

## Supporting Information

### Development of Thermal and Photochemical Strategies for Thiol-ene Click Polymer Functionalization

Luis M. Campos,<sup>1</sup> Kato L. Killops,<sup>1</sup> Ryosuke Sakai,<sup>1</sup> Jos M.J. Paulusse,<sup>1</sup> Denis Damiron,<sup>1,2</sup> Eric Drockenmuller,<sup>2</sup> Benjamin W. Messmore,<sup>1</sup>  
Craig J. Hawker\*<sup>1</sup>

*(1) Department of Chemistry & Biochemistry, Department of Materials, and Materials Research Laboratory, University of California, Santa Barbara, CA 93106, USA.*

*(2) Laboratoire des Matériaux Polymères et Biomatériaux (LMPB/IMP-UMR CNRS 5223), Université Claude Bernard Lyon 1, 15 Boulevard Latarjet, 69622 Villeurbanne Cedex, France*

#### Experimental Procedures

##### General Procedures for Thiol-ene Photoreactions.

**Ene-Functional Polymer + Thiol.** In a glass vial (diameter ca. 1 cm), the polymer, 5-10 eq. of thiol (with respect to the alkene), and 0.5 eq. of DMPA were dissolved in the minimal amount of the solvent required to solubilize all components. The solvents for each system are specified in Tables 1 and 2. The vial was sealed with a rubber septum, and the mixture was purged with argon for 5-10 min. Irradiation with a 365 nm UV lamp was carried out at specified time intervals (see Tables 1 and 2) while stirring.

##### General Procedures for Thiol-ene Thermal Reactions.

**Ene-Functional Polymer + Thiol.** In an ampoule, the polymer, 5-10 eq. of thiol (with respect to the alkene), and 0.5 eq. of AIBN were dissolved in the minimal amount of solvent required to solubilize all components. The mixture was degassed via three freeze-pump-thaw cycles, and subsequently flame-sealed. The ampoule was heated at 80 °C at specified time intervals (see Tables 1 and 2) while stirring.

**P(1-co-S) + Thioglycolic Acid (7) Adduct.** Specifics (photochemical): 50 mg of **P(1-co-S)** (0.044 mmol of ene), 20 mg of **7** (0.22 mmol), and 2.5 mg of DMPA (0.0098 mmol) were dissolved in 0.45 g of benzene. The product was precipitated into methanol to yield a white powder. Specifics (thermal): 50 mg of **P(1-co-S)** (0.044 mmol of ene), 18 mg of **7** (0.20 mmol), and 3.7 mg of AIBN (0.023 mmol) were dissolved in 0.45 g of benzene. The product was precipitated into methanol to yield a white powder.  $\delta_{\text{H}}$  ppm (500 MHz,  $\text{CD}_2\text{Cl}_2$ ): 7.30-6.35 (b,  $n \times 5\text{H}$ , aromatic of PSt), 4.45 (b, 2H, Ph- $\text{CH}_2$ -OR), 3.51 (b, 2H, -O- $\text{CH}_2$ -R), 3.29 (b, 2H, S- $\text{CH}_2$ -COOH) 2.73 (b, 2H, - $\text{CH}_2$ -S $\text{CH}_2$ COOH), 2.40-1.30 (b,  $n \times 3\text{H}$ , main chain; 4H, -O $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ -S-).

**P(1-co-S) + (3-mercaptopropyl)-trimethoxysilane (8) Adduct.** Specifics (photochemical): 52 mg of **P(1-co-S)** (0.049 mmol of ene), 52 mg of **8** (0.27 mmol), and 6 mg of DMPA (0.025 mmol) were dissolved in 0.60 g of chlorobenzene. The product was precipitated into methanol to yield a white powder. Specifics (thermal): 50 mg of **P(1-co-S)** (0.055 mmol of ene), 57 mg of **8** (0.29 mmol), and 4.8 mg of AIBN (0.029 mmol) were dissolved in 0.60 g of chlorobenzene. The product was precipitated into methanol to yield a white powder.  $\delta_{\text{H}}$  ppm (200 MHz,  $\text{CD}_2\text{Cl}_2$ ): 7.30-6.35 (b,  $n \times 5\text{H}$ , aromatic of PSt), 4.45 (b, 2H, Ph- $\text{CH}_2$ -OR), 3.62 (s, 9H, -Si(OCH<sub>3</sub>)<sub>3</sub>), 3.53 (b, 2H, -O- $\text{CH}_2$ -R), 2.62 (t, 4H, - $\text{CH}_2$ -S- $\text{CH}_2$ -), 2.30-1.30 (b,  $n \times 3\text{H}$ , main chain; 6H, -OCH<sub>2</sub>- $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ -S- $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ -), 0.81 (t, 2H, - $\text{CH}_2$ -Si(OCH<sub>3</sub>)<sub>3</sub>).

