660 Chem. Mater. 1990, 2, 660–669

Is There a Role for Organic Materials Chemistry in Nonlinear Optics and Photonics?

Paras N. Prasad*

Photonics Research Laboratory, Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

Bruce A. Reinhardt*

Polymer Branch, Materials Laboratory, Wright Research and Development Center, Dayton, Ohio 45433-6533

Received May 8, 1990

A review of the basic concepts and relevant scientific and technical issues in the new field of nonlinear optics and photonics is presented. The role the chemistry of organic materials may play in the development of new molecules with improved nonlinear optical properties is addressed. Numerous examples of chemical approaches are presented from our research as well as from other published work. We present our view on the question posed in the title. It is our intent to encourage the chemical community to become involved in the synthesis of novel organic/organometallic materials and bring to the attention of other disciplines the role materials chemistry may play in the development of the exciting area of nonlinear optics and photonics.

Nonlinear Optics and Photonics

The field of nonlinear optics and photonics has emerged as a new frontier of science and technology that has captured the imaginations of scientists and engineers worldwide. Photonics is the technology in which a photon instead of an electron is used to acquire, store, process, and transmit information.[1,2] It has been labeled as the technology for the 21st century. One can describe a photonic circuit, equivalent to an electronic circuit, where photons are conducted through channels. These channels can be fibers or channel waveguides imbedded in a film strip. Light can be switched from one channel to another at certain junction points. For optical switching at junctions, one needs to use nonlinear optical effects that allow the manipulation of light propagation, by application of an electric field or a laser pulse. In addition, nonlinear optical effects also give rise to frequency conversion, such as frequency doubling for high-density optical data storage and image analysis.

Photonics has many distinct merits over electronics. The most important advantage is the gain in speed. This increase in speed results from the fact that a photon travels much faster than an electron. Also, in photonic circuitry one can use three-dimensional connectivity to produce smaller integrated optical chips. Other advantages are that there is no electrical and magnetic interference, that the photonic circuits are fully compatible with the existing fiber optics networks, and that remote sensing and space applications are possible. Furthermore, there are new applications of photonics, such as in sensor protection against laser threats, which are not achievable from electronics alone.

Nonlinear optical processes occur when a medium is subjected to an intense light pulse such as that from a high peak power laser. The strong oscillating electric field of the laser creates a nonlinear polarization in the medium, yielding a nonlinear response.

Nonlinear optical processes can conveniently be viewed as dielectric phenomena. For a linear dielectric, application of an electric field polarizes the medium to produce a polarization P that is linearly proportional to the applied field, the proportionality constant $\chi^{(1)}$ being the linear susceptibility. If the electric field is due to an optical field, then the response is also described by a refractive index n. Thus at optical frequencies $n^2(\omega) = 1 + 4\pi\chi^{(1)}(\omega)$. For a plane wave propagation[3]

$$E = E_\omega(z,t) = E_0 \cos(kz - \omega t) \quad \text{or} \quad \tfrac{1}{2}[E_0 e^{i(\omega t - kz)} + \text{cc}] \qquad (1)$$

The refractive index n, the wave vector $k = n\omega/c$, and the phase velocity $v = c/n$ are all independent of the field strength E.

For a nonlinear dielectric one has the polarization[3]

$$P = \chi^{(1)}\cdot\vec{E} + \chi^{(2)}:\vec{E}\vec{E} + \chi^{(3)}\vdots\vec{E}\vec{E}\vec{E} + \text{higher order terms} = \chi_{\text{eff}}\cdot\vec{E} \qquad (2)$$

χ_{eff}, the effective susceptibility tensor, now depends on the field strength E. Therefore n, k, and v are all dependent on E. $\chi^{(2)}$ and $\chi^{(3)}$ are the second- and third-order nonlinear optical susceptibilities and, in general, are third- and fourth-rank tensors, respectively. Two important manifestations of optical nonlinearities are harmonic generation and refractive index modulation by electric and optical fields. Their origin can conveniently be explained by considering a plane wave propagation through the nonlinear medium. The polarization is then given by[4]

$$P = \chi^{(1)}E_0 \cos\alpha + \chi^{(2)}E_0^2 \cos^2\alpha + \chi^{(3)}E_0^3 \cos^3\alpha = \chi^{(1)}E_0 \cos\alpha + \tfrac{1}{2}\chi^{(2)}E_0^2(\cos 2\alpha + 1) + \chi^{(3)}E_0^3[\tfrac{3}{4}\cos\alpha + \tfrac{1}{4}\cos 3\alpha] \qquad (3)$$

where $\alpha = (kz - \omega t)$. Equation 3 shows that due to nonlinear optical effects, higher frequency components (2α and 3α terms) are generated that describe higher harmonic generation, examples being second harmonic generation due to $\chi^{(2)}$ and third-harmonic generation due to $\chi^{(3)}$. In addition, $\chi^{(3)}$ leads to a term with $\cos\alpha$ that describes the intensity dependence of refractive index. The dependence of refractive index on the electric field actually consists of two terms:[4] (i) one derived from $\chi^{(2)}$ that is linearly dependent on E and describes the electrooptic effect, also

---

(1) Clymer, B.; Collins, Jr., S. A. *Opt. Eng.* **1985**, *24*, 74.

(2) Stegeman, G. I. *Thin Solid Films* **1987**, *152*, 231.

(3) Shen, Y. R. *The Principles of Nonlinear Optics*; Wiley: New York, 1984.

(4) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1990.

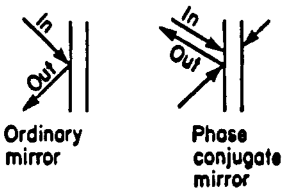


Figure 1. Comparison of reflections from an ordinary mirror and from a phase conjugate mirror.

known as Pockels effect, in which the application of an electric field modulates the refractive index; (ii) one derived from $\chi^{(3)}$ that is quadratically dependent on E and hence linearly dependent on I; it describes the optical Kerr effect. It is the latter that provides a mechanism for light control by light because an intense beam can be used to change the refractive index of the medium and influence either its own propagation or propagation of another beam of different or same frequency.

The intensity dependence of the refractive index can also be used in a degenerate four-wave mixing process.[3-5] With this process in the backward wave geometry, the nonlinear medium acts as a phase-conjugate mirror that reverses the direction of an incoming carrier wave when two counterpropagating waves of the same frequency are applied as shown in Figure 1. This process of phase conjugation corrects for any phase distortion of the carrier wave by reversing the phase in the outgoing beam. Since the process involves four optical waves of the same frequency, it is called degenerate four-wave mixing. In contrast, reflection for an ordinary mirror (also shown in Figure 1) does not reverse the path of the carrier wave and hence does not correct the phase distortion. This phase conjugation is of great significance in relation to real-time holography because using phase reversal one can correct for phase aberrations, introduced by various optical elements and/or environmental distortions, to reconstruct a high-quality image.

