Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Two Colours of Light Drive PET-RAFT Photoligation

Laura Delafresnaye, [a,b†] Kenward Jung, [c†] Cyrille Boyer*[c] and Christopher Barner-Kowollik*[a,b]

[a]Centre for Materials Science, Queensland University of Technology (QUT) 2 George Street, 4000 Brisbane, Queensland, Australia.

[b]School of Chemistry and Physics, Queensland University of Technology (QUT) 2 George Street, 4000 Brisbane, Queensland, Australia. christopher.barnerkowollik@qut.edu.au

[c]Centre for Advanced Macromolecular Design (CAMD) and Australian Centre for NanoMedicine (ACN), School of Chemical Engineering, The University of New South Wales, Sydney NSW 2052, Australia. cboyer@unsw.edu.au

[†]These authors contributed equally.

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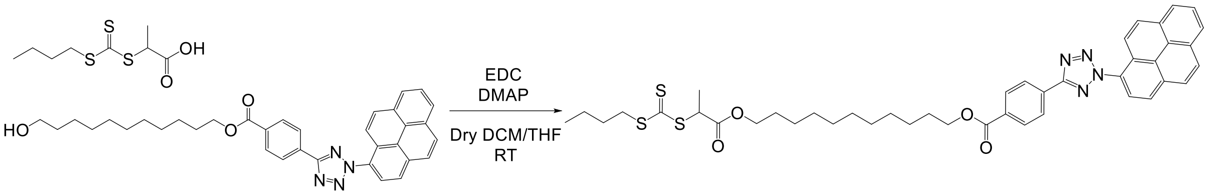
1. Synthesis

1.1. PAT-RAFT



11-hydroxyundecyl 4-(2-(pyren-1-yl)-2H-tetrazol-5-yl)benzoate (PAT-OH) and 2-(((butylthio)carbonothioyl)thio)propanoic acid (BTPA) were synthesized according to literature. In a round bottom flask, 840 mg (1.5 mmol, 1.0 eq.) PAT-OH, 410 mg (1.7 mmol, 1.15 eq.) BTPA, and 50 mg (0.4 mmol, 0.27 eq.) 4-dimethylaminopyridine (DMAP) were dissolved in 60 mL of a 3/1 mixture of dry DCM/THF. The solution was cooled to 0 °C and 340 mg (1.7 mmol, 1.18 eq.) 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) was added. The solution was allowed to reach ambient temperature, before being stirred for 24 h. Next, the solvent was removed *in vacuo* and the crude product dissolved in 30 mL of DCM. The solution mixture was washed with 30 mL hydrochloric acid 1M, saturated $NaHCO_3$ solution and brine. The combined organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica gel, cyclohexane/ethyl acetate, gradient 100/0 to 80/20) to obtain a black paste (647 mg; yield: 55.2%). ^1H, ^{13}C NMR and fluorescence spectra are reported in Figure S1-3.

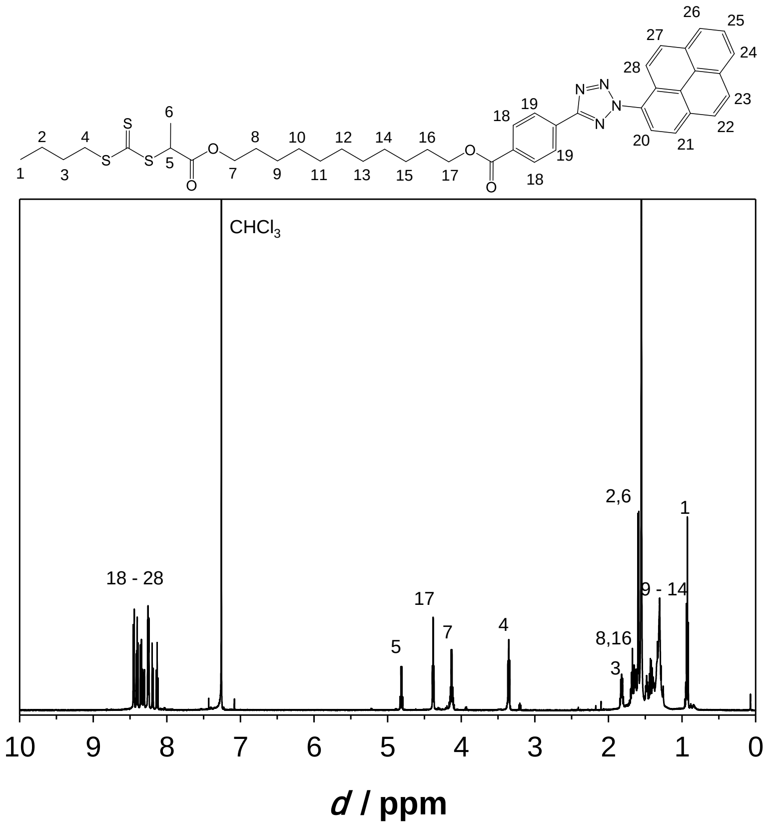


Figure S1. ^1H NMR spectrum of 11-((2-(((butylthio)carbonothioyl)thio)propanoyl)oxy)undecyl 4-(2-(pyren-1-yl)-2H-tetrazol-5-yl)benzoate (PAT-BTPA), 16 scans, 600 MHz, $CDCl_3$

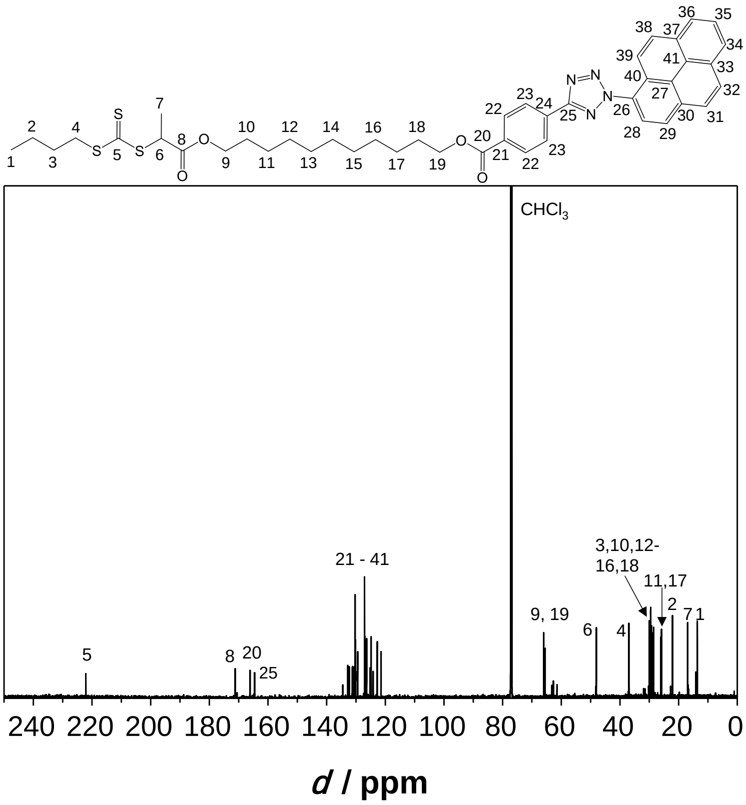


Figure S2. ^{13}C NMR spectrum of 11-((2-(((butylthio)carbonothioyl)thio)propanoyl)oxy)undecyl 4-(2-(pyren-1-yl)-2H-tetrazol-5-yl)benzoate (PAT-BTPA), 1024 scans, 600 MHz, CDCl$_3$

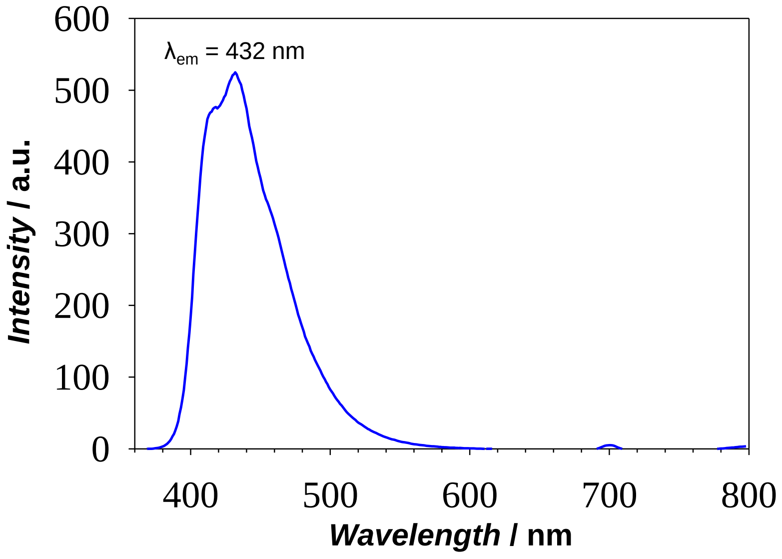


Figure S3. Fluorescence spectrum of 11-((2-(((butylthio)carbonothioyl)thio)propanoyl)oxy) undecyl 4-(2-(pyren-1-yl)-2H-tetrazol-5-yl)benzoate (PAT-BTPA) (λ$_{ex}$ = 349 nm, Medium voltage, THF, c = 1.23 10^{-5} g L^{-1}).

1.2. PET-RAFT polymerisation

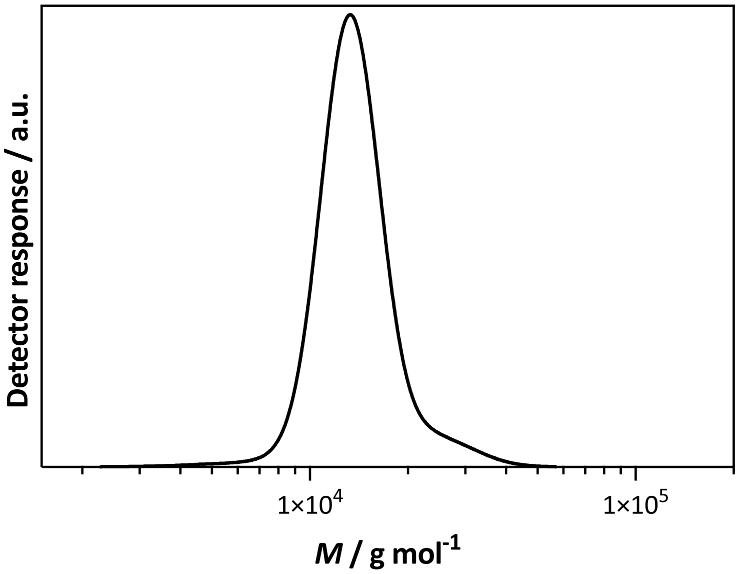


Figure S4. SEC traces of PMA$_1$ (DMAc-1, PMMA calibration).

