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The following objectives were defined and pursued: (1) Synthesis of chromophores characterized by large hyperpolarizability and good thermal stability, (2) covalent coupling of nonlinear optical chromophores to polymer matrices, (3) lattice hardening reactions which permit locking-in of electric field poling-induced macroscopic non-centrosymmetric order, (4) definition of mechanisms of optical nonlinearity and development of improved instrumentation to effect such characterization, (5) exploration of methods of enhancing optical nonlinearity and electromagnetic field intensities within materials(e.g., exploration of cascading effects and morphological resonances). Substantial success was achieved in each of these areas with more than sixty publications resulting from AFOSR support.

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TITLE: Development of Device Quality Nonlinear Optical Materials and Definition of Mechanisms of Optical Nonlinearity

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ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The following objectives were defined and pursued: (1) synthesis of chromophores characterized by large hyperpolarizability and good thermal stability, (2) covalent coupling of nonlinear optical chromophores to polymer matrices, (3) lattice hardening reactions which permit locking-in of electric field poling-induced macroscopic noncentrosymmetric order, (4) definition of mechanisms of optical nonlinearity and improved instrumentation to effect such characterization, and (5) exploration of methods of enhancing optical nonlinearity and electromagnetic field intensities within materials (e.g., exploration of cascading effects and morphological resonances). Substantial success was achieved in each area with more than sixty publications resulting from AFOSR support. Moreover, the following technological advances were demonstrated: (1) A thermally stable (to 100°C for 1000 hours) electro-optic modulator capable of broadband operation to 40 GHz and characterized by an electro-optic coefficient of 13 pm/V, (2) a write-read-erase optical memory based upon room temperature hole-burning exploiting morphological resonances, (3) a new sensor protection material, and (4) a fiber-optic amplifier.

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Personnel Associated With Project

A. Graduate Students (partial support)

1. Mark Becker
2. Paul Bryson
3. Mai Chen
4. Darin Files
5. Rima Ghosn
6. Aaron Harper
7. Joyce Laquindanum
8. Jerome Liang
9. Robert Montgomery
10. Youngsoo Ra
11. Linda Sapochak
12. Shajing Sun
13. Bo Wu
14. Chengzeng Xu

B. Theses Completed (USC Degrees)

1. Mai Chen, Ph.D.(Chemistry), 1992, "New polymers exhibiting stable and large optical nonlinearities."
2. Linda Sapochak, Ph.D.(Chemistry), 1992, "Studies of well-defined conjugated pi-electron subunits: Progress in material design for nonlinear optical applications."
3. Robert Montgomery, Ph.D.(Chemistry), 1992, "Synthesis of fused ring chromophores for nonlinear optical effects."
4. Yongqiang Shi, Ph.D.(EE), 1992, "Characterization and device applications of disperse red 19 containing second-order nonlinear optical polymers."
5. Paul Bryson, Ph.D.(Chemistry), 1993, "Electron spin resonance characterization of new delocalized pi-electron oligomers in oxidative and protonic doping."
6. Chengzeng Xu, Ph.D.(Chemistry), 1993, "Design, synthesis and characterization of novel organic nonlinear optical materials."
7. Mark Becker, M.S.(Chemistry) 1993, "A novel chromophore functionalized polyimide for nonlinear optical studies."
8. Bo Wu, Ph.D.(Chemistry), 1994, "Design, synthesis and characterization of polymeric materials with second order optical nonlinearity."

C. Postdoctoral Fellows

1. Robert Montgomery
2. Frederick Strohkendl (partial support)
3. Chengzeng Xu

D. Visiting Scholars Working on Project (No Support Provided from Federal Funds)

1. Professor Olga Todorowa, Bulgarian Academy of Sciences
2. Professor C.-S. Hsu, Department of Applied Chemistry, National Chiao Tung Univeristy, Hsinchu, Taiwan

E. Research Report

1. Development of Polymeric Electro-Optic Modulators. Our efforts involving the synthesis and processing of materials for the development of electro-optic modulators are reviewed in depth in the accompanying preprint, "Synthesis and Processing of Improved Organic Second Order Nonlinear Optical Materials for Applications in Photonics," which will be published in Chemistry of Materials. This manuscript also sets our work in the prespective of the worker of others and compares the state-of-the-art for the development of organic materials to that of competitive inorganic materials.

2. Exploitation of Morphological Resonances. Morphological resonances have been demonstrated in polystyrene beads coated with NLO chromophores (e.g., the aminosulfone azobenzene developed for electro-optic modulator applications). Write-read-erase optical memories exploiting room temperature spectral hole burning have been demonstrated (results have been independent communicated to program monitor and a patent application is under development). The chemical synthesis is described in the following paragraphs.

Write-read-erase memories derived from organic chromophores exploit one of four types of conformation changes[1]: (1) trans-cis isomerism as encountered in azobenzenes, (2) ring opening reactions such as encountered in the in benzospiropyrans, (3) keto-enol tautomerism as in benzophenone-type moieties, and (4) interconversion between twisted charge transfer conformations. We have shown that both the magnitude change in optical susceptibility and writing speed are influenced by the polymer network to which the chromophore is coupled and that these variables can be altered by systematic variation of the nature of the coupling element(s) which secure the chromophore to the polymer matrix. Thus, a central issue in chromophore design is functionalization for coupling to the appropriate polymer matrix. We have developed two rather different schemes for coupling write-read-erase chromophores (WRECs) to polystyrene microspheres (PSMSs). The first is to synthesize a chromophore terminated by a vinylbenzene (styrene) functionality. Such a chromophore can be used as a comonomer with styrene and divinylbenzene in the polymerization reaction to form PSMSs. A chromophore coating of controlled variable thickness is produced by altering the monomer feed during the controlled growth of PSMSs. Up to a given point the feed is vinylbenzene and divinylbenzene which is then switched for an appropriate period of time under controlled reaction conditions to vinylbenzene-chromophore and divinylbenzene feed.

The second approach is to derivatize the surface of PSMSs to permit covalent coupling of functionalized dyes. Their are two convenient schemes for functionalizing PSMS surfaces; the first yields a hydroxyl functionality[2] while the second yields an amine functionality[3]. Hydroxyl groups can subsequently be reacted with acylchlorides, isocynates, acetic anhydrides, silyl halides, etc. to provide a coupling between chromophore and the PSMS surface. Many of the same condensation reactions apply to amines. Functionalization of the other end of the chromophore permits subsequent layers of dyes to be incorporated. Several schemes for hydroxylation and amination have been demonstrated. Two representative approaches are given below:

Hydroxylation

$$\text{(PSMS)} + \text{NaBO}_3(4\text{H}_2\text{O}) \text{ ----------------------------> } \text{(PSMS)-(OH)x}$$

Amination

$$\text{Me}_3\text{SiN}_3 + 2\text{F}_3\text{CSO}_3\text{H} \text{ ----------> } \text{NH}_2\text{N}_2{}^{+-}\text{OSO}_2\text{CF}_3 + \text{Me}_3\text{SiOSO}_2\text{CF}_3$$

$$\text{(PSMS)} + \text{NH}_2\text{N}_2\text{+-OSO}_2\text{CF}_3 \text{ -----------> } \text{(PSMS)-(NH}_2)_x$$

Once hydroxylated beads are obtained, dyes can be coupled by condensation reactions such as the acyl chloride-hydroxyl reaction shown below

1. L. R. Dalton, L. S. Sapochak, M. Chen, and L. P. Yu, "Ultrastructure Concepts of Optical Integrated Microcircuits and Polymeric ElectronicsMaterials," and in Molecular Electronic Devices, Vol. II, K. Sienicki, ed. (CRC Press, Boca Raton, 1993) pp. 125-209.
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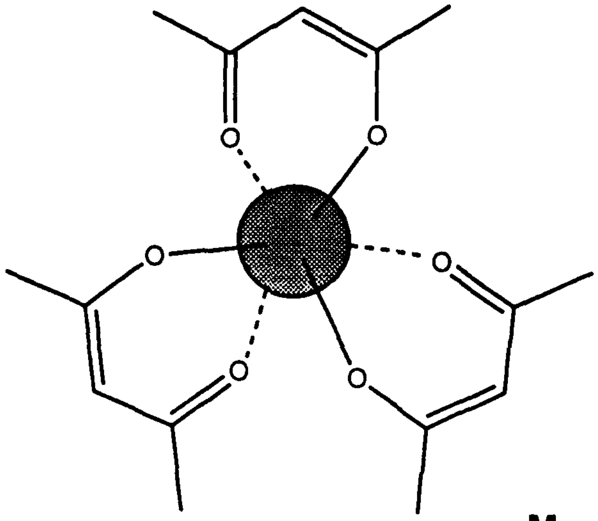
3. Development of Fiber-Optic Amplifiers. An effort was made to realize improved fiber optic amplifiers by achieving high levels of incorporation of rare earth ions into polymer matrices. Spectroscopic results have been independent communicated to the program monitor. In the following we describe preparation of materials.

In an effort to overcome the fundamental problem of low solubility of rare earth ions in waveguide materials (organic and inorganic polymers), we have chosen two approaches. Both are based upon preparing chelating agents which tightly bind rare earth ions. Such agents are then incorporating into processible waveguide materials either noncovalently to form composites or covalently to form homopolymer materials. We have examined a variety of chelating agents based upon metal binding either through oxygen or nitrogen ligands. In the following, we report results for incorporation exploiting acetylacetonate chelation. This material was found to be of interest because it prove possible to achieve both high loading and minimum perturbation of the optical spectrum from that obtained for rare earth ions doped in fiber optic cable (SiO_2 glass). Doping has been explored for a variety of rare earth ions but particularly for Er^{3+} and Pr^{3+}.

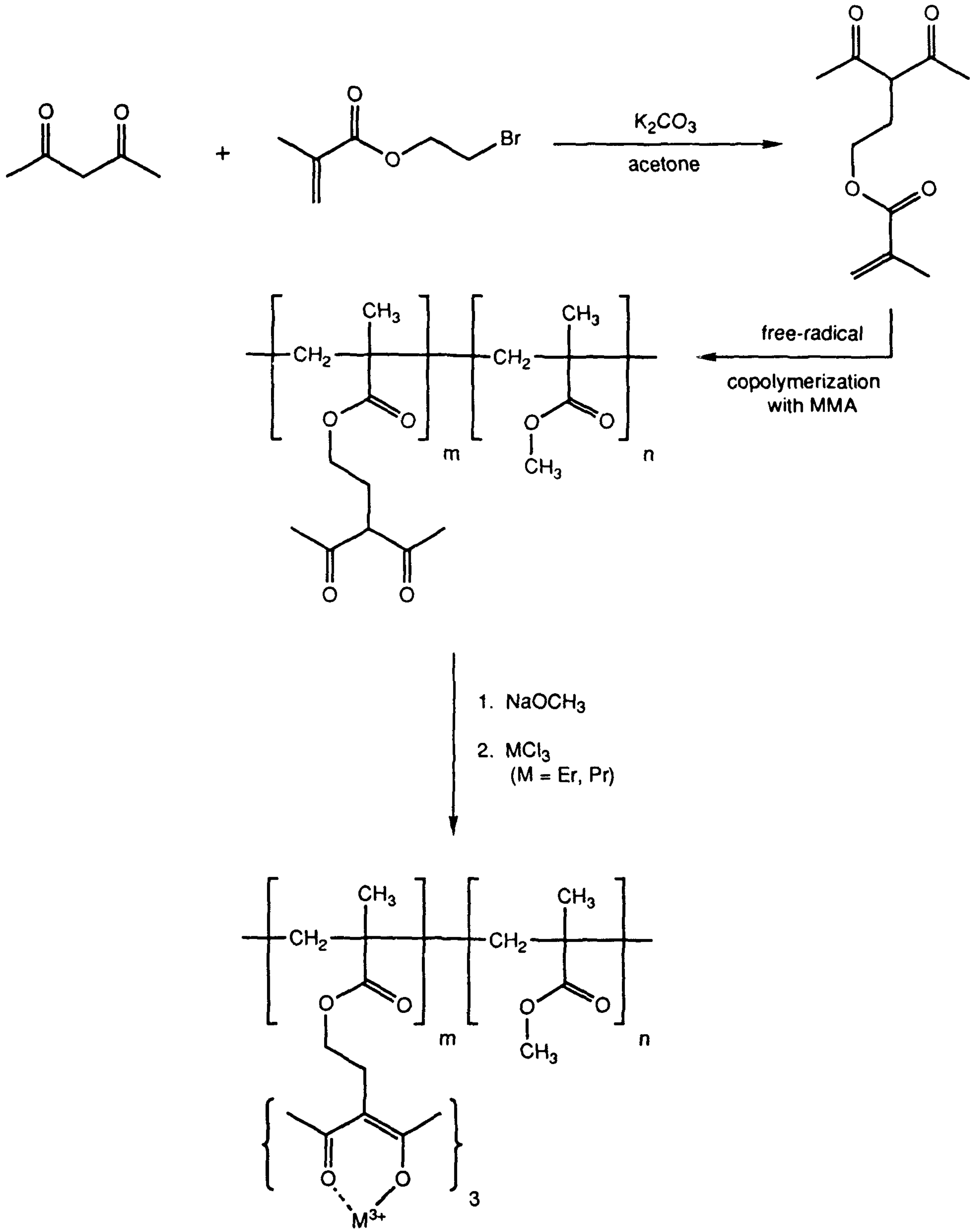
The first figure shows the physical blending of metallated acetylacetonate with the polymer poly(methylmethacrylate), PMMA, to form a guest-host composite which can then be processed into optical quality films (by spin casting) and fibers (by extrusion). Reasonably high levels of incorporation have been obtained without evidence of phase separation or precipitation.

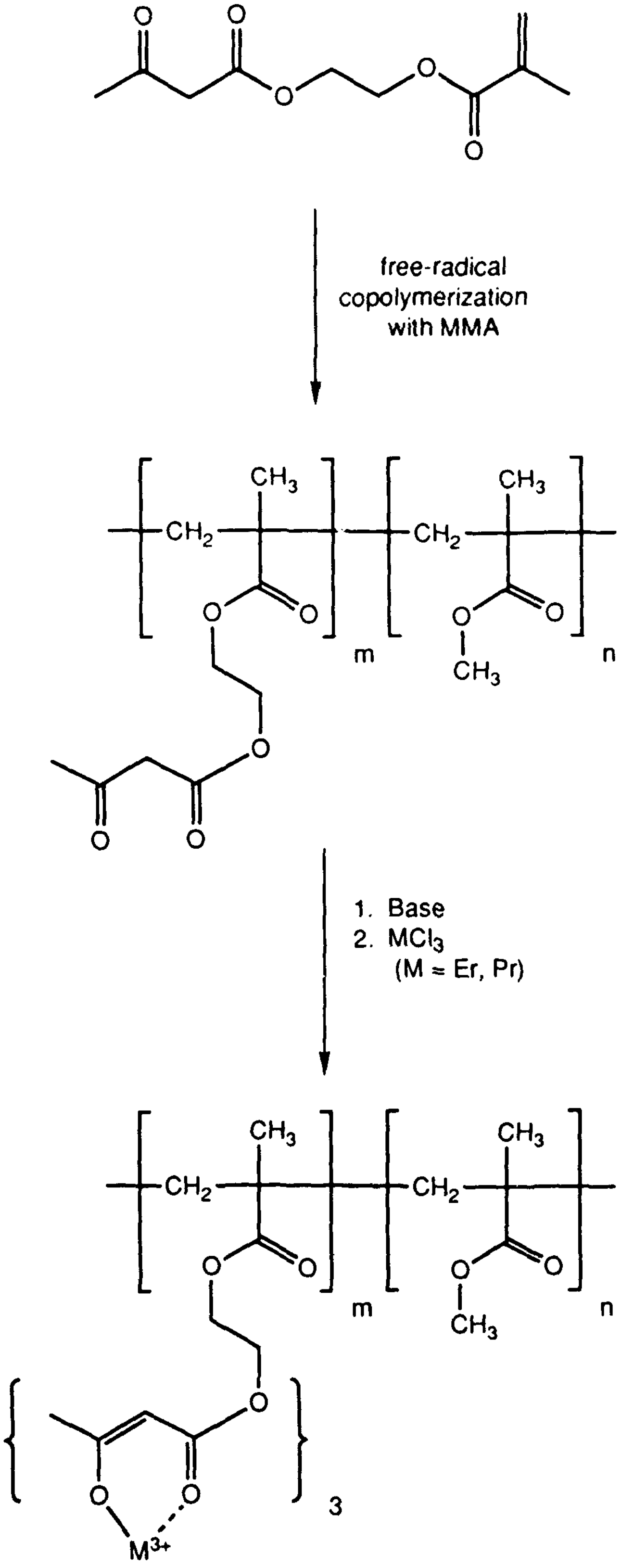
Even higher levels of incorporation can be obtained by covalent incorporation schemes shown in the second and third figures. These schemes circumvent all potential processing and operational problems associated with guest-host composites.



M = Er^{3+}, Pr^{3+}

$M(acac)_3$ + PMMA → guest-host composite


+
Br
K_2CO_3
acetone
free-radical
copolymerization
with MMA
CH_3
CH_2
m
n
1. $NaOCH_3$
2. MCl_3
(M = Er, Pr)
M^{3+}
3


free-radical
copolymerization
with MMA
CH$_3$
CH$_2$
m
n
1. Base
2. MCl$_3$
(M = Er, Pr)
3
M^{3+}

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

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Abstract

The various synthesis and processing steps required to fabricate prototype electro-optic modulators from polymeric materials containing nonlinear optical chromophores are discussed. 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, or by photochemical processing, (5) coupling of buried channel electro-optic modulators to fiber optic transmission lines by new concepts in photochemical processing and silicon V groove pigtailing, (6) deposition of metal drive electrodes and evaluation of resulting prototype modulators. While the main 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 (radar). The relative merits of organic and inorganic materials for electro-optic modulation applications are reviewed. Although consideration of poled polymer devices will primarily occupy our attention, other techniques for ultrastructure synthesis of noncentrosymmetric lattices are reviewed, including molecular self-assembly, sequential synthesis, and laser-assisted poling. An abbreviated overview of frequency doubling (second harmonic generation) applications is also given.

1. Introduction

Rapid developments in the telecommunications field are pressing the need for improved photonic components. 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, optically controlled antenna arrays, for example. 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.

Electro-optic polymers for optical modulation and switching is a research area that not only requires 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 electro-optic 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 radiofrequency (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 electro-optic 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., $LiNbO_3$), have the historical advantage as photonic materials and, to date, have dominated the optical technology.

This article attempts to provide insight into the potential role to be played by organic materials in new optical communication technologies and how these materials will compare to competitive inorganic materials. Particular attention is given to materials processing issues which are critical to the commercial success of organic electro-optic modulators (such as the integration of polymeric modulators into "networks") but which are not normally treated in scientific reviews of organic optical nonlinearity. Such processing activities are important for understanding the competitiveness of organic materials to currently utilized inorganic materials such as lithium niobate.

2. Chromophore Design and Synthesis

Molecular level polarization (induced dipole moment) can be represented by the following series expansion in the applied electric field, E,[1-3]

$$\mathbf{p} = \alpha E + \beta EE + \gamma EEE \qquad (1)$$

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

$$\mathbf{P} = \chi^{(1)}E + \chi^{(2)}EE + \chi^{(3)}EEE \qquad (2)$$

By symmetry, $\chi^{(2)} = 0$ for centrosymmetric lattices. Logically, it is to be expected that quantum mechanical calculations of hyperpolarizabilities would guide the design of nonlinear optical chromophores and indeed this has been the case. There is general agreement in the theoretical chemistry community[4-6] on the basic interactions which need to be included in the Hamiltonian in order to calculate first and second hyperpolarizabilities. Electron Coulomb interactions and correlations have proven to be important. When these interactions are considered in an approximate manner, one approach leads to the Pariser-Parr-Pople Hamiltonian which is the starting point for a number of perturbative theories. The dominant approach has been the "essential states" method which has been reviewed in depth.[4-5] More recently, a different approach based upon "anharmonic oscillators" has been introduced for the calculation of second hyperpolarizabilities.[7,8] The Hamiltonian employed is the same as for the essential states approach but the focus is upon the motion of charge carriers (treated as oscillators) in the presence of applied electric fields. The nonlinear mechanisms are attributed to the relative and center of mass motions of electron-hole pairs, electron-electron correlations, and hole-hole correlations. Saturation of optical nonlinearity with increasing chromophore length (e.g., as in polyene chains) is understood in terms of coherence lengths of the electron-hole system.

Although Zyss and coworkers[9-11] 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

(electron donor)-(π electron connective segment)-(electron acceptor)

Semiempirical quantum mechanical calculations of first hyperpolarizabilities, β, for such dipolar chromophores have proven quite successful in predicting trends in structure/function relationships.[4,5] Marder and Perry,[12-18] in particular, have been successful in using simple (two level) calculations to guide synthetic efforts aimed at optimizing molecular hyperpolarizabilities. Recall that 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

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

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 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 $\mu\beta = 446\text{-}580 \times 10^{-48}$ esu, continues to be a useful reference for assessing the optical nonlinearity of newly synthesized chromphores. 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, e.g., increasing the number of double bonds in the connective segment. In 1991, Marder and coworkers[13] demonstrated that there is an optimal combination of donor and acceptor strengths required to maximize μβ for a given connective segment and beyond that point, increasing the donor-acceptor strengths leads to a diminution of hyperpolarizability. In 1993, Gorman and Marder[14] 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 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 coworkers 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 μβ 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 μβ values an order of magnitude greater than DANS (see Table 1). It is clear that if the chromophores noted in Table 1 could be incorporated in high number density and with a high degree of noncentrosymmetric order into macroscopic lattices then electro-optic coefficients of several hundred picometers per volt could clearly be obtained. Note that electro-optic coefficients on the order of 400 pm/V at 820 nm have been measured for single crystals of the chromophore 4'-dimethylamino-N-methyl-4-stilbazolium tosylate.[19]

A problem encountered in efforts at optimizing optical nonlinearity is the fact that chemical modification to effect improvement in μβ often results in decreasing the optical gap. Since electro-optic modulator applications require a high degree of transparency at the operating wavelength, such reduction in optical gap can limit the application bandwidth of the modulator. This is particularly a problem for operation at diode laser wavelengths, e.g., 820 nm.

Recently, Marks, Ratner and coworkers[20] have pointed out the need to consider modification of chromophores by solvation when calculating hyperpolarizabilities.

It has been realized for some time that large molecular hyperpolarizability is a necessary but not sufficient condition for a chromophore to be considered for development of nonlinear optical devices. One of the most obvious requirements is that the chromophore 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. Short term and long term thermal material requirements are summarized in **Table 2**.

Garito and coworkers[21-23] have pursued the development of chromophores with exceptional thermal stability by considering fused ring systems. Jen et. al.,[24-26] Reinhardt and coworkers,[27] and Wright et. al.[28] have focused upon realizing improved thermal stability of chromophores by exploring the incorporation of heteroaromatic moieties. Wada et. al.[29] discuss achieving thermal stability by synthesizing supramolecular chromophores based on acceptor substituted carbazoles. Twieg and coworkers[30-33] 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 amines to aryl amines. It is interesting to note that the decomposition temperature of azobenzene chromophores with alkyl amine donor groups is determined by decomposition of the alkyl segment and not the azo moiety as widely assumed. It is not clear at this time that replacement of alkyl groups by aryl substituents is accomplished without some reduction in optical nonlinearity.

An obviously important 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)[1,24-26,34-39] and hyper-Rayleigh scattering[40-42] measurements. As both measurement techniques and extensive tabulations of data are reviewed elsewhere, we will not comment further (beyond introducing selected data, e.g., shown in Talble 1).

Of course, for chromophores to be of utility for nonlinear optical applications, they must be assembled into a noncentrosymmetric lattice (e.g., $\chi^{(2)} = 0$ for a centrosymmetric lattice). This assembly process can place an additional number of requirements on chromophore design. Let us now turn our attention to the many aspects of the assembly process. No attempt will be made at a comprehensive historical review but rather an introduction is provided to the various methods which have been pursued in the attempt to realize device quality organic nonlinear optical lattices.

3. Preparation of Noncentrosymmetric Lattices

We can somewhat arbitrarily define three general approaches to achieving noncentrosymmetric lattices of nonlinear optical chromophores; namely, (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. One can, of course, envision combination or hybrid versions of these techniques. All techniques are hindered by the repulsion of closely packed dipolar chromophores; indeed, this aspect is an important argument for considering octupolar chromophores. The precise effects of dipolar repulsion and various ordering forces can be understood within the framework of London theory[43] which we shall briefly review in our discussion of electric field poling.

3.1. Molecular Self-Assembly. Of course, when ordering forces are weak and numerous, such as in the case of Van der Waals interactions, it is not a simple matter to predict the formation of noncentrosymmetric structures. 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.[44] Some progress has been made in this arena by exploiting molecular asymmetry, chirality, hydrogen bonding, dipole reduction, changing counterions in organic or organometallic salts, and making use of noncentrosymmetric rearrangements in centrosymmetric organic crystals.[19,39,44-54] 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 which are unsuitable [illegible] preparation of optical samples.[47] Thus, progress in this area of research still appears [illegible]ted by the inability to obtain large, optical quality organic crystals containing noncentrosymmetric arrangements of chromophores.

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 coworkers[55] 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 coworkers[56-58] 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 coworkers[59] 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, Takshashi, and Kuroda[60] have recently investigated second harmonic generation from p-nitroaniline intercalated into tetramethylammonium saponite film under the influence of an electric field. A factor of 10^5 enhancement in second harmonic generation intensity was observed in the presence of an electric field compared to that observed with no field applied.

Lacroix and coworkers[61] have investigated incorporation of cationic chromophores into optically transparent MPS_3 (M = Mn, Cd) phases. Two nanocomposites of formula $M_{0.86}PS_3$(dimethyl-amino-N-methyl stilbazolium)$_{0.28}$ were synthesized and a nonlinear optical activity 750 times that of urea was recorded for the cadmium intercalate.

Numerous attempts have been made to obtain macroscopic noncentrosymmetric order by incorporating NLO chromophores into ordered phases, e.g., liquid crystalline materials. These efforts extend from the early work of Meredith, VanDusen, and Williams[62] doping DANS into a thermotropic nematic liquid crystalline polymer to the recent work of Wegner and coworkers[63,64] incorporating NLO chromophores into polymers which form two-dimensional layered structures. Swager and coworkers have discussed designing thermodynamically stable polar assemblies based on columnar liquid crystals.[65] Samulski et. al. have considered the influences of local anisotropy of liquid crystalline phases upon the temporal behavior of second order nonlinear optical activity.[66]

The problem with liquid crystalline hosts is that the intermolecular interactions within ordered phases provide alignment of chromophores but not typically into a noncentrosymmetric array. Noncentrosymmetric ordering typically requires the additional application of an electric poling field and relaxation of order occurs when the poling field is removed. In some cases, intermolecular potentials oppose poling forces to a greater extent than encountered in isotropic media. While the use of ordered phases is theoretically attractive, it has not yet been possible to identify molecular configurations which permit the successful reduction to practice of these concepts (at least not to the point of permitting simple fabrication of devices).

3.2. Sequential Synthesis Methods. We arbitrarily divide sequential synthesis methods into the following four categories: (1) traditional Langmuir-Blodgett methods, (2) techniques involving covalent coupling analogous to Merrifield methods, (3) sequential synthesis techniques exploiting ionic interactions, and (4) molecular beam epitaxy (MBE) methods. Of course since sequential synthesis techniques rely upon intermolecular interactions the concepts of molecular self-assembly are important. In some cases, we shall see that the application of external forces is also crucial to the realization of noncentrosymmetric order, e.g., MBE in the presence of an electric (poling) field.

Sequential synthesis methods afford the hypothetical advantage of permitting films of carefully controlled thickness to be prepared. In principle, films with thicknesses on the order of the wavelength of light can be prepared with tolerances on the order of the dimensions of one monolayer. Since the wave vector of a propagating mode in a waveguide is thickness dependent, such thickness control can be important, particularly for the phenomena of phase matching in frequency doubling applications. Because sequential synthesis methods involve hundreds or even thousands of steps, each step must proceed with very high efficiency to avoid the appearance of order-destroying defects.

3.2.1. Langmuir-Blodgett methods. Films from small amphiphilic molecules, fabricated by Langmuir-Blodgett methods, have been extensively investigated.[1,48-54,67-80] An amphiphilic molecule is one with 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. Swalen[73] 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 more stable, higher-quality films, several groups have explored the use of preformed polymers with the LB method.[74,75] Employing such an approach, Penner and coworkers[75] have prepared films containing as many as 262 layers. They have succeeded in fabricating waveguides using these films and have observed low optical loss (about 1 dB/cm) in contrast to previously reported LB film waveguides. While LB films have proven popular in demonstration of frequency doubling (second harmonic generation), we are unaware of electro-optic modulators constructed from such materials.

