories: (1) Langmuir-Blodgett methods, (2) techniques involving covalent coupling analogous to Merrifield methods, (3) sequential synthesis exploiting ionic interactions, and (4) molecular beam epitaxy (MBE) methods. Sequential synthesis methods afford the advantage of permitting films of carefully controlled thickness to be prepared. Films with thicknesses on the order of the wavelength of light can be prepared with tolerances of the dimensions of one monolayer. Since the wave vector of a propagating mode in a wavelength is thickness dependent, such control can be important, particularly for phase matching in frequency doubling applications. As sequential synthesis methods involve hundreds or even thousands of steps, each step must proceed with very high efficiency to avoid order-destroying defects.

3.2.1. Langmuir-Blodgett Methods. Films from small amphiphilic molecules, fabricated by Langmuir-Blodgett methods, have been extensively investigated.^{1,37,41-47,67-78} An amphiphilic molecule is one with

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a hydrophilic head group and a hydrophobic tail group; such a molecule will partition between aqueous and organic phases. When such molecules are spread on the surface of water and compressed laterally, they are compressed into an oriented film with polar head groups at the water surface and tails perpendicular to the surface. The layer is then transferred onto a substrate with the orientation determined by the wetting characteristics of the substrate. Swalen⁶⁹ has noted that a variety of forces determine the orientation and packing of the layers. A major limitation of LB films is their poor thermal and mechanical stability and the difficulty of obtaining films of thickness on the order of a micron due to increasing disorder with subsequent layers. In an effort to fabricate stable, high-quality films, several groups have explored the use of preformed polymers with the LB method.⁷⁰⁻⁷² Employing such an approach, Penner and co-workers^{71,72} have prepared films containing as many as 262 layers and have fabricated waveguides using these films which exhibit low optical loss (about 1 dB/cm) in contrast to previously reported LB film waveguides.

3.2.2. Sequential Synthesis by Covalent Coupling Reactions. Marks and co-workers^{79,80,84-86} have developed an organotrichlorosilane-based self-assembled multilayer deposition method which exploits covalent bonding and van der Waals forces to overcome dipole-dipole repulsion forces. The NLO chromophore is locked in place by siloxane condensation reactions. Salient features include (1) the introduction of an anchored benzyl iodide coupling layer, (2) the use of a bifunctional stilbazole chromophore precursor, and (3) the use of a chlorosilane reagent combined with a polyhydroxylic polymer to lock in and planarize the architecture as well as to provide a foundation for construction of the succeeding layer. Such deposition can be carried out on a variety of amorphous and single crystal substrates. Initial studies revealed a robust structure with $\chi^{(2)}$ values in excess of 10^{-7} esu. In more recent studies, Marks and co-workers⁸⁴⁻⁸⁶ have elaborated upon these

sequential synthesis procedures using in situ second harmonic generation (SHG) measurements to directly monitor the sequential assembly process. They find that the chromophoric layers undergo facile ion exchange and that with proper capping and cross-linking methodology, the poly(vinyl alcohol) step is no longer necessary. Reagents have been found which may be useful in lithographic/waveguide fabrication processes involving these films. Marks and co-workers have extended their studies to the investigation of different types of chromophores; we have also utilized the sequential synthesis techniques of Marks and co-workers using different chromophores.⁸⁷ Whitesell and Wang^{88,89} report a series of polymers based on β -amino acids, including poly(β -alanine), poly(*cis*- and *trans*-2-aminocyclohexanecarboxylic acid) and poly(anthranilic acid) grown on gold, using an aminothiols as the binder to the metal surface.⁹⁰ This method of sequential synthesis provides flexibility in introducing polar groups to anthranilic acid to enhance the magnitude of the molecular dipoles. The anthranilic acid group is also useful in controlling the spacing between chromophores.

3.2.3. Sequential Synthesis by Ionic Coupling. Katz and co-workers⁹¹⁻⁹⁷ have adapted the sequential synthesis procedure developed by Mallouk et al.^{98,99} for the fabrication of multiple polar dye monolayers on solid surfaces joined by zirconium phosphate-phosphonate interlayers. The layers are held together by ionic forces. Inorganic interlayers impart good orientational stability to the dye molecules with the onset of orientational randomization about 150 °C. In agreement with theory, the SHG intensity was found to be proportional to the thickness squared with no deviation observed through 32 layers. The observed second-order optical nonlinearities were on the order of those lithium niobate but were substantially less than those of stilbazolium dyes incorporated into LB materials. This observation reflects the relatively weak electron-withdrawing characteristics of the phosphonate group. More recently, Katz and co-workers have investigated the incorporation of high- β chromophores. The order parameters, $\langle \cos^3 \theta \rangle$, realized were approximately 0.2.

3.2.4. Sequential Synthesis by Organic Molecular Beam Epitaxy. This technique, which has been developed and popularized by Forrest and co-

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workers,^{100–105} depends upon van der Waals forces to guide the assembly of organic materials. This approach appears most attractive for third-order materials and the development of organic quantum well structures where the extent of exciton delocalization is controlled by the deposition process. For second-order materials, realization of noncentrosymmetric order typically requires the application of an electric (poling) field and some form of lattice stabilization is required. In recent work, Forrest and co-workers have introduced poling fields to their MBE fabrication scheme and have realized second-order nonlinear optical activity. This has also been accomplished by Yoshimura and co-workers,¹⁰⁶ who also chose co-deposited materials (pyromellitic dianhydride and 4,4'-diaminodiphenyl ether) which react to form a stable polymer lattice. Since the molecules are oriented by the electric field before being tightly inserted into polymer chains, alignment can be achieved without heating the polymer above its glass transition temperature.

3.3. Fabrication of Noncentrosymmetric Lattices by Electric Field Poling. The most popular method for the realization of macroscopic noncentrosymmetric order has been electric field poling of NLO chromophore containing polymers near the glass transition temperature, T_g , of the polymer matrix. Fabrication of electrooptic devices relies upon the macroscopic second-order susceptibility, $\chi^{(2)}$, which in turn is related to molecular hyperpolarizability, β , by the approximate relationship (we ignore the tensorial nature of the second-order NLO susceptibility)

$$\chi^{(2)} = NF\beta\langle\cos^3\theta\rangle \quad (4)$$

The requirement of noncentrosymmetric macroscopic symmetry appears in the polar order parameter $\langle\cos^3\theta\rangle$. F contains all local field effects. As it turns out, optimization of chromophore loading (number density N) and chromophore order is not always easily accomplished. The electrostatic repulsion between high dipole moment chromophores opposes optimization of both of these parameters; explicitly

$$\langle\cos^3\theta\rangle = (\mu E_p F / 5kT)(1 - L^2(W/kT)) \quad (5)$$

where E_p is the electric poling field and L is the Langevin function. The intermolecular potential associated with chromophore–chromophore interactions can be expressed as $W \cos \phi$ where ϕ is the angle between the chromophore dipole, μ , axis and the directional field from surrounding molecules (chromophores). London³⁶ has shown that interaction energy between two polarizable dipoles arises from three forces, namely, the van der Waals force, the orientational force, and the induction force. The statistically averaged potential

energy can be expressed as

$$W = 2\mu^4/(3r^6kT) + 2\mu^2\alpha/r^6 + 3la^2/4r^6 \quad (6)$$

where r is the average distance between chromophore dipoles and l is the ionization potential. Accurate calculations using the above theory are not trivial to carry out when corona poling is employed, and such calculations require modeling of polymer dynamics to assess the closest approach distance of the chromophores. Moreover, meaningful calculations require consideration of the nature of incorporation of chromophores into the polymer lattice, e.g., noncovalent incorporation to form composites or covalent incorporation to form homopolymers or copolymers. However, crude estimates of poling fields can be made which lead to the observation that reduction of $\langle\cos^3\theta\rangle$ can be significant for chromophore–chromophore average separations of 1 nm or less. Such small separations are not easily achieved in composite systems due to poor solubility of the chromophore in the host polymer but can quite readily be realized for covalent incorporation of chromophores.

3.3.1. NLO Chromophore/Polymer (Guest/Host) Composites. An attractive feature of chromophore/polymer composites is the ease with which such systems are prepared. Frequently, commercially available chromophores and polymers can be blended, spin cast into thin films, and poled near the glass transition temperature of the composite matrix. The first materials used in electric field poling experiments were composite materials.⁵⁶ Two significant problems were identified in early studies: (1) relatively rapid relaxation of poling-induced order with the concomitant loss of optical nonlinearity and (2) poor loading (number density) of the chromophore in the composite due to finite solubility of the chromophore in the host matrix. The first of these problems prompted intensive investigation of a number of chromophores in various polymer lattices,^{1,20,26,27,33,37,42–47,107–144} e.g., poly(methyl meth-

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acrylate) (PMMA) and polycarbonate lattices.^{107–109,112} A number of factors, including dopant size, guest–host interactions (e.g., hydrogen bonding), specific polymer relaxation mechanisms, void sizes, thermal history, etc., were found to influence the rate of loss of poling-induced order following removal of the poling field. However, for chromophores of relatively large sizes, the primary factor influencing the rate of relaxation of poling-induced order was the glass transition temperature of the composite material.^{26,27,113–116} Because of this observation, the use of composite materials has recently experienced a rebirth with the adoption of high- T_g polyimides for use as host lattices.^{113,120–130} Many fully cured polyimides are insoluble and must be processed as polyamic acids; three such polyamic acids are the LQ-2200 material (Hitachi) and Utradel 4212 or 3112 (Amoco). An exception to this observation concerning the solubility of polyimides is the isotropic poly(ether imide) Ultem (General Electric) which is fully imidized and still soluble in a variety of solvents. It has a T_g of 210 °C and excellent optical properties. Unfortunately, both polyamic acid precursor polymers and Ultem require high cure temperatures, and many chromophores are not chemically stable at such temperatures. Wu and co-workers¹²² have suggested that it is possible to circumvent this problem by using chemical instead of thermal imidization.

