Electro-optic phenomena in gelatin-based poled polymer

Z. Z. Ho, Ray T. Chen, and Robert Shih

Physical Optical Corporation, 2545 West 237th Street, Suite B, Torrance, California 90505

An electro-optic polymer with nitrophenol and photo lime gel has been constructed and demonstrated. The transmission spectrum of nitrophenol/gelatin shows an ultrawide optical bandwidth, from 340 to 2800 nm. A relatively stable and large electro-optic effect, $\gamma_{33} = 10$–40 pm/V, was observed at 632.8 nm. The poling stability is attributed to the two-dimensional cross-linked nature of the gelatin. This result indicates that both passive and active integrated optical devices can be fabricated onto the same polymer thin film to form a fully polymer-based miniature integrated optical circuit.

Formation of an integrated optical circuit requires a host material through which both passive and active integrated optical components (IOCs) such as waveguides, lenses, gratings, modulators, and switches can be fabricated. Previous research has shown that photo lime gel can be used to build completely passive IOCs. In this letter, the feasibility of demonstrating an electro-optic polymer based on the same host material is reported. A high speed electro-optic modulator can be built on the photo lime gel-based guest/host polymer.

Gelatin is a class of biopolymer which consists of thousands of 10–20 Å-long amino acids. Gelatin has been classified as a superpolymer[1] because of its extraordinary chemical and physical properties and its molecular structure. When a gelatin solution is subjected to temperatures below 30 °C, the solution becomes a soft gel. When the gel is dried, it becomes a rigid glass film that shows very little absorption and optical scattering. The remarkable fact is that biological gelatin has two extraordinary microstructural morphologies: (1) *Two-Dimensional Network*— molecules are partially aligned and cross linked with interchain hydrogen bonds to form a helical collagenlike sheet (Fig. 1) and (2) *Thermoplastic → Thermosetting*—the processible gelatin (thermoplastic form) can be readily transformed into a highly cross-linked and insoluble polymer (thermosetting form) using heat or UV radiation curing.

When gelatin is incorporated with ammonia dichromate, it becomes a widely used holographic recording material, dichromate gelatin (DCG). Holographic gelatin has attracted a great deal of interest because it has a variety of applications.[2,3] In recent years, gelatin has become increasingly important because of its potential for use in integrated holographic optical elements such as lenses,[4] grating couplers,[5] multiplexed gratings,[6] and optical interconnections.[7] Using polymer gelatin, high quality optical waveguides (with loss of <0.1 dB/cm)[8] have been fabricated on different high refractive index substrates, including insulators, semiconductors, and conductors. The feature which makes this waveguide application possible is the graded-index profile induced inside the gelatin layer by wet processing. A stepped-index profile would prohibit the formation of optical waveguides on high-index substrates. Wet processing, swelling, and dehydration, modify mass density distribution in gelatin thin films. As a result, the refractive index of the polymer thin film can be tuned from

~ 1.6 to ~ 1.4. In our recent letter,[9] we demonstrated 1-to-30 guided wave optical interconnections and a wavelength division demultiplexer using a highly multiplexed gelatin waveguide volume hologram. This technology provides guided wave massive fan-out capability for intraplane and intrachip optical interconnections. High quality passive integrated optical components, including planar and channel waveguides,[8,10] waveguide lenses,[4] multiplexed waveguided holograms,[9] three dimensional (3D) guiding layers[11] and board-to-board waveguide interconnections,[12] have been successfully demonstrated. In order to realize a fully polymer-based miniature integrated optical circuit on any substrate of interest, active devices such as waveguide modulators and switches are needed.

The search for materials with fast response times (< 1 ns), combined with a large electro-optic (EO) effect ($\Delta n > 10^{-4}$), and which are simple to process has been of intense interest for some time. EO materials, such as liquid crystal, photorefractive and piezoelectric materials, offer large EO effects but exhibit a switching time which is too slow (50 ns-ms) for practical applications. Also, the widely used inorganic crystalline (LiNbO$_3$) thin film is very difficult to process. In contrast, EO polymers offer excellent properties, including large EO coefficients ($\Delta n \cong 5 \times 10^{-4}$), low temperature processing (< 200 °C), and
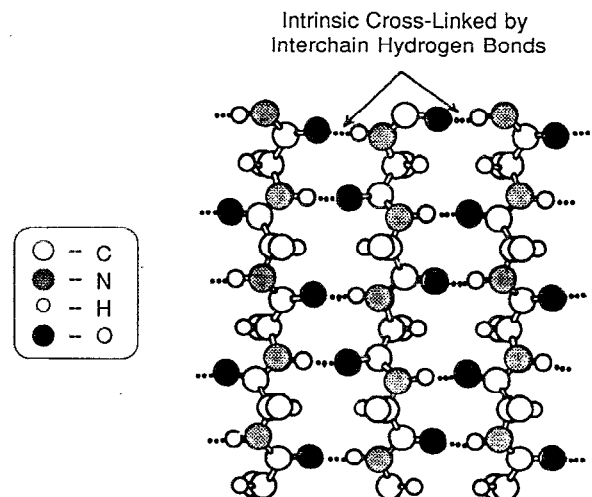
Intrinsic Cross-Linked by
Interchain Hydrogen Bonds

