

Measuring the Electro-Optic Coefficients of Bulk-poled Polymers

**by Robert C. Hoffman, Joshua A. Orlicki, George R. Martin,
Robert Lambeth, and MyVan Baranoski**

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14. ABSTRACT This report describes the construction of an optical test system to measure the electro-optic coefficients of poled polymers directly. The poling process in polymers is the spontaneous orientation of the dissolved dye molecule, the chromophore, in the presence of an applied electric field. This spontaneous orientation confers upon the poled polymer a variety of useful optical effects, the linear electro-optic effect being chief among them. The optical test system measures the electro-optic coefficient directly by measuring the relative retardance of one polarization, the p-polarization, relative to the other polarization present, the s-polarization. This method has advantages over previous methods that have relied on measuring the very weak second-harmonic signal emitted from poled polymers. This report describes the measurement of the electro-optic coefficient of a number of electro-optic chromophores synthesized in the Weapons and Materials Research Directorate (WMRD) and intended for use in electro-optic modulation devices.					
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1. Introduction

Poled polymers have been proposed for use in a number of electro-optics applications, such as telecommunications switching devices and devices that both emit and detect terahertz (THz) radiation. During the poling process, the chromophores in a guest-host polymer system spontaneously align in a strong applied electric field. The poling process is usually carried out near the glass transition temperature of the polymer host, i.e., the point at which the polymer host softens, allowing chromophore rotation and alignment to occur. However, when cooled below the glass transition temperature of the polymer host, the aligned chromophores become locked in their new orientation. When poled in this way, guest-host polymers can exhibit many useful electro-optic properties. Our investigations center on applications where a longer path length of poled guest-host polymer results in enhanced performance of the electro-optic device, i.e., in THz signal generation and detection and in large-aperture shutters. Many researchers have demonstrated that a longer optical path length, which is potentially available in bulk poled polymers, should allow improved THz power, sensitivity, and signal-to-noise ratio in both THz generators and detectors (1–5). In addition, bulk-poled guest-host polymers may open the possibility that inorganic nonlinear optical (NLO) crystals may be replaced in some applications.

An alternative approach to the high-voltage direct poling technique we used is optical poling (6–10). This method has also been shown to accomplish spontaneous chromophore alignment in thick sections of guest-host polymer. Rather than relying on a direct current (DC) electric field, as described in this work, optical poling relies on the large average electric field available in some continuous wave (CW) lasers and in femtosecond pulses. Unfortunately, optical poling has only been demonstrated in chromophores that undergo an optically induced *cis-trans* isomerization, such as Disperse Red 1 (DR1), and cannot be used for chromophores such as those described in this paper, or those used in poled guest-host polymers for ultrafast shutters and THz generation and detection.

Faced with the limitations of optical poling and the difficulties of processing and stacking large numbers of extremely thin corona-poled films for bulk applications, we chose the more direct approach of high-voltage DC contact poling (11). This method may, in principle, be employed to pole any polar chromophore in a guest-host system. To be sure, the larger electrode separation distance in slabs exceeding 1 mm thickness necessitates the use of much higher poling voltages than in thin films.

Once poled, the electro-optic coefficients r_{33} and r_{13} , among others, must be measured. Previously, we used the Maker fringe technique, which requires exacting and parallel sample surfaces. A faster, simpler technique was needed, and the direct electro-optic measurement by Sandalphon, et al. (12) provided the needed technique.

2. Theory of Direct Electro-optic Measurement

This experiment measures the modulation of the refractive index of a poled polymer sample by measuring the modulated intensity of a transmitted probe beam. The index of the sample is modulated by the application of a high-voltage alternating current (AC) field, and the s and p polarizations will see different changes in the refractive index. As a result, there will be a phase difference Ψ_{sp} introduced to the s and p polarizations as they pass through the sample.

