Supporting Information

The difference between photo-iniferter and conventional RAFT polymerization: high livingness enables the straightforward synthesis of multiblock copolymers

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Figure S1: UV-Vis spectrum of Xan in water.



Figure S2: Determination of chain transfer constants of NAM and Xan in water and DMF respectively. The target DP was set to 15 for the rection in DMF with a monomer concentration of 2 mol L⁻¹ and for

the reaction in water target DP was set to 25 and monomer concentration was 0.5 mol L⁻¹. The standard error for water was 0.0148 and for DMF 0.0266.



Figure S3: Example spectra for the determination of c_{tr} . The polymerization of NAM was performed in DMF using a thermal initiator. Monomer conversion was determined comparing the signals of the NAM side chain (red, constant) with the acrylic signals (green, decreasing over time). CTA consumption was determined using the signal of the Z group (CH₃, yellow) and measuring the decrease of the signals of the R-group (purple and blue).



Scheme S1: Formal reduction of thiocarbonylthio radical using a tertiary amine to temporally remove the radical from the PI-RAFT equilibrium.



Figure S4: Monomer conversion by NMR spectroscopy (400 MHz, D_20 or CHCl₃) before and after 1 h of UV (365 nm, 2 W) irradiation in water and DMF respectively.



Figure S5: SEC curves of polymerization reactions of NAM with xanthate CTA at a Monomer/CTA ratio of 50. Polymerization was performed in DMF under UV-initiation, or via an azo initiator. PI-RAFT was also performed in water and under the presence of triethylamine (NEt₃) in DMF.

| Number of | Irradiation | | | | Theoretical | | | | Targete | Cumulative |
|-----------|-------------|---------------------|--------------------|--------|-------------|-------------------------|------------------------|-----------------------------------|-----------|-----------------------|
| Number of | time | $V_{Water \ added}$ | V_{total} | Conv.ª | molecular | [Xan] | M_n^{b} | $\mathbf{\tilde{D}}^{\mathrm{b}}$ | d overall | DP (NMR) ^c |
| BIOCKS | ume | | | | weight | | | | DP | |
| | (h) | (mL) | (μL) | (%) | (g mol⁻¹) | (mmol L ⁻¹) | (g mol ⁻¹) | | | |
| 1 | 1.0 | 9.37 | 10.00 | 96.4 | 6,800 | 10.0 | 5,000 | 1.45 | 50 | 52 |
| 2 | 1.0 | 9.37 | 10.63 | 98.8 | 13,800 | 9.4 | 9,500 | 1.47 | 100 | 111 |
| 3 | 1.0 | 9.37 | 11.26 | 96.8 | 20,600 | 8.9 | 14,200 | 1.41 | 150 | 195 |
| 4 | 1.0 | 9.37 | 11.89 | 97.9 | 27,500 | 8.4 | 18,800 | 1.37 | 200 | 271 |
| 5 | 1.0 | 9.37 | 12.52 | 96.9 | 34,400 | 8.0 | 23,200 | 1.34 | 250 | 302 |
| 6 | 1.0 | 9.37 | 13.15 | 98.68 | 41,300 | 7.6 | 28,400 | 1.34 | 300 | 334 |
| 7 | 1.0 | 9.37 | 13.77 | 98.9 | 48,300 | 7.3 | 33,700 | 1.32 | 350 | 390 |
| 8 | 1.0 | 14.37 | 19.40 | 93.8 | 54,900 | 5.2 | 36,400 | 1.34 | 400 | 478 |
| 9 | 1.0 | 14.37 | 20.03 | 91.6 | 61,400 | 5.0 | 43,300 | 1.26 | 450 | 638 |
| 10 | 2.0 | 14.37 | 20.66 | 95.32 | 68,100 | 4.8 | 48,300 | 1.26 | 500 | 746 |
| 11 | 2.0 | 14.37 | 21.29 | 98.6 | 75,100 | 4.7 | 52,100 | 1.26 | 550 | 748 |
| 12 | 2.0 | 19.37 | 26.92 | 96.5 | 81,900 | 3.7 | 54,700 | 1.3 | 600 | 773 |
| 13 | 2.0 | 19.37 | 27.55 | 95.5 | 88,600 | 3.6 | 58,700 | 1.27 | 650 | 759 |
| 14 | 2.5 | 19.37 | 28.18 | 97.8 | 95,500 | 3.5 | 61,600 | 1.3 | 700 | 776 |
| 15 | 2.5 | 24.37 | 33.81 | 99.0 | 102,500 | 3.0 | 69,300 | 1.27 | 750 | 887 |
| 16 | 3.0 | 24.37 | 34.44 | 96.3 | 109,300 | 2.9 | 70,400 | 1.34 | 800 | 963 |
| 17 | 3.0 | 24.37 | 35.06 | 97.8 | 116,200 | 2.9 | 76,400 | 1.31 | 850 | 950 |
| 18 | 8.0* | 34.37 | 45.69 | 95.0 | 122,900 | 2.2 | 86,100 | 1.27 | 900 | 1063 |
| 19 | 4.5 | 34.37 | 46.32 | 95.4 | 129,500 | 2.2 | 87,200 | 1.29 | 950 | 1054 |
| 20 | 6.0 | 34.37 | 46.95 | 95.2 | 136,200 | 2.1 | 90,100 | 1.33 | 1000 | 1058 |

