

# Electro-optic characterization of nonlinear-optical guest–host films and polymers

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The Pockels coefficients  $r_{33}$  of four dyes for electro-optic applications are reported, including ones with stilbene, butadiene, azo, and hexatriene linkages between the charge donors and acceptors, with the charge donor being the amino group and the acceptor groups being the nitro and dicyanovinyl groups.  $r_{33}$  are reported for dyes as guest–hosts in poly(methyl methacrylate) and 50/50 copolymers with methyl methacrylate. The largest  $r_{33}$  is observed for the copolymer containing the amino donor, hexatriene linkage, and the dicyanovinyl acceptor group with a value of  $r_{33} = 18$  pm/V at 140 V/ $\mu\text{m}$  at a wavelength  $\lambda = 1.3$   $\mu\text{m}$ . We also find evidence that the dicyanovinyl hexatriene dyes in the copolymer are interacting with one another, causing a relative decrease in the copolymer's electro-optic efficiency compared with its value as a guest–host in poly(methyl methacrylate). The Pockels coefficient is measured by the ellipsometric reflection technique. We derive approximate analytic equations to analyze the reflected intensity and verify the validity of these approximations when the analyzing wavelength is far from the absorption of the dye. We also derive an approximate analytic expression for the optical retardation as a function of the ratio of the off-diagonal to the diagonal components of the Pockels coefficients  $r_{13}/r_{33}$  and also the finite birefringence of the poled film. We show that accurate knowledge of the ratio  $r_{13}/r_{33}$  is critical to obtaining accurate values of  $r_{33}$ . © 1996 Optical Society of America.

## 1. INTRODUCTION

Polymer-based electro-optic (EO) materials are attractive alternatives to crystals because of their ease of processing by spin coating onto wafers to make thin films with potentially high EO coefficients.<sup>1</sup> High concentrations of nonlinear-optical (NLO) dyes are covalently attached to a polymer backbone such as poly(methyl methacrylate) (PMMA) or polyimide to yield high EO coefficients after electric field poling. NLO dyes usually have large dipole moments of  $\sim 10$  D, and this may lead to large dipole–dipole interchromophore interactions. The resultant NLO activity may be quite different from the expected value based on a simple additivity model. To study this phenomenon we carried out a study of the EO properties of NLO polymers as a function of the concentration of the NLO dye molecule. At low concentrations the NLO dye was dissolved in PMMA as a guest–host, and at high concentrations it was covalently bonded to a PMMA back-

bone polymer. The dyes used had stilbene, butadiene, azo, and hexatriene linkages between the charge donors and acceptors. The charge donor was the amino group in all cases, and the acceptor groups were the nitro and dicyanovinyl groups. These dyes have some of the largest known hyperpolarizabilities.<sup>2–5</sup>

We used the ellipsometric reflection technique to measure the EO coefficients of the polymer films. A number of workers<sup>2,6–12</sup> have analyzed both theoretically and experimentally the reflection from a stratified thin-film structure in which the NLO film is sandwiched between a metal and an indium tin oxide (ITO) electrode. They derived equations for the reflectivity of the EO modulated signal as a function of incident angle in terms of the Fresnel coefficients and the Pockels coefficients.<sup>9–11</sup> They fitted these complex equations to the experimental data by computer and deduced the EO coefficients. Numerical calculations based on these exact models show that, when there is no absorption in the film and the

thickness of the film is less than the wavelength of the analyzing beam of light, the simple analytic equations deduced earlier<sup>2,6-8,12</sup> appear to be valid.<sup>9,11</sup> In this paper we extend and derive a more general analytic expression in terms of the two Pockels coefficients  $r_{33}$  and  $r_{13}$  and also the finite birefringence of the film. We start from the exact equations for a stratified medium and then introduce successive approximations. We give experimental evidence for the validity of the successive approximations.

## 2. ELECTRO-OPTIC EFFECT IN THIN POLYMER FILMS: EXPERIMENT AND THEORY

In this section we describe the experimental arrangement for measuring the EO coefficients and also state the key analytic results for the reflectivity from a stratified medium based on our approximations. The detailed derivation is given in Appendix A. We also report experimental results that support the approximations that we have introduced to simplify the complicated reflectivity equations.

### A. Experimental Arrangement

We carried out the Pockels measurements by using the setup depicted schematically in Fig. 1. A low-power diode laser (Melles Griot, wavelength  $\lambda = 1.3 \mu\text{m}$ ) whose polarization was at  $45^\circ$  to the plane defined by the incident and the reflected beams was reflected off the polymer sample at an angle of incidence of  $45^\circ$ . A Babinet-Soleil compensator (Karl Lambrecht) was used to adjust the relative retardations of the  $s$  and  $p$  waves between 0 and  $2\pi$ . The analyzer was crossed relative to the incident polarization. A signal generator (Stanford Research PS350) supplied 50 V rms with frequency 1 kHz across the  $2\text{-}\mu\text{m}$  thick polymer sample, and the modulated intensity signal was measured with a silicon detector and a lock in amplifier (Stanford Research Model SR530). The modulated reflected intensity  $dI^{\text{mod}}/dV$  was recorded at two settings of the Babinet-Soleil compensator,  $s1$  and  $s2$ , corresponding to retardations of  $\pi/2$  and  $3\pi/2$ , respec-

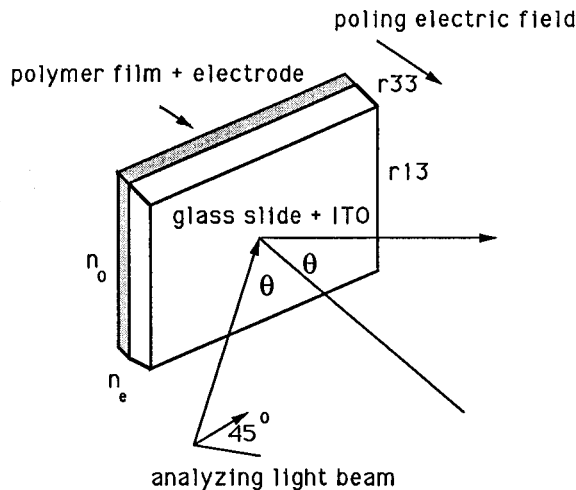


Fig. 1. Schematic of reflection from an EO film.

