SUPPORTING INFORMATION for

Role of Thiol Oxidation by Air in the Mechanism of the Self-Initiated Thermal Thiol-ene Polymerization

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Thiol-ene polymerization rate. The general thiol-ene polymerization rate expression is given below (see Cramer et al. Macromolecules 2003, 36, 7964-7969 for more details)

$$R_p = \sqrt{\frac{R_i}{2k_t}} \times \frac{1}{\sqrt{\frac{1}{(k_{add}[C=C])^2} + \frac{1}{(k_H[SH])^2} + \frac{1}{(k_{add}k_H[C=C][SH])}}}$$

R_i: initiation rate

k_t: rate constant for termination

k_H: rate constant for H-abstraction of thiols by carbon-centered radicals

k_{add}: rate constant for addition of thiyl radicals onto alkene

In the case of allyl ethers presented in the study, the addition rate constant is much greater than the H-abstraction rate constants ($k_{add} >> k_H$). For this particular case, the polymerization expression given below simplifies in a way that R_p becomes first order, and dependent only on thiol concentration (H-abstraction is the rate-limiting step).

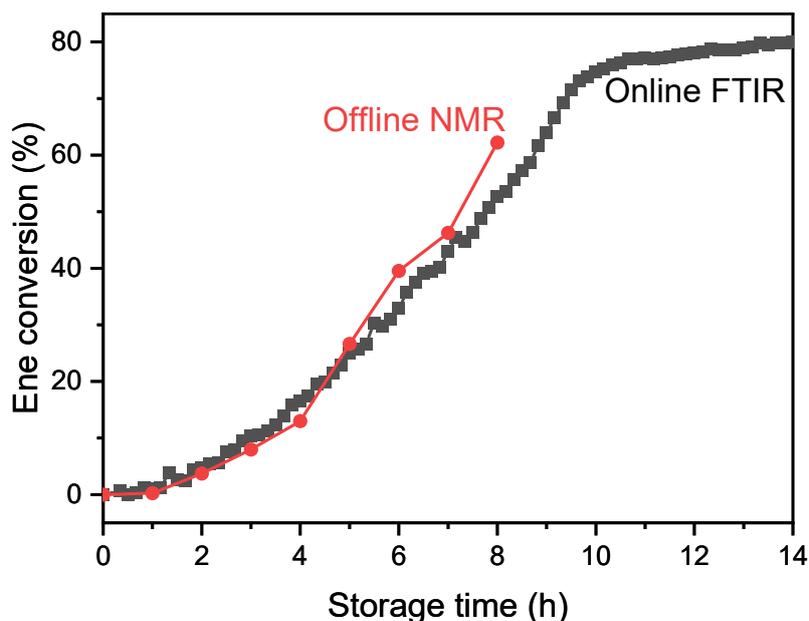$$R_p = \sqrt{\frac{R_i}{2k_t}} \times k_H[SH]$$

