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13. ABSTRACT (Maximum 200 words) Report developed under SBIR contract. A new scheme for a LD-3 nonlinear optical (NLO) polymer opto-electronic (OE) modulator/switch is presented in this Phase I that have an order of magnitude shorter interaction length than the conventional NLO polymer OE devices operating at TTL voltage levels. It utilized LD-3 NLO polymer as core layer and 3,4-Polyethylene-dioxythiophene (PEDOT) conductive polymer as cladding layers to realize an effective 1 μm separation between the electrodes. The polymer processing and spin coating parameters were determined and optimized to produce triple stack film (cladding/core/cladding) to meet the design requirements of the Mach-Zehnder (MZ) switch. It has been demonstrated theoretically that the construction of MZ switch is possible using LD-3 NLO polymer as core and conducting polymer as cladding layers. The electro-optical coefficient of LD-3 waveguide was measured to be 5 pm/V at 790 nm when film was electrode-poled at 80 V/μm. The higher value of electrooptical coefficient can be achieved by using higher poling voltage in the presence of conductive cladding layers.					
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1.0 INTRODUCTION

1.1 Goal

The effort in this program was directed towards developing material processing systems that possess the mechanical properties and processing characteristics for use in flexible electronic and photonic devices. The main goal was to demonstrate the feasibility of fabricating Mach-Zehnder (MZ) switch using LD-3 NLO polymer material as core and PEDOT/PSS conducting polymer as cladding layers.

1.2 Background

Today optical fibers are used for high rate data transfer over long distances for telecommunication applications. For localized electro-optical processing (e.g., communication between multiple processors on a computer motherboard chip or for cable television distribution) the optical modulation and switching possible in polymeric waveguide materials, being quite “flexible and rugged”, offer a powerful basis for optical processing and for fabrication of optical interconnects, switches and devices. Such photonic circuit applications can be successfully implemented in polymeric waveguide systems with low cost even for highly complex structures.

The new generation of polymer based nonlinear optical (NLO) materials have the potential to dramatically reduce the cost of fabricating integrated optical devices (IOD). These photonic circuits cover a wide range of important applications. Polymeric IOD's are well positioned to take advantage of the developments over the last decade in the field of optoelectronic devices and nonlinear optical materials.

Historically, nonlinear optics and the implementation of its useful effects have been largely based on materials of inorganic origin, semiconductors and single crystals. Unfortunately, the production of inorganic NLO materials is costly and they are not particularly compatible with silicon-based electronic circuit processing and the production of waveguides is nontrivial. Inorganic NLO materials can have moderate to reasonably high second-order nonlinear optical activity (governed by $\chi^{(2)}$). They also tend to have high dielectric constants, which limits the ultimate speed of electro-optic modulators constructed in these materials. The current commercial materials are inorganic (quartz, LiNbO₃, KH₂PO₄, LiB₃O₄, GaAs) [1].

Recently NLO polymeric materials have attracted great attention and interest for application in devices like electro-optic modulators, high efficiency directional beam couplers, optical switches, frequency mixers, fan-in and fan-out couplers, etc. The nonlinearity (or molecular hyperpolarizability) of the organic polymeric materials can be larger than that of the inorganic crystals [2-7]. NLO polymeric materials have several desirable properties and unique advantages over the bulk materials and crystals.

- Ultrafast response time (femtoseconds regime) due to the electronic origin of the nonlinearity.
- NLO polymeric materials are “easily” synthesized, and tailor-made chromophores may be made.
- High nonlinear optical coefficients $\rightarrow \chi^{(2)}$.

- Thin film deposition methods may be used to cover a large area of the substrate by spin casting a film from a solution of the NLO polymer. This offers flexibility in processing and lower cost of device fabrication.
- Thin polymer films can be polar aligned (poled) and crosslinked to produce a dipole locked-in 3D network of hyperpolarizable nonlinear optical units.
- Small changes in the chemical structure of the NLO-polymer may be used to alter/modify the optical properties such as, transparency, refractive index, optical nonlinearity, and dipole moment.
- Thin films may be deposited on virtually any substrate or on hybrid circuits thus offering promise of powerful technology for newer opto-electronic devices.
- These materials have low RF frequency dielectric constants (approximately equals to the square of the refractive index) which allows very high frequency electro-optic modulation and high laser damage thresholds.

Some of the important features of the integrated optical devices (IOD) based on polymeric NLO materials are compared [8] with lithium niobate (LiNb_3) and III-V based (gallium arsenide, GaAs) IOD's in Table 1. It is clear from table 1 that the IODs made on LiNbO_3 and polymeric NLO materials can easily replace GaAs substrate. In particular, the polymer IODs offer better performance characteristics for modulation speed (>100 GHz needed in military and space communication), channel densities and fabrication cost over LiNbO_3 and GaAs and IOC size is not limited by the size of the substrate. The modulation speed (multi-GHz range) is only limited by the drive and receiver electronics. Micro to macro IODs can be fabricated using polymer NLO materials, e.g., AdTech's LD-3 NLO polymerTM. It is expected that the production cost would be ten times less than a comparable inorganic solid state device. Multiple integrated optical devices may be incorporated on the same substrate using photolithographic technique and conventional IC manufacturing equipment. Thus, while new NLO device processing technology is required to develop the required devices, existing technologies and expertise play a vital role in the development process of polymeric NLO integrated optical devices.

Polymer Microstructure Waveguide Technology (PMWT) Technological Challenge

Polymer NLO materials offer unique time response ranging over 15 orders of magnitude. The physical mechanism giving rise to the different response times are:

- Large nonresonant electronic nonlinearities, femto (10^{-5}) to picosecond (10^{-12}) range
- Thermal and motional nonlinearities, nano (10^{-9}) to millisecond (10^{-3}) range
- Photochemical nonlinearities

The contribution of each of these nonlinear optical processes needs to be understood in order to design polymer NLO devices with ultrafast response time!

Another major attribute of the polymer NLO materials is their low dielectric constants compared to inorganic materials. The dielectric constant (in the RF and millimeter wave frequency range) is approximately 3 for polymers compared to 28 for LiNbO_3 . In polymer NLO waveguides, the fact that the dielectric constant nearly equals the refractive index squared means that the microwave

electrical modulation field and the optical field propagate at roughly the same phase and group velocities. The matching of the velocities means that the modulation efficiency is high in traveling wave devices (allowing fabrication of shorter devices that thus lowering the device loss) and that the

Table 1. NLO polymeric integrated optical devices vs. LiNbO₃ and GaAs [8]

Switches/Devices/Features	Polymer-NLO	Lithium niobate (LiNbO ₃)	Gallium arsenide (GaAs)
Planar Waveguide	Yes	Yes	Yes
Channel Waveguide	Yes	Yes	Yes
Electro-optic Modulator	Yes	Yes	Yes
Waveguide Amplifier	Yes	Yes	Yes
Waveguide Lens	Yes	Yes	Yes
Multiplexed Grating	Yes	No	No
Dielectric Constant	Low	High	High
Potential Modulation Speed (GHz)	> 100	~ 30	~ 30
Waveguide Propagation Loss (db/cm)	< 0.1	< 0.1	0.2 – 0.5
Channel Waveguide Density (Ch/cm)	1250	333	500
Integrated Circuit Size	Unlimited	Limited	Limited
Large Area Multiple Guiding Layer	Yes	No	No
Fabrication Cost	Low	High	High

modulation frequency can be made quite high without loss of modulation fidelity. Rapid loss of microwave-to-optical phase matching over even relatively short waveguide lengths due to large dielectric constant of LiNbO₃ results in higher drive voltages and higher power requirements in such devices and the modulation frequencies are limited to 8 to 24 GHz. By contrast; traveling waveguide modulators constructed of polymeric NLO materials can readily achieve a maximum frequency of >50 GHz in a single mode device and is limited only by the electrode losses. These high frequencies are accessible because of the lack of velocity mismatch in the modulator.

