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High net gain at 514 nm in a photorefractive polymer doped with a chalcone derivative

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We report on the photorefractive properties of a low T_g composite consisting of functionalized polysiloxane doped with a chalcone derivative. The high transparency of this doping molecule enabled the observation of high net gain at 514 nm. Orientational and Pockels contributions to the total refractive index variations were measured by frequency-dependent ellipsometry experiments. Finally, the field dependence of the gain coefficient is described using Kukhtarev's model for the space charge field with an effective trap density as a single fitting parameter. © *1997 American Institute of Physics.* [S0003-6951(97)03340-8]

The study of the photorefractive (PR) effect on polymers has kept growing these last years due to potential applications. Already great strides have been achieved in the optimization of these materials and their performances are now comparable to those of the best PR inorganics.[1,2] So far, the most efficient PR materials are photoconductive polymer matrix doped with photosentisizers and chromophores (i.e., molecules leading to quadratic nonlinearities). Such PR polymer exhibits a low glass transition temperature (T_g) since the high concentration of the guest chromophore acts as a plasticizer.

When a PR polymer is shined by two interfering beams with adequate frequency $\omega/2\pi$ for photogeneration and when an electric field E_0 is applied for photoconduction, then charge carriers redistribute according to the illumination grating, generating a spatially modulated space charge field E_{SC}. The coupling of optical and space charge fields via the EO process yields a refractive index grating that is spatially shifted in comparison to the illumination pattern. The EO effect requires noncentrosymmetry: in low T_g polymers, this can be easily obtained by electric poling since chromophores can move at room temperature. Orientation of rodlike chromophores by the space charge field also induces a refractive index modulation. Hence, the total refractive index modulation Δn has two contributions: the EO effect and the orientational birefringence.[3]

We have elaborated a new low T_g guest/host material. The matrix is polysiloxane with pendant carbazole groups. The choice of this material was justified by its photoconductive properties[4,5] and its low $T_g \approx 21$ °C allowing the mobility of the chromophores. We added (2,4,7-trinitro-9-fluorenylidene)malononitrile (98% pure Acros Chemical) as a photosensitizer in the proportion of one molecule for one thousand carbazole groups. The chromophore 4-[(E)-3-(4-methoxy-3-methylphenyl)-2-propenoyl]benzonitrile (MMOCC) is a chalcone derivative.[6,7] In solution in chloroform, it presents a maximum of absorption at λ_{max} = 364 nm and no absorption above 500 nm. Figure 1 presents the structures of these moieties.

For material preparation, the different components were mixed in chloroform and then the mixture was dried in a vacuum oven to ensure elimination of the solvent. The doped polymer was pressed between indium tin oxide (ITO) coated glass plates. Spacers ensured a 105 μm constant thickness of the sample. The chromophores tend to aggregate in the polymer, limiting the doping rate at 25 wt %, decreasing the PR performances. To eliminate the crystals, we heated the sample up to 165 °C (MMOCC melting point is $T_m \approx 160$ °C) for 1 min and then put it on a cold plate. Finally, the sample was sealed with glue. Above 15 wt % doping rate, recrystallization occurs after a week. A new heating of the sample is then needed to restore the sample's properties.

In these materials, we first performed frequency-dependent transmission ellipsometry measurements[8] in order to determine orientational birefringence and EO contributions to the refractive index modulation. The light source was a laser diode operating at $\lambda=670$ nm. The beam incidence angle on the sample is $\xi=45°$ and it was linearly polarized 45° to the incidence plane. The sample was placed between crossed polarizers. An applied electric field E_t induced a birefringence that modified the transmitted light in-
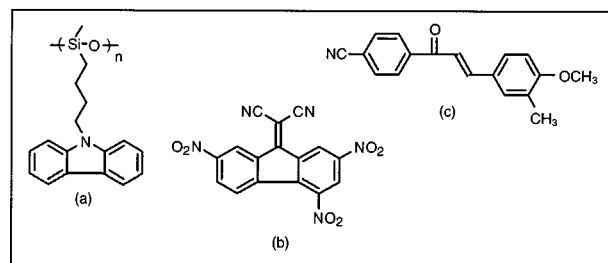

FIG. 1. (a) Polysiloxane with carbazole pendants, (b) (2,4,7-trinitro-9-fluorenylidene)malononitrile, (c) 4[(E)--3(4-methoxy-3-methylphenyl)-2-propenoyl] benzonitrile.