Table S1: Synthesis of NAM-based pseudo-multiblock with a DP of 50 per segment, 629 μ L of NAM were added per block. Water was used as a solvent.

*Transferred to a larger reaction vessel.

a) determined via ¹H-NMR in D₂0 (400 MHz).

b) determined via SEC in THF (Polystyrene calibration).

c) determined via 1 H-NMR in D₂0 (400 MHz) by comparing the signal of the R group (CH₃ at 1 ppm)

with the signal of the PNAM side chain (4 x CH_2 between 4.1 and 3 ppm).

| Number | Irradiation | | | | Theoretical | | | | Targeted | Cumulative |
|--------|-------------|------------------|--------------------|-------------------------|------------------------|-------------------------|------------------------|-----------------------------------|----------|-----------------------|
| of | time | $V_{Wateradded}$ | V_{total} | Conversion ^a | molecular | [Xan] | M_n^{b} | $\mathbf{\tilde{D}}^{\mathrm{b}}$ | overall | DP (NMR) ^c |
| Blocks | ume | | | | weight | | | | DP | |
| | (h) | (mL) | (μL) | (%) | (g mol ⁻¹) | (mmol L ⁻¹) | (g mol ⁻¹) | | | |
| 1 | 1.0 | 9.73 | 10.36 | 96.3 | 27,200 | 2.5 | 19,200 | 1.47 | 200 | 182 |
| 2 | 1.5 | 9.73 | 10.99 | 98.2 | 54,900 | 2.4 | 34,500 | 1.29 | 400 | 393 |
| 3 | 1.5 | 9.73 | 11.62 | 98.2 | 82,600 | 2.2 | 43,700 | 1.33 | 600 | 629 |
| 4 | 1.5 | 9.73 | 12.25 | 99.4 | 110,700 | 2.1 | 55,800 | 1.29 | 800 | 889 |
| 5 | 1.5 | 9.73 | 12.88 | 98.6 | 138,500 | 2.0 | 66,900 | 1.33 | 1000 | 1041 |
| 6 | 1.5 | 9.73 | 13.51 | 97.6 | 166,100 | 1.9 | 74,000 | 1.38 | 1200 | 1249 |
| 7 | 2.5 | 14.73 | 19.13 | 98.6 | 193,900 | 1.3 | 86,900 | 1.38 | 1400 | 1321 |
| 8 | 5.0 | 19.73 | 24.76 | 97.9 | 221,600 | 1.0 | 102,700 | 1.35 | 1600 | 1632 |
| 9 | 3.5 | 19.73 | 25.39 | 97.3 | 242,200 | 1.0 | 110,400 | 1.36 | 1800 | 1665 |
| 10 | 3.0 | 19.73 | 26.02 | 99 | 270,100 | 1.0 | 116,400 | 1.39 | 2000 | 1829 |
| 11 | 3.0 | 24.73 | 31.65 | 99.9 | 298,300 | 0.8 | 117,000 | 1.57 | 2200 | 2134 |
| 12 | 3.0 | 24.73 | 32.28 | 98.9 | 326,200 | 0.8 | 105,000 | 1.90 | 2400 | 1833 |

