Supporting information

Kinetic investigation of photoiniferter-RAFT polymerization in continuous flow using inline NMR analysis

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1 Experimental section

1.1 Materials

Methyl acrylate (MA) and methyl methacrylate were obtained from Sigma-Aldrich and passed through activated basic alumina column prior to use to remove inhibitor. 2,2'-Azobis(2-methylpropionitrile) (AIBN, $t_{1/2\text{-}10h}$ = 65°C (toluene), 98%) was obtained from Sigma-Aldrich and recrystalised from hexane prior to use. RAFT agents were synthesised, details below. All solvents, including anhydrous solvents, were obtained from either Chem-Supply, Fisher Scientific, VWR Chemical, or Sigma-Aldrich, and used as received. All deuterated solvents were obtained from or Sigma-Aldrich and used as received. Sodium 1-butanethiolate, carbon disulfide, (dimethylamino)pyridine (DMAP), 2-bromopropionic acid, 2-bromo-2-methylpropanoic acid, methyl-2-bromoproponate, sodium thiosulfate were obtained from Sigma Aldrich and used as received. N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) was obtained from Carbosynth and used as received. Iodine was obtained from Fisher and used as received. N-butylxanthic acid potassium salt was obtained from ABCR and used as received. Sodium hydride, 60% in oil was obtained STREM CHEMICALS UK and used as received.

1.2 Characterisation

1.2.1 Nuclear Magnetic Resonance (NMR) spectroscopy

^{1}H NMR spectra were recorded using a low field NMR spectrometer (60 MHz Magritek Spinsolve Ultra) using reaction monitoring suite with 7 µs excitation pulse, spectral width of 5 kHz (32,768 points), acquisition time of 6.4 s, repetition time 17 s and 2 scans. The spectrometer was shimmed using the powershim (40 min) setting with the standard solution of 10% D_2O in H_2O at the start of the day. The reaction monitor protocol (RMX) was used for data acquisition. All spectra were auto-phased and baseline correction was applied in the Spinsolve software prior to analysis.

Conversion for methyl acrylate was calculated as follows:

$$\alpha = \frac{[M]_0 - [M]_t}{[M]_t} = \frac{[P]_t}{[M]_t + [P]_t} = \frac{\int 1H_{polymer}}{\int 1H_{monomer} + \int 1H_{polymer}} = \frac{\frac{y-x}{3}}{\frac{y}{3}}$$

Equation 1 Monomer conversion, where $[M]_0$ is monomer concentration at time = 0, $[M]_t$ is monomer concentration at time = t, $[P]_t$ is polymer concentration at time t, x is integral of vinyl peaks of methyl acrylate and y is integral of methoxy peaks (monomer and polymer), see Figure 1.

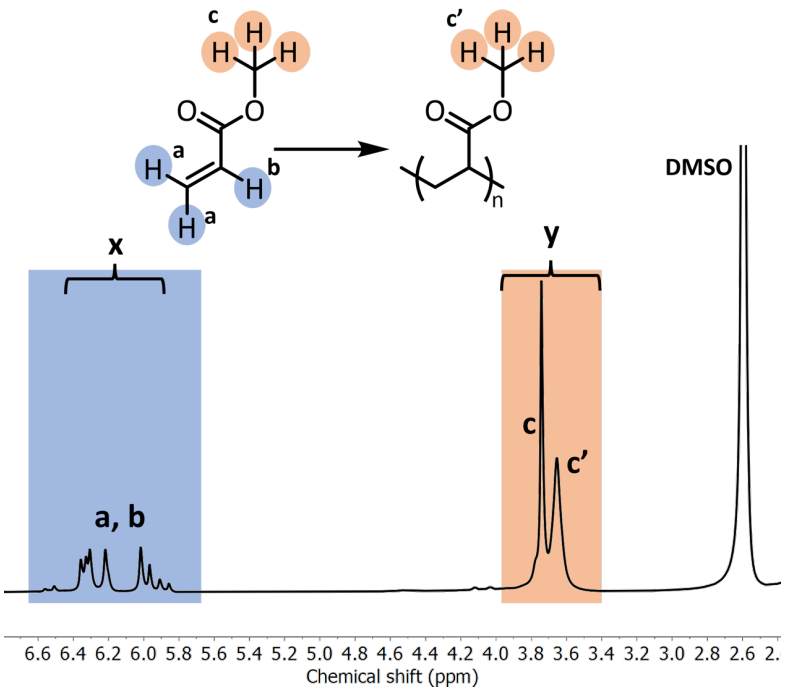


Figure 1 Assigned low field NMR spectrum of a partially converted PMA polymerization.

Conversion for methyl methacrylate was calculated analogously.

High field NMR spectra (offline) were recorded on 400 MHz Bruker Advanced III systems at 25°C using deuterated solvents – d-DMSO (99.9% D atom) or d-$CHCl_3$ (99.9 % D atom).

1.2.2 Size Exclusion Chromatography (SEC)

THF-SEC: PSS SECcurity2 GPC systems equipped with differential refractive index (DRI). The system was equipped with 3 x 5 µm SDV PSS analytical columns (50 x 8 mm) with varying porosity (1000 Å, 100 000 Å and 1 000 000 Å) and SDV 5.0 µm guard column. The eluent is THF, samples were run at 1ml/min at 40°C. Poly(styrene) narrow standards (PSS Laboratories) were used for calibration. Analyte samples were filtered through a PTFE membrane with 0.22 µm pore size before injection and sample solvent contained toluene as a flow marker. Respectively, experimental molar mass ($M_{n,SEC}$) and dispersity ($Đ$) values of synthesized polymers were determined by conventional calibration using PSS

WinGPC software and corrected against the Mark-Houwink-Sakurada (MHS) parameters of PMA reported literature values ($K = 10.2 \times 10^{-5}$, $dL \cdot g^{-1}$ and $\alpha = 0.74$).[1]

1.2.3 Ultraviolet/visible (UV-Vis) absorption spectroscopy

UV-Vis absorption spectra were recorded using Agilent Cary 60 UV-Vis spectrometer at 25°C in spectroscopy grade DMSO, scanning rate 600 nm/min, with automatic baseline correction.

1.3 Reactor set up

All experiments were performed using a single syringe pump (Fusion 100 Classic, Chemyx Inc) with a 10 mL SGE gastight syringe, and a custom-built flow reactor made of PFA tubing (1/16'' OD, 0.75 mm ID, 0.9 ml), wrapped around a glass beaker (Ø = 5.1 cm) and secured with cable ties (inner cable tie ring keeps the body of the tubing in place, outer cable tie ring secures inlet and outlet in place, see Figure 2B). Flow reactor was submerged in a thermostatic oil bath foil (Ø = 9 cm) wrapped with aluminium, and a blue LED array (λ_{max} = 455-460 nm, 10 W, LZ4-00B208, ams-OSRAM) placed 0.5 cm above the flow reactor. The LED array was connected to a heat sink (SK 577/20 SA, Fischer Elektronik) and a constant flow of compressed air was blowing over the heat sink to cool it down. The light intensity of the LED array was controlled with digital control DC power supply (RS PRO RS3005P, 0-30V, 0-5A) by changing the current. The light intensity [mW/cm^2] was measured using S401C Thermal Power Sensor (ThorLabs) pointed directly at the empty flow reactor, connected to a ThorLabs PM400 optical power meter set at 460 nm. The outlet of the flow reactor was passed through a hollow NMR tube, to keep the tubing stable, and directly through the benchtop NMR. Spectra were recorded every 17s and the dead volume between the reactor and the benchtop NMR was 0.34 ml. The syringe and tubing between the reactor and NMR were covered with aluminium foil to prevent any light exposure. Flow rates were preprogrammed using a python script, and the syringe pump was controlled with a Labview script, both available at GitHub: https://github.com/PRDMonash/ScreeningPlatform/tree/master[2]

