Supplementary Information

Monodisperse amphiphilic double crystalline block oligomers composed of linear alkyl chains and poly(vinyl alcohol) segments prepared by aldol-group transfer polymerization and recycling size-exclusion chromatography

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Experimental Section

Materials

Before use, 1,2-dichlorobenzene (Wako, >98%) was distilled from calcium hydride under reduced pressure. Octadecyl aldehyde (TCI, >95%), $ZnBr_2$ (Aldrich, 99.999%), sodium borohydride (TCI, >95%), hydrochloric acid (Wako, 35–37% in H_2O), butyllithium (TCI, *ca.* 20% in cyclohexane), *tert*-butyldimethylsilyl chloride (KANTO, >98%), and methanol (KANTO, >99.8%, dehydrated) were used as received. *tert*-Butyldimethylsilyl vinyl ether (TBSVE) was synthesized according to methods in the literature.[1,2] Dichloromethane (KANTO, >99.5%; H_2O <0.005%), THF (KANTO, >99.5%; H_2O <0.001%) and toluene (KANTO, >99.5%; H_2O <10 ppm) were dried and deoxygenized by passage through columns of Glass Contour Solvent Systems before use.

Aldol-group transfer polymerization (aldol-GTP)

Aldol-GTP was carried out by the syringe technique under dry nitrogen in a baked glass tube equipped with a three-way stopcock. A typical example of the polymerization procedure is given below. Polymerization was initiated by the addition of $ZnBr_2$ (2.0 mL of 200 mM solution in CH_2Cl_2/diethyl ether = 84/16 (v/v)) via a dry syringe into a monomer solution containing TBSVE (2.0 mL, 10.4 mmol), octadecyl aldehyde (0.56 g, 2.09 mmol), and 1,2-dichlorobenzene (0.63 mL) as an internal standard in CH_2Cl_2 (16.3 mL) at 0 °C. After 15 min, the polymerization was terminated with 10% triethylamine in CH_2Cl_2. The monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR with 1,2-dichlorobenzene as an internal standard (83%). The quenched reaction mixture was diluted with toluene, washed with distilled water to remove residual catalyst, evaporated to dryness under reduced pressure, and vacuum-dried to produce the oligomer ($M_n = 1300$, $Đ = 1.13$).

Reduction of the terminal aldehyde unit

Reduction of the terminal aldehyde unit of oligo(TBSVE) was carried out by the syringe technique under dry nitrogen in a round-bottom flask with a three-way stopcock. A typical example is given below. $NaBH_4$ (11 mg, 2 eq to the silyl unit), methanol (2.0 mL), and THF (8.0 mL) were added to fractionated oligo(TBSVE) (5 mer, 0.15 g), and the mixture was stirred for 2 h at 0 °C. The reaction mixture was diluted with CH_2Cl_2, washed with 1 M HCl aq., distilled water, and brine, evaporated to dryness under reduced pressure, and vacuum-dried to produce the product oligo(TBSVE) with a terminal alcohol unit (75 mg, 48% yield).

Deprotection of the silyl group

Deprotection of the TBS group of oligo(TBSVE) was carried out by the syringe technique under dry nitrogen in a round-bottom flask with a three-way stopcock. A typical example is given below. Aqueous HCl (~12 M, 0.049 mL) and THF (0.98 mL) were added to oligo(TBSVE) with a terminal alcohol unit (5 mer, 75 mg), and the mixture was stirred for 24 h at r.t. The reaction mixture was precipitated in acetonitrile, and the precipitate was vacuum-dried to give the product oligo(vinyl alcohol) (18 mg, 51% yield).

Measurements

^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECS-400 spectrometer operating at 400 MHz. The number-average molecular weight (M_n) and the molecular weight distribution ($Đ$) of the product oligo(TBSVE)s were determined using size-exclusion chromatography (SEC) in THF at 40 °C with two polystyrene gel columns (TSKgel MultiporeH$_{XL}$-M (7.8 mm i.d. × 30 cm × 2); flow rate of 1.0 mL min^{-1}) connected to a JASCO PU-2080 precision pump and a JASCO RI-2031 detector. The columns were calibrated against 10 standard polystyrene samples (Agilent Technologies; M_p = 580–3022000, $Đ$ = 1.02–1.23). Recycling preparative SEC was performed with a JAI LC-5060 liquid chromatograph equipped with JAI UV800LA UV and RI-700 LA detectors using JAIGEL-2HR (60 cm × 2.0 cm i.d.) × 2 columns and $CHCl_3$ as the eluent at room temperature. MALDI-TOF-MS was performed with a Bruker Autoflex Max system (linear mode) with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2- propenylidene]malononitrile (DCTB) as the ionizing matrix and sodium trifluoroacetate as the ion source. The glass transition temperatures (T_g: midpoint of the transition) of the polymers were recorded using a DSC250 differential scanning calorimeter (TA Instrument Inc.). Certified indium and sapphire were used for temperature and heat flow calibration. The samples were initially heated to 170 °C at 10 °C/min, equilibrated at this temperature for 5 min, and then cooled to –90 °C at 5 °C/min. After being held at this temperature for 5 min, the samples were reheated to 180 °C at 5 °C/min. All T_g values were obtained from the second scan after the thermal history was removed. Thermogravimetric analysis (TGA) was performed on a Q500 system (TA Instruments Inc.) at 5 °C/min under nitrogen gas flow.