Table S2: Synthesis of NAM-based Pseudo-Multiblock with a DP of 200 per segment, 629 μ L of NAM were added per block. Water was used as a solvent.

a) determined via 1 H-NMR in D₂0 (400 MHz).

b) determined via SEC in THF (Polystyrene calibration).

c) determined via ¹H-NMR in D_20 (400 MHz) by comparing the signal of the R group (CH₃ at 1 ppm) with the signal of the PNAM side chain (4 x CH₂ between 4.1 and 3 ppm).



Figure S6: Determination of C_{tr} of DMA and Xan in water. The target DP was set to 25 and monomer concentration was 0.5 mol L⁻¹. The standard error was 0.0422.

Table S3: Synthesis of multiblock copolymer from NAM, NiPAAm and DMA. Water was used as a solvent. Per block 0.5-1.5 mL of solution was removed as a sample, which was factored in monomer feeds.

| Nr of | | Mono | omer | | | | Theoretical | [Xan] | M_n^{b} | Ðb | Targeted |
|---------|-----------|--------|------|------------------|--------------------|--------------------|------------------------|-------------------------|------------------------|------|----------|
| Diselys | Irr. time | | | $V_{Wateradded}$ | V_{total} | Conv. ^a | molecular | | | | overall |
| BIOCKS | | | m | | | | weight | | | | DP |
| | (h) | | (mg) | (mL) | (mL) | (%) | (g mol ⁻¹) | (mmol L ⁻¹) | (g mol ⁻¹) | | |
| 1 | 1 | DMA | 248 | 4.74 | 5.00 | 98 | 2,600 | 20.0 | 1,700 | 1.22 | 25 |
| 2 | 1 | NiPAAm | 272 | 0.93 | 6.00 | 97 | 5,400 | 16.0 | 3,800 | 1.23 | 50 |
| 3 | 1 | NAM | 328 | 0.87 | 6.96 | 96 | 8,800 | 13.0 | 6,100 | 1.25 | 75 |
| 4 | 1 | DMA | 447 | 1.79 | 9.01 | 98 | 13,600 | 10.0 | 8,100 | 1.26 | 125 |
| 5 | 1 | NiPAAm | 499 | 1.71 | 11.02 | 97 | 19,100 | 8.0 | 11,600 | 1.25 | 175 |
| 6 | 1 | NAM | 611 | 1.62 | 12.98 | 95 | 25,800 | 6.7 | 17,500 | 1.21 | 225 |
| 7 | 1 | DMA | 845 | 3.38 | 17.04 | 99 | 35,600 | 5.0 | 20,100 | 1.19 | 325 |
| 8 | 1 | NiPAAm | 936 | 3.12 | 20.68 | 95 | 46,400 | 4.0 | 29,000 | 1.16 | 425 |
| 9 | 1 | NAM | 1139 | 3.02 | 24.21 | 96 | 96 59,900 | | 37,400 | 1.2 | 525 |
| 10 | 1 | DMA | 783 | 3.14 | 27.66 | 95 | 69,300 | 2.9 | 42,100 | 1.16 | 625 |
| 11 | 1.5 | NiPAAm | 878 | 3.00 | 31.04 | 97 | 80,300 | 2.5 | 50,500 | 1.16 | 725 |
| 12 | 2 | NAM | 1078 | 2.86 | 34.36 | 97 | 94,000 | 2.2 | 58,100 | 1.19 | 825 |
| 13 | 2 | DMA | 735 | 2.94 | 37.07 | 97 | 103,600 | 2.0 | 61,800 | 1.19 | 925 |

