Experimental

Unless stated otherwise, all commercial chemicals and solvents were used as received without further purification. Reagent chemicals were purchased either from Aldrich or Fisher Chemical Co, unless otherwise stated. All new compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. NMR spectra were taken on a Bruker ARX 400 spectrometer. All chemical shifts were reported relative to tetramethylsilane (TMS). UV-vis-NIR spectroelectrochemistry was carried out on a Shimadzu UV 3101PC UV-vis-NIR spectrophotometer. Melting points were measured using a capillary melting point apparatus (MelTemp from Laboratory Devices) and were uncorrected. Elemental analysis results were obtained from Desert Analytics Co. Light-scattering measurements were performed at a concentration of 8 mg mL^{-1} with Microtrac Ultrafine Particle Analyzer (Leeds & Northrup). Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed on a BAS 100B Electrochemical Analyzer in a three-electrode cell in a solution of Bu_4NBF_4 (0.1 M) in acetonitrile at a scan rate of 50 mV s^{-1}. The polymer films were coated on a glassy carbon disc electrode (0.5 cm^2) by casting the polymer solutions onto the electrode and then drying in vacuum. A Pt wire was used as the counter electrode and an $Ag/AgNO_3$ (0.1 M) electrode was used as the reference electrode. Its potential was corrected to the saturated calomel electrode (SCE) by measuring the ferrocene/ferrocenium couple in this system (0.31 V vs. SCE). For electrochromic device characterization, the top ITO glass slide acts as both the counter and the reference electrodes and the bottom ITO glass slide as a working electrode.

Electrochromic Device Fabrication: The polymer films were spin-coated onto ITO-coated glass plates (50 Ω/□). The film thickness was measured by a Dektak 8 profilometer. The viscous electrolyte was lithium perchlorate-plasticized by mixing with propylene carbonate and poly(methyl methacrylate) in acetonitrile (the ratio of the composition of $LiClO_4$/PC/PMMA/CH_3CN is 3:20:7:70 by weight). The mixture was stirred overnight at room temperature under an argon atmosphere.

2,9-Dibromo-benzo[c]thiophene-N-2′-ethylhexyl-4,5-dicarboxylimide (EHI-DBrITN): At 0–5 °C under an argon atmosphere, NBS powder (1.28 g, 7.2 mmol) was added slowly to a stirred solution of benzo[*c*]thiophene-*N*-2′-ethylhexy-4,5-dicarboxylic imide (EHIITN)[11] (1.10 g, 3.5 mmol) dissolved in a mixture of chloroform (50 mL) and acetic acid (50 mL). The mixture was stirred for 24 h at room temperature and then refluxed for an additional 2 h. The mixture was quenched with water, the organic layer was separated, and the water layer was extracted with chloroform (10 mL × 3). The combined chloroform extracts were neutralized with 5 % sodium bicarbonate solution and then washed again with distilled water. After drying with anhydrous magnesium sulfate and filtering, the solvent was evaporated and the residue was purified by column chromatography using methylene chloride: hexane (2:1) as eluent on silica to afford 1.3 g of a light yellow solid (78 %). mp, 173–175 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 ppm (s, 2H, Ar**H**), 3.63 ppm (d, 2H, J = 7.2 Hz, –NC**H**$_2$), 1.88 ppm (m, 1H, –NCH_2C**H**–), 1.29–1.36 ppm (m, 8H, –C**H**$_2$–), 0.86–0.92 ppm (m, 6H, –C**H**$_3$). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 167.4, 137.9, 127.2, 118.5, 109.9, 42.51, 38.13, 30.55, 28.50, 23.90, 23.01, 14.07, 10.44 ppm. Electron impact (EI) mass spectrometry (MS) *m*/*z* (%): 360 (100, M^+–C_8H_{17}), 471 (45, M^+–2), 473 (80, M^+), 475 (45, M+2). Anal. Calcd. for $C_{18}H_{19}Br_2NO_2S$: C, 45.86; H, 4.07; Br, 33.80; N, 2.97; S, 6.77. Found: C, 46.38; H, 4.08; Br, 32.16; N, 3.31; S, 6.47.

