

The Importance of Excess Poly(*N*-isopropylacrylamide) for the Aggregation of Poly(*N*-isopropylacrylamide)-Coated Gold Nanoparticles

Samuel T. Jones, Zarah Walsh-Korb, Steven J. Barrow, Sarah L. Henderson,
Jesús del Barrio, and Oren A. Scherman*

*Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge,
Lensfield Road, Cambridge CB2 1EW, United Kingdom. email: oas23@cam.ac.uk*

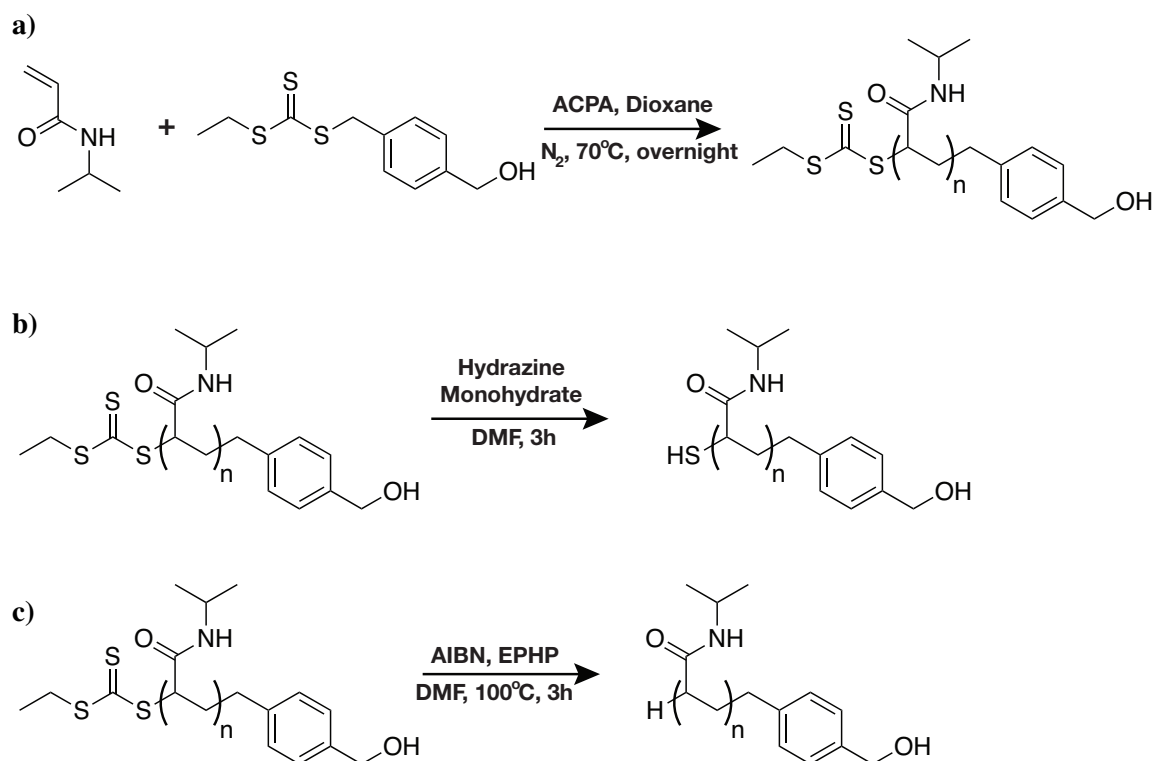


Figure S1: Reaction schemes for a) the RAFT polymerization of NIPAM with CTA-OH and ACPA in dioxane at 70 °C, b) cleavage of the PNIPAM-CTA using hydrazine to yield a thiol-terminated PNIPAM (HS-PNIPAM) and c) the homolytic cleavage of the PNIPAM-CTA by AIBN and addition of EPHP to yield a hydrogen terminated PNIPAM (H-PNIPAM).

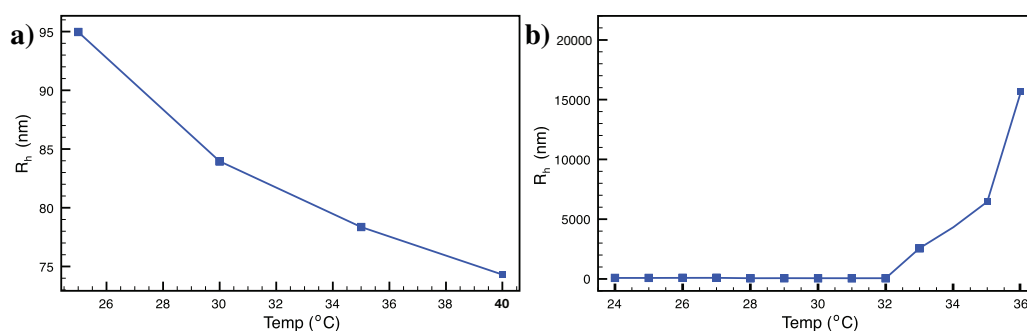
Table S1: Quantities of reagents used for the synthesis of SSS-PNIPAm-OH of different lengths.

