SUPPORTING INFORMATION

Synthesis of poly(caprolactone)-*block*-poly[oligo (ethylene glycol) methyl methacrylate] amphiphilic grafted nanoparticles (AGNs) as improved oil dispersants

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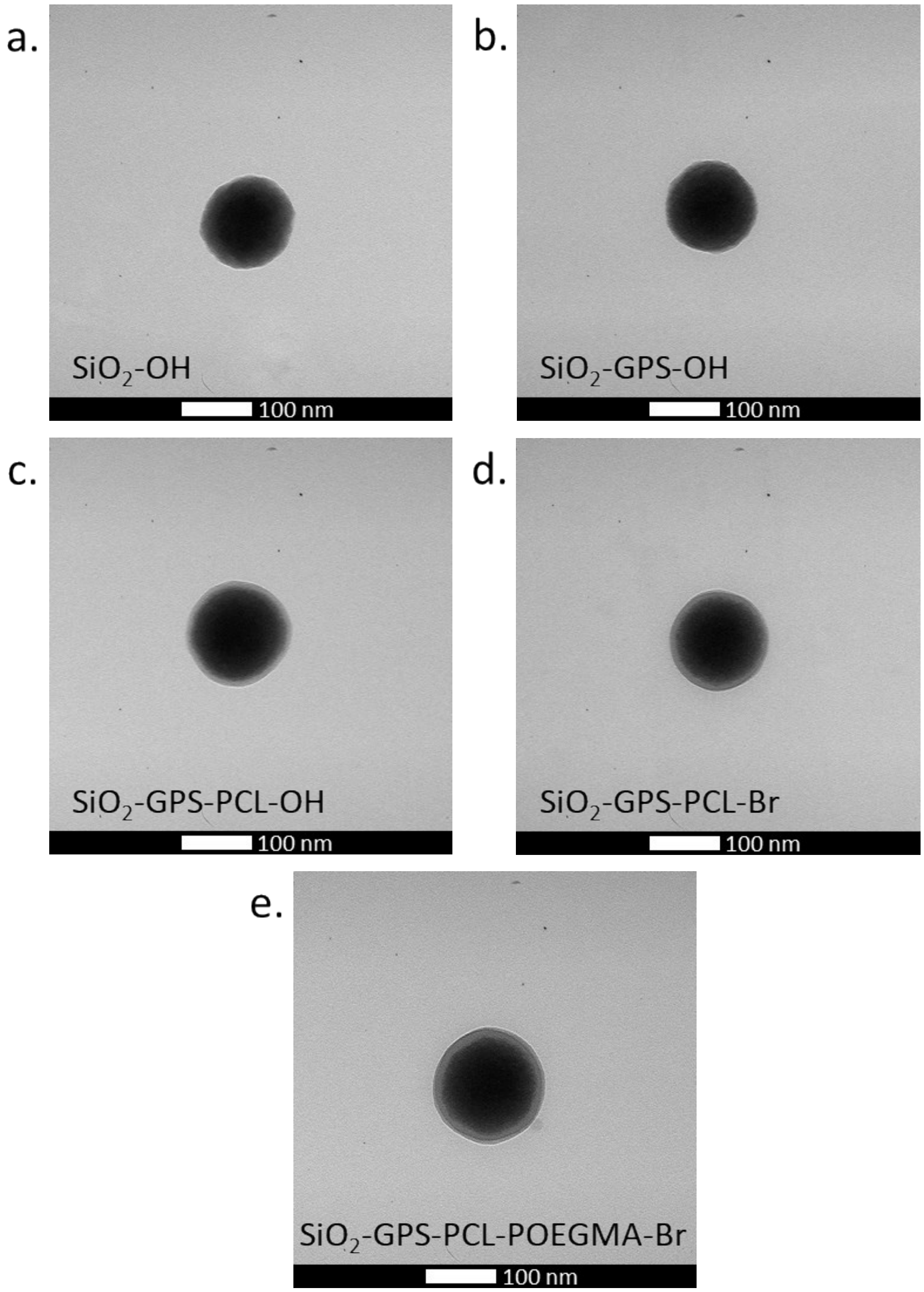

Results

Figure S1: Room temperature TEM images from Figure 3: A) SiO_2-OH, B) SiO_2-GPS-OH (1), C) SiO_2-GPS-PCL-OH (2a), D) SiO_2-GPS-PCL-Br (3a), E) SiO_2-GPS-PCL-POEGMA-Br NPs (4a)

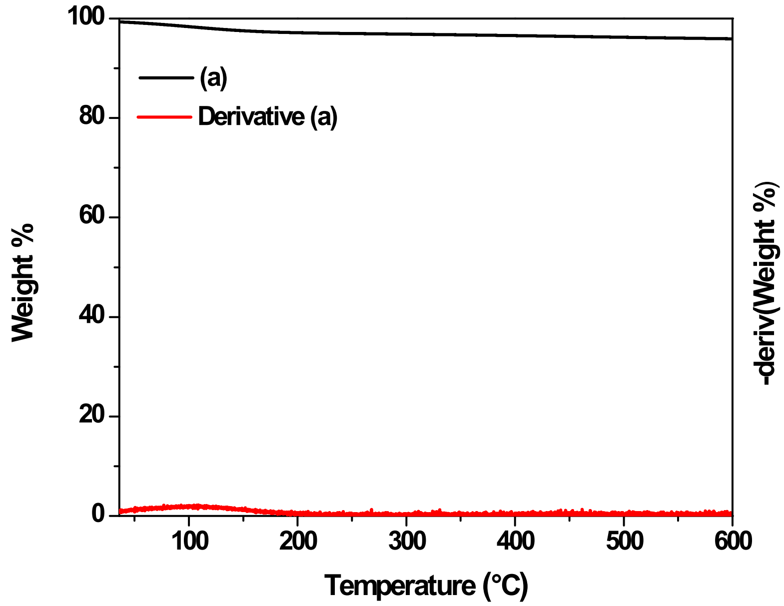

Figure S2: TGA measurements taken from Figure 4, shown as weight (%) vs. temperature (°C), of SiO_2-OH NPs (black) and the first derivative with respect to weight % (red)

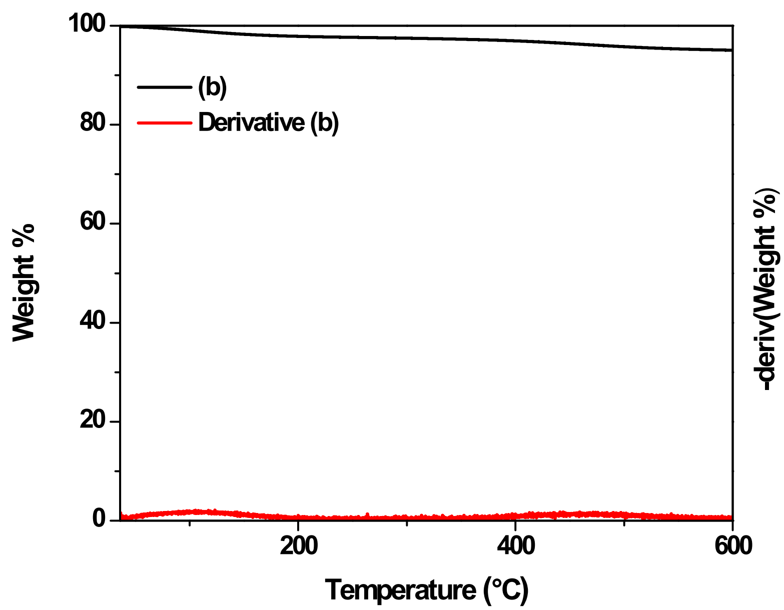

Figure S3: TGA measurements taken from Figure 4, shown as weight (%) vs. temperature (°C), of SiO_2-GPS-OH NPs (black) and the first derivative with respect to weight % (red)

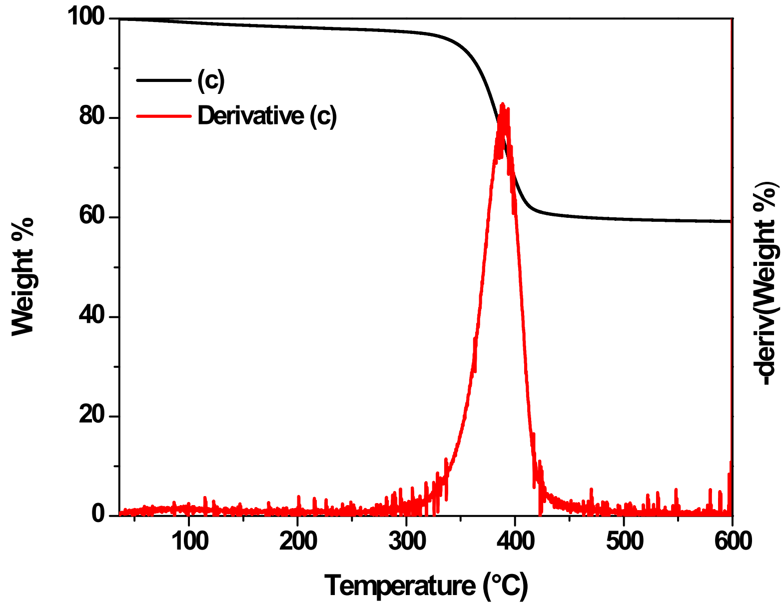

Figure S4: TGA measurements taken from Figure 4, shown as weight (%) vs. temperature (°C), of SiO_2-GPS-PCL-OH NPs (black) and the first derivative with respect to weight % (red)

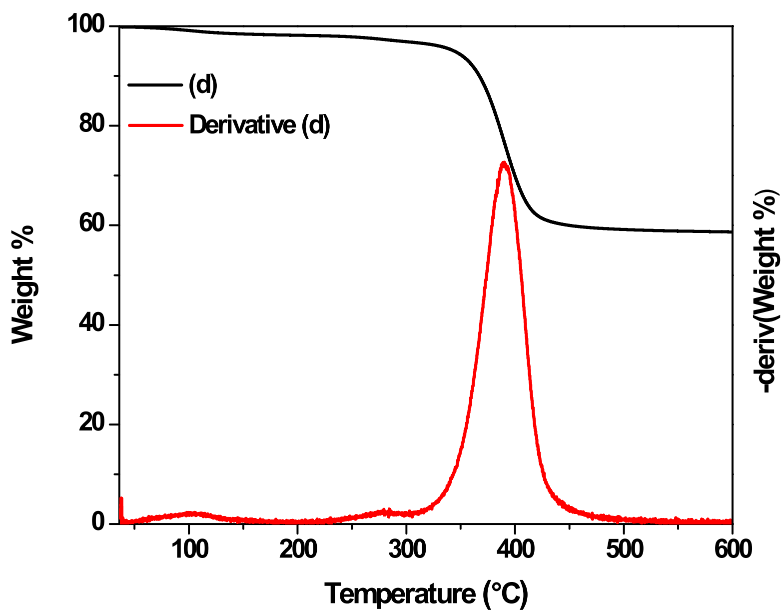

Figure S5: TGA measurements taken from Figure 4, shown as weight (%) vs. temperature (°C), of SiO_2-GPS-PCL-Br NPs (black) and the first derivative with respect to weight % (red)

