Supporting Information for:

Order-Disorder Transition in Supramolecular Polymer Combs/Brushes with Polymeric Side Chains

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1. Experimental Section

1.1. Materials.

Sodium ascorbate, copper (II) sulfate pentahydrate, *n*-butyl acrylate, 2-hydroxyethyl acrylate (HEA) , 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid 3-azido-1-propanol ester, 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanol, dibutyl tin dilaurate (DBTDL), *N*,*N*-dimethylformamide (anhydrous, DMF), hexamethyl diisocyanate (HDI) and *S*,*S*-Dibenzyl trithiocarbonate (DBTTC) were purchased from Aldrich. **T** (90 kg mol^{-1})[1], propargyl-DAT **5**[2], propargyl-UPy **1**[3] and Amino-1,8-naphthyridin-2(1H)-one[4] were synthesized by previously published methods. *α*,*α*′-azobis-(isobutyronitrile) (AIBN, Fluka, 99%) was recrystallized from methanol. Dichloromethane (DCM), methanol, hexane, chloroform (anhydrous) were purchased from Alfa Aesar.

1.2. Characterization

^{1}H (^{13}C) NMR spectra were recorded at room temperature on a Varian VXR (^{1}H: 400 MHz; ^{13}C: 100 MHz) spectrometer using deuterated solvents. Chemical shifts (δ) are reported in ppm, whereas the chemical shifts are calibrated to the solvent residual peaks. Gel permeation chromatography (GPC) measurements were performed in THF at 25 ^{o}C (1 mL/min) on a Spectra-Physics AS 1000, equipped with PLGel 5 μm x 30 cm mixed-C columns. Universal calibration was applied using a Viscotek H502 viscometer and a Shodex RI-71 refractive index detector. The GPC was calibrated using narrow disperse polystyrene standards (Polymer Laboratories).

Differential scanning calorimetry (DSC) measurements were done on a TA Instruments Q1000. The samples were heated from room temperature to 60 °C and kept there for 10 min to remove the thermal history. Then, they were cooled down to −70 °C with a rate of 5 °C min^{-1}, equilibrated for 15 min, and heated (10 °C min^{-1}) to 200 °C. The second heating cycle was repeated to check the reproducibility of the data.

Thermogravimetric analysis (TGA) To determine the thermal stability and decomposition behavior measurements were performed on a TA-Instruments D2500. Programmed heating from 30 °C to 700 °C was used at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere.

Variable-temperature FTIR (VT-FTIR) measurements were conducted on a Bruker IFS88 FTIR spectrometer. At each temperature, sample was left 10 min to equilibrate the temperature and then the spectrum was obtained.

DFT: Molecular geometries and hydrogen bonded complexes have been fully optimized using density functional theory (DFT) with the omega B97X-D functional / cc-PVDZ basis set as implemented in Q-Chem and the basis sets were corrected.

SAXS

SAXS experiments were performed at the MINA instrument in Groningen. The MINA instrument is equipped with a rotating Cu anode operating at 45 kV and 60 mA (x-ray wavelength λ = 1.54 Å). SAXS patterns were recorded using Vantec Bruker detectors with a 10min exposure time. The beam size on the sample was 0.25 mm. The sample temperature was controlled using a Linkam TMS600 hot stage. Two different sample-to-detector distances of 24 cm and 200 cm were used to cover an extended angular range. The beam center position at the detector and the exact sample-to-detector position (i.e. the scattering angles) were determined using the diffraction rings from a standard Silver Behenate powder. The data were radially integrated and merged into a single curve using a Matlab code.

Self-assembly:

For the self-assembly studies in solution, mixtures with different compositions of ODIN were prepared. Briefly, 3, 8, 21 mg ODIN was added under nitrogen to UPy solutions (3 mg UPy in 0.6 mL anhydrous $CDCl_3$) in 4 separate batches.

1.3. Synthesis of CTA-UPy **3**:

Synthesis of CTA-UPy **3** was performed under nitrogen atmosphere in a three-necked round bottom flask with an egg-shaped magnetic stirrer. Sodium ascorbate (93 mg, 0.47 mmol), copper (II) sulfate pentahydrate (48 mg, 0.19 mmol), azide functionalized RAFT agent **2** (800 mg, 1.79 mmol) and propargyl-UPy **1** (1g, 2.90 mmol) were added to the reaction flask and the flask was flushed 3 times with nitrogen. Anhydrous DMF (12 mL) was injected to the reaction mixture and was stirred at room temperature. Color of the mixture was changed from greenish brown to yellow after an hour. After three days, the mixture was poured into 150 mL 0.1M HCl and washed three times with DCM. The organic phase was then washed once with 150 mL brine, dried using $MgSO_4$ and the solvent was evaporated. The pure product was obtained using column chromatography (40:1 chloroform/methanol as eluent).

Yield: 62 % R_f = 0.1

^{1}H NMR (400 MHz, Chloroform-*d*) δ: 13.12 (1H, s, H_1), 11.84 (1H, s, H_2), 10.10 (1H, s, H_3), 7.63 (1H, s, H_4), 5.85 (1H, s, H_5), 5.16 (3H, s, H_6), 4.37 (2H, t, J = 7.0 Hz, H_7), 4.11 (2H, t, J = 5.72 Hz, H_8), 3.26 (4H, m, H_9), 3.14 (2H, m, H_{10}), 2.25 (2H, m, H_{11}), 2.22 (3H, s, H_{12}), 1.15-1.74 (33H, m, H_{13}), 0.87 (3H, t, J = 7.0 Hz , H_{14}). ^{13}C NMR (101 MHz, chloroform-*d*): δ: 222.00, 186.66, 172.72, 162.51, 154.49, 152.01, 142.37, 128.37, 109.99, 70.01, 62.34, 55.88, 47.37, 39.47, 36.47, 31.88, 29.60, 29.51, 29.41, 29.31, 29.07, 28.90, 27.83, 26.49, 25.33, 22.66, 19.43, 14.10.

1.4. Synthesis of CTA-DAT **6**:

Synthesis of CTA-DAT **6** was performed in a similar method as **3**. Under nitrogen atmosphere in a three-necked round bottom flask with an egg-shaped magnetic stirrer, sodium ascorbate (57.5 mg, 0.29 mmol), copper (II) sulfate pentahydrate (29.7 mg, 0.12 mmol), azide functionalized RAFT agent **2** (500 mg, 1.12 mmol) and propargyl-DAT **5** (285 mg, 1.12 mmol) were added. The flask was flushed 3 times with nitrogen. Anhydrous DMF (7 mL) was injected to the reaction mixture and was stirred at room temperature. After two days, the mixture was poured into 150 mL 0.1M HCl and washed three times with DCM. The organic phase was then washed once with 150 mL brine, dried using $MgSO_4$ and the solvent was evaporated. The pure product was obtained using column chromatography (95:5 DCM/methanol as eluent).

Yield: 58 % R_f = 0.16

^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.20 (1H, s, $H_{6,}$), 7.17 (2H, d, J = 8.2 Hz, H_3), 6.94 (2H, d, J = 8.2 Hz, H_4), 6.63 (4H, brs, H_1), 5.08 (2H, s, H_5), 4.39 (2H, t, J = 6.8 Hz, H_7), 4.04 (2H, t, J = 5.8 Hz, H_9), 3.55 (2H, s, H_2), 3.29 (2H, t, J = 7.3 Hz, H_{11}), 2.13 (2H, quin, J = 6.3 Hz, H_8), 1.62 (6H, s, H_{10}), 1.57 (2H, quin, J = 7.1 Hz, H_{12}), 1.21 (18H, m, H_{13}), 0.84 (3H, t, J = 6.6 Hz, H_{14}) ^{13}C NMR (101 MHz, chloroform-*d*) δ: 222.04, 193.73, 172.74, 167.08, 162.51, 144.01, 132.04, 130.29, 129.69, 114.83, 71.20, 62.32, 55.90, 37.03, 36.47, 31.88, 29.60, 29.51, 29.41, 29.30, 29.04, 28.88, 27.82, 26.17, 25.32, 22.65, 21.17, 14.10

1.5. RAFT polymerization of *n*-butyl acrylate using CTA-UPy **3** or CTA-DAT **6**:

A typical example of polymerization is as follows: in a schlenk flask with an egg-shaped magnetic stirrer, *n*-butyl acrylate (2.0 g, 15.63 mmol), AIBN (8.2 mg, 0.05 mmol), CTA-DAT **6** (340 mg, 0.5 mmol) and 2 mL anhydrous DMF was added. The reaction flask was closed using a septum and 3 times freeze-pump-thaw cycle was carried out following a nitrogen flush. The

schlenk flask was inserted in a preheated oil bath of 75 °C and stirred for 5 hours. Afterwards, it was quenched by plunging into liquid nitrogen. Then, it was precipitated into methanol/water mixture (90:10) to yield 1.5 g yellowish polymer oil.

D: ^{1}H NMR (400 MHz, Acetone-d_6) δ: 8.07 (1H, s, H_6), 7.22 (2H, d, J = 8.5 Hz, H_3), 6.97 (2H, d, J = 8.5 Hz, H_4), 5.95 (4H, brs, H_1), 5.14 (2H, s, H_5), 4.56 (2H, t, J = 6.9 Hz, H_7), 4.08 (50H, m, $H_{20,9}$), 3.60 (2H, s, H_2), 3.43 (2H, t, J = 7.4 Hz, H_{11}), 2.35 (22H, m, H_{19}), 2.13 (2H, m, H_8), 1.99 – 1.05 (180H, m, $H_{8,10,12,13,16,17,18}$), 0.94 (75H, m, $H_{14,15}$).

