

# The role of surface charge field in two-beam coupling in liquid crystal cells with photoconducting polymer layers

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In liquid crystal cells with photoconductive *poly(N-vinyl carbazole)* polymer layers, an external dc field can be completely screened by surface charge layers that develop at the liquid crystal–polymer interface. Under spatially modulated illumination, surface charge layers can be discharged in bright areas and lead to reorientation and spatially modulated Freedericksz transition. As a result, an asymmetric energy exchange in the photorefractive two-beam coupling process can take place. We propose a model to explain the origin of reorientation and phase shift in the two-beam coupling process, based on the profile and tilt of the refractive index grating. We also show that cells with just one photoconducting layer are more efficient than a typical design with two layers. © 2004 American Institute of Physics. [DOI: 10.1063/1.1778818]

## I. INTRODUCTION

Two-beam coupling has been widely investigated in different liquid crystal systems.<sup>1–3</sup> The electro-optic response and the buildup of a refractive index grating in liquid crystals' cells arise from the reorientation of molecules due to an induced space charge field<sup>4</sup> and this effect has been named the “orientational photorefractive effect” (or “photorefractive-like effect”).<sup>4–6</sup>

In this work, we focus our attention on structures containing liquid crystals and photoconducting polymer layers. The aim of our work was neither optimization nor achieving higher coupling coefficients than those reported earlier,<sup>2,3</sup> but to study the role of surface effects and their contribution to reorientation in the two-beam coupling process.

One of the arrangements for observing two-beam coupling involves the use of cells containing separate layers of liquid crystal and photoconductive polymer [*poly(N-vinyl carbazole)*], known as PVK, doped with the photosensitizer trinitrofluorene TNT.<sup>3,7</sup> The role of such a polymer is not only to impose order on liquid crystal molecules, but also to significantly contribute to the nonlinear response of the whole structure. Dopants such as TNF, pure C<sub>60</sub>, or mixtures<sup>8,9</sup> of C<sub>60</sub> and C<sub>70</sub> make PVK photosensitive to visible light. High photoconductivity of doped PVK means that upon exposure to light, any accumulated space charge field can be discharged. This photoinduced discharge process is, in fact, the basis of xerography.<sup>10</sup>

While it is widely accepted that the reorientation of liquid crystal molecules is responsible for the formation of a two-beam coupling grating, the actual mechanism of the electric field buildup inside the cell has not been explained in detail. For example, several groups have studied two-beam coupling in similar liquid crystal–photoconducting polymer systems, yet proposed different explanations of the mecha-

nism involved in the formation of the space charge field. Ono and co-workers<sup>11</sup> attributed the origin of the space charge field to the generation of charges in a PVK layer and their subsequent trapping in an insulating polyvinylalcohol (PVA) layer, adjacent to the PVK. PVA was reported as essential for the buildup of the space charge field. Mun and his group,<sup>12</sup> however, studied cells with different combinations of the alignment layers and dopants in both polymer and liquid crystal layers. They concluded that since charge photogeneration occurs in the liquid crystal bulk, followed by charge trapping at a PVK surface, PVA layers are not necessary. While the models of the mechanism of the space charge field proposed in these papers were quite different, both groups<sup>11,12</sup> assumed that dc electric field alone induced uniform reorientation of the liquid crystal director, followed by spatially modulated deviation of director. Light contributed to the buildup of space charge field and that field caused further reorientation of the director.

Moreover, in spite of some differences in theoretical models adapted, their experimental results were, in fact, very similar. The minor differences reported were most likely to be due to specific samples and measurement techniques used by the two groups. The experimental results<sup>11,12</sup> included the measurements of the diffraction and two-beam coupling gain. However, such data do not provide any direct evidence for a particular mechanism involved in the formation and change of reorientation grating. More detailed studies of light, electric field, and interaction geometry are needed to assess more fully the role of such surface effects.

Reorientation and two-beam coupling have also been investigated in liquid crystal cells with nonphotoconducting polymer layers.<sup>13,14</sup> The results of Pagliusi and co-workers highlighted the fundamental role of interfaces for two-beam coupling and light-induced reorientation. They carried out experiments in cells with different combinations of polymer

and liquid crystals, namely, polymers such as PVA and LQ1800, and liquid crystals E7 and BL001 from Merck. The effect of light and dc field induced reorientation of liquid crystals depended on the type of polymer alignment layer and the liquid crystal used. Their results indicate that accumulation of charges on surfaces adjacent to liquid crystals is not only limited to the case of photoconductive polymers. However, for the case of their specific structures, the field produced by these surface charges was much lower than that in cells with photoconducting polymers. Intensity dependent threshold of reorientation was also observed in cells with 5CB and Kapton polymer. Light-induced desorption of ions and change in their concentration was suggested as the cause of the redistribution and increase of electric field at surface<sup>15</sup> that, in turn, changed the anchoring energy of molecules.

