Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Tertiary Amine Catalysed Photo-induced Controlled Radical Polymerization of Methacrylates

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1. Experiments

Materials

Tris(2-aminoethyl)amine (96 %), formic acid (98 %), formaldehyde (25 %), sulfuric acid (H_2SO_4, 97 %), 1-dodecanethiol (>98 %), benzyl bromide (anhydrous, 99.8%), hydrochloric acid (HCl, 37 %), Aliquat® 336, carbon disulfide (CS_2, anhydrous, ≥99%), 2-cyano-2-propyl dodecyl trithiocarbonate (TTC-2, 97 %), *trans*-2-(3-(4-*tert*-Bbutylphenyl)-2-methyl-2-propenylidene)-malononitrile (DCTB, 98 %), silver trifluoroacetate (AgTFA, >99 %), sodium trifluoroacetate (NaTFA, >99 %), 3-mercaptopropionic acid (>99 %), *p*-toluenesulfonic acid monohydrate (PTSA, >98 %), dithiothreitol (DTT, >98 %), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 99 %) and trifluoroacetic acid (TFA, 99 %) were purchased from Sigma-Aldrich and used as received. Monomers methyl acrylate (MA, 99 %, Aldrich), methyl methacrylate (MMA, 99 %, Aldrich), ethyl methacrylate (EMA, 99 %, Aldrich), *n*-butyl methacrylate (*n*BuMA, 99 %, Aldrich), styrene (St, > 99 %, Aldrich) and oligo(ethylene glycol) methacrylate (OEGMA, M_n = 480 Da, Aldrich) were passed over basic alumina to remove inhibitors prior to use. *N*-isopropylacrylamide (NIPAM, 97 %, Aldrich) was recrystallized in hexane to remove inhibitors prior to use. Deuterated chloroform ($CDCl_3$, 99.8 %) was purchased from Cambridge Isotope Laboratories, Inc. Triethylamine (TEA) was distilled over calcium hydride under argon. Tetrahydrofuran (THF) was distilled from benzophenone and sodium metal under argon. AR grade sodium hydroxide (NaOH), potassium hydroxide (KOH), methanol (MeOH), ethanol (EtOH), formic acid, dichloromethane (DCM), chloroform, acetone, n-hexane, toluene, 1,4-dioxane, diethylether (DEE) and other solvents were purchased from Chem-Supply Pty. Ltd. and used without further purification. UV light sourceused for all experiments was a commercial nail-curing lamp ('Beaufly-nail lamp', 220V) fitted with 4 × 9W bulbs with λ_{max} ~ 365 nm.

Characterizations

Gel-Permeation Chromatography (GPC): GPC for THF mobile phase was conducted using a Shimadzu system fitted with a Wyatt DAWN DSP multi-angle laser light scattering detector (690 nm, 30 mW) and a Wyatt OPTILAB EOS interferometric refractometer (690 nm). THF was used as the eluent with three Phenomenex phenogel columns (500, 104, 106 Å porosity 5μm bead size) operated at 1 ml per minute at a column temperature of 45 °C. To process the GPC data, the program 'Astra' by Wyatt technologies was used. All samples were filtered through 0.45 μm nylon filters prior to injection. When DMF was used as an eluent, the GPC analysis was conducted on a Shimadzu liquid chromatography system equipped with a Shimadzu RID-10 refractometer (λ = 633 nm) and Shimadzu SPD-20A UV-vis detector using three identical Jordi columns (5 μm bead size, Jordi Gel Fluorinated DVB Mixed Bed) in series operating at 70°C. DMF with 0.05 mol·L^{-1} LiBr (> 99%, Aldrich) was employed as the mobile phase at a flow rate of 1 mL·min^{-1}. The system was calibrated using polystyrene standards. All samples were filtered through 0.45 μm nylon filters prior to injection.

Nuclear Magnetic Resonance (NMR) Spectroscopy: ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy were conducted on a Varian Unity 400 MHz spectrometer operating at 400 MHz, using the solvent deuterated chloroform ($CDCl_3$) (Cambridge Isotope Laboratories) as reference and sample concentrations of approximately 10 mg·mL^{-1}.

Matrix-assisted laser desorption/ionization time of flight (MALDI-ToF) mass spectroscopy: MALDI-ToF MS was performed on a Bruker Autoflex III Mass Spectrometer operating in positive linear mode; the analyte, matrix (DCTB) and cationisation agent (NaTFA) were dissolved in THF at concentrations of 10, 10, and 1 mg/mL, respectively, and then mixed in a ratio of 10:1:1. Then 0.3 μL of this solution was spotted onto a ground steel target plate and the solvent was allowed to evaporate prior to analysis. Flex Analysis (Bruker) was used to analyze the data.

