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The origin and nature of nonlinear optical effects in organic and polymeric materials is discussed. Approaches to the applications of these nonlinear optical effects in prototypical devices is explored.

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Nonlinear Optics and Organic Materials

Elizabeth Cavicchi, Jayant Kumar, Sai Kumar, Sukant Tripathy

In glancing through a flat windowpane we immediately confront light's interaction with glass, but ignore it. We assume that the world's image is not perceptibly altered when light passes through the glass. Yet glass does play tricks with light: a penny viewed through a variety of lenses may appear the same size, magnified, reduced, or blurred. The shape of glass dictates the distortion of the image. The fourteenth century craftspeople who first formed pieces of glass into lenses to assist deteriorating vision progressed by trial and error. Even Galileo improved the lenses of his pioneer telescope without benefit of a practical theory of optics, through the exacting labor of grinding glass. The optical industry flourished for centuries before theory could minutely chart the interaction between light and glass.

Contemporary optics research is distant from common experience, seeking clues far more subtle than the shape of a piece of glass, with techniques more esoteric than abrasive polishing of a glass lens. The traditional dominance of glass in optics is now challenged by a host of synthetic materials exhibiting unusual optical behavior. Laser light of unmatched brillance both probes and incites these novel effects. A detailed understanding of the nature of light, and how it interacts with matter, is essential to evince these effects. Although everyday optical tools--window panes and eyeglasses--may remain unaffected, such delicate engineering has thrust optics along routes far removed from the crudely empirical development of geometrical optics. This paper will follow some of the newly laid routes into the domain of organic materials, whose unusual responses to light undermine some of our intuitive assumptions about optics. The molecular structure of these organic materials can be custom designed to amplify their optical properties. Novel devices based on the optical phenomena manifested by organic materials may revamp facets of communications and information processing technologies.

Refraction and Linear Optics

Both familiar and novel optical properties of materials depend intimately on the character of light. A beam of light can be simply modelled as a stream of many packages, all moving in a straight line at the same speed. Each package, a photon, is a self propelled carrier of energy and momentum. The package is composed of a pair of perpendicular electric and magnetic field vectors whose magnitudes and directions oscillate periodically. The frequency of this oscillation dictates the "color", momentum, and energy content of the package; higher frequencies correspond to greater energy and momentum. The oscillations of different photons are "in phase" if their magnitudes peak simultaneously. If the peaks are aysnchronous, the field vectors cancel and the light disappears.

When light in air enters a denser, transparent material, such as glass, its electric field induces a slight separation between the positive and negative charges on each molecule in the material. Negative charges attempt to orient toward the instantaneous positive direction of light's field and vice versa. The *dielectric constant* ε is a measure of this response of charges in a material to an applied(usually dc) electric field. A small electric field, which reflects the molecules' spatial arrangement, is created by the polarization of charge. Its direction opposes the incident field; it oscillates asynchronously with light. This field, induced by light, in turn alters the direction and diminishes the magnitude of the field of light. As a consequence, the speed of light is reduced within the material. Light's fields perturb charges in the material to follow its dance and the material, through an induced field, perturbs light. Although this interaction occurs microscopically, it has a familiar macroscopic effect: *refraction*. When a pencil partially immersed in water appears crooked or a lens focuses a bright spot of light, we observe refraction.

The *index of refraction*, n, the ratio of light's speed in free space to its speed in a material, is a characteristic of the material. Although light of all "colors" travels at the same speed in free space, its speed inside a material varies slightly with "color"(i. e. frequency); the index of refraction is frequency dependent. When light's frequency approaches one of the material's built-in natural frequencies, the molecules oscillate sympathetically, absorbing more of light's energy. A prism sorts white light into a rainbow by deflecting the higher frequency bluer "colors" further from the path of the incoming beam. Ordinarily, a material's index of refraction is not affected by the brightness of the light shining on it. This enables us to use the same pair of binoculars to focus on a faint star at night and a bird in daylight(*1,2*).

Intensity-Dependent Nonlinear Effects

However, when laser light is directed upon a material, entirely different properties, microscopically sensitive to a precise match between light and the material, can be evoked. The high intensity of a laser beam can produce an electric field which rivals and disrupts the internal electric field of atoms in the material. The closely correlated oscillation phases or *coherence* of a laser beam produce a well defined field pattern, persistent in space and time. This can evoke complex, collective behavior in an ordered material system. The interaction between light and the material can now *drastically* alter each other in a unique fashion.

In conventional circumstances, when two light beams cross each other, the departing photons in one beam appear unaffected by the other beam . But if two light beams coincide while traversing certain special materials, the departing photons may become distinguishable from the incident photons. The first beam alters the material's optical behavior; the second beam, arriving while the influence of the first is still in sway, "sees" a different material. Its future course diverges from that observed in the absence of the first beam. Once the optical field has departed, the material gradually reverts to its unperturbed state; the duration of this relaxation is the material's characteristic *response time.* A light beam emerging from such an interaction is often qualitatively changed, for example in frequency or intensity, or refracted direction from the incident beam. This behavior is termed *nonlinear optics*; the input and output beams cannot be related by a simple proportionality(*3*).

A myriad of events occurring at the intimate scale of local interaction between light and the material can induce large-scale nonlinear effects. The laser beam's electric field can contort the shape of atoms by drawing the electrons toward its direction, or by inciting electrons to jump to a different electronic orbit. The atoms' arrangement in the three dimensional matrix of the material can shift, as the field pulls oppositely on the positively and negatively charged atoms. The field can induce an array of randomly oriented molecules to align uniformly along its direction. Bonds between atoms can be stretched or even be broken by the electric field. If the beam's intensity is increased, so is its electric field, evincing more pronounced distortions in the material. Yet a two-fold increase in light intensity will not induce a two-fold increase in distortion; the extent of distortion is contingent upon the material's inherent electronic properties. Any disruption of the material's charge configuration will be macroscopically observable as a change in light's speed and refraction.

A century ago, researchers found that strong electric fields could alter the optical properties of materials. Kerr showed that light passing through glass refracts differently along the direction of an applied electric field than along a perpendicular(*4*). Ordinarily, glass is isotropic; it exhibits the same refraction no matter what the angle of incident light. Pockels discovered the same behavior in crystals lacking a center of symmetry(*5*). However, it was not possible to change the way materials refract light using the electric field of light itself until the laser was invented. The light-induced optical effects can be more dramatic than the processes observed by Kerr and Pockels. An intense laser beam can induce a discontinuity in the way the material within and outside the beam's path refracts light. This discrepancy, for example, may create a lens embedded in the material which focuses the beam to a remarkable bright, narrow spot. The laser beam's energy, focused by the lens to a point, can even damage the material. In optical fibers, uncontrolled "self-focusing" of light, caused by the materials' nonlinearity, can disrupt both the transmission and the fiber.