3.2.2. Sequential Synthesis by Covalent Coupling Reactions. Marks and coworkers[81-88,90,91] 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. In this approach, 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 coworkers[86-88] 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 crosslinking methodology, the poly(vinylalcohol) step is no longer necessary. Reagents have been found which may be useful in lithographic/waveguide fabrication processes involving these films. In very recent work, Marks and coworkers[88] have extended their studies to the investigation of different types of chromophores. We have also pursued evaluation of the sequential synthesis techniques of Marks and coworkers using different chromophores than considered in their original work.[89] Although electro-optic modulators have yet to be fabricated from such materials, we view this approach as promising and certainly deserving of further exploration.

Whitesell and Wang[91] report a series of polymers based on β-amino acids, including poly(β-alanine), poly(cis and trans-2-aminocyclohexanecarboxylic acid) and poly(anthranlic acid) grown on gold, using an aminothiol as the binder to the metal surface.[92] This method of sequential synthesis provides flexibility in introducing polar groups to anthranlic acid to enhance the magnitude of the molecular dipoles. The anthranlic acid group is also useful in controlling the spacing between chromophores.

3.2.3. Sequential Synthesis by Ionic Coupling. Katz and coworker[93-96] have adapted the sequential synthesis procedure developed by Lee et. al.[97,98] 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 of lithium niobate but were substantially less than those of stilbazolium dyes incorporated into LB materials.[93] This observation reflects the relatively weak electron-withdrawing characteristics of the phosphonate group. More recently, Katz and coworkers[94] have investigated the incorporation of high β chromophores analogous to those used in electric field poling experiments. 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 coworkers,[99-104] depends, in its most simple version, 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 coworkers 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 coworkers[105] who also choose codeposited 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. Obviously, the ease of alignment in the gas phase is a potential advantage for chemical-deposition fabrication of second-order materials. Unfortunately, device quality second order organic materials simply have not been realized by MBE methods to this point in time.

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. This method is particularly attractive in that it can be applied quite generally with reasonably predictable results as will be illustrated in the following discussion. Let us first review general concepts relevant to generation of optical nonlinearity by electric field poling.

Fabrication of electro-optic devices relies upon the macroscopic second order susceptibility, $\chi^{(2)}$ which in turn is related to molecular hyperpolarizability, β, by the approximate relationship (for the moment we ignore the tensorial nature of the second order nonlinear optical susceptibility)

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

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. If chromophore loading could be easily optimized to point of approaching a pure chromophore lattice and if ordering efficiencies approaching perfect chromophore ordering could be achieved, it is quite clear that electro-optic coefficients in the range of hundreds of picometers per volt could be achieved with existing chromophores. For such values, the performance of second order materials begins to approach to within an order of magnitude the efficiency of liquid crystal materials in effecting modulation although the switching speed of second order materials is more than a million times faster than the switching speed of liquid crystal materials. If an electro-optic coefficient on the order of a thousand picometers per volt could be obtained, it is clear that major technological applications of second order nonlinear optical materials could be realized. For example, beam steering (spatial light modulation) applications as well as electro-optic modulation applications could be accomplished.

Unfortunately, the electrostatic repulsion between high dipole moment chromophores opposes optimization of both of these parameters. Since $\langle\cos^3\theta\rangle$ is defined by the competition between poling field-molecular dipole attractive interactions and dipole-dipole repulsive interactions, it is not a simple matter to estimate molecular order for a given poling field unless chromophore concentrations are sufficiently low that dipole-dipole interactions are unimportant. The preceding statement can be expressed approximately in a mathematical form as

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

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). London[43] 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 represented as

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

where r is the average distance between chromophore dipoles and I is the ionization potential. Accurate calculations using the above theory are not trivial to carry out when corona poling is employed and accurate calculations require some 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 approximate observation that reduction of $<\cos^3\theta>$ can be significant for chromophore-chromophore average separations of 1 nm or less (the exact values will vary with the magnitude of the applied field). 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.

Let us now turn our attention to consideration of the two general types of poled polymer materials considered for electro-optic modulator applications; namely, (1) chromophore/polymer composites; and (2) chromophores covalently incorporated into polymers either as pendants to the polymer main chain or as components of the polymer backbone.

3.3.1. NLO Chromophore/Polymer (Guest/Host) Composites. The most obviously attractive feature of chromophore/polymer composites is the ease with which such systems are prepared. Frequently, commercially available chromophores and polymers can simply be blended, spin cast into an appropriate thin films, and poled near the glass transition temperature of the composite matrix. As might be expected, the first materials for which electric-field poling was used to induced second order optical nonlinearity were composite materials, specifically, DANS dissolved in a thermotropic nematic liquid crystalline polymer.[62] Two significant problems with composite materials 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 guest in the host matrix. The first of these problems prompted intensive investigation of a number of chromophores in various polymer lattices,[1,21,30,31,39,44,49-54,106-144] e.g., polymethylmethacrylate (PMMA) and polycarbonate lattices[106-108,111]. A number of factors, including dopant (chromophore guest) 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.[30,31,112-115] 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.[112,120-129] 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) Utem (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 Utem require high cure temperatures and many chromophores are not chemically stable at such temperatures. Wu and coworkers[121] have suggested that it is possible to circumvent this problem by using chemical instead of thermal imidization.

However, 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 on the host lattice.

Wada and coworkers[29] report an effort to overcome some of the above mentioned disadvantages by synthesizing nonlinear optical supramolecules based on acceptor substituted carbazoles. Point-like, linear, cyclic, and starburst supramolecular structures have been explored.

The above mentioned limitations of guest/host composites provide motivation for the consideration of covalent incorporation of chromophores into polymer lattices.

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

3.3.2.1. Pendant Incorporation. The 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 (or side chains) to a main chain polymer.[107,145,146] 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 electro-optic 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.[1,39,44,48-54,107,109,115,145-180] As with guest host systems, an absolutely critical property is the thermal stability of the poling-induced order afforded by the final system. Thus, polyimides have proven to be among the most promising systems when additional crosslinking (lattice hardening) is not employed.[173-178] Covalent incorporation of NLO chromophores into polyimides dates from the work of Marks and coworkers.[173] Representative NLO-active polyimides developed at USC are shown in **Fig. 1** and representative thermal stability data are shown in **Fig. 2**.

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 principal axis colinear 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.[63,63,179,181-216] Also, the chromophore may be coupled, by two point attachment, into the polymer backbone such that the chromophore axis is orthogonal to the backbone axis (see **Fig. 3**).

For main-chain NLO polymers, 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, $\mu_{total} = N\mu$ 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 coworkers.[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 putative 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 crosslinking density as discussed in the next section on lattice hardening.

An interesting recent study is that of Robello and coworkers[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 two enhancement. The most significant advantage of the approach of Robello and coworkers 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 coworkers[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 coworkers synthesized a series of diethynyldiphenylsilicon polymers for this purpose 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.

Main-chain polymers in which the dipole moment of the NLO group is perpendicular to the polymer chain have been synthesized.[63,64] Such materials might be expected to be easier to pole. Unfortunately, without employing the lattice hardening procedures discussed in the next section, such polymers do not yield adequate thermal stability. In **Fig. 4**, we show such a polymer currently under development and evaluation at USC.

3.3.2.3. Lattice Hardening for the Stabilization of Poling-Induced Order. Due to the requirement for stability of optical nonlinearity at elevated temperatures (encountered both in processing and in long term operation), 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 solubility 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.

In sections 3.3 and 4, our separation of topics will at times appear to be rather arbitrary. For example, in our discussion of polyimides in sections 3.3.1 and 3.3.2.2,[120-129;173-176] we have already induced the concept of lattice hardening. The imidization reaction results in a significant increase in T_g and in the thermal stability of optical nonlinearity (see Fig. 2). Processing and poling can be executed on the polyamic acid form and then poling-induced noncentrosymmetric order can be locked-in by effecting imidization.

Both thermally and photochemically-induced crosslinking reactions have been used for many decades to harden polymers. As might be expected, these reactions can be adapted to the production of hardened NLO polymers.[44-54,112,115,120-129,173-176,217-261] Moreover, lattice hardening reactions can be carried out for guest/host (composite) materials, for polymers with pendant incorporation of chromophores, and for polymers incorporating the NLO chromophore as a component of the polymer main chain. Indeed, some of the references cited in the preceding section also explore lattice hardening protocols.

In the following discussion, we arbitrarily divide lattice hardening into the following categories: (1) Thermally-induced polymer crosslinking reactions, (2) photochemically-induced polymer crosslinking reactions, (3) sol-gel densification reactions, (4) stepwise processing using asymmetric reactions involving chromophores containing reactive functionalities at both donor and acceptor ends of the chromophore; the processing and hardening reactions can be separated as desired, (5) crosslinking reactions which lead to interpenetrating networks.

Since we have already alluded to lattice hardening by imidization[44,113,120-129,173-178] we will not repeat consideration of this class of hardening reaction although it could logically be treated under the category of thermally or chemically induced hardening reactions.

3.3.2.3.1. Thermally-induced Polymer Crosslinking Reactions.[44,48-54,115,217-234,245-250] 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.;[115] we find it convenient to group NLO epoxy materials according to the following five categories: (1) guest-host (composite) materials where crosslinking 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 crosslinking;[219,220] (3) materials which involve incorporation of the NLO chromophore into the epoxy polymer backbone independent of the crosslinking 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 crosslinking 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 (by Marks and coworkers[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 crosslinking was induced by heating briefly to 80°C before the poling field was applied; this is 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 non-hardened 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 coworkers[219,220] extended these studies to consider class 2 NLO epoxies (see above) 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 coworkers extended their investigation into a systematic study of the effect of crosslinking site on the temporal stability of poling-induced order for polymer-tethered NLO chromophores.[221]

Eich and coworkers[227] prepared class 4 NLO epoxies 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 on the order of 50 pm/V (at 1.06 μm [illegible]) reflects the increased chromophore loading. Good thermal stability to 80°C has been reported for these materials.

Marks and coworkers[221] have recently described another epoxy-NLO chromophore diamine system. 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 coworkers.[221] Solutions of the reagents were spin cast and precured to 100°C for 3 hours prior to corona poling. The final curing and poling were conducted at 130°C for 2 hours. 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 hours.

In addition to epoxy resins, a significant 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 a polyimide derivative.[222] In each of these cases, thermal stability was significantly improved by crosslinking. In **Fig. 5**, we illustrate the synthesis of a crosslinked polyurethane which has frequently been employed in the fabrication of prototype electro-optic modulators (to be discussed shortly). This material contains about 30 wt. % chromophore and is characterized by a d_{33} value of 120 pm/V (at 1.064 μm) and an r_{33} value of 13 pm/V (at 1.3 μm). Representative thermal stability data are shown in **Fig. 6**.

Marks and coworkers[222] have reported the development of 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 7×10^{20} cm^{-3} for the nitroaniline chromophore employed. Only 10-15% decay of the second-harmonic signal was observed over a 24 hour period. Other efforts focused on producing hardened polyimide lattices have already been alluded to and will not be discussed further here.[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. We shall divide our discussion of such materials into two parts. When the reactive functionalities at the two ends are sufficiently different to permit distinct two step processing, we can conveniently view the processing (spin casting and poling) step as distinct from the lattice hardening step. We shall defer the 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 coworkers[229] have investigated norbornenyl-4-carboxylates with 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 crosslinking studies were described.

Recently, we have investigated the tri and tetralinked systems shown in **Fig. 7**. 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. Representative thermal stability data are shown in **Fig. 8.** 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 Crosslinking.[235-248,257] The use of polyfunctional acylates and methacylates for photochemical crosslinking has been investigated by Robello and coworkers.[235] As might be expected, the first materials examined were guest/host systems. 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 (common to the various approaches to guest/host composites), there is, in some cases, the problem of chemical reactivity of the chromophore under the conditions of photochemical crosslinking.

An interesting variation of this approach is the work of Hayashi and coworkers[236] shown in **Fig. 9**. 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 hours at ambient temperatures.

We have also investigated photocrosslinkable acrylate containing NLO polymers[230,234] in our study of asymmetric reactivities; discussion of this system is deferred to the Section 3.3.2.3.4.

The cinnamate functionality is also well-known for its photoreactivity and use in the photoimaging industry. Matsuda and coworkers[237] 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 photocrosslinking step. This loss was subsequently reduced to less than 10% by use of a UV cutoff filter. A d_{33} value of 28 pm/V (at 1.064 μm) was measured for samples which exhibited approximately 70% decay of optical nonlinearity after three months at 25°C. This is a significant improvement over uncrosslinked guest/host systems.

Tripathy and coworkers[238-241] have also explored guest/host composite materials comprised of photoreactive NLO chromophores and the photocrosslinkable 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 weight %, without phase separation, have been reported for this system. The use of b-styrylacrylate groups, in place of cinnamates, permitted crosslinking 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 coworkers[242] have prepared terpolymers containing both the cinnamoyl crosslinking 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 crosslinking was followed by IR spectroscopy and observed to plateau at about 50% conversion. Although some chromophore decomposition was observed, an effective electro-optic coefficient of 7 pm/V (at 1.15 μm) was measured. No long term stability studies were reported.

Photocrosslinkable systems containing either the chromophore or the photoreactive functionality incorporated into the polymer main chain have been investigated. For example, Tripathy and coworkers[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 degrees of the glass transition temperature. Crosslinking was initiated by irradiation for 10 minutes or less at either 254 or 366 nm depending on the pendant crosslinker. d_{33} values in the range 3.2 to 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 to 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 (measured at ambient temperatures) of optical nonlinearities relative to uncrosslinked systems were observed; 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] **Fig. 10** illustrates the type of materials prepared; these were specifically developed to investigate photochemical processing to produced nonlinear optical waveguides and to achieve quasi-phase matched second harmonic generation. The photochemical processing aspect of these materials will be reviewed in sections 5 and 6. These materials suffer from the common defect of photocrosslinkable materials in that it is difficult to effect photocrosslinking without photochemical reaction of the NLO chromophore.

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 cowokers[262] 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 coworkers[263] 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 cowokers[264] 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 weight % which yielded a value of $\chi^{(2)}$ of 0.16 pm/V. 80% of the optical nonlinearity remained after 3 hours at ambient temperatures.

In a similar study, Prasad and coworkers[265] investigated the NLO activity of SiO_2-TiO_2 composite glasses containing up to 15 weight % of the chromophore NPP. Optical nonlinearity was assessed both by second harmonic generation and electro-optic 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 methylnitroaniline (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 SiO_2-TiO_2 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 coworkers[269] 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 coworkers[270] 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 4% decrease in optical nonlinearity was observed at 100°C after 1 hour.

A method of avoiding the problems associated with guest/host systems is that of covalent attachment of the chromophore to the lattice. Jeng and coworkers[271] 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 hours at 100°C.

Kim and coworkers[272] have prepared films containing the chromophores TDP and FPT by 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 coworkers[273] incorporated the chromophore N-[(3-(trimethoxysilyl)propyl]-4'-niroaniline 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 coworkers[274] 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 coworkers[27-] 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 hours 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 **Fig. 11**, we show the materials fabrication scheme used by Zang and coworkers[277] and representative thermal data are given in **Figs. 12 and 13**. The evolution of optical nonlinearity with heating, shown in Fig. 12, 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 Zang and coworkers 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, $<\cos^3\theta>$, 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 thermosetting 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. **Fig. 14** 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 phenomena 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 Figs. 12-14. 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 to opposing further chromophore alignment (see Fig. 14). The thermal stability realized with this sol-gel system is comparable to that of the polyimide/sol-gel interpenetrating networks of Tripathy and coworkers.[275]

Caldwell and coworkers,[276] employing a new chromophore N-methyl-N-[3-(triethoxysilyl)propyl]-4-tricyanovinylaniline, 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 minutes 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-dinitroanilne and observed d_{33} coefficients of 35-37 pm/V 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 **Fig. 15**; several representative examples of this approach are given in Figs. **16-18**. Representative thermal stability obtained by this approach is given in Fig. **19**. The material shown in Fig. 17 is now commercially available (AdTech). 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 coworkers[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 coworkers[279-282] have pioneered lattice stabilization by the synthesis of interpenetrating networks. Among the interpenetrating networks explored are epoxy/phenoxysilicon and polybismaleimide/phenoxylsilicon systems. These IPNs with the hybrid properties of a high glass transition temperature, an extensively crosslinked 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 coworkers realize an electro-optic coefficient of 6.5 pm/V at 1.3 mm and greater than 90% retention of optical nonlinearity even after 150 hours at 100°C. Moreover, a relative low optical loss of 2 dB/cm was observed.

Recently, Wright and coworkers[252] report the preparation of an NLO interpenetrating network based on polystyrene/poly(indole).

An IPN developed at USC is shown in **Fig. 20**. A key issue involved in the use of IPNs to stabilize noncentrosymmetric lattices is the compatibility of the polymers forming the IPN. Incompatibility can lead to phase separation and high optical loss.

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.[44,283] The basic concept of this procedure is illustrated in **Fig. 21**. This combined photochemical/poling processing was also used to effect periodic variations in $\chi^{(2)}$ to accomplish quasi-phased matched second harmonic generation.[44] Because of the restrictions placed upon poling configurations, we chose not to pursue this approach.

Sekkat and coworkers[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 photo-induced process.

Bauer and coworkers[287] also report exploiting photo-induced photochemical processes together with electric field poling to achieve phase matching in the fabrication of Langmuir-Blodgett films.

We shall see in the next section that photochemical reactions can be used to define buried channel waveguides. Spatially selective electric field poling can be used with such photo-induced reactions to optimize matching in transitioning between electro-optic modulator waveguides and fiber optic waveguides.

5. Fabrication of Small Buried Channel Waveguides (Electro-Optic Modulators)

To provide vertical confinement of light, a buried channel waveguide typically 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.

In sections 5 and 6, we shall see that the processing of buried channel waveguides of various dimensions (e.g., 1-3 μm and 5-10 μm) will be critically important for the development of organic electro-optic 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 critically dependent upon the ability to realize precise control of index of refraction variations within a material. We shall see that polymeric materials afford unique opportunities for shaping refractive index profiles necessary for the precise control of light in its travel through organic media; however, it is also well to note that fabrication techniques developed to achieve this control in inorganic glasses, crystalline insulators and semiconductors have been carefully worked out over many years. In comparison, the fabrication of organic polymer waveguide structures is a new field. To provide an organizational framework, we note that polymeric waveguides can be fabricated using a variety of procedures including (1) photochemical processing exploiting photo-induced conformational changes, (2) electron cyclotron resonance (ECR) and reactive ion etching (RIE) using the ions present in an oxygen plasma, (3) spatially-selective poling, and (4) laser ablation techniques including excimer lasers and other forms of UV irradiation. Electron beam ablation can also be employed but will not be considered here.

In selecting a process for waveguide definition and in the selection of cladding materials, one must take into account the entire modulator design and fabrication approach. In particular, for ultra high frequency operation the design of the electrodes determines the millimeter wave properties of the guiding structure (impedance, wave velocity, etc.) and determines the method of coupling the millimeter waves to the structure. These requirements on the electrode structure can place constraints on the optical waveguide design and therefore the entire modulator design should be completed before the approach to waveguide fabrication is determined.

5.1. Photochemical Processing. Such processing effects a change in refractive index of the material by producing a change either in p-electron density or nuclear density as the result of a photochemically-induced conformational change. Well-known photochemical processes include photo-induced trans-to-cis isomerization, ring opening reactions, keto-enol tautomerism, and interconversion between twisted charge transfer states.[44,305-327] Photo-induced polymerization is also used to fabricate waveguides. This can be accomplished either by a change in index between crosslinked and uncrosslinked 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] which will be discussed shortly. Our remaining discussion of photochemical processing will focus upon photo-induced change in index of refraction or birefringence.

We have made extensive use of conformational changes associate 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] In **Fig. 22**, we show birefringent patterned 5 µm wide waveguides and directional couplers as seen through cross polarizers.

One of the advantages of photochemical processing is the use of the upper electrode as a bleaching mask which assures 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 to 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 millitorr O_2 pressure and 45 watts of rf power which gives a polymer etch rate of 1300 Angstrons/min. In general, a slower the etch rate produces smoother and better quality etch walls. This technique was used to fabricate the buried channel nonlinear optical waveguide shown in **Fig. 23**. Single mode operation is assured by control of the waveguide width and control of the depth of the plasma etch. **Fig. 24** shows the calculation of ridge width vs. etch depth for single mode operation for two typical nonlinear optical polymers. This figure demonstrates that single mode waveguides can be fabricated with widths compatible with single mode optical fibers (5-10 μm) and the etch depth are compatible with the degree of control possible with RIE etching. Matching the vertical dimension of the waveguide to the typical fiber dimensions requires a transition waveguide or a focusing lens.

Temperatures reached by the material during RIE can easily be kept below the temperature which depoles the NLO material. In our studies, we have focused upon the materials synthesized according to the schemes shown in Figs. 1, 5, and 16. All of these materials exhibit long term stability to temperatures of 90°C and beyond. In our RIE processing, the substrate temperature does not exceed 60°C and we have not observed any degradation of performance of any of our EO polymers as the result of RIE processing.

There are a number of variations possible in waveguide fabrication by RIE. For example, channels can be etched in the lower cladding and later filled in with the EO polymer.

As an example of the quality of the structures that can be fabricated in a well controlled RIE system, we show in **Fig. 25** a waveguide Y junction etched in a polyurethane EO polymer (Fig. 5). Good quality Y junctions are important for the fabrication of Mach-Zehnder modulators as will be discussed shortly.

Reactive ion etching has the advantage of producing a channel structure that is stable with respect to subsequent UV radiation. Also, this approach is at least conceivably compatible with virtually any polymer synthesis scheme and is not limited by the requirement of a photochemically active moiety. In reality, the sharpness of channel walls obtained by RIE will vary with polymer structure so that this approach may not be suitable for all materials. Note also that the etch rate will vary with the structure of the hardened polymer employed. RIE etched waveguides can be readily observed under a microscope and this facilitates 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 etching 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. The accompanying SEM picture (**Fig. 26**) shows the dramatic improvement in vertical wall definition and smoothness which can be achieved relative to RIE by use of ECR etching. This improved smoothness translates into reduced waveguide optical loss.

5.3. Laser Etching. Eximer laser lithography, developed by Srinavasan,[328-333] utilizes pulsed excimer lasers operating at deep ultraviolet wavelengths (380 nm, 238 nm, 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 insure 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.[44,342,343] 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 assured. However, there is no control over the amount of index change since the material must be poled to the maximum amount to assure 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 Corporation) 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 assure 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. This is less of a problem for the case of electrode poling in the plane of the layers.

5.5. Other Methods. Franke et. al.[346] has described altering the refractive index of polymer films by ion implantation. Hybrid structures has 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 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 final steps of interconnecting the polymer optical devices with the electronics, attaching fiber inputs, and final packaging must be done using fabrication techniques compatible with the polymer and semiconductor devices. It is currently believed that these steps produce the highest temperatures and place the greatest demands on the template stability of the EO polymers. The integration of the well-developed existing semiconductor foundry technology with the high potential of polymer optical devices opens a promising new approach to high speed optoelectronics.

The advantages of this integration can also be seen when one considers the "silicon breadboard" approach to photonic circuits[348] 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, 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. In **Fig. 27** we show a $\Delta\beta$ optical switch and optical and electronic controls. The 2x2 optical switch is the basic building block of switching matrices and optical interconnects.

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 opto-electronics 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. However, we emphasize that all of the answers are not available to make a full comparison to the all-semiconductor approach. It is clear that the integrated polymer/semiconductor approach holds great promise and is certainly one of the top contenders.

We must deal with two issues involve in coupling electro-optic modulator waveguides to fiber optic transmission lines. The first is the mode matching problem while the second involves realizing mechanically stable connection. To achieve mode matching, we propose, among other alternatives, a novel photochemical processing strategy. To achieve mechanically stable coupling we pursue silicon V-groove technology.

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 radiation into the sample will depend upon radiation wavelength.[314,315,325-327,351-355] Explictly, 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]

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

$$-\partial C_{cis}(x,t)/\partial t = \partial C_{trans}(x,t)/\partial t = -\alpha C_{trans}(x,t)I(x,t) \quad (8)$$

where I(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 and very good description of the photochemical properties of the polymers of ref. 245. Representative data (see Fig. **28**) for light transmission and refractive index change as a function of depth into the film are gvien for polymer # 2 of reference 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 (**Fig. 29**), one finds (1) the lower cladding layer, (2) the unbleached, high 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 to 3 micron) waveguide of a high efficiency electro-optic 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 microns. However, large waveguide dimensions pose problems for single mode operation. Let us briefly review the criteria for single mode guiding.

For single mode operation, local gradients, if large, must be sufficiently *small in size* (0.5-1.5 mm 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 mm 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 1980's 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 large 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 multi-color 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 **Fig. 30**, we show a schematic representation of a switching node whose fabrication can be accomplished by a combination of multi-color photochemical processing and reactive ion 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 micro-patterning, 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 **Fig. 31**, we show one of our results for creating a V groove etched in silicon dioxide coated silicon substrates.

6.3. Integration with Electronics. Polymer electro-optic devices and optical waveguides have been fabricated on semiconductor substrates but 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 and reports of traveling wave intensity modulators at both 20 and 40 GHz which have been successfully fabricated and patterned on Si substrates.[361-372]

7. Simple Electro-Optic Modulator Device Concepts

An example of an application of electro-optic modulators is the interconnection of several computers, to share a large computational task or to share information, using wide bandwidth optical links. The key elements to achieve this interconnection network are opto-electronic circuits for transferring the data from the electronics of the computer to the optical links and back to the computer again. Similarly, the future of a very wide bandwidth, high capacity global communication network appears almost certainly to lie with optical communications. The key devices are again the opto-electronic ciricuits to add or remove information packets from the net and to route the information packets through the net to their proper address.

The basic operations of the opto-electronic circuits in these applications are to either modulate the electronic data onto an optical carrier and to later detect the modulation, or alternately, in the case of interconnection networks, to detect address headers or other electronic controls to switch packets on their correct path through the network. In the following paragraphs we will introduce two types of modulators and one routing switch (directional coupler). However, it is useful to first introduce some fundamental concepts.

The electro-optic (Pockel) effect results in a relative phase shift, $\Delta\phi$, of a optical beam passing through an EO material when an electric field is applied.

$$\Delta\phi = \pi n^3 r_{eff} VL/\lambda h \qquad (9)$$

where n is the index of refraction, r_{eff} is the effective electro-optic coefficient, V is the voltage of the applied modulation (electrical) signal, L is the modulation length, h is the gap distance between electrodes, and λ is the optical wavelength. The magnitude of the effective EO coefficient depends on the device geometry, the poling direction (if electric field poling is used to establish noncentrosymmetric order), the optical wave polarization, and the modulation scheme employed. The half-wave voltage-modulation length product is defined as

$$V_\pi L = \lambda h/n^3 r_{eff} \tag{10}$$

The $V_\pi L$ product is a measure of the modulation efficiency of the device. The lower the product, the higher the modulation efficiency.

A modulation of the intensity of the optical beam can be obtained either from interferometric effects or modal coupling changes due to phase modulation. Among various device architectures, integrated Mach-Zehnder interferometers, waveguide birefringent modulators and directional couplers are the most popular for high speed, broad bandwidth applications. As briefly analyzed in the following section, the modulation efficiency and the harmonic distortion are different from one to another.

7.1. Integrated Mach-Zehnder interferometer. An integrated Mach-Zehnder interferometer (see **Fig. 32a**) consists of two straight arms as modulation areas and two Y-branches (one splits the optical beam into two and the other combines the modulated beams together). The modulation electric field is applied to one arm or both arms to modulate the index of the waveguide and thus modulate the phase of the optical beam or beams. When the two beams combine coherently at the output (second Y branch), the interference of the two beams modulates the output intensity as (assuming no loss)

$$I_o = I_i \sin^2[(\phi_{ba} + \Delta\phi)/2] \tag{11}$$

where I_i and I_o are the input and output intensities, ϕ_{ba} is the phase difference between the two arms, and $\Delta\phi$ is the phase modulation produced by the EO effect. $\Delta\phi$ is zero when the modulation (electric) field is not applied. The required phase change for 100% modulation (to switch light "on" and "off") is a modulation field that produces $\Delta\phi = \pi$, which results in

$$(V_\pi L)_{MZ} = \lambda h/n^3 r_{33} \tag{12}$$

In analog signal applications, a DC bias voltage is applied to one arm to adjust ϕ_{ba}, and the modulation voltage is applied to the other arm. At proper DC bias voltage with $\phi_{ba} = \pi/2$ (the quadrature point) and when the modulation signal is small (not exceeding V_π), the output optical signal is linearly proportional to the input electric signal with small third-order and higher odd-order harmonic distortion terms.

$$I_o = I_i [1 - \Delta\phi + (\Delta\phi)^3/6 - (\Delta\phi)^5/120 + \ldots] \tag{13}$$

The modulation signal is a voltage signal and since the $\Delta\phi$ is proportional to V, the higher order terms in $\Delta\phi$ result in signal distortion. A linearization scheme is required which is essentially the correction of the third order term. From the above equation, we need either subtract a third order term from the output intensity or add a similar term in the modulation electric signals to cancel this distortion.