Although high- T_g lattices permit reasonable thermal stability of poling-induced optical nonlinearity to be realized, other disadvantages of composites remain. These include finite solubility, phase separation and

aggregation of chromophores, sublimation of chromophores at high processing temperatures, dissolution of chromophores with application of cladding layers, and a plasticizing effect of chromophores on the host lattice. Wada and co-workers²⁵ report an effort to overcome some of the above-mentioned disadvantages by synthesizing nonlinear optical supramolecules based on acceptor substituted carbazoles.

3.3.2. Covalent Incorporation of NLO Chromophores into Polymers. Such incorporation has varied from inclusion of chromophores as pendants to the polymer backbone (or main chain) to chromophore incorporation as an integral component of the backbone (with the chromophore axis either collinear or orthogonal to the backbone).

3.3.2.1. Pendant Incorporation. Early studies of guest/host systems suggested that improvement in both chromophore loading and the thermal stability of poling-induced noncentrosymmetric order could be achieved by covalent coupling of the NLO chromophores to the polymer lattice. This hypothesis was quickly verified by early studies where NLO chromophores were attached as pendants to a main chain polymer.^{108,145,146} In most cases, the T_g of the polymer with an NLO pendant was found to be substantially higher than that of a guest/host system containing the same concentration of chromophore molecules. Such systems permitted a significant improvement in optical nonlinearity with second harmonic generation coefficients, d_{33} , values greater than 25 pm/V and electrooptic coefficients, r_{33} , values greater than 5 pm/V routinely observed. NLO chromophores have been covalently attached to a variety of polymer backbones including PMMA, polystyrene, polyethylene, polyphosphazene, and polyamic acid.^{1,33,37,41–47,108,110,116,145–180} As with guest/host systems, a critical property is the thermal stability of the

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poling-induced order afforded by the final system. Thus, polyimides have proven to be among the most promising systems when additional cross-linking (lattice hardening) is not employed.¹⁷³⁻¹⁷⁸

3.3.2.2. Main-Chain Incorporation. Obviously, relaxation of poling-induced order could be further attenuated if both ends of the chromophore are anchored as is the case when the chromophore is incorporated into the polymer backbone with the chromophore principle axis collinear with the polymer backbone. It should be noted that the term "main-chain incorporation" is also used to describe the case where one end of the chromophore (e.g., the amine donor end) is coupled into the polymer main chain by two points of attachment.^{58-60,179,181-216} For main-chain NLO poly-

mers, large segmental motions of the polymer backbone are required for poling and for relaxation of the polymer; such polymers may also show improved tensile strength and mechanical properties relative to side-chain polymers. However, it was not restricted chromophore motion but rather the potential for cooperative interactions among chromophore dipoles, that motivated the first studies of main-chain chromophore incorporation. In these early studies,¹⁸¹⁻¹⁸⁹ the chromophores were incorporated into the polymer backbone in a "head-to-tail" manner with the hope that the dipole moment of the polymer chain would act as a single molecule, namely, $\mu_{\text{total}} = N\mu$ where N is the number of chromophore units and μ is the dipole moment of each chromophore. For this case, the second-order nonlinear optical susceptibility, $\chi^{(2)}$, would be expected to be approximately proportional to N^2 . This result is particularly attractive when it is realized that optical nonlinearity could (conceivably) be increased in this manner without incurring an associated reduction in the window of optical transparency (i.e., the optical gap); this assumes, of course, that the chromophores act as independent dipoles. Such enhancements may have been observed for a "head-to-tail" polymer in solution; however, enhancements have not been observed, to date, in thin films of "head-to-tail" polymers.¹⁸¹ This is not surprising for long polymers with entanglements since such intermolecular chain interactions would oppose the cooperative alignment of dipoles; this latter observation has been commented on by Xu and co-workers.²⁰⁵⁻²¹⁰ Indeed, these workers synthesized "head-to-head" and "random" main-chain polymers (as well as "head-to-tail" polymers) and demonstrated that, when sufficiently flexible segments are present, all these main-chain polymers can be effectively poled to produce materials with optical nonlinearities comparable to those obtained with side-chain (or pendant) incorporation. The puta-

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tive advantage of main chain polymers would be closer packing of polymer chains by avoiding perturbations of the pendant groups; such closer packing might permit realization of a greater cross-linking density.

An interesting recent study is that of Robello and co-workers,²¹² who observe that full (factor of 2) enhancements are not observed in rigid double-chromophore assemblies based on dibenzobicyclo[2.2.2]octadiene. Theoretically, this is not surprising since the dipoles are sufficiently close that they cannot be treated as independent as assumed in predicting the factor of 2 enhancement. The most significant advantage of the approach of Robello and co-workers is the possibility of achieving enhanced optical nonlinearity without a corresponding reduction in the window of optical transparency. Another study worthy of note is that of calix[4]-arenes by Kelderman et al.²¹¹

One of the more novel approaches to main-chain polymers is that of Lindsay and co-workers^{190-194,213-215} involving the synthesis of syndioregic or "accordion" polymers where chromophores are connected with U-shaped bridging groups designed to allow folding of the chromophores to produce roughly parallel dipole alignment. Another approach is the design of polymers where alignment of one dipolar segment requires alignment of an adjacent segment due to the geometric constraints of the connecting group. Bloor and co-workers synthesized a series of diethynyldiphenylsilicon polymers with the tetrahedral bonding on the Si atom in the connecting group expected to force the alignment of adjacent segments.²⁰³ Unfortunately, no such enhancements in optical nonlinearity were observed.

3.3.2.3. Lattice Hardening for the Stabilization of Poling-Induced Order. Due to thermal stability requirements, glass transition temperatures on the order of 300 °C may be required for certain device applications. It is difficult to realize such temperatures using the types of systems discussed above (section 3.3) since chromophore decomposition will frequently occur during processing (e.g., poling) near such temperatures. The ideal situation would be to develop a material which possesses a finite T_g and good stability in common organic solvents such that it can be processed into optical quality films, poled at modest temperatures, and then hardened into a high- T_g material which is solvent resistant. Of course, the hardening process must not degrade optical quality (e.g., result in increased light scattering), must not result in embrittlement or mechanical stress, must not result in significant shrinkage, etc.

Both thermally and photochemically induced cross-linking reactions have been used for many decades to harden polymers. As expected, these reactions can be adapted to the production of hardened NLO polymers.^{37,113,116,121-130,173-176,217-261} Lattice-hardening

reactions can be carried out for guest/host (composite) materials and for polymers with either pendant or main-chain incorporation of chromophores.

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3.3.2.3.1. Thermally Induced Polymer Cross-Linking Reactions.^{37,41-47,116,217-234,245-250} Epoxy resins represent one of the oldest and most extensively investigated hardened polymer materials. It is not surprising that the first efforts aimed at preparing hardened NLO polymeric materials involved such materials.^{217-221,227,228} Following Burland et al.,¹¹⁶ we find it convenient to group NLO epoxy materials according to the following five categories: (1) guest/host (composite) materials where cross-linking involves only the epoxy material and an external initiator but not the NLO chromophore;^{217,218} (2) materials where the NLO chromophore is tethered to the polymer backbone but is not involved in the actual cross-linking;^{219,220} (3) materials which involve incorporation of the NLO chromophore into the epoxy polymer backbone independent of the cross-linking sites;²²⁸ (4) materials created using difunctional epoxides and NLO diamines where the amine substituent is not only incorporated into the growing chain but is also involved in cross-linking the chains;^{221,227,228} and (5) materials formed from polyfunctional epoxides and polyamino-functionalized NLO initiators where many polymer chains can be linked together.

As might be expected, the first investigations (Marks and co-workers^{217,218}) involved guest/host systems. A commercial thermosetting epoxy, EPO-TEK 301-2 (diglycidyl ether of bisphenol A and a polyfunctional aliphatic amine-hardening agent) was mixed with either a DANS or azobenzene NLO chromophore. Partial cross-linking was induced by heating briefly to 80 °C before the poling field was applied; this was necessary to increase the viscosity and avoid dielectric breakdown with application of the poling field. Poling and curing were accomplished at elevated temperatures, and the poling field was maintained until the sample was cooled to room temperature. The temporal stability of the optical nonlinearity of these systems was observed to be considerably improved over nonhardened guest/host materials. However, the d_{33} (second harmonic generation coefficient) was small (0.04–0.4 pm/V), likely reflecting the poor solubility of the chromophores in the initial solution. Other potential disadvantages of this system (like guest/host systems in general) include potential phase separation, plasticization effects, and chromophore motion independent of the polymer matrix (including the potential for chromophores existing in void regions). Marks and co-workers^{219,220} extended these studies to consider class 2 NLO epoxides and observed an improvement in the thermal stability of optical nonlinearity relative to the class 1 guest/host materials. In both classes of epoxies, the thermal stability of the NLO activity tracked the extent of polymer vitrification as expected. Marks and co-workers have studied the effect of cross-linking site on the temporal stability of poling-induced order for polymer-tethered NLO chromophores.²²¹

Eich and co-workers²²⁷ prepared class 4 NLO epoxides, and Jungbauer et al.²²⁸ executed a variant of this approach. Utilization of a bis-epoxide also containing a bonded NLO chromophore allowed a significant increase in the chromophore density (63% by weight). Soluble prepolymers were obtained by melting the reagents and heating the mixture to 130 °C. The prepolymers were spin coated from diglyme and cured

at 120 °C in a corona field. A d_{33} value of the order of 50 pm/V (at 1.06 μm) likely reflects the increased chromophore loading. Good thermal stability to 80 °C has been reported for these materials. Marks and co-workers²²¹ describe another epoxy-NLO chromophore diamine system where the initiating amino substituents in the aminonitroazobenzene chromophore employed were insulated from the aromatic ring both to increase basicity and to avoid possible deleterious effects on the nonlinearity caused by electronic coupling of the initiating amino groups to aromatic π system of the chromophore. The molecular nonlinearity of this chromophore is significantly larger than that of the *p*-nitroaniline used in previous studies; however, this gain is offset by a reduced chromophore density in the final material. Both bisphenol A diglycidyl diether and a commercial oligomeric polyepoxide reagent were investigated by Marks and co-workers.²²¹ Solutions of the reagents were spin cast and precured to 100 °C for 3 h prior to corona poling. The final curing and poling were conducted at 130 °C for 2 h. The best preparation yielded a d_{33} value of 14.3 pm/V (at 1.064 μm). Thermal stability studies at 85 °C revealed 60% loss of optical nonlinearity after 1000 h.

