

Supporting Information

Irradiation Effects on Polymer-Grafted Gold Nanoparticles for Cancer Therapy

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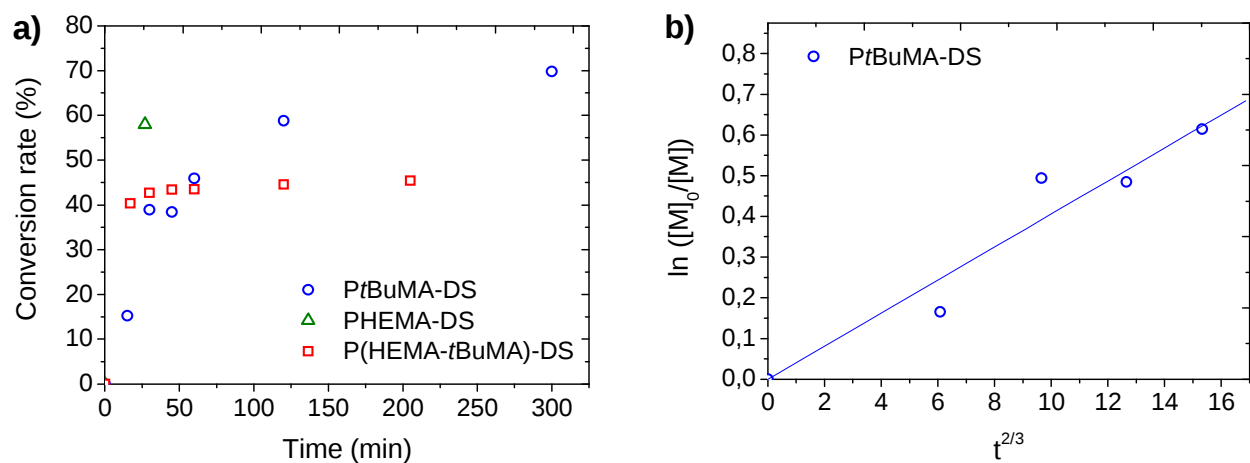


Figure S1. Kinetic plot of the conversion vs time for the polymerization of PtBuMA-DS, PHEMA-DS and P(HEMA-MAtBu)-DS (a) ; Kinetic plot of $\ln([M]_0/[M])$ vs $t^{2/3}$ for the polymerization of PtBuMA-DS (b).¹

