Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Self-assembled PHEA-based block copolymers for the synthesis of gold nanoparticles

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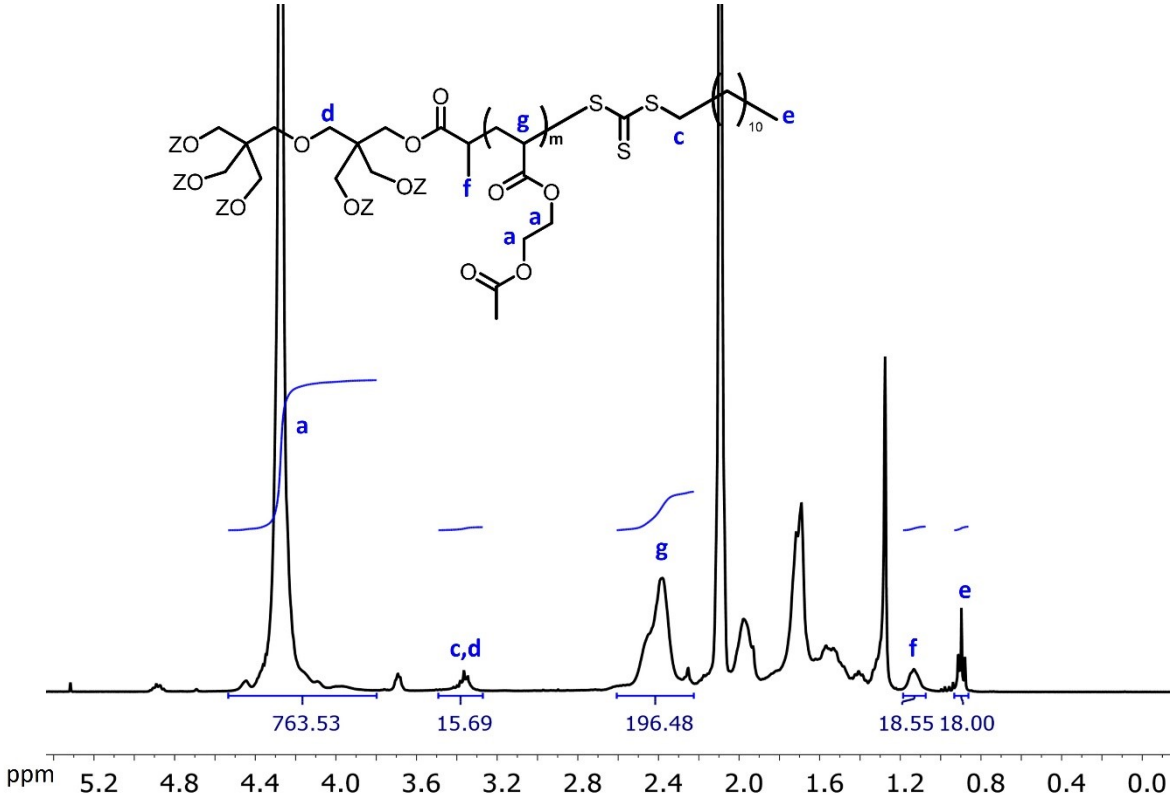

Fig. S1 ^{1}H NMR spectrum (400 MHz) in $CDCl_3$ of acetylated star-shaped $(PHEA_{32})_6$ polymers.

