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Investigation of Marine Derived DNA for use as a Cladding Layer in Electro-Optic Devices

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ABSTRACT

Deoxyribonucleic Acid (DNA) extracted and purified from salmon sperm was investigated for use in electro-optic devices as a cladding layer. This DNA material is derived from the waste product from salmon fisheries, thus it is a completely ‘green’ material. The experiments were conducted in two phases; material characterization and device characterization. Both of these phases conclude that this biologically-derived material is suitable for use in electro-optic waveguiding devices.

The marine based DNA has the material properties that make it a good candidate for use in the field of optoelectronics. The material has a refractive index less than that of common core materials such as poly(methyl)methacrylate and amorphous polycarbonates, which promotes waveguiding due to total internal reflection in the core material. Poling efficiency in these devices is directly related to the amount of voltage dropped across the core layer, thus, it is advantageous for the cladding material to have a lower resistivity and proper dielectric constant compared to the core material. The DNA shows a resistivity two orders of magnitude lower than common core materials. The poling process takes place at elevated temperatures, and the material shows no signs of degradation within 100°C of the poling temperatures. Device manufacturing requires certain solubility characteristics. The material must be resistant to common core material solvents for compatibility. Originally, the purified DNA was only water soluble, but it was modified through an ion exchange reaction with the cationic surfactant hexadecyltrimethylammonium chloride (CTMA). This modification makes the CTMA-DNA water insoluble, and soluble in many alcohol based solvents. Of these solvents, butanol produced the highest quality films through spin coating. The solution for device manufacturing was prepared as 5% (wt) DNA in 95% (wt) butanol.

The goal of novel materials in electro-optics requires them to not only have the suitable properties, but they must also perform well in the devices. The prime optical property in waveguiding is the complete transmission at guiding wavelengths. The DNA does not absorb an appreciable amount of light at a range of 300-1700nm. For a more precise approach of judging the material’s performance in electro-optic devices, a number of
experiments were conducted. DNA was analyzed as a cladding material for two different chromophore systems, Disperse Red 1 (DR1), and Cheng-Larry Dalton 1 (CLD1) in a PMMA guest/host system. A baseline device, comprised only of a 1.7µm layer of PMMA, was tested for non-linearity with each chromophore. The Teng and Man method was used, and the electro-optic coefficient, $r_{33}$, was found. Poling voltage and temperature were varied in order to monitor device behavior. Each chromophore baseline device showed the expected dependence on poling voltage and temperature. The $r_{33}$ value increased with increasing temperature and voltage. The second batch of devices included a 1µm thick DNA film as the cladding layer, directly on top of the substrate, with the core layer above. The same set of non-linearity experiments were performed for these devices, and were found to show the same dependence on poling voltage and temperature. Based on the dielectric properties of DNA, values of $r_{33}$ were calculated for the theoretical behavior of the devices. The recorded $r_{33}$ values were accurate within 5% of the calculated values with the DR1 chromophore, and within 20% with the CLD1 chromophore, hence showing good device reproducibility. The devices with DNA as the cladding layer also proved to be a more stable configuration, with no observed device short outs, as compared to numerous shorts in the baseline devices.

It is therefore concluded that marine based DNA material shows great promise for the electro-optics industry based upon these results.
I would like to thank my advisors, Dr. Stephen J. Clarson and Dr. James Grote for their guidance and advice throughout this research. This is a very exciting field, and I am privileged to be a part of it now and in the future. I would also like to thank my thesis committee, Dr. Jude Iroh, Dr. Michael Durstock, and Dr. Rodney Roseman.

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1.0 INTRODUCTION

1.1 BACKGROUND

The fields of electro-optic devices and non-linear optics have become a major area of development for many technologies. Some of these technologies include broadband telecommunications, optical storage, optical communication, and computing systems [1]. Current electronic devices for telecommunications and computing are limited in terms of bandwidth, speed, and power. Optics have stepped in to meet some of these needs through fiber optic technology. The missing link in the technologies lies in optical storage and optical switching.

Lasers provide many benefits in these technologies with their ability for high frequency response, high signal density, and excellent coherence [2]. These highly tuned lasers need a range of devices for incorporation into integrated electro-optic circuits. This is done through electro-optic devices. Electro-optic devices can utilize a number of principles to allow the device materials to undergo refractive index changes upon the application of an electric field. Among these principles lies non-linear optics.

Electro-optics provides an advantage as opposed to purely electronic or optic communications. Electro-optics combines the information carriers of electrons, as in electronics, and photons, as in optics. The interaction of electrons with photons is the basis for electro-optic and non-linear optic effects.
Novel materials are constantly being researched for use in electro-optic devices. In the research described in this thesis, marine based deoxyribonucleic acid (DNA) was investigated. The DNA is extracted from the waste product from salmon fisheries, and is therefore an inexpensive and environmentally friendly material.

1.2 NON-LINEAR OPTICS

The demonstration of the first laser in 1960 introduced the scientific community to the field of non-linear optics. Light, as it interacts with a material, has both a linear and a non-linear component. At low intensities, the non-linear component is small, and generally unnoticeable. However, with the advent of lasers, the intensity of the light increased dramatically, and the non-linear component became stronger and more noticeable [3]. Optical non-linearity is demonstrated when the material responds to the strength of an applied optical field in a non-linear manner.

As a beam of light interacts with a linear material, it causes the charges of the atoms in the material to oscillate at the frequency of the incident light. These charges either radiate light in the sample, or add heat to the material by radiation. Both refractive index and absorption are linear properties of these materials at low light intensities.

As shown by Mayer and Gires [4], the high intensity of laser light can cause a change in refractive index and electric permittivity. This proved that certain materials can show non-linearity with an increase in the light intensity. This effect is now commonly known as the Kerr effect.
Linear and non-linear optical effects can be explained mathematically by the relationship between the dipole moment per unit volume, or polarization, and the optical field. In general, polymer-based materials are electrically insulating with tightly bound electrons. The application of an external field in polymers will induce a dipole moment in the molecules. The bulk polarization is described by the following equation:

\[
P = -N \epsilon r
\]  

Where:  
\( P \) = polarization  
\( N \) = electron density  
\( \epsilon \) = electron charge  
\( r \) = displacement induced by external field

The induced polarization that opposes the external field lowers the internal field in the material. For low optical intensity, the polarization behaves linearly with the applied field as shown in equation (2) below [5]:

\[
P(t) = \chi^{(1)} E(t)
\]  

Where:  
\( P(t) \) = polarization  
\( \chi^{(1)} \) = linear susceptibility  
\( E(t) \) = applied optical field
This equation only applies to linear effects. In non-linear optics, the relationship is described as a power series of equation (3) [5]:

\[ P(t) = \chi^{(1)} E(t) + \chi^{(2)} E^{(2)}(t) + \chi^{(3)} E^{(3)} ... \]  

(3)

Where: \( \chi^{(2)} = \) second order non-linear susceptibility  
\( \chi^{(3)} = \) third order non-linear susceptibility

1.2.1 SECOND AND THIRD HARMONICS

The generation of the second harmonic in non-linear optics is shown in Figure 1.1. At high optical intensities, two photons of frequency \( \omega \) can be destroyed, and a single photon of frequency \( 2\omega \) can be created.

