Supporting Information

Investigating the Effect of End-Group, Molecular Weight, and Solvents on the Catalyst-Free Depolymerization of RAFT Polymers: Possibility to Reverse the Polymerization of Heat-Sensitive Polymers

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Table of Contents

Table of Figures

Methods

Materials. All materials were purchased from either Sigma Aldrich or Fischer Scientific unless otherwise stated. Benzyl methacrylate (BzMA, >98.0%) was purchased from Tokyo Chemical Industries. Monomers were filtered through basic alumina before use.

NMR spectroscopy. ^{1}H-NMR spectra were recorded on a Bruker Avance-300 spectrometer using acetone-$d_{6,}$ dimethyl sulfoxide-d_6, or $CDCl_3$ as the NMR solvent. Chemical shifts are given in ppm downfield from tetramethylsilane and referenced to residual solvent proton signals.

Size-exclusion chromatography (SEC). SEC was measured on Shimadzu equipment comprising a CBM-20A system controller, LC-20AD pump, SIL-20A automatic injector, 10.0 μm bead-size guard column (50 x 7.5 mm) followed by three KF-805L columns (300 x 8 mm, bead size: 10 μm, pore size maximum: 5000 Å), SPD-20A ultraviolet detector, and an RID-20A differential refractive index detector. The column temperature was maintained at 40 ℃ using a CTO-20A oven. The flow rate was set to 1 ml/min and with *N*, *N*-dimethylacetamide (DMAc, Acros, HPLC grade, with 0.03 w/v LiBr) as the eluent. The UV wavelength was set to 310 nm. Molecular weights were determined relative poly(methyl methacrylate) standards with molecular weights ranging from 5,000 to 1.5 x 10^6 g/mol (Agilent Technologies). All SEC samples were dissolved in DMAc and passed through 0.45 μm PTFE filters prior to analysis.

Polymerization of MMA using 2-cyano-2-propyl dithiobenzoate as the RAFT agent. A typical procedure for the polymerization is described. PMMA with different degrees of polymerization were synthesized by adjusting the MMA:RAFT agent ratio. Into a 25 mL round bottom flask, 157.9 mg of 2-cyanoprop-2-yl dithiobenzoate (713.4 μmol, 1 equiv) and 11.7 mg AIBN (71.3 μmol, 0.1 equiv) were dissolved in 5 mL toluene. Subsequently, 10.6 mL of MMA (10.0 g, 99.9 mmol, 140 equiv) and a stirrer bar were added, and the flask was sealed with a septum, prior to deoxygenation by nitrogen bubbling for 15 min. Polymerization was conducted in an oil bath at 70 °C for 4 h with a 400-rpm stirring rate. Samples were taken periodically under a nitrogen blanket for ^{1}H-NMR analysis and passed through a syringe filter (0.45 μm PTFE membrane) prior to SEC analysis. Polymerization was stopped at 45% conversion by removing the reaction from the oil bath and removing the septum.

Polymerization of MMA using 2-Cyano 2-propyl dodecyltrithiocarbonate as the RAFT agent. In a 15 mL vial, 57.5 mg of 2-Cyano 2-propyl dodecyltrithiocarbonate (166.5. μmol, 1 equiv) and 2.7 mg AIBN (16.6 μmol, 0.1 equiv) were dissolved in 1.3 mL toluene. Subsequently, 2.66 mL of

MMA (2.5 g, 25 mmol, 150 equiv) and a stirrer bar were added, and the flask was sealed with a septum, prior to deoxygenation by nitrogen bubbling for 15 min. Polymerization was conducted in an oil bath at 70 °C for 4.5 h with a 400-rpm stirring rate. Samples were taken periodically under a nitrogen blanket for ^{1}H-NMR analysis and passed through a syringe filter (0.45 µm PTFE membrane) prior to SEC analysis. Polymerization was stopped at 38% conversion by removing the reaction from the oil bath and removing the septum.

Polymerization of MMA using 2-Cyanobutan-2-yl 4-chloro-3,5-dimethyl-1H-pyrazole-1-carbodithioate as the RAFT agent. In a 15 mL vial, 143.7 mg of 2-Cyanobutan-2-yl 4-chloro-3,5-dimethyl-1H-pyrazole-1-carbodithioate (499.4 µmol, 1 equiv) and 8.2 mg AIBN (16.6 µmol, 0.1 equiv) were dissolved in 1.3 mL toluene. Subsequently, 2.66 mL of MMA (2.5 g, 25 mmol, 50 equiv) and a stirrer bar were added, and the flask was sealed with a septum, prior to deoxygenation by nitrogen bubbling for 15 min. Polymerization was conducted in an oil bath at 70 °C for 6 h with a 400-rpm stirring rate. Samples were taken periodically under a nitrogen blanket for ^{1}H-NMR analysis and passed through a syringe filter (0.45 µm PTFE membrane) prior to SEC analysis. Polymerization was stopped at 65% conversion by removing the reaction from the oil bath and removing the septum.

Polymerization of *tert*-butyl methacrylate using 2-cyano-2-propyl dithiobenzoate as the RAFT agent. In a 15 mL vial, 31.1 mg of 2-cyanoprop-2-yl dithiobenzoate (140.6 µmol, 1 equiv) and 2.3 mg AIBN (14.1 µmol, 0.1 equiv) were dissolved in 1.7 mL toluene. Subsequently, 3.4 mL of tBMA (3.0 g, 21.1 mmol, 150 equiv) and a stirrer bar were added, and the flask was sealed with a septum, prior to deoxygenation by nitrogen bubbling for 15 min. Polymerization was conducted in an oil bath at 70 °C for 7 h with a 400-rpm stirring rate. Samples were taken periodically under a nitrogen blanket for ^{1}H-NMR analysis and passed through a syringe filter (0.45 µm PTFE membrane) prior to SEC analysis. Polymerization was stopped at 43% conversion by removing the reaction from the oil bath and removing the septum.

