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Nonlinear optics and organic materials Part 2

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How much time left till 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 common visible indicator of the modification of light in a nonlinear interaction with matter. We'll now explore other novel devices based on nonlinear optical behavior of polymers that may eventually proliferate in the everyday components of our culture as has the liquid crystal display.

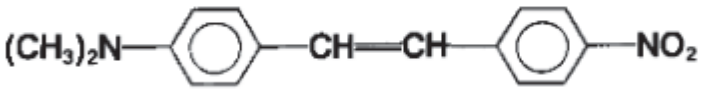
The invention of the laser has revealed a myriad branching cascade of related optical phenomena whose existence was demonstrated and probed by the laser's superior intensity, coherence, and monochromaticity. The oscillating electric fields of laser light are strong enough to compete with the inherent 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 asymmetric charge polarization under the influence of an external electric field, such as light, among other possibilities. Molecules or side groups with this configuration such as 3-methyl 4-nitroaniline (MNA) are able to sustain a large charge separation between excess positive charge at one end and negative charge at the other end, thus generating a molecular electric field that can, in turn, interact with the field of light. It may be possible to fine-tune the nonlinear response of a material to advantage in a given application by tinkering with the structure of the polymer 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 ($LiNbO3$) 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, are resistant to environmental degradation, and can be processed 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, 4-dimethylamino- 4'nitrostilbene (DANS)



is dissolved in an optically transparent matrix of polymers such as poly(methylmethacrylate) or polycarbonate. This matrix is termed a guest-host material because the active molecule is not chemically bonded with the polymer medium but is only homogeneously dispersed in it (5–10% by weight).

A liquid of a 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. However, the limited solubility of most active organics in the polymer and their tendency to segregate or migrate out of orientation imposes limitations on the choice of guest- host combinations and their suitability in applications.