Optical Harmonics

The seminal experiment in nonlinear optics was conducted by Franken in 1961(*6*). A beam of red light from a ruby laser was directed through a quartz crystal. Light emerging from the crystal included both a red and an ultraviolet component: the frequency of the ultraviolet component was precisely double that of the incoming red light. This doubled frequency is called the *second harmonic* in analogy with acoustics, where the higher harmonics of a fundamental tone are integer multiples of the fundamental's frequency. While the rich quality of musical sound derives from the simultaneous vibration of an instrument's string or air column at the fundamental and its harmonics, the world would look quite different if optical harmonics were commonplace. Light photons ordinarily do not interact with each other to change their frequency. White light which has passed through a piece of blue glass appears blue only because the glass absorbed all but the blue light; the glass did not transform photons of one "color" into another "color".

In the year following Franken's discovery, Bloembergen explicitly derived these optical effects by incorporating perturbing motions of electrons and charged atoms into the quantum mechanical model of light's interaction with matter. His study became the theoretical foundation of nonlinear optics, for which he was awarded the 1981 Nobel Prize(*7,8*).

A material exhibiting optical nonlinearities can override the noninteracting nature of photons. The material mediates the interaction; the energies of two incident photons may be added, producing a new photon at the combined energy. When the new photon is released, the difference in momentum between the incoming and outgoing photons may be absorbed by the matrix of the material. If two laser beams of different frequencies impinge upon a material, a light output of more diverse frequencies is possible. A material interacting with photons of inequal energy may emit that energy in a single photon at the total combined energy, or as several photons, splitting the total energy between them: for example, one bearing the difference energy and two at the lower of the two incident energies. The material facilitates these transformations without being affected itself; it acts as a catalyst.

When photon energies are combined to create photons of a new color, the light beam's refractive speed, which depends on "color", changes. The incident and resultant beams each travel at different speeds because of their different frequencies. At its creation, each new photon oscillates in phase with its parent photons. However, since the pace of the child beam differs from its parent, the oscillation phases of photons emitted by widely separated atoms will fall out of synchronization. These out-of-phase oscillations will cancel, diminishing the intensity of the new beam. In order for optical harmonics and mixture frequencies to be observable, the material's refractive properties must be manipulated to prevent phase cancellation. Sometimes by either heating or rotating the material, the speed of the incoming light travelling along one direction can be matched to that of the outgoing beam, travelling along a perpendicular. Then the phases of the newly created photons will remain synchronized. An even more stringent condition governs the combination of two photons with different frequencies to produce a third, or more. If the speeds of all three beams are not matched, phase cancellation will negate the effect(*9,10,11*).

Materials and Nonlinear Optics

Light and material must be tailored to precisely complement each other before these unusual effects can arise. Light's electric field interacts with and disrupts the electrical environment internal to the material. By systematically tweaking a material's molecular structure, its interaction with light can be analyzed. Insights derived from these studies of light and matter can shape the design of new materials with an enhanced nonlinear response to light.

The detection of nonlinear optical behavior in ordinary materials is elusive; ideally the material must possess superior optical quality--transparency, freedom from defects that scatter light, uniformity, a polished surface--in addition to sustaining the matching of light's refractive speeds. Inorganic materials traditionally associated with optics such as quartz and the new semiconductors initially received the dominant attention. For example lithium niobate, which can be grown as single crystals, satisfies many of these criteria; however, further enhancement of these properties is desirable. Several organic materials match--and may exceed--lithium niobate's efficiency in generating optical harmonics, yet deficiencies in other properties, such as phase matching ability, may hinder their practicality(*12*).

Table 1. Second Order Nonlinear Optical Properties

Material	n	ε	$d_{ij} \times 10^{-12}$ m/v
KDP	1.47	42	$d_{36} = 0.45$
$LiNbO_3$	2.3	78	$d_{22} = 2.3$
		32	$d_{33} = 40$
MNA (2 Methyl-4 nitroanaline)	1.8	4	$d_{11} \sim 250$
DAN (4-(N, N, dimethylamino-3-acetamonitrobenzene)	1.71	4	$d_{eff} \simeq 27$

Results of some comparative studies of the nonlinear optical behavior of inorganic and organic materials are summarized in the two tables. Table 1 lists parameters relevant to the production of second order optical harmonics: the index of refraction, n, the dielectric constant, ε, and a directionally dependent measure of the second order effect, d. Materials with a high dielectric constant ε, respond sluggishly to the stimulus of light's electric field. In this respect, MNA(methyl nitroanaline, see Figure 1), with a 1/20 lower dielectric constant and a hundred-fold higher second order coefficient than lithium niobate, would be preferable for applications in which a quick response time is critical to the operation of a device(The nature of these devices will be described later).

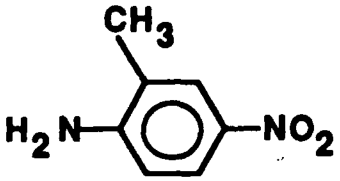


Figure 1. Molecular structure for MNA (2-methyl-4-nitroaniline) CH_3 and NH_2 are electron donors and NO_2 is electron acceptor

Table 2 gives characteristics pertinent to the third order harmonics: index of refraction n, a third order index n_2, and the response time. Again, the organic materials excel both in rate of response and in magnitude of the third order effect. Inorganic materials typically must compensate for changes in their electrical environment by shifting the position of atomic nuclei, a slower process than the electronic motions which perform the same function in organics. The inherently rapid electronic perturbations in organics--orders of magnitude faster than switching times in electronic devices--have potential for inclusion in information processing systems.

Table 2. Third Order Nonlinear Optical Properties

Material	n	n_2 (esu) (10^{-11})	Response Time (in seconds)
GaAs <100>	3.20	14.1	$< 10^{-12}$
Si <111>	3.44	8.8	$< 10^{-12}$
CS_2	1.59	1.1	$< 10^{-11}$
Fused Silica	1.458	0.0095	$\sim 10^{-14}$
PTS Polydiacetylene	1.88	80.0	$\sim 10^{-14}$
MNA (2 Methyl-4-Nitroanaline)	1.8	25.0	$\sim 10^{-14}$
p. nitroaniline		14.0	$\sim 10^{-14}$

The optical and electrical properties of a material directly proceed from the identity of its component parts--atoms and molecules--and from the arrangement of these parts into a superstructure. Inorganic materials are constituted of a limited range of atomic species; improvement of nonlinear performance must be sought through a change in crystal structure rather than by subtle modifications to the molecule. This is a daunting prospect, as the material may exist only in a specific crystal form; even if other structures exist, the effort to grow a new form of crystal is typically laborious, and protracted. Organic molecular structure, however, can be modified incrementally, by making small changes in the backbone or substituents. In this way, the chemist can fine-tune the material's response to light as well as its other chemical and mechanical properties.

