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Poled Polymer Films for Nonlinear Optics

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POLED POLYMER FILMS

Until recently, attempts to take advantage of the large second-order optical nonlinearities of certain conjugated organic molecules in devices were limited to neat crystalline materials, since the requirements for a noncentrosymmetric bulk phase could be met with molecular and polymeric crystals that happen to condense in a noncentrosymmetric point group.[1] The large dipoles that are often observed in these molecules made the growth of optical quality and robust crystals difficult. More recently, mixed systems consisting of the nonlinear optical molecules incorporated into polymer glasses, liquid crystals, and liquid crystal polymers have been investigated.[2] The difficulties in processing that are required to obtain optical quality materials are reduced. For second-order nonlinearities, an alignment process, such as electric field poling, is required to break the center of symmetry inherent in these materials. However, the reduction in number density and alignment attainable with realistic poling fields requires molecules with exceptionally large nonlinear optical susceptibilities in order to obtain bulk materials with nonlinear coefficients large enough to produce sensible devices.

As in molecular crystalline materials, the origin of the optical nonlinearities in guest-host polymer materials is traceable to the incorporated nonlinear optical moieties. However, the exact position and orientation of the moieties in the polymer host is not measurable as in crystalline materials. The relationship between the molecular and bulk susceptibility can be deduced from the thermodynamic potentials responsible for molecular motion during the poling and processing of the material. These potentials can be due to internal forces such as those responsible for liquid crystalline order, or external, such as those due to the poling field. Optical harmonic generation can be used to probe the molecular distributions that result from these forces to elicit the underlying molecular orientational order. The knowledge of this distribution, and the factors contributing to them are crucial since they determine the tensor components of the nonlinear susceptibility.[3] [4]

In organic molecular systems, such as molecular crystals and guest-host-polymer structures, 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 evaluating the thermodynamic average of the electronic contributions of the individual molecules (ignoring nonlocal effects):

$$P_i(t) = N<p_I(t)>_i \tag{1}$$

where N is the molecular density. In general, the molecules whose polarizations are summed using Eq. (1) exist within a thermal environment, so that the summation is expressed as a thermodynamic average, which, for an nth order nonlinear optical process is given by,

$$\chi^{(n)}_{ijkl\ldots} = N<\xi^{*}_{IJKL\ldots}>_{ijkl\ldots}, \tag{2}$$

where $<\xi^{*}_{IJKL\ldots}>_{ijkl\ldots}$ the ijkl...*th* component of the orientational average of the molecular nth order susceptibility, and where the * denotes that the local field effects have been included with the susceptibility. The indices I,J,K,L,...=x,y,z denote the molecular frame, and i,j,k,l,...=1,2,3 the laboratory frame. The orientational ensemble average for a tensor $\xi_{IJKL\ldots}$ is calculated using the following integral:

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$$<\xi_{IJKL\ldots}>_{ijkl\ldots} = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\psi \xi_{IJKL\ldots} a_{iI} a_{jJ} a_{kK} \cdots G(\phi,\theta,\psi), \tag{3}$$

where $G(\phi,\theta,\psi)$ is the normalized orientational distribution function which is a function of the Euler angles ϕ, θ, and ψ. The bulk nonlinear response of an 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

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. 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. 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 Legendre polynomials $P_l(\cos\theta)$,

$$G(\theta) = \sum_{l=0}^{\infty} \frac{(2l+1)}{2} A_l P_l(\cos\theta), \tag{4}$$

with the coefficients A_l determined from Eq. (4) as,

$$<P_l> \equiv A_l = \int_0^{\pi} \sin\theta d\theta G(\theta) P_l(\cos\theta). \tag{5}$$

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. 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,

$$\chi^{(2n)}_{ijk\ldots} = \sum_{m=0}^{n} u^{(2m+1)}_{ijk\ldots} <P_{2m+1}>,$$

$$\chi^{(2n+1)}_{ijkl\ldots} = \sum_{m=0}^{n+1} u^{(2m)}_{ijkl\ldots} <P_{2m}>. \tag{6}$$

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 N the number density. The *nth* rank tensor yields a limited number of distribution moments, and for a medium with zero odd-order $<P_l>$, even-order χ are zero.