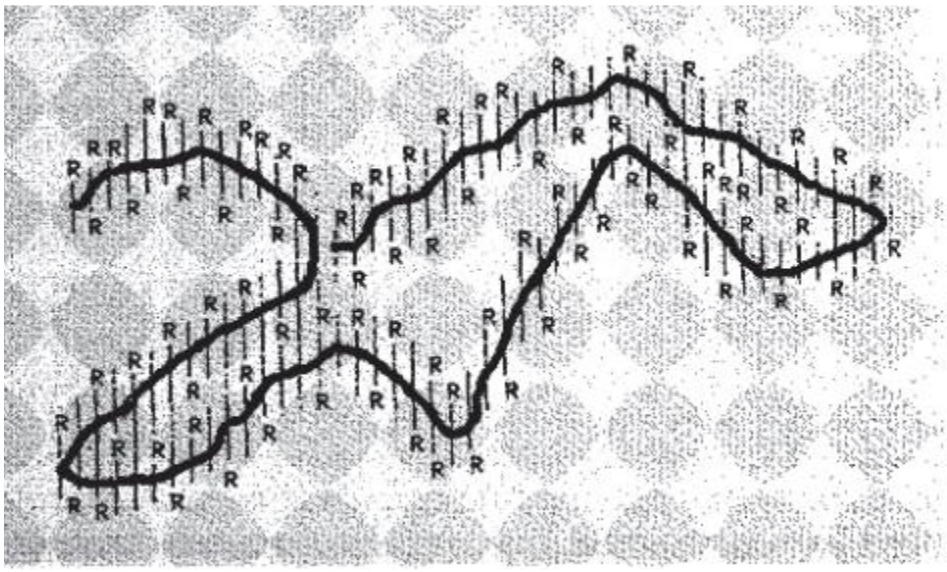


***Figure* 1. Flexible polymer backbone containing electroactive side groups (R)**

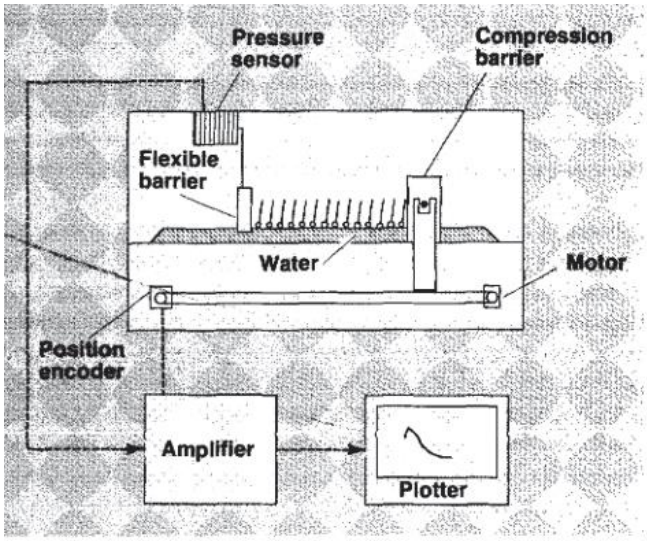


***Figure 2.* Schematic of Langmuir–Blodgett method**

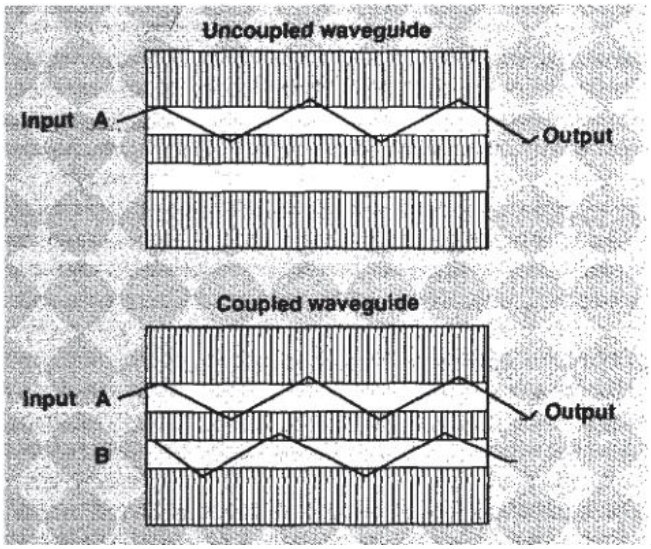


***Figure* 3. The index of refraction within the waveguide is higher than that of the surrounding shaded material. When two waveguides are coupled, some of the light input at channel A spills over and is output through channel B as schematically shown**

In an alternative approach, the active organic molecules may be covalently attached to the polymer backbone, analogous to the teeth of a comb (Figure 1). The polymer backbone may be devoid of nonlinear properties, as in the case of of acrylics, or it may be active, as the polydiacetylenes, thus enhancing the material's response to light. Its substituent teeth can be chemically modified following polymerization, allowing the chemist further flexibility. The comb-like structure can be processed by procedures used with guest-host materials: It can be heated, oriented in a field, and frozen in place.

If the comb teeth are not bulky and are 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, side chains 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.

Optical devices

A more intricate tactic is to devise a nonlinear monomer segment that also can 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 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 that is 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 shown in Figure 2. 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 may be suitable for application as waveguides in nonlinear optics experiments (1). The polydiacetylenes, attractive for their extraordinary nonlinear performance, have produced consistent films by this technique.

The diversity of nonlinear responses elicited from materials by light suggests many different applications. 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 on 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 speed of light transport by the signal (2).

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 the speed of light (3).

One example for the design of an optical switch regulated solely by fluctuations in the light beam's intensity is provided in Figure 3. A laser beam is

directed into a waveguide, in this example a thin channel of a nonlinear 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 intensity of the incoming beam 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 (4). 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 (5). The polydiacetylenes, with a fast response time of ~10-14s and high nonlinear index in their range of transparent frequencies, are candidate materials for this application.

