Investigation into the photolytic stability of RAFT agents and the implications for photopolymerization reactions

Supporting Information

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Experimental Data

Materials

Methyl acrylate (MA, Aldrich, 99%) was passed over basic alumina to remove inhibitors prior to use. 2-(((Butylthio)carbonothiolyl)thio)propanoic acid (TTC-1) was received from Dulux Group Australia and used as received. 2-(((Dodecylthio)carbonothiolyl)thio)propanoic acid (TTC-2) was received from Boron Molecular and used as received. 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (TTC-3), 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (TTC-4), 2-cyano-2-propyl dodecyl trithiocarbonate (TTC-5), and 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (DTB) were purchased from Sigma-Aldrich and used as received. Benzyl-((dodecylthio)carbonothiolyl)thio (TTC-6) was synthesized as described below and characterized via ^{1}H and ^{13}C NMR spectroscopy prior to use.[1] Carbon disulphide (CS_2), potassium hydroxide (KOH), 1-dodecanethiol, and benzyl bromide were all purchased from Sigma-Aldrich and used without further purification. Dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), acetone, toluene, and tetrahydrofuran (THF) were purchased from Chem-Supply Pty Ltd and used as received. Deuterated chloroform ($CDCl_3$, 99.99%) was purchased from Cambridge Isotope Laboratories Inc. The LED light source used for all experiments was a commercial strip lighting consisting of 300 LED bulbs with a 4.8W operating power. The light emission spectrum had a maximum around 460 nm as measured using a Maya 2000Pro spectrometer fitted with an optical fibre (OceanOptics 100UV) and an intensity at the working distance of ca. 1.5 mW/cm^2 as measured via a handheld visible light meter (Solarmeter Model 9.4).

Characterization

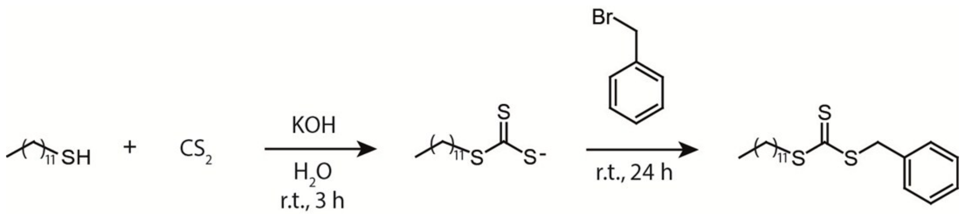
Nuclear Magnetic Resonance (NMR) spectroscopy. ^{1}H NMR was conducted on a Varian Unity 400 MHz spectrometer operating at 400 MHz. The deuterated solvent ($CDCl_3$) was used as a reference and all sample concentrations were approximately 10 mg/mL.

Gel Permeation Chromatography (GPC). GPC analysis was carried out on a Shimadzu liquid chromatography system equipped with a Wyatt OPTILAB DSP interferometric refractometer (690 nm) and Shimadzu SPD-10AVP UV-vis detector using three Phenomenex Phenogel columns (5 µm bead size) operating at 45°C. THF was used as eluent at a constant flow rate of 1 mL/min, and the system was calibrated using narrowly dispersed polystyrene standards of varying molecular weight.

UV-vis spectroscopy. UV-vis absorbance spectra were obtained using a Shimadzu UV-1800 Spectrophotometer and UVProbe software package. The wavelength range of 290-600 nm was selected with a slow scan speed and sampling interval of 1 nm.

Methods

Synthesis of benzyl-((dodecylthio)carbonothiolyl)thio (TTC-6).



To a solution of KOH (0.96 g, 17.2 mmol) in water (40 mL) in a 250 mL round bottom flask, 1-dodecanethiol (2.92 g, 14.4 mmol) was added and the mixture stirred to dissolve. CS_2 (1.7 mL, 28.8 mmol) was added dropwise to generate a straw yellow solution. The flask was then sealed and stirred at room temperature for 3 h. To the resulting deep orange solution, benzyl bromide (1.72 mL, 14.4 mmol) was added and a yellow solid immediately started precipitating. This mixture was then covered with foil and stirred at room temperature for a further 24 h. The reaction mixture was then transferred to a separating funnel and the product extracted three times with DCM (40 mL). The collected organic fraction was then washed sequentially with 30 mL portions of 0.5 M HCl, saturated NaCl, and milli-Q water before being dried over $MgSO_4$ overnight. The solids were removed via filtration and the DCM removed in vacuo. The resulting crude product (a viscous orange liquid) was then crystallized from a methanol/ethanol mixture (1:1, 50 mL) overnight at -18oC. The resulting yellow crystals were collected via filtration and dried in vacuo. Yield: 4.40 g (59%).^{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.