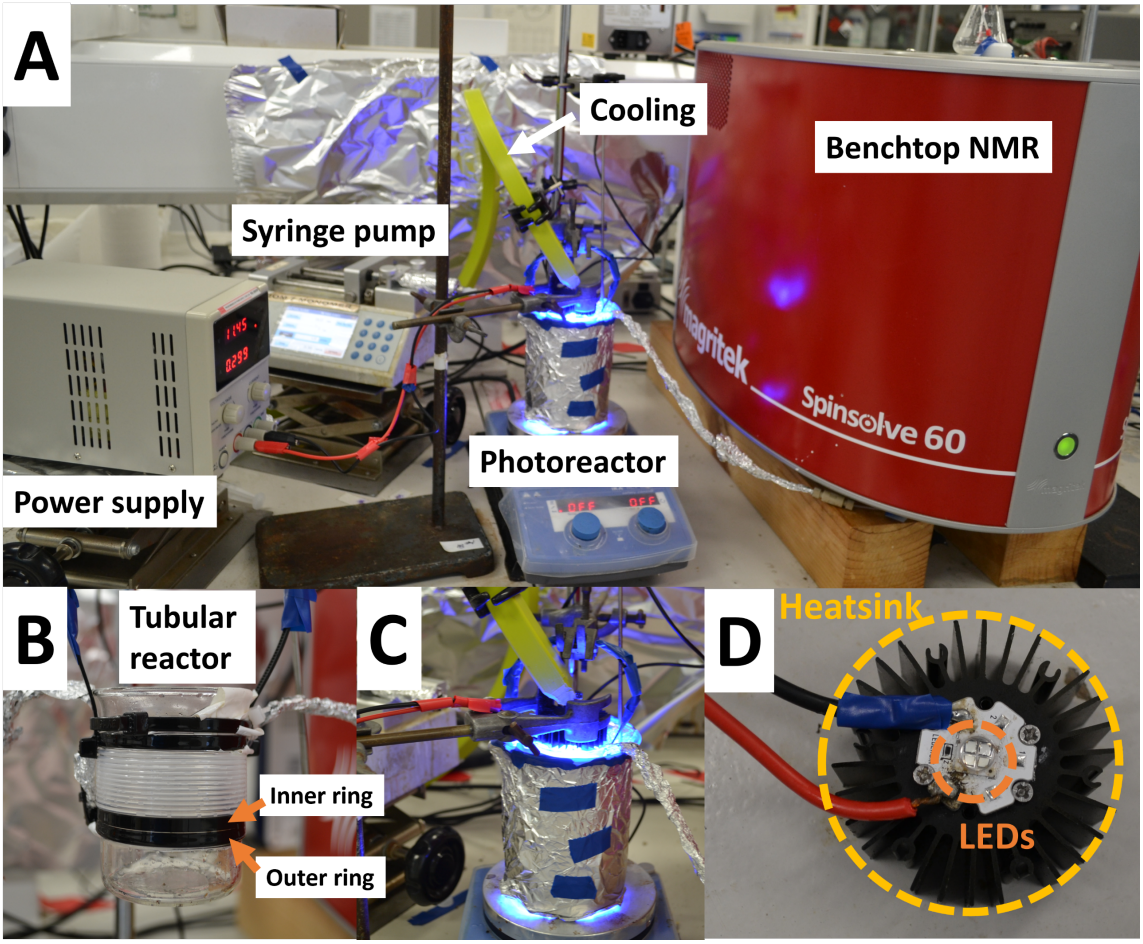


Figure 2 A Photo flow reactor set up consisting of power supply, syringe pump, photoreactor with cooling and benchtop NMR. B Close-up view of the tubular flow reactor. C Close-up view of the photoreactor. D Close-up view of the LED connected to a heatsink.

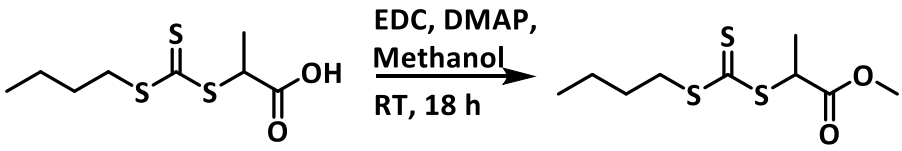
Table 1 Light intensity values for different current supply to the LED.

Current [A]	Light intensity [mW/cm^2]
0.15	5.3
0.25	8.6
0.3	9.8
0.35	11.2
0.4	12.5
0.5	15
0.6	17.6
0.7	20.1
0.8	22.2

1.4 Experimental procedures

1.4.1 Synthesis of methyl 2-(((butylthio)carbonothioyl)thio)propanoate (PMBTC)

Scheme 1 Synthesis of PMBTC.



2- (((Butylthio)-carbonothioyl)thio)propanoic acid (PABTC) was synthesised according to the literature[3] and recrystallised twice from hexane before use. 10.00 g of PABTC (1 eq, 42 mmol), 0.62 g (0.12 eq, 5 mmol) DMAP and 9.00 g (1.12 eq, 47 mmol) of EDC were dissolved in 100 ml of methanol and vigorously stirred at room temperature for 18 h. Then, methanol was removed in vacuo and the residue was redissolved in 100 ml of DCM and washed twice with water (50 ml each), dried over $MgSO_4$ and concentrated under vacuum. The crude product was purified by flash column chromatography on a silica column, 80/20 hexanes/ethyl acetate eluent to give pale orange oil (7.30 g, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.85 (q, *J* 7.2, 1H, CS*H*CH_3), 3.75 (s, 3H, OCH_3), 3.37 (t, *J* 7.2, 2H, CH_2S), 1.69 (quin, *J* 7.2, 2H, SCH_2CH_2), 1.60 (d, *J* 8, 3H, $CHCH_3$), 1.43 (h, *J* 7.2, 2H, CH_2CH_3), 0.94 (t, *J* 7.2, 3H, CH2C*H*3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 222.0 (C=S), 171.7 (C=O), 52.9 (OCH_3), 47.73 ($CHCH_3$), 37.0 (SCH_2),

29.9 (SCH_2CH_2), 22.1 (CH_2CH_3), 17.0 ($CHCH_3$), 13.6 (CH_2CH_3) ppm. ESI MS +ve: Calculated for $C_8H_{14}O_2S_3Na$, $[M+Na]^+$ 275.02. Found m/z 275.0

