ADMET and TAD Chemistry: A Sustainable Alliance

Supporting Information

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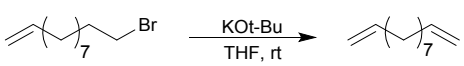
Experimental procedures

Used Products

Ethyl carbazate (4114-31-2, 98%), oxalylchloride (79-37-8, 98%) and triethylamine (121-44-8, 99%) were purchased from Acros. Butyl isocyanate (111-36-4, 98%), bromine (7726-95-6, reagent grade), chloroform (67-66-3, >99.8%), dibutyltin dilaurate (77-58-7, >95.0%), dichloromethane (DCM, 75-09-2, <99.8%), diethyl ether (60-29-7, >99.8%), dimethyl sulfoxide (DMSO, 67-68-5, >99.9%), ethyl acetate (EtOAc, 141-78-6, 99.7%), ethyl 4-aminobenzoate (94-09-7, 98%), hexane (110-54-3, >97.0%), HCl in dioxane (7647-01-0, 4M), methanol (67-56-1, >99.9%), 4,4'-methylenebis(phenyl isocyanate) (101-68-8, 98%), methyl 10-undecenoate (111-81-9, 96%), phenyl isocyanate (103-71-9, >98%), potassium hydroxide (1310-58-3, 90%), potassium tert-butoxide (865-47-4, >98.0%), silica gel (112926-00-8), sodium hydride (7646-69-7, 95%), tetrahydrofuran (THF, 109-99-9, >99.9%), toluene (108-88-3, 99.9%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (5807-14-7, 98%) and Zhan 1-C catalyst (918871-44-0, 95%) were purchased from Sigma-Aldrich. 1,4-diazabicyclo[2.2.2]octane (280-57-9, >98%), diphenylphosporyl azide (26386-88-9, >96%), ethyl vinyl ether (109-92-2, >98.0%) and 10-undecen-1-ol (112-43-6, >98.0%) were purchased from TCI Chemicals. Sodium sulfate anhydrous (7757-82-6, >99%) was purchased from Roth. Hydrochloric acid (7647-01-0, 36% p) was purchased from Chem Lab. 11-Bromo-undecene (7766-50-9, >95.0%) and 4-nitrophenyl isocyanate (100-28-7) were purchased from Fluorochem. $CDCl_3$ (865-49-6, 99.80%D), DMSO-d_6 (2206-27-1, 99.80%D) and THF-d_8 (1693-74-9, 99.50%D) were purchased from Eurisotop. O-Xylene (1330-20-7, >99.9%) was purchased from Fisher. Chemicals and reagent-grade solvents were used as received unless otherwise stated. Gaseous NO_2 was generated by thermal decomposition of $Pb(NO_3)_2$ (VWR, 10099-74-8, 99.0%) in a closed setup.[41]

Synthesis of monomers

Undeca-1,10-diene (M1).[8]

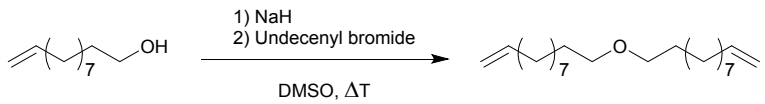


In a 500mL flask, potassium tert-butoxide (46 g, 410 mmol, 1.5 eq.) was added in portions to a solution of 11-bromo-1-undecene (63.988 g, 274 mmol, 1 eq.) in 190 mL THF. The reaction mixture was stirred for 2h under inert atmosphere at room temperature. The reaction was terminated with 1M HCl solution (136 mL) and the organic layer was concentrated in vacuo.

The product was distilled under reduced pressure at 70 °C to obtain pure undeca-1,10-diene (65%).

^{1}H NMR (300 MHz, CDCl3): δ (ppm) = 5.92 – 5.73 (m, 2H, H_2C=C*H*-), 5.07 – 4.87 (m, 4H, *H_2*C=CH-), 4.05 (q, 4H, =CH-C*H_2*-), 1.47 – 1.18 (m, 10H, aliphatic).

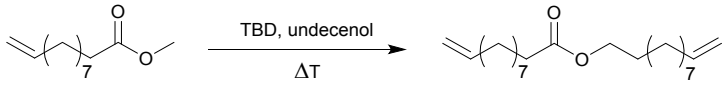
11-(undec-10-enoxy)undec-1-ene (M2). [8]



To a solution of 10-undecen-1-ol (36.5 g, 0.214 mol, 1 eq.) in 40 mL DMSO and 120 mL THF, NaH (7.3 g, 0.214 mol, 1 eq.) was added stepwise and let to stir at 70 °C for 1 h. After cooling down to room temperature, 11-bromo-1-undecene (50 g, 0.214 mol, 1 eq.) was added dropwise under inert atmosphere. Afterwards, the solution was refluxed overnight. The reaction mixture was taken into a separation funnel and the layers were separated. The water phase was extracted three times with diethyl ether, the collected organic layers were extracted once more with water and then concentrated in vacuo. The residue was filtered over silica with hexane, yielding a slightly yellow clear liquid. (58 %)

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 5.91-5.73 (m, 2H, H_2C=C*H*-), 5.06 – 4.87 (m, 4H, *H_2*C=CH-), 3.40 (t, 4H, -C*H_2*-O-C*H_2*-), 2.05 (q, 4H, =CH-C*H_2*-), 1.63 – 1.20 (m, 28H, aliphatic).

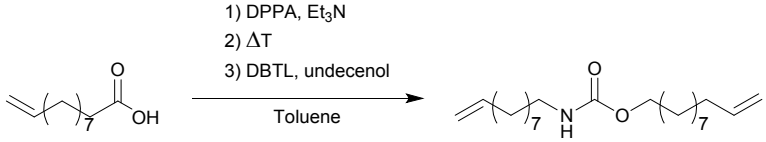
Undec-10-en-1-yl undec-10-enoate (M3). [7]



Methyl 10-undecenoate (45.89 g, 0.231 mol, 1 eq.), 10-undecenol (39.4 g, 0.277 mol, 1.2 eq.) and TBD (1.61 g, 0.012 mol, 0.05 eq.) were stirred under nitrogen flow at 80 °C for 5 h. After completion of the reaction, the solvent was removed in vacuo and the pure product (96%) was obtained via column chromatography (hexane:ethylacetate 9:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 5.90-5.72 (m, 2H, -C*H*=CH_2), 5.07-4.87 (m, 4H, C*H_2*=CH-), 4.06 (t, 2H, -C*H_2*-O-CO-), 2.30 (t, 2H, -C*H_2*-CO-O-), 2.05 (q, 4H, -C*H_2*-CH=CH_2), 1.62 (m, 2H, -C*H_2*-CH_2-O-CO-), 1.45-1.17 (m, 24H, aliphatic).

Undec-10-en-1-yl dec-9-en-1-ylcarbamate (M4).



15.9 g 10-undecenoic acid (0.087 mol, 1 eq.) was solubilized in 250 mL toluene and mixed with triethylamine (24.1 mL, 0.173 mol, 2 eq.) in a 500 mL flask. Diphenylphosporyl azide (25

g, 0.091 mol, 1.05 eq.) was added and the reaction mixture was stirred for 2 h at room temperature under inert atmosphere and subsequently refluxed for 4 h. Undec-10-en-1-ol (22.1 g, 0.130 mol, 1.5 eq.) and a catalytic amount of DBTL (100µL) were added and the mixture was stirred overnight at room temperature. The mixture was concentrated in vacuo and purified via chromatography on silica (eluent: hexane:ethyl acetate 9:1) to obtain the pure product (92%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 5.91-5.73 (m, 2H, -C*H*=CH_2), 5.05-4.88 (m, 4H, C*H*$_2$=CH-), 4.66-4.55 (s, b, 1H, -CO-N*H*-), 4.05 (t, 2H, -C*H*$_2$-O-CO-), 3.17 (q, 2H, -CO-NH-C*H*$_2$), 2.04 (q, 4H, -C*H*$_2$-CH=CH_2), 1.69-1.17 (m, 26H, aliphatic).

Polymer synthesis

Monomer feed (100 eq.) and Zhan 1-C (1 eq.) were introduced in a dry flask and stirred magnetically (500 rpm) at 80 °C under continuous vacuum until increase in viscosity made stirring impossible (3h-8h). The reaction was quenched with ethyl vinyl ether (EVE, 50 eq.) in THF, precipitated into a 1M HCl in methanol solution and dried overnight at 40°C under vacuum. All polymerisations had yields between 50 and 75%.

P1. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 5.49 – 5.29 (m, 2H, -*H*C=C*H*-), 2.09 - 1.85 (m, 4H, =CH-C*H*$_2$-), 1.42 – 1.12 (m, 10H).

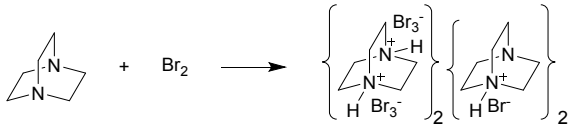
P2. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 5.43 – 5.30 (m, 2H, -*H*C=C*H*-), 3.39 (t, 4H, -C*H*$_2$-O-C*H*$_2$-), 2.09 - 1.90 (m, 4H, =CH-C*H*$_2$-), 1.64 – 1.18 (m, 28H).

P3. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 5.45-5.30 (m, 2H, -C*H*=C*H*-), 4.06 (t, 2H, -C*H*$_2$-O-CO-), 2.29 (t, 2H, -C*H*$_2$-CO-O-), 2.08-1.88 (m, 4H, =CH-C*H*$_2$-), 1.62 (m, 2H, -C*H*$_2$-CH_2-O-CO-), 1.44-1.14 (m, 24H).

P4. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 5.48-5.26 (m, 2H, -C*H*=C*H*-), 4.75-4.55 (s, b, 1H, -CO-N*H*-), 4.04 (t, 2H, -C*H*$_2$-O-CO-), 3.16 (q, 2H, -CO-NH-C*H*$_2$), 2.11-1.85 (m, 4H, =CH-C*H*$_2$-), 1.71-1.02 (m, 26H).

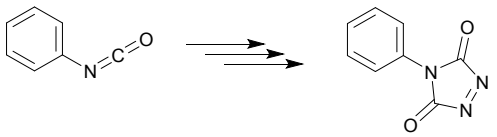
Synthesis of triazolinediones

DABCO-Br. [20]



In a 500 mL two-neck flask, 1,4-diazabicyclo[2.2.2]octane (6.73 g, 60.0 mmol, 1 eq.) was dissolved in chloroform (100 mL). In a next step, a solution of Br_2 (20.0 g, 0.125 mol, 2.1 eq.) in chloroform (100 mL) was added dropwise using an addition funnel. The resulting mixture was stirred under inert atmosphere for 1 hour. The yellow precipitate was filtered off, washed with chloroform (50 mL) and dried overnight in a vacuum oven at 40 °C to obtain 23.3 g of yellow powder (14.8 mmol, 99%).

