Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Highly 2,3-Selective and Fast Living Polymerization of Alkyl-, Alkoxy- and Phenylallene Using Nickel(II) Catalysts

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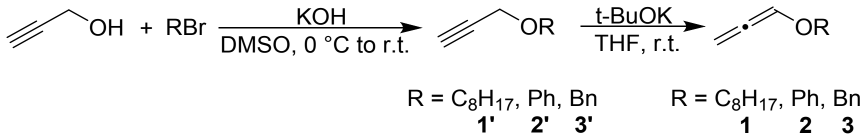
Experimental Procedures

General considerations. The ^{1}H NMR spectrum were recorded using an Agilent 600

MHz spectrometer {H}. Size exclusion chromatography (SEC) was performed on Waters 1515 pump and Waters 2414 differential refractive index (RI) detector. The eluent was tetrahydrofuran (THF) as the eluent at a flow rate of 0.8 mL/min. A series of two linear TSK gel GMHHR-H columns were used. M_n and M_w/M_n values were reported with reference to the polystyrene standards. FT-IR spectra were recorded on Perkin-Elmer Spectrum BX FT-IR system using KBr pellets at 25 °C. Differential scanning calorimetric (DSC) measurements were carried on a NETZSCH DSC 200F3 instrument. Poly-$\mathbf{1}_{100}$ and poly-$\mathbf{4}_{100}$ were first heated from -100 ℃ to 140 °C at a heating rate of 5 ℃/min under nitrogen atmosphere, poly-$\mathbf{2}_{100}$ and poly-$\mathbf{3}_{100}$ were first heated from -40 ℃ to 150 °C and the other samples were first heated from -20 ℃ to 240 ℃ at a heating rate of 10 ℃/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere at a heating rate of 10 °C/min from 25 ℃ to 800 °C using a NETZSCH STA 409 PC/PG instrument. Wide angle X-ray diffraction (WAXD, Rigaku D/max-2500 VB/PC apparatus, Japan) measurement was performed using Cu Kα radiation (λ = 1.54 Å) by graphite crystal. All solvents and chemicals were purchased from Sinopharm, Sigma-Aldrich and Aladdin Co. Ltd., and were purified by the standard procedures before used. The monomers **1-9**, Ni(II) catalyst, and the phosphine ligands **L1**, **L4** and **L5** were prepared according to reported literatures with slight modifications, and the structures were confirmed by ^{1}H NMR. [1-11] Ligands **L2**, **L3**, and **L6-L13** were obtained from Aladdin Co. Ltd. Tetrahydrofuran (THF) for polymerizations was further dried over sodium benzophenone ketyl, distilled onto lithium aluminum hydride under nitrogen atomosphere, and distilled under high vacuum just before use.

Synthetic Procedures

Scheme S1 Synthesis of monomers 1-3



Synthesis of 1-(prop-2-yn-1-yloxy) octane: Monomer **1-3** was prepared accordingly to Scheme S1 following the reported literature.[1-3] Taking monomer **1** as an example. Propargyl alcohol (3.70 g, 66.7 mmol) was added to a suspension of KOH (11.21 g, 200.0 mmol) in 100 mL DMSO at 0 ºC. After stirring for 30 min, 1-bromooctane (12.90 g, 66.7 mmol) was added at 0 ºC. Then, the reaction solution was warmed to room temperature and stirred for another 10 h. After the consumption of the materials completely, the resulting brown suspension was diluted with 200 mL water and extracted with diethyl ether three times (3 × 50 mL). The combined organic layer was washed with water (2 × 20 mL) and brine (2 × 20 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash chromatography using petroleum ether as eluent to afford the desired product as colorless liquid (7.89 g, 70% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ (ppm) 4.13 (s, 2H), 3.50 (t, 2H), 2.41 (s, 1H), 1.59 (t, 2H), 1.34 (m, 2H), 1.26 (m, 8H), 0.88 (t, 3H).

Synthesis procedure of monomer 1: *t*-BuOK (2.40 g, 21.4 mmol) was added batch-wise into a solution of 1-(prop-2-yn-1-yloxy) octane (3.00 g, 17.8 mmol) in 60 mL THF within 30 min at room temperature. The suspension was stirred at room temperature for 5 h, then filtered through a celite pad and washed with Et_2O (2 ×30 mL). The organic phase was combined and concentrated under reduced pressure. The crude was purified by flash chromatography using 0.5−0.8% diethyl ether in petroleum ether as eluent to afford monomer **1** as a colorless oil (2.04 g, 68% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ (ppm) 6.72 (t, J = 6.0 Hz, =CH, 1H), 5.42 (d, J = 5.4 Hz, $=CH_2$, 2H), 3.54 (t, J = 6.6 Hz, OCH_2, 2H), 1.63 (m, $OCH_2\mathit{CH_2}$, 2H), 1.26 (m, 10H), 0.88 (t, J = 7.2 Hz, CH_3, 3H).

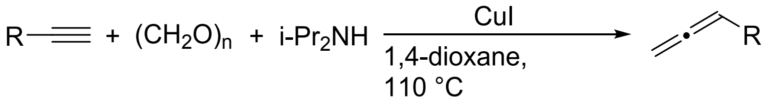
(Prop-2-yn-1-yloxy) benzene was purchased from Aladdin, and used for the synthesis of monomer **2** directly.

((Prop-2-yn-1-yloxy) methyl) benzene: ((Prop-2-yn-1-yloxy) methyl) benzene was prepared followed the similar procedure of 1-(prop-2-yn-1-yloxy) octane, which obtained as a colorless oil (81% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) 7.39−7.29 (m, ArH, 5H), 4.62 (s, CH_2, 2H), 4.20−4.17 (d, J = 2.4 Hz, OCH_2, 2H), 2.49−2.47 (t, J = 2.4 Hz, CH, 1H).

Monomer 2: Colorless oil, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) 7.35−7.32 (t, ArH, 2H), 7.09−7.06 (m, ArH, 3H), 6.87−6.85 (t, J = 6.0 Hz, =CH, 1H), 5.46−5.45 (d, J = 5.4 Hz, $=CH_2$, 2H).

Monomer 3: Colorless oil, 77% yield. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) 7.38−7.31 (m, ArH, 5H), 6.88−6.86 (t, J = 6.0 Hz, =CH, 1H), 5.51−5.50 (d, J = 5.4 Hz, $=CH_2$, 2H), 4.66–4.64 (d, J = 5.4 Hz, OCH_2, 2H).

Scheme S2 Synthesis of monomers 4-9



R = C_8H_{17}, Ph, *p*-BrC_6H_4, *p*-ClC_6H_4, *p*-$CH_3OC_6H_4$, *o*-$CH_3OC_6H_4$
4 **5** **6** **7** **8** **9**

Synthesis procedure of monomer 4-9: Monomer **4-9** was prepared accordingly to Scheme S2 following the reported literature with slight modification.$^{4–7}$ Taking Monomer **4** as an example. Paraformaldehyde (4.00 g, 136.0 mmol) and cuprous iodide (5.18 g, 27.2 mmol) was added in a 100 mL two-neck flask under N_2 atmosphere. Then, diisopropylamine (9.91 g, 97.9 mmol), dec-1-yne (7.52 g, 54.4 mmol) and dioxane (40 mL) were added. The solution was heated to 110 °C and refluxed for another 18 h until the substrates were completely consumed as indicated by thin layer chromatography (TLC) analysis. After the reaction flask was cooled to room temperature, the reaction solution was concentrated and diluted by water (10 mL). The pH value of the solution was adjusted to ca. 2 using HCl (1 N). Then the solution was extracted with Et_2O (3 × 30 mL). The organic phases were combined and washed with water (3 × 30 mL), saturated sodium chloride aqueous solution (3 × 30 mL). The combined organic phase was dried over $MgSO_4$ and the solvent was removed in vacuo. The residue was purified by silica gel chromatography using n-pentane as eluent to afford the monomer **4** as a colorless oil. (3.01 g, 36% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ (ppm) 5.13−5.06 (m, J = 10.2 Hz, =CH, 1H), 4.66−4.63 (m, J = 10.2 Hz, =CH_2, 2H), 2.00 (m, CH_2CH=, 2H), 1.44−1.20 (m, 12H), 0.90−0.86 (t, J = 6.6 Hz, CH_3, 3H)

Monomer **5**: 40% yield. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) 7.32−7.30 (m, ArH, 4H), 7.23−7.19 (m, ArH, 1H), 6.18 (t, J = 6.7 Hz, =CH, 1H), 5.16 (d, J = 6.7 Hz, =CH_2, 2H).

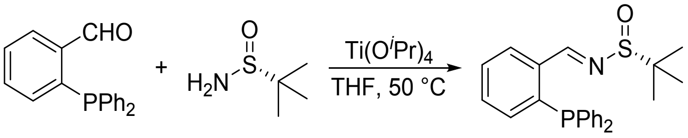
Monomer **6**: 46% yield. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) 7.43−7.41 (m, ArH, 2H), 7.17−7.15 (m, ArH, 2H), 6.11 (t, J = 7.2 Hz, =CH, 1H), 5.14 (d, J = 6.6 Hz, =CH_2, 2H).

Monomer **7**: 45% yield. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) 7.28−7.25 (m, ArH, 2H), 7.23−7.19 (m, ArH, 2H), 6.12 (t, J = 7.2 Hz, =CH, 1H), 5.14 (d, J = 6.6 Hz, =CH_2, 2H).

Monomer **8**: 39% yield. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) 7.23−7.21 (d, ArH, 2H), 6.86−6.85 (d, ArH, 2H), 6.12 (t, J = 7.2 Hz, =CH, 1H), 5.11 (d, J = 6.6 Hz, =CH_2, 2H), 3.80 (s, OCH_3, 3H).

Monomer **9**: 37% yield. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) 7.40−7.39 (d, ArH, 1H), 7.19−7.17 (t, ArH, 1H), 6.94−6.91 (d, ArH, 1H) 6.87−6.86 (t, ArH, 1H) 6.57 (t, J = 7.2 Hz, =CH, 1H), 5.11 (d, J = 6.6 Hz, =CH_2, 2H), 3.85 (s, OCH_3, 3H).

