

**Supplementary Materials for:**  
Mechanism and modelling of thermally initiated RAFT  
step-growth polymerization

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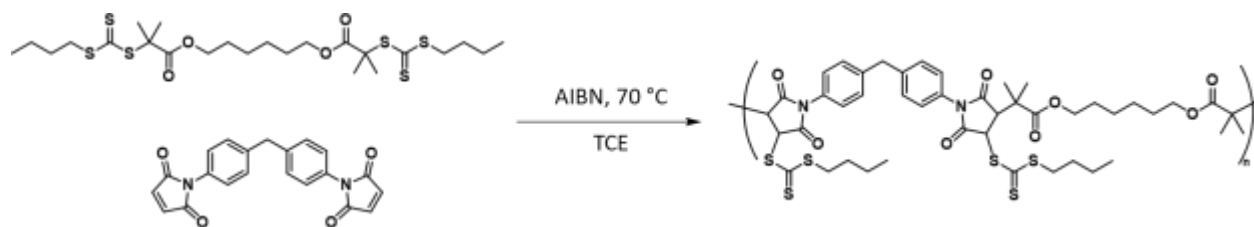
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## General considerations

Unless stated all reagents were purchased from commercial suppliers and used as received. Anhydrous dioxane was passed through activated basic aluminum oxide and discarded after several uses. All NMR spectrums were recorded on a Bruker 400 MHz spectrometer in  $\text{CDCl}_3$ . All NMR spectrums were processed using Mestrenova. Volumes of solvents (including initiator stock solution) were measured by weight based on densities reported by manufacturers. Initiator (AIBN) stock solution was prepared as 20 mg/ml in the solvent used for polymerization. For simplicity, molar concentration of the reacting species here is defined by moles of the reactants divided by the total volume of the solvent, without consideration for the volume taken up by non-solvent components. Experiments were carried out in either 3.7 ml scintillation vials with a diameter of 15 mm, or in 20 ml scintillation vials with a diameter of 28 mm. Reaction containers were sealed with a 14/20 rubber septum. Thermo Scientific digital baths (Digital Dry Baths/Block Heaters – PROMO, catalog number: 88870001) equipped with heat block (holds 15 x 16 mm diameter, catalog number: 88870106) were used to maintain constant temperature.

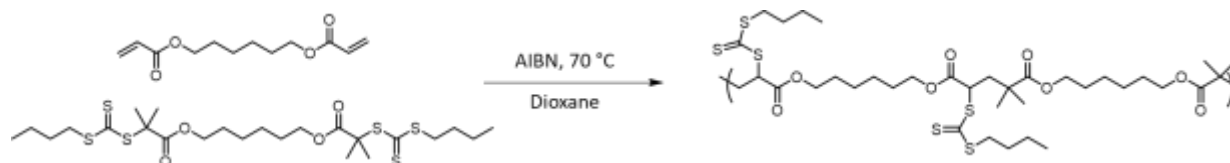
For kinetic analysis A 22-gauge, 4 inch hypodermic needle (air-tite product) was used to sample the reaction mixture under argon flow. Typically, a single needle and syringe was used to take sample for  $^1\text{H}$ -NMR spectroscopy, by drawing out approximately 50 to 100  $\mu\text{L}$  and dropping a few drops into a vial for  $^1\text{H}$ -NMR.

### Procedure for A<sub>2</sub> + B<sub>2</sub> RAFT step-growth polymerization with maleimide monomer:



Bifunctional monomer, **M<sub>2B</sub>** (250 mg, 0.698 mmol) was first charged into a 3.7 ml vial, followed by bifunctional CTA, **CTA<sub>2</sub>** (409.49 mg, 0.698 mmol). Next, 0.822 ml tetrachloroethane (TCE) and 0.911 ml AIBN stock solution (20 mg/ml in TCE) was added to target molar concentration of  $[M_2]_0:[CTA_2]_0:[AIBN]_0 = 0.5 : 0.5 : 0.05$  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 reaction vials were then purged with argon for 10 minutes and then placed inside the heat block at 70 °C.

### Procedure for A<sub>2</sub> + B<sub>2</sub> RAFT step-growth polymerization with acrylate monomer:



Bifunctional monomer, **M<sub>2F</sub>** (250 mg, 1.09 mmol) was first charged into a 3.7 ml vial, followed by bifunctional CTA, **CTA<sub>2</sub>** (642.03 mg, 1.10 mmol). Next, 0.397 ml 1,4-Dioxane and 0.464 ml AIBN stock solution (20 mg/ml in 1,4-dioxane) was added to target molar concentration of  $[M_2]_0:[CTA_2]_0:[AIBN]_0 = 1.0 : 1.0 : 0.05$  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 reaction vials were then purged with argon for 10 minutes and then placed inside the heat block at 70 °C.

### Determining $R_p$ for RAFT step-growth system

Equations 1-10 defined in the main text can be used to analytically solve for the rate of polymerization ( $R_p$ ). First consumption rates monomer and RAFT agent (equations 1 and 2) can be set equal, as shown below:

$$\frac{d[M]}{dt} = \frac{d[CTA]}{dt} \quad (S1)$$

$$-k_i[M][R\cdot] = -k_{add}[CTA][M\cdot] = -k_{frag}[CTA\cdot] \quad (S2)$$

Additionally, the steady state approximation can be invoked, allowing for equations 3-5 to 0, giving the following expression:

$$R_i = R_t = 2k_t[M\cdot]^2 + 2k_t[M\cdot][R\cdot] + 2k_t[M\cdot][CTA\cdot] + 2k_t[R\cdot]^2 + 2k_t[R\cdot][CTA\cdot] + 2k_t[CTA\cdot]^2 \quad (S3)$$

Equation S2 can be rearranged to give expressions for  $[M\cdot]$  and  $[CTA\cdot]$  (equations S4 and S5).

$$[M\cdot] = \frac{k_i[M][R\cdot]}{k_{add}[CTA]} \quad (S4)$$

$$[CTA\cdot] = \frac{k_i[M][R\cdot]}{k_{frag}} \quad (S5)$$

Equations S4 and S5 can be plugged into equation S3 to give the following expression for  $R_i$ :

$$R_i = k_t \left( \frac{k_i[M][R\cdot]}{k_{add}[CTA]} \right)^2 + k_t \left( \frac{k_i[M][R\cdot]}{k_{add}[CTA]} \right) [R\cdot] + k_t \left( \frac{k_i[M][R\cdot]}{k_{add}[CTA]} \right) \left( \frac{k_i[M][R\cdot]}{k_{frag}} \right) + 2k_t [R\cdot]^2 + 2k_t [R\cdot] \left( \frac{k_i[M][R\cdot]}{k_{frag}} \right) + 2k_t \left( \frac{k_i[M][R\cdot]}{k_{frag}} \right) \quad (S6)$$

Equation S6 can then be rearranged in terms of  $[R\cdot]$  to give equation S7, below:

$$[R\cdot] = \frac{1}{k_i[M]} \sqrt{\frac{R_i}{2k_t} \frac{1}{\frac{1}{\sqrt{(k_{add}[CTA])^2 + k_i[M]k_{add}[CTA]} + k_{add}[CTA]k_{frag}} + (k_i[M])^2 + k_i[M]k_{frag}} + \frac{1}{(k_{frag})^2}}}} \quad (S7)$$

As  $R_p$  can be defined by equation S8, an expression for  $R_p$  for RAFT step-growth can be solved for by plugging equation S7 into equation S8 to give equation S9.

$$R_p = -\frac{d[M]}{dt} = k_i [M][R\cdot] \quad (S8)$$

$$R_p = \sqrt{\frac{R_i}{2k_t}} \frac{1}{\sqrt{\frac{1}{(k_{\text{add}}[\text{CTA}])^2} + \frac{1}{k_i[\text{M}]k_{\text{add}}[\text{CTA}] + k_{\text{add}}[\text{CTA}]k_{\text{frag}} + (k_i[\text{M}])^2} + \frac{1}{k_i[\text{M}]k_{\text{frag}} + (k_{\text{frag}})^2}}} \quad (\text{S9})$$