Organic Materials and Nonlinear Optics

A conjugated backbone appears to be crucial to the ability of polymeric molecules to generate third harmonics. The pi electrons, smeared out along the backbone, react quickly to changes in the electrical environment imposed by another molecule, an electric field, or light. This quick response and the extensive spreading of the π-cloud is the source of a sizable, fast third order response in these quasi one-dimensional systems.

The class of polymer polydiacetylenes has emerged as one of the more promising prospects for third order nonlinear effects. The third order index n_2 of polydiacetylenes(Figure 2) is one of the larger indices demonstrated to hold within the range of a material's transparent frequencies. Their response time is predicted to be in the subpicosecond range(see Table 2). Organic molecules with other nonlinear behavior, such as second order effects, can be integrated into the diacetylene through the side groups. The pi-electrons are polarizable along the length of the macomolecular backbone. This extensive conjugation, both in the substituents and the backbone and their interplay together, may be responsible for a broad range of nonlinear phenomena not possible in a single monolithic inorganic system. The side groups, R and R' can be varied and modified to optimize their optical, mechanical, and processing properties(*13*).

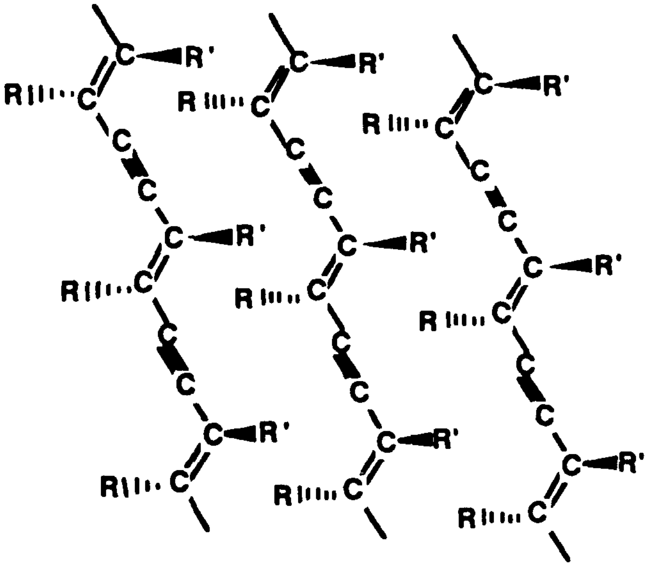


Figure 2. Polydiacetylene chains in a crystal; R is an electroactive side group and R' is a surfactive group

The *molecular hyperpolarizability* β is a measure of a molecule's *tendency to exhibit second harmonics. Two terms contribute to the* hyperpolarizability: an asymmetry term, β_{ass}, and a charge-transfer term, β_{ct}. A greater asymmetry in the way charge is distributed along a molecule will induce a more pronounced interaction with light's electric field. Second harmonics, however, will not occur at all if the molecule crystallizes or assembles with a center of symmetry. The charge-transfer term describes the extent to which light's field induces transitions from the molecule's ground state to its excited--or *resonance*--state. Since a crystal lattice of organic molecules is stabilized primarily by weak van der Waals forces, its *macroscopic second order behavior can be regarded as an* averaged sum of these molecular hyperpolarizabilities.

This correlation between structural and optical properties can be demonstrated by the example of DANS, or 4-dimethylamino-4'-nitro stilbene(Figure 3). The -C=C-bridging group confines the molecule to a plane, extending conjugation from end to end and stabilizing its resonance structure. In the resonance structure drawn in Figure 3, positive and negative charge are maximally separated, producing a large internal electric field. The electron-donating(dimethlylamino) and electron-withdrawing(nitro) groups create an asymmetry in charge. In this case, the charge transfer term dominates: for DANS the estimated value of $\beta_{ct}=3.8*10^{-32}$ esu is very close to the experimental determination of $\beta_{total}=4.5*10^{-32}$ esu.

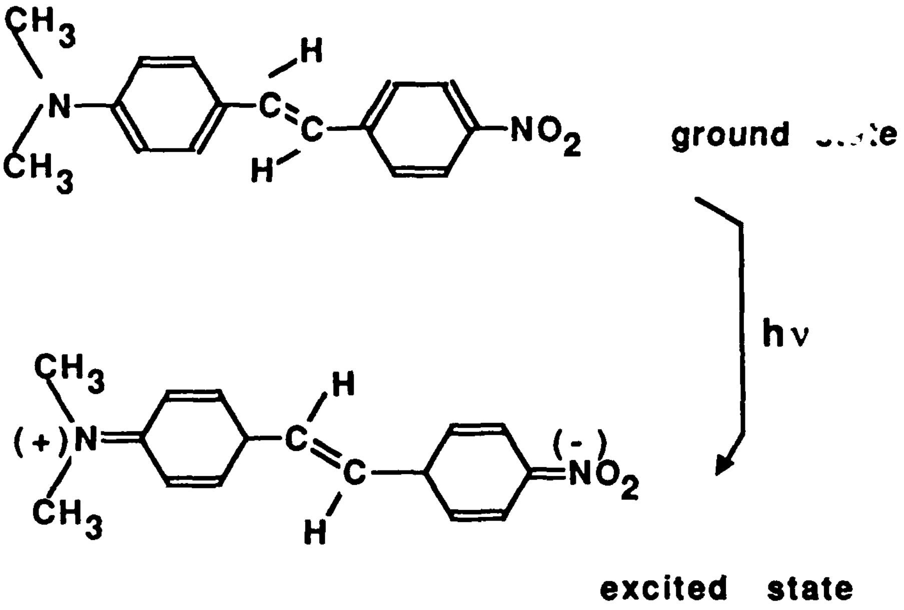


Figure 3. Molecular structures of the ground and resonance excited states for DANS (4-dimethylamino-4'nitro stilbene); $N(CH_3)_2$ is electron donor and NO_2 is electron acceptor

Key parameters extracted from the ultraviolet and visible spectrum of DANS confirm these results. The calculated probability of a transition from ground to resonance state(related to β_{ct}) is very high. In addition, the molecule's polarization--the separation of charge--in its resonance state is four times greater than in the ground state. This suggests that a molecule which admits a large charge separation in converting to its resonance state will possess a substantial hyperpolarizability. This observation is a possible blueprint for the design of molecules with enhanced nonlinear behavior. Its guidelines may assist in the selection of optimum molecular structures from the large palette of organic molecular structures available.

