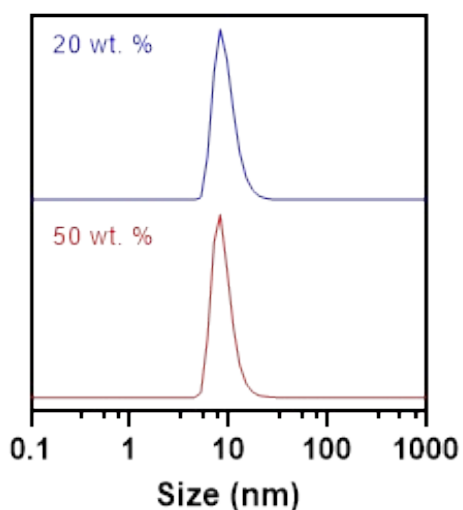


One pot synthesis of thiol-functional nanoparticles

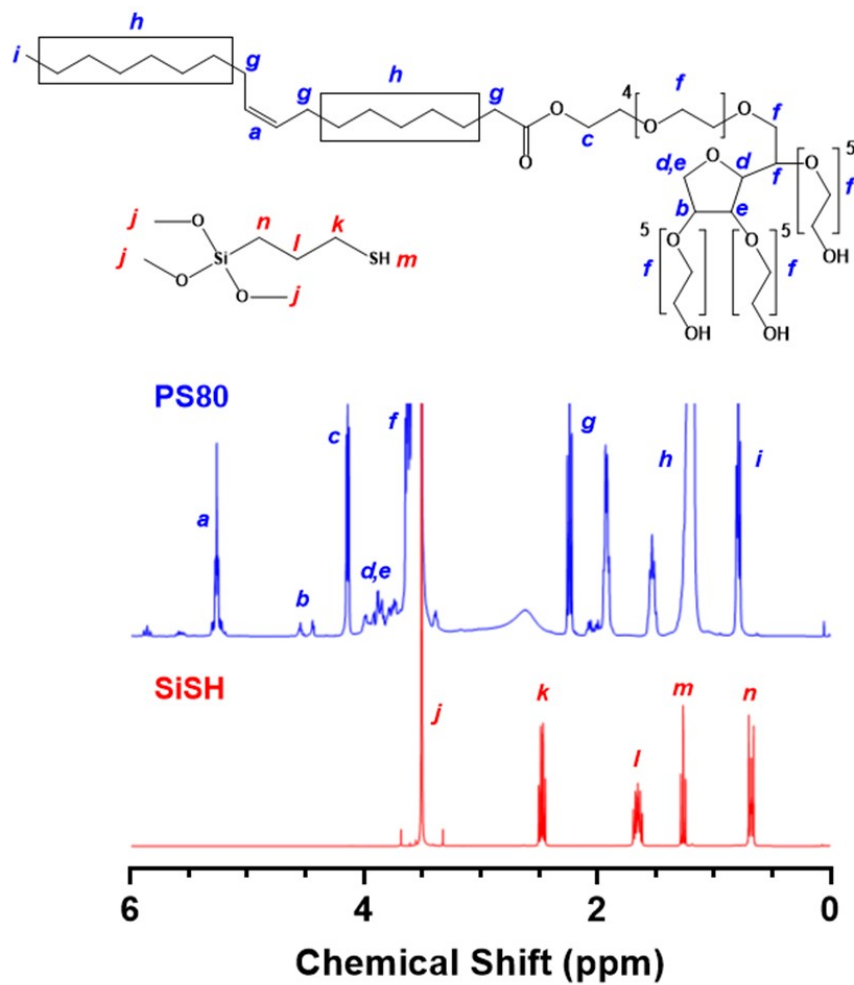
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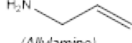
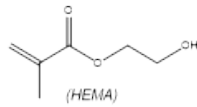
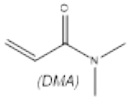
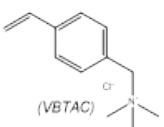
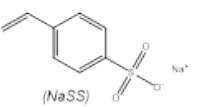
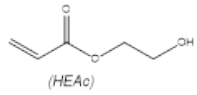
Supporting Information



