Supplementary Information for

**Strained alkyne polymers capable of SPAAC via ring-opening metathesis polymerization**

Rajeshwar Vasdev, Wilson Luo, Kyle Classen, Michael Anghel, Samantha Novoa, Mark S. Workentin*, and Joe. B. Gilroy*

*Department of Chemistry and the Centre for Advanced Materials and Biomaterials Research (CAMBR), The University of Western Ontario, London, Ontario, N6A 5B7, Canada. Email: joe.gilroy@uwo.ca, mworkent@uwo.ca*
Experimental Section
Materials and Methods

4-Butoxy-9-hydroxy-6,7-dihydro-1H-dibenzo[a,e]cyclopropa[c]-[8]annulen-1-one was prepared according to a published procedure. All other reagents were used as received and purchased from Sigma-Aldrich and Alfa Aesar. All common solvents and anhydrous drying agents were purchased from Caledon. Solvents were dried using an Innovative Technologies Inc. solvent purification system, collected under vacuum, and stored under a nitrogen atmosphere over 4 Å molecular sieves.

$^1$H and $^{13}$C{$_{^1}$H} NMR spectra were recorded on a Mercury 400 MHz spectrometer. $^1$H NMR spectra are reported as δ in units of parts per million (ppm) relative to CDCl$_3$ (δ 7.27, singlet). Multiplicities are reported as follows: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), m (multiplet), and bs (broad signal). Coupling constants are reported as $J$ values in Hertz (Hz). The number of protons (n) for a given resonance is indicated as nH and is based on spectral integration values. $^{13}$C{$_{^1}$H} NMR spectra are reported as δ in units of parts per million (ppm) relative to CDCl$_3$ (δ 77.00, t).

FT-IR spectra were recorded using a Perkin Elmer Spectrum 2 ATR FT-IR spectrometer by loading sample on to diamond platform. The background was subtracted from each spectrum.

UV-Vis absorption spectra were collected using a Varian Cary 300 Bio spectrophotometer. The solvent background was subtracted from each spectrum.

Emission spectra were collected using a Photon Technology International (PTI) QM-4 SE spectrofluorometer by dissolving the sample in spectroscopic grade CH$_2$Cl$_2$.

Gel permeation chromatography was conducted in DMF containing 10 mM LiBr and 1% NEt$_3$ flowing at 1 mL min$^{-1}$ for 30 min run times at 85 °C. The instrument was equipped with a Waters 515 HPLC pump and a Waters In-line Degasser AF. Materials were detected using a Wyatt Optilab Rex RI detector operating at 25 °C. The method employed two PLgel Mixed-D 5 µm (300 × 1.5 mm) columns connected to a PLgel guard column. Samples were dissolved in the above mobile phase at approximately 5 mg mL$^{-1}$ concentration and filtered through 0.22 µm PTFE syringe filters prior to injection using a 50 µL loop. Monodisperse polystyrene samples ranging in molecular weights of 580 to 170,800 g mol$^{-1}$ were used as calibration standards.

Thermal degradation studies were performed using a TA Instruments Q50 TGA. The sample was placed in a platinum pan and heated at a rate of 10 °C min$^{-1}$ from 25 °C to 1000 °C under a
flow of nitrogen (100 mL min\(^{-1}\)). Glass transition temperatures were determined using Differential Scanning Calorimetry (DSC) on a TA Instruments DSC Q2000. The polymer samples were placed in an aluminum Tzero pan and heated/cooled at 10 °C min\(^{-1}\) in their respective stability window under a flow of nitrogen (50 mL min\(^{-1}\)). The data reported were taken from the second heating/cooling cycle.

Photolysis experiments were conducted in a Luzchem (L2C-4V) equipped with 14 8W 350 nm lamps. Under these conditions samples for unmasking were irradiated for 10 min.

