

Supporting Information

The Bright and the Dark Side of the Sphere: Light-Stabilized Microparticles

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Contents

1	Materials	3
2	Instrumentation and Methods	3
2.1	Scanning Electron Microscopy	3
2.2	Nuclear Magnetic Resonance Spectroscopy	4
2.3	THF Size Exclusion Chromatography	4
2.4	Flash Column Chromatography	4
2.5	Particle synthesis setup.....	5
2.6	Online Light Scattering	5
3	Synthetic procedures	6
3.1	Synthesis of 4,4'-(hexane-1,6-diyl)bis(1,2,4-triazoline-3,5-dione) (BisTAD).....	6
3.2	Synthesis of 2-(methacryloyloxy)ethyl 2-naphthanoate (M1)	11
3.3	RAFT polymerization	12
3.4	Particle Synthesis	16
3.5	Particle degradation.....	16
3.6	Light-Stabilization.....	16
4	Additional Data	17
4.1	SEC Data	17
4.2	SEM Data	18
5	References	21

1 Materials

2-Hydroxyethyl methacrylate (50 ppm MEHQ, > 99 %, Sigma-Aldrich), 2-Cyanopropan-2-yl benzodithioate (97.0 %, Sigma-Aldrich), 2-Naphtoyl chloride (98.0 %, Combi-Blocks), Acetonitrile (HPLC grade, RCI Labscan), Ammonium chloride (Merck), Azobisisobutyronitrile (12 w% in acetone, recrystallized from ethanol, Sigma-Aldrich), Cyclohexane (Analytical reagent, Ajax Finechemicals), Dichloromethane (99.9 %, Fisher Chemical), N,N-Dimethylformamide (99.8 %, Thermo Fisher), Ethanol (99.5%, Ajax Finechemicals), Ethyl carbazate (97.0 %, Acros), Hexamethylene diisocyanate (>98 %, Sigma-Aldrich), Hydrochloric acid (32.0 %, Ajax Finechemicals), Isopropanol (99.8 %, Fisher Chemical), Methanol (99.8 %, Ajax Finechemicals), Methyl methacrylate (30 ppm MEHQ, 99.0 %, Sigma-Aldrich), Potassium carbonate (99.0 %, Chem Supply), Sodium Sulfate (99.0 %, Ajax Finechemicals), Toluene (99.8 %, Thermo Fisher), Trichlorocyanuric acid (99.8 %, Sigma-Aldrich), Triethylamine (99.0 %, Ajax Finechemicals), methacryloyl chloride (Sigma-Aldrich).

2 Instrumentation and Methods

2.1 Scanning Electron Microscopy

Scanning electron microscopy (SEM) images were recorded on a Tescan Mira3 Scanning Electron Microscope. Samples were dispersed in acetonitrile or toluene (about 5 mg mL⁻¹) by sonication for 30 s and then drop casted directly onto plasma cleaned aluminium SEM stubs. For detailed surface analysis, the drop casted samples were evaluated without conductive coating using a secondary electron detector in beam deceleration mode (BDM) at a working distance of 7 mm using an acceleration voltage of 1 kV. Scan speeds and line or image integration were adjusted to achieve acquisition times of 24 s per image. Analysis was done in ImageJ, with particle sizing and dispersity calculations based on counting a minimum of 200 particles, using the following equations:

$$D_n = \frac{\sum N_i D_i}{\sum N_i}$$

$$D_w = \frac{\sum N_i D_i^4}{\sum N_i D_i^3}$$

Where D_n is the number-average diameter, D_w is the weight-average diameter, N_i is the number of particles measured, and D_i is the diameter of the measured particle. The dispersity \mathcal{D} can then be calculated as

$$\mathcal{D} = \frac{D_w}{D_n}$$

2.2 Nuclear Magnetic Resonance Spectroscopy

^1H - and ^{13}C -spectra were recorded on a Bruker System 600 Ascend LH, equipped with a BBO-Probe (5 mm) with z-gradient (^1H : 600 MHz, ^{13}C 150 MHz). The signals are reported in chemical shift (δ = ppm, rounded to two decimals) relative to the solvent signal of CHCl_3 (7.26 ppm) or DMSO (2.5 ppm) for ^1H and ^{13}C spectra. Coupling constants (J) are reported in Hz. Spectra were processed using Mestrelab Reasearch S.L. MestReNova 11.

2.3 THF Size Exclusion Chromatography

SEC measurements were conducted on a PSS SECurity² system consisting of a PSS SECurity Degasser, PSS SECurity TCC6000 Column Oven (60 °C), PSS GRAM Column Set (8x150 mm 10 μm Precolumn, 8x300 mm 10 μm Analytical Columns, 10000 Å, 1000 Å and 30 Å) and an Agilent 1260 Infinity Isocratic Pump, Agilent 1260 Infinity Standard Autosampler, Agilent 1260 Infinity Diode Array and Multiple Wavelength Detector (A: 254 nm, B: 360 nm), Agilent 1260 Infinity Refractive Index Detector (35 °C). HPLC grade THF, stabilized with BHT, is used as eluent at a flow rate of 1 mL min⁻¹. Narrow disperse linear poly(styrene) (M_n : 266 g·mol⁻¹ to 2.52×10⁶ g·mol⁻¹) and poly(methyl methacrylate) (M_n : 202 g·mol⁻¹ to 2.2×10⁶ g·mol⁻¹) standards (PSS ReadyCal) were used as calibrants. All samples were passed over 0.22 μm PTFE membrane filters. Molecular weight and dispersity analyses were performed using the PSS WinGPC UniChrom software (version 8.2).

2.4 Flash Column Chromatography

Flash chromatography was performed on a Interchim XS420+ flash chromatography system consisting of a SP-in-line filter 20- μm , an UV-Vis detector (200-800 nm) and a SofTA Model 400 ELSD (55 °C dift tube temperature, 25 °C spray chamber temperature, filter 5, EDR gain mode) connected via a flow splitter (Interchim Split ELSD F04590). The separations were performed using an Interchim dry load column and an Interchim Puriflash 30 μm Silica HP column.