#### Apparent rate constants ( $k_{\text{app}}$ ) for Cases 1-4

Case 1:  $k_{\text{add}}, k_i \gg k_{\text{frag}}$

$$k_{\text{app}} = \sqrt{\frac{fk_d[\text{I}]}{k_t}} (k_{\text{frag}}) \quad (\text{S10})$$

Case 2:  $k_{\text{add}}, k_{\text{frag}} \gg k_i$

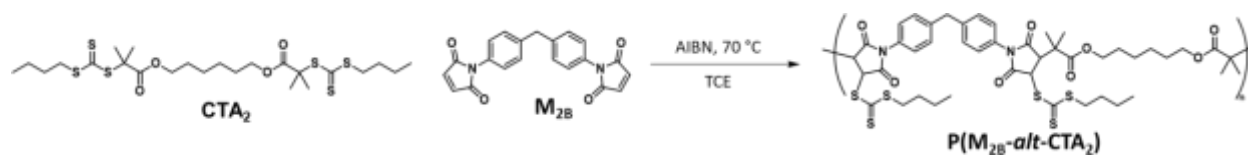
$$k_{\text{app}} = \sqrt{\frac{fk_d[\text{I}]}{k_t}} (k_i) \quad (\text{S11})$$

Case 3:  $k_{\text{frag}}, k_i \gg k_{\text{add}}$

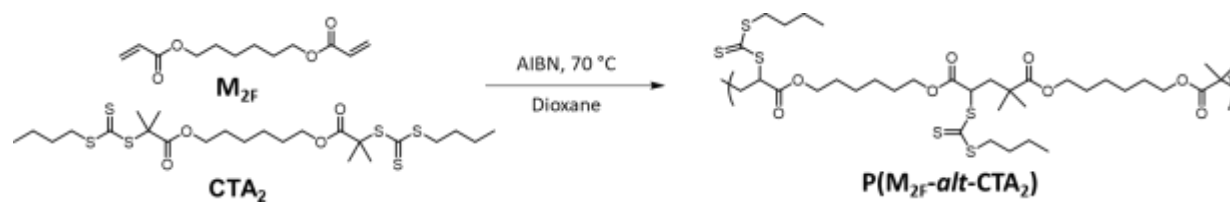
$$k_{\text{app}} = \sqrt{\frac{fk_d[\text{I}]}{k_t}} (k_{\text{add}}) \quad (\text{S12})$$

Case 4:  $k_{\text{frag}} \approx k_{\text{add}} \approx k_i$

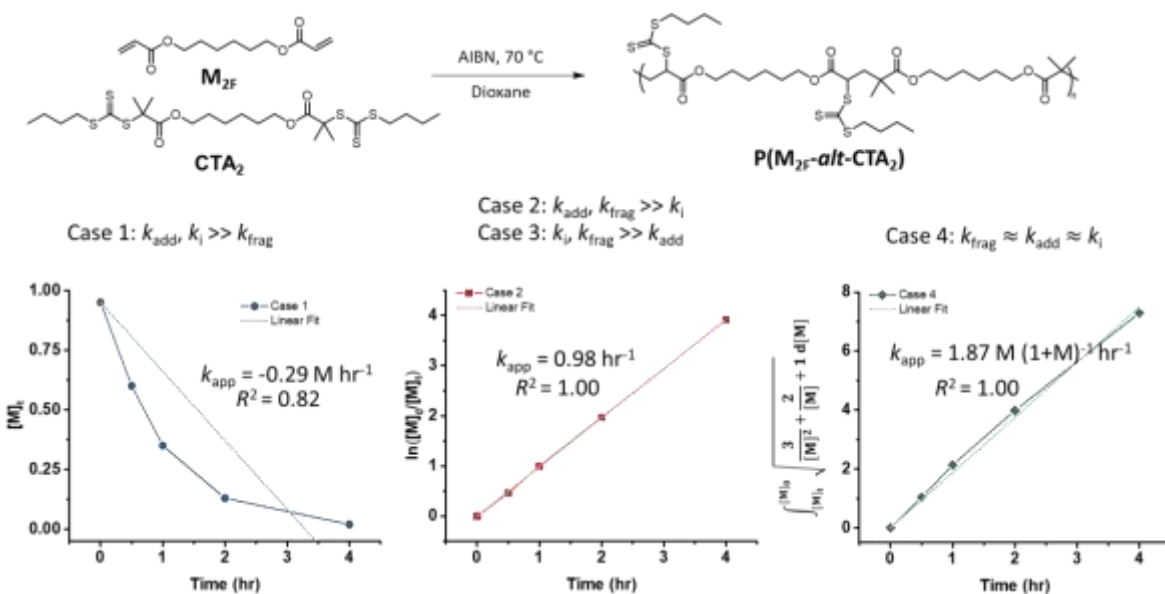
$$k_{\text{app}} = \sqrt{\frac{fk_d[\text{I}]}{k_t}} (k_{\text{case4}}) \quad (\text{S13})$$

**Table S1:** Kinetic analysis of A<sub>2</sub>+B<sub>2</sub> RAFT step-growth polymerization of M<sub>2B</sub> with CTA<sub>2</sub><sup>1</sup>

Case	$k_{app}$ (t0-1.0 hr)	$R^2$ (t0-1.0 hr)	$k_{app}$ (t0-2.0 hr)	$R^2$ (t0-2.0 hr)
1	$-1.97 \pm 0.37$ (M hr <sup>-1</sup> )	0.90	$-1.44 \pm 0.30$ (M hr <sup>-1</sup> )	0.57
2 & 3	$3.01 \pm 0.20$ (hr <sup>-1</sup> )	0.99	$2.27 \pm 0.25$ (hr <sup>-1</sup> )	0.96
4	$6.63 \pm 0.58$ ((1-M <sup>-2</sup> ) M hr <sup>-1</sup> )	0.99	$4.64 \pm 0.68$ (M (1+M) <sup>-1</sup> hr <sup>-1</sup> )	0.94

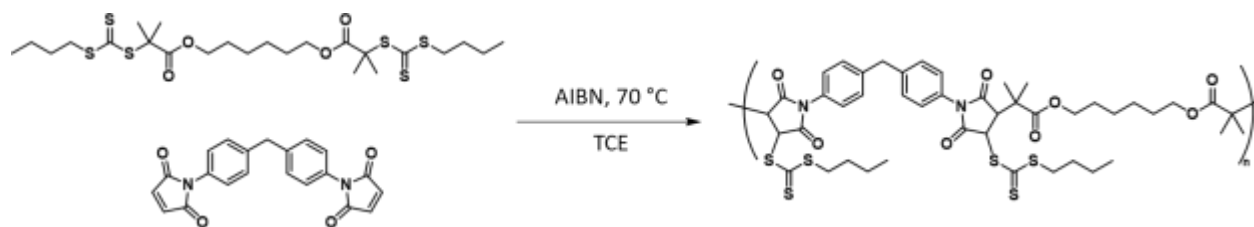
**Table S2:** Kinetic analysis of A<sub>2</sub>+B<sub>2</sub> RAFT step-growth polymerization of M<sub>2F</sub> with CTA<sub>2</sub> for various cases<sup>2</sup>

Case	$k_{app}$	$R^2$
1	$-0.29 \pm 0.05$ (M hr <sup>-1</sup> )	0.82
2 & 3	$0.98 \pm 0.01$ (hr <sup>-1</sup> )	1.00
4	$1.87 \pm 0.05$ (M (1+M) <sup>-1</sup> hr <sup>-1</sup> )	1.00