Molecular Materials for Nonlinear Optics

Nonlinear optical materials can be classified in two different categories:[4] (i) Molecular materials that consist of chemically bonded molecular units interacting in the bulk through weak van der Waals interactions. For these classes of materials, the optical nonlinearity is primarily derived from the molecular structure, and one can define microscopic nonlinear coefficients β and γ that are the molecular equivalents of the bulk susceptibilities $\chi^{(2)}$ and $\chi^{(3)}$. Examples of molecular materials are organic crystals and polymers.[4,5] (ii) Covalent and ionic bulk materials where the optical nonlinearity is a bulk effect. The examples of this class of materials are most inorganic systems, multiple quantum well semiconductors, and inorganic photorefractive crystals.[6] The molecular materials are emerging as an important class of materials because they provide flexibility to tailor their molecular structure and use molecular engineering to maximize the optical nonlinearity.[4,5,7]

For weak intermolecular coupling, one uses the oriented gas model and relates the microscopic nonlinearities such as γ with the bulk nonlinearity ($\chi^{(3)}$) with the consideration that the local field a molecule experiences in the bulk is different from the applied field due to the mutual polarization from electrons and nuclei of neighboring molecules. In such a case[4]

$$\chi^{(3)}(-\omega_4;\omega_1,\omega_2,\omega_3) = F(\omega_1)\,F(\omega_2)\,F(\omega_3)\,F(\omega_4)\sum_n\langle\gamma^n(\theta,\phi)\rangle \tag{4}$$

Equation 4 uses the convention for frequency dispersion representation of $\chi^{(3)}$ which indicates that three input waves of frequencies ω_1, ω_2, and ω_3 generate an output wave of frequency ω_4, the latter being written with a negative sign. The term $F(\omega_i)$ represents the local field correction factor at an optical frequency ω_i. For this correction factor, one often uses Lorentz approximation according to which[4,7]

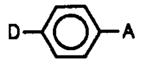
$$F(\omega_i) = (n_0^2(\omega_i) + 2)/3 \tag{5}$$

in which $n_0(\omega_i)$ is the linear refractive index at frequency ω_i. The summation n in eq 4 runs over all molecular sites to give orientational averaging of γ. The two limits are (i) all polymer chains aligned in the same direction in which case $\sum_n\langle\gamma^n(\theta,\phi)\rangle = N\gamma_{zzzz}$ and (ii) a completely amorphous polymer for which $\sum_n\langle\gamma^n(\theta,\phi)\rangle = {}^1/_5N\gamma_{zzzz}$. The term N represents the number density. In either case, a large value of γ produces a large $\chi^{(3)}$. Under this model, therefore, the optical nonlinearity of a materials is determined by its microscopic nonlinearity γ.

To take advantage of the flexibility offered by a molecular material, one needs to be able to project what chemical structures will contribute to optical nonlinearity. This is one area where our theoretical understanding still needs to be developed. However, by using existing theoretical models, we can make some structural projections. A useful model for second-order effect has been the two-level model. In this case one treats a molecule as having only two levels, a ground state, g, and an excited state, i. In such a case and far from resonance, β is given as [4,7,8]

$$\beta(-2\omega;\omega,\omega) = \left(\frac{3e^2}{2\hbar m}\right)\frac{\omega_{ig}^2}{(\omega_{ig}^2 - \omega^2)(\omega_{ig}^2 - 4\omega^2)}f\Delta\mu \tag{6}$$

In the above equation, f is the oscillator strength of the transition g → i and $\Delta\mu$ is the difference of dipole moment between the excited state and the ground state. Therefore, a molecular structure that possesses a low-lying excited state with a large oscillator strength and a more ionic character (to give large $\Delta\mu$) will possess large β. A suitable structure for this purpose is[4,7,8]



In the above structure, a conjugated unit (benzene ring in the above example) separates an electron-donor group (D) such as NH_2 and an electron acceptor group (A) such as NO_2. The lowest lying excited state in such structures involves a charge transfer from group D to group A, which gives rise to a large change of dipole moment.

Although a polymeric structure is not required, it is desirable both for mechanical strength and for ease of fabrication of device structures. For this reason, polymers with nonlinear active groups built into the side chain, as shown in Figure 2, are becoming very attractive materials.[4] In this example the nonlinear side group conforms to the molecular design in which a biphenyl π-electron structure separates an electron donor, oxy group, from an electron acceptor, nitro group.

Since $\chi^{(2)}$ is a third-rank tensor, it is nonvanishing only for noncentrosymmetric media. Therefore, to produce a net second-order nonlinear optical effect in a bulk sub-

---

(5) *Nonlinear Optical and Electroactive Polymers*; Prasad, P. N., Ulrich, D. R. Eds.; Plenum Press: New York, 1988.

(6) *Optical Nonlinearities and Instabilities in Semiconductors*; Haug, H., Ed.; Academic Press: London, 1988.

(7) *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: Orlando, 1987.

(8) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690.

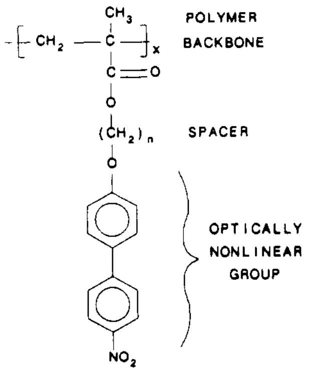


Figure 2. Optically nonlinear side-chain polymers.

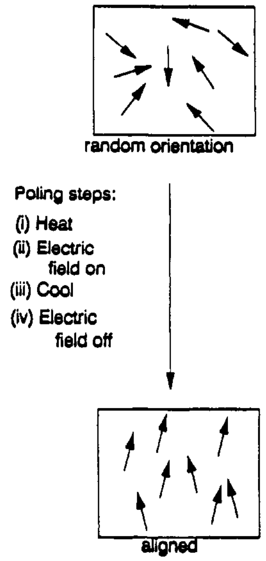


Figure 3. Electric field poling process.

stance, the medium must have a noncentrosymmetric ordering of dipoles, created either by spontaneous ordering or by electric field poling of the medium.[4,9,10] Electric field poling is a four-step process as shown in Figure 3. In the first step, the polymer, which has a random orientation of dipoles, is heated to a temperature at which molecular motions are significant. An electric field—typically 100 kV/cm—is applied to align the dipoles along the field direction. The field is kept on for some time, with the material remaining at a high temperature. The material is then cooled to lock the dipole orientation, and finally, the electric field is turned off. The resultant $\chi^{(2)}$ in an electrically poled system is maximum only when the largest component of the microscopic nonlinearity, β, tensor is along the direction of the molecular dipole. One important concern is reorientation of the ordered dipoles in the poled sample, which can be induced by various relaxation processes.[4] Therefore, current research is focusing on minimizing these dipolar relaxations by various methods.

For third-order nonlinear optical effects, the structural requirements are different. Extended π-conjugation is found to enhance the nonlinearity. Consequently, conjugated polymers have emerged as an important class of third-order nonlinear material.[4,5] Although order in polymeric structures does influence the third-order nonlinear behavior, it is not required. Therefore, even an amorphous polymer can be used for applications of third-order nonlinear optical effects.

Relevant Scientific and Technological Issues

Microscopic Understanding. The issues for second and third-order processes are somewhat different. For second-order processes, our microscopic understanding of optical nonlinearity is sufficiently developed that one can compute these nonlinearities using either simple models or more sophisticated quantum chemical calculations with some reasonable success.[4,7] Utilizing these theoretical models, one can design molecular structures for the synthesis of new materials that will have large microscopic nonlinearities. These calculations or theoretical modeling predict only that the microscopic nonlinearity β will be large. They do not, however, ensure that the molecules will form a noncentrosymmetric structure required to observe second-order processes from the bulk. Theoretical modeling is not sophisticated enough to predict molecular structures with both large β and noncentrosymmetric crystallization.

Another issue in theoretical modeling is the relationship between microscopic nonlinearity and the macroscopic (bulk) susceptibility.[4] One often uses the Lorentz model of local field as has been discussed above. Bulk effects such as intermolecular charge transfer and bulk excitations such as excitons and polaritons can produce substantial modifications of the nonlinear optical behavior. These issues have not fully been addressed.

