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Poled Electrooptic Photolime Gel Polymer Doped with Chlorophenol Red and Bromomethyl Blue Chromophores

Dave Gerold, Ray T. Chen, William A. Farone* and David Pelka**
Microelectronics Research Center
Dept. of Electrical and Computer Engineering
University of Texas at Austin, Austin, TX 78712-1084 (512) 471-4349

**Applied Power Concepts, Inc.*
2950 Airway Avenue, Suite A-12
Costa Mesa, CA 92626-6019 (714) 540-7332
***Novex Corp.*
2950 Airway Avenue, Suite A-12
Costa Mesa, CA 92626-6019 (714) 540-7332

Abstract

An electrooptic polymer with chlorophenol red dye and type-A photolime gel was demonstrated. The electrooptic coefficient γ_{33} in the direction of the poling field was measured to be 28 pm/V. Chlorophenol red in polymer showed a 1/e relaxation time constant of 820 hours, which is more stable than other dye demonstrated previously to be electrooptic in the same polymer.

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Electrooptic behavior in polymers is of interest because polymer-based electrooptically active material can be built of the same material used for passive devices such as optical waveguides. Electrooptic polymers have additional advantages over inorganic alternatives such as lithium niobate ($LiNbO_3$) in that electrooptic (EO) polymers have fast material response times (picoseconds), large EO coefficients (γ_{33} = 40pm/V), and flexible thin film processing.[1] On the other hand, to date polymer electrooptic coefficients typically relax over time. The EO polymer to be reported exhibited an electrooptic coefficient in the direction of the poling field (γ_{33}) of 28 pm/V. The 1/e relaxation time constant was measured to be 820 hours, which is longer than previous results for this polymer.

Previous work by Ho et al. with type-A photolime gel polymer used nitrophenol electrooptic dye.[2] The EO coefficient in that case decayed to 40% of its initial 38pm/V value within 5 days. A longer EO coefficient lifetime is desired for use in practical devices. Because of the promising large EO coefficient demonstrated, though, other materials from the same class as nitrophenol were investigated for use as electrooptic dyes in the same host material.

The chemical basis for nitrophenol's high electrooptic activity was ascribed to its conjugated electron structure, and to the ability of the nitrophenol molecule to orient properly within the biological polymer matrix. The chemical structures of the two chromophores, i.e., chlorophenol red and bromomethyl blue, are shown in figure 1. Chlorophenol red and bromomethyl blue, often used as acid-base reaction indicator dyes, were chosen for testing because they were in the same class as nitrophenol. All three compounds are highly conjugated and are non-centro-symmetric, both necessary properties for electrooptic behavior. They are also hydrophilic, a requirement for use with water soluble photolime gel polymer.

The photolime polymer employed has a wide transparent bandwidth.[3] When we added the selected chromophores to the host material, i.e., photolime gel, chlorophenol red and bromomethyl blue both absorbed in photolime gel below 600nm, as shown in figure 2.

To prepare the polymer films, very dilute solutions of 1.5g polymer, 0.1g to 0.2 g of EO dye, and 500ml water were prepared. The volume of solution needed to deposit the desired film thickness was calculated based on the polymer structure, which is a collagen that has repeating units 2800Å long and 14Å wide, with molecular weight of 300,000 g/mole.[4,5] The correct solution volume for a 5μm thick film was poured onto a quartz substrate with a 1000Å thick chrome thin film coating.

The chrome layer was used as the lower of two electrodes allowing the application of a poling electric field, used to align electrooptic dye molecules to the poling field. An indium-tin-oxide coated glass substrate was placed on top of the film to form the upper poling electrode. Indium-tin-oxide (ITO) is transparent and conductive (40 ohms/sq.).

Figure 3 shows the reflection geometry employed to detect and measure poling effects.[6] A 4 mW HeNe laser was polarized 45 degrees from the plane of incidence to equalize parallel and perpendicular optical field amplitudes. The laser beam was reflected off the chrome layer of the sample, which was located between two crossed polarizers. In this way a phase shift in one component of the optical field polarization relative to the orthogonal component caused polarization rotation as the beam propagated through the electrooptic film. The output intensity at the detector and after the crossed polarizer was then modulated. Following the optical path, the HeNe beam was transmitted through the first polarizer and then through the thickness of the polymer film. The beam was then reflected off the chrome layer and back up through the film, transmitted through a variable half-wave plate and analyzer, and finally detected.

