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13. ABSTRACT (Maximum 200 words)

During our Phase I research, we advanced materials synthesis and evaluation techniques needed to develop ferroelectric liquid crystals into a useful second-order nonlinear optical material. We developed a technique for determining the second-order nonlinear susceptibility by measuring the electro-optic coefficient r_{22} at 633 nm, using modulation frequencies between 100 KHz-100 MHz.

We evaluated two specially synthesized FLCs by measuring their r_{22} coefficients: previously existing MX-5679 and recently synthesized W-399, both based on a nitrobenzene hyperpolarizable moiety. Results show an increasing r_{22} with increasing spontaneous polarization. We also partially evaluated a new FLC material, W-371, with an ortho-situated nitroaniline hyperpolarizable moiety.

Since the liquid crystalline and the linear and nonlinear materials parameters FLCs have a temperature dependence, we examined existing FLC polymers for a FLC to glass phase and discovered a polymeric/FLC system that potentially could be used to reduce temperature dependent materials properties.

Our FLC synthesis efforts concentrated on synthesis of Hoffman-LaRoche compounds roche 1 and roche 2. Unfortunately, we were unable to duplicate their synthesis and instead developed an alternative core that could yield FLCs with a higher second-order nonlinear susceptibility.

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Development of Ferroelectric Liquid Crystals with Enhanced Nonlinear Optical Properties

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**Final Report
July 15, 1993 to March 15, 1994**

prepared for

Dr. Charles Y-C Lee

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I. Project Summary

Liquid crystals are an intermediate state of matter between solid and liquid possessing varying degrees of intrinsic molecular ordering. If liquid crystals have a ferroelectric phase, they have the minimal point group symmetry (C_2) needed to have a unique polar axis. Previous research at Displaytech and the University of Colorado demonstrated that hyperpolarizable molecules coupled to the ferroelectric polar order gives a phase with an enhanced $\chi^{(2)}$ -nonlinear susceptibility.

During our Phase I research, we advanced $\chi^{(2)}$ -enhanced ferroelectric liquid crystal (FLC) materials synthesis and evaluation techniques needed for our proposed Phase II work. We developed a technique for determining the $\chi^{(2)}$ -nonlinear susceptibility by measuring the electro-optic coefficient r_{22} at 633 nm, using modulation frequencies between 100 KHz-100 MHz. The technique can be adapted to 1150 nm. In addition, other tensor electro-optic coefficients can be measured. Redesign of FLC cell into traveling wave configuration will permit modulation frequencies up to 1 GHz.

We evaluated two $\chi^{(2)}$ -enhanced FLCs by measuring their r_{22} coefficients: previously existing MX-5679 and recently synthesized W-399, both based on a nitrobenzene hyperpolarizable moiety. Results show an increasing r_{22} with increasing spontaneous polarization. Full materials characterization will require temperature dependent r_{22} measurements.

We also partially evaluated a new $\chi^{(2)}$ -enhanced FLC material, W-371, with an ortho-situated nitroaniline hyperpolarizable moiety. Unfortunately, this liquid crystal material possesses a liquid crystalline phase that gives a twisted-grain boundary liquid crystalline phase that ruins liquid crystalline alignment in the smectic C^* phase. Phase I work did produce a liquid crystal alignment technique that is adaptable to this material; however, it requires a redesign of the FLC r -coefficient test cell and will not be further pursued until Phase II.

Since the liquid crystalline and the linear and nonlinear materials parameters FLCs have a temperature dependence, we examined existing FLC polymers for a FLC to glass phase and discovered a polymeric/FLC system that potentially could be used to reduce temperature dependent materials properties.

Our $\chi^{(2)}$ -enhanced FLC synthesis efforts concentrated on synthesis of Hoffman-LaRoche compounds roche 1 and roche 2. Unfortunately, we were unable to duplicate their synthesis and instead developed a promising $\chi^{(2)}$ -enhanced core that could yield FLCs.

Since $\chi^{(2)}$ -FLC materials have a relatively low non linearity, a strong nonlinear interaction requires an interaction volume with a large length² to cross-sectional area ratio. This requirement is met if we fabricate an optical fiber with a micron-sized, $\chi^{(2)}$ -enhanced FLC polymer core. This is the subject of our proposed Phase II research.

II. Introduction

Liquid crystals are an intermediate state of matter between solid and liquid possessing varying degrees of intrinsic molecular ordering. If liquid crystals have a ferroelectric phase, they have the minimal point group symmetry (C_2) needed to have a unique polar axis. Previous research at Displaytech and the University of Colorado demonstrated that hyperpolarizable molecules coupled to the ferroelectric polar order gives a phase with an enhanced $\chi^{(2)}$ -nonlinear susceptibility.¹

Since hyperpolarizable molecules incorporated into FLC molecules must be compatible with the FLC phase, the hyperpolarizability β cannot be as large as β molecules that are found in poled polymers; however, the FLC $\chi^{(2)}$ -nonlinear susceptibility is thermodynamically stable, unlike poled polymers.

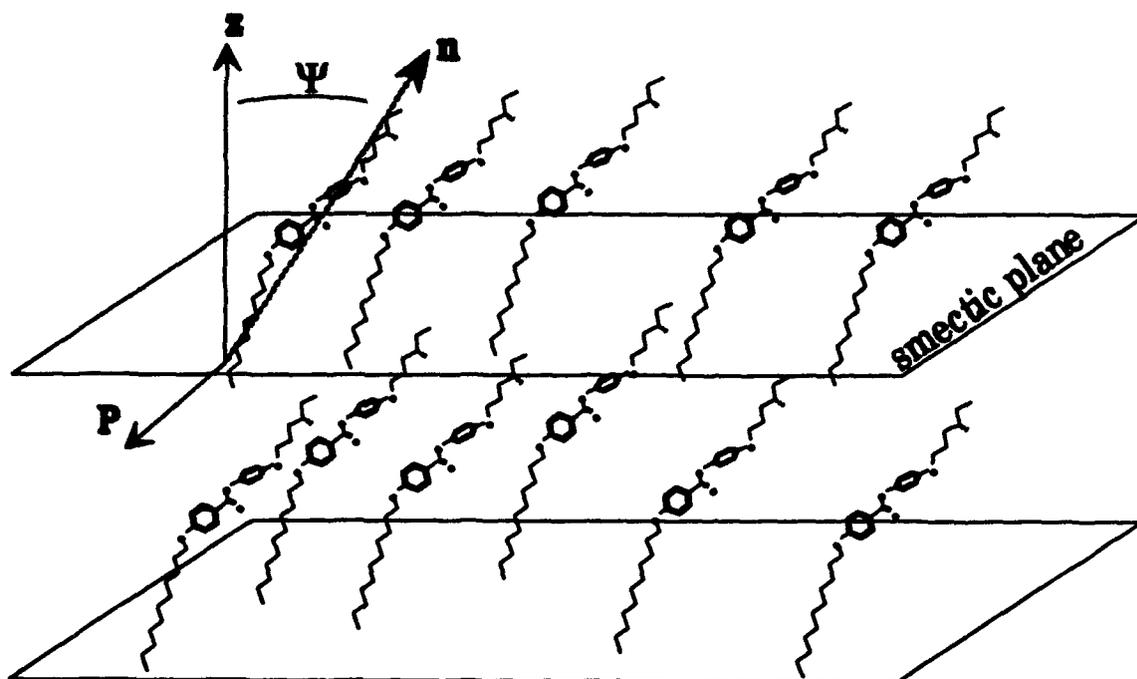
In addition to second-order nonlinear optical characteristics, FLC linear optical characteristics $\chi^{(1)}_{ij}$ can be adjusted by chemical synthesis or by mixing miscible liquid crystalline compounds with different linear susceptibilities α_{ij} .

During our Phase I research, we advanced $\chi^{(2)}$ -FLC materials synthesis and evaluation techniques needed for our proposed Phase II work.

A. FERROELECTRIC LIQUID CRYSTAL PHASE.

The ferroelectric liquid crystal (FLC) phase results from symmetry-enforced orientations of Z-shaped, optically anisotropic, chiral molecules *into a polar phase*. The Z-shaped molecules contain a "core" - one or more cyclic compounds - surrounded on each end by a "tail". At present, cyclic cores known to produce the smectic C* phase are benzene, cyclohexane, pyridine, and pyrimidine. The tails could be n-alkyl chains containing one or more chiral centers.