Fig. S1. Comparison between ene conversion determined by offline ^{1}H NMR (dots) and online FT-NIR (squares). A stoichiometric mixture (4 g) of dithiol **3** and diene **DAP** was placed in a 10 mL vial. 0.25 mL of the mixture was transferred to a quartz cuvette with an optical path 2 mm. Ene-conversion in this cuvette was monitored online using FT-NIR spectroscopy as described in detail in the main manuscript text. Aliquots were removed from the vial at different times, then placed in a NMR tube containing $CDCl_3$ and a ^{1}H NMR spectrum was recorded. In this case, ene conversion was determined by comparing the integrated resonance of the methylene protons in **DAP** at 4.75 ppm and that of the same methylene protons in the polymer at 4.25 ppm.
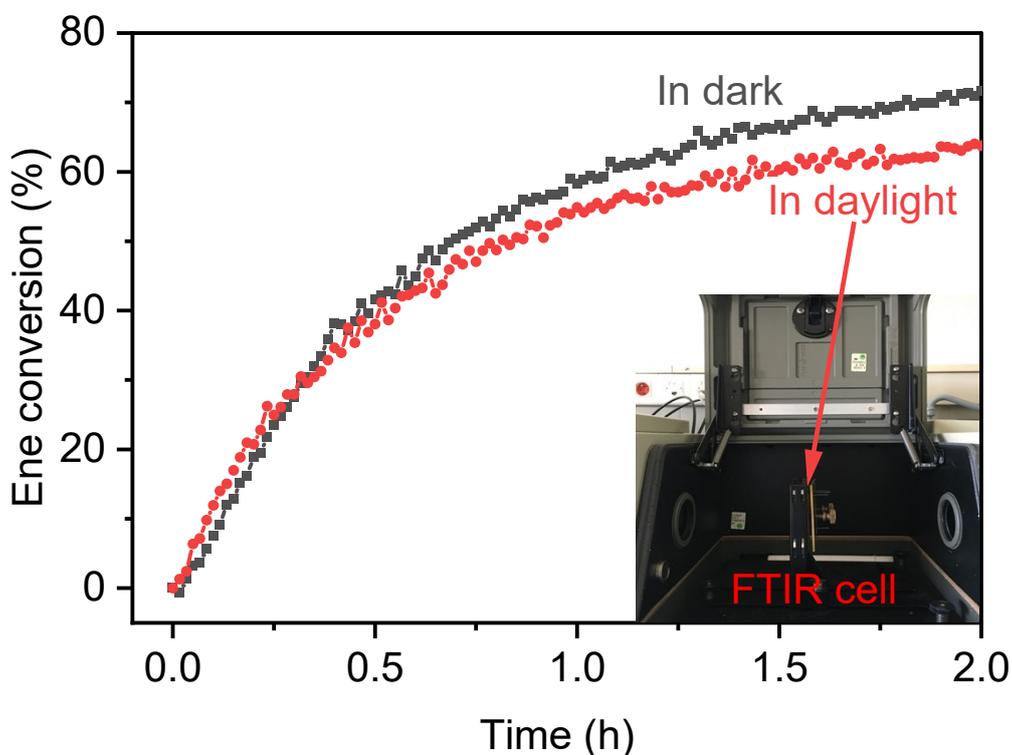