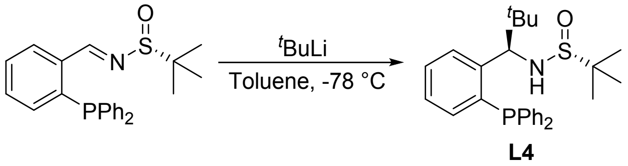
Scheme S3 Synthesis of ligand L1



L1

Synthesis procedure of ligand L1: The ligand **L1** was prepared according to literature with slight modification and confirmed by ^{1}H NMR.[8] To a flask containing a solution of the *tert*-butanesulfinamide (3.88 g, 32 mmol) in THF was added Ti(O^{i}Pr)$_4$ (2.73 g, 96 mmol), followed by the 2-(diphenylphosphino)-benzaldehyde (4.64 g, 16 mmol), and the reaction mixture was heated at 50 °C. Upon completion, the reaction mixture was allowed to cool to room temperature, diluted with EtOAc, and poured into brine with rapid stirring. The resulting suspension was filtered through a plug of Celite and the filter cake washed with EtOAc. The filtrate was transferred to a separatory funnel, and the organic layer was washed with an equal volume of brine. The organic phase was dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography (85/15 hexanes/EtOAc). **L1**: a light yellow solid, 82% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.12 (d, J = 4.8 Hz, 1H), 7.99−7.96 (m, 1H), 7.46−7.42 (m, 1H), 7.37−7.21 (m, 11H), 6.98−6.95 (m, 1H), 1.07 (s, 9H); $[\alpha]_D^{25} = -66.1$ (c = 0.30, $CHCl_3$).

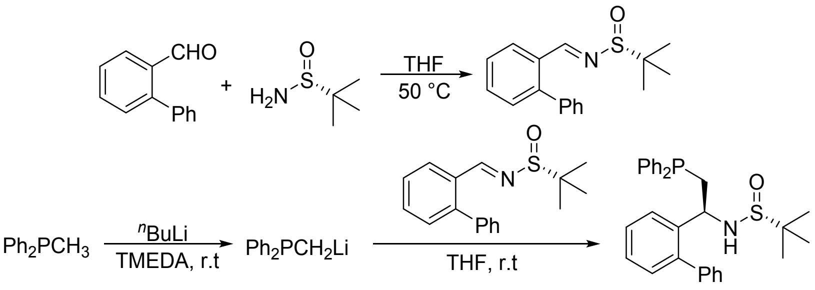
Scheme S4 Synthesis of ligand L4



L4

Synthesis procedure of ligand L4: The ligand **L4** was synthesized according to the literature with slight modification.[9] ^{t}BuLi (1.3 M in pentane, 9.6 mL, 1.1 eq.) was added to a solution of **L1** (4.44 g, 11.3 mmol, 1.0 eq.) in toluene (40 mL) at -78 °C. The mixture was stirred at -78 °C for 5 h until **L4** consumed completely as indicated by TLC analysis. Then, the reaction mixture was quenched by the addition of saturated NH_4Cl solution, and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 × 30 mL). The combined organic phase was dried over $MgSO_4$ and the solvent was removed in vacuo. The residue was purified by silica gel chromatography using petroleum ether/EtOAc (v/v = 5:1 to 3:1) as eluent to afford the **L4** as white solid (3.42 g, 67% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.45−7.33 (m, 7 H), 7.28−7.26 (m, 3 H), 7.24−7.11 (m, 4 H), 5.48−5.43 (m, 1 H), 3.55−3.52 (m, 1 H), 1.13 (s, 9 H), 0.96 (s, 9 H). $[\alpha]_D^{25}$ = 36.4 (c = 0.10, $CHCl_3$).

Scheme S5 Synthesis of ligand L5



Synthesis procedure of ligand L5: Ligand **L5** was synthesized according to the literature with slight modification and confirmed by ^{1}H NMR.[10] (64% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.56 (d, J = 7.9 Hz, 1H), 7.39−7.36 (m, 1H), 7.32−7.12 (m, 17H), 4.69−4.65 (m, 1H), 3.81 (d, J = 5.8 Hz, 1H), 2.58 (dd, J = 14.20, 8.69 Hz, 1H), 2.46−2.42 (dd, J = 14.20, 6.20 Hz, 1H), 1.12 (s, 9H). $[\alpha]_D^{25} = 20.6$ (c = 0.33, $CHCl_3$).

Preparation of the Ni(II) catalyst: Taking Ni(II)/**L4** as an example. In glovebox, a solution of commercial available $Ni(COD)_2$ (28.0 mg, 0.10 mmol) in toluene (2.0 mL) was treated with **L4** (45.0 mg, 0.10 mmol) and bromobenzene (11.0 μL, 0.1 mmol) at room temperature.[11] After the resulting mixture was stirred at room temperature for 15 min, it was directly used as an initiator for the polymerization of allene monomers without further purification. The other Ni(II)/**Ln** (n = 1-3 and 5-13) catalysts were prepared followed the similar procedure.

Typical polymerization procedure: Taking the polymerization of monomer **1** as an example. In glovebox, a solution of the as-prepared Ni(II)/**L4** catalyst in toluene (0.060 mL, 0.050 mol/L, 0.0030 mmol) was added to a solution of monomer **1** (50.0 mg, 0.30 mmol) in THF (1.5 mL) at room temperature. The concentrations of the monomer **1** and the catalyst were 0.20 mol/L and 0.050 mol/L respectively. The initial feed ratio of monomer **1** to catalyst was 100/1, and the reaction mixture was stirred at room temperature. After the polymerization solution was stirred for 40 min at 25 °C, it was precipitated into a large amount of menthol. The precipitated solid was collected by centrifugation and dried in vacuum at room temperature overnight, afforded poly-$\mathbf{1}_{100}$ as a white gelatinous solid (43.1 mg, 86% yield). SEC: M_n = 18.8 kDa, M_w/M_n = 1.09. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ (ppm) 6.24−5.75 (br, =CH, 1H), 3.89−3.39 (br, CH_2 of main chain, 2H), 3.00−2.10 (br, OCH_2, 2H), 1.82−1.45 (br, $OCH_2\mathit{CH_2}$, 2H), 1.45−1.03 (br, 10H), 1.00−0.66 (br, CH_3, 3H). FT-IR (KBr, 25 °C): 2927 ($\nu_{C–H}$), 1665 ($\nu_{C=C}$), 1468 ($\delta_{C–H}$), 1128 ($\nu_{C\text{-}O}$) cm^{-1}.

Poly-2$_{100}$: White solid, 76% yield. SEC: M_n = 13.3 kDa, M_w/M_n = 1.23. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) 7.23−6.98 (br, ArH, 2H), 6.98−6.58 (br, ArH, 2H), 6.58−6.09 (br, =CH, 1H), 3.57−2.27 (br, CH_2 of main chain, 2H). FT-IR (KBr, 25 °C): 3045 ($\nu_{Ar–H}$), 2904 ($\nu_{C–H}$), 1668 ($\nu_{C=C}$), 1488 ($\delta_{C–H}$), 1221 ($\nu_{C\text{-}O}$) cm^{-1}.

Poly-3$_{100}$: White solid, 78% yield. SEC: M_n = 15.4 kDa, M_w/M_n = 1.15. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) 7.45−6.72 (br, ArH, 5H), 6.05−5.29 (br, =CH, 1H), 4.70−3.75 (br, OCH_2, 2H), 3.07−1.75 (br, CH_2 of main chain, 2H). FT-IR (KBr, 25 °C): 2962 ($\nu_{C–H}$), 1667 ($\nu_{C=C}$), 1457 ($\delta_{C–H}$), 1096 ($\nu_{C\text{-}O}$), 1019 ($\nu_{C\text{-}O}$) cm^{-1}.

Poly-4$_{100}$: White gelatinous solid, 88% yield. SEC: M_n = 13.3 kDa, M_w/M_n = 1.07. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) 5.39−5.05 (br, =CH, 1H), 4.82−4.68 (br, =CH_2 of 1,2-polymerization, 0.2H), 2.90−2.31 (br, CH_2 of main chain, 2H), 2.15−1.80 (br, CH_2, 2H) 1.42−1.08 (br, 12H) 0.94−0.79 (br, CH_3, 3H). FT-IR (KBr, 25 °C): 2920 ($\nu_{C–H}$), 1461 ($\nu_{C=C}$), 1379 ($\delta_{C–H}$) cm^{-1}.

Poly-5$_{100}$: White solid, 89% yield. SEC: M_n = 9.3 kDa, M_w/M_n = 1.05. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) 7.24−6.78 (br, ArH, 5H), 6.62−5.99 (br, =CH, 1H), 3.45−2.62 (br, CH_2 of main chain, 2H). FT-IR (KBr, 25 °C): 3017 ($\nu_{Ar–H}$), 2899 (ν_{C-H}), 1605 ($\nu_{C=C}$), 1495 (δ_{C-H}) cm^{-1}.

Poly-6$_{100}$: White solid, 78% yield. SEC: M_n = 80.1 kDa, M_w/M_n = 1.51. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) 7.57−7.08 (br, *m*-C_6H_5Br, 2H), 7.08−6.40 (br, *o*-C_6H_5Br, 2H), 6.40−5.72 (br, =CH, 1H), 3.28−2.18 (br, CH_2 of main chain, 2H). FT-IR (KBr, 25 °C): 3030 ($\nu_{Ar–H}$), 2898 (ν_{C-H}), 1643 ($\nu_{C=C}$), 1489 (δ_{C-H}), 807 cm^{-1} (γ_{Ar-H}).

Poly-7$_{100}$: White solid, 84% yield. SEC: M_n = 18.6 kDa, M_w/M_n = 1.10. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) 7.22−6.89 (br, ArH, 2H), 6.89−6.45 (br, ArH, 2H), 6.45−5.55 (br, =CH, 1H), 3.39−2.12 (br, CH_2 of main chain, 2H). FT-IR (KBr, 25 °C): 3023 (ν_{Ar-H}), 2922 (ν_{C-H}), 1639 ($\nu_{C=C}$), 1488 (δ_{C-H}), 804 cm^{-1} (γ_{Ar-H}).

Poly-8$_{100}$: White solid, 80% yield. SEC: M_n = 14.2 kDa, M_w/M_n = 1.23. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ (ppm) 7.23−6.78 (br, ArH, 2H), 6.78−6.54 (br, ArH, 2H), 6.49−5.99 (br, =CH, 1H), 3.84−3.50 (br, OCH_3, 3H), 3.42−2.65 (br, CH_2 of main chain, 2H). FT-IR (KBr, 25 °C): 3289 (ν_{Ar-H}), 2925 (ν_{C-H}), 2855 (ν_{C-H} of OCH_3), 1741 ($\nu_{C=C}$), 1145 (ν_{C-O}), 880 cm^{-1} (γ_{Ar-H}).