O	– C
◉	– N
o	– H
●	– O

FIG. 1. The sheetlike structure of gelatin with intrinsic cross linking.
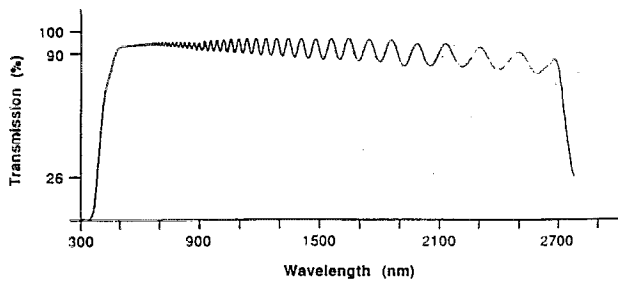
FIG. 2. The transmission spectrum of 10 μm nitrophenol/gelatin thin film.

FIG. 3. Electro-optic measurement setup.

fast response times (< 300 ps). In recent years, EO poled polymers have evoked international attention and effort. High glass transition temperature (T_g) polymers or cross-linked polymers have proved their effectiveness for stability enhancement. Unfortunately, their long-term EO stability is still a bottleneck for practical device applications.[13,14] While tremendous efforts have been put into the characterization of poled materials,[15-17] device research on EO polymers is still in its infancy. For the most part, this is due to the fact that the basic criteria for guided wave materials is that they have the capability to be integrated with other optoelectronic components. To the present, this aspect of most EO polymers has not be examined. Polymeric gelatin has been proved to be an excellent material for the fabrication of an array of guided wave optical elements, but no active EO device has been built in the gelatin media. The purpose of this letter is to describe the achievement of assembling an EO modulator by the incorporation of active EO materials in the highly cross-linked gelatin matrix.

The gelatin used in this experiment is known as type A gelatin, acid-treated protein derived from animal tissues. It has an isoelectric point between pH 7 and pH 9. Gelatin is soluble in aqueous solutions and insoluble in most organic solvents, such as benzene, acetone, petroleum ether, and absolute alcohol. This low solubility limits the use of a large number of EO dyes which are frequently water insoluble. In the experiment we describe here, 4-nitrophenol (NP) from Aldrich was selected as the active EO material. Nitrophenol has very high solubility in water (25 mg/ml) and can homogeneously disperse in gelatin matrix. The electronic acceptor NO_2 group and electron donor OH group form a linear dipole moment across the π conjugated electronic system. The molecular nonlinear hyperpolarizability of NP in solution has been gauged to be about 1/3 that of methyl nitroaniline (MNA) by measuring the electric-field-induced second-harmonic generation.[18] A solution containing polymer gelatin (30 g), nitrophenol (~20% to 30% by weight), and water (400 ml), was set in a water bath (60 °C) until it became clear. The solution was filtrated and spin coated on an aluminum (Al)/glass substrate. The absorption peak of NP is at 304 nm. The transmission spectrum of NP/gelatin thin film is shown in Fig. 2. It has a very wide optical bandwidth, from 350 to 2800 nm, which is much wider than most EO polymers. From the interference fringe, the thickness of the thin film was measured to be 10 μm. The thickness of polymer thin
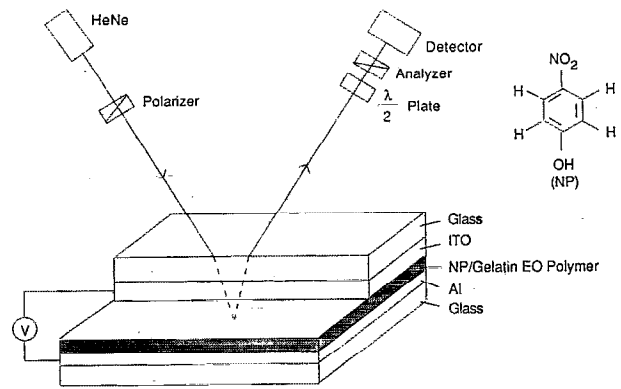
films can be varied from submicron to 100 μm by changing the ratio of water and gelatin or the speed of spin coating. The dry thin film was covered with an optically transparent indium tin oxide (ITO)/glass substrate. The Al and ITO electrodes served as poling fields as well as modulating fields. Although gelatin molecules are partially aligned microscopically, no macroscopic birefringence was found in the gelatin film before poling. The poling and curing processes were performed at the glass transition temperature (T_g), 60 to 70 °C, for 30 min.