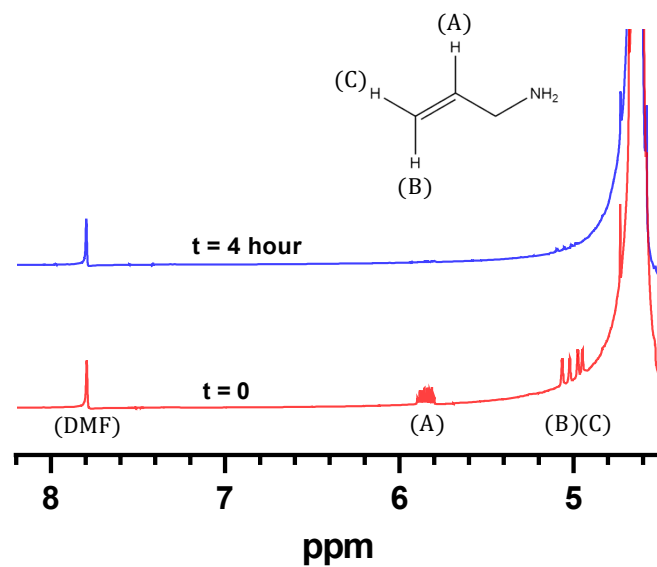
SI Figure 1. DLS traces and z-average sizes for PS80-SH nanoparticles before and after concentrating over 60°C heat for 6 hours. As shown, there was little to no change in the number average distribution of particle sizes. A slight increase from 22 to 27 nm in z-average size was observed.



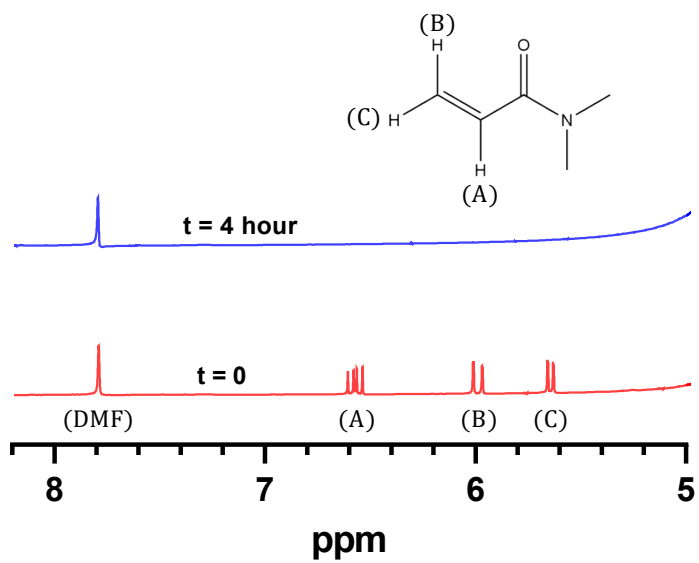
SI Figure 2. ^1H NMR and structures of starting reagents SiSH and PS80 in addition to peak assignments

Monomer	Thiol-to-Alkene Ratio	VA-086 conc. (wt%)	TEA conc. (wt%)	Time (hrs)	Conversion (%)
 (Allylamine)	0.5	0.5	0	4	94
 (HEMA)	0.5	0.5	0	4	99
 (DMA)	0.5	0.5	0	4	99
 (VBTA)	0.5	0.5	0	8	92
 (NaSS)	0.5	0.5	0	8	93
 (HEAc)	0.5	0	2.27	1	92

