Electronic Supplementary Material (ESI) for Soft Matter.

Dual-Reactive Nanogels for Orthogonal Functionalization of Hydrophilic Shell and Amphiphilic Network

Alexandra Gruber, [a] Lucila Navarro [a] and Daniel Klinger [a]*

[a]Institute of Pharmacy (Pharmaceutical Chemistry), Freie Universität Berlin,

Königin-Luise-Straße 2-4, 14195 Berlin, Germany

E-mail: daniel.klinger@fu-berlin.de

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1. Establishing a synthetic procedure for the preparation of reactive precursor particles with a hydrophilic PPEGMA corona

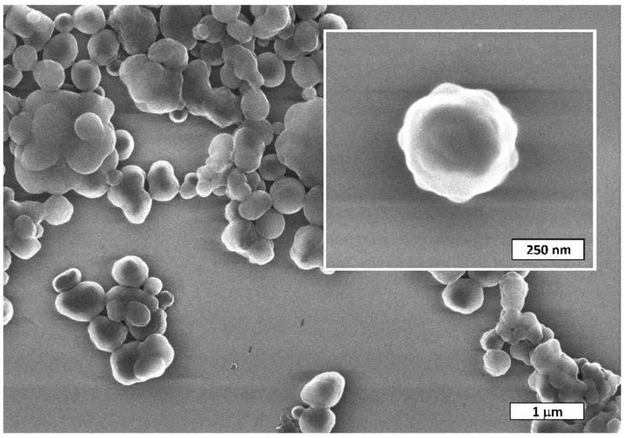


Figure S 1. SEM image of PPFPMA particles synthesized via emulsion polymerization with a reactive surfactant at 80°C result in raspberry like particles.

2. Monitoring the conversion of PPFPMA core to an amphiphilic interior

The successful conversion of the interior pentaflurophenyl esters (PFP) to the respective amides was followed by attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) on freeze dried particles. Upon functionalization the reactive PFP ester band disappear (1778 cm^{-1}) while new bands for the respective amides (1662 cm^{-1}) appear (Figure S 2).

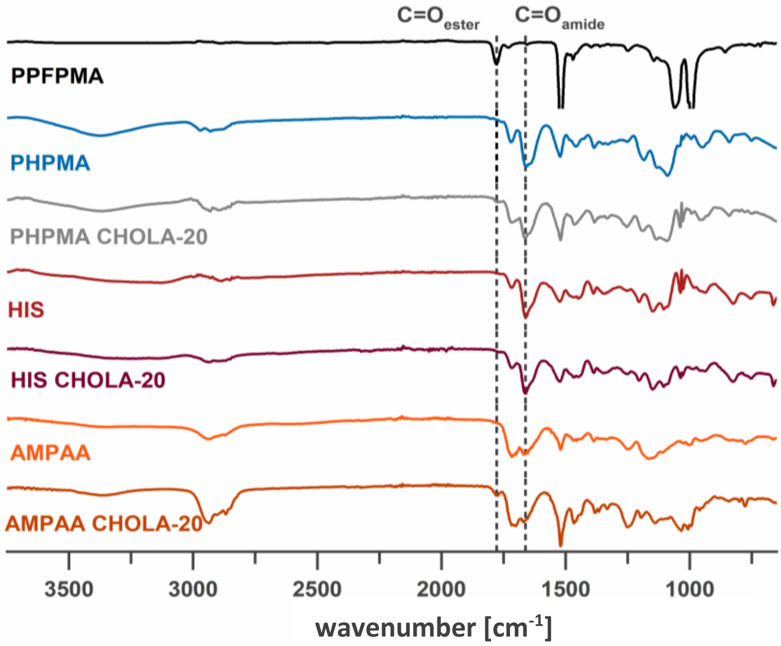


Figure S 2. Successful network functionalization of the NGs is demonstrated by the disappearance of the reactive PFP ester band and the simultaneous appearance of the amide bands in ATR-FTIR spectra.

