

Investigation of Polymers and Marine-Derived DNA in Optoelectronics[†]

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Our research in nonlinear optic (NLO) polymer-based electro-optic (EO) modulators has centered on optimizing device performance through the using of polymer cladding layers with higher relative conductivities than the NLO core material. We have demonstrated as much as a 10 times increase in the effective EO coefficient of electrode poled, guest/host NLO polymers, compared to using passive polymer claddings. We have achieved the lowest poling voltage to date for maximum EO coefficient, 300 V, for a two-layer waveguide structure consisting of a 2 μm thick NLO polymer layer and 2 μm thick conductive cladding layer. Optimized polymer cladding materials possessing the desired optical and electromagnetic properties we find need to be balanced with materials processability. In addition to the conventional polymer materials under investigation, a novel material, deoxyribonucleic acid (DNA), derived from salmon sperm, has shown promise in providing both the desired optical and electromagnetic properties, as well as the desired resistance to various solvents used for NLO polymer device fabrication. Our investigation also includes intercalation of fluorescent dyes, photochromic dyes, nonlinear optic chromophores, two-photon dyes, and rare earth compounds into a DNA-based host material and comparing results with poly(methyl methacrylate) (PMMA)-based host materials.

1. Introduction

Nonlinear optic (NLO) polymer-based electro-optic devices have achieved world record low half-wave voltages and high frequencies over the last 2–3 years.^{1–7} Part of the advancement is through the use of relatively more conductive polymers for the cladding layers.^{8–14} For electro-optic (EO) modulators, one wants an electric field induced phase retardation of π or 180° . For a transverse type EO modulator, the voltage necessary to realize this π phase retardation is defined as the half-wave voltage, $V\pi$, given by¹⁵

$$V\pi = (\lambda/d/n^3 r_{33} L \Gamma) \quad (1)$$

where λ is the operational wavelength, d is the thickness of the nonlinear optic core material, n is the refractive index of the

EO active core material after electric field poling, r_{33} is the electro-optic coefficient of the EO active core material, L is the length of the interaction region, and Γ is the modal overlap integral. For a given geometry, the half-wave modulation voltage $V\pi$ will be inversely proportional to the EO coefficient r_{33} . Therefore, to minimize $V\pi$ one must maximize r_{33} .

For guest/host NLO polymer materials, the value of the EO coefficient r_{33} is dependent on the degree of noncentrosymmetry in the NLO polymer, which is induced by electric field poling. The NLO film is heated to near its glass transition temperature T_g , at which point the molecules are free to align themselves along an applied dc electric field. An increase in this applied poling voltage causes the noncentrosymmetry, and hence r_{33} , of the NLO polymer film to increase. The sample is then cooled to room temperature while the application of the electric field is continued, which holds the molecules in place resulting in a poled material. The poling field is chosen to be as large as possible in order to maximize r_{33} , yet just less than that which would result in dielectric breakdown of the material. The typical poling field is 100 V/ μm .

When fabricating NLO polymer-based EO devices, one also introduces a top and bottom polymer cladding layer in addition to the NLO polymer core layer. To determine how much of the total applied voltage is dropped across the core material in this three-layer stack, one must consider the relative thickness and

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conductivity of the core and cladding materials. Assuming a standard ohmic voltage divider, the poling voltage can be given by⁸

$$V_{\text{PTotal}} = V_{\text{Pcore}}[(\rho_{\text{Core}} + \rho_{\text{CladB}}((d_{\text{CladB}}/d_{\text{Core}})) + \rho_{\text{CladT}}((d_{\text{CladT}}/d_{\text{Core}}))/\rho_{\text{Core}})] \quad (2)$$

where V_{PTotal} is the total applied poling voltage, V_{Pcore} is the poling voltage dropped across the core, ρ_{Core} , ρ_{CladB} , and ρ_{CladT} are the resistivities of the core, bottom cladding, and top cladding materials, and d_{Core} , d_{CladB} , and d_{CladT} are the thicknesses of the core, bottom clad, and top clad layers, respectively. This suggests that a cladding layer with a relative conductivity at least 1 order of magnitude higher than that of the NLO core layer will ensure that 80+% of the applied poling voltage will be dropped across the core layer and the risk for material breakdown will be minimized.

We have investigated various conductive and nonconductive polymer materials, over the last couple of years, suitable for use as cladding layers for NLO polymer-based optoelectronic devices. These include Baytron P blends, UV15LV, UFC170, and Epoxylite.^{9–11} The goal has always been to maximize the nonlinearity of the NLO core material, while minimizing the total poling voltage and the absorption loss. We have found, however, that we have had to balance the desired absorption loss, conductivity, and refractive index with the materials processability and materials compatibility.