In addition to epoxy resins, a number of other thermosetting reactions have been investigated producing polymers which can be viewed as modified polyurethanes,^{245-248,261} polyamides,^{223,224,254} and polyimides.²²² In each of these cases, thermal stability was significantly improved by cross-linking. We have synthesized a cross-linked polyurethane which contains about 30 wt % chromophore and is characterized by a d_{33} value of 120 pm/V (1.064 μm) and an r_{33} value of 13 pm/V (1.064 μm).²⁴⁵⁻²⁴⁷ Marks and co-workers²²² have prepared a polyimide type polymer by reacting a functionalized triamine with terminally functionalized bis-maleimide. Polymers characterized by glass transition temperatures as high as 236 °C were obtained by this approach; d_{33} values in the range 4.6–5.5 pm/V were measured at 1.064 μm , which is consistent with a number density of approximately $7 \times 10^{20} \text{ cm}^{-3}$ for the nitroaniline chromophore employed. Only 10–15% decay of the second-harmonic signal was observed over a 24 h period. A number of other such efforts exist.^{174-176,223,224,251,254,256}

Chromophores containing reactive functionalities at both ends have increasingly been exploited for the production of hardened NLO materials. When the reactive functionalities at the two ends are sufficiently different to permit distinct two-step processing, we can view the processing (spin casting and poling) step as distinct from the lattice hardening step. We defer discussion of such materials to section 3.3.2.3.4. When these steps are not well separated, the procedure is effected in a manner analogous to that described for epoxies. That is, the starting material is reacted under conditions to produce a viscous medium that can be spin cast and poled; then, further lattice hardening is effected. Betterton and co-workers²²⁹ have investigated norbornenyl-4-carboxylates with a tethered methacrylate containing an NLO functionality which can be selectively polymerized by ring-opening metathesis polymerization to produce macromonomers containing pendant methacrylate groups. Unfortunately, no cross-linking studies were described. Recently, we have

investigated the tri- and tetralinked systems. The r_{33} values lie in the range 16–17 pm/V (at 1.3 μm) for the tetralink material and 9–10 pm/V (at 1.3 μm) for the trilink material. No significant difference is observed in the thermal stability of optical nonlinearity for these two materials.

3.3.2.3.2. Lattice Hardening by Photochemical Cross-Linking.^{235–248,257} The use of polyfunctional acrylates and methacrylates for photochemical cross-linking has been investigated by Robello and co-workers.²³⁵ The first materials examined were again guest/host composites. Polymerization was initiated using a variety of photochemical electron-transfer sensitizer–activator combinations known to be effective for the hardening of polyfunctional acrylates. In addition to the problem of low chromophore solubility, there is the problem of chemical reactivity of the chromophore under the conditions of photochemical cross-linking. An interesting variation of this approach is the work of Hayashi and co-workers.²³⁶ Irradiation while corona poling at 60–70 °C led to a polymer with a d_{33} value of 3.6 pm/V (at 1.064 μm). The measured optical nonlinearity decayed to 50% after only 100 h at ambient temperatures. We have also investigated photo-cross-linkable acrylate containing NLO polymers^{230,234} in our study of asymmetric reactivities. The cinnamate functionality is also well-known for its photoreactivity and use in the photoimaging industry. Matsuda and co-workers²³⁷ have investigated guest/host composites created by dissolving various NLO chromophores in solutions of poly(vinyl cinnamate) or poly(4-vinylphenyl cinnamate). Unfortunately, significant NLO chromophore decomposition was observed during the photo-cross-linking step. This loss was subsequently reduced to less than 10% by use of a UV cutoff filter. A d_{33} of 28 pm/V (at 1.064 μm) was measured for samples which exhibited approximately 70% decay of optical nonlinearity after 3 months at 25 °C. Tripathy and co-workers^{238–241} have also explored guest/host composite materials comprised of photoreactive NLO chromophores and the photo-cross-linkable polymer poly(vinyl cinnamate). The potentially reactive bifunctionality of the NLO chromophores assures significant coupling to the densified polymer lattice. Chromophore loading densities up to 20 wt %, without phase separation, have been reported for this system. The use of β -styrylacrylate groups, in place of cinnamates, permitted cross-linking at longer irradiation wavelengths (e.g., 366 nm). For the highest chromophore loadings, a d_{33} value of 11.5–12.5 pm/V (at 1.54 μm) was observed. No loss of optical nonlinearity was observed over periods of several hours for temperatures as high as 85 °C. No chromophore decomposition was observed for short irradiation periods although decomposition was observed for longer periods. Muller and co-workers²⁴² have prepared terpolymers containing both the cinnamoyl cross-linking functionality and NLO chromophores covalently attached as side-chain tethers. The substituents were coupled by reaction of hydroxy-terminated functionalities with a 50/50 copolymer of methyl methacrylate and acryloyl chloride. The progress of cross-linking was followed by IR spectroscopy and observed to plateau at about 50% conversion. Although some chromophore decomposition was observed, an effective electrooptic coefficient of 7 pm/V (at 1.15 μm) was measured. No long-term stability studies were

reported. Photo-cross-linkable systems containing either the chromophore or the photoreactive functionality incorporated into the polymer main chain have been investigated. For example, Tripathy and co-workers^{243,244} have prepared nonlinear optical epoxies containing pendant cinnamoyl groups. Both linear and branched polymers were prepared and found to be soluble in common organic solvents. Glass transition temperatures ranged from 78 to 88 °C. The polymers were spin coated and corona poled within 5 °C of the glass transition temperature. Cross-linking was initiated by irradiation for 10 min or less at either 254 or 366 nm depending on the pendant cross-linker. d_{33} values in the range 3.2–8.8 pm/V (at 1.064 μm) were measured for the several polymers which also yielded corresponding r_{33} values in the range 2.4–5.0 pm/V (at 633 nm). The nonlinearities for branched systems were found to be larger than for linear systems due to greater chromophore density. Significant improvements in the stability (at ambient temperatures) of optical nonlinearities relative to un-cross-linked systems were observed, but studies at elevated temperatures were not reported. We have prepared a number of linear polymers containing photoreactive functionalities in the main-chain and NLO chromophores as pendants.²⁴⁵

3.3.2.3.3. Lattice Hardening through Sol–Gel Processing. Inorganic glasses, composed of oxides of silicon, aluminum, titanium, boron, zirconium, vanadium, etc., are rigid materials characterized by excellent optical clarity. These glasses can be prepared by low-temperature processing using the sol–gel procedure. A variety of NLO chromophores have been incorporated as guests into inorganic glass hosts by the sol–gel technique. In early studies of guest/host silicon dioxide films produced by the sol–gel process, Nakamura and co-workers²⁶² found that the chromophore 4'-(dimethylamino)-*N*-methyl-4-stilbazolium iodide could be incorporated into silicon dioxide glasses yielding third order nonlinear optical materials. Zyss and co-workers²⁶³ have used EFISH measurements to study the molecular environments at various stages in the sol–gel process. Covalent incorporation of the chromophores into the polymerizing media was observed to provide a more sensitive probe of the microscopic environments associated with various stages of the sol–gel process. Such chromophores were also less likely to participate in phase separation. Measurements of $\chi^{(2)}$ for 2,4-dinitroaniline chromophore covalently incorporated into a silicon dioxide glass yielded values in the range 0.7–3.2 pm/V (at 1.064 μm). One month later, a value of 0.02 pm/V was observed. Zyss and co-workers²⁶⁴ have investigated composites prepared from the NLO chromophore NPP and silica/zirconia glass prepared by the sol–gel method. Due to phase separation problems, their chromophore concentration was limited to approximately 4 wt % which yielded a value of $\chi^{(2)}$ of 0.16 pm/V. 80% of the optical nonlinearity remained after 3 h at ambient temperatures. In a similar study, Prasad and co-

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workers²⁶⁵ investigated the NLO activity of SiO₂-TiO₂ composite glasses containing up to 15 wt % of the chromophore NPP. Optical nonlinearity was assessed both by second harmonic generation and electrooptic measurements yielding values respectively of $\chi^{(2)} = 11$ pm/V (at 1.064 μm by SHG) and 2 pm/V (at 633 nm by E-O measurement). Unfortunately, the optical nonlinearity was observed to decay in a few hours at ambient temperatures. NLO chromophores have been incorporated into polyceram hosts prepared by the sol-gel process.²⁶⁶ Both 2-methyl-4-nitroaniline (MNA) and *p*-nitroaniline (PNA) have been doped into polycerams prepared by the hydrolysis of the comonomers tetraethoxysilane and (trimethoxysilyl)propyl-substituted poly(ethylene imine). Inorganic glass/organic polymer composites have been prepared by sol-gel techniques, e.g., sol-gel derived silicon dioxide glass/PMMA composites containing the NLO chromophore MNA.²⁶⁷ In a related study of SiO₂-TiO₂ composite glasses containing a variety of poly(*p*-phenylene vinylene) polymers doped with PNA, a d_{33} value of 11 pm/V (at 1.064 μm) was measured.²⁶⁸ The presence of polymer was necessary to prevent the loss of chromophore due to sublimation during the hardening of the gel. No thermal stability studies were reported. Kobayashi and co-workers²⁶⁹ have prepared optically transparent aluminum oxide glasses doped with the NLO chromophore MNA. The stability of the poled order in the cured alumina films exceeded that of many guest-host organic polymer systems and 80% of the second harmonic intensity remained after 5 days at ambient temperatures. Jeng and co-workers²⁷⁰ have shown that some of the processing problems associated with in situ sol-gel processing can be ameliorated by employing partially polymerized, soluble prepolymer precursors known as spin-on-glasses. For example, they have investigated guest/host composites prepared from the NLO chromophore DR1 and the prepolymer Accuglas 204 (Allied Signal). Although a significant quantity of the dye was lost by sublimation during processing, a d_{33} value of 1.54 pm/V (at 1.064 μm) and an r_{33} value of 0.7 pm/V (at 633 nm) were measured. Only a 4% decrease in optical nonlinearity was observed at 100 °C after 1 h. A method of avoiding the problems associated with guest/host systems is that of covalent attachment of the chromophore to the lattice. Jeng and co-workers²⁷¹ report such incorporation of a chromophore into the Accuglas system discussed above. The materials were poled and vitrified at 200 °C yielding a d_{33} value of 5.28 pm/V (at 1.064 μm). 45% of the optical nonlinearity was lost after 40 h at 100 °C. Kim and co-workers²⁷² have prepared films containing the chromophores TDP and FPT by

