

Supporting Information:
**Assessment of TEMPO as a Thermally Activatable
Base Generator and Its Use in Initiation of
Thermally-Triggered Thiol–Michael Addition
Polymerizations**

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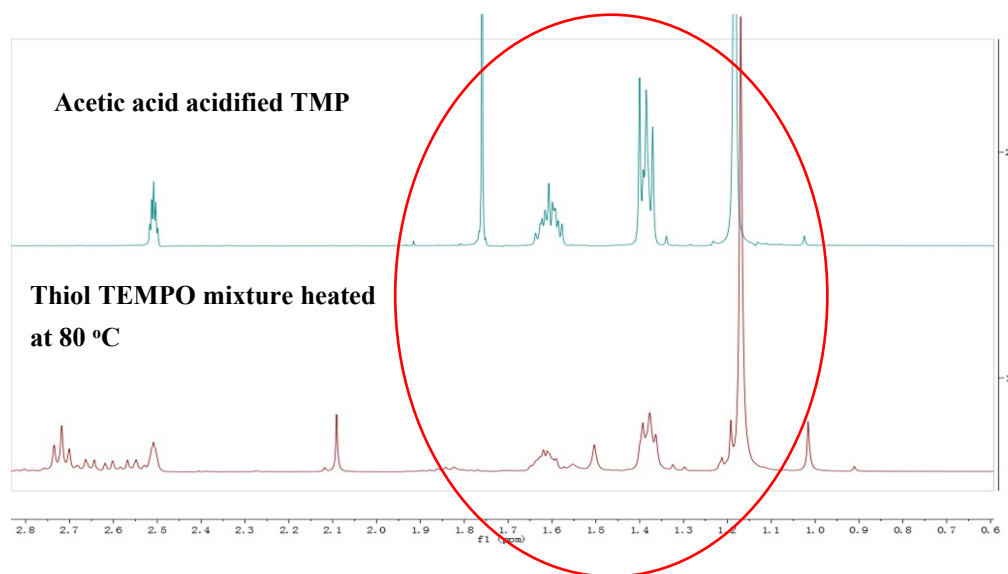


Figure S1. $^1\text{H-NMR}$ of oxidation-reduction reaction products of TEMPO and butyl 3-mercaptoproponate (BT) mixture (molar ratio of 1:4) heated to 60 degree for 30 min (tested in CDCl_3). Because of the odd spin number of TEMPO, no detectable NMR signal was observed but the solvent peak was observed prior to the reduction reaction. After redox reaction, 2,2,6,6-tetramethylpiperidine (TMP) is generated as a product and because of the much high basicity than BT, TMP is supposed to appear in an acidified form. Similar NMR peaks (1.15, 1.38, 1.63 ppm) can be observed in acetic acid acidified TMP. Herein, TMP generation during the redox reaction is confirmed. The generation of the TEMPO related side products may be responsible for the signal shift at 1.15 ppm

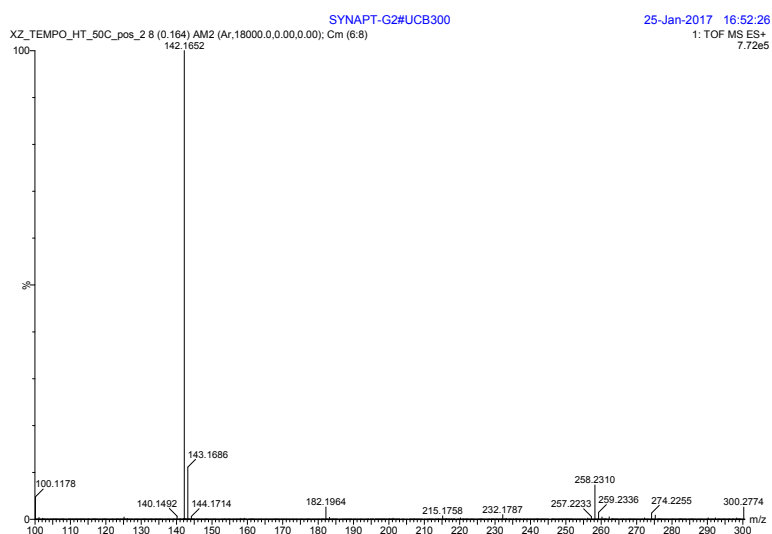


Figure S2. MS spectrum of oxidation-reduction reaction products of thermal TEMPO and butyl 3-mercaptoproponate (BT) mixture (molar ratio of 1:4) at 60 degree for 30

min. HRMS (ESI) m/z : $[M + H]^+$ calculated for $C_9H_{19}N$ is 142.15 and 142.1652 signal in the experiment indicates the generated TMP in the redox reaction.