Poly-9$_{100}$: White solid, 88% yield. SEC: M_n = 19.1 kDa, M_w/M_n = 1.15. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ (ppm) 7.60−7.32 (br, ArH, 1H), 7.14−6.81 (br, ArH, 1H), 6.81−6.61 (br, ArH, 2H), 6.61−6.19 (br, =CH, 1H), 3.73−3.28 (br, OCH_3, 3H), 3.28−2.62 (br, CH_2 of main chain, 2H). FT-IR (KBr, 25 °C): 3288 ($\nu_{Ar–H}$), 2930 (ν_{C-H}), 2852 (ν_{C-H} of OCH_3), 1745 ($\nu_{C=C}$), 1154 (ν_{C-O}), 753 cm^{-1} (γ_{Ar-H}).

Kinetic study for the polymerization of monomer 1: In glovebox, a solution of the Ni(II)/**L4** (0.0060 mmol) in toluene (0.12 mL) was added to the mixture of monomer **1** (100.0 mg, 0.60 mmol) and dimethyl terephthalate (30.0 mg, 0.15 mmol) in THF (3.0 mL) via a pipette ($[\mathbf{1}]_0$ = 0.20 mol/L, $[\mathbf{1}]_0/[\mathrm{Ni}]_0$ = 100). The polymerization solution was stirred at room temperature in glovebox and followed by measuring SEC and ^{1}H NMR of the aliquots taking out from the reaction solution at appropriate time intervals, and the removed sample was immediately quenched with excess methanol. The conversion of monomer **1** was calculated based on the peak area of unreacted **1** relative to that of the internal standard dimethyl terephthalate. The M_n and M_w/M_n values were estimated by SEC and reported as equivalent to polystyrene standards.

WAXD measurements.[12] The scanning range was 5-40° at a rate of 8°/min and a step length of 0.02. The WAXD samples were prepared using a hot stage containing a temperature controller, which were crystallized isothermally at 150 °C for 3 h.

Table S1 Results of kinetic study for the polymerization of monomer **1**[a]

run	time (min)	conversion (%)[b]	M_n (kDa)[c]	M_w/M_n[c]
1	2	31	3.9	1.07
2	4	50	8.9	1.06
3	7.5	67.2	13.1	1.07
4	11	79.3	17.9	1.10
5	19	92.2	23.1	1.05

[a]The polymerizations were carried out in THF at 25 °C according to Scheme 1 in the main text. [b]Confirmed by ^{1}H NMR in $CDCl_3$ at 25 °C. [c]The M_n and M_w/M_n values were

determined by SEC with reference to polystyrene standards.

Table S2 Results of poly-$\mathbf{1}_{100}$ using different Ni(II)/**Ln** as initiator[a].

run	ligand	Reaction time (h)	$M_{n,SEC}$ (kDa)[b]	$M_{n,thero}$ (kDa)	M_w/M_n[b]	yield[c] (%)	2,3-polymerization selectivity (%)[d]
1	**L2**	1	20.2	16.8	1.12	86	99.1
2	**L3**	1	19.6	16.8	1.25	74	97.8
3	**L5**	1.5	23.2	16.8	1.22	78	95.6
4	**L6**	48	–[e]	16.8	–[e]	–[e]	–[e]
5	**L7**	48	–[e]	16.8	–[e]	–[e]	–[e]
6	**L8**	36	22.2	16.8	1.13	66	99.3
7	**L9**	36	20.9	16.8	1.10	82	98.8
8	**L13**	6	17.4	16.8	1.10	72	77.0
9	**L4**($AgBF_4$)[f]	0.2	27.8	16.8	1.08	90	95.0
10	**none**	1	24.6	16.8	1.34	82	61.0

[a]The polymerizations were carried out in THF at 25 °C according to Scheme 1 in the main text, the feed ratio of Ni(II) to ligand was 1:1, and the initial feed ratio of monomer to catalyst was 100:1. [b]The M_n and M_w/M_n values were determined by SEC with reference to polystyrene standards. [c]Isolated yields. [d]Characterized by ^{1}H NMR in $CDCl_3$ at 25 °C. [e]No polymer could be isolated. [f]The feed ratio of ligand **L4** to $AgBF_4$ was 1:1.

Table S3 Results of poly-$\mathbf{1}_{100}$ using different solvents and temperatures during the polymerization.[a]

run	solvent	temperature (°C)	Reaction time (min)	$M_{n,SEC}$ (kDa)[b]	$M_{n,thero}$ (kDa)	M_w/M_n[b]	yield[c] (%)	2,3-selectivity (%)[e]
1	EtOH	25	50	16.9	16.8	1.07	76	98.1
2	$CHCl_3$	25	60	17.8	16.8	1.14	74	97.6
3	THF	0	360	–[d]	16.8	–[d]	–[d]	–[d]
4	THF	55	15	23.9	16.8	1.12	86	97.0

[a]The polymerizations were carried out in different solvents at 0 °C, 25 °C and 55 °C according to Scheme 1 in the main text, and the initial feed ratio of monomer to catalyst was 100:1. [b]The M_n and M_w/M_n values were determined by SEC with reference to polystyrene standards. [c]Isolated yields. [d]No polymer could be isolated. [e]Characterized by ^{1}H NMR in $CDCl_3$ at 25 °C.

Table S4 Results for poly-$\mathbf{4}_{100}$ and poly-$\mathbf{5}_{100}$ using different ratio of Ni(II) and **L4**[a].

run	polymer	$[Ni]_0/[\mathbf{L4}]_0$[b]	$M_{n,SEC}$ (kDa)[c]	$M_{n,thero}$ (kDa)	M_w/M_n[c]	Yield[d] (%)	2,3-selectivity (%)[e]
1	poly-$\mathbf{4}_{100}$	1:1	13.3	15.2	1.07	88	90.0
2	poly-$\mathbf{4}_{100}$	1:2	14.8	15.2	1.08	82	88.0
3	poly-$\mathbf{4}_{100}$	1:3	13.8	15.2	1.08	86	89.5
4	poly-$\mathbf{4}_{100}$	1:4	16.4	15.2	1.05	87	89.0
5	poly-$\mathbf{5}_{100}$	1:1	9.3	11.6	1.05	89	>99.9
6	poly-$\mathbf{5}_{100}$	1:2	9.4	11.6	1.05	92	>99.9

[a]The polymerizations were carried out in CH_2Cl_2 at 25 ℃ for 40 min according to Scheme 1 in the main text, the initial feed ratio of monomer to catalyst was 100:1. [b]The feed ratio of Ni(II) to **L4**. [c]The M_n and M_w/M_n values were determined by SEC with reference to polystyrene standards. [d]Isolated yields. [e]Characterized by ^1H NMR in $CDCl_3$ at 25 ℃.

Table S5 Results of poly-$\mathbf{4}_{100}$ using Ni(II)/**L4** as initiator in different solvents.[a]

run	solvent	$[Ni]_0/[\mathbf{L4}]_0$[b]	$M_{n,SEC}$ (kDa)[c]	$M_{n,thero}$ (kDa)	M_w/M_n[c]	yield[d] (%)	2,3-selectivity (%)[e]
1	CH_2Cl_2	1:1	13.3	15.2	1.07	88	90.0
2	THF	1:1	–[f]	15.2	–[f]	–[f]	–[f]
3	Toluene	1:1	15.3	15.2	1.12	78	91.5
4	DMSO	1:1	–[f]	15.2	–[f]	–[f]	–[f]
5	CH_2Cl_2	1:2	14.8	15.2	1.08	82	88.0
6	THF	1:2	–[f]	15.2	–[f]	–[f]	–[f]
7	Toluene	1:2	17.2	15.2	1.14	64	94.0
8	DMSO	1:2	–[f]	15.2	–[f]	–[f]	–[f]

[a]The polymerizations were carried out in different solvents at 25 ℃ for 40 min according to Scheme 1 in the main text. The initial feed ratio of monomer to catalyst was 100:1. [b]The feed ratio of Ni(II) to **L4**. [c]The M_n and M_w/M_n values were determined by SEC with reference to polystyrene standards. [d]Isolated yields. [e]Characterized by ^1H NMR in $CDCl_3$ at 25 ℃. [f]No polymer could be isolated.

Table S6 Results of poly-$\mathbf{4}_{100}$ using Ni(II)/**L4** as initiator at different temperatures.^{a}

run	solvent	Temp. (℃)	[Ni]$_0$/[**L4**]$_0$^{b}	$M_{\mathrm{n,SEC}}$ (kDa)^{c}	$M_{\mathrm{n,thero}}$ (kDa)	M_{w}/M$_{\mathrm{n}}$^{c}	Yield^{d} (%)	2,3-selectivity (%)^{e}
1	CH_2Cl_2	-10	1:1	–^{f}	15.2	–^{f}	–^{f}	–^{f}
2	CH_2Cl_2	-10	1:2	–^{f}	15.2	–^{f}	–^{f}	–^{f}
3	CH_2Cl_2	0	1:1	16.8	15.2	1.09	80	94.0
4	CH_2Cl_2	0	1:2	17.9	15.2	1.08	82	92.0
5	CH_2Cl_2	25	1:1	13.3	15.2	1.07	78	90.0
6	Toluene	-10	1:1	–^{f}	15.2	–^{f}	–^{f}	–^{f}
7	Toluene	-10	1:2	–^{f}	15.2	–^{f}	–^{f}	–^{f}
8	Toluene	0	1:1	–^{f}	15.2	–^{f}	–^{f}	–^{f}
9	Toluene	0	1:2	–^{f}	15.2	–^{f}	–^{f}	–^{f}
10	Toluene	25	1:1	15.3	15.2	1.12	78	91.5

^{a}The polymerizations were carried out in CH_2Cl_2 and toluene at different temperatures according to Scheme 1 in the main text, the initial feed ratio of monomer to catalyst was 100:1. ^{b}The feed ratio of Ni(II) to **L4**. ^{c}The M_n and M_w/M_n values were determined by SEC with reference to polystyrene standards. ^{d}Isolated yields. ^{e}Characterized by ^{1}H NMR in $CDCl_3$ at 25 ℃. ^{f}No polymer could be isolated.

