

Hierarchical Striped Walls Constructed by the Photo-polymerization of Discotic Reactive Building Blocks in the Anisotropic Liquid Crystal Solvents

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Equipments and experiments

Thermal stability of HABET compound was investigated by thermogravimetric analysis (TGA, Q-50, TA instrument). The scanning rate was kept at 10 °C/min from 30 °C to 600 °C under N₂. As shown in Figure S4, HABET began to degrade at 310 °C (estimated as 5 wt% weight loss). Thermal transition behavior was studied using differential scanning calorimetry (DSC, PYRIS Diamond DSC, Perkin-Elmer). For the DSC experiments, the sample weights were controlled to be about 4.0 mg and the pan weights were kept constant with a precision of ± 0.001 mg. The temperature and heat flow scales were calibrated using standard materials at different cooling and heating rates (in Table S1). Transition temperatures were determined using the onset temperatures. Heating experiments always preceded the cooling experiments to eliminate previous thermal histories, and the cooling and heating rates were always kept identical. The onset temperature was defined by the cross-point of the peak slope and the baseline in the DSC trace. The onset temperature during the cooling process was determined on the high-temperature side, while upon heating the onset temperature was determined on the low temperature side.

To investigate morphology on the micrometer length scales, optical textures of the ordered phases at different temperatures were observed with POM (Eclipse LV100POL, Nikon) coupled with a heating stage (FP 90, Mettler Toledo). Textures of the HABET molecules were monitored during a heat process from room temperature to 180 °C at a rate of 10 °C/min. To figure out molecular orientations in the macroscopically oriented film, a 530 nm retardation plate was additionally introduced at 45° to the orthogonally arranged polarizer and analyzer in POM. As shown in Figures S5, and S6, optical characteristics of the HABET networks at different cell gap was investigated by POM with the 530 nm retardation film. The patterned hierarchical structure was also observed using POM with the retardation films (Figures S7-S10).

1D WAXD experiments were conducted in the reflection mode of a Rigaku 12 kW rotating-anode X-ray (CuK α radiation) generator coupled with a diffractometer. The diffraction peak positions and widths were calibrated with silicon crystals in the high 2 θ -angle region (>15°) and silver behenate in the low 2 θ -angle region. To monitor the structural evolutions with temperature changes, a hot stage calibrated to be within ± 1 °C error was coupled to the diffractometer. Samples were scanned across a 2 θ -angle range of 1.5° to 35° at a scanning rate of 2°/min.

Utilizing a Rigaku X-ray imaging system with an 18 kW rotating anode X-ray generator, 2D WAXD patterned at different temperatures were obtained by irradiating X-ray perpendicular to the shear direction (SD) of macroscopically oriented HABET films. Silicon crystal powder, used as an internal reference, showed a diffraction ring at a 2 θ value of 28.466°. For the 2D WAXD experiment, the 30 min of exposure time was required for a high-quality pattern. In both 1D and 2D WAXD experiments, the background scattering was subtracted from the sample scans.

Chemical structure and purity of HABET were confirmed by proton (^1H) and carbon-13 (^{13}C) nuclear magnetic resonance (NMR, JNM-EX400, JEOL) in deuterated chloroform (CDCl_3).

Chemical shifts were quoted in part per million (ppm) with a reference of tetramethylsilane (TMS) and each NMR spectra were shown in Figures S1, and S2, respectively. Chemical structure of HABET was confirmed by the chemical shift and integration of $-\text{CH}=\text{CH}_2$ (5.18 ppm, 12H) and aromatic hydrogens of triphenylene (7.86 ppm, 6H). Molecular weight of HABET was confirmed by Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-ToF MS, Voyager DE PRO Spectrometer, PerSeptive Biosystems). As shown in Figure S3, molecular weight of HABET was determined to be 649.8 g/mol. Scanning electron microscopy (SEM, SUPRA 40VP, Carl Zeiss) was conducted to investigate the surface morphology of constructed hierarchical structure on the micrometer length scales. WCA was measured by contact angle analyzer (Phoenix-300, SEO). As shown in Figure S9, water contact angle (WCA) measurements of the macroscopically oriented hierarchical HABET-based polymer network structures at different cell gap were conducted. Introducing the 10 μl of water droplets on the hierarchical HABET morphology, the contact angle (θ), the advanced angle (θ_a), and the recession angle (θ_r) were calculated via the tangent method. Flow properties of HABET networks were also evaluated by WCA on the 45° tilted substrate.