Optical microscopy (OM)

For OM imaging, a 1 wt.% solution of oligomers in hexafluoroisopropanol was spin coated at 3000 rpm on 2 cm^2 glass coverslips (also used for the AFM analysis) previously cleaned in tetrahydrofuran, ethanol, and acetone for 10 minutes each. Morphological changes upon heating were observed using an Olympus BX51 optical microscope coupled with a Linkam LTS350 heating plate controlled by a Linkam TMS94 controller. Images were collected with a Sony Exwave HAD CCD camera interfaced with Pinnacle Studio version 9 software. The samples were heated from room temperature to 170 °C at a heating rate of 5 °C/min and then cooled to room temperature at the same rate.

Atomic force microscopy (AFM)

AFM imaging was performed in air at room temperature in tapping mode using a Bruker AFM Dimension Icon using Tespa-V2 cantilevers (resonance frequency of 320 kHz, spring constant of 37

N m^{-1}) with a nominal tip radius of 7 nm. All AFM images were 512×512 pixels in size. The samples were prepared according to the OM procedure.

Small-angle X-ray scattering (SAXS)

SAXS experiments were performed on a Xeuss- Xenocs X-ray scattering setup. The two-dimensional SAXS patterns were recorded using a high-sensitivity low-noise 2D detection (Pilatus 300K) at a distance of 368 mm from the sample, perpendicular to the X-ray parallel beam ($Cu_{K\alpha}$ radiation, λ = 0.15406 nm^{-1}). SAXS profiles were obtained after azimuthal integration of the 2D SAXS pattern. SAXS data were then reduced by performing necessary corrections (empty capillary subtraction, q-calibration, and intensity normalization). The resulting SAXS intensities are expressed in cm^{-1} versus q, the magnitude of the scattering vector is defined as $q = 4\pi.\sin\theta/\lambda$, where θ is the scattering angle.

Wide-angle X-ray scattering (WAXS)

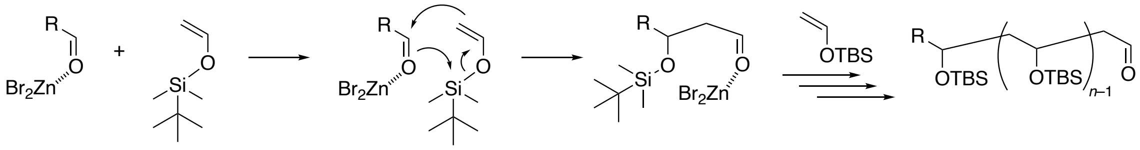
The crystalline structure of the samples was characterized by X-ray diffraction using a Thermo Electron ARL'XTRA diffractometer in Debye-Scherrer mode goniometer. Powder samples were placed in Mark glass capillaries (0.5 mm internal diameter from Hilgenberg, Germany) rotating at 30 rpm. The device was equipped with a linear Si(Li) solid detector (LYNXEYE XE-T) that filtered the $Cu_{K\alpha}$ radiation ($\lambda Cu_{K\alpha}$ = 1.5418 Å) of a standard European type X-ray tube (40 kV, 40 mA). XRD patterns were collected from 2° to 75° 2θ at a scan rate of 0.02° 2θ/s with a step size of 0.02° 2θ.

References

1 M. E. Jung and R. B. Blum, *Tetrahedron Lett.* 1977, **43**, 3791–3794.

2 L. Schreyer, P. S. J. Kaib, V. N. Wakchaure, C. Obradors, R. Properzi, S. Lee and B. List, *Science* 2011, **362**, 216–219.

Scheme S1 Reaction mechanism of aldol-GTP of TBSVE with RCHO as an initiator and $ZnBr_2$ as an activator.



