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

Aqueous (co)polymer stabilisers for size-controlled 2-5 nm gold nanoparticle synthesis with tuneable catalytic activity

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Supplementary Information

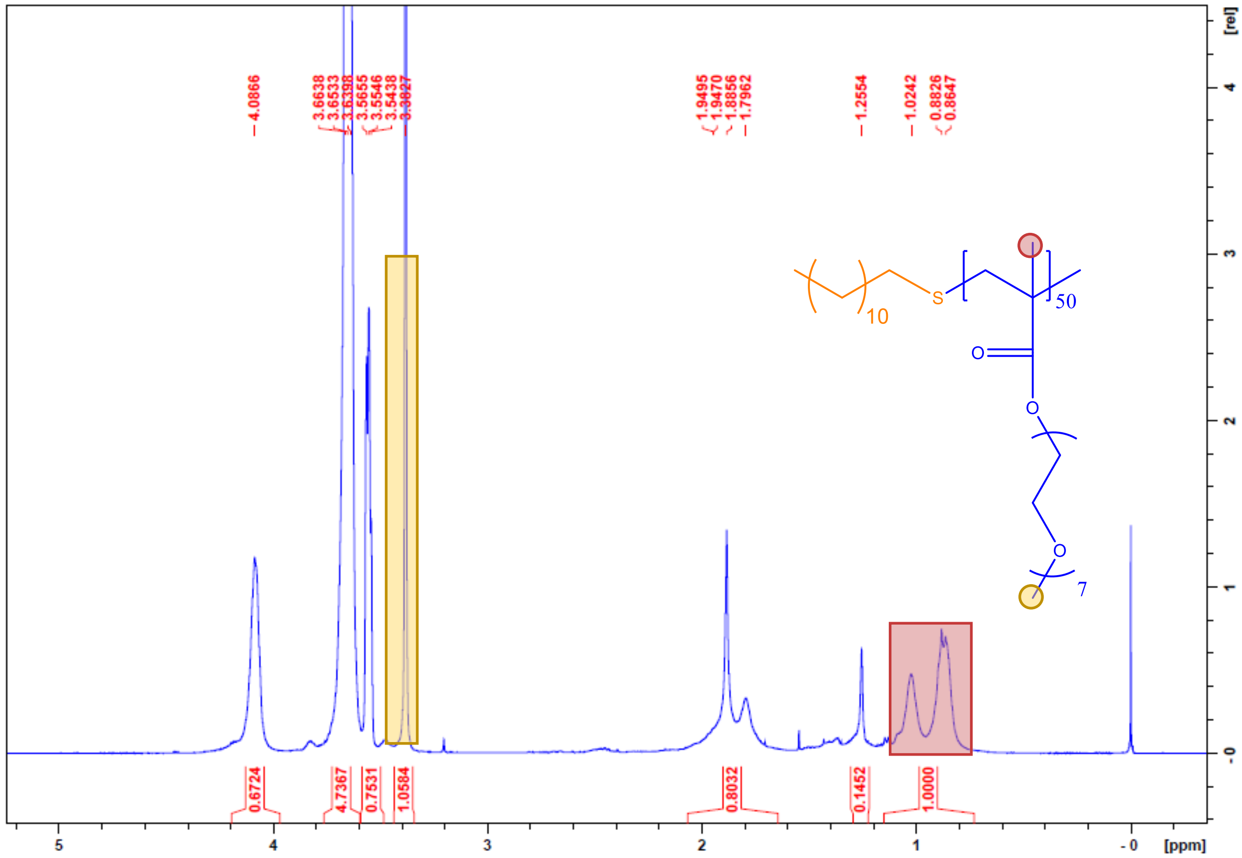

Figure S1. ^{1}H NMR spectrum of linear homo-polymer DDT-*p*(OEGMA$_{50}$)

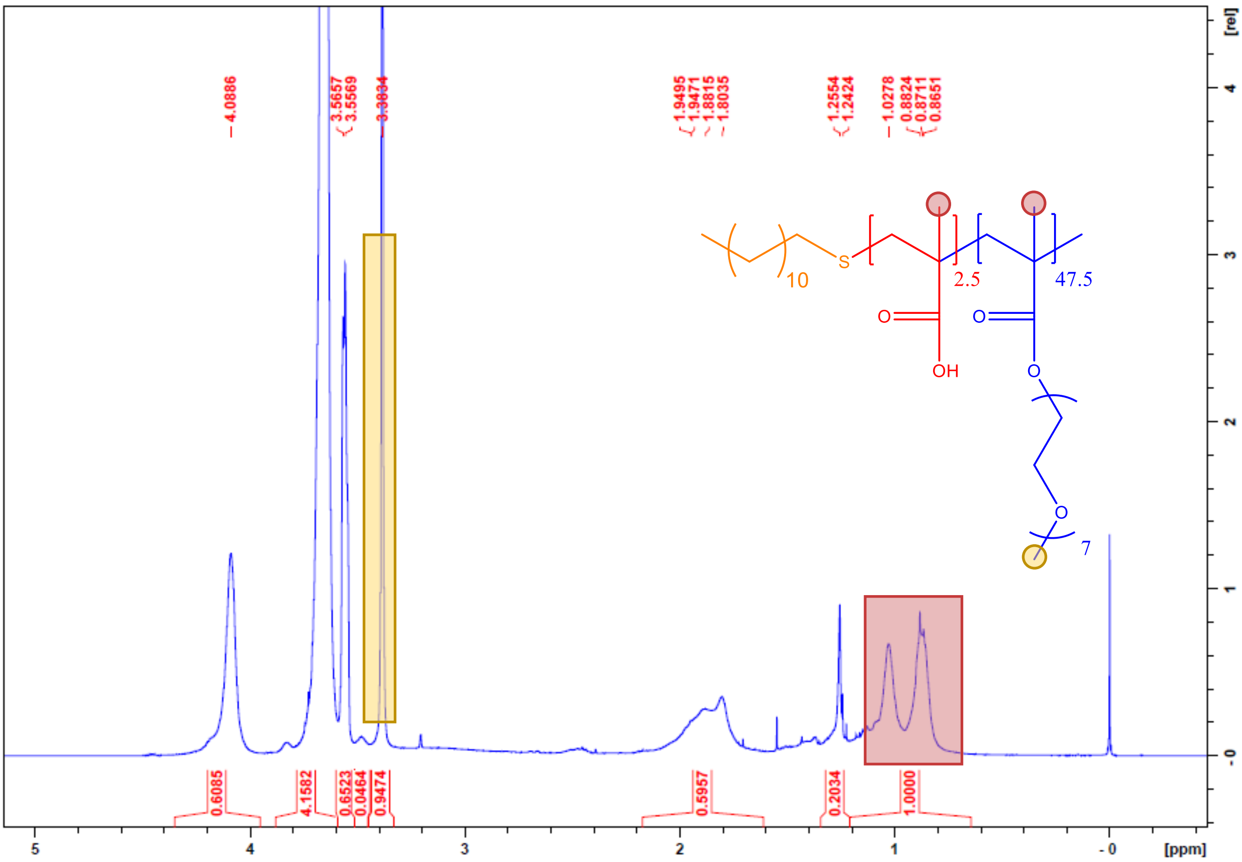

Figure S2. ^{1}H NMR spectrum of linear (co)polymer DDT-*p*(OEGMA$_{47.5}$-*co*-MAA$_{2.5}$)

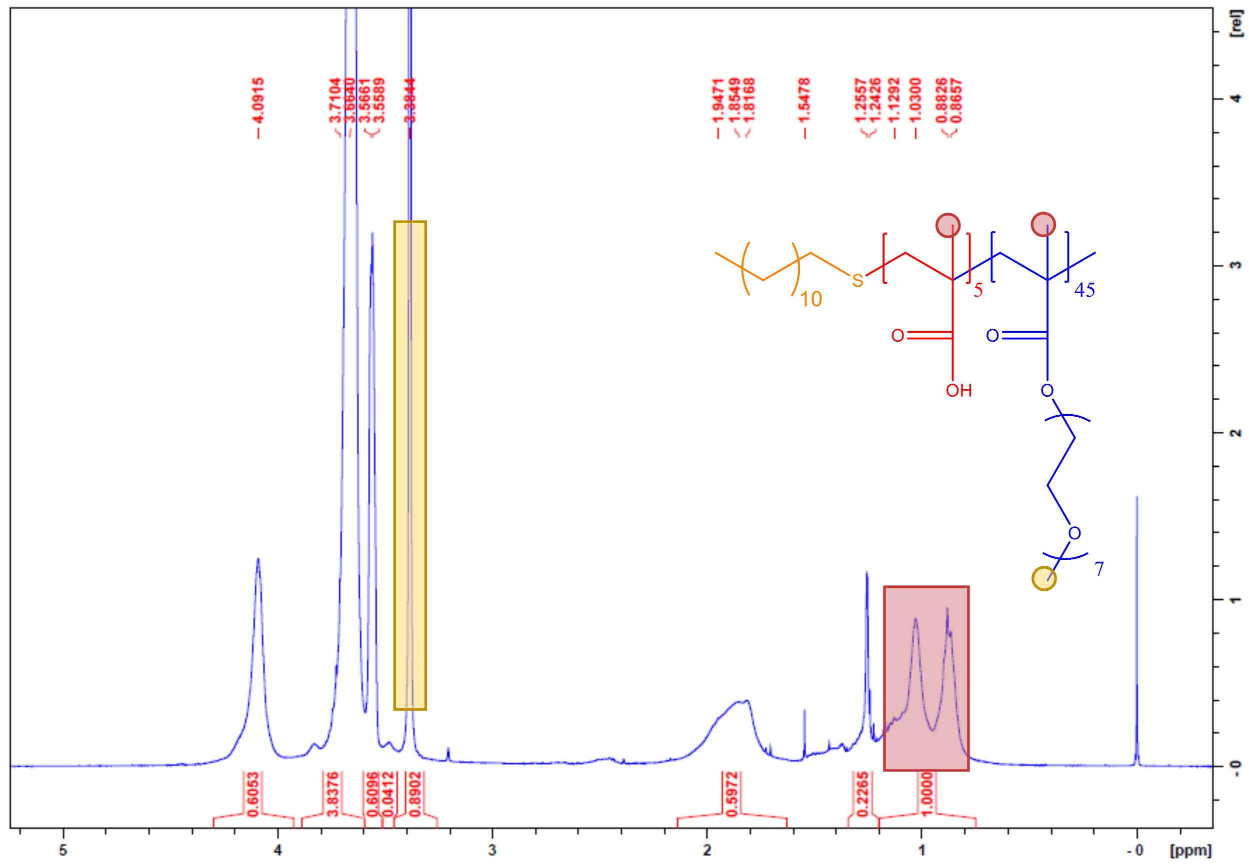

Figure S3. ^{1}H NMR spectrum of linear (co)polymer DDT-*p*(OEGMA$_{45}$-*co*-MAA$_5$)