Targeted M_n g/mol	PNIPAm /g (mmol)	ACPA /mg (μ mol)	CTA-OH /mg (μ mol)	1,4-dioxane /mL
15k	1.56 (13.8)	3.0 (10.7)	27.4 (106)	7
30k	2.62 (23.1)	2.5 (8.9)	22.8 (88.2)	10
60k	5.23 (46.2)	2.5 (8.9)	22.8 (88.2)	20

Table S2: Quantities of reagents used for the synthesis of SSS-PNIPAm-OH of different lengths.^a determined by NMR end-group analysis and ^b determined by GPC analysis.

M_n g/mol	Yield of SSS-PNIPAm /g (μ mol)	M_n^a g/mol	M_n^b g/mol	PDI ^b	% Yield /mg
15k	1.273 (84.9)	15,232	8,700	1.20	81.4
30k	2.265 (75.5)	35,052	17,000	1.14	86.5
60k	4.895 (81.6)	~	22,000	1.35	93.5

S.1 DLS of 5 nm AuNPs coated with 60K PNIPAm

**Figure S2:** Dynamic light scattering (DLS) data showing the change in hydrodynamic radius (R_h) as the temperature is increased for a) pure (*i.e.* all excess PNIPAm removed) 5 nm AuNPs coated by 60k-PNIPAm and b) the same 5 nm AuNPs coated with 60k-PNIPAm that have had 2.4 mg of free H-PNIPAm added.

S.2 Centrifuge wash cycle TGA analysis

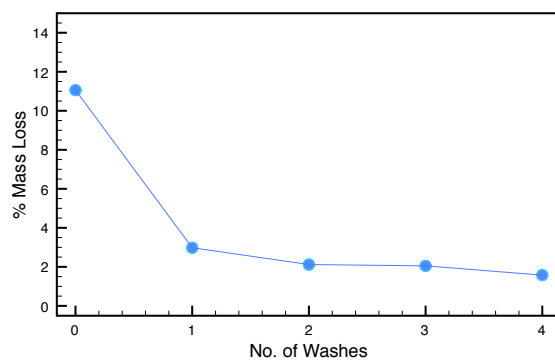


Figure S3: Thermogravimetric analysis (TGA) of PNIPAm coated 14 nm AuNPs before washing and after every sequential washing step. Washes were performed using the newly developed methanol wash approach and it can be seen that all free PNIPAm is removed after 4 washes.