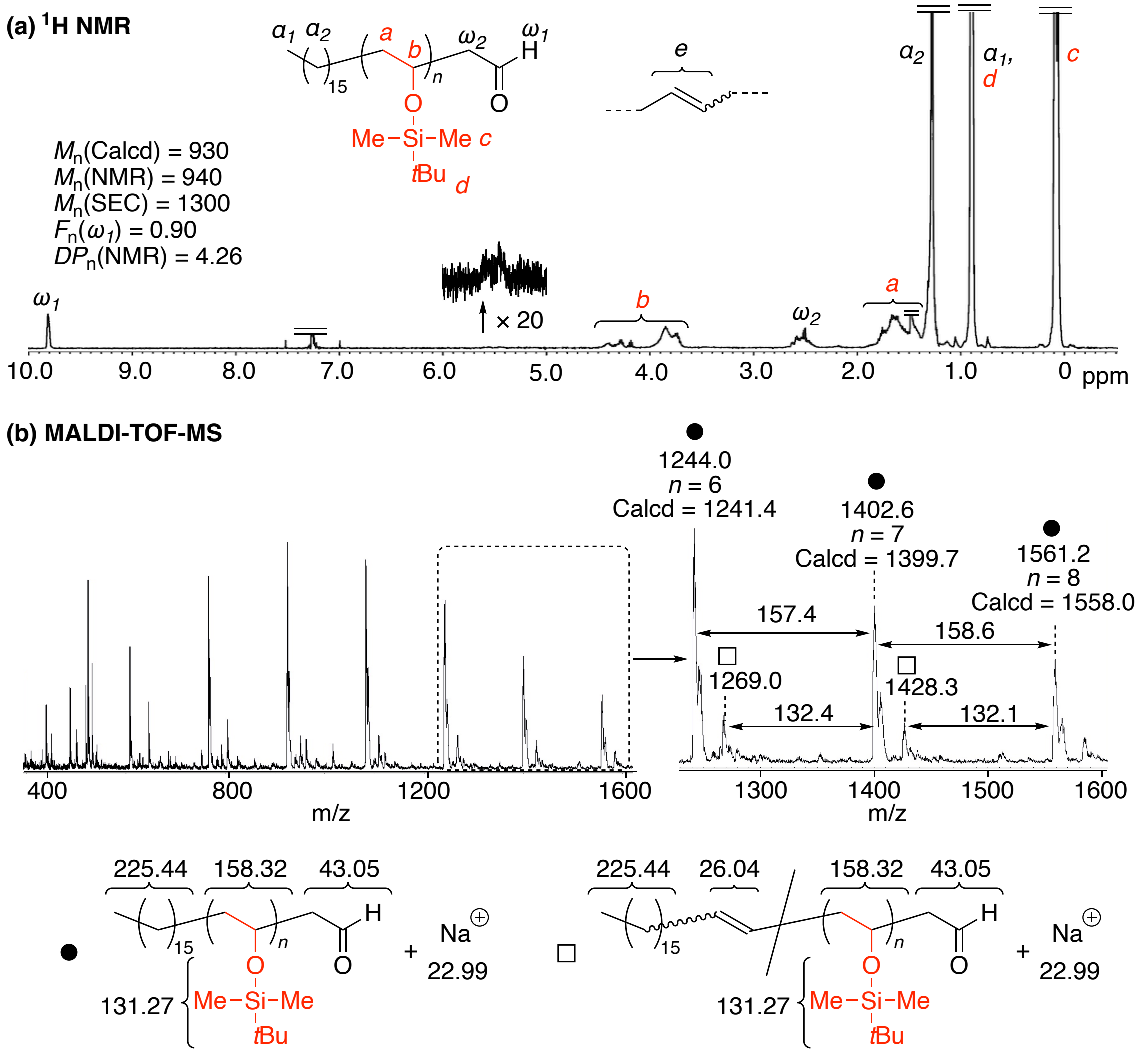


Fig. S1 (a) ^{1}H NMR and (b) MALDI-TOF-MS spectra of oligo(TBSVE) obtained by aldol-GTP of TBSVE.

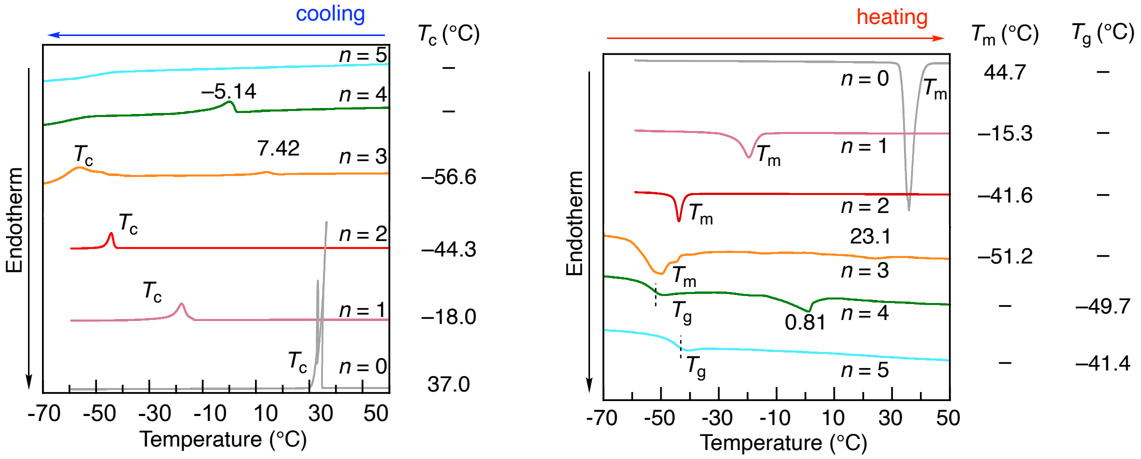


Fig. S2 DSC thermograms of monodisperse purified oligo(TBSVE)s bearing 1 to 5 TBSVE units (n = 1–5) and octadecyl aldehyde (n = 0).

