Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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This paper establishes a general framework relating nonlinear optical processes to the molecular orientational order within the material. The orientational order is described as an ensemble average of orthogonal functions transforming from the molecular to the macroscopic frames using a distribution function appropriate for the particular material class. These molecular additivity concepts can be applied to many materials including crystals, liquid crystals, polymer liquid crystals, Langmuir-Blodgett films, and polymer glasses. The literature is reviewed in the context of this description. Limitations, including inhomogeneity, defects, and quadrupole contributions are also discussed.

1. INTRODUCTION

Interest is growing in research aimed at developing new nonlinear optical materials for potential applications in the areas of telecommunications, computing, and imaging. The large nonlinear optical susceptibilities of certain organic molecules and polymers have stimulated considerable efforts toward the understanding of the nonlinear optical properties of these materials.[1–3] These susceptibilities have been traced to the electronic properties of the constituent molecules.[4] Much of the work on nonlinear optical properties of organic materials has been on molecular and polymeric crystals, where the positions of each atom and the bulk symmetries of the crystal are known exactly and make it possible to calculate the macroscopic nonlinear properties by summing over individual molecules.[5] Organic molecules, however, may be fabricated into materials characterized by order intermediate between a crystalline solid and an isotropic liquid. Thin ordered or-

ganic films with large nonlinear susceptibilities hold great potential for photonics applications, as thin films are compatible with existing electronics technology. Although an organic film may have less order than a crystalline solid, it is possible to impart a substantial nonlinear response by controlling orientational order. In addition, the possible ways to achieve order, either spontaneously or by applying an external force are numerous, owing to the flexibility of engineering the properties of a film, either by modifying or mixing the constituent molecules or changing the macroscopic symmetry of the material.

It is useful, therefore, to understand in a general way, the effects of macroscopic ordering on the nonlinear response. Such a framework is presented here in as nonspecific language as possible, in order that it can apply to various processes for making an ordered thin film. The relationship between macroscopic nonlinear optics and structural order is presented, applying these results to previous work addressing specific systems. The dependence of the second-order susceptibility on orientational ordering has been derived elsewhere in detail for doped polymers and liquid crystals poled by an external field.[6] The validity of the theory for poled doped polymer films has been confirmed. The dependence of third-order macroscopic nonlinear response on orientational order has also been previously calculated and measured in liquid crystalline and liquid crystal polymer systems.[7-13] Fluctuations in order parameters and bulk inhomogeneities of a medium contribute to its nonlinear optical response, and this has been calculated for second harmonic generation of nematic liquid crystals.[14]

The general dependence of nonlinear susceptibilities on macroscopic ordering of molecules in a medium is applied to several different materials including liquid crystals, liquid crystal polymers, glassy polymers, and Langmuir-Blodgett films. For each of these systems, data is presented on structural order and then related to measured nonlinear optical properties by modeling the nonlinear optical reponse of partially ordered ensembles of organic molecules.

2. INTRODUCTION TO NONLINEAR OPTICS

The application of an electric field to a material system causes the constituent charges to move in order to minimize total energy. In a molecular or atomic system, this results in ionization, excitation into a higher or lower energy state, or virtual excitation. Nonlinear optical measurements probe changes in the system's distribution of charge.

It is convenient to describe the induced charge distribution as an expansion in multipole moments, q_{lm},[15,16]

$$q_{lm} = \int Y^*_{lm}(\tau',\phi')r'^l\rho(\mathbf{x}')\mathrm{d}^3\mathrm{x}', \tag{1}$$

where $Y_{lm}(\tau',\phi')$ is a spherical harmonic function, r' the radial charge coordinate, $\mathbf{x}'$ the charge coordinate, $\rho(\mathbf{x}')$ the charge distribution function, and where * denotes complex conjugate.

A uniform electric field causes charges of opposite sign to move apart, resulting in a dipolar polarization. Since quadrupole charge distributions result from field gradients, only highly nonuniform fields yield a substantial quadrupolar redistribution of charge. Thus, dipolar polarization is dominant in bulk homogeneous materials. Near boundary surfaces, however, the electric field gradient can be large if the interface contains bound charge. This situation arises when two media of differing index of refraction are brought into contact. The electric field is discontinuous at the point of contact and the field gradients are large in a layer around the boundary surface. The thickness of this layer is material dependent and is usually on the order of a few molecules.[15]

Real physical systems possess charges that are bound in an anharmonic potential, which, for sufficiently intense electric fields, causes charge displacement to be nonlinear in the applied field. In the dipole approximation and for instantaneous response, the polarization, $\mathbf{P}$, is defined as the induced dipole moment per unit volume and is expressed as a Taylor series in the electric field, $\mathbf{E}$:

$$P_i(t) = \chi_i^{(0)} + \chi_{ij}^{(1)}(t)E_j(t) + \chi_{ijk}^{(2)}(t)E_j(t)E_k(t) + \chi_{ijkl}^{(3)}(t)E_j(t)E_k(t)E_l(t) + \cdots, \tag{2}$$

where $\chi^{(n)}$ is the nth order susceptibility, and where summation over repeated indices is implied. The first term in the expansion is the spontaneous polarization and the second term is responsible for linear optics. This paper will focus on the effects resulting from terms nonlinear in the electric field.

The quadrupole contribution to the nonlinear optical polarizability is of the form[14]

$$P_i = \Gamma_{ijkl}^{(2)}E_j\nabla_k E_l + \Gamma_{ijklm}^{(3)}E_jE_k\nabla_l E_m + \ldots, \tag{3}$$

where $\Gamma^{(n)}$ is the nth order susceptibility, and where ∇_k is the kth

component of the gradient operator. A film thinner than a few molecules, on a substrate, will experience a large field gradient throughout the film, so that the total polarizability will be a sum of both the dipole and quadrupole polarizabilities. Even in the absence of a film, the broken symmetry due to the interface can result in nonlinear optical polarizabilities. Assuming that the surface results in a total susceptibility $\chi_s^{(n)}$ and that the total film susceptibility (including both dipole and quadrupole polarizations) is $\chi_f^{(n)}$, the measured film susceptibility near the surface will be of the form,

$$\chi_{tot}^{(n)} = \chi_s^{(n)} + \chi_f^{(n)} + \chi_I^{(n)}, \tag{4}$$

where $\chi_I^{(n)}$ accounts for the interaction between the substrate and the film.

Typical experiments employ electric fields supplied by essentially monochromatic light sources. The fields, therefore, contain only a small number of Fourier components in frequency while the response is detected at one component through the use of filters or monochrometers. The ith component of the electric field E_i, can be expressed as a sum over the N Fourier components of the fields, $E_i^{\omega_m}$, at frequency ω_m,

$$E_i = \sum_{m=1}^{N} \frac{E_i^{\omega_m} + E_i^{-\omega_m}}{2}. \tag{5}$$

Substituting Eq. (5) into Eq. (2) results in

$$\begin{aligned} P_i^{\omega} = {} & \chi_i^{(0)} + \chi_{ij}^{(1)}(-\omega;\omega)E_j^{\omega} + \chi_{ijk}^{(2)}(-\omega;\omega',\omega'')E_j^{\omega'}E_k^{\omega''} \\ & + \chi_{ijkl}^{(3)}(-\omega;\omega',\omega'',\omega''')E_j^{\omega'}E_k^{\omega''}E_l^{\omega'''} + \cdots, \end{aligned} \tag{6}$$

where ω', ω'', and ω''' can take on any Fourier component $\pm\omega_m$ and where energy is conserved ($\omega = \omega' + \omega'' + \omega''' + \ldots$). The nth order susceptibility thus mixes n fields and results in a polarization at the frequency required by energy conservation, which in turn results in radiation at the same frequency and polarization direction.

The second-order term leads to either sum or difference frequency generation. The linear electro-optic or Pockels effect corresponds to mixing of fields at frequency $\omega' = \omega$ with a dc field, $\omega'' = 0$, resulting in polarization at ω, while second harmonic generation results from the mixing of two fields at the same frequency, $\omega' = \omega'' = \omega$, resulting in polarization at 2ω. Parametric mixing is the process where light at

frequency $\omega' = \omega_1$ and $\omega'' = \omega_2$ interacts through the material nonlinearity resulting in radiation at frequency $\omega = \omega_1 + \omega_2$. If one beam is much more intense than the other, a substantial portion of the weak beam can be "up-converted" to the sum frequency. This is useful in shifting light to frequencies that are more amenable to detection. The opposite process can be envisioned where the incoming light at frequency ω_1 results in two outgoing beams at frequencies ω_2 and $\omega_1 - \omega_2$. Since there is a continuum of frequencies, ω_2, that satisfies energy conservation, the intensity of light at any one of these frequencies is low. Phase space considerations require that a second beam of light passing through the medium at frequency ω', however, will cause all the light to radiate at frequencies $\omega_2 = \omega'$ and $\omega_1 - \omega'$. In this manner, the difference frequency between two applied fields can be generated.

There are two broad categories of phenomena that arise from the third order susceptibility, mainly sum frequency generation and self-action effects. An example of sum frequency generation is third harmonic generation where one incoming frequency, $\omega' = \omega'' = \omega''' = \omega$ results in radiated light at frequency 3ω. The self action effects are characterized by two incoming beams and two outgoing beams. The degenerate case corresponding to two incoming fields at frequency ω and two outgoing fields at frequency ω, and can be realized in a single beam of light. One of the incoming and outgoing fields can be thought of as deforming the material system while the second pair of fields "feel" the effects of this deformation. Thus, the light changes the material system which in turn causes the propagation of the light to change. This leads to an intensity dependent index of refraction which can result in self-focusing for localized beams and self-phase modulation in both localized and nonlocalized beams. Similarly, two-beam experiments can also probe self-action effects. An intense pump beam causes the index of refraction to change, while a weak beam probes this change. Other third order effects include degenerate four wave mixing, coherent anti-Stokes Raman scattering (CARS), dc induced second harmonic generation (DCSHG), two photon absorption and the quadratic electro-optic effect. Table I summarizes these nonlinear optical phenomena.

Higher order susceptibilities will lead to higher order harmonic generation, intensity dependent harmonic generation, sum frequency generation, multiphoton absorption, nonlinear intensity dependent index of refraction and any combination of the above. The discussion here will be limited to second- and third-order processes. All higher order processes can be understood qualitatively in terms of these lower order effects.