When investigating the Freedericksz transition and two-beam coupling in samples with pure PVK and PVK:C<sub>60</sub> alignment layers filled with E7 liquid crystal mixture, we have observed several features of this system. First, our results reveal a different picture of reorientation. In cells with at least one pure PVK polymer layer, the reorientation of the director by an external dc field is only transient. Depending on the experimental conditions, but less than 1 s after a dc field is applied, its influence on the liquid crystal bulk becomes negligible. We will show that this effect is due to accumulation of surface charge layers.

While the buildup of surface charge layers in other systems, for example, dye-doped liquid crystals, has been observed previously,<sup>16</sup> there are no reports, to the best of our knowledge on double charge layers capable of screening high electric fields in liquid crystal–photoconducting polymer structures. Moreover, we have observed that the threshold of reorientation for a sample with a PVK:C<sub>60</sub> alignment layer depended on incident light intensity. Additionally, we found that the direction of an easy axis on PVK was orthogonal to the rubbing direction.<sup>17</sup> Finally, we have observed that cells with just one photoconductive layer were as efficient, in terms of two-beam coupling, as cells with two photoconductive layers, the design adopted in all earlier publications.<sup>3,11,12</sup>

As expected, our experimental data on two-beam coupling, which we will present in detail in the following section, are in good agreement with previously published results.<sup>3,11,12</sup> Our data are also consistent with the results obtained in cells with nonphotoconducting polymer layers.<sup>13</sup>

## II. EXPERIMENT

### A. Preparation and deposition of polymer layers

We have developed a method of doping PVK with photosensitizer (C<sub>60</sub>) and depositing it as a thin and uniform layer onto ITO covered glass substrates. While C<sub>60</sub> is soluble in organic solvents or liquid crystals, its saturated concentration is highly dependent on the type of solvent.<sup>18</sup> After testing several solvents, we chose chlorobenzene which has a solubility of about 7 g/l at room temperature. PVK can be dissolved in a variety of organic solvents, but chlorobenzene was also chosen for PVK to avoid dropping down a C<sub>60</sub> sediment. This process occurs if a chlorobenzene/C<sub>60</sub> solu-

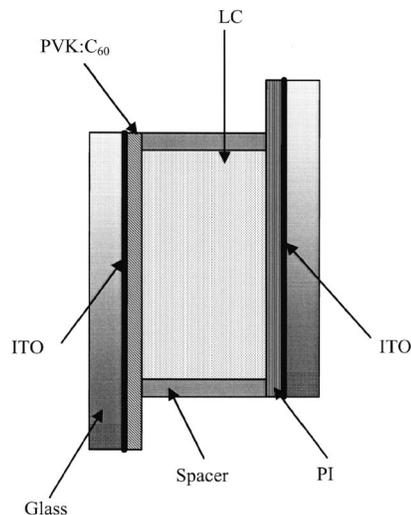


FIG. 1. Combined cell structure.

tion is mixed with another solvent. Doping of PVK with C<sub>60</sub> was achieved by adding a saturated concentration of C<sub>60</sub> solution to the PVK solution. Maximum estimated dopant concentration of C<sub>60</sub> in the PVK (dry layer) used in our experiments was approximately 14.9% by weight.

Polymer films were deposited onto clean ITO covered glass substrates by spin coating at 3000 rpm. The concentration of PVK solution was 20 g/l. After spin coating, substrates were dried at 90°C and 30 min and at 180°C for 60 min. The film thickness produced was of order 0.1 μm.

The substrates were unidirectionally rubbed with velour cloth to achieve planar homogeneous alignment of the liquid crystals. Uniform and stable alignment was achieved for cells with rubbed PVK substrates and subsequently filled with E7.

In some cells we also used polyimide (PI) as an alignment layer. Polyimide solution, dissolved additionally in acetone, was spin coated on substrates to produce a very thin, but uniform film. After prebaking and rubbing, it produced high quality and stable liquid crystal alignment.

### B. Liquid crystal–polymer cells

The cell configurations investigated included those with (i) both substrates having identical polymer layers and (ii) cells combining substrates with different polymer layers. In this paper we will refer to these types as “symmetrical” or “combined” cells, respectively. In our study, we mainly consider the second case, namely, a combined liquid crystal cell which has only one photoconductive polymer layer and one nonphotoconducting, namely, a rubbed PI.

In particular, our cells had (i) two symmetrically deposited PVK:C<sub>60</sub> layers on both substrates (a symmetrical cell); (ii) PVK:C<sub>60</sub> on one substrate and PI on the other substrate (a combined cell), or (iii) undoped PVK on one substrate and PI on the other substrate. Figure 1 presents a schematic diagram of a liquid crystal–polymer cell with one PVK:C<sub>60</sub> and one PI layer. For clarity, the substrate onto which light is incident first will be called the “input substrate.”