Locally, the molecules self-organize into smectic liquid crystal layers with the director \mathbf{n} tilted with respect to the smectic layer normal \mathbf{z} .² Within a smectic layer, the average orientation of the long axis of the molecules defines the director \mathbf{n} , which is approximately parallel to the extraordinary axis of the birefringent FLC medium ($\Delta n = 0.15$). The director \mathbf{n} makes an angle Ψ (tilt angle), typically 20 to 45 degrees with the layer normal \mathbf{z} . Since the molecules are chiral (non-superposable on their mirror images), the liquid crystalline phase has a polar order manifested through a spontaneous polarization \mathbf{P} , defined by: $\mathbf{P} = (\mathbf{z} \times \mathbf{n})P$. The spontaneous polarization magnitude is a function of the chiral center in addition to the net orientation of the dipole moment with respect to the polar axis of the FLC phase. A typical value of P for FLC mixtures optimized for surface stabilized switching is 30 nC/cm². A 3-D slice of the smectic C* phase is illustrated below, with an example of an early FLC molecule from the Boulder group.



B. $\chi^{(2)}$ -ENHANCED FERROELECTRIC LIQUID CRYSTALS

1. Hyperpolarizable cyclic cores.

The molecular second order hyperpolarizability β of the molecules in the FLC phase originates from electron donor (D) and acceptor (A) groups synthesized onto the core π -conjugated electron system (D π A subgroup).³ When driven by an applied electric field, the D π A subgroup has a nonlinear response – the polarization density occurs more readily when the applied field is such that the donor becomes positive, than when the field is such that the donor becomes negative.

In present $\chi^{(2)}$ -enhanced FLCs D π A subgroups are disubstituted benzene rings, with one or more donor (D) and acceptor (A) units situated ortho or para on the ring. The symmetry of the planar D π A subgroups above dictates that the hyperpolarizability tensor β is at most a two-dimensional system, coplanar with the benzene ring. For an ortho D π A subgroup, β is a two-dimensional system (symmetry group 2mm) with the ground state, excited state, and transition dipole moments all located in the plane. Parasubstituted subgroups are one dimensional (symmetry group 2) with the ground state, excited state, and transition dipole moments collinear and oriented approximately parallel to the donor-acceptor axis.

For the sake of simplicity, we will assume that we have a one dimensional D π A system. β_{yyy} resulting from charge transfer can be adequately described a two-state

model. The essential features of this model with respect to molecular D π A design are seen if we consider only second harmonic generation.

$$\beta_{xxx}(-2\omega, \omega, \omega) = \frac{3e^2 \hbar^2}{2m\epsilon_0} \frac{\Delta\mu \hbar \omega_{eg} f}{\left[(\hbar\omega_{eg})^2 - (2\hbar\omega)^2 \right] \left[(\hbar\omega_{eg})^2 - (\hbar\omega)^2 \right]}$$

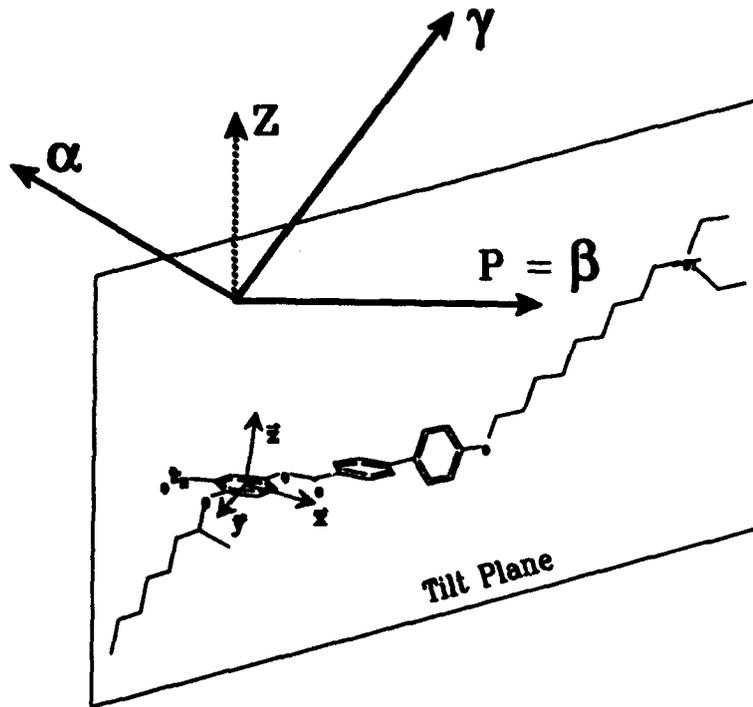
$\Delta\mu$ is the difference between the dipole moments between the ground and excited state, ω is the light frequency, f is the oscillator strength and ω_{eg} is the transition frequency of the nonresonant linearity.

Synthesizing stronger electron donor and acceptors into D π A subgroups can increase the oscillator strength and $\Delta\mu$. Longer D π A subgroups improves $\Delta\mu$ by increasing the charge separation; however, this also reduces ω_{eg} resulting in an increased light absorption at 2ω .

In addition to stringent phase matching considerations, second harmonic generation has the strictest nonlinear optical materials transparency requirement, since both the fundamental and second harmonic waves must be isolated from the resonant non linearity. It is easier to increase β for electro-optic modulation since only the carrier must be isolated from the resonant non linearity.

2. FLC $\chi^{(2)}$ -nonlinear susceptibility model.

As we have shown, appropriate chemical synthesis can produce an FLC with an enhanced $\chi^{(2)}$ nonlinear susceptibility if a substantial component of the D π A hyperpolarizability is oriented parallel to the polar axis of the FLC phase. Below is a representation of an $\chi^{(2)}$ -enhanced molecule in a ferroelectric phase showing the relative orientation between the hyperpolarizable core and the polar axis. Angles between the microscopic axes (x, y, z) attached to the hyperpolarizable core and the macroscopic FLC dielectric axes (α, β, γ) (in the weakly biaxial approximation) are shown.



This FLC $\chi^{(2)}$ nonlinear susceptibility is described by the van der Waals oriented gas model⁴. The nonlinear susceptibility $\chi^{(2)}(-2\omega; \omega, \omega)$ is a tensor sum of the molecular hyperpolarizabilities of N molecules, *independent* of any applied field E:

$$d_{ijk} = \frac{2}{V} f_i^{2\omega} f_j^{\omega} f_k^{\omega} \sum_s \sum_{ik} \langle C_{\bar{i}}^{(s)} C_{\bar{j}}^{(s)} C_{\bar{k}}^{(s)} \rangle \bar{\beta}_{ik}^{(s)}$$

where $d = 2\chi^{(2)}(-2\omega; \omega, \omega)$, β is the polar axis parallel to the spontaneous polarization P, γ is the acute bisectrix that is approximately parallel to n, and α is the remaining obtuse bisectrix of the weakly biaxial ferroelectric liquid crystal phase. V is the volume of the unit cell, f_i^{ω} are the local field factors, and the Cs are the direction cosines between the microscopic and macroscopic coordinate axis averaged over the molecular configurations in the unit cell smectic C* binding site. β is averaged over each molecular contribution. The sum (s) is carried over the two molecules per unit cell.

The local field factor f_i^{ω} for a spherical void is:

$$f_i^{\omega} = \frac{n(\omega)^2 + 2}{3}$$

Note that the local field factor goes as the square of the refractive indices. Actually, molecules that form an FLC phase are highly ellipsoidal (cigar shaped). In future research we must include the effect of void asymmetry on local field factors.