Polymerization of glycidyl methacrylate using 2-cyano-2-propyl dithiobenzoate as the RAFT agent. In a 15 mL vial, 31.1 mg of 2-cyanoprop-2-yl dithiobenzoate (140.6 µmol, 1 equiv) and 2.3 mg AIBN (14.1 µmol, 0.1 equiv) were dissolved in 1.7 mL toluene. Subsequently, 2.9 mL of GMA (3.0 g, 21.1 mmol, 150 equiv) and a stirrer bar were added, and the flask was sealed with a septum, prior to deoxygenation by nitrogen bubbling for 15 min. Polymerization was conducted in an oil bath at 70 °C for 5 h with a 400-rpm stirring rate. Samples were taken periodically under a nitrogen blanket for ^{1}H-NMR analysis and passed through a syringe filter (0.45 µm PTFE membrane) prior to SEC analysis. Polymerization was stopped at 50% conversion by removing the reaction from the oil bath and removing the septum.

Purification of PMMA and PGMA. PMMA and PGMA macroCTA were precipitated at least three times in cold methanol and vacuum-filtered using a Buchner funnel. The precipitates were dried in a vacuum oven for at least 12 h before use.

Purification of PtBMA. PtBMA was purified by diluting the polymerization solution with acetone and dialyzing against acetone in a dialysis membrane (molecular weight cut-off = 3500) for 48 h. The product was concentrated using a rotary evaporator and dried in vacuo for at least 12 h prior ot use.

General depolymerization procedure for PMMA, PtBMA, and PGMA. PMMA will be used as the model example to describe a typical depolymerization procedure. In a 125 ml schlenk tube, 21.5 mg of PMMA was dissolved in 40 ml 1,4-dioxane (5.17 mM of MMA repeat unit). 15 mg of 350 g/mol poly(ethylene glycol) monomethyl ether was added as an internal standard for ^{1}H NMR analysis. The schlenk tube was sealed with a rubber septum and deoxygenated by nitrogen bubbling for 20 min. The schlenk tube was then put into a 120 ^{o}C oil bath to start the reaction. The schlenk tube was submerged into the oil bath until the surface of the solution inside was submerged ~2 cm below the surface of the oil bath. To take samples, the reaction was periodically removed from the oil bath and quickly added to an ice bath until the solution cooled to room temperature. The solution was then sampled under a nitrogen blanket. For SEC samples, ~1 ml of the sample solution was blow-dried, dissolved in DMAc, and passed through a syringe filter (0.45 μm PTFE membrane).

Analysis of RI/UV SEC signal during depolymerization. Relative UV signals were analyzed by preparing SEC samples at the same concentration of the reaction mixture. Specifically, 3 ml of the reaction was sampled at various time points (including t_0, before the reaction was put into the oil bath) and dried by air blowing. The dried polymer residue was then redissolved into 1.2 ml of N, N-dimethylacetamide and analyzed with SEC. The RI/UV signal intensities for t_0 samples in dioxane, xylene, DMF, and DCB were confirmed to be near-identical (i.e. <2% deviation between RI samples and <2% between UV samples). The signal intensities for subsequent time points were not normalized and compared with each other. A 26-30% reduction in the RI intensity was observed at 50 min for dioxane, 1 h for xylene, and 2 h for DMF. A 4-6% reduction in the RI intensity was observed at 1 h for DMF and 8 h for DCB.

Determination of monomer conversion during polymerization. Monomer conversions were determined by NMR spectroscopy. The monomer vinyl signals were compared to the combined polymer and monomer ester signals (e.g., $-CH_3$ for PMMA, $-CH_2-$ for PGMA, $-(CH3)_3$ for PtBMA).

Determination of depolymerization conversion. Depolymerization conversions were determined in-situ by comparing the monomer vinyl signals to the polymer backbone $-CH_3$ signals (simply taking a sample in dioxane and re-dissolving it in deuterated acetone). In addition, an internal standard is added in each reaction to ensure accurate conversion calculation through an alternative way. Specifically, a second NMR sample was prepared by re-dissolving the dried reaction mixture (blowing the solvent with air). Conversions were then calculated by comparing the intensity of the backbone $–CH_3$ signals before and after depolymerization against a nonvolatile internal standard (methoxy-terminated polyethylene glycol). Depolymerization conversions from the two methods deviated by <5%.

Additional Data

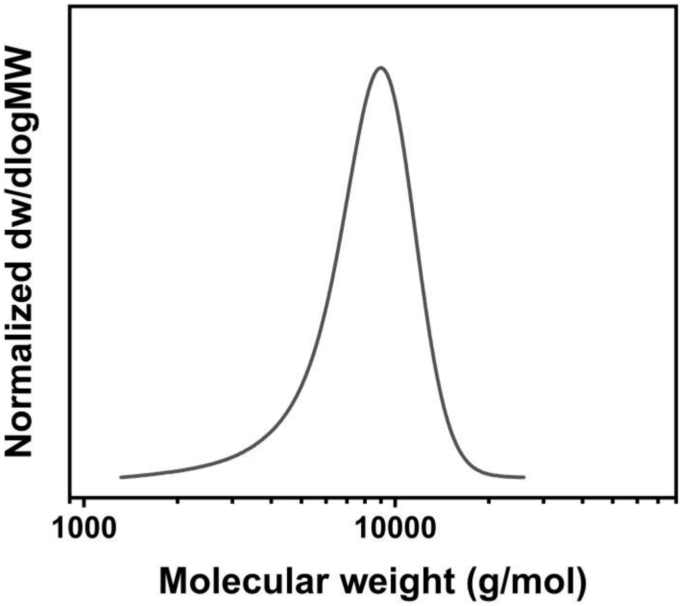

Figure S1. SEC trace of PMMA-DTB synthesized via RAFT polymerization with 2-cyano-2-propyl dithiobenzoate as the chain transfer agent ([CTA]:[AIBN]:[MMA] = 1:0.1:140) (M_n = 7,700; $Đ$ = 1.12).