| 14 | 2 | NiPAAm | 828 | 2.83 | 40.22 | 97 | 114,600 | 1.8 | 70,900 | 1.18 | 1025 |
|----|---|--------|------|------|-------|----|---------|-----|--------|------|------|
| 15 | 2 | NAM | 1020 | 2.70 | 43.33 | 96 | 128,200 | 1.7 | 77,700 | 1.2 | 1125 |
| 16 | 2 | DMA | 708 | 2.84 | 46.40 | 96 | 137,700 | 1.5 | 79,400 | 1.24 | 1225 |
| 17 | 6 | NiPAAm | 799 | 2.73 | 49.43 | 95 | 148,400 | 1.4 | 93,000 | 1.21 | 1325 |
| 18 | 8 | NAM | 967 | 2.56 | 51.36 | 96 | 162,000 | 1.3 | 92,600 | 1.26 | 1425 |
| 19 | 8 | DMA | 666 | 2.64 | 53.18 | 96 | 171,500 | 1.3 | 97,000 | 1.27 | 1525 |
| 20 | 8 | NiPAAm | 753 | 2.55 | 55.98 | 97 | 182,400 | 1.2 | 90,300 | 1.29 | 1625 |
| | | | | | | | | | | | |

a) determined via ¹H-NMR in D₂0 (400 MHz).

b) determined via SEC in THF (Polystyrene calibration).

Determination of the DP via NMR was not possible as the signals of NiPAAm strongly interfer with the signal of the end group.



Figure S7: Comparison of SEC traces of polymers (PNAM with Xanthate as CTA und PI-RAFT conditions (365 nm, 2W)) with a cumulative targeted DP of 1000.



Figure S8: SEC traces of PI-RAFT polymerization of NAM using Xan at varying monomer feeding rates (THF, PS calibration).



Figure S9: Investigation of multiblock 3 (Repeating sequence of DMA, NiPAAm, NAM) via aqueous SEC (0.3% formic acid, 0.1 mol L⁻¹ NaCl) using a poly(vinyl pyridine) (PVP) calibration as well as multi angle lights scattering (MALS) calibration.



Figure S10: NMR spectra of pseudo-multiblock synthesis using NAM with a DP of 50 per segment. The end group of Xan (CH_3 of the Z group) is visible throughout the process indicating a high livingness.



Figure S11: NMR spectra of pseudo-multiblock synthesis using NAM with a DP of 200 per segment. The end group of Xan (CH_3 of the Z group) is visible throughout the process indicating a high livingness.



Figure S12: NMR spectra of multiblock synthesis using NAM, NiPAAm, DMA with a DP of 25 to 100 per segment. The CH_3 group of NiPAAm overlaps with the end group of Xan (CH_3 of the Z group).

Experimental Part

Materials and Instrumentation

The chemicals used in this study were purchased from Sigma-Aldrich, Alfa Aesar, TCI (Tokio Chemical Industry), Acros Organics, Merck, Carl Roth and Fisher Chemicals. Inhibitor from monomers were removed via a short aluminum oxide column (*N*-acryloyl morpholine (NAM), dimethyl acrylamide (DMA)) or via recrystallization (*N*-isopropyl acrylamide (NiPAAm)) prior to polymerization.

Deionized water was used for all reactions in aqueous media, and *N*,*N*-dimethylformamide (DMF) was used in grade for peptide synthesis (> 99.8 %).

¹H-NMR spectra were recorded on a Bruker AVANCE NEO 400 MHz spectrometer in $CDCl_3$ or D_2O . Chemical shift values are reported in ppm, and the residual proton signal of the solvent was used as the internal standard.

Size exclusion chromatography (SEC) with simultaneous UV, and RI detection was performed with THF as the eluent at a flow of 1 mL min⁻¹ at room temperature; the stationary phase was a $300 \times 8 \text{ mm}^2$ PSS SDV linear M column. Solutions containing polymer samples were filtered through 0.45 µm Polytetrafluoroethylene filters; the injected volume was 100 µL. Polystyrene standards up to a molecular weight of 2,520,000 g mol⁻¹ (PSS, Mainz, Germany) were used for calibration.