This investigation of NLO materials for electro-optic, optical memory, and optical amplifier applications has also led us to a promising material, marine-based deoxyribonucleic acid (DNA). It is derived from waste material from the salmon fishing industry and is, therefore, abundant and inexpensive. It is also a green material. In addition, it has demonstrated optical and electromagnetic properties suitable for optical waveguide and device applications. Preliminary investigations have suggested that DNA may prove to be a more suitable material than the polymers currently being used for optical waveguide devices.^{16–18}

2. Experimental Section

2.1. Conductive Claddings. The guest NLO chromophores used for the study of conductive cladding layers were disperse red 1 (DR1) and Cheng Larry Dalton 1 (CLD1). The host polymers used were poly(methyl methacrylate) (PMMA) and poly[bisphenol A carbonate-co-4,4'-(3,3,5-triethyl cyclohexylidene) diphenol] (APC). The concentration of DR1 to host polymer was 10 wt %. The concentration of CLD1 to host polymer was 25 wt %.

The typical relative resistivity of these NLO polymers was on the order of $10^{12} \Omega\text{-cm}$ under poling conditions. Therefore, to verify eq 1, we had to identify suitable cladding materials with resistivities $\leq 10^{11} \Omega\text{-cm}$.

In previous research we demonstrated that selection of compatible conductive polymer cladding materials is crucial to device performance. We have experimentally verified that one can drop 95+% of the total applied poling voltage across the NLO core material by utilizing cladding materials with higher relative conductivities, hence maximizing the EO coefficient for electrode poled, guest/host NLO polymer systems. In addition, we have demonstrated the lowest total poling voltage to date for electrode poling, while realizing maximum EO coefficient.

This was demonstrated by performing poling experiments using both 10 wt % DR1 in PMMA and 25 wt % CLD1 in PMMA for the core and a conductive polymer for the cladding.

The conductive polymer used was a blend of 25 wt % Baytron P (poly(ethylene dioxythiophene) in poly(styrene sulfonate)), available from Bayer Corporation, in a solution of 15% poly(vinyl alcohol) (PVA) in H_2O . For these earlier experiments we used a structure consisting of a 45 nm thick indium tin oxide (ITO) bottom electrode on glass, a 2 μm thick 25 wt % Baytron P in PVA cladding layer, a 1.93 μm thick core layer of either DR1 or CLD1 in PMMA, and a 300 nm thick gold film layer for the top electrode. We also prepared a test structure using an Ultradel 4212 polyimide cladding with a resistivity 1 order of magnitude higher than 10 wt % DR1 in PMMA for comparison. These test structures were poled at 90 °C in air at various voltages, and the EO coefficients were measured at the Air Force Research Laboratory (AFRL) using the Teng and Mann technique (1 kHz modulation) at $\lambda = 0.780 \mu\text{m}$ for the DR1 in PMMA samples and at $\lambda = 1.3 \mu\text{m}$ for the CLD1 in PMMA samples and at the University of Southern California (USC) using the attenuated total reflection (ATR) technique at $\lambda = 1.06 \mu\text{m}$ for the CLD1 in PMMA samples. The results were compared with a control sample using a 1.93 μm thick DR1 in PMMA and CLD1 in PMMA layers sandwiched between the two electrodes. The resistivities of the materials in this study at a poling temperature of 90 °C and a poling field of 60 V/ μm were on the order of $10^{12} \Omega\text{-cm}$ for 25 wt % CLD1 in PMMA, $10^{13} \Omega\text{-cm}$ for polyimide, and $10^7 \Omega\text{-cm}$ for 25 wt % Baytron P in PVA. These poling experiments demonstrated the conductive polymer cladding concept. (See Figures 1 and 2.)

There was also excellent agreement between the AFRL and USC EO coefficient measurements. These poling experiments demonstrated the conductive polymer concept.

In order to achieve device stability at higher temperatures, new host materials with higher glass transition temperatures need to be used with the NLO chromophores. This, in turn, requires identification of new cladding materials as well. The host material identified for the CLD1 chromophore, for the current research, is poly[bisphenol A carbonate-co-4,4'-(3,3,5-triethyl cyclohexylidene) diphenol] (APC).

The solvents used to dissolve APC for this investigation were either dichloroethane or cyclopentanone. They produced good quality, low loss, 25 wt % CLD1 in APC optical films. However, both of these solvents dissolve PVA, which prevented Baytron P/PVA from being used as a viable bottom cladding layer.

In addition, APC has a T_g of 150 °C. This resulted in a poling temperature of 140–145 °C. PVA has a T_g of 90 °C and changes properties significantly at 145 °C. This prevented Baytron P/PVA from being used as a top cladding as well and, hence, rendered PVA as an unacceptable host for Baytron P for viable devices.

We then investigated alternative cladding materials, as well as new host materials for Baytron P, in order to optimize device performance and fabrication. The choice of these materials depended not only on the optical and electromagnetic properties of a given material but also on the solvent required for the material and temperature stability. In addition, materials used during device fabrication can include photoresists, developers, and etchants. Therefore, balances between the desired optical/electromagnetic properties and processability of the various materials become necessary. This made demonstration of a three-layer stack difficult.

