# Topochemical photo-reversible polymerization of a bioinspired monomer and its recovery and repolymerization after photo-depolymerization

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## Contents

Overall Synthetic Scheme for Compou	nds 1-3	3
General methods for characterization o	f Compounds 1-3	3
Synthesis of dimethyl 3,3'-(3,3'-(	butane-1,4-diyl)bis(5-methyl-2,4-dioxo-3,4-dihydropyrimidi	ine-
3,1(2 <i>H</i> )-diyl))dipropanoate (1)		4
Supplementary Characterization Dat	a	5
Compound 1 - 1H-NMR		5
Compound 1 - 13C-NMR		6
Thymine propanoate - <sup>1</sup> H-NMR		7
Thymine propanoate - 13C-NMR		8
Synthesis of dimethyl 3,3'-(3,3'-(h	nexane-1,6-diyl)bis(5-methyl-2,4-dioxo-3,4-dihydropyrimidi	ine-
3,1(2 <i>H</i> )-diyl)) (2)		9
Supplementary Characterization Dat	a	.10
Compound 2 - 1H-NMR		.10
Compound 2 - 13C-NMR		.11
Synthesis of 3,3'-(3,3'-(butane-1	,4-diyl)bis(5-methyl-2,4-dioxo-3,4-dihydropyrimidine-3,1(2	.H)-
diyl))dipropanamide (3)		.12
Supplementary Characterization Dat	a	.13
Compound 3 - 1H-NMR		.13
Compound 3 - 13C-NMR		.14
Thymine propanamide - 1H-NMR		.15
Thymine propanamide - 13C-NM	R	.16
Synthesis of poly(dimeth	yl 3,3'-(3,3'-(butane-1,4-diyl)bis(5-methyl-2,4-dioxo-3	3,4-
dihydropyrimidine-3,1(2H)-diyl))dig	propanoate) (poly-1)	.17

Supplementary Characterization Data
Poly-1 - 1H-NMR
Poly-1 - 13C-NMR
Gel Permeation Chromatography (GPC)
Oligomeric photo-products obtained upon irradiation of 220
Purification of poly-1 by serial precipitation
Depolymerization reactions
1. Solid-state depolymerization experiment
2. Cyclic irradiation experiments
Additional polymerization experiments with 1
Thermogravimetric Analysis (TGA)24
Dynamic Mechanical Thermal Analysis (DMTA)25
Ultraviolet-Visible Spectroscopy (UV-Vis)25
Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS).25
Powder x-ray diffraction (XRD)27
Crystal Data and Methods
References

**Overall Synthetic Scheme for Compounds 1-3** 

## **General methods for characterization of Compounds 1-3**

Melting points were determined using a Buchi B-545 melting point apparatus with a digital thermometer. Quoted melting points are uncorrected. Infrared spectra were recorded on a Perkin Elmer 1600 series Fourier Transform infrared spectrometer as KBr disks; or by using a Bruker Equinox 55 in ATR mode with diamond as the background reference. The infrared data were recorded in wavenumbers (cm<sup>-1</sup>). Proton Nuclear Magnetic Resonance (<sup>1</sup>H NMR) spectra were recorded at 400 MHz on a Bruker DPX-400 spectrometer. Carbon Nuclear Magnetic Resonance (<sup>13</sup>C NMR) spectra were determined from *J*-modulated Spin Echo experiments for X-nuclei coupled to <sup>1</sup>H in order to determine the number of attached protons. Low resolution electrospray ionisation mass spectra (ESI) were recorded on a

Micromass platform II API QMS Electrospray mass spectrometer with cone voltage 10 V, 25 V or 35 V. Analyses was performed in positive ( $ESI^+$ ) mode and negative mode ( $ESI^-$ ).

# Synthesis of dimethyl 3,3'-(3,3'-(butane-1,4-diyl)bis(5-methyl-2,4-dioxo-3,4dihydropyrimidine-3,1(2*H*)-diyl))dipropanoate (1)

Thymine propanoate was synthesized using a reported Michael's addition reaction between methyl acrylate and thymine <sup>1</sup>. Here, thymine (1.2 g, 9.4 mmole) was dissolved in anhydrous DMF (50 mL), using  $Et_3N$  (0.95 g, 9.4 mmole) as base. Methyl acrylate (1.6 g, 19 mmole) was added and the reaction was continued for 24 h at ambient temperature. The excess methyl acrylate and NEt<sub>3</sub> were removed under reduced pressure, and the solvent was evaporated to yield a white crystalline solid. The solid was washed with EtOH and hexane and dried in vacuo. Single crystals were obtained by slow cooling of a hot EtOH solution. The NMR spectral data were consistent with literature data.

