

Supporting Information

Mixed Mechanisms of Bond Exchange in Covalent Adaptable Networks: Monitoring the Contribution of Reversible Exchange and Reversible Addition in Thiol-Succinic Anhydride Dynamic Networks

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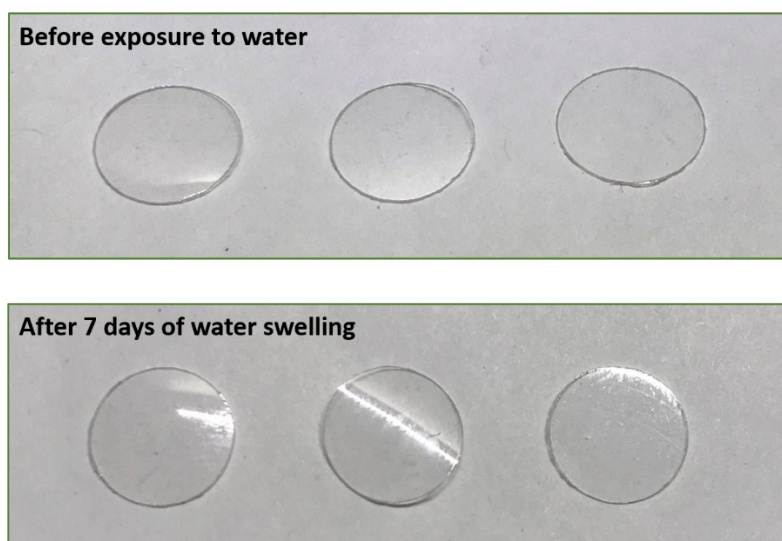


Figure S1. Water swelling study for ASA/PETMP dynamic photopolymer with 5 mol% DMAP catalyst. Polymer discs ($d = 10$ mm; $h = 0.25$ mm) were immersed in DI water for seven days. Water uptake was calculated by comparing the weights of the samples before and after water swelling. The average mass increase was assessed at 4.7 ± 0.4 % ($n = 3$).

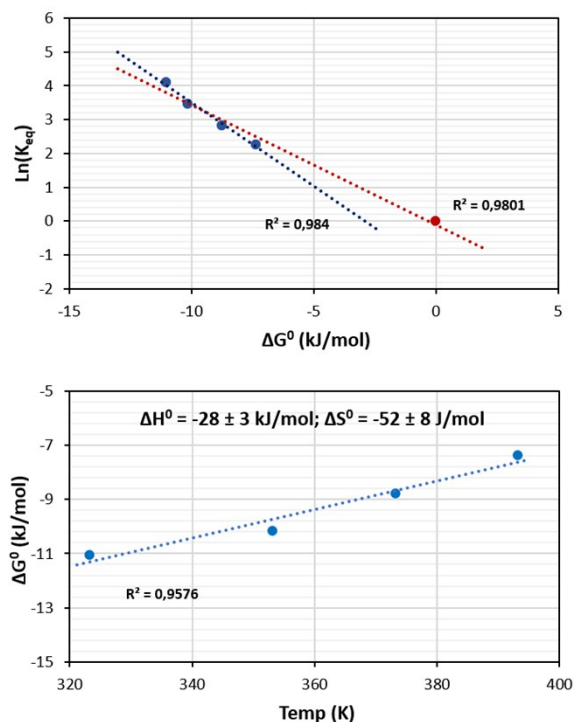


Figure S2. Standard free energy change (ΔG^0) in the function of $\ln(K_{eq})$ for ASA/BMP model reaction after 15 min equilibration time. The estimated enthalpy and entropy of the reaction are both overestimated. The experimental points diverge significantly when fitted on their own and when combined with the theoretical point $\Delta G^0 = 0$ at $K_{eq} = 1$.