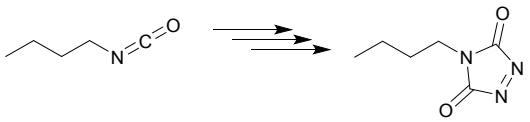
4-phenyl-1,2,4-triazoline-3,5-dione. [20]



A mixture of ethyl carbazate (10 g, 96.1 mmol, 1 eq.) and toluene (105 mL) was placed in a three neck flask (250 mL) and cooled in an ice bath. The flask was equipped with an addition funnel, containing 10.44 mL phenylisocyanate (96.1 mmol, 1 eq.), a mechanical stirrer and a bulb condenser. The mixture was put under inert atmosphere and the isocyanate was added slowly under vigorous stirring. After addition the mixture was stirred at room temperature for two hours, followed by 2 hours at 90°C. After cooling the reaction to room temperature, 4-phenyl-1-(ethoxycarbonyl) semicarbazide was filtered off and washed with toluene (96 %). Subsequently, the obtained 4-phenyl-1-(ethoxycarbonyl) semicarbazide (12.2 g, 60.0 mmol) was dissolved in 30 mL of an aqueous potassium hydroxide solution (4M) in a 50 mL flask under inert atmosphere. This mixture was refluxed for 1.5 hour (100°C), warm filtered, cooled to room temperature and acidified to pH 1 by addition of HCl. This mixture was cooled to room temperature to yield a white powder that was filtered off (95%). In a last step, a mixture of the just obtained 4-phenyl-1,2,4-triazolidine-3,5-dione (1 g, 5.64 mmol, 1 eq.), DABCO-Br (2 g, 1.27 mmol, 0.2 eq.) and dichloromethane (30 mL) was put in a flask (100 mL) under inert atmosphere and stirred for 2 hours at room temperature. The reaction mixture was filtered off, the residue washed with dichloromethane (2 × 30 mL) and the filtrate was concentrated in vacuo to obtain 4-phenyl-1,2,4-triazoline-3,5-dione (phenyl-TAD) as dark red crystals (92%). The temperature of the cooling bath should not exceed 50°C due to the volatility of the obtained compound.

^{1}H-NMR (300 MHz, DMSO-d_6): δ (ppm) = 7.45 – 7.60 (m, 5H, Ar-H).

4-butyl-1,2,4-triazoline-3,5-dione. [20]

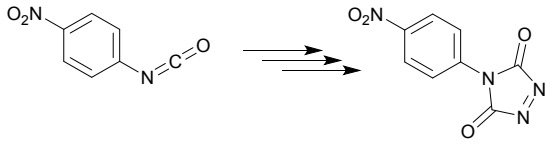


A mixture of ethyl carbazate (10 g, 96.1 mmol, 1 eq.) and toluene (105 mL) was placed in a three neck flask (250 mL) and cooled in an ice bath. The flask was equipped with an addition funnel, containing 10.8mL butylisocyanate (96.1 mmol, 1 eq.), a mechanical stirrer and a bulb condenser. The mixture was put under inert atmosphere and the isocyanate was added slowly under vigorous stirring. After addition, the mixture was stirred at room temperature for two hours, followed by 2 hours at 90°C. After cooling the reaction to room temperature, 4-butyl-1-(ethoxycarbonyl) semicarbazide (96%) was filtered off and washed with toluene. In a 50 mL flask, 4-butyl-1-(ethoxycarbonyl) semicarbazide (12.2 g, 60.0 mmol) was dissolved in 30 mL of an aqueous potassium hydroxide solution (4M) under inert atmosphere. This mixture was refluxed for 1.5 hour (100°C), warm filtered, cooled to room temperature and acidified until pH 1 by addition of hydrogen chloride. This mixture was cooled to room temperature to yield 4-butyl-1,2,4-triazolidine-3,5-dione (62%) as a solid white powder, that

was filtered off. A mixture of 4-butyl-1,2,4-triazolidine-3,5-dione (1 g, 6.36 mmol, 1 eq.), DABCO-Br (2 g, 1.27 mmol, 0.2 eq.) and dichloromethane (30 mL) was put in a flask (100 mL) under inert atmosphere and stirred for 2 hours at room temperature. The reaction mixture was filtered off, the residue washed with dichloromethane (2 × 30 mL) and the filtrate was concentrated in vacuo to obtain 4-butyl-1,2,4-triazoline-3,5-dione (72%). The temperature of the heating bath cannot exceed 50°C due to the volatility of the obtained compound.

^{1}H-NMR (300 MHz, DMSO-d6): δ (ppm) = 3.47 (t, 2H, N-CH2), 1.56 (m, 2H, N-CH2-CH2), 1.30 (m, 2H, CH3-CH2-CH2), 0.88 (t, 3H, CH3-(CH2)3).

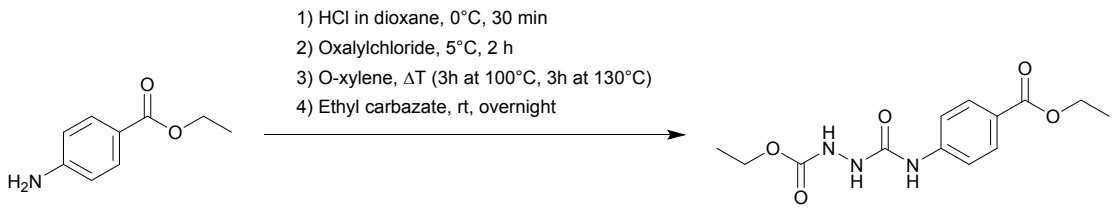
4-nitrophenyl-1,2,4-triazoline-3,5-dione. [20]



In a 50 mL two-neck flask, 4-nitrophenyl isocyanate (1 g, 6.1 mmol, 1 eq.) was dissolved in dry toluene (15 mL) and cooled in an ice bath for 30 min. Ethyl carbazate (0.634 g, 6.1 mmol, 1 eq.) in dry toluene (15 mL) was added dropwise over 10 minutes. The reaction mixture was brought to room temperature and allowed to stir for 8 hours, after which it was cooled in an ice bath. 4-nitrophenyl 1-(ethoxycarbonyl) semicarbazide (95%) was filtered off and used without any further purification in the next step. In a 5 mL flask, 4-nitrophenyl 1-(ethoxycarbonyl) semicarbazide (1 g, 3.7 mmol) was dissolved in 2.5 mL of an aqueous potassium hydroxide solution (4M) under inert atmosphere. This mixture was refluxed for 4 hours (100°C), warm filtered, cooled to room temperature and acidified to pH 1 by addition of HCl. This mixture was cooled to room temperature to yield a solid white powder (95%) that was filtered off.
^{1}H-NMR (300 MHz, DMSO-d_6): δ (ppm) = 10.17 (s, 2H, NH), 6.98 (d, 2H, Ar-H), 6.59 (d, 2H, Ar-H), 5.29 (s, 2H, NH_2).

In a last step, a mixture of the just obtained 4-nitrophenyl-1,2,4-triazolidine-3,5-dione (1 g, 4.5 mmol, 1 eq.), DABCO-Br (1.41 g, 0.9 mmol, 0.2 eq.) and dichloromethane (30 mL) was put in a flask (100 mL) under inert atmosphere, and stirred for 2 hours at room temperature. The reaction mixture was filtered off, the residue washed with dichloromethane (2 × 30 mL) and the filtrate, containing 4-phenyl-1,2,4-triazoline-3,5-dione, was used as such in the next steps, as evaporation of the solvent is not possible due to the reactivity of the product.

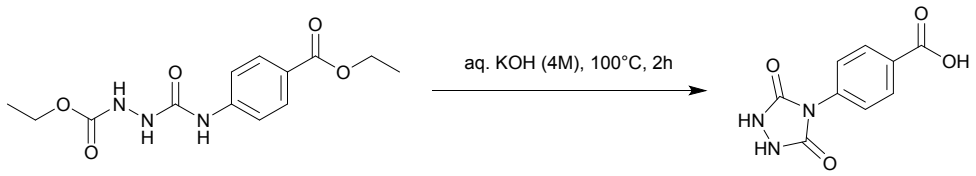
Ethyl 2-((4-(ethoxycarbonyl)phenyl)carbamoyl)hydrazine-1-carboxylate.[46]



In a two-neck 250 mL flask, (5.0 g, 30.3 mmol, 1 eq.) was solubilized in a mixture of HCl in dioxane (9.8 mL, 39.3 mmol, 1.3 eq.) and ethylacetate (120 mL) and stirred for 30 minutes at 0°C under inert atmosphere. Oxalylchloride (3.4 mL, 39.3 mmol, 1.3 eq.) was added and the mixture was stirred for 2 hours at 5 °C. Subsequently, o-xylene (100 mL) was added and the mixture was heated up to 100°C. After stirring for 3 hours, the reaction mixture was heated further and stirred for 3 hours at 130°C. Ethylcarbazate (3.15 g, 30.3 mmol, 1 eq.) in ethylacetate (60 mL) was added and the reaction mixture was stirred at room temperature overnight. The precipitate was filtered off and washed with o-xylene (2 x 50 mL). The resulting ethyl 2-((4-(ethoxycarbonyl)phenyl)carbamoyl)hydrazine-1-carboxylate was dried overnight under vacuum (4.8 g, 16.3 mmol, 57%)

^{1}H-NMR (300 MHz, DMSO-d6): δ (ppm) = 9.19 (s, 1H, NH), 8.98 (s, 1H, NH), 8.20 (s, 1H, NH), 7.85 (m, 2H, Ar-H), 7.61 (m, 2H, Ar-H), 4.26 (q, 2H, Ar-CO-O-C*H*2-CH3), 4.06 (q, 2H, NH-CO-O-C*H*2-CH3), 1.31 (t, 3H, Ar-CO-O-CH2-C*H*3), 1.19 (t, 3H, NH-CO-O-CH2-C*H*3).

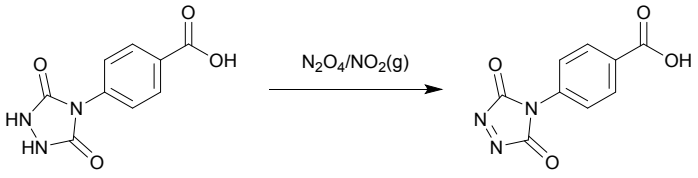
4-(3,5-dioxo-1,2,4-triazolidin-4-yl)benzoic acid. [46]



In a 25 mL flask, ethyl 2-((4-(ethoxycarbonyl)phenyl)carbamoyl)hydrazine-1-carboxylate (4.80 g, 16.3 mmol, 1 eq.) was dissolved in 15 mL of an aqueous potassium hydroxide solution (4M) under inert atmosphere. This mixture was refluxed for 2 hours (100°C), warm filtered, cooled to room temperature and acidified to pH 1 by addition of HCl. The obtained 4-(3,5-dioxo-1,2,4-triazolidin-4-yl)benzoic acid (3.58 g, 98%) was filtered off and dried under vacuum overnight.

