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SUPPORTING INFORMATION

Amino Acid Acrylamide Mimics: Creation of a consistent monomer library and characterization of their polymerization behaviour

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S1. Materials

Acrylic acid (Merck), Thionyl chloride (97 %, Sigma) and N,N-Dimethylformamide (DMF, Merck) were used as received. Tetrahydrofuran (THF, Chem-Supply) and Dichloromethane (DCM, Merck) were dried over molecular sieves. Triethylamine (Merck), isobutylamine (Merck), methylamine (2M solution in THF, Sigma), phenethylamine (Merck), isopentylamine (≥98%, Sigma), amino-2-propanol (93%, Sigma), β-alanine (99%, Sigma), 4-aminobutyric acid (>98%, Chem-Supply), S-methylisothiourea hemisulfate salt (98%, Sigma), di-tert-butyl dicarbonate (diBoc, 99+%, AK Scientific), 1,4-Diaminobutane (>98%, Chem-Supply), tetrapropyl ammonium bromide (98%, Sigma), ethanethiol (99+%, Fisher Scientific), 2-Bromopropionic acid (99+%, Fisher Scientific) and 2,2'-Azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride were used without further purification.

S2. Characterization

Gel Permeation Chromatography (GPC): Analysis of the molecular weight (distributions) of the samples was performed on a PSS SECcurity^2 GPC system operated by PSS WinGPC software, equipped with a SDV 5.0 µm guard column (50 x 8 mm), followed by three SDV analytical 5.0 µm columns with varying porosity (1000 Å, 100000 Å and 1000000 Å) (50 x 8 mm) and a differential refractive index detector using THF as the eluent at 40°C with a flow rate of 1 mL·min^{-1}. The SEC system was calibrated using linear narrow polystyrene standards ranging from 682 to 2.52 x 10^6 g·mol-1 PS (K = 14.1 x 10^{-5} dL·g^{-1} and α = 0.70).

Nuclear Magnetic Resonance (NMR): Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded in $CDCl_3$, DMSO-d_6 or D_2O on a Bruker Avance III nanobay NMR spectrometer (9.4 Tesla magnet) with a 5mm broadband autotunable probe with Z-gradients and BACS 60 tube autosampler operating at 400.20 MHz. The system has variable temperature capabilities. NMR spectra are collected and analysed in MestReNova software.
Monomer degradation analysis *via* ^{1}H NMR spectra were recorded periodically at a range of temperatures on a Bruker Avance III nanobay NMR spectrometer equipped with a 9.4 T magnet and 5 mm BBFO probe, operating at 400.20 MHz (^{1}H). Spectra of samples in DMSO-d_6 were acquire using the standard ^{1}H acquisition parameters: pulse program zg30 and 16 transients.

S3. Synthetic procedures

Synthesis of Acryloyl Chloride

Two separate stock solutions for Acrylic acid (1 M, 1 eq.), DMF (0.03 eq., 0.025 eq., 0.019 eq., 0.013 eq., 0.0064 eq.) and oxalyl chloride or thionyl chloride (1.1 M, 1.1 eq.) both in anhydrous THF were prepared under inert atmosphere and transferred into two separate 10 mL gastight syringes and placed in the holder of the syringe pump (Chemyx). The syringe pump delivered the reagent solutions with correct flowrates using PFA tubing (0.75 mm I.D., 1/16" O.D.). The two solutions were merged using a static y-shaped mixer (PEEK, P-512, Upchurch Scientific). Using the same diameter PFA tubing, the mixed reagents were passed to the reactor (6 mL Vol.) placed in an isothermal oil bath of 61 °C. The resulting crude reaction product was immediately used in following reactions without intermediate purification.

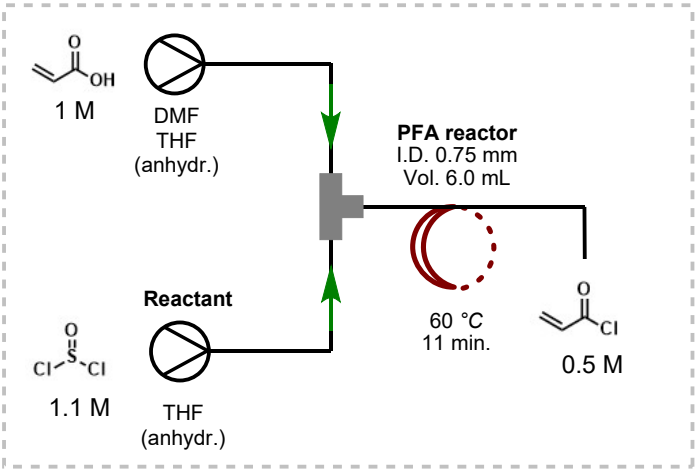
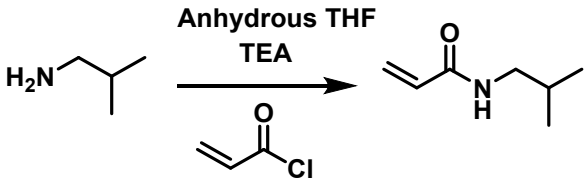


Figure S 1: Schematic overview of the reactor setup for the synthesis of acryloyl chloride

Synthesis of *N*-isobutylacrylamide



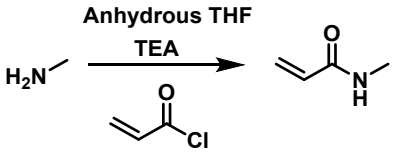
Scheme S 1: Reaction scheme for the synthesis of N-isobutylacrylamide.

Triethylamine (1.3834 g, 0.0137 mol, 4 eq.) and isobutylamine (0.250 g, 0.0034 mol, 1 eq.) were dissolved in anhydrous THF (30 mL) in a 100 mL 3-neck round bottom flask equipped with a magnetic stirrer. The flask was then placed in an ice bath at 0°C under a nitrogen atmosphere. The mixture was stirred vigorously to avoid salts fixating the stirrer bar. After cooling down of the solution, acryloyl chloride (9.3 mL, 0.0041 mol, 1.2 eq.) was added dropwise directly after synthesis. The reaction was then removed from the ice bath while the reaction solution was again exposed to air. Finally, the salt formed during the reaction was removed by filtration. The collected solution was purified using flash column chromatography on silica gel using petroleum ether: ethyl acetate (1/1) as eluent. The product was collected as a yellow oil, Scheme S 1 (0.2583 g, 59% yield).^{1}H NMR (600 MHz, DMSO-d_6) δ 8.04 (s, 1H), 6.24 (dd, J = 17.1, 10.1 Hz, 1H), 6.06 (dd, J = 17.1, 2.3 Hz, 1H),

5.56 (dd, *J* = 10.1, 2.3 Hz, 1H), 2.95 (t, *J* = 6.4 Hz, 2H), 1.70 (hept, *J* = 13.2, 6.6 Hz, 1H), 0.86 – 0.82 (d, 6H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 164.59, 131.90, 124.71, 46.11, 28.08, 20.12.

Figure S 2: Reactor cascade setup for the synthesis of acrylamide monomers

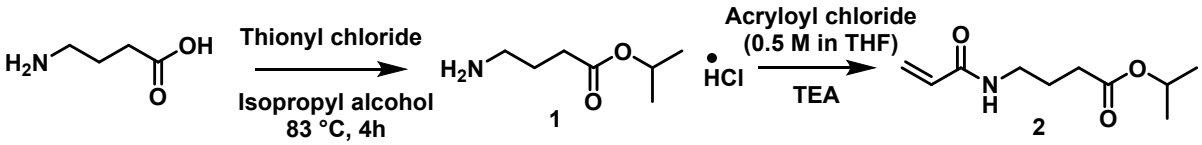
Synthesis of *N*-methylacrylamide



Scheme S 2: Reaction scheme for the synthesis of N-methylacrylamide.

Triethylamine (2.277 g, 0.0225 mol, 4 eq.), methylamine (2M solution in THF) (2.8125 mL, 0.0056 mol, 1 eq.), THF (25 mL) and acryloyl chloride (15 mL, 0.0067 mol, 1.2 eq.) were used. The procedure is identical as in 3.3.1. The collected solution was purified using flash column chromatography on silica gel using ethyl acetate: petroleum ether (1/1) as eluent. The product was collected as a yellow liquid, Scheme S 2 (0.1981 g, 42% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.02 (s, 2H), 6.18 (dd, *J* = 17.1, 10.0 Hz, 1H), 6.05 (dd, *J* = 17.1, 2.4 Hz, 1H), 5.55 (dd, *J* = 10.1, 2.4 Hz, 1H), 3.77 (t, *J* = 6.4 Hz, 0H), 2.65 (d, *J* = 4.8 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 164.58, 139.42, 131.80, 128.60, 128.32, 126.09, 124.93, 40.24, 35.07.

Synthesis of Isopropyl 4 - acrylamidobutanoate



Scheme S 3: Reaction scheme for the synthesis of Isopropyl 4 - acrylamidobutanoate

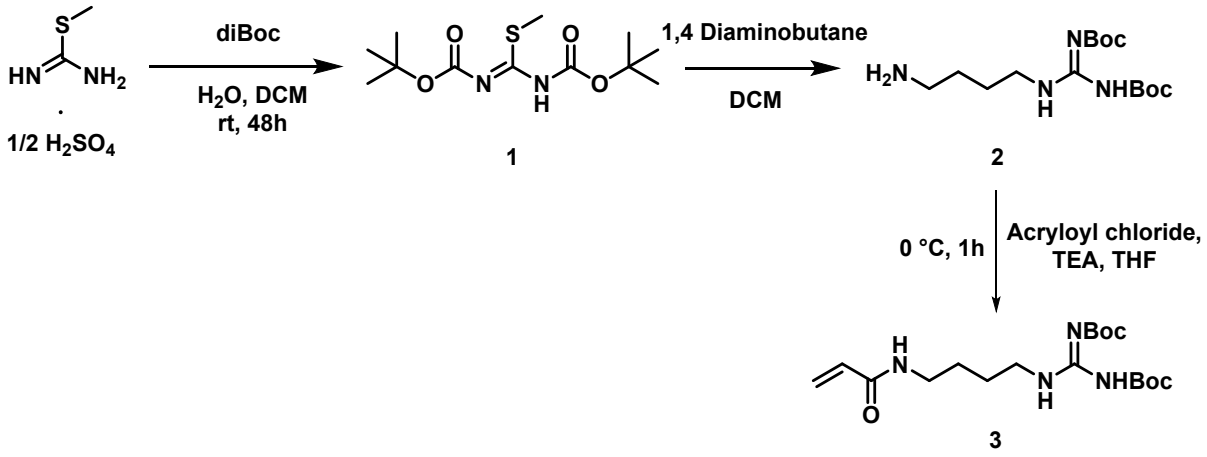
Synthesis of isopropyl 4-aminobutanoate hydrochloride (1)

To a suspension of 4 – aminobutyric acid (4 g, 0.0388 mol, 1 eq.) in isopropanol (116.52 mL), $SOCl_2$ (8,49 mL, 0.116 mol, 3 eq.) was added dropwise at 0 °C. The reaction mixture was refluxed at 83 °C for 4 h. The solvent was removed under vacuum to obtain the pure product **1** quantitatively as a white solid (6.935 g), Scheme S 3.

