

## Dark decay of holograms in photorefractive polymers

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The decay of holograms stored in photorefractive polymer composites based on poly(N-vinyl-carbazole) with and without extrinsic deep traps is investigated. The photorefractive phase shift is identified as one of the key parameters determining the dark decay dynamics. This has important implications for all kinds of photorefractive imaging applications including holographic data storage. A trade off will be required between accepting a certain degree of hologram distortion due to two-beam coupling on the one hand and achieving high hologram stability during idle periods in the dark with the external field applied on the other. © 2002 American Institute of Physics. [DOI: 10.1063/1.1492848]

The photorefractive (PR) effect is one of the most promising reversible holographic storage mechanisms.<sup>1</sup> Under nonuniform illumination, the refractive index of the photosensitive material is modulated due to the generation of mobile charge carriers in the bright regions, their subsequent redistribution, and eventual trapping in the dark areas. This gives rise to a space-charge field  $E_{SC}$ , which modulates the refractive index of the material through the linear electro-optic effect and orientational effects.<sup>2,3</sup> Photorefractivity in amorphous polymers has been intensively investigated,<sup>4,5</sup> and these systems have been widely recognized as potential active media in rewritable holographic optical memories for security applications,<sup>6</sup> in associative memories,<sup>7</sup> or in adaptive ultrasound sensors.<sup>8</sup> Due to the rather low dielectric constants of polymers ( $\epsilon < 10$ ), oppositely charged carriers show a rather strong tendency to recombine. As a result, only rather short storage times are anticipated. However, so far, the dark decay (referred to as “dd” hereafter) of the holograms in periods when the system is idle, i.e., held in the dark with the external field still applied, has been mostly neglected in literature on organic PR materials, even though it is important for the aforementioned applications. In this letter, we present systematic investigations of the dd of PR gratings in PR polymers. Our results will give evidence that the phase shift between the interference pattern and the recorded index grating, the commonly accepted fingerprint of photorefractivity, is one of the key parameters, yielding slower dd for a larger phase shift.

The investigated materials contained the photoconductor poly(N)vinylcarbazole (PVK, 39 wt %), the plasticizer N-ethylcarbazole (10 wt %), the eutectic mixture of two EO chromophores 2,5-dimethyl-4(p-nitrophenylazo)-anisole (25 wt %), and 3-methoxy-4(p-nitrophenylazo)-anisole (25 wt %), and finally the sensitizer 2,4,7-trinitro-fluorenone (TNF, 1 wt %). We also prepared a similar material doped

with 0.82 wt % (replacing PVK) of the commonly used hole conductor N,N'-bis(3-tolyl)-N,N'-diphenyl-benzidine (TPD), whose highest occupied molecular orbital levels are situated about 0.5 eV below those of PVK. Thus, TPD moieties constitute deep traps within the carbazole transport manifold, and therefore a longer storage time was expected. We refer to the materials as “C” without and “CT” with extrinsic traps. The glass-transition temperature was  $T_g = 14^\circ\text{C}$  (differential scanning calorimetry, heating rate 20 K/min) for both composites. The devices were sandwich structures of the PR composites between two transparent indium-tin-oxide-coated glass slides.<sup>4-8</sup> The active layer thickness was  $d = 125\ \mu\text{m}$ .

To determine the performance of the investigated materials degenerate four-wave-mixing and two-beam-coupling experiments were carried out using a HeNe laser ( $\lambda_0 = 633\ \text{nm}$ ). Holograms were recorded in tilted configuration with *s*-polarized writing beams (external tilt angles  $\alpha_1 = 50^\circ$  and  $\alpha_2 = 70^\circ$ , respectively, with respect to the sample normal). The internal intensities of the writing beams as determined from the half height width of their Gaussian profiles were similar ( $I_1 \approx I_2$ ), yielding a grating contrast close to unity. Prior to the writing process an electric field  $E_0$  was applied to the device, which was also preilluminated for 30 min by beam 2. Hereafter, beam 1 was switched on, and after writing the grating for a certain time  $t_{\text{rec}}$  both beams were switched off simultaneously.