3. Particle Characterization

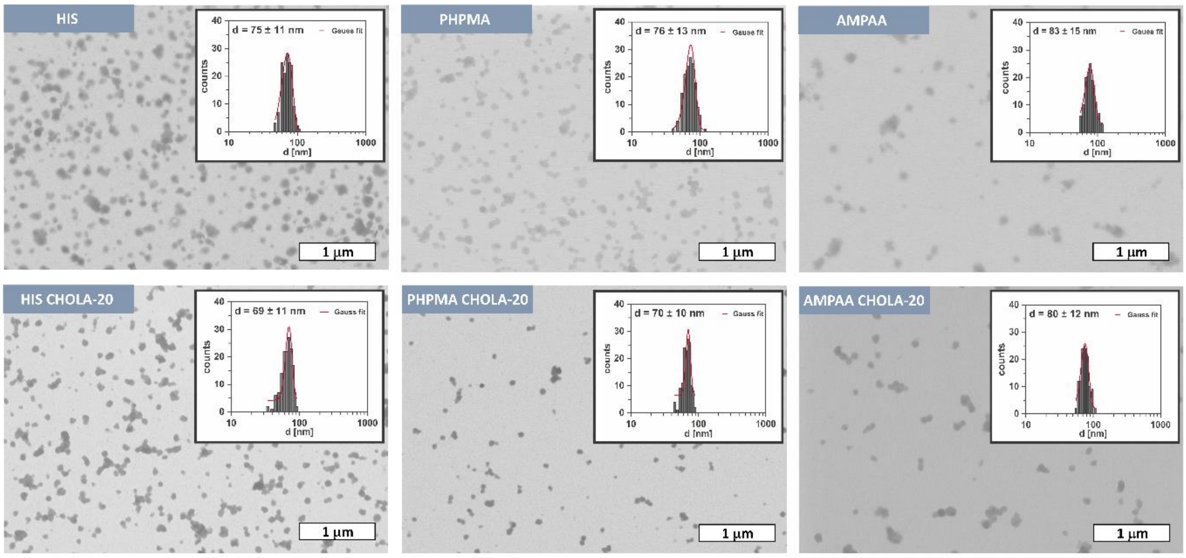


Figure S 3. Post-functionalization of reactive precursor particles gives access to well-defined NGs with different functionality. TEM images and statistical evaluation of 150 NGs show, that the overall hydrophilic NGs are only slightly bigger than their amphiphilic counterparts. Thus, showing the typical deformation of such soft particles, while the amphiphilic ones are more defined and show less deformation due to additional physical crosslinks.

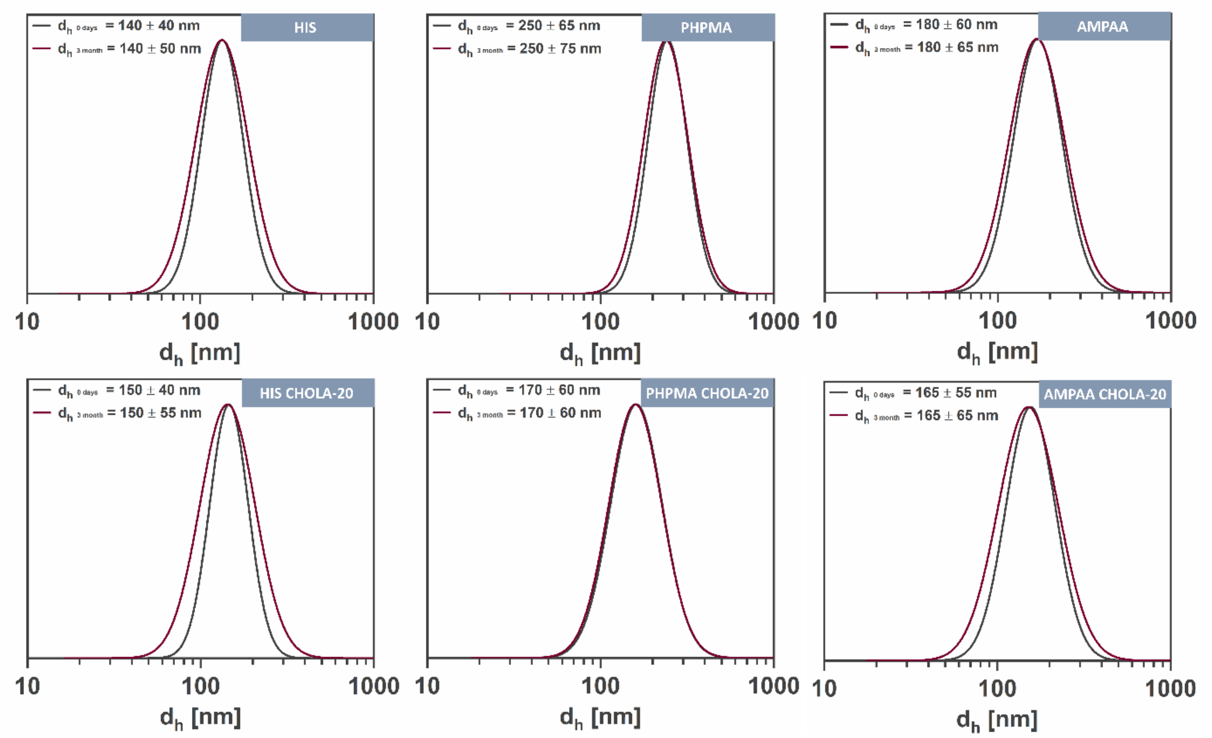


Figure S 4. DLS curves of NGs after 0 days (black) and 3 months (red) show colloidal stable NGs in water. Measurements are carried out at an angle of 90°. Error values represent the width of the size distribution as standard deviation.