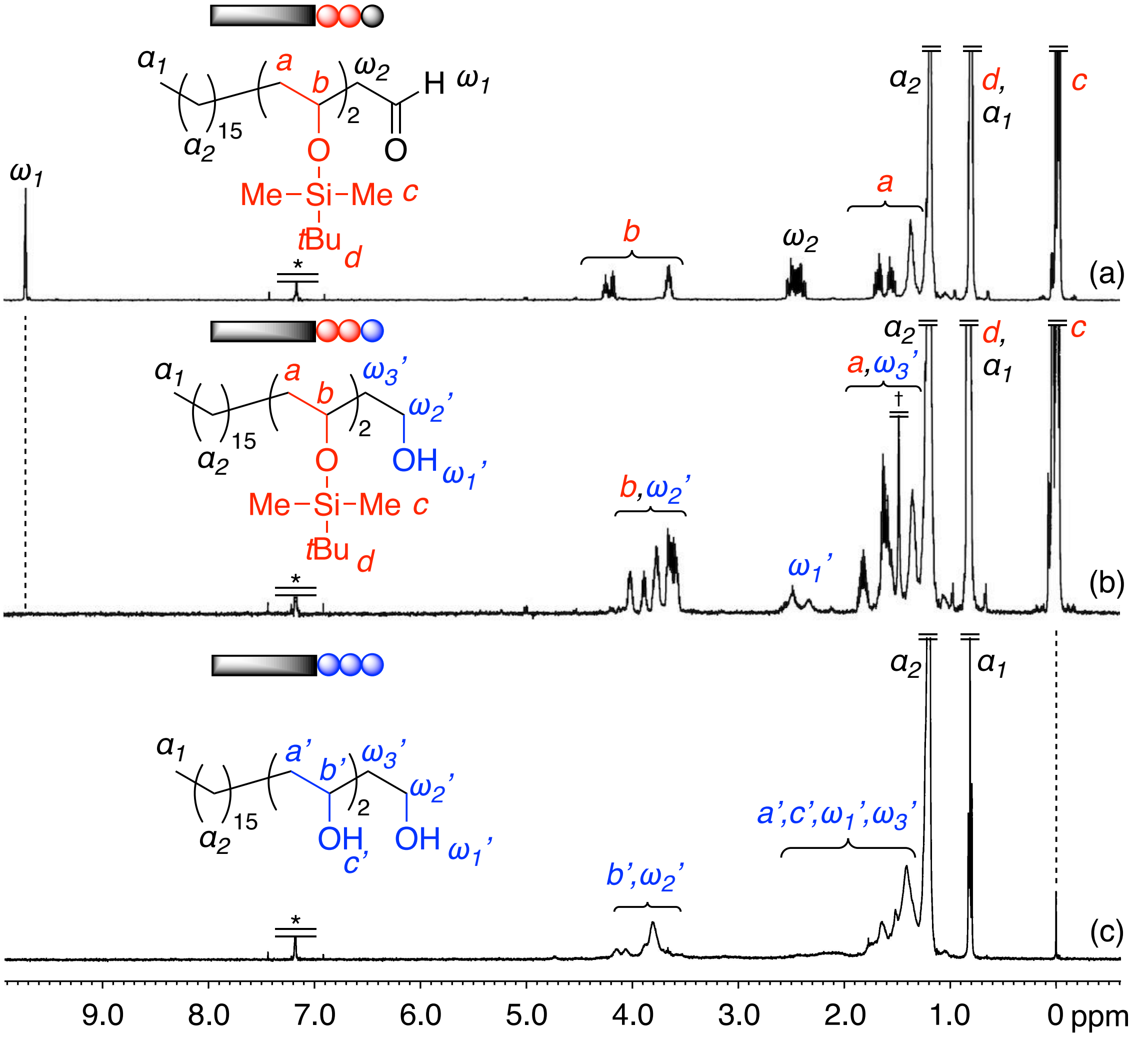


Fig. S3 ^{1}H NMR spectra of the original oligomer (n = 2) (a) and the oligomer obtained after reduction (b) and deprotection (c) ($CDCl_3$ at 55 °C). *$CHCl_3$ and †water.