Synthesis of isopropyl 4-acrylamidobutanoate (2)

Triethylamine (2.635 g, 0.026 mol, 4 eq.), **1** (1.05 g, 0.0065 mol, 1 eq.), anhydrous THF (13.5 mL) and acryloyl chloride (0.5 M solution in THF, 16.5 mL, 0.0078 mol, 1.2 eq.) were used. After addition of acryloyl chloride, the mixture was stirred at 0 °C for 2h. The reaction mixture was washed with 5% $NaHCO_3$, brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude was purified using flash column chromatography on silica gel using ethyl acetate: petroleum ether (1/1) as eluent. The product was collected as a yellowish oil, Scheme S 4. ^{1}H NMR (600 MHz, DMSO-d6) δ 8.09 (s, 1H), 6.19 (dd, J = 17.1, 10.2 Hz, 1H), 6.06 (dd, J = 17.1, 2.2 Hz, 1H), 5.56 (dd, J = 10.1, 2.2 Hz, 1H), 4.88 (hept, J = 6.3 Hz, 1H), 3.13 (q, J = 6.9 Hz, 2H), 2.27 (t, J = 7.5 Hz, 2H), 1.67 (p, J = 7.3 Hz, 2H), 1.17 (d, J = 6.3 Hz, 6H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 173.13, 165.82, 131.03, 126.19, 68.00, 39.17, 32.29, 24.61, 21.87.

Synthesis of 1,3-Di-Boc-guanidinobutyl acrylamide



Scheme S 4: Reaction scheme for the synthesis of 4-[2,3-Bis(tert-butoxycarbonyl)guanidino]butylacrylamide .

Synthesis of 1,3-Bis(tert-butoxycarbonyl)-2-methyl-2-thiopseudourea (1)

S-methylthiourea hemisulfate (5 g, 0.036 mol, 1 eq.) was dissolved and stirred in a biphasic mixture of saturated $NaHCO_3$ solution (39.5 mL) and DCM (84 mL). Next, di-tert-butyl dicarbonate (15.63 g, 0.072 mol, 2 eq.) dissolved in DCM (60 mL) was added. The mixture was allowed to react for 48h at room temperature. Subsequently, the organic phase was isolated and the aqueous layer was washed with DCM (3 x 20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo. The crude solid was dissolved in a 1:9 mixture of EtOH and water and stirred for 1h. Subsequently, the mixture was cooled to 0 °C. The precipitate was filtered via vacuum filtration and washed with water. Purification via column chromatography using Petroleum ether: $CHCl_3$ (15:85) as eluent yield the pure product **1** as a white solid, Scheme S 4 (8.2 g, 78.44%). ^{1}H NMR (600 MHz, Chloroform-d) δ 2.40 (s, 3H), 1.52 (s, 18H).

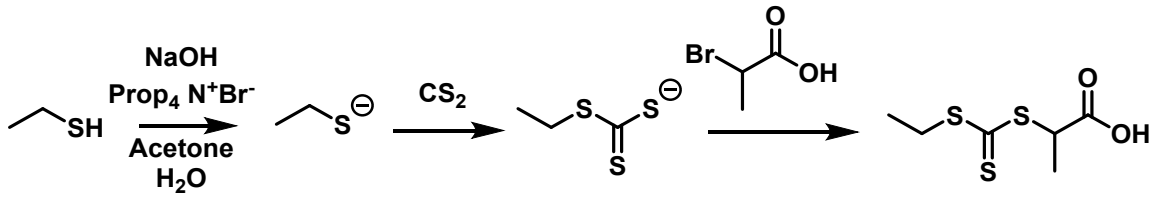
Synthesis of 2-[2,3-Bis(tert-butoxycarbonyl)guanidino]butylamine (2)

1,4-Diaminobutane (0.322 g, 0.3672 mL, 0.00365 mol, 1 eq.) was dissolved in 3.122 mL DCM. Next, **1** (0.3713 g, 0.00128 mol, 0.35 eq.) was dissolved in 2.53 mL DCM and added dropwise to the solution. After addition, the reaction mixture was allowed to react for 4h at room temperature. After reaction, the mixture was washed with water (3 x 10 mL) and brine (2 x 10 mL), dried over $MgSO_4$ and concentrated in vacuo to yield the pure product **2** as a white solid, Scheme S 4 (0.361 g, 85.35%). ^{1}H NMR (600 MHz, Chloroform-d) δ 11.47 (s, 1H), 8.33 (s, 1H), 3.45 – 3.37 (m, 2H), 2.72 (t, J = 7.0 Hz, 1H), 1.73 (s, 2H), 1.61 (dt, J = 15.0, 7.4 Hz, 2H), 1.47 (s, 20H) (S1.8.).

Synthesis of 4-[2,3-Bis(tert-butoxycarbonyl)guanidino]butylacrylamide (3)

Triethylamine (1.41 g, 0.0139 mol, 3 eq.), **2** (1.5313 g, 0.00463 mol, 1 eq.), anhydr. THF (15 mL) and acryloyl chloride (0.5 M solution in THF 11.71 mL, 0.0056 mol, 1.2 eq.) were used. After addition of acryloyl chloride, the mixture was stirred at 0 °C for 2h, and then at room temperature overnight. Saturated $NaHCO_3$ (30 mL) was added and the aqueous layer was extracted with DCM (3 x 25 mL). The organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure the crude product was purified using flash column chromatography on silica gel using ethyl acetate: petroleum ether (2/8 to 8/2) as eluent. Finally, the purified product was re-crystallized from Et_2O at < 5°C to afford pure 4-[2,3-Bis(tert-butoxycarbonyl)guanidino]butylacrylamide as a white solid (0.5 g, 28% yield), Scheme S 4. ^{1}H NMR (600 MHz, Chloroform-d) δ 11.44 (s, 1H), 8.36 (t, J = 5.3 Hz, 1H), 6.81 (s, 1H), 6.24 (dd, J = 17.0, 1.9 Hz, 1H), 6.17 (dd, J = 17.0, 10.0 Hz, 1H), 5.56 (dd, J = 10.0, 1.9 Hz, 1H), 3.39 – 3.32 (m, 4H), 1.57 (dq, J = 23.1, 6.6 Hz, 4H), 1.45 (d, J = 5.2 Hz, 19H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.61, 163.32, 156.40, 153.26, 131.25, 125.93, 83.30, 79.51, 40.15, 39.16, 28.29, 28.07, 27.11, 25.57. MS. $[M+Na]^+$ 407.2265 (calculated), 407.2261 (found).

Synthesis of 2-(propionic acid)ylethyl trithiocarbonate (PAETC)



Scheme S 5: Reaction scheme for the synthesis of the chain transfer agent 2-(propionic acid)ylethyl trithiocarbonate (PAETC)

NaOH (2.3058 g, 57.05 moles, 1 eq.) and tetrapropyl ammonium bromide (1.2474 g, 4.564, 0.08 eq.) were dissolved in 25 mL of H_2O. Next, ethanethiol (3.54 g, 57.05 moles, 1 eq.) was added, followed by the addition of 200 mL of acetone. Subsequently, CS_2 (4.3435 g, 57.05 moles, 1 eq.) was added and the combined solution was stirred for 30 minutes.

Next, Bromopropionic acid (8.7263 g, 57.05 moles, 1 eq.) was added dropwise and the mixture allowed to react overnight. Next, the acetone was removed under reduced pressure and 100 mL HCl (1M solution) and 100 mL of water were added, resulting in the formation of an orange oil. The water was decanted of and the remaining oil was concentrated in vacuo. The pure product was crashed out by adding water to the oil and cooling it down overnight. The solid product was filtered and dried under high vacuum, Scheme S 5. ^{1}H NMR (600 MHz, Chloroform-d) δ 4.87 (q, J = 7.4 Hz, 1H), 3.38 (q, J = 7.4 Hz, 2H), 1.64 (d, J = 7.4 Hz, 3H), 1.37 (t, J = 7.4 Hz, 3H).

Thermal RAFT polymerization of amino acid mimics

In a typical procedure, 2,2'-Azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044) (0.025 eq.), PAETC (1 eq.), monomer (10, 25, 50 or 100 eq.) and the reaction solvent dioxane/water (4:6 or 7:3 v/v) were added in a glass vial and sealed with a rubber septum. The solution was degassed for 15 min by Ar purging. Next, the prepared solution was loaded into a 1 mL gastight syringe and placed in the holder of a syringe pump (chemyx). The syringe pump delivered the reaction solution with the correct flowrate into a 25 µL tubular reactor (Idex, Peek tube Yellow, 1/32" OD x .007" ID) submerged in an oil bath of 90 °C (Figure 5). Samples of the crude reaction mixture were collected after various reaction times. 2-3 drops of the crude reaction mixture were withdrawn and analysed by ^{1}H NMR and GPC.

Figure S 3: Picture of the simple reactor setup for the thermal RAFT polymerization screening reactions of 4 model monomers in the current work

PhotoRAFT polymerization of 1,3-di-boc-guanidinobutyl acrylamide

In a typical procedure, Benzoin (0.1 eq.), CDP-TTC(1 eq.), monomer (10, 25, 50 or 100 eq.) and the reaction solvent dioxane/water (8:2 v/v%) were added in a glass vial and sealed with a rubber septum. The solution was degassed for 15 min by Ar purging. Next, the stock solution was equally divided over 5 GPC vials and each vial was degassed for an additional 2 minutes before being placed before a TL-D 15W BLB 1SL/25 (Phillips) with a peak emission at 365 nm. A constant flow of pressurized air was applied throughout the reactor in order to keep the ambient temperature around ~30 °C. Samples of the crude reaction mixture were collected after various reaction times. 2-3 drops of the crude reaction mixture were withdrawn and analysed by ^{1}H NMR and GPC.