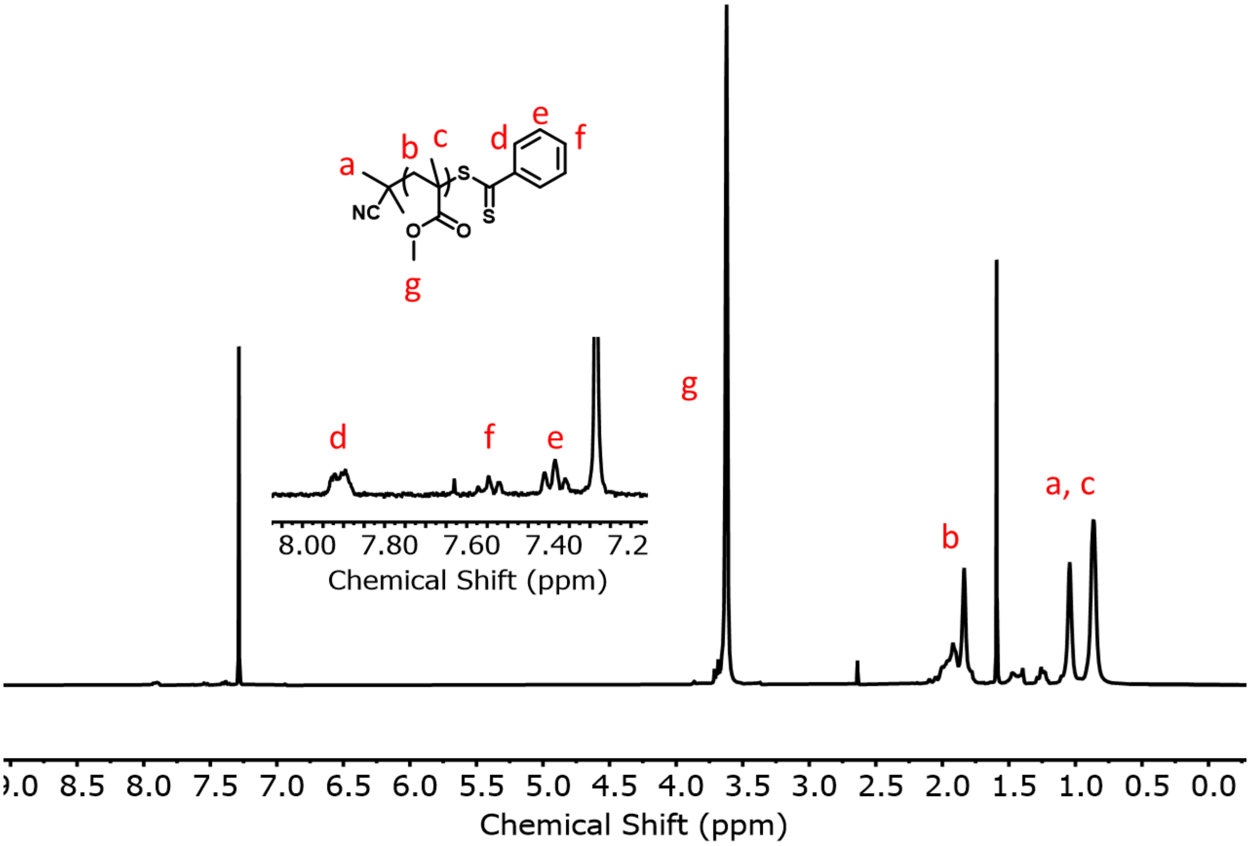

Figure S2. ^{1}H-NMR spectrum of purified PMMA-DTB prior to depolymerization.

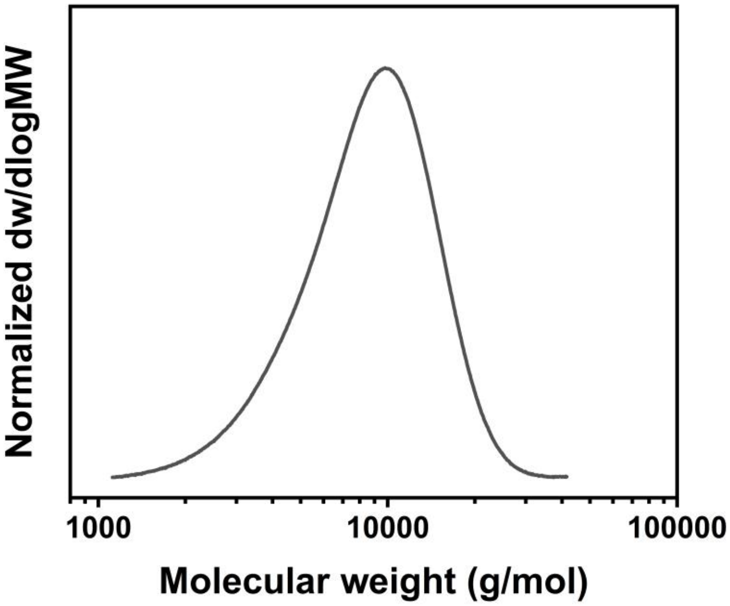

Figure S3. SEC trace of PMMA-TTC synthesized via RAFT polymerization with 2-cyano 2-propyl dodecyltrithiocarbonate as the chain transfer agent ([CTA]:[AIBN]:[MMA] = 1:0.1:140) (M_n = 7,400; $Đ$ = 1.30).