Visible light photopolymerization protocol

In a typical experiment, a 25 mL Schlenk was charged with MA (1.5 mL, 16.7 mmol), the chosen thiocarbonylthio compound (0.167 mmol), and DMSO (typically 50 vol% to monomer). The reaction mixture was degassed by 3 successive freeze-pump-thaw cycles before being back-filled with UHP-Ar (note: sparging with N_2 or Ar in a flask or vial could also be employed, however we found that polymerization results were inconsistent using these methods of degassing). The sealed Schlenk was then placed in the light source and irradiated while stirring at room temperature. Samples were taken via degassed syringe under an Ar blanket. The extracted samples were immediately diluted with $CDCl_3$ or THF for NMR and GPC analysis, respectively. Monomer conversion was estimated from ^{1}H NMR by comparing the integrals of the peaks corresponding to the polymer backbone (δ_H ~ 1.5 ppm, *t*, 2H –[C$\boldsymbol{H}_2$-CH]$_n$- and δ_H ~ 2.2 ppm, *s*, 1H, -[CH$_2$-C$\boldsymbol{H}$]$_n$-) to those corresponding to the unsaturated acrylate double bond (δ_H ~ 5.7 ppm, *s*, 1H, H$_2$C=C$\boldsymbol{H}$).

UV-vis degradation studies.

Reactions were carried out in the same fashion as for a typical photopolymerization but in the absence of monomer. The extracted samples were prepared for UV-vis analysis by careful dilution of a known volume of reaction mixture with fresh DMSO to give TTC concentrations of 1 mM and 0.1 mM for observing the n→π* and π→π* absorption bands, respectively. The amound of degradation was calculated using the initial absorption value at a fixed wavelength close to the λ_{max} of 310 nm for the 0.1 mM solutions. Subsequent absorption values at this wavelength were then reported as a percentage of the initial value.

Additional Figures

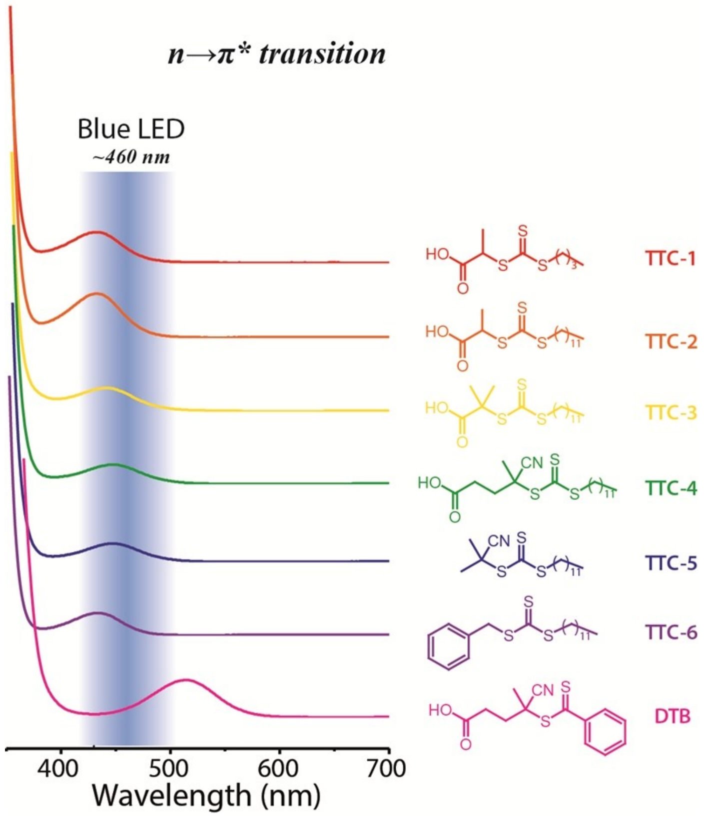


Figure S1: Absorption spectra of thiocarbonylthio compounds used in this study and blue LED emission wavelength range (shaded area) that illustrates the emission-absorption overlap with each thiocarbonyl's n→π* absorption band.

