Supporting Information

Microscale manipulation of bond exchange reactions in photocurable vitrimers with a covalently attachable photoacid generator

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Materials and methods

Materials

All chemicals were used as received without additional purification. *N*-hydroxy-1,8-naphthalimide and dimethylformamide (DMF) were supplied by TCI Europe (Haven, Belgium). Thionyl chloride, 4-tert-butylcatechol, sodium styrenesulfonate, pyridine, 4-methylbenzene-1-sulfonyl chloride, 1,4-butanedithiol, toluene, ethylene glycol (EG) and dichloromethane were supplied by Sigma Aldrich (St. Louis, USA). Ethyl acetate, cyclohexane and anhydrous sodium sulfate were purchased by Carl Roth (Karlsruhe, Germany). Pentaerythritol tetrakis(3-mercaptopropionate) partially esterified with an average degree of 75 % (PETMPOH) was kindly provided by Bruno Bock (Marschacht, Germany) as a custom synthesis. Ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate (TPO-L) was obtained from IGM Resins B.V. (Waalwijk, Netherlands). Perstorp Holding AB (Malmö, Sweden) supplied trimethylolpropane diallyl ether 90 (TMPDE) free of charge. Silanizing agents (3-acryloxypropyl)trimethoxysilane and 3-(trimethoxysilyl)-1-propanethiol were obtained from ABCR GmbH (Karlsruhe, Germany).

Synthesis of photoacid generators (PAGs)

*Synthesis of 2-[(4-ethenylbenzene-1-sulfonyl)oxy]-1H-benzo[de]isoquinoline-1,3(2H)-dione (PAG-**Vi**).*

4-tert-butylcatechol (0.13 g, 0.8 mmol), thionyl chloride (37.6 g, 316.6 mmol) and 27 mL DMF were added into a flask and stirred at 0 °C under nitrogen for 20 minutes. Sodium styrenesulfonate (10.0 g, 36.4 mmol) was added slowly and the reaction was stirred at room temperature for 24 h. Subsequently, the mixture was poured into 100 mL deionized water. The organic layers were extracted with 100 mL toluene and dried over anhydrous sodium sulfate. After filtration, the solvent was evaporated. The obtained product was dissolved in 100 mL CH_2Cl_2 and 2 mL pyridine and *N*-hydroxy-1,8-naphthalimide (4.8 g, 22.5 mmol) were added. The mixture was then stirred at room temperature under nitrogen for 30 min. After filtration, the solvent was evaporated under vacuum. After purification by flash chromatography on silica gel using cyclohexane:CH_2Cl_2 = 2:1, the product was obtained as a colorless solid (4.5 g, 52.7 %).

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.52 (dd, J = 15.5, 7.7 Hz, 4H), 8.02 (d, J = 8.2 Hz, 2H), 7.91 (t, J = 7.8 Hz, 2H), 7.81 (d, J = 8.2 Hz, 2H), 6.91 (dd, J = 17.6, 11.0 Hz, 1H), 6.15 (d, J = 17.7 Hz, 1H), 5.58 (d, J = 10.9 Hz, 1H) ppm.

^{13}C-NMR (76 MHz, $CDCl_3$, δ): 159.62, 143.87, 135.59, 135.04, 133.06, 131.68, 131.55, 129.43, 127.48, 127.09, 126.73, 121.86, 119.51 ppm.

FT-IR (cm^{-1}): 3069, 1730, 1700, 1583, 1377, 1325, 1195, 1179.

*Synthesis of 2-[(4-methylbenzene-1-sulfonyl)oxy]-1H-benzo[de]isoquinoline-1,3(2H)-dione (PAG-**Me**)*

4-methylbenzene-1-sulfonyl chloride (2.10 g, 11.0 mmol) and 1 mL pyridine were added to a mixture of *N*-hydroxy-1,8-naphthalimide (2.13 g, 10 mmol) and 25 mL CH_2Cl_2. The solution was refluxed and stirred for 8 h. The completion of the reaction was monitored by TLC.

Subsequently, the mixture was filtered and the solvent was removed under vacuum. Purification with flash chromatography on silica gel using CH_2Cl_2:EtOAc = 10:1 yielded the product as a white crystal powder (2.73 g, 74.4 %).

^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.63 (d, J = 7.3 Hz, 2H), 8.29 (d, J = 7.8 Hz, 2H), 8.05 (d, J = 8.3 Hz, 2H), 7.80 (t, J = 7.8 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 2.52 (s, 3H) ppm.

^{13}C NMR (76 MHz, $CDCl_3$, δ): 159.94, 146.48, 135.22, 132.40, 132.29, 131.94, 129.89, 129.54, 127.58, 127.25, 122.38, 21.94 ppm.

FT-IR (cm^{-1}): 1731, 1705, 1584, 1513, 1435, 1388, 1327, 1229, 1181, 1154, 1117.

Synthesis of 4-{2-[(4-sulfanylbutyl)sulfanyl]ethyl} benzene-1-sulfonyl)oxy]-1H-benzo[de]isoquinoline-1,3(2H)-dione (PAG-Th)

2-[(4-vinylphenyl-1-sulfonyl)oxy]-1H-benzo[de]isoquinoline-1,3(2H)-dione (PAG-**Vi**, 100 mg, 0.26 mmol) and 1,4-butanedithiol (1000 mg, 8.18 mmol) were stirred for 2 h at 90 °C. Obtained clear solution was cooled to room temperature and 10 ml of cyclohexane were added. The mixture was allowed to stir for 1 h, before the formed precipitate was filtered and washed with 3 x 10 ml of cyclohexane to give a white crystal solid (94 mg, 71.3 %).

^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.64 (d, J = 7.2 Hz, 2H), 8.29 (d, J = 8.1 Hz, 2H), 8.13 (d, J = 12.9 Hz, 2H), 7.80 (t, J = 7.7 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 3.13 – 2.92 (m, 2H), 2.93 – 2.73 (m, 2H), 2.75 – 2.61 (m, 1H), 2.53 (dd, J = 15.1, 7.8 Hz, 4H), 1.74 – 1.50 (m, 4H) ppm.

^{13}C NMR (76 MHz, $CDCl_3$, δ): 159.94, 146.48, 135.22, 132.40, 132.29, 131.94, 129.89, 129.54, 127.58, 127.25, 122.38, 21.94 ppm.

FT-IR (cm^{-1}): 2924, 2854, 1727, 1700, 1583, 1513, 1434, 1410, 1371, 1323, 1223, 1194, 1177, 1145, 1114.

Preparation of resin formulations

The synthetized PAGs (1, 2.5 or 5 mol% from PETMPOH) were added to PETMPOH and mixed at 80 °C with a magnetic stirrer until complete dissolution. The resulting solution was cooled down to room temperature and TPO-L (1 mol% per thiol group) and TMPDE were added. All formulations were prepared with a stoichiometric ratio of 1:1 of "ene" to thiol functionalities and are summarized in Table S1. The prepared mixture was stirred for additional 10 minutes until being homogenous and subsequently ultrasonicated for 1 minute for degassing.

Table S1. Compositions of studied formulations.

	PETMPOH, eq	TMPDE, eq	TPO-L, eq	PAG-Vi, eq	PAG-Me, eq	PAG-Th, eq
Reference	1	1.5	0.03	-	-	-
PAG-Vi-5	1	1.475	0.03	0.05	-	-
PAG-Me-5	1	1.5	0.03	-	0.05	-
PAG-Th-5	1	1.525	0.03	-	-	0.05

Photomask assisted patterning

Photomask assisted patterning was performed by curing a polymer film between a surface modified glass substrate and a quartz photomask (TOPPAN PHOTOMASK INC., France) with a 0.01 mm spacer. The glass substrates were modified by exposure to oxygen plasma utilizing a plasma etching system Femto-BR-200-PCCE7-c (Diener Electronics GmbH, Germany) with an oxygen pressure of 0.1 mbar, a gas flow of 5 mL min^{-1} and a power of 200 W applied for 15 minutes. Subsequently, the plasma activated glass substrates were treated with a 2 wt% solution of 3-(trimethoxysilyl)-1-propanethiol in toluene at 70 °C for 14 h. To reduce the adhesion of polymer film to the photomask, Chemrelease R&B EZ (Chem-Trend Deutschland GmbH, Germany) as release agent was applied. Curing was performed by 405 nm LED light exposure (Opsytec Dr. Gröbel, 79.3 mW cm^{-2}) for 30 seconds (total exposure dose is 0.28 J cm^{-2}). After curing, the sample was irradiated with 365 nm LED light (Opsytec Dr. Gröbel, 215.1 mW cm^{-2}) for 1 minute through the photomask in order to achieve micropatterned activation of the acidic catalyst (total exposure dose is 12.94 J cm^{-2}).