S.3 TEM of Initiator AuNPs

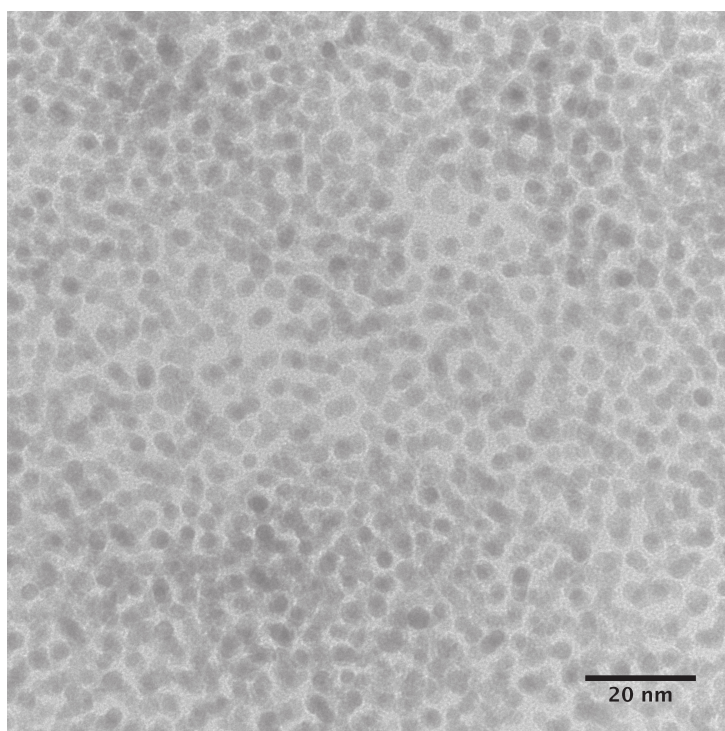


Figure S4: Transmission electron micrograph (TEM) of initiator coated AuNPs

S.4 TEM of PNIPAm coated AuNPs

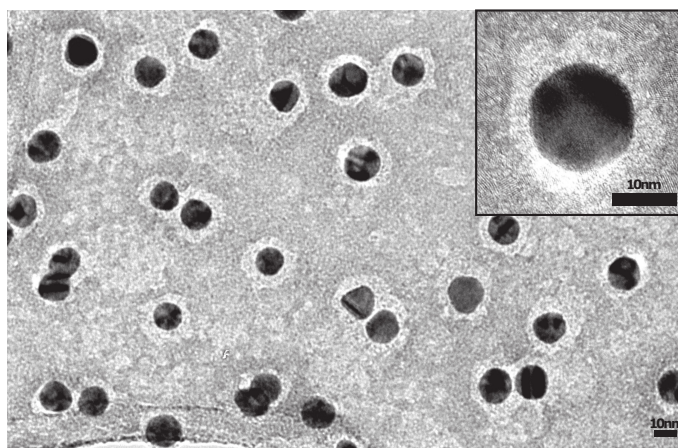


Figure S5: Transmission electron micrograph (TEM) of PNIPAm coated AuNPs that have been stained with uranyl acetate. Lighter regions around each AuNP is on account of the presence of attached PNIPAm.

S.5 Graft-from PNIPAm-AuNPs

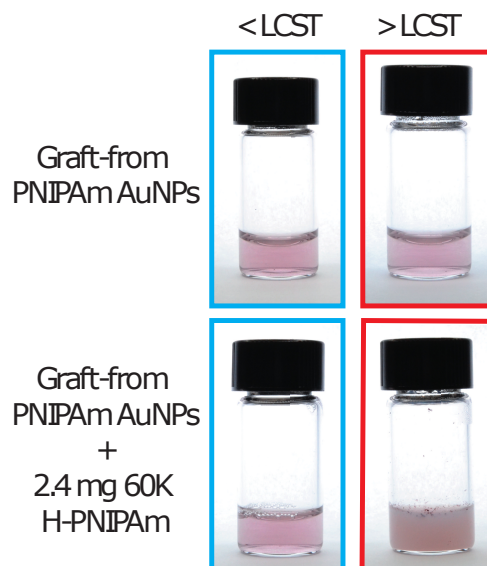


Figure S6: Graft-from PNIPAm-AuNPs without (top row) and with (bottom row) free polymer and below (blue) and above (red) the LCST of PNIPAm.