Fig. S2. Dependence of monomer (alkene) conversion on storage time for stoichiometric polymerization of bulk **DAA**-**1** performed under air. Polymerization was carried out at ambient temperature in the dark (squares) and in daylight (dots). For this latter case, the FTIR chamber was left open during the 2 hours of data acquisition (without exposure to artificial light source).
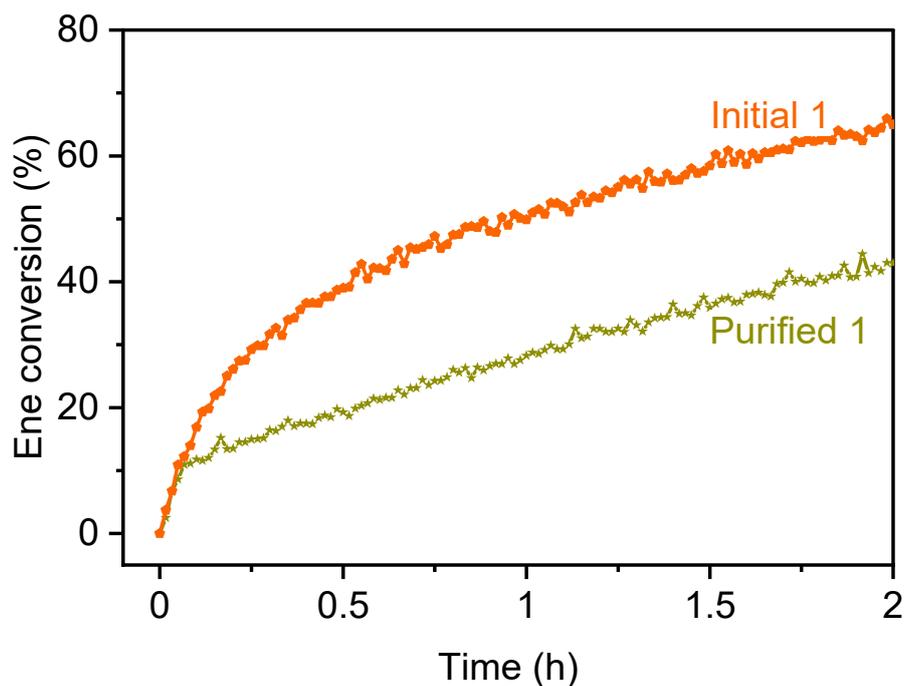
Fig. S3. Dependence of ene conversion versus time on the thiol stoichiometric polymerization of **DAA**-**1**. Dithiol **1** was purified after passing through an aluminum oxide column (activated, neutral, Brockmann I, 150 mesh, Sigma Aldrich Product number 199974). Briefly, 5 g of dithiol **1** was passed through a short column (12 mm ID) packed with 5 g of aluminum oxide.
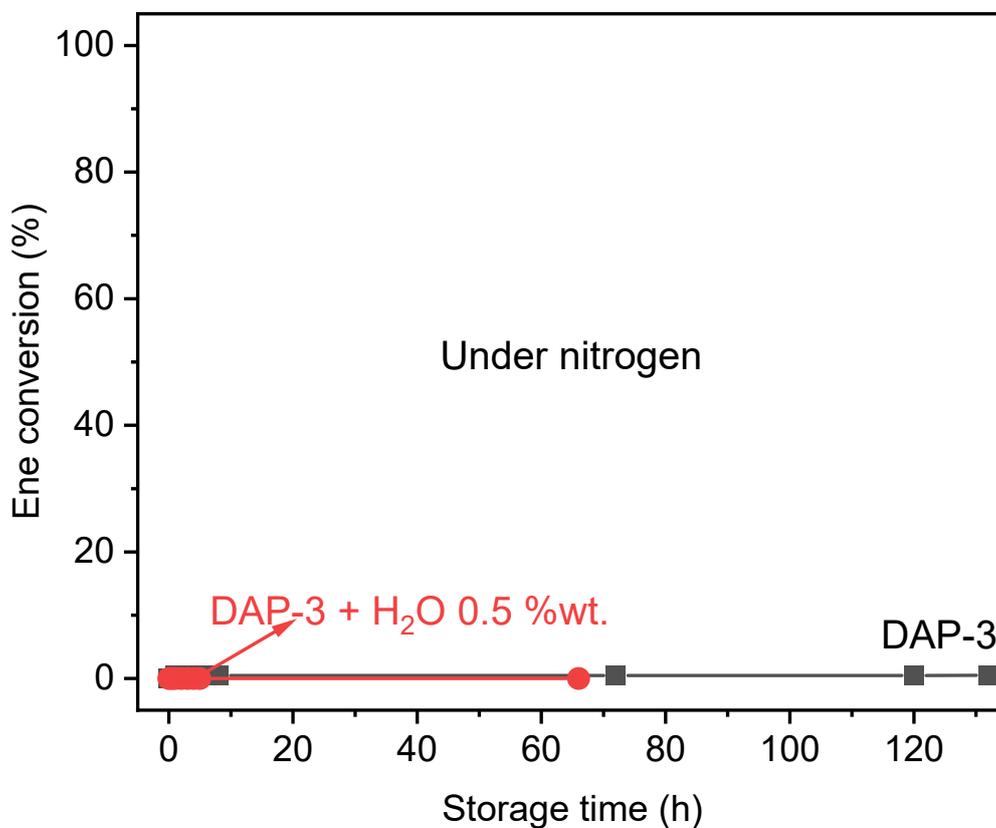