**Figure S1:** Kinetic analysis of  $A_2+B_2$  RAFT step-growth polymerization of  $M_{2F}$  for various fittings cases (left Case 1, middle Case 2 and 3, and left Case 4).<sup>2</sup>

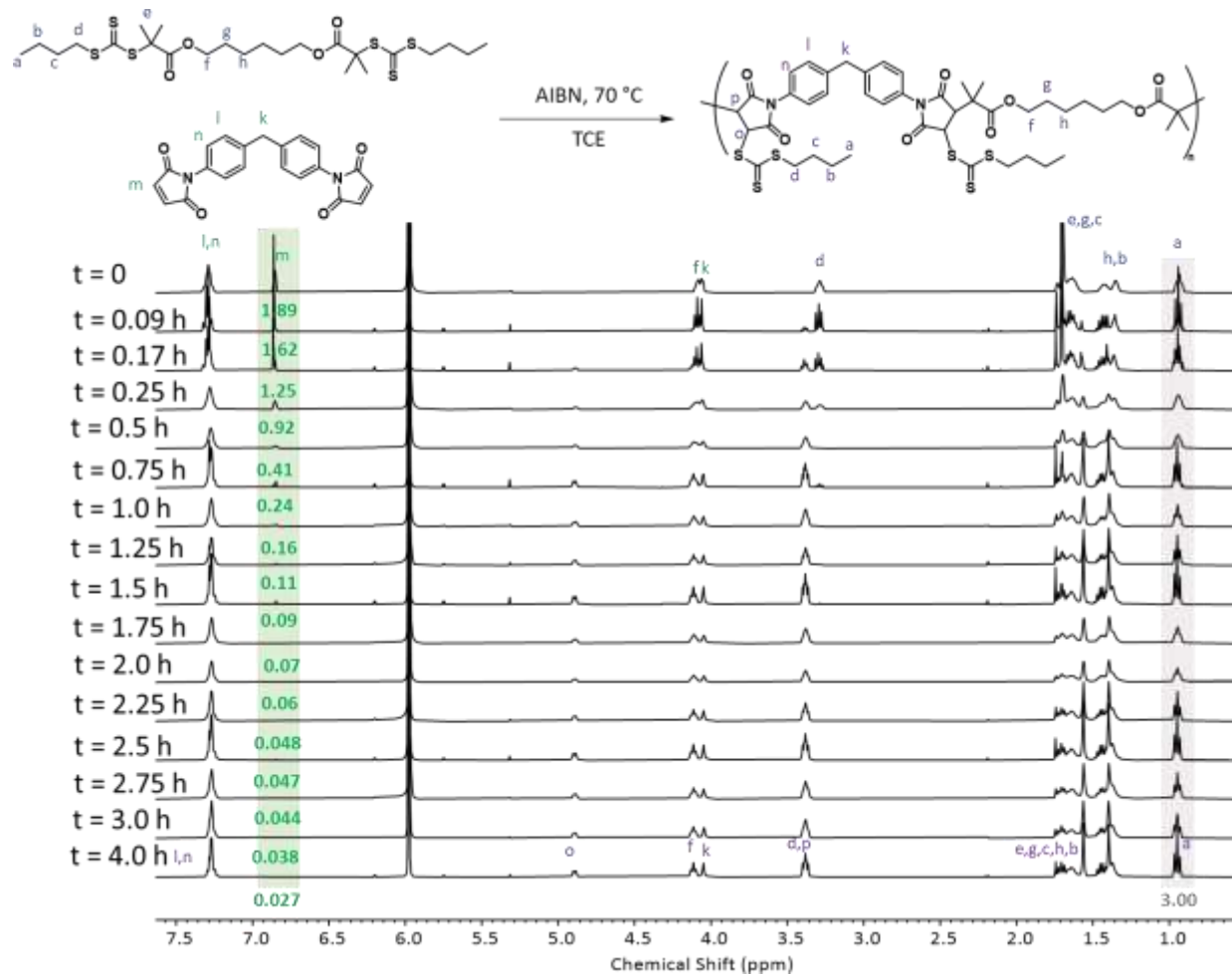
**Table S3:** Kinetic analysis of A<sub>2</sub>+B<sub>2</sub> RAFT step-growth polymerization of M<sub>2B</sub> with CTA<sub>2</sub>



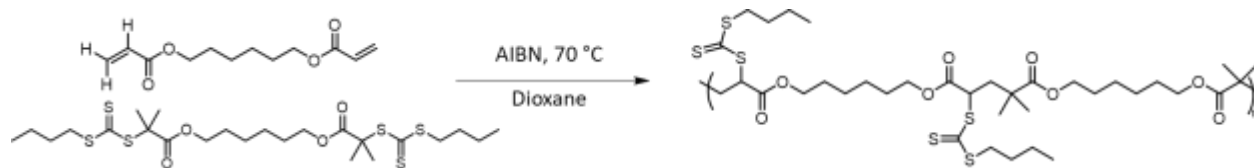
Time (hr) <sup>a</sup>	<i>p</i> <sup>b</sup>
0	0
0.09	0.142
0.17	0.341
0.25	0.512
0.5	0.782
0.75	0.872
1.0	0.918
1.25	0.943
1.5	0.953
1.75	0.964
2.0	0.971
2.25	0.975
2.5	0.976
2.75	0.977
3.0	0.980
4.0	0.986

<sup>a</sup> Duration of the polymerization. <sup>b</sup> Monomer conversion determined by <sup>1</sup>H-NMR.