^{1}H-NMR (300 MHz, DMSO-d6): δ (ppm) = 12.63 (broad, 1H, COOH), 10.68 (s, 2H, NH), 8.03 (d, 2H, Ar-H), 7.65 (d, 2H, Ar-H).

4-(3,5-dioxo-1,2,4-triazol-4-yl)benzoic acid**.** [46]

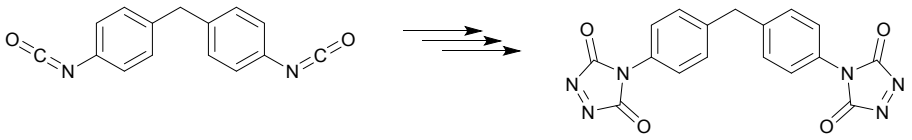


In a 250 mL flask, 4-(3,5-dioxo-1,2,4-triazolidin-4-yl)benzoic acid (0.7 g, 3.2 mmol, 1 eq.) was suspended in 100 mL of dried ethyl acetate. 5 g (excess) Na_2SO_4 was added, the mixture was cooled to 0°C and gaseous NO_2 was bubbled through the solution for 15 minutes, until no further change in colour was observed. Excess of NO_2 was removed by a stream of argon. The

red solution was filtered and the solvent was removed in vacuo to obtain pure 4-(3,5-dioxo-1,2,4-triazol-4-yl)benzoic acid (0.66 g, 3.0 mmol, 94%) as a red powder.

^{1}H-NMR (300 MHz, DMSO-d6): δ (ppm) = 10.06 (broad, 1H, COOH), 8.14 (d, 2H, Ar-H), 7.58 (d, 2H, Ar-H).

4,4'-(4,4'-diphenylmethylene)-bis-(1,2,4-triazoline-3,5-dione).[20]



A mixture of ethyl carbazate (40 g, 0.384 mol, 2 eq.) and toluene (300 mL) was placed in a three neck flask (1 L) and cooled in an ice bath. The flask was equipped with an addition funnel, containing 48.0 g of 4,4'-methylenebis(phenyl isocyanate) (0.192 mol, 1 eq.) dissolved in 200 mL of toluene, a mechanical stirrer and a bulb condenser. The mixture was put under inert atmosphere and the isocyanate was added slowly under vigorous stirring. After addition, the mixture was stirred at room temperature for two hours, followed by 2 hours at 90°C. After cooling the reaction to room temperature, 4,4'-(4,4'-diphenylmethylene)-bis-(carbethoxysemicarbazide) (98 %) was filtered off and washed with toluene. In a 1 L flask, the obtained 4,4'-(4,4'-diphenylmethylene)-bis-(carbethoxysemicarbazide) (86.2 g, 0.188 mol) was dissolved in 330 mL of an aqueous potassium hydroxide solution (4M) under inert atmosphere. This mixture was refluxed for 1.5 hour (100°C), warm filtered, cooled to room temperature and acidified to pH 1 by addition of HCl. This mixture was cooled to room temperature to yield a white powder that was filtered off (99%). In a last step, a mixture of the just obtained 4,4'-(4,4'-diphenylmethylene)-bis-(urazole) (2 g, 5.64 mmol, 1 eq.), DABCO-Br (5 g, 3.18 mmol, 0.58 eq.) and dichloromethane (30 mL) was put in a flask (100 mL) under inert atmosphere, and stirred for 2 hours at room temperature. The reaction mixture was filtered off, the residue washed with dichloromethane (2 × 30 mL) and the filtrate was concentrated in vacuo to obtain 4,4'-(4,4'-diphenylmethylene)-bisTAD as pink crystals (98%). The temperature of the cooling bath should not exceed 50°C due to the volatility of the obtained compound.

^{1}H-NMR (300 MHz, DMSO-d6): δ (ppm) = 7.48 (d, 4H, Ar-H), 7.38 (d, 4H, Ar-H), 4.11 (s, 2H, Ar-CH_2-Ar).

Polymer modification

200 mg of polymer was dissolved in 2 mL of THF and the appropriate amount of TAD component in a minimal amount of THF was added. Stirring was continued until the red colour disappeared. The obtained polymers were precipitated in methanol. The texture of the polymers ranged from powdery to slimy and fibrous, depending on the TAD compound and the degree of functionalisation.

Crosslinking

100 mg of polymer was dissolved in 0.3 mL of THF and the appropriate amount of bisTAD crosslinker in 0.2 mL THF was added and stirred until gelation occurred. The gel was left at

room temperature until the colour faded. The obtained networks were dried overnight under vacuum at 40°C prior to thermal analysis.

Materials & Methods

^{1}H-NMR spectra were recorded in $CDCl_3$, DMSO-d_6 or THF-d_8 on a Bruker Avance 300 (300 MHz). Chemical shifts are presented in parts per million (δ) relative to $CDCl_3$ (7.26 ppm), DMSO-d_6 (2.50 ppm) or THF-d_8 (3.58 and 1.73 ppm) as internal standard. The resonance multiplicities are described as s (singlet), d (doublet), t (triplet), q (quadruplet) or m (multiplet). *HR-MAS analyses* were recorded in THF-d_8 and were performed on a Bruker Avance II 700 spectrometer (700 MHz) using a HR-MAS probe equipped with a ^{1}H, ^{13}C, ^{119}Sn and gradient channel. Samples were spun at a rate of 6 kHz. All spectra were measured with an acquisition time of 1.136 s in which 32 768 fid points were obtained, leading to a spectral width of 20.6 ppm. *Thermogravimetric analysis (TGA)* was performed using a Mettler-Toledo TGA/SDTA851e equipment. Samples (5 to 10 mg) were heated in a nitrogen atmosphere with a heating rate of 10 K min^{-1} going from 25°C to 600°C. For the analysis of the thermograms, the STARe software of Mettler-Toledo was used. All curves are blank corrected. *Differential scanning calorimetry (DSC)* analyses were performed with a Mettler Toledo instrument 1/700 under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The glass transition temperatures were determined from midpoints in the second heating using the STARe software of Mettler-Toledo. *IR spectra* were collected using a Perkin–Elmer Spectrum1000 FTIR infrared spectrometer with a diamond ATR probe.

Supplementary Figures and Tables

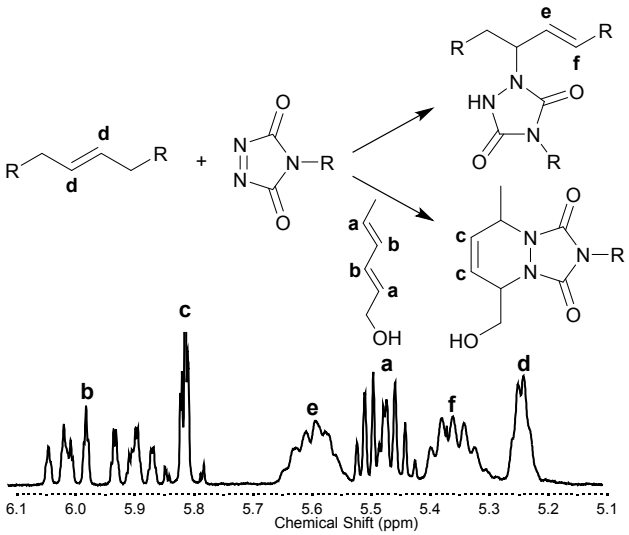


Figure S 1 – Modification kinetics: Quenching with HDEO makes analysis via ^{1}H-NMR possible; Conversions were obtained by comparison of the signals at 5.50 ppm (e, 1 olefinic proton after modification) and 5.25 ppm (d, 2 olefinic protons before modification) as these signals show no interference with the HDEO signals (a, b, c).

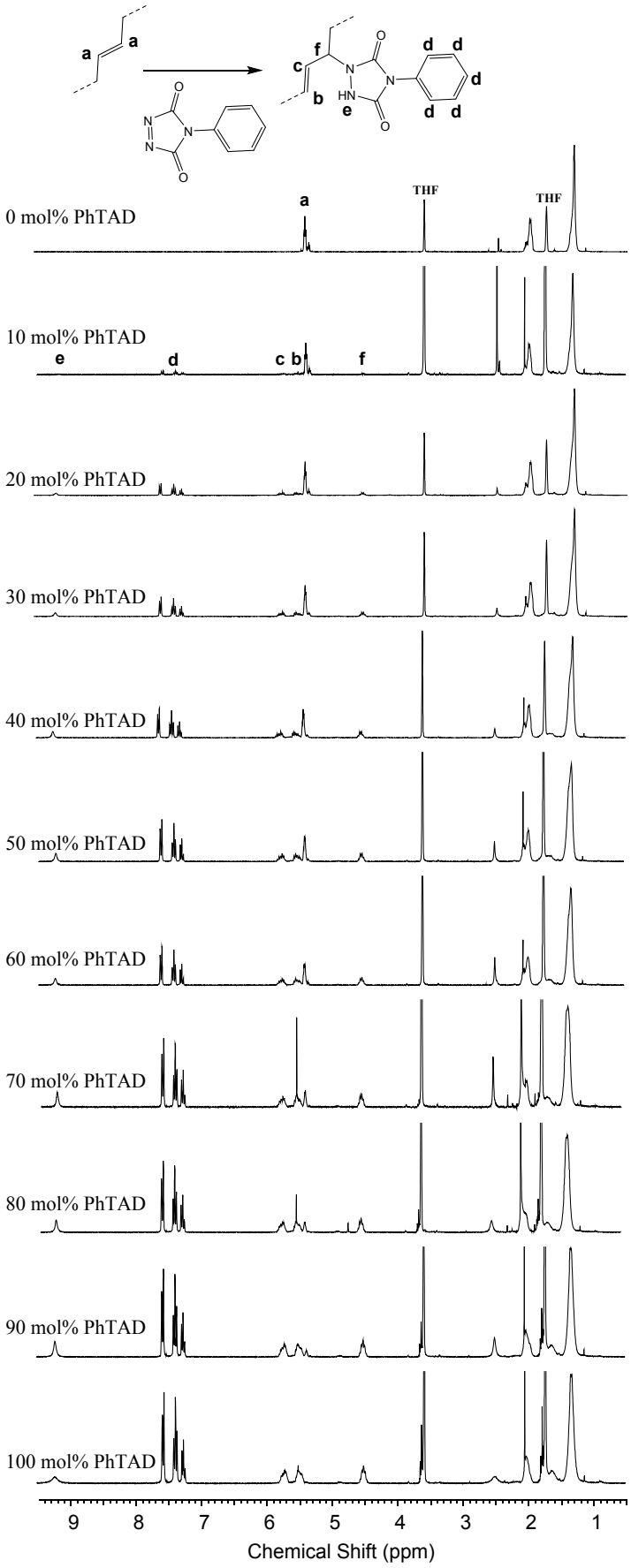


Figure S 2 - Full spectra of the systematic modification of P1 with PhTAD (THF-d_8).