**Synthetic Procedures**

**NHS-activated endo-monomethyl-5-norbornene-2,3-dicarboxylate**

*Endo*-monomethyl-5-norbornene-2,3-dicarboxylate (1.00 g, 5.10 mmol), 4-dimethylaminopyridine (0.12 g, 1.02 mmol), *N*,*N*-dicyclohexylcarbodiimide (1.26 g, 6.12 mmol), N-Hydroxysuccinimide (0.70 g, 6.1 mmol) were dissolved in dry THF (40 mL) under argon. The reaction mixture was stirred at 22 °C for 16 h. Upon completion of the reaction, the THF was evaporated, replaced with CH\(_2\)Cl\(_2\), solids were removed by gravity filtration and the filtrate was concentrated *in vacuo*. The crude product was purified by column chromatography (5% MeOH/CH\(_2\)Cl\(_2\)) to give NHS-activated *endo*-monomethyl-5-norbornene-2,3-dicarboxylate as a white solid. Yield = 1.30 g, 87%.

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 6.49–6.47 (dd, \(J = 5.6 \& 3.1\) Hz, 1H), 6.21–6.19 (dd, \(J = 5.6 \& 2.9\) Hz, 1H), 3.66–3.63 (dd, \(J = 10.2 \& 3.5\) Hz, 1H), 3.61 (s, 3H), 3.42–3.39 (m, 1H), 3.38–3.35 (dd, \(J = 10.2 \& 3.3\) Hz, 1H), 3.25–3.24 (m, 1H), 2.81 (s, 4H), 1.60–1.56 (dt, \(J = 8.9\) Hz, 1H), 1.43–1.41 (m, 1H). \(^{13}\)C\(^{\{1\}H}\) NMR (CDCl\(_3\), 100 MHz): \(\delta\) 172.0, 169.2, 168.2, 137.3, 133.5, 52.0, 49.4, 49.0, 48.1, 45.8, 44.9, 25.8. FT-IR (ATR, cm\(^{-1}\)): 2982, 2949, 1786, 1730, 1434, 1371, 1216, 1071, 1041, 752, 649. HRMS: calculated for [C\(_{12}\)H\(_{15}\)NO\(_6\)]\(^+\), [M]\(^+\): 293.0899, found 293.0903.
Cyclopropenone-masked monomer 1

4-Butoxy-9-hydroxy-6,7-dihydro-1H-dibenzo[a,e]cyclopropa[c]-[8]annulen-1-one\(^1\) (0.430 g, 1.34 mmol) and \(\text{K}_2\text{CO}_3\) (0.223 g, 1.61 mmol) were dissolved in \(\text{CH}_3\text{CN}\) (50 mL). Endo-monomethyl-5-norbornene-2,3-dicarboxylate (0.472 g, 1.61 mmol) was dissolved in \(\text{CH}_3\text{CN}\) (15 mL) and added to reaction mixture. The reaction mixture was stirred at 22 °C for 16 h and upon completion concentrated \textit{in vacuo}. The crude product was purified by column chromatography (silica gel, 15% EtOAc/CH\(_2\)Cl\(_2\)) to give compound (1) as an off-white solid. Yield = 0.487 g, 73%.

\(^1\text{H} \text{NMR (CDCl}_3, \text{400 MHz):} \delta 8.01–7.96 (m, 2H), 7.21–7.14 (m, 2H), 6.92–6.91 (m, 2H), 6.46–6.43 (m, 1H), 6.26–6.25 (m, 1H), 4.07–4.05 (t, 2H), 3.67 (s, 3H), 3.53–3.49 (m, 2H), 3.39–3.35 (t, 2H), 3.32–3.29 (d, J = 12 Hz, 2H), 2.63–2.61 (m, 2H), 1.84–1.79 (m, 2H), 1.59–1.49 (m, 3H), 1.45–1.44 (m, 1H), 1.02–0.99 (t, 3H). \(^{13}\text{C} \{^1\text{H} \text{NMR (CDCl}_3, \text{100 MHz):} \delta 172.5, 170.6, 162.3, 153.7, 153.1, 147.9, 147.0, 144.9, 141.2, 136.0, 135.5, 134.7, 134.4, 122.9, 120.9, 120.2, 116.1, 115.8, 112.3, 116.1, 67.9, 51.7, 48.6, 48.2, 47.9, 46.8, 46.1, 37.2, 36.6, 30.9, 19.0, 13.7. \text{FT-IR (ATR, cm}^{-1}\text{):} 2954, 2933, 2875, 1847, 1763, 1734, 1728, 1566, 1343, 1254, 1112. \text{HRMS: calculated for [C}_{31}\text{H}_{30}\text{O}_{6}^+\text{, [M]}^+: 498.2042, found 498.2032. UV-Vis [\lambda_{max} = 341 (\log \varepsilon = ca. 4.12) and 323 nm in CH}_2\text{Cl}_2\text{]}\]

