Supporting Information

RAFT polymerization by the radical decarboxylation of carboxylic acids

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I. Materials and Characterizations

Methyl acrylate (MA) (99%, Sigma-Aldrich or Alfa Aesar), butyl acrylate (BA) (99%, Sigma-Aldrich), N,N-dimethylacrylamide (DMA) (99%, Sigma-Aldrich), methyl methacrylate (MMA) (Sigma-Aldrich), N-isopropylacrylamide (NIPAM) (97%, Sigma-Aldrich) were purified by passing through basic alumina to remove inhibitor. Other chemicals such as N-Cbz-phenylalanine (99%, Sigma-Aldrich), Fmoc-Met-OH (Mimotopes), Fmoc-Ser-(tBu)-OH (Mimotopes), trans-4-(4-Chlorophenyl)cyclohexanecarboxylic Acid (Aaron Chem), 2-phenylpropanoic acid (Aaron Chem), isobutyric acid (99%, Sigma-Aldrich), pivalic acid (99%, Sigma-Aldrich), 3,4-Dihydro-2H-benzopyran-3-carboxylic acid (Aaron Chem), 3,4-Dihydro-2H-benzopyran-3-carboxylic acid (Aaron Chem), glycyrrhetinic acid (Combi-Blocks), 3R-N-[tert-Butyloxycarbonyl]-3-amino-4-(2,4,5-trifluorophenyl)-butanoic acid (Chiral Quest), 10-(3,5-Dimethoxyphenyl)-9-mesityl-1,3,6,8-tetramethoxy-acridin-10-i um tetrafluoro-borate (95%, Sigma-Aldrich and BLD Pharm), N,N-Dimethylacetamide (DMF, Thermo Scientific) and dimethylsulfoxide (DMSO, Thermo Scientific) were dried and stored over molecular sieves (beads, 0.4 nm). Bis(dithiobenzoyl) disulfide was prepared according to the literature procedure.1

Gel permeation chromatography (GPC)/ size exclusion chromatography (SEC): Number-average molecular weight (Mn) and dispersity (Mw/Mn) of the resulting polymers were determined using a Shimadzu size exclusion chromatography (SEC), which was performed on a system comprising a Shimadzu LC-20AT pump, Shimadzu RID-20A refractive index detector, and SPD-20A UV–visible detector. The SEC is equipped with a guard column (WAT054415) and 3 × Waters SEC columns (WAT044238, WAT044226 and WAT044235, 300 mm × 7.8 mm), providing an effective molecular weight range of 100–600 000 g mol⁻¹. The eluent is DMF with 10 mM LiBr and is eluted at 1 mL min⁻¹ for 45 min in total. The samples were dissolved in DMF with 10 mM LiBr, filtered through 0.20 μm syringe filters. A calibration curve was obtained from a series of poly(methyl methacrylate) (PMMA) standards with low dispersity. Nuclear magnetic resonance (NMR) spectroscopy: NMR spectra were recorded in acetone-d₆ or DMSO-d₆ or CDCl₃ on a Bruker DRX400 NMR spectrometer operating at 400 MHz for proton and 100 MHz for
carbon nuclei, or Bruker DRX600 NMR spectrometer operating at 600 MHz for proton and 151 MHz for carbon nuclei. Residual acetone, DMSO, and CDCl₃ were used as the internal standard for ¹H-NMR spectra (2.05 ppm for acetone, 2.50 ppm for DMSO, 7.26 ppm for CDCl₃). For ¹³C NMR spectra the central peak in the acetone septet and singlet (29.84 ppm and 206.26 ppm), the central peak in the DMSO-d₆ septet (39.52 ppm), and the central peak in the CDCl₃ triplet (77.16 ppm) were used as internal standard. NMR data were recorded as follows: chemical shift (δ) (multiplicity, coupling constant(s) J (Hz), relative integral), where multiplicity is defined: s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, t = triplet, td = triplet of doublets, tdd = triplet of doublet of doublets, q = quartet, qu = quintet, sep = septet, m = multiplet or combinations thereof, and prefixed br = broad. DOSY-NMR spectra were recorded on a Bruker DRX400 NMR spectrometer operating at 400 MHz (D20 = 0.2 delays and P30 = 750 pulse). DOSY NMR spectra were analysed by Topspin 3.6.2 software. Mass spectroscopy: High resolution mass spectrometry (HRMS) was performed on a Bruker BioApeX 47e FTMS fitted with an analytical electrospray source using NaI for accurate mass calibration.