The exact form of the $u^{(l)}_{ijk\ldots}$ are determined from the thermodynamic potentials acting on the ensemble. For a Gibbs distribution,

$$G(\theta) = \frac{\exp[-U/kT]}{\int d\Omega \exp[-U/kT]}. \tag{7}$$

The U is the mean-field potential describing the internal and external forces acting on the ensemble. For instance, the potential,

$$U = -m^{*}E_{P}P_{1}(\cos\theta) + bP_{2}(\cos\theta) \tag{8}$$

where the first term can describe an electric poling field, and the second term can describe internal liquid crystalline forces if b is positive, or other types of axial forces. The actual distribution or the nature of the thermodynamic potentials can be deduced from nonlinear optical measurements.

Second harmonic generation was measured for a thin corona-poled film of a dicyanovinyl azo dye incorporated in the side-chain methacrylate polymer shown in Figure 1. Measurements were performed at a wavelength of 1.58 μm as a function of incident angle for both p- and s-polarized incident light. From these measurements the form and magnitude of the second harmonic coefficient tensor were determined, as shown in Table 1. The molecular distribution implied by the data is consistent with a thermodynamic potential containing only the dipolar orienting energy acting during poling.

The magnitudes of the second harmonic coefficients in Table 1 are considerably larger than films previously reported.[3] This increase is due to the incorporation of a new nonlinear optical dye[5] and the introduction of corona poling. In addition, the side-chain polymer optical nonlinearity due to poling was found to be considerably more stable than films with molecules dissolved in a polymer matrix.

POLING UNDER UNIAXIAL STRESS

The formalism above can be used to describe the effects of electric field poling of a material under uniaxial stress.[6] Thus, second harmonic generation is used to study the rheological properties of the doped polymer, or, conversely the stress can be used to control the nonlinear optical properties of the polymer. The stress is introduced formally using the potential given in Eq. (8), where b describes the stress potential, which is an axially symmetric potential.

In order to examine the effect of compressive stress applied perpendicular to the plane of a polymer film, the formalism leading to Eq. (6) is applied in three steps.[7] First, the susceptibility is calculated assuming an undetermined poling and stress potential. The second order susceptibility tensor for a one dimensional molecule is related to the first and third order parameters:[8]

$$\chi^{(2)}_{333} = N\beta^{*}_{zzz}\left[\frac{3}{5}<P_{1}> + \frac{2}{5}<P_{3}>\right] \tag{9}$$

and

$$\chi^{(2)}_{113} = \chi^{(2)}_{131} = \chi^{(2)}_{311} = N\beta^{*}_{zzz}\left[\frac{1}{5}<P_{1}> - \frac{1}{5}<P_{3}>\right] \tag{10}$$

where β^{*}_{zzz} is the local field corrected hyperpolarizability. If a material possesses axial order as described by $<P_2>$ and $<P_4>$, electric field poling results in,[3]

$$\chi^{(2)}_{333} = N\beta^{*}_{zzz}\frac{m^{*}_{z}E_{p}}{kT}\left[\frac{1}{5} + \frac{4}{7}<P_{2}> + \frac{8}{35}<P_{4}>\right], \tag{11}$$

and

$$\chi^{(2)}_{113} = \chi^{(2)}_{131} = \chi^{(2)}_{311} = N\beta^{*}_{zzz}\frac{m^{*}_{z}E_{p}}{kT}\left(\frac{1}{15} + \frac{1}{21}<P_2> - \frac{4}{35}<P_4>\right), \tag{12}$$

where E_p is the magnitude of the poling field and m^{*}_{z} the magnitude of the local field corrected molecular dipole moment.

Experimentally determined order parameters can be used to calculate the tensor ratio. A dipole experiences a polar force in the presence of an electric field and results in a nonzero $<P_1>$ in contrast to the effects of stress described in terms of the potential b, which results in a nonzero value of $<P_3>$ in the presence of the field.[7] The ratio $\alpha = <P_3>/<P_1>$ can be shown to be a function of the stress and can be used to determine the orientational order of the molecules.[7] Figure 2 shows the dependence of the orientational distribution function on the stress for a fixed poling field.

Second harmonic generation is used to determine the ratio of the order parameters, α. The angular dependence of the second harmonic is measured as a function of incident angle for both s- and p-polarized fundamental and p-polarized second harmonic.[9] The ratio of the second harmonic power for the two input polarizations can be used to determine a, the tensor ratio of the second order susceptibility. The doped films are made by spin coating on Indium Tin Oxide (ITO) coated substrates, and pressing two such coated substrates into a sandwich above the glass transition temperature. The poling field is applied with the ITO electrodes when above the transition temperature and removed after reaching room temperature. Table 2 shows the properties of the two measured films.

