Electronic Supplementary Material (ESI) for Chemical Science.

Precise Modulation of Molecular Weight Distribution for Structure Engineering

Rui Tan,[a] Dongdong Zhou,[a] Baolei Liu,[c] Yanxiao Sun,[a] Xinxin Liu,[a] Zhuang Ma,[a] Deyu Kong,[a] Jinlin He,[c] Zhengbiao Zhang,[c] and Xue-Hui Dong[a, b]*

[a] South China Advanced Institute of Soft Matter Science and Technology, School of Molecular Science and Engineering, South China University of Technology, Guangzhou 510640, China

[b] State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China

[c] College of Chemistry, Chemical Engineering and Materials Science, Soochow University Suzhou, 215123, China

*Corresponding author: xdong@scut.edu.cn

1. Materials and Methods.

The following chemicals are used as received: $_D$-camphorsulfonic acid (TCI), benzyl alcohol (Bn, TCI), *tert*-butyldimethylsilyl chloride (TBDMSCl, TCI), imidazole (TCI), Pd/C (10 wt%, Aldrich), *N*, *N*'-diisopropylcarbodiimide (DIC, Aldrich). 4-(Dimethylamino)Pyridinium-4-toluenesulfonate (DPTS) was synthesized according to literature[1]. Anhydrous solvents, including toluene, dimethylformamide (DMF), dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), were obtained with an INERT Pure Solv System (Inert Corporation, USA). Automated column chromatography was conducted on a SepaBean^{TM} machine T (SanTai Technologies, China) with an automated variable-wavelength UV-VIS detector (200 ~ 400 nm).

^{1}H-NMR spectra were recorded on Bruker 400 MHz spectrometers using $CDCl_3$ (Cambridge) as deuterated solvent. The spectra were referenced to the residual proton impurities in the $CDCl_3$ at d 7.27 ppm.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-ToF) mass spectra (MS) were acquired on an UltrafleXtreme MALDI-ToF mass spectrometer (Bruker Daltonics, Germany) equipped with an Nd:YAG smart beam-II laser with 355-nm wavelength and 200 Hz firing rate using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCBT, Aldrich, >98%) as matrix. The cationizing agent sodium trifluoroacetate was prepared in ethanol at a concentration of 10 mg/mL. The matrix and cationizing salt solutions were mixed in a ratio of 10/1 (v/v). The instrument was calibrated prior to each measurement with external PMMA at the molecular weight under consideration. All samples were dissolved in $CHCl_3$ at a concentration of 10 mg/mL.

Size exclusion chromatography (SEC) analyses were conducted on a Tosoh HLC-8320 instrument equipped with three TSKgel columns (SuperH2000, SuperH3000, and SuperH4000) in series, a double flow type RI detector, and a UV-8320 UV detector, under an eluent flow rate of 0.6 mL/min (THF). Regular SEC calibrations were conducted with polystyrene standards (Polymer Laboratories). Dispersed *o*LLAs were further calibrated using discrete *o*LLA library as standards.

Differential scanning calorimetry (DSC) data were collected using DSC Q20 (TA Instruments). Discrete and dispersed *o*LLAs samples were heated to 180 °C for 15 minutes, followed by

isothermal crystallization at a certain temperature on a Linkam heating stage (LTS420) for 12 hours. The prepared samples (typically ~3 mg) were weighed and sealed in aluminum pans, and heated from 40 to 150 °C with a heating rate of 5 °C/min.

Small angle X-ray scattering (SAXS) was performed on Shanghai Synchrotron Radiation (SSRF), beamline BL16B1. The incident X-ray photon energy was 10 keV, producing X-rays with a wavelength (λ) of 0.124 nm and a photo flux of 1×10^{11} phs/s. The beam size is less than 0.4×0.5 mm^2. Scattered X-rays were captured on a 2-dimensional Pilatus detector. The instrument was calibrated with diffraction patterns from silver behenate.

Wide angle X-ray diffraction (WAXD) was performed on an X-ray diffractometer custom-made by Rigaku (Japan) with an ultrahigh-intensity microfocus rotating anode X-ray generator (FR-X), using a copper $K\alpha$ X-ray source at a voltage of 45 kV and a current of 66 mA. The source produces X-rays with a wavelength (λ) of 0.154 nm. Scattered X-rays were captured on a Hybrid Pixel 2-dimensional detector (HyPix-6000C, Rigaku). The instrument was calibrated using a silicon standard.

2. Syntheses of Discrete *o*LLAs.

Synthesis of HO-LLA$_2$-Bn (**2**). L-(-)-lactide **1** (50.00 g, 346.91 mmol) and benzyl alcohol (56.33 g, 520.95 mol) was dissolved in ~ 100 mL of toluene under an argon atmosphere in a 250 mL round-bottom flask. D-Camphorsulfonic acid (0.15 g, 0.646 mmol) was added and stirred for 8 h at 80 °C. The reaction was then quenched by washing with $NaHCO_3$ saturated solution (3 × 100 mL). The aqueous layers were combined and extracted with ethyl acetate (EtOAc, 3 × 100 mL). The combined organic layers were further washed with NaCl (3 × 50 mL) and dried with $MgSO_4$ overnight. After removal of the solvent in vacuo, the crude material was purified by automated column chromatography using hexane/EtOAc (gradient 90/10 to 80/20) as eluent. The pure product **2** was obtained as a colorless oil (61.26 g, 70%). ^{1}H-NMR (400 MHz, $CDCl_3$, *δ*): 7.40-7.30 (5H, Ar-*H*), 5.23 (1H, OC*H*(CH_3)CO), 5.21 (1H, Ar-C*H*$_2$O), 5.15 (1H, Ar-C*H*$_2$O), 4.34 (1H, HOC*H*(CH_3)CO), 2.67 (1H, *H*OCH), 1.54 (3H, OCH(C*H*$_3$)CO), 1.44 ppm (3H, HOCH(C*H*$_3$)CO).

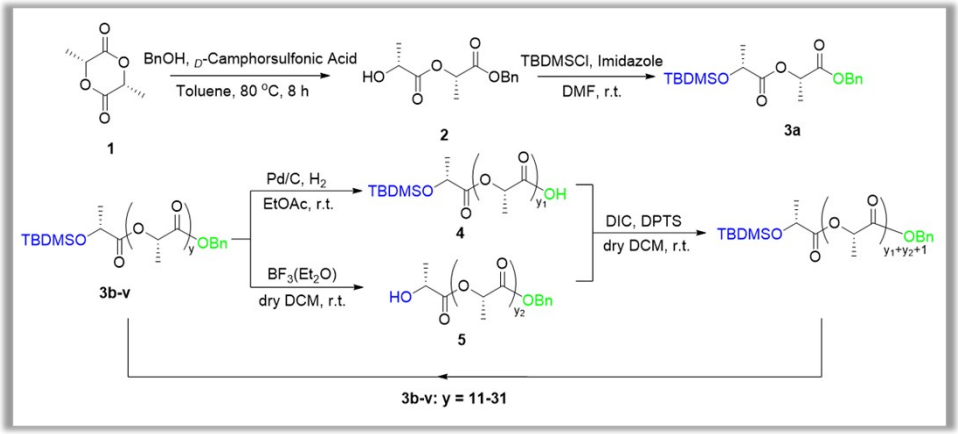
Synthesis of TBDMSO-LLA$_2$-Bn (**3a**). HO-LLA-Bn (**2b**) (30.04 g, 119.08 mmol) and Imidazole (36.48 g, 535.86 mmol) were dissolved in dry DMF (100 mL) in a 250 mL 2-necked round bottom flask under argon atmosphere. Tertbutyldimethylsilyl chloride (TBDMSCl, 44.87 g, 297.74 mmol) were then added and stirred overnight at room temperature. The mixture was quenched by adding saturated $NaHCO_3$ (200 mL) and extracted with EtOAc (3 × 150 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed in vacuo, giving crude product as colorless oil. The crude material was purified by automated column chromatography using hexane/EtOAc (gradient 100/0 to 90/10) as eluent. Pure **3a** was obtained as a colorless oil (39.28 g, 90%).^{1}H-NMR (400 MHz, $CDCl_3$, *δ*): 7.40-7.30 (5H, Ar-*H*), 5.23 (1H, OC*H*(CH_3)CO), 5.21 (1H, Ar-C*H*$_2$O), 5.15 (1H, Ar-C*H*$_2$O), 4.34 (1H, TBDMS-OC*H*(CH_3)CO), 1.54 (3H, OCH(C*H*$_3$)CO), 1.44 ppm (3H, TBDMS-OCH(C*H*$_3$)CO), 0.90 (s, 9H, (C*H*$_3$)$_3$C-Si(CH_3)$_2$), 0.10 (s, 3H, (CH_3)$_3$C-Si(C*H*$_3$)$_2$), 0.08 ppm (s, 3H, (CH_3)$_3$C-Si(C*H*$_3$)$_2$).

General procedures for synthesizing HO-LLA$_{y2}$-Bn (**5**). Take HO-LLA$_6$-Bn as an example. The oligomer TBDMSO-LLA$_6$-Bn (9.82 g, 15 mmol) was dissolved in anhydrous DCM (75 mL, 0.2 M) in a 250 mL round-bottom flask under argon atmosphere. BF_3-etherate (9.5 mL, 75 mmol) was then slowly added at 0 °C and the mixture was allowed to return to room temperature. The solution

became light yellow and was further stirred overnight. The reaction was quenched by adding saturated $NaHCO_3$ (150 mL). The organic layer was separated and washed with saturated NaCl solution (2 × 150 mL) and dried with $MgSO_4$. After removal of solvent in vacuo, the crude product was purified by column chromatography using *n*-hexane/ethyl acetate (gradient 100/0 to 80/20) as eluent to give the pure material **5e** (90%).

General procedures for synthesizing TBDMSO-LLA$_{y1}$-COOH (**4**). Take TBDMSO-LLA$_{16}$-COOH as an example. Benzyl protected oligomer **3f** (6.88 g, 5 mmol) was dissolved in ethyl acetate (35 mL, 0.15 M). Palladium (0.027 g, 10% on carbon, 0.5% eq of Pd) was added and purged with argon. The mixture was then stirred under a hydrogen atmosphere at room temperature. The black suspension was filtered through a thick layer of celite and washed with EtOAc (100 mL in small portions). After removal of solvent in vacuo, product **4f** were obtained in high purity (95%).

General procedures for synthesizing TBDMSO-LLA$_y$-Bn (**3**). Take TBDMSO-OLLA$_{22}$-Bn as an example. TBDMS protected oligomer **4f** (2.62 g, 2.04 mmol), benzyl protected oligomer **5e** (1.08 g, 2 mmol), and DPTS (0.30 g, 1 mmol) were dissolved in dry DCM (15 mL) in a round-bottom flask in a glove box. *N*,*N*'-Diisopropylcarbodiimide (DIC, 0.63 g, 5 mmol) was added slowly at 0 °C. The mixture was stirred at room temperature overnight. The reaction was quenched by washing with saturated NaCl solution (70 mL). The organic layer was dried with $MgSO_4$. The solvent was removed in vacuo, giving the crude product **3l** as a light-yellow oil. Purification by column chromatography using DCM/ethyl acetate (gradient 100/0 to 95/5) as eluent gave the pure material (73%).



