

Enhancement of Electrooptic Coefficient of Doped Films through Optimization of Chromophore Environment

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The dependence of electrooptic (EO) coefficient on electronic properties of the host polymer and specific chromophore–host interactions were examined. The r_{33} of 10 wt % Disperse Red 1 (DR1)- and 4-(dicyanomethylene)-2-methyl-6-(*p*-(dimethylamino)stryryl)-4*H*-pyran (DCM)-doped poly(2-vinyl pyridine) films (6.4 and 5.8 pm/V, respectively) was up to 70% larger than comparable poly(methyl methacrylate)-doped films (3.7 and 3.9 pm/V, respectively) and as much as a factor of 12 larger than comparable polystyrene-doped films (0.5 and 0.4 pm/V, respectively). The variation in EO coefficient was addressed by quantifying the effects of resonance enhancement, local field factors, field responsivity of the host, and specific guest–host interactions. Resonance enhancement and local field effects account for 20–25% of this variation. In contrast, the largest variations in r_{33} were associated with specific chromophore–host and chromophore–chromophore interactions. These influence the molecular miscibility and thus alter the effective chromophore concentration and therefore the EO coefficient. An ultimate EO coefficient of 15 pm/V for a 25 wt % DR1–P2VP system was obtained in which specific secondary interactions (hydrogen bonding) occur between chromophore and host. Additionally, synergy between chromophore and a field responsive host (P2VP) may facilitate chromophore orientation and subsequent stability. These results demonstrate the potential associated with modification of guest–host interactions in chromophore-doped polymer films for the development of highly nonlinear, stable EO materials.

Introduction

High-speed electrooptical (EO) modulators are currently of commercial interest for a variety of applications including electronic-to-optical signal transduction, satellite communications, and telecommunications.¹ Current electrooptic modulators are being designed using second-order nonlinear optical crystals such as lithium niobate and potassium dihydrogen phosphate.² However, polymer systems offer an attractive alternative to these materials, including a low dielectric constant, processing ease, and large nonlinearities. Issues associated with the magnitude and stability of the EO coefficient, thermal oxidative stability, and optical loss are currently limiting the commercialization of these polymer modulators.^{1,3}

In general, an electrooptic polymer system is comprised of a nonlinear optical (NLO) chromophore dis-

tributed throughout an amorphous polymer matrix. Second-order nonlinear effects require an asymmetric alignment of the chromophore. Typically, the order is imposed using electric field poling, where a static field is applied across a film while above its glass transition temperature. The static poling field can be applied either from corona discharge^{4,5} or by parallel electrodes.^{6,7} The field induces alignment of the molecular dipoles in the polymer melt leading to an asymmetric orientational distribution of the NLO chromophore. Before the poling field is withdrawn, the film is cooled below the glass transition temperature to freeze the orientation of the chromophore. Traditional systems contain chromophores homogeneously dispersed in a host (guest–host system). This past decade researchers have demonstrated that covalently attaching the dye to the polymer chain improves chromophore isolation and the stability of the imposed asymmetric order,^{8,9} albeit

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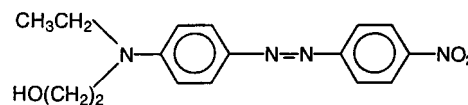
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at considerable increase in synthetic effort relative to traditional guest–host systems.

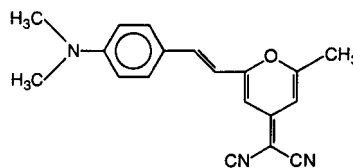
A majority of the efforts addressing the issues limiting the use of EO polymers have concentrated on modifications to the chromophore, specifically to enhance molecular nonlinearities^{10,11} and reduce chromophore–chromophore interactions in the bulk state.¹² The relatively smaller number of efforts that have examined different host matrixes have concentrated on the relative stability of chromophore orientation.^{13,14} Only a few efforts have specifically examined the host–guest interactions and their role in optimizing the molecular environment of a specific chromophore in various hosts. Lackritz et al. quantified the free volume and polymer restriction influences on dipolar orientation using rotational Brownian motion to determine the chromophore orientation.¹⁵ This study was confined to one system [4-(dimethylamino)-4'-nitrostilbene (DANS)-doped poly(methyl methacrylate) (PMMA)] and did not address how the parameters associated with the host would scale with different matrixes. Very recently researchers have reported larger second-order effects in polycarbonate (PC)-doped systems when compared to similarly processed PMMA films. The improved properties were correlated to chromophore–host interactions (specifically hydrogen bonding) and the ability to orient the main-chain polymer repeat units.^{16–18} In general though, systematic studies of molecular structure–processing–property relationships across a broad range of molecular structures, both for the host polymer and chromophore, are scarce because of the numerous molecular and processing factors that contribute to the final nonlinearity of the material. Thus, comparison of results from previous independent studies is difficult.