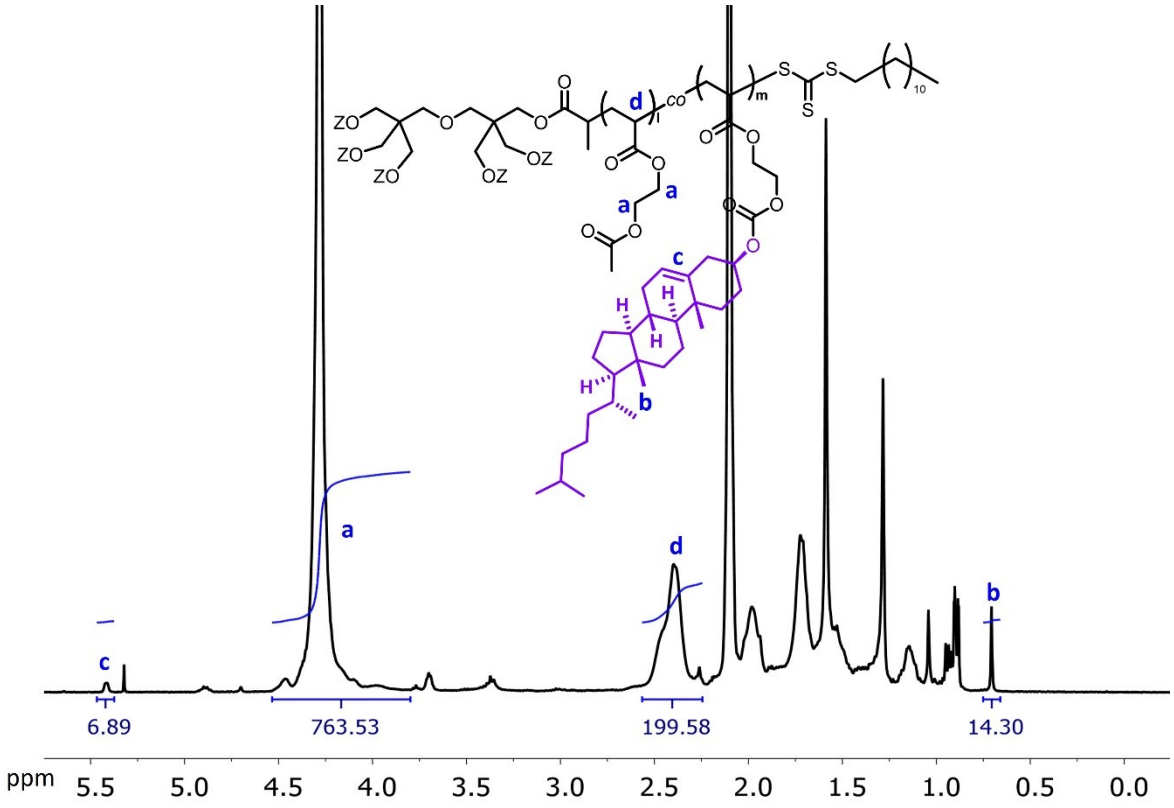

Fig. S2 ^{1}H NMR spectrum (400 MHz) in $CDCl_3$ of acetylated star-shaped ($PHEA_{32}$-*co*-$PChol_{2\%})_6$ polymers.
The peak "*b*" at 0.68 ppm is attributed to the methyl hydrogen in cholesterol. The peak "*a*" at 4.25 ppm corresponds to the methylene hydrogens in PHEA. The percentage of cholesterol substitution was calculated from the integration ratios of the peaks at 4.2 ppm and 0.68 ppm.

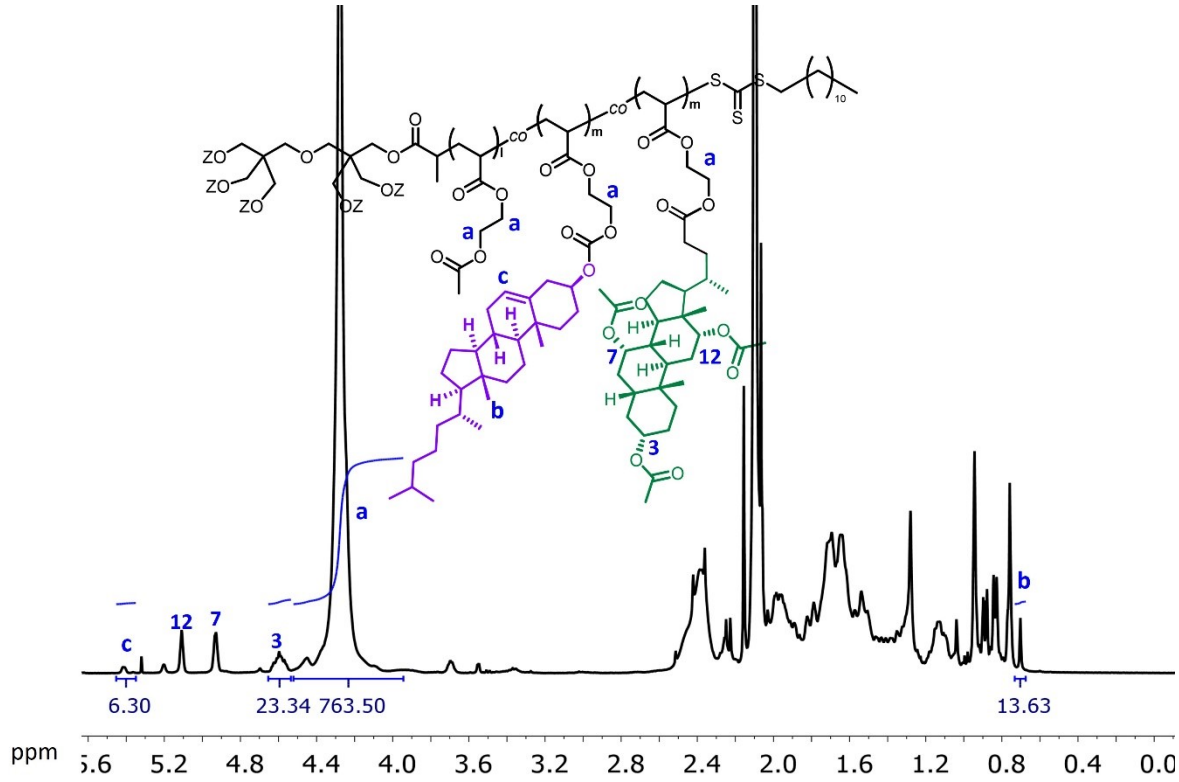

Fig. S3 ^{1}H NMR spectrum (400 MHz) in $CDCl_3$ of acetylated star-shaped ($PHEA_{32}$-*co*-$PChol_{2\%}$-*co*-$PCAE_{13\%}$)$_6$ polymers.
The peak "*3*" at 4.57 ppm is attributed to the hydrogen in the cholic acid. The peak "*a*" at 4.25 ppm corresponds to the methylene hydrogens in PHEA. The percentage of cholic acid substitution was calculated from the integration ratios of the peaks at 4.57 ppm and 4.2 ppm.