Organic materials satisfy other practical requirements for nonlinear optics. They may be selected and tailored to be transparent to light of frequencies convenient for experimentation and applications. The frequency range from near-infrared to visible, uncommon among inorganics, is of particular interest at present. In addition, light usually travels at markedly disparate refractive speeds when it is directed along different axes in organic crystals; this phenomenon is termed *birefringence*. This facilitates the effort to match the phases of the incident beam with the optical harmonic, necessary to prevent cancellation of the harmonic(*14*). Although organic molecules can be designed with an asymmetric structure, such as DANS, often they crystallize in a symmetric configuration. This precludes production of second harmonics. Alternative techniques for crystal growth must be devised to circumvent this drawback. A recently developed technique embeds active molecules within a polymer host, where, following alignment in an electric field, they are available for use in nonlinear experiments. This remarkable approach bypasses the stringent demands of crystal growing.

In part II, our attention shifts from the theoretical foundations of nonlinear optical behavior in polymers to the more practical agenda of processing these materials and incorporating them into optical devices. The techniques of casting, crystallization, and thin-film multi-layer growth are adapted for the production of the appropriate form of the polymer which retains its nonlinear function. Through the active component of an optical device, i. e., the nonlinear material, a light beam or imposed electric field operates on the incident light by switching it or altering its information content. The emergent light beam bears the imprint of the nonlinear interaction as a change in its frequency, direction, or intensity.

Nonlinear Optics and Organic Materials
Part 2

Elizabeth Cavicchi, Jayant Kumar, Sai Kumar, Sukant Tripathy

How much time left 'til lunch?

How many miles per gallon this past week?

Before answering one of these questions, you will probably glance automatically at figures imaged on a surface by nonlinear optical phenomena--the liquid crystal display. In many watches or calculators, the screen is made from a thin liquid crystal layer sandwiched between two glass plates. In one display configuration, the inner surface of each glass plate is lined with a transparent conducting grid. Variations in the electrical signal at each point on the grid can reorient the liquid crystal molecules and change their optical absorption. The inexorable progression of digits marking seconds of time is a commonplace, visible indicator of the modification of light in a nonlinear interaction with matter. Part II of this article will explore other novel devices based on nonlinear optical behavior of polymers which may eventually proliferate in the everyday components of our culture as has the liquid crystal display.

The invention of the laser has revealed a myriad branching cascade of related optical phenomena whose existence was demonstrated and probed by the laser's superior intensity, coherence, and monochromaticity. The oscillating electric fields of laser light are strong enough to compete with the inherent electric fields of atoms and molecules in a sample. The interaction between incident light and a material perturbs both: light's frequency or direction may be altered, while the atom's electronic cloud may become distorted, creating a charge dipole or even flipping the molecule's orientation in space. The incident light beam is qualitatively distinguishable from the emergent light beam: light has undergone a nonlinear interaction while traversing the material.

Some organic materials have exhibited pronounced nonlinear optical behavior. These effects appear to be augmented in polymers with a conjugated backbone or with side groups that are susceptible to assymetric charge polarization under the influence of an external electric field, such as light, among other possibilites. Molecules or side groups with this configuration(such as methyl nitroanaline) are able to sustain a large charge separation between excess positive charge at one end, and negative at the other, thus generating a molecular electric field that can, in turn, interact with light's field. It may be possible to fine-tune the nonlinear response of a material to advantage in a given application by tinkering with the polymer's structure in modifying its side groups or backbone geometry. The current interest in organic nonlinear materials derives from this multifaceted potential for molecular "engineering".

Processing Techniques for Organic Materials

Despite their exceptional nonlinear response to laser light, organic materials have not yet supplanted inorganics such as lithium niobate in applications. The crystalline forms of organic molecules are often characterized by poor mechanical strength and rapid degradation when subjected to radiation and reactive chemicals. Organic polymers, however, are notably resilient, resistant to environmental invasion, and manipulatable into objects of desirable shape. This suggests a research strategy to incorporate active organics exhibiting nonlinear optical properties into polymeric structures, thus synergizing the advantages of both.

In one method of achieving a nonlinear polymer system, the active organic(for example, DANS) is dissolved in an optically transparent matrix of polymers such as poly(methylmethacrylate) or poly-carbonate. This matrix is termed a *guest-host material* because the active molecule is not chemically bonded with the polymer medium, but only homogenously dispersed in it(5-10% by weight).

A liquid of guest-host preparation can be poured onto a mold and solidified by cooling, polymerization, or solvent evaporation, or spin coated on suitable substrates. In the next step, the thin film produced by either method is heated above its glass transition temperature and subjected to a strong electric field. The active organics align with the field and are frozen in position as the film cools, producing a useful material for nonlinear optics experiments, as depicted in Figure 4. However, the limited solubility of most active organics in the polymer and their tendency to segregate or migrate out of orientation impose limitations on the choice of guest-host combinations and their suitablity in applications.

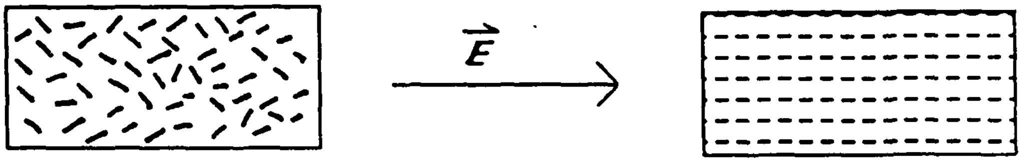


Figure 4. Influence of applied electric field ($\vec{E}$) on the molecular orientation in a guest-host matrix

In an alternative approach, the active organic molecules may be covalently attached to the polymer backbone, analogous to the teeth of a comb(Figure 5). The polymer backbone may be devoid of nonlinear properties, such as the acrylics, or it may be active as the polydiacetylenes are, thus enhancing the material's response to light. Its substitutent teeth can be chemically modified following polymerization, allowing the chemist further flexibility. The comblike structure can be processed by procedures used with guest-host materials: heated, oriented in a field, and frozen in place.