Scheme S1. Syntheses of discrete *o*LAs *via* an iterative exponential growth route.

Table S1. Molecular Data of Discrete *oligo*-L-Lactic acids

Sample	x	M_n [a](Da)	$Đ$ [b]	d [c](nm)	d_c [d](nm)	T_m [e](°C)	ΔH_m [e](J/g)
oLLA$_{12}$	12	1087.2	< 1.00001	4.64	3.73	63.6	49.8
oLLA$_{13}$	13	1159.2	< 1.00001	4.85	3.94	75.6	54.4
oLLA$_{14}$	14	1231.3	< 1.00001	5.26	4.35	83.7	53.4
oLLA$_{15}$	15	1303.3	< 1.00001	5.49	4.58	87.2	53.8
oLLA$_{16}$	16	1375.4	< 1.00001	5.88	4.97	92.4	54.7
oLLA$_{17}$	17	1447.5	< 1.00001	6.10	5.19	97.7	57.0
oLLA$_{18}$	18	1519.5	< 1.00001	6.32	5.41	105.1	69.3
oLLA$_{19}$	19	1591.6	< 1.00001	6.69	5.78	109.0	61.5
oLLA$_{20}$	20	1663.7	< 1.00001	6.96	6.05	111.1	62.3
oLLA$_{21}$	21	1735.7	< 1.00001	7.33	6.42	116.8	60.0
oLLA$_{22}$	22	1807.8	< 1.00001	7.61	6.70	119.7	64.8
oLLA$_{23}$	23	1879.9	< 1.00001	8.04	7.13	122.0	77.9
oLLA$_{24}$	24	1951.9	< 1.00001	8.31	7.40	123.9	66.3
oLLA$_{25}$	25	2024.0	< 1.00001	8.50	7.59	127.4	69.9
oLLA$_{26}$	26	2096.0	< 1.00001	8.96	8.05	131.2	71.1
oLLA$_{27}$	27	2168.1	< 1.00001	9.18	8.27	134.1	74.0
oLLA$_{28}$	28	2240.2	< 1.00001	9.39	8.48	135.5	81.0
oLLA$_{29}$	29	2312.2	< 1.00001	9.77	8.86	136.6	68.7
oLLA$_{30}$	30	2384.3	< 1.00001	10.27	9.36	139.1 [f]	72.7
oLLA$_{31}$	31	2456.4	< 1.00001	10.45	9.54	141.6 [f]	72.3
oLLA$_{32}$	32	2528.4	< 1.00001	10.55	9.64	143.3 [f]	69.9

[a]Calculated molecular weight. [b]Dispersity calculated from the relative peak intensities in the MALDI-ToF MS spectra. [c]Lamellar thickness, calculated based on $d = 2\pi/q^*$. [d]Crystal thickness calculated as $d_c = d - d_a$. [e]Melting temperature (T_m) and heat of fusion (ΔH_m), determined with DSC. [f]Multiple transitions were observed (see Figure S3). oLLA samples were isothermally crystallized at $T_c \approx T_m$ - 20 °C.

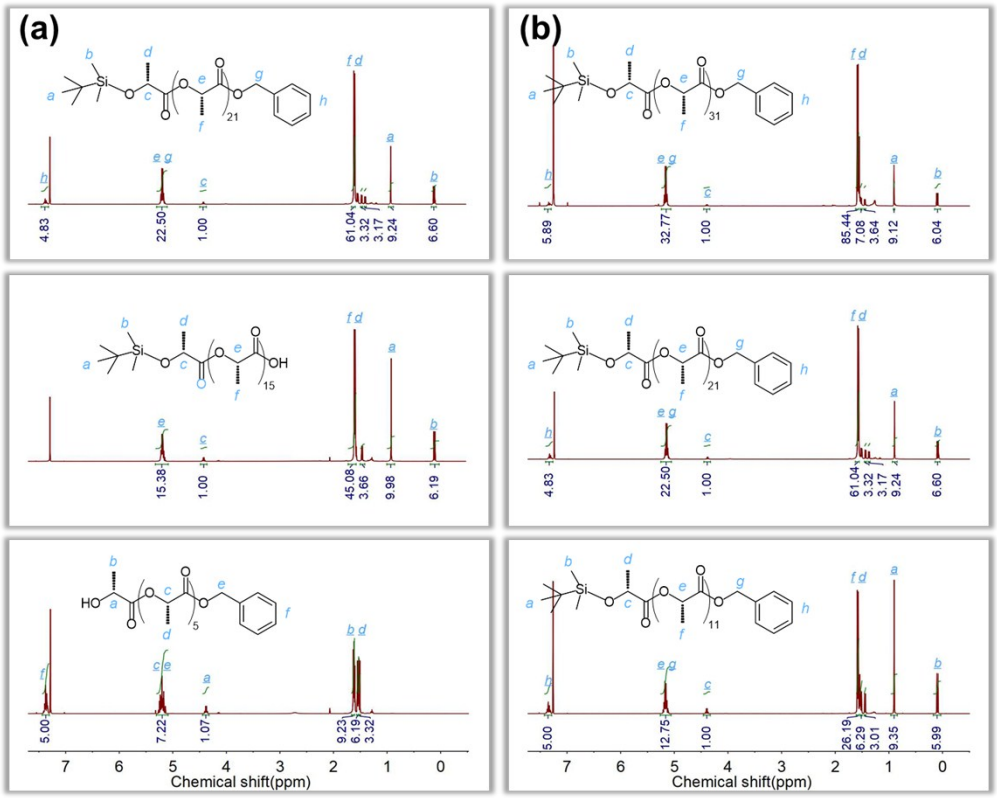


Fig. S1. ^{1}H NMR spectra of (a) intermediate and final compounds of a typical iterative growth cycle, and (b) representative spectra of oLA$_x$ with x = 12, 22, and 32. Other samples have similar spectra except integrations.

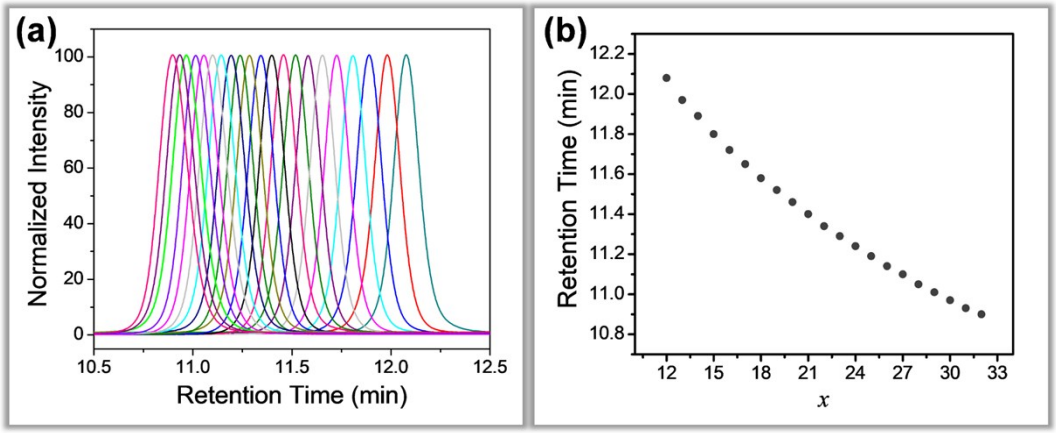


Fig. S2. (a) SEC elution profiles of oLA$_x$ (x = 12 to 32, from right to left), and (b) non-linear correlation between peak position and number of repeat units (x).

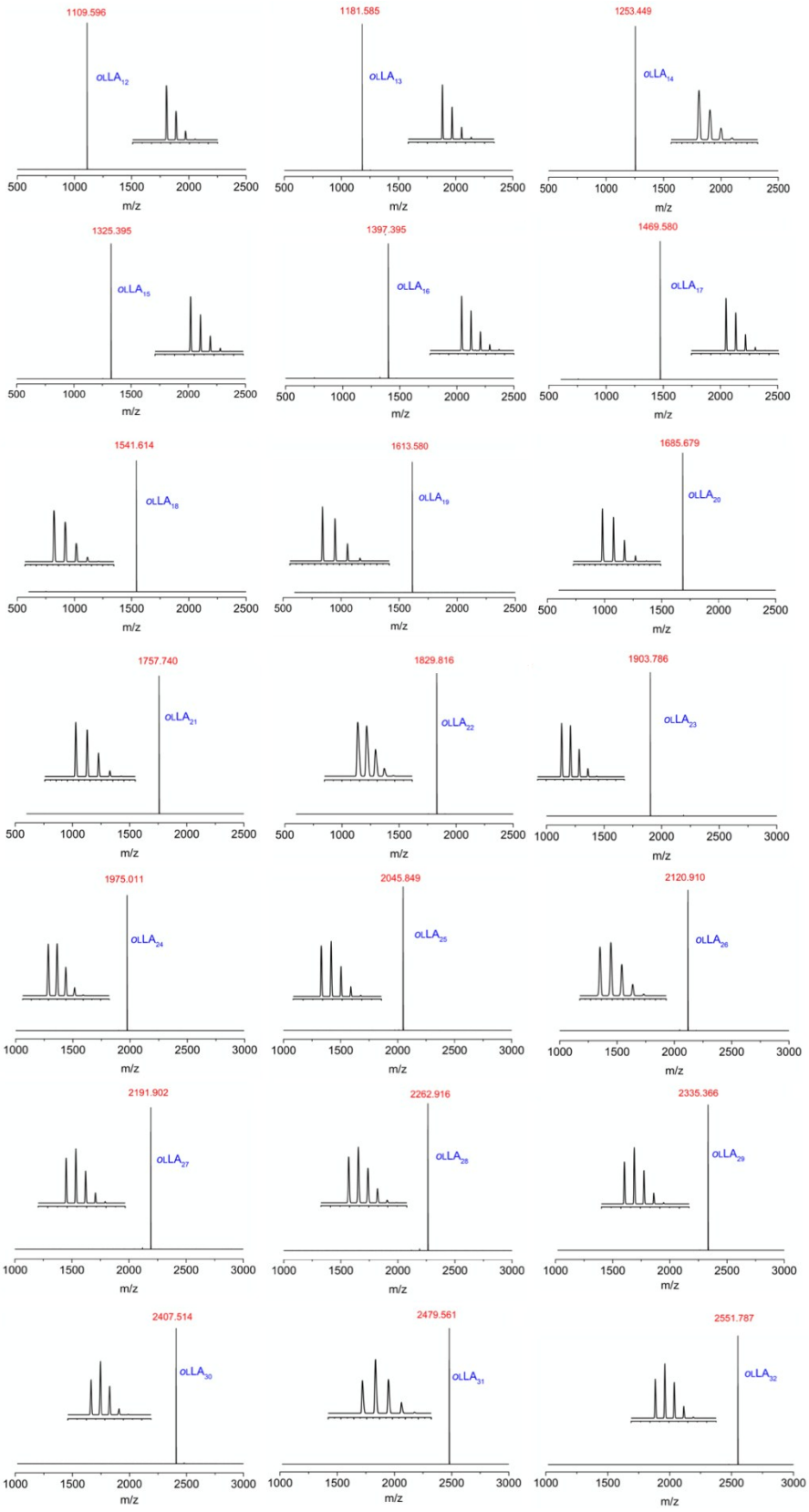


Fig. S3. MALDI-ToF mass spectra of discrete *o*LLA$_x$ (x from 12 to 32)

3. Crystallization Behaviors of Discrete *o*LLAs.

Discrete *o*LLAs were heated to about 30 K above the equilibrium melting temperature for 10 minutes, followed by crystallizing isothermally at a fixed crystallization temperature (*e.g.*, 60 °C). Meanwhile, to avoid potential polymorphism and/or kinetic trapping, an isothermal crystallization process with T_c to be about 20 K below the melting temperature (T_m) of each discrete *o*LLA was also adopted.