Table S1. Calibration data for DSC using indium as a standard sample at different scan rate

Scan rate (°C/min)	Cooling onset (°C)	Cooling Δ (°C)	Heating onset (°C)	Heating Δ (°C)	Cooling ΔH (°J/g)	Heating ΔH (J/g)
1	152.0	4.5	156.1	0.5	-28.5	28.0
5	152.1	4.5	156.4	0.3	-28.5	27.6
10	152.1	4.6	156.5	0.1	-27.8	20.0

$$T_{\text{real}} = T_{\text{measured}} + \Delta T. \Delta H_{\text{In}} = 28.45 \text{ J/g}$$

Table S2. Experimental and calculated crystallographic parameters of HABET at 25 °C

<i>(hkl)</i>	2θ (degree)		d-spacing (nm)	
	Calc ^a	Exptl ^b	Calc ^a	Exptl ^b
(100)	4.42	4.43	2.00	2.00
(110)	5.07	5.12	1.74	1.72
(020)	6.36	6.39	1.39	1.38
($\bar{1}$ 20)	8.24	8.08	1.07	1.09
(200)	8.85	8.88	1.00	0.99
($\bar{2}$ 20)	11.61	11.39	0.76	0.78
(300)	13.30	13.30	0.66	0.66
(240)	14.41	14.44	0.61	0.61
($\bar{3}$ 20)	15.58	15.40	0.57	0.57
($\bar{2}$ 40)	16.58	16.50	0.54	0.54
(400)	17.76	17.80	0.50	0.50
(430)	18.89	18.96	0.47	0.47
($\bar{3}$ 40)	19.78	19.73	0.45	0.45
(440)	20.30	20.86	0.43	0.43
(360)	21.69	21.85	0.41	0.41
($\bar{1}$ 70)	23.48	23.43	0.38	0.38
(201)	25.45	25.47	0.35	0.35
(001)	27.14	26.78	0.33	0.33
(251)	30.21	30.27	0.30	0.30

^aThe calculated data listed are based on the triclinic unit cell. ^bThe accuracy of the experimental data is ± 0.005 nm.

Table S3. Experimental and calculated crystallographic parameters of HABET at 100 °C

<i>(hkl)</i>	2θ (degree)		d-spacing (nm)	
	Calc ^a	Exptl ^b	Calc ^a	Exptl ^b
(100)	5.58	5.59	1.58	1.58
(110)	9.75	9.68	0.91	0.91
(200)	11.16	11.18	0.79	0.79
(120)	14.90	14.82	0.59	0.60
(220)	19.59	19.39	0.45	0.46
(211)	24.90	24.99	0.36	0.36
(001)	26.05	25.59	0.34	0.34

^a The calculated data listed are based on the triclinic unit cell. ^b The accuracy of the experimental data is ±0.005 nm.

Table S4. Experimental and calculated crystallographic parameters of HABET at 140 °C

<i>(hkl)</i>	2θ (degree)		d-spacing (nm)	
	Calc ^a	Exptl ^b	Calc ^a	Exptl ^b
(100)	5.58	5.59	1.58	1.58
(110)	9.67	9.68	0.91	0.91
(200)	11.17	11.18	0.79	0.79
(210)	14.78	14.74	0.60	0.60
(130)	20.20	20.26	0.44	0.44
(001)	24.73	24.73	0.36	0.36

^a The calculated data listed are based on the triclinic unit cell. ^b The accuracy of the experimental data is ±0.005 nm.