Fig. S4. Effect of water on the ene conversion for the self-initiated polymerization of **3**-**DAP** under nitrogen (^{1}H NMR data); in the absence of water (squares), with added water (dots).
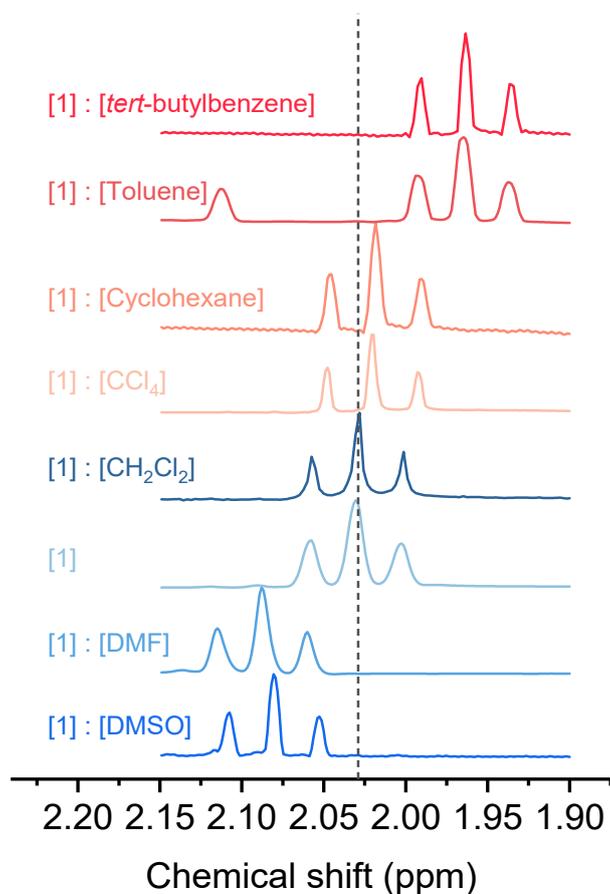
Fig. S5. The chemical shift of the sulfhydryl proton in thiol **1** in CDCl$_3$ was observed after adding an excess of solvent (24 equiv). A downfield shift (DMF, DMSO) corrsponds to a negative chemical shift ΔHz, while a upfield shift (CCl$_4$, toluene, tert-butylbenzene) corrsponds to a positive chemical shift ΔHz.
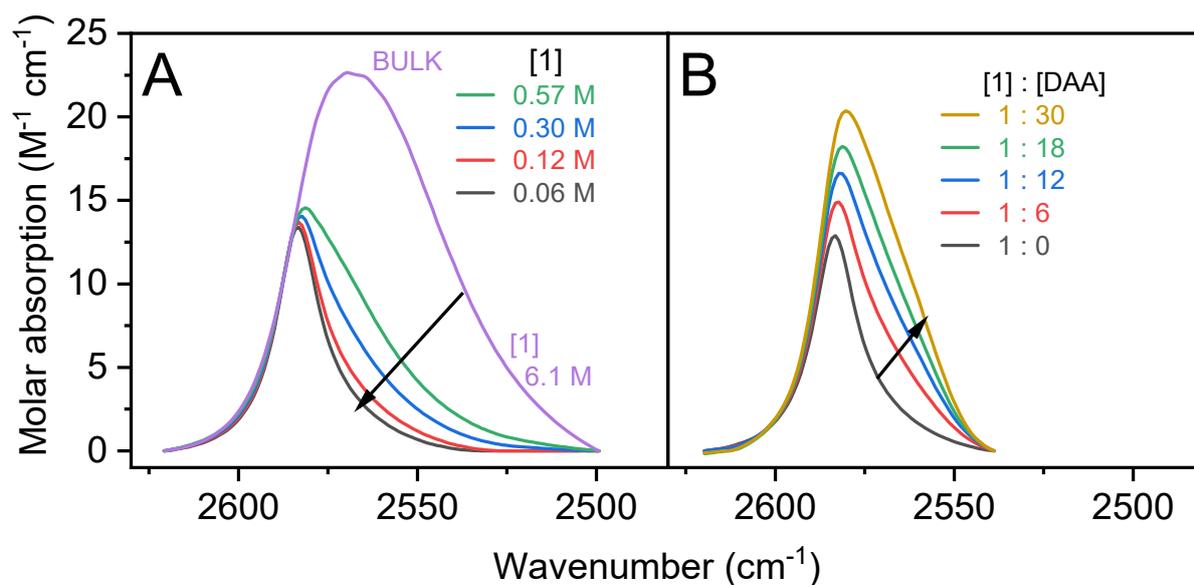