Synthesis of tris(2-(dimethylamino)ethyl)amine (Me_6TREN)

Tris(2-(dimethylamino)ethyl)amine (Me_6TREN) was prepared according to the literature.[1] Tris(2-aminoethyl amine) (12 mL, 80 mmol) was placed in a round-bottom flask containing HCl in MeOH (100 mL, 3 M). After reaction at room temperature for 1 hour, the solid residue was collected by filtration. The solid was washed with MeOH and dried *in vacuo*. 18 g of the solid was dissolved in a mixture of H_2O, formic acid and formaldehyde (1 : 6 : 6, volume ratio). The reactant was stirred at 120 °C until CO_2 release had stopped. The resulting solution was dissolved in 10 % NaOH solution (200 mL). The oily layer was extracted in DEE, followed by evaporation of DEE. Me_6TREN was collected from vacuum distillation at 70 ºC as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ_H ppm): 2.58-2.52 (t, 2H, $(CH_3)_2NC\boldsymbol{H_2}CH_2$-), 2.34-2.30 (t, 2H, $(CH_3)_2NCH_2C\boldsymbol{H_2}$-), 2.18-2.14 (s, 6H, $(C\boldsymbol{H_3})_2$N-). ^{13}C NMR (400 MHz, $CDCl_3$, δ_C ppm): 57.5, 53.0, 45.9.

Synthesis of benzyl dodecyl carbonotrithioate (TTC-2)

TTC-2 was synthesized as previously reported.[2] To a round bottom flask containing 1-dodecanethiol (2.92 g, 14.4 mmol) was added a solution of KOH (0.97 g, 17.3 mmol in 40 mL of Milli-Q water), followed by the dropwise addition of carbon disulfide (1.73 mL, 28.8 mmol). The colour of the solution mixture gradually turned yellow upon addition of carbon disulfide. The mixture was left to stir for 3 h at 25 ºC until the colour of the solution changed from yellow to orange. Subsequently, benzyl bromide (1.72 mL, 14.4 mmol) was added to the reaction mixture and the solution was left to stir for another 24 h at 25 ºC. By the end of the reaction, the colour of the solution became yellow. The crude product in the solution mixture was extracted with $CHCl_3$ (40 mL). Next, the organic phase was washed with 0.5 M HCl solution (30 mL), brine (30 mL) and Milli-Q water (30 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo*. The product was recrystallized from MeOH:EtOH (1:1, 50 mL) overnight at -18 ºC and recovered by filtration to afford the product as yellow crystals (4.60 g, yield = 86%).^{1}H NMR (400 MHz, $CDCl_3$, δ_H ppm): 7.36-7.25 (m, 5H, Ar***H***), 4.61 (s, 2H, PhC$\boldsymbol{H_2}$S-), 3.37 (t, 2H, -SC$\boldsymbol{H_2}CH_2$-), 1.76-1.17 (m, 20H, -C$\boldsymbol{H_2}$-), 0.89 (t, 3H, C$\boldsymbol{H_3}$-). ^{13}C NMR (400 MHz, $CDCl_3$, δ_C ppm): 223.7, 135.1, 129.2, 128.6, 127.7, 41.3, 37.0, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 29.1, 28.9, 28.0, 22.7, 14.1.

Synthesis of 2,2'-(thiocarbonyl-bis(sulfanediyl))-bis(2-methylpropanoic acid) (TTC-3)

TTC-3 was synthesized via a procedure reported in the literature.[3] Carbon disulfide (5.378 g, 70.64 mmol), chloroform (21.558 g, 0.180 mol), acetone (9.536 g, 0.180 mol), and Aliquat® 336 (1.101 g, 2.72 mmol) were dissolved in hexane (50 mL) in a 250 mL round bottom flask under a nitrogen atmosphere. The flask was placed in an ice/water bath. After the solution was cooled in an ice water bath for 20 min, a 50% NaOH aqueous solution (18.5 g, 0.23 mol) was added dropwise into the flask. The mixture turned a deep yellow colour after ~ 15 min and then a brownish red colour after 1 h. The reaction was allowed to proceed at 0 °C overnight. Deionized water (100 mL) was added into the flask, followed by dropwise addition of a concentrated HCl solution (30 mL) until the solution was acidic. The organic layer was separated and bubbled with nitrogen to remove the volatiles. The resultant slurry was filtered

by vacuum filtration, and the collected solid was stirred in toluene/hexanes (v/v: 50/50). 2,2'-(thiocarbonylbis(sulfanediyl))bis(2-methylpropanoic acid) was obtained as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$, δ_H ppm): 1.67 (m, 12H, -C***H*****$_3$**). ^{13}C NMR (400 MHz, $CDCl_3$, δ_C ppm): 180.0, 55.8, 25.14.