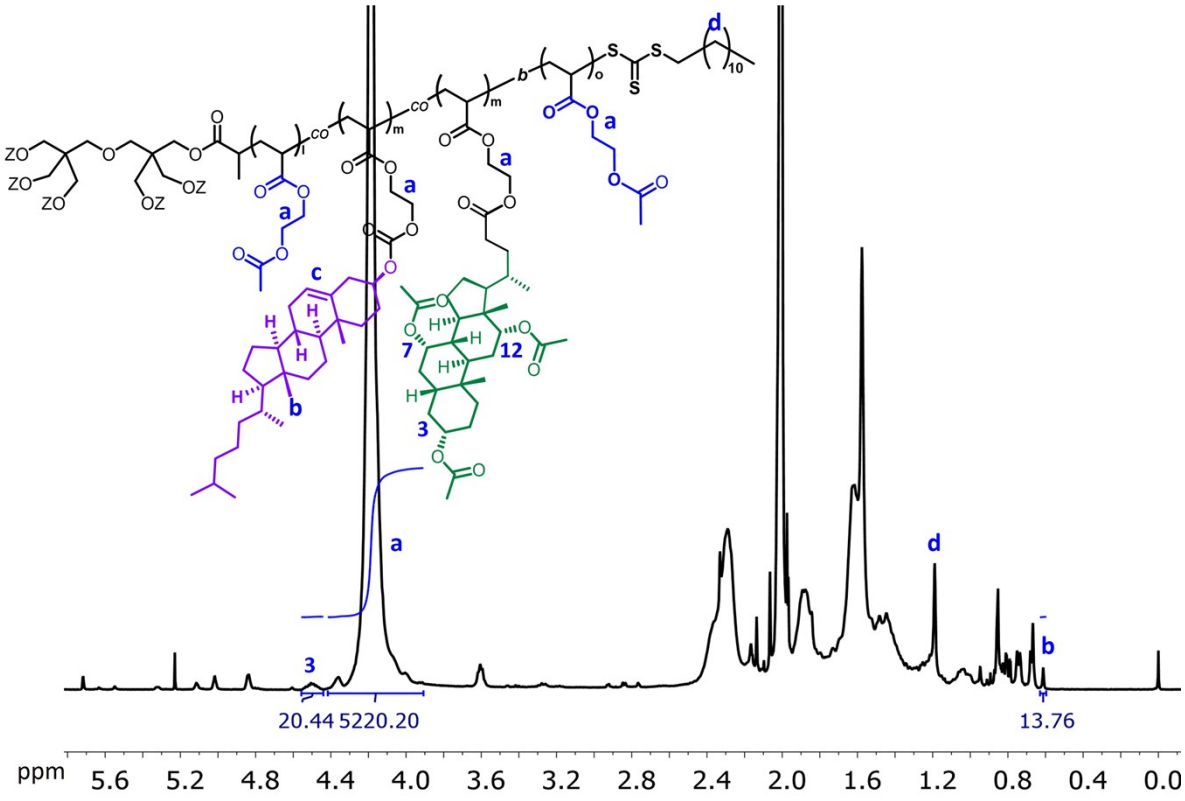

Fig. S4 ^{1}H NMR spectrum (400 MHz) in $CDCl_3$ of acetylated star-shaped ((PHEA$_{32}$-*co*-PChol$_{2\%}$-*co*-PCA$_{13\%}$)-*b*-PHEA$_{186}$)$_6$ or COP **1** polymers (Table 1, entry 1).

		Size (d.nm):	% Number:	St Dev (d.nm):
Z-Average (d.nm): 92.01	Peak 1:	10.21	100.0	2.765
PdI: 0.410	Peak 2:	0.000	0.0	0.000
Intercept: 0.988	Peak 3:	0.000	0.0	0.000

Result quality : Refer to quality report

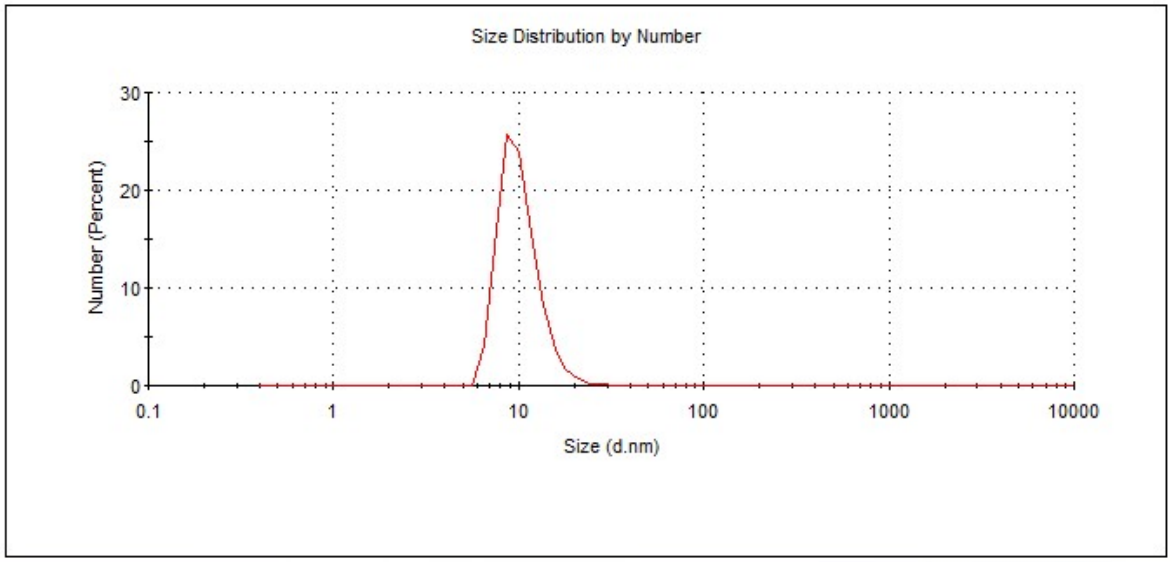

Fig. S5 DLS particle size distribution recorded for sample COP-**2** at 25 °C (*c*=0.5 g/L in distilled water).