Fig. S6. (**A**) S-H stretching mode (v(SH)) of thiol **1** in CCl$_4$ at different concentrations. At [**1**] = 0.06 M, solvent-thiol and thiol-thiol interaction are assumed to be minimal. (**B**) Effect of increasing amount of **DAA** on the v(SH) of thiol **1** initially dissolved in CCl$_4$ at 0.06 M.

Explanation about Fig. S5.

Another approach to study the solvation of a given thiol is the examination of the effects of increasing amount of solvent (or alkene) on its FTIR spectrum. **Fig. 5A** begins by showing the S-H stretching mode (v(SH)) of thiol **1** without solvent. For this neat thiol, the band is centred at 2569 cm^{-1} and is quite broad because of H-bonding interactions where the sulfur atom acts as the H acceptor (SH•••S).[1] Dilution with an apolar solvent such as CCl$_4$ causes a gradual narrowing of the S-H stretching band, as well as a marked shift to higher frequency (2583 cm^{-1}) indicative of minimal solvent-solute interactions. These observations are consistent with the progressive disruption of hydrogen-bonded complexes between thiol molecules. Below 0.06 M, the position and shape of the S-H stretching band no longer changes reflecting that most thiol molecules are thus in the monomeric (free molecules). Starting from this solution of **1** at 0.06 M in CCl$_4$, **Fig. 5B** shows the effects of increasing amount of **DAA** on the S-H stretching mode. As more **DAA** is added, the originally sharp feature progressively broadens, moves to lower frequencies, and becomes more intense. This evolution is consistent with the formation of hydrogen bonds between the SH proton of **1** and the π electrons of C=C bonds of **DAA** acting as H acceptor, as already evidenced by NMR data.[2] Electron density transfer from olefin to the thiol causes a weakening of the S−H bond with a resultant red shift, elongation of the S−H bond and higher intensity in the SH stretching band. It should be noted that a similar trend is found when **DAA** is replaced by **DVE** and also **DAP** (**Fig. S6**). This supports the existence of analogous H-bonding interactions in other thiol-ene systems (SH•••C=C) with π electrons acting as H acceptor.

Experimental section - Thiol solvation by FTIR spectroscopy. For the analysis of neat thiols, **1** was sandwiched between two quartz plates using a 100 μm Teflon O-ring. The FTIR spectrum was recorded at room temperature on a Bruker FTIR (IFS66/s) spectrometer in the 2000-4000 cm^{-1} region with a DTGS detector. For the analysis of diluted solutions, 480 μL of CCl$_4$ was placed in a 2-mm thick quartz cuvette (volume: 700 μL, width 10 mm) closed by a septum stopper. Known volumes of the dithiol **1** were then injected (5 - 25 μL) into the cuvette to vary the concentration (0.06 – 0.57 M). The FTIR spectra were recorded after each injection. To study the influence of the diene on the S-H stretching mode of **1**, a CCl$_4$ solution of thiol **1** of concentration 0.06 mM was placed in a 2-mm thick spectroscopic cuvette. Known volumes of the diene of interest were added to the cuvette to obtain a molar excess relative to the thiol varying between 6 and 30 times. The FTIR spectra were then recorded for each injection.