In this paper, we summarize current efforts to systematically examine the influence of the host polymer on the final EO response. The influence of the dopant on T_g , sub- T_g relaxations, free volume, and inhomogeneities of the applied field associated with inhomogeneities in the film are all factors to consider when addressing experimental variation associated with the polymer host. In addition, the host polymer will induce changes in the electronic spectrum and alter the local field around the chromophore as well as dictate the molecular miscibility of the chromophore. Concentrating on the latter issues, the relationship between the magnitude of the EO coefficient and the properties of the host matrix is discussed for two common EO



$\mu=7.5$ Debye
 $\beta_0=50$ E-30 esu
 MW=314 g/mol

(a)



$\mu=8.6$ Debye
 $\beta_0=58$ E-30 esu
 MW=303 g/mol

(b)

Figure 1. Chemical structures and selected properties of (a) DR1 and (b) DCM. The hyperpolarizabilities (β_0) shown are zero frequency values observed through EFISH.¹⁹

Table 1. Characteristics of Host Polymers

polymer	MW (g/mol)	n_o ²⁰	ϵ ^{20,21}	T_g (°C)
PMMA	130 000	1.49	3.60	105
P(S _{0.7} MMA _{0.3})	270 000	1.51	2.58	105
PS	530 000	1.58	2.55	100
PtBMA	138 000	1.46	2.74	107
PCHMA	65 000	1.51	2.58	105
P2VP	200 000	1.59	4.91	104

chromophores (4-(dicyanomethylene)-2-methyl-6-(*p*-(dimethylamino)stryryl)-4*H*-pyran (DCM) and Disperse Red 1 (DR1)) and in six different hosts with similar α -glass transition temperatures (100–105 °C). The advantages of molecularly designing specific guest–host interactions are emphasized.

Experimental Section

Two common electrooptic chromophores with different molecular architectures but comparable molecular weight, hyperpolarizability and dipole moment were examined. Commercially available DR1 (Aldrich ~95%) and DCM, seen in Figure 1, were used without further purification. A series of polymers with comparable glass transition temperatures were chosen to minimize variations associated with processibility. These polymers represented two general architectures, acrylates (poly(cyclohexyl methacrylate) (PCHMA, Scientific Polymer Products), poly(*tert*-butyl methacrylate) (PtBMA, Scientific Polymer Products), and poly(methyl methacrylate) (PMMA, Scientific Polymer Products), and vinyl polymers with aryl pendants (poly(2-vinylpyridine) (P2VP, Scientific Polymer Products) and polystyrene (PS)). In addition poly(styrene-methyl methacrylate) (P(S_{0.7}MMA_{0.3}), Polysciences) copolymer was chosen to examine the mean field nature of the local molecular environment. Characteristics of the polymers are summarized in Table 1. Glass transition temperatures were verified by differential scanning calorimetry.

Films were spun-cast from solutions, consisting of 8–12 wt % polymer in cyclopentanone. Chromophore content varied from 0.1 to 30 wt % of the polymer.²² Prior to film spinning

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the solutions were filtered using a 0.7- μm cartridge to remove large particulates. The substrates for spin coating varied with respect to characterization method (quartz slides for electronic spectroscopy, soda lime glass with a 3000- \AA -thick ITO layer for EO measurements, and NaCl pellets for infrared spectroscopy). The films were dried in a vacuum oven at 80 $^{\circ}\text{C}$ for 12 h. Film thickness was determined using a Dektak II profilometer. For electric field poling and EO characterization a 1000- \AA gold layer was evaporated on the surface of the films to serve as an electrode and a reflection layer.

Electronic spectroscopy was performed using a Hewlett-Packard 8453A photodiode array spectrophotometer. Spectra were acquired between 200 and 1100 nm and normalized to the thickness of the film. Infrared spectrums from 4000 to 450 cm^{-1} were obtained using a Bruker IFS28 FTIR spectrometer. All FTIR spectra, except the pure DR1, were normalized with respect to the C-H stretching peak at 3000 cm^{-1} , which is proportional to the relative thickness of the film. The spectrum for pure DR1 was obtained using a KBr pellet containing 1 wt % DR1.

An asymmetric chromophore alignment was induced using electric field poling with parallel electrodes (ITO and Au). Initially films were annealed 20 $^{\circ}\text{C}$ above the poling temperature (115 $^{\circ}\text{C}$) and allowed to equilibrate for 10 min to erase any processing history. Films were slowly cooled to 30 $^{\circ}\text{C}$ at a rate of 3 $^{\circ}\text{C}/\text{min}$ and subsequently heated to the poling temperature (T_p) at a rate of 5 $^{\circ}\text{C}/\text{min}$. When the sample reached T_p the poling voltage was applied and the sample was allowed to equilibrate for 10 min. The sample was subsequently cooled at 3 $^{\circ}\text{C}/\text{min}$ to room temperature, and the poling field was withdrawn.