Another mechanism (based on liquid crystals) for switching light 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 crystal light valve are shown schematically in Figures 4 and 5. 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°. Following reflection, the light retraverses L and is rotated further by 45°. It is blocked by the analyzer.

Subsequently, if an electric field is applied across the

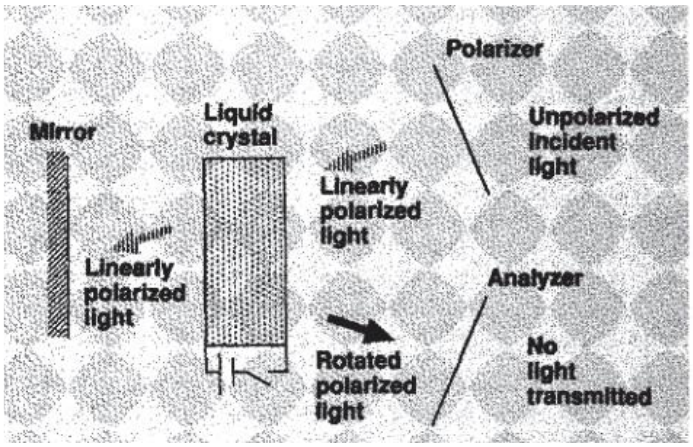


***Figure* 4. The "off" state of a liquid crystal light valve. Linearly polarized light, rotated by 90° in two passes through the liquid crystal, is stopped by the analyzer**

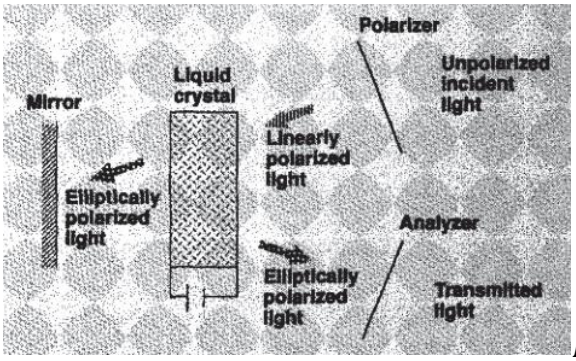


***Figure* 5. The "on" state of a liquid crystal light valve. Application of an electric field to the liquid crystal transforms the linearly polarized light passing through it to elliptically polarized light. One component of the elliptically polarized light is transmitted by the analyzer**

liquid crystal, the long molecules will reorient and 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 5). Because this switch depends on 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 (6).

The ability to transform the frequency of light from one regime to another (e.g., from visible to ultraviolet) has evident practical import. A device that

performs this operation is schematically simple: a single crystal. However, the crystal's orientation with respect to the laser beam is critical.

Detection of the barmonic (i.e., the multiple of the incident frequency) is only possible when the velocities of the incident light and the harmonic along the chosen crystal axis are matched. Urea (NH_2CONH_2) and MNA crystallize in forms lacking a center of symmetry to 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 that 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.

One popular scheme for modulating light, the Mach-Zender interferometer, consists of a waveguide of a nonlinear material split into channels that reunite (Figure 6). 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 (10^{-11} s) are possible (7-9).

In a Mach-Zender device, the waveguide channels are fabricated from a material that responds to an applied electric field with a pronounced change in index of refraction. A DANS guest-host system could be prepared

