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A.K.M. Rahman, B.K. Mandal, X.F. Zhu, J. Kumar and S.K. Tripathy

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A.K.M. Rahman, B.K. Mandal, X.F. Zhu,
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OPTICAL AND ELECTRO-OPTICAL PROPERTIES OF A PHOTOCROSS-LINKABLE POLYMER.

A. K. M. Rahman, B. K. Mandal*, X. F. Zhu, J. Kumar, and S. K. Tripathy*
University of Lowell, Departments of Physics and Chemistry · Lowell, MA 01854, U.S.A.

ABSTRACT

Planar waveguides from a photocross-linkable polymer have been fabricated on glass and SiO_2 on silicon using the spin coating process. The polymer has been cross-linked by exposure to UV radiation ($\lambda = 254nm$). Prism coupling technique has been used to couple a laser beam into the waveguide structure. The waveguiding parameters such as number of modes, loss, thickness, and index of refraction of the polymer have been determined before and after crosslinking. The refractive index of the polymer before cross-linking differs significantly from that after cross-linking. No anisotropy has been observed in the refractive indices for the uncross-linked or cross-linked samples. The refractive index and thickness of the polymer film before and after cross-linking have also been measured using an ellipsometer and found to be in very good agreement with those obtained by the prism coupling technique. Dye molecules with large second order hyperpolarizability were utilized as guests into the photocross-linkable polymer matrix for second order nonlinear optical applications. Electro-optic properties of this polymeric system are reported.

INTRODUCTION

Organic nonlinear optical (NLO) polymers are potential candidates for second order nonlinear optical and electro-optic devices [1-2]. These NLO polymers provide a number of advantages over inorganic NLO materials including lower dielectric constant and greater processing flexibility. Extensive studies have been made on two types of poled NLO polymers such as guest-host systems and side chain polymers [3-7]. The side chain polymers are significantly more stable than the guest-host systems, but they still suffer from slow relaxation of nonlinearity over a period of time.

The stability of the poling induced nonlinearity is very critical to device application. Recently, Eich et al. [7] have developed a cross-linked epoxy system in which this relaxation problem has been overcome by thermal cross-linking of NLO polymers in the poled orientation. However, in order to achieve an efficient epoxy system, one needs to control the molecular weight of the epoxy prepolymer. Furthermore, very long curing and poling cycles (~20 h) at high temperature (~140°C) are necessary. More recently, a different approach to obtain a stable cross-linked polymer system by photochemical reaction has been reported by Mandal et al. [9-10]. In this technique NLO molecules and photosensitive polymer are processed in the same way as the guest-host systems and photocross-linking is then performed by exposing to UV radiation subsequent to poling.

In this paper we have presented waveguiding properties of a photosensitive polymer, polyvinyl cinnamate (PVCN) before and after photocross-linking. NLO molecules of a new azo dye 3-cinnamoyloxy-4-[4(N,N-diethylamino)-2-cinnamoyloxy phenyl azo] nitrobenzene (CNNB-R) were introduced into the PVCN matrix. Electro-optic coefficients of poled and cross-linked PVCN containing CNNB-R have been determined.

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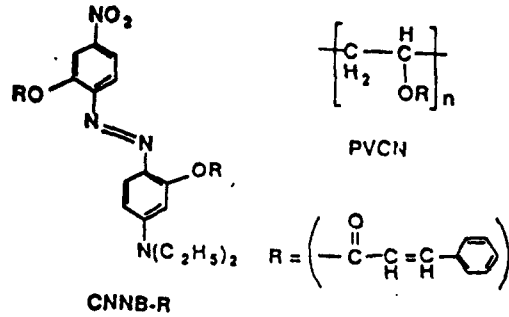
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Figure 1. Structures of new azo dye CNNB-R (guest) and PVCN (host)