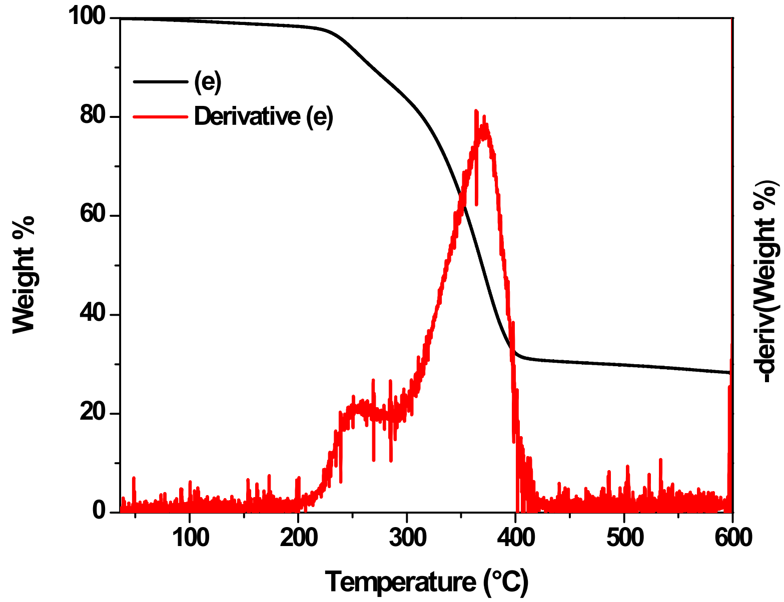

Figure S6: TGA measurements taken from Figure 4, shown as weight (%) vs. temperature (°C), of SiO_2-GPS-PCL-POEGMA-Br NPs (black) and the first derivative with respect to weight % (red)

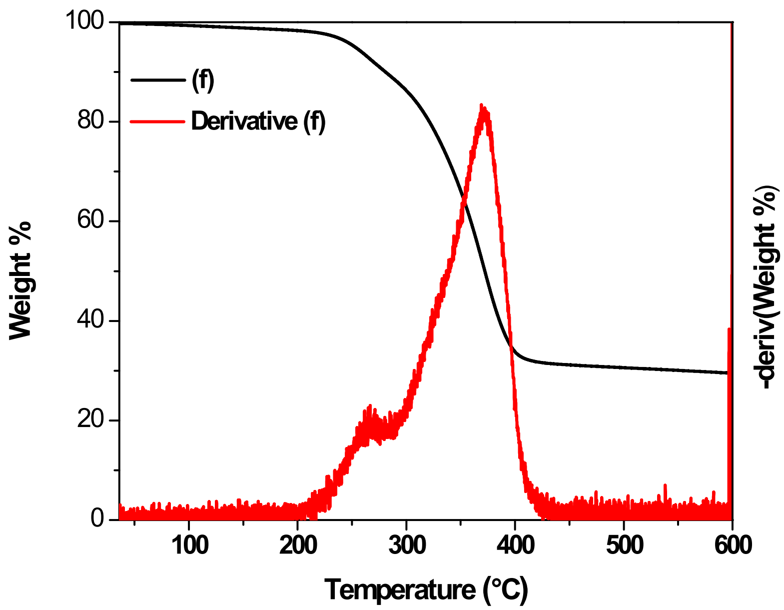

Figure S7: TGA measurements taken from Figure 4, shown as weight (%) vs. temperature (°C), of SiO_2-GPS-PCL-POEGMA-Br NPs (black) and the first derivative with respect to weight % (red) after being dried and redispersed in deionized water four times

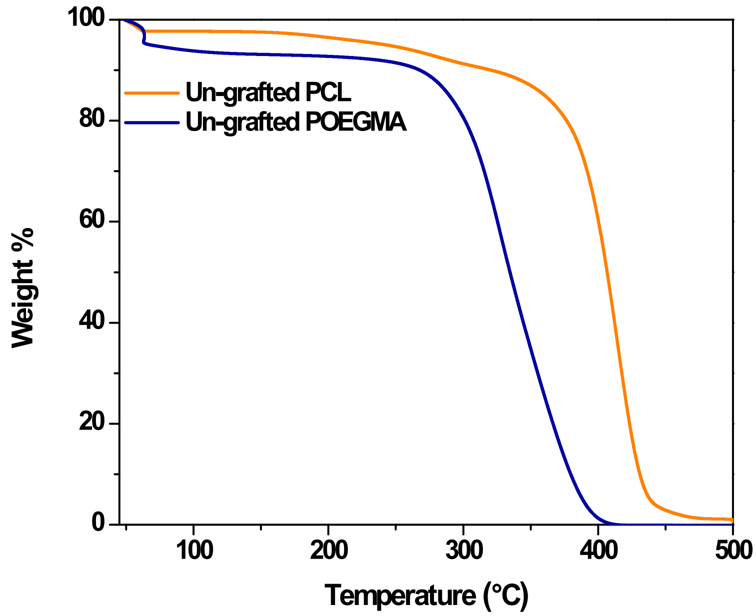

Figure S8: TGA measurements, shown as weight (%) vs. temperature (°C), of un-grafted PCL (gold) and un-grafted POEGMA (purple)

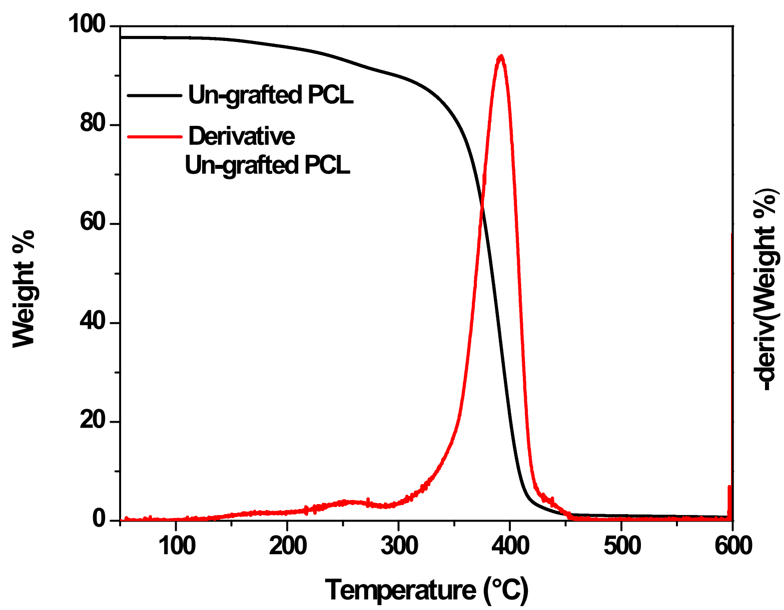

Figure S9: TGA measurements, shown as weight (%) vs. temperature (°C), of un-grafted PCL (black) and the first derivative with respect to weight % (red)

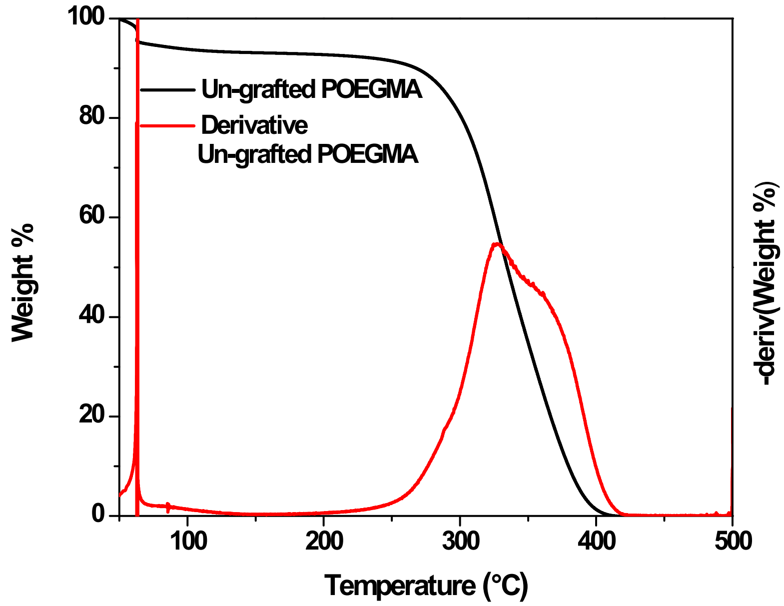

Figure S10: TGA measurements, shown as weight (%) vs. temperature (°C), of un-grafted POEGMA (black) and the first derivative with respect to weight % (red)

Table S1: Decomposition temperatures assignments, measured from TGA first derivative plots

Decomposition temp	***Samples observed:***	***Species***
100	SiO_2 NP, SiO_2-GPS NP	*water*
475	SiO_2-GPS NP	*GPS*
400	SiO_2-GPS-PCL NP	*PCL*
275	SiO_2-GPS-PCL-Br NP, SiO_2-GPS-PCL-POEGMA-Br NP, SiO_2-GPS-PCL-POEGMA-Br NP (redisp)	*POEGMA*
250	ungrafted PCL	
325	ungrafted POEGMA	
375	ungrafted POEGMA	
275	SiO_2-GPS-POEGMA-Br NP	
350	SiO_2-GPS-POEGMA-Br NP	

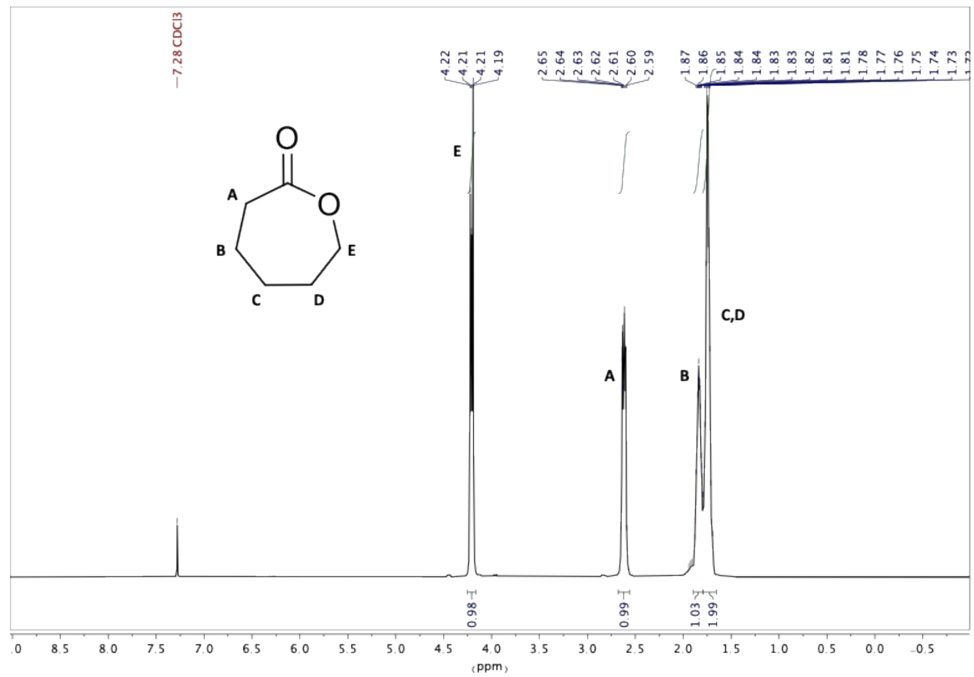

Figure S11: ^{1}H NMR spectrum of ε-caprolactone monomer with peaks at: 1.7 ppm (C, D CH_2 γ, δ position), 1.9 ppm (B CH_2 β position), 2.6 ppm (A CH_2 α position), and 4.2 ppm (E CH_2 ε position)