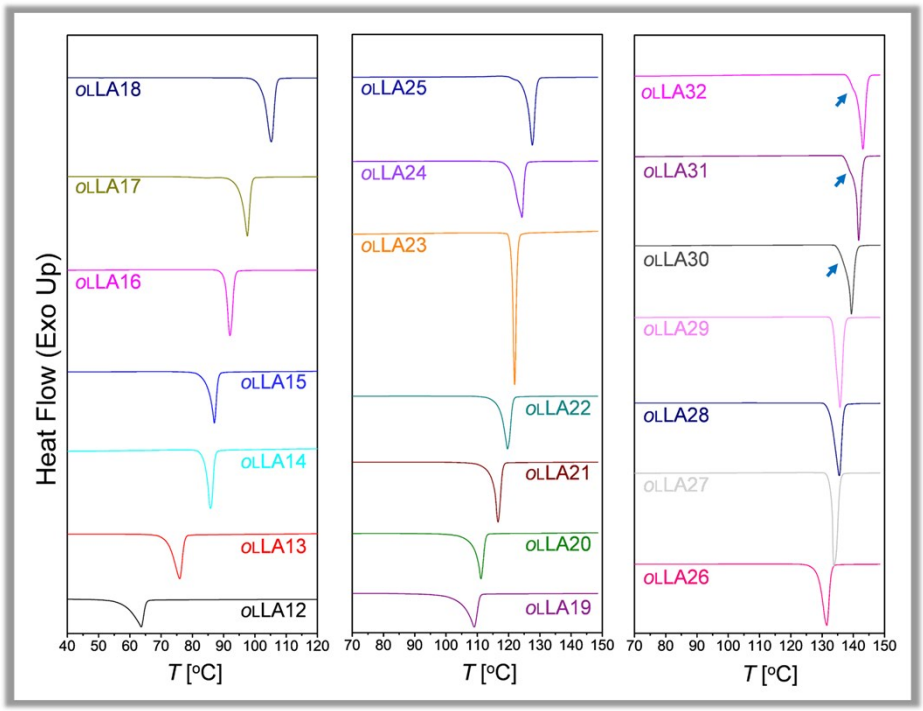


Fig. S4. DSC thermograms of discrete *o*LLA$_x$ (heating rate: 5 °C /min, vertically offset for clarity). Arrows indicate melting-recrystallization transition of ill-defined crystals.

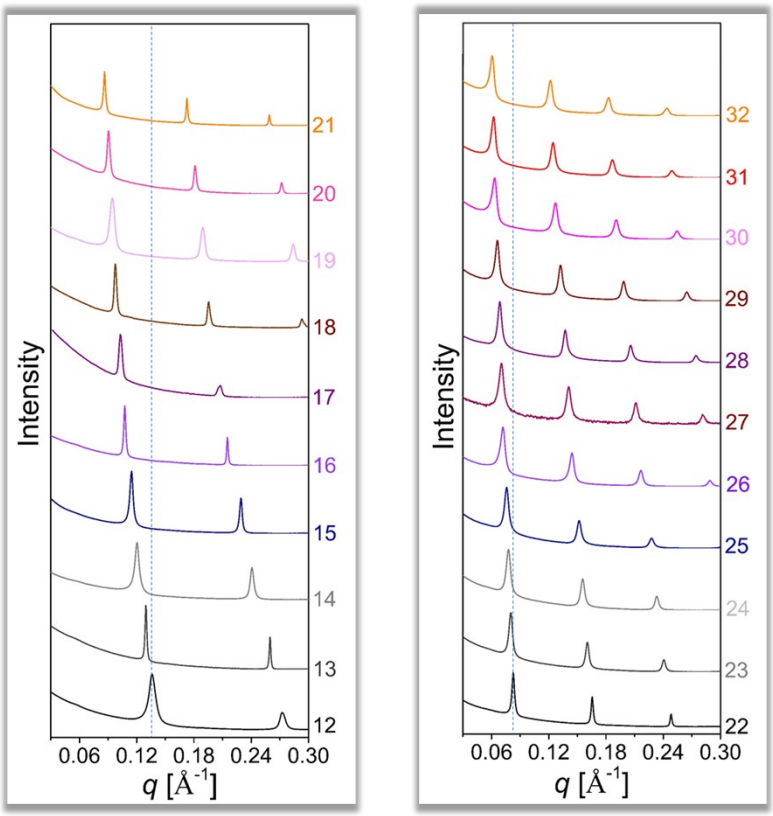


Fig. S5. SAXS patterns of *o*LLA$_x$ (vertically offset for clarity). Number of repeat units (*x*) is labelled on the right side.

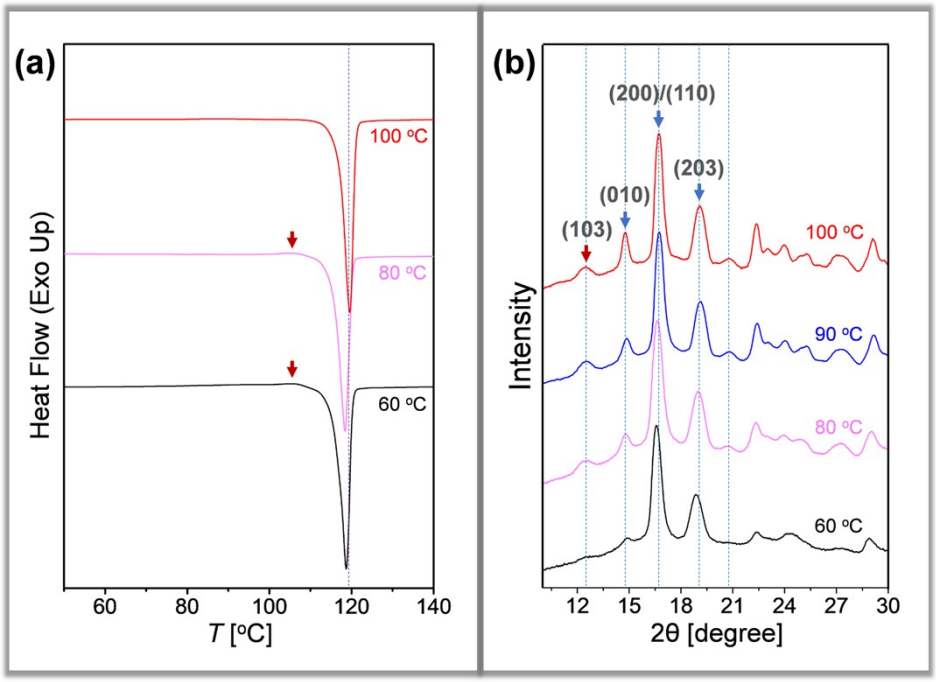


Fig. S6. DSC thermograms (a) and WAXD patterns (b) of *o*LLA$_{22}$ crystallized at different temperatures. Spectra were vertically offset for clarity. Arrows in (a) indicate *α′* to *α* form transition.

4. Modulation of Dispersity.

Dispersed samples were prepared through precision blending. As a prerequisite, the concentration of the oLLA$_x$ stock solutions has to be carefully measured. Simply weighing by high precision balance was not sufficient. To improve accuracy, we took advantage of absorption of the Bn protecting group to calibrate the concentration.

Preparation of calibration curves. To establish a work function, a series of oLLA$_4$ solutions were prepared. Specifically, 2.072, 6.187, 8.702, 10.590, 12.035, and 14.537 mg of oLLA$_4$ was accurately weighed on an electronic balance (Sartorius MSA6.6S-0CE-DM, Sartorius, German) with an accuracy of 0.001 mg, and added into separate 5 mL volumetric flasks. 5 mL of THF was then added. The UV-vis absorption spectra of these solutions were recorded on UV-vis-NIR spectrophotometer (UV-3600Plus, Shimadzu, Japan). The characteristic absorption peak arising from the benzyl end group (258 nm, see Fig. S7a) was used for calibration. The absorption intensity at 258 nm increases linearly with the solution concentration (Fig. S7a). Similar linear response was also recorded in the case of oLLA$_8$ and oLLA$_{16}$, indicating that the absorption is not sensitive to the number of repeat units (Fig. S7). A quantitative measurement of concentration can thus be achieved for all the oLLAs by using Beer-Lambert law.

$$A = kc + b$$

where A is the absorbance at 258 nm, c is the molar concentration of the benzyl group (*i.e.*, molar concentration of oLLA). The slope, k, was determined to be 211.8 M^{-1}, and b was 0.02.