tively, between the  $s$  and  $p$  waves, and the average of the two signals was taken. The compensator was used to adjust the total retardation in the optical system (sum of compensator and polymer static birefringence) to be equal to  $\phi^{\text{comp}} = \pi/2 (s1)$  or  $\phi^{\text{comp}} = 3\pi/2 (s2)$ . At this setting it can be shown that the modulated intensity  $dI^{\text{mod}}/dV$  at  $s1$  and  $s2$  is linearly proportional to the EO modulated retardation  $d\phi^{\text{eo}}/dV$ . We measured the continuous-wave (cw) intensity of the reflected beam  $I_{\text{max}}$  by removing the analyzer and recording the signal on the silicon detector with a dc voltmeter. We prepared the EO polymer sample by spin coating a  $2\text{-}\mu\text{m}$  thick NLO polymer from the solvent hexanone onto an ITO-coated glass slide and then drying the slide in an oven. Then a thin layer of gold was deposited in vacuum (Edwards) onto the polymer film. The gold electrode served a dual purpose: It poled the polymer near its glass transition temperature and acted as a mirror for reflecting the analyzing  $\lambda = 1.3 \mu\text{m}$  light beam. The absorption of the polymers at  $\lambda = 1.3 \mu\text{m}$  was low and could be neglected in the analysis of this experiment.

### B. Approximate Analytic Expressions for Reflectivity from a Multilayer Stack

In our model we consider the two interfaces whose Fresnel reflectivities are expected to be voltage dependent, namely, the glass-polymer ( $r_{\text{gp}}$ ) and the polymer-metal ( $r_{\text{pm}}$ ) interfaces (see Fig. 1).  $r_{\text{pm}}$  is expected to be much greater than  $r_{\text{gp}}$ . Expressions for the Fresnel reflection coefficients can be found in the literature.<sup>13,14</sup> The phase retardation experienced by the ordinary and the extraordinary waves is given by<sup>14</sup>  $\phi_e = (4\pi d/\lambda) n_e(\theta_e)\cos\theta_e$  and  $\phi_o = (4\pi d/\lambda) n_o\cos\theta_o$ , respectively, where  $d$  is the thickness of the sample and  $n_e$  and  $n_o$  are the extraordinary and ordinary refractive indices, respectively. We also assume that there is no absorption in the sample because in our experiments the analyzing wavelength was from a near-infrared laser and far from the absorption maximum of the dyes. It can be shown that the reflected intensity  $I$  incident upon the detector is given by (see Appendix A)

$$I = I_{\text{max}} \sin^2(\phi/2), \quad (1)$$

where  $I_{\text{max}} = r_{\text{pm}}^o r_{\text{pm}}^e$  is the cw reflected signal and  $\phi$  is the total retardation in the optical system, given by

$$\phi = \phi^{\text{eo}} + \phi^{\text{comp}}. \quad (2)$$

$\phi^{\text{eo}} = \phi_e - \phi_o$  denotes the difference in phase retardations between  $\phi_e$  and  $\phi_o$  and comes from the static birefringence induced by poling and the EO Pockels effect.  $\phi^{\text{eo}}$  is much less than that owing to the compensator because  $\phi^{\text{comp}} = \pi/2$  or  $\phi^{\text{comp}} = 3\pi/2$  during measurement.

### C. Experimental Verification of Eq. (1)

We show that the modulated reflected signal has two components, which come from the EO effect and the Fresnel reflectivity at the polymer-metal electrode interface. We calculate the modulated signal  $dI^{\text{mod}}/dV$  when a sinusoidal voltage  $V$  is applied across the polymer sample during measurement. Differentiating Eq. (1) and normalizing by  $I_{\text{max}}$ , we obtain

$$\frac{1}{I_{\max}} \frac{dI^{\text{mod}}}{dV} = \frac{\sin(\phi^{\text{comp}})}{2} \frac{d\phi^{\text{eo}}}{dV} + \frac{\sin^2(\phi^{\text{comp}}/2)}{I_{\max}} \frac{dI_{\max}}{dV}. \quad (3)$$

The second term is usually much less than the first term and accounts in an approximate way for the modulation of the Fresnel reflection terms, because they are also functions of the refractive indices. To test the validity of Eq. (3) we carried out a number of optical experiments in which we measured  $dI^{\text{mod}}/dV$  as a function of compensator setting. Figure 2 is an experimental plot of the cw and the modulated intensities,  $I_{\max}$  and  $dI^{\text{mod}}/dV$ , respectively, as a function of the compensator retardation  $\phi^{\text{comp}}$ . Note that the cw intensity reflected from the sample is typically 100–1000 greater than  $dI^{\text{mod}}/dV$ , so the latter has been arbitrarily scaled to plot on the same graph. The cw intensity has a  $\sin^2(\phi^{\text{comp}}/2)$  [see Eq. (1)] dependence, whereas  $dI^{\text{mod}}/dV$  has a  $\sin(\phi^{\text{comp}})$  dependence, on compensator setting [see Eq. (3)]; note that in Fig. 2  $dI^{\text{mod}}/dV$  at  $s_1$  and  $s_2$  (corresponding to  $\phi^{\text{comp}} = \pi/2$  and  $\phi^{\text{comp}} = 3\pi/2$ ) are equal and symmetrical, which means that  $dI_{\max}/dV = 0$  in Eq. (3). The shape of the curve  $dI^{\text{mod}}/dV$  on the compensator setting deserves some comment. It is almost zero whenever the cw signal is a maximum or a minimum, and there is also a cusp. It is actually a  $\sin(\phi^{\text{comp}})$  function that goes from a positive to a negative sign, but because the lock-in amplifier reads only an amplitude, the curve registers on the lock-in amplifier as a  $180^\circ$  phase change.