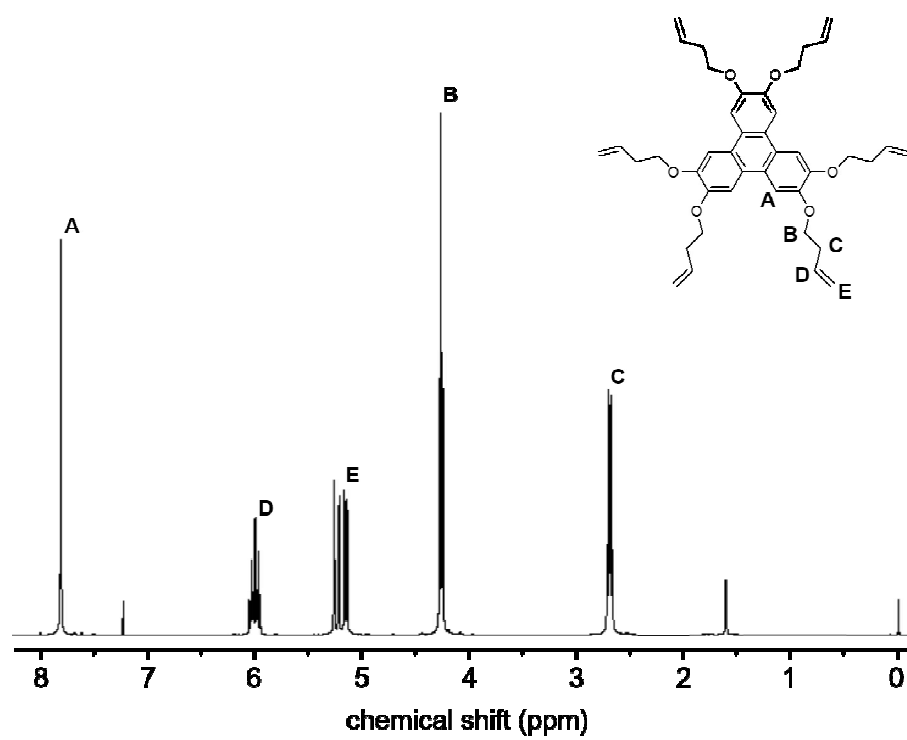


Figure S1. A set of ^1H NMR spectra of HABET

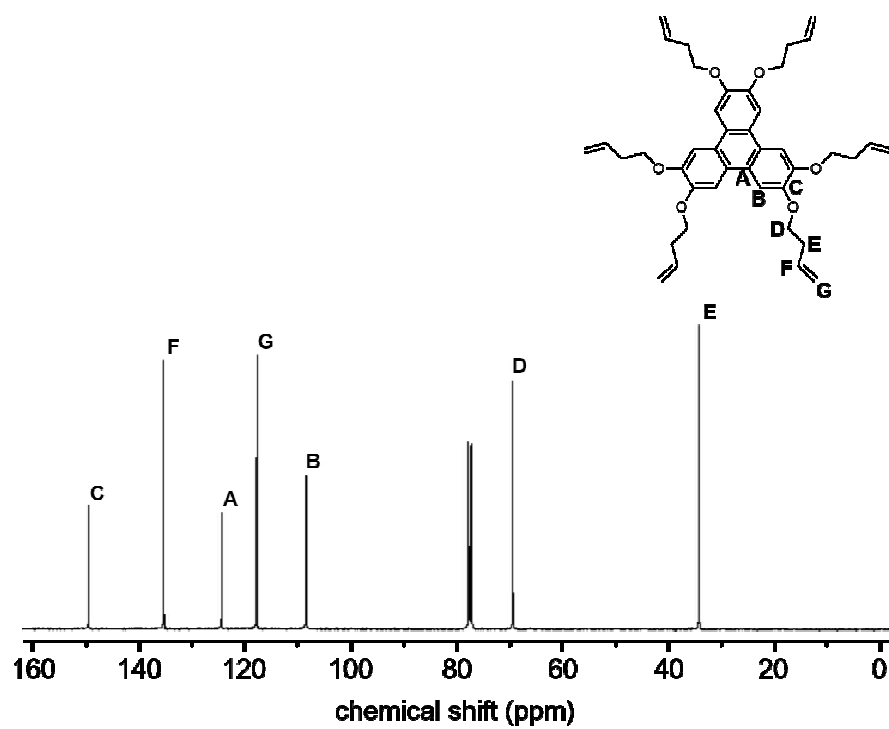


Figure S2. A set of ^{13}C NMR spectra of HABET