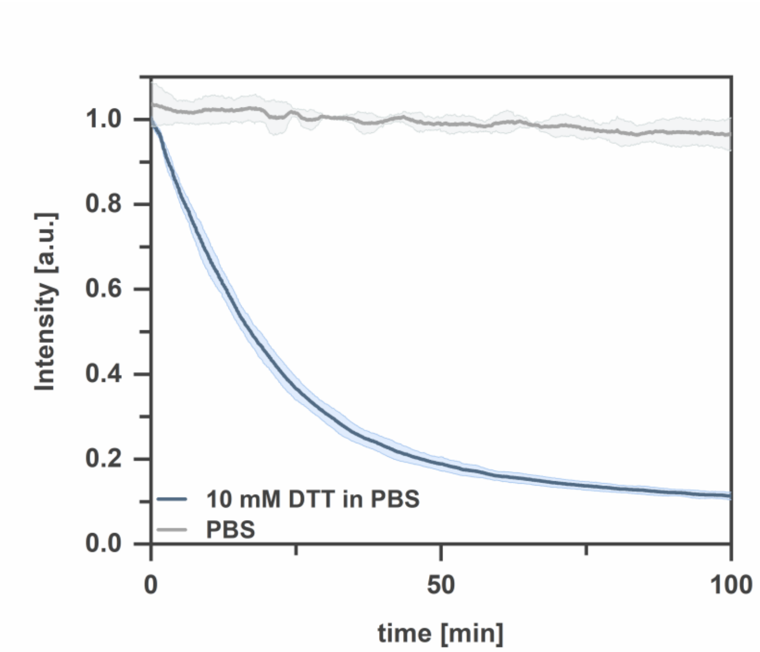
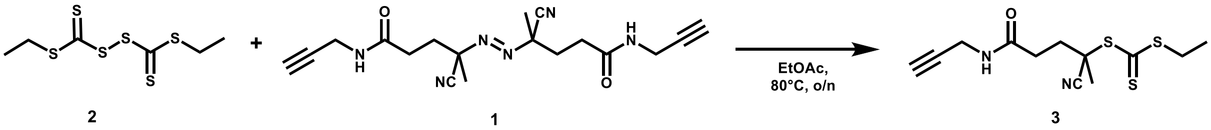


Figure S 5. Turbidity measurements of PHPMA NGs based on reactive precursor particles synthesized via emulsion polymerization with SDS as surfactant treated with 10 mM DTT show a strong decrease in the intensity. Thus, indicating the cleavage of the redox-responsive crosslinker followed by disintegration of the NG network. Solid line represents the average of 3 turbidity measurements. Colored area represents the error as standard deviation.

4. Characterization data

4.1 Alkyne modified chain transfer agent



Scheme S 1 Reaction scheme of alkyne chain transfer agent (3).