Some of the state-of-art devices that could be manufactured with the second order ($\chi^{(2)}$) polymeric NLO materials are:

- **Travelling-wave Mach-Zehnder Electro-optic Modulator**

No velocity mismatch implies higher frequency devices are possible with polymeric NLO material

- **Electro-optic Bragg cell**

High speed radar signal processing – 20 GHz as a target

- **Second Harmonic Generation**

High efficiency frequency doubling, especially of a Diode Laser

The recent successful developments in synthesizing various polymeric NLO materials with large second order nonlinearities (hyperpolarizability) have made the polymer thin films viable candidates for integrated optics. The most fundamental electro-optic device is an electro-optic modulator. A thin film waveguide electro-optic modulator normally uses one of the three modulating systems. These are:

- Mach-Zehnder interferometer
- Directional coupler
- Rotation of the optical polarization

The Mach-Zehnder configuration is the most common design, and high frequency traveling wave devices have been constructed matching the optical and the microwave phase velocities [9-12]. Some characteristics of a Mach-Zehnder modulator using LiNbO_3 and polymeric NLO material are compared in the following table (Table 2).

Table 2. Mach-Zehnder electro-optic modulator using LiNbO_3 and polymeric NLO material

PARAMETERS	LiNbO_3	POLYMER NLO
Switching Voltage (V)	3.5 – 10.5	0.7 – 1.3
Power Requirement (W)	0.6 – 5	0.03
Maximum Frequency (GHz)	8 - 24	>50

There is also a great need in both commercial and military (US Air Force) domain for a compact diode laser source in the 450-500 nm region for optical data storage. The highly efficient, almost colorless NLO materials (transparent between 400 and 2000 nm) are prime candidates for frequency doubling of existing laser diodes.

Why Polymeric NLO Materials?

The polymeric NLO materials are relatively easy to synthesize compared to growing single crystals or bulk crystalline materials. These can be easily purified and therefore chemically pure, reproducible materials may be guaranteed. They are also cost effective to produce. The polymeric

NLO materials have high electro-optic coefficients. For new generation polymeric NLO materials, an electro-optic coefficient in the range 10-30 pm/V is common.

NLO polymers have several attractive potential characteristics, which many researchers have tried to capitalize on over the past decade. These include a high EO coefficient for low voltage operation, a low dielectric constant for high-speed modulation, low temperature processing for integration of optics with electronics, excellent index match to optical fibers and simplified fabrication for lower cost. However, several barriers have prevented them from progressing much further than research devices.

Some of the potential benefits/commercial applications of the present research efforts are outlined:

- To produce a cohesive capability to supply tailored NLO material to users, devices to system developers and design data to the technology community.
- Generation of new flexible electronic and photonic devices to decrease in delivered cost, increase data speed, reduce weight, and reduce electrical power requirements over those devices used in the current electronic design.
- The dual applications include multimode optical fibers, optical switches, optical modulators, and intra-inter computer connects, and sensors.
- Commercial applications in the field of optical interconnects, waveguides matching closely the properties of glass multimode optical fibers, optical switches, optical modulators, intra-inter-computer connects, sensors.
- NLO polymeric material offers compact packaging and high efficiency.

1.3 Technical Objectives

The voltage necessary to realize a π phase shift change is defined as half wave voltage and is given by $V_{\pi} = (\lambda d)/(n^3 r_{33} L)$.

Current properties for the NLO polymers include an EO coefficient $r_{33} = 11-26$ pm/V at $\lambda = 830$ nm, a propagation loss of 1-2 db/cm at $\lambda = 830$ and a long-term poling retention temperature stability of $>80^{\circ}\text{C}$. These properties should be adequate for the development of a competitive OE integrated optic device. Substituting the properties of various competing materials into above equation gives one a good material comparison. These are presented in Table 3.

From Table 3 it is clear that the NLO polymer is not being utilized to its full potential. **If one could find a way to reduce the electrode separation for the NLO polymer devices, the switching voltage could be reduced.** For $d = 1$ μm , using the above parameters, $L = 1.5$ mm and the voltage-length is reduced to 7.5 V-mm. Thus, an integrated optic OE device using currently available NLO polymers has the potential of having the lowest switching voltage for any integrated optic OE modulator/switch demonstrated to date.

Table 3. NLO material comparison

Material	V_{π} (V)	λ (nm)	N	r_{33} (pm/V)	D (μm)	L (mm)	Voltage-length (V-mm)
Bulk III-V Semiconductor	5	830	3.42	1.5	2	5.6	28
LiNbO ₃	5	830	2.2	32	9	4.4	22
MQW III-V Semiconductor	5	830	3.42	4.7	2	1.8	9
NLO Polymer	5	830	1.63	26	8	12	60

1.4 Phase I Project Tasks

Through the performance of the following tasks, we plan to accomplish the objectives and reach the goal of the proposed nonlinear optical (NLO) polymer opto-electronic (OE) modulator/switch project under Phase I.

Task 1 - Define and Establish Structures and Requirements

The geometry for straight and curved structures for single and multimode operations will be theoretically determined and the design, structure, and dimensions of waveguides and modulator/switch requirement will be established in the planned structure.

Task 2 - Measurements of Thin Films

Uniform thin films of LD-3 NLO Polymer™ will be cast and the parameters will be optimized for fabrication in Task 3. The characteristics of the thin films, especially the electro-optic (EO) coefficient, loss parameter, dielectric constant and refractive index will be measured. Chemical formula changes will be examined to solve problems as they are encountered.

Task 3 - Fabricate Modulator/Switches

Using the data from Task 1 and Task 2 the modulator/switch will be fabricated. To fabricate the lowest switching voltage integrated optic OE modulator/switch, we will demonstrate the feasibility of decreasing the core thickness and increase the conductivity of the cladding layers in order to pole the core layer in the conventional triple stack polymer device configuration to its full NLO value. Chemical formula changes will be examined to solve problems as they are encountered.

Task 4 - Test and Evaluate

The optical characteristics of devices fabricated under Task 3 will be tested with particular reference to attenuation, propagation and bending losses, coupling efficiencies and cross talk. Chemical formula changes will be examined to solve problems as they are encountered.

Task 5 - Prepare Final Report

1.5 Phase I Work Plan

To help develop and produce the lowest switching voltage integrated optic OE modulator/switch, we have investigated the feasibility of decreasing the core thickness to 1 μm and rendering the cladding layers conductive. Several researchers have recently increased the conductivity of the cladding layers in order to pole the core layer in the conventional triple stack polymer device configuration to its full NLO value. This conductivity is adequate for poling, but not adequate enough to act as switching electrodes. Using conductive polymers, such as polyethylene dioxythiophene polystyrene sulfonate (PEDOT) and doped polyanilene, we have been able to achieve a conductivity of 0.05 $\Omega\text{-cm}$, which is roughly on the order of Ge. This conductivity has also been shown to remain constant over a wide temperature range.

In addition to good conductivity, PEDOT has demonstrated good transmissivity, 80% at 830 nm for a 1.5 to 2 μm thickness. Planer waveguide losses using PEDOT as the cladding layers have been measured at 8-11 dB/cm, which is well within what is necessary for these particular devices.

In order to align the moieties to attain the nonlinearity of the material, one needs to pole the polymer with a dc poling voltage. The level of this poling voltage is typically 150-200 V/ μm . Hence, for a conventional triple stack device configuration, where the electrode separation is typically 6-10 μm , one can expect a poling voltage of 900-2000 volts. Voltage levels of these magnitudes prevent the ease of integration of optics with electronics. Poling experiments using conductive polymers have been performed using PEDOT as the cladding layers and PMMA/DR1 for the core. Poling at 150 V/ μm , we have been able to achieve an EO coefficient equal to that when poling only a single layer of the NLO polymer. This is also twice as high as that which can be achieved for a conventional triple stack device using passive polymer cladding layers. In addition, since we effectively have a 1 μm separation between the electrodes, the total poling voltage for this new scheme for an NLO polymer OE device is only 150 volts as opposed to 900-2000 volts for conventional NLO polymer OE devices.

Spin Casting of Thin Film on Substrates

In order to fabricate high-speed optical switches and waveguides from NLO polymer, it is necessary to produce uniform thin film. In contrast to older methods of fabricating thin films for waveguides by epitaxially grown materials, a high-cost technique, the production of thin films from NLO polymer is based on simple cost-effective procedure of spin coating from organic solutions of NLO polymer, followed by vacuum drying and electric field poling. The level of poling induces orientational order in the film, which in turn affects the electro-optic coefficient and the coupling between the waveguides [14]. Furthermore, the total active length of the poled waveguide influences the propagation loss. Hence, it is necessary to measure and optimize properly, all of the pertinent parameters of a device fabrication for total evaluation of the technology.

