

Molecular-Scale Soft Imprint Lithography for Alignment Layers in Liquid Crystal Devices

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ABSTRACT

We describe molecular-scale soft nanoimprint lithographic replication of rubbed polyimide substrates to form alignment layers for liquid crystal devices. Systematic studies of the surface relief morphology of the polyimide and molded structures in three different polymers illustrate good lithographic fidelity down to relief heights of several nanometers, and with some capabilities at the level of ~ 1 nm. Collective results of experiments with several polymer formulations for molds and molded materials and process conditions indicate that this molecular-scale fidelity in replication can be used to produce surfaces that will effectively align liquid crystal molecules. Good electro-optical responses from liquid crystal light modulators that are formed in this manner suggest utility for fundamental studies and potential practical application.

Nanoimprint lithography provides an appealing route to the fabrication of many classes of nanoscale devices for use in electronics, optics, microfluidics, and biology.^{1–5} These techniques are firmly established as research tools in these areas and, in some cases, they are also being explored for commercial manufacturing in photonics, data storage, and certain segments of microelectronics. The fundamental aspects that define the ultimate limits in the resolution of these approaches are of both basic and applied interest. For the case of imprinting with hard (i.e., high modulus) molds, studies that use molds formed from superlattices of GaAs/Al_xGa_(1–x) and from structures defined by high-resolution electron beam lithography indicate the ability to form features with lateral dimensions down to ~ 5 nm.^{6,7} Substantially smaller length scales have been explored with soft molds. In one set of experiments, casting and curing prepolymers to the elastomer poly(dimethylsiloxane) (PDMS) against individual single-walled carbon nanotubes (SWNTs) with diameters as small as ~ 0.7 nm yield PDMS molds with surface relief structures defined by the SWNTs.^{8,9} Soft nanoimprint lithography with these molds demonstrates an ability to form features with lateral and vertical dimensions in the 1–2 nm range, likely limited by the average distance between cross-links in the cured PDMS.^{8,9} Related studies using molds made of polyfluoroether elastomers produced similar results.^{10,11} Other studies report the use of PDMS

molds created with templates consisting of step edges in crystalline substrates and of latent images in layers of resist to achieve comparable resolution in the vertical dimension.^{12,13}

These basic studies reveal capabilities for imprinting (i.e., surface relief replication by molding) at the molecular scale that could create new application opportunities. One long-range possibility, for example, might involve the formation of surface relief structures that could serve as engineered sites for molecular recognition. In this paper, we explore an extremely simple, but important, application of this type. In particular, we use molecular-scale soft imprint lithography to form oriented features of relief with dimensions as small as ~ 1 nm and then employ these structures as alignment layers for liquid crystal devices. The paper begins with a description of the fabrication procedures and results of soft imprint lithography using different mold materials and molding conditions. We then summarize the use of these molded features for aligning commercially available liquid crystal materials and for incorporating them into electro-optic modulators.

Early work on liquid crystals demonstrated that mechanically rubbed surfaces of polyimide (PI) can align liquid crystal molecules and that this alignment can propagate into the bulk of the liquid crystal film via intermolecular interactions.¹⁴ Empirically optimized rubbing procedures represent the simplest and most widely used methods to form liquid crystal devices, even though the nature of interactions

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between the liquid crystals and the rubbed surfaces are only partially understood.^{15,16} In one model, these interactions have their origins in the surface topography on the substrate,¹⁷ rather than or perhaps in addition to specific chemical interactions with aligned polymer chains that might be created during the rubbing procedure.¹⁸ Although chemical interactions can play a dominant role in some cases (e.g., certain photoexposed alignment layers^{19,20}), the importance of topography has been shown clearly in experiments that use grating-type relief structures to achieve good alignment.^{21–25} In these studies, the gratings had periods in the range of micrometers to hundreds of nanometers, with relief depths between a few tens and a few hundreds of nanometers. Although such structures show the role of topography, they do not directly address the mechanisms with rubbed polyimide due to the vastly different nature of the relief features associated with these two cases. In addition, their value for practical applications is limited due to the diffraction and/or scattering that can occur upon transmission through or reflection from these gratings. In the present work, we show that the relief associated with conventional rubbed polyimide alignment layers has dimensions that extend down to the 1 nm range and that this relief can be replicated directly, using the techniques of molecular-scale soft imprint lithography, into a range of other polymers. Results indicate that these imprinted polymers can serve as effective alignment layers for commercial liquid crystal materials in a manner that avoids any significant diffraction or scattering. Comparisons of performance obtained in these cells to those that use rubbed PI provide insights into the mechanisms for alignment.

Figure 1 illustrates the procedures for molecular-scale soft imprint lithography using molds derived from rubbed PI templates and the fabrication of liquid crystal (LC) cells with molded alignment layers. Fabrication of the template began with spin coating a layer of polymer. A commercially available polyimide (Matrimid 5218; Ciba-Geigy, Tarrytown, NJ) was first dissolved in *r*-butyrolactone (Sigma-Aldrich, St. Louis, MO) to a concentration of 5% (w/v).²⁶ Unlike a polyimide prepolymer such as polyamic acid, Matrimid 5218 is a commercially available thermoplastic polyimide (PI) obtained by the polycondensation of 3,3',4,4'-benzophenone tetracarboxylic dianhydride and a mixture of two rigid cycloaliphatic indane-type monomers, 5- and 6-amino-1-(4'-aminophenyl)-1,3,3-trimethylindane.²⁷ This material can be obtained in the form of a powder that is soluble in a variety of common solvents. The PI solution was spin-cast onto substrates at 5000 rpm for 60 s. Heating on a hot plate at 250 °C for 2 h removed the solvent and created solid films of polyimide. The thicknesses were ~80 nm, as measured by profilometry (Dektak 3030). Rubbing this film gently by hand in one direction with a velvet cloth (Jo-Ann Fabric and Craft Stores, Urbana, IL) generated oriented grooves. The inset image near the top of Figure 1 shows an atomic force microscope (AFM) image (5 $\mu\text{m} \times 5 \mu\text{m}$) of a representative area. The morphological anisotropy, also shown in the two-dimensional power spectrum, is associated with the physical modification induced by directional rubbing. The relief

