Supplementary Information

SET-LRP from Programmed Difunctional Initiators Encoded with Double Single-Cleavage and Double Dual-Cleavage Groups

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1. Structural Characterization of Initiators 1-3

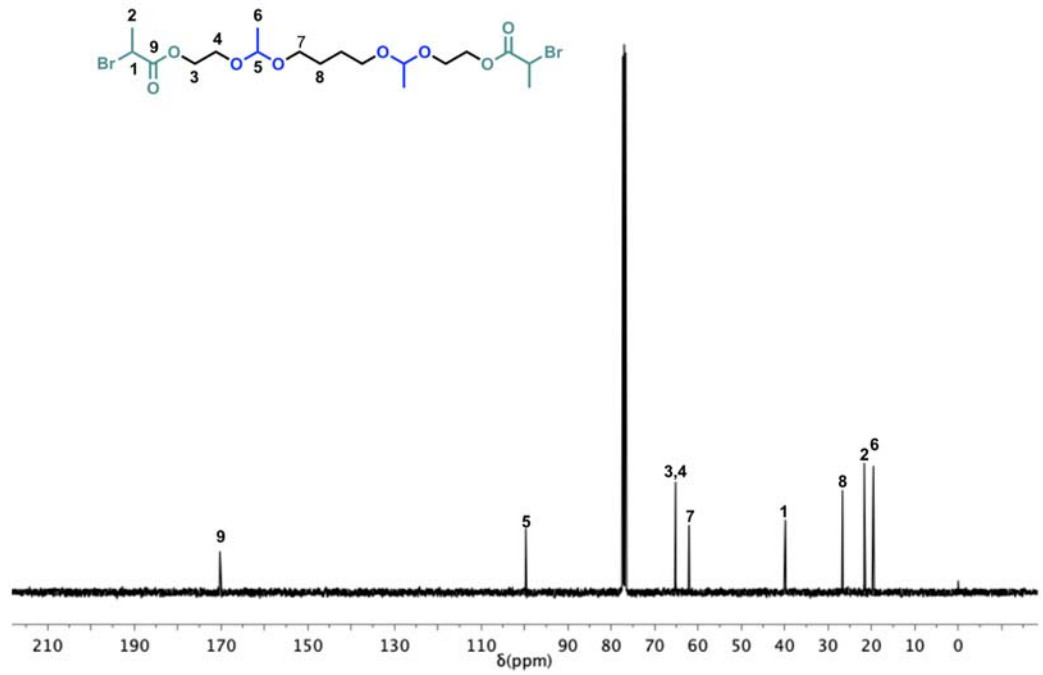

Figure S1. ^{13}C-NMR spectrum of **1** in $CDCl_3$.

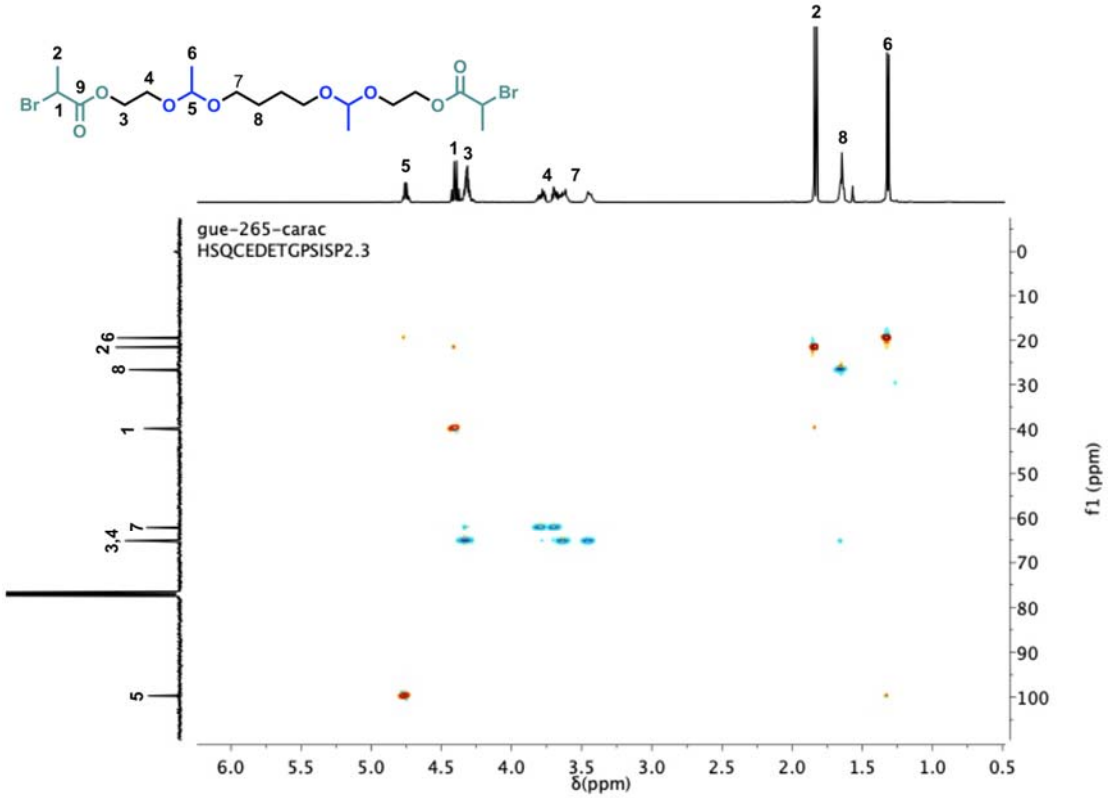

Figure S2. HSQCAD spectrum of **1** in $CDCl_3$.