DEVICE CONSIDERATIONS

The geometry of poled polymer films is amenable to the formation of guided-wave electro-optic and nonlinear optical devices. Therefore, a measurement of optical properties in a waveguide geometry is an important preliminary step to devices, and it has indeed been found that poled polymers do possess the requisite properties.

Measurements of the linear optical properties of dye/polymer films indicate that these materials can be considered for use in near-infrared devices. It is found that the index of refraction is positively correlated to the concentration of the dye species. Typical indices range from 1.5 to 1.6 for dye incorporated methacrylate polymers.

Waveguiding in films of Disperse red 1 in PMMA is impossible at $\lambda=632.8nm$ owing to dye absorption due to electronic excitations. However, losses as low as $0.3dB/cm$ are found at $\lambda=1.06\mu m$ wavelength.

The intrinsic flexibility of guest-host systems allows for simultaneous optimization of various optical properties. Along these lines we have been invesigating anomalous dispersion phase-matched second harmonic generation as a method of producing efficient nonlinear optical devices.

The possibility of obtaining phase-matched frequency multiplication by employing anomalous dispersion associated with a strong absorption allowing one component of a mixture to cancel the normal dispersion of another component was proposed over 25 years ago.[10] Anomalous-dispersion phase-matching is extremely desirable in that the phase-matching is completely independent of the propagation characteristics of the optical beams; thus, reductions in efficiency due to orientation, beam overlap, spatial dispersion, and beam walk-off are absent. Furthermore, any tensor coefficient in such a material could be phase-matched with the fields polarized along principle dielectric axes. These factors would allow for high conversion efficiencies without critical beam propagation constraints.

We have demonstrated anomalous-dispersion phase-matched second harmonic generation for the first time using electric field induced second harmonic generation (EFISH) in a liquid solution of Foron Brilliant Blue S-R (FBB). This dye has a sharp absorption maximum near 620 *nm* and a deep absorption minimum near 450 *nm*.

Anomalous-dispersion phase-matched second harmonic generation at 0.954μm was accomplished in an electric-field-aligned acetonitrile solution in which the concentration of FBB was varied. Acetonitrile was chosen because it is relatively nondispersive, transparent in the visible, is a good solvent, is nonhydroxylic, and is noncorrosive toward the cell's electrodes. The EFISH experiment was performed in acetonitrile as a function of concentration of Foron Brilliant Blue S-R at a fundamental wavelength of 0.954 μm. The dispersion ($n_{2\omega}-n_{\omega}$) for measurements at various concentrations was determined from the coherence length, and is plotted in Figure 3. The intercept for zero dispersion was determined from this plot to be at approximately 0.044 *M*, and the molar dispersivity was found to be 0.2313 M^{-1}. A 0.1 *M* solution was prepared and EFISH measured on dilution of this stock. The concentration dependence is shown in Figure 4. The peaked behavior indicating a factor of 50 enhancement at approximately 0.045 *M* is consistent with the extrapolation in Figure 3, and clearly signifies phase-matched second harmonic generation.

Table 1. Nonlinear optical properties of side-chain dicyanovinyl azo methacrylate polymer film.

THICKNESS	REFRACTIVE INDEX	d_{33}	d_{31}	d_{31}/d_{33}
(μm)	λ=0.8μm	(10^{-9}*esu*)	(10^{-9}*esu*)	
1.8	1.58	51	17	1/3

Table 2. Film parameters for PMMA doped with disperse red 1 dye.

