

Supporting Information

Spontaneous generation and long-range patterning of polymeric surface toroids

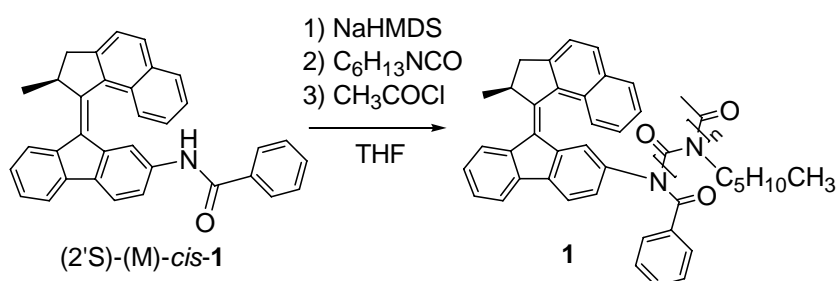
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Methods

The synthesis and characterization of compound **1** was previously reported.¹ *n*-Hexyl isocyanate was dried over CaH₂ and vacuum distilled before use, THF was distilled under N₂ after refluxing with sodium for 5 h. The polymerizations were carried out in a flame-dried schlenk tube under N₂-atmosphere. At room temperature, sodium bis(trimethylsilyl)amide (28 μL of a 1.0 M solution in THF, 28 μmol,) was added to a solution of (2'*S*)-(M)-*cis*-**1** (13 mg, 28.1 μmol) in THF (4 mL). After cooling the red-colored solution to -90°C, *n*-hexyl isocyanate (410 μL, 0.36 g, 2.8 mmol) was added, upon which the mixture slowly turned more viscous. After 45 min acetyl chloride (20 μL, 22 mg, 0.28 mmol) and pyridine (22.6 μL, 22.1 g, 0.28 mmol) were added to the mixture, which was then allowed to warm to room temperature. The mixture was then poured in MeOH (100 mL) and the precipitated poly(*n*-hexyl isocyanate) was filtered off, washed three times with MeOH and dried *in vacuo*, which yielded a yellow solid (280 mg, 79%).
¹H NMR (400 MHz, CDCl₃) δ: 0.85 (3H, s), 1.25 (6H, b), 1.6 (2H, b), 3.7 (2H, b), 6.6-8.0 (low intensity signals: aromatic protons motor).
¹³C NMR (100 MHz, CDCl₃) δ: 14.0 (q), 22.6 (t), 26.2 (t), 28.4 (t), 31.5 (t), 48.5 (t), 156.8 (s).



Preparation of films

Compound **1** was dissolved in freshly distilled toluene or THF, or fresh UV grade chloroform (Aldrich) at concentrations of 0.050 mg/ml to 0.001 mg/ml solvent. Samples were aged for one day prior to surface deposition. To ensure that the polymer was dissolved, samples were rapidly mixed prior to deposition by withdrawing and releasing solution from a pipet. Approximately 5 μ l drops were placed on freshly cleaved mica or a freshly prepared gold surface and allowed to dry under ambient conditions.