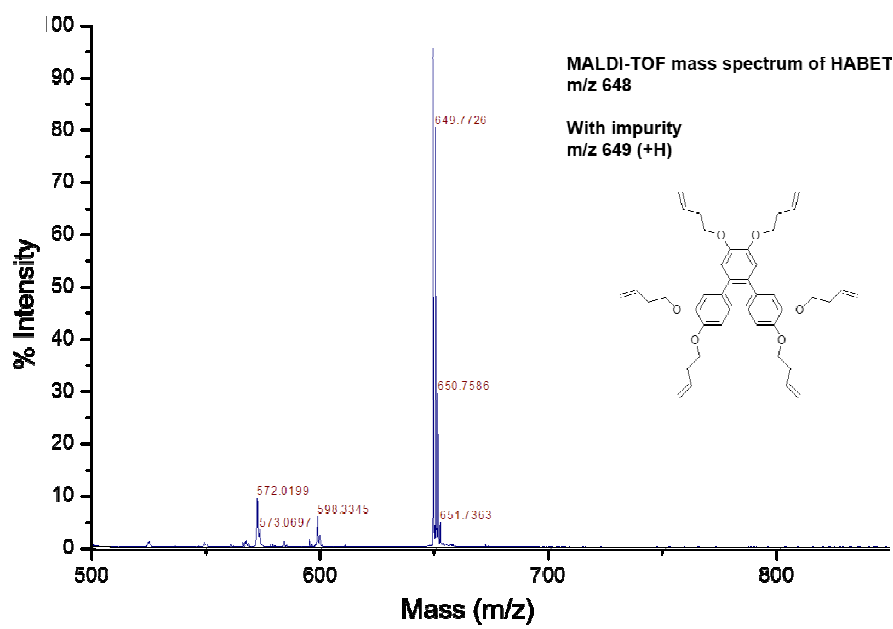


Figure S3. MALDI-ToF MS spectra of HABET

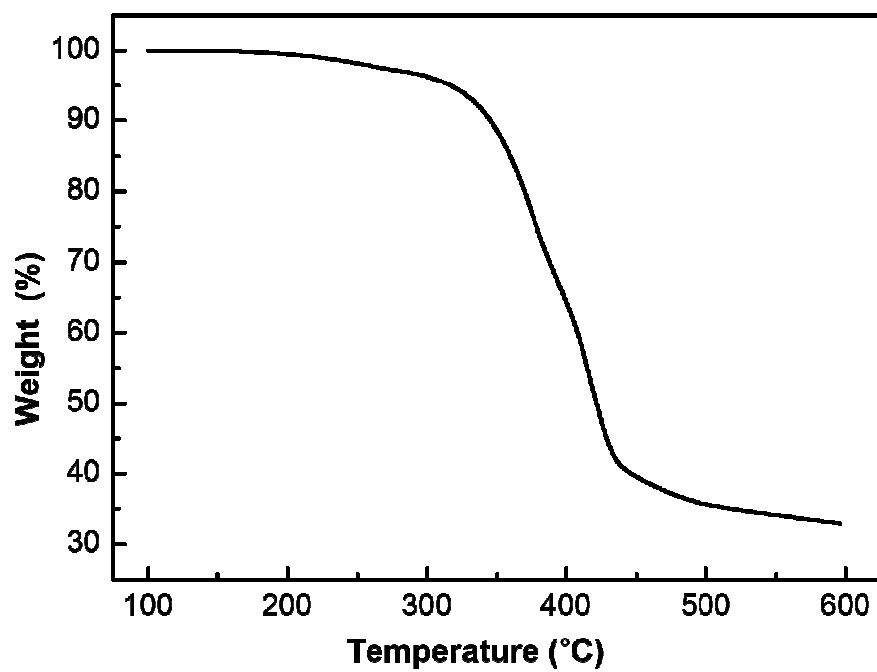


Figure S4. TGA of HABET. The 5 wt% weight loss is detected at 310 °C.