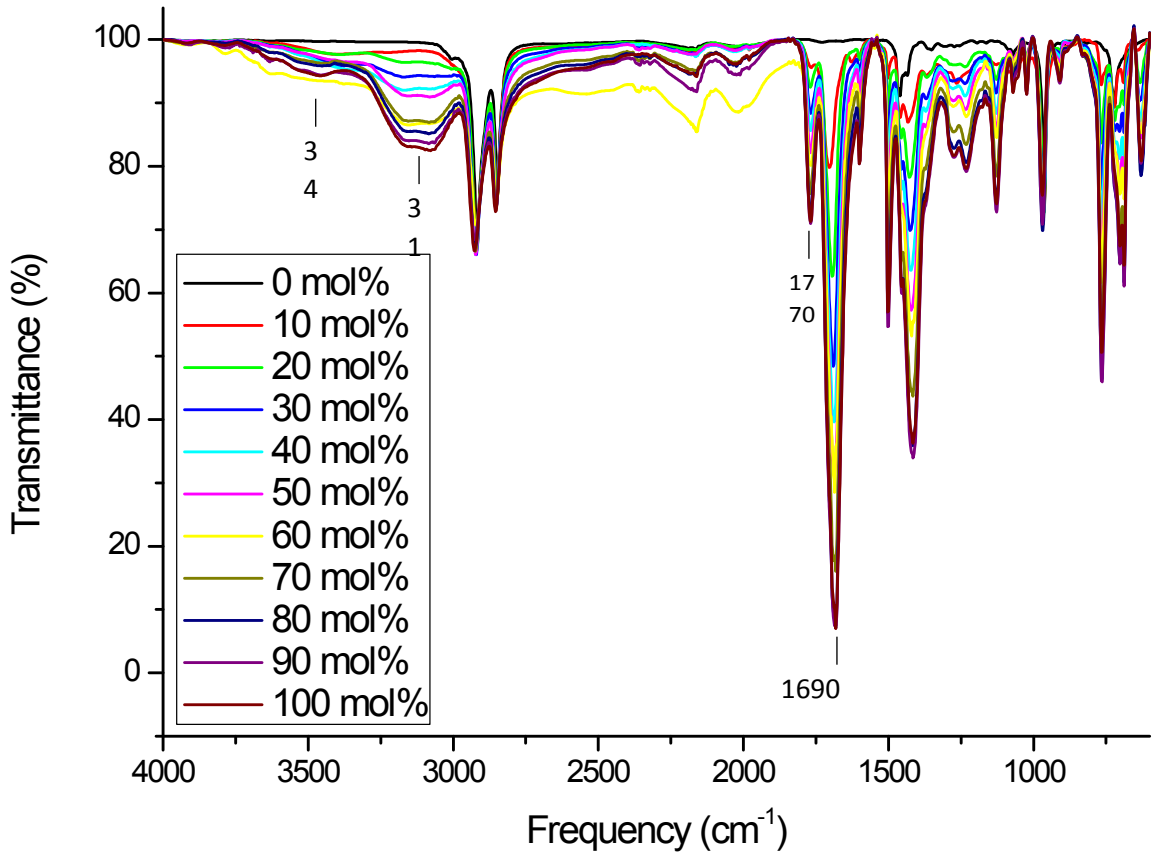


Figure S 3 - IR-spectra of the systematic modification of P1 with PhTAD with varying degrees of modification. Increasing modification leads to the increase of C=O stretches (1690 cm^{-1} and 1770 cm^{-1}) and N-H stretches (3400 cm^{-1} and 3140 cm^{-1}).

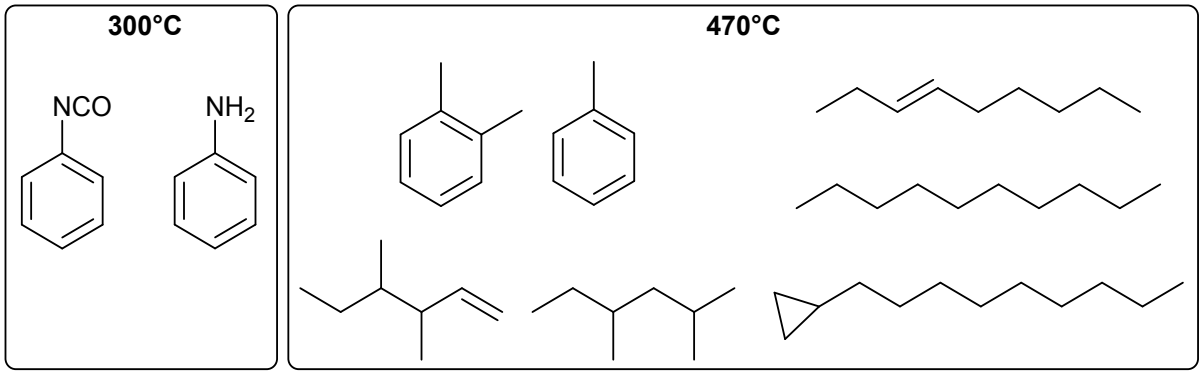


Figure S 4 - Overview of possible degradation products found in TGA-MS.

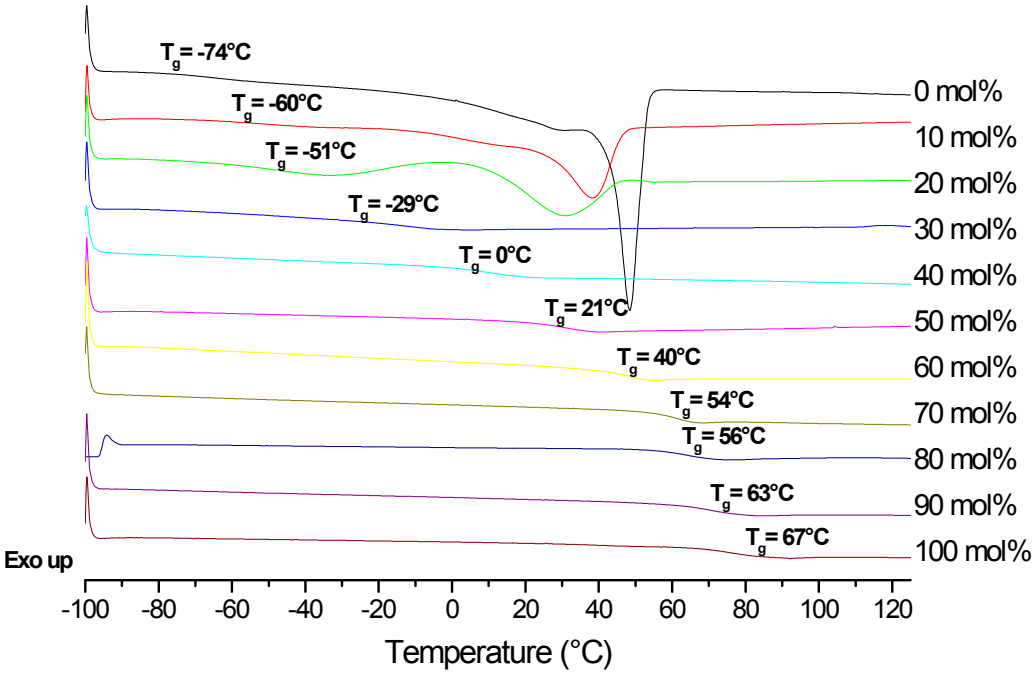


Figure S 5 - Raw DSC data of the systematically modified polymers with modification degrees ranging from 0 mol% PhTAD to 100 mol% PhTAD. An increasing T_g and decreasing crystallinity with increasing degree of modification are observed.

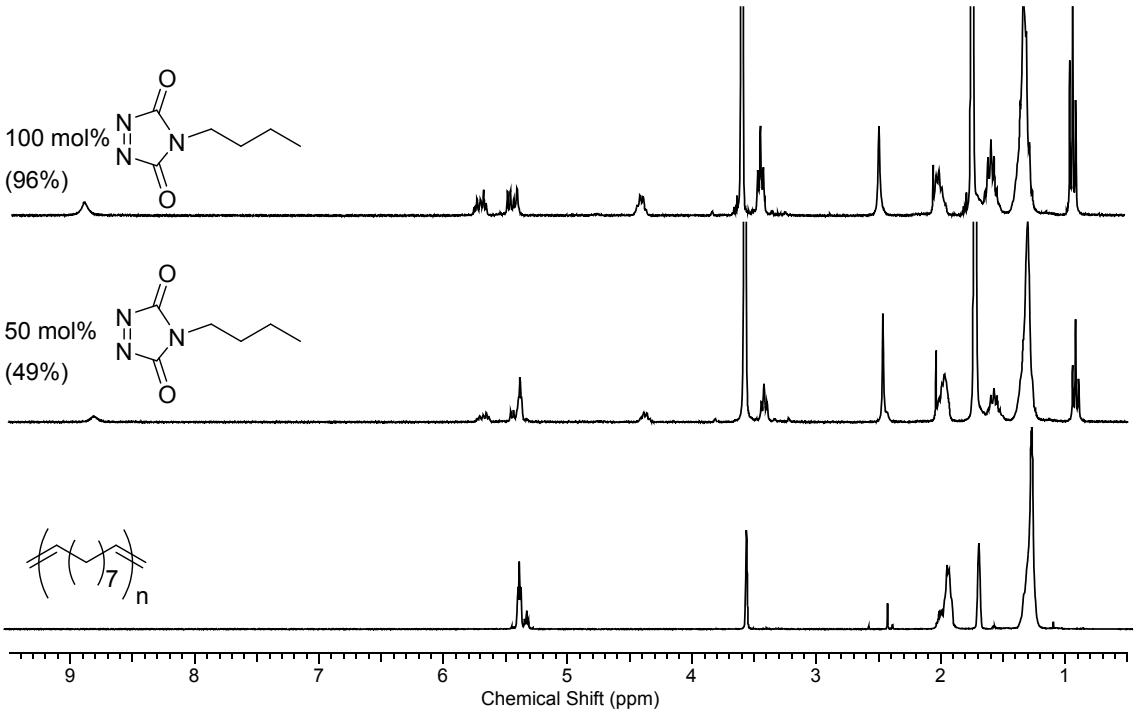


Figure S 6 - Modification of P1 with BuTAD - NMR spectra (THF-d_8).