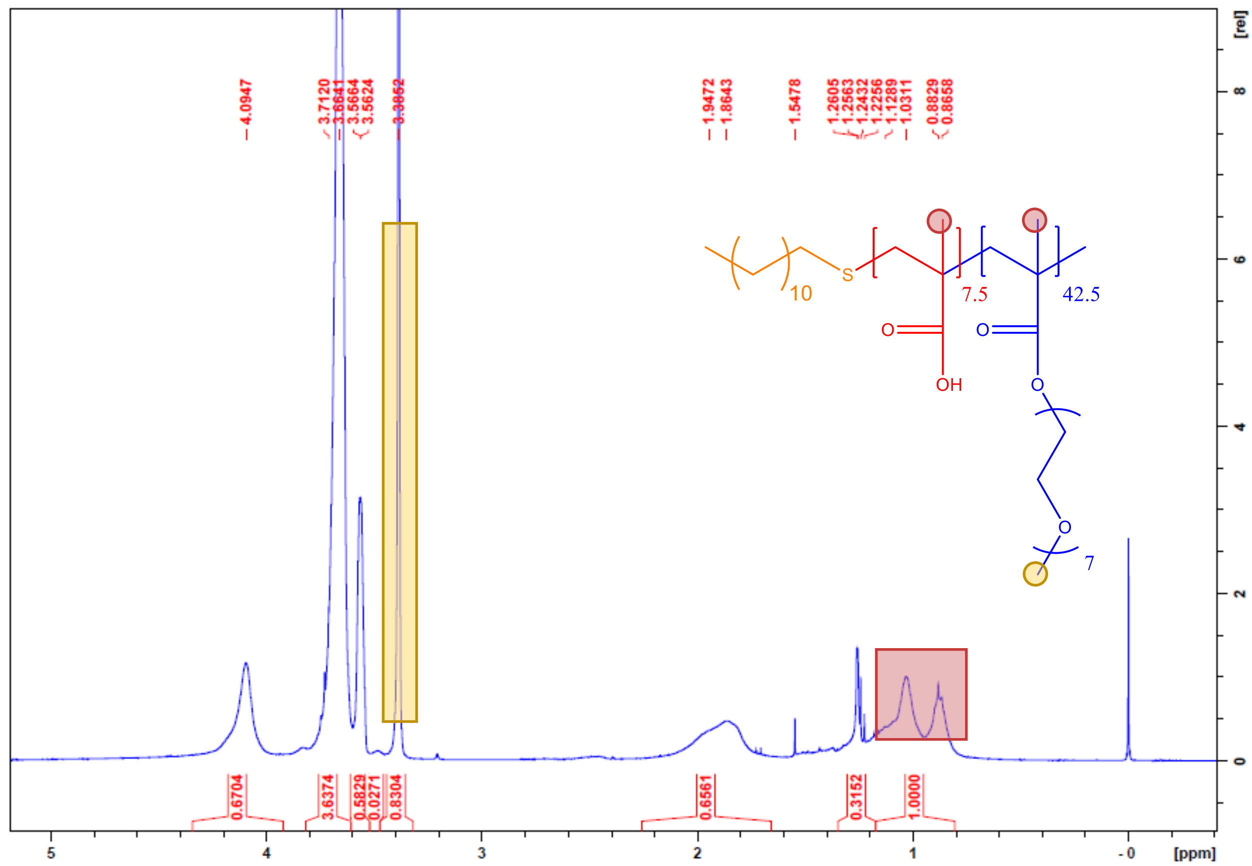

Figure S4. ^{1}H NMR spectrum of linear (co)polymer DDT-*p*(OEGMA$_{42.5}$-*co*-MAA$_{7.5}$)

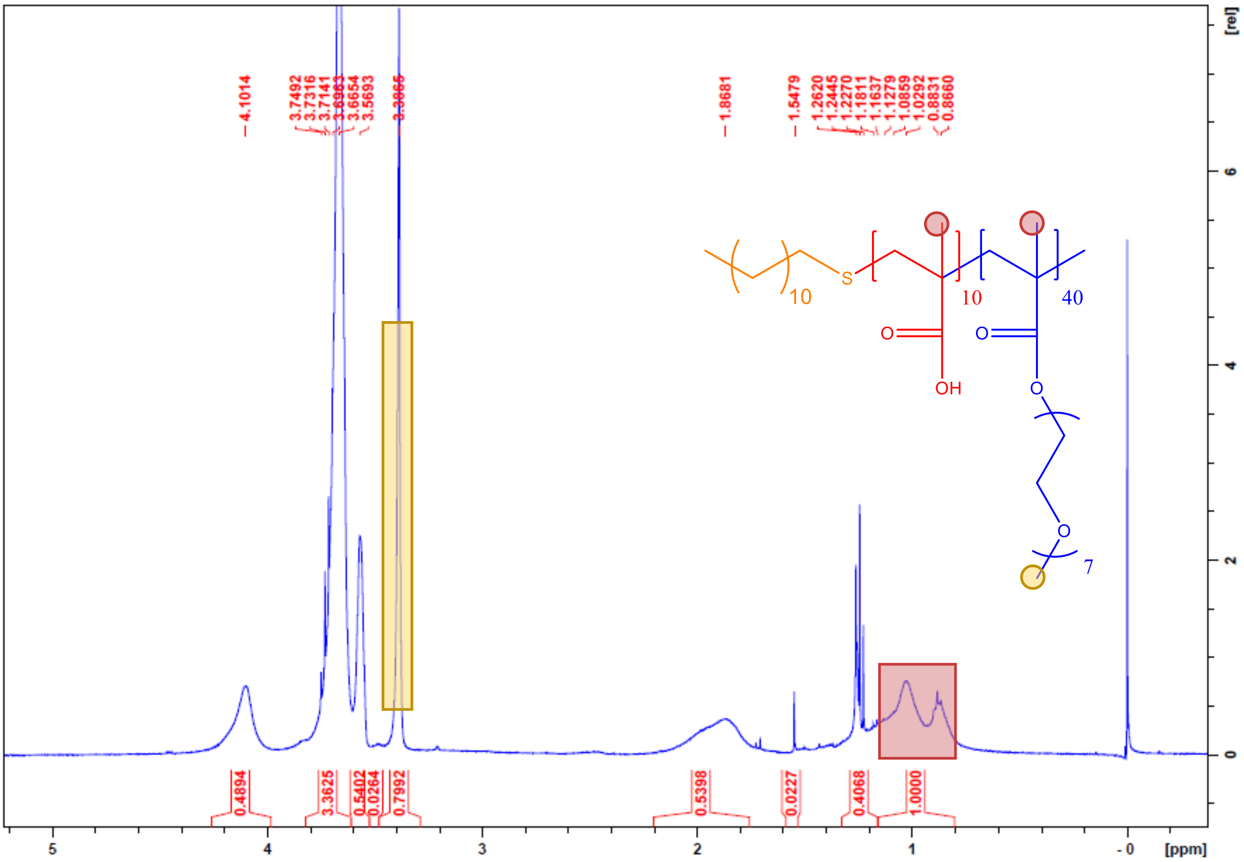

Figure S5. ^1H NMR spectrum of linear (co)polymer DDT-*p*(OEGMA$_{40}$-*co*-MAA$_{10}$)

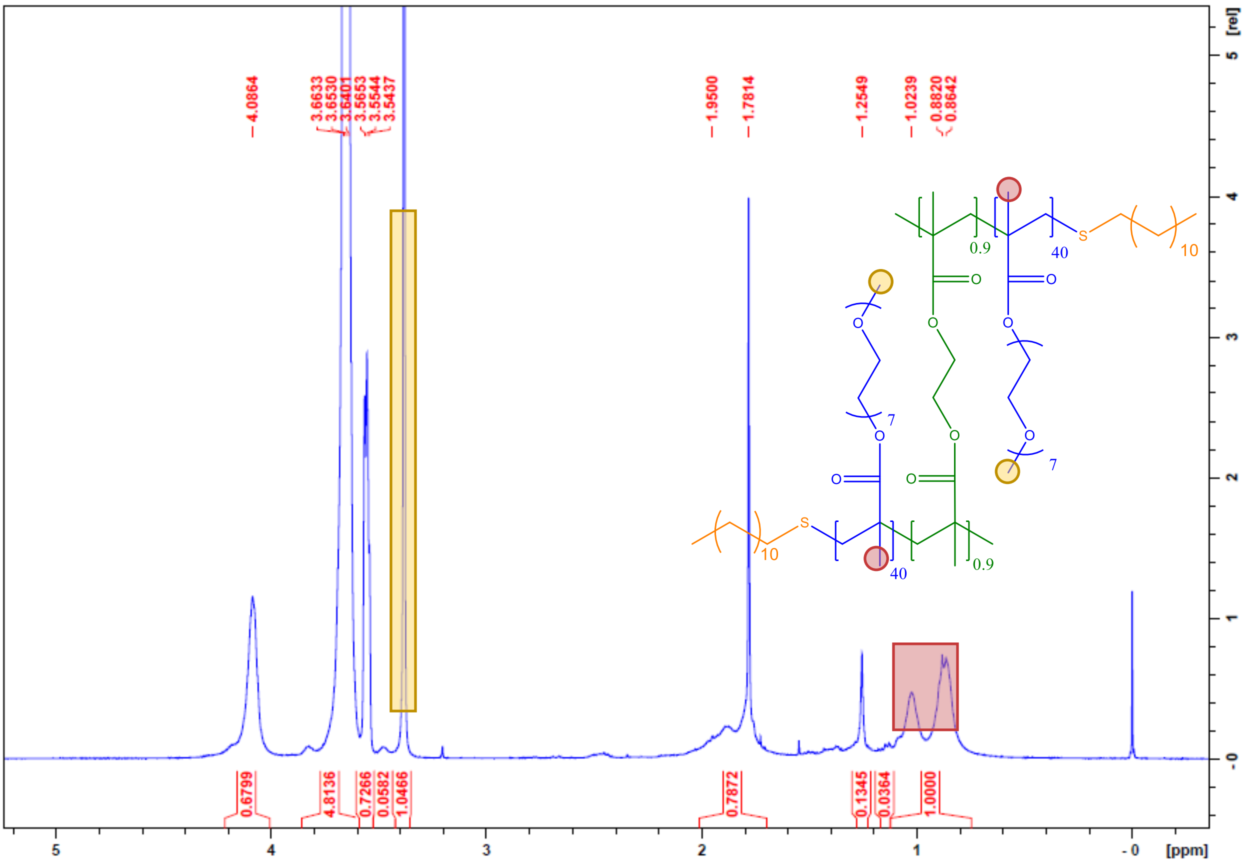

Figure S6. ^1H NMR spectrum of branched (co)polymer DDT-*p*(OEGMA$_{50}$-coEGDMA$_{0.8}$)

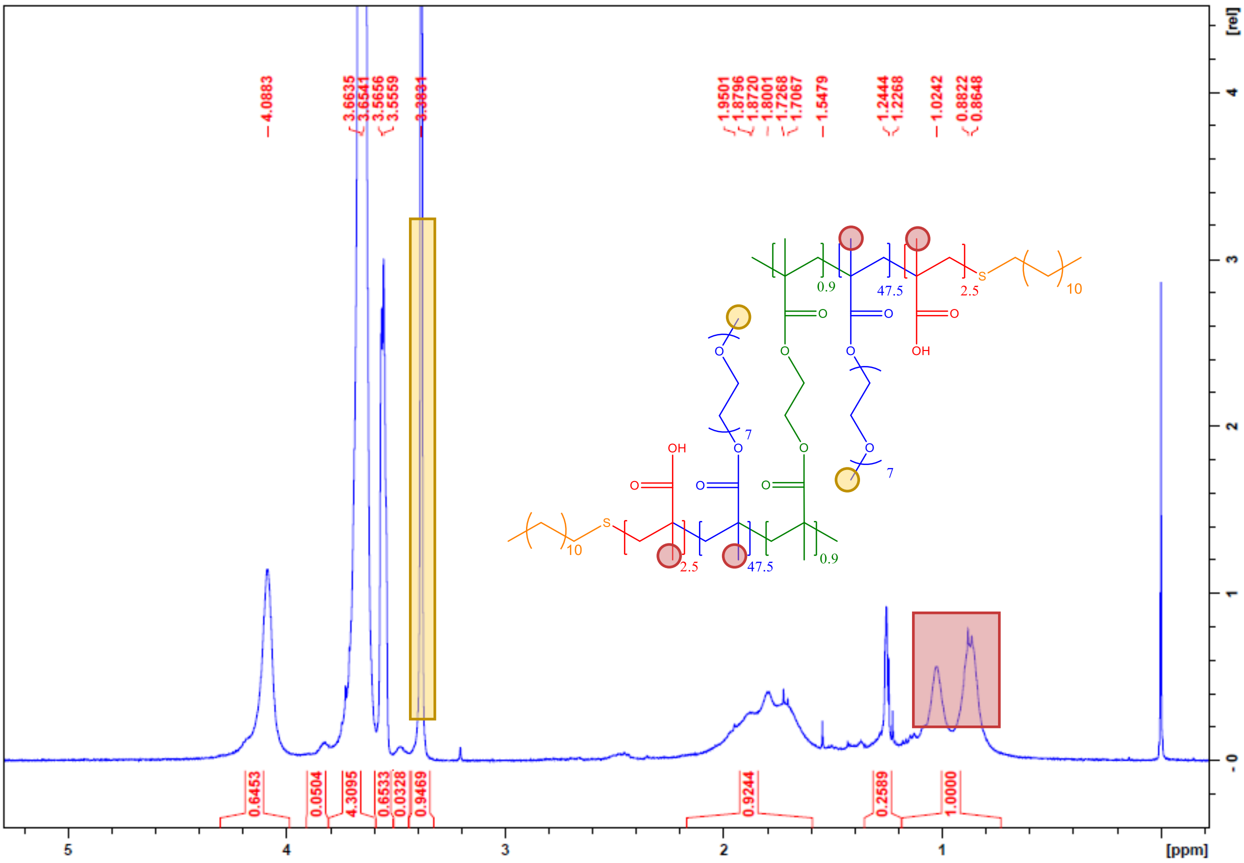

Figure S7. ¹H NMR spectrum of branched (co)polymer DDT-*p*(OEGMA$_{47.5}$-*co*-MAA$_{2.5}$-*co*-EGDMA$_{0.9}$)

