Patterning of Crystalline Organic Materials by Electrohydrodynamic Lithography

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The control of semi-crystalline polymers in thin films and in micrometer-sized patterns is attractive for (opto-)electronic applications. Electro-hydrodynamic lithography (EHL) enables the structure formation of organic crystalline materials on the micrometer length scale while at the same time exerting control over crystal orientation. This gives rise to well-defined micro-patterned arrays of uniaxially aligned polymer crystals. This study explores the interplay of EHL structure formation with crystal alignment and studies the mechanisms that give rise to crystal orientation in EHL-generated structures.

1. Introduction

Elegantly designed micro- and nanostructures are essential for the fabrication of high-performance devices, including integrated circuits, displays and sensor arrays. The key to the realization of these and other applications is the availability of a scalable lithographic technique. Substantial progress has been made in developing micro-and-nanopatterning processes^[1-4] over the past decade. While the vast majority of micro- and nanofabrication schemes utilize macromolecular resists, several methods have been extended to pattern nonpolymeric materials, such as glasses, ceramics, ferroelectric and crystalline materials, because of the interesting physical properties these materials can offer. Particularly interesting is the patterning of crystalline materials into design structures because of their importance in optoelectronic applications^[5] and bio-macromolecular immobilization.^[6] For instance, optically active, semicrystalline conjugated polymers are competitive candidates for field-effect transistors (FETs), solar cells and light emitting diodes.^[7,8] In particular, in thin-film FETs, the mobility of charge carriers has been shown to be directly

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dependent on the orientation of semicrystalline chains.^[9,10] The morphological organization of crystalline polymers into regular surface structures has also been demonstrated to strongly influence the selective adsorption behavior of proteins on surfaces.^[11] In thin films, nano-imprint lithography has beed used to partially align semi-crystalline polymers,^[12] including conjugated polymers for photovoltaic applications.^[13–15] Despite these promising results, the development of a simple robust route towards the fabrication of surface patterns containing aligned organic crystals remains a considerable challenge.

The increasing need for low-cost and high-throughput pattering methods of various materials led to the development of alternative lithographic techniques.^[16–18] Initially established to pattern highly viscous amorphous polymers with a resolution down to 100 nm, electro-hydrodynamic lithography (EHL)^[4] has recently been extended to a broad range of materials, including ceramics,^[19] nanocomposites,^[20] and low-viscosity resists with fast pattern formation kinetics.^[21] The generic nature of this straight-forward technique extends its applicability to an even larger class of materials. Here, we demonstrate the use of the EHL method to generate welldefined micrometer-sized patterns of organic crystals and study the interplay of electro-hydrodynamic pattern formation and crystal alignment.

The EHL method makes use of a capacitor device that includes a polymer-film-covered electrode opposed by a second electrode with a topographic design pattern, shown in **Figure 1**. The application of a voltage U across the two capacitor plates gives rise to an electric field $E_{\rm f}$ that varies laterally across the device. The reduced distance between

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Figure 1. EHL pattern replication of a structured electrode: A) A thin film in a capacitor assembly is liquefied and the amplification of instability is triggered by applying a voltage *U*. B) The heterogeneous force field directs the electro-hydrodynamic instability towards the protruding structures and generates liquid columnar bridges between the two electrodes. C) Coarsening of the pillars results in a positive replica of the master pattern. In unstructured regions, the film remains stable on a much longer timer scale.

downward protruding parts of the structured electrode and the film locally enhances the electric field, triggering film destabilization and focusing the electro-hydrodynamic instability towards these protrusions. This yields a pillar pattern spanning the capacitor gap at the locations of the smallest interelectrode distances (Figure 1B), which eventually, by coalescence generates a replicated pattern of the upper electrode. The final structure is a positive replica of the structured electrode (Figure 1C) as opposed to negative replication achieved by conventional imprinting techniques. The final height of the polymer structure is determined by the plate spacing.

In this work the EHL technique is used to pattern crystalforming polymers. This results in the formation of surface structures which contain anisotropically oriented polymer chains perpendicular to the substrate. Positional control of the generated morphologies can be adjusted by varying a number of experimental parameters, such as the initial film thickness, inter-electrode spacing, electric field strength, surface tension, and lateral periodicity of the master electrode. The orientation of the crystalline *c*-axis is governed by key process parameters such as the electrostatic torque. Our study is a model study on generic polymers, which may pave the way for the control of crystal morphology in the technologically more relevant conjugated polymer systems.