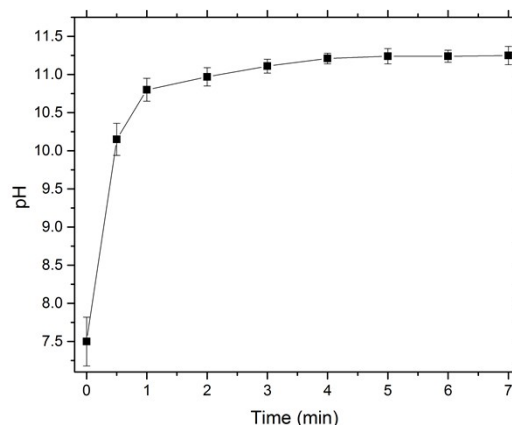


Figure S3a. pH monitoring of the base generation in TEMPO and BT mixture (molar ratio of 1:4) upon heat (50 °C) at different reaction times. Mixed with a methanol/water mixture (volume ratio of 1:9), the concentration of TEMPO is diluted to 0.1 M in this pH test. This pH measurement describes the trend of base evolution in the system but this pH value does not represent the actual pH given the presence of the organic medium.

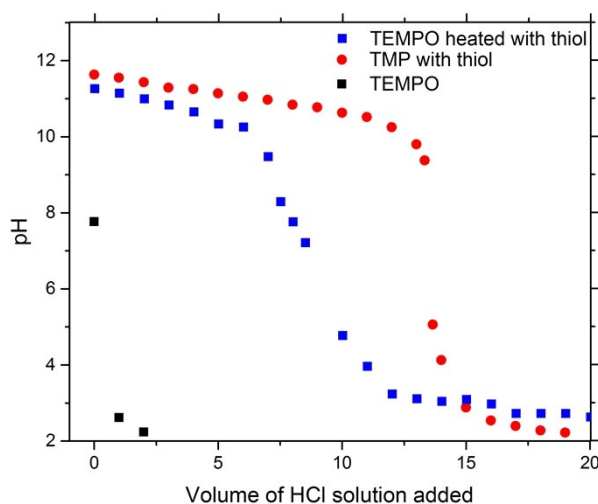


Figure S3b. Titration experiments of pure TEMPO, TMP/BT mixture (molar ratio of 1:4), and TEMPO/BT (molar ratio of 1:4) thermal reaction product solutions using 0.5 M HCl solution. All systems were diluted to 0.1 M with respect to TEMPO and TMP concentrations. The pH value measured for the solution of pure TEMPO, TMP/BT mixture (molar ratio of 1:4), and TEMPO/BT (molar ratio of 1:4) thermal reaction product is 7.77, 12.08, 11.63, respectively. The pH of the pure TEMPO in this medium was 7.7 and the titration of it consumed almost no acid solution. In contrast, the pure amine (TMP) and thiol (BT) mixture and the TEMPO/BT mixture (after being heated to 50 °C for 20 min) showed much higher pH values.

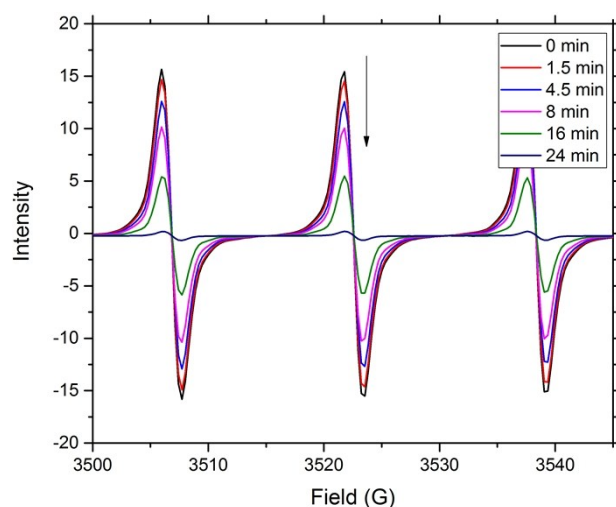


Figure S4a. EPR spectra obtained in diluted TEMPO/BT/ DEGDE mixture (1.5 mg TEMPO dissolved in 5mL BT and 15 mL DEGDE mixture) at 1.5, 4.5, 8, 16, 24 minute heated at 50 °C. The decreasing trend can be observed and the analysis of the degradation kinetics is shown in Figure S5. [TEMPO] = 0.96 mM in buytl 3-mercaptoproponiate.

