

Recent Advances in Photorefractive Polymers

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ABSTRACT

Photorefractive composites derived from conducting polymers offer the advantage of dynamically recording holograms without the need for processing of any kind. Thus, they are the material of choice for many cutting edge applications, such as updatable three-dimensional (3D) displays and 3D telepresence. Using photorefractive polymers, 3D images or holograms can be seen with the unassisted eye and are very similar to how humans see the actual environment surrounding them. Absence of a large-area and dynamically updatable holographic recording medium has prevented realization of the concept. The development of a novel nonlinear optical chromophore doped photoconductive polymer composite as the recording medium for a refreshable holographic display is discussed. Further improvements in the polymer composites could bring applications in telemedicine, advertising, updatable 3D maps and entertainment.

Keywords: Photorefractive polymers, holography, 3D display, nonlinear materials, high diffraction efficiency materials.

1. INTRODUCTION

The photorefractive (PR) effect, originally discovered in inorganic crystals more than 40 years ago, initially drew attention as a perceived detriment to non-linear applications in these materials [1, 2]. First, the process was reversible though also fixable, allowing both read/write and read-only applications, as opposed to standard photographic films which could only be written once. Second, the non-local nature of the process allowed coupling and energy transfer to occur between two coherent beams. Organic polymer materials compared to inorganic materials have the inherent advantages of ready manipulation of component formulations to suit a given application and low cost [3, 4]. The structural constraints were also relaxed in polymers, allowing them to be custom made into different geometries, and samples can be made much larger than is typical for crystals. The dielectric constant is also smaller, which reduces the electric field screening of trapped charges and increases the quality factor. The highly customizable doping process is also easier compared to crystals, where dopants are typically expelled during crystal growth. PR polymers now outperform inorganic counterparts in diffraction efficiency, two-beam coupling gain, and sensitivity.

Due to this tremendous progress many applications have appeared, including optical communication[5] and imaging through scattering media [6], all with different material challenges that can be met by these highly versatile polymers. Recently, they have been shown to function in dynamic holographic displays [7], which are of use in medical imaging, industrial design, defense applications, and air traffic control, among other emerging areas such as telepresence. Unlike other permanent media for recording holograms, PR polymers are reversible and require no post-processing. They demonstrate fast response time, long persistence, and high diffraction efficiency, which are necessary material properties for such an application. However, progress in other areas has not been as rapid, particularly in the area of sensitivity. In the visible, the sensitivity is still orders of magnitude smaller than that of permanent films used for recording static holograms.

Here we discuss the recent progress in the field of photorefractive polymers, including new hole-transporting polymers for reduced glass transition temperature (T_g) and high mobility. Particularly, a bis-triarylamine side-chain host polymer exhibits less deep trapping leading to stable dynamics independent of the illumination history. New composites

with excellent sensitivity in the near IR wavelengths have extended the range of high performing polymers beyond the visible. Finally, some material considerations necessary for specific applications are also taken into account, such as pulsed writing for high speed operation of many devices, and updatable holographic displays. Optimized materials have been shown to exhibit good performance even under single pulse nanosecond writing times, enabling operation at 100Hz or more, which is faster than CW recording schemes.

2. PR POLYMER COMPONENTS

In a typical PR guest-host system, a hole-transporting polymer matrix is doped with a photo-reducible molecule (photo-sensitizer) that can either absorb light or form a charge-transfer complex with the hole-transport polymer. Upon excitation the photo-sensitizer injects a hole into the transport system and a NLO chromophore subsequently produces the field-dependent refractive index. As the highest index modulations arise from birefringence produced by the dynamic orientation of the chromophores, a T_g close to room temperature is a desired property. Small molecules are often added to the mixture to act as plasticizers thereby lowering T_g .

Considerable advances have been accomplished in photorefractive polymer composites since their first discovery. A variety of different types of functional materials have been developed with large gain and high efficiency, such as guest-host composites, fully-functionalized polymers, polymer-dispersed liquid crystals, and amorphous glasses. This paper will focus on guest-host composites. Guest-host composites delegate the functions required for photorefractivity to separate polymer constituents, allowing a high degree of customizability and wide range of material parameters to be achieved. This versatility generally comes at the cost of potential phase separation due to the mixing of polar and non-polar molecules. Hence, careful material manipulations should be undertaken to achieve high quality photorefractive polymer composites.