Two-photon absorption direct laser writing

Films were obtained by spin-coating (4000 rpm) the resin solutions (50 wt% in toluene) on modified silicon wafer substrates. The modification of silicon wafers consisted of three steps. First, exposure of the wafer to oxygen plasma utilizing a plasma etching system Femto-BR-200-PCCE7-c (Diener Electronics GmbH, Germany) with an oxygen pressure of 0.1 mbar, a gas flow of 5 mL min^{-1} and a power of 200 W applied for 15 minutes. After the treatment, the substrates were placed in a 10 wt% solution of (3-acryloxypropyl)trimethoxysilane in toluene at 70 °C for 14 h. The silanized surface was additionally treated with a 2 wt% solution of TPO-L in PETMPOH upon 405 nm LED light irradiation (Opsytec Dr. Gröbel, 79.3 mW cm^{-2}) for 120 seconds (total exposure dose is 1.12 J cm^{-2}) in order to obtain a surface with thiol functionalities for enhanced adhesion of the thiol-ene formulation. The curing of the spin-coated films was performed by 405 nm light irradiation (Opsytec Dr. Gröbel, 79.3 mW cm^{-2}) for 30 seconds (total exposure dose is 0.28 J cm^{-2}). Direct laser writing was performed using the two-photon lithography system PPGT 2 (Photonic Professional GT2, NanoScribe GmbH & Co. KG, Eggstein, Leopoldshafen, Germany) with the 20x Objective (Plan-Apochromat 20x N.A. 1.4 Oil DIC, Carl Zeiss AG, Oberkochen, Germany). For the preparation of the print files via the printer's associated software, a slicing distance of 100 nm was used with hatching of 200 nm and with a shifted scanning direction of 90° between each printed layer. For the optimization of writing parameters, the set of experiments was performed with variation of the scanning speed (100, 250, 500, 1000, 5000 µm s^{-1}) and writing laser power (20, 30 and 40 mW).

Surface structure development

After patterned activation of the acid, the development was performed by immersing the sample in ethylene glycol (EG) at 100 °C for 1 h. The treated samples were washed with deionized water and then dried in vacuum oven at 80 °C for 1 h to remove residual EG and water.

Extraction procedure

Extractions of PAGs from cured samples were performed by immersing the cured samples in CH_2Cl_2 for 7 days. Then the mixtures were filtered and the solvent was evaporated. Residual extract was subsequently analyzed with TLC and GC-MS. Gas chromatography coupled with simultaneous mass-spectrometry was performed by injection of 1 μL of sample solution (splitless mode, 250 °C) into a Trace 1300 gas chromatograph (Thermoscientific, USA), coupled with a ISQ 7000 mass spectrometer (Thermoscientific, USA). The separation was performed using a TG-5MS column (Thermoscientific, USA) with 30 m length × 0.25 mm i.d. × 0.25 μm film thickness. The oven program started at 50 °C with 1 minute in isothermal mode followed with subsequent heating to 250 °C with a heating rate of 10 °C min^{-1} and a final isothermal step at 250 °C for 19 minutes under a constant carrier gas flow of 1.3 mL min^{-1}. The mass spectrometer was operated in electron-impact (EI) mode with ionization energy equal to 70 eV in the scan range 35–500 amu. The scan rate was 0.15 s per scan. The temperature of the transfer line and ionization chamber were set to 250 °C and 300 °C, respectively.

Tailoring of material stiffness

Samples were prepared with a resin formulation containing 5 mol% PAG-**Vi**. A film was cured between two glass plates with 0.1 mm spacer. To reduce the adhesion of the polymer film to the glass, Chemrelease R&B EZ (Chem-Trend Deutschland GmbH, Germany) release agent was applied. Curing was performed by exposition of the sample to 405 nm LED light (Opsytec Dr. Gröbel, 79.3 mW cm^{-2}) for 60 seconds (total exposure dose is 0.56 J cm^{-2}). After curing, all resulted films were thermally post-cured at 150 °C for 24 hours. To obtain activated samples, post-cured films were irradiated with 365 nm LED light (Opsytec Dr. Gröbel, 215.1 mW cm^{-2}) for 1 minute (total exposure dose is 12.94 J cm^{-2}). All films were cut with a blade in rectangular specimens (0.1 x 5 x 40 mm) for further modification.

To decrease the Young's modulus, the samples were treated in EG at 100 °C for 30 minutes and subsequently washed with deionized water. In order to remove residual water and EG, the samples were dried at 100°C under vacuum for 1 h.

To increase the Young's modulus, the samples were immersed in a saturated solution of adipic acid in acetone for 72 h. Then, the samples were removed from the solution and dried at room temperature to remove the acetone. The dried specimens were allowed to stay under vacuum at 150 °C for 4 h to enable esterification reaction between adipic acid and free hydroxyl groups and to shift the equilibrium by removing the eliminated water.

The tensile testing was performed on a Physica MCR501 rheometer (Anton Paar, Austria) with extensional fixture UXF12/CTD upon o strain rate of 10 % min^{-1} at room temperature. The modulus of elasticity (Young's modulus) was determined as the slope of linear fit line of the data obtained from 2% to 4 % of deformation. The elongation at break was determined as strain at breaking point. For each experimental condition, 7 specimens were tested in order to perform statistical analysis of mechanical testing data.

Characterization methods

^{1}H and ^{13}C nuclear magnetic resonance spectra (NMR) were recorded on a Avance III 300 MHz spectrometer (Bruker, USA) with deuterated $CDCl_3$ as solvent and trimethylsilane (TMS) as internal standard.

^{1}H NMR spectra for kinetics evaluation were recorded on a Bruker 200 MHz spectrometer. Samples were prepared in CH_3CN-d_3 with a concentration of 0.01 M. Irradiation of the sample was performed using the light of a Hamamatsu Spitlight HgXe Lamp (λ_{max} = 365 nm, power density 4500 mW cm^{-2}) directly inside the NMR probe head by guiding the light via a quartz rod. Scans of the samples upon irradiation were taken every 20 seconds.

Photocuring Kinetic studies of resin formulations were followed by FTIR spectroscopy utilizing a Vertex 70 spectrometer (Bruker, USA). 16 scans were accumulated in transmission mode from 4000 to 900 cm^{-1} with a resolution of 4 cm^{-1} and the absorption peak areas were determined with SpectraGryph software. 10 µL of the resin was placed between two CaF_2 discs and cured with light from a LED source with the wave length of 405 nm (Opsytec Dr. Gröbel, 2.4 mW cm^{-2} and 9.4 mW cm^{-2}) with varying irradiation times. Evaluation of the curing process was performed by calculating the integral area of the bands in the range 2650-2450 cm^{-1} for thiol and 1655-1630 cm^{-1} for C=C groups referring to the carbonyl group oscillations at 1740 cm^{-1}.

Kinetic studies of PAGs activation was performed similarly by irradiation of fully cured samples with 365 nm light (Opsytec Dr. Gröbel, 215.1 mW cm^{-2}) with increasing irradiation times.

UV-Vis experiments were conducted on a Varian (Palo Alto, USA) Cary 50 UV-Visible Spectrophotometer in the range of 200-800 nm at a scan rate of 600 nm min^{-1} and a recording interval of 1.0 nm using a quartz cuvette with an optical path length of 10 mm. The absorption spectra of synthetized PAGs were recorded at a concentration of 40 µM in acetonitrile. Activation of PAGs in acetonitrile solution was performed by irradiation of cured samples with 365 nm light (Opsytec Dr. Gröbel, 215.1 mW cm^{-2}) with varying irradiation times. Evaluation of the PAG activation process by means of UV-vis spectroscopy was performed by calculating the integral area of the peak in the range 285 – 385nm.

Thermal gravimetrical analysis was carried out with a TGA/DSC3+ thermogravimetric analyzer (Mettler Toledo, USA). The measurements were performed under nitrogen atmosphere in temperature range from 30 °C to 900 °C with a heating rate of 10 °C min^{-1}.

Differential scanning calorimetry measurements were carried out with a DSC 4000 instrument (PerkinElmer, USA). All the measurements were performed with a heating rate of 10 °C min^{-1} under nitrogen flow of 50 mL min^{-1}. The polymers' glass transition temperature (T_g) was measured in temperature range from −60 °C to 50 °C and was determined from the second heating run as an inflection point of DSC curve. Melting points of synthetized PAGs were measured in a temperature range from 30 °C to 260 °C and were determined from the first heating run as a peak onset of the DSC curve

Relaxation measurements were performed using the Physica MCR501 rheometer (Anton Paar, Austria) with plate-plate geometry with torque deformation of 3 % and normal force of 10 N at temperatures between 90 °C and 130 °C. The specimens were cured upon 405 nm irradiation (Opsytec Dr. Gröbel, 79.3 mW cm^{-2}) for 1 minute per side (total exposure dose was 1.13 J cm^{-2}), followed by thermal post-curing at 100 °C for 1 h, in a silicon mold to obtain cylindrical samples

with a diameter of 10 mm and a height of 1 mm. Activation of PAGs was performed by irradiation of cured samples with 365 nm light (Opsytec Dr. Gröbel, 215.1 W cm^{-2}) for 15 minutes (total exposure dose was 194.13 J cm^{-2}).