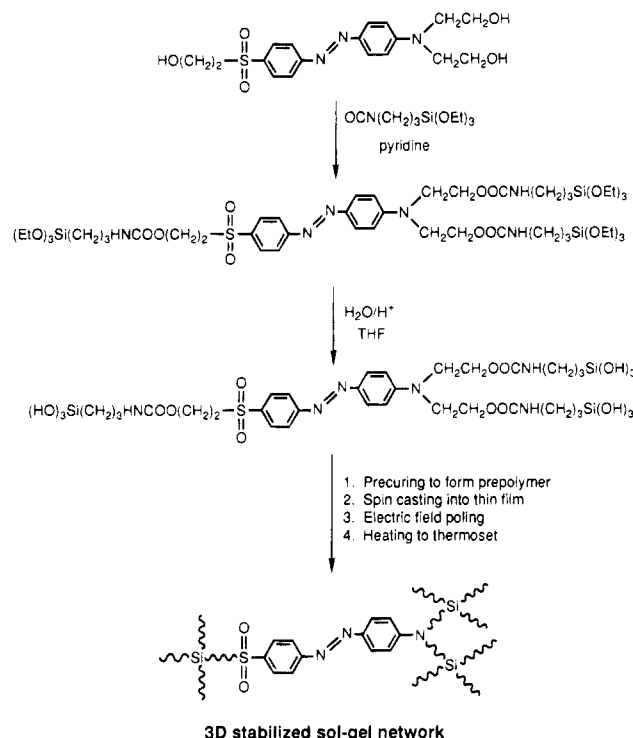


Figure 1. Synthesis of NLO chromophores covalently incorporated into a hardened sol-gel network is shown.

copolymerization with tetraethoxysilane and tetramethoxysilane. The films were cured and corona poled at 120 °C yielding d_{33} values (at 1.064 μm) of 9.1–11.7 pm/V (TDP) and 0.8–1.3 pm/V (FPT). Unfortunately, thermal stability data were not reported. In like manner, Claude and co-workers²⁷³ incorporated the chromophore *N*-[3-(trimethoxysilyl)propyl]-4'-nitroaniline into a sol-gel matrix prepared by hydrolysis of trimethoxysilane in dimethylacetamide. A d_{33} value of 13 pm/V at 1.064 μm was measured, but the thermal stability of the optical nonlinearity was not reported. Nandi and co-workers²⁷⁴ have prepared composite films containing nanoclusters of silicon dioxide and titanium dioxide in a polyimide host by curing polyamic acid precursors in the presence of orthosilicate and orthotitanate esters. Tripathy and co-workers²⁷⁵ have also investigated such composites by curing polyamic acid precursors in the presence of functionalized trimethoxysilanes. A d_{33} value of 13.7 pm/V was measured for the cured film. Only 27% reduction in optical nonlinearity was observed after 168 h at 120 °C. No signal loss was observed at ambient temperatures over the same period of time. We have also investigated the covalent incorporation of chromophores,^{276–278} including high $\mu\beta$ chromophores, into inorganic glasses using sol-gel processing methodology. In Figure 1, we show the materials

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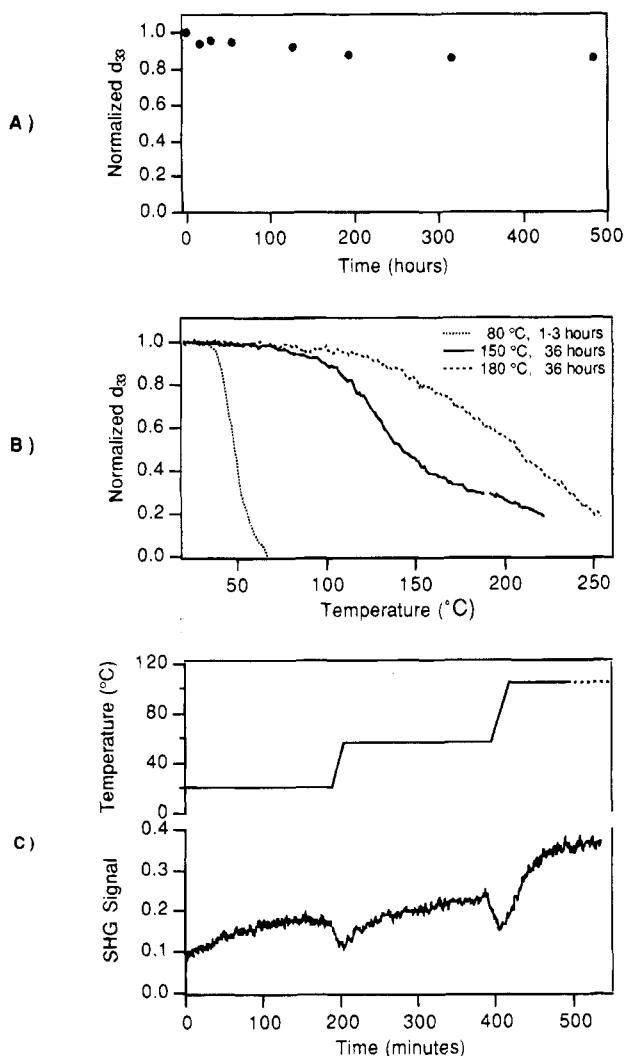


Figure 2. (A) Temporal stability of the NLO optical activity of the hardened material of Figure 11 is shown for aging at 100 °C. SHG is used to follow the thermal stability of the optical nonlinearity. (B) Dynamic thermal stability measurements are shown; the SHG signal is monitored while heating the sample at a rate of 10 °C/min. Notice the dependence of the stability of the optical nonlinearity (chromophore order) upon cure conditions shown in the upper right of the figure. (C) Effect of poling protocol is illustrated for two protocols. Top: in the first (not shown), the temperature is raised directly to 180 °C in the presence of the poling field while in the protocol shown the temperature is raised in steps of 20–30 °C until a temperature of 180 °C is finally reached. Bottom: the SHG signal response is shown for the “step” poling protocol. The final optical nonlinearity realized by the step protocol is 1.5 times that obtained by directly heating to 180 °C.

fabrication scheme used by Yang and co-workers,²⁷⁷ and representative thermal data are given in Figure 2. The evolution of optical nonlinearity with heating, shown in Figure 2, is partly due to incomplete curing. Support for this contention is provided by observation of an increase in infrared bands (measured by FT-IR) associated with Si–O–Si. Covalent chromophore incorporation by the scheme of Yang and co-workers permits 35% chromophore loading to be achieved. This high loading likely accounts for the moderately large second harmonic coefficient (27 pm/V) observed. The change in optical spectra upon poling suggests an alignment factor, $\langle \cos^3 \theta \rangle$, of 0.34 which is also consistent with the observed d_{33} coefficient and the hyperpolarizability of the chromophore. It is worthwhile to briefly discuss the

importance of poling protocol when preparing thermo-setting or thermally hardened materials. Care must be exercised so that lattice hardening is not effected before a reasonable degree of noncentrosymmetric order is introduced by electric field poling. Figure 2 illustrates the change in second harmonic signal with stepped increases in temperature. This stepped increase in temperature yields an optical nonlinearity 1.5 times that obtained by simply ramping the temperature to 180 °C while applying the poling field. The drop in SHG intensity immediately following a stepped increase in temperature likely reflects the onset of ionic conductivity associated with the transient increase in mobility accompanying the temperature jump. This phenomenon is to be expected considering the relationship between glass transition temperature and sample temperature through the kinetics of the vitrification process. The dependence of glass transition temperature upon thermal curing is experimentally evident from Figure 2. The decrease in SHG is reversed as the lattice-hardening reaction proceeds at the elevated temperature and ultimately levels off as the lattice is hardened to the point of opposing further chromophore alignment. The thermal stability realized with this sol–gel system is comparable to that of the polyimide/sol–gel interpenetrating networks of Tripathy and co-workers,²⁷⁵ Caldwell and co-workers,²⁷⁶ employing a new chromophore *N*-methyl-*N*-[3-(triethoxysilyl)propyl]-4-tricyanovinyl-aniline, record an r_{33} value of 14.3 pm/V (at 1.523 μm). This value decreases to 5.4 pm/V after heating for 30 min at 140 °C. Shea et al.²⁷⁸ report preparation of organic bridged polysilsesquioxane xerogels as nonlinear optical materials. They investigate the covalent incorporation of two chromophores, 4-nitroaniline, and 2,4-dinitroaniline and observed d_{33} coefficients of 35–37 and 9–10 pm/V, respectively. The r_{33} values at 1.3 μm were found to be 9–10 and 2–2.5 pm/V, respectively.

3.3.2.3.4. Stepwise Processing Using Asymmetric Reactions Based on DEC Chromophores. The general scheme for exploiting asymmetric functionalities terminating NLO chromophores is shown in Figure 3. The most obvious examples of stepwise processing involve use of an addition reaction in one step and a condensation reaction in the other step. The other alternative is to use to functionalities which undergo the same class of reaction (e.g., condensation) but exhibit significantly different reactivities. An example of this approach is the work of Francis and co-workers^{225,226,249} in which a bifunctional (hydroxyl and amine reactive functionalities) NLO chromophore is reacted with a polyfunctional isocyanate [tris(hexamethylene isocyanate) isocyanurate] to produce a hardened polyurethane. Although some degradation of the chromophore occurred during processing, an r_{33} value of 3–4 pm/V (at 1.3 μm) was obtained. Chromophore decomposition made it difficult to access loss of optical nonlinearity from chromophore reorientation.