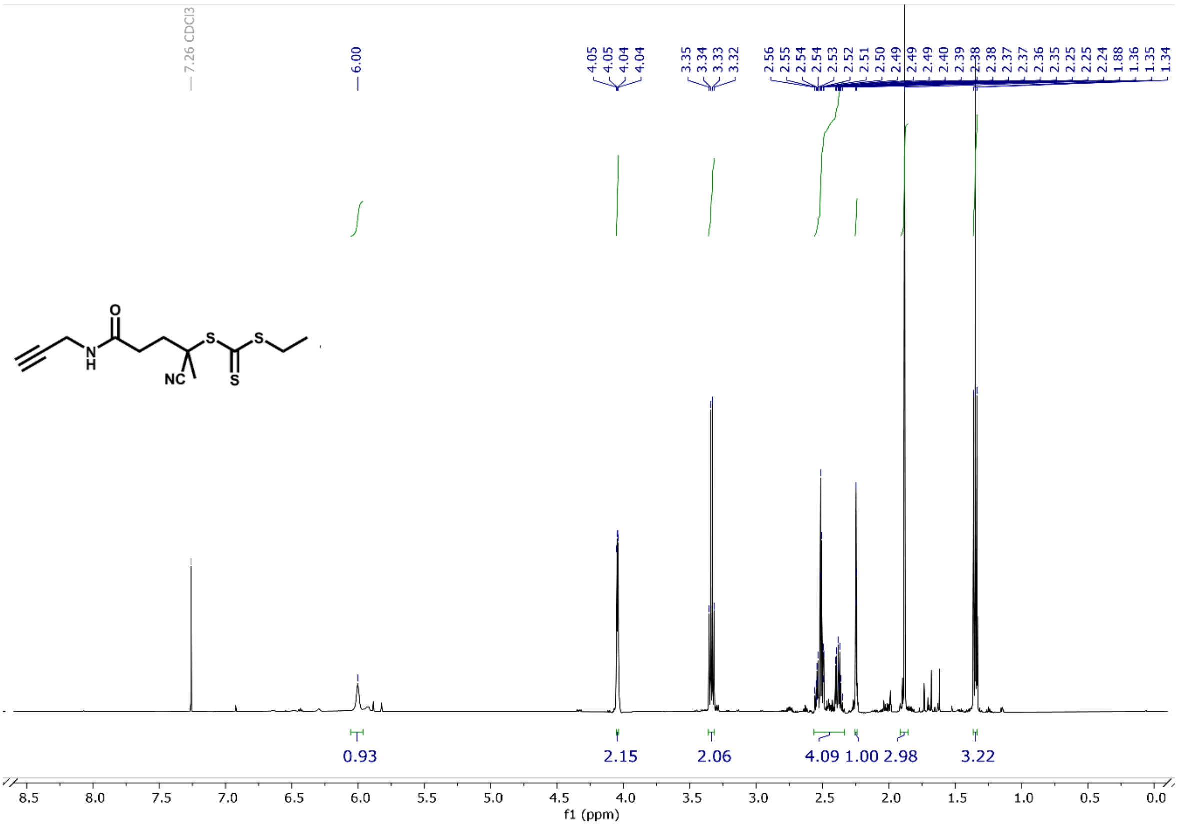


Figure S 6. ^{1}H NMR of alkyne modified chain transfer agent (**3**).

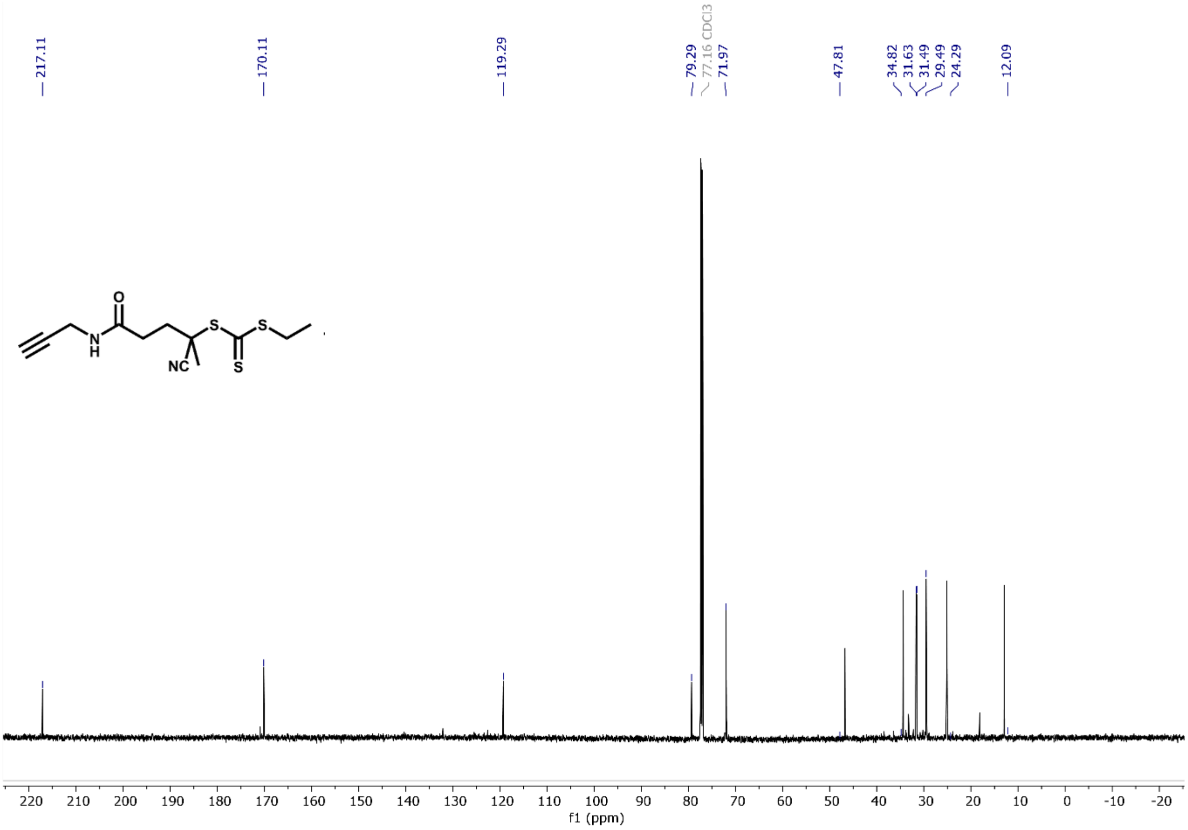


Figure S 7. ^{13}C NMR of alkyne modified chain transfer agent (**3**)

