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Article

# Highly Ordered Sub-10 nm Patterns Based on Multichain Columns of Side-Chain Liquid Crystalline Polymers

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Supporting Information

ABSTRACT: The development of nanotechnology relies crucially on the ability to fabricate materials with desired nanostructures. Because of their precise side-chain structure and versatile ordered morphologies, side-chain liquid crystalline polymers can provide a novel material platform to obtain sub-10 nm structures via their self-assembly. Here we show that for a newly designed side-chain liquid crystalline (LC) polynorbornene (P1) with a slim hemiphasmid mesogen microphase separation between the main and side chains drives the spontaneous formation of hexagonal columnar phase  $(\Phi_{\rm h})$ 



composed of cylinders with a uniform diameter of 8.3 nm. At every cross section of the cylinder there are more than a dozen P1 chains laterally bundled together. The cylinders can grow axially when more chains join in becoming extraordinarily long to over several micrometers. Simple shearing can produce P1 thin films with very good orientation of the  $\Phi_h$  phase at the macroscopic scale. More interestingly, we show that directed self-assembly of graphoepitaxy of P1 also provides an efficient route to obtain the patterned cylinders, making its applications in nanotechnology highly possible.

# INTRODUCTION

In the past half century, the systematic exponential increase of the density of transistors on integrated circuits ("Moore's law") has enabled the manufacture of powerful personal computers and mobile devices that have become indispensable in society.<sup>1</sup> To maintain Moore's law, fabrications of smaller features at a lower cost are highly desirable, which presents a great challenge to both science and technology.<sup>2-4</sup> There has been tremendous progress on the traditional "top-down" methods, represented by photolithography.<sup>5,6</sup> However, significant difficulties still exist in the top-down technology to produce patterns meeting the requirement of next-generation semiconductor devices with sub-10 nm half-pitch length.<sup>2,7</sup> One possible route to alleviate the difficulties is to employ "bottomup" technology, in which the structures are obtained by assembling individual components together.<sup>8,5</sup>

The cornerstone of "bottom-up" methods is the building blocks of self-assembly. In the past decades, diverse building blocks ranging from small molecules<sup>10-12</sup> to natural<sup>13-15</sup> or synthetic polymers<sup>16–18</sup> have been explored as candidates for the development of nanostructured materials. Among those, the deeply studied one is block copolymers (BCPs), which are macromolecules composed of chemically different blocks linked together. The competition between the repulsion and the connectivity of the different blocks enables BCPs to

spontaneously form well-ordered nanostructures at the length scale of 10–100 nm.<sup>9,17,19</sup> Directed self-assembly (DSA) of BCPs has been identified as a candidate technology for nextgeneration nanopatterning by the International Technology Roadmap for Semiconductor (ITRS).<sup>2,20-22</sup> An exquisite DSA pattern based on some BCPs (e.g., polystyrene-b-poly(methyl methacrylate)<sup>23</sup>) has approached the requirements for semiconductor manufacturing. However, when shrinking the domain size to sub-10 nm, the DSA process of BCPs becomes complex and time-consuming.<sup>3,24-26</sup> Furthermore, the small domain size requires BCPs with a rather low molecular weight (MW), which in turn weakens the segregation strength, leading to degrading of the ordered pattern formation with sharp domain boundaries.<sup>3,19</sup> In this context, low-MW compounds with precise chemical structure and well-organized molecular packing at the nanometer scale provide appealing alternative building blocks for the construction of nanoscopic patterns. Recently, it has been reported that liquid crystalline (LC) small molecules<sup>2,27</sup> and giant molecules<sup>28,29</sup> can form well-ordered nanostructures with periods around 5 nm, even though their processability of pattern formation needs to be improved.<sup>2</sup>

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Figure 1. Chemical structure of monomer M1 and the corresponding polymer P1. Schematic illustration of multichain column and the orientation obtained by mechanical shearing and graphoepitaxy.