Sample	*n*-butyl acrylate g(mmol)	AIBN mg(mmol)	CTA mg(mmol)	DMF mL	Conversion %	Yield g
D3400	2.0(15.63)	8.2(0.05)	340(0.5)	2	87	1.5
D4100	2.0(15.63)	5.6(0.034)	246(0.34)	2	71	1.2
D15600	2.0(15.63)	1.3(0.008)	62(0.08)	2	69	1.3

U: ^{1}H NMR (400 MHz, Acetone-d_6) δ: 12.99 (1H, s, H_1), 11.88 (1H, s, H_2), 10.21 (1H, s, H_3), 7.98 (1H, s, H_4), 5.86 (1H, s, H_5), 5.09 (1H, s, H_6), 4.56 (2H, t, H_7), 4.09 (99H, m, H_8), 3.62 (3H, m, H_9), 3.44 (2H, m, H_{10}), 3.14 (2H, m, H_{11}), 2.18 – 2.50 (49H, m, H_{12}), 1.18-2.01 (210H, m, H_{13}), 0.94 (135H, m, H_{14}).

Sample	*n*-butyl acrylate g(mmol)	AIBN mg(mmol)	CTA mg(mmol)	DMF mL	Conversion %	Yield g
U4500	2.0(15.63)	6.6(0.04)	311(0.4)	2	86	1.4
U12500	2.0(15.63)	2.1(0.013)	102(0.13)	2	80	1.4
U26000	2.0(15.63)	1.0(0.006)	49(0.06)	2	79	1.5

1.6. Synthesis of PnBa **9**:

In a schlenk flask with an egg-shaped magnetic stirrer, *n*-butyl acrylate (1.0 g, 7.82 mmol), AIBN, CTA **8** ([CTA]/[AIBN]:10/1), 2 mL anhydrous DMF was added. The reaction flask was closed using a septum and 3 times freeze-pump-thaw cycle was carried out following a nitrogen flush. The schlenk

flask was inserted in a preheated oil bath of 75 °C and stirred for 5.5 hours. Afterwards, it was quenched by plunging into liquid nitrogen. Then, it was precipitated into methanol/water mixture (90:10) to yield yellowish polymer oil.

^{1}H NMR (400 MHz, Acetone-d_6) δ: 4.01 (55H, m, H_9), 2.26 (29H, m, H_{11}), 1.20-2.00 (210H, m, H_{12}), 0.91 (82H, m, H_{13}).

Sample	*n*-butyl acrylate g(mmol)	AIBN mg(mmol)	CTA mg(mmol)	DMF mL	Conversion %	Yield g
9(2700)*	1.0(7.82)	4.76(0.029)	112(0.29)	2	78	0.67
9(8300)	1.0(7.82)	1.48(0.009)	35(0.09)	2	74	0.71
9(9500)	1.0(7.82)	1.15(0.007)	29(0.07)	2	71	0.73

*sample **9(Mn)** later is called ODMn (i.e: **9(2700)** is **OD2700** after functionalization with ODIN)

1.7. Synthesis of ((1-(6-Isocyanatohexyl)-3-(7-oxo-7,8-dihydro-1,8-naphthyridin-2-yl)urea) (ODIN)) **10**

4g (0.025 mol) 7-amino-1,8-naphthyridin-2(1H)-one was added to a 100 mL three-necked round bottom flask equipped with an egg-shaped magnetic stirrer. The solids were allowed to dry for one hour under vacuum. The flask was kept under nitrogen atmosphere by 3 consequent vacuum/nitrogen cycles. 60 mL HDI (0.37 mol) was added to the reaction flask. The reaction mixture was heated to 110 °C while stirring. After 19h the reaction mixture was cooled down to room temperature. Then, it was precipitated in 500 mL hexane. The precipitate was filtered off and the traces of HDI was removed by distillation under reduced pressure (0.01 mbar) at 130 °C. (84% yield)

^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.15 (1H, s, H_1), 9.63 (1H, s, H_2), 8.98 (1H, t, J = 8.0 Hz, H_7), 7.88 (1H, d, J = 8.5 Hz, H_4), 7.75 (1H, d, J = 9.4 Hz, H_5), 6.83 (1H, d, J = 8.5 Hz, H_3), 6.31 (1H, dd, J = 9.3, 1.9 Hz, H_6), 3.0-3.3 (4H, m, H_8), 1.1-1.6 (8H, m, H_9).

^{1}H NMR (400 MHz, Chloroform-d) δ: 12.75 (1H, s, H_1), 11.22 (1H, s, H_2), 8.19 (1H, d, J = 8.8 Hz, H_3), 7.80 (1H, d, J = 8.8 Hz, H_4), 7.70 (1H, d, J =

9.3 Hz, H_5), 6.45 (1H, d, J = 9.3 Hz, H_6), 5.93 (1H, s, H_7), 3.05-3.45 (4H, m, H_8), 1.25-1.75 (8H, m, H_9).

^{13}C NMR (101 MHz, DMSO-d_6): δ 163.52, 154.69, 154.24, 139.52, 138.56, 127.06, 119.32, 108.14, 106.96, 40.01, 39.34, 30.51, 30.03, 26.66, 26.63.

1.8. Synthesis of polymer **OD**

A 100 mL three necked round bottom flask was equipped with a reflux condenser and an egg-shaped magnetic stirrer and put under nitrogen atmosphere. 300 mg PnBa and 3 equivalent of ODIN **10** was added to the reaction flask under nitrogen atmosphere. Then, 10 mL of anhydrous chloroform and 2 droplets of DBTDL was added to the reaction mixture. The reaction mixture was refluxed overnight and then, hexane was added (3 mL) and the unreacted extra ODIN **10** was isolated by centrifugation at 4500 rpm for 30 minutes. The solution was collected and the solvent was removed under reduced pressure. A yellow solid was obtained.

Yield: 294 mg

^{1}H NMR (400 MHz, Acetone-d_6) δ: 12.89 (1H, s, H_1), 11.25 (1H, s, H_2), 8.19 (1H, s, H_3), 7.80 (1H, d, J = 8.8 Hz, H_4), 7.70 (1H, d, J = 9.3 Hz, H_5), 6.53 (1H, d, J = 9.3 Hz, H_6), 6.03 (1H, s, H_7), 4.79 (1H, s, H_8), 4.01 (55H, m, H_9), 3.27 (7H, m, H_{10}), 2.26 (29H, m, H_{11}), 1.20-2.00 (210H, m, H_{12}), 0.91 (82H, m, H_{13}).

1.9. Synthesis of 2-(((6-(3-(7-oxo-7,8-dihydro-1,8-naphthyridin-2-yl)ureido)hexyl)carbamoyl)oxy)ethyl acrylate **12**:

A 100 mL three necked round bottom flask was equipped with a reflux condenser and an egg-shaped magnetic stirrer. ODIN **10** (300 mg, 0.9 mmol) and HEA (522 mg, 4.5 mmol) was added to the reaction flask under nitrogen atmosphere. Then, 10 mL of anhydrous chloroform and 2 droplets of DBTDL was added to the reaction mixture. The reaction mixture was refluxed overnight and then, the reaction mixture was precipitated in hexane to remove the catalyst. Then, the crude product was dissolved in 6 mL DMSO and precipitated in water. The pure product was obtained after filtration and after it was kept in vacuum oven overnight.

^{1}H NMR (400 MHz, Chloroform-d) δ: 12.77 (1H, s, H_1), 11.20 (1H, s, H_2), 8.18 (1H, d, J = 8.7 Hz, H_7), 7.80 (1H, d, J = 8.8 Hz, H_6), 7.70 (1H, d, J =

9.3 Hz, H_5), 6.51 – 6.38 (2H, m, $H_{4,14}$), 6.21 – 6.09 (1H, m, H_{13}), 5.95 (1H, s, H_3), 5.85 (1H, dd, J = 10.4, 1.5 Hz, H_{15}), 4.86 (1H, s, H_{10}), 4.36 – 4.28 (4H, m, $H_{11,12}$), 3.31 (2H, q, J = 6.6 Hz, H_8), 3.19 (2H, q, J = 6.8 Hz, H_8), 1.83 – 1.16 (8H, m, H_9).

^{13}C NMR (101 MHz, DMSO-d_6) δ: 172.70, 160.97, 159.51, 152.87, 140.08, 137.70, 131.37, 127.86, 125.28, 105.38, 100.79.

Yield: 66 %

1.10. RAFT polymerization of acrylate **12**:

Synthesis of **O** was carried out via polymerization of acrylate **12** initiated by AIBN and DBTTC as the chain transfer agent. To a Schlenk tube containing a magnetic stirrer, acrylate **12** (1 g, 2.24 mmol), DBTTC (4.64 mg, 0.016 mmol) and AIBN (0.26 mg, 0.0032 mmol) and DMF (9 mL) were added followed by four times free-pump-thaw cycles. Then, the reaction mixture was inserted in a pre-heated oil bath of 75 ^{o}C and stirred for 36 hours. Subsequently the reaction mixture was precipitated in a methanol, filtered and dried in vacuum oven overnight.