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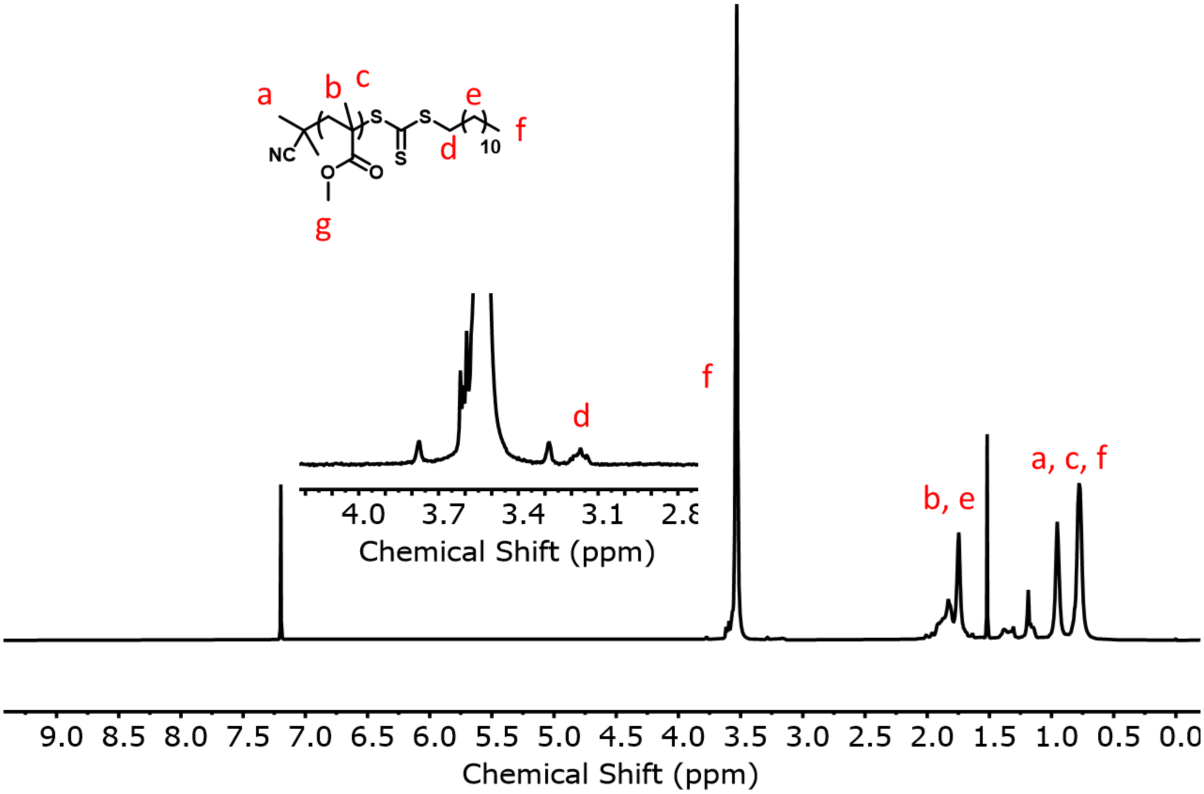

Figure S4. ^{1}H-NMR spectrum of purified PMMA-TTC prior to depolymerization.

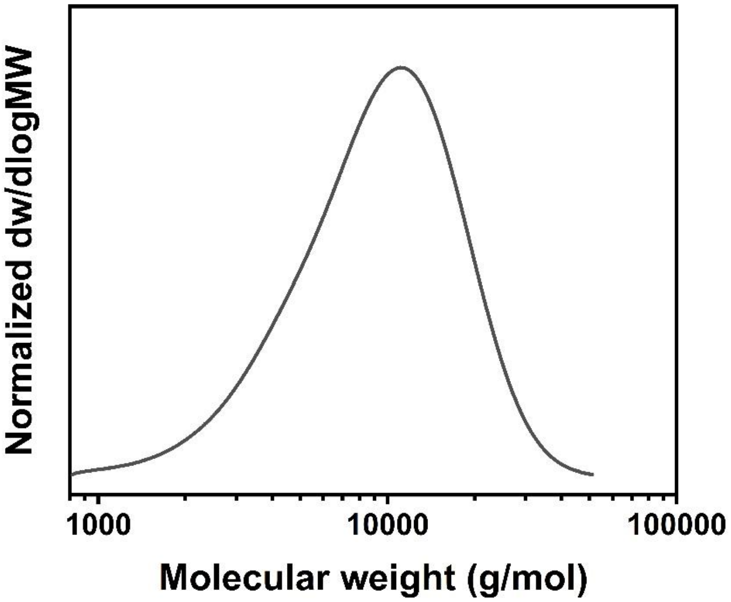

Figure S5. SEC trace of PMMA-pyrazoleCD synthesized via RAFT polymerization with cyanobutan-2-yl 4-chloro-3,5-dimethyl-1H-pyrazole-1-carbodithioate as the chain transfer agent ([CTA]:[AIBN]:[MMA] = 1:0.1:50) (M_n = 7,400; $Đ$ = 1.50).