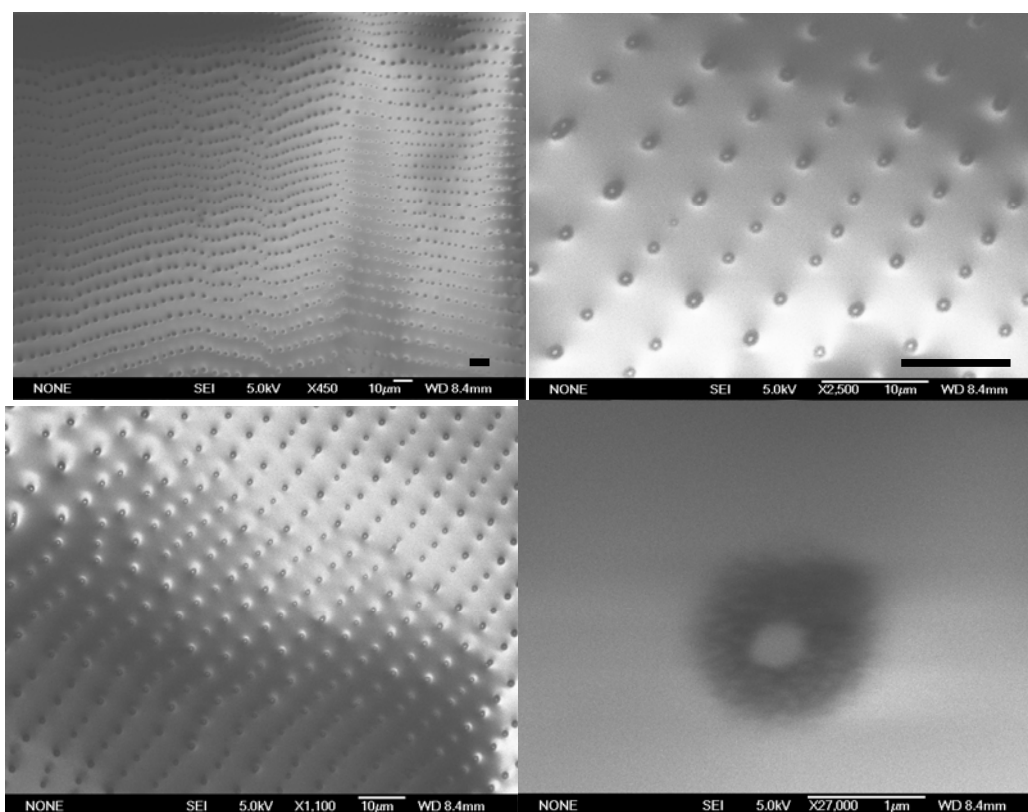
Imaging

Samples were examined with atomic force, scanning electron and optical microscopy. In some cases it was possible to observe toroidal features with optical microscopy. AFM images were obtained with a PicoScan LE (Molecular Imaging) atomic force microscope in tapping mode. Tips with a force constant of 60 N/m were used. Images were scanned at rates ranging from 1-2 lines per second. SEM images were obtained with a JEOL scanning electron microscope. A voltage of 5 kV was used. The optical micrographs were recorded using an Olympus BX 60 microscope equipped with crossed polarizers and a Sony 3CCD DXC 950 P digital camera attached to a PC running Matrox Inspector 8.0 imaging software.

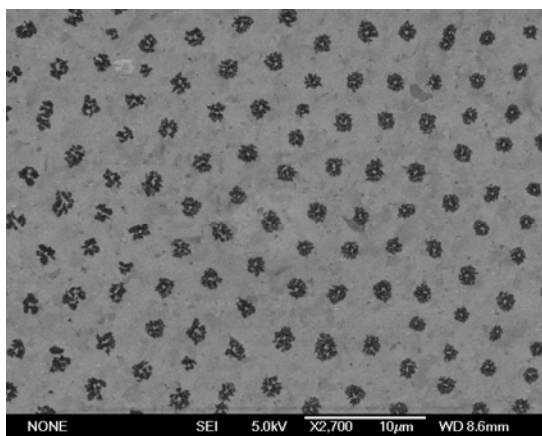
Spectroscopic measurements

CD spectroscopy was performed on a Jasco 815 CD spectrometer. Solution measurements were performed in UV grade CHCl_3 (Aldrich). Surface measurements were prepared by spin-coating solution used for CD measurement (see below) at 500 RPM for one minute onto a clean quartz slide. The solution was first concentrated to dryness and then dissolved in 400 μ l distilled toluene. The background spectrum of the uncoated quartz was taken before casting the film. Quartz was cleaned immersing overnight in a piranha solution (7:3 by volume $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$). **Caution:** Piranha reacts violently with organic matter.