References. 1. J. G. David and H. E. Hallam, *Spectrochimica Acta*, 1965, **21**, 841–850. **2** . M. C. R. Symons and G. P. Archer, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 2499–2509.
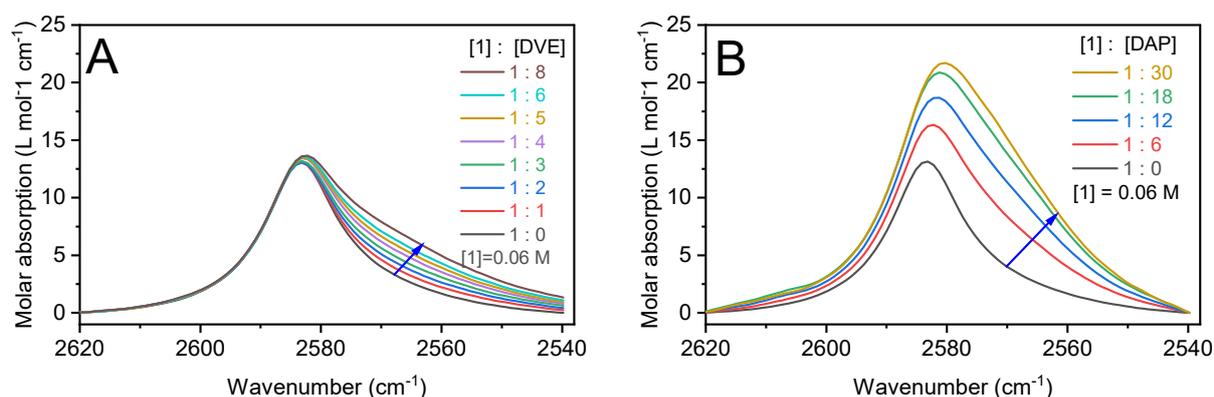