S.6 Free P[NIPAM-*co*-HEAm] with 60K PNIPAm-coated AuNPs

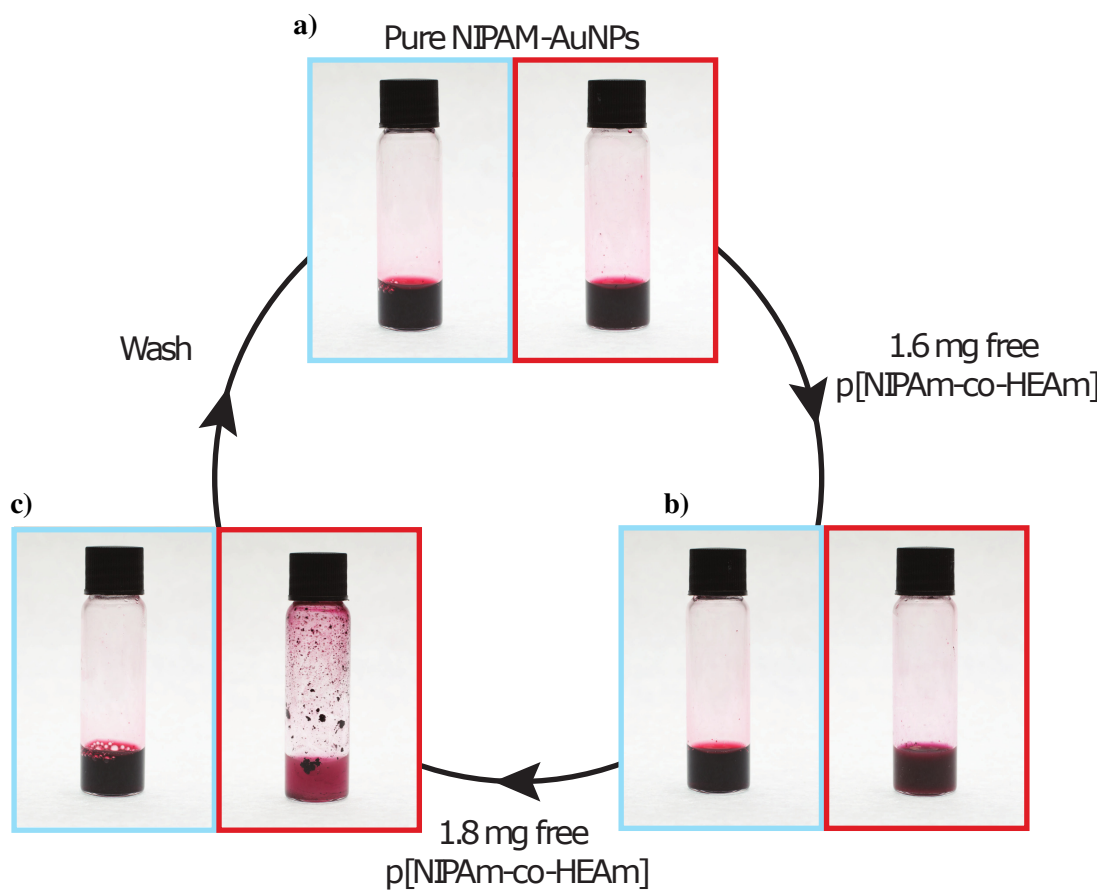


Figure S7: 14 nm 60K-PNIPAm coated AuNPs taken above (red) and below (blue) the LCST of a) pure PNIPAm-AuNPs, b) PNIPAm-AuNPs after the addition of 1.6 mg P[NIPAM-*co*-HEAm] and c) PNIPAm-AuNPs after the addition of a further 1.8 mg P[NIPAM-*co*-HEAm].

S.7 UV-vis Studies

S.7.1 Result of changing the free polymer size

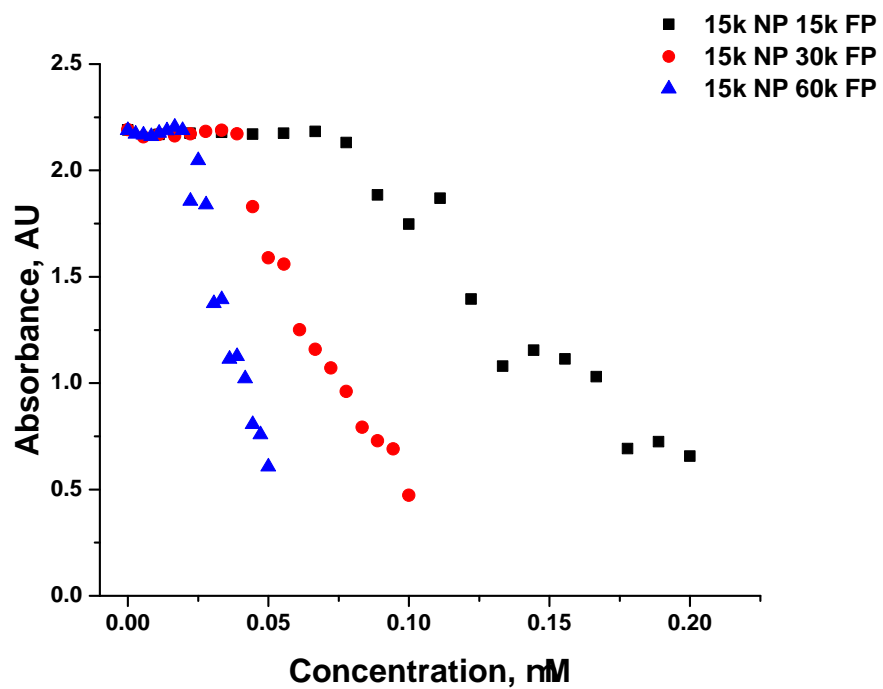


Figure S8: 14 nm 15k-PNIPAm coated AuNPs mixed with free PNIPAm of differing lengths. Black - 15k free polymer, blue - 30k free polymer and red - 60k free polymer.