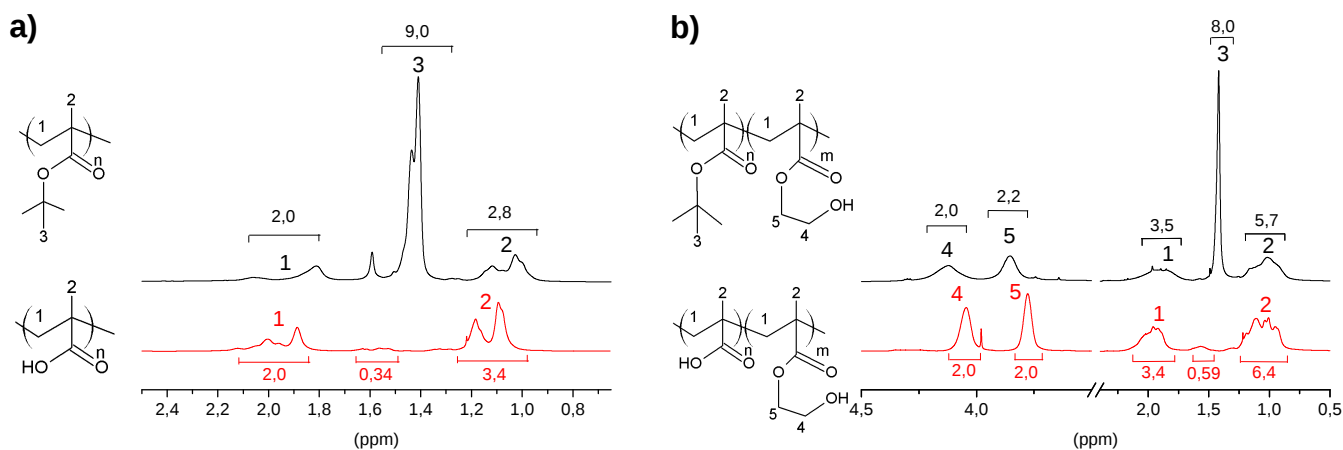


Figure S2. ¹H NMR spectra of polymeric ligands before (black spectra) and after hydrolysis (red spectra): PMAAtBu-DS and PMAA-DS (a); P(HEMA-MAtBu)-DS and P(HEMA-MAA)-DS (b).

¹ Fischer, H. The Persistent Radical Effect In "Living" Radical Polymerization. *Macromolecules* **1997**, *30*, 5666-5672.

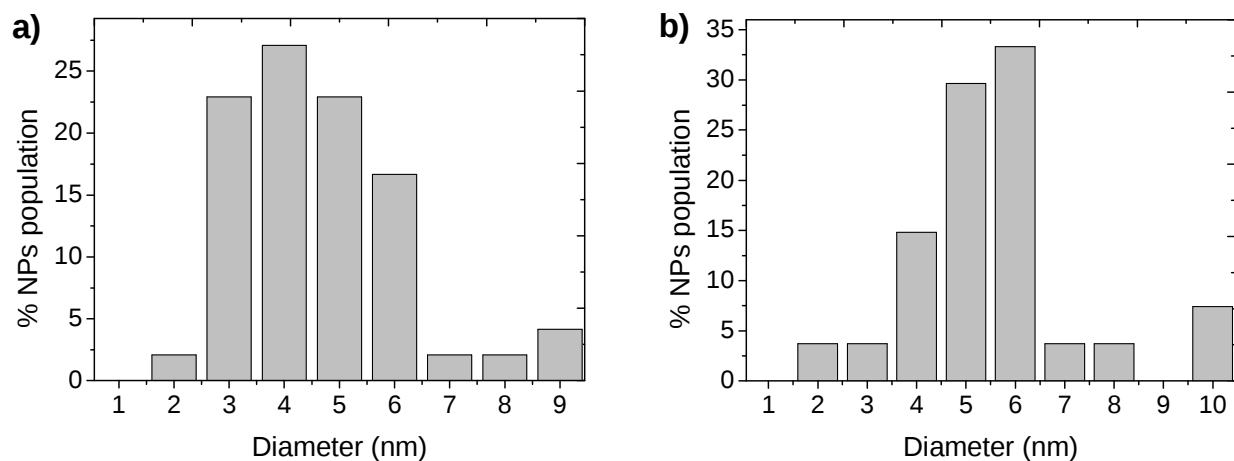


Figure S3. Size distribution diagrams of PMAA-AuNPs (a) and P(HEMA-MAA)-AuNPs (b) obtained by TEM analysis.

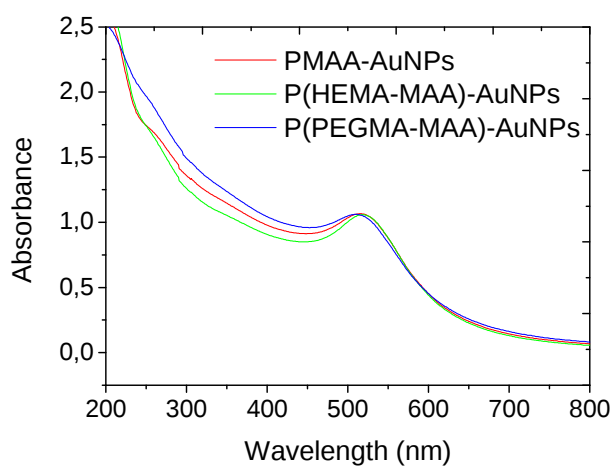


Figure S4. UV-Vis spectra of polymer-grafted AuNPs in water (0.17 mg/mL).