The experiment was performed in the reflection geometry[19] (see Fig. 3) with a 3 mW HeNe laser beam polarized at 45° to the plane of incidence, so that the parallel and perpendicular components of the optical field were equal in amplitude. The beam reflected from the Al coating was propagated through a half-wave plate, an analyzer, and into a photodiode. The analyzer was set at a cross-polarization angle with respect to the polarizer. The half-wave plate was used to generate $\pi/2$ phase retardation between x and y polarizations of the laser beam. When the phase shift, ψ, is biased at $\pi/2$ with a $\lambda/2$ plate, the output intensity is approximately linearly related to the phase retardation as well as to the applied modulating voltage. The ratio between the modulated intensity, I_m, and the dc signal, I_c, can be expressed as

$$I_m/I_c = (2\pi/\lambda)2d\Delta n(\sin^2\theta/\cos\theta), \qquad (1)$$

where θ is the angle of incidence, d is the thickness of the polymer film, and Δn is the birefringence introduced by the modulation field. I_c is the output intensity at $\pi/2$ phase shift. This intensity can be obtained by rotating the $\lambda/2$ plate. This birefringence is given by

$$\Delta n = 1/2(n_3^3\gamma_{33} - n_1^3\gamma_{31})V/d, \qquad (2)$$

where n_1 and n_3 are refractive indices along the directions perpendicular and parallel to the poling electric field, respectively. For an initially isotropic system, the corresponding EO coefficients for light polarized perpendicular and parallel to the surface plane are related to γ_{31} and γ_{33}, $\gamma_{33} = 3\gamma_{31}$. This assumption can be justified because nitrophenol is randomly dispersed in the polymer matrix. Therefore, we have
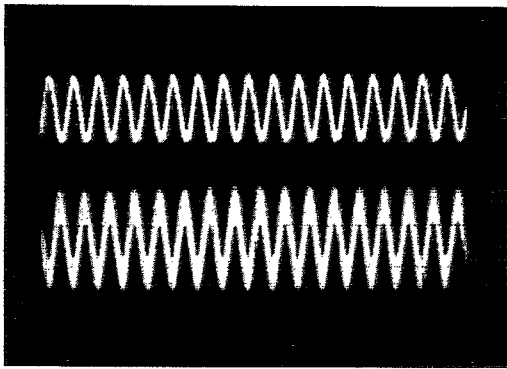
Ho, Chen, and Shih   5

FIG. 4. The optical signal from a HeNe laser is modulated and displayed on an oscilloscope.

$$\gamma_{33} = 3\lambda I_m \cos\theta / 4\pi(n^3) V_m I_c \sin^2\theta, \tag{3}$$

where V_m is the modulating voltage.

The electrooptic effect of NP/gelatin polymer was observed with a poling field of 400 V across a 10-μm-thick film. The optical modulation signal from a HeNe laser was displayed on an oscilloscope (see Fig. 4). The upper curve is 3.3 MHz rf modulation with a V_{p-p} of 90 V. The bottom curve is the corresponding modulated optical signal. Based on Eq. (3), the EO coefficient of NP/gelatin, γ_{33}, of 10–40 pm/V was obtained at 632.8 nm with a direct current. The spread in EO coefficient is due to variations in film thicknesses, dye concentrations, and poling fields. The index change introduced by the modulation field is 1–4$\times 10^{-4}$. This value is comparable to many poled polymers and inorganic LiNbO$_3$. The major reason for the large nonlinear effect is the high concentration of EO moieties, 35% by weight of NP, that can be incorporated into the gelatin matrix without any cluster appearing. This concentration is much higher than that in most guest/host systems ($\approx$15%). Effective poling may account for additional EO enhancement. For guest/host systems, the typical poling efficiency is between 10% and 20%. Poling efficiency for short-axis molecules, such as NP, is believed to be higher. This is because the short-axis molecule is subjected to a smaller axial force potential. Thus the molecules can be rotated and aligned more easily.