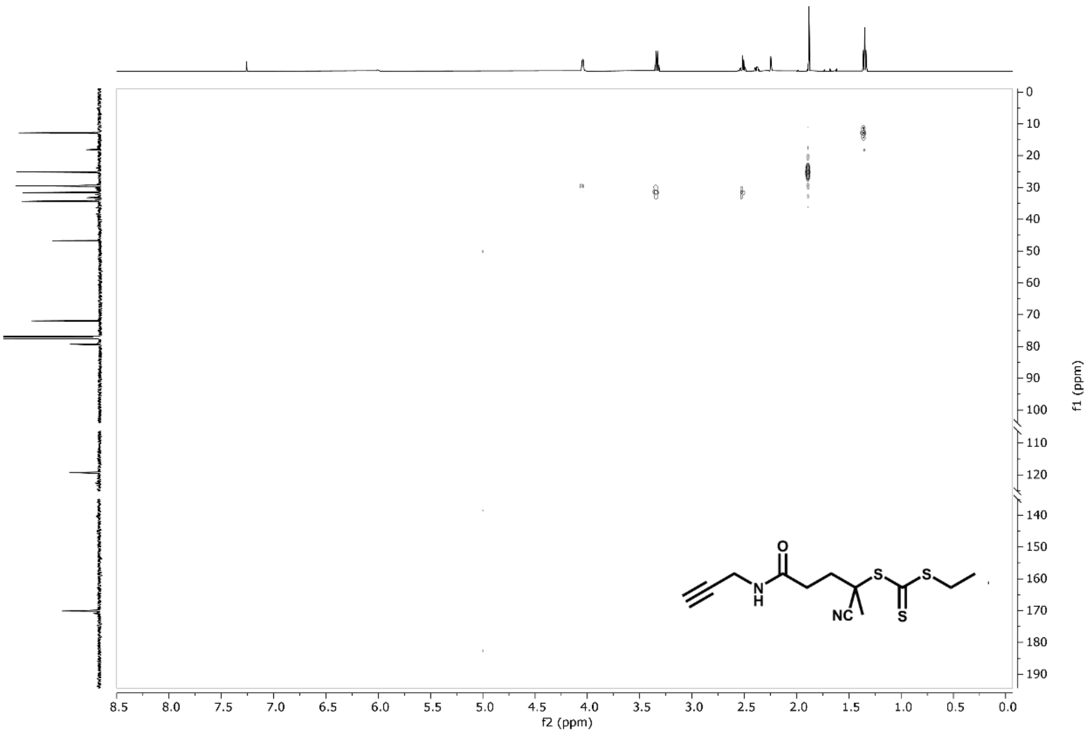


Figure S 8. HMQC of alkyne modified chain transfer agent (**3**)