Aqueous SEC was measured on an instrument from PSS (Mainz, Germany) using set of NOVEMA Max columns (1 x 30 Å, 8 x 3000 mm; 2 x 1000 Å, 8 x 300 mm) including RI and UV (280 and 309 nm), as well as a 7-angle MALS detector (SLD 7000). Water with 0.3 Vol% formic acid and 0.1 mol L⁻¹ NaCl was used as the eluent and poly(vinyl pyridine) was used as calibration. For MALS measurements, dn/dc was determined by performing different injections varying the injections volume and thus the injected sample amount. The area under the RI-curve was integrated and fitted against injected mass to determine the dn/dc (slope of the linear regression). For multiblock 3 (block 20) the dn/dc was found to be 0.282.

A UVP Hand Lamp, EL Serie, 2UV[™] Twin model (UVPA95-0271-02) with 254 and 365 nm emission wavelength and a power of 4 W was used for light induced polymerization experiments. The 365 nm tube was used exclusively for polymerization.

A LA-100, RS232 syringe pump from HLL Landgraf Laborsysteme in combination with 3 mL disposable syringes with a 10 mm diameter were used for feeding experiments.

Experimental Procedures

2-((Ethoxycarbonothioyl)thio)propionic acid (Xan)

Potassium ethyl xanthogenate (15 g, 93.5 mmol) was loaded into a round bottom flask and the reaction volume was purged with nitrogen. In another flask 2-bromopropionic acid (2.8 mL, 31.1 mmol) was dissolved in dry acetonitrile (30 mL) and purged with nitrogen. The solution was then added to the

xanthogenate over a period of 20 min under stirring while cooling the reaction mixture to 0°C in an ice bath. The reaction was left to stir overnight. After that a light brown solid was formed which was filtered off and the solvent from the filtrate was evaporated. The resulting orange solid was dissolved in 150 mL of dichloromethane (DCM) and washed with a saturated aqueous sodium carbonate solution (3 x 90 mL). The organic phase dried over sodium sulfate and DCM was removed via evaporation yielding a yellow liquid. The product was purified by silica column chromatography (9:1, hexane : acetic acid) to yield an off-white solid (4.52 g, 74.9 %). ¹H-NMR (CDCl₃, 400 MHz): δ = 11.2 ppm (s, 1H, COO<u>H</u>), δ = 4.6 ppm (q, 2H, CH₃-CH₂-O), δ = 4.4 ppm (q, 1H, S-<u>CH(</u>CH₃)-COOH) δ = 1.6 ppm (d, 3H, <u>CH₃-CH</u>), δ = 1.4 ppm (t, 3H, J = 9 Hz, <u>CH₃-CH₂</u>).

General Polymerization Procedure

Monomer (after inhibitor removal), Xan, solvent and in the case of thermal polymerization azo initiator were mixed in a glass vial (5 mL, Pyrex) or a 1-necked round bottom flask (50/100 mL) and sealed with a rubber septum. Oxygen was removed by purging with nitrogen gas via a needle for 10 min prior to polymerization. Magnetic stirring was used for reactions in round bottom flasks, in vials no stirring was used.

Thermally induced polymerization reactions

When using water as a solvent, 2,2'-[Azobis(1-methylethyliden)]bis[4,5-dihydro-1Himidazoldihydrochlorid (VA-044) was used as an initiator at a temperature of 70°C for 2 h, and 4,4'-Azobis(4-cyanovaleric acid) (ACVA) at 75°C (16 h) was used when working in DMF. Polymerization mixtures were heated in an oil bath. Polymerization was stopped by removal of the sample from the oil bath.

Photo-induced polymerization reactions

After degassing, samples were placed in front of an UV-Lamp (2 W, 365 nm) with an approximate distance of 1 cm from the light source. Polymerization was stopped by removal of the sample from the light source. Due to heat generation of the lamp the temperature of the polymerization mixture was slightly elevated (~30 °C).

Determination of the chain transfer constant

Monomer, CTA, azo initiator and solvent were mixed in a 1-necked round bottom flask (50 mL) with a magnetic stirrer and sealed with a rubber septum. When using DMF as a solvent, 4,4'-Azobis (4-cyanovaleric acid) (ACVA) was used as initiator at a temperature of 70°C for 3 h, and 2,2'-Azobis[2-methylpropionamidin]dihydrochloride (V-50) at 60°C for 3 h was used when working in water.