2.5 Particle synthesis setup

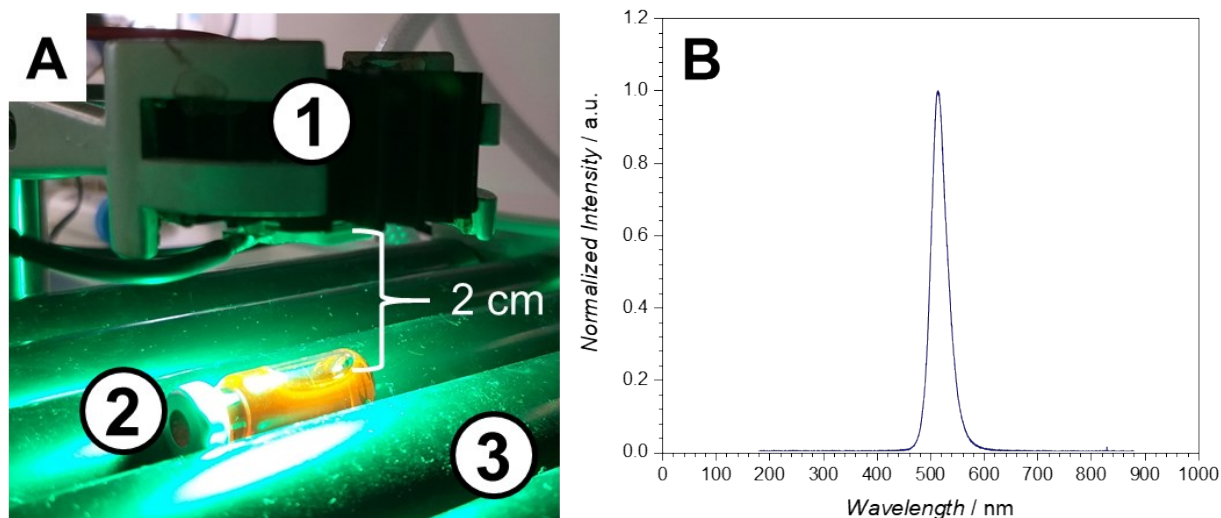


Figure S1. (A) Image of the particle synthesis setup; 1: 10 W 525 nm LED, intensity at 2 cm distance = 9.77 mW cm^{-2} , 2: sample and 3: bottle roller. The sample is placed on the bottle roller at 2 rpm and irradiated from above with the LED in 2 cm distance for 1 h. (B) Emission spectrum of the 10 W 525 nm LED.

2.6 Online Light Scattering

Online light scattering measurements were performed using a customized setup equipped with a 7 mW CW HeNe laser (Melles Griot) directed at the side of the photovial containing the reaction solution, as depicted in Figure S2. The 142° backscattered radiation was collected using a $400 \mu\text{m}$ UV-Vis optics fibre (Ocean Optics P400-025-SR) fitted with a collimating lens and connected to a spectrometer (Ocean Optics Flame-T) which was used to isolate the scattered laser irradiation from any undesired LED irradiation. Spectra were recorded every 250 ms (10 ms integration time, 25 average) and processed with a moving average function in Matlab® to remove any undesired scatter from the bottle roller or surface of the photovial.

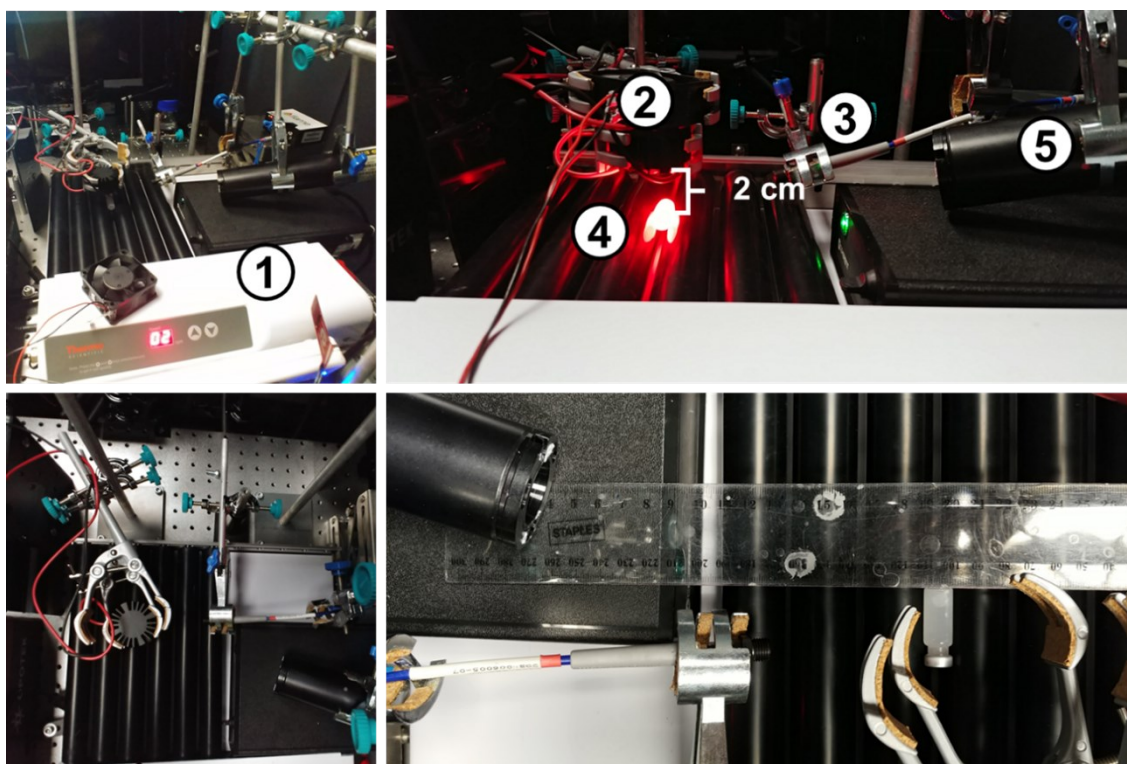
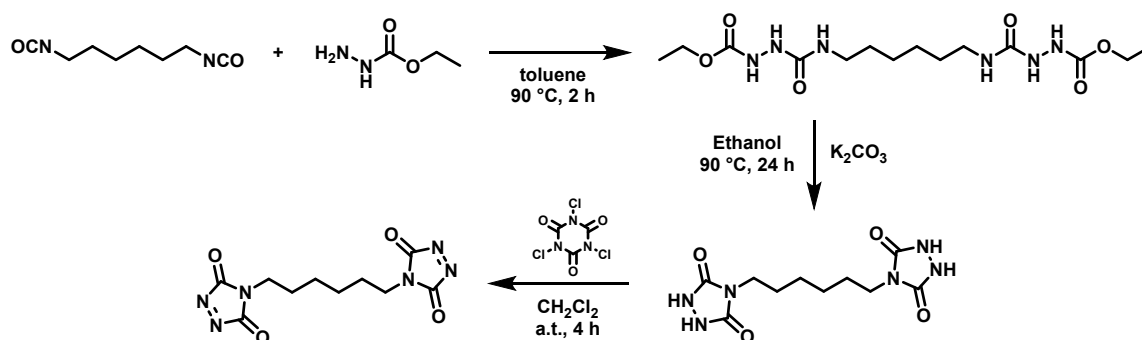


Figure S2. 1: Bottle roller (2 rpm), 2: 10 W 525 nm LED, 3: Optic fibre and collection lens, 4: Sample, 5: CW HeNe Laser.

3 Synthetic procedures

3.1 Synthesis of 4,4'-(hexane-1,6-diyl)bis(1,2,4-triazoline-3,5-dione) (**BisTAD**)



The synthesis of **BisTAD** was adapted from a literature procedure, which is outlined below.^[1] Due to its high reactivity, the linker was freshly synthesized from a stable urazole precursor for each set of experiments and was stored in the freezer for up to 5 days. The reported precursor synthesis is based on a procedure first established by Cookson *et al.*^[29] where semicarbazides, yielded from simple addition of ethyl carbamate to isocyanates, undergoes a base-catalyzed ring closure reaction to afford the respective urazole. The urazole can then be readily oxidized through *in situ* generated chlorine species from trichlorocyanuric acid.

