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# Design of optimized photorefractive polymers: A novel class of chromophores

Rüdiger Wortmann, Constantina Poga, Robert J. Twieg, Christian Geletneky, Christopher R. Moylan, Paul M. Lundquist, Ralph G. DeVoe, Patricia M. Cotts, Hans Horn, Julia E. Rice, and Donald M. Burland *IBM Almaden Research Center*, 650 Harry Road, San Jose, California 95120-6099

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It is demonstrated that the microscopic mechanism of the photorefractive (PR) effect in organic composites with low glass transition temperatures involves the formation of refractive index gratings through a space-charge field-modulated Kerr effect. A tensorial formulation of the macroscopic aspects of the PR Kerr effect and its microscopic interpretation is presented. The second-order dipole orientation term containing the anisotropy of the first-order optical polarizability  $\alpha(-\omega;\omega)$  is shown to yield the dominant contribution to the Kerr susceptibility  $\chi^{(3)}(-\omega;\omega,0,0)$ . A class of special chromophores having negligible second-order polarizabilities  $\beta(-\omega;\omega,0)$  and large dipole moments  $\mu$  has been identified in order to optimize this term. These chromophores are not subject to the efficiency-transparency tradeoff typically encountered with second-order nonlinear optical (NLO) chromophores, providing highly transparent materials with large PR Kerr response. Contrary to previous approaches in this field, the best-performing PR polymers are then expected to employ chromophores that would be useless for second-(negligible order applications β). We report PR of the material 30% 2,6-di-n-propyl-4H-pyran-4-ylidenemalononitrile (DPDCP): 15% N,N'-bis(3-methylphenyl)-N,N'-bis(phenyl)benzidine (TPD):55% poly(methyl methacrylate) (PMMA):0.3% C<sub>60</sub> as an illustration of this principle. A 100  $\mu$ m thick film of this material exhibits a steady-state diffraction efficiency of  $\eta$ =25% and net two-beam coupling of  $\Gamma$ =50 cm<sup>-1</sup> at a bias field of 100 V/ $\mu$ m and a wavelength of 676 nm. The macroscopic Kerr susceptibility of the material is related to molecular electronic properties of the chromophore DPDCP which were independently determined by experiments in solution and by quantum chemical calculations. © 1996 American Institute of Physics. [S0021-9606(96)50547-7]

#### I. INTRODUCTION

The photorefractive (PR) effect has long been known in noncentrosymmetric inorganic crystals such as LiNbO<sub>3</sub>.<sup>1</sup> In PR crystals the interference pattern produced by two intersecting coherent beams generates a nonuniform space-charge field  $E_{sc}$  by photogeneration of free carriers and subsequent carrier drift and diffusion processes.<sup>2,3</sup> As a consequence, the refractive index of the material is modulated by the interaction of the field  $E_{sc}$  with the Pockels susceptibility  $\chi^{(2)}(-\omega;\omega,0)$  of the crystal. The refractive index grating is spatially displaced from the intensity grating, by as much as  $\pi/2$  rad (nonlocality of the PR effect). The PR effect gives rise to a variety of two- and four-wave mixing phenomena, and has potential technological importance for a variety of optical signal processing schemes.<sup>2,3</sup> Recent developments in enabling technologies for high-density holographic optical data storage<sup>4</sup> have stimulated research on PR materials, with the goal of identifying inexpensive holographic materials.

Photorefractivity in organic materials was demonstrated only recently, first in molecular crystals<sup>5,6</sup> and later in polymer systems.<sup>7</sup> In particular, PR polymers have attracted growing interest<sup>8</sup> because of their ease of sample fabrication and large diffraction efficiencies.<sup>9,10</sup> While the PR effect in molecular crystals and in permanently electric field-poled polymers can be described in a similar fashion as in inor-

ganic crystals, the origin of the photorefractivity of organic composites or polymers with low glass transition temperatures  $T_g$  can be quite different. These low- $T_g$  materials are isotropic in the absence of an externally applied bias field  $E_{h}$ . Therefore, the first-order electro-optical (Pockels) susceptibility  $\chi^{(2)}(-\omega;\omega,0)$  vanishes for reasons of symmetry and the second-order electro-optical (Kerr) susceptibility  $\chi^{(3)}(-\omega;\omega,0,0)$  governs the nonlinear response. These materials are poled in situ and the diffraction grating is created by the combined effect of the fields  $E_b$  and  $E_{sc}$ .<sup>11</sup> In contrast to crystalline systems, reorientation of the dipolar chromophores is an important, sometimes even dominant, mechanism in these materials.<sup>11</sup> In order to distinguish clearly the PR effect through  $\chi^{(2)}(-\omega;\omega,0)$  in intrinsically noncentrosymmetric materials (such as permanently poled polymers) from that in isotropic low- $T_g$  materials through the Kerr susceptibility  $\chi^{(3)}(-\omega;\omega,0,0)$ , we will use the nomenclature photorefractive Pockels effect for the former and photorefractive Kerr effect for the latter. The PR Kerr effect incorporates both the "conventional" PR mechanism and the so-called "orientational enhancement" mechanism.<sup>11</sup>

In this paper we present a fully tensorial formulation of the PR Kerr effect, providing a convenient formalism for the calculation of diffraction efficiencies for various geometries. We also present a detailed microscopic interpretation of the



FIG. 1. Molecule-fixed coordinate system and resonance structures for DMDCP (*R*-methyl), DEDCP (R=ethyl), and DPDCP (R=n-propyl).

PR Kerr effect in terms of the relevant molecular linear and nonlinear optical properties. This approach allows the identification of the dominant molecular contributions and a better establishment of design criteria for the optimization of functional dyes for organic PR materials. These general principles are illustrated with a prototype chromophore, 2,6-di*n*-propyl-4H-pyran-4-ylidenemalononitrile (DPDCP, Fig. 1). The linear and nonlinear optical properties of this compound are obtained from a complete set of refractive index, permittivity, depolarized Rayleigh scattering, electric field-induced second harmonic generation (EFISH), and UV-VIS spectroscopic measurements, and quantum chemical calculations.

#### **II. MACROSCOPIC THEORY OF THE** PHOTOREFRACTIVE KERR EFFECT

The PR Kerr effect is the local response of the medium to the space-charge modulated static electric field. In this section we present a tensorial formulation of the PR Kerr effect and employ it in the calculation of diffraction efficiencies for different geometries and polarization conditions.

The principal indices of refraction of the medium at frequency  $\omega$ ,  $n_{\alpha}^{(\omega)}$ , are related to its first-order susceptibility  $\chi^{(1)}_{\alpha\alpha}(-\omega;\omega)$  by the equation

$$n_{\alpha}^{(\omega)} = \sqrt{1 + \operatorname{Re}[\chi_{\alpha\alpha}^{(1)}(-\omega;\omega)]},\tag{1}$$

where  $\alpha$  indicates the polarization direction of the light. In a PR experiment, the total electric field E is a superposition of a static or slowly varying field  $\mathbf{E}_0$  and an optical field with amplitude  $\mathbf{E}_{\omega}$  and frequency  $\omega$ . The time dependence of the total field is given by

$$\mathbf{E}(t) = \mathbf{E}_0 + \frac{1}{2} \left[ \mathbf{E}_{\omega} e^{-i\omega t} + (\mathbf{E}_{\omega})^* e^{i\omega t} \right], \tag{2}$$

where \* indicates complex conjugation. The static field itself is a superposition of the externally applied bias field  $\mathbf{E}_b$  and the spatially periodic space-charge field with amplitude  $\mathbf{E}_{sc}$ and grating vector  $\mathbf{K}_{G}$ 

$$\mathbf{E}_0 = \mathbf{E}_b + \mathbf{E}_{sc} \cos(\mathbf{K}_G \cdot \mathbf{r}). \tag{3}$$

This spatially varying space-charge field is generated by internal charge separation<sup>2</sup> produced by a spatially varying optical field  $\mathbf{E}_{\omega}$ . The Fourier component at frequency  $\omega$  of the polarization induced by the field  $\mathbf{E}(t)$  in the medium is given by

$$P_{\mu}^{(\omega)} = \left[\chi_{\mu\alpha}^{(1)}(-\omega;\omega) + \Delta\chi_{\mu\alpha}^{(1)}(-\omega;\omega)\right] E_{\alpha}^{(\omega)}, \qquad (4)$$

where (sum convention used for repeated indices)

$$P_{\mu}^{(\omega)} = [\chi_{\mu\alpha}^{(1)}(-\omega;\omega) + \Delta\chi_{\mu\alpha}^{(1)}(-\omega;\omega)]E_{\alpha}^{(\omega)}, \qquad (4)$$