For third-order processes, the theoretical understanding is even more limited.[4] The quantum chemical approaches do not predict satisfactory agreement with the experimental values. There is a qualitative understanding that π-electron conjugation enhances the nonlinearity. Ab initio calculations have a sound theoretical foundation. However, they cannot be applied to large molecules. One has to rely on semiempirical methods, but these methods are not yet at a stage at which they can be used with any confidence to predict the third-order nonlinearity.

Materials Perspectives. From a materials point of view, some organic crystals are showing promise as highly efficient frequency doublers.[7] The magnitude of $\chi^{(2)}$ for many organic crystals is significantly larger than that of the available inorganic materials.[7,11] Yet, we are not at a stage where these materials are widely used. The reason is the availability of optical quality and defect-free crystals of these materials. Their environmental stability is also a concern.

One concern is the optical transparency of organic materials.[4] As one uses a more conjugated structure to enhance the value of β, there is a big tradeoff in that the lowest lying π–π^* optical transition shifts to the longer wavelength. As a result, the region of optical transparency in the visible–UV range reduces.

For electrooptic applications, prototype electrooptic modulators with large band width have been reported.[12] They have used electrically poled polymers. A major concern here is the dipolar relaxation of the poled polymer, which would lead to a reduction of the bulk $\chi^{(2)}$ value. Although one can think of device structures that can be periodically recharged by poling, this is not a practical solution in most cases.

Third-order materials are even further away from being ready for device applications. The relevant issues are high optical nonlinearities and fast response time. Efforts in

---

(9) Meredith, G. R.; Van Dusen, J. G.; Williams, D. J. *Macromolecules* **1982**, *15*, 1385.

(10) Singer, K. D.; Sohn, J. E.; Lalama, S. J. *Appl. Phys. Lett.* **1986**, *49*, 248.

(11) Garito, A. F.; Singer, K. D. *Laser Focus* **1982**, *80*, 59.

(12) Hass, D.; Yoon, H.; Man, H.-T.; Gross, G.; Mann, S.; Parson, N. *SPIE Proc.* **1989**, *1147*, 222. Man, H.-T.; Chiang, K.; Hass, D.; Teng, C. C.; Yoon, H. N. *SPIE Proc.* **1990**, *1213*.

the past have focused on conjugated polymeric structures that have large γ derived from π-electron contribution and fast response time.[4,5] This ad hoc approach based only on π-conjugation, however, has stifled the progress because the largest nonresonant $\chi^{(3)}$ observed so far in conjugated structures has been only $<10^{-9}$ esu. This value is not large enough for any practical devices, which would like to use only a small switching energy. One, therefore, has to find ways, other than conjugation alone, to enhance optical nonlinearity by several orders of magnitude. Another problem encountered is that of high optical losses in nonlinear polymer wave guides and fibers. Our work with conjugated polymers has shown that the losses arise from residual absorption due to a broad distribution of conjugation length and defects as well as from domain structures (refractive index inhomogeneity) which leads to light scattering.

Another problem encountered is that most conjugated polymers with large $\chi^{(3)}$ are insoluble and not processible. Ideal materials will have large $\chi^{(3)}$ and be processible into high optical quality device structures.

Role of Materials Chemistry

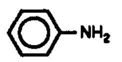
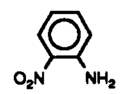
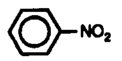
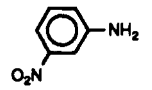
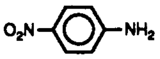
In this section, we provide our answer to the question posed in the title of this article. In our judgement organic materials chemistry will play a very important role in addressing the relevant issues and providing guidance to the development of this area. Some of these key roles are discussed here with suitable examples.

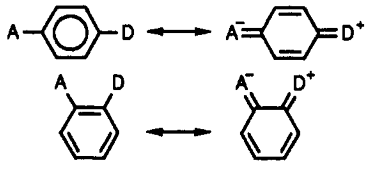
Microscopic Understanding of Optical Nonlinearities. Synthetic chemists and chemical engineers can contribute greatly to our microscopic understanding of optical nonlinearity by producing systematically derivatized and sequentially built molecular structures. A systematic correlation of experimentally measured nonlinearities on these model compounds will provide valuable input for understanding the dependence of optical nonlinearity on specific functional groups, the relation between microscopic nonlinearity and bulk susceptibility, the importance of intermolecular charge transfer, and other effects such as metal chelation.

There have been several excellent pioneering efforts using the molecular structural variation approach that already have identified structural characteristics for molecular design to enhance the microscopic nonlinearities β and γ. In addition, experimental measurements of β and γ on these systematically varied structures have also provided a basis for testing the predictions of various theoretical models in order to establish their reliability. As discussed above, the microscopic structural requirements for second-order and third-order optical nonlinearities are not the same. For this reason, we discuss the systematic studies for second- and third-order effects separately.

For the second-order effect, a considerably large number of molecular structures have been investigated that have established the importance of intramolecular charge transfer, relative positions of the electron donor and acceptor groups, and the length of π-electron delocalization on the value of β. One of the earliest studies provided some excellent experimental evidence of the relationship between donor–acceptor charge transfer through the π system and the magnitude of β. Experimental measurements were carried out on a series of aminonitrobenzene derivatives using electric field induced second harmonic generation (EFISH) in solution.[13] These values are compared in Table I. Although this study involved only a few compounds, the powerful effect of highly conjugated donor and acceptor groups is easily observed. The meta isomer, for which no charge-transfer resonance structures can be written, shows a greatly decreased β when compared to the ortho and para isomers, for which charge-transfer resonance structures can be written. The 4-fold difference in magnitude between the ortho and para isomers can be attributed to the number of double bonds

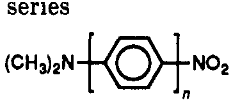
Table I. Experimental β Values for Substituted Nitroanilines

struct	$10^{31}\beta$, esu	struct	$10^{31}\beta$, esu
	7.9		64
	19.7		
	42		211



(total number of π electrons) involved in the resonance between the donor and acceptor groups. This investigation demonstrates how structure–property studies even when involving only a few variations in structure can provide adequate data to formulate basic concepts and predict property trends. Dulcic and Sauteret[14] investigated, using the EFISH technique, the effect of variation in the relative strengths of the donor and the acceptor on the β values of the para-disubstituted benzene derivatives. The measured β values clearly establish the trend that within a series where the bridging group is constant, the β value increases with the increasing donor and acceptor strengths. This study showed that $N(CH_3)_2$ and NO_2 act as the strong electron-donating and electron-accepting substituents, respectively.

Experimental studies of β in sequentially built structures have also provided valuable information on the effect of increase of conjugation length on β. For the (dimethylamino)polyphenyl series



both the experimental and theoretical studies have been made[15] to determine the dependence of β on n. The β value increases monotonically with increasing value of n reaching a maximum between $n = 2$ and 3 and then decreases. This effect can be attributed to first the increase of conjugation length and then a reduction due to the effect of twisting of phenyl rings in higher polyphenyls, which reduces the efficiency of π-conjugation from one phenyl ring to another.[16]

The β values have also been measured for conjugated structures in which a double bond is replaced by a triple bond. One such example is given here:[17]

---

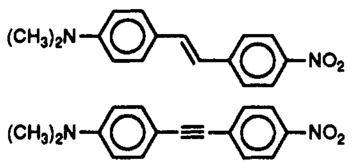
(13) Levine, B. F. *Chem. Phys. Lett.* **1976**, *37*, 516.

(14) Dulcic, A.; Sauteret, C. *J. Chem. Phys.* **1978**, *69*, 3453.