depths ranged from <1 nm to ~20 nm. The widths were between <50 nm, limited by the resolution of the AFM, and several hundred nanometers (Supporting Information, Figure S1). These films can be used directly as templates for generating molds for soft nanoimprint lithography. This process involves casting a liquid prepolymer to the mold material against the rubbed PI, curing the prepolymer and then peeling the resulting soft mold away from the PI. For the work described here, we used two different formulations of PDMS. The first, which we refer to as s-PDMS, consisted of a low cross-link density version of PDMS with a relatively low modulus of ~2–3 MPa (Sylgard 184, Dow Corning). The second, h-PDMS, was a more highly cross-linked variant with a modulus of ~10–15 MPa (Gelest Inc.). For the s-PDMS molds, we poured a mixture of the prepolymer (A/B = 1:10, Sylgard 184, Dow Corning) onto the rubbed PI and cured the material at 70 °C for 2 h. For the h-PDMS molds, we spin cast a ~3 μm thick layer of the prepolymer (3.4 g of 7–8% vinylmethylsiloxane copolymer, 100 μg of 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane, 50 μg of platinum catalysts, 1 g of 25–30% (methylhydrosiloxane)-dimethylsiloxane copolymer) onto the PI and then cured it at room temperature for 24 h. To facilitate handling, we cast and cured a ~5 mm thick backing of s-PDMS onto the h-PDMS to produce a mechanically robust, composite structure.

Each type of mold was used to imprint relief structures onto spin-cast layers of ultraviolet (UV) and thermally curable polymer materials according to procedures illustrated in Figure 1. In all cases, the curing was performed with the PDMS molds in physical contact with the films. The polymers included a photocurable polyurethane formulation (NOA 73, Norland Inc.), a thermally curable epoxy (SU-8 2, Microchem Corp.) and phototcurable acrylate/methacrylate formulation (SK9, Summers Optical Inc.). The polyurethane (PU) includes a prepolymer, a chain extender, a catalyst, and an adhesion promoter. Ultraviolet light illumination causes the polymer to undergo chain extension and cross-linking to yield a set PU with Shore D hardness of 60.²⁸ The SU8 is a well-known negative photoresist.²⁹ Photogenerated acids created by exposure to UV light initiate cross-linking polymerization reactions upon heating. SK-9 is a low-viscosity liquid acrylate/methacrylate photopolymer.³⁰ In each case, the fabrication began with spin-casting thin films (1–2 μm) of the liquid prepolymers onto well-cleaned glass slides. Placing the PDMS molds against these films led to conformal contact, driven by generalized adhesion forces^{31–33} and capillary flows without applied pressure. In some cases, lightly pressing the molds facilitated the removal of trapped air bubbles via diffusion through the gas permeable PDMS. For the case of PU, the photocuring occurred by UV exposure (365 nm, 14 mW/cm² for ~1 h) through the transparent PDMS molds while in contact with the PU. Similar procedures were used with SK-9. For SU8, the films with PDMS on top were first baked at 65 °C for 1 min and then at 95 °C for 1 min. The films were then exposed to UV light (365 nm, 14 mW/cm²) for 20 s to generate the acid and then cross-linked at 65 °C for 1 min and 95 °C for another 1 min.