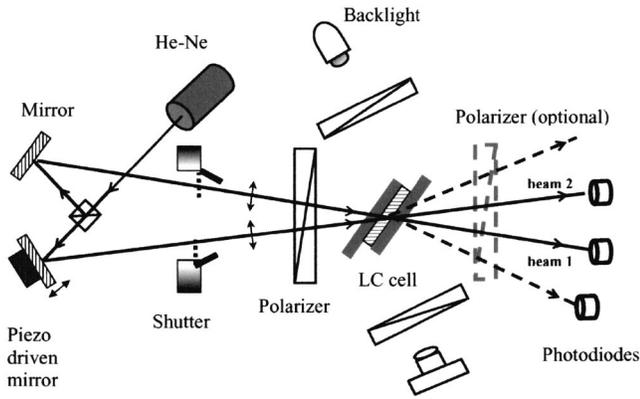


FIG. 2. Experimental setup.

All the cells were  $30\ \mu\text{m}$  thick and filled with pure (undoped) E7 liquid crystal mixture. In our discussion we assume that the liquid crystal remains pure, neglecting its possible contamination by diffusion from polymer layers.

### C. Experimental setup

Figure 2 shows a schematic diagram of the experimental setup, which was designed to carry out different measurements without the need for substantial tuning or adjusting of optical elements. The computer controlled data acquisition system allowed us to monitor simultaneously the intensity of transmitted as well as diffracted beams. A cell was mounted on a rotation stage and could be precisely turned by a stepper motor around the vertical axis (perpendicular to the plane containing the incident beams) at the point of intersection of the incident beams. This setup was designed to measure the transmitted intensity dependence on the angle of incidence. A set of electromagnetic relays controlled both the application of an electric field to the cell electrodes as well as shutters that were used to block and unblock the incident beams. A dc power supply and a wave form generator were used to apply dc and ac electric fields, respectively. The phase of one of the beams could be controlled by a piezo driver connected to the wave form generator. We used this option for the measurement of phase shift using the moving-grating method.<sup>19</sup> Current flow through a cell was measured by a Keithley multimeter. Two additional crossed polarizers and a backlight source, placed off axis, were used for visual (or charge coupled device monitoring) observation of a cell.

Intensity gratings with grating spacing  $\Lambda$  equal to  $58\ \mu\text{m}$ , or  $7\ \mu\text{m}$ , were created via interference of two horizontally polarized beams at  $633\ \text{nm}$ , or  $543\ \text{nm}$ , from a He-Ne laser. The experiment was carried out at very low incident light intensities with typical values varying from  $2.8$  to as low as  $70\ \mu\text{W}/\text{cm}^2$ .

## III. RESULTS

### A. Fredericksz transition threshold

Our investigations started with measurements of light and dc field induced changes in birefringence (optical Fredericksz transition). Using the setup with the backlight and a cell placed between cross polarizers, we were able to observe

the changes in liquid crystal orientation. Cells with at least one PVK covered substrate revealed some unusual features of the optical Fredericksz transition. The volume of liquid crystal could be completely screened from the external electric field because of surface charge layers that build up at the liquid crystal-polymer interface. As such a surface charge field could completely block the external electric field and no Fredericksz transition was observed. Even for high fields, in our case, up to  $56\ \text{V dc}$  ( $1.9\ \text{V}/\mu\text{m}$ ), we did not observe any reorientation. However, when the PVK was sensitized with  $\text{C}_{60}$ , and therefore became photoconductive in the visible, this transition was characterized by a threshold. This threshold proved to be strongly dependent on light intensity, decreasing for higher light intensities. When an ac field was applied, the usual, uniform Fredericksz transition took place. The director reoriented with an ac field and remained in the new position as long as the ac field was applied. With an external dc field applied to the whole cell, the reorientation was observed but only in the area illuminated by a laser beam. The remaining, nonilluminated area of the cell remains unchanged, despite the applied dc field.

We measured in detail the changes in reorientation with increasing light intensity and the results are presented in Fig. 3. For these measurements a liquid crystal cell was placed between crossed polarizers with its director at  $45^\circ$  with respect to their transmission axes. We observed a strong shift in the Fredericksz transition threshold, depending on the incident light intensity. For low light intensities, the threshold shifted towards higher voltages. As a result, the Fredericksz transition was not observed for low voltages. For higher light intensities, the threshold was shifted towards lower voltages. For weak incident beams, such as  $70\ \mu\text{W}/\text{cm}^2$ , the threshold could be as high as  $20\ \text{V}$ , but it decreased significantly, to  $\approx 5\ \text{V}$ , for higher intensities such as  $2.8\ \text{mW}/\text{cm}^2$ . The threshold for high intensities ( $\text{mW}/\text{cm}^2$ ) tended towards the threshold measured with the ac field. In the limit of very weak light incident intensity, below  $\sim \mu\text{W}/\text{cm}^2$ , such as from the backlight source or in the areas outside the illuminated spot, no reorientation was observed. Moreover, in cells containing pure PVK, even with high light intensities (several  $\text{mW}/\text{cm}^2$ ), there was no reorientation observed.