TABLE I

Nonlinear optical effects

	Effect	*Susceptibility*
First-order	Linear optics	$\chi^{(1)}(-\omega;\omega)$
Second-order	Parametric Mixing	$\chi^{(2)}(-\omega_1-\omega_2;\omega_1,\omega_2)$
	Second Harmonic	$\chi^{(2)}(-2\omega;\omega,\omega)$
	Linear Electro-optic Effect	$\chi^{(2)}(-\omega;0,\omega)$
	Optical Rectification	$\chi^{(2)}(0;\omega,-\omega)$
Third-order	Third Harmonic	$\chi^{(3)}(-3\omega;\omega,\omega,\omega)$
	Sum Frequency	$\chi^{(3)}(-\omega_1-\omega_2-\omega_3;\omega_1,\omega_2,\omega_3)$
	Optical Kerr Effect	$\chi^{(3)}(-\omega;\omega,\omega,-\omega)$
	Pump-Probe Kerr Effect	$\chi^{(3)}(-\omega_2;\omega_1,\omega_2,-\omega_1)$
	DC SHG	$\chi^{(3)}(-2\omega;0,\omega,\omega)$
	Quadratic Electro-Optic Effect	$\chi^{(3)}(-\omega;0,0,\omega)$
	CARS	$\chi^{(3)}(-\omega,-\omega;2\omega-\omega_1,\omega_1)$

The nonlinear optical properties of a material are determined by bulk symmetry properties, which are described by the arrangement of the constituent components. In van der Waals materials, relevant parameters include density, orientation, local field environment and intrinsic nonlinear properties of the nonlinear optical species. Conversely, the nonlinear optical properties of the bulk material can be used to infer microscopic material properties. An understanding of these properties can be used to optimize the nonlinear optical properties of "man-made" systems.

3. ORGANIC MATERIALS

Over the past decade, it has become apparent that organic molecules possess exceptionally large molecular nonlinear optical susceptibilities.[1] In order to form a bulk system which takes advantage of these large nonlinearities, the molecules must be assembled in a favorable structure. For device applications, however, there are other constraints which are not always compatible with maximizing the bulk susceptibility. Important considerations include optical quality, processability, and stability. As an example, one can greatly increase the material nonlinearity by matching the light frequency to a material resonance. Unfortunately, this can lead to losses that preclude its usefulness in devices.

Crystalline systems are densely packed and highly ordered structures. For this reason, a great deal of effort has been focused on

producing organic crystals for use in second-order nonlinear optical devices. Second- and all even-order optical processes require materials lacking an inversion symmetry operation. Unfortunately, many organic molecules form centrosymmetric crystals. Furthermore, the optical quality tends to be poor and leads to large scattering losses.[17] Work is in progress to improve optical quality and orientation to make organic crystals appropriate for guided-wave devices. Thin crystalline films of polydiacetylene monomer have been grown under shear to induce alignment in the film plane.[18] The optical characteristics of films produced with this technique look promising. Furthermore, polymerization of the crystalline monomer enhances the nonlinear optical susceptibility as measured by the third-order process of degenerate four wave mixing through increased conjugation length.

Another system with crystalline-like order is the Langmuir-Blodgett (LB) film. These films are fabricated one monolayer at a time and therefore offer a controlled process. Multilayers usually form centrosymmetric structures with each successive layer aligned opposite in direction to the previous layer. A second-order nonlinear material can be formed by using a nonlinear optical material in alternate layers, thus leaving a noncentrosymmetric configuration of the nonlinear optical molecules.[19]

Since isotropic materials offer high optical quality, noncentrosymmetric systems that are almost isotropic and possess a substantial second order nonlinear optical susceptibility may be applicable in photonic devices. A polymer host doped with a nonlinear organic molecular guest with large nonlinear susceptibility can be poled to form such a material.[20] A uniform electric field is used to align the molecular dipoles above the glass transition temperature where molecular motion is enhanced. The field is removed when the sample is cooled below the transition temperature in order to lock in the polarization. These materials have been shown to possess high optical quality.[21] Work is now in progress to maximize the nonlinear properties, which can be controlled by adjusting the film processing parameters.

Alignment and stability of component systems can be enhanced by selecting appropriate guest and host materials. For increased alignment, a liquid crystal host or a single component optically nonlinear liquid crystal may be appropriate. Further improvement in alignment and stability may be gained by reacting the guest into the host. Other possible combinations include the use of a liquid crystal polymer where the nonlinear optical species consists of liquid crystalline molecules.

4. NONLINEAR OPTICAL PROPERTIES AND STRUCTURAL ORDER

The intrinsic optical nonlinearities of some organic molecules may be exploited by engineering films of such molecules in order to obtain structural symmetries which maximize the bulk nonlinear response. This engineering of structure must begin by formalizing the relationship between the molecular and bulk properties in order to define the aspects of order which are relevant to the desired nonlinear optical process. The bulk nonlinear susceptibilities, $\chi^{(n)}$, of Eq. (2) for an organic medium are derived from the nonlinear character of individual molecular units. The molecular polarization in analogy to the bulk polarization of Eq. (2) is given by

$$p_I(t) = \mu_I^0 + \alpha_{IJ}(t)F_J(t) + \beta_{IJK}(t)F_J(t)F_K(t) + \gamma_{IJKL}(t)F_J(t)F_K(t)F_L(t) + \ldots, \quad (7)$$

where $F_m(t)$ is the *local* electric field, μ_I^0 the molecular ground state dipole moment, $\alpha_{IJ}(t)$ the linear polarizability, and $\beta_{IJK}(t)$ and $\gamma_{IJKL}(t)$ the two lowest order nonlinear optical susceptibilities or hyperpolarizabilities. In most of the organic materials studied to date, the nonlinear optical moieties do not interact strongly. These interactions are dominated by dipolar, or van der Waals forces, so that the macroscopic polarization is calculated by summing over the contributions of the individual molecules:

$$P_i(t) = \frac{1}{V}(\Sigma p_I(t))_i, \quad (8)$$

where V is the volume per molecule.

Specific aspects of order can aid in evaluating the sum in Eq. (8). In general, structural order in a thin film of molecules can be of several types. Positional order characterizes the translational symmetries between molecular centers of mass. This includes the packing symmetry of a crystal, or for layered, non-crystalline media such as Langmuir-Blodgett films and smectic liquid crystals the translational symmetries arising from the layers or bilayers. Orientational order characterizes molecular alignment in the ensemble relative to a fixed reference frame, while conformational order characterizes the *intra*-molecular bond orientations which affect the packing of molecular units. Since intermolecular interactions are small, the molecular iden-

tity is preserved and positional order is subsumed in macroscopic local field factors, thus leading to the additivity given in Eq. (8). Furthermore, typical nonlinear optical moieties are often conformationally rigid, even though parts of the molecule containing them may be free to move. This implies that the nonlinear optical properties, since they involve the nonlinear optical moiety only, should not explicitly depend on the overall conformational order. The positional and conformational order, however, may indirectly affect the nonlinear optical properties since they can enhance the orientational order, affect the volume that the molecule occupies, and contribute to local fields. For instance, a densely packed film with in-plane crystalline symmetry, such as a higher ordered smectic liquid crystal or a Langmuir-Blodgett film, restricts rotational motion when compared with a film possessing arbitrary translational symmetry.

In general, the molecules whose polarizations are summed using Eq. (8) exist within a thermal environment, so that the summation is expressed as a thermodynamic average, which, in second-order, is

$$\chi^{(2)}_{ijk} = N \langle \beta^*_{IJK} \rangle_{ijk}, \tag{9}$$

where N is the molecular density, $\langle \beta^*_{IJK} \rangle_{ijk}$ the ijkth component of the orientational average of the molecular second order susceptibility, and where the * denotes that the local field effects have been included with the susceptibility. The indices $I,J,K = x,y,z$ denote the molecular frame, and $i,j,k = 1,2,3$ the laboratory frame. Similarly, the third-order susceptibility is given by

$$\chi^{(3)}_{ijkl} = N \langle \gamma^*_{IJKL} \rangle_{ijkl}, \tag{10}$$

where $\langle \gamma^*_{IJKL} \rangle_{ijkl}$ is the orientationally averaged third-order hyperpolarizability. The orientational ensemble average for a tensor T (in our case β_{IJK} or γ_{IJKL}) is calculated using the following integral:

$$\langle T_{IJK\ldots} \rangle_{ijk\ldots} = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\psi T_{IJK\ldots} a_{iI} a_{jJ} a_{kK} \cdots G(\phi,\theta,\psi), \tag{11}$$

where $G(\phi,\theta,\psi)$ is the normalized orientational distribution function which is a function of the Euler angles ϕ, θ, and ψ and where A_{mM} are components of the rotation matrix.[22] The bulk nonlinear response of an anisotropic organic medium, then, is determined by the local

field corrected molecular hyperpolarizabilities, the density of molecular units, and the orientational distribution of the molecules. It should be noted here that the use of a thermodynamic ensemble average implies that each particle experiences an average potential such as calculated by mean field theory. However, if short range interactions are strong enough to cause aggregation, then consideration of these interactions is required in the ensemble averages.[23] This case is not considered in this paper.

For crystalline materials, the distribution function is approximated by a delta function specifying the molecule within the lattice with the orienting angles being the direction cosines between the crystallographic and molecular reference frames. Here, $\chi^{(2)}$ is[5]

$$\chi^{(2)}_{ijk} = N_u f_i^{\omega 3} f_j^{\omega 1} f_k^{\omega 2} \times \sum_{I,J,K} \sum_{s=1}^{n} \cos(i,I(s))\cos(j,J(s))\cos(k,K(s))\beta_{IJK}(s). \quad (12)$$

The summation is performed over n molecules (indexed by s) in the unit cell. The hyperpolarizability of each molecule is projected from the molecular reference frame to the crystal frame. The factors $f_i^{\omega 3}$, $f_j^{\omega 1}$, and $f_k^{\omega 2}$ are local field factors assumed diagonal in the crystalline frame at the field frequencies, ω_3, ω_1, and ω_2, which correct for the effect of neighboring molecules on the hyperpolarizability. The structural order of the nonlinear medium determines the macroscopic nonlinear susceptibility through the unit cell density, N_u, and spatial orientation of each molecule in calculating the contribution of its β to each tensor component of $\chi^{(2)}$.[5] Eq. (12) can be generalized for an nth order process in a crystal, leading to,

$$\chi^{(n)}_{ijkl\ldots} = N_u f_i^{\omega_{n+1}} f_j^{\omega_n} \cdots f_m^{\omega 1} \sum_{I,J,K,L\ldots} \sum_{s=1}^{n} a_{iI(s)} a_{jJ(s)} a_{kK(s)} \cdots \xi_{IJKL\ldots}(s), \quad (13)$$

where $\xi_{IJKL\ldots}$ is the nth order hyperpolarizability in the frame of the molecule.