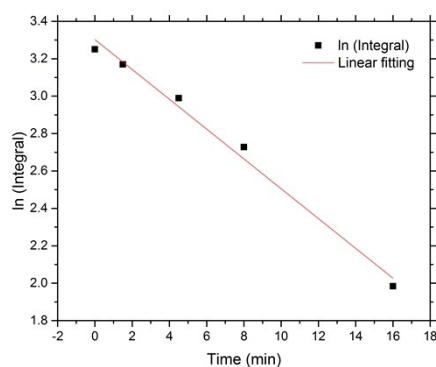


Figure S4b. EPR signal integrals plotted as a function of time during the thermal oxidation-reduction reaction. TEMPO/ BT/DEGDE mixture heated with varying at 0, 1.5, 4.5, 8, 16, 24 minute heated at 50 °C. [TEMPO] = 0.96 mM presented in buytl 3-mercaptoproponiate products and the half life time is estimated to be 530 seconds by linear fitting analysis.

Figure S5-11 describe the used data for table 1. Linear fitting was applied to simulate the TEMPO thermal degradation at its initial stage (conversion < 80%) and evaluate the half-time of TEMPO during the thermal redox reaction.

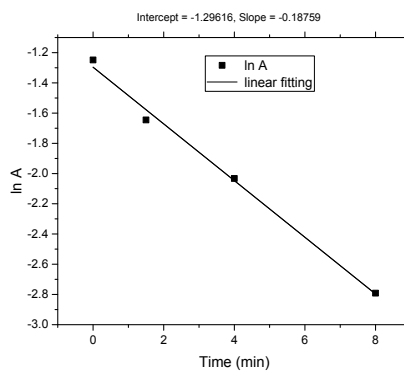
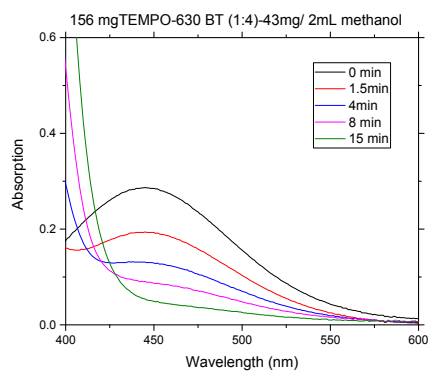


Figure S5. TEMPO/BT (molar ratio of 1:4) thermal redox reaction at 50 °C

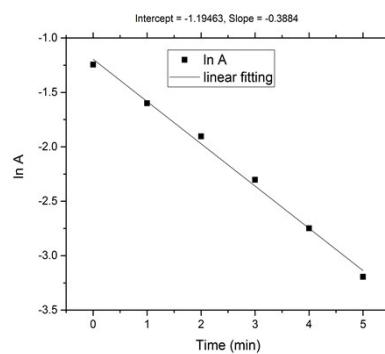
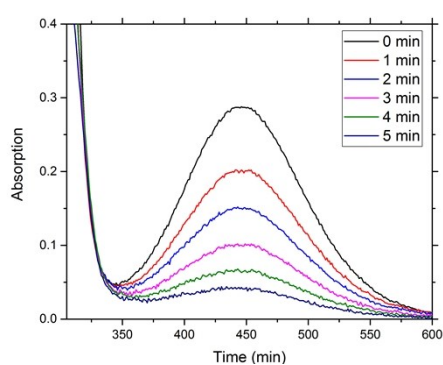


Figure S6. TEMPO/HT (molar ratio of 1:4) thermal redox reaction at 50 °C

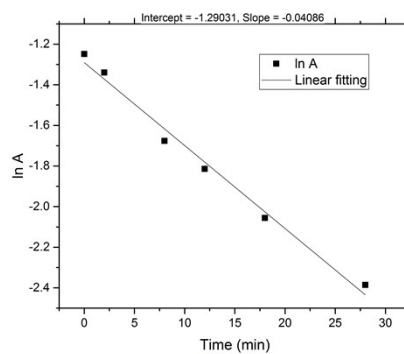
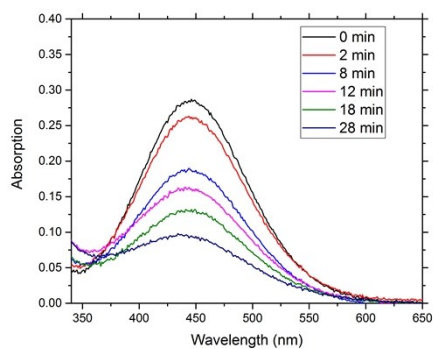