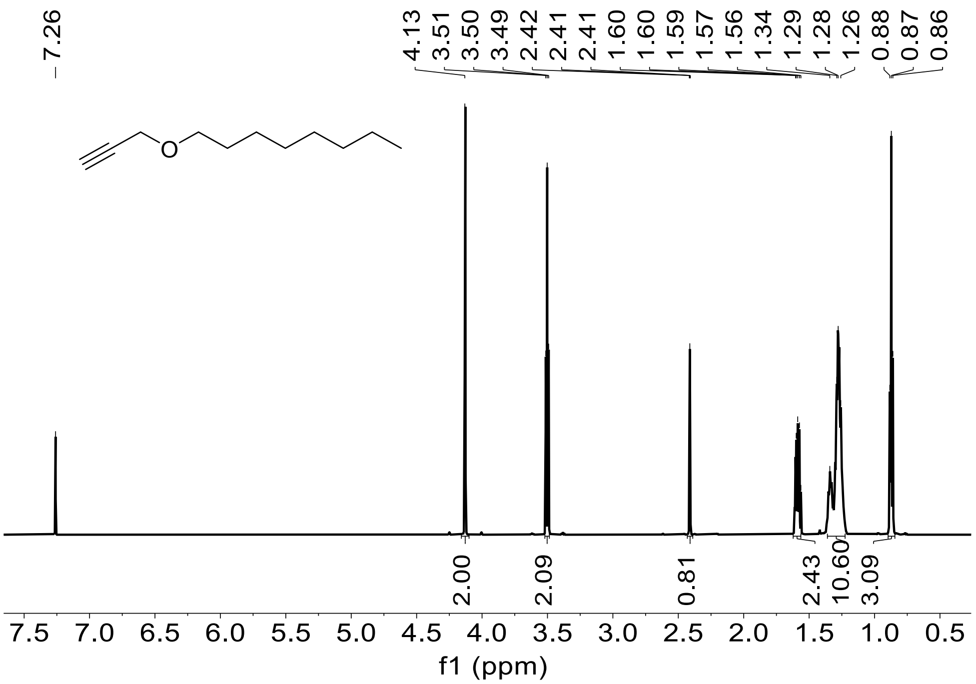


Fig. S1 ^{1}H NMR (600 MHz) spectrum of 1-(prop-2-yn-1-yloxy) octane recorded in $CDCl_3$ at 25 °C.

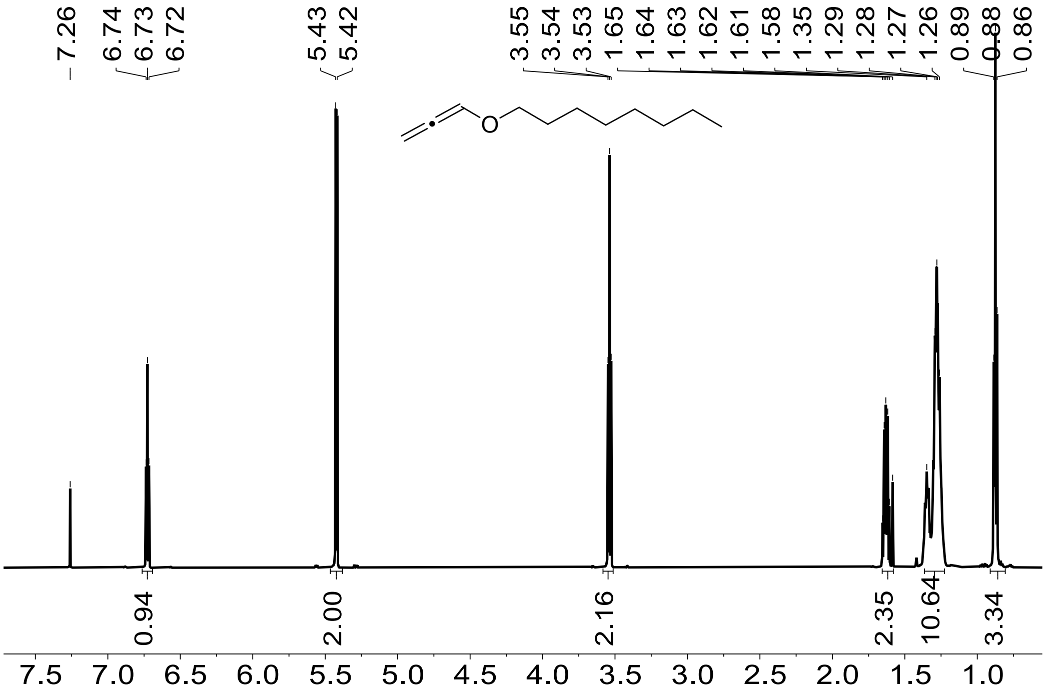


Fig. S2 ^{1}H NMR (600 MHz) spectrum of monomer **1** recorded in $CDCl_3$ at 25 °C.

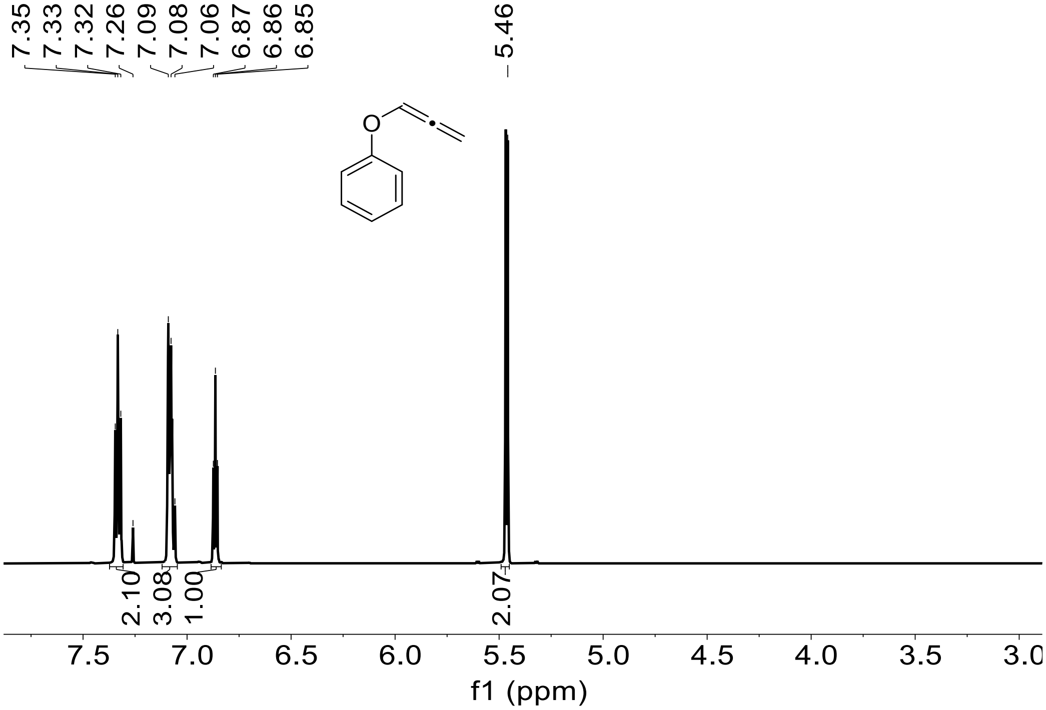


Fig. S3 ^{1}H NMR (600 MHz) spectrum of monomer **2** recorded in $CDCl_3$ at 25 °C.

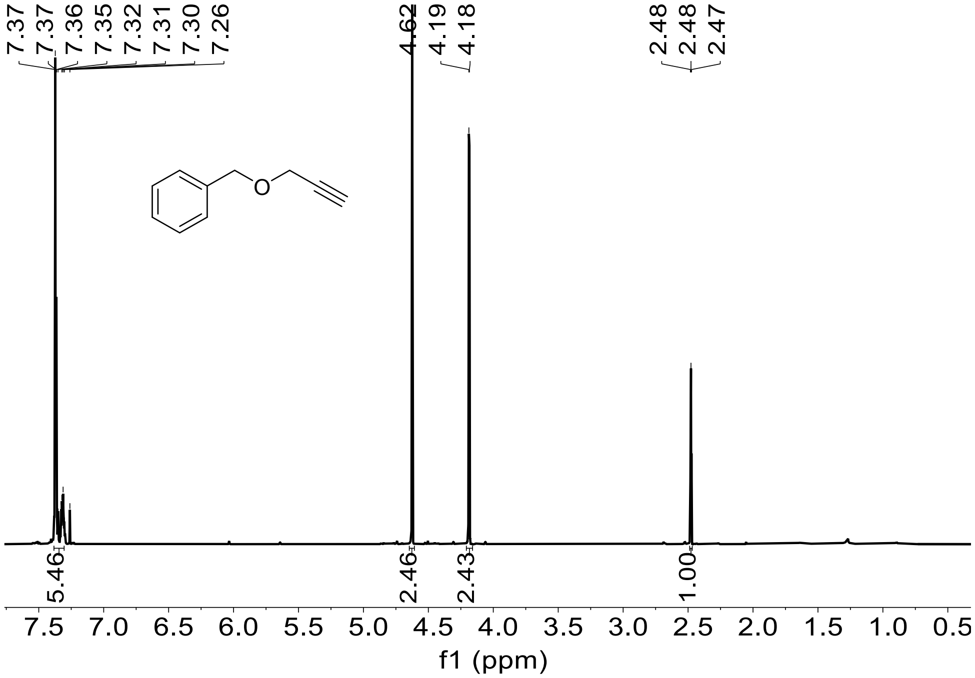


Fig. S4 ^{1}H NMR (600 MHz) spectrum of ((prop-2-yn-1-yloxy) methyl) benzene recorded in $CDCl_3$ at 25 °C.

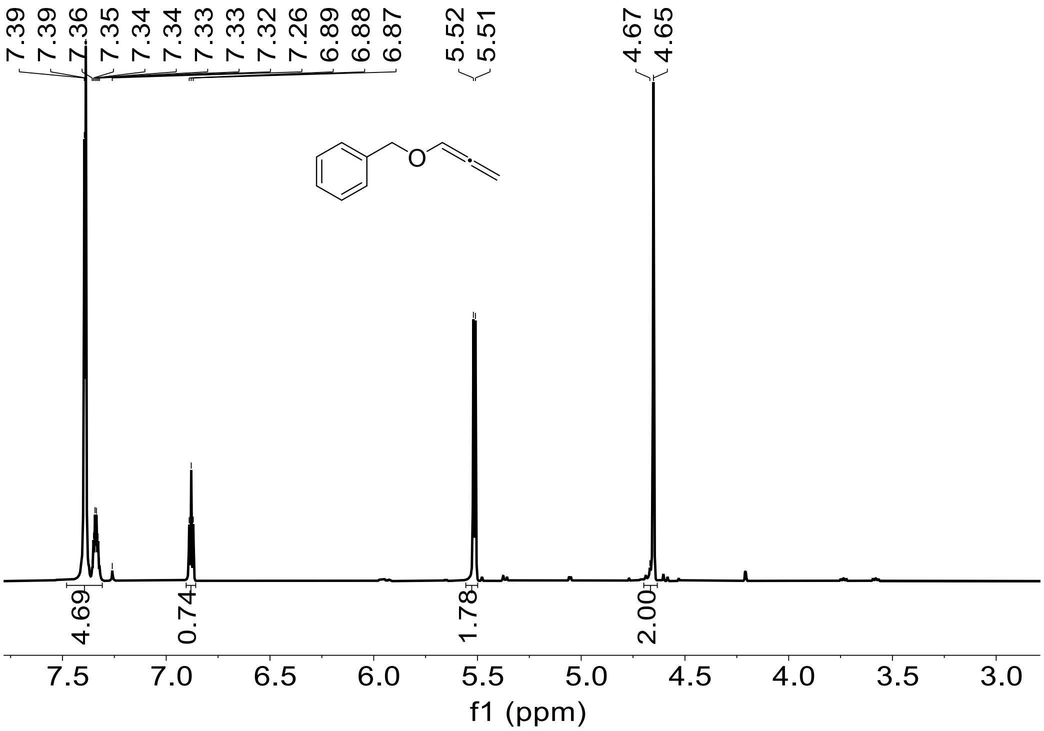


Fig. S5 ^{1}H NMR (600 MHz) spectrum of monomer **3** recorded in $CDCl_3$ at 25 °C.