General procedure for TAC Pi-RDRPs

In a typical experiment, a 25 mL Schlenk tube was charged with monomer (i.e. MMA: 0.94g, 1.0 mL, 9.4 mmol), TTC (i.e. TTC-1, 34.5 mg, 0.094 mmol), Me_6TREN (5.4 mg, 6.3 µL, 0.023 mmol) and DMSO (1 mL, 50 vol% w.r.t monomer), [MMA]:[TTC]:[Me_6TREN] = 100:1:0.25. The reaction mixture was degassed by 2 freeze-pump-thaw cycles then back-filled with argon.The UV light source (λ_{max} ~ 365 nm, 4 × 9W) was then switched "on", and the reaction mixture was stirred under positive argon pressure. Samples were taken at timed intervals *via* degassed syringe and immediately diluted with either $CDCl_3$ or THF, for NMR and GPC analysis respectively. MMA conversion was estimated from ^{1}H NMR by integrating the peaks corresponding to the polymer methyl group (δ_H = 3.42 ppm, m, 3H, -OC***H*****$_3$**) and the protons corresponding to the unsaturated methyacrylate double bond (δ_H = 5.35-6.0 ppm, m, 2H, ***H*****$_2$**C=C-). These peaks account for all protons derived from the monomer species, from which the percentage of remaining unreacted monomer can be calculated.

"On"/"Off"experiments

"On"/"Off" reactions were set up in same fashion as for synthesis of linear polymers, however at a given reaction time the UV light source was turned off and the Schlenk tube covered completely in aluminium foil and placed into a home-made 'dark box' for a designated time period. The polymerization was re-activated by irradiating the reaction mixture with UV again. Samples were taken at timed intervals via degassed syringe under argon protection and immediately diluted with either $CDCl_3$ or THF, for NMR and GPC analysis respectively.

***In situ* chain extension to prepare *psuedo*-diblock copolymers.**

The *in situ* chain extension experiment was as follows. After 8 hours polymerization, a 1:1 (v/v) mixture of degassed MMA (100 eq.) used for block copolymerization and DMSO was added to the reaction mixture *via* degassed syringe. Samples were taken after another 12 hours and measured using ^{1}H NMR and GPC analysis.

2. Light Source

UV source used for all experiments was a commercial nail-curing lamp ('Beaufly-nail lamp', 220V) fitted with 4 × 9W bulbs with $\lambda_{max} \sim 365$ nm.

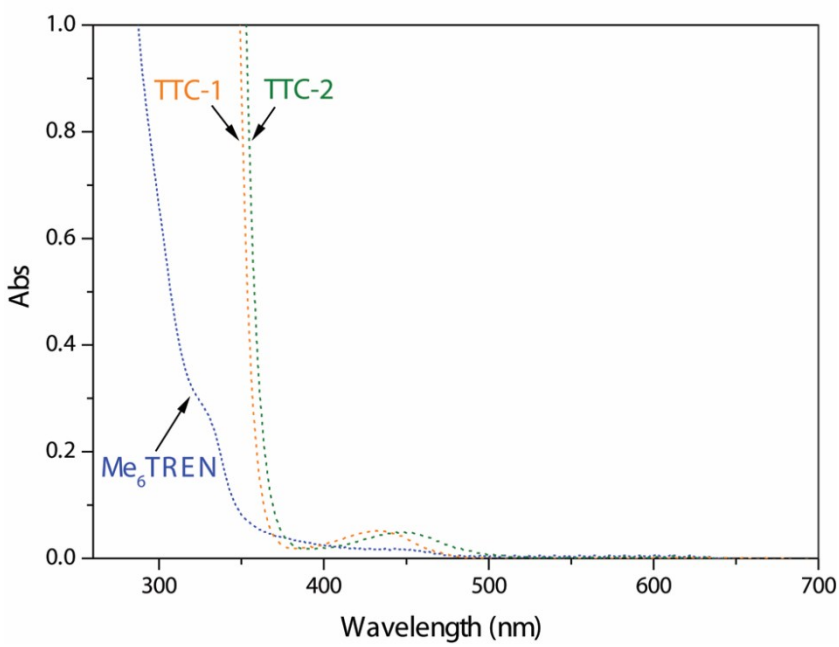

Figure S1. Absorption spectra of TTC-1, TTC-2 and Me_6TREN (0.01 mmol/mL, dot).

3. Kinetic Study of PMMA for Figure 1

In this experiment, a 25 mL Schlenk tube was charged with MMA (1.0 g, 1.07 mL, 10 mmol), TTC-1 (34.5 mg, 0.1 mmol), Me_6TREN (5.75 mg, 6.7 μL, 0.025 mmol) and DMSO (50 vol % w.r.t monomer). The reaction mixture was degassed by 2 freeze-pump-thaw cycles then back-filled with argon.After polymerization, the MMA conversion was estimated from ^{1}H NMR by integrating the peaks corresponding to methyl group at δ_H = 3.5-3.7 ppm, (s, 3H, -COOC***H₃***) and the protons corresponding to the unsaturated methacrylate double bond (δ_H = 5.3-6.0 ppm, m, 3H, C***H₂***=C(CH_3)-). These peaks account for all protons derived from the monomer species, from which the percentage of remaining unreacted monomer can be calculated. The theoretical molecular weight was calculated using the equation S1.

$$M_{n,th} = [M]_0/[TTC]_0 \times \%\ conv. \times M_{r,M} + M_{r,TTC} \qquad (S1)$$

where $[M]_0$ and $[TTC]_0$ are the initial concentrations of monomer and TTC respectively, % conv. is the monomer conversion estimated from ^{1}H NMR, $M_{r,M}$ and $M_{r,TTC}$ are the molecular weights of monomer and TTC, respectively.