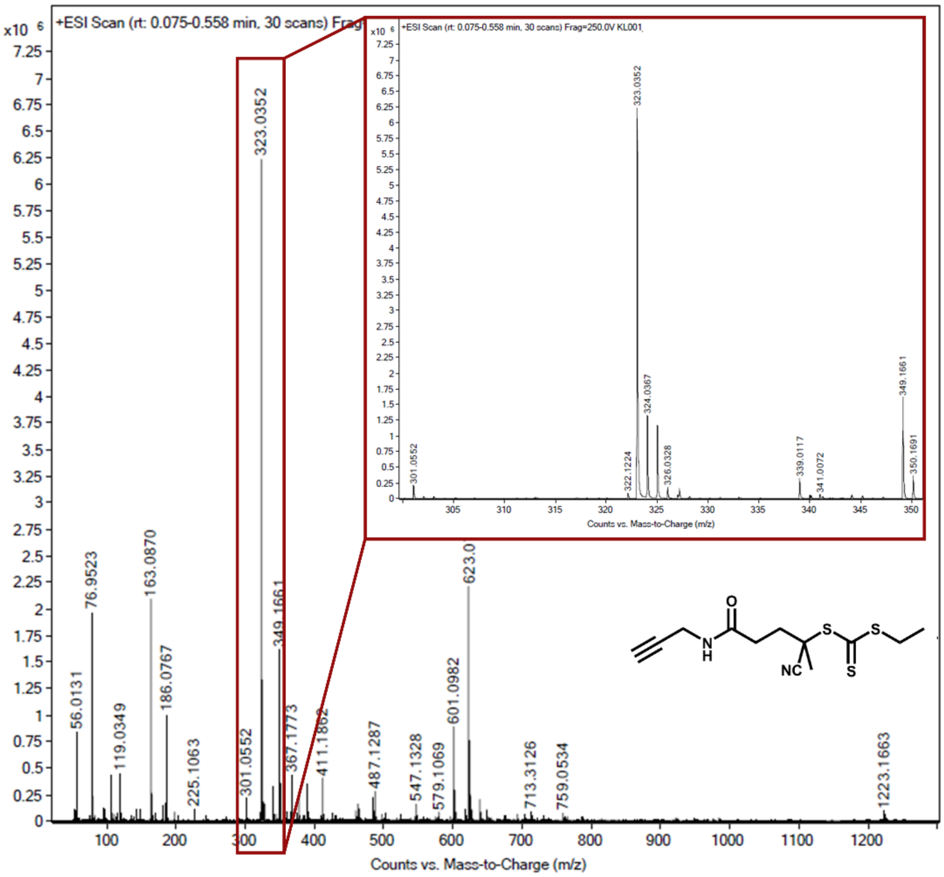
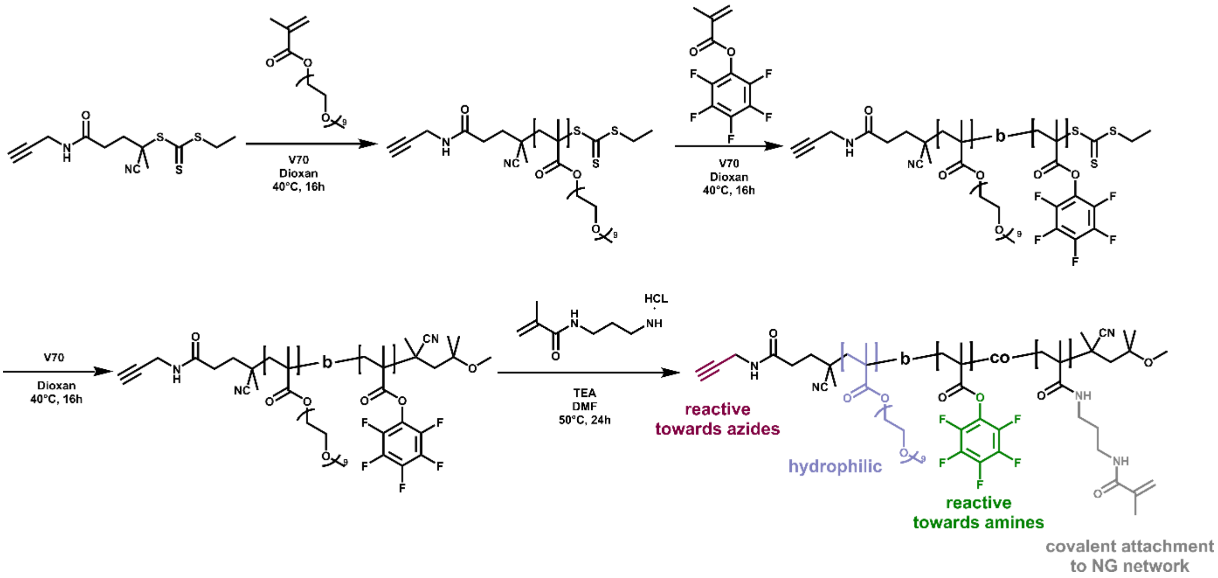


Figure S 9. ESI-MS spectra of alkyne modified chain transfer agent (**3**).

4.2 Reactive surfactant



Scheme S 2. Reaction scheme of the synthesis of the dual reactive block copolymer surfactant.

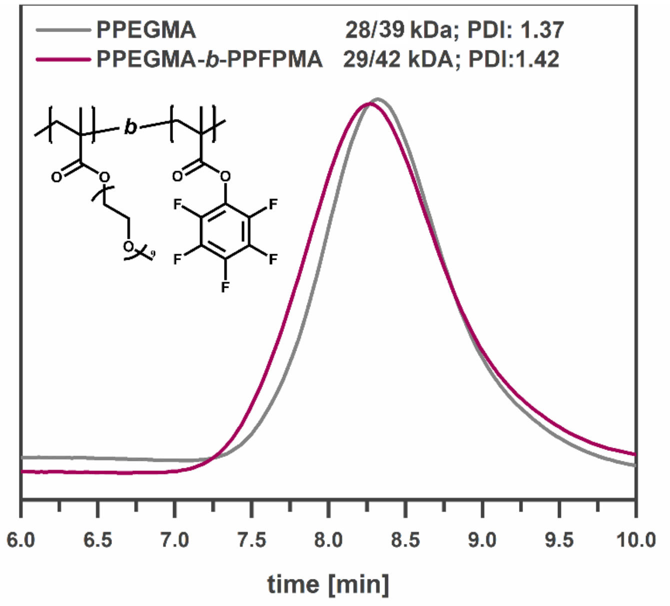


Figure S 10. GPC measurements indicate only negligible chain extension of the PPEGMA macro-raft.