 $\Delta \chi^{(1)}_{\mu\alpha}(-\omega;\omega) = 2 \chi^{(2)}_{\mu\alpha\beta}(-\omega;\omega,0) E^{(0)}_{\beta}$  $+3\chi^{(3)}_{\mu\alpha\beta\gamma}(-\omega;\omega,0,0)E^{(0)}_{\beta}E^{(0)}_{\gamma}+\cdots$ (5)

is the change of the first-order susceptibility induced by the static field  $\mathbf{E}_0$ , the Greek indices denoting Cartesian tensor components in the laboratory frame. The susceptibilities  $\chi^{(1)}$ ,  $\chi^{(2)}$ , and  $\chi^{(3)}$  in the preceding equations use the convention recommended by Butcher and Cotter.<sup>12</sup>

The second-order susceptibility  $\chi^{(2)}$  gives rise to the PR Pockels effect in noncentrosymmetric materials. In isotropic centrosymmetric materials,  $\chi^{(2)}$  vanishes and the nonlinear response of the medium is due to the Kerr susceptibility  $\chi^{(3)}(-\omega;\omega,0,0)$  only. The third-order susceptibility  $\chi^{(3)}$  of an isotropic medium has 21 nonvanishing tensor components of which only three are independent.<sup>12</sup> The general symmetry relations<sup>12</sup> between these can be written using Kronecker  $\delta$ symbols in the compact form<sup>13</sup>

$$\chi^{(3)}_{\mu\alpha\beta\gamma} = \chi^{(3)}_{ZZXX} \delta_{\mu\alpha} \delta_{\beta\gamma} + \chi^{(3)}_{ZXZX} \delta_{\mu\beta} \delta_{\alpha\gamma} + \chi^{(3)}_{ZXXZ} \delta_{\mu\gamma} \delta_{\alpha\beta}$$
(6)

with the additional linear relationship

$$\chi_{ZZZZ}^{(3)} = \chi_{ZZXX}^{(3)} + \chi_{ZXZX}^{(3)} + \chi_{ZXXZ}^{(3)}.$$
(7)

The Cartesian indices in Eqs. (6) and (7) refer to an arbitrarily chosen laboratory frame. In the particular case of  $\chi^{(3)}(-\omega;\omega,0,0)$  two components are identical because of intrinsic permutation symmetry in the last two indices;  $\chi^{(3)}_{ZXZX} = \chi^{(3)}_{ZXXZ}$ . The most general Kerr susceptibility of an isotropic medium therefore has only two independent components  $\chi^{(3)}_{ZZXX}$  and  $\chi^{(3)}_{ZZZZ}$ , and is of the form<sup>13</sup>

$$\chi^{(3)}_{\mu\alpha\beta\gamma}(-\omega;\omega,0,0) = \chi^{(3)}_{ZZXX}\delta_{\mu\alpha}\delta_{\beta\gamma} + \frac{1}{2}(\chi^{(3)}_{ZZZZ} - \chi^{(3)}_{ZZXX}) \times (\delta_{\mu\beta}\delta_{\alpha\gamma} + \delta_{\mu\gamma}\delta_{\alpha\beta}).$$
(8)

Using Eqs. (3), (5), and (8) it is straightforward to calculate the diffraction efficiency  $\eta$  of photorefractive gratings observed in four-wave mixing (FWM) experiments for various geometries and polarization conditions.

The geometry of the FWM experiment of this work has been described previously.<sup>11</sup> The internal angles of incidence of writing beams 1 and 2 are denoted  $\theta_1$  and  $\theta_2$ , and the angle of the grating vector relative to the surface normal is  $\theta_G$ . The laboratory frame was chosen with the z axis parallel to the surface normal, the xz plane as the plane of incidence, and y normal to this plane. The polarization unit vectors of the reading beam 3 and the diffracted beam 4 are then  $\mathbf{e}_{3}^{(s)} = \mathbf{e}_{4}^{(s)} = (0,1,0)^{T}$  (*T* indicates tensor transposition) for *s*-polarized reading, and  $\mathbf{e}_3^{(p)} = (\cos \theta_2, 0, \sin \theta_2)^T$  and  $\mathbf{e}_4^{(p)} = (\cos \theta_1, 0, \sin \theta_1)^T$  for *p*-polarized reading. The grating vector is  $\mathbf{K}_G = K_G$  (sin  $\theta_G$ , 0, cos  $\theta_G$ )<sup>T</sup>, the bias field  $\mathbf{E}_b = E_b(0,0,1)^T$ , and the space-charge field  $\mathbf{E}_{sc} = E_{sc}$  $\times (\sin \theta_G, 0, \cos \theta_G)^T \cos(\mathbf{K}_G \cdot \mathbf{r}).$ 

The diffraction efficiency  $\eta$  for Bragg-matched readout of a slanted thin transmission grating of thickness d has been shown<sup>11,14</sup> to be the following:

$$\eta = \sin^2[H(e_3 \cdot e_4)(e_3 \cdot \Delta \chi^{(1)} \cdot e_4)] \tag{9}$$

with

$$H = \frac{\pi d}{2n\lambda_0 (\cos \theta_1 \cos \theta_2)^{1/2}}.$$
 (10)

For the geometry specified above, the results for s-polarized and p-polarized reading are

$$\eta_s = \sin^2[H\Delta\chi_{YY}^{(1)}],\tag{11}$$

$$\eta_p = \sin^2 [H \cos(\theta_1 - \theta_2)) (\cos \theta_1 \cos \theta_2 \Delta \chi_{XX}^{(1)} + \sin(\theta_1 + \theta_2) \Delta \chi_{XZ}^{(1)} + \sin \theta_1 \sin \theta_2 \Delta \chi_{ZZ}^{(1)})]. \quad (12)$$

The relevant tensor components are easily obtained from Eqs. (3), (5), and (8) and contain spatial Fourier components at 0  $\mathbf{K}_G$ , 1  $\mathbf{K}_G$ , and 2  $\mathbf{K}_G$ . The results for the 1  $\mathbf{K}_G$  component are:

$$\Delta \chi_{XX}^{(1)} = \Delta \chi_{YY}^{(1)} = 6 \chi_{ZZXX}^{(3)} E_b E_{sc} \cos \theta_G, \qquad (13)$$

$$\Delta \chi_{XZ}^{(1)} = \Delta \chi_{ZX}^{(1)} = 3(\chi_{ZZZZ}^{(3)} - \chi_{ZZXX}^{(3)}) E_b E_{sc} \sin \theta_G, \quad (14)$$

$$\Delta \chi_{ZZ}^{(1)} = 6 \chi_{ZZZZ}^{(3)} E_b E_{sc} \cos \theta_G.$$
<sup>(15)</sup>

The preceding equations can be used to calculate the diffraction efficiency  $\eta$  for various polarization conditions. In particular, one obtains for the polarization anisotropy of the 1 **K**<sub>G</sub> grating in the low diffraction limit:

$$\frac{\eta_p}{\eta_s} = \cos^2(\theta_1 - \theta_2) \left[ \cos \theta_1 \cos \theta_2 + \frac{\chi_{ZZZ}^{(3)}}{\chi_{ZZXX}^{(3)}} \sin \theta_1 \sin \theta_2 + \frac{1}{2} \left( \frac{\chi_{ZZZZ}^{(3)}}{\chi_{ZZXX}^{(3)}} - 1 \right) \tan \theta_G \sin(\theta_1 + \theta_2) \right]^2.$$
(16)

This expression is equivalent to Eq. 25 of Ref. 11.