Figure S 4: Picture of the simple reactor setup for the photoRAFT polymerization of 4-[2,3-Bis(tert-butoxycarbonyl)guanidino]butyl acrylamide

S4. ^{1}H NMR and ^{13}C NMR

N-isobutylacrylamide

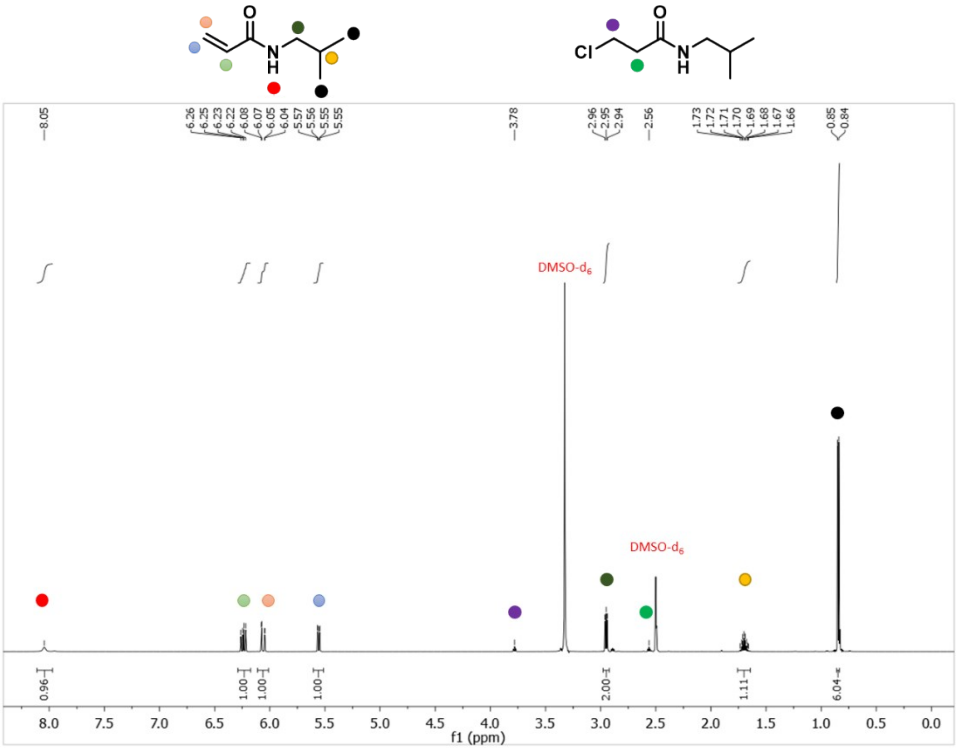


Figure S 5: ^{1}H NMR spectrum of *N*-isobutyl acrylamide

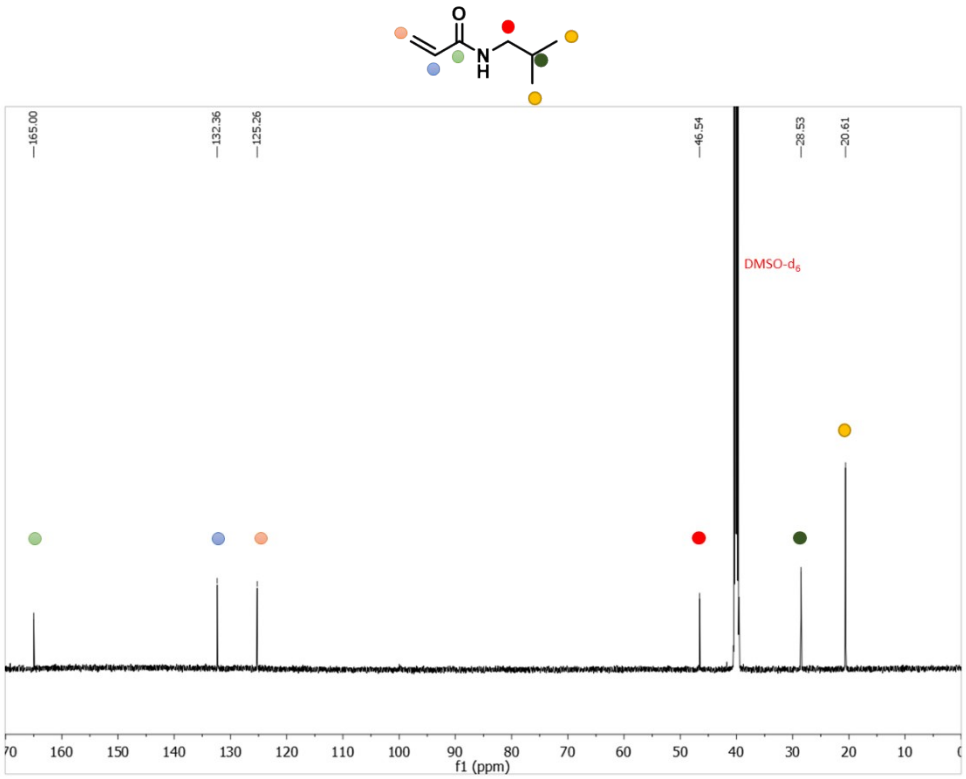


Figure S 6: ^{13}C NMR spectrum of *N*-isobutyl acrylamide

N-methyl acrylamide

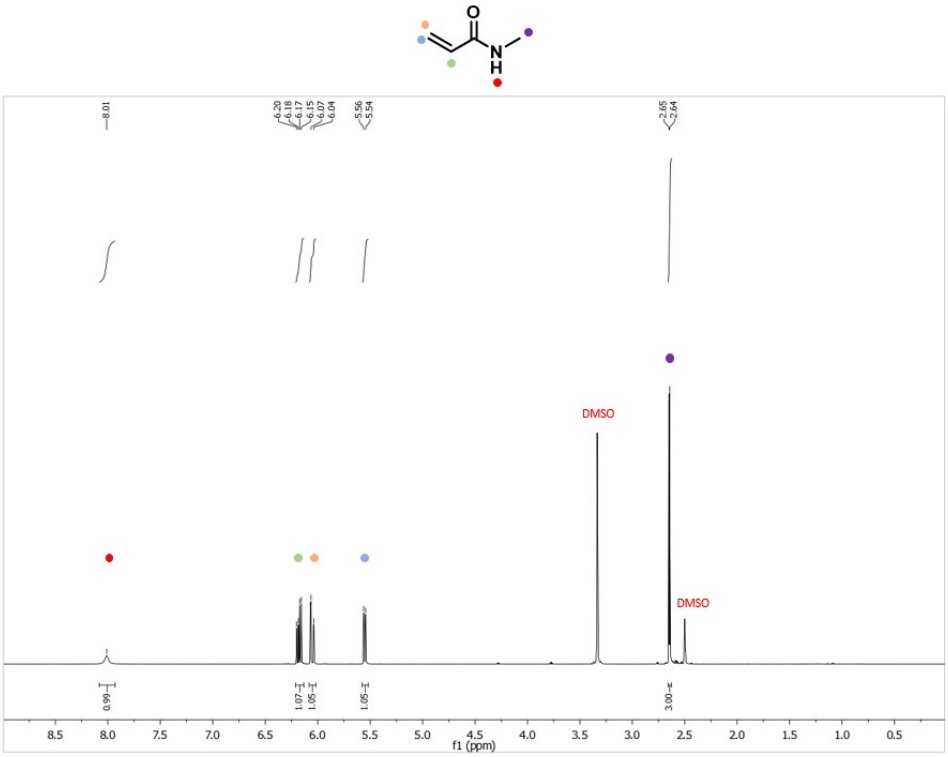


Figure S 7: ^{1}H NMR spectrum of *N*-methyl acrylamide

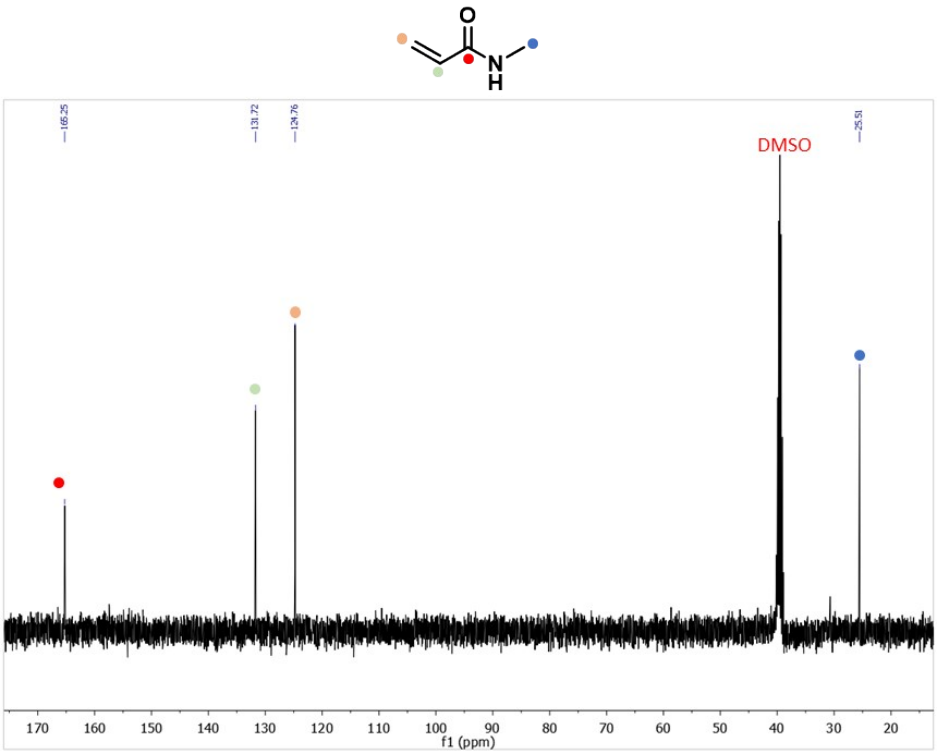


Figure S 8*:* ^{13}C NMR spectrum of *N*-methyl acrylamide

Isopropyl 4 - acrylamidobutanoate

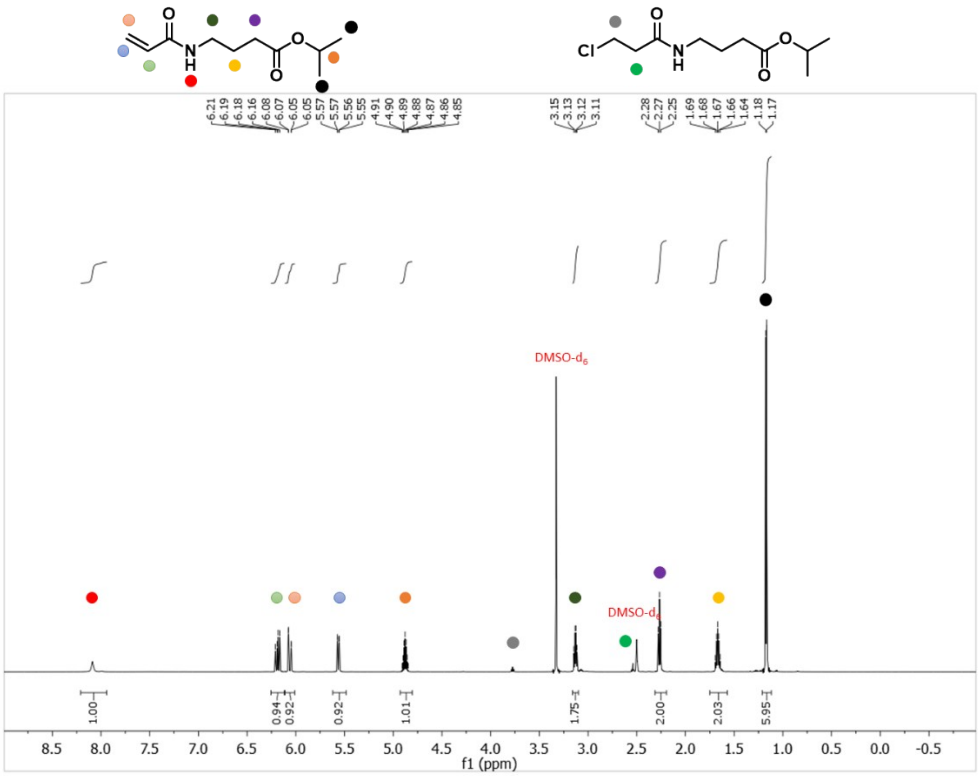


Figure S 9: ^{1}H NMR spectrum of Isopropyl 4-acrylamidobutanoate

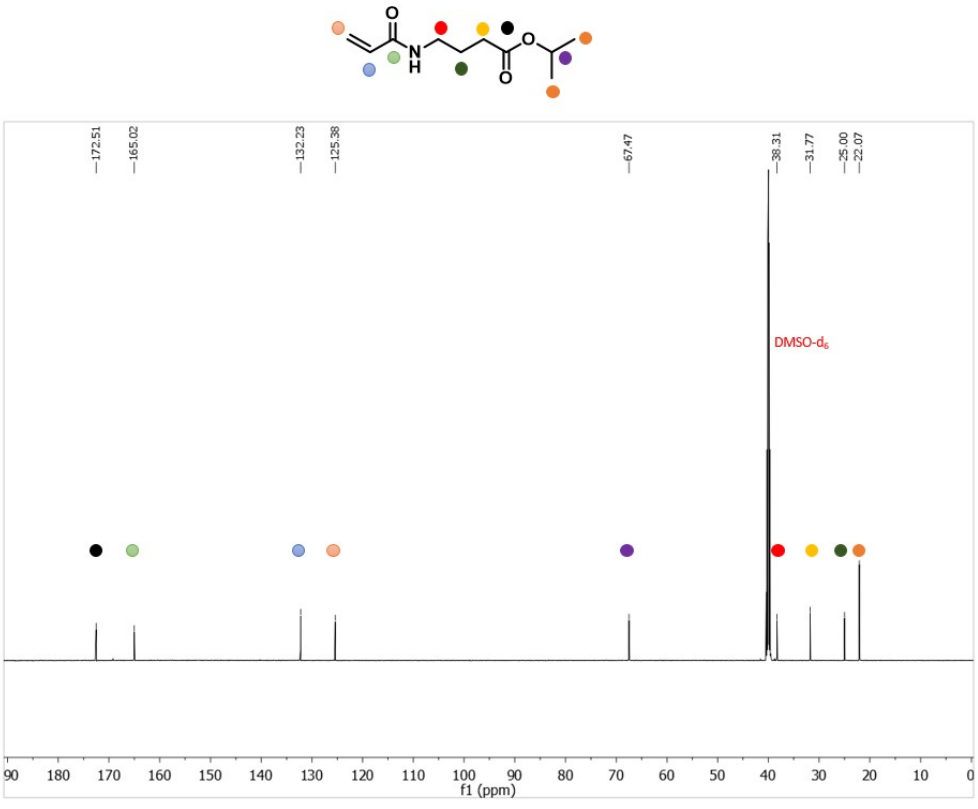


Figure S 10*:* ^{13}C NMR spectrum of Isopropyl 4-acrylamidobutanoate

1,3-di-boc-guanidinobutyl acrylamide

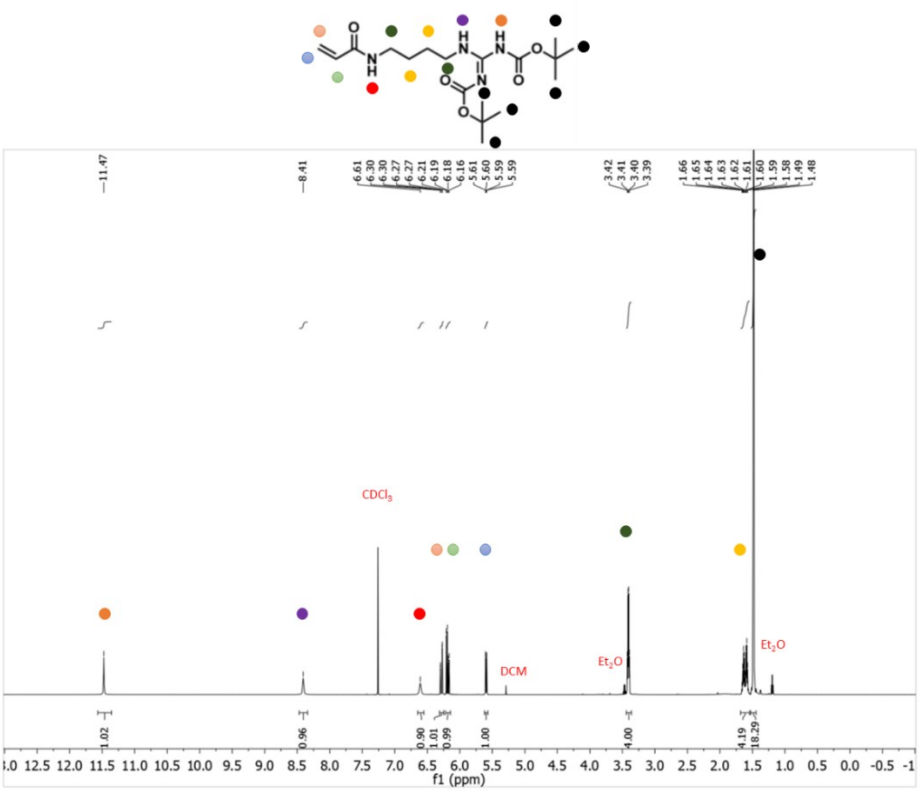