(15) Morley, J. D.; Docherty, V. J.; Pugh, D. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1351, 1357.

(16) Berkovic, G.; Shen, Y. R.; Schadt, M. *Mol. Cryst. Liq. Cryst.* **1987**, *150B*, 607.

(17) Buckley, A.; Chol, E.; Demartino, R.; Leslie, T.; Nelson, G.; Stamartoff, J.; Stuetz, D.; Yoan, H. *Polym. Mater. Sci. Eng.* **1986**, *54*, 502.



These studies have lead to the conclusion that the triple bond actually acts as a potential barrier to π-electron delocalization, reducing the β value.

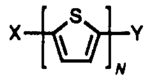
Recently, Cheng et al.[18] have used EFISH and third harmonic generation studies of benzene, stilbene, and the arene derivatives to conduct a systematic investigation of the structure–property relations, especially issues concerning donor–acceptor strength, charge-transfer, conjugation length, planarity, aromaticity, and heteroatom substitution. They focus on the variations of both β an γ in their systematic studies. Their work again confirms the importance of low-lying charge-transfer excitations in giving rise to large second-order nonlinearities in para donor-acceptor substituted benzenes. Cheng et al. also show that the extended and planar structure makes *trans*-stilbene a very effective conjugated backbone. Therefore, the *trans*-stilbene derivatives are found to provide the higher volume normalized nonlinearity in their study.

Compared to the extensive amount of research conducted on synthesis and characterization of new molecular structures for second-order nonlinear processes, the scope of synthesis of new molecular materials and their characterization for third-order nonlinear optical properties have received rather limited attention. As discussed above, the nonresonant third-order nonlinearity has to be significantly enhanced if organic structures have to find application in all optical processing of information. Consequently, there is even a greater need for the study of structure–property relationship for third-order nonlinear optical processes using systematically derivatized and sequentially built structures. Therefore, materials chemistry involving design and synthesis of novel structures is expected to play an important role in the development of third-order nonlinear optical materials.

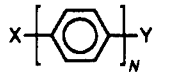
An earlier experimental study by Hermann et al.[19] and theoretical work by Rustagi and Ducuing[20] established the importance of extended π-electron conjugation in achieving large γ values. A conjugated polymer provides a structure framework for extensive delocalization of the π-electrons and hence can be expected to exhibit large third-order nonlinearity. Sauteret et al.[21] reported the first investigation of a conjugated polymer where they studied third-harmonic generation in polydiacetylene and reported a strong dependence of $\chi^{(3)}$ on the π-electron conjugation. Since then much of the work in the development of $\chi^{(3)}$ organic materials has focused on conjugated polymers. In our view, it is time now to identify, by a systematic structure–property correlation, other functionalities for enhancing the nonlinearity.

One study particularly noteworthy from the viewpoint of correlation of molecular structure with γ is that by Stevenson et al.[22] on compounds containing aromatic heterocyclic groups. Stevenson et al. prepared and investigated the polarizabilities and hyperpolarizabilities of a large number of cyanines, thiazole, benzthiazole, and their aza-substituted derivatives by third-harmonic generation. To understand the structure–property relationship and more specifically the role of aza substitution, they analyzed the results using the anharmonic oscillator model of Mehendale and Rustagi.[23] In the anharmonic oscillator model, the nonlinear response of a molecule is related to the anharmonic terms in the potential well in which an electron moves around the nucleus. The cubic anharmonic term relates to the second-order coefficient β, and the quartic term relates to the third-order coefficient γ. Mehendale and Rustagi,[23] using a free-electron model, showed that, for moderate conjugation length, $\gamma = K\alpha^{7/3}$ in which K is the anharmonicity factor, which is an indicator of the intrinsic anharmonicity of the π-electrons, and α is the linear polarizability. Their work suggests that enhancement of γ in a linear conjugated structure can be achieved by structural modifications that increase the anharmonicity factor. A symmetric aza substitution in the cyaninelike structure produces this effect by introducing a spatially periodic potential. Similarly, the incorporation of the nitrogen linkage in the chain between the benzthiazole groups seems to greatly increase the magnitude of γ.

With an objective to understand the structure–property relationship, Zhao et al.[24,25] investigated the third-order nonlinearity of systematically derivatized and sequentially built thiophene and benzene structures as shown here:



thiophene oligomers
X, Y = H, NO₂, I
N = 1–6



benzene oligomers
N = 1–3

They used femtosecond degenerate four-wave mixing at a wavelength of 602 nm on THF solutions of these materials. The advantage of the solution measurement is that in addition to yielding the orientationally averaged γ value, it also provides information on the sign of γ and whether it is a complex quantity. Their measurement yielded a positive value for all those compounds that do not absorb at 602 nm. This sign is what various microscopic theories predict for a nonresonant γ value. Close to an electronic resonance, the real part of γ often becomes negative. In the case of an electronic resonance, γ is complex, the imaginary part relating to nonlinear absorption. In the case of benzene oligomers, the measurement could not be performed for oligomers with $N > 3$ because of the difficulty in solubilizing them.

Zhao et al.[24] fitted the dependence of orientationally averaged $\langle\gamma\rangle$ for the thiophene oligomers to the following power law in N, the number of repeat units:

$$\langle\gamma\rangle = A + B(N - \delta)^C$$

Their analysis yields an exponent of ~4, which is to be compared with a value of 5 predicted by the free-electron model[20] and 3.5 predicted by ab initio calculations.[26] For the benzene oligomers, the increase in the γ value with increasing N is not as fast and the value appears to level

---

[18] Cheng, L.-T.; Tam, W.; Meredith, G. R.; Rikken, G. L. J. A.; Meijer, E. W. *SPIE Proc.* **1989**, *1147*, 61.

[19] Hermann, J. P.; Ricard, D.; Ducuing, J. *Appl. Phys. Lett.* **1973**, *23*, 178.

[20] Rustagi, K. C.; Ducuing, J. *Opt. Commun.* **1974**, *10*, 258.

[21] Sauteret, C.; Hermann, J. P.; Frey, R.; Pradere, F.; Ducuing, J.; Baughman, R. H.; Chance, R. R. *Phys. Rev. Lett.* **1976**, *36*, 956.

[22] Stevenson, S. H.; Donald, D. S.; Meredith, G. R. *Nonlinear Optical Properties of Polymers*; Heeger, A. J., Orenstein, J., Ulrich, D. R., Eds.; Materials Research Society Symposium Proceedings; Materials Research Society: Pittsburgh, 1988; Vol. 109, p 103.

[23] Mehendale, S. C.; Rustagi, K. C. *Opt. Commun.* **1979**, *28*, 359.

[24] Zhao, M.-T.; Singh, B. P.; Prasad, P. N. *J. Chem. Phys.* **1988**, *89*, 5535.

[25] Zhao, M.-T.; Samoc, M.; Singh, B. P.; Prasad, P. N. *J. Phys. Chem.* **1989**, *93*, 7916.

[26] Chopra, P.; Carlacci, L.; King, H. F.; Prasad, P. N. *J. Phys. Chem.* **1989**, *93*, 7120.

