

NONLINEAR OPTICS OF ORGANIC AND POLYMER MATERIALS

Exotic multiexciton strings, electron correlation effects and custom-designed nonlinear optical molecules are some of the developments resulting from initial efforts toward active control of light-matter interactions in nonlinear organic systems. The potential applications are equally diverse and exciting.

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Over the past decade the study of nonlinear optical processes in organic and polymer systems has enjoyed rapid and sustained growth. One indication of that growth is the increase in the number of articles published in refereed society journals. The four-year period 1980–83 saw the publication of 124 such articles. For the four-year period a decade later the production of articles in the field had grown to 736—nearly a sixfold increase. In part, the rapid growth of the field can be attributed to the technological promise and interesting physical properties of these materials.^{1–3} Because of their large optical nonlinearities and mechanical, chemical, thermal and optical stability, organic nonlinear optical materials are the leading practical materials for fabricating optoelectronic devices. They also have proven to be excellent subjects in which to study many-body electron correlation effects and exotic states like polarons, excitons and even coherently propagating multiexciton strings.

Progress in realizing the potential of these materials has been enhanced by the development of a concerted international research effort based on the following steps:

- ▷ obtaining a fundamental understanding of the basic physics of nonlinear optical and electro-optic processes in organic materials

- ▷ based on that understanding, synthesizing innovative organic materials having large nonlinear optical and electro-optic coefficients and exhibiting high thermal, mechanical, chemical and photo stabilities

- ▷ using these materials to engineer polymer-based integrated optoelectronic devices that can be manufactured with standard processes in existing microelectronics facilities for making integrated circuits.

This approach has worked very well for organic non-

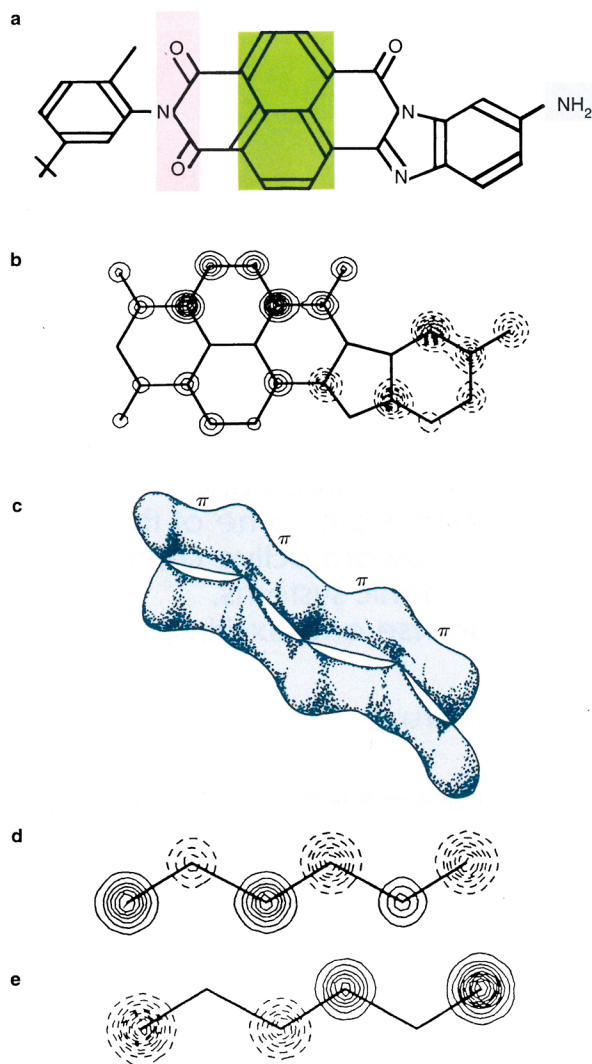
linear optical materials because, unlike in inorganic systems, where nonlinear phenomena arise from band structure effects, in organic and polymer systems nonlinear optical effects originate in the virtual electron excitations occurring on the individual molecular, or polymer chain, units. This allows researchers to employ ultrastructure synthesis, a new level of molecular design in which molecular assembly is controlled down to the placement of individual substituent groups, to optimize the nonlinear optical properties of organic systems while preserving the thermal, mechanical and chemical properties that have made organic materials so useful in industry. Our present level of understanding makes viable the computer-aided molecular design of new nonlinear optical chromophores (so called because these dye-like compounds give rise to color in organic substances) that can be substituted into polymers and other organic molecules. One can then incorporate these chromophores into thin films and fibers using existing low-cost processing techniques.

