SUPPORTING INFORMATION

Providing Polyurethane Foams with Functionality: A Kinetic Comparison of Different “Click” and Coupling Reaction Pathways

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I. CuAAC modification of the yne-functionalized PU foam

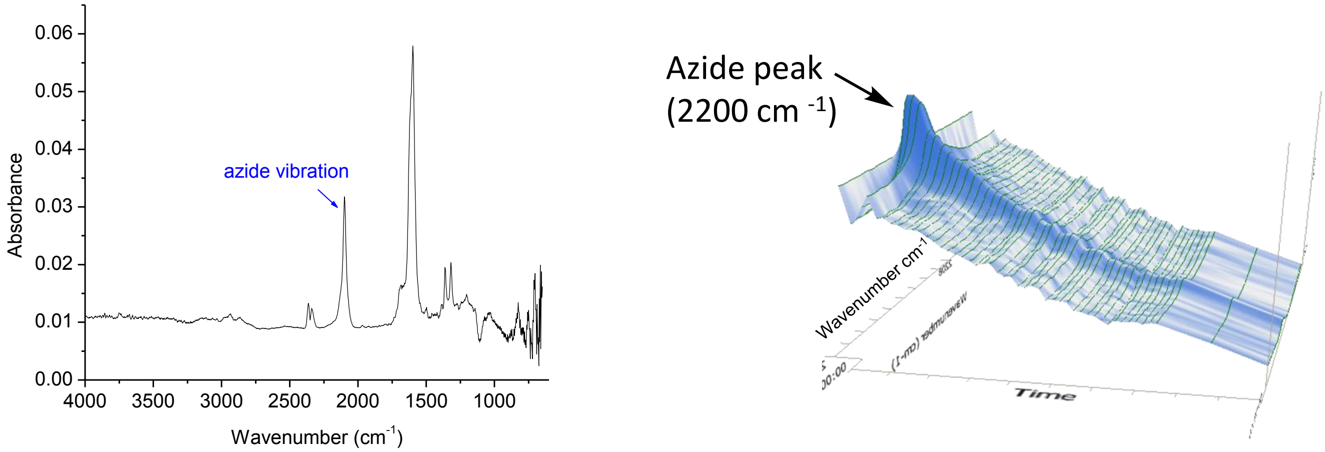


Fig. S1. Illustration of the FT-IR absorbance spectrum of the reaction mixture (left) and online FT-IR waterfall plot (right) for the CuAAC reaction between benzyl azide and the alkyne functionalized PU foam.

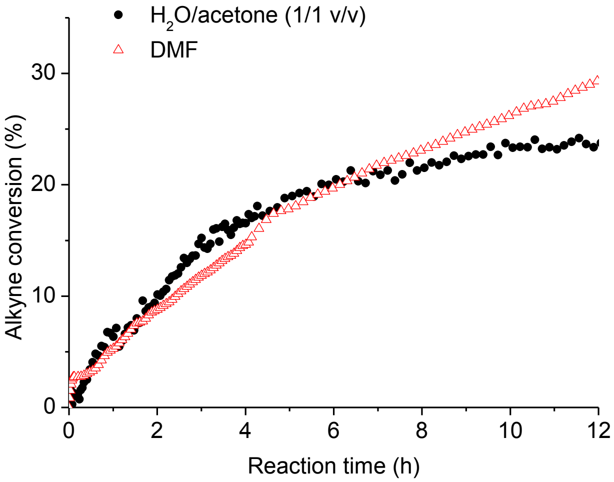


Fig. S2. Alkyne conversion as a function of time for CuAAC reactions of benzyl azide with the yne-functionalized PU foam in DMF and H_2O/acetone, at 50 ^{o}C using 1.2 equiv. of azide and 0.1/0.2 equiv. of $CuSO_4$, $5H_2O$/Na_{asc} with respect to alkyne.