For noncrystalline materials, the form of the orientational distribution function determines the nonlinear optical properties, and depends on the details of the interaction between molecules which is generally not known *a priori*. In fact, as is shown presently, nonlinear optical measurements can be employed to probe the moments of the

distribution. The form of the orientational distribution function used in averaging over the molecular ensemble reflects the macroscopic symmetry of the medium. In the most general case, when the distribution is a function of all three Euler angles, $G(\phi,\theta,\psi)$ can be expanded in terms of Wigner functions.[12] For a uniaxial phase with its symmetry axis parallel to the z-axis, the orientational distribution function $G(\phi,\theta,\psi)$ is independent of ϕ, and can be expanded in terms of spherical harmonics. Many nonlinear optical moieties have a large component of β along the ground state dipole moment, resulting in uniaxial symmetry where $G(\theta,\psi)$ is independent of ψ. $G(\theta)$ is then expanded in terms of orthonormal functions, such as Legendre polynomials $P_l(\cos\theta)$,

$$G(\theta) = \sum_{l=0}^{\infty} \frac{(2l+1)}{2} A_l P_l(\cos\theta), \tag{14}$$

with the coefficients A_l determined from Eq. (14) as,

$$\langle P_l \rangle \equiv A_l = \int_0^{\pi} \sin\theta d\theta G(\theta) P_l(\cos\theta). \tag{15}$$

The A_l are ensemble averages of the P_l and are defined as microscopic order parameters. For systems whose order is characterized solely by θ, the distribution of molecules is represented by the summation over successively higher orders of P_l. The odd-ordered polynomials P_l give the "polar" order. If molecular dipoles are arranged centrosymmetrically so that the net moment is zero, these terms are all zero. The even P_l give the angular distribution of molecules without distinguishing dipolar direction. These features can be seen in the polar plots of the first four nontrivial Legendre polynomials shown in Figure 1. General expressions for the even and odd order nonlinear susceptibilities are written in terms of $P(\theta)$ for axially symmetric molecules in an optically uniaxial medium,

$$\begin{aligned} \chi^{(2n)}_{ijk\ldots} &= \sum_{m=0}^{n} u^{(2m+1)}_{ijk\ldots} \langle P_{2m+1} \rangle, \\ \chi^{(2n+1)}_{ijkl\ldots} &= \sum_{m=0}^{n+1} u^{(2m)}_{ijkl\ldots} \langle P_{2m} \rangle. \end{aligned} \tag{16}$$

In these expressions, $u^{(k)}_{lmn\ldots} = N\xi^{(k)}_{lmn\ldots}$ where $\xi^{(k)}_{lmn\ldots}$ are linear combinations of local field-corrected molecular hyperpolarizabilities and

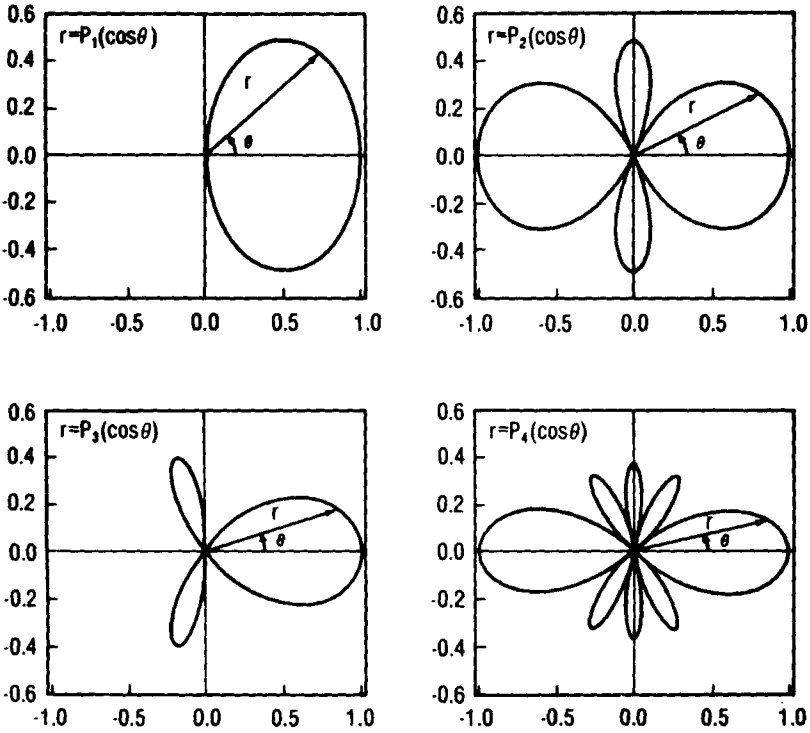

FIGURE 1 Polar plots of the Legendre polynomials, P_l, for $l = 1$ to 4. Length of vector r represents probability density of the distribution in the θ direction.

N the number density. The nth rank tensor yields a limited number of distribution moments, and for a medium with zero odd-order $\langle P_l \rangle$, even-order χ's are zero.

The assumptions leading to Eq. (16) apply to homogeneous uniaxial liquid crystal and liquid crystal polymer phases that are not optically active, and to Langmuir-Blodgett films whose in-plane crystalline order has correlation lengths much smaller than the coherence length appropriate for the nonlinear optical process. In addition, Eq. (16) is always nonzero for odd-order susceptibilities of isotropic materials and even-order susceptibilities of poled materials. Azimuthally symmetric uniaxial materials possessing a center of inversion are described by the point group ∞/mmm. The symmetry operations of this group include an infinite-fold rotation axis, an infinite number of mirror planes including the axis, a mirror plane normal to the axis, and a two-fold rotation about any line perpendicular to the axis. The direction labeled 3 is defined as the unique axis and 1 and 2 are

TABLE II

$\chi^{(3)}$ components for point group ∞/mmm[24]

	1	2	3	4	5	6
1	$\chi^{(3)}_{1111}$	$\chi^{(3)}_{1122}$	$\chi^{(3)}_{1133}$	0	0	0
2	$\chi^{(3)}_{2211}$	$\chi^{(3)}_{1111}$	$\chi^{(3)}_{1133}$	0	0	0
3	$\chi^{(3)}_{3311}$	$\chi^{(3)}_{3311}$	$\chi^{(3)}_{3333}$	0	0	0
4	0	0	0	$\chi^{(3)}_{2323}$	0	0
5	0	0	0	0	$\chi^{(3)}_{2323}$	0
6	0	0	0	0	0	$2(\chi^{(3)}_{1111}-\chi^{(3)}_{1122})$

Row and column labels: 1 = 11; 2 = 22; 3 = 33; 4 = 23,32; 5 = 31,13; 6 = 12,21.

indistinguishable due to the uniaxial symmetry. The non zero components for third-order processes in point group ∞/mmm are shown in Table II. The tensor symmetries for the isotropic point group ($\langle P_2\rangle = \langle P_4\rangle = 0$) are similar to those of point group ∞/mmm with the additional symmetries of $\chi^{(3)}_{2323} = \chi^{(3)}_{1212} = 2(\chi^{(3)}_{1111} - \chi^{(3)}_{1122})$, $\chi^{(3)}_{1111} = \chi^{(3)}_{3333}$, and $\chi^{(3)}_{1122} = \chi^{(3)}_{1133}$.[24] Materials which exhibit even-order nonlinear optical susceptibilities, include Langmuir-Blodgett films, poled liquid crystals, poled liquid crystal polymers, and poled isotropic polymers. All of these materials belong to the point group ∞mm which exhibits an infinite-fold rotation axis and an infinite number of mirror planes including the axis. The non zero tensor components are shown in Table III.

When the thermodynamic average of Eq. (9) is evaluated for the second order susceptibility, Eq. (16) is of the form

$$\chi^{(2)}_{ijk} = N\,(\xi^{(1)}_{ijk}\,\langle P_1\rangle + \xi^{(3)}_{ijk}\,\langle P_3\rangle), \tag{17}$$

TABLE III

$\chi^{(2)}$ components for point group ∞mm[24]

	1	2	3
1	0	0	$\chi^{(2)}_{311}$
2	0	0	$\chi^{(2)}_{311}$
3	0	0	$\chi^{(2)}_{333}$
4	0	$\chi^{(2)}_{113}$	0
5	$\chi^{(2)}_{113}$	0	0
6	0	0	0

Row and column labels: 1 = 11; 2 = 22; 3 = 33; 4 = 23,32; 5 = 31,13; 6 = 12,21

where the coefficients $\xi_{ijk}^{(i)}$ are given by

$$\xi_{333}^{(1)} = \frac{1}{5}\left[\{\beta_{xxz}^*\} + \{\beta_{yyz}^*\} + 3\beta_{zzz}^*\right] \tag{18}$$

and

$$\xi_{333}^{(3)} = \frac{1}{5}\left[-\{\beta_{xxz}^*\} - \{\beta_{yyz}^*\} + 2\beta_{zzz}^*\right], \tag{19}$$

where the curly brackets denote the permuted sum,

$$\{\beta_{IIJ}^*\} = \beta_{IIJ}^* + \beta_{IJI}^* + \beta_{JII}^*, \tag{20}$$

and where summation notation is not used. The only other non zero coefficients are

$$\xi_{113}^{(1)} = \frac{1}{10}\left[-\{\beta_{xxz}^*\} - \{\beta_{yyz}^*\} + 2\beta_{zzz}^* + 5(\beta_{xxz}^* + \beta_{yyz}^*)\right] \tag{21}$$

$$\xi_{113}^{(3)} = \frac{1}{10}\left[\{\beta_{xxz}^*\} + \{\beta_{yyz}^*\} - 2\beta_{zzz}^*\right] \tag{22}$$

$$\xi_{131}^{(1)} = \frac{1}{10}\left[-\{\beta_{xxz}^*\} - \{\beta_{yyz}^*\} + 2\beta_{zzz}^* + 5(\beta_{xzx}^* + \beta_{yzy}^*)\right] \tag{23}$$

$$\xi_{131}^{(3)} = \frac{1}{10}\left[\{\beta_{xxz}^*\} + \{\beta_{yyz}^*\} - 2\beta_{zzz}^*\right] \tag{24}$$

$$\xi_{311}^{(1)} = \frac{1}{10}\left[-\{\beta_{xxz}^*\} - \{\beta_{yyz}^*\} + 2\beta_{zzz}^* + 5(\beta_{zxx}^* + \beta_{zyy}^*)\right] \tag{25}$$

and

$$\xi_{311}^{(3)} = \frac{1}{10}\left[\{\beta_{xxz}^*\} + \{\beta_{yyz}^*\} - 2\beta_{zzz}^*\right]. \tag{26}$$

For a one dimensional molecule, where the only nonvanishing coefficient is β_{zzz}^*, the macroscopic second order susceptibility, $\chi^{(2)}$, can be written in the form

$$\chi_{333}^{(2)} = N\beta_{zzz}^*\left(\frac{3}{5}\langle P_1\rangle + \frac{2}{5}\langle P_3\rangle\right) \tag{27}$$

and

$$\chi^{(2)}_{113} = \chi^{(2)}_{131} = \chi^{(2)}_{311} = N\beta^*_{zzz}\left(\frac{1}{5}\langle P_1\rangle - \frac{1}{5}\langle P_3\rangle\right). \tag{28}$$

In the limit where $\langle P_1\rangle = \langle P_3\rangle = 1$ corresponding to total alignment, the bulk susceptibility reflects the molecular symmetry, i.e. $\chi^{(2)}_{333} = N\beta^*_{zzz}$ and $\chi^{(2)}_{113} = \chi^{(2)}_{131} = \chi^{(2)}_{311} = 0$.