Origins of optical nonlinearity

The origin of the outstanding nonlinear optical properties of organic systems is the relative ease with which light fields affect the motions of the electrons that take part in the delocalized, multicenter bonds characteristic of unsaturated organic compounds: the π electrons. Because π electrons are not tightly bound to the individual positive nuclear sites, their paths, or orbitals, extend over long distances, spanning an entire molecule or even a macroscopic solid. Figure 1c shows the π -electron distribution of all-*trans*-hexatriene, a linear polyene. (A polyene is a hydrocarbon chain in which three of each carbon's valence electrons bond covalently to a hydrogen and the two nearest carbons, respectively, while the remaining valence electron contributes to a delocalized π -electron distribution along the carbon chain.)

Because the nonlinear optical responses in organic materials originate primarily from π -electron excitations

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Molecules with π -electron systems can exhibit nonlinear optical effects when these electrons are optically excited. To show second-order effects the molecule must be noncentrosymmetric. The high-temperature-stable nonlinear optical chromophore 1,8-naphthoylene-(3'-amino)-benzimidazole-4,5-dicarbox-N-(2,5-di-tert-butyl)phenylimide (a) is noncentrosymmetric by virtue of the presence of an NH₂ donor group (blue) and an imide acceptor group (red). The naphthalene ring (green) serves as both a π bridge and part of the acceptor. The contour diagram of the electron-charge-density difference between the first excited state and the ground state (b) shows that on excitation charge is depleted from the donor and transferred to the acceptor (greater densities of dashed lines correspond to greater depletion; greater densities of solid lines to greater excess). Third-order effects are seen in centrosymmetric molecules like all-*trans*-hexatriene, the delocalized π ''' electron clouds for which are shown in c. An electron-transition-density matrix diagram (d) shows modulated charge separation, corresponding to a moderate nonlinear response, when this molecule is excited to its first excited state (1^1A_g) from the ground state (1^1B_u). The transition diagram between the ground state and the two-photon state 5^1A_g (e) shows a large charge transfer, corresponding to a large nonlinear optical response. **Figure 1**

second-order molecular nonlinear optical susceptibility $\beta_{ijk}(-\omega; \omega_1, \omega_2)$. Likewise, a third-order effect (like the Kerr effect, where a photon is modulated by a term quadratic in the dc electric field) will depend on $\gamma_{ijkl}(-\omega; \omega_1, \omega_2, \omega_3)$.

The time-dependent *quantum* perturbation expansion generates an expression for the second-order coefficient β or the third-order coefficient γ with terms proportional to the transition moments between eigenstates of the unperturbed system. These terms describe virtual transition sequences through the excited-state manifold that are critical to understanding the origin and mechanism of nonlinear optical effects.

Theory of second-order processes

Because even-order electric dipole coefficients are zero for centrosymmetric molecules, one must make organic molecular and polymer-chain structures noncentrosymmetric for them to exhibit second-order nonlinear optical effects. One usually does this by chemically attaching electron donor and acceptor groups at diametrically opposed positions in the structure, a molecular analog to p- and n-type doping in semiconductors. The recently developed high-thermal-stability electro-optic chromophore shown in figure 1a serves as a timely example.⁴ The molecular ground state dipole moment that results from the symmetry lowering points nearly uniaxially across the central rings from the donor NH₂ group to the acceptor imide group.

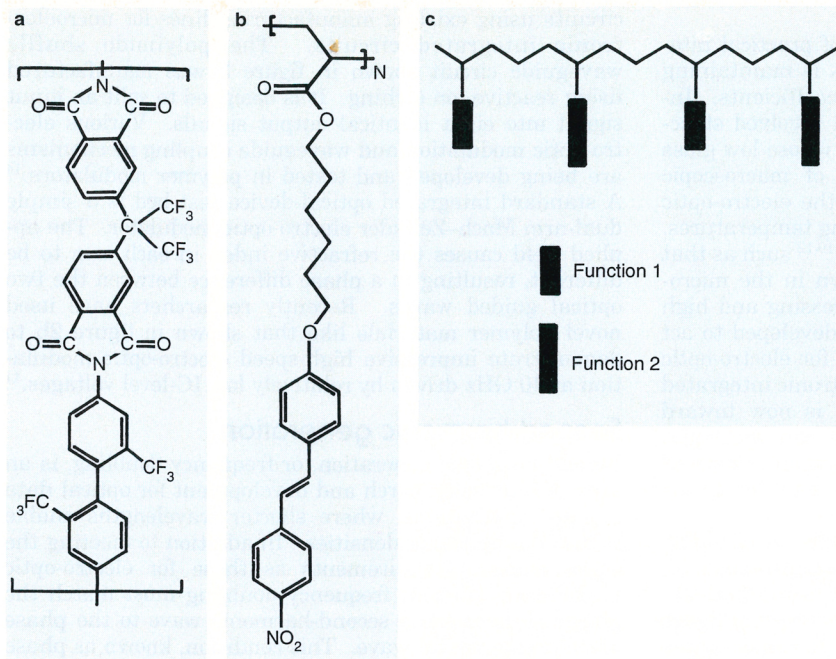
The standard technique for measuring β in dipolar gases and liquids is dc-induced second-harmonic generation.⁵ In this technique, one measures the second-harmonic light after applying a dc electric field across the sample to align the dipolar molecules and break the natural centrosymmetry of the macroscopic assembly. Recently, Belgian researchers have developed a new hyper-Rayleigh scattering technique⁶ to overcome the inability of dc induced second-harmonic generation to determine β for nondipolar or ionic compounds. In hyper-Rayleigh scattering, one measures the incoherent second-harmonic scattered light from a solution with no need of an applied electric field. This new technique has been applied to many systems, including not only dipolar molecules but also ionic materials, octupolar molecules, polymers and