Here, we intend to demonstrate that a side-chain liquid crystalline polymer (SCLCP) can also be employed as the building block for the highly ordered nanostructures. SCLCPs bear calamitic or discotic pendant groups, which can form the mesophases like smectic or columnar  $(\Phi)$  phase with periods below 10 nm.<sup>16,30-32</sup> Similar to other synthetic polymers, SCLCPs are inevitably polydisperse. However, worthy to emphasize is that the polydispersity only exists in the SCLCP main chains, whereas the mesogenic side chains have precise chemical structures as small molecules. The anisotropic shape and interaction of the mesogens facilitate the nanosegregation between the main and side chains. Consequently, the selfassembled structure of SCLCPs can be largely determined by the side-chain characteristic, resulting in uniform domain size (3-10 nm).<sup>30</sup> From this perspective, SCLCP shall be a good building block to obtain nanostructured materials. However, various types of defects could exist in the LC phases. In the smectic phases of SCLCP, long-range order could be disrupted by layer undulations and localized defects like edge dislocations. Similar situations could be encountered in  $\Phi$ phases of the SCLCPs with pendant discotic mesogens.<sup>30,33</sup> When considering the application of SCLCPs in nanoscopic pattering, it is vital to remove the defects as much as possible. Moreover, it requires that the orientation of ordered structures of SCLCPs can be well manipulated.

Herein, we report that the  $\Phi$  phase based on the "multichain column" of SCLCP can be fabricated into highly ordered sub-10 nm patterns. In biological systems,<sup>34</sup> the self-assembled cylindrical or columnar structures are abundant in tissues like neurofilaments, microtubules, and collagen.<sup>15,35,36</sup> Intriguingly, inside these biomaterials the columns are composed of several polypeptide chains assembled together rather than one single chain. This multichain construction enables the column to grow along the axial direction, reaching lengths as long as a few micrometers. Similar construction of materials can also be seen in daily life, such as the long yarns of fabrics that are obtained from spanned short fibers of cotton or silk. Inspired by these observations, we hypothesize that once the  $\Phi$  phase of SCLCPs takes several bundled chains,<sup>37</sup> namely, "multichain column", as the LC building block, the column length will not be limited by the molecular weight (MW) of the polymers, and it could also be as long as a few micrometers. Moreover, packing of the uniform columns could result in the significantly improved long-range ordering of the  $\Phi$  phase. Together with suitable molecular design, this SCLCP-based columnar nanostructure can provide a superior platform for nanomaterials.

The  $\Phi$  phases composed of multichain columns have been proposed in several supramolecular and synthetic polymer

systems. Examples include the axial bundle  $\Phi$  phases formed by bolaamphipiles,<sup>12</sup> the supramolecular column of coiled coil appeared in the hairy-rod polymers,<sup>38</sup> and the  $\Phi$  phase with  $\alpha$ helical bundles found in peptide-dendron hybrids.<sup>39</sup> Recently, we have illustrated that hemiphasmid SCLCPs, of which the side chain contains a rod-like mesogen and a fan-like end group,<sup>40</sup> exhibit  $\Phi$  phases based on the multichain columns.<sup>16,41-43</sup> Here, for the first time to apply the columns or cylinders of SCLCP in sub-10 nm patterning, we designed and synthesized a new hemiphasmid SCLCP (P1, see Figure 1), which bears the backbone of polynorbornene and the side chain with a long and slim wedge shape. It is observed that, independent of the MW, P1 can form hexagonal columnar phase  $(\Phi_{\rm h})$  with regulated column diameter of 8.3 nm. The thick column was due to that the column contains more than a dozen chains laterally associated together. Along the axial direction the columns could be several micrometers long, as identified by atomic force microscopy (AFM), and their growth process was also tracked. More importantly, the long columns can be easily oriented by mechanical shearing or the DSA method of graphoepitaxy, forming highly ordered pattern with large area. This result demonstrates an excellent processability of P1 for nanopattern formation. Based on these features, this special kind of SCLCPs provides an excellent candidate for various applications of nanotechnology.

