Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

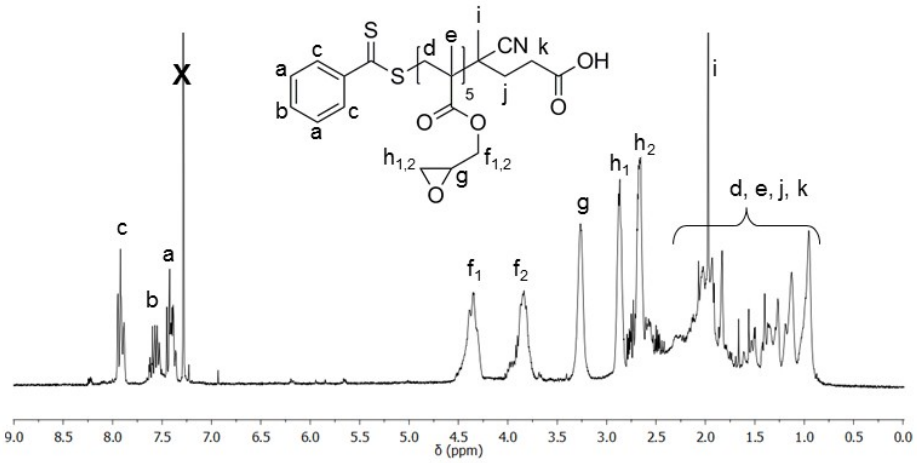

Figure S1: ^{1}H NMR spectra of poly(glycidyl methacrylate) as recorded in $CDCl_3$.

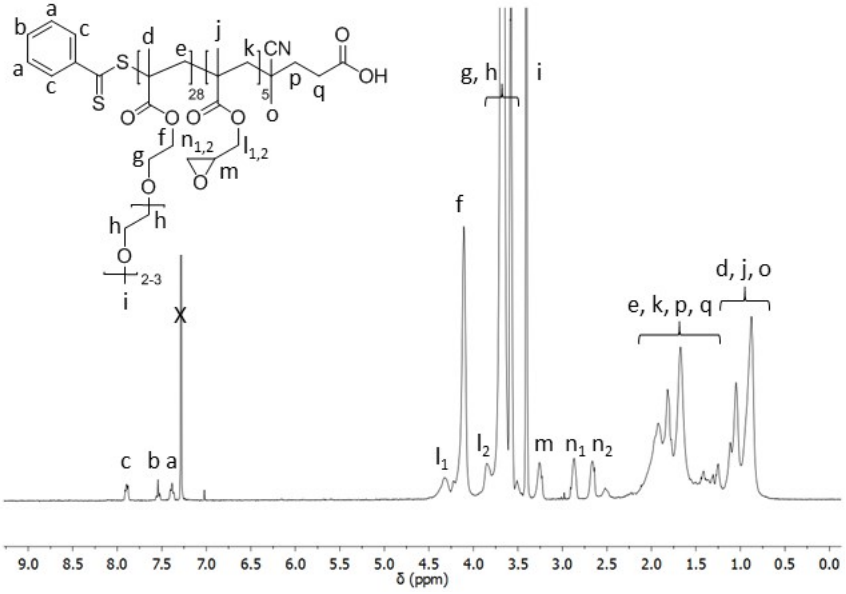

Figure S2: ^{1}H NMR spectra of PGMA-b-POEGMA as recorded in $CDCl_3$.