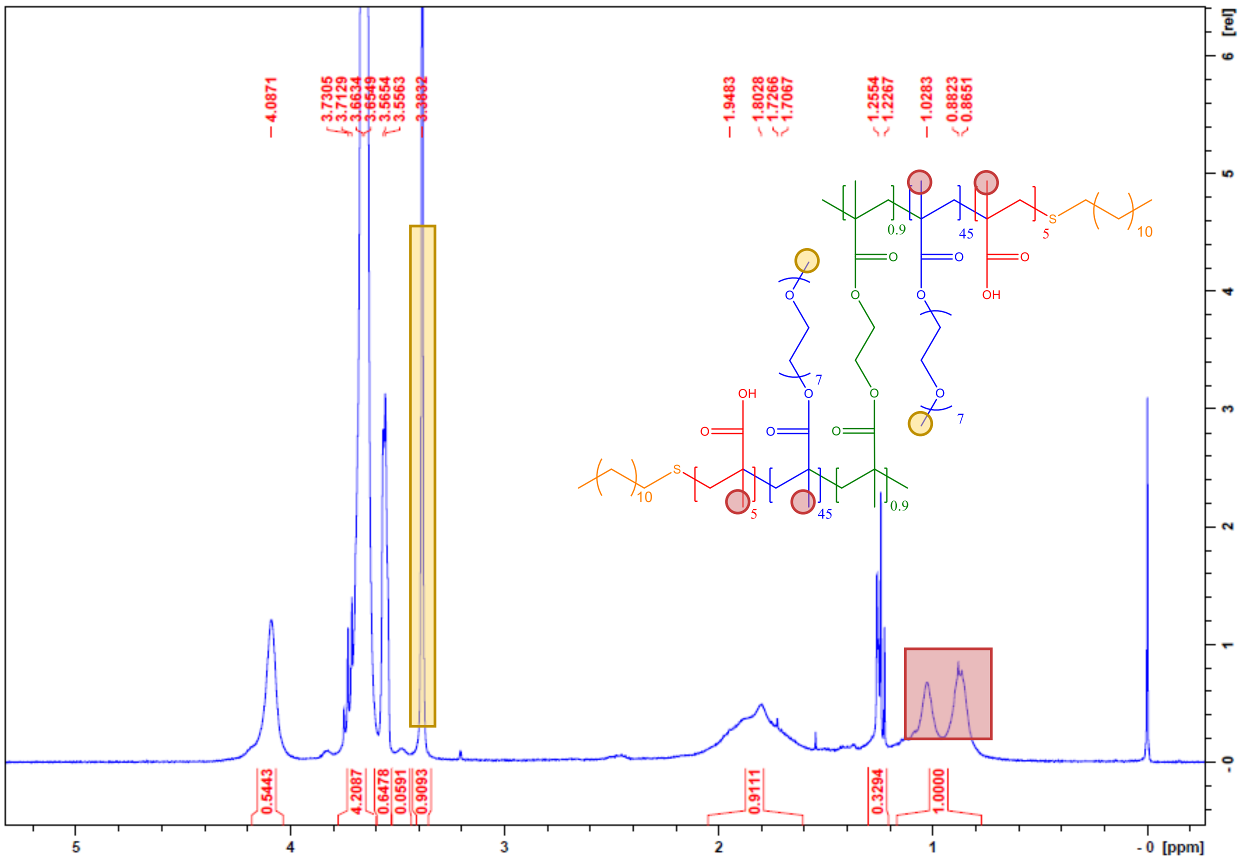

Figure S8. ¹H NMR spectrum of branched (co)polymer DDT-*p*(OEGMA$_{45}$-*co*-MAA$_{5}$-*co*-EGDMA$_{0.9}$)

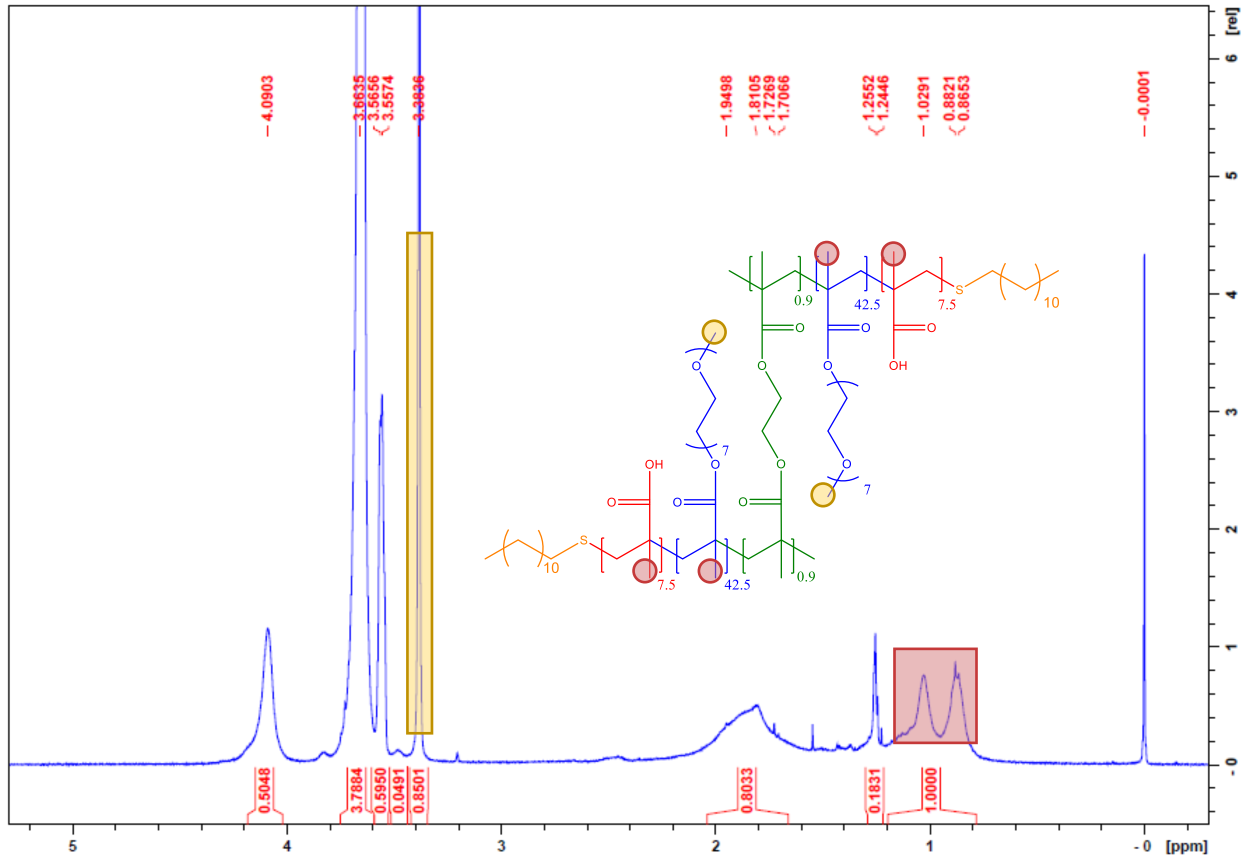

Figure S9. ^{1}H NMR spectrum of branched (co)polymer DDT-*p*($OEGMA_{42.5}$-*co*-$MAA_{7.5}$-*co*-$EGDMA_{0.9}$)

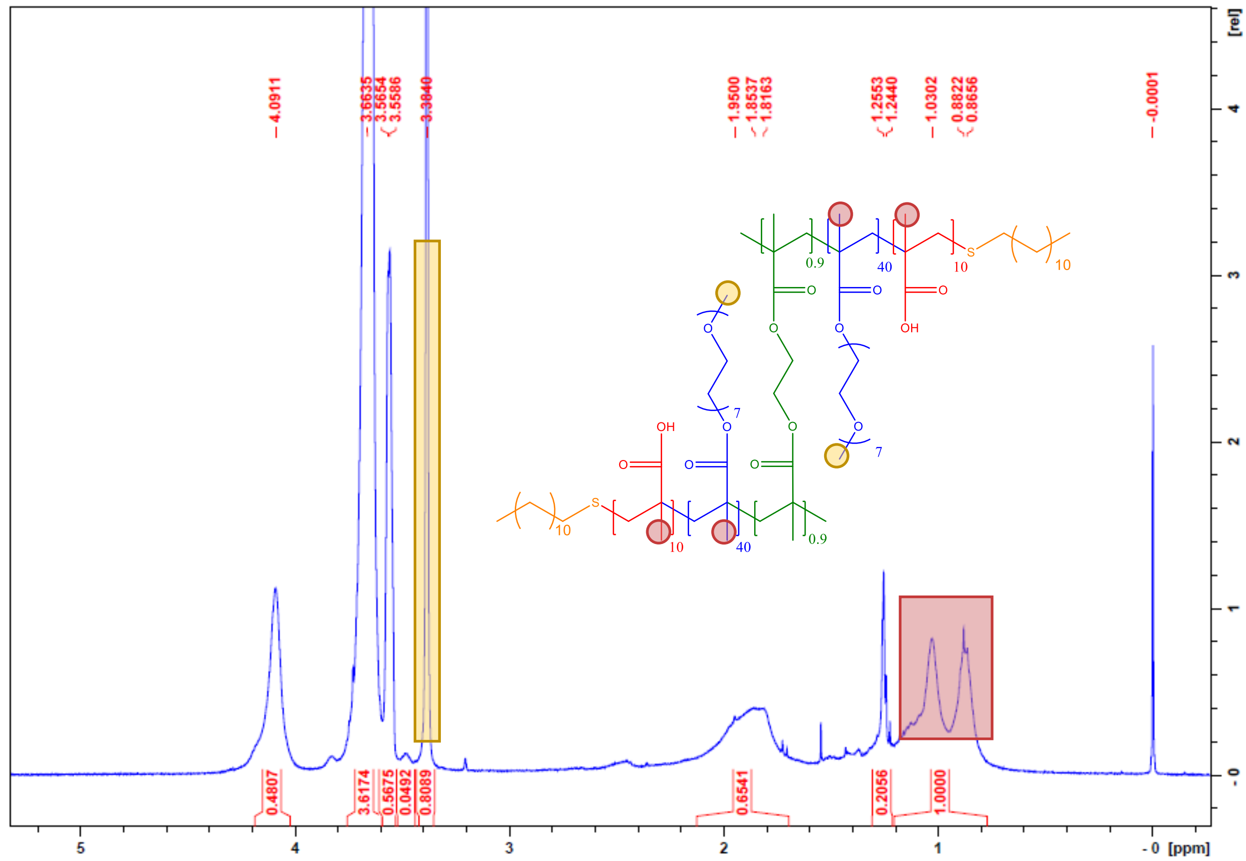

Figure S10. ^{1}H NMR spectrum of branched (co)polymer DDT-*p*($OEGMA_{40}$-*co*-MAA_{10}-*co*-$EGDMA_{0.9}$)