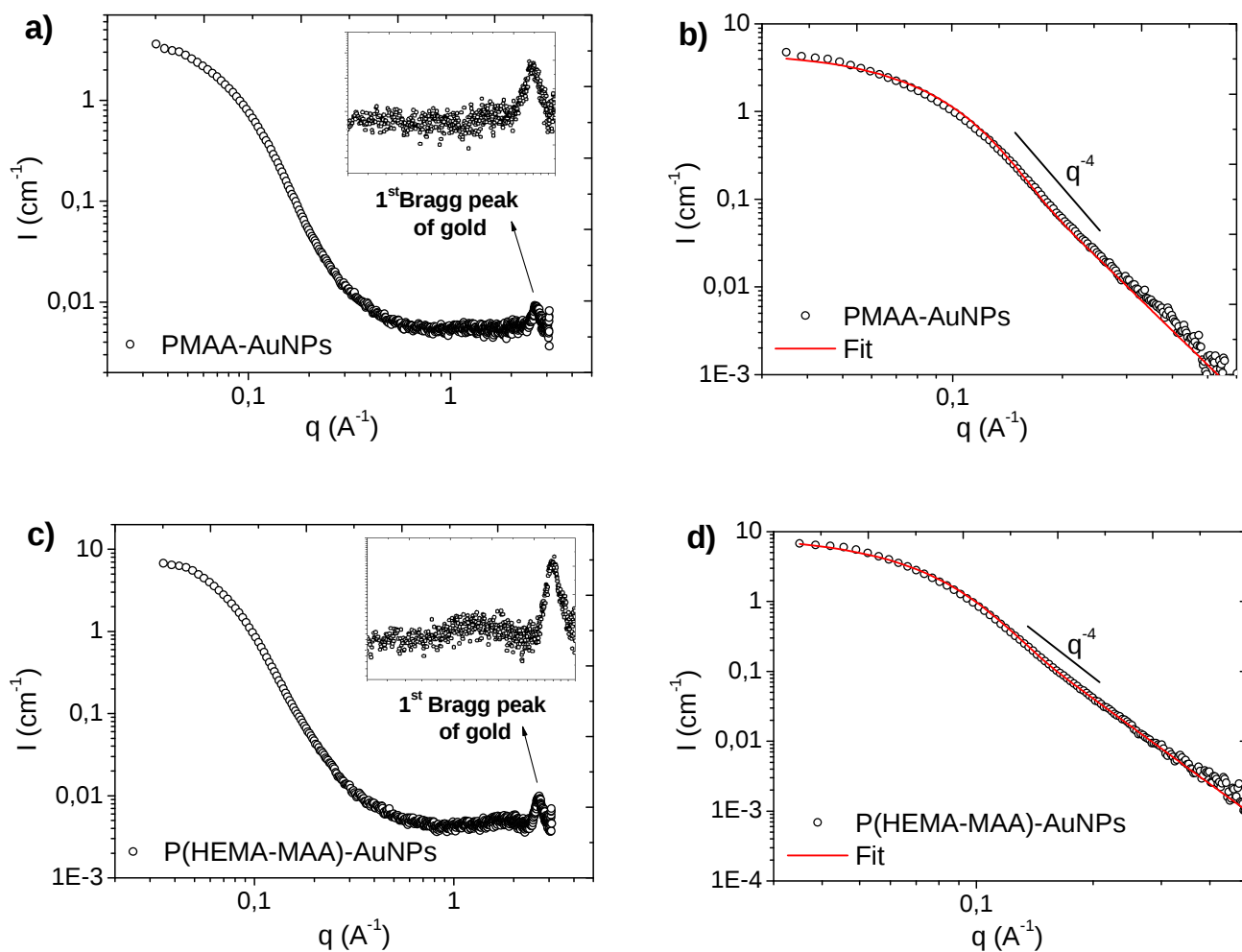


Figure S5. Raw SAXS spectra of PMAA-AuNPs (a) and P(HEMA-MAA)-AuNPs (c) with linear insert of the 1st Bragg peak of gold; Treated SAXS spectra and corresponding fits of PMAA-AuNPs (b) and P(HEMA-MAA)-AuNPs (d). Parameters used for the fits were the following: $R=15$ $\text{\AA}$ and $\text{PDI}=0.5$ (Gaussian distribution) for PMAA-AuNPs; $R=20.637$ $\text{\AA}$ and $\text{PDI}=0.3$ (lognorm distribution) for P(HEMA-MAA)-AuNPs.

