# Quasinondestructive Readout in a Photorefractive Polymer

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(Received 25 April 1994)

An important physical phenomenon, quasinondestructive reading, has been observed for the first time in a photorefractive polymeric material, PMMA (poly-methylmethacrylate):DTNBI (1,3-dimethyl-2,2-tetramethylene-5-nitrobenzimidazoline):$C_{60}$. In addition, a maximum steady-state diffraction efficiency of 7% (125 $\mu$m sample thickness) and a net two-beam coupling gain of 16 $cm^{-1}$ are observed in this polymer. A two-trap-level model, in which the levels are populated sequentially, qualitatively mimics the intensity-dependent decay rate and the transition to quasinondestructive reading.

PACS numbers: 42.40.Ht, 42.70.Ln, 42.70.Nq, 78.66.Qn

Since the first photorefractive (PR) polymer was reported several years ago [1], further research on the materials and mechanisms has produced dramatic progress in improving virtually all response parameters [2] so that, for several potential applications, the PR polymers reported to date are competitive with inorganic PR crystals. At the same time, there has been renewed interest in developing volume holographic memory systems based on PR materials [3]. One problem that must be overcome in any practical memory system is the gradual erasure of the information stored in the material during readout (destructive readout) which occurs in all PR materials, inorganic as well as organic. Mechanisms of nondestructive readout or prolonged reading [4–7], as well as various methods for fixing PR gratings [8–11] in inorganics, have been the subject of much recent research. Since PR polymers are relatively new and they differ from the conventional inorganic crystals in many respects (for example, by having a field-dependent photogeneration quantum efficiency and mobility), there is continuing interest in understanding the novel aspects of photorefractivity in polymers.

Here we report a novel physical effect, quasinondestructive readout (QNDR), in a PR polymer for the first time. By QNDR, we mean that the erasure rate at low intensity is far smaller than expected simply by the reduction in probing intensity alone, and, in addition, revelation (grating growth during reading) is also observed. The new material consists of an inert poly(methylmethacrylate) (PMMA) host into which 33 wt.% 1,3-dimethyl-2,2-tetramethylene-5-nitrobenzimidazoline (DTNBI) and 0.2 wt.% of the fullerene molecule $C_{60}$ are added. The DTNBI functions as *both* the nonlinear optical (NLO) chromophore and as the hole transport agent in this guest-host polymer mixture. This polymer is one example of an entire class of new PR polymer materials utilizing molecules which act as dual-function dopants, described in detail elsewhere [12]. $C_{60}$ acts to sensitize the generation of mobile charge [13] by formation of a charge transfer complex with DTNBI which has an absorption peak at 720 nm. The samples in which the PR properties were studied are preirradiated 125 $\mu$m thick films (sandwiched between transparent electrodes [14]) which have a glass transition temperature of ~45 °C (measured by differential scanning calorimetry), which allows the NLO chromophores to orient in the presence of an external field $E_0$ at room temperature to establish a nonzero electro-optic coefficient [2]. The photoconductivity of the sample $\sigma_{ph}/I$ is $\sim 3 \times 10^{-14}$ $(\Omega\,cm)^{-1}/(W/cm^2)$ at 676 nm and $E_0 = 4$ V/$\mu$m and at $I = 0.03$ W/$cm^2$. The absorption coefficient $\alpha$ of the polymer is 12 $cm^{-1}$ at 676 nm.

The PR properties of PMMA:DTNBI:$C_{60}$ are characterized by the usual holographic optical techniques of four-wave mixing (FWM) and two-beam coupling (2BC). In either technique, two continuous wave writing beams ($\lambda = 676$ nm, 6 mW power, 750 $\mu$m spot diameter) from a $Kr^+$ laser are overlapped in the sample using a tilted geometry described previously [2] (grating wavelength 1.6 $\mu$m), in order to provide a projection of the grating wave vector along the direction of $E_0$ (which is 40 V/$\mu$m, unless otherwise noted). In the FWM experiments, the writing beams are *s* polarized and the grating is probed with a *p*-polarized reading beam (676 nm, 750 $\mu$m spot diameter) of adjustable power counterpropagating to one of the writing beams. In the 2BC experiments, the intensities of the *p*-polarized writing beams exiting the sample are monitored directly.