Fig. S7. S-H stretching mode of thiol **1** in CCl$_4$ ([**1**] = 0.06 M) and in the presence of an increasing concentration of DVE (**A**), or DAP (**B**). Data were presented after a̶ background subtraction of the spectrum from a corresponding diene solution in the absence dithiol **1**.
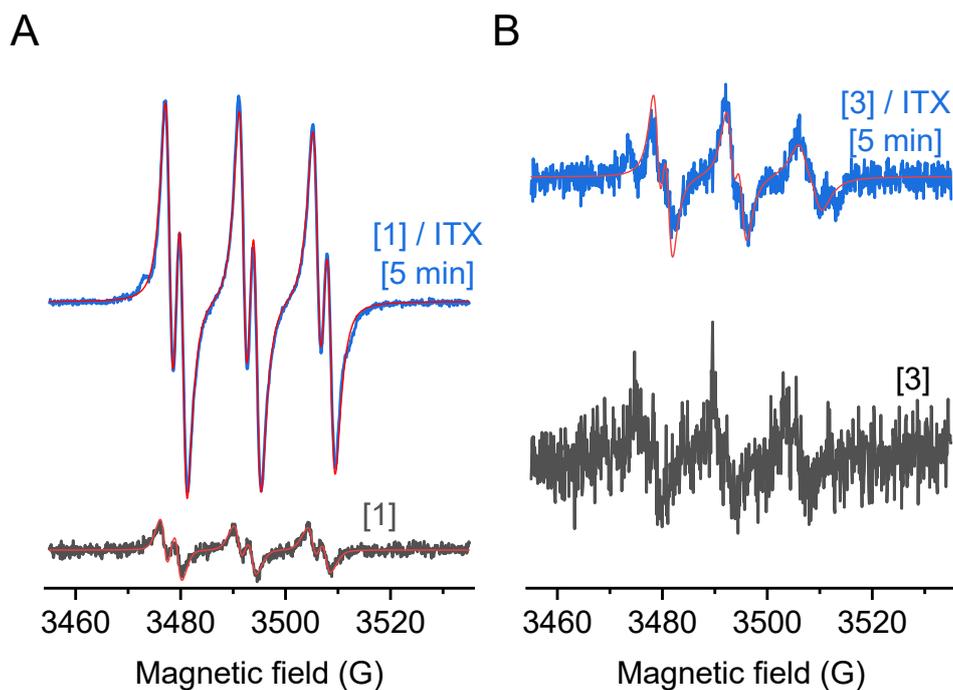
Fig. S8. The EPR spectra of the mixture 30 mM PBN, 100 mM thiol (**1** or **3**) in tert-butylbenzene with or without ITX (10 mM). The samples containing ITX were irradiated at 385 nm (2.7 mW cm^{-2}) for 5 min to generate the thiyl radical via H-abstraction. The experiment involving ITX shows a similar but increased EPR signal compared to the system without sensitizer (ITX).
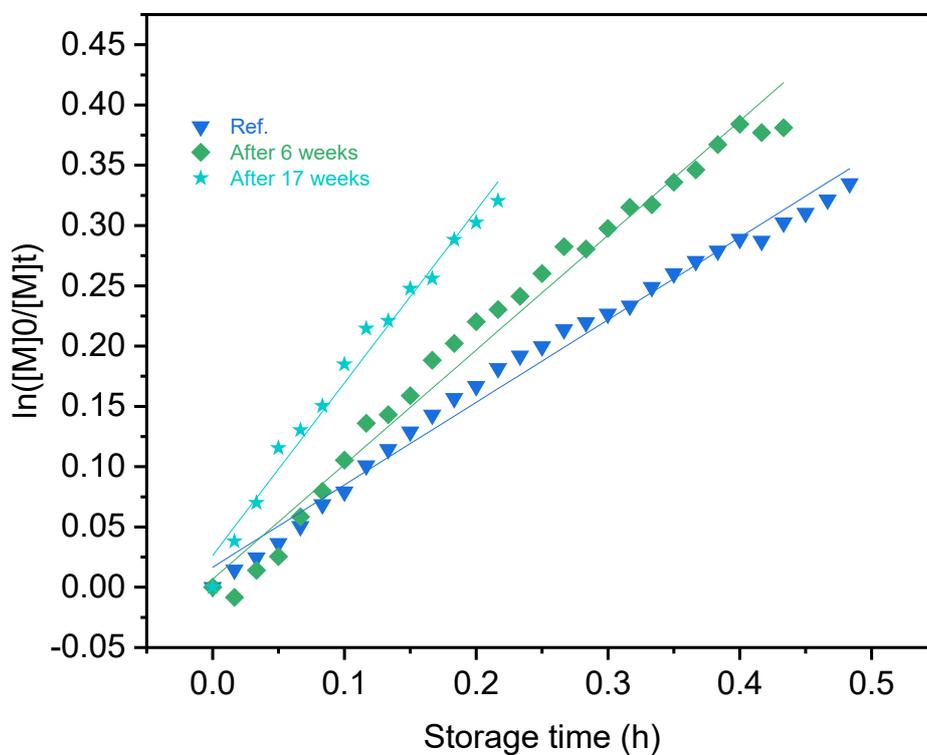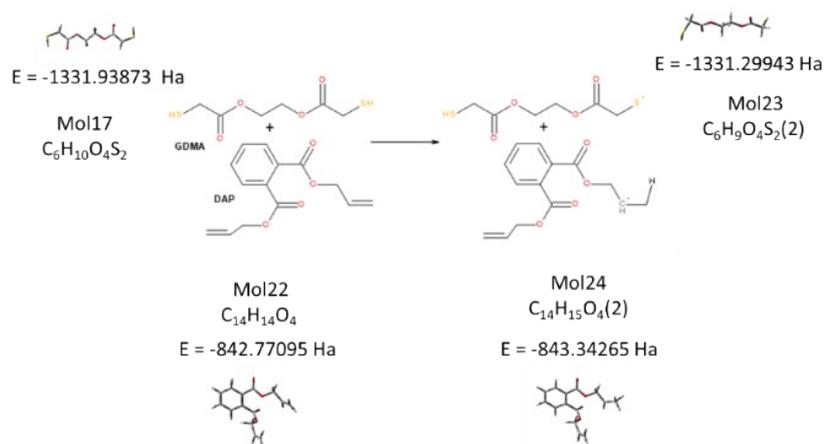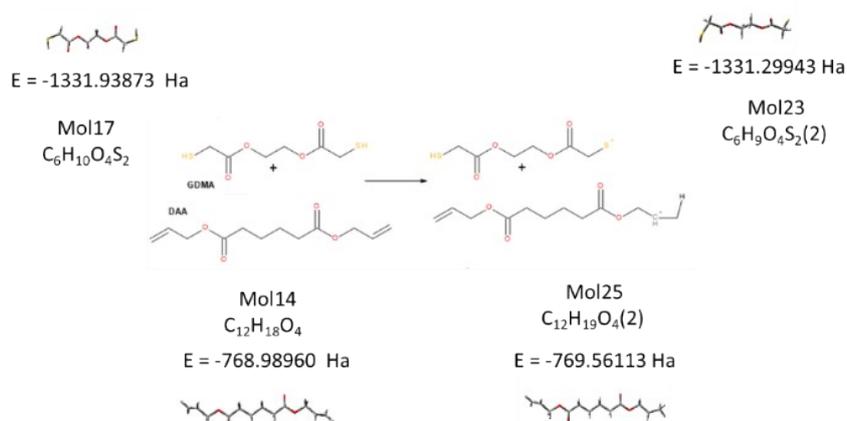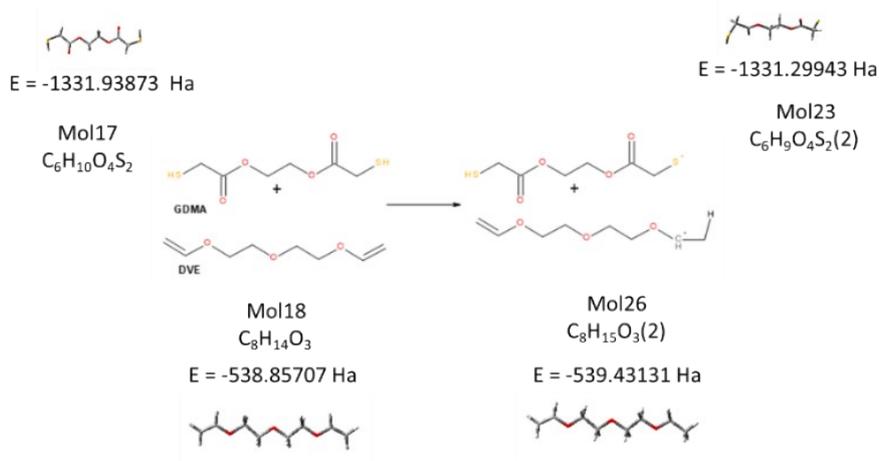