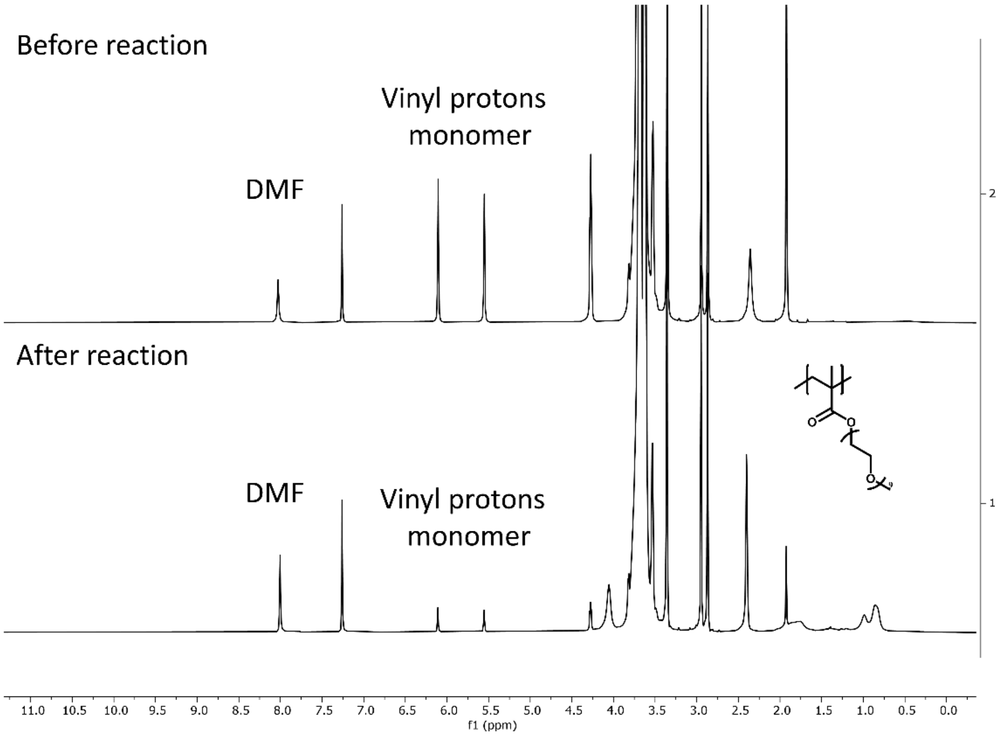


Figure S 11. ^{1}H NMR show a conversion of 83 % for the polymerization of PEGMA. For this, ^{1}H NMR were taken of the reaction mixture before and after the synthesis and the integrals of the vinyl protons of the monomer were compared to each other using DMF as internal standard. This corresponds to 25 kDa PPEGMA$_{500}$ block.

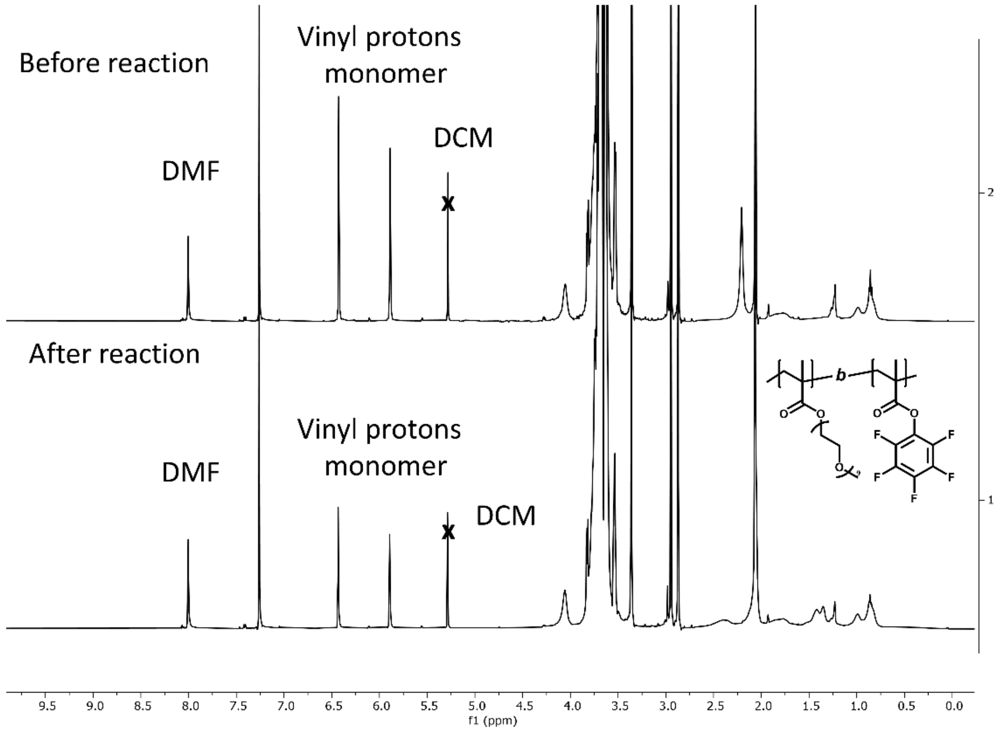


Figure S 12. ^{1}H NMR show a conversion of 45% for the polymerization of PFPMA initiated by PPEGMA macro raft. For this, ^{1}H NMR were taken of the reaction mixture before and after the synthesis and the integrals of the vinyl protons of the monomer were compared to each other using DMF as internal standard. This corresponds to a 9 kDA PFPMA block.