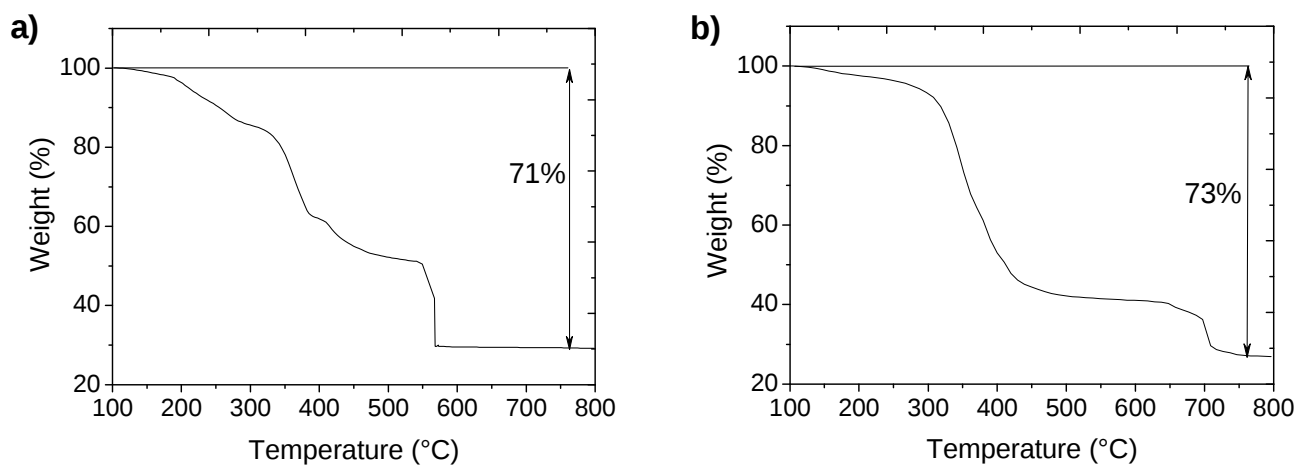


Figure S6. TGA analysis of PMAA-AuNPs (a) and P(HEMA-MAA)-AuNPs (b).