4,4'-(hexane-1,6-diyl)bis(1-(ethoxycarbonyl) semicarbazide)

A mixture of ethyl carbazate (16.2 g, 155.6 mmol, 2.00 eq.) in 100 mL toluene was placed under inert atmosphere and stirred at room temperature. To this, a solution of hexamethylene diisocyanate (12.5 mL, 77.8 mmol, 1.0 eq.) in 50 mL toluene was added dropwise. Following complete addition, the resulting mixture was heated at 90 °C for 2h and cooled to room temperature. The resulting waxy solid was filtered off, washed with toluene (2 x 75 mL) and dried overnight in a vacuum at 40 °C to yield 4,4'-(hexane-1,6-diyl)bis(1-(ethoxycarbonyl) semicarbazide) as a white powder (26.5 g, 90 %). ¹H NMR (600 MHz, DMSO-*d*₆) δ [ppm]: 1.17 (t, 6H, CH₃, J = 7.1 Hz), 1.22 (m, 4H, N-CH₂-CH₂-CH₂), 1.35 (m, 4H, N-CH₂-CH₂), 2.97 (q, 4H, N-CH₂, J = 14.5, 6.6 Hz), 4.01 (q, 4H, CH₃-CH₂, J = 14.2, 7.1 Hz), 6.28 (s, 2H, CH₂-NH), 7.60 (s, 2H, C(O)-NH), 8.34 + 8.70 (s, 2H, C(O)-NH). ¹³C NMR (150 MHz, DMSO-*d*₆) δ [ppm]: 14.56 (CH₃), 26.06 (CH₂), 29.88 (CH₂), 38.99 (CH₂), 60.33 (CH₂), 156.92 (C), 158.24 (C).

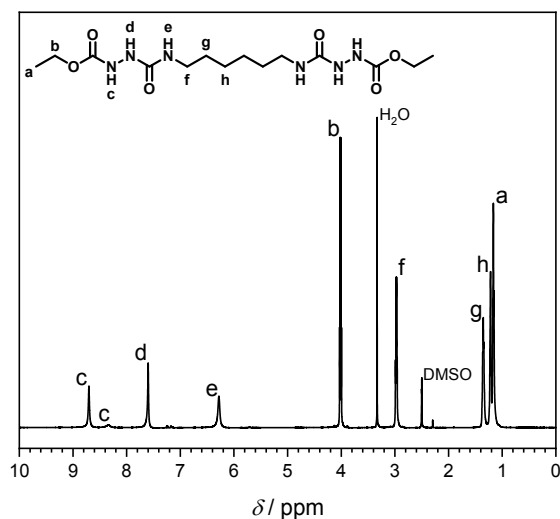


Figure S3. ¹H NMR spectrum of 4,4'-(hexane-1,6-diyl)bis(1-(ethoxycarbonyl) semicarbazide) recorded in DMSO-*d*₆.

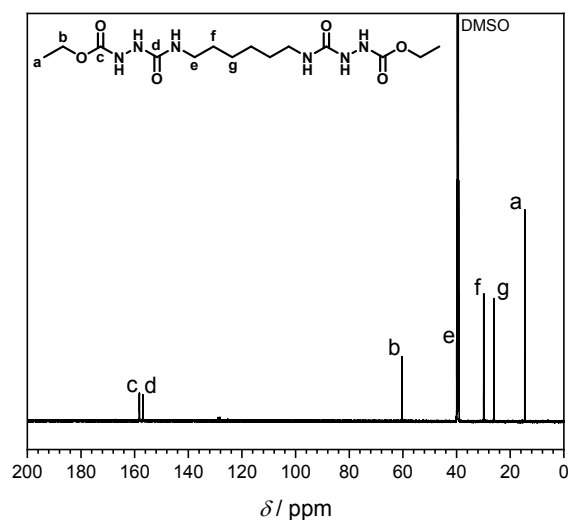


Figure S4. ^{13}C NMR spectrum of 4,4'-(hexane-1,6-diyl)bis(1-(ethoxycarbonyl) semicarbazide) recorded in $\text{DMSO-}d_6$.

4,4'-(hexane-1,6-diyl)bis(1,2,4-triazolidine-3,5-dione)

Next, a suspension of the obtained 4,4'-(hexane-1,6-diyl)bis(1-(ethoxycarbonyl) semicarbazide) (10.0 g, 26.6 mmol, 1.0 eq.) and potassium carbonate (12.4 g, 98.8 mmol, 3.4 eq.) in 300 mL ethanol was placed under inert atmosphere and heated to reflux at 90 °C for 24 h. The resulting mixture was filtered warm, washed with methanol and the filtrate was cooled to room temperature before acidifying to pH 1 by addition of hydrochloric acid (5-6 N) solution in isopropanol. Filtration of the precipitated salts followed by solvent removal *in vacuo* and overnight drying in a vacuum oven gave 4,4'-(hexane-1,6-diyl)bis(1,2,4-triazolidine-3,5-dione) as a white powder (5.54 g, 73 %). ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ [ppm]: 1.24 (m, 4H, $\text{N-CH}_2\text{-CH}_2\text{-CH}_2$), 1.49 (t, 4H, $\text{N-CH}_2\text{-CH}_2$, $J = 6.8$ Hz), 3.32 (t, 4H, N-CH_2 , $J = 7.1$ Hz), 10.0 (s, 4H, NH). ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ [ppm]: 25.60 (CH_2), 27.44 (CH_2), 37.80 (CH_2), 155.08 (C).

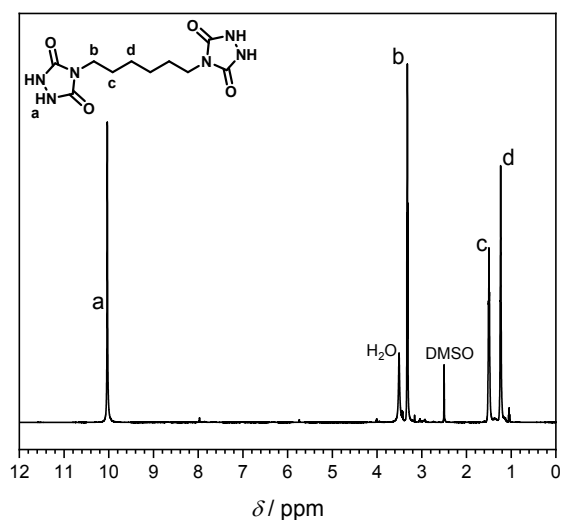


Figure S5. ¹H NMR spectrum of 4,4'-(hexane-1,6-diyl)bis(1,2,4-triazolidine-3,5-dione) recorded in DMSO-*d*₆.

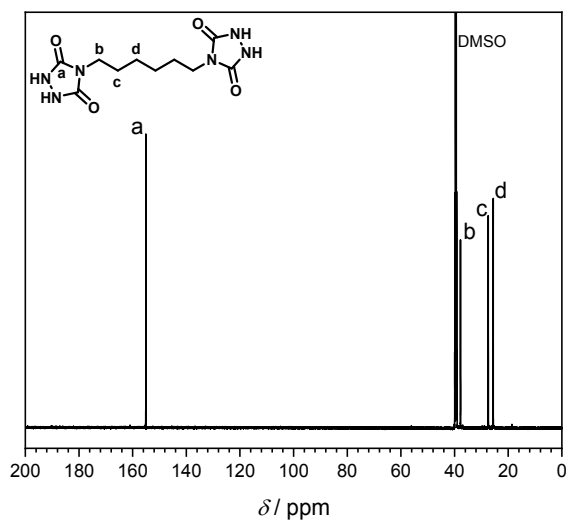


Figure S6. ¹³C NMR spectrum of 4,4'-(hexane-1,6-diyl)bis(1,2,4-triazolidine-3,5-dione) recorded in DMSO-*d*₆.