**P(1-co-S) + 1-Adamantanethiol (9) Adduct.** Specifics (photochemical): 50 mg of **P(1-co-S)** (0.055 mmol of ene), 65 mg of **9** (0.39 mmol), and 7 mg of DMPA (0.027 mmol) were dissolved in 0.40 g of chlorobenzene. The product was precipitated into hexanes to yield a white powder. Specifics (thermal): 50 mg of **P(1-co-S)** (0.053 mmol of ene), 45 of mg **9** (0.27 mmol), and 4.5 mg of AIBN (0.027 mmol) were dissolved in 0.40 g of chlorobenzene. The product was precipitated into hexanes to yield a white powder.  $\delta_{\text{H}}$  ppm (500 MHz,  $\text{CD}_2\text{Cl}_2$ ): 7.30-6.35 (b,  $n \times 5\text{H}$ , aromatic of PSt), 4.45 (b, 2H, Ph- $\text{CH}_2$ -OR), 3.53 (b, 2H, -O- $\text{CH}_2$ -R), 2.59 (b, 2H, - $\text{CH}_2$ -S-R), 2.30-0.85 (b,  $n \times 3\text{H}$ , main chain; 4H, -OCH<sub>2</sub>- $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ -S-; 15H, adamantane).

**P(1-co-S) + Fmoc-Cysteine (10) Adduct.** Specifics (photochemical): 50 mg of **P(1-co-S)** (0.055 mmol of ene), 93 mg of **10** (0.27 mmol), and 7.5 mg of DMPA (0.029 mmol) were dissolved in 0.20 g of DMF and 0.20 g of chlorobenzene. The product was precipitated into methanol to yield a white powder. Specifics (thermal): 50 mg of **P(1-co-S)** (0.053 mmol of ene), 91 of mg **10** (0.26 mmol), and 4.3 mg of AIBN (0.027 mmol) were dissolved in 0.20 g of DMF and 0.20 g of chlorobenzene. The product was precipitated into methanol to yield a white powder.  $\delta_{\text{H}}$  ppm (200 MHz,  $\text{CD}_2\text{Cl}_2$ ): 7.80 (b, 2H, fluorene Ph), 7.63 (b, 2H, fluorene Ph), 7.42 (b, 2H, fluorene Ph), 7.35 (b, 2H, fluorene Ph), 7.30-6.35 (b,  $n \times 5\text{H}$ , aromatic of PSt), 5.85 (b, 1H, -S- $\text{CH}_2$ -CH(COOH)-NH-), 4.65 (b, 1H, -OCH<sub>2</sub>-CH-fluorene), 4.45 (b, 2H, Ph- $\text{CH}_2$ -OR), 4.25 (b, 2H, OCH<sub>2</sub>-fluorene), 3.48 (b, 2H, -O- $\text{CH}_2$ -R), 3.07 (b, 2H, -S- $\text{CH}_2$ -CH(COOH)-), 2.60 (b, 2H, - $\text{CH}_2$ -S- $\text{CH}_2$ -), 2.30-1.30 (b,  $n \times 3\text{H}$ , main chain; 4H, -OCH<sub>2</sub>- $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ -S-).

**P(1-co-S) + Thioglycerol (11) Adduct.** Specifics (photochemical): 50 mg of **P(1-co-S)** (0.053 mmol of ene), 30 mg of **11** (0.28 mmol), 7 mg of DMPA (0.027 mmol) were dissolved in 0.45 g of DMF. The product was precipitated into methanol to yield a white powder. Specifics (thermal): 50 mg of **P(1-co-S)** (0.055 mmol of ene), 30 mg of **11** (0.28 mmol), 4.5 mg of AIBN (0.027 mmol) were dissolved in 0.45 g of DMF. The product was precipitated into methanol to yield a white powder.  $\delta_{\text{H}}$  ppm (200 MHz,  $d_6$ -DMSO): 7.30-6.35 (b,  $n \times 5\text{H}$ , aromatic of PSt), 4.73 (b, 1H, -OH), 4.55 (b, 1H, -OH), 4.45 (b, 2H, Ph- $\text{CH}_2$ -OR), 3.58 (b, 1H, -S- $\text{CH}_2$ -CH(OH)- $\text{CH}_2$ OH), 3.38 (b, 2H, -O- $\text{CH}_2$ -R; 2H, -S- $\text{CH}_2$ -CH(OH)- $\text{CH}_2$ OH), 2.73 (b, 2H, - $\text{CH}_2$ -S $\text{CH}_2$ -), 2.60 (b, 2H, - $\text{CH}_2$ -S- $\text{CH}_2$ -), 2.30-1.10 (b,  $n \times 3\text{H}$ , main chain; 4H, -O $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ -S-).

**P(3-co-MMA) + Thioglycolic Acid (7) Adduct.** Specifics (photochemical): 50 mg of **P(3-co-MMA)** (0.048 mmol of ene), 23 mg of **7** (0.25 mmol), 5 mg of DMPA (0.020 mmol) were dissolved in 0.30 g of chlorobenzene. The product was precipitated into methanol to yield a white powder. Specifics (thermal): 50 mg of **P(3-co-MMA)** (0.048 mmol of ene), 22 mg of **7** (0.24 mmol), 4 mg of AIBN (0.024 mmol) were dissolved in 0.30 g of chlorobenzene. The product was precipitated into methanol to yield a white powder.  $\delta_{\text{H}}$  ppm (200 MHz,  $\text{CDCl}_3$ ): 4.03 (b, 2H, -O- $\text{CH}_2$ -), 3.62 (s,  $n \times 3\text{H}$ , -O $\text{CH}_3$ ), 3.36 (b, 2H, - $\text{CH}_2$ -S- $\text{CH}_2$ -), 2.68 (b, 2H, - $\text{CH}_2$ -S- $\text{CH}_2$ -), 2.15-0.75 (b,  $n \times 5\text{H}$ , main chain; 4H, -O $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ -S-).