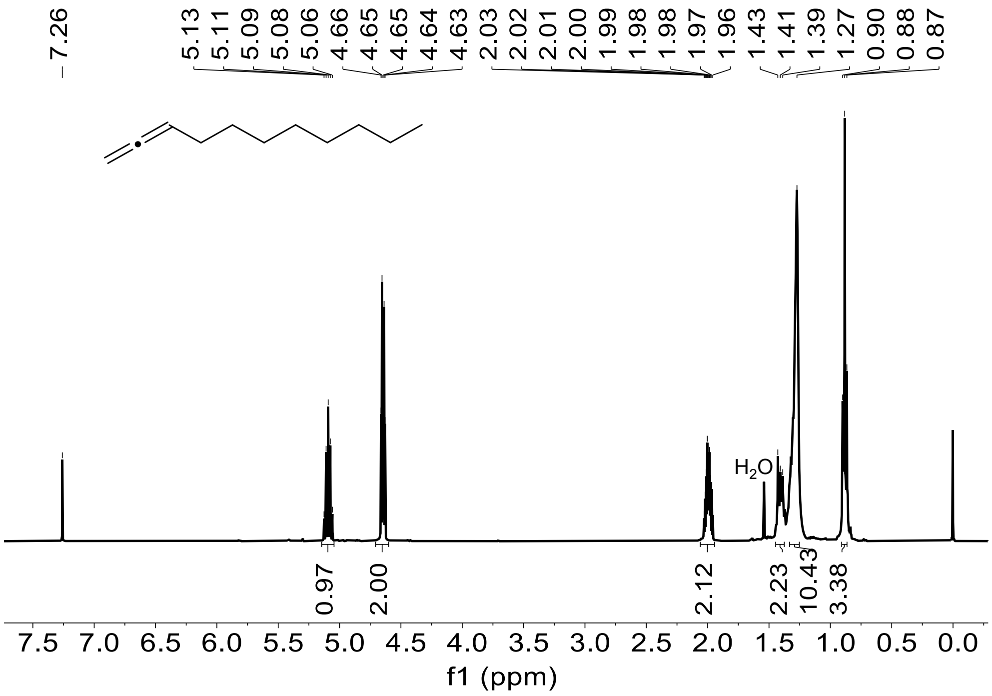


Fig. S6 ^{1}H NMR (600 MHz) spectrum of monomer **4** recorded in $CDCl_3$ at 25 °C.

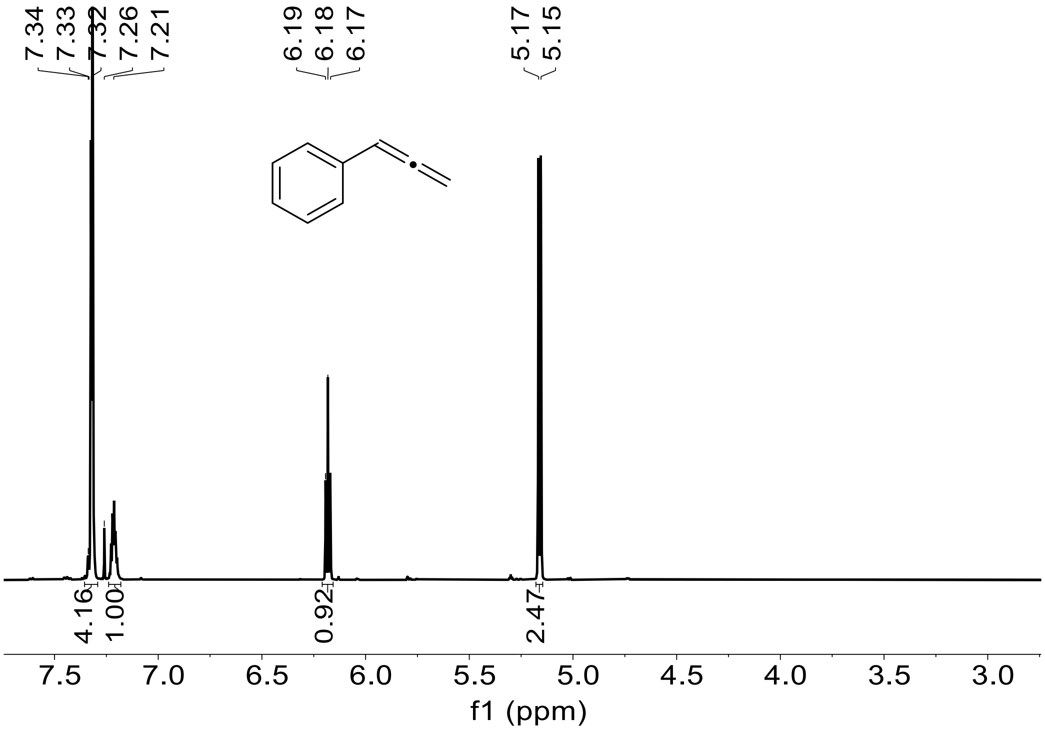


Fig. S7 ^{1}H NMR (600 MHz) spectrum of monomer **5** recorded in $CDCl_3$ at 25 °C.

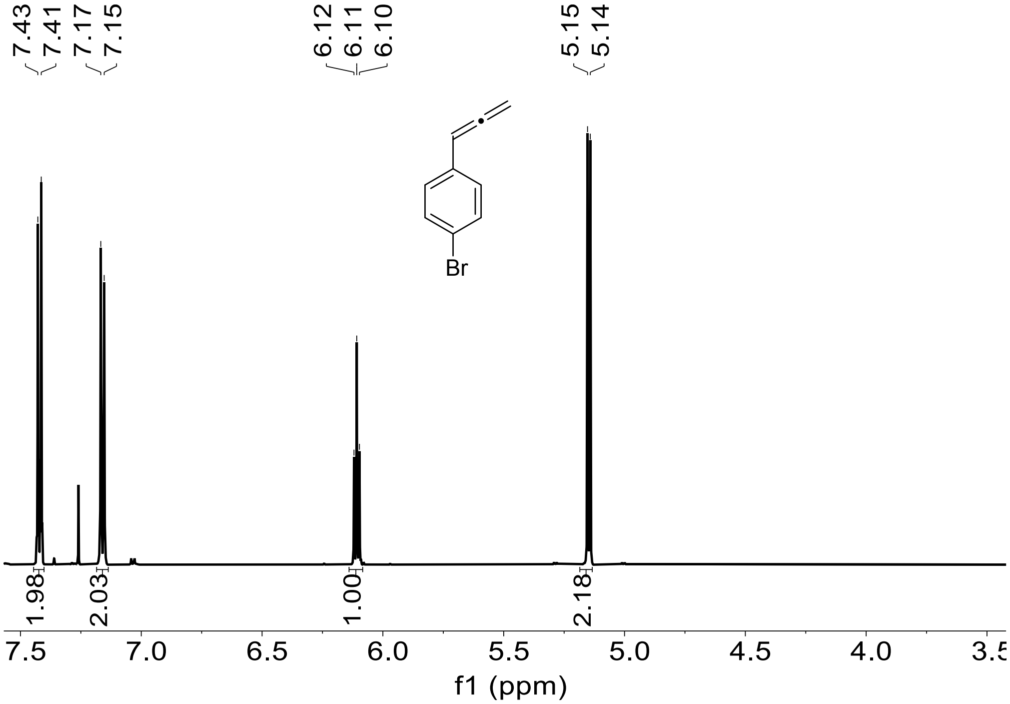


Fig. S8 ^{1}H NMR (600 MHz) spectrum of monomer **6** recorded in $CDCl_3$ at 25 °C.

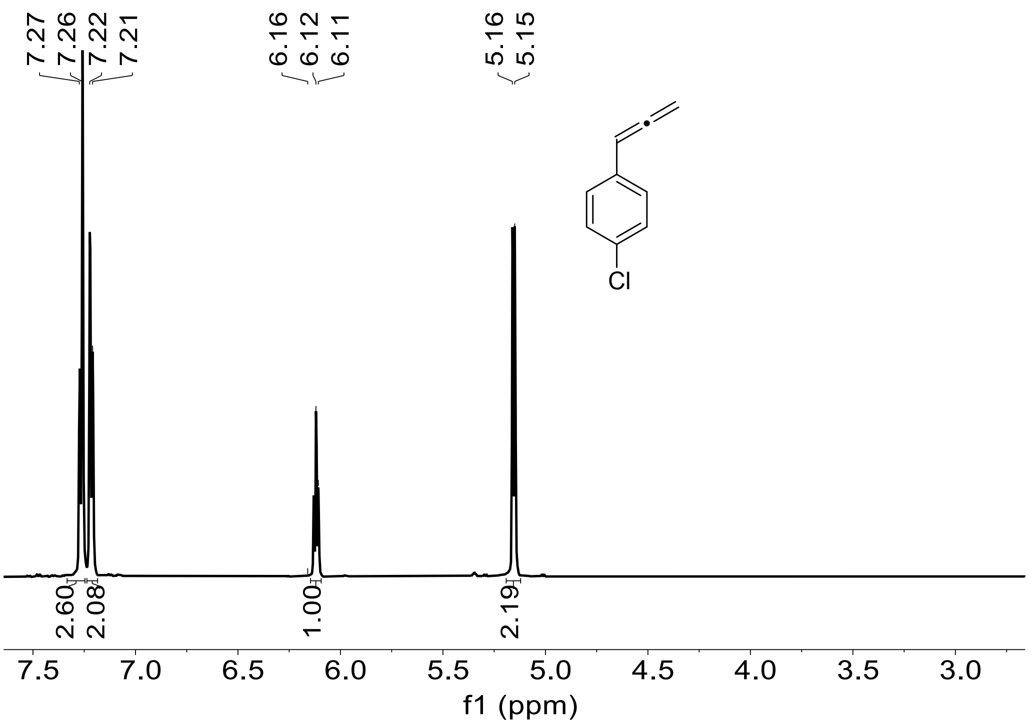


Fig. S9 ^{1}H NMR (600 MHz) spectrum of monomer **7** recorded in $CDCl_3$ at 25 °C.