Figure S 11: ^{1}H NMR spectrum of 1,3-Di-Boc-Guanidinobutyl acrylamide

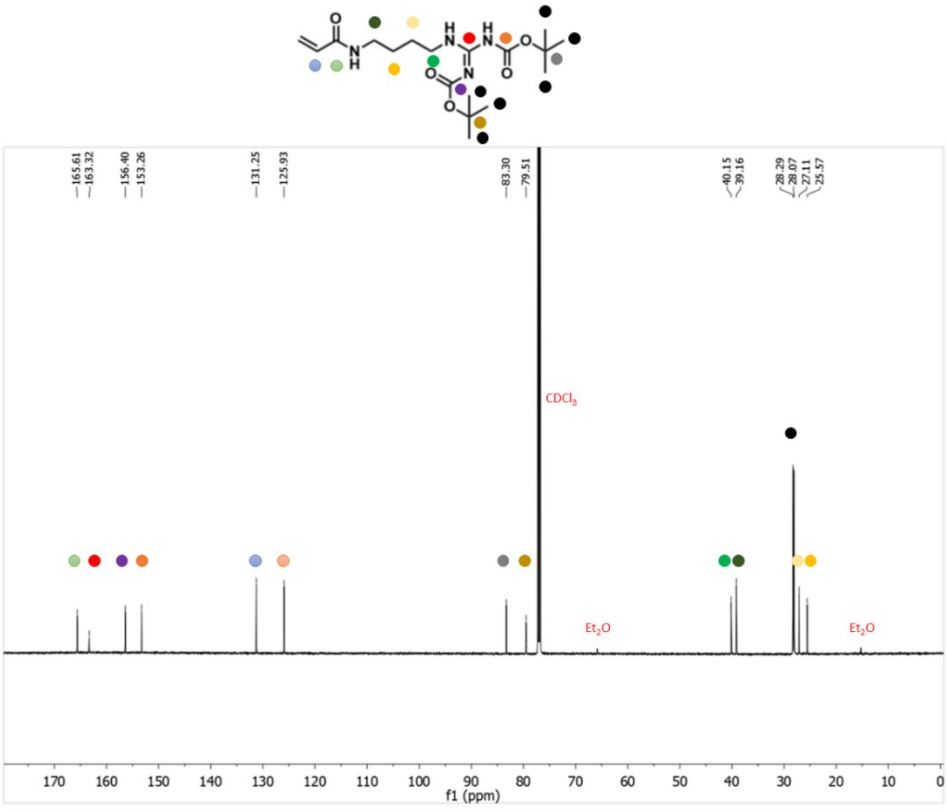


Figure S 12: ^{13}C NMR spectrum of 1,3-Di-Boc-Guanidinobutyl acrylamide

S5. RAFT polymerization screening

RAFT polymerization of 2-Hydroxyethyl acrylamide

Table S 1: Summary of RAFT polymerization conditions for N-Hydroxyethyl acrylamide using PAETC as the RAFT agent. Reaction conditions: T = 90 °C, solvent = H_2O:Dioxane (6:4), Initiator = VA-044, reaction time = 15 min.

DP	[Monomer] (mol L^{-1})	[CTA] (mol L^{-1})	[CTA]/[initiator] ratio	Conversion (%)	$M_{n\ (theoretical)}$ g mol^{-1}	$M_{n\ (H\ NMR)}$ g mol^{-1}
10	1.66	0.1657	40	86	1176	972.5
25	1.66	0.06628	40	92	2793	2133
50	1.66	0.03314	40	86	5055	3662
100	1.66	0.01657	40	77	/	N.A.

RAFT polymerization of *N*-Isobutyl acrylamide

Table S 2: Summary of RAFT polymerization conditions for N-Isobutyl acrylamide using PAETC as the RAFT agent. Reaction conditions: T = 90 °C, solvent = H_2O:Dioxane (3:7), Initiator = VA-044, reaction time = 15 min.