**P(3-co-MMA) + (3-mercaptopropyl)-trimethoxysilane (8) Adduct.** Specifics (photochemical): 52 mg of **P(3-co-MMA)** (0.049 mmol of ene), 52 mg of **8** (0.27 mmol), 6 mg of DMPA (0.023 mmol) were dissolved in 0.50 g of chlorobenzene. The product was precipitated into methanol to yield a white powder. Specifics (thermal): 36 mg of **P(3-co-MMA)** (0.057 mmol of ene), 56 mg of **8** (0.29 mmol), 5 mg of AIBN (0.03 mmol) were dissolved in 0.50 g of chlorobenzene. The product was precipitated into methanol to yield a white powder.  $\delta_{\text{H}}$  ppm (200 MHz,  $\text{CDCl}_3$ ): 4.00 (b, 2H, -O- $\text{CH}_2$ -), 3.65 (s,  $n \times 3\text{H}$ , -O $\text{CH}_3$ ), 3.52 (s, 9H, -Si(O $\text{CH}_3$ ) $_3$ ), 2.59 (b, 4H, - $\text{CH}_2$ -S- $\text{CH}_2$ -), 2.10-0.75 (b,  $n \times 5\text{H}$ , main chain; 4H, -O $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ -S-).

**P(3-co-MMA) + 1-Adamantanethiol (9) Adduct.** Specifics (photochemical): 50 mg of **P(3-co-MMA)** (0.048 mmol of ene), 53 mg of **9** (0.31 mmol), 6 mg of DMPA (0.023 mmol) were dissolved in 0.40 g of chlorobenzene. The product was precipitated into hexanes to yield a white powder. Specifics (thermal): 50 mg of **P(3-co-MMA)** (0.048 mmol of ene), 40 mg of **9** (0.24 mmol), 4 mg of AIBN (0.024 mmol) were dissolved in 0.40 g of chlorobenzene. The product was precipitated into hexanes to yield a white powder.  $\delta_{\text{H}}$  ppm (500 MHz,  $\text{CDCl}_3$ ): 5.81 (b, residual ene), 5.13 (b, residual ene), 4.02 (b, 2H, -

C(O)O-CH<sub>2</sub>-), 3.63 (s, n × 3H, -OCH<sub>3</sub> main chain), 2.60 (b, -CH<sub>2</sub>-S-Ad), 2.43 (b, -O-CH<sub>2</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>), 2.15-0.80 (b, n × 5H, main chain; 15H, adamantane).

**P(3-co-MMA) + Fmoc-Cysteine (10) Adduct.** Specifics (photochemical): 50 mg of **P(3-co-MMA)** (0.048 mmol of ene), 82 mg of **10** (0.24 mmol), 7 mg of DMPA (0.027 mmol) were dissolved in 0.20 g of DMF and 0.20 g of chlorobenzene. The product was precipitated into methanol to yield a white powder. Specifics (thermal): 39 mg of **P(3-co-MMA)** (0.062 mmol of ene), 107 mg of **10** (0.31 mmol), 5 mg of AIBN (0.03 mmol) were dissolved in 0.20 g of DMF and 0.20 g of chlorobenzene. The product was precipitated into methanol to yield a white powder. δ<sub>H</sub> ppm (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 7.83 (b, 2H, Fmoc), 7.65 (b, 2H, Fmoc), 7.57-7.28 (b, 4H, Fmoc), 5.98 (b, 1H, NH), 4.67 (b, 1H, Fmoc), 4.45 (b, 2H, Fmoc), 4.28 (b, 2H, Fmoc), 4.01 (b, 2H, -O-CH<sub>2</sub>-), 3.66 (b, n × 3H, -OCH<sub>3</sub> main chain), 3.12 (b, 2H, -S-CH<sub>2</sub>-CH(COOH)-), 2.68 (b, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-S-), 2.15-0.80 (b, n × 5H, main chain; 4H, -OCH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-S-).

**P(3-co-MMA) + Thioglycerol (11) Adduct.** Specifics (photochemical): 50 mg of **P(3-co-MMA)** (0.048 mmol of ene), 27 mg of **11** (0.25 mmol), 5 mg of DMPA (0.020 mmol) were dissolved in 0.30 g of DMF. The product was precipitated into methanol to yield a white powder. Specifics (thermal): 51 mg of **P(3-co-MMA)** (0.049 mmol of ene), 27 mg of **11** (0.25 mmol), 5 mg of AIBN (0.027 mmol) were dissolved in 0.30 g of DMF. The product was precipitated into methanol to yield a white powder. δ<sub>H</sub> ppm (200 MHz, CDCl<sub>3</sub>): 5.82 (b, residual ene), 5.17 (b, residual ene), 4.05 (b, 2H, -O-CH<sub>2</sub>-), 3.90 (b, thioglycerol), 3.79 (b, thioglycerol), 3.64 (b, n × 3H, -OCH<sub>3</sub> main chain), 2.78 (b, thioglycerol), 2.66 (b, -O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-S-CH<sub>2</sub>-), 2.15-0.80 (b, n × 5H, main chain; 4H, -OCH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-S-).