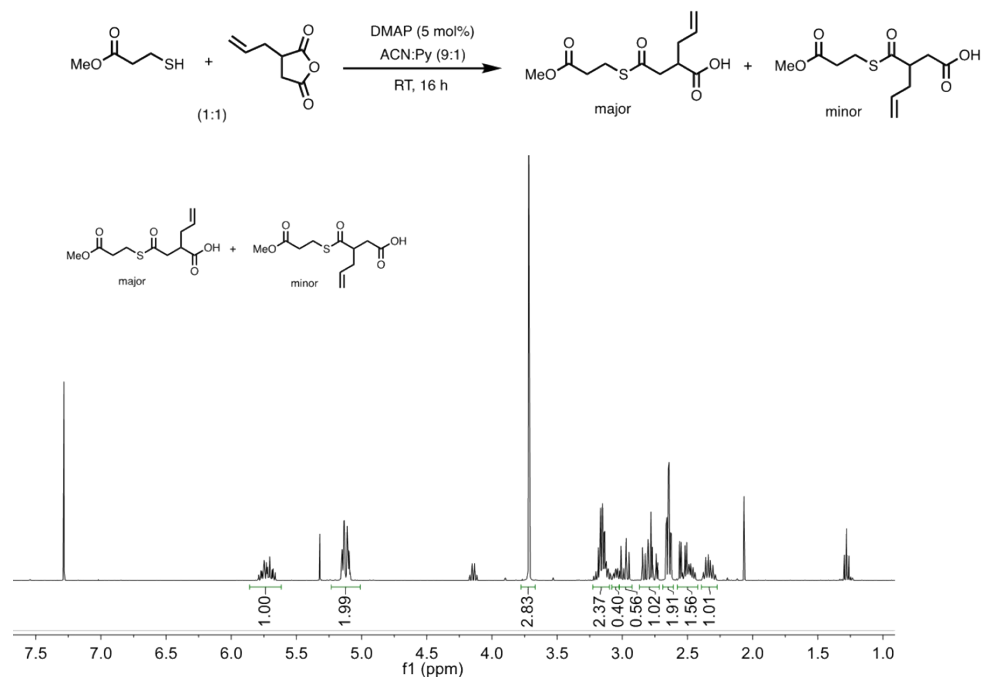


Figure S3. The NMR of the adduct of allyl succinic anhydride (ASA) and methyl 3-mercaptopropionate (MMP). (a) NMR of isolated mixture of isomeric thiol-anhydride products.

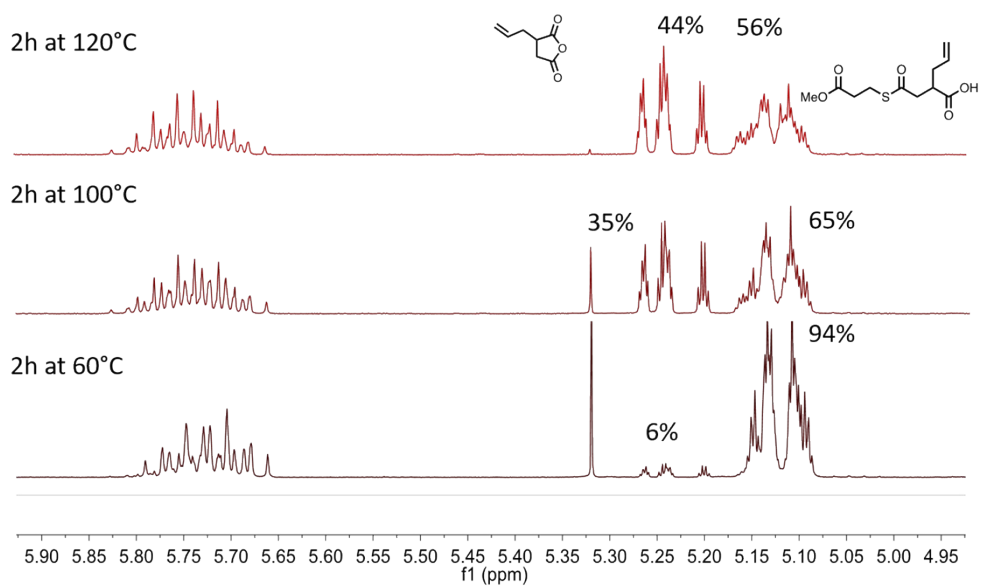


Figure S4. Thiol-anhydride reaction reversibility observed after 2 h at 60, 100 and 120 °C in the presence of 5 mol% DMAP. Because of side reactions (Figure S3) the equilibrium was changed resulting in overestimated conversions values.