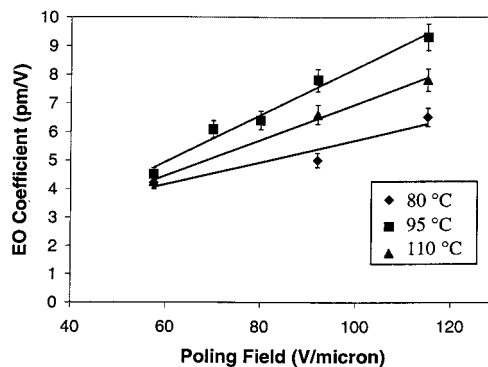
The electrooptic response was monitored in situ during the poling procedure using a modified reflection method initially proposed by Teng and Man.^{23,24} A polarization rotator was used to equate the s- and p-orthogonal components ($I_s = I_p$) of a 780-nm incident beam from a Phillips laser diode. A 1 kHz ac voltage, supplied by a Hewlett-Packard 8116A function generator, modulated the EO response and thus the polarization of the beam as it is reflected through the film. A Babinet-Soliel phase compensator retarded the s- and p-waves before they passed through an analyzer and onto a photodetector. A Stanford Research SR530 lock-in amplifier monitored the intensity change ($\Delta I(\Omega)$) at the frequency of the modulating electric field (Ω). The electrooptic coefficient of the polymer (r_{33}) is related to $\Delta I(\Omega)$ by²³

$$r_{33} = \frac{3\lambda\sqrt{n^2 - \sin^2\alpha} \Delta I(\Omega)}{4\pi n^2 \alpha V_{\text{mod}} I_0} \quad (1)$$

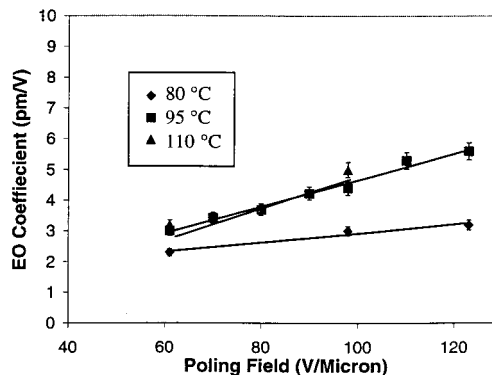
where λ is the wavelength of characterization, α is the angle of incidence, I_0 is the intensity at the photodetector, n is the refractive index of the polymer, and V_{mod} is the modulating voltage. Here, r_{33} is assumed to be $3r_{13}$. The measured r_{33} is related to the fundamental second-order susceptibility ($\chi^{(2)}$) of the material³:

$$r_{33} = \frac{-2}{n^4} \chi_{33}^{(2)} \quad (2)$$

The reported r_{33} corresponds to the observed response directly after removal of the poling field at room temperature. Meas-



(a)



(b)

Figure 2. The dependence of r_{33} on processing conditions for 10% DR1 doped in (a) P2VP and (b) PMMA. Solid lines are linear least-squares fit to the data.

urement of r_{33} on two similarly processed films of equal chromophore concentration was reproducible to within $\pm 5\%$.

Stability studies were used to determine the influence of the host on the relaxation of the chromophore alignment. Chromophore orientation was achieved by heating the sample to the poling temperature of 95 $^{\circ}\text{C}$ and applying an 80 $\text{V}/\mu\text{m}$ static poling field for 10 min. The sample was cooled to 30 $^{\circ}\text{C}$ and the poling voltage was withdrawn. The decay of the EO coefficient was monitored for 500 min.

Results

Numerous molecular and processing factors contribute to the final nonlinearity of the EO polymer film. Thus to systematically examine the influence of molecular architecture and intermolecular interactions on the EO response of various guest-host systems, the dependence of nonlinearity on processing for each of the systems must be initially understood. Figure 2 shows the affect of various processing conditions on the EO coefficient of PMMA and P2VP films doped with 10 wt % DR1. At a single poling temperature, r_{33} is proportional to the magnitude of the applied poling field, E_p . This reflects the increasing torque ($\propto \mu E_p$) applied to the chromophore dipole (μ) with increasing field. The proportionality is also temperature-dependent, reflecting the competition between decreasing host viscosity and increasing entropic disorder with increasing temperature. r_{33} initially increases with poling temperature, suggesting that a higher degree of chromophore orientation is achieved in a more mobile host. However for $T_p = 110$ $^{\circ}\text{C}$, r_{33} is unchanged in PMMA and decreases in P2VP relative to $T_p = 95$ $^{\circ}\text{C}$. The greater orientation

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(22) PMMA films containing up to 25 wt % chromophore were optically clear after spinning and remained transparent for greater than 1 year. No higher loadings were examined. P2VP films containing up to 30 wt % chromophore were also stable greater than 1 year. However, visible phase separation indicated by cloudiness of the film was observed for 50 wt % DR1 in P2VP immediately after spinning.

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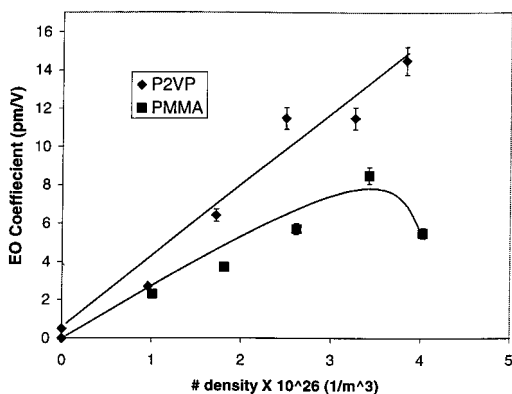


Figure 3. Concentration dependent EO coefficient for PMMA and P2VP films doped with DR1.