2.1 Charge Transporting Agent (CTA)

The CTA is an oxidizable host polymer that can efficiently transport charges leading to charge separation and the non-local nature of the PR effect. In the vast majority of samples, the holes are the most mobile carriers, though electron transport and trapping has also been studied. To be effective, the CTA should be chosen such that the charge transporting moieties are highly conjugated with delocalized π -electrons. It should also be an electron donor capable of accepting a hole from the sensitizer molecule (in the case of hole transport). The latter condition requires the HOMO level to be above that of the sensitizer to energetically facilitate charge transfer. Transport through the CTA will occur as electrons are transferred between charged and neutral moieties. The CTA is generally included with a high enough loading for transport to occur via hopping. Electric fields are applied since the mobility is highly field dependent.

The chemical structures of some typical transporting agents are shown in Figure 1. Carbazole-containing polymers are very common and highly successful, such as poly(vinyl carbazole) (PVK), which the first high performance composites utilized [8], and polysiloxane-based (PSX) [9] polymers. A few other conjugate polymers have drawn attention as well, due to the generally higher drift mobilities and reduced polarity leading to more stable mixing. Triarylamine-containing side chain polymers, such as poly(acrylic tetraphenyldiaminobiphenyl) (PATPD) have been as successful as PVK-based samples, and the response time is not dependent on the history of illumination [10]. Others include poly(phenylene vinylene) (PPV) copolymers, which have also shown superior steady-state performance compared to PVK systems.

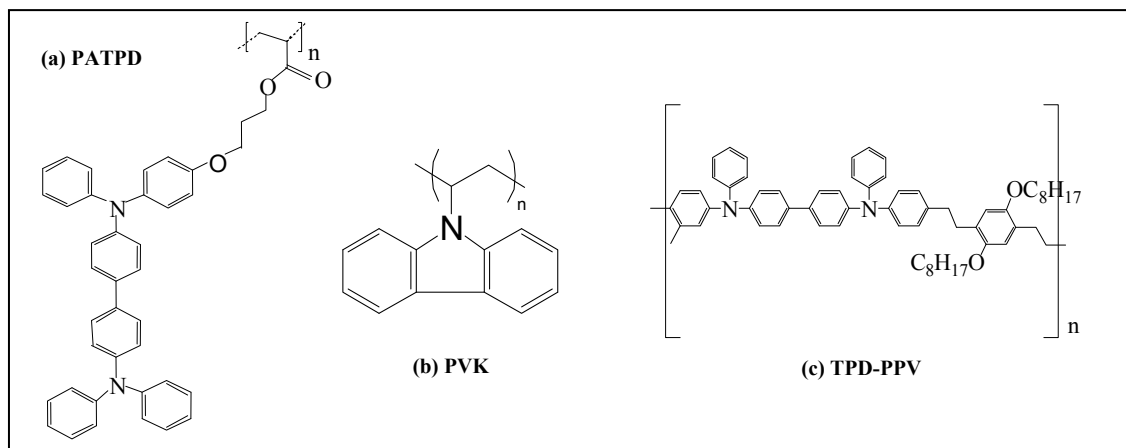


Figure 1. Some commonly used hole transporting polymers. (a) Tetraphenyl-diaminobiphenyl (TPD) pendant group attached to a polyacrylate backbone through an alkoxy linker. (b) poly(n-vinyl carbazole) (PVK). (c) poly(arylene vinylene) copolymer (TPD-PPV).