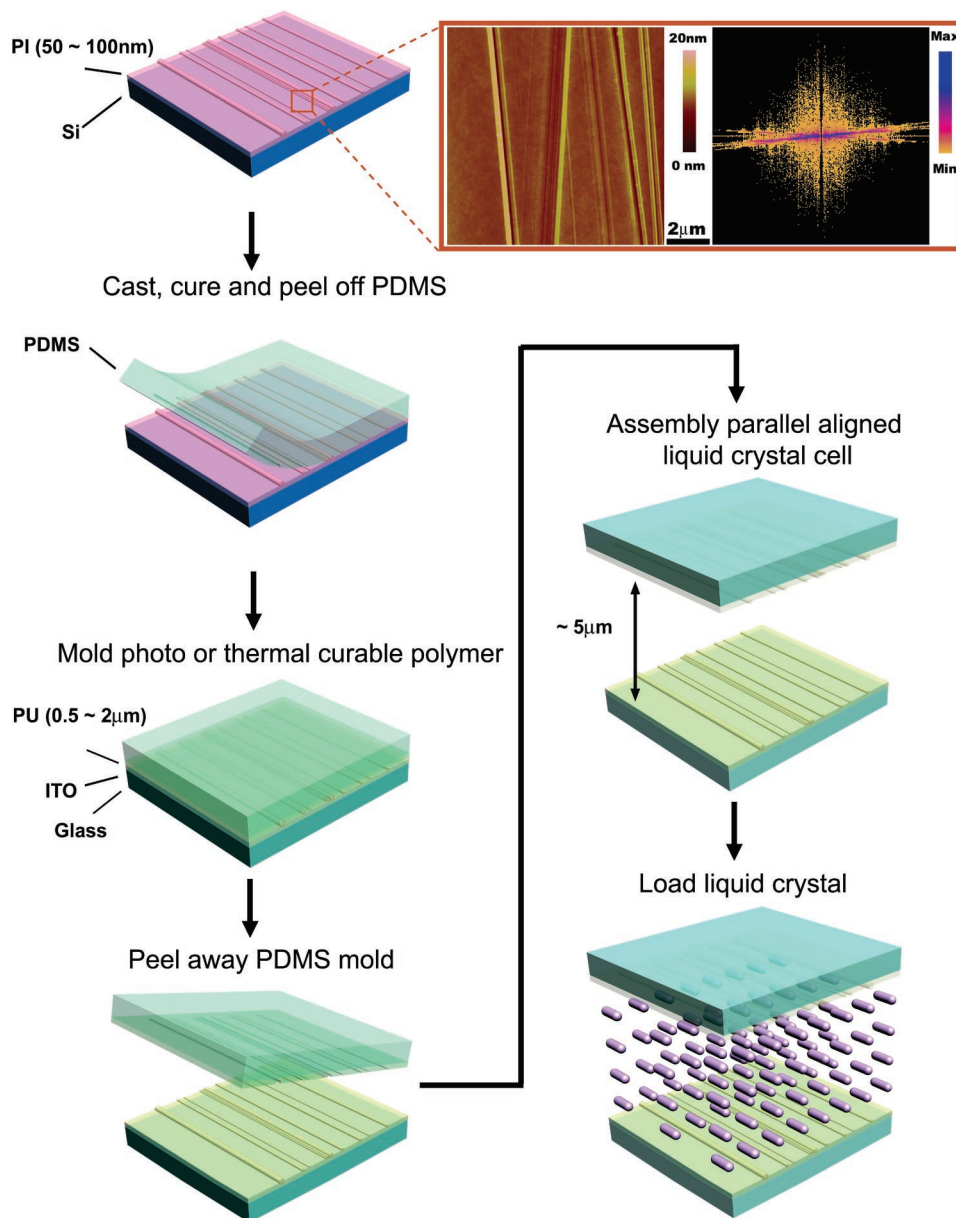


Figure 1. Schematic illustration of the fabrication of a PDMS mold from a mechanically rubbed sheet of polyimide, use of this mold to create replicas of the associated relief structures in another polymer, and implementation of these molded polymers as alignment layers in liquid crystal devices. The inset shows the surface profile measured by atomic force microscopy and a two-dimensional power spectrum of a piece of rubbed polyimide.

Removing the PDMS molds from the cured polymer films completed the imprint process. A individual mold could be used in this fashion to imprint many polymer films.

Liquid crystal cells fabricated with imprinted polymer films and with the rubbed PI films that were used as the templates provided a means to evaluate directly, in a one to one fashion, the role of relief in the alignment process. The device fabrication began by producing glass slides with imprinted polymer alignment layers. Clamping oriented pairs of these slides together with glass fibers spacers ($5\ \mu\text{m}$ diameter silica spacers, Sekisui Chemical Co., Ltd., Japan) formed the cells. A UV curable glue (SK9, Summers Optical Inc.) was placed along the edge of the cell and then cured into a solid form to hold the cells together after removing the clamps. Measuring Fabry–Perot resonances in visible

light transmission through the cells using a Cary 5G UV–vis spectrophotometer (Varian Instruments, Sugar Land, TX) provided a convenient way to measure directly the distances between the slides.³⁴ Cells had spacings of $4.9 \pm 0.1\ \mu\text{m}$, consistent with the geometry of the spacers. The liquid crystal material was 4'-n-pentyl-4-cyanobiphenyl (5CB), which has a clearing point of $35.3\ ^\circ\text{C}$.²⁶ Heating the cells to $\sim 40\ ^\circ\text{C}$ on a hot plate and then placing a drop of 5CB at their edges led to filling by capillary action. Cooling the cells after this filling process caused a phase transformation of the 5CB from its isotropic to nematic state. For measurements of the electro-optical response, the imprinted alignment layers were formed on indium tin oxide (ITO) coated glass substrates, which exhibited sheet resistances of $\sim 100\ \Omega/\square$ or less. Characterization of the LC cells involved several measure-

