Supplementary information

Nanoconfinement in miniemulsion increases reaction rates of thiol-ene photopolymerization and yields high molecular weight polymers

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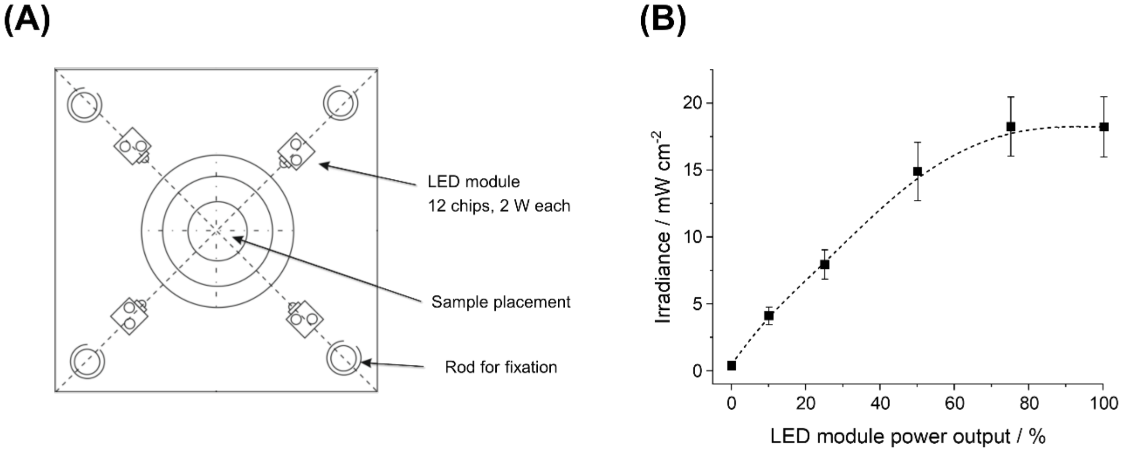

Figure S1. UV-LED module employed for the photopolymerization of the thiol-ene monomer-mixtures. A) Scheme of the top view of the photoreactor, with 4 LED modules with 12 chips each, and rods for the fixation of reaction vessels. B) UV-irradiance measured at the distance of the sample placement, from 10 to 100% of the total power output. Measured with a ThorLabs S120VC photodiode power sensor.

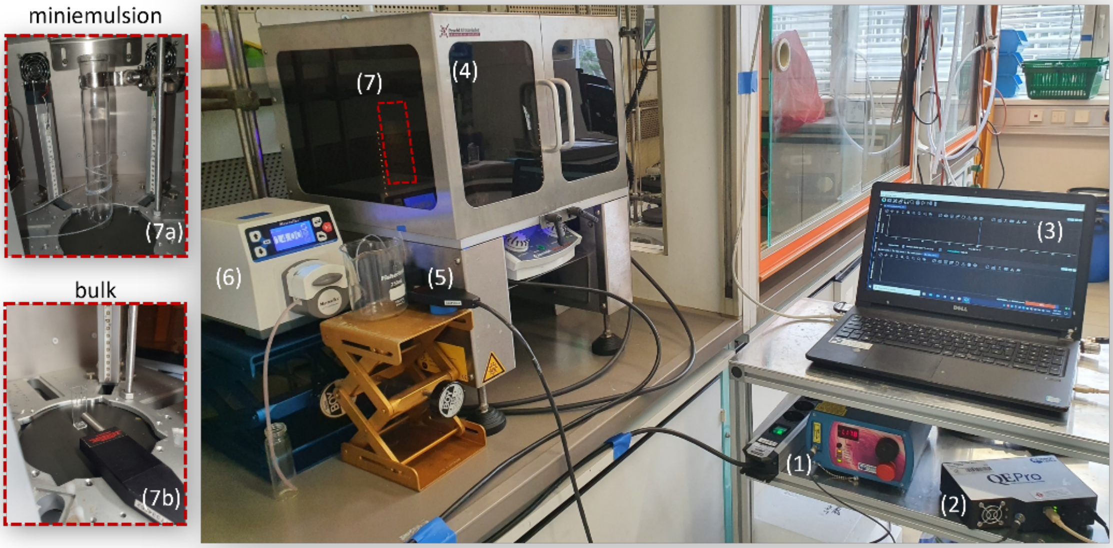

Figure S2. Reaction setup: 1) 785 nm laser source, 2) Raman detector, 3) Raman software, 4) UV-reactor chamber, 5) External Raman probe, coupled by optical fibers to the (1) and (2), 6) peristaltic pump for miniemulsion experiments, 7) Interior of the reaction chamber: a) UV-transparent tubing for miniemulsion, and b) Cuvette for bulk experiments.