II. Synthesis of RAFT Precursor

Scheme S1. Synthesis of bis(3,5-dimethyl-1H-pyrazole-1-ylthiocarbonyl) disulfide (4)

Step 1. Synthesis of 3,5-dimethylpyrazole

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\[ \text{N}_2\text{H}_4 \cdot \text{xH}_2\text{O} \rightarrow \text{H}_3\text{C} \begin{array}{c} \text{O} \\ \text{O} \end{array} \text{CH}_3 \rightarrow \begin{array}{c} \text{N} \\ \text{H} \end{array} \begin{array}{c} \text{N} \\ \text{H} \end{array} \text{C} \begin{array}{c} \text{S} \\ \text{S} \end{array} \text{K} \text{THF, 0°C, 0.5 h} \]
```

Acetylacetone (3 mL, 30 mmol, 1 equiv.) was added to a round bottom flask containing ±25 mL of tetrahydrofuran (THF). The solution was stirred and placed in an ice bath. Hydrazine hydrate (1 mL, 33 mmol, 1.1 equiv.) was added dropwise to the cold acetylacetone solution. The mixture was stirred at 0-5 °C for 30 minutes. White precipitate was filtered and washed with petroleum benzine, and then dried under reduced pressure (2 g, 69% yield).

¹H NMR (600 MHz, CDCl₃) δ 5.81 (s, 1H), 2.26 (s, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 144.44, 104.26, 12.25.

Step 2. Synthesis of potassium 3,5-dimethyl-1H-pyrazole-1-carbodithioate