**P(ACL-co-CL) + Thioglycolic Acid (7) Adduct.** Specifics (photochemical): 40 mg of **P(ACL-co-CL)** (0.036 mmol of ene), 17 mg of **7** (0.18 mmol), 2 mg of DMPA (0.008 mmol) were dissolved in 0.25 g of chlorobenzene. The product was precipitated into methanol to yield a white powder. Specifics (thermal): 41 mg of **P(ACL-co-CL)** (0.037 mmol of ene), 18 mg of **7** (0.20 mmol), 3 mg of AIBN (0.018 mmol) were dissolved in 0.25 g of chlorobenzene. The product was precipitated into methanol to yield a white powder. δ<sub>H</sub> ppm (500 MHz, CDCl<sub>3</sub>): 4.91 (b, 1H, -CH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-S-), 4.08 (t, n × 2H, -CH<sub>2</sub>-O-C(O)-), 3.26 (s, 2H, -S-CH<sub>2</sub>-COOH), 2.68 (b, 2H, -CH<sub>2</sub>-S-CH<sub>2</sub>-COOH), 2.33 (t, -O-C(O)-CH<sub>2</sub>-), 1.85-1.30 (complex m, n × 10H, main chain; 4H, -CH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-S-).

**P(ACL-co-CL) + (3-mercaptopropyl)-trimethoxysilane (8) Adduct.** Specifics (photochemical): 40 mg of **P(ACL-co-CL)** (0.036 mmol of ene), 36 mg of **8** (0.182 mmol), 1.9 mg of DMPA (0.0073 mmol) were dissolved in 0.25 g of chlorobenzene. The product was precipitated into methanol to yield a white powder. Specifics (thermal): 40 mg of **P(ACL-co-CL)** (0.036 mmol of ene), 36 mg of **8** (0.18 mmol), 3 mg of AIBN (0.02 mmol) were dissolved in 0.25 g of chlorobenzene. The product was precipitated into ether to yield a white powder.  $\delta_{\text{H}}$  ppm (500 MHz,  $\text{CDCl}_3$ ): 4.91 (b, 1H,  $-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{S}-$ ), 4.08, (t,  $n \times 2\text{H}$ ,  $-\text{CH}_2-\text{O}-\text{C}(\text{O})-$ ), 3.61 (s, 9H,  $-\text{Si}(\text{OCH}_3)_3$ ), 2.53 (m, 4H,  $-\text{CH}_2-\text{S}-\text{CH}_2-$ ), 2.33 (t,  $n \times 2\text{H}$ ,  $-\text{O}-\text{C}(\text{O})-\text{CH}_2-$ ), 1.85-1.30 (complex m,  $n \times 10\text{H}$ , main chain; 4H,  $-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{S}-$ ), 0.78 (t, 2H,  $-\text{CH}_2-\text{Si}(\text{OCH}_3)_3$ ).

**P(ACL-co-CL) + 1-Adamantanethiol (9) Adduct.** Specifics (photochemical): 40 mg of **P(ACL-co-CL)** (0.036 mmol of ene), 31 mg of **9** (0.182 mmol), 1.9 mg of DMPA (0.0073 mmol) were dissolved in 0.25 g of chlorobenzene. The product was precipitated into hexanes to yield a white powder. Specifics (thermal): 40 mg of **P(ACL-co-CL)** (0.036 mmol of ene), 31 mg of **9** (0.18 mmol), 3 mg of AIBN (0.02 mmol) were dissolved in 0.25 g of chlorobenzene. The product was precipitated into hexanes to yield a white powder.  $\delta_{\text{H}}$  ppm (500 MHz,  $\text{CDCl}_3$ ): 5.75 (m, residual ene), 5.08 (m, residual ene), 4.90 (m, 1H,  $-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{S}-$ ), 4.08, (t,  $n \times 2\text{H}$ ,  $-\text{CH}_2-\text{O}-\text{C}(\text{O})-$ ), 2.53 (m, 2H,  $-\text{CH}_2-\text{S}-\text{C}_{10}\text{H}_{15}$ ), 2.30 (t,  $n \times 2\text{H}$ ,  $-\text{O}-\text{C}(\text{O})-\text{CH}_2-$ ), 2.05 (b, 2H,  $-\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$ ), 1.84 (b, 2H,  $-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{S}-$ ), 1.80-1.30 (complex m,  $n \times 10\text{H}$ , main chain; 4H,  $-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{S}-$ ).