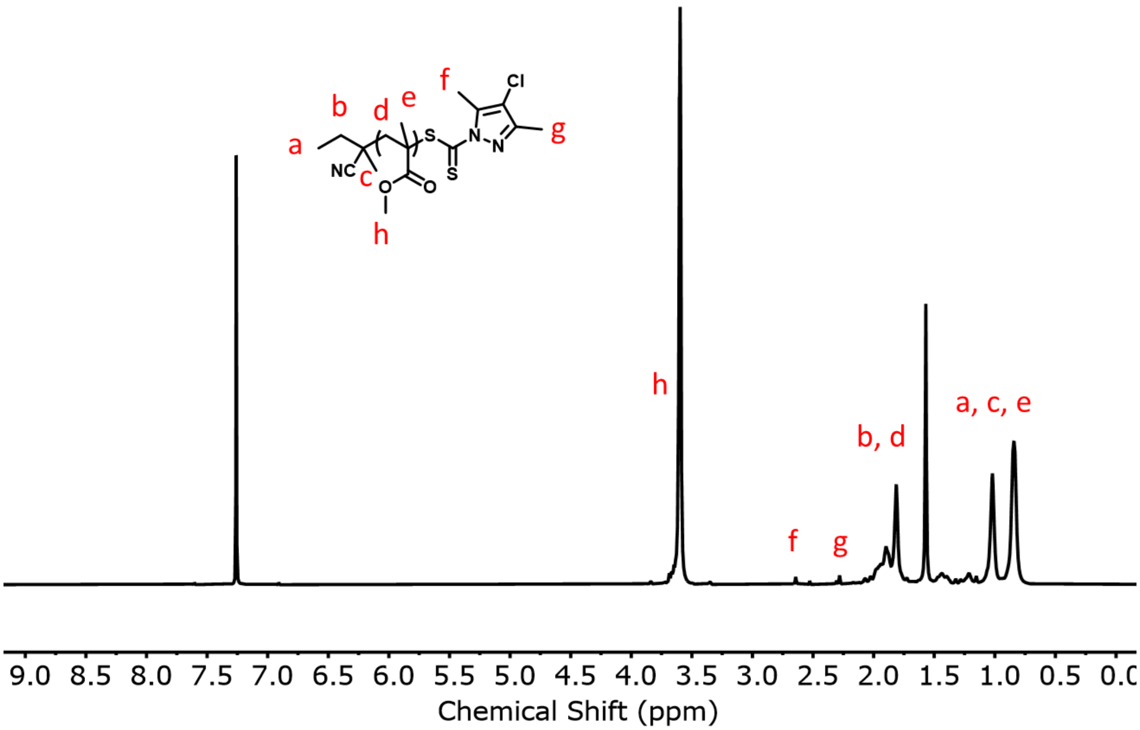

Figure S6. ^{1}H-NMR spectrum of purified PMMA-pyrzaoleCD prior to depolymerization.

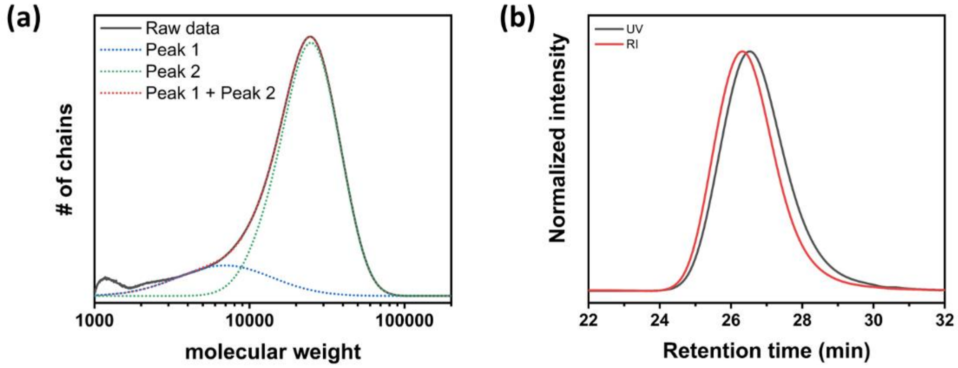

Figure S7. (a) Deconvolution of the SEC trace of chain-extended pyrazoleCD-PMMA. The y-axis was normalized to the number of chains by dividing the RI intensity by the respective molecular weight. Deconvolution was performed using MATLAB and the fractional area of Peak 1 was used to calculate the fraction of non-extended chains. (b) Normalized RI and UV SEC traces of chain-extended pyrazoleCD-PMMA.

Another approach to calculating livingness is by using the equation

$$L = \frac{[\mathrm{CTA}]_0}{[\mathrm{CTA}]_0 + 2f[\mathrm{I}]_0\left(1 - e^{-k_d t}\right)\left(1 - \frac{f_c}{2}\right)}$$

where L is the livingness, $[\mathrm{CTA}]_0$ is the concentration of RAFT agent, f is the initiation efficiency, $[\mathrm{I}]_0$ is the concentration of the initiator, k_d is the decomposition constant of the initiator, t is the reaction time, and f_c is the coupling factor. Setting $[\mathrm{CTA}]_0/[\mathrm{I}]_0 = 10$, $f = 0.5$, $k_d = 0.0000385$ (calculated based on a half-life of 5 h), t = 21,600 s, $f_c = 0$, we get a livingness of 97%.