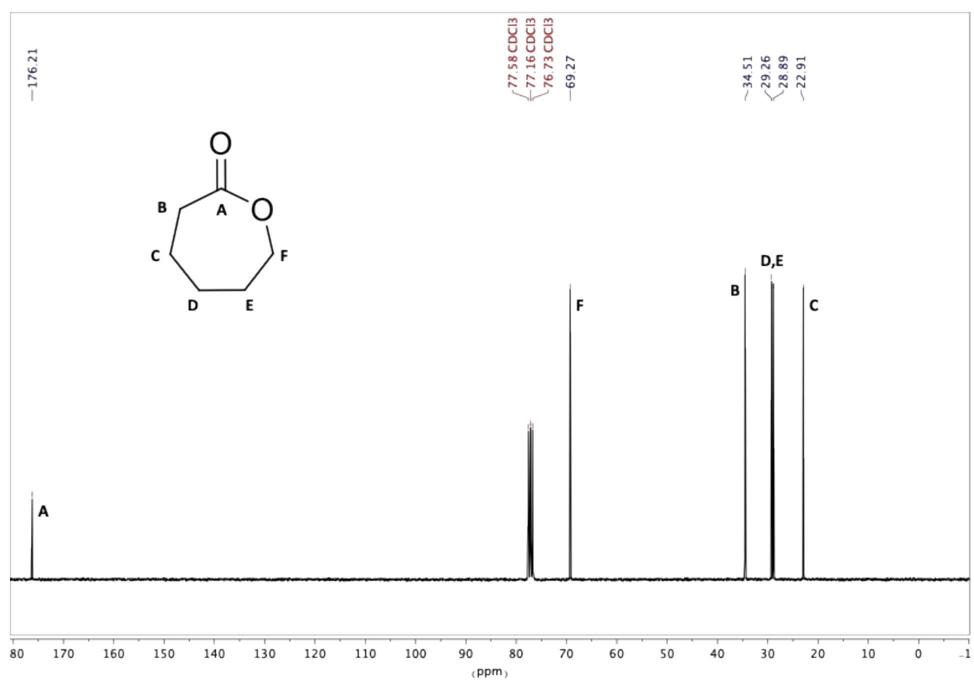

Figure S12: ^{13}C NMR spectrum of ε-caprolactone monomer with peaks at: 22.9 ppm (C CH_2 β position), 28.9 ppm (D CH_2 γ position), 29.3 ppm (E CH_2 δ position), 34.5 ppm (B CH_2 α position), 69.3 ppm (F CH_2 ε position), and 176.2 ppm (A C(O))

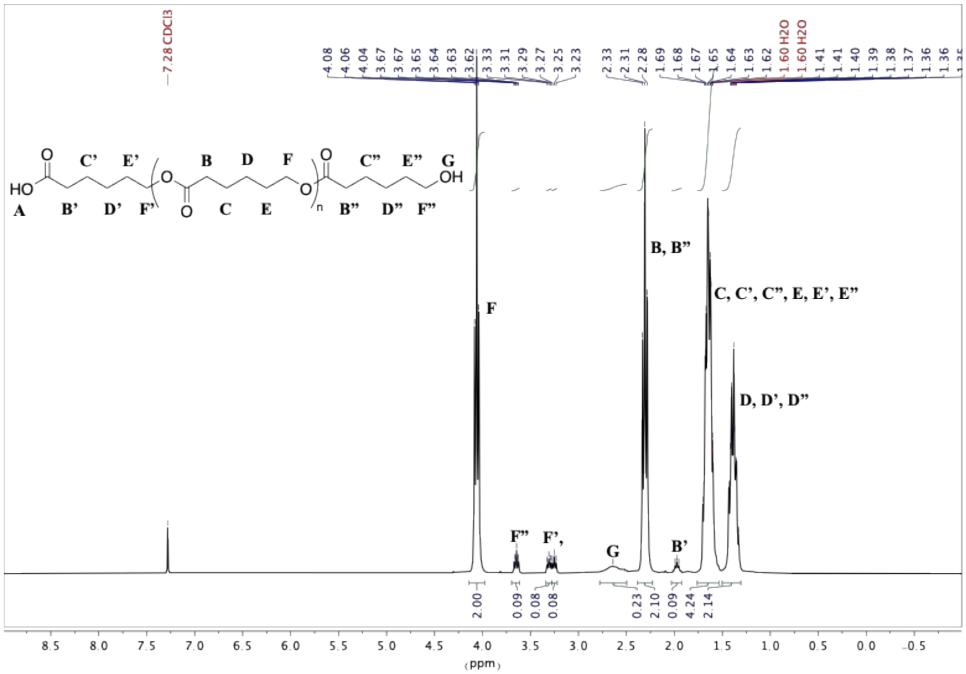

Figure S13: [1]H NMR spectrum of water-initiated un-grafted PCL (Scheme 3-A, sample 2A and 2C) generated in situ with peaks at: 1.39 ppm (D, D', D" CH_2 γ position), 1.66 ppm (C, C', C", E, E', E" CH_2 β, δ position), 2.1 ppm (B', B" CH_2 α position), 2.31 ppm (B CH_2 α position), 3.3 ppm (F' CH_2 ε position), 3.65 ppm (F" CH_2 ε position), and 4.06 ppm (F CH_2 ε position)

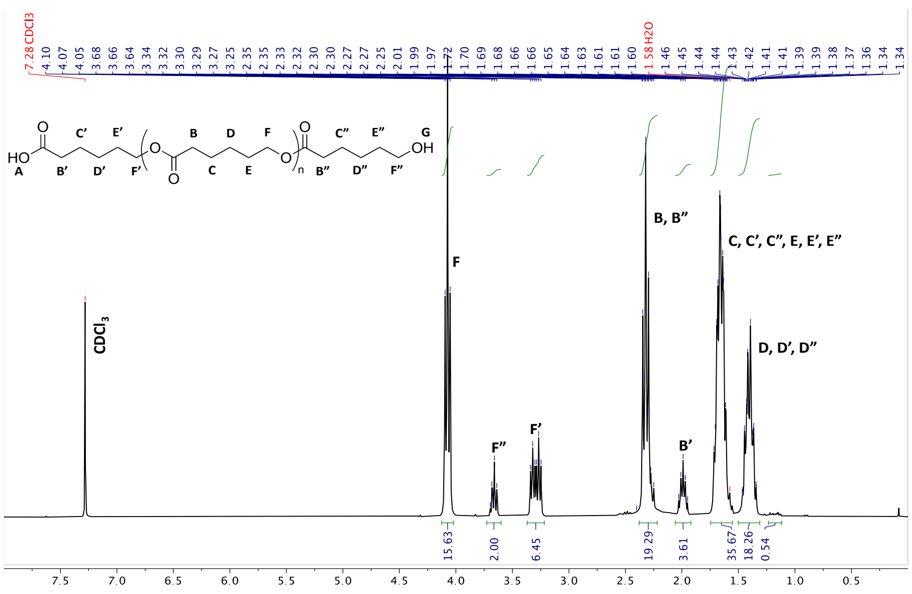

Figure S14: [1]H NMR spectrum of water-initiated un-grafted PCL (Scheme 3-A, sample 2B) generated in situ with peaks at: 1.39 ppm (D, D', D" CH_2 γ position), 1.66 ppm (C, C', C", E, E', E" CH_2 β, δ position), 2.1 ppm (B', B" CH_2 α position), 2.31 ppm (B CH_2 α position), 3.3 ppm (F' CH_2 ε position), 3.65 ppm (F" CH_2 ε position), and 4.06 ppm (F CH_2 ε position)

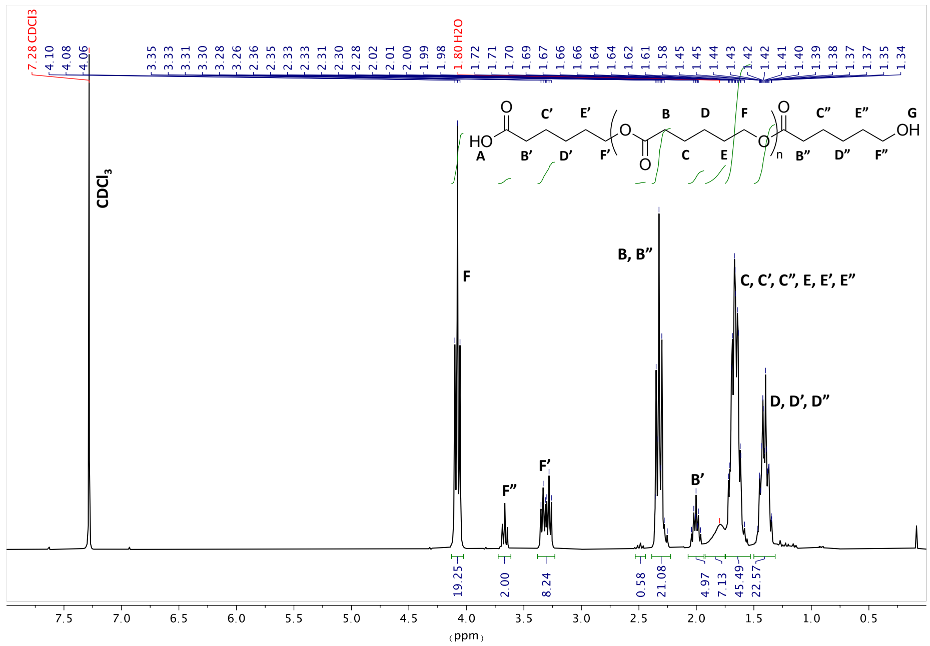

Figure S15: [1]H NMR spectrum of water-initiated un-grafted PCL (Scheme 3-A, sample 2D) generated in situ with peaks at: 1.39 ppm (D, D', D'' CH_2 γ position), 1.66 ppm (C, C', C'', E, E', E'' CH_2 β, δ position), 2.1 ppm (B', B'' CH_2 α position), 2.31 ppm (B CH_2 α position), 3.3 ppm (F' CH_2 ε position), 3.65 ppm (F'' CH_2 ε position), and 4.06 ppm (F CH_2 ε position)

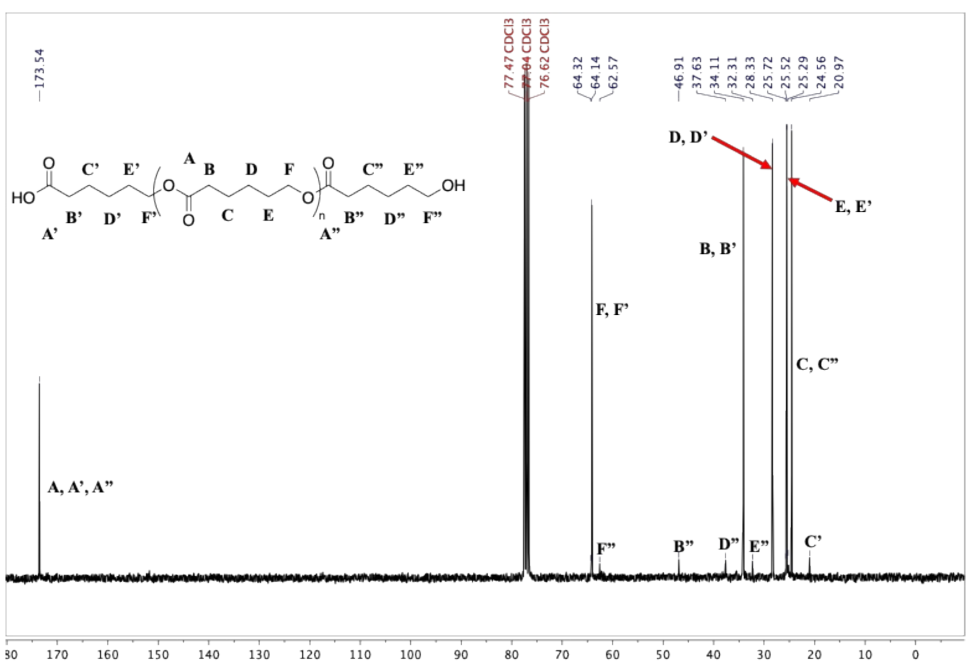

Figure S16: [13]C NMR spectrum of water-initiated PCL (Scheme 3-A, sample 2A) generated in situ with peaks at: 24.6 ppm (C, C', C'' CH_2 β position), 25.5 ppm (E, E' CH_2 δ position), 28.3 ppm (D, D', D'' CH_2 γ position), 32.3 ppm (E'' CH_2 δ position), 34.1 ppm (B, B', B'' CH_2 α position), 62 ppm (F'' CH_2 ε position), 64.2 ppm (F, F' CH_2 ε position), and 173.6 ppm (A, A'' C(O))