The third harmonic generation occurs in a similar fashion and is shown in Figure 1.2 [5]. Here, three photons of frequency \( \omega \) are destroyed, and a single photon of frequency \( 3\omega \) is created.

1.2.2 ELECTRO-OPTIC EFFECT

The electro-optic effect occurs when a material’s index of refraction varies with the application of an external electrical field. It is the second order non-linear susceptibility from equation (3) that is responsible for this phenomenon. Materials whose refractive
Figure 1.1. Schematic of second harmonic generation

Figure 1.2. Schematic of third harmonic generation
indices change linearly with the applied electric field undergo what is referred to as the Pockels effect. The non-linear polarization of the Pockels effect is described as follows:

\[ P_i(\omega) = 2 \sum_{jk} \chi^{(2)}_{ijk}(\omega = \omega + 0)E_j(\omega)E_k(0) \]  

(4)

Where: \( E(\omega) = \) optical field

\( E(0) = \) electrical field

Through a mathematical model using an index ellipsoid [5], the Pockels effect is described in terms of refractive index through the general expression below:

\[
\left(\frac{1}{n_x^2}\right)_1 x^2 + \left(\frac{1}{n_y^2}\right)_2 y^2 + \left(\frac{1}{n_z^2}\right)_3 z^2 + 2\left(\frac{1}{n_n^2}\right)_4 yz + 2\left(\frac{1}{n_n^2}\right)_5 xz + 2\left(\frac{1}{n_n^2}\right)_6 xy = 1
\]  

(5)

Substituting the Cartesian coordinates of \( x, y, \) and \( z \) yields the relations [5]:

\[
\left(\frac{1}{n^2}\right)_1 = \left(\frac{1}{n_x^2}\right)_x
\]  

(6)

\[
\left(\frac{1}{n^2}\right)_2 = \left(\frac{1}{n_y^2}\right)_y
\]  

(7)

\[
\left(\frac{1}{n^2}\right)_3 = \left(\frac{1}{n_z^2}\right)_z
\]  

(8)
Upon application of the electric field, the change in refractive index is generally stated as:

\[
\Delta \left( \frac{1}{n^2} \right)_i = \sum_j r_{ij} E_j \quad (9)
\]

Where: \( r_{ij} \) = rate at which the term \( 1/n^2 \) changes with increasing electric field

Expanding this expression out to matrix form yields:

\[
\begin{bmatrix}
\Delta \left( \frac{1}{n^2} \right)_1 \\
\Delta \left( \frac{1}{n^2} \right)_2 \\
\Delta \left( \frac{1}{n^2} \right)_3 \\
\Delta \left( \frac{1}{n^2} \right)_4 \\
\Delta \left( \frac{1}{n^2} \right)_5 \\
\Delta \left( \frac{1}{n^2} \right)_6 \\
\end{bmatrix} =
\begin{bmatrix}
r_{11} & r_{12} & r_{13} \\
 r_{21} & r_{22} & r_{23} \\
 r_{31} & r_{32} & r_{33} \\
 r_{41} & r_{42} & r_{43} \\
 r_{51} & r_{52} & r_{53} \\
 r_{61} & r_{62} & r_{63} \\
\end{bmatrix}
\begin{bmatrix}
E_x \\
E_y \\
E_z \\
\end{bmatrix} \quad (10)
\]

Rotational symmetry makes a number of the \( r_{ij} \) tensors become zero. For a guest/host uniaxial polymer system, the matrix is simplified to the following:
\[
\begin{bmatrix}
0 & 0 & r_{13} \\
0 & 0 & r_{23} \\
0 & 0 & r_{33} \\
0 & r_{42} & 0 \\
r_{51} & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}
\]

(11)

Therefore,

\[
\Delta \left( \frac{1}{n^2} \right)_1 = r_{13} E_3
\]

(12)

\[
\Delta \left( \frac{1}{n^2} \right)_{31} = r_{33} E_3
\]

(13)

For this reason, the system involved in this set of experiments focuses solely on the \( r_{13} \) and \( r_{33} \) values. Derivation of a usable experimental value of \( r_{33} \) can be found in Section 2.2.1.

1.3 MOLECULAR CHARACTERISTICS

1.3.1 POLARIZABILITY

The nonlinear response of a material to an electric field, either optically or electrically induced, is a result of molecular polarization. This polarization, \( p \), is induced by the electric field, \( E \), as described by equation (4) below [2]:

\[
\Delta \left( \frac{1}{n^2} \right)_1 = r_{13} E_3
\]
\[ p_i = \mu_{g,i} + \varepsilon_0 \left( \alpha_{ij}^{(1)} E_j + \beta_{ijk}^{(2)} E_j E_k + \gamma_{ijkl}^{(3)} E_j E_k E_l + \ldots \right) \]  \hspace{1cm} (4)

Where:

\( \mu_{g,i} \) = ground state dipole moment

\( \alpha_{ij} \) = polarizability tensor

\( \beta_{ijk} \) = second order polarizability tensor

\( \gamma_{ijkl} \) = second order hyperpolarizability tensor

1.3.2 BONDING

The driving force of the nonlinearity of a molecule is electronic asymmetry. The polarizability of a molecule is dependent on the types of bonding and types of end groups. Covalent bonds such as those between carbon atoms are very stable due to the localization of the electron charge density. However, \( \pi \) bonds are more delocalized, and have electrons that are much more mobile than those in covalent bonds. This enables electronic asymmetry upon the application of an electric field, creating a dipole moment for the molecule. Another route to an inherent dipole moment is through end groups. Substituting an electron donor on one end of the molecule, and an electron acceptor on the other end of a \( \pi \) bonded system creates a polarizable molecule. When the electric field is applied in this system, charge flows toward the electron acceptor end group, causing an asymmetric response to the field, and thus nonlinearity. Davydov et. al discovered this property and the second harmonic generation from a benzene ring with a donor and acceptor on either end in 1970 [19].
These organic polymers with \( \pi \)-conjugated bonds exhibit the fast response times necessary for optical switching in the range of picoseconds. Figure 1.3 [5] shows both the linear and non-linear response of a \( \pi \)-conjugated bonded molecule to an applied electric field.