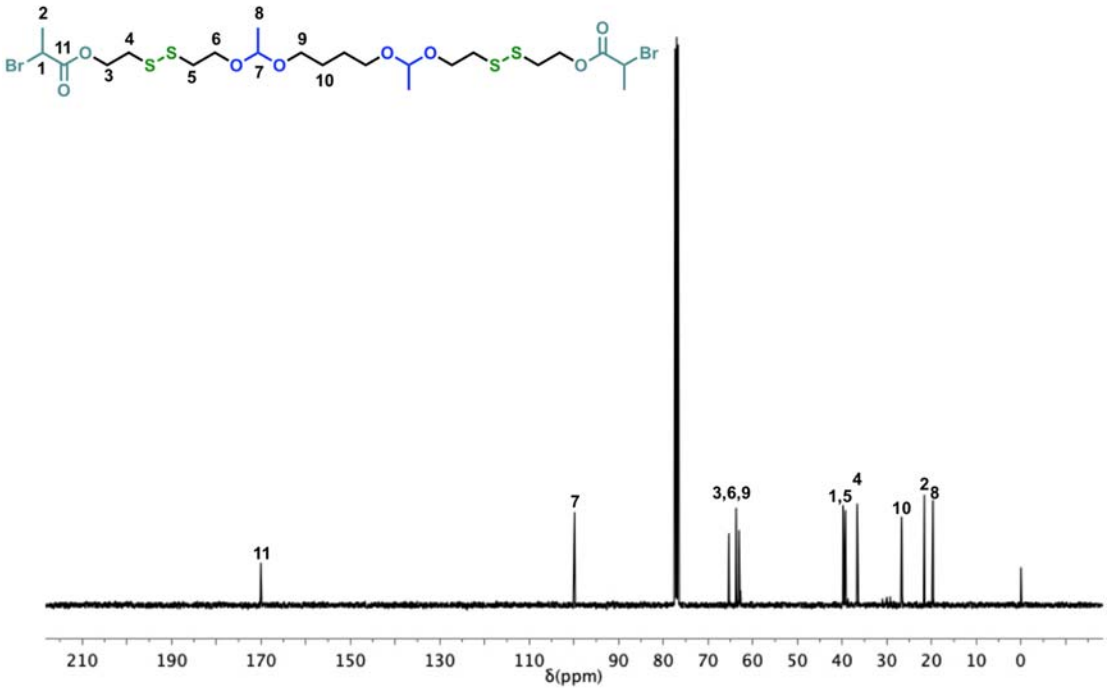

Figure S3. ^{13}C-NMR spectrum of **2** in $CDCl_3$.

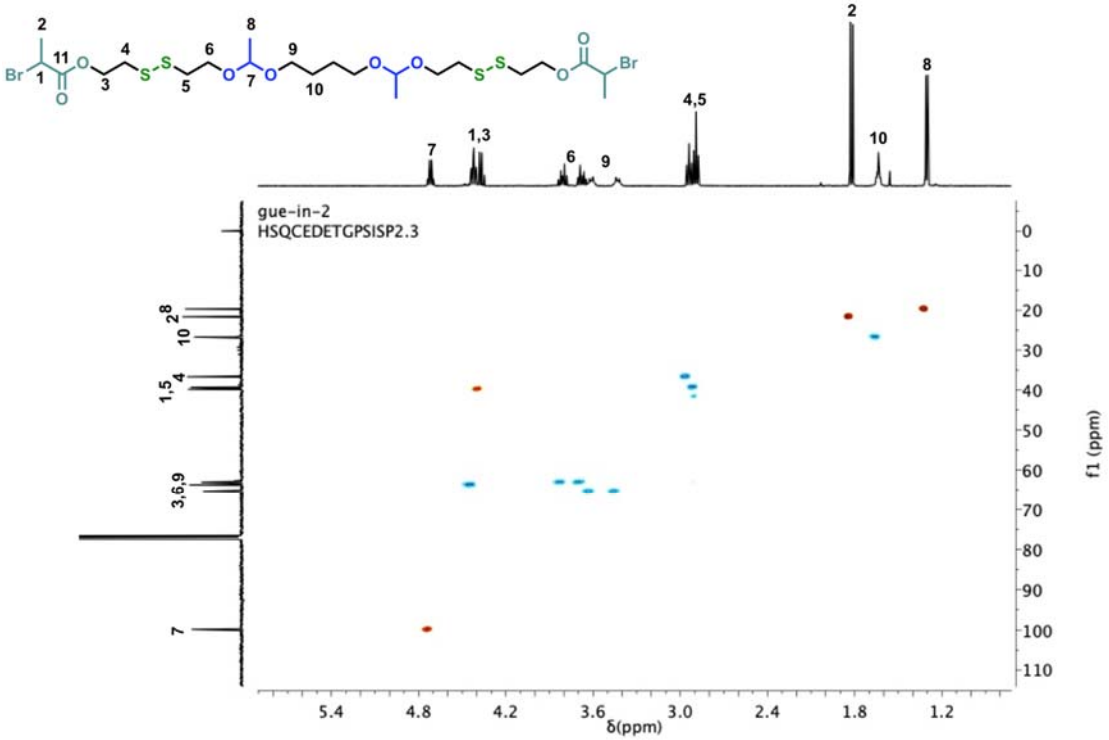

Figure S4. HSQCAD spectrum of **2** in $CDCl_3$.