DP	[Monomer] (mol L^{-1})	[CTA] (mol L^{-1})	[CTA]/[initiator] ratio	Conversion (%)	$M_{n\ (theoretical)}$ g mol^{-1}	$M_{n\ (SEC)}$ g mol^{-1}	$Đ$
10	1.66	0.1657	40	93	1366	847	1.13
25	1.66	0.06628	40	90	3005	1846	1.15
50	1.66	0.03314	40	83	5364	3772	1.25
100	1.66	0.01657	40	74	9403	6522	1.18

RAFT polymerization of *N*-methyl acrylamide

Table S 3: Summary of RAFT polymerization conditions for N-methyl acrylamide using PAETC as the RAFT agent. Reaction conditions: T = 90 °C, solvent = H_2O:Dioxane (6:4), Initiator = VA-044, reaction time = 15 min.

DP	[Monomer] (mol L^{-1})	[CTA] (mol L^{-1})	[CTA]/[initiator] ratio	Conversion (%)	$M_{n\ (theoretical)}$ g mol^{-1}	$M_{n\ (H\ NMR)}$ g mol^{-1}
10	1.66	0.1657	40	88	910	847
25	1.66	0.06628	40	82	1906	1827
50	1.66	0.03314	40	79	3498	4040
100	1.66	0.01657	40	68	5892	N.A.

RAFT *polymerization* of Isopropyl-4-acrylamidobutanoate

Table S 4: Summary of RAFT polymerization conditions for Isopropyl 4 – acrylamidobutanoate using PAETC as the RAFT agent. Reaction conditions: T = 90 °C, solvent = H_2O:Dioxane (3:7), Initiator = VA-044, reaction time = 15 min.

DP	[Monomer] (mol L^{-1})	[CTA] (mol L^{-1})	[CTA]/[initiator] ratio	Conversion (%)	M_n (theoretical) g mol^{-1}	$M_{n\ (SEC)}$ g mol^{-1}	$Đ$
10	1.66	0.1657	10	92	2000	1476	1.12
25	1.66	0.06628	25	86	4394	2824	1.14
50	1.66	0.03314	50	59	5951	3171	1.18
100	1.66	0.01657	100	49	9746	6580	1.26

RAFT polymerization of 1,3-di-boc-guanidinobutyl acrylamide

Table S 5: Summary of RAFT polymerization conditions for 1,3-Di-Boc-Guanidinobutyl acrylamide using PAETC as the RAFT agent. Reaction conditions: T = ~30 °C, solvent = 1,4-Dioxane, Initiator = Benzoin, reaction time = 8 hours.

DP	[Monomer] (mol L^{-1})	[CTA] (mol L^{-1})	[CTA]/[initiator] ratio	Conversion (%)	M_n (theoretical) g mol^{-1}	$M_{n\ (SEC)}$ g mol^{-1}	$Đ$
10	0.45	0.045	20	99	4000	3935	1.10
25	0.45	0.018	20	98	10000	6883	1.12
50	0.45	0.009	20	98	20000	12420	1.21
100	0.45	0.0045	20	98	40000	13620	1.22

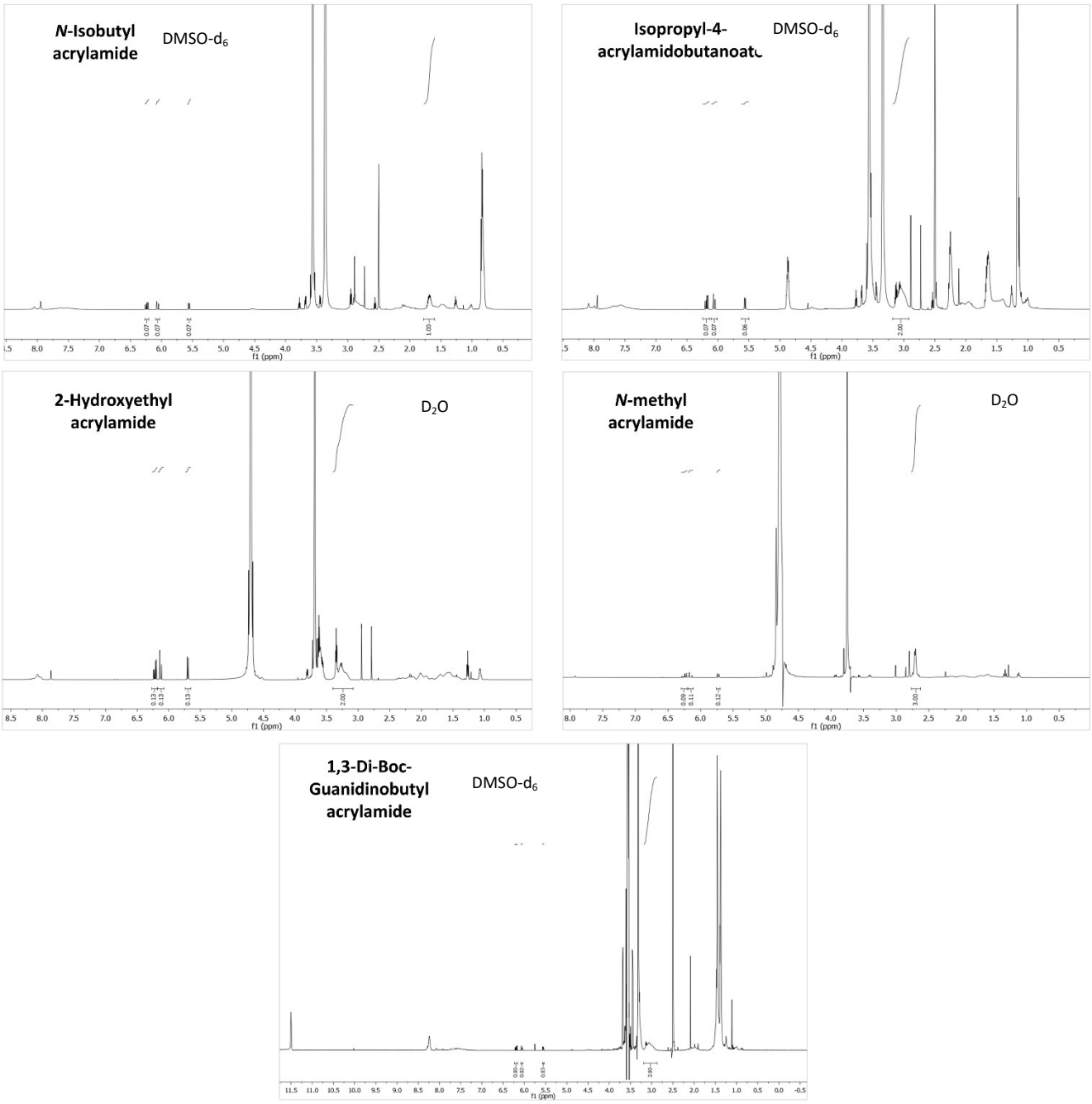


Figure S 13: Determination of the monomer conversions of homopolymers of the different model monomers via ^{1}H NMR in either DMSO-d_6 or D_2O: comparing the average integration of the vinyl peaks (monomer) to the integration of a backbone peak as reference integrated for one, two or three (depending on the monomer) protons (polymer backbone). For each reaction a reference sample at 0 minutes reaction time (T_0) was taken to which the vinyl integration were compared. The monomer conversion (p) was calculated using the following formula:

S6. SEC analysis

N-isobutyl acrylamide

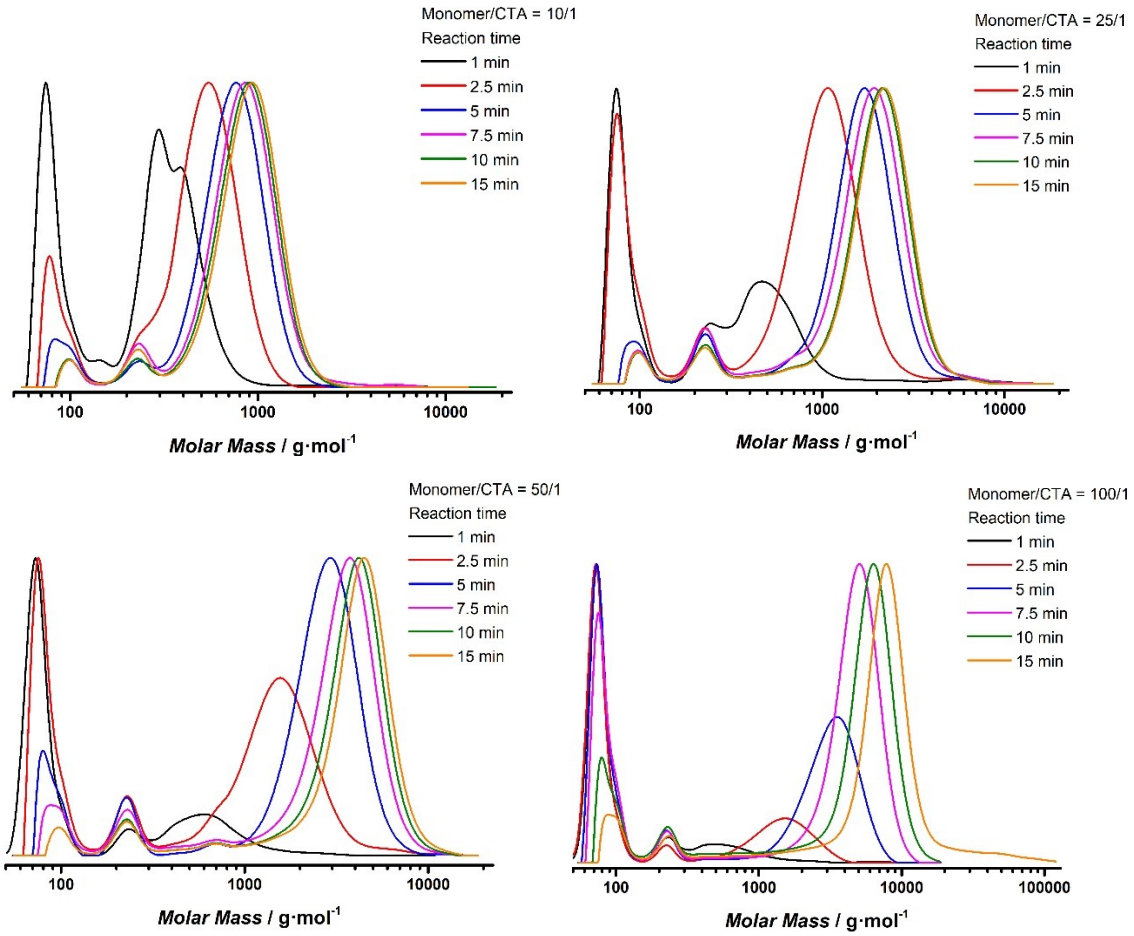


Figure S 14: Overview of monomer to RAFT variations at different reaction times for *N*-isobutyl acrylamide indicating the reduction of the monomer peak and emerging of the polymer molecular weight distribution

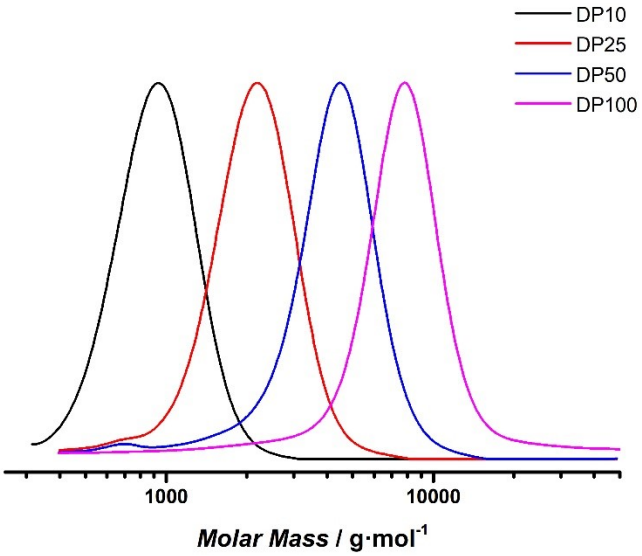


Figure S 15: Molecular weight distributions of the different monomer to RAFT agent ratios after 15 min reaction time for *N*-isobutylacrylamide.