2. Methods

Polycaprolactone (PCL) and poly(dimer acid-*co*-1,6-hexanediol-*co*-adipic acid) (PDHA) were purchased from Sigma-Aldrich. Highly polished p-doped silicon (Si) wafers, with $\langle 100 \rangle$ crystal orientation (Wafernet Gmbh, Eching, Germany) were used as substrates. Patterned silicon wafers were obtained from X-lith eXtreme Lithography, Ulm, Germany). Chloroform (Fischer Inc.) was used as the main solvent.

Film thicknesses ranging from 40 to 350 nm (±10 nm) were generated by spin-coating onto silicon substrates from chloroform solutions with typical concentrations of 2–3% polymer by weight. Prior to spin-coating, the substrates were cleaned in a 'piranha' solution consisting of 3:1 H_2SO_4 (98%): H_2O_2 (30%), followed by thorough rinsing with deionised water and drying under nitrogen. Substrates as well as top-electrodes were snow-jet cleaned immediately before film deposition and device assembly. Planar as well as topographically structured top-electrodes were mounted facing the polymer-covered substrate, leaving a thin air gap, *d* (Figure 1). Silicon oxide colloids were used as spacers to

adjust d. Both capacitor electrodes were electrically contacted using silver paint (Electrodag 1415M). A constant voltage of 80 V was applied across the two electrodes of the capacitor. In some experiments, the upper electrode was substituted by a thick Kapton CR (DuPont) sheet (27.0 µm) with a thermally evaporated 50 nm thick Au layer on the reverse side. In these experiments conformal contact of the top electrode with the film was established by a thin layer (~3.0 µm) of poly(dimethylsiloxane) (PDMS, Sylgard 184, Dow Corning) that was spin-cast and thermally crosslinked on the front side of the Kapton sheet. Since, the overall distance between the Au and the film substrate (i.e., the two electrodes) was ~30 µm, a much higher voltage of 4.5 kV was applied to achieve a comparable field in the polymer film as in the experimental configuration of Figure 1. After quenching to room temperature which induces the crystallization of the polymer, the electric field was disconnected and the upper electrode was removed.

The resist viscosities were measured using a 1° cone and plate rheometer (Physica MCR 501, Anton Paar) at temperatures above the melting point of each polymer. A Zeiss AXIO Imager was used for light microscopy and an Olympus BX51 optical polarizing microscope was used to investigate the optical textures of the crystalline material. The optical anisotropy of oriented samples was evaluated with regard to variations of the intensity of reflected or transmitted light using a spectrometer (QE6500, Ocean Optics) that was attached to the microscope. The microscope halogen lamp acted as an illumination source for the spectroscopic measurements. Linear polarization measurements were obtained using achromatic polarizers (Thorlabs, Inc.) in cross and parallel configurations. The maximum intensity of reflected polarized light corresponds to the chains oriented parallel to the polarizing filter, with minima for chain orientations perpendicular to the filter. The sample topography was analyzed by tappingmode atomic force microscopy (AFM) (Veeco, Dimension 3100). For transmission electron microscopy (TEM) crosssectional imaging, the crystalline film was embedded in Spurr epoxy resin. The substrate was removed and the film was sectioned using diamond knife in a Leica Ultracut Microtome, yielding sections with thicknesses of 40-100 nm. The cross-sections were analyzed using a FEI Technai 20 TEM (LaB₆) at an acceleration voltage of 200 kV in diffraction mode. The obtained diffraction patterns were analyzed using Digital Micrograph image (Gatan v3.3) processing software and a computer program for the simulation of polycrystalline electron diffraction patterns and phase identification (JECP/ PCED).^[22]

