Time-scale invariance of the reorientation dynamic in photorefractive polymers

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Abstract

Under the influence of an applied electric field, dipoles reorientate to provide most of the index contrast of holograms in photorefractive polymer composites. The poling transient is commonly described by modified exponential functions. Either a KWW stretched exponential or a bi-exponential function is required to fit adequately the observed behavior. Moreover, when the analysis was performed for data that extended over 3 orders of magnitude in time then at least 5 time constants were required. We show that the dispersive rotational dynamic is, in fact, described by a power law, and hence does not have characteristic lifetimes. The dispersive rotation of dipoles is described simply and accurately using a time-dependent diffusion coefficient. This gives an excellent agreement between theory and measurement. This has important implications for the characterization of the transient response of any electro-optic process or device based on the rotation of dipoles in a dispersive amorphous material such as a polymer or glass.

Introduction

Since their discovery 10 years ago, photorefractive polymers have generated a great deal of interest because of their potential application in, amongst other things, holographic data storage and image processing. In 1994, it was shown that the holographic diffraction efficiency obtainable in a photorefractive polymer composite could be increased from the sub-percent level to almost unity by the inclusion of reorientable dipoles [1]. These dipoles tend to align with the space charge field formed by the photorefractive material in response to patterned illumination. The local refractive index change caused by this dipole reorientation generates the bulk of the index modulation in the material, thus greatly amplifying the photorefractive effect. The rate of hologram formation is an important performance parameter for many of the proposed applications because it determines, for example, the writing speed possible in a holographic data storage system. However, dipole reorientation, and therefore hologram formation in high performance photorefractive polymer composites, has not been well understood. This lack of understanding of the reorientation process has made the reliable assessment and comparison of high performance photorefractive materials difficult. Furthermore, not knowing how a growing space-charge field effects reorientable dipoles has restricted the investigation of the processes that underlie field formation, such as charge generation, transport and trapping.

Until now, the poling transient in photorefractive polymers has been most commonly described by one of two modified exponential functions: either the bi-exponential [2] or the Kohlrausch-Williams-Watts (KWW) or stretched exponential [3]. Overall, it has become conventional to fit a bi-exponential to the poling transient and then cite the smaller of the two resultant time constants as the characteristic time [2]. This procedure is empirical and the value of the time constant depends not only on the material under study but also on the particular experimental conditions, such as poling field strength and the duration of the experiment. Moreover, a recent analysis [4] has shown that, when 3 orders of magnitude of time are considered, at least 5 time constants are required to describe the response of dipoles in a photorefractive polymer material.

In this work, an analytical description of the response to an applied field of a collection of dipoles in an amorphous medium is presented. The analysis derives a power law time-dependence for the poling transient, rather than an exponential, and shows that the dynamic response of a polymer composite can be characterized by a single material parameter: the diffusion constant. An excellent agreement was found between this theory and experiment. The experimental verification was performed for a reorientable dipole in both poly(N-vinylcarbazole) and polycarbonate as the amorphous media.

Theory

The degree of alignment of a collection of dipoles with the applied field can be characterized by a set of n order parameters, A_n, which are defined as the nth degree Legendre polynomial averaged over the angular distribution of the dipoles [5]:

$$A_n = \langle P_n(\cos\theta) \rangle \qquad (1)$$

where θ is angle between the symmetry axis of the dipole and the applied field. The rotational diffusion

equation describes the transient properties of these order parameters:

$$\frac{1}{D}\frac{\partial A_n}{\partial t} = -n(n+1)A_n + u\frac{n(n+1)}{2n+1}\left[A_{n-1}(t) - A_{n+1}(t)\right] \quad (2)$$

where D is the diffusion coefficient and u is the 'balance parameter' and is given by:

$$u = \mu E/kT \quad (3)$$

where μ is the dipole moment, E is the applied electric field, k is Boltzmann's constant and T is the temperature. In general, equation (1) is not analytically solvable but for typical values of u the values of A_n are vanishingly small for $n>2$ and, moreover, because the population of dipoles is constant $A_0=1$. Thus, the rotational diffusion equation is reduced to a system of two simultaneous, first-order, inhomogeneous differential equations in the dependent variables A_1 and A_2. For material systems which do not display rotational dispersion, such as dipoles in weak solution, the diffusion coefficient is a constant and consequently the solution of equation (2) consists of bi-exponential expressions for A_1 and A_2 [5]. Transients for the order parameters are thus characterized by definite time constants. This work, however, will describe the case of dispersive media by considering a diffusion coefficient that is a function of time.