Conversion: 55%

Yield: 430 mg

^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.18 (62H, s, H_1), 9.64 (68H, s, H_2), 8.99 (67H, s, H_3), 7.88 (73H, d, J = 8.5 Hz, H_6), 7.75 (72H, d, J = 9.4 Hz, H_5), 6.80 (68H, d, J = 8.5 Hz, H_7), 6.29 (79H, d, J = 9.5 Hz, H_4), 5.71 (80H, s, H_{10}), 4.00-4.40 (m, $H_{11,12}$), 1.00-3.30 (m, $H_{8,9,13,14}$).

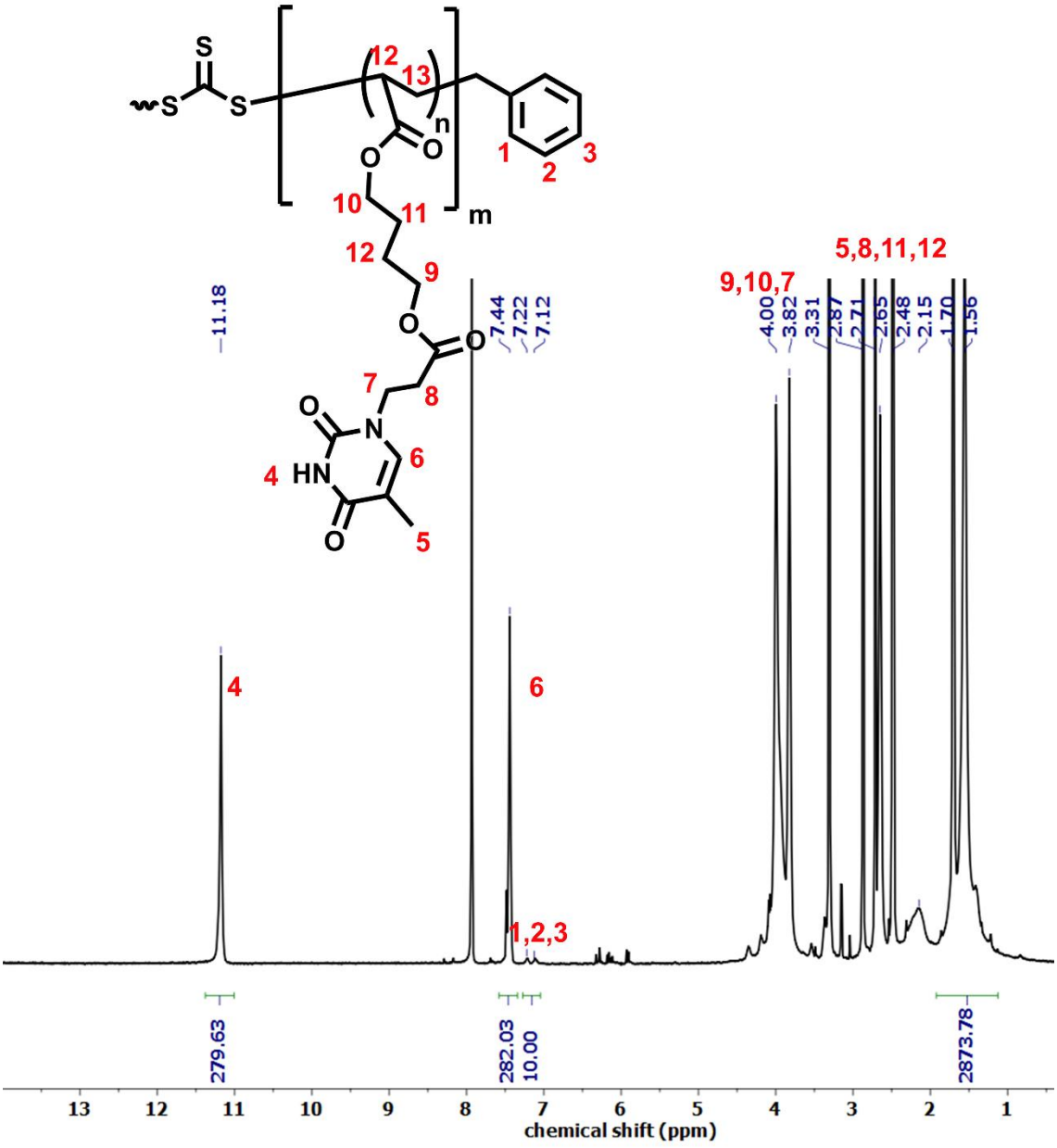
1.11. Synthesis of **T**:

Synthesis of **T** was carried out via polymerization of the required amount of THY (4.00 g, 12.35 mmol) initiated by AIBN (0.49 mg, 0.003 mmol) and DBTTC (9.6 mg, 0.03 mmol) as the chain transfer agent. To a Schlenk tube containing a magnetic stirrer, DBTTC, and AIBN in 5 mL DMF, the required amounts THY (4.00 g, 12.35 mmol) was added followed by four freeze–pump–thaw cycles. Then, the reaction mixture was inserted in a preheated

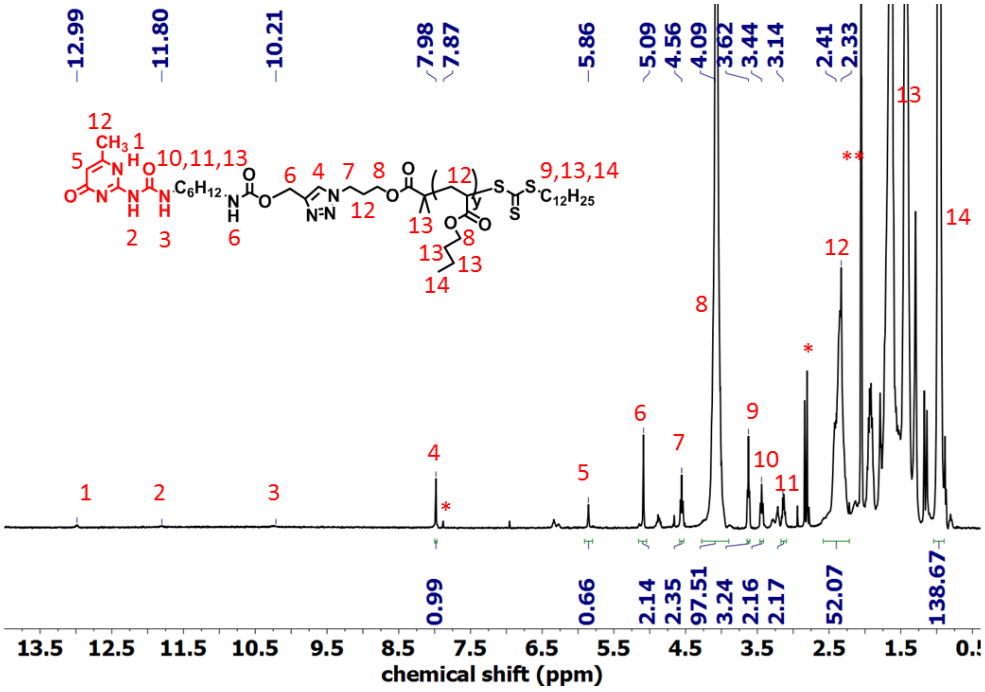
oil bath of 70 °C and stirred for 7 h. Subsequently the reaction mixture was precipitated in a methanol–water mixture and recovered via centrifugation. The polymers were dried under vacuum and yielded the desired product.

68% conversion, 2.52 g yield

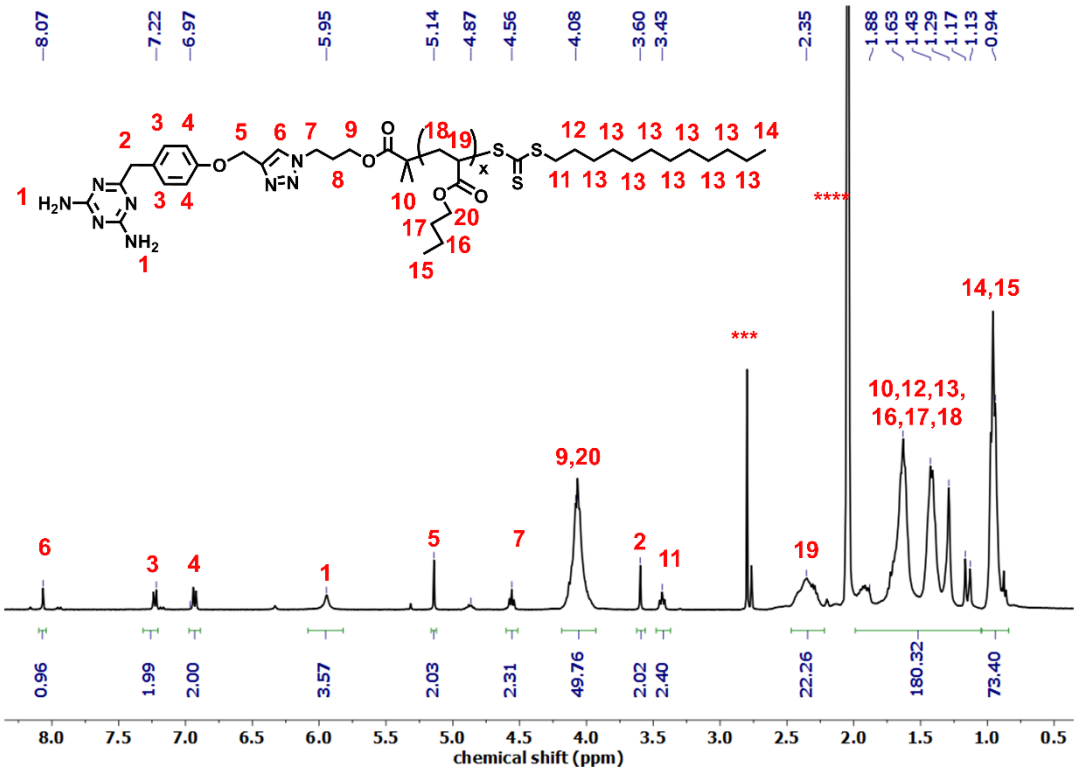
^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.19 (280H, s, H_{10}), 7.44 (280H, s, H_6), 7.10-7.30 (67H, m, $H_{1\text{-}3}$), 3.70-4.10 (1680H, m, $H_{7,9,10}$), 1.00-3.50 (2520H, m, $H_{5,8,11,12}$).