Table 2. r_{33} of Guest–Host Systems (10 wt % Chromophore, $T_{\text{poling}} = 95\text{ }^{\circ}\text{C}$, $E_{\text{poling}} = 80\text{V}/\mu\text{M}$)

polymer	r_{33} (pm/V)	
	DR1	DCM
PMMA	3.7	3.9
P(S _{0.7} MMA _{0.3})	3.5	3.9
PS	0.5	0.4
PtBMA	2.6	
PCHMA	3.3	3.4
P2VP	6.4	5.8

provided by improved chromophore mobility competes with increased entropic forces favoring randomization at this elevated temperature.

Although there is variation with processibility, the relative magnitude of r_{33} depends on the host matrix for all processing conditions (Figure 2: $r_{33}(\text{P2VP}) > r_{33}(\text{PMMA})$). Figure 3 summarizes the general enhancement of r_{33} for DR1 in P2VP relative to PMMA for various concentrations (1–25 wt %). For the concentrations examined P2VP results in a higher r_{33} than PMMA. Table 2 summarizes the general results obtained for the different hosts containing 10 wt % chromophore using one set of processing conditions. The EO response is comparable for both chromophores in a given host but varies between hosts, emphasizing the large role the host polymer plays in determining r_{33} . P2VP results in the highest r_{33} whereas PS results in the lowest r_{33} .

Figure 4 shows the relaxation of r_{33} for 10 wt % doped PMMA and P2VP films at 30 °C and the corresponding fit to a biexponential relaxation model. In the biexponential relaxation model, the decrease in electrooptic response, r_{33} , relative to the response upon field removal (r_{33}^0) is expressed as²⁵

$$r_{33}/r_{33}^0 = a \exp(-t/\tau_1) + (1 - a) \exp(-t/\tau_2) \quad (3)$$

where τ_1^{-1} and τ_2^{-1} are the relaxation rates and a is the relative proportion of the two relaxation of processes. Previous efforts have associated the rapid relaxation, τ_1 , to various contributions including the release of surface charge, chromophore rotation in polymer free volume, and third-order effects.^{26,27} The slow component,

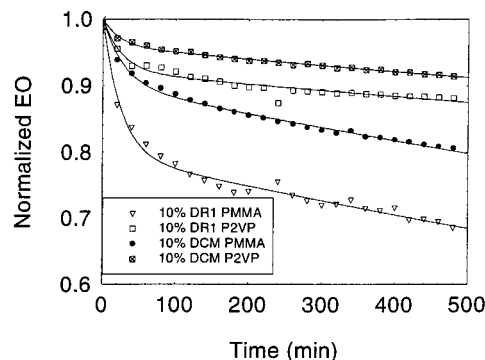


Figure 4. The decay of r_{33} at room temperature for PMMA and P2VP films doped with 10 wt % DR1 and 10 wt % DCM (every 20th data point is marked to distinguish between curves). The solid lines correspond to the biexponential decay model (eq 3).

Table 3. Relative Stability of r_{33} (Biexponential Decay Model, Eq 3)

EO polymer	a	τ_1 (min)	τ_2 (min)	t (50% loss) (min)	% loss (500 min)
10% DR1 PMMA	0.207	25	3382	1560	32
10% DR1 P2VP	0.079	26	9785	5977	12
10% DCM PMMA	0.101	29.2	4170	2446	20
10% DCM P2VP	0.0413	23.5	10100	6575	12

τ_2 , is attributed to rotation of the dipole due to polymer mobility.^{26,27} Table 3 summarizes the model parameters associated with the relaxation data in Figure 4. The fast relaxation of all four films were essentially equal, suggesting that surface charge dissipates at roughly the same speed after withdrawal of the poling field. In both hosts the alignment of DCM is more stable than DR1, which further demonstrates the rotational mobility of the chromophore will vary with molecular size and architecture.¹⁷ Finally, τ_2 depends markedly on the host. Generally, τ_2 is smaller for PMMA films than for P2VP films, indicating a more stable alignment of chromophores in P2VP.

Although pure PMMA and P2VP have a similar glass transition temperature, direct comparison of room-temperature chromophore relaxation requires an examination of the β -relaxations.²⁸ β -transitions in polymers are often associated with localized motion of pendant groups, which may facilitate chromophore relaxation. The β -transition temperature of pure PMMA was observed at 70²⁸ and 110 °C²⁹ for dielectric spectroscopy measurements at 0.451 and 10 kHz, respectively. Comparatively, P2VP exhibits a β -transition temperature via dielectric spectroscopy of 40 °C at 10 kHz.³⁰ The lower temperature β -relaxation of P2VP relative to PMMA implies a more dynamic local chromophore environment at room temperature and potentially greater relaxation rates (τ_2^{-1}). The opposite behavior is observed and indicates that additional factors, such as field responsive host and/or guest–host interactions, may dominate relaxation behavior.

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Table 4. Absorption Maximum and Relative Resonance Enhancement

polymers	DR1		DCM	
	λ_{\max} (nm)	Δr_{33} (%)	λ_{\max} (nm)	Δr_{33} (%)
PMMA	486	0	459	0
P(S _{0.7} MMA _{0.3})	486	0	464	2.0
PS	474	-4.3	467	3.3
PCHMA	486	0	460	0.3
P2VP	505	8.7	474	6.5

Discussion

The observed variation of r_{33} for DR1 and DCM in various hosts is discussed with regard to the influence of the host on the local molecular environment of the chromophore. This includes resonance enhancement (induced changes in the electronic spectrum of the chromophore), local field effects (Lorentz–Lorenz and Onsager factors), nanoscopic phase segregation (non-ideal random copolymers), nonisotropic medium (field-responsive matrix), and specific guest–host interactions (hydrogen bonding).