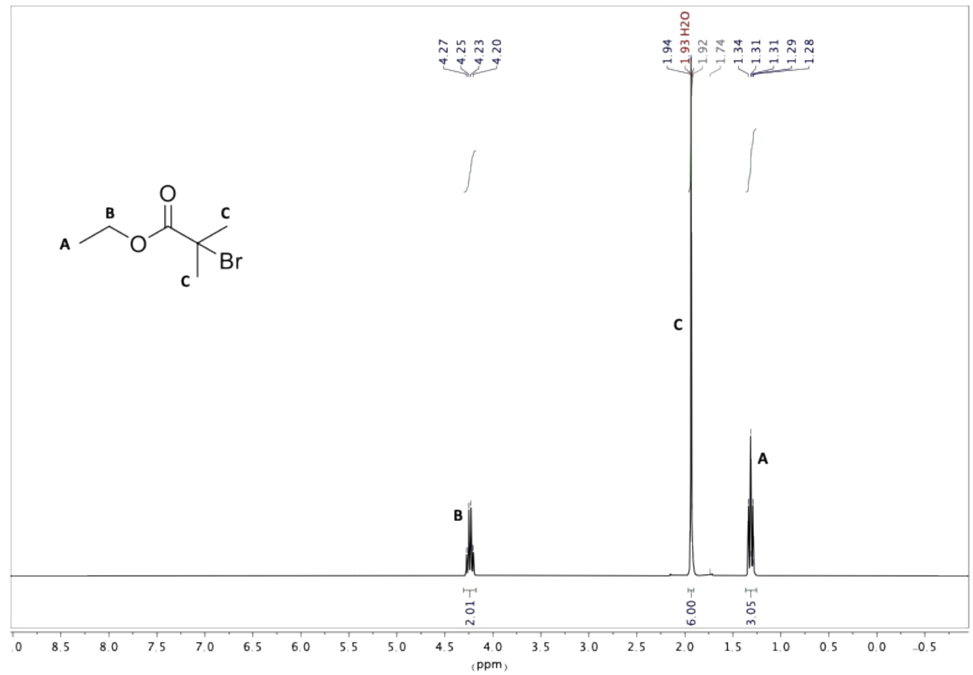

Figure S17: ^{1}H NMR spectrum of ethyl 2-bromoisobutyrate (EBiB) with peaks at: 1.3 ppm (A CH_3-CH_2), 1.9 ppm (C $(CH_3)_2$-C(Br)), and 4.2 ppm (B CH_3-CH2-O)

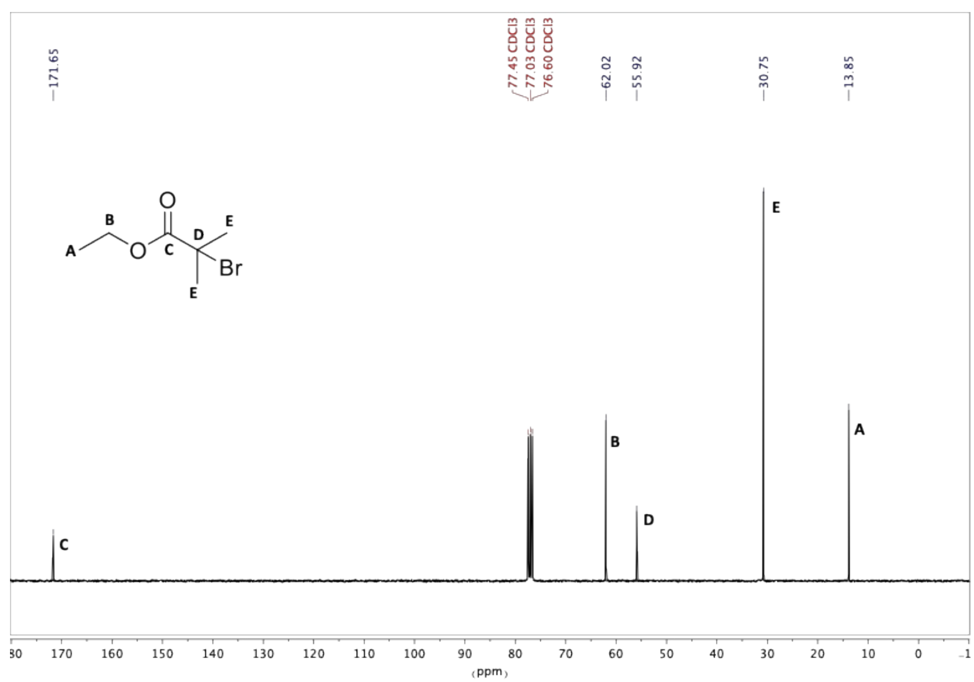

Figure S18: ^{13}C NMR spectrum of ethyl 2-bromoisobutyrate (EBiB) with peaks at: 13.9 ppm (A CH_3-CH_2), 30.8 ppm (E $(CH_3)_2$-C(Br)), 55.9 ppm (D C(O)-C$(CH_3)_2$-Br), 62.0 ppm (B CH_3-CH_2-O), and 171.7 ppm (C O-C(O)-C$(CH_3)_2$)

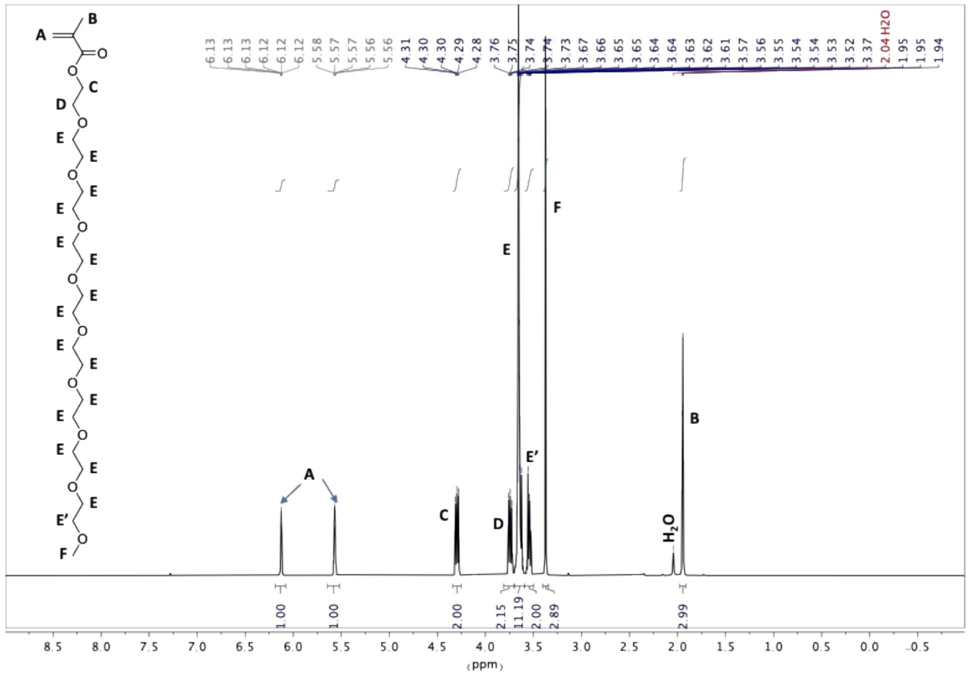

Figure S19: [1]H NMR spectrum of oligo(ethylene glycol) mono-methyl ether methacrylate (OEGMA) with peaks at: 1.9 ppm (B CH_3-C), 3.4 ppm (F O-CH_3), 3.5 ppm (E' CH_2-CH_2-O(CH_3)), 3.6 ppm (E CH_2-CH_2-O(CH_2)), 3.7 ppm (D CH_2-CH_2-CH_2), 4.3 ppm (C CH_2-CH_2-CH_2), 5.6 and 6.1 ppm (A CH_2-CH_2-CH_2)

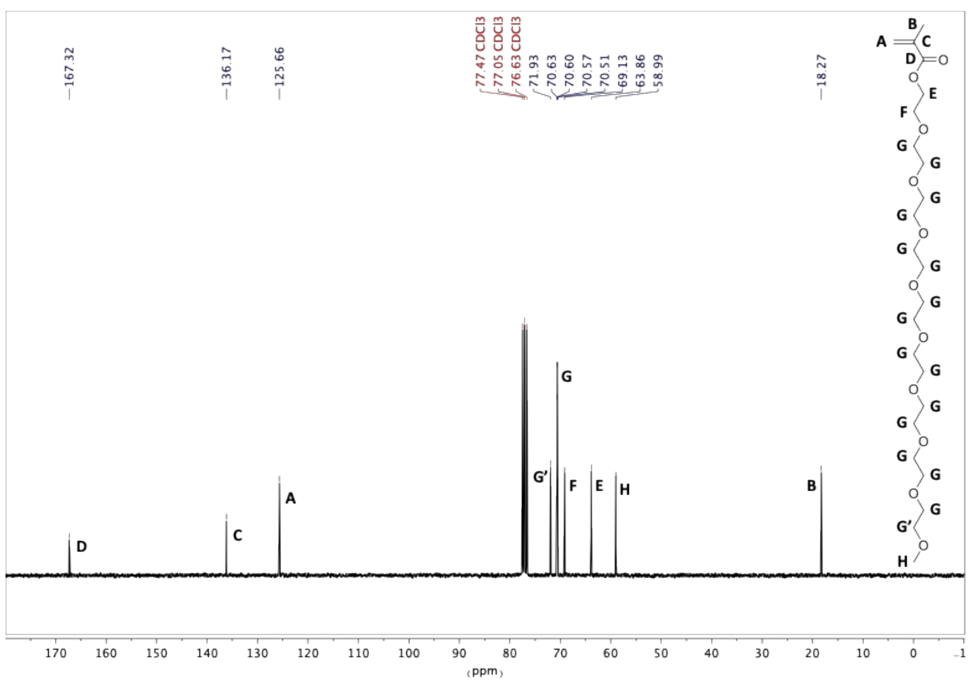

Figure S20: [13]C NMR spectrum of oligo(ethylene glycol) mono-methyl ether methacrylate (OEGMA) with peaks at: 18.3 ppm (B CH_3-C), 58.9 ppm (H O-CH_3), 63.9 ppm (E O-CH_2-CH_2), 69.1 ppm (F CH_2-CH_2-O), 70.6 ppm (G O-CH_2-CH_2-O), 71.9 ppm (G' CH_2-CH_2-O), 125.7 ppm (A CH_2-C(CH_3)), 136.2 ppm (C CH_2-C(CH_3)-C(O)), and 167.3 ppm (D C(CH_3)-C(O)-O)