#### III. MICROSCOPIC INTERPRETATION OF THE PHOTOREFRACTIVE KERR EFFECT

In the model of additive molecular contributions, the macroscopic susceptibility  $\chi^{(3)}(-\omega;\omega,0,0)$  may be represented as a sum of terms that are proportional to the concentrations  $c_J$  of the different constituents J of the medium

$$\chi^{(3)}_{\mu\alpha\beta\gamma}(-\omega;\omega,0,0) = \frac{1}{\epsilon_0} \sum_{N}^{J=1} \zeta^{(3)}_{J\mu\alpha\beta\gamma}(-\omega;\omega,0,0)c_J,$$
(17)

where  $\zeta_{J\mu\alpha\beta\gamma}^{(3)}$  are molar third-order polarizabilities of the component *J* and  $\epsilon_0$  is the permittivity of free space. The quantities  $\zeta_{J\mu\alpha\beta\gamma}^{(3)}$  can be calculated on the basis of a specific molecular model and are closely related to partial molar quantities that are well known in the formalism of chemical thermodynamics.<sup>13,15</sup> They do not, however, necessarily satisfy the Euler theorem of homogeneous functions.<sup>15</sup> The molar polarizabilities can be derived from<sup>13</sup>

$$\zeta_{J\mu\alpha\beta\gamma}^{(3)}(-\omega;\omega,0,0) = \frac{N_A}{3} \lim_{|E|\to 0} \frac{\partial^3}{\partial E^{(\omega)}_{\alpha} \partial E^{(0)}_{\beta} \delta E^0_{\gamma}} \langle w_J p_{J\mu}^{(\omega)} \rangle,$$
(18)

where  $N_A$  is Avogadro's constant and  $\langle \rangle$  denotes a statistical-mechanical average calculated with the orienta-

tional distribution function  $w_J$  given in Eq. (28) below. The Fourier components  $p_{J\mu}^{(\omega)}$  of the induced dipole of the constituent *J* are

$$p_{J\mu}^{(\omega)} = \overline{\alpha}_{J\mu\alpha}(-\omega;\omega)E_{\alpha}^{(\omega)} + \overline{\beta}_{J\mu\alpha\beta}(-\omega;\omega,0)E_{\alpha}^{(\omega)}E_{\beta}^{(0)} + \frac{1}{2}\overline{\gamma}_{J\mu\alpha\beta\gamma}(-\omega;\omega,0,0)E_{\alpha}^{(\omega)}E_{\beta}^{(0)}E_{\gamma}^{(0)} + \cdots$$
(19)

with  $\overline{\alpha}_J$ ,  $\overline{\beta}_J$ , and  $\overline{\gamma}_J$  being effective first-, second-, and thirdorder polarizabilities of the molecules of type J in the medium in the Taylor series convention.<sup>16</sup> Applying Lorentz local field corrections, the effective polarizabilities are related to those of the free molecules by

$$\overline{\alpha}_{J}(-\omega;\omega) = L_{\omega}\alpha_{J}(-\omega;\omega), \qquad (20)$$

$$\overline{\beta}_{J}(-\omega;\omega,0) = L_{\omega}L_{0}\beta_{J}(-\omega;\omega,0), \qquad (21)$$

$$\overline{\gamma}_J(-\omega;\omega,0,0) = L_{\omega} L_0^2 \gamma_J(-\omega;\omega,0,0), \qquad (22)$$

with Lorentz factors  $L_{\omega}$  at frequencies 0 and  $\omega$ 

$$L_{\omega} = \frac{\epsilon_{\omega} + 2}{3}.$$
 (23)

More refined local field corrections and effects of the static reaction field on effective molecular properties in condensed media have been described elsewhere.<sup>13,17</sup>

The energy of a molecule with permanent dipole  $\mu_J$  and static polarizability  $\alpha_J(0;0)$  in a static external field is orientation dependent:

$$\Delta W_J(\mathbf{E}_0) = -\bar{\mu}_{J\gamma} E_{\gamma}^{(0)} - \frac{1}{2} \bar{\bar{\alpha}}_{J\beta\gamma}(0;0) E_{\beta}^{(0)} E_{\gamma}^{(0)} - \cdots$$
(24)

with the effective quantities

$$\bar{\bar{\mu}}_{J} = \frac{\epsilon_{0}(\epsilon_{\infty}+2)}{2\epsilon_{0}+\epsilon_{\infty}} \mu_{J}, \qquad (25)$$

$$\bar{\bar{\alpha}}_{J}(0;0) = \frac{3\epsilon_{0}^{2}(\epsilon_{\infty}+2)}{(2\epsilon_{0}+1)(2\epsilon_{0}+\epsilon_{\infty})} \alpha_{J}(0;0), \qquad (26)$$

in Onsager's local field approximation.<sup>13,18–20</sup> The canonical distribution function describing the molecular orientation is, to second order in the static field<sup>13</sup>

$$w_{J}(\tau) = \frac{\exp(-\Delta W_{J}/kT)}{\langle \exp(-\Delta W_{J}/kT) \rangle}$$

$$= 1 + \frac{1}{kT} \,\overline{\mu}_{J\gamma} E_{\gamma}^{(0)} + \frac{1}{6k^{2}T^{2}} \left[ 3\bar{\bar{\mu}}_{J\beta}\bar{\bar{\mu}}_{J\gamma} - \bar{\bar{\mu}}_{J}^{2} \delta_{\beta} \delta_{\gamma} \right] E_{\beta}^{(0)} E_{\gamma}^{(0)} + \frac{1}{6kT} \left[ 3\bar{\bar{\alpha}}_{J\beta\gamma} - tr(\bar{\bar{\alpha}}_{J}) \delta_{\beta} \delta_{\gamma} \right] E_{\beta}^{(0)} E_{\gamma}^{(0)} + \cdots$$

$$(28)$$

and consists of four terms corresponding to an isotropic contribution, a first-order and a second-order dipole orientation, and an orientation contribution arising from the anisotropy of the static polarizability. Using standard methods of orientational averaging<sup>21</sup> one obtains from Eqs. (18), (19), and (28) the two independent third-order molar polarizabilities

TABLE I. Linear and nonlinear optical properties of DPDCP and pNA.

		DPDCP	pNA
$\lambda_{a_{s}}$	(nm)	352 <sup>a</sup>	354 <sup>j</sup>
$\mu_{ag}$	$(10^{-30} \text{ Cm})$	21 <sup>a</sup>	16 <sup>j</sup>
$\mu$	$(10^{-30} \text{ Cm})$	24.6 <sup>b</sup>	20.8 <sup>j</sup>
$tr[\alpha(-\omega;\omega)]$	$(10^{-40} \text{ CV}^{-1} \text{ m}^2)$	110 <sup>c</sup>	57 <sup>j,k</sup>
$\delta \alpha_R$	$(10^{-40} \text{ CV}^{-1} \text{ m}^2)$	$26^{d}$	$10^{\rm f}$
$\alpha_{xx}(-\omega;\omega), \alpha_{yy}(-\omega;\omega), \alpha_{zz}(-\omega;\omega)$	$(10^{-40} \text{ CV}^{-1} \text{ m}^2)$	21, 38, 51 <sup>e</sup>	13, 19, 25 <sup>j,k</sup>
$\delta \alpha_{\kappa}$	$(10^{-40} \text{ CV}^{-1} \text{ m}^2)$	$22^{\rm f}$	$10^{\rm f}$
$\alpha^{(\tilde{\mathrm{TLM}})}(-\omega;\omega)$	$(10^{-40} \text{ CV}^{-1} \text{ m}^2)$	19 <sup>g</sup>	11 <sup>g</sup>
$\beta(-2\omega;\omega,\omega)$	$(10^{-50} \text{ CV}^{-2} \text{ m}^3)$	$-2(2)^{h}$	27 <sup>j,1</sup>
$\beta(-\omega;\omega,0)$	$(10^{-50} \text{ CV}^{-2} \text{ m}^3)$	$\sim 0^{i}$	23 <sup>i</sup>
$4\mu^2 \delta \alpha_{\nu}/(3k^2T^2)$	$(10^{-60} \text{ CV}^{-3} \text{ m}^4)$	105 000	34 000
$6\mu\beta(-\omega;\omega,0)/(kT)$	$(10^{-60} \text{ CV}^{-3} \text{ m}^4)$	$\sim 0$	7 000

Second-order polarizabilities  $\beta$  are given in the Taylor series definition<sup>16</sup> and SI units. SI to cgs unit conversions are:  $\mu$ ,  $10^{-30}$  Cm=0.2998×10<sup>-18</sup> esu;  $\alpha$ ,  $10^{-40}$  Cm<sup>2</sup> V<sup>-1</sup>=0.089 88×10<sup>-23</sup> esu;  $\beta$ ,  $10^{-50}$  Cm<sup>3</sup> V<sup>-2</sup>=2.694×10<sup>-30</sup> esu.

<sup>a</sup>From UV-VIS absorption in CHCl<sub>3</sub>.

<sup>b</sup>From permittivity measurements in CHCl<sub>3</sub>. <sup>c</sup>From refractive index measurements in CCl<sub>4</sub> at  $\lambda$ =633 nm.

<sup>d</sup>From depolarized Rayleigh scattering in CCl<sub>4</sub> at  $\lambda$  =633 nm.

<sup>e</sup>From  $tr[\alpha]$  and  $\delta \alpha_R$  with an estimated value of  $\alpha_{rr}$ .

<sup>f</sup>Calculated from  $\alpha_{xx}$ ,  $\alpha_{yy}$ , and  $\alpha_{zz}$ .

<sup>g</sup>Calculated for  $\lambda = 676$  nm from  $\mu_{ag}$  and  $\lambda_{ag}$  with Eq. (37).