3. Results and Discussion

Figure 1 summarizes the principle of the experimental procedure. To demonstrate the versatility of our approach, two crystalline materials were selected for EHL patterning: PCL and the amphiphilic PDHA. The low softening temperatures and viscosities of the two samples (PCL: glass transition temperature, $T_g = -59$ °C, crystallization temperature, $T_c = 47$ °C, melting temperature, $T_{\rm m} = 58$ °C, and viscosity, $\eta = 1.2$ Pa·s; PDHA: $T_{g} = 20$ °C, $T_{c} = 35$ °C, $T_{m} = 47$ °C, and $\eta = 0.55$ Pa·s) result in a short annealing-quenching cycle, enabling highspeed EHL patterning. PCL is a biodegradable low-cost material which is often used for bio-sensing applications and bio-absobable surgical devices. Generally, the liquefaction of a film is achieved by annealing the material above the softening point, followed by preserving the formed structures by cooling to the solid state. In the present approach solidification is achieved by gradual quenching of the generated pattern to its crystalline state.

Films and experimental assemblies of both materials were prepared in a similar manner. Initially, a thin film was spin-cast onto a silicon wafer acting as bottom electrode. The film was opposed by a structured second electrode, leaving an air gap and forming a capacitor-like set-up. Subjecting the assembly to thermal annealing well above the melting temperature equilibrates the film, erasing all structural spherulitic features, thereby providing a homogeneous film prior to the EHL patterning. Then, a constant voltage is applied across the liquefied film. The electric field gives rise to a surface instability which is amplified. The surface undulations are drawn towards the protruding electrode structures, eventually bridging the two electrodes, thereby replicating the electrode structure. Quenching the sample below its melting point terminates the lithographic process and induces crystallization, generating a well-defined pattern of the crystalline polymer. Figure 2 shows a PCL square grid with a square



width of $\approx 2.9 \pm 0.4 \,\mu\text{m}$ (Figure 2A,B) and a PDHA lines pattern ($\approx 1.1 \pm 0.3 \,\mu\text{m}$ in width, Figure 2E,F). AFM images reveal structure heights of 75 ± 3.0 nm and 180 ± 17 nm, respectively. The structured electrodes have lateral feature dimensions of 3.0 μm for the cross-hatched structure (Figure 2A, left) and 1.0 μm (Figure 2E, left) for the line pattern. The replicated patterns in the polymer film are formed over the entire electrode area (i.e., 150 $\mu\text{m} \times 150 \,\mu\text{m}$, see Supporting Information (SI)) and are highly reproducible. The electrostatically induced structure formation in the polymer film is not limited to wavelengths around the intrinsic instability wavelength, and a large range of lateral structural features can be replicated for otherwise identical experimental parameters.

Well-ordered structures with nearly vertical walls, comprising stacks of crystals were obtained for both PCL (Figure 2B) and PDHA (Figure 2F). While the crystalline PCL texture of the formed patterns is evident in the optical microscopy images, polarized optical microscopy (POM) is required to reveal the crystalline nature of the PDHA line pattern (Figure 2F, inset). This suggests that the grain size of crystals forming the PDHA pattern is finer compared to PCL.

To further investigate the crystalline orientation within the formed pattern, electron diffraction of thin sample sections was performed. The electron beam was normal to the film surface. In this transmission geometry only reflections from lattice planes perpendicular to the film plane are observable. Figure 2C and G show diffraction patterns of patterned PCL and PDHA films, respectively. The illuminated area was 350 μ m², i.e., approximately 5–7 lines were imaged for both pattern types (cf. Figure 2B,F). For both replicated structures of PCL (Figure 2C) and PDHA (Figure 2G) a set of nested rings have formed in the diffraction plane, indicating polycrystalline samples.

All observable diffraction rings for PCL can be indexed as (hk0)-reflections of the orthorhombic PCL crystal structure.^[23] The two inner-most rings were indexed as (110) and



Figure 2. AFM images of a master electrode (left) and the replicated structures (right) of PCL (A) and PDHA (E) with corresponding cross-sections determining lateral and vertical dimensions of the pattern. Optical micrographs reveal well-defined crystalline EHL-generated patterns of PCL (B) and of PDHA in (F). The POM images enable the visualization of the crystalline texture of the line pattern (F, inset). Diffraction patterns for a large area of the PCL (C) and PDHA (G) patterns. Selected area diffraction pattern obtained with an aperture of 3.0 µm of a single PCL crystal in (D) and with a 1.0 µm aperture diameter of a single PDHA crystal in (H).