```
\[ \text{H}_3\text{C} \begin{array}{c} \text{N} \\ \text{H} \end{array} \begin{array}{c} \text{N} \\ \text{H} \end{array} \text{C} \begin{array}{c} \text{S} \\ \text{S} \end{array} \text{K} \rightarrow \text{H}_3\text{C} \begin{array}{c} \text{N} \\ \text{H} \end{array} \begin{array}{c} \text{N} \\ \text{H} \end{array} \text{C} \begin{array}{c} \text{S} \\ \text{S} \end{array} \text{K} \text{CS}_2 \text{KOH (1 eq.), THF, rt, 0.5 h} \]
```

SI-3
A 50 mL of THF was added to a round bottom flask containing 3,5-dimethylpyrazole (2 g, 20.80 mmol, 1 equiv.), followed by the addition of potassium hydroxide (KOH, 1.17 g, 20.8 mmol, 1 equiv.). While stirring the mixture at room temperature, carbon disulfide (CS₂, 1.4 mL, 22.8 mmol, 1.1 equiv.) was added dropwise. The color changed from white to yellow and then reddish orange. The orange precipitate was collected by filtration and washed with diethyl ether and chloroform after 30 minutes reactions. The solid was dried overnight under reduced pressure to give light orange powder (1.95 g, 44% yield).

**1H NMR** (600 MHz, DMSO) δ 5.78 (s, 1H), 2.44 (s, 3H), 2.05 (s, 3H).

**13C NMR** (151 MHz, DMSO) δ 220.10, 143.71, 137.58, 106.58, 14.83, 13.25.

**Step 3. Synthesis of bis(3,5-dimethyl-1H-pyrazole-1-ylthiocarbonyl)disulfide (6)**

In a round bottom flask, potassium 3,5-dimethyl-1H-pyrazole-1-carbodithioate (1.95 g, 9.26 mmol, 1 equiv.) was dissolved in 100 mL methanol (MeOH) to give reddish orange solution. Iodine flakes (I₂, 1.18 g, 4.63 mmol, 0.5 equiv.) were added to the potassium salt solution. The reaction mixture was stirred for 2 hours at room temperature. Yellow precipitate formed was filtered and washed with MeOH. The solid was then dried under reduced pressure to give a yellow solid (400 mg, 25% yield).

**1H NMR** (600 MHz, DMSO) δ 6.54 (s, 2H), 2.62 (s, 6H), 2.30 (s, 6H).

**13C NMR** (151 MHz, DMSO) δ 192.65, 153.42, 146.42, 114.66, 16.49, 13.30.

**Scheme S2. Synthesis of Bis(decanesulfanylthiocarbonyl) disulfide (5)**

A solution of NaOH (400 mg, 10 mmol, 1 equiv., 2.5 M) was added slowly to a round bottom flask containing 1-decanethiol (2.11 mL, 10 mmol, 1 equiv.) in diethyl ether (14 mL) under rigorous stirring. This colorless solution was stirred for 30 minutes and then cooled down to 5-10 °C before the addition of carbon disulfide (CS₂) (0.72 mL, 12 mmol, 1.2 equiv.), resulting in a yellow solution. This solution was stirred for 30 minutes, and 10 mL of diethyl ether was added to it before the slow addition of iodine (1.259 mg, 5 mmol, 0.5 equiv.). The reaction mixture was stirred at room temperature for 1.5 hours. After that, 14 mL of diethyl ether was added to the reaction mixture, and the ether phase was washed two times with an aqueous solution of sodium thiosulfate to remove excess iodine and dried over anhydrous magnesium.
sulfate. The solvent was removed under reduced pressure to give a yellow oil. The product was purified by silica gel chromatography, eluted in hexane to give the desired product, which was then crystallised from cold acetone by doing a quick deep in a liquid nitrogen to afford a yellow solid of Bis(decanesulfanyl-thiocarbonyl)disulfide (734 mg, 15% yield).

$^1$H NMR (600 MHz, CDCl$_3$) δ 3.30 (t, $J = 6.0$ Hz, 4H), 1.69 (qu, $J = 6.0$ Hz, 4H), 1.47 – 1.20 (m, 28H), 0.88 (t, $J = 6.0$ Hz, 6H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 221.74, 38.48, 32.02, 29.66, 29.57, 29.43, 29.23, 29.09, 27.51, 22.82, 14.26.
III. Polymerization procedures

Scheme S3. General synthesis of Photo-RAFT polymerization of methyl acrylate initiated by photoinduced decarboxylation of non-activated carboxylic acids

N-Cbz-phenylalanine 1a (18 mg, 0.06 mmol), RAFT precursor 4 (20.6 mg, 0.06 mmol), and photocatalyst PC3 (1.9 mg, 0.003 mmol) were added to a dried microwave tube equipped with a stir bar. Under a nitrogen atmosphere, degassed anhydrous DMSO (1.30 mL) was added, followed by a degassed methyl acrylate (0.54 mL, 6 mmol). The reaction mixture was stirred at room temperature and irradiated by green LED light (552 nm, 75% light intensity, reaction vial was placed 5 cm from the light source). After stirring the reaction overnight, an aliquot was taken to determine the monomer conversion by 1H-NMR spectroscopy (99% conversion). The crude reaction was diluted with acetonitrile and precipitation from a large amount of water (2 times). The resulting polymer was purified by dissolving in a small amount of THF and precipitated from a large amount of ether (2 times), then dried under vacuum to give poly(methyl acrylate) (2a and 3).