The rule of thumb we followed was the following: the core and cladding materials must withstand short-term poling temperatures ranging from 90 to 200 °C; the bottom cladding material must be resistant to cyclopentanone and dichloroethane and may have to be resistant to photoresists, etchants, and

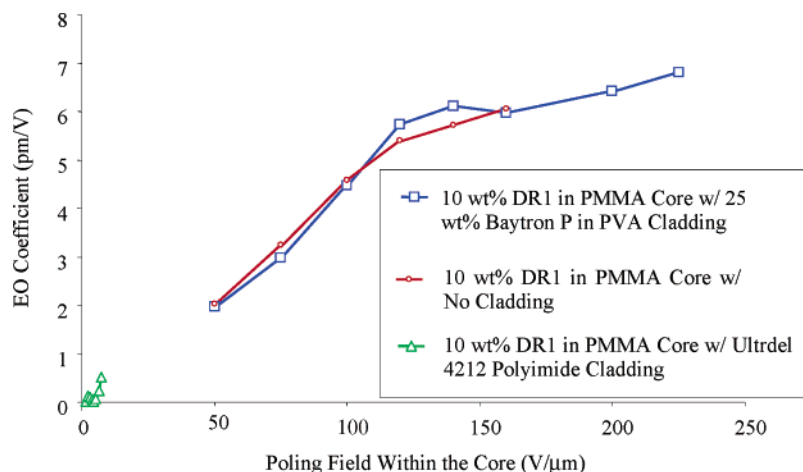


Figure 1. Electro-optic coefficient for 10 wt % DR1 in PMMA vs poling field within the NLO core layer at $\lambda = 780$ nm.

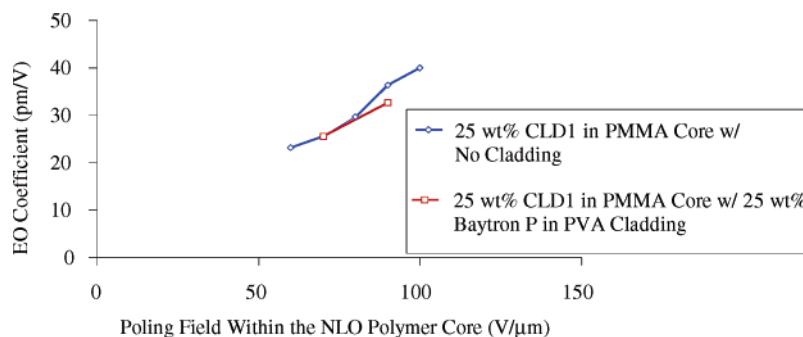


Figure 2. Electro-optic coefficient for 25 wt % CLD1 in PMMA vs poling field at $\lambda = 1.3$ μm .

developers, depending on the fabrication process; the solvent used for the top cladding must not dissolve PMMA or APC, the core material; the top cladding material may also have to be resistant to photoresists, developers, and etchants; in addition, protective layers may be needed between the claddings and core.

2.2. DNA Cladding Material. DNA materials used for this investigation were processed at the Chitose Institute of Science and Technology (CIST).^{16,17} The DNA was isolated from salmon sperm and purified, and the protein content was reduced. We started with frozen salmon sperm. The sperm was homogenized and given an enzymatic treatment to degrade the proteins by protease. Holding the pH level at 7.5 eliminated proteins. The material then underwent a carbon treatment for decolorization. It was filtered, and ethanol was added to precipitate the DNA. The purified DNA was filtered from the ethanol and freeze-dried. The purified DNA dissolves only in water. It does not dissolve in any organic solvent, except a strong acidic solvent such as trifluoromethanesulfonic acid. This is not compatible with waveguide device fabrication, so we performed additional processing to render it more suitable for device fabrication.

The processing was accomplished by precipitating the purified DNA in water with a cationic surfactant complex, hexadecyltrimethylammonium chloride (CTMA), by an ion exchange reaction, replacing the sodium cation of the DNA. This was done at both CIST and AFRL. The resulting DNA–lipid complex became water insoluble and more mechanically stable due to the long alkyl chain of the CTMA. The average molecular weight of the resulting DNA–lipid complex measured $M_w = 500\,000$, the purity measured assay = 96%, and the protein content measured 2%.

By adding the CTMA complex, DNA–CTMA could now be dissolved using solvents more compatible with device fabrication, such as chloroform, ethanol, methanol, butanol, or

a chloroform/alcohol blend. For a bottom cladding layer, any of these solvents work; however, since optical waveguides require a top cladding layer as well, we focused on ethanol, methanol, and butanol, since these solvents do not dissolve poly(methyl methacrylate) (PMMA) or poly[bisphenol A carbonate-co-4,4'-(3,3,5-triethyl cyclohexylidene) diphenol] (APC), which are currently being used as host materials for NLO polymer films. Since butanol has the highest boiling point of the three alcohol solvents, it produced the highest quality and most uniform films. In addition, the alcohol solvents ensured that the NLO/PMMA or NLO/APC core layer would not be dissolved, suggesting that the DNA–CTMA complex would be a suitable top cladding material, as well as a bottom cladding material.

At AFRL we mixed 10 wt % DNA–CTMA to butanol at 60 °C for 1 h, until the DNA–CTMA complex was dissolved. We then filtered the solution through a 0.2 μm filter. The DNA–CTMA complex was then spun onto uncoated glass slides, 50 nm indium tin oxide coated glass slides, and SiO₂ coated Si substrates.