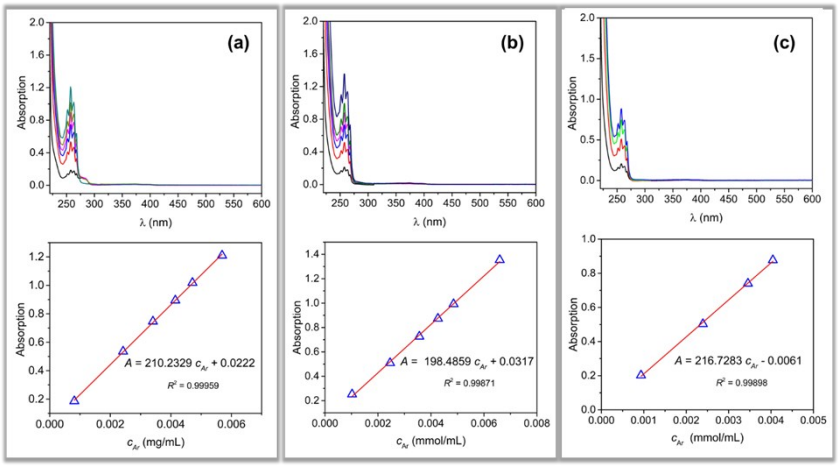
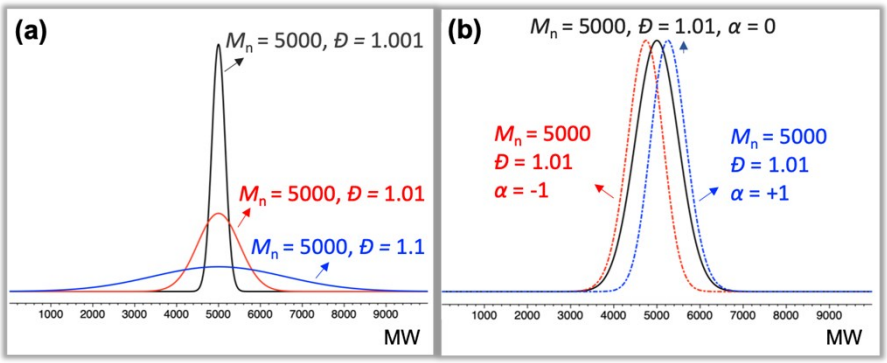


Fig. S7. UV-vis spectra of oLLA solution in THF and corresponding calibration curves: (a) oLLA$_4$ solution, (b) oLLA$_8$ solution, and (c) oLLA$_{16}$ solution.

Preparation of *o*LLA$_x$ stock solutions. Approximately 50 mg of *o*LLA$_x$ was accurately weighed on an electronic balance (Sartorius MSA6.6S-0CE-DM, Sartorius, German). The powder was then transferred into a 20 mL bottle glass with a PTFE sealing plug. 10 mL of THF was added through a pipette. The accurate concentration of the solution was further calibrated by UV-vis spectra as discussed.

Preparation of samples with varying *Đ*. Take the *o*LLA$_{22}$(1.01) as an example. Molar content of each component can be calculated by Eq. 2 and Eq. 3 (listed in Table S2). Fraction lower than 2 mol% will be neglected. Given a total mass (*e.g.*, 50 mg), the actual weight of each component, as well as the mass of corresponding stock solution, can be determined. Based on the recipe, each stock solution was weighed on an electronic balance (ME204, METTLER TOLEDO, Switzerland), and mixed in a 20 mL vial. To ensure high precision, all the operation was conducted under saturated THF atmosphere. THF was then removed in vacuo. Similar approaches were adopted to prepared samples with symmetric (Table S2) and asymmetric distribution (Table S3) with varying M_n and *Đ*.



Scheme S2. Molecular weight distribution generated based on *Gaussian* distribution (a, Eq. 2) and *skew-normal* distribution (b, Eq. 4).

Table S2-1. Composition of Symmetrically Dispersed Samples with Varying *Đ* (*x* = 19)

	1.001[a]	1.003	1.005	1.007	1.01	1.02	1.04	1.06	1.10
oLLA$_{12}$	0.000[b]	0.000	0.000	0.000	0.001	0.010	0.026	0.032	0.035
oLLA$_{13}$	0.000	0.000	0.000	0.001	0.005	0.020	0.036	0.040	0.039
oLLA$_{14}$	0.000	0.000	0.002	0.006	0.014	0.035	0.048	0.048	0.044
oLLA$_{15}$	0.000	0.001	0.010	0.021	0.035	0.056	0.060	0.056	0.048
oLLA$_{16}$	0.000	0.015	0.040	0.058	0.072	0.081	0.072	0.063	0.052
oLLA$_{17}$	0.009	0.084	0.112	0.120	0.120	0.104	0.081	0.069	0.055
oLLA$_{18}$	0.205	0.234	0.208	0.186	0.163	0.121	0.088	0.072	0.057
oLLA$_{19}$	**0.571**	**0.330**	**0.255**	**0.216**	**0.181**	**0.128**	**0.090**	**0.074**	**0.057**
oLLA$_{20}$	0.205	0.234	0.208	0.186	0.163	0.121	0.088	0.072	0.057
oLLA$_{21}$	0.009	0.084	0.112	0.120	0.120	0.104	0.081	0.069	0.055
oLLA$_{22}$	0.000	0.015	0.040	0.058	0.072	0.081	0.072	0.063	0.052
oLLA$_{23}$	0.000	0.001	0.010	0.021	0.035	0.056	0.060	0.056	0.048
oLLA$_{24}$	0.000	0.000	0.002	0.006	0.014	0.035	0.048	0.048	0.044
oLLA$_{25}$	0.000	0.000	0.000	0.001	0.005	0.020	0.036	0.040	0.039
oLLA$_{26}$	0.000	0.000	0.000	0.000	0.001	0.010	0.026	0.032	0.035

Table S2-2. Composition of Symmetrically Dispersed Samples with Varying *Đ* (*x* = 22)

	1.001[a]	1.003	1.005	1.007	1.01	1.02	1.04	1.06	1.10
oLLA$_{14}$	0.000[b]	0.000	0.000	0.000	0.001	0.009	0.022	0.028	0.030
oLLA$_{15}$	0.000	0.000	0.000	0.001	0.003	0.016	0.030	0.034	0.034
oLLA$_{16}$	0.000	0.000	0.001	0.003	0.009	0.027	0.039	0.040	0.038
oLLA$_{17}$	0.000	0.000	0.004	0.011	0.022	0.042	0.048	0.047	0.041
oLLA$_{18}$	0.000	0.004	0.018	0.031	0.045	0.060	0.058	0.053	0.044
oLLA$_{19}$	0.000	0.027	0.054	0.068	0.078	0.079	0.066	0.058	0.047
oLLA$_{20}$	0.021	0.101	0.119	0.121	0.116	0.096	0.073	0.062	0.049
oLLA$_{21}$	0.227	0.223	0.192	0.170	0.147	0.108	0.078	0.064	0.050
oLLA$_{22}$	**0.503**	**0.290**	**0.225**	**0.190**	**0.159**	**0.112**	**0.079**	**0.065**	**0.050**
oLLA$_{23}$	0.227	0.223	0.192	0.170	0.147	0.108	0.078	0.064	0.050
oLLA$_{24}$	0.021	0.101	0.119	0.121	0.116	0.096	0.073	0.062	0.049
oLLA$_{25}$	0.000	0.027	0.054	0.068	0.078	0.079	0.066	0.058	0.047
oLLA$_{26}$	0.000	0.004	0.018	0.031	0.045	0.060	0.058	0.053	0.044

oLLA$_{27}$	0.000	0.000	0.004	0.011	0.022	0.042	0.048	0.047	0.041
oLLA$_{28}$	0.000	0.000	0.001	0.003	0.009	0.027	0.039	0.040	0.038
oLLA$_{29}$	0.000	0.000	0.000	0.001	0.003	0.016	0.030	0.034	0.034
oLLA$_{30}$	0.000	0.000	0.000	0.000	0.001	0.009	0.022	0.028	0.030

Table S2-3. Composition of Symmetrically Dispersed Samples with Varying *Đ* (*x* = 24)

	1.001[a]	**1.003**	**1.005**	**1.007**	**1.01**	**1.02**	**1.04**
oLLA$_{16}$	0.000 [b]	0.000	0.000	0.000	0.002	0.012	0.025
oLLA$_{17}$	0.000	0.000	0.000	0.001	0.005	0.020	0.032
oLLA$_{18}$	0.000	0.000	0.002	0.005	0.013	0.031	0.040
oLLA$_{19}$	0.000	0.001	0.007	0.015	0.027	0.044	0.048
oLLA$_{20}$	0.000	0.007	0.024	0.037	0.049	0.060	0.056
oLLA$_{21}$	0.001	0.035	0.061	0.073	0.080	0.077	0.063
oLLA$_{22}$	0.031	0.108	0.121	0.119	0.112	0.091	0.069
oLLA$_{23}$	0.236	0.214	0.182	0.160	0.138	0.101	0.072
oLLA$_{24}$	**0.466**	**0.269**	**0.208**	**0.176**	**0.147**	**0.104**	**0.074**
oLLA$_{25}$	0.235	0.214	0.182	0.160	0.138	0.101	0.072
oLLA$_{26}$	0.030	0.108	0.121	0.119	0.112	0.091	0.069
oLLA$_{27}$	0.001	0.035	0.061	0.073	0.080	0.077	0.063
oLLA$_{28}$	0.000	0.007	0.024	0.037	0.049	0.060	0.056
oLLA$_{29}$	0.000	0.001	0.007	0.015	0.027	0.044	0.048
oLLA$_{30}$	0.000	0.000	0.002	0.005	0.013	0.031	0.040
oLLA$_{31}$	0.000	0.000	0.000	0.001	0.005	0.020	0.032
oLLA$_{32}$	0.000	0.000	0.000	0.000	0.002	0.012	0.025

[a]Dispersity (*Đ*). [b]Molar fraction calculated based on Eq. 2 and Eq. 3. Color code: central fraction (orange), fractions with molar content > 2% (blue), and fractions with molar content < 2% (grey).

Table S3-1. Composition of Asymmetrically Dispersed *o*LLA$_{19}$ with Varying α ($Đ$ = 1.01).

	$\alpha = 0$ [a]	+1	-1	+2	-2	+3	-3
***o*LLA$_{14}$**	0.014 [b]	0.000	0.028	0.000	0.028	0.000	0.028
***o*LLA$_{15}$**	0.035	0.002	0.068	0.000	0.070	0.000	0.070
***o*LLA$_{16}$**	0.072	0.013	0.131	0.000	0.143	0.000	0.144
***o*LLA$_{17}$**	0.120	0.044	0.196	0.008	0.231	0.001	0.239
***o*LLA$_{18}$**	0.163	0.106	0.220	0.060	0.266	0.028	0.298
***o*LLA$_{19}$**	**0.181**	**0.181**	**0.181**	**0.181**	**0.181**	**0.181**	**0.181**
***o*LLA$_{20}$**	0.163	0.220	0.106	0.266	0.060	0.298	0.028
***o*LLA$_{21}$**	0.120	0.196	0.044	0.231	0.008	0.239	0.001
***o*LLA$_{22}$**	0.072	0.131	0.013	0.143	0.000	0.144	0.000
***o*LLA$_{23}$**	0.035	0.068	0.002	0.070	0.000	0.070	0.000
***o*LLA$_{24}$**	0.014	0.028	0.000	0.028	0.000	0.028	0.000
***o*LLA$_{25}$**	0.005	0.009	0.000	0.009	0.000	0.009	0.000
***o*LLA$_{26}$**	0.001	0.002	0.000	0.002	0.000	0.002	0.000

Table S3-2. Composition of Asymmetrically Dispersed *o*LLA$_{22}$ with Varying α ($Đ$ = 1.01).