4,4'-(hexane-1,6-diyl)bis(1,2,4-triazoline-3,5-dione)

Finally, a mixture of 4,4'-(hexane-1,6-diyl)bis(1,2,4-triazolidine-3,5-dione) (200 mg, 0.7 mmol, 1.0 eq.) and trichloroisocyanuric acid (108 mg, 0.46 mmol, 0.65 eq.) in 5 mL dichloromethane was placed under inert atmosphere and stirred at room temperature. After 4 h, the resulting mixture was filtered and washed with dichloromethane (2 x 10 mL). Solvent

removal in vacuo, keeping the temperature below 35 °C, gave the **BisTAD** as a pink powder (130 mg, 66 %), which was stored in a dark recipient at -18 °C. ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ [ppm]: 1.29 (m, 4H, N- $\text{CH}_2\text{-CH}_2\text{-CH}_2$), 1.55 (m, 4H, N- $\text{CH}_2\text{-CH}_2\text{-CH}_2$), 3.46 (t, 4H, N- $\text{CH}_2\text{-CH}_2\text{-CH}_2$, $J = 7.2$ Hz). ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ [ppm]: 25.24 (CH_2), 26.46 (CH_2), 40.51 (CH_2), 160.13 (C).

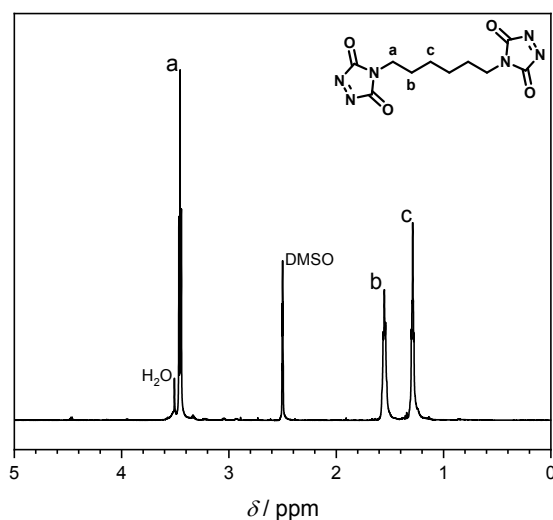


Figure S7. ^1H NMR spectrum of 4,4'-(hexane-1,6-diyl)bis(1,2,4-triazoline-3,5-dione) recorded in $\text{DMSO-}d_6$.

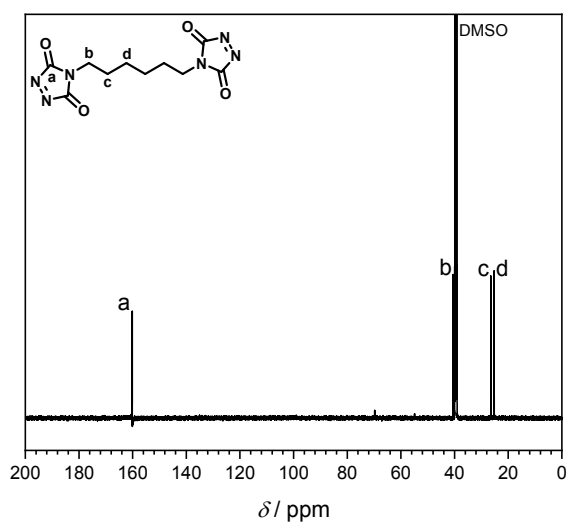
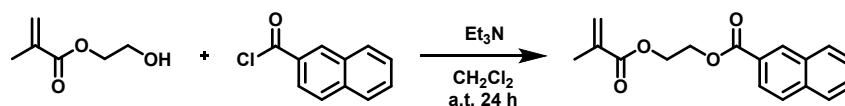


Figure S8. ^{13}C NMR spectrum of 4,4'-(hexane-1,6-diyl)bis(1,2,4-triazoline-3,5-dione) recorded in $\text{DMSO-}d_6$.

3.2 Synthesis of 2-(methacryloyloxy)ethyl 2-naphthanoate (**M1**)



The synthetic procedure was adapted from literature.^[1]

2-Naphthoyl chloride (5.00 g, 26.2 mmol, 1.0 eq.) was dissolved in dry dichloromethane (50 mL) and cooled to 0 °C. Triethylamine (4.02 mL, 28.9 mmol, 1.1 eq.) was added to the cool solution, followed by the dropwise addition of 2-hydroxyethyl methacrylate (3.50 mL, 28.9 mmol, 1.1 eq.). The reaction mixture was stirred overnight and was allowed to warm to ambient temperature. Subsequently, 20 mL of an aqueous saturated ammonium chloride solution was added to quench the reaction and the organic phases were separated. The organic phase was dried with Na₂SO₄ and the solvent removed in vacuum. The crude product was purified with flash chromatography using a gradient (silica, ethyl acetate:cyclohexane 0:100 -> 15:85). 2-(methacryloyloxy)ethyl 2-naphthanoate was obtained as a white powder (4.73 g, 64 %). ¹H NMR (600 MHz, CDCl₃) δ [ppm]: 1.97 (dd, 3H, CH₃, J = 0.5 (x2) Hz), 4.55 (m, 2H, Ar-CO-O-CH₂), 4.64 (m, 2H, Ar-CO-O-CH₂-CH₂), 5.60 (quin, 1H, C=CH, J = 1.6 Hz), 6.17 (dq, 1H, C=CH, J = 1.7, 0.9 Hz), 7.52-7.65 (m, 2H, ArH), 7.88 (m, 1H, ArH), 7.96 (m, 1H, ArH), 8.06 (dd, 1H, ArH, J = 8.5, 1.7 Hz), 8.62 (s, 1H, ArH). ¹³C NMR (150 MHz, CDCl₃) δ [ppm]: 18.19 (CH₃), 62.36 (CH₂), 62.65 (CH₂), 125.08 (CH), 126.01 (CH₂), 126.58 (CH), 126.96 (C), 127.66 (CH), 128.10 (CH), 128.25 (CH), 129.27 (CH), 131.15 (CH), 132.35 (C), 135.49 (C), 135.85 (C), 166.36 (C), 167.07 (C).

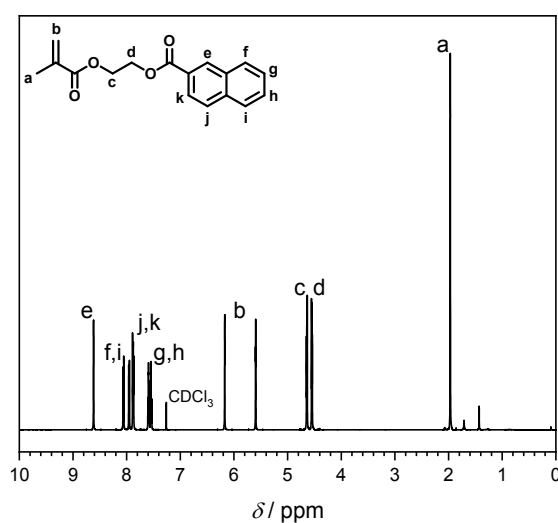


Figure S9. ¹H NMR spectrum of 2-(methacryloyloxy)ethyl 2-naphthanoate recorded in CDCl₃.