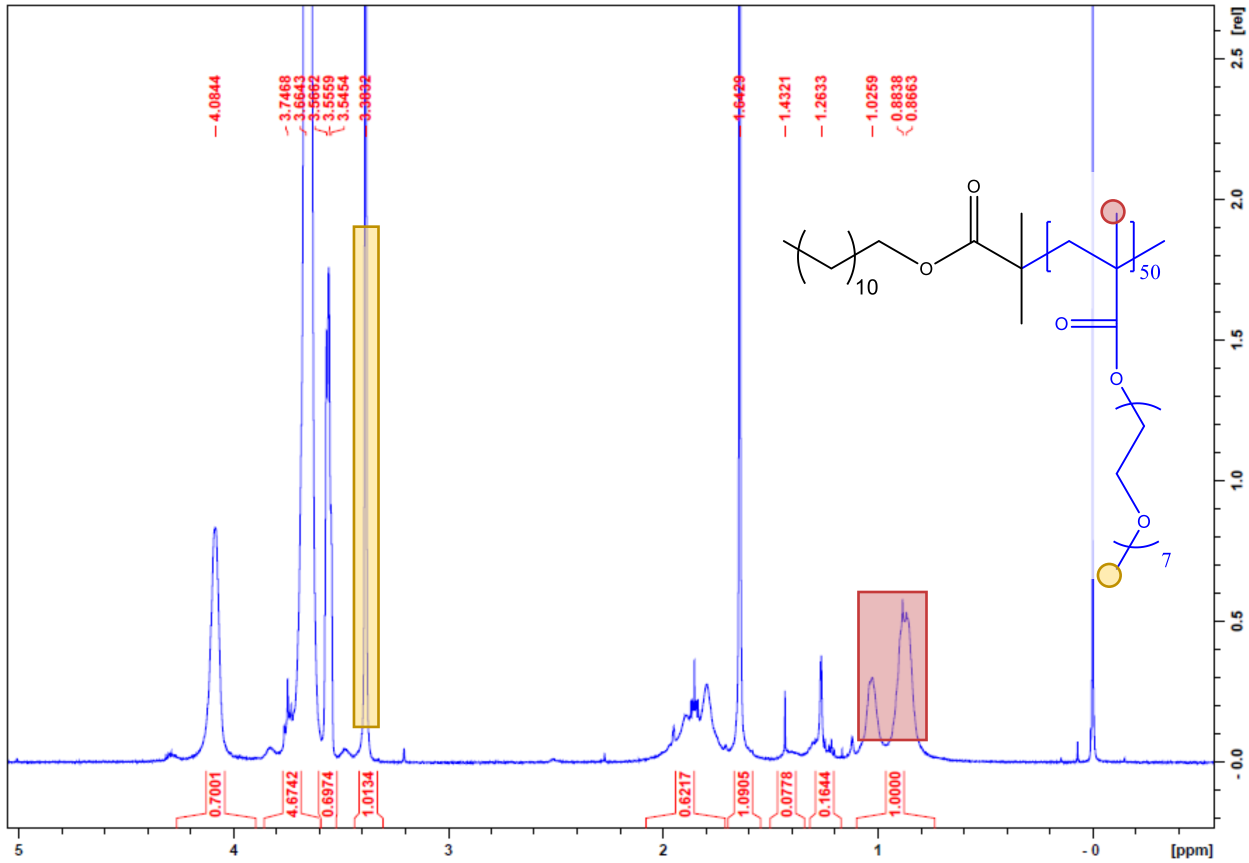

Figure S11. ^{1}H NMR spectrum of linear homo-polymer DBIB-*p*($OEGMA_{50}$)

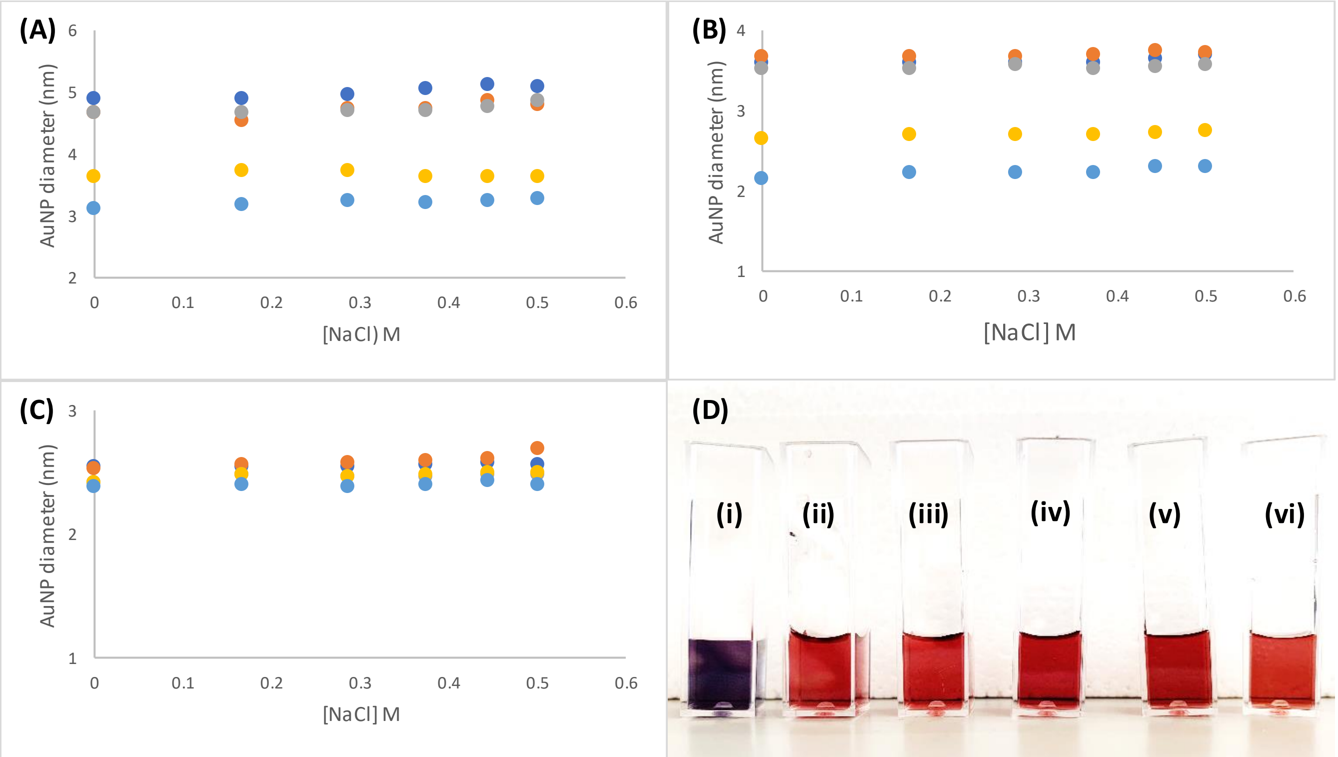

Figure S12. Salt stability studies for AuNP dispersions prepared with linear polymeric stabilisors at (a) 9:1, (b) 18:1 and (c) 35:1 P:Au mass ratios. Plots represent NaCl titrations for AuNP solutions baring polymeric structures with varying MAA:OEGMA ratio; DDT-*p*($OEGMA_{50}$) (dark blue); DDT-*p*($OEGMA_{47.5}$-*co*-$MAA_{2.5}$) (orange); DDT-*p*($OEGMA_{45}$-*co*-MAA_{5}) (grey); DDT-*p*($OEGMA_{42.5}$-*co*-$MAA_{7.5}$) (yellow); DDT-*p*($OEGMA_{40}$-*co*-MAA_{10}) (light blue). Green corresponds to the UV-vis trace of the control AuNP sample baring no polymeric stabiliser. (d) shows a photograph of solutions following addition of 0.55 M NaCl to AuNPs baring (i) no polymeric stabiliser; (ii) DDT-*p*($OEGMA_{50}$); (iii) DDT-*p*($OEGMA_{47.5}$-*co*-$MAA_{2.5}$); (iv) DDT-*p*($OEGMA_{45}$-*co*-MAA_{59}); (v) DDT-*p*($OEGMA_{42.5}$-*co*-$MAA_{7.5}$); (vi) DDT-*p*($OEGMA_{40}$-*co*-MAA_{10}).