<sup>h</sup>From EFISH in CHCl<sub>3</sub> at  $\lambda = 1907$  nm.

<sup>i</sup>Calculated for  $\lambda = 676$  nm from  $\beta(-2\omega;\omega,\omega)$  by using Eqs. (32)–(34). <sup>j</sup>From Ref. 23.

<sup>k</sup>At  $\lambda$ =589 nm in dioxane.

<sup>1</sup>From EFISH in dioxane at  $\lambda = 1064$  nm.  $\beta$  values are given in T convention, Ref. 16.

 $\zeta_{JZZXX}^{(3)}(-\omega;\omega,0,0)$ 

$$= \frac{N_A}{90} \left\{ \overline{\gamma}_{Jrrtt} + \frac{2}{kT} \,\overline{\bar{\mu}}_{Jr} \overline{\beta}_{Jrtt} - \frac{1}{3k^2 T^2} \left[ 3 \overline{\bar{\mu}}_{Jr} \overline{\bar{\mu}}_{Jt} \overline{\alpha}_{Jrt} - \overline{\bar{\mu}}_{Jr} \overline{\bar{\mu}}_{Jr} \overline{\bar{\mu}}_{Jr} \overline{\bar{\alpha}}_{Jrt} \right] - \frac{1}{3kT} \left[ 3 \overline{\bar{\alpha}}_{Jrt} \overline{\alpha}_{Jrt} - \overline{\bar{\alpha}}_{Jrr} \overline{\alpha}_{Jtt} \right] \right\}, \quad (29)$$

 $\zeta_{IZZZZ}^{(3)}(-\omega;\omega,0,0)$ 

$$= \frac{N_A}{90} \left\{ \overline{\gamma}_{Jrrtt} + \frac{6}{kT} \,\overline{\bar{\mu}}_{Jr} \overline{\beta}_{Jrtt} + \frac{1}{3k^2 T^2} \left[ 6 \overline{\bar{\mu}}_{Jr} \overline{\bar{\mu}}_{Jt} \overline{\alpha}_{Jrt} - 2 \overline{\bar{\mu}}_{Jr} \overline{\mu}_{Jr} \overline{\alpha}_{Jtt} \right] + \frac{1}{3kT} \left[ 6 \overline{\bar{\alpha}}_{Jrt} \overline{\alpha}_{Jrt} - 2 \overline{\bar{\alpha}}_{Jrr} \overline{\alpha}_{Jtt} \right] \right\},$$
(30)

where the Latin indices refer to Cartesian tensor components in the molecule-fixed frame and index permutation symmetry was assumed for the tensors  $\beta$  and  $\gamma$ . Four molecular terms therefore contribute to the PR Kerr effect. They are of type  $\gamma$ ,  $\mu\beta$ ,  $\mu^2\alpha$ , and  $\alpha\alpha$ , and arise from the four different orientation contributions in Eq. (28). The preceding equations represent an accurate description of the Kerr effect in dilute solutions. For highly viscous or rigid polymer systems with high concentrations of dopants, orientation correlations become important and the assumption of independently and freely reorienting molecules can be regarded as an approximation only. In addition, effects of electrostriction which are neglected in Eqs. (29) and (30) can sometimes be important. Nevertheless, these equations are useful in estimating the Kerr response of organic PR materials with low  $T_g$ , in the identification of the dominant contributions, and in establishing design criteria for its optimization, as will be discussed below.

#### IV. OPTIMIZATION OF FUNCTIONAL DYES FOR ORGANIC PR MATERIALS

It is illustrative to estimate the different contributions to the molar Kerr susceptibility for a typical chromophore such as 4-nitroaniline (pNA). The linear and nonlinear electric properties<sup>22,23</sup> of this prototype NLO-phore were taken from the literature and are collected in Table I. Neglecting local field effects and correcting for the different dispersion behavior of  $\beta(-2\omega,\omega,\omega)$  and  $\beta(-\omega;\omega,0)$  [see Eqs. (33) and (34) below], one obtains for the molar susceptibility using Eq. (30)  $\zeta_{ZZZZ}^{(3)} = 240 \times 10^{-36} \text{ C m}^4/\text{V}^3 \text{ mol at the Kr}^+ \text{ laser}$ wavelength of 676 nm. The contributions of the  $\gamma$ ,  $\mu\beta$ ,  $\mu^2\alpha$ , and  $\alpha\alpha$  terms to  $\zeta_{ZZZZ}^{(3)}$  are found to be 0.4%, 14%, 84%, and 1%, respectively. This example demonstrates that the dominant contribution in low- $T_g$  organic materials is, in many cases, due to the  $\mu^2 \alpha$  term ("birefringence orientational contribution"), with the  $\mu\beta$  term ("electrooptical contribution") being of minor importance, contrary to what was assumed in early investigations of PR polymers. Contributions of the  $\gamma$  and  $\alpha \alpha$  terms are usually negligible. It is, therefore, appropriate to introduce the approximations

$$\zeta_{ZZXX}^{(3)}(-\omega;\omega,0,0) \approx \frac{N_A}{90} \left\{ \frac{2}{kT} \,\bar{\bar{\mu}}\overline{\beta}(-\omega;\omega,0) - \frac{2}{3k^2T^2} \,\bar{\bar{\mu}}^2 \delta \overline{\alpha}_K(-\omega;\omega) \right\}, \quad (29a)$$

$$\zeta_{ZZZZ}^{(3)}(-\omega;\omega,0,0) \approx \frac{N_A}{90} \left\{ \frac{6}{kT} \,\bar{\mu}\overline{\beta}(-\omega;\omega,0) + \frac{4}{3k^2T^2} \,\bar{\mu}^2 \delta \overline{\alpha}_K(-\omega;\omega) \right\}, \quad (30a)$$

where the index for the constituent *J* and the Cartesian indexes of the molecular tensors have been omitted for reasons of simplicity. It is implied in Eqs. (29a) and (30a) that the dipole is oriented along the *z* axis, which is also assumed to be the main axis of the polarizability ellipsoid, and that the vector part of the second-order polarizability refers to the component along the dipole axis  $[\bar{\beta}_z = \beta_{zzz} + \beta_{zxx} + \beta_{zyy}]$ . The  $\mu^2 \alpha$  term contains the anisotropy of the optical polarizability  $\alpha(-\omega;\omega)$  in the form

$$\delta \alpha_K = \alpha_{zz} - \frac{1}{2} (\alpha_{xx} + \alpha_{yy}). \tag{31}$$

As will become apparent below, it is, in fact, quite difficult to design one-dimensional (1D) NLO chromophores for which the  $\mu\beta$  term dominates. It thus seems appropriate instead to focus design strategies on optimization of the  $\mu^2 \delta\alpha$ term, as will now be discussed.

It is well known that the second-order polarizability  $\beta$  of dipolar "charge-transfer" 1D NLO-phores with extended  $\pi$ -conjugated systems can be reasonably approximated by the two-level model (TLM, see, e.g., Ref. 22 and references therein) taking into account only the ground and the first optically allowed excited singlet state. The following expressions can be readily derived using the methods of time-dependent perturbation theory<sup>13</sup>

$$\beta_0^{(\text{TLM})} = \frac{6\Delta\mu(\mu_{ag})^2}{\left(\hbar\,\omega_{ag}\right)^2},\tag{32}$$

$$\beta^{(\text{TLM})}(-\omega;\omega,0) = \beta_0^{(\text{TLM})} \frac{\omega_{ag}^2 (3\omega_{ag}^2 - \omega^2)}{3(\omega_{ag}^2 - \omega^2)^2},$$
 (33)

$$\beta^{(\text{TLM})}(-2\omega;\omega,\omega) = \beta_0^{(\text{TLM})} \frac{\omega_{ag}^4}{(\omega_{ag}^2 - \omega^2)(\omega_{ag}^2 - 4\omega^2)},$$
(34)

with  $\beta_0^{(\text{TLM})}$  being the TLM approximation to the static  $\beta$ ,  $\Delta\mu$ , and  $\mu_{ag}$  the change of the dipole and the transition dipole of the electronic excitation from the ground state  $|g\rangle$  to the excited state  $|a\rangle$ , and  $\hbar\omega_{ag}$  the transition energy.