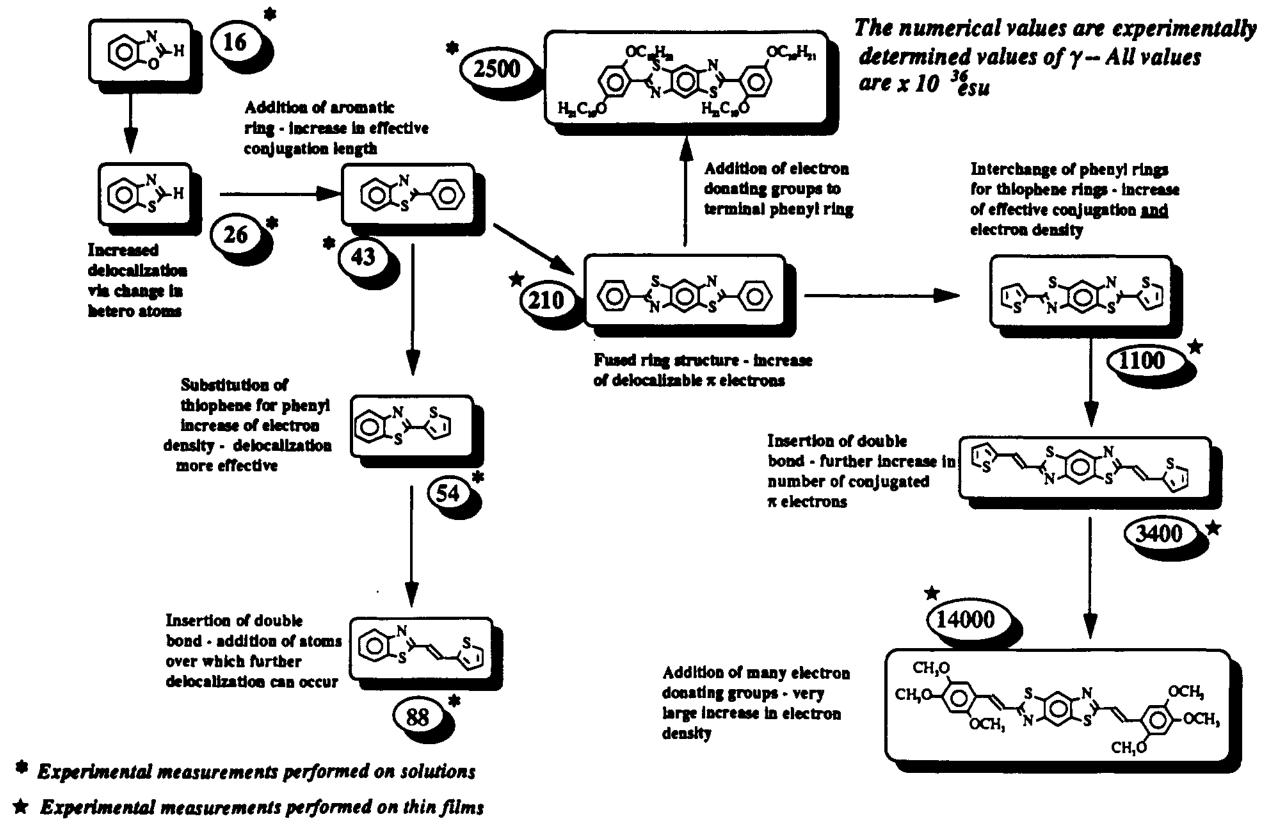


Figure 4. Flow chart of structural modifications to increase γ for benzothiazole model compounds.

off at $N \geq 3$. This result establishes that the π-conjugation through the thiophene unit is much more effective than through the benzene unit, possibly due to the noncoplanarity of benzene rings in the latter case. The experimental results reported by Zhao et al.[25] also suggests that substitution by nitro and iodo groups (which are electron rich) enhances the third-order optical nonlinearity of the thiophene units.

Due to a lack of adequate experimental structure–NLO property data on aromatic heterocyclic compounds in the literature, we began a combined study in our laboratories to fill this void. We have thus far been able to evaluate the third-order nonlinear optical properties of a large number of systematically varied model compounds. At the onset of the investigation it was decided that the following criteria needed to be strictly adhered to for the study to be meaningful: (1) The model compounds for study had to be well characterized and highly pure. (2) The method of measurement had to be designed to distinguish purely nonresonant electronic nonlinearity from other types of nonlinearity. (3) A correlation of values measured on different forms (e.g., solution or thin films) must be made. The method chosen for the model compound measurement was femtosecond degenerate four-wave mixing. The femtosecond time resolution provides the opportunity to distinguish electronic $\chi^{(3)}$ processes from other types of nonlinearities with slower response. Details of the synthesis, preparation of samples, calculations, and experimental measurements are presented in the accompanying paper.[27] In this review we will summarize the experimental results and offer some discussion on the systematic correlation of the structures with these measured values. We assign the difference in the nonlinearity to the variation in chemical structure, since all measurements are made under nonresonant conditions. The power-dependence study along with the time decay behavior and lack of any imaginary contributions as inferred from the concentration dependence analysis suggests that no one- and two-photon resonances are encountered for these model compounds at the wavelength of study (602 nm). To simplify the understanding of the various correlations and to understand the structural building methodology employed to increase the value of γ, it is advantageous to examine schematic flow charts for both benzothiazole and *N*-phenylbenzimidazole model compounds as presented in Figures 4 and 5. If one examines the upper left corner of the flow chart in Figure 4 it can be concluded that if a less electronegative atom such as sulfur is incorporated into the heterocyclic part of these molecules the electronic delocalization improves from oxygen to sulfur and γ increases. This effect may be due in part to the participation of the d orbital and the ease of polarization of the electrons in the sulfur atom. This increased aromaticity of benzothiazole is also exemplified in the proton NMR spectra of similar compounds.[28]

As one moves along the flow chart from benzothiazole to 2-phenylbenzothiazole it can be seen that the substitution of a phenyl group for a hydrogen causes almost a 2-fold increase in γ. This is a direct result from both an increase in effective conjugation length and the total number of π electrons.

As one moves down the chart from the 2-phenyl derivative to the compound that contains a double bond and a thiophene unit, γ increases by approximately a factor of 2. This increase is again due to the extension of conjugation and higher electron density derived from sulfur. It also shows that olefinic bonds are highly effective in

---

(27) Zhao, M.-T.; Samoc, M.; Prasad, P. N.; Reinhardt, B. A.; Unroe, M. R.; Prazak, M.; Evers, R. C.; Kane, J. J.; Jariwala, C.; Sinsky, M. *Chem. Mater.*, following paper in this issue.

(28) DiModica, G.; Barni, E.; Gasco, A. *J. Heterocycl. Chem.* **1965**, *2*, 457.