Kinetic Study

Table S1. Kinetic study of Photo-RAFT polymerization of methyl acrylate initiated by N-Cbz-phenylalanine

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time (h)</th>
<th>Mon. Conv</th>
<th>Mn, GPC (g/mol)</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>14%</td>
<td>3,360</td>
<td>1.05</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>27%</td>
<td>5,170</td>
<td>1.09</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>36%</td>
<td>6,062</td>
<td>1.15</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>53%</td>
<td>8,318</td>
<td>1.15</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>74%</td>
<td>11,687</td>
<td>1.13</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>84%</td>
<td>13,302</td>
<td>1.15</td>
</tr>
</tbody>
</table>

*Shimadzu size exclusion chromatography (SEC), DMF, using 10 mM of LiBr in DMF and poly(methyl methacrylate) standards

N-Cbz-phenylalanine 1a (18 mg, 0.06 mmol), RAFT precursor 4 (20.6 mg, 0.06 mmol), and photocatalyst PC3 (1.9 mg, 0.003 mmol) were added to a dried Schlenck tube equipped with a stir bar. Under nitrogen atmosphere, degassed anhydrous DMSO (1.3 mL) was added, followed by a degassed methyl acrylate (0.54 mL, 6 mmol). The reaction mixture was stirred at room temperature and irradiated by green LED light (552 nm, 75% light intensity, reaction vial was placed 5 cm from the light source). Aliquots were taken at several points in the range of 6 hours for 1H-NMR and GPC analysis.

Scheme S4. Chain extension experiment
The macroinitiator (poly(methyl acrylate) **2a**: $M_{n,GPC} = 16,600$ g/mol; $Đ = 1.15$) (50 mg, 0.0033 mmol, 1 equiv.) was placed in a dried microwave tube equipped with a stir bar under a nitrogen atmosphere. Degassed anhydrous DMSO (0.85 mL) was added, followed by the addition of 500 equivalents of degassed methyl acrylate (0.15 mL, 1.65 mmol, 500 equiv.). An aliquot of the reaction mixture at time zero was taken and analyzed by $^1$H-NMR spectroscopy. The reaction then was stirred overnight under green LED light irradiation. An aliquot of the crude reaction was taken before isolating the chain extended polymer to determine the monomer conversion by $^1$H-NMR analysis (88% monomer conversion). The crude mixture was diluted by acetonitrile and precipitation from a large amount of water (2 times). The resulting polymer was purified by dissolving in a small amount of THF and precipitated from a large amount of ether (2 times), then dried under vacuum to give the chain-extended poly(methyl acrylate).

**“On/off” experiment**

Table S2. “On-off” experiment of Photo-RAFT polymerisation of methyl acrylate initiated by N-Cbz-phenylalanine

<table>
<thead>
<tr>
<th>No.</th>
<th>Polymerisation time (hours)</th>
<th>Monomer conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0-0.5 (on)</td>
<td>9%</td>
</tr>
<tr>
<td>2</td>
<td>0.5-2 (on)</td>
<td>16%</td>
</tr>
<tr>
<td>3</td>
<td>2-3 (off)</td>
<td>16%</td>
</tr>
<tr>
<td>4</td>
<td>3-4 (on)</td>
<td>19%</td>
</tr>
<tr>
<td>5</td>
<td>4-5 (off)</td>
<td>19%</td>
</tr>
<tr>
<td>6</td>
<td>5-7 (on)</td>
<td>39%</td>
</tr>
<tr>
<td>7</td>
<td>7-8 (off)</td>
<td>39%</td>
</tr>
<tr>
<td>8</td>
<td>8-9 (on)</td>
<td>49%</td>
</tr>
</tbody>
</table>

*N-Cbz-phenylalanine* **1a** (18 mg, 0.06 mmol), RAFT precursor **4** (20.6 mg, 0.06 mmol), and photocatalyst **PC3** (1.9 mg, 0.003 mmol) were added to a dried Schlenck tube equipped with a stir bar. Under nitrogen atmosphere, degassed anhydrous DMSO (1.3 mL) was added, followed by a degassed methyl acrylate (0.54 mL, 6 mmol). The reaction mixture was stirred at room temperature and irradiated by green LED light. Aliquots were taken (Table S2) to determine the monomer conversion by $^1$H-NMR spectroscopy.
Scheme S5. Polymerisation of alternative monomers

