Visible Light Mediated Controlled Radical Polymerization in the Absence of Exogenous Radical Sources or Catalysts

Supporting Information

Thomas G. McKenzie, Qiang Fu, Edgar H. H. Wong, Dave E. Dunstan, Greg G. Qiao*.

Polymer Science Group, Department of Chemical and Biomolecular Engineering, The University of Melbourne, Parkville, VIC 3010, Australia

E-mail: gregghq@unimelb.edu.au

Supporting Data

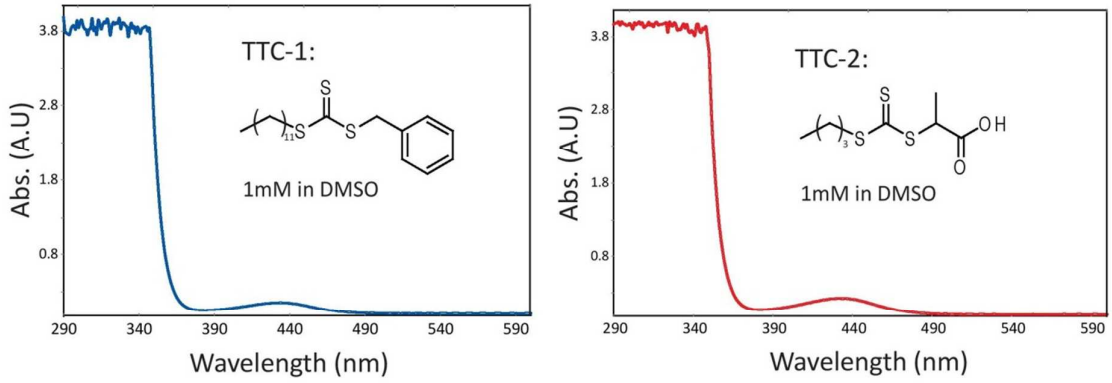

Figure S1: Absorption spectra of trithiocarbonates used in this study that clearly illustrates the distinctive n→π* peak in the visible region.

Figure S2: Visible light photoreactor used in this study which was constructed from a commercial LED strip light wound around the inside of a beaker.