2,5-Bis(tributylstannyl)-3,4-ethylenedioxythiophene: This compound was prepared according the literature procedure [12]. Colorless liquid; bp, 140 °C/0.15 mmHg. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.11 ppm (s, 4H, –OC**H**$_2$), 1.52–1.58 ppm (m, 12H, –SnC**H**$_2$–), 1.30–1.36 ppm (m, 12H, –C**H**$_2$–), 1.06–1.10 ppm (m, 12H, –C**H**$_2$), 0.87–0.91 ppm (t, 18H, J = 7.2 Hz, –C**H**$_3$). ^{13}C NMR ($CDCl_3$): δ 148.3, 115.8, 64.65, 28.93, 27.23, 13.72, 10.51 ppm. EI, MS *m*/*z* (%): 720 (5, M^+), 663 (100, M^+-C_4H_9), 473 (35, M^+-$SnBu_4$), 291 (18, M^+-473). Anal. Calcd. for $C_{30}H_{58}O_2SSn_2$: C, 50.03; H, 8.12; S, 4.45; Sn, 32.96. Found: C, 50.37; H, 8.29; S, 4.23; Sn, 32.46.

Poly(3,4-ethylenedioxythiophene)-benzo[c]thiophene-N-2′-ethylhexyl-4,5-dicarboxylic imide (PEDOT-EHIITN): 2,5-Bis(tributylstannyl)-3,4-ethylenedioxythiophene (1.468 g, 2.04 mmol) and 2,5-dibromo- benzo[*c*]thiophene-*N*-2′-ethylhexy-4,5-dicarboxylic imide (DiBrEHIITN) (0.946 g, 2.00 mmol) were dissolved in 20 mL of tetrahydrofuran (THF) under an argon atmosphere,. A catalytic amount of dichlorobis(triphenylphosphine)palladium(II) [$PdCl_2(PPh_3)_2$] (30 mg, 0.04 mmol) was added and the mixture was refluxed for 48 h. After cooling, the reaction mixture was poured into methanol (100 mL). The black precipitate was then collected by centrifugation. After washing several times with methanol, the crude polymer was further purified by redissolving in chloroform and repeatedly precipitated with methanol to afford a blue–black solid powder. The polymer was extracted with methanol, acetone, THF, and finally with chloroform using a Soxhlet extractor. The polymer was further purified by dissolving it in chloroform and precipitating it with methanol, followed by centrifugation. After drying under vacuum overnight at 40 °C, the purified polymer was obtained as deep blue powder (650 mg, yield: 71 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.64–7.02 ppm (br, 2H, Ar**H**), 3.51–4.82 ppm (br, 6H, OC**H**$_2$, –NC**H**$_2$), 0.85–1.88 ppm (br, 15 H, –C**H**$_2$, –C**H**$_3$), ^{13}C NMR ($CDCl_3$): δ 167.7, 138.3, 134.2, 128.4, 126.1, 118.7, 110.5, 65.40, 42.12, 38.20, 30.57, 28.62, 23.90, 23.02, 14.13, 10.43 ppm. Anal. Calcd. for $C_{24}H_{23}NO_4S_2$: C, 63.55; H, 5.11; N, 3.09; S, 14.14. Found: C, 60.56; H, 5.66; N, 3.13; S, 12.92. The molecular weight $\overline{M}_w$ of the polymer was determined to be 47 000 g mol^{-1}, determined using a light-scattering measurement.

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Patterned Microstructures of Porous Silicon by Dry-Removal Soft Lithography

By *Donald J. Sirbuly*, *Geoffrey M. Lowman*, *Brian Scott*, *Galen D. Stucky*, and *Steven K. Buratto**

Luminescent nanoporous silicon remains a broadly studied material due to its potential as an active component in optical or optoelectronic devices.[1,2] Recently, applications in sensor devices[3] and biomaterials[4] have fueled research into ways to controllably pattern the morphology of porous silicon (PSi) thin films. One route to patterned microstructured materials that has shown wide relevance is the family of microcontact printing techniques, collectively known as soft lithography.[5,6]

[*] Prof. S. K. Buratto, D. J. Sirbuly, G. M. Lowman, B. Scott, Prof. G. D. Stucky
Department of Chemistry and Biochemistry
University of California
Santa Barbara, CA 93106-9510 (USA)
E-mail: buratto@chem.ucsb.edu