on individual molecular or polymer-chain units, each unit can be viewed essentially as an independent source of nonlinear optical response. One can calculate the optical response of a macroscopic condensed assembly like a solid by simply summing these individual responses, averaged over their orientations. The nonlinear optical responses of inorganic materials, arising from collective band structure effects, are not so easy either to calculate or to optimize.

Under nonresonant conditions the frequencies of the input and output optical fields (greater than 10^{14} Hz) are below π -electron resonances but well above any vibrational and rotational modes. This means that the nonlinear optical responses are due exclusively to the responses of the electrons in the molecule to the applied electric fields. Classically, one can expand p_i , the molecular response to a local field $\mathbf{E}$, in terms of the components of $\mathbf{E}$:

$$p_i(\omega) = \mu_i + \alpha_{ij}(-\omega)E_j(\omega) + \beta_{ijk}(-\omega; \omega_1, \omega_2)E_j(\omega_1)E_k(\omega_2) + \gamma_{ijkl}(-\omega; \omega_1, \omega_2, \omega_3)E_j(\omega_1)E_k(\omega_2)E_l(\omega_3) + \dots$$

A second-order process (such as second-harmonic generation, in which two input photons of the same frequency interact with the molecule to generate a single photon with twice the frequency) will be proportional to the



Novel polymers can be synthesized to fulfill many different functions. **a:** The high-glass-transition-temperature fluorinated polyimide 6FDA/TFDB maintains its nonlinear optical properties throughout its manufacture into integrated optoelectronic circuits. (Courtesy of T. Matsuura, Nippon Telephone and Telegraph, and S. Nara, Hitachi Chemical). **b:** A polymer with an acrylate backbone, a six-carbon-site spacer chain and the nonlinear optical side group 4-methoxy-4'-nitrostilbene is a prime candidate for a high-frequency electro-optic modulator. (Courtesy of G. Mohlmann, AKZO-NOBEL.) **c:** In general, one can make a polymer multifunctional by substituting different functional groups along the polymer backbone. Such groups (represented here by boxes of different size) can confer, for example, piezoelectric, pyroelectric, electro-optic, electrically conductive or photoconductive functions on the molecule. (Courtesy of R. Norwood, Hoechst Celanese.) **Figure 2**

proteins, that cannot be measured by dc-induced second-harmonic generation and has led to greater understanding of nonlinear optical processes.

Understanding the basic physical mechanisms of nonlinear optical processes has naturally led to the development of highly efficient computational methods that allow researchers for the first time to explore reliably the second-order optical properties of π -conjugated structures.⁷ For many structures theoretical calculations reveal that large second-order effects result from highly asymmetric, charge-correlated excited states. Often the dominant contribution to the second-order susceptibility β involves the first π -electron excited state. Figure 1b shows a representative topographical contour map calculated using Cray C-90 facilities at the Pittsburgh Supercomputing Center. The map illustrates the redistribution of π -electron density accompanying optical excitation to the first π -electron excited state of the new chromophore. On excitation electron density in the vicinity of the electron-donor amino group on the right is transferred to the region of the electron acceptor on the left, resulting in a large charge separation and an associated large optical transition moment. Such diagrams clearly illustrate the microscopic origin and mechanism of second-order optical responses in π -electron systems. They also suggest ways in which the second-order nonlinear response might be maximized at the macroscopic as well as the microscopic level.