The diffraction efficiency $\eta$, defined as the power of the diffracted beam divided by the power of the reading beam before the sample, is shown as a function of time in Fig. 1 for two different reading intensities, 0.1 W/$cm^2$ (open circles) and $2 \times 10^{-5}$ W/$cm^2$ (filled circles). For either case, $\eta$ increases from 0 as writing begins at $t = 0$, with a characteristic grating growth time $\tau_g$ (defined as the $1/e$ growth time of the refractive index modulation) of approximately 20 s at 1 W/$cm^2$ writing intensity and saturates at a steady-state diffraction efficiency $\eta_{ss} = 1.6\%$. The growth time is greatly increased from that of PR polymers based on the charge conducting host poly(*n*-vinyl carbazole) (PVK) [14], which is consistent with the order of magnitude decrease in photoconductivity of PMMA:DTNBI:$C_{60}$. The steady-state diffraction efficiency is strongly field dependent, increasing from $2 \times 10^{-5}\%$ at $E_0 = 0$ V/$\mu$m to 7% at $E_0 = 56$ V/$\mu$m.

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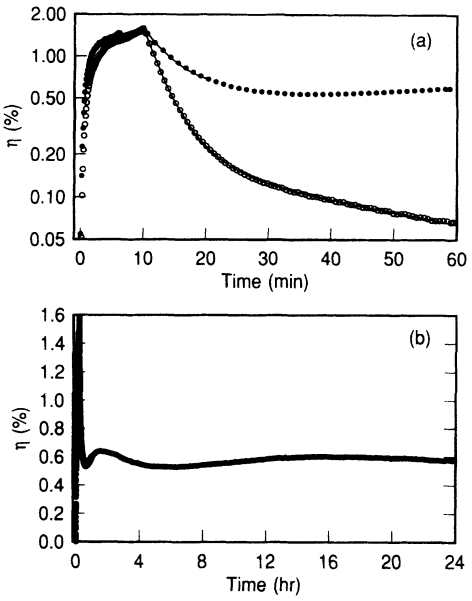


FIG. 1. (a) Diffraction efficiency $\eta$ vs time in PMMA:DTNBI:$C_{60}$. The writing beams are turned on at $t = 0$ and blocked at $t = 10$ min. At 0.1 W/cm$^2$ reading intensity (open circles) the decay of $\eta$ during reading is given by Eq. (1) (solid line), while at $2 \times 10^{-5}$ W/cm$^2$ (filled circles) the initial exponential decay (solid line between 10 and 20 min) is followed by revelation. The long-time behavior of the grating read at $2 \times 10^{-5}$ W/cm$^2$ is shown in (b).

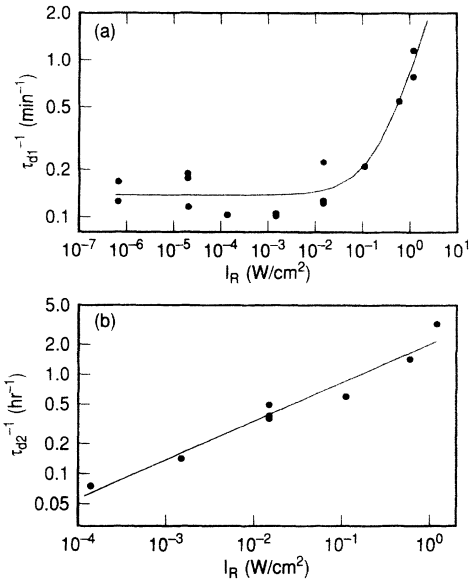


FIG. 2. (a) $\tau_{d1}^{-1}$ shown as a function of reading (i.e., erasing) intensity. The solid line is a fit to the data using Eq. (2). (b) $\tau_{d2}^{-1}$ shown as a function of intensity above $10^{-4}$ W/cm$^2$, where a biexponential decay is observed. The solid line is a power law fit showing $\tau_{d2}^{-1} \propto I_R^{0.4}$.