IN constructing the Y branches of a MZ interferometer, care must be exercised in avoiding optical loss by keeping the bend angles small.

7.2. Integrated birefringent EO modulator. The integrated birefringent EO modulator is an extension of the longitudinal bulk EO modulator to guided optical beams. The modulator (see **Fig. 32b**) consists of a single mode nonlinear optical (NLO) polymer waveguide and an analyzer. When the modulation field is applied to the waveguide in the poling direction, the refractive index of the waveguide will experience different changes along different directions and therefore the birefringence of the waveguide is modulated by the electric field.

$$\Delta n(TE) = n^3 r_{13} V/2h \qquad \Delta n(TM) = n^3 r_{33} V/2h$$

$$\Delta\phi(TE/TM)_{sp} = 2\pi \Delta n L/\lambda = \pi V L(n^3 r_{13} - n^3 r_{33})/\lambda h \qquad (14)$$

In order to obtain intensity modulation, the input beam is 45 degree polarized to excite both TE and TM modes. An analyzer converts the polarization modulation into an intensity modulation signal. The output intensity of a lossless birefringent EO modulator is given by

$$I_o = I_i \sin^2[(\phi_{sp} + \Delta\phi_{sp})/2] \qquad (15)$$

where ϕ_{sp} is the built-in phase delay between TE and TM modes, and $\Delta\phi_{sp}$ is the modulated phase delay. The $V_\pi L$ product is (assuming $r_{33} \approx 3\, r_{13}$)

$$(V_\pi L)_{BR} = 1.5\lambda h/n^3 r_{33} = 1.5(V_\pi L)_{MZ} \qquad (16)$$

Compared with the Mach-Zehnder modulator, the modulation efficiency of the birefringent modulator is lower since $V_\pi L$ is 1.5 times higher in the BR modulator. A birefringent modulator can be biased at its quadrature point by an external compensator. At this point and when the modulation signal is small, the harmonic distortion is the same as for a Mach-Zehnder device.

7.3 EO directional couplers. Directional couplers (see **Fig. 32c**) consist of two side-by-side waveguides separated by only a few microns. The overlap of the guided waves in the two waveguides couples energy back and forth between the waveguides. When the rf (electrical) voltage is applied, the modulation is obtained by modulating either the phase difference or the coupling coefficient. A directional coupler is a four-terminal device which allows two inputs and two outputs. The information of the optical beams can be exchanged between the two waveguides. When only one input terminal is used, the output intensities of the waveguides are[303,304]

$$I_1(L) = I_o \{\kappa^2/[\kappa^2 + (\Delta\beta/2)^2]\} \sin^2\{L\sqrt{[\kappa^2 + (\Delta\beta/2)^2]}\} \qquad (17a)$$

$$I_2(L) = I_o \{1 - \kappa^2/[\kappa^2 + (\Delta\beta/2)^2]\} \sin^2\{L\sqrt{[\kappa^2 + (\Delta\beta/2)^2]}\} \qquad (17b)$$

where κ is the coupling coefficient, $\Delta\beta$ is the phase mismatch between the two waveguides, and L is the coupling length. From the above equation, the complete power crossover occurs when $\Delta\beta = 0$ and $\kappa = (\pi/2) + m\pi$, where m = 0, 1, 2, ... To turn the coupling "off" by the applied electrical field, one requires

$$\Delta\beta L = (4m + 3)^{1/2}\pi \qquad (18)$$

or

$$V_\pi L_c = (4m + 3)^{1/2}\lambda h/n^3 r_{33} \qquad (19)$$

The smallest voltage required for switching occurs when m = 0, which is 1.7 times larger than that of a Mach-Zehnder device. However, to achieve high bandwidth, an additional voltage penalty must be paid when driving a directional coupler in the vertical geometry. For high frequency operation, microstrip drive electrodes are required. Because of the proximity of the two electrodes in this switch configuration, the fringe fields from the microstrip extend beyond the upper waveguide. The upper waveguide is thus partially driven with the same polarity as the lower waveguide. Hence, an even larger voltage must be applied to effect switching. Obviously, the response of a directional coupler has all orders of harmonic distortion terms. Linearization schemes must correct both second and third order harmonic terms.

An important area of activity which deserves more attention is that of improved device design. This aspect is illustrated by a recent paper by Garito and coworkers which presents an improved design for a directional coupler.[21]

In **Table 3**, we summarize the features of different electro-optic modulators.

8. Fabrication and Evaluation of a Prototype Birefringence Modulator

As most modulators have been fabricated in a Mach-Zehnder configuration, let us, in this discussion, illustrate the birefringence modulator which can be used either as a phase or a birefringence 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. The analyzer shown in Fig. 32b converts the polarization modulation into an amplitude modulation. Representative modulation signals are shown in **Figs. 33 and 34**. These signals were detected using an InGaAs p-i-n photodetector (Fermionics FD80S) and monitored by a Hewlett-Packard HP8652A spectrum analyzer. Although these signals were obtained using thick cladding layers (total device thickness approximately 15 microns) and the modulator uses only 2/3 of the available r_{33} nonlinearity, a half-wave V_π voltage of 35 volts was obtained using a 15 mm electrode (this corresponds to an electro-optic coefficient of 12 pm/V which was expected for the azobenzene incorporated polymer used). This birefringence modulator has been operated to frequencies as high as 40 GHz and has been operating for well over one year with no apparent degradation in performance. The expected upper limit on modulation frequency (greater than 40 GHz) is set by modulator design and not by limitations of the polymer EO material.

For the sake of completeness, it is appropriate to review the fabrication of the modulator used to obtain the data shown in Figs. 33 and 34. The nonlinear optical material is an azobenzene containing polyurethane processed according to the procedure shown in Fig. 5. Fused quartz slides (ESCO products, Inc.) were used as substrate materials. A layer of gold (approximately 0.5 micron thick) was sputtered using an argon plasma sputtering system. The lower and upper polymer claddings were cast from commercial polyurethane (Epoxylite 9653-1). Note that a critical component of electro-optic modulators is the cladding material. it must have a lower index than the core EO material and must not have a substantially higher resistivity than the core material. A higher resistivity makes it difficult to pole the core material. The lower cladding was first spin-cast on the gold coated substrate and was baked at 90°C for several hours. The NLO material was dissolved in dioxane and was spin cast into approximately one micron films using a spin speed of approximately 1000 rpm. The film was then heated and poled using a corona discharge set-up with needle to plane distance of approximately 2 cm. A 5.5 KV voltage was applied. The temperature was raised to approximately 160°C and the hardening reaction initiated. The NLO waveguide was then defined by RIE as discussed above. The top cladding layer was spun on top of the etched surface and was cured at room temperature. The upper electrode with dimensions of 15 mm length and 30 microns width was defined photolithographically and was plated to 5 micron thickness to reduce DC resistance.

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 volts (depending on the chromophore used, cladding layer thickness, processing conditions, electrode design, etc.).[361-372] Performance at wavelengths from 0.83 to 1.3 microns has been evaluated. Commercial application will require further improvement in V_π, namely, reduction of required drive voltages to digital voltage levels. A critical area of focus for the realistic achievement of modulation at frequencies above 50 GHz is electrode design as losses at electrodes appear to be the limiting factor in the frequency range 50-100 GHz.

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 to 2 dB/cm while bulk losses for materials have typically been in the range 0.1 to 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 decribed 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 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]

9. Alternative Device Applications

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

9.1 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 **Fig. 35**) would be comprised completely of low dielectric components, metallic antennas are traditionally attached to the electro-optic modulator of a photonic system to enhance field gain. Hilliard and coworkers[373,374] have proposed employing a low dielectric (polystyrene polymer) Luneburg lens to achieve the necessary gain; thus, they propose a completely low-dielectric electromagnetic field sensor (see **Figs. 36 and 37**).

Photonic electromagnetic field sensors consist of a laser source providing an optical signal which is sent through an electro-optic modulator and then to a photodetector/amplifier via optical fiber transmission lines. As already discussed, the information content (frequency, amplitude, phase) of the radiofrequency field passing through an EO modulator can be transferred by the Pockel effect to light passing through the modulator. The modulated optical signal is converted to an electrical signal by the photodetector and is amplified to produce an RF output directly proportional to the measured field. Usually some form of amplification is required to increase the rf field strength to a sufficient level to permit reasonable modulation efficiency; here we will focus upon amplification employing a low dielectric Luneburg lens. A Luneburg lens is a spherically-shaped, broadband dielectric device that focuses an incident planar electromagnetic wave entering one side of the lens onto a spot on the opposite side of the lens. The dielectric constant of the Luneburg lens varies quadratically with the radius from a maximum value of 2 at the center of the lens to a minimum value of 1 at the lens surface. according to $\varepsilon_r = 2 - (r/a)^2$ where ε_r is the relative dielectric constant of the lens, r is the radial location within the lens, and a is the radius of the lens. In practice, the Luneburg lens is often implemented in concentric shells of polystyrene, each shell comprising a continuous dielectric constant.

Electro-optic 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 amount of field energy passing from the Luneburg lens to the modulator can be quantified by the reflection coefficient of the materials comprising the lens and modulator. The reflection coefficient for fields in dielectric media passing from medium 1 into medium 2 (at a planar interface, each with a relative dielectric constant of ε_{r1} and ε_{r2}) is

$$\rho = [(\varepsilon_{r1})^{1/2} - (\varepsilon_{r2})^{1/2}]/[(\varepsilon_{r1})^{1/2} + (\varepsilon_{r2})^{1/2}] \qquad (20)$$

Although the lens/modulator interface is not a planar surface, the above equation is a good approximation at microwave and millimeter wave frequencies. 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, $|\rho|^2$, is about 50%. Organic polymers have the lowest dielectric constant (approximately 3 to 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.

9.2. Electro-Optic Modulators as Voltage Sensors. Recently, Grune and coworkers[375] have described the application of polymeric modulators as voltage sensors. While this application greatly relaxes the requirement on electro-optic coefficient (0.01 to 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. They also note that cost will be an important consideration since a considerable amount of material will be used in each sensor. Modulators must also be able to withstand corrosive chemical environments and lightning voltage surges.

9.3. 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 electro-optic 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.[44,376] 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, $n_{2\omega}$, indices. 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 us[44] 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 with be given to phase matching by the method of counter-propagating 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.[44] Such periodic variation in $\chi^{(2)}$ has been accomplished by a number of procedures. For example, Gunter and coworkers[380] 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 coworker[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 coworkers.*[44,282,385,386] A periodic poling could also be accomplished, although somewhat laboriously, by using RIE to create periodic channels in a poled and hardened polymer, these channel 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 coworkers[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 counter propagating beams. For the case of degenerate frequencies, the second harmonic beam is radiated orthogonal to the waveguide. For the counter-propagating 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. Miayatta and coworkers[387] 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 coworkers[388] 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.

10. Concluding Remarks

In **Table 4**, we summarize the comparison of organic and inorganic materials in terms of bandwidth and modulation efficiency. A superficial evaluation of this table would suggest that organic materials are clearly the materials of choice for development of electro-optic modulators. However, it must be kept in mind that commercial organic modulators have yet to be developed and no "in field" evaluations are available. Indeed, although promising starts have been made in the many disciplines involved in fabricating organic modulators and integrating these modulators into networks, much more work is required. Moreover, progress is required in all aspects that we have reviewed in the preceding paragraphs. High $\mu\beta$ chromophores have yet to be incorporated into hardened (high T_g) polymer matrices to an extent that materials are available for subsequent steps of device fabrication. Although impressive starts at processing waveguide structures in organic materials have been made, much remains to be learned and scalable processing procedures have not yet been developed. Development of modulators operating above 40 GHz is essentially a virgin field which will require serious consideration of electrode design and fabrication before significant success can be realized even in the demonstration of prototype devices. Nevertheless, it is not unreasonable to anticipate that during the next two to five years modulators operating to 100 GHz will be realized and significant system integration of components such as directional coupler switches will be achieved. The next two years should witness the realization of modulators characterized by electro-optic coefficients in the range of 30-60 pm/v and long term thermal stability to temperatures on the order of 150°C or greater. However, it is likely that the degree of commercial utilization of organic nonlinear optical materials in the near future will be determined more by economic factors than by technological considerations.

The synthetic and processing methods of materials chemistry suggest solutions to all of the problems facing the commercial development of electro-optic modulators. From another perspective, the potential application of organic polymeric materials to the fabrication of electro-optic modulators has stimulated considerable research into topics such as ultrastructure synthesis and photochemical processing. Indeed, a number of systematic investigations of lattice dynamics have evolved from efforts to realize thermally stable second order, nonlinear optical lattices. This aspect of NLO research has been recently reviewed by Burland and coworkers.[115] Corn and Higgins[389] have reviewed the use of second harmonic generation as a probe of surface chemistry. Electro-optic modulation studies, conducted as a function of frequency, provide direct insight into lattice dynamics and piezoelectric effects. Studies of electro-optic modulation in the frequency range 50-100 GHz should stimulate the characterization of dielectric properties of polymeric materials in this frequency regime. Such data should prove useful not only for the development of electro-optic modulators, but also electron paramagnetic resonance spectrometers operating in this region. Instrumentation used in the characterization of optical nonlinearity has recently become commercially available (Sopra Inc.)[390] which is a likely consequence of research efforts motivated by the desire to realize second order nonlinear optical devices based upon organic materials. Clearly, a very synergistic relationship has developed between organic materials research and device fabrication efforts.

A synergistic relationship also exists between research focused upon π-electron nonlinear optical materials and π-electron materials being developed for applications involving electrical conductivity and superconductivity, photoconductivity, photorefractivity, light emitting diodes, optical memories, etc. The relationships that exist between studies of various physical phenomena are often evident in the proceedings of conferences dealing with solid state organic materials.[391]

In the preceding paragraphs, we have not attempted to provide a comprehensive review of the many topics discussed but rather we have attempted to provide an introduction to key concepts and to provide some insight into the status of various research endeavors. For more detailed information, the reader is referred to the proceedings of various conferences (SPIE, MRS, EMRS, ACS, OSA, IEEE, OMNO, NATO, Frontiers in Polymer Research, etc.) which provide in depth information. Our discussion has been clearly biased toward the presentation of our own work since it is this work to which we have the greatest access and can provide the most current review. For a more balanced overview, the reader is strongly encouraged to consult the literature cited.

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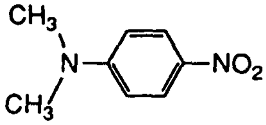
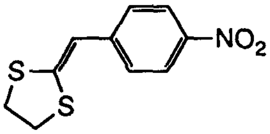
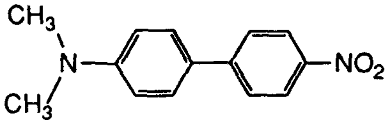
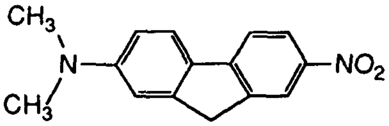
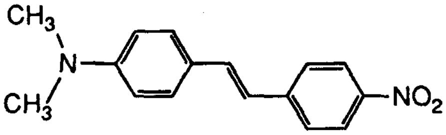
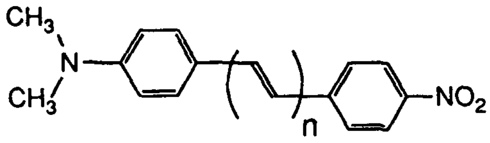
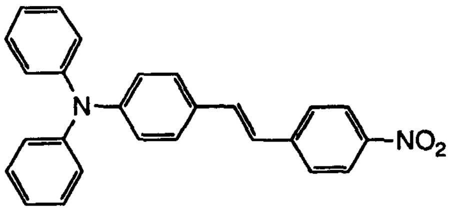
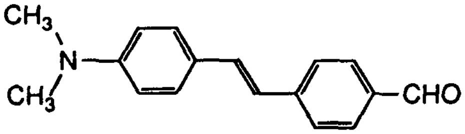
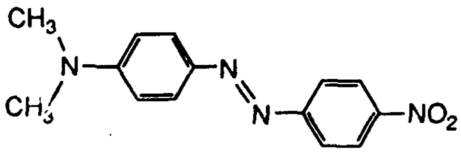
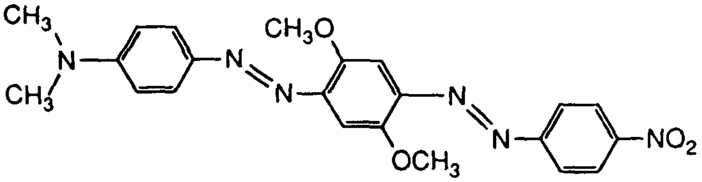
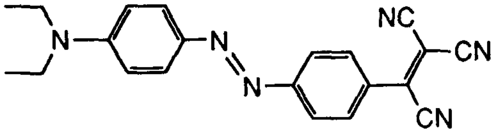
Table 1. Representative NLO chromophores and their corresponding $\mu\beta$ values

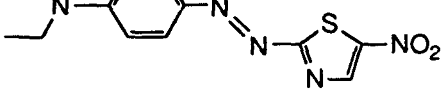
Chromophore		Nonlinearity	Reference
		$\mu\beta = 140 \times 10^{-48}$ esu (1.3 μm)	a
		$\mu\beta = 358 \times 10^{-48}$ esu (1.3 μm)	a
		$\mu\beta = 275 \times 10^{-48}$ esu (1.907 μm)	b
		$\mu\beta = 330 \times 10^{-48}$ esu (1.907 μm)	b
		$\mu\beta = 580 \times 10^{-48}$ esu (1.907 μm)	c
	n = 1	$\mu\beta = 482 \times 10^{-48}$ esu (1.907 μm)	d
	n = 2	$\mu\beta = 813 \times 10^{-48}$ esu (1.907 μm)	d
	n = 3	$\mu\beta = 1074 \times 10^{-48}$ esu (1.907 μm)	d
	n = 4	$\mu\beta = 1700 \times 10^{-48}$ esu (1.907 μm)	d
		$\mu\beta = 788 \times 10^{-48}$ esu (1.907 μm)	e
		$\mu\beta = 84 \times 10^{-48}$ esu (1.907 μm)	d
		$\mu\beta = 800 \times 10^{-48}$ esu (1.58 μm)	f



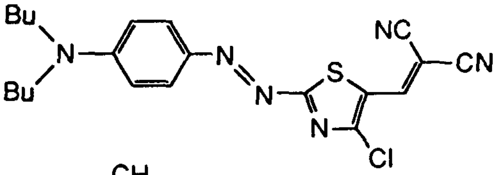
$\mu\beta = 1040 \times 10^{-48}$ esu (1.064 μm) g



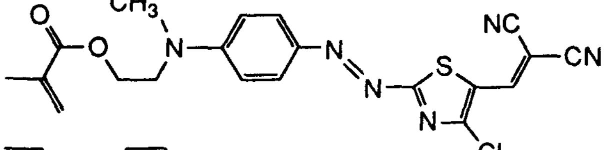
$\mu\beta = 4100 \times 10^{-48}$ esu (1.58 μm) f



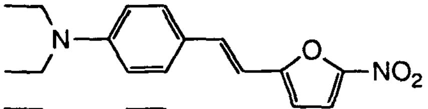
$\mu\beta = 2190 \times 10^{-48}$ esu (1.58 μm) f



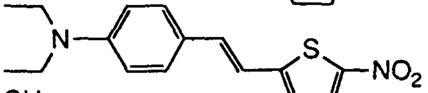
$\mu\beta = 5320 \times 10^{-48}$ esu (1.58 μm) f



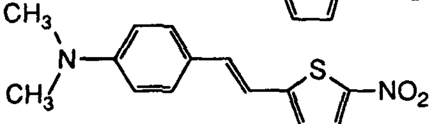
$\mu\beta = 1658 \times 10^{-48}$ esu (1.907 μm) h



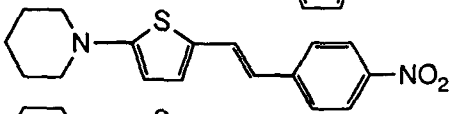
$\mu\beta = 560 \times 10^{-48}$ esu (1.907 μm) i



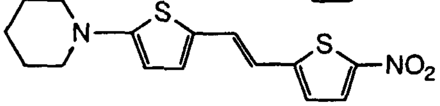
$\mu\beta = 700 \times 10^{-48}$ esu (1.907 μm) i



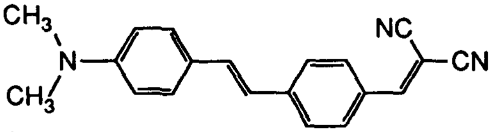
$\mu\beta = 600 \times 10^{-48}$ esu (1.907 μm) c



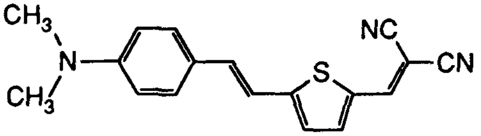
$\mu\beta = 660 \times 10^{-48}$ esu (1.907 μm) c



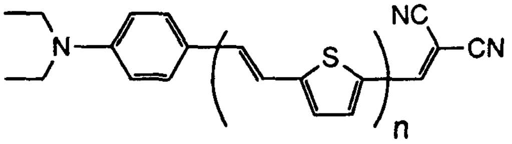
$\mu\beta = 1040 \times 10^{-48}$ esu (1.907 μm) c



$\mu\beta = 1100 \times 10^{-48}$ esu (1.907 μm) c

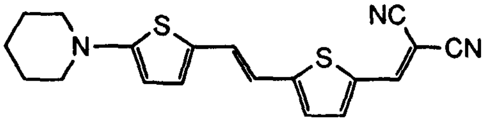


$\mu\beta = 1300 \times 10^{-48}$ esu (1.907 μm) c

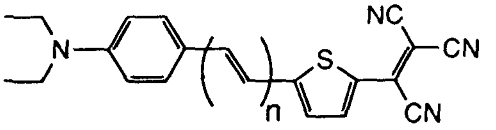


n = 2 $\mu\beta = 2300 \times 10^{-48}$ esu (1.907 μm) j

n = 3 $\mu\beta = 3800 \times 10^{-48}$ esu (1.907 μm) j

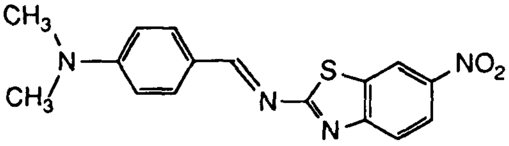


$\mu\beta = 2600 \times 10^{-48}$ esu (1.907 μm) c

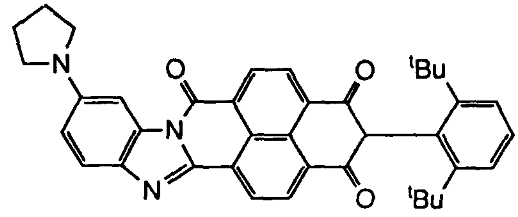


n = 1 $\mu\beta = 6200 \times 10^{-48}$ esu (1.907 μm) k

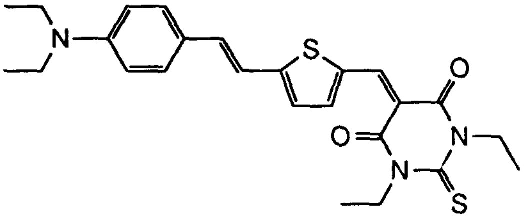
n = 2 $\mu\beta = 9100 \times 10^{-48}$ esu (1.907 μm) k



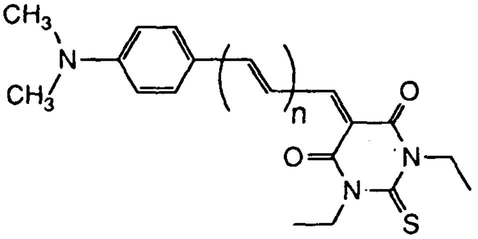
$\mu\beta = 640 \times 10^{-48}$ esu (1.064 μm) g



$\mu\beta = 1500 \times 10^{-48}$ esu (1.907 μm) l



$\mu\beta = 2400 \times 10^{-48}$ esu (1.907 μm) k

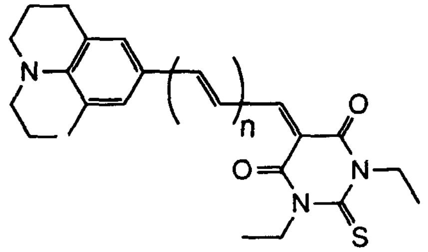


n = 0 $\mu\beta = 370 \times 10^{-48}$ esu (1.907 μm) d

n = 1 $\mu\beta = 1457 \times 10^{-48}$ esu (1.907 μm) d

n = 2 $\mu\beta = 3945 \times 10^{-48}$ esu (1.907 μm) d

n = 3 $\mu\beta = 9831 \times 10^{-48}$ esu (1.907 μm) d

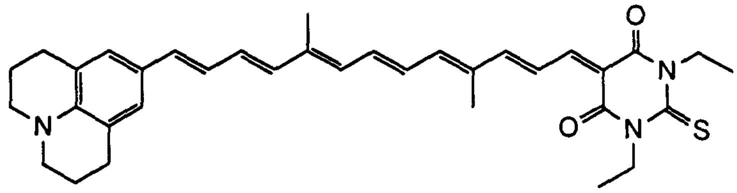


n = 0 $\mu\beta = 609 \times 10^{-48}$ esu (1.907 μm) d

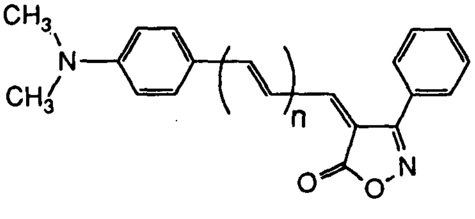
n = 1 $\mu\beta = 2210 \times 10^{-48}$ esu (1.907 μm) d

n = 2 $\mu\beta = 7152 \times 10^{-48}$ esu (1.907 μm) d

n = 3 $\mu\beta = 19086 \times 10^{-48}$ esu (1.907 μm) d



$\mu\beta = 34770 \times 10^{-48}$ esu (1.907 μm) d

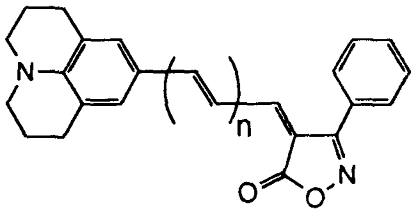


n = 0 $\mu\beta = 312 \times 10^{-48}$ esu (1.907 μm) d

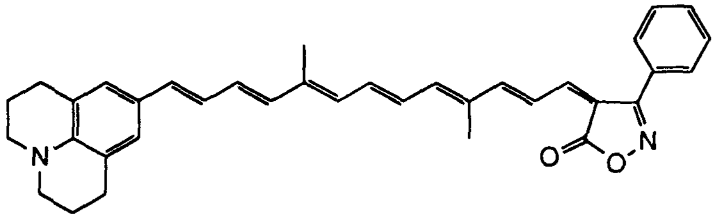
n = 1 $\mu\beta = 1202 \times 10^{-48}$ esu (1.907 μm) d

n = 2 $\mu\beta = 3156 \times 10^{-48}$ esu (1.907 μm) d

n = 3 $\mu\beta = 8171 \times 10^{-48}$ esu (1.907 μm) d



n = 0	$\mu\beta$ = 488 x 10^{-48} esu (1.907 μm)	d
n = 1	$\mu\beta$ = 1638 x 10^{-48} esu (1.907 μm)	d
n = 2	$\mu\beta$ = 5812 x 10^{-48} esu (1.907 μm)	d
n = 3	$\mu\beta$ = 9750 x 10^{-48} esu (1.907 μm)	d



$\mu\beta$ = 28500 x 10^{-48} esu (1.907 μm) d

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a Katz, H.E., *et al., J. Am. Chem. Soc.* **109**, 6561(1987)

b Cheng, L.-T., *et al., J. Phys. Chem.* **95**, 10643(1991)

c Rao, V.P., *et al.*, in *Nonlinear Optical Properties of Organic Materials V*; Williams, D.J., Ed.; Proc. SPIE, 1992; Vol 1775, p. 32

d Marder, S.R., *et al., Science* **263**, 511(1994)

e Tweig, R.J., *et al., Mat. Res. Soc. Symp. Proc.* **328**, 421(1994)

f Dirk, C.W., *et al., Chem. Mater.* **2**, 700(1990)

g Xu, C., Ph.D. Thesis, University of Southern California, Los Angeles, 1993

h Ra, Y.S., personal communication

i Cheng, L.-T., *et al., J. Phys. Chem.* **95**, 10643(1991)

j Jen, A.K.-Y., *et al., J. Chem. Soc. Chem. Commun.* .90(1993)

k Jen, A.K., *et al., Mat. Res. Soc. Symp. Proc.* **328**, 413(1994)

l Yamada, S., *et al., Mat. Res. Soc. Symp. Proc.* **328**, 523(1994)

Table 2. Temperature requirements for opto-electronic integration

Operation (Long Term)	-40 to 125°C (Military Specification) 20 to 100°C (Commercial)
Processing & Packaging (Short Term, 1-10 minutes)	
Wire Bonding	100 to 150°C
Solder Bonding	150 to 200°C
Hermetic Packaging	150 to 250°C

Table 3. Comparison of key features of E-O modulators

	Mach-Zehnder interferometer	Birefringent modulator	Directional coupler
r_{eff}	r_{33} or r_{13}	$r_{33}-r_{13}$	r_{33} or r_{13}
$V\pi$	low $V_{\pi MZ}$	medium $1.5 \times V_{\pi MZ}$	high $1.73 \times V_{\pi MZ}$
modulation power	low P_{MZ}	medium $1.25 \times P_{MZ}$	high $3 \times P_{MZ}$
harmonic distortion	odd terms	odd terms	all terms

Table 4. Critical parameters characterizing electro-optic modulators

Velocity Mismatch $L_{max}f_m = c/2(n - \sqrt{\varepsilon_{eff}})$

GaAs	$LiNbO_3$	Polymer
40 GHz-cm	6 GHz-cm	130 GHz-cm

Modulation Efficiency $(\phi/E_m)(\lambda_0/\lambda_m) = n^3r/(n - \sqrt{\varepsilon_{eff}})$

GaAs	$LiNbO_3$	Polymer
1.7×10^{-4}	1.3×10^{-4}	12×10^{-4}

FIGURE CAPTIONS

Fig. 1. Two synthetic schemes for preparing polyimides with covalently incorporated nonlinear optical chromophores are shown.