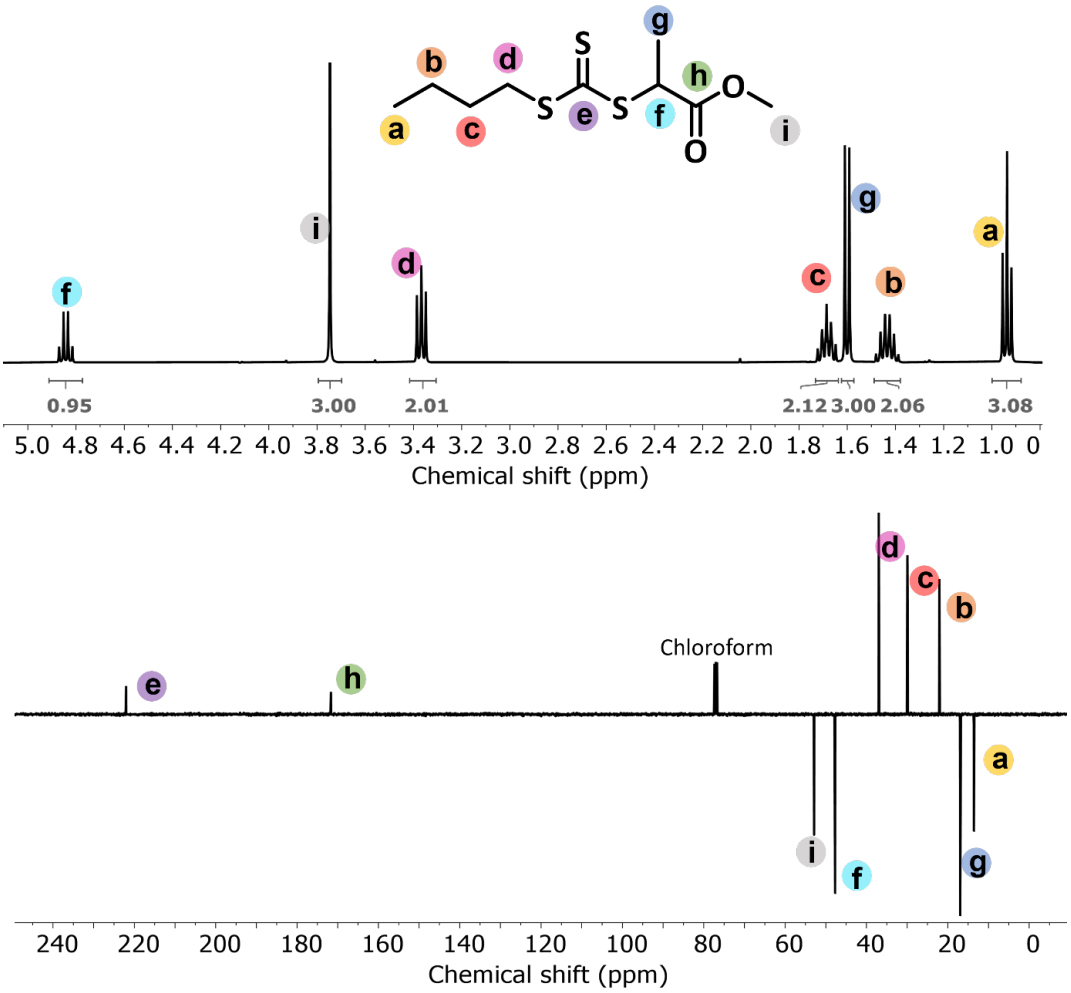
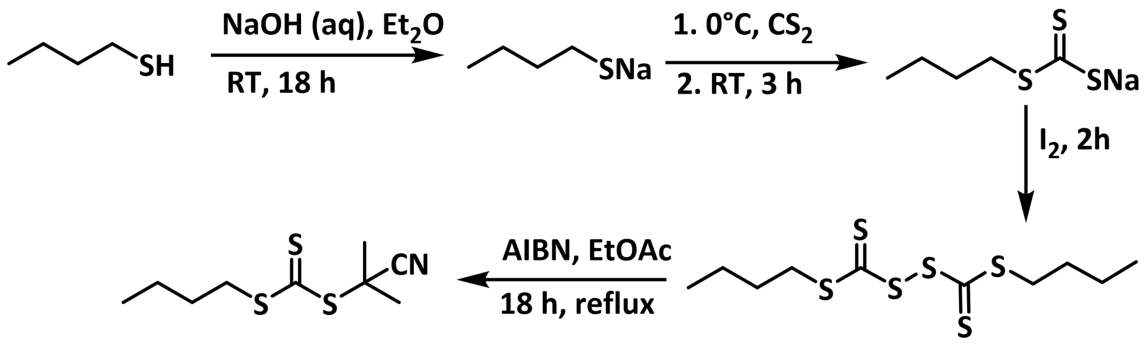


Figure 3 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra ($CDCl_3$) of PMBTC.

1.4.2 Synthesis of Butyl (2-cyano-2-propyl) trithiocarbonate (BCN-TTC)

Scheme 2 Synthesis of BCN-TTC



25 ml of 1-butanethiol (1 eq, 0.23 mol) and 350 ml diethyl ether were charged into a round bottom flask equipped with a stirrer bar and a rubber septum. Slowly, aqueous solution of sodium hydroxide (10.21 g, 1.1 eq, 0.26 mol in 40 ml of water) was added and solution was stirred overnight. The solution was cooled down on ice bath and carbon disulfide (14.65 ml, 1.05 eq, 0.24 mol) was added dropwise via syringe over 10 min. The reaction was brought up to room temperature and stirred for further 3 h after which 32.38 g of solid iodine (0.55 eq, 0.128 mol) was added portion-wise and stirred at room temperature for 2 h. The reaction mixture was subsequently washed with thiosulfate, until no further colour changes of the organic layer were observed, water (1x 100 ml) and brine (2 x 100 ml). The organic layer was dried over $MgSO_4$ and solvent removed under vacuum to give bis(butylsulfanylthiocarbonyl) disulfide as dark orange oil which was used without further purification (crude yield 81%, 31.1 g). Bis(butylsulfanylthiocarbonyl) disulfide (5 g, 1eq, 151 mmol) and AIBN (1.5 eq, 3.73 g) were dissolved in 150 ml of ethyl acetate in a three neck round bottom flask fitted with thermometer and water condenser. The solution was purged with nitrogen for 30 min, water condenser was equipped with a nitrogen filled balloon before it was heated up and refluxed for 18 h. Solvent was removed under vacuum. Crude product was dissolved in hexane to precipitate out excess of AIBN and its decomposition products. The resulting solution was filtered, concentrated and RAFT agent was purified by silica flash chromatography using hexane/ethyl acetate gradient, starting with 100% hexane, concentrated, and dried under high vacuum to give a red oil, 53% yield, 3.77 g. The resulting RAFT agent was stored in the freezer under nitrogen.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.35 (t, *J* 7.4, 2H, C*H*$_2$S(C=S)), 1.87 (s, 6H, (C*H*$_3$)$_2$C(CN)), 1.72 – 1.64 (m, 2H, C*H*$_2$CH$_2$CH$_3$), 1.49 – 1.39 (m, 2H, C*H*$_2$CH$_3$), 0.94 (t, *J* 7.4, 3H, CH$_2$C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 217.8 (C=S), 120.4 (CN), 42.4 (*C*(CN)(CH$_3$)$_2$), 36.6 (SCH$_2$), 29.8 (SCH$_2$*C*H$_2$), 27.1 ((*C*H$_3$)$_2$C(CN)), 22.1 (*C*H$_2$CH$_3$), 13.7 (CH$_2$*C*H$_3$)