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ADVANCED MATERIALS

Soft lithography has predominantly been used to deposit patterned self-assembled monolayers (SAMs) and other materials on a variety of substrates including silicon.[7–10] In this procedure a patterned elastomeric stamp made from poly(dimethylsiloxane) (PDMS) is "inked" with molecules that are then transferred to a substrate upon physical contact. The patterned SAM can in turn be used as a passivating layer for wet etching or selective deposition of metals. In recent years, alternate methods for pattern formation have been reported on which take advantage of a clean elastomeric stamp as an active element for pattern formation.[11,12] This procedure involves using a clean PDMS stamp as a mask for near-field optical lithography or patterned evaporation. In this communication, we outline a new procedure to directly pattern a luminescent PSi substrate by dry-removal soft lithography. We demonstrate the ability to pattern PSi on a Si substrate with various feature sizes and dimensions using no more than a clean PDMS stamp. Furthermore, we will exhibit the ability to create patterned PSi on other substrates by dry removal onto the PDMS stamp, followed by deposition onto a free-standing flexible polymer film.

Patterning PSi using a simple method such as dry removal leaves luminescent material connected to the original Si substrate. The removed film can then be transferred to another substrate, opening up a host of possible applications for both the removed and remaining PSi film. One could imagine creating a patterned linear array where each strip of PSi can be addressed separately to create an "on-chip" sensor that can detect many analytes simultaneously. In addition, one could take advantage of the emission characteristics of PSi and to create a patterned multicolor display. This could be accomplished either by chemically functionalizing different portions of the patterned porous Si surface, or through subsequent etching of the entire wafer to obtain a variety of emission colors. Another promising new application of patterned PSi is its use in carbon nanotube field-effect transistors (CNFETs).[13] Researchers at IBM have used porous silicon patterned by traditional lithography techniques as a substrate for growth of carbon nanotubes that are subsequently used as field emitters in an FET structure. Patterning the PSi layer in these devices by dry removal would make the process cheaper and easier, compared to other more elaborate lithography techniques.

A schematic representation of the procedure is depicted in Figure 1. A p-type single-crystal silicon wafer is anodically etched to produce a thin film of PSi as previously reported.[14] Samples are etched for 10–20 s at a current density of 25 mA cm^{-2} in a solution containing 15 % hydrofluoric acid and 10 % hydrogen peroxide/ethanol. After etching, the entire sample is dried and heated on a copper plate at a constant temperature of ~80 °C. A clean PDMS stamp, cast from a silicon master, with patterned features ranging in size from 3–100 μm, is then brought into contact with the heated wafer for 15–20 min. The stamp is subsequently peeled from the substrate surface, removing PSi from the areas that make physical contact with the stamp (Route I). Figure 1 (Route I) contains an optical micrograph showing fluorescence from the

