

**Electro-Optic Coefficients of Guest-Host Poled Polymers Containing
Chromophores with Large First Hyperpolarizabilities:
A Test of the Two-State, Oriented-Gas Model**

J. Skindhøj,^a G. Bourhill,^a S. Gilmour,^a B. G. Tiemann,^{a,b} K. Mansour,^a
K. J. Perry,^a L.-T. Cheng,^c S. R. Marder,^{a,b} and J. W. Perry^{*a,b}

^a Jet Propulsion Laboratory, California Institute of Technology, Pasadena,
CA 91109, U. S. A.

^b Beckman Institute, California Institute of Technology, Pasadena, CA
91125, U. S. A.

^c Central Research and Development, Dupont Co., Wilmington, Delaware
19880-0356, U. S. A.

Abstract

The electro-optic, r_{33} , coefficients of poled poly(methylmethacrylate) films containing dyes with first hyperpolarizabilities that span nearly two orders of magnitude have been determined at 820 and 1300 nm by modulated ellipsometry. The observed electro-optic coefficients compare reasonably well with those calculated from the molecular first hyperpolarizabilities using a two-state dispersion, oriented-gas model, but the values at 1300 nm for several of the dyes with longest wavelength absorptions are lower than predicted by up to a factor of four. Nonresonant r_{33} values up to 11 pm/V were obtained with 2 mole percent dye and poling fields of 1 MV/cm.

* To whom correspondence should be addressed.

Electro-optic polymers are of considerable interest for optical modulator, switch and electric field sensor applications¹⁻³. Such materials must be thermally stable, under elevated operating and processing temperatures, and must have large nonlinear optical coefficients, to afford adequate sensitivity. These needs have driven intensive research efforts that have resulted in advances in the design of molecules with large hyperpolarizabilities, and in the synthesis of nonlinear optical molecules and polymer systems with improved thermal stability.⁴

The availability of molecules with large hyperpolarizabilities^{5,6} could, at high number densities, lead to polymers with large macroscopic nonlinear coefficients exceeding those of LiNbO_3 and, at lower number densities, moderate nonlinearities, that would be adequate for a number of applications. At low number densities, the thermal and mechanical properties are dominated by the host or backbone polymer, while the nonlinearity is dominated by the dye molecules, and aggregation of dye may be reduced. Such a separation of primary and secondary properties facilitates the design and preparation of materials with a specific combination of properties.

In this paper we report that guest/host polymers based on a low concentration of molecules with large hyperpolarizabilities can indeed result in reasonably large electro-optic coefficients. We also show that a model based on an oriented-gas picture and a two-state dispersion is reasonably good for predicting the electro-optic coefficients (at two disparate wavelengths) of guest/host poled polymers for a series of dyes with hyperpolarizabilities varying by two orders of magnitude. However, some deviations are observed for the dyes with the longest wavelength absorptions and raise questions

about the general validity of the simple two-state dispersion model based on the absorption maximum.

The structures of the chromophores examined in this study are shown in Figure 1. The preparation and hyperpolarizabilities of these compounds have been reported previously, except for 5[1], 5[2], 10[0], and 10[1].⁵⁻¹¹ 5[1] and 5[2] were prepared by the same method as 5[0],¹⁰ and the preparation of 10[0] and 10[1] followed that of compounds 9[n] and 11[n].¹¹ The scalar product of the ground-state dipole moment, μ , and the first hyperpolarizability, β , of each compound was measured by electric field induced second harmonic generation (EFISH) in chloroform at 1907 nm as reported elsewhere.¹²

Poly(methylmethacrylate) (PMMA) thin films of 1 μ m thickness containing 2 mole percent guest chromophore were prepared by spin-coating a chlorobenzene solution of dye and PMMA at 800 rpm for two minutes onto glass slides possessing a 0.7cm wide indium-tin-oxide (ITO) strip. Residual solvent was removed by baking under reduced pressure for three hours at 110 $^{\circ}$ C.¹³ A 0.7 cm wide, 200 nm thick aluminum strip, perpendicular to the ITO strip, was vacuum deposited on top of the polymer film, forming a 0.7 x 0.7 cm² active-area of ITO-polymer-aluminum sandwich. Thermopoling was accomplished by applying 100V for two minutes while holding the polymer at 120 $^{\circ}$ C on a hot plate. Samples were subsequently thermally quenched by removing the sample from the hot plate while maintaining this field .