The effect of the dc field and light-dependent threshold could be explained by the buildup of a surface charge layer on the PVK-liquid crystal interface that generates a field capable of screening the external dc up to at least  $56\ \text{V}$ . This is a strong blocking of a dc field induced Fredericksz transition.

Moreover, the magnitude of the photoinduced shift in the Fredericksz transition threshold too is very large.

We studied the dynamics of light-induced and a dc field induced reorientation to gain further insight into the nature of these surface charge layers. While no reorientation was observed at a slow rampup of a dc field without an incident laser beam, an instantaneous application of a dc field caused a transient reorientation. This transient Fredericksz transition corresponded to the penetration of electric field inside the liquid crystal, before any surface charge layers could develop. A second transient transition was observed when the

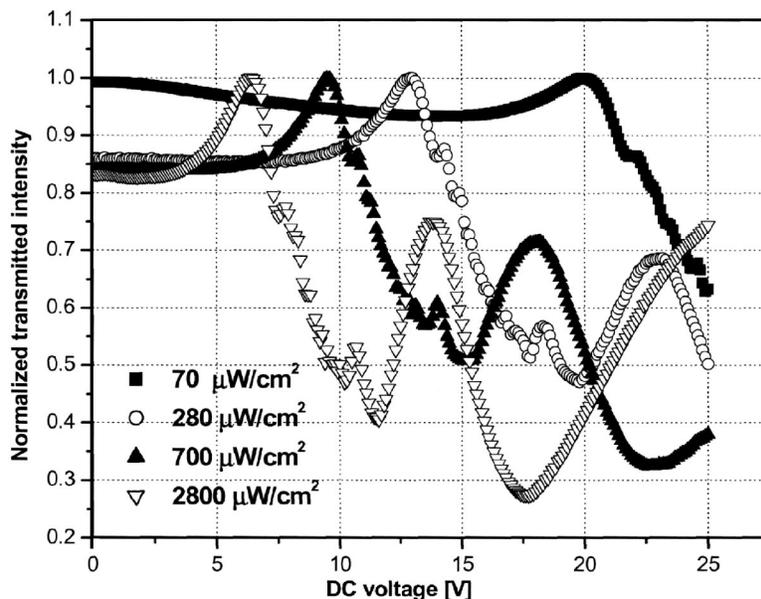


FIG. 3. Transmittance as a function of an external dc voltage for different incident light intensities. The initial director is at  $45^\circ$  vs the polarizer and analyzer transmission axes.

dc field was removed from the cell. This Freedericksz transition could be the result of uncompensated potential of surface charge layer.

### B. Two-beam coupling

Following a study of Freedericksz transition, we concentrated on the measurement of two-beam coupling gain and diffraction. The two incident beams were *p* polarized, intersecting in the plane of the sample and producing an interference pattern. The setup was modified by removing the second polarizer, so the intensities of transmitted beams and first-order diffracted beams could be monitored.

Asymmetric energy exchange was observed when the cell was tilted away from normal incidence and a dc field was applied. We measured the dependencies of two-beam coupling on the external dc field, the angle of incidence, as well as the intensity of incident light.

We measured a two-beam coupling gain that exceeded 1.6. The two-beam coupling gain (also known as gain ratio

$G$ ) is defined as  $G = I_{\text{probe+pump}} / I_{\text{probe-pump}}$ , where  $I_{\text{probe+pump}}$  is the intensity of the probe beam in the presence of the pump beam and  $I_{\text{probe-pump}}$  is the intensity of the probe beam in the absence of the pump beam. The measured value of gain was higher in a combined cell than in a symmetrical cell. The symmetrical cell design had been used in all previous work, but, as our results suggest, there is no benefit in having two PVK photoconducting layers, as one layer is sufficient. In fact, the analysis of the two-beam coupling grating buildup is much simpler in the case of a single active layer.

