

## Dual-Mode Switching of Diffraction Gratings Based on Azobenzene-Polymer-Stabilized Liquid Crystals\*\*

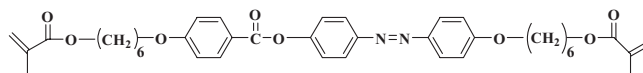
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Switchable diffraction gratings are of interest for a number of optical and photonic applications. Liquid crystals (LCs) are the materials of choice for making such gratings.<sup>[1–10]</sup> Generally, switching between high and low diffraction efficiency is made possible by applying an electric field across the LC cell, altering the LC orientational state or texture. In recent years, the LC materials exploited for electrically switchable diffraction gratings include polymer-dispersed liquid crystals (PDLC),<sup>[3,4]</sup> cholesteric liquid crystals (CLC) with or without a covalent polymer network,<sup>[5–7]</sup> and self-assembled LC gels.<sup>[8]</sup> In the search for new LC materials for switchable diffraction gratings, it should be of fundamental interest to develop materials that can be used to prepare gratings whose diffraction efficiency can be switched not only by an electric field but also by light; i.e., dual-mode switching. The control of diffraction of light by using light and the coupling or combination of electrical and optical switching may lead to new applications. In this communication, we report the discovery of such a material, namely azobenzene-polymer-stabilized liquid crystals (Azo-PSLCs).

Generally, PSLCs are low-molecular-weight LCs that contain a low-concentration polymeric network formed by polymerization of a reactive monomer dissolved in the LC host.<sup>[11–13]</sup> The polymeric networks in PSLCs have the primary effect of stabilizing the LC orientation or texture induced by the treated surfaces of the cell. When the polymer used in PSLCs contains the azobenzene chromophore in its structure, the resultant material is an Azo-PSLC that is photoactive because of the *trans*–*cis* photoisomerization of azobenzene.<sup>[14]</sup> We have shown that the azobenzene-polymer network can be used to align the LC host, which could also be a ferroelectric liquid crystal (FLC),<sup>[15]</sup> with no need for treated surfaces. In the present study, the exploitation of Azo-PSLCs for optically and electrically switchable diffraction gratings is based on the

following considerations: Upon exposing a homogeneous mixture composed of an azobenzene monomer, a photoinitiator, and a LC to light through a grating photomask, photopolymerization occurs only in irradiated regions. Similarly to the preparation of gratings with PDLCs<sup>[3]</sup> and other studies using photopolymerization-induced phase separation,<sup>[16]</sup> the polymer formation in irradiated areas should result in diffusion of the monomer from non-irradiated areas into the irradiated areas, expelling the LC from the irradiated areas as more polymer forms and solidifies. The consequence of this process should be the segregation of the polymer from the LC host, leading to the formation of a permanent grating. However, it is likely that a small amount of the azobenzene monomer would remain dissolved in the LC in the non-irradiated area and can be polymerized further on flood irradiation. If the concentration of the azobenzene-polymer network in the LC regions is low, the LC may be aligned by rubbed surfaces and switched by an electric field, and the LC orientation can be altered through the photoisomerization of azobenzene groups. Should this condition be fulfilled, optical and electrical dual-mode switching of the diffraction grating may be possible.

In this design, the concentration of azobenzene monomer before polymerization must be quite high (>10 wt.-%). All the azobenzene monomers used in our previous Azo-PSLC studies<sup>[14,15]</sup> are non-mesogenic and have limited solubility in the LC hosts. To overcome this problem, we have prepared the liquid-crystalline azobenzene dimethacrylate monomer, whose chemical structure is shown in Scheme 1.