The test sample film stack chosen forms a parallel plate electrode capacitor structure with polymer as the dielectric, and was used to pole experimental samples. Figure 4 is a schematic of the sample geometry. The upper positive electrode was ITO. The lower ground electrode was chrome on quartz. With this structure, the poling electric field was oriented normal to the polymer film plane, neglecting fringing at electrode edges. The entire electrode structure sat on a hotplate used to heat the polymer above its glass transition temperature and to allow dipoles associated with different chromophores to be aligned within the polymer.

Voltage was applied to the electrodes while heating the sample to above the polymer's glass transition temperature, which is 76°C before dehydration and ~180°C after laser cross-linking and dehydration. Arcing at electrode edges limited applied fields to 50 V/μm. When an intensity shift was observed at the output polarizer, it was confirmed to be due to electrooptic (EO) behavior by turning the voltage off and on. This helped insure that spurious effects such as fringe movement or thermooptic effects were not causing the intensity shift. When an EO effect was observed, heat was maintained until the intensity shift plateaued and was then removed. We observed that the intensity shift plateaued within 10-15 seconds for non-dehydrated polymer samples that exhibited their change at 76° C. The electric field was maintained across the samples until they cooled to room temperature (23-24° C). The dipole alignment and polarization were thus "frozen-in" and the EO coefficient was then measured.

To measure the EO coefficient the variable half-wave plate was rotated to shift the output intensity vs. phase shift response to its most linear region. A sinusoidal modulation was applied to the electrodes, causing the small signal modulated intensity I_{ac} to be superimposed on the average intensity I_{DC}.

In our measurements, the electrooptic coefficient parallel to the poling field (γ_{33}) was found according to[2]

$$\gamma_{33} = 3\lambda\, I_{ac} \cos\theta \,/\, (4\pi n^3 V_{ac} I_{DC} \sin^2\theta) \tag{1}$$

where $\lambda = 0.632\mu m$, the HeNe laser wavelength, θ is the incident angle from sample normal, n is the polymer index of refraction before modulation, and V_{ac} is the modulation voltage amplitude. Thus the electrooptic coefficient γ_{33} was measured by recording I_{ac} and I_{DC}, as indicated in figure 5. The modulating voltage V_{ac} was a 122 volt rms (172 volt amplitude) 60Hz sinusoid.

In order to estimate the sensitivity of γ_{33} measurement to experimental parameters, the first order differential was derived with respect to θ, n, I_{ac}, and I_{DC}. The result is

$$\partial(\gamma_{33})/\partial(\theta) = 3/4\ (I_{ac}\lambda)(1 + \cos^2\theta) \,/\, (I_{DC}\pi n^3 V_{ac} \sin\theta(\cos^2\theta - 1)) \tag{2}$$

We consider ($\Delta\theta^*(\partial(\gamma_{33})/\partial(\theta))$), or the change in γ_{33} measurement vs. working incident angle, given operating conditions $\Delta\theta = 1$ degree, $n=1.55$, $I_{ac}= 18.5$mV, $I_{DC} = 260$mV, $\lambda = 632.8$nm, and $V_{ac} = 170$V amplitude (actual experimental conditions). For these conditions, we see that this measurement is sensitive to incident angles near the normal ($\theta=0$ degrees), and that it is best to work at angles closer to grazing incidence. The total differential was then computed from (2) and the differentials of (1) with respect to n, I_{ac}, and I_{DC}. $\Delta\gamma_{33}$, the total γ_{33} measurement error, was then computed for the same operating conditions using errors $\Delta\theta = 1$ degree, $\Delta n = 0.05$, $\Delta I_{DC} = 5$mV, and $\Delta I_{ac}=$ 5mV, all realistic worst errors for our apparatus. For our experimental equipment, working at incident angles greater than roughly 60 degrees will keep EO coefficient measurement error due to parameters of equation (1) below 1pm/V.