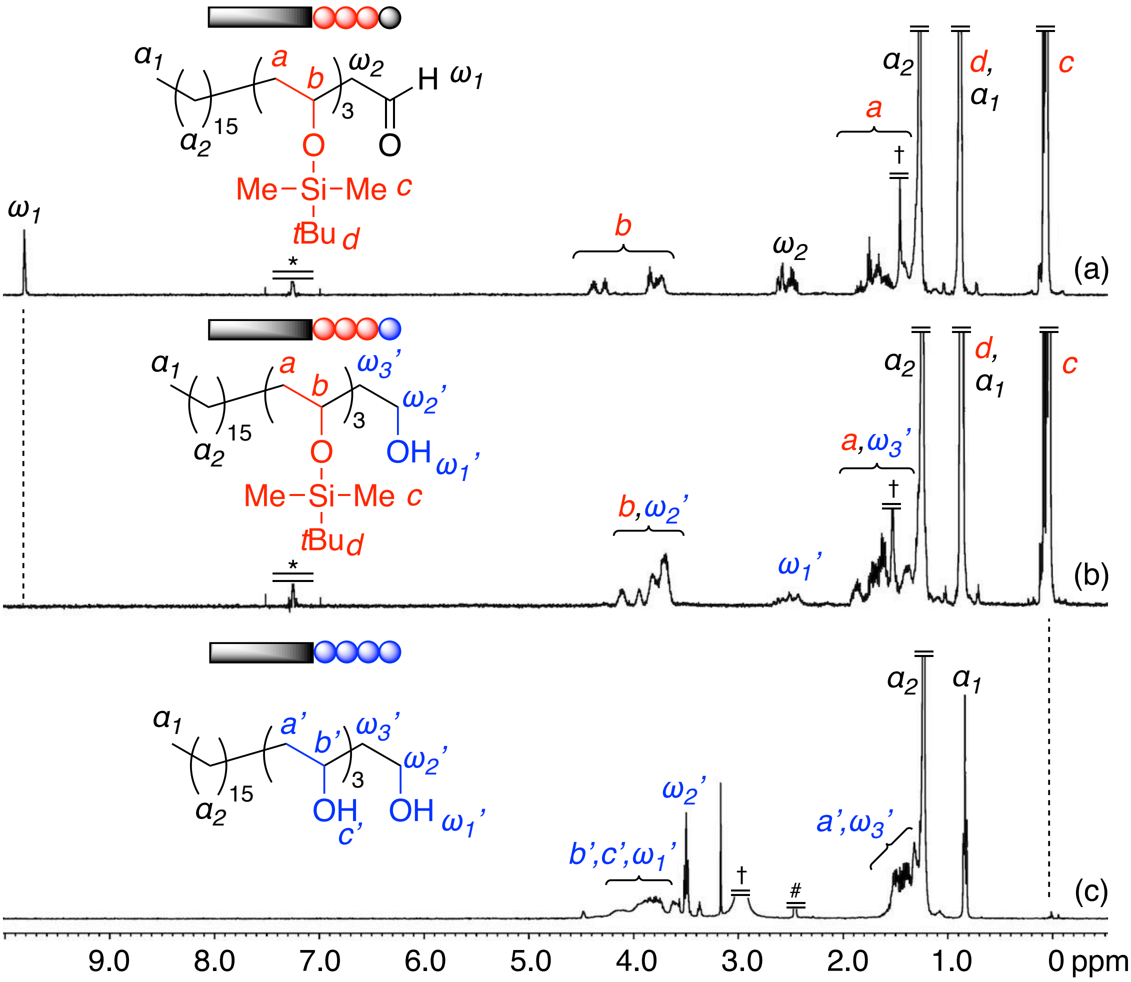


Fig. S4 ^{1}H NMR spectra of the original oligomer ($n = 3$) (a) and the oligomer obtained after reduction (b) and deprotection (c) ($CDCl_3$ at 55 °C for a and b, DMSO-d_6 at 100 °C for c). *$CHCl_3$, †water, and $^\#$DMSO.

