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Analytical form for holographic contrast growth in photorefractive polymers

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ABSTRACT An analytical form for holographic contrast growth in photorefractive polymer composites under constant illumination is presented. The transient is a convolution of the exponential growth of the space-charge field and the rotational response of the chromophores in the amorphous host. Under this formalism, the contrast growth is fully characterised by just two parameters: the rise time of the space-charge field and the rotational diffusion constant of the material. There is excellent agreement between theory and experiment. Using this description of holographic index growth, the reciprocal relationship between rise time and intensity is confirmed.

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Since their discovery ten years ago, there has been a great deal of interest in photorefractive polymers because they are candidate materials for, amongst other applications, high-density holographic data storage. An important advance was made in 1994 [1], when it was discovered that the holographic diffraction efficiency achievable from a photorefractive polymer could be increased from less than one percent to almost unity by including re-orientable chromophores within the composite. These chromophores are dipolar and attempt to align themselves with the space-charge field formed by the photorefractive effect in response to patterned illumination. This chromophore re-orientation causes a local change in refractive index and is responsible for most of the index modulation in the material, thus greatly amplifying the photorefractive effect [2]. Holographic growth rate is an important performance parameter for many of the proposed applications, determining the writing speed possible in a holographic data storage system, for instance. Although the re-orientational enhancement effect has greatly improved photorefractive polymer performance, it also has limited the interpretation of the holographic growth dynamics because the form of the chromophore re-orientation transient has not been known. Consequently, it has been difficult to reliably assess and compare different photorefractive materials. Further, without a good understanding of chromophore re-orientation, the investigation of the underlying processes, such as charge generation and transport, has been restricted.

Holographic growth transients in photorefractive polymers have been, up to now, normally characterised by a fit to either a bi-exponential [3–5] or the Kohlrausch–Williams–Watts (i.e. stretched) exponential [6]. Overall, it has become most common to use a bi-exponential fit and then quote the shorter of the two resultant time constants as the characteristic time. However, this procedure is empirical and the time constant depends not only on the material under study but also on the specific experimental conditions, such as poling field strength, write-beam intensity and pre-illumination. Very recently, however, an analytical description of the rotational response to the application stepwise of a constant applied field has been reported [7] for chromophores in an amorphous medium. The analysis derives a power-law time dependence for the field-induced birefringence, rather than an exponential, in contrast to previous descriptions [8–10]. It was shown in [7] that the dynamic response of a polymer composite can be characterised by a single material parameter: the diffusion constant. Excellent agreement was found between this theory and experiment. The experimental verification was performed using a chromophore in poly(N-vinylcarbazole) (PVK), which is an amorphous medium commonly used as a host material for photorefractive composites. Therefore, the theory presented in [7] can be used to analyse the response of the chromophores in a photorefractive composite to a constant field, when applied as a step function. This theory has not yet been applied directly to the case of the holographic contrast formation. Holographic contrast in a photorefractive polymer composite depends linearly on the space-charge field amplitude, under conditions of a steady poling field. According to the standard theory [11, 12], the space-charge field inside a photorefractive material grows exponentially with the onset of patterned illumination.

In this paper, an analytical description of the rotational response to an exponentially growing electric field of a collection of pre-poled dipoles in an amorphous medium will be reported. This dynamic corresponds to the

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growth in holographic index contrast in a photorefractive polymer composite in which the electro-optic effect is due to the re-orientation of chromophores. The general transfer function for rotating chromophores in an amorphous medium will also be given and the experimental verification of the theory will be detailed.

The index contrast of a photorefractive grating is proportional to the square of $\boldsymbol{E}_{\rm res}$, the resultant of the photorefractive space-charge field, $\boldsymbol{E}_{\rm sc}(z, t)$, and the poling field, $\boldsymbol{E}_{\rm pol}$, applied to the sample, i.e.

$$\Delta n \propto \boldsymbol{E}_{\rm res}^2 = E_{\rm pol}^2 + 2\boldsymbol{E}_{\rm pol}\cdot\boldsymbol{E}_{\rm sc}(t)\cos(\boldsymbol{K}\cdot z) + E_{\rm sc}^2(t)\cos^2(\boldsymbol{K}\cdot z) \qquad (1)$$

where $\boldsymbol{K}$ is the grating vector, set in this case to be parallel to the z-axis. The first-order diffraction efficiency from this grating is determined by the first Fourier (i.e. $1\boldsymbol{K}$) component of the index contrast, Δn_1. Hence, Δn_1 is proportional to the product of $E_{\rm pol}$ and $E_{\rm sc}(t)$ [2]:

$$\Delta n_1 \propto E_{\rm pol} E_{\rm sc}(t) \qquad (2)$$

Charge diffusion is negligible compared to drift in photorefractive polymers and so to a good approximation a space-charge field does not build up in the absence of a poling field. For this reason, a constant poling field is commonly applied to the polymer sample before photorefraction is initiated. Hence, it is quite general to describe the evolution of $\Delta n_1(t)$ as the response of a system of dipoles driven by $E_{\rm sc}(t)$ only. That there is a linear relation between the response and the driving function is crucial to the following analysis because it allows linear convolution theory to be used. (In contrast, the second-order diffraction efficiency, which depends on the second ($2\boldsymbol{K}$) Fourier component of the index contrast, Δn_2, is proportional to the square of the space-charge field and therefore in that case linear convolution theory is not valid.) The strategy for this analysis then is: to determine the transfer function for the re-orientable dipolar chromophores and then to convolve this with the space-charge field transient as described by the standard theory of photorefractivity.

The transfer function may be found by identifying and deconvolving the response of the chromophores to a known driving function. An analytical form for the response of re-orientable chromophores to a field applied as a step function has already been identified [7] and the simple nature of the driving function makes this response an obvious candidate for deconvolution. It was shown in [7] that in dispersive media, such as polymers and glasses, chromophore re-orientation produces an index change in response to a step-function field, $\Delta n_{\rm step}$, given by

$$\Delta n_{\rm step}(t) = k\frac{u^2}{15+u^2}\left\{1 + \frac{\tau_1}{\tau_2-\tau_1}t^{s_1} - \frac{\tau_2}{\tau_2-\tau_1}t^{s_2}\right\} \qquad (3)$$

where t represents time, k is a material constant and

$$s_{1,2} = -\frac{1}{\tau_{1,2}} = -2D_0\left(2 \mp \sqrt{1-u^2/5}\right); \quad u = \mu E_{\rm pol}/k_{\rm B}T \qquad (4)$$

where μ is the dipole moment, $E_{\rm pol}$ is the applied poling field, $k_{\rm B}$ is Boltzmann's constant and T is the absolute temperature. The diffusion constant, D_0, is related to the diffusion coefficient, D, by $D = D_0/t$ for $t \geq 1$. The restriction $t \geq 1$ (i.e. the field is applied at time $t = 1$) ensures that the temporal evolution of $A_2(t)$ is well behaved (see (3)); in principle, however, arbitrarily small units of time could be used and thus the onset of poling can be arbitrarily close to $t = 0$. D_0 is the initial value of the diffusion coefficient, the value of which is determined by the units of time used.

The transient described by (3) strictly corresponds to an experiment in which an initially unpoled sample has a single field applied to it as a step function. A precise correspondence with holographic recording would require the application of a spatially varying step-function field to a pre-poled sample, with the two fields being, in general, not parallel. However, the form of the transient is the same in both cases. The parallelism of the two fields and the condition $\boldsymbol{K} \to 0$ form a specific example of the general case and do not alter the transient. We can regard (3) to be the response of chromophores to a constant poling field and a step-function field. Mathematically, this is possible because the Laplace transform of a step function at $t = 0$ (which we are arbitrarily close to) and a constant are identical. Physically, typical poling fields only slightly perturb the angular distribution of chromophores (for instance, using the analysis and parameter values presented in [10], an applied field of 50 V/μm alters the average angle between field direction and chromophore axis by $\sim 1°$). Hence, pre-poling is not expected to appreciably alter the dynamic behaviour of the chromophores. The validity of this approach will be ultimately supported by the excellent agreement between theory and experiment described below.

To emphasise the correspondence between (2) and (3), for the purposes of this analysis $\Delta n_{\rm step}(t)$ is regarded to be the response to a constant poling field and an equal-magnitude step-function field, $E_{\rm step}(t) = E_{\rm pol} \times U(t)$, where $U(t)$ is the unit step function, i.e. $\Delta n_{\rm step}(t) \propto E_{\rm pol}E_{\rm step}(t) = E_{\rm pol}E_{\rm pol}U(t)$. The corresponding transfer function can be found by calculating the Laplace transform of (3) and dividing through by the transform of a step-function poling field, i.e. $E_{\rm pol}/p$, where p is the transform variable. This approach assumes that the system is linear, which is not strictly true in the present case because the time constants, τ_1 and τ_2, are functions of the field. However, both time constants are only very weak functions of u under experimental conditions ($\sqrt{(1-u^2/5)} \sim 0.995$ for typical parameters [10]) and can therefore be well approximated as independent of the driving field. Similarly, since $u \ll 15$ then $u^2/(u^2+15) \sim u^2/15$. Under these approximations, (3) can be linearly deconvolved into a transfer and a signal (step) function. Hence, in transform space the transfer function, $T(p)$, is