Cyclopropenone-masked polymer 2

Under a nitrogen atmosphere, monomer 1 (0.25 g, 0.50 mmol) was dissolved in dry CH\(_2\)Cl\(_2\) (24.5 mL) in a Schlenk flask. G3 (4.4 mg, 1% mol) was also dissolved in dry and degassed CH\(_2\)Cl\(_2\) (24.5 mL) in a separate Schlenk flask. The catalyst solution was added to the monomer solution and stirred for 8 h at 22 °C. Catalysis was terminated by the addition of ethyl vinyl ether (25 equiv.) with stirring for 30 min. The catalyst was removed by passing the reaction mixture through a plug of neutral alumina (CH\(_2\)Cl\(_2\)) to give the crude polymer. The crude polymer was dissolved in CH\(_2\)Cl\(_2\) (10 mL) and precipitated in ice-cold pentane (50 mL) to afford polymer 2 as an off-white solid. Yield = 0.190 g, 76%.
\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.00–7.90 (bs, 2H), 7.20–7.09 (bs, 2H), 6.91–6.79 (bs, 2H), 5.91–5.35 (bs, 2H), 4.05–3.95 (bs, 2H), 3.69–3.62 (bs, 3H), 3.38–3.11 (bs, 5H), 2.60–2.39 (bs, 2H), 2.07–1.87 (bs, 2H), 1.77–1.72 (bs, 3H), 1.49–1.47 (bs, 2H), 0.98–0.96 (bs, 3H). FT-IR (ATR, cm\(^{-1}\)): 2953, 2924, 2870, 1847, 1729, 1600, 1556, 1348, 1255, 1122. UV-Vis \([\lambda_{\text{max}} = 342 \text{ (log } \varepsilon = \text{ ca. 4.3}) \text{ and } 322 \text{ nm in CH}_2\text{Cl}_2]\). Concentration used in UV-vis was calculated by taking mass of polymer/monomer MW and was ca 8 \(\times\) 10\(^{-5}\) M. GPC (DMF vs. polystyrene standards): \(M_n = 41,640 \text{ g mol}^{-1}, M_w = 87,190 \text{ g mol}^{-1}, D = 2.09\).

**Time-dependent ROMP of cyclopropenone-masked monomer 1**

According to the procedure described above, monomer 1 underwent ROMP. Aliquots were removed after 1, 2, 4, 6, and 8 h, passed through a short plug of neutral alumina and analyzed by GPC and \(^1\)H NMR spectroscopy without precipitation to produce Table 1, Fig. 2a, and Fig. S14.

**Variation of feed molar ratio**

According to the procedure described above, a series of ROMP reactions with different molar feed ratios of monomer to catalyst were conducted. The catalyst loading was varied in each reaction (0.8, 1.0, 1.2, 2.0, and 4.0 mol%), which corresponded to monomer:catalyst ratios of 125, 100, 83, 50, and 25. After purification via passing the solution through a neutral alumina plug and precipitation, samples were analyzed by GPC to produce Fig. 2b.

**Strained alkyne monomer M3**

Monomer 1 (9.8 mg, 0.020 mmol) was dissolved in glass distilled CH\(_2\)Cl\(_2\) (250 mL) and purged with argon for 15 min. The solution was irradiated in the photochemical Luzchem (L2C-4V) using 350 nm light for 10 min with stirring. Strained alkyne monomer M3 was isolated as a pale-yellow oil and characterized without further purification. Yield = 9.3 mg, 100%.