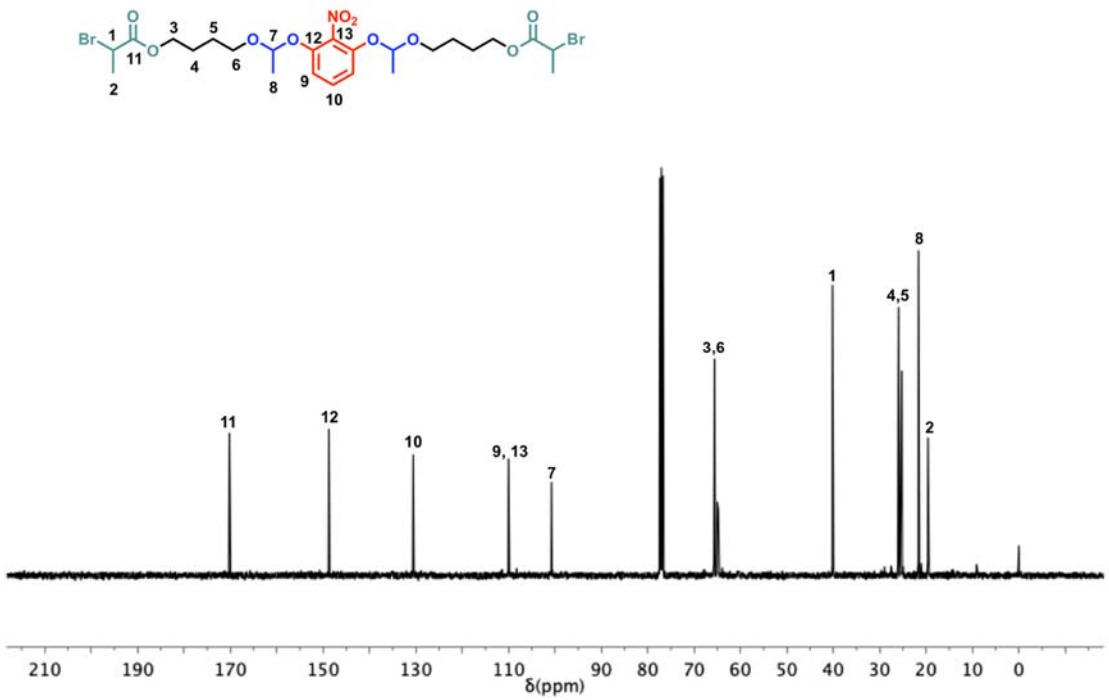

Figure S5. ^{13}C-NMR spectrum of **3** in $CDCl_3$

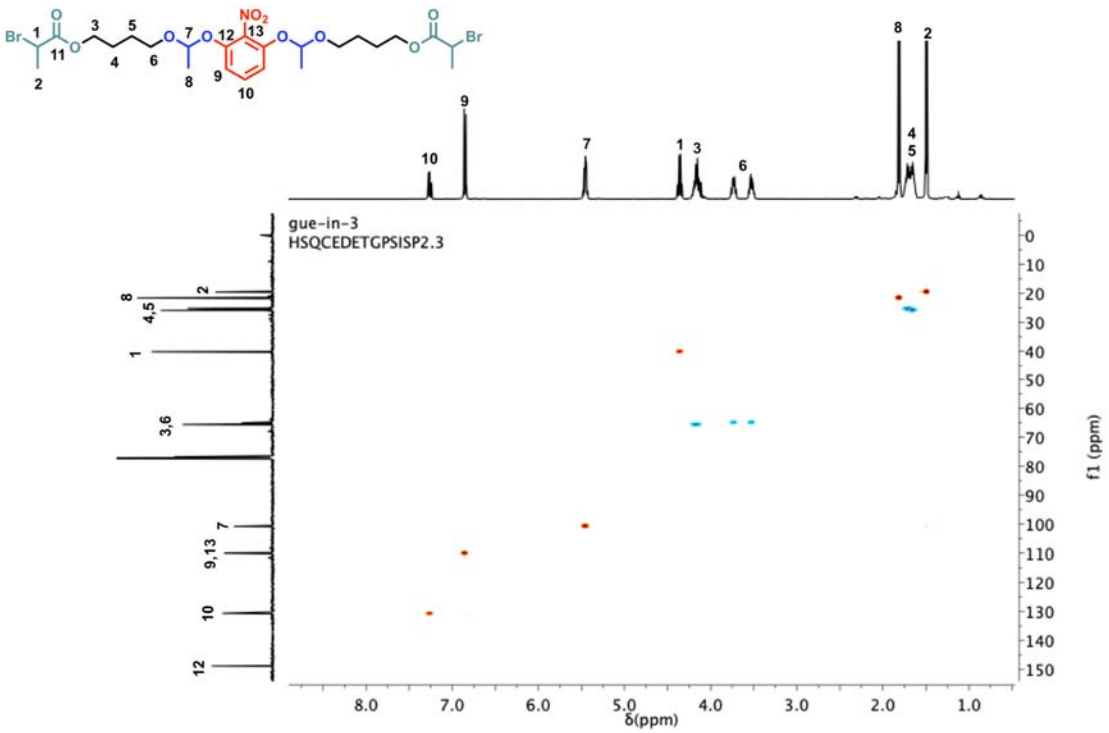

Figure S6. HSQCAD spectrum of **3** in $CDCl_3$.