To evaluate DNA–CTMA's potential as an optical waveguide material, the refractive index of DNA–CTMA was measured at both 0.633 μm and 1.550 μm , the transmissivity was measured as a function of wavelength, the resistivity was measured as a function of temperature, and the dielectric constant was measured as a function of frequency.¹⁸ In addition, we tested the film's resistance to various organic solvents used for polymer waveguide fabrication.

We added various concentrations of optical dyes to the DNA–CTMA complex to evaluate intercalation and material compatibility. These dyes included fluorescent dye 4-[4-(dimethylamino)styryl]-1-dococylpyridinium bromide (DMASDPB), photochromic dye spiropyran, rare earth metal compound Eu–

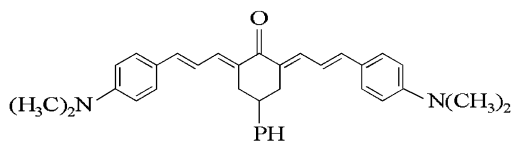


Figure 3. Two-photon dye 1433.

FOD, NLO chromophores disperse red 1 (DR1) and Cheng Larry Dalton 1 (CLD1), and two-photon dye 1433. (See Figure 3.)

3. Results and Discussion

3.1. Conductive Claddings. Potential alternative materials to Baytron P that we investigated included a UV curable epoxy, UV15LV, available from Master Bond, a UV curable polymer, UFC170, available from URAY, and a heat curable epoxy, Epoxylite, available from Epoxylite. Potential alternative host materials for Baytron P included poly(vinylpyrrolidone) (PVP) and poly(4-vinylphenol) (P₄VP), both available from Aldrich.

We found that UV15LV is resistant to dichloroethane and cyclopentanone after it is UV cured and baked at 150 °C for 1 h. It has a refractive index of 1.51 at $\lambda = 1.55 \mu\text{m}$, and we measured 4 dB/cm loss at $\lambda = 1.55 \mu\text{m}$. It is stable above 200 °C and is also resistant to AZ5214 photoresist, AZ400 developer, and chromium and gold etchant. Preliminary conductivity measurements indicated that the conductivity is ~ 2 to 3 orders of magnitude greater than APC under poling conditions. However, preliminary EO measurements for a two-layer CLD1: APC/UV15LV waveguide structure suggested to us that the conductivity of UV15LV might be closer to that of APC under poling conditions. Further testing needs to be performed. This told us that UV15LV is a suitable bottom cladding material, but depending on the conductivity, higher poling voltages may be required. UV15LV will dissolve APC and, hence, is not a suitable top cladding material without the use of a protective layer.

We found that UFC170 is resistant to dichloroethane and cyclopentanone after it is UV cured and baked at 120–150 °C for 30 min. It has a refractive index of 1.49 at $\lambda = 1.55 \mu\text{m}$, and we measured 3 dB/cm loss at $\lambda = 1.55 \mu\text{m}$. It is stable above 200 °C and is also resistant to AZ5214 photoresist, AZ400 developer, and chromium and gold etchant. Preliminary conductivity measurements indicated that the conductivity is on the same order as that of APC under poling conditions. Further testing needs to be performed. Also, UFC170 does not dissolve APC, therefore, it is a suitable material for both the top and bottom claddings without need of protective layers, however, higher poling voltages are necessary due to its low conductivity.

Devices have been fabricated using UV15LV for the bottom cladding and UFC170 for the top cladding with promising results. The lowest $V\pi$'s to date have been reported using this combination. This is adequate for the present, but materials with better optical and electromagnetic properties are desired in the future.

Epoxylite, when temperature cured, was also found to be resistant to the various solvents used for the NLO polymer core material; however, the resistivity of Epoxylite was found to be 3 orders of magnitude greater than that of UV15. This would require higher poling fields. Tests are currently underway to correlate resistivity with poling efficiency.

We found that 25 wt % Baytron P in poly(4-vinylphenol) (P₄VP) can be dissolved in ethanol. It will also dissolve in dichloroethane and cyclopentanone. It has a refractive index of 1.58 at $\lambda = 1.55 \mu\text{m}$, and we measured 4 dB/cm loss at $\lambda =$

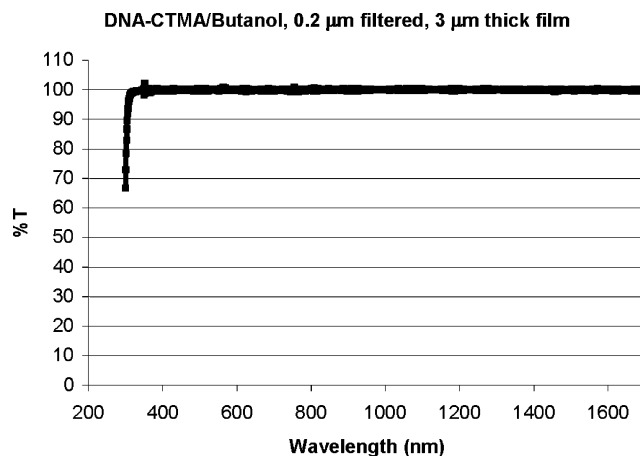


Figure 4. Transmissivity of a 3 μm thick DNA-CTMA thin film.