The electro-optic coefficients, r_{33} , of the poled films were determined at 820 and 1300 nm using modulated ellipsometry.^{14,15} Briefly, light polarized at 45 $^{\circ}$ to the plane of incidence was passed through the glass, ITO and polymer

layers and was reflected from the aluminum back through the various layers. The polymer birefringence induces a phase-difference, Ψ_{sp} , between the s- and p-wave components of the light. The reflected beam then passed through a variable phase retarder and a polarizer, crossed with the incident polarization, and was finally detected by a Si or Ge photodiode detector for 820 or 1300 nm light, respectively. The detected intensity depends on Ψ_{sp} and was modulated via the linear electro-optic effect by applying an ac modulating voltage, V_m , (20V(rms) at 3000 (330) Hz for 820 (1300) nm measurements) across the polymer. Measurements of the dc and modulated signal intensities were made as a function of the variable phase retardation. The modulated intensity, I_m , was obtained at the points where the dc signal is at 50% transmittance, $I_{1/2}$, which corresponds to a Ψ_{sp} of $\pi/2$ or $3\pi/2$. The electro-optic coefficient was calculated using¹⁴

$$r_{33} = \frac{3\lambda}{4\pi} \frac{1}{V_m n^2} \frac{(n^2 - \sin^2\theta)^{1/2}}{\sin^2\theta} \frac{I_m}{I_{1/2}} \quad (1)$$

where λ is the optical wavelength, θ is the angle of incidence, and n is the polymer refractive index. In using this equation, it is implicitly assumed that $r_{33} = 3r_{13}$. The real and imaginary parts of r_{33} were obtained by taking half the difference and sum of the I_m values at the $\pi/2$ and $3\pi/2$ positions, respectively.¹⁶ The r_{33} values in this paper were obtained at a large angle of incidence, $\theta = 65^\circ$, to minimize multilayer interference effects.¹⁷

The experimentally determined values for $\mu\beta$, λ_{max} in CHCl_3 solution and in PMMA films, and the real part of r_{33} at 820 and 1300 nm for the chromophores studied are summarized in Table I. For comparison, data for

the well known dye Disperse Red 1 (DR1) is included. The r_{33} values for the DR1/PMMA films are in accord with the values reported in the literature, after adjusting for the dye concentration.^{18,19} The hyperpolarizabilities and their dependence on structure for most of the dyes in Table 1 have been discussed previously.⁵⁻¹¹

Generally speaking it can be seen that the r_{33} values of the various compounds track the $\mu\beta$ values relatively well and that rather large r_{33} values are obtained at both wavelengths, considering the low dye loading. While values of $\text{Re}(r_{33})$ as high as 31 pm/V at 820 nm are observed, the compounds with the three largest values, 4[3], 7[3] and 9[1], exhibited complex r_{33} values with large imaginary components; for example, $\text{Im}(r_{33})$ was 54 pm/V for 4[3] and 13 pm/V for 7[3]. On the other hand, for the remaining dyes the imaginary component was $\leq 6\%$ of the real part, and thus essentially nonresonant values up to 11 pm/V were obtained at 820 nm. The values at 1300 nm were essentially real and smaller, with the largest being about 6 pm/V. These results suggest that very large electro-optic coefficients (perhaps as high as 35 pm/V at 1300 nm) may be achieved with the most nonlinear chromophores studied here through increased loading. A large electro-optic coefficient (10.8 pm/V at 1520 nm) for a relatively low dye loading (12 wt. %) in a guest/host polymer has recently been reported by Wong and Jen, who used a tricyanovinyl analog of 8 in a polyimide host.²⁰

The r_{33} values determined at 820 and 1300 nm were compared with those predicted from the molecular hyperpolarizability using the standard two-state oriented-gas model as described by Singer *et al.*¹⁸ First, experimental $\beta(\text{EFISH})$ values were scaled, using a dispersion model, to give $\beta(\text{EO})$ values.