Figure S7. TEMPO/HT (molar ratio of 1:4) thermal redox reaction at 35 °C

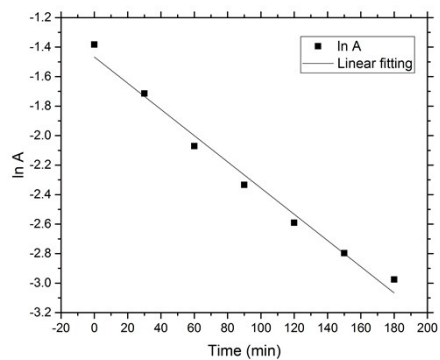
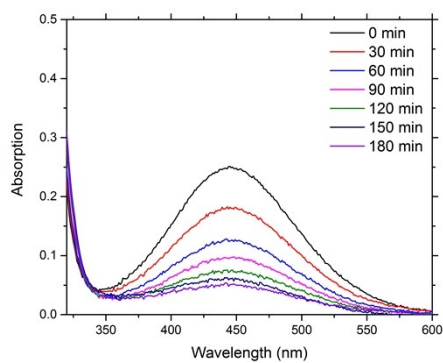


Figure S8. TEMPO/HT (molar ratio of 1:4) thermal redox reaction at 23 °C

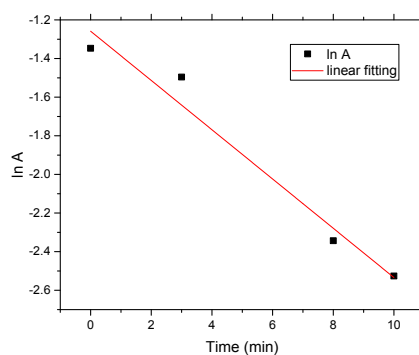
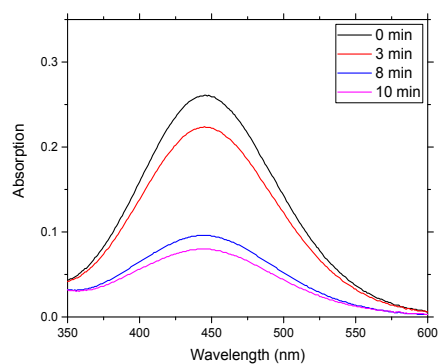


Figure S9. TEMPO/HT (molar ratio of 1:4) thermal redox reaction at 40 °C

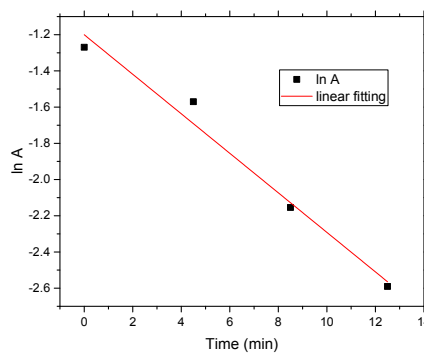
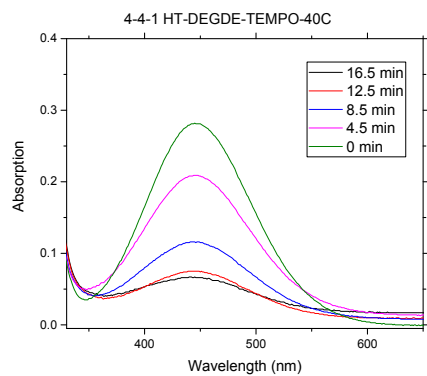


Figure S10. TEMPO/HT/DEGDE (molar ratio of 1:4:4) thermal redox reaction at 40 °C