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(200) reflections, followed by (210) and (020) planes for the third and fourth rings, the (120) and (310) planes for the fifth ring and the (400) and (410) planes for the sixth and seventh rings, respectively. Diffraction patterns recorded from different areas of the patterned PCL films invariably showed only (hk0)-reflections.

Note that the diffraction rings of the PCL pattern are made up of discrete spots, while PDHA diffraction produced a more continuous ring pattern, indicating smaller crystal grains in comparison to PCL. When imaging a smaller area, individual single-crystalline grains become apparent. A selected area diffraction (SAD) pattern in Figure 2D was recorded from a 3.0-µm-wide area on the PCL sample. The different spots can again be assigned to different (hk0)reflections. The absence of (h00) and (0k0) reflections with odd h and k as well as the lattice parameters a = 0.74 nm and b = 0.50 nm agree with published values.^[23] Electron diffraction therefore demonstrates that PCL crystals are uniaxially aligned during the patterning process with the *c*-axis (i.e., the chain axis) parallel to the film normal. A comparison of Figure 2C and D indicates a grain size of approximately 3.0 µm.

Similarly, SAD diffraction patterns were obtained from single PDHA crystals (Figure 2H) with a selected diffraction area width of 1.0 μ m, indicating smaller (~1- μ m-wide) aligned PDHA grains. The spots form a slightly distorted hexagon, which were assigned to the (020) and (110) crystal planes. Again, an alignment of the crystal *c*-axis almost parallel to the film normal is found.

Both SAD patterns correspond to *c*-axis-aligned single crystals, albeit of different crystal dimensions, which is in agreement with the optical observation of Figure 2D,G. For both crystal types, chains were highly aligned along the electric field vector, i.e., normal to the film surface.

The alignment of structurally anisotropic fluids by EHL is well known. For example carbon nanotubes dispersed in a polymer matrix align normal to the film surface through a combination of shear flow and an electric field induced torque.^[20] Similarly, cylindrical or lamellar block-copolymers morphologies align in electric fields through an interplay of the same forces.^[24] The system discussed here is different, however, because the EHL experiment was carried out in the molten state of the polymers, where structure of the polymers is isotropic. Crystallization sets in only after pattern formation is complete.

Three possible mechanisms can lie at the origin of the observed crystal *c*-axis orientation: 1) EHL pattern formation induces shear- and elongational flow in the film, which could pre-align the chains perpendicular to the film surface. This pre-alignment facilitates the formation of *c*-axis oriented crystals upon quenching below the melting point. 2) During the temperature quench, the forming crystals exhibit anisotropic dielectric properties which have an orientation-dependent free energy of a crystal in an electric field,^[25] similar to polymers with anisotropic magnetic properties in magnetic fields.^[26,27] This may cause the crystal nuclei to rotate into a preferred orientation upon nucleation. 3) Crystallization of polymers in confined geometries can show macroscopic alignment (kinetic "gate effect"^[28]). In thin films, 2D

confinement selects the fast growing crystallization direction to lie in the plane of the film.

Before experimentally testing these three mechanisms, it is useful to estimate the potential role of the first two mechanisms, i.e., flow-induced chain alignment and crystallite rotation induced by dielectric anisotropy. Flow is known to enhance crystallization rates and to align crystals.^[29] For polymers, these effects appear above a molecular-weight-dependent critical strain rate.^[29,30] For PCL with $M_n = 80\ 000\ \text{g mol}^{-1}$, shear rates as low as $\dot{\gamma} \leq 1\ \text{s}^{-1}$ applied during a quench from $T = 80\ ^{\circ}\text{C}$ to $T = 46\ ^{\circ}\text{C}$ enhance crystallization.^[31]

Note however, that the at the temperature of the EHL experiments, the polymers are in their (non-crystalline) random-coil conformation. It is therefore necessary to estimate the timescale on which a possible flow-induced alignment of a chain decays. The longest time scale in a random coil polymer melt is the reptation time^[32]

$$u_{\rm rep} \approx \frac{\langle L \rangle^2}{D} = \frac{\zeta b^2 N^3}{k_{\rm B} T N {\rm e}},$$
(1)

with the friction coefficient $\zeta = 6\pi\eta R_g$ and the radius of gyration of the coils $R_g = a\sqrt{N}$. For PCL the degree of polymerization was $N \approx 88$. Using a monomer size $a \approx 1$ nm and $\eta = 1.2$ Pa·s, we find at T = 75 °C a value of τ_{rep} of around 10 ms. Since the samples are kept in the molten state substantially longer after EHL pattern formation has finished, before a quench to room temperature, the effect of flowinduced chain alignment on polymer crystallization is likely to be negligible.