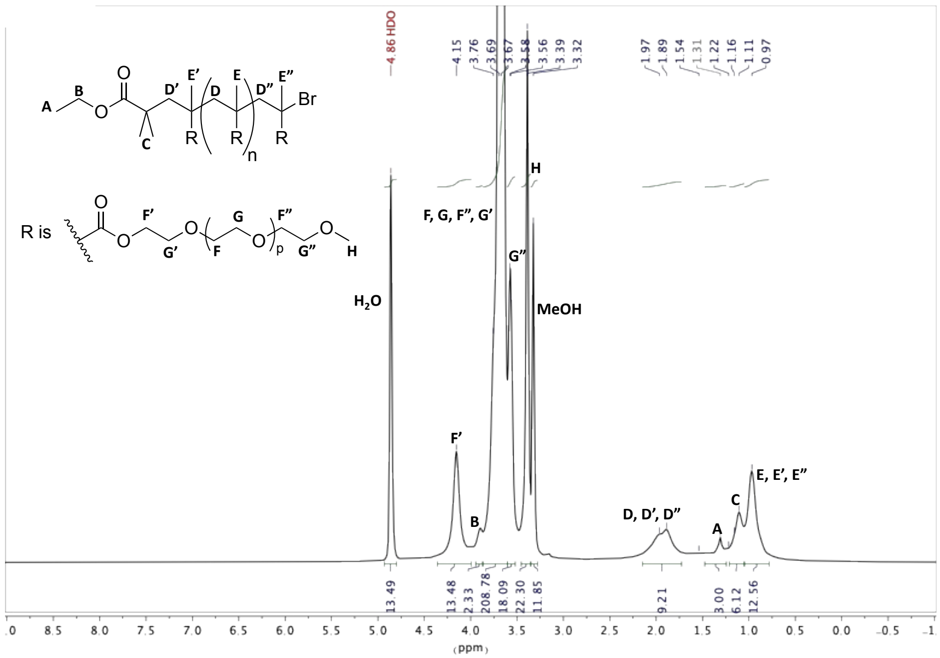

Figure S21: [1]H NMR spectrum of EBiB-initiated POEGMA (Scheme 3-B, sample 4A) generated in situ with peaks at: 0.95 ppm (E, E', E'' CH_3-$C(R)_3$), 1.1 ppm (C $(CH_3)_2$-$C(R)_2$), 1.31 ppm (A CH_3-CH_2-O), 1.9 ppm (D, D', D'' $C(CH_3)$-CH_2-$C(CH_3)$), 3.4 ppm (H CH_2-O-CH_3), 3.58 ppm (G'' O-CH_2-CH_2-O), 3.67 ppm (F, F'', G O-CH_2-CH_2-O), 3.76 ppm (B CH_3-CH_2-O), and 4.15 ppm (F' O-CH_2-CH_2-O)

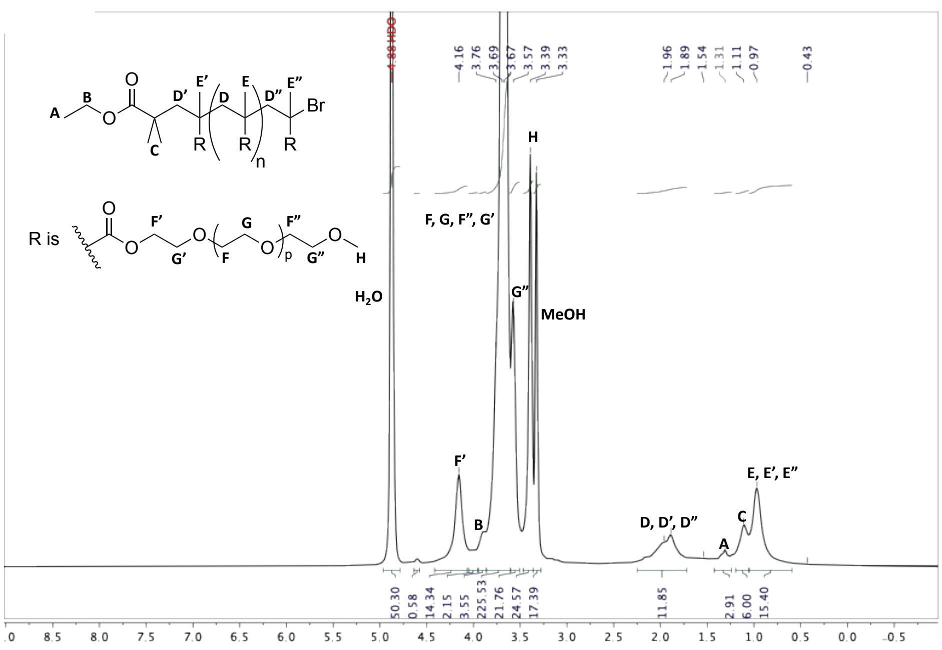

Figure S22: [1]H NMR spectrum of EBiB-initiated POEGMA (Scheme 3-B, sample 4B) generated in situ with peaks at: 0.95 ppm (E, E', E'' CH_3-$C(R)_3$), 1.1 ppm (C $(CH_3)_2$-$C(R)_2$), 1.31 ppm (A CH_3-CH_2-O), 1.9 ppm (D, D', D'' $C(CH_3)$-CH_2-$C(CH_3)$), 3.4 ppm (H CH_2-O-CH_3), 3.58 ppm (G'' O-CH_2-CH_2-O), 3.67 ppm (F, F'', G O-CH_2-CH_2-O), 3.76 ppm (B CH_3-CH_2-O), and 4.15 ppm (F' O-CH_2-CH_2-O)

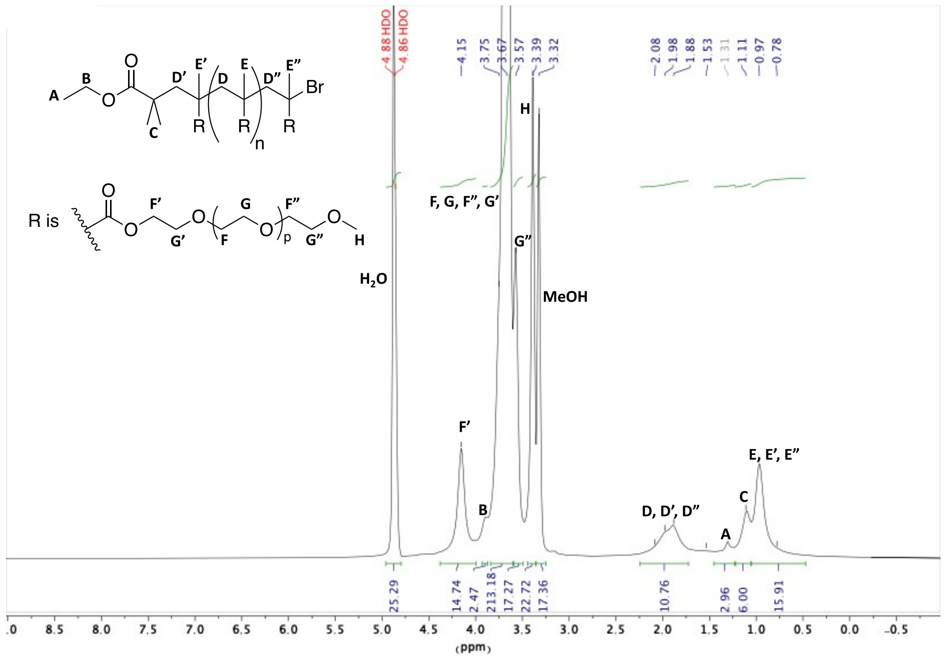

Figure S23: ^1H NMR spectrum of EBiB-initiated POEGMA (Scheme 3-B, sample 4C) generated in situ with peaks at: 0.95 ppm (E, E', E'' CH_3-$C(R)_3$), 1.1 ppm (C $(CH_3)_2$-$C(R)_2$), 1.31 ppm (A CH_3-CH_2-O), 1.9 ppm (D, D', D'' $C(CH_3)$-CH_2-$C(CH_3)$), 3.4 ppm (H CH_2-O-CH_3), 3.58 ppm (G'' O-CH_2-CH_2-O), 3.67 ppm (F, F'', G O-CH_2-CH_2-O), 3.76 ppm (B CH_3-CH_2-O), and 4.15 ppm (F' O-CH_2-CH_2-O)

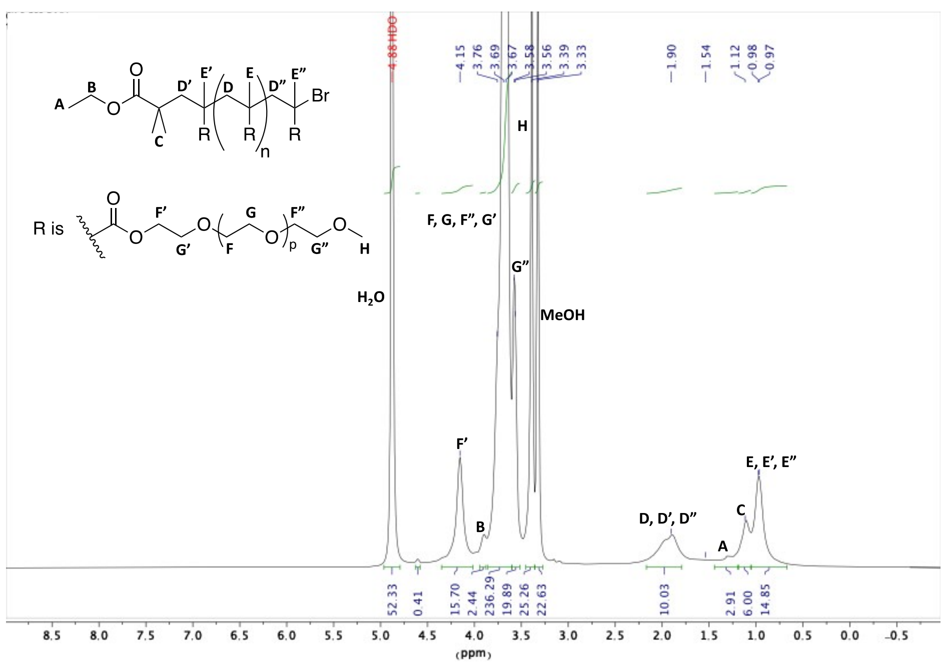

Figure S24: ^1H NMR spectrum of EBiB-initiated POEGMA (Scheme 3-B, 4D) generated in situ with peaks at: 0.95 ppm (E, E', E'' CH_3-$C(R)_3$), 1.1 ppm (C $(CH_3)_2$-$C(R)_2$), 1.31 ppm (A CH_3-CH_2-O), 1.9 ppm (D, D', D'' $C(CH_3)$-CH_2-$C(CH_3)$), 3.4 ppm (H CH_2-O-CH_3), 3.58 ppm (G'' O-CH_2-CH_2-O), 3.67 ppm (F, F'', G O-CH_2-CH_2-O), 3.76 ppm (B CH_3-CH_2-O), and 4.15 ppm (F' O-CH_2-CH_2-O)

