

Complementary grating dynamics in photorefractive polymers with Alq₃

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ABSTRACT

The electron transporting molecule tris(8-hydroxyquinoline) aluminum (Alq₃) was introduced into a photorefractive composite in a low density to study the effects of electron traps on the performance. Compared to a control sample, Alq₃ samples exhibited higher dielectric strength, over-modulation at reduced voltage, and increased writing speed. Transient measurements indicated grating revelation via decay of a competing grating. The dynamics are consistent with a bipolar charge transport model. Overall, Alq₃ improves the sensitivity, trapping, and breakdown voltage without significant losses in absorption or phase stability.

Keywords: Photorefractive polymers, holography, competing gratings

1. INTRODUCTION

The photorefractive (PR) effect was first observed in crystals in 1967¹, and in organic polymer more than twenty years later². The realization of its potential utility was immediate, and since that time a wide range of applications³ have been studied, such as optical amplification, correlation, image correction, communication, and dynamic holographic displays. PR polymers in particular have gained interest due to the low cost, ease and range of tunability of optical and electronic properties, and increased figure of merit over inorganic materials. Large diffraction efficiencies, fast response times, and long persistency^{4,5} have all been demonstrated.

In the PR effect, a modulation of the refractive index of the material is induced by the interference pattern of two coherent light beams. Charges are generated in the bright regions, which then transport via hopping until they recombine or become trapped in dark regions. The separation and trapping leads to the development of a space-charge (SC) field with the same spatial distribution as the light, with a phase shift due to the transport. Nonlinear and/or birefringent molecules will align to this field, creating a macroscopic index modulation.

Many studies on material properties have been performed over the years by many groups an effort to improve the steady-state and dynamics performance. In particular, it has been shown that the introduction of tris(8-hydroxyquinoline) aluminum (Alq₃) increases the two-beam coupling gain and response time by acting as a trap for the electrons, allowing more efficient and faster charge separation⁶⁻⁷. Here, we report the addition of Alq₃ leads to the formation of competing grating. The mechanisms and theory of complementary grating dynamics via bipolar charge transport are briefly reviewed, and the potential benefit to various applications of such a device are discussed.

2. EXPERIMENTAL DETAILS AND RESULTS

The polymer host matrix for the PR composite samples studied is poly(acrylic tetraphenyldiaminobiphenol) (PATPD). It has a polyacrylate backbone with the well-known hole-transporting tetraphenyldiaminobiphenol-type (TPD) pendant group attached through an alkoxy linker. The chromophore 4-homopiperidinobenzylidenemalononitrile (7-DCST) was added to provide refractive index change and to act as a charge sensitizer at 532nm. The composite also included N-ethyl carbazole as a plasticizer and C₆₀ for further charge sensitization. Alq₃ was also added to provide electron traps and at a low concentration to prevent transport in the Alq₃ itself. The compositions of samples with and without Alq₃ are shown

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in Table 1. The samples were prepared by melt processing the mixture between two indium-tin-oxide coated glass slides, with 105 μ m spacer beads used to set the thickness. The absorption coefficient of each sample is approximately 160 cm⁻¹ at 532nm. Both samples exhibited phase stability for a several months.

Table 1. Weight percentage of each component in the samples studied.

Label	PATPD	7-DCST	ECZ	C ₆₀	Alq ₃
A	54.5	30	15	0.5	0
B	53.5	30	15	0.5	1.0

Degenerate four-wave mixing (DFWM) measurements were performed on these samples at 532nm. Each writing beam was s-polarized with an intensity of 100 mW/cm². The external angle between the beams was 360 and the sample was tilted by 550. The reading beam was p-polarized with an intensity of about 1 mW/cm². To measure the steady-state diffraction efficiency, the voltage was ramped up over about 5 minutes and the reading beam continuously monitored. Sample A showed 40% efficiency at 6kV, while sample B was over-modulated (almost 90%) at 4.5kV. No overmodulation was observed in sample A, but it was not possible to apply voltages higher than 6kV since these samples tended to suffer dielectric breakdown more often than B. This is expected given the higher trap density.

The transient efficiencies for each sample are shown in Figure 1. In this measurement, the 6kV was applied for about 30s prior to illumination. After recording for 4 minutes, the writing beams were blocked and the grating allowed to decay.

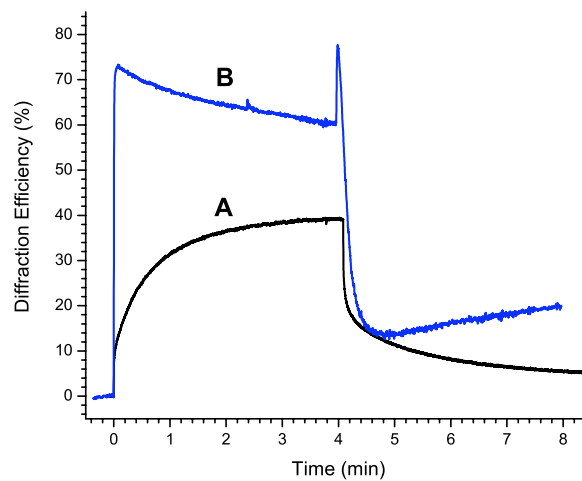


Figure 1. DFWM transients at 532nm demonstrating effects of Alq₃ on grating dynamics. Sample B is faster and exhibits evidence of grating revelation.