The grating growth time and $\eta_{ss}$ are unaffected by the value of the reading intensity.

Proof of the PR nature of these gratings is given by the observation of asymmetric two-beam coupling [2]. With equal writing beam intensities before the sample, an increase in the intensity in one beam of $\gamma_0 = I/I_{(t=0)} = 1.2$ is observed ($E_0 = 40$ V/$\mu$m), accompanied by an approximately equal decrease in the intensity of the second beam. Using a beam path length of 140 $\mu$m (oblique geometry), a 2BC gain coefficient of $\Gamma = 28$ cm$^{-1}$ is calculated [2,14], yielding a net gain of 16 cm$^{-1}$, the largest net gain of any organic PR material reported to date [14,15].

For reading (and consequent erasing) intensities greater than $10^{-4}$ W/cm$^2$, the decay of the diffraction efficiency $\eta$ is well characterized by the square of a biexponential

$$\eta(t) = \left[A \exp\left(-\frac{t}{\tau_{d1}}\right) + B \exp\left(-\frac{t}{\tau_{d2}}\right)\right]^2, \qquad (1)$$

where $\tau_{d1}$ is the faster characteristic decay time, and $\tau_{d2}$ is the slower characteristic decay time. A fit to the data with a reading intensity of 0.1 W/cm$^2$ is shown in Fig. 1(a) (line through open circles), with $\tau_{d1} = 285$ s and $\tau_{d2} = 6060$ s. The grating lifetimes of PMMA:DTNBI:$C_{60}$ are greatly enhanced over those of previously reported PR polymers [2]. Figure 2 shows the behavior of the decay rates as a function of the reading intensity $I_R$. The value of $\tau_{d1}^{-1}$ [Fig. 2(a)] decreases with decreasing $I_R$ down to 0.1 W/cm$^2$, below which $\tau_{d1}^{-1}$ becomes independent of $I_R$. The slow decay rate $\tau_{d2}^{-1}$ is shown in Fig. 2(b) for $I_R$ greater than $10^{-4}$ W/cm$^2$, the region over which a biexponential decay is observed. Over this power range, $\tau_{d2}^{-1}$ increases as $I_R^{0.4}$ (solid line).

As $I_R$ is decreased below $10^{-4}$ W/cm$^2$, the shape of the decay profile changes in a striking way. The decay profile for $I_R = 2 \times 10^{-5}$ W/cm$^2$ (100 nW reading power) is shown in Fig. 1 (filled circles). There is a rapid decrease in $\eta$ when the writing beams are blocked at 600 s, which is described by a single exponential decay ($\tau_{d1}$), as shown in Fig. 1(a) (line through solid circles between 10 and 20 min), which is independent of intensity. The solid line in Fig. 2(a) shows a fit of $\tau_{d1}^{-1}$ over the complete intensity range using the expression

$$\tau_{d1}^{-1} = \tau_{d1,\min}^{-1} + BI_R, \qquad (2)$$

with the values $\tau_{d1,\min}^{-1} = 0.14 \pm 0.05$ min$^{-1}$ and $B = 0.7 \pm 0.2$ cm$^2$/W min.

In contrast to data taken at intensities above $2 \times 10^{-5}$ W/cm$^2$, after the initial rapid decay $\eta$ begins to slowly increase again, as is shown in Figs. 1(a) and 1(b). This increase, referred to as grating revelation, is clearly visible in Fig. 1(b) between 0.5 and 2 h. At longer times, $\eta$ again decreases slightly and remains essentially unchanged at approximately 35% of the peak value as the PR grating is read out continuously. (The variation in $\eta$ on the 4 to 24 h scale is within the long-term drift of the laser intensity.) The power law behavior of $\tau_{d2}^{-1}$ observed above $10^{-4}$ W/cm$^2$ [shown in Fig. 2(b)] predicts a decay time for $\eta$ of ~10 h at an erasing intensity of $2 \times$