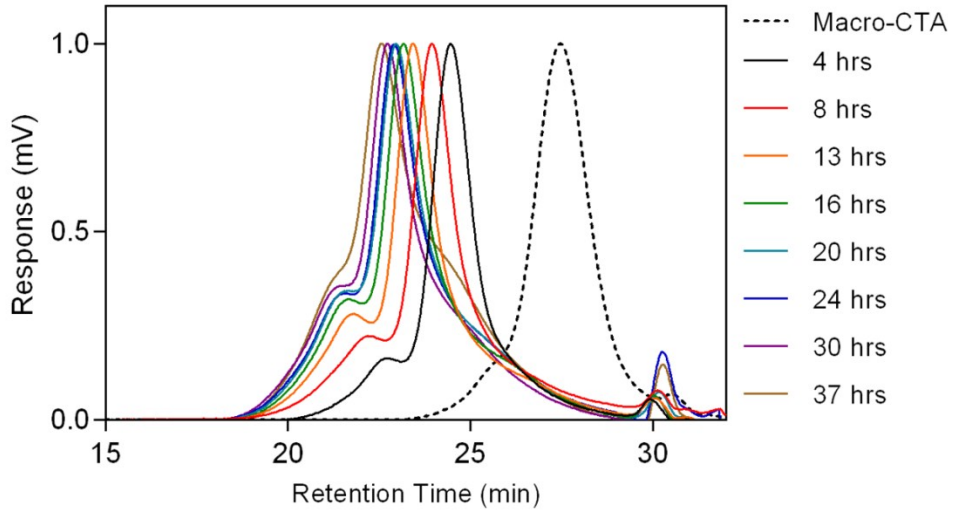

Figure S3: Evolution of SEC traces versus polymerization times for PGMA-*b*-POEGMA-*b*-PST.

Table S1: Conjugation of furfuryl mercaptan to epoxide surface-functional polymeric nanoparticles. Morphologies: micelle (M), filomicelle (FM), and vesicle (V).

Polymer	DP (^{1}H NMR)			Furfuryl mercaptan	TEM shape	
	GMA	OEGMA	ST	Conjugation (%)	Before conjugation	After conjugation
PGMA-*b*-POEGMA-*b*-PS	5	28	132	18%	M	M
	5	28	220	22%	FM	FM
	5	28	264	17%	V	V

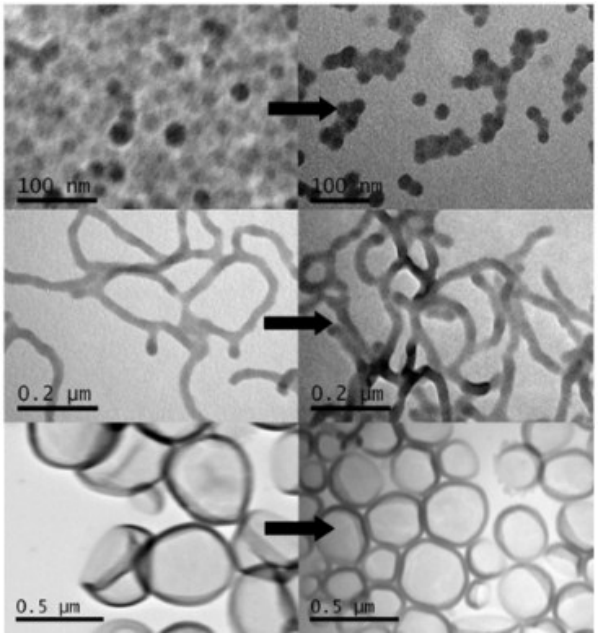

Figure S4: TEM confirmed stability of each morphology after conjugation of furfuryl mercaptan.