Earlier studies on the temporal stability of the LD3 films has established that the poled films retain over 95% of their SHG at 100°C over 1400 hours. This guarantees the stability of the devices to be fabricated under Phase I for a period of several years at ambient condition. The advantage of LD3 over other NLO material is that once it is crosslinked and poled the thermodynamic relaxation of the dipolar alignment is negligible.

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2.0 DEFINE AND ESTABLISH STRUCTURES AND REQUIREMENTS

2.1 Overview

The goal of this work was to design a three-stack, 2- μm -wide waveguide structure consisting of a nonlinear optical (NLO) polymer core and symmetrical cladding layers of a slightly conducting polymer deposited onto a conducting substrate. This structure is configured into an input channel that splits into two straight, parallel channels that, after an appropriate distance, rejoin into a single output channel. On one of the parallel channels a gold electrode is deposited. By raising the temperature of this Mach-Zehnder (MZ) switch/modulator to an appropriate high value and applying sufficient voltage to this channel, roughly 100-200 V/ μm , the NLO polymer becomes poled, that is, a permanent electric polarization is induced. If the conducting cladding layers have a conductivity that is at least 10^3 times greater than that of the core material, essentially all of the applied voltage appears across the core. By maintaining the temperature and voltage for an extended period approximately one to three hours, the polarization is permanent after the temperature is returned to the ambient value. This device splits injected plane polarized light into the two parallel channels, which, with no voltage applied to the poled channel, recombines constructively in the output channel. The switch/modulator is “on.” Upon applying a small amplitude voltage, 5 V or less, between the substrate and the gold electrode on the poled channel, the phase of the light is shifted as the light propagates along this channel. If the length of the parallel channels is appropriate, this light will be 180° out of phase from the light entering the output leg from the unpoled channel. This will cause cancellation of the forward propagating wave. The switch/modulator is “off.” Sketches of this design are given in Figure 1.

The waveguide MZ switch/modulator design is not new in of itself. What is new is an all-polymer MZ device. There are several important issues that need settling before there is reasonable hope that

such a device can be fabricated and made to work. Nevertheless, it is straightforward to develop a paper design that works. This is shown in Figures 2a and 2b for the “on” and “off” states. This design is a “channel” design in that the core is imbedded in a thick layer of the cladding material. The other possible design is the “ridge” design in which the waveguide structure is imbedded in air on all sides. The ridge design raises two concerns: 1) it is not clear that this structure can actually be made without damaging the device during the fabrication; 2) There is concern for the mechanical and performance stability of the device if left exposed to the atmosphere. It must be sealed in some manner, which may end up making it a channel design.

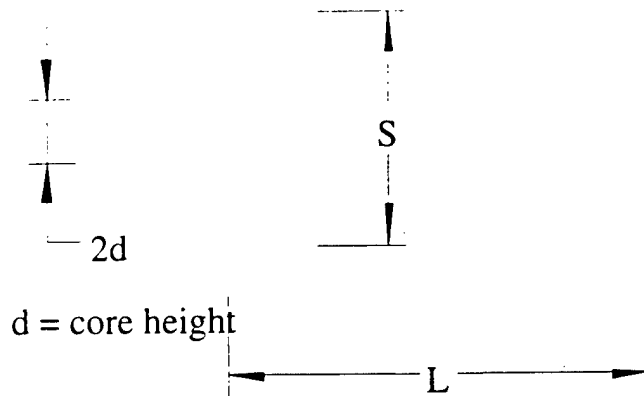


Figure 1. Rectangular waveguide design for a Mach-Zehnder photonic switch/modulator

2.2 Design of a DC MZ Switch

The design of a dc MZ switch shown in Figure 2 illustrates a possible selection of parameters centered on the information that is available on the LD-3 NLO polymer that is supplied by Ad Tech Systems Research. This design is for 850-nm light polarized normal to the substrate. The index of refraction was obtained from two published values for the poled polymer using the Sellmeier equation. The index plot and data are given in Figure 3 and Table 4.¹ This design assumes that whole device has been poled. This, in principle, could be done by using “corona poling” to simultaneously pole all the devices on a given substrate. The gold electrodes would then be applied after the poling. The effect of this procedure on the slightly conducting cladding layers and the surrounding medium is not known. The design was developed in the period of January through February 1999, using the BeamPROP software package.² The parameters for this model are as follows, where the side index $n_3 = n_2$:

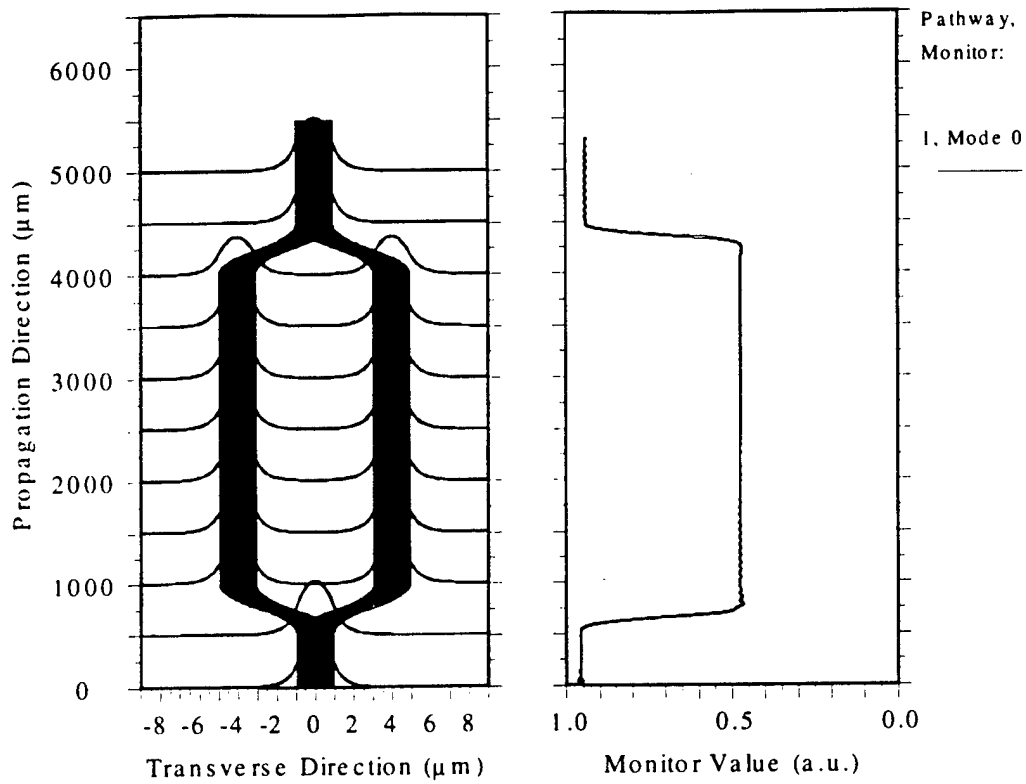


Figure 2(a). Mach-Zehnder switch in "on" state.