$10^{-5}$ W/cm$^2$, which is clearly not observed in Fig. 1(b). From the measured long-term drift of the laser intensity, a lower limit on the decay time $\tau_{d2}$ of the data shown in Fig. 1(b) is estimated to be approximately 300 h. The absence of any observable decay in $\eta$ over nearly 24 h of continuous reading represents the first QNDR process observed in a PR polymer. The low reading intensity required for QNDR provides $\sim 2 \times 10^9$ photons/s at the detector, which may limit the usefulness of this material in some storage applications, depending upon the number of bits per hologram, the number of holograms, and the available reading time.

After 24 h of constant reading, the diffraction efficiency of the grating which remains can still be gated using the external applied field as for other PR polymers [2]. When $E_0$ is decreased from 40 to 0 V/$\mu$m, $\eta$ loses >95% of its value, decreasing from 0.6% to $2.5 \times 10^{-2}$%. This is due to the fact that the electro-optic coefficient vanishes as the sample loses the orientational order induced by the external field. The small residual grating which remains is due to a residual field which remains across the sample because of trapped bulk space charge; applying a field of between $-20$ and $-30$ V/$\mu$m across the sample causes this residual grating to vanish. As the field is reapplied across the sample, orientational order (and the $r$ coefficient) is restored and the diffraction efficiency recovers its initial value. The grating remaining after 24 h can be rapidly erased by a strong erasing beam (1 W/cm$^2$) to $\eta$ less than $1 \times 10^{-5}$%, with a biexponential decay with time constants roughly a factor of 2 larger than those shown in Fig. 2 at 1 W/cm$^2$.

Grating revelation has been observed in numerous inorganic PR crystals [4,5,7,9–11], as well as two polymeric PR materials [16,17], and in all cases this behavior generally results from the presence of two charge gratings. In both of the polymeric materials, competition of a second grating with the primary grating was observed during writing, and $\eta$ increased immediately after the writing beams were blocked (the secondary grating was revealed as the primary grating was erased). In the first PR polymer in which revelation was reported, the secondary grating was attributed to ionic motion in response to the PR space-charge field [16], a mechanism similar to that postulated to occur in several inorganics [4,7,10,11]. In the second polymer a two-trap model was proposed to explain the grating revelation [17]. The grating revelation and QNDR reported here for PMMA:DTNBI:$C_{60}$ are distinctly different from that for the previous PR polymers. No competition is observed during writing, and, in contrast to Ref. [17] where a sufficiently high intensity reading beam was required for revelation, here revelation occurs only at sufficiently low reading intensity. Since the secondary grating in PMMA:DTNBI:$C_{60}$ can be easily erased with high reading intensities, it is unlikely that ionic motion is responsible for the secondary grating.

To provide a first attempt at developing a mechanism for the QNDR process, we have used simple rate equations to study a straightforward model with two sequentially connected hole trap levels, as holes are generally the dominant carrier in PR polymers [2]. An energy level diagram of the model is shown in Fig. 3, where $I_R$ is the intensity of the reading (erasing) beam. Level 1 initially stores the charge grating, is relatively shallow, and can be easily emptied (to the transport states of the material) thermally (with rate $k_4$, where the temperature dependence is implicitly assumed) and optically (with rate $k_3 I_R$). Level 2 is populated only by level 1 (with rate $k_1$), and it is a deep charge storage level not emptied thermally but emptied weakly by light (with rate $k_2 I_R$), which distinguishes this model from that in Ref. [17]. One possible physical realization of this situation may be that the deep trapping sites are initially shallow sites, which are stabilized by slow structural rearrangements of the surrounding polymer driven by the charge occupation of the site. The characteristics of this straightforward model are readily apparent. The index of refraction modulation is assumed to be proportional to the sum of populations in levels 1 and 2. The initial decay of the trapped charge grating is dominated by the depopulation of level 1 to the transport states, where the charges no longer contribute to the spatially modulated trapped charge grating. The model predicts that the initial decay of the trapped charge grating will be exponential, with a decay rate given by $\tau_{d1}^{-1} = k_4 + k_3 I_R$. This is the behavior observed experimentally [Fig. 2(a)], and, from the fit to the data [Eq. (2)], the values for the rates which control the population transfer to the transport states are found to be $k_3 = 42 \pm 12$ cm$^2$/W s and $k_4 = 8.3 \pm 3.0$ s$^{-1}$. For $k_1 \geq k_4$, as the intensity is lowered, more charges will be able to escape from level 1 to the deep storage level 2.