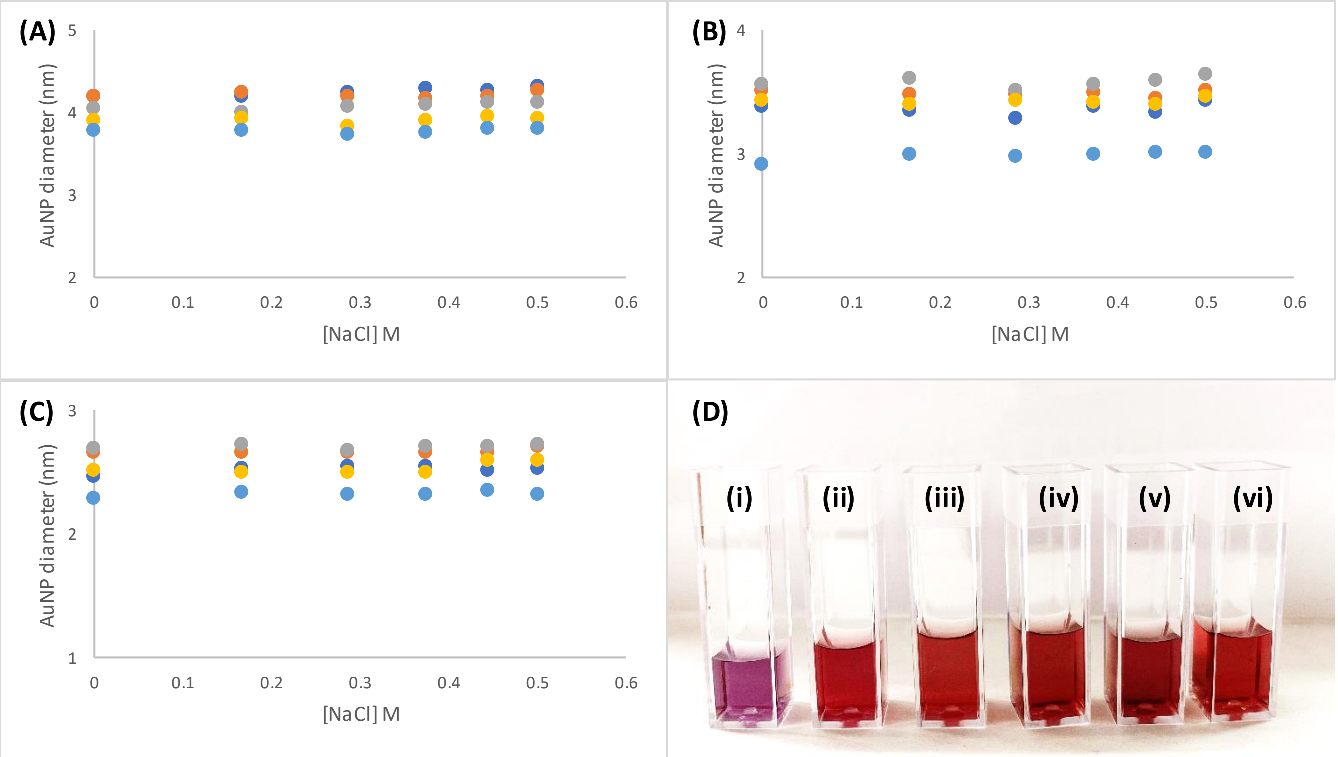

Figure S13. Salt stability studies for AuNP dispersions prepared with branched polymeric stabilisors at (a) 9:1, (b) 18:1 and (c) 35:1 P:Au mass ratios. Plots represent NaCl titrations for AuNP solutions baring polymeric structures with varying MAA:OEGMA ratio; DDT-*p*($OEGMA_{50}$-*co*-$EGDMA_{0.9}$) (dark blue); DDT-*p*($OEGMA_{47.5}$-*co*-$MAA_{2.5}$-*co*-$EGDMA_{0.9}$) (orange); DDT-*p*($OEGMA_{45}$-*co*-MAA_{5}-*co*-$EGDMA_{0.9}$) (grey); DDT-*p*($OEGMA_{42.5}$-*co*-$MAA_{7.5}$-*co*-$EGDMA_{0.9}$) (yellow); DDT-*p*($OEGMA_{40}$-*co*-MAA_{10}-*co*-$EGDMA_{0.9}$) (light blue). Green corresponds to the UV-vis trace of the control AuNP sample baring no polymeric stabiliser. (d) shows a photograph of solutions following addition of 0.55 M NaCl to AuNPs baring (i) no polymeric stabiliser; (ii) DDT-*p*($OEGMA_{50}$-*co*-$EGDMA_{0.9}$); (iii) DDT-*p*($OEGMA_{47.5}$-*co*-$MAA_{2.5}$-*co*-$EGDMA_{0.9}$); (iv) DDT-*p*($OEGMA_{45}$-*co*-MAA_{5}-*co*-$EGDMA_{0.9}$); (v) DDT-*p*($OEGMA_{42.5}$-*co*-$MAA_{7.5}$-*co*-$EGDMA_{0.9}$); (vi) DDT-*p*($OEGMA_{40}$-*co*-MAA_{10}-*co*-$EGDMA_{0.9}$).

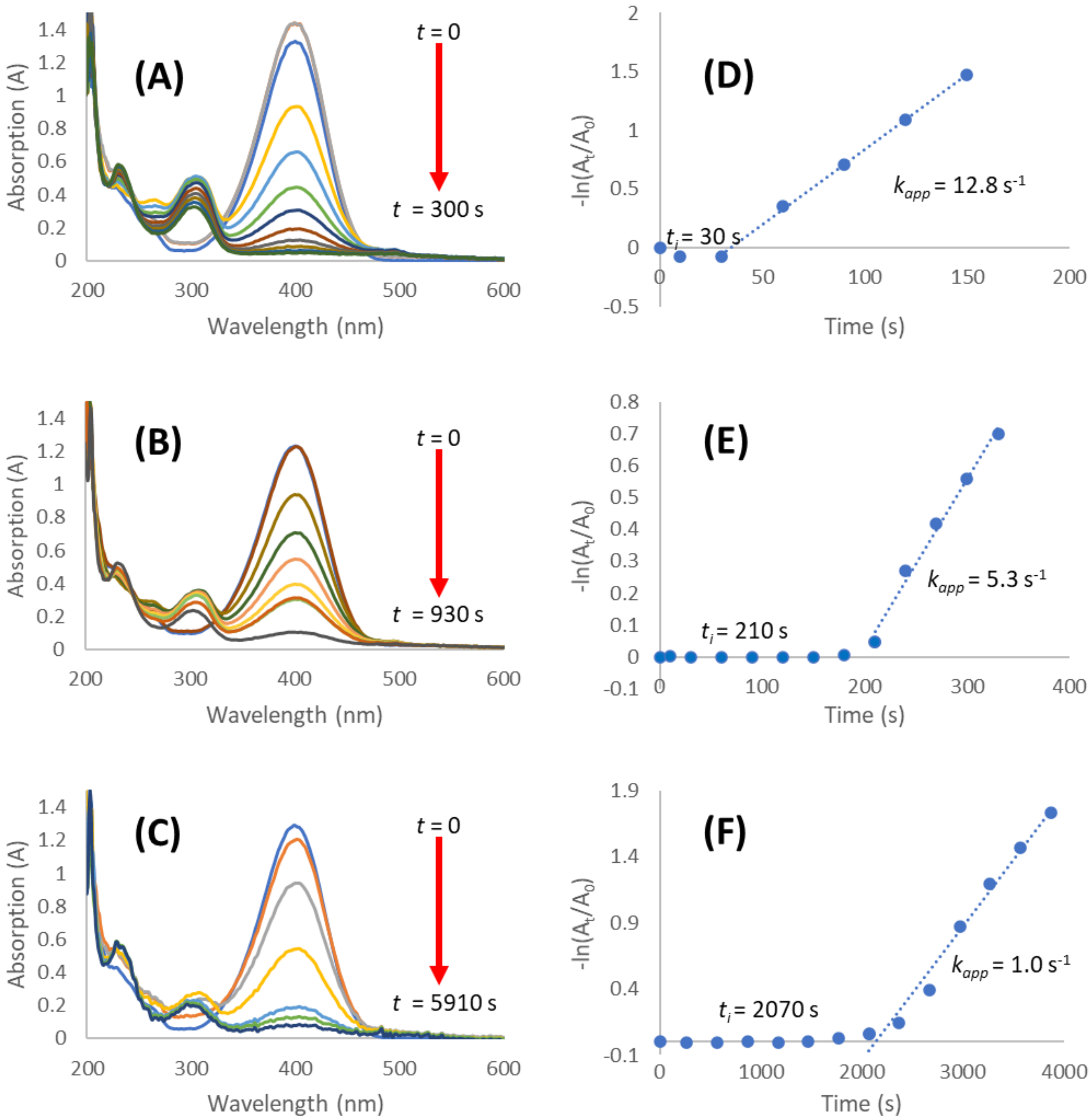

Figure S14. DDT-*p*(OEGMA$_{50}$) catalytic reduction of 4-NP to 4-AP. A - C show UV-vis absorption traces for (A) 9:1, (B) 18:1 and (C) 35:1 P:Au mass ratios. D – F show -ln(A_t/A_o) vs. t plots used to determine apparent rate constant (k_{app}) and induction times (t_i) for (D) 9:1, (E) 18:1 and (F) 35:1 P:Au mass ratios.

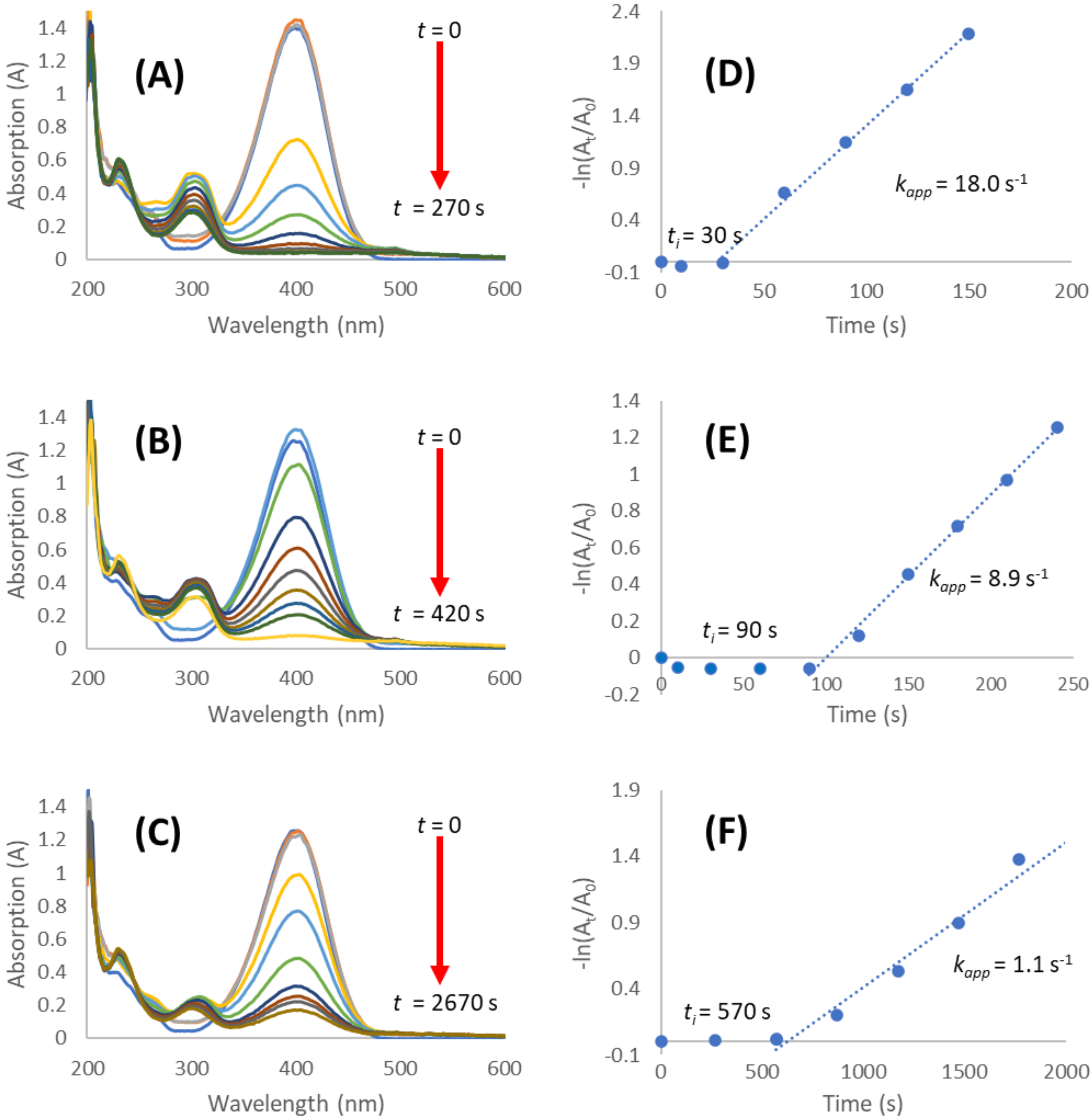

Figure S15. DDT-*p*(OEGMA$_{47.5}$-*co*-MAA$_{2.5}$) catalytic reduction of 4-NP to 4-AP. A - C show UV-vis absorption traces for (A) 9:1, (B) 18:1 and (C) 35:1 P:Au mass ratios. D – F show -ln(A_t/A_o) vs. t plots used to determine apparent rate constant (k_{app}) and induction times (t_i) for (D) 9:1, (E) 18:1 and (F) 35:1 P:Au mass ratios.