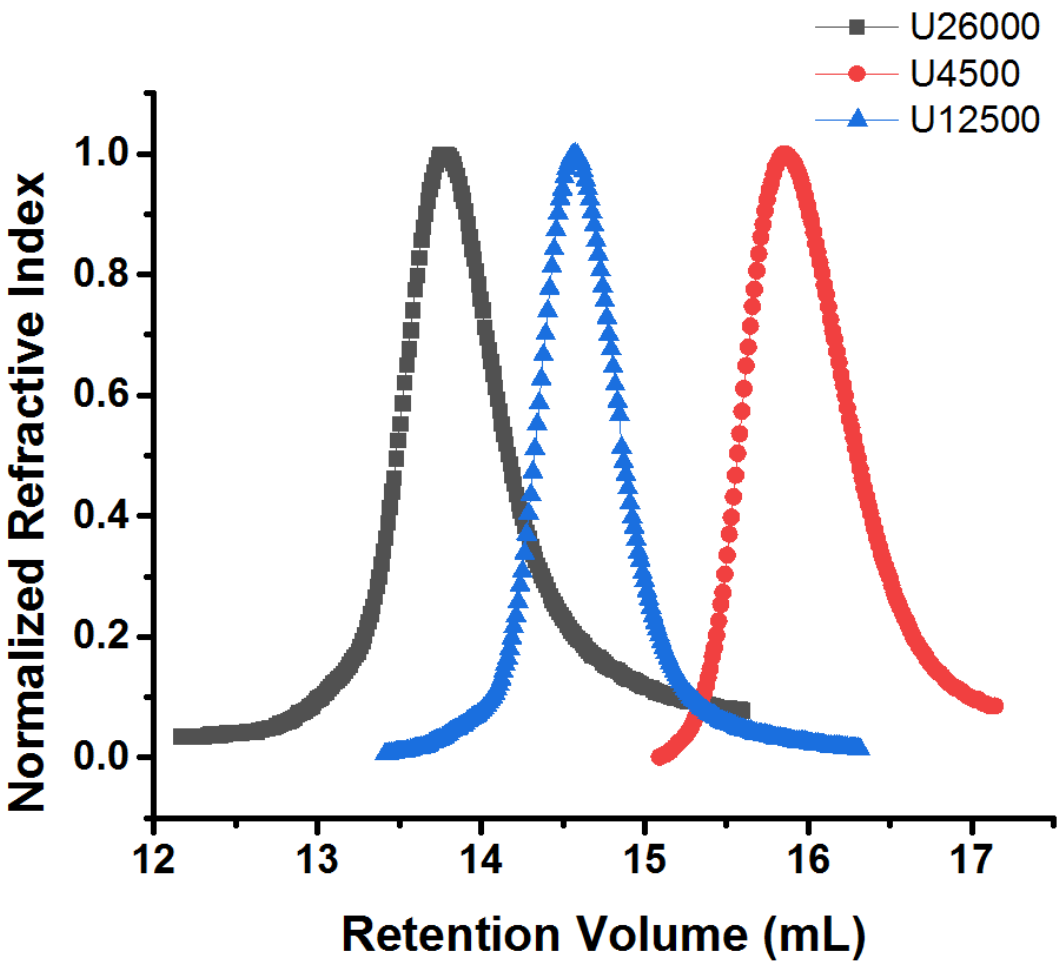
2. Supplementary Figures and Tables



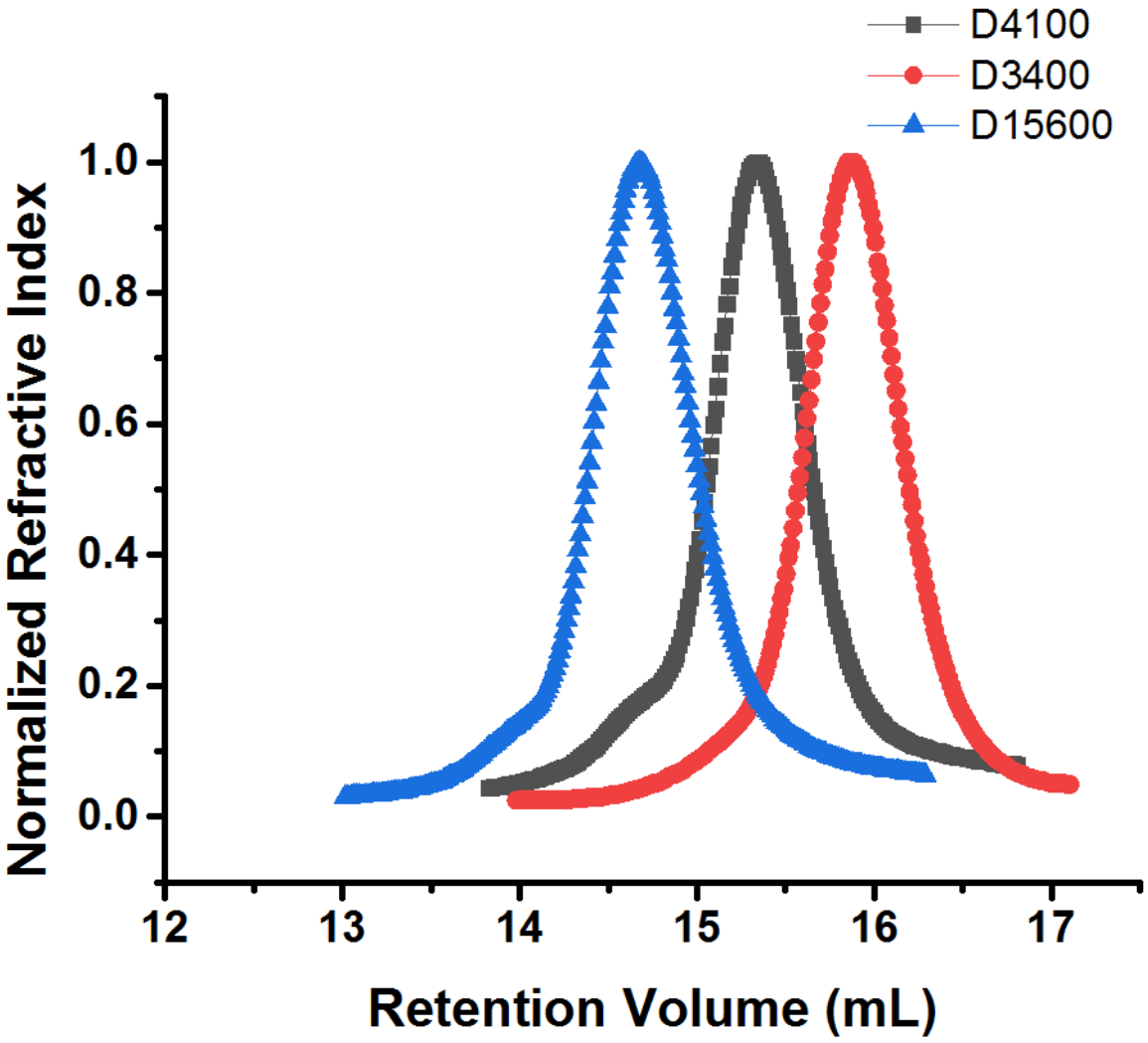
S1. ^{1}H NMR spectrum of polymer **U**



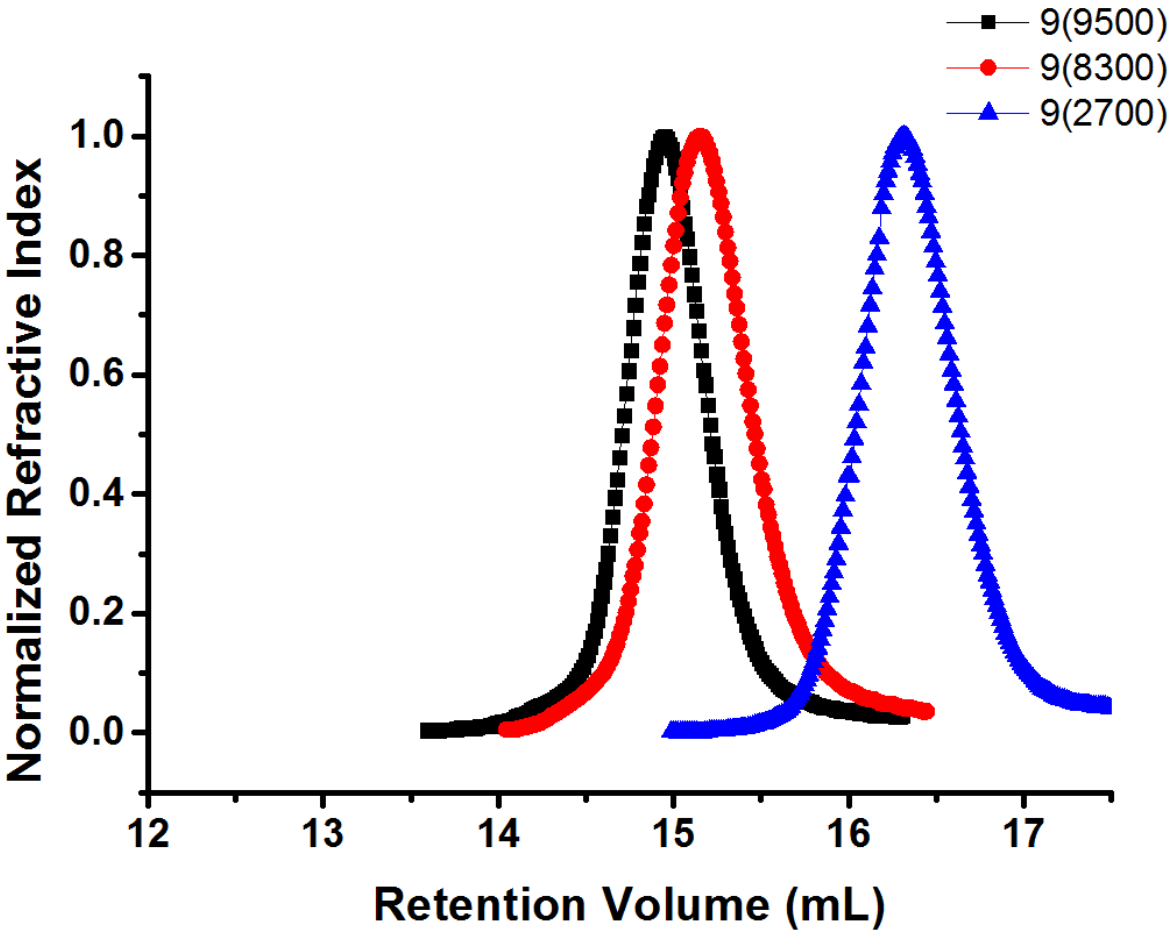