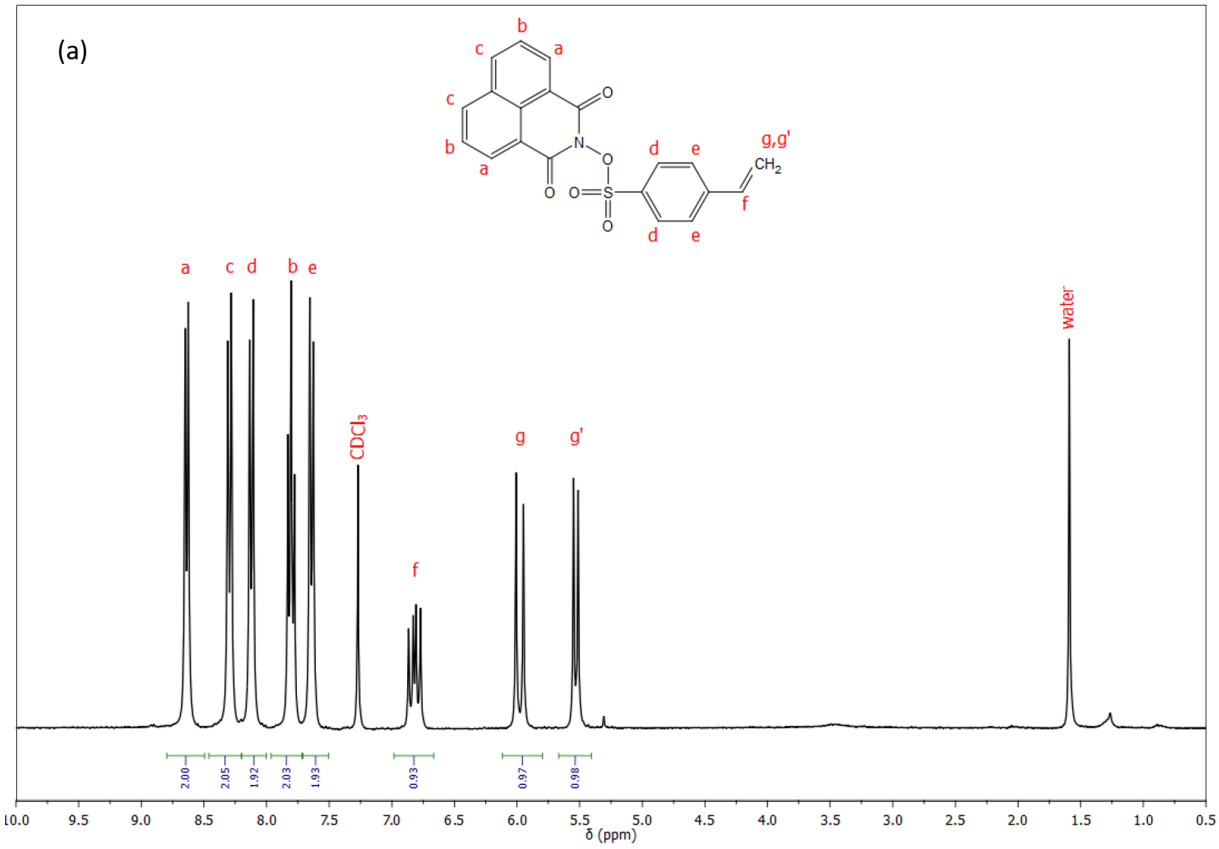
The obtained data of the stress relaxation time was modeled against reversed temperature according to the Arrhenius equation:

$$\tau(T) = \tau_0 \cdot e^{-\frac{E_a}{RT}}, \quad \text{(S1)}$$

where E_a is the activation energy of the relaxation process, τ is the relaxation time, T the temperature (in K), τ_0 the characteristic constant, R the universal gas constant, equal to 8.314 kJ $mol^{-1}K^{-1}$. The obtained linear models of the ln(τ) on the 1/T were used for the calculation of the activation energy (E_a) and the vitrification temperature (T_v).

Surface topography measurements were carried out with the 3D optical surface metrology system Leica DCM8 (Leica Microsystems, Germany). The images were taken with a Mirau 50x objective using the focus variation mode, with green light.

Results



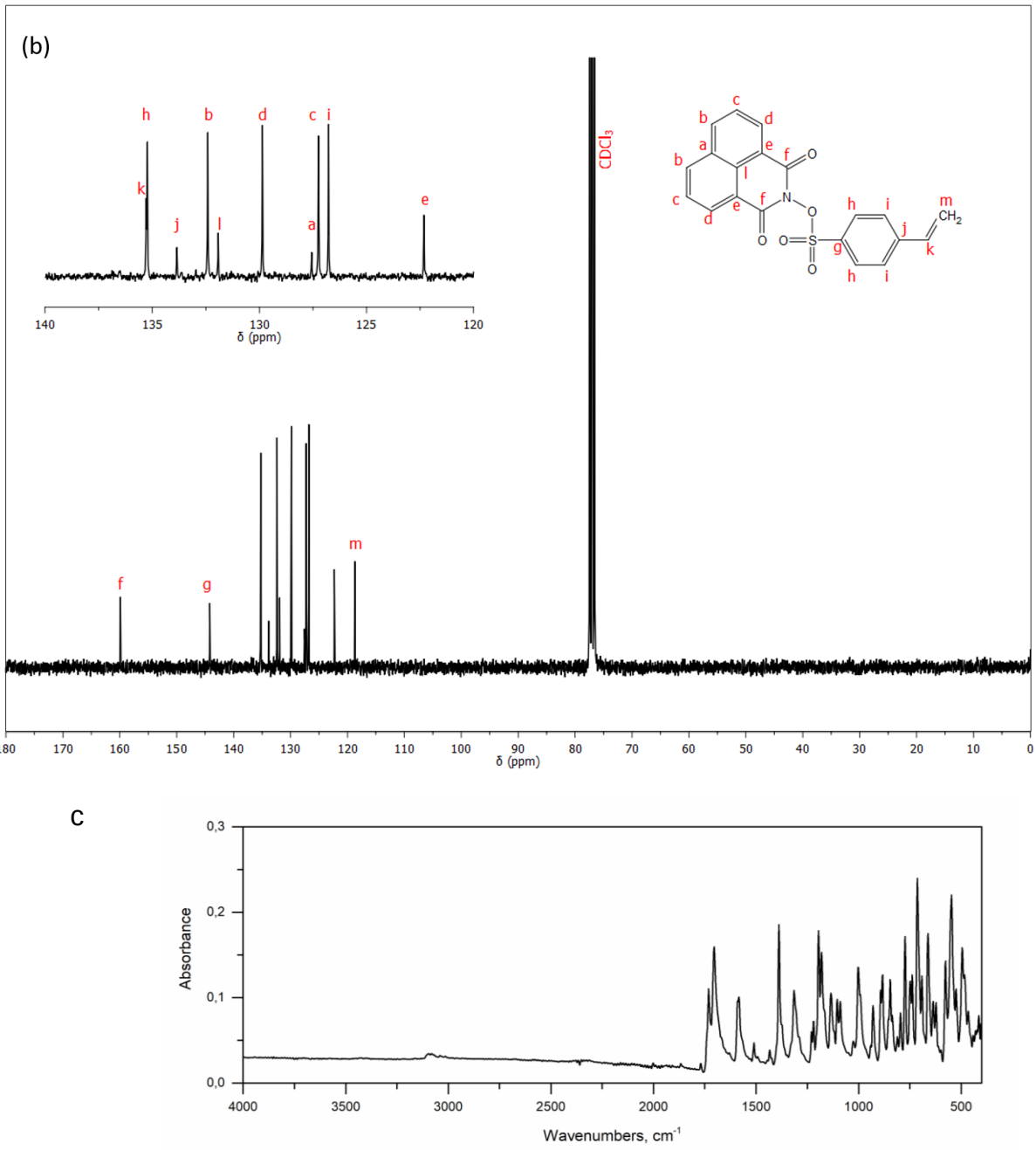
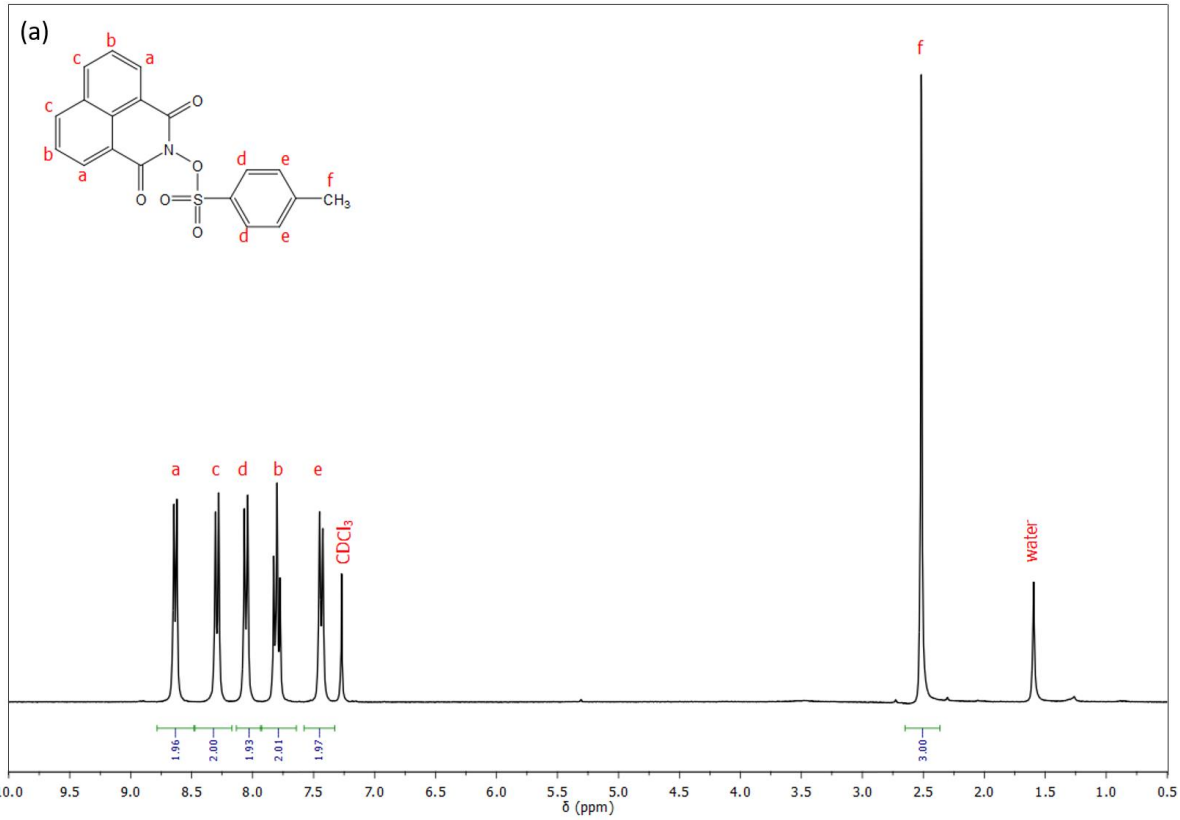