1.55 μm . It is stable above 200 °C. It will dissolve in AZ5214 photoresist, AZ400 developer, and chromium and gold etchant. Baytron P in P₄VP is as conductive as Baytron P in PVA under poling conditions. This suggests that Baytron P in P₄VP may be a suitable top and bottom cladding material with the use of a top protective layer.

We then added a 4,4'-methylenebis(*N,N*-dyglycidylaniline) cross-linker to the Baytron P in P₄VP blend using dimethylformamide solvent. It was baked at 180 °C for 30 min. This blend was resistant to dichloroethane and cyclopentanone. It has a refractive index of 1.58 at $\lambda = 1.55 \mu\text{m}$, and we measured 4 dB/cm loss at $\lambda = 1.55 \mu\text{m}$. It is stable above 200 °C. Cross-linked Baytron P in P₄VP is as conductive as Baytron P in PVA under poling conditions. This suggests that Baytron P in P₄VP may be a suitable bottom cladding material. Dimethylformamide will dissolve APC and, hence, is not a suitable top cladding material without use of a protective layer, provided that a new lower temperature cross-linker could be identified, since the curing temperature for 4,4'-methylenebis(*N,N*-dyglycidylaniline) is 180 °C.

We found that 25 wt % Baytron P in poly(vinylpyrrolidone) (PVP) can be dissolved in ethanol. It will also dissolve in dichloroethane and cyclopentanone. It has a refractive index of 1.53 at $\lambda = 1.55 \mu\text{m}$, and we measured 4 dB/cm loss at $\lambda = 1.55 \mu\text{m}$. It is stable above 200 °C. It will dissolve in AZ5214 photoresist, AZ400 developer, and chromium and gold etchant. Baytron P in PVP is as conductive as Baytron P in PVA under poling conditions. This suggests that Baytron P in PVP may be a suitable top cladding material with the use of a top protective layer but is not a suitable bottom cladding material.

We then were able to achieve success using the PVP with the addition of a cross-linker and wetting agent. This allowed us to fabricate the first three-layer stack using conductive polymers for both the top and bottom claddings. The conductive cladding layers used in this three-layer stack configuration are a mixture of several chemicals. The host material was 15 wt % PVP in ethanol (ETH). The PVP/ETH blend was mixed using a rotator at room temperature, until the PVP was completely dissolved. Then 20 wt % of a modified Baytron P solution was added to make up the Baytron P/PVP conductive polymer. This solution was then mixed using a rotator placed within a 70 °C oven for 5 min. The mixture was filtered in a class 1000 clean room, first through a 1 μm GF/B glass fiber filter, and then through a 0.2 μm PTFE filter to eliminate particulates.

The modified Baytron P solution was a blend of 42 wt % regular grade Baytron P, 3.2 wt % 1-methyl-2-pyrrolidinone, 1.7 wt % Silquest A 187 (a silane available from Crompton

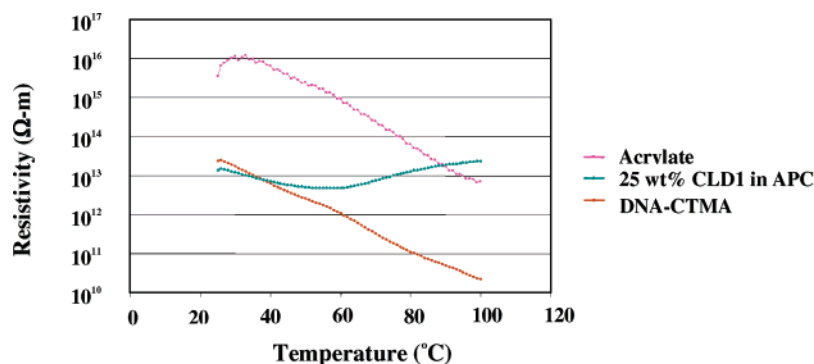


Figure 5. Resistivity vs temperature for acryliclate cladding material, DNA-CTMA complex and 25 wt % CLD1 in APC NLO polymer material.

Corporation), 52.5 wt % isopropyl alcohol, and 0.6 wt % Bayowet FT 219 (a fluorosurfactant available from Bayer Corp.). Mixing was performed under constant agitation in a beaker with a magnetic stirrer at room temperature.

1-Methyl-2-pyrrolidinone was used as an agent to assist film formation by increasing the gel-particle to gel-particle intermingling. This is necessary since Baytron P is not truly a mixture, but rather a gel-particle-in-water solution. Additionally, 1-methyl-2-pyrrolidinone aids in surface wetting and increases the overall conductivity of the mixture. Silquest A 187 was used because it is a cross-linking and adhesive agent for polycarbonate materials. Silquest not only made the Baytron P/PVP resistant to the organic solvents used in the NLO core material but also helped prevent the cladding layers from peeling away off both the NLO polymer core layer and the bottom ITO electrode. Isopropyl alcohol was used in order to increase the drying rate of the blend by assisting the movement of water through and out of the film. Bayowet FT 219 was used as the primary wetting agent for this modified Baytron P blend. Without the wetting agent we observed that the Baytron P/PVP would not coat the surface of the DR1/APC core layer.