THIN FILM PREPARATION

The structural formulae of PVCN and azo dye CNNB-R are shown in Figure 1. PVCN and PVCN doped with CNNB-R were dissolved in a mixed solvent of chlorobenzene and toluene in the ratio of 3:1 (by volume). The solution in both cases was filtered using a 0.2 μm teflon filter. Films were prepared by spin-coating the solution on glass, silicon oxide on silicon and indium tin oxide (ITO) substrates. The solution viscosities and spin speeds were adjusted to produce films that are typically 1.0-1.2 μm thick. The spin-coated samples were baked for about 12 hours at 50°C under vacuum to remove residual solvent.
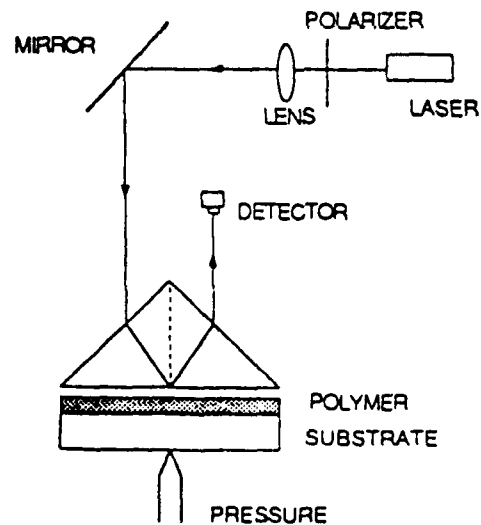
Figure 2. Schematic of waveguiding experiment using a prism coupler

LINEAR OPTICAL PROPERTIES

Linear optical properties of PVCN were investigated using waveguiding technique. Thin film planar waveguides were fabricated on glass and SiO_2 on silicon with the polymer as the guiding layer. A rutile prism was used to couple a light beam into the waveguide structure. The schematic of the waveguiding experiment using a prism coupler is shown in Figure 2. The reflected intensity from the prism was monitored as a function of the external angle of incidence. The coupling angles were obtained from the reflected intensity minima for both transverse electric (TE) and transverse magnetic (TM) polarizations. The dispersion

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equation of a planar waveguide structure for each polarization was solved to determine thickness and refractive index of PVCN film [11]. Two TE or TM Modes were observed for PVCN film on glass using a 633nm He-Ne source. Figures 3(a) and 3(b) show reflected intensity versus external angle of incidence for TE_0 and TE_1 modes. Figures 4(a) and 4(b)

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show reflected intensity versus external angle of incidence for TM_0 and TM_1 modes. The well resolved minima demonstrate the excellent optical quality of the film. The refractive index and thickness of PVCN before photocross-linking were found to be 1.60 and 1.16μm respectively using a 633nm He-Ne source.
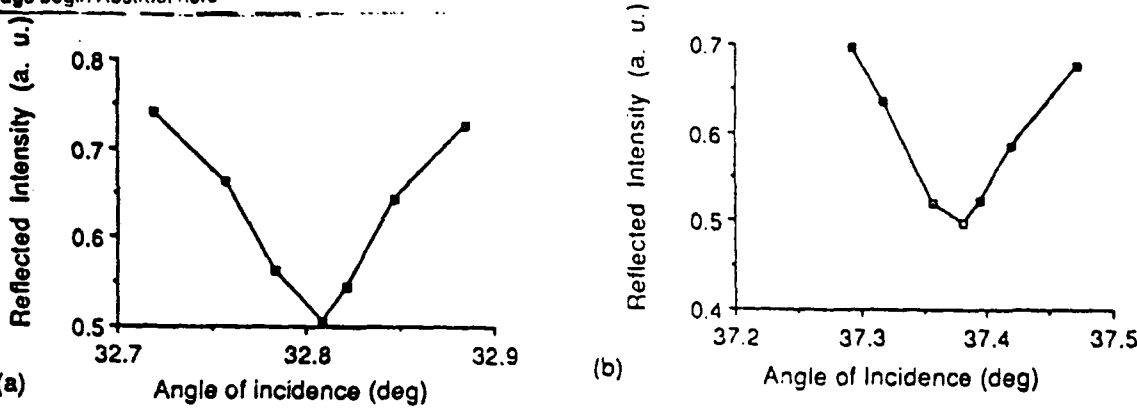
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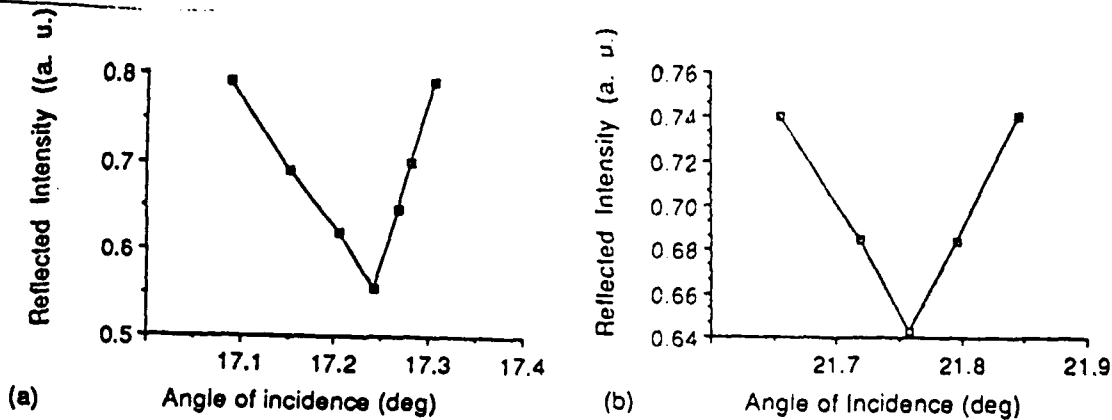Figure 3. Reflected intensity vs angle of incidence for (a) TE_0 mode and (b) TE_1 mode