Figure 4 shows a typical example of the probe and pump beam intensity dependence on applied external dc electric field. Both incident beams had the same intensity of  $17 \text{ mW/cm}^2$ , so the incident intensity ratio  $m$  was equal to 1. In principle, therefore, either of the incident beams could be called probe or pump. A typical two-beam coupling experiment in liquid crystal cells operates in the Raman-Nath (thin) grating regime and as a result several diffraction orders of the beams will be evident. For example, each beam could be

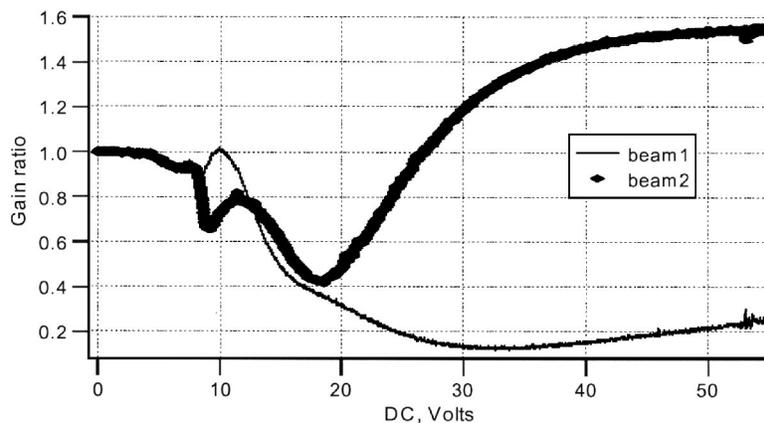


FIG. 4. Two-beam coupling ratio. The angle of incidence is equal to  $-25^\circ$  vs the cell normal. Beam 2 is incident at a smaller angle (to the cell normal) than beam 1.

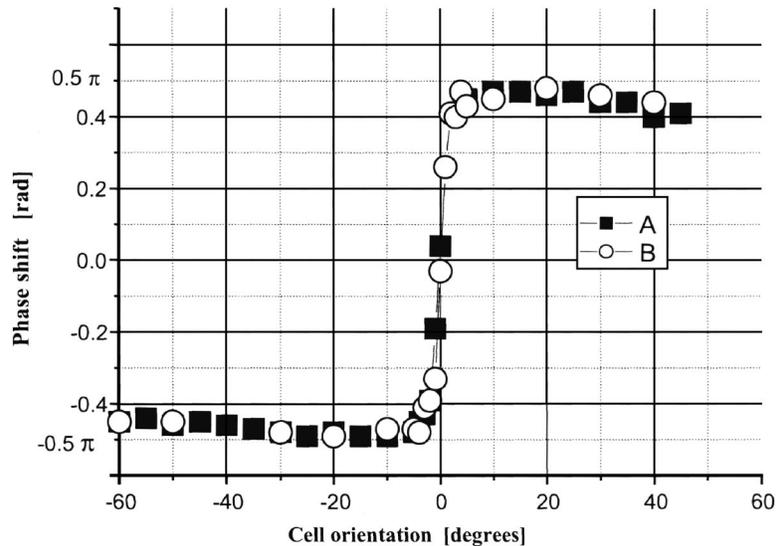


FIG. 5. Dependence of the phase shift on cell orientation. Curves A and B were measured for positive and negative dc bias on the PVK:C<sub>60</sub> substrate, respectively.

diffracted into several orders and this diffraction could cause both beams to experience a net loss (even with gain present). Moreover, for a weak probe and a strong pump beam ( $m \gg 1$ ), some diffracted orders of the pump beam could propagate along the probe beam direction, giving an apparent increase in the probe beam intensity. As a result, the real magnitude of the beam coupling gain could be difficult to extract simply by the measurement of the probe beam intensity. Careful monitoring of pump and probe beam intensities,<sup>20</sup> with and without the other beam present, can help, however, to estimate the net value of energy exchange between the two beams.

In order to demonstrate the nonlocal nature of the refractive index grating and confirm that the gain we measured originated from the two-beam coupling process, we carried out measurements involving a phase shift between the interference pattern and the reorientation (refractive index) index grating. The maximum gain in this case is observed when the phase shift is equal to  $\pi/2$ , as reported earlier.<sup>21</sup>

Figure 5 presents the results of the phase shift measurements versus the relative cell orientation. Except for the case

of  $0^\circ$ , the phase shift was approximately equal to  $\pi/2$ , namely, the optimum value to achieve high two-beam coupling gain. We observed that the phase shift changed quite dramatically at a small deviation from the  $0^\circ$  orientation, reaching the value of  $\pi/2$  and remaining fairly constant irrespective of orientation. Over a range of  $-60^\circ$  to  $+60^\circ$ , and irrespective of the dc bias, the changes in phase shift were approximately the same. Figure 6 presents the two-beam coupling gain dependence on the cell orientation. It is interesting to note that the gain does not follow the same dependence on cell orientation as does the phase shift, despite the fact that the standard photorefractive two-beam coupling theory predicts that gain is directly proportional to sine of the phase shift.<sup>21</sup> The gain increased gradually and had a maximum value at an orientation angle of approximately  $25^\circ$ , for both directions of the cell rotation. This dependence did not show any dramatic changes around  $0^\circ$  orientation. As can be seen, there was no change in the direction of energy transfer with the change of polarity of the applied dc field, but changing the cell orientation changed the direction of energy transfer.