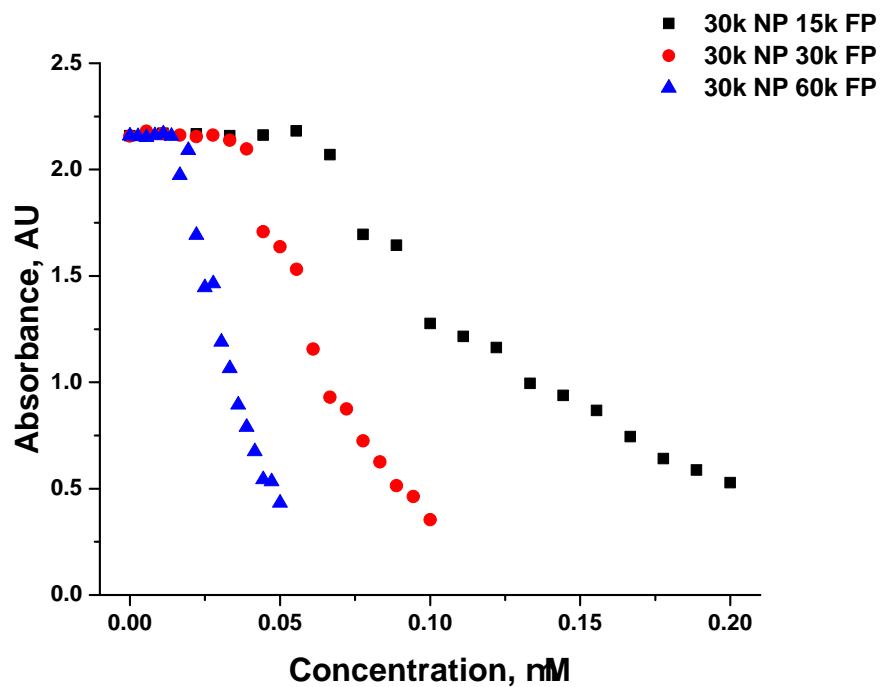


Figure S9: 14 nm 30k-PNIPAm coated AuNPs mixed with free PNIPAm of differing lengths. Black - 15k free polymer, blue - 30k free polymer and red - 60k free polymer.

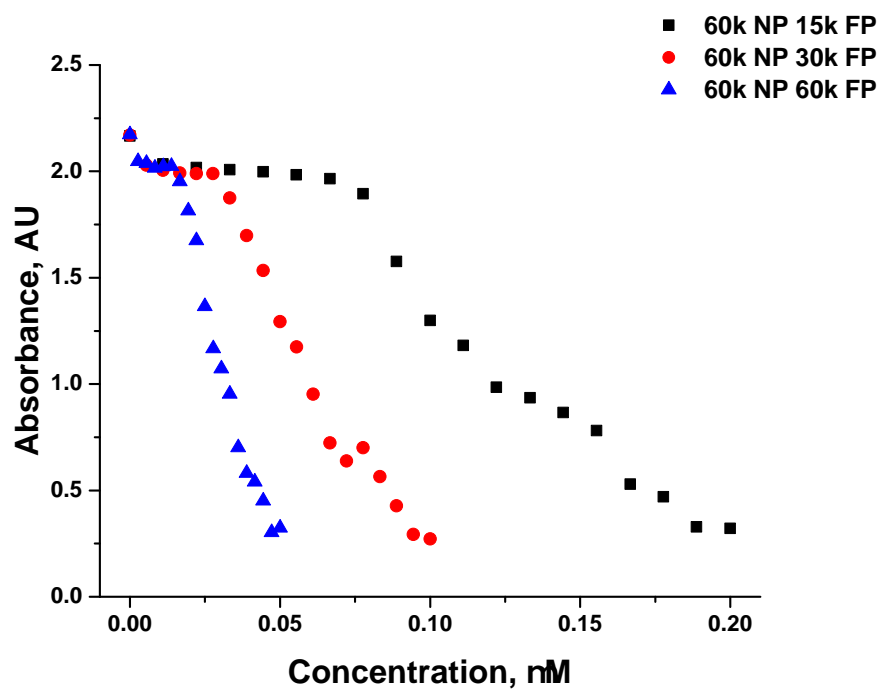


Figure S10: 14 nm 60k-PNIPAm coated AuNPs mixed with free PNIPAm of differing lengths. Black - 15k free polymer, blue - 30k free polymer and red - 60k free polymer.