# RESULTS AND DISCUSSION

Synthesis and Polymerization. Synthesis and molecular characterization of the norbornene monomer (M1, Figure 1) are shown in the Supporting Information. M1 is a hemiphasmid LC molecule composed of a rod-like mesogen and a half-disk group. To obtain a longer and slimmer wedge-shaped hemiphasmid, we lengthened the rod segment using two biphenyl groups, which was further linked to the end group of a typical mini-dendron. Two methyleneoxy groups were used as the linkers in M1. Hemiphasmid molecules reported previously are usually rigid, as the rod and half-disk are connected by an ester group.<sup>40</sup> Our design uses two methyleneoxy units as the linkers, giving the molecule more flexibility as well as better self-assembly ability.<sup>18</sup> M1 can be polymerized by ring-opening metathesis polymerization (ROMP), having perfect controllability with Grubbs thirdgeneration catalyst.44 To examine the MW effect, we synthesized a series of samples with different MWs (Figure S1). In this work, two samples with the degrees of polymerization (DPs) of 30 (P1<sub>L</sub> with MW = 33000, PDI = 1.09) and 420 ( $P1_{H}$  with MW = 420000, PDI = 1.25) are selected for the detailed study (MW was determined by using static solution light scattering, Figure S2).



Figure 2. Phase transition and structure of P1. (a) DSC second heating curves of P1<sub>H</sub> and P1<sub>L</sub>. (b) XRD results of P1<sub>H</sub> and P1<sub>L</sub> before and after annealing (original state: precipitate from methanol and dry under vacuum). (c, d) AFM results of P1<sub>H</sub> and P1<sub>L</sub> after annealing. (e, f) GI-XRD patterns of (c) and (d), respectively. Scale bar: 100 nm.

**Phase Behavior of P1.** Figure 2a presents the differential scanning calorimetry (DSC) second heating traces of  $P1_H$  and  $P1_L$ . While the low-temperature endotherm below 0 °C could be attributed to the melting of alkyl tails on the side chains, the high-temperature peak was associated with the LC–isotropic transition, giving the isotropic temperature ( $T_i$ ) at ~200 °C. Between these two endotherms, a stepwise shift of baseline was observed to start at around 100 °C. Combining with the rheology result of  $P1_H$  (Figure S3), we attributed the stepwise change of heat capacity to glass transition, which could cause the shear storage modulus (G') to decrease more than 2 orders of magnitude.<sup>45</sup> The  $T_i$  and glass transition temperature ( $T_g$ ) of P1 were reduced with decreasing MW.

The phase structure of P1 was examined by using onedimensional (1D) X-ray diffraction (XRD). Solid P1 samples obtained by precipitation or solution casting without further thermal treatment showed no sign of ordered structures (Figure 2b). A broad scattering peak at 7.2 nm was observed, which should be due to the local segregation between the wedge-shaped side chains and polynorbornene main chains. After annealing at 200 °C (Figure 2b), the 1D XRD profile of **P1**<sub>H</sub> exhibited diffraction peaks with the *q* ratio ( $q = 4\pi \sin \theta / d\pi$ )  $\lambda$ , with  $2\theta$  the scattering angle and  $\lambda$  the X-ray wavelength) of 1: $\sqrt{3.2}$ , indicating a  $\Phi_{\rm h}$  phase with an *a* parameter of 8.33 nm. Despite a lower  $T_{ii}$ , **P1**<sub>L</sub> after annealing at 160 °C showed the 1D XRD profile almost identical to  $P1_{H'}$  giving the same a parameter. This result indicated clearly that at the sub-10 nm scale the ordered structure of P1 is independent of MW of the polymers.

Thin films of P1 could be easily obtained by spin coating, demonstrating excellent film-forming ability. The thickness of flat thin films on silicon substrates could be controlled by the spin rate and the concentration of toluene solutions (the thicknesses of P1 films were  $\sim 100$  nm in this study). The phase structures and morphologies of annealed film samples were analyzed by grazing-incidence XRD (GI-XRD) and atomic force microscopy (AFM), respectively. For P1<sub>H</sub>, GI-XRD results (Figure 2e) showed a typical diffraction pattern of  $\Phi_{\rm h}$  phase with columns lying on the surface, giving the same lattice parameter as that obtained from the 1D XRD of bulk samples. The AFM results (Figure 2c and Figure S4) unambiguously confirmed the GI-XRD results. Strikingly, extremely long (at least >1  $\mu$ m) and almost perfect cylinders could be observed, with the diameter consistent with the diffraction result. Although the cylinders of P1<sub>L</sub> were shorter than  $P1_{H}$  and contained more defects (Figure 2d,f), the length could still be as long as several hundred nanometers, which was 1 order of magnitude longer than the contour length ( $\sim$ 14 nm) of  $\mathbf{P1}_{\mathbf{L}}$  with the DP of 30.