Isopropyl 4-acrylamidobutanoate

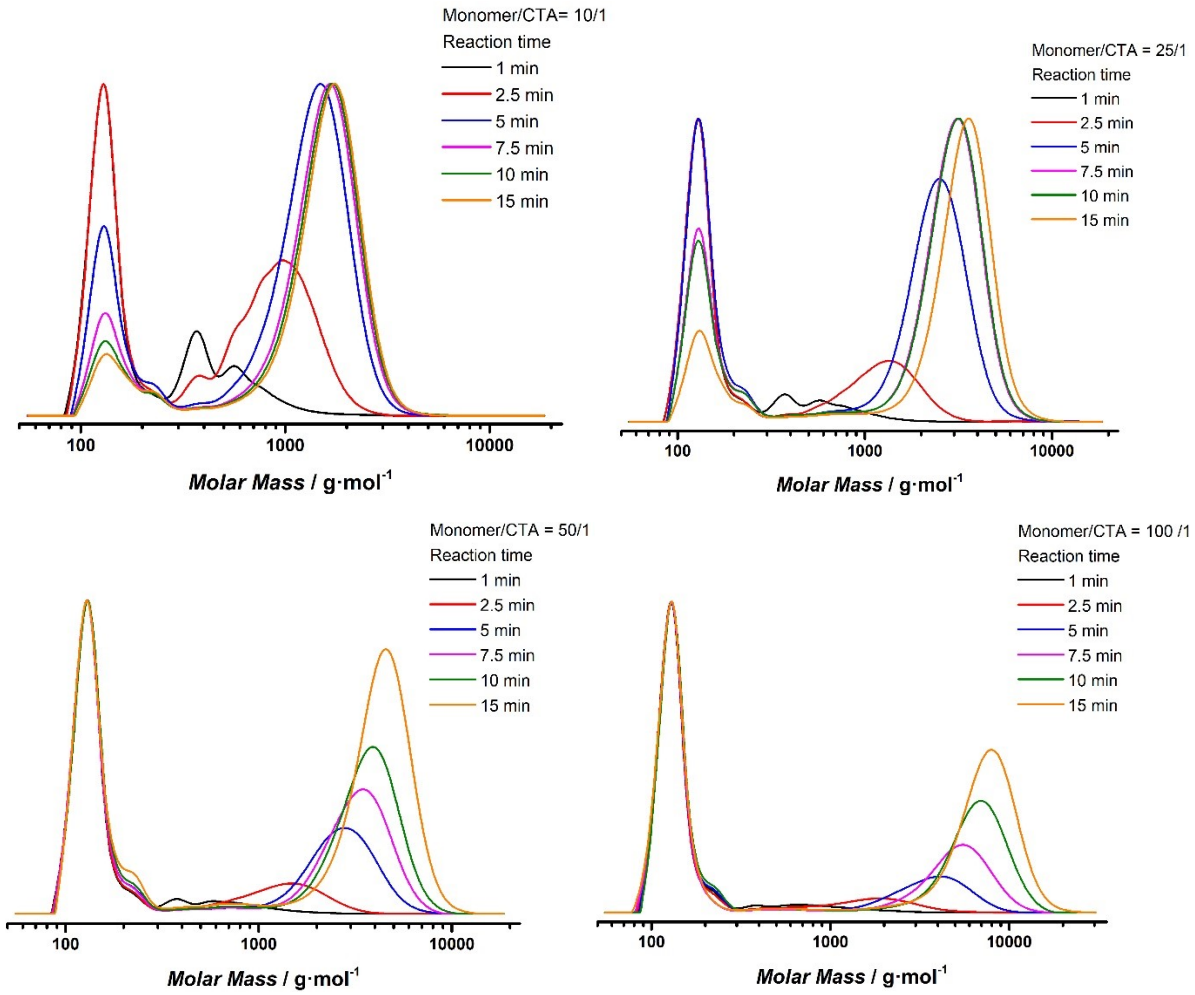


Figure S 16*:* Overview of monomer to RAFT variations at different reaction times for Isopropyl 4-acrylamidobutanoate indicating the reduction of the monomer peak and emerging of the polymer molecular weight distribution

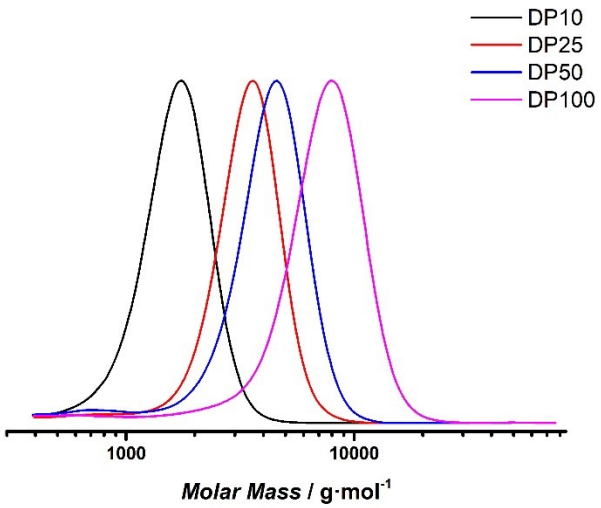


Figure S 17*:* Molecular weight distributions of the different monomer to RAFT agent ratios after 15 min reaction time for *N*-isobutyl acrylamide.

1,3 di-boc-guanidinobutyl acrylamide

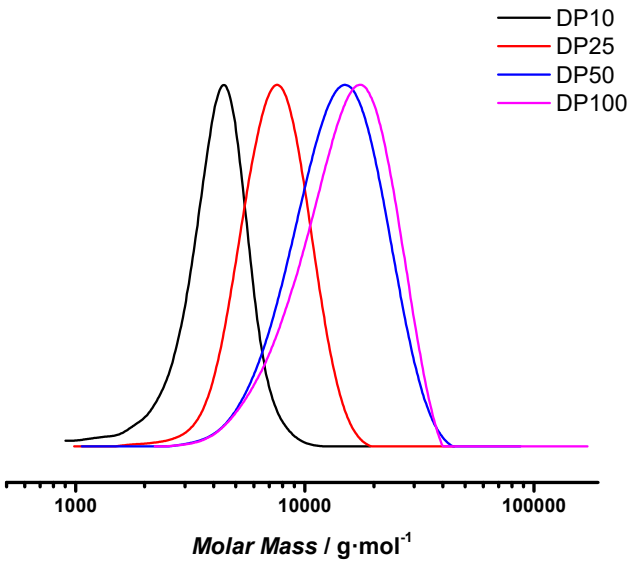


Figure S 18: Molecular weight distributions of the different monomer to RAFT agent ratios after 8 hour reaction time for 1,3-di-boc-guanidinobutyl acrylamide

S7. ^{1}H NMR analysis of 1,3-di-boc guanidinobutyl acrylamide degradation

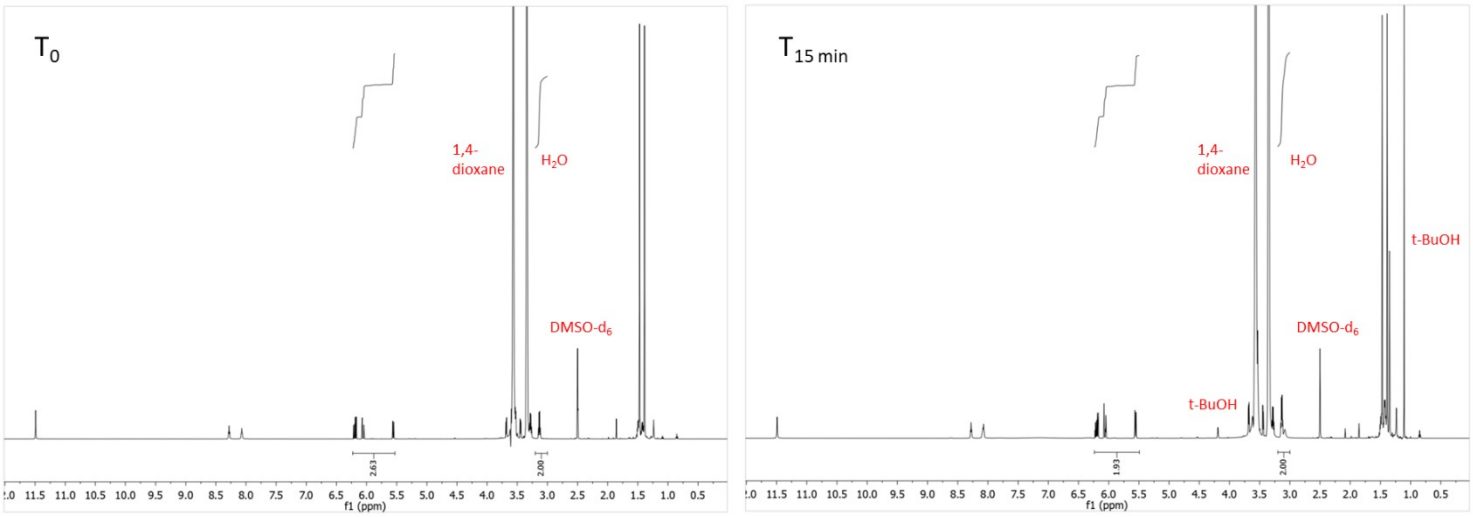


Figure S 19: ^{1}H NMR spectra (in DMSO-d_6) of crude reaction mixture for the thermal RAFT polymerization of 1,3-di-boc guanidinobutyl acrylamide with PAETC and VA-044 as CTA and radical initiator respectively in a Dioxane:H_2O (8:2) mixture taken before (T_0 – left figure) and after 15 minutes reaction time (T_{15min} – right figure) at 90 °C. Monomer conversion was determined by using the formula on page 16 and indicated 26% monomer conversion. Clear tert-Butanol peaks are present in the 15 minute sample indicative of the monomer deprotection.