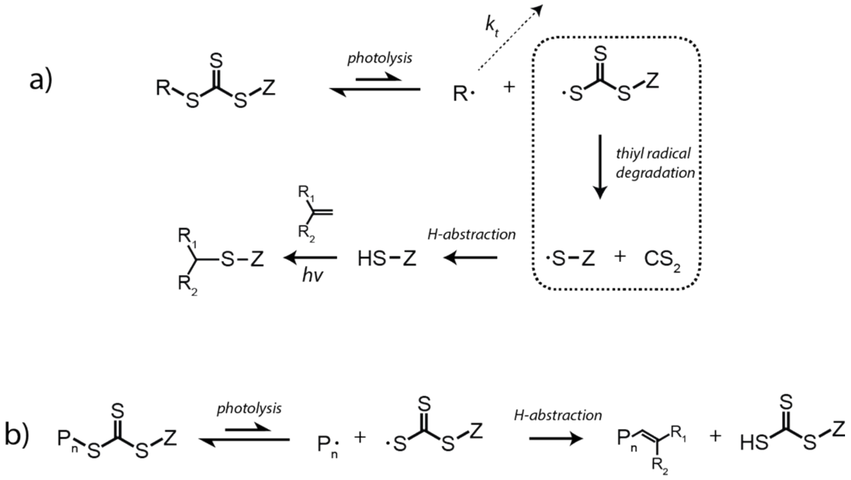


Figure S2: a) Proposed mechanism of trithiocarbonate (TTC) degradation under visible light irradiation.[2] H-abstraction typically occurs as a termination reaction of the active radical (R•),[3] thus contributing to a broadening of the polymer disperisty and loss of control observed under conditions where degradation is considered to be significant. B) Potential pathway for polymeric-TTC degradation via formation of unsaturated *ω* chain end as is observed in studies of thermal degradation.[4]

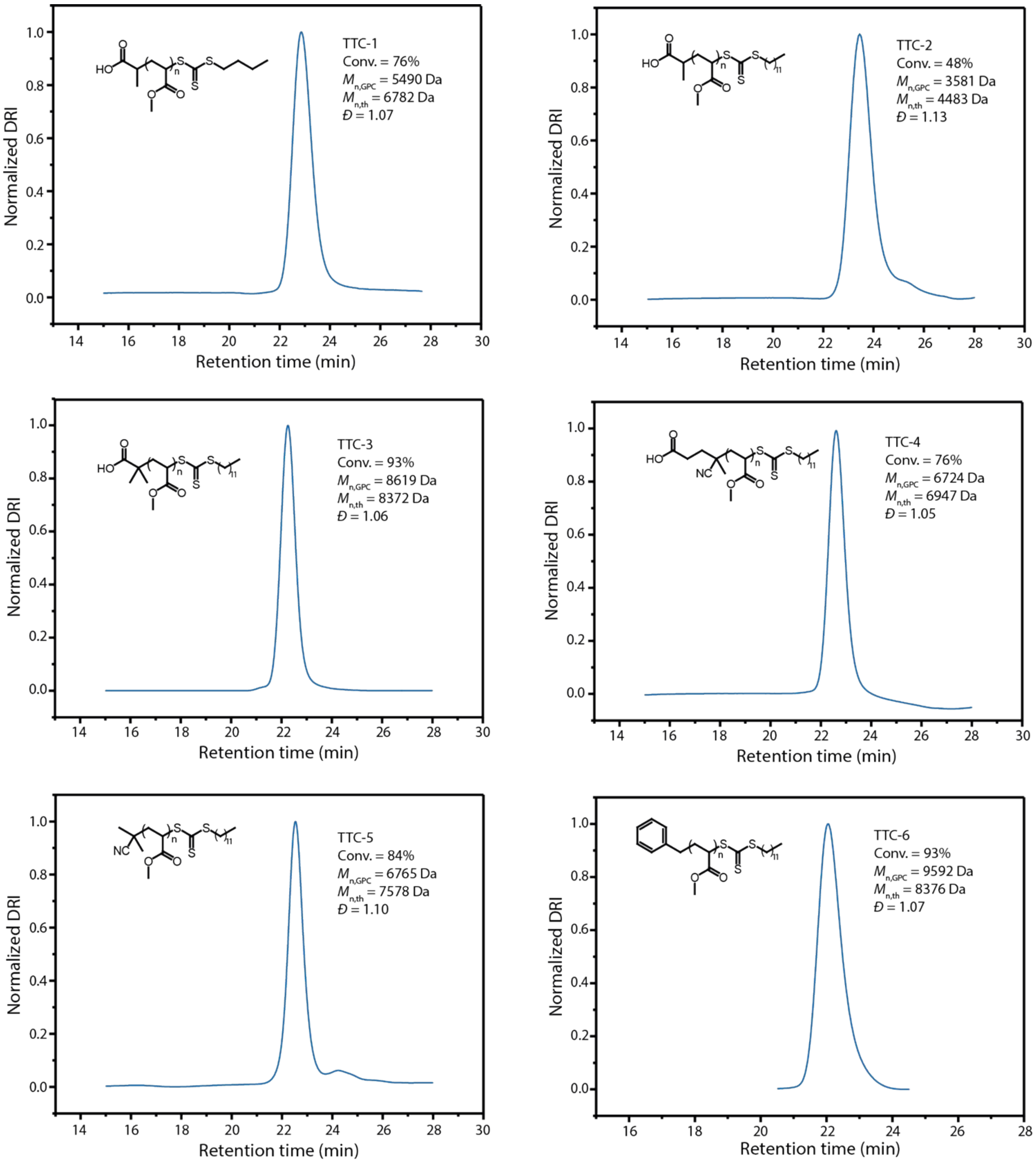


Figure S3: GPC (DRI) chromatograms and molecular structure for each trithiocarbonate (TTC) investigated in this study.

References

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