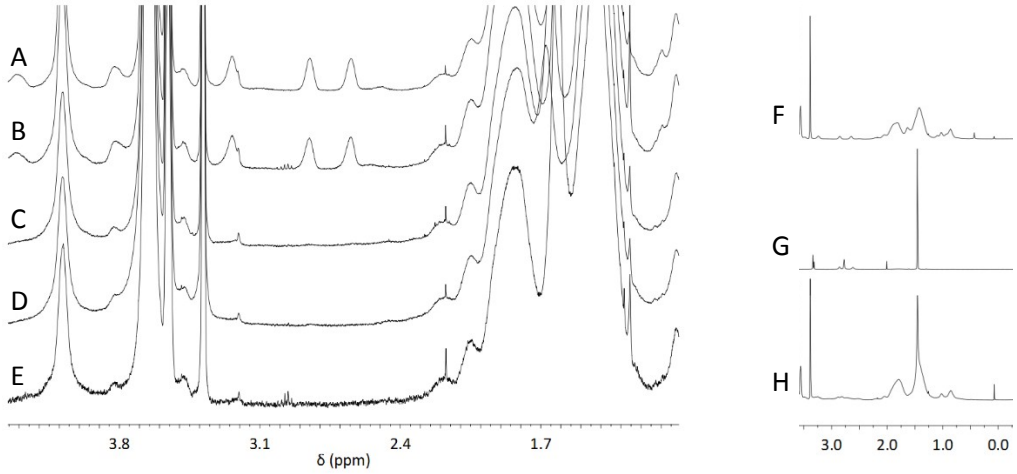

Figure S5: Left: ^{1}H NMR study of the conjugation of a primary amine, propargylamine, to the epoxide surface-functional polymeric nanoparticles. (A) epoxide surface-functional polymeric nanoparticles, showing oligoethylene glycol methyl ether NMR signals between δ 4.1 – 3.3 ppm, and epoxide NMR signals at δ3.24, 2.85, and 2.65 ppm; (B) after reaction conditions of 50 °C overnight; (C) 10 eq. of propargylamine and 6 eq. of triethylamine (per epoxide); (D) 10 eq. of propargylamine; (E) 6 eq. of triethylamine. Right: ^{1}H NMR study of the conjugation of 4-aminobutyl-DOTA-tris (t-butyl ester) to the epoxide surface-functional polymeric nanoparticles: (F) epoxide surface-functional polymeric nanoparticles, showing the polymer backbone NMR signals; (G) 4-aminobutyl-DOTA-tris (t-butyl ester), showing the large proton NMR signal for the t-butyl groups; (H) conjugation of NH_2-DOTA(tBu) to the polymeric nanoparticle.

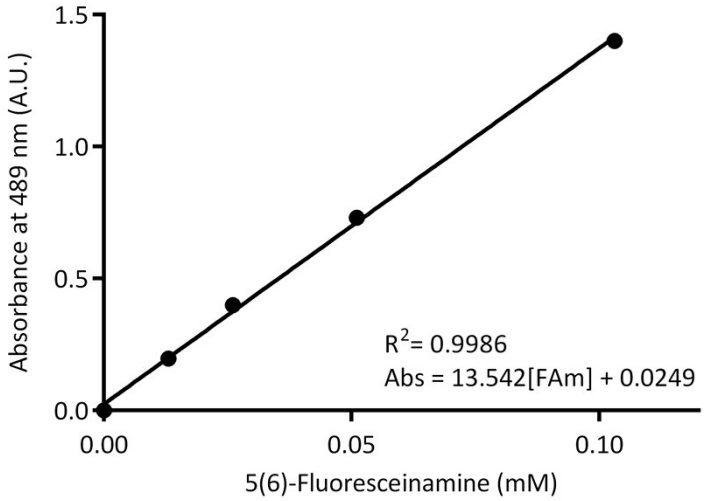

Figure S6: Calibration curve of FAm with R^2 of 0.9986.

Table S2: Conjugation of 5(6)-fluoresceinamine to epoxide surface-functional polymeric nanoparticles. Morphologies: micelle (M), filomicelle (FM), and vesicle (V).

Polymer	DP (^{1}H NMR)			5(6)-Fluoresceinamine	TEM shape	
	GMA	OEGMA	ST	Conjugation (%)	Before conjugation	After conjugation
PGMA-*b*-POEGMA-*b*-PS	5	28	132	26	M	M
	5	28	220	23	LW	LW
	5	28	264	19	V	V

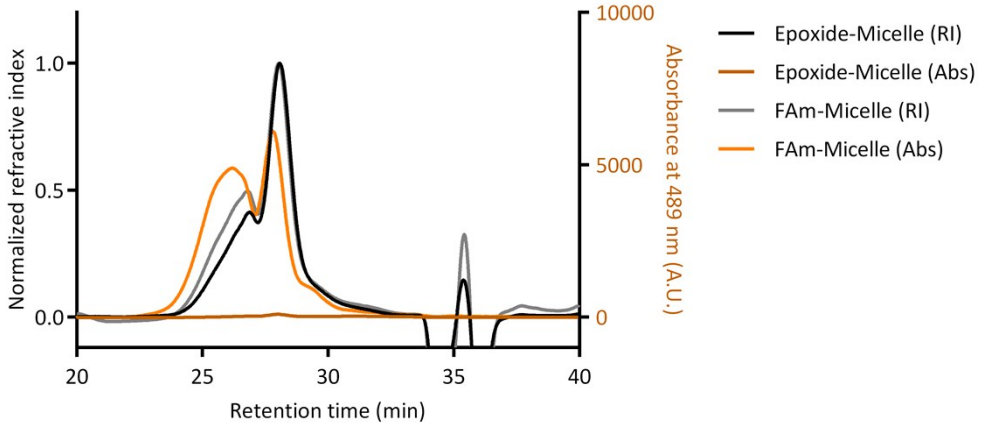

Figure S7: Size-exclusion chromatograms in DMAc of polymer before and after 5(6)-fluoresceinamine conjugation, on the left axis the refractive index is displayed and on the right axis absorbance at 489 nm.