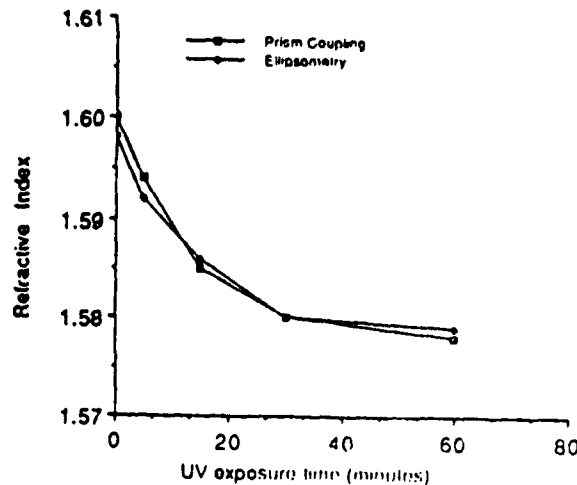Figure 4. Reflected intensity vs angle of incidence for (a) TM_0 mode and (b) TM_1 mode

Figure 5. Refractive index vs UV exposure time (I=2mW/cm^2) for PVCN

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The cross-linking of PVCN was performed by irradiating UV light ($\lambda = 254nm$) with an intensity of approximately $2mW/cm^2$ on the film surface. Waveguiding technique was used to determine refractive indices of PVCN at $\lambda = 633nm$ as a function of UV exposure time. The changes in refractive index vs UV exposure time is plotted in Figure 5. The refractive index of PVCN decreases with photocross-linking. The decrease in the index of refraction is due to the loss of unsaturated double bonds which are converted into saturated four membered rings as a result of intermolecular cross-linking. No anisotropy was observed in PVCN before and after photocross-linking.

1st page begin Abstract here The refractive indices of PVCN before and after photocross-linking were also measured at 633 nm using an ellipsometer and are plotted in Figure 5. The values of refractive indices were found to be in very good agreement with those obtained by the waveguiding technique.

Waveguide loss of PVCN was determined using an experimental setup shown in Figure 6. A fiber bundle was used as a probe to collect light scattered from the waveguide. The fiber was held at right angle to the waveguide and scanned along the length of the bright streak formed by the guided beam. The distance between the fiber end-face and the waveguide surface was kept constant during scanning and light passing through the fiber was monitored as a function of position. Loss was evaluated assuming [12]

$$I = I_0 \exp(-\alpha z)$$

where I is the intensity of scattered light at any point, z along the length of the waveguide, I_0 is the intensity at z = 0, and α is the attenuation coefficient. A plot of ln(I) versus z for PVCN is shown in Figure 7. The waveguide loss for PVCN was found to be 3 dB/cm at 633nm wavelength. This loss is mostly due to scattering because the absorption loss for this polymer at 633nm wavelength is negligible.

XYZ TRANSLATOR

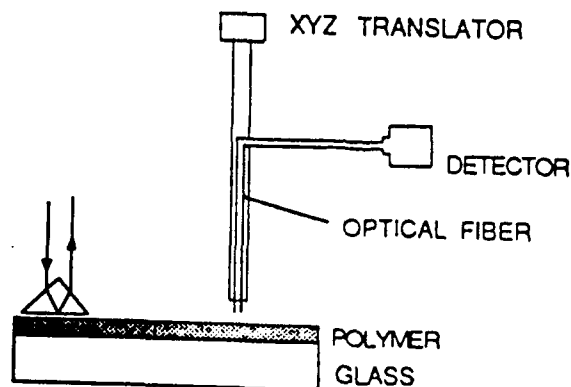DETECTOR

OPTICAL FIBER

POLYMER

GLASS

Figure 6. Schematic of waveguiding loss measurement system

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ELECTRO-OPTIC MEASUREMENTS

The electro-optic coefficients of PVCN doped with 10% CNNB-R were measured using the reflection method of Teng and Man [13]. Schematic of experimental setup for this method is shown in Figure 8. A thin film ($1\mu m$) of PVCN doped with CNNB-R was spun onto ITO coated glass. The polymer films were poled using both the corona poling and parallel electrode poling techniques.