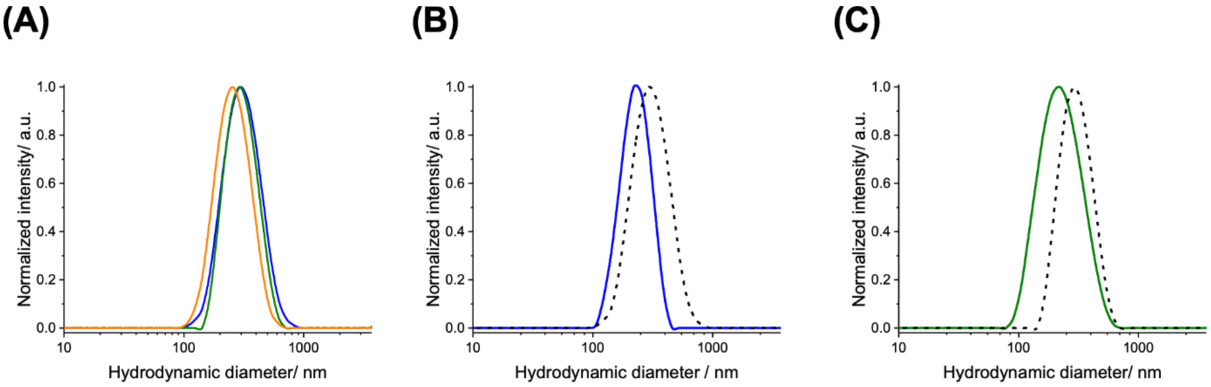

Figure S3. Size distributions obtained by DLS for A) the droplets of the monomer mixtures of EDDT-1,4DAc (orange), EDDT-DAA (blue), and EDDT-DVA (green), B) the droplets (dashed line) and NPs (continuous line) of EDDT-DAA (blue) and C) EDDT-DVA (green).

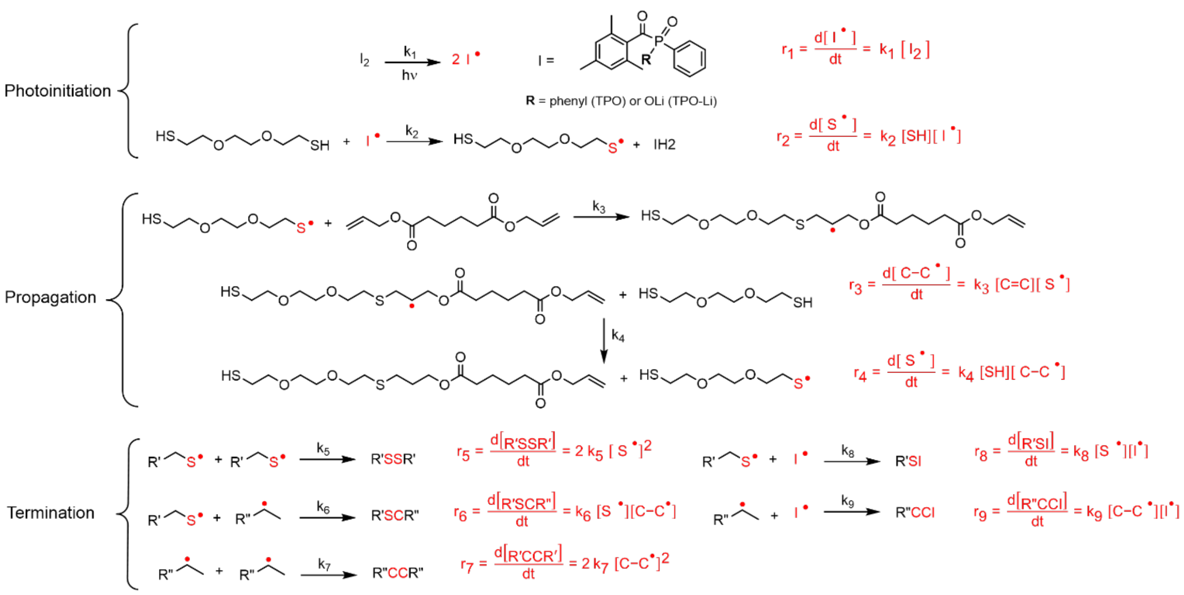

Figure S4. Extended mechanism of thiol-ene reaction of the system EDDT-DAA. The following approximations were used to analyze the kinetics: (1) Both radicals formed from the homolysis of TPO are equally reactive ≈ 2 I*, (2) Pseudo-steady-state assumption $\frac{d\,[S^*]}{dt} = \frac{d\,[C^*]}{dt} = 0$, (3) $r_3 = r_4$, and (4) all termination steps are equally likely to occur.[45]