Mp 131.6-133.2 °C, lit. 134-136 °C.<sup>2</sup> Yield: 1.73 g (86 %). MS (ESI): Calcd for  $[C_9H_{12}N_2O_4]^+$ : m/z 212.1; Found: m/z 213.1 (M+1), 235.2 (M+Na). <sup>1</sup>H-NMR (400 MHz, D<sub>6</sub>-DMSO):  $\delta_H$  1.74 (d, J = 1.2 Hz 3H, C5-CH<sub>3</sub>), 2.68 (t, J = 8.0 Hz 2H, CH<sub>2</sub>-C=O), 3.85 (t, J = 6.8 Hz 2H, N1-CH<sub>2</sub>), 7.49 (d, J = 1.2 Hz 1H, C6H), 11.21 (s, 1H, N3H). <sup>13</sup>C-NMR (100 MHz, D<sub>6</sub>-DMSO):  $\delta_C$  11.93 (C5-<u>C</u>H<sub>3</sub>), 32.58 (<u>C</u>H<sub>2</sub>CO), 43.72 (N1-CH<sub>2</sub>), 51.54 (O-CH<sub>3</sub>), 108.24 (C5), 141.80 (C6), 150.78 (C2=O), 164.29 (C4=O), 171.21 (prop. C=O). Selected IR bands (ATR, cm<sup>-1</sup>): 3154 m, 3097 m, 3023m, 2997 m, 2957 m, 2885 m, 2859 w, 2829 m, 2774 w, 1753 s, 1706 s, 1655 s, 1382 s, 1358 s, 1255 m, 1230 s, 1217 s, 1198 s.

Thymine propanoate  $(3.00 \text{ g}, 14.8 \text{ mmol})^1$  was dissolved in anhydrous dimethylformamide (15 mL). K<sub>2</sub>CO<sub>3</sub> (2.44 g, 17.8 mmol) was added, and the mixture was stirred for a short time before the addition of 1,4-diiodobutane (1.84 g, 5.94 mmol). The reaction was allowed to continue for 48 h at 70 °C. At this time, the reaction mixture was cooled and decanted into d.H<sub>2</sub>O (100 mL). The crude solids were isolated by filtration and recrystallised from EtOH to give the title compound. Further amounts of the monomer could be obtained by extracting the filtrate with CHCl<sub>3</sub>. The organic phases were then dried over MgSO<sub>4</sub>, and the solvent was removed under diminished pressure. The residues were then twice recrystallised from hot EtOH.

Yield: 2.14 g (75%). Mp. 189.7-191.9 °C. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$  1.68 (m, J = 3.2 Hz, 4H, alk. core CH<sub>2</sub>), 1.90 (d, J = 1.2 Hz, 6H, C5-CH<sub>3</sub>), 2.77 (t, J = 6.4 Hz, 4H, CH<sub>2</sub>-C=O), 3.70 (s, 6H, O-CH<sub>3</sub>), 3.96 (t, J = 6.4 Hz, 8H, N3-CH<sub>2</sub>, N1-CH<sub>2</sub>), 7.14 (d, J = 1.2 Hz 2H, C6H). <sup>13</sup>C-NMR (100 MHz,

CDCl3):  $\delta$ C 12.93 (C5-<u>C</u>H<sub>3</sub>), 25.19 (alk. core CH<sub>2</sub>), 32.89 (<u>C</u>H<sub>2</sub>-C=O), 41.00 (N3-CH<sub>2</sub>), 45.74 (N1-CH<sub>2</sub>), 51.94 (O-CH<sub>3</sub>), 109.42 (C5), 139.32 (C6H), 151.24 (C2=O), 163.69 (C4=O), 171.85 (ester C=O). IR (KBr, cm<sup>-1</sup>): 3450 m, 2968 m, 2936 m, 1732 s, 1700 s, 1662 s, 1640 s, 1470 m, 1454 m, 1430 m, 1406 m, 1392 m, 1376 m, 1360 m, 1214 s, 1202 s. UV (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max} = 268$  nm. MS (ESI) calcd for [C<sub>22</sub>H<sub>23</sub>N<sub>4</sub>O<sub>8</sub>]<sup>+</sup>: m/z 478.2; found: m/z 479.1 (M+1), 501.1 (M+Na), 502.1 (M+Na+1). CHN Analysis (calcd, found for C<sub>22</sub>H<sub>23</sub>N<sub>4</sub>O<sub>8</sub>): C (55.22, 55.35), H (6.32, 6.28), N (11.71, 11.64).

## **Supplementary Characterization Data**



#### **Compound 1 - 1H-NMR**





#### Supplementary information, S7



# Synthesis of dimethyl 3,3'-(3,3'-(hexane-1,6-diyl)bis(5-methyl-2,4-dioxo-3,4dihydropyrimidine-3,1(2*H*)-diyl)) (2)

The previously synthesized thymine propanoate (2.99 g, 14.8 mmol) was dissolved in acetonitrile (40 mL) at 80 °C. K<sub>2</sub>CO<sub>3</sub> (2.46 g, 17.8 mmol) was added, and the mixture was stirred for 5 min before the addition of dibromohexane (1.44 g, 5.90 mmol). After 48 h, the reaction mixture was decanted into CH<sub>2</sub>Cl<sub>2</sub>. The solids were removed by filtration, and the solvents were evaporated from the filtrate. The residues were dissolved in THF (15 mL) and precipitated using hexane (15 mL). A crystalline sample of the monomer was obtained by slow evaporation of an aqueous solution containing 20% ethanol.