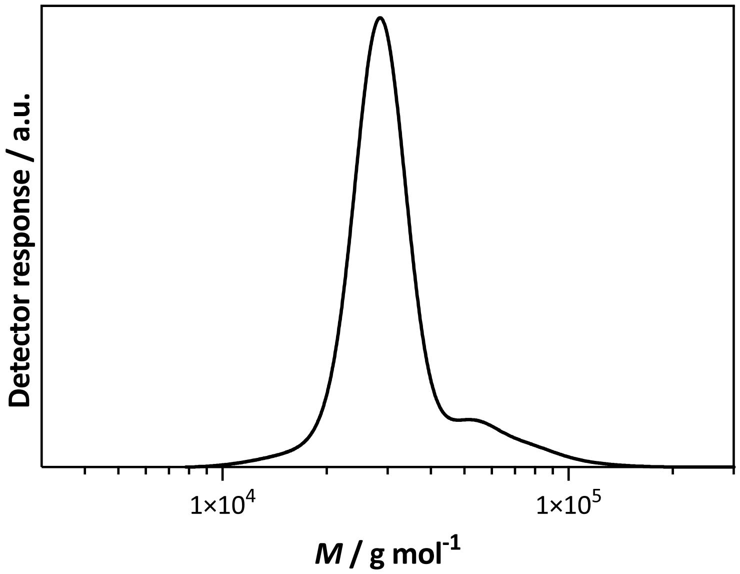


Figure S5. SEC traces of PMA$_2$ (DMAc-1, PMMA calibration).

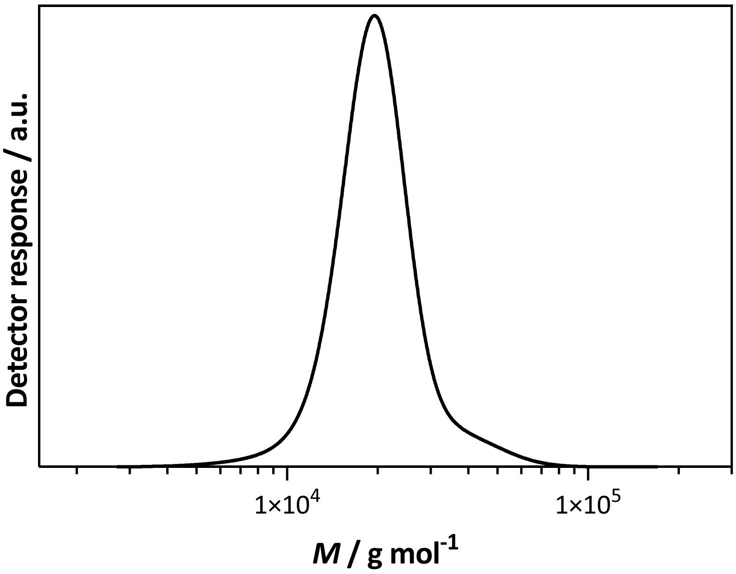


Figure S6. SEC traces of PDMA$_1$ (DMAc-1, PMMA calibration).

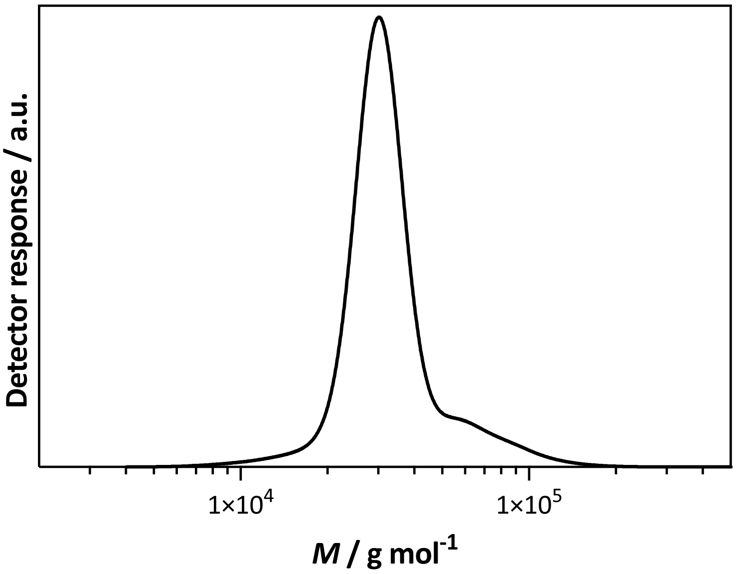


Figure S7. SEC traces of PDMA$_2$ (DMAc-1, PMMA calibration).

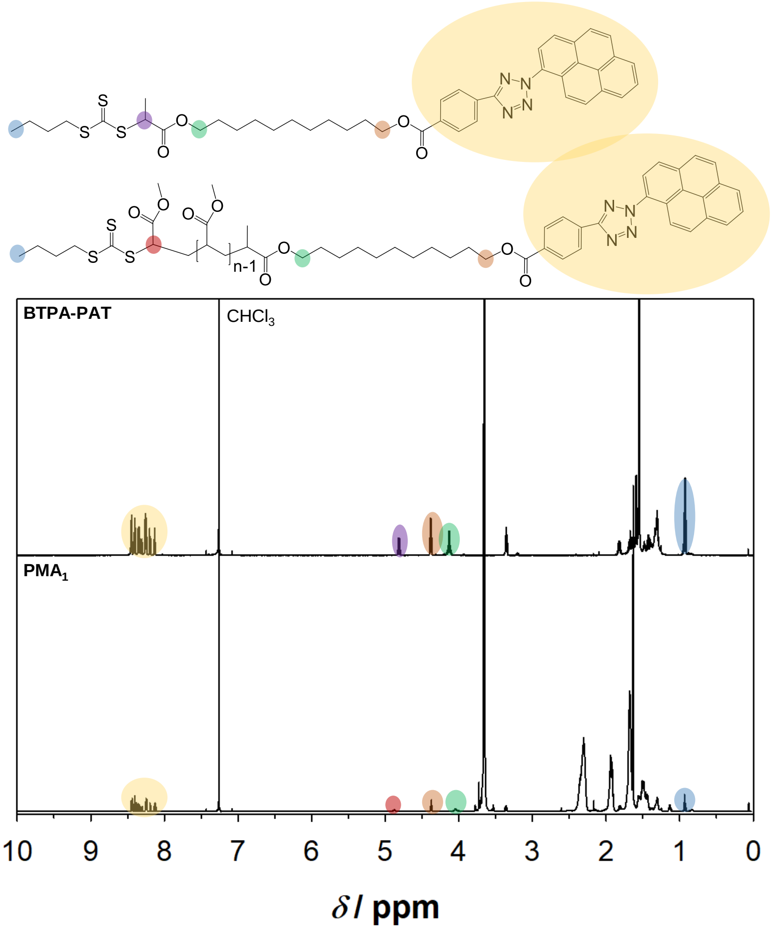


Figure S8. ^{1}H NMR analysis of BTPA-PAT and PMA$_1$ polymer, 32 scans, 600 MHz, CDCl$_3$. Protons of interest are highlighted in the chemical structure and spectra.

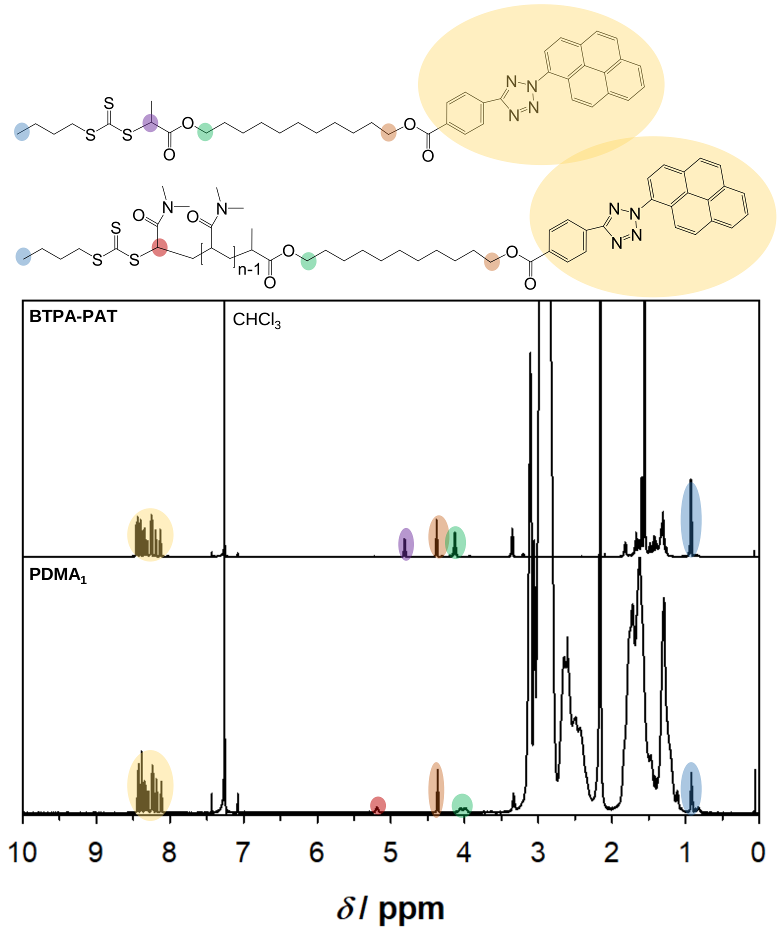
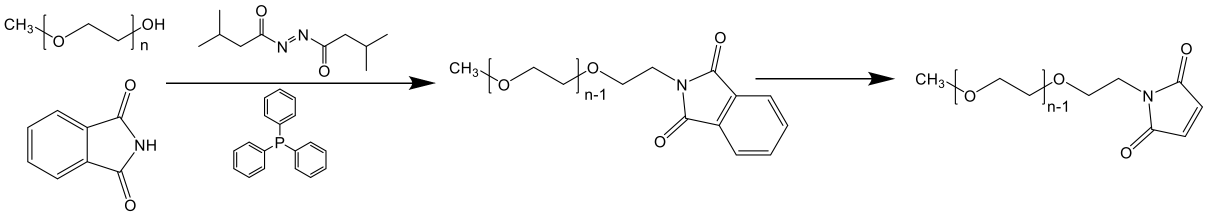