After considering the C_2 symmetry of the smectic C* phase, the nonlinear susceptibility coefficients are:

$$d_{\beta\beta\beta} = \frac{2}{v} f_{\beta}^{2\alpha} f_{\beta}^{\alpha} f_{\beta}^{\alpha} \sum_i \langle C_{\beta y_i}^3 \rangle$$

$$d_{\beta\gamma\gamma} = \frac{2}{v} f_{\beta}^{2\alpha} f_{\gamma}^{\alpha} f_{\gamma}^{\alpha} \sum_i \langle C_{\beta y_i} C_{\gamma y_i}^2 \rangle$$

$$d_{\beta\alpha\alpha} = \frac{2}{v} f_{\beta}^{2\alpha} f_{\alpha}^{\alpha} f_{\alpha}^{\alpha} \sum_i \langle C_{\beta y_i} C_{\alpha y_i}^2 \rangle$$

$$d_{\alpha\beta\gamma} = \frac{2}{v} f_{\alpha}^{2\alpha} f_{\beta}^{\alpha} f_{\gamma}^{\alpha} \sum_i \langle C_{\alpha y_i} C_{\beta y_i} C_{\gamma y_i} \rangle$$

where $C_{\beta y}$ is the direction cosine between the β axis and the y axis of the s th molecule. Noting that the spontaneous polarization P is:

$$P_{\beta} = \frac{1}{v} \sum_i p_i \langle C_{\beta y_i} \rangle$$

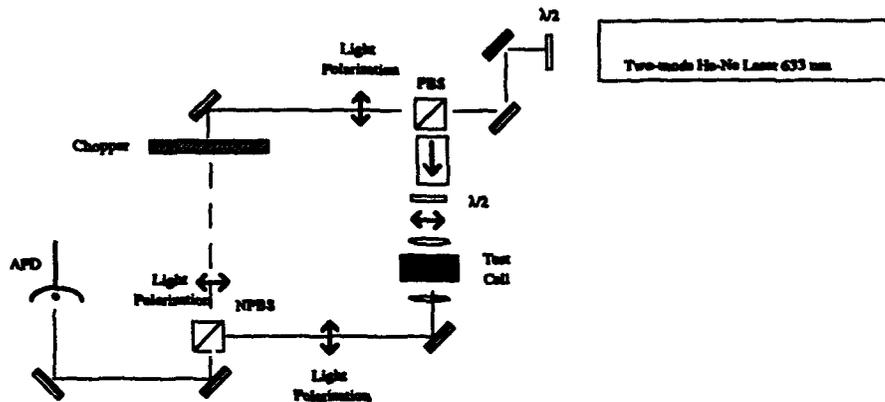
where p_i is the dipole moment, $C_{\beta y}$ is the direction cosine between the β axis and the y axis of the s th molecule. Thus, an increase in the spontaneous polarization of the FLC phase can be an indicator of an increased nonlinear susceptibility.

III. Phase I Results

A. DEVELOPMENT OF TECHNIQUE FOR EVALUATING FLC $\chi^{(2)}$ - NONLINEAR SUSCEPTIBILITY.

1. Description of technique.

Using the light output from a 633 nm He-Ne laser, the radio-frequency (RF) output from a synthesized frequency source, and a small optically uniform sample of $\chi^{(2)}$ - enhanced FLC, we developed a technique for measuring the electro-optic coefficient r_{22} of ferroelectric liquid crystals. A schematic of our evaluation apparatus is shown below.



Light from a 0.5 mW 633 nm He-Ne gas discharge laser with flat, *polarization insensitive* windows is directed through a polarizing beamsplitter (PBS). If the laser is built such that only two modes will lase within the gain profile, competition between the orthogonal, linearly polarized modes ensures they will lase at frequencies separated by the free spectral range (≈ 720 MHz) of the laser cavity. The laser is rotated until one of the longitudinal modes corresponds to the PBS s-polarized wave, and the other corresponds to the orthogonally polarized p-wave. One of these waves can serve as the unmodulated carrier (frequency f_c) and the other the local oscillator (frequency $f_{LO} = f_c + 720$ MHz).

After transiting an optical diode and a half-wave plate, the carrier is directed through the $\chi^{(2)}$ FLC thin film at right angles to the modulating electric field produced by a high frequency source (frequency f_m). The spectral density of the light exiting the FLC test cell is determined by mixing the modulated carrier with a local oscillator (frequency f_{LO}) on a fast photo diode. Photo current from the photo diode is analyzed by a spectrum analyzer yielding the modulated carrier spectral density. After tuning the spectrum analyzer local oscillator to a frequency equal to $f_{LO} - f_m - f_c$, the rms phase retardation Γ is determined from the ratio of the spectral density at ($f_{LO} - f_m - f_c$) to the spectral density at ($f_{LO} - f_c$). The electro-optic modulation coefficient r is determined from the cell geometry parameters, such as electrode spacing d and FLC sample thickness l , light

wavelength λ , index of refraction n , and rms drive voltage V . Using this technique, we measured r_{22} as small as 0.1 pm/V.

Because this technique demands an optically uniform FLC sample, and because the liquid crystal alignment uniformity in one thermotropic liquid crystal phase strongly depends on the alignment uniformity in the previous thermotropic phase, we have used this technique only on liquid crystals with well-behaved alignment characteristics. When cooled, a well-behaved liquid crystal has a thermotropic phase sequence such as: isotropic (I) \Rightarrow chiral nematic (N^*) \Rightarrow smectic A \Rightarrow ferroelectric smectic C^* ; or I \Rightarrow A \Rightarrow C^* .

Phase II refinements of the evaluation method include adapting the FLC cell into a traveling RF wave configuration that will allow modulation frequencies up to 1 GHz. With better liquid crystal alignment and by mounting the RF test cell on a rotating stage, we can also measure the r_{23} and r_{21} electro-optic coefficients. Temperature control will allow a full temperature-dependent characterization of $\chi^{(2)}$ FLC monomers for validation of order-dependent nonlinear susceptibility model. Development of a polarization-stabilized He-Ne laser at 1.15 μm will allow r measurements at light wavelengths closer to actual commercial use.

2. FLC r -coefficient evaluation cell.

The idea behind the FLC r -coefficient evaluation cell is to provide an optically uniform sample of FLC with a known optic axis orientation; thus, measurements of the rms phase shift can be connected to individual tensor r -coefficients knowing RF field, light polarization and propagation direction relative to the optic axes.

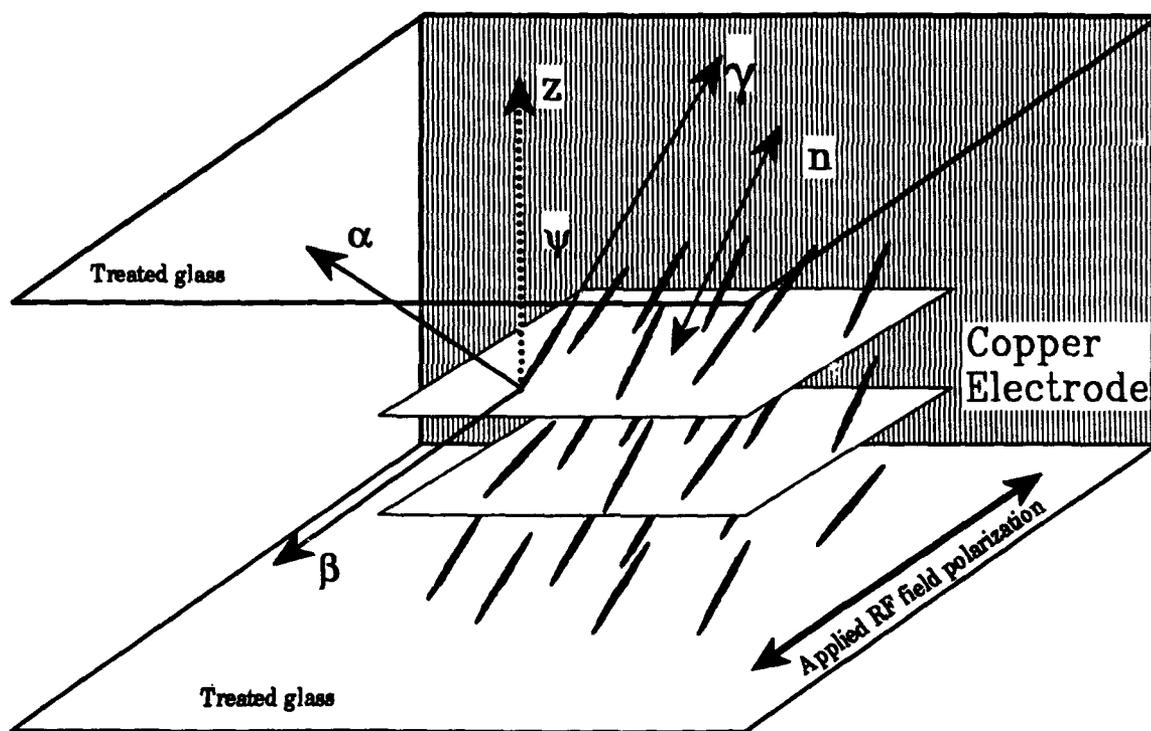
The evaluation cell consists of two glass plates sandwiching two, 50 μm thick electrically isolated copper electrodes approximately 1 cm square. FLC to be evaluated is placed between the copper electrodes. A first generation r -coefficient evaluation cell is shown in the photograph below.