		Size (d.nm):	% Number:	St Dev (d.nm):
Z-Average (d.nm): 45.76	Peak 1:	14.21	100.0	2.673
PdI: 1.000	Peak 2:	0.000	0.0	0.000
Intercept: 0.951	Peak 3:	0.000	0.0	0.000

Result quality : Refer to quality report

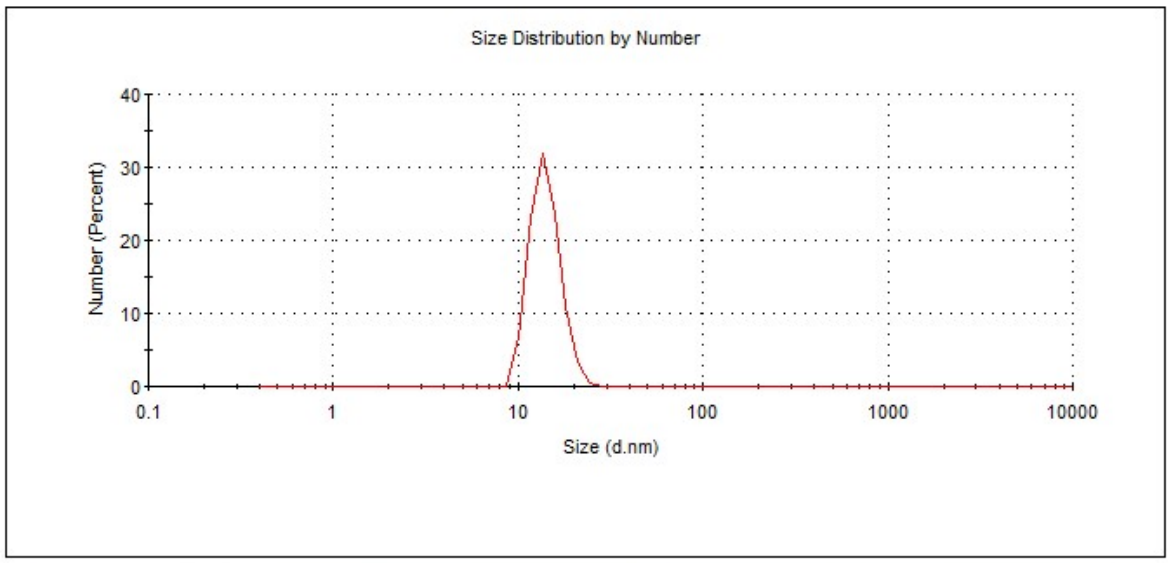

Fig. S6 DLS particle size distribution recorded for sample COP- **1** at 25 °C (*c*=0.5 g/L in distilled water).

		Size (d.nm):	% Number:	St Dev (d.nm):
Z-Average (d.nm): 80.44	Peak 1:	19.61	100.0	5.585
PdI: 0.507	Peak 2:	0.000	0.0	0.000
Intercept: 0.874	Peak 3:	0.000	0.0	0.000

Result quality : Refer to quality report

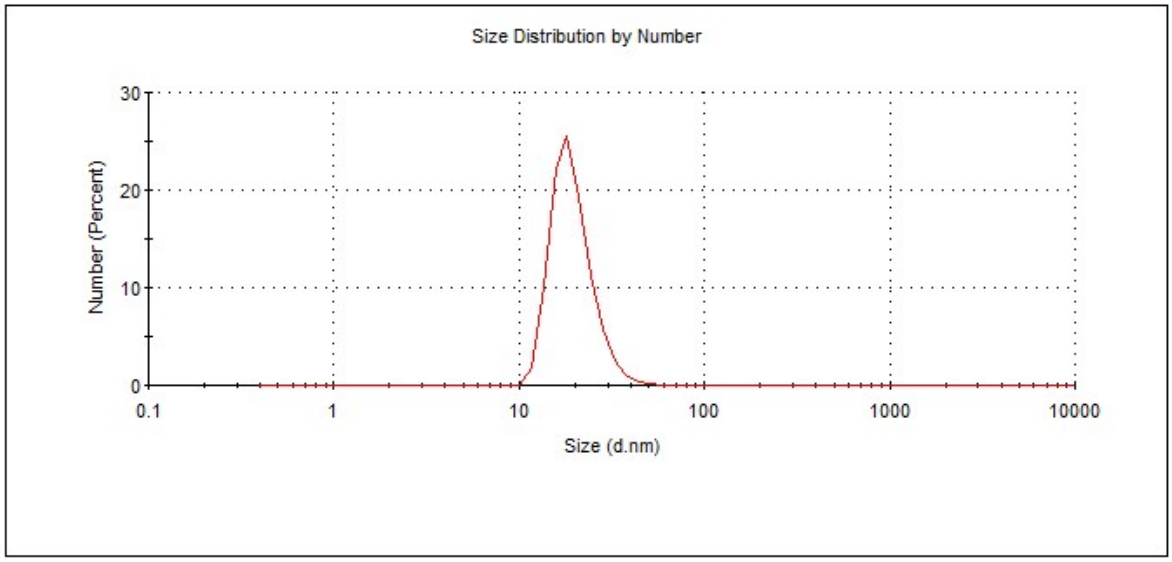

Fig. S7 DLS particle size distribution recorded for sample COP **2**@AuNPs at 25 °C (*c*=0.5 g/L in distilled water).

		Size (d.nm):	% Number:	St Dev (d.nm):
Z-Average (d.nm): 76.33	Peak 1:	21.01	100.0	5.795
PdI: 0.639	Peak 2:	0.000	0.0	0.000
Intercept: 0.860	Peak 3:	0.000	0.0	0.000