Figure S9. ^{1}H NMR analysis of BTPA-PAT and PDMA$_1$ polymer, 32 scans, 600 MHz, CDCl$_3$. Protons of interest are highlighted in the chemical structure and spectra

1.3. PEG-maleimide



In a round bottom flask, 1.0 g of poly(ethylene glycol) methyl ether (average M_n 1,900 g mol^{-1}, 0.5 mmol, 1.0 eq.) and 414 mg triphenylphosphine (PPh$_3$, 1.6 mmol, 3.0 eq.) were dissolved in 5 mL of dry THF. The solution was then put on ice and stirred for 5 minutes. Next, 315 mL of diisopropyl azodicarboxylate (DIAD, 1.6 mmol, 3.0 eq.) was added dropwise to the solution and was stirred for another 5 minutes. Next, a solution of 264 mg of phthalimide (1.8 mmol, 3.4 eq.) in 5 mL of dry THF was added dropwise to the solution. The reaction was allowed to stir overnight at room temperature. To remove the unreacted PEG, the crude was precipitated in freezing diethyl ether. The retro Diels-Alder was then performed under reflux in toluene for 3 hours hours at 110 °C to obtain a white powder (NMR: 77-93% conversion)

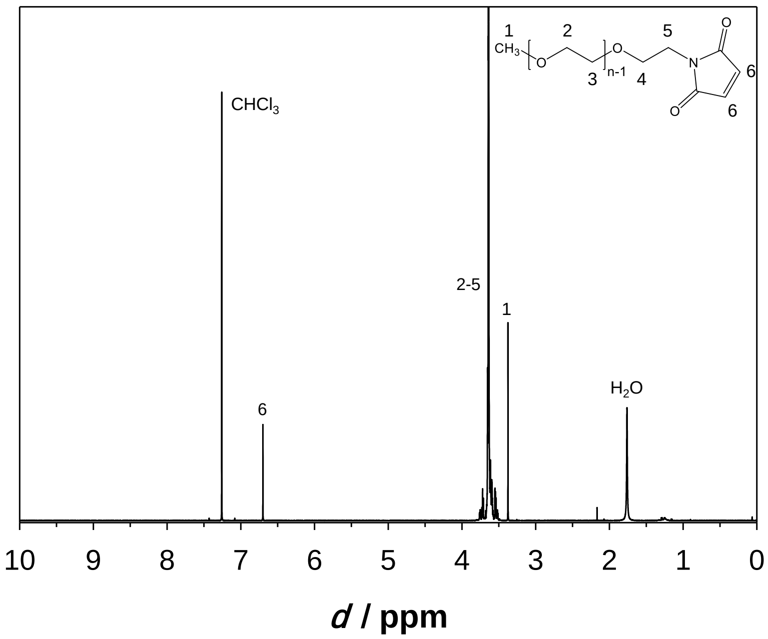


Figure S10. ^{1}H-NMR spectrum of poly(ethylene glycol) methyl ether maleimide (PEG-mal), 16 scans, 600 MHz, $CDCl_3$

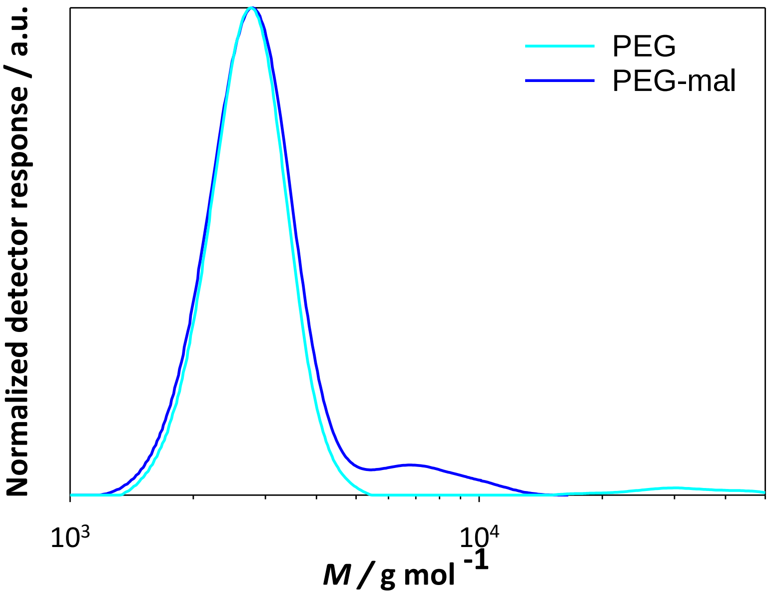


Figure S11. SEC traces of poly(ethylene glycol) methyl ether (PEG) and poly(ethylene glycol) methyl ether maleimide (PEG-mal) (DMAc-2, PMMA calibration).

2. Photoligation results

2.1. Photoligation set-up

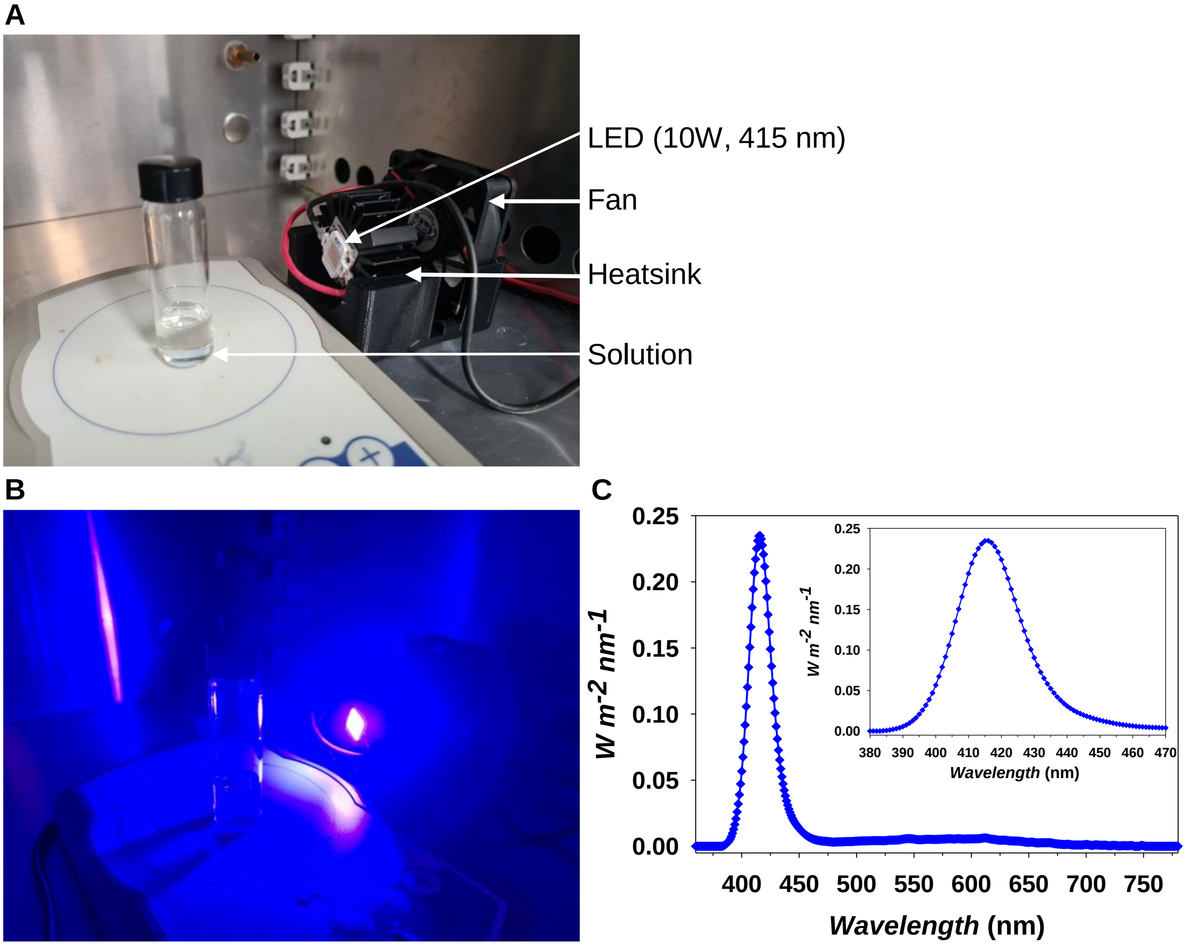


Figure S12. The photoligation set-up consists of a 10W LED (415 nm) mounted on a heatsink. The distance between the LED and the sample is 80 mm and the LED is cooled using a fan. A. Picture of the set-up with LED off. B. Picture of the set-up with LED on. C. Spectrum of the blue LED.