Fig. 2. The thermal stability of nonlinear optical data for a polymer prepared according to the scheme shown in Fig. 1A is shown for the polyamic acid and polyimide forms of the NLO polymer. Optical nonlinearity is assessed by measurement of the second harmonic generation efficiency (d_{33}) as a function of heating the polymer materials at a rate of 10°C/min. This is referred to as the "rapid" or "dynamic" assay of the thermal stability of an NLO-active polymer lattice and can be contrasted with measurement of thermal stability assayed by observing the optical nonlinearity at a fixed temperature as a function of time. The dynamic assay is analogous to thermal gavimetric analysis (TGA) for assessing the chemical stability of a material. See ref. 175 for a more complete description of the dynamic thermal assay of optical nonlinearity used to obtain the data shown in this figure.

Fig. 3. This figure illustrates three types of incorporation of chromophores into the polymer main chain. A.) The most common type of incorporation involves incorporating the chromophore such that the chromophore axis is colinear with the local polymer backbone axis. This is achieved with reactive functionalities at both the donor and acceptor ends of the chromophore. B.) The donor end is attached by two points of attachment to the polymer backbone. C.) The chromophore is incorporated into the polymer main chain by two points of attachment but in a manner such that the chromophore axis is orthogonal to the local backbone axis. Attachment occurs at the middle rather than the ends of the chromophore.

Fig. 4. The preparation of a three dimensional stabilized polymer network, with the chromophore and local polymer axes orthogonal, is shown.

Fig. 5. The preparation of thermoset NLO polyurethane is shown.

Fig. 6. The temporal stability of the optical nonlinearity (normalized SHG coefficient) of the thermoset NLO polyurethane of Fig. 5 is shown at ambient temperature and at 90°C.

Fig. 7. The preparation of stabilzed three dimensional NLO lattices from (A) tri and (B) tetra functionalized monomers is shwon.

Fig. 8. The stability of optical nonlinearity for tri and tetralinked chromophores as a function of time and temperature is shown. Data obtained by aging the tri and tetralink samples in air at 100°C are shown in the upper graph (a) while data obtained the dynamic assay technique are shown in the lower graph (b). The stability of optical nonlinearity is measured by recording second harmonic generation efficiency.

Fig. 9. Photocrosslinking in linear polymethacrylates is shown. Adapted from ref. 236.

Fig. 10. Syntheses of main chain photocrosslinkable NLO polymers are shown.

Fig. 11. The synthesis of NLO chromophores covalently incorporated into a hardened sol-gel network is shown.

Fig. 12. The temporal stability of the NLO optical activity of the hardened material of Fig. 11 is shown for aging at 100°C. SHG is used to follow the thermal stability of the optical nonlinearity.

Fig. 13. Dynamic thermal stability measurements are shown for the sol-gel material of Fig. 11. The SHG signal is monitored while heating the sample at a rate of 10°C/min. Notice the obvious dependence of the stability of the optical nonlinearity (chromophore order) upon cure conditions shown in the upper right of the figure.

Fig. 14. The effect of poling protocol is illustrated to the material of Fig. 11. Two protocols were evaluated. Upper: 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° to 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.

Fig. 15. General schemes for producing hardened lattices utilizing DEC chromophores are shown. A.) The prepolymer is produced through a condensation reaction and the crosslinking reaction is a free radical addition reaction. B.) The prepolymer is produced by an addition reaction while the crosslinking 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 then crosslinking 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.

Fig. 16. The use of a DEC chromophore with addition and condensation reactions to produce a hardened NLO lattice is shown. An addition reaction is carried out to yield a processible prepolymer which is spin cast into optical quality films and poled near the glass transition temperature. Lattice hardening is effected by a condensation reaction. This material has exhibited long term stability of optical nonlinearity to 125°C.

Fig. 17. Similar to Fig. 16 but the procedure is modified to permit incorporation of a nitro acceptor group in the chromophore.

Fig. 18. Similar to Fig. 16 but the procedure is modified to permit incorporation of a high $\mu\beta$ chromophore.

Fig. 19. The temporal stability of NLO polymer matrices prepared according to Fig. 17 is shown for aging in air at 100°C. Note that the relaxation of poling-induced order is greatly retarded in the crosslinked (hardened) polymer material. When assayed by the dynamic method of assessing the thermal stability of NLO activity, the hardened sample retains full optical nonlinearity to approximately 175°C at which point the optical nonlinearity rapidly decays to approximately 20% (at 200°C) of the original value of 14 pm/V (at 1.3 μm).

Fig. 20. A scheme for preparation of an IPN is shown.

Fig. 21. A schematic representation of laser-assisted poling is given. The upper diagram illustrates the effect on chromophore orientation of irradation with plane-polarized light.

Note that the chromophores, because of the symmetry and rigidity, have been approximated as simpe dipoles. Plane polarized light orients the dipoles orthogonal to the polarization direction since the transition moment for trans-to-cis isomerization in azobenzenes depends upon the angle between the chromophore dipole axis and the electric field vector of the light field. The lower diagram shows the same process but with the addition of an electric poling field. Note that both the photochemical process and the poling process act to orient chromophores in the direction of the poling field.

Fig. 22. (A) A schematic diagram of defining birefringent cladding waveguides is shown. The refractive index profiles are shown for TE and TM modes. (B) A polarization microscope photograph of the birefringent cladding waveguides and directional couplers defined in the Disperse Red 19 chromophore containing thermoset polymer (Fig. 5) thin film. The analyzer and a half-waveplate were adjusted to null the light from exposed areas.

Fig. 23. Side view of an NLO waveguide prepared by RIE. The brightest area is the gold ground electrode. The polymer of Fig. 5 was used in the fabrication of this structure.

Fig. 24. The waveguide structure and single mode operation dimensions are shown for (left) a disperse red 19 containing polyurethane thermoset polymer with clear polyurethane claddings and for (right) a disperse red 19 containing polyimide with polyimide claddings.

Fig. 25. A top view of Y-branch waveguides defined by RIE in an thermosetting polymer containing a covalently incorporated aminosulfone chromophore is shown. (B) The improvement in waveguide wall definition realized with a reduction in RIE rate is shown.

Fig. 26. 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.

Fig. 27. Schematic of the breadboard concept for integrated polymer/semiconductor opto-electronics is shown for a polymer 2X2 cross-over $\Delta\beta$ switch.

Fig. 28. 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.

Fig. 29. An 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.

Fig. 30. A schematic representation of a high bandwidth opto-electronic device with a high speed polymer optical switch is shwon. Multicolor lithography is used to eliminate the optical losses due to device-fiber mismatch through fine control of mode size, shape, and support.

Fig. 31. Fiber-waveguide coupling exploiting V-groove positioning is shown.

Fig. 32. Schematic representations are given for (a) a Mach-Zehnder interferometer, (b) a birefringent modulator, and (c) a directional coupler. In (b) the optical input to the birefringence modulator is polarized at 45° and excites both TE and TM modes. The applied voltage modulates the output polarization. Intensity modulation is achieved using polarizing components at the output.

Fig. 33. A spectrum analyzer scan of the detected and down-converted optical modulation signal from a birefringent modulator (fabricated from the materials of Fig. 5) is shown. A local oscillator at 20 GHz was mixed with the detector output. The displayed signal at 17 GHz signifies an optically modulated signal at 17 + 20 = 37 GHz.

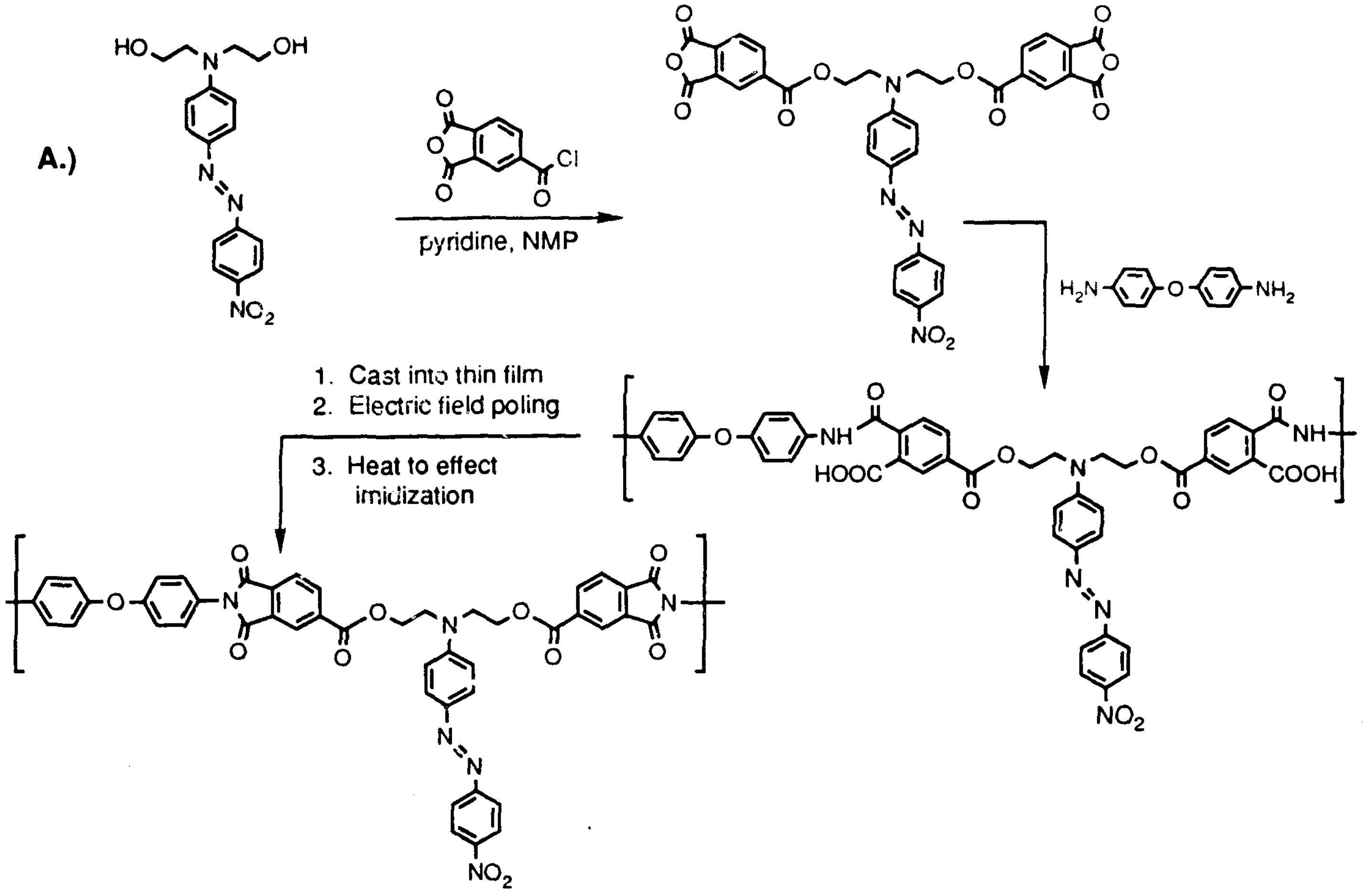
Fig. 34. The relative response of a birefirngent modulator output (signal shown in Fig. 33) as a function of frequency is shown to 19 GHz. Modulation signals have been observed to 40 GHz with this modulator and the modulator has been operational for over a year with no detectable degradation in performance. Within experimental error, the response appears to be flat.

Fig. 35. A block diagram of a photonic sensor system is given.

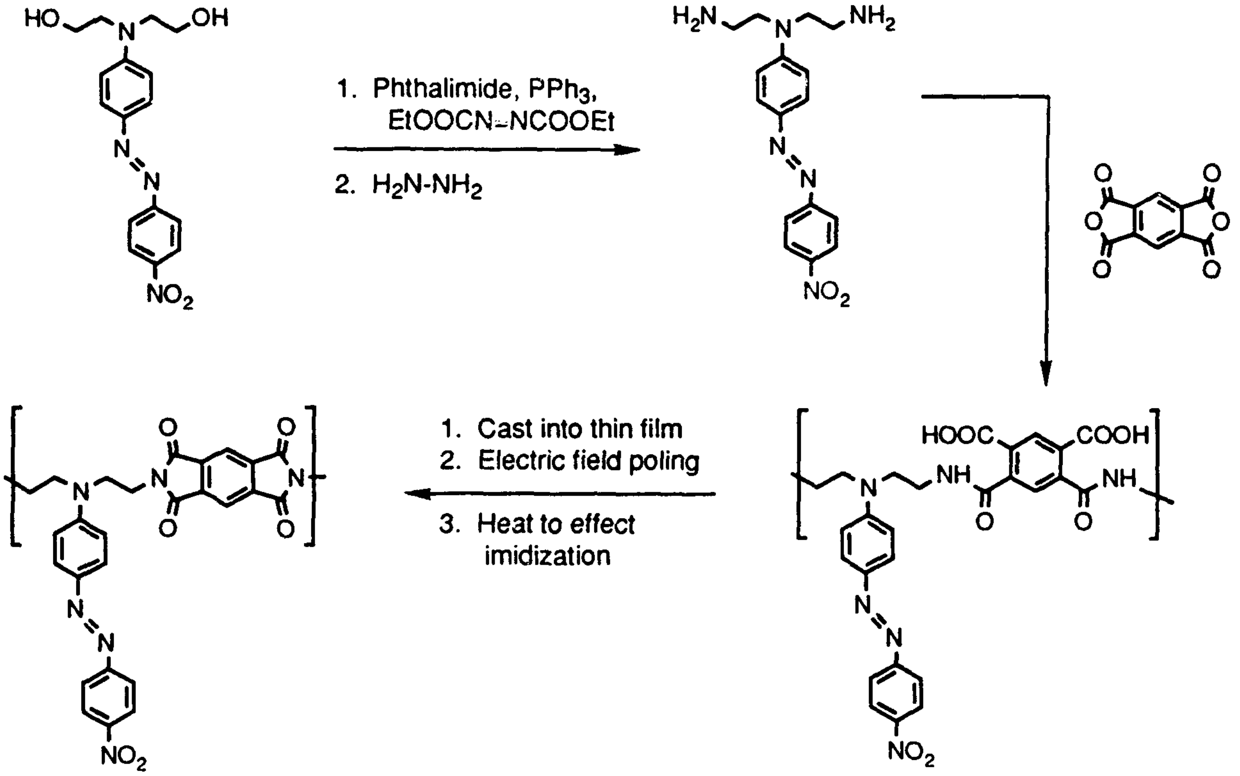
Fig. 36. A schematic representation of the use of a Luneburg lens with a single photonic sensor is shown.

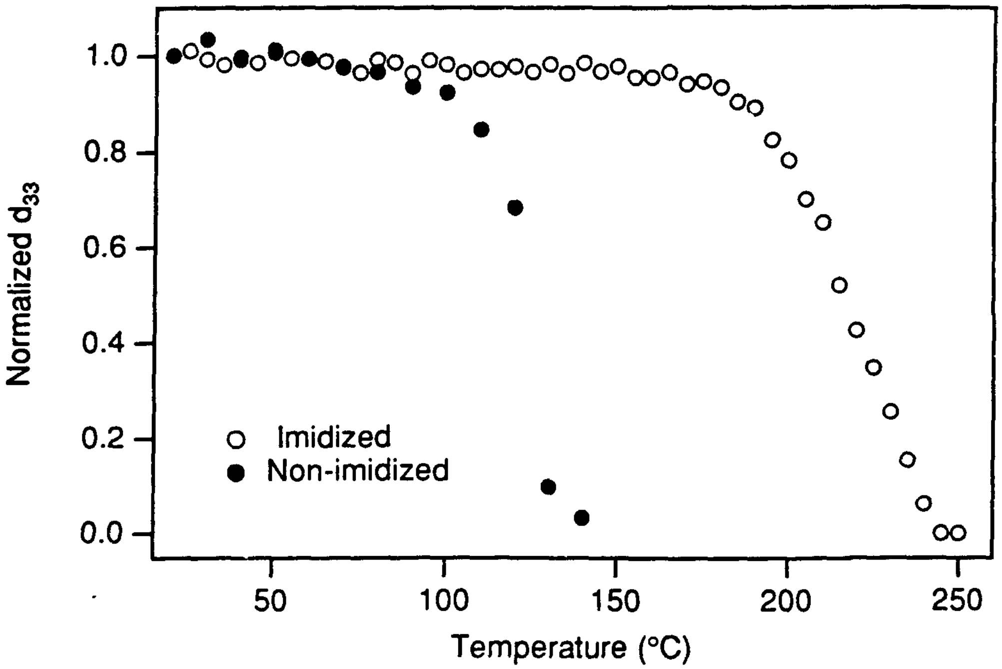
Fig. 37. The use of multiple photonic sensors with a Luneburg lens is shown.

A.)

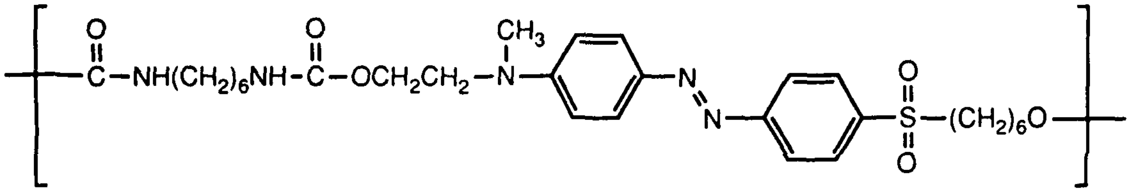

pyridine, NMP
1. Cast into thin film
2. Electric field poling
3. Heat to effect imidization

B.)


1. Phthalimide, PPh3, EtOOCN=NCOOEt
2. H2N-NH2
1. Cast into thin film
2. Electric field poling
3. Heat to effect imidization

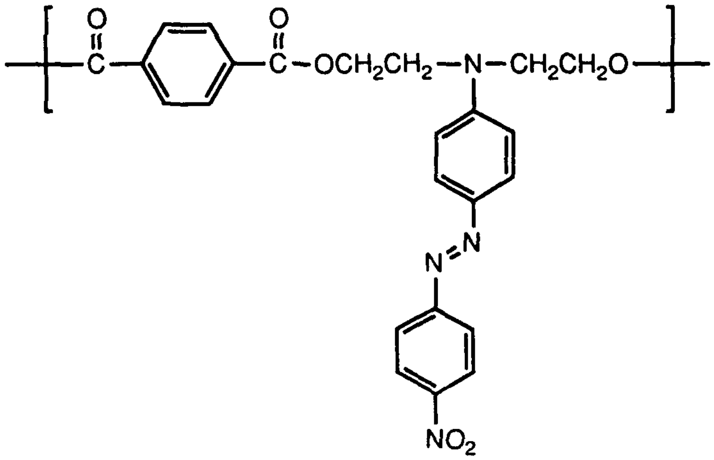

1.0
0.8
0.6
0.4
0.2
0.0
Normalized d_{33}
○ Imidized
● Non-imidized
50
100
150
200
250
Temperature (°C)

A.)



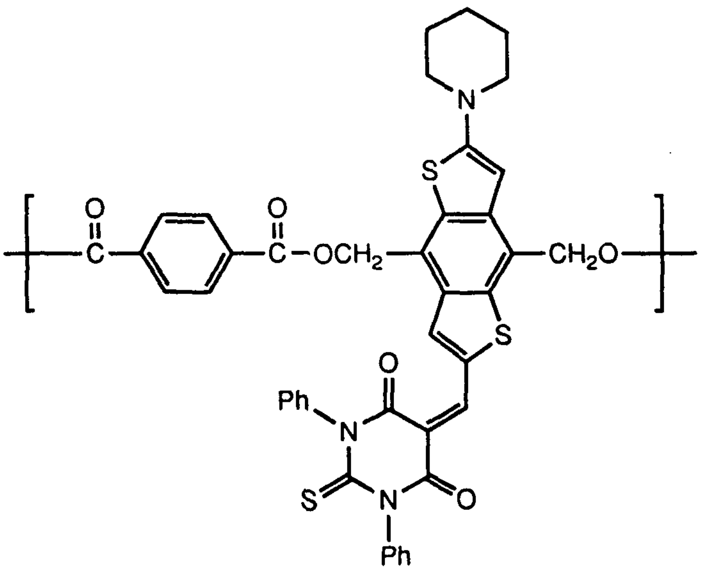
O
C
NH(CH2)6NH
O
C
OCH2CH2
CH3
N
N
N
O
S
O
(CH2)6O

B.)



O
C
O
C
OCH2CH2
N
CH2CH2O
N
N
NO2

C.)



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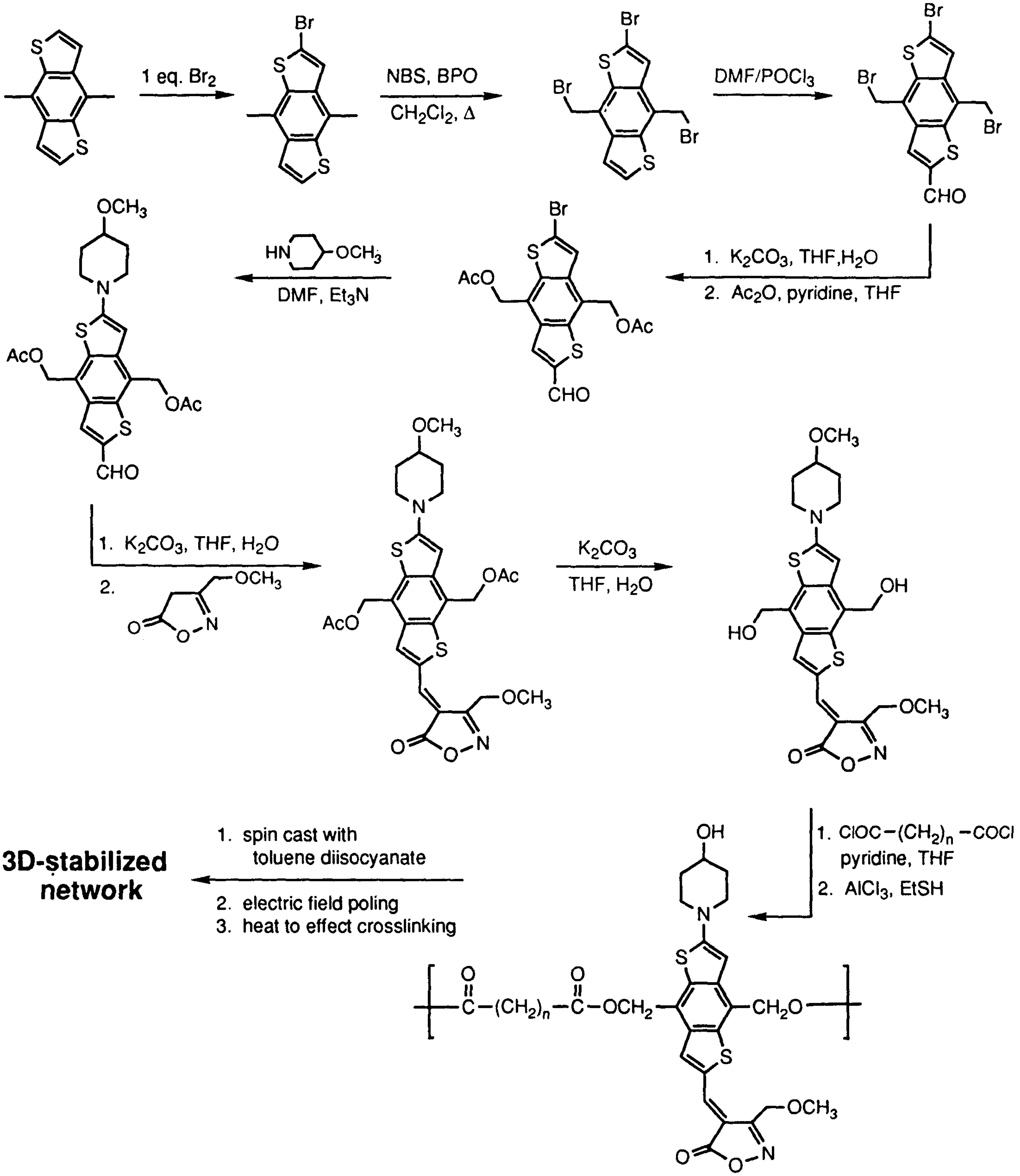
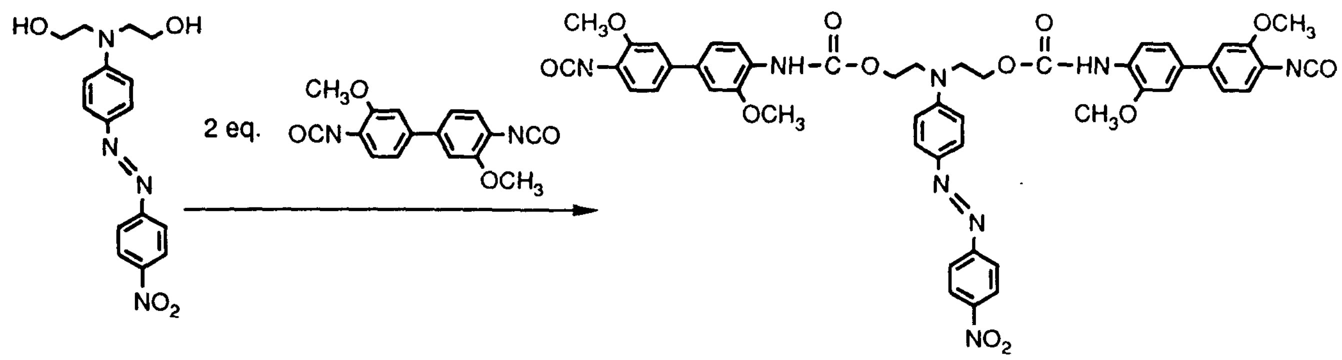
S
S
O
C
O
C
OCH2
CH2O
O
Ph
N
S
N
O
Ph



1 eq. Br2
NBS, BPO
CH2Cl2, Δ
DMF/POCl3
1. K2CO3, THF,H2O
2. Ac2O, pyridine, THF
HN⟨⟩-OCH3
DMF, Et3N
1. K2CO3, THF, H2O
2.
K2CO3
THF, H2O
1. ClOC–(CH2)n–COCl
pyridine, THF
2. AlCl3, EtSH
1. spin cast with
toluene diisocyanate
2. electric field poling
3. heat to effect crosslinking
3D-stabilized network
Br
S
CHO
AcO
OAc
OCH3
N
O
OH
HO
C–(CH2)n–C–OCH2
CH2O

A.)