Sample A rises to 67% of the steady-state value in about 40s, while it takes the Alq₃ sample only 200ms. The other significant difference is the recovery of the efficiency in B after several minutes of decay. The decay for A was measured for about 10 mins without any sign of this recovery.

3. DISCUSSION

This recovery is typically associated with a competing grating^{8,9}. A single grating is insufficient to describe the existence of two extrema with a second over-modulation peak that is not observed in the steady-state DFWM. Furthermore, the transport of one type of charge carrier is also insufficient to reveal the second grating, as the two will add in phase making them indistinguishable.

It is believed that during the writing a weak competing grating is formed. The slight decay observed during writing is due a combination of this and that the over-modulation occurs at a lower voltage than used during the transients. When

the grating is allowed to decay in the dark, the initial rise and then quick fall is from the over-modulation as the index passes through the steady-state value at 4.5kV giving the maximum efficiency. The primary grating continues to decay until the SC field reaches a minimum (not zero due the phase mismatch of the two gratings), and eventually reverses sign as the competing grating becomes dominant. This then continues to be revealed as the primary decays. This behavior is modeled theoretically in Bashaw *et al.*¹⁰ and following papers in PR crystals. In general, the dynamics of the field will exhibit two sets of time constants, which depend on the recombination rates, charge generation and trapping rates, and mobilities of both species. The behaviour cannot be expressed using separate time constants for electrons and holes, except for the case of trap-limited field. The space-charge field takes the form of

$$E_{sc}(t) \propto \left[N_{sc}^+ e^{-\Gamma_e t} + P_{sc}^+ e^{-\Gamma_h t} \right] \quad (1)$$

for the decay, and something similar for the rise. The coefficients are the steady-state trapped charge densities for electrons (N) and holes (P). There is a minus sign implicit in the P coefficient. For PR polymers, each component would have two time constants to include effects occurring on both long and short time scales.

There are three primary regimes of this model. If the strongest grating is the slowest, then the SC field will go through a reversal during writing as the weak grating buildups first but is eventually overcome by the stronger. If both gratings have the same magnitude, the efficiency will exhibit some non-zero dynamics but the steady-value will be zero. If the strongest grating is the fastest, then the SC field will reverse only during the decay, as the strongest grating decays first. It is the latter case that applies to the dynamics observed in these samples. The SC field is not trap-limited so the behavior of each grating cannot be assigned exclusively to electrons or holes.

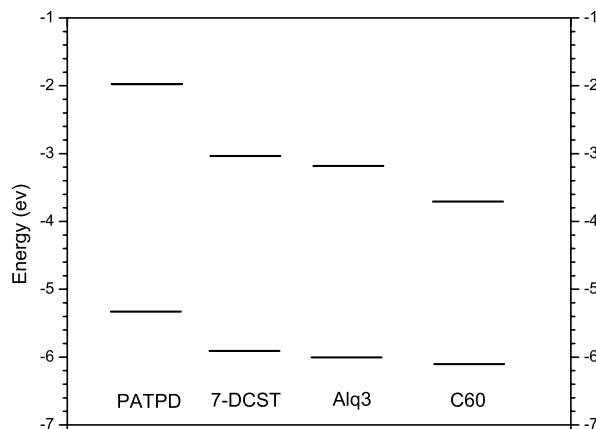


Figure 2. HOMO and LUMO levels of components in the samples studied.

The energy levels of the components are shown in Figure 2. At 532nm, electron-hole pairs are generated in both the 7-DCST and the C₆₀. Holes can be injected into the PATPD transport levels and become trapped in conformational structures or C₆₀ anions. Electrons in the C₆₀ will remain in the LUMO given the energy levels, but in the 7-DCST they can be injected into either the Alq₃ or neutral C₆₀. Given that C₆₀ has a higher molecular weight, smaller loading, and can be reduced via illumination, the number density of Alq₃ is at least 4 times larger, and thus be the primary electron trapping site. This interpretation is supported by the fact that at 633nm, the absorption of 7-DCST is greatly reduced (absorption coefficient of 40 cm⁻¹) and no complementary grating dynamics are observed on time scales of about 10 mins. It is expected that the electron transport necessary for the formation of the competing grating is occurring via the chromophore, though direct measurements are needed.

4. CONCLUSION

Evidence of bipolar charge transport leading to competing grating dynamics in PR polymers with Alq₃ has been observed. The grating manifests itself as a recovery of the efficiency after a decay time of a couple minutes, which is not

seen in samples without Alq₃. This has several beneficial applications involving holography. It can increase the sensitivity of PR polymers, which is orders of magnitude less than static photographic emulsions, improves the trap density necessary for reflection geometries and pulsed laser writing, and increases the dielectric breakdown strength, which is often the limiting factor real-world applications.

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