2.2. NMR

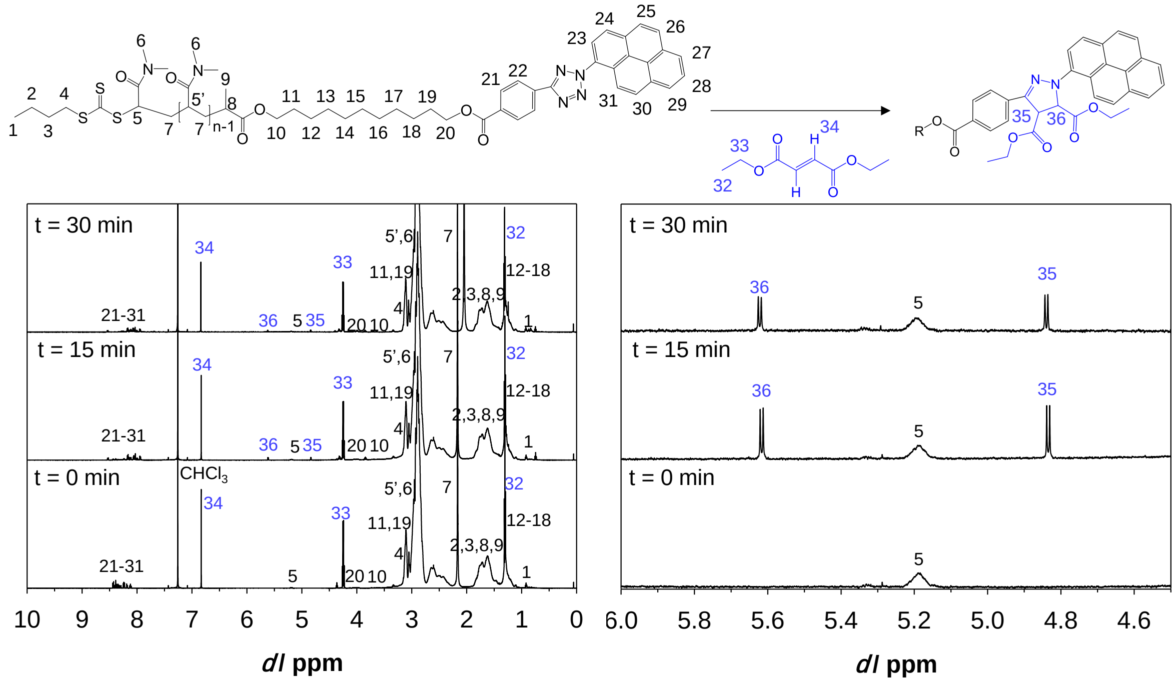


Figure S13. ^{1}H NMR spectrum of PDMA$_1$ before and after photoligation with diethyl fumarate recorded in CDCl$_3$ at 600 MHz (32 scans) after 0, 15 and 30 min of irradiation (10W blue LED, λ = 415 nm). The right spectrum shows a zoom on the 4.5 – 6.0 ppm region to clearly see protons 35 and 36. The rearomatised reaction product is not shown.

Table S1. Integrals of proton resonances H_5, $H_{21\text{-}31}$, H_{33}, H_{34}, H_{35} and H_{36} at different times (PDMA$_1$). The integral for the H_{33} resonance has been set to 4.00 for the calculation of the conversion.

Time	**$\int H_{34}$ (2H)**	**$\int H_{33}$ (4H)**	**$\int H_{21\text{-}31}$ (13H)**	**$\int H_5$ (1H)**	**$\int H_{36}$ (1H)** [a]	**$\int H_{35}$ (1H)** [a]	**Eq. Fum/Tz**[b]	**Conversion X_t (%)**[c]
0 min	1.88	4.00	2.99	0.20	/	/	4.34 eq.	0%
15 min	1.53	4.00	3.03	0.07	0.05	0.07		81%
30 min	1.51	4.00	2.72	0.26	0.16	0.14		85%

[a] With prolonged irradiation time, the pyrazoline adduct can undergo rearomatisation, meaning the integrals for H_{35} and H_{36} decrease over time.

[b] Based on 13 protons integrals (eq = 13/2.99).

[c] Calculated as follows

$$\int H34_{X=100\%} = \int H34_{X=0\%} - \frac{\int H34_{X=0\%}}{eq.}$$

$$X_t(\%) = \frac{(\int H34_{X=0\%} - \int H34_t)}{(\int H34_{X=0\%} - \int H34_{X=100\%})} \times 100\%$$

Where $\int H34_{X=0\%}$, $\int H34_t$ and $\int H34_{X=100\%}$ are the integrals of proton H_{34} at 0, *t* and 100% conversion.

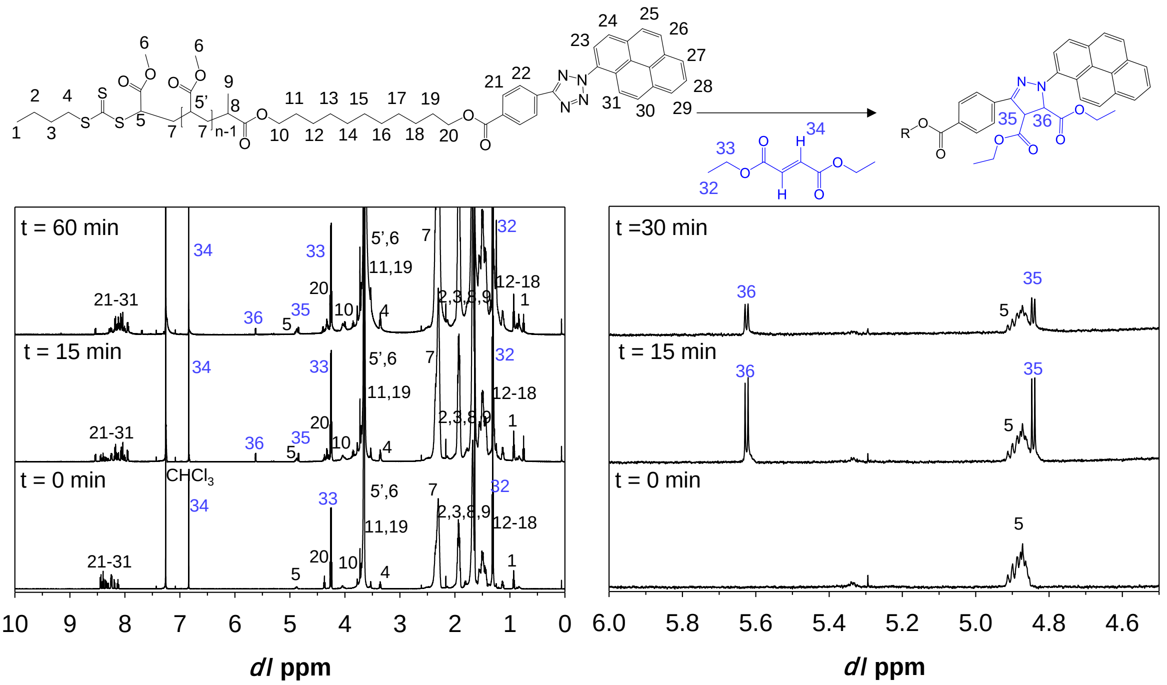


Figure S14. ^{1}H NMR spectrum of PMA$_1$ before and after photoligation with diethyl fumarate recorded in CDCl$_3$ at 600 MHz (32 scans) after 0, 15 and 30 min of irradiation (10W blue LED, λ = 415 nm). The right spectrum shows a zoom on the 4.5 – 6.0 ppm region to clearly see protons 35 and 36. The rearomatised reaction product is not shown.

Table S2. Integrals of proton resonances H_5, H_{21-31}, H_{33}, H_{34}, H_{35} and H_{36} at different times (PMA$_1$). The resonance for H_{33} has been set to 4.00 for the calculation of the conversion.

Time	**$\int H_{34}$ (2H)**	**$\int H_{33}$ (4H)**	**$\int H_{21-31}$ (13H)**	**$\int H_5$ (1H)**	**$\int H_{36}$ (1H)** [a]	**$\int H_{35}$ (1H)** [a]	**Eq. Fum/Tz**[b]	**Conversion X_t (%)**[c]
0 min	1.99	4.00	5.67	0.50	/	/	2.3 eq.	0
15 min	1.38	4.00	5.66	0.53	0.23	0.27		71
30 min	1.13	4.00	5.74	0.46	0.36	0.20		100

[a] With prolonged irradiation time, the pyrazoline adduct can undergo rearomatisation, meaning the integrals for H_{35} and H_{36} decrease over time.

[b] Based on 13 protons integrals (eq = 13/5.67).

[c] Calculated as follows

$$\int H34_{X=100\%} = \int H34_{X=0\%} - \frac{\int H34_{X=0\%}}{eq.}$$

$$X_t(\%) = \frac{(\int H34_{X=0\%} - \int H34_t)}{(\int H34_{X=0\%} - \int H34_{X=100\%})} \times 100\%$$

Where $\int H34_{X=0\%}$, $\int H34_t$ and $\int H34_{X=100\%}$ are the integrals of proton H_{34} at 0, *t* and 100% conversion.