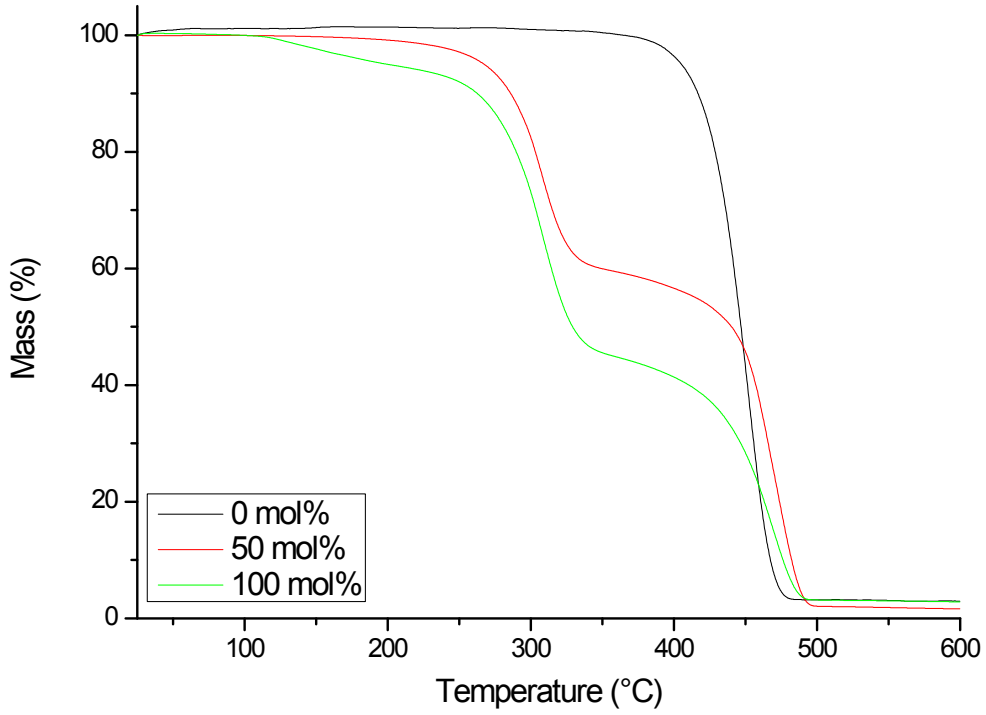


Figure S 7 - Modification of P1 with BuTAD - TGA thermograms.

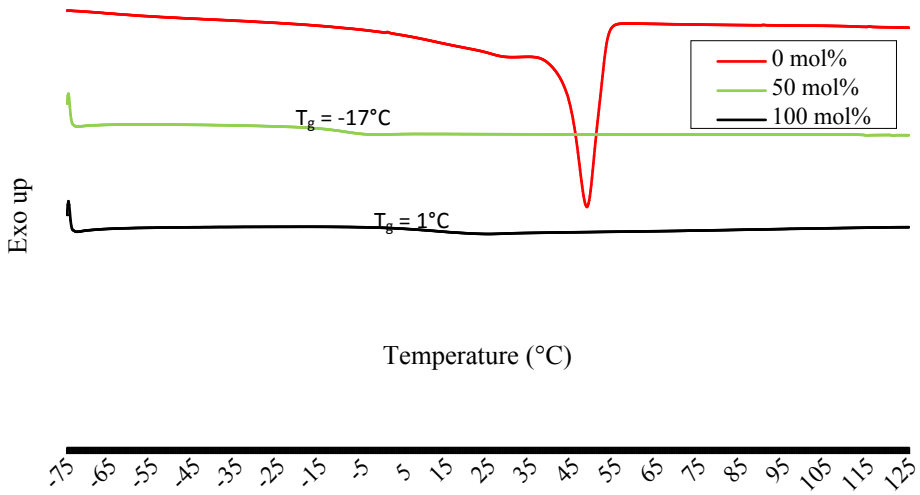


Figure S 8 - Modification of P1 with BuTAD – DSC data.

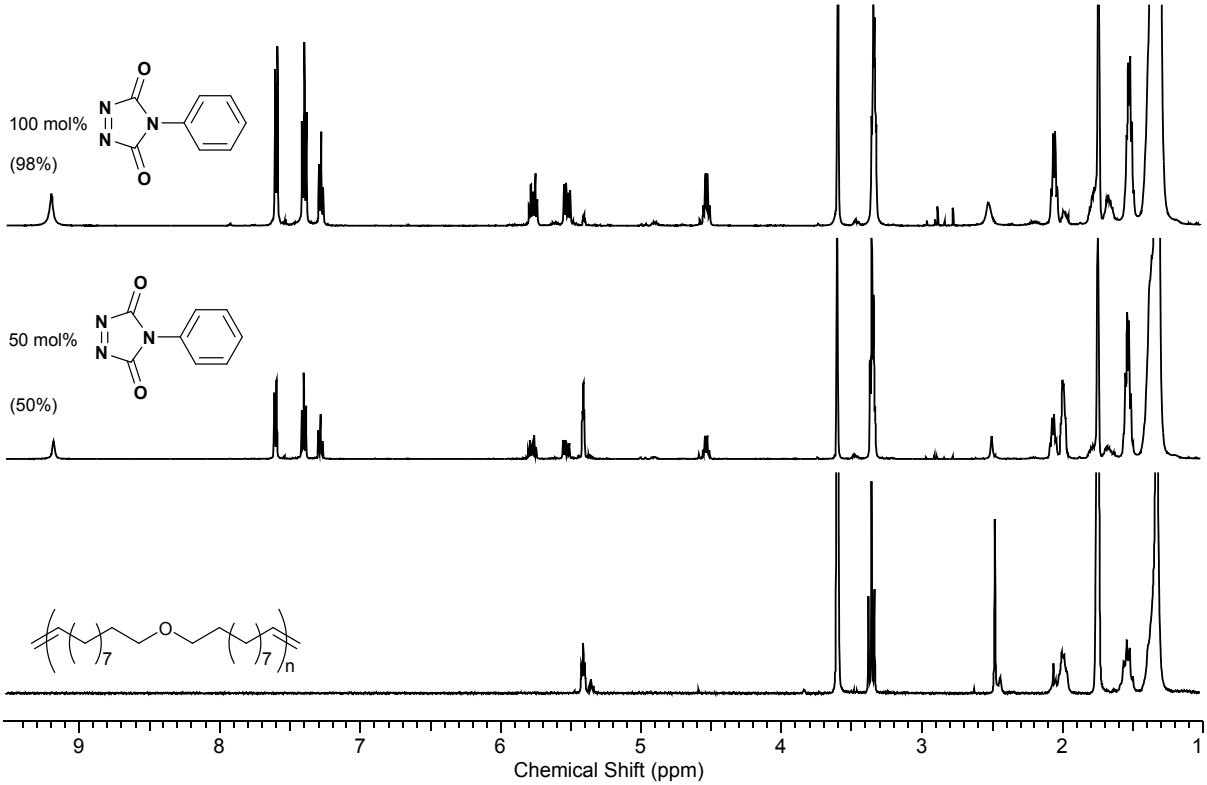


Figure S 9 - Modification of P2 with PhTAD – NMR spectra in THF-d_8 with targeted and experimentally observed (between brackets) functionalisation degree.

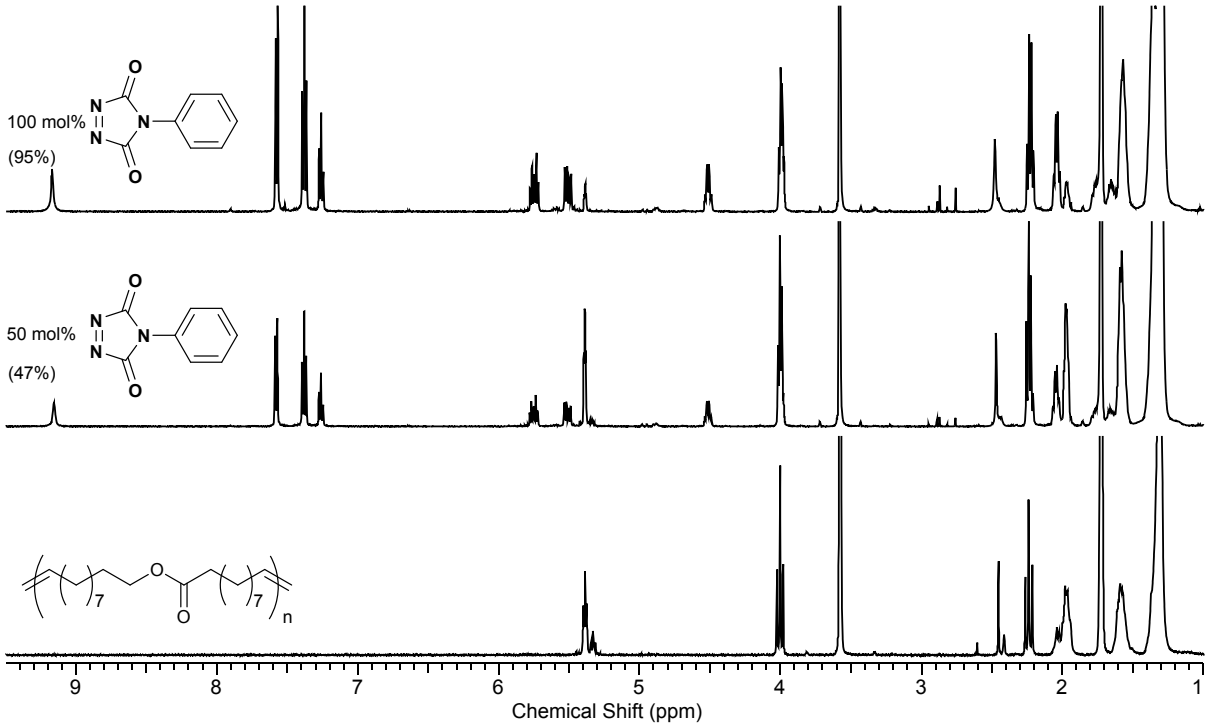


Figure S 10 - Modification of P3 with PhTAD – NMR spectra in THF-d_8 with targeted and experimentally observed (between brackets) functionalisation degree.