S2. ^{1}H NMR spectrum of polymer **D**



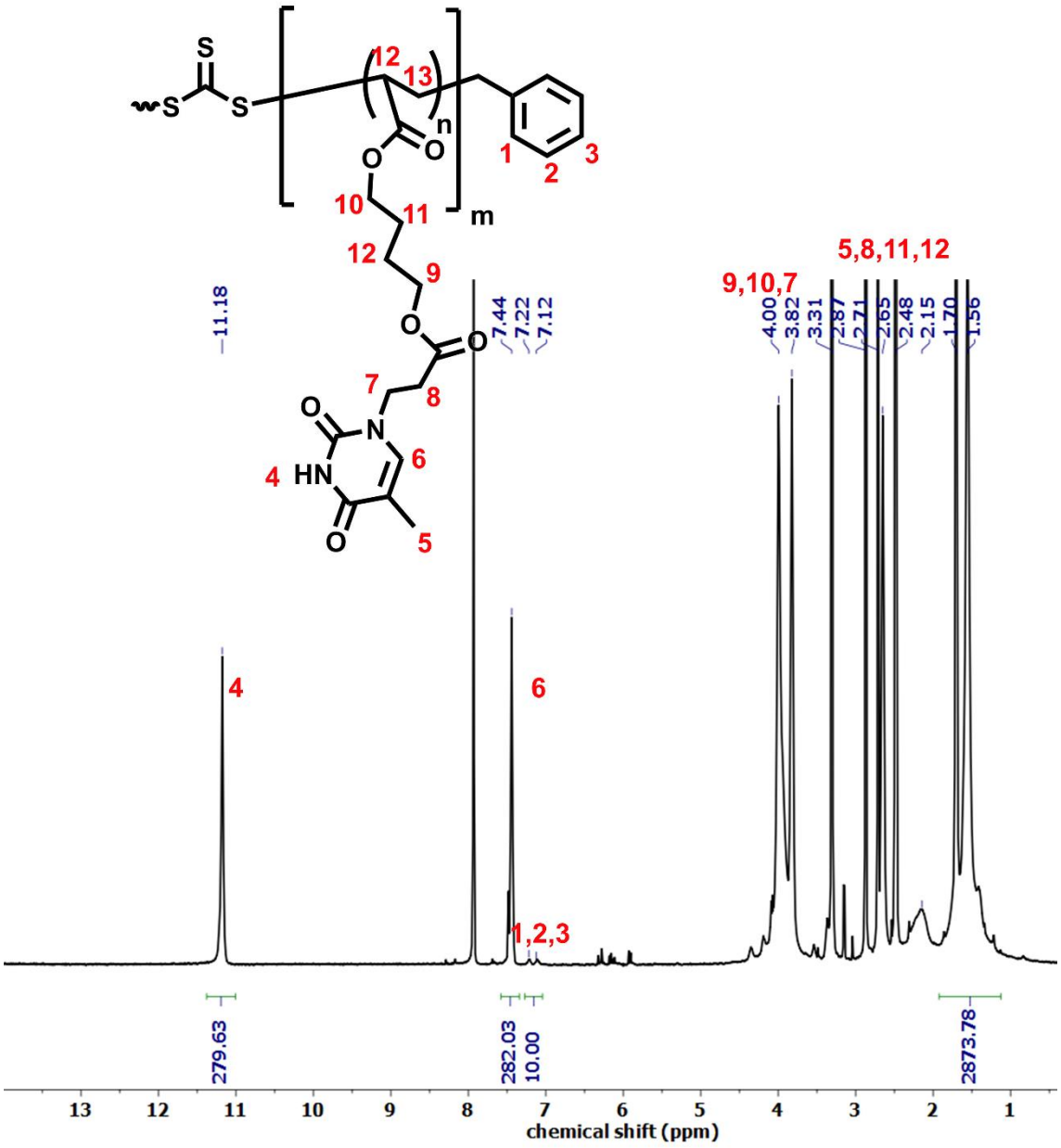
S3. GPC traces of polymer **U**



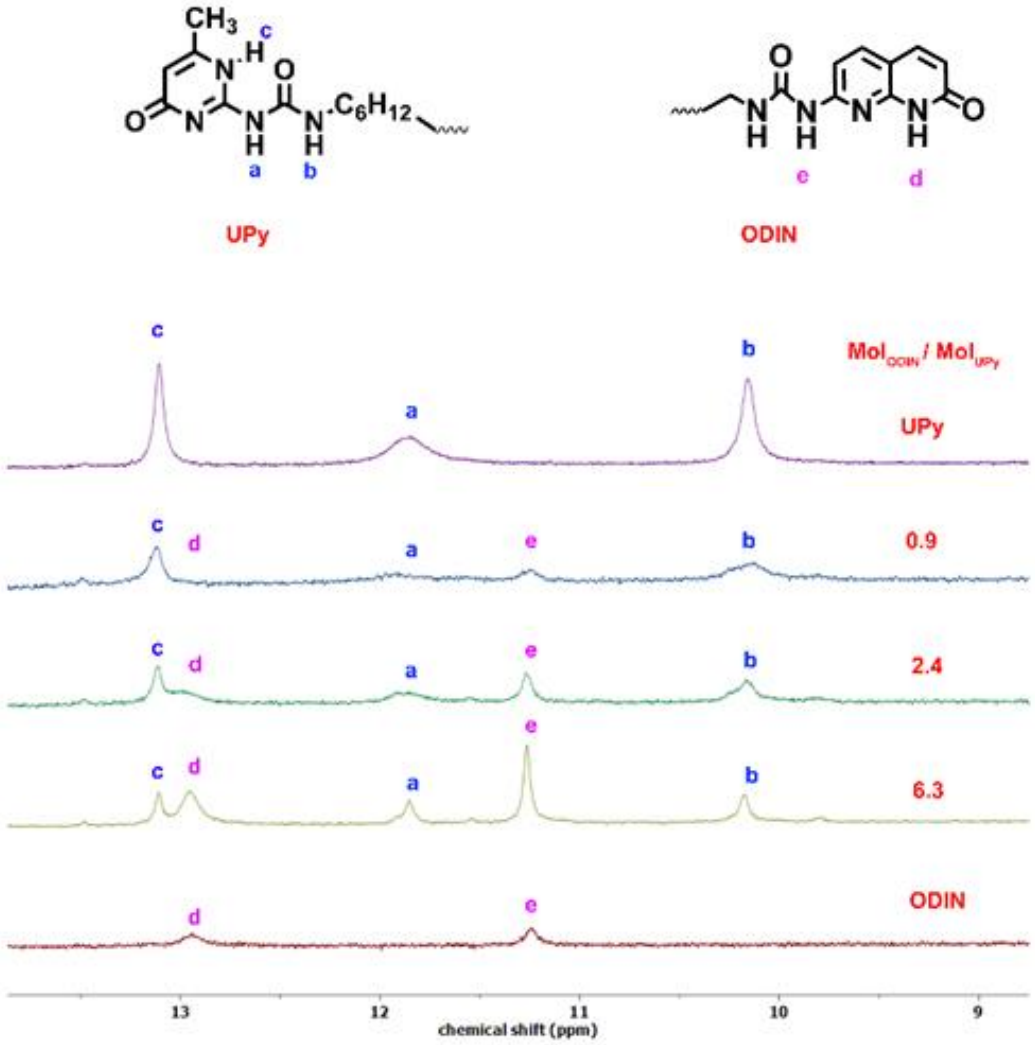
S4. GPC traces of polymer **D**



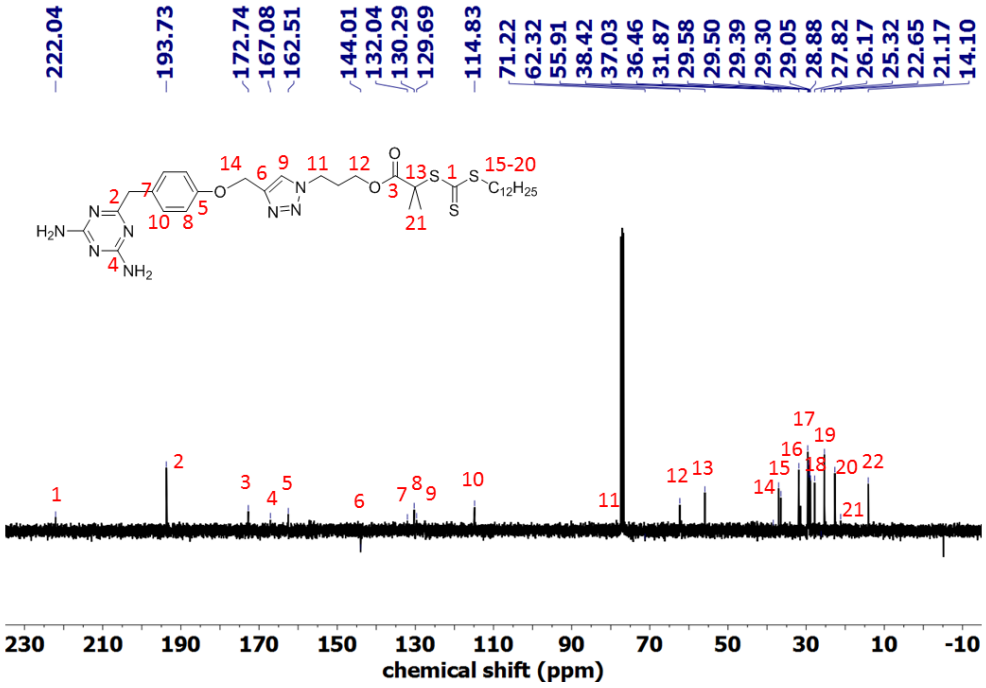