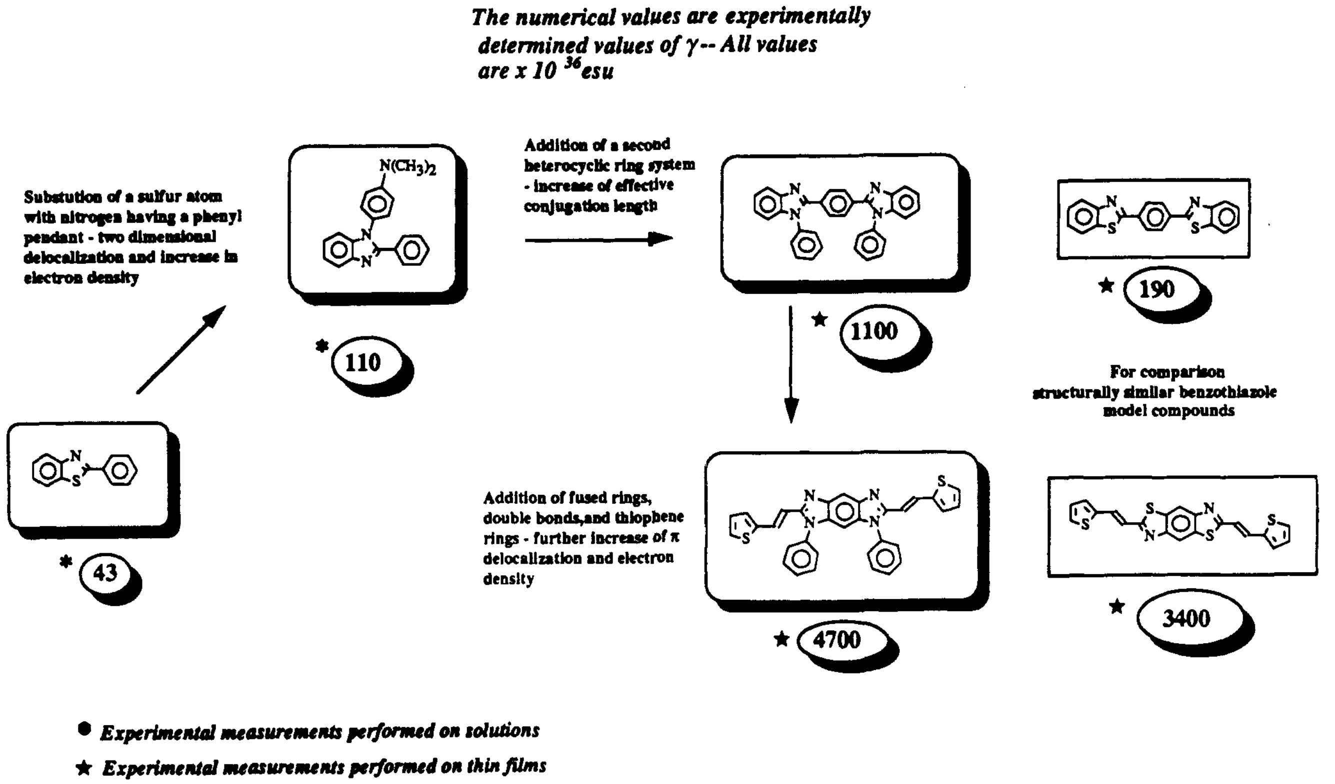


Figure 5. Flow chart showing variation of experimental γ values with structure for N-phenylbenzimidazole model compounds.

increasing the conjugation length.

If one moves right from 2-phenylbenzothiazole to compounds containing three fused rings, another significant increase in γ is realized. Again, it is the extension of conjugation in the fused ring system and the increased number of π electrons that are the major contributing factors. With the addition of long-chain alkoxy groups in the 2 and 5 positions of the terminal phenyl rings an increase in solubility is observed along with an increase in γ. Clearly, the introduction of an alkoxy group enriches the electron density in the π conjugation of this compound because of the electron-donating nature derived from the lone s-electron pair of the alkoxy group.

As one again moves across the table to the model compound containing three fused rings with two terminal thiophene groups, γ is again increased by a factor of 5. Once again the ease in polarization of the electrons around the sulfur atoms and the increased effective conjugation of thiophene compared to benzene are the factors that bring about this major increase in γ.

Moving down the chart, the insertion of double bonds between the thiophene rings and the benzobisthiazole nucleus produces a 3-fold increase in γ due to the large further increase in conjugation length.

Finally, upon the substitution of electron-rich trimethoxy-substituted phenyl rings for thiophene, an additional 4-fold increase in γ is realized. Although this compound is still under investigation, it appears that the donating ability of the methoxy groups in the 4 positions on the terminal phenyl rings has a much stronger influence in the enhancement of γ than do the alkyoxy groups on other position of the same rings.

In Figure 5 a flow chart showing the effect that structure has on the experimental value of γ for N-phenylbenzimidazole model compounds is presented. On the left side of the chart it can easily be seen that as a nitrogen atom containing an electron-rich phenyl pendant is substituted for a sulfur atom, there is a 3-fold increase in the experimental value of γ. The introduction of the pendant phenyl group on the heteroatom provides both extended conjugation and increased electron density to the molecule. This pendant phenyl group approach introduces a two-dimensional nature to π-electron structure. The pendant group also helps in improving the solubility.

Moving to the right, the addition of a second heterocyclic group containing a pendant phenyl group increases γ by an order of magnitude. The γ value of this compound, when compared to the γ value of a benzothiazole model compound of similar structure shows the impact of the incorporation of the pendant phenyl groups.

As we move down the table to the fused ring N-phenylbenzimidazole containing double bonds and thiophene terminal groups, γ is again increased, this time by a factor of 4. Again the inclusion of double bonds and thiophene units causes an increase in γ similar to those increases produced by the same structural units in other model compounds. The contribution of the pendant phenyl is again demonstrated by a comparison with a structurally similar benzobisthiazole model compound.

The above systematic correlations, utilizing experimental observations, enable us to make the following important conclusions that will help us in guiding the design of new nonlinear materials:

(a) A thiophene ring in a conjugated structure is found to be much more effective than a phenyl ring or other heteroaromatic rings such as furan or pyridine in increasing optical nonlinearity.

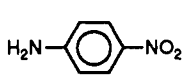
(b) An olefinic double bond provides a highly effective π-delocalization and consequent increase of the third-order nonlinear coefficient.

(c) Grafting of pendant aromatic groups through attachment to a nitrogen atom in a fused heteroaromatic ring provides a means for producing two-dimensional π-conjugation. Our experimental observation indicates that such a structural change leads to not only enhancement but also improved solubility.

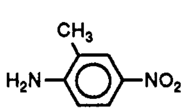
(d) The substitution of an alkoxy pendant group on an aromatic or heterocyclic ring is found to enhance $\chi^{(3)}$, presumably, because of the electron-donating nature of the alkoxy group. It also leads to improved solubility due to an increase in the free volume of the molecule.

Noncentrosymmetric Crystallization by Appropriate Derivatization and Novel Molecular Assemblies. Even with a molecular structure exhibiting large microscopic nonlinearity β, the corresponding bulk structure has to be noncentrosymmetric for the medium to exhibit second-order nonlinear optical effect (nonvanishing $\chi^{(2)}$). Materials chemistry can play an important role in the design and preparation of noncentrosymmetric bulk phase. The three important approaches used for the development of materials for second-order nonlinear optics are crystal growth including inclusion complexes, electrical poling of polymers, and deposition of Langmuir–Blodgett films.[4]

The organic crystals offer the advantages of highly specific arrangements of molecules and density of packing in a crystalline state to maximize bulk nonlinearity. Chemical derivatization has been used to introduce asymmetric unit and noncentrosymmetric crystallization.[4] A simple example is provided by nitroaniline, which forms a centrosymmetric crystal, and its derivative 2-methyl-4-nitroaniline (MNA), which forms noncentrosymmetric (monoclinic, m) crystals.[7] MNA exhibits one of the highest $\chi^{(2)}$.

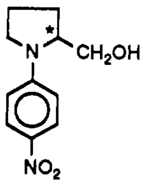


4-nitroaniline



2 methyl-4-nitroaniline (MNA)

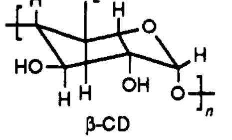
The strategy for ensuring noncentrosymmetric crystal structure by incorporating a chiral substituent has been successfully used in many cases. Probably, the most successful example of the use of chirality in crystal design is provided by N-(4-nitrophenyl)-L-prolinol (NPP):



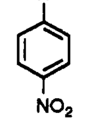
NPP

Zyss et al.[29] found that a combination of the chiral substituent and hydrogen-bonding character of the prolinol group leads to nearly optimal orientation of the molecule within the unit cell for phase-matched interactions.