The transmitted intensity I_t through the sample is:

$$I_t = I_i \sin^2 \left(\frac{\Psi_{SB} + \Psi_{sp}}{2} \right), \quad (1)$$

where I_i is the incident intensity and Ψ_{sp} is the phase difference introduced by the s and p polarizations, and Ψ_{SB} is the phase difference introduced by the Soleil-Babinet compensator. A plot of intensity versus phase difference of the s and p polarizations is shown in figure 1. At points A and B on the curve, where the intensity is $I_i/2$, the response is the most linear. Applying an AC modulating voltage at these points will yield a phase difference of $\delta\Psi_{sp}$, which results in a modulation of the transmitted modulation I_m . For small levels of modulation, I_m is related to $\delta\Psi_{sp}$ by:

$$\frac{I_m}{\delta\Psi_{sp}} \approx \frac{I_i}{2} \sin(\Psi_{SB} + \Psi_{sp}). \quad (2)$$

At points A and B on the curve in figure 1, the relationship between the measured intensity modulation and the modulation of the difference in the s and p polarizations after the probe beam passes through the sample is:

$$\frac{I_m}{I_i/2} \approx \delta\Psi_{sp}. \quad (3)$$

For a single pass through the sample the phase difference between the s and p polarizations is:

$$\Psi_{sp} = \Psi_p - \Psi_s = \left(\frac{2\pi d}{\lambda} \right) [n_p \cos(\alpha_p) - n_s \cos(\alpha_s)], \quad (4)$$

where $\alpha_{s,p}$ is the angle of incidence inside the sample with respect to the sample normal for both s and p polarizations. The applied field perpendicular to the sample, so then $n_s = n_o$, and n_p is related to n_o and n_e by:

$$\frac{1}{n_p^2} = \frac{\sin^2(\alpha_p)}{n_e^2} + \frac{\cos^2(\alpha_p)}{n_o^2}. \quad (5)$$

Using the relation $n_{p,s} \sin(\alpha_{p,s}) = \sin(\theta)$ such that $\alpha_{p,s} = \sin^{-1}[\sin(\theta)/n_{p,s}]$, where θ is the angle of incidence. By approximating $n_o \approx n_e \approx n$, the expression for $\delta\Psi_{sp}$ can be simplified.

Assuming all effects are purely EO, then:

$$\Delta n_o = -\frac{1}{2}n^3 r_{13} E \quad (6)$$

$$\Delta n_e = -\frac{1}{2}n^3 r_{33} E, \quad (7)$$

also assuming that $r_{33} = 3r_{13}$. This approximation is valid for poled films with symmetry $C_{\infty v}$, in which there are no nearby resonances, thus Kleinmann symmetry applies:

$$\delta \Psi_{sp} = \frac{2\pi d}{\lambda G} |\Delta n_e - \Delta n_o| = \frac{2\pi n^3 d r_{33} E_{AC}}{3\lambda G}, \quad (8)$$

where E_{AC} is the applied voltage and:

$$G = \frac{n[n^2 - \sin^2 \theta]^{\frac{1}{2}}}{\sin^2 \theta} \quad (9)$$

is a geometrical factor that accounts for the angle of incidence and refraction within the polymer. If the modulation is entirely due to the EO effect then using the approximation in equations 3 and 8 we get:

$$r_{33} = \frac{I_m 3\lambda G}{I_i \pi n^3 V_{AC}}, \quad (10)$$

where the substitution $E_{AC} = V_{AC}/d$ has been made. For typical poled polymers with $n = 1.5$ then $G = 3.97$. Assuming $\lambda = 658$ nm, and $V_{AC} = 480$ V RMS, then $r_{33} = I_m/I_i$ multiplied by a constant, which is approximately 1.75×10^{-12} m/V for the parameters described. For the purposes of performing the experiment, $I_i = I_{\max} - I_{\min}$, the difference in the highest and lowest points on the transmitted intensity curve in figure 1, obtained by adjusting the Soleil-Babinet compensator to trace out the curve in figure 1.