\[ \text{N-Cbz-phenylalanine 1a (18 mg, 0.06 mmol), RAFT precursor 4 (20.6 mg, 0.06 mmol), and photocatalyst PC3 (1.9 mg, 0.003 mmol) and a solid monomer (100 equivalents) were added to a dried microwave tube equipped with a stir bar. Under a nitrogen atmosphere, degassed anhydrous DMSO was added, followed by a degassed monomer (6 mmol). The reaction mixture was stirred at room temperature and irradiated by green LED light (552 nm, 75% light intensity, reaction vial was placed 5 cm from the light source). After stirring the reaction overnight, an aliquot was taken to determine the monomer conversion by \textsuperscript{1}H-NMR spectroscopy. The crude reaction was diluted with acetonitrile and precipitation from a large amount of water (2 times). The resulting polymers were purified by dissolving in a small amount of THF and then precipitated in certain solvents as described in Table S3 to give purified polymers (7a-d).} \]

Table S3. Conditions for polymerisation of the alternative monomers and their isolation

<table>
<thead>
<tr>
<th>Monomer</th>
<th>( V_{\text{monomer}}/V_{\text{DMSO}} ) (mL/mL)</th>
<th>Solvents for precipitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA</td>
<td>0.86/0.21</td>
<td>cold methanol</td>
</tr>
<tr>
<td>MMA</td>
<td>0.64/0.28</td>
<td>cold methanol</td>
</tr>
<tr>
<td>DMA</td>
<td>0.62/1.22</td>
<td>diethyl ether</td>
</tr>
<tr>
<td>NIPAM</td>
<td>Solid/0.62</td>
<td>diethyl ether</td>
</tr>
</tbody>
</table>
IV. NMR Spectra of RAFT precursors

**Figure S1** - Bis(3,5-dimethyl-1H-pyrazole-1-ylthiocarbonyl)disulfide (4) – 1H-NMR (600 MHz, DMSO-d$_6$)

**Figure S2** - Bis(3,5-dimethyl-1H-pyrazole-1-ylthiocarbonyl)disulfide (4) – $^{13}$C-NMR (151 MHz, DMSO-d$_6$)
**Figure S3** - Bis-(decanesulfanylthiocarbonyl) disulfide (5) - $^1$H-NMR (600 MHz, CDCl$_3$)

**Figure S4** - Bis-(decanesulfanylthiocarbonyl) disulfide (5) - $^{13}$C-NMR (151 MHz, CDCl$_3$)
V. NMR Spectra and GPC traces of polymers

Figure S5. $^1$H-NMR of poly(methyl acrylate) 2a (400 MHz, Acetone-d$_6$)

Figure S6. GPC traces of poly(methyl acrylate) 2a
**Figure S7.** $^1$H-NMR of poly(methyl acrylate) 2b (400 MHz, Acetone-d$_6$)

**Figure S8.** GPC trace of poly(methyl acrylate) 2b
Figure S9. $^1$H-NMR of poly(methyl acrylate) 2c (400 MHz, Acetone-$d_6$)

Figure S10. GPC trace of poly(methyl acrylate) 2c
**Figure S11.** $^1$H-NMR of poly(methyl acrylate) 2d (400 MHz, Acetone-$d_6$)

**Figure S12.** GPC traces of poly(methyl acrylate) 2d
Figure S13. $^1$H-NMR of poly(methyl acrylate) 2e (400 MHz, Acetone-$d_6$)

Figure S14. GPC trace of poly(methyl acrylate) 2e
Figure S15. $^1$H-NMR of poly(methyl acrylate) 2f (400 MHz, Acetone-$d_6$)

Figure S16. GPC trace of poly(methyl acrylate) 2f
**Figure S17.** $^1$H-NMR of poly(methyl acrylate) 2g (400 MHz, Acetone-$d_6$)

**Figure S18.** GPC trace of poly(methyl acrylate) 2g
Figure S19. $^1$H-NMR of poly(methyl acrylate) 2h (400 MHz, Acetone-$d_6$)

Figure S20. GPC trace of poly(methyl acrylate) 2h
**Figure S21.** $^1$H-NMR of poly(methyl acrylate) 2I (400 MHz, Acetone-$d_6$)

**Figure S22.** GPC trace of poly(methyl acrylate) 2I
Figure S23. $^1$H-NMR of poly(methyl acrylate) 2j (400 MHz, Acetone-$d_6$)

Figure S24. GPC trace of poly(methyl acrylate) 2j
Figure S25. $^1$H-NMR of poly(methyl acrylate) 2k (400 MHz, Acetone-$d_6$)

Figure S26. GPC traces of poly(methyl acrylate) 2k
Figure S27. $^1$H-NMR of poly(butyl acrylate) (pBA) (400 MHz, Acetone-d$_6$)

Figure S28. GPC traces of poly(butyl acrylate) (pBA)
Figure S29. $^1$H-NMR of poly(methyl methacrylate) (pMMA) (400 MHz, DMSO-d$_6$)

Figure S30. GPC traces of poly(methyl methacrylate) (pMMA)
Figure S31. $^1$H-NMR of poly(N,N-dimethylacrylamide) (pDMA) (400 MHz, DMSO-$d_6$)

Figure S32. GPC traces of poly(N,N-dimethylacrylamide) (pDMA)
Figure S33. $^1$H-NMR of poly(N-isopropylacrylamide) (pNIPAM) (400 MHz, D$_2$O)

Figure S34. GPC traces of poly(N-isopropylacrylamide) (pNIPAM)
VI. DOSY NMR

Figure S32. Dosy NMR of poly(methyl acrylate 2a)
VII. ESI Mass Spectroscopy

Electrospray ionisation mass spectrometry (ESI-MS) was used to analyze the structure of the resulting polymer, which was taken from the reaction mixture at lower monomer conversion (32% conversion). The MS spectra can be seen in Figure S35, confirming the poly(methyl acrylate) with the desired α- and ω-endgroups (1480.5538 calcd. for n=12, found 1480.5561, [M+Na⁺]) and a side product of poly(methyl acrylate) containing a pyrazole ring at α-end and thiocarbonylthio moiety at ω-end (1493.5702 calcd. for n=14, found 1493.5704, [M+Na⁺]).

Reference

1. Imamura, Y.; Yamago, S., Role of Lewis Acids in preventing the degradation of dithioester-dormant species in the RAFT polymerization of acrylamides in methanol to enable the successful dual control of molecular weight and tacticity. Polymer Chemistry 2021, 12 (37), 5336-5341.