II. Thiol-ene and thiol-yne modifications of the ene- and yne-functionalized PU foams

II.1. Model reactions

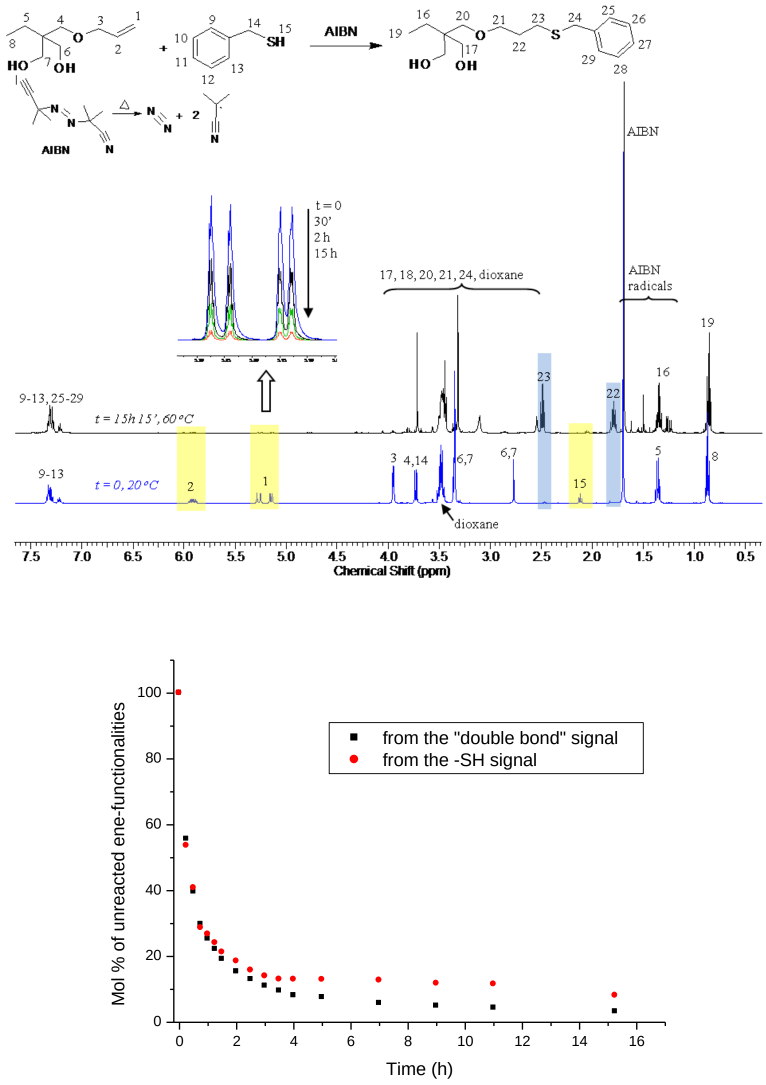


Fig. S3. ^{1}H NMR spectra (upper part) of the reaction between BM and TMPME and the mol% of unreacted "ene" functional groups (lower part) as a function of reaction time. The reaction was monitored by online ^{1}H NMR (Bruker AM500, 500 MHz) in dioxane-d8, at 60 ^{o}C, with c_{ene} = 0.47 mol/L, 1.05 equiv. of BM with respect to TMPME, and 0.23 mol/L of initiator AIBN.