Table S1. TAC Pi-RDRP of MMA as a function of irradiation time[a].

Entry	Polymerization time (min)	Conv.[b] (%)	$M_{n,th}$[b] (kDa)	$M_{n,\ GPC}$[c] (kDa)	M_w/M_n[c]
1	30	4.5	0.8	0.9	1.31
2	60	22.7	2.6	2.9	1.29
3	120	50.0	5.4	5.7	1.26
4	240	82.8	8.6	8.9	1.25

[a] Supplementary data to Figure 1. [b] Determined by ^{1}H NMR. [c] Determined by THF GPC.

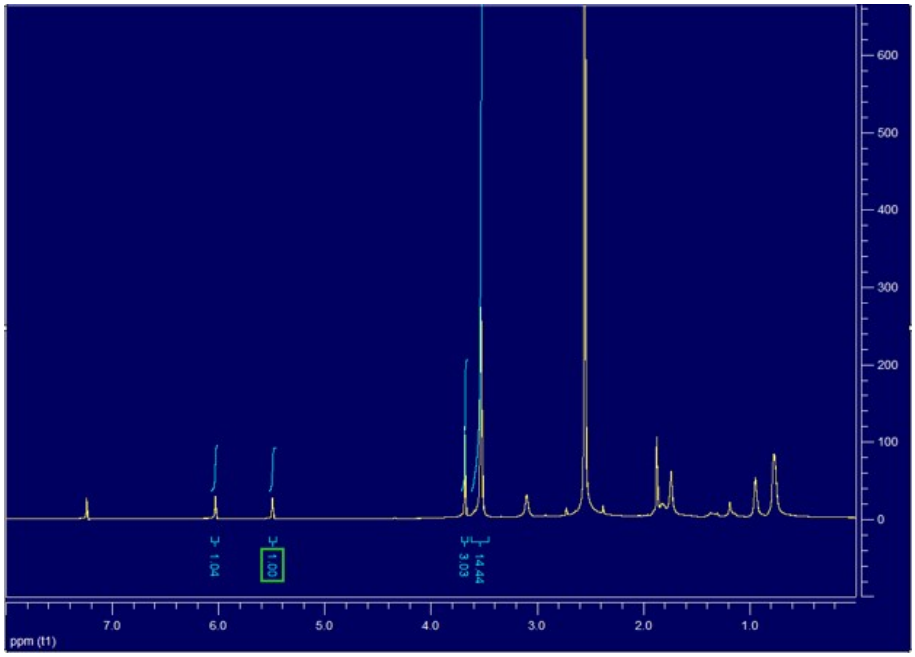

Figure S2. ^{1}H NMR spectrum of crude PMMA (Entry 4, Table S1).

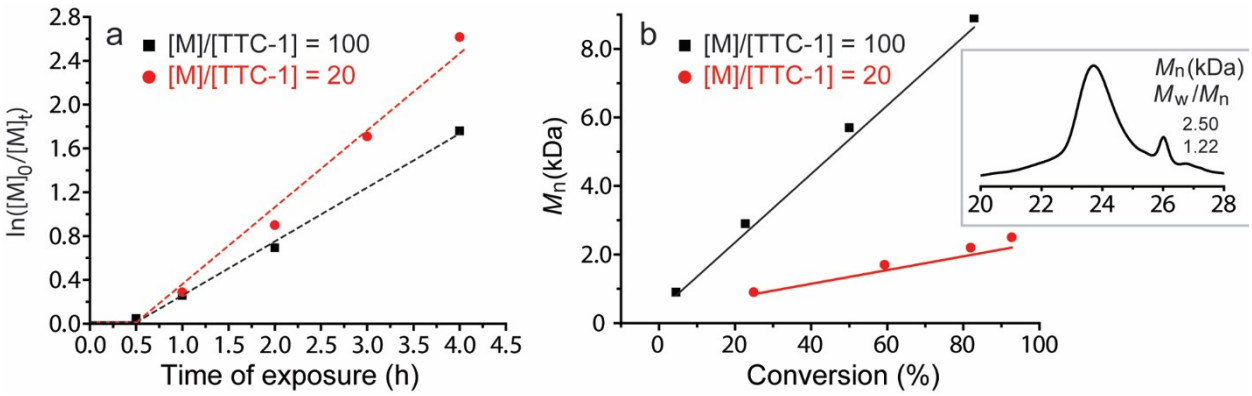

Figure S3. Kinetic plots for the TAC Pi-RDRPs of MMA using different [M]/[TTC-1] ratios. (a) $\ln([M]_0/[M]_t)$ *vs.* reaction time and (b) molecular weights *vs.* conversion. All M_ns were obtained from GPC analysis. The solid lines represent the theoretical molecular weight based on NMR analysis. The insert chart shows the GPC trace of PMMA prepared using [M]/[TTC-1] = 20 ratio (at 92 % conversion).

