Hybrid Photorefractive Material Composed of Layered Conjugated Polymer and Dye-Doped Liquid Crystal Films

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The development of photorefractive materials for modern optical signal processing applications such as image amplification, phase conjugate mirrors, and dynamic holography has recently generated wide interest.[1−7] The photorefractive effect results from the creation of a space-charge field in a nonlinear optical material produced by the photogeneration of ion pairs in the illuminated fringes of an optical interference pattern followed by differential diffusion or drift of the opposite charges and subsequent charge trapping. The resultant space-charge field modulates the refractive index of the nonlinear optical material, which leads to asymmetric energy exchange (two-beam coupling) between the two laser beams that generate the interference pattern in the material. Research on photorefractive polymers[1,8,9] and doped liquid crystals (LCs)[3−7] seeks to optimize optical nonlinearity, charge generation, and charge trapping, while moving toward near-infrared wavelengths of interest to optical communications. Films of homeotropically aligned (i.e., perpendicular to a surface), dye-doped, nematic LCs exhibit significant photorefractive effects.[3,6,10] In addition, homogeneously aligned (i.e., parallel to a surface), nematic LCs containing no added dye dopants are also photorefractive.[11−13] The rapid reorientational response of LCs to a space-charge field generated in these materials is one of the principal advantages to using LCs for photorefractive materials. In addition, the use of very low voltages applied to these materials to induce charge transport, usually less than 2 V, is another attractive feature relative to other photorefractive materials. It is well-known that unidirectionally rubbed thin polymer films align LCs along the rubbing direction.[14,15] Here we report photorefractivity in a multifunctional layered material consisting of a nematic LC film doped with an electron acceptor that absorbs red light and a rubbed conjugated polymer film that aligns the doped LC as well as functions as an electron donor and charge transport agent.

A solution of poly(2,5-bis(2′-ethylhexyloxy)-1,4-phenylenevinylene (BEH-PPV) ($M_n = 87$ kDa) in 3/1 (v/v) xylenes/chloroform was spin-coated onto conductive indium tin oxide (ITO) coated glass (Delta Technologies, 100 ohms/sq) to give a film about 100 nm thick. The polymer layer was rubbed unidirectionally using velvet cloth. Two of these polymer-coated ITO glass slides were used to construct a cell in which the rubbed direction of the polymer coatings were parallel, and a path length of 26 μm was established using a cellulose triacetate spacer (Figure 1). A eutectic mixture of 35% 4′-(*n*-octyloxy)-4-cyanobiphenyl (8OCB) and 65% 4′-(*n*-pentyl)-4-cyanobiphenyl (5CB) containing 0.027 mM 1,7-bis(*N*-piperidinyl)-3,4;9,10-perylenebis(dicarboximide) (6PDI), a green dye whose synthesis and characterization are presented elsewhere,[16] was introduced into the cell. The rubbed BEH-PPV layer aligns the LC director in these optically clear cells in a direction parallel to the rubbing direction (Figure 1), as verified using polarized light spectroscopy.

An optical interference pattern was generated in the cell by crossing two 7.5 mW, 1 mm diameter, p-polarized beams from a He:Ne laser operating at 632.8 nm at angle $\theta = 0.53°$, which fixes the grating spacing at $\Lambda_g = 37\ \mu$m. The normal to the cell is tilted at $\beta = 30°$ relative to the bisector of the two crossed laser beams. The tilt angle ensures that there will always be a component of the direction of charge migration along the grating wave vector. Illumination of the cell with 633 nm light selectively excites only 6PDI because the optical absorbance of both BEH-PPV layers together at 633 nm is $A = 1.5$ cm^{-1}, while that of the 6PDI is $A = 33$ cm^{-1}. Selective excitation of the 6PDI electron acceptor is critical to the successful generation of a reversible photorefractive grating in this material because excitation of the BEH-PPV polymer layer alone over a period of several hours results in irreversible grating formation due to thermal or photochemical damage of the BEH-PPV film. These absorption gratings are easily distinguished from photorefractive gratings (see below). Two-beam coupling experiments were conducted in the thin grating (Raman−Nath) regime, which results in multiple diffracted beams emerging from the cell for each incident beam. The beam-coupling ratio is the gain (or loss) of energy in each zero-order beam

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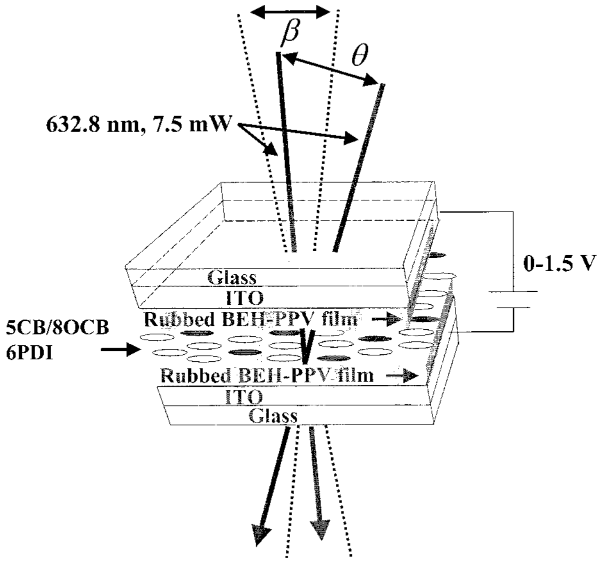

Figure 1. Schematic representation of the layered structure of the polymer and LC films within the photorefractive cell as well as the geometry of the input beams.