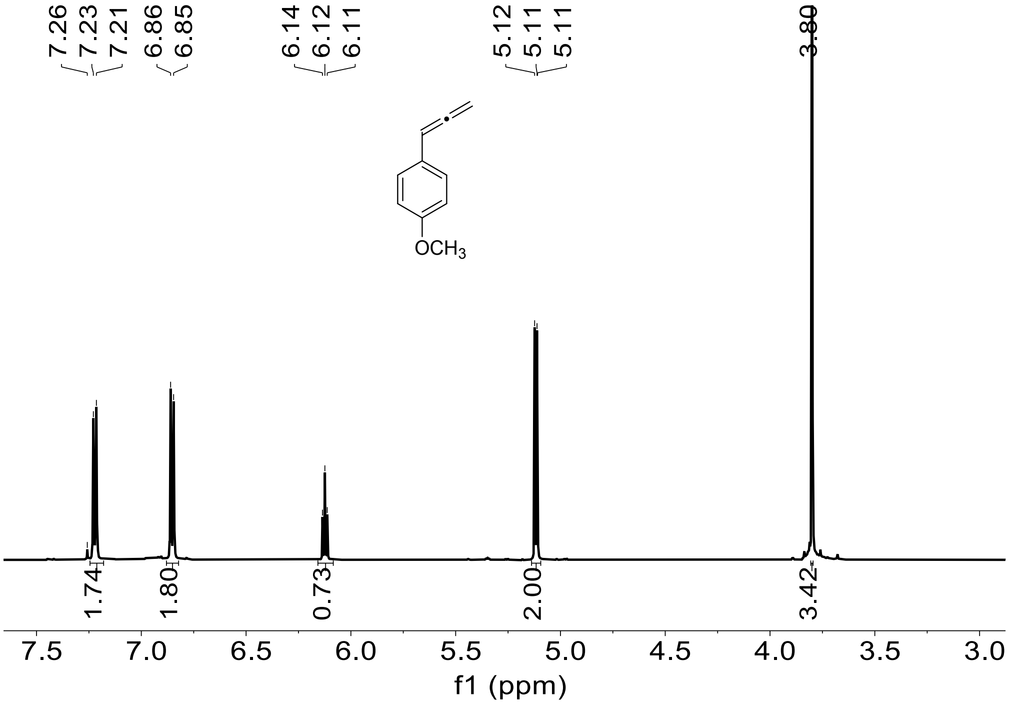


Fig. S10 ^{1}H NMR (600 MHz) spectrum of monomer **8** recorded in $CDCl_3$ at 25 °C.

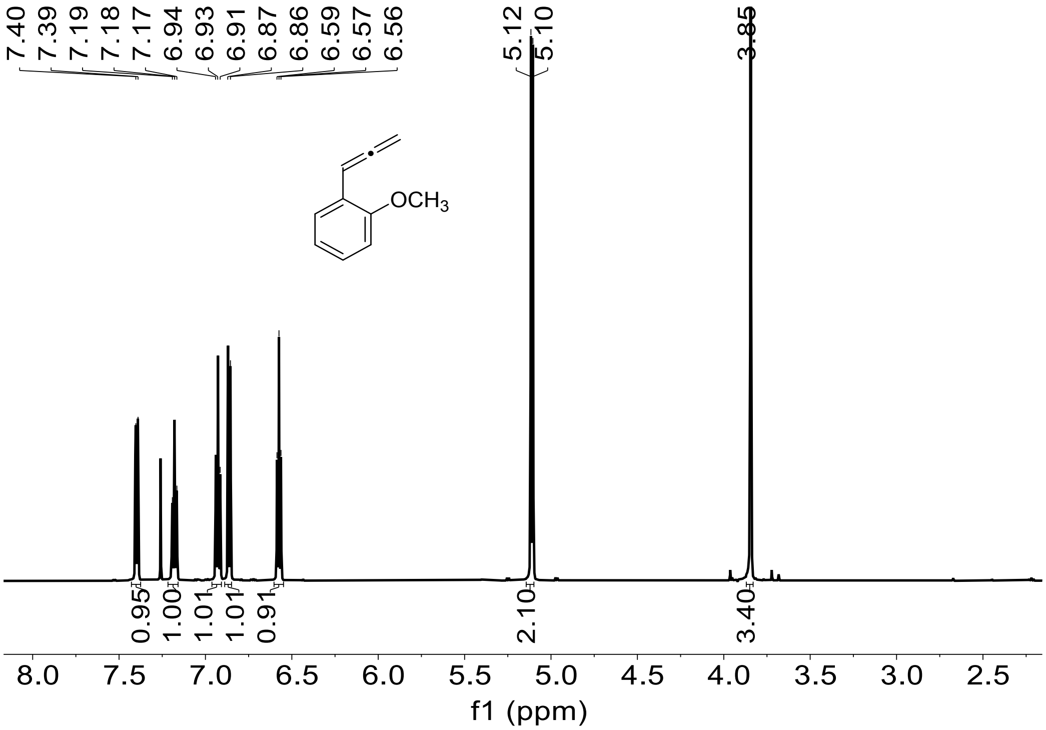


Fig. S11 ^{1}H NMR (600 MHz) spectrum of monomer **9** recorded in CDCl$_3$ at 25 °C.

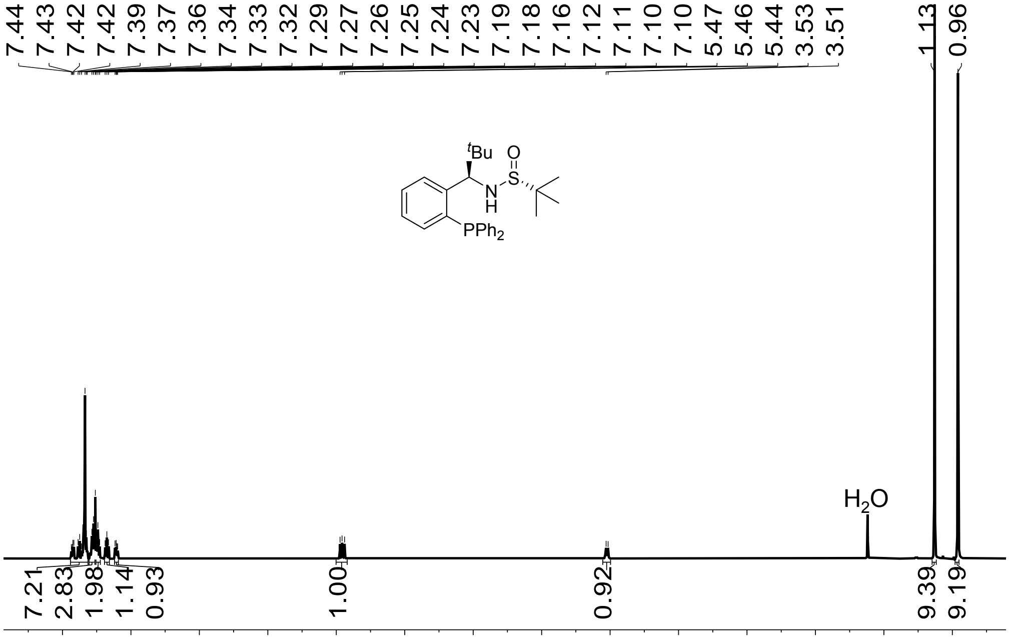


Fig. S12 ^{1}H NMR (600 MHz) spectrum of ligand **L4** recorded in CDCl$_3$ at 25 °C.

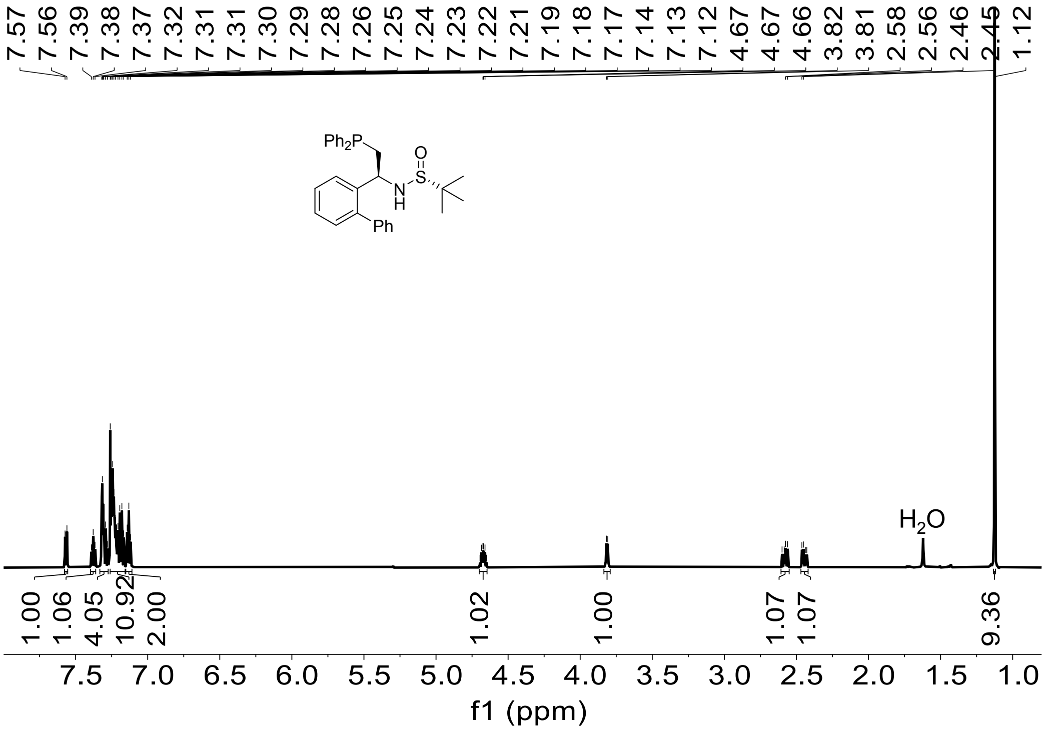


Fig. S13 ^{1}H NMR (600 MHz) spectrum of ligand **L5** recorded in CDCl$_3$ at 25 °C.