Liquid crystal optic axes alignment is accomplished by pretreating the glass surfaces adjacent the liquid crystal with an agent that produces a self-assembled monolayer

(SAM) on the glass surface; thus, liquid crystal molecules interacting with the SAM tend to orient themselves normal to the glass surface. Furthermore, the copper electrodes surfaces adjacent the FLC are directionally polished to promote liquid crystal alignment parallel to the liquid crystal alignment induced by the SAM.

Considering that the minimal rms phase shift that can be observed is 10^{-4} radians, the limit on the maximum electrode separation d to sample thickness l ratio is approximately 1:1. Our previous research has shown that FLC cells can be homeotropically aligned in sample up to 100 microns thick; furthermore, optical alignment quality improves with thinner cells. We therefore chose to make our evaluation cells 50 μm thick, with a 25 μm electrode spacing. A cut-away drawing depicting the FLC optic axes orientation, glass and copper surfaces, RF field orientation and light polarization direction is show below.



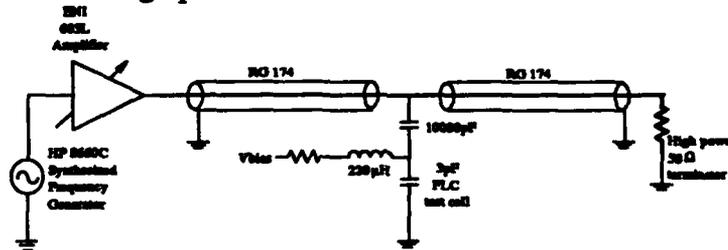
Local layer structure cut-away section of $\chi^{(2)}$ -enhanced ferroelectric liquid phase in r-coefficient FLC test cell, showing the relationship between average molecular direction (double headed arrow n) of liquid crystal molecules (dark rods), smectic layers (planes), smectic layer normal (z), the tilt angle y between z and n , the polarization direction and two-fold C_2 axis (β), the acute (α) and obtuse bisectrix (γ) of the biaxial FLC phase. Note grooves in Cu electrode parallel to z .

Because this technique demands an optically uniform FLC sample with a known optic axes orientation, and because the liquid crystal alignment uniformity in one

thermotropic liquid crystal phase strongly depends on the alignment uniformity in the previous thermotropic phase, we have used this technique only on liquid crystals with well-behaved alignment characteristics. When cooled, a well-behaved liquid crystal has a thermotropic phase sequence such as: isotropic (I) \Rightarrow chiral nematic (N*) \Rightarrow smectic A \Rightarrow ferroelectric smectic C* ; or I \Rightarrow A \Rightarrow C*. Materials with I \Rightarrow C* or with I \Rightarrow TGBA \Rightarrow C* phase transitions tend to be ill-behaved and difficult to align.

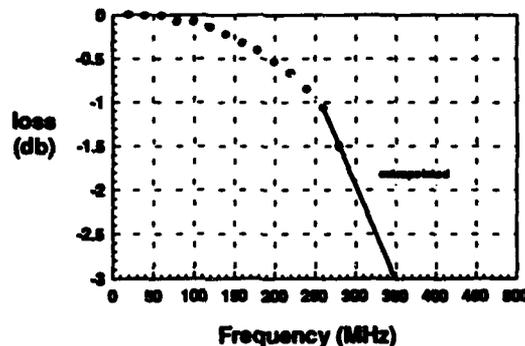
3. Electrical circuit.

A schematic of the equivalent electrical circuit is shown below. An HP 8660C synthesized frequency source is connected to an ENI 603L power amplifier with 40 db gain and 35 dbm power saturation point. This combination drives a 125 cm cable connected to the FLC r-coefficient cell. The cell is biased by a small electric field (< 0.5 V/ μ m) that unwinds the FLC and produces an optically uniform FLC sample. On the other side of the FLC cell is a high power 50 Ω terminator.



We checked the frequency response of our transmission line/FLC r-coefficient cell combination using two different methods. First, by measuring the difference between incident RF power at the output of the ENI amplifier and the transmitted RF power through to the 50 Ω terminator; second by comparing incident power at the ENI amplifier to the voltage measured across the copper electrodes using a fast Tektronix oscilloscope and high-frequency probe combination. Out to 250 MHz, we noticed virtually no difference between the two measurements. Below is a typical FLC r-coefficient frequency response of our transmission line/FLC r-coefficient cell combination, measured using the first technique. Note that out 100 MHz, frequency response is virtually flat.

Frequency Response of Cell #4

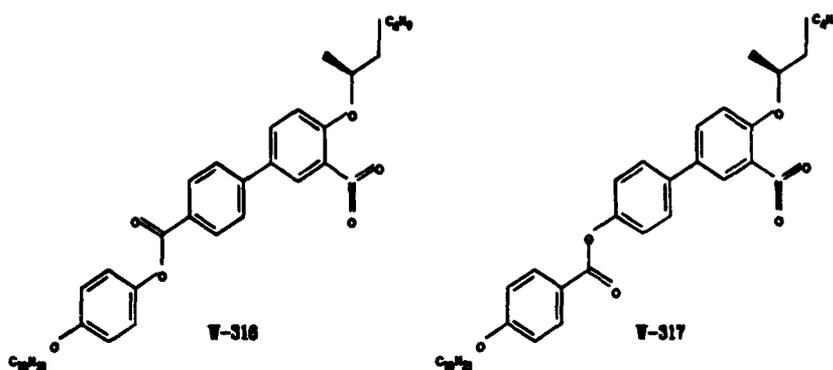


To avoid any possible deleterious RF effects, we generally restricted our r -coefficient measurements to no less than 100 MHz.

4. 633 nm electro-optic coefficients.

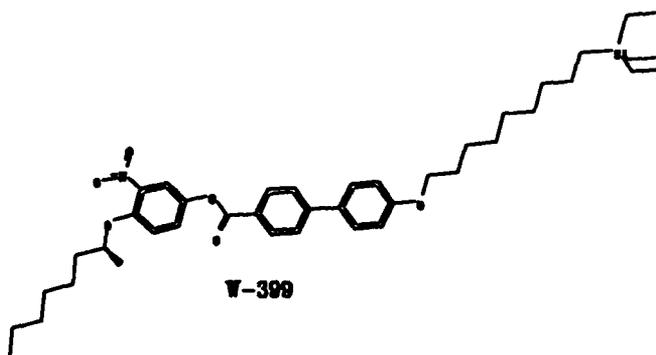
We evaluated two $\chi^{(2)}$ -enhanced FLC mixtures during our phase I work; first, we made measurements of the spontaneous polarization magnitude P v.s. temperature; second, we measured the electro-optic coefficient r_{22} using modulation frequencies between 100 KHz and 100 MHz at room temperature.

The first FLC, MX-5679, consists of a 1:1 mixture of the two compounds below. Note that the $D\pi A$ nitrogroup is attached to the biphenyl side of the FLC core.



$\chi^{(2)}$ -enhanced FLC mixture MX-5679, with a phase sequence: $I \Rightarrow 79^\circ \Rightarrow A \Rightarrow 45^\circ \Rightarrow C^* \Rightarrow < 0^\circ \Rightarrow X$.

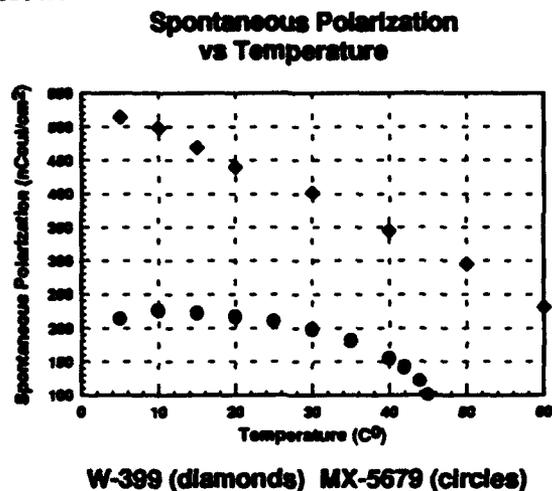
The second FLC, received from Walba at the University of Colorado, consists of the pure compound W-399 shown below. Note that the $D\pi A$ nitrogroup is attached to the biphenyl benzoate side of the FLC core.