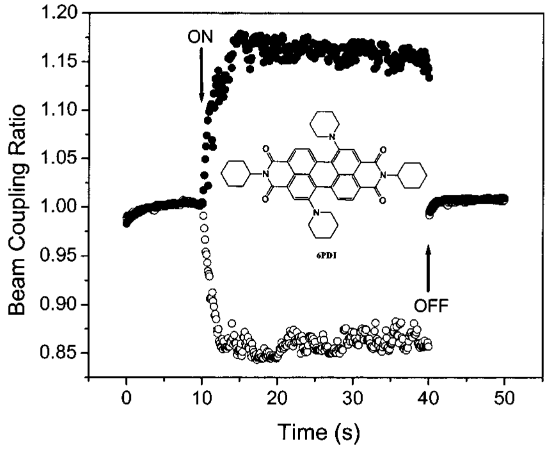

Figure 2. Asymmetric two-beam coupling data for 0.027 mM 6PDI in a homogeneously aligned 5CB/8OCB mixture in the cell illustrated in Figure 1 with 1.2 V applied.

emerging from the cell relative to its incident energy and is monitored by a photodiode. A maximum of 1.5 V dc was applied across the cell to induce charge transport, corresponding to an electric field of only 0.58 kV/cm.

The concentrations of 6PDI and the polymer film thickness were both varied to find the optimum photorefractive performance, which is illustrated in Figures 2 and 3. Figure 2 shows the onset of two-beam coupling within the BEH-PPV/6PDI/LC composite characteristic of the photorefractive effect, when both laser beams strike the cell at 10 s, and the disappearance of the effect when one of the beams is blocked at 40 s. Two-beam coupling occurs only when the external electrical field is applied and p-polarized light is used, which supports the fact that the observed two-beam coupling is due formation of a photorefractive grating and is not due to a thermal or absorption grating.[3,17] Figure 3 plots the first-order diffraction efficiency (η) of the photorefractive grating, which is the ratio of the intensity of the first diffracted beam to that of the incident beam as a function of applied voltage. The diffraction efficiency increases monotonically as expected reaching a value of about 4% at 1.5 V applied. Despite the relatively low diffraction efficiency observed, the inset to Figure 3 shows that the beam-coupling ratio reaches about 30% as the applied voltage is increased to 1.5 V. Thus, asymmetric energy exchange is reasonably efficient. We report beam-coupling ratios rather than exponential gain coefficients for photorefractive materials in the thin grating regime because the gain coefficient is poorly defined for thin gratings.

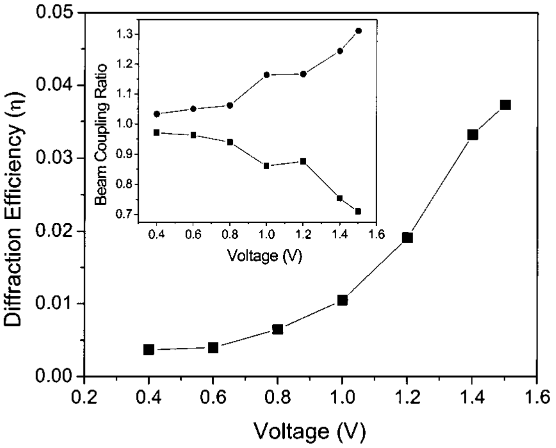

Figure 3. First-order diffraction efficiency (η) of the photorefractive grating for the BEH-PPV/6PDI/LC system. The inset shows the dependence of the beam-coupling ratio on voltage applied to the cell.

Photoexcitation of 6PDI produces its lowest excited singlet state, ^{1*}6PDI, which has an energy of 1.77 eV.[16] Electron transfer from the BEH-PPV polymer film to nearby ^{1*}6PDI molecules results in formation of 6PDI$^-$ ($E_{\mathrm{RED}} = -0.64$ V vs SCE)[16] and hole injection into the polymer layer ($E_{\mathrm{OX}} = 0.9$ V vs SCE). Previous work from our laboratory on homeotropically aligned nematic LCs, in which both BEH-PPV and a naphthalene-1,8:4,5-bis(dicarboximide) electron acceptor are dissolved, showed that the space-charge field in these composites is created by diffusion of the reduced electron acceptor in the LC as well as hole transport by drift through the conjugated BEH-PPV structure.[18] In this study we have shown that the BEH-PPV polymer can serve as a solid-state alignment agent for LCs, as well as an electron donor, and a hole transport material, which greatly simplifies photorefractive device construction.

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