In order to appreciate the effects of orientational order on $\chi^{(3)}$, a "one-dimensional" molecule (only $\gamma^{(3)*}_{zzzz}$ appreciable) can be considered where $\chi^{(3)}_{3333}$ reduces to:

$$\chi^{(3)}_{3333} = N\gamma^*_{zzzz}\left(\frac{1}{5} + \frac{4}{7}\langle P_2\rangle + \frac{8}{35}\langle P_4\rangle\right). \tag{29}$$

The enhancement in $\chi^{(3)}_{3333}$ where $\langle P_2\rangle = \langle P_4\rangle = 1$ is a factor of 5 over the case when $\langle P_2\rangle = \langle P_4\rangle = 0$.

For second-order processes $\chi^{(2)}$ is linear in $\langle P_1\rangle$ and $\langle P_3\rangle$, which describe polar order, thus ensuring that $\chi^{(2)}$ is zero in centrosymmetric materials. However, it is possible to impart a nonzero $\chi^{(2)}$ by poling a centrosymmetric material with an external electric field, thereby inducing nonzero odd terms.[20,25] The process of poling is shown in Figure 2, where the temperature of the material is raised beyond a material phase transition, T_g, where molecular motion is enhanced. The material is cooled with an electric field applied, thus locking in a permanent polarization. Polymer glasses, liquid crystals and liquid crystal polymers may be processed in this manner. The susceptibility, $\chi^{(2)}$, can be calculated for a mixture of species labeled by u, by considering a Gibbs distribution,

$$G_u(\Omega, E_p) = \sum_v \frac{\exp\left[-\frac{1}{kT}\left(U_{uv} - \mathbf{m}^*_\mathbf{u}\cdot\mathbf{E}_\mathbf{p}\right)\right]}{\int d\Omega \exp\left[-\frac{1}{kT}\left(U_{uv} - \mathbf{m}^*_\mathbf{u}\cdot\mathbf{E}_\mathbf{p}\right)\right]}, \tag{30}$$

where $\mathbf{m}^*_\mathbf{u}$ is the molecular dipole moment of molecule u including corrections arising from the local poling field, $\mathbf{E}_\mathbf{p}$. The term U_{uv} is the mean-field interaction potential between molecular species u and v. If $\mathbf{m}^*\cdot\mathbf{E}_\mathbf{p} < kT$, then the dipolar energy exponential factor can be expanded in a Taylor series and the first term retained. After expanding the distribution function in terms of Legendre polynomials,

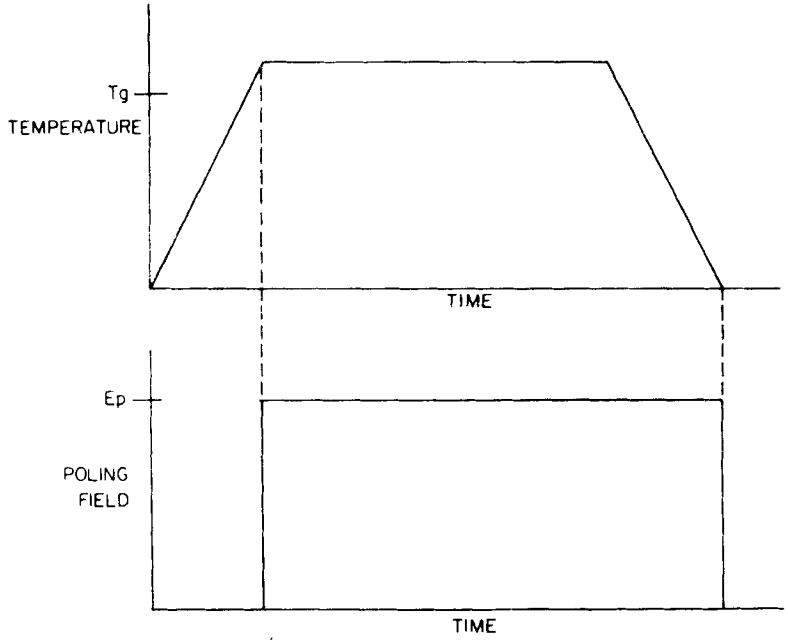

FIGURE 2 Process for electric field poling of films.

the second-order susceptibility is given by,[6]

$$\chi^{(2)}_{ijk} = \nu^{(0)}_{ijk} \langle P_0 \rangle + \nu^{(2)}_{ijk} \langle P_2 \rangle + \nu^{(4)}_{ijk} \langle P_4 \rangle. \tag{31}$$

The coefficients of the $\langle P_l \rangle$ contain the interaction energy of the external field with the molecular dipoles. This results in even-order susceptibilities depending on even-order Legendre polynomials. Detailed examples of this are shown in Section 5. In a multiple component system, the nonlinear susceptibility is additive over its components. The microscopic order parameters of the composite system, however, may be enhanced by the interaction of the components.

We have shown how molecular susceptibilities and bulk structural properties of molecular ensembles contribute to the net nonlinear response of the ensemble. It has been assumed that the material is homogeneous, which is not necessarily applicable for liquid crystals and Langmuir-Blodgett films. The nonlinear susceptibilities, $\chi^{(2)}$ and $\chi^{(3)}$ are then affected by the inhomogeneities due to spatial dispersion of the orientational director. For example, a layered system with a bilayer repeat unit which is ideally centrosymmetric may exhibit sec-

ond-order nonlinear effects due to internal interfaces, while order parameter fluctuations in nematic liquid crystals result in nonzero second-order susceptibilities in unpoled samples. In addition, field gradients in a material can lead to a large quadrupolar polarization. Such effects can be seen near interfaces between dissimilar dielectric media and in structural singularities.

5. SPECIAL MATERIAL CLASSES

The considerations discussed in the previous section have been applied to several material classes. In this section, the effects of orientational order on the nonlinear optical properties of poled polymer films, LB films, liquid crystals, liquid crystal polymers and guest host composites are discussed.

5.1 Liquid Crystals

Liquid crystals represent a state of matter intermediate between isotropic fluids and crystalline solids. All liquid crystals exhibit some degree of orientational order due to intermolecular interactions, and various states of liquid crystalline order have been identified, some of which are depicted in Figure 3.[23] The simplest is the nematic state which is characterized only by orientational order in which an inversion invariant unique axis is defined within the bulk liquid crystalline state. In this phase, the intermolecular potential often possesses axial symmetry with respect to both the molecular and bulk coordinate frames, so that the material order is described by one polar angle, as discussed above. When the mesogenic molecules possess a chiral center, the short range orientational correlations are augmented by a longer range twist leading to cholesteric nematic mesophases. The molecular director, **n**, then depends on position within the liquid crystal. Smectic mesophases have orientational order and, in addition, are characterized by nonzero positional ordering in that they are layered structures. Smectic C is a biaxial phase where the molecules are oriented at a tilt angle with respect to the layer normal and are positioned randomly within a layer. The assumption of uniaxial symmetry does not hold because of the nonzero tilt and the expansion of the distribution function in terms of Legendre polynomials cannot be used. In smectic A, however, the layer normal coincides with the orientational director within the layers such that the phase is uniaxial. Smectic B is characterized by orientation about the normal to the

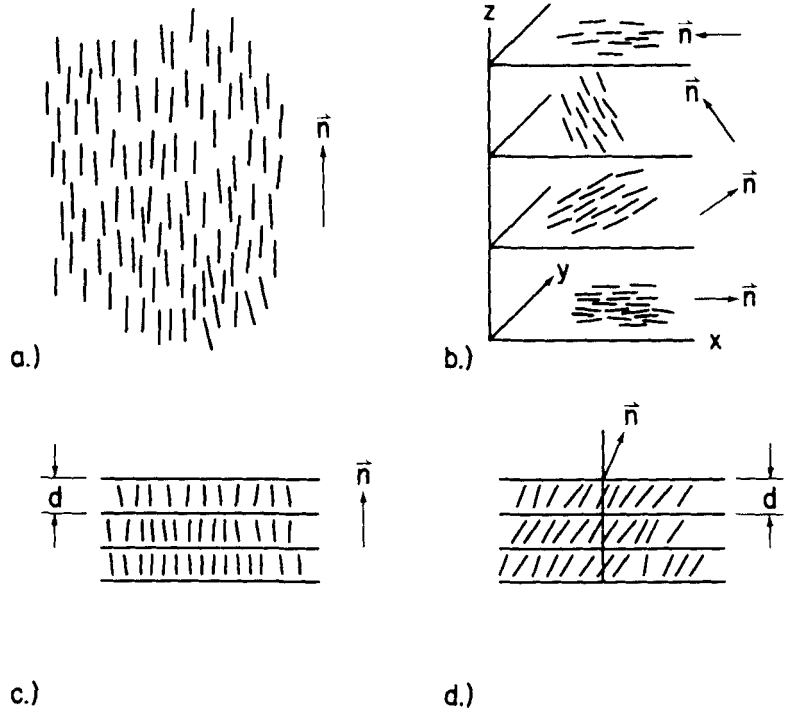

FIGURE 3 Types of liquid crystalline order: a) nematic, b) cholesteric, c) smectic A, and d) smectic C.

layers, but unlike smectics A and C has hexagonal ordering which extends out to an effectively infinite correlation length within the layers. Given this long range order, the overall symmetry is uniaxial and the distribution function is only a function of θ. Other smectic phases have been observed.[23] The phase diagram of a single material may contain one or more of the liquid crystalline forms, and thus exhibit several mesophases. In nematics and smectics, the director $\mathbf{n} = -\mathbf{n}$ which requires that the odd-order $\langle P_n \rangle$ are zero since the material is centrosymmetric. In ferroelectric liquid crystals this is not the case.[26] As stated earlier, the formalism leading to Eq. (16) applies to uniaxial phases that are not optically active, which, for liquid crystals, includes the nematic and non-tilted smectic phases.