Figure S1. (a) ^{1}H and (b) ^{13}C NMR (300 MHz, $CDCl_3$) and (c) FTIR spectra of PAG-**Vi**.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a
c
d
b
e
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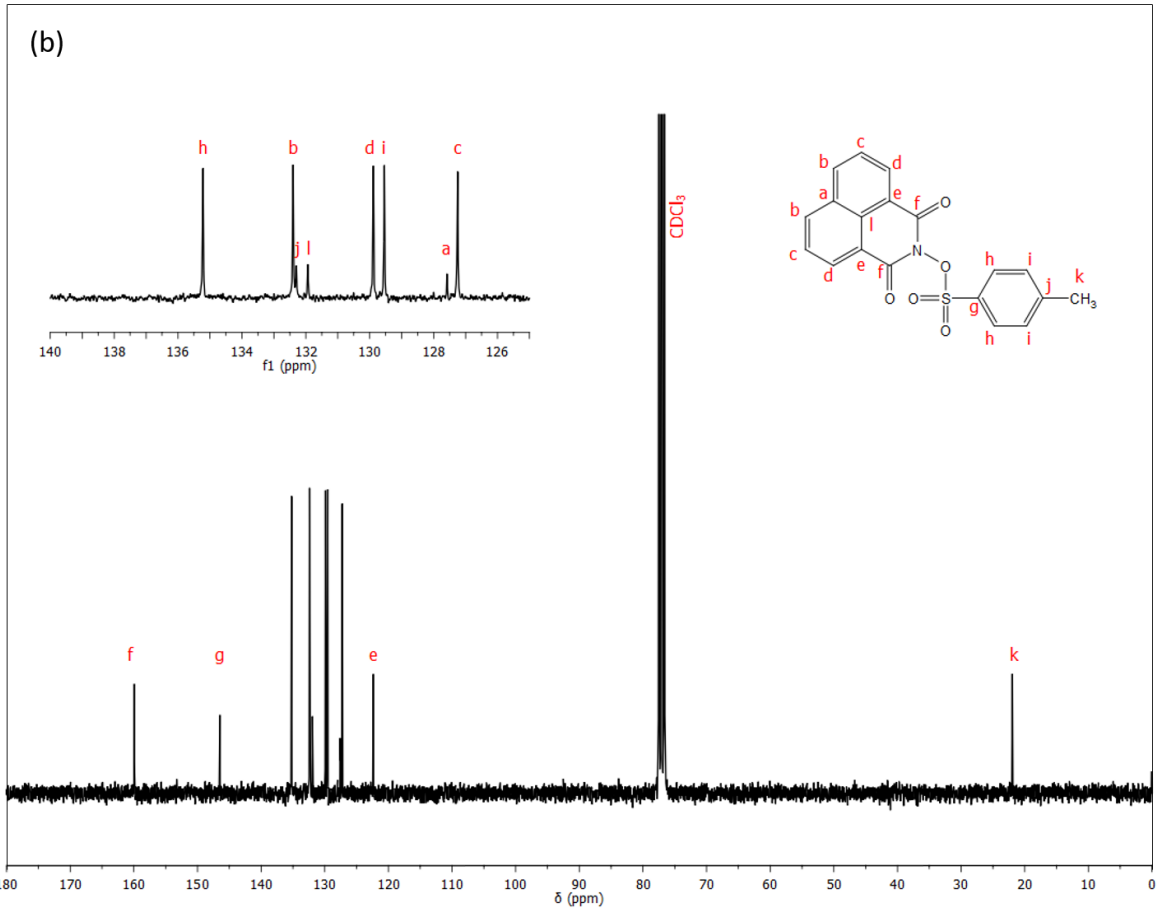
1.93
2.01
1.97
3.00
δ (ppm)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b
d i
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j l
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f
g
e
k
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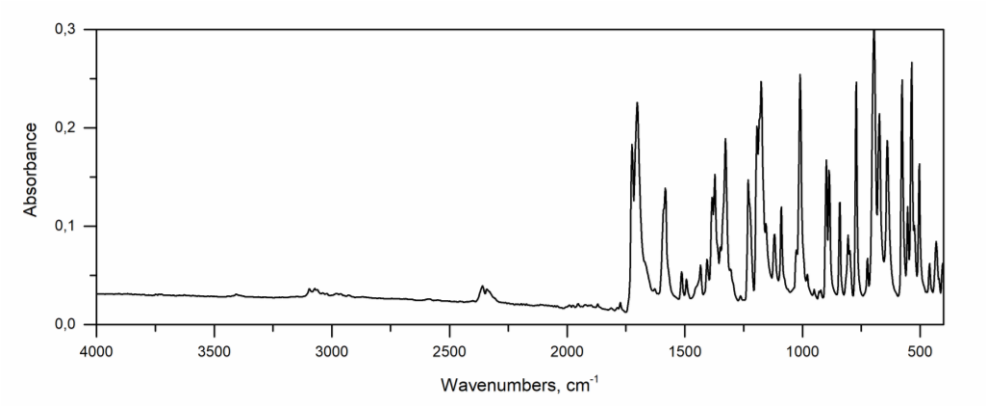
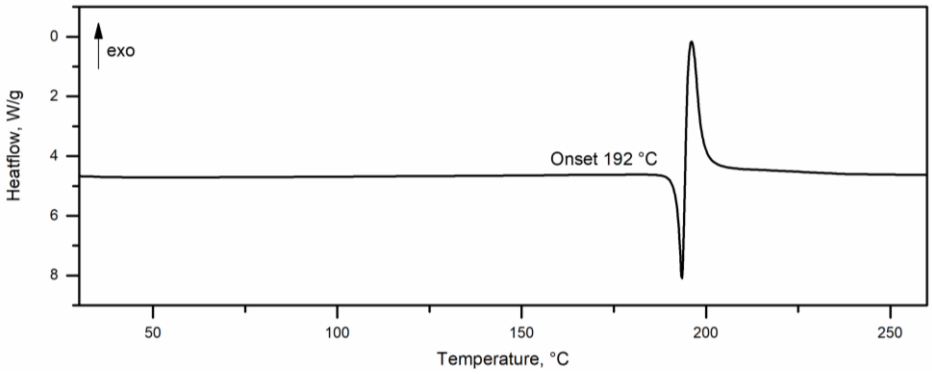