S5. GPC traces of PnBa **9**



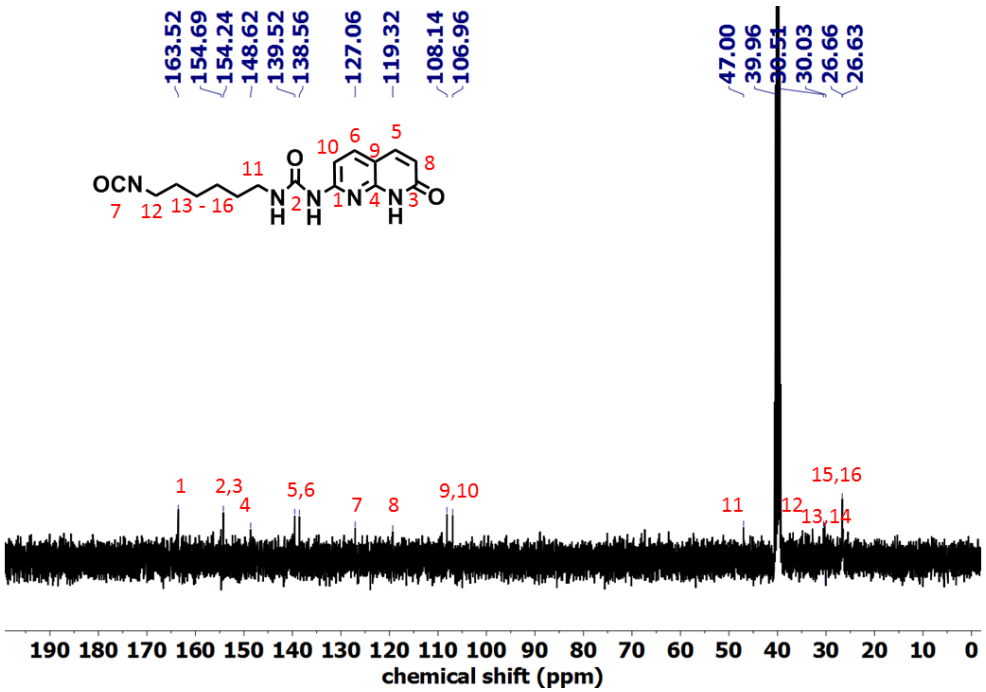
S6. ^{1}H NMR spectrum of polymer **T**



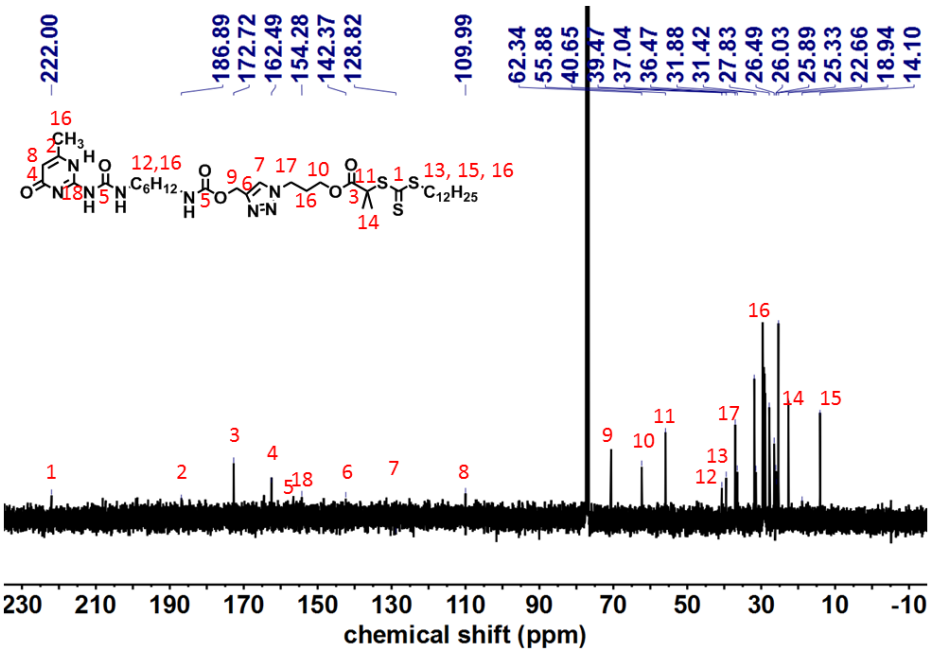
S7. ^{1}H NMR titration of UPy and ODIN **10**



