Electronic Supplementary Material (ESI) for Polymer Chemistry.

# Supplementary Materials for:

# Photo-mediated RAFT step-growth polymerization with maleimidic monomers

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## General considerations

Unless stated all reagents were purchased from commercial suppliers and used as received. Butyl acrylate (BA) and anhydrous dioxane were passed through activated basic aluminum oxide and discarded after several uses. All NMR spectrums were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$. All NMR spectrums were processed using Mestrenova. The wavelength of the emitted from LEDs was determined using an emission spectrophotometer (Edinburgh Instruments, model FLS-920) equipped with a cooled PMT (Hamamatsu, R2658) with spectra corrected for instrument response. UV-Vis absorbance spectrum of the RAFT agents were recorded using UV-Vis spectrometer (SHIMADZU, model UV-2600) in dioxane.

For kinetic analysis A 22-gauge, 4 inch hypodermic needle (air-tite product) was used to sample the reaction mixture under argon flow. Typically, a single needle and syringe was used to take sample for both THF-SEC and $^1$H-NMR spectroscopy, by drawing out approximately 50 to 100 µL and dropping a few drops into a vial for $^1$H-NMR and the remaining mixture left in the needle was flushed out with THF (or vice versa) in a separate vial for SEC analysis.

## Photo-reactor set-up

The photoreactor consists of 20 cm length strip of 12 x 5050 SMD LED light (12 volt, purchased from JOYLIT) wrapped around 20 ml scintillation vials with inner lid diameter of 15 mm and outer dimensions of 27.5 x 58 mm (diameter x length), 1 cm from the bottom of the vial. The wavelengths for the blue, green, and red LED lights are 458 nm, 514 nm, and 625 nm, respectively. These were placed in a light masking container secured by a Velcro tape with cooling plate underneath the photo-reactor. Reaction mixture were placed in 3.7 ml scintillation vials with outer dimensions of 15 x 45 mm (diameter x length) and secured with a 14/20 rubber septa with the head flanking 2 mm past the outer diameter of the vial. These were placed inside the placed inside the photo-reactor (**Fig. S1**). The distance of the reaction mixture from the light source is approximately 6 mm.

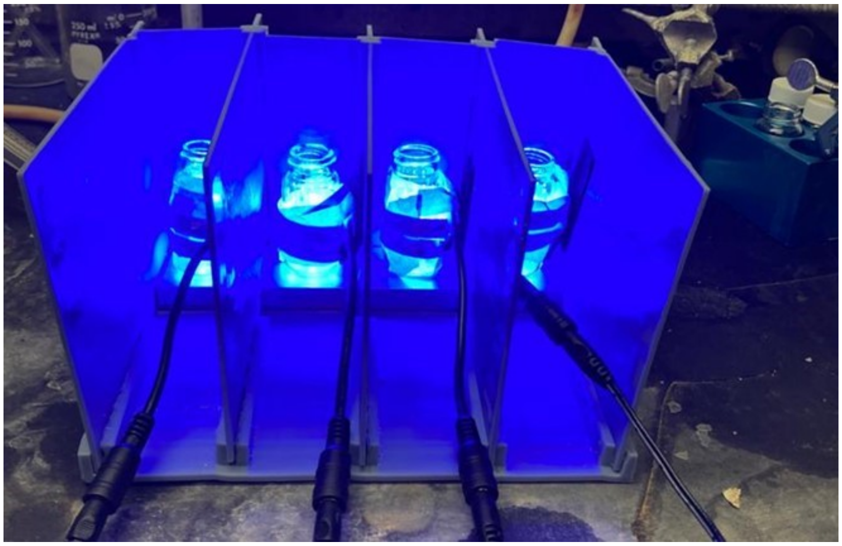


**Figure S1**: Photograph of the photoreactor used for the kinetic studies (without the reaction vials).

## Molecular weight characterization

Conventional SEC analysis of the crude polymerization mixture was carried out using polystyrene calibration in THF. SEC chromatograms were measured on a Waters 2695 separations module liquid chromatograph equipped with two Agilent ResiPore columns (linear SEC separation range up to 500k) maintained at 35°C, and a Waters 2412 refractive index detector. THF (with BHT as the inhibitor) was used as the mobile phase and the flow rate was set to 1 ml/min. Some experiments used THF without BHT, and separate calibration curves were created and used for this de-inhibited THF to ensure accuracy of the results. All samples were run with 100 µL injection volume.

## Theoretical average molecular weight

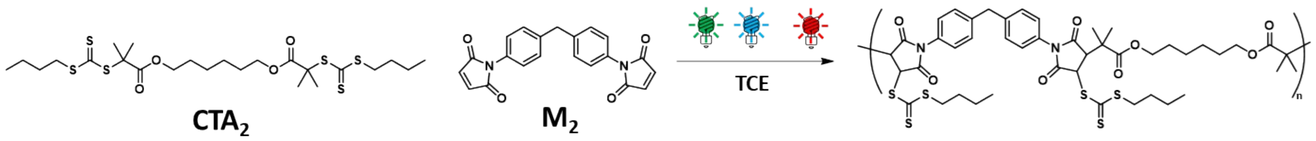
The evolution of number-average ($M_n$), weight-average ($M_w$) and Z-average ($M_z$) molecular weight of the crude reaction mixture were determined by SEC analysis. These were plotted together with conversion determined by $^1$H-NMR with expected molecular averages for linear step-growth polymerization according to Flory's equation which assumes no cyclization:[1]

$$M_{n,th} = M_0 \frac{1}{1-p}$$

$$M_{w,th} = M_0 \frac{1+p}{1-p}$$

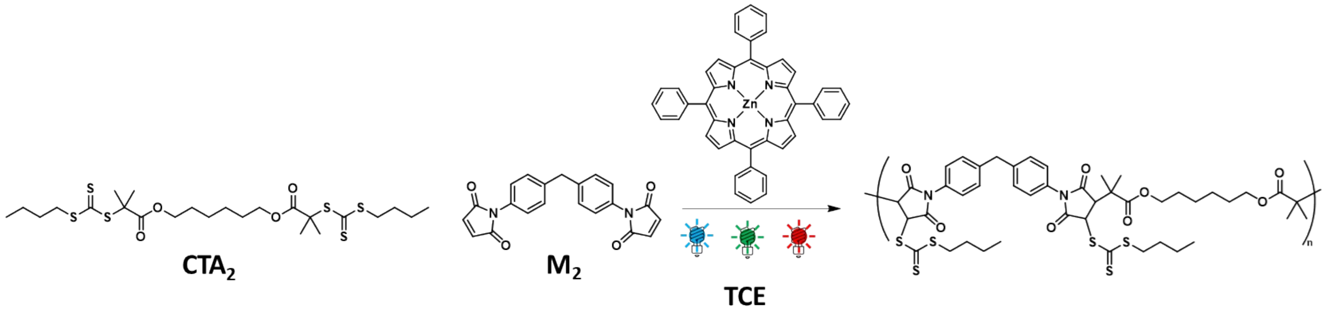
$$M_{z,th} = M_0 \frac{1+4p+p^2}{1-p^2}$$

## Procedure for $A_2$ + $B_2$ RAFT-Iniferter step-growth polymerization:



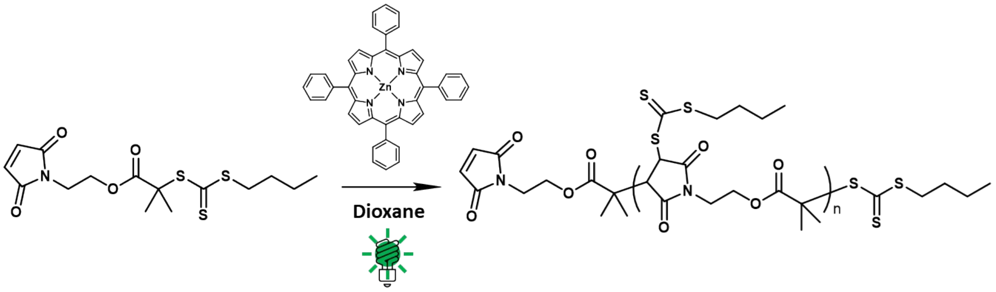
Master mix of the reaction mixture was prepared accordingly: Bifunctional monomer, **$M_2$** (870 mg, 2.43 mmol) was first charged into the vial, followed by bifunctional CTA, **$CTA_2$** (1425 mg, 2.43 mmol). Next, 4.856 ml tetrachloroethane (TCE) was added to target molar concentration of $[M_2]_0$:$[CTA_2]_0$ = 0.5 : 0.5 M (without consideration for the volume taken up by non-solvent components). The vial was then equipped with a stir bar and rubber septum, which was gently heated to 40 °C until $M_2$ was completely solubilized. 2.0 ml was aliquoted into a 3.7 ml scintillation vial per reaction. These were then purged with argon for 10 minutes and then placed inside the photoreactor. Monomer conversion (*p*) was determined by $^1$H-NMR spectroscopy by integrating C*H*=C*H* maleimide ring proton(s) relative to C*H*$_3$ at 0.96 ppm on the Z-group of the CTA.

## Procedure for $A_2$ + $B_2$ PET-RAFT step-growth polymerization:



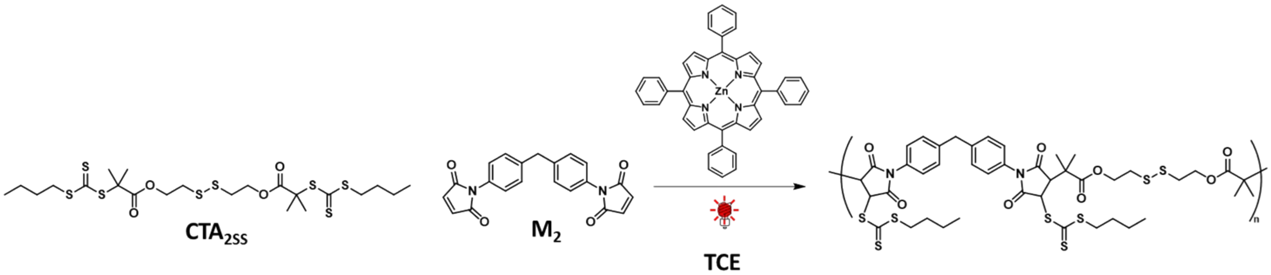
Master mix of the reaction mixture was prepared accordingly: **$M_2$** (2000 mg, 5.58 mmol) was first charged into the vial, followed by **$CTA_2$** (3275.9 mg, 5.58 mmol). Next, 9.270 ml TCE and 1.892 ml zinc tetraphenylporphyrin (ZnTPP) stock solution (20 mg/ml in TCE) were added to target molar concentration of $[M_2]_0$:$[CTA_2]_0$:$[ZnTPP]_0$ = 0.5 : 0.5 : 0.005 M (without consideration for the volume taken up by non-solvent components). The vial was then equipped with a stir bar and rubber septum, which was gently heated to 40 °C until $M_2$ was completely solubilized. 2.0 ml was aliquoted into a 3.7 ml scintillation vial per reaction. These were then purged with argon for 10 minutes and then placed inside the photoreactor. Monomer conversion (*p*) was determined by $^1$H-NMR spectroscopy by integrating C*H*=C*H* maleimide ring proton(s) relative to C*H*$_3$ at 0.96 ppm on the Z-group of the CTA.

**Procedure for AB PET-RAFT step-growth polymerization:**



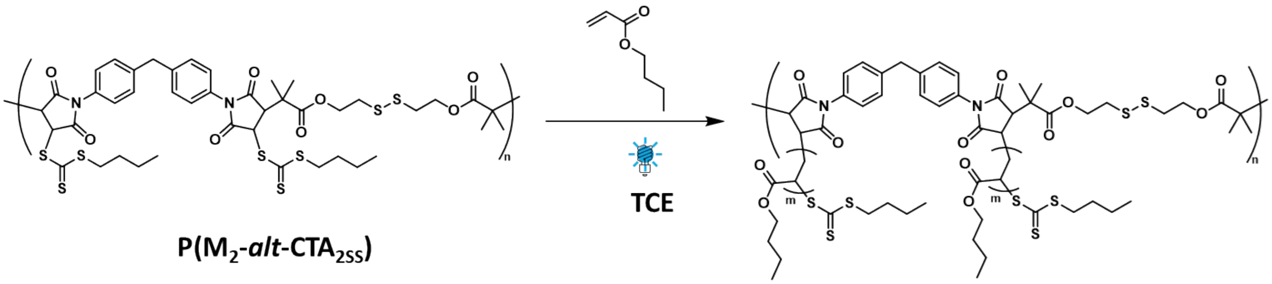
**MCTA** (250 mg, 0.698 mmol) was first charged into 3.7 ml scintillation vial, followed by 0.214 ml dioxane and 0.451 ml zinc tetraphenylporphyrin (ZnTPP) stock solution (5 mg/ml in dioxane) were added to target molar concentration of [**MCTA**]$_0$:[ZnTPP]$_0$ = 1 : 0.005 M (without consideration for the volume taken up by non-solvent components). The vial was then equipped with a stir bar and rubber septum. The solution was then purged with argon for 10 minutes and then placed inside the photoreactor. Monomer conversion ($p$) was determined by $^1$H-NMR spectroscopy by integrating C$H$=C$H$ maleimide ring proton(s) relative to C$H_3$ at 0.92 ppm on the Z-group of the CTA. Additional note: the dioxane was passed through aluminum oxide to remove inhibitors and peroxides (if any formed), prior to its use. ZnTPP stock solution was sonicated to assist the solubilization in dioxane and stored in absence of light.