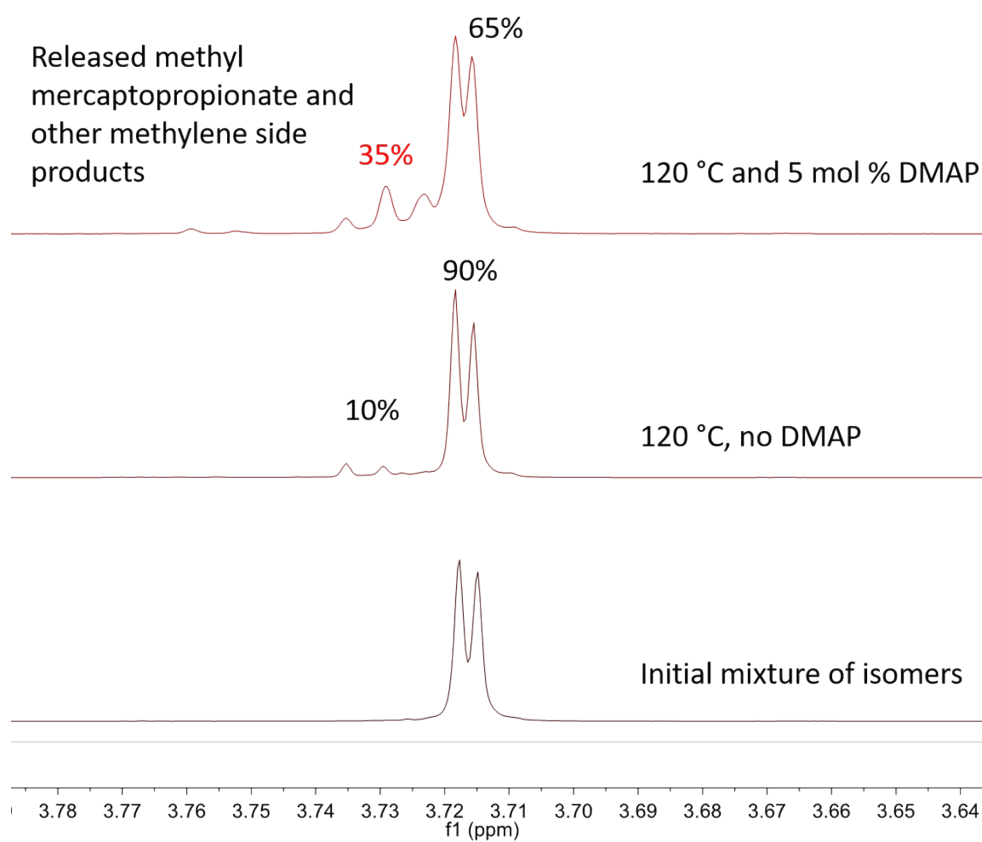


Figure S5. MMP side products detected in the NMR after 2 h equilibration time at 120 °C for ASA/MMP.

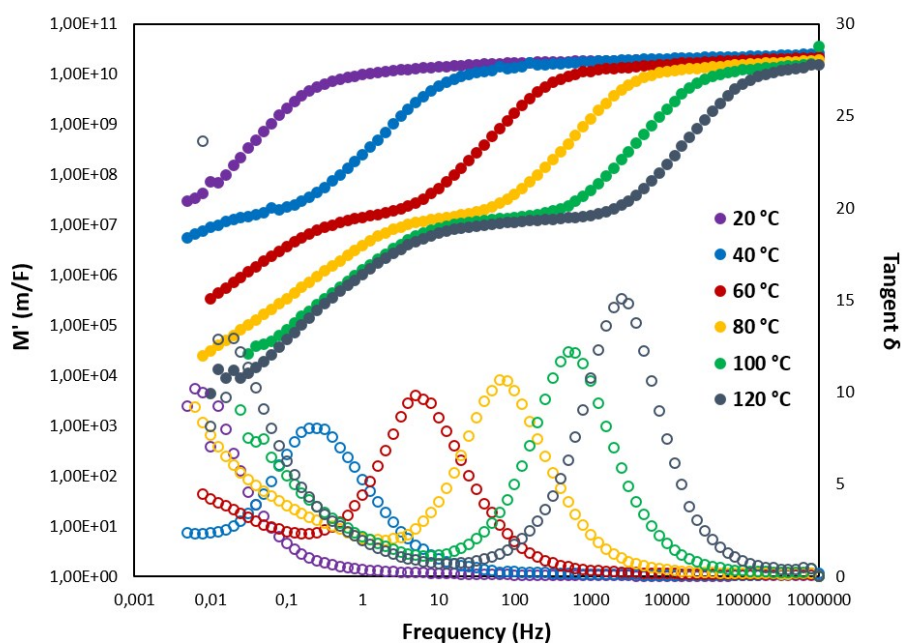


Figure S6. Dielectric modulus (filled circles) and tangent delta (open circles) for a stoichiometric ASA/PETMP dynamic photopolymer with 5 mol% DMAP catalyst.