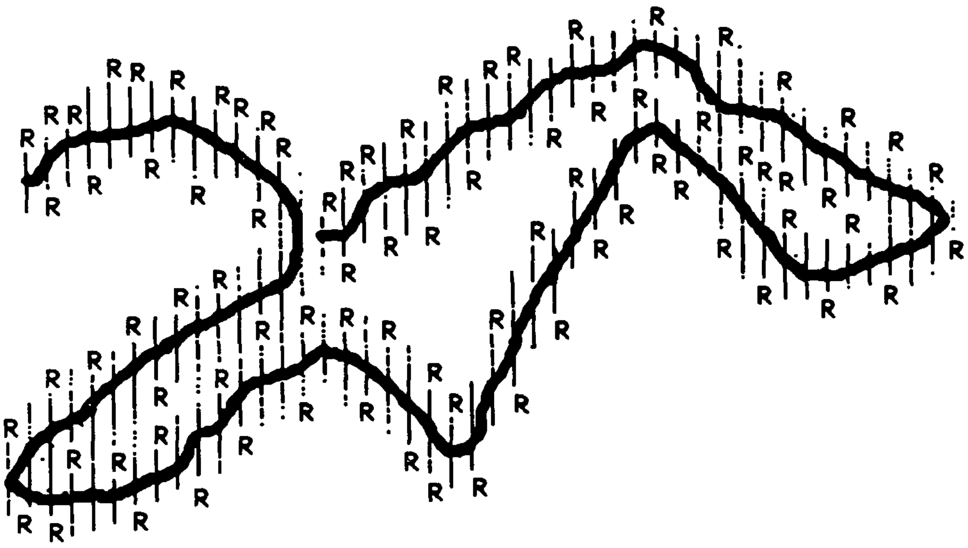


Figure 5. Flexible polymer backbone containing electroactive side groups (R)

If the comb teeth are not bulky and of appropriate shape, the polymer may exhibit liquid crystalline behavior. The charged or polarizable teeth are susceptible to alignment when subjected to suitable fields. The polymer backbone accommodates side group motion through internal rotations of its own. The polymer units may spontaneously align in solution. Subsequent application of an electric field or heat will induce a reorientation of the polymer chains. The ordering of polymers in liquid crystals is highly anisotropic: backbones along one axis, sidechains along another. As a result of this pronounced spatial anisotropy, light directed along different crystal axes travels at different rates. This property of birefringence may assist in achieving conditions appropriate for phase matching.

A more intricate tactic is to devise a nonlinear monomer segment that can also be polymerized into a well organized structure by treatment with heat or radiation. If the monomers are constructed with a head of an active moiety and a polar tail at the other end, the polar tails will automatically align on a water surface, creating a sheet of head-up, active monomers. Just as soap spreads across a water surface to a molecular thin layer, so a droplet of these monomers suspended in a volatile solvent will spread over the water surface to a film, one molecular unit thin. This loose film of monomers can be compressed by a barrier sweeping across the surface to form a uniform, monolithic film as diagramed in Figure 6. A glass slide gently dipped through the monomer-water interface will acquire a monolayer coating, which can be thickened by successive dipping. Afterwards, the monomers may be polymerized in place by exposure to radiation. This technique for the fabrication of multilayer polymer samples, the *Langmuir-Blodgett method,* allows precise control of film thickness and molecular organization. The resultant films have high optical quality and are suitable for application as waveguides in nonlinear optics experiments(*15*). The polydiacetylenes, attractive for their extraordinary nonlinear performance, have produced consistent films by this technique.