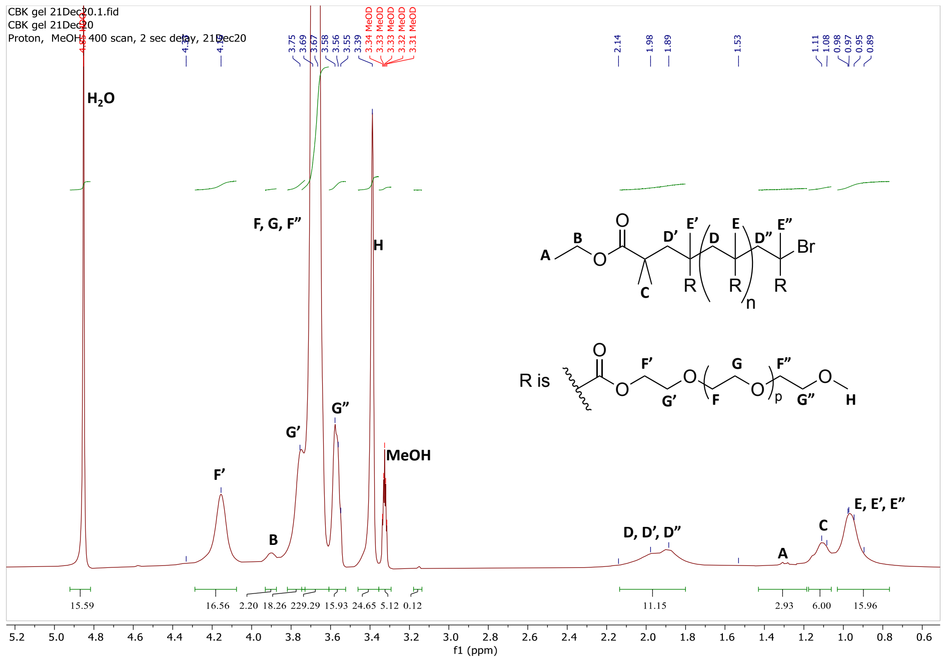

Figure S25: [1]H NMR spectrum of EBiB-initiated POEGMA (Scheme 3-B, sample 6) generated in situ with peaks at: 0.95 ppm (E, E', E" CH_3-$C(R)_3$), 1.1 ppm (C $(CH_3)_2$-$C(R)_2$), 1.31 ppm (A CH_3-CH_2-O), 1.9 ppm (D, D', D" $C(CH_3)$-CH_2-$C(CH_3)$), 3.4 ppm (H CH_2-O-CH_3), 3.58 ppm (G" O-CH_2-CH_2-O), 3.67 ppm (F, F", G O-CH_2-CH_2-O), 3.76 ppm (B CH_3-CH_2-O), and 4.15 ppm (F' O-CH_2-CH_2-O)

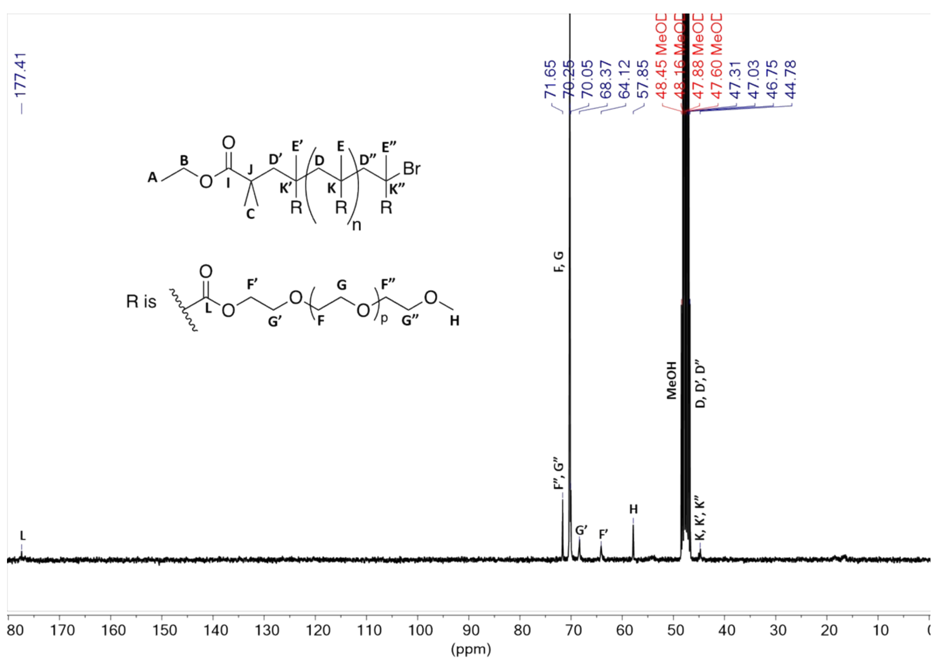

Figure S26: [13]C NMR spectrum of EBiB-initiated POEGMA (Scheme 3-B, sample 4A) generated in situ with peaks at: 44.78-46.75 ppm (K, K', K" CH_2-$C(CH_3)$-CH_2), 47.31 ppm (D, D', D" $C(CH_3)$-CH_2-$C(CH_3)$), 57.85 ppm (H O-CH_3), 64.12 ppm (F' O-CH_2-CH_2-O), 68.37 ppm (G' O-CH_2-CH_2-O), 70.05-70.25 ppm (F, G O-CH_2-CH_2-O), and 71.65 ppm (F", G" O-CH_2-CH_2-O), 177.41 ppm (L $C(CH_3)$-C(O)-CH_2)

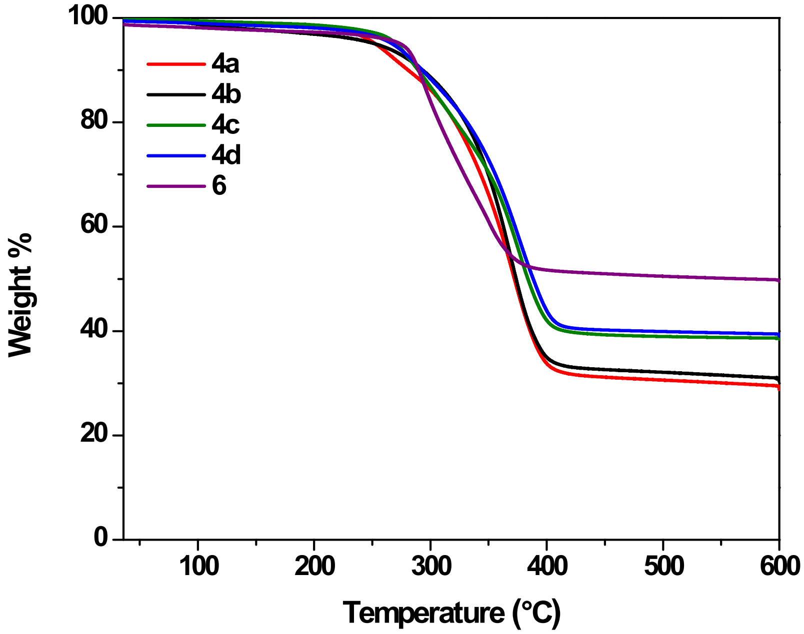

Figure S27: TGA measurements, shown as weight (%) vs. temperature (°C), of SiO_2-GPS-PCL-POEGMA-Br NPs (Samples 4a-d) alongside SiO_2-GPS-POEGMA-Br NPs (Sample 6)

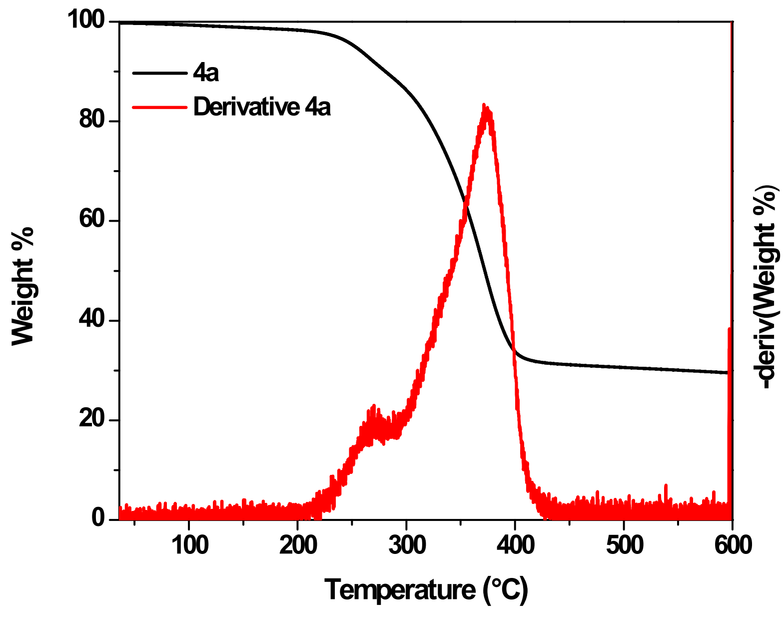

Figure S28: TGA measurements (black), shown as weight (%) vs. temperature (°C), of SiO_2-GPS-PCL-POEGMA-Br NPs (Samples 4a) alongside the first derivative with respect to weight percent (red)

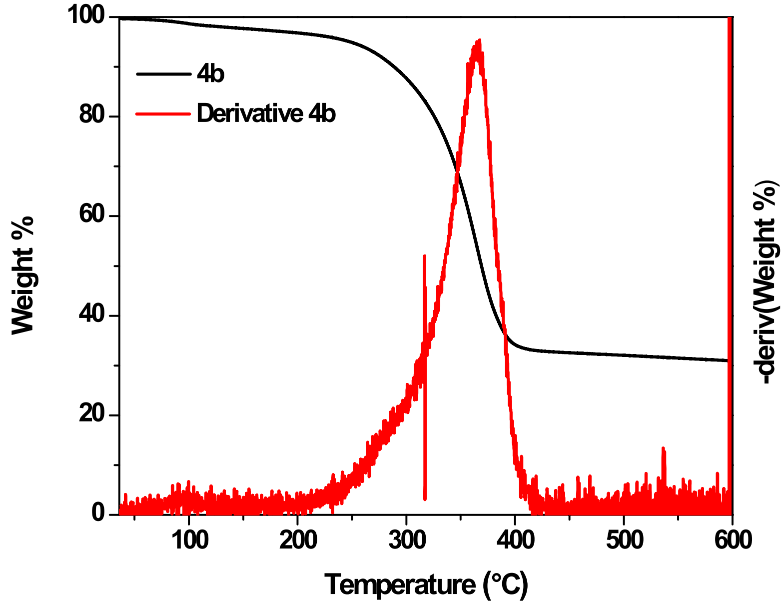

Figure S29: TGA measurements (black), shown as weight (%) vs. temperature (°C), of SiO_2-GPS-PCL-POEGMA-Br NPs (Samples 4b) alongside the first derivative with respect to weight percent (red)

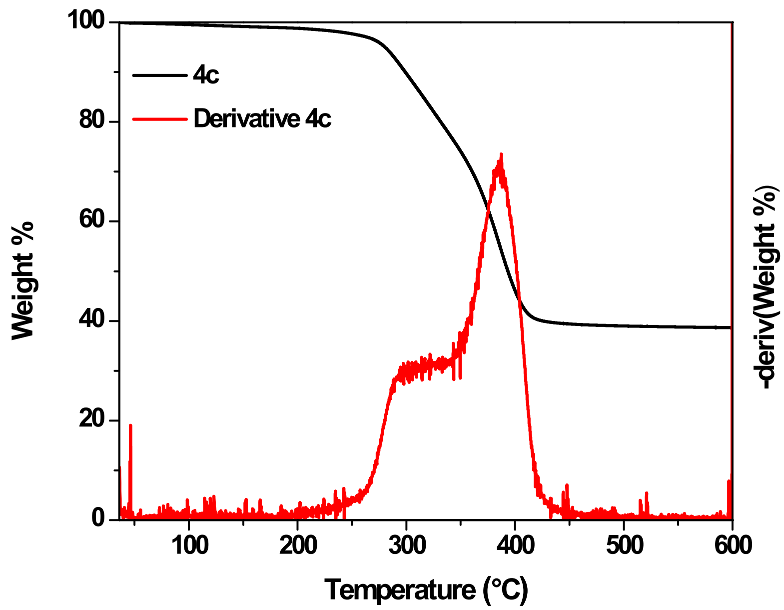

Figure S30: TGA measurements (black), shown as weight (%) vs. temperature (°C), of SiO_2-GPS-PCL-POEGMA-Br NPs (Samples 4c) alongside the first derivative with respect to weight percent (red)