We found from our many measurements of guest–host and polymer films that the results of Fig. 2 are atypical. Figure 3 is a result obtained from one of our samples in which the intensities at  $s_1$  and  $s_2$  are not equal. The degree of asymmetry is large in Fig. 3 but serves to illustrate our observations. We can easily account for this asymmetry by invoking the second term in Eq. (3), which includes  $dI_{\max}/dV$ . From Eq. 3 the modulated signals at  $s_1(\phi^{\text{comp}} = \pi/2)$  and  $s_2(\phi^{\text{comp}} = 3\pi/2)$  are given by

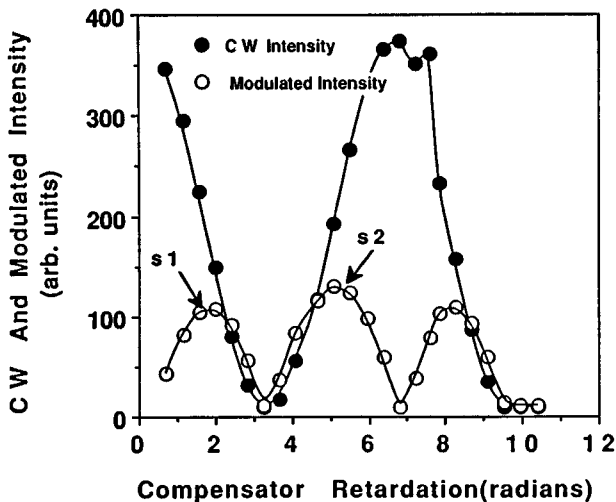


Fig. 2. cw and modulated intensity versus compensator retardation: The amplitudes are equal at  $s_1$  and  $s_2$ , corresponding to compensator retardations of  $\pi/2$  and  $3\pi/2$ .

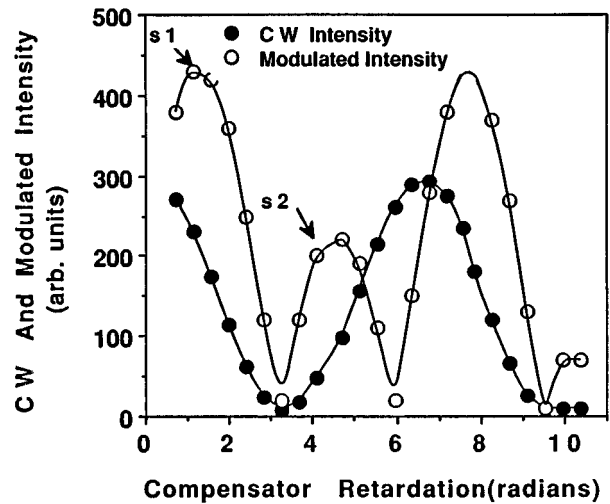


Fig. 3. cw and modulated intensity versus compensator retardation: The amplitudes at  $s_1$  and  $s_2$  are not equal.

$$\frac{1}{I_{\max}} \left( \frac{dI^{\text{mod}}}{dV} \right)_{s_1} = \frac{1}{2} \left[ \frac{1}{I_{\max}} \frac{dI_{\max}}{dV} + \frac{d\phi^{\text{eo}}}{dV} \right], \quad (4a)$$

$$\frac{1}{I_{\max}} \left( \frac{dI^{\text{mod}}}{dV} \right)_{s_2} = \frac{1}{2} \left[ \frac{1}{I_{\max}} \frac{dI_{\max}}{dV} - \frac{d\phi^{\text{eo}}}{dV} \right]. \quad (4b)$$

In Eq. 4(b) the second term is negative, and there is a  $180^\circ$  change in phase as measured by a lock-in amplifier. However, because the lock-in amplifier always measures a positive amplitude (irrespective of its phase), we can average the two expressions in Eq. (4) to obtain

$$\frac{d\phi^{\text{eo}}}{dV} = \frac{1}{I_{\max}} \left[ \left( \frac{dI^{\text{mod}}}{dV} \right)_{s_1} + \left( \frac{dI^{\text{mod}}}{dV} \right)_{s_2} \right]. \quad (5)$$

Throughout our study we measured the modulated EO signals  $dI^{\text{mod}}/dV$  that corresponded to the compensator settings  $s_1(\pi/2)$  and  $s_2(3\pi/2)$  and averaged the two signals. According to Eq. (5) this yields  $d\phi^{\text{eo}}/dV$ . A similar expression was derived by Levy *et al.*<sup>9</sup> and Chollet *et al.*<sup>11</sup>

To check further the internal consistency of our model and approximations, we performed an additional experiment by removing the analyzer and recording the modulated reflected intensity when a sinusoidal voltage was applied across the sample. If the modulated intensity was of purely EO origin, no signal should be observed. The fact that there is a signal  $dI_{\max}/dV$  in the absence of the analyzer means that there is a modulated reflectivity. We discount the possibility of modulated absorption because the analyzing wavelength ( $1.3 \mu\text{m}$ ) is far from the absorption of these polymers. To account for this we subtract Eq. (4a) and (4b) from each other to quantify the asymmetry of the modulated signal. Thus

$$\frac{1}{I_{\max}} \left( \frac{dI_{\max}}{dV} \right) = \frac{1}{I_{\max}} \left[ \left( \frac{dI^{\text{mod}}}{dV} \right)_{s_1} - \left( \frac{dI^{\text{mod}}}{dV} \right)_{s_2} \right]. \quad (6)$$

Equation (6) predicts that the difference of the modulated signals at  $s_1$  and  $s_2$  (obtained with the analyzer present) is equal to the modulated reflected intensity  $dI_{\max}/dV$  (obtained with analyzer removed). Figure 4 is

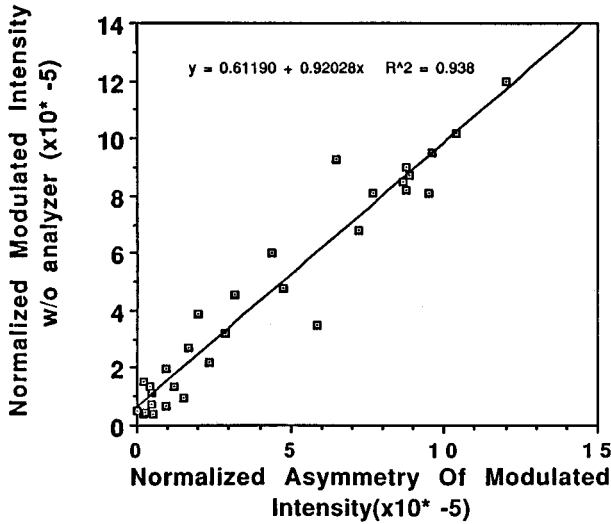


Fig. 4. Normalized modulated intensity without an analyzer versus normalized asymmetry of modulated intensity with an analyzer: verification of Eq. (6).

a plot of experimental values of  $(1/I_{\max})(dI_{\max}/dV)$  versus the asymmetry of the modulated signals at  $s_1$  and  $s_2$  for many samples studied during the course of this research. The slope is 0.94, clearly showing the validity of Eq. (6) and the theoretical model to analyze this experiment. Chollet *et al.*<sup>11</sup> also derived an expression similar to Eq. (6) but did not verify it experimentally.