II. 2. Illustrated ^{1}H NMR spectra for reactions on functionalized PU foams

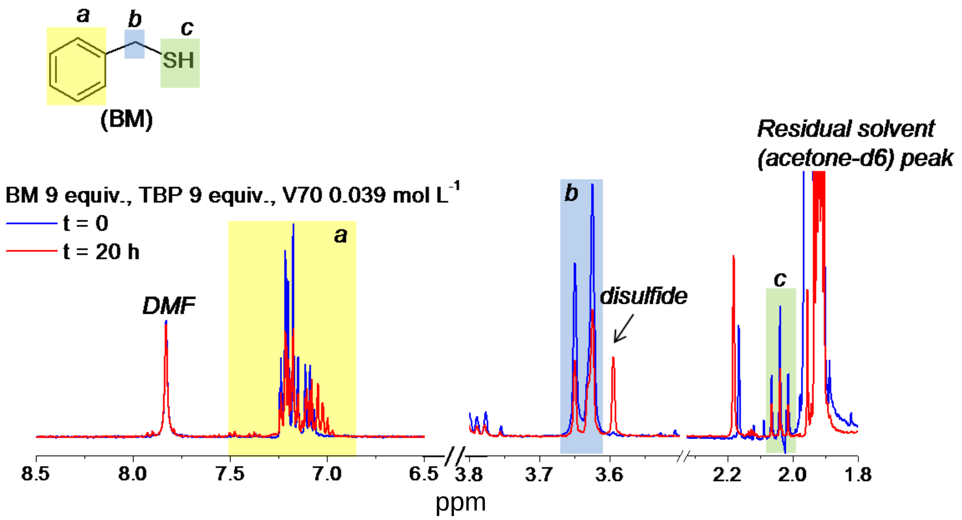


Fig. S4. Illustration of the ^{1}H NMR spectra, intensity-normalized to the DMF peak, of the reaction mixture of the alkene-functionalized PU foam and BM, in acetone-d6 using the V-70 thermal initiator, as a function of time.

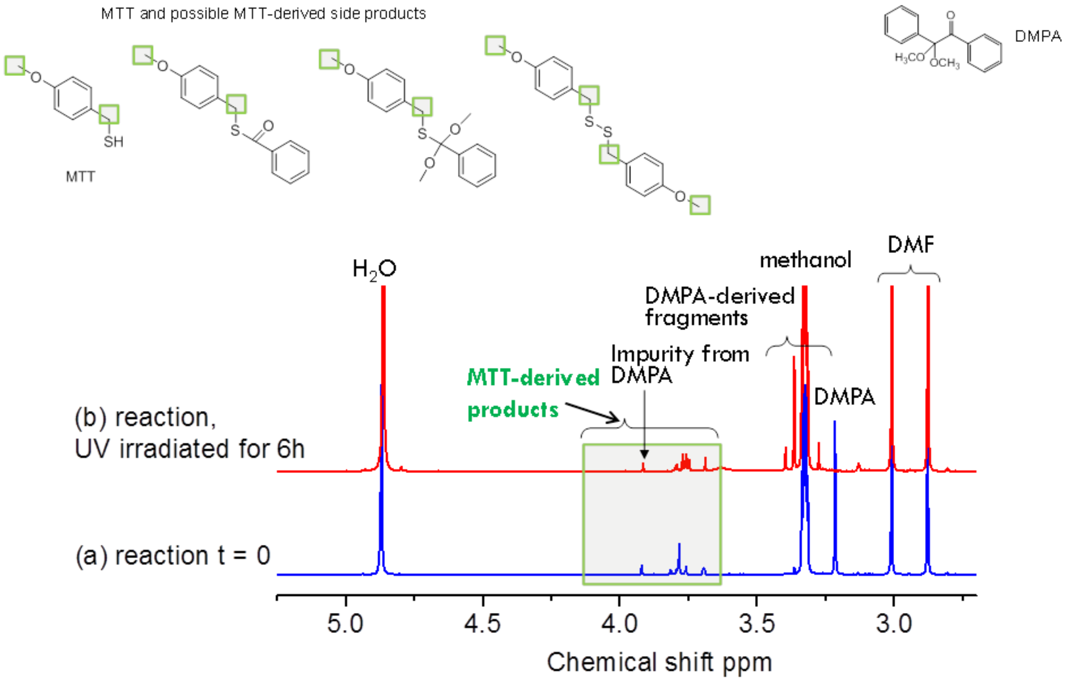


Fig. S5. Illustration of the ^{1}H NMR spectra of the reaction mixture of the alkene-functionalized PU foam and MTT (1.2 equiv. relative to alkene), in methanol-d4 using the DMPA photoinitiator, as a function of time.