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.26–7.22 (dd, \(J = 10.2 \& 8.3 \) Hz, 2H), 7.09–7.07 (dd, \(J = 5.0 \& 2.3 \) Hz, 1H), 6.99–6.96 (dt, \(J = 8.3 \) Hz, 1H), 6.89–6.88 (d, \(J = 2.5 \) Hz, 1H), 6.79–6.76 (dd, \(J = 8.5 \& 2.7 \) Hz, 1H), 6.44–6.40 Hz (m, 1H), 6.29–6.25 (m, 1H), 3.99 (t, \(J = 8 \) Hz, 2H), 3.71–3.60 (m, 3H), 3.54–3.44 (m, 2H), 3.31–3.12 (m, 4H), 2.44–2.41 (m,
2H), 1.82–1.75 (m, 1H), 1.58–1.42 (m, 3H), 1.26 (s, 2H), 0.99 (t, J = 8 Hz, 3H). \(^{13}\text{C}\{\text{^1}\text{H}}\) NMR (CDCl\(_3\), 100 MHz): \(\delta\) 172.7, 171.0, 158.9, 155.2, 154.3, 149.8, 135.4, 134.8, 126.9, 126.3, 122.9, 121.8, 119.5, 116.7, 115.4, 111.9, 111.8, 109.5, 77.2, 67.8, 51.8, 48.7, 48.2, 46.8, 46.3, 36.5, 36.4, 31.3, 19.2, 13.8. FT-IR (ATR, cm\(^{-1}\)): 2959, 2923, 2865, 1758, 1734, 1556, 1487, 1176, 1146.

HRMS: calculated for [C\(_{30}\)H\(_{30}\)O\(_5\)]\(^+\), [M]\(^+\): 470.2093, found 470.2082. UV-Vis (\(\lambda_{\text{max}}\) = 319 (log \(\varepsilon\) = ca. 4.1) and 304 nm in CH\(_2\)Cl\(_2\)).

**Strained alkyne polymer 3**

Cyclopropenone-masked polymer 2 (10 mg, 0.020 mmol) was dissolved in glass distilled CH\(_2\)Cl\(_2\) (250 mL) and purged with argon for 15 min. The solution was irradiated in the photochemical Luzchem (L2C-4V) using 350 nm light for 10 min with stirring. Compound (3) was isolated as a pale-yellow oil and characterized without further purification. Yield = 9.3 mg, 99%.

\(^1\text{H} \)NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.20 (bs, 2H), 7.01 (bs, 1H), 6.87 (bs, 1H), 6.75 (bs, 1H), 6.00–5.42 (bs, 2H), 3.98–3.89 (bs, 2H), 3.67–3.61 (bs, 3H), 3.40–3.07 (bs, 4H), 2.45–2.28 (bs, 1H), 2.03 (bs, 1H), 1.75 (bs, 2H), 1.47 (bs, 2H), 1.32–1.20 (bs, 4H), 0.99–0.84 (bs, 6H). FT-IR (ATR, cm\(^{-1}\)): 2954, 2924, 2870, 2253, 2164, 1734, 1561, 1482, 1216, 1137, 894, 726. UV-Vis (\(\lambda_{\text{max}}\) = 320 and 303 nm in CH\(_2\)Cl\(_2\)).

**Benzyl-functionalized monomer M4a (both regioisomers)**

Strained alkyne monomer M3 (10 mg, 0.021 mmol) was dissolved in glass distilled CH\(_2\)Cl\(_2\) (2 mL). Benzyl azide (3 mg, 0.02 mmol) was added to the reaction mixture, which was stirred for 30 min. After solvent removal in vacuo, the crude product was purified by column chromatography (silica gel, 5% EtOAc/CH\(_2\)Cl\(_2\)) to give compound M4a as a yellow oil. Yield = 12 mg, 95%.