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tensity. A Babinet–Soleil–Bravais compensator was inserted between the polarizers to optimize these intensity variations. The field E_t was composed by a dc (offset) E_0 and a modulated component $E_{\text{mod}} \cos \Omega t$. The resulting Δn along and perpendicular to the poling direction is given by (1)[8]

$$\Delta n = \frac{2\pi}{n}\left(\frac{3}{2} B E_{\text{pol}}^2 + \frac{4}{3} C E_{\text{pol}} E_t\right), \tag{1}$$

where n is the mean refractive index. Contributions to Δn arising from orientational birefringence and the Pockels EO effect are contained, respectively, in coefficients B and C[8]

$$B = \frac{2}{45} N f_\infty f_0^2 \Delta\alpha(\omega)\left(\frac{\mu_0}{k_B T}\right)^2 \tag{2}$$

$$C = \frac{1}{5} N f_0^2 f_\infty^2 \beta(\omega)\left(\frac{\mu_0}{k_B T}\right), \tag{3}$$

where $\Delta\alpha(\omega)$ stands for the change in linear polarizability along and perpendicular to the ground-state dipole μ_0, $\beta(\omega)$—a short-hand notation for $\beta(-\omega;\omega,0)$—is the projection of the vector part of the quadratic hyperpolarizability tensor along μ_0; $f_0 = \epsilon(n^2+2)/(2\epsilon+n^2)$ and $f_\infty = (n^2+2)/3$ are the Onsager and Lorentz–Lorenz local field correction factors. For this experiment, we used a 20 wt % doped sample which corresponds to a chromophore density of $N = 5.6 \times 10^{20}$ cm^{-3}. The mean refractive index value, $n = 1.61 \pm 0.03$, was obtained by the minimum deviation method using a doped polymer filled glass prism. The relative dielectric constant $\epsilon = 3.7$ was determined from capacitive measurements at 120 Hz. At low modulation frequency $\Omega/2\pi$, both dc and modulated fields act on the chromophores so that the poling field is equal to the total field: $E_{\text{pol}} = E_t$. At high frequency, the modulated field can no longer align the chromophores and then: $E_{\text{pol}} = E_0$. Expressions of maximum light modulation at Ω in the high frequency (HF) and low frequency (LF) limits are given by Eqs. (4) and (5)[8]

$$I(\Omega)^{\text{HF}} = K E_{\text{mod}} E_0 \tfrac{2}{3} C \tag{4}$$

$$I(\Omega)^{\text{LF}} = K E_{\text{mod}} E_0 (\tfrac{3}{2} B + \tfrac{4}{3} C), \tag{5}$$

where $K = (4\pi^2 l I_0)/(\lambda G n)$, l is the sample thickness, I_0 is the maximum of transmitted light intensity obtained by adjusting the compensator, $G = n\sqrt{n^2 - \sin^2\xi}/\sin^2\xi = 4.7$. Figure 2 presents the variations of the maximum light modulation at Ω and 2Ω with voltage values of $V_0 = V_{\text{mod}} = 1000$ V. Special care has been taken to reach well defined plateaus at low and high frequencies. These conditions are met at 5 mHz and 1 kHz (see Fig. 2).