II.3. Conversion plots for thiol-ene and thiol-yne reactions on functionalized PU foams

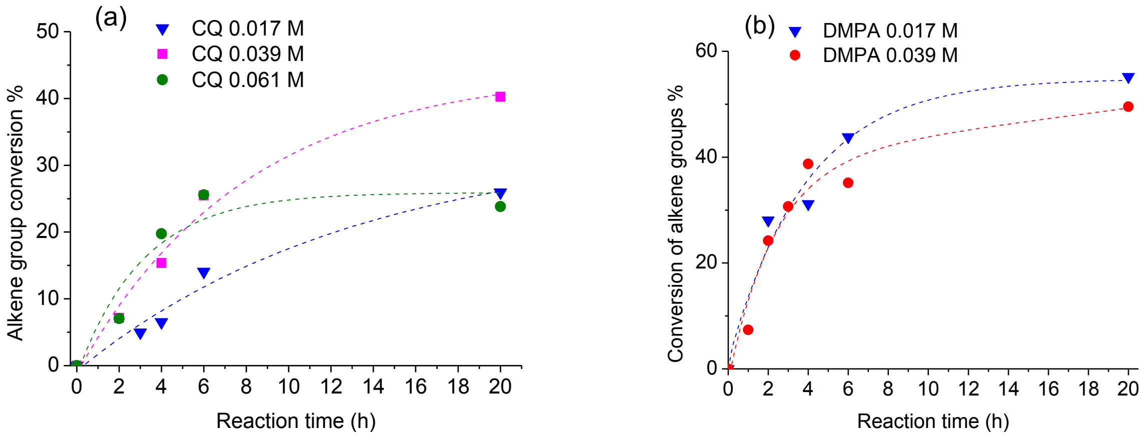


Fig. S6. Alkene conversion as a function of time for reactions of MTT with the alkene-functionalized PU foam at different photoinitiator concentrations under (a) VIS and (b) UV light irradiation (thiol/alkene and reducing agent/thiol molar ratios of 1.2 and 10, respectively). Symbols are experimental data while dashed lines are guides to the eye.

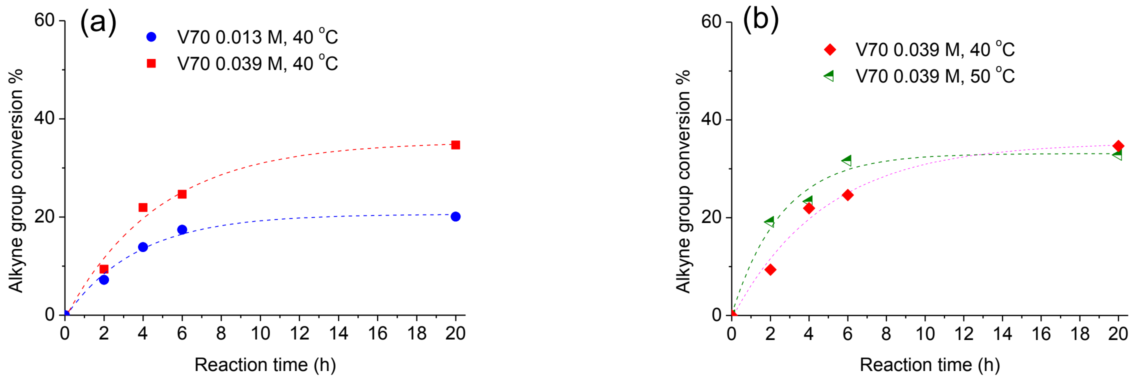


Fig. S7. Conversion of alkyne groups, each reacted with two thiols, as a function of time for reactions of BM with the alkyne-functionalized PU foam at different (a) initiator concentrations and (b) temperatures. Thiol/alkyne and reducing agent/thiol molar ratios were 2.4 and 10, respectively. Symbols are experimental data while dashed lines are guides to the eye.