Yield: 0.98 g (33%). Mp: 139.3-140.9°C. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$  1.37 (p, *J* = 3.6 Hz, 4H, alk. core CH<sub>2</sub>), 1.60 (p, *J* = 7.2 Hz, 4H, alk. CH<sub>2</sub>), 1.90 (d, *J* = 1.2 Hz, 6H, C5-CH<sub>3</sub>), 2.76 (t, *J* = 6.2 Hz, 4H, CH<sub>2</sub>-C=O), 3.69 (s, 6H, O-CH<sub>3</sub>), 3.90 (t, *J* = 6.2 Hz, 4H, N1-CH<sub>2</sub>), 3.96 (t, *J* = 7.6 Hz, 4H, N3-CH<sub>2</sub>), 7.13 (d, *J* = 1.2 Hz, 2H, C6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  12.96 (C5-CH<sub>3</sub>), 26.58 (alk. core CH<sub>2</sub>), 27.41 (alk. CH<sub>2</sub>), 32.91 (CH<sub>2</sub>-C=O), 41.29 (N3-CH<sub>2</sub>), 45.76 (N1-CH<sub>2</sub>), 51.96 (O-CH<sub>3</sub>), 109.46 (C5), 139.23 (C6H), 151.24 (C2=O), 163.67 (C4=O), 171.86 (ester C=O). IR (ATR, cm<sup>-1</sup>): 3409 wb, 3085 w, 2954 m, 1732 m, 1696 m, 1662 s, 1637 s, 1509 m, 1460 m, 1429 m, 1381 m, 1355 m, 1203 s. MS (ESI) calcd for [C<sub>24</sub>H<sub>34</sub>N<sub>4</sub>O<sub>8</sub>]<sup>+</sup>: m/z 506.2; found: m/z 529.1 (M+Na), 530.1 (M+Na+1), 531.1 (M+Na+2). CHN Analysis (calcd, found for C<sub>24</sub>H<sub>34</sub>N<sub>4</sub>O<sub>8</sub>): C (56.91, 57.01), H (6.77, 6.53), N (11.06, 10.92).

## **Supplementary Characterization Data**







# Synthesis of 3,3'-(3,3'-(butane-1,4-diyl)bis(5-methyl-2,4-dioxo-3,4-dihydropyrimidine-3,1(2*H*)-diyl))dipropanamide (3)

Thymine propanamide was first prepared by aminolysis of thymine propanoate (1.0 g, 4.7 mmol). The ester was added to concentrated  $NH_4OH$  (15 mL), and then shaken in a capped flask until dissolution (approx. 5 min). The amide crystallized from the crude mixture as large colourless needles, which were subsequently collected by filtration. The crystalline solids were recrystallised from hot  $d.H_2O$ , to obtain the pure amide.

Mp 233.9-235.8 °C, lit. (not reported). Yield: 0.48 g (52 %). MS (ESI): Calcd for  $[C_8H_{11}N_3O_3]^+$ : m/z 197.1; Found: m/z 220.1 (M+Na). <sup>1</sup>H-NMR (400 MHz, D<sub>6</sub>-DMSO):  $\delta_H$  1.72 (d, J = 0.8 Hz, 3H, C5-CH<sub>3</sub>), 2.42 (t, J = 6.8 Hz, 2H, CH<sub>2</sub>-C=O), 3.80 (t, J = 6.8 Hz, 2H, N1-CH<sub>2</sub>), 6.89 (s, 1H, amide NH), 7.40 (s, 1H, amide NH), 7.43 (d, J = 1.2 Hz, 1H, C6H), 11.19 (s, 1H, N3H). <sup>13</sup>C-NMR (100 MHz, D<sub>6</sub>-DMSO):  $\delta_C$  11.96 (C5-<u>C</u>H<sub>3</sub>), 33.91 (<u>C</u>H<sub>2</sub>-C=O), 44.39 (N1-CH<sub>2</sub>), 107.92 (C5), 142.01 (C6H), 150.75 (C2=O), 164.35 (C4=O), 171.69 (prop. C=O). IR (KBr, cm<sup>-1</sup>): 3410 m, 3364 m, 3232 m, 3188 m, 3078 m, 3048 w, 2964 w, 2932 w, 2804 w, 1686 s, 1672 s, 1658 s, 1618 sh, 1472 m, 1464 m, 1448 w, 1434 w, 1386 m, 1362 m, 1242 m, 1218 m.