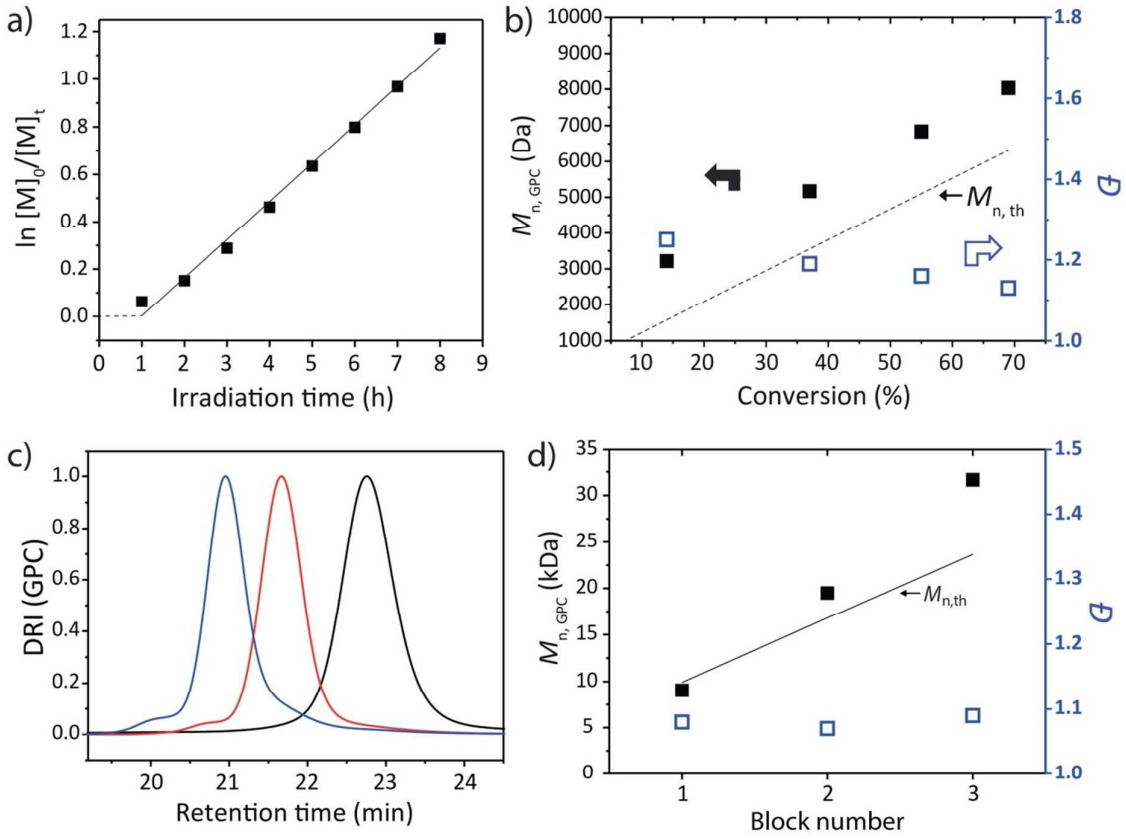

Figure S2: UV light source for photocontrolled radical polymerization; a) Semi-logarithmic plot showing linear evolution of monomer conversion with irradiation time following an induction period of < 1 h. b) Molecular weight and dispersity values at different monomer conversions. c) and d) Chain extension experiments via in situ monomer addition in one-pot to yield pseudo-triblock copolymer.

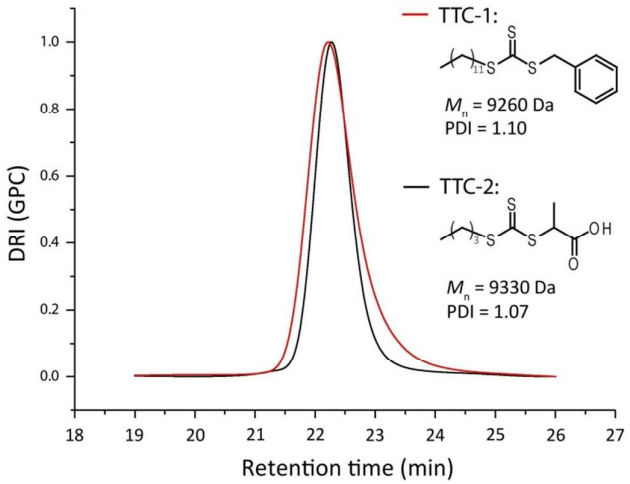

Figure S3: Overlay of GPC DRI chromatograms of the resultant PMA formed (at >95% monomer conversion) using different TTC compounds.

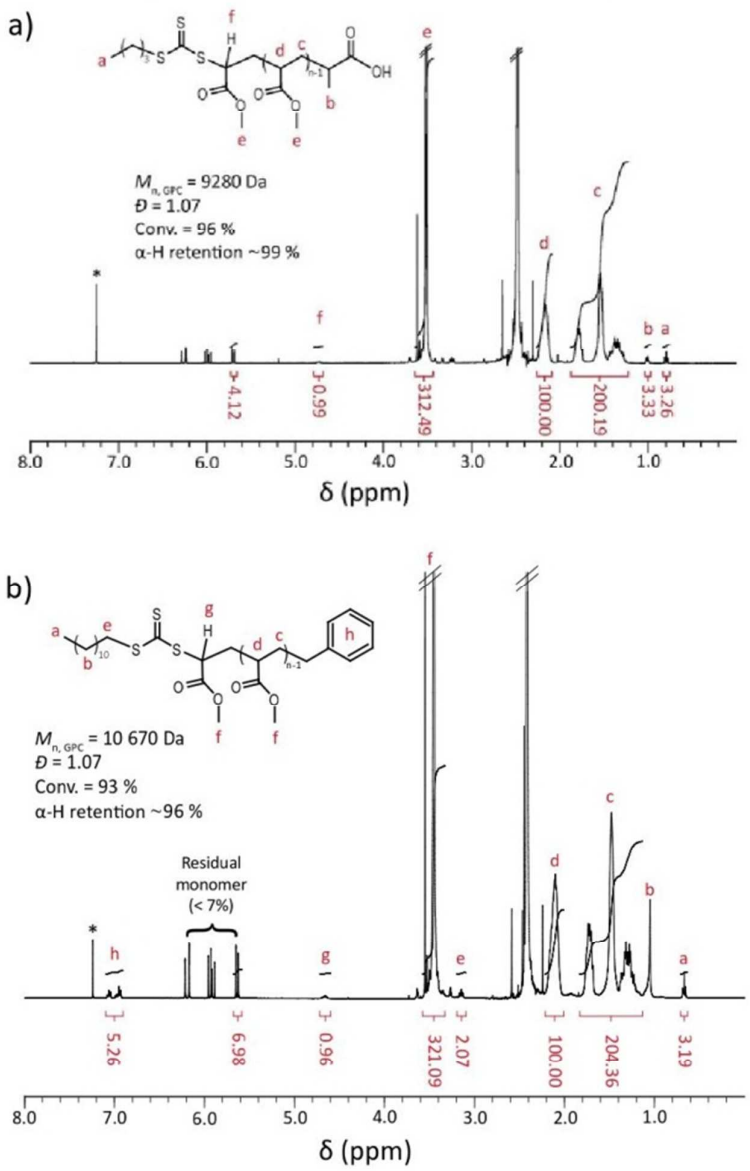

Figure S4: ^{1}H NMR of PMA formed using a) TTC-1 and b) TTC-2. High α-H retention observed even at high monomer conversion as indicated by peak area conversions of polymer backbone peaks (**d**, δ_{ppm}~2.1, -C***H***, and **c**, δ_{ppm}~1.1-1.8, -C$\boldsymbol{H_2}$), TTC terminal methyl group (**a**, δ_{ppm}~0.8, -C$\boldsymbol{H_3}$), and single proton α to the thio end group (**f/g**, δ_{ppm}~1.1, f_{th} = 1.00).