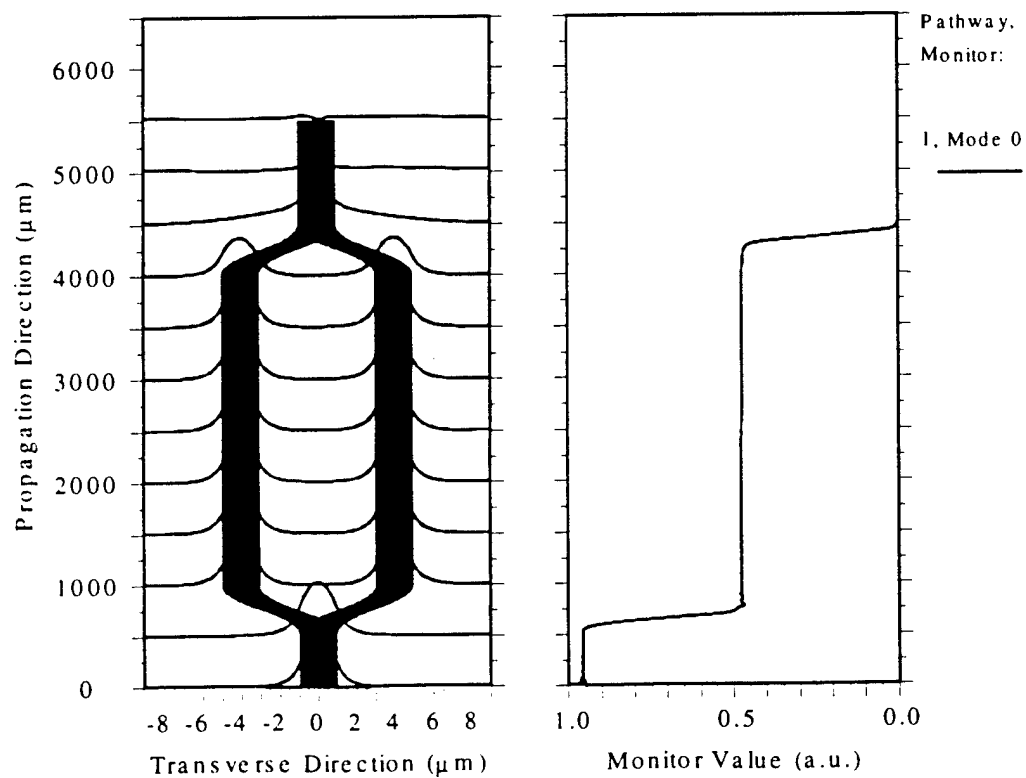


Figure 2(b). Mach-Zehnder switch in "off" state.

Structure: Channel (i.e. NLO polymer imbedded in the cladding)
 Launch Mode: TM Mode 00
 Wavelength, λ : 850 nm
 Core index, n_1 : 1.622
 Clad index, n_2 : 1.59
 Core height, d : 1 μm
 Core width, $b = 2d$: 2 μm
 Clad height: 2 μm above and below the core
 Channel spacing, S : 8 microns (center to center)
 EO coefficient, r_{33} : 20 pm/V
 Interaction length, L : 3 mm
 DC switch voltage, V_S : 5 V

The spacing of the two straight channels was the minimum value that showed no interaction between the channels as determined by BeamPROP. The value of the clad index was obtained from the solutions to rectangular waveguide equations. These solutions give the dependence of the propagation constant β on the frequency parameter $V = kd(n_1^2 - n_2^2)^{1/2}$ for each allowed mode of wave propagation in the waveguide, where $k = 2\pi/\lambda$.³ For this design effort, the only unknown in V is n_2 . The normalized form for β provides the most useful way to characterize the waveguide performance versus n_2 . The normalized propagation constant $b = (\beta^2 - n_2^2 k^2) / [(n_1^2 - n_2^2) k^2]$. By

Table 4. Fit of the Sellmeier equation to Reference No. 1 values for poled LD-3 (shown in bold italics)

λ (μm)	n_1 (LD-3)
0.5	1.748
<i>0.532</i>	<i>1.719</i>
0.55	1.705
0.6	1.673
0.65	1.648
0.7	1.628
0.75	1.612
0.8	1.599
0.85	1.588
0.9	1.578
0.95	1.571
1	1.564

1.05	1.558
<i>1.064</i>	<i>1.557</i>
1.1	1.554
1.15	1.549
1.2	1.545
1.25	1.542
1.3	1.539
1.35	1.537
1.4	1.534
1.45	1.532
1.5	1.530
1.55	1.528
1.6	1.527

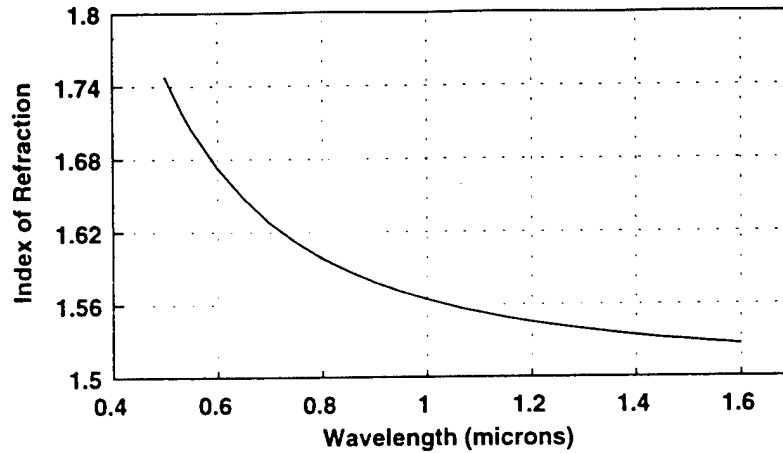


Figure 3. Plot of the index data for poled LD-3 from Table 1.

plotting this constant against V , it can be clearly determined what range of the cladding refractive index, n_2 , will support a guided wave in the waveguide structure.

The interaction length, L , for the design in Figure 2 is the value found from BeamPROP to give the "off" condition. The TTL switching voltage of 5 V applied to the electrode was chosen. This voltage is to produce a change in the "bulk" index n_1 of Δn over the interaction length, L , such that the phase of the wave is shifted by 180° relative to the initial phase entering the straight section from the input channel. BeamPROP provided $\Delta n = -2.125 \times 10^{-4}$ as the value necessary to produce the "off" state. To achieve this π phase shift, the theoretical value of L is $L = \lambda / (2 |\Delta n|) = 2.0$ mm. However, BeamPROP required that to achieve the "off" state $L = 3.0$ mm. This discovery revealed that the guided waves actually see an effective core index that is smaller than the bulk index given by n_1 . This means that a larger interaction length, L , is required than that predicted by the theory from the change in the bulk index. Other waveguide designs were examined and were found to demonstrate the same characteristic.

Figure 4 shows the normalized propagation constant for the fundamental TM mode, b_{00} , plotted versus the clad index, n_2 , for three wavelengths in the "ridge" type structure. The values of n_1 in Table 1 were used here. For the waveguide to support this mode, b_{00} must be greater than zero. As n_2 approaches n_1 , the mode approaches cutoff. In this region most of the field energy of the mode is traveling outside the core and, therefore, giving inefficient propagation. The desired operating point is near the maximum of the b_{00} plot. In Figure 4(a) for $\lambda = 850$ nm, this would be at value of $n_2 \approx 1.53$. As can be seen in Figures 4(b) and (c), the required clad index changes significantly for the infrared wavelengths of interest in waveguide communication systems. These results underline the importance of making index measurements in the spectral region of interest.

The electro-optical coefficient of interest here, r_{33} , is related to this index change and switching voltage, V_S , by $\Delta n = -n_1^3 r_{33} V_S / 2d$. For the values used here, the required electro-optical coefficient

is $r_{33} = 20$ pm/V. This coefficient is higher than the 11 pm/V value reported by Ad Tech for poled LD-3 at 1300 nm. Unfortunately, there are no supporting published values for this coefficient at any wavelength. We carried out preliminary measurements of this coefficient at 790 nm with Dr. Grote's help. A value of $r_{33} = 5$ pm/V was obtained with electrode poling of LD-3 at 80 V/ μ m. It is projected that using conductive cladding layers, twice the poling voltage should be possible giving 10 pm/V at 790 nm. A predictive model⁴ gives for the wavelength dispersion in r_{33} to be $r_{33} \propto [3 - (\lambda_m/\lambda)^2]/[1 - (\lambda_m/\lambda)^2]^2$. From this expression, we estimate $r_{33} = 6.7$ pm/V at 1550 nm. The basic effect of these low values of r_{33} would be to increase the length of the interaction region, L. However, it is hoped that further poling efforts and measurements of the coefficient will reveal higher values.

2.3 Transmission and Refractive Index Issues

Preliminary spectrophotometer measurements were made on PEDOT and LD-3 films to confirm that these materials have adequate light transmission characteristics. Figures 5 and 6 present these spectra for the two materials, which confirm that these materials have good transmissivity. However, more data is needed to ensure that the absorption losses are <25 dB/cm for a 5-mm-long device.

A potentially important issue is that the refractive index of a poled polymer changes with the degree of poling, that is, with the resulting value of r_{33} . Dr. Zhang of the University of Southern California provided the data given in Figure 7 for poled films of the NLO polymer CLD/PMMA.⁵ The refractive index change from unpoled to the maximum poling is 0.036.