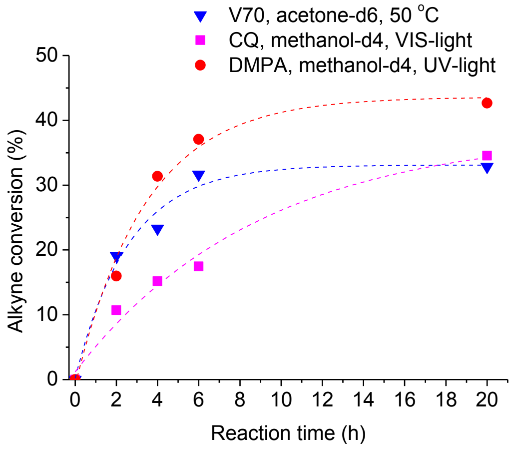
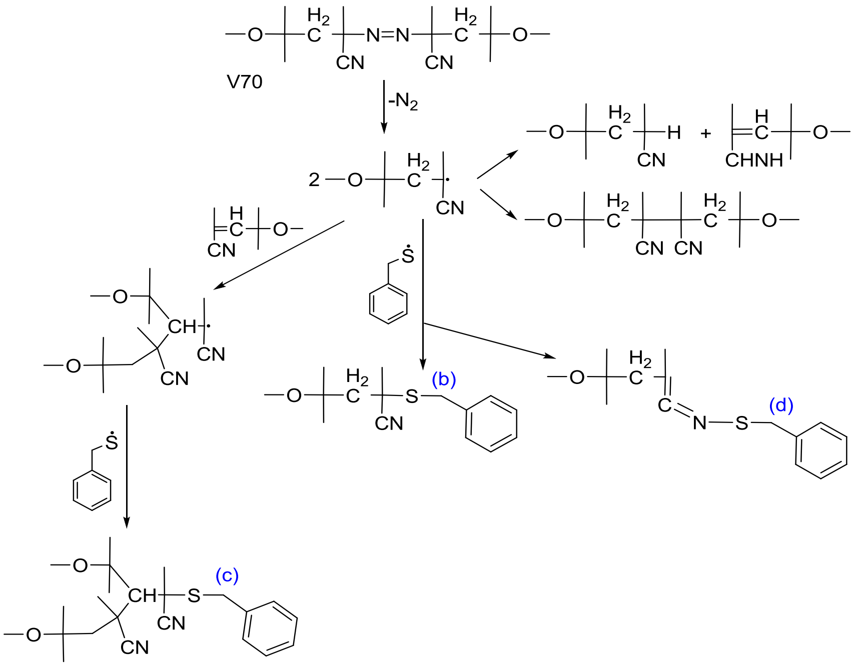


Fig. S8. Conversion of alkyne groups, each reacted with two thiols, as a function of time for reactions of BM with the yne-functionalized PU foam using different initiators. Thiol/alkyne and reducing agent/thiol molar ratios were 2.4 and 10, respectively. Symbols are experimental data while dashed lines are guides to the eye.

II.4. Scheme demonstrating possible side reactions in the thiol-ene functionalization



$RS^- + H\dot{O}{-}\dot{O} \longrightarrow RS^\bullet + \dot{O}{-}O^-$

$RS^\bullet + \dot{O}{-}O^- \longrightarrow RSO_2^-$

$RSH + \dot{O}{-}O^- \longrightarrow RS^\bullet + HOO^-$

$RSH + HOO^- \longrightarrow RS^\bullet + HO^- + HO^\bullet$

$RS^\bullet + HO^\bullet \longrightarrow RSOH$

$RSH + HO^\bullet \longrightarrow RS^\bullet + H_2O$

$2\ RS^\bullet \longrightarrow RSSR$ (a)

$RSOH + RSH \longrightarrow RSSR$

$RS^\bullet \xrightarrow{O_2} RSO_2^\bullet \xrightarrow{RSH} RSO_2H + RS^\bullet$

$I^\bullet \xrightarrow{O_2} I{-}O{-}O^\bullet \xrightarrow{RSH} I{-}OOH + RS^\bullet$

(I = V70-derived radicals)

Scheme S1. Possible side reactions occurring during the functionalization of the alkene-functionalized PU foam with BM.