The samples with chlorophenol red and bromomethyl blue in polymer were poled and the initial EO coefficients were measured at $\lambda = 632.8$nm. Results are summarized in table 1. Both materials showed electrooptic behavior, but the chlorophenol red showed the highest coefficient. A higher concentration of dye was expected to increase EO coefficient, as seen in the third chlorophenol red sample. Also, the bromomethyl blue sample, with only 0.005 g/ml dye concentration, showed a coefficient similar to that from the 0.01 g/ml concentration chlorophenol red samples, suggesting that bromomethyl blue was more electrooptic. Samples with the higher 0.01 g/ml bromomethyl blue concentration were indeed prepared but their dye crystallized too readily on the film surface during drying. This solubility limitation could be improved in future work by the addition of organic solvents to manipulate the drying process. The higher concentration bromomethyl blue samples therefore did not show expected EO coefficient, and chlorophenol red was chosen for the subsequent tests.

A 0.02 g/ml concentration chlorophenol red sample was tracked over time to show the EO decay as dipole alignment relaxed towards a randomized state. Some EO data variations were observed, due to imperfect electrical contact to the chrome electrode, which oxidizes if arcing is allowed to occur. The sample, nonetheless, showed a longer lasting electrooptic coefficient than reported previously for nitrophenol doped polymer. The new sample's electrooptic behavior relaxed with a 1/e time constant of 820 hours at room temperature. Further improvements in the EO coefficient stability are expected through chemical or UV exposure to cross-link and fix the position of the polymer matrix.

In conclusion, we demonstrated large electrooptic coefficients in type-A photolime gel polymer thin films doped with chlorophenol red indicator dye by using bulk electrode poling procedures and ac-modulated reflection geometry measurements. An 820 hour 1/e lifetime was observed, well beyond previous results with this particular versatile polymer. This result was obtained without any cross-linking performed to stabilize the molecular dipole alignment within the polymer host matrix. As stated, cross-linking through chemical processing or UV-illumination is expected to extend the electrooptic polymer stability even further.

References

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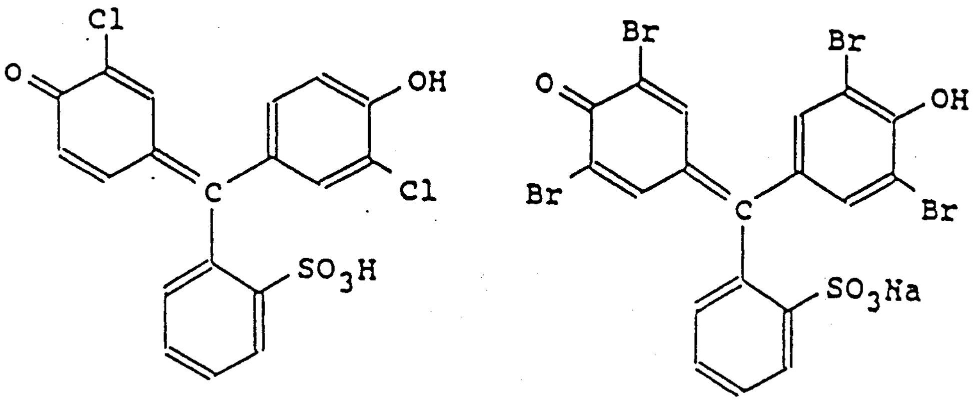
Volume	Dye	Normalized Concentration	γ33, Immediately After Poling
Chlorophenol Red			
20ml	0.2 g	0.01 g/ml	11 pm/V
10ml	0.1 g	0.01 g/ml	12 pm/V
10ml	0.2 g	0.02 g/ml	28 pm/V
Bromomethyl Blue			
20ml	0.1 g	0.005 g/ml	16 pm/V