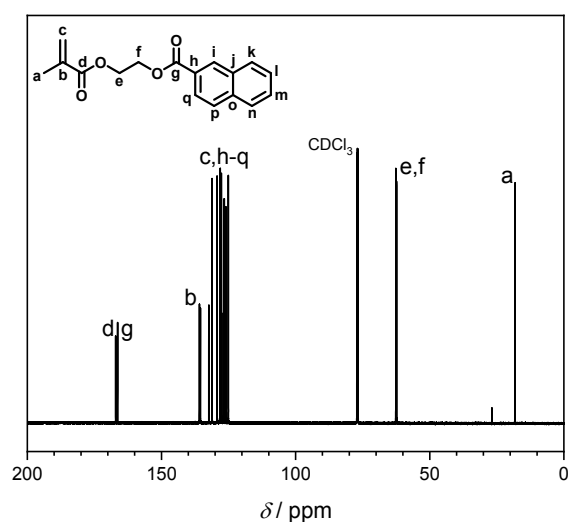
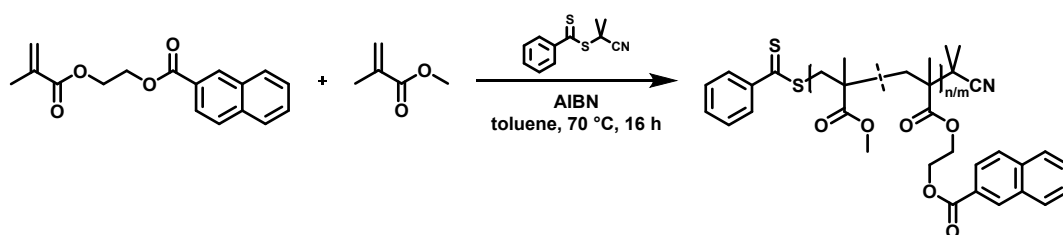


Figure S10. ^{13}C NMR spectrum of 2-(methacryloyloxy)ethyl 2-naphthanoate recorded in CDCl_3 .

3.3 RAFT polymerization



Methyl methacrylate was passed through a basic aluminium oxide column prior to use to remove any inhibitor. In a small vial the respective amounts of methyl methacrylate, **M1**, 2-cyanopropan-2-yl benzodithioate (CTA) and azobisisobutyronitrile (AIBN) listed in **Table S1**, were dissolved in toluene. The vial was sealed and the reaction solution was purged with inert gas for 15 min and the polymerization was carried out at 70 °C for 16 h. The reaction was quenched by freezing the vial in liquid nitrogen and opening to air. 2 mL of toluene was added and the polymer was precipitated in ice cold methanol 3 times. The residue was filtered off and dried at 40 °C under vacuum overnight. ^1H NMR (600 MHz, CDCl_3) δ [ppm]: 0.75-2.25 (CH_3 + CH_2 polymer backbone), 3.24-3.70 (O- CH_3), 4.10-4.65 (4H, CH_2), 7.45-7.65 (2H, ArH), 7.77-8.11 (4H, ArH), 8.50-8.67 (1H, ArH).

Table S1. Amounts of monomer, CTA, initiator and solvent used to obtain **P1-P8** as well as conversions of the respective synthesis. Conversion was measured gravimetrically.

	MMA [μL]	M1 [mg]	CTA [mg]	AIBN [mg]	Toluene [mL]	Conversion [%]
P1	576	385	15	2.23	1.2	75
P2	576	385	30	4.46	1.2	82
P3	576	385	60	8.92	1.2	80
P4	288	192.5	60	8.92	0.6	47
P5	576	192.5	15	2.23	1	76
P6	576	192.5	30	4.46	1	79
P7	576	192.5	60	8.92	1	70
P8	288	96	60	8.92	0.5	26

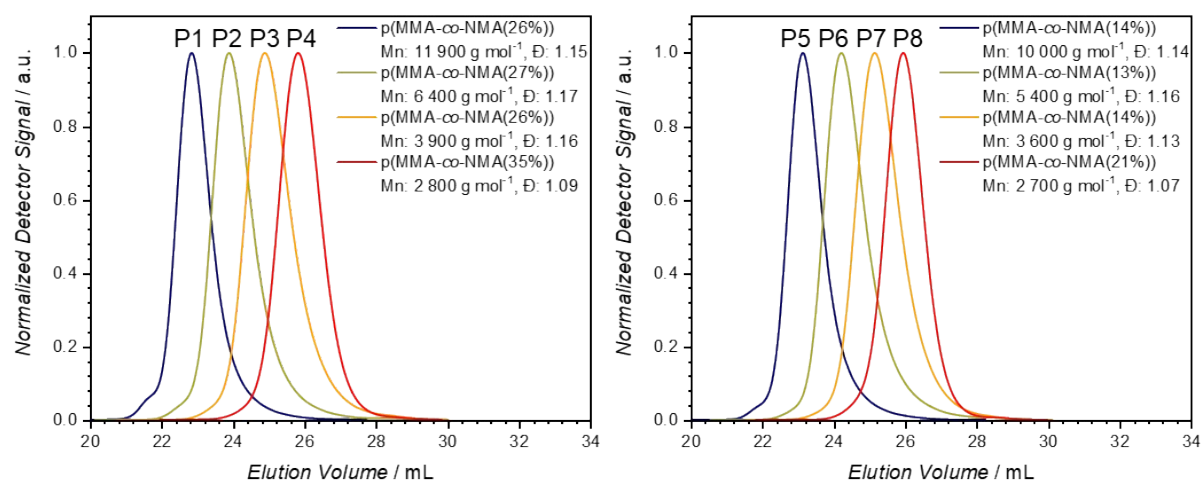


Figure S11. SEC elugrams of **P1-P8** recorded in THF, calibrated with PMMA standards.

Calculation of theoretical molar mass^[2]

The theoretical molar mass of the RAFT polymerization was calculated by:

$$M_{n,theo} = \frac{[M]_0 p M_M}{[CTA]_0} + M_{CTA}$$

Where $[M]_0$ represents the initial monomer concentration, M_M and M_{CTA} represent the molar mass of the monomer and the CTA respectively, $[CTA]_0$ represents the initial CTA concentration and p the monomer conversion.

Calculation of functional monomer per polymer chain

Using the fraction X of functional groups in the polymer determined from the ^1H NMR spectra (from signals a and b in Figure S12) and the M_n determined by SEC, the average number of functional groups $n(\text{M1})$ per polymer chain could be calculated by:

$$n(\text{M1}) = \frac{M_n(\text{Polymer}) - M(\text{CTA})}{X(\text{MMA}) \cdot M(\text{MMA}) + X(\text{M1}) \cdot M(\text{M1})} \cdot X(\text{M1})$$

Where $M(\text{CTA})$, $M(\text{MMA})$ and $M(\text{M1})$ are the molar masses of the CTA, methyl acrylate and M1 respectively.