In general, the mesophase is not homogeneous, but displays a rich structure of defects. This structure can lead to interesting nonlinear optical properties, but also leads to optical scattering which limits the length of useful optical propagation. The defect structure can be reduced by surface and field alignment techniques, but the light scat-

tering is still substantial enough to reduce the utility of most liquid crystals for guided-wave applications.[27] Nonetheless, various second- and third-order nonlinear optical effects have been observed. These have been previously reviewed.[8,28]

Third-order nonlinear optical processes in liquid crystals have been studied for important scientific and technological reasons. All materials exhibit these effects, regardless of symmetry. Of prime technological interest, are Kerr, or quadratic electro-optic effects.[8,28,29] These effects can range in frequency from dc to optical frequencies. The observed electro-optic effects are large, and are due to large scale molecular motions. As such, however, the time response is slow, usually longer than microseconds. This time response limits the applicability of liquid crystals for the type of switching required for data processing and communication, but has not limited the widepread applicability of liquid crystals in display technology.[27,30,31] It is the "freezing" out of the slow processes that allows the fast electronic linear electro-optic response to dominate, resulting in interest in "frozen" oriented liquid crystal structures.[17,32]

Many third-order phenomena have been observed and studied in liquid crystals.[8,28] The intensity-dependent refractive index has been studied due to its technological importance as the basis for liquid crystal displays. For low frequency modulation, the applied field causes a large change in the refractive index and birefringence. The susceptibility is seen to depend on the dielectric anisotropy, the incident intensity, and the elastic constants of the liquid crystal. In addition, optical Kerr phenomena have been observed in nematic liquid crystals due to both molecular and electronic motion, and to thermal effects.[8,28,33] The optical Kerr phenomena observed include degenerate wave mixing, phase conjugation, self-focusing, self-phase modulation, and optical bistability.

As detailed above, the nonlinear optical properties of orientationally ordered materials can be related to those of the constituent molecules. These relationships are expressed, as in Eq. (16), in terms of the microscopic order parameters, $\langle P_n \rangle$, which can be measured separately using other methods or can be deduced from the component dependence of the nonlinear optical properties. As shown in Eq. (16), order parameters up to $\langle P_n \rangle$ can be measured by a property related to an nth rank tensor. Order parameters have been measured using dielectric or magnetic anisotropy, magnetic resonance techniques, and x-ray and neutron scattering techniques.[10,12] The use of nonlinear optical properties to deduce order parameters requires a detailed knowledge of the local fields especially since nonlinear op-

tical susceptibilities depend on high powers of local field factors. Recent studies have begun to attack this problem.[7,10] For instance, isotropic local field factors have been shown to be inadequate, and recent results suggest that local field factors do not depend on the macroscopic anisotropy of the bulk.[7] Further work on both theory and the experimental comparison of order parameter determination by techniques relatively sensitive and insensitive to local fields are necessary to understand the local field problem in liquid crystals. This is important in order to use nonlinear optics as a tool for structural studies of liquid crystals, as well as to realize the potential of liquid crystals as nonlinear optical materials.

Several third-order nonlinear optical processes have been employed in order to study the orientational order of liquid crystals. In particular, they have been used to measure the $\langle P_2 \rangle$ and $\langle P_4 \rangle$ orientational order parameters. Among the first methods employed was Raman scattering, which probes the phonon modes, and allows the order parameters to be deduced from the depolarization ratios of scattered Raman intensity.[12,34] Several types of liquid crystals were evaluated, yielding the order parameters listed in Table IV. Subsequent studies of the orientational order were carried out using dc induced second harmonic generation, again relating the observed harmonic generation to orientational order parameters.[11,35,36] Another third-order measurement to deduce orientational order is two-photon dichroism.[10] With a knowledge of the $\langle P_2 \rangle$ order parameter, the linear optical anisotropy, and the local field anisotropy, the $\langle P_4 \rangle$ parameter can be deduced from the two-photon dichroism. Finally, recent measurements of optical third harmonic generation in liquid crystals have been employed to deduce the orientational order of a nematic with the results also listed in Table IV.[7] As shown in Table IV, all of the techniques used to determine $\langle P_2 \rangle$ are in reasonable agreement. The agreement is less apparent in $\langle P_4 \rangle$ due mostly to the model for the local field. Raman scattering shows some variation in the parameters determined from different modes.[12] In light of Table IV and Eqs. (16), it is clear that smectics possess larger nonlinear optical susceptibilities than nematics, and, as indicated by the BBCA-MBBA mixture, the effect of mixing two components is minimal.

For second-order nonlinear optical phenomena, the effects of liquid crystal symmetry and structure are paramount. In nematic liquid crystals, only orientational order is present, which results in the symmetry operations including an infinite-fold rotation with an infinity of mirror planes containing the director, and a mirror plane normal to it. The normal mirror plane implies that $\mathbf{n} = -\mathbf{n}$ so that nematics

are centrosymmetric and do not exhibit second-order nonlinear optical properties in the electric dipole approximation. However, second harmonic generation has been observed in nematic phases,[13,14,36–41] and is consistent with that expected from quadrupole radiation given by the polarization:[14,36]

$$P_i^{NL} = \Gamma_{ijkl} E_j \nabla_k E_l. \tag{32}$$

Non-uniformly aligned liquid crystals, possess terms in the nonlinear polarization due to broken symmetry from the various discontinuities and gradients found within the liquid crystal.[13,14,38,41] These broken symmetries result in variations of $\mathbf{n}(\mathbf{r})$ over $\mathbf{r}$ such as splay, twist, and bend fluctuations within the liquid crystals, which, when on length scales shorter than the coherence length characteristic of the nonlinear optical process, produce the sources of nonlinear polarization responsible for second-order effects. For cholesteric nematics, the variation of $\hat{n}$ with position breaks the center of symmetry and leads to second harmonic generation,[8,37,40] while, for ferroelectric liquid crystals, the presence of a permanent polarization allows for second harmonic generation in the electric dipole approximation.[39]

The linear electro-optic effect also represents a second-order nonlinear optical process, where the modulating field is at a much lower frequency than the optical field, and the nonlinear susceptibility depends on atomic and molecular motion. As in second harmonic generation, the centrosymmetric structures do not exhibit the effect in the electric dipole approximation, but the spatial dispersion of the director permits the modulating field to couple to the various gradients of the director allowing effects linear in the applied field. Defect-free samples exhibit only quadrupole effects in second-order, so that measurements of the change in refractive index due to an applied field are dominated by the quadratic electro-optic effect.

As mentioned previously, "frozen" liquid crystals oriented with electric fields may be of technological interest for fast switching and data processing applications, and optical parametric devices. These second-order nonlinear optical materials could be formed with molecules exhibiting large hyperpolarizabilities, which consist of electron donors and acceptors fixed to the ends of extended pi-electron systems. Such molecules can be viewed, to a reasonable approximation, as "one-dimensional," that is only β^*_{zzz} and m^*_z are non-zero. This symmetry is consistent with the axial nature assumed in the previous sections.[42] With these assumptions, Eq. (31) can be rewritten for the

TABLE IV

Order parameters of liquid crystals

Material	Phase*	Method†	$-\Delta T$‡	$\langle P_2 \rangle$	$\langle P_4 \rangle$
5CB[1]	N	DC	0	0.34	−0.12
			5	0.5	0.09
			10	0.58	0.12
		RS	0		−0.1
			5		0.05
			10		0.09
MBBA[2]	N	RS	4	0.455–0.470	(−0.002)–0.023
			10	0.506–0.546	0.078–0.092
			16	0.561–0.601	0.141–0.157
		TH	0	0.34	0
			5	0.43	0.1
			10	0.50	0.18
			20	0.6	0.25

BBCA–MBBA[3]	N	RS	4	0.430–0.465	(−0.087)–(−0.079)
			15	0.582–0.591	0.039–0.049
			25	0.638–0.650	0.109–0.154
40.8[4]	SB	RS	10.2(SB–SA)	0.918–0.922	0.805–0.817
			2.2(SB–SA)	0.907–0.913	0.779–0.797
	SA	RS	12.7(SA–N)	0.804–0.808	0.515–0.525
			4.2(SA–N)	0.730–0.736	0.384–0.395
	N	RS	13.9(N–I)	0.678–0.680	0.302–0.319
			7.5(N–I)	0.599–0.610	0.180–0.192

*N = nematic; SA = smectic A; SB = smectic B; I = isotropic.

†DC = two-photon dichroism; RS = Raman scattering; TH = optical third harmonic generation.

‡Temperature below indicated phase transition.

[1]4-cyano-4′-pentylbiphenyl (5CB) DC from S. D. Durbin and Y. R. Shen, *Phys. Rev. A*, **30**, 1419 (1984). RS from K. Miyano, *J. Chem. Phys.*, **69**, 4807 (1978).

[2]N-(*p*′-methoxybenzylidene)-*p*-cyanoaniline (MBBA) RS from S. Jen, N. A. Clark, P. S. Pershan and E. B. Priestly, *J. Chem. Phys.*, **66**, 4635 (1977). Range indicates parameters determined from different Raman lines. TH from K. Y. Wong and A. F. Garito, *Phys. Rev. A* **34**, 5051 (1986).

[3]20% N-(*p*′-butoxybenzylidene)-*p*-cyanoaniline (BBCA) in MBBA RS from S. Jen, N. A. Clark, P. S. Pershan and E. B. Priestly, *J. Chem. Phys.*, **66**, 4635 (1977). Range indicates parameters determined from different Raman lines.

[4]N-(*p*′-butoxybenzylidene)-*p*-*n*-octylaniline (40.8) RS from S. Jen, N. A. Clark, P. S. Pershan and E. B. Priestly, *J. Chem. Phys.*, **66**, 4635 (1977). Range indicates parameters determined from different Raman modes.

nonzero components as[6]

$$\chi^{(2)}_{333} \sim N \frac{\beta^*_{zzz} m^*_z E_p}{kT} \times \left(\frac{1}{5} + \frac{4}{7} \langle P_2 \rangle + \frac{8}{35} \langle P_4 \rangle \right), \tag{33}$$

and

$$\chi^{(2)}_{311} = \chi^{(2)}_{113} = \chi^{(2)}_{131} \sim N \frac{\beta^*_{zzz} m^*_z E_p}{kT} \times \left(\frac{1}{15} + \frac{1}{21} \langle P_2 \rangle - \frac{8}{70} \langle P_4 \rangle \right). \tag{34}$$

For liquid crystals, all terms in Eqs. (33) and (34) contribute, and, in the limit when the order parameters are unity, the term in parentheses in Eq. (33) becomes one, so that, assuming similar local field effects, a susceptibility five times that of materials where $\langle P_2 \rangle = \langle P_4 \rangle = 0$ is obtained. In addition, the term in parentheses in Eq. (34) becomes zero, and that tensor component vanishes, reflecting the molecular symmetry. As seen in Table IV, the order parameters of liquid crystals are found to be less than one. For instance, far from the phase transition of a typical nematic, MBBA, $\langle P_2 \rangle \sim 0.6$ and $\langle P_4 \rangle \sim 0.25$.[7,12] The component $\chi^{(2)}_{333}$ is about three times that obtained when $\langle P_2 \rangle = \langle P_4 \rangle = 0$, while the other components are about the same. For certain smectic liquid crystals, the order parameters can be as high as $\langle P_2 \rangle \sim 0.9$ and $\langle P_4 \rangle \sim 0.8$.[12] Here, $\chi^{(2)}_{333}$ and $\chi^{(2)}_{311}$ are about 4.5 and 0.3 times that of the case where $\langle P_2 \rangle = \langle P_4 \rangle = 0$, respectively.