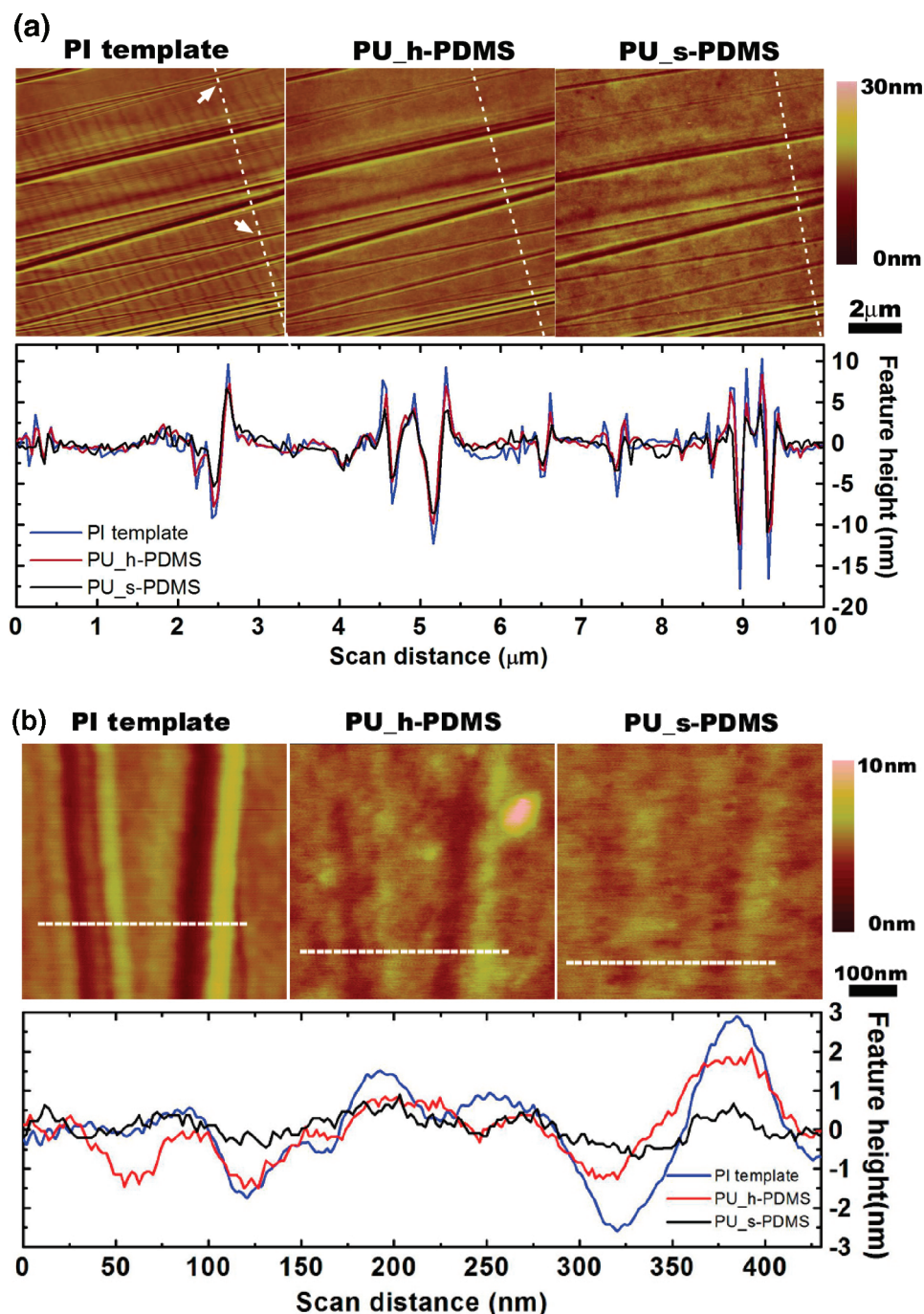


Figure 2. (a) Atomic force micrographs of structures of relief in a mechanically rubbed polyimide film (PI template) and those in molded layers of polyurethane formed with molds of high and low modulus formulations of PMDS (h-PDMS and s-PDMS, respectively). The linecuts, collected at identical locations in the respective structures, illustrate the high level of fidelity in the fabrication process. (b) High-resolution atomic force micrographs of small regions of the same samples shown in (a). The results highlight the limits in resolution (defined in this case by the degree to which heights of relief features are reproduced accurately) of replication techniques that use PDMS.

ments, including contrast ratio and order parameter, as described in detail subsequently.

Figure 2 presents AFM images and analysis of the imprinted relief structures in PU and their comparison to the rubbed PI template. For these experiments, a single template was used for fabricating the s-PDMS and h-PDMS molds to allow for direct comparison. Detailed atomic force microscope imaging of the templates shows that there is little degradation (less than 0.2 nm height loss) associated with fabrication of a mold (Supporting Information, Figures S2,

S3). The images show that the imprinted PU layers accurately reproduce the overall structures of surface relief on the rubbed PI in this range of length scales. Carefully choosing linecuts that connect pairs of intersection points (highlighted by arrows in the images) of adjacent grooves enables a stringent comparison of the imprinted structures. The plot in Figure 2a shows representative results. The resolution (i.e., minimum lateral and vertical dimensions) and fidelity (i.e., lateral and vertical dimensions compared to those on the rubbed PI template) are remarkably good for feature sizes

in this range, i.e., 1–20 nm for both s-PDMS and h-PDMS molds. To compare further and to reveal the limits, we examined high-resolution AFM scans, as shown in Figure 2b. The line cut analysis in this case involved selecting positions that match distances between two neighboring grooves. The results of Figure 2b show clearly the superior replication capabilities of h-PDMS compared to s-PDMS. In particular, s-PDMS molds yield shallower features and rougher surfaces in the imprinted structures than h-PDMS molds. In the case of h-PDMS, the imprinting process exhibits abilities to replicate features that have heights approaching the 1 nm range, although the replicated structures do not recover the full height of the template in this regime.