3.3.2.3.5. Lattice Hardening by Development of Interpenetrating Networks. Tripathy and co-workers^{279–282}

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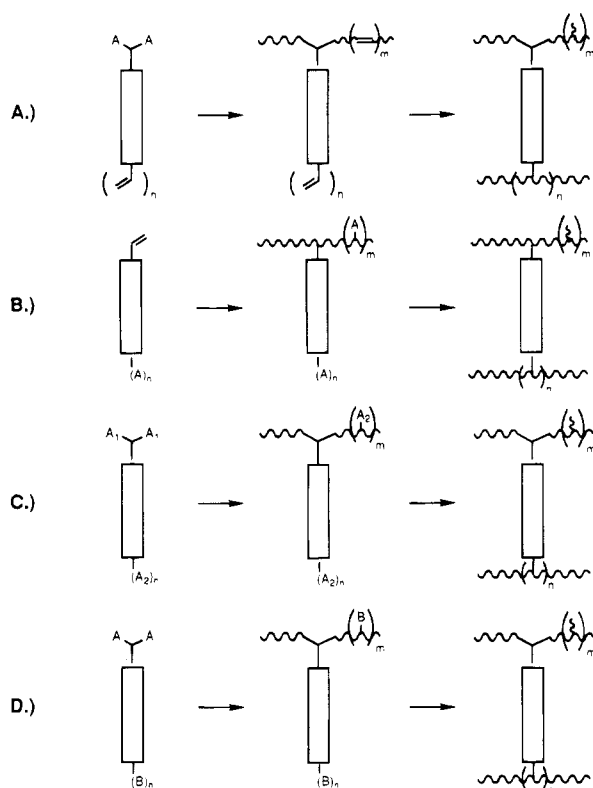


Figure 3. General schemes for producing hardened lattices utilizing DEC chromophores are shown. (A) The prepolymer is produced through a condensation reaction and the cross-linking reaction is a free radical addition reaction. (B) The prepolymer is produced by an addition reaction while the cross-linking reaction can be condensation or addition. (C) A_1 and A_2 are the same functionality but with different reactivities. A condensation or addition reaction is effected at some temperature T_1 , and then cross-linking is carried out at some temperature T_2 where $T_2 > T_1$. (D) A and B are different functionalities but react via similar mechanisms.

have pioneered lattice stabilization by the synthesis of interpenetrating networks. Among the interpenetrating networks explored are epoxy/phenoxy-silicon and polybismaleimide/phenoxy-silicon systems. These IPNs with the hybrid properties of a high glass transition temperature, an extensively cross-linked network, and permanent entanglements, exhibited excellent temporal stability of optical nonlinearity even at elevated temperatures (100–110 °C). In their most recent work, Tripathy and co-workers realized an electrooptic coefficient of 6.5 pm/V at 1.3 μm and greater than 90% retention of optical nonlinearity even after 150 h at 100 °C. Moreover, a relatively low optical loss of 2 dB/cm was observed. Recently, Wright and co-workers²⁵² report the preparation of an NLO interpenetrating network based on polystyrene/poly(indole).

4. Laser-Assisted Poling

Lasers have been used to effect photochemical reactions which can facilitate the realization of noncentrosymmetric order when used in conjunction with electric field poling. In 1990, we demonstrated that trans-cis-trans interconversion (e.g., accomplished with polarized light from an argon ion laser) effected

in the presence of an electric field led to improved poling efficiency.^{37,283} This combined photochemical/poling processing was also used to effect periodic variations in $\chi^{(2)}$ to accomplish quasi-phased-matched second harmonic generation.³⁷ Sekkat and co-workers^{284–286} have conducted a much more systematic investigation of laser-assisted poling of azobenzene chromophores in a variety of polymer hosts. In particular, they have demonstrated that polar order can be achieved at room temperatures as well as by processing near the glass transition temperature. In their most recent work, they discuss their results within the framework of a phenomenological theory of the photoinduced process. Bauer and co-workers²⁸⁷ also report exploiting photoinduced photochemical processes together with electric field poling to achieve phase matching in the fabrication of LB films.

5. Fabrication of Small Buried Channel Waveguides (Electrooptic Modulators)

To provide vertical confinement of light, a buried channel waveguide requires upper and lower cladding layers composed of lower index materials with a middle layer of higher index material. To provide horizontal confinement, a higher index channel in the middle (or guiding) layer must be surrounded by lower index material. Processing of buried channel waveguides of various dimensions (e.g., 1–3 and 5–10 μm) is critically important for the development of organic electrooptic modulators and for integrating these devices with fiber optic transmission lines. The theoretical basis for developing such structures is well understood^{288–304} and is dependent upon the ability to realize precise control of index of refraction variations within a material. Polymeric waveguides can be fabricated using a variety

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of procedures including (1) photochemical processing exploiting photoinduced conformational changes, (2) electron cyclotron resonance (ECR) and reactive ion etching (RIE) using ions present in an oxygen plasma, (3) spatially selective poling, and (4) laser ablation techniques using excimer lasers and other forms of UV irradiation. Electron beam ablation can also be used.

5.1. Photochemical Processing. Such processing effects a change in refractive index of the material by producing a change either in π -electron density or nuclear density as the result of a photochemically induced conformational change. Well-known photochemical processes include photoinduced trans-to-cis isomerization, ring-opening reactions, keto-enol tautomerism, and interconversion between twisted charge transfer states.^{37,305-327} Photoinduced polymerization is also used to fabricate waveguides which can be accomplished either by a change in index between cross-linked and un-cross-linked regions, or more commonly exposure through a mask is used to produce a channel of polymerized material and a corresponding rib structure is obtained by using an appropriate solvent to dissolve the unpolymerized (protected by the mask) regions.³¹⁶⁻³¹⁸ Although a photochemical reaction is involved, the end result is analogous to laser ablation.³²⁸⁻³³³ We have made extensive use of conformational changes associated with the induction of trans-

to-cis isomerization in azobenzenes.³²⁴⁻³²⁷ Waveguides can be made single mode by control of the transverse size and control of Δn via UV exposure time. For disperse red chromophores, we have reported large UV patterned changes in the index of refraction (Δn approximately 0.2) and, by using polarized light, we have achieved patterned control of the material birefringence.^{324,326,327} One of the advantages of photochemical processing is the use of the upper electrode as a bleaching mask which ensures alignment of the electrode and optical waveguide. Of course, this may only be possible for low-frequency devices since for very high frequencies the electrode structure required for good signal impedance matching and efficient signal coupling may not be compatible with the desired waveguide dimensions. The primary disadvantage of photochemical processing is the requirement of a photochemically active component and residual sensitivity of the device structure of extraneous radiation over the lifetime of the device. Of course, such effects can be minimized by appropriate packaging. The decoupling of NLO and photochemical Δn effects can be accomplished by chemical design. A number of workers have discussed photochemical processing employing a variety of chromophores.³⁰⁵⁻³²³

5.2. Reactive Ion Etching and Electron Cyclotron Resonance Etching. RIE is a plasma dry etch process commonly used in the processing of semiconductor devices. The etching of organic materials can be accurately controlled in an RIE system using oxygen as the reactive agent. This method does not change the index of refraction but rather etches a ridge or a trough which acts as the waveguide. In RIE systems, ions of the reactive gas are created by an rf plasma discharge. In our experiments, we pattern commercially available photoresist directly onto the poled polymer film to act as the etch mask. The photoresist is baked for short times and then patterned in a mask aligner using masks made of standard photolithography materials. After the proper exposure, the photoresist is developed in an inorganic developer. The etching is done in a Plasma Technology RIE instrument; typical conditions are 100 mTorr of O₂ pressure and 45 W of rf power which gives a polymer etch rate of 1300 Å/min. In general, a slower etch rate produces smoother and better quality etch walls. Single-mode operation is ensured by control of the waveguide width and control of the depth of the plasma etch. RIE etched waveguides can be observed under a microscope facilitating the visual alignment of the electrodes to the optical waveguide and the visual alignment of pigtailed fibers for optical coupling to the waveguide. A recent improvement in dry plasma etch-

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Oxygen Plasma Etching of Ridge Waveguide Structures in Electrooptic Polymers

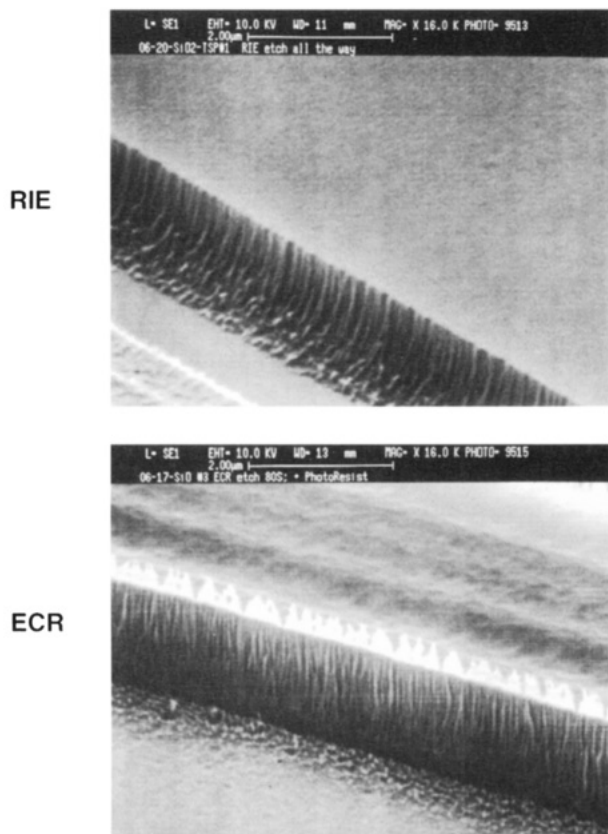


Figure 4. SEM pictures of waveguides fabricated by RIE (top) and ECR (bottom) are shown. Note that the ECR sample in the picture is partially covered with etched photoresist. The polymer surface underneath the resist and the ECR-etched polymer surface are both very smooth.

ing is electron cyclotron resonance (ECR) etching. These instruments provide a higher degree of control of the energy of the reactive ions and produce smoother, more controlled etching (which translates into reduced optical loss). The accompanying SEM picture (Figure 4) shows the dramatic improvement achieved by use of ECR etching.