Using a two-state dispersion factor and a factor of 2 needed to convert from the phenomenological hyperpolarizability, used to analyze the experimental results,¹² to the hyperpolarizability as defined in the perturbation expansion²¹ gives:

$$\beta(-\omega, \omega, 0) = 2 \beta(-2\omega', \omega', \omega') \frac{(3\omega_p^2 - \omega^2)(\omega_0^2 - \omega'^2)(\omega_0^2 - 4\omega'^2)}{3\omega_0^2(\omega_p^2 - \omega^2)^2} \quad (2)$$

where we have allowed for different EFISH fundamental (ω') and EO optical (ω) frequencies, as well as different resonance frequencies in solution (ω_0) and in the polymer (ω_p). In the oriented gas model, r_{33} is given by:

$$r_{33} = \left[\frac{4 N f_0 f \omega^2}{n^4} \right] \left[\frac{P}{5} - \frac{P^3}{105} \right] \beta(\text{EO}) \quad (3)$$

where N is the chromophore number density, $f_0 = \epsilon(n^2 + 2)/(n^2 + 2\epsilon)$, $f = (n^2 + 2)/3$, and $P = f_0 \mu E_p / kT$, where E_p is the poling field, in the truncated form of the order parameter.

Figure 2 displays reasonably good agreement between predicted and experimental $\text{Re}(r_{33})$ values at 820 nm. This is somewhat surprising considering that the model does not include damping and that substantial $\text{Im}(r_{33})$ components were observed for several dyes. At 1300 nm (Figure 3) there is again reasonably good agreement, except for a few dyes, 4[3], 7[3], and 10[1], where the predicted coefficients are consistently higher than experiment. These dyes exhibited the largest values of λ_{max} within their respective series of compounds.

These observations raise a question about using the simple two-state dispersion scaling of $\mu\beta(\text{EFISH})$ to calculate $\mu\beta(\text{EO})$ and the electro-optic coefficients for such dyes with long conjugation lengths and long wavelength absorptions. Gadret *et al.*¹⁶ and Chollet *et al.*¹⁷ have observed low energy resonances in the dispersion of the electro-optic coefficient of nonlinear optical polymers well below the absorption maximum, that do not correlate with a feature in the observed in the linear absorption. Such observations suggest that there would be problems with the simple two-state dispersion model for molecules where the EFISH harmonic or EO optical frequencies approach the absorption band edge, as we observe. In order to develop a better predictive ability for such molecules, measurements and an understanding of the dispersion and resonances of the hyperpolarizability and the electro-optic coefficient are needed.

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40; 5[1], 89; 5[2], 41; 6[0], 84; 7[0], 89; 7[1], 90; 7[2], 98; 7[3], 88.; 8-11[1], 100;
DR1, 90.

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Table I. Absorption maximum, λ_{\max} , $\mu\beta$, and $\text{Re}(r_{33})$ values at 820 and 1300 nm for the chromophores studied. The estimated uncertainty in $\mu\beta$ and r_{33} is $\pm 15\%$. λ_{\max} are reported for dyes in chloroform solution and in PMMA films. For 10[0], 10[1] and 11[1], the $\text{Im}(r_{33})$ dominated the electro-optic response at 820 nm, precluding the determination of the real part. The r_{33} values in this table have not been corrected for chromophore loss during sample preparation.