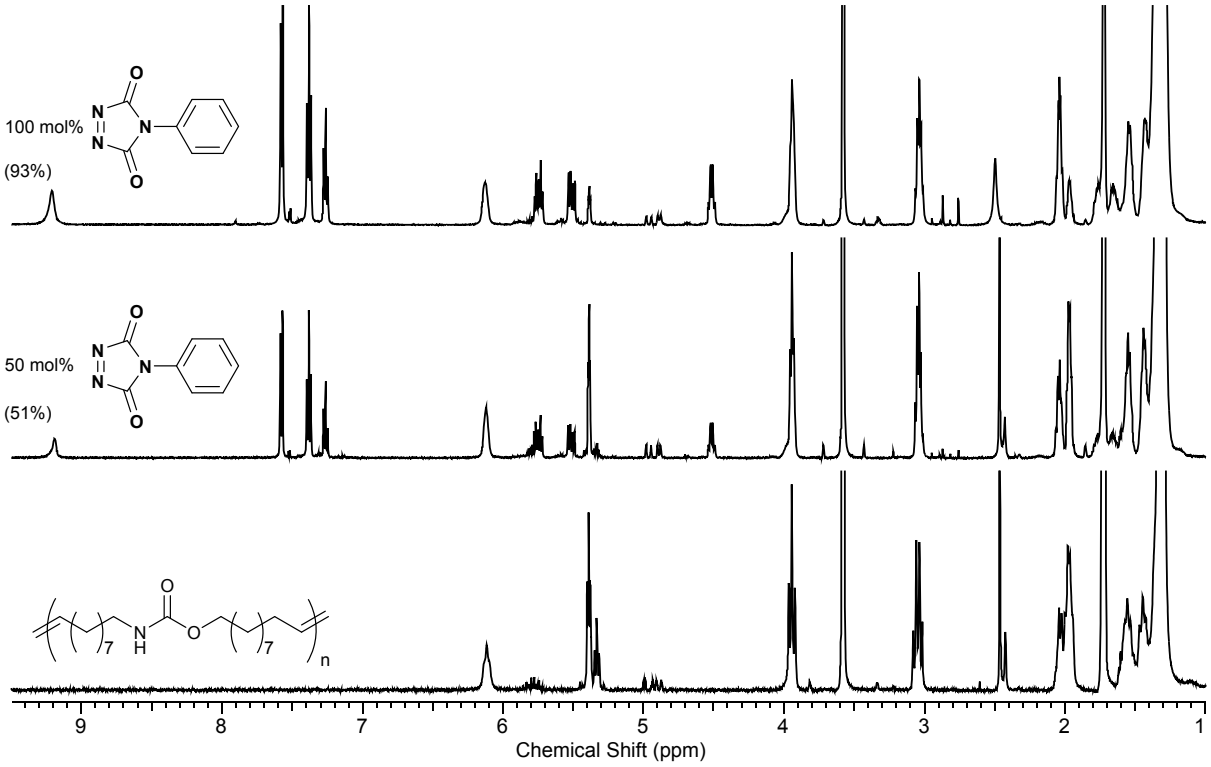


Figure S 11 - Modification of P4 with PhTAD – NMR spectra in THF-d_8 with targeted and experimentally observed (between brackets) functionalisation degree.

Table S 1 - SEC analysis of PhTAD functionalised P2-P4 polymers.

Polymer	PhTAD (mol%)	M_n (measured) (kDa)	M_n (expected) (kDa)	Đ
P2	0	20.0	/	3.5
	50	19.3	25.9	2.3
	100	22.9	31.9	2.8
P3	0	9.9	/	3.3
	50	22.6	12.7	2.1
	100	23.1	15.5	2.5
P4	0	4.9	/	1.3
	50	11.7	5.9	2.0
	100	14.5	7.1	2.1

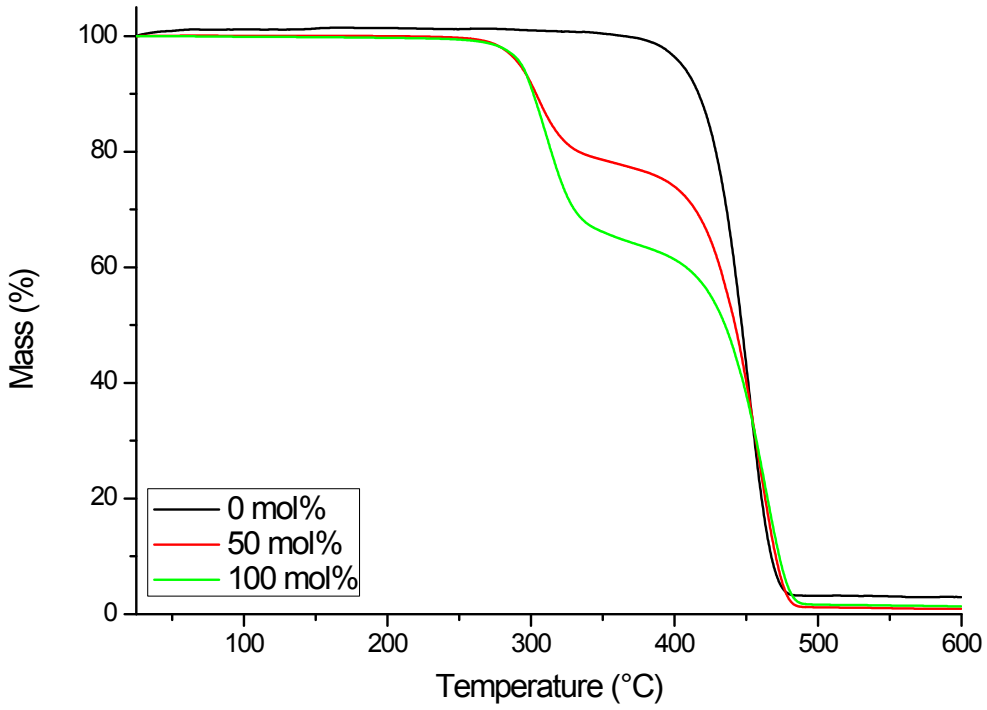


Figure S 12 - Modification of P2 with PhTAD – TGA thermograms.

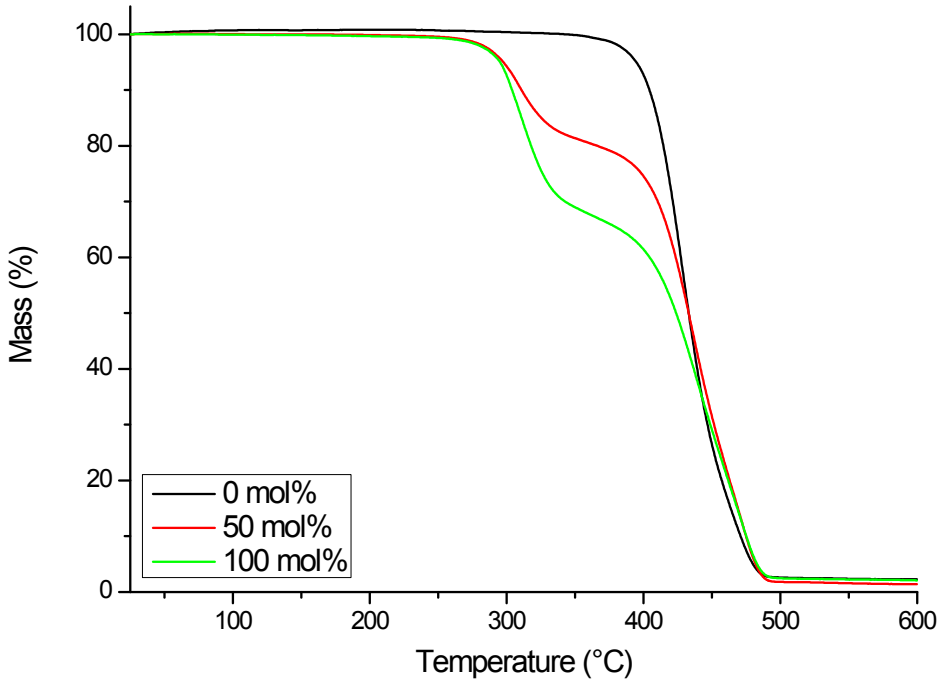


Figure S 13 - Modification of P3 with PhTAD – TGA thermograms.

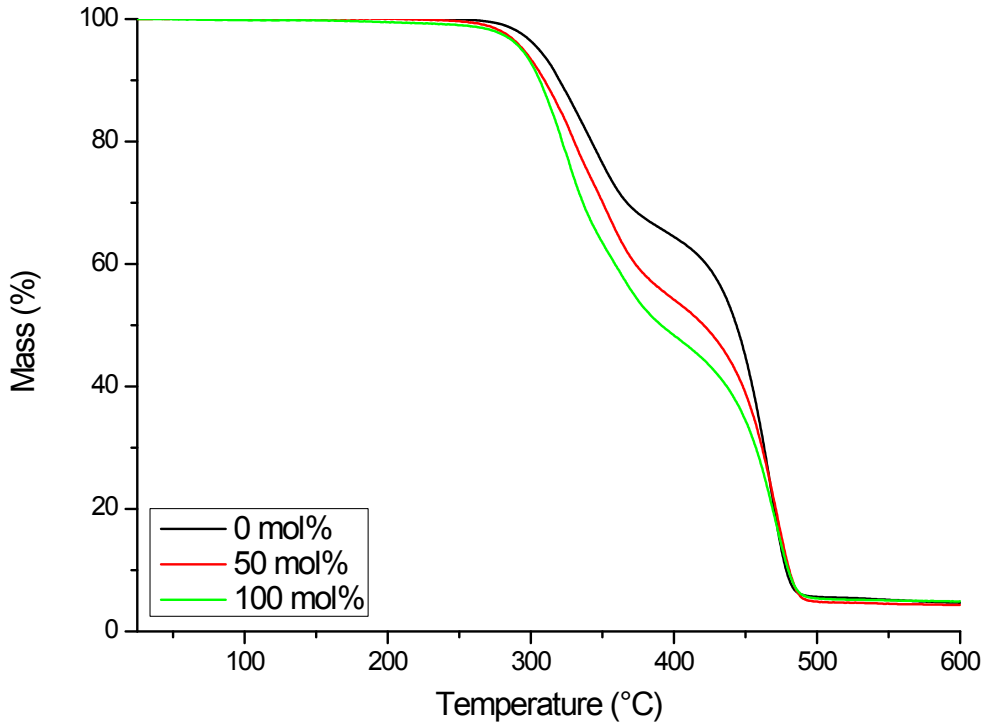


Figure S 14 - Modification of P4 with PhTAD – TGA thermograms.

Table S 2 - Calculated ($m_{PhTAD,calc}$) and experimentally observed ($m_{loss,300°C}$) mass loss for PhTAD modified P2 and P3 at 300°C.

Modification degree	**50 mol% PhTAD**		**100 mol% PhTAD**	
	$m_{PhTAD,calc}$ (%)	**$m_{loss,\ 300°C}$ (%)**	**$m_{PhTAD,calc}$ (%)**	**$m_{loss,\ 300°C}$ (%)**
P2	23.0	22	37.4	34
P3	22.2	19	36.3	32

Table S 3 - Calculated ($m_{x\text{-}TAD,calc}$) and experimentally observed ($m_{loss,300°C}$) mass loss for Bu-TAD and NO_2-PhTAD modified P1 at 300°C.