For first-order polarizabilities, it is, in general, necessary to take contributions of higher excited  $\pi$  states and of  $\sigma$ electrons explicitly into account. Nevertheless, the TLM contribution to  $\alpha$  is often substantial and is always a lower bound since all contributions to  $\alpha_{xx}$ ,  $\alpha_{yy}$ , and  $\alpha_{zz}$  are positive. The TLM contribution can be estimated by applying the following equations:

$$\alpha_0^{(\text{TLM})} = \frac{2\mu_{ag}^2}{\hbar\omega_{ag}},\tag{35}$$

$$\alpha^{(\text{TLM})}(-\omega;\omega) = \alpha_0^{(\text{TLM})} \frac{\omega_{ag}^2}{(\omega_{ag}^2 - \omega^2)}.$$
(36)

In the case of PNA  $\alpha^{(\text{TLM})}$  contributes about 40% to  $\alpha_{zz}$  (cf. Table I). For the moment, we assume that the off-axis components of the polarizability,  $\alpha_{xx}$  and  $\alpha_{yy}$ , and those of the second-order polarizability,  $\beta_{zxx}$  and  $\beta_{zyy}$ , are negligible. Equations (35) and (36) can, therefore, be used as a guiding principle to design functional dyes with optimized anisotropy of  $\alpha$ .

One-dimensional dipolar NLO-phores are usually  $\pi$ -conjugated donor-acceptor systems with resonance structures similar to those displayed in Fig. 1 for DPDCP. To a first approximation, the ground and excited states can each be represented by a linear combination of a neutral  $|n\rangle$  and a zwitterionic wave function  $|z\rangle$ 

$$|g\rangle = c|z\rangle - (1 - c^2)^{1/2}|n\rangle,$$
 (37)

$$|a\rangle = c|n\rangle + (1 - c^2)^{1/2}|z\rangle,$$
 (38)

where *c* is the mixing coefficient and zero differential overlap,  $\langle n|z\rangle = 0$ , is assumed. This description is reasonable for weakly interacting molecular complexes or spiro-conjugated charge-transfer compounds.<sup>24</sup> For  $\pi$ -conjugated systems, the approximation will be crude in general, but nevertheless some qualitative trends can be derived from it. The transition dipole and the change of the dipole upon electronic excitation are

$$\mu_{ag} = \langle a | \mu | g \rangle = -c(1-c^2)^{1/2} \Delta, \tag{39}$$

$$\Delta \mu = \langle a | \mu | a \rangle - \langle g | \mu | g \rangle = (1 - 2c^2) \Delta, \qquad (40)$$

where  $\Delta$  is the difference between the dipole moments of the neutral and the zwitterionic states, equal to the maximum change of the dipole upon excitation in the given system. Equations (39) and (40) allow for a straightforward estimation of the TLM polarizabilities in Eqs. (32)–(35). The results are displayed in Fig. 2 as a function of the mixing coefficient. The transition energy was assumed to be constant. The predictions of this simple model are that  $\alpha$  is maximized when  $\beta$  is zero. Similar trends were recognized in a two-state four-orbital model by Marder et al.<sup>25</sup> The maximum for  $\alpha$  occurs when the coefficient c is equal to  $2^{-1/2}$  and the neutral and the zwitterionic wave functions contribute equally to the ground and excited state. Since this situation is naturally present in symmetric cyanine dyes, it is sometimes called the "cyanine limit." At the same time, the change of the dipole upon excitation is zero and the magnitude of the transition dipole is maximized. The nature of the electronic excitation changes from a "charge transfer" (CT) to a "charge resonance" (CR) transition. Geometry changes upon excitation tend to be small in such CR systems. As a consequence, Franck-Condon progressions are short and the optical absorption spectra are unusually sharp.

Let us briefly examine some of the approximations of this model. It is assumed that  $\delta \alpha_K$  is modeled by  $\alpha_{zz}$ . The



FIG. 2. Relative TLM polarizabilities  $\alpha_0^{(\text{TLM})}$ ,  $\beta_0^{(\text{TLM})}$ , and  $\gamma_0^{(\text{TLM})}$  as a function of the mixing coefficient *c*.

off-axis contributions to the polarizability,  $\alpha_{xx}$  and  $\alpha_{yy}$ , are generally non-negligible. For molecules that maximize the transition dipole (along the permanent dipole axis, z) and that are predominantly one-dimensional in nature, however, the value of  $\frac{1}{2}(\alpha_{xx} + \alpha_{yy})$  should be substantially smaller than  $\alpha_{zz}$ . For pNA, the difference is almost a factor of 2 (see Table I). It should also be emphasized that molecules that maximize  $\alpha^{(\text{TLM})}$  will minimize  $\beta$ , within the two-level model. Thus,  $\beta$  may not in actual fact be zero, due to contributions to all three components ( $\beta_{zxx}$ ,  $\beta_{zyy}$ , and  $\beta_{zzz}$ ) from higher-order states.

Functional dyes that are close to the limiting case described above meet the requirements for optimizing the PR Kerr effect. They combine a high polarizability anisotropy  $\delta \alpha_K$  with a large resonantly enhanced ground state dipole moment  $\mu$  and maximize the  $\mu^2 \alpha$  term in Eqs. (29) and (30). This optimization is achieved while maintaining a short conjugation length, which allows a small molecular size resulting in fast and efficient reorientation of the chromophore in the polymer environment.

A molecular figure of merit for photorefractive chromophores may be defined based on Eq. (30a). Substituting  $w\rho N_A/M$  for N, where w is the weight fraction of chromophore in the material,  $\rho$  is the density of the material, and M is the molecular weight of the chromophore, and retaining only terms involving molecular parameters, the figure of merit F is determined [Eq. (41)],

$$F = \frac{9kT\bar{\bar{\mu}}\beta(-\omega;\omega,0) + 2\bar{\bar{\mu}}^2\delta\bar{\alpha}_k(-\omega;\omega)}{kTM}.$$
(41)

If one extracts explicit definitions of the coefficients  $C_{EO}$  and  $C_{BR}$  from Ref. 11 and adds them together to get the coefficient *C*, and makes the same substitution and similar simplifications as above, one arrives at an identical expression for the molecular figure of merit *F*.

Because of the sharpness of the optical spectra, it is easy to find chromophores that are nonabsorbing at the applied laser wavelength. The vanishing dipole change upon excitation also results in reduced absorption losses in the material, since bathochromic shifts (solvatochromism<sup>26</sup>) and polar environment-induced broadening of the absorption band are minimized. The functional dye DPDCP (Fig. 1) is an example of a system designed with these considerations in mind.

#### **V. SYNTHESIS**

DPDCP was prepared by a four-step synthesis following the methods of Deshapande,<sup>27</sup> Yates *et al.*,<sup>28</sup> and Woods<sup>29</sup> as shown in Scheme I:



**1** was obtained in 40%-50% yield by heating a threefold excess of 1,3-acetonedicarboxylic acid with *n*-propionic anhydride and a few drops of concentrated sulfuric acid to 100 °C for 20–30 min. After this time, the dark brown mixture was allowed to cool down to room temperature and the crude product was precipitated by addition of a small amount of water. **1** was isolated as a light brown solid after filtration, washing with cold water, and air drying.

The decarboxylation step was carried out by heating 1 in a 10% aqueous solution of sodium carbonate (pH must be kept basic) for 30 min at 100 °C and an additional period of 1.5 h at 80–90 °C. After cooling to room temperature, the yellow solution was acidified with 30% acetic acid. Since 2 did not crystallize after cooling to room temperature, it was isolated by extraction of the aqueous reaction mixture with ethyl acetate. The organic layer was dried over magnesium sulfate and the solvent was evaporated to provide 2 as a light brown oil in 70% yield.

For the second decarboxylation, **2** was boiled in 12 N hydrochloric acid for at least 12 h. Reaction progress was readily monitored by thin layer chromatography. After cooling to room temperature, the brown solution was neutralized with solid sodium carbonate and extracted with chloroform. The 2,6-*n*-dipropyl- $\gamma$ -pyrone **3** was obtained as a brown oil in 80% yield after evaporation of the solvent from the dried organic layer.