Optimizing second-order effects

Once one understands the underlying physical mechanisms of second-order processes, one can use this understanding to optimize the desired effect. Three key parameters that often determine β are the transition energy, dipole moment difference and transition moment between the ground state and first π -electron excited state. To enhance β one has to decrease the transition energy and increase the two moment parameters. Typical ways to do this are to increase the strength of the electron-donor and acceptor substituents and to increase the conjugation length of the π bridge that spans from donor to acceptor.

Realization of bulk materials having large macroscopic second-order optical response χ_2 requires not only

molecular constituents with large microscopic second-order susceptibility β but also macroscopic noncentrosymmetric assemblies aligned so that the individual tensor components of β add constructively. Other than standard crystal growth, the most popular approach for attaining such structures is electric-field-induced alignment of glassy amorphous polymer films, which is particularly important because of the ease of film processing, the ability to form multilayers and the compatibility with standard semiconductor device manufacturing steps. In this approach⁸ one applies a dc electric field across a polymer film sample that is heated above its glass transition temperature (the temperature above which a material tends to become rubber-like) to allow the dipolar chromophores to align with the field. One then lowers the temperature through the glass transition temperature to room temperature to lock in the noncentrosymmetric orientational order. One can greatly reduce the intrinsic thermal relaxation that could eventually destroy the noncentrosymmetry by using polymer systems with intrinsically high glass transition temperatures. An elegant example currently under development^{9,10} is the class of optical polyimides with glass transition temperatures greater than 300–400 °C. (See figure 2a.)

Linear electro-optic effect

The first applications of π -conjugated organic materials will likely be based on the linear electro-optic properties of aligned glassy polymers in integrated optoelectronic circuits.¹¹ The electro-optic effect is a second-order optical process in which an externally applied dc or low-frequency electric field couples to the optical electric field to change the refractive index of the polymer material. For a fixed electric field the phase change induced by a nonlinear material is proportional to a figure of merit n^3r/ϵ , where n is the refractive index of the material, r is the electro-optic coefficient and ϵ is the dielectric constant. The large electro-optic coefficients and low dielectric constants characteristic of organic materials lead to figures of merit for organic polymer materials that typically range from 20 to 80. In contrast, the figures of merit for the inorganic materials lithium niobate (LiNbO_3) and gallium arsenide

are 9.1 and 4.2, respectively.

The main challenge to development of practical integrated optic devices using poled polymers is maintaining the thermal stability of the electro-optic coefficients. Initial proof-of-principle device efforts often involved structures similar to polymethyl methacrylate, whose low glass transition temperatures lead to a loss of macroscopic alignment and a consequent decrease in the electro-optic coefficient at device assembly and operating temperatures. Recent efforts have shown that polyimides^{10,12} such as that shown in figure 2a, which are well known in the microelectronics industry for their ease of processing and high thermal and chemical stabilities, can be developed to act as both passive waveguides and as hosts for electro-optic chromophores in active regions of optoelectronic integrated circuits. The focus of current research is now toward designing electro-optic chromophores that can withstand the stringent thermal and chemical conditions required in polyimide-based fabrication processes and device assembly steps.

Several major advances in the development of highly stable electro-optic chromophores have recently been reported.^{4,13} One involves a new class of high-thermal-stability electro-optic chromophores like that shown in figure 1a. These chromophores were designed for their structural similarity to polyimide repeat units and consequent easy incorporation into host polyimides.⁴ Other new important high-temperature-stable classes of electro-optic chromophores are donor-acceptor-substituted heteroaromatic structures¹³ having large second-order microscopic responses. These new high-thermal-stability electro-optic chromophores are the first realization of large-electro-optic-coefficient guest molecules able to withstand real semiconductor device fabrication conditions.

High-performance electro-optic polymers present a unique technological opportunity: They allow one to design and build novel optoelectronic integrated devices and

circuits using existing manufacturing lines for microelectronic integrated circuits. The polyimide shuffle waveguide circuit shown in figure 3 was manufactured using reactive-ion etching. It is designed to split an input signal into eight identical output signals. Various electro-optic modulation and waveguide coupling mechanisms are being developed and tested in polymer modulators.¹⁴ A standard integrated optical-device test bed is a simple dual-arm Mach-Zehnder electro-optic modulator. The applied field causes the refractive index in each arm to be different, resulting in a phase difference between the two optical guided waves. Recently researchers have used novel polymer materials like that shown in figure 2b to demonstrate impressive high-speed electro-optic modulation at 40 GHz driven by relatively low IC-level voltages.¹⁴