S.7.2 Result of Changing the Size of the Polymer Coating

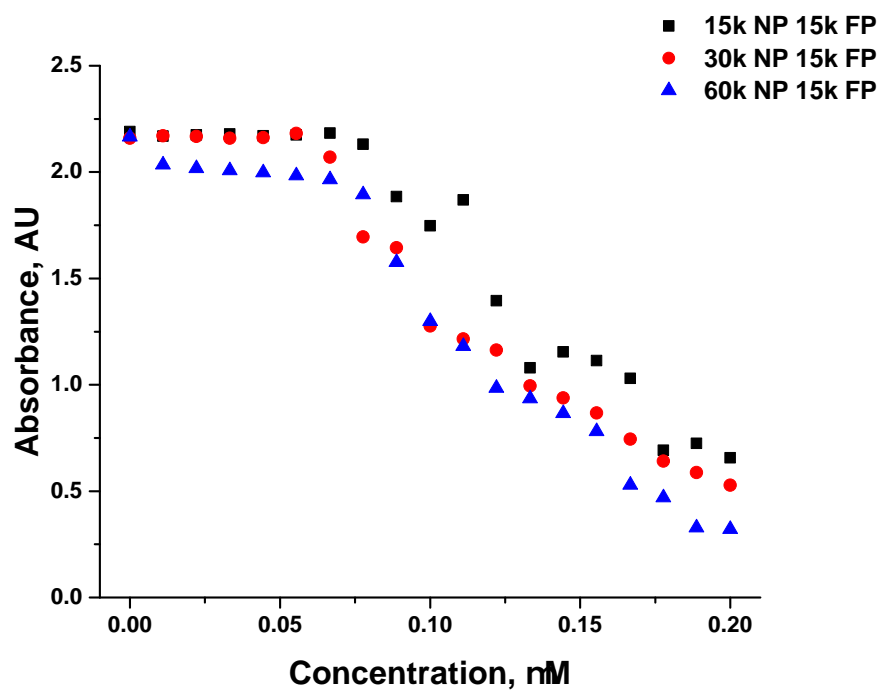


Figure S11: 14 nm AuNPs coated with different sized PNIPAm mixed with free 15k-PNIPAm.

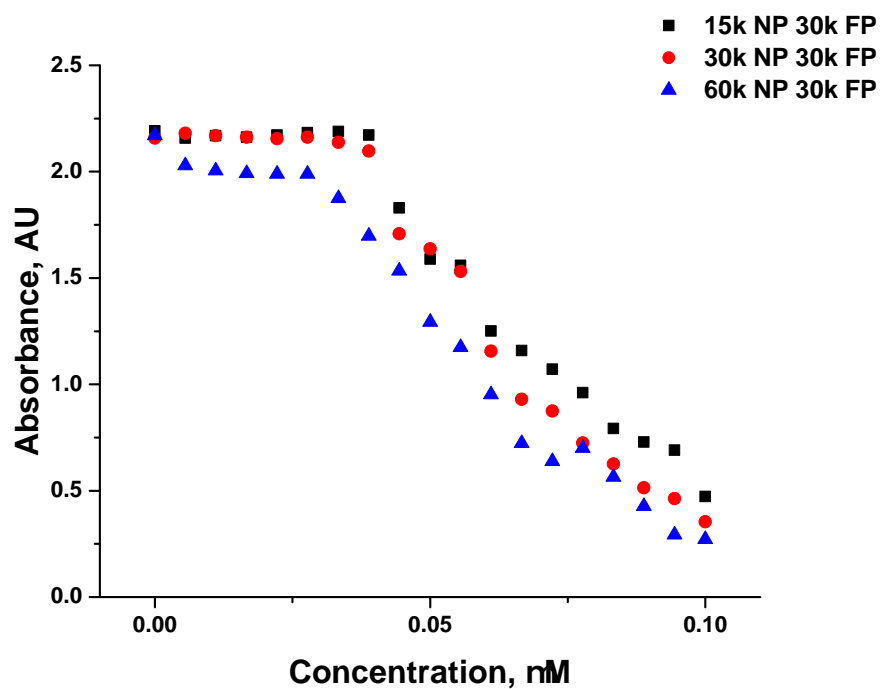


Figure S12: 14 nm AuNPs coated with different sized PNIPAm mixed with free 30k-PNIPAm.