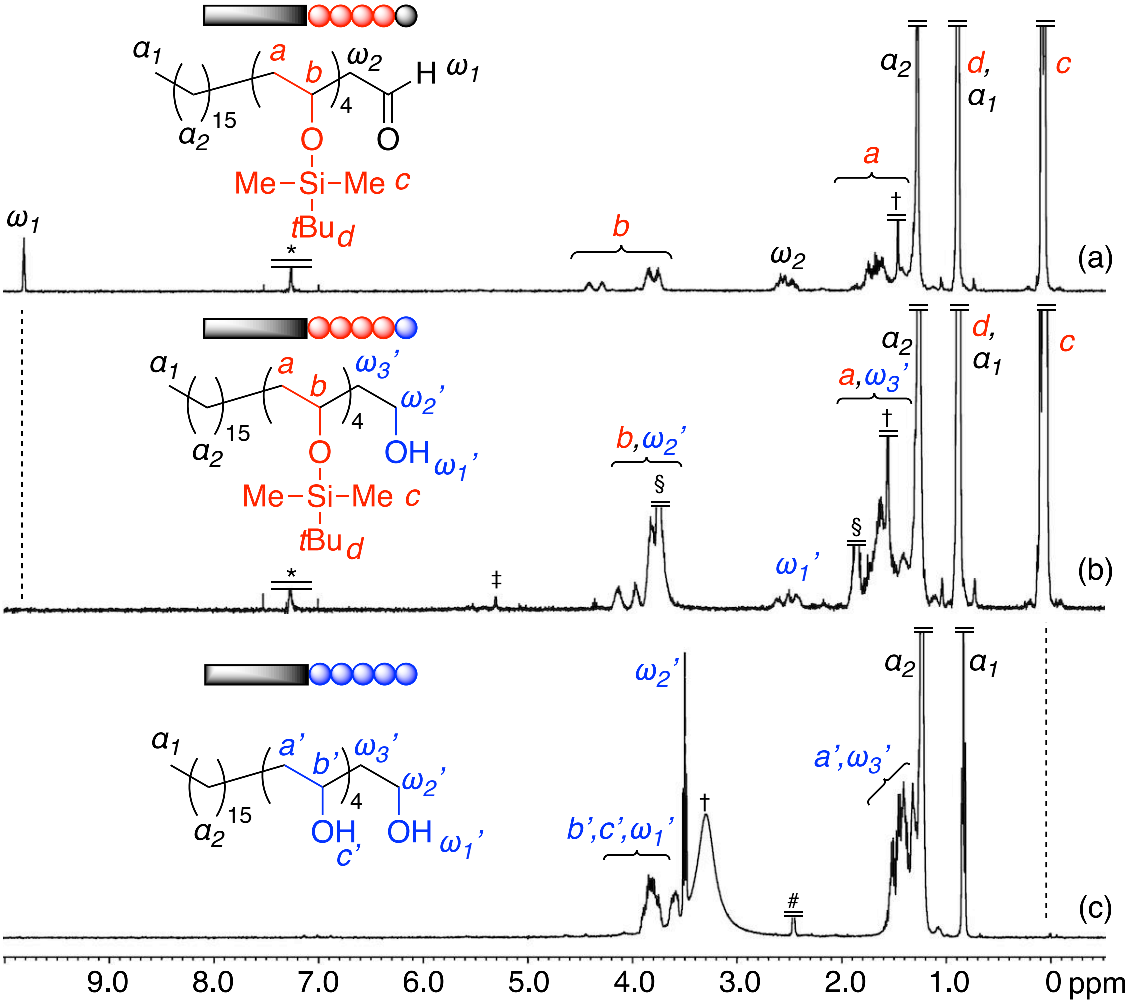


Fig. S5 ^{1}H NMR spectra of the original oligomer ($n = 4$) (a) and the oligomer obtained after reduction (b) and deprotection (c) (CDCl$_3$ at 55 °C for a and b, DMSO-d_6 at 100 °C for c). *CHCl$_3$, †water, ‡CH$_2$Cl$_2$, §THF, and $^\#$DMSO.

Table S1 Solubility of oligo(vinyl alcohol)s with C16 alkyl chain at 1wt%.

	Toluene	Chloroform	THF	Acetone	MeOH	DMSO	Water	HFIP
$n = 1$	✓✓	✓✓	✓✓	×	×	—	—	—
$n = 2$	✓✓	✓✓	✓✓	✓	✓	—	—	—
$n = 3$	✓✓	✓✓	✓✓	✓✓	✓✓	—	—	—
$n = 4$	×	×	✓	✓	✓	✓[a]	×	✓✓
$n = 5$	×	×	×	×	×	✓[a]	×	✓✓

✓✓: soluble at r.t., ✓: soluble at elevated temperature, ×: insoluble

[a] Examined at 0.1 wt%

Table S2 Position of the crystallisation and melting temperature (T_m and T_c) of the alkyl chains (1) and VA segments (2) for the purifies oligomers with increased number of the original TBSVE units (n = 1 to 5) and as well as 1-dodecanol (n = 0) and the unseparated products (n = 2.9).

Entry	T_{c1}(°C)	T_{m1}(°C)	T_{c2}(°C)	T_{m2}(°C)
▬ n = 2.9	64.3	71.9	64.3	71.9
▬ n = 5	48.6	54.2	106.3	112.1
▬ n = 4	48.2	53.3	95.1	100.2
▬ n = 3	54.6	57.0	81.2	84.9
▬ n = 2	56.4	62.8	40.4	45.9
▬ n = 1	65.4	71.6	65.4	71.6
▬ n = 0	55.0	58.9	55.0	58.9