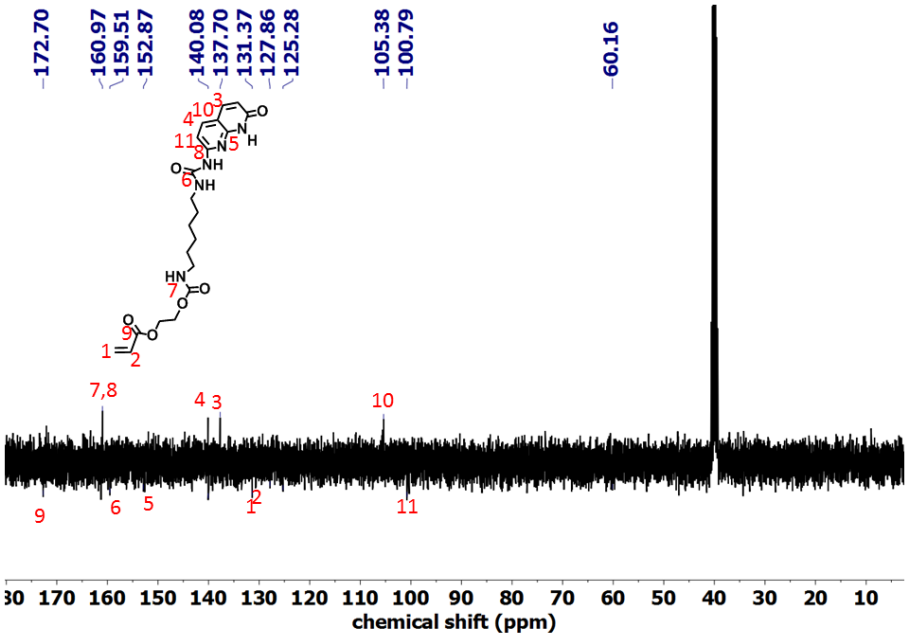
S8. ^{13}C NMR spectrum of **6**



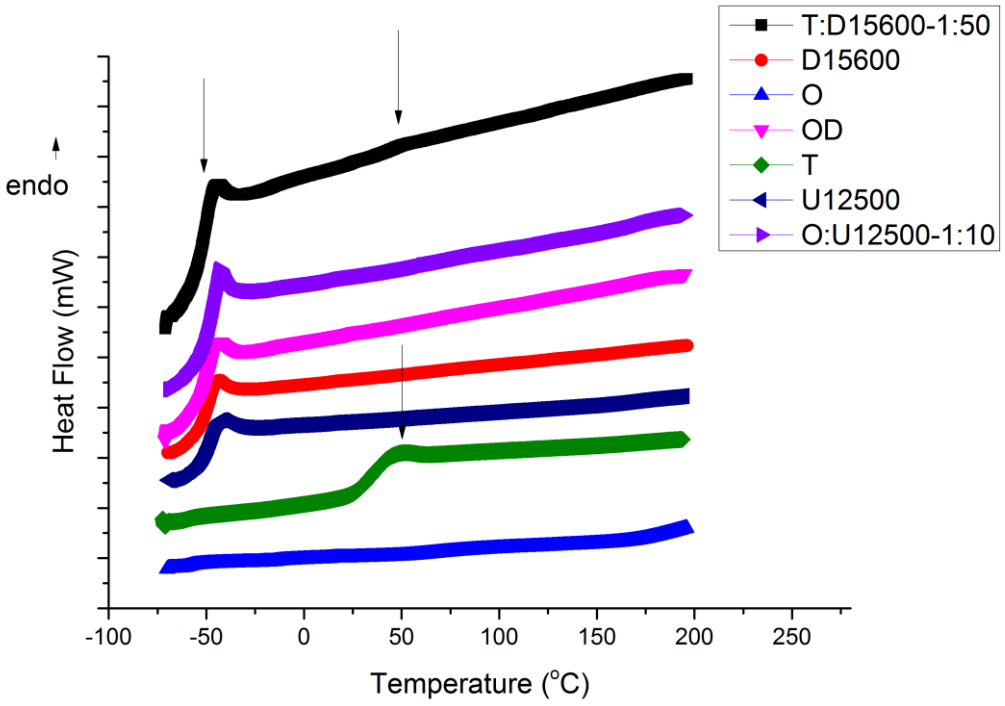
S9. ^{13}C NMR spectrum of **10**



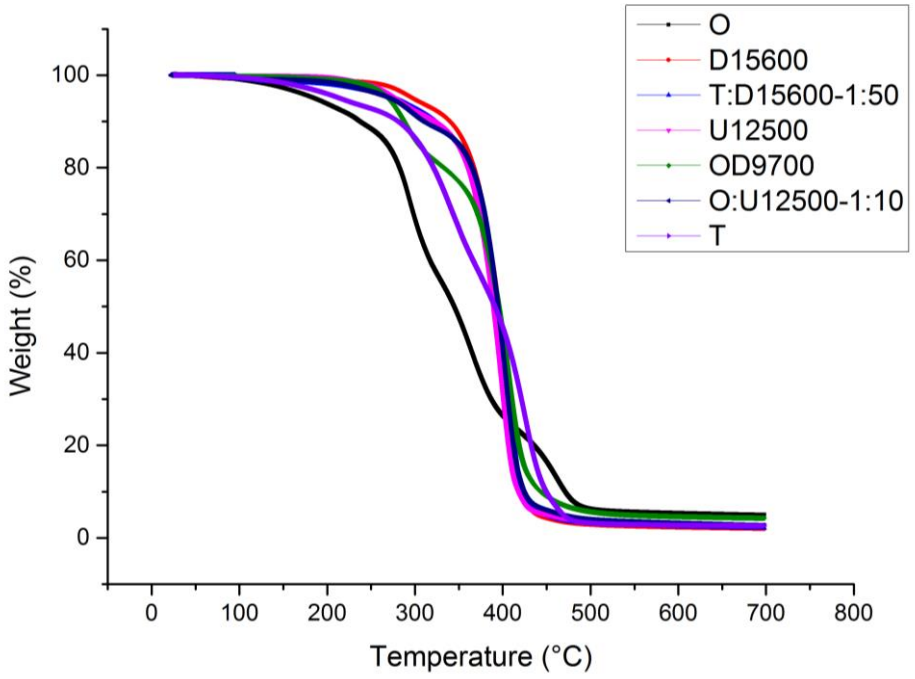
S10. ^{13}C NMR spectrum of **3**



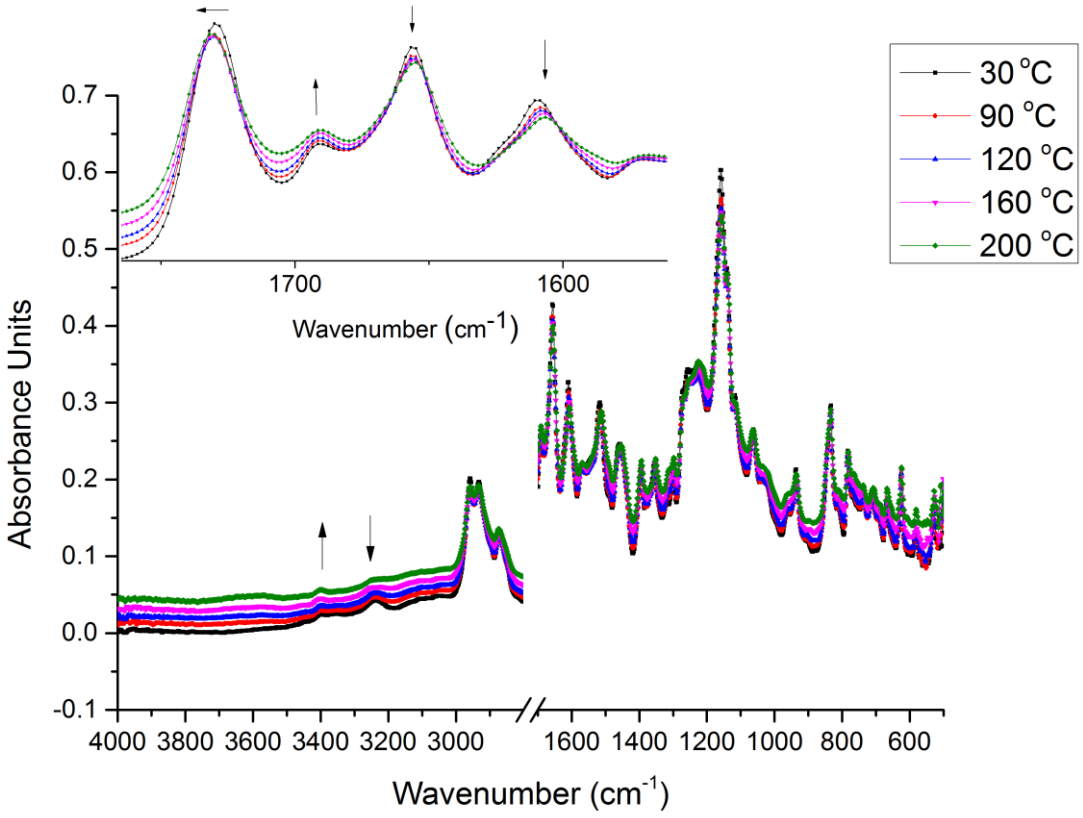
S11. ^{13}C NMR spectrum of **12**



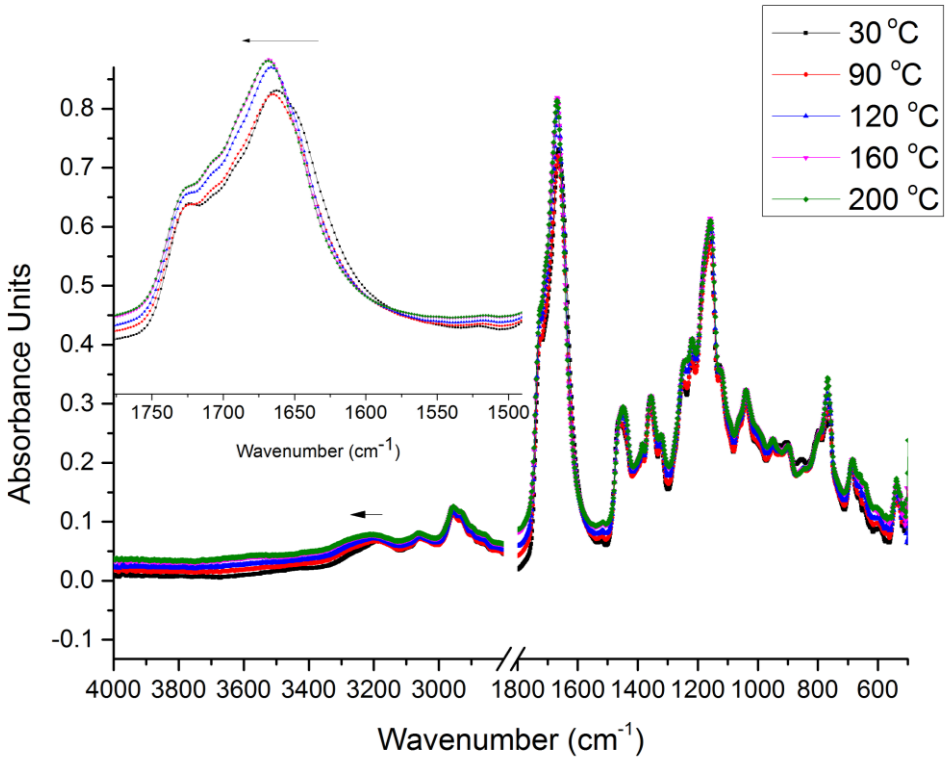
S12. DSC thermograms of **T:D15600-1:50**, **O**, **T**, **OD9700**, **D15600**, **U12500**, **O:U12500-1:10**.



