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Chromophore Design for Photorefractive Applications

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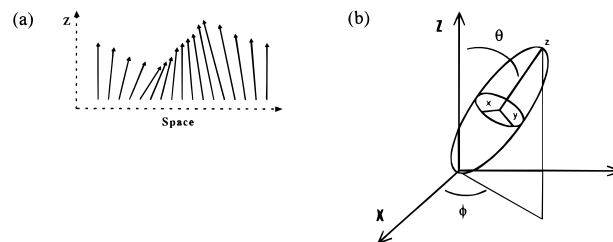of Technology, Pasadena, California 91109*

Active organic polymers are emerging as key materials for advanced information and telecommunication technology.[1] Owing to their high performance, structural flexibility, and light weight, polymers are expected to play a major role in optical technology especially when large-scale manufacturing of devices at low cost is crucial. Multifunctional nonlinear optical polymers and molecular assemblies are intensively investigated for electrooptic and photorefractive applications.[2−5]

In the field of electrooptic polymers, a commonly used figure of merit of chromophores for electrooptic applications is $\beta\mu/M$ where β is the first hyperpolarizability of the molecule, μ its dipole moment, and M its molecular weight. Recently, we proposed the BOA (bond order alternation) model as a simple way to optimize the magnitude of the $\beta\mu$ product in chromophores by adjusting the strength of the donor and acceptor substituents.[6−9] With the development of highly efficient photorefractive polymers,[3] that combine electrooptic and photoconducting properties, interest in nonlinear optical chromophore design has gained additional momentum. Due to the orientational effects evidenced in low glass transition temperature (T_g) photorefractive polymers,[2] the design criteria or figure of merit of chromophores for photorefractive applications differ from those discussed above for purely electrooptic applications. In this paper, we report results from calculations performed using the INDO/SCDCI method on $(CH_3)_2N(CH=CH)_4CHO$ in the presence of an external field to modulate the ground state polarization and concomitantly BOA. On the basis of the computation results on this molecule, we discuss the general design guidelines for the optimization of chromophores for low T_g photorefractive polymers.

The basic properties for photorefractivity include photosensitivity, photoconductivity, and electrooptic activity.[10] Polymers we developed[3] showed nearly 100% four-wave mixing diffraction efficiency in 105 μm thick and net gain coefficients in excess of $\Gamma = 200$ cm^{-1} at an applied field of 90 V/μm. In

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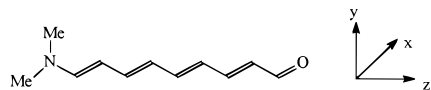(7) Gorman C. B.; Marder, S. R. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 11297.
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Figure 1. (a) Periodic orientational distribution of the chromophores in low glass transition temperature photorefractive polymers. (b) Schematic structure of rodlike chromophores in the laboratory frame {X, Y, Z}; {x, y, z} is the frame attached to the molecule.

traditional photorefractive materials, the refractive index modulation arises solely from the space−charge field acting on the electrooptic (Pockels) effect of the material.[11] Thus, the molecular figure of merit developed for high T_g photorefractive polymers, is related to $\beta\mu/M$ as discussed above for purely electrooptic polymers. In contrast, photorefractive polymers with a low T_g, exhibit an orientational contribution to the refractive index modulation. Accordingly, the figure of merit and the design criteria for the chromophores change. The so-called orientational enhancement effect[10] is due to the ability of the chromophores to orient at room temperature under the influence of the total electric field which is the superposition of the internal modulated field and the externally applied field. As a result, in steady state, after photorefractive hologram formation, the molecules have no longer a uniform orientation but can have an orientation that is spatially modulated both in magnitude and in direction as shown in Figure 1a. That periodic orientation of the chromophores doubles the effect of the electrooptic contribution and, more importantly, leads to a modulated birefringence that significantly enhances the total refractive index modulation. This modulated birefringence can be easily understood by recalling that a macroscopic change in orientation of rodlike molecules with a polarizability anisotropy $\Delta\alpha$ (see Figure 1b) leads to refractive index changes. In the frame of the oriented gas model[12] the change in refractive index induced by a poling field applied along a Z axis for an optical wave polarized along that axis is given by

$$\Delta n_Z^{(1)} = \frac{2\pi N F^{(1)}}{n} \Delta\alpha[\langle\cos^2\theta\rangle - 1/3] \approx \frac{4\pi N F^{(1)}}{45n}\Delta\alpha\left(\frac{\mu E}{kT}\right)^2 \quad (1)$$

where n is the refractive index, E the poling field, θ is the orientation angle, $F^{(1)} = (n^2 + 2)/3$ is the Lorentz−Lorenz local field correction factor, and N the density of chromophores. On a microscopic level, the new figure of merit for chromophores that leads to the orientational refractive index changes described by eq 1 is consequently $\Delta\alpha\mu^2$. When both the orientational birefringence and the electrooptic effects contribute to the total refractive index modulation amplitude, the new figure of merit FOM becomes

$$\text{FOM} = [A(T)\Delta\alpha\mu^2 + \beta\mu] \quad (2)$$

where $A(T) = 2/9kT$ is a numerical scaling factor. For the purpose of this study, the temperature was set to 300 K, which is a typical operating temperature for low T_g photorefractive polymers.