**Procedure for $A_2$ + $B_2$ PET-RAFT step-growth polymerization with degradable backbone:**



**M$_2$** (250 mg, 0.698 mmol) was first charged into 3.7 ml scintillation vial, followed by disulfide tethered bifunctional CTA, **CTA$_{2SS}$** (434.6 mg, 0.698 mmol). Next, 1.159 ml TCE and 0.237 ml zinc tetraphenylporphyrin (ZnTPP) stock solution (20 mg/ml in TCE) were added to target molar concentration of [**M$_2$**]$_0$:[**CTA$_{2SS}$**]$_0$:[ZnTPP]$_0$ = 0.5 : 0.5 : 0.005 M (without consideration for the volume taken up by non-solvent components). The vial was then equipped with a stir bar and rubber septum, which was gently heated to 40 °C until M$_2$ was completely solubilized. The solution was then purged with argon for 10 minutes and then placed inside the photoreactor. Monomer conversion ($p$) was determined by $^1$H-NMR spectroscopy by integrating C$H$=C$H$ maleimide ring proton(s) relative to C$H_3$ at 0.96 ppm on the Z-group of the CTA. For purification, the reaction mixture was diluted in approximately equal volume of chloroform and precipitated directly into 50 ml centrifuge tube with diethyl ether and collected with centrifugation. After discarding the supernatant, the polymers were redissolved in chloroform and then reprecipitated again in diethyl ether twice.

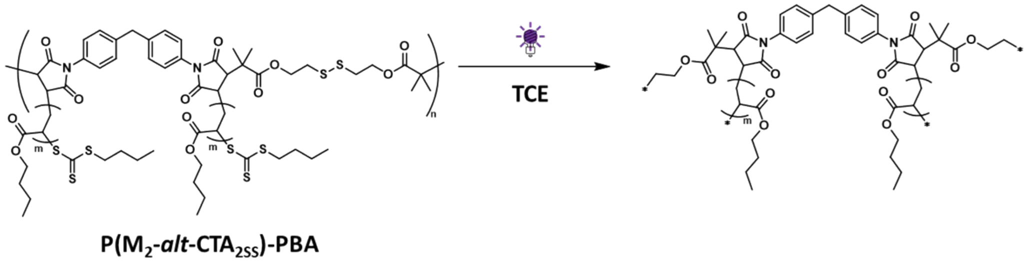
**Procedure for grafting from degradable backbone with RAFT-iniferter polymerization:**



**P($M_2$-*alt*-$\text{CTA}_{2SS}$)**

Isolated P($M_2$-*alt*-$\text{CTA}_{2SS}$) (23 mg, 0.098 mmol) was charged into a 3.7 ml scintillation vial, followed by n-butyl acrylate (BA) (250 mg, 3.90 mmol). Next, 0.386 ml dioxane was targeting molar concentrations of $[M]_0$ : $[CTA]_0$: = 3 M :0.075 M (taking into account volume of the monomer). The vial was then equipped with a magnetic stir bar and secured by rubber septum. The solution was purge with argon for 10 minutes, prior to placing the reaction mixture in a photoreactor ~~an oil bath set to 65°C~~. After 1 hour the monomer conversion reached 20 % and the polymer was isolated by precipitating into methanol with few drops of water.

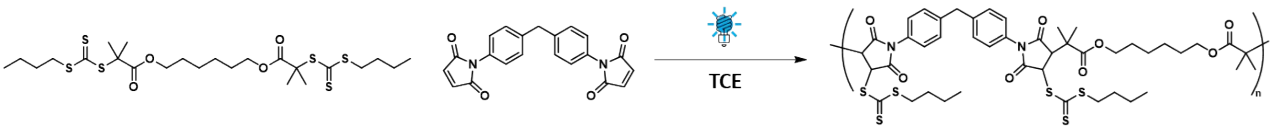
**Procedure for brush backbone degradation with UV light:**



**P($M_2$-*alt*-$\text{CTA}_{2SS}$)-PBA**

Isolated P($M_2$-*alt*-$\text{CTA}_{2SS}$)-PBA (5.9 mg, 0.74 µmol) was charged into a 3.7 ml scintillation vial, followed by 0.59 ml THF. The vial was then equipped with a magnetic stir bar and secured by rubber septum. The solution was purged with argon for 10 minutes, prior to placing the reaction mixture in an ultraviolet light photoreactor overnight for 18.5 hours.

**Table S1**: Kinetic analysis of $A_2$+$B_2$ RAFT-Iniferter step-growth polymerization using blue lights



| Time (hr) [a] | $p$ [b] | $M_{w,th}$ [c] | $M_w$ [d] | $M_w/M_n$ [d] | $M_z/M_w$ [d] |
|---|---|---|---|---|---|
| 0 | 0 | 473 | 400 | 1.01 | 1.01 |
| 0.5 | 0.416 | 1.1k | 1.2k | 1.64 | 1.79 |
| 1.0 | 0.530 | 1.5k | 1.6k | 1.69 | 1.76 |
| 2.0 | 0.739 | 3.2k | 2.8k | 2.03 | 1.84 |
| 4.0 | 0.885 | 7.8k | 7.0k | 2.53 | 1.96 |
| 8.0 | 0.951 | 18.7k | 11.3k | 2.72 | 1.95 |
| 16.0 | 0.977 | 40.7k | 20.1k | 3.49 | 2.20 |
| 48.0 | 0.981 | 50.4k | 16.0k | 3.37 | 2.16 |

[a] Duration of the polymerization. [b] Monomer conversion determined by $^1$H-NMR. [c] Theoretical value according to Flory's equation.[1] [d] Determined by THF-SEC analysis using polystyrene calibration.

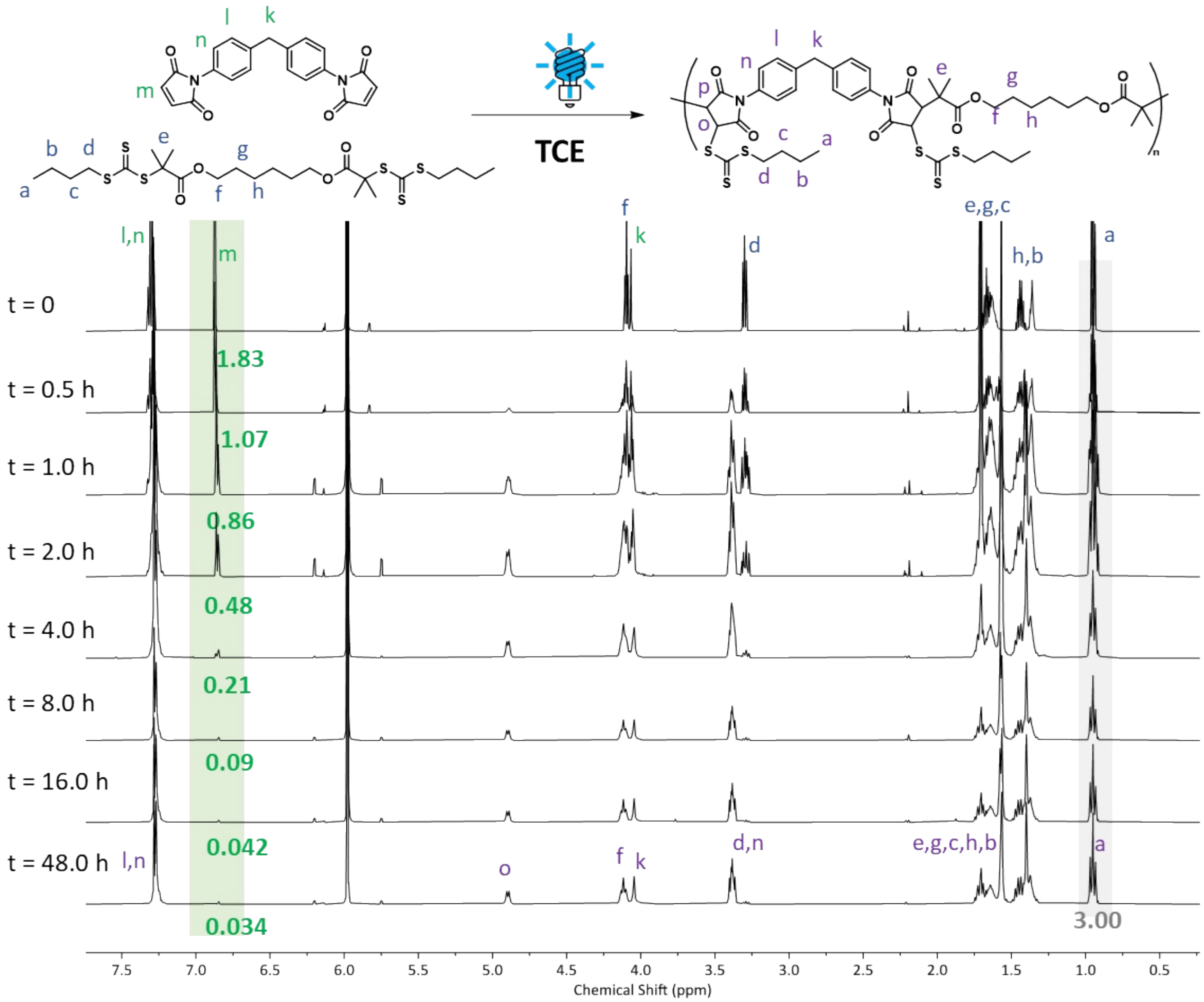
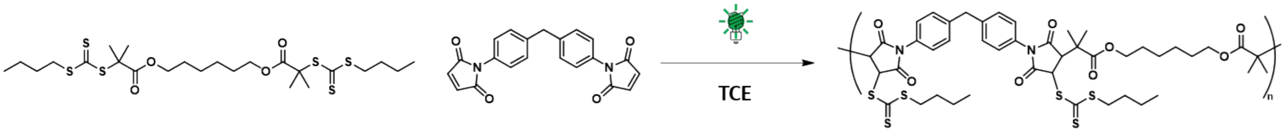


**Figure S2**: $^1$H-NMR ($CDCl_3$, 400 MHz) analysis of $A_2$+$B_2$ RAFT-iniferter step-growth polymerization using blue light. The numbers correspond to relative integral of the monomer peak (green region) with respect to the Z-group $CH_3$ (grey region) as 3 for reference.

**Table S2**: Kinetic analysis of $A_2$+$B_2$ RAFT-Iniferter step-growth polymerization using green lights



| Time (hr) [a] | $p$ [b] | $M_{w,th}$ [c] | $M_w$ [d] | $M_w/M_n$ [d] | $M_z/M_w$ [d] |
|---|---|---|---|---|---|
| 0 | 0 | 473 | 400 | 1.01 | 1.01 |
| 0.5 | 0.403 | 1.1k | 756 | 1.26 | 1.32 |
| 1.0 | 0.491 | 1.4k | 1.2k | 1.45 | 1.45 |
| 2.0 | 0.721 | 2.9k | 2.2k | 1.76 | 1.54 |
| 4.0 | 0.874 | 7.0k | 5.4k | 2.05 | 1.61 |
| 8.0 | 0.956 | 21.1k | 11.6k | 2.39 | 1.62 |
| 16.0 | 0.975 | 37.9k | 15.5k | 2.74 | 1.70 |
| 48.0 | 0.985 | 61.2k | 16.0k | 2.96 | 1.77 |

[a] Duration of the polymerization. [b] Monomer conversion determined by $^1$H-NMR. [c] Theoretical value according to Flory's equation.[1] [d] Determined by THF-SEC analysis using polystyrene calibration.