**D. Approximate Analytic Expression for Optical Retardation in a Birefringent Film**

Consider a uniaxial EO medium of thickness  $d$  that has been poled with static refractive indices  $n_{es}$  (along poling direction) and  $n_{os}$  (normal to the poling direction). During the measurement of EO coefficients a modulating voltage  $V$  is applied across thickness  $d$ , and the refractive indices of the slab change according to the relations<sup>13</sup>

$$n_e = n_{es} - \frac{1}{2}n_{es}^3 r_{33} V/d, \tag{7}$$

$$n_o = n_{os} - \frac{1}{2}n_{os}^3 r_{13} V/d,$$

where  $r_{33}$  and  $r_{13}$  are the Pockels coefficients of the slab. To obtain an expression for the modulated phase retardation  $d\phi^{eo}/dV$  in a film with finite birefringence it is convenient to define the ratio of the nonlinear susceptibilities:

$$\alpha = \frac{\chi_{zxx}^2}{\chi_{zzz}^2} = \frac{n_{os}^4 r_{13}}{n_{es}^4 r_{33}}, \tag{8}$$

where  $\chi^2$  is the nonlinear susceptibility. The ratio of off-diagonal-to-diagonal susceptibility has a nominal value of 1/3 according to the Debye model of independent dipoles oriented by an electric poling field,<sup>15</sup> which would be expected to be true in the case of a dilute concentration of dyes dissolved in a polymer (guest-host system). When the concentration is higher one could expect deviations from 1/3 because of aggregation and restricted motion. The resultant expression for  $d\phi^{eo}/dV$  is (see Appendix B)

$$\frac{d\phi^{eo}}{dV} = \frac{2\pi r_{33}(\alpha n_{es}^2 - n_{os}^2)}{\lambda} \frac{\sin^2 \theta}{(n_{os}^2 - \sin^2 \theta)^{1/2}} D(\alpha, \theta), \tag{9}$$

where  $D$  is given by

$$D(\alpha, \theta) = 1 + \frac{n_{es}^2 - n_{os}^2}{2(n_{os}^2 - \sin^2 \theta)} \left[ \frac{\alpha n_{es}^2}{\alpha n_{es}^2 - n_{os}^2} - \frac{\sin^2 \theta}{n_{es}^2} \right] - \frac{3(n_{es}^2 - n_{os}^2)^2 \sin^2 \theta}{8(n_{os}^2 - \sin^2 \theta)^2} + \dots \tag{10}$$

In the limit of zero static birefringence, i.e.,  $n_{es} = n_{os}$  and  $D(\alpha, \theta) = 1$ , Eq. (9) simplifies to

$$\frac{d\phi^{eo}}{dV} = \frac{2\pi n^2 [r_{31} - r_{33}]}{\lambda} \times \frac{\sin^2 \theta}{(n^2 - \sin^2 \theta)^{1/2}}, \tag{11}$$

where  $n$  is the average refractive index in the limit of low poling voltage. Equation (11) was first derived in Ref. 6 and used to deduce EO coefficients in guest-host films and polymers.<sup>2</sup> An analogous expression was also derived for the Kerr effect and used to deduce the Kerr constant of polymer-dispersed liquid crystal composites.<sup>12</sup> The subsequent derivation in Ref. 7 is incorrect. Levy *et al.*<sup>9</sup> and Chollet *et al.*<sup>11</sup> also derived Eq. (11), using a somewhat different approach.

In Fig. 5 we evaluate the magnitude of  $D$  [Eq. (10)] as a function of  $\theta$  and  $\alpha$  for the case of 50/50 DANS/methyl methacrylate (DANS/MMA) copolymer when it is poled at 160 V/ $\mu\text{m}$  [see Fig. 6 for the chemical structure of the polymer]. The refractive indices for this polymer are  $n_{es} = 1.71$  and  $n_{os} = 1.60$  at a wavelength  $\lambda = 1.3 \mu\text{m}$ . We note that the larger the  $\alpha$  value, the greater the change of  $D$  with incident angle  $\theta$ . The neglect of the finite birefringence will result in a 15% error (at most) in the EO coefficient for the case of a moderately poled film (<150 V/ $\mu\text{m}$ ) consisting of DANS-like NLO dyes. It is also clear from Eq. (9) that the biggest source of error in obtaining EO coefficients is the often made assumption that  $\alpha = 1/3$ .

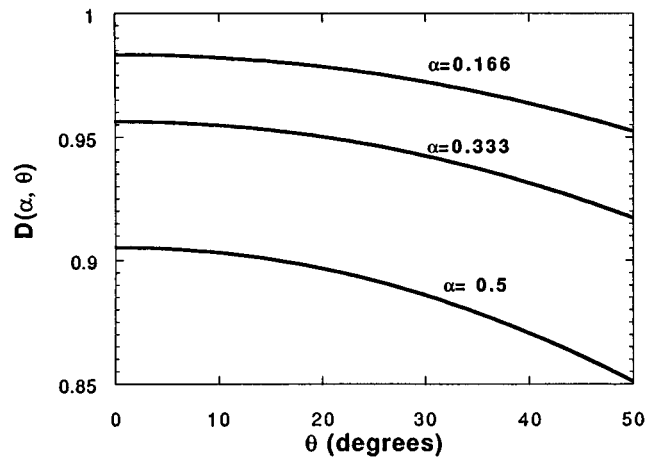


Fig. 5. Deviation function  $D$  versus angle of incidence for different values of  $\alpha$ . The refractive indices used in the calculation are those of DANS polymer poled at 160 V/ $\mu\text{m}$ .