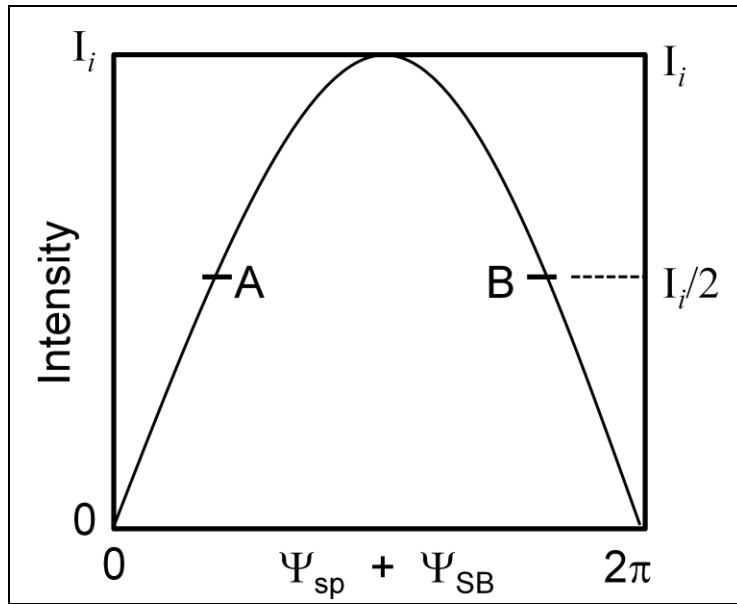


Figure 1. Transmitted intensity vs. phase shift $\Psi_{sp} + \Psi_{SB}$ for the s and p polarizations after the probe beam passes through the sample.

3. Sample Preparation

The chromophores used in this study (figure 2) were DR1 ((E)-2-(ethyl(4-((4-nitrophenyl) diazenyl)phenyl)amino)ethanol), ANS ((E)-4-(4-nitrostyryl)aniline), and MNS ((E)-1-methoxy-4-(4-nitrostyryl)benzene), either as a simple guest-host system or as a copolymer system with a ring-opening metathesis polymer backbone (ROMP) (13). Pelletized polymethylmethacrylate (PMMA) was produced by CYRO Industries (Acrylite H15) and distributed by AMCO Plastics. All other chemicals were obtained from Sigma Aldrich or Alfa Aesar, and were used as received without further purification. MNS was synthesized according to procedures in references (13).

The production of guest-host polymer samples above 1 mm in thickness requires the use of a compounder and an injection molding machine; conventional thin-film polymer techniques such as spin casting or solution casting are unsuitable. To facilitate production of these samples, an approximately 1:1 mixture of PMMA and chromophore was dissolved in a common solvent (acetone) and cast into an aluminum tray (45 mm diameter). As the solvent evaporated, tack-free films formed over a period of about 1 day at room temperature in a fume hood and were further dried in an oven at 60 °C to drive off residual solvent. The films were broken into small pieces and fed into the compounder, along with virgin PMMA, to achieve the desired chromophore content.