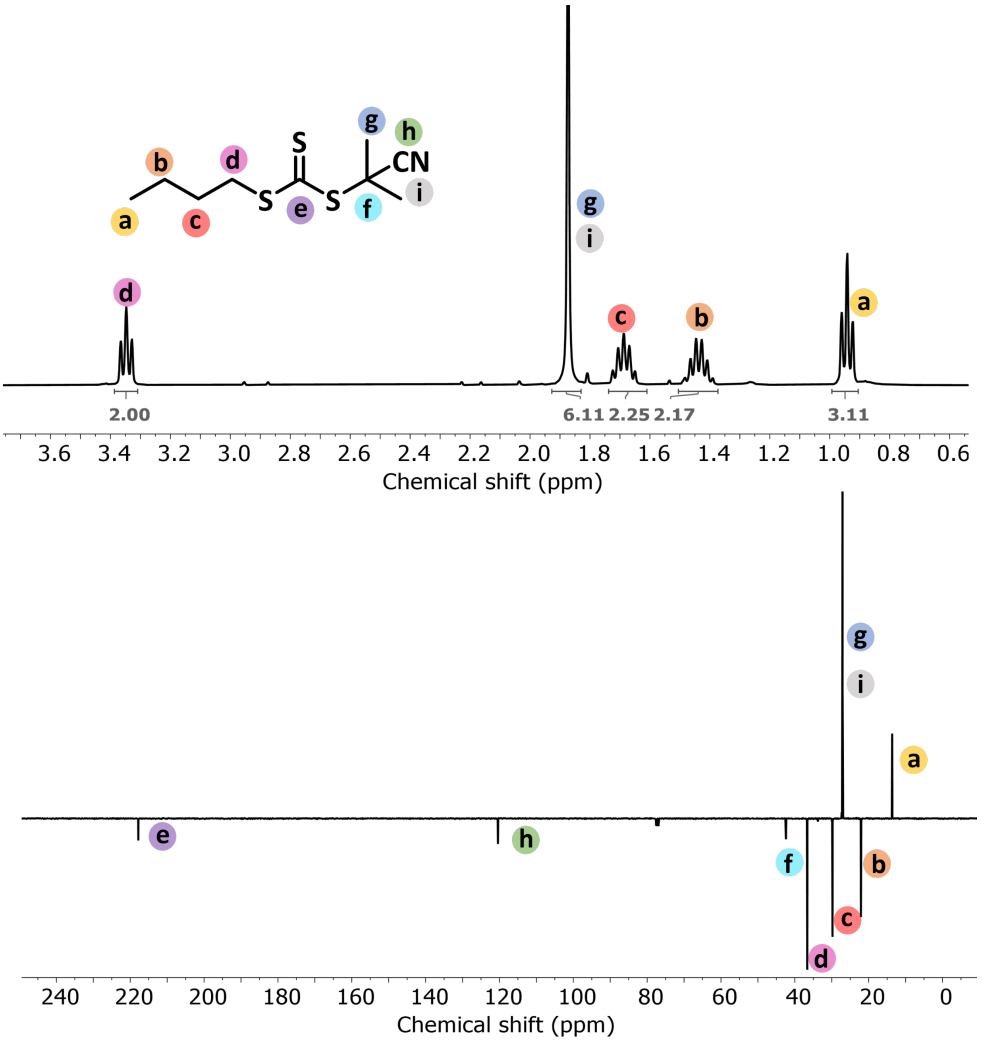
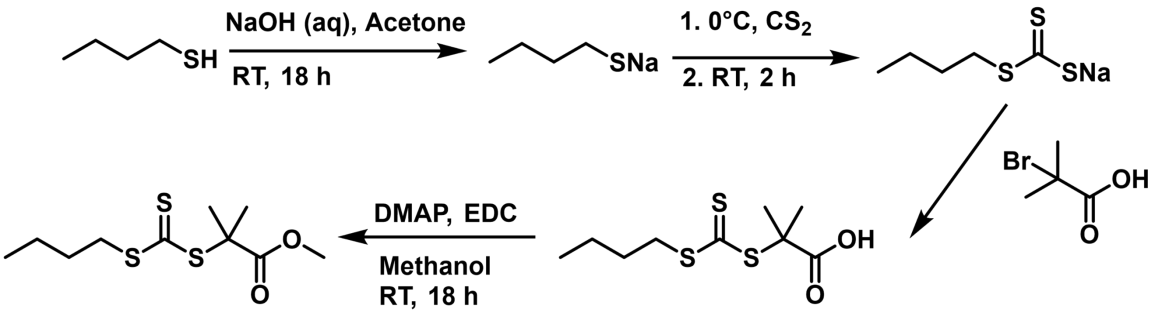


Figure 4 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra ($CDCl_3$) of BCN-TTC.

1.4.3 Synthesis of 2-(butylthiocarbonothioylthio)-2-methylpropanoate (BDMMT)

Scheme 3 Synthesis of BDMMT.



Aqueous solution of sodium hydroxide (9.28 g, 1 eq, 0.23 mol in 40 ml of water) was slowly added to a mixture of 1-butanethiol (25 ml, 1 eq, 0.23 mol) and acetone (15 ml) and the solution was vigorously stirred at room temperature overnight. The solution was cooled on ice bath and carbon disulfide

(15.34 ml, 1.1 eq, 0.26 mol) was added dropwise via syringe over 10 min and the reaction was left at room temperature for further 2 h. The solution was cooled down in an ice bath and 2-bromo-2-methylpropanoic acid (38.74 g, 1 eq, 0.23 mol) was added slowly followed by addition of further 9.28 g of sodium hydroxide in 40 ml of water. The solution was left to stir overnight at room temperature after which the reaction mixture was diluted with 100 ml of water before being washed twice with hexane. The aqueous layer was then cooled down on ice bath and concentrated hydrochloric acid was added dropwise until pH 2 was reached and yellow precipitate formed. The solid was collected by vacuum filtration, washed twice with cold water and dried to give 2-(butylthiocarbonothioylthio)-2-methylpropionic acid as yellow powder (34.86 g, crude yield 60%) which was used without further purification. 34.5 g of BDMAT (1 eq, 137 mmol), 2.0 g (0.12 eq, 16 mmol) DMAP and 29.4 g (1.12 eq, 153 mmol) of EDC were dissolved in 200 ml of methanol and vigorously stirred at room temperature for 18 h. Then, methanol was removed in vacuo and the residue was redissolved in 200 ml of DCM and washed twice with water (2 x 70 ml), brine (2 x 70 ml) dried over $MgSO_4$ and concentrated under vacuum. The crude product was purified by flash column chromatography on a silica column, gradient 80/20 hexanes/ethyl acetate eluent to orange oil (21.45 g, 59% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.71 (s, 1H, OCH_3), 3.29 (t, *J* 7.4, 2H, $CH_2S(C=S)$), 1.69 (s, 6H, $(CH_3)_2CH$), 1.67-1.62 (m, 2H, $CH_2CH_2CH_3$), 1.42 (quin, *J* 7.4, 2H, CH_2CH_3), 0.93 (t, *J* 7.4, 3H, CH_2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.1 (C=S), 173.0 (COOH), 55.6 ($C(CH_3)_2$), 52.8 (OCH_3), 36.4 (SCH_2), 29.9 (SCH_2CH_2), 25.2 ($C(CH_3)_2$), 22.0 (CH_2CH_3), 13.6 (CH_2CH_3).