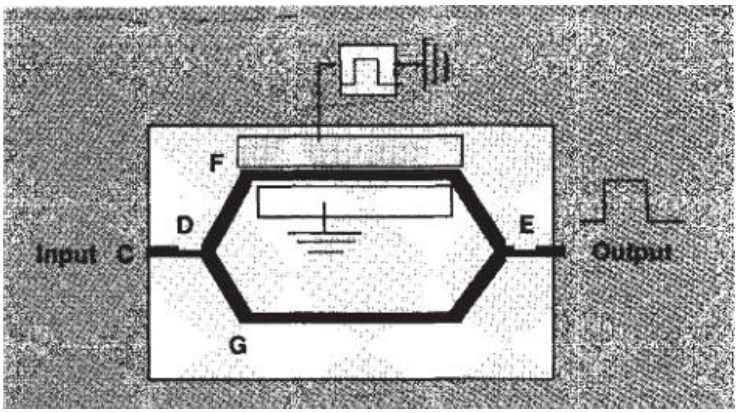
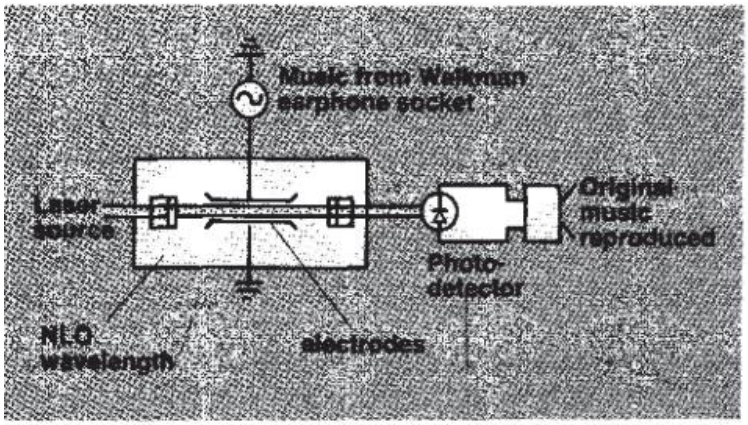


***Figure* 6. A Mach-Zender interferometer. The light input at C is divided at D into two channels: F and G. The material in channel F is subjected to an electric field, which changes its index of refraction. The phase of light that traversed channel F does not match the phase of light from channel G. When the two beams are combined at E, their phases partially cancel, resulting in a reduced output**



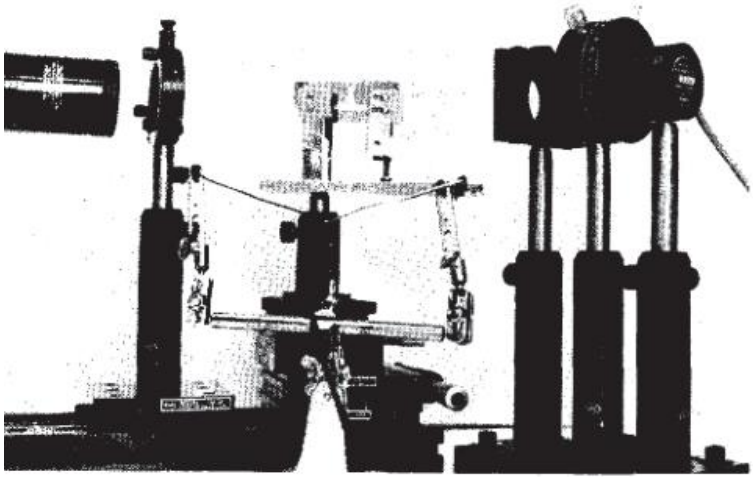


***Figure* 7. Diagram of a demonstration of organic nonlinear materials designed by the Advanced Photonics Division of Hoechst Celanese and a photograph of the apparatus. NLO nonlinear optics**

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.

The optical devices described above already exist, either as prototypes or as manufactured components. The Advanced Photonics unit of Hoechst Celanese based in Summit, N.J. (10), has designed the effective demonstration of its nonlinear polymeric materials shown in Figure 7. 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 audio output of the device.

Several other companies are marketing products that incorporate the unique properties of nonlinear organic materials. Liquid crystal devices and materials are available from Displaytech Inc. *(11*). Cleveland Crystals *(12*) supplies an extensive range of crystals grown in their labs for scientific and industrial applications. 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 new 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. The efficiency of an interaction 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 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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