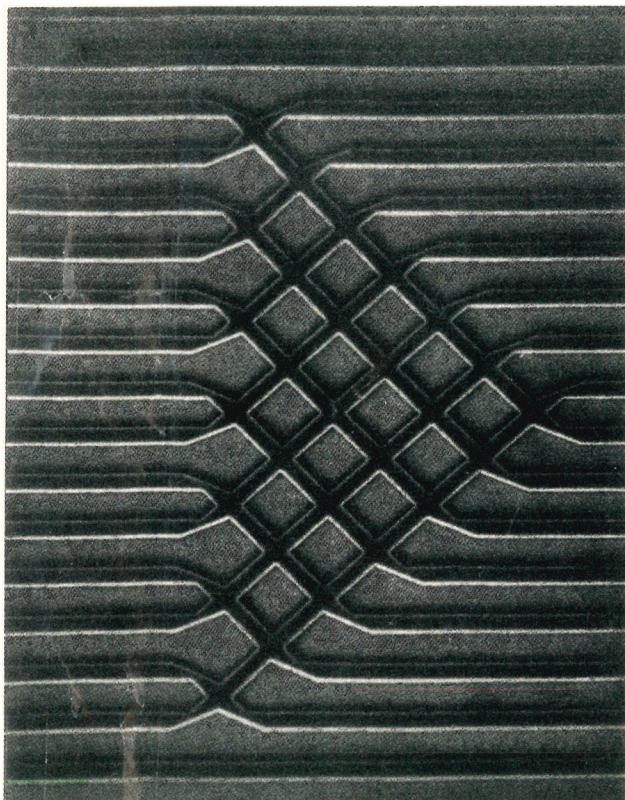
Second-harmonic generation

Second-harmonic generation, or frequency doubling, is an area of intense research and development for optical data storage applications, where shorter wavelengths enable higher data packing densities. In addition to meeting the same material requirements as those for electro-optic modulators, efficient frequency doubling must match the phase of the created second-harmonic wave to the phase of the fundamental wave. This condition, known as phase matching, results in the conversion of a high proportion of the input light to the output second harmonic. In practice one can achieve phase matching by selecting a material with an optical birefringence that cancels the natural optical dispersion, leading to equal refractive indexes at the fundamental and second-harmonic frequencies. Since the second-harmonic output is proportional to the square of the frequency-doubling coefficient divided by the cube of the refractive index, this number provides a convenient figure of merit for comparing frequency-doubling materials. The low index values (1.3–1.8) that characterize organic materials give them a distinct advantage over inorganic materials, with their relatively large values (2.0–2.5).

Various approaches are being pursued for achieving efficient second-harmonic generation. They include filling hollow-core optical fibers with crystalline organic material and forming spatially periodic polymer films in which alternate layers are polarized in opposite directions to achieve quasi-phase-matching.¹⁵ Waveguides composed of such films have been used to simultaneously achieve phase matching and improve the optical field overlap between the propagating waveguide modes.¹⁶

Currently applications of second-harmonic generation are centered on doubling the frequency of laser diode sources operating in the 800-nm range to the blue spectral region near 400 nm. The main issue associated with blue- or violet-light generation is optical transparency at the fundamental and harmonic wavelengths. Most materials with high second-harmonic-generation efficiency show significant absorption in the blue or violet. Researchers¹ have recently demonstrated efficient blue-light generation below 400 nm using highly efficient organic single crystals.

Optoelectronic circuits can be manufactured from organic nonlinear optical polymers using standard microelectronics processing techniques. This polyimide rib waveguide structure was manufactured using reactive-ion etching and is meant to split an input signal into eight identical output signals. (Courtesy of A. Husain, Advanced Research Projects Agency, and B. Booth, Du Pont.) **Figure 3**