2. SET-LRP of MA initiated with 1-3

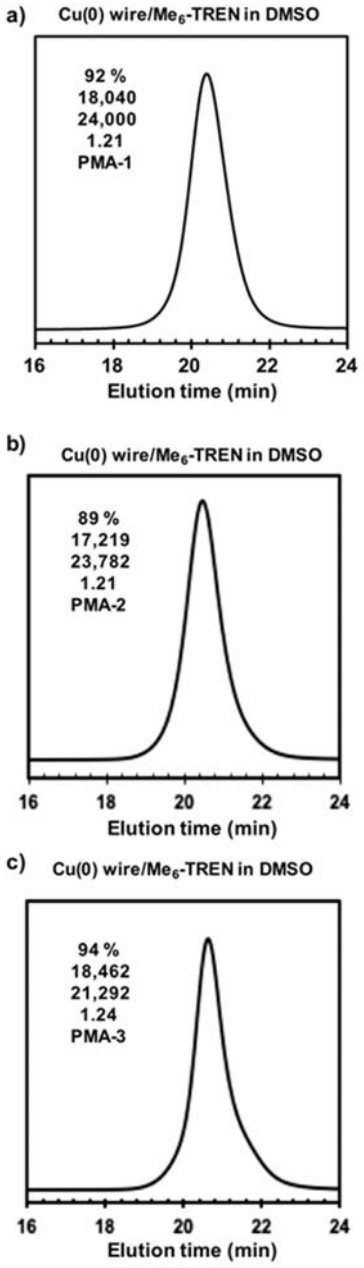

Figure S7. GPC traces of PMAs obtained by SET-LRP of MA initiated with (a) **1**, (b) **2** and (c) **3** in DMSO. Reaction conditions: MA = 1 mL, DMSO = 0.5 mL, $[MA]_0/[\mathbf{1}, \mathbf{2} \text{ or } \mathbf{3}]_0/[Me_6\text{-TREN}]_0$ = 222/1/0.1 using 12.5 cm of hydrazine-activated Cu(0) wire (20-gauge diameter). Numbers shown in each panel correspond to monomer conversion, M(th), M_n(GPC), and M_w/M_n, respectively, from the top to bottom.

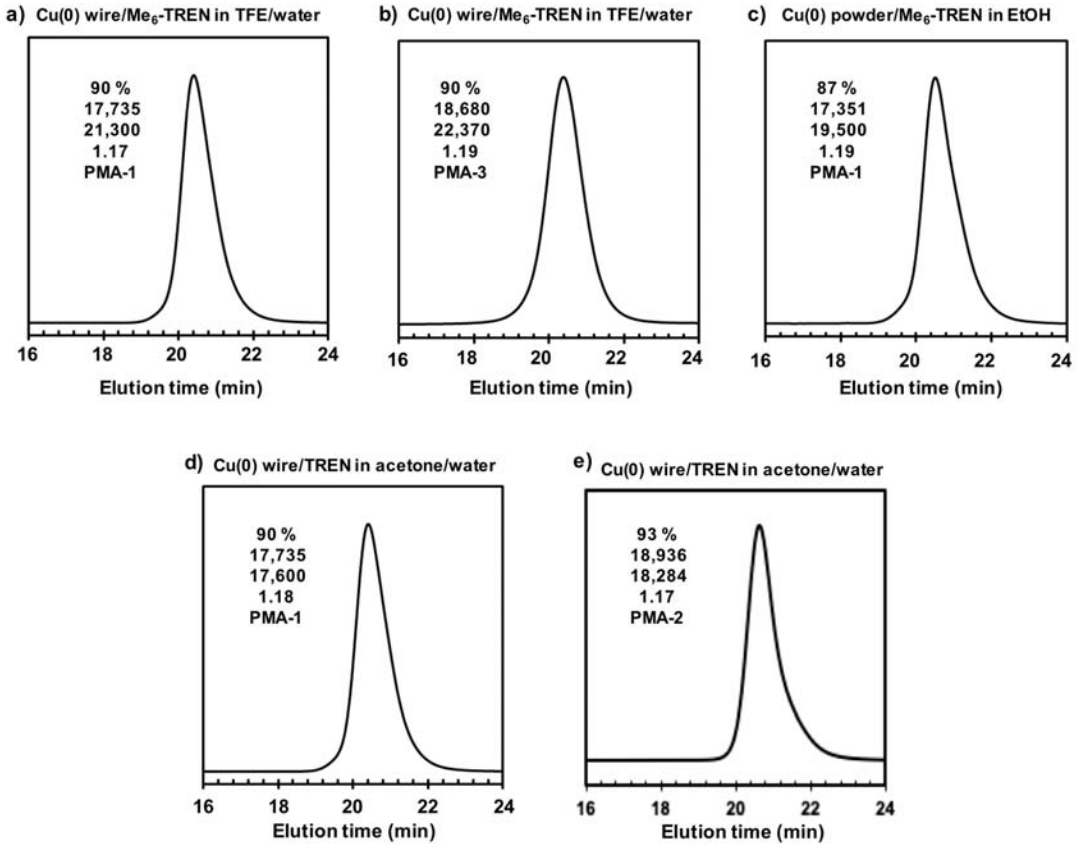

Figure S8. GPC traces of PMAs obtained by SET-LRP initiated with **1** (a, c, d), **2** (e), and **3** (b) catalyzed by hydrazine-activated Cu(0) wire or Cu(0) powder at 25 ºC. Reaction conditions: MA = 1 mL, solvent = 0.5 mL and $[MA]_0/[\mathbf{1}$ or $\mathbf{3}]_0/[Me_6\text{-TREN}]_0$ = 222/1/0.2 (a, b), $[MA]_0/[Cu(0)]_0/[\mathbf{1}]_0/[Me_6\text{-TREN}]_0$ = 222/1/0.1/0.2 (c) and $[MA]_0/[\mathbf{1}$ or $\mathbf{2}]_0/[Me_6\text{-TREN}]_0/[Cu(II)Br_2]_0$= 222/1/0.4/0.2 (d,e). Solvent: TFE/water (9/1, v/v) in (a, b), EtOH in (c), and acetone/water (8/2, v/v) in (d, e).