The second mechanism relies on the anisotropic dielectric constant of a polymer crystal. To this end, we follow a similar calculation that considers a polymer crystal with an anisotropic magnetic susceptibility in a magnetic field.^[27] The free energy of a crystal with volume V in an electric field \vec{E} is given by

$$F = F_0 - 2\varepsilon_0 \int_{V} \vec{E} \vec{\varepsilon} \vec{E} d^3 r, \qquad (2)$$

with the matrix $\tilde{\varepsilon}$ the anisotropic dielectric constant of the crystal. Defining ϑ as the angle between the electric field and the crystal *c*-axis (i.e. the polymer chain backbone) and defining $\varepsilon_a \approx \varepsilon_b < \varepsilon_c$, the angle-dependent part of the free energy is $F(\vartheta) = -V/2\varepsilon_0 E^2 \Delta \varepsilon \cos^2 \vartheta$, with $\Delta \varepsilon = \varepsilon_c - 0.5 \cdot (\varepsilon_a + \varepsilon_b)$. With this choice of parameters, the *c*-axis orientation of the crystal parallel to the electric field lines is energetically preferred. Comparing the difference $\Delta F = F(\vartheta = 90^\circ) - F(\vartheta = 0^\circ) \sim k_{\rm B}T$ with the thermal energy gives an estimate for the minimum volume of a crystal that aligns in the electric field. Furthermore, the time needed to rotate a sphere with dielectric anisotropy $\Delta \varepsilon$ in a viscous liquid with viscosity η in an electric field with strength *E* is given by^[27]

$$\tau = \frac{6\eta}{\varepsilon_0 \Delta \varepsilon E^2}.$$
(3)

In the absence of values for ε_i (*i* = a,b,c) for PCL, we have to resort to several approximations to estimate the minimum volume and the rotation time. The crystal structure of PCL in

the a-b plane is very similar to polyethylene (PE) and PCL, like PE, forms negatively birefringent spherulites,^[33] i.e. the refractive index along the chain axis is highest. If we approximate ε_i (PCL) $\approx \varepsilon_i$ (PE) $\approx n_i^2$ (PE), the above quantities can be estimated. The refractive indices of PE are $n_{\rm a} \approx n_{\rm b} \approx 1.52$ and $n_c \approx 1.55$. For an electric field of 80 V over 75 nm we find at T = 60 °C a volume of $V \approx 1 \text{ nm}^3$ where free energy difference $\Delta F = F(\vartheta = 90^\circ) - F(\vartheta = 0^\circ)$ becomes comparable to the thermal energy. With the viscosity $\eta = 1.2$ Pa·s of PCL at T =70 °C, a rotation time of $\tau = 10^{-4}$ s is estimated. Both, the small volume and the fast rotation time indicate that this alignment mechanism may well be active in our experiments.

To experimentally address the question, which of the three proposed crystal alignment mechanisms is dominant, an additional series of measurements was performed. Since PCL is a well-studied crystalline polymer we will limit the further discussion to this polymer only. Two new sample types were prepared. First, a thin PCL film was annealed above it melting point and quenched to its crystalline state. In this experiment neither flow nor electric field effects act on the sample, leaving crystallization confinement as only possible cause for crystal alignment. Second, rather than leaving an air gap in the capacitor, the top electrode was brought into direct conformal contact with the crystal polymer film (see Section 2). This sample was exposed to the same



Figure 3. Electron diffraction patterns and corresponding relative integral intensities of: A) EHL structured films, B) a film crystallized in the absence of an applied electric field, and C) a sample crystallized in an applied electric field, but in the absence of an air-gap. D) Comparison of relative intensities of the diffraction patterns in A–C to a random PCL powder.^[23] E) Assignment of diffraction rings to the *c*-axis inclination angles with respect to the [001] orientation.

temperature and electric field cycle as the EHL samples. In this device geometry, only hydrodynamic flow is suppressed, with the electric field and film confinement acting on the PCL crystals during the temperature quench.