HO
N
OH
N
N
NO2
2 eq.
CH3O
OCN
NCO
OCH3
CH3O
OCN
NH-C-O
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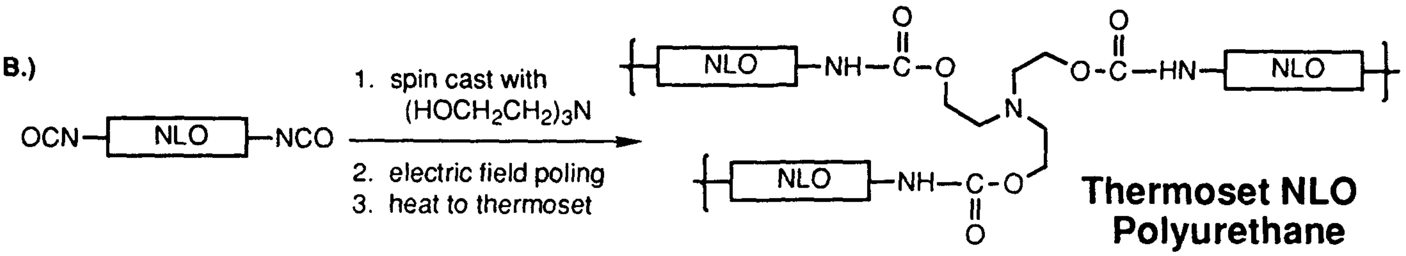
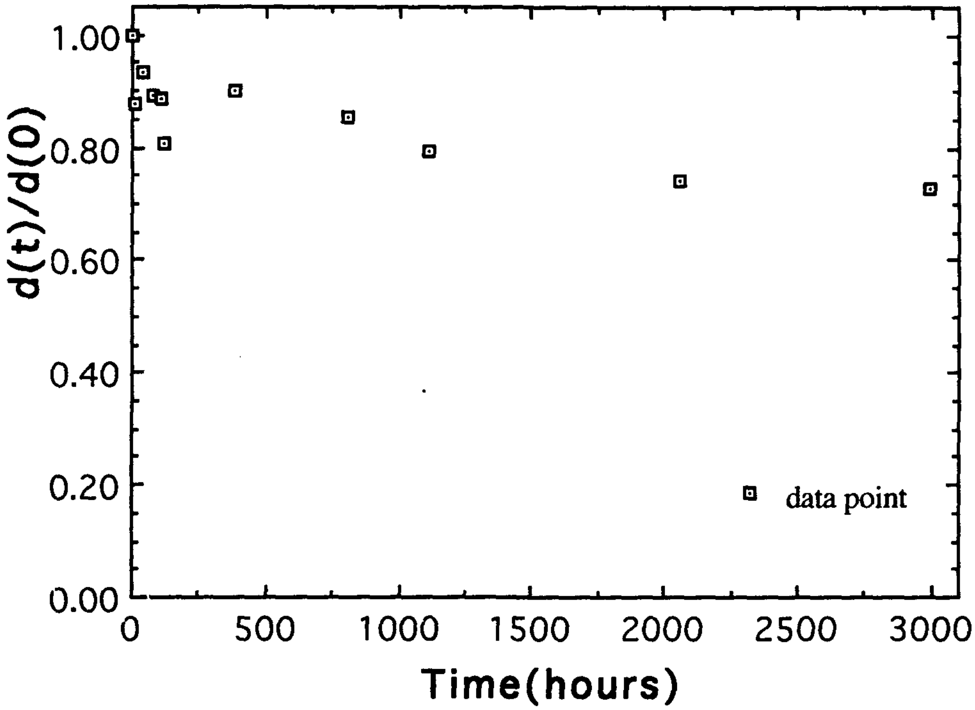
N
O-C-HN
O
OCH3
NCO
OCH3
CH3O
N
N
NO2

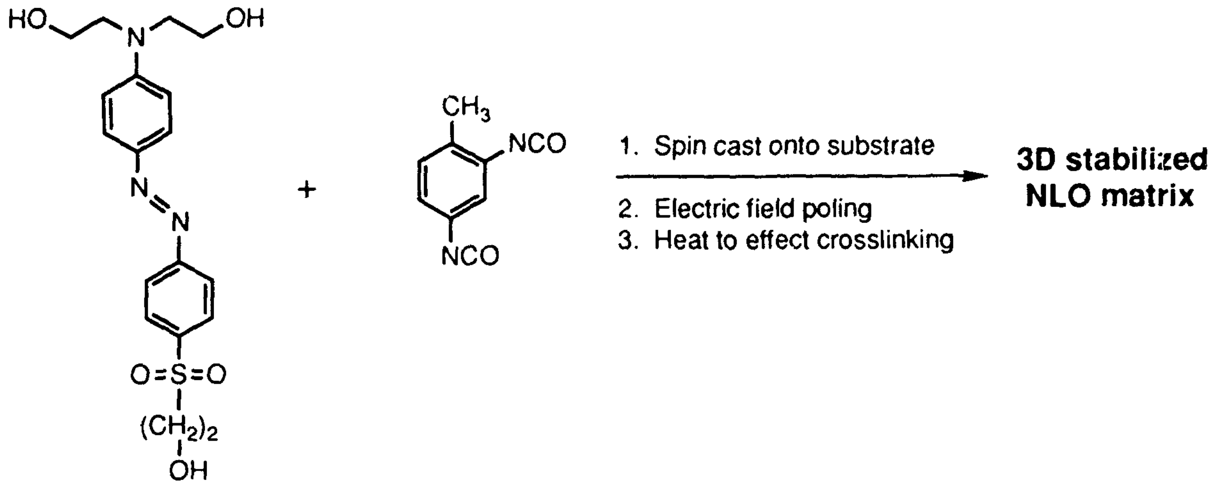
B.)


OCN
NLO
NCO
1. spin cast with (HOCH2CH2)3N
2. electric field poling
3. heat to thermoset
NLO
NH-C-O
O
N
O-C-HN
O
NLO
NLO
NH-C-O
O
Thermoset NLO Polyurethane

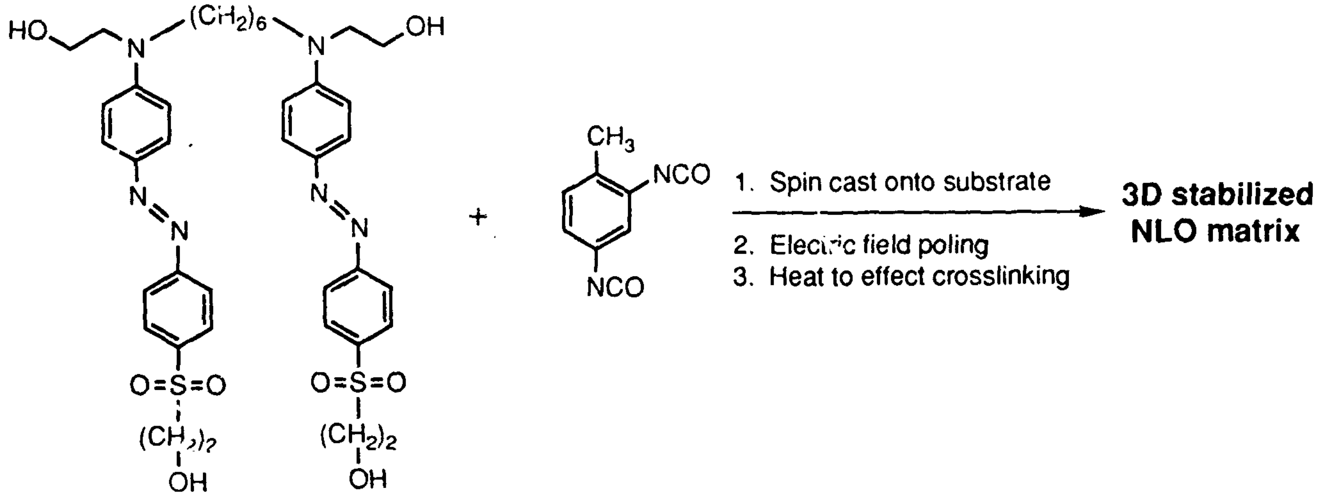
Temporal stability of the thermosetting polymer at 90°
(200°C setting temperature, 12KV poling field)

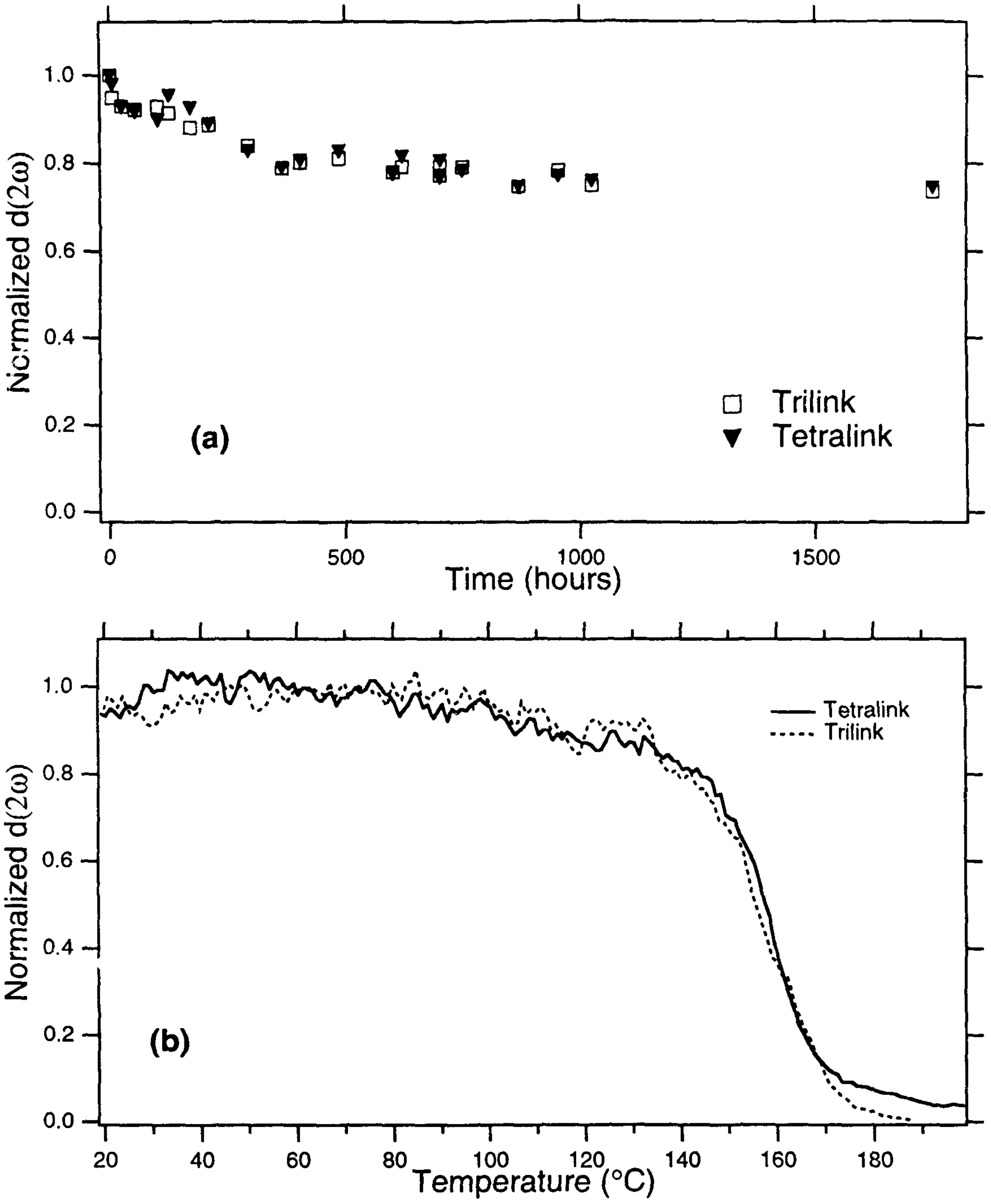


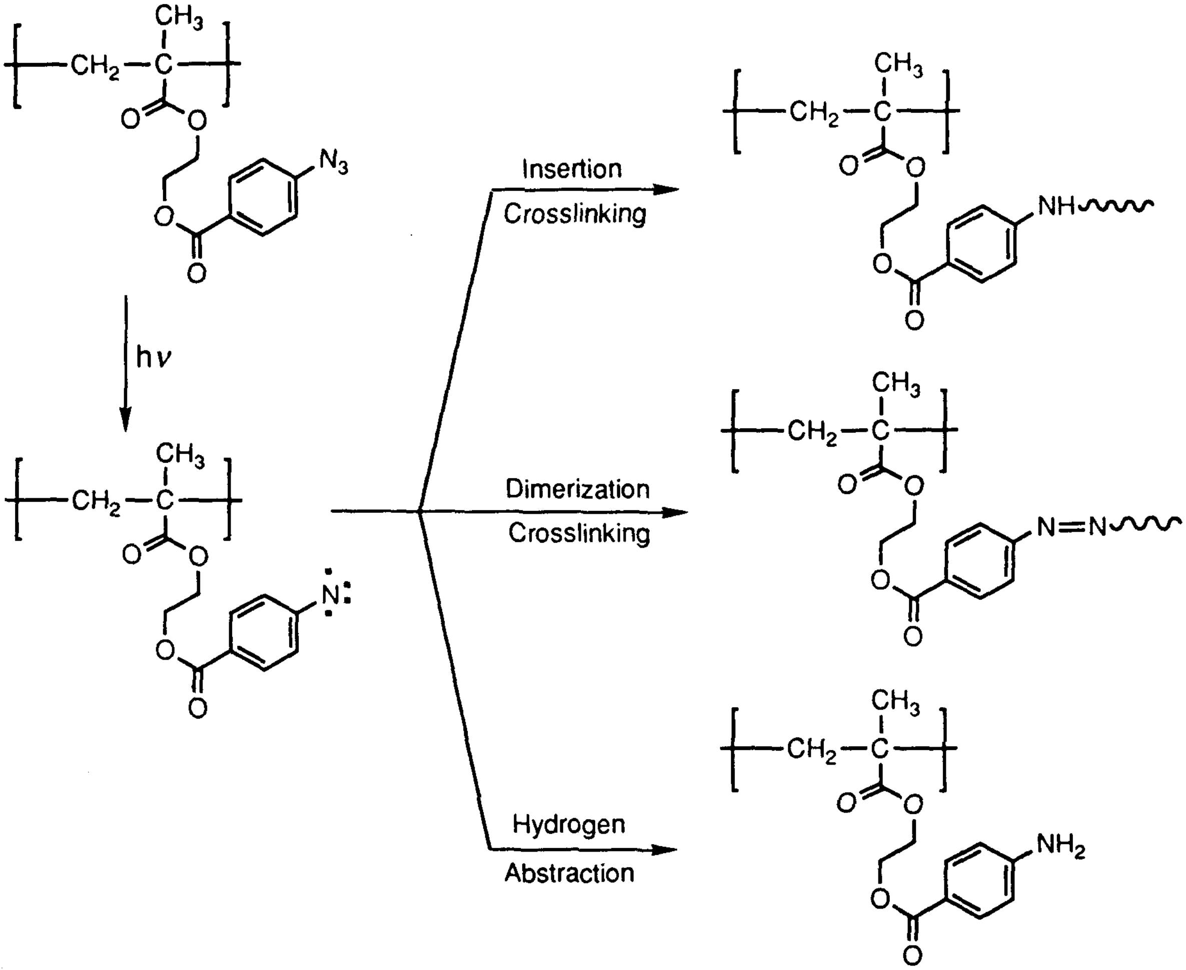
A.)


HO
N
OH
N
N
O=S=O
$(CH_2)_2$
OH
+
CH_3
NCO
NCO
1. Spin cast onto substrate
2. Electric field poling
3. Heat to effect crosslinking
3D stabilized
NLO matrix

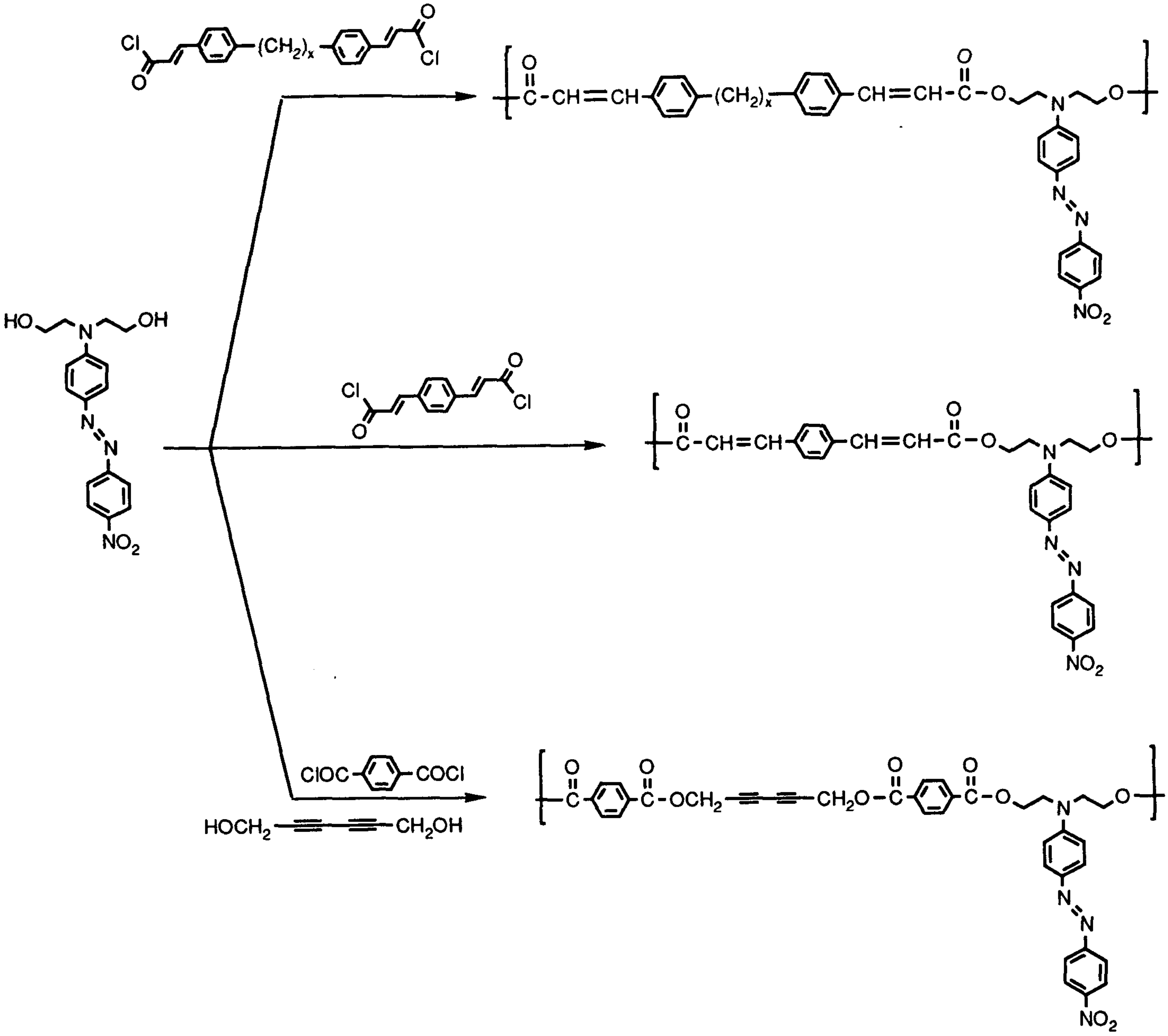
B.)


HO
N
$(CH_2)_6$
N
OH
N
N
N
N
O=S=O
O=S=O
$(CH_2)_2$
$(CH_2)_2$
OH
OH
+
CH_3
NCO
NCO
1. Spin cast onto substrate
2. Electric field poling
3. Heat to effect crosslinking
3D stabilized
NLO matrix

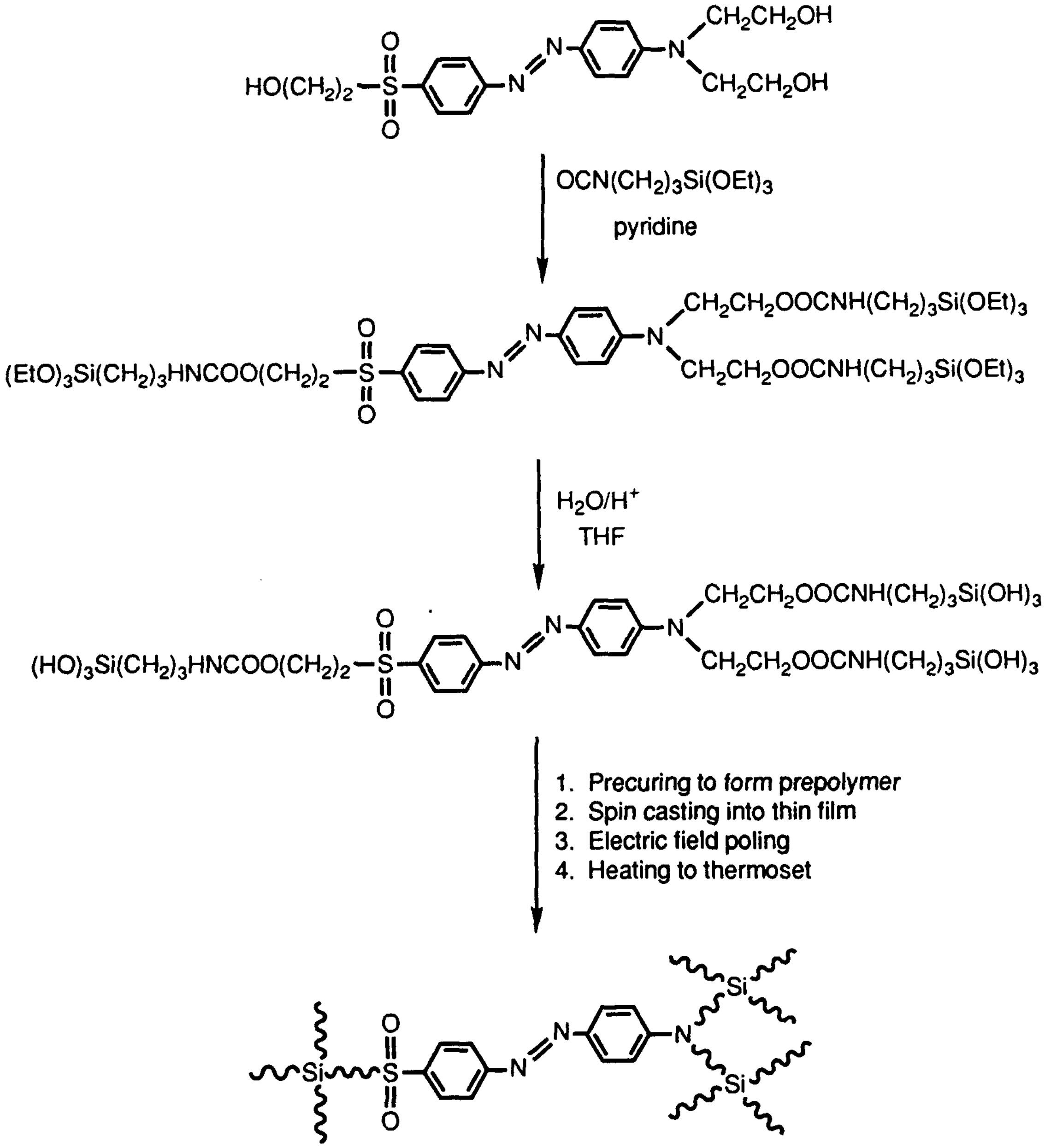

Normalized d(2ω)
1.0
0.8
0.6
0.4
0.2
0.0
0
500
1000
1500
Time (hours)
(a)
□ Trilink
▼ Tetralink
Normalized d(2ω)
1.0
0.8
0.6
0.4
0.2
0.0
20
40
60
80
100
120
140
160
180
Temperature (°C)
(b)
Tetralink
Trilink



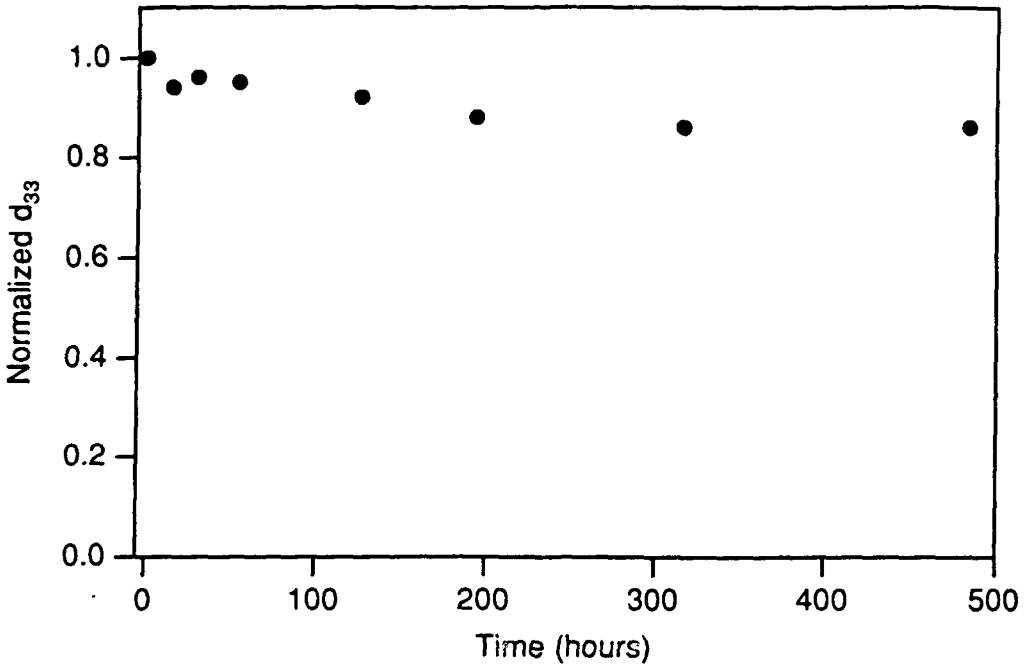
CH3
CH2
C
O
O
N3
hν
Insertion
Crosslinking
NH
Dimerization
Crosslinking
N=N
Hydrogen
Abstraction
NH2