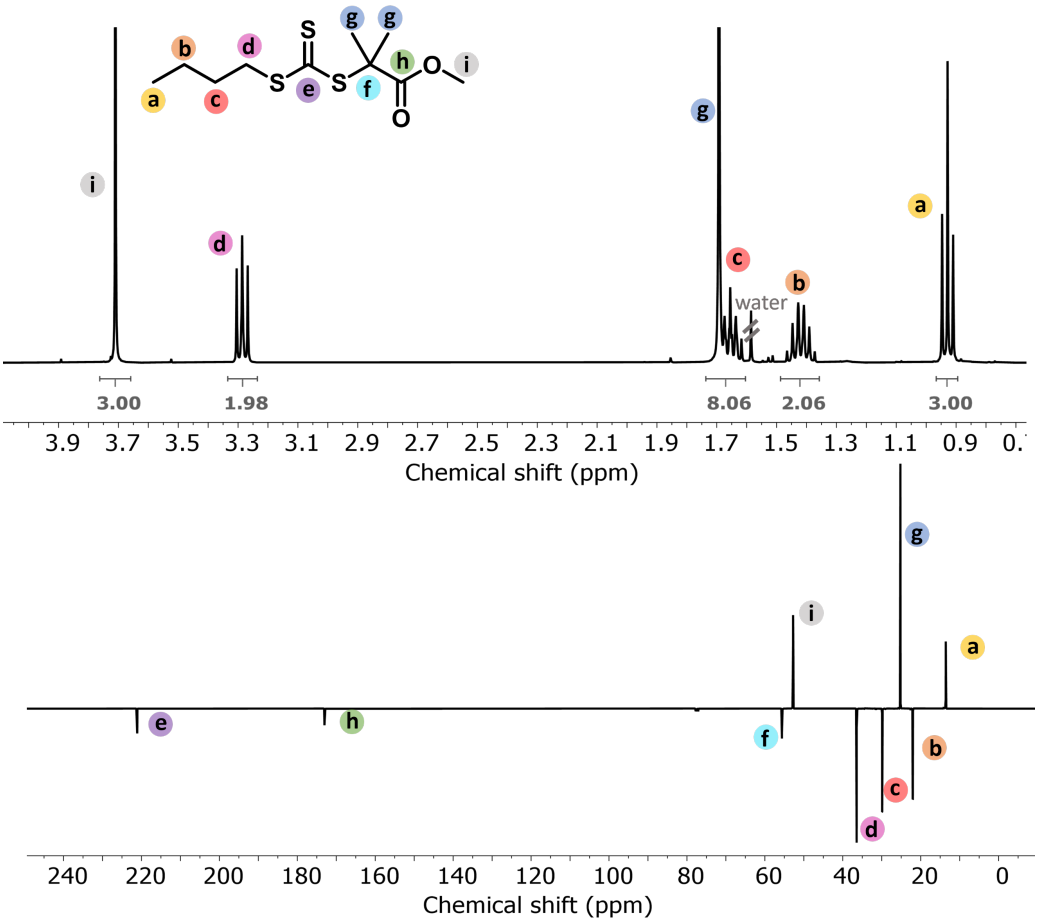
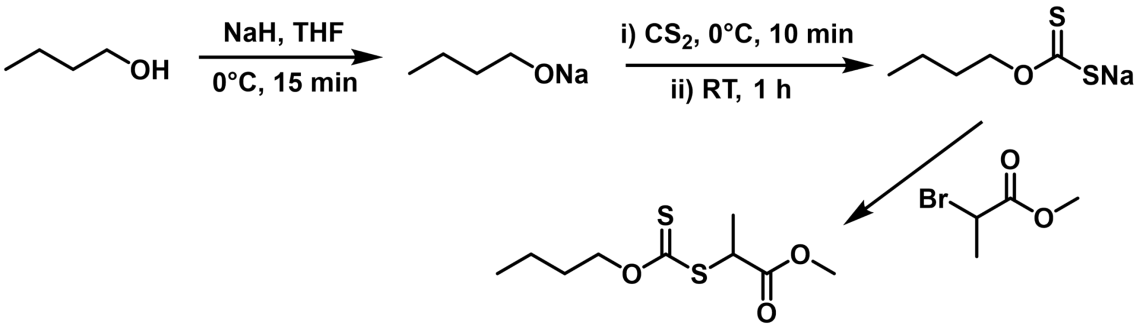


Figure 5 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra ($CDCl_3$) of BDMMT.

1.4.4 Synthesis of O-butyl S-methyl 2-propionylxanthate (PMB-Xan)

Scheme 4 Synthesis of PMB-Xan.



2-neck round bottom flask equipped with a balloon was charged with 60 wt% mineral oil suspension sodium hydride (4.81 g, 120 mmol, 1.1 eq). The flask was degassed and cooled down on ice bath and 100 ml of anhydrous THF was added via cannula transfer. Then, 10 ml of anhydrous 1-butanol (109 mmol, 1 eq) were added dropwise via degassed syringe. Solution was stirred at 0°C for 15 min until no further outgassing was observed. Balloon was vented and carbon disulfide (7.23 ml, 120 mmol , 1.1

eq) was added dropwise over 10 min and stirred for further 1 h at room temperature. Methyl-2-bromoproponate (13.41 ml, 1.1 eq, 120 mmol) was then added and stirred for 2 h. The resulting suspension was filtered to remove precipitated salts and THF was removed in vacuo. The residue was redissolved in ethyl acetate (100 ml), washed with water (1 x 10ml) and brine (2 x 100 ml). The organic layer was dried over magnesium sulfate and solvent removed under vacuum. Crude product was purified via silica flash column chromatography hexane/ethyl acetate 9:1 gradient to give pure product as pale yellow oil (41% yield, 10.5 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.61-4.55 (m, 2H, OCH_2), 4.40 (q, *J* 7.4, 1H, $SCH(CH_3)$), 3.76 (s, 1H, OCH_3), 1.78 (quin, *J* 7.3, 2H, OCH_2CH_2), 1.57 (d, *J* = 7.4 Hz, 3H, $SCH(CH_3)$), 1.44 (h, *J* 7.4, 2H, CH_2CH_3), 0.96 (t, *J* = 7.4 Hz, 1H, CH_2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.8 (CS), 171.6 (CO), 74.1 (OCH_2), 52.6 (OCH_3), 46.8 ($SCCH_3$), 30.0 (OCH_2CH_2), 19.1 (CH_2CH_3), 16.9 (CCH_3), 13.6 (CH_2CH_3) ppm