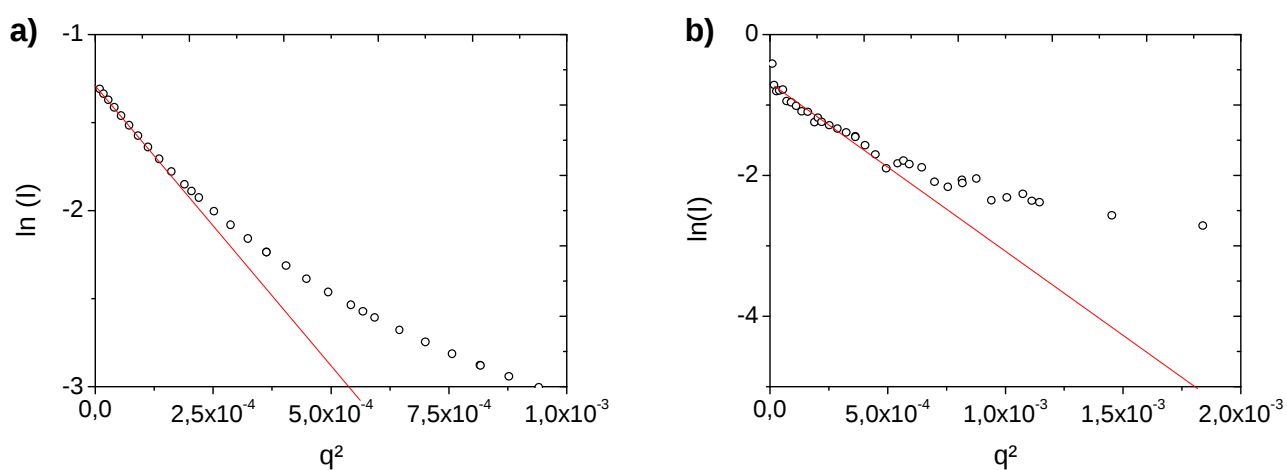
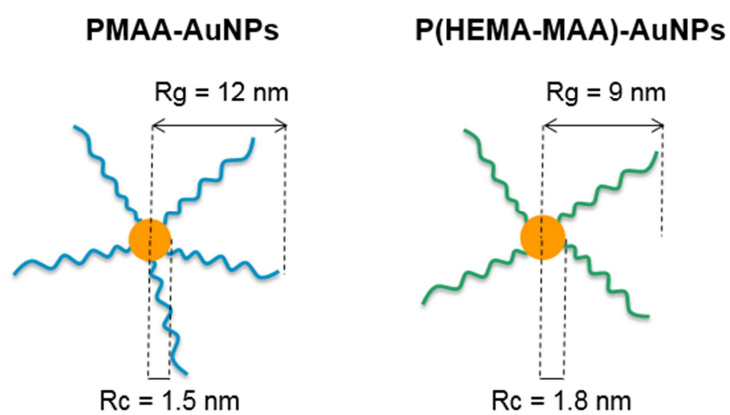


Figure S7. Guinier plots for PMAA-AuNPs (a) and P(HEMA-MAA)-AuNPs (b).



Scheme S1. Size and structure of nano-objects.

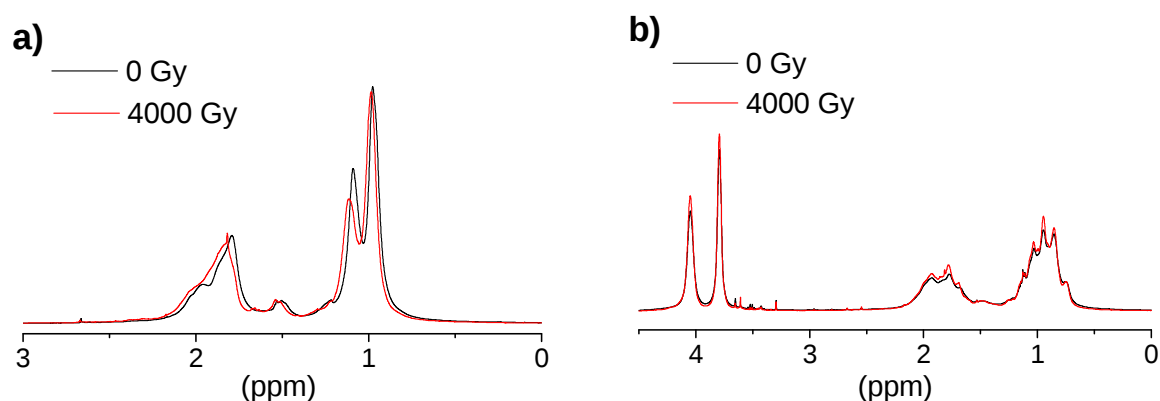


Figure S8. ^1H NMR spectra before and after irradiation of PMAA-AuNPs (a) and P(HEMA-MAA)-AuNPs (b).

Table S1. M_n and PDI values obtained from SEC measurements for PMAA-AuNPs and P(HEMA-MAA)-AuNPs before and after irradiation.

Polymer	Dose (Gy)	Grafted chains		Free chains		Initial ligands	
		M_n (g/mol)	PDI	M_n (g/mol)	PDI	M_n (g/mol)	PDI
PMAA	0	4900	1.6	3800	1.1	4600	1.1
	4000	2900	1.2	2600	1.3	2500	1.2
	20000	2500	1.1	1900	1.2	2200	1.2
P(HEMA-MAA)	0	5500	1.4				
	4000	5600	1.3				
	20000	3100	1.3				

Table S2. Scission and degrafting yields obtained for PMAA-AuNPs and PHEMA-PMAA-AuNPs.