The core layer we used consisted of 10 wt % DR1, in a mixture of 15 wt % APC in cyclopentanone. The APC/cyclopentanone solution was mixed using a rotator in a 70 °C oven until dissolved. DR1 was then added to the APC/cyclopentanone solution and mixed using a rotator at 70 °C until thoroughly blended (about 5 min). The mixture was then filtered through a 0.2 μ m PTFE filter.

The three-layer structure was created on a glass substrate. A 5 mm wide, 45 nm thick layer of ITO was sputtered on the glass surface. The ITO acted as the bottom poling electrode. A 2.9 μ m thick layer of the modified Baytron P/PVP was then spin coat deposited for the bottom cladding layer. The sample was then placed in a covered Pyrex dish, dried for 5 min in a 120 °C nitrogen atmosphere oven, and then transferred to a 120 °C vacuum oven for 90 min. A 3.2 μ m thick layer of DR1/APC was then spun on top of the bottom cladding layer and baked using the same parameters as for the Baytron P/PVP layer. A 2.9 μ m thick modified Baytron P/PVP layer was then spun on top of the DR1/APC for the second cladding layer and baked under the same parameters as before. The sample was then placed in the vacuum oven overnight near room temperature to remove any residual water and solvents. Finally, 5 mm wide top poling electrodes consisting of 10 nm chromium (Cr) plus 50 nm Au were deposited normal to the direction of the ITO electrode. This yielded several 5 mm \times 5 mm square volumes of polymer between the electrodes. The Cr was deposited for better adhesion to the polymer. Without the Cr, the top electrodes would crinkle during the poling process.

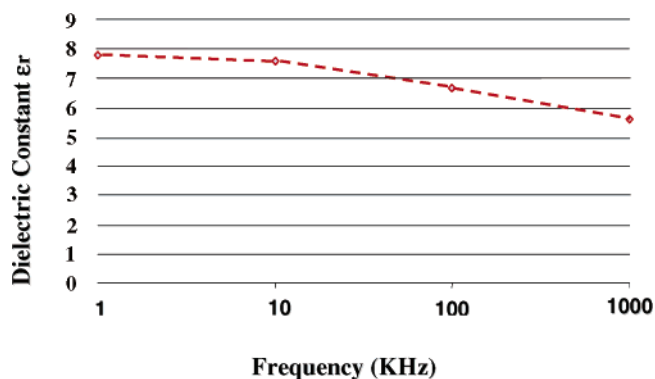


Figure 6. Dielectric constant vs frequency for DNA-CTMA complex.

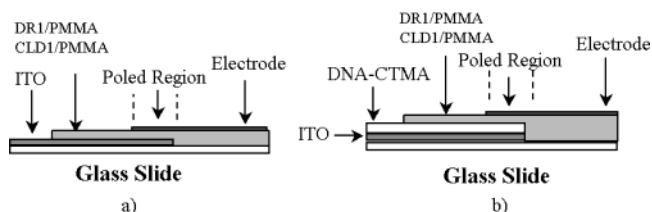


Figure 7. Device architecture of (a) baseline sample and (b) cladding sample.

The samples were then poled in a nitrogen atmosphere at 145 °C on a programmable hotplate. The hotplate, sample, and probes were encased in a plastic and metal container, with flow holes for the nitrogen outflow. The temperature was increased from room temperature to 120 °C in 10 min. After reaching 120 °C, 50 V dc was applied while monitoring the current. The sample was held at this temperature for 5 min while the current settled. The temperature was then ramped up to 145 °C in 10 min. After reaching 145 °C, the voltage was ramped up to 160 V dc, in 20 V increments. Two minutes after reaching 160 V dc, the sample was then cooled to room temperature with 160 V dc still applied. At room temperature the voltage was ramped down to zero. The 160 V dc provided 50 V/ μ m across the core layer. We also prepared a control sample with only a 3.2 μ m layer DR1/APC between the poling electrodes. This sample was poled under the same conditions as the three-layer structure.