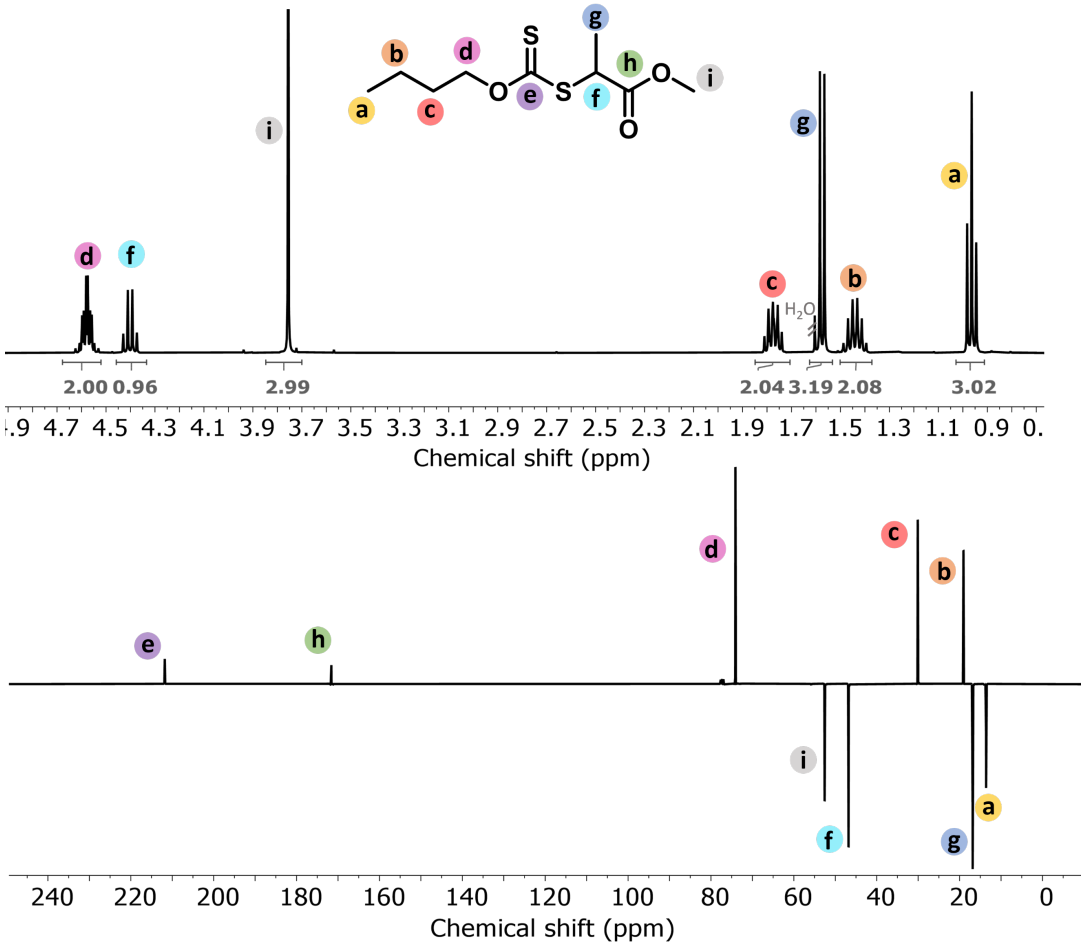
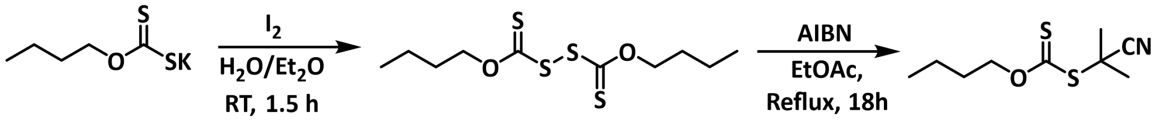


Figure 6 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra ($CDCl_3$) of PMB-Xan.

1.4.5 Synthesis of O-butyl S-(2-cyanopropan-2-yl) xanthate (BCN Xan)

Scheme 5 Synthesis of BCN-Xan.



To a solution of n-butylxanthic acid potassium salt (35 g, 186 mmol, 1 eq) in 150 ml of deionised water and 50 ml of diethyl ether, solid iodine (26 g, 103 mmol, 0.55 eq) was added slowly. Reaction mixture was vigorously stirred at room temperature for 1.5 h after which it was extracted with additional 50 ml of diethyl ether, washed with concentrated sodium thiosulfate solution, until no further colour changes of the organic layer were observed, water (1x 100 ml) and brine (2 x 100 ml). The organic layer was dried over $MgSO_4$ and solvent removed under vacuum to give xanthate disulfide as pale yellow oil which was used without further purification (crude yield 63%, 17.5 g). Disulfide (17.5 g, 59 mmol, 1 eq) and AIBN (19.3 g, 118 mmol, 2 eq) were dissolved in 200 ml of ethyl acetate in a three neck round bottom flask fitted with thermometer and water condenser. The solution was purged with nitrogen for 30 min, water condenser was equipped with a nitrogen filled balloon before it was heated up and refluxed for 18 h. Solvent was removed under vacuum, redissolved in hexane and vacuum filtered to remove leftover AIBN and its decomposition products. Filtrate was dried under vacuum and crude product was purified via silica flash column chromatography hexane/ethyl acetate 4:1 gradient to give pure product as pale-yellow oil (82% yield, 21 g, total yield 52 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.69 (t, *J* 6.8 Hz, 2H, OCH_2), 1.95 – 1.85 (m, 2H, OCH_2CH_2), 1.76 (s, 6H, $C(CN)(CH_3)_2$), 1.56 – 1.45 (m, 2H, CH_2CH_3), 0.99 (t, *J* 7.4 Hz, 3H, CH_2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.0 (CS), 121.1 (CN), 74.7 (OCH_2), 40.8 ($C(CN)(CH_3)_2$), 29.9 (OCH_2CH_2), 27.3 ($C(CN)(CH_3)_2$), 19.2 (CH_2CH_3), 13.7 (CH_2CH_3) ppm