4. SupplementaryData to Table 1

In this study, a 25 mL Schlenk tube was charged with monomer, TTC, Me_6TREN and solvent (50 vol % w.r.t monomer), [M]/[TTC] = 100. The reaction mixture was degassed by 2 freeze-pump-thaw cycles then back-filled with argon before the UV light source was switched on. Samples were taken at timed after 24 h and immediately diluted with either $CDCl_3$ or THF, for NMR and GPC analysis, respectively.

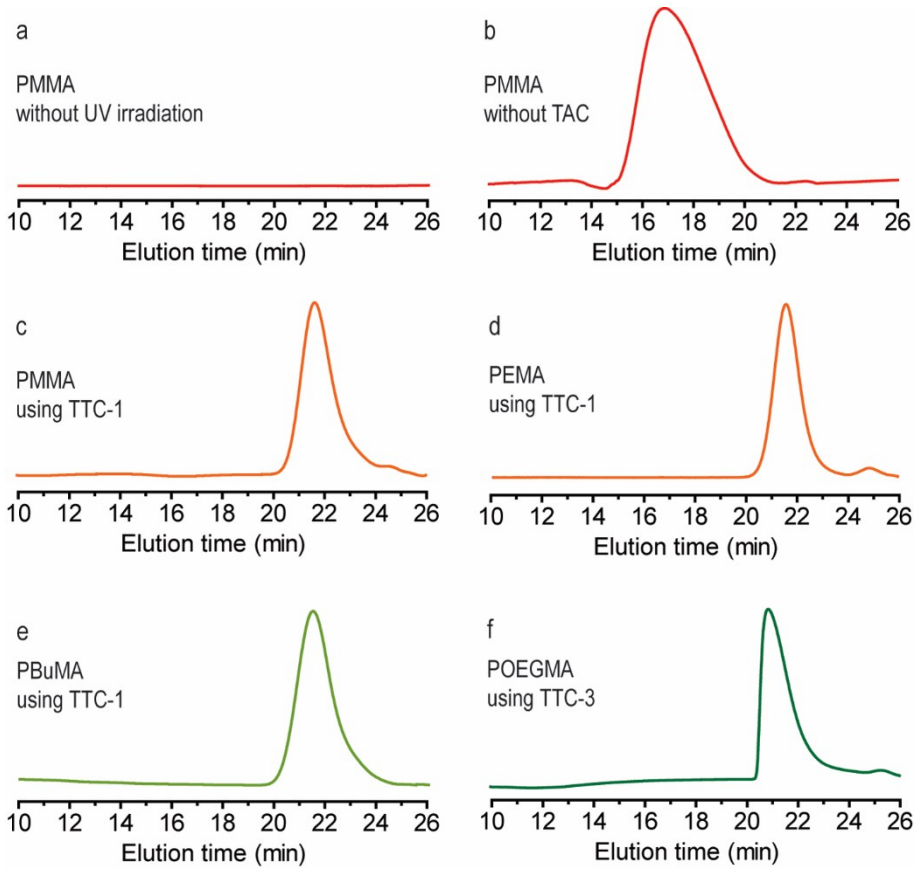

Figure S4. GPC (THF) traces of polymethacrylayes obtained from TAC Pi-RDRPs (a-f correspond to Entry 1-6 in Table 1).