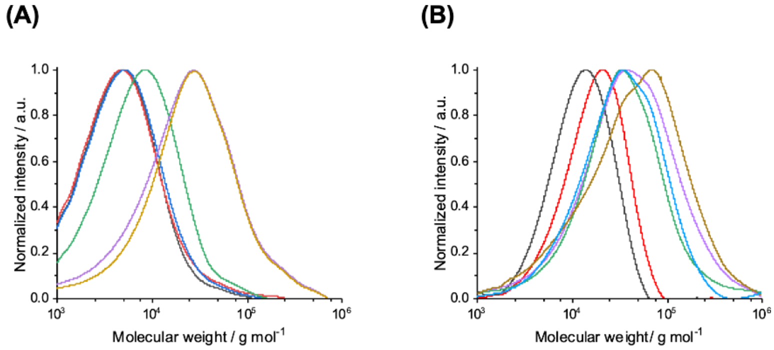

Figure S5. GPC plots of the molecular weight distribution of the polymers obtained from the polymerization of EDDT-DAA after 0.5 (gray), 1 (red), 2 (blue), 5 (green), 10 (lilac), and 30 min (beige) of reaction in A) bulk and B) miniemulsion reported in Figure 4.

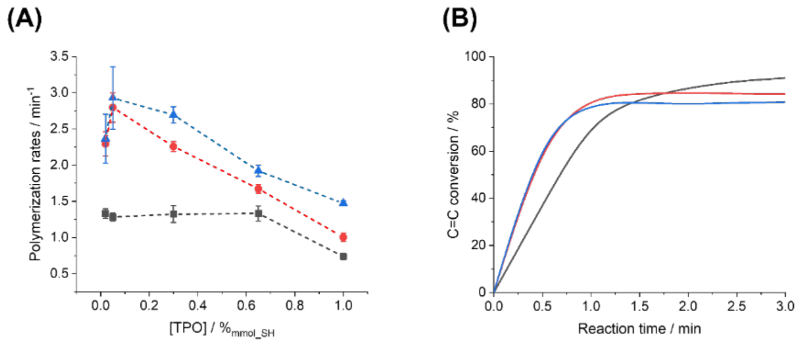

Figure S6. Effect of the concentration of photoinitiator and irradiance in the reaction of the system EDDT-DAA in bulk: A) Polymerization rates as a function of [TPO] at different UV-irradiance: 4 mWcm^{-2} (gray squares and dashed line), 7 mWcm^{-2} (red circles and dashed line), 15 mWcm^{-2} (blue triangles and dashed line). B) Conversion of C=C double bonds over time at different UV-irradiance for [TPO] = 0.05 %$_{mmol\_SH}$: 4 mWcm^{-2} (gray line), 7 mWcm^{-2} (red line), 15 mWcm^{-2} (blue line). Polymerization rates of the system EDDT-DAA in bulk.