\(^1\text{H} \)NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.53–7.50 (d, J = 8.0 Hz, 1H), 7.25–7.24 (m, 2H), 7.09–7.08 (m, 3H), 6.97–6.88 (m, 2H), 6.78–6.72 (m, 2H), 6.37–6.35 (m, 1H), 6.27–6.25 (m, 1H), 5.59–5.47 (m, 2H), 3.98–3.94 (m, 2H), 3.61 (s, 3H), 3.49–3.40 (m, 2H), 3.27–2.64 (m, 4H), 2.32–2.18 (m, 1H), 2.08–2.05 (m, 1H), 1.81–1.74 (m, 2H), 1.54–1.25 (m, 5H), 1.00–0.07 (m, 3H). \(^{13}\text{C}\{\text{^1}\text{H}}\) NMR
Benzyl-functionalized polymer 4a (both regioisomers)

Cyclopropenone-masked polymer 2 (33 mg, 0.067 mmol) and benzyl azide (11 mg, 0.080 mmol) and was dissolved in CH$_2$Cl$_2$ (250 mL) and purged with argon for 15 min. The solution was irradiated in the photochemical Luzchem (L2C-4V) using 350 nm light for 10 min. The reaction was monitored by UV-Vis absorption spectroscopy. After solvent removal, the crude polymer was dissolved in CH$_2$Cl$_2$ (10 mL) and precipitated in ice-cold pentane (50 mL) to afford benzyl-functionalized polymer as a yellow solid. Yield = 40 mg, 98%.

The product was characterized by $^1$H NMR spectroscopy in CDCl$_3$ (Fig. S23). Because of the broadness of the signals this was done by comparing the spectrum to that of the monomer M4a. FT-IR (ATR, cm$^{-1}$): 3368, 2924, 2855, 1734, 1605, 1457, 1206, 1132. UV-Vis ($\lambda_{\text{max}} = 257$ nm in CH$_2$Cl$_2$). $M_n = 44,780$ g mol$^{-1}$, $M_w = 100,900$ g mol$^{-1}$, $D = 2.43$.

Ferrocene-functionalized monomer M4b (both regioisomers)

Strained alkyne monomer M3 (10 mg, 0.021 mmol) was dissolved in glass distilled CH$_2$Cl$_2$ (2 mL). Azidomethylferrocene (5 mg, 0.02 mmol) was added to the reaction mixture, which was then stirred for 30 min. After solvent removal, the crude product was purified by column chromatography (silica gel, pure CH$_2$Cl$_2$ followed by pure EtOAc) to give compound M4b an orange solid (12 mg, 81% yield).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.48–7.38 (m, 1H), 7.22–7.07 (m, 2H), 6.93–6.83 (m, 2H), 6.75–6.63 (m, 1H), 6.47–6.34 (m, 1H), 6.27–6.25 (m, 1H), 5.26 (s, 2H), 4.29–4.00 (m, 7H), 3.93–3.83 (m, 2H), 3.67–3.60 (m, 2H), 3.50–3.39 (m, 2H), 3.31–3.23 (m, 3H), 3.00–2.72 (m, 3H), 1.82–1.69 (m, 3H), 1.62–1.38 (m, 4H), 1.31–1.29 (m, 2H), 1.03–0.93 (m, 3H).
of both regioisomers, there are additional carbon signals for many of the carbon environments.

$^{13}$C{\textsuperscript{1}H} NMR (CDCl$_3$, 100 MHz): δ 173.0, 171.4, 171.2, 160.4, 159.0, 151.8, 150.5, 146.9, 146.2, 143.5, 143.3, 139.3, 139.2, 135.9, 135.7, 135.1, 135.0, 134.8, 133.6, 133.1, 132.7, 130.5, 130.4, 127.9, 124.5, 123.6, 123.2, 123.1, 122.5, 120.1, 120.0, 119.5, 118.7, 116.7, 115.9, 113.0, 112.6, 69.2, 68.8, 68.0, 67.8, 60.6, 53.7, 52.1, 52.0, 49.0, 48.5, 47.1, 46.9, 46.5, 36.7, 36.6, 33.2, 31.9, 31.6, 30.0, 29.6, 29.3, 25.5, 22.9, 21.3, 19.5, 14.5, 14.1. FT-IR (ATR, cm$^{-1}$): 3071, 2949, 2934, 2865, 1739, 1610, 1511, 1343, 1250, 1201, 1151, 1003, 820, 736.