This degree of change will significantly impact the device performance. We expect to see a similar result in the refractive index of poled LD-3. The plot given in Figure 3 for poled LD-3 is based solely on extrapolated data. Clearly more reliable data is needed. To accurately determine the required interaction length, which directly impacts the mask layout, measured values or good approximations of poled and unpoled indices of refraction of LD-3 at the desired wavelengths are needed.

These uncertainties also extend to the refractive indices of the PEDOT material that was the initial choice for the slightly conductive polymer cladding. This material may not be compatible with LD-3 at longer wavelengths than 850 nm. No information is available at this time regarding the wavelength of the one reported index value for PEDOT of $n = 1.53$. Furthermore, there is circumstantial evidence regarding the measurement procedure that this value is an effective index rather than a bulk value. New measurements are essential to establishing switch/modulator designs that have a reasonable probability of operating.

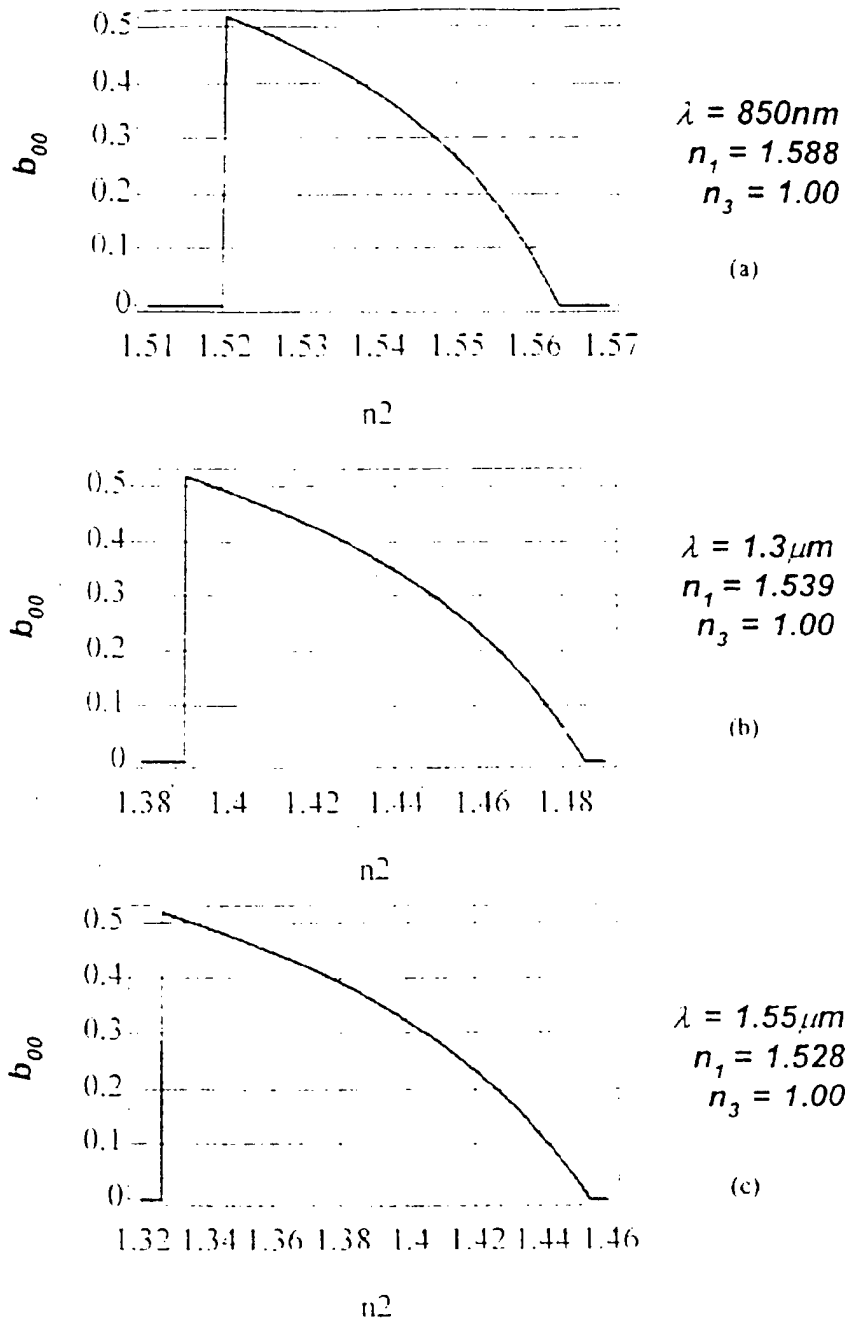


Figure 4. Normalized propagation constant plots for a “ridge” waveguide immersed in air ($n_3=1$) at three wavelengths using the index values in Table 1 for the core index, n_1

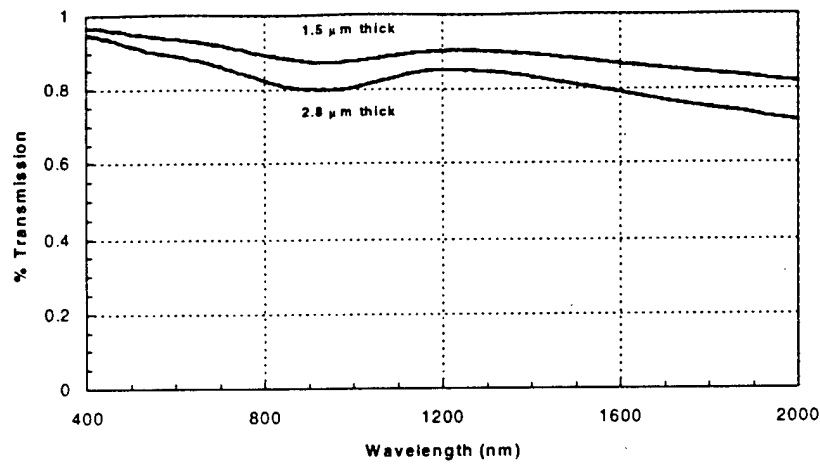


Figure 5. Transmission spectra of two PEDOT films of 1.5 and 2.8 μm thickness

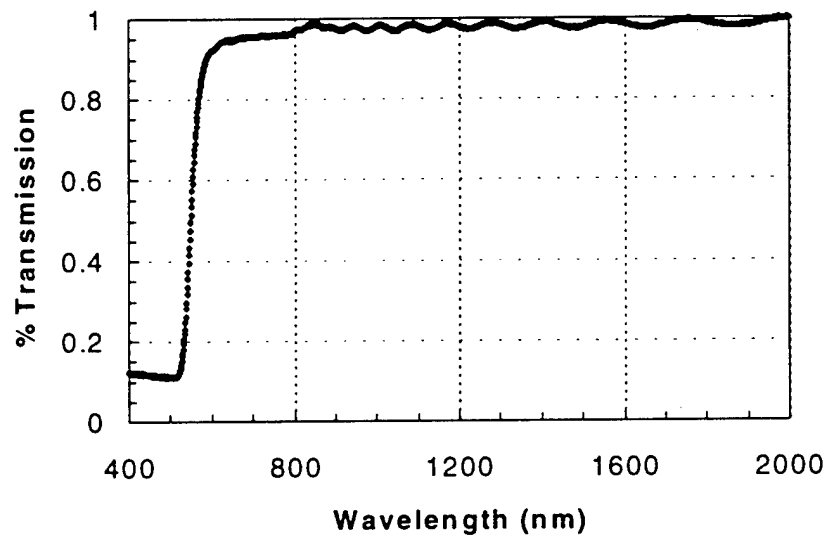


Figure 6. Transmission spectrum of a 1- μm thick crosslinked LD-3 film

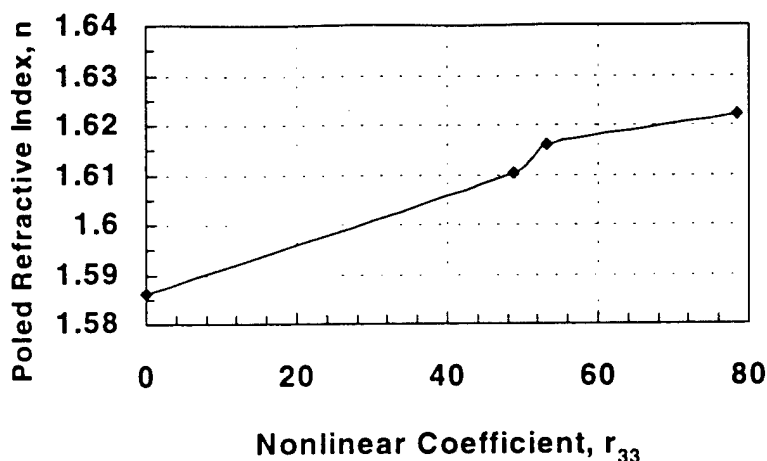


Figure 7. Dependence of the poled refractive index of the NLO polymer CLD/PMMA on degree of poling from Reference No. 5