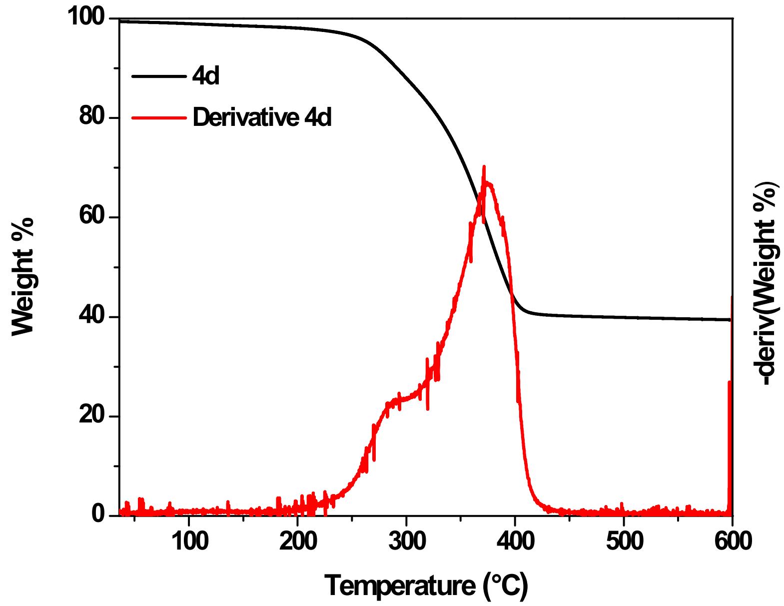

Figure S31: TGA measurements (black), shown as weight (%) vs. temperature (°C), of SiO_2-GPS-PCL-POEGMA-Br NPs (Samples 4d) alongside the first derivative with respect to weight percent (red)

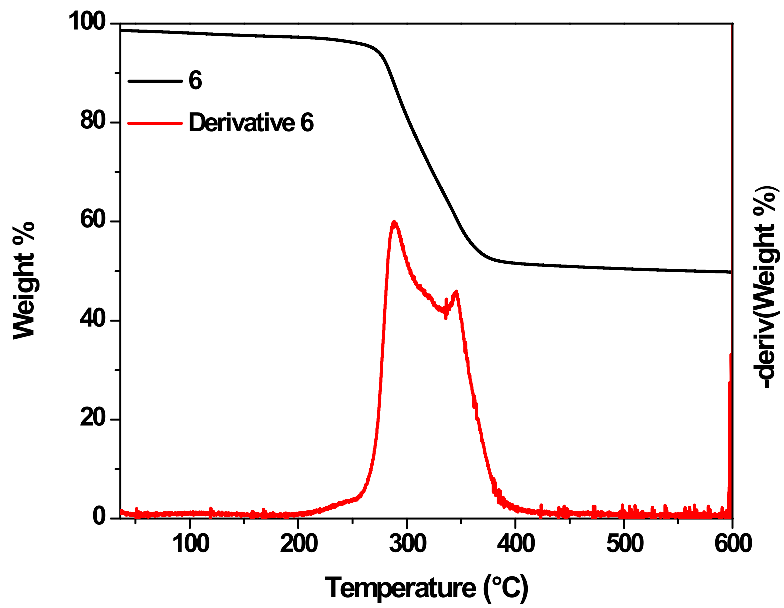

Figure S32: TGA measurements (black), shown as weight (%) vs. temperature (°C), of SiO_2-GPS-POGEMA-Br NPs (Sample 6) alongside the first derivative with respect to weight percent (red) before HF treatment to remove the silica NP core

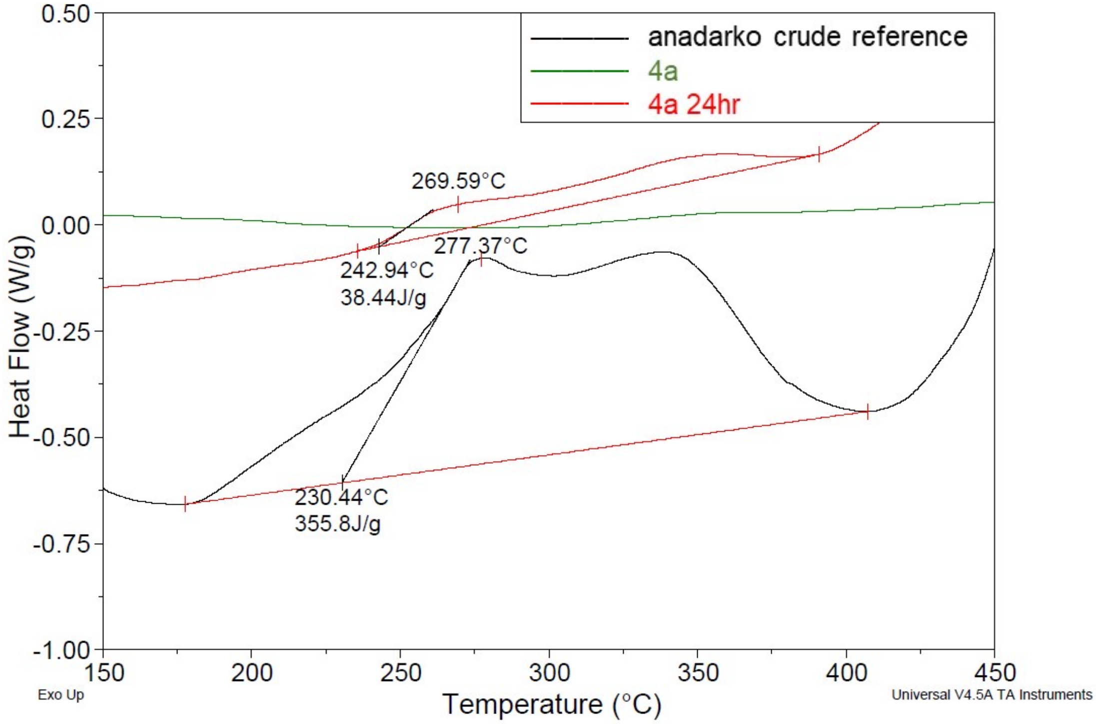

Figure S33: Sample 4a without oil exposure (green) and after 24 hr of oil exposure (red) compared the Anadarko crude oil reference showing a 30:1 oil:NP uptake in a 24 hr testing window

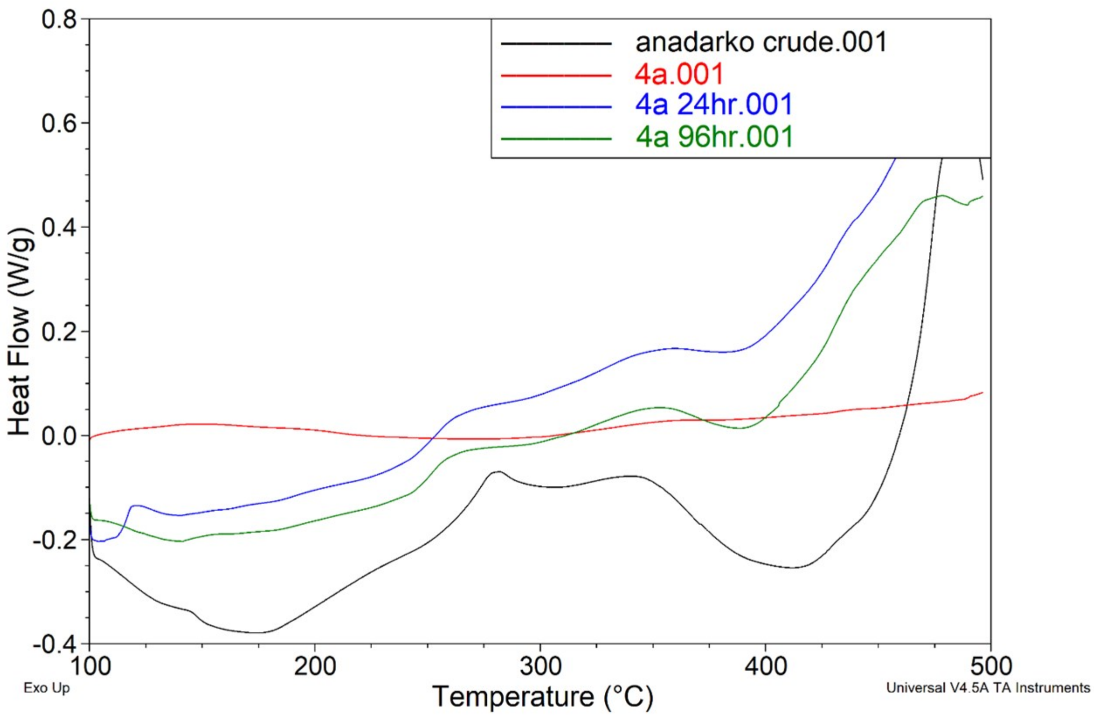

Figure S34: Sample 4a without oil exposure (red) and after 24 hr (blue) and 96 hr (green) of oil exposure compared the Anadarko crude oil reference

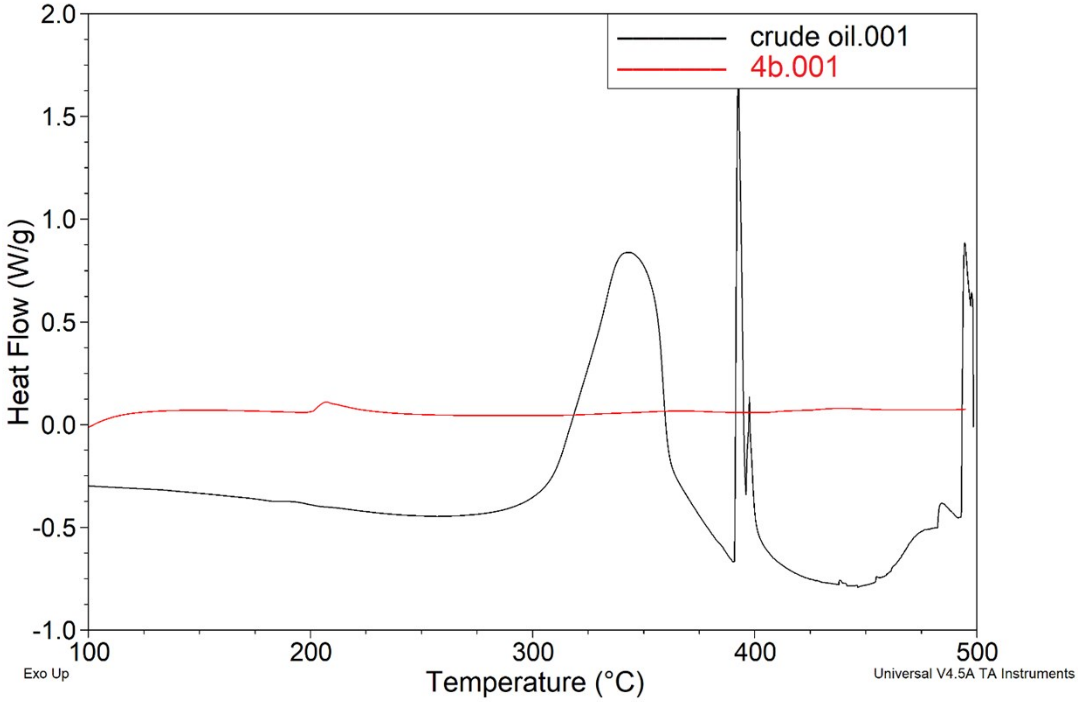

Figure S35: Sample 4b exposed to BP crude oil for 72 hr (red)