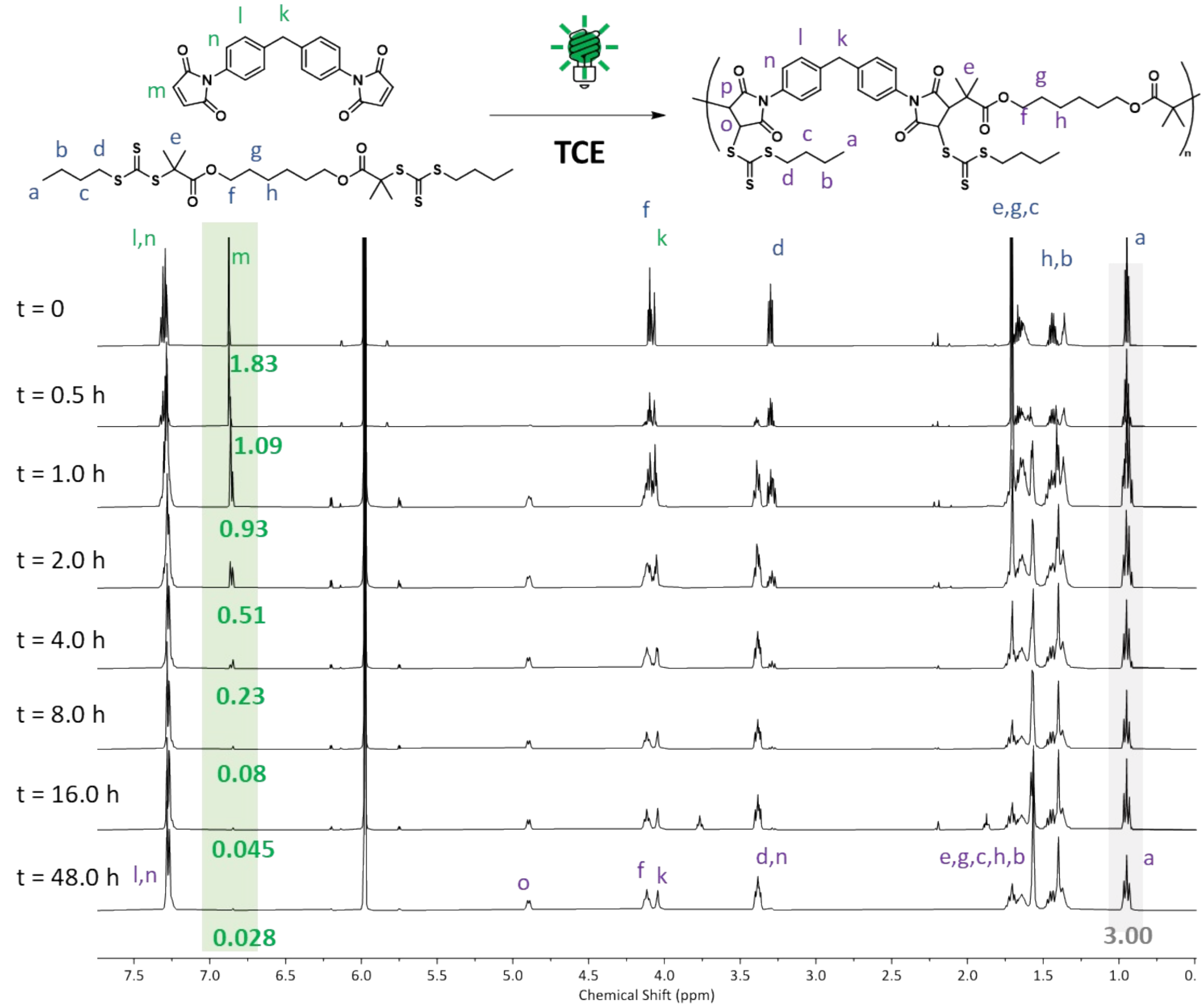
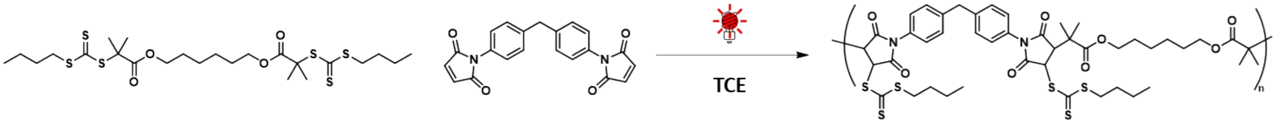


**Figure S3**: $^1$H-NMR ($CDCl_3$, 400 MHz) analysis of $A_2$+$B_2$ RAFT-iniferter step-growth polymerization using green light. The numbers correspond to relative integral of the monomer peak (green region) with respect to the Z-group C$H_3$ (grey region) as 3 for reference.

**Table S3**: Kinetic analysis of $A_2$+$B_2$ RAFT-Iniferter step-growth polymerization using red lights



| Time (hr) [a] | $p$ [b] | $M_{w,th}$ [c] | $M_w$ [d] | $M_w/M_n$ [d] | $M_z/M_w$ [d] |
|---|---|---|---|---|---|
| 0 | 0 | 473 | 400 | 1.01 | 1.01 |
| 0.5 | 0.018 | 489 | 404 | 1.01 | 1.01 |
| 1.0 | 0.025 | 497 | 521 | 1.21 | 1.24 |
| 2.0 | 0.141 | 627 | 408 | 1.01 | 1.01 |
| 4.0 | 0.310 | 897 | 831 | 1.30 | 1.36 |
| 8.0 | 0.501 | 1.4k | 1.3k | 1.48 | 1.48 |
| 16.0 | 0.656 | 2.3k | 2.0k | 1.68 | 1.57 |
| 48.0 | 0.760 | 3.5k | 3.1k | 1.88 | 1.63 |

[a] Duration of the polymerization. [b] Monomer conversion determined by $^1$H-NMR. [c] Theoretical value according to Flory's equation.[1] [d] Determined by THF-SEC analysis using polystyrene calibration.

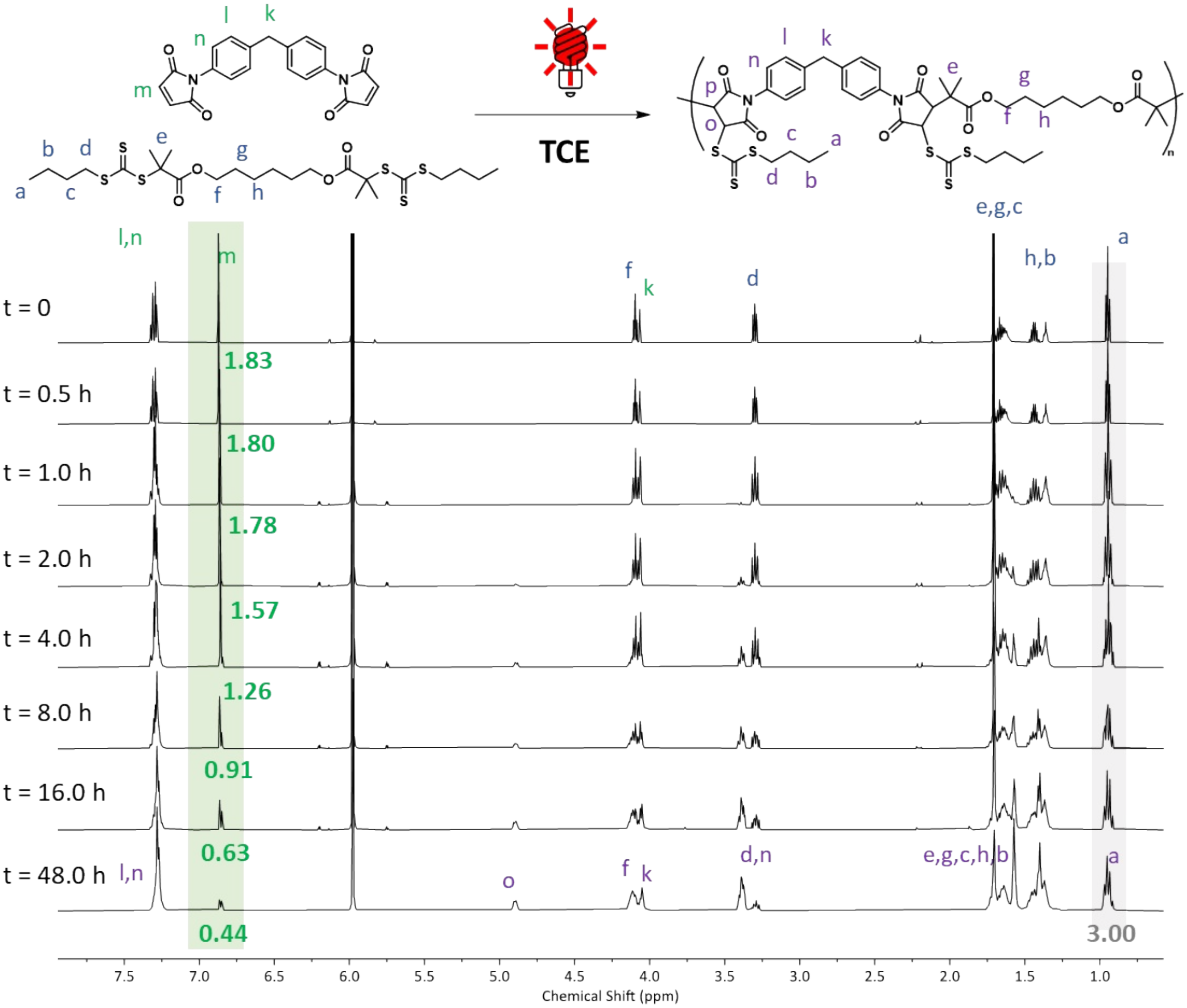


**Figure S4**: $^1$H-NMR ($CDCl_3$, 400 MHz) analysis of $A_2$+$B_2$ RAFT-iniferter step-growth polymerization using red light. The numbers correspond to relative integral of the monomer peak (green region) with respect to the Z-group $CH_3$ (grey region) as 3 for reference.

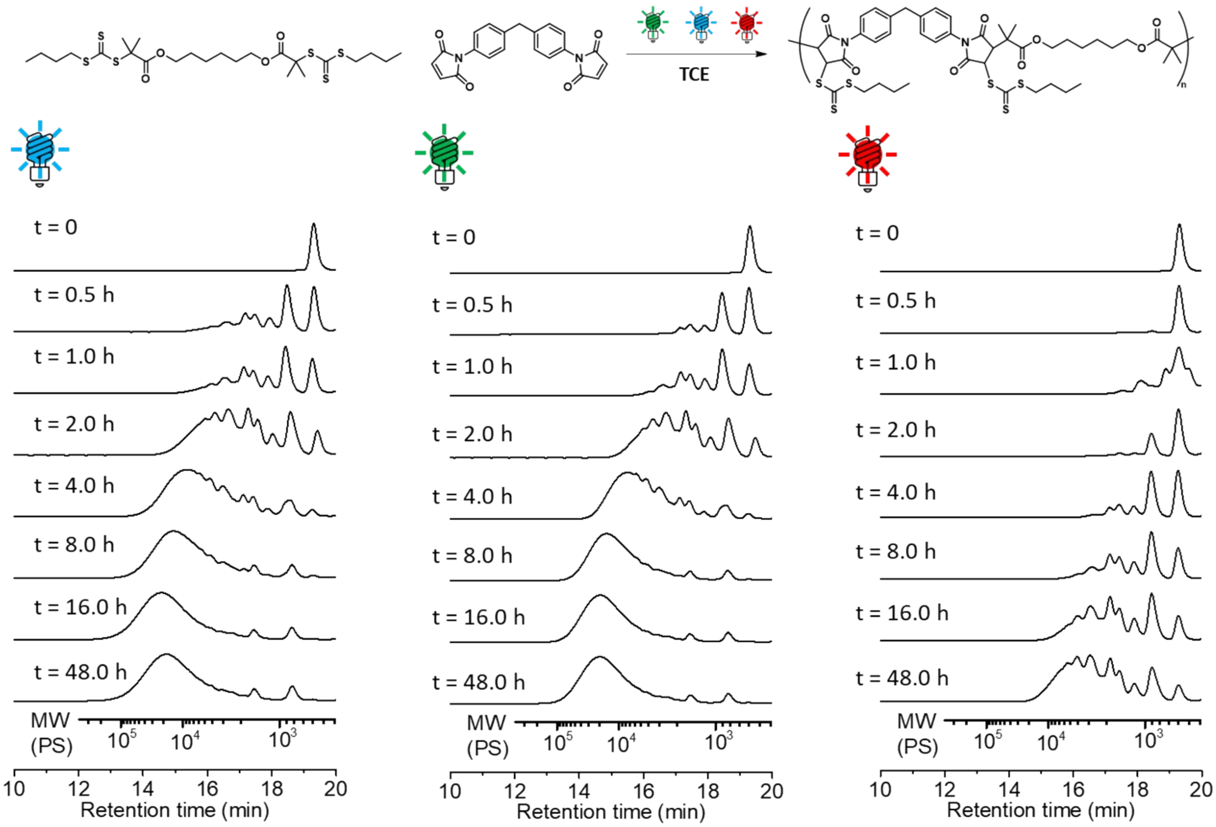
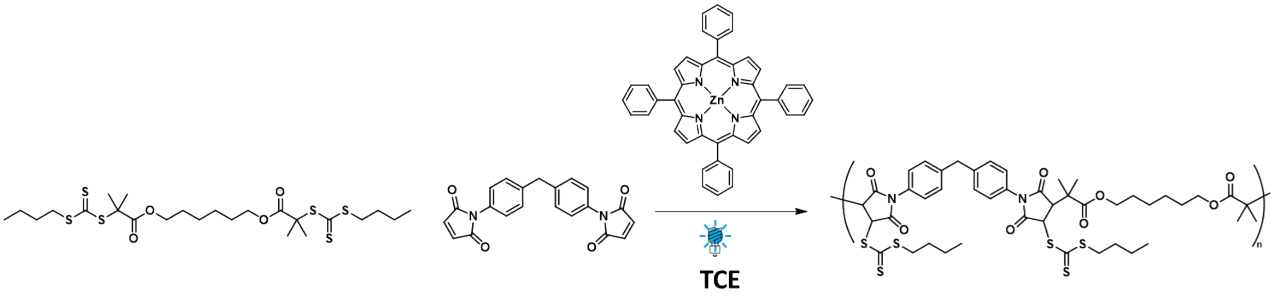