Resonance Enhancement. The enhancement of the electrooptic coefficient near resonance of the $\pi \rightarrow \pi^*$ transition is associated with the wavelength dependence of the molecular hyperpolarizability, β . Chromophore–solvent and chromophore–chromophore interactions have a mitigating effect on the excited and ground-state energy levels of a chromophore. This alters the energy of $\pi \rightarrow \pi^*$ transition in organic compounds,³¹ which not only alters the fundamental optical absorption wavelength, but also enhances the inherent molecular nonlinearities.³² In EO films, the solid host solvates the chromophore, and therefore similar effects to those observed in solution are expected. Shifting of the electronic absorption maximum toward the optical operating frequency (resonance enhancement) will increase the effective nonlinearity of the dispersed chromophore and therefore the r_{33} of the polymer film, albeit at the expense of increased absorptive loss and reduction of optical stability of the chromophore.

The polymers used as hosts for DR1 and DCM represent a broad polarity range and the resulting spectral shifts are quantified in Table 4. The electronic absorption spectra are shown in Figure 5. The relative red (bathochromic) shift observed in the P2VP correlates to the more polar environment created by the pyridine pendent. The DR1-doped PS film displayed a slight high-energy shoulder which is dependent on chromophore concentration. Supplementary infrared spectra indicate that strong intermolecular hydrogen bonds form between the nitro and hydroxyl groups of DR1, indicating the presence of head–tail aggregates in these films. This suggests that PS does not completely solvate DR1, even at modest loading (10 wt %). Note that in this case conventional microscopy (optical or electronic) or X-ray diffraction is insufficient to resolve these morphological inhomogeneities and spectroscopic techniques must be employed to determine blend morphology.

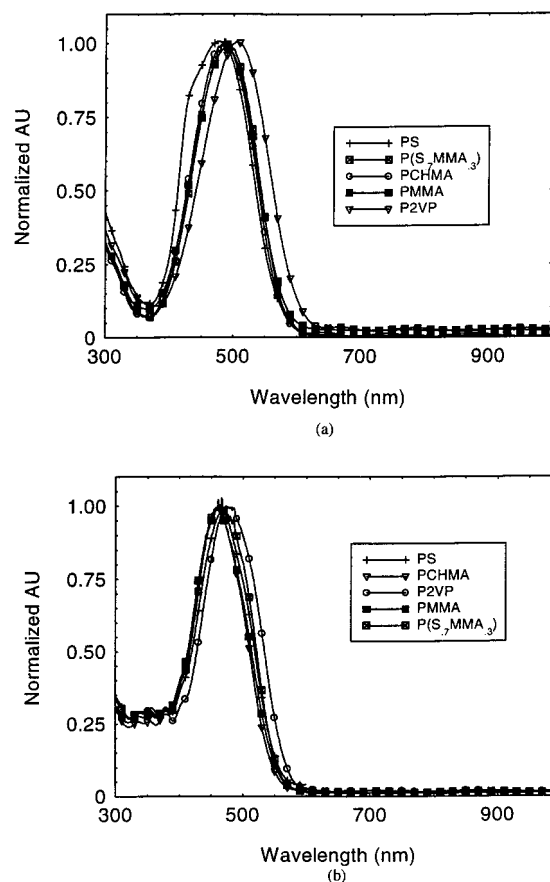


Figure 5. The electronic spectrum of (a) 10 wt % DR1 and (b) 10 wt % DCM dispersed in various polymer hosts (Table 1). The ordinate is normalized absorbance, and every 20th data point is marked to distinguish between curves.

The variation of r_{33} associated with this resonance enhancement can be estimated by³³

$$DF = \frac{\left(3 - \frac{\lambda_{\max}^2}{\lambda_2}\right)}{\left(3 - \frac{\lambda_{\max}^2}{\lambda_2}\right)} \quad (4)$$

where λ_{\max} is the wavelength of the absorption maximum and λ is the characterization wavelength (785 nm). The dispersion factor, DF, quantifies the resonance enhancement of r_{33} with respect to perfectly nonresonance conditions and is frequently used to estimate the r_{33} of a particular polymer system at various operating frequencies. Complementary, eq 4 quantifies the variation in r_{33} expected by the spectral shifts observed in various hosts. The relative variation of r_{33} relative to the well-studied host polymer PMMA ($\Delta r_{33} = (r_{33}^{\text{host}} - r_{33}^{\text{PMMA}})/r_{33}^{\text{PMMA}} \times 100$) is summarized in Table 4. Even for the most dramatic host-induced spectral shift (8.7%), the anticipated enhancement is modest and only slightly above the uncertainty inherent in the characterization method. In general, the resonance enhancement is not substantial at the optical characterization frequencies removed from λ_{\max} . It only become significant for operating frequencies close to the absorption peak,

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which is not a viable approach to enhance r_{33} due to high absorptive loss and decrease in optical stability of the chromophore.