The final condensation of the  $\gamma$ -pyrone with malononitrile was carried out by heating **3** with a slight excess of malononitrile in acetic anhydride to 140 °C for at least 2 h. Reaction progress was readily monitored by thin layer chromatography. Compound **4** was isolated by adding water and extraction of the aqueous reaction mixture with ethyl acetate. The organic layer was dried over magnesium sulfate and concentrated by rotary evaporation. Characterization of **4**: mp. (DSC, 20 °C/min): 68 °C. <sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$ =0.91 (*t*, 6H, <sup>3</sup>*J*<sub>H,H</sub>=7.3 Hz, -CH<sub>2</sub>--CH<sub>2</sub>--CH<sub>3</sub>), 1.65 (six, 4H, <sup>3</sup>*J*<sub>H,H</sub>=7.4 Hz, -CH<sub>2</sub>--CH<sub>2</sub>--CH<sub>3</sub>), 2.48 (*t*, 4H, <sup>3</sup>*J*<sub>H,H</sub>=7.3 Hz, -CH<sub>2</sub>--CH<sub>2</sub>--CH<sub>3</sub>), 2.48 (*t*, 4H, <sup>3</sup>*J*<sub>H,H</sub>=7.3 Hz, -CH<sub>2</sub>--CH<sub>2</sub>--CH<sub>3</sub>),  $\delta$ =13.4 (*s*, -CH<sub>2</sub>--CH<sub>2</sub>--CH<sub>3</sub>), 20.3 (*s*, -CH<sub>2</sub>--CH<sub>3</sub>), 35.5 (*s*, -CH<sub>2</sub>--CH<sub>2</sub>--CH<sub>3</sub>), 58.1 (*s*(NC)<sub>2</sub>--C=C-), 106.2 (*s*, (NC)<sub>2</sub>--C=C-), 166.6 (*s*, -CH=-C(Pr)--O-).

## VI. CHARACTERIZATION OF THE FUNCTIONAL DYE DPDCP

The molecular linear and nonlinear optical properties of DPDCP were thoroughly investigated by a combination of experimental techniques. The results are summarized in Table I. The dipole moment was determined from the concentration dependence of the relative permittivity<sup>15,30</sup> ( $\epsilon_r$ ) of solutions of DPDCP in chloroform using the Guggenheim<sup>31,32</sup> method. The dipole moment was found to be  $\mu_z = 24 \times 10^{-30}$  C m (7.3 D), which is significantly larger than the value of  $12 \times 10^{-30}$  C m (3.6 D) expected from an estimation based on group dipole moments. This indicates a strong enhancement of the dipole moment due to zwitterionic resonance structures as mentioned previously. The second-order polarizability  $\beta(-2\omega;\omega,\omega)$  was measured in the same solvent by EFISH as previously described.<sup>31</sup> The observed  $\beta$  is small, as expected for a chromophore in the charge resonance limit. The UV-VIS absorption spectrum was recorded in chloroform solution on an HP8452A UV-VIS spectrophotometer. DPDCP exhibits a strong absorption in the UV with a maximum at 352 nm, and is essentially transparent above 400 nm (Fig. 3). The transition dipole  $\mu_{ag}^{(z)}$  is  $21 \times 10^{-30}$  C m (6.3 D) as determined from the integrated absorption.<sup>22,26</sup> This value is large for a chromophore of such a small size, again indicating resonant contributions as implied by Eq. (39). Neither the position nor the intensity of the absorption band changes significantly in solvents of higher permittivity such as acetone or acetonitrile, as expected from the theory of solvatochromism<sup>26,33</sup> for an excitation with a negligible change of the dipole moment upon excitation. This is consistent with  $\beta^{(TLM)} \sim 0$ , according to Eq. (32).

The tensor trace of the first-order polarizability  $\alpha(-\omega;\omega)$  was determined by refractive index measurements<sup>15,30</sup> at 632.8 nm in tetrachloromethane solution with an Abbe-3L refractometer (Bausch & Lomb). Information on the anisotropy  $\delta\alpha_R(-\omega;\omega)$  of the first-order optical polarizability defined by

$$\delta \alpha_R^2 = \frac{1}{2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2]$$
(42)

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FIG. 3. Optical absorption spectrum of DPDCP in  $\mathrm{CHCl}_3$  at room temperature.

was determined by depolarized Rayleigh scattering in the same solvent following the method of Vuks.<sup>34</sup> This experiment was carried out with a BI-DS light scattering apparatus (Brookhaven Instruments Corporation) operating at 632.8 nm. Diphenylacetylene ( $\delta \alpha_R = 22.5 \times 10^{-40} \text{ CV}^{-1} \text{ m}^2$ )<sup>34</sup> was used as an external calibration standard. Remarkably, the observed anisotropy of DPDCP,  $26 \times 10^{-40} \text{ CV}^{-1} \text{ m}^2$ , is larger than that of the rod-shaped molecule diphenylacetylene.

The refractive index and the depolarized Rayleigh scattering experiments yield only two equations for the three components of the tensor  $\alpha$ , so the component perpendicular to the molecular plane,  $\alpha_{xx}$ , was estimated from the group and bond polarizabilities given by Stuart.<sup>35</sup> The reliability of this method has been verified.<sup>15,30,34</sup> The components  $\alpha_{yy}$ and  $\alpha_{zz}$  were then calculated from  $tr(\alpha)$  and  $\delta \alpha_R$ ; results are listed in Table I. Estimated values for  $\alpha_{yy}$  and  $\alpha_{zz}$  were 38 and  $33 \times 10^{-40}$  CV<sup>-1</sup> m<sup>2</sup>, respectively. The discrepancy between the estimated and experimental  $\alpha_{zz}$  can be attributed to the TLM contribution of the CR transition which is  $\alpha^{(\text{TLM})}(-\omega; \omega) = 19 \times 10^{-40} \text{ CV}^{-1} \text{ m}^2$ , Eq. (37). This contribution is not included in the group and bond additivity scheme. The Kerr anisotropy  $\delta \alpha_K$  can now be calculated to be  $22 \times 10^{-40}$  CV<sup>-1</sup> m<sup>2</sup>, which is larger than the Rayleigh anisotropy  $\delta \alpha_R$ . Only for rod-shaped molecules with  $\alpha_{\perp} = \alpha_{xx} = \alpha_{yy}$  and  $\alpha_{\parallel} = \alpha_{zz}$  are the anisotropies identical,  $\delta \alpha_R = \delta \alpha_K = \alpha_{\parallel} - \alpha_{\perp}$ , Eqs. (31) and (41).

It is interesting to note that  $\alpha^{(\text{TLM})}$  contributes about 40% to the long axis polarizability  $\alpha_{zz}$  and that the polarizability anisotropy  $\delta \alpha_K$  is almost entirely due to  $\alpha^{(\text{TLM})}$  in both DPDCP and pNA. This suggests that the determination of  $\alpha^{(\text{TLM})}$  from UV-VIS spectroscopic measurements can be used as a screening method in the search for chromophores with high  $\delta \alpha_K$ . Table I provides a comparison of the different molecular contributions to the molar susceptibilities  $\zeta^{(3)}$ in Eqs. (29) and (30). The  $\mu^2 \delta \alpha_K$  term of DPDCP is about three times larger than that of pNA<sup>36</sup> due to its 18% larger dipole moment and its two times larger polarizability anisotropy. The  $\mu\beta$  term of DPDCP is nearly zero because of its nearly vanishing second-order polarizability. For pNA, the  $\mu\beta$  term is significant, but contributes only about 17% to  $\zeta^{(3)}$ .

TABLE II. Results of quantum chemical calculations (MP2) of dipole moments and static first- and secondorder polarizabilities of DMDCP and pNA.

		DMDCP	pNA <sup>a</sup>
$\mu$	$(10^{-30} \text{ Cm})$	26.7	22.9
$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$	$(10^{-40} \text{ CV}^{-1} \text{ m}^2)$	13.1, 24.2, 35.6	9.5, 17.3, 26.1
$trace(\alpha)$	$(10^{-40} \text{ CV}^{-1} \text{ m}^2)$	72.9	52.9
$\delta lpha_K$	$(10^{-40} \text{ CV}^{-1} \text{ m}^2)$	16.9	12.7
$\delta \alpha_R$	$(10^{-40} \text{ CV}^{-1} \text{ m}^2)$	19.5	14.3
$\beta_{zxx}, \beta_{zyy}, \beta_{zzz}^{b}$	$(10^{-50} \text{ CV}^{-2} \text{ m}^3)$	0.00, 1.58, 2.04	-0.15, -0.25, 6.60
$\beta = \beta_{zxx} + \beta_{zyy} + \beta_{zzz}^{b}$	$(10^{-50} \text{ CV}^{-2} \text{ m}^3)$	3.61	6.20
$4\mu^2 \delta \alpha_K / (3k^2T^2)$	$(10^{-60} \text{ CV}^{-3} \text{ m}^4)$	95 000	52,500
$6\mu\beta/(kT)$	$(10^{-60} \text{ CV}^{-3} \text{ m}^4)$	1400	2070

<sup>a</sup>From Ref. 42.

<sup>b</sup>Given in T convention, Ref. 16.