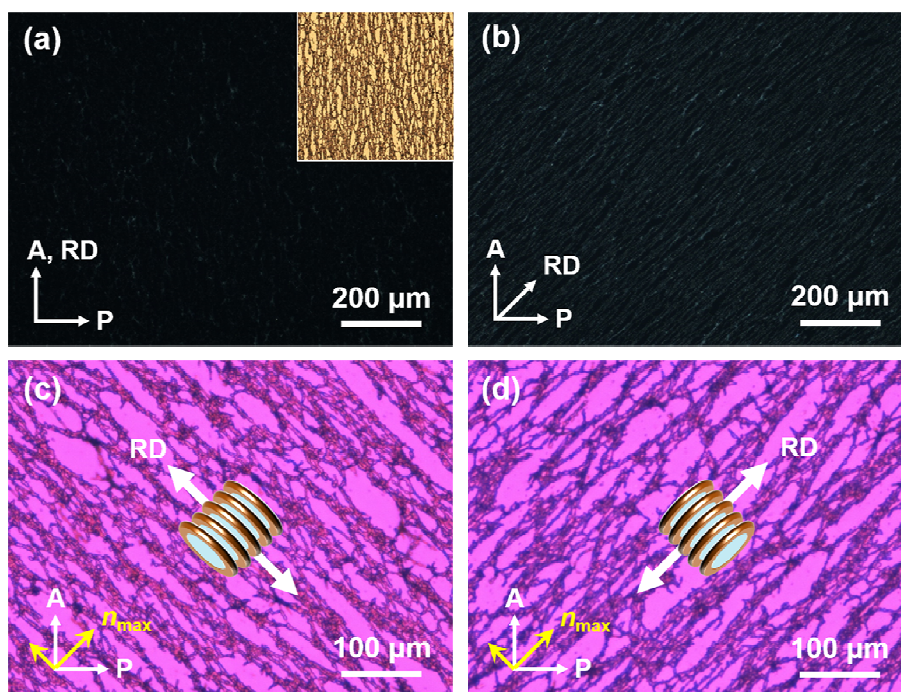


Figure S5. Morphological observations of the macroscopically oriented hierarchical HABET-based polymer network structures that fabricated in cell which have 10 μm cell gap. POM images are taken when the rubbing direction (RD) is (a) parallel to analyzer (A) or (b) 45° away from A. Inset of (a) is OM image of HABET networks. POM images are taken with a 530 nm retardation plate when the RD is (c) perpendicular or (d) parallel with the maximum refractive axis (n_{max}) of the retardation plate.

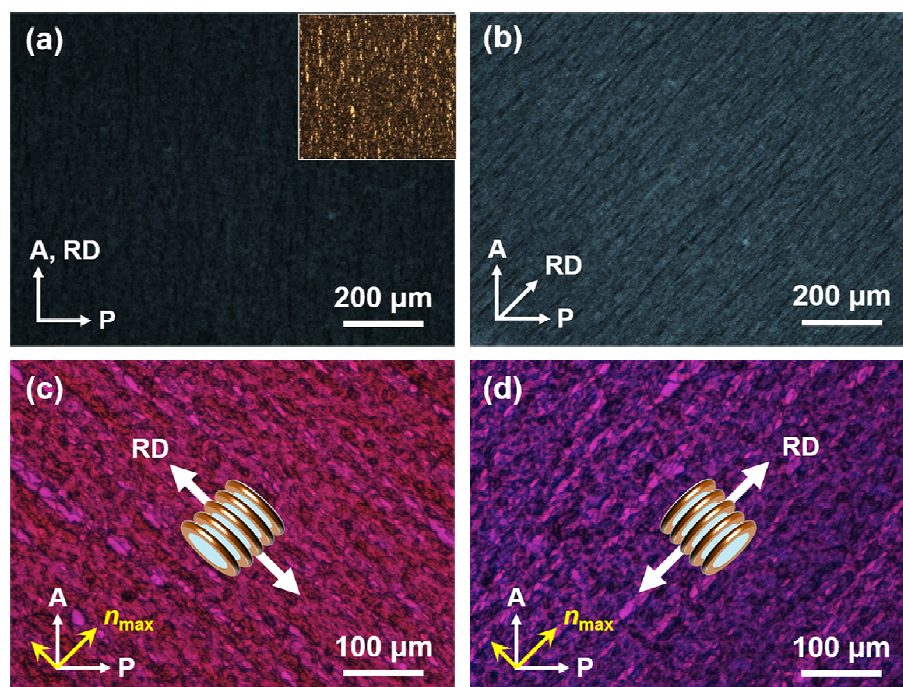


Figure S6. Morphological observations of the macroscopically oriented hierarchical HABET-based polymer network structures that fabricated in cell which have 50 μm cell gap. POM images are taken when the rubbing direction (RD) is (a) parallel to analyzer (A) or (b) 45° away from A. Inset of (a) is OM image of HABET networks. POM images are taken with a 530 nm retardation plate when the RD is (c) perpendicular or (d) parallel with the maximum refractive axis (n_{max}) of the retardation plate.

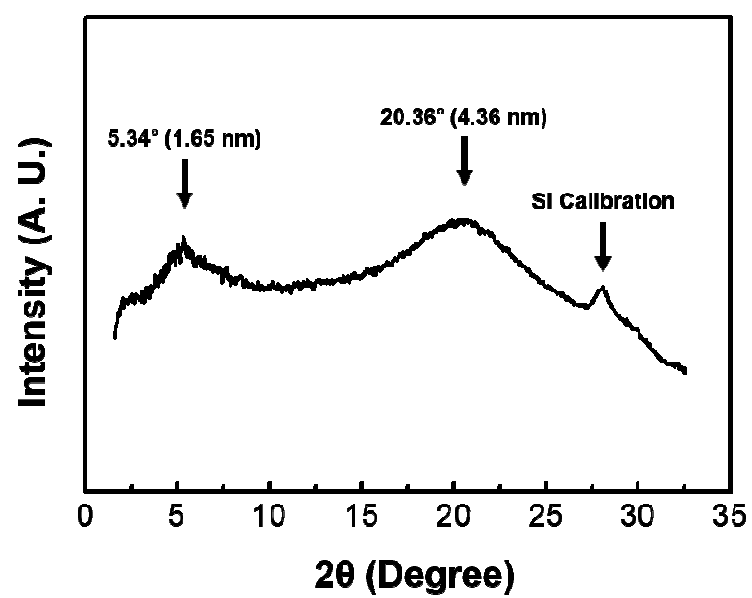


Figure S7. 1D WAXD pattern of HABET polymer networks.