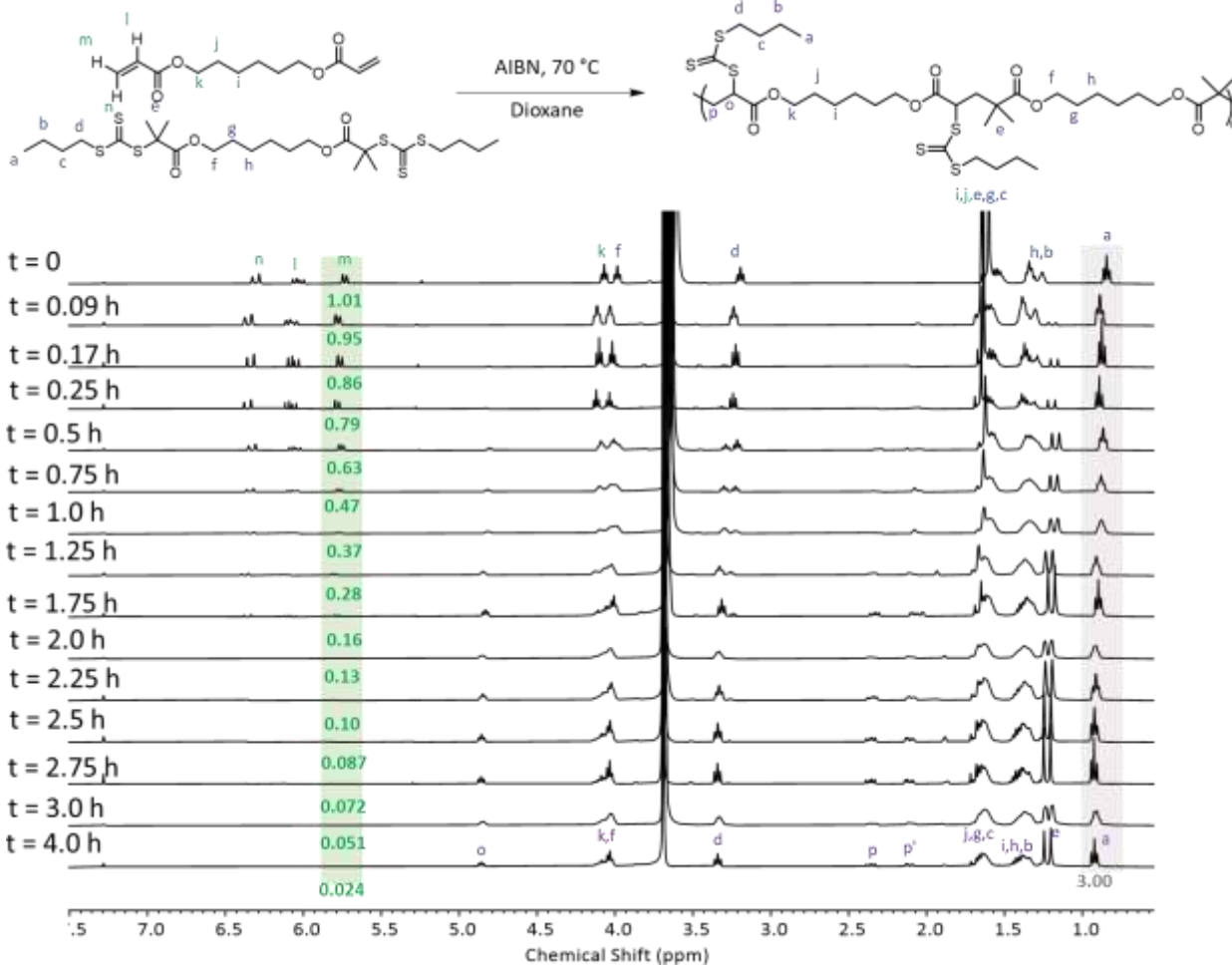


**Figure S2:**  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz) analysis of  $\text{A}_2+\text{B}_2$  RAFT-iniferter step-growth polymerization with  $\text{M}_{2\text{B}}$  and  $\text{CTA}_2$ . The numbers correspond to relative integral of the monomer peak (green region) with respect to the Z-group  $\text{CH}_3$  (grey region) as 3 for reference.

**Table S4:** Kinetic analysis of A<sub>2</sub>+B<sub>2</sub> RAFT step-growth polymerization of M<sub>2F</sub> with CTA<sub>2</sub>

Time (hr) <sup>a</sup>	<i>p</i> <sup>b</sup>
0	0
0.09	0.057
0.17	0.153
0.25	0.217
0.5	0.380
0.75	0.540
1.0	0.640
1.25	0.721
1.75	0.840
2.0	0.873
2.25	0.897
2.5	0.914
2.75	0.929
3.0	0.950
4.0	0.976

<sup>a</sup> Duration of the polymerization. <sup>b</sup> Monomer conversion determined by <sup>1</sup>H-NMR.

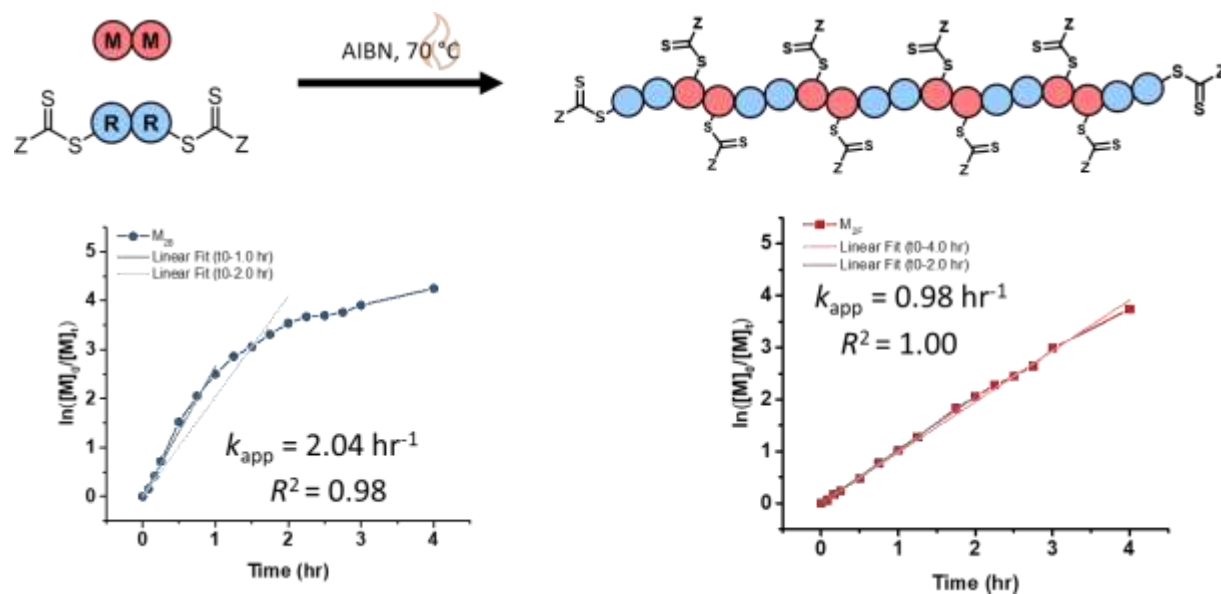


**Figure S3:**  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz) analysis of  $\text{A}_2+\text{B}_2$  PET-RAFT step-growth polymerization with  $\text{M}_{2\text{F}}$  and  $\text{CTA}_2$ . The numbers correspond to relative integral of the monomer peak (green region) with respect to the Z-group  $\text{CH}_3$  (grey region) as 3 for reference.

**Table S5:** Kinetic analysis of  $\text{A}_2+\text{B}_2$  RAFT step-growth polymerization of  $\text{M}_{2\text{B}}$  and  $\text{M}_{2\text{F}}$  with  $\text{CTA}_2$

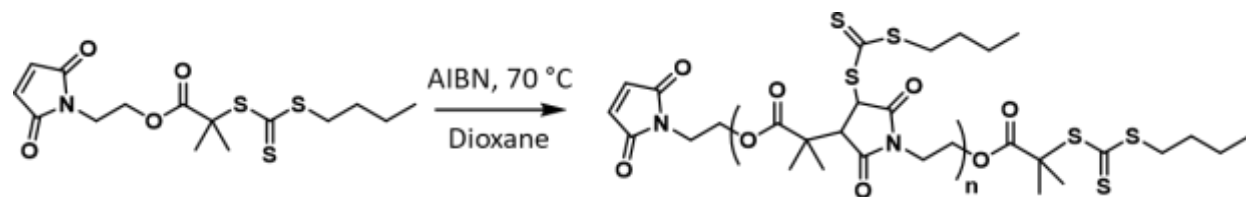


Monomer	$k_{\text{app}}$ (t0-2.0 hr) ( $\text{hr}^{-1}$ )	$R^2$ (t0-2.0 hr)	$k_{\text{app}}$ (t0-4.0 hr) ( $\text{hr}^{-1}$ )	$R^2$ (t0-4.0 hr)
$\text{M}_{2\text{B}}$	$2.65 \pm 0.08$	1.00	$2.04 \pm 0.10$	0.98
$\text{M}_{2\text{F}}$	$1.03 \pm 0.01$	1.00	$0.98 \pm 0.01$	1.00