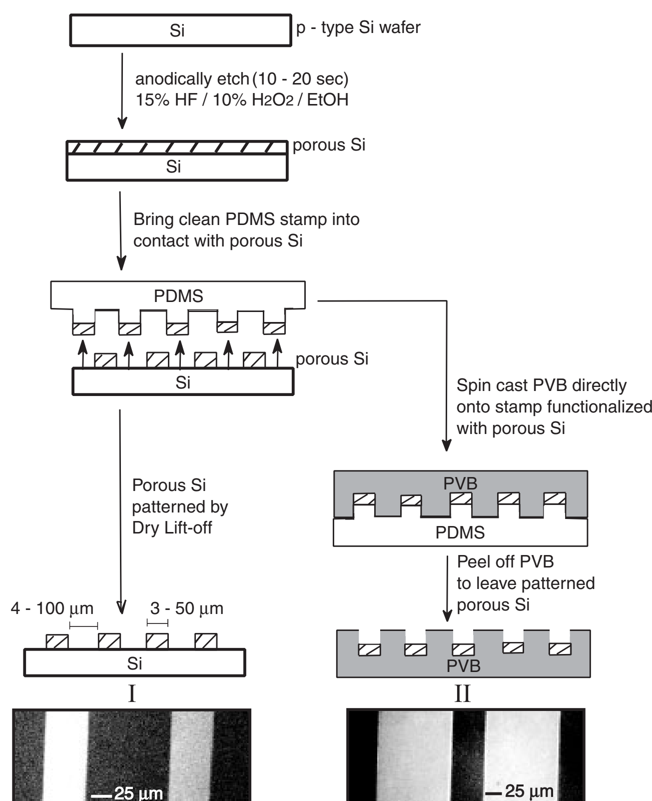

Fig. 1. Scheme for the fabrication of patterned PSi by dry removal with an elastomer stamp. A p-type silicon wafer is anodically etched for 10–20 s in 15 % HF/10 % H_2O_2/ethanol. This process creates a very thin layer of luminescent PSi (~50 nm). A prefabricated PDMS stamp with feature sizes ranging from 3–100 μm is brought into physical contact with the PSi film heated to 80 °C. (Route I) The stamp is lifted from the substrate, leaving patterned PSi on the Si wafer. Below route I is an optical image of 50 μm wide lines of PSi patterned by dry removal directly on a Si wafer. (Route II) After peeling from the silicon substrate, the PSi that has been removed retains the pattern of the posts on the PDMS stamp. A hydrophobic polymer film PVB is spin-cast directly on the stamp surface. Peeling the PVB film from the stamp results in a flexible polymer substrate with PSi bound in a pattern inverse to that of route I. An optical micrograph (shown below route II) shows fluorescence from PSi removed from the Si wafer and deposited on a flexible PVB substrate.

remaining, unaffected areas of PSi. Figure 1 (Route II) illustrates how the removed areas of PSi can subsequently be used to create patterned free-standing polymer thin films. A solution of the hydrophobic polymer poly[(vinyl butyral)-*co*-(vinyl alcohol)-*co*-(vinyl acetate)] (PVB) in ethanol is spun or drop-cast directly on the stamp surface. The solvent is allowed to evaporate leaving a thin film that can be peeled from the stamp, taking with it the areas of PSi originally lifted from the silicon wafer. This process is confirmed by the optical image shown below Route II. It is clear that the patterned PSi removed by the cast PVB film is the inverse of that in Route I. Additional studies are needed to confirm if any physical changes occur in the PSi network during the transferring process. This ongoing investigation will focus on the internal structure of the film on the PDMS stamp, and subsequently on the PVB film. From optical studies, however, we can conclude that no residual PSi is left after transferring to the PVB, and that the luminescent properties (i.e., lineshape and spectral position) of the Si nanostructures remain unaltered.

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A closer examination of a patterned PSi sample shows the degree of precision afforded from this simple procedure. Figure 2 displays characterization data from a patterned PSi substrate created by dry removal using a PDMS stamp with rows that are 3 μm wide. The fluorescence micrograph in Figure 2A shows the consistency of the pattern over a larger area. The inset shows a higher magnification confocal micrograph of the emission from the PSi. Fluorescence spectra collected from the bright and dim areas in Figure 2A are presented in Figure 2C. The emission is broad and centered at 650 nm (full width at half maximum 120 nm), which is typical for a PSi sample etched at a low current density.[15] There remains some residual PSi emission from the dim areas of the pattern at long integration times (60 s) as evidenced in the lower-intensity spectrum in Figure 2C. An atomic force microscopy (AFM) image of the same patterned PSi sample in Figure 2A is shown in Figure 2B. AFM clearly differentiates between the morphology of the PSi untouched by the stamp and that of the bare substrate left behind after the stamp is peeled from the surface. In this image the smooth morphology (root mean square (rms) roughness = 2.3 nm) corresponds to the untouched luminescent PSi, and the rough morphology (rms roughness = 12.9 nm) results from the removal of PSi. The line cut in Figure 2D (white line in Fig. 2B) clearly indicates the 3 μm line pattern left by the PDMS stamp and a film height of ~50 nm. The electron micrograph in Figure 2E provides a sharp distinction between the two morphologies seen in these patterned films.