**Scheme 1.** Liquid-crystalline azobenzene dimethacrylate monomer.

This azobenzene monomer has the following phase-transition temperatures (°C) on heating: Cr S 99 N145 Iso (Cr, S, N, and ISO stand for crystalline, smectic, nematic, and isotropic, respectively) Additionally, its *trans*–*cis* photoisomerization in tetrahydrofuran (THF) is almost 100%.<sup>[17]</sup> As much as 30 wt.-% of the monomer can be readily dissolved in nematic LCs because the compatibility is enhanced by the liquid crystallinity of both components. The nematic LC used in this study was BL006 (Merck), which is a eutectic mixture of several LC compounds. This nematic LC has an ordinary refractive index,  $n_o$ , of 1.53, with a large birefringence,  $\Delta n$ , of 0.286 (589 nm, 20 °C), a positive dielectric anisotropy,  $\Delta\epsilon$ , of 17.3, and a nematic-isotropic transition temperature,  $T_{N-ISO}$ , of 115 °C. The photoinitiator used was Irgacure 784, (bis(eta.5-2,4-cyclopentadien-1-yl)-bis(2,6-difluoro-3-(1H-pyrrol-1-yl)-phenyl) titanium, Ciba Speciality Chemicals) which can initiate polymerization upon visible-light irradiation because of its absorption at wavelengths  $\lambda > 450$  nm. The visible-light photopolymerization is necessary in order to minimize the interference by absorption of the LC host and the azobenzene mono-

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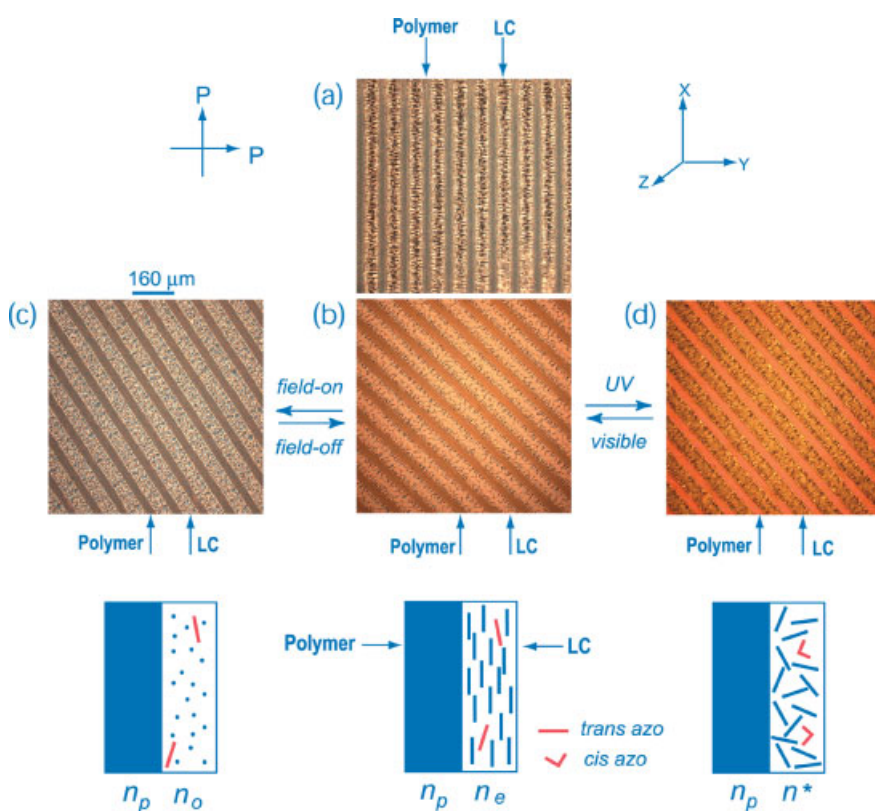
mer in the UV region (maximum absorption  $\lambda_{\text{max}} = 354$  nm in THF for the LC azobenzene monomer). We found that this combination of materials indeed allows the preparation of optically and electrically switchable gratings. Before presenting the results of our diffraction measurements, the preparation method, as well as the origin of the dual-mode switching of diffraction efficiency, are first explained in Figure 1, using as an example a mixture containing 15% of the azobenzene monomer and 2% of the photoinitiator.