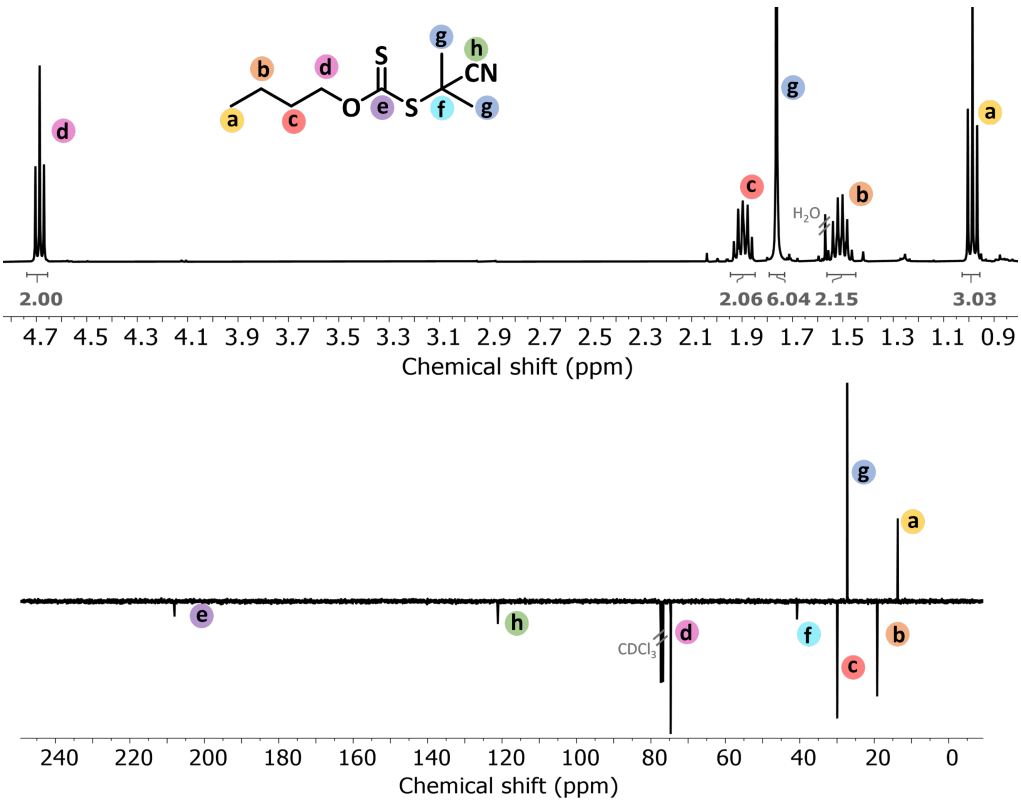


Figure 7 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra ($CDCl_3$) of BCN-Xan.

1.4.6 General procedure for timesweep kinetics of methyl methacrylate and methyl acrylate polymerization

A 20 ml vial covered with aluminium foil was charged with PMBTC RAFT agent (126.1 mg, 0.50 mmol, 1 eq), MMA (2500 mg, 24.97 mmol, 50 eq) and DMSO (6230 mg), giving concentrations [MMA] = 3 M, [PMBTC] = 0.06 M. Methyl acrylate experiments were carried out in the same manner, for an exemplar reaction solution see Table 2. The vial was sealed with a rubber septum and degassed by sparging with argon for 5 min. The solution was immediately transferred to a 10 ml gas tight syringe wrapped with aluminium foil and preflushed with argon. The syringe was connected to the flow reactor and placed in the syringe pump. The LED and its cooling were turned off. The flow reactor, submerged in an oil bath preheated to 70 °C, was prefilled with reaction mixture. Between the runs, the reactor was flushed with fresh DMSO. The experiment was initiated via the software and flow rates were controlled with Python script, as reported previously.[2,4] Stabilisation time was 1.3 x τ_{start}, for standard experiments, the reactor was stabilised at 0.45 ml/min for 2.6 min. After stabilisation time, the flow rate was reduced to 0.225 ml/min and run for 4 min, after this time the flow rate was reduced again (for details about timesweep ranges see Table 3). Standard screening were performed with 4 consecutive timesweeps as combination of smaller range timesweeps gives more reliable data.[4] NMR spectra were recorded every 17 s. Python software automatically extracts NMR data and assigns it to

timesweep (and corresponding residence time) or dead volume/stabilisation time, for software details see reference 2 (NMR-only mode). The only modification was data synchronisation; in the previously reported method, data was synchronised using the NMR scan number as the time unit[2] while here we used experiment time as given by the NMR software, with precise timing of each NMR scan. After reaching final steady-state conditions, samples were collected manually at the outlet for high field NMR and SEC analysis.

Table 2 Reaction solution for methyl acrylate polymerization.

Reagent	MW [g/mol]	Mass [mg]	Moles [mmol]
MA	86.09	2185	25.38
PMBTC	252.41	128	0.51
DMSO	78.13	6776	-

Table 3 Details of timesweep ranges, τ – residence time, ν – flow rate.

Timesweep	τ_{start} [min]	τ_{end} [min]	ν_{start} [ml/min]	ν_{end} [ml/min]
Timesweep 1	2	4	0.45000	0.22500
Timesweep 2	4	8	0.22500	0.11250
Timesweep 3	8	16	0.11250	0.05625
Timesweep 4	16	30	0. .05625	0.03000

1.4.7 General procedure for batch kinetics of methyl methacrylate and methyl acrylate thermal polymerization

A 10 ml vial equipped with was a stirrer bar was charged with BCN TTC RAFT agent (69.9 mg, 0.30 mmol, 1 eq), MMA (1500 mg, 14.98 mmol, 50 eq), AIBN (4.9 mg, 0.03 mmol, 0.1 eq) and DMSO (3 740 mg), giving concentrations [MMA] = 3 M, [BCN TTC] = 0.06 M. Methyl acrylate experiments were carried out in the same manner. The vial was sealed with a rubber septum and degassed by sparging with nitrogen for 10 min. The vial was placed in an oil bath pre-heated to 70 °C. Time points were taken under nitrogen blanket. Conversion was measured with ^{1}H NMR and molecular weight and dispersity were measured with THF SEC.

1.4.8 UV-vis study - molar absorption coefficients of RAFT agents

Absorbance values at 460 nm and maxima of n to π ∗ transitions for trithiocarbonate RAFT agents were measured. To establish molar absorption coefficient, UV vis spectra of samples of different

concentrations prepared by serial dilutions were measured, giving absorbance between 0 and 1. Molar absorption coefficients were determined by a linear plot of absorbance vs concentration using Beer-Lambert Law.

2 Supplementary figures

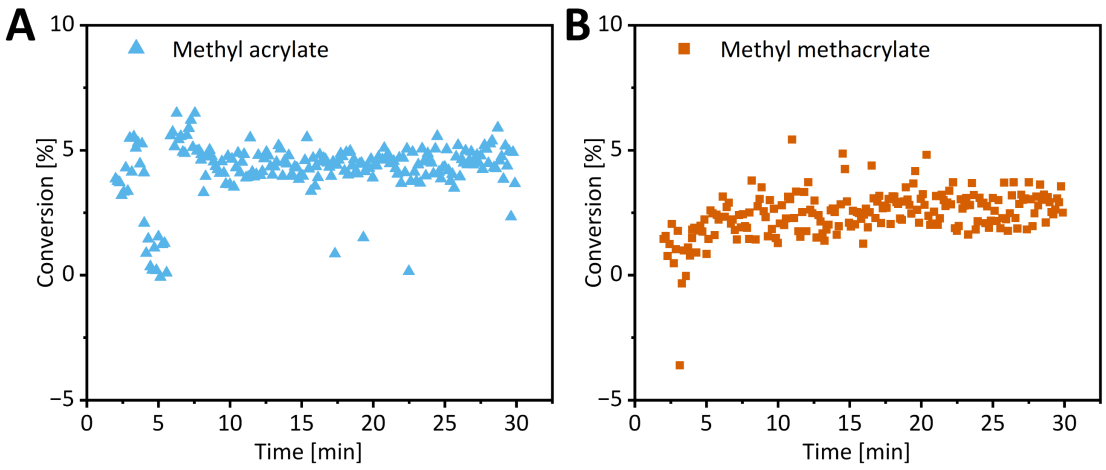


Figure 8 Control photoreaction with no RAFT agent: A – methyl acrylate, B – methyl methacrylate. Noisy NMR signal for fast flow rate (short residence times) for methyl acrylate leads to deviation in conversion.