Thymine propanamide (1.35 g, 6.8 mmol) was dissolved in anhydrous DMF (10 mL) at 70 °C.  $K_2CO_3$  (1.13 g, 8.2 mmol) was added, and the mixture was stirred for 5 min before the addition of diiodobutane (0.84 g, 2.7 mmol). After 48 h, the insoluble white material was collected by filtration. The solids were suspended in d.H<sub>2</sub>O to dissolve  $K_2CO_3$  and precipitate the products. The insoluble material was collected by filtration, washed with d.H<sub>2</sub>O, and recrystallised from hot MeOH.

Yield: 0.90 g (73%). Mp: 241.9-243.6°C. <sup>1</sup>H-NMR: (400 MHz, D<sub>6</sub>-DMSO)  $\delta$  1.48 ((m, 4H, alk. core CH<sub>2</sub>), 1.78 (s, 6H, C5-CH<sub>3</sub>), 2.45 (t, *J* = 6.8 *Hz*, 4H, <u>CH<sub>2</sub>-C=O</u>), 3.79 (m, 4H, 2 x N3-CH<sub>2</sub>), 3.86 (t, *J* = 6.8 Hz, 4H, N1-CH<sub>2</sub>), 6.89 (s, 2H, amide NH), 7.39 (s, 2H, amide NH), 7.50 (s, 2H, C6H). <sup>13</sup>C-NMR (100 MHz, D<sub>6</sub>-DMSO):  $\delta_{C}$  12.61 (C5-CH<sub>3</sub>), 24.71 (alk. core CH<sub>2</sub>), 33.77 (CH<sub>2</sub>-C=O), 45.53 (N1-CH<sub>2</sub>, N3-CH<sub>2</sub> under DMSO), 107.15 (C5), 140.68 (C6H), 150.66 (C2=O), 163.09 (C4=O), 171.65 (amide C=O). IR (KBr, cm-1): 3405 (v N-H), 3213 (v N-H), 2949 (v CH, CH2), 2923 (v CH, CH2), 1668 (v C=O), 1629 (v C=O). MS (ESI): Calcd for [C<sub>20</sub>H<sub>28</sub>N<sub>6</sub>O<sub>6</sub>]<sup>+</sup>: m/z 448.2; Found: m/z 471.1 (M+Na), 472.1 (M+Na+1). CHN Analysis (calcd, found for C<sub>20</sub>H<sub>28</sub>N<sub>6</sub>O<sub>6</sub>): C (53.56, 53.61), H (6.29, 6.15), N (18.74, 18.68).

## **Supplementary Characterization Data**



#### Supplementary information, S13

## Compound 3 - 13C-NMR





#### Supplementary information, S15



Synthesis of poly(dimethyl 3,3'-(3,3'-(butane-1,4-diyl)bis(5-methyl-2,4-dioxo-3,4dihydropyrimidine-3,1(2*H*)-diyl))dipropanoate) (poly-1)

Crystalline **1** was spread into a thin layer (approx. 1 mm thick) on a pyrex petri dish. The uncovered sample was irradiated with an Ultraviolet Products CL1000M UV-crosslinker lamp (302 nm) that produced mid-range UV-wavelengths centred at 302 nm (0-850 J.cm<sup>-2</sup>). The crystalline material was agitated periodically during the irradiation to ensure even as possible UV-exposure. Photoreactions were monitored by <sup>1</sup>H-NMR and GPC. The average polymer molecular weights and irradiation doses of "as-polymerized" samples used for NMR, UV-VIS, and thermoanalytical experiments are shown in **Supplementary Table T 1**.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$  1.36 (s, 6H, C5-CH<sub>3</sub>), 1.61 (br. app. s, 4H, core N3 alkyl (CH<sub>2</sub>)<sub>2</sub>, H<sub>2</sub>O), 2.60 (dt, *J* = 16.75, 5.56 Hz, 2H, N1-C-CH<sub>2</sub>), 2.77 (dt, *J* = 16.84, 7.26 Hz, 2H, N1-C-CH<sub>2</sub>), 3.25 (dt, *J* = 13.72, 7.03 Hz, 2H, N1-CH<sub>2</sub>), 3.66 (s, 6H, O-CH<sub>3</sub>), 3.85 (br. t, 4H, 2 x N3-CH<sub>2</sub>), 3.94 (s, 2H, C6H), 4.00 (dt, *J* = 14.27, 6.39 Hz, 2H, N1-CH<sub>2</sub>). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  14.34, 18.37 (CH<sub>3</sub>), 25.63 ((CH<sub>2</sub>)<sub>2</sub>), 31.89 (N1-C-CH<sub>2</sub>), 32.15 (C-CH<sub>3</sub>), 40.74 (2 x N3-CH<sub>2</sub>), 43.82 (N1-CH<sub>2</sub>), 45.81 (N1-CH<sub>2</sub>), 51.84 (O-CH<sub>3</sub>), 61.98 (2 x CH), 151.36 (C=O), 171.90 (C=O).