Second-order nonlinear optical effects have been observed in "frozen" nematics containing a nonlinear optical dye, and have been found to be in qualitative agreement with Eqs. (33) and (34).[32] The polarization is found to be unstable in the presence of intense optical fields. In addition, properties of "frozen" nematics have been investigated.[43] Quantitative studies of "frozen" oriented liquid crystals in light of the theory above have yet to be carried out, and would be especially useful in determining the validity of the mean-field approximation for specific materials.

5.2 Isotropic Materials

Nonlinear optical materials can also be formed from isotropic materials by incorporating nonlinear optical molecules into them. Examples of these are molecule-doped polymer glasses, which can be applied to both second- and third-order nonlinear optical processes. In isotropic materials, $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are zero; nonetheless, substantial nonlinear susceptibilities can be obtained. For third-order processes,

the material need not be oriented since centrosymmetric materials will produce these effects, while for second-order processes, the material must be oriented. This can be done in a polymer glass by raising the temperature above the glass-rubber transition temperature, applying an electric field, and then cooling to room temperature. Orientational polarizations have been imparted using this method.[20,44]

In poled polymer glasses, the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are zero, so that only the first term of Eq. (33) contributes for $\chi^{(2)}_{333}$ and the other components of $\chi^{(2)}_{ijk}$ are exactly 1/3 of $\chi^{(2)}_{333}$ as in Eq. (34).[6] Here, the local field effects are reasonably well characterized, and the local field effects factor out as:

$$\beta^*_{zzz}(-\omega_3;\omega_1,\omega_2)\, m^*_z = f^{\omega 3} f^{\omega 1} f^{\omega 2} f^0 \beta_{zzz}(-\omega_3;\omega_1,\omega_2)\mu_z. \quad (35)$$

The local fields at optical frequencies can be described with Lorenz-Lorentz type expressions

$$f^\omega = \frac{n^2_\omega + 2}{3}, \quad (36)$$

and that of the dipole in the presence of the local static poling field by the Onsager expression,

$$f^0 = \frac{\epsilon(n^2_\infty + 2)}{n^2_\infty + 2\epsilon}, \quad (37)$$

where ϵ is the static dielectric constant, μ_z the molecular dipole moment, and n_∞ and n_ω are optical indices of refraction.[45]

In isotropic materials, the integral in the orientational average of Eq. (11) can be evaluated exactly without expanding the dipolar energy in a Taylor series. It is found that

$$\chi^{(2)}_{333} \sim N f^{\omega 3} f^{\omega 1} f^{\omega 2} \beta_{zzz}(-\omega_3;\omega_1,\omega_2) L_3(p), \quad (38)$$

where $L_3(p)$ is the third-order Langevin function whose series expansion for a "one-dimensional" molecule is given by[46]

$$L_3(p) = \frac{p}{5} - \frac{p^3}{105} + \cdots, \quad (39)$$

where

$$p = \left(\frac{\epsilon(n_\infty^2 + 2)}{n_\infty^2 + 2\epsilon}\right)\frac{\mu_z E_p}{kT}. \tag{40}$$

The first term in Eq. (39) is identical to the first term in Eq. (33), and Eq. (39) shows that the next term in the Langevin function is small if $\mu_z E_p < kT$.

Second harmonic generation in poled molecule-doped polymer films has been measured, and the results are consistent with the theory.[20] Since the films represent a non-interacting composite system, the susceptibility is given by Eq. (30) with $U_{\mu\nu} = 0$, where the measured susceptibility is the sum of the susceptibilities of the polymer and the dye. Indeed, it has been found that the film susceptibilities are linear in the number density of nonlinear optical moieties, and extrapolate to a nonzero value corresponding to the contribution of the polymer. It should be noted that glassy polymer thin films are homogeneous, and are thus appropriate for guided-wave propagation.

Third order nonlinear optical properties of doped polymer films have been determined by picosecond transient grating studies.[47] Time resolved measurements show that the electronic part of the response is shorter than $2ps$.

5.3 Liquid Crystal Polymers

Liquid crystalline mesophases possess a high degree of orientational order as defined by the even-order order parameters. High speed device applications require that the slow molecular reorientational processes be frozen. The incorporation of liquid crystal molecules into a polymer structure results in a system with a high degree of locked-in order below the glass transition temperature, and thus combines the favorable properties of both liquid crystals and polymer glasses. In this section, the orientational order of nonlinear optical molecules incorporated into a liquid crystal polymer structure is described, with emphasis on the resulting nonlinear optical properties.

One method of determining orientational order is through dichroism measurements, where the macroscopic order parameter, S_D, is defined as

$$S_D = \frac{A_\parallel - A_\perp}{A_\parallel + 2A_\perp}, \tag{41}$$

where $A_\perp$ and $A_\parallel$ are the peak absorptions measured perpendicular and parallel to the director, respectively. The microscopic order parameter, $\langle P_2 \rangle$, is determined from S_D if the local field effects are properly taken into account.

In the isotropic phase, the local field factors are calculated by assuming that the bulk can be described by an average isotropic dielectric environment, resulting in scalar local field factors which relate the microscopic fields to the macroscopic fields through a constant multiplicative factor. In the mesophase, the local field tensor may not be diagonalizable in the molecular coordinate system, so that the microscopic and macroscopic order parameters may not be equivalent.[10] Therefore, nonlinear optical properties can only be estimated from the results of measurements of the macroscopic order parameter, S_D.

One method of producing liquid crystalline films with homogeneous planar alignment employs magnetic field poling with the aid of surface treatment.[48] The substrates used are rubbed, polyimide coated glass plates, and the films are cooled from the isotropic phase to the mesophase in the presence of a magnetic field. In liquid crystal polymers, the cooling is continued until the sample is below the glass transition temperature of the polymer, locking in the orientation.

The nonlinear species can either be chemically reacted into the liquid crystal polymer or dissolved into a guest-host mixture. In either case, the interaction between the nonlinear optical moiety and the liquid crystal molecule enhances the orientation of the nonlinear optical moieties. The amount of order imparted will depend on the guest, the host and how the system is assembled. The results of a series of measurements of the macroscopic order parameters as a function of molecule size and environment can be used to optimize the order and orientation of the composite system.

Such studies were performed on liquid crystal polymers shown schematically in Figure 4. These random co-polymers are formed from substituted hexylacrylate monomers, one containing a mesogenic group and the other containing a dye. In the mesophase, the mesogenic side groups orientationally order the dye side groups. The resultant orientational order can be compared with similarly prepared guest-host mixtures of the dye in the liquid crystal side chain homopolymer to determine the effects of the backbone.

Eight different copolymers shown in Figure 5 were formed by copolymerizing one of the corresponding four dichroic dye monomers (#1–#4) with either a nematic or smectic monomer corresponding to #5 and #6 respectively, and aligned by magnetic field poling on

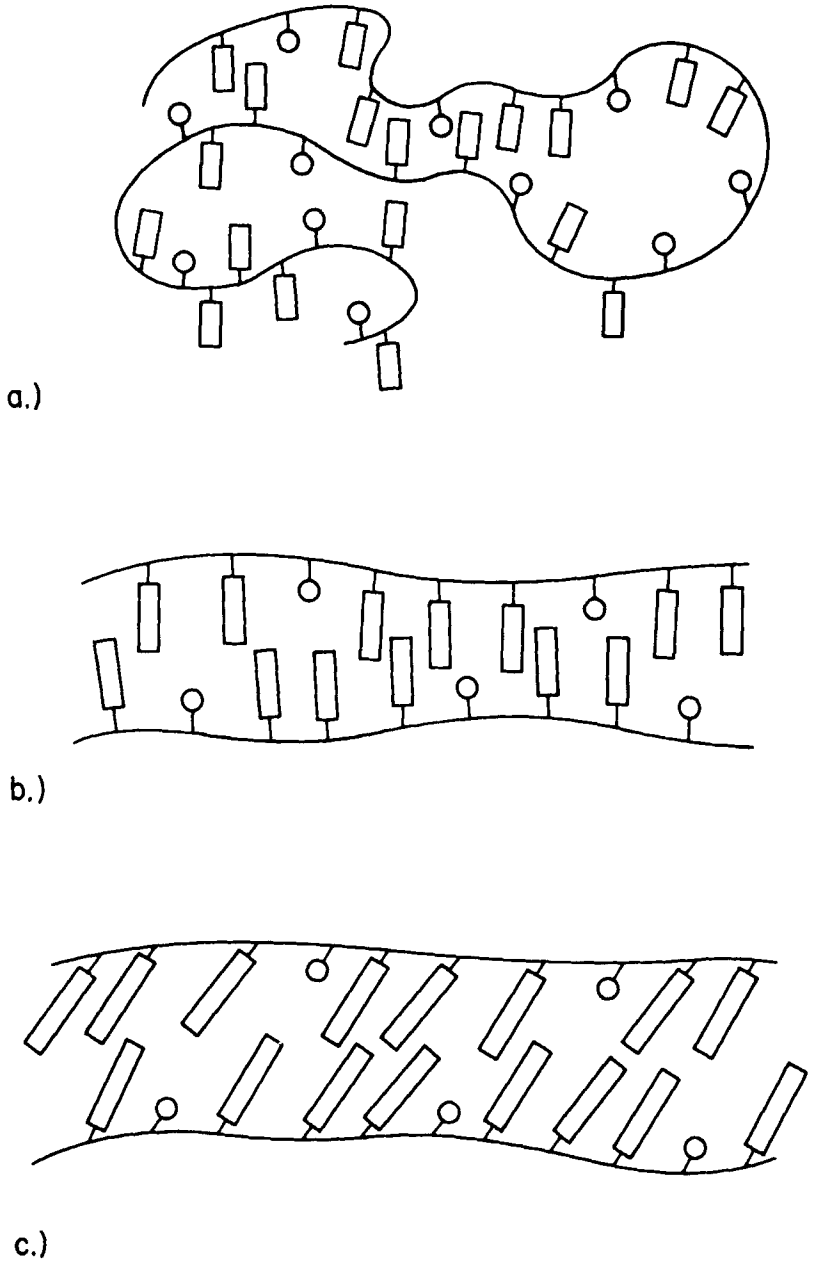

FIGURE 4 Schematic of a liquid-crystalline side-chain polymer, where the rectangles represent mesogenic units, and circles the nonlinear optical moieties. a) nematic order, b) smectic A order, c) smectic C order.

surface treated substrates.[48] The order parameters of the dyes in smectic copolymers were found to be larger than the order parameters of the dyes in nematic copolymers. This is consistent with the order parameters of nematic and smectic phases of pure liquid crystals. In both cases the dye concentrations were 2.0% by weight.

Guest-host mixtures of the nematic (#5) or smectic (#6) homopolymers and the dyes (#1, #2, #4) were aligned with the techniques described above. As seen in Table V, the smectic mixtures possess higher order than the nematic. On average, the polymer backbone does not affect the order, although the smectic guest-host system possesses a marginally higher order parameter than the corresponding copolymer. These effects may be due to the lower dye concentrations of 0.3% by weight used in the guest-host mixtures. It can be concluded that the polymer backbone and the concentrations have little effect on the order parameters in this concentration range.