2.2 Nonlinear chromophores

The chromophore provides the modulation of the refractive index in response to the development of the space-charge field. It can in general achieve this either through orientational birefringence or the linear Pockels electro-optic effect. Thus, the molecule must have either a large linear polarizability anisotropy (birefringence) or first hyperpolarizability (electro-optic), and in both cases must have a large ground state dipole moment. A widely accepted expression for quantifying the chromophore quality and optimizing these two contributions to the index modulation is given by

$$FOM = \frac{1}{M_W} \left[9\mu\beta + 2 \frac{\mu^2 \Delta\alpha}{k_B T} \right]$$

where M_W is the molar mass of the chromophore, μ is the dipole moment, β is the second order polarizability, $\Delta\alpha$ is the linear polarizability anisotropy, k_B is Boltzmann's constant, and T is the temperature. A two-state four-orbital model assuming non-interacting electrons predicts that the hyperpolarizability maximizes for specific donor and acceptor strengths for the given conjugated bridge. A few of the commonly used chromophores are shown in Figure 2.

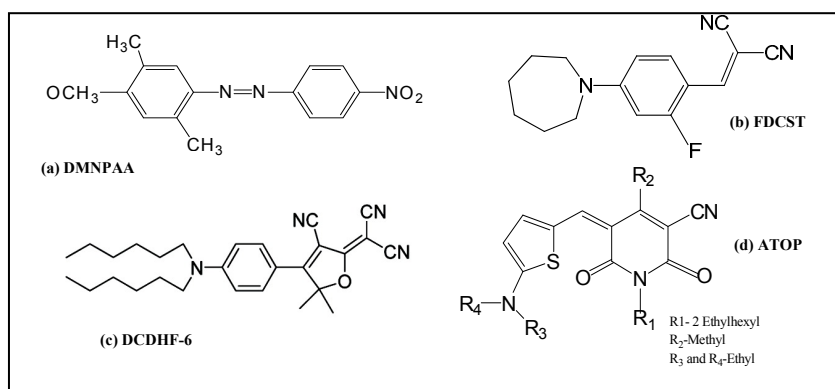


Figure 2. Some high-performing chromophores. (a) 2,5-dimethyl-4-(p-phenylazo)anisole (DMNPAA). (b) a fluorinated dicyanostyrene 4-homopiperidino benzylidene malonitrile (FDCST). (c) 2-dicyanomethylene-3-cyano-2,5-dihydrofuran (DCHHF-6). (d) amino thienyl-dioxopyridine (ATOP).

2.3 Sensitizer

Photogeneration of charges is provided by a molecule with proper absorption at the wavelength of interest. This sensitizer will form a charge transfer complex with the CTA, allowing the charges to be efficiently transferred between the separate functional components. In the case of primarily hole conduction, the sensitizer will inject a hole into the material by accepting an electron, becoming reduced. For the PR effect to be reversible, it should also be oxidizable to allow it to return to the original state. The sensitizer must have its HOMO well below that of the CTA to ensure efficient transfer. Marcus' theory describes the physics of this charge-transfer process [11]. In order to obtain large photogeneration efficiency, the difference between the ionization potential of the donor and acceptor should be large.

2.4 Plasticizer

Since the orientational birefringence is the largest source of index modulation, the T_g of the material must be at or near the operating temperature, which is usually room temperature. Usually the T_g of composites with high molecular weight polymers are much higher than room temperature. To counter-act this, plasticizers may be added to the composite to reduce the T_g . They do not typically participate in charge generation and trapping, and are thus inert, though they do reduce the functional volume by diluting the charge transport matrix.

3. SAMPLE PREPARATION AND DEVICE FABRICATION

An effective PR polymer composite comprises a host polymer with high charge mobility and carefully selected components that provide all the functionalities needed to achieve PR response. The preparation of the polymer composite is carried out by dissolving all the components in a common solvent, evaporating off the solvent using a rotary evaporator, and then completely drying the sample in a vacuum oven. The dried product is then melted between glass plates several times to ensure uniform mixing. A small portion of this composite is sandwiched by melting between two ITO glass finger electrodes with the desired film thickness set by glass spacer beads placed in between the ITO coated substrates. The assembled sample is rapidly cooled down to room temperature to avoid crystallization of the composite. The devices are sealed with epoxy to limit the exposure of the material to the environment.