	$\alpha = 0$ [a]	+1	-1	+2	-2	+3	-3
***o*LLA$_{16}$**	0.009 [b]	0.000	0.018	0.000	0.018	0.000	0.018
***o*LLA$_{17}$**	0.022	0.001	0.043	0.000	0.044	0.000	0.044
***o*LLA$_{18}$**	0.045	0.005	0.084	0.000	0.089	0.000	0.089
***o*LLA$_{19}$**	0.078	0.018	0.137	0.001	0.154	0.000	0.155
***o*LLA$_{20}$**	0.116	0.049	0.182	0.013	0.219	0.002	0.229
***o*LLA$_{21}$**	0.147	0.101	0.192	0.062	0.231	0.034	0.260
***o*LLA$_{22}$**	**0.159**	**0.159**	**0.159**	**0.159**	**0.159**	**0.159**	**0.159**
***o*LLA$_{23}$**	0.147	0.192	0.101	0.231	0.062	0.260	0.034
***o*LLA$_{24}$**	0.116	0.182	0.049	0.219	0.013	0.229	0.002
***o*LLA$_{25}$**	0.078	0.138	0.018	0.154	0.001	0.156	0.000
***o*LLA$_{26}$**	0.045	0.084	0.005	0.089	0.000	0.089	0.000
***o*LLA$_{27}$**	0.022	0.043	0.001	0.044	0.000	0.044	0.000
***o*LLA$_{28}$**	0.009	0.018	0.000	0.018	0.000	0.018	0.000

Table S3-3. Composition of Asymmetrically Dispersed *o*LLA$_{24}$ with Varying α ($Đ$ = 1.01).

	$\alpha = 0$ [a]	+1	-1	+2	-2	+3	-3

$o_L LA_{18}$	0.013 [b]	0.000	0.025	0.000	0.025	0.000	0.025
$o_L LA_{19}$	0.027	0.002	0.052	0.000	0.054	0.000	0.054
$o_L LA_{20}$	0.049	0.007	0.092	0.000	0.099	0.000	0.099
$o_L LA_{21}$	0.080	0.021	0.138	0.002	0.157	0.000	0.159
$o_L LA_{22}$	0.112	0.052	0.173	0.016	0.209	0.003	0.221
$o_L LA_{23}$	0.138	0.098	0.177	0.063	0.212	0.037	0.238
$o_L LA_{24}$	**0.147**	**0.147**	**0.147**	**0.147**	**0.147**	**0.147**	**0.147**
$o_L LA_{25}$	0.138	0.177	0.098	0.212	0.063	0.238	0.037
$o_L LA_{26}$	0.112	0.173	0.052	0.209	0.016	0.221	0.003
$o_L LA_{27}$	0.080	0.138	0.021	0.157	0.002	0.159	0.000
$o_L LA_{28}$	0.049	0.092	0.007	0.099	0.000	0.099	0.000
$o_L LA_{29}$	0.027	0.052	0.002	0.054	0.000	0.054	0.000
$o_L LA_{30}$	0.013	0.025	0.000	0.025	0.000	0.025	0.000

[a]Asymmetric parameter (α). [b]Molar fraction calculated based on Eq. 2, Eq. 3, and Eq. 4. Dispersity is fixed at $Đ$ = 1.01. Color code: central fraction (orange), fractions with molar content > 2% (blue), and fractions with molar content < 2% (grey).

Table S4-1. Molecular Characterization of Symmetrically Dispersed *o*LLA Samples (*x* = 19).

Sample[a]	M_n [b]	Đ		T_c = 60 °C[f]			T_c = 80 °C[f]					
				d [g]	T_m [h]	ΔH_m [i]	d_1 [g]	$T_{m,1}$ [h]	ΔH_{m1} [i]	d_2 [g]	$T_{m,2}$ [h]	ΔH_{m2} [i]
*o*LLA$_{19}$ [e]	1591.6 [e]	< 1.0001 [e]		6.66	109.2	62.3	6.66	109.5	63.0	--	--	--
*o*LLA$_{19}$(1.001)	1590	1.004 [c]	1.001 [d]	6.70	105.8	58.3	6.66	105.0	56.9	--	--	--
*o*LLA$_{19}$(1.003)	1590	1.005	1.002	6.72	105.6	51.2	6.73	104.9	56.2	--	--	--
*o*LLA$_{19}$(1.005)	1580	1.007	1.002	6.75	105.3	47.3	6.72	104.8	55.4	--	--	--
*o*LLA$_{19}$(1.007)	1590	1.009	1.004	6.76	105.7	46.0	6.75	104.7	55.0	--	--	--
*o*LLA$_{19}$(1.01)	1580	1.012	1.005	6.77	105.7	45.0	6.79	105.1	54.3	--	--	--
*o*LLA$_{19}$(1.02)	1570	1.020	1.010	6.87	105.5	41.2	--	105.4	44.5	--	67.3	2.7
*o*LLA$_{19}$(1.04)	1590	1.029	1.015	6.90	108.6	40.5	7.17	107.4	45.0	5.50	70.0	3.2
*o*LLA $_{19}$(1.06)	1580	1.039	1.024	7.02	108.2	40.7	--	108.3	39.2	--	68.9	5.0
*o*LLA$_{19}$(1.10)	1580	1.053	1.028	7.31	111.1	33.9	7.70	110.1	37.5	5.38	65.9	5.9

[a]Sample label *o*LLA$_x$(*Đ*), where *x* refers to the number of repeat units, *Đ* is the dispersity. [b]Number average molecular weight (Da) measured by SEC using discrete *o*LLA library as calibration. [c]Dispersity measured by SEC using discrete *o*LLA library as calibration. [d]Dispersity measured by MADLI-ToF. [e]Discrete *o*LLA$_{19}$, adopted from Table S1. [f]Crystallization temperature (T_c). [g]Lamellar thickness, nm, calculated based on $d = 2\pi/q^*$. [h] Melting temperature (°C) and [i] heat of fusion (J/g), determined with DSC.

Table S4-2. Molecular Characterization of Symmetrically Dispersed *o*LLA Samples (*x* = 24).

Sample[a]	M_n [b]	Đ		T_c = 60 °C[f]			T_c = 100 °C[f]		
				d [g]	T_m [h]	ΔH_m [i]	d [g]	T_m [h]	ΔH_m [i]
*o*LLA$_{24}$ [e]	1951.9 [e]	< 1.0001 [e]		7.96	126.2	53	8.10	126.1	70.5
*o*LLA$_{24}$(1.001)	1930	1.004[c]	1.001[d]	7.96	123.2	59.7	8.17	123.2	70.8
*o*LLA$_{24}$(1.003)	1940	1.006	1.001	8.08	123.2	62.3	8.27	122.7	67.8
*o*LLA$_{24}$(1.005)	1930	1.008	1.003	8.08	120.0	59.9	8.27	121.4	61.4
*o*LLA$_{24}$(1.007)	1930	1.009	1.004	8.06	120.3	59.7	8.31	121.2	65.8
*o*LLA$_{24}$(1.01)	1930	1.011	1.007	8.10	121.7	54.1	8.33	121.3	60.8
*o*LLA$_{24}$(1.02)	1930	1.026	1.013	8.18	122.7	45.5	8.41	121.9	59.4
*o*LLA$_{24}$(1.04)	1930	1.028	1.013	8.21	123.3	43.1	8.49	123.0	54.7

[a]Sample label *o*LLA$_x$(*Đ*), where *x* refers to the number of repeat units, *Đ* is the dispersity. [b]Number average molecular weight (Da) measured by SEC using discrete *o*LLA library as calibration. [c]Dispersity measured by SEC using discrete *o*LLA library as calibration. [d]Dispersity measured by MADLI-ToF. [e]Discrete *o*LLA$_{24}$, adopted from Table S1. [f]Crystallization temperature (T_c). [g]Lamellar thickness, nm, calculated based on $d = 2\pi/q^*$. [h] Melting temperature (°C) and [i] heat of fusion (J/g), determined with DSC.

Table S5-1. Molecular Characterization of Asymmetrically Dispersed *o*LLA Samples (*x* = 19).

Sample[a]	M_n [b]	Đ		T_c = 80 °C [e]		
				d [f]	T_m [g]	ΔH_m [h]
oLLA$_{19}$(**-3**)	1450	1.008 [c]	1.001 [d]	6.32	93.1	44.2
oLLA$_{19}$(**-2**)	1460	1.010	1.005	6.37	93.8	45.4
oLLA$_{19}$(**-1**)	1470	1.011	1.005	6.44	94.3	43.6
oLLA$_{19}$(**0**)	1570	1.012	1.005	6.77	105.1	54.3
oLLA$_{19}$(**+1**)	1660	1.010	1.004	7.17	109.4	55.8
oLLA$_{19}$(**+2**)	1680	1.007	1.002	7.25	111.1	51.0
oLLA$_{19}$(**+3**)	1690	1.007	1.002	7.26	111.3	52.4

[a]Sample label oLLA$_x$(**α**), where *x* refers to the number of repeat units, *α* is the asymmetric parameter. [b]Number average molecular weight (Da) measured by SEC using discrete *o*LLA library as calibration. [c]Dispersity measured by SEC using discrete *o*LLA library as calibration. [d]Dispersity measured by MADLI-ToF. [e]Crystallization temperature (T_c). [f]Lamellar thickness, nm. [g]Melting temperature (°C) and [h]heat of fusion (J/g), determined with DSC.

Table S5-2. Molecular Characterization of Asymmetrically Dispersed *o*LLA Samples (*x* = 24).

Sample[a]	M_n [b]	Đ		T_c = 100 °C [e]		
				d [f]	T_m [g]	ΔH_m [h]
oLLA$_{24}$(**-3**)	1780	1.008 [c]	1.002 [d]	7.67	116.9	60.6
oLLA$_{24}$(**-2**)	1790	1.008	1.004	7.69	116.7	56.4
oLLA$_{24}$(**-1**)	1820	1.010	1.004	7.74	116.9	61.3
oLLA$_{24}$(**0**)	1920	1.011	1.007	8.08	120.3	60.8
oLLA$_{24}$(**+1**)	2020	1.009	1.003	8.45	126.5	71.3
oLLA$_{24}$(**+2**)	2060	1.007	1.003	8.65	127.9	70.5
oLLA$_{24}$(**+3**)	2140	1.007	1.002	8.96	130.8	69.6

[a]Sample label oLLA$_x$(**α**), where *x* refers to the number of repeat units, *α* is the asymmetric parameter. [b]Number average molecular weight (Da) measured by SEC using discrete *o*LLA library as calibration. [c]Dispersity measured by SEC using discrete *o*LLA library as calibration. [d]Dispersity measured by MADLI-ToF. [e]Crystallization temperature (T_c). [f]Lamellar thickness, nm. [g]Melting temperature (°C) and [h]heat of fusion (J/g), determined with DSC.