References:

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2. BeamPROP, version 1.1, "A CAD program for design and simulation of photonic integrated circuits," (Columbia University and RSoft, Inc.) 1996.
3. D. Marcuse, *Theory of dielectric optical waveguides* (Academic Press, New York, 1974).
4. Singer, Kuzyk and Sohn, "SKS predictive model for r_{33} " (private communication, 1987).
5. Cheng Zhang, Organic Polymer Chemistry Group, Chemistry Department, University of Southern California (private communication, 1999).

3.0 POLYMER PROCESSING FOR THIN FILM MEASUREMENTS

The main effort here was in preparing spin coated specimens and measuring the resulting substrate-mounted thin films using a profilometer. Issues that relate to the solution concentration, spin speed, and spinning time were solved, which gives the parameters needed to produce a desired film thickness.

3.1 Materials

Baytron P solution, a conductive polymer solution, was obtained from Bayer Corporation and used as received. The Baytron P is an aqueous solution containing 0.5 wt.% 3,4-polyethylenedioxythiophene (PEDOT) and 0.8 wt.% polystyrenesulfonate (PSS). Poly(vinyl alcohols) (PVA) (99 + % pure) having four different average molecular weight distributions were obtained in the hydrolyzed form from Aldrich and used as received. The average molecular weights

of PVA were $M_w = 31k-50k, 89k-98k, 85k-146k$ and $124k-186k$. Cyclohexanone (99 + %), ACS reagent grade, was obtained from Aldrich. Cyclohexanone was freshly distilled (dry cyclohexanone) prior to use. Methanol (99.9% pure) and acetone (histological grade) were obtained from Fisher Scientific and used without any further purification. 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, a crosslinking material for LD-3 NLO polymer, was obtained from Pfaltz & Baur Inc. and used as received. ACS reagent grade Water was obtained from Aldrich and used as received.

The indium-tin oxide (ITO) coated float glass substrate was obtained from Thin Film Devices, Inc., Anaheim, California. The properties of the ITO coated float glass, as reported by the manufacturer, are given in Table 5.

Table 5. Characteristic properties of ITO coated glass slide

Properties	Description
Substrate diameter	50 ± 0.25 mm
Substrate thickness	1.524 mm
Indium-Tin oxide coating thickness	3000 Å, sputter coated
Resistivity of ITO coating	10 ohm/sq nominal
Transmission	65% at 550 nm
Coating defects	80/50
Non-Uniformity of coatings	$\pm 5\%$

3.2 Preparation and Spin Coating the Cladding Material

A 10 wt.% aqueous solution of PVA was prepared and blended with Baytron P solution to obtain a conductive cladding solution. The resulting cladding solution was stirred for at least 4 hours at a slightly elevated temperature ($\sim 40^\circ\text{C}$) to allow for thorough mixing of PVA with PEDOT/PSS. The cladding solution was then cooled to room temperature and syringe filtered, first through a $2.0 \mu\text{m}$ prefilter and then with a $0.45 \mu\text{m}$ fine filter. The filtered conductive cladding solution was then spin cast on to the substrate surface.

In order to obtain a uniform coating with desired film thickness, a series of cladding solution mixtures, having various PEDOT/PSS solution to PVA solution weight ratios, were prepared. Also, the PVA molecular weight in the conductive cladding solution mixture was varied in order to optimize the cladding layer thickness. For this purpose, PVA having four different molecular weight distributions, $31k-50k, 89k-98k, 85k-146k$ and $124k-186k$, were used.

To obtain a uniform and complete coating of desired thickness, the coating parameters such as, cladding solution composition, coating speed, coating time and sample volume used were optimized. The substrate surface was completely covered with the cladding solution as described below. For a given cladding solution composition, sample-volume and spin time, the spin speed was varied to obtain a series of spin coated samples having different coating thicknesses. The coating thickness was measured using a SLOAN DEKTAK II profilometer. A calibration curve (thickness vs. spin

speed) was then constructed. Once the calibration curve was obtained, appropriate spin speed was selected to obtain the desired film thickness.

3.3 Substrate Preparation and Spin Coating Technique

The substrate was mounted and centered on the sample stage of the spin machine. While spinning at 1000 rpm, the substrate surface was spray rinsed first with acetone and then with methanol. The compressed nitrogen gas (N₂) was blown over the substrate surface several times to dry off the surface completely. The vacuum pump attached to spin machine generated good vacuum in the range of 25-28 inch Hg to hold the sample down while it was spinning. The predetermined spin speed, acceleration and de-acceleration rates were set on the spin machine. The acceleration was set at a maximum rate where the pre-set spinning speed was attained in an approximately less than a second and the de-acceleration was set at a maximum rate where sample comes to a complete rest in less than a second at the end of the spinning cycle. Once all the adjustable parameters were set on the spin machine, the test solution was evenly spread over the whole substrate surface using a clean and dry pasteurized glass pipet and the spin machine was started. At the end of the spin cycle, the sample was dried and film thickness was measured.

3.4 Spin Coating the LD-3 NLO Polymer

The LD-3 NLO polymer is soluble in dry cyclohexanone and other organic solvents. 1.0 g of LD-3 polymer was dissolved in 10.0 mL of dry cyclohexanone. The solution was slightly heated and constantly stirred using a magnetic stir bar to completely dissolve LD-3 NLO polymer. The solution was cooled to room temperature after LD-3 was completely dissolved in cyclohexanone. 0.6 g of crosslinker (3,3'-dimethoxy-4,4'-biphenylene diisocyanate) was then added to the LD-3 solution. The solution was constantly stirred using a magnetic stir bar until the crosslinker was completely dissolved in the solution (for about 0.5 hour). The resulting LD-3/crosslinker solution was immediately syringe filtered, first through a 2.0 µm prefilter and then through a 0.2 µm fine filter. Within one hour after it was made, the filtered LD-3/crosslinker solution was spin cast on to the substrate surface. For about 1.0 mL of sample volume the spinning time was set at 90 seconds and the spinning speed was varied to obtain a calibration curve similar to the cladding layer. The spin cast film was vacuum dried overnight at room temperature and thickness was measured. After the thickness of the dried film was measured, the film was cured at 150°C for 2 hours and thickness was measured again to see if any reduction in the film thickness has taken place as a result of further solvent removal.

3.5 Adhesion Test

It is imperative that the spin coated cladding films and LD-3 films maintain their structural integrity in an electro-optic device for a long period of time. Simple adhesion tests were carried out using a Scotch Tape™ (3M) to test the bonding between cladding layer and substrate and between cladding layer and LD-3 film.

LD-3 NLO polymer containing a crosslinker was spin coated on to the glass substrate and dried overnight in a vacuum oven at room temperature and then a layer of PEDOT/PSS/PVA film was spin coated on top of it. A total of six such samples were prepared. Three samples were subjected to the cure cycle; 150°C for 2 hours in air and three other samples were left uncured inside the desiccator. One samples each from cured and uncured conditions were exposed to de-ionized water. Two samples each from cured and uncured conditions were exposed to cyclohexanone. After 24 hours of exposure in de-ionized water and cyclohexanone, the film quality was visually evaluated and a simple adhesion test was performed using a Scotch Tape™ (3M) to test the integrity of the film.