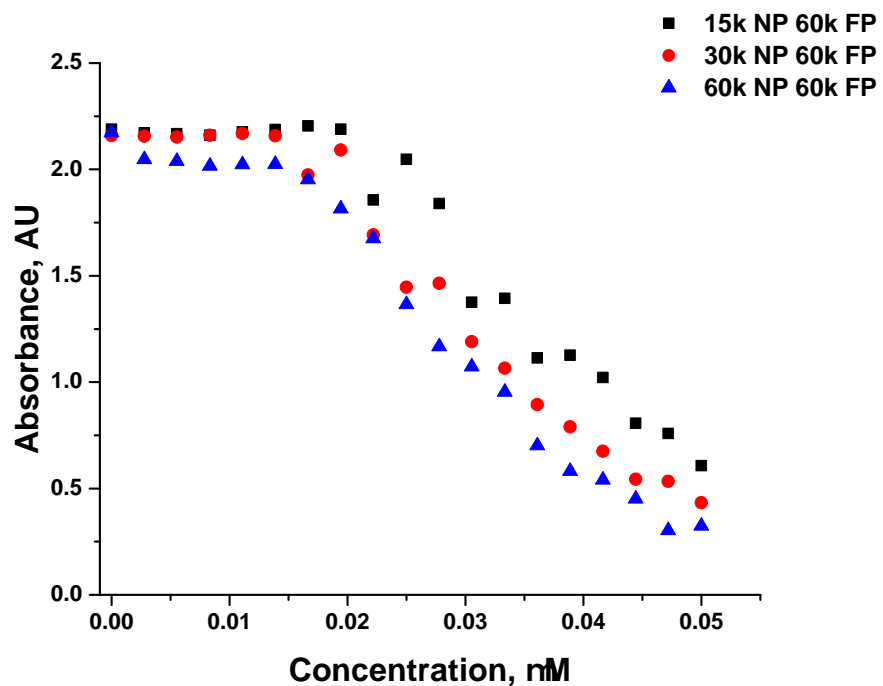


Figure S13: 14 nm AuNPs coated with different sized PNIPAm mixed with free 60k-PNIPAm.

S.7.3 Overview of UV-Vis data

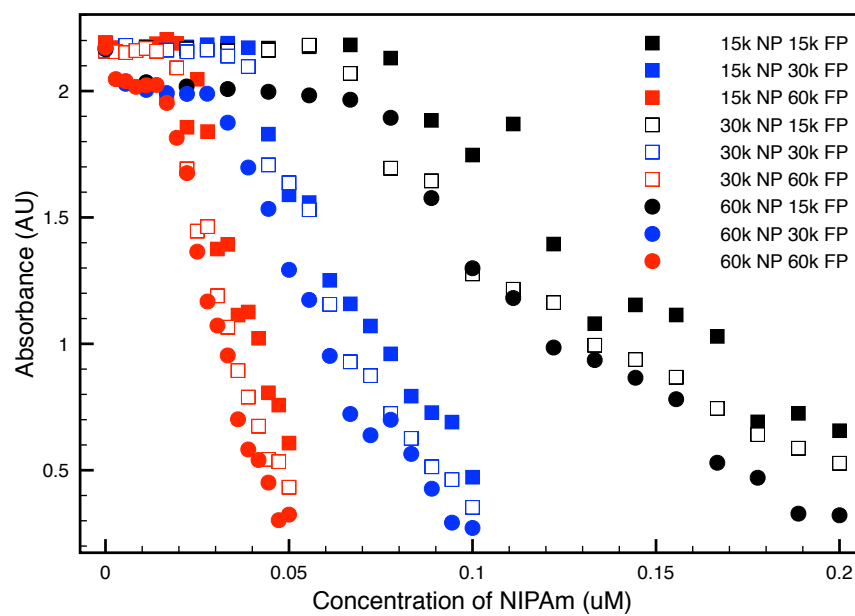


Figure S14: Overview of UV-Vis data collected in this study.

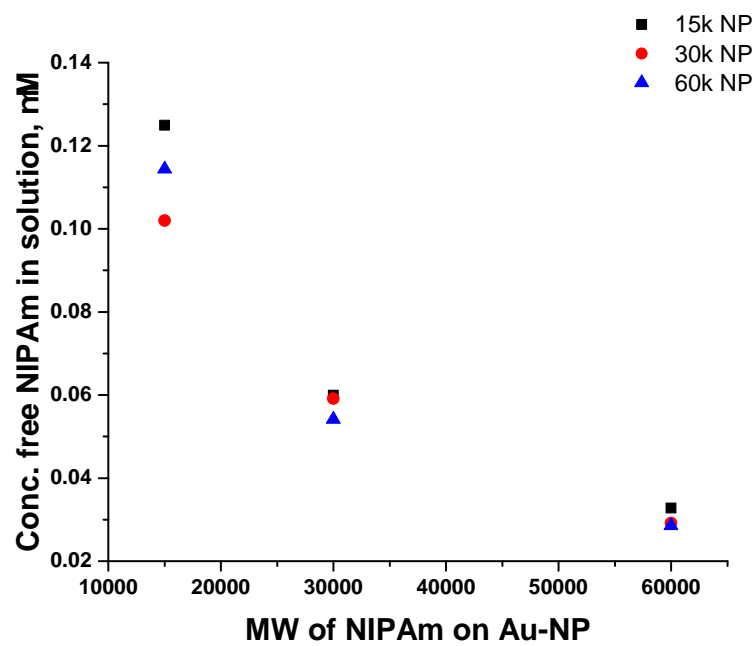


Figure S15: Calibration curve generated from the UV-Vis data collected in this study.