HRMS: calculated for [C$_{41}$H$_{41}$FeN$_3$O$_5$]$^+$, [M]$^+$: 711.2396, found 711.2381.

**Ferrocene-functionalized polymer 4b (both regioisomers)**

Cyclopropenone-masked polymer 2 (44 mg, 0.088 mmol) and azidomethylferrocene (30 mg, 0.12 mmol) and was dissolved in CH$_2$Cl$_2$ (250 mL) and purged with argon for 15 min. The solution was irradiated in the photochemical Luzchem (L2C-4V) using 350 nm light for 10 min. The reaction was monitored by UV-Vis absorption spectroscopy. After solvent removal, the crude polymer was dissolved in CH$_2$Cl$_2$ (10 mL) and precipitated in ice-cold pentane (50 mL) to afford ferrocene-functionalized polymer 4b as a yellow solid. Yield = 60 mg, 95%. The product was characterized by $^1$H NMR in CDCl$_3$ (Fig. S32). Because of the broadness of the signals this was done by comparing the spectrum to that of the monomer M4b.

FT-IR (ATR, cm$^{-1}$): 3437, 3092, 2959, 2924, 2865, 2242, 1739, 1605, 1511, 1206, 1137, 983, 914, 820, 721. $M_n = 50,890$ g mol$^{-1}$, $M_w = 110,600$ g mol$^{-1}$, $D = 2.17$.

**Pyrene-functionalized monomer M4c (both regioisomers)**

Strained alkyne monomer M3 (10 mg, 0.021 mmol) was dissolved in glass distilled CH$_2$Cl$_2$ (2 mL). Azidomethylpyrene (6 mg, 0.023 mmol) was added to the reaction mixture, which was stirred for 30 min. After solvent removal, the crude product was purified by column chromatography (silica gel, pure CH$_2$Cl$_2$ followed by pure EtOAc) to give compound M4c as a beige solid (14 mg, 90% yield).
\[1\text{H NMR (CDCl}_3, 400 MHz): \delta 8.21–8.16 (m, 3H), 8.10–8.00 (m, 5H), 7.59–7.49 (m, 2H), 7.16–7.04 (m, 1H), 6.97–6.92 (m, 1H), 6.86–6.75 (m, 1H), 6.70–6.67 (m, 1H), 6.59 (s, 1H), 6.36–6.34 (m, 1H), 6.26–6.24 (m, 1H), 3.92–3.89 (t, 8 Hz, 2H), 3.60 (s, 3H), 3.48–3.38 (m, 2H), 3.28–3.22 (m, 2H), 3.15–3.03 (m, 1H), 2.91–2.75 (m, 1H), 2.65–2.58 (m, 1H), 1.77–1.70 (m, 2H), 1.56–1.38 (m, 5H), 1.31–1.30 (m, 1H), 0.99–0.93 (m, 3H). Due to the presence of both regioisomers, there are additional carbon signals for many of the carbon environments. \[\text{\textsuperscript{13}C\{\textsuperscript{1}H\} NMR (CDCl}_3, 100 MHz): \delta 172.6, 170.7, 160.1, 158.8, 151.6, 150.3, 146.9, 146.2, 142.8, 139.2, 139.0, 135.1, 134.8, 134.4, 133.5, 132.7, 132.6, 131.3, 131.1, 130.5, 130.2, 130.0, 128.4, 128.2, 128.1, 127.7, 127.5, 127.3, 126.4, 126.1, 125.5, 125.4, 124.7, 124.6, 124.5, 123.8, 123.2, 122.0, 119.2, 118.0, 116.3, 115.7, 112.8, 112.4, 67.7, 67.5, 60.4, 53.4, 51.7, 50.4, 48.7, 48.2, 46.7, 46.6, 46.3, 36.1, 36.0, 32.7, 31.2, 19.2, 14.2, 13.8. FT-IR (ATR, cm\(^{-1}\)): 3043, 2954, 2924, 2865, 1753, 1739, 1605, 1511, 1339, 1260, 1196, 1146, 845, 701. HRMS: calculated for [C\(_{47}\)H\(_{41}\)N\(_3\)O\(_5\)]\(^+\), [M\(^+\): 727.3046, found 728.3112. UV-Vis in CH\(_2\)Cl\(_2\) (\(\lambda_{\text{max}}\) = 346, 329, 315, 278 and 267 nm in CH\(_2\)Cl\(_2\)).