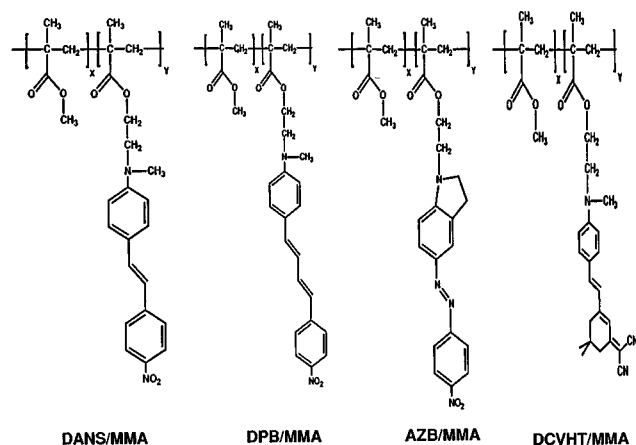


Fig. 6. Molecular structures of the dyes and polymers used in this study.

Levy *et al.*<sup>9</sup> derived an expression similar to Eq. (11) and verified its validity as a function of incident angle  $\theta$  when the incident wavelength  $\lambda$  was far from the absorption maximum of the dye molecule (see Fig. 4 of Ref. 9). When the incident wavelength was near the absorption maximum Levy *et al.*,<sup>9</sup> Chollet *et al.*,<sup>11</sup> and Morichere *et al.*<sup>10</sup> observed significant deviations from Eq. (11) when they did angle scans and instead used the full Fresnel expressions for stratified media to deduce the EO coefficients. In our research the analyzing wavelength, 1.3  $\mu\text{m}$ , was far from the absorption maximum of the dyes used, so we did not do angle scans of the reflected intensity. We kept the angle at  $45^\circ$  and used Eqs. (5) and (9) to deduce the EO coefficients of the polymers and the guest-host samples.

### 3. NONLINEAR-OPTICAL POLYMERS, DYES, AND GUEST-HOST SAMPLE PREPARATION

The polymer structures studied in this paper are shown in Fig. 6 and were 50/50 copolymers of MMA and DANS/MMA, 1-[4-[N-methyl-N-(2-methacryloyloxyethyl)-amino]-phenyl]-4-(4-nitrophenyl)-butadiene (DPB/MMA), 1-(2-methacryloyloxyethyl)-5-(4'-nitrophenylazo)-indoline (AZB/MMA) and amino dicyanovinyl hexatriene (DCVHT/MMA). The synthesis of these polymers is described elsewhere.<sup>2</sup> All the dyes in these polymers have the same amino donor group but differ from DANS because the molecule is made longer, thereby increasing the transition dipole moment (DPB), the amino group is restricted to planar position and the azo is substituted for the stilbene bond (AZB), and the acceptor is changed from nitro to dicyanovinyl group (DCVHT).

For guest-host film studies the NLO-containing monomers were dissolved in PMMA as follows: A 7% (w/w) of high molecular weight PMMA (Aldrich) was dissolved in cyclohexanone. Then the NLO dye was dissolved such that its concentration relative to the PMMA was 3%, 6%, or 12% w/w. Most of the guest-host studies were carried out on the 12%-w/w samples. The solutions were spun coated onto ITO-coated glass to give film thicknesses of

$\sim 2 \mu\text{m}$ . The samples were placed in an oven at  $120^\circ\text{C}$  for 3 h in a nitrogen atmosphere to dry the films. Then gold electrodes were deposited in an Edwards vacuum deposition coater, wires were attached to the ITO and gold electrodes, and the samples were poled at a temperature  $5^\circ$  below the glass transition temperature  $T_g$  of these polymers to avoid excessive conduction.

### 4. ULTRAVIOLET-VISIBLE SPECTRA BEFORE AND AFTER DRYING OF GUEST-HOST FILMS

It is well known that small molecules such as *p*-nitroaniline sublime when they are dissolved as guest-hosts in PMMA and heated to its  $T_g$ . Furthermore, when the films are at ambient temperature the molecules tend to crystallize or diffuse to the surface of the film. For this reason we measured ultraviolet-visible spectra of the NLO dyes before and after drying off the solvent. Figure 7 shows the ultraviolet-visible spectra of DCVHT guest-host films before and after drying in the oven at  $120^\circ\text{C}$  for 3 h. One sees very little difference, which means that the dye was not subliming from the PMMA film. We also measured the spectra of dried films as a function of concentration of NLO dye. Figure 8 shows

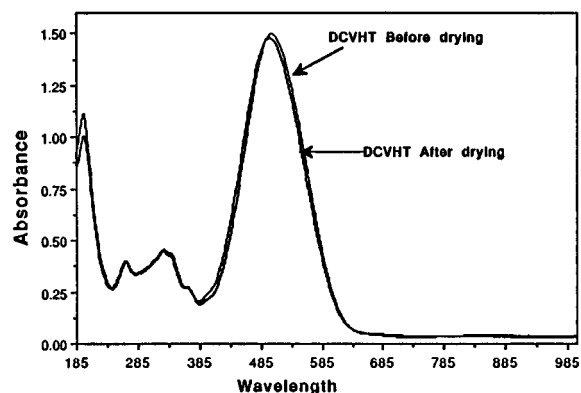


Fig. 7. Absorption spectra of 12% w/w guest host of DCVHT in PMMA before and after drying at  $120^\circ\text{C}$  in an oven.