The TEM diffraction patterns of the two samples are shown in **Figure 3**B and C. Qualitatively comparing Figure 3A–C, we note the following: 1) The diffraction rings of all three samples exhibit an intensity pattern, 2) the number and location, and 3) the relative averaged intensities of the ring in Figure 3A–C vary. This is indicative of partial crystal orientation in all three samples, but the degree (and possibly orientation) of crystal alignment differ in the three samples.

Thin polycrystalline films with randomly oriented crystals exhibit a characteristic electron diffraction pattern (DP) consisting of a sequence of homogeneous rings corresponding to the structure factor. The absence of rings or an intensity variation within the rings indicate the presence of (partial) crystal alignment with respect to the electron beam. The averaged intensities of the electron diffraction rings from thin polycrystalline films depend on the orientation distribution of the crystallites contributing to the DP. The extent of preferred orientation can therefore be determined by measuring the diffraction ring relative intensities even when the preferred orientation is only partial.^[34]

The integrated intensity distribution was determined for each of the three samples in Figure 3A–C as described in.^[22,35] The x-ray powder pattern of randomly oriented PCL was used as a reference.^[23] The relationship between x-ray and electron diffraction intensities allows such a comparison.^[36]

The examination of the DPs in Figure 3 reveals that the relative intensities of the rings in Figure 3A–C vary markedly from powder spectrum^[23] (Figure 3D). The only rings seen in Figure 3A are from (hk0) reflection planes and they are much stronger compared to powder spectrum. These intensities stem from a *c*-axis aligned crystal orientation in the EHL patterned PCL samples.

Also for the two other sample types in Figure 3B and C, several ring intensities differ from the powder spectrum. In particular, the (020), (120), (400), (410), and (202) rings in Figure 3B and (011), (021), (027), (310), and (127) rings Figure 3C are enhanced. Most of the enhanced intensity in Figure 3B correspond to the (hk0) Bragg planes, while (0kl) reflexes are enhanced in Figure 3C. The enhancement of the (0kl) signal is indicative of an *c*-axis inclination with respect to

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the film normal. The anisotropy of PCL crystal orientation in Figure 3B and C is further evidenced by the fact that several rings of the PCL powder are missing in these spectra. While both samples have a lower degree of orientation compared to the EHL sample in Figure 3A, all three samples show a strong texture stemming from partial crystal alignment.

For an electron beam striking the plane of the film at perpendicular incidence, the surface normal is parallel to the beam. Since the [001] axis is perpendicular to the sample surface, families of Bragg planes are inclined with specific angles with respect to this axis. For the orthorombic system, the angle α at which a plane is inclined to this axis is given by^[37]

$$\tan \alpha = l/\sqrt{h^2 + k^2}.$$
(4)

Partially oriented films (Figure 3B,C) have zone axes inclined to the electron beam axis, but with insufficient orientation to cause the disappearance of rings. While planes having α in the 0° to 45° range (Figure 3E) reflect with relatively high intensities, reflections from the (*hk7*) planes for which $\alpha > 50^\circ$ have much decreased intensities.

The results from Figure 3 allow the following conclusions: While patterns of Figure 3A stem from crystal alignment parallel to the film normal, the diffraction patterns in Figure 3B and C are also indicative of a nonrandom texture of the crystals in the films, with orientation distributions ranging from 0° to $\approx 74^{\circ}$. The sample crystallized in presence of an electric field only (Figure 3C) consists predominantly of crystals with the $\langle hk0 \rangle$ direction aligned with the surface normal. $\langle 0kl \rangle$ crystal orientations with nonzero l index, however, are strong in the case of the field-free sample (Figure 3B). Moreover, since the intensity of the $\{hkl\}$ ring is proportional to the multiplicity of the occurrence of the $\{hkl\}$ planes, a higher relative intensity of the (hk0) reflections in Figure 3C in comparison to Figure 3B point towards a higher degree of vertical c-axis orientation in the sample exposed to the electric field, but lower relative to the EHL patterned structures.