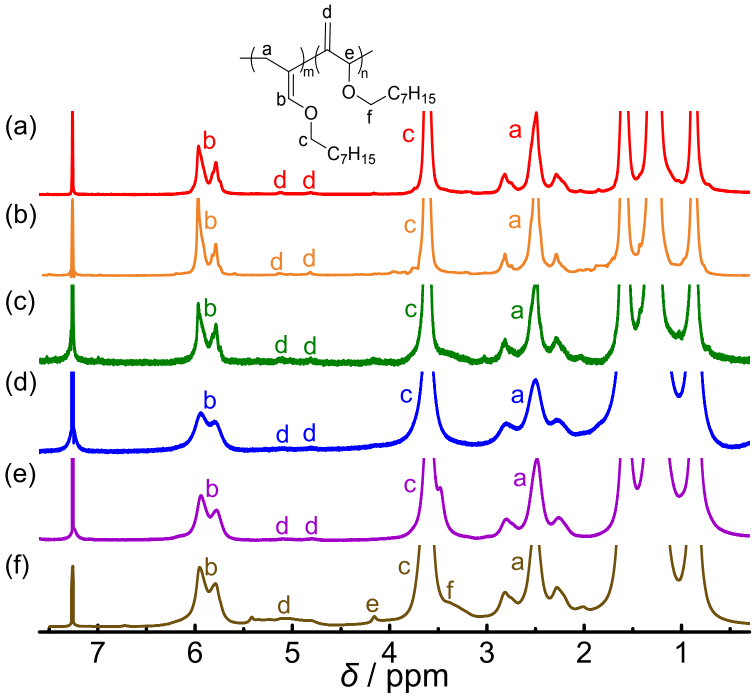


Fig. S14 ^{1}H NMR (600 MHz) spectrum of poly-**1**$_{100}$ obtained from ligands **L2** (a); **L3** (b); **L5** (c); **L8** (d); **L9** (e); **L13** (f) respectively recorded in CDCl$_3$ at 25 °C.

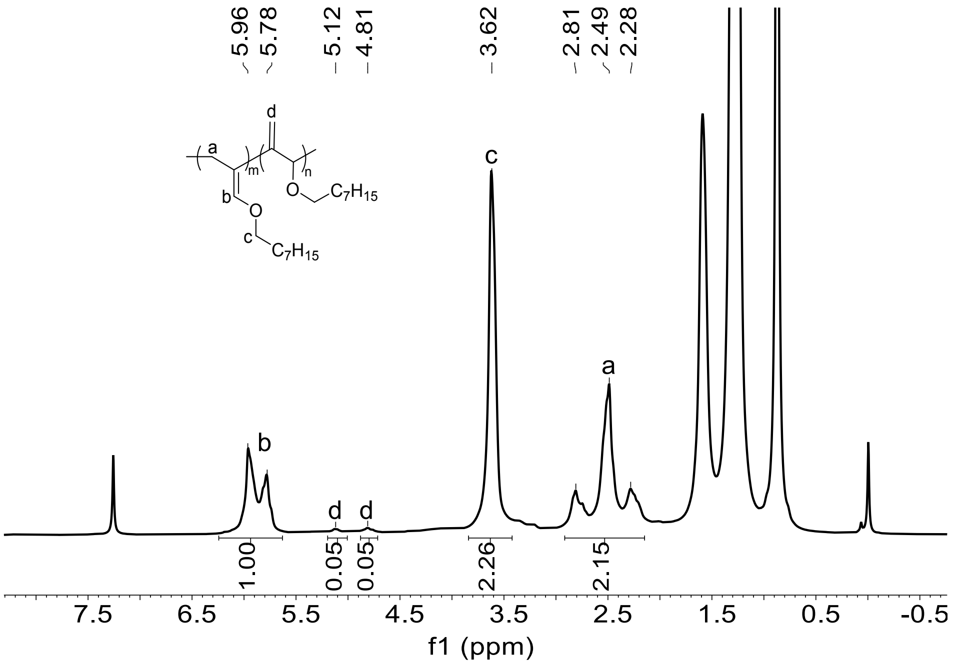


Fig. S15 ^{1}H NMR (600 MHz) spectra of poly-$\mathbf{1}_{100}$ obtained from Ni/**L4** catalyst by adding $AgBF_4$ (1 equiv.) recorded in $CDCl_3$ at 25 °C.

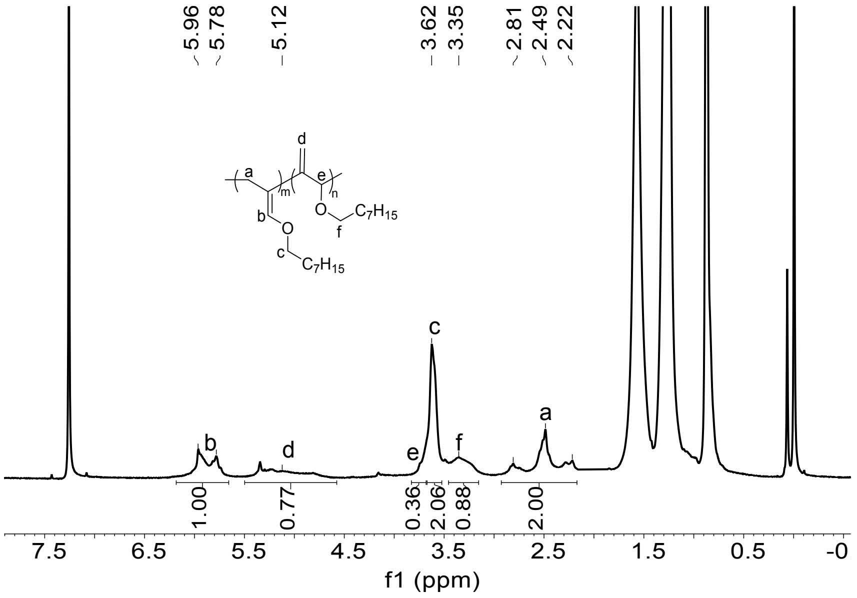


Fig. S16 ^{1}H NMR (600 MHz) spectra of poly-$\mathbf{1}_{100}$ obtained from Ni catalyst without any ligands recorded in $CDCl_3$ at 25 °C.

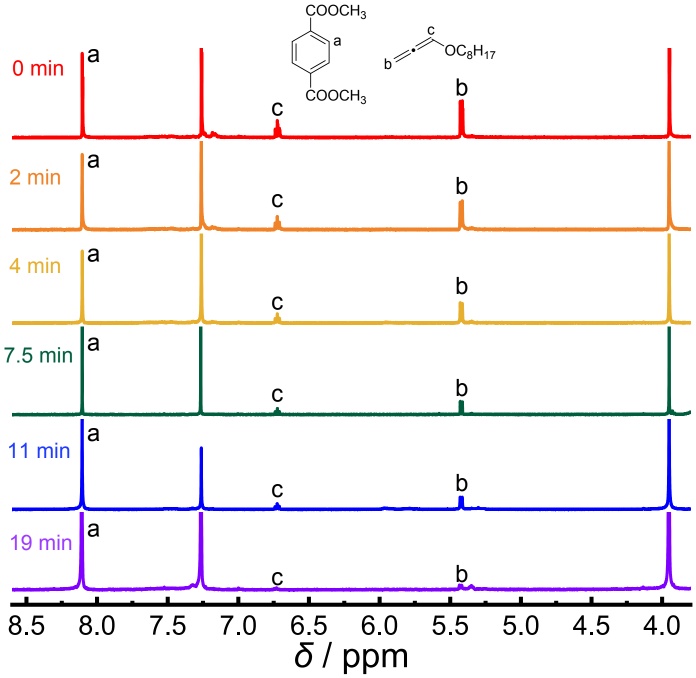


Fig. S17 ^{1}H NMR spectra of samples taken at different times in kinetic study for the polymerization of **1** (dimethyl terephthalate as internal standard).

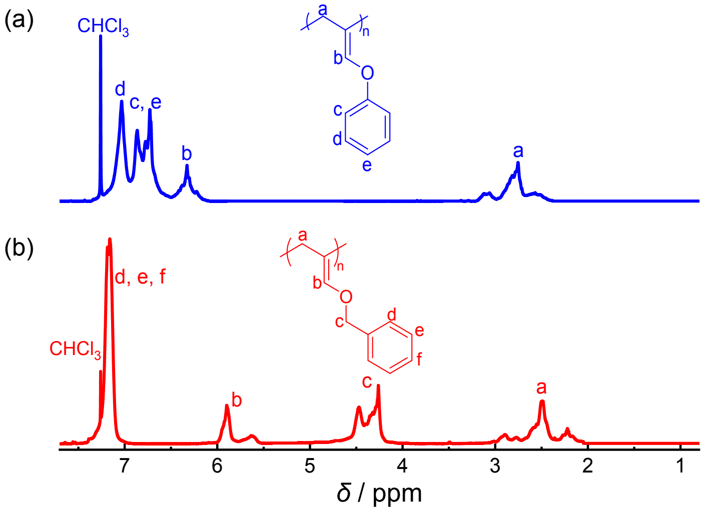


Fig. S18 ^{1}H NMR (600 MHz) spectra of poly-**2**$_{100}$ (a) and poly-**3**$_{100}$ (b) recorded in CDCl$_3$ at 25 °C.

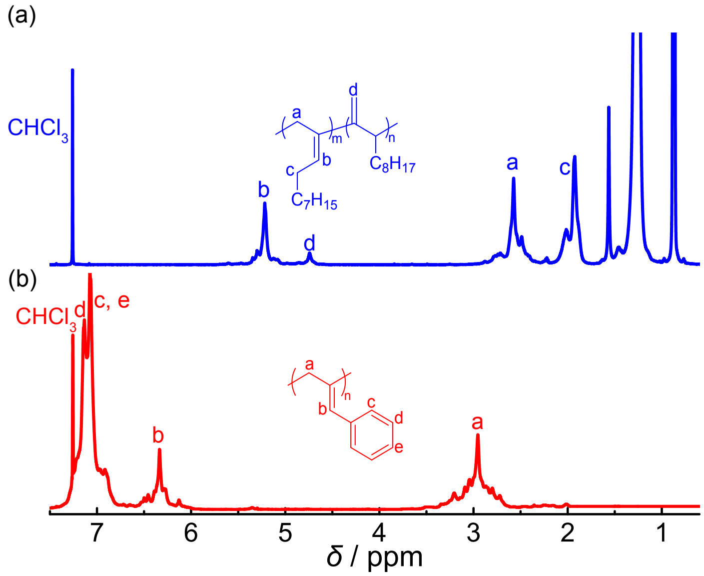


Fig. S19 ^{1}H NMR (600 MHz) spectra of poly-$\mathbf{4}_{100}$ (a) and poly-$\mathbf{5}_{100}$ (b) recorded in $CDCl_3$ at 25 °C.