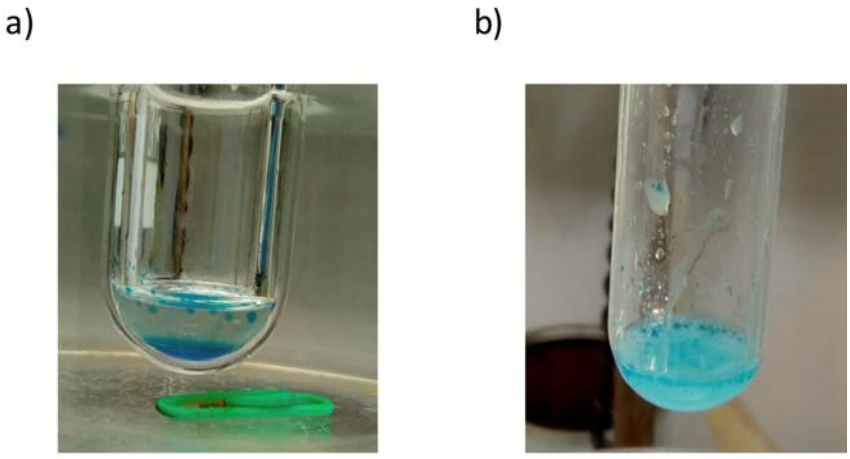

Figure S9. Visualization of the biphasic reaction mixture taking place during the SET-LRP of MA initiated with **1** in acetone/water mixtures (8/2, v/v) using hydrazine activated Cu(0) wire/TREN/ Cu(II)Br_2 as catalytic system: (a) Initial mixture before deoxygenation procedure and (b) polymerization mixture after 30 min reaction (90% conversion). SET-LRP "programmed" biphasic systems are based on aqueous mixtures of both disproportionating and non-disproportionating organic solvents. This concept relies on the unexpected immiscibility of water containing Cu(II)Br_2 and ligand with most of organic solvents including water-miscible solvents (e.g. alcohols, acetone, acetonitrile). Under these conditions, activation, disproportionation and deactivation events occurs in different compartments. Activation step takes place in the organic phase generating the Cu(I)X species which due to the low solubility migrates to the aqueous phase, containing ligand and Cu(II)Br_2 leading at the same time the disproportionation step and the subsequent generation of Cu(0) and Cu(II)Br_2. In this scenario, deactivation of growing radicals into dormant species is basically an interfacial process occurring at the interface between organic and aqueous phase. Partition of reagents in two phases are advantageous since they minimize side reaction presents in homogeneous systems due to the accumulation of Cu(II)Br_2. Even more remarkable is that this concept allowed the use of poor or non-disproportionating solvents in Cu(0)-mediated SET-LRP due to the key disproportionation step take place in the water phase.