In an amorphous material the microscopic environment for each dipole will be unique and this is the cause of the rotational dispersion. Some dipoles will be able to rotate with relatively little hindrance whilst others will find it much more difficult to align themselves with the applied field. The diffusion coefficient represents an average for the ensemble of dipoles. When the field is first applied, each dipole begins to rotate, however, those dipoles that can rotate most freely reach thermal equilibrium after a certain time. This leaves only the more slowly rotating dipoles to contribute to the transient, reducing the effective value of D. A time dependent diffusion coefficient is therefore plausible but what form does the dependence take? There is a close analogy between the dispersive rotation of dipoles in and the transit of charge carriers through an amorphous material. A packet of charge travelling through an amorphous medium exhibits dispersion in its transit time due to the wide distribution of hopping times between sites. The average mobility of the moving packet of charge carriers decreases with time as the fast moving charges complete their journey, leaving in motion only those carriers that have encountered a hopping site with a long dwell time. This phenomenon has been well explained [6,7] by a hopping time distribution, φ, which has the form:

$$\varphi(t) \propto t^{-1\pm\alpha} \quad (4)$$

where α is a constant. The value of α ranges between 0, which represents complete disorder, and 1 for an ordered motion. The transition from the $+\alpha$ to the $-\alpha$ form occurs when a certain fraction of the charges have reached the destination electrode and are removed from the material. By analogy, we propose the time dependence of the diffusion coefficient for dipoles rotating in a dispersive medium to be:

$$D(t) = D_0/t \qquad (for\ t\geq 1) \quad (5)$$

where D_0 is the initial value at $t=1$ and depends on the material used and the time-scale of the experiment. This form corresponds to the completely disordered environment for the translational case. The choice of form for the time dependence of the diffusion coefficient will be borne out by the excellent agreement between theory and experiment.

If equation (5) is substituted into equation (2) then the rotational diffusion equations have variable coefficients; in comparison, for the time-independent diffusion coefficient case then the system has only constant coefficients. This important difference affects the form of the solution and causes a remarkable change in the dynamic. The solution for $D=D_0/t$ may be found by making the substitution $t=e^z$ to give, for the dispersive case:

$$A_1(t) = A_1^\infty\left\{1 + \frac{\tau_1}{\tau_2-\tau_1}t^{s_1} - \frac{\tau_2}{\tau_2-\tau_1}t^{s_2}\right\}$$
$$- 2D_0\frac{u}{3}\frac{\tau_2\tau_1}{\tau_2-\tau_1}\left[t^{s_1} - t^{s_2}\right] \quad (6)$$

$$A_2(t) = A_2^\infty\left\{1 + \frac{\tau_1}{\tau_2-\tau_1}t^{s_1} - \frac{\tau_2}{\tau_2-\tau_1}t^{s_2}\right\}$$

where

$$s_{1,2} = -\frac{1}{\tau_{1,2}} = -2D_0\left(2\mp\sqrt{1-u^2/5}\right) \quad (7)$$

and

$$A_1^\infty = \frac{5u}{15+u^2}$$
$$A_2^\infty = \frac{u^2}{15+u^2} \quad (8)$$

The order parameters now have a power law, rather than a bi-exponential, dependence on time. There is no characteristic lifetime associated with a power law, in contrast to an exponential. The transient is now completely specified by just two parameters: the diffusion constant, D_0, and the balance parameter, u. The ultimate $(t\to\infty)$ value of the order parameters is determined entirely by the magnitude of the balance parameter. In contrast, the shape of the transient depends mostly on the value of the diffusion constant with only a weak dependence on the balance parameter. This form of power law time dependence is similar to that seen in dispersive charge transport, which is responsible for the observed time-scale invariant behavior [6,7].

Experiment

The reorientation of dipoles under the influence of an applied field affects the birefringence of a sample by enhancing the polarizability of a material in a preferred direction. It has been shown [5] that the field-induced birefringence, Δn, is proportional to the second order parameter, $A_2(t)$. Applying a field to a sample of amorphous material that contains re-orientable dipoles and monitoring the consequent birefringence transient allows the theory described above to be verified experimentally. In this work, a transmission ellipsometer was used to measure the birefringence change due to an applied field in a number of different materials that contained re-orientable dipoles.