The observations from Figure 3 provide insight in the crystal alignment process in PCL thin films. The different diffraction patterns of all three samples are indicative that two of the three discussed alignment processes are responsible for PCL c-axis alignment in thin films. The diffraction texture of the film annealed in the absence of an electric field shows that confinement itself influences crystal orientation. The dominance of $\langle 0kl \rangle$ crystal orientations are indicative of a *c*-axis director that lies predominantly in the plane of the film. Quenching the sample from the isotropic melt in the presence of an electric field gives rise to a director parallel to the film normal (and to the electric field). This finding is reminiscent to the alignment often found in liquid crystals, where an initial orientation is achieved by the appropriate treatment of the confining surfaces, and is later switched by the application of an electric field.

While this comparison clearly demonstrates the role of the electric field in polymer crystallization, the degree of orientation order in the planar film quenched in the presence of an electric field is lower compared to the EHL-patterned sample. Despite the somewhat different setup, the annealing and quenching protocol was the same for both samples, as was the electric field of $\sim 1 \times 10^9$ V/m. As discussed above, the crystal alignment must be different from orientation effects in structured liquids (block-colplymers, nanotubes) because flow-induced forces act on the isotropic melt, and chain stretching and alignment effects are too short-lived to be significant.

Apart from its rheological history, the EHL sample differs from the continuous film by its lateral structure. A comparison of Figure 2A and D reveals that the crystal size of the polycrystalline PCL of ~3 μ m is comparable to width of the cross-hatched lines of $\approx 2 \mu$ m. This suggests an interplay of crystal orientation with the micro-structure of the film. Two possible mechanisms are likely: 1) Because of "missing neighbors" in one lateral direction, the rotation of the forming crystals in the electric field during the temperature quench is facilitated (i.e., accelerated) compared to a homogenous film where viscous dissipation is higher. 2) Because of the anisotropic surface energy of most crystals, a better alignment of the crystals in the EHL-patterned lines might be energetically favorable. The detailed interplay of these two effects is subject to further studies.

4. Conclusion

This study introduces a straightforward technique to pattern semi-crystalline organic materials while simultaneously inducing a well-defined crystalline order within the formed structures. The exposure of liquefied films to a heterogeneous electric field gives rise to micrometer- and submicrometersized patterns which can be lithographically controlled. EHL allows tuning and manipulation of the position of the formed patterns while aligning the polymer *c*-axis within the formed structures. This patterning technique presents a successful combination of bottom-up and top-down approaches based on the electro-hydrodynamic generation of surface patterns in thin crystalline films, yielding uniaxially aligned crystallites with the polymer backbone parallel to the surface normal.

While the crystal alignment is predominantly driven by the electric field, rotating a confinement-induced in-plane *c*-axis into an out-of-plane orientation, the EHL-induced crystal alignment is superior compared to a film which is exposed to the electric field only. This improved alignment arises most likely from the EHL lateral structure size, which kinetically, and possibly in terms of the surface free energy, enhances crystal alignment.

Based on earlier EHL work, feature sizes down to 100 nm can be achieved, over areas of several square centimeters.^[4,38] A further reduction in feature size may be possible for conducting or leaky dielectric materials.^[39] The latter observation is particularly interesting in the context of semiconducting conjugated polymers for photovoltaic devices.

The application of EHL patterning to anisotropic polymer crystals is attractive because it extends this technique towards functionalities that cannot be achieved with amorphous or polycrystalline materials. The orientation of crystals within the micrometer-sized pattern can be used to strongly influence their mechanical, electronic, optical, and ferroelectric properties. Moreover, the possibility of obtaining aligned functional crystalline materials that are patterned with submicrometer resolution may be attractive for semiconductor architectures, which require a large surface area, morphological control, and high charge carrier mobility. EHL pattering and control of crystal orientation in a conjugated polymer has been successfully accomplished, and a study of the interplay of chain orientation and device performance are currently underway. The design and fabrication of functional semiconducting materials with desired nanopatterns, orientations, and shapes may also have potential applications in photocatalysis, biochemical sensors, photochromism, and display technology.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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