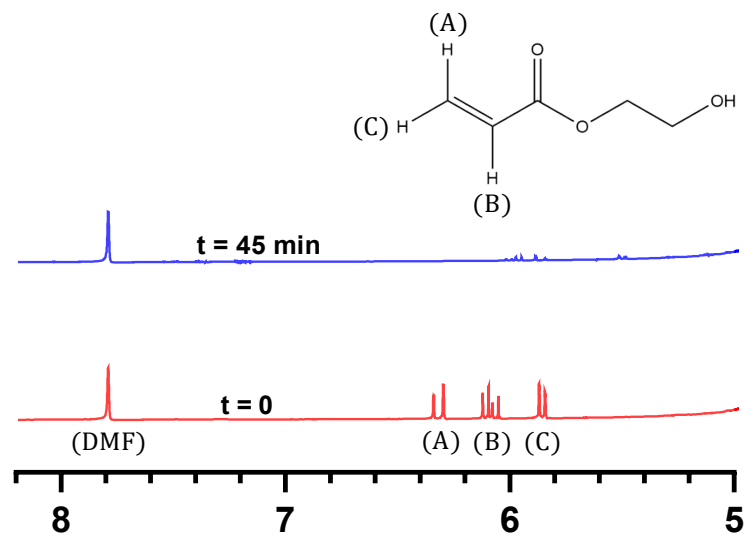
SI Figure 4. Summary of monomer conjugation trials including conditions, reactions times and conversions



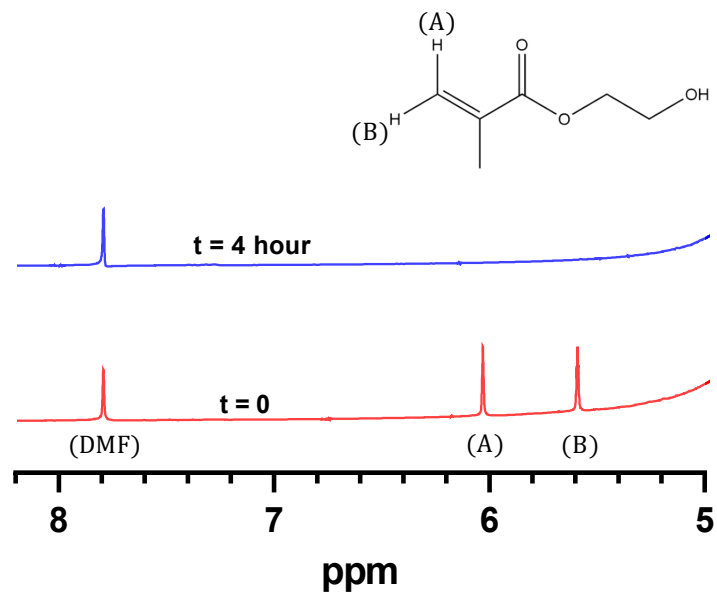
SI Figure 5. ¹H NMR spectra of allylamine before (red) and after (blue) thiol-ene reaction



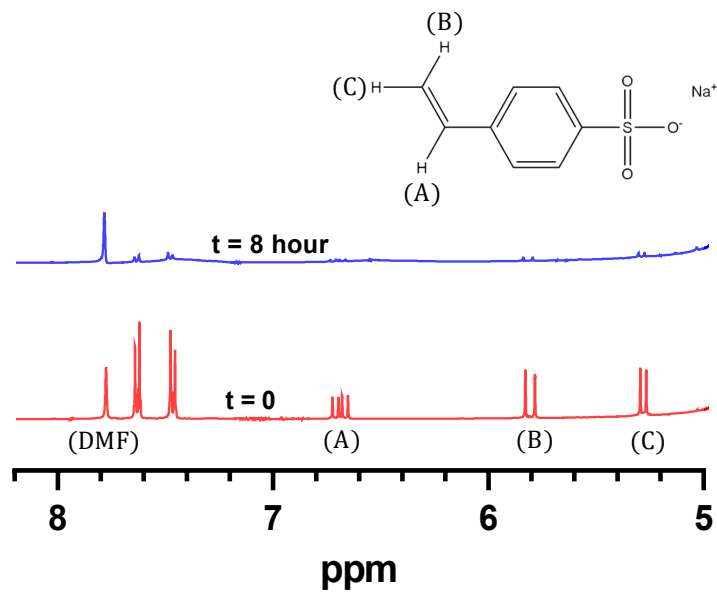
SI Figure 6. ¹H NMR spectra of N,N-dimethylacrylamide before (red) and after (blue) thiol-ene reaction