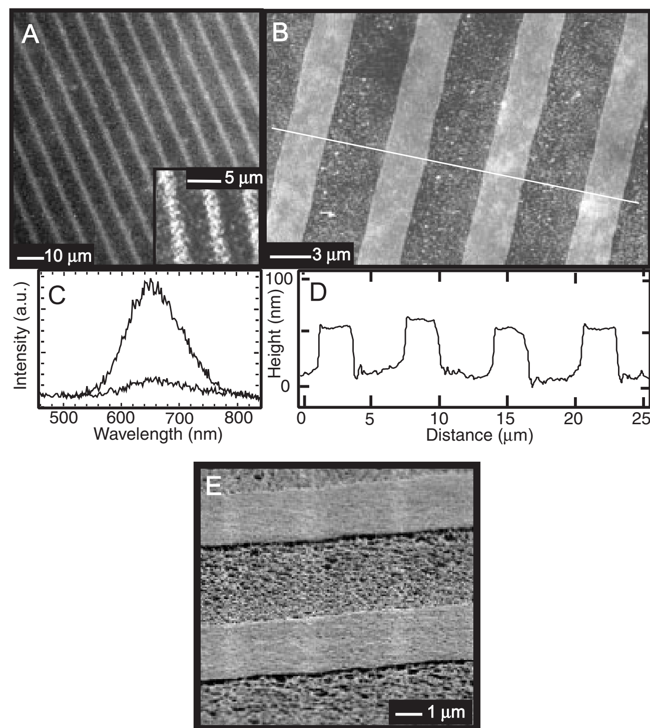

Fig. 2. A) Optical micrograph (80 × 80 μm) of emission from patterned PSi on a silicon wafer. The inset shows a confocal micrograph of a magnified area of the same film. B) AFM image of the same film. The pattern shown here has features 4 μm in width where porous silicon has been removed, leaving 3 μm wide patterned porous silicon strips. Inset shows a magnified portion of a patterned edge. C) Fluorescence spectra from a contrasting bright-and-dim region in image (A). D) Cross-section of the solid white line shown in (B). E) Scanning electron microscopy image of the same sample mention above.

To verify the versatility of the procedure, we explored stamping a second time, after a primary line pattern had been created. We chose to stamp in a direction orthogonal to the initial stamp orientation in order to produce small square posts. Figure 3A shows a reflection contrast optical image from a region on the Si substrate, where PSi was removed in a two-step process. Interestingly the spacing between the posts in one direction differs from the other. In both steps a clean stamp, patterned with the same features, was used. The Si wafer was simply rotated 90° between stamps. It is important to note that the PSi surface is not perfectly planar. During the etching process, there is a slight current gradient near the outside of the sample. The anodized region of PSi is circular with a diameter of 80 mm (the size of our electrochemical cell). The outer third of the etched region experiences ~0.3–0.5 times the current density of the inner two thirds. This leads to a higher outer edge and better contact during stamping. A larger region of the stamp is in contact with the PSi surface when the patterned lines run down the slope. In contrast, if the patterned lines run orthogonal the slope, the spacing between the untouched PSi ends up being narrower, as seen in Figure 3A. The fluorescence image in Figure 3B shows a small magnification of the patterned PSi posts. The spectra in Figure 3C where collected from a bright post and a dark region in between the posts. Note that the shapes of the posts are not perfect squares since this two-step process requires complete contact in both directions. Sharper features would be seen if a stamp patterned initially with squares were used.

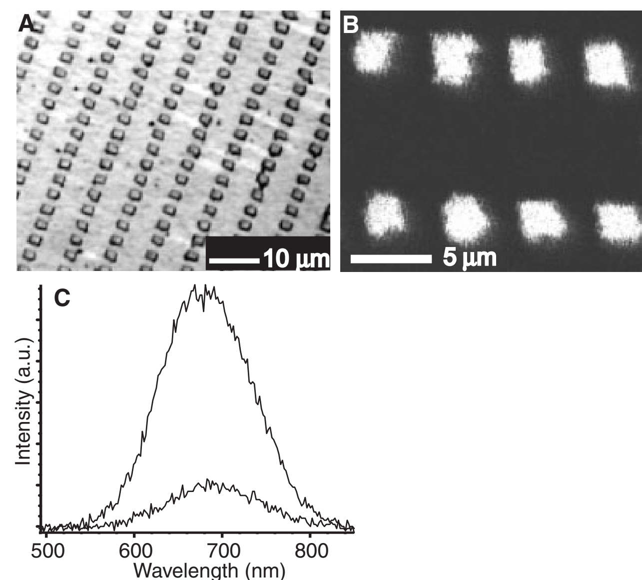

Fig. 3. A) White-light reflection micrograph of a PSi sample patterned by stamping a second time in a direction orthogonal to the first stamping. B) Confocal fluorescence image after zooming in on a region in (A). C) Spectra taken from a bright post and a dark region in between the posts.

In summary, we have developed a simple dry-removal technique for PSi films that uses nothing more than a dry PDMS

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stamp. We have demonstrated that after bringing a PDMS stamp in contact with a freshly etched PSi film, the stamp can be peeled away from the surface leaving untouched luminescent PSi patterned on the silicon substrate. The removed film can then be transferred to a flexible free-standing polymer film, while retaining its luminescence properties.