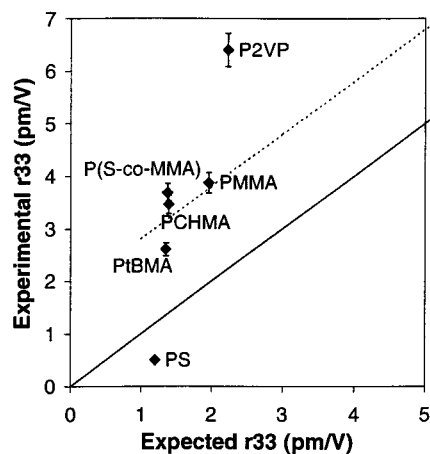
Local Field Effects. The dielectric properties of the host medium have a substantial effect on the magnitude of the local electric field experienced by a chromophore during alignment and modulation. The influence of the dielectric properties of the host polymer on the magnitude of the modulating and poling electric fields experienced by isolated chromophore can be estimated using Lorenz–Lorentz and Onsager local field factors. Using these factors, Singer et al. developed a mean-field expression relating the molecular hyperpolarizability (β) of a system of isolated dipoles (μ) in an isotropic medium to the macroscopic nonlinear response, r_{33} associated with a set of processing conditions (E_p , T):³³

$$r_{33} = \left(2N\beta \frac{\mu E_p}{5kT} \right) \left(\frac{f(0)^2 f(\omega)^2}{n_\omega^4} \right) \quad (5)$$

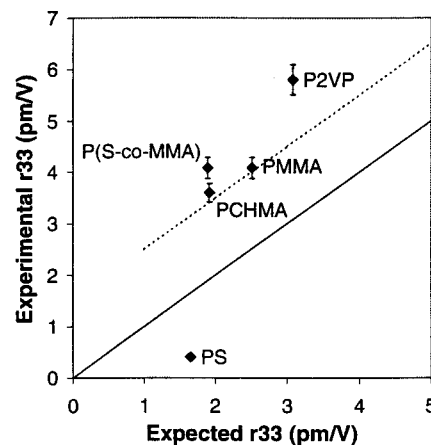
N , E_p , k , and T are the number density of chromophores, static poling field, Boltzmann's constant and poling temperature, respectively. $f(\omega)$ is the Lorenz–Lorentz local field factor for optical frequencies, $f(0)$ is the Onsager local field factor for a static field. For convenience, the terms that reflect the contribution from the chromophores are grouped in the first parentheses of eq 5 and will be collectively referred to as B^{chromo} . F^{host} refers to the host-dependent factors in the second parenthesis. B^{chromo} includes properties inherent to the chromophore (μ , β) and the response of the chromophore to poling conditions (E_p , T). Local field factors embodying the dielectric properties of the host are grouped in F^{host} . Note that the mean-field nature of this expression ignores host–guest interactions and specific dipole–dipole interactions between chromophores.

Figure 6 compares the host-dependent behavior expressed in eq 5 with experimental results for 10 wt % DR1- and DCM-doped films. Since B^{chromo} is the same for all the systems, changes in the expected r_{33} are directly proportional to host-dependent properties (local field factors) associated with F^{host} . Direct correlation (solid line) between the data and eq 5 is poor. Qualitatively, the relationship among the acrylate systems scales with eq 5 (dash line). Enhancement of nonlinear response of 10–15% can be realized through enhancement of local electric fields associated with the dielectric properties of the matrix. In the extreme, local field factors can account for the 20–25% increase in r_{33} of DCM in P2VP relative to DCM in PMMA. For inorganics where a larger range of dielectric constants are available, enhancements exceeding a factor of 4 resulting from localization of electric fields have been predicted for Maxwell–Garnett, Bruggeman, layered, and fractal geometries.^{34,35}

Intermolecular Interactions. In general, the mean-field model (eq 5) fails to describe the relationships for PS, PVP, and the PS–PMMA copolymer. Specific interactions, such as secondary interactions with directional character (weak acid–base or strong hydrogen



(a)



(b)

Figure 6. The EO coefficient of 10 wt % (a) DR1 and (b) DCM as a function of the host polymer. The expected r_{33} was calculated using eq 5 and a direct correlation was assumed for the solid line. A constant vertical offset (dotted line) is necessary for qualitative agreement with experiment.

bonding) and variations in the local molecular environment, such as via nanoscopic phase segregation, will result in substantial deviations from the simple mean-field treatment of chromophore environment.

As previously discussed the relatively nonpolar nature of PS leads to poor solvation of the highly polar chromophores. The observed head–tail aggregates of DR1 reduce the effective chromophore concentration, reducing N and thus r_{33} . Similar aggregation of DCM is expected to account for the low r_{33} in DCM-doped PS.