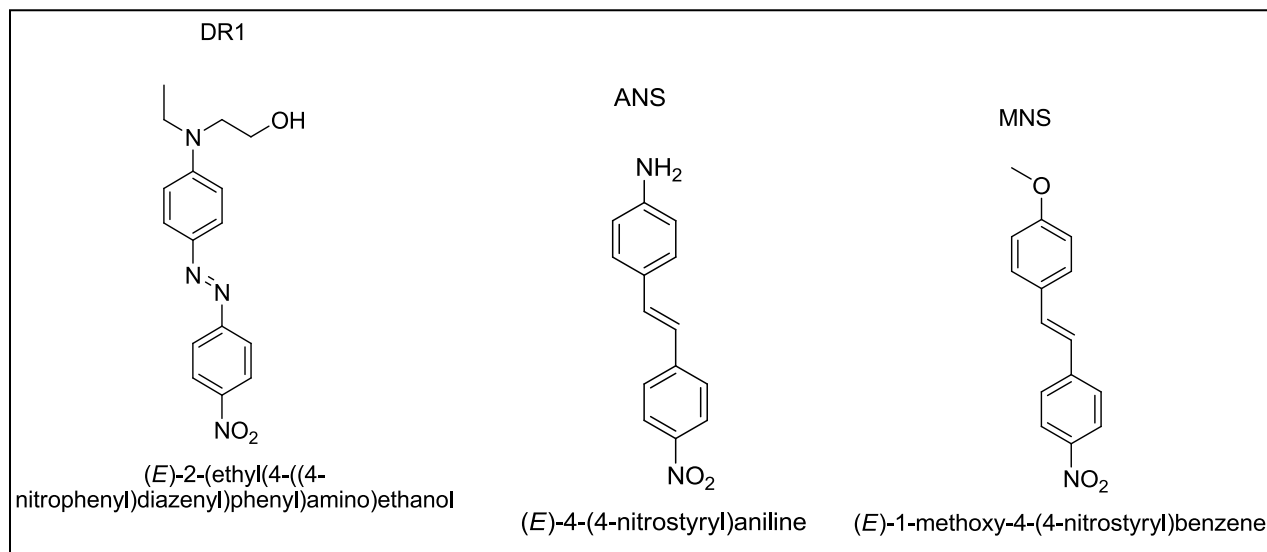


Figure 2. Chromophores used in poled guest-host system.

The polymer samples were processed on a DSM Xplore 15 cc Micro-Compounder, consisting of a clamshell barrel with two conical screws and a 15 mL recirculation pathway to allow for extended processing intervals. The Xplore system is equipped with a pressure transducer, which measures the downforce exerted by the polymer melt, roughly correlating with the viscosity of

the melt. Sample plaques were prepared using a DSM Xplore 12 mL Injection Molding Machine, equipped with a mold yielding 2.5 cm squares, approximately 1 mm thick.

A representative procedure for the preparation of a compounded guest/host system is described below. Beginning with a pre-heated (235 °C) clean barrel and screws, a known quantity of virgin PMMA was used to purge the compounder and the recirculation pathway, removing any residual particulates or polymer from the cleaning process. The extrudate was recovered and weighed, yielding a measure of remaining polymer in the compounder. The pre-mixed chromophore/polymer blend and virgin PMMA were charged into the compounder to provide approximately 15 g total material for processing, and screw rotation was maintained at 100 rpm. After the final addition of the chromophore and PMMA, the feed-port was closed and the polymer melt was compounded for 15 min and maintained under a gentle N₂ purge at about 5 L/min. During this time, the barrel temperature was reduced from 235 °C to 200 °C because of plasticization of the PMMA by the chromophore. The viscosity of the melt dropped significantly after chromophore addition, and a drop in temperature was required to permit sufficient shearing of the melt to ensure homogenization of the melt.

After processing for 15 min, the extrudate was collected in the heated transfer line/plunger assembly used by the DSM Xplore 12 mL injection molding system. The transfer line had been pre-heated to 230 °C, and the extrudate was fed into the transfer line until the pressure transducer measured less than 600 N. The transfer line was then placed into the cradle for the injection molder, and the polymer was injected into a room temperature mold using an 8 bar/10 bar injection pressure (8 bar initial impulse with 10 bar following to ensure full mold fill). Total injection cycle time for each sample was about 10 s. The parts were removed from the mold immediately by applying pressure to the runner of the injected part, and no mold release was required. Individual plaques were removed from the injection tab and were then wrapped in aluminum foil to prevent damage to the surface of the plaque. A small sample was broken off from the injection runner to permit analysis by DSC for glass transition temperature (T_g) determination. The T_g values were measured using a Perkin Elmer Q1000 DSC, with a 0 °C–150 °C heat-cool-heat cycle, heating at 10 °C/min heat and cooling at 20 °C/min. The transition temperature is reported as the inflection point of the transition taken from the second heat cycle. Measured values of T_g were 83.0 °C and 76.9 °C for the 10% MNS and 15% MNS, respectively.

We accomplished chromophore alignment by the use of a poling fixture of our own invention (figure 3), which consists of two nylon blocks fabricated into a clamp-like device, secured by two nylon screws. Polished copper electrodes, each 2 cm in diameter, were inserted into the fixture through holes drilled into the clamp. The copper electrodes have rounded edges to prevent undesired electric field concentrations. The copper electrodes were carefully polished as flat as possible; during the poling process, the smooth surfaces were impressed upon the polymer