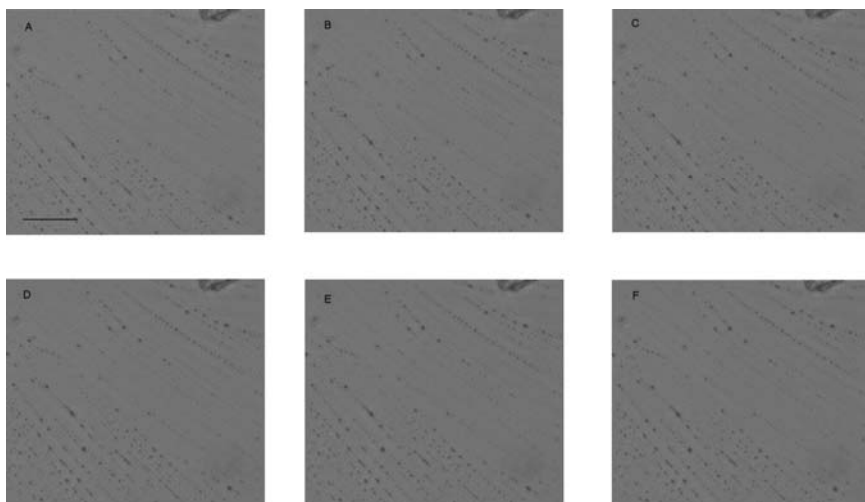
(a)



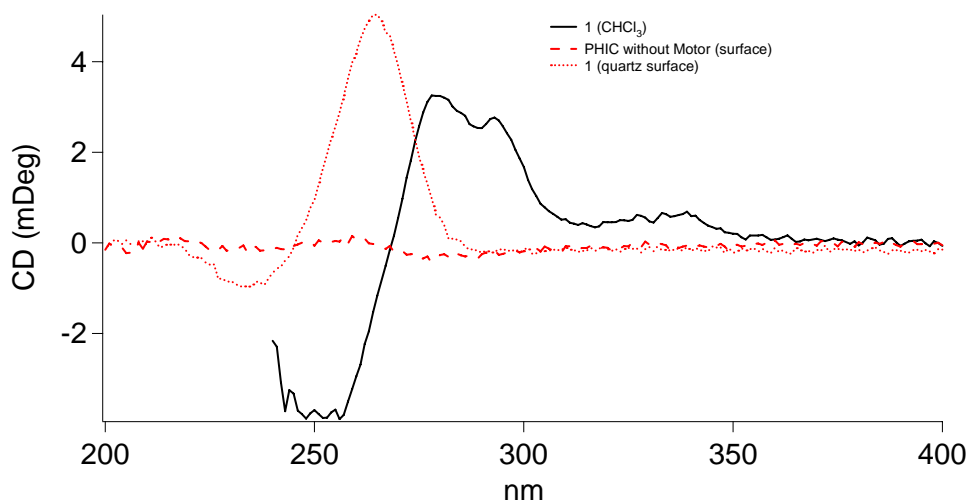
(b)



S1: SEM images of films prepared by evaporating a toluene solution containing **1** on (a) mica and (b) Au.



S2: Optical microscope images show long-range ordered aggregates on quartz from a drop-cast solution of **1** in toluene. Heating the aggregates produces no major change in structure up to 70°C. The surface was heated to the following temperatures A) 25.6 °C B) 39.9 °C C) 50.1 °C D) 60.4 °C E) 65.0 °C F) 70.0 °C. The scale bar equals 50 µm.



S3: CD spectroscopy of **1** in chloroform, on a quartz surface and unmodified PHIC on a quartz surface.

1. Pijper, D. & Feringa, B.L. Molecular transmission: Controlling the twist sense of a helical polymer with a single light-driven molecular motor. *Angew. Chem. Int. Ed.* **46**, 3693-3696 (2007).