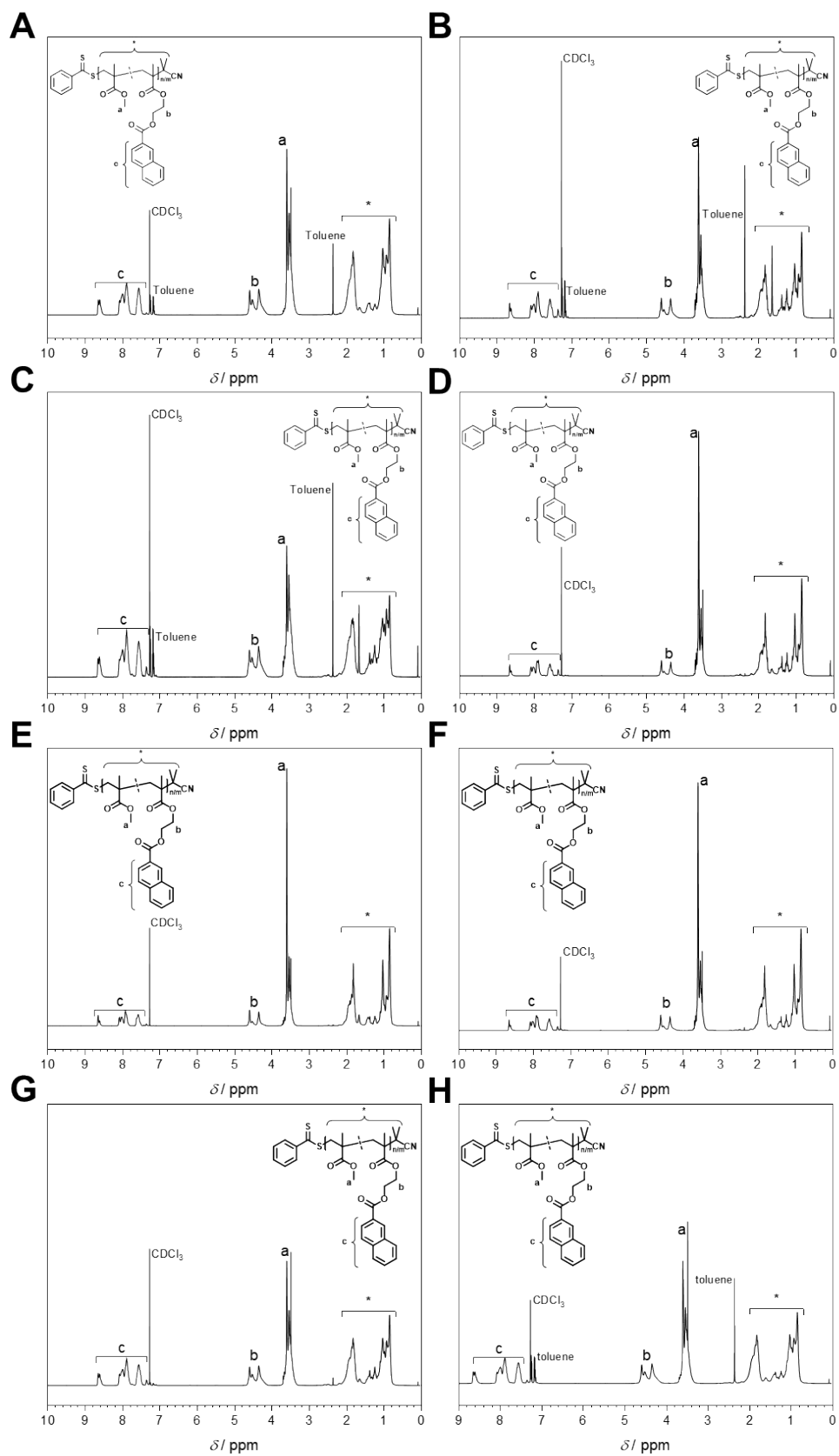
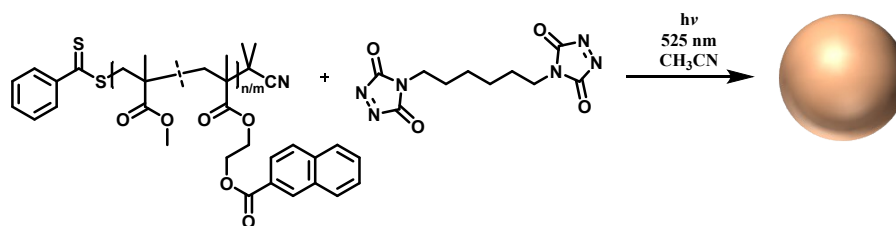


Figure S12. ^1H NMR spectra of **P1-P8** recorded in CDCl_3 .

3.4 Particle Synthesis



Particles were synthesized by adding the desired amount of BisTAD to a small crimp vial (1 eq. = 3.75 mg, 2 eq. = 7.5 mg, 3 eq. = 9.22 mg, 4 eq. = 15 mg, in respect to the total molar amount of naphthalene units). Polymer was subsequently added from a stock solution in acetonitrile ($c = 5 \text{ mg/mL}$) for a total reaction volume of 1.5 mL. The vial was sealed and purged with inert gas for 5 min. The vial was then placed on the bottle roller setup shown in Figure S1 and irradiated for 1 h. The particles were obtained by repeated centrifugation and redispersion in acetonitrile.

For kinetic studies, a stock solution of polymer and BisTAD was distributed over 6 vials, sealed and purged with inert gas for 5 min. The reaction was carried out for 1, 5, 10, 15, 30 and 60 min respectively.

3.5 Particle degradation

To monitor the particle degradation, previously prepared particles were dispersed in toluene ($c = 1 \text{ mg/mL}$) and stirred in the dark. SEM samples were taken after the respective time without further purification.

3.6 Light-Stabilization

For light-stabilization experiments, the particles were dispersed in toluene ($c = 1 \text{ mg/mL}$) and put on the bottle roller setup. SEM samples were taken after the respective time without further purification.