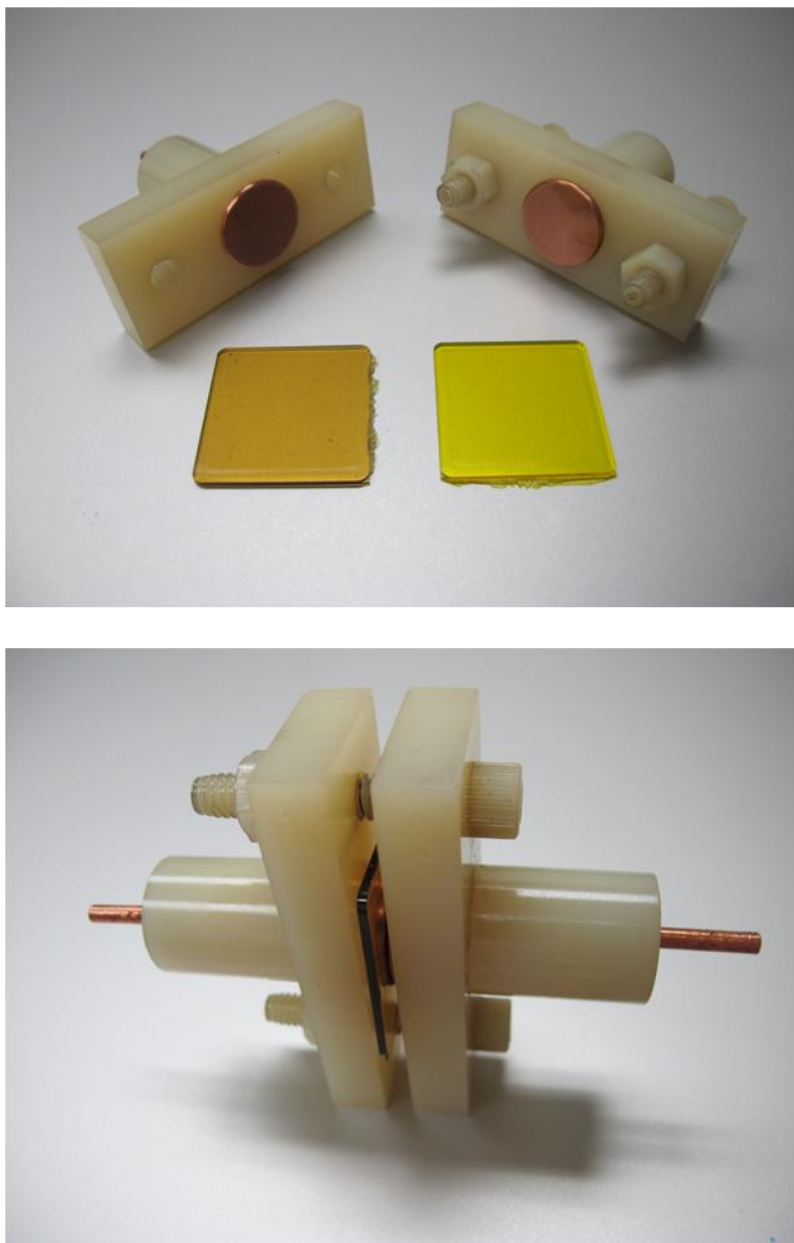


Figure 3. Poling clamp open, showing polymer plaques (top); poling clamp closed (bottom).

plaques, eliminating the need for any post-poling polishing steps. The two nylon screws allow one to adjust the tension against the polymer plaque and to ensure that the copper electrodes are seated parallel to the faces of the plaque. High-voltage connections were made by securing the high-voltage leads from the high-voltage power supply to the poling fixture by copper alligator clamps. This was done so that the poling fixture can easily be removed from the silicone oil bath to access the sample. The copper electrodes are considerably smaller (2 cm) than the polymer plaques (2.5 cm) to allow the extra polymer material to increase the hold-off voltage of the polymer in the clamp.