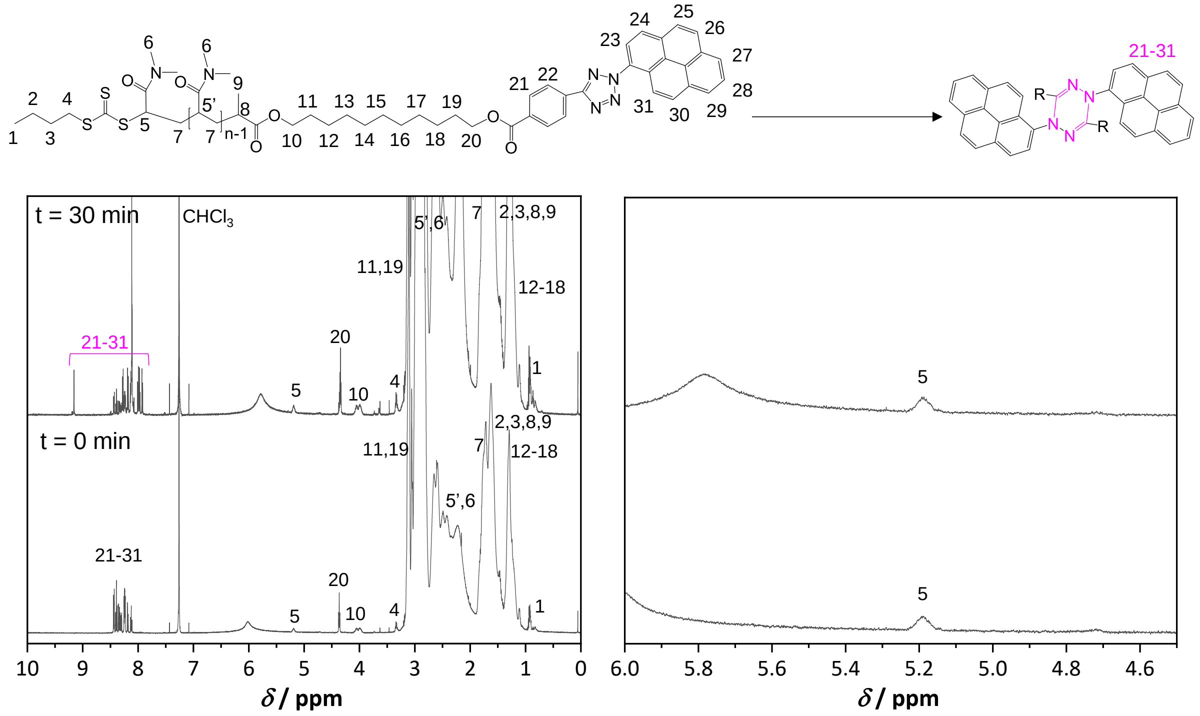


Figure S15. ^{1}H NMR spectrum of PDMA$_1$ before and after photoligation without dipolarophile (dimerisation) recorded in CDCl$_3$ at 600 MHz (32 scans) after 0 and 30 min of irradiation (10W blue LED, λ = 415 nm). The right spectrum shows a zoom on the 4.5 – 6.0 ppm region to clearly see the absence of protons of the pyrazoline adduct.

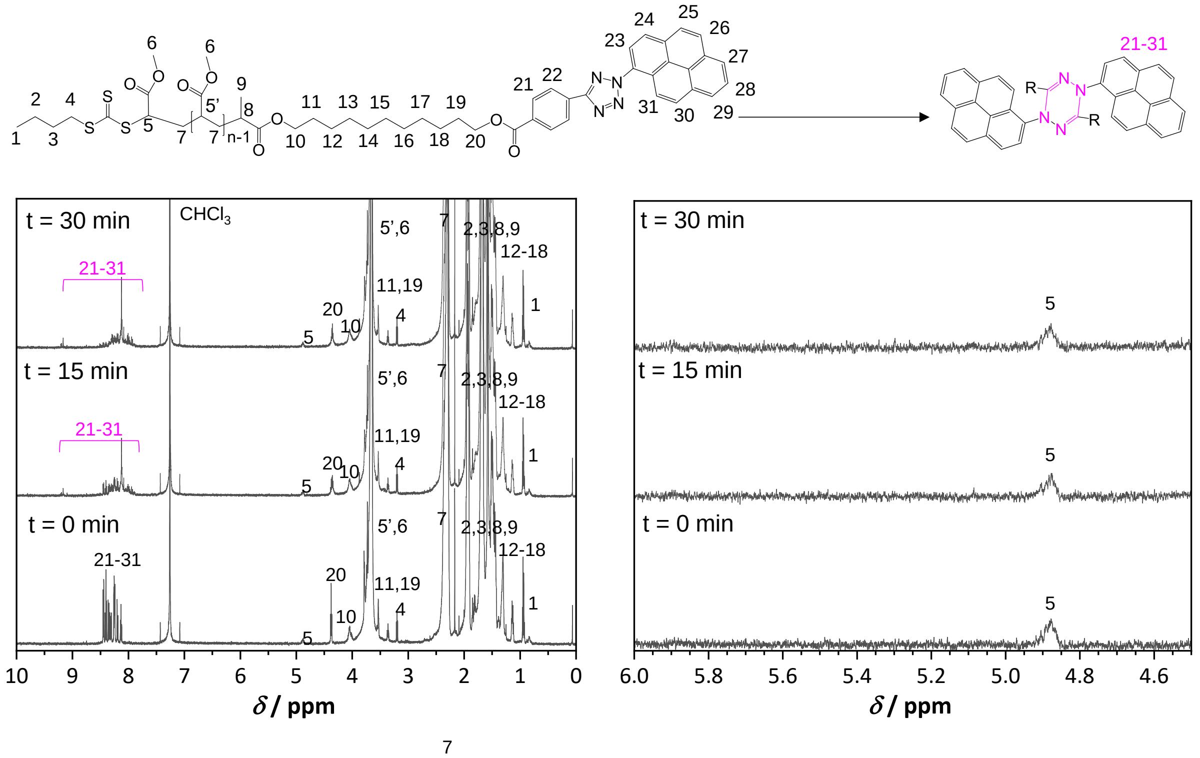


Figure S16. ^{1}H NMR spectrum of PMA$_1$ before and after photoligation without dipolarophile (dimerisation) recorded in CDCl$_3$ at 600 MHz (32 scans) after 0, 15 and 30 min of irradiation (10W blue LED, λ = 415 nm). The right spectrum shows a zoom on the 4.5 – 6.0 ppm region to clearly see the absence of protons of the pyrazoline adduct.

2.3. Fluorescence

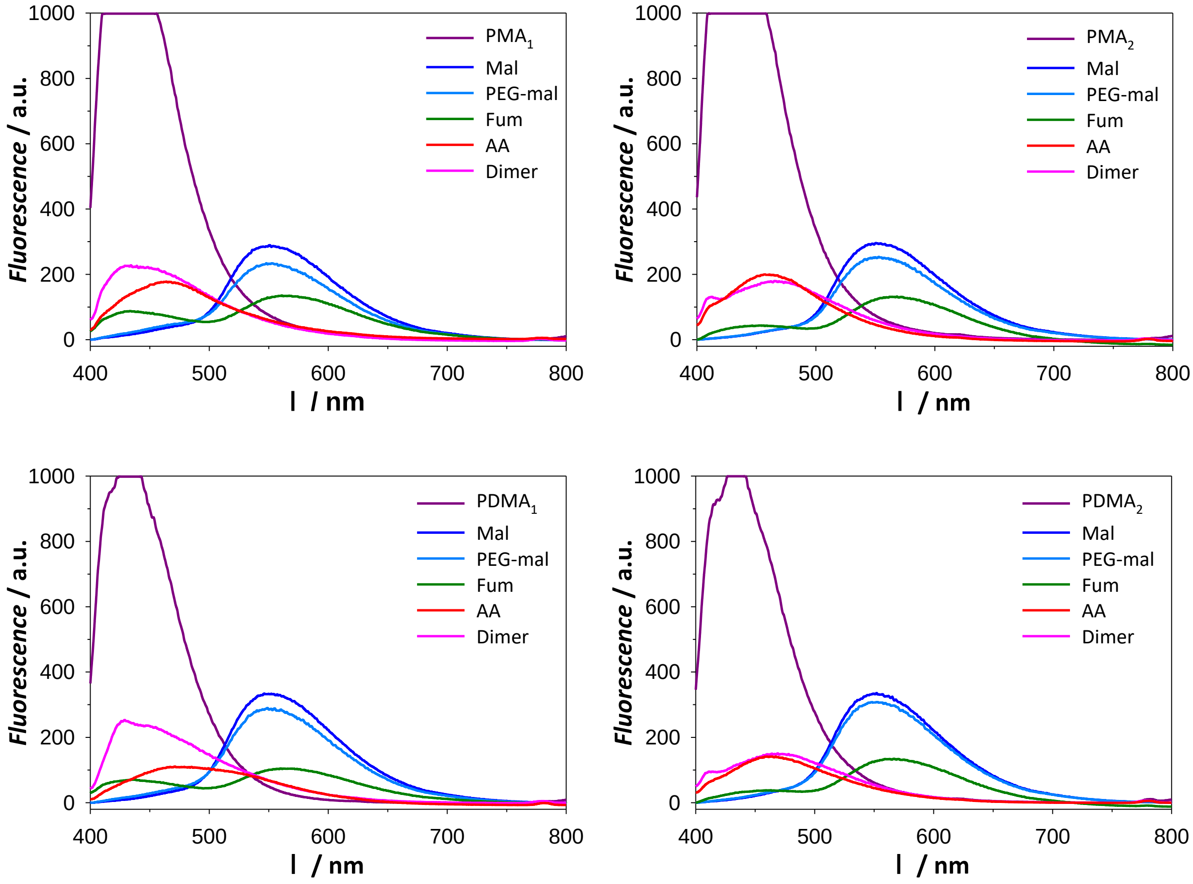


Figure S17. Post-modification of PMA and PDMA polymers synthesised by PET-RAFT polymerisation via ligation under blue light (λ = 415 nm) with a maleimide (mal), a PEG-maleimide (PEG-mal), diethyl fumarate (fum), acetic acid (AA) and without any dipolarophile (dimer). Fluorescence spectra were recorded after 30 min of irradiation (λ_{ex} = 390 nm, MV).