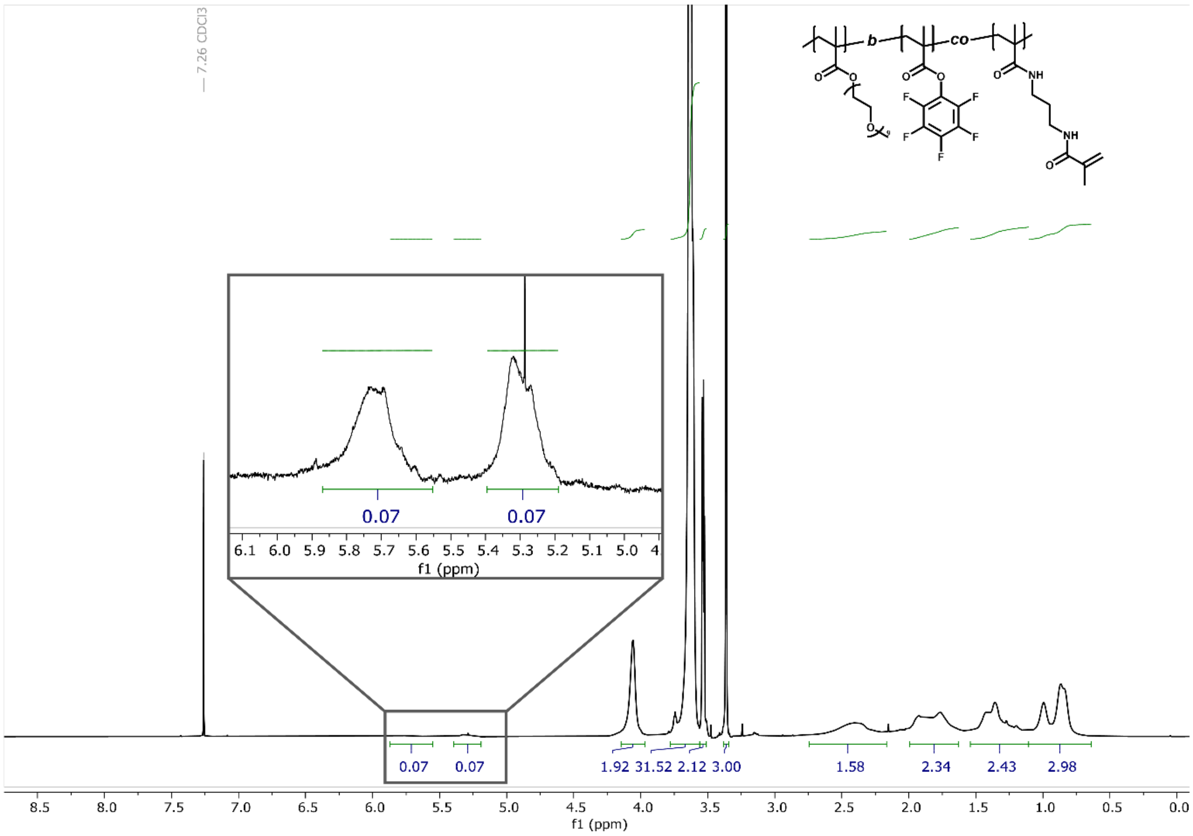


Figure S 13. ^{1}H NMR of reactive block copolymer surfactant indicate a functionalization with around 3 APMA groups.

5. Parameters for post-functionalization PPFPMA core

Table S 1. Parameters for post-functionalization reaction of PPFPMA precursor particles with PEGMA corona

Sample name	**Hydrophilic group R**				**Hydrophobic CHOLA**		
	Type of hydrophilic group R	**eq**	**n [mmol]**	**m [mg]**	**eq**	**n [mmol]**	**m [mg]**
HIS	HIS	3	1.18	132	-	-	-
HIS CHOLA-20	HIS	2.4	0.95	106	0.6	0.24	112
PHPMA	HPA	3	1.18	89	-	-	-
PHPMA CHOLA-20	HPA	2.4	0.95	71	0.6	0.24	112
AMPAA	AMPAA	3	1.18	197	-	-	-
AMPAA CHOLA-20 (seq.)	AMPAA	2.8	1.11	183	0.2	0.08	38