3.6 Results and Discussion on Polymer Processing

Thickness Measurements

A typical profilometer trace of LD-3 NLO polymer film with crosslinker, spin coated on to a glass slide, is shown in Figure 8. The film was deposited from solution containing 0.050 g of LD-3 NLO polymer and 0.022 g of crosslinker dissolved in 1.0 mL of Cyclohexanone. The coating parameters were set at 1000 rpm for 90 seconds for a 1.0 mL sample-volume. The film thickness was measured to be about 0.6 μm after the film was cured at 150°C for 2 hours. The thickness vs. spin speed calibration curve for LD-3 NLO polymer with and without crosslinker are shown in Figures 9 and 10, respectively. The LD-3 NLO polymer film without crosslinker was deposited from solution prepared in cyclohexanone (0.1 g/mL). The film was baked at 150°C for 2 hours in air prior to thickness measurements. The LD-3 NLO polymer film with crosslinker was deposited from solution containing 0.1 g of LD-3 NLO polymer and 0.6 g of crosslinker dissolved in 1.0 mL of Cyclohexanone. The film was cured at 150°C for 2 hours in air prior to thickness measurements. The thickness of the LD-3 NLO polymer film was found to decrease by 5-9% when LD-3 coated specimens vacuum dried overnight at room temperature were further baked at 150°C for 2 hours. This result indicates that overnight vacuum drying at room temperature is not sufficient to remove solvent (cyclohexanone) completely from the LD-3 film.

It is obvious from the calibration curve that to produce a 1.0 μm thick crosslinked LD-3 polymer film the spinning speed should be set at 1500 rpm for 90 seconds for a 1.0 mL sample-volume.

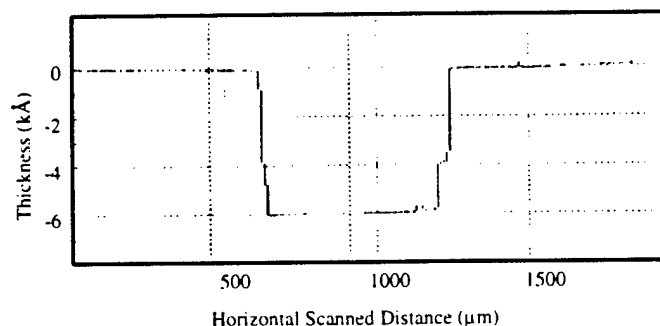


Figure 8. A typical profilometer trace of LD-3 NLO polymer film with crosslinker spin coated on to a microscope glass slide

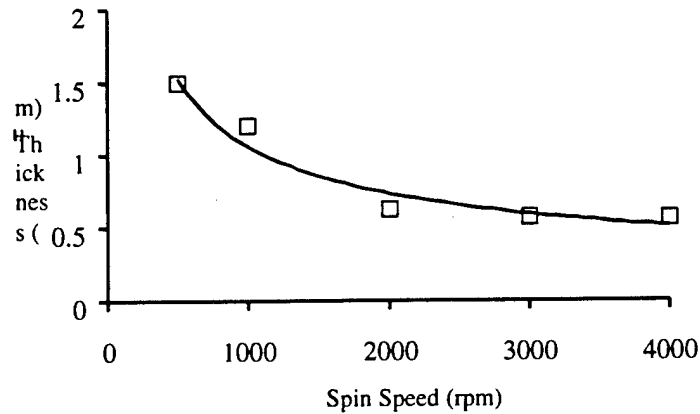


Figure 9. Thickness vs. spin-speed calibration curve for LD-3 NLO polymer film without crosslinker, spin coated on to a microscopic glass slide

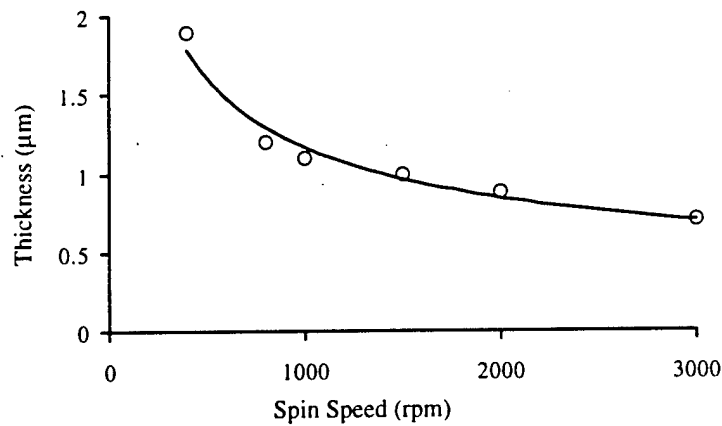


Figure 10. Thickness vs. spin-speed calibration curve for LD-3 NLO polymer film with crosslinker spin coated on to a microscopic glass slide

Figure 11 is a typical profilometer trace of the cladding layer spin coated on to a glass slide. The film was deposited from the polymer blend prepared by mixing 10 wt.% PVA solution (MW = 31k-50k) with PEDOT/PSS solution in a 17 to 100 volume ratio. The coating parameters were set at 1000 rpm for 180 seconds for 1.0 mL of sample volume.

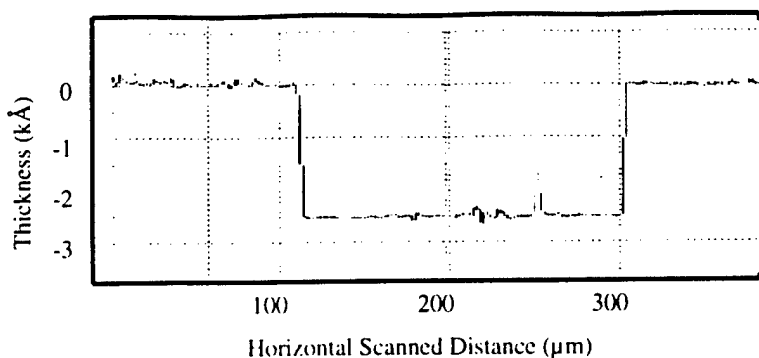


Figure 11. A typical profilometer trace of PEDOT/PSS/PVA film spin coated on to a microscopic glass slide

Figure 12 shows the influence of volume ratio (10 wt.% PVA solution (MW = 124k-186k) to PEDOT/PSS solution in a polymer blend) on the thickness of the cladding layer. The spin speed was set at 1000 rpm for 180 seconds for a 1.0 mL of sample-volume. It is clear from Figure 12 that with the increase in PVA solution to PEDOT/PSS solution volume-ratio the thickness of the film increases.

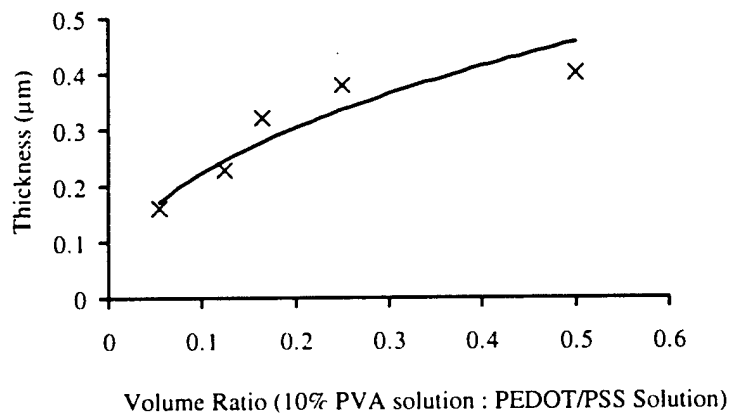


Figure 12. The influence of volume ratios, 10 wt.% PVA solution to PEDOT/PSS solution in a polymer blend, on the cladding layer thickness

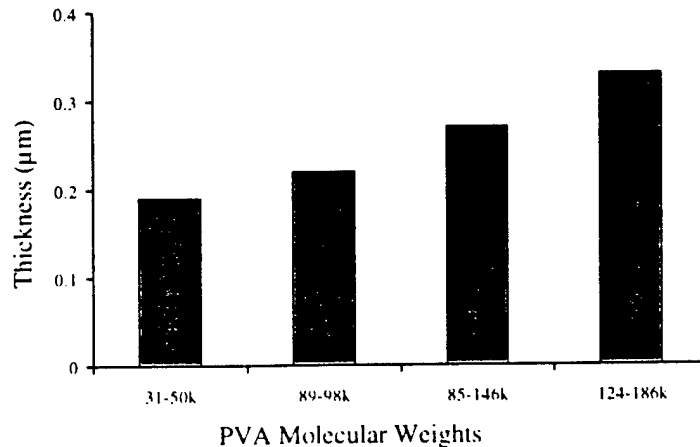


Figure 13. The influence of PVA molecular weights on the thickness of the cladding layer

Figure 13 shows the influence molecular weights of PVA on the thickness of the cladding layer. It is clear from the above figure that increasing the PVA molecular weights in a polymer blend, prepared by mixing a 10 wt.% PVA solution with PEDOT/PSS solution in a 17 to 100 volume ratio, increases the thickness of the cladding layer. It is clear from Figures 12 and 13 that in order to obtain a much thicker cladding film ($\approx 2.0 \mu\text{m}$) the viscosity of the cladding solution must be further increased by increasing the concentration and/or the molecular weight of PVA in the cladding solution.