$\chi^{(2)}$ -enhanced FLC W-399, with a phase sequence $I \Rightarrow 94^\circ \Rightarrow A \Rightarrow 68^\circ \Rightarrow C^* \Rightarrow < 5^\circ \Rightarrow X$.

Spontaneous polarization measurements.

Measurements of the magnitude of the spontaneous polarization measurements as a function of temperature were made using the triangular wave technique.⁵ Results for the two FLCs are shown below.

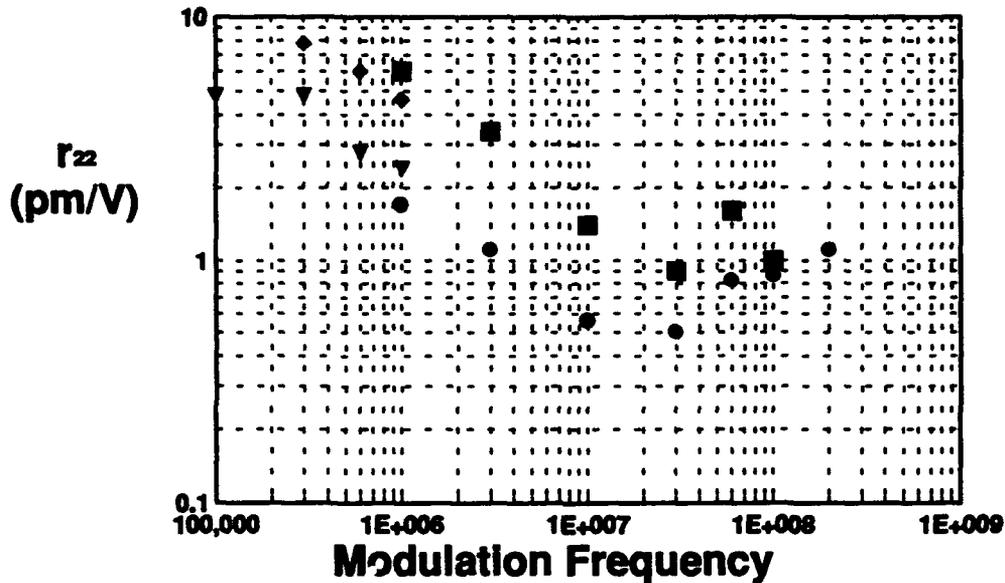


Changing the nitrosubstitution from the 1-methylheptyl side of the MX-5679 constituents to the decane side of W-399 core increases P. Since the magnitude of the spontaneous polarization increases with increasing polar order $C_{\beta\gamma}$, we expect a subsequent increase in the nonlinear susceptibility.

Electro-optic coefficients.

The FLC nonlinear susceptibility is determined from measurements of the 633 nm r_{22} electro-optic coefficients, measured in the manner described in previous sections. Results for our two FLCs are shown below.

MX-5679 vs W-399



MX-5679 Triangles BK 3010 source Circles HP 8660/ENI 603L source
 W-399 Diamonds BK 3010 source Squares HP 8660/ENI 603 L source

Note that as the frequency source is changed at 1 MHz, there is a slight discrepancy in measured r_{22} values between sources.

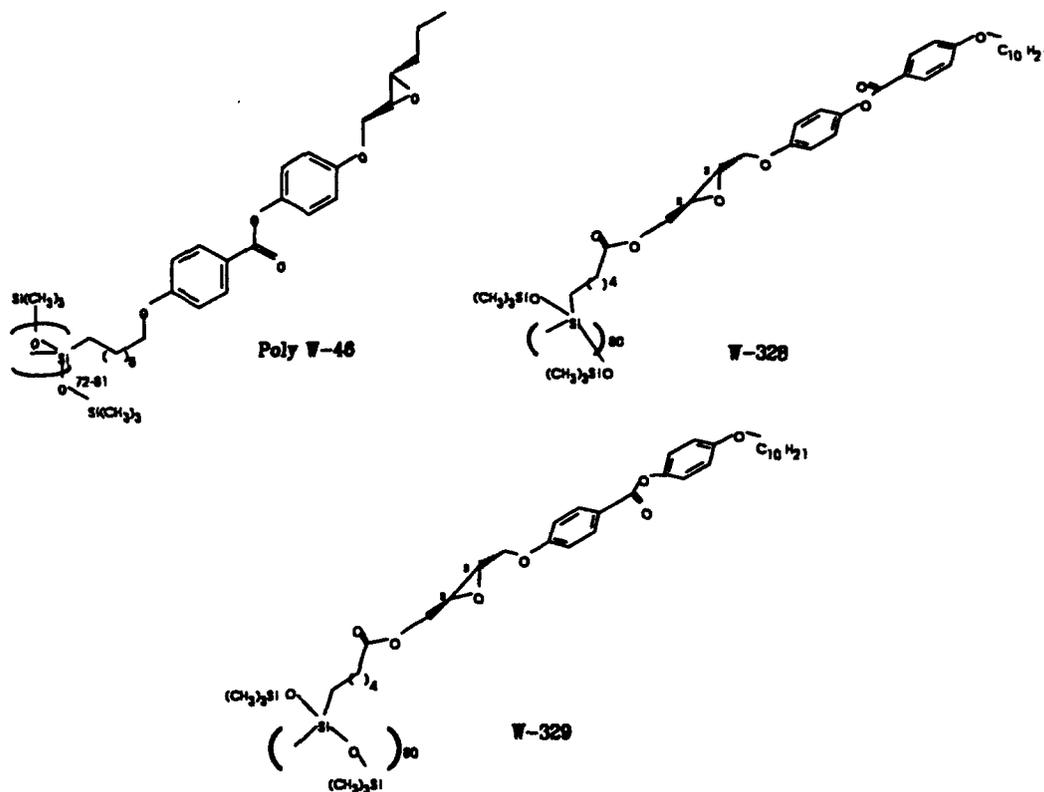
We attribute the r_{22} frequency dependence to residual nuclear motion electro-optic modulation in an imperfect aligned liquid crystal sample at 100 KHz, decreasing to a remnant purely electronic electro-optic modulation at MHz frequencies. Frequency dependence does not appear to be due to varying frequency response of the FLC test cell/amplifier combination. However, a redesign of r -coefficient test cell into traveling wave configuration will remove any unwanted frequency response and illuminate the source of the frequency dependence.

We attribute increases in r_{22} of W-399 over MX-5679 due to an increased polar orientation of the $D\pi A$ subgroup; spontaneous polarization magnitude P goes as C_{py} , while r_{22} goes as $(C_{py})^3$. A full analysis of the difference in r_{22} between MX-5679 and W-399 must include order parameter temperature dependence, because the relative increase in r_{22} depends on the initial value of the order parameter at a given temperature.