The order parameter for a bisazo dye (#7) in the nematic phase of copolysiloxane (#8) has been found to be $S_D = 0.42$ while that of the monomeric dye in the homopolymer is $S_D = 0.54$.[49] The lower value in the polymer bonded dye has been attributed to an incomplete motional decoupling of dye and polymer backbone due to the shortness of the spacer. Both deuterium NMR and spin probe measurements show that the smectic homopolymer (#6), in Table V, has an order parameter of $S_N = 0.85$ and $S_S = 0.92$.[50,51] The smectic guest-host mixtures have orientational order in this range.

The large order parameters in the smectic polymer result in enhanced third-order optical properties, and electric field poling of this type of material should lead to second-order nonlinear optical prop-

TABLE V

Order parameters of liquid crystal polymer systems (data from Ref. 48)

	#5 Reacted	#6 Reacted	#5 Guest-Host	#6 Guest-Host
Dye #1	$S_D = 0.67$	$S_D = 0.78$	$S_D = 0.67$	$S_D = 0.84$
Dye #2	$S_D = 0.61$	$S_D = 0.77$	$S_D = 0.56$	$S_D = 0.79$
Dye #3	$S_D = 0.58$	$S_D = 0.68$		
Dye #4	$S_D = 0.72$	$S_D = 0.84$	$S_D = 0.76$	$S_D = 0.87$
No Dye		$S_N = 0.85$		
		$S_S = 0.92$		

S_D is the order parameter as determined from dichroism. S_N is the order parameter as determined from deuterium NMR. S_S is the order parameter as determined from spin probe.

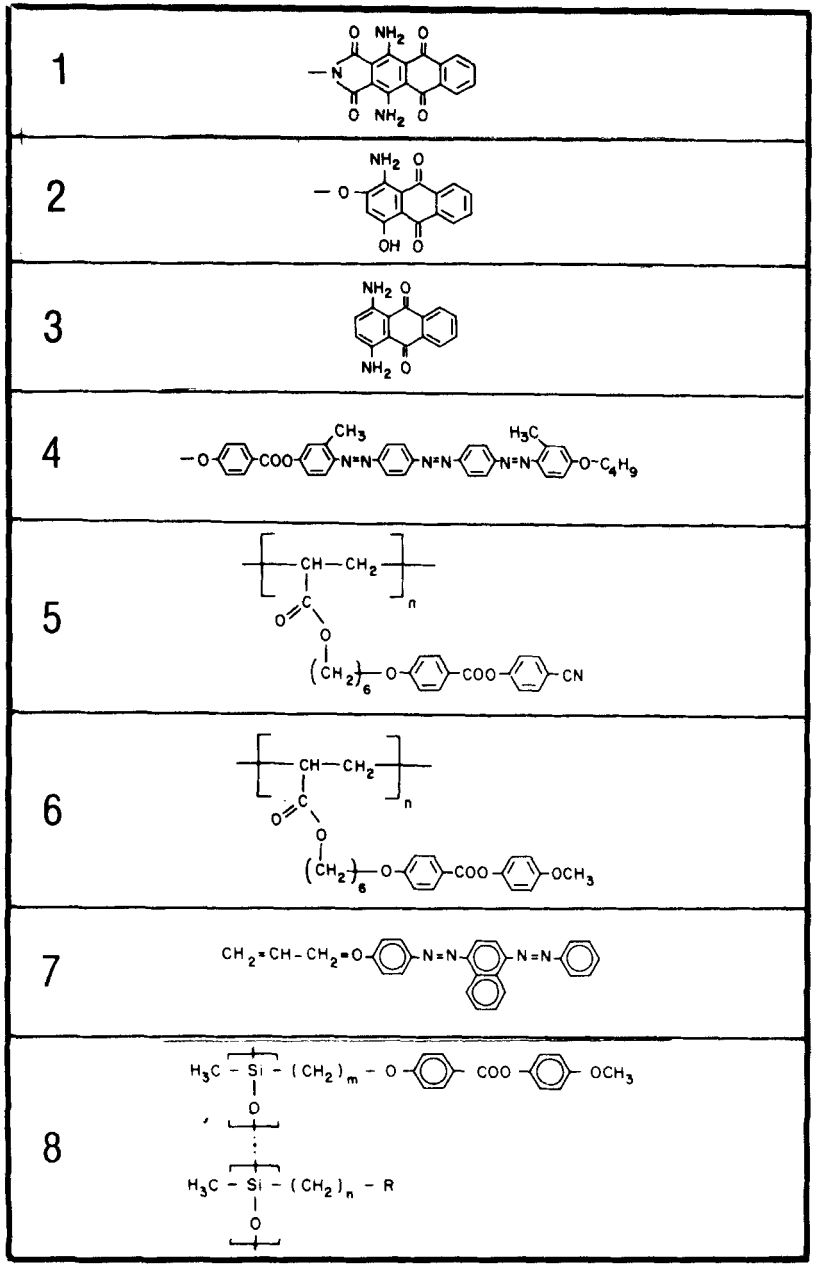

FIGURE 5 Liquid crystal polymer components (from Ref. 48).

erties that are enhanced relative to poled isotropic materials. For a one dimensional nonlinear dye molecule, the value of $\chi^{(2)}_{333}$ is three times greater for $S_D = 0.8$ (assuming $\langle P_2 \rangle = 0.8$) than for the isotropic case neglecting $\langle P_4 \rangle$. The lifetime of the covalently bound orientationally ordered dye may be enhanced over the guest-host solution by restricting rotational motion.

It may be advantageous to fabricate nonlinear optical mesogenic units that can be cross linked in order to lock-in the orientational order. To this end, mesogenic units consisting of a divinyldiacetylene terminated with nonlinear optical groups have been fabricated.[52] A DSC calorimetric thermogram of one of these materials, 1,8-bis[*p*-propylphenyl]-octa 1,7-dien-3,5-diyne (DVDA3), exhibits a nematic phase above 160°C, and at temperatures above 210°C, the diacetylene polymer forms from the mesogenic monomer.

A series of DVDA systems was synthesized and found to form both centrosymmetric and noncentrosymmetric films.[52] An aligning field was applied to a film located between glass plates coated with indium tin oxide (ITO) electrodes. The sample was heated until the mesophase was fully polymerized. The measured third-order susceptibility was about two to three orders of magnitude larger than quartz. No mention was made of the third-order susceptibility in the isotropic case as compared to the polymerized film, but the resulting polymerized films were reported to possess high optical quality.

The third-order susceptibility of other liquid crystal polymer films, namely polybenzimidazole (PBI) and polybenzthiazole (PBT), were evaluated by third harmonic generation.[53] The PBT films had a susceptibility of $\chi^{(3)} = 50 - 100 \times 10^{-12}$ esu and the PBI films were measured to be $\chi^{(3)} = 0.8 \pm .5 \times 10^{-12}$ esu. The optical quality of PBI was superior to that of PBT. The lower value of the nonlinear optical susceptibility of PBT was attributed to its tendency to form helical structures. The third order susceptibility of PBT was also measured using degenerate four-wave mixing, where the angular dependent measurement showed an anisotropy in the nonlinear susceptibility which was attributed to the material anisotropy.[54]

In side-chain liquid crystal polymer structures, the nonlinear optical susceptibility may not be given by the simple model if the interactions between the polymer backbone and the molecule are sufficiently strong to affect the nonlinear optical properties of the molecule. Here, the nonlinear optical moieties are not independent so that the sum in Eq. (8) does not hold, and collective effects become important on the molecular scale.

5.4 Langmuir-Blodgett Films

Highly ordered thin films can be fabricated using the Langmuir-Blodgett technique, where the structural properties are a result of the deposition process. The resulting order is derived from the externally applied surface pressure on a monolayer of molecules spread at an air-water interface. This ordered layer is then deposited one molecular layer at a time as shown in Figure 6. Since the order is supplied by an outside force, control of the final structure can be effected. The relatively high molecular density within a molecular layer, the high degree of orientational order, as well as the ability to grow structures in monolayer increments represent favorable properties for the application of Langmuir-Blodgett films to nonlinear optics.

Nonlinear optical properties of thin films deposited from the air-water interface can be measured by harmonic generation experiments. Since the nonlinear optical susceptibility of a thin organic film depends on the density and orientational order of the constituent molecules, nonlinear optical measurements can provide structural information on monolayers and multilayers. Second and third harmonic generation experiments provide information on the first four order parameters, so that a reasonable approximation to the orientational distribution function of molecules in a LB film can be obtained. Results from other experiments designed to measure order parameters augment harmonic generation data. Furthermore, the intensity of second harmonic generation from a thin film is also correlated with the molecular hyperpolarizability and density of molecules so that independent measurements of these using dc induced second harmonic generation[45] and pressure-area isotherms, respectively, can yield detailed information on the structure of the films. This information can further the basic understanding of Langmuir-Blodgett films, as well as provide a basis for engineering nonlinear optical devices.

In a medium of axially symmetric molecules, where the molecular hyperpolarizability is along the molecular axis and the orientational distribution in the azimuthal plane is random, the nonvanishing components of $\chi^{(2)}_{ijk}$ are written from Eqs. (27)–(28) as linear combinations of the first- and third-order Legendre polynomials,[55]

$$\chi^{(2)}_{\perp\perp\perp} = N\beta^*_{zzz}\left(\frac{2}{5}\langle P_3\rangle + \frac{3}{5}\langle P_1\rangle\right),$$

$$\chi^{(2)}_{\perp\parallel\parallel} = \chi^{(2)}_{\parallel\perp\parallel} = \chi^{(2)}_{\parallel\parallel\perp} = \frac{1}{5}N\beta^*_{zzz}(\langle P_1\rangle - \langle P_3\rangle). \tag{42}$$