Figure 1 shows the experiment set-up. The birefringence transient induced in a sample by an electric field applied as a step function was measured by observing the transmittance, through crossed polarizers, of plane-polarized light. The birefringence induced by the field causes a change of the polarization state of the light during propagation through the sample that results in a change in the transmission through the experiment. This technique is described in more detail in Ref. [8].
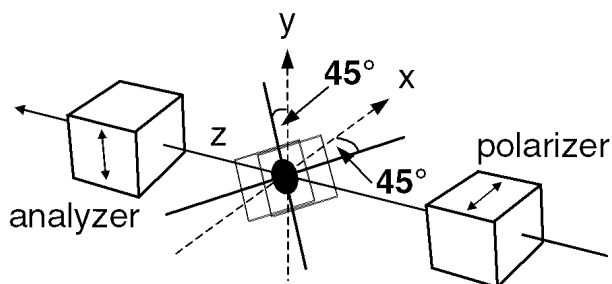

Figure 1. Experimental set-up. A sample is placed between two crossed Glan-Taylor polarizers, with the sample normal oriented such that it is at an angle of 45° from the x-axis and from the axis of propagation of the plane-polarised light beam (632.8 nm He-Ne laser). The sample is then rotated 45° about the y-axis. Measuring the transmission through the ellipsometer monitors the field-induced response of the birefringence.

Three different amorphous materials were used as hosts: poly(N-vinylcarbazole) (PVK), a mixture of PVK and its monomer ethylcarbozole (ECZ), and polycarbonate. Each of these hosts was doped with a high percentage (40-47.5 wt.%) of the chromophore 1-(2'-ethylhexyloxy)-2,5-dimethyl-4-(4"nitrophenylazo)benzene (EHDNPB), which acts as the reorientable dipolar molecule. A small amount (0.5 wt.%) of the sensitisor, C_{60}, was also included to produce a fully functional photorefractive polymer composite.

Each sample consisted of the composite material sandwiched between two glass plates coated with indium tin oxide electrodes on the inner surfaces. The exact composition for each material, the thickness of each sample and the magnitude of field applied are given in the appropriate figure caption.

Results

The experimental birefringence response for the PVK, PVK + ECZ and polycarbonate samples are shown in Figures 2 to 4, respectively. A millisecond time-scale was used in each case. A least squares fit was performed on each data set using equation (6) as the fitting function; the fit and the resulting residuals are also shown on each figure. This fit used the estimate from the literature [5] that $u/E \cong 8.7 \times 10^{-3}$ J.μm/V. Since $A_2(t)$ is only a weak function of u, only an estimate of u is necessary for a good fit. Thus, only 2 fitting parameters were used: the diffusion constant, D_0, and a scaling factor between A_2 and the birefringence change. The value of the diffusion constant, and the associated statistical error, found from the fit is shown in Table 1 for each material.
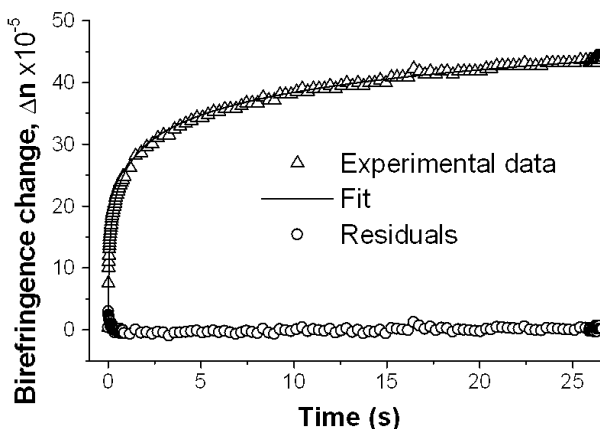

Figure 2. Transmission ellipsometer data showing the field-induced birefringence of a sample containing 40 wt.% EHDNPB in a PVK host. The sample had a thickness of 50 μm and a 2.0 kV step function was applied across the electrodes; thus the field applied was 40 V.μm[1]. For clarity, only every fifth point has been plotted.