Film #	Dye Number Density N ($10^{20}/cm^3$)	Thickness $\ell(\mu m)$	Poling Field $E_a(MV/cm)$	Stress $T_S(dyne/cm^2)$ ×10^7	a
1	2.42	4.0	0.60	0.00	0.33
2	1.08	4.9	0.25	3.71	0.7

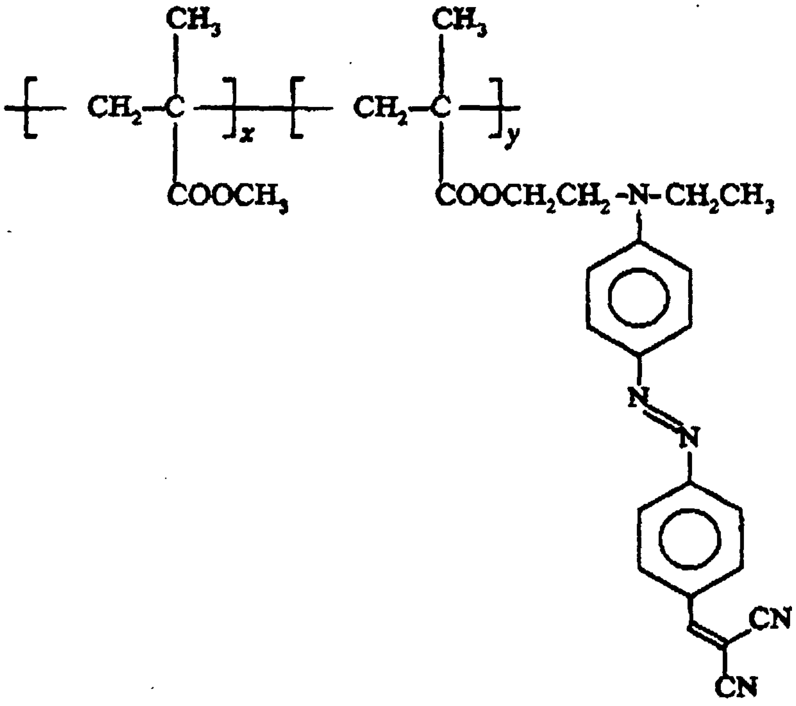


Figure 1. Side-chain dicyanovinyl azo methacrylate polymer.

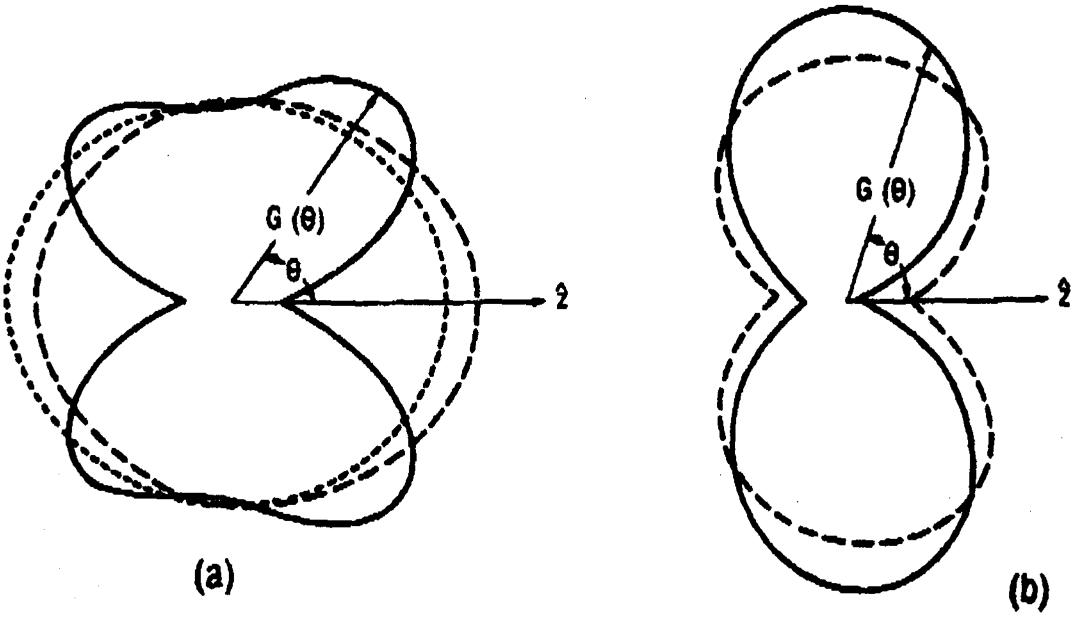


Figure 2. Polar plot of the distribution function, $G(\theta)$, as a function of the polar angle, θ. The length of the vector from the origin to the curve shows the magnitude of the distribution function in that direction. The curves shown are for (a) the isotropic film (dotted curve), the poled film with no pressure (dashed curve), the poled film under pressure (solid curve, $b/kT=0.5$) (b) $b/kT=1.0$ (dashed curve), and $b/kT=1.5$ (solid curve). $E_p=0.20 MV/cm$ in all poled samples.