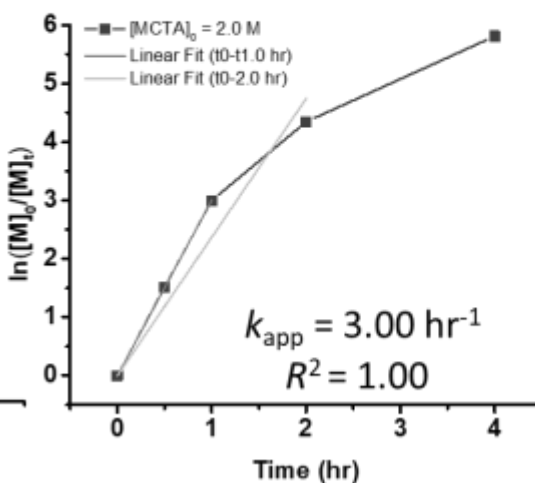
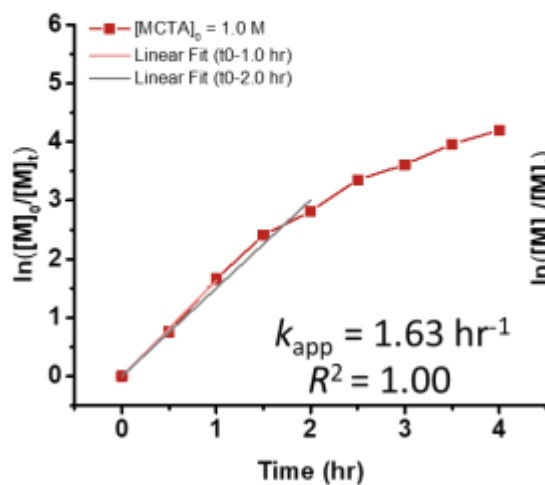
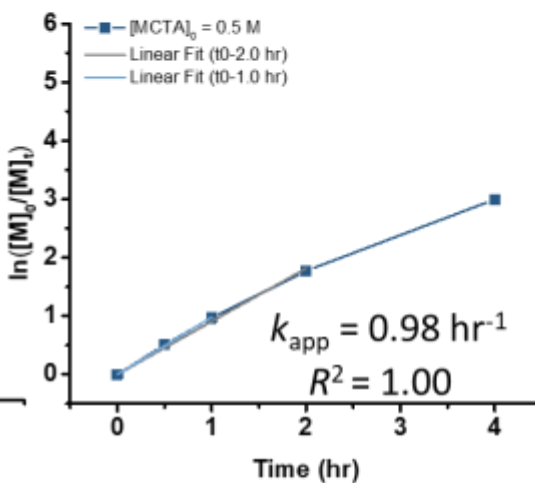
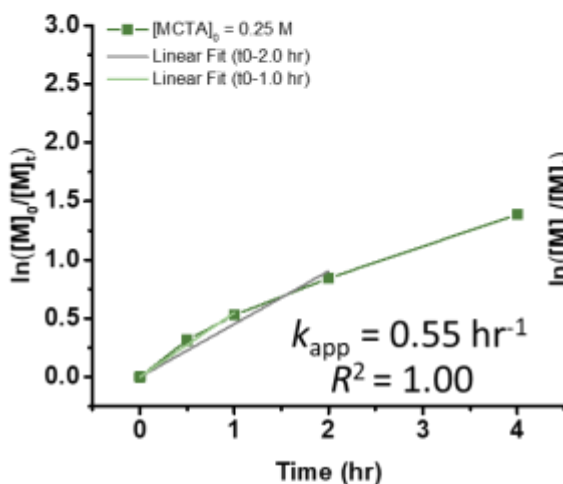
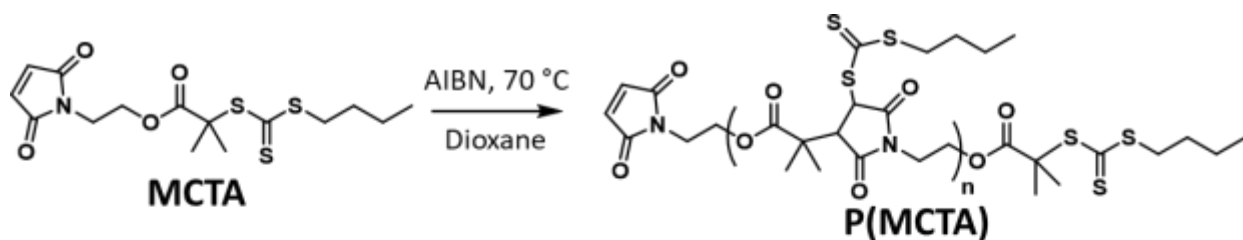


**Figure S4:** Kinetic analysis of  $A_2+B_2$  RAFT step-growth polymerization (**left**  $M_{2B}$  with  $CTA_2$ , **right**  $M_{2F}$  with  $CTA_2$ ).

**Table S6:** Kinetic analysis of AB RAFT step-growth polymerization of MCTA, where  $[MCTA]_0/[AIBN]_0 = 20^3$

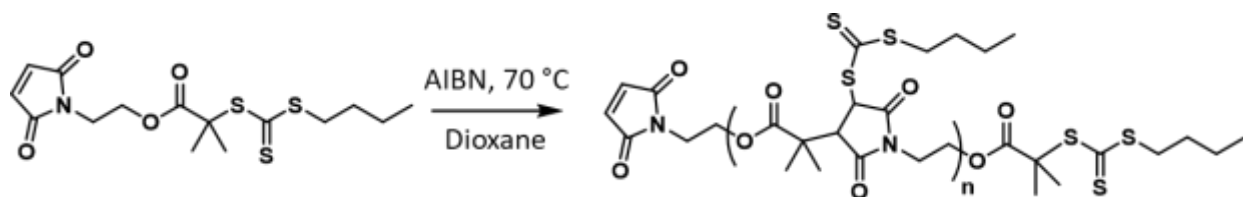


Concentration (M)	$k_{app}$ (t0-1.0 hr) (hr <sup>-1</sup> )	$R^2$ (t0-1.0 hr)	$k_{app}$ (t0-2.0 hr) (hr <sup>-1</sup> )	$R^2$ (t0-2.0 hr)
0.25	$0.55 \pm 0.03$	1.00	$0.45 \pm 0.03$	0.98
0.5	$0.98 \pm 0.02$	1.00	$0.91 \pm 0.02$	1.00
1.0	$1.63 \pm 0.04$	1.00	$1.50 \pm 0.05$	1.00
2.0	$3.00 \pm 0.01$	1.00	$2.37 \pm 0.20$	0.98