**P(ACL-co-CL) + Fmoc-Cysteine (10) Adduct.** Specifics (photochemical): 40 mg of **P(ACL-co-CL)** (0.036 mmol of ene), 62 mg of **10** (0.182 mmol), 1.9 mg of DMPA (0.0073 mmol) were dissolved in 0.20 g of DMF. The product was precipitated into methanol to yield a white powder. Specifics (thermal): 33 mg of **P(ACL-co-CL)** (0.030 mmol of ene), 51 mg of **10** (0.15 mmol), 2.5 mg of AIBN (0.015 mmol) were dissolved in 0.20 g of DMF. The product was precipitated into methanol to yield a white powder.  $\delta_{\text{H}}$  ppm (500 MHz,  $\text{CDCl}_3$ ): 7.78 (b, 2H, Fmoc), 7.62 (b, 2H, Fmoc), 7.45-7.32 (b, 4H, Fmoc), 6.15 (b, 1H, NH), 5.47 (b, 1H, Fmoc), 4.89 (b, 1H,  $-\text{CH}(\text{R})-\text{C}(\text{O})\text{O}-$ ), 4.67 (b, 1H, Fmoc), 4.45 (b, 2H, Fmoc), 4.25 (t,  $n \times 2\text{H}$ , main chain), 4.06 (b, 1H, Fmoc), 3.09 (b, 2H,  $-\text{S}-\text{CH}_2-\text{CH}(\text{COOH})-$ ), 2.31 (t,  $n \times 2\text{H}$ , main chain), 1.72-1.20 (b,  $n \times 6\text{H}$ , main chain; 4H,  $-\text{OCH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{S}-$ ).

**P(ACL-co-CL) + Thioglycerol (11) Adduct.** Specifics (photochemical): 40 mg of **P(ACL-co-CL)** (0.036 mmol of ene), 20 mg of **11** (0.182 mmol), 1.9 mg of DMPA (0.0073 mmol) were dissolved in

0.20 g of chlorobenzene. The product was precipitated into methanol to yield a white powder. Specifics (thermal): 31 mg of **P(ACL-co-CL)** (0.028 mmol of ene), 16 of mg **11** (0.15 mmol), 3 mg of AIBN (0.018 mmol) were dissolved in 0.20 g of chlorobenzene. The product was precipitated into methanol to yield a white powder.  $\delta_{\text{H}}$  ppm (500 MHz,  $\text{CDCl}_3$ ): 5.75 (m, residual ene), 5.10 (m, residual ene), 4.93 (m, 1H,  $-\text{CH}(\text{R})-\text{C}(\text{O})\text{O}-$ ), 4.09 (t,  $n \times 2\text{H}$ , main chain), 2.32 (t,  $n \times 2\text{H}$ , main chain), 1.80-1.30 (b,  $n \times 6\text{H}$ , main chain; 4H,  $-\text{OCH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{S}-$ ).

**e-PS + Thioglycolic Acid (7) Adduct.** Specifics (photochemical): 120 mg of **e-PS** (0.02 mmol), 18.4 mg of **7** (0.20 mmol), 1.0 mg of DMPA (0.004 mmol) were dissolved in 0.30 g of benzene. The product was precipitated into methanol to yield a white powder. Specifics (thermal): 120 mg of **e-PS** (0.02 mmol), 18.4 mg of **7** (0.20 mmol), 1.6 mg of AIBN (0.01 mmol) were dissolved in 0.30 g of benzene. The product was precipitated into methanol to yield a white powder.  $\delta_{\text{H}}$  ppm (200 MHz,  $\text{CDCl}_3$ ): 7.26-6.30 (b,  $n \times 5\text{H}$ , aromatic of PSt), 4.48 (b, 1H, methyne adjacent to  $-\text{Br}$ ), 3.33 (s, 2H,  $-\text{CH}_2-\text{COOH}$ ), 2.73 (t, 7.22 Hz, 2H,  $-\text{CH}_2-\text{SCH}_2\text{COOH}$ ), 2.29-0.81 (b,  $n \times 3\text{H}$ , main chain).  $\delta_{\text{H}}$  ppm (200 MHz,  $\text{CDCl}_3$ ): 7.26-6.30 (b,  $n \times 5\text{H}$ , aromatic of PSt), 4.48 (b, 1H, methyne adjacent to  $-\text{Br}$ ), 3.27 (s, 2H,  $-\text{CH}_2-\text{COOH}$ ), 2.67 (t, 2H,  $-\text{CH}_2-\text{SCH}_2\text{COOH}$ ), 2.48-1.05 (b,  $n \times 3\text{H}$ , main chain).

**e-PS + (3-mercaptopropyl)-trimethoxysilane (8) Adduct.** Specifics (photochemical): 90.0 mg of **e-PS** (0.015 mmol), 29.5 mg of **8** (0.15 mmol), 0.77 mg of DMPA (0.003 mmol) were dissolved in 0.30 g of chlorobenzene. The product was precipitated into methanol to yield a white powder. Specifics (thermal): 90.0 mg of **e-PS** (0.015 mmol), 29.5 mg of **8** (0.15 mmol), 1.2 mg of AIBN (0.008 mmol) were dissolved in 0.30 g of chlorobenzene. The product was precipitated into methanol to yield a white powder.  $\delta_{\text{H}}$  ppm (200 MHz,  $\text{CDCl}_3$ ): 7.43-6.37 (b,  $n \times 5\text{H}$ , aromatic of PSt), 4.51 (b, 1H, methyne adjacent to  $-\text{Br}$ ), 3.62 (s, 9H,  $-\text{OCH}_3$ ), 2.58 (m, 4H,  $-\text{CH}_2\text{SCH}_2-$ ), 2.43-0.63 (b,  $n \times 3\text{H} + 6\text{H}$ , main chain + methylene protons derived from **8**).