1.4 ELECTRO-OPTIC POLYMER SYSTEMS

Research has focused on the development of electro-optic polymers over the last two decades [1]. Thus far, a suitable polymer has not been developed for this application. The core polymer must have the proper thermal and optical properties for incorporation into a device. The current focus is on the development of non-linear optical chromophores. These materials are non-centrosymmetric molecules with high dipole moments. The chromophore must be resistant to rotation once it is aligned, meaning it must be fairly resistant to thermal, optical, and humidity fluctuations. Along with these characteristics, the chromophore must also be optically transparent at telecommunications wavelengths [22, 23]. However, the advantage to this method is that the researcher is flexible to which polymer they choose for the core layer. The chromophore can either be dispersed (guest/host system) or chemically attached to the core polymer, thus giving it the non-linear optical properties.

Chromophore design not only involves the need for a high dipole moment, but they must also translate into a high electro-optic coefficient. Electrostatic interactions and molecule
Figure 1.3. Linear and Nonlinear response of conjugated molecules to an electric field
de-alignment can hinder the electro-optic effect. Chromophore development has focused on molecule conformations such as dendrimers [1, 6-7] and liquid crystals [8].

1.4.1 POLY(METHYL)METHACRYLATE – CORE

Poly(methyl)methacrylate is a common polymer for use in optics [9-12]. The advantages for using PMMA are high optical transparency, relatively low glass transition temperature ($T_g$), high resistivity, and low optical loss. These physical values can be found in the Section 3.1. The structure of PMMA is shown in the Figure 1.4.

1.4.2 CHROMOPHORE – DISPERSE RED 1

A common chromophore used in polymer based non-linear optics is Disperse Red 1 (DR1) [13-16, 36]. The PMMA/DR1 system is very common in non-linear optics, and is a consistent reference point for experimentation [17, 18]. DR1 has a backbone which is stabilized by the $\pi$-conjugated system of two benzene rings and a nitrogen/nitrogen double bond. The donor and acceptor end groups are the $-\text{N}_2\text{O}$ and $-\text{OH}$ groups. The structure of DR1 can be seen in Figure 1.5 [20].

The molecular formula for DR1 is $C_{16}H_{18}N_4O_3$, and the chemical name is N-Ethyl-N-(2-hydroxyethyl)-4-(4-nitrophenylazo)aniline. The molecular weight is 314 g/mol, it melts at 160-162°C, and has an absorbance at 502nm.
Figure 1.4. Structure of Poly(methyl)methacrylate
Figure 1.5. Chemical structure of Disperse Red 1
1.4.3 CHROMOPHORE – CHENG-LARRY DALTON 1

With the concept of a donor – \( \pi \) conjugated molecule – acceptor structure for non-linear optic molecules firmly in place, many researchers have begun development of novel chromophore materials. Among these researchers are Cheng Zhang and Larry R. Dalton at the University of Southern California. They developed a chromophore which was aptly named Cheng-Larry Dalton 1, or CLD-1 [21]. CLD-1 is a phenyltetraene based chromophore with a molecular nonlinearity of \( 14065 \times 10^{-48} \) esu at 1.9\( \mu \)m. The structure of the molecule is in Figure 1.6, with 85% trans and 15% cis conformations [21].

The CLD-1 molecule exhibits a large first hyperpolarizability and large dipole moment, but it also has another very important characteristic. The molecule has very bulky tert-butylidimethylsilyl (TBDMS) groups on one of the ends to help eliminate the strong interchromophore interactions which can lead to insolubility. The bulky nature of the CLD-1 molecule also helps the thermal aggregation of the poled guest-host system.

1.4.4 POLING

Now that the theory of nonlinear optical effects has been discussed, and the organic molecular characteristics identified, the overall system can be defined. There are two common ways of incorporating the NLO chromophore into an organic electro-optic devices. The first is by chemically attaching the chromophore molecule to the host polymer [38-41]. Michelotti et. al did this by synthesizing a DR-1 and PMMA side-chain co-polymer [13]. The second common method is dispersing the chromophore in the polymer.
Figure 1.6. Structure of Cheng-Larry Dalton-1
host. The chromophore is simply dissolved into the polymer solution. A schematic of the chromophore molecules dispersed in the polymer matrix is shown in Figure 1.7.

After the guest (NLO chromophore) host (PMMA) system has been created and cast onto a substrate, it still has no macroscopic first hyperpolarizability (second order non-linearity) component. In order to achieve this, the non-centrosymmetric chromophore molecules must be aligned making the overall material anisotropic. This is achieved by heating the guest-host system close to the host’s glass transition temperature and applying a strong electric field. This aligns the permanent dipole moment of the chromophore molecules in the direction of the field, thus giving the material anisotropy (Figure 1.8). Once the alignment is complete, the guest-host system is cooled down below the glass transition temperature with the electric field still applied. As the host polymer cools, the mobility of both the host and the guest decreases to the point where the molecules are again ‘frozen’ into place.

With a poled guest-host system, the electro-optic (EO) coefficient becomes non-zero. Again, electro-optics are the ability of a material to undergo a refractive index change with the application of an electric field. The Pockels effect described in Section 1.2.2 showed for a polymer guest-host system, the EO coefficients $r_{13}$ and $r_{33}$ describe the NLO activity of a material. The refractive index is uniaxial with the long axis parallel to the poling direction ($n_e$, direction 3), and with the short axis perpendicular to the poling direction ($n_o$, directions 1 and 2). When a modulating voltage is applied, $E_{mod}$, the EO coefficients can be described by the following relations [24]:

\[ 21 \]
Figure 1.7. Schematic of randomly dispersed chromophore in a polymer matrix

Figure 1.8. Schematic of aligned chromophore molecules in a polymer matrix with applied voltage
\[
\delta n_e = -\frac{1}{2} n_e^3 r_{33} E_{\text{mod}} = \frac{1}{n_e} \chi_{333}^2 E_{\text{mod}} = \frac{1}{n_e} NF \beta \left( \cos^3 \theta \right) E_{\text{mod}} \quad (5)
\]

\[
\delta n_o = -\frac{1}{2} n_o^3 r_{13} E_{\text{mod}} = \frac{1}{n_o} \chi_{113}^2 E_{\text{mod}} = \frac{1}{n_o} NF \beta \left( \frac{1}{2} \cos \theta \sin^2 \theta \right) E_{\text{mod}} \quad (6)
\]

Where:

- \( N \) = number density of hyperpolarizable groups
- \( F \) = factor for local field effects
- \( \theta \) = angle between the permanent dipole moment and the poling field

For typical values of \( \theta \), the term of \( \left( \cos^3 \theta \right) \) is much greater than \( \left( \frac{1}{2} \cos \theta \sin^2 \theta \right) \). For this reason, the EO coefficient \( r_{33} \) becomes the dominant factor in evaluating the NLO properties of an EO material [24].