To probe how the FOM varies as a function of the BOA which is related to the extend of charge transfer or polarization in the ground state of the molecule, we analyzed the results of semiempirical INDO (intermediate neglect of differential over-

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Figure 2. Structure of the cyanine molecule investigated in this work.

lap) calculations[8] performed on $(CH_3)_2$ $N(CH=CH)_4CHO$ in the presence of an external field applied along the long axis z of the molecule (Figure 2). At each field strength, the geometry was optimized and a value of BOA was determined. Electronic states were calculated using configuration interaction with full single and limited double configuration excitations. Then, $\Delta\alpha$ and β were evaluated using the sum over states (SOS) approach derived from perturbation theory, using the 30 lowest energy states to obtain converged values.[8] As discussed previously,[6–9] $\beta\mu$ exhibits two extrema with a negative maximum at a value of roughly 0.2BOA, which corresponds to molecules that are somewhat polarized beyond the BOA $= 0$, cyanine limit (Figure 3). The calculations indicate that $\alpha_{zz} \gg \alpha_{xx}$, α_{yy}, thus $\Delta\alpha \approx \alpha_{zz}$. Previously, we have shown[8] that α_{zz} exhibits a peak at BOA $= 0$ for this molecule. In addition, we have demonstrated[8] that μ essentially increases linearly with BOA over the region considered in this study, and thus, μ^2 increases quadratically with BOA. As a consequence, $\Delta\alpha\mu^2$ has its peak shifted to greater polarization (higher BOA) than is observed at the cyanine limit and exhibits a peak at roughly the BOA where $\beta\mu$ peaks. However, it is important to note that the two contributions are opposite in sign. It is therefore necessary to consider their relative magnitudes. Such a comparison is shown in Figure 3a where we have plotted $A(T)\Delta\alpha\mu^2$ and $\beta\mu$ as a function of BOA. As can be seen from Figure 3a, in the region where $A(T)\Delta\alpha\mu^2$ and $\beta\mu$ are peaked, the magnitude of $A(T)\Delta\alpha\mu^2$ is over 80 times higher than that of $\beta\mu$. As a result, the contribution of the $\beta\mu$ term is almost negligible and $[A(T)\Delta\alpha\mu^2 + \beta\mu] \approx A(T)\Delta\alpha\mu^2$ for this molecule. FOM as a function of BOA is shown in Figure 3b.

In conclusion, our calculations suggest that for linear polymethines of this length, one should synthesize molecules which are somewhat polarized beyond the cyanine limit. Such molecules will lead to high refractive index changes due to orientational effects in low T_g photorefractive polymers. One caveat of this analysis that will be important as the technology allows for the incorporation of longer molecules with significantly higher $\beta\mu$ values is the fact that $\beta\mu$ will scale more rapidly with length than will $A(T)\Delta\alpha\mu^2$. This will reduce the ratio of $A(T)\Delta\alpha\mu^2$ to $\beta\mu$ and consequently shift the peak of $[A(T)\Delta\alpha\mu^2$
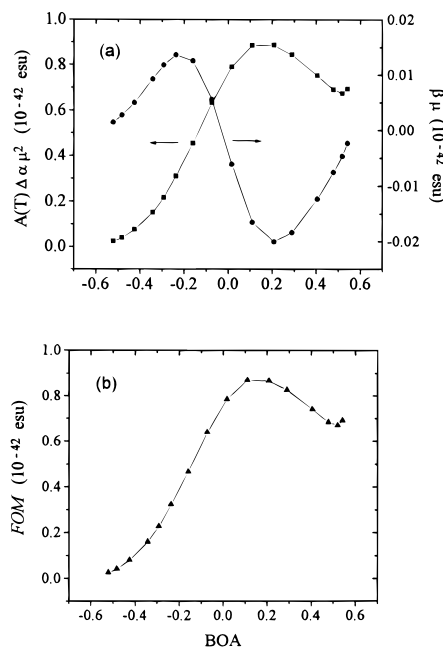
Figure 3. Electrooptic ($\beta\mu$) and orientational ($A(T)\Delta\alpha\mu^2$) contributions (a), and FOM (b) as a function of BOA for the cyanine molecule whose structure is shown in Figure 2.

$+ \beta\mu]$ to lower values of BOA. However, for molecules of the length that are currently being considered for visible and near-IR photorefractive applications, this effect should only be a minor perturbation. By following this design strategy for the active dye dopant molecules, we recently developed new photorefractive polymers with an unprecedented level of performance.[13] Our results validate the design rationale presented in this paper.

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