Supporting Information

Nucleophilic thiol-Michael chemistry and hyperbranched (co)polymers: synthesis and ring-opening metathesis (co)polymerization of novel difunctional exo-7-oxanorbornenes with in situ inimer formation

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1. Experimental Procedure and Characterization of Compounds and polymers

Real-time $^1$H NMR monitoring of thiol-Michael adduct ROMP kinetics

Homopolymerization of M1

Using M1 (32.9 mg, 0.047 mmol) and RuCl$_2$(PCy)$_3$CHPh (2.9 mg, 0.0035 mmol for a targeted molecular weight of 10,000). **PM1**: $^1$H NMR (300 MHz, CD$_2$Cl$_2$, ppm): $\delta$ = 1.69-1.75 (m, 4H), 2.43-2.68 (m, 4H), 3.33-3.76 (m, 12H), 4.31-5.05 (m, 8H), 5.84-6.12 (m, 4H), 7.28-7.33 (m, 4H). $M_n$ (NMR) = 10,956; $M_n$ (DMAC GPC) = 23,634; $M_w$ = 33,166, PDI = 1.40; c/t ratio = 26.5/73.5.

Homopolymerization of M3

Using M3 (28.8 mg, 0.041 mmol) and RuCl$_2$(PCy)$_3$CHPh (2.7 mg, 0.0032 mmol for a targeted molecular weight of 10,000). **PM3**: $^1$H NMR (300 MHz, CD$_2$Cl$_2$, ppm): $\delta$ = 1.63-1.93 (m, 4H), 2.60-2.83 (m, 12H), 3.39-3.80 (m, 12H), 4.26-5.04 (m, 8H), 5.81-6.13 (m, 4H). $M_n$ (NMR) = 6329; $M_n$ (DMAC GPC) = 17,316;
M_w = 26,126, PDI = 1.50; c/t ratio = 30.0/70.0.

Homopolymerization of M4
Using M4 (12.9 mg, 0.025 mmol) and RuCl_2(PCy_3)_2CHPh (1.1 mg, 0.0013 mmol for a targeted molecular weight of 10,000). PM4: 1H NMR (300 MHz, CD_2Cl_2, ppm): δ = 1.28-2.06 (m, 20H), 2.51-2.74 (m, 5H), 3.01-3.37 (m, 5H), 3.79-3.90 (m, 3H), 4.21-5.23 (m, 3H), 5.85-6.12 (m, 2H), 6.35-6.82 (m, 1H), 7.19-7.51 (m, 1H). M_n (NMR) = 17,106; M_n (DMAC GPC) = 10,045; M_w = 13,705, PDI = 1.36; c/t ratio = 33.9/66.1.

Homopolymerization of M5
Using M5 (11.5 mg, 0.025 mmol) and RuCl_2(PCy_3)_2CHPh (1.0 mg, 0.0012 mmol for a targeted molecular weight of 10,000). PM5: 1H NMR (300 MHz, CD_2Cl_2, ppm): δ = 1.68-2.27 (m, 6H), 3.23-3.40 (m, 2H), 4.08-5.08 (m, 5H), 5.77-6.12 (m, 2H), 7.34-7.78 (m, 8H). M_n (NMR) = 9555; M_n (DMAC GPC) = 16,128; M_w = 25,844, PDI = 1.60; c/t ratio = 27.8/72.2.
See our previous report1.

See our previous report1.

See our previous report1.
Copolymerization of M1/M6 (25:75)
Using M1 (8.7 mg, 0.0125 mmol), M6 (27.9 mg, 0.0375 mmol) and RuCl₂(PCy₃)₂CHPh (3.1 mg, 0.0037 mmol for a targeted molecular weight of 10,000).

Copolymerization of M1/M6 (50:50)
Using M1 (17.4 mg, 0.025 mmol), M6 (18.6 mg, 0.025 mmol) and RuCl₂(PCy₃)₂CHPh (3.0 mg, 0.0036 mmol for a targeted molecular weight of 10,000).

Copolymerization of M1/M6 (75:25)
Using M1 (26.1 mg, 0.0375 mmol), M6 (9.3 mg, 0.0125 mmol) and RuCl₂(PCy₃)₂CHPh (2.96 mg, 0.0035 mmol for a targeted molecular weight of 10,000).

STAT P(M1+M6): ¹H NMR (300 MHz, CD₂Cl₂, ppm): δ = 1.58-1.91 (m, 12H), 2.44-2.81 (m, 22H), 3.42-3.45 (m, 7H), 4.28-5.11 (m, 13H), 5.83-6.75 (m, 6H), 7.26-7.51 (m, 4H). Mₙ (NMR) = 9162; c/t ratio = 28.0/72.0.
Copolymerization of M3/M7 (25:75)
Using M3 (8.85 mg, 0.0125 mmol), M7 (43.3 mg, 0.0375 mmol) and RuCl₂(PCy₃)₂CHPh (4.36 mg, 0.0052 mmol for a targeted molecular weight of 10,000).

Copolymerization of M3/M7 (50:50)
Using M3 (17.7 mg, 0.025 mmol), M7 (28.8 mg, 0.025 mmol) and RuCl₂(PCy₃)₂CHPh (3.9 mg, 0.0047 mmol for a targeted molecular weight of 10,000).