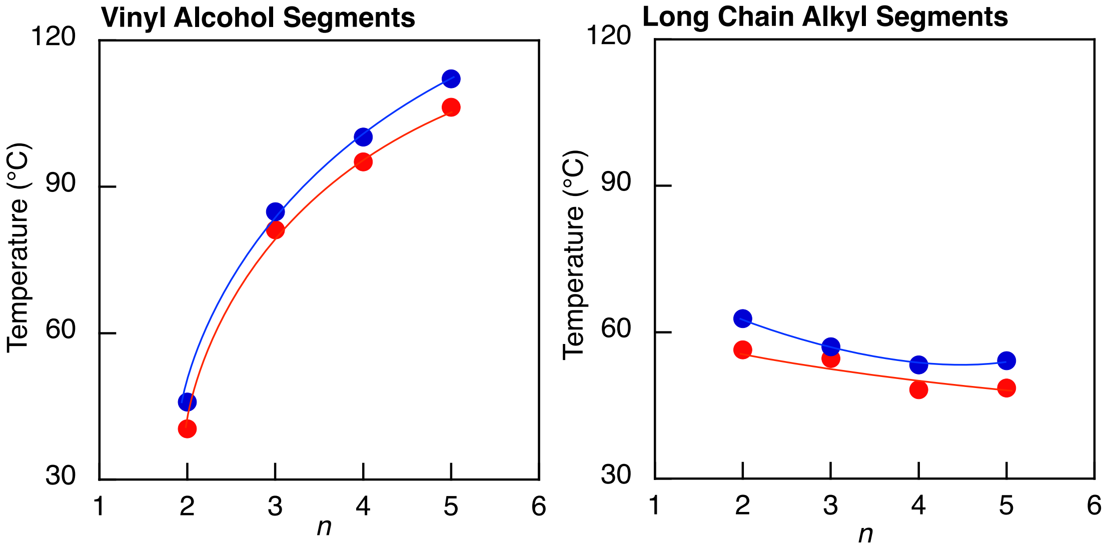


Fig. S6 Evolution of the T_c (red) and T_m (blue) for the vinyl alcohol segments (left) and alkyl chains segments.

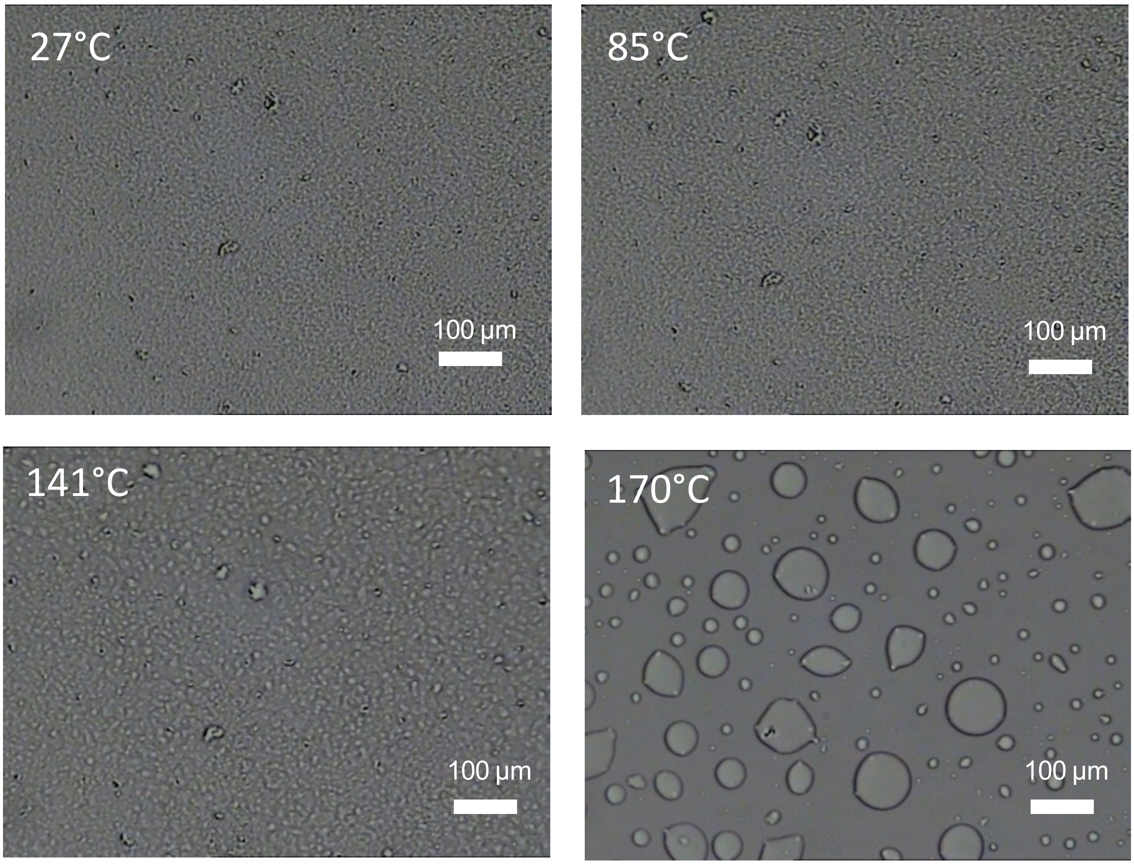


Fig. S7 Optical microscopy micrograph of oligomers bearing 5 VA units showing flowing for T > TODT.