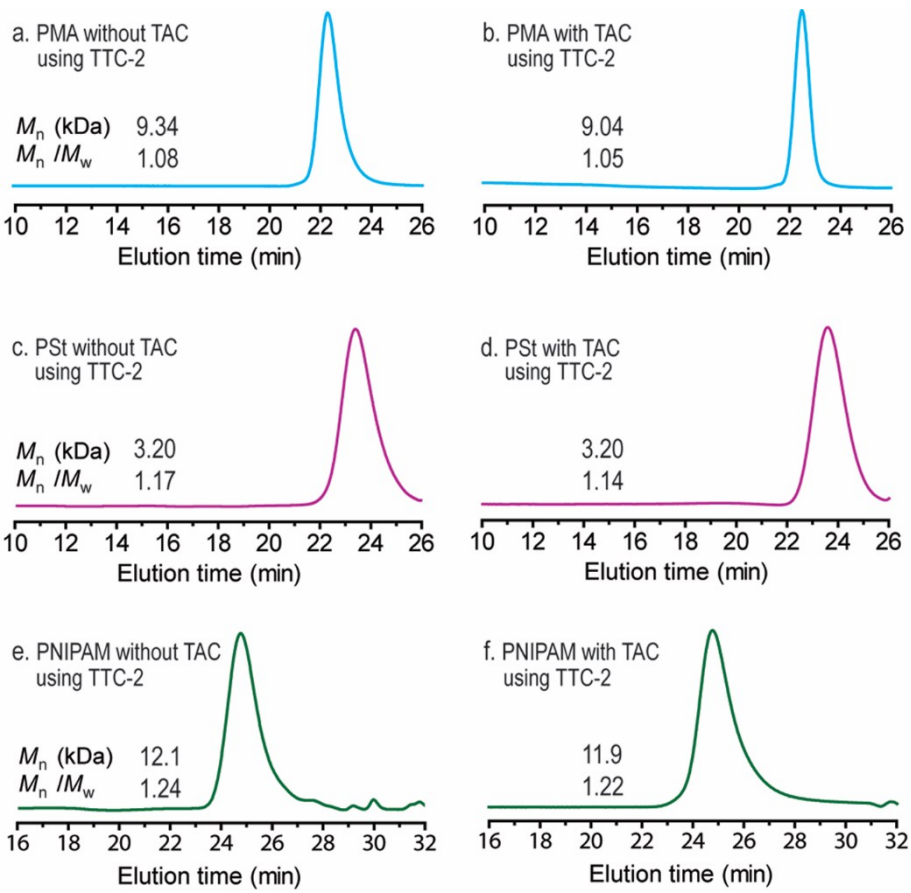

Figure S5. GPC (THF) traces of PMA and PSt prepared by Pi-RAFT polymerization (a,c) and TAC Pi-RDRP (b,d). GPC (DMF) traces of PNIPAM prepared by Pi-RAFT polymerization (e) and TAC Pi-RDRP (f).

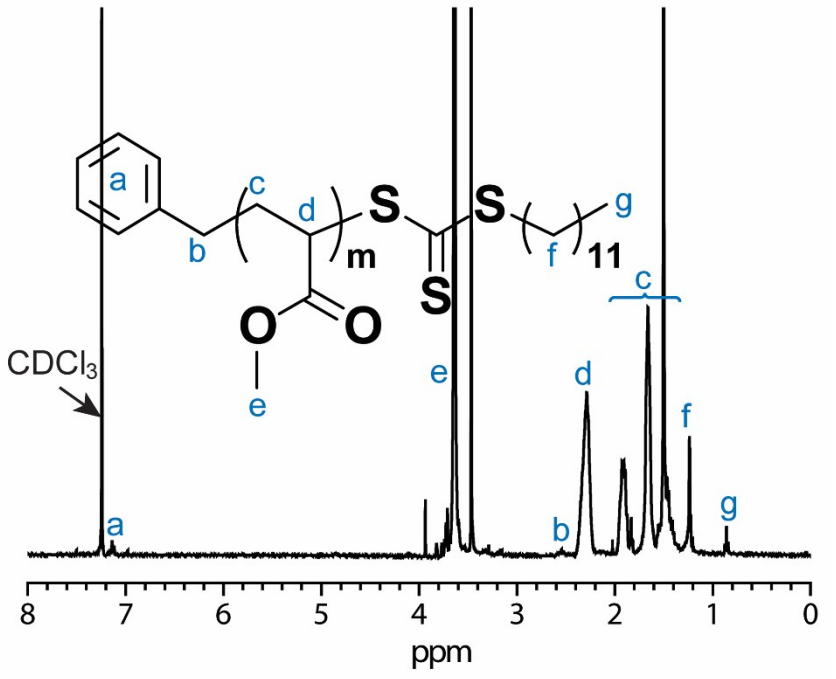

Figure S6. ^{1}H NMR spectrum of purified PMA (a in Fig. S4).

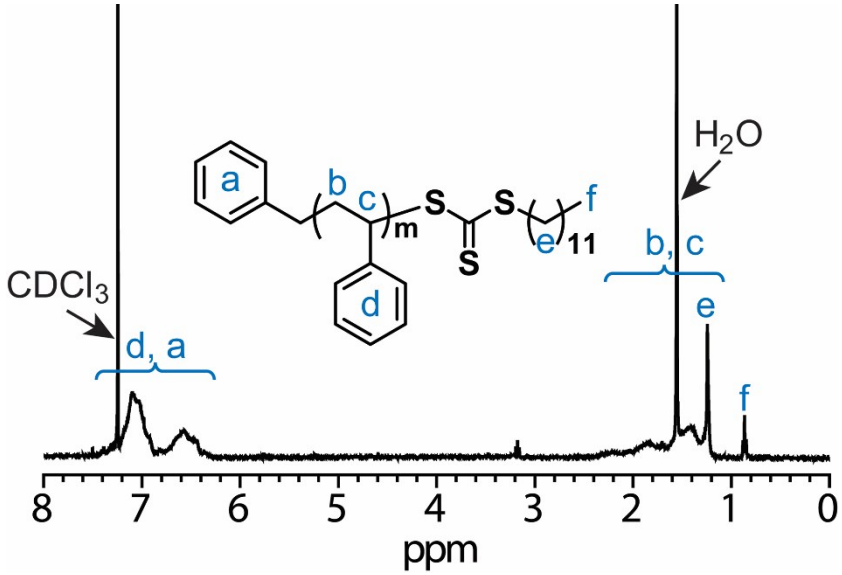

Figure S7.[1]H NMR spectrum of purified PSt (c in Fig. S4).