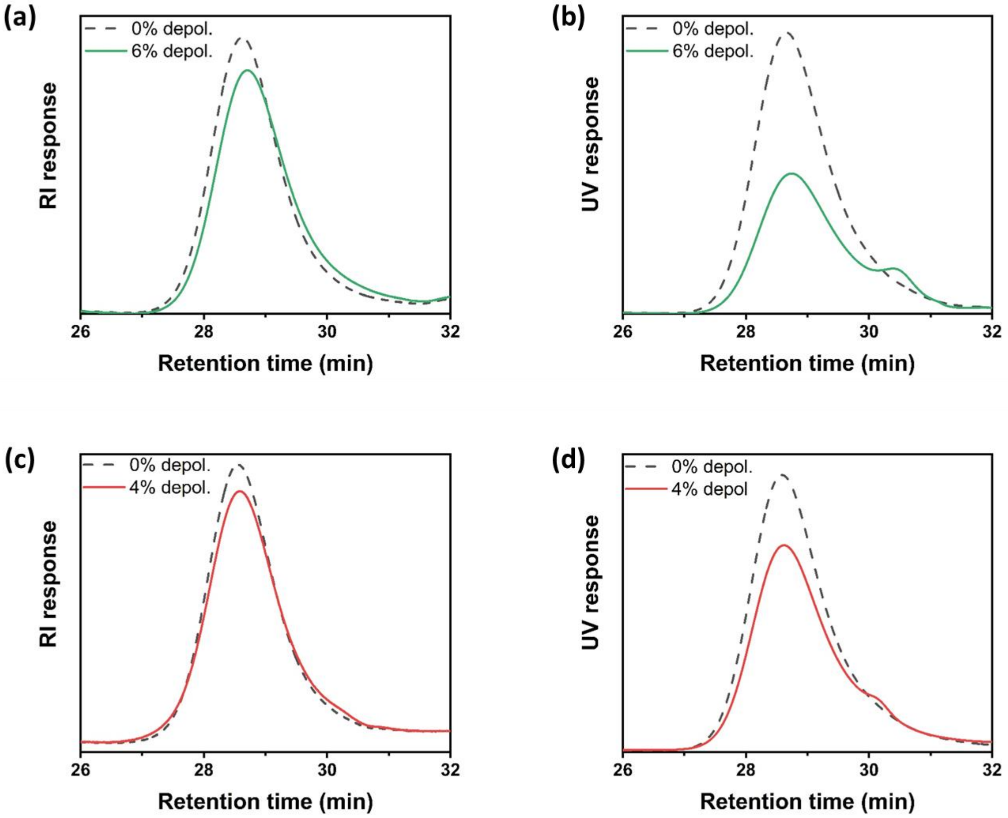

Figure S8. RI and UV SEC traces of PMMA-DTB before and after depolymerization in (a), (b) DCB and (c), (d) DMF. The reduction in the UV signal was 46% for DCB at 6% depolymerization and 18% for DMF at 4% depolymerization.

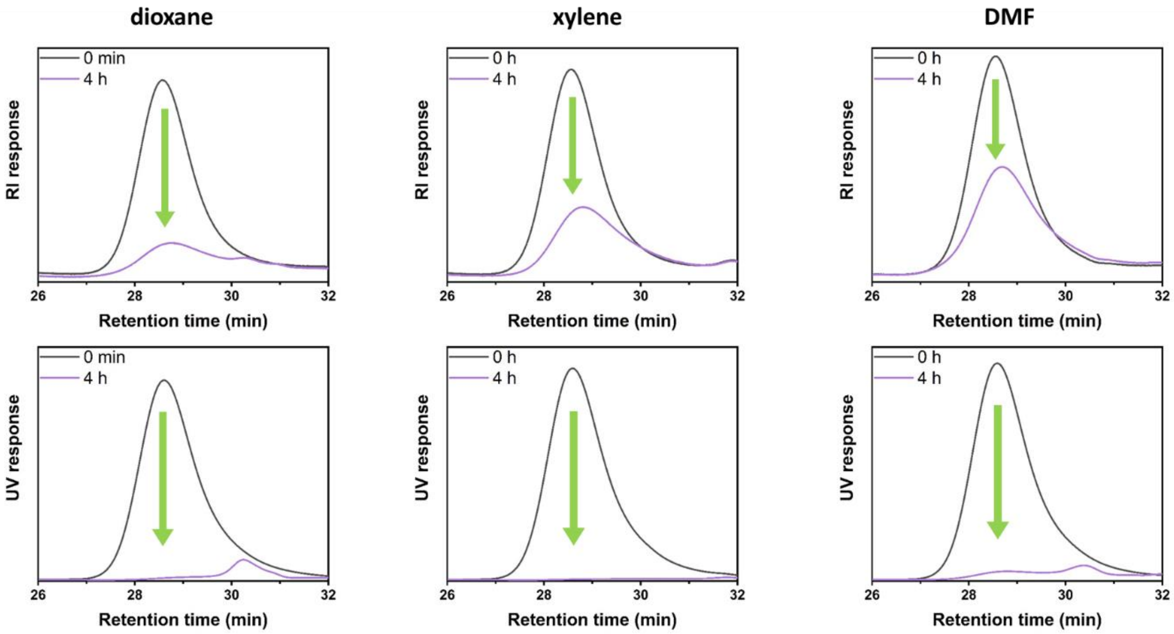

Figure S9. RI and UV SEC traces before (black) and after (purple) depolymerization in dioxane, xylene, and DMF.

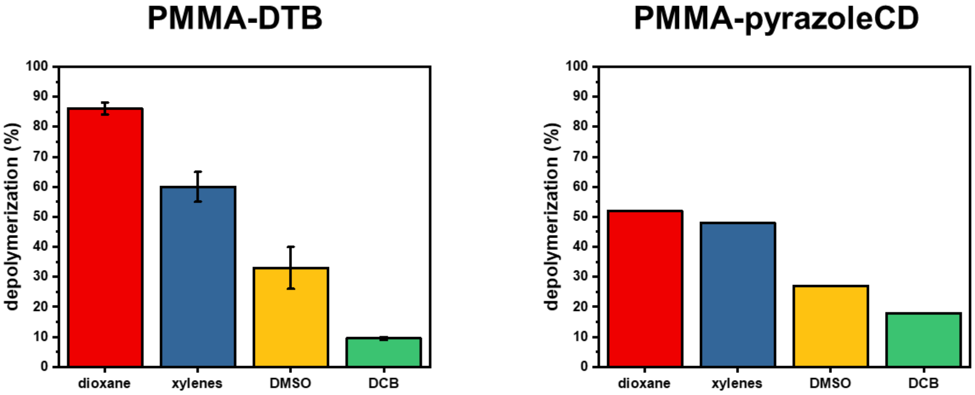

Figure S10. Final depolymerization conversions of PMMA-DTB (left) and PMMA-pyrazoleCD (right) in dioxane, xylenes, DMSO, and DCB. Depolymerization reactions were conducted at 5 mM and 120 ℃.