Table 1

Measured Electrooptic Coefficients Immediately After Poling Process

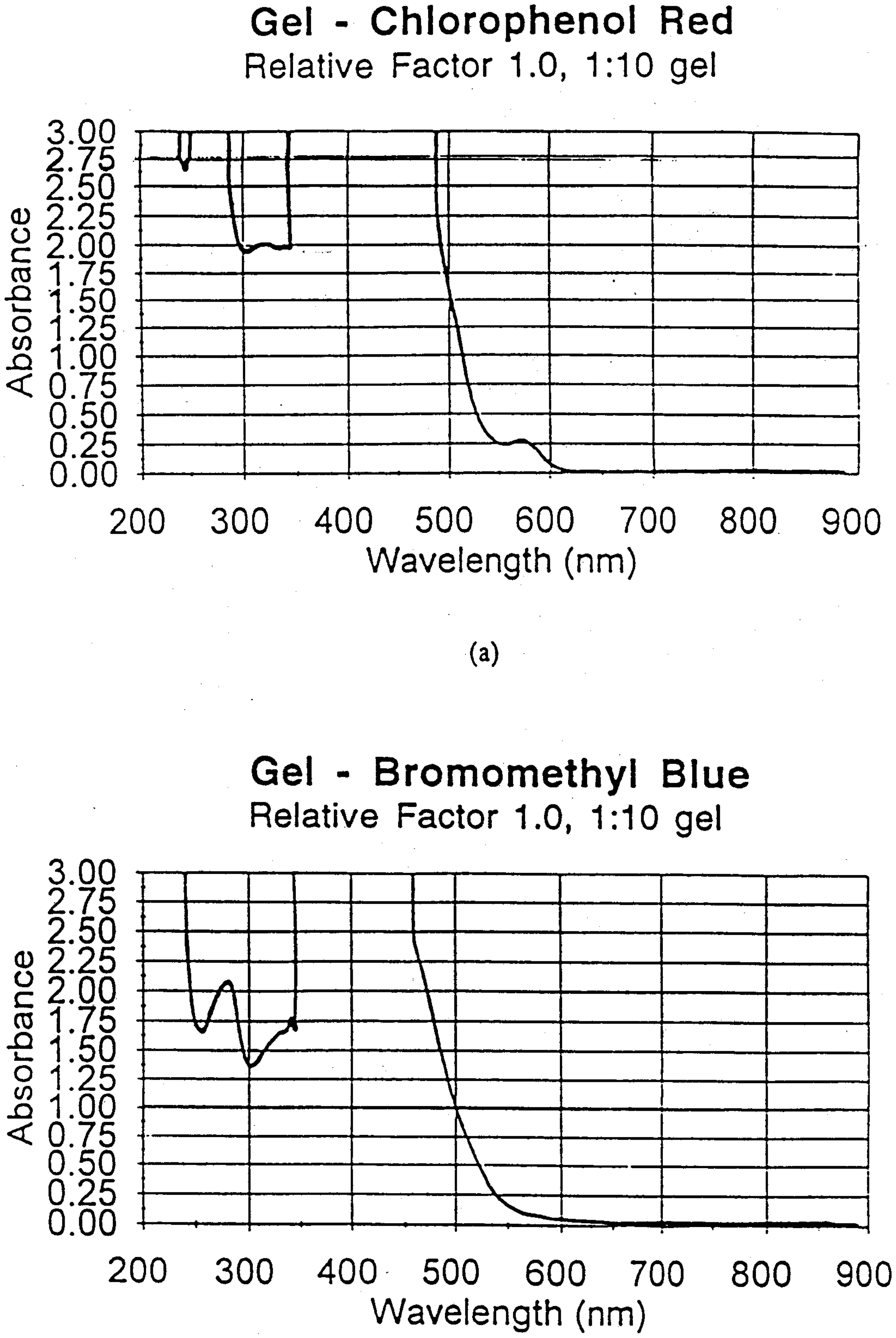


Chlorophenol Red

Bromophenol Blue

Figure 1

Chemical Structure of Dyes Incorporated Into Polymer



(a)

(b)