Similar nanoscopic phase segregation can occur with regard to a host polymer containing dissimilar constituents. The similar nonlinearity between PMMA and P(S_{0.7}MMA_{0.3}) indicate that the local molecular environment of the chromophore is more PMMA rich than PS (Table 2). Different reactivities of methyl methacrylate and styrene may lead to a blocky (nonrandom) copolymer. This nanoscopic nonuniformity would lead to segregation of the chromophores in PMMA-rich regions and thus similar behavior to homopolymer PMMA-doped DR1 or DCM films. Control of nanoscale structure affords the ability to maximize functionality of the host, by creating regions that optimize the molecular environment of the chromophore within regions that maxi-

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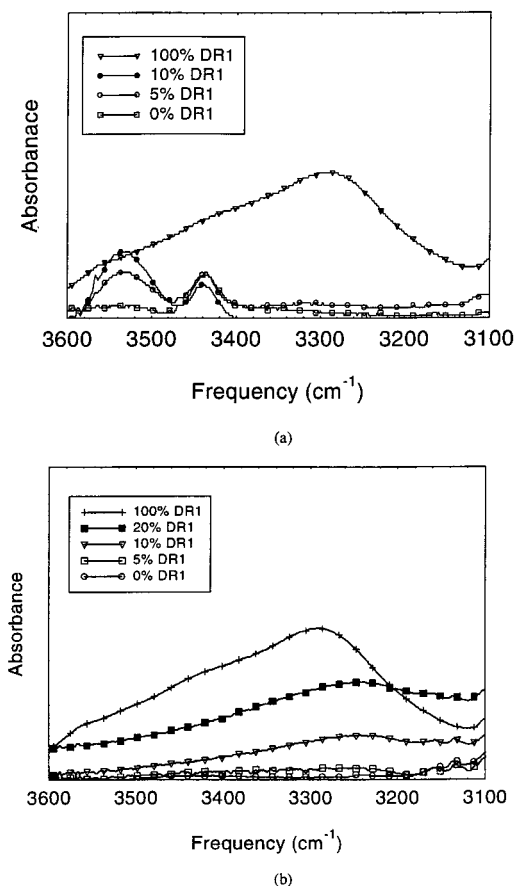


Figure 7. Infrared spectrum ($3600\text{--}3100\text{ cm}^{-1}$) of the hydroxyl stretching region for concentrations varying from 5 to 20 wt % of DR1 dispersed in (a) PMMA and (b) P2VP. (Every 20th data point is marked to distinguish between curves.)

mize structural performance or environmental stability of the EO film, while maintaining optical clarity.

In contrast to nanoscale segregation of chromophore or polymer, secondary interactions between chromophore and polymer will result in direct coupling of the structure and dynamics of the guest and host. These interactions may increase the magnitude and stability of r_{33} by improving miscibility and homogeneity of chromophore distribution as well as altering cooperative relaxations and poling efficiency. Many common chromophores and hosts may exhibit this coupling. For example, DR1 (Figure 1) may serve as a hydrogen bond donor (free hydroxyl group attached to the amino acceptor) or as a hydrogen-bond acceptor (nitro donor group). Furthermore, the pyridine group of P2VP is susceptible to hydrogen bonding with free hydroxyl groups.^{36,37}

Evidence for the presence of hydrogen bonding in DR1–P2VP and the absence of hydrogen bonding in DR1–PMMA was found using infrared spectroscopy, Figure 7. The hydroxyl-stretching band in DR1 is sensitive to hydrogen-bond interactions. A completely “free” hydroxyl group will produce a sharp peak around $3650\text{--}3584\text{ cm}^{-1}$, while hydrogen bonding will engender a broadening of the band along with a shift to lower

wavenumbers.³⁸ The relative strength of the interaction is proportional to the magnitude of the shift. Pure DR1 in powder form exhibits a broad peak at 3289 cm^{-1} , indicative of a relatively strong hydrogen bond formed between the hydroxyl and nitro group in crystalline DR1. When DR1 is dispersed in P2VP, a shift of the hydroxyl band to lower wavenumbers is observed. Figure 7b shows a broad peak at 3230 cm^{-1} for the doped P2VP, a 50 cm^{-1} shift when compared to the crystalline chromophore. Additionally, this peak scales with chromophore concentration. These results indicate that the hydrogen bonding between chromophore and host is even stronger than observed in crystalline DR1. Furthermore, the absorption associated with the nitro group (not shown) verifies the absence of chromophore–chromophore aggregates such as observed in DR1–PS systems. Finally, FTIR spectra collected at temperatures up to $160\text{ }^{\circ}\text{C}$ indicated that the hydrogen bond between DR1 and P2VP remains up to $160\text{ }^{\circ}\text{C}$ and is present during processing temperatures used for the chromophore alignment.

In contrast, when DR1 is dispersed in PMMA (Figure 7a), the hydroxyl band is shifted to higher wavenumbers. Two discrete peaks are observed, one at 3450 cm^{-1} associated with pure polymer and other at 3533 cm^{-1} associated with DR1. The 3450 cm^{-1} peak correlates to a small percentage of PMMA repeat units containing carboxyl groups.³⁹ The fairly sharp peak at 3533 cm^{-1} is associated with the “free” hydroxyl group of DR1 and scales with chromophore concentration. This suggests that the chromophores are well dispersed, a condition that has traditionally been assumed for DR1–PMMA systems and necessary to obtain a high degree of molecular orientation and thus nonlinear response in guest–host systems.