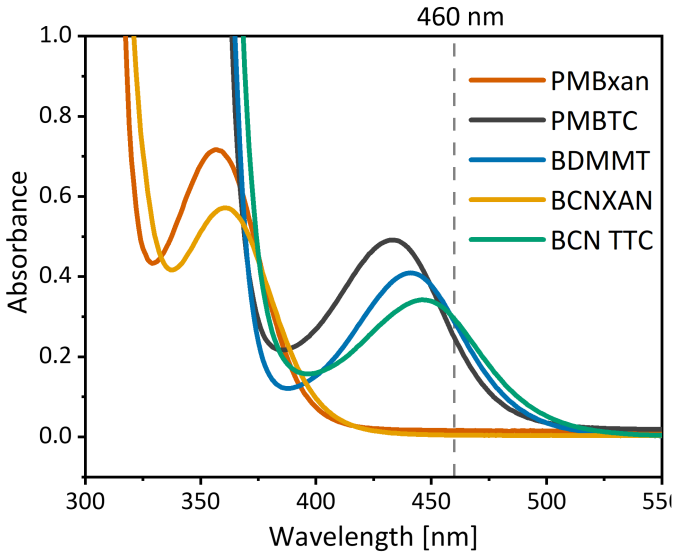


Figure 9 UV-vis spectra of RAFT agents in DMSO, 10 mM concentration.

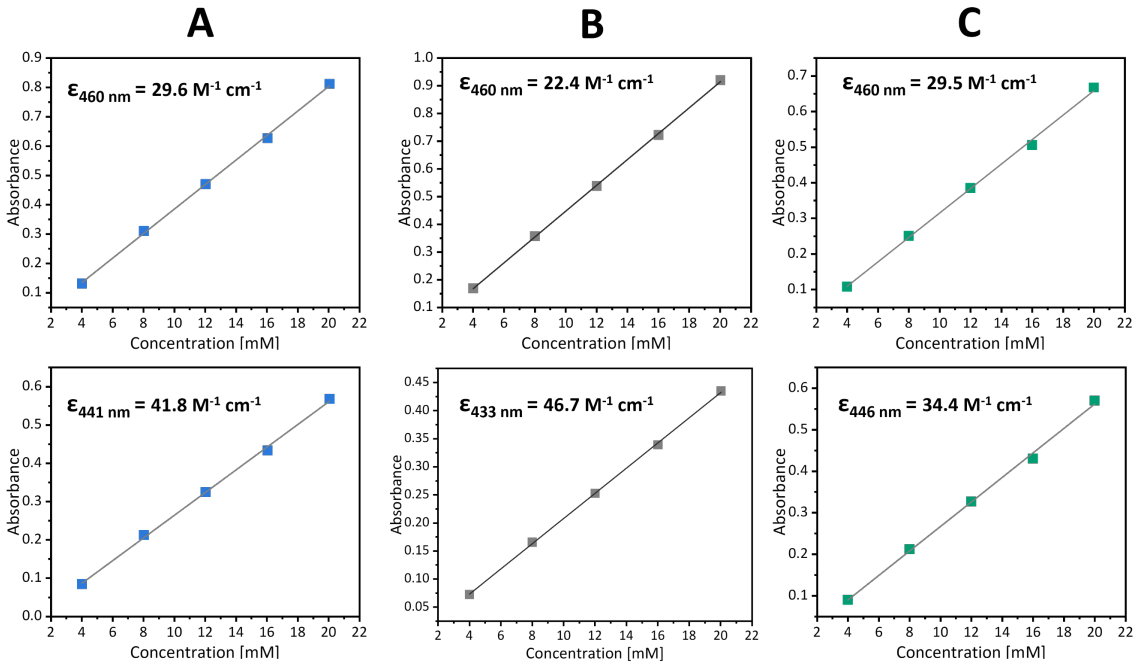


Figure 10 Beer-Lambert plots for the n→π* transition maxima and 460 nm wavelengths for RAFT agents: A: BDMMT, B: PMBTC, C: BCN-TTC

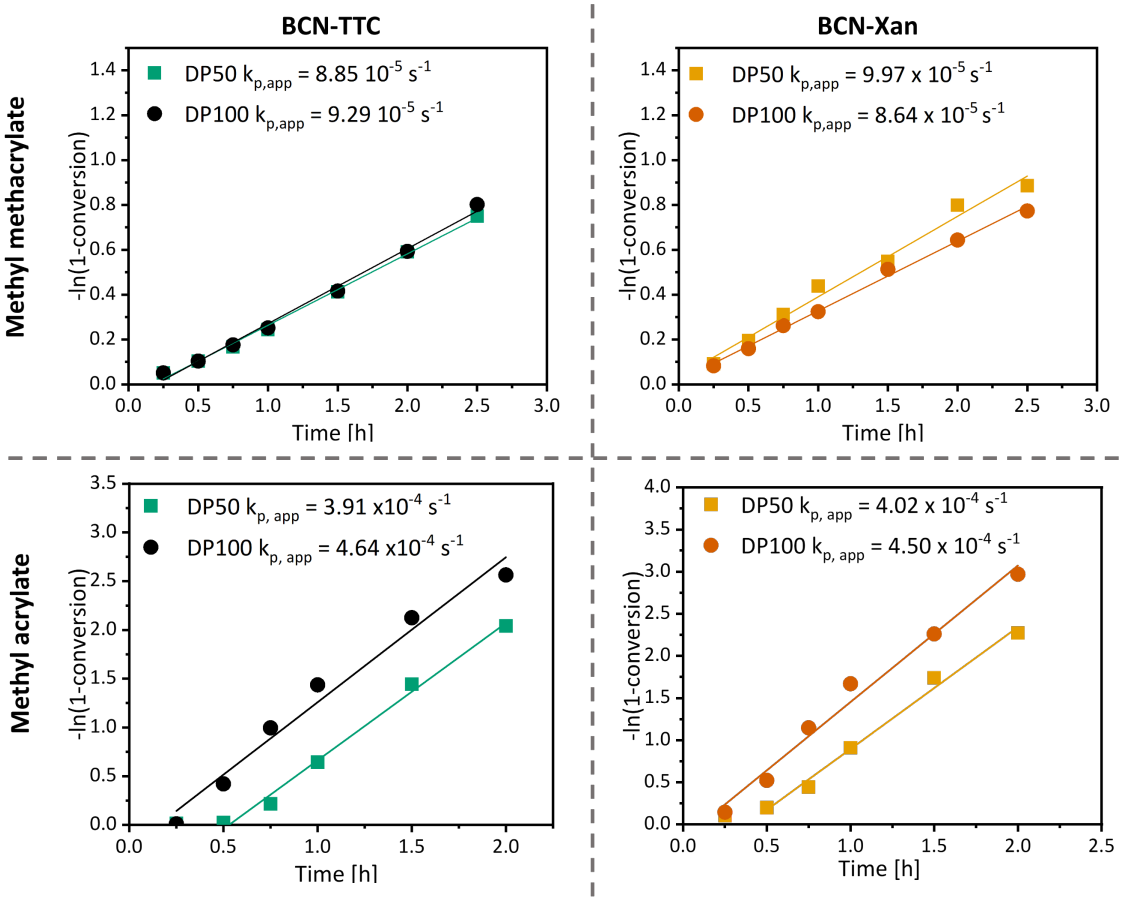


Figure 11 Pseudo first-order kinetic plots for thermal polymerization of methyl acrylate and methyl methacrylate with BCN-TTC and BCN-Xan RAFT agents in DMSO, [monomer] = 3 M, [monomer]/[AIBN] = 500, 70 °C.

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