Result quality : Good

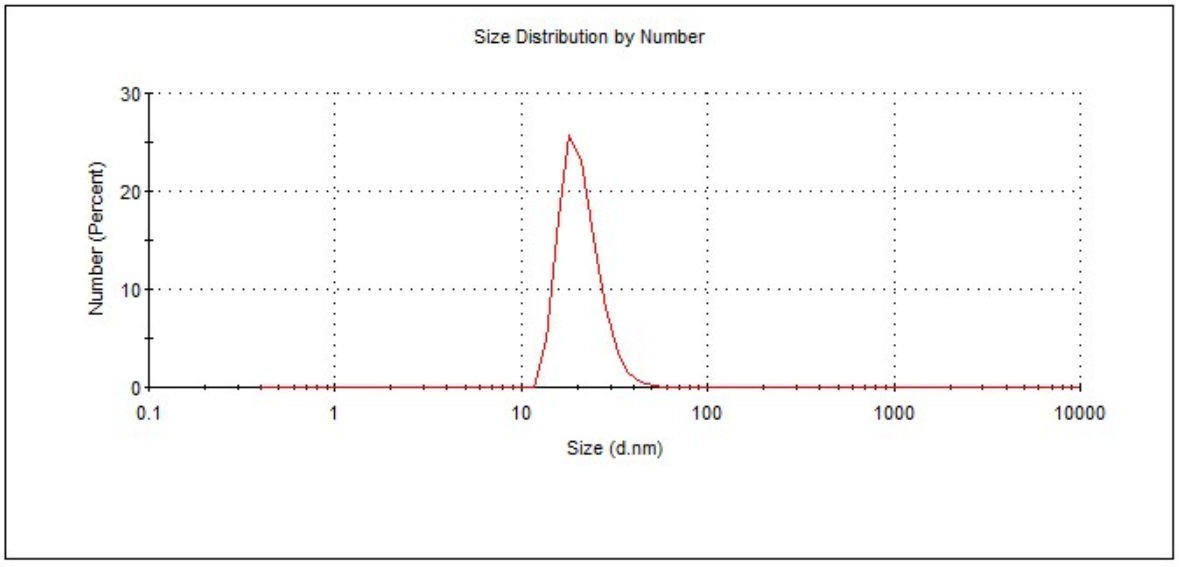

Fig. S8 DLS particle size distribution recorded for sample COP **2**@AuNPs at 20 °C (*c*=4.0 g/L in distilled water).

		Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): -4.53	Peak 1:	-4.53	100.0	3.78
Zeta Deviation (mV): 3.78	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm): 0.237	Peak 3:	0.00	0.0	0.00

Result quality : Good

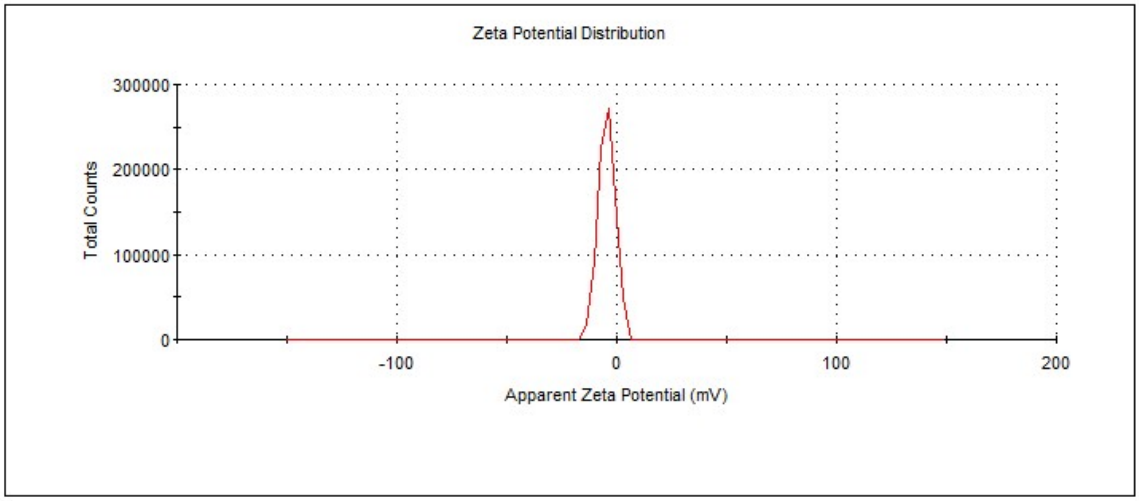

Fig. S9 Zeta potential data for sample COP **2**@AuNPs at 20 °C (*c*=1 g/L in distilled water).

		Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): -4.77	Peak 1:	-4.77	100.0	3.52
Zeta Deviation (mV): 3.52	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm): 0.238	Peak 3:	0.00	0.0	0.00

Result quality : Good

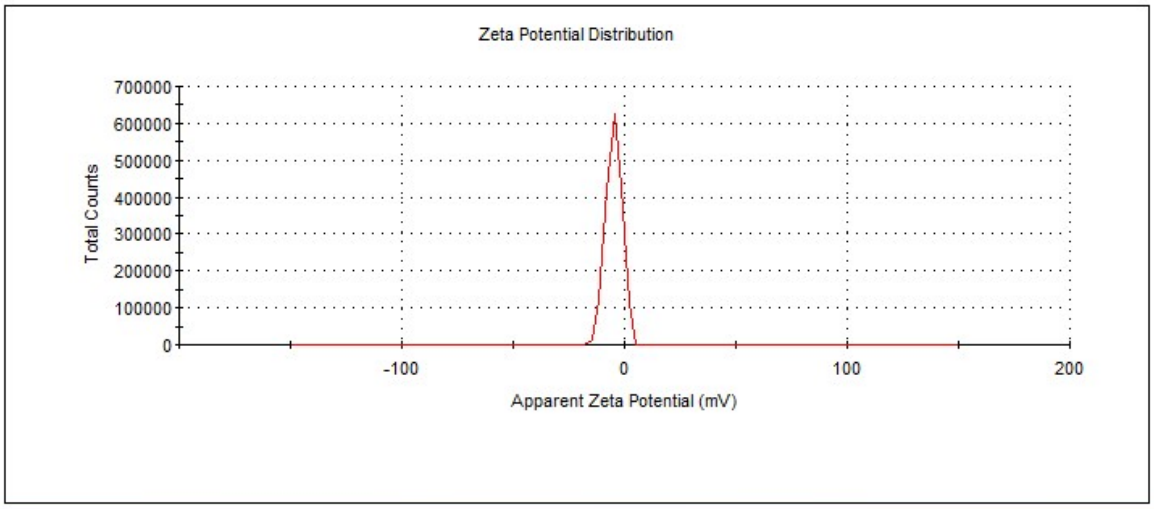

Fig. S10 Zeta potential data for sample COP **2**@AuNPs at 20 °C (*c*=4 g/L in distilled water).