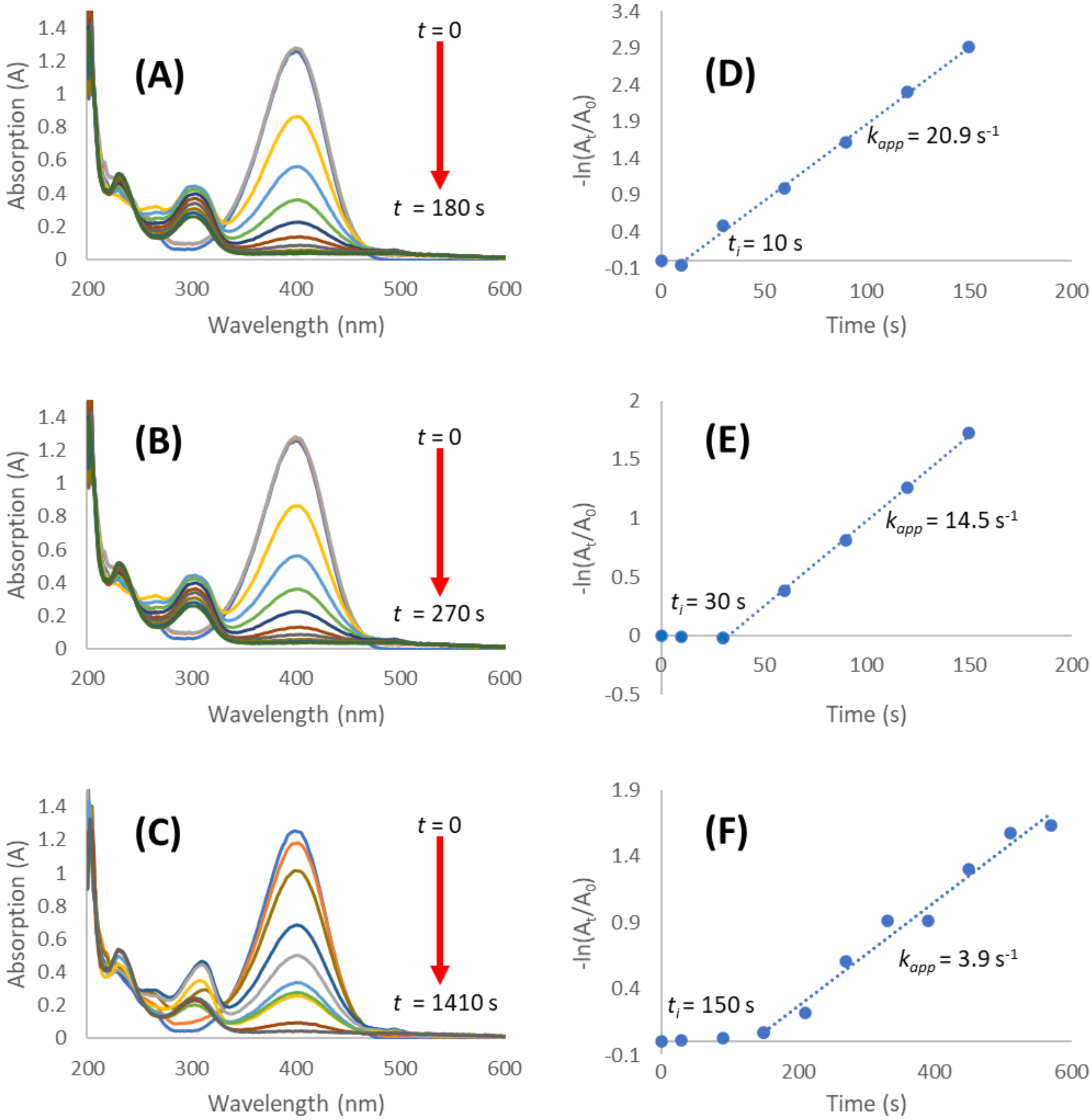

Figure S16. DDT-*p*(OEGMA$_{45}$-*co*-MAA$_{5}$) catalytic reduction of 4-NP to 4-AP. A - C show UV-vis absorption traces for (A) 9:1, (B) 18:1 and (C) 35:1 P:Au mass ratios. D – F show -ln(A_t/A_o) vs. t plots used to determine apparent rate constant (k_{app}) and induction times (t_i) for (D) 9:1, (E) 18:1 and (F) 35:1 P:Au mass ratios.

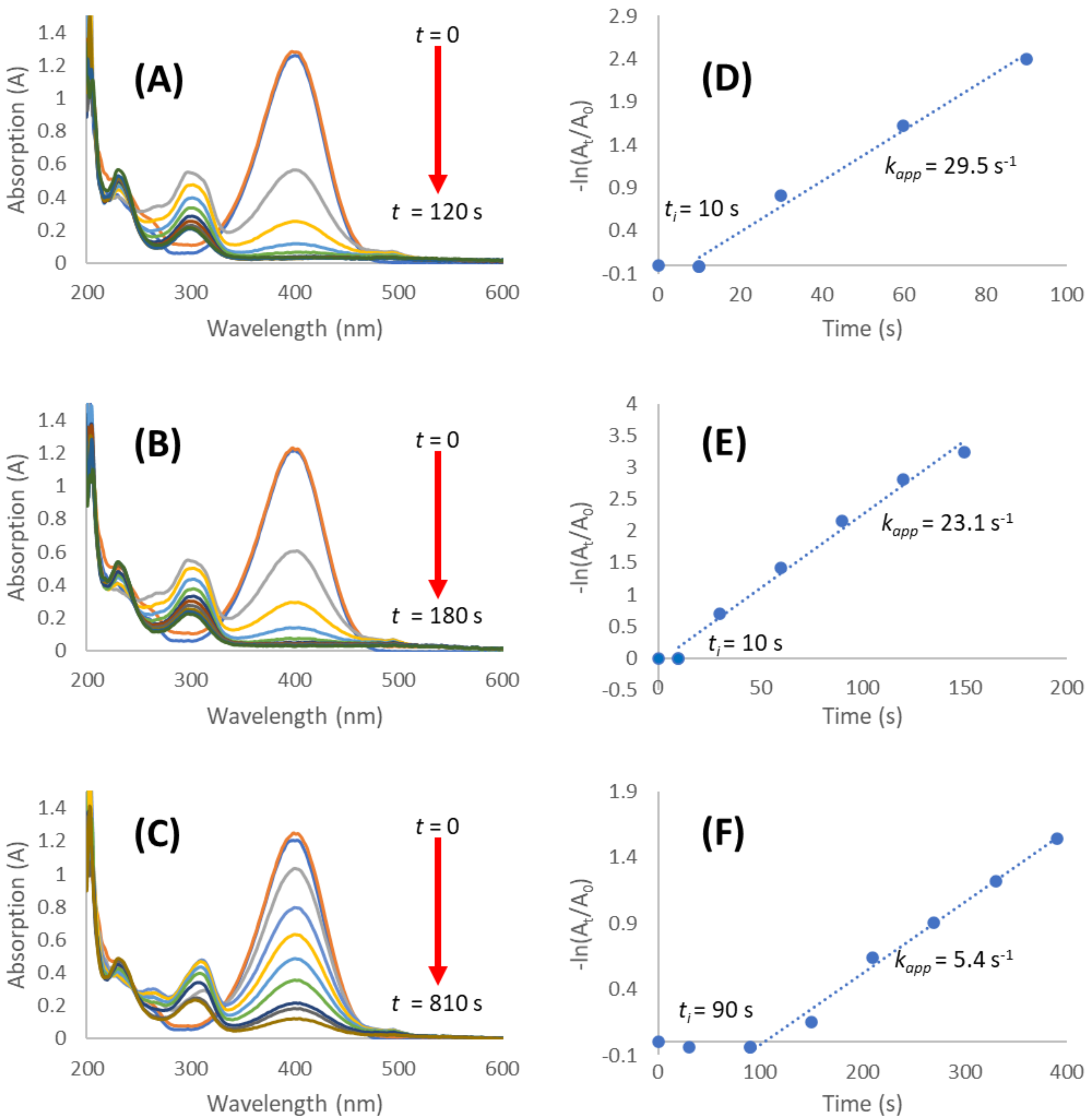

Figure S17. DDT-*p*(OEGMA$_{42.5}$-*co*-MAA$_{7.5}$) catalytic reduction of 4-NP to 4-AP. A - C show UV-vis absorption traces for (A) 9:1, (B) 18:1 and (C) 35:1 P:Au mass ratios. D – F show -ln(A_t/A_o) vs. t plots used to determine apparent rate constant (k_{app}) and induction times (t_i) for (D) 9:1, (E) 18:1 and (F) 35:1 P:Au mass ratios.

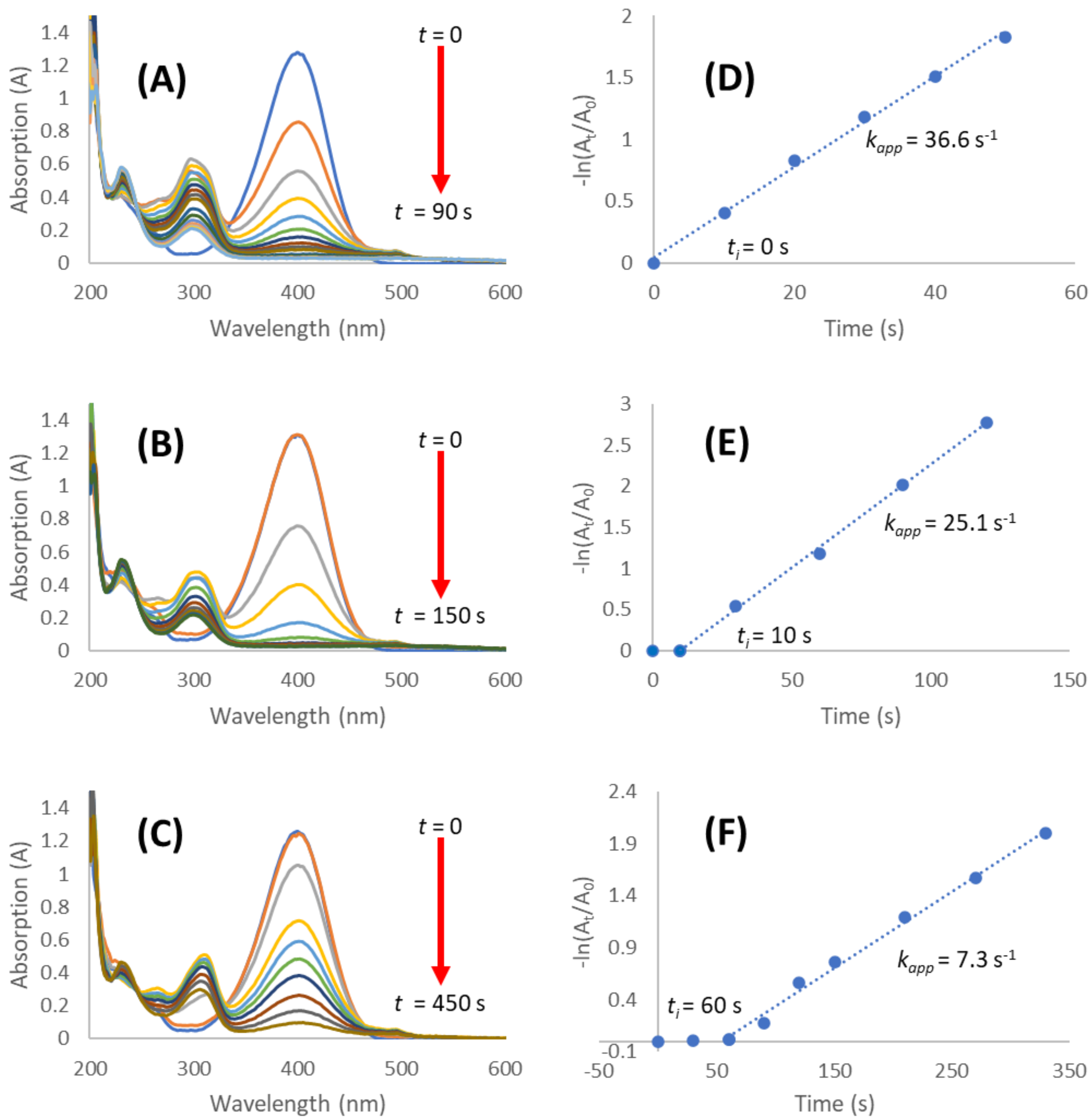

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Figure S18. DDT-*p*(OEGMA$_{40}$-*co*-MAA$_{10}$) catalytic reduction of 4-NP to 4-AP. A - C show UV-vis absorption traces for (A) 9:1, (B) 18:1 and (C) 35:1 P:Au mass ratios. D – F show -ln(A_t/A_o) vs. t plots used to determine apparent rate constant (k_{app}) and induction times (t_i) for (D) 9:1, (E) 18:1 and (F) 35:1 P:Au mass ratios.