Modification degree	**50 mol%**		**100 mol%**	
	$m_{x\text{-}TAD,calc}$ (%)	**$m_{loss,\ 300°C}$ (%)**	**$m_{x\text{-}TAD,calc}$ (%)**	**$m_{loss,\ 300°C}$ (%)**
Bu-TAD	38.4	40	55.5	56
NO_2-PhTAD	47,0	42	63,9	58

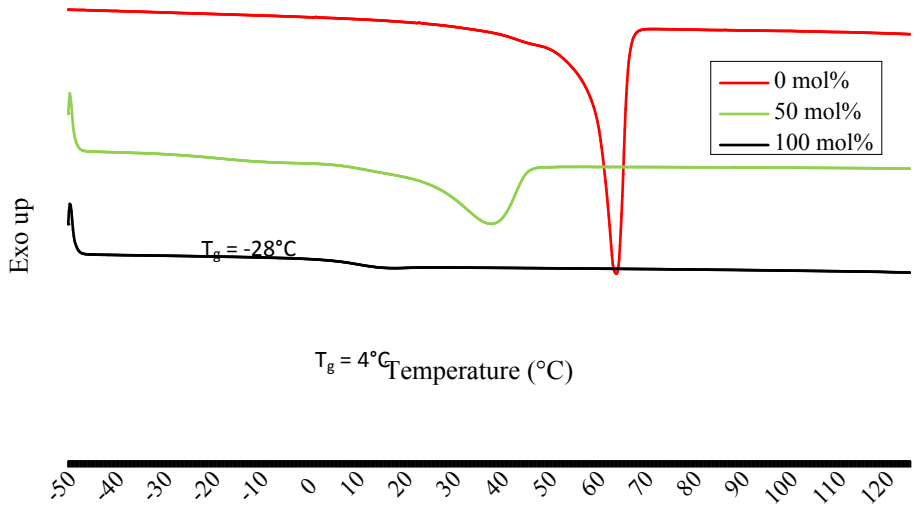


Figure S 15 - Modification of P2 with PhTAD – DSC data.

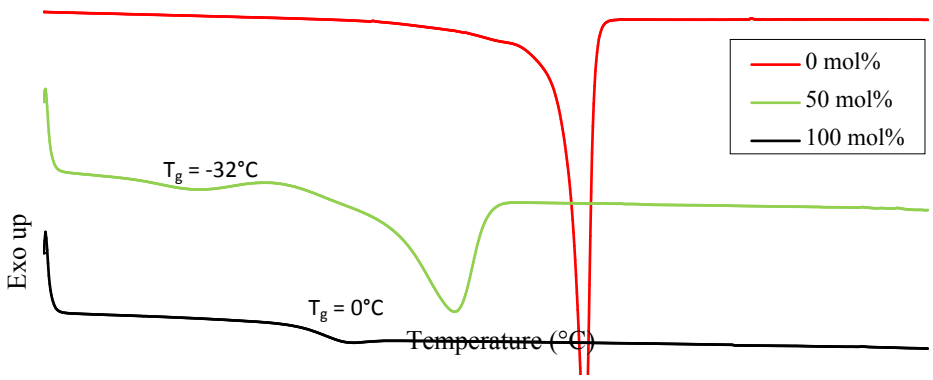


Figure S 16 - Modification of P3 with PhTAD – DSC data.

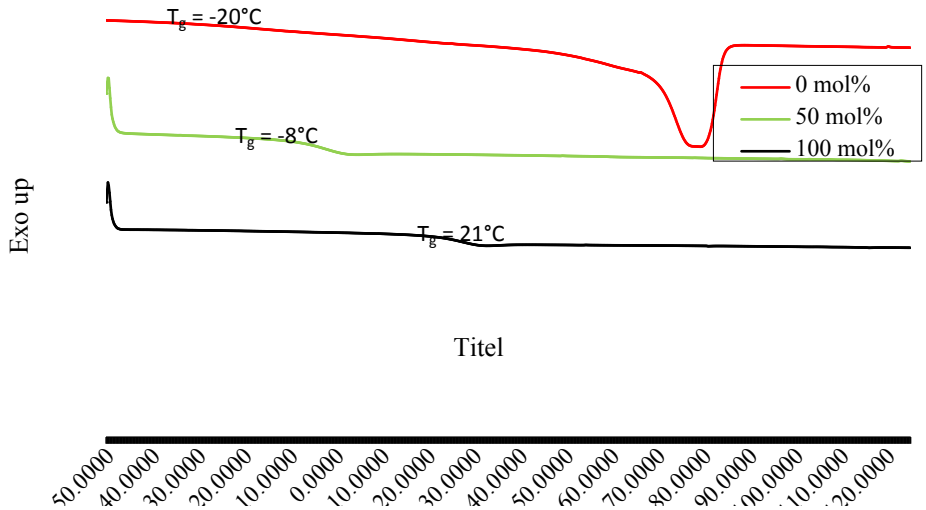


Figure S 17 - Modification of P4 with PhTAD – DSC data.

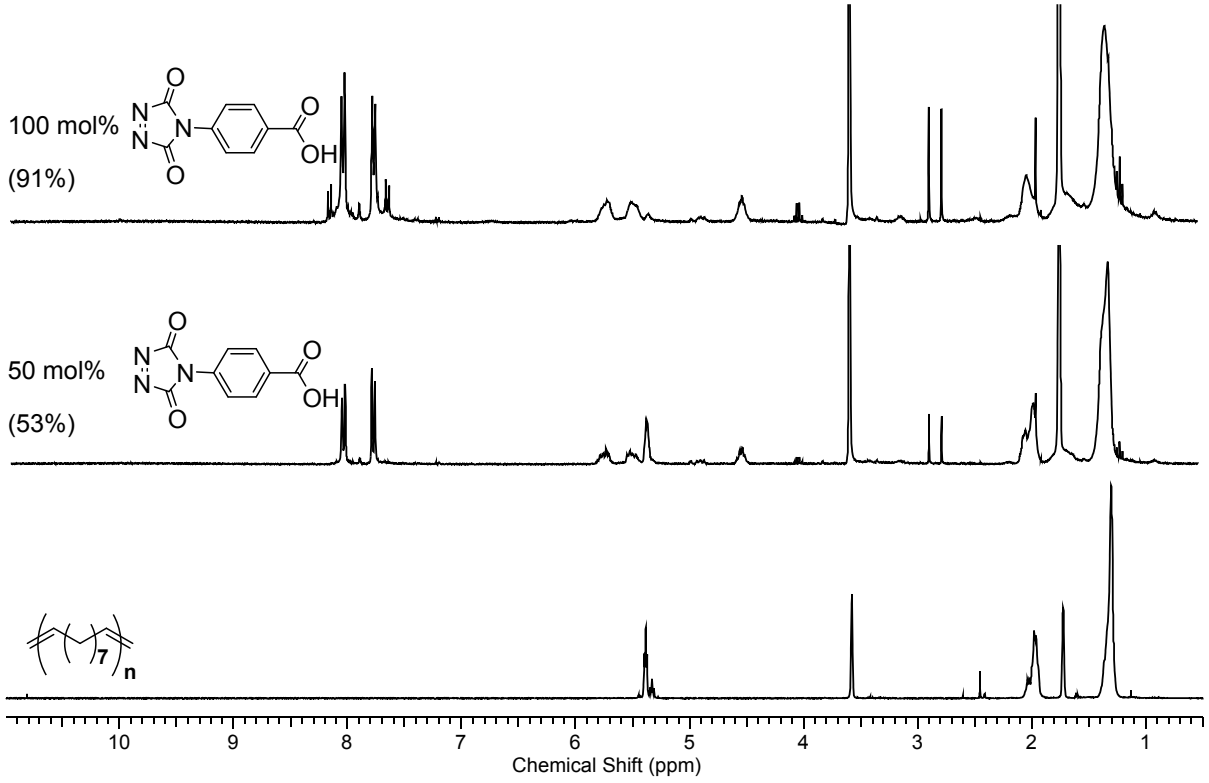


Figure S 18 - Functionalisation of P1 with COOH-PhTAD - NMR data (THF-d_8). The COOH and urazole protons can only be seen upon zooming.

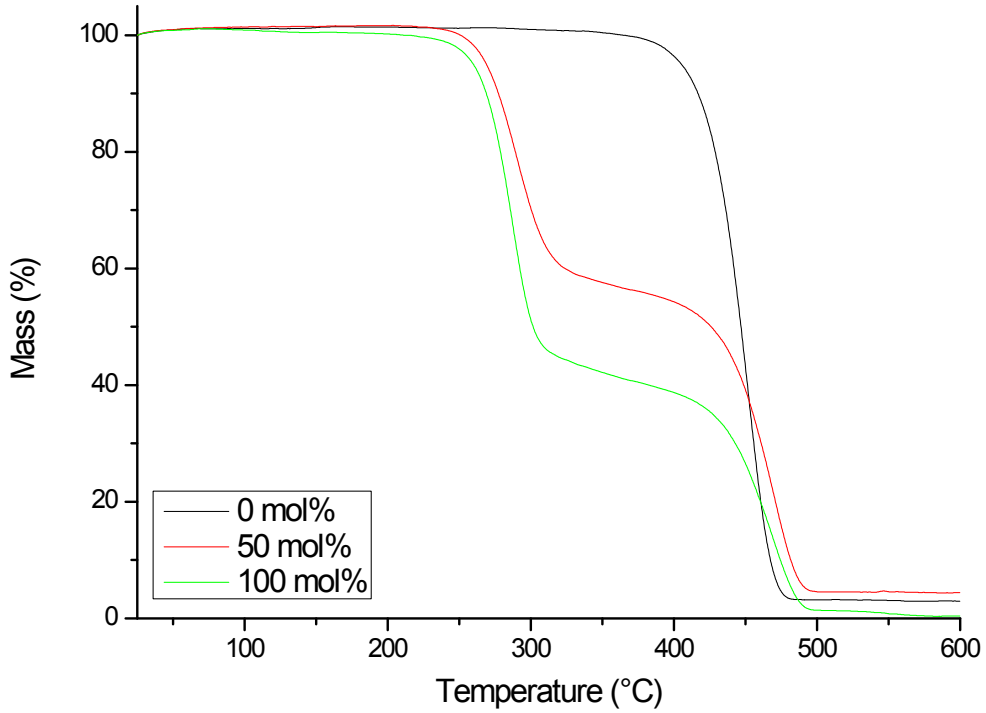


Figure S 19 - Functionalisation of P1 with NO_2-PhTAD - TGA thermograms.