Preparation of bromide precursor (3-((2-bromopropanoyl)oxy)-2-(((2-bromopropanoyl)oxy)methyl)-2-methylpropanoic acid).

2,2-bis(hydroxymethyl)propionic acid (1 g, 7.46 mmol) was dissolved in dry THF (20 mL), and pyridine was then added (1.48 g, 18.7 mmol). This solution was ice-cooled, and 2-bromopropionyl bromide (1.64 mL, 15.66 mmol in 2 mL of dry THF) was added dropwise. After complete addition, the reaction mixture was maintained in an ice bath for one hour, then at ambient temperature for 24 hours. The white suspension was filtered to remove the triethylammonium bromide. The THF was eliminated under reduced pressure. The product was re-dissolved in 20 mL of CH_2Cl_2, transferred to a separating funnel, and washed successively with a 0.01 M HCl solution (20 mL) and water (20 mL). The organic phase was dried over Na_2SO_4 and filtered. After

solvent evaporation under reduced pressure, the bromide precursor was obtained as a thick oil (65% yield).

*Synthesis of CTA-**Y*** (2-methyl-3-((2-(((propylthio)carbonothioyl)thio)propanoyl)oxy)-2-(((2-(((propylthio)carbonothioyl)thio)propanoyl)oxy)methyl)propanoic acid). Propanethiol (1.0 g, 13.15 mmol) was dissolved in THF (10 mL), and triethylamine (3.66 mL, 26.31 mmol) was added. This solution was cooled with ice/water, and CS_2 was added dropwise (1.368 mL, 18 mmol). Next, the bromide precursor was added to the solution (2.59 g, 6.4 mmol) and stirred overnight at room temperature. The salt was removed by filtration, and the filtrate was evaporated under reduced pressure. Next, the product was dissolved in 20 mL of CH_2Cl_2 and washed with 20 mL of HCl (0.01 M) and water. The water in the product was removed by drying from Na_2SO_4. After evaporation of the solvent under reduced pressure, the CTA-**Y** was purified using column chromatography on silica gel (the product was recovered with ethyl acetate). The CTA-Y was obtained as a yellow sticky oil (75%).

*CTA Y***.** ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 4.84 (CH_3-C***H***-S, q, 2H), 4.29 (-COO-CH_2-, m, 4H), 3.34 (-CH_2C***H***$_2$-S, t, 4H), 1.73 (-S-CH_2-C***H***$_2$, sext, 6H), 1.59 (C***H***$_3$-CH-S, d, 6H), 1.28 (C***H***$_3$C**,** s, 3H), 1.02 (C***H***$_3$$CH_2$-, t, 6H) (See Fig. S11). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): selected peaks: 221 (***C***=S), 178 (***C***OOH), 170 (***C***=O), 65.97 (-COO-**C**H_2-), 13.45 (***C***H_3CH_2-) (See Fig. S12).

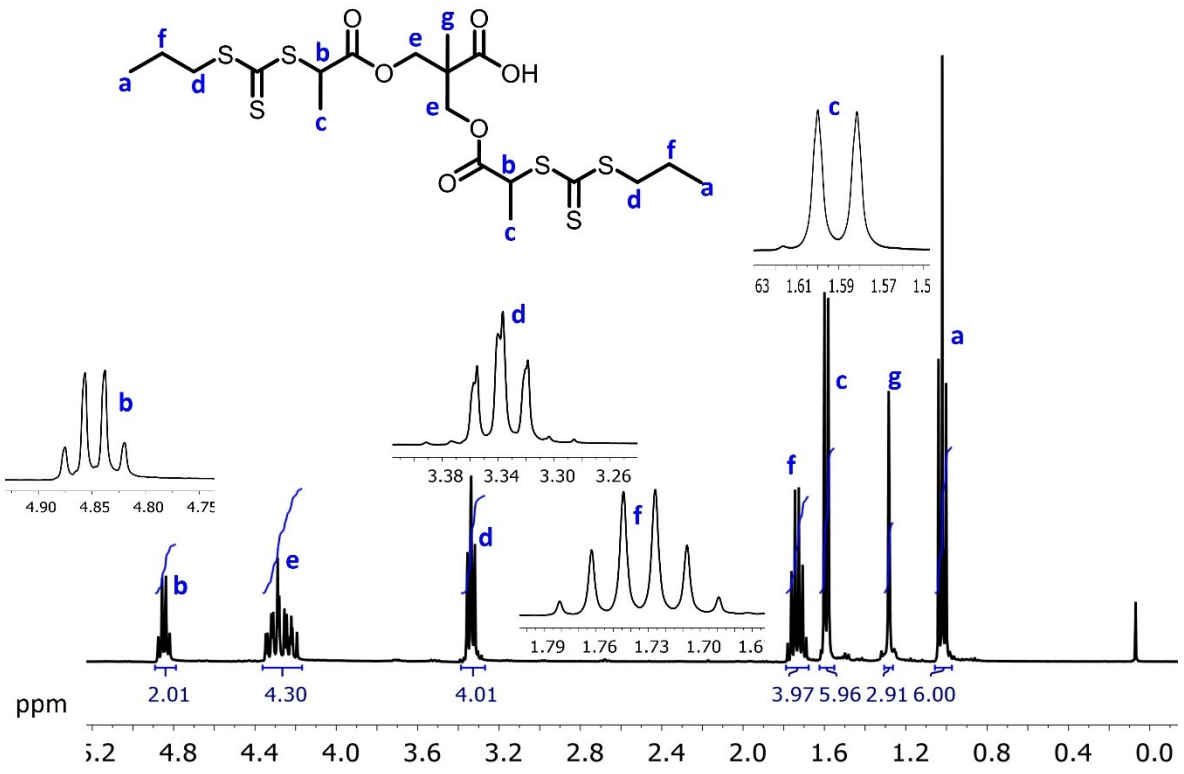

Fig. S11 ^{1}H-NMR (400 MHz) spectrum of *CTA-**Y*** (2-methyl-3-((2-(((propylthio)carbonothioyl)thio)propanoyl)oxy)-2-(((2(((propylthio)carbonothioyl)thio)propanoyl)oxy)methyl)propanoic acid) in $CDCl_3$.