The long-time decay of the trapped charge grating is dominated by the decay of the charges trapped in

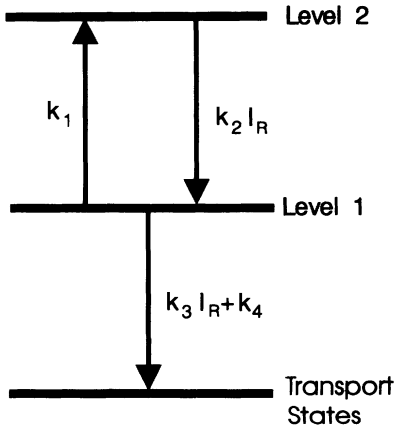


FIG. 3. Energy level diagram of the two-trap-level model proposed to explain the intensity dependence of the grating decay times and the transition to QNDR. Charges trapped in trap level 1 can empty into the transport states both thermally and optically, while charges trapped in level 2 must be photoexcited back to level 1 before they can be liberated.

level 2 to the transport states (via level 1). At high intensities, and for $k_3 \geq k_2$, the model predicts a long-time exponential decay with a decay rate given by $\tau_{d2}^{-1} = k_2 I_R$. At much lower intensities, the charges which are photoexcited from level 2 to level 1 will preferentially by promoted back to level 2 (for $k_1 \geq k_4$). The decay rate then becomes a superlinear function of the intensity, falling faster than linearly as $I_R$ is reduced. The transition at $k_1 \approx k_3 I_R + k_4$ represents the transition from destructive to QNDR which is observed experimentally in PMMA:DTNBI:$C_{60}$ at $I_R = 10^{-4}$ W/cm$^2$. Finally, the model predicts that the grating which is read without appreciable decay at low reading intensities should be easily erasable at high intensities.

Two features observed in the data are not reproduced by this simple model. The first is the sublinear dependence of the long-time decay rate $\tau_{d2}^{-1}$ on the intensity of the erasing beam [Fig. 2(b)]. Sublinear dependences of grating response times have been observed previously [13,16] and were attributed to the presence of shallow traps in the polymer. In the present case, this sublinear dependence may be the result of a more complex trap structure than that shown in Fig. 3, including perhaps distributions of trap levels due to the structural disorder of the polymer. The second feature not reproduced by the model is the grating revelation which occurs at low reading intensities [Fig. 1(b)]. Such gratings may arise from the motion of charges liberated into the transport states and retrapped at different spatial positions. Since there is no spatial component to the model, it is not expected to reproduce this revelation. It is hoped that presentation of the characteristics of this novel physical effect will stimulate further theoretical study of the underlying mechanism.

In summary, we have demonstrated QNDR over a period of at least 24 h in the photorefractive polymer PMMA:DTNBI:$C_{60}$ at sufficiently low reading intensity. In addition, at high reading intensities, grating lifetimes are also greatly enhanced over those of previous PR polymers. No explicit fixing scheme, such as thermal cycling to induce ionic motion [10,11] or a structural phase transition [8] or electric field pulsing [9], is required to achieve this novel fixed grating, which can be quickly erased by application of a sufficiently intense erasing beam. The steady-state diffraction efficiency of this polymer is among the largest reported to date, as are the two-beam coupling gain coefficient and the net two-beam coupling gain. The essential features of the grating decay as well as the transition to the QNDR regime can be qualitatively modeled with a simple two-trap-level model, in which the deep trap level is sequentially populated from the shallower level.

We acknowledge ARPA Contract No. DAAB07-91-C-K767 for partial support of this work.

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