Figure S2. (a) ^{1}H and (b) ^{13}C NMR (300 MHz, $CDCl_3$) and (c) FTIR spectra of PAG-**Me**.

a



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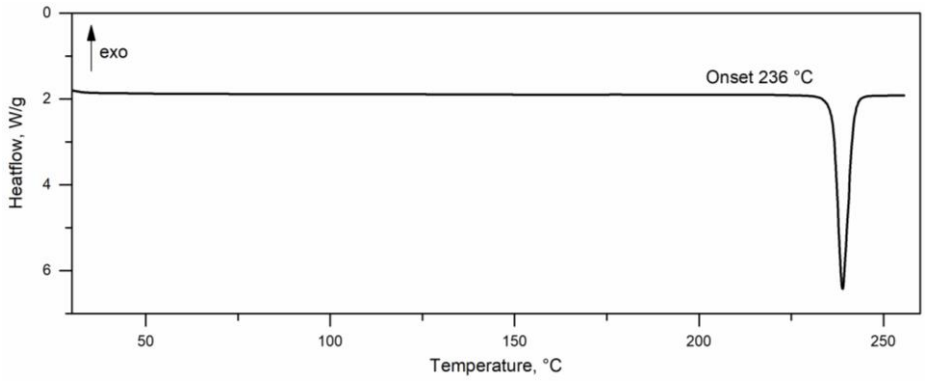
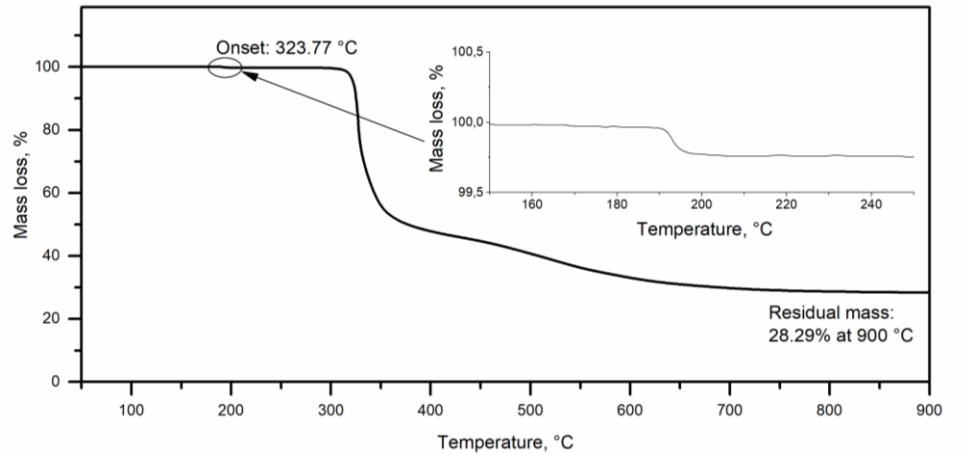


Figure S3. DSC scans of (a) PAG-**Vi** and (b) PAG-**Me**.

a



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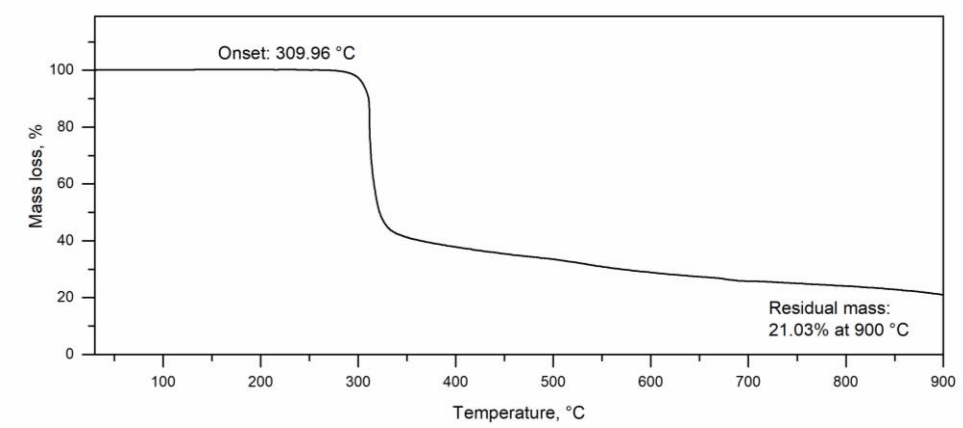


Figure S4. TGA curves of (a) PAG-**Vi** and (b) PAG-**Me**.

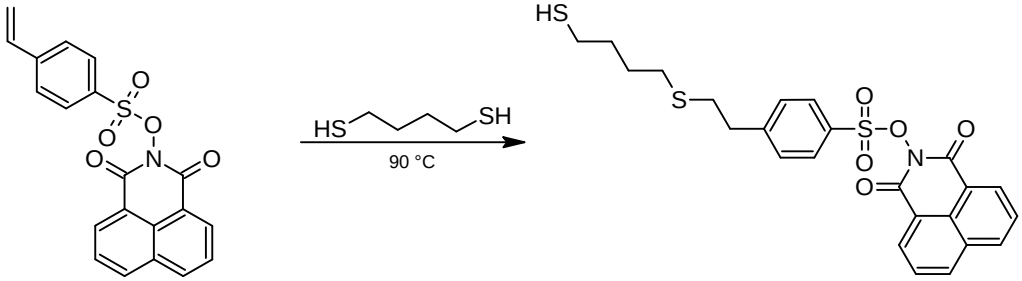
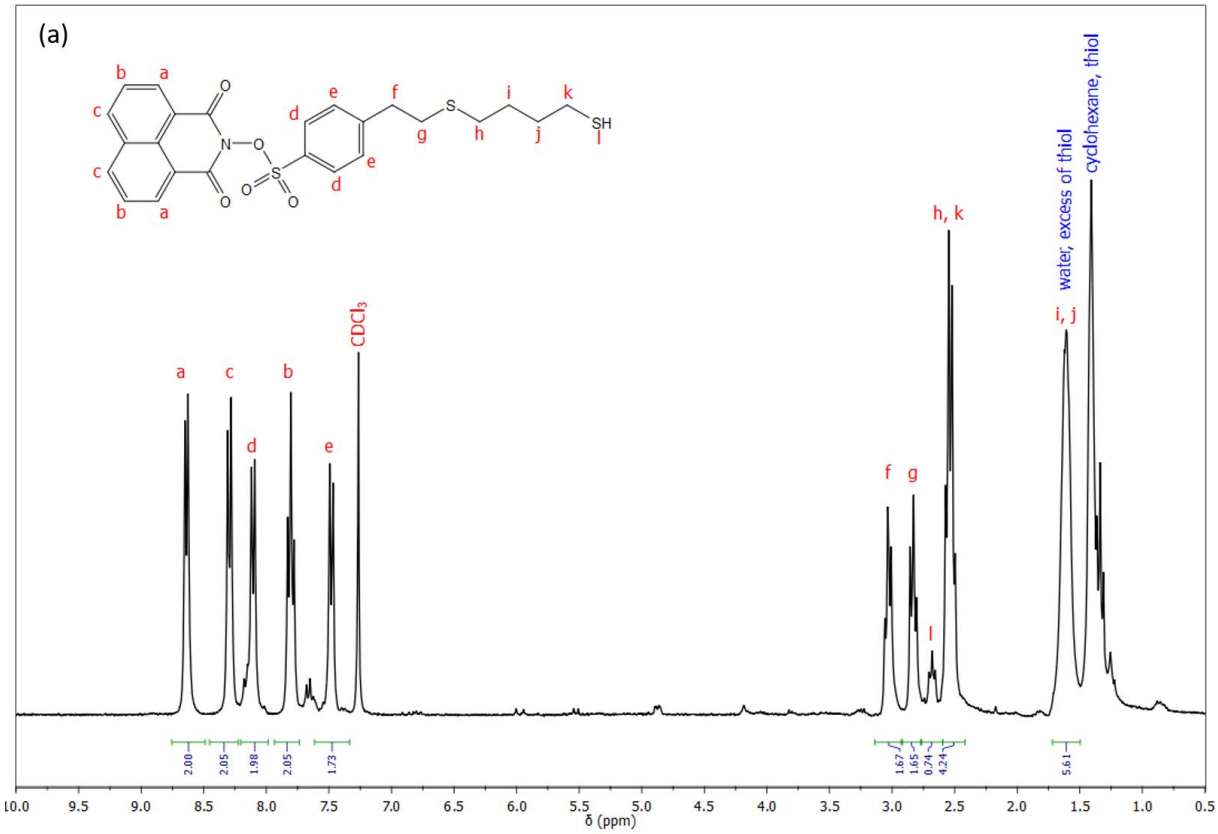


Figure S5. Reaction scheme of the PAG-**Th** synthesis.