		PMAA	P(HEMA-MAA)
Calculated scission yields with respect to the dose received by the solution (mol.J^{-1})	Grafted chains	1.6×10^{-7}	2.7×10^{-8}
	Free chains	1.6×10^{-7}	/
	Initial ligands	2.0×10^{-7}	/
Calculated degrafting yields (near-surface scission events)	With respect to the dose received by the solution (mol.J^{-1})	1.1×10^{-8}	4.8×10^{-8}
	With respect to the dose received by NPs (molecules per 100 eV)	~ 10	~ 50

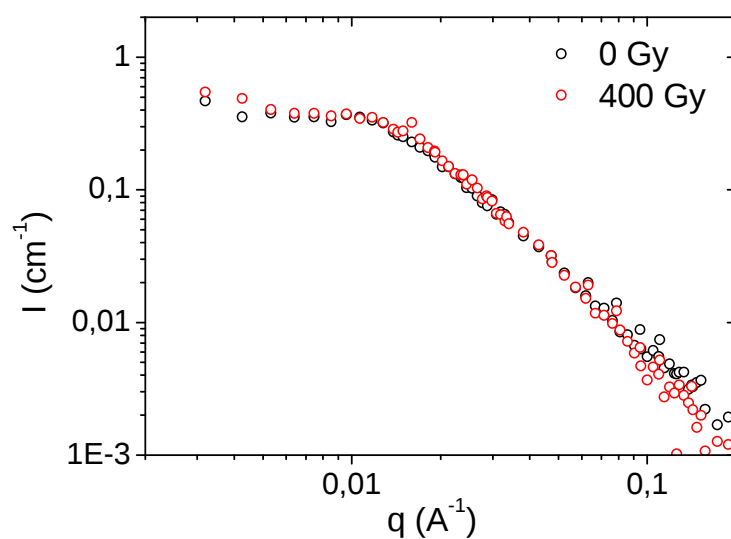


Figure S9. SANS spectra of PMAA-AuNPs before and after irradiation (400 Gy).

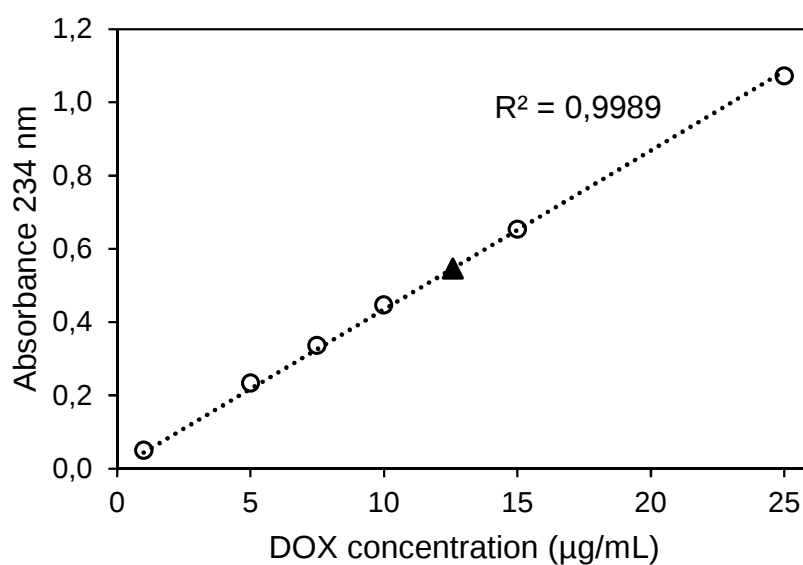


Figure S10. UV-vis calibration curve of PMAA-AuNPs (0.13 mg/mL) associated with increasing concentrations of DOX (○). Absorbance values correspond to the 234 nm peak of DOX. Concentration of grafted DOX (▲) was estimated using this calibration curve.