**Figure S5**: THF-SEC (normalized dRI) analysis of $A_2$+$B_2$ RAFT-iniferter step-growth polymerization with blue (left), green (middle) and red (right). The molecular weight is relative to polystyrene calibration.

**Table S4**: Kinetic analysis of $A_2$+$B_2$ PET-RAFT step-growth polymerization using blue lights



| Time (hr) [a] | $p$ [b] | $M_{w,th}$ [c] | $M_w$ [d] | $M_w/M_n$ [d] | $M_z/M_w$ [d] |
|---|---|---|---|---|---|
| 0 | 0 | 473 | 410 | 1.06 | 1.06 |
| 0.5 | 0.189 | 693 | 631 | 1.32 | 1.53 |
| 1.0 | 0.362 | 1.0k | 473 | 1.11 | 1.15 |
| 2.0 | 0.452 | 1.3k | 1421 | 2.03 | 2.18 |
| 4.0 | 0.636 | 2.1k | 2947 | 2.74 | 2.62 |
| 8.0 | 0.753 | 3.4k | 4489 | 2.97 | 2.45 |
| 16.0 | 0.872 | 6.9k | 9038 | 3.56 | 2.66 |
| 24.0 | 0.935 | 14.1k | 13254 | 4.20 | 3.68 |
| 48.0 | 0.962 | 24.4k | 17523 | 4.02 | 2.35 |

[a] Duration of the polymerization. [b] Monomer conversion determined by $^1$H-NMR. [c] Theoretical value according to Flory's equation.[1] [d] Determined by THF-SEC analysis using polystyrene calibration.

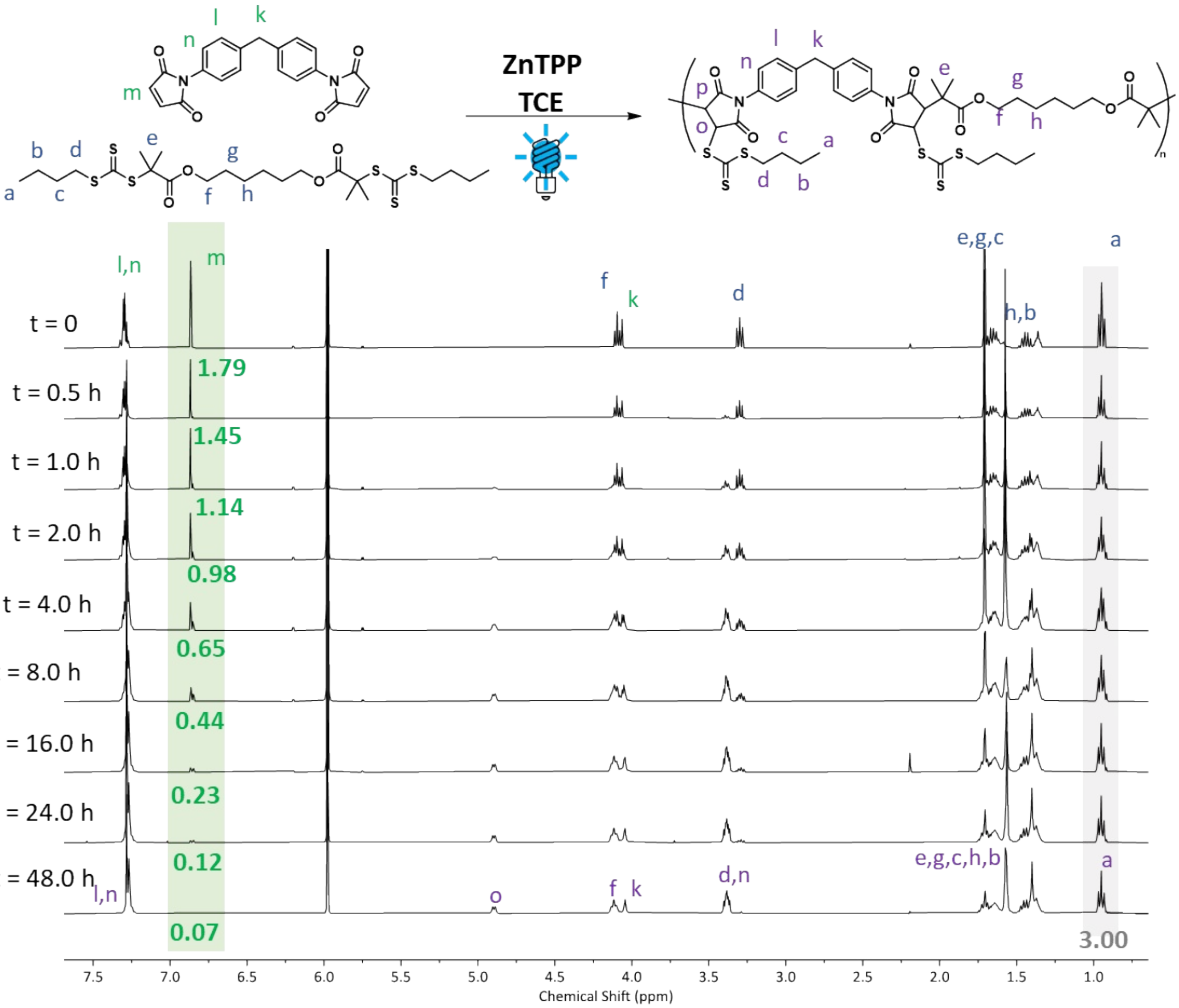
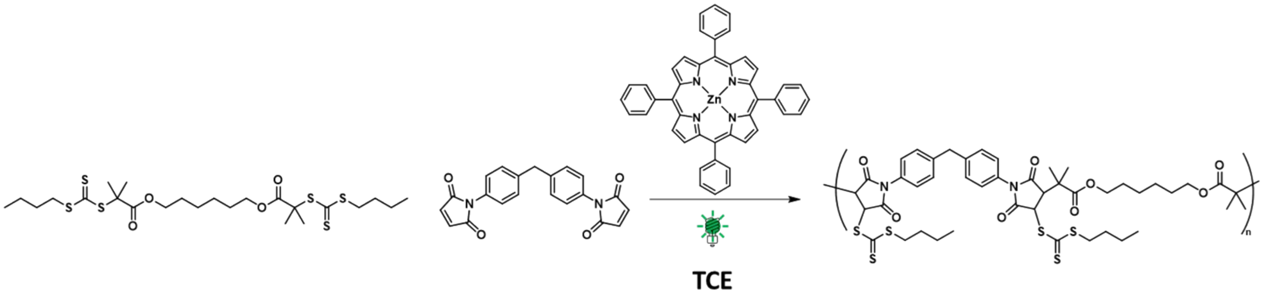


**Figure S6**: $^1$H-NMR (CDCl$_3$, 400 MHz) analysis of A$_2$+B$_2$ PET-RAFT step-growth polymerization using blue light. The numbers correspond to relative integral of the monomer peak (green region) with respect to the Z-group C$H_3$ (grey region) as 3 for reference.

**Table S5**: Kinetic analysis of $A_2$+$B_2$ PET-RAFT step-growth polymerization using green lights



| Time (hr) [a] | $p$ [b] | $M_{w,th}$ [c] | $M_w$ [d] | $M_w/M_n$ [d] | $M_z/M_w$ [d] |
|---|---|---|---|---|---|
| 0 | 0 | 473 | 400 | 1.03 | 1.03 |
| 0.5 | 0.105 | 583 | 499 | 1.16 | 1.20 |
| 1.0 | 0.206 | 718 | 649 | 1.28 | 1.34 |
| 2.0 | 0.416 | 1.1k | 1.0k | 1.48 | 1.50 |
| 4.0 | 0.598 | 1.9k | 1.7k | 1.67 | 1.63 |
| 8.0 | 0.722 | 2.9k | 3.9k | 2.07 | 1.75 |
| 16.0 | 0.932 | 13.5k | 10.7k | 3.17 | 2.76 |
| 24.0 | 0.964 | 25.9k | 13.8k | 3.11 | 2.49 |
| 48.0 | 0.978 | 42.4k | 24.2k | 4.72 | 3.12 |

[a] Duration of the polymerization. [b] Monomer conversion determined by $^1$H-NMR. [c] Theoretical value according to Flory's equation.[1] [d] Determined by THF-SEC analysis using polystyrene calibration.