5.3. Laser Etching. Excimer laser lithography, developed by Srinivasan,³²⁸⁻³³³ utilizes pulsed excimer lasers operating at deep ultraviolet wavelengths (380, 238, or 193 nm) to remove organic material very effectively and cleanly. Rib waveguides have been prepared with sharply defined vertical walls. The advantages and disadvantages of this technique are similar to RIE. Care must be taken to ensure that the active region temperature does not exceed the depoling temperature of the polymer or, alternately, the polymer must be poled after the laser etch process. This technique is most suitable for producing large (e.g., 10 μm) multimode waveguide structures.

5.4. Spatially Selective Poling. When polymer materials are poled, the dipole alignment produces a birefringence with a slightly higher index in the poling direction. By selective area poling, waveguides can thus be defined for modes with the optical polarization in the

same direction as the poling field.^{37,342,343} Lytel et al.³⁴³ have fabricated a two-dimensional single-mode waveguide by poling a dichroic dye in PMMA with a spatially defined electric field to increase the refractive index of the TE mode within the defined region. This approach has the advantage that the electrodes used for poling can also be used as the signal electrodes, and therefore the alignment of the waveguide to the electrodes is always ensured. However, there is no control over the amount of index change since the material must be poled to the maximum amount to ensure a large EO coefficient. This fixes the difference between the poled and unpoled material. This approach does eliminate the need for a photochemically active moiety, but unlike RIE and laser etching techniques, it is not readily amenable to the fabrication of buried channel waveguide structures. An interesting variation to allow small Δn buried channel waveguide structures through spatially selective poling with strong electric fields is the use of claddings which also pole and similarly increase the index of refraction in the poling direction. An example is provided by the HCC 1232A cladding polymer (Hoechst Celanese Corp.) for use with the HCC 1232 NLO polymer.^{344,345} Such a cladding polymer can maintain a small Δn over a wide range of poling voltages and has been examined for the formation of buried channels using spatially selective poling with electric fields in excess of 100 V/ μm . It has recently become clear that the selection and the properties of the cladding materials is not a trivial problem. A cladding material with the proper index of refraction, properties that allow it to be spin cast and cured on top of active polymer materials without degrading the active material, and with sufficiently high conductivity to ensure the poling voltage is applied to the active layer is not easy to find. The cladding material conductivity is an important parameter for the case of electrode poling perpendicular to the layers. The poling electric field will be small inside the active polymer waveguide layer if the conductivity of this layer is higher than that of the cladding layers.

5.5. Other Methods. Franke et al.³⁴⁶ has described altering the refractive index of polymer films by ion implantation. Hybrid structures have been developed where semiconductor processing techniques have been employed to define waveguide geometries in inorganic materials which were subsequently filled with polymeric materials.³⁴⁷

6. Fabrication of Large Buried Channel Waveguides (Coupling to Fiber Optic Lines)

An advantage of organic polymer materials relative to inorganic materials is that materials with large EO effects and good optical quality can be integrated on the same substrate with the high-speed drive and signal-processing electronics. The processing steps for the polymer device and the projected temperature stability

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of the polymer materials are compatible with this integration. In contrast only hybrid integration using separate optical and electronic modules connected via cables or flip-chip bonding is possible using crystalline dielectrics such as LiNbO_3 . The true significance of this can be seen when one considers that there are well-established and highly developed VLSI semiconductor foundries from which one can have fabricated state-of-the-art high-speed integrated semiconductor electronic circuits built to custom design. This technology could become available for high-speed optoelectronic circuits by developing techniques of fabricating polymer optical switch/modulators and other polymer integrated optical devices onto the Si or GaAs substrate which already contains the control, drive, and interface integrated electronics.

The advantages of this integration can also be seen when one considers the "silicon breadboard" approach to photonic circuits³⁴⁸ wherein the Si substrate contains the electronic circuitry, the optical modulator/switch, the optical sources and/or the optical fiber inputs, and the electrical controls or inputs. The EO polymer films can be easily spun onto almost any substrate, including semiconductors, and the modulators or other optical structures fabricated in the polymer and then connected via wire bonds to the previously fabricated electronic control circuitry. The optical inputs are connected via fiber and V-groove positioning or from on-chip lasers via waveguides.

It is important to compare the polymer/semiconductor integrated approach to the other two approaches to photonic switching: Dielectrics (LiNbO_3) and semiconductors (GaAs). LiNbO_3 is a well-developed EO material which is single crystalline and hence cannot be readily grown on other substrates. Consequently, the only integration path for LiNbO_3 is through hybrid integration in which the LiNbO_3 modulator is flip-chip bonded to a substrate or alternately the electronics, lasers, and modulators are interconnected via cables and fibers.³⁴⁹ The second approach to integrated optoelectronics involves development of all-semiconductor systems which rely primarily on GaAs or related compounds for both the optical and electronic devices.³⁵⁰ While many of the technical issues remain to be resolved, the polymer/semiconductor integrated approach has some important advantages over the semiconductor systems. The EO effects are large in polymers and have the possibility of going much higher, the technology for waveguide fabrication is currently more advanced for the polymers, and the coupling between fibers and polymers is easier to achieve because of the lower index of refraction of the polymers.

6.1. Photochemical Processing for Modulator/Fiber Coupling. Photochemical processing can be used to fabricate a buried channel waveguide directly without deposition of a cladding layer. The procedure involves two-step, two-color processing with change of the mask between steps. The development of a buried channel of nonlinear optical material by this procedure depends upon the fact that the penetration of the

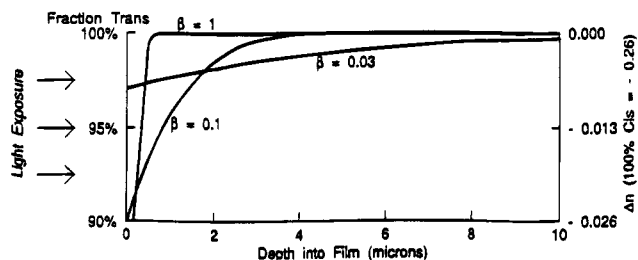


Figure 5. Refractive index profiles in an azobenzene containing polymer resulting from change in optical filtering of the light source after equal exposure times. Changes in the effective absorption coefficient (β) provide corresponding changes in the Δn profiles in the polymer film.

radiation into the sample will depend upon radiation wavelength.^{314,315,325-327,351-355} Explicitly, the time-dependent spatial concentrations of bleached and unbleached NLO chromophores in films can be modeled to good approximation by the following coupled equations:³⁵⁵

$$\frac{\partial l(x,t)}{\partial x} = -l(x,t)[a_{\text{cis}}C_{\text{cis}}(x,t) + a_{\text{trans}}C_{\text{trans}}(x,t) + a_{\text{poly}}C_{\text{poly}}(x,t)] \quad (7)$$

$$-\frac{\partial C_{\text{cis}}(x,t)}{\partial t} = \frac{\partial C_{\text{trans}}(x,t)}{\partial t} = -\alpha C_{\text{trans}}(x,t) l(x,t) \quad (8)$$

where $l(x,t)$ is the depth- and time-dependent light intensity, the a 's are molar absorption for the cis and trans forms of the NLO chromophore and other absorption by the polymer, the C 's are depth- and time-dependent concentrations, and α is the photoconversion rate per unit intensity. For example, these equations provide a very good description of the photochemical properties of the polymers of ref 245. Representative data (see Figure 5) for light transmission and refractive index change as a function of depth into the film are given for polymer no. 2 of ref 245. Let us now see how the above features of the photochemical process can be used to develop buried channel waveguides without the deposition of an upper cladding layer. The first step involves use of a mask to protect a channel of high-index, nonlinear optical material from the top of the film to the bottom. Radiation at a wavelength characterized by low absorption (hence good penetration through the film) is used to reduce the index of refraction of the material around the protected region. The low absorption must, of course, be offset by a long exposure time to achieve effective bleaching. Following this step, the mask is removed and the unbleached region is exposed to radiation of a wavelength corresponding to (or closer to) the absorption maximum. Electromagnetic radiation of such a wavelength has a shallow penetration depth so it bleaches (with short exposure time) only the uppermost region creating a buried channel of unbleached, nonlinear optical material. Moving from the bottom to the top of the material (Figure 6), one finds (1) the lower cladding layer, (2) the unbleached, high-