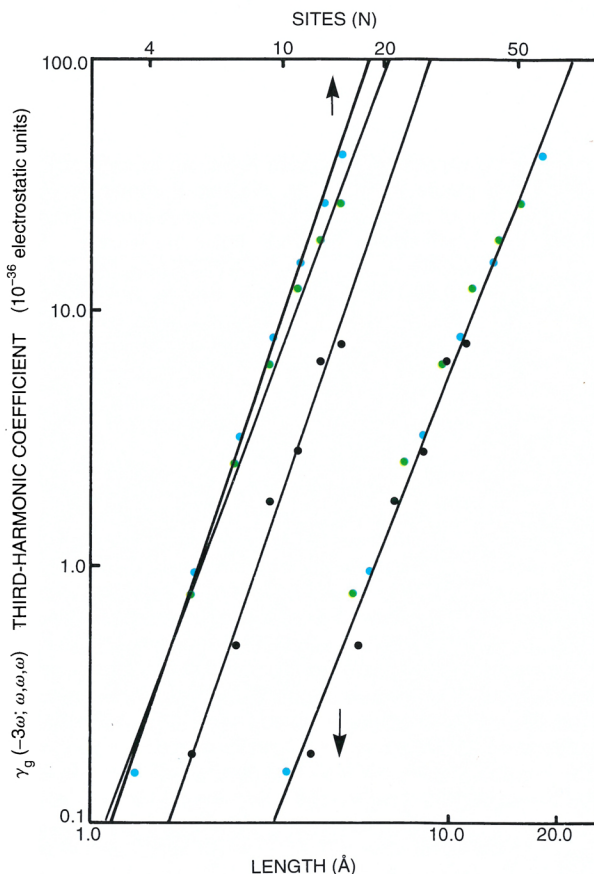
Such organic materials may be used in terabit optical data storage applications.

Theory of third-order processes

Since the odd terms of the dipole expansion are nonzero regardless of the symmetry of the molecule, third-order optical effects occur naturally in all optical media. The large, ultrafast, nonresonant third-order optical responses γ of π -conjugated organic and polymeric systems are determined by electron correlation effects among the π -electrons.¹⁷ For linear chains, explicit consideration of these effects leads to results for the magnitude, sign, dispersion and chain-length dependence for γ in agreement with experiment.¹⁸ Most importantly, virtual π electron transitions that involve previously unknown, strongly correlated, high-energy two-photon states are essential to the determination of γ and consequently of the macroscopic third-order response χ_3 . Descriptions based on independent-particle models, which entirely neglect electron-electron repulsions and correlations, miss these states and thus the underlying mechanism for third-order processes.

The physical origin of the nonresonant third-order response is best illustrated by centrosymmetric linear chains like the six-site chain HT (*trans*-hexatriene) of figure 1c. The π -electron states possess definite parity. One-photon states have a parity different from the ground state. Two-photon states have the same parity as the ground state. Quantum many-electron sum-over-states calculations reveal the primary role of the highly correlated two-photon π -electron states. For short chains like HT, two types of competing third-order virtual excitation processes almost exclusively determine γ . The type-I processes are of the form $S_0 \rightarrow S_1 \rightarrow S_0 \rightarrow S_1 \rightarrow S_0$, where S_0 is the ground state and S_1 is a one-photon excited state. The intermediate state is S_0 itself, and the process makes a negative contribution to γ . For the type-II processes, $S_0 \rightarrow S_1 \rightarrow S_2 \rightarrow S_1 \rightarrow S_0$, the intermediate state S_2 is a high-energy, strongly correlated, two-photon state. The contour diagrams for HT in figures 1d and 1e illustrate the electron density redistribution for the virtual transitions $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_2$, which are important to the type-I and II terms, respectively. The transition $S_0 \rightarrow S_1$ yields a somewhat modulated π -electron charge redistribution and an associated radiative moment for the transition of 6.6 debye. In contrast, the transition $S_1 \rightarrow S_2$ produces large charge separation along the chain axis and an associated large transition moment of 11.4 debye, which dominates the positive type-II contributing term in γ . The type-II process makes a larger, positive contribution to γ and therefore determines the overall sign of γ to be positive, a result that is corroborated by experiment.

The electron correlation mechanism, which has been shown experimentally to hold for chains of moderate length, causes γ to increase supralinearly with increased chain length L . The log-log plot of $\gamma_g(-3\omega; \omega, \omega, \omega)$ (the isotropically averaged third-harmonic response) versus chain length L shown in figure 4 demonstrates that γ_g varies approximately as $L^{3.5}$, independent of the chain's conformation.¹⁹ Figure 4 also shows that cyclic ring structures possess a length dependence similar to that of linear polyenes, evidence that the effective length over which charge can be separated determines the nonlinear optical response. Increased charge separation increases the number of virtual excitation processes and the transition moments between the principal virtual states, and it decreases the excitation energies of those states. This is why γ increases rapidly with increased chain length. In fact, this mechanism for third-order processes in linear chains and cyclic rings is generalizable to many other



Calculated log-log plot of isotropically averaged $\gamma_g(-3\omega; \omega, \omega, \omega)$ at an input energy $\hbar\omega$ of 0.65 eV versus the number of carbon sites and correlation length L for *trans* (blue), *cis* (green) and cyclic (black) polyenes.¹⁹ For all three polyene series, the third-harmonic coefficient γ_g varies approximately as $L^{3.5}$, showing that third-order nonlinear optical effects are much more sensitive to the physical length of the chain than to its conformation. **Figure 4**