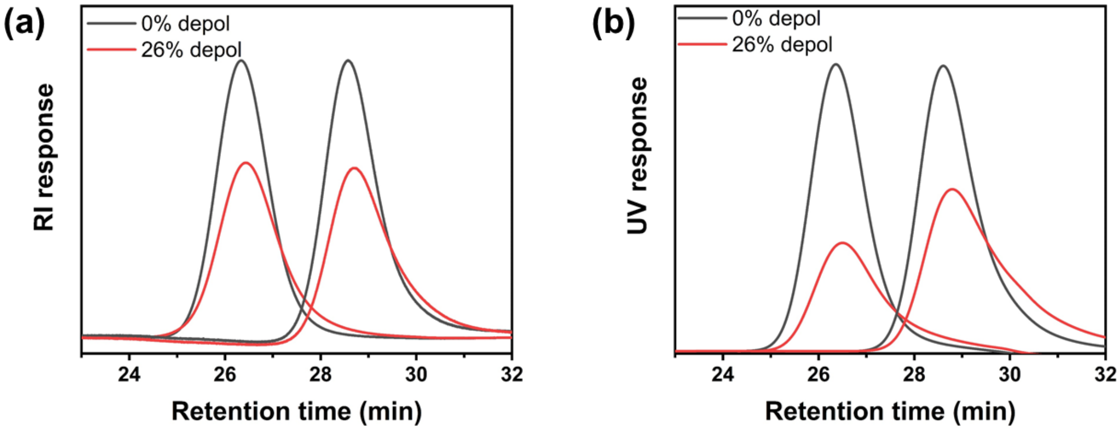

Figure S11. Comparison of the SEC (a) RI and (b) UV signals of DP75 (right trace) and DP260 PMMA (left trace) at the same depolymerization conversion (26%). A larger decrease in the UV signal is observed for the DP260 compared with that of the DP75 (52% vs 23%).

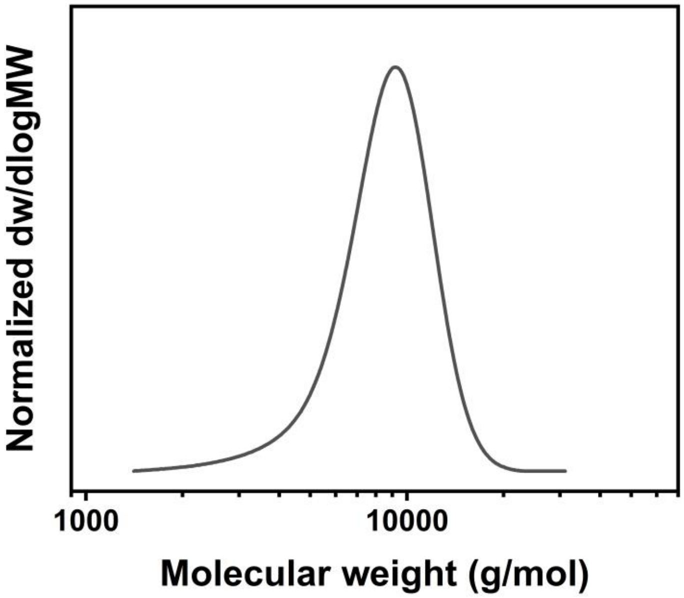

Figure S12. SEC trace of PtBMA-DTB synthesized via RAFT polymerization with 2-cyano-2-propyl dithiobenzoate as the chain transfer agent ([CTA]:[AIBN]:[MMA] = 1:0.1:150).