We have determined the PR gain Γ using the two beam coupling experiment.[9] In this technique, two interfering beams create a refractive index grating via the PR effect. Since the refractive index grating is shifted in comparison to the illumination pattern, the diffraction of the two beams involves asymmetric energy exchange:[9]

$$\frac{I_t^+(l)}{I_t(l)} = \frac{[I_p(0)/I_t(0)+1]\exp(\Gamma l)}{I_p(0)/I_t(0)+\exp(\Gamma l)} \exp(-\alpha l), \tag{6}$$

where α is the sample absorption; $I_t^+(l)$ and $I_t(l)$ are the test beam intensities after the sample, respectively, with and
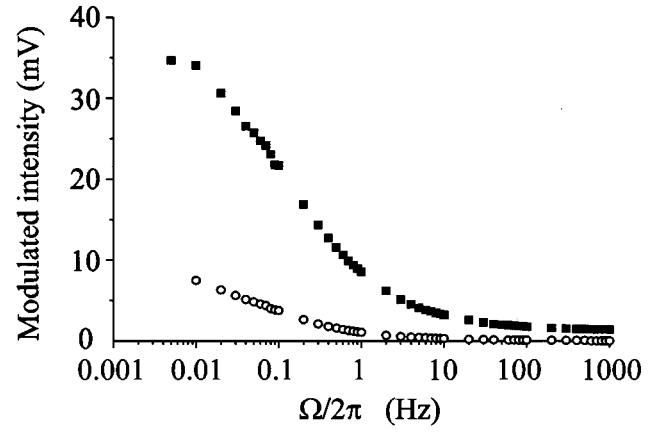

FIG. 2. Variation of the modulated intensity with the modulation voltage frequency. The sample was 20 wt % chromophore doped: (squares) intensity modulation detected at Ω, (circles) intensity modulation detected at 2Ω.

without dc voltage applied; $I_t(0)$ and $I_p(0)$ are the test and pump beam intensities before the sample. The measurements were performed at 633 nm and the absorption coefficient of the 20% doped sample we used for this experiment was $\alpha_{633} = 16$ cm^{-1}. Pump beam power density was 14 mW/cm^2 and pump to test intensity ratio was $I_p(0)/I_t(0) = 300$. Both beams were p polarized, and their incidence angles were 77° for the pump and 40° for the test beam. The variation of Γ as a function of applied voltage V_0 has been plotted in Fig. 3.

It appears from the ellipsometry experiment that only the orientational and Pockels EO contributions to refractive index variation Δn are significant. We have derived the following values for molecular parameters: $\mu_0^2 \Delta\alpha(\omega) = 8.7 \times 10^{-58}$ e.s.u. and $\mu_0 \beta(\omega) = 3.3 \times 10^{-46}$ e.s.u. Γ is proportional to the amplitude Δn_{NL} of the refractive index grating [see Eq. (7)]:

$$\Gamma = \frac{4\pi}{\lambda}(\hat{e}_p \cdot \hat{e}_t)\Delta n_{\text{NL}} \sin \Psi, \tag{7}$$

where $\Psi = \arg(E_{\text{SC}})$ is the refractive index grating shift relative to the illumination grating, $\hat{e}_p$ and $\hat{e}_t$ the polarization vectors, respectively, of the pump and test beams. When
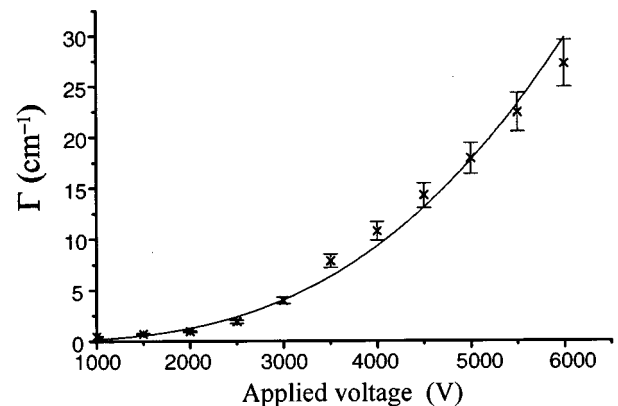

FIG. 3. Variation of the photorefractive Γ gain with the applied voltage at 633 nm. The sample was 20 wt % chromophore doped. Solid line corresponds to the Kukhtarev model adjustment.