The recorded hologram was probed by a *p*-polarized beam counterpropagating to beam 1. Due to the erasure of the PR grating upon uniform illumination, we took the following precautions to reasonably approximate “real” dd: First, the reading beam had more than 3 (at lowest recording intensity) up to more than 5 (at highest recording intensity) orders of magnitude lower time-averaged intensity ( $\sim 250\ \text{nW/cm}^2$ ) than the recording beams. Second, the read beam was only applied from time to time using a fast magnetical shutter. Between the readouts, the sample was held in the dark. Overall, the read beam was on for less than 8% of the total time the grating decay was monitored. The read beam

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was chopped, and the internal diffraction efficiency  $\eta_{\text{int}}$  was determined utilizing lock-in amplifiers.  $\eta_{\text{int}}$  was calculated according to:

$$\eta_{\text{int}} = I_D / (I_D + I_T). \quad (1)$$

with  $I_D$  as the power of the diffracted and  $I_T$  as the power of the transmitted reading beam. From the  $\eta_{\text{int}}$ , we calculated the refractive index modulation  $\Delta n_p$  according to<sup>9</sup>

$$\Delta n_p = (\text{asin} \sqrt{\eta_{\text{int}}} \cdot (\cos \alpha_1 + \cos \alpha_2) \cdot \lambda'_0) / (2 \cdot \pi \cdot d). \quad (2)$$

The PR gain coefficient  $\Gamma_s$  was calculated according to<sup>10</sup>

$$\Gamma_s = d^{-1} [\ln(I_1/I_{10}) \cos \alpha_1 - \ln(I_2/I_{20}) \cos \alpha_2]. \quad (3)$$

Here  $I_{1,2}$  are the intensities of the recording beams 1 and 2 after passing the device, and  $I_{i0}$  are the corresponding values without grating. Estimates of the phase shift  $\phi$  were obtained by substituting  $\Delta n_s$  and  $\Gamma$  in<sup>1</sup>

$$\phi = \text{asin}(\Gamma_s \lambda_0 / (2 \pi \Delta n_s)), \quad (4)$$

accounting for the polarization anisotropy of the chromophores ( $\Delta n_p / \Delta n_s = -2, 2$ ).<sup>11,3</sup> The experimental data were normalized to the index modulation achieved at the end of recording and fitted by bi- or triexponential decay functions. In order to obtain a unified measure for the general decay dynamics, we calculated the combined logarithmic averages of the relaxation times  $\langle \tau \rangle$  according to<sup>12</sup>

$$\langle \tau \rangle = \exp \left( \sum_i A_i \cdot \ln \tau_i \right); \quad \sum_i A_i = 1. \quad (5)$$

The dd kinetics was found to be at least two orders of magnitude slower than the relaxation of the orientational order of the dipoles in the material. The latter was similar in both materials as determined by independent transmission ellipsometric experiments.<sup>12</sup> This proves that the grating decay is governed exclusively by the decay of the PR space-charge field, i.e., essentially by the recombination of oppositely charged carriers. The decay curves exhibit multiexponential behavior in contrast to earlier results on a low-molecular-weight glass, where a simple monoexponential behavior was observed.<sup>13</sup> However, these latter results are somewhat questionable, since the read beam was rather strong and applied at all times. Therefore, low intensity erasure was performed rather than a reasonable approximation of dark decay.

According to a theoretical framework proposed by Cui *et al.*<sup>14</sup> covering the erasure process in PVK-based PR polymers, the (thermal) detrapping coefficient  $\alpha_T$  determines the PR grating decay kinetics for the case of vanishing zero-order hole density, which also applies to the dd. Presuming charged sensitizers as the dominant PR trap species,<sup>15</sup> Poole-Frenkel behavior is implied for the field dependence of  $\alpha_T$  leading to accelerated dd as a function of increasing external field  $E_0$ . Our findings agree with these considerations, however, the dependence is much more pronounced in material CT as compared to C [Fig. 1(a)].

