Supporting Information

Functional, sub-100 nm polymer nanoparticles via thiol-ene miniemulsion photopolymerization

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Table S1. Typical SDS stock solution formulation to prepare samples with various concentrations of organic phase.

SDS Stock Solution	Mass (g)	Weight %
SDS	0.578 (2.00 mmol)	0.600
DI water	90.0	99.4

Table S2. Sample preparation for varying the amount of organic phase with 20 mM SDS.

SDS Stock (mL)	DI Water (μL)	Organic Stock (μL)
9	500	500
9	600	400
9	650	350
9	700	300
9	725	275
9	750	250
9	775	225
9	800	200
9	815	185
9	825	175
9	850	150
9	900	100
9	950	50
9	975	25

Effect of Various Concentrations of SDS
The organic concentration was kept constant at 2.5 % (v/v) while the relative amounts of SDS stock (Table SI-3) and DI water were adjusted to maintain 10 mL total volume (Table SI-4).

Table S3. Aqueous formulation to prepare samples at a variety of SDS concentrations.

SDS Stock Solution	*Mass (g)*	*Weight %*
SDS	2.38 (8.00 mM)	2.5
DI water	90.0	97.5

Table S4. Samples preparation for varied SDS concentration with a constant organic stock.

[SDS] (mmol)	*SDS Stock (μL)*	*DI Water (μL)*	*Organic Stock (μL)*
0.80	9000	750	250
0.40	4500	5250	250
0.20	2250	7500	250
0.10	1125	8625	250
0.05	562.5	9187.5	250
0.025	281.25	9468.75	250

Effect of Sonication Time
Samples with 2.5 % of organic and 20 mM of SDS were prepared while the sonication time was varied from 5, 10, 15, 20, 25, 30, 45, 60 minutes.

Effect of Sonication Amplitude (Intensity setting)
Samples with 2.5 % of organic and 20 mM of SDS were prepared by varying amplitude setting from 5, 10, 15, 20, 25 percent.

Effect of inhibitor
Samples with 20 mM of SDS and 2.5 % organic phase were prepared with varying amounts of inhibitor (MEHQ) ranging from 0 to 60 mg. The samples were emulsified at 10 % amplitude for 20 minutes.

Effect of hexadecane
Two different organic phases with and without hexadecane were prepared following Table SI-1. Samples with 20 mM of SDS were prepared using 2.5 % with and without hexadecane. The samples were then placed into an ice bath and sonicated at 10 % amplitude for 20 minutes. The samples then place in the dark for different amount of time ranging from 0, 3, 6, and 72 hours before curing.

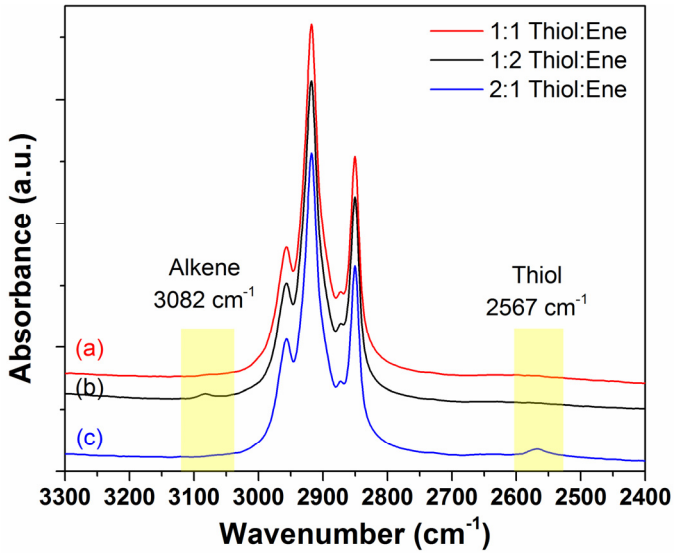

Figure S1. FTIR spectra of thiol-ene nanoparticles obtained after photopolymerization of miniemulsions containing (a) 1:1 stoichiometric ratios of thiol and alkene functional groups, (b) 1:2 thiol to alkene, and (c) 2:1 thiol to alkene. As expected, the 1:1 samples shows complete conversion of thiol (2567 cm^{-1}) and alkene (3082 cm^{-1}) functional groups.