The thermal stability of the poled EO response has been a critical issue in the practical application of poled polymers. The high T_g and cross-linked polymers has been used to reduce the diffusion of EO groups, and thus increase the thermal stability. The typical EO decay curve of guest/host polymers shows an initial fast decay to 20% within 5 days, followed by a slower decay. The EO stability of NP/gelatin shows that 40% of the original birefringence persists 5 days after poling at room temperature. As shown

in Fig. 1, gelatin has 2D sheetlike structures held by intermolecular hydrogen bonds. During the thermal curing process, these chemical bonds in NP/gelatin can be further crosslinked and enhanced to form a rigid and irreversible thermosetting polymer. The observed results indicate that the highly cross-linked hydrogen bonds are responsible for the EO stability. In addition to the above intrinsic cross linking, it is known that gelatin can be hardened and rendered insoluble by cross linking between chromium ions and amino-acid groups (in DCG) into a more stable 3D network. We are currently characterizing the stability enhancement by cross linking the poled gelatin with dichromate under exposure to laser radiation. Further results will be presented in future publications.

In conclusion, we have successfully constructed and demonstrated an EO modulator in biopolymeric gelatin. Nitrophenol was chosen as the active EO moiety and was shown to have a large EO effect. The planar structure of the gelatin plays an important role in the stability of the EO group in the polymer matrix. Optical birefringence was generated with a poling field at temperatures between 60 and 70 °C. The results illustrate that active EO devices can be integrated into holographic gelatin films. This project is partially supported by NSF and the Department of Energy.

[1] T. C. Lubensky and P. A. Pincus, Phys. Today, Oct (1984), p. 44.
[2] J. R. Magarinos and D. J. Coleman, Opt. Eng. 24, 769 (1985).
[3] B. J. Chang, Opt. Eng. 19, 642 (1980).
[4] R. T. Chen, Final Report to Harry Diamond Lab, Contract. No. DAAL01-91-C-0034, 1991.
[5] R. T. Chen, W. Phillips, T. Jannson, and D. Pelka, Opt. Lett. 14, 892 (1989).
[6] R. T. Chen. H. Lu, D. Robinson, and T. Jannson, Appl. Phys. Lett. 57, 2071 (1990).
[7] R. T. Chen, M. R. Wang, G. Sonek, and T. Jannson, Opt. Eng. 30, 622 (1991).
[8] R. T. Chen, Proc. SPIE 1774, 10 (1992).
[9] R. T. Chen, M. R. Wang, and T. Jannson, Appl. Phys. Lett. 57, 2071 (1990).
[10] R. T. Chen, Proc. SPIE 1374, 20 (1990).
[11] R. T. Chen, L. Sadovnik, T. Jannson, and J. Jannson, Appl. Phys. Lett 58, 1 (1991).
[12] R. T. Chen, H. Lu, D. Robinson, Z. Sun. T. Jannson, D. Plant, and H. Fetterman, Appl. Phys. Lett. 60, 536 (1992).
[13] Nonlinear Optical Properties of Organic and Polymeric Materials, edited by D. J. Williams, ACS Symposium Series 233 (American Chemical Society, Washington, DC, 1983).
[14] Organic Moleculars for Nonlinear Optics and Photonics, edited by J. Messier, F. Kajzar, and P. Prasad, (NATO ASI Series, 1987), Vol. 194.
[15] D. Haas, H. Yoon, H. T. Man, G. Cross, S. Mann, N. Parsons, Proc. SPIE 1147, 222 (1989).
[16] R. D. Small, K. D. Singer, J. E. Sohn, M. G. Kuzyk, and S. J. Lalama, Proc. SPIE 682, 160 (1986).
[17] Y. Shuto, M. Amano, and T. Kaino, Jp. J. Appl. Phys. 30, 320 (1991).
[18] L. T. Cheng, W. Tam, G. R. Meredith, G. L. J. A. Rikken, and E. W. Meijer, Proc. SPIE 1147, 62 (1989).
[19] C. C. Teng and H. T. Man, Appl. Phys. Lett. 56, 1734 (1990).