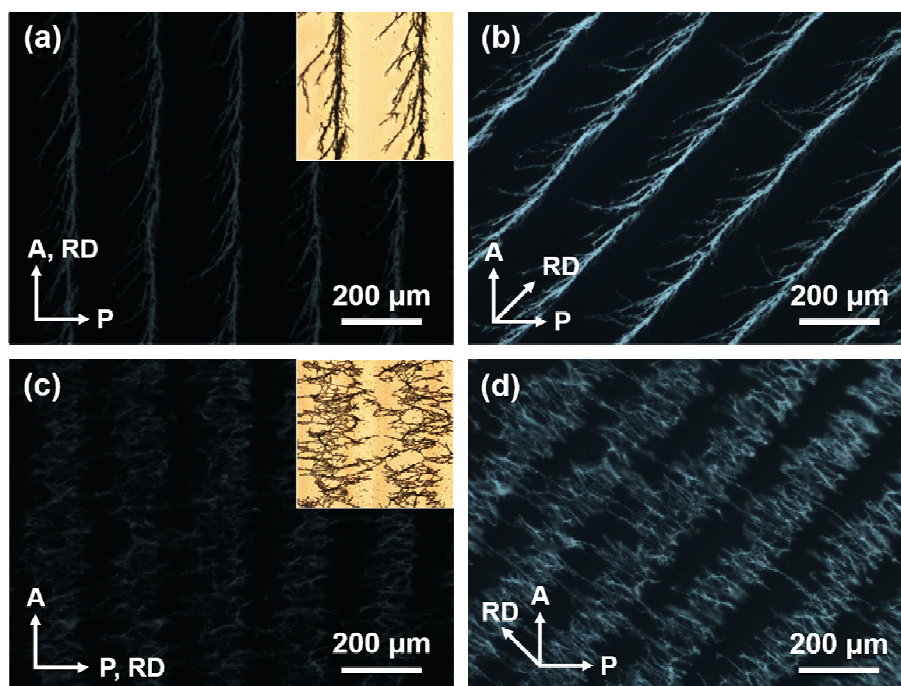


Figure S8. Morphological observations of the stripe-patterned hierarchical HABET-based polymer network structures that fabricated in cell which have 10 μm cell gap. POM images are taken when the RD is parallel to the long axis of the stripe-patterned photo mask: RD is (a) parallel to the analyzer (A) or (b) 45° away from A. POM images are taken when the RD is perpendicular to the long axis of the stripe-patterned photo mask: RD is (c) parallel to the polarizer (P) or (d) 45° away from P. Insets of (a) and (c) are OM image of HABET networks.