The homogeneous mixture of LC/monomer/initiator was first filled into an indium tin oxide (ITO)-coated, unidirectionally rubbed electro-optical cell with a gap of 10  $\mu\text{m}$ . A photomask with alternating transparent and non-transparent stripes (40  $\mu\text{m}$  wide) was stuck onto the cell with the stripes aligned parallel to the rubbing direction, and the whole setup was placed inside a microscope hot-stage. After the mixture was heated to 125  $^{\circ}\text{C}$ , corresponding to the isotropic phase of BL006, a beam of visible light at  $\lambda = 540$  nm ( $\sim 2.8$   $\text{mW cm}^{-2}$ ) was directed through the photomask for photopolymerization (duration: 1 h). The cell was then cooled to room temperature

under irradiation, and after the removal of the photomask a flood irradiation was applied to the whole sample to complete the polymerization of the remaining monomer. Figure 1a shows a polarizing optical micrograph of the cell placed with the rubbing direction parallel to one of the crossed polarizers (along the  $x$ -axis). It is clear that a grating was formed as a result of the polymerization-induced segregation. Polymer stripes were found in the irradiated regions, which are well-separated from the LC concentrated in the non-irradiated regions and have clear boundaries. The orientation of the LC molecules in the rubbing direction in the LC regions is revealed by the extinction in these areas. As illustrated in the schematics under the micrographs, this grating should diffract the probe light (a He-Ne laser at  $\lambda = 633$  nm) propagating along the  $z$ -axis (normal incidence) with the electric vector parallel to the fringes ( $x$ -axis), because the probe light essentially sees the extraordinary refractive index of the LC,  $n_e$ , in the LC regions, and the mean refractive index of the polymer,  $n_p$ , in the polymer regions, with  $n_e$  larger than  $n_p$  ( $n_e$  should be similar to the ordinary refractive index of the LC,  $n_o$ , i.e.,

around 1.5). This large refractive-index modulation can be controlled either by an electric field or by an excitation light for the photoisomerization of azobenzene. In order to better explain the mechanisms, Figure 1b shows the polarizing optical micrograph of the same grating rotated by approximately 45 $^{\circ}$  with respect to the crossed polarizers. At this alignment, the oriented LC molecules in the non-irradiated areas appear bright by allowing light to pass through, and the remaining azobenzene-polymer network is visible as denser zones under the optical microscope. When an electric field was applied across the cell, as shown in Figure 1c, the part of the LC molecules that is far from polymer walls was aligned in the field direction, i.e., perpendicular to the plane of the cell (homeotropic orientation), and consequently appeared dark under crossed polarizers. In this state, the probe light sees essentially  $n_o$  and  $n_p$  in the two neighboring regions, and this sharp decrease in the refractive-index modulation should result in a drop of the diffraction efficiency. The electrical switching of the refractive-index modulation was reversible, as the initial planar orientation of LCs was recovered when the electric field was turned off.

On the other hand, the depth of the refractive-index modulation of the grating in Figure 1 could also be reversibly changed by using two different wave-