A measurement of r_{33} was then made using the Teng and Mann setup, at room temperature. The measurement was taken at 20 V applied at 1 kHz. For the triple stack, r_{33} was measured to be 0.54–0.75 pm/V. The single-layer DR1/APC APC film had a measured r_{33} of 0.55 pm/V. Several sample regions were measured for each sample. These values, although small, indicated that most of the applied poling voltage was across the core layer using the modified Baytron P conductive

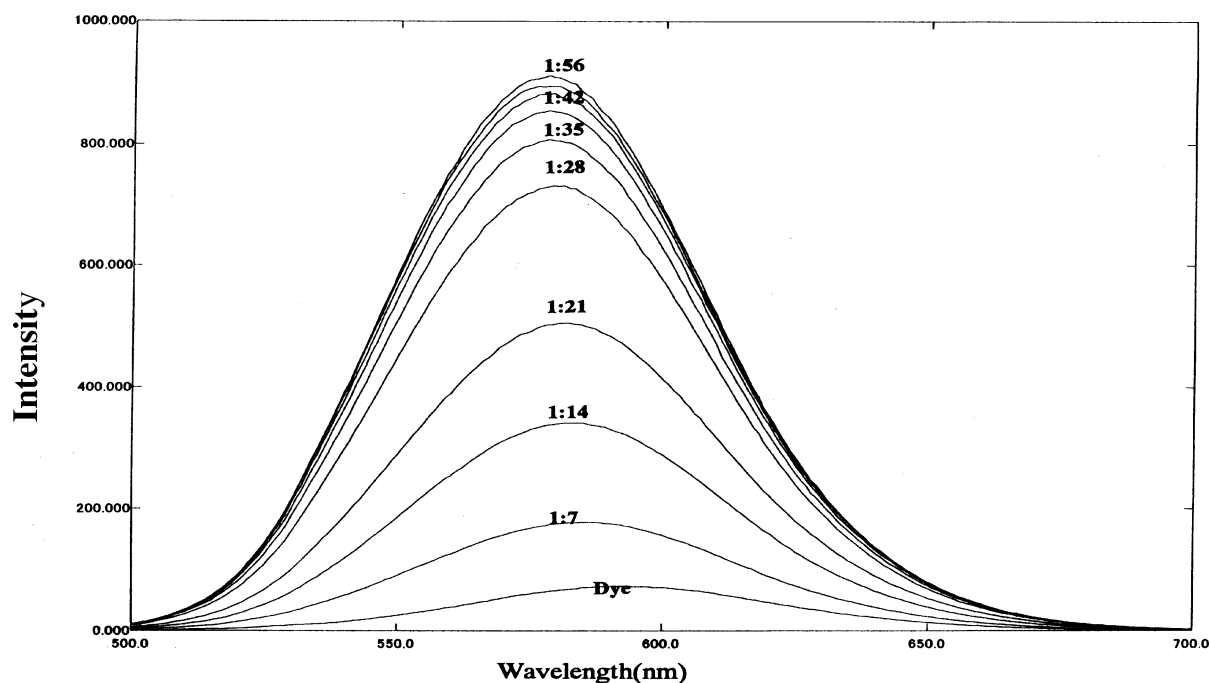


Figure 8. Fluorescence vs wavelength for various ratios of DMASDPB in DNA-CTMA.

TABLE 1: Electro-Optic Coefficient Using DNA-CTMA Cladding Layer

sample	r_{33} (measured)	r_{33} (calculated)
1.8 μm thick 10 wt % DR1 in PMMA no cladding	4.6 pm/V ($\pm 10\%$) ($\lambda = 633$ nm)	
1.7 μm thick 10 wt % DR1 in PMMA 1 μm thick DNA-CTMA	3.7 pm/V ($\pm 10\%$) ($\lambda = 633$ nm)	3.5 pm/V ($\pm 10\%$) ($\lambda = 633$ nm)
1.7 μm thick 10 wt % CLD1 in PMMA no cladding	4.9 pm/V ($\pm 10\%$) ($\lambda = 1550$ nm)	
1.7 μm thick 10 wt % CLD1 in PMMA 1 μm thick DNA-CTMA	4.3 pm/V ($\pm 10\%$) ($\lambda = 1550$ nm)	3.6 pm/V ($\pm 10\%$) ($\lambda = 1550$ nm)

claddings. However, the optical losses using Baytron P were observed to be too excessive for a viable device. Further testing is planned.

3.2. DNA Cladding Material. We first tested the DNA-CTMA film's resistance to cyclopentanone, dichloroethane, toluene, and tetrahydrofuran. These are typical solvents used for polymer-based optical waveguide materials. We found that these solvents had no visible effects on the DNA-CTMA film, indicating resistance to these types of solvents.

We measured the optical transmissivity of the 3 μm thick DNA-CTMA film using a Cary spectrophotometer. Figure 4 is a plot of the spectrophotometer data. As can be seen in Figure 4, the DNA-CTMA film demonstrated excellent transmissivity over a broad wavelength range.

We measured the refractive index of the DNA-CTMA thin film at two different wavelengths. At $\lambda = 633$ nm, $n = 1.526$ and at $\lambda = 1550$ nm, $n = 1.48$.

The resistivity of the 3 μm thick DNA-CTMA film measured 2 orders of magnitude less resistive than the acrylate cladding material and the 25 wt % Cheng Larry Dalton 1 (CLD1) in poly[bisphenol A carbonate-co-4,4'-(3,3,5-triethyl cyclohexylidene) diphenol] (APC) NLO polymer, all measured at the Lockheed Martin facility in Sunnyvale, CA. (See Figure 5.)

Figure 6 is a plot of the dielectric constant of DNA-CTMA versus frequency.