Another important avenue to prepare a novel noncentrosymmetric crystalline structure is by incorporating the molecules with large β into inclusion matrices such as cyclodextrin, zeolite, etc. This approach was first demonstrated by Tomaru et al.,[30] who prepared the complexes of β-cyclodextrin (β-CD) and various nitroaniline derivatives such as N-methyl-4-nitroaniline (HMNA):



β-CD



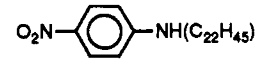
HMNA

The guest, by itself, crystallizes in a centrosymmetric group, and the β-cyclodextrin by itself exhibits on a small nonlinearity. The 1:1 complex, in contrast, exhibits a very strong second-order nonlinearity. Since this work, several additional inclusion hosts with a variety of organic and organometallic guest structures have been studied.[31,32]

Another approach useful for preparing noncentrosymmetric crystalline structures is the use of molecular salts of organic cations with β-enhancing structures.[33] The option to vary the anions allows one to change the monopole interactions which may override the dipolar effects usually responsible for centrosymmetric crystallization of molecular structures with large β. A more recent work reports preparation of organic salts with very large $\chi^{(2)}$ as determined by powder second harmonic generation.[34]

Polymeric structures offer a greater flexibility in chemical modification of both the side chain and the main chain. In addition, they exhibit the flexibility of fabrication into various physical shapes (fibers, films, etc.). Most polymers, however, have amorphous domains, not suitable for second-order optical nonlinearity. A successful approach has been to use the electric field poling technique, described above, to align the molecular dipole and consequently generate a noncentrosymmetric alignment. The electric field poling approach has been applied to cases where a molecule with large β is molecularly dispersed in a polymer matrix as well as to a situation where the nonlinear group is incorporated in the polymer structure.[4] The advantage of the latter type of system is that large concentrations of the nonlinear groups can be introduced without any phase separation. An important material design for electric field poling is the syntheses of side-chain polymers, as mentioned earlier, in which the nonlinear molecular moieties with large β are attached as a pendant group through a flexible spacer to the polymer backbone. Eich et al. recently have shown that organic glasses can also be electrically poled.[35]

The Langmuir–Blodgett film approach offers the orientational advantages of the crystalline state, with an enhanced degree of materials design flexibility.[4] The Langmuir–Blodgett approach uses a transfer of the monolayer films of an amphiphilic molecular structure from an air–water interface to a substrate. In the monolayer form, amphiphilic molecules will always yield a noncentrosymmetric structure. The molecular design for this approach involves the synthesis of amphiphilic derivatives of molecular structure with large β. A simple modification is to simply introduce a long alkyl chain (hydrophobic tail). A suitable simple example investigated in our laboratory is the following derivative of 4-nitroaniline:[36]



This material when spread on water phase orients itself, with the molecular axes at an angle and the hydrophobic tail protruding out of the water subphase. The noncentrosymmetric structure in the monolayer form yields a net

---

(29) Zyss, J.; Nicoud, J. F.; Coquillay, M. *J. Chem. Phys.* **1984**, *81*, 4160.

(30) Tomaru, S.; Zembatsu, S.; Kawachi, M.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1207.

(31) Wang, Y.; Eaton, D. F. *Chem. Phys. Lett.* **1985**, *120*, 441.

(32) Tam, W.; Eaton, D. F.; Calabrese, J. C.; Williams, I. D.; Wang, Y.; Anderson, A. *Chem. Mater.* **1989**, *1*, 128.

(33) Meredith, G. R. In *Nonlinear Optical Properties of Organic and Polymeric Materials*; Williams, D. J., Ed.; American Chemical Society: Symposium Ser. 233, 1983, p 30.

(34) Marder, S. R.; Perry, J. W.; Schaefer, W. P. *Science* **1989**, *245*, 626.

(35) Eich, M.; Looser, H.; Yoon, D. Y.; Twieg, R.; Bjorklund, G.; Baumert, J. C. *J. Opt. Soc. Am. B* **1989**, *6*, 1590.

(36) Geisler, T.; Wijekoon, K. J.; Prasad, P. N.; Rosenheilde, S.; Ramanujam, P. S., unpublished results.

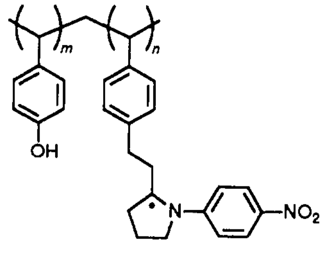
$\chi^{(2)}$ and thus generates second harmonic. Successively deposited multilayer films of this compound also generate second harmonic because a tilt in the molecular axis with respect to the surface normal produces net dipole along the surface.

In many cases, however, successive deposition generates cancellation of the nonlinearity between two successive layers due to antiparallel alignment of the chromophores. Girling et al.[37] used an alternating layer concept for the fabrication of noncentrosymmetric multilayers. They deposited alternate layers of the nonlinear active merocyanine and nonlinear-inactive spacer ω-tricosenoic acid.

Neal et al.[38] have shown that by selecting a spacer in which the donor–acceptor groups are oppositely arranged, an alternate layer Langmuir–Blodgett film structure can be built in which the nonlinearities derived from these alternate layers are additive. It has also been reported[39] that by special choice of the structure, one can form multilayer Langmuir–Blodgett films that involve a head-to-tail (z-type) arrangement, which avoids the cancellation of the nonlinearities between the successive layers.

Another approach for preparing novel molecular assemblies for second-order effects has recently been described by Azoz et al.[40] The technique involves the use of temperature gradient zone melting (TGZM) to grow aligned crystals of 4-nitroaniline (MNA) in a transparent polymer matrix such as poly(methyl methacrylate) or poly(vinylcarbazole). In this type of composite material the host polymer imparts mechanical integrity to the normally fragile MNA crystals. The advantages of these materials are reported to be the following: (1) Very transparent and nonscattering films in the visible, (2) excellent stability with no decrease in activity for over 1 year, and (3) with careful design of the host material the index of refraction of that host can be matched with that of the guest.

Chemical Processing To Reduce Dipolar Relaxation in Solid Polymers. In the case of poled polymers for second-order nonlinear processes, a major issue is the long-term stability of the induced metastable dipole aligned state. Dipole–dipole interaction is unfavorable in this configuration, and dipolar relaxation occurs to produce randomization of dipoles in the polymeric phase. Chemical processing can be used to minimize this dipolar relaxation and overcome the loss of alignment. Ye et al.[41] showed that by using an appropriate structure capable of hydrogen bonding, one can considerably increase the stability of poled structures. They prepared the following copolymer in which the composition n was varied between 0.15 and 0.48:

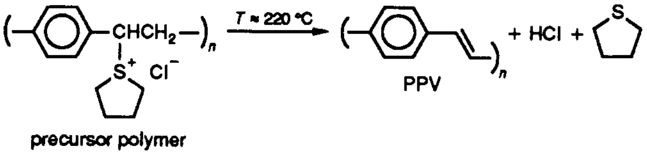


The hydrogen bonding between the OH group and the electron-rich amine unit produces a weak cross-linked network that contributes to the enhanced stability of the poled structure.

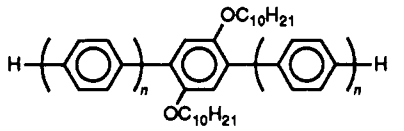
Recently, Robello et al.[42] and Eich et al.[43] used an approach where photoinduced cross-links in multiacrylic systems or diepoxide–diamine condensation reactions leads to considerable increase in the stability of poling. Also, Hubbard et al.[44] recently used an approach in which a high-β guest is dispersed in an optically transparent host matrix that can simultaneously be poled and chemically cross-linked. In this work, a two-component optically transparent thermosetting epoxy, IPO-TEK 301-2, was employed as the cross-linkable host matrix.