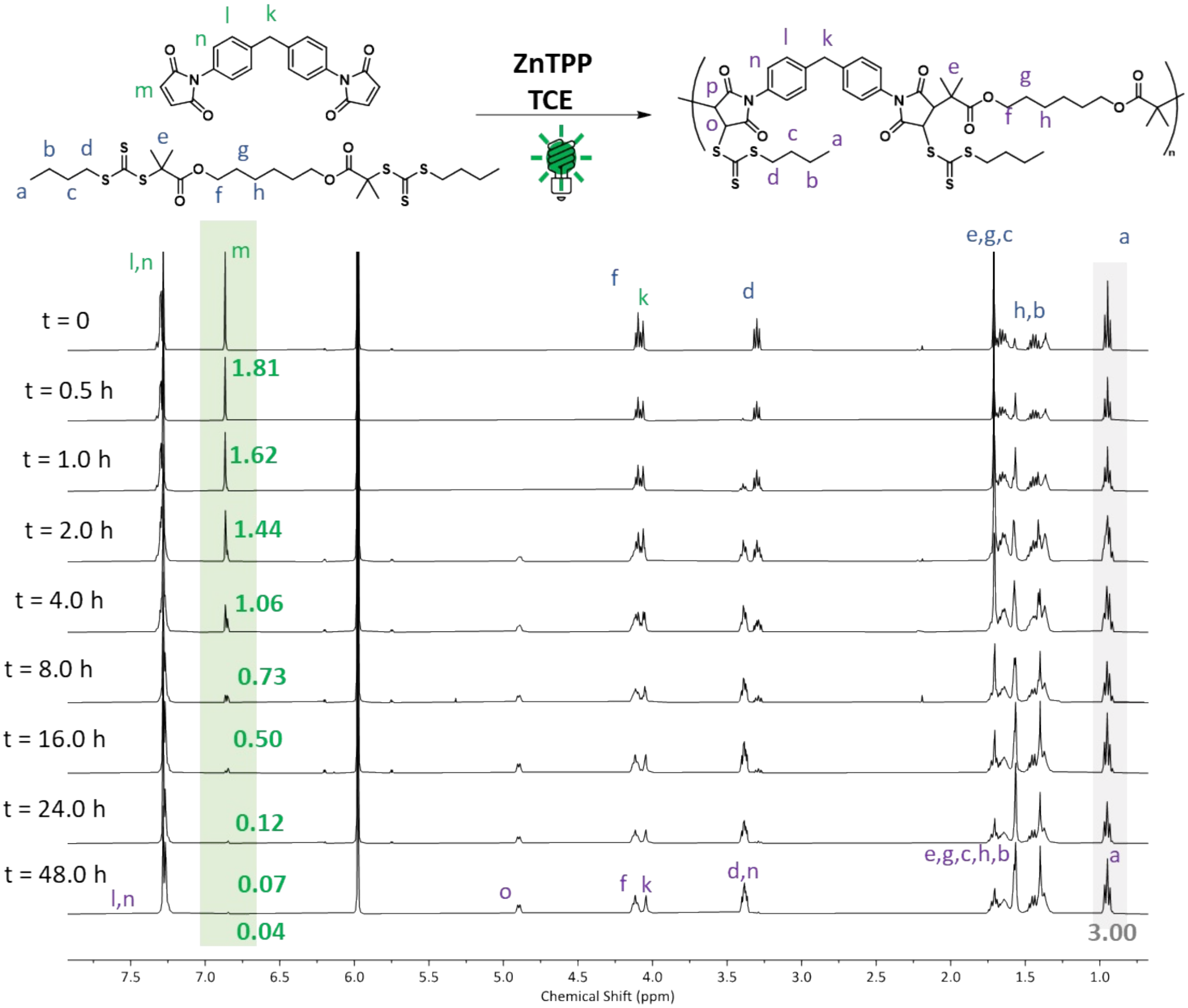
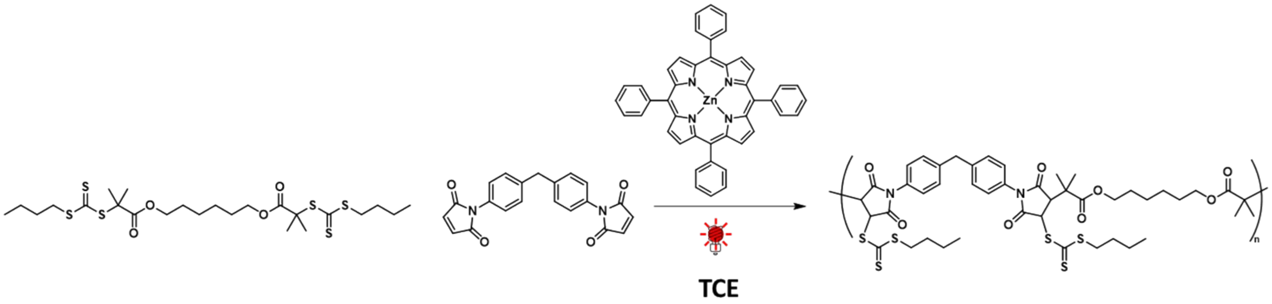


**Figure S7**: $^1$H-NMR (CDCl$_3$, 400 MHz) analysis of A$_2$+B$_2$ PET-RAFT step-growth polymerization using green light. The numbers correspond to relative integral of the monomer peak (green region) with respect to the Z-group C$H_3$ (grey region) as 3 for reference.

**Table S6**: Kinetic analysis of $A_2$+$B_2$ PET-RAFT step-growth polymerization using red lights



| Time (hr) [a] | $p$ [b] | $M_{w,th}$ [c] | $M_w$ [d] | $M_w/M_n$ [d] | $M_z/M_w$ [d] |
|---|---|---|---|---|---|
| 0 | 0 | 473 | 410 | 1.06 | 1.06 |
| 0.5 | 0.014 | 486 | 405 | 1.04 | 1.02 |
| 1.0 | 0.109 | 588 | 516 | 1.14 | 1.18 |
| 2.0 | 0.185 | 687 | 742 | 1.30 | 1.33 |
| 4.0 | 0.485 | 1.4k | 1.3k | 1.56 | 1.51 |
| 8.0 | 0.809 | 4.5k | 3.9k | 2.01 | 1.67 |
| 16.0 | 0.878 | 7.2k | 11.4k | 2.80 | 2.07 |
| 24.0 | 0.963 | 24.8k | 18.4k | 3.18 | 2.64 |
| 48.0 | 0.990 | 93.4k | 27.3k | 3.98 | 2.33 |

[a] Duration of the polymerization. [b] Monomer conversion determined by $^1$H-NMR. [c] Theoretical value according to Flory's equation.[1] [d] Determined by THF-SEC analysis using polystyrene calibration.

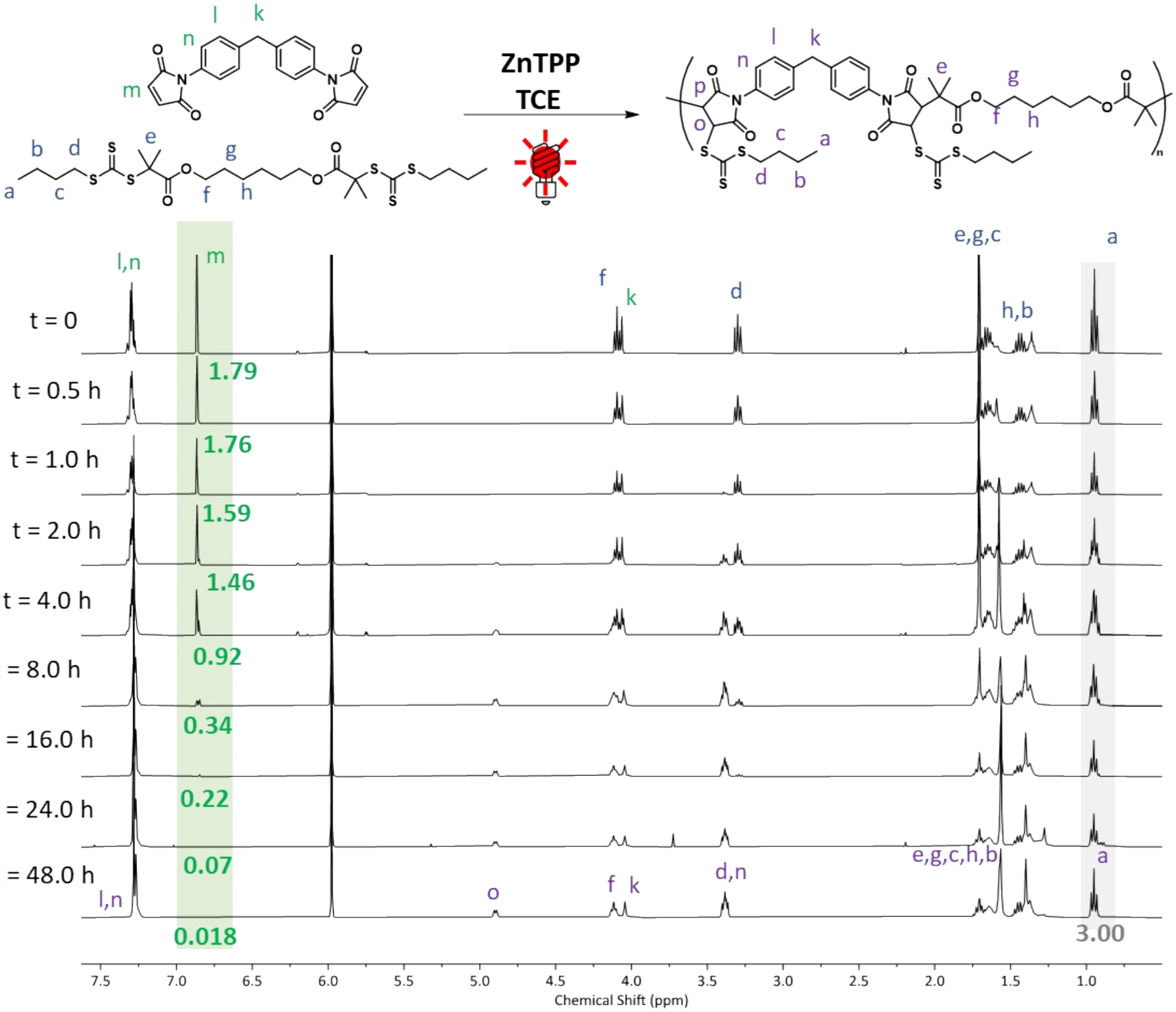


**Figure S8**: $^1$H-NMR ($CDCl_3$, 400 MHz) analysis of $A_2$+$B_2$ PET-RAFT step-growth polymerization using red light. The numbers correspond to relative integral of the monomer peak (green region) with respect to the Z-group $CH_3$ (grey region) as 3 for reference.

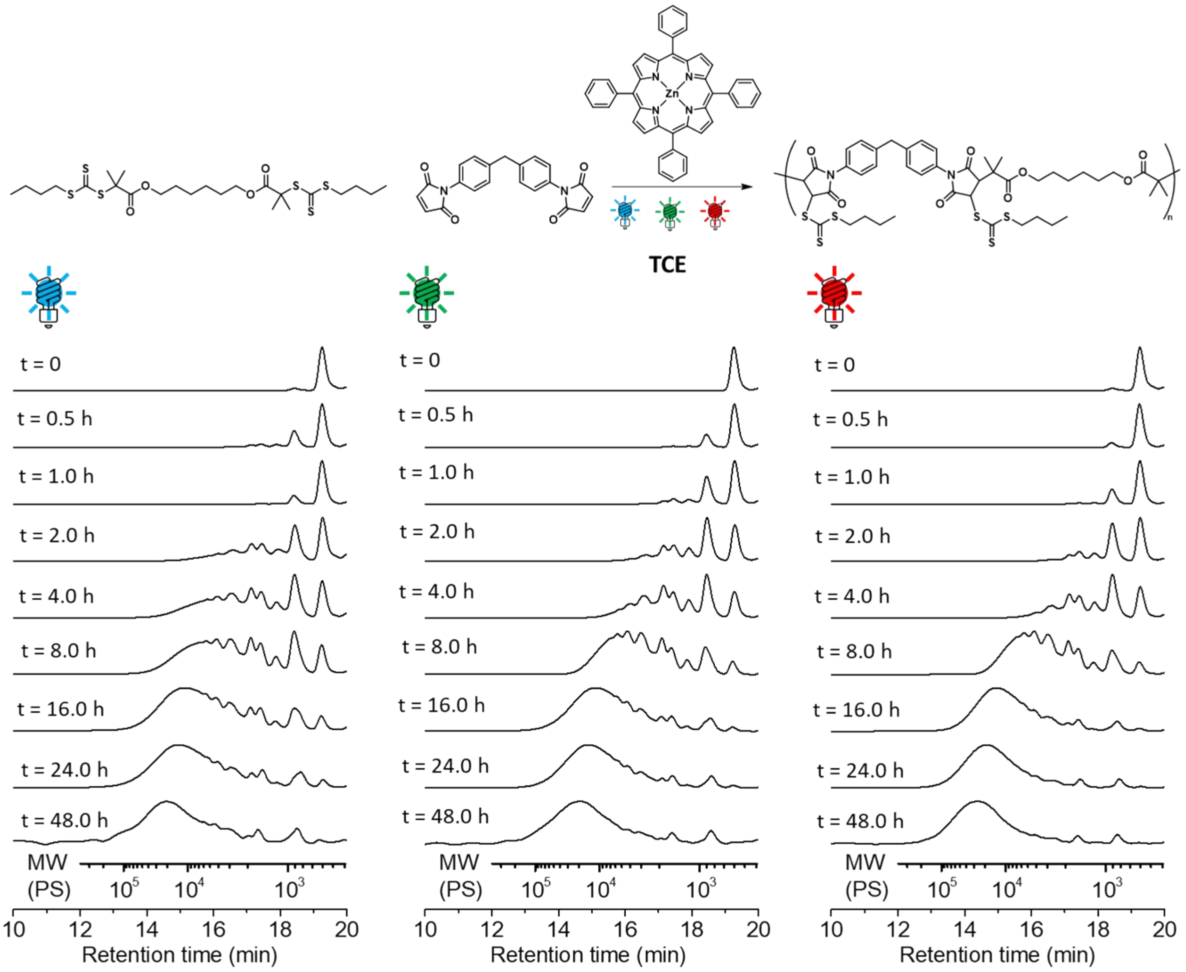
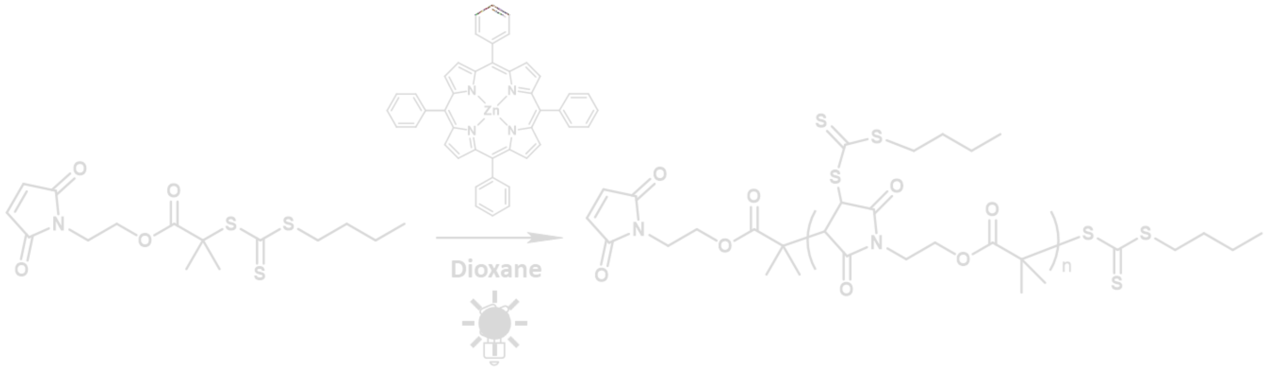


**Figure S9**: THF-SEC (normalized dRI) analysis of $A_2$+$B_2$ PET-RAFT step-growth polymerization with blue (left), green (middle) and red (right). The molecular weight is relative to polystyrene calibration.