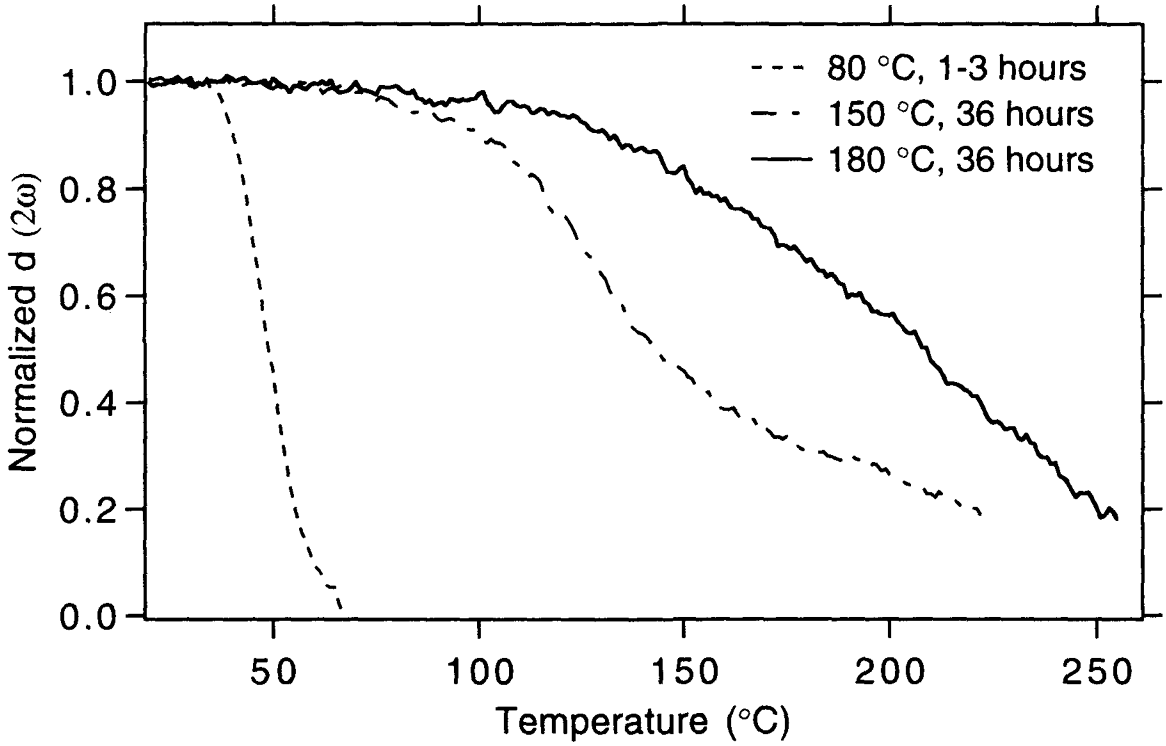


HO
OH
N
N
N
NO2
Cl
O
(CH2)x
Cl
ClOC
COCl
HOCH2
CH2OH
C
CH=CH
C
O
OCH2
CH2O

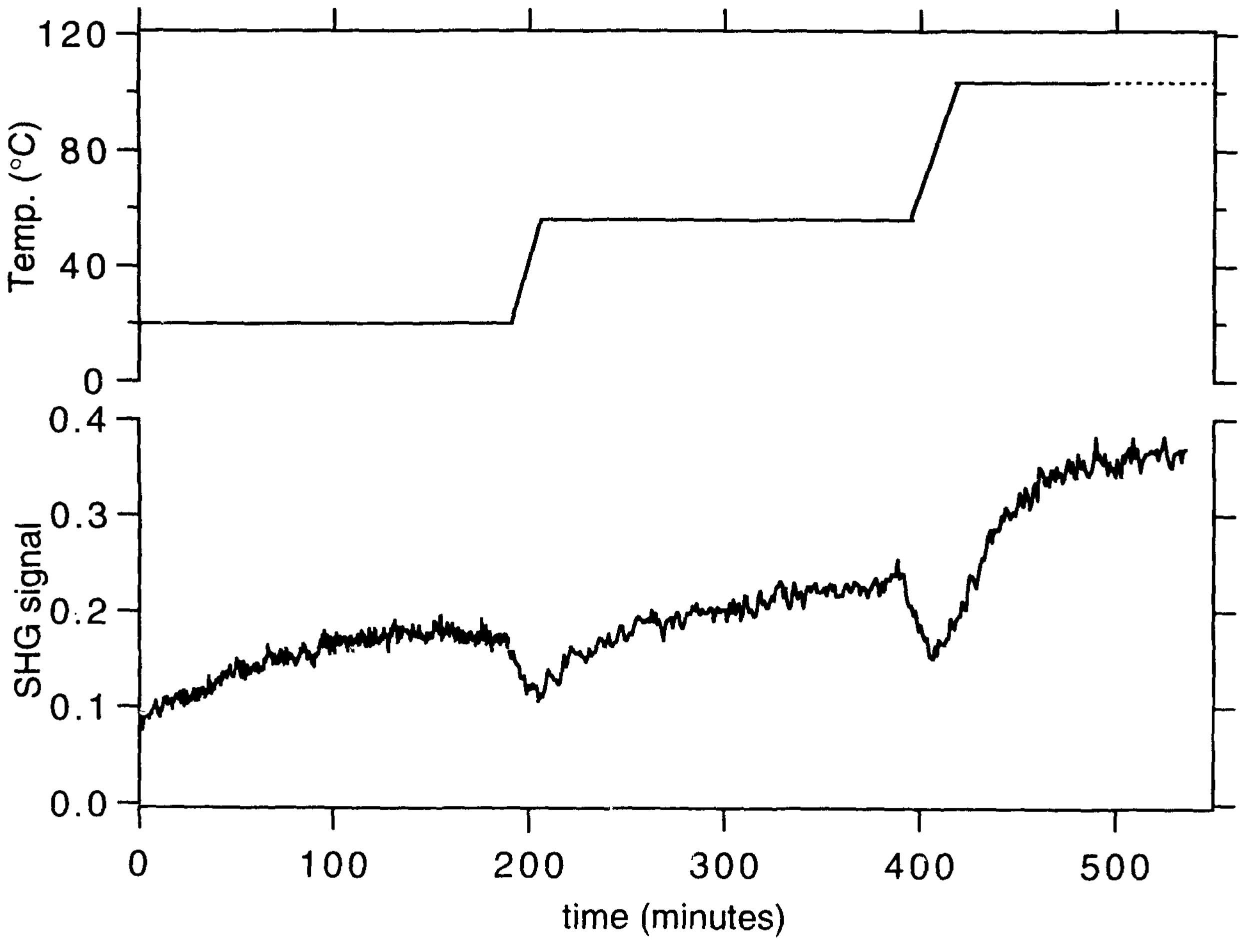


3D stabilized sol-gel network

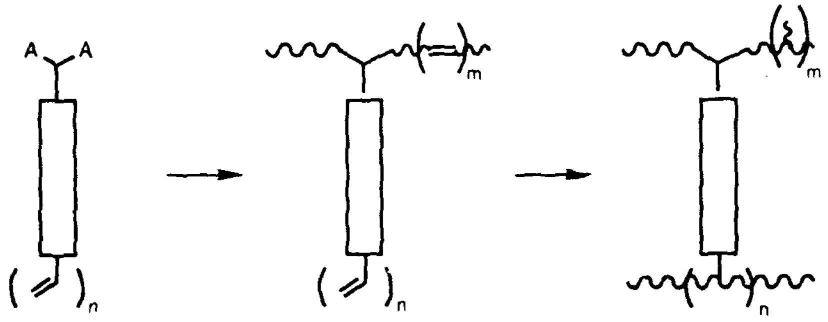

Normalized d_{33}
1.0
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
500
Time (hours)



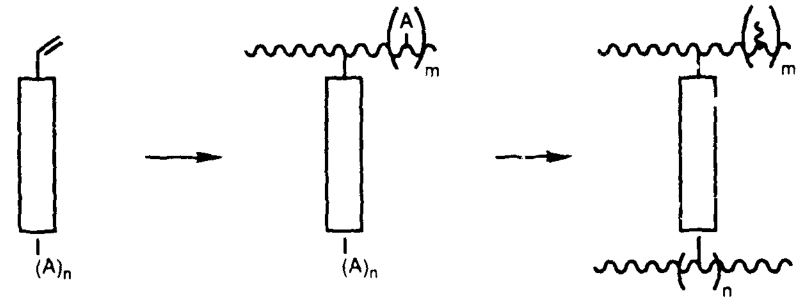
80 °C, 1-3 hours
150 °C, 36 hours
180 °C, 36 hours
Normalized d (2ω)
1.0
0.8
0.6
0.4
0.2
0.0
50
100
150
200
250
Temperature (°C)


120
80
40
0
Temp. (°C)
0.4
0.3
0.2
0.1
0.0
SHG signal
0
100
200
300
400
500
time (minutes)

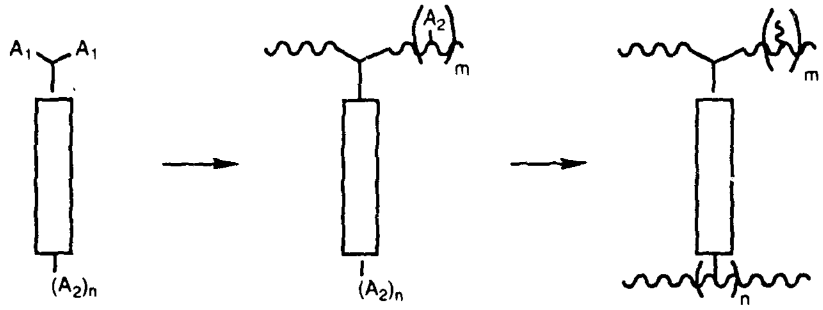
A.)



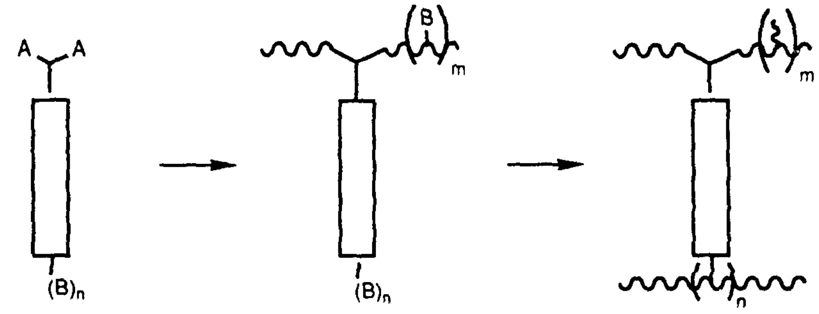
B.)

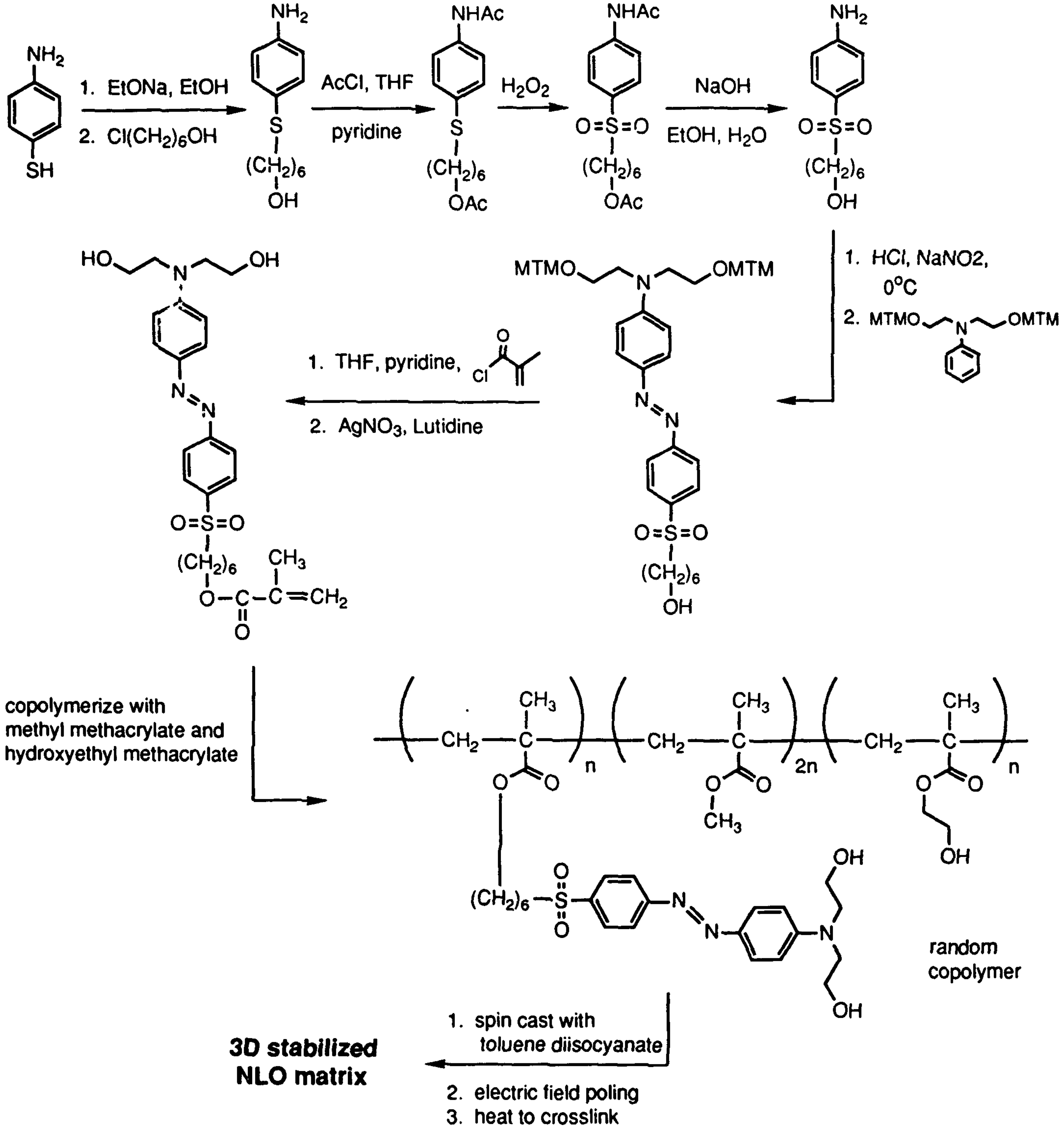


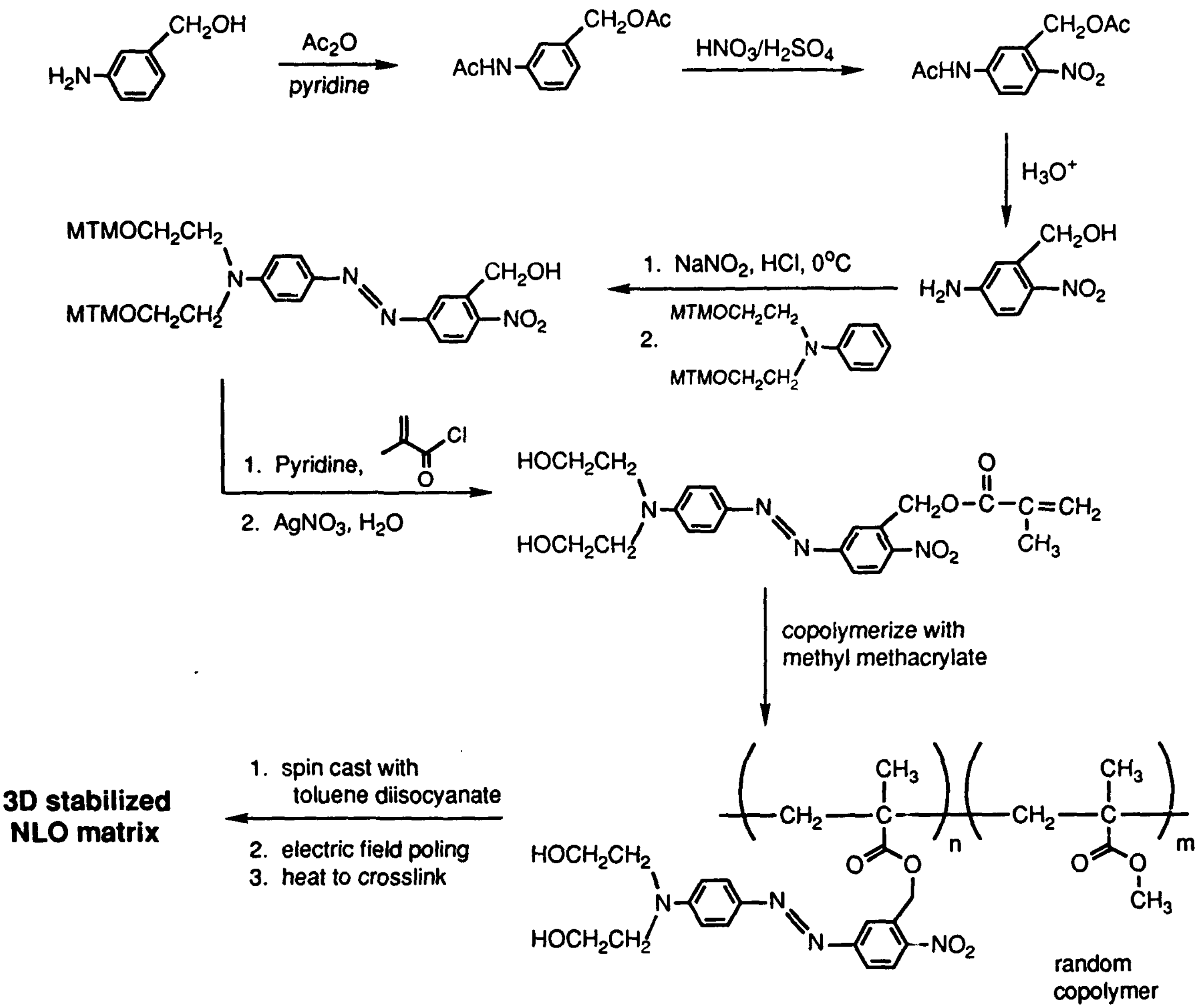
C.)

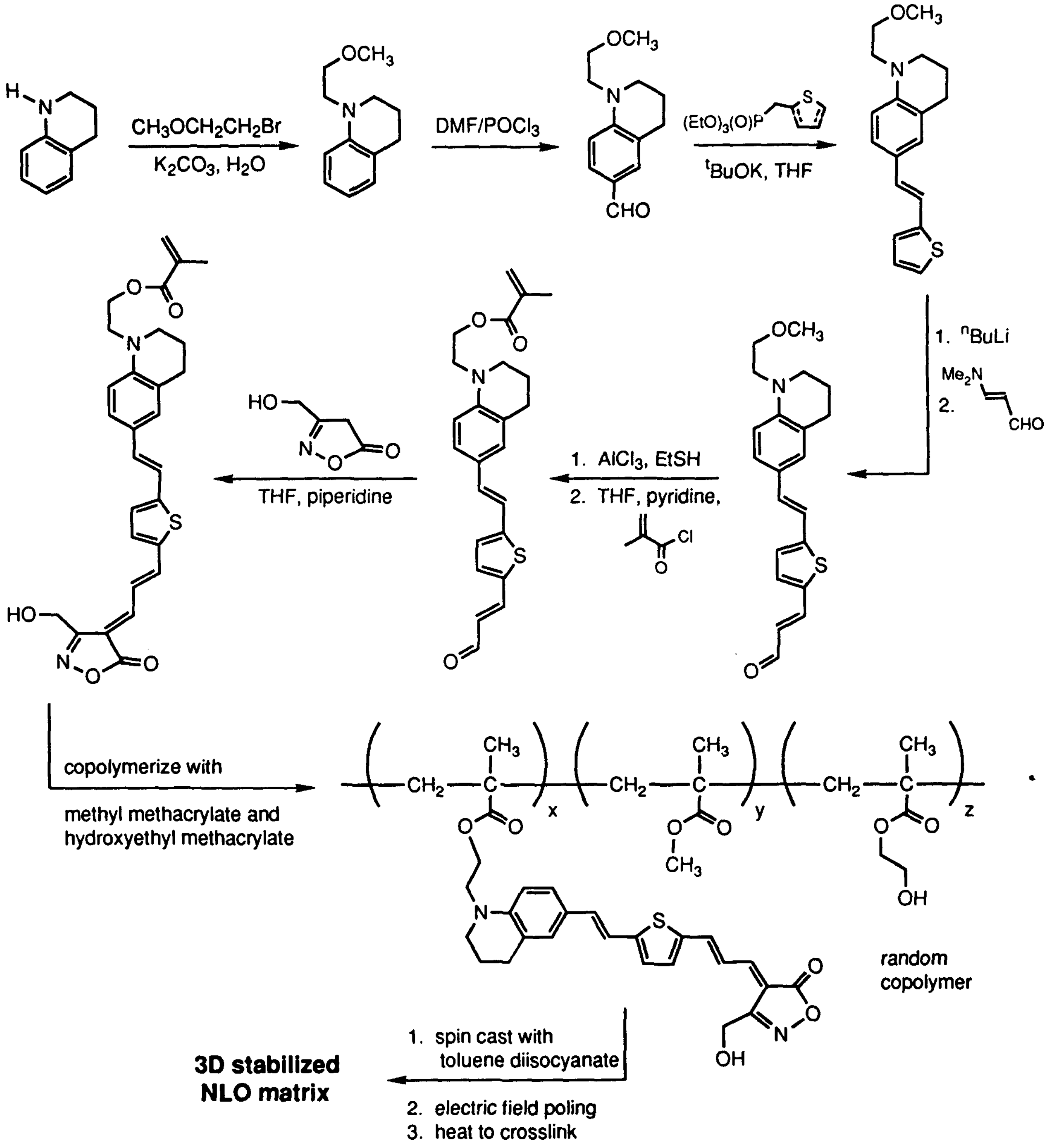


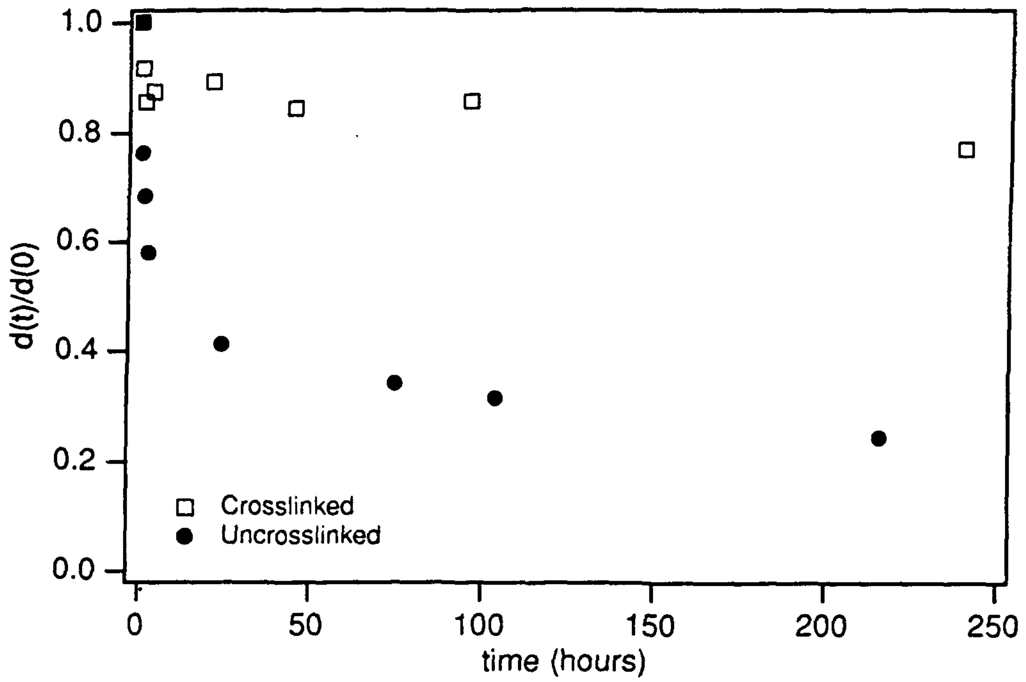
D.)

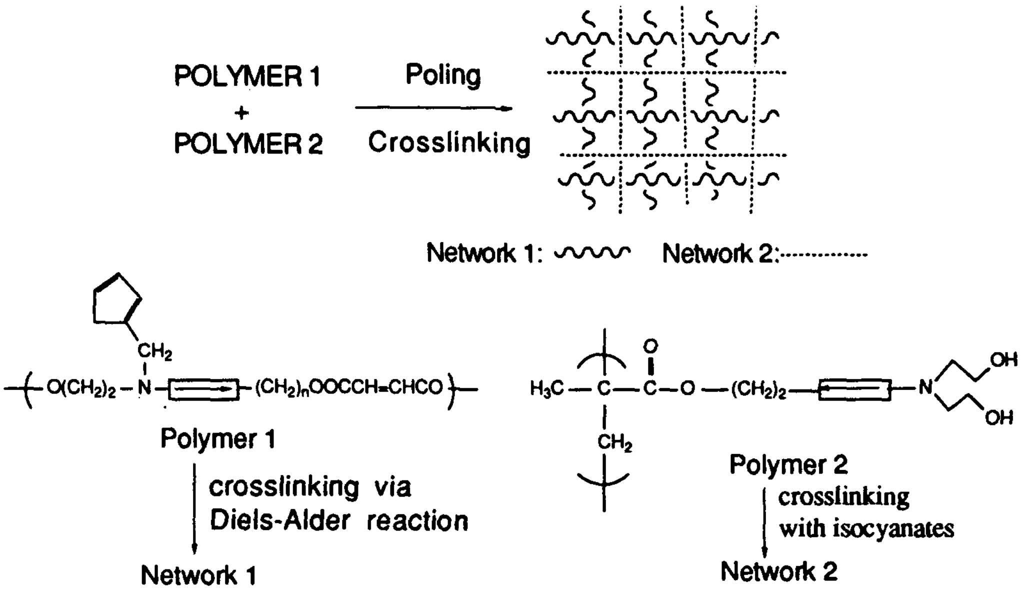



NH2
SH
1. EtONa, EtOH
2. Cl(CH2)6OH
NH2
S
(CH2)6
OH
AcCl, THF
pyridine
NHAc
S
(CH2)6
OAc
H2O2
NHAc
O=S=O
(CH2)6
OAc
NaOH
EtOH, H2O
NH2
O=S=O
(CH2)6
OH
1. HCl, NaNO2, 0°C
2. MTMO N OMTM
MTMO N OMTM
N=N
O=S=O
(CH2)6
OH
1. THF, pyridine, Cl O
2. AgNO3, Lutidine
HO N OH
N=N
O=S=O
(CH2)6
CH3
O-C-C=CH2
O
copolymerize with methyl methacrylate and hydroxyethyl methacrylate
CH2 C CH3 n
CH2 C CH3 2n
CH2 C CH3 n
O O
O O CH3
O O OH
(CH2)6 S O O
N=N
N
OH
OH
random copolymer
1. spin cast with toluene diisocyanate
2. electric field poling
3. heat to crosslink
3D stabilized NLO matrix

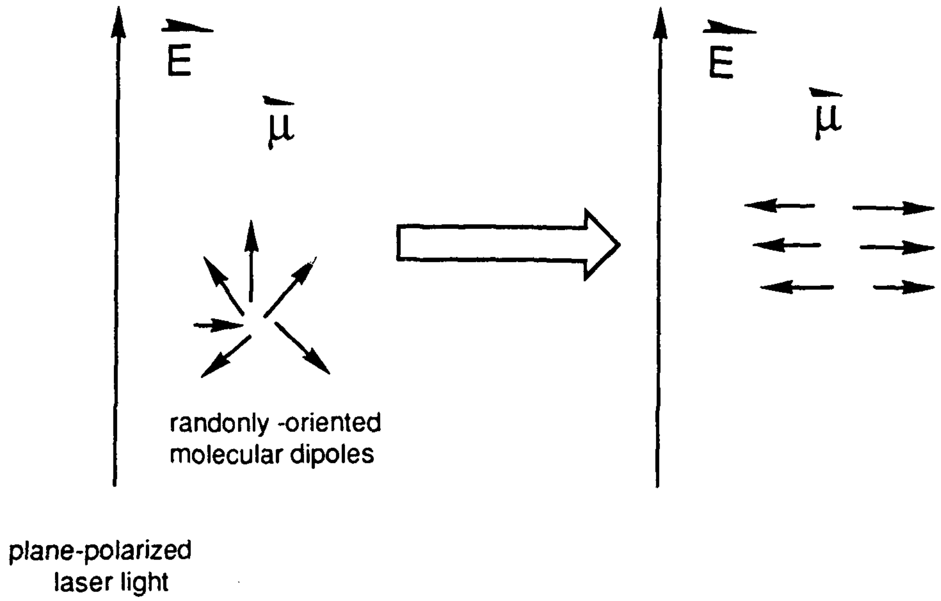

CH2OH
H2N
Ac2O
pyridine
CH2OAc
AcHN
HNO3/H2SO4
NO2
H3O+
1. NaNO2, HCl, 0°C
2. MTMOCH2CH2 N MTMOCH2CH2
MTMOCH2CH2
MTMOCH2CH2
N
N
1. Pyridine,
Cl
O
2. AgNO3, H2O
HOCH2CH2
HOCH2CH2
CH2O-C-C=CH2
CH3
copolymerize with
methyl methacrylate
CH2
CH3
C
O
n
m
random
copolymer
1. spin cast with
toluene diisocyanate
2. electric field poling
3. heat to crosslink
3D stabilized
NLO matrix


CH3OCH2CH2Br
K2CO3, H2O
DMF/POCl3
(EtO)3(O)P
tBuOK, THF
OCH3
CHO
1. nBuLi
Me2N
2.
CHO
1. AlCl3, EtSH
2. THF, pyridine,
Cl
HO
THF, piperidine
copolymerize with
methyl methacrylate and
hydroxyethyl methacrylate
CH3
CH2
C
x
y
z
OH
random
copolymer
1. spin cast with
toluene diisocyanate
2. electric field poling
3. heat to crosslink
3D stabilized
NLO matrix

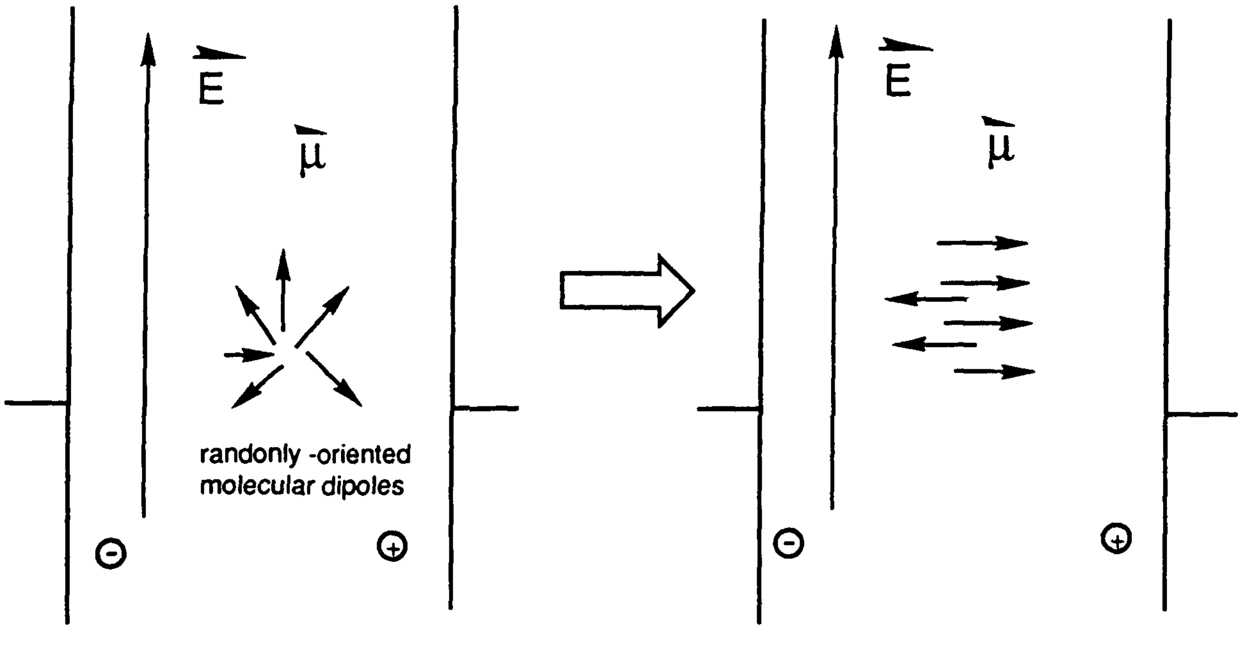

1.0
0.8
0.6
0.4
0.2
0.0
d(t)/d(0)
0
50
100
150
200
250
time (hours)
□ Crosslinked
● Uncrosslinked