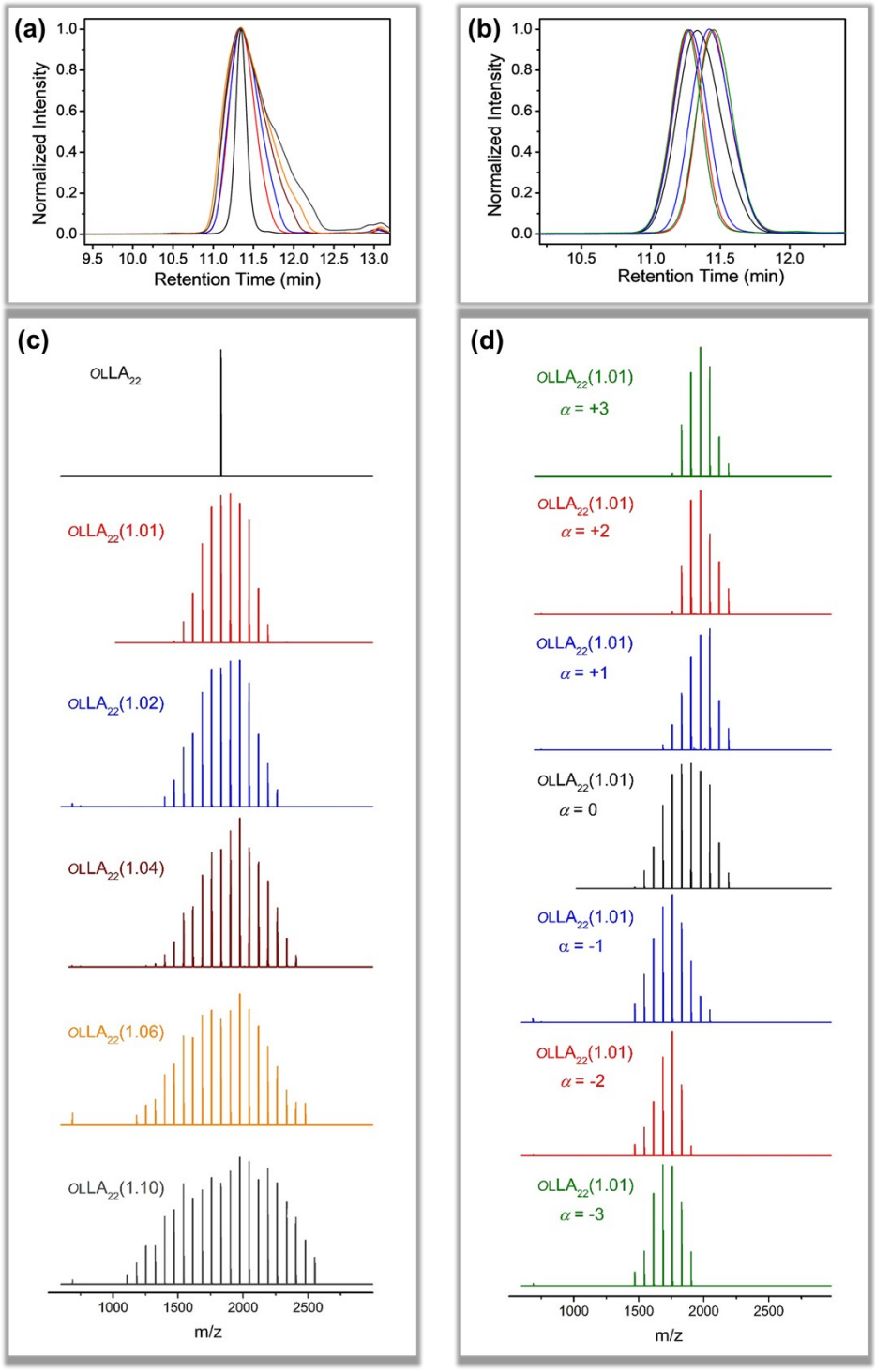


Fig. S8. SEC traces (a, b) and corresponding MALDI-ToF mass spectra (c, d) of symmetrically (a, c) and asymmetrically (b, d) dispersed *o*LLA$_{22}$ series samples (Table 1 and Table 2).

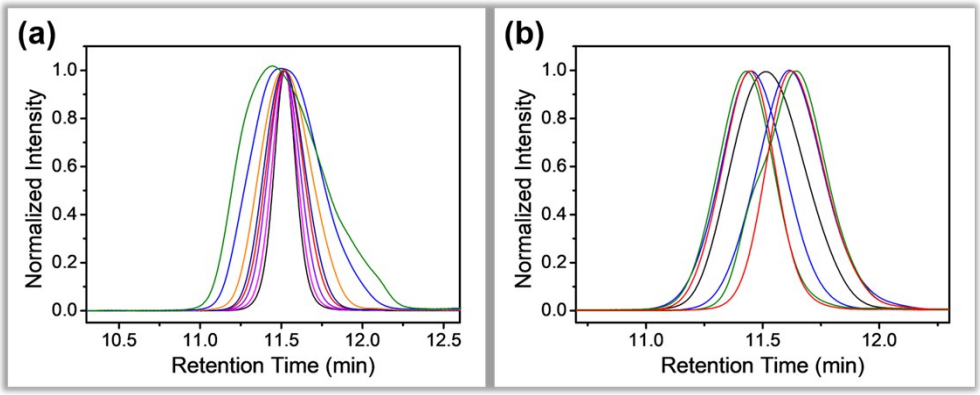


Fig. S9. SEC traces of symmetrically (a) and asymmetrically (b) dispersed *o*LLA$_{19}$ series samples.

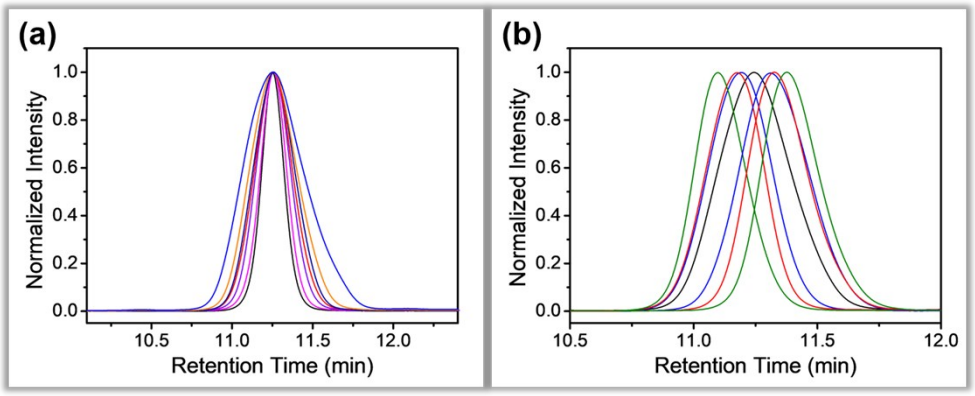


Fig. S10. SEC traces of symmetrically (a) and asymmetrically (b) dispersed *o*LLA$_{24}$ series samples.

5. Effects of Dispersity Width on Crystallization.

Table S6. T_m^H **and** T_m^L **of Dispersed *o*LA Blends.**

Sample[a]	T_{mb}^H	T_{mc}^L	Sample	T_m^H	T_m^L	Sample	T_m^H	T_m^L
*o*LA$_{19}$(1.001)	111.1	105.1	*o*LA$_{22}$(1.001)	123.9	111.1	*o*LA$_{24}$(1.001)	131.2	119.7
*o*LA$_{19}$(1.003)	116.8	97.7	*o*LA$_{22}$(1.003)	127.4	109.0	*o*LA$_{24}$(1.003)	134.1	116.8
*o*LA$_{19}$(1.005)	119.7	92.4	*o*LA$_{22}$(1.005)	127.4	109.0	*o*LA$_{24}$(1.005)	135.5	111.1
*o*LA$_{19}$(1.007)	122.0	87.2	*o*LA$_{22}$(1.007)	131.2	105.1	*o*LA$_{24}$(1.007)	135.5	111.1
*o*LA$_{19}$(1.01)	122.0	87.2	*o*LA$_{22}$(1.01)	131.2	105.1	*o*LA$_{24}$(1.01)	136.6	109.0
*o*LA$_{19}$(1.02)	123.9	83.7	*o*LA$_{22}$(1.02)	135.5	92.4	*o*LA$_{24}$(1.02)	139.1	105.1
*o*LA$_{19}$(1.04)	131.2	63.5	*o*LA$_{22}$(1.04)	139.1	83.7	*o*LA$_{24}$(1.04)	143.3	92.4
*o*LA$_{19}$(1.06)	131.2	63.5	*o*LA$_{22}$(1.06)	139.1	83.7	*o*LA$_{24}$(1.06)	--	--
*o*LA$_{19}$(1.10)	131.2	63.5	*o*LA$_{22}$(1.10)	139.1	83.7	*o*LA$_{24}$(1.10)	--	--

[a]Sample label *o*LA$_x$(*Đ*), where *x* refers to the number of repeat units, *Đ* is the dispersity. [b]Melting temperature (°C) of the longest component. [c]Melting temperature (°C) of the shortest component.

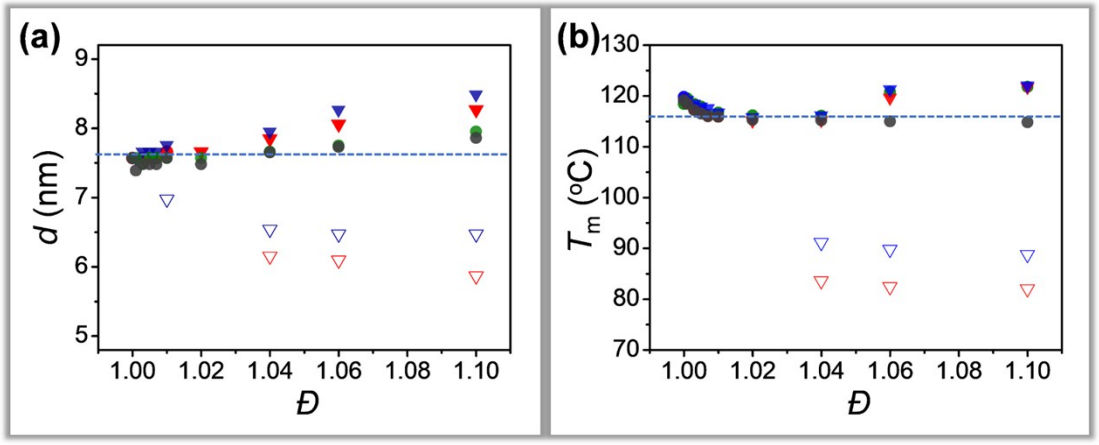


Fig. S11. The relationship between lamellar thickness (*d*) and *Đ* (a), and between melting temperature (T_m) and *Đ* (b) for *o*LA$_{22}$ series samples crystallized at 60 °C (grey), 80 °C (olive), 100 °C (red), and 110 °C (blue): solid circles (region I), triangles (region II).

