Supplementary Information (SI) for Polymer Chemistry.

Supplementary Information

Trioxanes as photodegradable motifs for additive manufacturing

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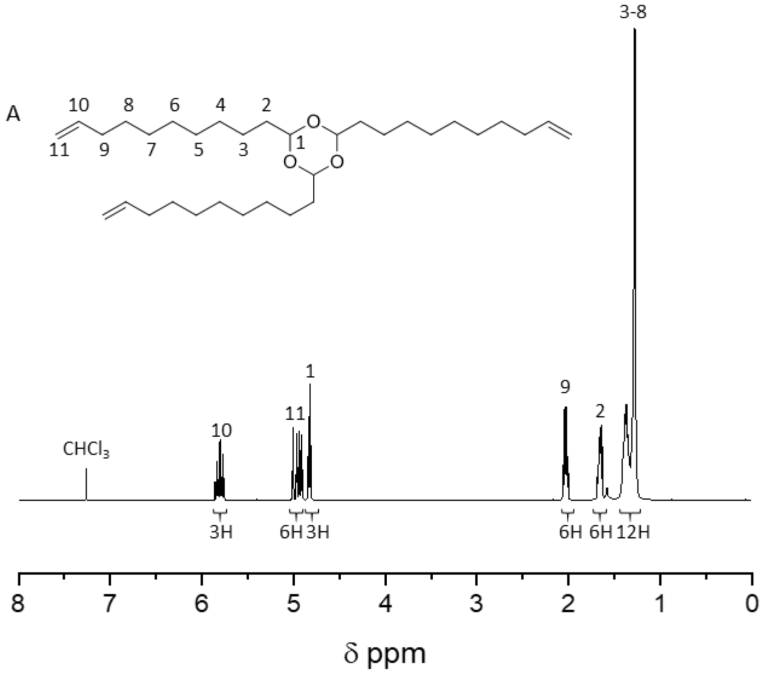
1. NMR characterization of monomer and reference compound

1.1. Trioxane-containin ene-crosslinker



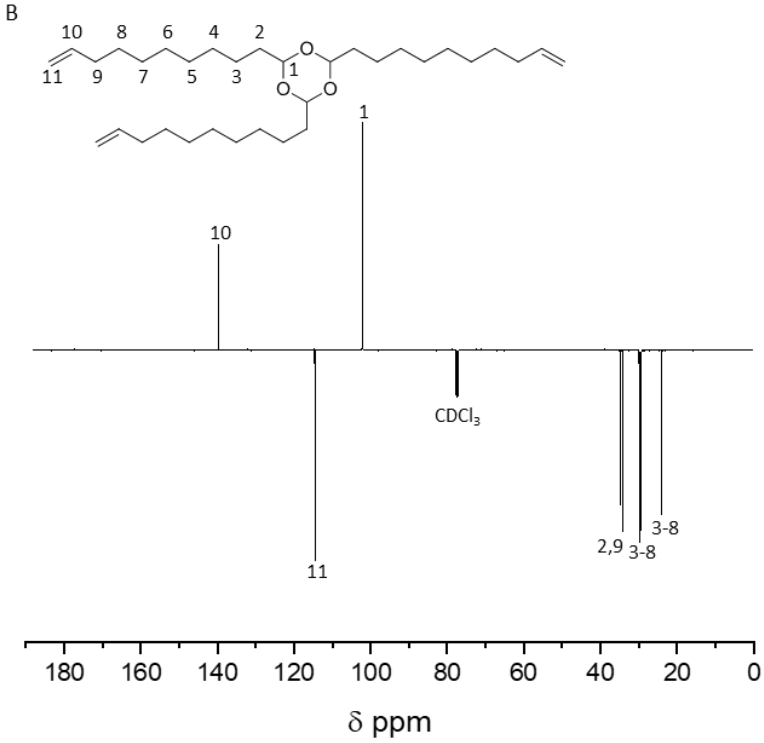


Figure S1: *A) ^{1}H and B) ^{13}C(APT)- NMRs of the product (400 MHz, CDCl$_3$)*