II.5. Information on the initiators used for thiol-ene and thiol-yne reactions

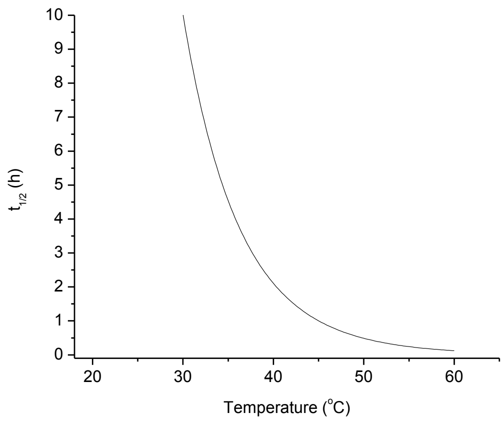


Fig. S9. Half-life time of V-70 as a function of temperature

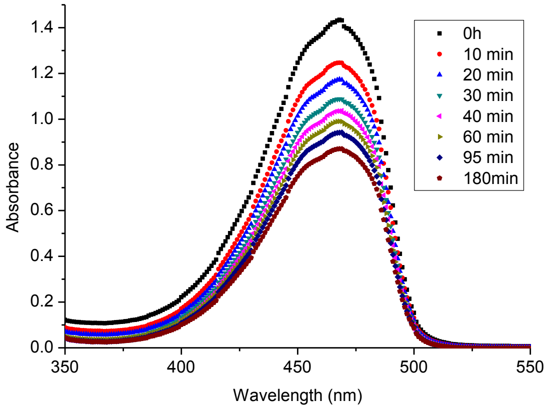


Fig. S10. UV-VIS spectral changes during the VIS light irradiation of a solution of 0.2 M of CQ in tetrahydrofuran, using a home-designed VIS light setup.

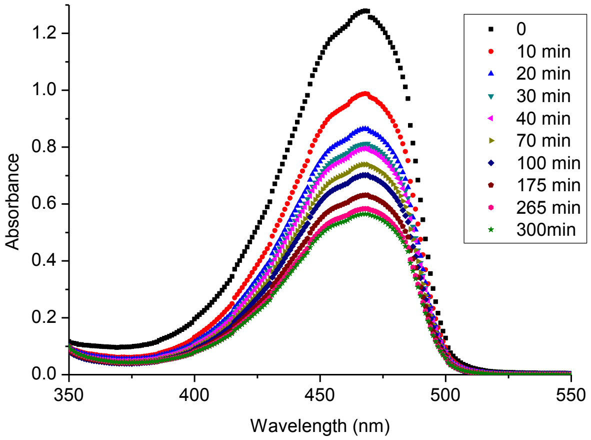


Fig. S11. UV-VIS spectral changes during the VIS light irradiation of a solution of 0.039 M of CQ in methanol in the presence of 0.0105 M of MTT, using a home-designed VIS light setup.