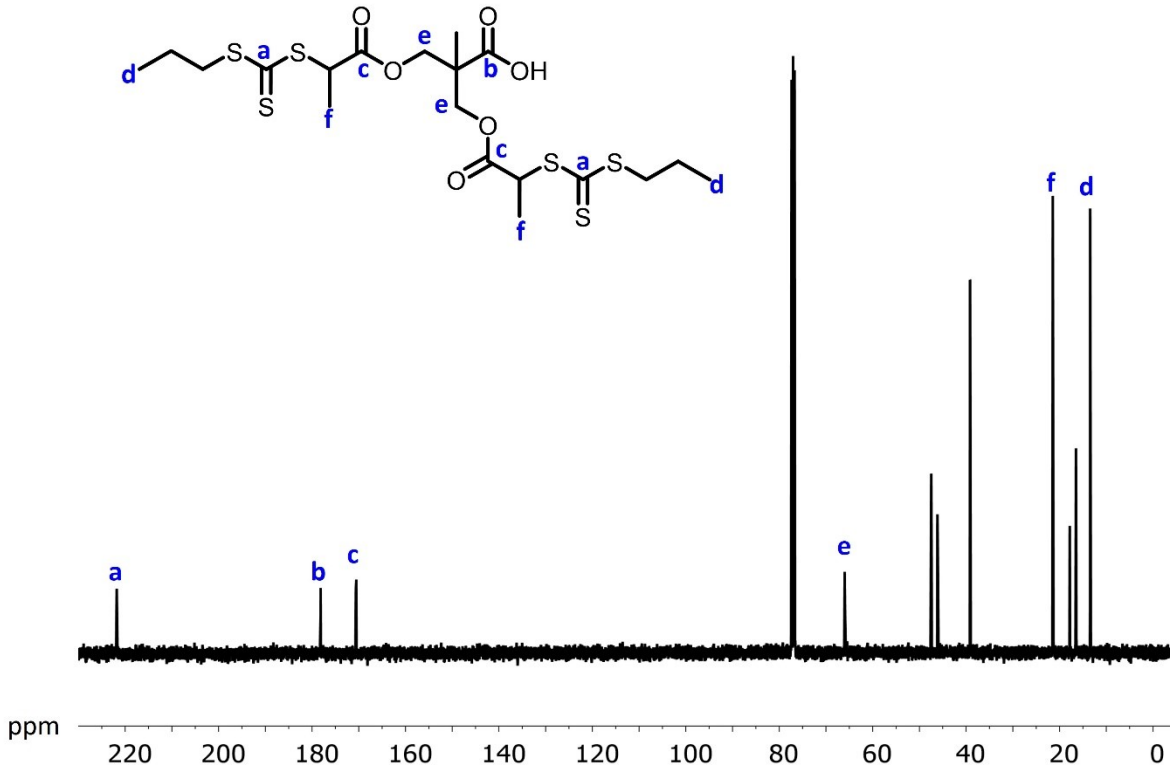

Fig. S12 ^{13}C-NMR (100 MHz) spectrum of *CTA-**Y*** (2-methyl-3-((2-(((propylthio)carbonothioyl)thio)propanoyl)oxy)-2-(((2(((propylthio)carbonothioyl)thio)propanoyl)oxy)methyl)propanoic acid) in $CDCl_3$.