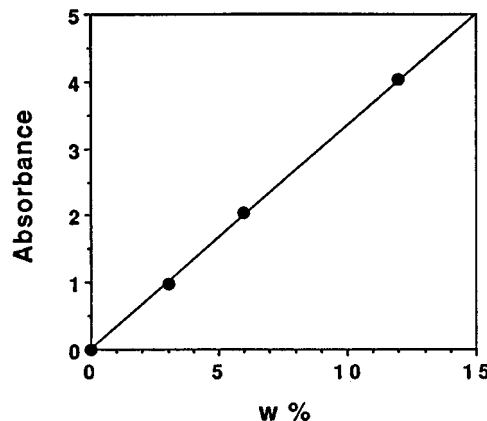


Fig. 8. Absorption at  $\lambda_{\text{max}} = 515 \text{ nm}$  versus concentration of DCVHT in PMMA.

that the peak absorbance at 515 nm increases linearly with concentration, indicating again that there is no sublimation of the dyes because of film heating or crystallization at ambient temperature. We conclude that the method of film preparation does not lead to the degradation or sublimation of the dyes. The absence of new absorption peaks and the linear dependence of absorption versus concentration are also evidence that no aggregation of dyes was occurring up to 12% w/w. This was confirmed for all four dyes studied in this paper.

## 5. RESULTS OF ELECTRO-OPTIC COEFFICIENTS OF GUEST-HOSTS AND POLYMERS

Figure 9 shows the  $r_{33}$  of the 12% w/w guest-host films versus the poling electric field  $E_p$ . There is a linear dependence on  $E_p$  up to the highest value used for poling (140 V/ $\mu$ m). Table 1 reports the  $r_{33}$  values at 3%, 6%, and 12% w/w of dye in PMMA at  $E_p = 100$  V/ $\mu$ m.  $r_{33}$  of the guest-host films were deduced with the assumption that  $\alpha = 1/3$ , i.e.,  $r_{13} = 1/3r_{33}$ . Although one would have to measure the two components separately to verify this assumption, circumstantial evidence points to its validity. We noted above that the ultraviolet-visible absorption maximum scaled linearly with concentration of dye in PMMA and that no new absorption peaks appeared, which is indicative that no aggregation of dye was occurring. In Fig. 9 the slope is a measure of the dyes' EO activity relative to DANS. The ratios are DCVHT:AZB:DPB:DANS = 3.17:1.67:1.47:1. DCVHT has the largest activity because of the strength of the dicyanovinyl acceptor group and the length of the molecule. AZB has a larger activity than DANS because of the presence of the azo bond, and the amino group is fixed in the plane of the molecule. DPB has a larger activity than DANS because of its longer length, so the transition dipole moment is larger.

Figure 10 shows the results of  $r_{33}$  versus poling voltage for the four copolymers depicted in Fig. 6. Again, there is linear dependence of  $r_{33}$  on poling field, and one can attain large values of  $r_{33} = 25$  pm/V at 140 V/ $\mu$ m for the copolymer DCVHT. Table 1 gives  $r_{33}$  values of these co-

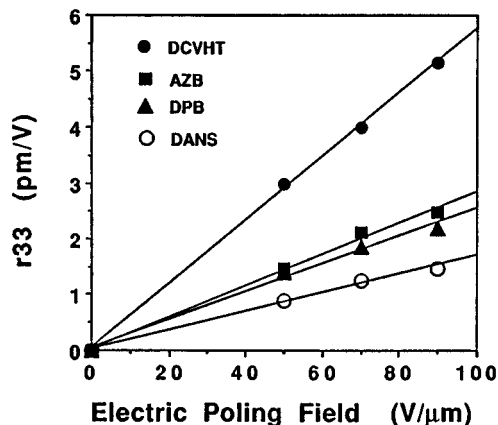


Fig. 9.  $r_{33}$  versus poling field for the four dyes as 12% w/w guest-hosts in PMMA.

**Table 1. Pockels Constants  $r_{33}$  (pm/V) of 3%, 6%, and 12% w/w Dye in PMMA as Guest-Host<sup>a</sup> and Dye/MMA 50/50 Copolymers at  $\lambda = 1.3$   $\mu$ m and a Poling Electric Field of 100 V/ $\mu$ m**

	DANS <sup>b</sup>	DPB <sup>b</sup>	AZB <sup>b</sup>	DCVHT <sup>b</sup>
3% G/H <sup>c</sup>	—	—	0.6	1.2
6% G/H <sup>c</sup>	—	—	1.8	2.2
12% G/H <sup>c</sup>	1.7	2.5	2.85	5.4
57% (50/50 copolymer) <sup>c</sup>	8.5	11.3	14	16.4
57% (50/50 copolymer) <sup>d</sup>	7.9	—	—	12.9

<sup>a</sup> G/H.

<sup>b</sup> Chemical structures of dyes and copolymers shown in Fig. 6.

<sup>c</sup>  $r$  calculated from Eq. (9) with  $n_{es} = n_{os}$  and  $\alpha = 1/3$ .

<sup>d</sup>  $r$  calculated from Eq. (9).  $n_{es}$ ,  $n_{os}$ ,  $\alpha$ , and  $D$  values are given in text.

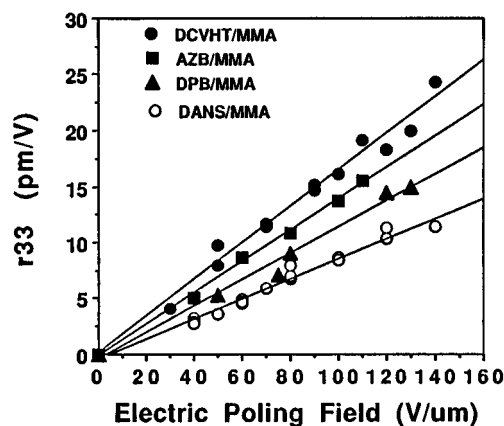


Fig. 10.  $r_{33}$  versus poling field for the four copolymers shown in Fig. 6.

polymers at 100 V/ $\mu$ m based on the assumption that  $r_{33} = 1/3r_{13}$  in Eq. (9). In the case of the copolymer AZB/MMA Nahata *et al.*<sup>4</sup> reported  $r_{33} = 7$  pm/V at 50 V/ $\mu$ m and at a concentration of  $1.6 \times 10^{21}$ /cm<sup>3</sup>, which corresponds to a 50/50 mole fraction concentration. Because the Pockels coefficient increases linearly with poling field one can extrapolate their value to 14 pm/V at 100 V/ $\mu$ m, in excellent agreement with value reported here.