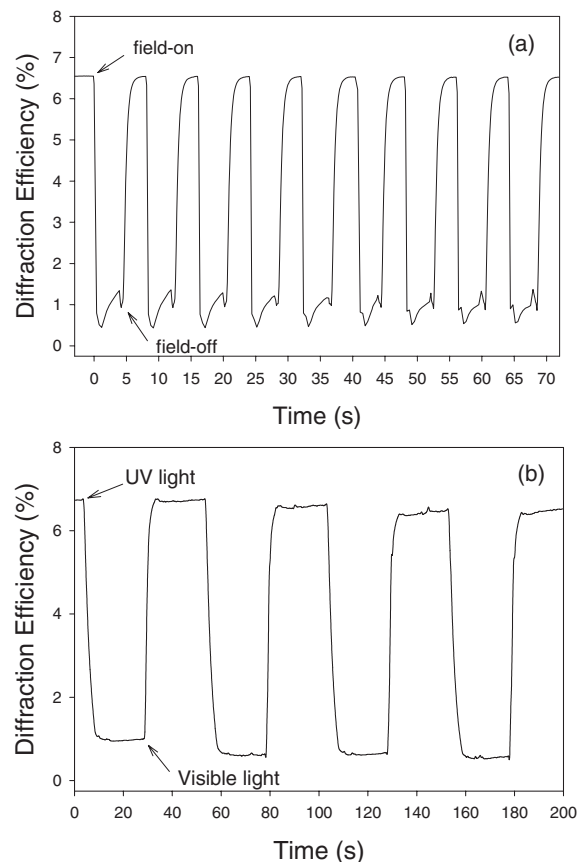


**Figure 1.** Polarizing optical micrographs showing an electrically and optically switchable diffraction grating prepared with an azobenzene-polymer-stabilized nematic liquid crystal (15 wt.-% polymer). a) The grating with fringes parallel to one of the crossed polarizers (P), with LC molecules being oriented in the rubbing direction ( $x$ -axis); b) the same grating rotated by an angle of about 45 $^{\circ}$ ; c) the grating in (b) subjected to an alternating current (AC) field (1000 Hz, 40 V peak-to-peak), the LC molecules being oriented in the field direction ( $z$ -axis); d) the grating in (b) exposed to UV light ( $\lambda = 365$  nm, 20  $\text{mW cm}^{-2}$ ), resulting in the nematic-to-isotropic phase transition of the LC. The schematic illustrations beneath show the various orientational states of the LC molecules and the corresponding refractive-index modulation of the grating for probe light propagating along the  $z$ -axis and polarized along the  $x$ -axis.

lengths of light. By illumination with UV light ( $\lambda = 360$  nm), azobenzene groups in the polymeric network in the LC regions undergo a *trans*-*cis* photoisomerization. Contrary to the elongated *trans* form, the contracted *cis* isomer of azobenzene is not compatible with the nematic phase, and the disturbing effect can induce the photochemical nematic-isotropic phase transition at room temperature.<sup>[18]</sup> This was indeed observed in our experiment. Figure 1d shows the significant change in contrast induced by the UV light. The LC molecules are disordered and appear dark under crossed polarizers. When this happens, the probe light mainly experiences the average refractive index of the LC,  $n^* = (2n_o + n_e)/3$ , which should also be close to  $n_p$ , leading to a drop of the diffraction efficiency. This optical switching was also reversible. When illuminated with visible light ( $\lambda = 440$  nm), the *cis*-*trans* back-photoisomerization of azobenzene occurred, and the initial surface-induced LC orientation was recovered.

However, it should be emphasized that the polymer and LC stripes forming the grating in Figure 1 are actually polymer-rich and LC-rich regions. As already mentioned, azobenzene polymer remaining in the LC regions is noticeable in Figure 1b, which may also contain some unreacted monomer. Likewise, the polymer regions can confine LC molecules, whose switching under the electric field is responsible for the darker appearance of the polymer stripes in Figure 1c. On the basis of the morphology of the azobenzene-polymer network revealed by polarizing optical microscopy,<sup>[15]</sup> the amount of polymer remaining in the LC regions was estimated to be around 3%. At this point, we do not know how much LC is in the polymer areas because of difficulty in the characterization (attempts to open the cell resulted in the destruction of the grating). Nevertheless, as will be shown below, the experimental confirmation of both electrical and optical switching of the diffraction grating in Figure 1 corroborates quite well with the analysis of the index-modulation changes without taking into account the remaining polymer or LC, which suggests that the residual amount of polymer in the LC region, and vice versa, was minor and did not determine the behavior of the switchable grating. Note that in a control experiment, the reversible photochemical nematic-isotropic phase transition of BL006 was observed with 2% of the azobenzene-polymer network.

Measurements of the switching of diffraction efficiency with an electric field and two different wavelengths of light were carried out. An example of the results is given in Figure 2, corresponding to the grating shown in Figure 1. Figure 2a shows multiple cycles of electrical switching between the high (6.5%) and low (0.5%) first-order (+1) diffraction efficiency in response to a square-wave electric field alternating between 0 V (field off) and 40 V (field on). The low diffraction state is somewhat unstable, which is likely related to some dynamic instability of the LC in the direct current (DC) electric field. Under the conditions used, at the field-on state, the time for the diffraction drop (from 90% to 10% of the initial efficiency) was estimated to be about 110 ms, while at the field-off state, the diffraction recovery (from 10% to 90%) needed about 1 s. The electrical switching can be repeated many