The formation of such long cylinders or columns with a few defects is first observed for SCLCPs, implying that the **P1** column should not be a single chain. Worth mentioning is that in the systems like mesogen-jacketed LC polymers<sup>32,46,47</sup> and comb<sup>48,49</sup> or dendronized polymers<sup>18,50</sup> the "single-chain column" is usually the building block of the columnar LC phase. In these SCLCPs, bulky side groups crowdedly pack around the main chain, forcing the main chain to take an extended conformation.<sup>32</sup> Such a shape-persistent SCLCP chain in turn acts as a cylindrical unit, i.e., "single-chain



Figure 3. Molecular packing scheme of P1 and M1. (a) Reconstructed relative 2D electron density map (EDM) of P1. The color from blue to red represents the electron density from low to high. (b) Molecular models of single chain of P1 with 20 repeating units. Left image: top view, the diameter of the column is 8.1 nm; right image: front view, the length of 20-mer is 9.1 nm and thus the length of repeating unit is 0.46 nm. (c) 1D XRD pattern of M1 after annealing. (d) 3D EDM of M1 in  $Im\bar{3}m$  cubic phase and its 2D section at the (200) plane (upper right).

column", in the  $\Phi$  phase.<sup>49,50</sup> In this case, however, the length of columns is determined by the main-chain length. It hardly exceeds 200 nm, roughly corresponding to about 1000 monomer units connected together on the main chain. Because the column length distribution depends on the MW polydispersity, numerous defects appear in the  $\Phi$  phases constituting of single-chain columns.<sup>33</sup>

**Molecular Packing of P1.** Two-dimensional (2D) XRD results indicated that the **P1** samples oriented by mechanical shearing exhibited hexagonal diffractions on the direction perpendicular to the shear direction (Figure S5). The high angle scattering mainly from the interference between the side chains was somewhat concentrated on the shear direction at 0.44 nm. These observations indicated that the column axis, and thus the polymer main chain, was aligned along the shear direction, while the side chains tended to perpendicular to the column axis.

The number of repeating units  $(Z_{rep})$  packed in a unit cell can be estimated by assuming a hexagonal unit cell with a =8.33 nm and c = 0.44 nm and using the expression  $Z_{rep} = (N_A/$ M) $(a^2 c \sin 60^\circ)\rho$ , with  $N_A$  Avogadro's number, M the molar mass of repeating unit, and  $\rho$  the density of P1 (1.03 g cm<sup>-3</sup> as measured). This gives a remarkably large value of  $Z_{\rm rep} \sim 16$ , indicating that 16 repeating units are packed in a 0.44 nm thick stratum of the column. It is physically impossible that all of the units are from the same polynorbornene main chain. In other words, these packed repeating units shall be from different chains. The reconstructed 2D relative electron density map (EDM, Figure 3a) of the  $\Phi_h$  phase indicated that the P1 polymers self-assembled to form supramolecular column with a "core-shell-corona" structure. In terms of the chemical structure of P1, the alkyl chains with the lowest electron density at the side-chain ends should form the corona (blue

region), while the polymer main chains and the aromatic mesogens form the core and shell, respectively. The projection of one repeating unit on the polynorbornene chain axis is ~0.44 nm, which could be confirmed by the molecular simulation of a single chain of P1 (Figure 3b and Figure S6). Therefore, the aforementioned  $Z_{\rm rep}$  value of ~16 becomes nearly equivalent to the number of chains in each column unit.

Obviously, the multichain column of P1 is related to the wedge-shaped hemiphasmid side chain. We noted from 1D XRD that the monomer M1 could form a highly ordered cubic phase with  $Im\bar{3}m$  symmetry (Figure 3c). On the basis of the "three networks" model proposed for the  $Im\overline{3}m$  cubic phase by Ungar et al.,<sup>51</sup> we reconstructed the 3D relative EDM of M1 (Figure 3d). With the aliphatic parts of M1 as the matrix, three continuous networks composed of the aromatic parts (~40% volume ratio) could be found in the EDM. Two of them (yellow and purple) are identical and separated by the middle network (red). The cubic phase with  $Im\overline{3}m$  symmetry is regarded as the most complex LC phase, and only a few examples were reported.<sup>51</sup> The formation of the continuous networks indicates that M1 possesses the high self-assembly ability. This may be attributed to the semiflexible nature<sup>18</sup> of the hemiphasmid M1. The ether linkages may adopt proper conformations to satisfy the delicate molecular packing, facilitating the long-range ordered complex structure.