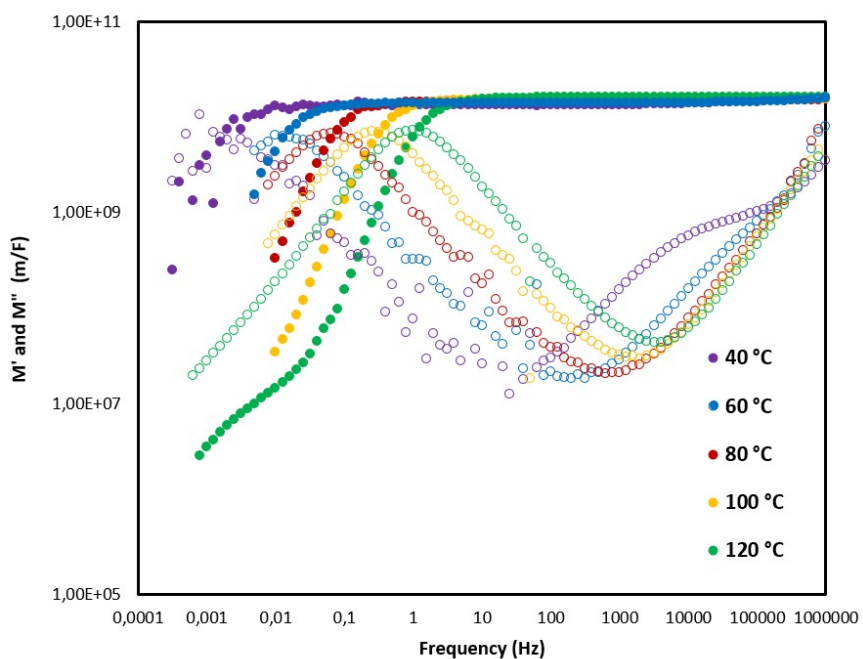


Figure S7. Dielectric modulus (filled circles) and dielectric loss (open circles) for a stoichiometric thiol-ene non-dynamic photopolymer (HDT/TTT).

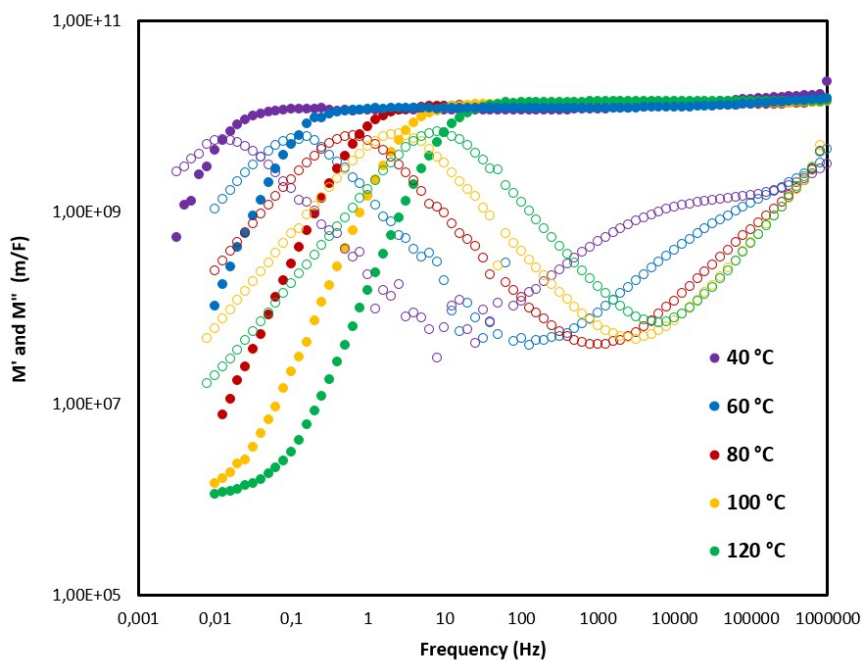


Figure S8. Dielectric modulus (filled circles) and dielectric loss (open circles) for an off- stoichiometric thiol-ene non-dynamic photopolymer (TMPTMP/TTT).