Thus, in contrast to DR1–PMMA systems in which the chromophore is dispersed in the polymer matrix, DR1 is specifically attached through a hydrogen bond to the pendant pyridine of the P2VP chain. Assuming hydrogen-bond formation occurs for an equivalence of DR1 and pendant pyridine, a maximal loading of 75 wt % may ideally be achieved. In the highest loaded system (25 wt %), roughly a third of the pendants from the polymer chain contain a DR1 molecule. Direct coupling of DR1 to the polymer matrix will greatly alter chromophore mobility and miscibility. The decrease in r_{33} at high concentrations of DR1 in PMMA (Figure 3) has been attributed to dipole–dipole interactions that effectively reduce the active chromophore concentration as well as the overall orientation parameter of the chromophores.¹² The hydrogen bonding ostensibly improves chromophore separation at all concentrations, maintaining a maximal chromophore–chromophore distance and therefore delaying dipole–dipole interactions to higher concentrations. The absence of a hydrogen-bond donor on DCM and thus an inability to directly coordinate with the matrix leads to a relatively lower r_{33} of DCM in P2VP relative to DR1.

The specific guest–host coupling may also influence the temporal stability of chromophore alignment. Stability will likely be enhanced with the addition of

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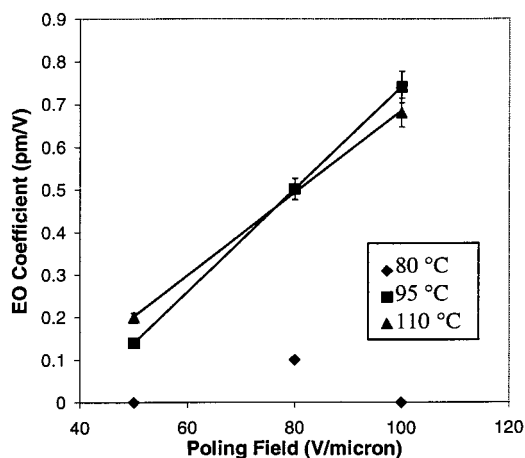


Figure 8. The processing dependence of the EO coefficient of undoped P2VP.

multiple hydroxyl groups on the chromophore. Cross-linking via specific secondary interactions is common in hydrogels and polyelectrolytes. Opportunities afforded by specific secondary interactions such as combining the processing ease of guest–host systems and the temporal stability of cross-linked matrixes through a temperature-dependent three-dimensional H-bonded network are currently under investigation.

Orientable Matrix. Finally consider the influence of an anisotropic, electric-field-responsive matrix in contrast to conventional isotropic, nonresponsive matrixes. The responsive matrix may act to enhance chromophore orientation and stability by constructively adding an additional bias to the orientation potential energy function.⁴⁰ Under the proper processing conditions, second-order effects can be observed from pure P2VP, which are associated with the chromophoric properties of pyridine (calculated to be $\mu = 1.9$ D and $\beta_0 = 0.26E - 30$ esu).^{41,42} Figure 8 shows the r_{33} for pure P2VP for various processing conditions (E_p , T). Side-group alignment occurs at a minimum poling temperature (above 80 °C), and does not improve at temperatures above T_g . These results indicate that the polymer is electric field-responsive and local molecular orientation can be induced. Similar second-order effects from pyridine containing polymers have been reported elsewhere.^{41,42} For the specific systems examined herein, simple superposition of the r_{33} of pure P2VP to the DR1- and DCM-doped system only accounts for a 5–8% enhancement of the EO response.

An orientable matrix may act as a template to aid chromophore orientation or to redistribute free volume anisotropically around the chromophore, increasing the activation barrier to reorient after alignment. In addition to different sub- T_g relaxation temperatures, this

may partially account for the enhanced nonlinearly and stability observed with P2VP (Figures 2–4). A similar approach of using an orientable matrix has been investigated in liquid crystal (LC) systems as a route to improved chromophore orientation and stability.⁴⁰ It was concluded from this work that the potential energy of the chromophore to align with an applied field is reduced in an anisotropic medium. The unique aspect of P2VP is that anisotropy is induced during processing, whereas the anisotropy is present before processing in LC systems. Relative to LC systems, orienting the matrix along with the chromophore will minimize defect structures and scatter associated with LC systems. This may be significant when addressing optical quality of the final film or the stability of the imposed order. Note that the relatively small enhancement of r_{33} of DCM-doped P2VP relative to DR1-doped P2VP suggests that the contribution of an orientable matrix to the magnitude of r_{33} may be minor or may be sensitive to the chromophore shape.

Conclusion

The r_{33} of 10 wt % DR1- and DCM-doped P2VP films was up to 70% larger than PMMA and as much as a factor of 12 larger than PS (shown in Table 2). Although relative shifts in the electronic spectrum were observed in these films, changes in the resonance enhancement were relatively small (less than 8%). Only 20–25% of the host-dependent variation may be attributed to local field effects, which were quantified using the model developed by Singer et al. The majority of the variation is associated with intermolecular interactions and chromophore miscibility. Careful consideration of host–guest interactions will enable substantial increases of r_{33} by enhancing chromophore separation and retention of asymmetric order. For example, the pyridine side group of P2VP provided an active hydrogen-bonding site for the free hydroxyl group in DR1. The resulting guest–host interaction increased chromophore separation, enhancing the effective chromophore concentration.

In general, use of secondary interactions offer some advantages relative to current covalent attachment of chromophores, such as enhanced flexibility in processing and formulation, and to covalent cross-linked systems, such as minimization of reaction products and volume change. These results demonstrate the potential associated with modification of guest–host interactions for the development of highly nonlinear, stable EO polymer systems.

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