(a)
a
c
b
d
f
g
h, k
l
i, j
CDCl3
water, excess of thiol
cyclohexane, thiol
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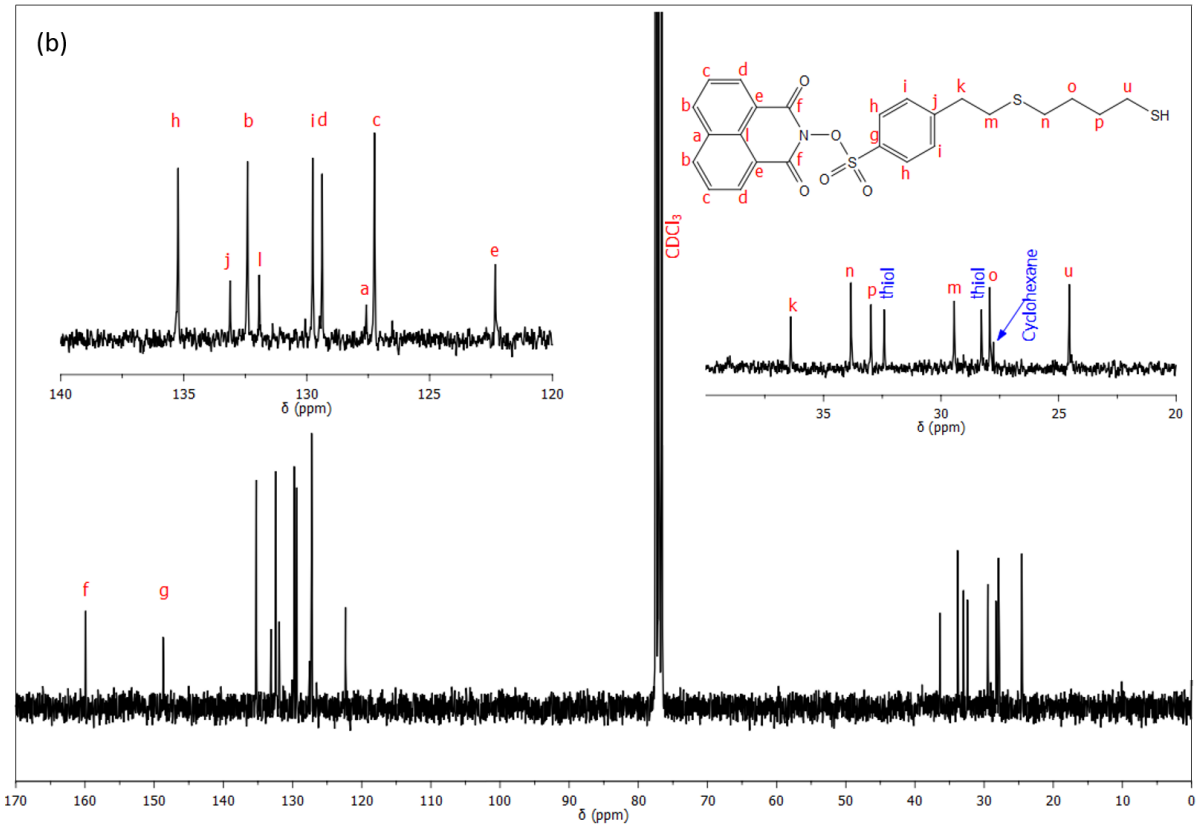
2.05
1.73
1.67
1.65
0.74
4.24
5.61
δ (ppm)


(b)
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i d
c
j
l
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δ (ppm)
δ (ppm)

c

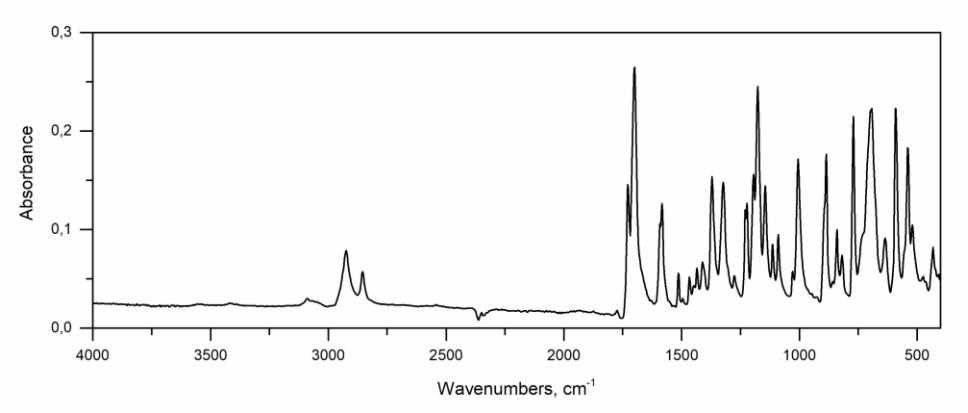


Figure S6. (a) ^{1}H and (b) ^{13}C NMR (300 MHz, $CDCl_3$) and (c) FTIR spectra of PAG-**Th**.

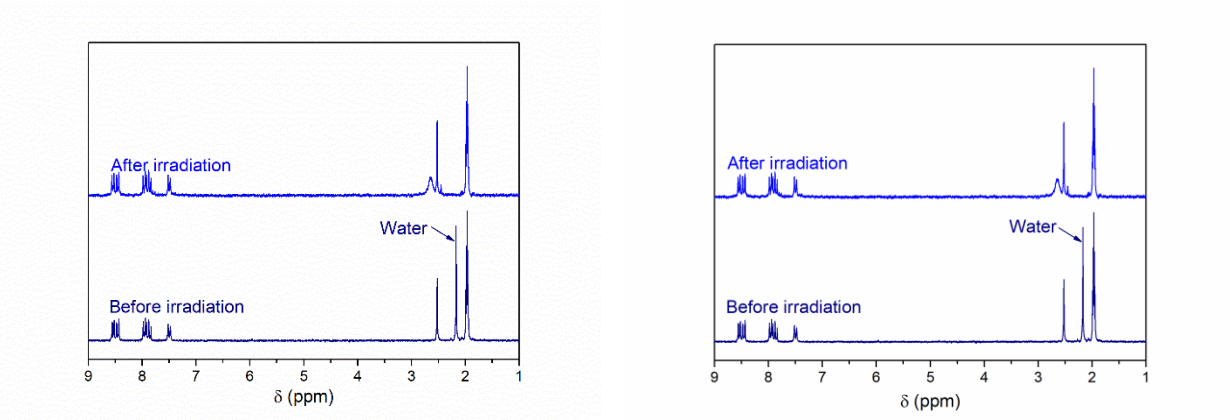


Figure S7. ^{1}H NMR (200 MHz, CD_3CN) spectra of (a) PAG-**Me** and (b) PAG-**Th** prior to and after UV irradiation (365 nm).