2.4. UV-Vis absorbance

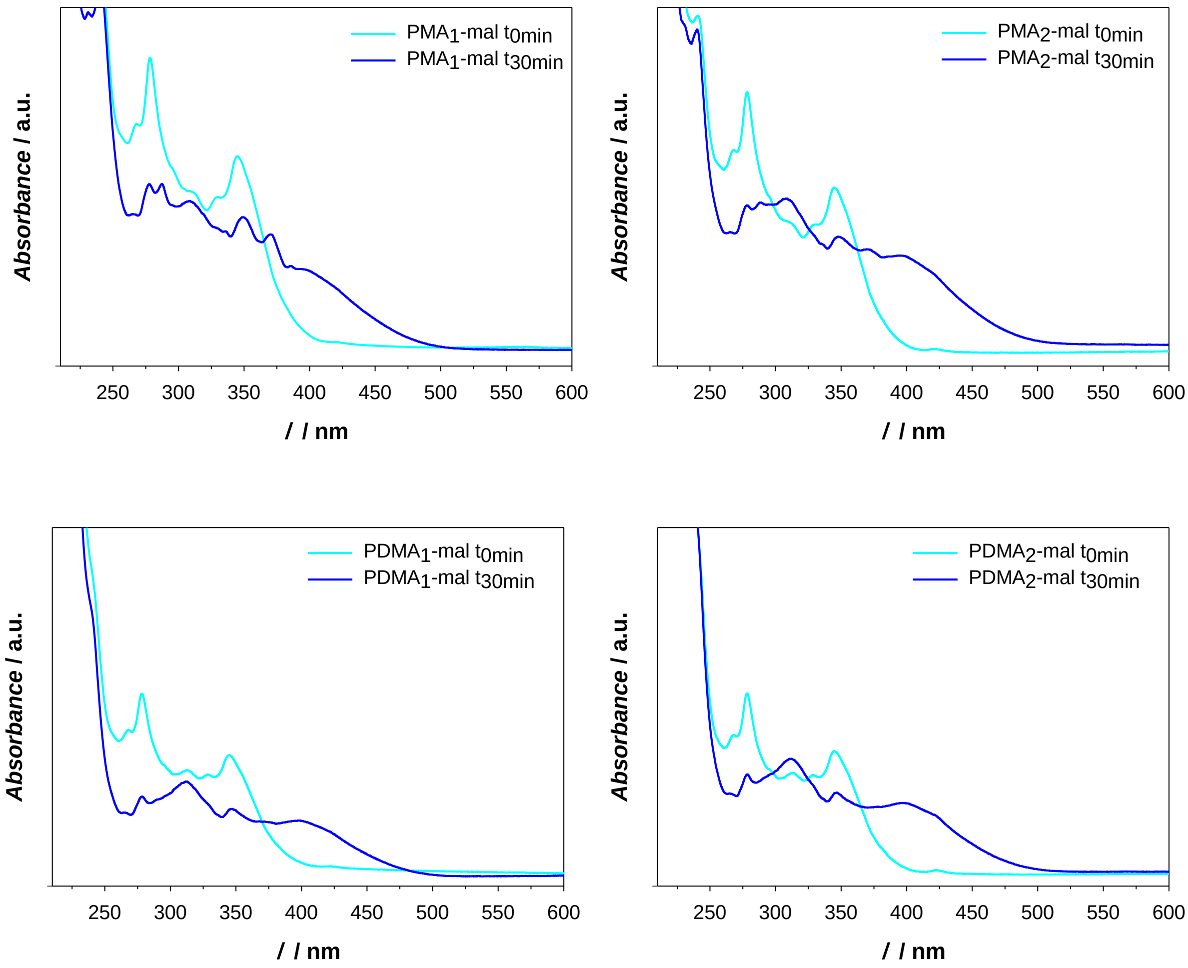


Figure S18. UV-Vis spectra of PMA and PDMA polymers before and after ligation with maleimide (mal) under blue light (λ = 415 nm, 30 min).

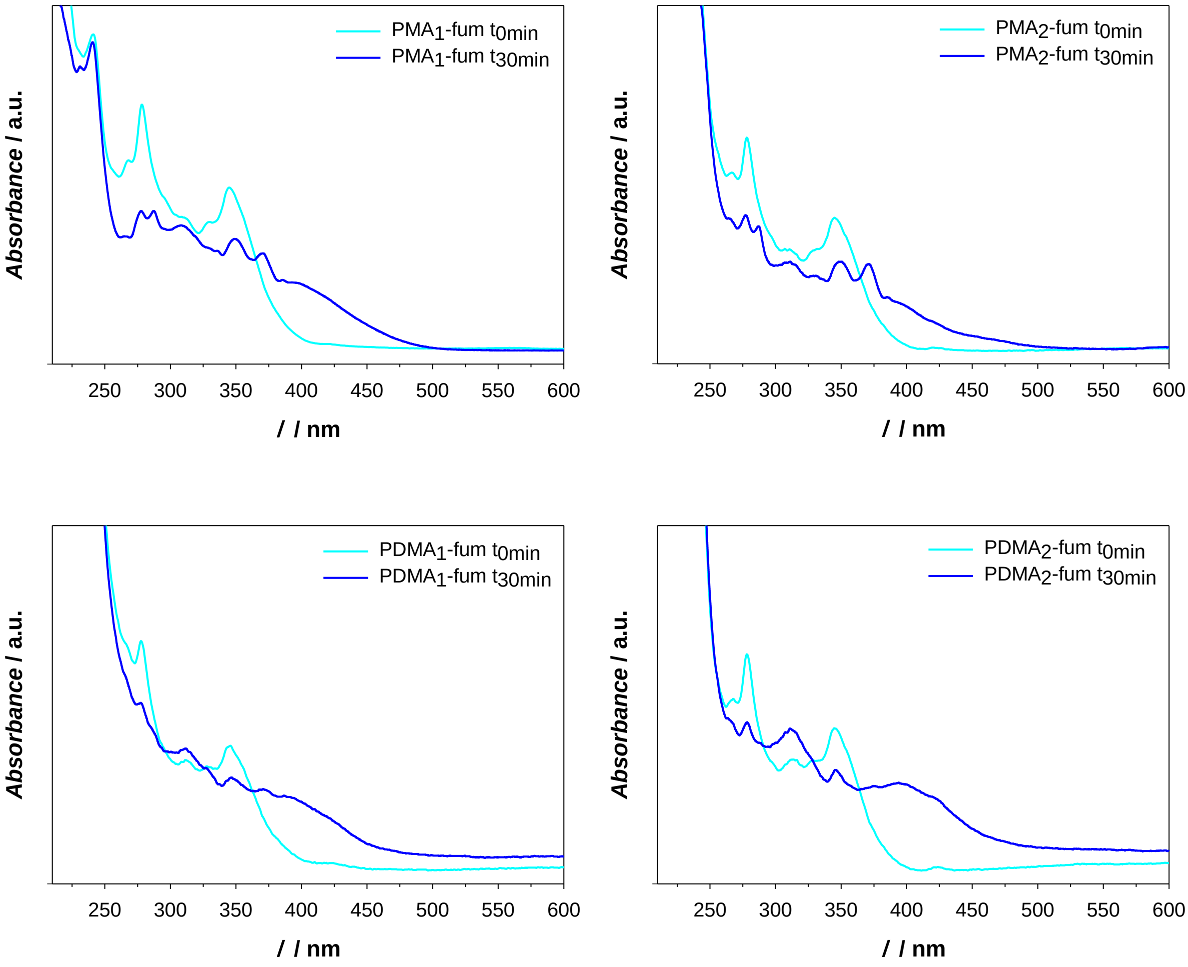


Figure S19. UV-Vis spectra of PMA and PDMA polymers before and after ligation with fumarate (fum) under blue light (λ = 415 nm, 30 min).

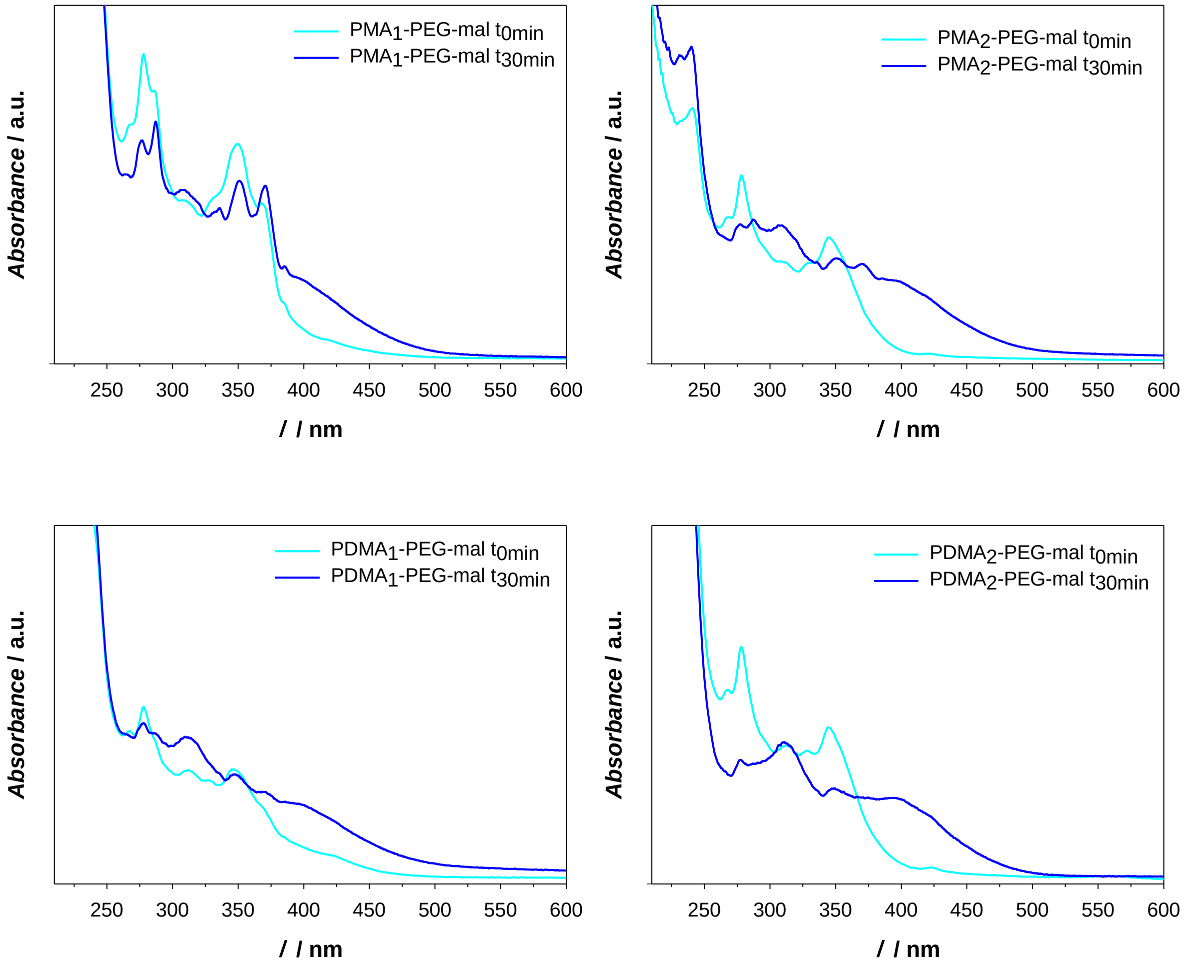


Figure S20. UV-Vis spectra of PMA and PDMA polymers before and after ligation with PEG-maleimide (PEG-mal) under blue light (λ = 415 nm, 30 min).