**e-PS + 1-Adamantanethiol (9) Adduct.** Specifics (photochemical): 60 mg of **e-PS** (0.01 mmol), 16.8 mg of **9** (0.10 mmol), 1.3 mg of DMPA (0.005 mmol) were dissolved in 0.20 g of chlorobenzene. The product was precipitated into methanol to yield a white powder. Specifics (thermal): 60 mg of **e-PS** (0.01 mmol), 16.8 mg of **9** (0.10 mmol), 0.8 mg of AIBN (0.005 mmol) were dissolved in 0.20 g of chlorobenzene. The product was precipitated into methanol to yield a white powder.  $\delta_{\text{H}}$  ppm (500 MHz,

CDCl<sub>3</sub>): 7.33-6.21 (b, n × 5H, aromatic of PSt), 4.42 (b, 1H, methyne adjacent to -Br), 2.47 (t, 2H, -CH<sub>2</sub>S-adamantyl), 2.41-0.82 (b, n × 3H + 15H, main chain + methyne and methylene protons derived from **9**).

**e-PS + Fmoc-Cysteine (10) Adduct.** Specifics (photochemical): 70.0 mg of **e-PS** (0.012 mmol), 42.0 mg of **10** (0.12 mmol), 1.8 mg of DMPA (0.007 mmol) were dissolved in 0.25 g of chlorobenzene. The product was precipitated into methanol to yield a white powder. Specifics (thermal): 122 mg of **e-PS** (0.02 mmol), 70.0 of mg **10** (0.20 mmol), 1.7 mg of AIBN (0.010 mmol) were dissolved in 0.25 g of chlorobenzene. The product was precipitated into methanol to yield a white powder. δ<sub>H</sub> ppm (500 MHz, CDCl<sub>3</sub>): 7.67 (d, 2H, aromatic of Fmoc), 7.52 (b, 2H, aromatic of Fmoc), 7.30 (m, 2H, aromatic of Fmoc), 7.22 (m, 2H, aromatic of Fmoc), 7.21-6.08 (b, n × 5H, aromatic of PSt), 4.61-4.09 (m, 5H, methyne adjacent to -Br + methyne and methylene protons derived from Fmoc group + methyne adjacent to -COOH), 3.48-2.47 (m, 4H, -CH<sub>2</sub>SCH<sub>2</sub>-), 2.30-0.78 (b, n × 3H, main chain).

**e-PS + Thioglycerol (11) Adduct.** Specifics (photochemical): 60 mg of **e-PS** (0.01 mmol), 10.8 mg of **11** (0.10 mmol), 1.3 mg of DMPA (0.005 mmol) were dissolved in 0.25 g of DMF. The product was precipitated into methanol to yield a white powder. Specifics (thermal): 111 mg of **e-PS** (0.020 mmol), 20 mg of **11** (0.19 mmol), 1.5 mg of AIBN (0.009 mmol) were dissolved in 0.25 g of DMF. The product was precipitated into methanol to yield a white powder. δ<sub>H</sub> ppm (200 MHz, CDCl<sub>3</sub>): 7.43-6.39 (b, n × 5H, aromatic of PSt), 4.51 (b, 1H, methyne adjacent to -Br), 3.50-3.95 (b, 3H, -CH(OH)CH<sub>2</sub>OH), 2.70-2.87 (m, 2H, -SCH<sub>2</sub>CH(OH)CH<sub>2</sub>OH) 2.63 (t, 2H, -CH<sub>2</sub>SCH<sub>2</sub>CH(OH)-), 2.49-0.90 (b, n × 3H, main chain).

**e-PMMA + Thioglycolic Acid (7) Adduct.** Specifics (photochemical): 163 mg of **e-PMMA** (0.022 mmol), 20.0 mg of **7** (0.22 mmol), 2.7 mg of DMPA (0.011 mmol) were dissolved in 0.30 g of benzene. The product was precipitated into hexane to yield a white powder. Specifics (thermal): 163 mg of **e-PMMA** (0.022 mmol), 20.0 mg of **7** (0.22 mmol), 1.8 mg of AIBN (0.011 mmol) were dissolved in 0.30 g of benzene. The product was precipitated into hexane to yield a white powder. δ<sub>H</sub> ppm (400 MHz, CDCl<sub>3</sub>): 3.60 (b, n × 3H, methoxy PMMA), 3.12 (s, 2H, CH<sub>2</sub>S), 2.65 (t, 2H, SCH<sub>2</sub>), 2.10-0.70 (b, n × 5H, main chain).