Improved Processibility through Materials Chemistry. Materials chemistry can be used to produce polymeric structures that are easily processible into device structures. One approach is to devise a soluble precursor route in which a device structure is fabricated with a soluble precursor polymer which is then converted (by heat or radiation treatment) into the final polymer.

Poly(p-phenylenevinylene), commonly abbreviated as PPV and investigated in our laboratory for high third-order optical nonlinearity,[45] has been processed by using a water-soluble sulfonium polyelectrolyte polymer precursor. The precursor can be cast into a device structure (e.g., film) by using solution processing. Then it can be converted into the final conjugated polymer PPV upon heating when the following E1CB elimination takes place:[46]



Another useful approach is derivatization of the present polymer structure to make it more soluble. Pendant long alkyl or alkoxy chains have been found to render increased solubility to a polymeric structure.[47,48] In our work we have used this approach for the study of both polythiophene and polyphenyls. Here we discuss polyphenyls. In the case of unsubstituted polyphenyls, the third-order nonlinear measurements were limited to terphenyl due to the drastically reduced solubility of p-quarterphenyl. We found that the incorporation of only two oxydecyl groups on the central phenyl ring produced a substantial lowering of the melting point as well as a large increase in solubility:



An increase in solubility is especially important for the pentamer (n = 2) and heptamer (n = 3). These higher

---

(37) Girling, I. R.; Kolinsky, P. V.; Cade, N. A.; Earls, J. D.; Peterson, I. R. *Opt. Commun.* **1985**, *55*, 289.

(38) Neal, D. B.; Petty, M. C.; Roberts, G. G.; Ahmad, M. M.; Feast, W. J.; Girling, I. R.; Cade, N. A.; Kolinsky, P. V.; Peterson, I. R. *Electron Lett.* **1986**, *22*, 460.

(39) Popovitz-Biro, R.; Hill, K.; Landau, E. M.; Lahav, M.; Laserowitz, L.; Sagiv, J. *J. Am. Chem. Soc.* **1988**, *110*, 2672.

(40) Azoz, N.; Calvert, P. D.; Kadim, M.; McCaffery, A. J.; Seddon, K. R. *Nature* **1990**, *344*, 49.

(41) Ye, C.; Minami, N.; Marks, T. J.; Yang, J.; Wong, G. K. *Macromolecules* **1988**, *21*, 2899.

(42) Robello, D. R.; Ulman, A.; Willand, C. S. U.S. Patent 4,796,971, 1989. Robello, D. R.; Scozzafova, M.; Willand, C. S.; Ullman, A. ACS Symposium on New Materials for Nonlinear Optics, Boston, April, 1990.

(43) Eich, M.; Reck, B.; Yoon, D. Y.; Wilson, C. G.; Bjorklund, G. C. *J. Appl. Phys.* **1989**, *66*, 3241.

(44) Hubbard, M. A.; Marks, T. J.; Yang, J.; Wong, G. K. *Chem. Mater.* **1989**, *1*, 167.

(45) Singh, B. P.; Prasad, P. N.; Karasz, F. E. *Polymer* **1988**, *29*, 1940.

(46) Gagnon, D. R.; Capistran, J. D.; Karasz, F. E.; Lenz, R. W.; Antoun, S. *Polymer* **1987**, *28*, 567.

(47) Jen, K. Y.; Oboodi, R.; Elsenbaumer, R. L. *Polym. Mater. Sci. Eng.* **1985**, *53*, 79.

(48) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212.

oligomers show interesting manifestations of one- and two-photon resonances. The results are especially interesting for the heptamer (n = 3) because even in solution an upconverted blue emission is observed possibly due to two-photon absorption.

Control of Optical Losses by Using Structurally Homogeneous Materials. Conjugated polymeric structures because of the distribution of conjugation lengths and chain lengths are structurally inhomogeneous which cause absorption and scattering losses. An alternative approach for third-order nonlinear optical materials can be the use of well-defined oligomeric structures or segmented (block polymer and copolymer) polymeric structures.

Our measurements on sequentially built model compounds indicate a leveling-off of the γ value as the oligomer size is increased.[24,25] An extrapolation of γ values of thiophene oligomers indicates that the $\chi^{(3)}$ value for N = 9 oligomer should be the same as that for a long-chain polymer.[24] Clearly, the effective conjugation lengths in these high molecular weight polymers are not large, limited possibly by a chemical defect or rotation along the single bond. In the case of poly(p-phenylene) the effective conjugation length is projected to be even more limited. Therefore, one can achieve the same effective nonlinearity by preparing a well-defined optimum length oligomer that can be appropriately derivatized to make it soluble. We have used this approach for polyphenyls as discussed above where alkoxy substitution was used on the central ring to make the homogeneous heptamer structure. Alternatively, one can incorporate an optimum length oligomeric conjugated segment into a polymeric structure by preparing block copolymers.

In our systematic investigation of sequentially built aromatic heterocyclic model compounds (discussed above and in more detail in the accompanying paper), we observe that the $\chi^{(3)}$ value of some of these conjugated oligomers already approaches that of many aromatic heterocyclic polymers such as poly(p-phenylenebenzobisthiazole).[49]

Molecular Composites Approach for Optimization of Materials Quality and Nonlinearity. For photonics applications, there is a need for multifunctional materials that simultaneously exhibit many necessary physical and chemical properties. Use of polymer blends and molecular composites is one approach by which one can optimize the various functionalities necessary for a given application. An example is a molecular composite where the optical nonlinearity is derived from one component, while the second component helps improve the optical quality and optical damage threshold.

Here we discuss one specific example of photonics application, nonlinear optical waveguide for all optical switching circuit. One can use a conjugated polymer that has a large nonresonant $\chi^{(3)}$ and exhibits femtosecond response time. However, the conjugated polymers are generally optically highly lossy. Conversely, inorganic glasses, particularly silica, form excellent photonic media because of the extremely low optical losses achievable. These glasses, however, have very low $\chi^{(3)}$.

One can naturally think of a composite of an inorganic glass and a conjugated polymer in which both the optical quality and high $\chi^{(3)}$ are optimized. An inorganic glass and an organic polymer are generally found to be incompatible for forming a composite, and phase separation occurs. Recently, our research effort using sol–gel chemical processing of glasses has produced, to our knowledge, the first compatible blend between the silica glass and a conjugated polymer, poly(p-phenylenevinylene).[50] This composite is homogeneously mixed over large composition ranges and can be cast in the form of films for planar waveguide configurations in which optical losses are significantly reduced. This success opens up an area of materials chemistry of new exotic composites of inorganic glasses and organic polymers for many technological applications.

Conclusion

In conclusion, molecular engineering and chemical synthesis of novel structures as well as materials processing are expected to play a major role in the development of this new and highly exciting area. It is our hope that this article will sufficiently stimulate the interest of materials chemists to actively contribute to this field.

Acknowledgment. The work performed at SUNY, Buffalo, was supported by the Air Force Office of Scientific Research, Directorate of Chemical and Atmospheric Sciences and Polymer Branch, Air Force Wright Materials Laboratory, Wright Research and Development Center through Contract Number F49620-90-C-0021.

---

(49) Rao, D. N.; Swiatkiewicz, J.; Chopra, P.; Ghoshal, S. K.; Prasad, P. N. *Appl. Phys. Lett.* **1986**, *48*, 1187.

(50) Wung, C. J.; Pang, Y.; Prasad, P. N.; Karasz, F. E. *Polymer*, in press.