In the case of the two copolymers 50/50 DANS/MMA and 50/50 DCVHT/MMA we can recalculate more-accurate values of  $r_{33}$  by using Eq. (9) and some of the data reported by Norwood *et al.*<sup>5</sup> They used an interferometric method to measure  $r_{13}$  and  $r_{33}$  of DANS/MMA 35/65 copolymer. They obtained  $r_{13}/r_{33} = 0.3$ . We assume that this value applies to the copolymer 50/50 DANS/MMA. Also,  $n = 1.636$ ,  $n_{es} = 1.665$ , and  $n_{os} = 1.622$  for the copolymer at 100 V/ $\mu$ m and  $\lambda = 1.3$   $\mu$ m. Therefore  $\alpha = n_{os}^4 r_{13} / n_{es}^4 r_{33} = 0.26$ , and the deviation function  $D = 0.99$  [Eq. (11)]. Substituting these parameters into Eq. (9), we calculate a new  $r_{33}$  for 50/50 DANS/MMA of 7.9 pm/V at 100 V/ $\mu$ m, which is 6.5% lower than the value based on the assumption that  $r_{13} = 1/3r_{33}$ . In the case of the copolymer 50/50 DCVHT/MMA Norwood *et al.*<sup>5</sup> obtained  $r_{13}/r_{33} = 0.17$ . Also,  $n = 1.669$ ,  $n_{es} = 1.6876$ , and  $n_{os} = 1.660$  for this copolymer at 100 V/ $\mu$ m and  $\lambda = 1.3$   $\mu$ m. Therefore  $\alpha = 0.158$  and  $D = 0.98$ . Substituting these param-

eters into Eq. (9), we obtain a new  $r_{33}$  for 50/50 DCVHT/MMA of 12.9 pm/V at 100 V/ $\mu\text{m}$ , which is 21% lower than the value based on the assumption that  $r_{13} = 1/3r_{33}$ . For this polymer Norwood *et al.*<sup>5</sup> reported that  $r_{33} = 14$  pm/V at 100 V/ $\mu\text{m}$ , which is 8% higher than the value reported here. These recalculated values of  $r_{33}$  are also given in Table 1. DCVHT/MMA 50/50 copolymer has an  $r_{33}$  of 18 pm/V at a poling field of 140 V/ $\mu\text{m}$  based on the recalculated parameters of  $\alpha = 0.158$  and  $D = 0.98$ .

The relative ratios of the Pockels coefficients of the 50/50 copolymers are DCVHT:AZB:DPB:DANS/MMA = 1.9:1.63:1.3:1. It is interesting to note that the ratios relative to DANS are comparable with those of the guest-host materials, except for DCVHT/MMA. In the case of DCVHT/MMA the ratios relative to DANS/MMA are 1.83 (copolymer) and 3.2 (guest-host), respectively. The deviation of  $r_{13}/r_{33}$  from 1/3 is the result of dipolar and steric interactions that favor antiparallel orientation of NLO chromophores in this copolymer,<sup>16</sup> whereas in the guest-host systems the dyes are far apart and are oriented independently in an electric field.

## 6. CONCLUSIONS

The ellipsometric reflection technique is a useful method for evaluating the EO coefficients of poled films. Previous workers<sup>9–11</sup> derived exact equations for analyzing the results of this experiment based on the Fresnel reflection coefficients from a multilayer polymer film and used a computer to fit their equations to the experimental data. In this paper we derived approximate analytic equations for the reflectivity and verified their validity when the wavelength of measurement was far from the absorption of the dye molecule. Our results are in agreement with those of Levy *et al.*<sup>9</sup> and Chollet *et al.*<sup>11</sup>. We also derived approximate analytic expressions for the optical retardation of an EO film as a function of the ratio  $r_{13}/r_{33}$  and the birefringence of the film. We conclude that the common assumption that the ratio equals 1/3 is the biggest potential source of error in the reported literature values of  $r_{33}$ . The ratio of 1/3 comes from a theoretical model of independent dipoles orienting in an electric field. The neglect of the birefringence of poled films is a smaller source of error and causes an error of less than 15% in moderately poled films (<150 V/ $\mu\text{m}$ ).

We report the Pockels constant of four NLO dyes as guest-hosts and as copolymers. Guest-host studies at low concentration allow one to deduce the relative NLO activity of dye molecules independently of the influence of aggregation between dyes and the backbone polymer. The assumption that  $r_{13}/r_{33} = 1/3$  applies to these guest-host films. A dye molecule based on the amino and dicyanovinyl groups as donor and acceptor, respectively, and on hexatriene as the conjugated linkage group (DCVHT), had a NLO activity 3.2 times the value of the DANS dye. However, when this dye was attached as part of a PMMA copolymer its activity was only 1.8 times the value of a copolymer with DANS attached to it. DCVHT dye appears to interact with itself at high concentrations, causing a decrease in NLO activity. The three other dyes studied in this paper gave the same relative NLO activities in a copolymer as in a guest-host film.

## APPENDIX A

It can be shown<sup>10</sup> that the reflected electric field is given by

$$E^{o,e} = r_{gp} + r_{pm} \exp(-i\phi_{o,e}), \quad (\text{A1})$$

where interference between the front and back surfaces is neglected. After the light is reflected by the glass-polymer-metal multilayer structure, it is passed through a Babinet-Soleil compensator with a phase retardation  $\phi^{\text{comp}}$  and finally through an analyzer crossed relative to the initial incident polarization. The normalized intensity of light coming through the analyzer is given by

$$I = 1/4[E^o(E^o)^* + E^e(E^e)^* - \exp(i\phi^{\text{comp}})E^o(E^e)^* - \exp(-i\phi^{\text{comp}})E^e(E^o)^*], \quad (\text{A2})$$

where \* denotes the complex conjugate. Substituting Eq. (A1) into Eq. (A2), one obtains the normalized intensity

$$I = 1/4 \left[ 4r_{pm}^o r_{pm}^e \sin^2 \left( \frac{\phi^{eo} + \phi^{\text{comp}}}{2} \right) + (r_{pm}^o - r_{pm}^e)^2 + 2r_{gp}^o r_{pm}^o \cos \phi_o + 2r_{gp}^e r_{pm}^e \cos \phi_e - 2r_{gp}^o r_{pm}^e \times \cos(\phi^{\text{comp}} + \phi_e) - 2r_{gp}^e r_{pm}^o \cos(\phi^{\text{comp}} - \phi_o) + 4r_{gp}^o r_{pm}^e \sin^2 \left( \frac{\phi^{\text{comp}}}{2} \right) + (r_{gp}^o - r_{gp}^e)^2 \right]. \quad (\text{A3})$$