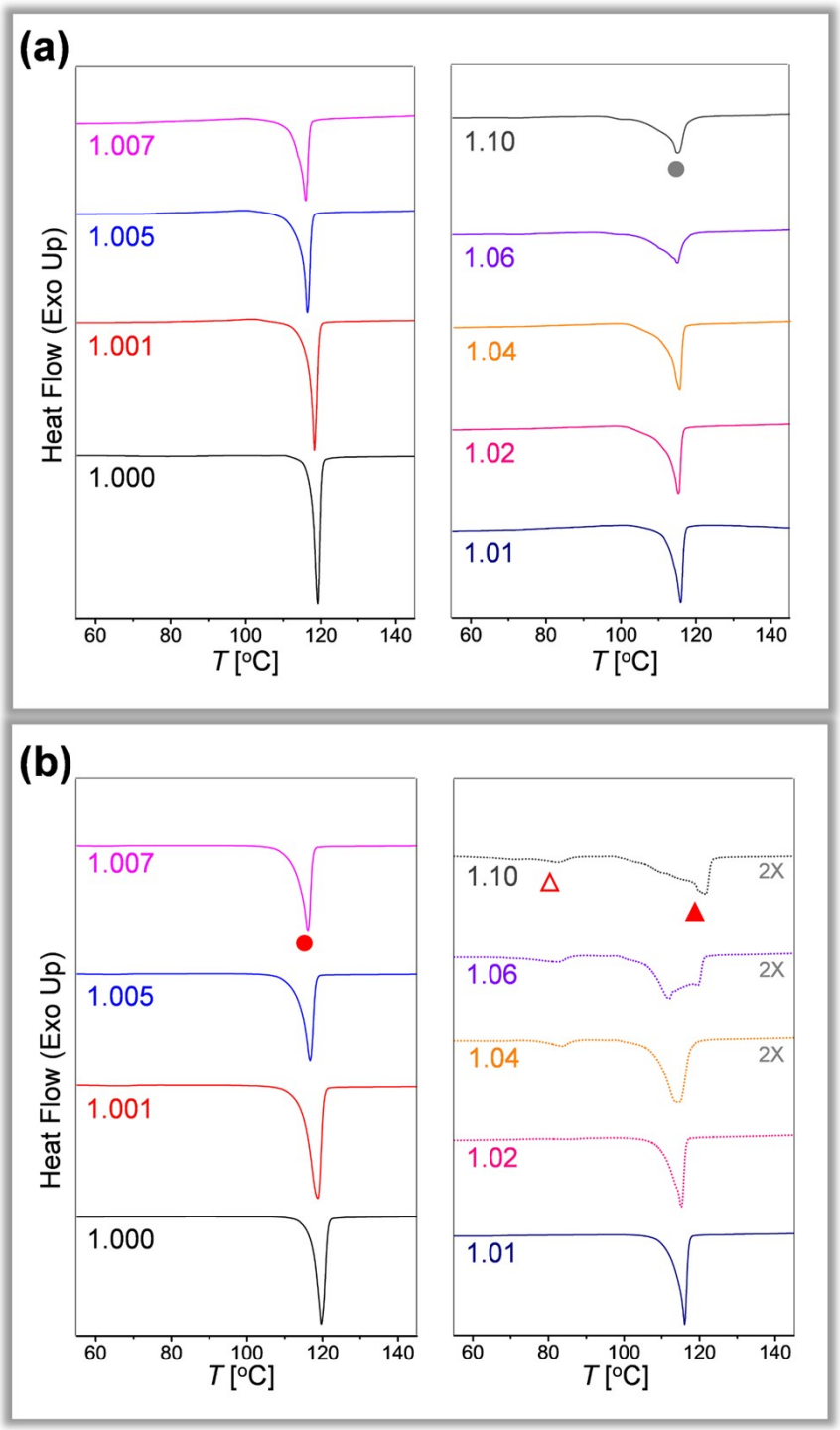


Fig. S12. DSC thermograms of symmetrically dispersed *o*LLA$_{22}$ with varying *Đ* crystallized at 60 °C (a) and 100 °C (b): solid line (region I), dash line (region II).

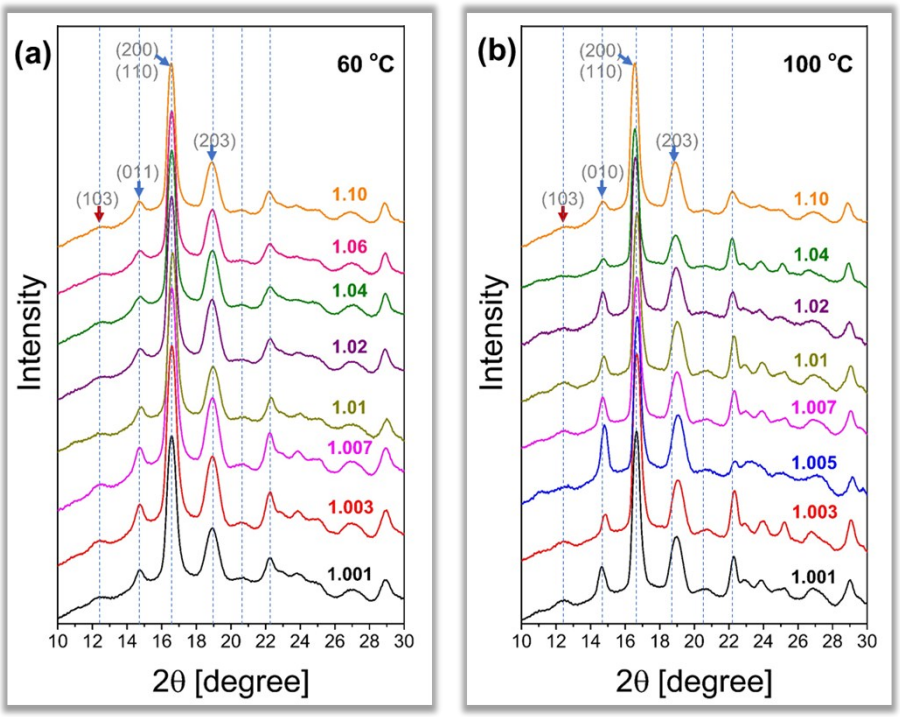


Fig. S13. WAXD patterns of symmetrically dispersed *o*LLA$_{22}$ samples (Table 1) crystallized at 60 °C (a) and 100 °C (b).

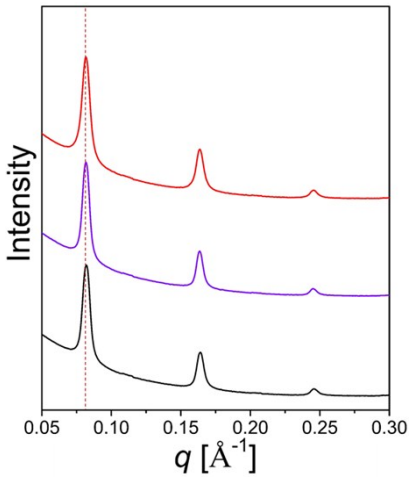


Fig. S14. SAXS patterns of *o*LLA $_{22}$(1.01) crystallized at 60 °C (black), and subsequently annealed at 80 °C (violet) and 90 °C (red).

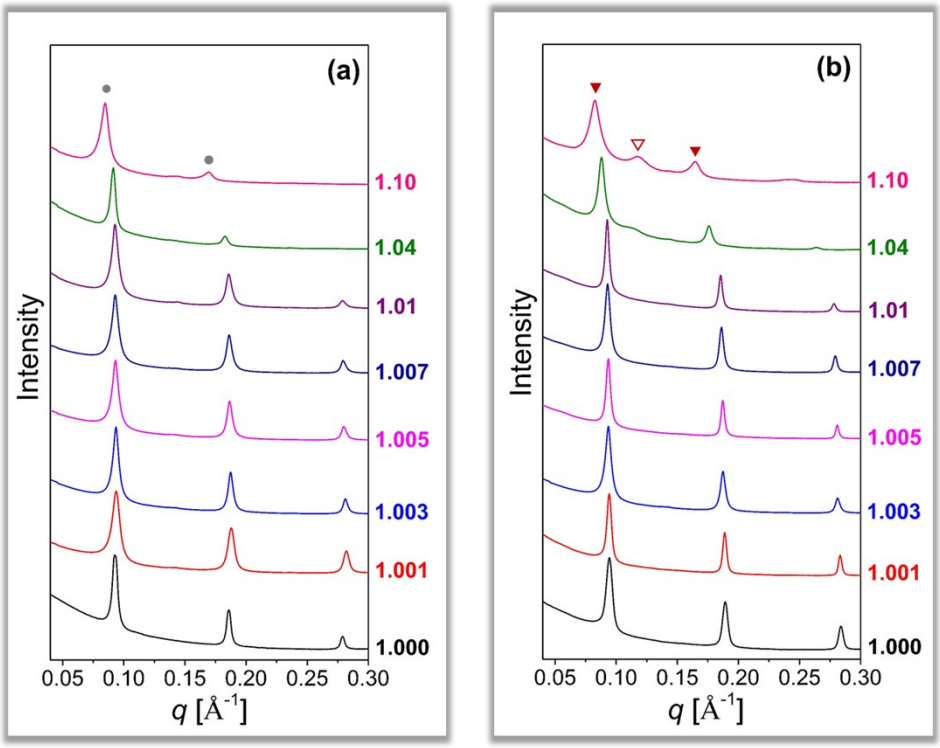


Fig. S15. SAXS patterns of *o*LLA$_{19}$ series with varying *Đ* crystallized at 60 (a) and 80 °C (b).

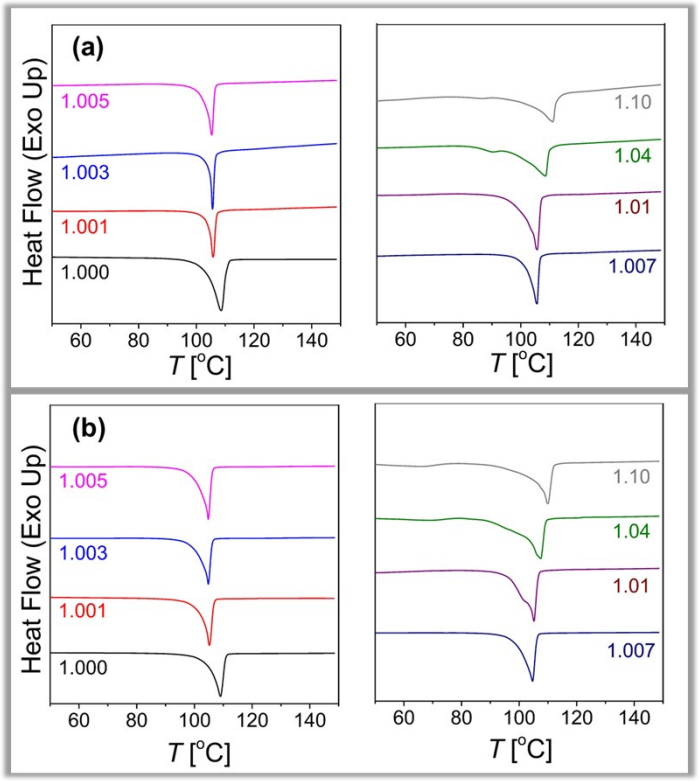


Fig. S16. DSC thermograms of symmetrically dispersed *o*LLA$_{19}$ with varying *Đ* crystallized at 60 °C (a) and 80 °C (b), respectively.