Statistical analysis of many grooves in the imprinted structures and the templates yields additional insights into the process. Figure 3a shows a graph of the heights of selected features in the imprinted structures as a function of the heights of those same features in the template. The results show that the imprinted structures do not fully replicate the heights. The h-PDMS molds offer the best results by this metric. Increasing the temperature of the step in the imprinting process when the molds are in contact with the PU improves the fidelity in the replication of the feature heights but increases the background roughness. (Here, the 70 °C corresponds to the case when the molds are placed in contact with the PU in a vacuum oven at 70 °C for 2 h before ultraviolet exposure. UV exposure occurs after cooling to room temperature.) Although the viscosity of the PU prepolymer is reduced by the heating, systematic studies of molding with formulations of the PU that have systematically different viscosities show little correlation between imprinting fidelity and viscosity for the range of parameters studied here. (Supporting Information, Figure S4). The temperature could have the effect of reducing the surface tension and/or of increasing the surface energy to result in improved wettability of the mold by the PU. Additional work is needed to clarify this issue.

Figure 3b shows two-dimensional power spectra of the PI template and imprinted PU replicas. The background roughness suggested by the off-axis portions of the power spectra can be quantified by measuring directly the roughness in parts of the templates and imprinted layers that were (nominally) unaffected by the rubbing process. The root-mean-squared roughness data appears in Figure 3c. The results show clearly that the roughness of the imprinted structures is higher than that in the templates and that the roughness associated with the s-PDMS molds is higher than that of the h-PDMS molds. The differences in the average distances between cross-links in the s-PDMS and h-PDMS materials are likely responsible for much of the differences observed in the roughness and other aspects of the imprinting with these two types of molds.^{8,9}

The utility of these imprinted layers for liquid crystal devices can yield additional insights into the imprinting process as well as the possible use of such a manufacturing approach for this application. Figure 4a presents optical micrographs from liquid crystal cells with rubbed polyimide and imprinted polyurethane alignment layers. In each case,

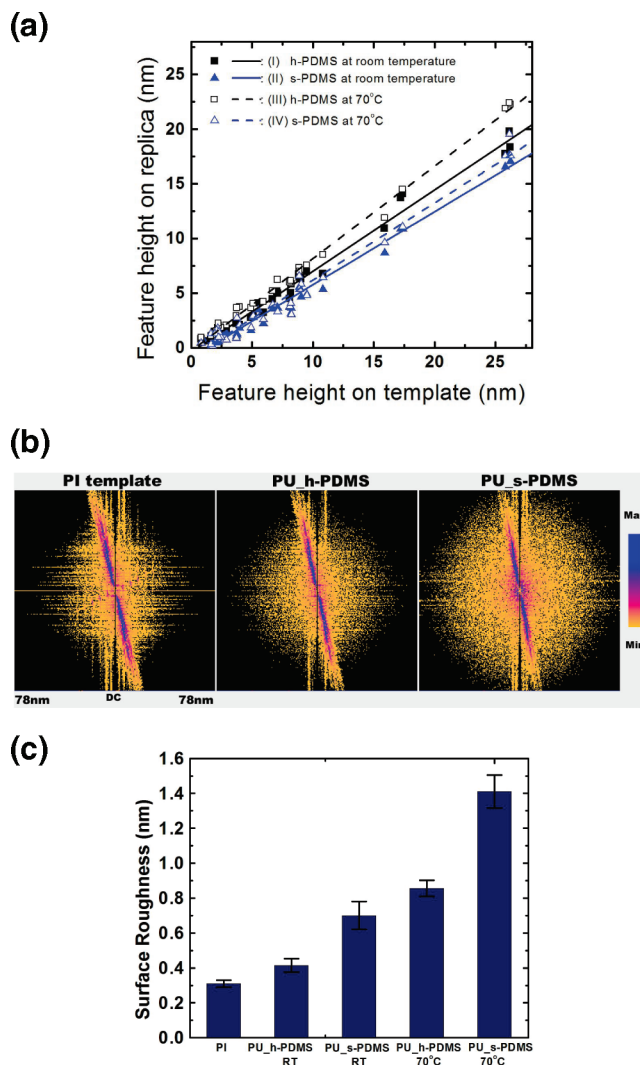


Figure 3. (a) Graph of the feature height observed in a replica molded structures of polyurethane (y-axis) as a function of the height of the corresponding features in the rubbed polyimide layer that was used as the template to create the PDMS molds (x-axis). Several cases are shown here, including bilayer molds of h-PDMS/s-PDMS (I, III) and single layer molds of s-PDMS stamp (II, IV). (I, II, III, and IV) correspond to the cases that the molding was performed at room temperature and 70 °C, respectively. Lines are linear fits to the data. (b) Two-dimensional power spectra of a rubbed polyimide surface (left frame) and corresponding molded structures in polyurethane formed using h-PDMS and s-PDMS molds (middle and right frames, respectively). (c) Root-mean-squared surface roughness measured by atomic force microscopy on the surfaces ($1 \mu\text{m} \times 1 \mu\text{m}$ areas) of rubbed polyimide (PI) and polyurethane molded with both s-PDMS and h-PDMS at room temperature and at 70 °C.

the assembled LC cells were rotated and observed using an optical microscope with crossed polarizers. As the cell rotates, bright and dark states of the LC cell appear alternatively. The maximum bright (45° to the polarizer) and dark (0° to the polarizer) states were observed for LC cells with rubbed polyimide and molded PU. The spatial uniformity of the images in these two states (Figure 4a) indicates good, homogeneous, in-plane alignment of the liquid crystal layers for all cases. Cells without any alignment layer show the expected brightly colored Schlieren structures.^{35,36} An