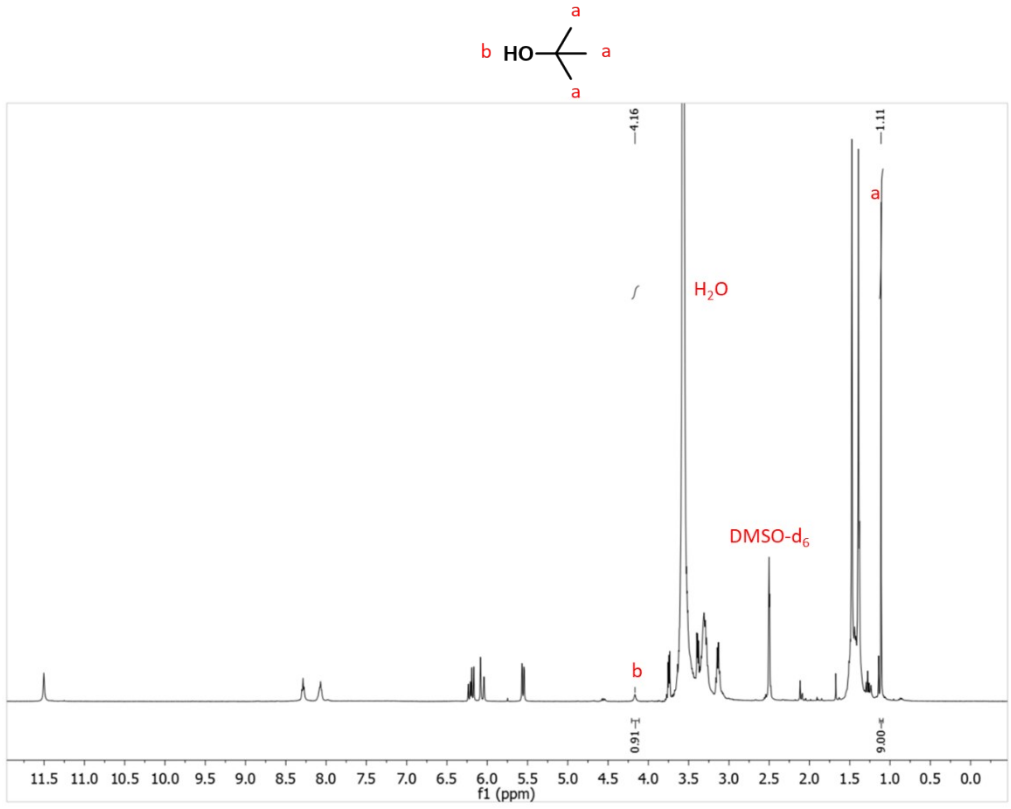


Figure S 20*:* ^{1}H NMR spectrum of a crude polymerization reaction mixture of 1,3-di-boc guanidinobutyl acrylamide conducted for 48 hours at 45 °C in 1,4-Dioxane. No monomer conversion was observed after 48 hours of reaction time and two peaks at 4.36 and 1.11 ppm appeared and indicated the presence of tert-butanol in the sample.

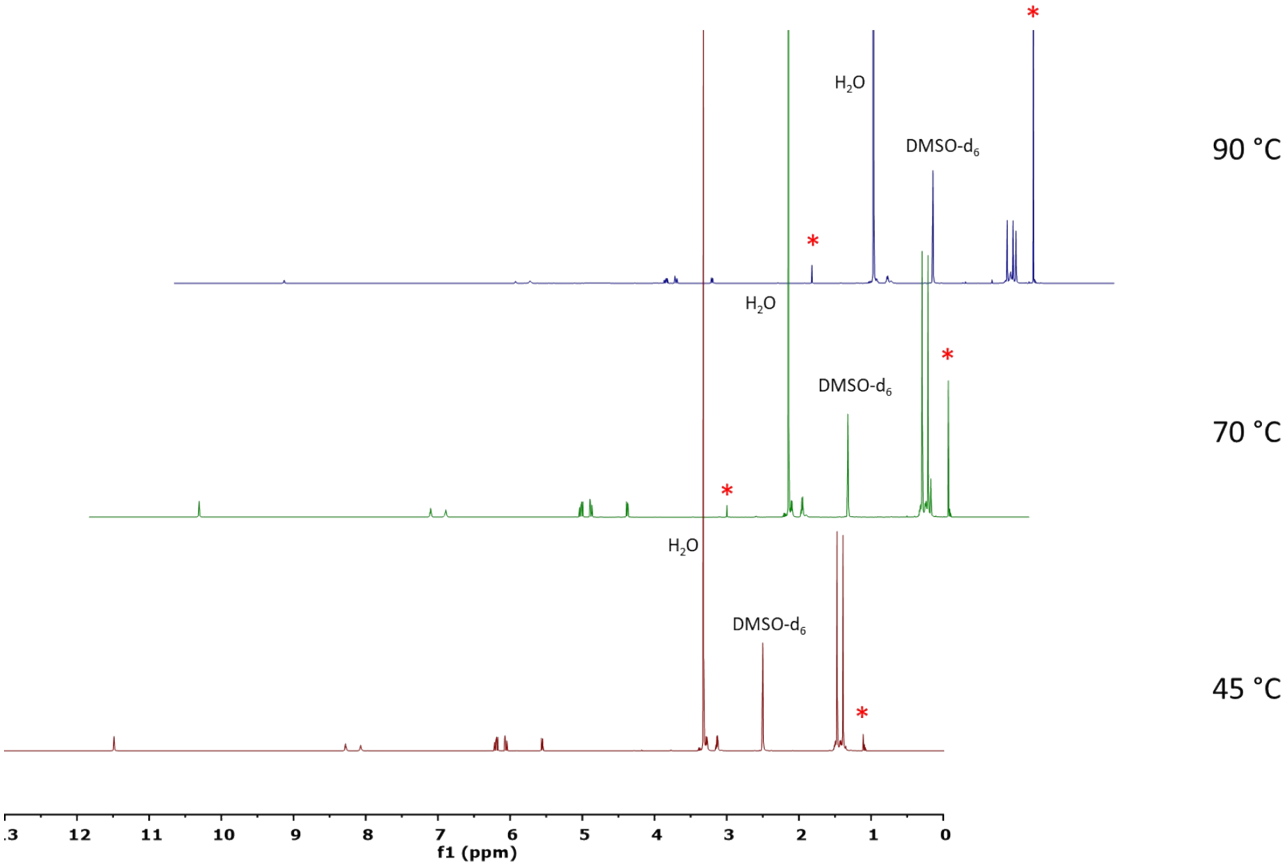


Figure S 21: ^{1}H NMR spectra of 1,3-di-boc guanidinobutyl acrylamide in DMSO-d_6 after 15 min exposure to 45, 70 or 90 °C. An amount of monomer was dissolved in DMSO-d_6 in an NMR tube. The tube was subsequently submerged in an oil bath set to the desired temperature. After 15 minutes the tubes were taken out of the oil bath and cooled in a cool water bath. The samples were then analysed ^{1}H NMR. Peaks associated with tert-Butanol are highlighted with a red asterisk. Higher temperatures resulted in larger amounts of tert-butanol formed.

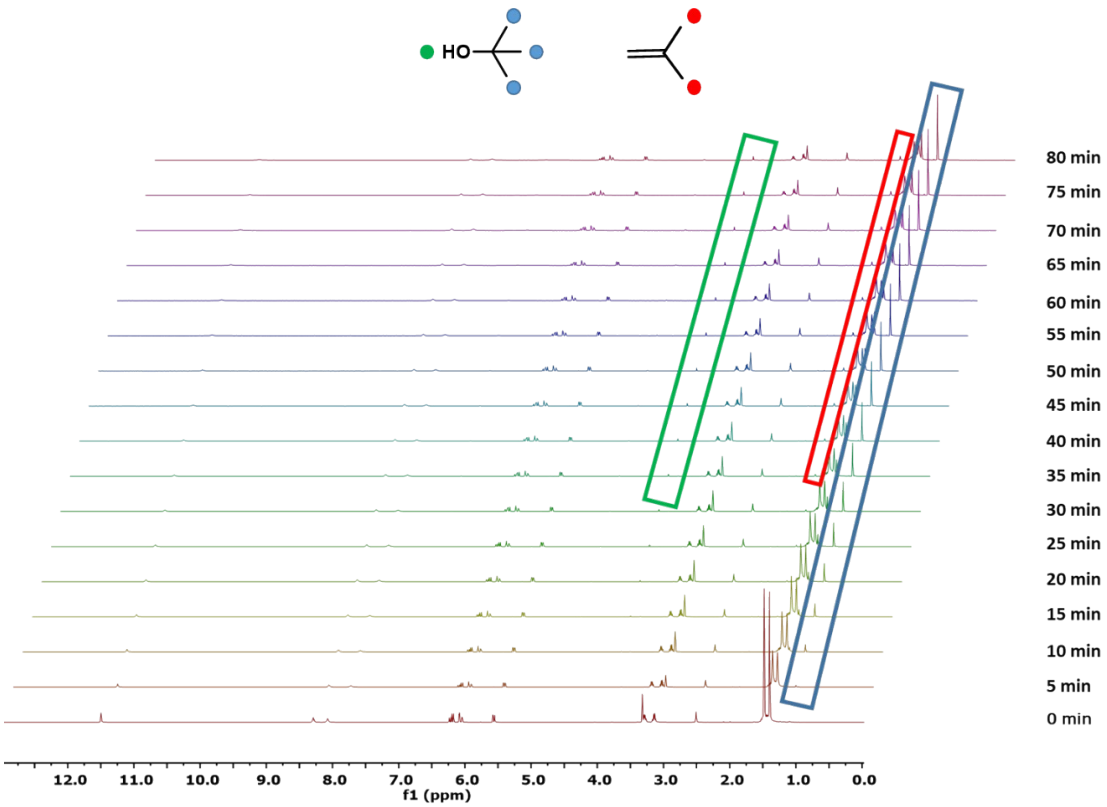


Figure S 22: Evolution of monomer deprotection and subsequent tert-butanol and isobutylene formation monitored via ^{1}H NMR analysis in DMSO-d_6 at a constant temperature of 70 °C at 5 minute intervals. The 0 minute sample was measured at room temperature (25 °C). Deprotection of the monomer under elevated temperatures is confirmed by the clear decrease of the singlets at 1.41 and 1.49 ppm which represent both tert-butyl groups of both Boc-protection groups of the monomer over time. Moreover, a singlet at 1.11 ppm, indicative of the tert-butyl group in tert-butanol, appears and increases in intensity over time. Tert-butanol is generated from the reaction of tert-butyl cations (generated through the deprotection of the Boc groups of the monomer) with water molecules in the solvent. Finally, 2 singlets at 4.65 and 1.7 ppm appear after 5 minutes (only visible in figure from 25 min sample trace) which are indicative of the presence of isobutylene which is formed through an elimination reaction of tert-butyl cations. The clear difference in peak intensity between isobutylene and tert-butanol indicates that the formation of tert-butanol happens faster.