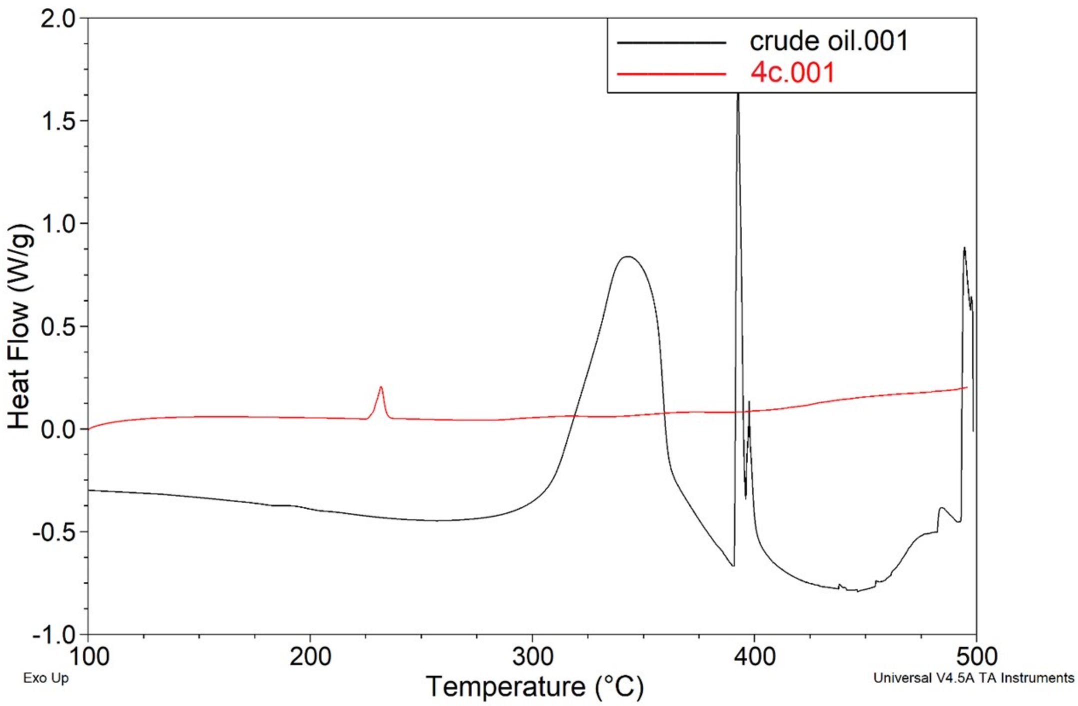

Figure S36: Sample 4c exposed to BP crude oil for 72 hr (red)

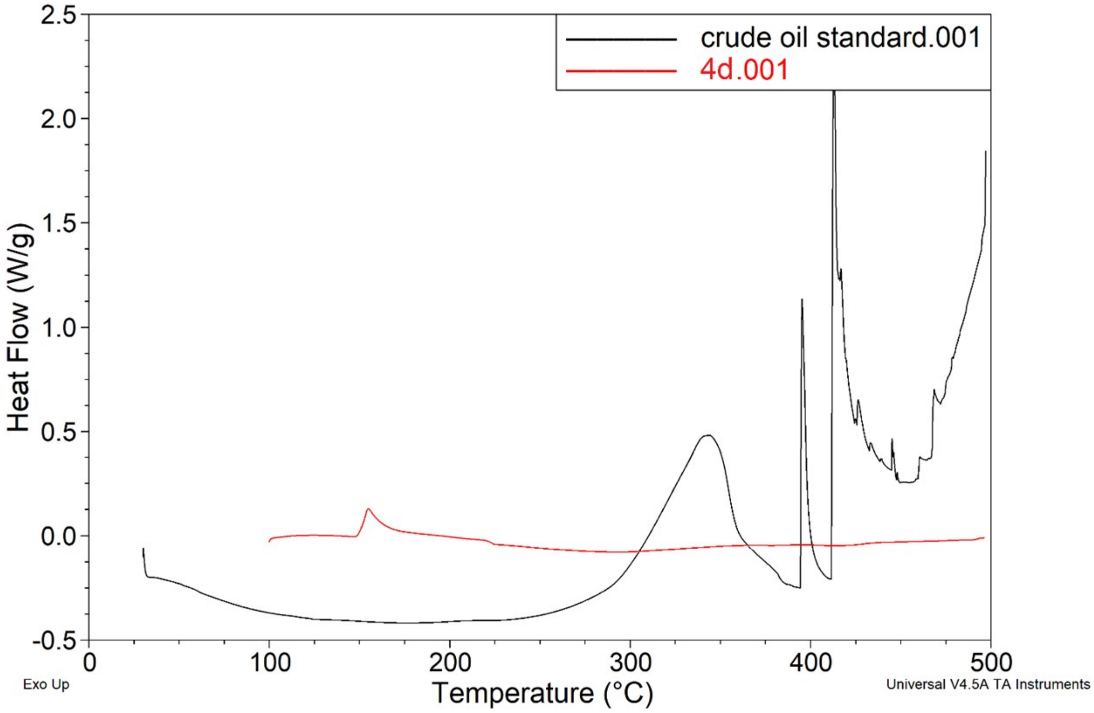

Figure S37: Sample 4d exposed to BP crude oil for 72 hr (red)

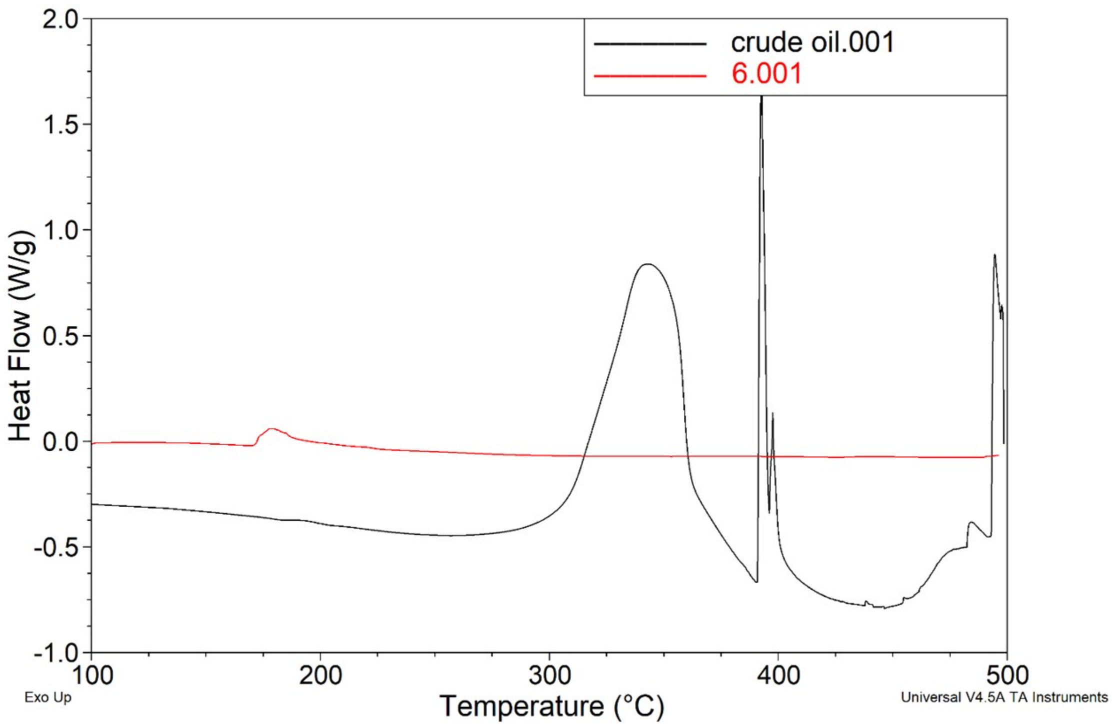

Figure S38: Sample 6 exposed to BP crude oil for 72 hr (red)

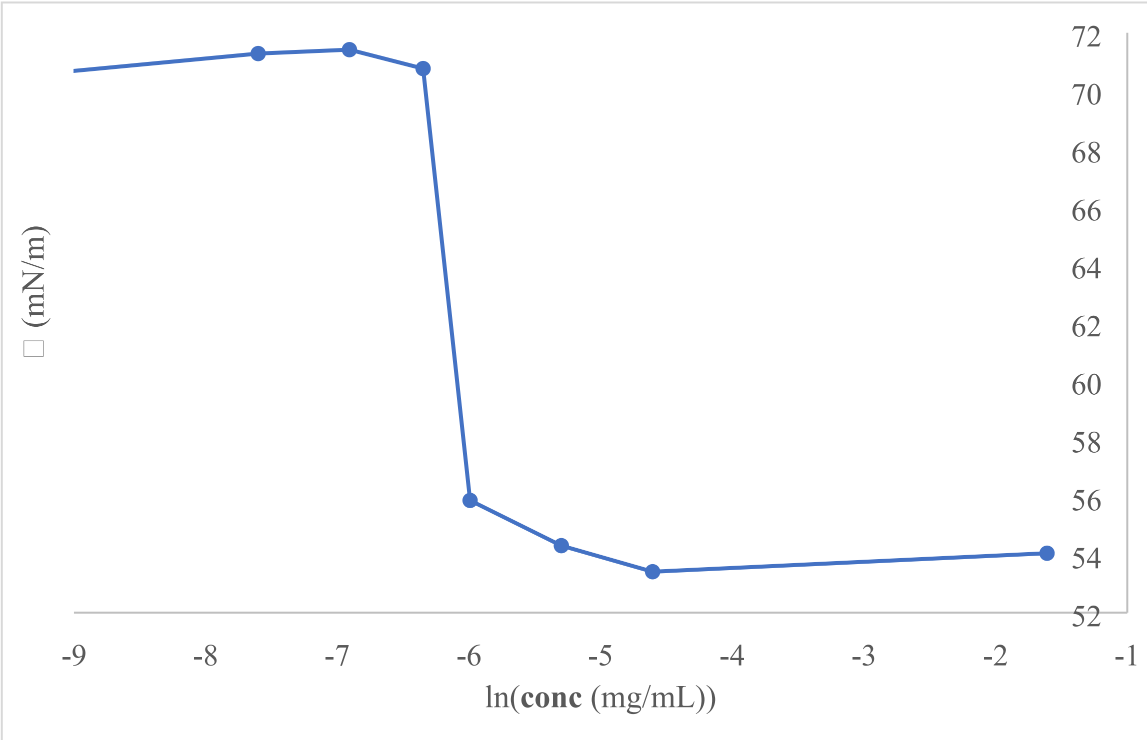

*Figure S39: A plot of surface tension (**Γ**, mN/m) vs. the natural log of concentration (mg/mL) for SiO_2-GPS-PCL-POEGMA-Br nanoparticles*