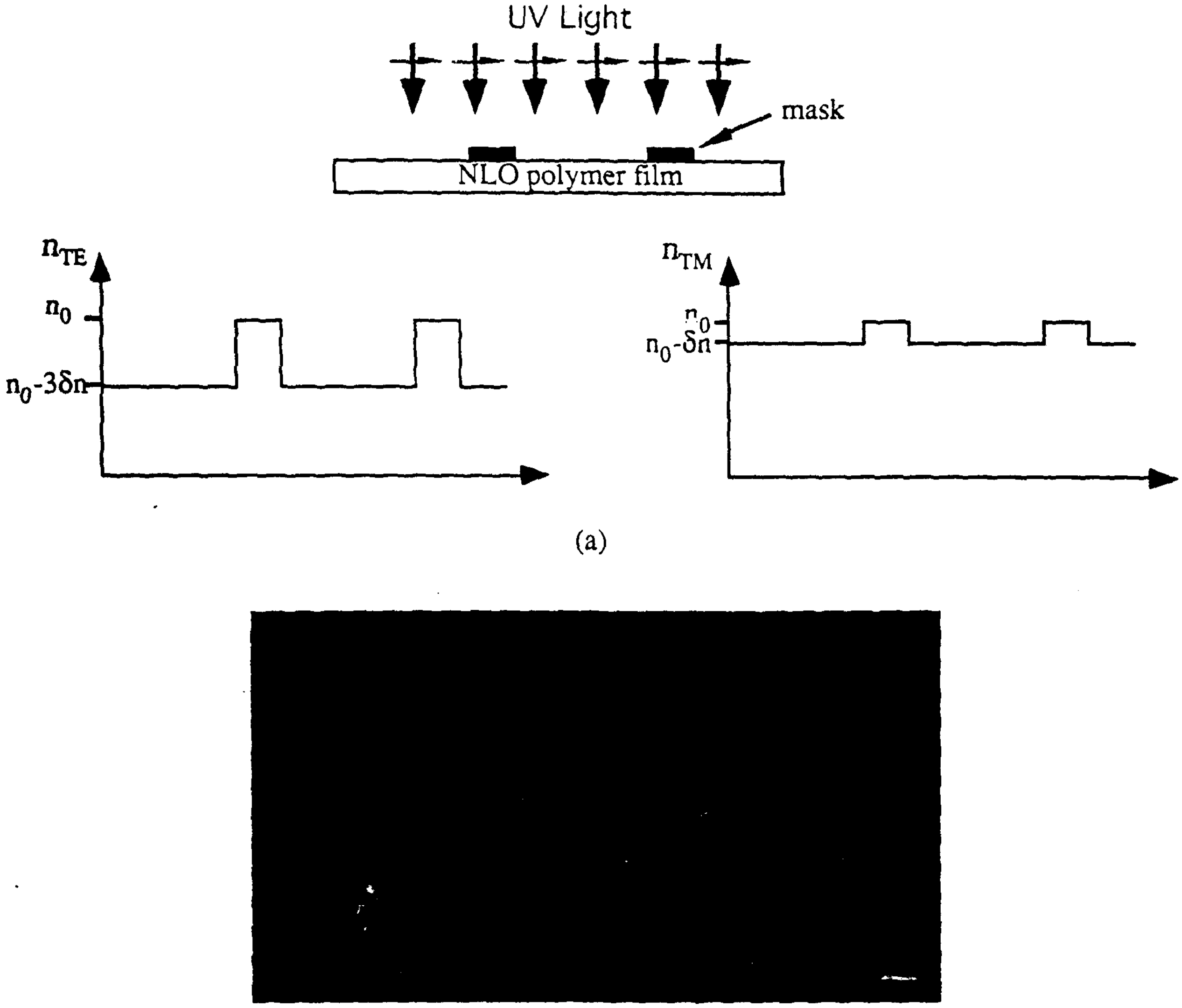

POLYMER 1
+
POLYMER 2
Poling
Crosslinking
Network 1:
Network 2:
CH2
O(CH2)2 – N
(CH2)nOOCCH=CHCO
Polymer 1
crosslinking via
Diels-Alder reaction
Network 1
O
H3C — C — C — O — (CH2)2
N
OH
OH
CH2
Polymer 2
crosslinking
with isocyanates
Network 2

No Electric Field



With Electric Field



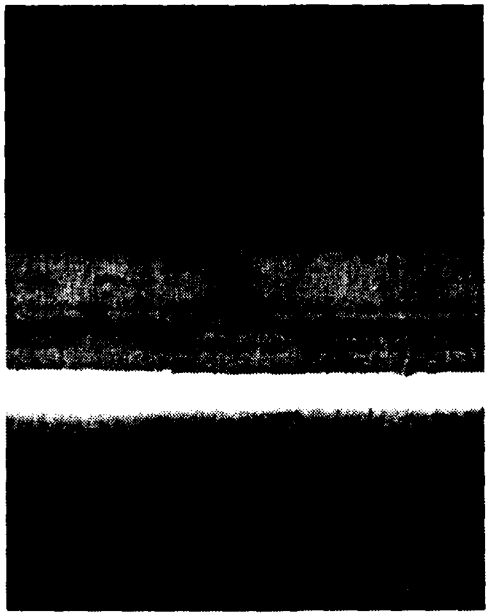


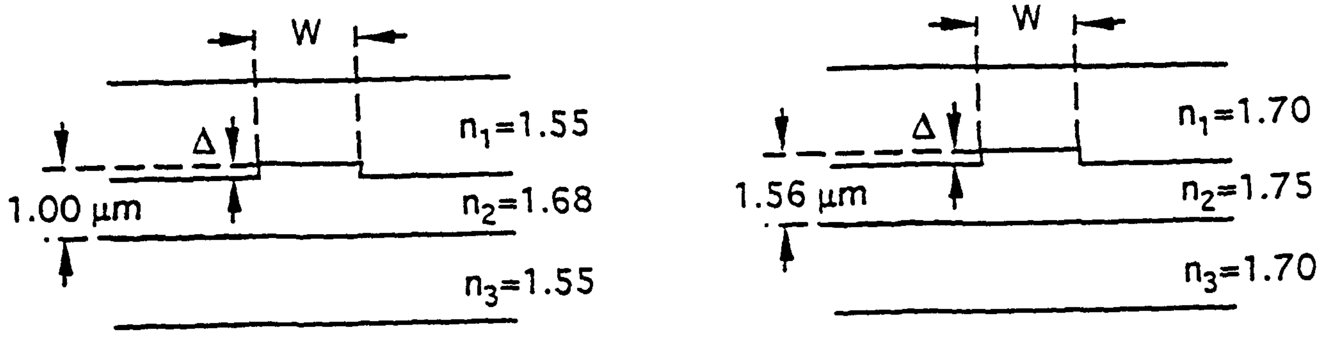
(a)

(b)

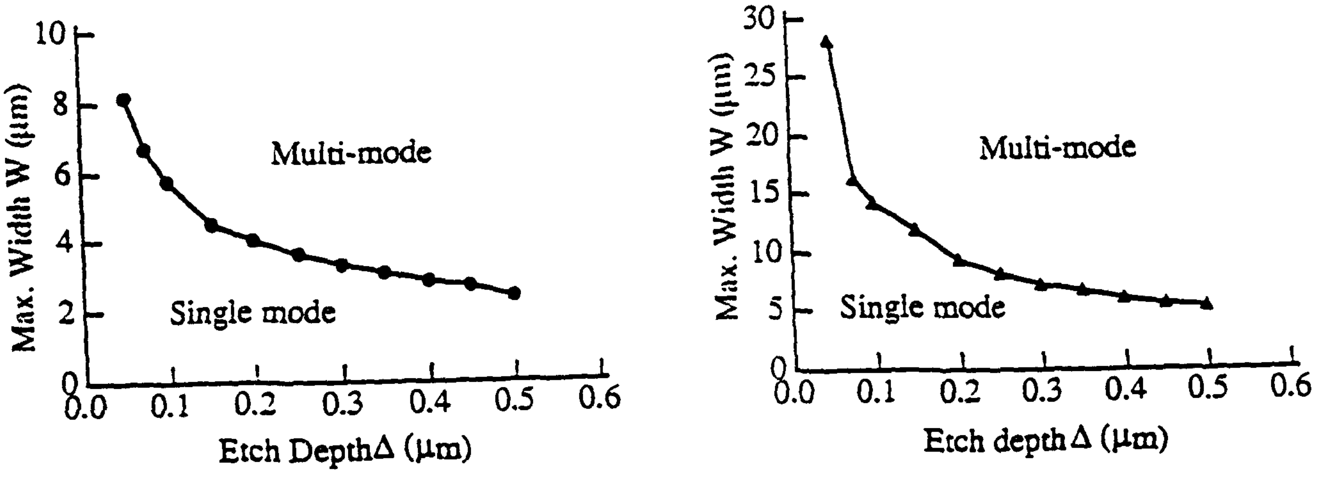
Birefringent Cladding Waveguides and Directional Couplers

CROSS LINKED POLYMER ELECTRO-OPTIC BURIED CHANNEL RIDGE WAVEGUIDE FABRICATED BY REACTIVE ION ETCHING



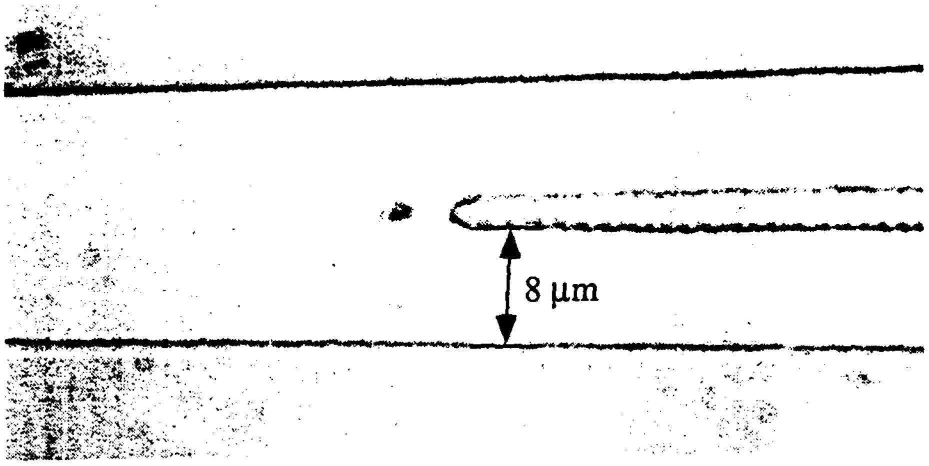

W
n_1=1.55
Δ
n_2=1.68
1.00 μm
n_3=1.55
W
n_1=1.70
Δ
n_2=1.75
1.56 μm
n_3=1.70

(a)

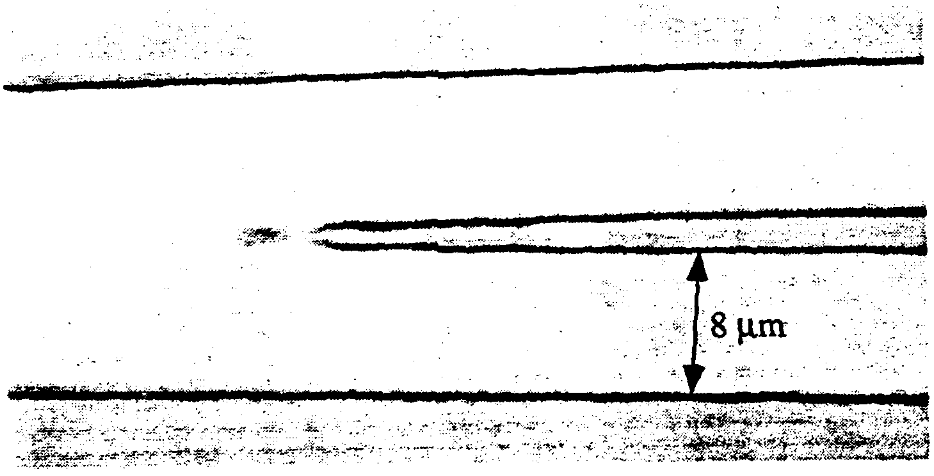

Max. Width W (μm)
0
2
4
6
8
10
Multi-mode
Single mode
0.0
0.1
0.2
0.3
0.4
0.5
0.6
Etch DepthΔ (μm)
Max. Width W (μm)
0
5
10
15
20
25
30
Multi-mode
Single mode
0.0
0.1
0.2
0.3
0.4
0.5
0.6
Etch depth Δ (μm)

(b)

RIE Etched Y Junctions



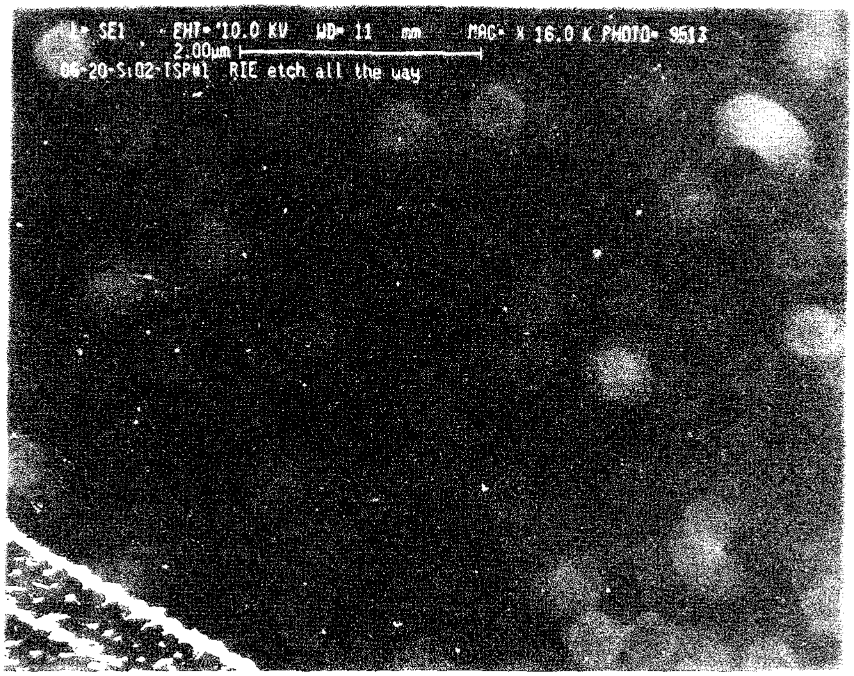
a. Early Work



b. Improved Process Control

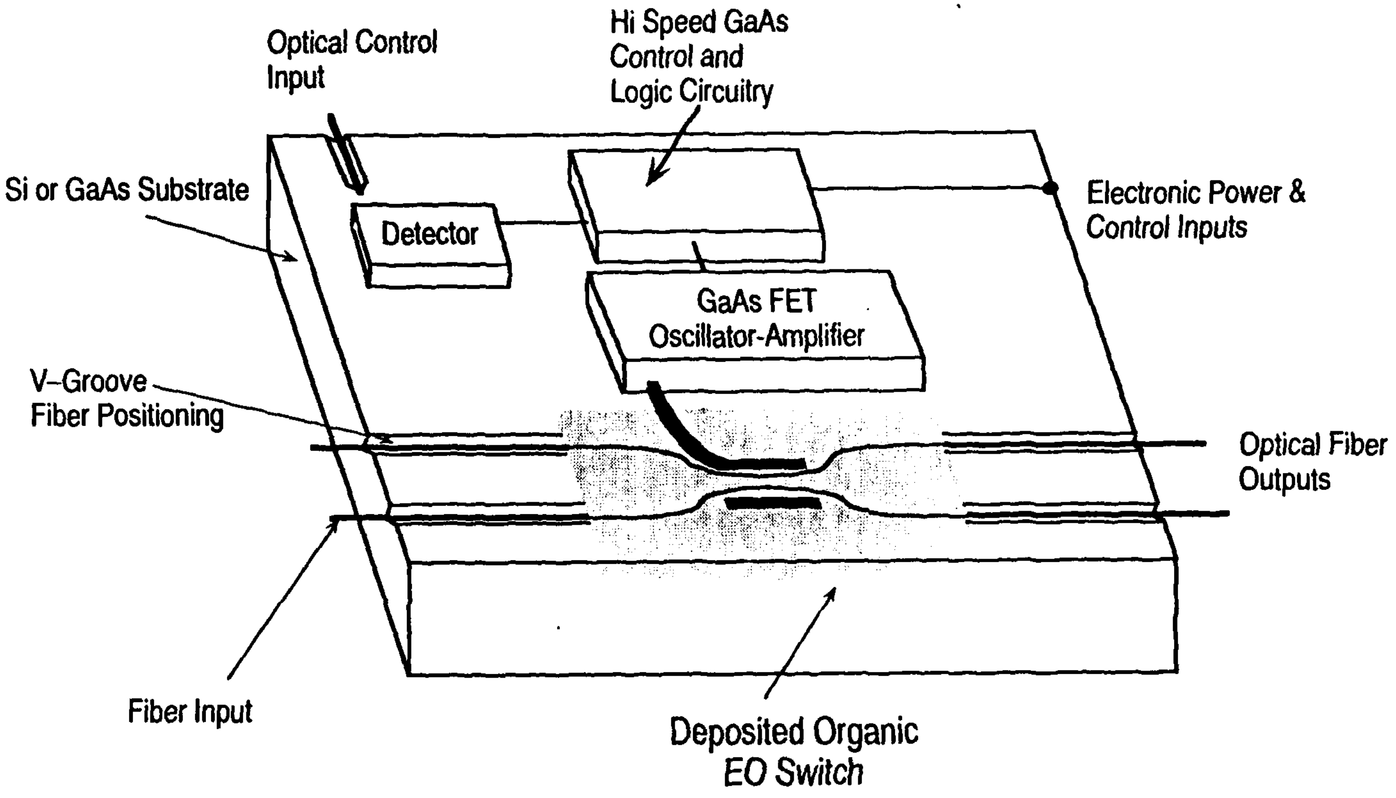
Oxygen Plasma Etching of Ridge Waveguide Structures in Electrooptic Polymers

RIE

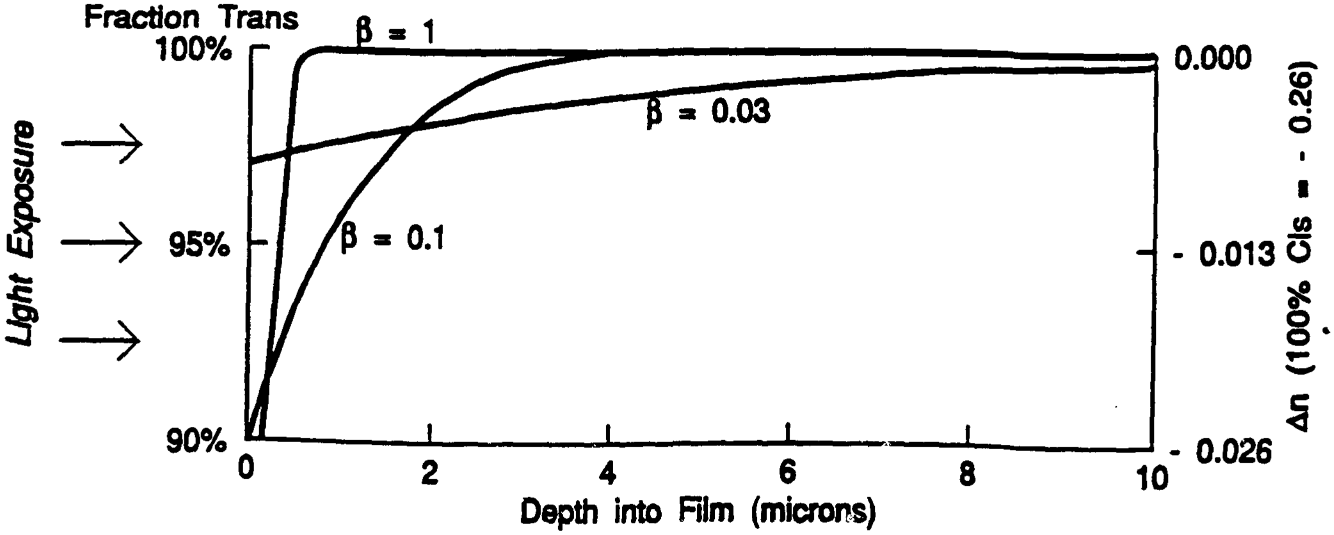


ECR

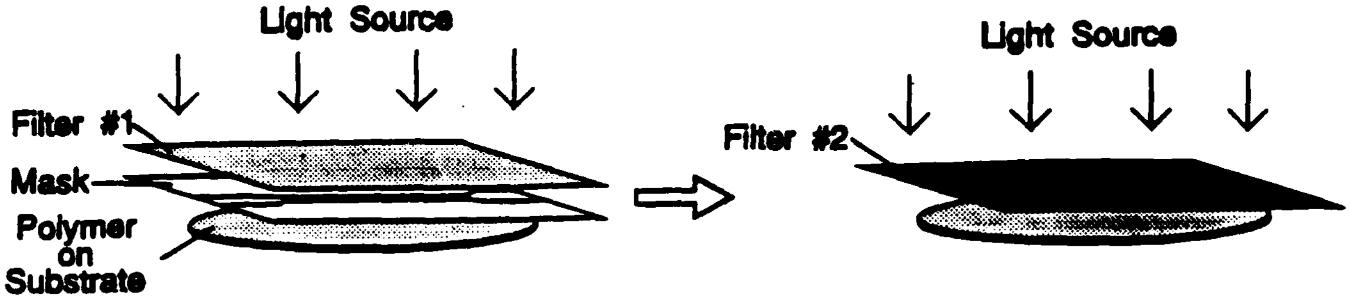
Concept of Polymer-Semiconductor Integrated Optoelectronics



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

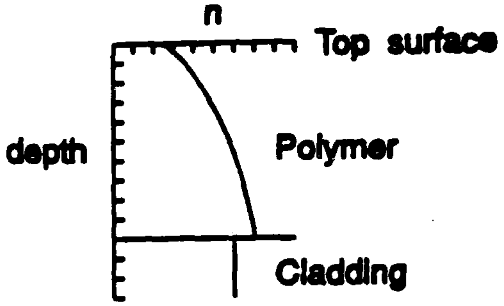


Fraction Trans
100%
95%
90%
Light Exposure
β = 1
β = 0.1
β = 0.03
0.000
- 0.013
- 0.026
Δn (100% Cis = - 0.26)
0
2
4
6
8
10
Depth into Film (microns)

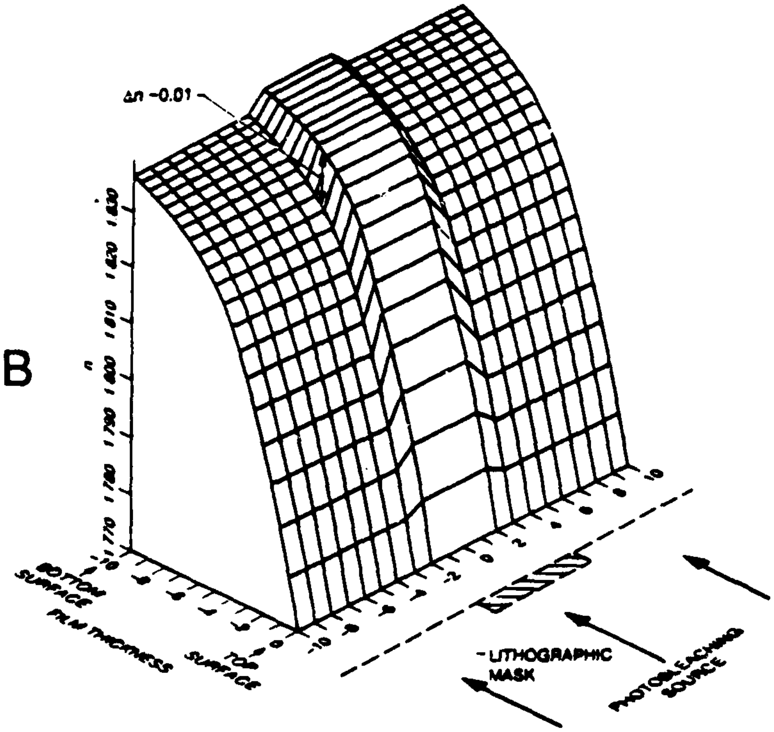


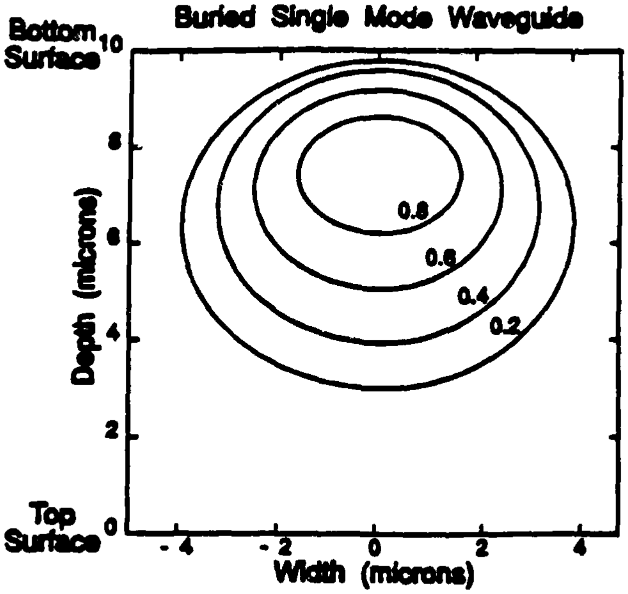
A

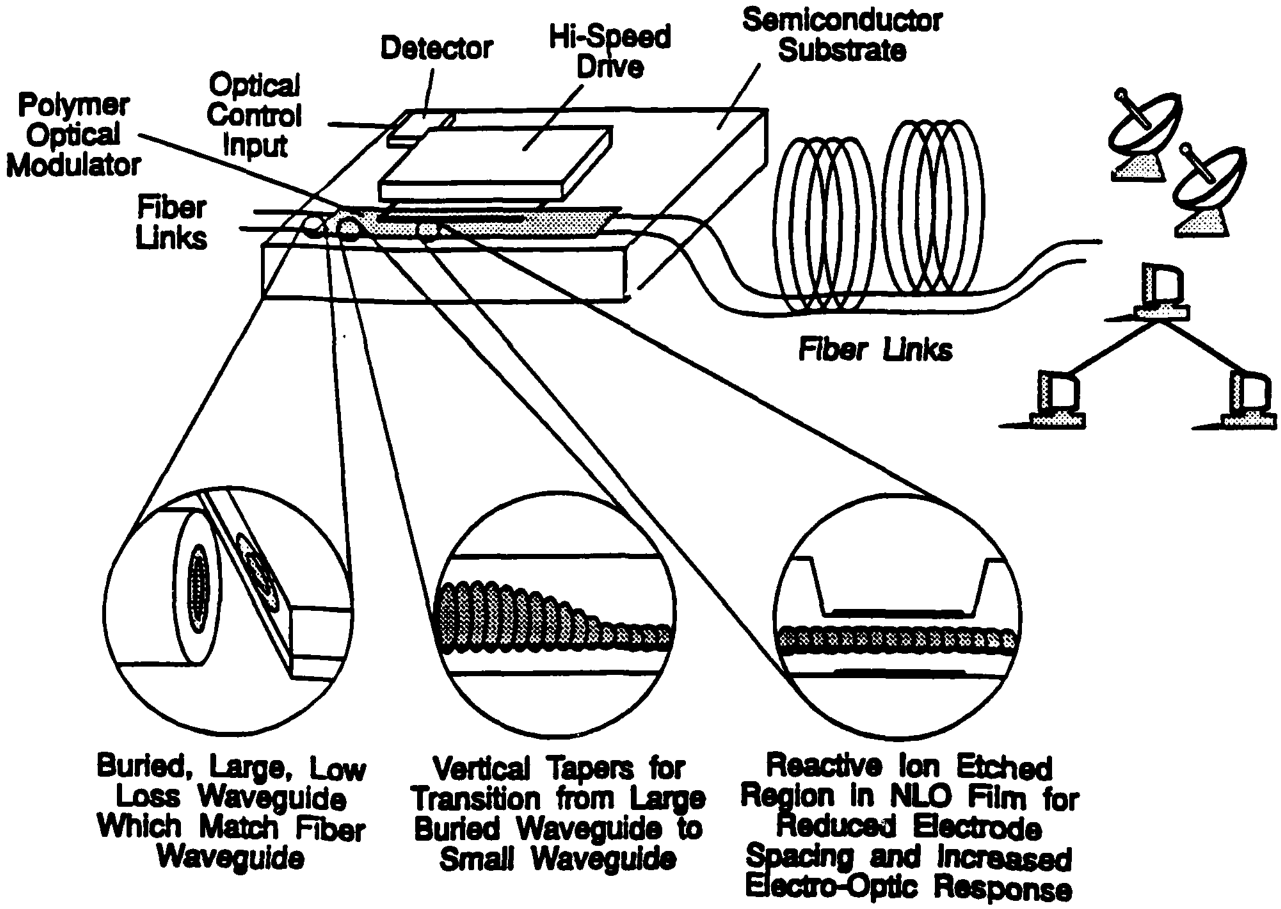
Small Δn gradients (large mode size)
Buried single-mode waveguides
All optical processing using standard lithography
Single cladding layer
Reduced thin film stresses
Reduced processing and higher yields