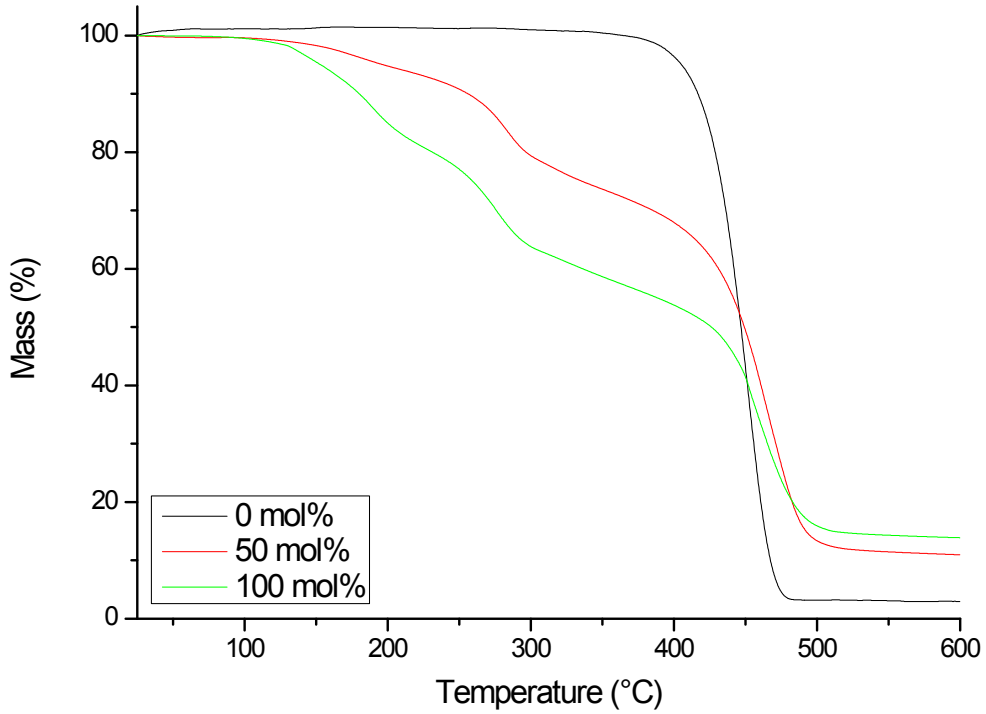


Figure S 20 - Functionalisation of P1 with COOH-PhTAD - TGA thermograms.

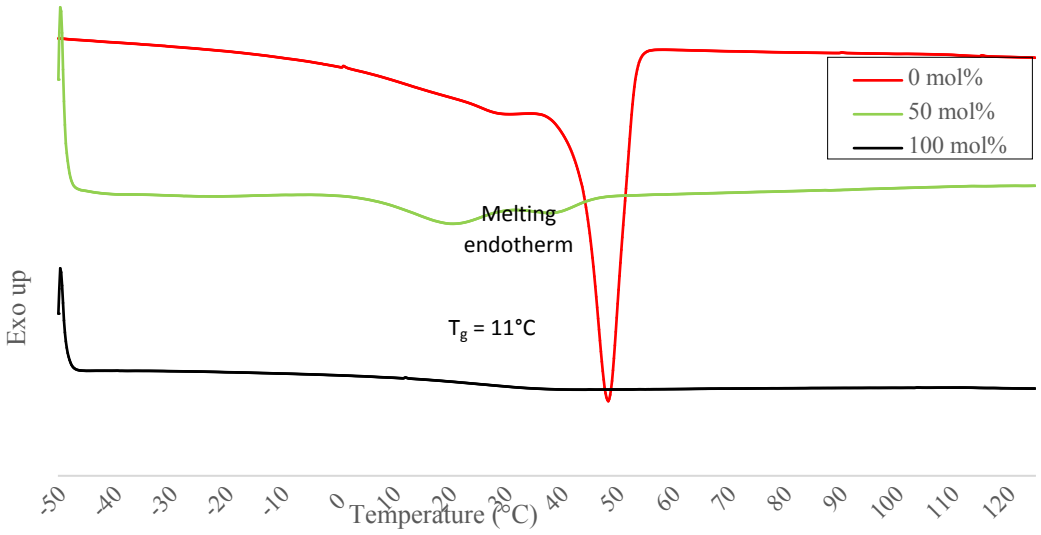


Figure S 21 - Functionalisation of P1 with NO_2-PhTAD – DSC data.

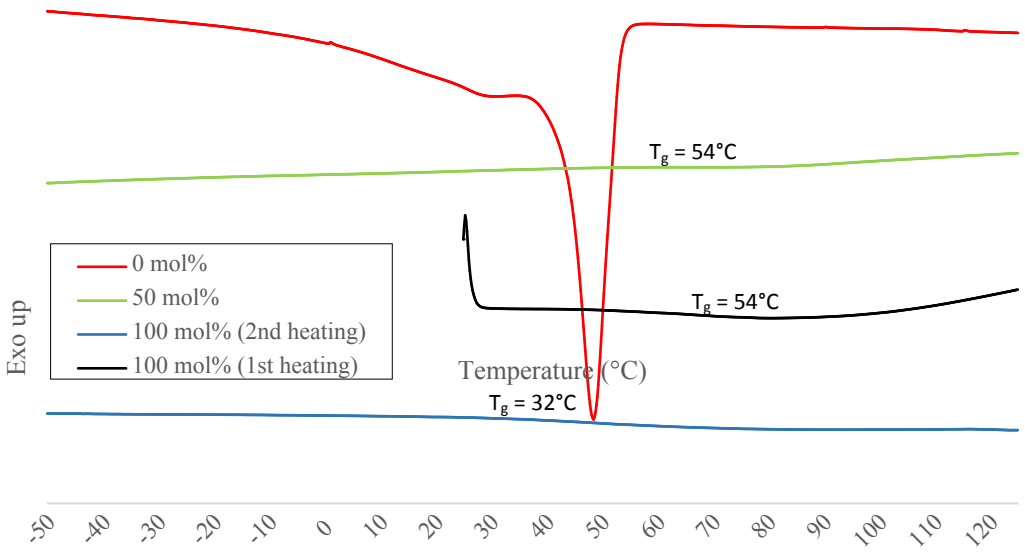


Figure S 22 - Functionalisation of P1 with COOH-PhTAD - DSC data.

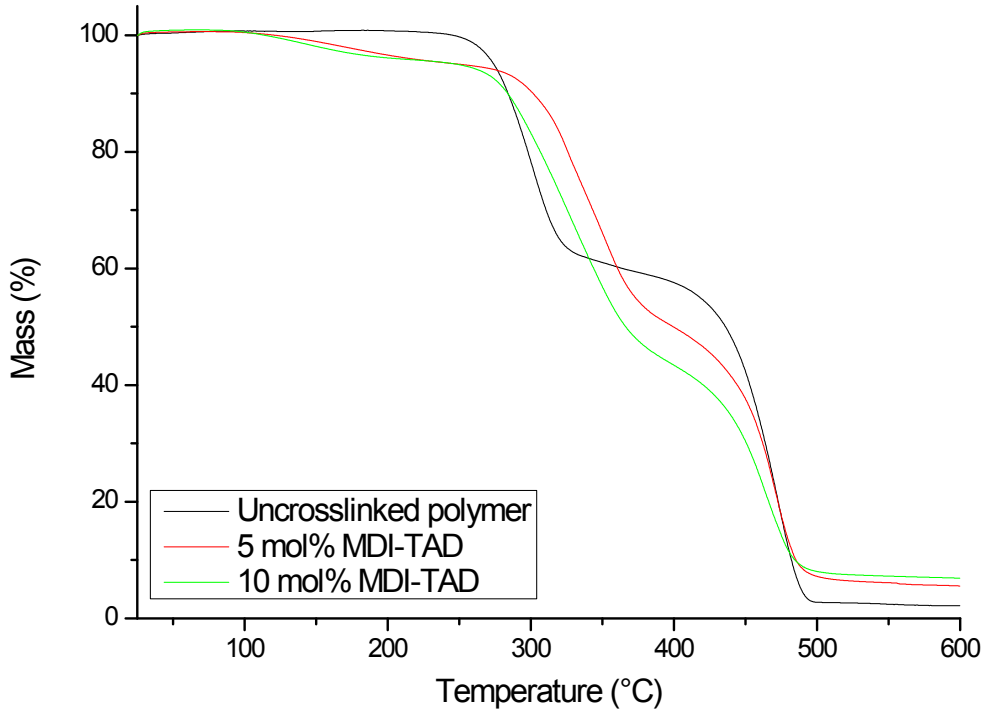


Figure S 23 - Example of crosslinking of 50 mol% PhTAD modified P1 with 5 and 10 mol% MDI-TAD - TGA data.

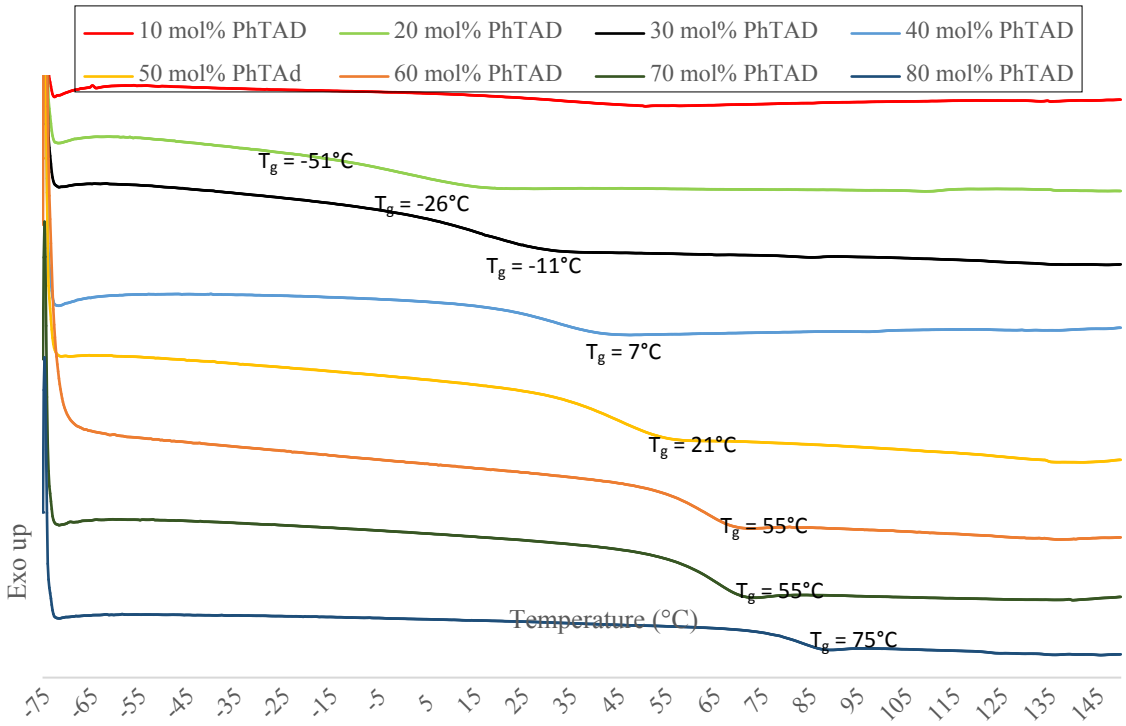


Figure S 24 – DSC analysis of PhTAD modified P1 crosslinked with 5 mol% MDI-TAD.