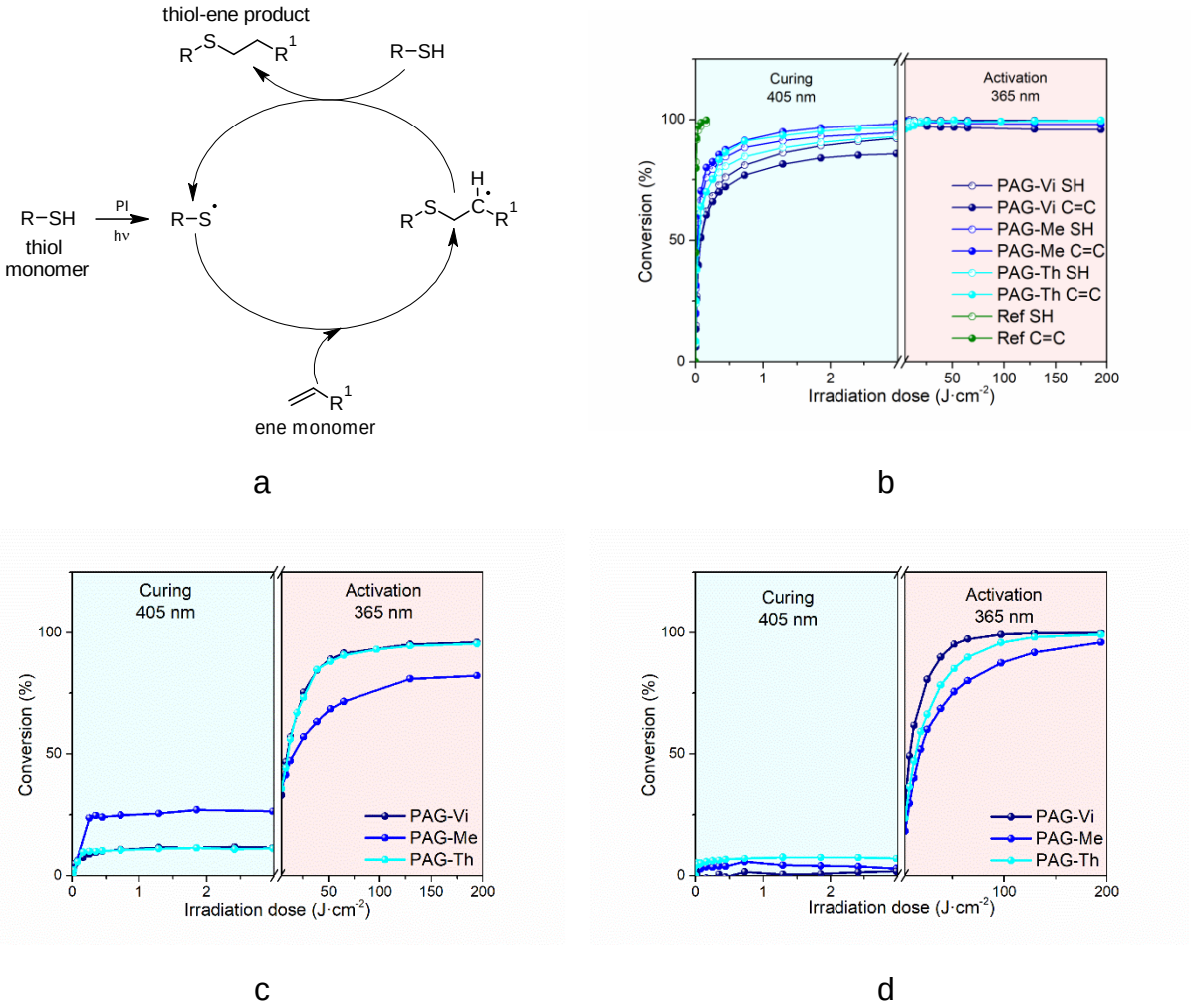
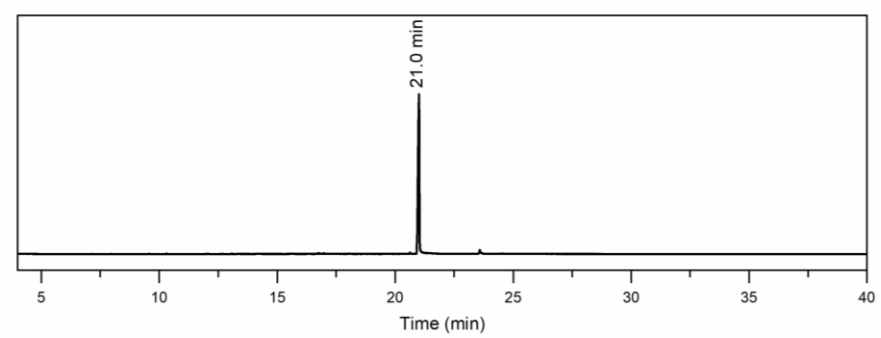


Figure S8. (a) Reaction scheme of the radical-mediated thiol-ene polymerization; (b) Monitoring the conversion of thiol and C=C groups in formulations upon light irradiation as obtained from FTIR measurements; Following the conversion of the synthetized PAGs to acid in fully cured thiol-ene photopolymers upon irradiation (405 and 365 nm) by (c) FTIR and (d) UV-vis spectroscopy.

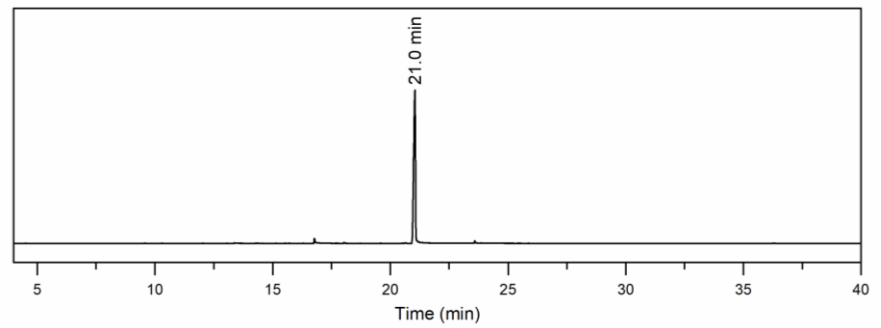
Table S2. Glass transition temperatures of the cured formulations with PAGs prior to and after activation with UV light (365 nm).

Concentration of PAG, mol%	PAG-**Vi**		PAG-**Me**	
	Non-activated, °C	Activated, °C	Non-activated, °C	Activated, °C
0 (reference)	-19.9			
5	-26.6	-21.8	-28.3	-19.6

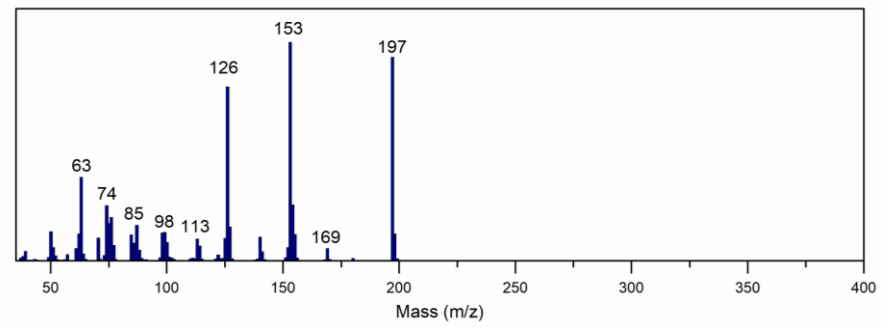
a


21.0 min
5
10
15
20
25
30
35
40
Time (min)

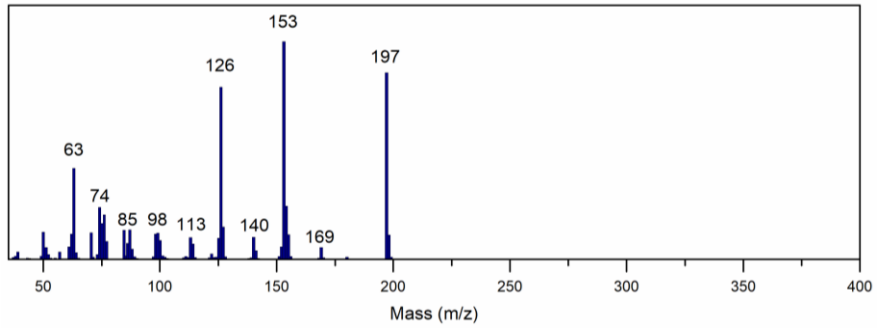
b


21.0 min
5
10
15
20
25
30
35
40
Time (min)

c


153
197
126
63
74
85
98
113
169
50
100
150
200
250
300
350
400
Mass (m/z)

d


153
126
197
63
74
85
98
113
140
169
50
100
150
200
250
300
350
400
Mass (m/z)

e

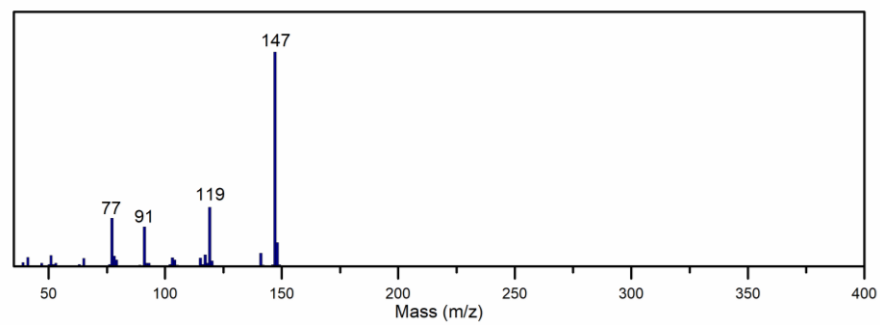


Figure S9. GC chromatograms of (a) PAG-**Vi** and (b) PAG-**Me**. MS plots of the GC peak at 21 min observed for (c) PAG-**Vi** and (d) PAG-**Me** and at 23 min for the extract of reference material (containing no PAG).