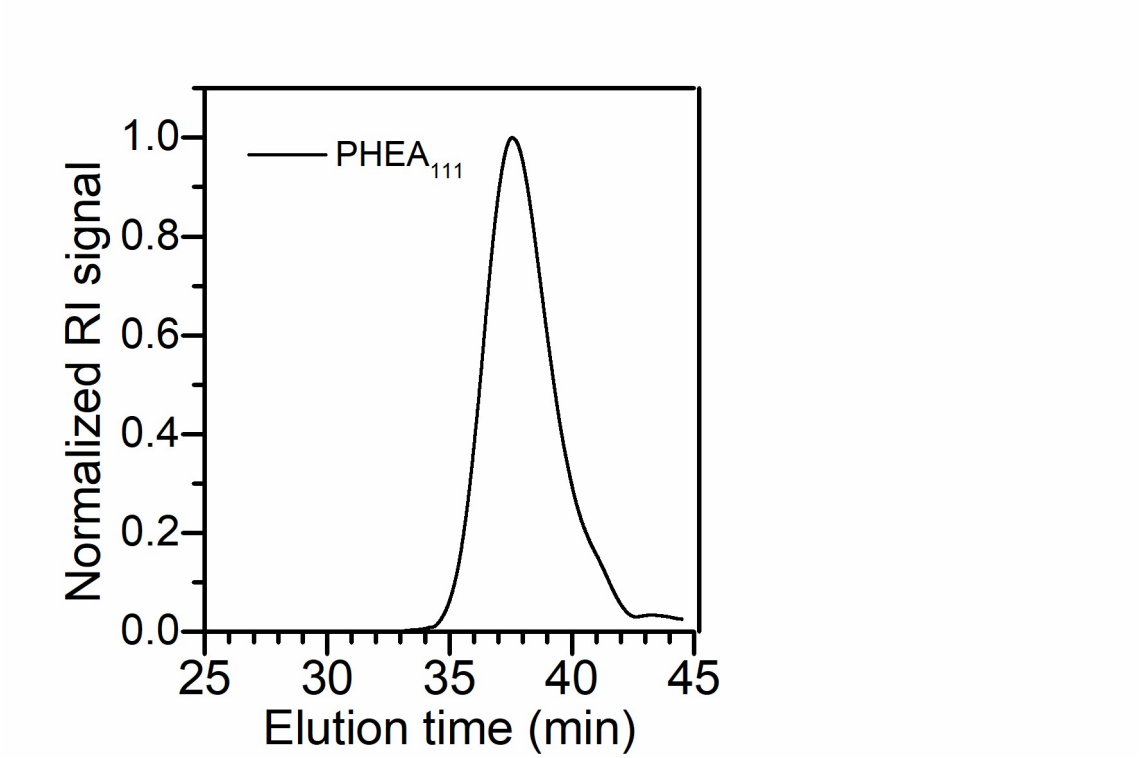

Fig. S13 Normalized GPC traces in THF for $PHEA_{111}$ polymer. M_{nGPC}=12,880 g/mol and $Đ$=1.14.

a) b)

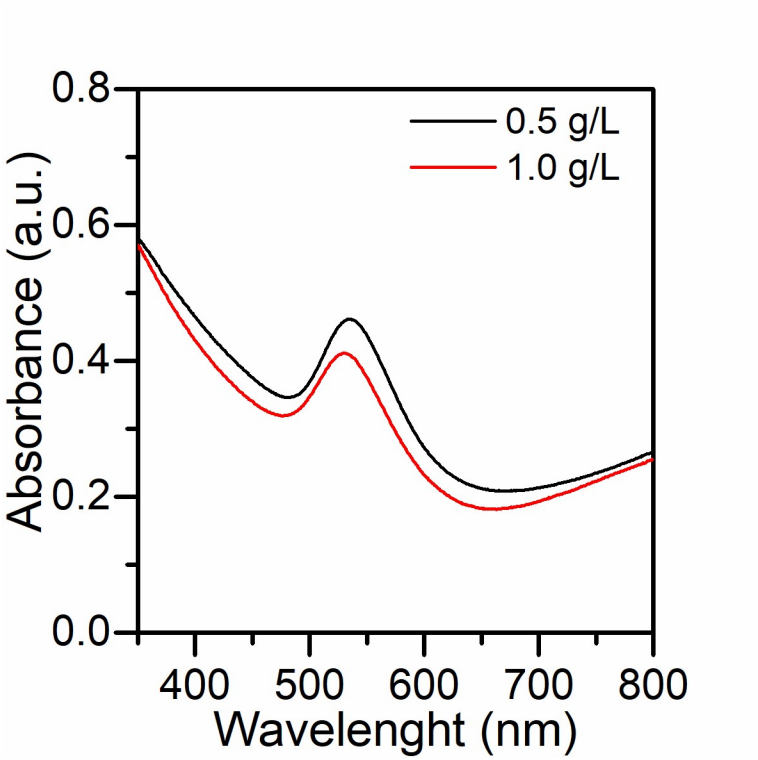

Fig. S14 AuNPs synthesized at 70 °C using with concentration of 0.5 g/L and 1 g/L) of lineal PHEA homopolymer as a reducing and stabilizing agent. a) UV-vis spectra and photograph.

		Size (d.nm):	% Number:	St Dev (d.nm):
Z-Average (d.nm): 166.3	Peak 1:	3.216	99.8	0.5429
PdI: 0.945	Peak 2:	9.461	0.2	1.696
Intercept: 0.919	Peak 3:	0.000	0.0	0.000

Result quality : Refer to quality report

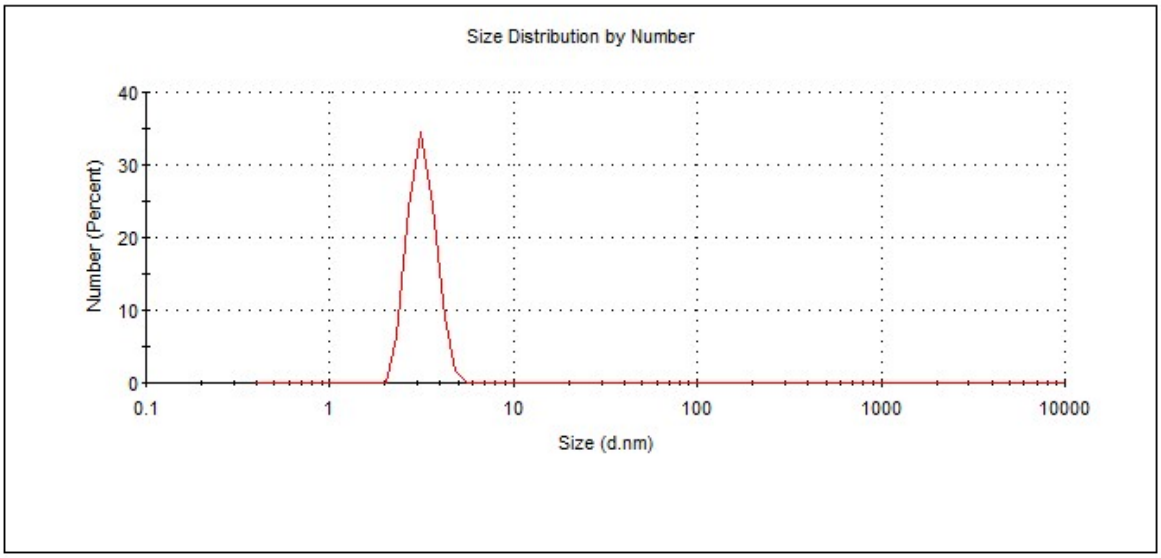

Fig. S15. DLS particle size distribution recorded for $PHEA_{111}$ PHEA@AuNPs at 25 °C (*c*=1.0 g/L in distilled water).