After polymerization, the intrinsic self-assembly ability of the side chains persists in **P1**. The microphase separation tendency between the main and side chains drives the polymers to form large columns. It is worth to mention that the side chain of **P1** contains two biphenyl groups, resulting in the longer and slimmer "wedge" than other hemiphasmid groups reported.<sup>40–43</sup> Consequently, the supramolecular column of **P1** becomes thicker (diameter of 8.33 nm), and more chains (~16

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Figure 4. Phase transition of  $P1_L$ . (a) 1D XRD profiles of  $P1_L$  recorded upon heating. (b) 1D XRD profiles of  $P1_L$  recorded at different times during isothermal annealing at 110 °C.



Figure 5. Column-growth process of  $P1_{H}$ . (a-f) AFM images of  $P1_{H}$  on silicon substrate after annealing at 135 °C for 0, 4, 8, 12, 16, and 36 h, respectively. Scale bar: 100 nm.

chains) are involved in to fully fill the space of column unit. This molecular packing scheme is essential to the possibility of forming ultralong columns.

**Growth of Ultralong Columns of P1.** One distinct feature of **P1** is the extremely long length of columns in its  $\Phi_h$ phase. As it is much longer than the chain contour length (~14 and ~200 nm for **P1**<sub>L</sub> and **P1**<sub>H</sub>, respectively), the columns must result from a continuously packing of polymers along the column axis, similar to the cylindrical biomaterials mentioned in the Introduction. With as many as ~16 chains laterally associated together at every cross section of the column, intertwining of the main chains and interlocking of the wedgeshaped side chains are unavoidable, forming the interconnected structure of the different chains within the column. Kinetics of the column growth was investigated by using XRD and AFM, starting from the disordered samples. Interestingly, a transient state was identified prior to the formation of the columnar structure. Upon heating of P1<sub>L</sub>, the scattering halo centered at 7.2 nm gradually broadened, and a new broad peak at ~10.2 nm becomes distinct at 130 °C (Figure 4a). Further heating quickly leaded to the hexagonal diffractions. The peak at 10.2 nm was more evidenced during isothermal annealing of P1<sub>L</sub> at its  $T_g$  of 110 °C (Figure 4b). It appeared at 30 min and disappeared after 1200 min when the hexagonal diffractions developed. Note that the two broad peaks at 10.2 and 7.2 nm have the *q* ratio of  $1:\sqrt{2}$ , suggesting a spherical structure similar to the micelle phase of BCP. For P1<sub>H</sub>, though the two peaks were not observed, the full width at half-maximum (fwhm) of the scattering at 7.2 nm exhibited an



**Figure 6.** Large area orientation of **P1** columns by mechanical shearing. (a) AFM image reflecting the uniform orientation in the area of  $2.2 \times 6.7 \mu m^2$  which contains five different images ( $2.2 \times 2.2 \mu m^2$ ) marked by dashed lines. (b, c) AFM scan results of the selected areas in (a); the insets give the FFT result of the AFM images. (d) GI-XRD pattern of the sample shown in panel a and the azimuthal integration of the second- and third-order diffractions (red curve below). Scale bar: 100 nm.

anomalistic increase when temperature reached the glass transition range, implying a hidden new peak developed on the left side of the scattering (Figure S7). These results indicated the existence of a transient state of spherical fluctuations during the transition from disordered state to  $\Phi_h$  phase of P1.

The column growing from spherical structure was confirmed by AFM (Figure 5). The surface of the as-cast  $P1_{H}$  film was rather smooth with the root-mean-square average height deviation of 0.56 nm (Figure 5a). Some disordered wormlike entities were faintly discernible. Interestingly, after the film was annealed at 135 °C for 4 h (Figure 5b), many dots with a diameter of  $\sim 10$  nm appeared, and some of them were connected together as a "pearl necklace". The dots should correspond to the spherical fluctuation happened in bulk. When increasing the annealing time (Figure 5c-e), these dots merged into short cylinders, which may be bended, folded, or branched and could grow along the columnar axis gradually. Finally, after a long enough time annealing (i.e., 36 h, Figure 5f), the defects between short cylinders were largely eliminated and long cylinders were formed. Elevating the annealing temperature would greatly shorten the time for forming the perfect cylinders. For example, annealing at 200 °C (slightly below the  $T_i$  of  $P1_H$ ) the long cylinder could appear in 5 min (Figure 2c and Figure S4). For P1<sub>L</sub>, the evolution from disorder to dot to cylinder could also be observed (Figure S8).