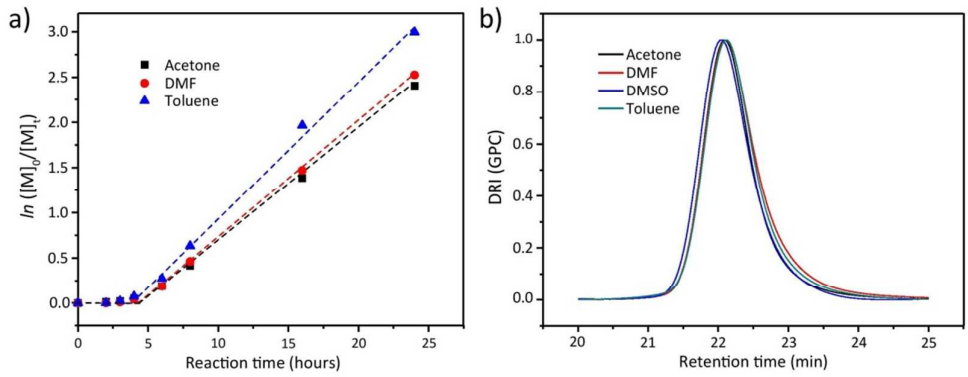

Figure S5: a) Kinetic plots for the photopolymerization of methyl acrylate in various solvents under irradiation from blue LED light source. b) Overlay of GPC DRI chromatograms of the resultant PMA formed (at >95% monomer conversion) in different solvents.

Table S1: Experimental conditions and characterization data for linear PMA homopolymer (Entries 1-5) and pseudo-hexablock PMA-*b*-PMA-*b*-PMA-*b*-PMA-*b*-PMA-*b*-PMA polymer (Entries 6-10) synthesized *via* visible light photoactivated polymerization.

Entry	*Monomer*	*Light*	*TTC*[a]	*Solvent*	$[M]_0/[TTC]_0$	*t* (h)	*%conv.*[b]	$M_{n,th}$ (Da)[c]	$M_{n,GPC}$ (Da)[d]	$Đ$[d]
1	MA	Vis.	1	DMSO	100	4	15	1660	3100	1.23
2	MA	Vis.	1	DMSO	100	6	40	3813	5230	1.16
3	MA	Vis.	1	DMSO	100	8	64	5879	6950	1.12
4	MA	Vis.	1	DMSO	100	10	79	7171	8545	1.11
5	MA	Vis.	1	DMSO	100	12	89	8032	9260	1.10
6	MA (Block 1)	Vis.	1	DMSO	100	16	93	8980	10670	1.07
7	MA (Block 2)	Vis.	1	DMSO	100	16	96	17600	21700	1.05
8	MA (Block 3)	Vis.	1	DMSO	100	16	96	26200	36500	1.07
9	MA (Block 4)	Vis.	1	DMSO	100	24	94	34800	45700	1.10
10	MA (Block 5)	Vis.	1	DMSO	100	24	93	43400	61350	1.12
11	MA (Block 6)	Vis.	1	DMSO	100	24	92	52000	80800	1.13

[a]See Figure S1 for TTC molecular structures. [b]Obtained by ^{1}H NMR characterization. [c]Calculated via the equation: $M_n = [M]_0/[TTC]_0 \times M_w^M \times \%conv. + M_w^{TTC}$, where $[M]_0$, $[TTC]_0$, M_w^M, %conv., and M_w^{TTC} correspond to the initial monomer and trithiocarbonate concentrations, molar mass of monomer, monomer conversion, and molar mass of trithiocarbonate, respectively. [d]Molecular weight and dispersity values determined by GPC analysis based on calibration by monodisperse polystyrene standards.

***Gel characterization*[1]**

Swelling ratio (q_w) calculated via:

$$\boldsymbol{qw = \frac{m(wet)}{m(dry)}}$$

Where *m(wet)* is mass after swelling with good solvent (water in this case), and *m(dry)* is mass after drying to constant weight.

Swelling degree percentage (%SD) calculated via:

$$\boldsymbol{\%SD = \frac{[m(wet) - m(dry)]}{m(dry)} \times 100}$$

References

1 H. Zhou and J. A. Johnson, *Angew. Chem.* **2013**, *125*, 2291-2294.