### 1.4.5 APPLYING ELECTRO-OPTICS

Equation (5) shows how the EO coefficient effects the refractive index of a NLO material. The speed of light traveling through a material depends on the interaction of the electric field component of the light with the electric components of the material. Because of the first order hyperpolarizability nature of NLO materials, the electric charges within the material change upon application of an external electric field. Through tuning of the system and device structure, the speed of light in the material can
be controlled by an external electric field. The phase shift for plane polarized light due to
the field is shown in equation (7) below [25]:

\[
\Delta \phi = \frac{n^3 r_{33}VL}{\lambda}
\]  

(7)

Where: \( \Delta \phi \) = phase shift of light
\( V \) = external electric field
\( L \) = length of the material
\( \lambda \) = wavelength of light

Of particular interest is the external field required to change the light wave by 180°, or \( \pi \).
This value is commonly known as \( V_{\pi} \), and is shown in equation (8) below [25]:

\[
V_{\pi} = \frac{\lambda h}{n^3 rL}
\]  

(8)

Where: \( h \) = spacing between electrodes

1.5 ELECTRO-OPTIC DEVICES

1.5.1 WAVEGUIDE DESIGN

The geometry for many of the electro-optic devices in use is a planar waveguide [26].
This allows for very thin layers of material to be deposited on a single, planar substrate.
The layer where the light is confined in the waveguide is known as the core. This is the layer that will house the guest-host polymer system described in section 1.4.4. A schematic of a simple waveguide device is shown in Figure 1.9.

Cladding layers are used primarily in waveguides to confine the light to the core. This is achieved by the differences between the refractive indices of the layers.

The light will be confined to the core as long as the following relationship is maintained:

\[
 n_1 > n_2 \geq n_3
\]  

(8)

With the proper selection of materials for the waveguide, total internal reflection can be achieved within the core. A schematic showing the light travel through the waveguide is shown in Figure 1.10.

Selection of materials for each layer is very important when designing a waveguide EO device. The cladding and core layers must have the proper refractive index shown in equation (8). Each layer must be able to withstand the operating temperature of the device without any degradation or weight loss. The layers must also be optically transparent at the modulating wavelength. Any losses due to scattering or absorption within the layers will reduce the output intensity. Since total internal reflection is not likely in a planar waveguide, the cladding layers also contribute to optical losses.
Figure 1.9. Schematic of a planar waveguide
Figure 1.10. Schematic of total internal reflection in a waveguide
The evanescent tail of the light travels through the cladding layers, while the rest of the light wave is confined to the core.

1.5.2 SIMPLE DEVICE STRUCTURES

Combining the planar waveguide and electro-optic materials allows for the design of a wide array of devices. One of the most common device structures is the Mach Zehnder modulator shown in Figure 1.11 [27]:

In Steier’s device, PU-FTC is the guest-host system, while NOA73 and Epoxylite are the cladding layers. Light enters the device at intensity \(I_{in}\) and travels to the ‘Y’ junction. At this junction, the light splits evenly to both arms and recombines at the end ‘Y’ junction at intensity \(I_{out}\). One of the arms of the device has an electrode where an external electric field can be applied. The light in the Mach Zehnder device is related by the following equation [27, 28]:

\[
I_{out} = I_{in} \sin \left( \frac{\phi_{ba} + \Delta \phi}{2} \right) \tag{9}
\]

Where: \(\phi_{ba}\) = phase difference between the arm without the electric field and \(\Delta \phi\)

\(\Delta \phi\) = defined in equation (7)

If no electric field is applied, then the light will recombine completely at the end of the device where \(I_{in} = I_{out}\). When an electric field with a value of \(V_{\pi}\) is applied, as defined in
Figure 1.11. Schematic of a Mach Zehnder modulator
equation (8), then the phase of the light in each arm will be off by 180°. This causes the light to add destructively at the second Y junction, and \( I_{\text{out}} = 0 \).

A second common device in electro-optics is a directional coupler which acts as an optical router. The coupler is shown in Figure 1.12 [28]. In the directional coupler, two guided waves are separated by a few microns. The proximity creates an interaction between the two waves and couples the energy back and forth between the guides. Application of a low frequency voltage will control this interaction and direct the light to either of the output ports \( I_1 \) or \( I_2 \), depending on the field.

1.6 CLADDING LAYER – DNA

Research by Naoya Ogata of the Chitose Institute of Science and Technology (CIST) introduced marine based DNA to the field of optical materials [31,32]. In Hokkaido Japan, over 200,000 tons of salmon is fished per year. Of that, over 15,000 tons of the processes salmon is considered waste product. Through the process detailed below, DNA can be extracted and purified from the sperm in the waste product for use as an optical material.

Frozen salmon sperm is first homogenized for ease of extraction. It is then fed into a reactor where the proteins are degraded through enzymatic treatment by protease. The proteins are then eliminated from the material by maintaining a pH of 7.5 for a period of time. The reactor is pictured in Figure 1.13a.
Figure 1.12. Schematic of an EO directional coupler
The resulting material contains purified DNA. In order for a material to present good optical properties along a wide range of wavelengths, colorization must be controlled. Thus, this material must undergo decolorization through carbon treatment. This is done in the equipment in Figure 1.13b:

The final step in the extraction process of the marine DNA is precipitation of the decolorized mixture with ethanol, and final filtration. The resulting product is purified salmon DNA seen in Figure 1.14.

One of the necessary properties of optical materials is good processability and compatibility. Processability includes properties such as hydrophobicity, wettability, vapor pressure etc. Compatibility deals mostly with solubility in organic solvents, and is very important in multi-film processing. The cladding layer is the first layer deposited on the substrate. If the second layer is spin coated onto the cladding layer, then the cladding must be resistant to the solvent of the second layer.

The purified DNA$^{-}\text{Na}^+$ is soluble only in water and very acidic organic compounds [33]. Water is a very poor solvent for spin coating, so modification of the DNA was necessary. Through an ion-exchange reaction with the cationic surfactant hexadecyltrimethyl-ammonium chloride (CTMA$^+\text{Cl}^-$), the DNA becomes water insoluble, and soluble in alcohol based organic solvents such as butanol and ethanol. Ogata diagrams the reaction as shown in Figure 1.15.
Figure 1.15. Diagram of DNA-CTMA ion exchange reaction
Figure 1.13a. Picture of DNA Reactor

Figure 1.13b. Picture of Decolorization and Filtering Equipment
Figure 1.14. Picture of Extracted and Purified Salmon DNA
The large CTMA molecules that are now attached to the DNA provides greater molecular stability. The modifications of the DNA make the molecule more stable and more compatible for multi-layered device manufacturing [33].

2.0 EXPERIMENTAL

2.1 DEVICE DESIGN

The goal of the research was to investigate the use of a novel cladding layer in an electro-optic device. In order to do this, a simple device structure was needed that is easily processable, can be consistently manufactured, and is economical from a time and monetary state. As stated in section 1.5.1, the planar waveguide is the most common geometry for electro-optic devices. This is the geometry used for these experiments.