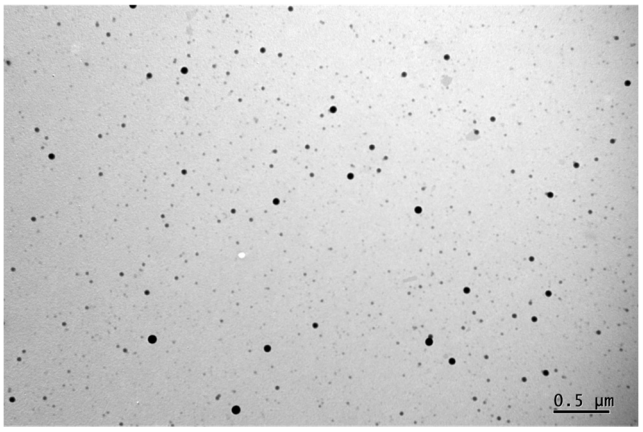

Figure S2. Lower magnification TEM image of thiol-ene nanoparticles synthesized at 2.5 wt. % organic fraction.

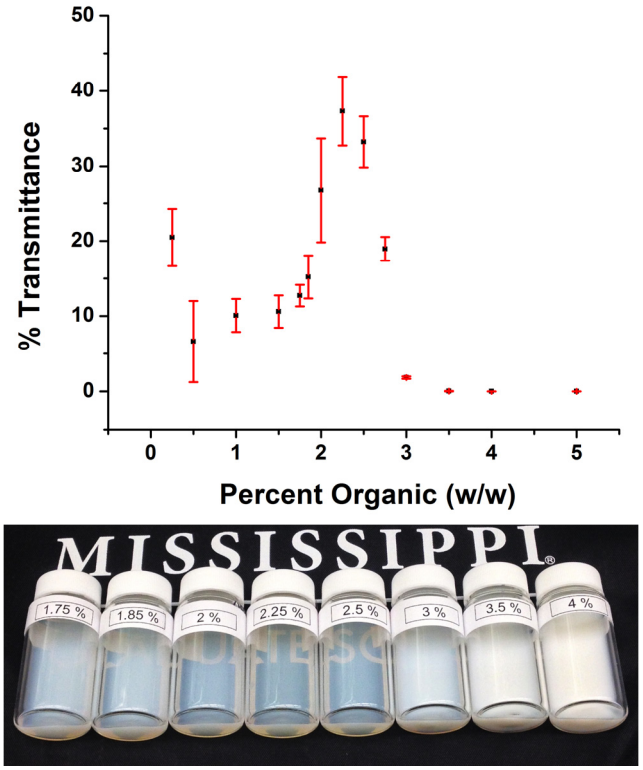

Figure S3. Percent transmittance of thiol-ene miniemulsions as a function of organic weight fraction in the formulation.

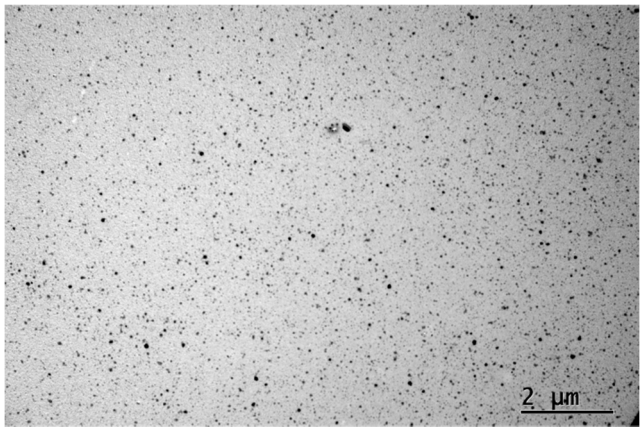

Figure S4. TEM image of thiol-ene nanoparticles synthesized with stoichiometric excess of thiol groups.