#### **VII. QUANTUM CALCULATIONS**

The geometry of DMDCP, in which the *n*-propyl groups of DPDCP have been replaced by methyl groups, was optimized in  $C_{2\nu}$  symmetry using the MB3LYP density functional<sup>37,38</sup> in conjunction with the 6-31G\* basis set.<sup>39,40</sup> The dipole and (hyper)polarizability calculations were performed at this optimized geometry using second-order perturbation theory (MP2) together with a double-zeta quality basis set  $[3s_{2p}/2s]$  augmented with diffuse polarization functions ( $\alpha_d$  for C, N, and O=0.2 and 0.05). This basis was shown to give results in agreement with larger basis sets for the polarizabilities of pNA.<sup>41,42</sup> We have chosen to use second-order perturbation theory since it is important to calculate the hyperpolarizabilities of conjugated organic molecules with theoretical methods that include the effects of electron correlation. For example, for pNA the electron correlation contribution is responsible for 50% of the value of  $\beta$ . The (hyper)polarizabilities were calculated from finite difference calculations of the MP2 energy and MP2 dipole moment (where the dipole moment is defined as the first derivative of the energy with respect to an external electric field). The field strengths used were 0.0, 0.000 667, 0.002 a.u. Analysis of the values based on finite difference of energies versus finite difference of dipole moment indicates that the error based on finite field differentiation is not significant (less than 1% for  $\beta$ ).

The values of the electrical properties (in the static field limit) of DMDCP are reported in Table II together with those for pNA.<sup>41</sup> There are two important points to examine in the context of this work. First, how do the theoretical values compare and contrast for DMDCP and pNA, and second, how do the calculations compare with experiment? We can address the first point predominantly from examination of the calculated gas phase properties in the static field limit. Of main interest is the magnitude of the contribution to the photo refractive Kerr effect from the " $\mu^2 \delta \alpha_K$ " term and the " $\mu\beta$ " term, as summarized in the last two lines of Table II. It is clear that for both molecules the larger contribution comes from the " $\mu^2 \delta \alpha_K$ " term and that the " $\mu \beta$ " term is considerably smaller even for pNA where  $\beta$  is considered significant (in the context of nonlinear processes). For this latter term to play an equivalent role in the photorefractive Kerr effect,  $\beta$  would have to be at least ten times larger. Thus, these calculations support the assumption that concentrating on maximization of the " $\mu^2 \delta \alpha_K$ " contribution is a more profitable approach to optimizing the chromophore for PR applications. If the " $\mu\beta$ " contribution has the same sign as " $\mu^2 \delta \alpha_K$ ," this will increase the total value, but probably by only 10%. Examination of the individual moments shows that DMDCP has a larger dipole moment and a larger polarizability anisotropy  $\delta \alpha_K$  than pNA. It is interesting to note that the sum of  $\alpha_{xx}$  and  $\alpha_{yy}$  is close to  $\alpha_{zz}$  for both molecules, so that the anisotropy  $\delta \alpha_K$  is about 1/2  $\alpha_{zz}$ . Thus, DMDCP has a larger polarizability anisotropy since  $\alpha_{zz}$  is 40% larger than for pNA. We note that in order to maximize the anisotropy, we must aim to increase  $\alpha_{zz}$  without significantly increasing  $\alpha_{xx}$  or  $\alpha_{yy}$ , since these latter components are not negligible for these molecules. Finally, if we sum the major contributions to the photorefractive Kerr effect from these theoretical calculations, we see that DMDCP is almost two times more effective than pNA.

Let us turn now to comparison of the calculated values for DMDCP with the experimental results for DPDCP (as reported in Table I). The comparison between the calculated and experimental para-nitroaniline values has been discussed at length (see, for example, Ref. 41) and only comments pertinent to the DMDCP discussion will be raised. First, we chose to evaluate the properties of DMDCP rather than DPDCP to make the calculations more computationally tractable. The difference between the DMDCP values and those of DPDCP is expected to be small, since the major contribution to the polarizabilities arises from the mobility of the  $\pi$ electrons in the conjugated system. We note that the dipole moment overestimates the experimental value by 9%, not unexpected since this is also seen for pNA. If we first examine  $\delta \alpha_R$ , which may be directly compared with experiment, we note good agreement (19.5 vs  $18.1 \times 10^{-50}$  CV<sup>-1</sup> m<sup>2</sup>). Comparison of *trace*  $\alpha$  with *trace*  $\alpha(-\omega;\omega)$  shows that the theoretical static value is about 34% smaller than the experimental value at 633 nm. It is unlikely that the frequency dependence is responsible for more than 10%-20% of this difference. It is possible that the remaining difference could be attributed to the replacement of the methyl groups (DMDCP) by *n*-propyl groups (DPDCP). There is reason-

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able agreement for the percentage contributions of the individual components of  $\alpha$  to the *trace*  $\alpha$ . Since *trace*  $\alpha$  is underestimated theoretically, however, so also is  $\delta \alpha_K$ . We note though that, most importantly, experiment and theory are in clear agreement on the increasing trend of " $\mu^2 \delta \alpha_K$ " between DPDCP and pNA.

There is a considerable difference between theory and experiment in the prediction of  $\beta$ . We will discuss this difference, but it should be realized that since the " $\mu\beta$ " contribution to the photorefractive Kerr effect is so much smaller than the " $\mu^2 \delta \alpha_K$ " contribution, this discrepancy does not have any impact on the conclusions in this paper. First, we note that there is a difference of more than a factor of 3 between  $\beta_{calc}$  and  $\beta_{exp}$  for pNA. This difference is mainly due to the fact that the experiments are done in polar solvents, whereas the calculations refer to gas-phase species.<sup>13,43</sup> We note that the long axis component of  $\beta$  ( $\beta_{777}$ ) for DMDCP is three times smaller than for pNA and that it is the other in-plane component  $\beta_{zyy}$  that is responsible for the overall  $\beta$  of DMDCP being less than a factor of 2 smaller than for pNA. Given the fact that DPDCP is much less of a "charge-transfer" molecule than pNA, it is possible that the solvent effect for DPDCP is smaller and, therefore, that there is a much wider difference in hyperpolarizability between these two molecules in solution. This rationale is borne out by the fact that the charge resonance transition of DPDCP does not solvatochromically shift in a polar environment.

#### VIII. PHOTOREFRACTIVE PROPERTIES OF THE DOPED POLYMER SYSTEM DPDCP:TPD:PMMA:C<sub>60</sub>

A doped polymer material consisting of 30% DPDCP, 15% TPD, 55% PMMA, and 0.3%  $C_{60}$  was chosen as a model system to illustrate the potential of functional dyes in the CR limit for PR organic materials. DPDCP was characterized as a transparent, highly dipolar chromophore with large anisotropy of the optical polarizability and negligible second-order nonlinearity (Table I). Poly(methylmethacrylate) (PMMA, purchased from Aldrich,  $M_W = 33000$ , secondary standard) was used as an inert polymer binder with good optical quality and low scattering. N, N'-bis(3-methylphenyl)-N, N'-bis(phenyl)benzidine(TPD, purchased from H. W. Sands) was employed as an efficient charge transport agent (CTA).<sup>44,45</sup> The fullerene  $C_{60}$  (Aldrich) was used as a sensitizer with low absorption at 676 nm for the photogeneration of free carriers.<sup>46,47</sup>

Hole mobilities in vapor-deposited glasses and doped polymers containing TPD were investigated recently, and charge transport in these materials was demonstrated to occur via a simple disorder-controlled hopping mechanism.<sup>44,45</sup>  $C_{60}$  was observed to form a charge transfer complex with TPD in organic nanocomposites and multilayer structures,<sup>48</sup> the maximum of the CT band lying near 675 nm. The function of  $C_{60}$  in the photogeneration of charges and in charge transport processes have also been investigated in photoconducting<sup>46</sup> and photorefractive<sup>47</sup> polymers.

Samples for PR studies were prepared by casting the polymer from solution onto glass plates coated with indium

tin oxide (ITO). After evaporation of the solvent (nitrobenzene), the plates were assembled face to face at an elevated temperature of ~135 °C, at which the material is a viscous liquid, using 100  $\mu$ m spacers. The resulting samples were of good optical quality and almost transparent throughout the visible region. The absorption coefficient  $\alpha$  at 676 nm was 2 cm<sup>-1</sup>.

The dark conductivity  $\sigma_{\text{dark}}$  of samples of DPDCP: PMMA:TPD: $C_{60}$  was measured to be typically 3.2  $\times 10^{-12} (\Omega \text{ cm})^{-1}$ . The specific photoconductivity  $\sigma_{\text{ph}}/I$  at 676 nm was  $1.2 \times 10^{-12} (\Omega \text{ cm})^{-1}/(\text{W/cm}^2)$  at a bias field of 5 V/ $\mu$ m and  $3 \times 10^{-12} (\Omega \text{ cm})^{-1}/(\text{W/cm}^2)$  at  $E_b = 30 \text{ V}/\mu\text{m}$ .