3. Mid-Chain Cleavage of PMA-1, PMA-2, PMA-3 and Mixtures

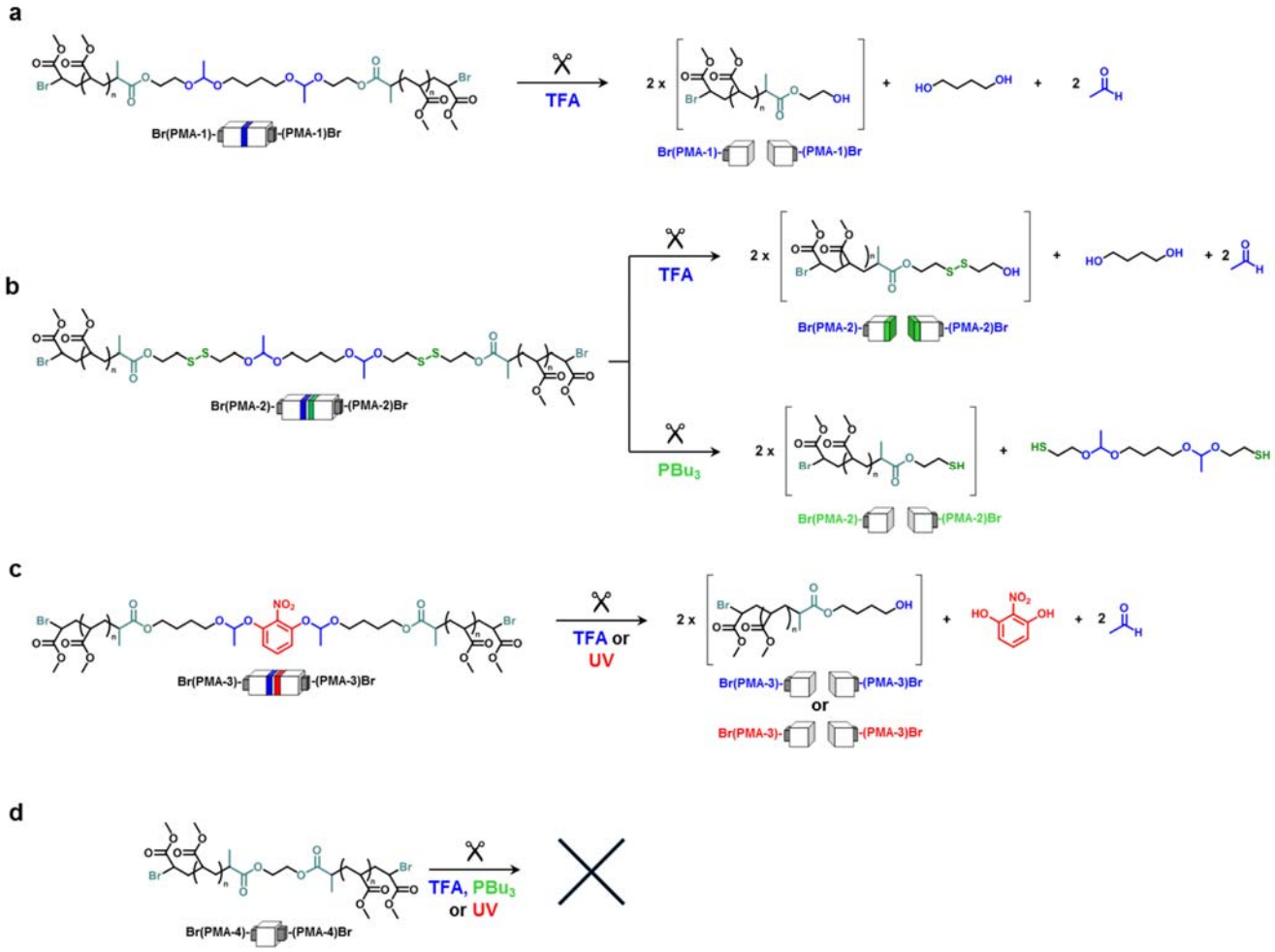

Figure S10. Schematic illustration of the mid-chain cleavage of PMA-**1**, PMA-**2** and PMA-**3** under various mild reaction conditions. BPE is stable to acidic, reductive and UV-light treatments.