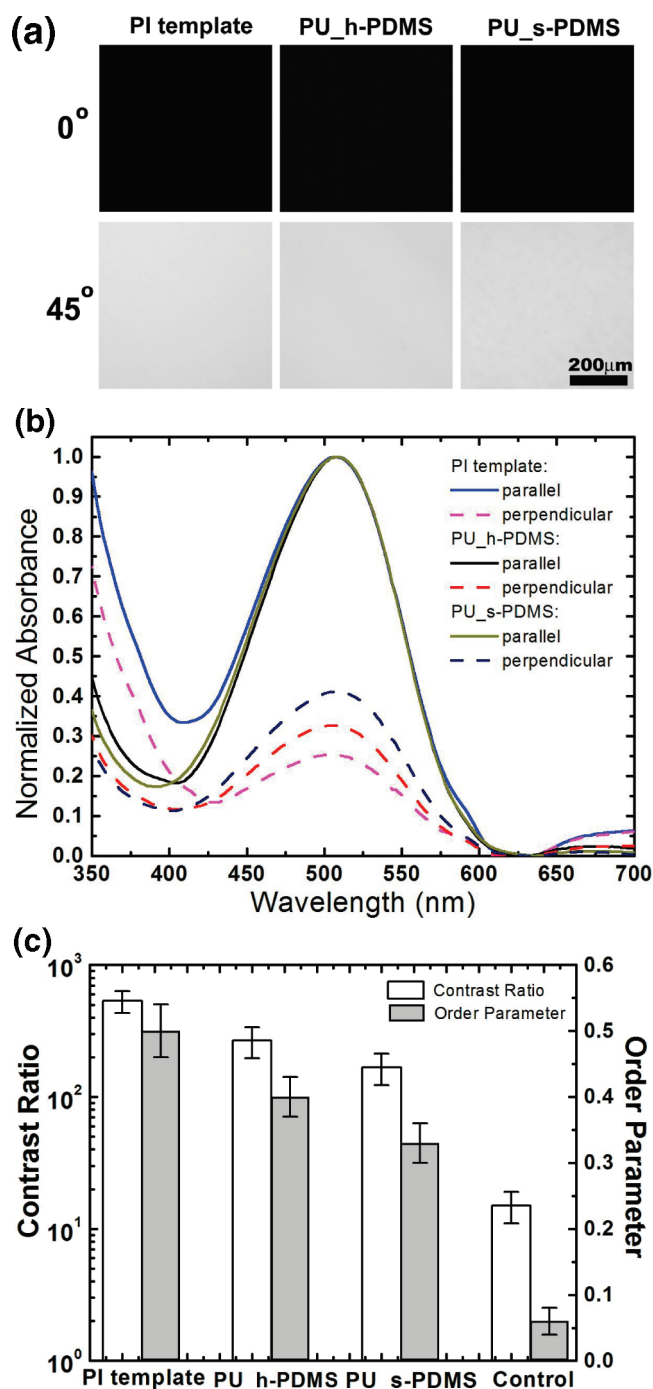


Figure 4. (a) Optical transmission micrographs measured between crossed polarizers of liquid crystal (LC) cells (thickness $\sim 5 \mu\text{m}$) that use the nematic liquid crystal 5CB and alignment layers consisting of rubbed polyimide films (PI template) and polyurethane (PU) films molded with h-PDMS and s-PDMS molds at room temperature. The designation 0° corresponds to the case that the direction of the relief structures on the alignment layers lie parallel to the analyzer. The designation 45° corresponds to a direction 45° to the analyzer. (b) Polarized absorption spectra (normalized to the peak absorbance measured in configuration where the incident polarization is parallel to the LC alignment direction) of LC cells (thickness $20 \mu\text{m}$) with PI and molded PU alignment layers. These cells contain 5CB with a small concentration of a dye that orients with the liquid crystal (DR1). (c) Comparison of contrast ratios and order parameters for LC cells that use different alignment layers. The control corresponds to a cell assembled using an alignment layer that consists of a layer of polyimide that has not been mechanically rubbed.

optical setup, including a green laser (532 nm, BRT-20-E, Brimrose Inc., Baltimore, MD), polarizers (25706 Glan-Thompson Cube Polarizer, Oriel Instruments), a precision rotation stage (Newport model RSX-1 rotation stage), and a photodiode (Silicon PIN 7781-2 photodiode, Throlabs Inc.) coupled with a chopper (HMS Light Beam chopper 230, Ithaco Inc., Ithaca, NY) and lock-in amplifier (SR 830 DSP lock-in amplifier, Stanford Research Systems) was used to determine the contrast ratio for each type of cell. The contrast ratio was measured by rotating the LC cell between two crossed polarizers and measuring the maximum (45° to the polarizer) and minimum (0° to the polarizer) intensity of light passing through the cell. The measurements (Figure 4b) show that all the LC cells generate good contrast ratio, while PU molded with h-PDMS mold offers a lower contrast ratio than rubbed PI but higher than PU molded with s-PDMS. Calculation of optical retardation based on birefringence data (0.19 for 5CB) and cell thickness ($\sim 5 \mu\text{m}$) shows that the LC cell functions approximately as a half-wave plate, with slightly less phase retardation, for the case of perfect alignment. Experimental measurement shows a contrast ratio of ~ 900 for a commercial half-wave plate. The contrast ratio provides a measure of the LC alignment quality.