Compound	λ_{\max} (nm)		$\mu\beta$ (EFISH) (10^{-48} esu)	r_{33} (pm/V)	
	CHCl ₃	PMMA		820 nm	1300 nm
1[2]	479 ^a	477	480 ^a	1.5	0.6
1[3]	562 ^a	530	2100 ^a	3.6	-
2[0]	433 ^b	428	250 ^b	1.0	-
2[1]	490 ^b	473	690 ^b	2.8	-
2[2]	523 ^b	504	1500 ^b	6.8	-
2[3]	546 ^c	524	3800 ^c	11	-
3[0]	470 ^d	463	280 ^d	1.0	0.6
3[1]	533 ^d	504	880 ^d	3.7	2.5
3[2]	554 ^d	533	2000 ^d	4.6	1.3
4[0]	501 ^e	495	420 ^e	1.8	1.2
4[1]	572 ^e	556	1500 ^e	6.0	-
4[3]	620 ^e	582	9800 ^e	31	5.0
5[0]	480 ^d	484	370 ^d	0.7	-
5[1]	574	562	1300	5.4	-
5[2]	618	586	3300	9.1	2.5
6[0]	522 ^e	517	610 ^e	2.3	-
7[0]	477 ^e	475	310 ^e	1.2	0.8
7[1]	532 ^e	518	1200 ^e	5.0	-
7[2]	566 ^e	548	3100 ^e	10	-
7[3]	581 ^e	567	8200 ^e	23	5.0
8	540 ^f	520	1200 ^f	3.8	1.7
9[0]	590 ^g	566	1900 ^g	6.6	2.7
9[1]	608 ^g	580	2900 ^g	16	3.3
10[0]	660	630	3700	-	3.9
10[1]	670	644	7100	-	6.0
11[0]	626 ^g	602	2500 ^g	12	4.9
11[1]	648 ^g	622	4100 ^g	-	5.3
DR1	480 ^b	487	340 ^b	1.3	1.0

^aRef. 7, ^bRef. 8, ^cRef. 9, ^dRef. 10, ^eRef. 5, ^fRef. 6, ^gRef. 11.

Figure Captions

Figure 1. Structures and labeling scheme for the compounds investigated. Et \equiv C₂H₅. For compounds 3[0] and 4[0] the electron donor is Et₂N whereas the donor for 1[2] is (n-C₄H₉)₂N.

Figure 2. Predicted (filled circles, with line as a guide) and experimental (open circles) r_{33} coefficients at 820 nm versus electro-optic $\mu\beta$ values. The experimental r_{33} data have been corrected for chromophore degradation¹³ during sample processing. In calculating the electro-optic coefficients, the hyperpolarizabilities were multiplied by a factor of 0.64 to account for the revised value for the d coefficient of quartz, which was used as a standard.

Figure 3. Predicted (filled circles, with line as a guide) and experimental (open circles) r_{33} coefficients at 1300 nm versus electro-optic $\mu\beta$ values. Details are as for Figure 1.