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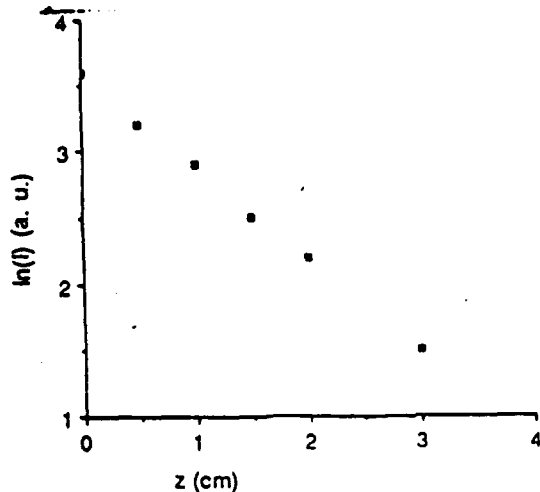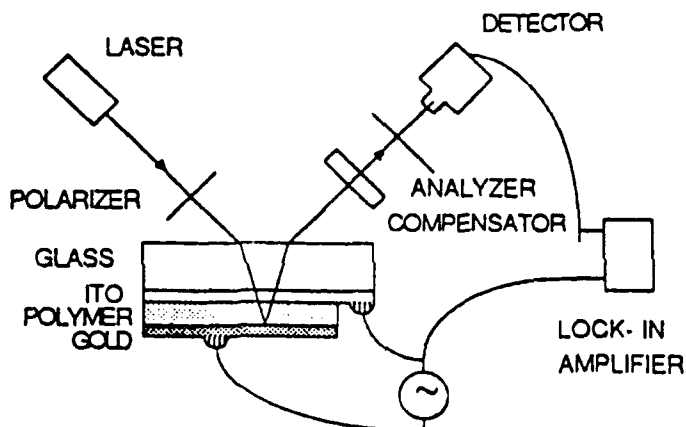1st page start Authors here

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Figure 7. Plot of ln(I) vs z for PVCN

Figure 8. Experimental arrangements to measure electro-optic coefficients

In the corona poling technique, the wire-to-plane electrode configuration was used. The poling temperature was 70°C which is less than the glass transition temperature T_g ($T_g = 80°$ C). The polymer was poled for about 4 minutes and subsequently cross-linked for 10 minutes by UV irradiation without changing the poling field. The sample was then cooled down to room temperature under the poling field and with the UV lamp on. A thin layer (60nm) of polyvinyl alcohol (PVA) was deposited on top of the sample by spin coating PVA solution in water to fill the pinholes generated during corona poling. Gold film of 40 nm thickness was evaporated on top of the PVA layer. Gold and ITO served as top and bottom electrodes for modulating field for electro-optic measurements.

In the parallel electrode poling technique, gold electrode was first evaporated on top of the polymer layer. The sample was heated to 70°C and a voltage was applied between gold and ITO electrodes. The poling and cross-linking were then performed using the procedure described earlier.

The electro-optic coefficient is given [13] by

$$r_{33} = \left[3\lambda I_m (n^2 - \sin^2\theta)^{3/2} \right] / \left[4\pi v_m I_c (n^2 - 2\sin^2\theta)n^2 \sin^2\theta \right]$$

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where λ is the wavelength in vacuum, n is the refractive index of the polymer film, I_m is the amplitude of modulated intensity, I_c is the half maximum intensity, v_m is the amplitude of modulating voltage applied, and θ is the angle of incidence with respect to the normal to the plane of the sample. In the present calculations, $n_e = n_o = n$ has been assumed. The r_{33} coefficient for the corona poled sample (10%, CNNB-R) was found to be 4.5pm/V at 633nm wavelength. The r_{33} coefficients for parallel electrode poled film at 633 nm wavelength were 2.0pm/V and 0.9pm/V for poling fields of 60V/μm and 45V/μm respectively.

CONCLUSION

The photoreactive polymer, PVCN forms a good optical quality film. Its refractive index decreases upon photocross-linking by as much as 0.02. PVCN offers significant advantages in processing and photolithographic patterning steps that are necessary for fabricating devices. The poled and cross-linked PVCN polymer containing CNNB-R shows stable nonlinearity. Although, the electro-optic coefficients for this system for low concentration of dye are not large, they can be increased significantly by increasing the concentration of CNNB-R in PVCN or using alternate NLO molecular subunits.

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