The first sample was taken as t = 0 value. Through purging the flask with nitrogen gas via a needle for 10 min oxygen was removed. Polymerization mixtures were heated in an oil bath. Samples were taken

after defined times through a needle while purging with nitrogen. Consumption of CTA and monomer was determined via ¹H-NMR spectroscopy.

Variation of targeted DP

For variation of targeted DPs, NAM was diluted with solvent (DMF or water) to reach a monomer concentration of 2 mol L⁻¹. Xan was weighed in directly (low targeted DPs) or added via stock solution in the respective solvent (high targeted DPs, 5 mg mL⁻¹) to reach the respective monomer/CTA ratio. In the latter case the volume of the stock solution was subtracted from the added solvent. Polymerizations were performed photo-initiated or thermally using respective azo-initiators at a CTA/I ratio of 5. ACVA at 75°C for 16 h was used in DMF and 2,2'-[Azobis(1-methylethyliden)]bis[4,5-dihydro-1H-imidazoldihydrochlorid] (VA044) at 70°C for 2h was used in water.

Conversion was determined directly from reaction solution via NMR (diluted with $CDCl_3$ for samples in DMF or D_2O for samples in water). For this, signals of the acrylic protons (6.71-5.52 ppm) were referenced with signals associated with the entirety of monomer in the reaction solution (e.g. for NAM: signals of the side chain CH_2 -groups between 4 and 3 ppm). Samples were dried under vacuum prior to SEC measurements in THF (PS calibration).

Table S4: Reaction conditions for polymerization of NAM and Xan with different M/CTA ratios in DMF. The monomer concentration was 2 mol L^{-1} in each case. In case of thermal RAFT polymerization, the ratio of CTA to initiator was 5. The overall reaction volume was 1 mL.

| M/CTA | Concentration | Concentration | M_{theo} | M _n | Ð | Conv. | M _{theo} (PI)* | M _n | D | Conv. |
|-------|---------------|---------------|------------|----------------|-----------|-------|-------------------------|----------------|-----------|-------|
| | of CTA | of Initiator | (thermal)* | (Measu | red, ther | mal) | | (Mea | sured, PI |) |
| | (mm ol 1 -1) | (mm ol 1 -1) | (a mol-1) | (a mol-1) | | (0/) | | (a mol-1) | | (0/) |
| | (mmor L -) | (mmor L -) | (g moi -) | (g moi -) | | (%) | | (g moi -) | | (%) |
| 5 | 400 | 80 | 800 | 800 | 1.47 | 99.9 | 700 | 1,000 | 1.33 | 71.0 |
| 10 | 200 | 40 | 1,400 | 1,200 | 1.70 | 99.9 | 1,500 | 1,600 | 1.49 | 91.0 |
| 20 | 100 | 20 | 2,500 | 1,900 | 1.85 | 99.8 | 2,800 | 2,800 | 1.58 | 94.0 |
| 50 | 40 | 8 | 6,000 | 5,000 | 1.62 | 99.3 | 7,000 | 5,300 | 1.67 | 96.8 |
| 100 | 20 | 4 | 11,900 | 9,100 | 1.64 | 99.5 | 13,800 | 9,000 | 1.74 | 96.6 |
| 200 | 10 | 2 | 23,600 | 13,000 | 1.72 | 99.5 | 28,200 | 20,300 | 1.66 | 99.4 |
| 500 | 4 | 0.8 | 58,400 | 20,000 | 1.81 | 99 | 68,400 | 30,300 | 1.99 | 96.7 |
| 1000 | 2 | 0.4 | 116,400 | 23,100 | 1.98 | 98.9 | 139,800 | 40,900 | 2.12 | 99.0 |
| 2000 | 1 | 0.2 | 226,500 | 26,700 | 1.98 | 96.3 | 274,900 | 55,000 | 2.34 | 97.4 |
| 5000 | 0.4 | 0.08 | 419,100 | 38,300 | 1.72 | 71.3 | 679,800 | 59,900 | 2.73 | 96.4 |
| | | | | | | | | | | |

* Calculated for respective conversion.