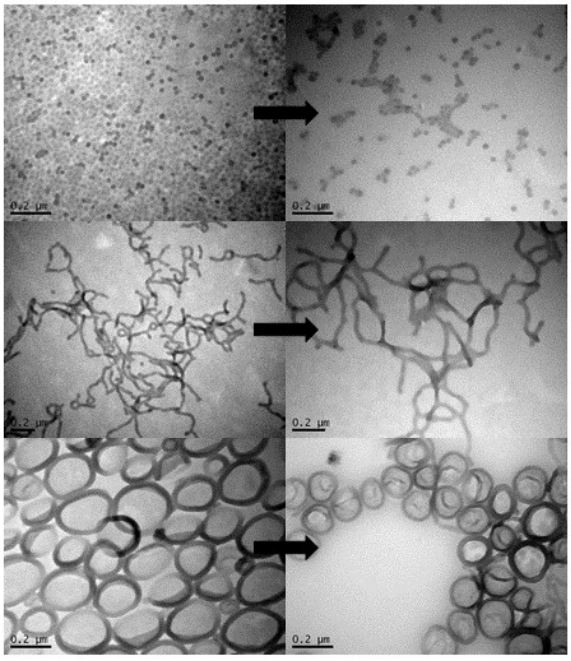

Figure S8: Transmission electron micrographs showing the different morphologies before and after fluorophore conjugation.

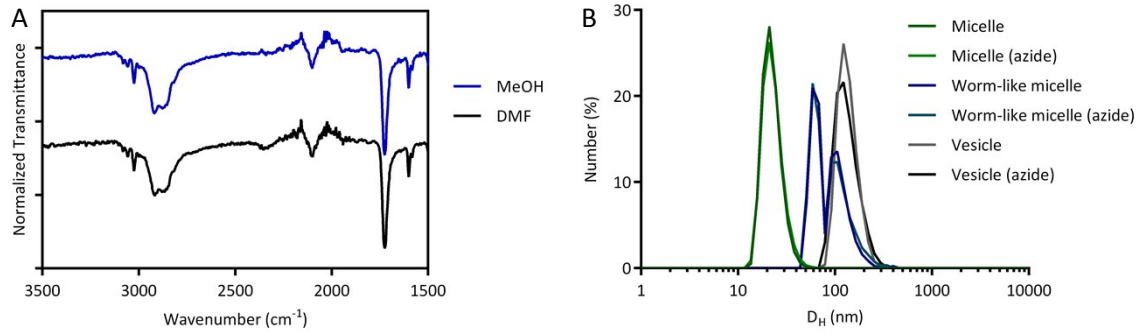

Figure S9: (A) ATR FTIR spectra of polymer after ring-opening with sodium azide in methanol (MeOH, self-assembled nanoparticles) and in *N,N*-dimethylformamide (DMF, dissolved polymer) showing similar efficiency; (B) dynamic light scattering showing stability of self-assembled nanoparticles upon ring-opening.

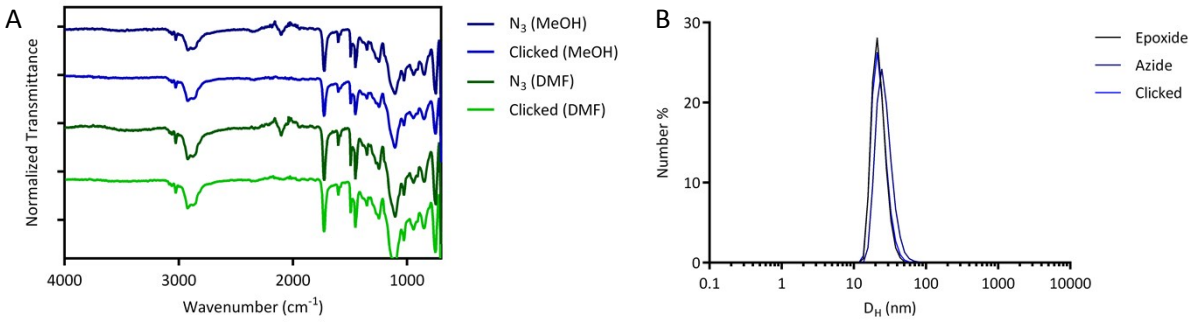

Figure S10: (A) ATR FTIR of azide-functional polymers in methanol (micelles) or DMF (dissolved), before and after CuAAC click reaction with propargylamine. (B) Number-average distribution in DLS of epoxide-functional, azide-functional and propargyl-clicked polymeric micelles.