**Figure 2.** Switching of the first-order diffraction efficiency for the grating in Figure 1 ( $80 \mu\text{m}$  for polymer line and LC line combined) by means of a) a square-wave electric field between 0 V (off state) and 40 V (on state); and by b) UV light ( $365 \text{ nm}$ ,  $20 \text{ mW cm}^{-2}$ ) and visible light ( $\sim 440 \text{ nm}$ ,  $26 \text{ mW cm}^{-2}$ ) with an irradiation time of 5 s.

times. The speed of switching diffraction from high to low efficiency is determined by the speed at which the LC molecules change from the surface-induced in-plane orientation to the homeotropic (or tilted) orientation, which is influenced by the applied voltage. On removal of the field, the reverse change is governed by the relaxation rate of the LC returning to its initial in-plane orientation.

Figure 2b shows the reversible optical switching of diffraction efficiency upon irradiation with UV and visible light. For this experiment, the irradiation light was directed at an angle to the normal of the cell in order to prevent the irradiation light from directly entering the photodetector used to measure the intensity of the diffracted probe light. The UV light ( $\sim 20 \text{ mW cm}^{-2}$ ) was turned on for 5 s, which was enough to induce the nematic-isotropic phase transition, resulting in the drop of the diffraction efficiency. The high-diffraction state was recovered by turning on the visible light ( $\sim 26 \text{ mW cm}^{-2}$ ) for 5 s, restoring the oriented nematic phase. With the 5 s irradiation used, the actual diffraction drop and recovery times were about 3.4 s and 1.4 s, respectively. Similar to electrical switching, optical switching can be realized for many cycles

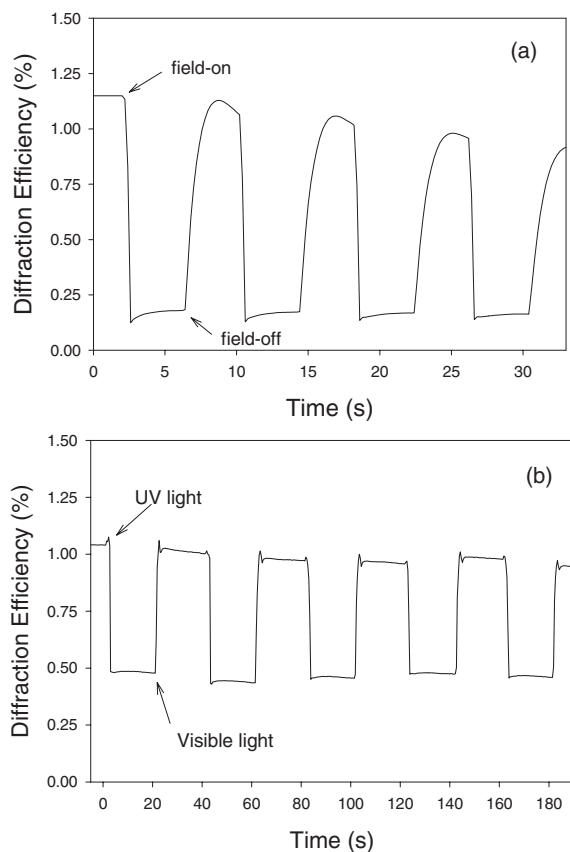
without significant degradation of the grating performance. For switching with UV light, the switching speed is determined by the photochemical nematic–isotropic phase transition.<sup>[18]</sup> The reverse switching under the action of visible light is dictated by the reorientation of LC molecules induced by the rubbed surfaces after the *trans*–*cis* back-isomerization (resulting from visible light) is complete. Increasing the intensities of UV and visible light can increase the speed of optical switching. It is noted that the remnant diffraction (low-diffraction state) is similar for both electrical and optical switching, which is consistent with the analysis of the index-modulation changes as discussed above (Fig. 1). The results in Figure 2 thus confirm that both an electrical field and two wavelengths of light can be used to reversibly switch the diffraction efficiency of gratings prepared using this Azo-PSLC. Note also that for both modes of switching, varying the voltage or the intensity of light can switch the diffraction efficiency to different levels. To maintain the low-diffraction state in the electric-field mode, the applied voltage needs to be maintained. By contrast, to maintain the low-diffraction state when using UV light, continuous excitation is not required. However, the stability is limited by the thermally induced *cis*–*trans* back-isomerization. For the LC azobenzene monomer used, the thermal relaxation of the *cis* isomer is slow, taking hours to complete in solution.<sup>[17]</sup> Consequently, the low-diffraction state in the absence of UV excitation is quite stable. Should a long-period stability of the low-diffraction state be required, an intermittent short-time UV excitation is enough to prevent the interconversion of the *cis* isomer to the *trans* isomer. It is worthwhile mentioning that, in a control experiment, we were able to obtain gratings using a commercial LC diacrylate monomer from Merck (RM257) that contains no azobenzene. Although an electrical switching of the diffraction efficiency was observed, no changes could be achieved using UV or visible light.