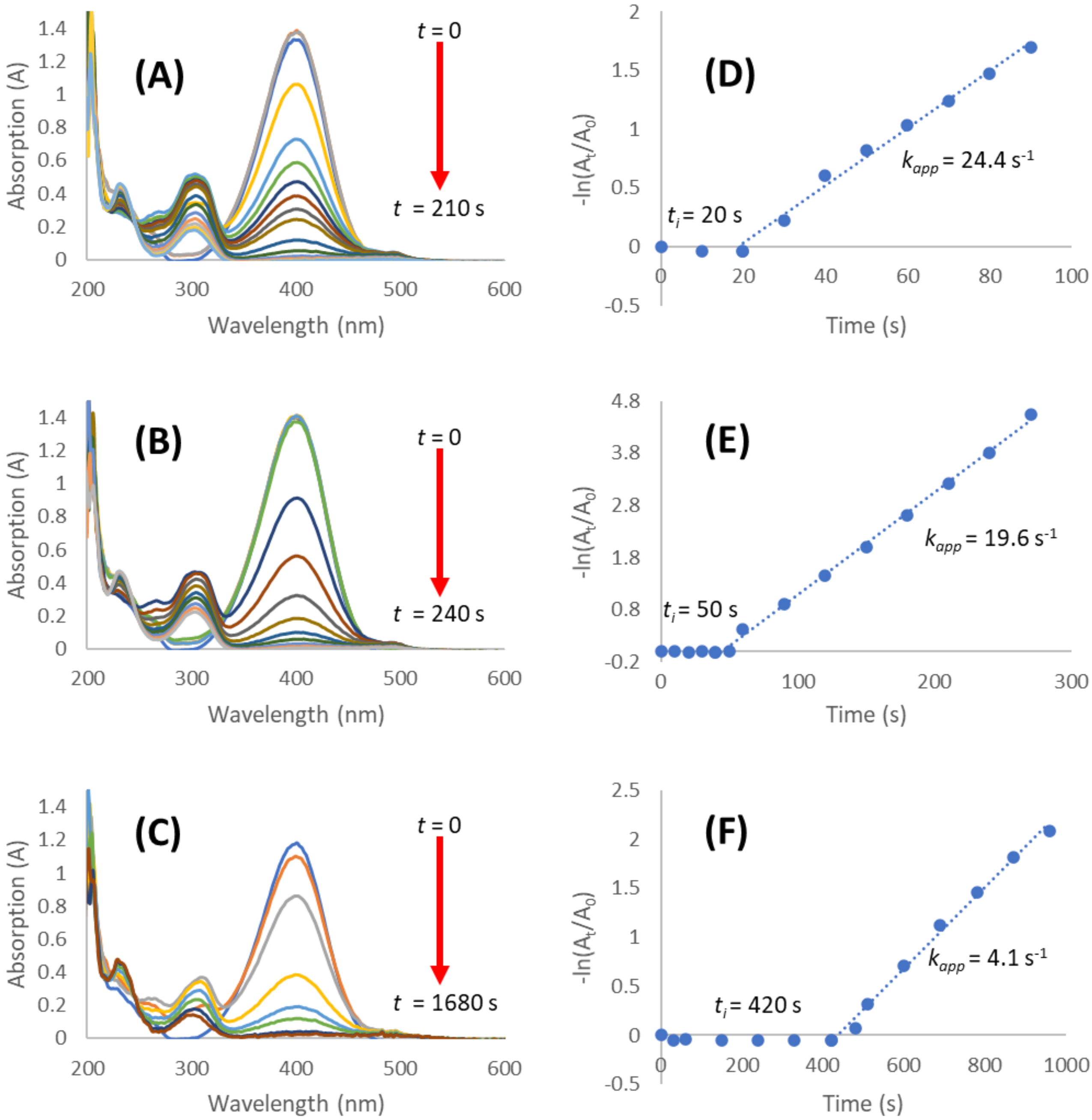

Figure S19. DDT-*p*($OEGMA_{50}$-*co*-$EGDMA_{0.9}$) catalytic reduction of 4-NP to 4-AP. A - C show UV-vis absorption traces for (A) 9:1, (B) 18:1 and (C) 35:1 P:Au mass ratios. D – F show -ln(A_t/A_o) vs. t plots used to determine apparent rate constant (k_{app}) and induction times (t_i) for (D) 9:1, (E) 18:1 and (F) 35:1 P:Au mass ratios.

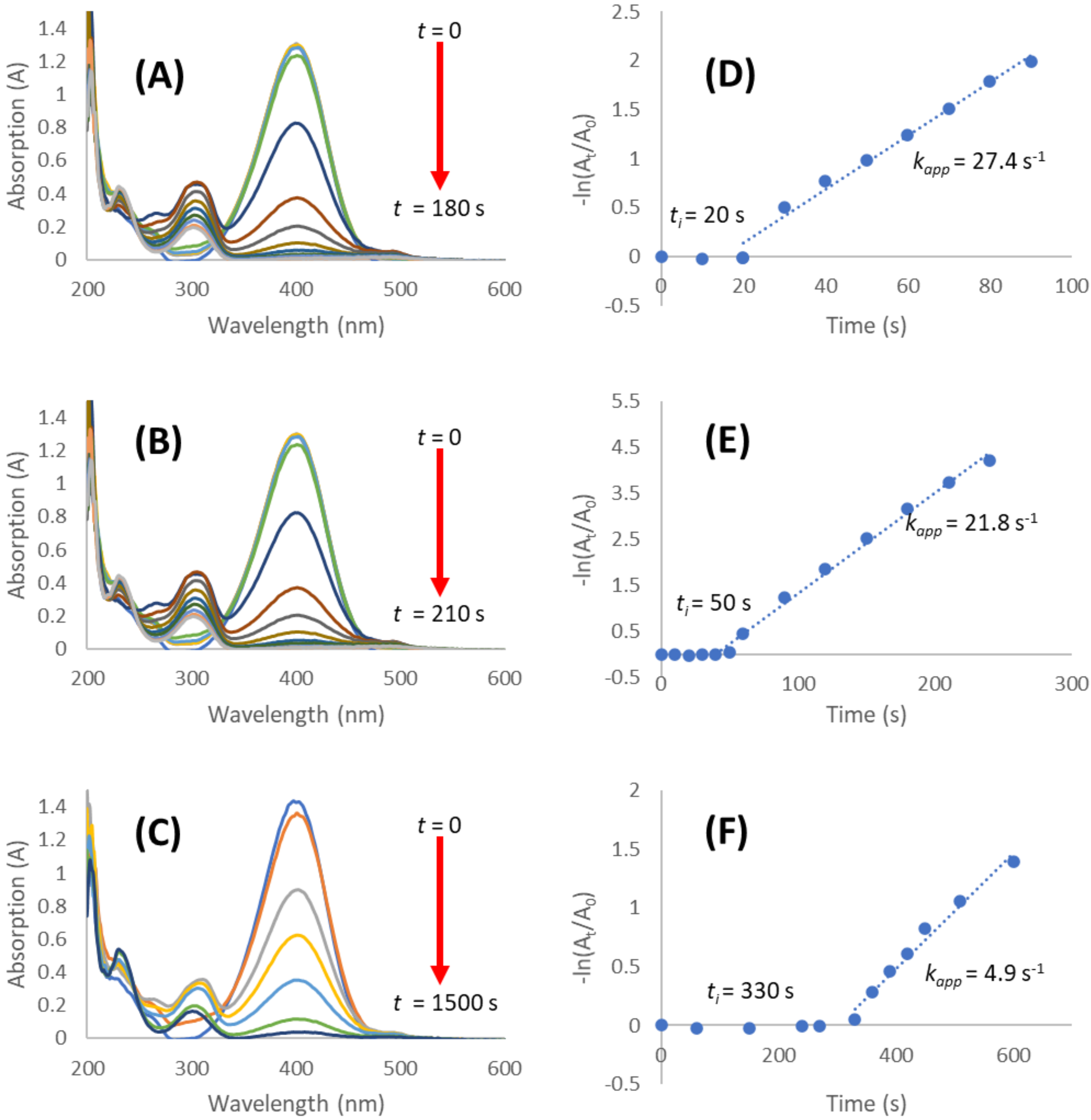

Figure S20. DDT-*p*($OEGMA_{47.5}$-*co*-$MAA_{2.5}$-*co*-$EGDMA_{0.9}$) catalytic reduction of 4-NP to 4-AP. A - C show UV-vis absorption traces for (A) 9:1, (B) 18:1 and (C) 35:1 P:Au mass ratios. D – F show -ln(A_t/A_o) vs. t plots used to determine apparent rate constant (k_{app}) and induction times (t_i) for (D) 9:1, (E) 18:1 and (F) 35:1 P:Au mass ratios.

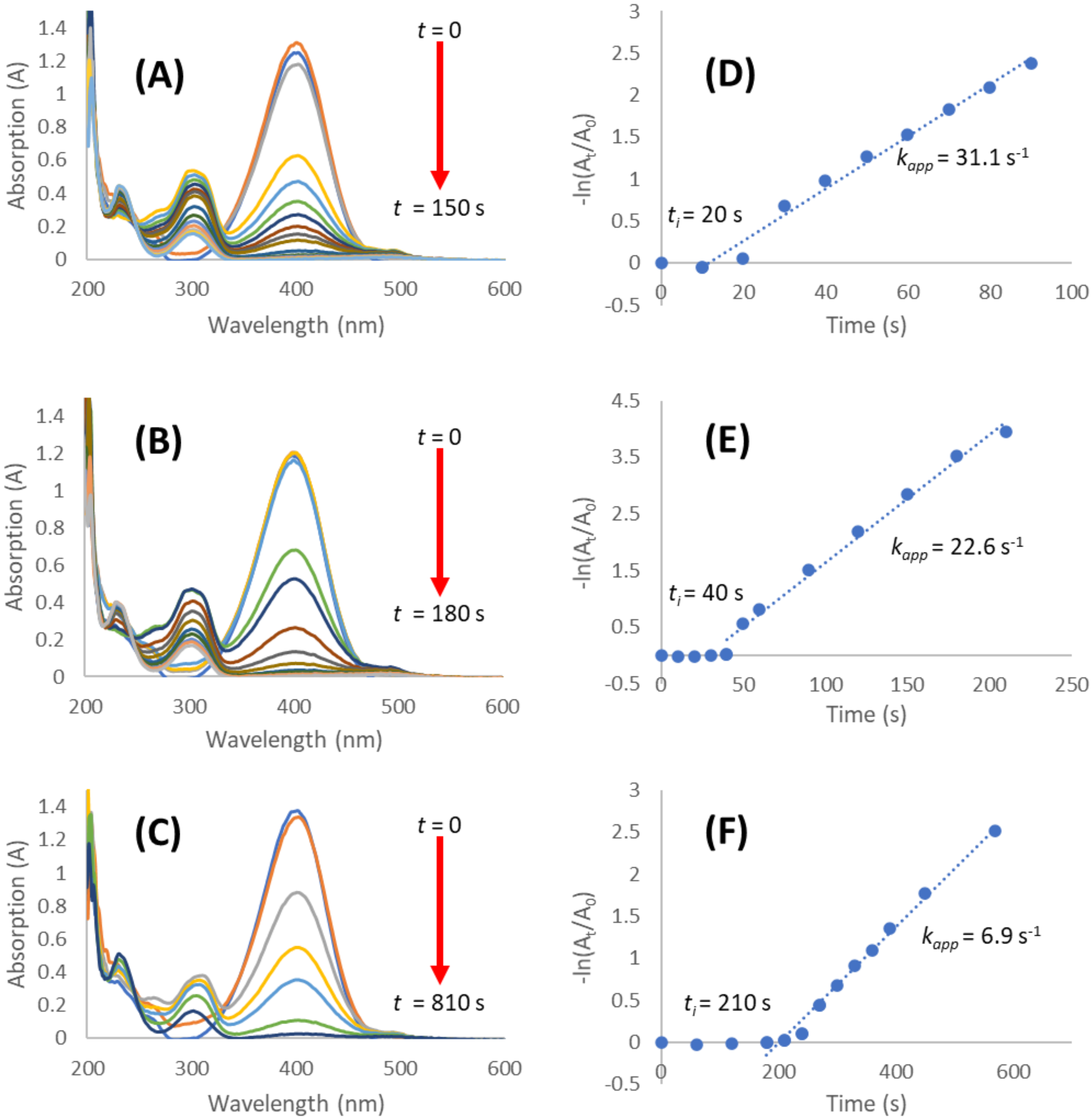

Figure S21. DDT-*p*($OEGMA_{45}$-*co*-MAA_5-*co*-$EGDMA_{0.9}$) catalytic reduction of 4-NP to 4-AP. A - C show UV-vis absorption traces for (A) 9:1, (B) 18:1 and (C) 35:1 P:Au mass ratios. D – F show -ln(A_t/A_o) vs. t plots used to determine apparent rate constant (k_{app}) and induction times (t_i) for (D) 9:1, (E) 18:1 and (F) 35:1 P:Au mass ratios.