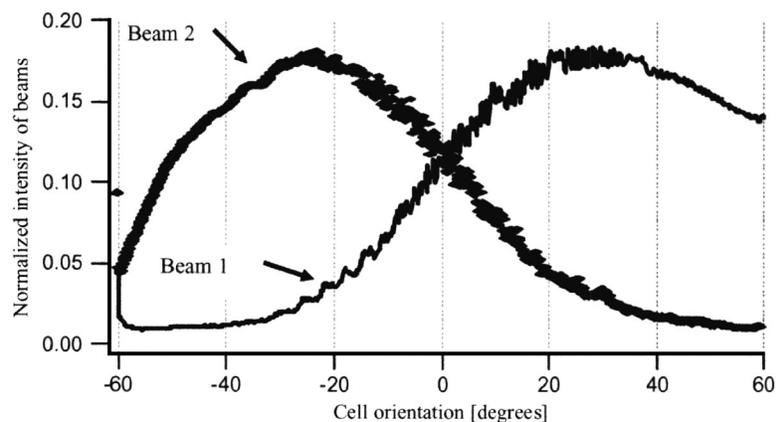


FIG. 6. Dependence of two-beam coupling gain on cell orientation tilt, measured at 55 V dc, for both beams presented. Incident intensities of beams are approximately equal. If external dc field is absent, there is no energy exchange and little dependence of transmitted intensity on cell orientation.

We will analyze the mechanisms behind the gain and phase shift dependence on the tilt angle in the following section, which is devoted to a detailed discussion of our results.

## IV. DISCUSSION

### A. Surface charge layers

Our experimental results indicate that the mechanism behind the exchange of energy in two-beam coupling in PVK: C<sub>60</sub> and (or PVK) and E7 is closely related to processes taking place at the liquid crystal–polymer interfaces. These processes, rather than bulk effects, drive the reorientation of liquid crystal molecules. We suggest a qualitative model to explain the observed features of the Fredericksz transition threshold and two-beam coupling. As explained in the Experiment, without any incident light, but with a dc field applied, no reorientation takes place and the Fredericksz transition threshold for this liquid crystal–polymer system is very high. This is due to surface charge (screening) layers that build up near the polymer–liquid crystal interfaces. The field they create can completely screen the effect of an external electric field. While for most standard polymers the voltage required to initiate reorientation is in the range of 0–2 V, typically,<sup>14</sup> in case of PVK, either undoped or doped, but without illuminating beams, much stronger voltage is needed. We applied up to 56 V (1.9 V/ $\mu\text{m}$ )—the maximum voltage, available on our programmable power supply—and we were not able to induce any reorientation.

The lack of reorientation in case of undoped PVK, even with strong illumination by visible light, could be understood via the photoconductivity profile of this polymer. Without any dopants PVK photoconductivity can only be observed under UV illumination.<sup>22</sup> In the visible regime, it behaves like an excellent insulator, with very low conductivity. Hence, pure PVK did not show any detectable surface discharge upon illumination due to its low charge generation efficiency in the visible regime. Its remarkable improvement in photosensitivity<sup>23</sup> was evident when doped with sensitizers. PVK doped with C<sub>60</sub> is, in fact, extremely photosensitive to incident light and reorientation starts when a sample is illuminated even with weak (as low as a few  $\mu\text{W}/\text{cm}^2$ ) laser beams (Fig. 4). The observed decrease in the Fredericksz transition threshold voltage can be explained, again by PVK photoconductivity, which is proportional to light intensity.

In case of PVK, its high photoconductivity is accompanied by low dark conductivity, and that results in well-defined states of blocking and discharge of surface charge layers. However, the presence and discharge of similar surface charge layers in systems described in previously published papers could be identified. The results by Pagliusi and Cipparone<sup>13,14</sup> obtained in liquid crystal cells with nonphotoconducting polymer layers showed the dc field threshold of reorientation being approximately 20 times smaller than the one observed in our experiments. Even in the absence of photoconductivity in the polymers they used (PVA and LQ 1800) surface charge layers developed at interfaces. The process of charge injection from electrodes by a dc field and the migration of ions present in liquid crystals was used to ex-

plain surface layer buildup and discharge. It is clear that, first of all, surface charge layers can develop on various interfaces and, second, that this process does not require light. The magnitude of the field that surface charge layers create strongly depends on the properties of the polymer used. This field can become very high and easier to control, when polymers such as PVK are used, with very low dark conductivity and high photoconductivity. In fact, our results are a report on optically induced Fredericksz transition with high threshold, induced and explained by discharging surface layers via polymer photoconductivity. We suggest that this selective discharging effect is mostly responsible for two-beam coupling gain, rather than just the photorefractive effect proposed for hybrid liquid crystal–PVK structures in earlier reports.<sup>3,11,12</sup>

### B. Surface charge field effect on two-beam coupling

Our qualitative model of the effect of surface charge layers on two-beam coupling is the easiest to understand in the case of a combined cell (with one PVK:C<sub>60</sub> layer and one PI layer). In this type of cell, surface charge, and hence the electric field, is spatially modulated only on the input side of the cell. The second output substrate has uniform charge and is not photosensitive. Therefore, we can neglect the effect of photoconductivity or modulated charge on that second substrate. In a symmetrical cell, the spatial electric field distribution and the liquid crystal orientational grating are much more complex because of two active surfaces.