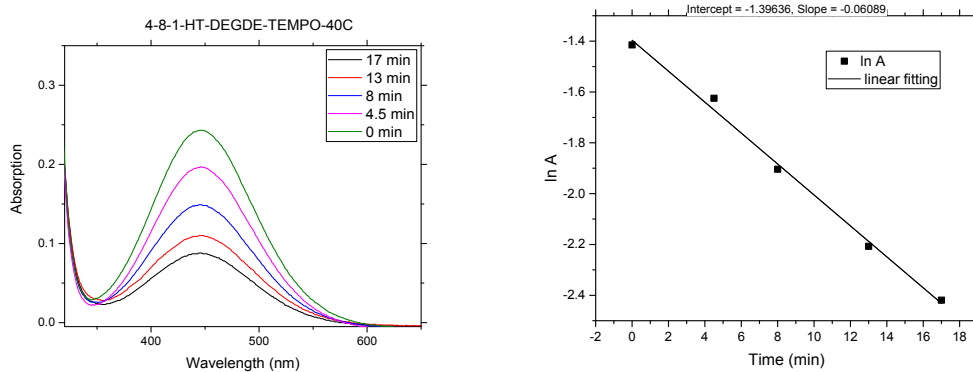


Figure S11. TEMPO/HT/DEGDE (molar ratio of 1:4:8) thermal redox reaction at 40 °C

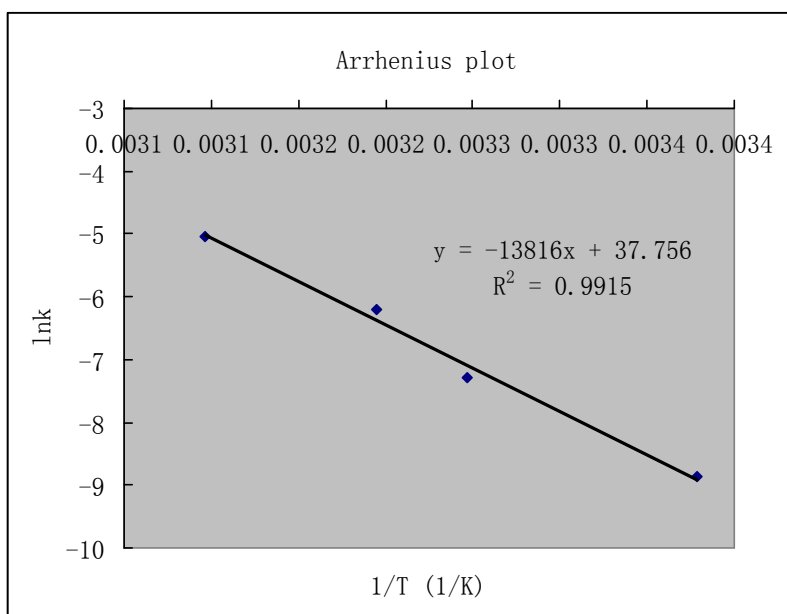


Figure S12. A plot of the natural log of the rate constant for TEMPO/HT (molar ratio of 1:4) reaction at different temperatures (23 °C, 35 °C, 40 °C and 50 °C) versus the inverse of the temperature in kelvin is a straight line with a slope equal to $-E_a/R$.