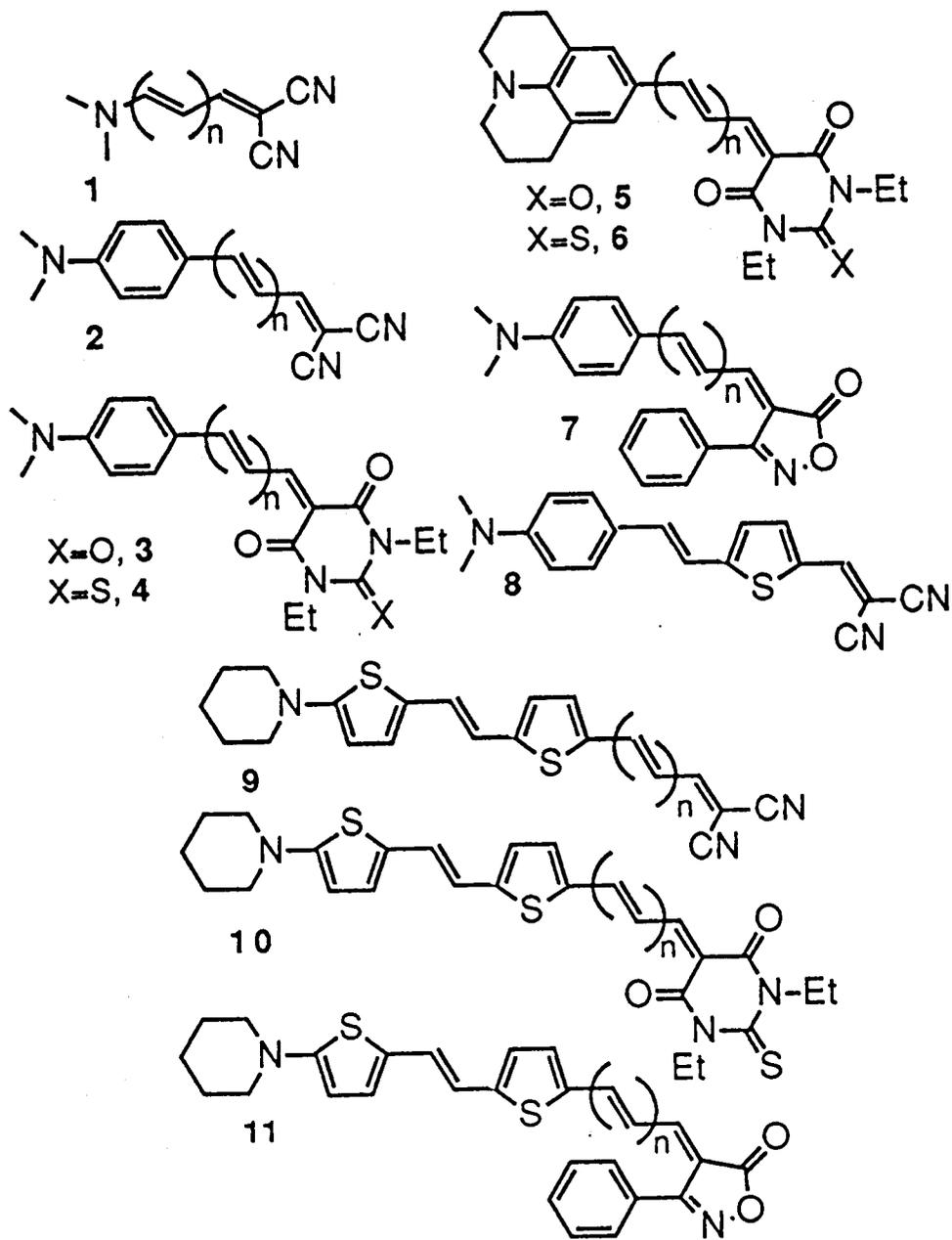


Figure 1. Skindhøj et al. Appl. Phys. Lett.