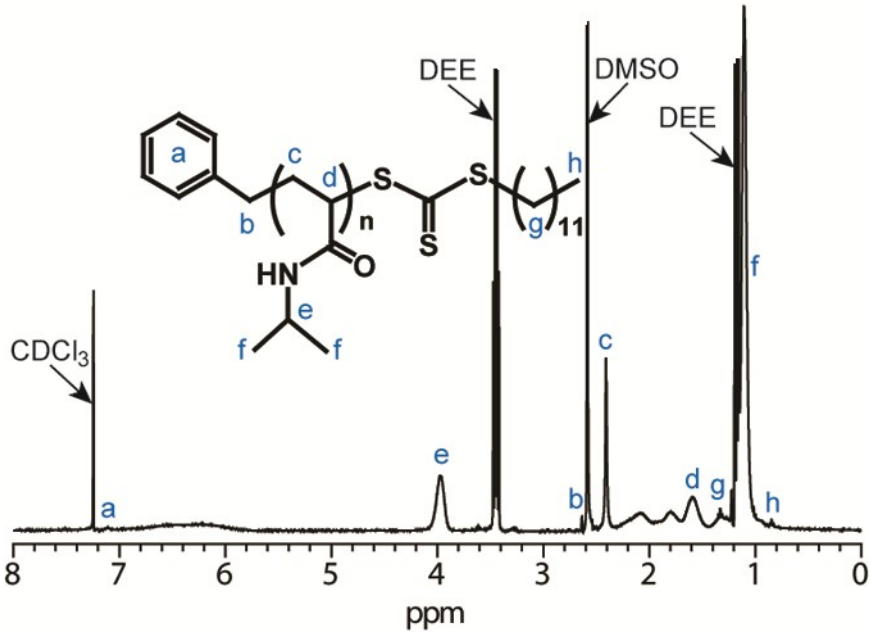

Figure S8.[1]H NMR spectrum of purified PNIPAM (e in Fig. S4).

5. Experimental for Figure 2

"On"/"Off" reactions were set up in same fashion as for synthesis of linear polymers, however at a given reaction time the UV light source was turned off and the Schlenk tube covered completely in aluminium foil and placed into a home-made 'dark box' for a designated time period. The polymerization was re-activated by irradiating the reaction mixture with UV again. Samples were taken at timed intervals *via* degassed syringe under argon protection and immediately diluted with either $CDCl_3$ or THF, for NMR and GPC analysis respectively.

Table S2. *ON/OFF* experiments of PMMA[a].

Entry	Time(h)	UV irradiation	MMA Conv.[b] (%)
1	1	On	23.9
2	2	Off	24.6
3	3	On	47.6
4	4	Off	48.0
5	5	On	68.1
6	6	Off	70.0

[a] Supplementary data to Figure 2. [b] Determined by ^{1}H NMR.

6. Supplementary Data to Figure 3

Table S3. *In situ* chain extension experiments of PMMA-*b*-PMMA[a].

Entry	Feed ratio [MMA]: [(macro)TTC]	Time (h)	Conv.[b] (%)	M_{nGPC}[c] (kDa)	M_w/M_n[c]
i	100	8	92	10.2	1.31
ii	100	12	96	20.5	1.29

[a] Supplementary data to Figure 3. [b] Determined by ^{1}H NMR. [c] Determined by THF GPC.

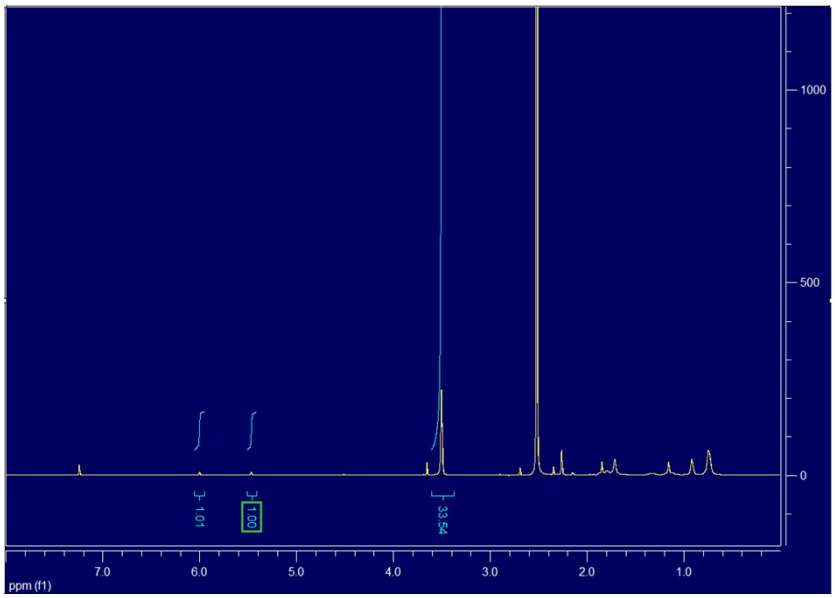

Figure S9. ^{1}H NMR spectrum of crude PMMA.