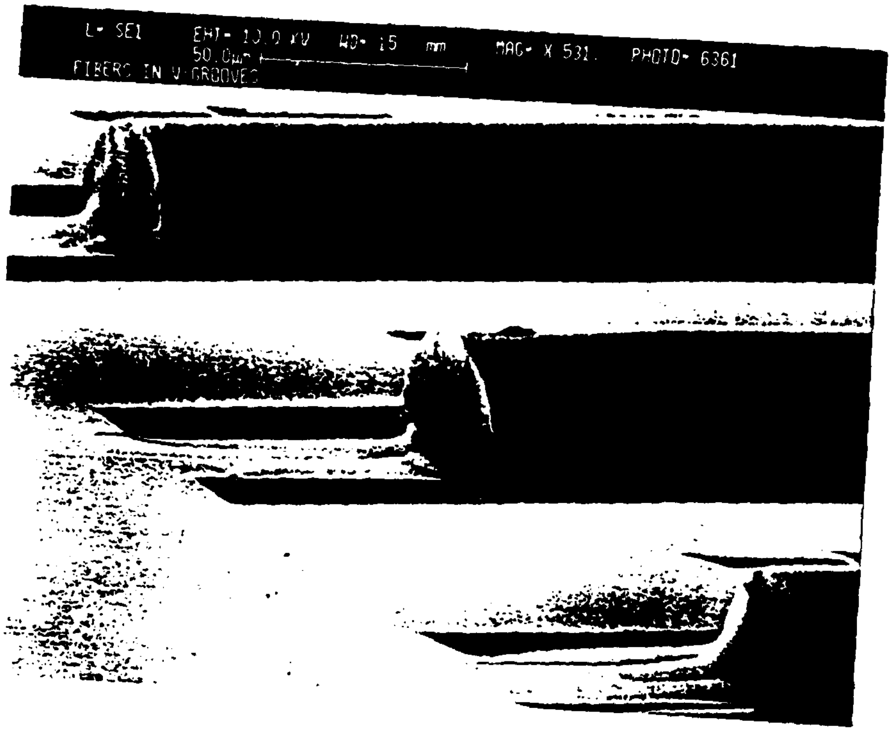
B

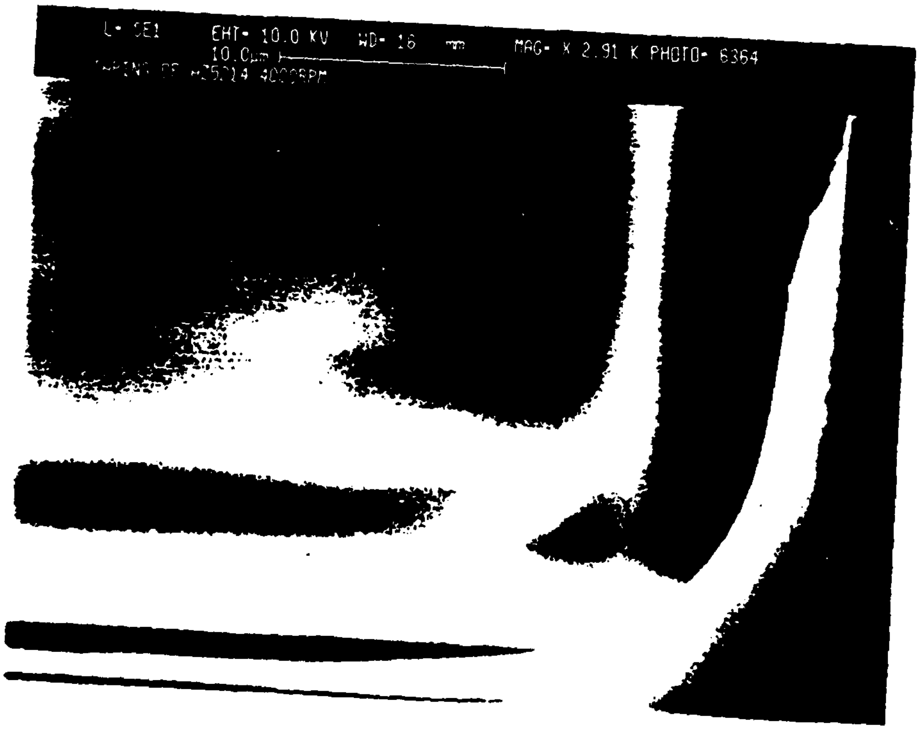




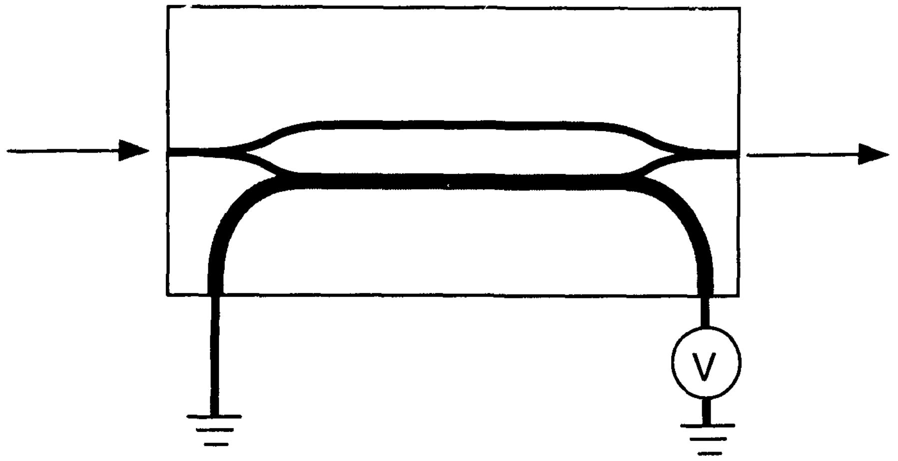

Detector
Hi-Speed Drive
Semiconductor Substrate
Optical Control Input
Polymer Optical Modulator
Fiber Links
Fiber Links
Buried, Large, Low Loss Waveguide Which Match Fiber Waveguide
Vertical Tapers for Transition from Large Buried Waveguide to Small Waveguide
Reactive Ion Etched Region in NLO Film for Reduced Electrode Spacing and Increased Electro-Optic Response

Spin-Coated Tapered Polymer Waveguide Array

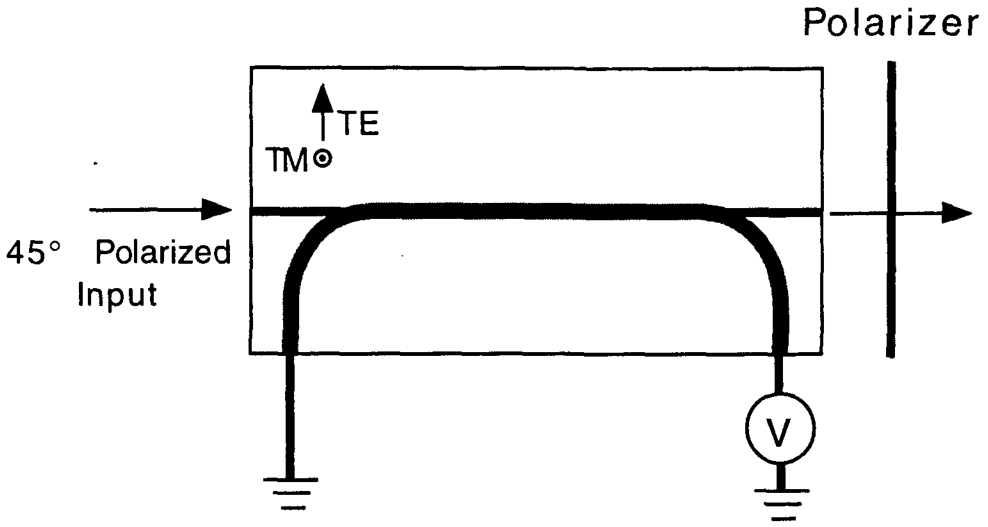




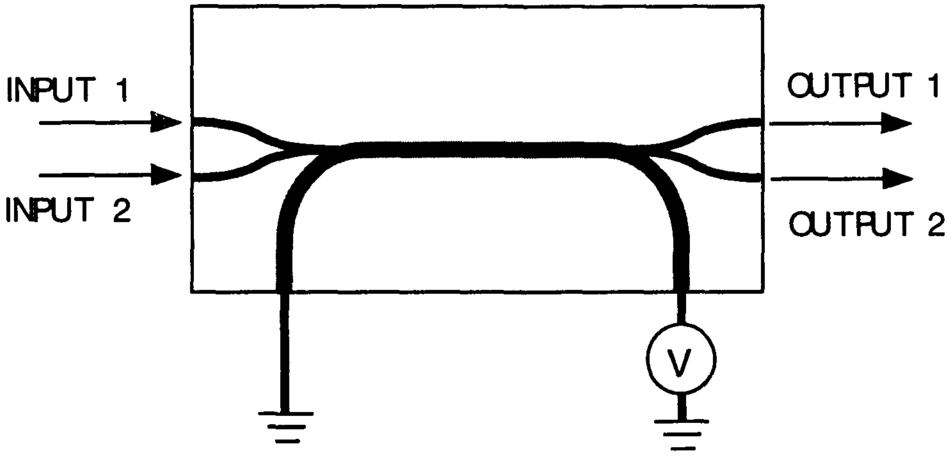
Tapered end
(side view)


V

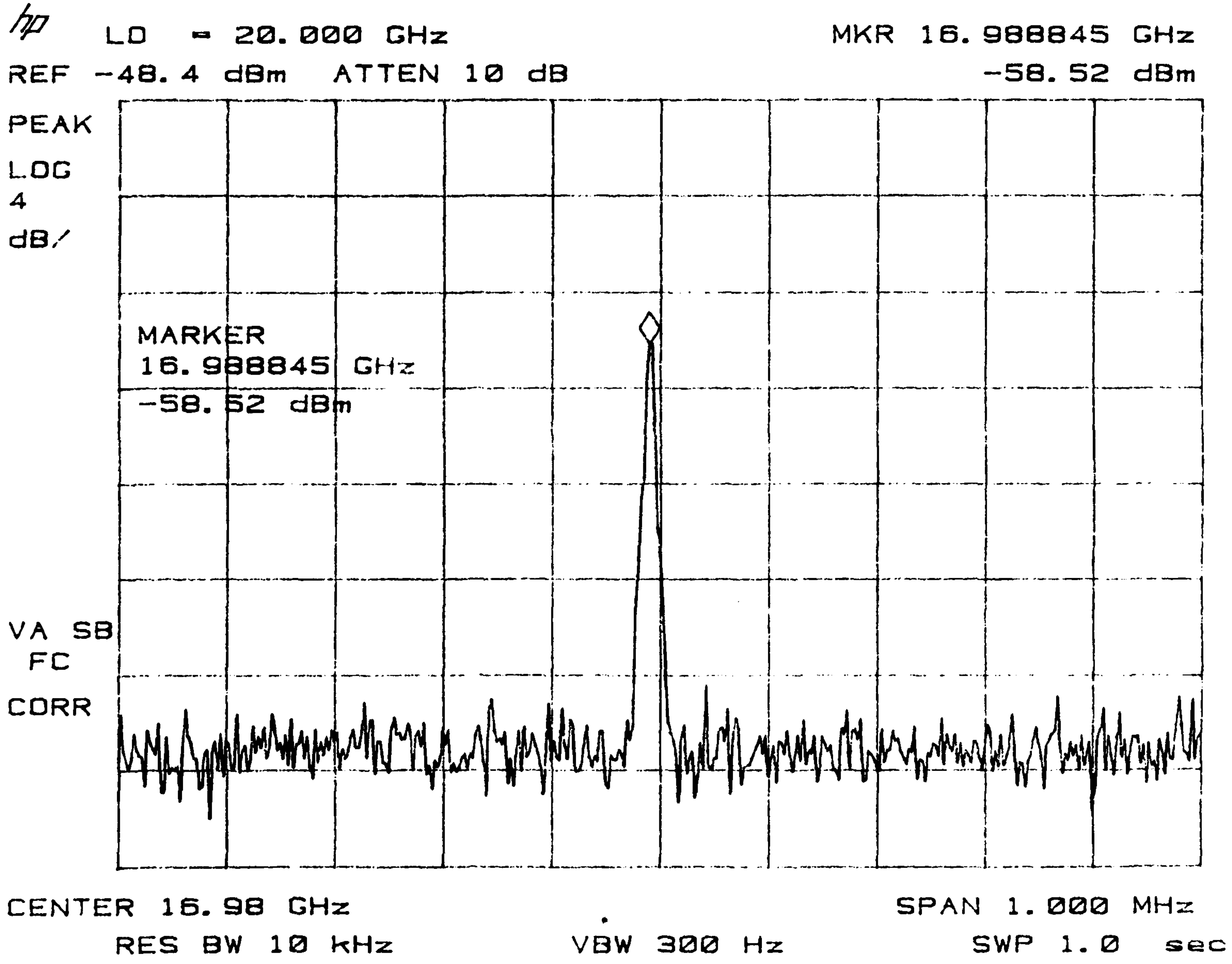
(a)

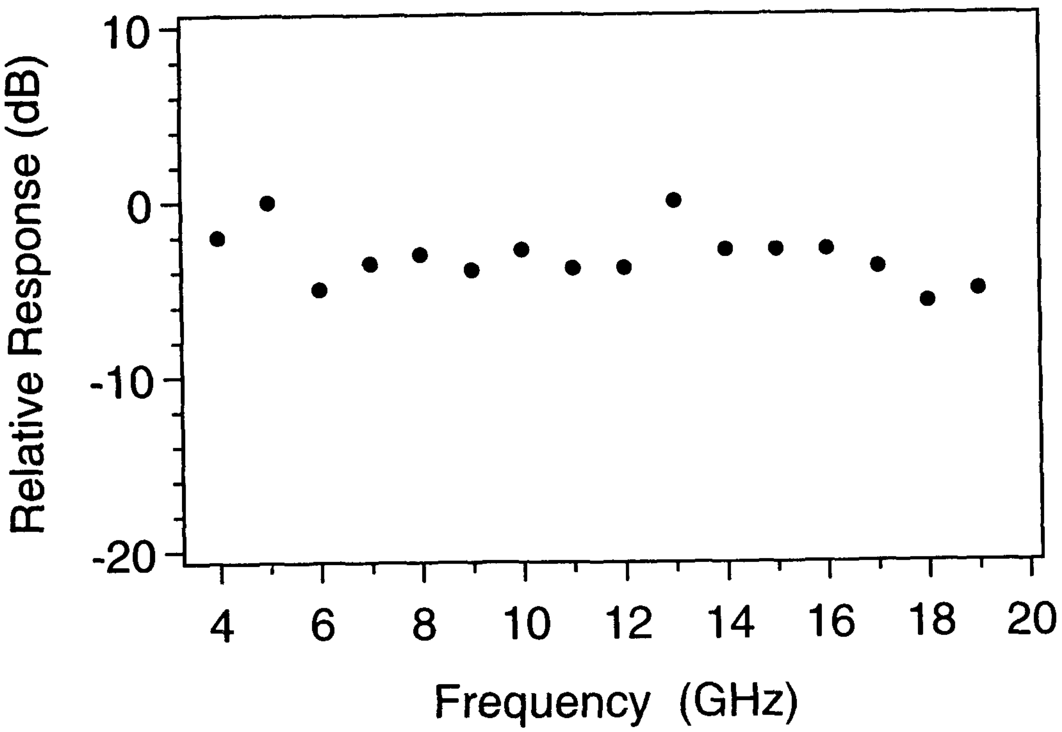

Polarizer
TE
TM
45° Polarized Input
V

(b)

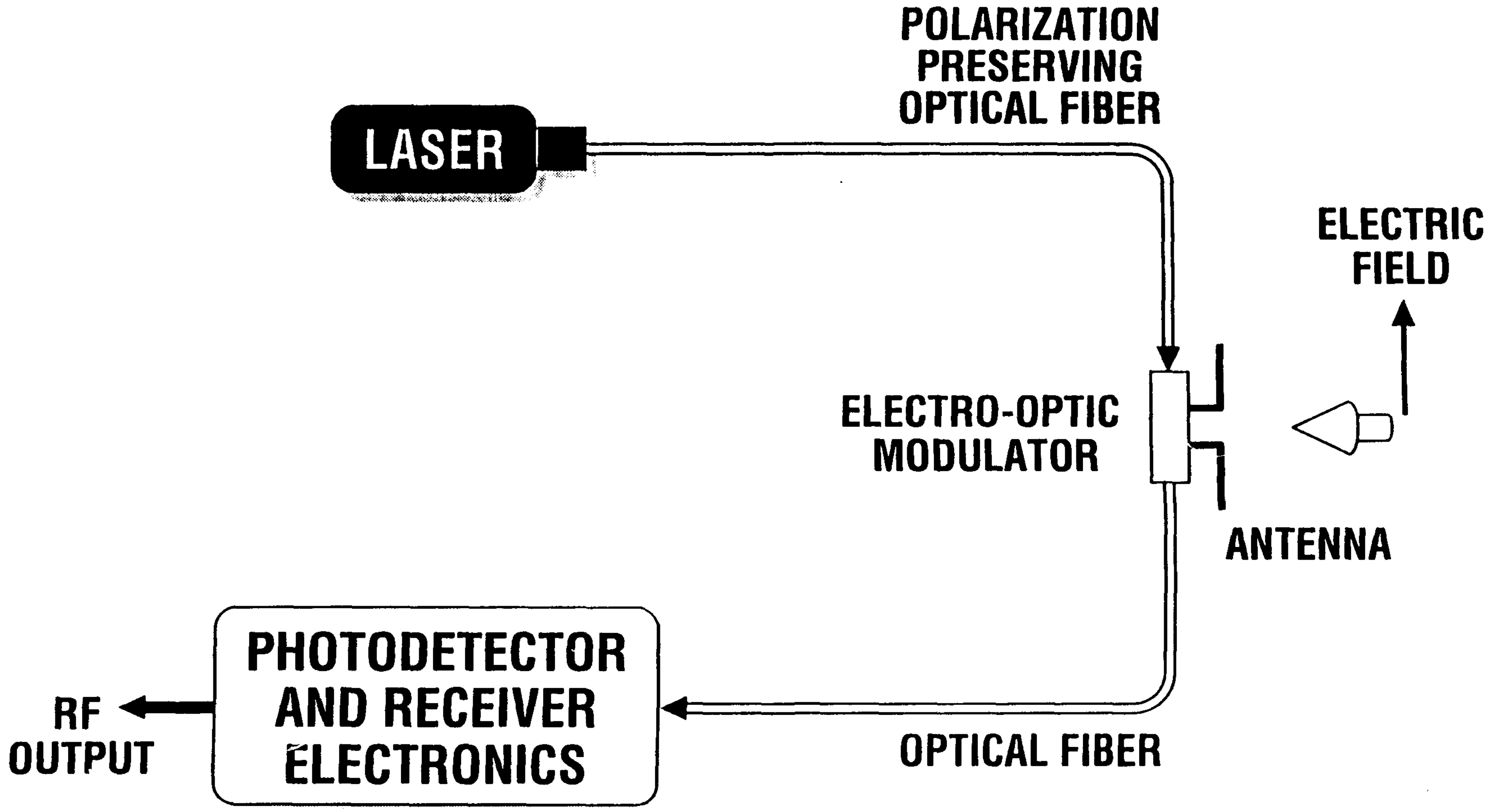

INPUT 1
INPUT 2
OUTPUT 1
OUTPUT 2
V

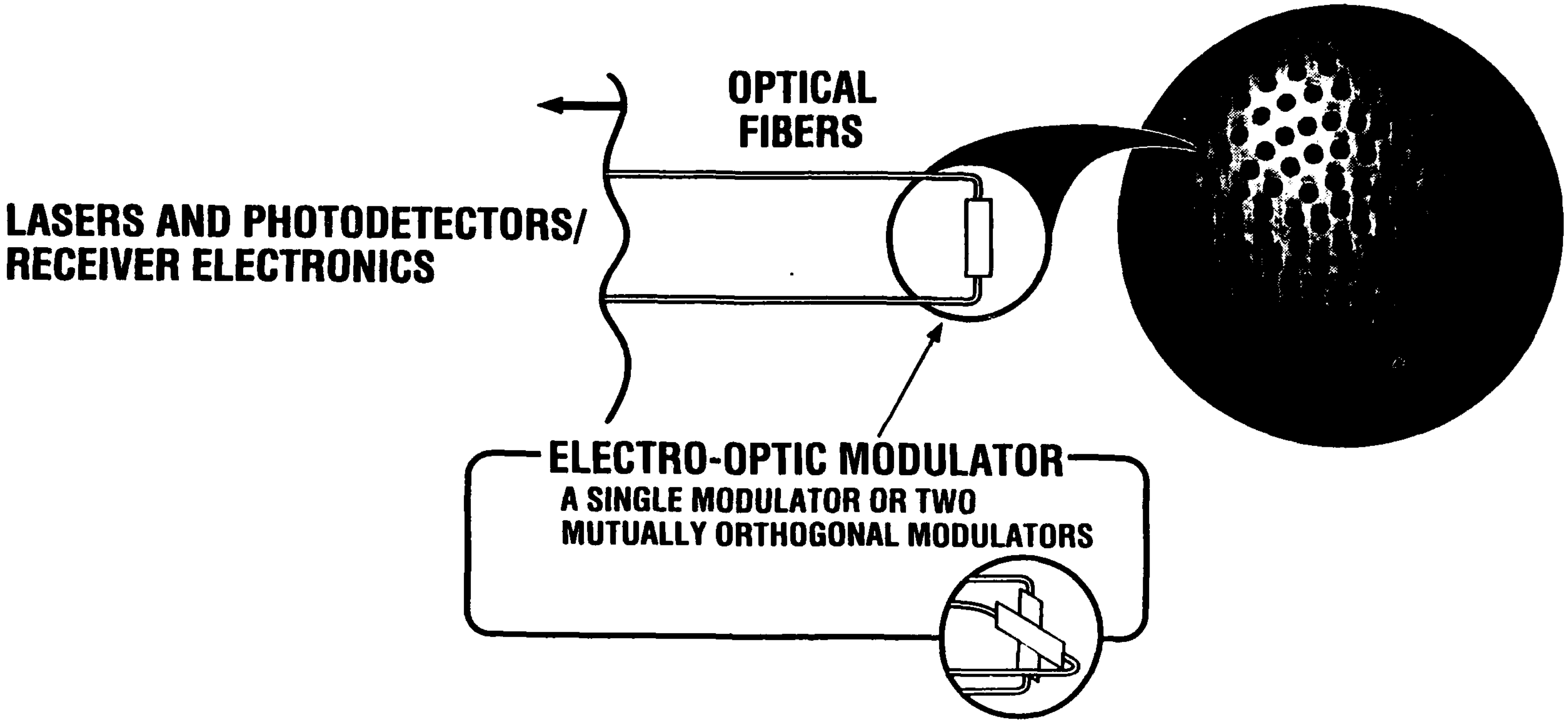
(c)

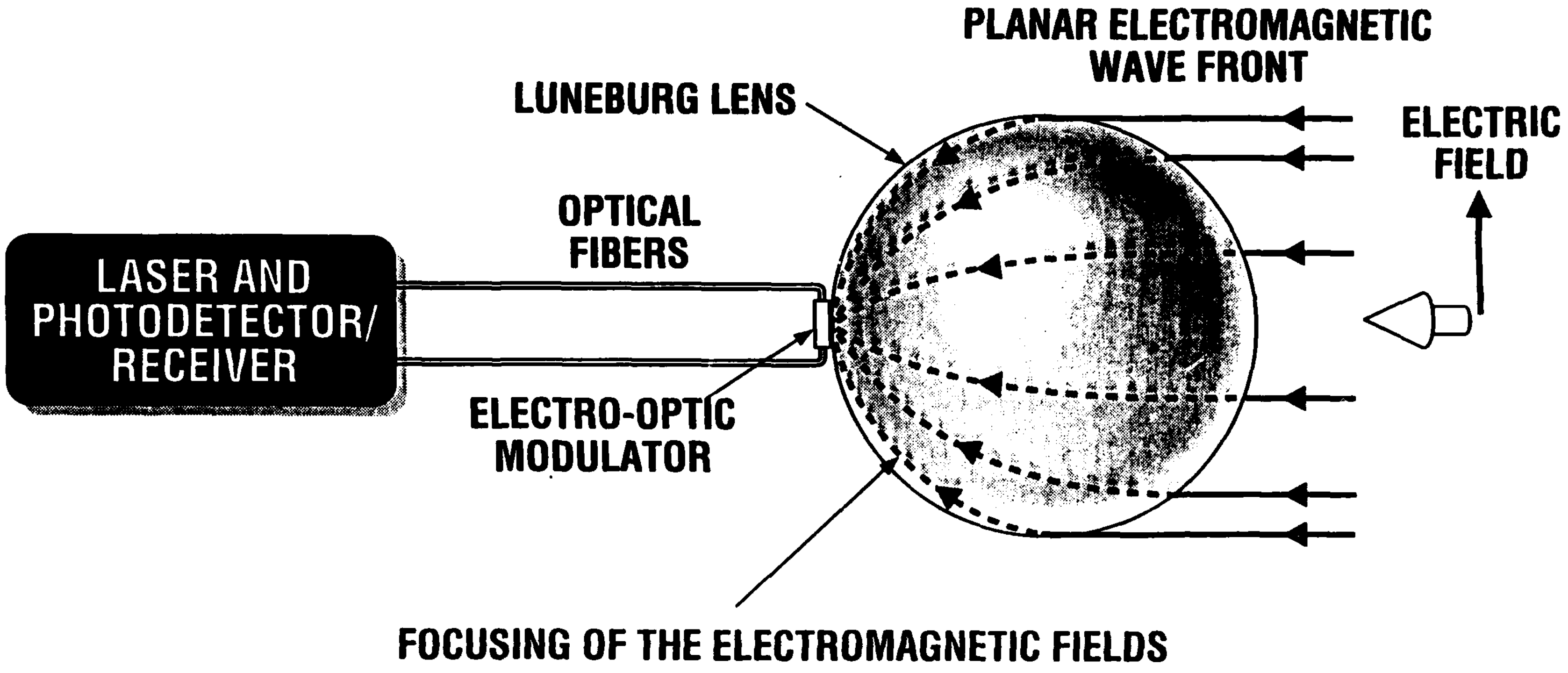

hp
LO = 20.000 GHz
MKR 16.988845 GHz
REF -48.4 dBm ATTEN 10 dB
-58.52 dBm
PEAK
LOG
4
dB/
MARKER
16.988845 GHz
-58.52 dBm
VA SB
FC
CORR
CENTER 16.98 GHz
SPAN 1.000 MHz
RES BW 10 kHz
VBW 300 Hz
SWP 1.0 sec



10
0
-10
-20
Relative Response (dB)
4
6
8
10
12
14
16
18
20
Frequency (GHz)


POLARIZATION PRESERVING OPTICAL FIBER
LASER
ELECTRIC FIELD
ELECTRO-OPTIC MODULATOR
ANTENNA
PHOTODETECTOR AND RECEIVER ELECTRONICS
RF OUTPUT
OPTICAL FIBER


OPTICAL
FIBERS
LASERS AND PHOTODETECTORS/
RECEIVER ELECTRONICS
ELECTRO-OPTIC MODULATOR
A SINGLE MODULATOR OR TWO
MUTUALLY ORTHOGONAL MODULATORS


PLANAR ELECTROMAGNETIC WAVE FRONT
LUNEBURG LENS
ELECTRIC FIELD
OPTICAL FIBERS
LASER AND PHOTODETECTOR/ RECEIVER
ELECTRO-OPTIC MODULATOR
FOCUSING OF THE ELECTROMAGNETIC FIELDS