4 Additional Data

4.1 SEC Data

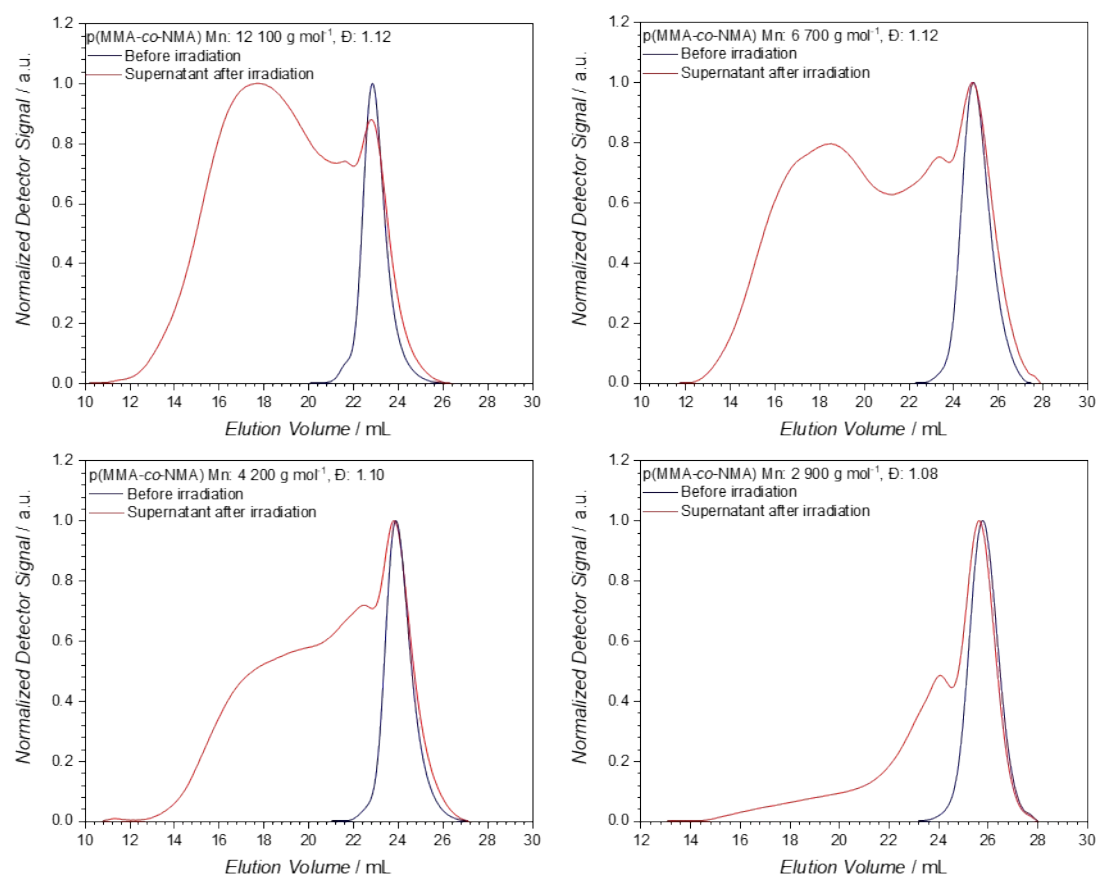


Figure S13. SEC elugrams of prepolymers **P1-P4** before irradiation and of the supernatant after 1 h irradiation with 10 W 525 nm LED. All elugrams were recorded in THF, calibrated with PMMA standards.

4.2 SEM Data

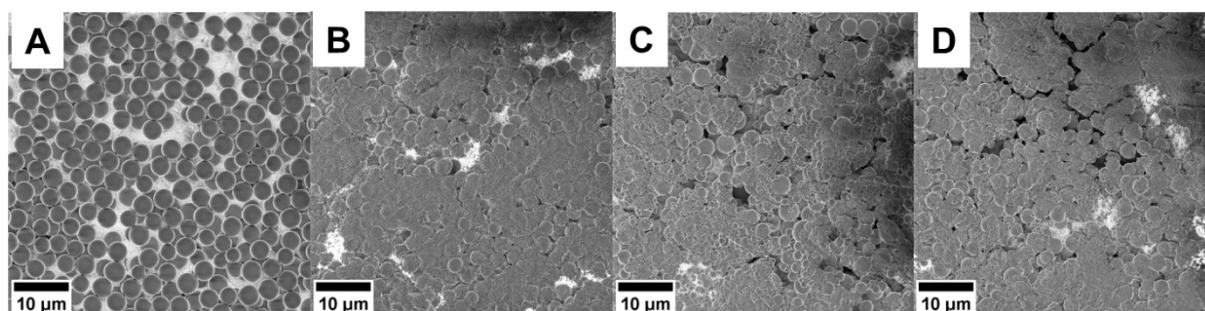


Figure S14. SEM images of particles synthesized with various equivalents of **BisTAD** linker. (A) 1 eq., (B) 2 eq., (C) 3 eq., and (D) 4 eq.

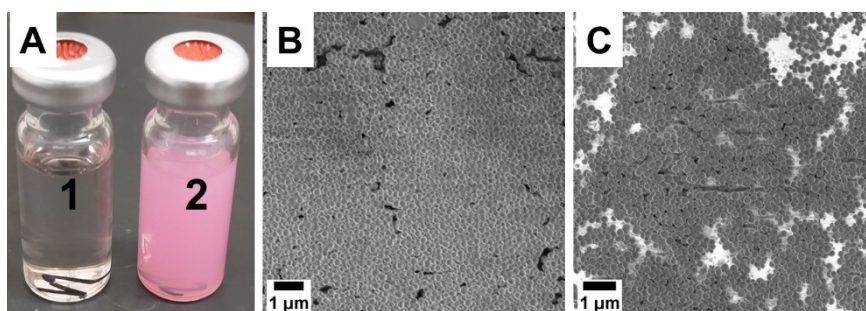


Figure S15. Blank experiment; (A) picture of reaction vials after 1 h irradiation with 10 W 525 nm LED; 1: **P2** in acetonitrile ($c = 5$ mg/mL), 2: **BisTAD** in acetonitrile ($c = 2.5$ mg/mL). (B) SEM image of particles synthesized from **BisTAD**, $D_n = 403$ nm, (C) SEM image of **BisTAD** particles after stirring in toluene for 7 days in the dark.

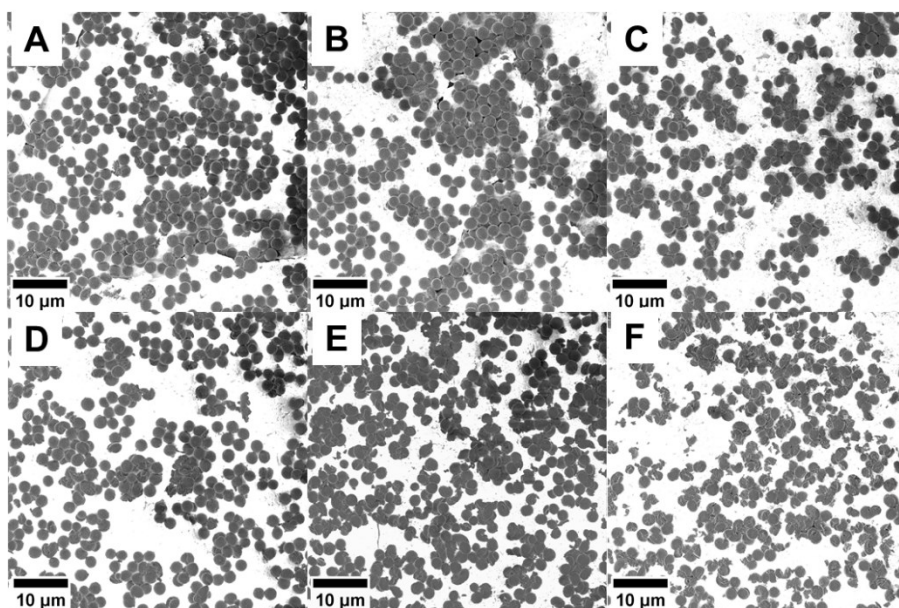


Figure S16. SEM images of MS1 after (A) 1 day, (B) 2 days, (C) 3 days, (D), 4 days, (E) 7 days and (F) 14 days in the dark dispersed in toluene.

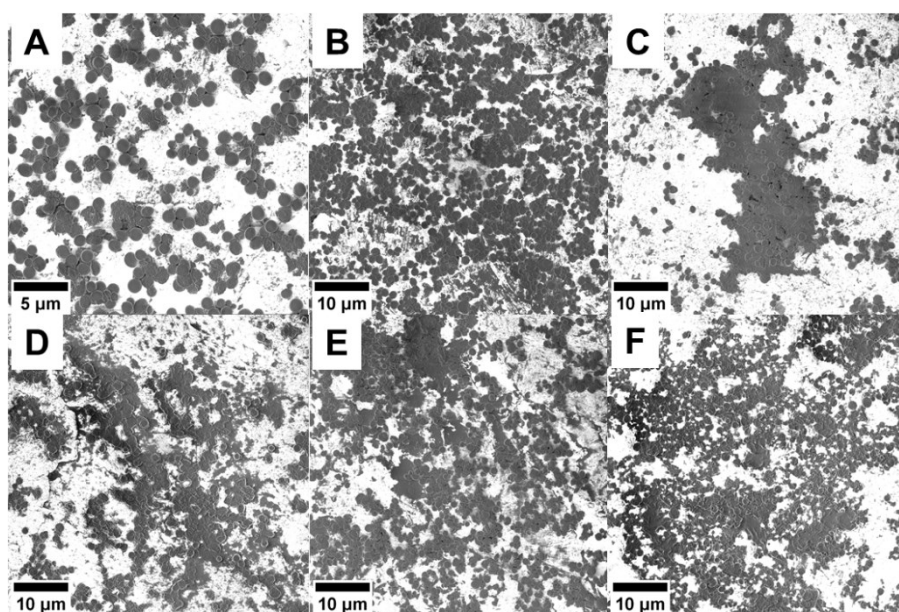


Figure S17. SEM images of MS2 after (A) 3 days, (B) 4 days, (C) 5 days, (D), 6 days, (E) 7 days and (F) 10 days in the dark dispersed in toluene.