**e-PMMA + (3-mercaptopropyl)-trimethoxysilane (8) Adduct.** Specifics (photochemical): 38.2 mg of **e-PMMA** (0.0051 mmol), 10 mg of **8** (0.051 mmol), 0.3 mg of DMPA (0.001 mmol) were dissolved

in 0.20 g of chlorobenzene. The product was precipitated into hexane to yield a white powder. Specifics (thermal): 153 mg of **e-PMMA** (0.020 mmol), 40 mg of **8** (0.20 mmol), 1.0 mg of AIBN (0.010 mmol) were dissolved in 0.30 g of chlorobenzene. The product was precipitated into hexane to yield a white powder.  $\delta_{\text{H}}$  ppm (400 MHz,  $\text{CDCl}_3$ ): 3.60 (b,  $n \times 3\text{H}$ , methoxy PMMA & 9H,  $\text{Si}(\text{OCH}_3)_3$ ), 2.52 (t, 2H,  $\text{CH}_2\text{S}$ ), 2.48 (t, 2H,  $\text{SCH}_2$ ), 2.10-0.70 (b,  $n \times 5\text{H}$ , main chain).

**e-PMMA + 1-Adamantanethiol (9) Adduct.** Specifics (photochemical): 44.6 mg of **e-PMMA** (0.0059 mmol), 10.0 mg of **9** (0.059 mmol), 0.3 mg of DMPA (0.0012 mmol) were dissolved in 0.20 g of chlorobenzene. The product was precipitated into hexane to yield a white powder. Specifics (thermal): 134 mg of **e-PMMA** (0.018 mmol), 30 mg of **9** (0.178 mmol), 1.5 mg of AIBN (0.009 mmol) were dissolved in 0.30 g of chlorobenzene. The product was precipitated into hexane to yield a white powder.  $\delta_{\text{H}}$  ppm (400 MHz,  $\text{CDCl}_3$ ): 3.60 (b,  $n \times 3\text{H}$ , methoxy PMMA), 2.49 (d, 2H,  $\text{CH}_2\text{S}$ ), 2.10-0.70 (b,  $n \times 5\text{H}$ , main chain).

**e-PMMA + Fmoc-Cysteine (10) Adduct.** Specifics (photochemical): 44 mg of **e-PMMA** (0.006 mmol), 20 mg of **10** (0.058 mmol), 0.30 mg of DMPA (0.001 mmol) were dissolved in 0.25 g of chlorobenzene. The product was precipitated into hexane to yield a white powder. Specifics (thermal): 153 mg of **e-PMMA** (0.020 mmol), 70 mg of **10** (0.204 mmol), 1.7 mg of AIBN (0.001 mmol) were dissolved in 0.25 g of chlorobenzene. The product was precipitated into hexane to yield a white powder.  $\delta_{\text{H}}$  ppm (400 MHz,  $\text{CDCl}_3$ ): 7.74 (d, 2H, aromatic of Fmoc), 7.58 (b, 2H, aromatic of Fmoc), 7.36 (m, 2H, aromatic of Fmoc), 7.29 (m, 2H, aromatic of Fmoc), 4.56 (m, 1H, CH Fmoc), 4.32 (m, 2H,  $\text{CH}_2$  Fmoc), 4.19 (t, 1H,  $\text{CHCOOH}$ ), 2.88 (d, 2H,  $\text{CHCH}_2\text{S}$ ) 2.57 (m, 2H,  $\text{CH}_2\text{CH}_2\text{S}$ ) 2.00-0.75 (b,  $n \times 5\text{H}$ , main chain).

**e-PMMA + Thioglycerol (11) Adduct.** Specifics (photochemical): 69.3 mg of **e-PMMA** (0.0092 mmol), 10.0 mg of **11** (0.093 mmol), 0.5 mg of DMPA (0.0018 mmol) were dissolved in 0.25 g of benzene. The product was precipitated into hexane to yield a white powder. Specifics (thermal): 139 mg of **e-PMMA** (0.019 mmol), 20 mg of **11** (0.185 mmol), 1.52 mg of AIBN (0.009 mmol) were dissolved in 0.30 g of benzene. The product was precipitated into hexane to yield a white powder.  $\delta_{\text{H}}$  ppm (400 MHz,  $\text{CDCl}_3$ ): 3.60 (b,  $n \times 3\text{H}$ , methoxy PMMA), 2.73-2.61 (m, 2H,  $-\text{SCH}_2\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})$ ), 2.63 (t, 2H,  $\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2(\text{OH})$ ), 2.10-0.70 (b,  $n \times 5\text{H}$ , main chain).

**e-PEG + Thioglycolic Acid (7) Adduct.** Specifics (photochemical): 120 mg of **e-PEG** (0.024 mmol), 22.1 mg of **7** (0.24 mmol), 2.3 mg of DMPA (0.0090 mmol) were dissolved in 0.30 g of benzene. The product was precipitated into diethyl ether to yield a white powder. Specifics (thermal): 120 mg of **e-PEG** (0.024 mmol), 22.1 mg of **7** (0.24 mmol), 2.5 mg of AIBN (0.015 mmol) were dissolved in 0.30 g of benzene. The product was precipitated into diethyl ether to yield a white powder.  $\delta_{\text{H}}$  ppm (200 MHz,  $\text{CDCl}_3$ ): 3.61 (b,  $n \times 4\text{H}$ , methylene of PEG), 3.34 (s, 3H, -OMe). 2.71 (t, 2H,  $-\text{CH}_2-\text{SCH}_2\text{COOH}$ ), 1.84 (m, 2H,  $-\text{CH}_2-\text{CH}_2\text{SCH}_2\text{COOH}$ ).