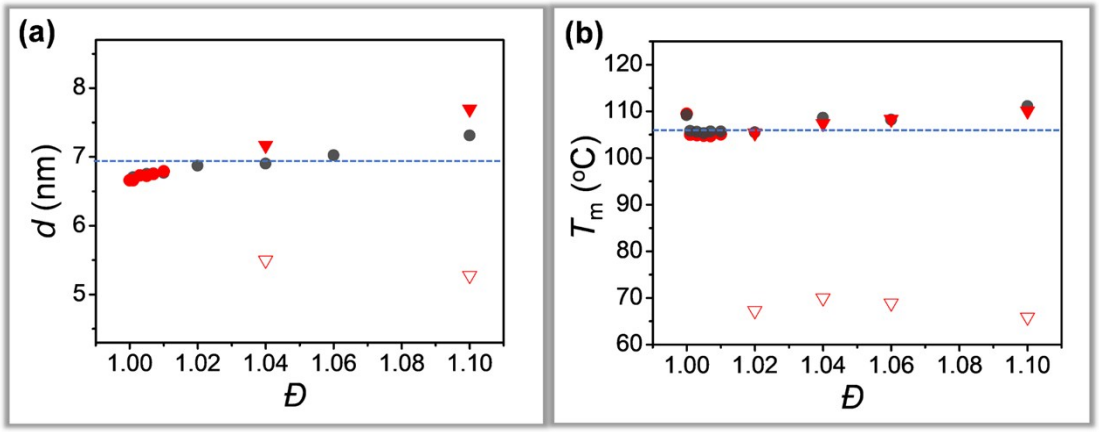


Fig.S17. The relationship between lamellar thickness (*d*) and *Đ* (a), and between melting temperature (T_m) and *Đ* (b) for *o*LLA $_{19}$ series samples crystallized at T_c = 60 °C (grey) and 80 °C (red): solid circles (region I), triangles (region II). See Table S4-1.

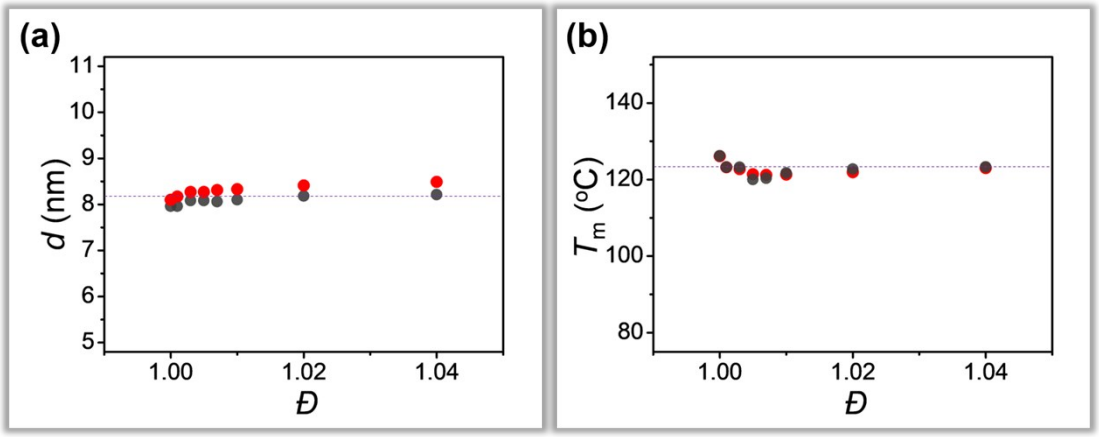


Fig. S18. The relationship between lamellar thickness (*d*) and *Đ* (a), and between melting temperature (T_m) and *Đ* (b) for *o*LLA$_{24}$ series samples crystallized at T_c = 60 °C (grey) and 100 °C (red). See Table S4-2.

6. Effects of Dispersity Symmetry on Crystallization.

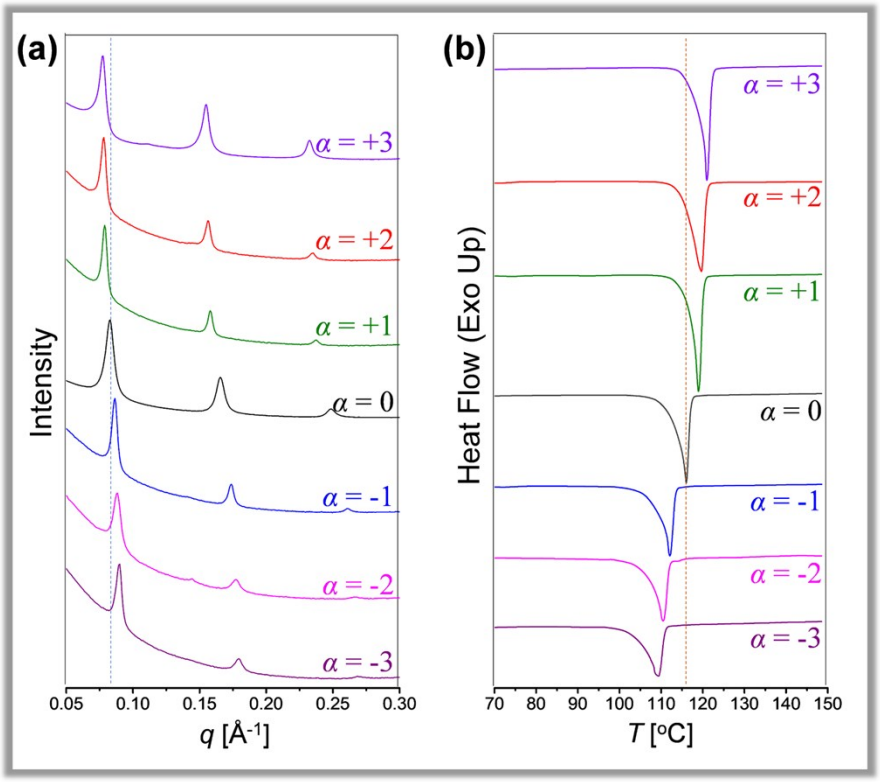


Fig. S19. SAXS patterns (a) and DSC thermograms (b) of asymmetrically dispersed *o*LLA$_{22}$ samples with varying α (see Table 2).

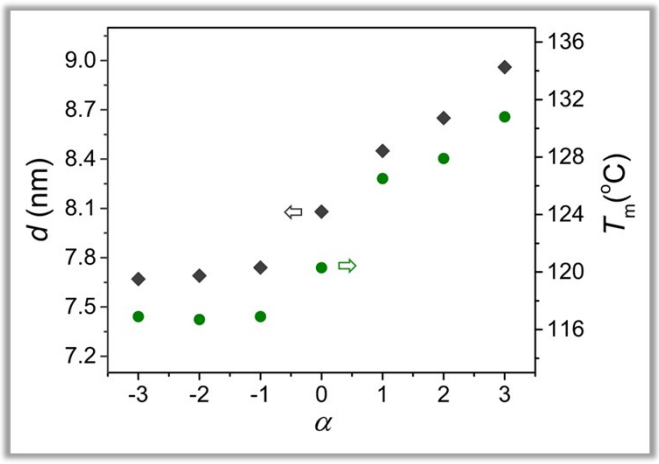


Fig. S20. The plot of lamellar thickness (d, grey) and melting temperature (T_m, olive) of asymmetrically dispersed *o*LLA$_{19}$ samples as a function of α.

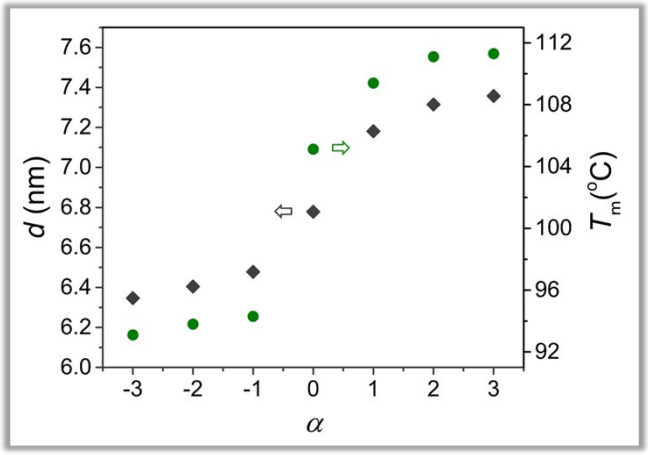


Fig. S21. The plot of lamellar thickness (*d*, grey) and melting temperature (T_m, olive) of asymmetrically dispersed *o*LLA$_{24}$ samples as a function of *α*.

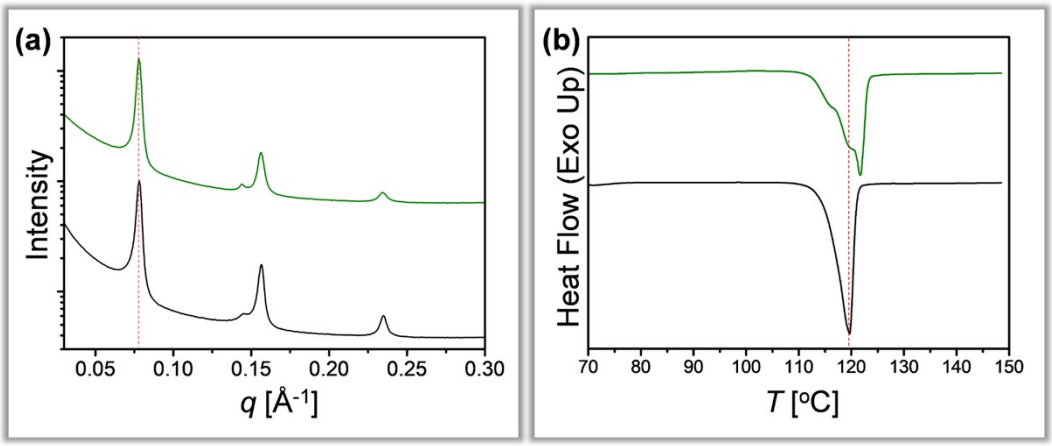


Fig. S22. SAXS patterns (a) and DSC thermograms (b) of asymmetrically dispersed *o*LLA$_{22}$(**+2**) (*Đ* = 1.01, black) and symmetrically dispersed *o*LLA$_{24}$(1.01) (olive) crystallized at 80 °C.

Reference

[1] Zhou, J.; Defante, A. P.; Lin, F.; Xu, Y.; Yu, J.; Gao, Y.; Childers, E.; Dhinojwala, A.; Becker, M. L. *Biomacromolecules* **2015**, *16*, 266-274.