1.2. Reference compound

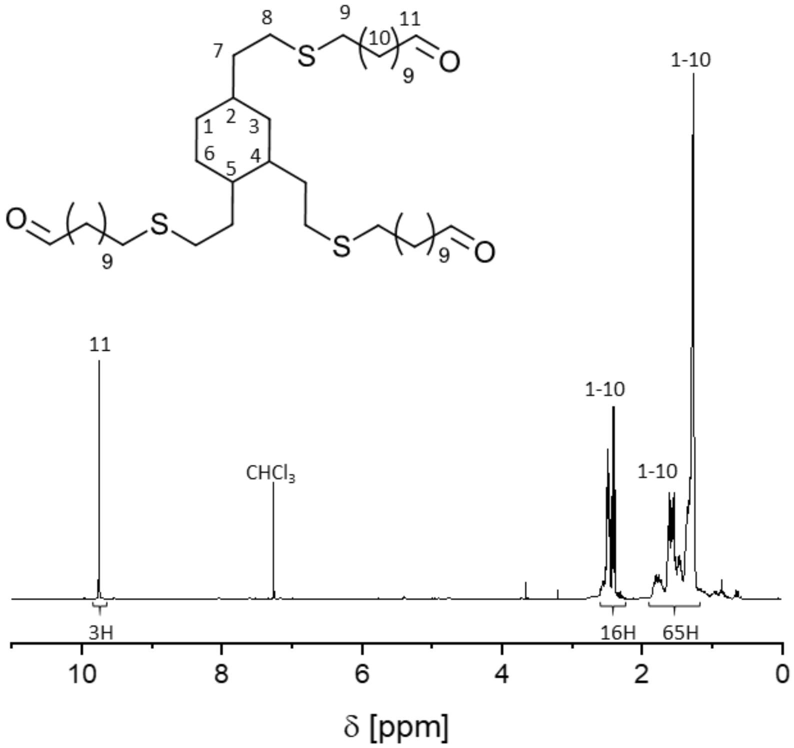


Figure S2: *^{1}H NMR of the reference aldehyde (400 MHz, CDCl$_3$)*

2. Photorheology measurements

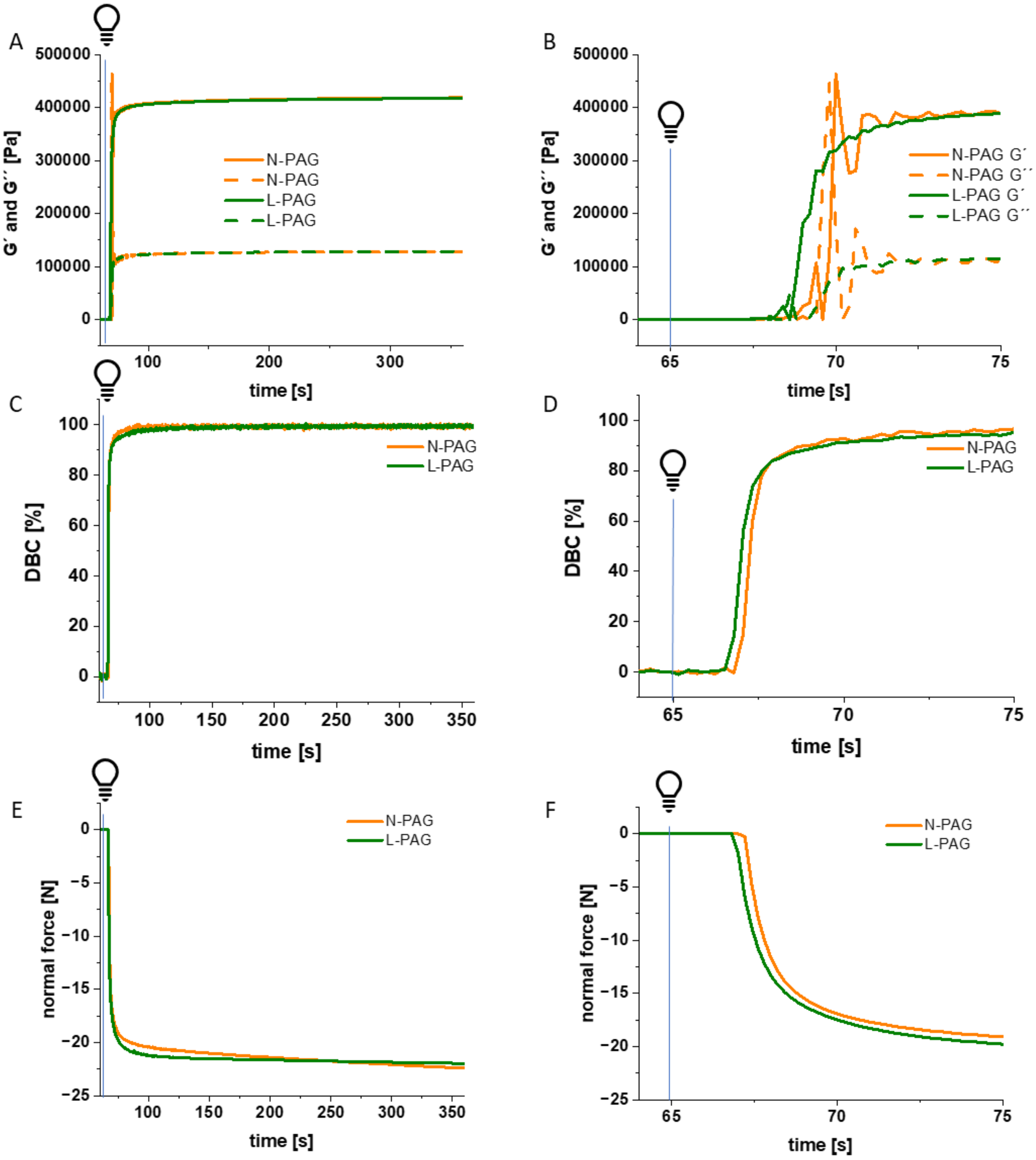


Figure S3: *Photorheology curves: storage and loss moduli A) over the entire measured time range and B) zoomed-in version of the steep section, double bond conversion (DBC) C) over the entire measured time range and D) zoomed-in version of the steep section, normal force E) over the entire measured time range and F) zoomed-in version of the steep section. Vertical line at 65 s indicates start of irradiation (385 nm 50 mW cm*$^{-2}$*)*