For the EO coefficient measurements using the Teng and Man method (see section 2.2.1), it is necessary to have a transparent substrate bottom electrode. For this application, a 2”x1” glass substrate was used with low resistivity indium tin oxide (ITO) as the bottom electrode. Directly above the ITO electrode would lie the first polymer film. In order to test the efficacy of the cladding layer, both a baseline device and the test device structure were needed. The baseline consisted of only one polymer film, which was the guest-host layer. The test structure would include the cladding layer directly above the ITO electrode, with the guest-host layer above the cladding layer. The top layer of the device is a gold electrode. A cross section of the baseline device is shown in figure 2.1a, and the test device in figure 2.1b.
Figure 2.1. Schematic of device design a) baseline, b) ‘doublestack’
The layering of the device is straightforward, but the electrode patterning can be customized a number of different ways. One of the frustrations with laboratory scale EO device manufacturing is repeatability. A common occurrence as simple as an air bubble entrained in a polymer film can cause a short circuit in the entire device. This creates the need for multiple poling sites on a single device. With this in mind, an electrode pattern was developed and is shown in Figure 2.2. In this pattern, there are 10 potential spots on the device for poling. This greatly increases the percentage of usable devices. Using aluminum foil and insulating tape (scotch), any one of the potential poling areas can be connected to the proper voltage source.

2.1.1 DEVICE PROCESSING

The manufacturing of the EO devices begins with the substrate. For this work, glass substrates with low-resistivity ITO were provided by Wright Patterson Air Force Base Research Labs. This ITO layer was unpatterned with a thickness of approximately 250nm. The ITO is patterned by a chemical etching process. The entire substrate is covered with a highly adhesive cellulose tape, and the proper pattern following Figure 2.2 is cut out. The area exposed to the atmosphere is the area where the ITO is not desired. The chemical etchant is a solution of 3 parts hydrochloric acid to 1 part nitric acid. This pinkish solution is transferred to a glass slide holder, where the substrates were completely immersed. After 3 minutes, the substrates are removed and immediately rinsed with deionized water. The substrates were then dried, and
Figure 2.2. Schematic of electrode patterning – a) cross pattern of ITO and gold electrodes, b) net result of 10 possible circuits
the tape is cleaned off with a combination of acetone and a razor blade. The result of this
effort is a glass substrate with a patterned ITO electrode.

With all of the factors that can impede the quality EO devices, cleaning becomes a very
important step in device processing. Through much effort, an efficient substrate cleaning
process was developed. The first step is to clean the substrates in a Microclean/DI water
solution with a soft brush. This will eliminate the large particles and any remnants left
over from the etching process. This step is followed by a series of cleaning steps in an
ultrasonic batch. The first ultrasonic cleaning is with acetone, followed by a DI water
rinse. The second round is with methanol, followed by a DI water rinse, and then with DI
water in the ultrasonic bath. The substrates are then either immediately used in the next
processing step, or are kept in a clean room until needed.

There are a number of methods for deposition of polymer thin films. A simple method
employed in this research is spin coating. In this process, the clean substrate is placed on
a vacuum chuck where it can spin at a controlled speed. A polymer solution is dispersed
onto the substrate by pipetting. Once the substrate is completely covered, the spin
coating machine begins rotating at a programmed speed. After spinning, the solvent must
be completely evaporated away from the surface. There are quite a few variables
involved for such a simple deposition method. The spin coating machine controls the
speed of the chuck, the time of the spin, and rate of the ramp up to the set speed. All of
these variables are completely material dependent. Some polymers need a slow ramp rate
to produce a uniform film, some need an immediate rapid spin.
The polymer must be dissolved into a solvent for spin coating. Choice of this solvent and the ratio of solvent to polymer is important to device fabrication. The solvent system must have two major characteristics: it must produce high quality films, and must be compatible with the deposition of additional layers. If a layer is being deposited onto another polymer that has already been cast, then the cast polymer must not be soluble in the solvent used for spin coating. This would destroy the interface, and most likely cause loss of the previously cast polymer. Volatility is also key to spin coating. A solvent must be volatile enough that it will rapidly evaporate away from the polymer during drying, but not so volatile that it evaporates away before the spin coater starts. These are the reasons that water and chloroform are avoided as solvents if possible. The water is hard to evaporate from the surface, and can easily entrain air bubbles during drying, which causes short circuits. Chloroform solutions must be applied while the spin coater is rotating because of its high volatility. This hurts the repeatability and quality of deposition.

For these experiments, the polymers used for device processing are Polymethylmethacrylate (PMMA), Salmon derived DNA, and mixtures of PMMA and the chromophores Disperse Red 1 (DR1) and Cheng-Larry Dalton 1 (CLD-1). The solvent systems were optimized in Table 2.1. Spin curves are presented in Section 3.2.1.

The PMMA solutions were both formed the same way. PMMA (15% by wt) and cyclopentanone (85% by wt) were combined and shaken until completely dissolved. The
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Chromophore</th>
<th>Wt. % Polymer in solution</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>DR1 (10% wt to PMMA)</td>
<td>15%</td>
<td>Cyclopentanone</td>
</tr>
<tr>
<td>PMMA</td>
<td>CLD-1 (10% wt to PMMA)</td>
<td>15%</td>
<td>Cyclopentanone</td>
</tr>
<tr>
<td>DNA</td>
<td>N/A</td>
<td>5%</td>
<td>Butanol</td>
</tr>
</tbody>
</table>

Table 2.1. Polymer/Solvent systems used for device design
chromophore was then added to the dissolved solution at 10% (by wt) to PMMA and shaken again until completely dissolved. For the DNA solution, DNA (5% by wt) was added to butanol (95% by wt) and shaken under 60°C until completely dissolved. Each solution was equated to room temperature and all visible air bubbles escaped before any spin coating was done.

In the test devices, a 1µm DNA layer is deposited onto the clean substrate. After the proper evaporation time and cool down, a 1.7µm PMMA/chromophore layer is deposited. DNA is not soluble in cyclopentanone, so the interface between the two films will remain intact. The spin coating machine parameters and solvent evaporation procedures for each system are defined in section 3.2.1.

The final step in device processing is the deposition of the top electrode. This is done by sputtering. A paper mask was generated to fit the pattern shown in Figure 2.2 and taped onto the substrate. The masked substrate is then placed in the sputtering machine, and a 3000Å gold electrode is deposited. The final product from all these processing steps is seen in Figure 2.3.

2.2 EXPERIMENTAL METHODS

2.2.1 TENG AND MAN

The concept of measuring the electro-optic coefficient of a polymer NLO material is to measure the phase shift of the transverse electric (TE) and transverse magnetic (TM)
Figure 2.3. Pictures of Devices: a) CLD1/PMMA Baseline, b) CLD1/PMMA with DNA doublestack, c) DR1/PMMA Baseline
modes of a laser beam through material while an external modulating field is applied. C. Teng and H. Man developed a simple reflection technique for determination of the EO coefficient in NLO polymer films [29, 30]. This process does not require waveguiding, and can be carried out during or after the poling process. The experimental setup is shown in Figure 2.4 [29]. The actual experimental setup is shown in Figure 2.5.