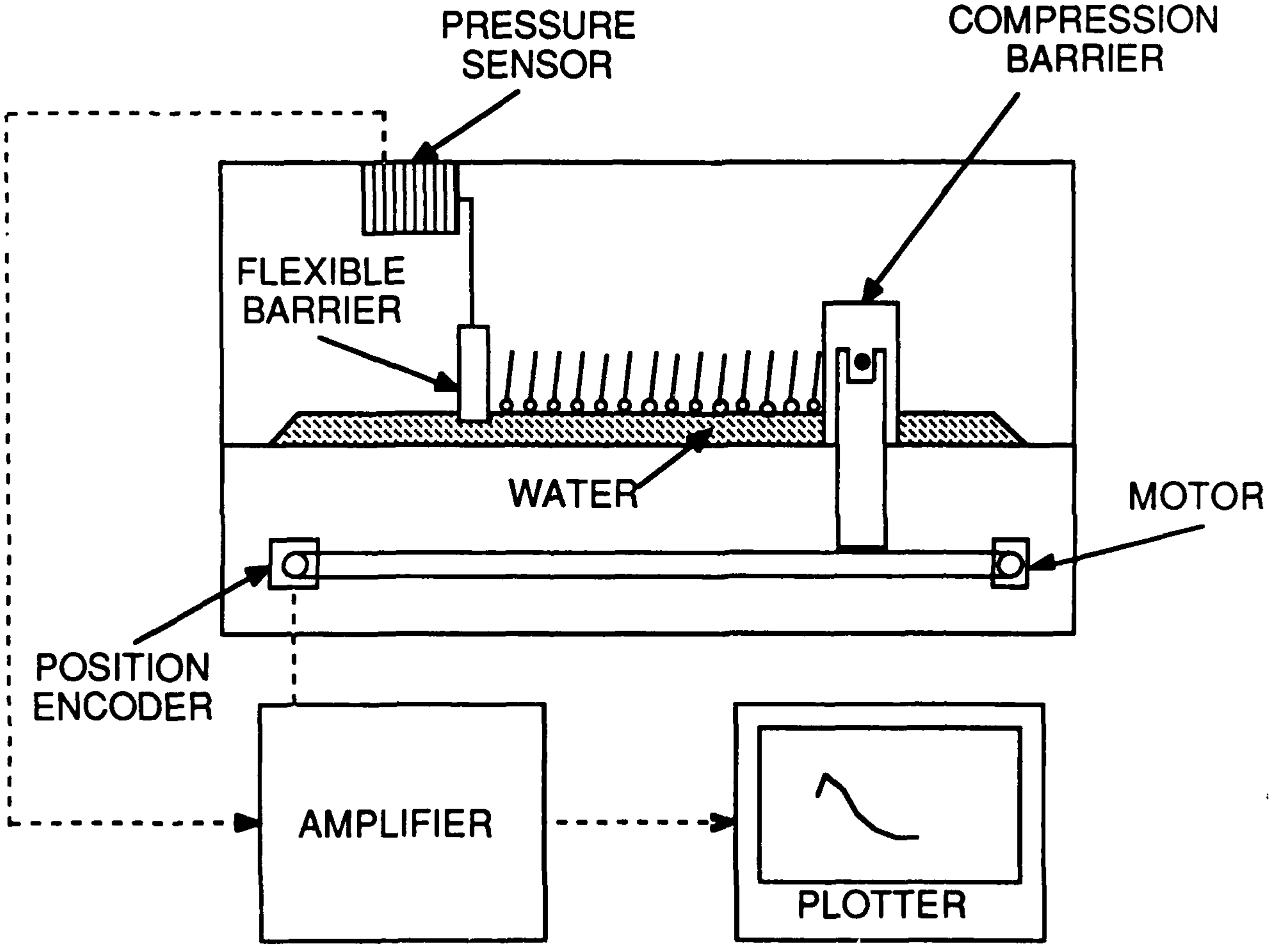


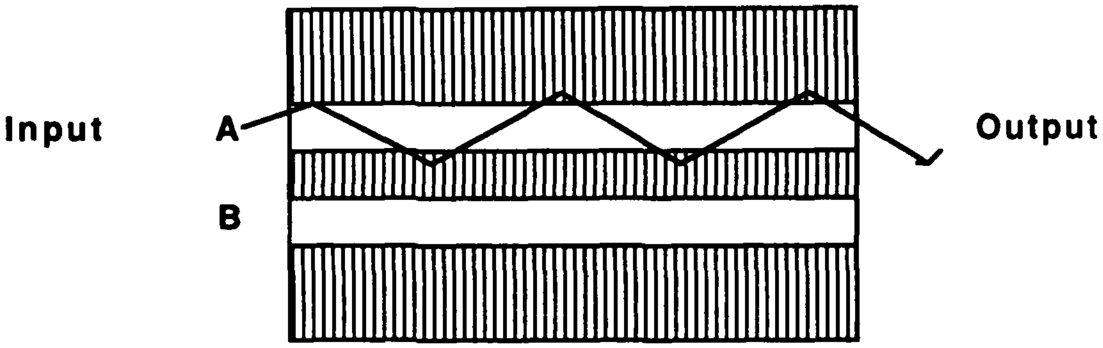
Figure 6. Schematic of Langmuir-Blodgett method.

Optical Devices

The diversity of nonlinear responses elicited from materials by light suggests application to many contexts. One of the most alluring quests is to replace electronic devices with optical analogues. The optical fiber, bearing information as a modulated light beam, emulates a current-carrying wire with increased information capacity and speed. The installation of optical cables as long telephone lines capitalizes upon these assets. At present, however, the optical signal carried on the fiber must be converted to an electrical signal for manipulation and decoding. An *all-optical switch*, which processes light by light, would circumvent this conversion complexity, without sacrificing the signal's speed of light transport(*16*).

An optical switch must function macroscopically much like a mechanical switch: the setting corresponding to "on" must allow light to pass through, while "off" blocks transmission. Current strategies for achieving precise, rapid switching of a light beam are dramatically more sophisticated than Galileo's use of a lantern shutter in his attempt to determine light's speed(*17*).

Uncoupled Waveguide



Coupled Waveguide

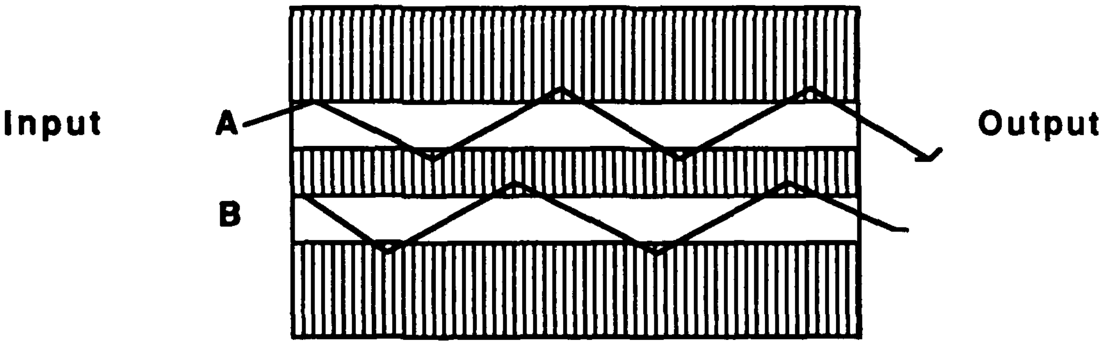


Figure 7. The index of refration within the waveguide is much higher than that of the surrounding, shaded material. When two waveguides are coupled, some of the light input at channel A "spills over" and is output through channel B.

One example for the design of an optical switch regulated solely by fluctuations in the light beam's intensity is provided in Figure 7. A laser beam is directed into a *waveguide*, a thin channel of a nonlinear(in this example) material whose index of refraction, higher than the surrounding substrate, confines the light beam within that channel. However, as light propagates by zig-zag reflections down channel **A**, it slightly exceeds the confines at each reflection. When another waveguide **B** of high refractive index is situated parallel and very close to **A**, some of the light from **A** will "spill over" into **B**. Both waveguides will output light: they are coupled together. The waveguide geometry can be so constructed that all the light from **A** is transferred to **B.** In this case, a light input in channel **A** results in light output through **B**.

A variation in the incoming beam's intensity alters the index of refraction in the waveguide if it is composed of a nonlinear material. Once the refractive index is increased above a threshold value, the waveguides abruptly decouple, like the flip of a switch. This breakdown of coupling between **A** and **B** eliminates light output from **B**: the transmission of light has been switched(*18*). The switching speeds(potentially up to 10^{-13}s) for such a device are determined, not by waveguide length, but by the characteristic response time of the constituent material to changes in optical intensity(*19*). The polydiacetylenes, with a fast response time and high nonlinear index in their range of transparent frequencies, are candidate materials for this application.

Another mechanism for switching light, based on liquid crystals, is a component of many commercially available image processing systems. This device, controlled by an applied electric field, screens out light by exploiting its *polarization*. The oscillation of the electric vector of linearly polarized light is confined to a plane; if it impinges upon a grating(*analyzer*) oriented perpendicular to that plane, no light is transmitted. However, when elliptically polarized light falls upon an analyzer, the component parallel to the grating is transmitted. The "off" and "on" states of a liquid cystal light valve are shown schematically in Figures 8 and 9. The long molecules composing the liquid crystal **L** are initially aligned so that the oscillation plane of linearly polarized light passing through it will be rotated by 45^{o}. Following reflection, the light retraverses **L** and is rotated further by 45^{o}. It is blocked by the analyzer.