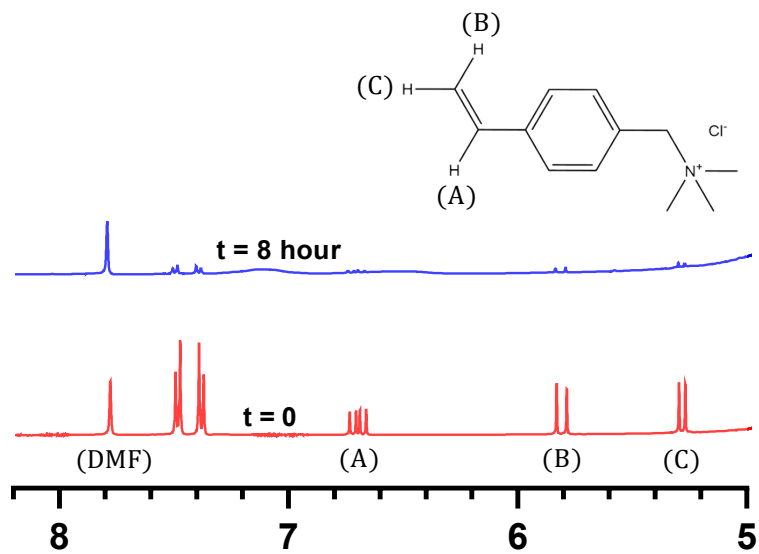
SI Figure 7. ^1H NMR spectra of 2-hydroxyethyl acrylate before (red) and after (blue) thiol Michael reaction



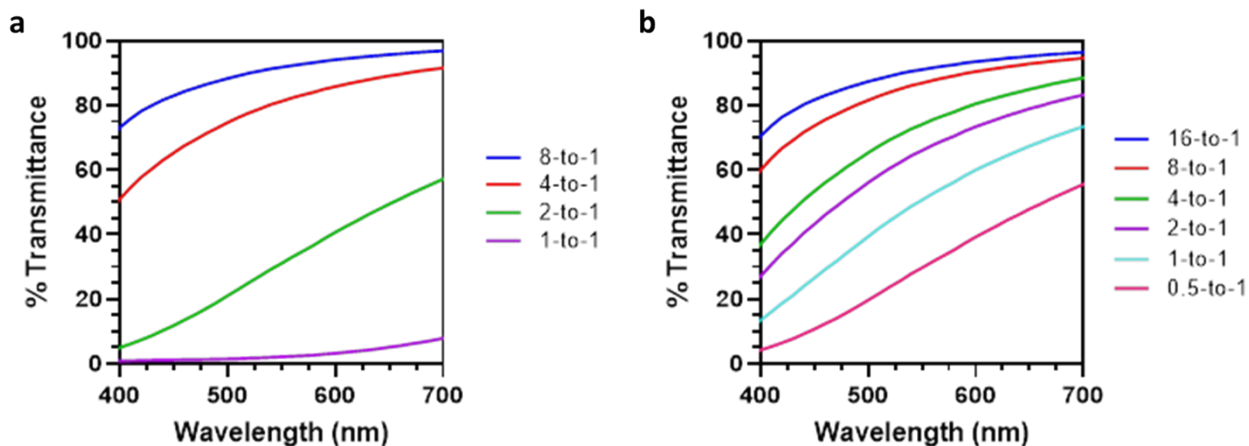
SI Figure 8. ^1H NMR spectra of hydroxyethyl methacrylate before (red) and after (blue) thiol-ene reaction



SI Figure 9. ^1H NMR spectra of sodium 4-vinylbenzenesulfonate before (red) and after (blue) thiol-ene reaction



SI Figure 10. ^1H NMR spectra of (vinylbenzyl)trimethylammonium chloride before (red) and after (blue) thiol-ene reaction



SI Figure 11. Change in % transmittance as a function of alkene-to-thiol ratio for resins with fixed 40 wt% PEGdMA concentration (a) and resins with fixed 50 wt% solids concentration. As the alkene-to-thiol ratio is reduced towards unity, % transmittance of light through the material over the entire visible range is reduced, indicating the material is transitioning from transparent to opaque.



SI Figure 12. Curing and 3D printing of BMAP/PS80-SH resins. As shown on the left, the resins were transparent and stiff when cured in plates under UV light. However, the resin completely gelled / cured during printing as shown in the middle. On the right, the faint outline of the intended print (dogbone) could be seen under light embedded in a gel-like matrix.