The test device is fabricated as detailed in section 2.1.1. The device is placed in a sample holder with the back side (glass substrate) facing the laser beam. The beam enters the device at an angle $\theta = 45^\circ$, where it propagates through the glass substrate, ITO layer, and polymer film. The laser beam then reflects off the gold electrode and travels back through the device layers. The incident angle of the laser is set at $45^\circ$ so the amplitude of the s-wave (perpendicular) and p-wave (parallel) components are equal. The beam exiting the device then travels through a Soleil-Babinet compensator, an analyzer, and then to a detector. The detector runs to a lock-in amplifier where the modulation of the laser beam is measured.

With the Soleil-Babinet compensator, the intensity of the laser beam picked up at the detector is described in the following relation [29]:

$$I_o = 2I_c \sin^2 \left( \frac{\psi_m}{2} \right)$$  \hspace{1cm} (10)

Where: $I_c = \text{half of the maximum intensity}$
Figure 2.4. Schematic of Teng and Man Experimental Setup
Figure 2.5. Teng and Man Experimental Setup: a) Electronics, b) Optics
\[ \Psi_{sp} = \text{phase retardation between the s and p waves due to the Soleil-Babinet compensator} \]

The refractive indices in this system are defined as:

\[
\left( \frac{1}{n_p} \right) = \frac{\sin^2 \alpha_p}{n_e^2} + \frac{\cos^2 \alpha_p}{n_o^2} \quad (11)
\]

\[ n_s = n_o \quad (12) \]

\[ \sin \theta = n_p \sin \alpha_p \quad (13) \]

Where: 
- \( n_p \) = p-wave refractive index
- \( n_e \) = perpendicular refractive index
- \( n_o \) = parallel refractive index
- \( n_s \) = s-wave refractive index
- \( \alpha_p \) = refraction angle of the p-wave

The application of a modulating voltage (AC) causes a phase shift in the s and p waves of the laser due to the EO induced refractive index change. This phase shift naturally changes the path length of the laser. With the symmetry approximation of refractive indices such that \( n_o \approx n_p \approx n \), the two equations are derived [29]:
\[ \delta \psi_{sp} = \delta \psi_p - \delta \psi_s = \Gamma_m \sin \omega_m t \]  \hspace{1cm} (14)

\[ \Gamma_m = \frac{2\pi m V_m r_{33}}{3 \lambda d} \left( s - \frac{4d^2 \sin^2 \theta}{sn^2 \left( 1 - \frac{\sin^2 \theta}{n^2} \right)} \right) \sin^2 \alpha_p \]  \hspace{1cm} (15)

Where: \( V_m \) = modulating voltage

\( d \) = distance between electrodes

\( s \) = change in path length

The phase retardation is at its most linear point at the half intensity value shown in Figure 2.6 [29].

Therefore, the ratio of the modulated beam intensity to the half intensity is approximately equal to the induced phase retardation. With this approximation, the experimental value for the electro-optic coefficient \( r_{33} \) is as follows [29]:

\[ r_{33} = \frac{3\lambda I_m}{4\pi V_m I_c n^2} \cdot \frac{\left( n^2 - \sin^2 \theta \right)^{3/2}}{\left( n^2 - 2 \sin^2 \theta \right)} \cdot \frac{1}{\sin^2 \theta} \]  \hspace{1cm} (16)

2.2.2 SPIN COATING

A spin coating machine was used for this research for the deposition of all thin films.

The unit features a circular vacuum chuck, and spins up to a maximum speed of 4000
Figure 2.6. Output intensity vs. Phase retardation for use in Teng and Man
RPM. Three separate spin rates are programmable in one cycle. The variables for these spin rates are RPM, ramp time, and hold time.

### 2.2.3 DIELECTRIC MEASUREMENTS

Dielectric measurements of DNA at different frequencies were provided by Lockheed Martin.

### 2.2.4 PROFILOMETRY

Profilometry is an experimental method for determining the thickness of polymer films. A substrate with a polymer film is scored with a razor blade. The scoring is such that the polymer film is completely removed from a small section of the substrate. The stylus from the profilometry machine is scanned across a set section of the surface. This scan maps the surface level, and will show a ‘plateau’ over the film, and a ‘dip’ where the film was scored. This change in elevation is measured, which gives the thickness of the polymer film. Profilometry is also a good tool for overall surface roughness of films.

### 2.2.5 RESISTIVITY MEASUREMENTS

The conductivity/resistivity of films in electro-optic devices is important for the efficiency of the poling process. In order for the poling process to be efficient, a majority of the poling voltage must be dropped over the core layer. Grote, Drummond et al. showed that using conductive cladding layers increased the poling efficiency over 2 times [34, 35]. However, there is a tradeoff. Most commercial conductive polymers have large absorptions in the visible spectrum. The increased efficiency in poling using conductive
polymers leads to large optical losses. It is advantageous to use a cladding layer that is less resistive (more conductive) than the core layer.

The effects of the resistivity of each layer on the overall device can be seen directly in Equation (17) below:

\[
V_{p(\text{total})} = V_{p(\text{core})} \left[ \frac{\rho_{\text{core}} + 2 \rho_{\text{clad}} \left( \frac{d_{\text{clad}}}{d_{\text{core}}} \right)}{\rho_{\text{core}}} \right]
\]

(17)

Where:

- \( V_{p(\text{total})} \) = Total Applied Voltage
- \( V_{p(\text{core})} \) = Desired Voltage drop across the core
- \( \rho \) = Resistivity
- \( d \) = Thickness

The resistivity measurements were taken in a custom setup shown in Figure 2.7. The setup consists of a high voltage supply and a Keithly ampmeter/voltmeter, both of which are controlled by a computer. The specimen area consists of a grounded hotplate and positive and negative connections, all in an insulated container in a nitrogen atmosphere. The container also has copper wiring around the inside to act as a Faraday cage.
Figure 2.7. Resistivity Experimental Setup
2.2.6 THERMAL ANALYSIS

The thermal analysis for these experiments was done using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The scans were done by WPAFB labs. As described previously, the glass transition temperature is pertinent to the poling process. Also, since the devices are heated during the process, it is necessary to analyze the thermal behavior of each material.

2.2.7 SPECTROPHOTOMETRY

Spectrophotometry was done using a Hitachi model U-4001. This maps out the absorption of a material over a set spectrum of wavelengths. This is one of the most important pieces of data for waveguide devices. The materials selected for the devices must not absorb at the guiding wavelengths.

3.0 RESULTS

3.1 MATERIALS CHARACTERIZATION

3.1.1 THERMAL ANALYSIS

The thermogravimetric analysis data shows the range of temperature stability for a material. There must be no appreciable weight loss in the material around the operating device temperature. Another important temperature to monitor is the poling temperature. If a guest-host layer is poled at around 80°C, in the case of PMMA, then all the other layers in the device must be stable at this temperature. All of the materials involved in
this research are stable past 150°C. This is shown in the following 4 TGA scans in Figures 3.1a-d.