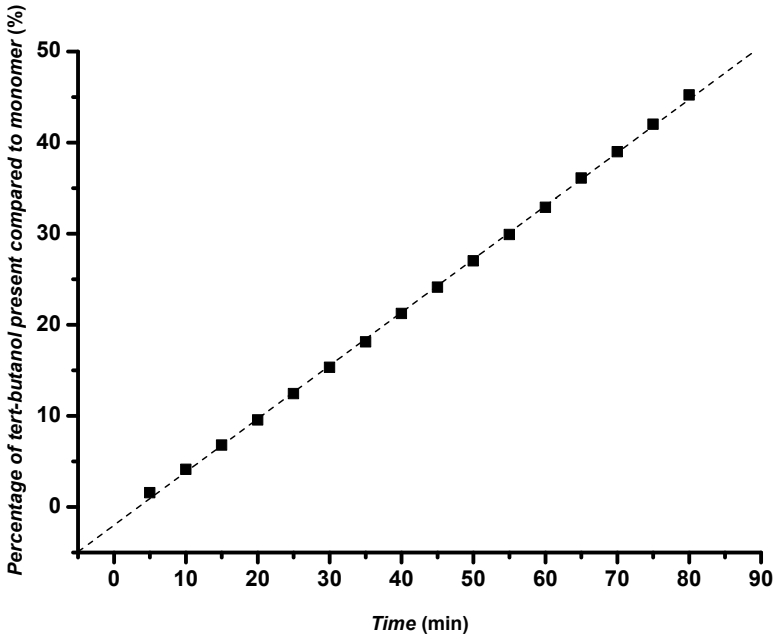


Figure S 23: Percentage of tert-butanol formation compared to monomer over time.

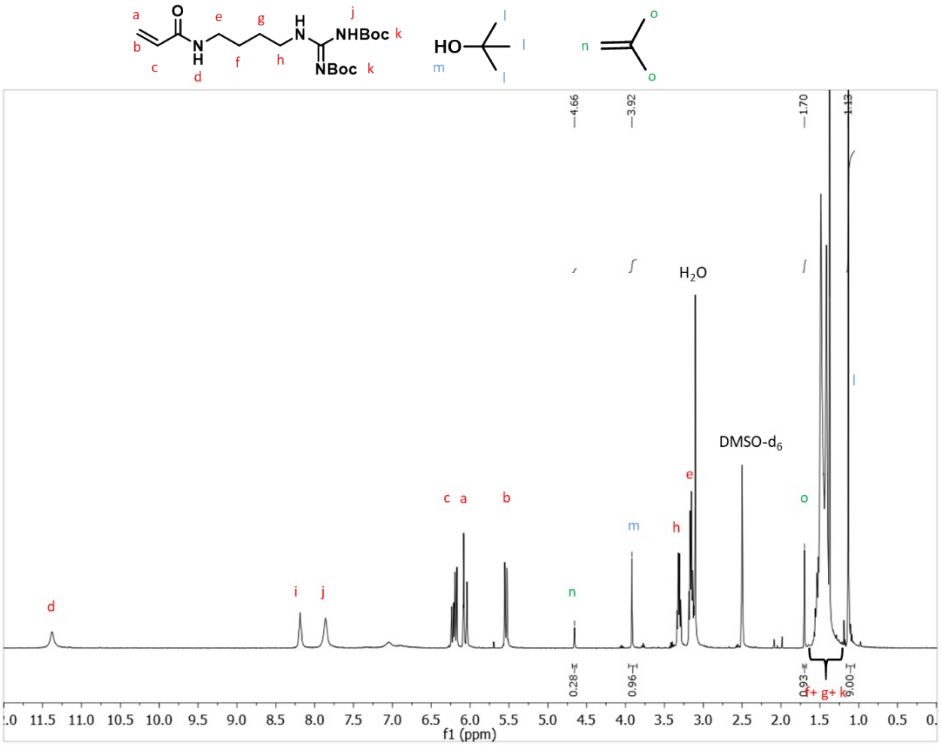


Figure S 24: ^{1}H NMR spectrum of 1,3-di-boc guanidinobutyl acrylamide after exposure to 70 °C for 80 minutes in DMSO-d_6. Additional peaks indicative of the presence of tert-butanol (3.92 ppm –O**H** and 1.13 ppm –C**H$_3$** , 1:9 integration ratio) and isobutylene (4.66 ppm =C**H$_2$** and 1.70 ppm –C**H$_3$**, 1:3 integration ratio) were observed. The presence of both tert-butanol and isobutylene confirm the deprotection of the guanidinium functionality of the monomer.

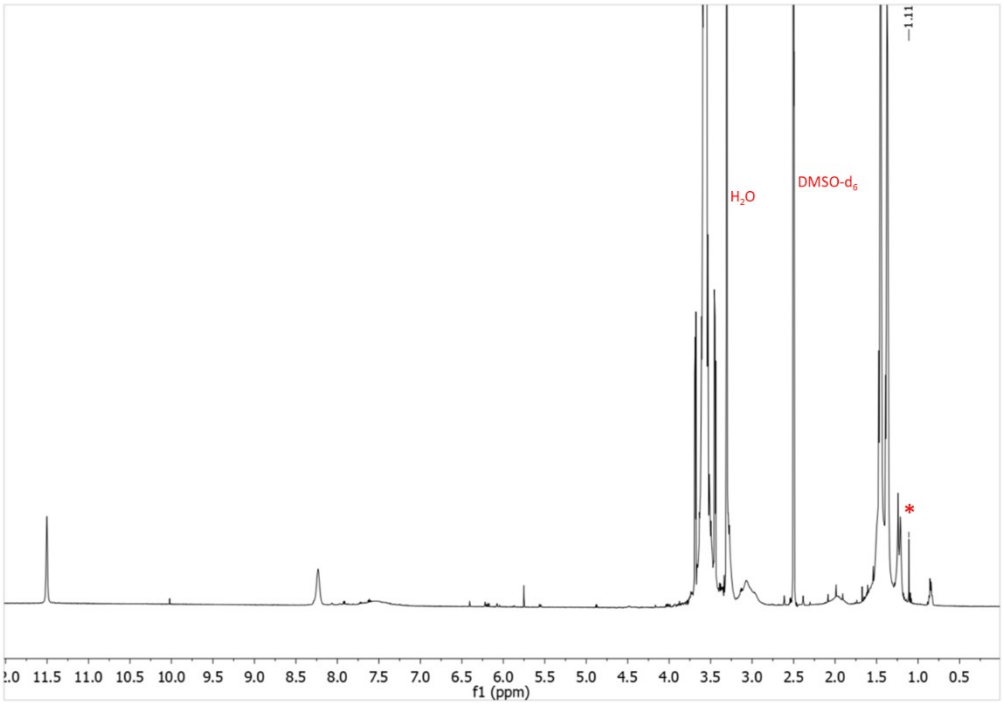


Figure S 25: ^{1}H NMR spectrum of poly(1,3-di-boc guanidinobutyl acrylamide) (DP10) generated through a photoRAFT reaction conducted in 36W Coscelia Nail Dryer UV LED (365 + 405 nm) lamp for 24 hours. The photo activated polymerization reaction resulted in high monomer conversion and small amounts of deprotection as indicated by the low intensity of the singlet at 1.11 ppm.

S8. TGA analysis of 1,3-di-boc guanidinobutyl acrylamide

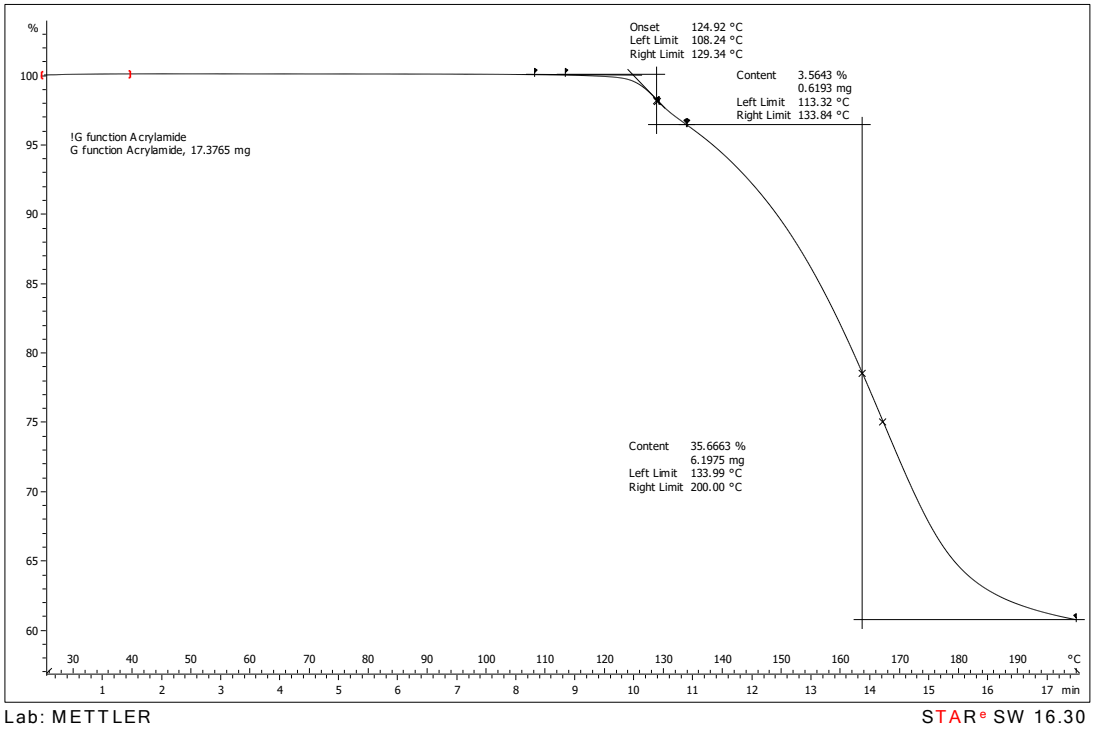


Figure S 26: Dynamic Thermogravimetric analysis (TGA) of 1,3-di-boc-guanidinobutyl acrylamide monomer