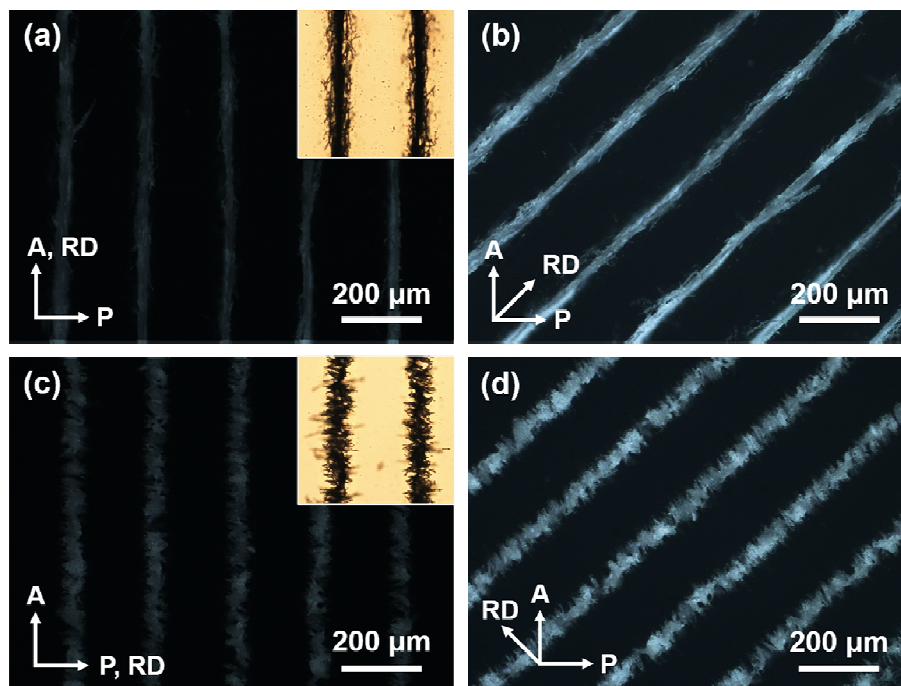


Figure S9. Morphological observations of the stripe-patterned hierarchical HABET-based polymer network structures that fabricated in cell which have 50 μm cell gap. POM images are taken when the RD is parallel to the long axis of the stripe-patterned photo mask: RD is (a) parallel to the analyzer (A) or (b) 45° away from A. POM images are taken when the RD is perpendicular to the long axis of the stripe-patterned photo mask: RD is (c) parallel to the polarizer (P) or (d) 45° away from P. Insets of (a) and (c) are OM image of HABET networks.

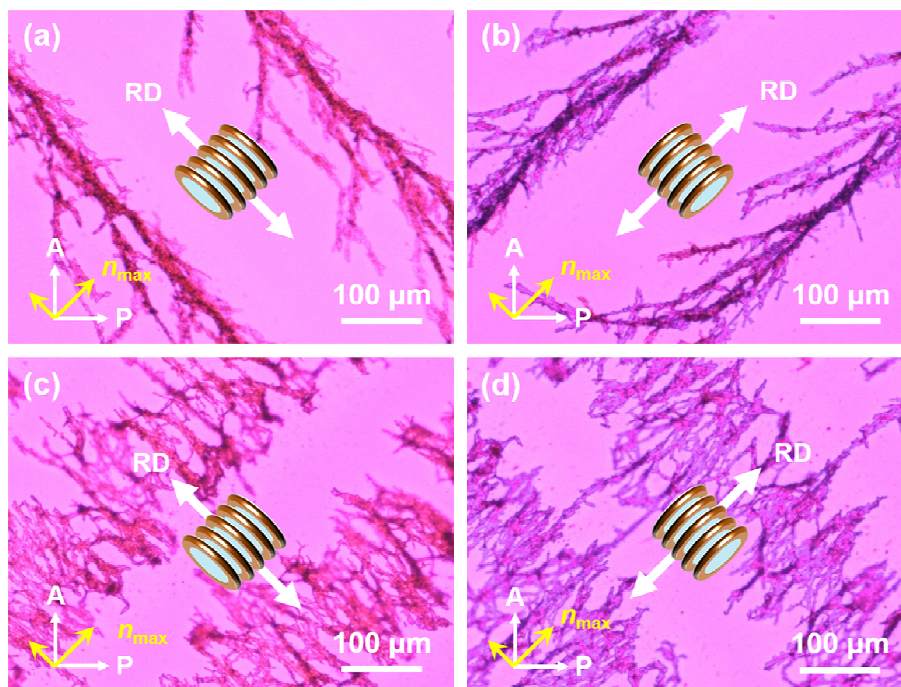


Figure S10. POM morphological observations of the stripe-patterned hierarchical HABET-based polymer network structures that fabricated in cell which have 10 μm cell gap with a 530 nm retardation plate. RD is parallel to the long axis of the stripe-patterned photo mask: RD is (a) perpendicular or (b) parallel to the maximum refractive axis (n_{max}) of the retardation plate. RD is perpendicular to the long axis of the stripe-patterned photo mask: RD is (c) perpendicular or (d) parallel to the n_{max} .