Supplementary Table T 1 Average polymer molecular weights determined by GPC, and irradiation doses of "as-polymerized" samples used for NMR, UV-VIS, and thermoanalytical experiments

Entry	Irradiation dose	Polymer <i>M</i> <sub>n</sub>	$M_{ m w}/M_{ m n}$
1	0.5 kJ.cm <sup>-2</sup>	1.9 x 10 <sup>4</sup>	4.0
2	0.85 kJ.cm <sup>-2</sup>	$3.0 \times 10^4$	5.3

## **Supplementary Characterization Data**



### Poly-1 - 13C-NMR



#### **Gel Permeation Chromatography (GPC)**

The molecular weight of irradiated samples were determined by gel permeation chromatography performed on a Tosoh Ecosec HLC-8320GPC equipped with a refractive index (RI) detector, using Tosoh alpha 4000 (450 Å pore size) and 2000 (125 Å pore size) columns. DMF containing 10 mM LiBr was used as the solvent. Calibration curves were obtained using poly(styrene sulfonic acid sodium salt) standards. Unless specified, the quoted values for polymer  $M_n$  and polymer  $M_w/M_n$  were determined by integration of the polymer peak.

<u>Sample preparation</u>: Approximately 5 mg of sample was dissolved in 1.5 mL DMF containing 10 mM LiBr. "As-polymerized" materials were obtained directly from the reacted solids and analysed without purification. "Purified samples" were obtained by the method of serial precipitation, as per the procedure described on **p. S21**.

#### Oligomeric photo-products obtained upon irradiation of 2

Crystalline 2 (100 mg) was spread into a thin layer on a pyrex petri dish. The uncovered sample was irradiated with an Ultraviolet Products CL1000M UV-crosslinker lamp (302 nm) that produced mid-range UV-wavelengths centred at 302 nm (0.85 kJ.cm<sup>-2</sup>). The crystalline material was agitated periodically during the irradiation to ensure even as possible UV-exposure. The photo-products of the irradiation were determined by GPC (**Supplementary Figure S 1**).

Referring to Error! Reference source not found., the GPC chromatogram of irradiated 2 clearly shows the formation of low molecular weight oligomeric photo-products ( $M_n 2.6 \times 10^3$ ,  $M_w/M_n 5.2$ ).



Supplementary Figure S 1GPC chromatograms of monomer 2 and the irradiated sample 2 (302 nm, 0.85 kJ.cm<sup>-2</sup>)

#### Purification of poly-1 by serial precipitation

Purification of **poly-1** was achieved by the serial precipitation of polymer samples. This procedure involved dissolving 1-2 g of material in 15 mL CHCl<sub>3</sub>. The highest molecular weight portion of the sample was precipitated, upon addition of hexane (5 mL), and the suspension was centrifuged at 4000 rpm for 10 min to give a polymer pellet. The supernatant was decanted into a new Falcon tube, and then diluted with 5 mL hexane in order to precipitate the next molecular weight fraction. The process of centrifugation (4000 rpm, 10 min), removal and dilution of the supernatant with hexane (5 mL), was repeated a further 8 times. The obtained polymer pellets from each centrifugation step were then washed twice using 5 mL portions of the solvent mixture used for their isolation. The washed pellets were then dried under vacuum at ambient temperature (24 h) to give the purified polymer samples. The average polymer molecular weight and sample polydispersity was determined using GPC. If further purification was required, the serial precipitation was repeated using smaller portions of hexane (eg. 2 mL portions added instead of 5 mL portions). **Supplementary Figure S 2** shows the GPC chromatograms obtained after 1-round of serial precipitation.



Supplementary Figure S 2 Exemplary GPC chromatograms of purified samples obtained from 1-round of serial precipitation

#### **Depolymerization reactions**

The depolymerizations were performed by the irradiation of polymer samples (either as solids or as suspensions in MeCN) using a CL1000S UV-crosslinker lamp (Ultraviolet Products), coupled with two optical filters. A 250 nm shortpass optical filter (Asahi Spectra Co.) provided polychromatic light < 260 nm, while the second 230 nm bandpass filter provided UV <240 nm (eSource Optics, 50230FBB). Due to the use of these filters, precise energy doses for the depolymerization reactions are unknown.

#### 1. Solid-state depolymerization experiment

"As polymerized" solids (50 mg) were spread into a thin layer in a petri dish and were covered with the optical filters. The light-source was turned on, and the solids were irradiated for a period corresponding to 1.4 kJ.cm<sup>-2</sup> (prior to optical filtration). Periodically the depolymerized solids were sampled, and the solids were subjected to GPC analysis (without purification). The average molecular weight of the polymer ( $M_n$ ) was followed throughout the irradiation period, giving the depolymerization curve shown in **Supplementary Figure S 3.** Even after the long period of exposure to short wavelength UV, the polymer failed to depolymerize completely, and only underwent a 65 % decrease to molecular weight (compared to the starting polymer).