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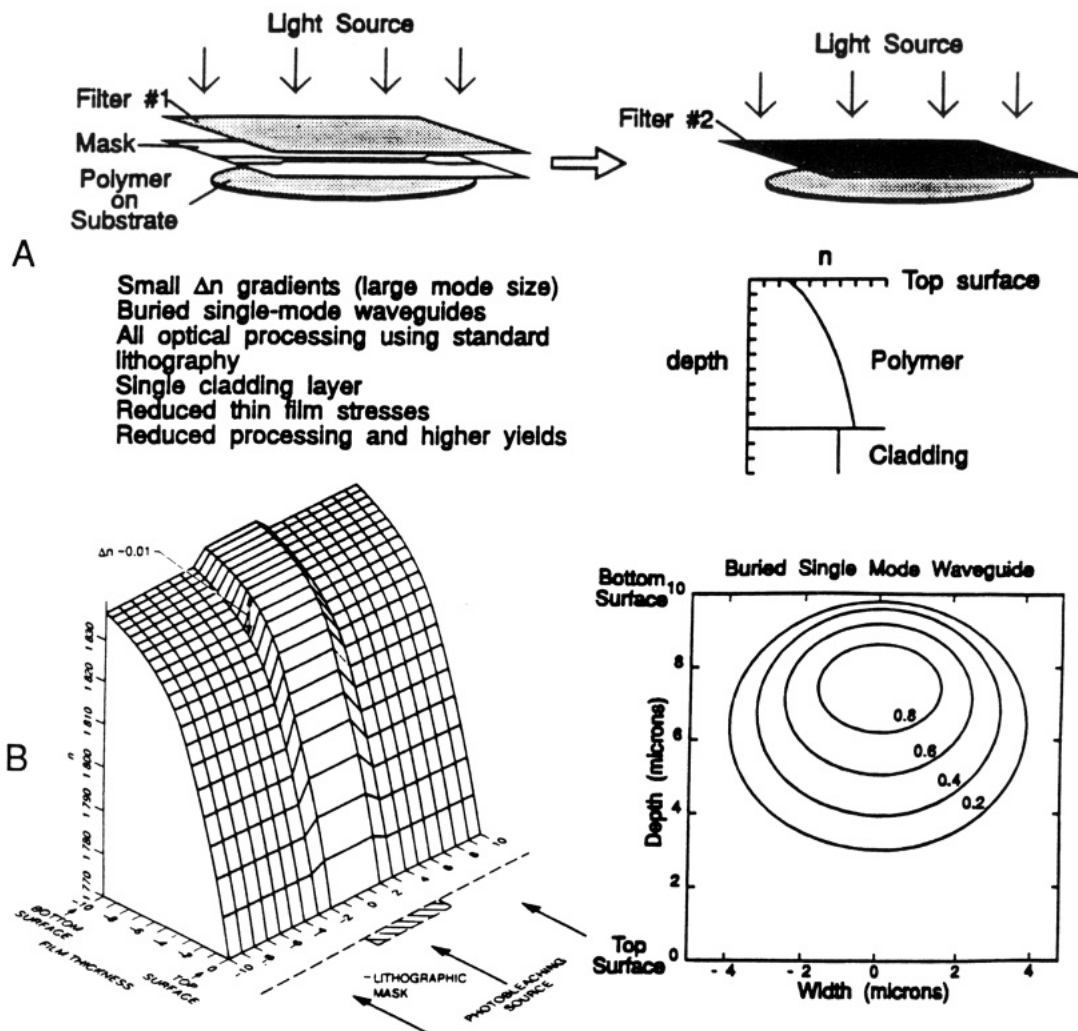


Figure 6. Example of two-color lithography using light-field and dark-field waveguide masks is shown. The resulting small lateral ridge in the high-index, back region of the polymer film forms a large, buried, single-mode waveguide. Top: the two color photoprocessing scheme is schematically represented. Bottom: refractive index and single-mode light profiles are shown.

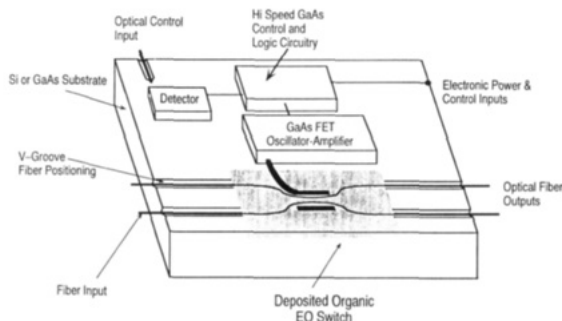
index, nonlinear optically active channel, and (3) the bleached, low-index upper layer. A serious problem in system integration is that of coupling the rather small (e.g., 1–3 μm) waveguide of a high efficiency electrooptic modulator to the large-waveguide structure of a fiber optic transmission line. The most logical approach to this procedure is to develop a tapered waveguide structure progressing from a few microns to approximately 8–10 μm . However, large waveguide dimensions pose problems for single-mode operation. For single-mode operation, local gradients, if large, must be sufficiently small in size (0.5–1.5 μm for refractive index differences between 0.5 and 1.5). This is fine for small device dimensions but leads to a gross mismatch with the larger mode sizes of optical fibers because these have small, graded index (small Δn) cores. This mismatch has been a persistent problem to device development with NLO polymer materials because unless polymer claddings are closely matched in index, single-mode operation requires small waveguide dimensions which mismatch fiber mode sizes. Early innovations to make thick films with small Δn claddings and boundaries (0.01–0.03 for 10 μm waveguide dimensions) for channel waveguides led to innovations in specialized claddings such as NLO polymer blends, e.g., the HCC 1232-1232A polymers developed in the late 1980s by Hoechst Celanese.³⁴⁵ A number of methods for creating large

single-mode (small Δn) waveguides have been developed including reactive ion etching (RIE) of ribs in small Δn claddings^{337,356} and induced birefringence in small Δn claddings.^{342,344} An inherent shortcoming of all approaches to make large single-mode waveguides in thin films stems directly from the need for small Δn boundaries. This necessitates thick cladding layers because single modes are strongly evanescent in small Δn claddings; however, thick claddings result in low device efficiency because of large electrode spacings. Moreover, serious fabrication difficulties (cracking of film laminates, solvent damage, and other stress-related problems) are encountered with thick claddings.

The multicolor photolithography technique mentioned above is ideally suited for processing buried channel (small Δn) waveguides without the requirement of cladding layers. Small Δn gradients can be realized by exploiting the known penetration profiles of electromagnetic radiation of various wavelengths into the photoactive polymer material. In Figure 7, we show a schematic representation of a switching node whose fabrication can be accomplished by a combination of multicolor photochemical processing and reactive ion

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Concept of Polymer-Semiconductor Integrated Optoelectronics



Polymer EO modulator/switch fabricated directly on substrate which contains driver/processing electronics and fiber positioning

Figure 7. Schematic representation of a high-bandwidth optoelectronic device with a high-speed polymer optical switch is shown. Multicolor lithography is used to eliminate the optical losses due to device-fiber mismatch through fine control of mode size, shape, and support.

etching. Several novel ideas have been reported for improving the coupling between the fiber and the waveguide which are applicable to polymeric materials. These include matching lenses fabricated on the fiber tip or in the organic polymer via micropatterning, using multiple coupling structures, and using layered structures to increase the transverse mode size.³⁵⁷⁻³⁵⁹

6.2. Silicon V Groove Technology. This technology is the most developed and most successful method of accurately and repeatably connecting fibers to integrated optical waveguides.³⁶⁰ In Figure 8, we show one of our results for creating a V-groove etched in silicon dioxide coated silicon substrates. This figure shows many 100 μm wide V-grooves with 80 μm cladding diameter fibers in some of them. The substrate is Si covered with 4 μm of SiO_2 which also acts as the lower cladding. The fiber is first laid down, then UV curable epoxy is used to hold it in place. Fabrication is completed by a matching V-groove piece on top of the fibers in the V-groove. This piece ensures further mechanical stability for the spinning process and the final packaging.

6.3. Integration with Electronics. Polymer electrooptic devices and optical waveguides have been fabricated on semiconductor substrates, not with the goal of integration but rather to take advantage of the easy and accurate cleavage and etching of the semiconductor substrate. The clean cleavage can make possible butt coupling into the polymer waveguide and V-groove etching can make accurate alignment of a coupling fiber possible. There have been reports of low-loss passive polymer waveguides and active EO waveguides fabricated on silicon.³⁶¹⁻³⁷²

7. Fabrication and Evaluation of a Prototype Birefringence Modulator

As most modulators have been fabricated in a Mach-Zehnder configuration, let us consider a birefringence

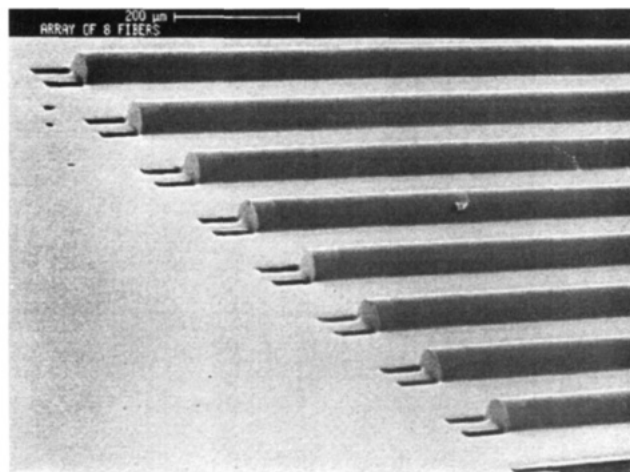


Figure 8. Fiber-waveguide coupling exploiting V-groove positioning is shown.

modulator which can be used either as a phase or an amplitude modulator. If the input is either a pure TE or a pure TM mode, the device acts as a phase modulator. If the input beam excites both TE and TM modes, the birefringence of the waveguide is changed by the applied voltage and the output polarization changes according to the modulation field. An analyzer converts the polarization modulation into an amplitude modulation. A representative modulation signal is shown in Figure 9. This birefringence modulator has been operated to frequencies as high as 60 GHz and has been operating for well over 1 year with no apparent degradation in performance. Both Mach-Zehnder and birefringent modulator designs have been evaluated to frequencies approaching 40 GHz and require V_π voltages in the range 10–50 V (depending on the chromophore used, cladding layer thickness, processing conditions, electrode design, etc.).³⁶¹⁻³⁷² Optical loss is a crucial parameter; measured losses for modulator waveguides operating in the wavelength region 1.3–1.5 μm have typically been on the order of 1–2 dB/cm while bulk losses for materials have typically been in the range 0.1–0.5 dB/cm. The additional losses are due to the roughness of the waveguide walls or ripples in the surface interface between the cladding and the core. The techniques which we have described hold promise for reducing losses of modulator waveguides to those of the bulk materials. Losses at 0.8 μm will likely be limited to values of 1 dB/cm or greater by intrinsic absorption