When an external dc field is applied across the cell, a surface charge layer builds up on the liquid crystal–PVK interface and a field with a sign opposite to the externally applied dc field is created. This leads to screening of liquid crystals from the dc field. If a cell is illuminated with, for example, an interference pattern, the screening layer is selectively discharged in the area of bright fringes. This allows the dc field to penetrate and reach the liquid crystal molecules. An electric field, equal to the difference between the externally applied field and the remaining surface charge field, induces the Fredericksz transition, which is spatially modulated. The director reorientation is related to the electric field pattern and gives rise to a corresponding refractive index grating. If the cell is not tilted, there is no significant shift between the intensity pattern and the reorientation grating. In this case, the liquid crystal director reorientation is local (coincides with the intensity modulation) and perpendicular to the plane of the cell.

In the first approximation, for a combined liquid crystal, this effect does not depend on the dc bias polarity. The liquid crystal director will be deviated near the bright fringes incident on the input substrate, irrespective of the dc field bias. A nonzero phase shift appears when the cell is tilted, namely, when the pattern of intensity modulation is tilted from the electric field (director) modulation and the cell tilt, rather than the dc field polarity, is the most important factor contributing to the phase shift. As a result of this geometrical mismatch between intensity and electric field modulation, the two-beam coupling gain can build up. Its magnitude will mostly be determined by the intensity distribution at the in-

put (PVK:C<sub>60</sub>) substrate and magnitude of dc field applied. While the formation of space charge layers occurs for both positive and negative bias applied to the PVK:C<sub>60</sub> substrate, higher gain was observed when positive dc bias was applied. This is most likely related to the transport properties of PVK:C<sub>60</sub>, with its high hole conductivity and poor electron mobility.<sup>22</sup> Moreover, C<sub>60</sub> is a good hole donor in photoinduced intramolecular processes and therefore PVK:C<sub>60</sub> is dominated by hole conductivity.

The buildup and discharge of surface charge layers was confirmed by the results obtained with an applied ac field. When an ac field of, for example, 1 kHz, was applied, the surface charge layer was practically eliminated, with the threshold of the Freedericksz transition being at  $\approx 3$  V. We observed the liquid crystal to be uniformly reoriented across the entire cell area. There was no diffraction and no light-induced modulation of reorientation, and the value of this threshold was not dependent on light intensity.

As presented in the Experiment, the phase shift we measured was close to  $\pi/2$ —the optimum value for gain—for approximately all angles of a cell orientation, while the magnitude of gain increased with the increasing angle of cell orientation. We suggest that the lack of correspondence between these two dependencies could be explained by considering the geometry of the interference and refractive index gratings. Even a small tilt from the bisector between incident beams creates a geometrical mismatch between the two gratings. This mismatch depends on the penetration depth into the sample and the profile of reorientation (refractive index) grating, which is nonuniform through the thickness of the cell. This profile also depends on the applied dc field. As a result, the conditions for the optimum energy exchange will, most likely, be fulfilled somewhere in the liquid crystal bulk, namely, in a region where one grating happens to be phase shifted by  $\pi/2$ . Since gain strongly depends on phase shift, the contributions from other regions, with smaller phase shifts will be correspondingly small and the  $\pi/2$  phase shifted region will automatically dominate and provide the strongest contribution. By rotating the cell further, another part of the liquid crystal bulk will be  $\pi/2$  phase shifted with respect to the interference pattern, but as the net result on probe intensity comes from the whole bulk of liquid crystal, this change in the position of the contributing regions will only have a negligible effect on the measured intensity.

In the case of a symmetrical cell (PVK:C<sub>60</sub> on both substrates), the annihilation of the surface charge layers occurs in different places on both substrates and the exact visualization of the form of the refractive index modulation is more difficult.

This qualitative model is the first step in gaining a better understanding of photorefractive and photoconductive phenomena taking place at polymer–liquid crystal interfaces. However, the role of surface charge field that builds up inside PVK:C<sub>60</sub> will need to be analyzed further. Theoretical modeling and optimization of experimental parameters, such as cell thickness or grating spacing has to be established to determine the full potential of these polymer–liquid crystal structures for efficient beam coupling and pattern writing.

Moreover, our studies of PVK:C<sub>60</sub> and E7 structures can be regarded as a base to further optimization of these structures. In particular, the promising results<sup>24</sup> on liquid crystals doped with C<sub>60</sub> and carbon nanotubes showed “supra” nonlinearity with  $n_2 > 1$  cm<sup>2</sup>/W. In our further work, we intend to use these dopants in polymer–liquid crystal structures as well as explore functionalized forms of C<sub>60</sub> that show better solubility.