Differential Scanning Calorimetry (DSC) shows the transition temperatures polymer materials. Since the basis of the poling step involves the glass transition temperature ($T_g$), the DSC data is very relevant to device design. The $T_g$ for each material used in the devices were found and listed below in Table 3.1 and DSC scans shown in Figure 3.2.

### 3.1.2 SPECTROPHOTOMETRY

The results from the spectrophotometry show generally how the materials will behave optically at a range of wavelengths. For these experiments, each device material was scanned with the absorption results listed in Table 3.2 and Figures 3.3. DNA proves to be a good material optically with no noticeable absorptions. Both chromophores, DR1 and CLD1, have significant absorptions in the lower region. Since DR1 absorbs below 625nm, a Helium-Neon laser is used for waveguiding with a wavelength of 633nm. CLD1 absorbs up to 975nm, so a laser with a wavelength of 1.55µm is used.

### 3.1.3 RESISTIVITY

The resistivity of two films were recorded using the technique described in Section 2.2.5. A constant voltage of 5V was applied, and the resistivity was recorded for 10 minutes at 6 second increments. The results shown in Figure 3.4 [33, 42] show that the DNA has a
a) Weight vs. Temperature for PMMA

b) Weight vs. Temperature for PMMA/CLD1 guest/host system
c) Weight vs. Temperature for PMMA/DR1 guest/host system

d) DNA

Figure 3.1. TGA scans of a) PMMA, b) PMMA with DR1, c) PMMA with CLD1, d) DNA
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Glass Transition Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>78°C</td>
</tr>
<tr>
<td>PMMA / DR1</td>
<td>61.5°C</td>
</tr>
<tr>
<td>PMMA / CLD1</td>
<td>63°C</td>
</tr>
<tr>
<td>DNA</td>
<td>56.5°C</td>
</tr>
</tbody>
</table>

Table 3.1. Experimental values of Glass Transition Temperatures
a) DSC scan of PMMA at 10°C/min

b) DSC scan of PMMA/DR1 at 10°C/min
c) DSC scan of PMMA/CLD1 at 10°C/min

d) DSC scan of DNA at 10°C/min

Figure 3.2. DSC Scans of a) PMMA, b) PMMA/DR1, c) PMMA/CLD1, d) DNA
### Table 3.2. Absorption Ranges of all device materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Absorbing Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>None</td>
</tr>
<tr>
<td>PMMA and DR1</td>
<td>&lt; 625nm</td>
</tr>
<tr>
<td>PMMA and CLD1</td>
<td>&lt; 975nm</td>
</tr>
<tr>
<td>DNA</td>
<td>None</td>
</tr>
</tbody>
</table>
Absorption Scan: PMMA

Absorption Scan: PMMA and DR1

a)

b)
Figure 3.3. Spectrophotometry Results of a) PMMA, b) PMMA/DR1, c) PMMA/CLD1, d) DNA
Figure 3.4. Resistivity of DNA at a range of temperatures
resistivity much less than a typical APC core layer, as well as a typical acrylate cladding layer, especially near poling temperatures >70°C.

3.1.4 DIELECTRIC CONSTANT

The dielectric constant of DNA was measured at different frequencies. These results are shown in Figure 3.5, with values of 7.8 at 1 kHz, and 5.6 at 1 MHz [42].

3.1.5 REFRACTIVE INDICES

Optical materials for waveguiding must be chosen with the refractive index in mind. In order for a three layer waveguide to propagate light, the refractive indices of each layer must adhere to equation (8) in the Waveguide section above. The refractive indices are listed in Table 3.3 [42]. Since the refractive index of DNA is lower than the core, PMMA, it is a good candidate for use as a cladding layer.

3.2 DEVICE CHARACTERIZATION

3.2.1 SPIN CURVES

Spin coating is a good technique for depositing films with a thickness on the order of microns. Obtaining a good quality film at a desired thickness is more of an art form than a science. There are four basic variables for optimizing spin coating: ratio of polymer to solvent, speed of spinning, ramping, and duration. Each polymer-solvent system behaves somewhat differently during deposition, so these four variables must be determined for each system. However, there are some obvious rules of thumb. The higher the ratio of
Figure 3.5. Dielectric Constant of DNA at a range of frequencies
<table>
<thead>
<tr>
<th>Material</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>1.491 at 1.55µm</td>
</tr>
<tr>
<td>DNA – 3,000,000 MW</td>
<td>1.53 at 633nm, 1.48 at 1.55µm</td>
</tr>
</tbody>
</table>

Table 3.3. Refractive Index Values
polymer to solvent, the thicker the solution, thus the thicker the film. The slower the spinning, the thicker the film. And finally, the shorter the duration, the thicker the film (typically).

For this research, the spin coating parameters were fairly easy to optimize. The only stipulation for deposition was to adhere a high quality film between 1 and 2 microns in thickness. For the core, PMMA, 1.7 microns was the desired thickness. Each of the variables was optimized first simply for quality of film. Table 3.4 lists the results of the optimization.

After the variables were optimized for film quality, spin curves were constructed to reach the desired film thickness. Again, the core layer was desired at 2µm, whereas the DNA layer was desired at any thickness between 1 and 2µm with high quality. The ramping and speed parameters for both materials are set by film quality. Therefore, the spin curves were used to determine the length of spinning.

The spin curves for PMMA and DNA are shown in Figures 3.6a and 3.6b. The resulting spin parameters are in Table 3.5.

3.2.2 ELECTRO-OPTIC COEFFICIENTS

The defining characteristic of the non-linearity of an electro-optic material is the $r_{33}$ value, as defined in Section 2.2.1. Using the Teng and Man technique also described in
<table>
<thead>
<tr>
<th>Variable</th>
<th>PMMA-Chromophore</th>
<th>DNA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polymer to Solvent ratio</strong></td>
<td>Set at 15% polymer to 85% solvent</td>
<td>Unable to filter solution at high percentages of DNA (&gt;8%). Low amounts of DNA would not adhere to the substrate. Maximized at 5%</td>
</tr>
<tr>
<td><strong>Speed</strong></td>
<td>Optimized at 1000 RPM for film quality.</td>
<td>Optimized at 1000 RPM for film quality. Faster speeds would leave uncoated areas, slower speeds introduced air bubbles.</td>
</tr>
<tr>
<td><strong>Ramping</strong></td>
<td>Slow ramp up was vital to the film quality. Films were very uneven with a slow ramp. 25 second ramp at 600 RPM optimized</td>
<td>A fast ramp was necessary for good film quality. Again, slow ramping introduced air bubbles. 5 second ramp at 500 RPM followed by a 5 second hold were optimized.</td>
</tr>
</tbody>
</table>

Table 3.4. Spin Coating Film Quality Parameters
<table>
<thead>
<tr>
<th>Material</th>
<th>Spin Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>25 second ramp to 600 RPM</td>
</tr>
<tr>
<td></td>
<td>10 second spin at 1000 RPM</td>
</tr>
<tr>
<td>DNA</td>
<td>5 second ramp to 500 RPM</td>
</tr>
<tr>
<td></td>
<td>5 second hold at 500 RPM</td>
</tr>
<tr>
<td></td>
<td>5 second ramp to 1000 RPM</td>
</tr>
<tr>
<td></td>
<td>5 second hold at 1000 RPM</td>
</tr>
</tbody>
</table>

Table 3.5. Spinning Film Thickness Parameters
Figure 3.6. Spin curves for a) PMMA, b) DNA
that section, the $r_{33}$ values were found experimentally for varying materials, poling temperatures, and poling voltages.