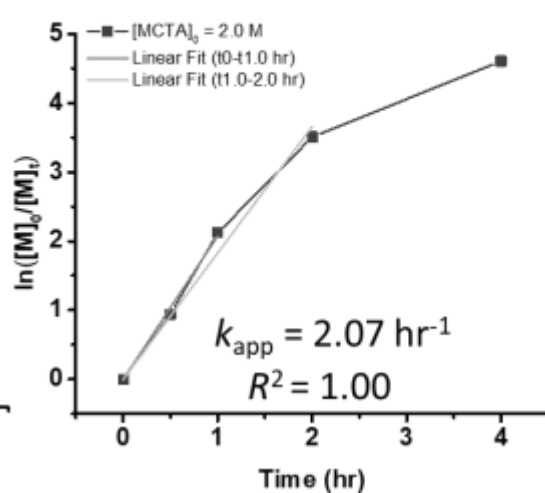
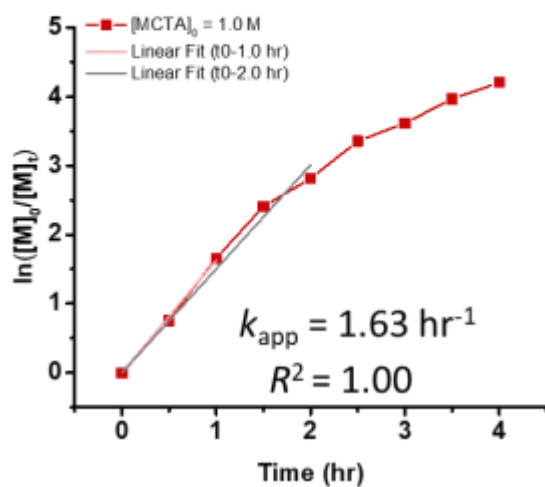
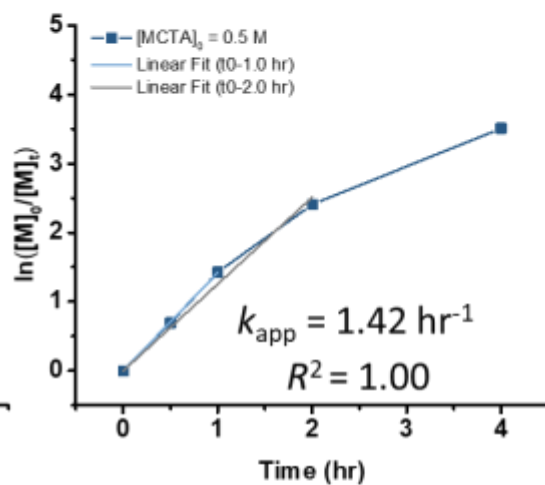
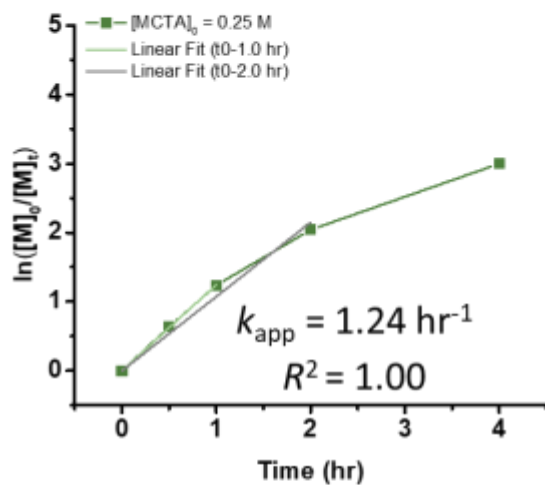
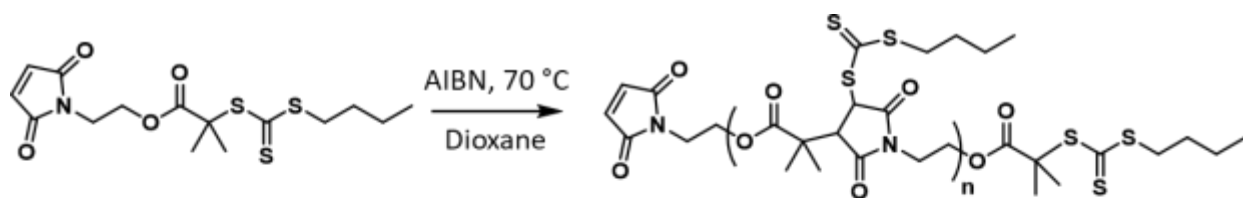


**Figure S5:** Kinetic analysis of AB RAFT step-growth polymerization of MCTA at various monomer concentrations (**top left**  $[MCTA]_0 = 0.25 \text{ M}$ , **top right**  $[MCTA]_0 = 0.5 \text{ M}$ , **bottom left**  $[MCTA]_0 = 1.0 \text{ M}$ , **bottom right**  $[MCTA]_0 = 2.0 \text{ M}$ ), where  $[MCTA]_0/[AIBN]_0 = 20$ .<sup>3</sup>

**Table S7:** Kinetic analysis of AB RAFT step-growth polymerization of MCTA, where  $[AIBN]_0 = 0.05 \text{ M}^3$

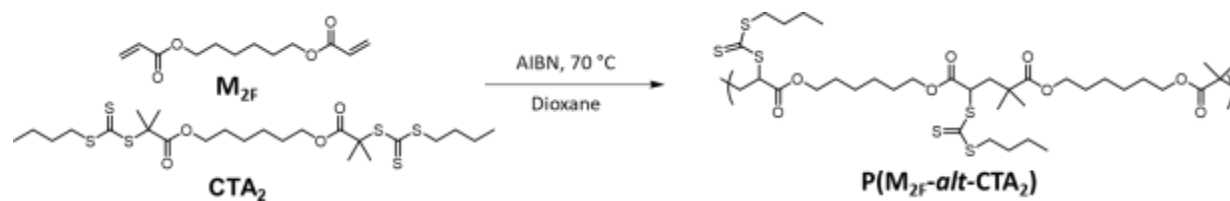


Concentration (M)	$k_{app}$ (t0-1.0 hr) ( $\text{hr}^{-1}$ )	$R^2$ (t0-1.0 hr)	$k_{app}$ (t0-2.0 hr) ( $\text{hr}^{-1}$ )	$R^2$ (t0-2.0 hr)
0.25	$1.24 \pm 0.01$	1.00	$0.45 \pm 0.03$	0.99
0.5	$1.42 \pm 0.01$	1.00	$1.26 \pm 0.05$	1.00
1.0	$1.63 \pm 0.04$	1.00	$1.50 \pm 0.05$	1.00
2.0	$2.07 \pm 0.07$	1.00	$1.83 \pm 0.08$	0.99



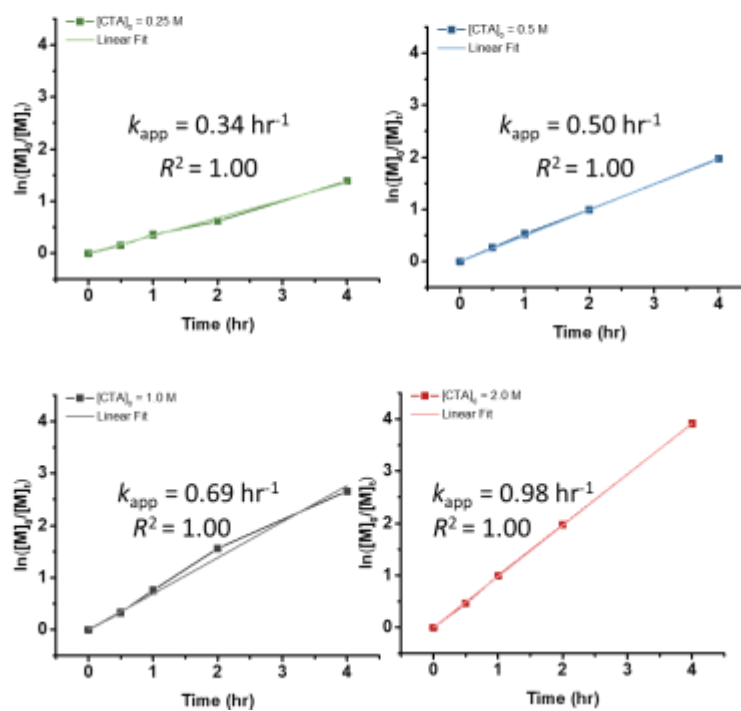
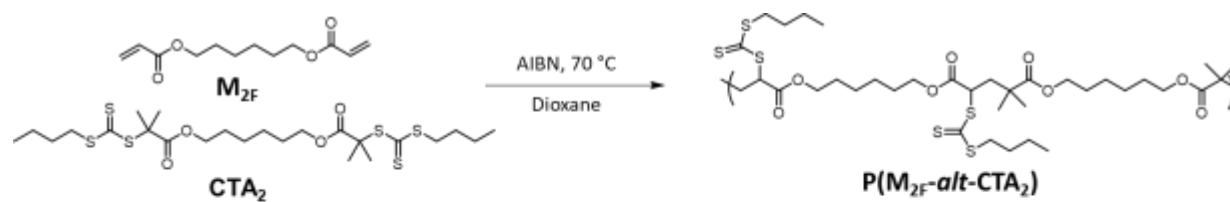
**Figure S6:** Kinetic analysis of AB RAFT step-growth polymerization of MCTA at various monomer concentrations (**top left**  $[MCTA]_0 = 0.25$  M, **top right**  $[MCTA]_0 = 0.5$  M, **bottom left**  $[MCTA]_0 = 1.0$  M, **bottom right**  $[MCTA]_0 = 2.0$  M), where  $[AIBN]_0 = 0.05$  M.<sup>3</sup>