For this purpose, the cladding layer was deposited from a polymer blend prepared by mixing a 10 wt.% PVA solution (MW = 85k-145k) with PEDOT/PSS solution in a **70 to 30 weight-ratio** (approximately 100 to 46 volume ratio). The spin cast film was vacuum dried at 70°C for 1 hour prior to thickness measurements. There was no change in the thickness of the vacuum dried (at 70°C for 1 hour) cladding layer when it was further baked at 150°C for 2 hours. This result indicates that vacuum drying at 70°C for 1 hour is sufficient to remove solvent (water) completely from the cladding layer. The thickness vs. spin speed calibration curve for cladding layer is shown in Figures 14. From calibration curve it is apparent that a $2.0 \mu\text{m}$ thick cladding layer can be spin coated on to a substrate by setting the spin speed to 500 rpm and spin time to 180 seconds for a 1.0 mL of sample-volume.

Adhesion Test

Samples, which were cured at 150°C for 2 hours did not show any signs of solvent attack. The integrity of the film was maintained even after they were immersed in water and cyclohexanone for about 24 hours. However, samples which were not cured and exposed to water and cyclohexanone for 24 hours showed some degree (20-25% of film area) of delamination of the top PEDOT coating in each exposure conditions. The adhesion test suggests that the cured LD-3 coating is very well bonded to the substrate and to the cladding layer (PEDOT/PSS/PVA coating) and is durable. In a curing process the hydroxyl groups of LD-3 NLO polymer and crosslinker (3,3'-dimethoxy-4,4'-biphenylene diisocyanate) reacts with each other to form a network of urethane linkage. So, it is

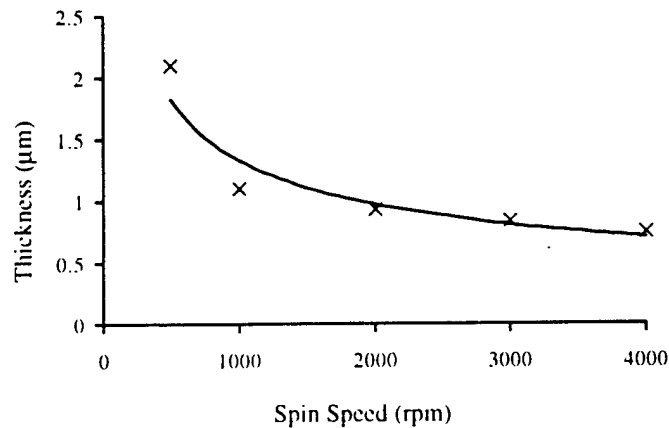


Figure 14. Thickness vs. spin-speed calibration curve for cladding material (PEDOT/PSS)

possible that during the curing process the crosslinker in LD-3 film may very well react with the hydroxyl groups of PVA in the cladding layer also and form a urethane linkage at the interface. The formation of urethane linkage across the interface of LD-3 layer and cladding layer may thus provide a good adhesion between the two layers. A schematic of the possible urethane linkage formation at LD-3 film/cladding layer interface is shown in Figure 15.

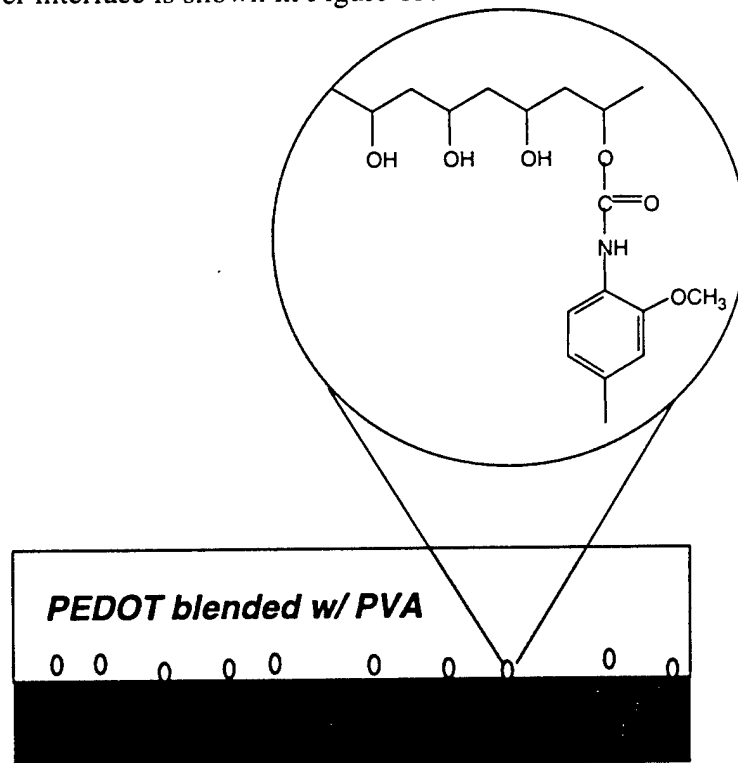


Figure 15. A schematic diagram showing urethane crosslink between core LD-3 layer and cladding layer

4.0 SUMMARY, CONCLUSIONS AND FUTURE WORK

4.1 Summary and Conclusions

Uniform, durable and well-bonded thin films of PEDOT/PSS/PVA and LD-3 were successfully spin coated on to a glass/ITO substrate. Triple stack incorporating 1.0 μm thick crosslinked LD-3 NLO polymer sandwiched between two 2.0 μm thick cladding layers (PEDOT/PSS films) was successfully fabricated.

We have been able to show that within the range of the data made available at the outset of this contract, it is possible to construct a MZ switch using an NLO polymer core with slightly conducting cladding polymers. The designs that were explored indicated, however, that there was a need for multi-wavelength values of the refractive indices more accurate than originally available. On the other hand, the spin parameters needed to make films to meet the design requirements of the MZ switch were determined as well as a preliminary measurement of the electro-optical coefficient of an electrode-poled LD-3 waveguide. Electrode poling is an important feature of this MZ switch design. Also, many details concerning the performance of the device were uncovered. This includes especially the requirement of a longer interaction length than predicted by theory and the change in the index with degree of poling. Neither of these important facts was known at the start of this work.

Without adequate data to design a switch that has a reasonable probability of operating, there simply was no basis for proceeding to mask fabrication. This situation is further exacerbated by the need for etching parameters for the target polymers. For a given mask design to have a chance to succeed, the impact of the processing steps on the final structure must be known.

4.2 Future Work

All experimental parameters needed for the development of communication networks using optimized nonlinear optical (NLO) polymer opto-electronic (OE) modulator/switch and the future prototype development of directional waveguides, splitters, decouplers, and Mach Zehnder modulators under the follow-on STTR Phase II program. This will include a feasibility road map to reach the NLO Polymer material goals for this program. These proposed new generation of electronic devices will decrease delivered device cost, increase data speed, reduce weight, and reduce electrical power requirements over those devices used in current electronic designs.

Once we have developed and optimized all conditions necessary for the fabrication of the modulator/switch, planar channel waveguides, optical fiber cable splitters, and decouplers and tested their optical characteristics, the development and fabrication of optical modulators of Mach Zehnder type and waveguide directional coupler switches will follow during the Phase II of the project. Testing and modification of studies will be carried out to determine the frequency range of operation of the Mach-Zehnder modulators. The commercial impact of the proposed technology and development on optical communication, data processing, sensing and interconnects is expected to be very large.

Following the Phase II development, commercialization of the technology and products (waveguides, interconnects, optical buses, switches, couplers and modulators) will be vigorously pursued.