$$\begin{aligned} T(p) &= \frac{p}{E_{\rm pol}} \times \int_0^\infty \Delta n_{\rm step}(t)\,{\rm e}^{-pt}{\rm d}t \\ &= k\frac{\mu}{k_{\rm B}T}\frac{u}{15}\left\{1+\left(\frac{\tau_1}{\tau_2-\tau_1}\right)\frac{\Gamma(s_1+1)}{p^{s_1}} - \left(\frac{\tau_2}{\tau_2-\tau_1}\right)\frac{\Gamma(s_2+1)}{p^{s_2}}\right\} \end{aligned} \qquad (5)$$

where $\Gamma(x)$ is the gamma function. The transfer function is composed of a normalised response function (the terms in the curly brackets) and a pre-factor, which depends on the constant magnitude of the poling field, $E_{\rm pol}$.

According to the standard model of photorefractivity, the space-charge field grows exponentially from the onset of patterned illumination and has the form

$$E_{\mathrm{sc}}(t) = E_0 \left(1 - \exp\left(-\frac{t}{\tau_{\mathrm{sc}}}\right)\right) \tag{6}$$

where E_0 is the constant amplitude factor for the field dynamic and τ_{sc} is the rise time of the space-charge field, which is, in general, a complex quantity. In the terms of this analysis, τ_{sc} is assumed to be a constant at all times and for all values of space-charge field. In most cases the space-charge field is not collinear with the poling field and the effect of the change of resultant field strength on charge-generation efficiency may be neglected in the first instance. The driving function in this case, i.e. (6), is not affected by the nature of the response function. Thus, the response of $\Delta n_1(t)$ to $E_{\mathrm{sc}}(t)$ can be found by finding the Laplace transform of (6), multiplying the result by (5) and finally performing an inverse Laplace transformation on the product, in other words convolving the signal and transfer function, to get

$$\Delta n_1(t) \propto \frac{u_{\mathrm{sc}} u}{15} \left\{ \begin{array}{l} \left(1 + \left(\frac{\tau_1}{\tau_2 - \tau_1}\right) t^{s_1} - \left(\frac{\tau_2}{\tau_2 - \tau_1}\right) t^{s_2}\right) \\ - \exp\left(-\frac{t}{\tau_{\mathrm{sc}}}\right) \left(1 + \frac{\gamma(s_1+1, -t/\tau_{\mathrm{sc}})}{\tau_1 - \tau_2} (-\tau_{\mathrm{sc}})^{s_1} - \frac{\gamma(s_2+1, -t/\tau_{\mathrm{sc}})}{\tau_1 - \tau_2} (-\tau_{\mathrm{sc}})^{s_2}\right) \end{array} \right\} \tag{7}$$

where $u_{\mathrm{sc}} = \mu E_0 / k_{\mathrm{B}} T$ and $\gamma\,(s_n + 1, -t/\tau_{\mathrm{sc}})$ is the incomplete gamma function (limits 0 to $-t/\tau_{\mathrm{sc}}$).

The above theory has been verified using a degenerate four-wave-mixing (DFWM) experiment. Two coherent, equal-intensity, writing beams interfere within a sample of photorefractive material to produce a sinusoidal illumination pattern. The material responds by forming a refractive-index grating, which diffracts some fraction of a probe beam. The efficiency of diffraction is determined by the magnitude of the index contrast of the grating or hologram. In our experiment, a field and one of the writing beams are initially applied to the sample whilst the second writing beam is blocked. The growth of the holographic index contrast was measured by monitoring the first-order diffraction efficiency after the second writing beam is unblocked, thus causing the space-charge field to begin to form. (If both writing beams were initially blocked then theoretically the build-up dynamics of the charge carriers would have an effect on the contrast-growth curve. However, measurements suggest that the hole lifetime in similar materials is less than a millisecond [13] at high poling fields and hence the carrier build-up transient is expected to have a negligible effect on the observed growth in holographic contrast. The initially dark experimental situation should therefore also be well described by (7)). A schematic of the experimental set-up is shown in Fig. 1. The photorefractive polymer composite used consisted of 47.5 wt. % of the chromophore 1-(2′-ethylhexyloxy)-2,5-dimethyl-4-(4″nitrophenylazo)benzene (EHDNPB), 0.5 wt. % of C_{60} which acts as the photosensitiser, and the photoconductor was the host material PVK.