Experimental

Porous silicon films were prepared by anodically etching a p-type Si (100) wafer, resisitivity ~10 Ω cm, in a 15 % HF/10 % H_2O_2/ethanol electrolyte. Samples were etched 15–25 s at current densities of 20–25 mA cm^{-2}. Near the end of each etch (the last 1–2 s) the current density is ramped by a factor of two. This weakens the PSi/Si interface by nearly electropolishing the surface. Prior to etching, the silicon wafers were cleaned/sonicated in methanol and/or acetone. PDMS stamps were cleaned/sonicated in ethanol and blown dry with nitrogen. Etched PSi samples were placed on a heated copper block (~80 °C) for 5 min before stamping to ensure dryness. The PDMS stamp was then placed on the PSi sample for 15–20 min and removed by peeling in the direction parallel to the line pattern. Patterned samples were carefully washed with ethanol and blown dry with nitrogen.

A saturated PVB (Aldrich average $\overline{M}_w$ = 50 000–80 000 g mol^{-1}) solution was prepared by dissolving the polymer in ethanol. PVB films were created by drop-casting or spin-casting ~300 L of the saturated solution on the PDMS stamp.

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Relationship Between the Electro-Optic Performance of Polymer-Stabilized Liquid-Crystal Devices and the Fractal Dimension of Their Network Morphology

By *Ingo Dierking**

The electro-optic performance of polymer-stabilized cholesteric textures (PSCTs), namely the diffuse reflectivity, diffuse transmittance, threshold voltage, and response time, was investigated in relation to a *quantitative* measure of the morphology of the stabilizing polymer network, its fractal dimension. It is demonstrated that the reflectivity approaches a saturation value as the polymer network becomes increasingly space-filling. At the same time the transmittance exhibits saturation behavior for decreasing fractal dimensions and strongly decreases as the polymer structure becomes space-filling. The threshold electric field for switching the liquid crystal diverges on approaching a space-filling polymer structure, while it retains a finite saturation value for decreasing fractal dimensions, in accordance with the commonly observed threshold behavior of non-stabilized systems. The dependence of the electro-optic decay time verifies our interpretation, as decreasing switching times are observed for increasingly space-filling polymer structures. Universal scaling relations are proposed to relate the electro-optic performance of PSCTs to their polymer network morphology. These are verified by experimental data from three independent sample preparation series, varying the curing temperature, the UV curing intensity, and the UV irradiation time for the network formation process over a wide parameter range.

[*] Dr. Ingo Dierking
Schuster Laboratory
Department of Physics and Astronomy
University of Manchester
Oxford Road, Manchester M13 9PL (UK)
E-mail: dierking@reynolds.ph.man.ac.uk

Liquid-crystal/polymer composites[1–3] have attracted increasing interest over the last years, not only due to their promising properties for reflective display applications based on polymer-stabilized cholesteric textures,[4,5] but also with respect to fundamental insights concerning pre-transitional phenomena and elastically induced properties.[6,7] Polymer-stabilized liquid crystals (PSLCs) are obtained by dissolving a relatively small amount of a bifunctional photo-reactive (mesogenic) monomer, generally between 1–10 wt.-%, in a low-molar-mass liquid-crystal host material, together with a photo-initiator. The monomer molecules align along the liquid-crystal director field and are subsequently polymerized by UV irradiation of the sample. The polymer network prepared in this way acts as a template for the liquid-crystal order and follows the original director configuration, as has been demonstrated by optical methods, scanning electron microscopy (SEM), and confocal microscopy for a variety of different systems, including nematic, cholesteric, and smectic materials.[8–13] Elastic interactions between the liquid crystal and the phase-separated polymer network stabilize the liquid-crystal director field in which the network was formed. This is the basis of the electro-optic effect of polymer-stabilized cholesteric textures (PSCTs), utilized in reverse-mode reflective displays:[4] at zero electric field the helix of a long-pitch cholesteric liquid crystal is oriented with its twist axis perpendicular to the substrate plane and the device is transparent at optical wavelengths. Application of an electric field above a certain threshold breaks up the uniformly twisted orientation of the liquid crystal and light-scattering is observed; the device appears opaque with a certain reflectivity. For these devices no polarizers are employed, i.e., the electro-optic effect observed does not rely on electric-field-induced changes of the birefringence, in contrast to common liquid-crystal devices. Removal of the applied electric field results in a rapid reorientation of the liquid crystal back to its original director configuration,

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