**Table S7**: Kinetic analysis of AB PET-RAFT step-growth polymerization using green lights



| Time (hr) [a] | $p$ [b] | $M_{\mathrm{w,th}}$ [c] | $M_{\mathrm{w}}$ [d] | $M_{\mathrm{w}}/M_{\mathrm{n}}$ [d] | $M_{\mathrm{z}}/M_{\mathrm{w}}$ [d] | $M_{z,th}$ [c] | $M_{\mathrm{z}}$ [d] |
|---|---|---|---|---|---|---|---|
| 0 | 0 | 380 | 260 | 1.01 | 1.01 | 380 | 260 |
| 0.5 | 0.13 | 490 | 350 | 1.16 | 1.26 | 590 | 440 |
| 1.0 | 0.25 | 630 | 470 | 1.32 | 1.38 | 830 | 650 |
| 2.0 | 0.46 | 1.0k | 750 | 1.55 | 1.50 | 1.55 | 1.1k |
| 4.0 | 0.73 | 2.5k | 1.7k | 1.93 | 1.67 | 3.6k | 2.8k |
| 12.0 | 0.96 | 20k | 9.3k | 4.49 | 2.10 | 28k | 19.5k |
| 24.0 | 0.99 | 70k | 30k | 10.7 | 2.97 | 112k | 88.4k |

[a] Duration of the polymerization. [b] Monomer conversion determined by $^{1}$H-NMR. [c] Theoretical value according to Flory's equation.[1] [d] Determined by THF-SEC analysis using polystyrene calibration.

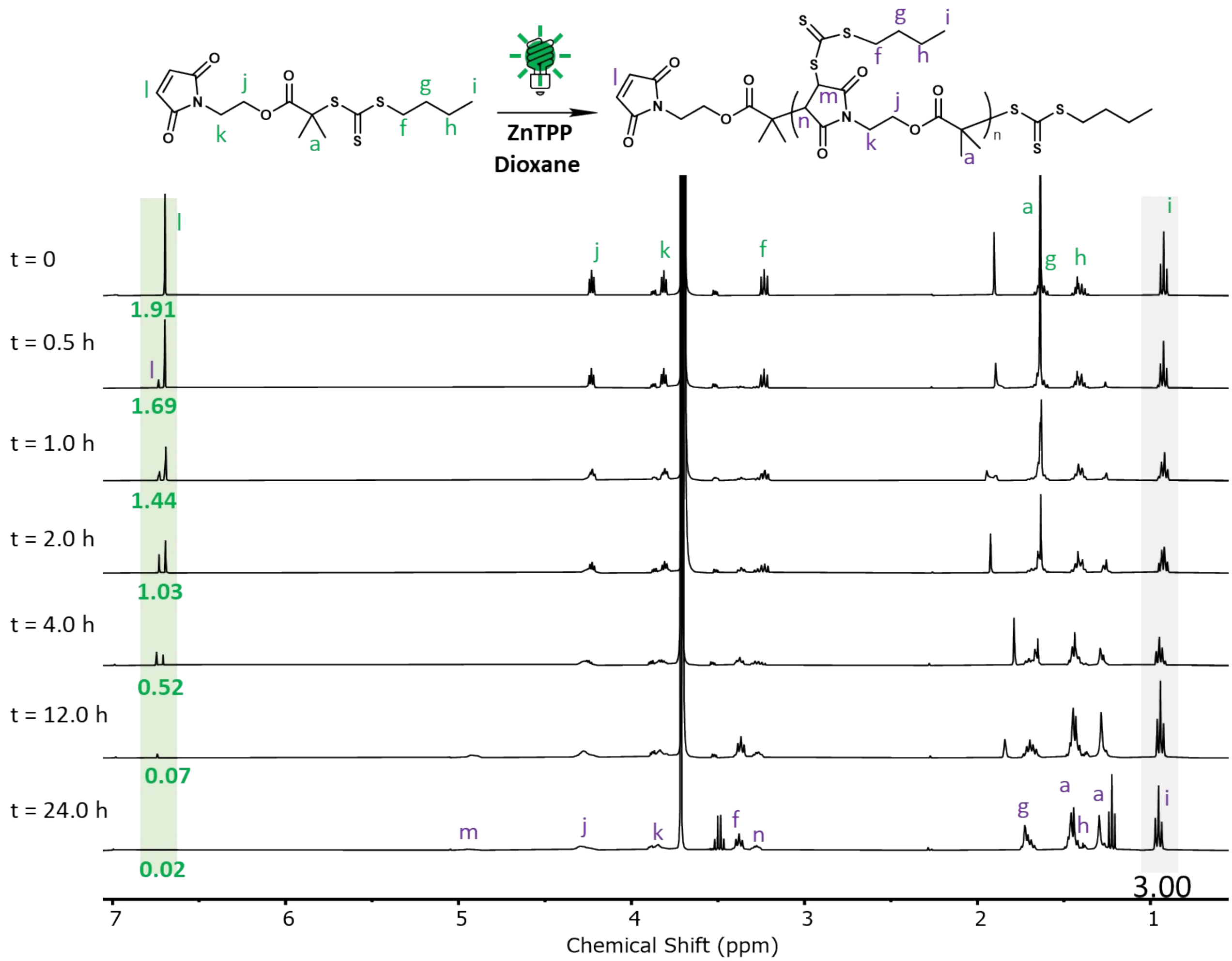


**Figure S10**: $^1$H-NMR ($CDCl_3$, 400 MHz) analysis of AB PET-RAFT step-growth polymerization using red light. The numbers correspond to relative integral of the monomer peak (green region) with respect to the Z-group C$H_3$ (grey region) as 3 for reference.

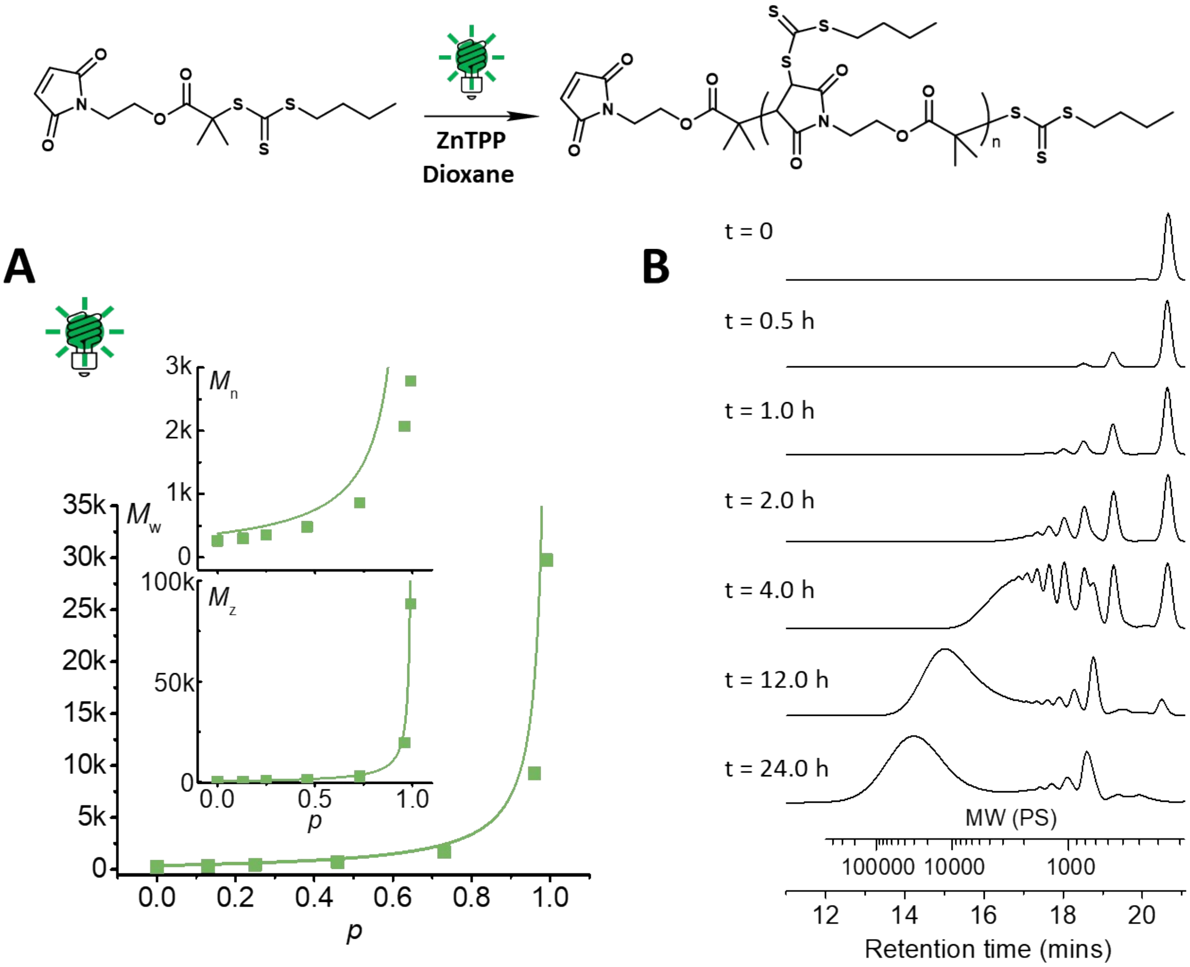
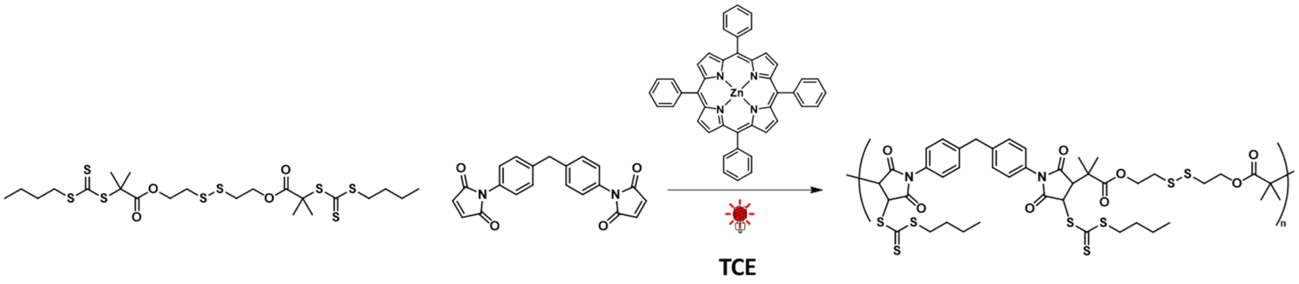


**Figure S11**: A) Evolution of molecular weight averages with conversion of AB PET-RAFT step-growth polymerization under green light **B**) THF-SEC (normalized dRI) chromatograms. The molecular weight is relative to polystyrene calibration.