3. IR-comparison trioxane monomer and 10-undecenal

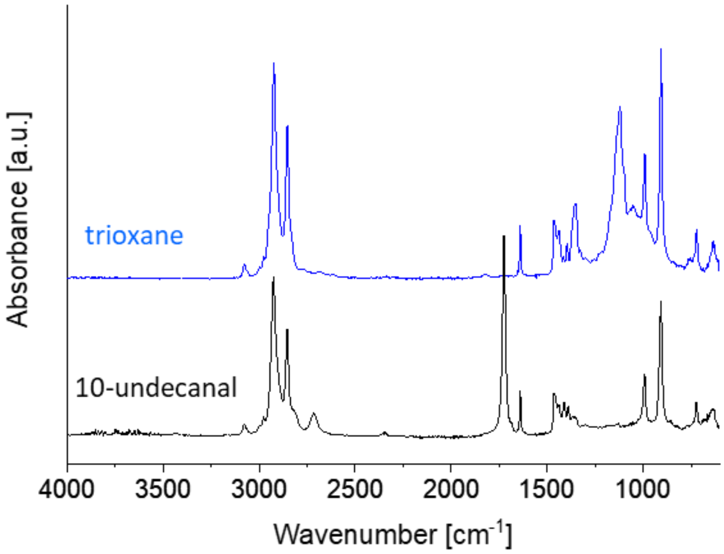


Figure S4: *IR spectra of trioxane and reference aldehyde 10-undecanal*

4. IR comparison different stages from formulation to degraded polymer

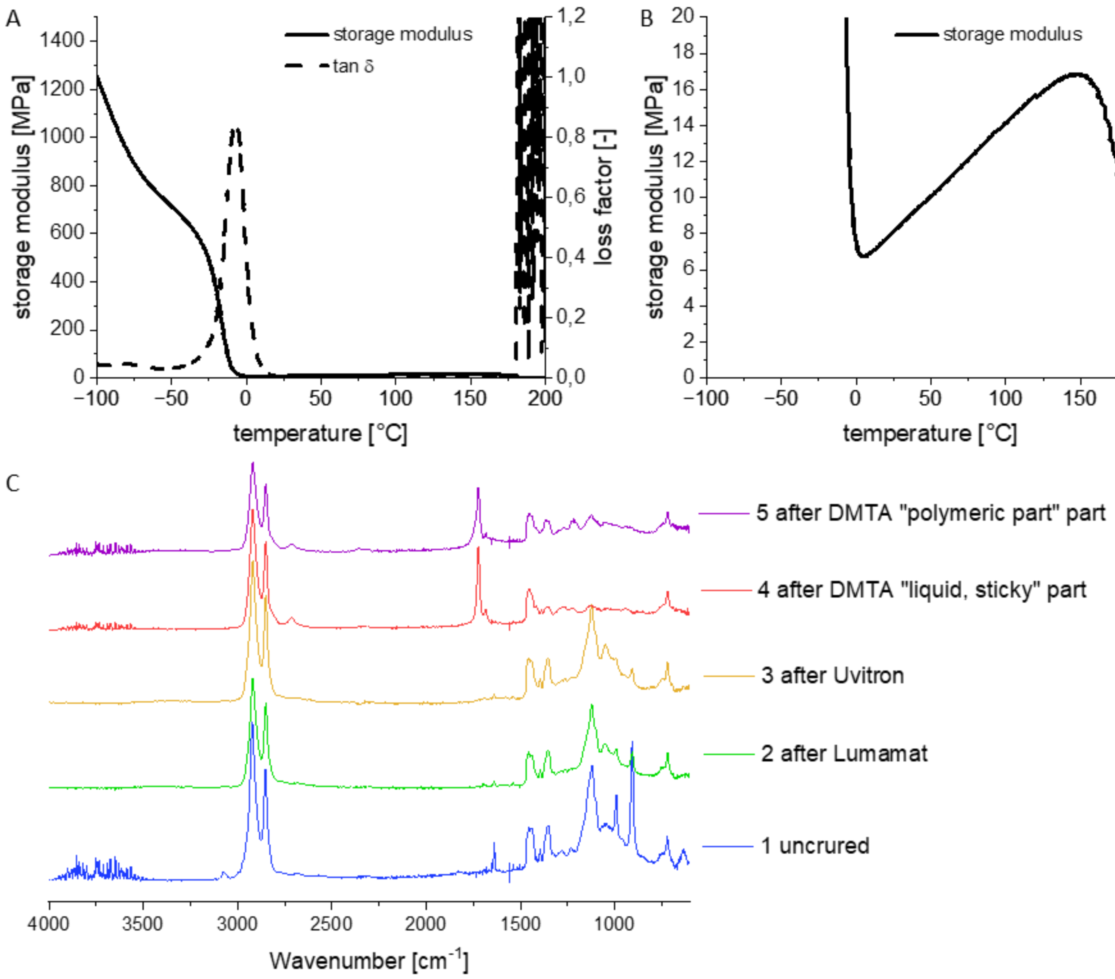


Figure S5: *ATR-IR tracking of polymerization and degradation (bottom to top): 1 (blue): uncured formulation; 2 (green): formulation after Lumamat (400 nm- 500 nm) curing to photopolymerize the formulation; 3 (orange): polymer after UV-oven (Uvitron; 320 nm – 500 nm); DMTA specimen melted partly in the DMTA and therefore there consisted of a liquid (4, red) and a polymeric part (5, purple).*

After the degradation studies of the trioxane monomer in solution, an **N-PAG** DMTA specimen was prepared by thiol-ene polymerization of the trioxane-based ene-crosslinker with the trithiol. To see if the trioxane ring would open by just UV irradiation, ATR-IR measurements were performed. The UV irradiation is strongest on the surface of the sample, therefore UV-light induced degradation was expected to occur on the surface and ATR-IR was chosen as analysis method.

The absence of a carbonyl peak at 1724 cm^{-1} in the intact polymer network **L-PAG** confirmed that there is no trioxane degradation and that this curing method is suitable for the polymer (**Figure S5** 2, 3). To check the thermo-mechanical behaviour the specimen was measured on the DMTA with the standard program that ranges from -100 °C – 200 °C with a heating range of 2 K min^{-1}. During this analysis, a