The PR properties of DPDCP:PMMA:TPD:C<sub>60</sub> were investigated by using the holographic optical techniques of four-wave mixing (FWM)<sup>47</sup> and two-beam coupling (2BC).<sup>49</sup> The continuous-wave writing beams 1 and 2 ( $\lambda$ =676 nm, 6 mW) were overlapped in the sample, the external angles of incidence being 60° and 30° as in previous studies.<sup>11</sup> This geometry corresponds to internal angles of  $\theta_1 = 33.5^{\circ}$  and  $\theta_2 = 18.6^\circ$  in the polymer (index of refraction n = 1.57) and a grating period of  $\Lambda_G = 1.66 \ \mu m$ . The spot diameter (FWHM) of the weakly focused writing beams at the sample was determined with a silicon photodiode array (Reticon RL0512G) to be 760  $\mu$ m. The writing beams were s-polarized in the FWM experiment and the grating was probed with a *p*-polarized beam 3 (676 nm, 16  $\mu$ W, spot diameter 370  $\mu$ m) counterpropagating to beam 2. The smaller spot size of beam 3 was chosen in order to guarantee complete overlap of beam 3 with the grating. Diffraction efficiencies were corrected for reflection losses at the outer surfaces of the sample. In 2BC experiments, the writing beams 1 and 2 were p-polarized and their intensities were monitored directly.

Samples of DPDCP:PMMA:TPD: $C_{60}$  exhibited steadystate diffraction efficiencies  $\eta_p$  of up to 25% at a bias field of 100 V/ $\mu$ m. This corresponds to an index modulation in the PR grating of  $\Delta n = (e_3 \cdot \Delta_{\chi}^{(1)} \cdot e_4)/(2n) = 0.0010$  [calculated from Eqs. (1), (9), and (10)]. The index modulation showed a quadratic dependence,  $\Delta n \sim E_b^{2.06 \pm 0.05}$ , on the applied bias field (Fig. 4), indicating proportionality of  $E_{\rm sc}$  and  $E_b$ . This behavior is predicted by the standard PR model when the trap density-limited space-charge field  $E_q$  is much larger than both the bias field and the diffusion field  $E_d \sim 0.1$ V/ $\mu$ m.<sup>8</sup>

The initial growth of the PR grating was single exponential,  $\eta^{1/2} \propto 1 - \exp(-t/\tau_r)$ , with a characteristic rise time  $\tau_r$ . This functional dependence is consistent with the conventional single carrier model for the formation of the spacecharge field  $E_{\rm sc}$ .<sup>50</sup> The rise time  $\tau_r$  was 850 ms at  $E_b$ =50 V/ $\mu$ m. The inverse rise time  $\tau_r^{-1}$  was a sublinear function of the writing intensity,  $\tau_r^{-1} \sim I^{0.42}$ , similar to observations in other systems.<sup>8</sup>

The photorefractive nature of the observed gratings was confirmed by two-beam coupling and grating-phase measurements.<sup>5,49</sup> In these experiments, gratings were written with two writing beams of equal intensity. Figure 5 shows the transmitted intensities of beams 1 and 2 in the steady state (at negative times), with beam 1 being amplified



FIG. 4. Refractive index modulation  $\Delta n$  and two-beam coupling gain  $\Gamma$  as a function of the bias field  $E_b$ . The curves are quadratic fits.

by asymmetric energy transfer. The two-beam coupling coefficient (energy transfer coefficient) showed a quadratic dependence,  $\Gamma \sim E_b^{2.05 \pm 0.22}$ , on the bias field. Because of the low absorption coefficient  $\alpha$  of the material, net two beam coupling,  $\Gamma > \alpha$ , was achieved at very low fields,  $E_b \ll 20$  $V/\mu$ m.

Starting at time zero in Fig. 5, the sample was translated for 2 s with rate 3.2  $\mu$ m/s. The resulting periodic intensity variations of beams 1 and 2 were clearly out of phase, consistent with a dominant index grating. Fitting of these curves, as described in Ref. 49, was impeded by grating decay and intensity fluctuations. Typical phase shifts between index and intensity gratings could thus be determined only to be between 60° and 90° at fields greater than 30 V/ $\mu$ m, corroborating the PR origin of the index gratings.

Some estimates of the PR properties of the material can be made on the basis of Eqs. (11)-(15), (17), and (20)-(30). For the actual FWM geometry and the material properties of



FIG. 5. Two-beam coupling and grating phase measurement. The transmitted intensities of beams 1 and 2 are shown as a function of the translation time. The signal for negative times is the steady state. The translation starts at time zero, the rate being 3.2  $\mu$ m/s.

this work,  $\theta_1 = 33.5^\circ$ ,  $\theta_2 = 18.6^\circ$ ,  $\theta_G = 64.0^\circ$ , sample thickness  $d = 100 \ \mu\text{m}$ , refractive index n = 1.57, density  $\rho = 0.9 \ \text{g cm}^{-3}$ ,  $\epsilon^{\infty} \sim n^2$ ,  $\bar{\mu} \sim 2\mu$  (assumed), molecular weight of DPDCP  $M = 228.3 \ \text{g mol}^{-1}$ , one obtains

$$\eta_s \approx 1.91 \times 10^5 \times (\chi_{ZZXX}^{(3)} E_b E_{sc})^2,$$
 (43)

$$\eta_p \approx 1.73 \times 10^5 \times (\chi_{ZZZZ}^{(3)} E_b E_{sc})^2,$$
 (44)

where a contribution of less than 2% of  $\chi_{ZZXX}^{(3)}$  in Eq. (43) was neglected. Thus, with  $\eta_p$  and  $\eta_s$ , one probes in this geometry almost exclusively  $\chi_{ZZZZ}^{(3)}$  and  $\chi_{ZZXX}^{(3)}$ , respectively. From Eqs. (43) and (44), one expects the depolarization ratio to be  $\eta_p/\eta_s=3.6$  in the limit of the purely "birefringent"  $\beta$ -less chromophore DPDCP, Eqs. (29) and (30). In good agreement with this prediction, we observed experimentally the ratio  $4.0\pm1.6$ . A quantitative estimate of the diffraction efficiency and the index modulation assuming a maximum space-charge field of  $E_{sc}=E_b \cos \theta_G$  based on Eqs. (17), (30a), and (44) yields  $\eta_p=7\%$  and  $\Delta n=0.00055$  at  $E_b=50$  V/ $\mu$ m. The observed index modulation was  $\Delta n \sim 0.0003$  (Fig. 4). This is a reasonable agreement, in view of the approximate character of the outlined theory for highly doped polymer systems and the small index changes involved.

#### **IX. CONCLUSIONS**

We have demonstrated photorefractivity in a low- $T_g$ polymer system where the dopant chromophore DPDCP has a negligible second-order polarizability  $\beta$ . The modulation of the refractive index in this material was shown to be due to the interaction of the square of the total electric field in the material with the Kerr susceptibility  $\chi^{(3)}(-\omega;\omega,0,0)$ , the total electric field being a superposition of the bias field and the spatially periodic space-charge field. A tensorial formulation of the photorefractive Kerr effect and its microscopic interpretation was presented. A molecular figure of merit for photorefractive chromophores was derived [Eq. (41)]. Predictions of the theory were in reasonable agreement with experimental findings. The second-order dipole orientation term containing the anisotropy of the first-order optical polarizability and the square of the dipole moment was shown to provide the major molecular contribution to PR performance. Functional dyes in the charge resonance limit, DPDCP representing a prototype, were identified to optimize this term. These dyes combine high dipole moments with a large polarizability anisotropy which is produced by the intense CR transition. The CR transition in DPDCP contributes 37% to the long axis polarizability and 86% to the polarizability anisotropy, assuming that the contribution from higher-order states is equivalent for  $\alpha_{xx}$ ,  $\alpha_{yy}$ , and  $\alpha_{zz}$ . Experimental values of the dipole moment and first-order polarizability of DPDCP were in good agreement with those obtained from quantum chemical calculations. The ground state of DPDCP is stabilized by contributions of aromatic resonance structures and no significant change of the dipole moment occurs upon excitation in the CR band. As a consequence, the CR transition occurs at high energy in the UV region and does not solvatochromically shift in a polar environment. Highly transparent and efficient PR polymers can, therefore, be devised on the basis of functional dyes in the CR limit. Since it is possible in this limit to achieve large anisotropies of the polarizability for relatively short molecules, it can also be expected that efficient PR materials with fast orientational response can be prepared.

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