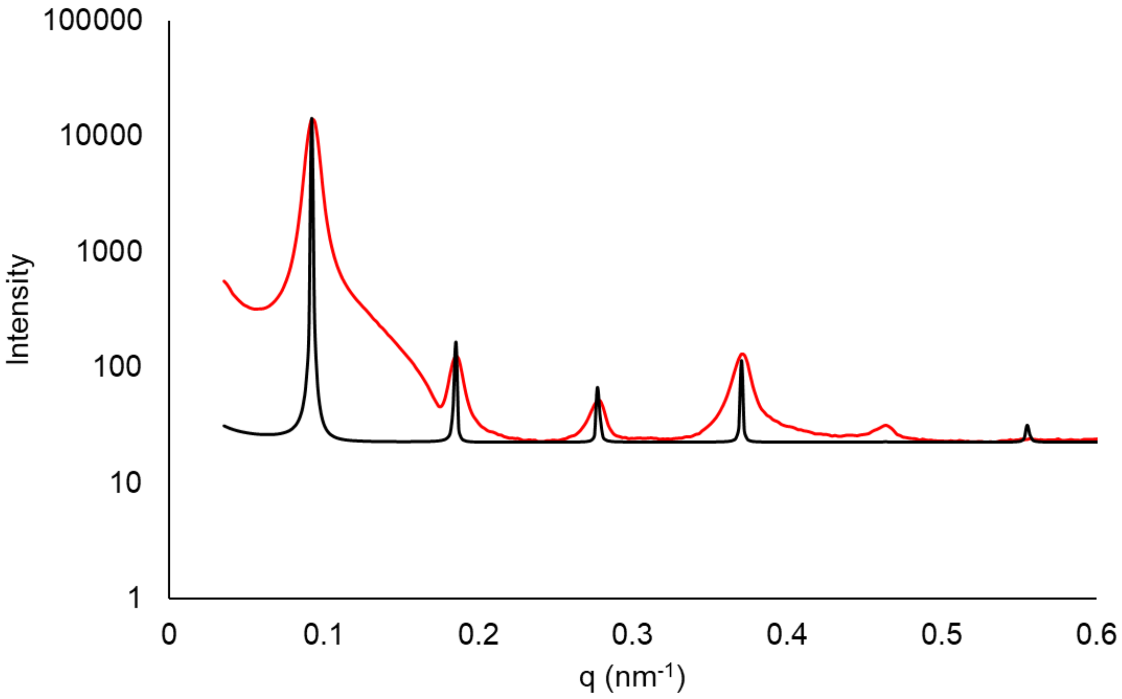


Fig. S8 Experimental (red) and simulated (black) SAXS profile. The SAXS profile was simulated using the scattering model of a lamellar paracrystal available on Irena analysis toolbox (1) for small angle scattering data, compatible with Igor Pro software (Wavemetrics, Inc.) The position and relative intensities of maxima visible on the SAXS profile were obtained with a model composed of 2.7 nm thick infinite lamella, stacked with a repeating distance of 6.8 nm. Additional scattering at small angles and larger peak in the experimental profile width can be explained by the presence of lamellar with finite length and limited number of stackings. Distorted lamellae and/or non-crystalline domains bringing disorder in the system may also account for such behaviour.
https://usaxs.xray.aps.anl.gov/software/irena

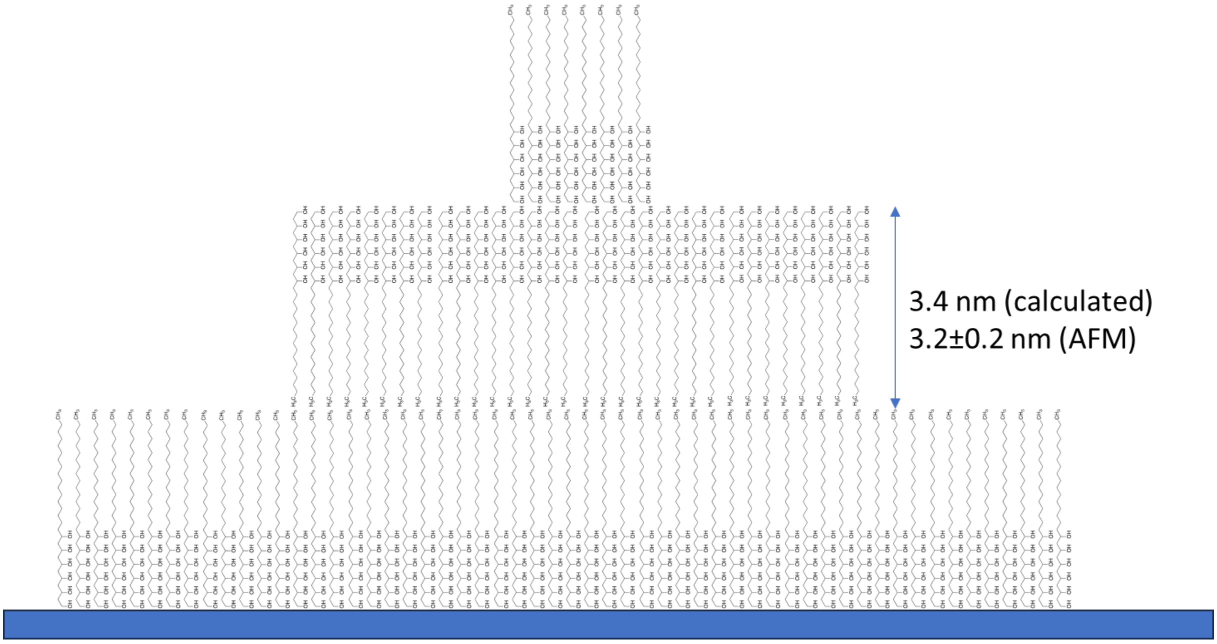


Fig. S9 Proposed model of the surface morphology resulting from the vertical self-assembly of oligomers (here with *n* = 5 VA units), in good agreement with the formation of flat stacked terraces observed by AFM.