Copolymerization of M3/M7 (75:25)
Using M3 (26.6 mg, 0.0375 mmol), M7 (14.42 mg, 0.0125 mmol) and RuCl₂(PCy₃)₂CHPh (3.43 mg, 0.0041 mmol for a targeted molecular weight of 10,000).

STAT P(M3+M7): ¹H NMR (300 MHz, CD₂Cl₂, ppm): δ = 0.62-2.01 (m, 50H), 2.61-2.86 (m, 18H), 3.40-3.80 (m, 22H), 4.11-5.15 (m, 12H), 5.89-6.48 (m, 6H), 7.31-7.50 (m, 1H). Mₙ (NMR) = 11,673; c/t ratio = 30.6/69.4.
Copolymerization of M1/M4 (50:50)

Using M1 (17.4 mg, 0.025 mmol), M4 (12.9 mg, 0.025 mmol) and RuCl₂(PCy₃)₂CHPh (2.5 mg, 0.0030 mmol for a targeted molecular weight of 10,000).

STAT P(M₁+M₄): 'H NMR (300 MHz, CD₂Cl₂, ppm): δ = 1.28-1.85 (m, 32H), 2.46-2.72 (m, 12H), 3.30-3.77 (m, 12H), 4.20-5.06 (m, 12H), 5.82-6.12 (m, 6H), 7.28-7.51 (m, 4H). Mₙ (NMR) = 12,381; Mₙ (DMAC GPC) = 26,200; Mₙ = 63,500, PDI = 2.42; c/t ratio = 24.6/75.4.
Copolymerization of M3/M5 (50:50)

Using M3 (17.7 mg, 0.025 mmol), M5 (11.5 mg, 0.025 mmol) and RuCl₂(PCy₃)₂CHPh (2.4 mg, 0.0029 mmol for a targeted molecular weight of 10,000).

STAT P(M3+M5): ¹H NMR (300 MHz, CD₂Cl₂, ppm): δ = 1.28-2.82 (m, 22H), 3.78-3.79 (m, 16H), 4.29-5.07 (m, 11H), 5.84-6.14 (m, 6H), 7.38-7.76 (m, 8H). Mₙ (NMR) = 29,379; Mₙ (DMAC GPC) = 28,100, Mₘ = 73,950, PDI = 2.63; c/t ratio = 28.8/71.2.
Determination of ROMP kinetics via an aliquot approach

ROMP kinetics via an aliquot approach of M1/M6 (25:75)
Using M1 (0.087 g, 0.125 mmol), M6 (0.279 g, 0.375 mmol) and RuCl₂(PCy₃)₂CHPh (30.6 mg, 0.037 mmol for a targeted molecular weight of 10,000). Aliquots were withdrawn periodically (at 2, 5, 10, 15, 20, 25, 30, 35, 40, 50, 65 and 90 min, with intervals based on prior kinetic experiments).

ROMP kinetics via an aliquot approach of M1/M6 (50:50)
Using M1 (0.17 g, 0.25 mmol), M6 (0.185 g, 0.25 mmol) and RuCl₂(PCy₃)₂CHPh (29.7 mg, 0.035 mmol for a targeted molecular weight of 10,000). Aliquots were withdrawn periodically (at 2, 5, 10, 20, 30, 40, 60, 80, 100, 120, 150, 180 and 200 min, with intervals based on prior kinetic experiments).

ROMP kinetics via an aliquot approach of M1/M6 (75:25)
Using M1 (0.26 g, 0.375 mmol), M6 (0.093 g, 0.125 mmol) and RuCl₂(PCy₃)₂CHPh (29.5 mg, 0.035 mmol for a targeted molecular weight of 10,000). Aliquots were withdrawn periodically (at 2, 5, 10, 20, 30, 40, 60, 80, 100, 120, 150, 180 and 200 min, with intervals based on prior kinetic experiments).

ROMP kinetics via an aliquot approach of M3/M7 (25:75)
Using M3 (0.089 g, 0.125 mmol), M7 (0.433 g, 0.375 mmol) and RuCl₂(PCy₃)₂CHPh (43 mg, 0.051 mmol for a targeted molecular weight of 10,000). Aliquots were withdrawn periodically (at 2, 5, 10, 15, 20, 25, 30, 35, 40, 50, 67 and 90 min, with intervals based on prior kinetic experiments).

ROMP kinetics via an aliquot approach of M3/M7 (50:50)
Using M3 (0.177 g, 0.25 mmol), M7 (0.288 g, 0.25 mmol) and RuCl₂(PCy₃)₂CHPh (38.9 mg, 0.046 mmol for a targeted molecular weight of 10,000). Aliquots were withdrawn periodically (at 2, 5, 10, 20, 30, 40, 60, 80, 100, 130, 150, 180 and 200 min, with intervals based on prior kinetic experiments).

ROMP kinetics via an aliquot approach of M3/M7 (75:25)
Using M3 (0.266 g, 0.375 mmol), M7 (0.144 g, 0.125 mmol) and RuCl₂(PCy₃)₂CHPh (34.3 mg, 0.041 mmol for a targeted molecular weight of 10,000). Aliquots were withdrawn periodically (at 2, 5, 10, 20, 30,
40, 60, 80, 100, 120, 150, 180 and 200 min, with intervals based on prior kinetic experiments).
2. Copies of $^1$H- and $^{13}$C spectra

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3. References