It is conceivable that the column growth from the disordered state could only take place at or above  $T_{\rm g}$  due to the chain mobility. The appearance of spherical or dot-like patterns was unexpected. One possible mechanism is that when the chain segment motion starts locally, the already rather active side chains tend to assemble into spheres first because of their wedge shape. However, as the  $\Phi_{\rm h}$  phase is stable, the spherical

packing patterns would relax to form the columns. Assuming that the two scattering peaks with a q ratio of  $1:\sqrt{2}$  arise from a simple cubic structure, the sphere diameter is ~10 nm, in agreement with that measured by AFM (Figure 5b and Figure S8). In this case, one sphere contains nearly 500 repeating units, which is much larger than the DP of **P1**, meaning that the sphere should involve many chains. When the transient spheres merged together to be the columns, this many-chain construction should remain.

The AFM observation suggested that the ultralong column resulted from the linking of short columns, accompanied by the elimination of defects. Similar to what happened in the cylindrical phase of BCPs, these processes could reduce the free energy. For P1, the particular interchain interaction inside the column could be an additional reason for the ultralong column growth. The "pearl necklace" in Figure 5b indicated that the dots were linked together. The linkage must be the chains joining the adjacent dots. We measured the persistence length  $(L_p)$  of P1 using static solution light scattering. The remarkably large  $L_P$  of 18 nm (Figure S2) indicated that P1 was quite rigid. While a single rigid chain has large interspace surrounding the backbone (see Figure 3b), other chains will invade. Consequently, in the column the main chains will cross over and the large side chains will interlock with each other. Such an interaction could take place throughout the space. We could assume that certain precursors of columns existed in the disordered state, as the wormlike entities shown in Figure 5a. The broad scattering at 7.2 nm of the amorphous P1 may be associated with the packing of column precursors (Figure 2b). It should be easier for the longer chains, which could involve in more column precursors, to render longer columns, as the comparison of  $P1_H$  and  $P1_L$  showed.



Figure 7. Spontaneous orientation of P1 by graphoepitaxy. (a, c) AFM results of P1<sub>H</sub> in graphoepitaxial trenches with 150 and 280 nm width, respectively. (b, d) AFM scan results of the selected area in panels a and c, respectively. Scale bar: 100 nm.

Highly Oriented P1 Columns by Mechanical Shearing. As the column diameter depends only on the chemical structure of repeating units, the P1 chains assembled to form sub-10 nm columns with negligible diameter fluctuations in the  $\Phi_{\rm h}$  phase. Moreover, ultralong columns with just a few defects could be obtained. These two prominent characteristics make P1 a good candidate for applications in nanotechnology. One necessary requirement for many such applications is good orientation of the columns or cylinders.<sup>11,52</sup> Taking advantage of the excellent processability, we oriented the P1 columns by simple shearing. For example, the shearing of  $\mathbf{P1}_{\mathrm{H}}$  was done above its  $T_g$  (i.e., ~150 °C) when the samples became relatively soft due to the decreased modulus. After annealing at 180 °C, the 2D XRD results indicated that the columns of P1 were aligned along the shear direction. Quantitative analysis of the azimuthal scanning data of the (10) diffraction indicated that the Herman Stein orientation factor  $f_{10}$  was -0.38, rather close to the value of -0.5 for the ideal orientation (Figure S5).