**Supplementary Figure S 3** Follows the solid state depolymerization of an "as polymerized" poly-1 sample over an irradiation dose of  $1.4 \text{ kJ.cm}^{-2}$  (prior to optical filtration).

#### 2. Cyclic irradiation experiments

The "as polymerized" solids (**P1**) were suspended in MeCN (50 mg in 10 mL) in a sealable quartz cell. The quartz cell was laid on its side and covered with the optical filters. The light-source was turned on and the suspensions were irradiated to achieve a total dose of 0.85 kJ.cm<sup>-2</sup> (prior to optical

filtration). After irradiation the clear solution was quantitatively transferred to a 25 mL round bottomed flask and the solvent was evaporated by rotary evaporator to give solid residues (**D1**). A 5 mg sample of the residues was taken and subjected to GPC analysis (without purification). The remaining solid residues were dissolved in acetonitrile (1 mL, 60 °C), cooled to ambient temperature, ultrasonicated and then transferred to a petri-dish. The solvent was evaporated in the open air, and the resulting solids were repolymerized using 302 nm UV (0.85 kJ.cm<sup>-2</sup>) to give **P2**. A portion of the "as polymerized" **P2** material was taken and subjected to GPC analysis (without purification). The remaining material was depolymerized and then repolymerized (as described above) to give **D2** and **P3**, respectively. The corresponding GPC chromatograms and summary data are presented in **Supplementary Figure S 4**.

Referring to **Supplementary Figure S 4**, the P2 chromatogram shows that the sample contains a small amount of residual monomer. The presence of monomer in the "as-polymerized" sample is attributed to the difficulties relating to recrystallization of the small sample and the presence of amorphous (hence non-reactive) monomer. Since the monomer peak area relates to only 2.3 % of the polymer peak area, and according to the typical procedure for quantification of *polymer* molecular weight, the polymer peak in the *P2 chromatogram* was integrated as a single, unimodal peak to give the reported value,  $M_n 1.9 \times 10^4$ .



**Supplementary Figure S 4** GPC chromatograms obtained from the cyclic irradiation experiment, and the corresponding values determined for  $M_n$  and  $M_w/M_n$  after each polymerization and depolymerization step.

#### Additional polymerization experiments with 1

The polymerization of 1.6 g of **1** (0 - 850 J.cm<sup>-2</sup>) was followed using GPC. Samples of the irradiated material were periodically collected and then directly subjected to GPC measurement without purification. The total sample  $M_n$  (closed circles) was determined by the integration of all components in the GPC chromatogram (i.e. monomer, dimer, oligomers and polymers). Monomer

conversion percentages were determined by comparison of the monomeric and total photoproduct peak areas. The molecular weight distribution of the photo-products  $(M_w/M_n)$  was also followed as a function of monomer conversion. **Supplementary Figure S 5** clearly indicates that the polymerization occurs via a step-polymerization mechanism. The gradual build-up of high molecular weight polymer and the formation of intermediate sized molecules suggest that the polymerization follows step-growth mechanism. The broad polydispersity of the photo-products was also shown to vary throughout the irradiation. The polydispersity increased proportionally with the photo-product molecular weight – but as the monomer conversion increased to values greater than 80%, the polydispersity of the photoproducts decreased, and in this particular case reached  $M_w/M_n XX (M_n XX)$  at 100% monomer conversion.



**Supplementary Figure S 5** GPC results indicate a step polymerization mechanism for the formation of **poly-1** (dark circles); the changes to photo-product polydispersity (open circles) are also shown as a function of monomer conversion.

#### Thermogravimetric Analysis (TGA)

Analyses were performed using a Perkin Elmer TGA7 thermogravimetric analyzer equipped with TAC 7/DX thermal analysis controller to measure weight changes in sample materials as a function of temperature. The TGA curves were recorded on Pyris software. The weight of the platinum sample pan was calibrated before each sample analysis. All tests were performed at a constant heating rate of 40°C.min<sup>-1</sup> under argon (flow rate: 20 mL.min<sup>-1</sup>) over a temperature range from room temperature to 600°C (temperature accuracy: 1-2 °C).

#### **Dynamic Mechanical Thermal Analysis (DMTA)**

Measurements were performed on a Rheometrics Mark IV DMTA instrument, operated in tensilemode at 1 Hz. A strip of poly-**1** film (100  $\mu$ m thick), measuring 10 .00 x 10.02 mm was heated from 20 - 120°C, at a rate of 3°C.min<sup>-1</sup>. Sample displacement gave the storage modulus (E'), the loss modulus (E'') and tan  $\delta$  (E''/E'). The peak in the tan  $\delta$  curve was taken as the glass transition temperature.

#### Ultraviolet-Visible Spectroscopy (UV-Vis)

UV-Vis spectra were recorded on a Hitachi U1800 spectrophotometer over a wavelength range of 1100-220 nm. Dichloromethane solutions of the monomer and polymer (3-5 x  $10^{-5}$  M monomer equiv.) were measured in sealable-quartz cuvettes (l = 1 cm).