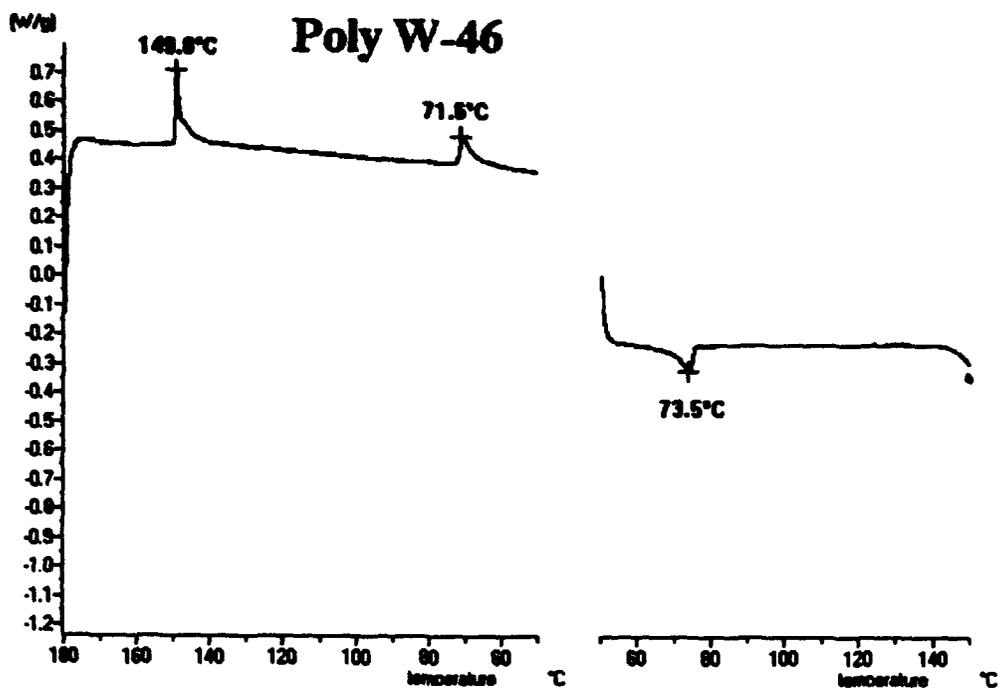
B. FLC POLYMERIC SYSTEMS WITH FLC-GLASS TRANSITION.

$\chi^{(2)}$ -enhanced FLCs are a promising nonlinear optical material; however, before we make commercially useful devices, we must mitigate temperature dependence and light loss. Light losses (due to thermal fluctuations), nonlinear susceptibility temperature dependence, high-frequency dielectric resonances, and possible liquid crystal alignment dependence on drive field all can be reduced or eliminated by "freezing" the liquid crystal directors into a quenched smectic C* state.

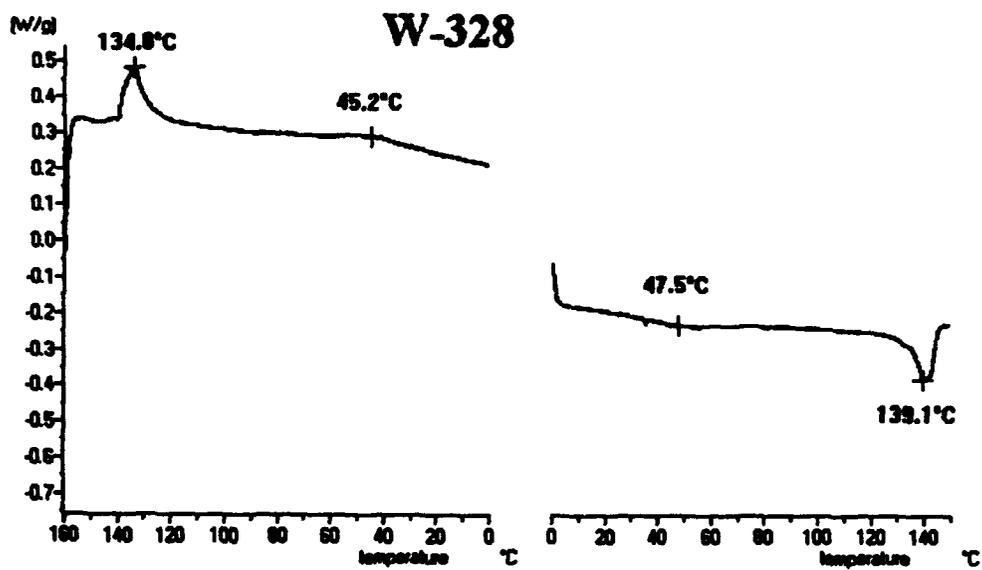
In Phase I, we examined polymerization as a potential quenching method. Using a differential scanning calorimeter (DSC), we made measurements on the following three compounds received from Walba at the University of Colorado.

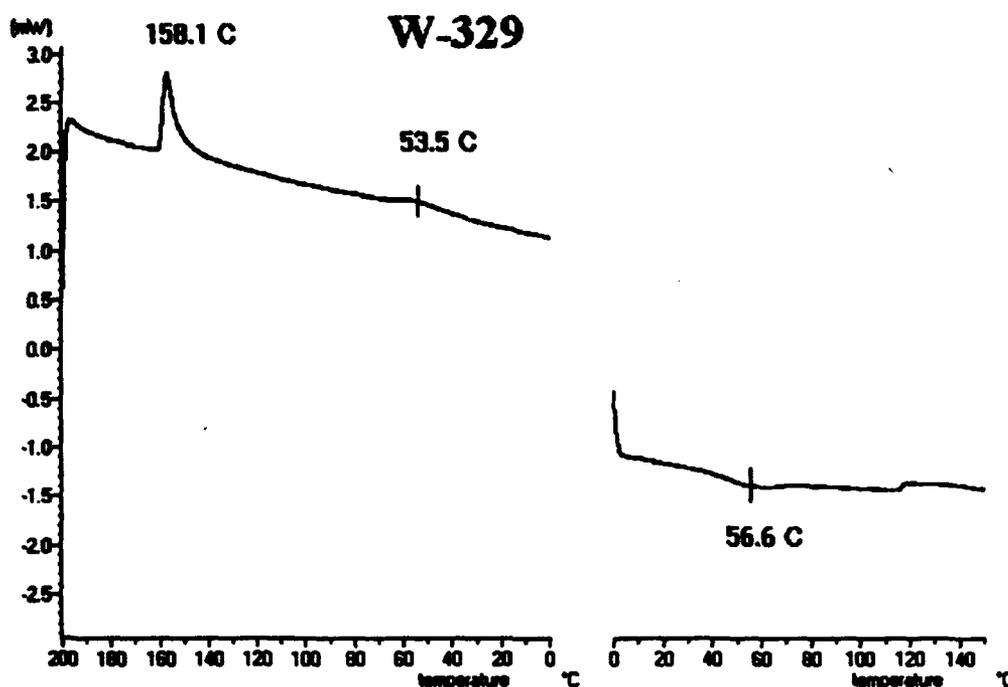


The first compound, W-46, was thought to have an FLC-to-glass phase transition above room temperature; using a rapid cool, the DSC showed a FLC-to-crystal phase transition near 70° (see DSC below).



The remaining two compounds, W-328 and W-329, did show the characteristic DSC signature of a glass phase transition near 50° (see DSCs below).





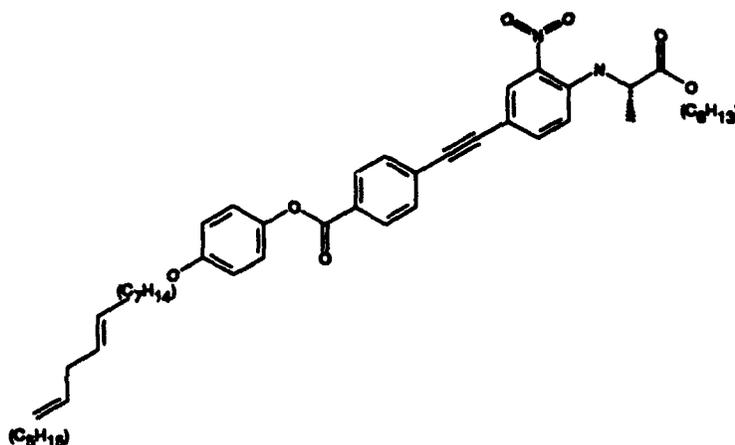
Unfortunately, these molecules have a small hyperpolarizability and are not suitable for nonlinear optical applications.

These results helped us identify a polymeric class of compounds that, for a limited class of FLC mesogens, will give an FLC-to-glass phase transition. In Phase II, we will synthesize $\chi^{(2)}$ -active mesogens into this polymeric system and create a temperature stabilized $\chi^{(2)}$ -enhanced FLC polymer.