4. PHOTOREFRACTIVE CHARACTERIZATION

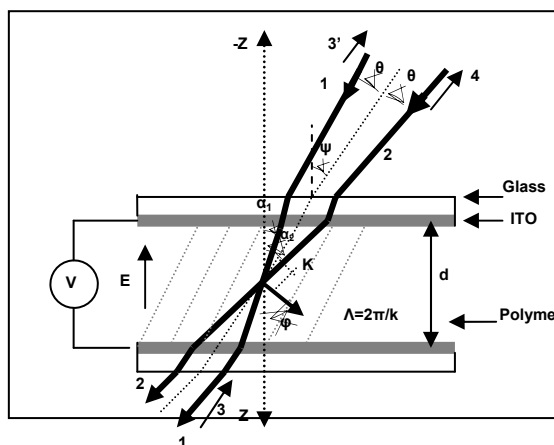


Figure 3. The slanted transmission geometry used for photorefractive four-wave mixing. Writing beams 1 and 2 intersect within the sample. The reading beam 3 partially diffracts from the grating to produce beam 3' which is counterpropagating with respect to beam 1 and beam 4 is the transmitted beam counterpropagating with respect to beam 2.

Steady state four-wave mixing has frequently been used as a technique for characterizing PR polymers. The intensity of the diffracted beam is monitored as a function of the applied field. In a four-wave mixing experiment, as shown in Figure 3, a reading beam (3) is diffracted from the grating written by two interfering writing beams (1 and 2) which are incident from one side of the sample. The sample surface is usually tilted 60° (ψ) with respect to the sample bisector. The writing beam incident angles are α_1 and α_2 . The grating vector is given by k and a is the sample thickness. A low intensity reading beam is used to minimize its effect on the grating compared to the writing beams; the reading to writing beam intensity ratio is generally 1:10. The reading beam can be at the same or a different wavelength from the writing beams and its direction has to be adjusted to satisfy the Bragg condition. A well-known configuration is degenerate four-wave mixing where all beams have the same wavelength and the reading beam (3) partially diffracts from the grating written by the writing beams to produce a fourth beam (3'). In this configuration, the diffracted beam (3') is counterpropagating with respect to the writing beam (1) and the Bragg phase-matching condition is automatically fulfilled. Beam 4 is the transmitted beam counterpropagating with respect to the second writing beam (2). When the readout wavelength is different from the writing beams, it is called non-degenerate four wave mixing. A careful selection of the polarizations and relative powers of the writing and reading beams maximizes the visibility of the phase grating and minimizes the interaction between the writing and reading beams. The strength of the grating is expressed in terms of the diffraction efficiency which can either be internal or external. The internal diffraction efficiency is defined as the ratio of intensity of the diffracted beam to that of the transmitted beam in the absence of a grating ($\eta_{int} = I_{diff} / I_{tran}$). The external diffraction efficiency is the ratio of the diffracted beam intensity to the incident intensity ($\eta_{ext} = I_{diff} / I_{inci}$).

5. PR POLYMER FOR APPLICATIONS

There are many proposed applications for organic PR polymers, for which all the previous material developments will assist to various degrees. They include tissue imaging, beam cleanup and dynamic displays. In this section, we will discuss the specific material aspects required to realize some of these applications, namely pulsed writing required for many high speed devices, and holographic displays.

5.1 Pulsed writing

One of the primary advantages of recording a grating with pulsed writing beams is that sufficient writing energy can be delivered in much shorter amounts of time than in CW. This will decrease the writing time but also makes the entire process very insensitive to vibration which can provide even further improvements in speed. The issue of decreasing overall writing time then transfers from delivering enough energy in a given time, to developing lasers with higher repetition rates. This requires a material that can respond to such brief impulses.

In one of the previous studies conducted [12], a PR composite consisting of PATPD/7-DCST/ECZ/C₆₀ (54.5/25/20/0.5 wt.%), 105 micrometer thick, was illuminated with two 532nm writing beams about 1ns in duration (total fluence of 4 mJ/cm²). Under single pulse exposure, a maximum diffraction efficiency of 56% was observed in 1.8ms after illumination, as charge transport, trapping, and chromophore orientation continued after illumination. An applied field of 95 V/micrometer was used in a standard geometry with a 60° slant and an inter-beam angle of 20°. In CW recording, the same sample exhibits near 100% efficiency with a response time of 4ms under a similar fluence.