Figure 3. Dispersion versus concentration for solutions of Foron Brilliant Blue S-R in acetonitrile.

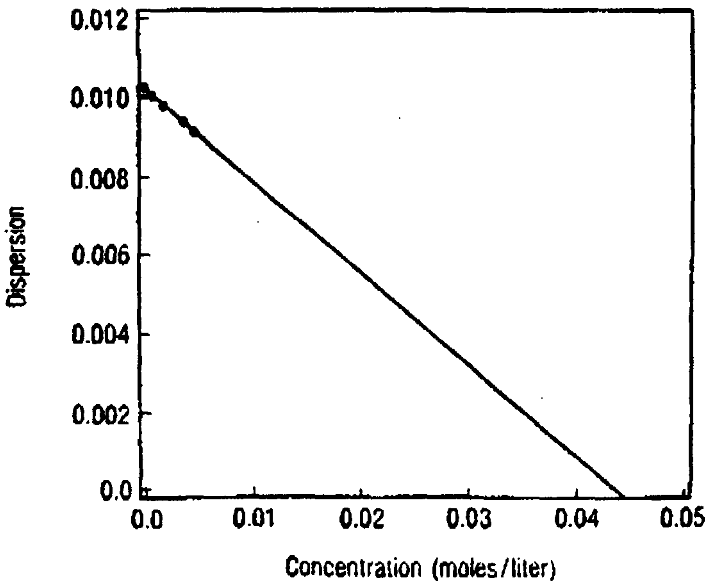
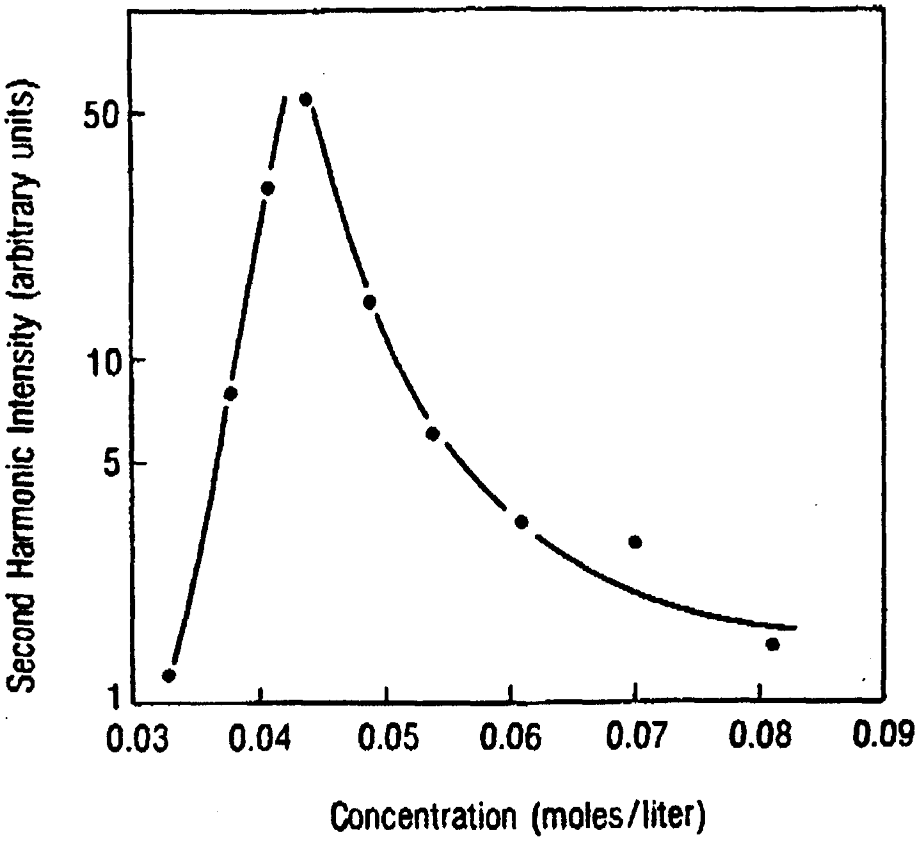


Figure 4. Second harmonic intensity versus concentration for solutions of Foron Brilliant Blue S-R in acetonitrile near the anomalous-dispersion phase-matched condition.



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