**Table S8:** Kinetic analysis of A<sub>2</sub>+B<sub>2</sub> RAFT step-growth polymerization of M<sub>2F</sub> with CTA<sub>2</sub> for various concentrations, where [CTA]<sub>0</sub>/[AIBN]<sub>0</sub> = 40<sup>2</sup>



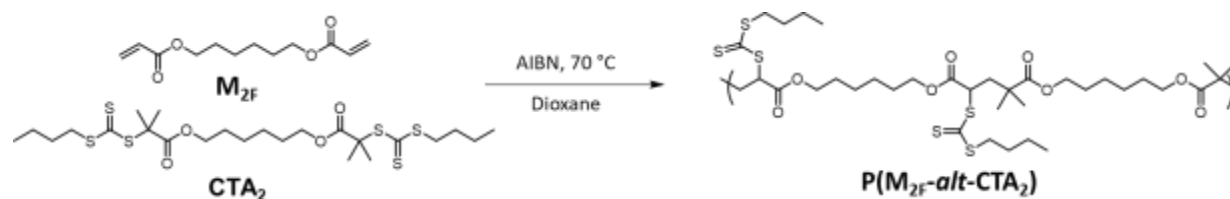
Concentration (M)	$k_{app}$ (hr <sup>-1</sup> )	$R^2$
0.25	0.34 ± 0.05	1.00
0.5	0.50 ± 0.01	1.00
1.0	0.69 ± 0.02	1.00
2.0	0.98 ± 0.01	1.00



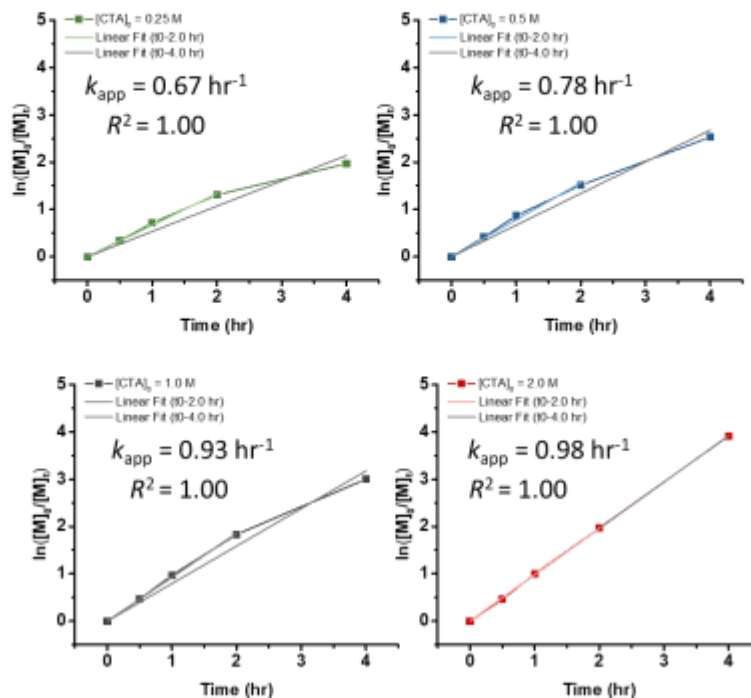
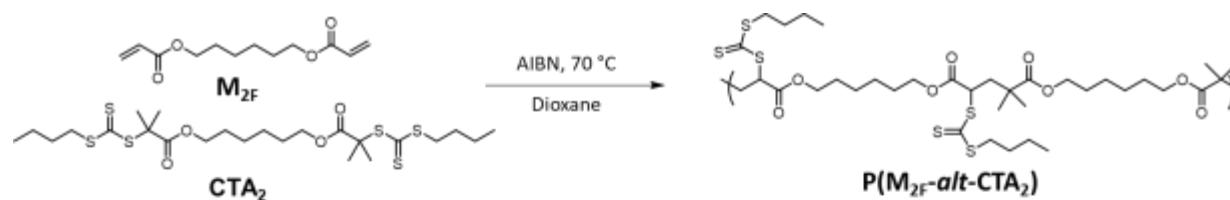


**Figure S7:** Kinetic analysis of  $A_2+B_2$  RAFT step-growth polymerization of  $M_{2F}$  at various monomer concentrations (**top left**  $[MCTA]_0 = 0.25$  M, **top right**  $[MCTA]_0 = 0.5$  M, **bottom left**  $[MCTA]_0 = 1.0$  M, **bottom right**  $[MCTA]_0 = 2.0$  M), where  $[CTA]_0/[AIBN]_0 = 40$ .<sup>2</sup>

**Table S9:** Kinetic analysis of A<sub>2</sub>+B<sub>2</sub> RAFT step-growth polymerization of M<sub>2F</sub> with CTA<sub>2</sub> for various concentrations, where [AIBN]<sub>0</sub> = 0.05 M<sup>2</sup>



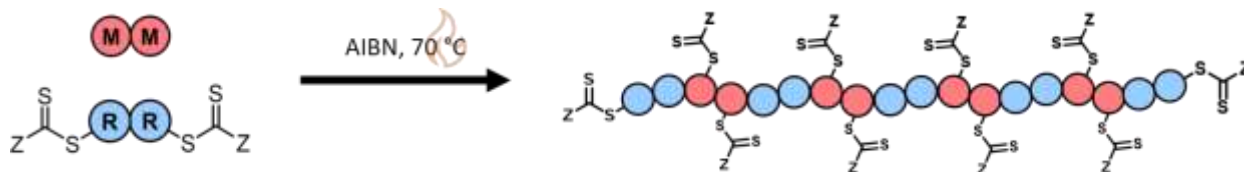
Concentration (M)	$k_{app}$ (t0-1.0 hr) (hr <sup>-1</sup> )	$R^2$ (t0-1.0 hr)	$k_{app}$ (t0-2.0 hr) (hr <sup>-1</sup> )	$R^2$ (t0-2.0 hr)
0.25	0.67 ± 0.01	1.00	0.54 ± 0.04	0.98
0.5	0.78 ± 0.03	1.00	0.67 ± 0.03	0.99
1.0	0.93 ± 0.01	1.00	0.79 ± 0.04	0.99
2.0	0.98 ± 0.01	1.00	0.98 ± 0.01	1.00



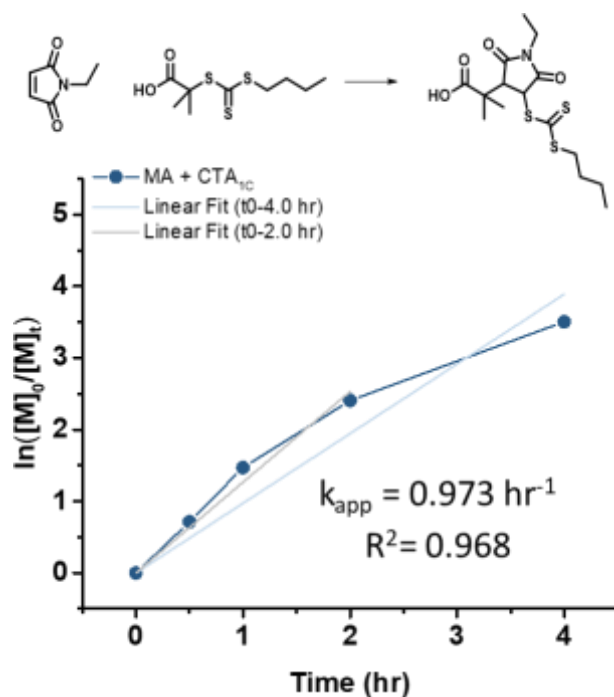
**Figure S8:** Kinetic analysis of  $A_2+B_2$  RAFT step-growth polymerization of  $M_{2F}$  at various monomer concentrations (**top left**  $[MCTA]_0 = 0.25 \text{ M}$ , **top right**  $[MCTA]_0 = 0.5 \text{ M}$ , **bottom left**  $[MCTA]_0 = 1.0 \text{ M}$ , **bottom right**  $[MCTA]_0 = 2.0 \text{ M}$ ), where  $[AIBN]_0 = 0.05 \text{ M}$ .<sup>2</sup>