**Synthesis of pyrene-functionalized polymer 4c (both regioisomers)**

Cyclopropenone-masked polymer 2 (45 mg, 0.090 mmol) and azidomethylpyrene (25 mg, 0.097 mmol) and were dissolved in CH\(_2\)Cl\(_2\) (250 mL) and purged with argon for 15 min. The solution was irradiated in the photochemical Luzchem (L2C-4V) using 350 nm light for 10 min. The reaction was monitored by UV-Vis absorption spectroscopy. After solvent removal, the crude polymer was dissolved in CH\(_2\)Cl\(_2\) (10 mL) and precipitated into ice-cold pentane (50 mL) to afford pyrene-functionalized polymer 4c as a yellow solid. Yield = 50 mg, 77%.

The product was characterized by \(^1\text{H NMR} \text{ spectroscopy in CDCl}_3\) (Fig. S39). Because of the broadness of the signals this was done by comparing the spectrum to that of the monomer M\(_4\)c. FT-IR (ATR, cm\(^{-1}\)): 3043, 2959, 2870, 2361, 2257, 1734, 1605, 1205, 1132, 904, 845, 726. UV-Vis in CH\(_2\)Cl\(_2\) (\(\lambda_{\text{max}}\) = 346, 329, 315, 277 and 266 nm). M\(_n\) = 33,710 g mol\(^{-1}\), M\(_w\) = 84,860 g mol\(^{-1}\), D = 2.52.
Fig. S1  $^1$H NMR spectrum of NHS-activated endo-monomethyl-5-norbornene-2,3-dicarboxylate in CDCl$_3$. Asterisks denote residual solvent signals.

Fig. S2  $^{13}$C($^1$H) NMR spectrum of NHS-activated endo-monomethyl-5-norbornene-2,3-dicarboxylate in CDCl$_3$. Asterisk denotes solvent signal.
**Fig. S3**  FT-IR spectrum of NHS-activated *endo*-monomethyl-5-norbornene-2,3-dicarboxylate.

**Fig. S4**  $^1$H NMR spectrum of cyclopropenone-masked monomer 1 in CDCl$_3$. Asterisks denote residual solvent signals.
Fig. S5. $^{13}\text{C}$\{H\} NMR spectrum of cyclopropenone-masked monomer 1 in CDCl$_3$. Asterisk denotes solvent signal.

Fig. S6. FT-IR spectrum of cyclopropenone-masked monomer 1.
**Fig. S7** UV-Vis absorption spectrum of cyclopropenone-masked monomer 1 (orange), strained alkyne monomer M3 (blue), benzyl-functionalized monomer M4a (pink), and ferrocene-functionalized monomer M4b (black) in CH$_2$Cl$_2$. Spectra were normalised at 220 nm.

**Fig. S8** UV-Vis absorption spectrum of cyclopropenone-masked polymer 2 (orange), strained alkyne polymer 3 (blue), benzyl-functionalized polymer 4a (pink), and ferrocene-functionalized polymer 4b (black) in CH$_2$Cl$_2$. 
Fig. S9 $^1$H NMR spectrum of cyclopropenone-masked polymer 2 in CDCl$_3$. Asterisks denote residual solvent and grease signals.

Fig. S10 FT-IR spectrum of cyclopropenone-masked polymer 2.
Fig. S11  GPC trace obtained for cyclopropenone-masked polymer 2 in DMF.

Fig. S12  TGA analysis of cyclopropenone-masked polymer 2.
Fig. S13  DSC analysis of cyclopropenone-masked polymer 2.