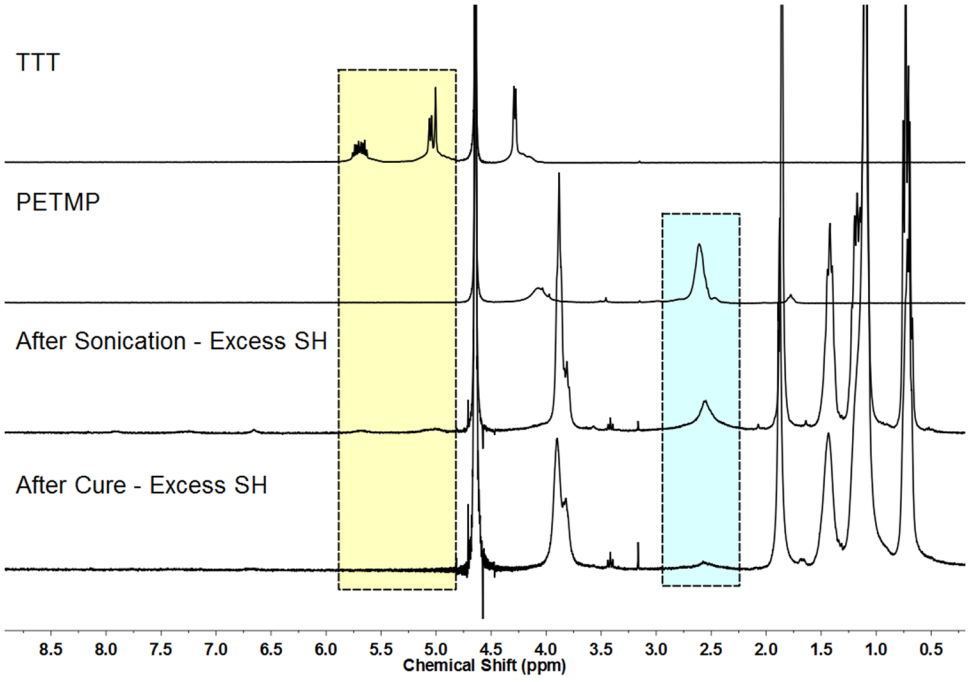

Figure S5. ^{1}H NMR of TTT and PETMP starting materials, miniemulsion containing excess PETMP (2:1 thiol:ene) prior to UV exposure, and miniemulsion containing excess PETMP after UV exposure. The lower spectrum confirms the presence of thiol (~ 2.5 ppm) remaining on the nanoparticles, and the complete consumption of the alkene. See Figure S1 for complimentary FTIR data.

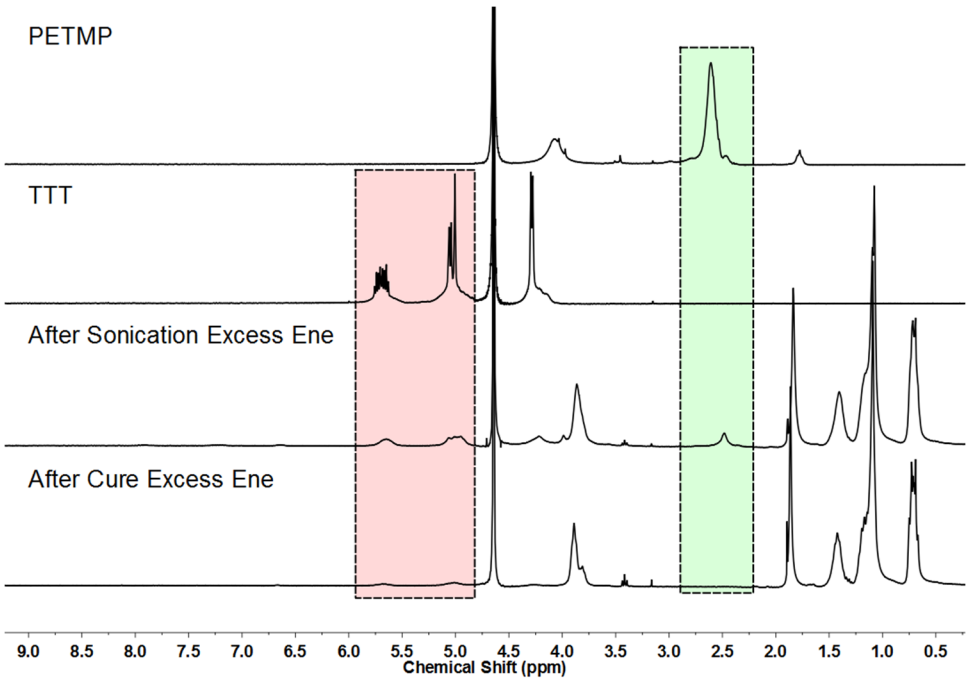

Figure S6. ^{1}H NMR of TTT and PETMP starting materials, miniemulsion containing excess TTT (1:2 thiol:ene) prior to UV exposure, and miniemulsion containing excess TTT after UV exposure. The lower spectrum confirms the presence of alkene (5.0 – 5.8 ppm) remaining on the nanoparticles, and the complete consumption of the thiol at 2.5 ppm. See Figure S1 for complimentary FTIR data.