Fig. S9. Effect of thiol aging time on monomer (alkene) conversion for stoichiometric polymerization of bulk **DAA-1**. The experiment was performed under air and at ambient temperature **DAA** with dithiol **1**. Ref. corresponds to a freshly opened thiol bottle.

ΔH = 42.42 kcal mol⁻¹

ΔH = 42.53 kcal mol⁻¹

ΔH = 40.83 kcal mol⁻¹

Fig. S10. Calculated reaction enthalpy $\Delta_r H$ (DFT calculation, method uB3LYP - Base 6-31G*) for MAH of thiol **1** by alkene **DAA**, **DAP** and **DVE**. It is found that the reaction enthalpy of a H-atom transfer of thiol **1** to alkene amounts to $\Delta_r H_{298} \approx 42$ kcal/mol and does not vary significantly with the nature of the alkene.

Table S1. Dependence of self-initiated polymerization rate of **DAA**-1 (1:1 equiv) on impurities (relative to polymerization rate of a system without solvent). Dibutyl disulfide (TCI, > 98.5%), cumyl hydroperoxide (TCI, 80.5%), copper (II) sulfate pentahydrate (Carl Roth, >99%) were used as impurities.

Run	Concentration of impurity (M)	Relative R_p (h^{-1})[a]
Bulk **DAA**:**1** (Reference)	-	1 ± 0.2
+ Water	0.52	5.5 ± 0.2
+ Dibutyl disulfide	0.05	0.8 ± 0.2
+ Cumyl hydroperoxide	0.10	1.1 ± 0.2
+ Cu^{2+}	1.56×10^{-5}	6.8 ± 0.2

[a] Relative to the polymerization rate in bulk