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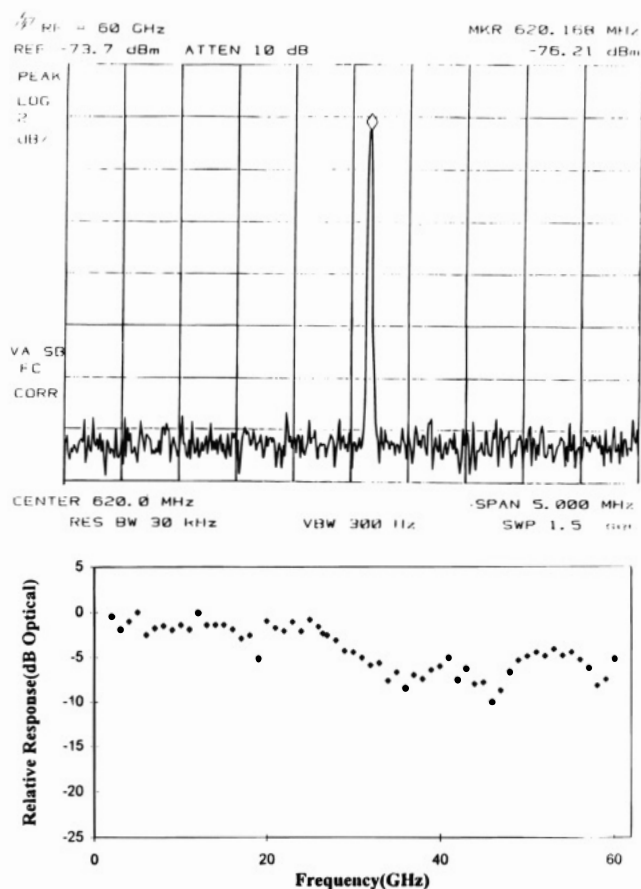


Figure 9. (a, top) Spectrum analyzer scan of the detected and down-converted 60 GHz optical modulation signal from a birefringent modulator fabricated from the thermosetting polymer of reference 247 is shown. (b, bottom) The relative response of a birefringent modulator output as a function of frequency to 60 GHz is shown. This modulator has been operational for over a year with no detectable degradation in performance. The variation in modulation signal with frequency reflects the characteristics of the metal electrodes and not the polymeric material.

of the chromophore unless new chromophores are developed. An effort to synthesize chromophores with large optical nonlinearity and improved transparency has been described recently.²¹²

8. Alternative Device Applications

In this section, we mention three additional applications: photonic detection of electromagnetic radiation, voltage sensing, and frequency doubling.

8.1. Photonic Detection of Electromagnetic Radiation. Conventional methods of detecting electromagnetic fields require metal electrodes which have the disadvantage of distorting the fields to be measured. An attractive alternative is the use of dielectric EO materials and to detect the fields using the EO effect on a sensing optical beam. Low dielectric constant EO materials distort the field less than the metal electrodes. Although an ideal photonic sensor (see Figure 10) would be comprised completely of low dielectric components, metallic antennas are traditionally attached to the electrooptic modulator of a photonic system to enhance field gain. Hilliard and co-workers^{373,374} have proposed

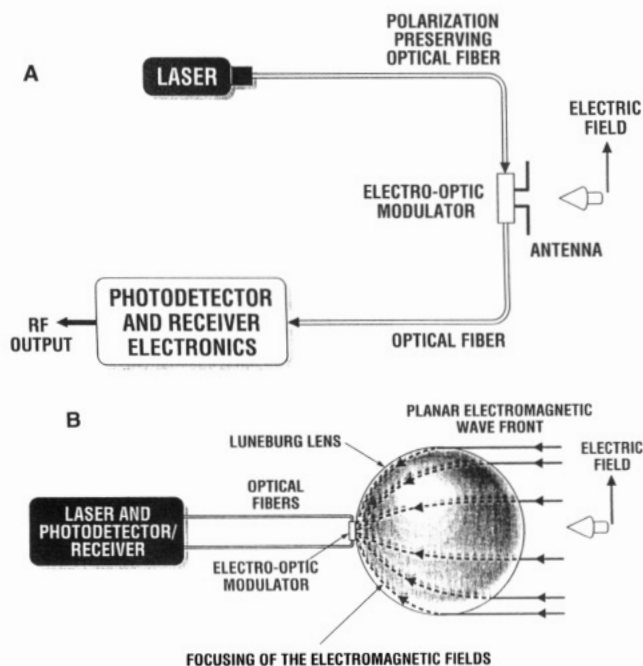


Figure 10. (a) Block diagram of a photonic sensor system is given. (b) Schematic representation of the use of a Luneburg lens with a single photonic sensor is shown.

employing a low dielectric (polystyrene polymer) Luneburg lens to achieve the necessary gain; thus, they propose a completely low-dielectric electromagnetic field sensor.

Electrooptic modulator sensors can be placed on the surface of a Luneburg lens either as single elements or as units consisting of two mutually orthogonal modulators (for detecting polarization of the electromagnetic wave front). The angle-of-arrival of the electromagnetic wave fronts is determined by noting which sensors are most strongly modulated. EO modulators can be placed over the entire surface of the lens to provide 4π steradian angle-of-arrival coverage or placed over a subsection of the lens surface to provide a narrower field-of-view. In the case of 4π steradian coverage, aperture blockage, which would occur with metal antennas, is reduced because the modulators covering the lens surface on the side of field incidence are effectively transparent to the fields. This allows fields to penetrate into the lens and be focused onto the modulators on the opposite side.

Maximum energy coupling into the EO modulator can be achieved by minimizing the reflection of fields at the surface of the modulator. The relative dielectric constant of a common inorganic EO modulator material, e.g., LiNbO_3 , ranges from 28 to 80. Assuming a value of 30, the reflection coefficient for fields passing from the lens surface to the modulator is 0.7. The percentage of incident energy density reflected to the source is about 50%. Organic polymers have the lowest dielectric constant (approximately 3–3.5) of all known EO materials resulting in about 7% reflected energy density. Moreover, organic polymers are manufacturable as thin films which make them capable of being conformably interfaced to the spherical surface of the Luneburg lens.

(373) Hilliard, D.; Mensa, D. *Proc. IEEE Ant. Prop. Soc. Symp.* **1992**, 2, 720.

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8.2. Electrooptic Modulators as Voltage Sensors. Recently, Skindhøj and co-workers³⁷⁵ have described the application of polymeric modulators as voltage sensors. While this application greatly relaxes the requirement on electrooptic coefficient (0.01–1 pm/V), the coefficient must show less than 0.2% fluctuation over a 20 year life span, sometimes under daily thermal cycling fluctuations of greater than 20 °C and must be able to withstand lightning voltage surges.

8.3. Frequency Doubling. Frequency doubling (or second harmonic generation, SHG) of the well-developed infrared semiconductor lasers through electronic optical nonlinearities in organic materials, which must compete with the rapidly developing semiconductor lasers in the visible, has many of the same material requirements as electrooptic modulation; namely, large $\chi^{(2)}$, good processibility, low optical loss (at both the fundamental and second harmonic wavelengths), good thermal and environmental stability, and low cost.^{37,376} While SHG does not require the design and deposition of metal electrodes, it does require index of refraction or velocity matching ($L|n_{\omega} - n_{2\omega}| < \lambda/4$, preferably $\rightarrow 0$) of the fundamental, n_{ω} , and the harmonic, $n_{2\omega}$, indexes. This has been accomplished in a variety of ways including by (1) modal waveguide dispersion and birefringence, (2) quasi-phase matching, (3) anomalous dispersion, (4) Cerenkov radiation, and (5) counter-directed waves. The first four methods have been previously reviewed by us³⁷ and by others.³⁷⁶ We will mention only a few selected studies which illustrate recent application and modification of these methods. A somewhat more detailed discussion will be given to phase matching by the method of counterpropagating waves.^{376–379}

Let us first briefly comment on the quasi-phase-matching method. Quasi-phase-matching is achieved by creating a periodic variation of $\chi^{(2)}$ which periodically corrects for the fundamental and second harmonic phase difference. This, in turn, results in a finite second harmonic power as has been discussed elsewhere.³⁷ Such periodic variation in $\chi^{(2)}$ has been accomplished by a number of procedures. For example, Gunter and co-workers³⁸⁰ have recently used the Langmuir–Blodgett deposition technique with the sign of $\chi^{(2)}$ inverted between successive layers to achieve quasi-phase-matching. Khanarian and co-workers^{381,382} have realized quasi-phase-matching employing periodic poling; more recently, they report the adaptation of this procedure to the preparation of free-standing films.^{383,384} A technique which is quite analogous to periodic poling

is photochemical irradiation through a periodic mask to produce a periodic variation in $\chi^{(2)}$ as effected by Dalton and co-workers.^{37,282,385,386} A periodic poling could also be accomplished, although somewhat laboriously, by using RIE to create periodic channels in a poled and hardened polymer, these channels could be filled with an unhardened NLO polymer, then this polymer could be poled with an electric field of reverse polarity relative to the original poling field.

Stegeman and co-workers^{376–379} have demonstrated SHG by the overlap and mixing of two oppositely propagating fundamental beams in a waveguide. The angle of radiation of the sum beam from the waveguide depends upon the frequencies of the counterpropagating beams. For the case of degenerate frequencies, the second harmonic beam is radiated orthogonal to the waveguide. For the counterpropagating geometry, molecular alignment in the plane of the film is required which, in turn, requires in-plane poling with parallel electrodes. In a recent paper, Stegeman and Otomo^{378,379} discuss the importance of cladding layers in the poling procedure. When used with nonresonant optical nonlinearities, the counterpropagating geometry is inherently less efficient than the copropagating geometry. This is a consequence of the different geometric factors. However, Stegeman and Otomo^{378,379} note that since, in the counterpropagating case, light transverses only the thickness of the film, it is possible to operate close to resonance absorptions and benefit from the associated large enhancements.

One of the major problems associated with phase matching by modal dispersion is the severe tolerances placed on waveguide dimensions. Miyatta and co-workers³⁸⁷ have recently discussed a five-layer waveguide structure that attempts to address this liability of phase matching by modal dispersion. In a similar way, Asai and co-workers³⁸⁸ increased the efficiency of Cerenkov type radiation, in which the second harmonic radiates into the substrate at a specific angle, by using a layer waveguide with $\chi^{(2)}$ inversion between layers.

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