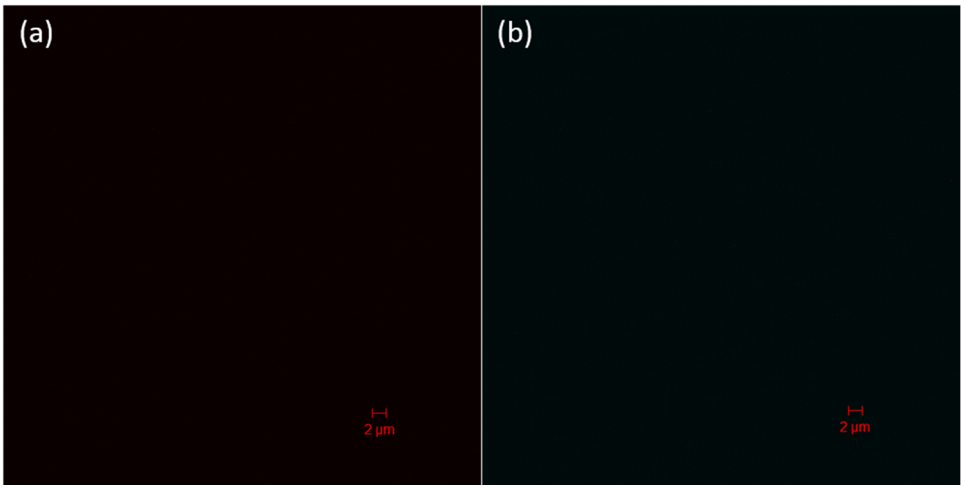

Figure S7. Confocal fluorescence control experiments for nanoparticle postpolymerization functionalization: (a) Thiol-functionalized nanoparticles (synthesized with excess 2:1 excess thiol:ene) were exposed to sulphorhodamine B (without maleimide) using the same reaction conditions as for Texas Red C2 maleimide. (b) Alkene-functionalized nanoparticles (synthesized with excess 1:2 excess thiol:ene) were exposed to 7-methoxy-4-methylcoumarin (without thiol) using the same reaction conditions as for 7-mercapto-4-methylcoumarin. After washing, the absence of nanoparticles in the fluorescence images in (a) and (b) shows that covalent attachment, rather than physisorption is responsible for nanoparticle fluorescence when employing reactive fluorescent tags.

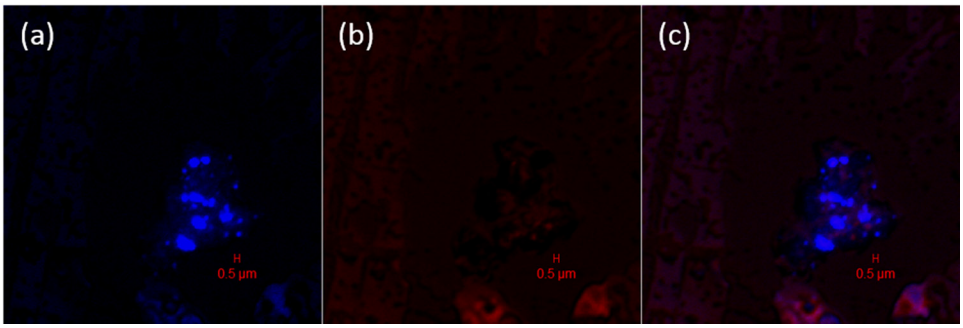

Figure S8. Control experiments for nanoparticle postpolymerization functionalization: Alkene-functionalized nanoparticles (synthesized with excess 1:2 excess thiol:ene) were reacted with 7-mercapto-4-methylcoumarin in the presence of the non-reactive dye sulphorhodamine B to show that the non-reactive dye is not physisorbing onto the surface of the nanoparticles. (a) Image at excitation (λ_{ex}=405 nm) for 7-mercapto-4-methylcoumarin, (b) image at excitation (λ_{ex}=543 nm) for sulphorhodamine B, and (c) composite overlaid image.