A Spellman 120 kV high-voltage DC power supply (Model SL120P60) was used to supply the high voltage required for poling. The power supply has an adjustable current overlimit setting that is designed to prevent continuous arcing. The overlimit was set at about 250 μA . Once the limit is exceeded, an internal circuit breaker shuts off the high voltage. The poling fixture was connected to the power supply, as described above, and then immersed in Dow-Corning 710 silicone oil contained in a 2 L Pyrex reaction flask. A Teflon cup was placed in the bath to prevent arcing to the walls of the oven, and Teflon sheathing lines the inside of the reaction flask. The entire bath/sample assembly was then placed in a Cascade Tek TO-3 oven for poling. The temperature was controlled with a Watlow temperature controller. The temperature was set to the inflection point of the glass transition temperature T_g , with the temperature rising from ambient to T_g over the course of 2 h and then maintained near T_g for approximately 10 min. The voltage was increased to 70–90 kV and applied throughout the entire poling process. As the fields near the clamp are large, and any thermocouple device will act as an undesirable ground and suffer damage, the temperature next to the poling clamp was measured with a conventional mercury thermometer. The current through the plaques ranged from 1–5 μA during poling, with the plaques conducting higher currents as the temperature approached T_g . At the end of the poling process, when the temperature reached approximately 40 $^{\circ}\text{C}$, the samples were removed from the oil bath and trimmed of excess unpoled material.

4. Sample Measurement

The optical setup used to measure the electro-optic coefficient is shown in figures 4 and 5. A diode laser or diode pumped solid state (DPSS) laser source is used as the light source for the measurement. The setup is designed to allow sources to be easily changed, and the sources available are diode lasers at 830 nm and 650 nm, and a DPSS laser at 532 nm. The laser source passes through a half-wave plate and then through a calcite polarizer oriented at $+45^{\circ}$ with respect to the table vertical. The light then passes through the sample, which is rotated to permit a 45° angle of incidence (figure 5, inset). Once through the sample, the modulated light passes through a Soleil-Babinet (S-B) compensator, which provides continuous retardance of the *s* and *p* polarizations. After the S-B compensator is another calcite polarizer oriented at -45° to the table vertical. The sample consists of two patterned indium tin oxide (ITO) on glass, with the bulk poled sample placed between them. The ITO surfaces contact the sample on both sides. The glass-ITO slides are compressed to the sample using two spring clamps to ensure good contact. A Hewlett-Packard Model 3325A signal generator provides a clean sine wave signal to the Trek Model 2220 high-voltage amplifier. The voltage from the high-voltage amplifier is connected to the sample, and in most cases the voltage applied to the sample is 480 V RMS. The voltage applied to the sample causes a periodic modulation of the relative phase of the *s* and *p* polarizations, thus resulting in the modulated intensity reaching the detector, as described in section 2. The modulated signal then arrives on the detector, where it is processed by the lock-in

amplifier, a Stanford Research Systems SR830 DSP. It is crucial that all voltages be RMS, otherwise significant errors will be introduced. The value of $I_i = I_{\max} - I_{\min}$, the difference in the highest and lowest points on the transmitted intensity curve in figure 1, is obtained by adjusting the Soleil-Babinet compensator to trace out the curve in figure 1, although only the highest and lowest values are needed. This portion of the measurement is a DC measurement obtained from the digital voltmeter (DVM). The value of I_m is obtained directly from the lock-in amplifier and is the modulated AC signal. At this point, the calculation of r_{33} is simple once n , G , λ , and V_{AC} are known.