Table S5: Reaction conditions for polymerization of NAM and Xan with different M/CTA ratios in water.The monomer concentration was 2 mol L^{-1} in each case. In case of thermal RAFT polymerization, theratio of CTA to initiator was 5. The overall reaction volume was 1 mL.

| M/CTA | Concentration | Concentration | M_{theo} | Mn | Ð | Conv. | M_{theo} | M _n | Ð | Conv. |
|-------|-------------------------|-------------------------|------------------------|-----------|-----------|-------|------------|----------------|------|-------|
| | of CTA | of Initiator | (thermal)* | (Measur | ed, therr | mal) | (PI)* | Measured, PI) | | |
| | | | | | | | | | | |
| | (mmol L ⁻¹) | (mmol L ⁻¹) | (g mol ⁻¹) | (g mol⁻¹) | | (%) | | (g mol⁻¹) | | (%) |
| 10 | 200 | 40 | 1,400 | 1,000 | 1.55 | 99.9 | 1,400 | 1,200 | 1.49 | 99.5 |
| 20 | 100 | 20 | 2,500 | 2,100 | 1.46 | 99.2 | 2,500 | 2,000 | 1.48 | 99.9 |
| 50 | 40 | 8 | 6,100 | 4,700 | 1.35 | 99.9 | 6,100 | 5,200 | 1.40 | 99.9 |
| 100 | 20 | 4 | 11,900 | 9,700 | 1.38 | 99.8 | 11,900 | 11,300 | 1.39 | 99.9 |
| 200 | 10 | 2 | 23,700 | 17,800 | 1.48 | 99.9 | 23,700 | 23,200 | 1.44 | 99.9 |
| 500 | 4 | 0.8 | 58,800 | 43,800 | 1.90 | 99.7 | 58,900 | 101,300 | 1.74 | 99.9 |
| 1000 | 2 | 0.4 | 113,800 | 111,000 | 2.08 | 96.7 | 116,600 | 239,300 | 2.29 | 99.1 |
| 2000 | 1 | 0.2 | 232,800 | 177,500 | 2.31 | 99.0 | 208,600 | 285,100 | 2.13 | 88.7 |
| 5000 | 0.4 | 0.08 | 587,100 | 264,000 | 2.25 | 99.9 | 379,700 | 506,400 | 1.88 | 64.6 |
| | | | | | | | | | | |

* Calculated for respective conversion.

Variation of Xan concentration at constant DP

For variation of Xan concentration at constant DP (50), a stock solution of NAM (1107 μ L, 8 mmol, 4 mol L⁻¹) and Xan (31 mg, 0.16 mmol) in solvent (993 μ L) was prepared. 1 mL of the solution was used at this concentration, the remaining stock was diluted with solvent to reach different total monomer concentrations (2, 1, 0.5, 0.25 mol L⁻¹). In case of thermally initiated polymerization reactions, initiator (ACVA or VA044 at a CTA/I ratio of 5) was added via a stock solution after dilution to maintain a constant concentration in all samples. For reactions in the presence of amin base Triethylamine was added in a 3-fold excess to the CTA before degassing.

Table S6: Reaction conditions for polymerization of NAM and Xan at constant targeted DP (50) in water. In case of thermal RAFT polymerization, the ratio of CTA to initiator was 5. The overall reaction volume was 1 mL.

| Concentration | Concentration | Concentration | M _n | Ð | Conv. | M _n | Ð | Conv. |
|-------------------------|------------------------|-------------------------|------------------------|------|-------|----------------|------|-------|
| of CTA | of monomer | of Initiator | (thermal) | | | (PI) | | |
| (mmol L ⁻¹) | (mol L ⁻¹) | (mmol L ⁻¹) | (g mol ⁻¹) | | (%) | (g mol⁻¹) | | (%) |
| 80 | 4 | 16 | 4,900 | 1.63 | 99.9 | 5,400 | 1.58 | 99.9 |
| 40 | 2 | 8 | 5,300 | 1.37 | 99.4 | 4,900 | 1.50 | 99.9 |
| 20 | 1 | 4 | 5,100 | 1.31 | 99.9 | 4,700 | 1.44 | 99.9 |
| 10 | 0.5 | 2 | 4,900 | 1.30 | 98.9 | 4,700 | 1.41 | 98.9 |
| 5 | 0.25 | 1 | 4,900 | 1.28 | 98.6 | 4,600 | 1.41 | 96.6 |
| | | | | | | | | |