π -conjugated structures, including rigid-rod polymers, polydiacetylenes, polythiophenes, ladder polymers, C_{60} and novel dye chromophores. Figure 5 shows the good agreement between experiment and the electron correlation description for the broad dispersion of χ_3 for π -conjugated polydiacetylene (poly-4BCMU) polymer chains.¹⁸

The supralinear dependence of γ on L is the primary reason for the intense interest in π -conjugated linear chains as third-order optical materials. However, this behavior continues only to lengths of approximately 50–100 Å, or equivalently 50–100 carbon atom sites, with little to be gained beyond this limit. It is this general finding that has spurred recent exploratory efforts to find new ways to enhance γ and χ_3 of π -conjugated structures.

Enhancement of third-order processes

Second-order optical effects in π -conjugated organic and polymer materials are more than adequate for device applications such as optoelectronic integrated circuits and second-harmonic generation. This is not the case for third-order optical properties, which provide the basic

means for controlling light with light, as in optical bistability²⁰ and phase conjugation. Figure 6 shows projected path-length and macroscopic-third-order-response requirements for applications in fiber optic networks. Even assuming little or no optical loss, currently available third-order effects do not satisfy device requirements. Attempts to increase γ and, in turn, χ_3 in organic and polymer systems by increasing the conjugation length have reached an upper limit. The largest value of γ , observed in polydiacetylenes, is almost a decade old. Recent searches for materials with larger third-order effects have proved futile.

A number of approaches in fundamentally new directions have been tried to enhance γ . Among the mechanisms being studied are populated excited states, new collective excitations and bond-length alternation.²¹

Compared with the ground state S_0 , the nonresonant χ_3 of a π -conjugated structure can be enhanced by orders of magnitude or even change sign when a metastable first or second electronic excited state (S_1 or S_2) is optically pumped and then populated for times long enough to permit nonresonant measurements of χ_3 (that is, measurements at frequencies different from the resonant pump frequency). Such enhancements have been observed for nonresonant third-harmonic generation and degenerate four-wave mixing in organometallic discs and polyene chains.

Our understanding of nonlinear optical processes in organic systems was advanced by the recent discovery of entirely new elementary excitations in an organic crystal in which electron charge transfer occurs in one dimension along the molecular stacking axis. These experiments have shown the existence of coherently propagating strings of excitons, which are the counterpart of excited states in individual molecules and polymers. As the exciton number density increases, strings of two, three and even more excitons form and propagate coherently through the material. The nonlinear optical responses associated with the new exciton strings, as well as those associated with more familiar collective excitations such as polarons and bipolarons, are being explored as possible sources for increasing γ of linear chains.

Researchers have also recently proposed that the nonresonant γ can be further increased by controlling bond-length alternation, the difference in length between carbon-carbon single and double bonds in a π -conjugated

molecular structure. Changing the alternation may markedly alter the electronic charge density distribution of the molecular ground state. For optimized alternation, enhancements of γ by up to a factor of five are possible.

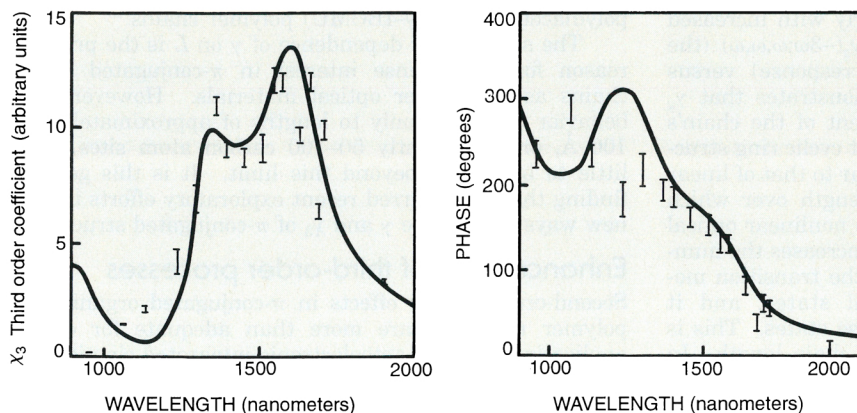
Photorefractive effects

The early 1990s witnessed the first investigations of photorefractive effects in organic and polymer materials.^{22,23} Photorefraction results in a periodically varying index of refraction, effectively creating an index-of-refraction grating. Such a grating has many uses: It can couple two input beams of light or link three input beams of light in a four-wave mixing scheme to produce phase-conjugate waves. (See the article by Jack Feinberg in *PHYSICS TODAY*, October 1988, page 46.) Recent studies have demonstrated that organic and polymeric materials can be used in photorefractive devices.