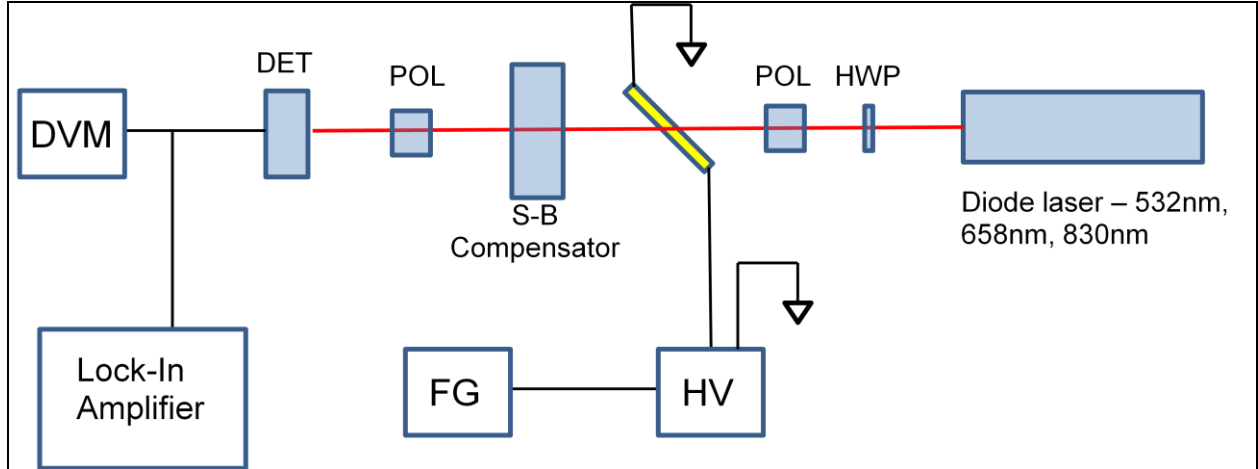


Figure 4. Electro-optic measurement setup based upon Sandalphon et al.

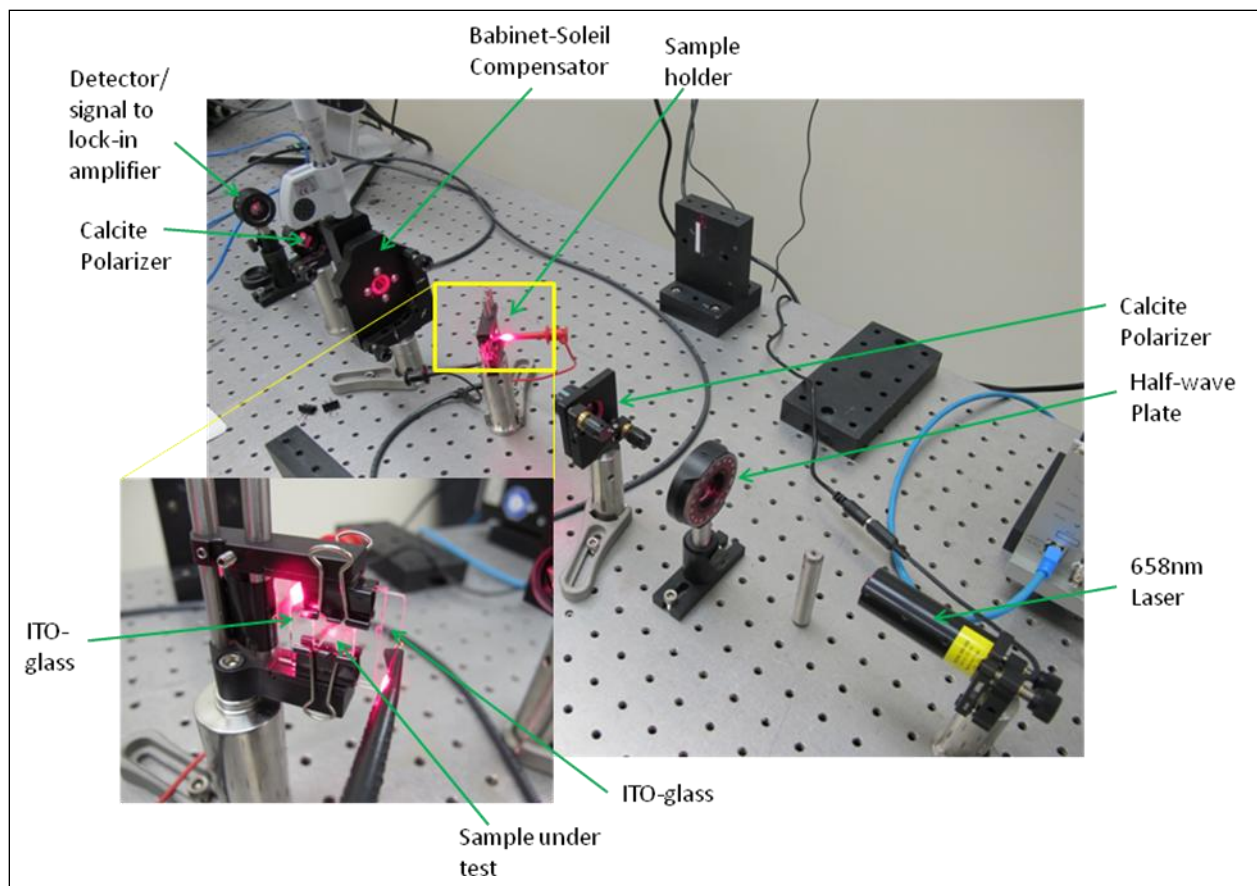


Figure 5. Photo of electro-optic measurement setup showing sample detail.