Fig. S14  GPC traces obtained for aliquots taken from the ROMP of cyclopropenone-masked monomer 1 at various times.
**Fig. S15**  \(^1\)H NMR spectrum of strained alkyne monomer M3 in CDCl\(_3\). Asterisks denote residual solvent signals.

**Fig. S16**  \(^{13}\)C\(_{\{1\}^1\}\) NMR spectrum of strained alkyne monomer M3 in CDCl\(_3\). Asterisk denotes solvent signal.
**Fig. S17**  
FT-IR spectrum of strained alkyne monomer M3.

**Fig. S18**  
$^1$H NMR spectrum of strained alkyne polymer 3 in CDCl$_3$. Asterisks denote residual solvent signals.
**Fig. S19**  FT-IR spectrum of strained alkyne polymer 3.

**Fig. S20**  $^1$H NMR spectrum of benzyl-functionalized monomer M4a in CDCl$_3$. Asterisks denote residual solvent signals.
Fig. S21 $^{13}$C{$^1$H} NMR spectrum of benzyl-functionalized monomer M4a in CDCl$_3$. Asterisk denotes residual solvent signal.

Fig. S22 FT-IR spectrum of benzyl-functionalized monomer M4a.
**Fig. S23**  \(^1\)H NMR spectrum of benzyl-functionalized polymer 4a in CDCl₃. Asterisks denote residual solvent signals. Because of the broadness of the spectrum, it was characterized by direct comparison of the chemical shifts and rough integration to the spectrum of the corresponding monomer M4a.

**Fig. S24**  FT-IR spectrum of benzyl-functionalized polymer 4a.
Fig. S25  TGA analysis of benzyl-functionalized polymer 4a.

Fig. S26  DSC analysis of benzyl-functionalized polymer 4a.
**Fig. S27** $^1$H NMR spectrum of ferrocene-functionalized monomer M4b in CDCl$_3$. Asterisks denote residual solvent signals.

**Fig. S28** $^{13}$C\{H\} NMR spectrum of ferrocene-functionalized monomer M4b. Asterisk denotes residual solvent signal.
**Fig. S29**   FT-IR spectrum of ferrocene-functionalized monomer M4b.

**Fig. S30**   UV-Vis absorption spectrum of strained alkyne monomer M3 (blue) and ferrocene-functionalized monomer M4b (black) in CH$_2$Cl$_2$ with expansion showing the long wavelength absorption of the ferrocene moiety.
**Fig. S31**  UV-Vis absorption spectrum of strained alkyne polymer 3 (blue) and ferrocene-functionalized polymer 4b (black) in CH$_2$Cl$_2$ with expansion showing the long wavelength absorption of the ferrocene moiety.

**Fig. S32**  $^1$H NMR spectrum of ferrocene-functionalized polymer 4b in CDCl$_3$. Asterisks denote residual solvent signals. Because of the broadness of the spectrum, it was characterized by direct comparison of the chemical shifts and rough integration to the spectrum of the corresponding monomer M4b.
Fig. S33  FT-IR spectrum of ferrocene-functionalized polymer 4b.

Fig. S34  TGA analysis of ferrocene-functionalized polymer 4b.
Fig. S35  DSC analysis of ferrocene-functionalized polymer 4b.

Fig. S36  $^1$H NMR spectrum of pyrene-functionalized monomer M4c in CDCl$_3$. Asterisks denote residual solvent signals.
**Fig. S37** $^{13}$C\{H\} NMR spectrum of pyrene-functionalized monomer M4c. Asterisk denotes solvent signal.

**Fig. S38** FT-IR spectrum of pyrene-functionalized monomer M4c.
**Fig. S39**  
$^1$H NMR spectrum of pyrene-functionalized polymer 4c in CDCl$_3$. Asterisk denotes residual solvent signal. Because of the broadness of the spectrum, it was characterized by direct comparison of the chemical shifts and rough integration to the spectrum of the corresponding monomer M4c.

**Fig. S40**  
FT-IR spectrum of pyrene-functionalized polymer 4c.
Fig. S41  TGA analysis of pyrene-functionalized polymer 4c.

Fig. S42  DSC analysis of pyrene-functionalized polymer 4c.
Reference