Figure 2

Optical Absorption of (a) Chlorophenol Red and (b) Bromomethyl Blue in Polymer

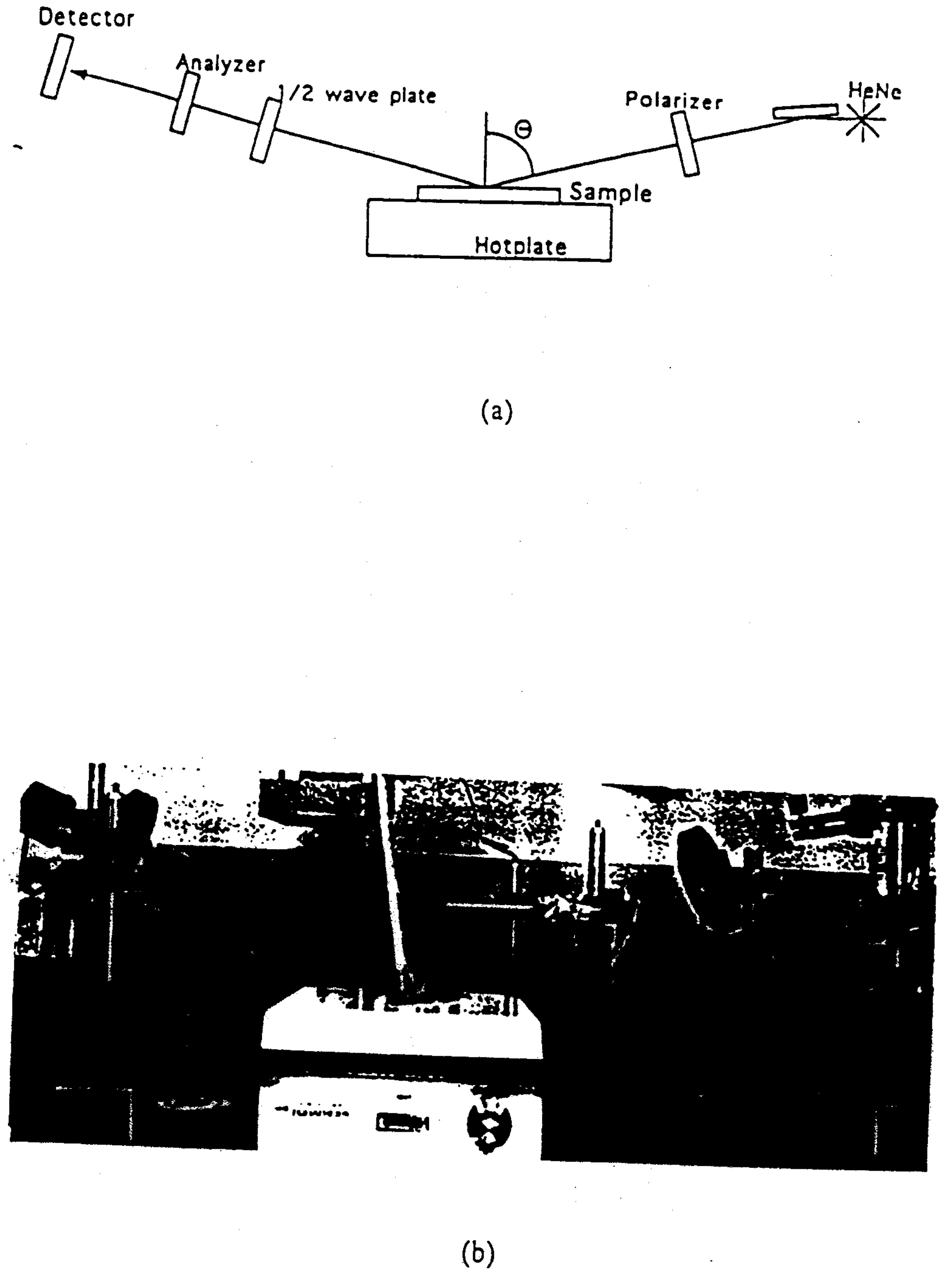


Figure 3

Reflection Geometry Electrooptic Measurement System; (a) sketch, (b) photo