decrease in storage modulus starting at 160 °C, with a loss factor starting at 175 °C was recorded, which was deemed unfeasible. This result can be caused by slipping, breaking or melting of the specimen. Opening the device confirmed partial melting of the sample starting from 160 °C, which can explain the observed decrease in storage modulus.

Both the molten and the solid parts of the DMTA sample were measured on the ATR-IR and confirmed the formation of an aldehyde peak at 1724 cm^{-1} in line with the expected degradation reaction (**Figure S5** 4, 5).

5. Stability study of cured polymers

IR spectra of three polymers were measured, after storing them at 25 °C for 110 days and compared to the reference aldehyde, which was also taken as benchmark for 100% degraded trioxane groups and compared to a polymer without PAG, that was measured directly after curing it (**Figure S5**). For evaluation, the area of the carbonyl peak at 1700 cm^{-1} was compared to the area of the C-H stretch bands at 2900 cm^{-1} to yield a relative peak area. The relative peak area of the freshly synthesised polymer without PAG was taken as 0% degradation and was subtracted from the relative peak areas before comparing them to the reference compound to obtain a degree of degradation (D, Equation 1).

$$D = \frac{\frac{A_{1700,\ 110d}}{A_{2900\,cm^{-1},\ 110d}} - \frac{A_{1700,no\,Pag}}{A_{2900\,cm^{-1},no\,PAG}}}{\frac{A_{1700,ref}}{A_{2900\,cm^{-1},\ ref}}} \qquad [1]$$

$A_{1700,110d}$ … area of the carbonyl peak in the sample after 110 days (1700 cm^{-1})