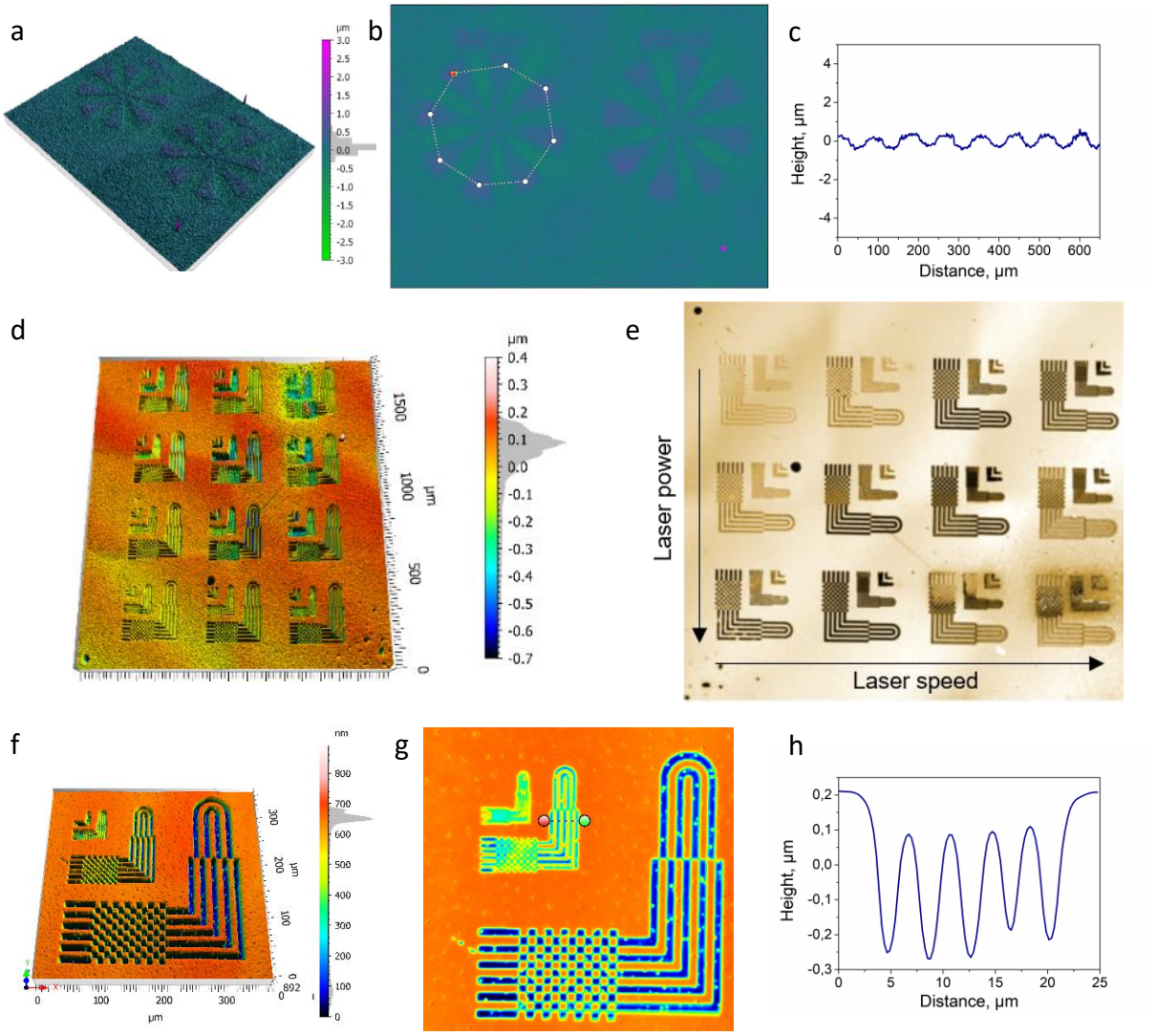


Figure S10. Analysis of a film with 5 mol% PAG-**Me** patterned via photomask (365 nm) and subsequent development in EG: (a) 3D reconstruction of surface topography scans, (b) surface topography scans with marked profile pathway, (c) related surface profile; (d,e) Optimization of laser parameters used in direct TPA laser writing by varying the laser power (20 – 40 Mw) and scanning speed (250 – 1500 µm min^{-1}); Analysis of a film with 5 mol% PAG-**Vi** patterned via direct TPA laser writing (intensity: 20 mW, scanning speed: 500 µm s^{-1}) and subsequent development in EG: (f) 3D reconstruction of surface topography scans; (g) surface topography scans with marked profile pathway; (h) related surface profile.

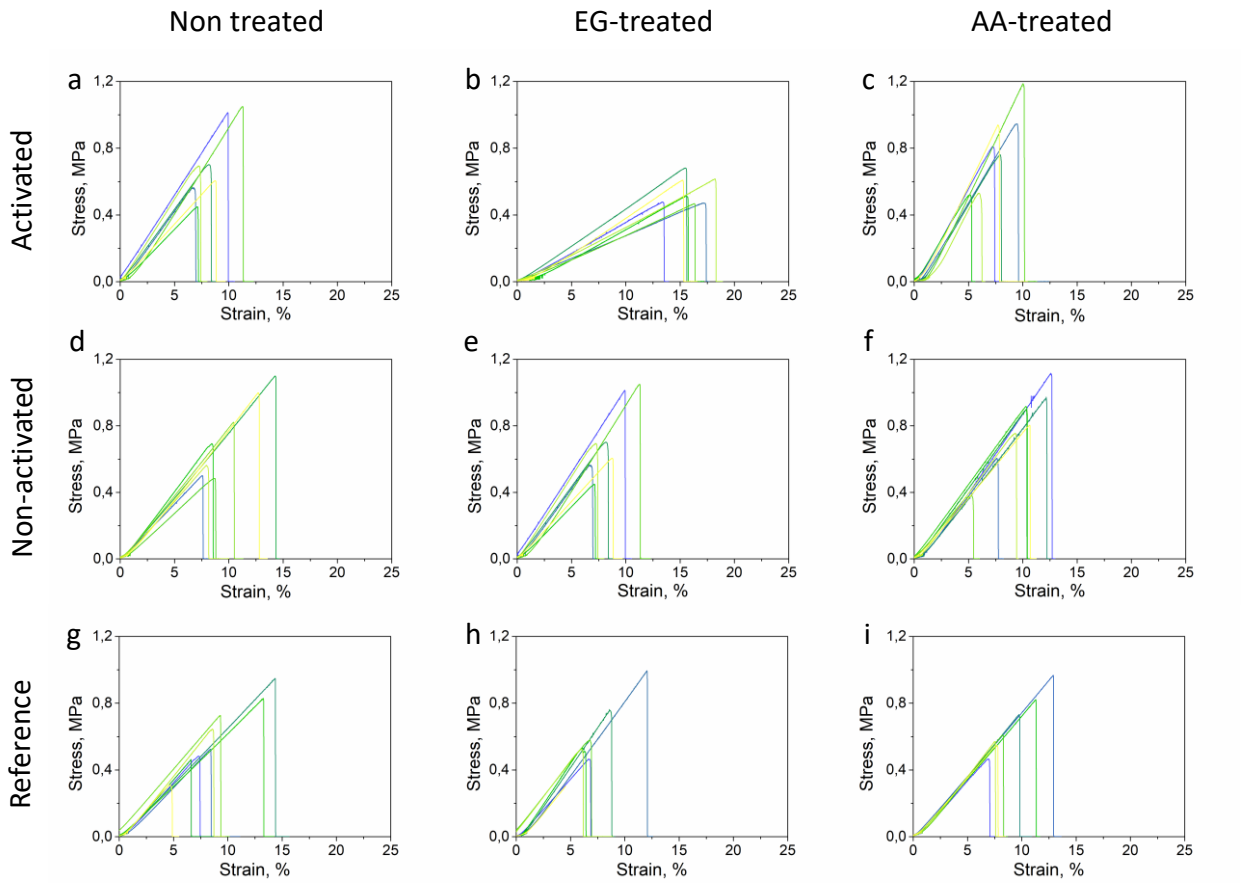


Figure S11. Stress-strain curves of tested samples: (a) post-cured activated samples containing 5 mol% PAG-**Vi** without treatment; (b) post-cured activated samples containing 5 mol% PAG-**Vi** after treatment in ethylene glycol and subsequent washing in water and drying in vacuum; (c) post-cured activated samples containing 5 mol% PAG-**Vi** after treatment in adipic acid saturated solution with subsequent drying in vacuum; (d) post-cured non-activated samples containing 5 mol% PAG-**Vi** without further treatment; (e) post-cured non-activated samples containing 5 mol% PAG-**Vi** after treatment in ethylene glycol with subsequent washing in water and drying in vacuum; (f) post-cured non-activated samples containing 5 mol% PAG-**Vi** after treatment in adipic acid saturated solution with subsequent drying in vacuum; (g) post-cured reference samples without further treatment; (h) post-cured reference samples after treatment in ethylene glycol and subsequent washing in water and drying in vacuum; (i) post-cured reference samples after treatment in adipic acid saturated solution and subsequent drying in vacuum.