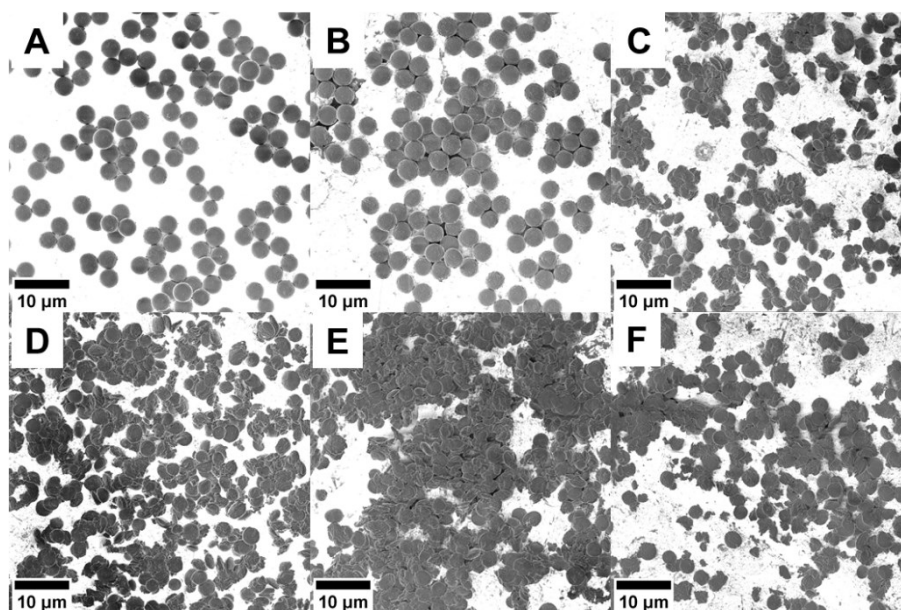


Figure S18. SEM images of MS3 after (A) 1 days, (B) 2 days, (C) 3 days, (D), 4 days, (E) 7 days and (F) 14 days in the dark dispersed in toluene.

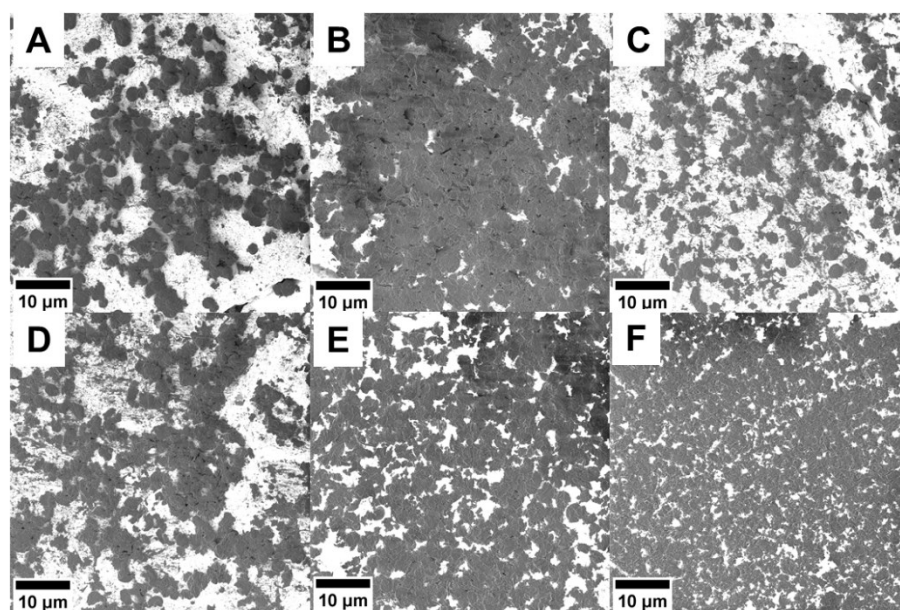


Figure S19. SEM images of MS4 after (A) 3 days, (B) 4 days, (C) 5 days, (D), 6 days, (E) 7 days and (F) 10 days in the dark dispersed in toluene.

4.3 Additional Data

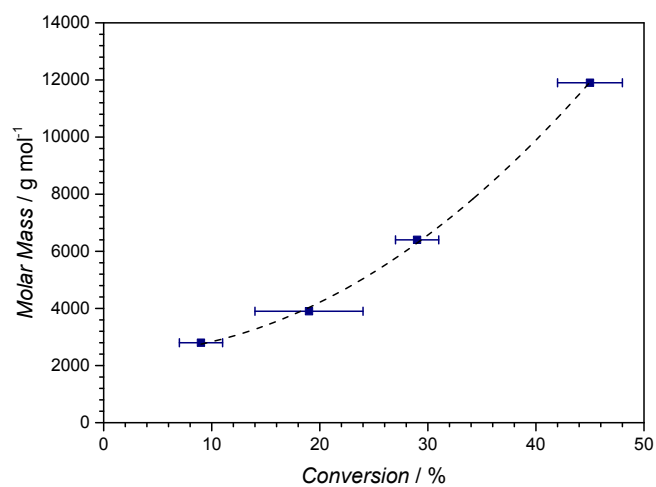


Figure S20. Prepolymer molecular weight plotted vs the polymer conversions after the particle synthesis (cf. Table 2).

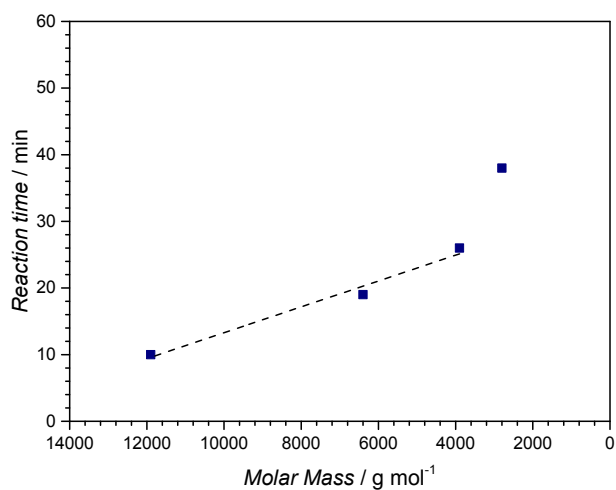


Figure S21. Reaction time after which particle precipitation is observable, plotted vs prepolymer molecular weight.

5 References

- [1] H. A. Houck, E. Blasco, F. E. Du Prez, C. Barner-Kowollik, *J. Am. Chem. Soc.* **2019**, *141*, 12329.
- [2] S. Perrier, *Macromolecules* **2017**, *50*, 7433.