The order parameter more directly addresses the question of alignment quality. The order parameter is given by:^{37,38} $S_{\text{dichr}} = (D - 1)/(D + 2)$, $D = A_{\parallel}/A_{\perp}$, where D is the dichroic ratio, $A_{\parallel}$ and $A_{\perp}$ is the absorbance for light polarized parallel and perpendicular to the liquid crystal director, respectively. The liquid crystal material studied here (i.e., 5CB) is highly transparent in the visible range but has strong absorption features in the ultraviolet between 300 and 350 nm.^{39,40} Measurement of dichroic ratio of a pure nematic phase such as 5CB is a difficult task, however, even in this range. In particular, due to very high absorption coefficients of electronic transitions, the LC layer thickness required for measurement without causing saturation in the detector is about 100 nm.⁴¹ We used, instead, the guest–host technique in which dye molecules are dissolved, at low concentrations, in the LC.^{42,43} The dye molecule has its absorption bands in the visible spectral range, where the host LC is highly transparent. Disperse Red 1 (DR1 or 4-[N-ethyl-N-(2-hydroxyethyl)amino-4'-nitroazobenzene]) is used typically due to its excellent stability and large polarity. The LC materials were prepared by mixing DR1 (Sigma-Aldrich) and 5CB to obtain a concentration of DR1 at 1% (w/v). Heating the stirred mixture of 5CB and DR1 on a hot plate at 80°C for 10 min formed a homogeneous solution. The DR1 molecules, in their stable trans form, have a rod shape similar to that of the LC molecules and also tend to become aligned parallel to the LC director axis via the guest–host effect. Measurement of dichroic ratio, as performed using a Cary 5G UV–vis spectrophotometer (Varian Instruments, Sugar Land, TX) and a Glan-Taylor CaCO_3 polarizer (GT10 (220–2500 nm), Thorlabs Inc.), provided a means to evaluate the order parameter. Figure 4b shows the polarized absorption spectra for LC cells with the director axis parallel and perpendicular to the light polarization direction and the control case without any alignment. The spectrum shows the maximum absorption

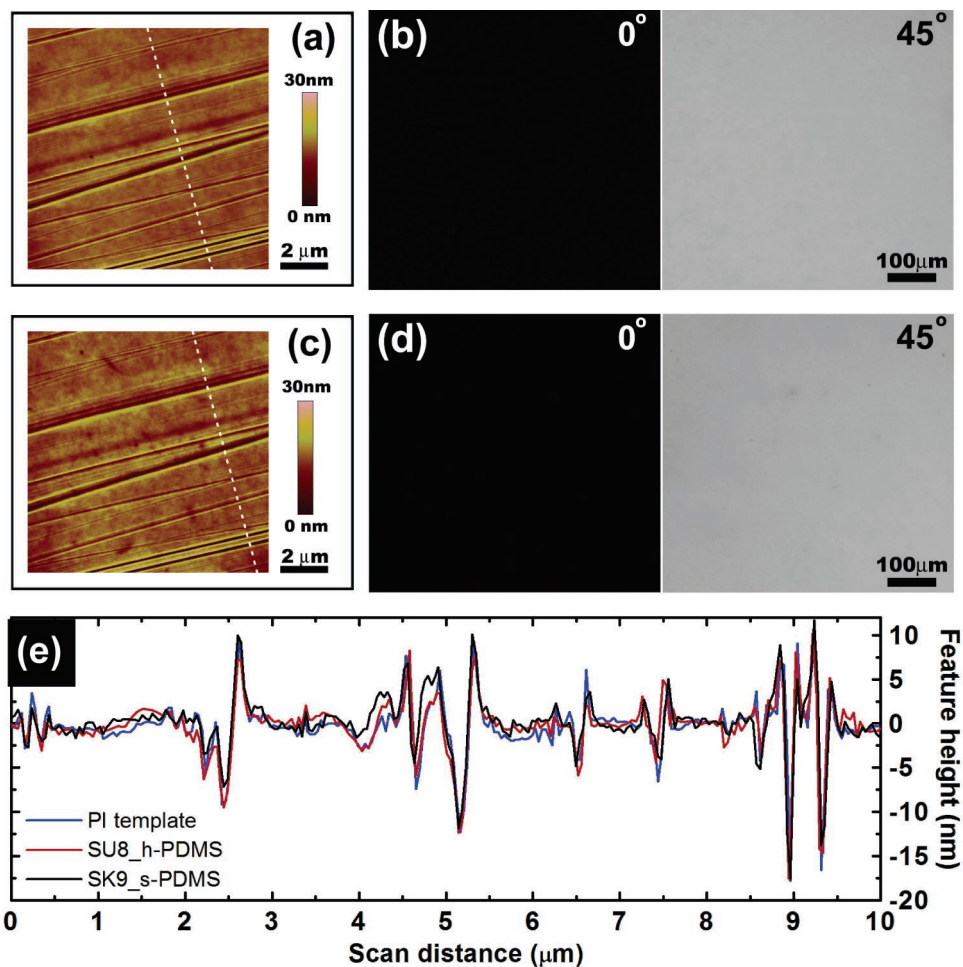


Figure 5. (a) Atomic force micrographs of structures of relief molded on a layer of epoxy (SU-8) formed using a h-PDMS mold generated with a rubbed polyimide (PI) template. (b) Optical transmission micrographs measured between crossed polarizers of liquid crystal (LC) cells (thickness $\sim 5 \mu\text{m}$) that use the nematic liquid crystal 5CB and alignment layers consisting of the molded SU-8. The designation 0° corresponds to the case that the direction of the relief structures on the alignment layers lie parallel to the analyzer. The designation 45° corresponds to a direction 45° to the analyzer. (c, d) Results similar to those in (a) and (b) for the polymer poly(acrylate/methacrylate) (SK-9) (e) Linecuts, collected at identical locations in the respective structures, including the PI template, that illustrate the high level of fidelity in the fabrication process.