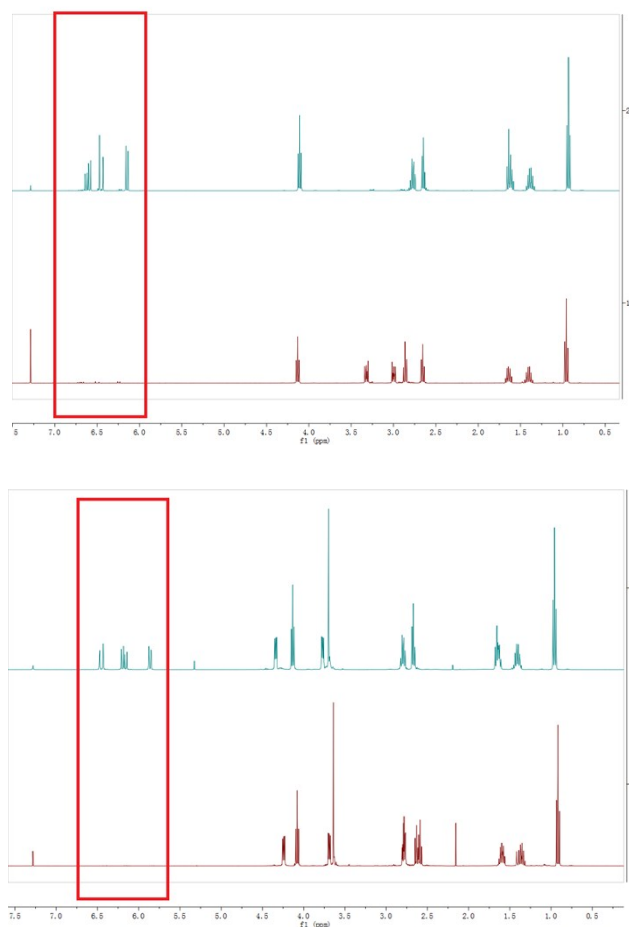


Figure S13. The model reactions of the TEMPO catalyzed thiol-Michael reactions (Table 2) monitored with $^1\text{H-NMR}$ (before and after reactions). (Top) The butyl 3-mercaptoproniate and DVS reaction catalyzed by 1 wt% TEMPO at 80 °C for 90 minutes; (Bottom) The butyl 3-mercaptoproniate and TEGDA reaction catalyzed by 2 wt% TEMPO at 80 °C for 90 minutes.

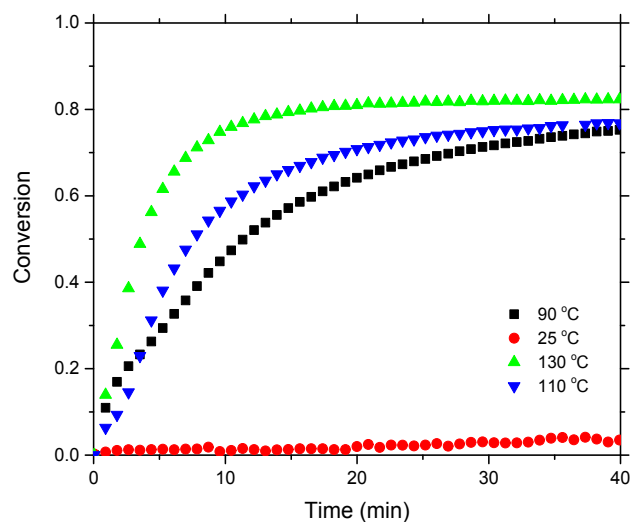


Figure S14. TEMPO catalyzed thermal thiol-Michael polymerization in

stoichiometric PETMP/TEGDA system. Thiol-acrylate based thiol-Michael polymerization exhibited much higher stability. However, the system also requires higher temperature for TEMPO induced thermal curing reaction.

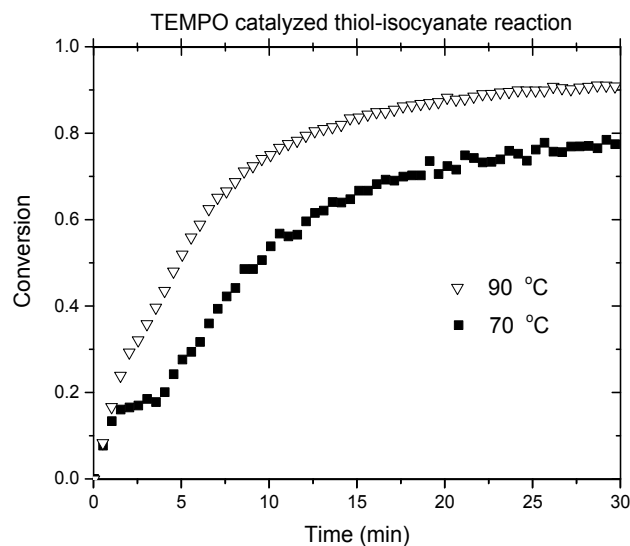


Figure S15. TEMPO catalyzed thermal thiol-isocyanate polymerization reaction at different temperatures. And in contrast, weak bases (TEA) will also cause explosive reaction during thiol-isocyanate coupling reaction.

Table S1. TEMPO thermal redox reaction measured by EPR indicating the first order degradation character. ^aTEMPO heated without thiol moieties in DMSO solution and determined with NMR. ^bTEMPO tested in EPR experiments. ^cTEMPO tested in UV-Vis experiments

Components	Molar ratio	TEMPO concentration	Temperature (°C)	k_d (s ⁻¹)
TEMPO ^a	-	0.064 M	80	-
TEMPO/BT ^b	Pure thiol solvent	0.96 mM	50	7.3×10^{-3}
TEMPO/BT/DEGDE ^b	HT/ DEGDA= 1:4	0.48 mM	50	1.3×10^{-3}
TEMPO/HT ^c	1:4	7.04 M	50	6.5×10^{-3}