Finally, we performed a thermogravimetric analysis (TGA) of the DNA-CTMA complex which showed material stability up to 230 $^{\circ}\text{C}$ and 10% water absorption in air at room temperature.

These results suggest that DNA-CTMA is a good potential candidate optical waveguide material. With its resistance to the organic solvents used for polymer device fabrication, we explored its use as a cladding material for NLO polymer-based EO modulators.

Poling experiments were conducted using DNA-CTMA (butanol solvent) as a cladding layer and both DR1-PMMA and CLD1-PMMA as the NLO polymer core material. (See Figure 7.)

The films were spin deposited. We electrode poled both the control sample and cladding sample using the same parameters. The poling temperature was set at 80 $^{\circ}\text{C}$, and the poling field was set at 80 V/ μm . The EO coefficient was measured using the Teng and Mann technique. Table 1 contains the results of this experiment.

The calculated values for the EO coefficient using the DNA-CTMA cladding layer were 7% and 15% less than the measured values for the DR1 in PMMA and CLD1 in PMMA cores, respectively, suggesting that the poling efficiency was $> 90\%$ using a DNA-CTMA cladding layer. High poling efficiency, along with the anticipated optical propagation loss, and with resistance to those solvents used for PMMA and APC, render DNA-CTMA an excellent candidate for a bottom cladding material for NLO polymer devices. In addition, the fact that the alcohol solvents used for DNA-CTMA do not dissolve PMMA or APC render DNA-CTMA an excellent candidate for a top cladding material as well.

3.3. DNA Dye Intercalation. We blended DMASDPB dye to DNA-CTMA using an ethanol solvent, cast thin films, and measured the fluorescence as a function of dye concentration. (See Figure 8.)

The pumping wavelength was 1064 nm. One can see in Figure 7 that the maximum fluorescence was achieved for 1.8%

DMAADPB in DNA-CTMA. This corresponds to the 1:56 ratio in Figure 8. We also compared these results to a sample with 1.8% DMAADPB in PMMA and found that in solution the fluorescence for both samples was comparable. However, after casting films, the fluorescence measured 2 orders of magnitude higher for DMAADPB in DNA-CTMA.

Spiropyran-intercalated DNA-CTMA films were cast using an ethanol solvent, and their photochromic responses were measured. They exhibited a rapid response toward an irradiation by UV light, which we found could be repeated many times. We tested repeatability for 300 cycles, suggesting that novel DNA-based optical memory films might be possible.

A two-photon dye, sample 1433, being developed for cancer detection, optical limiting, and optical memory (See Figure 3), was blended with DNA-CTMA using a 2:1 chloroform/butanol solvent mixture. Then 1% dye in DNA-CTMA film was spin deposited and excited using 1064 nm laser with a 100 mJ pulse energy, 5 ns pulse length, at a 5 Hz repetition rate. Two-photon excitation was observed but not quantified.

NLO chromophores DR1 and CLD1 were mixed with DNA-CTMA using a 2:1 chloroform/butanol solvent blend. The samples were spin deposited on indium tin oxide (ITO) coated glass slides producing 5 μm thick films. The chromophore concentration used was 10% for both DR1 and CLD1. The samples were electrode poled at 50 $^{\circ}\text{C}$ with an applied electric field of 54 V/ μm . We achieved an EO coefficient of 2.13 pm/V at $\lambda = 633$ nm for the DR1 in DNA-CTMA sample. This is comparable to the EO coefficient of DR1 in PMMA films with the same concentration of DR1 and under the same poling parameters. We were unable to record any data for the CLD1 in DNA-CTMA samples. This could be due to the fact that the spacing between the ribs of the DNA was 0.2 nm and the length of the CLD1 chromophore was also 0.2 nm. We will investigate reducing the length of the chromophore.

The rare earth metal element europium (Eu) was found to form a stable and strong chelation with the DNA-CTMA complex. Thin films of Eu-FOD in DNA-CTMA were cast using an ethanol solvent. These samples exhibited strong amplification of fluorescence at 614 nm when irradiated with UV light. The amplification we achieved for the Eu-FOD in DNA-CTMA film was more than 100 times that of comparable Eu-FOD dissolved PMMA films. In addition, relaxation times of the fluorescence of the Eu-FOD in DNA-CTMA films were twice as long as those for Eu-FOD in PMMA films.

4. Conclusions

In summary, we have envisaged a new scheme for electrode poled NLO polymer EO devices that utilizes conductive polymers for the cladding layers, to maximize and enhance the poling efficiency. We have identified a proof-of-concept conductive polymer, Baytron P, cladding material for NLO polymer-based devices with adequate conductivity but excessive absorption. We have demonstrated the lowest poling voltage to date for electrode poling (300 V for a 2 μm thick film).

Identifying and/or developing optimal cladding materials will be crucial for viable NLO polymer-based devices. DNA-CTMA is a promising novel material for use as both a top and bottom cladding layer for NLO polymer-based EO devices as well as a core material host for nonlinear optical dyes. It has demonstrated excellent optical and electromagnetic properties thus far and has demonstrated excellent processability and compatibility characteristics.

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References and Notes

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