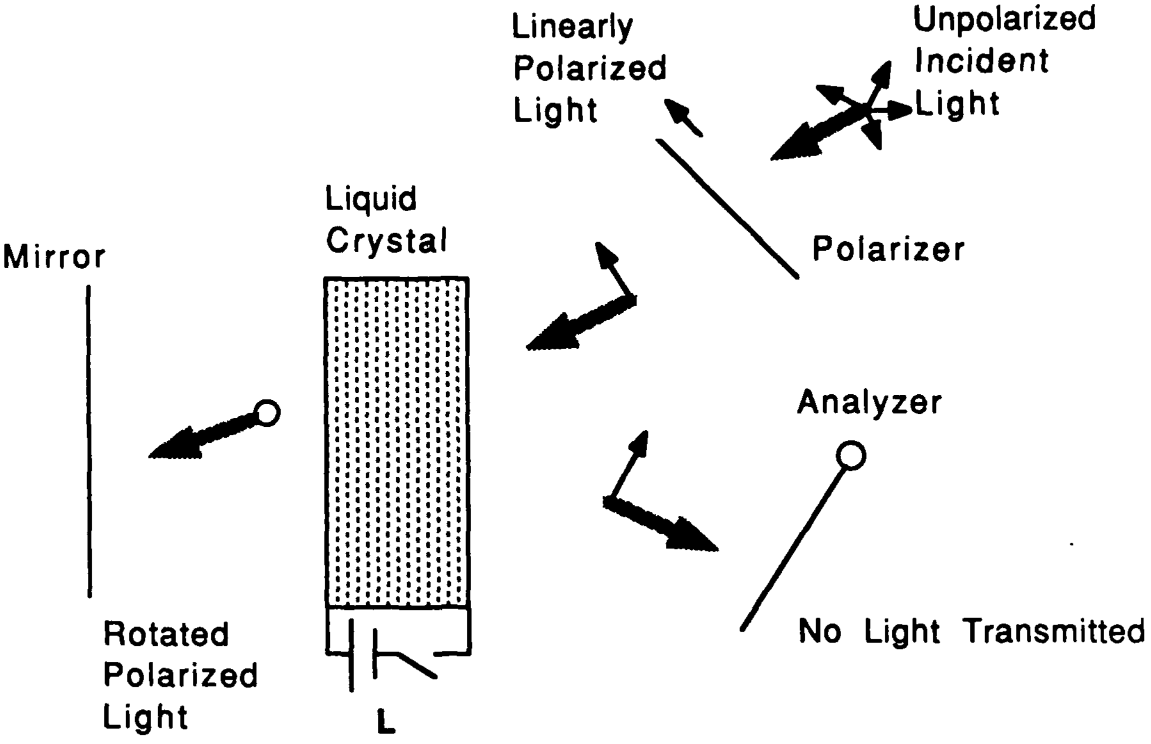


Figure 8. The "Off" state of a Liquid Crystal Light Valve. Linearly polarized light, rotated by 90 degrees in two passes through the liquid crystal, is stopped by the analyzer.

Subsequently, if an electric field is applied across the liquid crystal, the long molecules will reorient. The material becomes birefringent. This field-induced orientation of the molecules may transform linearly polarized light to elliptically polarized light. If this effect is attained, one component of the elliptically polarized light will emerge from the analyzer: the device will output light(Figure 9). Since this switch depends upon a "moving part"--repositioning of molecules and molecular fragments--it is inherently slower than the preceding example by several orders of magnitude. Typical response times are tenths of milliseconds, however, relatively small fields are adequate to achieve switching*(20)*.

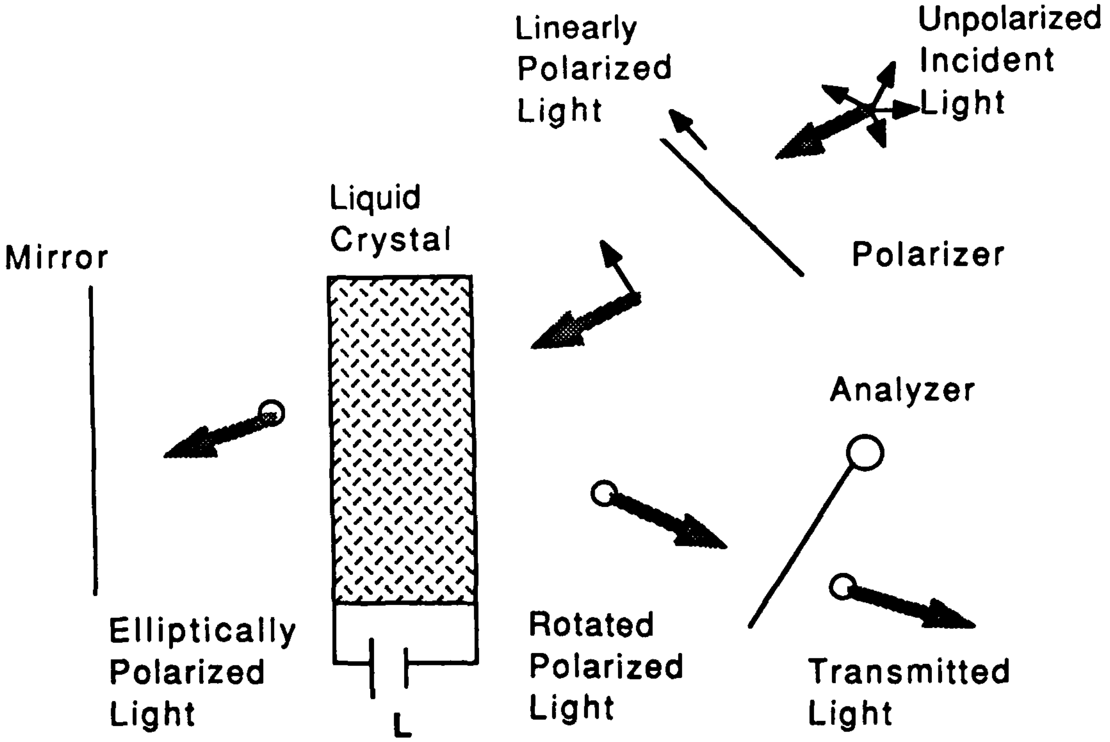


Figure 9. The "On" State of a Liquid Crystal Light Valve. Application of an electric field to the liquid crystal transforms the linearly polarized light passing through it to elliptically polarized light. One component of the elliptically polarized light is transmitted by the analyzer.

The ability to transform light's frequency from one regime to another(for example, from visible to ultraviolet) has evident practical import. A device which performs this operation is schematically simple: a single crystal(Figure 10). However, the crystal's orientation with respect to the laser beam is critical. Detection of the harmonic is only possible when the velocities of the incident light and the harmonic along the chosen crystal axis are matched. Urea($NH_2C_2NH_2$) and MNA(described above) crystallize in forms lacking a center of symmetry which produce an efficient second harmonic signal.

A continuous, uniform light beam is not useful for information transfer. However any of its observable properties, including intensity, frequency, phase, or polarization, may be deliberately modified to impart an information content to the beam. A *modulator*, a device which performs this function, is at the crux of any system based on optically transmitted signals. The modulator transposes coded information from an electrical, acoustic, or magnetic signal onto a light beam.