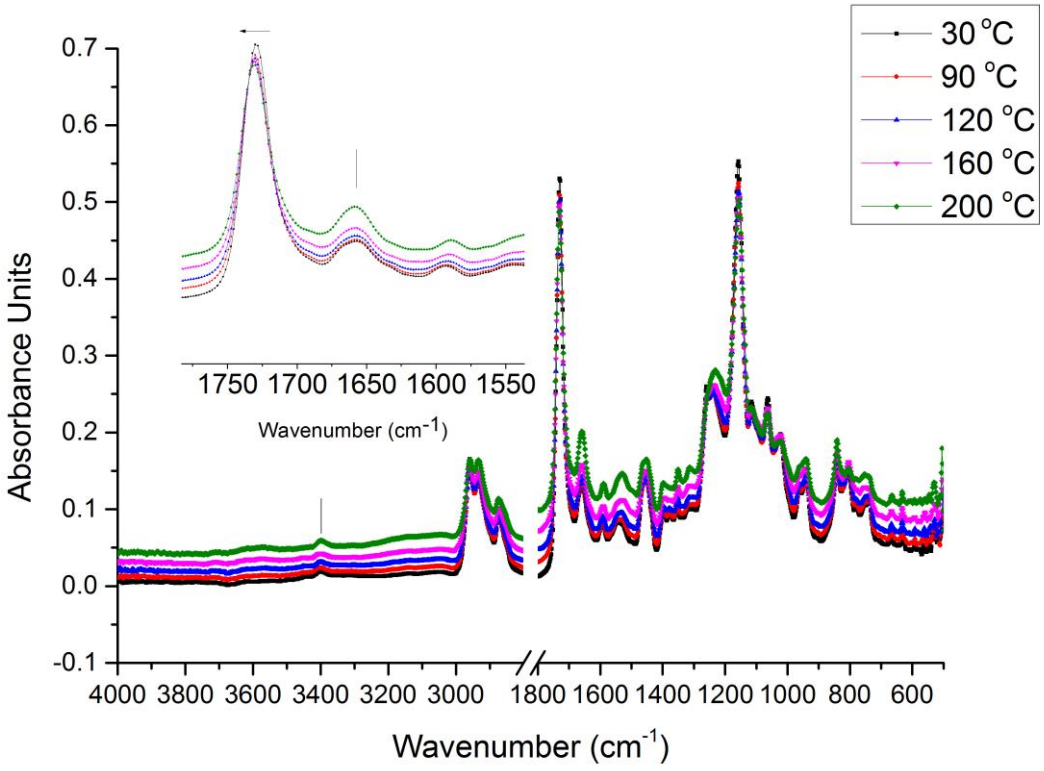
S13. TGA thermograms of **T:D15600-1:50**, **O**, **T**, **OD9700**, **D15600**, **U12500**, **O:U12500-1:10**.



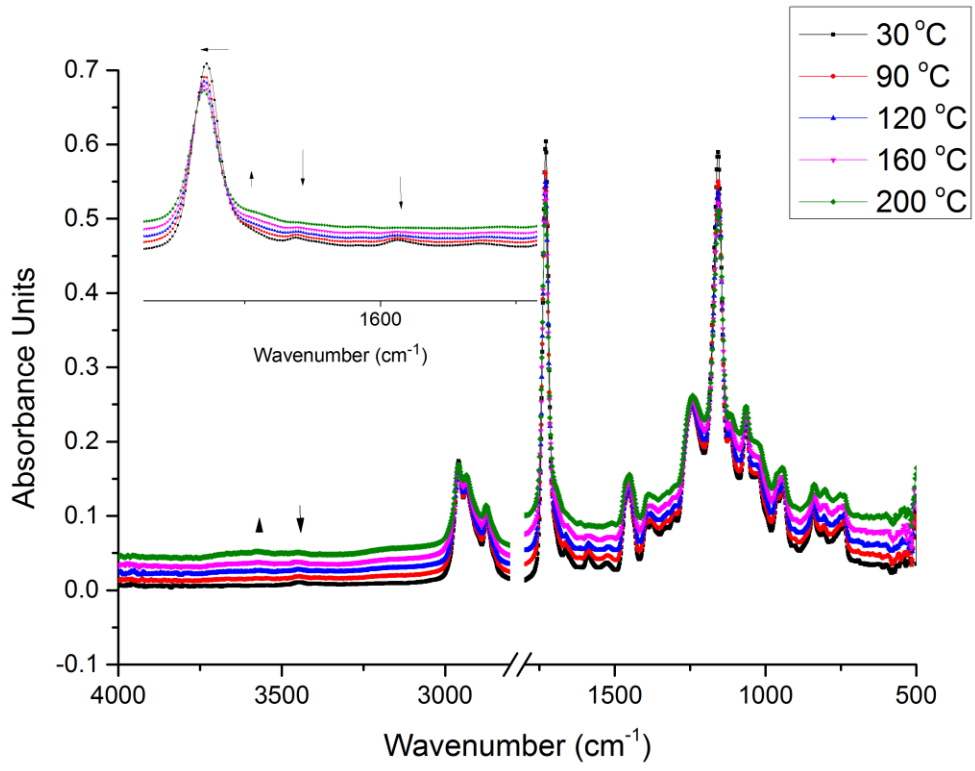
S14. Variable temperature FT-IR spectra of **O**



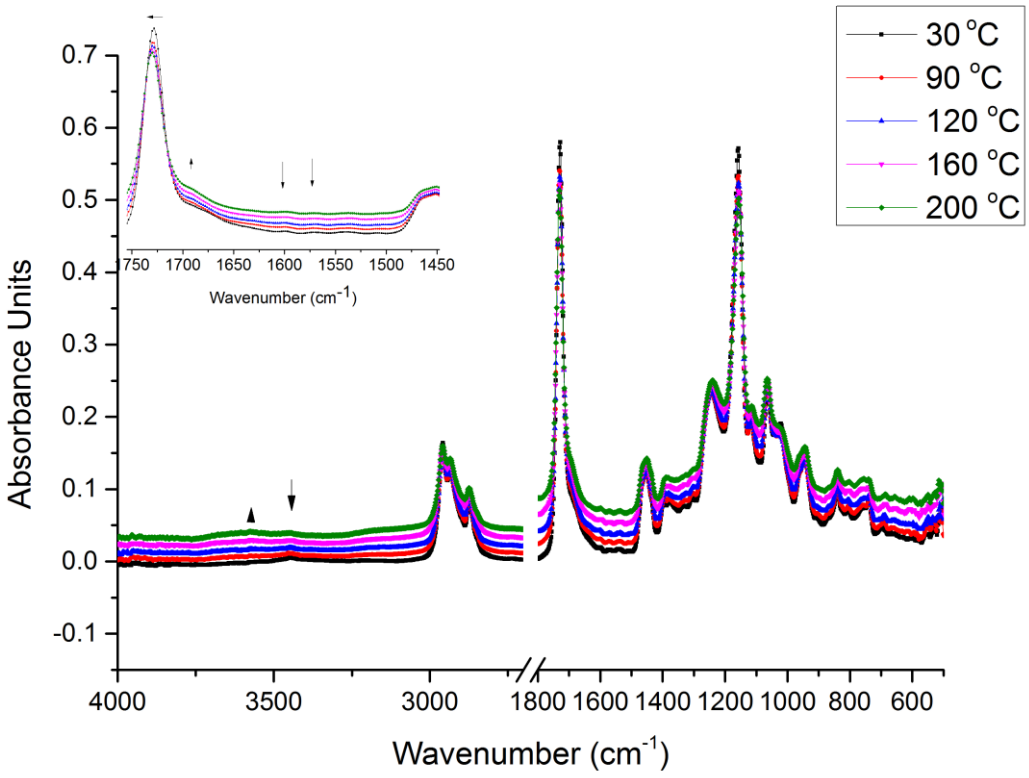
S15. Variable temperature FT-IR spectra of **T**



S16. Variable temperature FT-IR spectra of **OD9700**



S17. Variable temperature FT-IR spectra of **O:U12500-1:10**



S18. Variable temperature FT-IR spectra of **T:D15600-1:50**

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