S.8 DLS of Graft-from PNIPAm-AuNPs in the presence of salt

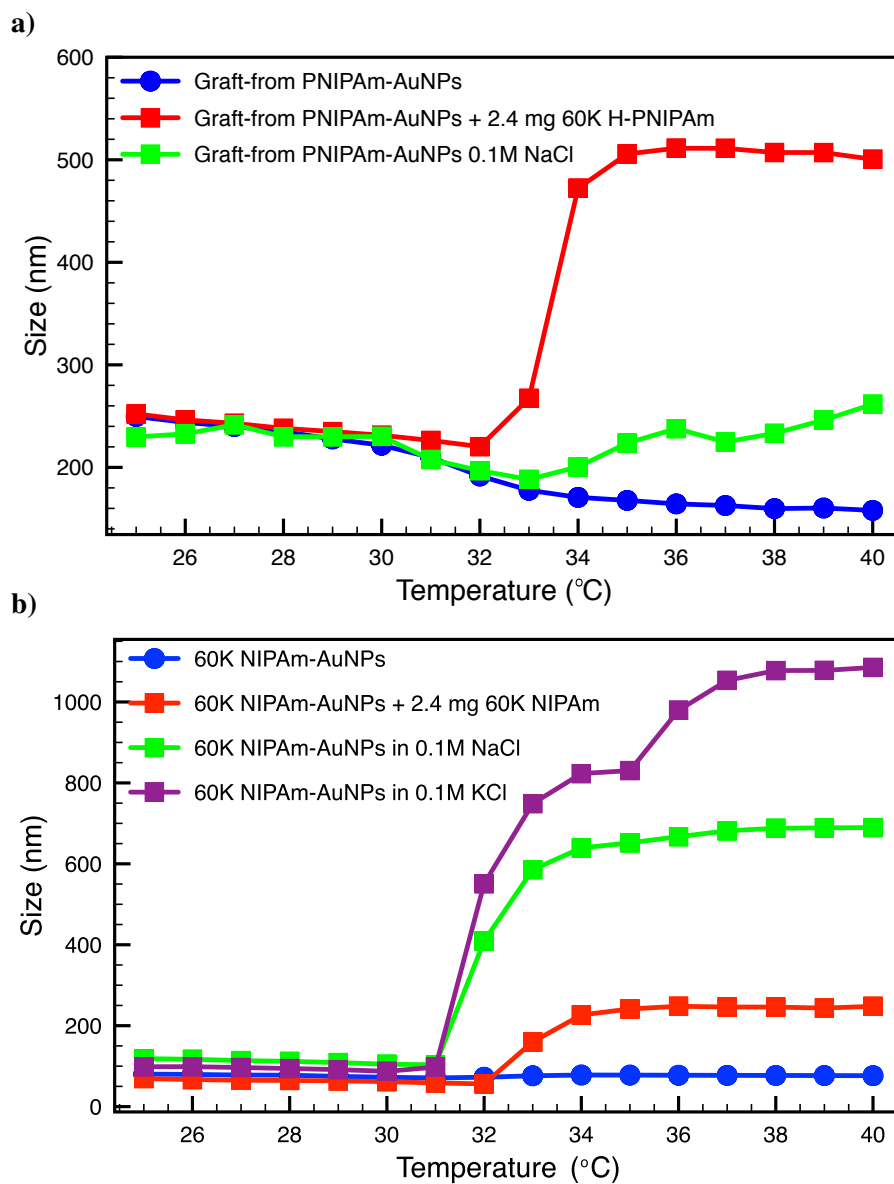


Figure S16: Dynamic light scattering (DLS) data showing the change in hydrodynamic radius (R_h) as the temperature is increased for a) graft-from PNIPAm AuNPs, including the effect of salt addition, and b) graft-to PNIPAm-AuNPs, including the effect of salt addition, before (blue circles) and after (red squares) the addition of $40 \mu\text{mol}$ (2.4 mg) of free 60k H-PNIPAm.