To achieve improved grating performance in terms of the diffraction efficiency and switching behavior (speed and stability), there are several requirements for the material and the preparation conditions. First, the LC ideally should have a large birefringence with its  $n_o$  equal to  $n_p$ . This will provide high diffraction efficiency for the grating formed after polymerization and no (or negligible) diffraction when an electric field or UV light is applied. Second, upon photopolymerization the polymer should segregate as thoroughly as possible from the LC to form the periodic grating structure. Under the conditions and with the materials used, there was always a small amount of the azobenzene polymer remaining in the LC regions. However, it is likely that even with complete separation of the polymer from the LC, mesogenic azobenzene groups at the interface between the two regions could accomplish the optical switching. While ensuring the optical switching of diffraction, the absence or presence of merely a small amount of the azobenzene-polymer network in the LC regions is desirable. It means that a homogeneous LC orientation can be induced by rubbed surfaces, which determines the high-diffraction state, and that the transformation from the homogeneous to homeotropic orientation of LC molecules

can develop without interaction with the polymer. This allows the electrical switching of diffraction to be governed by the behavior of pure nematic LC. Moreover, several other factors were found to affect the grating: 1) Polymerization in the isotropic phase resulted in better gratings, probably as a result of the higher fluidity that favors the diffusion or transport of the monomer and thus the segregation between polymer and LC. 2) A long polymerization time (1–2 h) was necessary to complete the reaction with the visible-light photoinitiator (Irgacure 784). 3) A concentration of 15–20 % of the azobenzene monomer was necessary. At higher concentrations, the segregation between polymer and LC was not sufficient; too much polymer remained in LC regions to allow good surface alignment of the LC. At lower concentrations, the amount of polymer in irradiated areas was not sufficient to yield large polymer stripes. As can be noted from Figure 1, for the grating obtained with 15 % azobenzene monomer, the solidified polymer stripes are narrower than the LC bands.

Finally, gratings with periods of less than 30  $\mu\text{m}$  cannot be prepared with a photomask when the sample is inside the electro-optical cell. This is due to the diffraction of light by the grating photomask before hitting the sample.<sup>[8]</sup> Preliminary investigations showed that holographic gratings with smaller periods could also be recorded using Azo-PSLC following the same procedure, and the diffraction efficiency could be switched both electrically and optically. Figure 3 shows the electrical and optical switching of the first-order diffraction efficiency with a 5  $\mu\text{m}$  period grating prepared with an interference pattern generated by an Ar-ion laser ( $\lambda = 514 \text{ nm}$ ,  $85 \text{ mW cm}^{-2}$  per pumping beam) for photopolymerization. The diffraction remained in the Raman–Nath regime. The same switching conditions as in Figure 2 were used, except that the UV and visible light was applied for 2 s. Although the diffraction efficiency and the switching performance of this holographic grating are not as good as the large-period gratings obtained using a photomask, measurement of the grating-formation dynamics showed that the holographic grating had the same origin as described earlier in Figure 1. On cooling the cell from the isotropic phase of BL006 (125 °C) after a 20 min exposure to the interference pattern, diffraction was observed once the LC entered the nematic phase. Diffraction increased as the temperature was decreased as a result of the increasing difference between  $n_e$  and  $n_p$  at lower temperature. And, similar to the large-period grating in Figure 1, the diffraction efficiency was highly dependent on the polarization of the probe light, decreasing with increasing angle between the polarization and the fringes of the grating, and reaching the lowest level when the polarization was perpendicular to the fringes. Under a polarizing optical microscope, the 5  $\mu\text{m}$  grating was observable, but the sample appeared quite heterogeneous, with the presence of droplets and defect regions much larger than the period of the grating, which led to the diminished performance of the grating. The conditions for recording holographic gratings remain to be optimized. For example, we anticipate that using more-efficient visible-light photoinitiators for faster photopolymerization