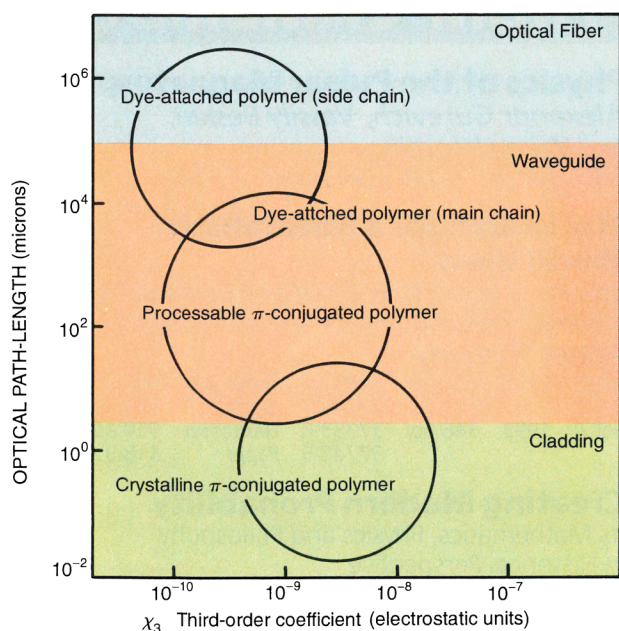
The materials design and sequential synthesis that went into these studies illustrate the strengths and versatility of organic materials. Four processes must occur in a photorefractive material—generation of charge carriers by input light, transport of the charge carriers, trapping of the charge carriers in the dark regions, and electro-optic response. Polymer systems in which photorefractive effects are studied typically consist of thin films of semiconducting polymers doped with charge-donating and nonlinear optical molecules. One can optimize the four processes needed for photorefraction almost independently, by changing the backbone or the dopant molecules. In inorganic systems the properties of crystals cannot be changed so easily, because nonlinear optical and conduction properties are intimately tied to the crystal band structure. Recently researchers have fabricated photorefractive devices based on the charge-transporting polymer poly(*N*-vinylcarbazole) doped with charge generation and electro-optic chromophores. These devices have shown response times and diffraction grating efficiencies²³ (a measure of the effectiveness of the photorefractive process in a material) close to those of inorganic devices. Research into organic polymer-based photorefraction is still in its infancy, and the rapid progress in this field is expected to continue.

Controlling light with light and beyond

It is clear that π -conjugated organic nonlinear optical materials represent a major advance for high technology



Spectral dispersions of the magnitude (a) and phase (b) of the third-order nonlinear optical coefficient χ_3 of poly-4BCMU chains show the qualitative agreement between experiment (data with error bars) and calculations that explicitly account for electron correlation effects (curves).¹⁸ (Courtesy of G. Stegeman, University of Central Florida, and S. Mazumdar, University of Arizona.) **Figure 5**



Possible application areas for third-order nonlinear optical polymers. For example, crystalline π -conjugated polymers can be applied as cladding layers, while soluble π -conjugated polymers are best suited for waveguide applications. (Courtesy of T. Kaino, Nippon Telephone and Telegraph.) **Figure 6**

in the areas of integrated optoelectronic circuits, high-speed fiber optics, and advanced packaging. That development would not have been possible without long-term commitments by government and industry worldwide, especially by the Air Force Office of Scientific Research, the Advanced Research Projects Agency and the National Science Foundation in the US. One can gauge the success of the worldwide effort to realize the promise of nonlinear optical organic materials in the realm of second-order nonlinear effects by the fact that high-performance electro-optic polymer films are now practical materials for the low-cost, reliable fabrication of integrated optoelectronic devices having high bandwidth, low capacitance and low power requirements.

While third-order effects in currently available materials are still orders of magnitude away from realistic device applications, there is reason to expect that the approach taken in the development of second-order effects will prove effective in this realm as well. Investigations into the mechanisms of third-order processes have provided clear, direct evidence that many-body electron correlations are essential to a complete understanding of these processes in π -electron systems. Models must take such effects into account if they are to calculate correctly the magnitude, the dispersion or even the sign of these nonresonant responses. Novel approaches are now being explored to using these insights to enhance nonresonant χ_3 values. With the prospect of future investigations into the photorefractive effect in organic and polymer systems, we are optimistic that the field will continue its rapid progress.

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