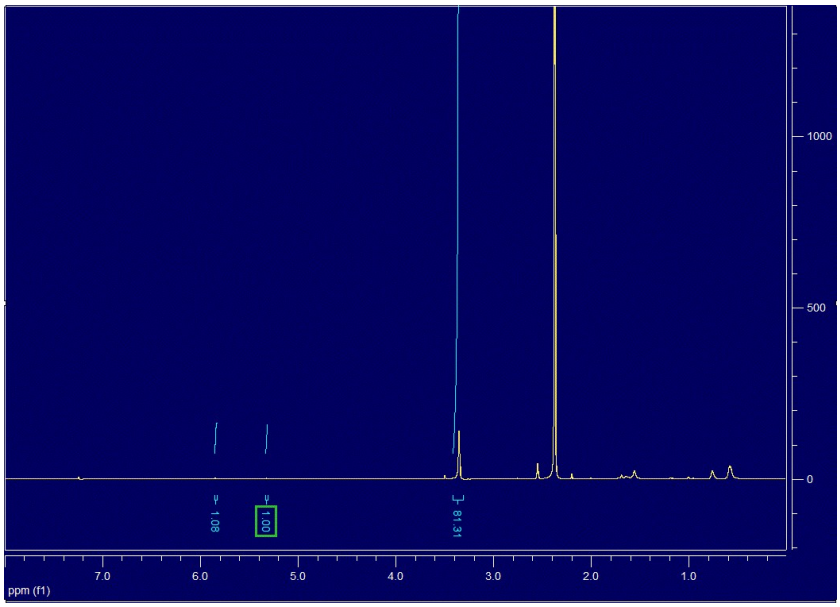

Figure S10. ^{1}H NMR spectrum of crude PMMA-*b*-PMMA.

7. Supplementary Data to Figure 4

Table S4. The effects on the TAC Pi-RDRPs[a].

Entry	Time (h)	Solvent	TACs[b]	Conv.[c] (%)	$M_{n,th}$[c] (kDa)	$M_{n,GPC}$[d] (kDa)	M_w/M_n[d]
1	0.5			4.5	0.8	0.9	1.31
2	1	DMSO	Me_6TREN	22.7	2.6	2.9	1.29
3	2			50.0	5.4	5.7	1.26
4	4			82.8	8.6	8.9	1.25
5	1			18.1	1.0	1.0	1.32
6	2	Dioxane	Me_6TREN	40.4	1.4	1.5	1.32
7	3			60.2	2.0	2.1	1.31
8	4			72.1	3.0	3.3	1.30
9	1			6.0	0.9	1.0	1.35
10	2	Toluene	Me_6TREN	16.6	2.0	2.2	1.32
11	3			30.2	3.4	3.7	1.30
12	4			40.4	4.4	4.7	1.26
13	1			22.4	2.6	2.8	1.32
14	2.2	DMSO	PMDETA	56.6	6.0	6.3	1.30
15	3			68.7	7.2	7.5	1.28
16	3.8			79.8	8.3	8.7	1.26
17	1			24.7	2.8	3.0	1.33
18	2	DMSO	TEA	48.7	5.2	5.5	1.30
19	3			70.2	7.4	7.7	1.28
20	4			81.2	8.5	8.9	1.26

[a] Supplementary data to Figure 4. [b] Molar ratio with respect to TTC-1 was adjusted to give the same molar amount of R_3N for each experiment (*i.e.* 0.25 eq. for Me_6TREN, 0.33 eq. for PMDETA, and 1 eq. for TEA). [c] Determined by ^{1}H NMR. [d] Determined by THF GPC.

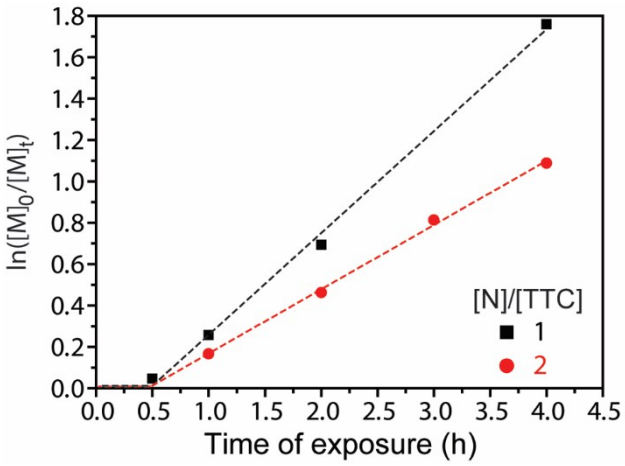

Figure S11. Kinetic plots for the TAC Pi-RDRPs of MMA using different amount of amine (Me_6TREN). The molar ratio [N] with respect to [TTC-1] was adjusted to 2 and 1 eq., respectively.

Reference

1. M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, **5**, 41-44.
2. E. H. H. Wong, S. J. Lam, E. Nam and G. G. Qiao, *ACS Macro. Letters*, 2014, **3**, 524-528.
3. J. T. Lai, D. Filla and R. Shea, *Macromolecules*, 2002, **35**, 6754-6756.