$\phi^{eo} = \phi_e - \phi_o$  denotes the difference in phase retardations between  $\phi_e$  and  $\phi_o$  and comes from the static birefringence induced by poling and the EO Pockels effect. Equation (A3) is the general expression for the intensity coming through the analyzer. It is complicated by the fact that  $r_{gp}$  is not equal to 0 (a small percentage is reflected by the glass and the polymer) and that  $r_{pm}$  is not equal to 1, as would be expected for a highly reflective metal. Furthermore, the reflection coefficients are not equal for the ordinary and the extraordinary waves. The leading term has a coefficient  $(r_{pm}^o)^2$ , which is of order 1. The next term is the difference of  $r_{pm}^o$  and  $r_{pm}^e$  for the two polarizations and is expected to be smaller than the first term. The next four terms have coefficients of the form  $r_{gp} r_{pm}$ , and they are expected to be smaller than the first two terms of Eq. (3) because  $r_{gp} \ll r_{pm}$ . Finally, the last two terms have the smallest values, as they have coefficients of the form  $(r_{gp})^2$  that are  $\ll 1$ .

One should use Eq. (A3) to analyze EO effects in thin films. However, the resulting expressions are complicated and do not provide an insight into the underlying key effects. We approximate Eq. (A3) by the leading term only and neglect all the other terms because the latter are expected to make smaller contributions. This approximation applies when the  $\sin^2[(\phi^{eo} + \phi^{\text{comp}})/2]$  expression in the leading term is of order 1 because  $\phi^{\text{comp}} = \pi/2$  or  $\phi^{\text{comp}} = 3\pi/2$  when measurements are made. The total intensity  $I$  incident upon the detector is then given by

$$I = I_{\text{max}} \sin^2(\phi/2), \quad (\text{A4})$$

where  $I_{\text{max}} = r_{pm}^o r_{pm}^e$  is the cw reflected signal and  $\phi$  is the total retardation in the optical train, given by

$$\phi = \phi^{eo} + \phi^{\text{comp}}. \quad (\text{A5})$$

## APPENDIX B

The phase retardation between *s* and *p* waves depicted in Fig. 1 is given by<sup>14</sup>

$$\phi^{\text{eo}} = \frac{4\pi d}{\lambda} [n_e(\theta_e)\cos\theta_e - n_o\cos\theta_o]. \quad (\text{B1})$$

If the beam is transmitted through the slab then the phase retardation is 1/2 of the above value. In Eq. (5)  $\theta_{o,e}$  refers to the internal angle in the slab that the ordinary and the extraordinary waves make and is related to the angle of incidence  $\theta$  by Snell's law:

$$\sin\theta = n_o\sin\theta_o, \quad \sin\theta = n_e(\theta_e)\sin\theta_e. \quad (\text{B2})$$

Furthermore, the angular dependence of  $n_e$  is given by

$$n_e(\theta_e) = \frac{1}{\left(\frac{\sin^2\theta_e}{n_e^2} + \frac{\cos^2\theta_e}{n_o^2}\right)^{1/2}}. \quad (\text{B3})$$

Combining Eqs. (B2) and (B3), we arrive at the following expressions that will be used to evaluate Eq. (B1):

$$n_e(\theta_e)\cos\theta_e = \left(n_o^2 - \frac{n_o^2}{n_e^2}\sin^2\theta\right)^{1/2},$$

$$n_o\cos\theta_o = \sqrt{n_o^2 - \sin^2\theta}. \quad (\text{B4})$$

The two expressions above differ because of the permanent and EO induced birefringence in the sample. Inasmuch as this is generally a small quantity relative to the indices, we let  $x = (n_e^2 - n_o^2)/n_e^2$ , and so we can expand Eq. (B1) as a Taylor series in  $x$ , so the phase retardation becomes

$$\phi^{\text{eo}} = \frac{4\pi d}{\lambda} \left[ \frac{x\sin^2\theta}{2(n_o^2 - \sin^2\theta)^{1/2}} - \frac{x^2\sin^4\theta}{8(n_o^2 - \sin^2\theta)^{3/2}} + \dots \right]. \quad (\text{B5})$$

This is the general expression for the retardation that includes the static birefringence  $\Delta n_s = n_{\text{es}} - n_{\text{os}}$  induced by poling and the EO birefringence induced by the measuring voltage  $V$ . We proceed by differentiating Eq. (B5) with respect to the applied voltage  $V$  to obtain the following expression:

$$\frac{d\phi^{\text{eo}}}{dV} = \frac{2\pi r_{33}(n_{\text{es}}^2 - n_{\text{os}}^2)}{\lambda} \frac{\sin^2\theta}{(n_{\text{os}}^2 - \sin^2\theta)^{1/2}} D(\alpha, \theta), \quad (\text{B6})$$

where  $D$  is given by

$$D(\alpha, \theta) = 1 + \frac{n_{\text{es}}^2 - n_{\text{os}}^2}{2(n_{\text{os}}^2 - \sin^2\theta)} \left( \frac{\alpha n_{\text{es}}^2}{\alpha n_{\text{es}}^2 - n_{\text{os}}^2} - \frac{\sin^2\theta}{n_{\text{es}}^2} \right) - \frac{3(n_{\text{es}}^2 - n_{\text{os}}^2)^2 \sin^2\theta}{8(n_{\text{os}}^2 - \sin^2\theta)^2} + \dots \quad (\text{B7})$$

and  $\alpha$  by

$$\alpha = \frac{\chi_{zxx}^2}{\chi_{zzz}^2} = \frac{n_{\text{os}}^4 r_{13}}{n_{\text{es}}^4 r_{33}}. \quad (\text{B8})$$

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