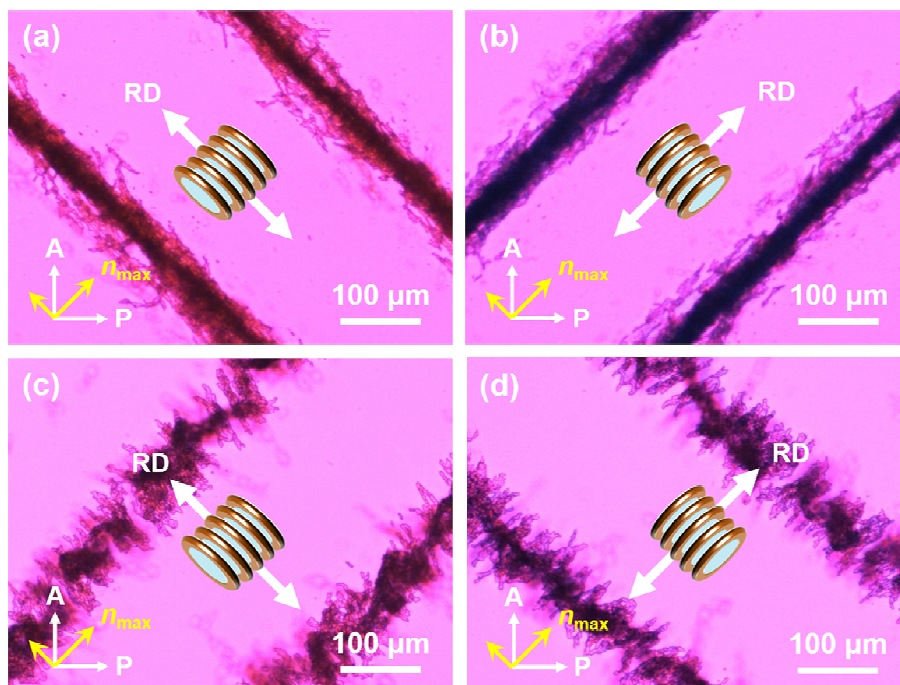


Figure S11. POM morphological observations of the stripe-patterned hierarchical HABET-based polymer network structures that fabricated in cell which have 50 μm cell gap with a 530 nm retardation plate. RD is parallel to the long axis of the stripe-patterned photo mask: RD is (a) perpendicular or (b) parallel to the maximum refractive axis (n_{max}) of the retardation plate. RD is perpendicular to the long axis of the stripe-patterned photo mask: RD is (c) perpendicular or (d) parallel to the n_{max} .

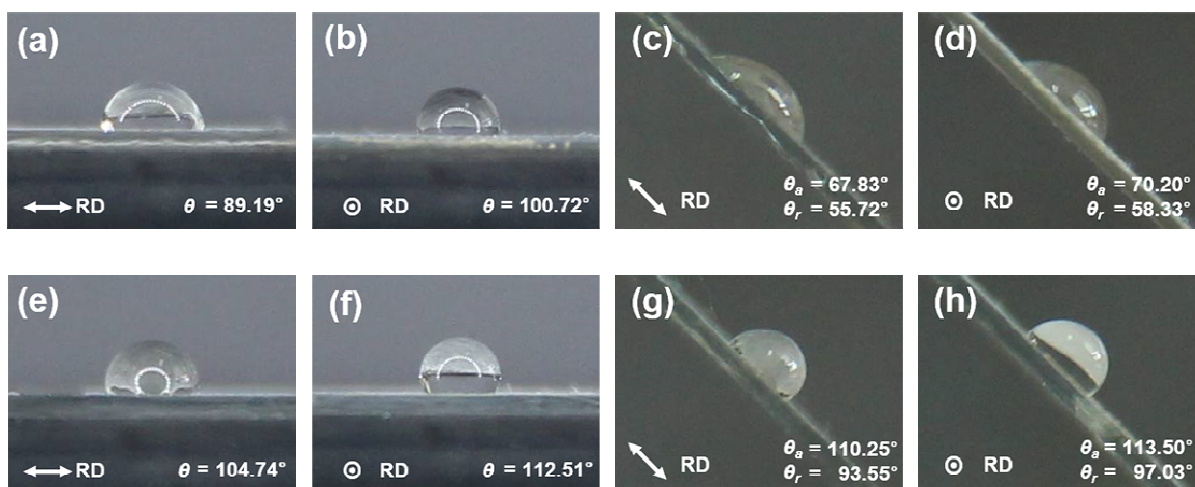


Figure S12. Contact angle measurements of the macroscopically oriented hierarchical HABET-based polymer network structures: water droplets on the HABET-based polymer network structures that fabricated in the LC cells with the (a, b, c, d) 10 μm and (e, f, g, h) 50 μm cell gap, which images are observed (a, c, e, g) perpendicular or (b, d, f, h) parallel to the RD. Images of c, d, g and h are taken by 45°-tilting the a, c and e samples, respectively. Here, θ , θ_a , and θ_r stand for contact angle, advancing angle and recession angle, respectively.