III. DA modification of the furan-functionalized PU foams

III.1. Model reactions

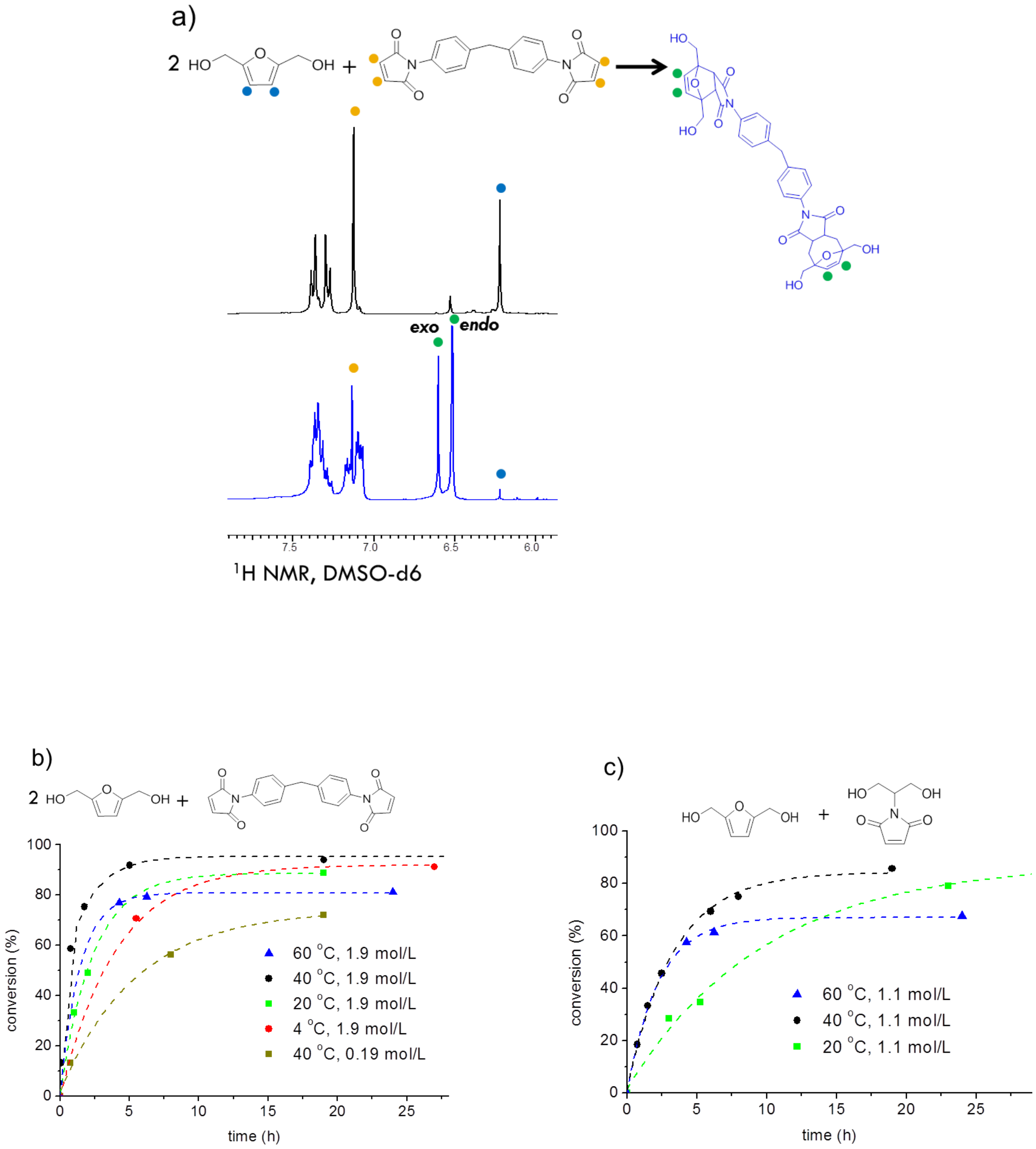


Fig. S12. Demonstrated ^{1}H NMR spectra (a) and reaction conversions (b and c) for the model DA reactions of 2,5-bis-(hydroxymethyl)furan with different maleimide compounds in DMSO-d6 and at varying temperatures and concentrations. Symbols are experimental data while dashed lines are guides to the eye.