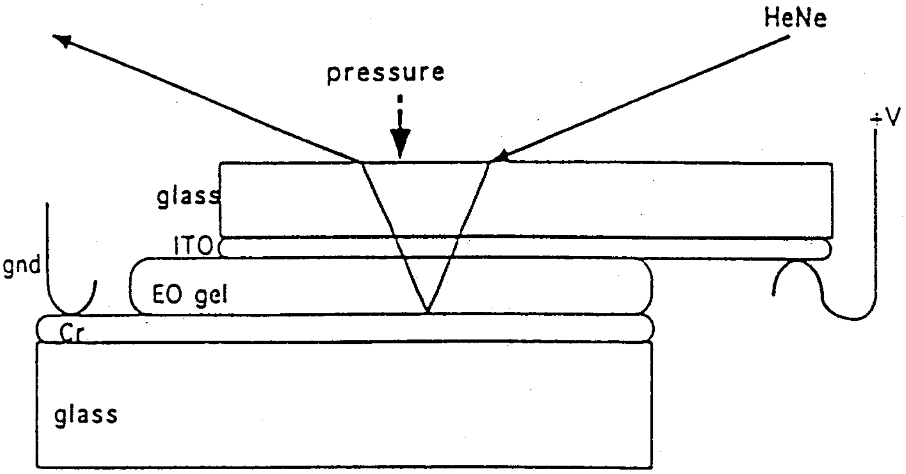


Figure 4

Film Stack for Electrooptic Coefficient Measurement

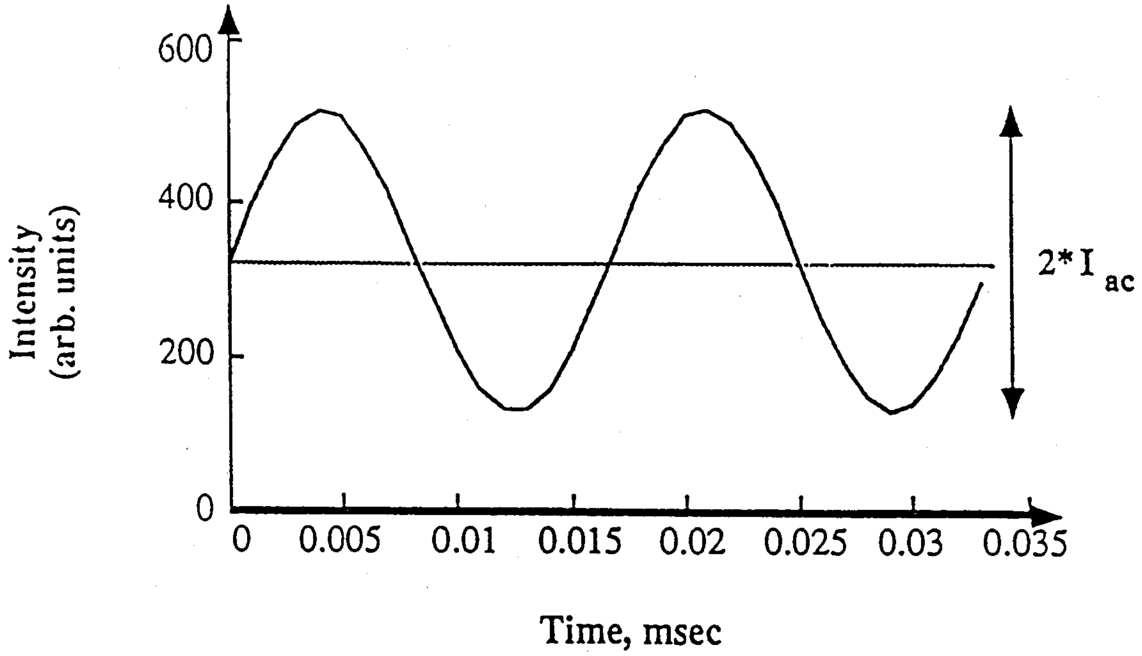


Figure 5

Modulated Intensity Output Used For Electrooptic Coefficient Measurement