**Figure 3.** a) Electrical switching of the first-order diffraction efficiency for a holographic grating with a 5  $\mu\text{m}$  period using a square-wave electric field between 0 V (off state) and 40 V (on state). b) Optical switching of the same grating using UV light (360 nm, 20  $\text{mW cm}^{-2}$ ) and visible light ( $\sim 440$  nm, 26  $\text{mW cm}^{-2}$ ), with an irradiation time of 2 s.

may improve the segregation between the azobenzene polymer and the LC. More investigations are underway.

To summarize, we report, for the first time, the preparation of diffraction gratings using Azo-PSLC whose diffraction efficiencies can be switched by both an electric field and different wavelengths of light. The control of light diffraction with light was identified to originate from the reversible *trans*-*cis* photoisomerization of the azobenzene chromophore incorporated into a LC-polymer network. While at this stage the dual-mode switchable diffraction gratings may appear to be mainly of fundamental interest, and the performance of such gratings needs to be improved by further studies, we believe diffraction gratings with combined electrical and optical switching capability may be exploited for such device applications as, for example, electrically controllable UV-visible image conversion.

### Experimental

The synthesis and characterization of the liquid crystal (LC) azobenzene dimethacrylate monomer is reported elsewhere [17]. To dissolve the monomer in BL006, the two components, together with Irgacure 784, were dissolved in tetrahydrofuran (THF), and the solvent

was removed in a vacuum oven at 40 °C. The homogeneous mixture was filled in the 10  $\mu\text{m}$  gaps of a unidirectionally rubbed, indium tin oxide (ITO)-coated cell (E.H.C. Japan) at 80 °C by the capillary effect; the cell was sealed after filling. To obtain a grating, a grating photomask (5 mm  $\times$  5 mm, 40  $\mu\text{m}$  wide stripes) was fixed on one side of the cell with tape; the cell was placed on a microscope hot-stage (Instec) and heated to 125 °C. Once the heating started, unpolarized visible light was applied to the sample through the mask to photopolymerize the monomer in the irradiated regions using a UV-vis spot curing system (Novacure, N2001) combined with a visible interference filter (540 nm, 10 nm bandwidth, Oriol). The photopolymerization was continued for 1–2 h at 125 °C. Then, the cell was cooled to room temperature by opening the cover of the hot stage while under irradiation. The gratings were observed on a polarizing optical microscope (Leitz DMR-P). To record holographic gratings, an optical setup similar to that described elsewhere was employed [19]. An Arion laser ( $\lambda = 514$  nm) was used to produce the interference pattern for photopolymerization under similar conditions; the two beams were polarized parallel to the fringes of the grating (s-s geometry).

To measure the diffraction efficiency of the grating, a low-intensity He-Ne laser (633 nm, 4 mW) was used as the probe light (normal incidence). The first-order diffraction signal,  $I_d$ , was monitored using a high-speed photodetector (Displaytech) connected to a digital oscilloscope (Tektronix, TDS 420A). The diffraction efficiency was calculated as the ratio of  $I_d$  to the intensity of the laser beam before reaching the cell. For the measurements of the electrical switching of diffraction, a high-voltage waveform generator (WFG500, FLC Electronics) was used to apply either alternating current (1000 Hz), square wave, or pulsed electric fields through the cell. The optical-switching measurements were performed using another curing system (Exfo Lite) in which two band-pass filters (365 nm and 400–500 nm) could be interchanged quickly to produce UV and visible light centered at about 365 nm and 440 nm, respectively. The irradiating light was directed at an angle to the cell to prevent it from directly entering the photodetector.

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