$A_{2900\ 110d}$… area of the peak at 2900 cm^{-1} in the sample after 110 days (2900 cm^{-1})

$A_{1700,noPAG}$… area of the carbonyl peak of a freshly cured sample without PAG (1700 cm^{-1})

$A_{2900,noPAG}$ … area of the peak at 2900 cm^{-1} of a freshly cured sample without PAG (2900 cm^{-1})

$A_{1700,ref}$ … area of the carbonyl peak of the reference aldehyde (1700 cm^{-1})

$A_{2900,ref}$ … area of the peak at 2900 cm^{-1} of the reference aldehyde (2900 cm^{-1})

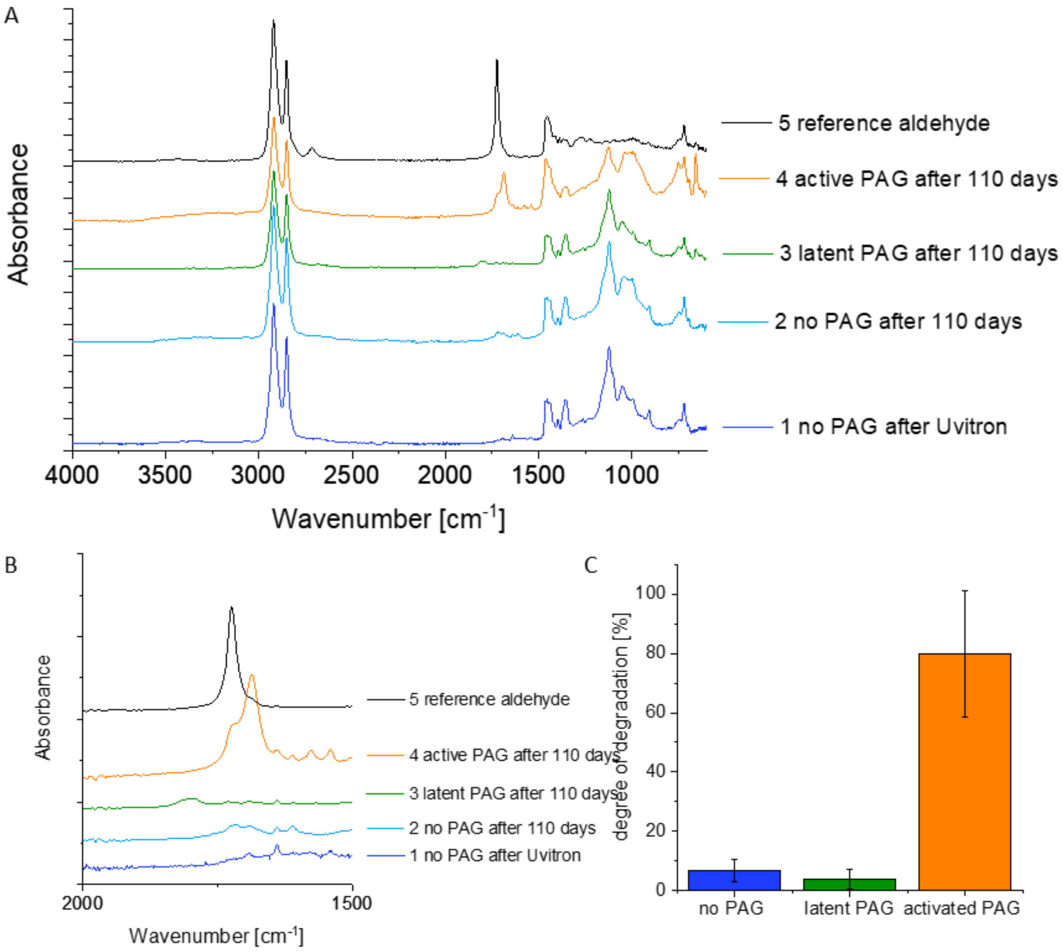


Figure S6: *Degradation study of polymers made of the trioxane monomer and the thiol CHTT for specimen containing latent (green, 3) or activated photoacid generator (PAG; orange, 4) compared to the reference aldehyde (5, black) and a freshly cured polymer with (1, dark blue) and without (light blue, 2) PAG: A) full spectrum B) carbonyl peak C) Calculated degree of degradation (D) of trioxane groups after 100 days.*

The data shows that the polymer with activated PAG has a high degree of degradation around 80%, even though no heat was applied to this system. The polymers without PAG and with latent PAG do not show a peak in the carbonyl region. The recorded degree of degradation could also correspond to noise in the spectrum and can be seen as minimal for the two polymers.