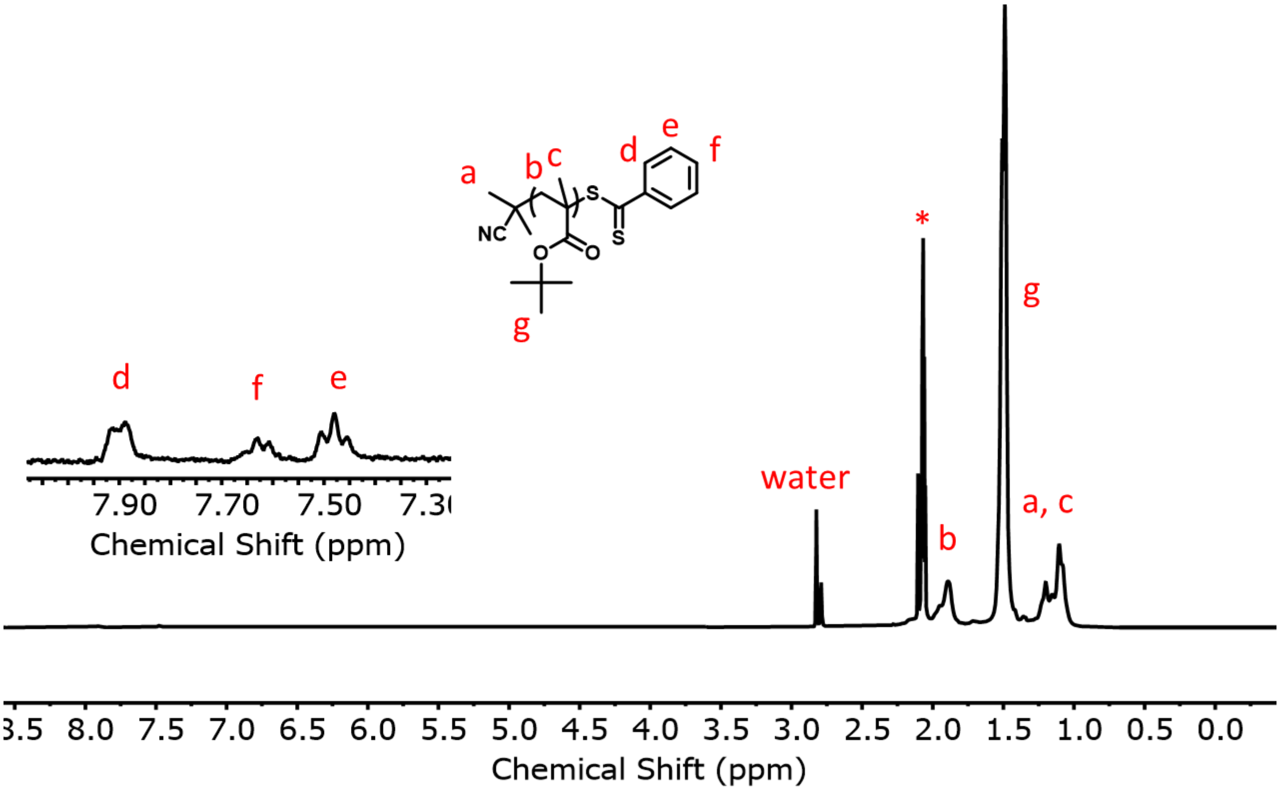

Figure S13. ^{1}H-NMR spectrum of purified PtBMA-DTB prior to depolymerization.

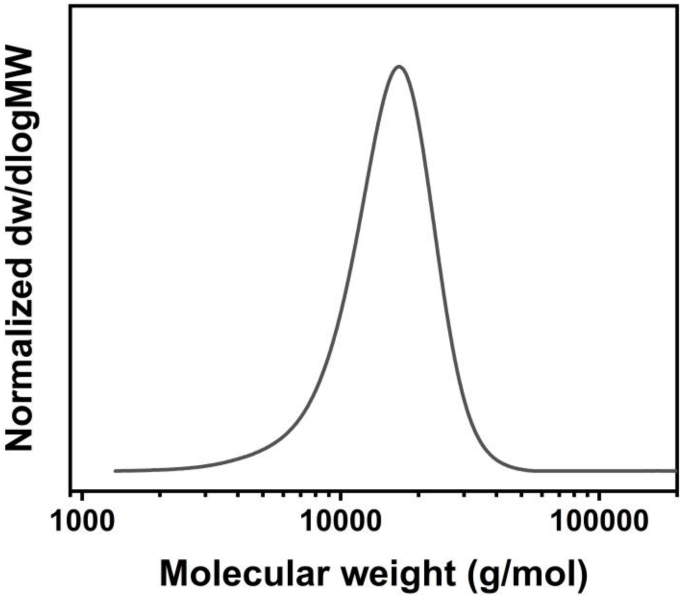

Figure S14. SEC trace of PGMA-DTB synthesized via RAFT polymerization with 2-cyano-2-propyl dithiobenzoate as the chain transfer agent ([CTA]:[AIBN]:[MMA] = 1:0.1:150).

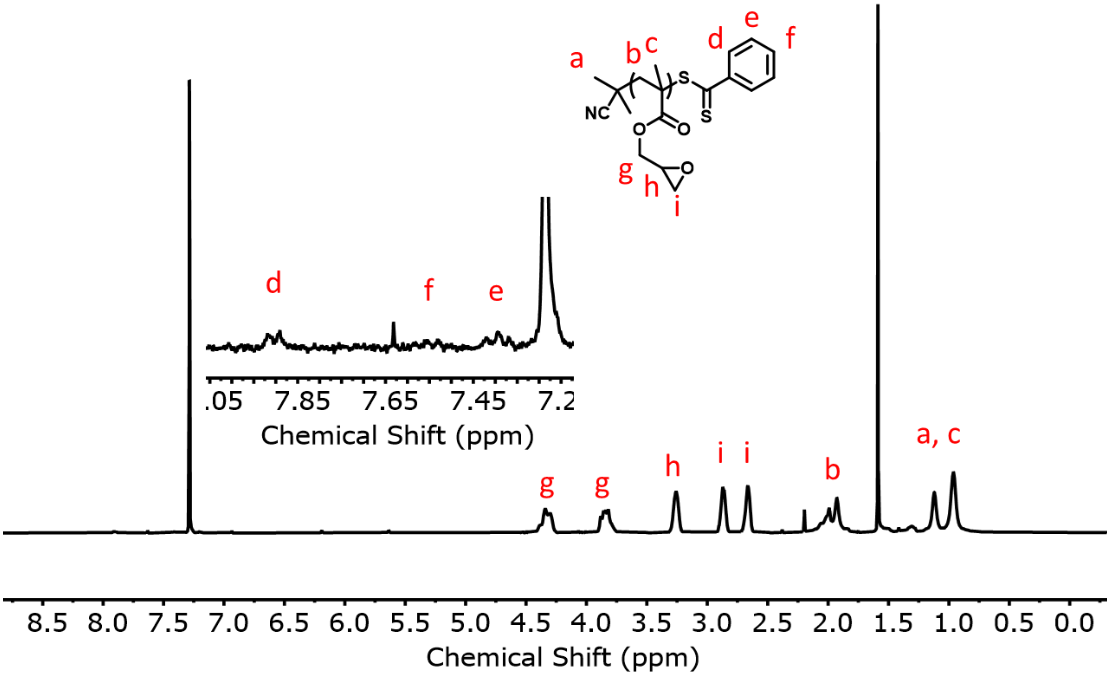

Figure S15. ^{1}H-NMR spectrum of purified PGMA-DTB prior to depolymerization.