III.2. Reactions on the furan-functionalized PU foams

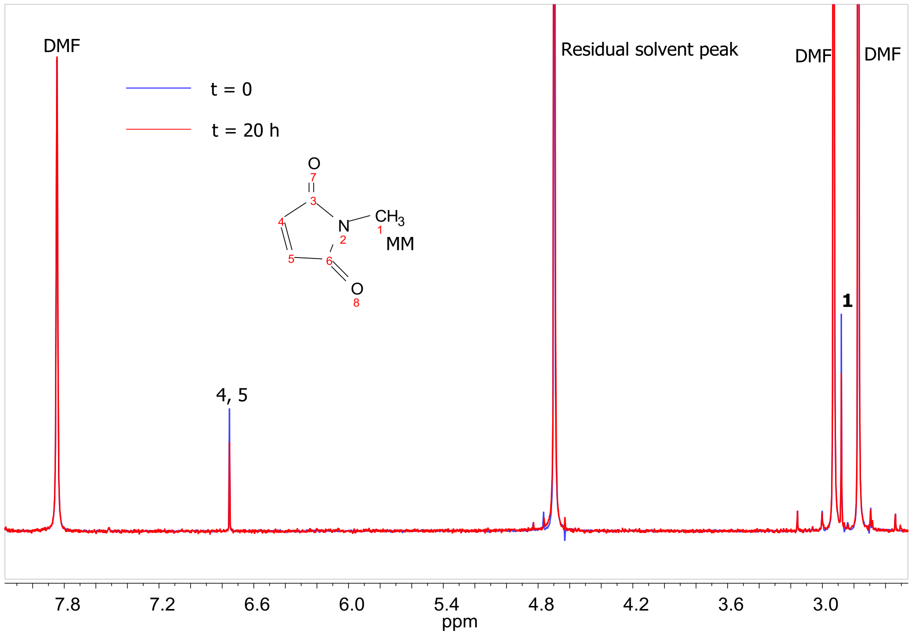


Fig. S13. Illustrated ^{1}H NMR spectra, intensity-normalized to the DMF peak, of the reaction mixture of the furan-functionalized PU foam and MM (1.2 equiv. relative to furan) in D_2O at 40 ^{o}C.

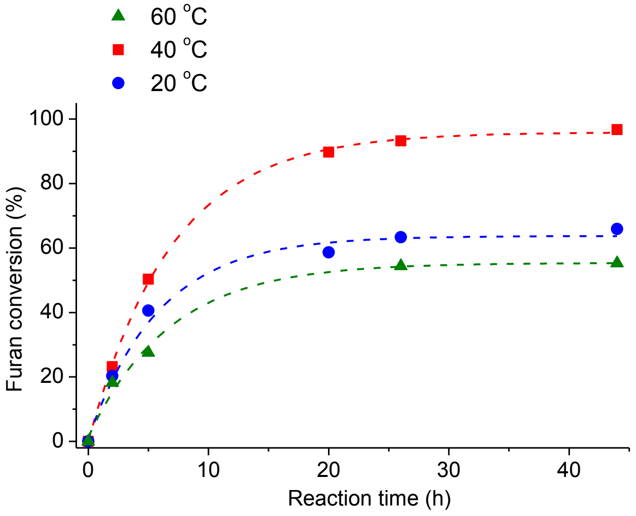


Fig. S14. Furan conversion as a function of time for reactions of MM with the furan-functionalized PU foam with 9 equiv. of MM with respect to furan in D_2O at varied temperatures. Symbols are experimental data while dashed lines are guides to the eye.

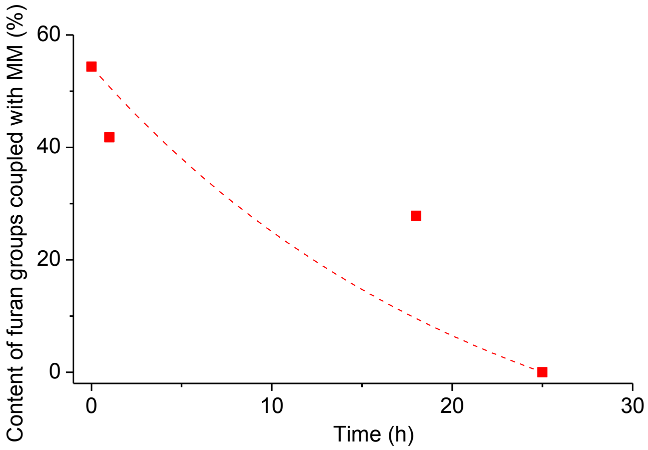


Fig. S15. Conversion of the retro-DA reaction at 100 °C in D_2O to detach MM from the PU foam, which was previously coupled with MM via the DA reaction using 1.2 equiv. of MM with respect to furan, in D_2O at 40 °C for 44 h. Symbols are experimental data while dashed lines are guides to the eye.