C. $\chi^{(2)}$ -ENHANCED FERROELECTRIC LIQUID CRYSTAL SYNTHESIS.

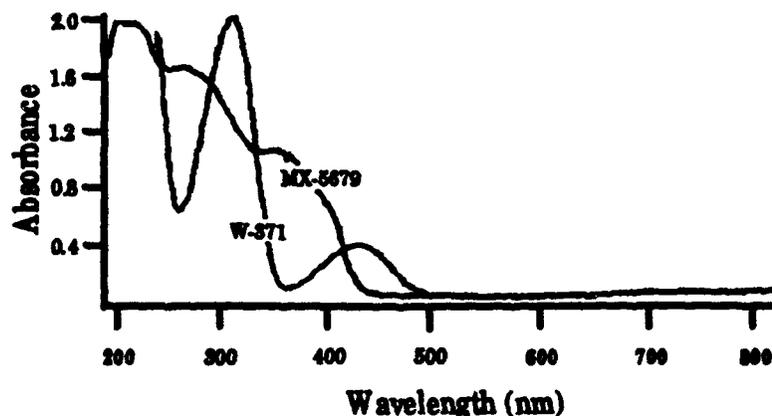
1. Ortho-nitroaniline $\chi^{(2)}$ -enhanced FLC.

In the past, all thermodynamically stable $\chi^{(2)}$ -enhanced FLCs contained only nitrobenzene electron donor-acceptor (D π A) subgroups. Recently, Jim Rego, a member of Walba's group at the University of Colorado, synthesized a new FLC compound containing an ortho-nitroaniline D π A subgroup. Labeled W-371, the idea behind this compound is to increase the overall FLC nonlinear susceptibility by incorporating a D π A group with a larger hyperpolarizability than nitrobenzene, and specifically increase $\chi^{(2)}_{23}$ by altering the local field factor. FLCs with tolane cores have higher extraordinary refractive indices.



Evaluation of this new FLC compound revealed a liquid crystal phase sequence: $I \Rightarrow 70^\circ \Rightarrow N \Rightarrow 69^\circ \Rightarrow \text{TGBA} \Rightarrow 47^\circ \Rightarrow C^*$, where TGBA is the "twisted grain boundary smectic A", a phase with the same local smectic layer ordering as the normal smectic A, but with the additional supermolecular structure of twists in the smectic layers on the order of tens of nanometers.⁶ This phase is highly light scattering and complicates both the uniform optical alignment of the smectic C^* phase and the subsequent electro-optic coefficient evaluation. Polarization measurements near the A- C^* phase transition indicate a moderate increase in spontaneous polarization, suggesting an increase in nonlinear susceptibility. Complete spontaneous polarization characterization in the C^* phase requires the use of a different measurement technique,⁷ as switching is virtually absent in the C^* phase due to high viscosity.

Below is a graph comparing the relative absorbency vs. wavelength between W-371 and MX-5679 in methanol. MX-5679 has a nitrobenzene D π A, while W-371 has an ortho-nitroaniline as a D π A; the redshift of the absorption resonance responsible for enhanced $\chi^{(2)}$ -nonlinear susceptibility is evident. W-371 should be an excellent candidate electro-optic material for modulating 633 nm.

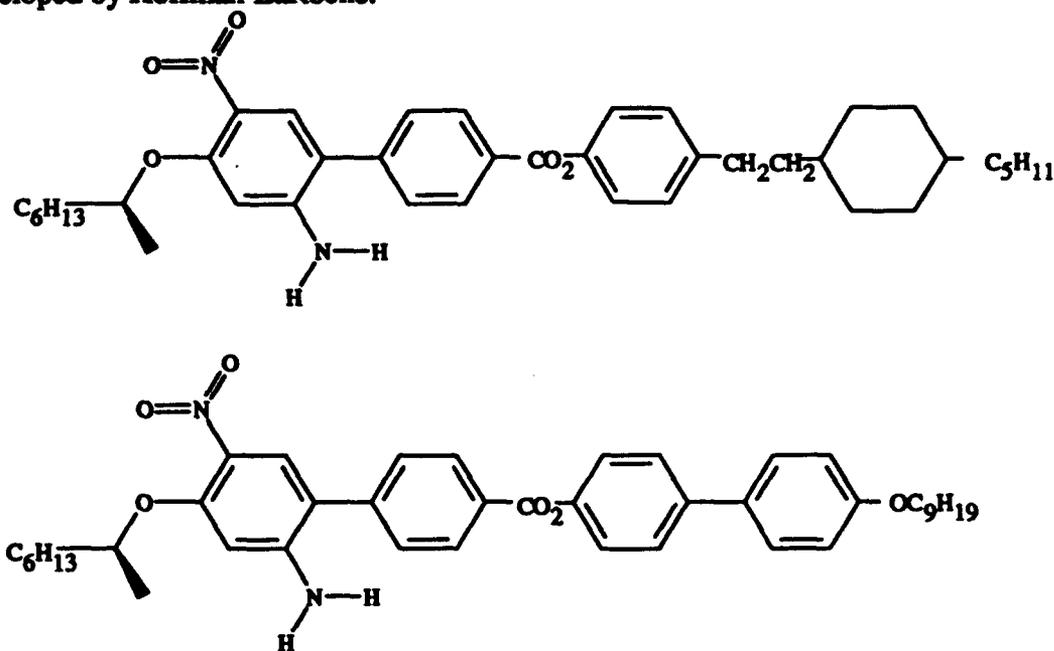


Since W-371 is our first attempt at altering the nonlinear susceptibility through the local field factors, we must continue our evaluation efforts on this reticent material.

On going W-371 alignment experiments that use a DC. electric field to unwind the TGBA helix have produced a uniform optical sample in the C* phase; however, using electric fields requires a slight redesign of the electro-optic evaluation cell and thus will not be pursued until Phase II.

2. $\chi^{(2)}$ - Ferroelectric Liquid Crystal Synthesis.

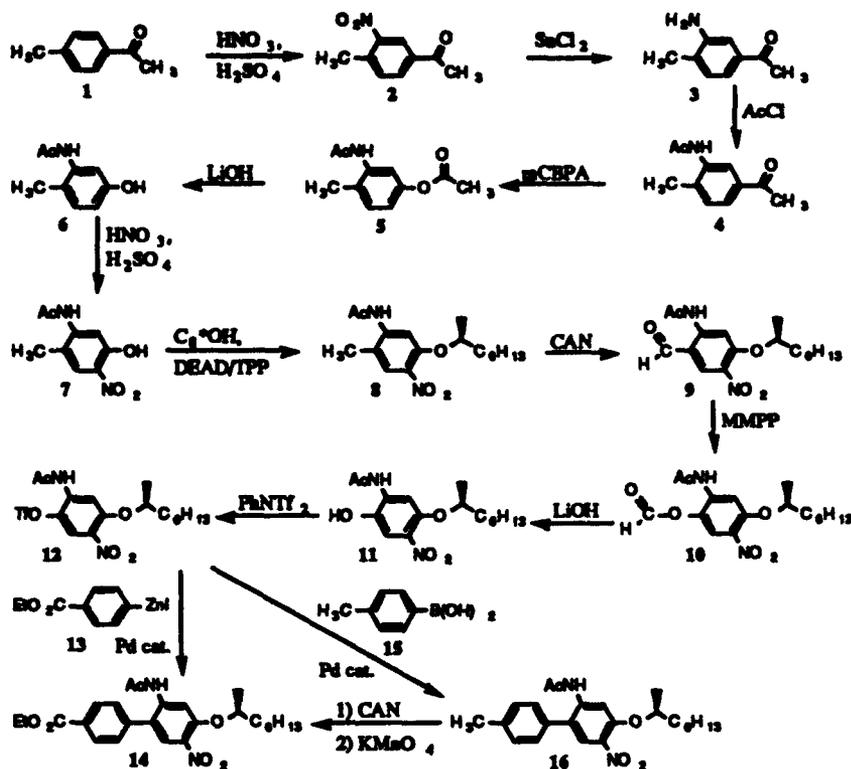
The original goal of the Phase I synthesis effort was to synthesize constituents of a liquid crystal mixture, roche 1 and roche 2, containing paranitroaniline D π A groups, developed by Hoffman-LaRoche.



Roche 1 (bottom) and Roche 2 (top).

Although these compounds do not exhibit a thermodynamically stable FLC phase, they are the first candidate FLC molecules that contain a para-disubstituted hyperpolarizable core.⁸

We envisioned synthesizing the Roche compounds using the reaction scheme outlined in Scheme 1 shown below.



Scheme 1. Attempted synthesis of Roche 1.