Surprisingly, the dd is faster in material CT than in C, whereas the recording process is much slower (about a factor of 5–6) in CT. The latter is in general agreement with earlier results reported by Malliaras *et al.*<sup>16</sup> This finding may indicate, that even though the TPD content is small (about

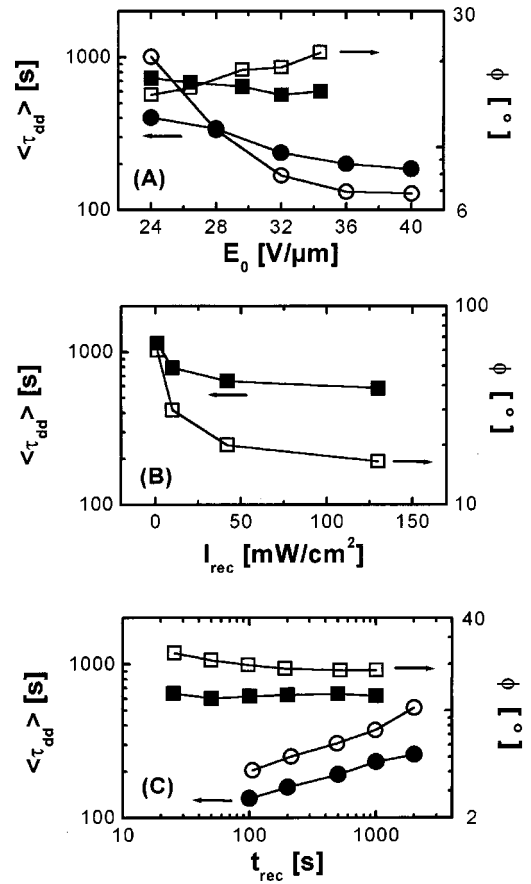


FIG. 1. Dependence of the averaged dd time constants  $\langle \tau_{\text{dd}} \rangle$  (solid symbols, left-hand side axis) and the PR phase shift  $\phi$  (open symbols, right-hand side axis) for material C (squares) and CT (circles): (a) on the electric field for  $t_{\text{rec}} = 500$  s (C) and  $t_{\text{rec}} = 1500$  s (CT) at  $I_{\text{rec}} = 42$  mW/cm<sup>2</sup>; (b) on the recording intensity for  $t_{\text{rec}} = 500$  s (C) and at  $E_0 = 32$  V/μm; and (c) on the recording time at  $E_0 = 32$  V/μm and  $I_{\text{rec}} = 42$  mW/cm<sup>2</sup>. The lines are to guide the eye.

$10^{21}$  cm<sup>-1</sup>, one extrinsic trap per 100 transporting sites) it may contribute to charge transport in the dark. By contrast, the photoconductivity proceeds through the cabazole manifold and is hindered by the trapping in TPD, and therefore the recording in CT is slower than in C.

It was even more striking that in both materials, the dd depended strongly on the intensity of the recording (!) beams  $I_{\text{rec}} = I_1 + I_2$  [Fig. 1(b)]. Since at a given  $E_0$ , the thermal detrapping coefficient is a characteristic material constant, we propose that the recombination of charge carriers might depend on the displacement  $\Delta$  between the positive and negative carrier distributions. Assuming that the negative carriers were immobile and would remain on the TNF sites where they were initially generated, in zero-order approximation (i.e., neglecting recombination effects), the PR phase shift  $\phi$  would correspond to half of the displacement  $\Delta$  and could, therefore, serve as a qualitative measure for  $\Delta$ . Accordingly, a larger  $\phi$  would reflect a larger  $\Delta$  with reduced mutual overlap between of the positive and negative carrier clouds and, thus, a reduced number of potential recombination sites available near a mobile charge carrier. As a result, the average number of recombination events should be reduced, and the dd would take longer. We estimated  $\phi$  from concomitant gain measurements during recording using Eq. (4). Indeed,  $\phi$  increases strongly with decreasing  $I_{\text{rec}}$  [Fig. 1(b)].