Quantitative temporal characteristics were obtained by fitting the curve to a modified exponential function. Since grating formation and decay are occurring at the same time, each of which is typically characterized by two time constants, a total of four time constants were used:

$$\Delta n \propto [1 - m_1 \exp(-t/t_1) - (1 - m_1) \exp(-t/t_2)] \times [m_2 \exp(-t/t_3) + (1 - m_2) \exp(-t/t_4)]$$

$$\eta \propto \sin^2(B\Delta n^2)$$

All the fit parameters for single pulse illumination are shown in Figure 4. The fast time constant was 300μs, with a weighting factor of 0.54. The slowest time constant for the decay portion was 74.4ms. The effect of pulse energy was

studied by writing with different fluences. The fact that the peak power is also changing will not affect the PR process, since the number of charges generated is only affected by the total number of photons absorbed

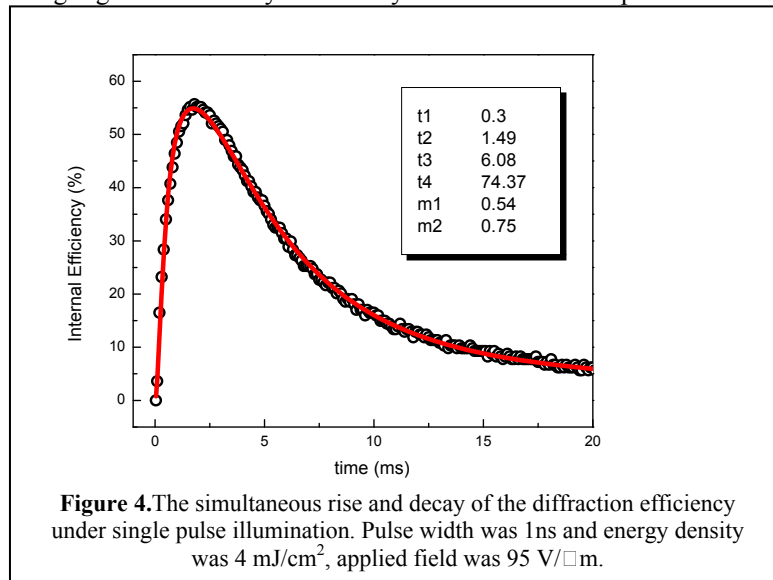


Figure 4. The simultaneous rise and decay of the diffraction efficiency under single pulse illumination. Pulse width was 1ns and energy density was 4 mJ/cm², applied field was 95 V/μm.

which are independent of writing intensity.

A primary goal of such a device is to operate at the fastest possible speed for the desired application, at least as fast as the repetition rate, which can be around hundreds of Hz. To achieve this goal, the grating must form to a significant extent and decay within 10ms so that new information can be recorded. The grating forms within 1-2ms, and the decay can be accelerated by uniform illumination. Gated illumination for 5ms with a CW 532nm beam was used. Since it cannot be present during the grating formation, a variable time delay is used for the gating. At an energy density of 6 mJ/cm², the entire write-read-erase process was completed within 10ms. The delay as well as the intensity and nature (cw or pulsed) of the erasing can be adjusted to optimize the signal-to-noise ratio during the reading process.

While this constitutes a significant increase in the dynamic response, some applications will require even faster writing times, such as those involving large area devices and storage. A recent report [13], shows a grating written with 130 fs pulses at 800nm in PVK samples sensitized with TNFM. With an average intensity of 3.5 mW/cm², the diffraction efficiency reported is 2%, lower than for the PATPD samples under ns exposure, but much higher repetition rates are achievable (80 MHz) with these lasers; this would require materials with response times on the order of 10 ns. However, as faster lasers are used, the spectral bandwidth increases, which may reduce contrast from unintentional spectral multiplexing.