This particular route was chosen because much of it had already been done at the University of Colorado. Thus, methylacetophenone 1 was chosen as the starting material. This compound could be nitrated using nitric and sulfuric acids to give an 88% yield of product 2. The nitro group was reduced in 82% yield, using tin (II) chloride, to give amine 3. The amine was then mono-acetylated to give the amide 4. It was at this stage that we ran into our first problem. The reactions were monitored by TLC, and we expected the product to have a higher Rf than the starting material. When the product's Rf was significantly lower than the starting material, we interpreted the new spot as a degradation product. To further complicate matters, the diacetylated product co-elutes with the starting material, so it appeared that none of the desired reaction had occurred. We were eventually able to solve this problem, and realized a 74% yield from this reaction.

The next step in the reaction scheme was oxidation of the ketone to an acetate using metachloroperoxybenzoic acid (mCPBA). This reaction proceeded smoothly, giving 51% of the acetate 5. Hydrolysis of this acetate with lithium hydroxide gave 93% of the phenol 6. The phenol could then be nitrated using nitric acid and sulfuric acid, to give 32% yield of the nitrophenol 7. We later determined that the yield of this reaction could be improved to 41% by using nitronium tetrafluoroborate. The phenol could then be transformed into the chiral ether 8 using 2-octanol under Mitsunobu reaction conditions. A 70% yield was obtained in this last reaction.

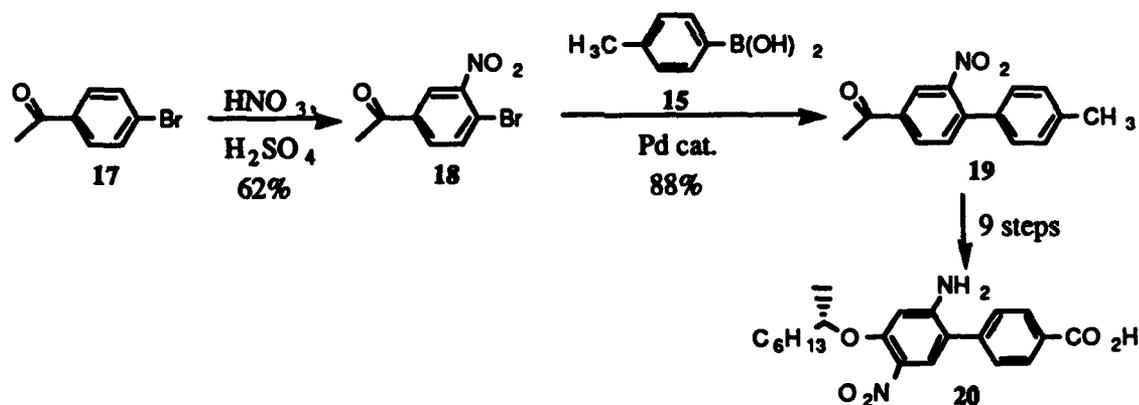
The methyl group was then oxidized to aldehyde 9, in 71% yield, using cerium ammonium nitrate (CAN). The aldehyde then underwent a Baeyer-Villiger oxidation to the formate under the influence of magnesium monophtalate. Under these reaction

conditions, the formate **10** was also hydrolyzed to give the phenol **11**, in an overall yield of 70%. The phenol was then treated with trifluoromethanesulfonic imidazole⁹ to give the key intermediate, triflate **12**.

Studies¹⁰ had shown that aryl triflates could be coupled with a variety of metaloaryl species. We had, earlier in the project, tried a coupling using zincate **13** and a model aryl triflate, but had gotten a disappointing 10% yield from the reaction. We believe that this was due to difficulty in making the zincate. An alternative route, where a boronic acid was used in place of a metaloaryl species, was also investigated with a model compound. Thus, a boronic acid much like tolueneboronic acid **15** was treated with the model aryl triflate and a palladium catalyst, giving a reasonable 52% yield of a diaryl product. Although this route would not directly give the carboxylate **14**, we were confident that the methyl group could be oxidized to an aldehyde using CAN, and further oxidized to an acid using potassium permanganate.

With the triflate **12** and tolueneboronic acid **15** in hand, the coupling reaction was attempted. Unfortunately, no product resulted from this reaction. We believe that this failure was due to steric hindrance caused by the amide, but were unable to hydrolyze the amide off of compound **12**. Hydrolysis of the imide at an earlier step prevented the final triflation. Thus, we were stranded just a few steps short of our goal.

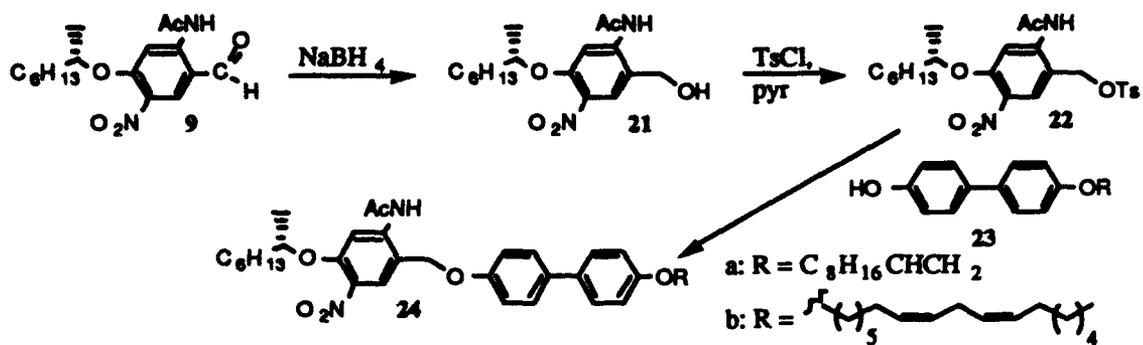
Later work has shown that an alternative route, where the two aryl compounds are coupled early in the synthesis, shows great promise. Unfortunately, time did not allow further exploration of this route. This synthesis route is outlined in Scheme 2.



Scheme 2.

The starting material for the new route to Roche 1 is bromoacetophenone **17**. This material can be nitrated using a combination of nitric and sulfuric acids to give the nitrated compound **18** in 62% yield. This compound can then be coupled to tolueneboronic acid **15** to give the diaryl compound **19** in 88% yield. Further elaboration of this compound into carboxylic acid **20** should be relatively straightforward, using reactions equivalent to those used in the original synthesis.

Since the attempted synthesis of Roche 1 was unsuccessful, we decided to try to salvage the synthesis by making other nitroanilines which would have a reasonable chance of having high NLO activity. These compounds are shown in Scheme 3.



Scheme 3. The synthesis of some nitroaniline ethers.

The aldehyde **9** could be easily reduced to give the methylenehydroxy compound **21**. After tosylation to give the tosylate **22**, this compound could be coupled with either of two phenols to give ethers **24a** and **24b**. Unfortunately, neither of these compounds had smectic C phases.

IV. Conclusions and Recommendations for Future Research

Phase II evaluation method refinements include adapting the FLC cell into a traveling RF wave configuration that will allow modulation frequencies up to 1 GHz. With better liquid crystal alignment and by mounting the RF test cell on a rotating stage, we can also measure the r_{23} and r_{21} electro-optic coefficients. Temperature control will allow a full temperature-dependent characterization of $\chi^{(2)}$ -FLC monomers for validation of order-dependent nonlinear susceptibility model. Finally, development of a polarization-stabilized He-Ne laser at 1.15 μm will allow r -coefficient measurements at light wavelengths closer to actual commercial use.

Phase II $\chi^{(2)}$ -FLC materials synthesis should concentrate on increasing hyperpolarizability of FLC molecules and their integration into temperature stabilizing polymers. The W-399 hyperpolarizable core could be integrated into the poly(siloxane) polymer identified as producing FLC-to-glass phase transition. The only $\chi^{(2)}$ -enhanced molecule containing a disubstituted core that produces a thermodynamically stable FLC phase is W-371. Future $\chi^{(2)}$ -enhanced molecular design must fully utilize para-disubstituted benzene system like roche 1 and 2.

Finally, since the FLC $\chi^{(2)}$ -nonlinear susceptibilities are considered modest, strong $\chi^{(2)}$ -nonlinear interactions requires an interaction volume with a large length² to cross-sectional area ratio. This requirement is met if we fabricate an optical fiber with a micron sized $\chi^{(2)}$ -enhanced FLC polymer core.

V. References

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