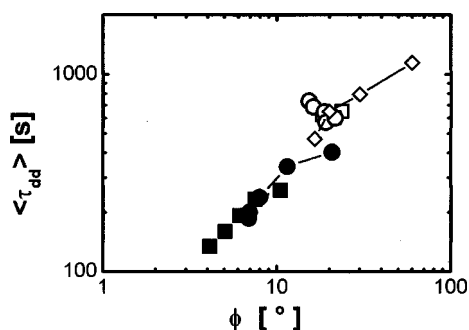


FIG. 2. Averaged dd time constants  $\langle \tau_{dd} \rangle$  of material C (open symbols) and material CT (solid symbols) as a function of the corresponding PR phase shifts  $\phi$ . Details of the particular experimental parameters are explained in the captions of Fig. 1. The lines are to guide the eye.

1(b), open symbols] and yields the slower dd in agreement with our explanation.

We now check this interpretation for the field dependence. With increasing field,  $\phi$  decreases in CT [Fig. 1(a)], and, since simultaneously the decay becomes faster, which is in agreement with the given interpretation. By contrast, in C,  $\phi$  increases slightly when the field increases, which should lead to a slowing of dd, but instead the dd is even slightly accelerated by the field. Obviously, in this case, the phase-shift effect is compensated by the field-induced decrease of  $\alpha_T$  as discussed herein. For comparison, in the doped material CT, both of these effects cooperate accelerating the dd at higher fields.

Recently, we discovered a strong dependence of the erasure kinetics on the recording time in undoped PVK-based materials.<sup>7,17</sup> Therefore, we expected a similar influence on the dd kinetics, which, surprisingly, was not the case for C [Fig. 1(c)]. This finding also shows that the dd kinetics is independent of the actual strength of the hologram (i.e., the number of charges involved in the space-charge field), which varies by a factor of almost 5 from the shortest to the longest recording time applied. In contrast, in the doped material CT, the dd does depend on the recording time. Both of these findings can also be explained by the phase-shift effect, since  $\phi$  increases strongly with time in CT, while it varies little in C [Fig. 1(c)].

Figure 2 compiles the data for all experiments discussed in a master plot. The dark decay times  $\langle \tau_{dd} \rangle$  show a clear dependence on the estimated phase shifts  $\phi$ . The fact that the observed trend is consistent even for both investigated materials indicates that the PR phase shift represents a dominant factor for the dd behavior. We may estimate that the longest  $\langle \tau_{dd} \rangle$  is in the order of 2000 s in our material for the maximum phase shift of  $90^\circ$ .

In conclusion, we have performed a systematic investigation of the dark decay in PR polymers. The dd was found to be governed by the decay of the space-charge field and—mostly remarkably—depended on the phase shift of the PR

grating. This is particularly important for the application of PR polymers. In order to store distortion-free images, the energy transfer between the write beams (two-beam-coupling “gain”) is undesired, because it leads to fringe bending and contrast loss of the hologram.<sup>1</sup> To avoid this, small gain coefficients  $\Gamma$  are required, which are (simultaneously assuming large index modulation amplitudes) correlated with small PR phase shifts. The latter, however, yield a fast dd of the recorded information as the results in this letter clearly demonstrate. Thus, a trade off between these counteracting trends is necessary. The phase-shift effects may even vary in different areas of an image (e.g., due to different intensities, fringe visibility  $m$ , etc.), leading to time-dependent contrast and distortion of images subjected to idle periods during processing, where dd can take place.

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