Two different devices were tested for non-linearity. Baseline devices of a single spin coated core layer of PMMA and a chromophore (both CLD1 and DR1) were manufactured. This layer was 1.7µm thick. The second device type was a doublestack consisting of a 1µm layer of DNA with a 1.7µm core layer. Each device type, four in total, was tested at a variety of temperatures and voltages. To describe the behavior of the device with poling voltage, the temperature was held at 80°C while the poling voltage was varied at 80, 82, 84, and 86 V/µm. Conversely, for behavior with poling temperature, the voltage was held at 80V/µm while the temperature was varied at values of 80, 84, and 90°C.

This data (Figures 3.7a-h) shows that the devices behave logically. As the poling voltage increases, so does the EO coefficient, likewise for poling temperature. The key point is that the doublestack devices behaved like the baseline devices. The DNA cladding layer did not hinder the non-linearity of the guest-host system.

The DNA cladding layer performance was evaluated by calculating the expected $r_{33}$ value of the device based on the dielectrics and the baseline value. This is calculated using a modified version of Equation (8) shown below in Equation (18):
EO Coefficient vs. Poling Voltage: PMMA/DR1

EO Coefficient vs. Poling Voltage: Doublestack PMMA/DR1 and DNA
EO Coefficient vs. Poling Voltage: PMMA/CLD1

c)

EO Coefficient vs. Poling Voltage: Doublestack PMMA/CLD1 and DNA

f)
EO Coefficient vs. Poling Temperature: PMMA/CLD1

Figure 3.7. EO Coefficients, a) Baseline with DR1 at 80C, b) Doublestack with DR1 at 80C, c) Baseline with DR1 at 80V, d) Doublestack with DR1 at 80V, e) Baseline with CLD1 at 80C, f) Doublestack with DR1 at 80C, g) Baseline with CLD1 at 80V, h) Doublestack with CLD1 at 80V
\[ V_\pi = \frac{\lambda}{n^3 r_{33} L \Gamma} \left( d_{\text{core}} + d_{\text{clad}} \sqrt{\frac{\varepsilon_{r_{\text{Core}}}}{\varepsilon_{r_{\text{Clad}}}}} \right) \]  

(18)

Where: \( d = \) Layer Thickness

\( \varepsilon_r = \) Dielectric Constant

Using Equation (18), a ratio can be calculated to determine the theoretical electro-optic constant results for a doublestack device based on the results from a single stack device. The results of this show that the DNA cladding layer behaved theoretically within 10% of the actual experimental values (Table 3.6). This is acceptable considering the large amount of error possible through the process. Each processing step introduces error, and there are several steps in the manufacturing of these test devices.
<table>
<thead>
<tr>
<th>Device Structure</th>
<th>Actual r33 (pm/V)</th>
<th>Calculated r33 (pm/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline with DR1</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>Doublestack with DR1</td>
<td>3.7</td>
<td>3.5</td>
</tr>
<tr>
<td>Baseline with CLD1</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>Doublestack with CLD1</td>
<td>4.3</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Table 3.6. Actual EO Coefficient values vs. calculated
4.0 SUMMARY AND CONCLUSIONS

Marine derived DNA has proven to be a novel material for use in electro-optic devices as a cladding layer. Though much further investigation must be done, the preliminary results are positive. A number of material properties are necessary for use in electro-optic devices. The optical properties needed for a cladding material are a refractive index lower than the core, and little optical loss due to absorptions. The electrical properties of the material are low resistivity as compared to the core layer, and electrical stability at high voltages and temperatures. Finally, the material must have a number of performance properties. It must be resistant to a number of common solvents for device manufacturing, it must not degrade near poling and/or operating temperatures, and must not absorb a large amount of moisture from the atmosphere.

The following table (4.1) summarizes the properties of DNA [33]:

<table>
<thead>
<tr>
<th>Property</th>
<th>Type</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive Index</td>
<td>Optical</td>
<td>1.53 at 633nm, 1.48 at 1550nm</td>
</tr>
<tr>
<td>Absorption</td>
<td>Optical</td>
<td>~100% Transmission at both 633nm and 1550nm</td>
</tr>
<tr>
<td>Resistivity</td>
<td>Electrical</td>
<td>2 orders of magnitude lower than the resistivity of typical core materials</td>
</tr>
<tr>
<td>Dielectric Constant</td>
<td>Electrical</td>
<td>7.8 at 1kHz, 5.6 at 1MHz</td>
</tr>
<tr>
<td>Degradation Temperature</td>
<td>Material</td>
<td>&gt;200°C</td>
</tr>
<tr>
<td>Solvent Resistance</td>
<td>Material</td>
<td>Water, Cyclopentanone</td>
</tr>
<tr>
<td>Solubility</td>
<td>Material</td>
<td>Soluble in most alcohol based solvents</td>
</tr>
</tbody>
</table>

Table 4.1. Properties of DNA
The marine derived DNA also performed well in the electro-optic device. Based on the material properties, the cladding layer behaved as expected in the device within 10%. The experimental values were actually 10% higher than the calculated values, which might suggest the material has a lower dielectric constant than was recorded.

The electro-optic devices with DNA as the cladding layer showed the common dependence of poling voltage and temperature on poling efficiency. The doublestack devices were also more stable in experimentation than the baseline samples, with zero device failures, as opposed to numerous failures of baseline devices.
5.0 SUGGESTIONS FOR FUTURE WORK

Further experimentation is needed in the area of biologically-derived materials for use in electro-optics. These results are promising for the area, however much is yet to be determined. In terms of the marine derived DNA, we need to look at the performance of the cladding layer with respect to the molecular weight. For these experiments, 3MM g/mol DNA was used because of availability. It is possible that some material properties will differ with molecular weight.

Work must also be done in the manufacturing area of electro-optic devices. As shown in the Mach-Zehnder diagram in Figure 1.11, the cladding layer must be etched to form the desired shapes. Both chemical and plasma etching should be investigated, with attention given to the surface modification of the DNA layer.
REFERENCES


[34] J. Grote, The United States of America as represented by the Secretary of the Air Force, U.S. Patent 5,892,859 (Apr. 6, 1999).