**Table S10:** Kinetic analysis of A<sub>2</sub>+B<sub>2</sub> RAFT step-growth polymerization with maleimide monomers<sup>1,3</sup>

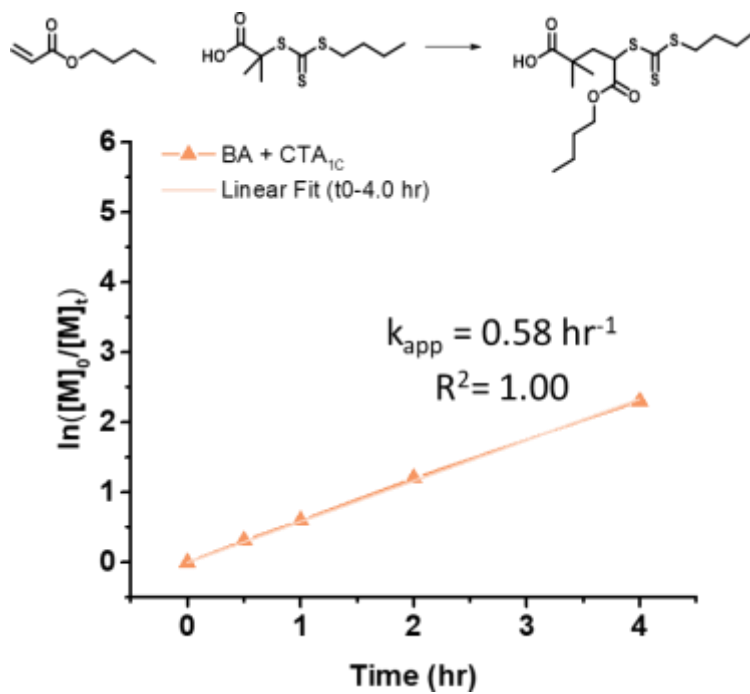
Monomer	$k_{app}$ (t0-1.0 hr) (hr <sup>-1</sup> )	$R^2$ (t0-1.0 hr)	$k_{app}$ (t0-2.0 hr) (hr <sup>-1</sup> )	$R^2$ (t0-2.0 hr)
M <sub>2A</sub>	2.06 ± 0.03	1.00	1.96 ± 0.04	1.00
M <sub>2B</sub>	3.01 ± 0.20	0.99	2.27 ± 0.25	0.96
M <sub>2C</sub>	0.66 ± 0.02	1.00	0.53 ± 0.04	0.98
M <sub>2D</sub>	3.31 ± 0.27	0.99	2.68 ± 0.23	0.98
M <sub>2E</sub>	1.64 ± 0.04	1.00	1.51 ± 0.05	1.00

**Table S11:** Kinetic analysis of A<sub>2</sub>+B<sub>2</sub> RAFT step-growth polymerization with various diacrylate monomers<sup>2</sup>

Monomer	$k_{app}$ (t0-2.0 hr) (hr <sup>-1</sup> )	$R^2$ (t0-2.0 hr)	$k_{app}$ (t0-4.0 hr) (hr <sup>-1</sup> )	$R^2$ (t0-4.0 hr)
M <sub>2F</sub>	1.38 ± 0.03	1.00	1.22 ± 0.05	1.00
M <sub>2G</sub>	1.02 ± 0.01	1.00	0.91 ± 0.03	1.00
M <sub>2H</sub>	1.60 ± 0.03	1.00	1.39 ± 0.05	0.99
M <sub>2I</sub>	1.01 ± 0.03	1.00	1.01 ± 0.02	1.00



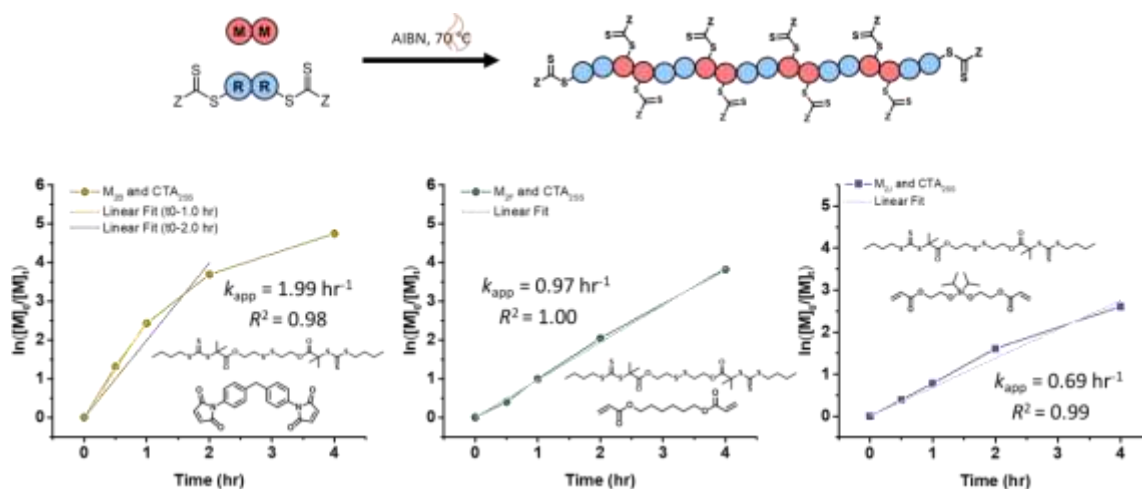
**Figure S9:** Kinetic analysis of RAFT-SUMI of *N*-ethyl maleimide (MA) with BDMAT (CTA<sub>1C</sub>).<sup>3</sup>



**Figure S10:** Kinetic analysis of RAFT-SUMI of butyl acrylate (BA) with BDMAT (CTA<sub>1C</sub>).<sup>2</sup>

**Table S12:** Kinetic analysis of RAFT-SUMI with various monomers (MA and BA) with CTA<sub>1C</sub><sup>2,3</sup>

Monomer	$k_{app}$ (t0-2.0 hr) (hr <sup>-1</sup> )	$R^2$ (t0-2.0 hr)	$k_{app}$ (t0-4.0 hr) (hr <sup>-1</sup> )	$R^2$ (t0-4.0 hr)
MA	$1.27 \pm 0.06$	0.99	$0.97 \pm 0.09$	0.97
BA	$0.58 \pm 0.01$	1.00	---	---



**Figure S11:** Kinetic analysis of A<sub>2</sub>+B<sub>2</sub> RAFT step-growth polymerization of various monomers with RAFT Agent CTA<sub>2SS</sub> (**left** M<sub>2B</sub>, **middle** M<sub>2F</sub>, **left** M<sub>2I</sub>).<sup>2, 4, 5</sup>

**Table S12:** Kinetic analysis of A<sub>2</sub>+B<sub>2</sub> RAFT step-growth polymerization for diacrylate and maleimide monomers with various CTA<sub>2SS</sub><sup>2, 4, 5</sup>



Monomer	$k_{app}$ (t0-1.0 hr) (hr <sup>-1</sup> )	$R^2$ (t0-1.0 hr)	$k_{app}$ (t0-2.0 hr) (hr <sup>-1</sup> )	$R^2$ (t0-2.0 hr)
M <sub>2B</sub>	2.47 ± 0.06	1.00	1.99 ± 0.16	0.98
M <sub>2F</sub> <sup>a</sup>	---	---	0.97 ± 0.02	1.00
M <sub>2J</sub> <sup>a</sup>	---	---	0.69 ± 0.03	0.99

<sup>a</sup> Fitting from 0 hr to 4.0 hr.

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