**Table S8**: Kinetic analysis of $A_2$+$B_2$ PET-RAFT step-growth polymerization with degradable bifunctional CTA under red light



| Time (hr) [a] | $p$ [b] | $M_{w,th}$ [c] | $M_w$ [d] | $M_w/M_n$ [d] | $M_z/M_w$ [d] |
|---|---|---|---|---|---|
| 0 | 0 | 491 | 580 | 1.01 | 1.01 |
| 0.5 | 0.034 | 526 | 590 | 1.01 | 1.01 |
| 1.0 | 0.061 | 555 | 610 | 1.03 | 1.03 |
| 2.0 | 0.128 | 635 | 673 | 1.08 | 1.10 |
| 4.0 | 0.390 | 1.1k | 880 | 1.15 | 1.21 |
| 8.0 | 0.476 | 1.4k | 1.2k | 1.29 | 1.36 |
| 16.0 | 0.755 | 3.5k | 2.5k | 1.64 | 1.58 |
| 24.0 | 0.870 | 7.1k | 5.5k | 2.03 | 1.66 |
| 48.0 | 0.991 | 110k | 24.1k | 3.24 | 2.41 |

[a] Duration of the polymerization. [b] Monomer conversion determined by $^1$H-NMR. [c] Theoretical value according to Flory's equation.[1] [d] Determined by THF-SEC analysis using polystyrene calibration.

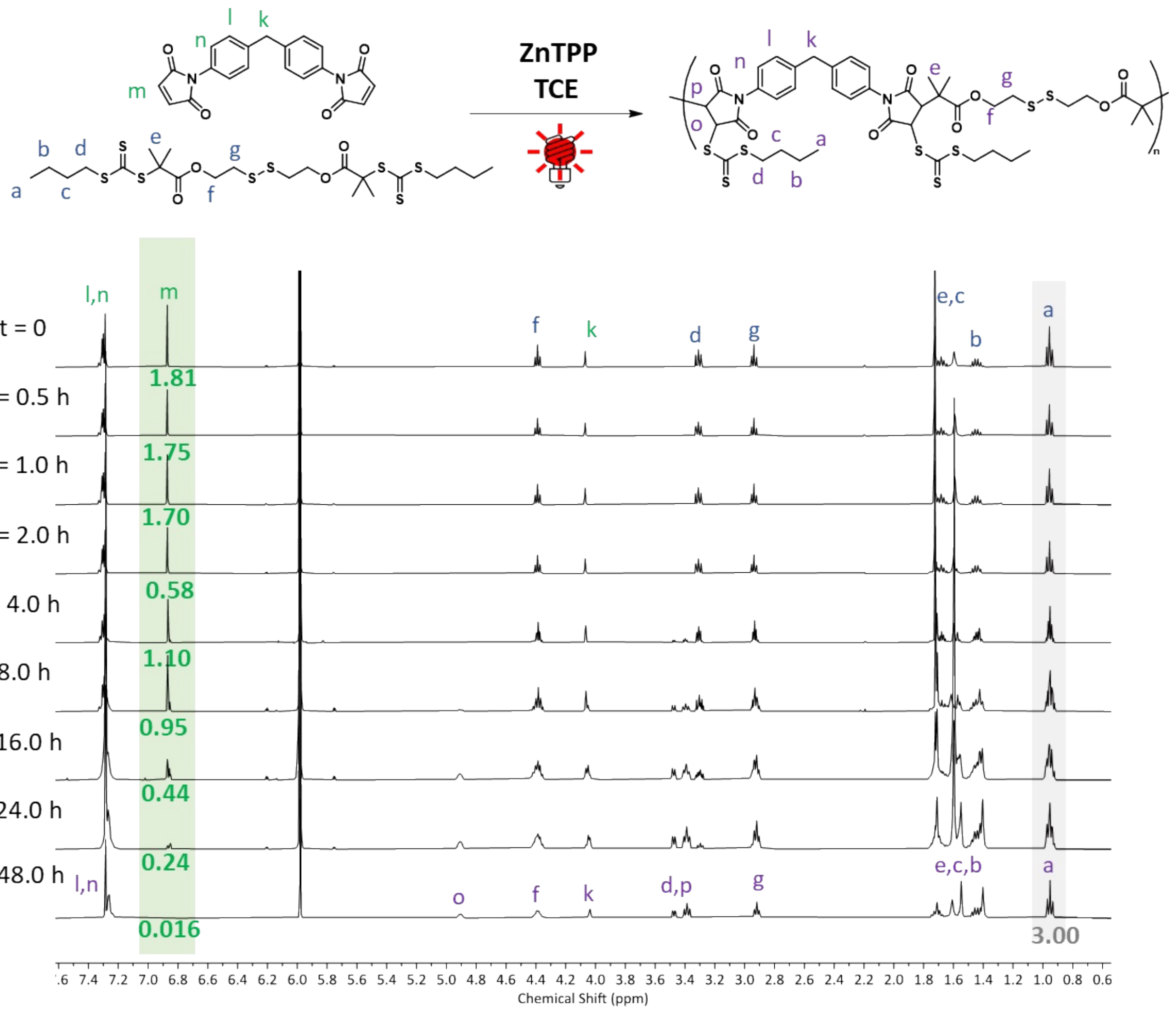


**Figure S12**: $^1$H-NMR (CDCl$_3$, 400 MHz) analysis of A$_2$+B$_2$ PET-RAFT step-growth polymerization using red light with degradable bifunctional CTA. The numbers correspond to relative integral of the monomer peak (green region) with respect to the Z-group C$H_3$ (grey region) as 3 for reference.

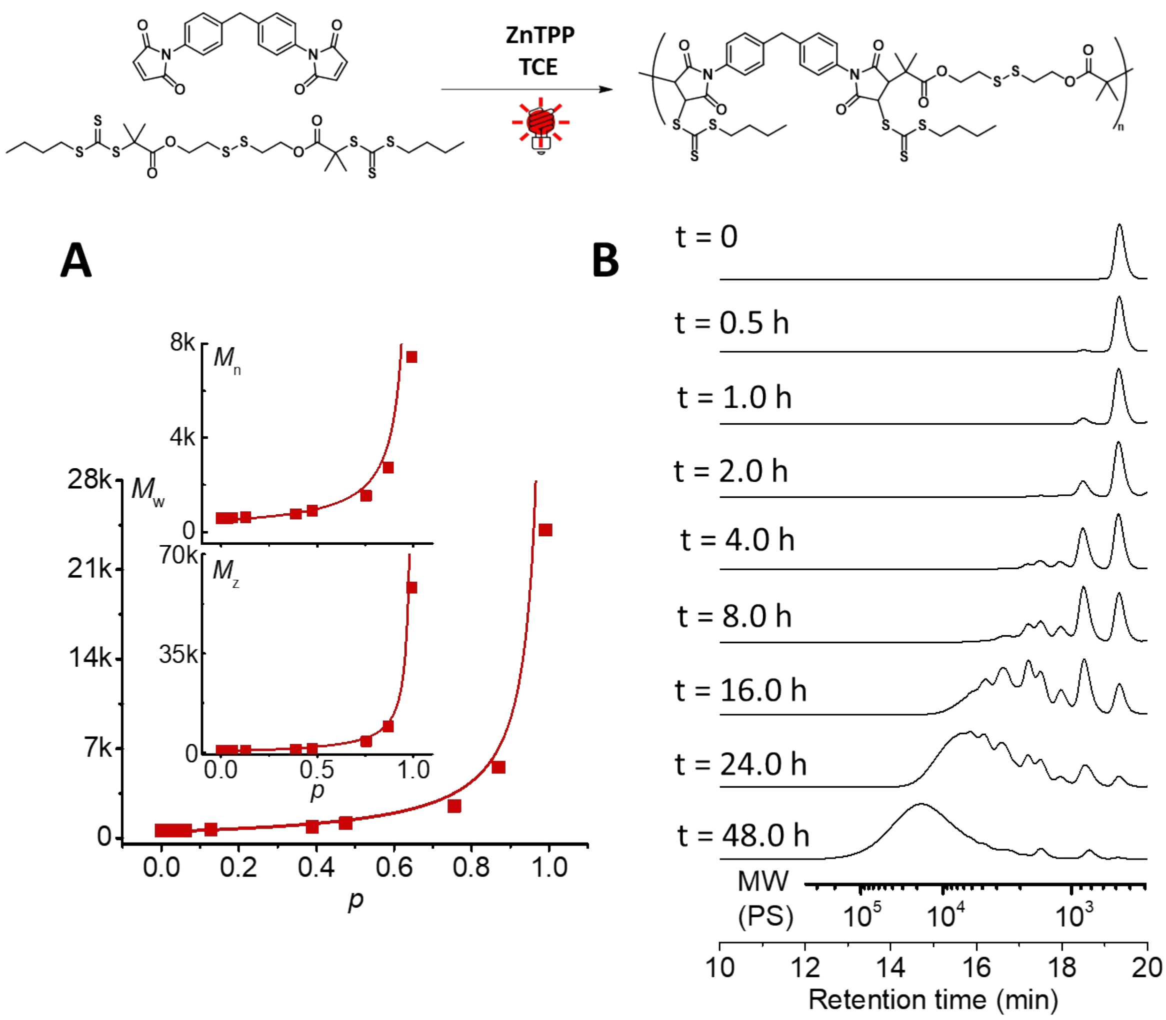


**Figure S13**: A) Evolution of molecular weight averages with conversion of $A_2$+$B_2$ PET-RAFT step-growth polymerization under red light with degradable bifunctional CTA **B**) THF-SEC (normalized dRI) chromatograms. The molecular weight is relative to polystyrene calibration.