A typical index-contrast transient is shown in Fig. 2; a least-squares fit of (7) to the data is also shown, as well as the corresponding residuals. There is very good agreement between theory and experiment. The index-contrast growth was measured and analysed in this way for a range of writing-beam intensities. The rate of formation of the space-charge field, $R_{\mathrm{sc}} = 1/\tau_{\mathrm{sc}}$, is plotted against total writing-beam intensity

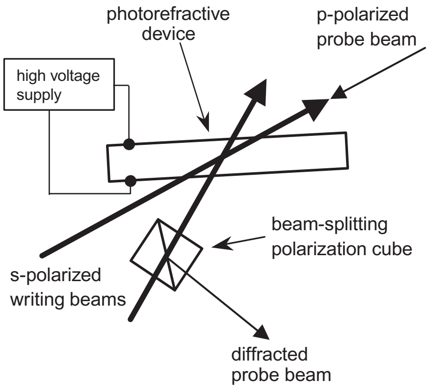

FIGURE 1 Schematic of the degenerate four-wave-mixing experiment. The two equal-intensity, *s*-polarised write beams intersect at an angle, external to the photorefractive device, of 20° and their bisector forms an angle of 65° with the device normal. The *p*-polarised probe beam is partially diffracted by the grating formed in the device in response to the interfering write beams and this fraction is measured by a photodiode (not shown). The photorefractive device consists of a 67-μm-thick sample of polymer composite sandwiched between two glass plates that have a conductive coating on the inside surface. A high-voltage supply maintains a field of 65 V/μm across the sample

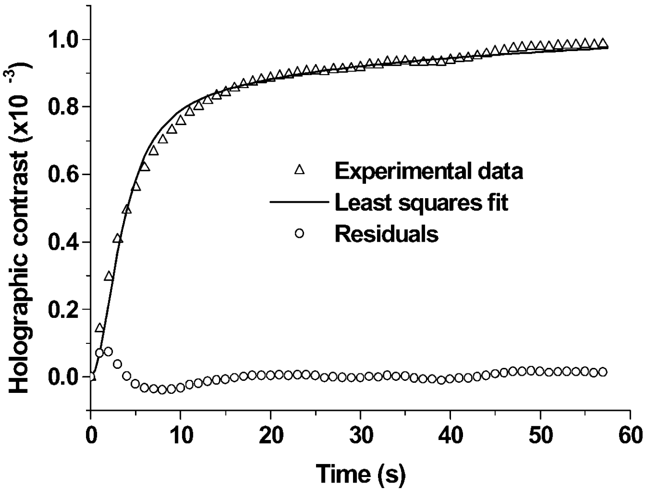

FIGURE 2 Growth in holographic contrast. The experimentally measured holographic contrast transient is shown for a total write-beam intensity of 0.09 W/cm^2. The fit of (7) to the data and the corresponding residuals are also shown. The fit utilised a value $D_0 = 0.059$ (ms time scale) measured by transmission ellipsometry [7], an effective field of 26 V/μm (see [14]) and $u/\boldsymbol{E} = 8.7 \times 10^{-3}$ μm/V from [10]

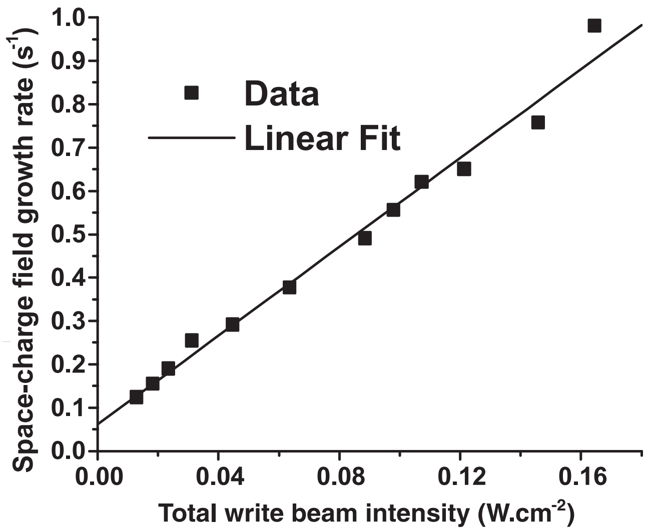

FIGURE 3 Rate of space-charge-field growth as a function of total write-beam intensity. The intensity is calculated from the total write-beam power and the beam-spot size projected onto the photorefractive device

in Fig. 3. As predicted by the standard theory of photorefractivity [11, 12], the space-charge field forms at a rate proportional to the intensity of illumination. This result further verifies that index-contrast transients are well described by (7).

We have presented an analytical description of the index-contrast transient in a photorefractive polymer composite containing re-orientable chromophores in an amorphous host. The analytical result fits the data well and is in agreement with the standard theory of photorefractivity. Therefore, reliable values of the space-charge field rise time can be extracted from index contrast transient data, for the first time. This will allow the performance of different materials to be assessed and compared in a consistent way and also provide a useful tool with which to investigate the underlying processes of photorefractivity in polymers.

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