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both beams are p polarized, it is straightforward to derive the following relation for the refractive index modulation from Ref. 10:

$$\Delta n_{NL} = \frac{2\pi}{n}|E_{SC}|E_0[B(\cos^2\theta+1)+\tfrac{4}{3}C(4\cos^2\theta-1]\sin\varphi,$$

(8)

$\theta=(\alpha_p-\alpha_t)/2$ and $\varphi=(\alpha_t+\alpha_p)/2$, α_p and α_t being the pump and test beams angles inside the material. In order to compare the orientational birefringence and Pockels EO contributions to Γ in our sample it is convenient to calculate the following ratio:

$$\frac{\mu_0^2\Delta\alpha(\omega)}{6f_\infty\mu_0\beta(\omega)k_BT}\frac{\cos^2\theta+1}{4\cos^2\theta-1}$$

(9)

for the two beam coupling experiment geometry $\cos^2\theta\approx1$. We have found for this chalcone derivative that orientational birefringence dominates refractive index modulation with a contribution 4.5 times higher than that of the Pockels EO effect. For comparison, we have also calculated the value of this ratio for 2,5-dimethyl-4-(p-nitrophenylazo)anisole (DMNPAA) chromophore incorporated in a poly (N-vinyl carbazole) (PVK) matrix. We have found for this chromophore and for experimental conditions used in Ref. 1 that orientational birefringence also dominates refractive index modulation, with a contribution four times larger than that of the Pockels EO effect. The expression of space charge field E_{SC} has been determined by Kukhtarev:[9]

$$E_{sc}=\frac{E_q(E_0\sin\varphi+iE_d)}{E_q+E_d-iE_0\sin\varphi},$$

(10)

where $E_q=eN_{eff}/\epsilon\epsilon_0k_g$ is the maximum field, $E_d=k_gk_BT/e$ is the diffusion field, N_{eff} the effective trap density, and k_g the grating wave vector norm. It seems that this expression for E_{sc} remains valid in PR polymers.[11] As can be seen from Fig. 3, theoretical variation of Γ vs V_0 given by Eq. (10) fits well with experimental data for $N_{eff}=9.4\times10^{17}$ cm^{-3}. This value is higher than effective trap densities measured in other PR polymers.[2,11]

Net gain $\Gamma-\alpha$ can be achieved at 633 nm with the 20 wt % doped sample with the $\alpha_{633}=16$ cm^{-1} absorption coefficient (see Fig. 3). We have observed an enhancement of net gain by shifting the incident wavelength to $\lambda'=514$ nm. Here, pump beam power density was 60 mW/cm^2 and pump

to probe ratio was 100. The incident angles were 81° for the pump beam and 47° for the probe beam. For the same 20 wt % doped sample, we have obtained a PR gain $\Gamma=48$ cm^{-1} by applying 6 kV, whereas the absorption was $\alpha_{514}=26$ cm^{-1}. This increase of Γ from 30 to 48 cm^{-1} is consistent with the $1/\lambda$ dependence of Γ and with the dispersion enhancements of $\Delta\alpha(\omega)$ and $\beta(\omega)$ described by the two-level factors.[12] With a 25 wt % doped sample, we have obtained $\Gamma=56$ cm^{-1} for an absorption of $\alpha_{514}=30$ cm^{-1} and $V_0=6$ kV. To the best of our knowledge, this is the highest net gain obtained at this wavelength.

In conclusion, we have prepared a new low T_g PR polymer doped with a chalcone derivative having high transparency in the visible range. We have shown that the PR gain is dominated by orientational contribution. We have also described the dependence of Γ on applied voltage by using the Kukhtarev model. Finally, the transparency of the chromophore has allowed observation of an important net PR gain of 26 cm^{-1} at 514 nm. Now, we are about to synthesize new chalcone derivatives to enhance the solubility. This would allow us to increase the doping rate and improve the sample stability.

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