Supplementary Figure S 6 UV-Vis spectra of 1 and the poly-1 (after 302 nm UV irradiation for 0.5 kJ.cm<sup>-2</sup>).

## Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS)

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were performed on a Bruker AutoflexIII MALDI-TOF mass spectrometer.

<u>Sample preparation</u>: The purified polymer samples were dissolved in CHCl<sub>3</sub> at a concentration of 1 mg.mL<sup>-1</sup>. A stock solution of the matrix was prepared by dissolving 10 mg of (E)-2-(3-(4-(tert-butyl)phenyl)-2-methylallylidene)malononitrile (DCTB) in 1 mL CHCl<sub>3</sub>. The polymer and matrix solutions were combined in the ratio of 10  $\mu$ L to 10  $\mu$ L, respectively. A 0.5  $\mu$ L aliquot of the mixture was then applied to the stainless steel sample plate and air-dried at ambient temperature (20 °C).

<u>Measurements:</u> Measurements were performed at an acceleration voltage of 19 kV, in positive ion linear mode. Suitable values for laser power, gain and laser shots were determined for each sample set as below in **Supplementary Table T 2Error! Reference source not found.** 

ID	GPC $M_{\rm n}$ and $M_{\rm w}/M_{\rm n}$	Laser power (%)	Gain	Laser shots
a	$M_{\rm n} 3.2 {\rm x} 10^3, M_{\rm w}/M_{\rm n} 1.1$	30%	x10	2,000
b	$M_{\rm n}  4.7 { m x} 10^3,  M_{\rm w} / M_{\rm n}  1.1$	40%	x10	3,000
c	$M_{\rm n} 7.0 {\rm x} 10^3, M_{\rm w}/M_{\rm n} 1.1$	50%	x20	4,000
d	$M_{\rm n} 1.6 {\rm x} 10^4, M_{\rm w}/M_{\rm n} 1.4*$	50%	x20	11,000

Supplementary Table T 2 MALDI-TOF MS Analyte details and measurement parameters

\*Further fractionation by GPC and subsequent MALDI-TOF analysis did not improve the quality of the MALDI-TOF spectrum



**Supplementary Figure S 7** Assignment of key ions in the MALDI-TOF MS of purified polymer sample **b** ( $M_n$  4.7x10<sup>3</sup>,  $M_w/M_n$  1.1)



**Supplementary Figure S 8** MALDI-TOF MS Spectra of the three other purified polymer samples (**a**, **c** and **d**). GPC sample details (**a**)  $M_n$  3.2x10<sup>3</sup>,  $M_w/M_n$  1.1, (**c**)  $M_n$  7.0x10<sup>3</sup>,  $M_w/M_n$  1.1, (**d**)  $M_n$  1.6x10<sup>4</sup>,  $M_w/M_n$  1.4. The uncorrected spectrum for **d** shows a build-up of material near m/z 1.6x10<sup>4</sup>, but after baseline correction (inset) it is lost to the baseline noise. Only ions up to m/z 10,584 could be observed after the correction.

#### Powder x-ray diffraction (XRD)

A Philips PW series diffractometer was used for powder diffraction measurements with Cu Ka radiation. The diffractometer was operated using Phillips Diffraction Software – PC-APD v3.6j. Powdered samples were analysed between 2 $\theta$  angles of 5°- 80°.



Supplementary Figure S 9 Comparison of powder XRD spectra for 1 (black) and poly-1 (red).

#### **Crystal Data and Methods**

CCDC depositions 841955, 841956 and 841957 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. As the individual crystal sizes were small (i.e. in the range of 40-60  $\mu$ m) or produced weak diffraction patterns, structural analyses were performed on the MX1 micro-crystallography beam-line at the Australian Synchrotron, Clayton, Victoria. The end station comprised a  $\varphi$  goniostat with a Quantum 210r area detector. Data were collected using the Blue Ice GUI<sup>3</sup> and processed using the XDS software.<sup>4</sup> Due to hardware constraints (fixed detector angle, minimum detector distance) the maximum obtainable resolution at the detector edge was approximately 0.81Å. The structures were solved and refined using the programs SHELXS-97<sup>5</sup> and SHELXL-97<sup>6</sup>, respectively. The program X-Seed<sup>7</sup> was used as an interface to the SHELX programs, and for preparation of the figures. Plausible positions of hydrogen atoms in water molecules and the amide, were located in the difference Fourier map, and were refined such that O-H distances were restrained to reasonable values (0.88-0.98Å); all other hydrogen atoms were placed in calculated positions using a standard riding model.