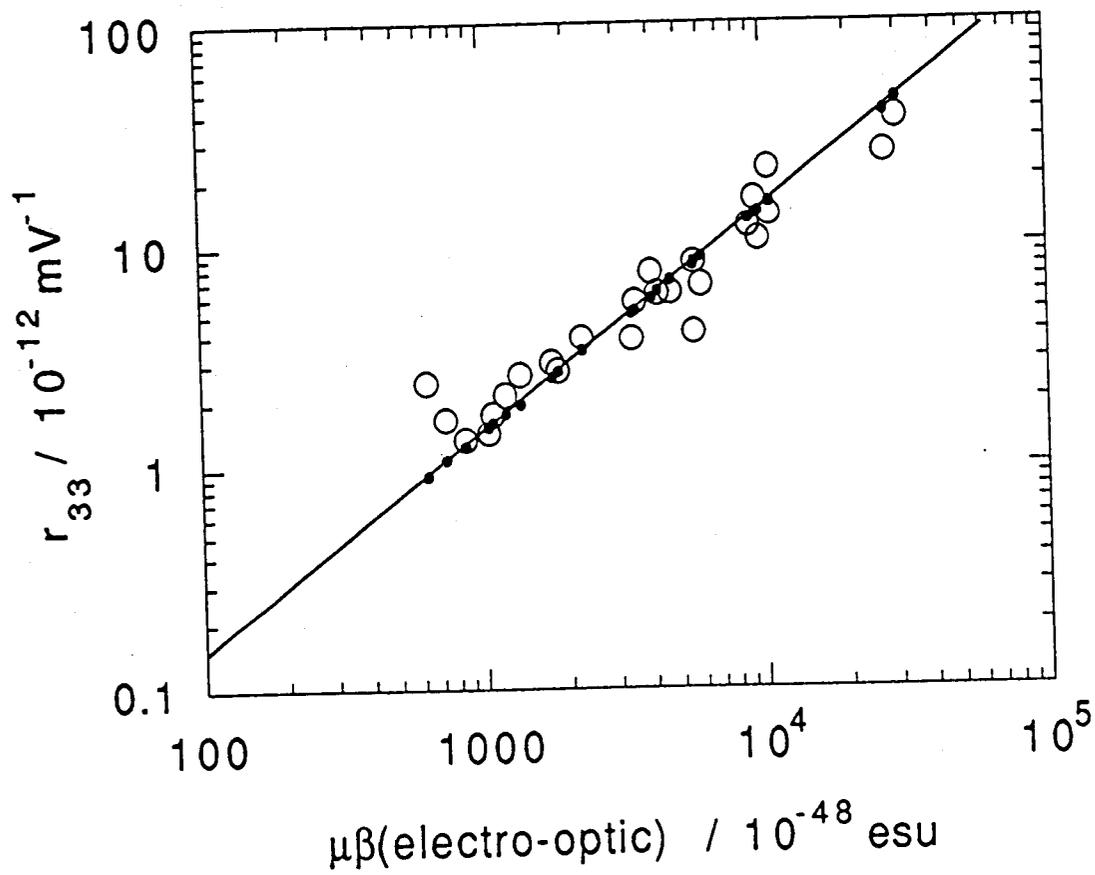


Figure 2. Skindhøj et al. Appl. Phys. Lett.

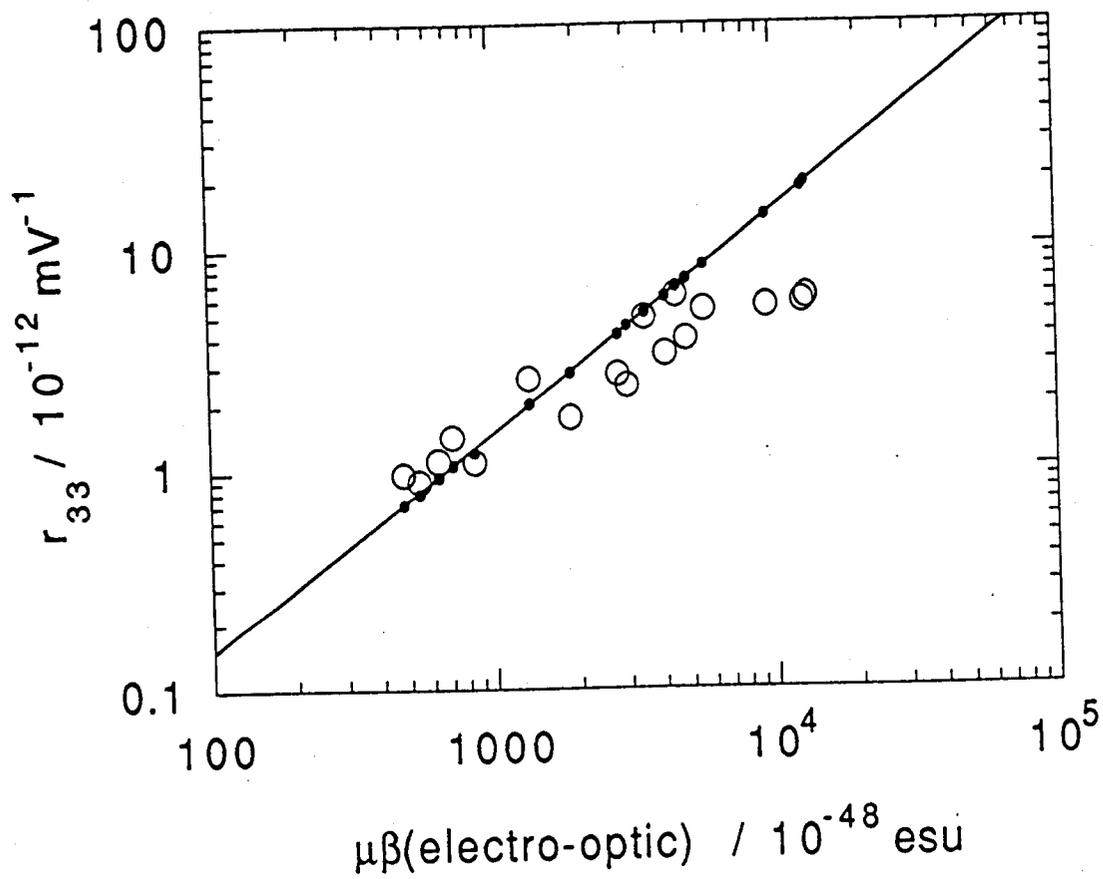


Figure. 3. Skindhøj et al Appl. Phys. Lett.