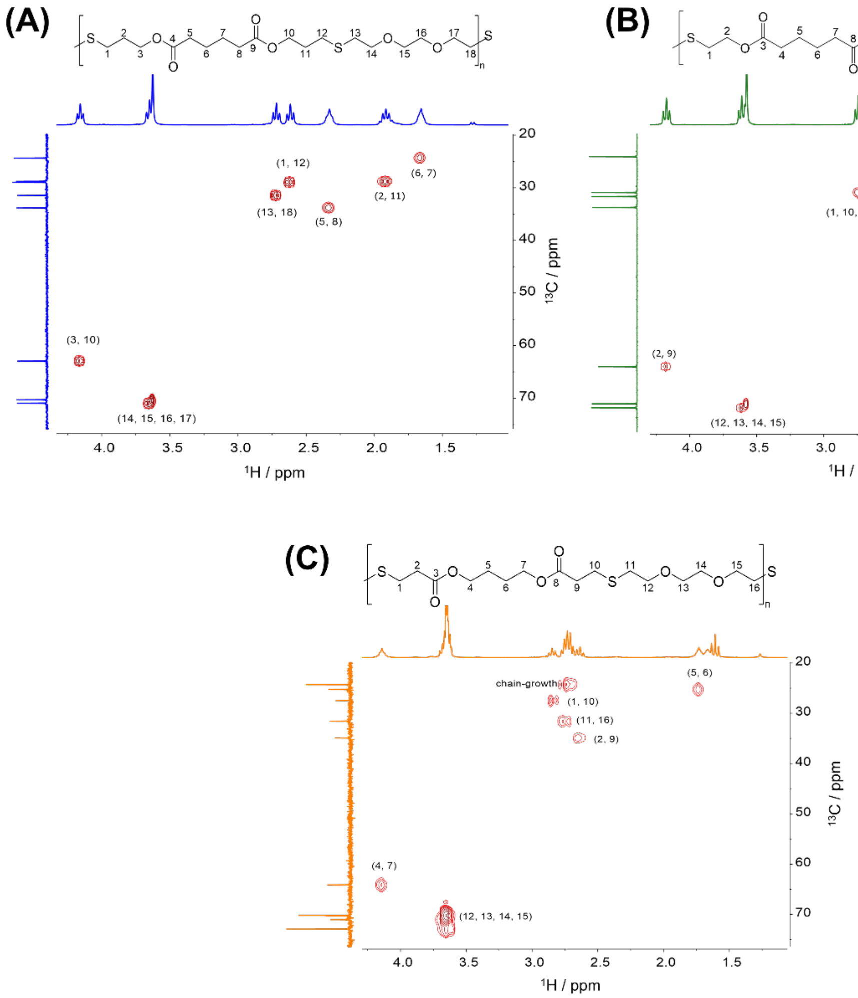

Figure S7. HSQC spectra of the polymers in $CDCl_3$ obtained by thiol-ene photopolymerization of A) EDDT-DAA, B) EDDT-DVA, and C) EDDT-1,4DAc. A) and B) exhibit no detectable signs of homopolymerization, whereas C) exhibits peaks originating from both the formation of the polythioether and the crosslinking of acrylic moieties by chain-growth homopolymerization (peak labeled chain growth), leading to the formation of a crosslinked network. The sample for NMR analysis of the crosslinked polymer sample (C) was prepared by first mechanically grinding the polymer in a fine powder and then swelling this powder in CDCl3

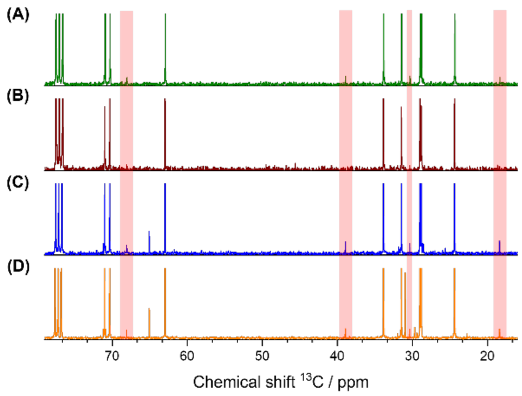

Figure S8. ^{13}C-NMR spectra of the polymers obtained by photopolymerization of the system EDDT-DAA at (A-B) stoichiometry ratio of monomers in (A) bulk (green) and (B) miniemulsion (brown), and at (C-D) off-stoichiometry ratio of monomers in (C) bulk (blue) and (D) miniemulsion (orange). The shaded areas highlight the peaks originating from the chain-growth radical homopolymerization of the enes, and demonstrate the absence of homopolymerization in during the miniemulsion of the stoichiometric monomer mixture in B.