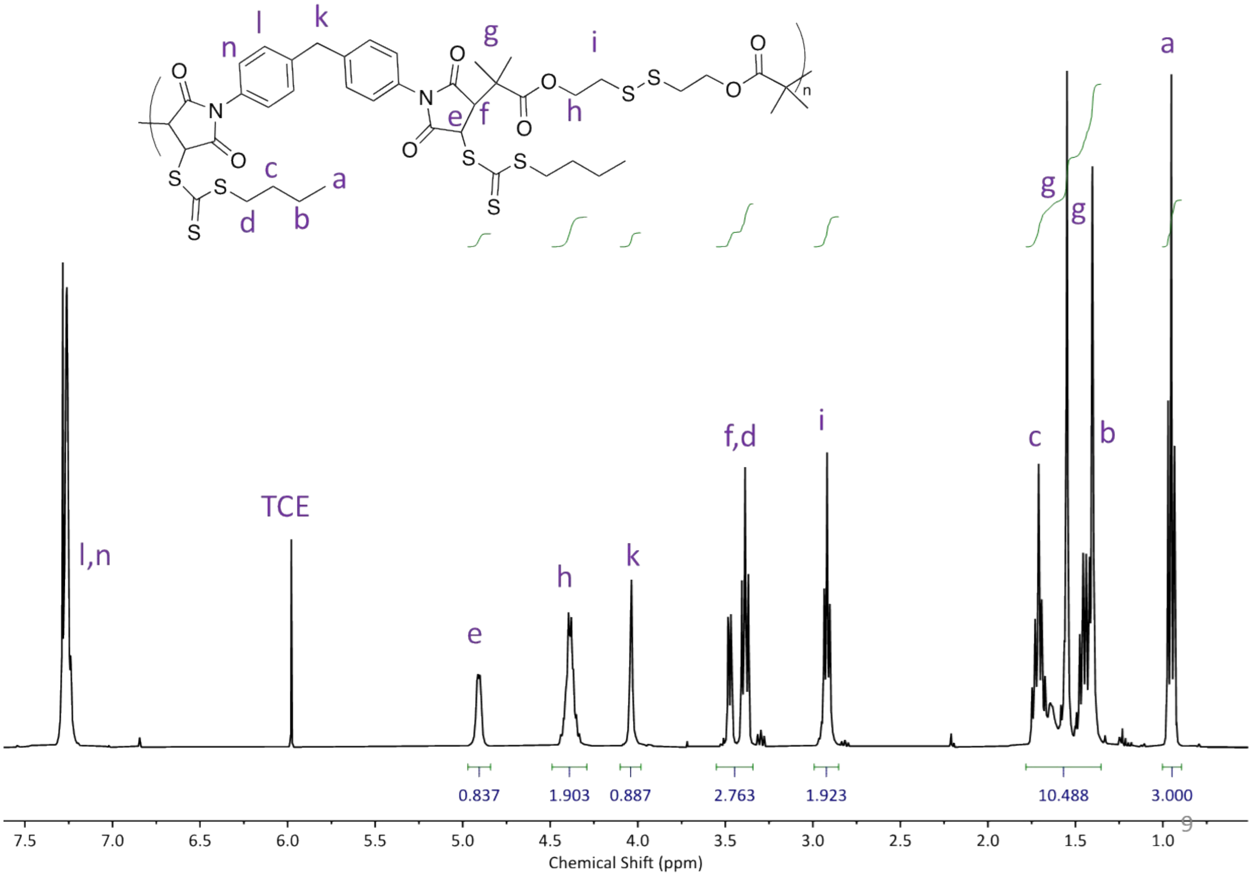


**Figure S14**: $^1$H-NMR ($CDCl_3$, 400 MHz) of isolated P(**M$_2$**-*alt*-**CTA$_{2SS}$**).

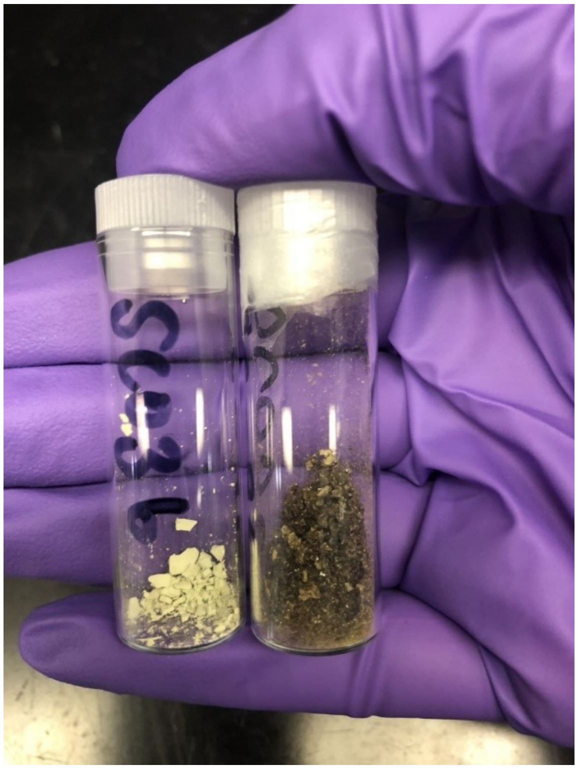


**Figure S15**: Before (left) and after (right) passing P($\mathbf{M_2}$-*alt*-$\mathbf{CTA_{2SS}}$) through aluminum oxide to remove some of the ZnTPP.

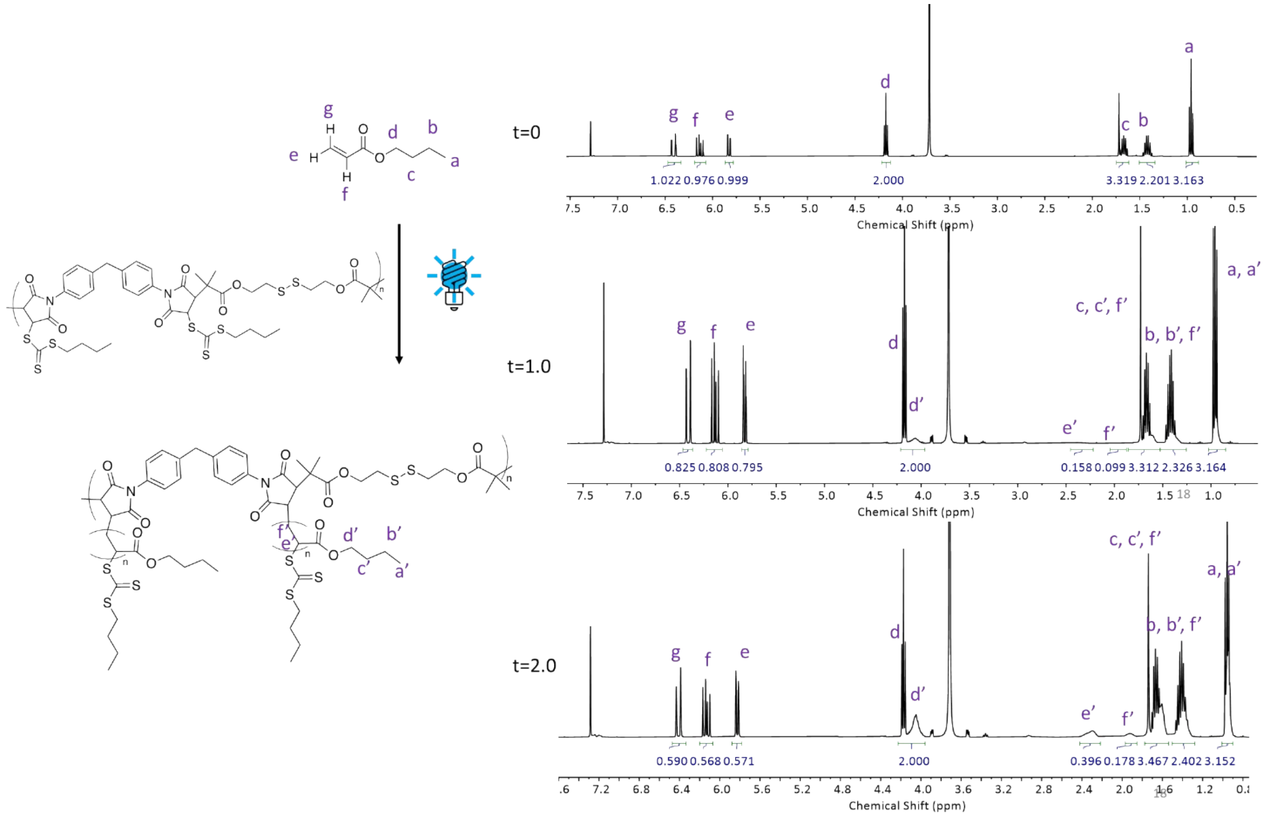


**Figure S16**: $^1$H-NMR (CDCl$_3$, 400 MHz) analysis of RAFT polymerization of Butyl Acrylate using blue light to graft from P(M$_2$-alt-CTA$_{2SS}$) backbone. The integrals of vinyl proton (H$_e$) with respect to monomeric and polymeric-OCH$_2$ signal (H$_d$ and H$_{d'}$) was used to determine monomer conversion.

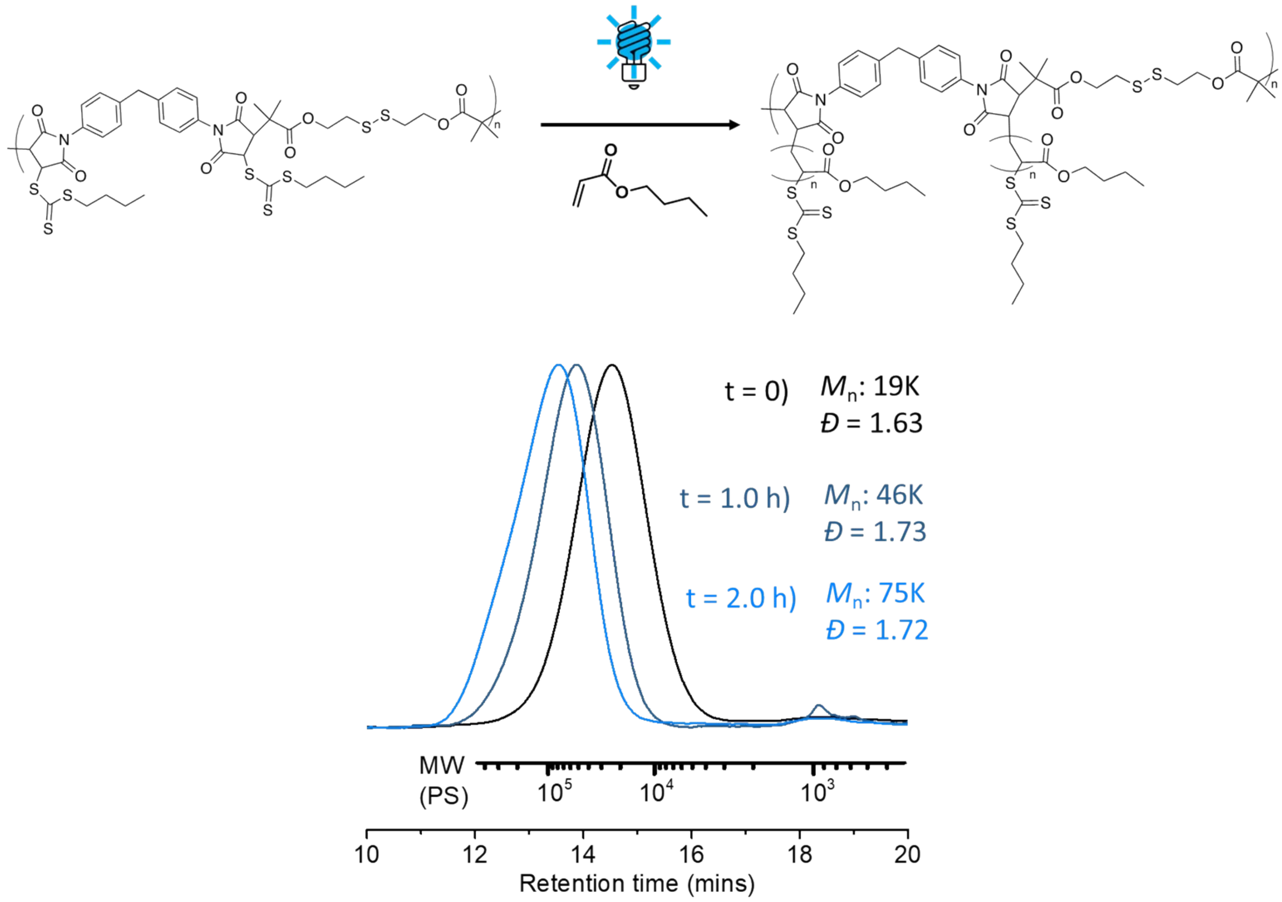


**Figure S17**: THF-SEC (normalized dRI) chromatograms of RAFT polymerization of Butyl Acrylate using blue light to graft from P($M_2$-alt-$CTA_{2SS}$) backbone. The molecular weight is relative to polystyrene calibration.

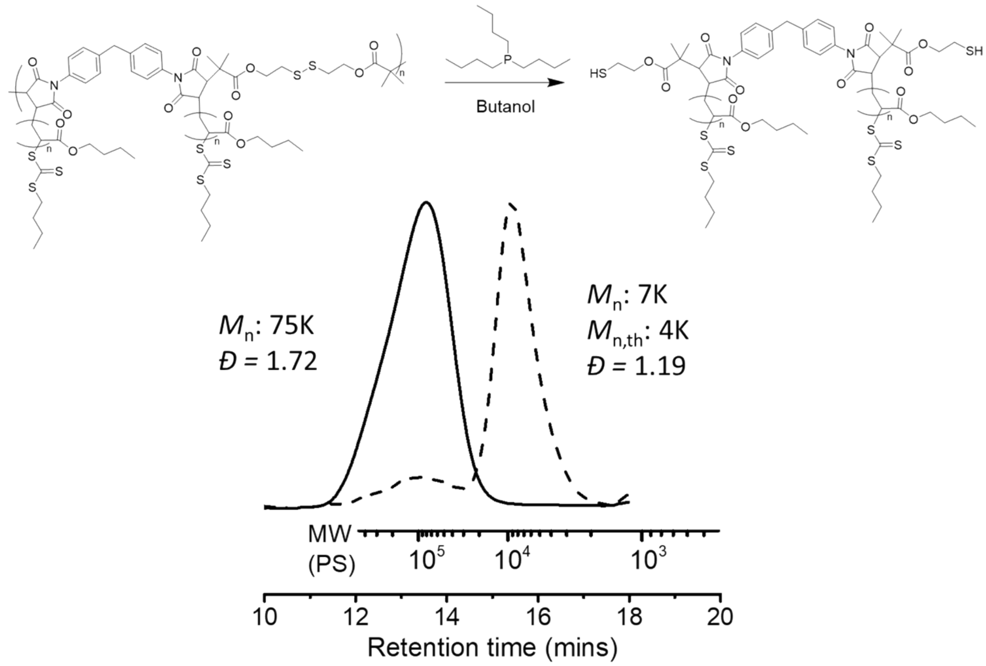


**Figure S18**: THF-SEC (normalized dRI) chromatograms of complete cleavage of the graft copolymer backbone using tributyl phosphine as the reducing agent for comparison (dashed line). The molecular weight is relative to polystyrene calibration. The theoretical $M_n$ is consistent with experimental $M_n$. Note, the trace at low retention time is artefact of baseline due to relatively weak signal.

**References:**

1. Flory, P. J., Molecular Size Distribution in Linear Condensation Polymers. *J. Am. Chem. Soc.* **1936,** *58*, 1877−1885.