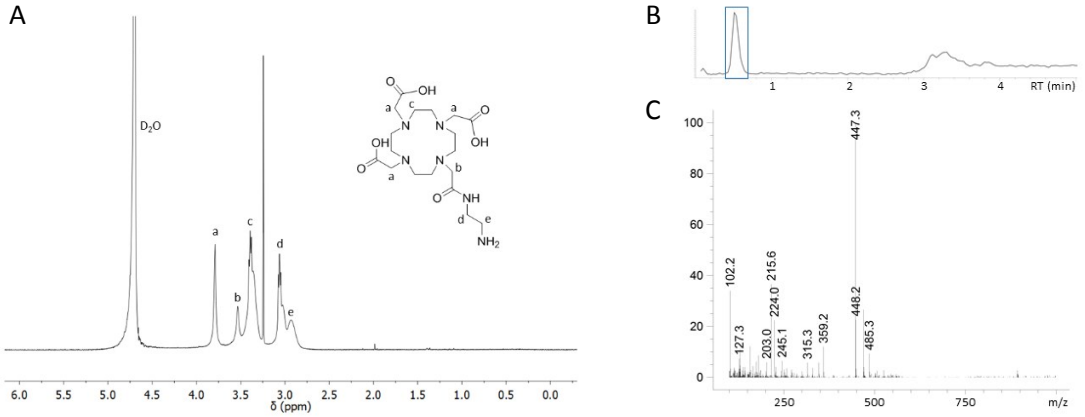

Figure S11: (A) ^{1}H NMR spectra of 4-aminobutyl-DOTA recorded in deuterium oxide, demonstrating complete removal of the *tert*-butyl ester protection groups at δ 1.41 ppm. (B) API-ESI positive mode chromatogram with (C) mass spectrum of main signal (M + H, 447.3).

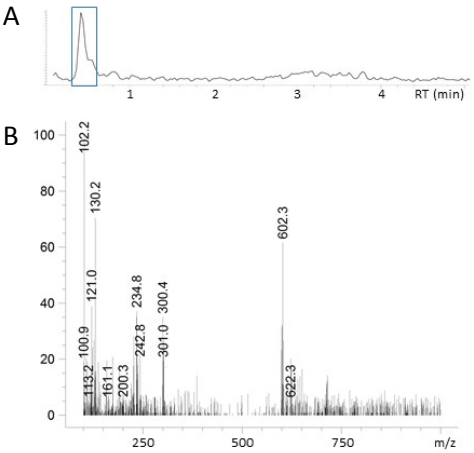

Figure S12: (A) API-ESI positive mode chromatogram with (B) mass spectrum of main signal (M + H, 602.3) representing 4-aminobutyl-DOTA(Gd).

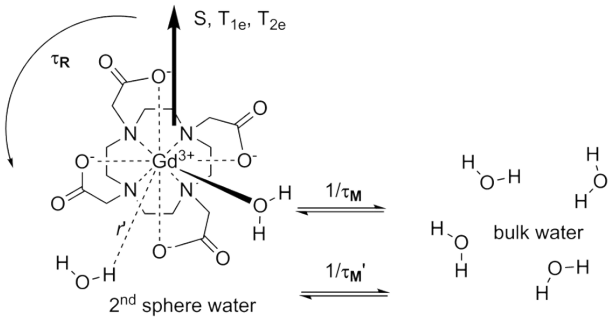

Figure S13: Factors influencing solvent water relaxation, adapted from Caravan *et al*.[1] The metal complex has an inner sphere of nitrogen and oxygen atoms from the DOTA ligand and a coordinated water molecule. There is a distinct second hydration sphere with Gd–H distance r, and water molecules from both spheres undergo exchange with bulk water at rates $1/\tau_M$ and $1/\tau_M'$ for first- and second-sphere exchange.

References

1. P. Caravan, *Chem Soc Rev*, 2006, **35**, 512-523.