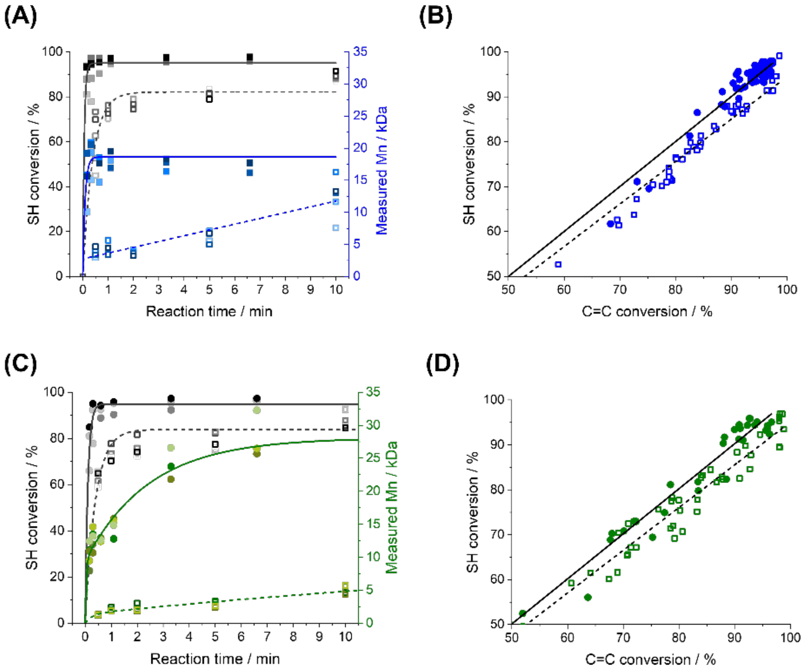

Figure S9. Study of the polymerization of EDDT-DAA (A,B) and EDDT-DVA (C,D) by the consumption of the thiol moieties. (A, C) Kinetics of the conversion of thiols (left axis, black) and evolution of the $\overline{M}_n$ of the resulting polymer (right axis, blue/green) in bulk (dashed line, opened symbols) and in miniemulsion (solid line, closed symbols). (B, D) Comparison of the conversions of thiols and carbon-carbon double bonds in each system for polymerization carried out in miniemulsion (solid circle) and in bulk (open squares).

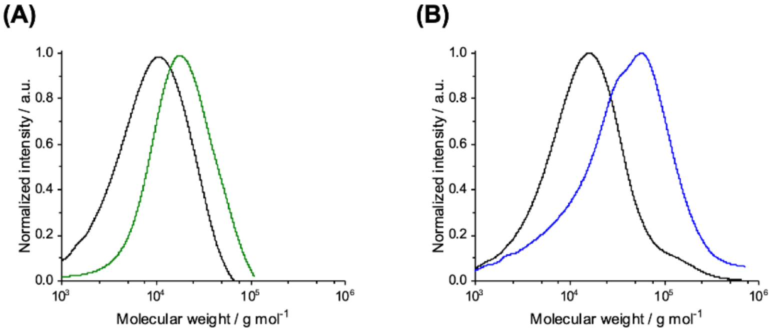

Figure S10. GPC plots of the molecular weight distribution of the polymers obtained after 10 minutes of polymerization in bulk (black) and miniemulsion of A) EDDT-DVA (green) and B) EDDT-DAA (blue) monomer mixtures, at UV-irradiance of 15 mW·cm^{-2}.

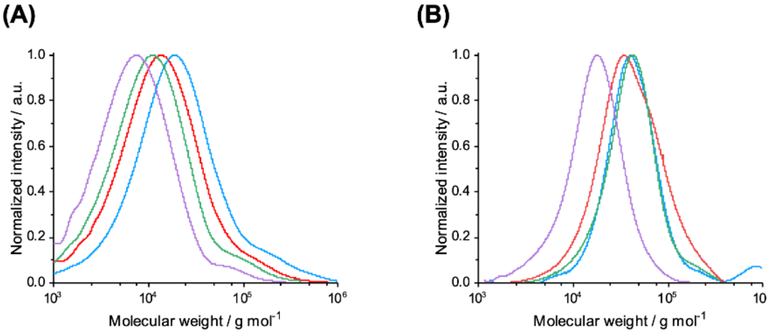

Figure S11. Molecular weight distribution measured by GPC for the polymers obtained from the polymerization of EDDT-DAA at different SH/CC molar fractions: 0.90 (blue), 0.95 (red), 1.00 (black dashed line), 1.05 (green), and 1.10 (lilac) for reactions performed in A) bulk and B) miniemulsion presented in Figure 8.

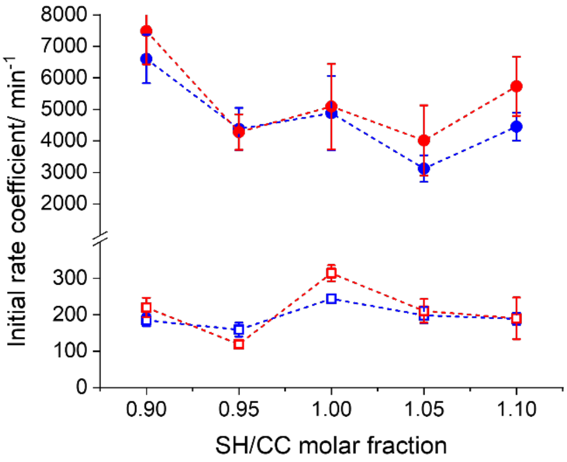

Figure S12. Rate coefficients for the polymerization of mixtures of EDDT and DAA in different stoichiometric ratios performed in bulk (open symbols) and in miniemulsion (closed symbols) calculated from the conversion of thiol (red) and ene (blue) groups.