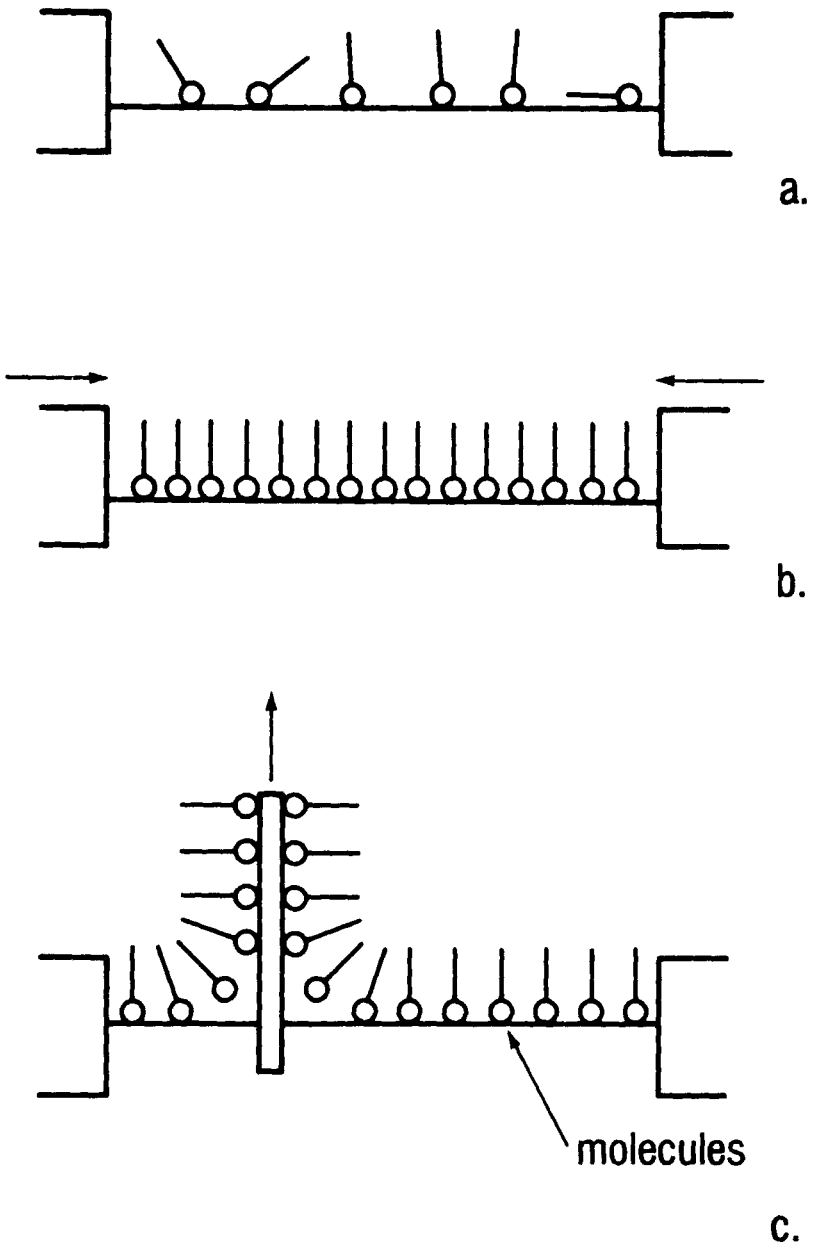

FIGURE 6 Langmuir-Blodgett deposition process. a) molecules spread at the air-water interface, b) compressed monolayer, c) transfer to substrate.

$\perp$ and $\parallel$ refer to directions perpendicular and parallel to the surface and z is the molecular axis. The third-order susceptibility is expressed in terms of thermodynamic averages of the even Legendre polynomials as shown in Eq. (16). Since LB films are "two dimensional," the local field factors are small when compared to bulk systems, as has been shown in a floating monolayer of sodium dodecylnaphthalene sulfonate.[55] In a medium with azimuthal symmetry, polarization dependent measurements can be used to decouple $\langle P_1 \rangle$ and $\langle P_3 \rangle$. The most probable tilt angle from the axis normal to the film plane can be calculated from the order parameter using an assumed distribution function.[55] In Langmuir-Blodgett layers, the in-plane crystalline order is characterized by correlation lengths much smaller than the coherence length of the nonlinear optical process.[56] Nonlinear optical measurements average over the domains so that it is possible to assume azimuthal symmetry.

The tilt angle of molecular axis from the surface normal of sodium-dodecylnapthalene-sulfonate has been measured by second harmonic generation in a monolayer at the water-air interface as a function of surface pressure.[55] Calculations, assuming either a delta function or Lorentzian distribution about the tilt angle θ, yield the same tilt angle within 10%. The orientation of the molecules varies continuously with increasing surface pressure and approaches a limiting value of roughly 30°.[55] Tilt angles have been measured in the same way for monolayers and bilayers of merocyanine and hemicyanine molecules on glass substrates. Assuming a delta function molecular distribution, a tilt angle was calculated at two different molecular densities for each compound. The minimum tilt angle is 9° for merocyanine and 20° for hemicyanine.[57,58] In another experiment, the tilt angle of a bilayer film of alternating layers of hemicyanine and nitrostilbene was compared with the tilt angles found for pure monolayers of each. The bilayer system exhibits a smaller net tilt angle and enhanced nonlinear response,[59] which represents an example of a composite system where the net orientational order is increased due to interaction between the two components. The parameters $\langle P_1 \rangle$ and $\langle P_3 \rangle$ were calculated using delta function distributions from the measured tilt angles. Table VI summarizes these calculations for films compressed to about 30 dynes/cm. The values for density and angle illustrate that on both aqueous and solid substrates, increased compression of the monolayer increases both molecular density and orientational order of the molecules, thereby increasing the nonlinear response of the film. These data suggest that the orientatioal order of the molecules in the Langmuir monolayer is coupled to changes in density. It is also clear from

TABLE VI

Polar order in monolayers (data from Ref. 59)

Molecule	θ (degree)	N (cm^{-2})	$\langle P_1 \rangle$	$\langle P_3 \rangle$
SDNS[1]	30	$2.5x10^{14}$	0.87	0.34
MC[2]	9.1	$5.4x10^{14}$	0.99	0.94
HC[3]	24	$4.0x10^{14}$	0.91	0.53
NS[4]	30	$4.0x10^{14}$	0.87	0.34
HC/NS[5]	23	$8.0x10^{14}$	0.92	0.57

[1]sodium-dodecylnapthalene monolayer on air-water interface.
[2]merocyanine monolayer on glass.
[3]hemicyanine monolayer on glass.
[4]nitrostilbene monolayer on glass.
[5]hemicyanine/nitrostilbene bilayer on glass.

these results that assuming a molecular orientation normal to the surface is not valid and leads to an underestimation of the value of β.

The effects of varying the point of attachment of long chains to a dye molecule on the orientation of the dye at the surface have been studied using pressure-area isotherms at the air-water interface and infrared absorption dichroism on multilayers of five azobenzene derivatives containing one or two stearylamino groups at different positions.[60] The dichroism data yield the orientation of the azo dye which is consistent with the area per molecule deduced from the pressure-area isotherm. The tilt angle of the long axis of the chromophore varies from almost lying flat on the surface to 30° from the normal to the surface. It is significant that changing the molecular shape profoundly influences the orientation of the molecule and limits the extent to which the dye aligns along the normal. In fabricating thin films of nonlinear optical dyes, similar experiments should be used to optimize the orientational order of the film. Usually nonlinear optical dyes are modified by the addition of long hydrocarbon chains to make them suitable candidates for Langmuir-Blodgett deposition. Varying the final steric "footprint" of the molecule is an additional way of controlling the density and orientational order of the film for optimization of the nonlinear optical properties of that film.

Both linear and nonlinear optical methods have been used to find the first four orientational order parameters in multilayers of a series of amphiphilic azoxy compounds with different end groups.[61–64] This work is unique in that both even- and odd-order parameters are measured in the same films, and thus indicate if the deposition is centrosymmetric or noncentrosymmetric. The linear Stark effect where

the shift in absorption under an applied electric field is measured, is the method used to obtain the odd-order parameters. Linear dichroism and the nonlinear Stark effect are measured to find $\langle P_2 \rangle$ and $\langle P_4 \rangle$. These results are summarized in Table VII for films 65 layers thick. In addition, electric field induced second harmonic generation has been measured for polydiacetylene multilayers.[65]

Measurements of second harmonic from a bilayer of hemicyanine, a structure thought to be centrosymmetric, give a nonzero signal.[58,66] The nonzero signal has been explained by differences in structure leading to incomplete cancellation between molecules in the two layers.[58] Inhomogeneities in a medium which is locally centrosymmetric lead to a net noncentrosymmetric ordering. This agrees with linear Stark effect measurements on a bilayer of merocyanine which produced a nonzero signal indicating structural asymmetry in the bilayer.[67] The dependence of second harmonic generation on number of layers has also been measured and a saturation in the dependence of signal on number of layers observed.[66] The second harmonic intensity in noncentrosymmetric films should vary with the square of the film thickness.[68] Measurements of second harmonic from multilayers of varying number of layers do not agree with this.[58,66] Third harmonic generation from polydiacetylene Langmuir-Blodgett films, however, varies quadratically with film thickness to 0.5 μm.[69]

The application of Langmuir-Blodgett films to nonlinear optics should benefit greatly from both theoretical and experimental work aimed at understanding the structural order in monolayers and multilayers, including in-plane positional order, orientational order, and the dependence of order and defects on number of layers. Nonlinear optical measurements can be useful tools for understanding this structure. Furthermore, the formalism of orientational order parameters aids in understanding the film structure, and provides a framework relevant to nonlinear optical processes.

TABLE VII

Order parameters of azo dye multilayers (data from Refs. 61–64)

End Groups	$\langle P_1 \rangle$	$\langle P_2 \rangle$	$\langle P_3 \rangle$	$\langle P_4 \rangle$
COOH	0.28	0.42	0.08	0.1
SO_2NH_2	0.72	0.57	0.15	−0.1
$SO_2N(C_2H_5)_2$	0.4	0.4	0.03	
PS[1]	0.26	0.06	−0.09	

[1]PS piperidinyl sulfamide.

6. CONCLUSIONS

The large nonlinear optical susceptibilities of many organic nonlinear optical materials arise from the electronic structure of the constituent molecules which is only slightly perturbed by the surrounding structure. Thus, the bulk nonlinear polarization is a sum over the molecular polarizations corrected for the effects of local fields. This additivity implies that only the orientational order of the molecules and density explicitly determine the nonlinear optical properties. The orientational order can be expressed as thermal averages of orthogonal functions, yielding expressions which relate microscopic order parameters to nonlinear susceptibilities. These expressions have been applied to a variety of structures including crystals, liquid crystals, liquid crystal polymers, isotropic materials, and Langmuir-Blodgett films, forming a common language with which to express the effects of order on nonlinear optical processes. This formalism can act as a guide to the study and optimization of structures for technological application as well as providing a method for determining the orientational order using nonlinear optics.

In addition to the order found in the homogeneous bulk, other aspects of the structure of materials can lead to sources of nonlinear polarization. These include the field gradients at interfaces, as well as the spatial dispersion within the material. This dispersion can be relatively gradual, such as found in cholesteric liquid crystals, or abrupt, as found in orientational defects in non-uniformly aligned nematic liquid crystals. A great deal of work in nonlinear optical materials has focused on crystals, which are generally homogeneous. However, with the increasing interest in liquid crystalline materials, and Langmuir-Blodgett films, the effects of inhomogeneities must be addressed, requiring supporting structural studies. The presence of inhomogeneities is important not only for determining the nonlinear optical properties, but also for the linear propagation of light, which will impact greatly on the potential applicability of these materials to photonic devices.

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