5. Results and Discussion

We first tested DR1, an easy-to-pole chromophore in PMMA, concentration 10% by weight, and routinely obtain values of r_{33} around 5.6 pm/V, in good agreement with values from the literature. The value of 5.64pm/V (standard deviation = 1.06) for DR1 is a composite of 36 different measurements taken in different sample holders on different days, demonstrating the utility and repeatability of the experiment, and compares favorably to the value of 6.1 pm/V observed in 10% DR1/PMMA samples in our previous experiment using the well-established Maker fringe method (13). Next we tested methoxy nitrostilbene and alkoxy nitrostilbene in simple guest-host polymers and in ROMP copolymer hosts as well. The summary of the results obtained is in table 1.

Table 1. Results of electro-optic measurements of guest-host chromophores

Sample ID	Composition	R_{33}
DR1	10% DR1 in PMMA	5.64pm/V (SD = 1.06)
MHB-153-9C-D	10% alkoxy nitrostilbene/ ROMP polymer	<0.15pm/V
MHB-I-150-B	10% alkoxy nitrostilbene/ ROMP polymer	<0.15pm/V
IV-248-A2	15% methoxy nitrostilbene in PMMA	<0.15pm/V
IV-248-B	15% methoxy nitrostilbene in PMMA	0.65pm/V
CDR-I-030	10% methoxy nitrostilbene/ PMMA with Diels-Alder cross-links	<0.15pm/V

It is clear from the data in table 1 that the chromophores in ROMP based polymers suffer from low values of r_{33} . The r_{33} values we observe for similar concentrations of ANS and MNS in PMMA as simple guest-host polymers, 0.7 to 1.75 pm/V (532 nm), using the Maker fringe technique (14), are commensurate with the values observed in this experiment, when the different source wavelengths are considered. Depoling, or spontaneous thermal randomization of the chromophores, was also observed in the ROMP samples in this experiment, as well as the samples in (14) when using the Maker fringe technique to make the measurement. The depoling was observed to take place over a period of a few hours.

To remedy the situation with the depoling of chromophores, we are switching to a different ROMP system with additional co-monomers designed to enhance the T_g of the polymer and improve thermal stability. In addition, we have begun exploring high T_g PMMA-based linear and hyperbranched polymers where the chromophores are covalently bound to the polymer backbone. The chromophores are attached through a post-polymerization process. The chromophore is attached through reaction with an isocyanate group appended to the polymer backbone to produce a urethane linkage. The resulting urethane linkage can hydrogen bond with other urethanes and improve thermal stability.

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List of Symbols, Abbreviations, and Acronyms

AC	alternating current
ANS	((E)-4-(4-nitrostyryl) aniline)
DC	direct current
DSC	differential scanning calorimetry
CW	continuous wave
DPSS	diode pumped solid state
DR1	Disperse Red 1
DVM	digital voltmeter
EO	electro-optical
ITO	indium tin oxide
NLO	nonlinear optical
MNS	((E)-1-methoxy-4-(4-nitrostyryl) benzene)
PMMA	polymethylmethacrylate
RMS	root-mean-square
ROMP	ring-opening metathesis polymer
T _g	glass transition temperature
THz	terahertz

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1	US ARMY RESEARCH LAB ATTN RDRL SEE M A G MOTT BLDG 207 Z3D-46-20 2800 POWDER MILL RD ADELPHI MD 20783-1197

ABERDEEN PROVING GROUND

3	US ARMY RESEARCH LAB ATN RDRL WMM G J A ORLICKI G R MARTIN R LAMBETH
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