Discussion

Figures 2 to 4 show that the theory detailed above describes well the response of the dipoles to an applied field. The residuals can be attributed to detector noise everywhere except for the very first few points in each transient. The first data point of the transient was assumed to be at exactly $t=1$ even though the precise moment the field was applied may have occurred between samples. Hence, a systematic error is introduced to the initial part of the fit in this way. Moreover, the field cannot be applied instantaneously as is assumed in the analysis and this too introduces a systematic error in the early part of the fit. This error is more pronounced for the PVK+ECZ based sample because it has the quickest initial rise. Nevertheless, the agreement between theory and experiment is very good and consequently the response of the dipoles to the applied electric field may be characterized by a single material parameter: the diffusion constant. The monomer ECZ acts as a plasticizer in PVK, increasing dipolar rotational mobility

and hence leading to a greater diffusion constant. As expected, the value of measured D_0 was indeed greater for the PVK+ECZ than for PVK only sample (see Table 1).
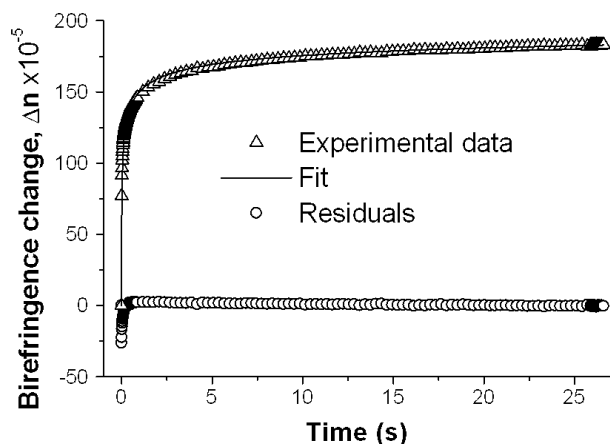

Figure 3. Transmission ellipsometer data showing the field-induced birefringence of a sample containing 40 wt.% EHDNPB in host consisting of 25 wt.% ECZ and 35 wt.% PVK. The sample had a thickness of 53 μm and a 2.1 kV step function was applied across the electrodes, giving a poling field of 40 V.μm^{-1} For clarity, only every fifth point has been plotted.
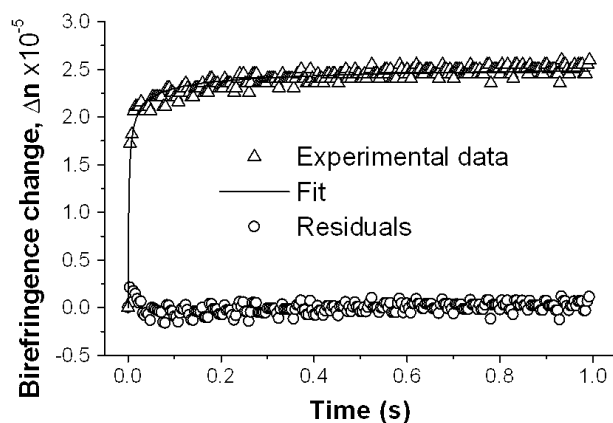

Figure 4. Transmission ellipsometer data showing the field-induced birefringence of a sample containing 47.5 wt.% EHDNPB in a polycarbonate host. The sample had a thickness of 70 μm and a 6.0 kV step function was applied across the electrodes, giving a poling field of 86 V.μm^{-1}. For clarity, only every 20th point has been plotted.

Table 1. Diffusion constants for each of the materials .

Material	Diffusion Constant, D_0
PVK	0.0363(1)
PVK + ECZ	0.1178(4)
Polycarbonate	0.41(1)

Summary and conclusions

A simple and exact analytical description of the rotational response of dipoles to an applied electric field in amorphous media has been found. This analysis describes the transient in terms of a power law time-dependence; a power law description has no characteristic times and is invariant with time-scale. Experimental verification of the theory was achieved by monitoring the field-induced birefringence change in a polymer composite that contains re-orientable dipoles. An excellent agreement was found between theory and experiment. A single material parameter, the diffusion constant, can now be used to characterize the response of host-dipole composites. The diffusion constant, D_0, is dimensionless and is equivalent to the diffusion coefficient at unit time; its magnitude therefore depends on the units of time used. The reorientation rates of dipoles in amorphous host materials can now be reliably assessed and compared by the use of this parameter. Moreover, this new theory will allow complex phenomena that may involve dipolar reorientation, such as the photorefractive effect in polymer composites, to be properly interrogated and thus increase the understanding of the underlying processes.

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Biography

David Binks was born in Preston, UK in 1971. He received a BSc. (Hons) in Physics from the University of Manchester in 1992. After working in industry for 3 years, he returned to Manchester University, gaining a PhD in 1998. He is presently a Research Associate in the Department of Physics and Astronomy at Manchester, most recently investigating dynamical processes in photorefractive polymer composites.