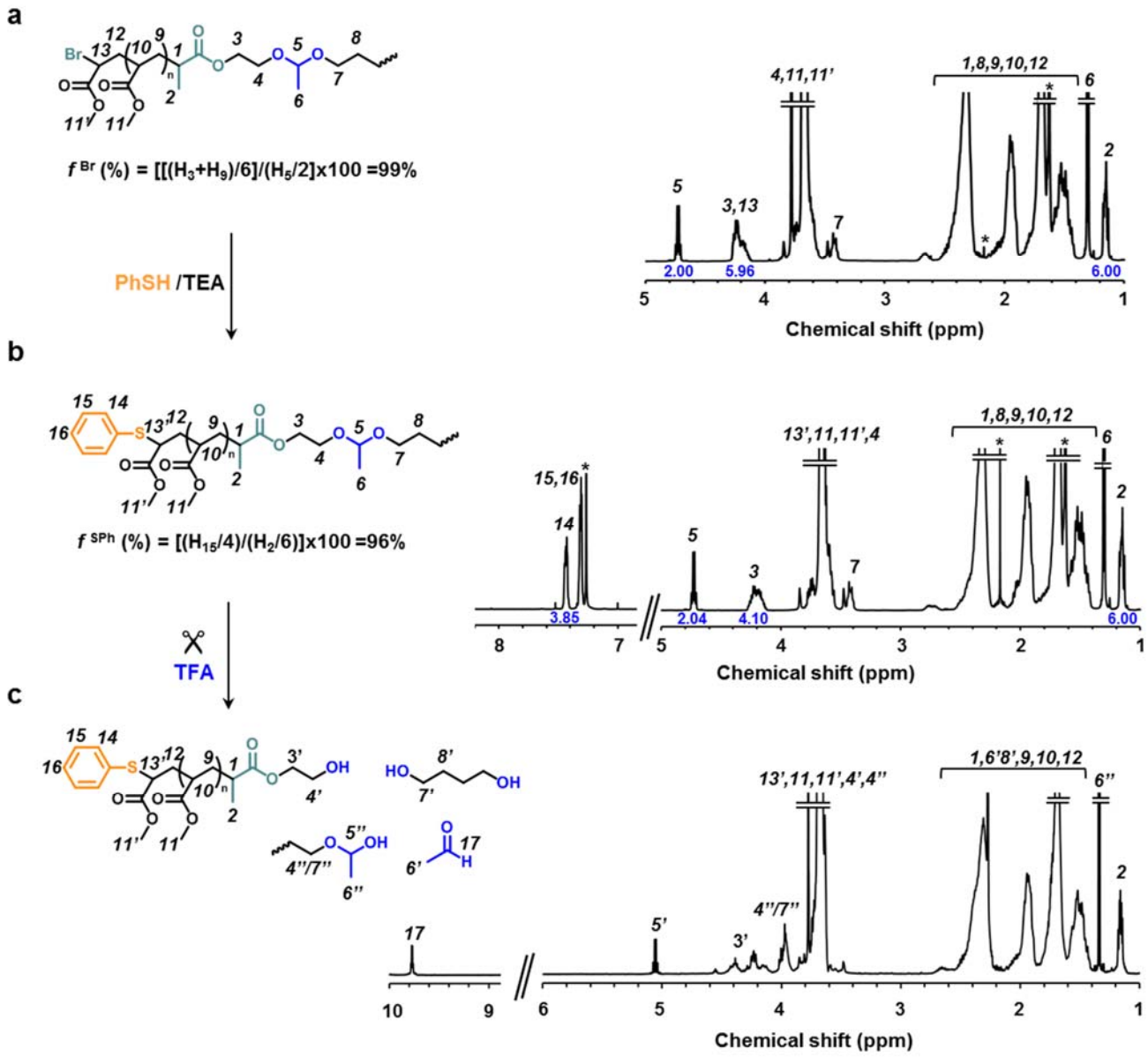

Figure S11. ^{1}H NMR spectra of PMA-**1** (a) isolated at 97% monomer conversion ([MA]$_0$/[**1**]$_0$/[Me$_6$-TREN]$_0$ = 50/1/0.2 in DMSO), (b) after thio-bromo "click" reaction at chain ends using thiophenol, and (c) after acid-catalyzed hydrolysis of the thioetherified polymer using TFA in THF. ^{1}H NMR resonances from residual solvents are indicated with "*".

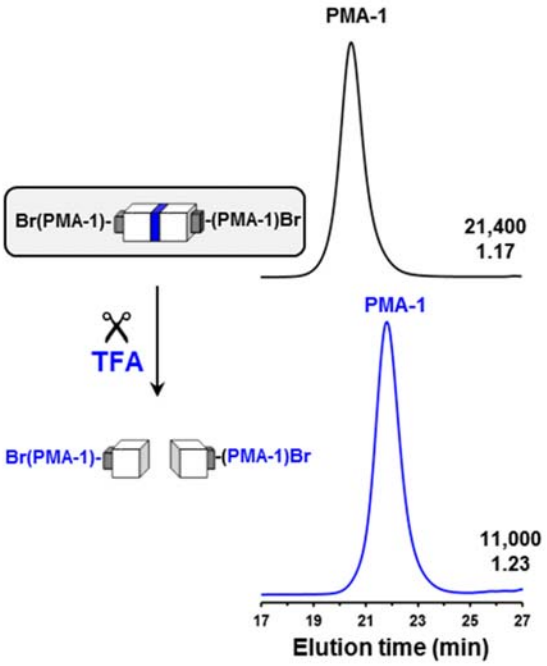

Figure S12. GPC traces for PMA-**1** (M_n = 23,640 g mol^{-1}, M_w/M_n = 1.24) before (black) and after (blue) acid treatment to promote mid-chain cleavage. Numbers shown in each panel correspond to M_n (GPC) and M_w/M_n, respectively, from the top to bottom. Bond cleavage information: TFA treatment produces the selective acid hydrolysis of acetal linkages. The expected degradation products are shown in Figure S10a.

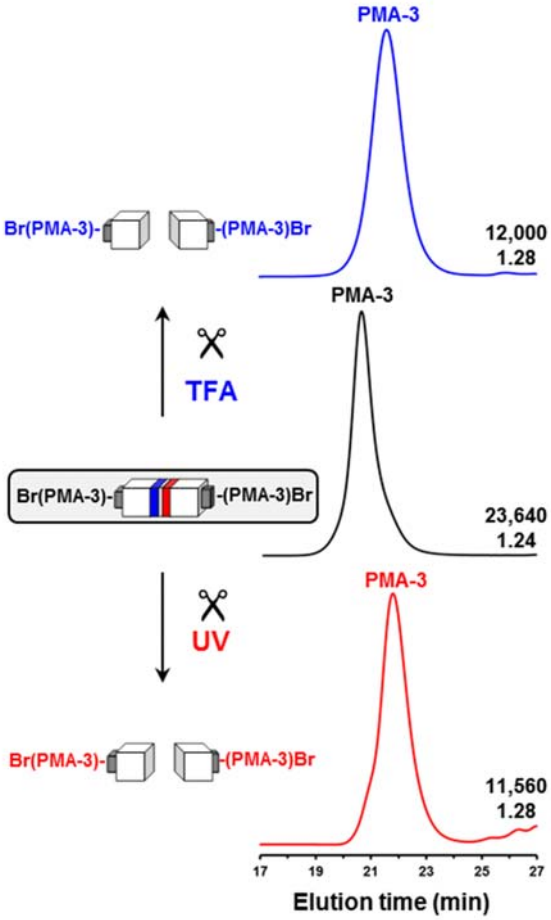

Figure S13. GPC traces for PMA-**3** (M_n = 23,640 g mol^{-1}, M_w/M_n = 1.24) before (black) and after acid (blue) or reductive (red) treatments to promote mid-chain cleavage. Numbers shown in each panel correspond to M_n (GPC) and M_w/M_n, respectively, from the top to bottom. Bond cleavage information: both TFA and UV light treatments cleave 2-nitroresorcinol-derived acetal junctions. The expected degradation products are shown in Figure S10c.