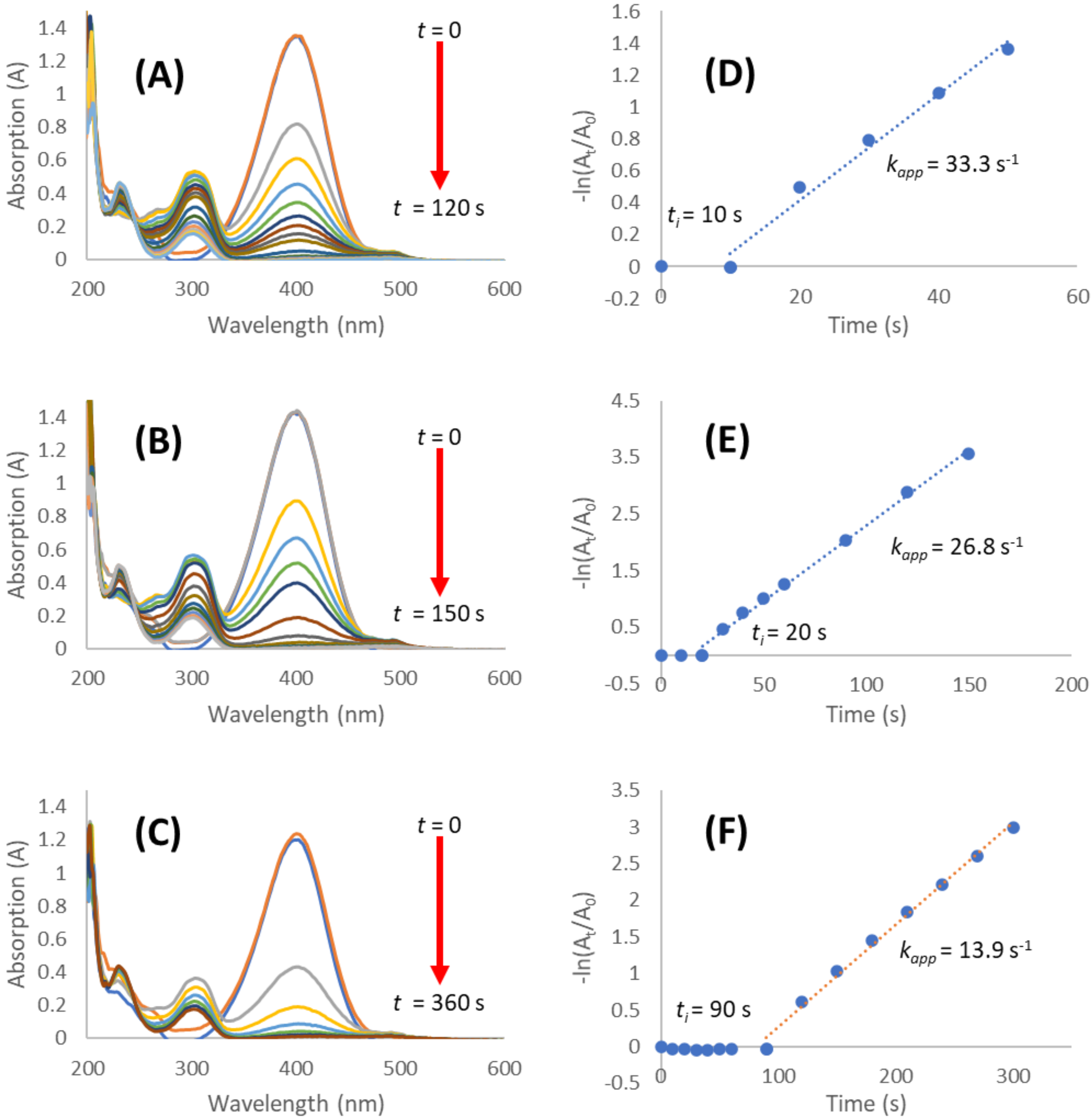

Figure S22. DDT-*p*(OEGMA$_{42.5}$-*co*-MAA$_{7.5}$-*co*-EGDMA$_{0.9}$) catalytic reduction of 4-NP to 4-AP. A - C show UV-vis absorption traces for (A) 9:1, (B) 18:1 and (C) 35:1 P:Au mass ratios. D – F show $-\ln(A_t/A_o)$ vs. t plots used to determine apparent rate constant (k_{app}) and induction times (t_i) for (D) 9:1, (E) 18:1 and (F) 35:1 P:Au mass ratios.

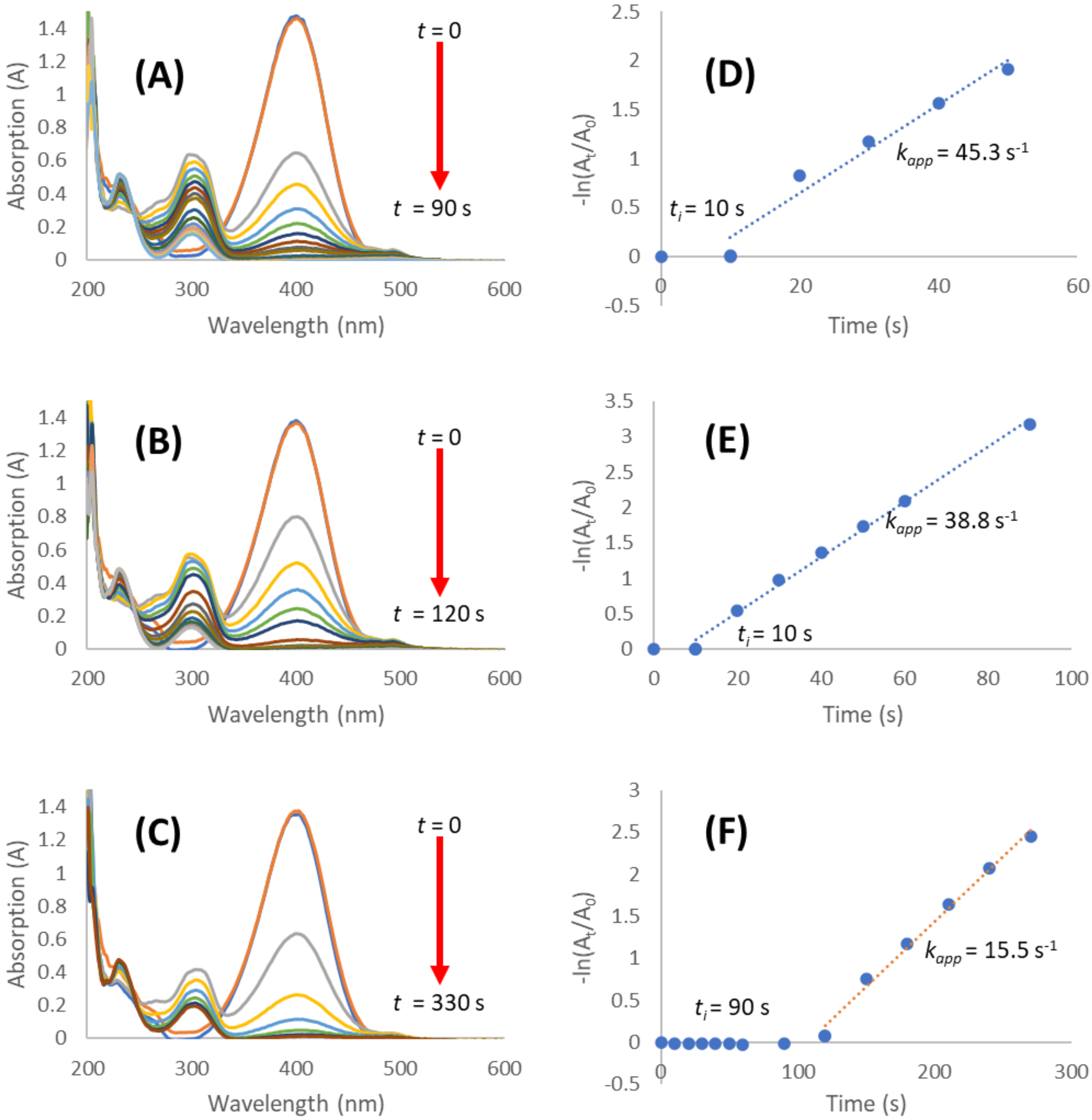

Figure S23. DDT-*p*(OEGMA$_{40}$-*co*-MAA$_{10}$-*co*-EGDMA$_{0.9}$) catalytic reduction of 4-NP to 4-AP. A - C show UV-vis absorption traces for (A) 9:1, (B) 18:1 and (C) 35:1 P:Au mass ratios. D – F show -ln(A_t/A_o) vs. t plots used to determine apparent rate constant (k_{app}) and induction times (t_i) for (D) 9:1, (E) 18:1 and (F) 35:1 P:Au mass ratios.

Table S1. Calculated apparent rate constants (k_{app}) and induction times (t_i) for each AuNP solution prepared using the library of employed polymeric stabilisers for the catalytic reduction of 4-NP to 4-AP, determined by UV-vis spectroscopy.

Linear Homo-polymers and (co)polymers				**Branched (co)polymers**			
Structure	P:Au	k_{app} (s^{-1})	t_i (s)	**Structure**	P:Au	k_{app} (s^{-1})	t_i (s)
DDT-*p*($OEGMA_{50}$)	9:1	12.8	30	DDT-*p*($OEGMA_{50}$-*co*-$EGDMA_{0.9}$)	9:1	24.4	20
	18:1	5.3	210		18:1	19.6	50
	35:1	1.0	2070		35:1	4.1	420
DDT-*p*($OEGMA_{47.5}$-*co*-$MAA_{2.5}$)	9:1	18.0	30	DDT-*p*($OEGMA_{47.5}$-*co*-$MAA_{2.5}$-*co*-$EGDMA_{0.9}$)	9:1	27.4	20
	18:1	8.9	90		18:1	21.8	50
	35:1	1.1	570		35:1	4.9	330
DDT-*p*($OEGMA_{45}$-*co*-MAA_{5})	9:1	20.9	10	DDT-*p*($OEGMA_{45}$-*co*-MAA_{5}-*co*-$EGDMA_{0.9}$)	9:1	31.1	20
	18:1	14.5	30		18:1	22.6	40
	35:1	3.9	150		35:1	6.9	210
DDT-*p*($OEGMA_{42.5}$-*co*-$MAA_{7.5}$)	9:1	29.5	10	DDT-*p*($OEGMA_{42.5}$-*co*-$MAA_{7.5}$-*co*-$EGDMA_{0.9}$)	9:1	33.3	10
	18:1	23.1	10		18:1	26.8	20
	35:1	5.4	90		35:1	13.9	90
DDT-*p*($OEGMA_{40}$-*co*-MAA_{10})	9:1	36.6	0	DDT-*p*($OEGMA_{40}$-*co*-MAA_{10}-*co*-$EGDMA_{0.9}$)	9:1	45.3	10
	18:1	25.1	10		18:1	38.8	10
	35:1	7.3	60		35:1	15.5	90