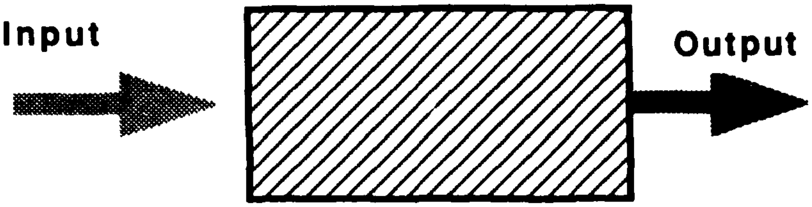


Figure 10. A single crystal exhibiting second harmonics. The frequency of the incoming light is changed(doubled) in passage through the crystal.

One popular scheme for modulating light, the *Mach-Zender interferometer*, consists of a waveguide of a nonlinear material which is split into channels that reunite, as depicted in Figure 11. A coherent beam of light enters the device at **C** and is divided by the waveguide into two beams, ideally of equal amplitude, at **D**. The beam in channel **F** is subjected to a modulating(encoded) electric field; the other is not. The index of refraction in channel **F** changes, creating a discrepancy between the speed of light in the two channels. As a result the two initially coherent beams fall out of synchronization with each other: their phases are mismatched at **E** and the beams partially cancel. The difference in phase of the two beams at **E** is proportional to the induced change in index of refraction in **F**. By regulating the index change, the phase difference at **E** can be controlled; thus light from the two channels will totally cancel in the device output. This device is, in principle, an electronically controlled switch: switching rates of up to tens of picoseconds are possible(*21,22,23*).

In a Mach-Zender device, the waveguide channels are fabricated from a material which responds to an applied electric field with a pronounced change in index of refraction. A DANS guest-host system could be prepared as a spin coated film within the channel. If the sample is heated beyond its glass transition temperature, an electric field can align the DANS molecules in the desired direction within the channel. Upon cooling, this orientation will be frozen in place. Alternatively, organic materials could be processed into waveguide geometries by several methods including the Langmuir-Blodgett technique, or by growing single crystals from solution or from melt.

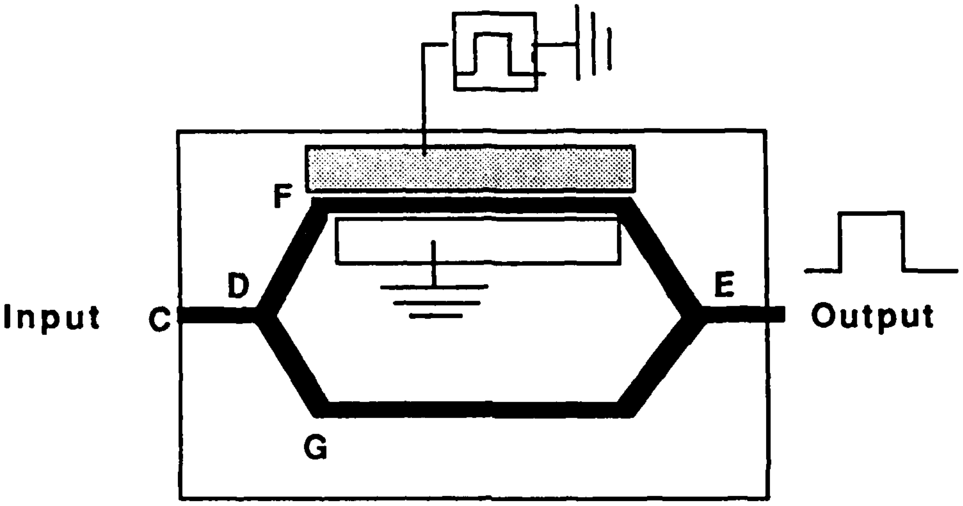


Figure 11. A Mach-Zender Interferometer. The light input at C is divided at D into two channels: F and G. The material in channel F is subjected to an electric field, which changes its index of refraction. The phase of light which traversed channel F does not match the phase of light from channel G. When the two beams are combined at E, their phases partially cancel, resulting in a reduced output.

The optical devices described above already exist, either as prototypes or manufactured components. The Advanced Photonics unit of Hoechst Celanese based in Summit, New Jersey(*24*), has designed the effective demonstration of their nonlinear polymeric materials shown in Figure 12. The audio signal from a Walkman radio applies a changing electrical voltage between two electrodes separated by a layer of nonlinear material. The material's index of refraction changes in step with variations in the applied field, thus creating a phase difference between two oscillation modes of light traveling in the layer. This optical phase difference is converted at the photodetector to a modulated electrical signal that, when fed to a loudspeaker, reproduces the original music. The polymer has facilitated the translation of a signal from audio to electrical to optical and back to electrical and audio without compromising its fidelity. An ordinary listener, without specialized knowledge, can appreciate the practicality of this set of transformations for communications applications by hearing the device's audio output.

Several other companies are marketing products which incorporate the unique properties of nonlinear organic materials. Liquid crystal devices and materials are available from Displaytech Inc. (*25*). Cleveland Crystals(*26*) supplies an extensive range of crystals grown in their labs for scientific and industrial applications(Figure 13). Their stock includes both inorganic and organic crystals with nonlinear optical properties. In addition, they have facilities for the fabrication and testing of laser-optic components such as harmonic generators.

Preliminary studies of organic materials have demonstrated their exceptional nonlinear response to light. Empirically based inference on how the form of a molecule relates to its function may guide the design of new organics, optimized to perform a specific role in this developing technology.

Conclusion

Our picture of the interaction between light and matter has been enriched in detail by the retinue of nonlinear phenomena first manifested by laser light. The effect is mutually induced: the electric field of light distorts molecular structure, which in turn alters some features of the beam. An interaction's efficiency at producing nonlinear effects can be finely tuned by incremental adjustments in the material. Organic materials, whose structure--like a microscopic lego set--can be remodelled at will, may merit prominence in the effort to devise components based on the physics of nonlinear optics.

The novel optical behavior of organic materials could invert the hierarchy of materials employed in communications technology. Engineering plastics have seen service primarily as passive components: housing for computers, packaging for microelectronic devices, and simply as insulators for current carrying cables. Silicon-based materials have been at the top of the hierarchy, directly engaged in the conduct and manipulation of information. In the future, molecularly engineered plastics may constitute the key active components, such as modulators and switches, that process the crucial decisions of our complex world. Further, just as the laser engendered a branch of physics, the tailor-made materials themselves may reveal new, unexpected physical and chemical phenomena.

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