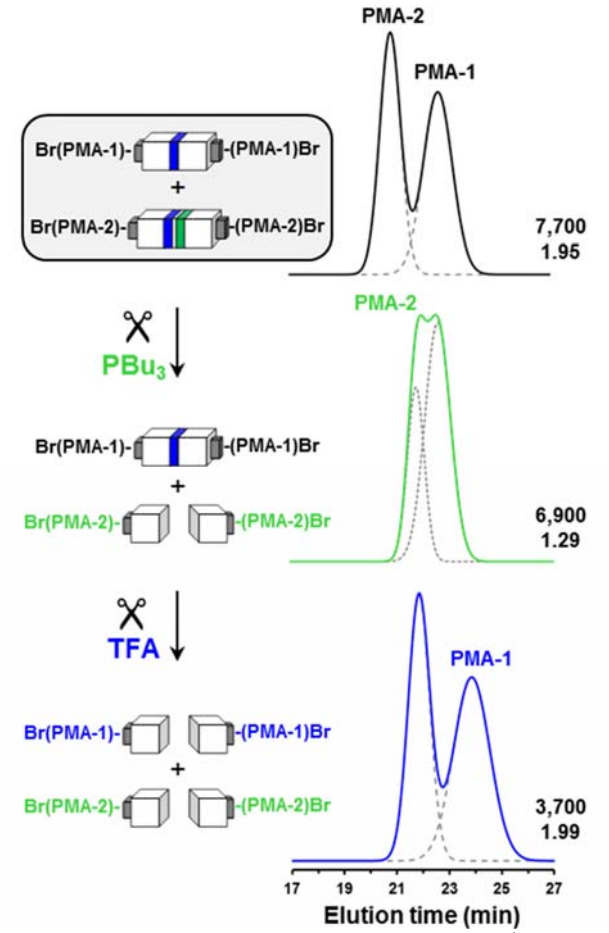

Figure S14. GPC traces for a mixture of PMA-**1** (M_n = 5,300 g mol^{-1}, M_w/M_n = 1.18) and PMA-**2** (M_n = 23,300 g mol^{-1}, M_w/M_n = 1.21) before (black) and after sequential reductive (green) and acid (blue) treatments to promote independent mid-chain cleavage. Numbers shown in each panel correspond to multi-peak M_n (GPC) and M_w/M_n, respectively, from the top to bottom. The individual component from the fits to a multi-peaks Gaussian distribution are also shown by grey dashed lines. Bond cleavage information: PBu_3 and TFA treatments produce the selective cleavage of disulfide and acetal linkages, respectively. The expected degradation products are shown in Figure S10a,b.

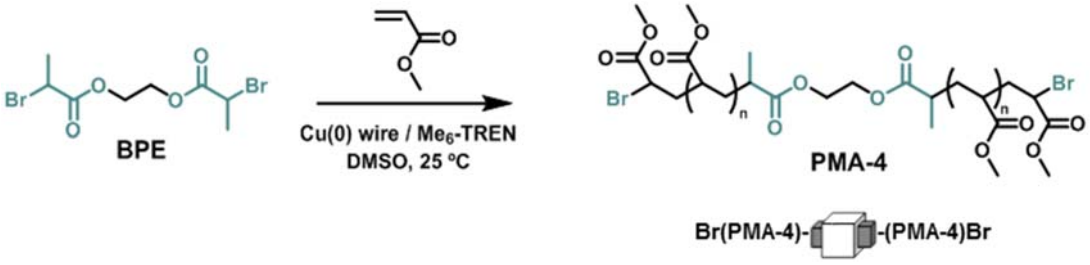

Figure S15. SET-LRP of MA initiated with conventional BPE difunctional initiator. Reaction conditions: MA = 1 mL, DMSO = 0.5 mL, $[MA]_0/[BPE]_0/[Me_6\text{-TREN}]_0$ = 600/1/0.2 using 12.5 cm of hydrazine-activated Cu(0) wire (20-gauge diameter).

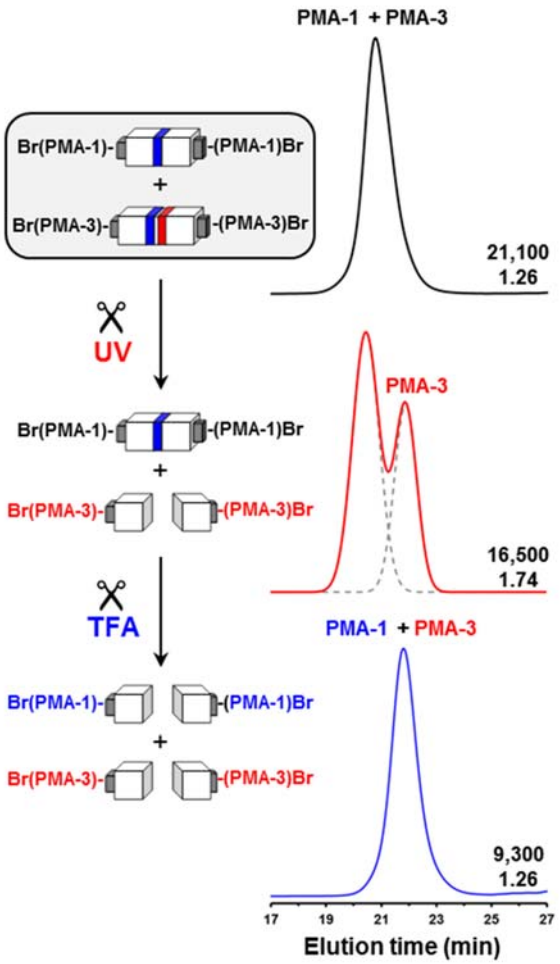

Figure S16. GPC traces for a mixture of PMA-**1** (M_n = 21,400 g mol^{-1}, M_w/M_n = 1.17) and PMA-**3** (M_n = 23,640 g mol^{-1}, M_w/M_n = 1.24) before (black) and after sequential UV (red) and acid (blue) treatments to promote independent mid-chain cleavage. Numbers shown in each panel correspond to multi-peak M_n (GPC) and M_w/M_n, respectively, from the top to bottom. The individual component from the fits to a multi-peaks Gaussian distribution are also shown by grey dashed lines. Bond cleavage information: both TFA and UV light treatments cleave 2-nitroresorcinol-derived acetal junctions. The expected degradation products are shown in Figure S10a,c.