Furthermore, we investigated the shear-induced orientation in **P1** thin films on the silicon substrate. To decrease the shear temperature and also to get a smoother film for morphological observation by AFM, a piece of **P1**<sub>H</sub> was placed on the silicon substrate in the toluene atmosphere. After the sample absorbed the solvents and became a little soft, strong shearing was applied by hand at room temperature, leaving a thin film on the substrate. As toluene volatilized quickly, the orientation of the **P1** chains was frozen in a large sample area. Exemplified by Figure 6a with the area of  $2.2 \times 6.7 \ \mu\text{m}^2$ , the AFM result clearly showed that all the columns throughout the sample area were of the same orientation (Figure 6b,c). With the X-ray incident beam along the shearing direction, the GI-XRD pattern depicted a very good  $\Phi_h$  structure (Figure 6d). The sharp (*hk*) diffractions at different azimuthal angles had very similar intensities. This suggests that simple shearing has a great potential to produce the "single crystal-like" domain at the macroscopic scale. We may attribute this result to the unique interconnection of **P1** chains, which could retain the alignment after the chains flowed along the shearing direction.

Spontaneous Orientation in Graphoepitaxial Trenches. Graphoepitaxy is a widely used method for the DSA of BCPs and LC molecules. Compared to the chemical epitaxy which is usually complex, graphoepitaxy is more convenient, although somewhat less efficient.<sup>17,21</sup> However, our preliminary result demonstrated that this simple DSA method could lead P1 to a very good oriented pattern. Two graphoepitaxial trenches (depth of ~300 nm) prepared by electron-beam lithography were used here, with the width of 150 and 280 nm, respectively. A 1 wt % toluene solution of  $P1_{H}$  was spin-coated onto the patterned wafers followed by annealing at 180 °C for 1 h. AFM revealed that P1 chains covered both the plateaus and trenches (Figure 7a,c). On the plateaus the columns packed randomly, similar to that shown in Figure 2c. By contrast, the columns inside the trenches were well arranged with the column axis perpendicular to the trench edge (Figure 7b,d).

Such a perpendicular orientation was observed in some discotic LC molecules after topological guiding.<sup>53</sup> Similar to small molecules, we propose that the perpendicular alignment of **P1** is related to the surface energy difference between the silicon substrate and different parts of the supramolecular

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column. With the "core-shell-corona" structure, the column side surface is covered by the hydrophobic alkyl tails. Only can the polar groups of ether and ester on the column end be exposed, which could interact more favorably with the hydrophilic silicon surface. Confined in the thin film, the columns or cylinders usually lie down rather than stand up, as found in experiments. When the columns are placed in the trench, column ends will prefer contacting with the trench edge to further reduce the free energy. Intuitionally, such a surface anchoring should be quite weak. However, the current observation showed that the anchoring effect could lead the columns to remain in the perpendicular orientation throughout the trenches with the width at least close to 300 nm. Note that just simple annealing could result in the spontaneous orientation of P1 columns. This graphoepitaxy result suggested the great applicability of this hemiphasmid SCLCP in nanotechnology, while further efforts like introducing functional structure or designing suitable etching methods are desirable.

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In summary, we have designed and synthesized a new hemiphasmid side-chain liquid crystalline polymer P1, which could form a  $\Phi_{\rm h}$  phase with a unit cell size of a = 8.33 nm. At every cross section of the column, there should be  $\sim 16$  chains laterally bundled together. Formation of the supramolecular column resulted from the nanosegregation between the main and side chains. The column has the core of main chains, which is surrounded by the slim wedge-shaped side chains. Attributed to the precise chemical structure of side chains, the column diameter remains uniform independent of the polymer molecular weight. The columns in  $\Phi_h$  phase could grow axially to as long as several micrometers. A transient state with spherical fluctuations was observed during the column growth from the disordered state to  $\Phi_{\rm h}$  phase. More meaningfully, we validated that high orientation of the extraordinarily long columns could be achieved in large area by using simple mechanical shearing. Furthermore, self-assembly directed by graphoepitaxy could result in the spontaneous perpendicular orientation of the P1 columns in the silicon trenches. The results reported here have clearly demonstrated that welloriented nanostructures with excellent long-range order at sub-10 nm length scale could be obtained from the multichain columns of SCLCPs. SCLCPs with rationally designed mesogenic side chains can provide the promising candidate for the patterning of sub-10 nm nanostructures, such as wellordered and oriented nanowires and nanopores.<sup>10,28,54</sup>

# ASSOCIATED CONTENT

## **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.9b00910.

All experimental and calculational details (PDF)

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# Notes

The authors declare no competing financial interest.

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