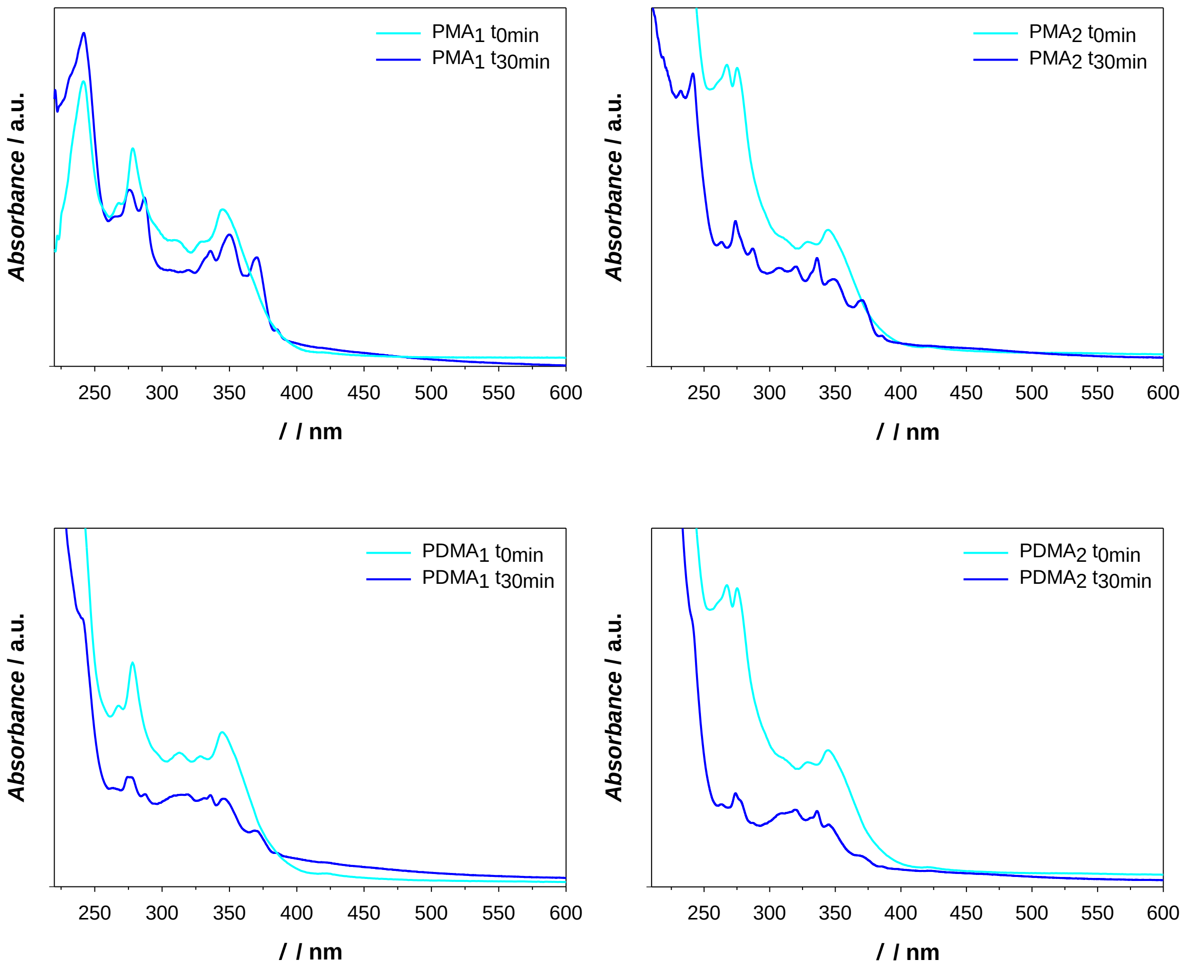


Figure S21. UV-Vis spectra of PMA and PDMA polymers before and after self-dimerisation under blue light (λ = 415 nm, 30 min).

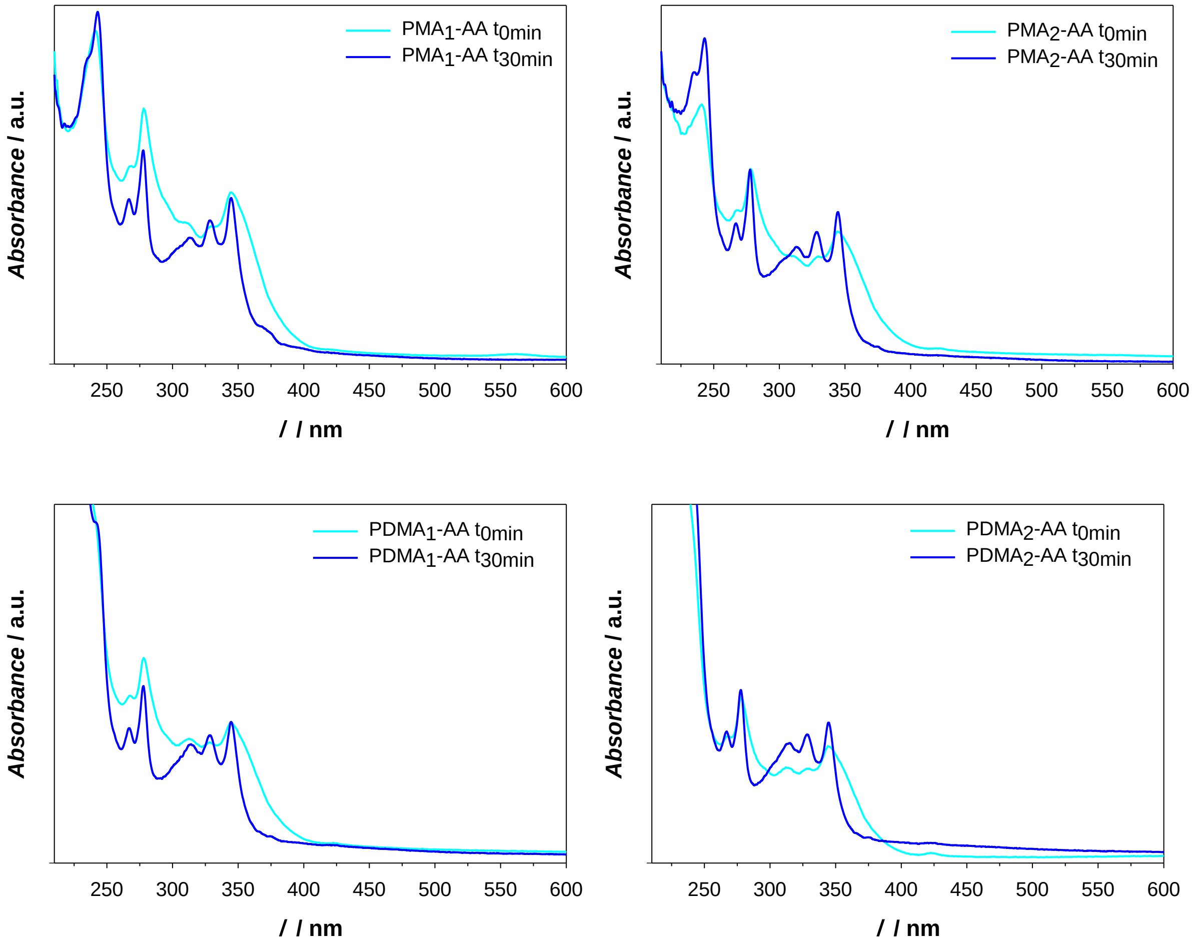


Figure S22. UV-Vis spectra of PMA and PDMA polymers before and after ligation with acetic acid (AA) under blue light (λ = 415 nm, 30 min).

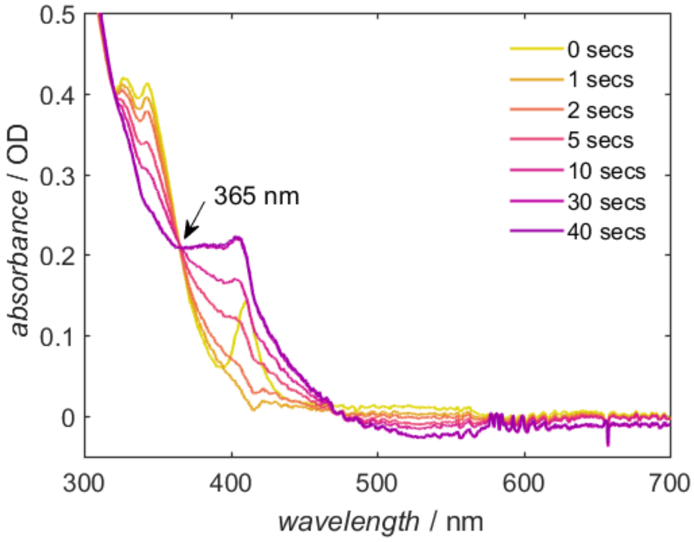


Figure S23.. Online UV-Vis spectra of PMA_2 with ethyl fumarate while irradiated under blue light (λ = 415 nm, THF). The arrow shows the isosbestic point at 365 nm. The spectrum at 0 s (yellow) shows a peak at 415 nm, which corresponds to the blue LED employed. As soon as the reaction occurs, the product absorbs at this wavelength and the peak disappears. Note that the baseline is slightly shifted to negative value due to the fluorescence nature of the product.