*Crystal data for 1*: C<sub>22</sub>H<sub>30</sub>N<sub>4</sub>O<sub>8</sub>, M = 478.50, Colourless Prism, 0.02 × 0.02 × 0.02 mm<sup>3</sup>, monoclinic, space group  $P2_1/c$  (No. 14), a = 9.5800(19), b = 16.550(3), c = 7.6900(15) Å,  $\beta = 112.13(3)^\circ$ , V = 1129.4(4) Å<sup>3</sup>, Z = 2,  $D_c = 1.407$  g/cm<sup>3</sup>,  $F_{000} = 508$ , goniostat with quantum 210r detector, synchrotron radiation,  $\lambda = 0.71253$  Å, T = 100(2)K,  $2\theta_{max} = 54.4^\circ$ , 15282 reflections collected, 2341 unique (R<sub>int</sub> = 0.0558). Final *GooF* = 1.051, RI = 0.0446, wR2 = 0.1147, R indices based on 2190 reflections with I >2sigma(I) (refinement on  $F^2$ ), 156 parameters, 0 restraints. Lp and absorption corrections applied,  $\mu = 0.108$  mm<sup>-1</sup>. The completeness measured for **1** is low (0.93) due to the hardware limitations of the synchrotron beamline (i.e. fixed detector angle, minimum detector distance). However, the amount of observed data is close to 100% and yields a more than satisfactory refinement (RI = 0.0446).

*Crystal data for* **2**: C<sub>24</sub>H<sub>36</sub>N<sub>4</sub>O<sub>9</sub>, M = 524.57, Colourless Prism,  $0.02 \times 0.02 \times 0.02 \text{ mm}^3$ , monoclinic, space group *C*2/*c* (No. 15), a = 22.4706(5), b = 9.3600(19), c = 16.0501(3) Å,  $\beta = 131.959(3)^\circ$ , V = 2510.3(5) Å<sup>3</sup>, Z = 4,  $D_c = 1.388$  g/cm<sup>3</sup>,  $F_{000} = 1120$ , goniostat with quantum 210r detector, synchrotron radiation,  $\lambda = 0.710699$  Å, T = 173(2)K,  $2\theta_{max} = 50.0^\circ$ , 15754 reflections collected, 2179 unique (R<sub>int</sub> = 0.0422). Final *GooF* = 1.087, *R1* = 0.0459, *wR2* = 0.1191, *R* indices based on 1961 reflections with I >2sigma(I) (refinement on  $F^2$ ), 174 parameters, 0 restraints. Lp and absorption corrections applied,  $\mu = 0.107$  mm<sup>-1</sup>.

Crystal data for 3:  $C_{80}H_{116}N_{24}O_{26}$ , M = 1829.97, Colourless Needle,  $0.025 \times 0.005 \times 0.005$  mm<sup>3</sup>, tetragonal, space group  $P4_2/n$  (No. 86), a = b = 22.260(3), c = 4.7700(10) Å, V = 2363.6(7) Å<sup>3</sup>, Z = 1,  $D_{\rm c} = 1.286$  g/cm<sup>3</sup>,  $F_{000} = 972$ , goniostat with quantum 210r detector, synchrotron radiation,  $\lambda =$ 0.710702 Å, T = 100(2)K,  $2\theta_{max} = 50.0^{\circ}$ , 28507 reflections collected, 2084 unique (R<sub>int</sub> = 0.1751). Final GooF = 1.133, RI = 0.0751, wR2 = 0.2148, R indices based on 1532 reflections with I >2sigma(I) (refinement on  $F^2$ ), 164 parameters, 9 restraints. Lp and absorption corrections applied,  $\mu$  $= 0.098 \text{ mm}^{-1}$ . Several attempts to model the residual electron density located in the cavities of the molecular columns were attempted. The final refinement contained water molecules that were disordered about a 4-bar symmetry element, with isotropic oxygen and fixed hydrogens. Two significant, additional electron density peaks (1.6 and 1.3) remained at <sup>1</sup>/<sub>4</sub>, <sup>1</sup>/<sub>4</sub>, <sup>3</sup>/<sub>4</sub> and <sup>1</sup>/<sub>4</sub>, <sup>1</sup>/<sub>4</sub>, <sup>1</sup>/<sub>4</sub>, respectively. These were attributed to further unresolved disorder in the water molecules. Although the refined water molecules do not appear to be coordinated to the main structure, it is possible that the atoms form hydrogen bonds with O14 and due to disorder, they were simply not observed. Water molecules participating in unobserved hydrogen bonds could also account for the larger atom displacement parameter of carbonyl O14. The displacement of O14 occurs in a direction perpendicular to the C=O bond, which may again be indicative of unobserved hydrogen bonds with water molecules. Alternatively, the general disorder of the water molecules could also produce a larger-than-normal atom displacement for O14, particularly if the amide carbonyl group had to

slightly reorient to accommodate the water molecules. As only very small, weakly diffracting crystals were obtained for **5**, a large proportion of essentially "unobserved" reflections were used in the refinement which probably lead to the elevated value for  $R_{int}$  (0.175). Nevertheless, a satisfactory refinement was obtained (*R1* = 0.0751).

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