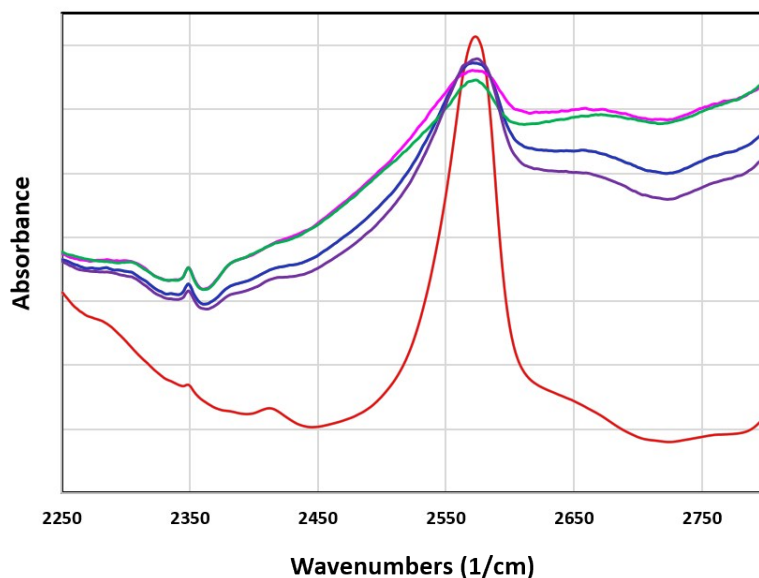


Figure S9. Broadening of the IR signal during thiol-anhydride ring opening reaction. Initial mixture contained ASA (2M) and PETMP (1M) and no DMAP (red). Addition of DMAP (5 mol %) initiates the thiol-anhydride reaction which was monitored over 1 h time (purple – 20 min reaction time, pink – 1 h reaction time). Such broadening in the IR signal hinders thiol conversion analysis.

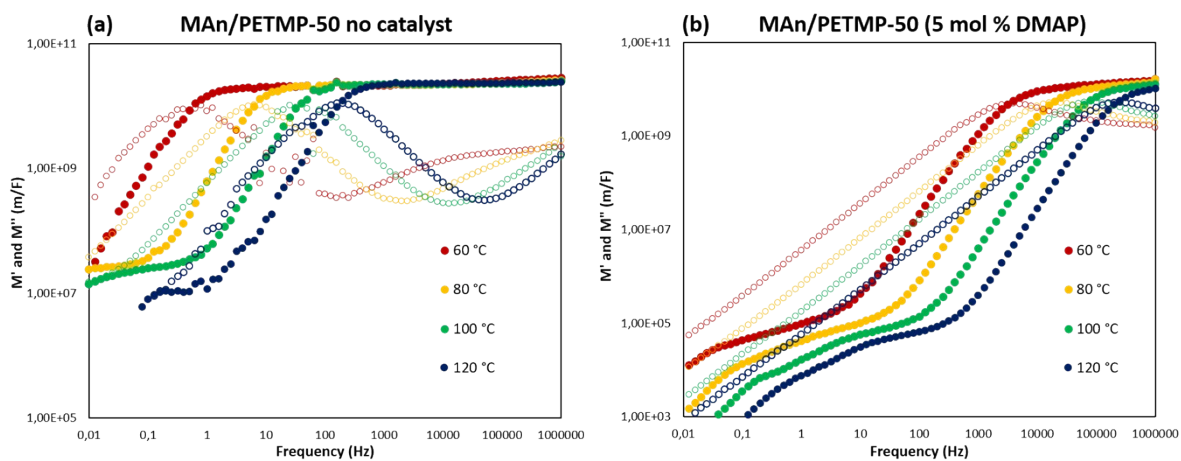


Figure S10. Dielectric modulus (filled circles) and dielectric loss (open circles) as a function of frequency for MAn/PETMP-50 dynamic networks without catalyst (a) and with 5 mol % DMAP (b). Evident is shift of the dielectric modulus-loss crossover points toward higher frequencies when the network becomes more dynamic.