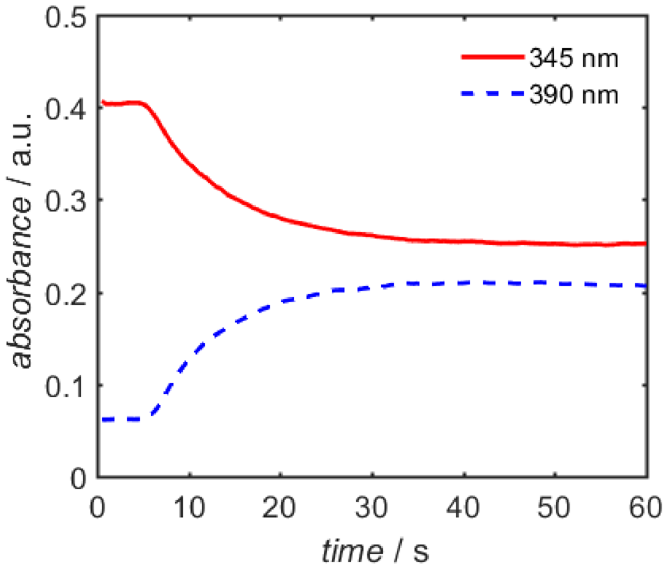


Figure S24. Absorbance over time at two specific wavelengths (345 and 390 nm) based on the online UV-Vis spectra of PMA_2 with ethyl fumarate while irradiated under blue light (λ = 415 nm, THF) (Figure S23).

2.5. SEC

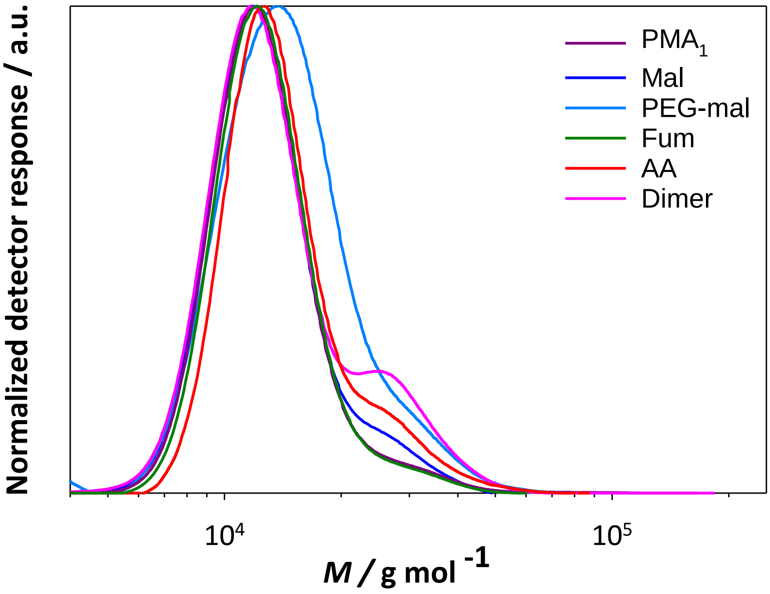


Figure S25. Normalised SEC traces of PMA_1 polymer before and after photoligation (THF, PMMA calibration)

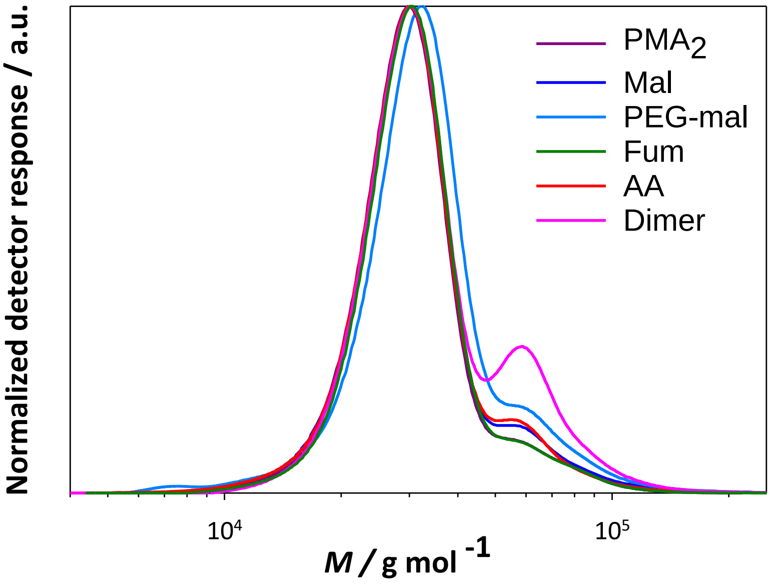


Figure S26. Normalised SEC traces of PMA_2 polymer before and after photoligation (THF, PMMA calibration)

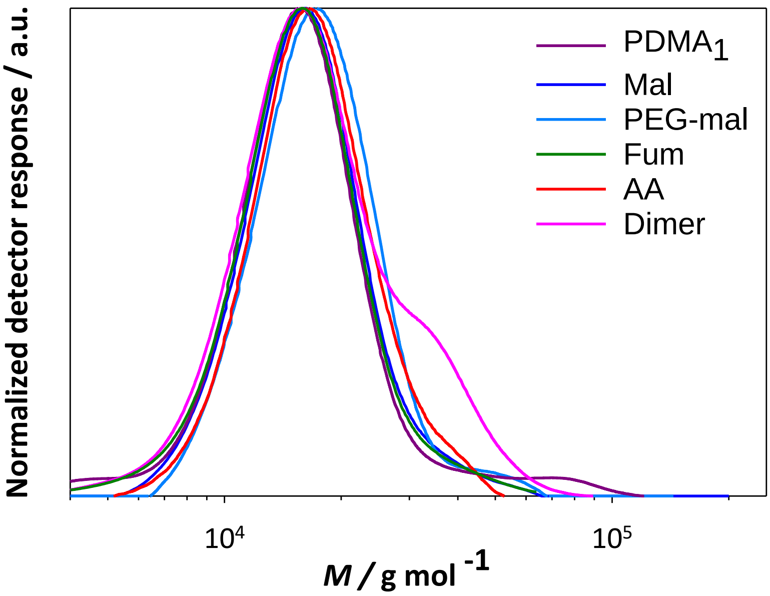


Figure S27. Normalised SEC traces of $PDMA_1$ polymer before and after photoligation (DMAc-2, PMMA calibration)

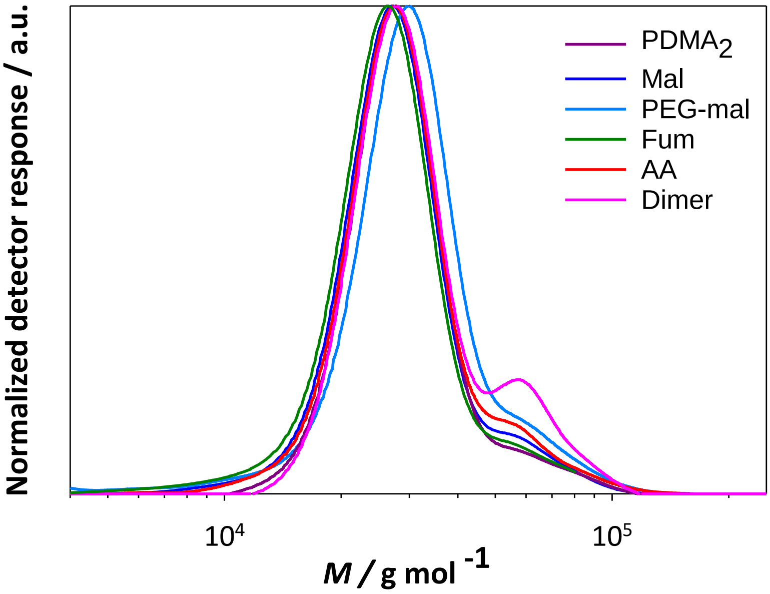


Figure S28. Normalised SEC traces of $PDMA_2$ polymer before and after photoligation (DMAc-2, PMMA calibration)

Table S3. Number-average (M_n) and weight-average (M_w) molecular weight and polydispersity ($Đ = M_w/M_n$) of the PEG-mal, PMA$_1$, PMA$_2$, PDMA$_1$ and PDMA$_2$ before and after photoligation.

Polymer	**M_n / g mol^{-1}**	**M_w / g mol^{-1}**	**$Đ$**
PEG-mal	2 800	2 900	1.04
PMA$_1$	12 000	13 500	1.12
PMA$_{1}$- PMA$_1$	12 700	15 100	1.19
	(11 000/24 000)		
PMA$_1$-AA	13 400	15 200	1.13
PMA$_1$-fum	12 200	13 500	1.12
PMA$_1$-mal	12 100	13 600	1.12
PMA$_1$-PEG-mal	12 600	15 400	1.22
PMA$_2$	28 500	32 500	1.14
PMA$_{2}$- PMA$_2$	31 400	37 600	1.19
	(30 600/58 900)		
PMA$_2$-AA	28 600	33 300	1.16
PMA$_2$-fum	29 200	33 000	1.13
PMA$_2$-mal	29 100	33 800	1.16
PMA$_2$-PEG-mal	30 200	36 300	1.20
PDMA$_1$	14 200	17 800	1.15
PDMA$_{1}$- PDMA$_1$	15 500	19 400	1.25
	(15 700/34 000)		
PDMA$_1$-AA	14 100	16 200	1.14
PDMA$_1$-fum	14 300	16 900	1.18
PDMA$_1$-mal	15 100	17 300	1.15
PDMA$_1$-PEG-mal	16 200	18 500	1.14
PDMA$_2$	26 000	30 100	1.18
PDMA$_{2}$- PDMA$_2$	28 900	34 600	1.19
	(26 600/59 400)		
PDMA$_2$-AA	26 900	31 200	1.16
PDMA$_2$-fum	24 500	28 000	1.18
PDMA$_2$-mal	25 400	29 900	1.16
PDMA$_2$-PEG-mal	28 800	33 400	1.16

Only the polymers reacted with the acetic acid were precipitated in diethyl ether to remove unreacted acid (in excess) and avoid contaminations of the SEC columns. One may note that the M_n are slightly lower with AA which can be explained by reaction of polymer-AA with the column material. PMA polymers were analysed via SEC THF. PEG and PDMA polymers were analysed via SEC DMAc-2. M_n, M_w and $Đ$ were determined using PMMA standards.