at 504 nm for DR1 anisotropic absorption with calculated dichroic ratio of 4.0 for rubbed PI alignment layers, 3.0 for PU imprinted layer from h-PDMS mold, and 2.5 for PU layer from s-PDMS mold. LC cells fabricated using glass and rubbed PI, molded PU formed with h-PDMS, molded PU formed with s-PDMS, and unrubbed PI exhibited order parameters of 0.50, 0.40, 0.33, and 0.06, respectively. These trends suggest that the differences in the alignment quality result, at least partly, from differences in the surface relief structures. Relative strengths of chemical interactions between the LC molecules and the polymer layers are also likely important. The 5CB molecule is approximately 1.8 nm in length and approximately 0.25 nm in diameter. These dimensions are comparable with those of the chemical repeat unit of the main chain backbone (e.g., aromatic ring) for polyimide.

To explore further this important of chemistry, and to demonstrate the general applicability of the soft imprinting procedures, we formed imprinted alignment layers with other polymers. Figure 5 shows AFM images of imprinted layers of SU-8 and SK9 using the same h-PDMS mold. Both

polymers show good fidelity in the replicated relief structures comparable to the polyurethane replicas. Optical micrographs exhibit levels of alignment that are somewhat worse, in both cases, than results obtained with rubbed PI and imprinted PU (Figure 4). The measured order parameter is ~ 0.2 for each case, suggesting that surface chemistry may play a role in liquid crystal alignment. For instance, compared to polyimide and polyurethane, SU8 is an epoxy resin that forms highly cross-linked three-dimensional network structures through cationic polymerization. Although the structure contains phenyl rings, its highly cross-linked nature may make it less favorable for aligning liquid crystal molecules compared to PI and PU. SK-9 is based on acrylate/methacrylate chemistry and its exact chemical structure is not available from the manufacturer. Further study will be required to provide additional insights into these issues; studies with surfaces terminated with different functional groups, for example, could yield additional insights.

Functioning devices can be built with these imprinted alignment layers. Figure 6 presents the electro-optical responses of liquid crystal cells made using the rubbed

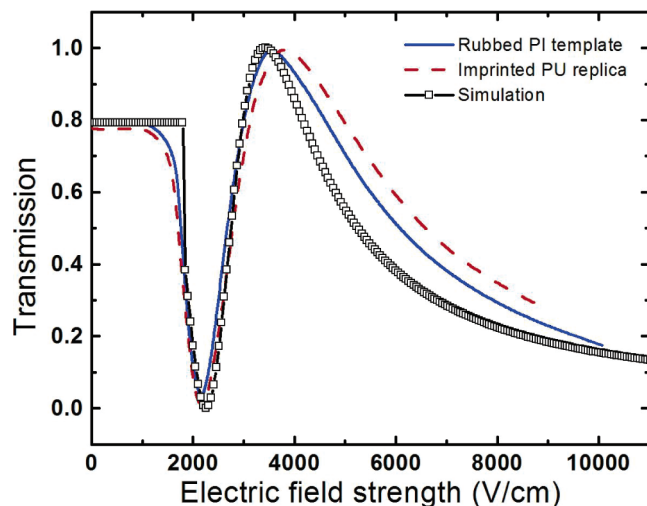


Figure 6. Electro-optical response of parallel aligned liquid crystal cells (thickness $5\ \mu\text{m}$) made from rubbed polyimide films and from molded polyurethane films as alignment layers. An ac driving voltage with a frequency of 400 Hz was used.

polyimide and PU imprinted using h-PDMS. These measurements used an alternating square wave voltage with a frequency of 400 Hz (BK Precision 4017 function generator) applied to ITO electrodes. For these parallel aligned LC cells, the optical retardation (δ) decreases with increasing root-mean-squared voltage. The intensity of light that passes through the cells placed between crossed polarizers oscillates like the square of the sine of optical retardation.⁴⁴ The transmission, T , can be expressed as: $T = \sin^2(\delta/2) = \sin^2(\pi d \Delta n / \lambda)$,³⁷ where δ is the optical retardation, d is the cell thickness, λ is the wavelength, and $\Delta n = n_{\parallel} - n_{\perp}$ is the birefringence of 5CB. Applying an electric field in the out-of plane direction changes LC alignment from planar to homeotropic, resulting in decrease of birefringence. The measurements indicate similar electro-optic responses in LC cells with rubbed polyimide and imprinted PU alignment layers (Figure 6). These experimental results are in good agreement with the simulated data calculated from the elastic continuum theory and the Jones matrix methods (open square dots in Figure 6). Compared to the PI case, the PU cell requires a higher voltage to achieve a similar dark state due to differences in the thicknesses of the alignment layers in these two cases (PI layer thickness is 80 nm; PU layer thickness is $1.65\ \mu\text{m}$).

In summary, this paper demonstrates several aspects of molecular-scale soft imprint lithography and its use in the area of liquid crystals. The results provide some insights into basic aspects of the alignment process, and they demonstrate the practical feasibility of soft imprinting for this class of application. Additional improvements in the fidelity of molding process and its direct application to polyimide materials might improve the technical outlook for realistic applications, and also clarify further the mechanisms of alignment. These and other areas represent promising directions for future work.

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Supporting Information Available: The detailed AFM measurement of templates and replicas before molding and after molding and viscosity effects on molding fidelity. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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