**e-PEG + (3-mercaptopropyl)-trimethoxysilane (8) Adduct.** Specifics (photochemical): 50.9 mg of **e-PEG** (0.010 mmol), 20.0 mg of **8** (0.10 mmol), 0.52 mg of DMPA (0.0020 mmol) were dissolved in 0.25 g of chlorobenzene. The product was precipitated into diethyl ether to yield a white powder. Specifics (thermal): 100 mg of **e-PEG** (0.02 mmol), 39.3 mg of **8** (0.20 mmol), 1.6 mg of AIBN (0.01 mmol) were dissolved in 0.30 g of chlorobenzene. The product was precipitated into diethyl ether to yield a white powder.  $\delta_{\text{H}}$  ppm (200 MHz,  $\text{CDCl}_3$ ): 3.63 (b,  $n \times 4\text{H} + 9\text{H}$ , methylene of PEG +  $-\text{Si}(\text{OCH}_3)_3$ ), 3.37 (s, 3H, -OMe). 2.56 (m, 4H,  $-\text{CH}_2\text{SCH}_2-$ ), 1.80 (m, 4H,  $-\text{CH}_2\text{CH}_2\text{S CH}_2\text{CH}_2-$ ), 0.73 (t, 2H,  $-\text{CH}_2\text{Si}-$ ).

**e-PEG + 1-Adamantanethiol (9) Adduct.** Specifics (photochemical): 59.4 mg of **e-PEG** (0.012 mmol), 20.0 mg of **9** (0.12 mmol), 0.6 mg of DMPA (0.0024 mmol) were dissolved in 0.25 g of chlorobenzene. The product was precipitated into diethyl ether to yield a white powder. Specifics (thermal): 44.6 mg of **e-PEG** (0.0089 mmol), 15.0 mg of **9** (0.089 mmol), 0.7 mg of AIBN (0.0045 mmol) were dissolved in 0.25 g of chlorobenzene. The product was precipitated into diethyl ether to yield a white powder.  $\delta_{\text{H}}$  ppm (400 MHz,  $\text{CDCl}_3$ ): 3.60 (b,  $n \times 4\text{H}$ , PEG), 2.55 (t, 2H,  $\text{CH}_2\text{S}$ ), 2.05 (m, adamantane), 1.84 (m, adamantane), 1.67 (m, adamantane).

**e-PEG + Fmoc-Cysteine (10) Adduct.** Specifics (photochemical): 29 mg of **e-PEG** (0.006 mmol), 20 mg of **10** (0.058 mmol), 0.30 mg of DMPA (0.001 mmol) were dissolved in 0.10 g of DMF and 0.10 g of chlorobenzene. The product was precipitated into diethyl ether to yield a white powder. Specifics (thermal): 102 mg of **e-PEG** (0.020 mmol), 70 mg of **10** (0.204 mmol), 1.67 mg of AIBN (0.010 mmol) were dissolved in 0.20 g of DMF and 0.20 g of chlorobenzene. The product was precipitated into diethyl ether to yield a white powder.  $\delta_{\text{H}}$  ppm (400 MHz,  $\text{CDCl}_3$ ): 7.73 (m, 2H, aromatic of Fmoc), 7.59 (m, 2H, aromatic of Fmoc), 7.35 (m, 2H, aromatic of Fmoc), 7.26 (m, 2H, aromatic of Fmoc), 4.61 (m, 1H, CH

Fmoc), 4.43 (b, 2H, CH<sub>2</sub> Fmoc), 4.21 (t, 2H, CHCOOH), 3.60 (b, n × 4H, PEG), 2.90 (d, 2H, CHCH<sub>2</sub>S) 2.62 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>S).

**e-PEG + Thioglycerol (11) Adduct.** Specifics (photochemical): 46.2 mg of **e-PEG** (0.0092 mmol), 10.0 mg of 11 (0.093 mmol), 0.5 mg of DMPA (0.0018 mmol) were dissolved in 0.10 g of DMF and 0.10 g of chlorobenzene. The product was precipitated into diethyl ether to yield a white powder. Specifics (thermal): 46.2 mg of **e-PEG** (0.0092 mmol), 10.0 mg of 11 (0.093 mmol), 0.8 mg of AIBN (0.0046 mmol) were dissolved in 0.10 g of DMF and 0.10 g of chlorobenzene. The product was precipitated into diethyl ether to yield a white powder.  $\delta_{\text{H}}$  ppm (400 MHz, CDCl<sub>3</sub>): 3.80-3.45 (b, n × 4H, PEG, CH<sub>2</sub>OH & CH thioglycerol), 2.71 (b, 2 × 2H, CH<sub>2</sub>S), 1.79 (b, 2H, CH<sub>2</sub>CH<sub>2</sub>S).