5.2 Updatable 3D Holographic Displays

Three-dimensional perception is fundamental to the human interaction with the world, since our brains are accustomed to processing more than just a single image to understand a situation. There are many applications where 3D displays would yield a significant advantage in terms of adaptation and functionality, including medical imaging, industrial design, and terrain mapping.

Current popular 3D imaging techniques rely on stereoscopic rendering that requires special eye-wear, at the expense of user fatigue and lack of depth. Holographic displays can reproduce very high quality images without these drawbacks, but to date have been made with either static photopolymers [14] or dynamic media with small-size and low resolution.

Organic PR polymers have the potential to bridge this gap between speed and viewing experience, with large diffraction efficiencies, fast writing times, large area, phase stability, and reversible recording process. Recently, just such a composite has been demonstrated, combining all of these properties [7] into the first updatable holographic 3D

display based on PR polymers. A copolymer is used as the hole-transporting agent to reduce the phase separation, allowing increased loading of the chromophores. The copolymer consists of a polyacrylic backbone with pendant groups tetraphenyldiaminobiphenyl-type (TPD) and carbaldehyde aniline (CAAN) attached through an alkoxy linker (PATPD-CAAN) in a ratio of 10:1. A fluorinated dicyanostyrene (FDCST) NLO chromophore was added to provide sufficient refractive index change and charge generation at the wavelength of interest (532nm). ECZ was also used to reduce the glass-transition temperature to room temperature. The ratios of PATPD:CAAN/FDCST/ECZ were 50/30/20 wt.%. The display film was 105micrometer thick with an active area of 4inches \times 4inches for the display. It showed no phase separation in an accelerated aging test at 60°C for 7 days, nor any degradation or damage for several months over hundreds of write/erase cycles. The absorption coefficient at 532nm is 90cm⁻¹.

This sample showed approximately 90% diffraction efficiency for a 105 μ m at 4kV in the standard slanted transmission geometry at 532nm. This sample was slower than the fast PR composites, though at 9kV an intermediate peak is reached after 1s of writing. This permits writing the display at this voltage and sets the time scale of the recording process. Even though this peak is only at 10%, it is not the steady-state diffraction efficiency.

The hologram for the 3D display is generated using integral image holography. More details on the writing system, including the optical setup, recording parameters, and hogel generation are discussed in the previous literature [7]. Briefly, dozens of 2D perspectives of an object are processed on a computer and then optically multiplexed onto the recording medium in a manner such that when reconstructed, the sensation of depth is created via parallax. The reference and object beam interfere in the sample in a Fourier transform geometry. The hologram is written by successively recording approximately 120 holographic pixels, or “hogels” side by side. Given the geometry of the human vision, horizontal parallax only is used, so the hogels are vertical stripes. 532nm light is used with a total writing intensity of 0.1 W/cm². Given the transients, each hogel is written for 1s, so the overall writing time is then 3-4 minutes for a 4inch \times 4inch sample. After writing, the sample is translated to a new position and the hologram read using a 650nm LED lamp. The image is visible for about 3 hours of continuous viewing, but erasing can be done at any time by illuminating the sample with a homogeneous beam at 532nm. Some images produced by this process are shown in Figure 5.



Figure 5. 2D images of the 3D holographic images produced from updatable display setup. Images are taken at different camera locations to demonstrate occlusion and parallax. The right-most images are one frame from the computer model used to generate the holograms.

6. CONCLUSIONS

Photorefractive polymers have advanced to such a level that devices with large figures-of-merit are readily available. They outperform their inorganic counterparts in diffraction efficiency, sensitivity and two beam coupling gain. They are attractive for the reversibility of the process, sensitivity from the visible to the infrared, and highly customizable fabrication, so that new ideas can be tried with relative ease. Thus, the current forefront of the research is on developing materials for specific applications and assessing their performance in real-world schemes. In particular, recent applications that have been demonstrated include 3D holographic displays with potential medical, military, and industry uses, and accurate imaging through highly scattering media such as tissue for non-invasive diagnoses.

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