## V. CONCLUSIONS

In conclusion, we have showed strong surface charge field build up on the polymer–liquid crystal interface in PVK:C<sub>60</sub> and E7 liquid crystal cells, following the application of a dc field. We demonstrated that surface charge layers could be selectively discharged via PVK:C<sub>60</sub> photoconductivity and lead to reorientation gratings in the bulk of the liquid crystal. Similar effects occur at other polymer–liquid crystal interfaces, but their magnitude is approximately an order of magnitude smaller. The reorientation grating is  $\pi/2$  phase shifted from the interference pattern and as a result a high two-beam coupling gain can be observed. This optimum phase shift is created in some regions in the volume of liquid crystal when a sample is tilted away from the bisector of two incident beams. We proposed that the process of buildup and discharge of surface charge layer is responsible for two-beam coupling gain.

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<sup>1</sup>G. P. Wiederrecht, *Annu. Rev. Mater. Res.* **31**, 139 (2001).

<sup>2</sup>I. C. Khoo, H. Li, and Y. Liang, *Opt. Lett.* **19**, 1723 (1994).

<sup>3</sup>S. Bartkiewicz, A. Miniewicz, F. Kajzar, and M. Zagorska, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **322**, 9 (1998).

<sup>4</sup>I. C. Khoo, H. Li, and Y. Liang, *Opt. Lett.* **19**, 1723 (1994); *IEEE J. Quantum Electron.* **32**, 525 (1996).

<sup>5</sup>I. C. Khoo, *Opt. Lett.* **20**, 2137 (1995).

<sup>6</sup>S. Slussarenko, *Europhys. Lett.* **56**, 672 (2001).

<sup>7</sup>S. Bartkiewicz, K. Matczyszyn, A. Miniewicz, and F. Kajzar, *Opt. Commun.* **187**, 257 (2001).

<sup>8</sup>Y. Wang *Nature (London)* **356**, 585 (1992).

<sup>9</sup>F. Li, Y. Li, Z. Guo, C. Long, F. Bai and D. Zhu, *J. Appl. Polym. Sci.* **72**, 209 (1999).

<sup>10</sup>J. H. Dessauer and H. E. Clark, *Xerography and Related Processes* (The Focal, New York, 1965).

<sup>11</sup>H. Ono and N. Kawatsuki, *Appl. Phys. Lett.* **71**, 1162 (1997).

<sup>12</sup>J. Mun, C.-S. Yoon, H. W. Kim, S.-A. Choi, and D. Kim, *Appl. Phys. Lett.* **79**, 1933 (2001).

<sup>13</sup>P. Pagliusi and G. Cipparrone, *Appl. Phys. Lett.* **80**, 168 (2002).

<sup>14</sup>P. Pagliusi and G. Cipparrone, *J. Appl. Phys.* **93**, 9116 (2003).

<sup>15</sup>V. Boichuk, S. Kucheev, J. Parka, V. Reshetnyak, Y. Reznikov, I. Shiy-anovskaya, K. D. Singer, and S. Slussarenko, *J. Appl. Phys.* **90**, 5963 (2001).

<sup>16</sup>A. Sugimura, N. Matsui, Y. Takahashi, H. Sonomura, H. Naito, and M. Okuda, *Phys. Rev. B* **43**, 8272 (1991).

<sup>17</sup>M. Kaczmarek and A. Dyadyusha, *J. Nonlinear Opt. Phys. Mater.* **12**, 547 (2003).

<sup>18</sup>V. N. Bezmel'nitsyn, A. V. Eletsii, and M. V. Okun', *Usp. Fiz. Nauk* **168**, 1195 (1998).

<sup>19</sup>R. S. Cudney, G. D. Bacher, R. M. Pierce, and J. Feinberg, *Opt. Lett.* **17**,

67 (1992).

<sup>20</sup>J. E. Hall and D. A. Higgins, *Rev. Scient. Meth.* **73**, 2103 (2002).

<sup>21</sup>P. Gunter and J. P. Huignard, *Photorefractive Materials and Their Applications* (Springer, Berlin, 1988), Vols. 1 and 2.

<sup>22</sup>W. E. Moerner *et al.*, *Annu. Rev. Mater. Sci.* **27**, 585 (1997); *Chem. Phys.*

*Lett.* **291**, 553 (1998).

<sup>23</sup>D. P. West, M. D. Rahn, C. Im, and H. Bassler, *Chem. Phys. Lett.* **326**, 407 (2000).

<sup>24</sup>I. C. Khoo, J. Ding, Y. Zhang, K. Chen, and A. Diaz, *Appl. Phys. Lett.* **82**, 3587 (2003).