Table S7: Reaction conditions for polymerization of NAM and Xan at constant targeted DP (50) in water in the presence of NEt₃. In case of thermal RAFT polymerization, the ratio of CTA to initiator was 5. The overall reaction volume was 1 mL.

| Concentration | Concentration | Concentration | Concentration | M _n | Ð | Conv. | M _n | Ð | Conv. |
|-------------------------|------------------------|-------------------------|-------------------------|------------------------|------|-------|------------------------|------|-------|
| of CTA | of monomer | of Initiator | of NEt_3 | (thermal) | | | (PI) | | |
| (mmol L ⁻¹) | (mol L ⁻¹) | (mmol L ⁻¹) | (mmol L ⁻¹) | (g mol ⁻¹) | | (%) | (g mol ⁻¹) | | (%) |
| 80 | 4 | 16 | 12 | 15,700 | 3.64 | 91.6 | 66,500 | 1.80 | 89.0 |
| 40 | 2 | 8 | 6 | 21,200 | 2.33 | 99.9 | 36,900 | 2.07 | 98.7 |
| 20 | 1 | 4 | 3 | 20,000 | 2.09 | 99.9 | 31,900 | 1.98 | 98.8 |
| 10 | 0.5 | 2 | 1.5 | 20,100 | 1.84 | 99.9 | 25,300 | 2.14 | 97.7 |
| 5 | 0.25 | 1 | 0.75 | 20,500 | 1.69 | 99.9 | 24,600 | 1.99 | 93.0 |

Synthesis of (pseudo-)multiblock copolymers

Monomer (NAM, NiPAAm or DMA, 0.5 mol L⁻¹) was dissolved in water to obtain a total volume of 10 mL) in a round bottom flask (50 or 100 mL). The reaction solution was closed using a rubber septum and purged with nitrogen. Polymerization was performed under UV light irradiation. The reaction time was set to 1 h for the initial block. After this time a sample was withdrawn and the conversion was determined via NMR as described above, as well as SEC measurements were performed. If the conversion was found to be high (above 90%), the next monomer was added. If the conversion was insufficient, irradiation was continued after oxygen removal. In case of chain extension, monomer was added directly (for pseudo-multiblocks) or as a 1 mol L⁻¹ solution in water for the multiblock copolymer. For pseudo multiblocks, the reaction solution was diluted when stirring became impossible due to increased viscosity. The new reaction time was set to the time required for the former block. The process was repeated until the desired number of blocks have been installed. The theoretical molecular weight was determined adding molecular weights of all blocks, which in turn were determined using the targeted DP and the actual conversion.

Feeding experiments

In a 50 mL round bottom flask, Xan (1.5 mg, 0.075 mmol) was dissolved in water (1 mL) under stirring. The flask was closed by a rubber seal and purged with nitrogen. A stock solution of NAM (94.5 µL mL⁻¹) in water (3 mL) was prepared in a glass vial and sealed using a rubber septum. The stock solution was purged with nitrogen and 2.5 mL of it were loaded into plastic syringe and placed into a syringe pump. The syringe was connected to the solution of a xanthate via a needle in a way, that monomer stock would drip into the stirred polymerization solution upon addition. 2 mL of monomer stock solution were added per reaction. The solution containing the xanthate was irradiated over the whole reaction with a UV lamp. The reaction time varied according to the feeding rate between 1 and 30 h. Irradiation was maintained 10 min after feeding was completed. For a reaction with immediate monomer addition, both solutions (1 mL containing Xan and 2 mL containing NAM) were mixed before purging and irradiation.