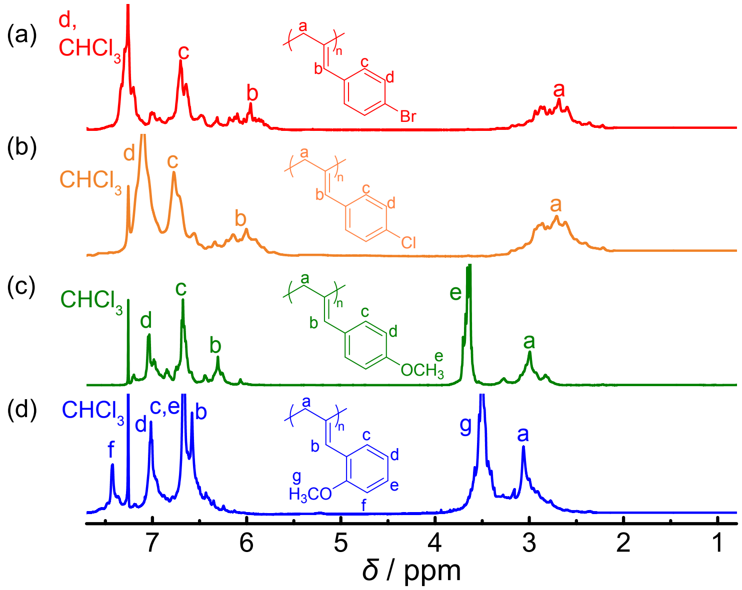


Fig. S20 ^{1}H NMR (600 MHz) spectra of poly-$\mathbf{6}_{100}$ (a), poly-$\mathbf{7}_{100}$ (b) poly-$\mathbf{8}_{100}$ (c) and poly-$\mathbf{9}_{100}$ (d) recorded in $CDCl_3$ at 25 °C.

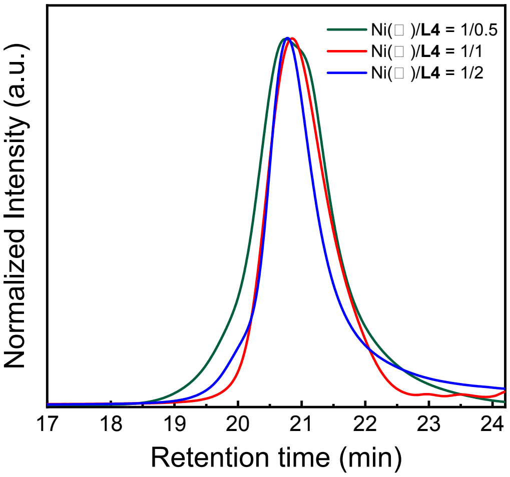


Fig. S21 SEC of poly-**1**$_{100}$ prepared from the polymerization of monomer **1** in THF at room temperature using Ni(II)/**L4** catalyst with different ratio of Ni(II) and **L4**.

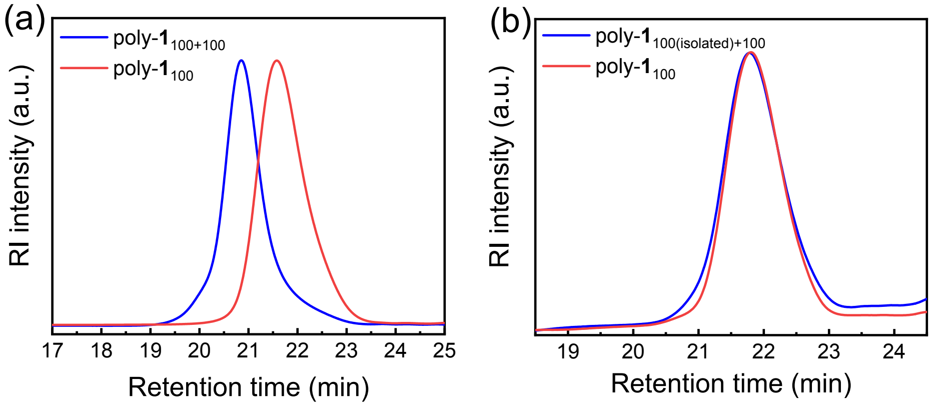


Fig. S22 SEC of poly-**1**$_{100}$ and poly-**1**$_{100+100}$ prepared by (a) addition of monomer **1** continuously without isolating the precursor poly-**1**$_{100}$ and (b) addition of monomer **1** to the solution of the isolated poly-**1**$_{100}$ in THF at room temperature using Ni(II)/**L4**.

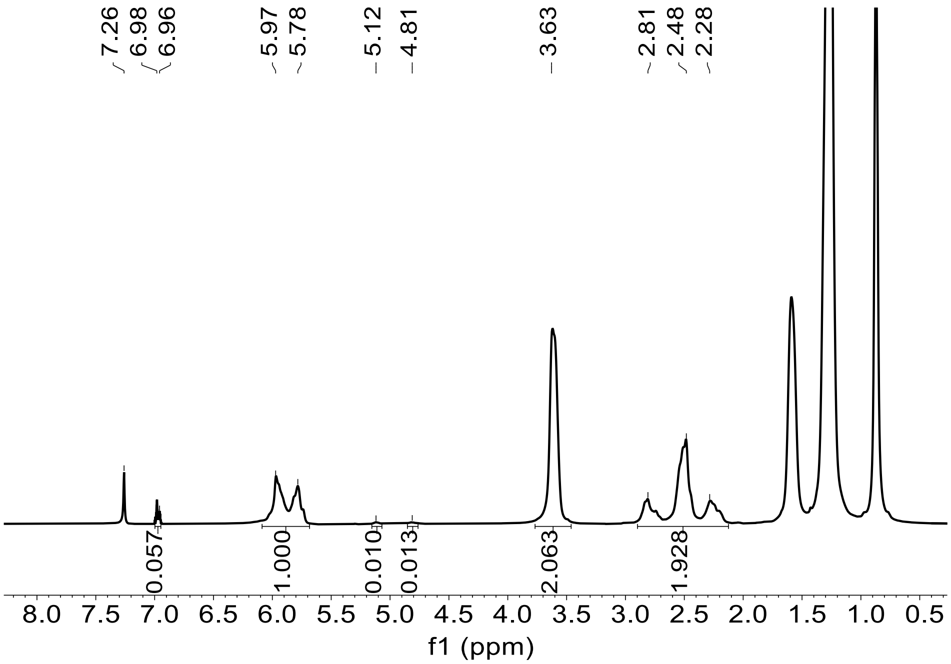


Fig. S23 ^{1}H NMR (600 MHz) spectra of poly-$\mathbf{1}_{90}$ and its phenyl end group obtained from Ni/**L4** catalyst recorded in $CDCl_3$ at 25 °C.

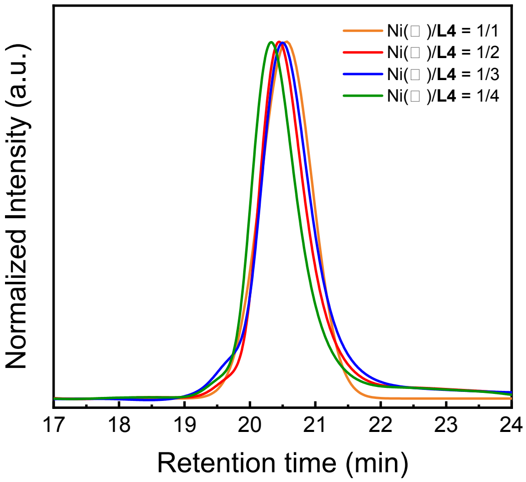


Fig. S24 SEC of poly-$\mathbf{4}_{100}$ prepared in CH_2Cl_2 at room temperature using Ni(II)/**L4** catalyst with different ratio of Ni(II) and **L4**.

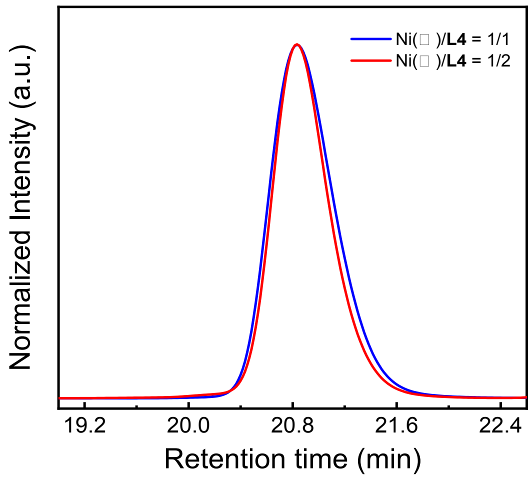


Fig. S25 SEC of poly-**5**$_{100}$ prepared in CH_2Cl_2 at room temperature using Ni(II)/**L4** catalyst with different ratio of Ni(II) and **L4**.

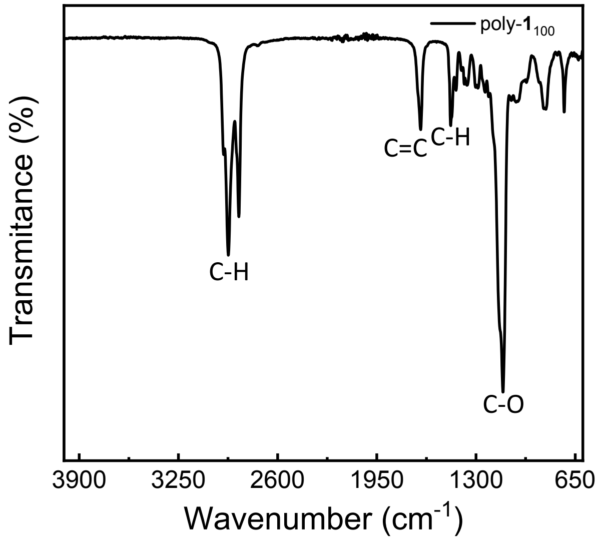


Fig. S26 FT-IR spectrum of poly-**1**$_{100}$ measured at 25 °C using KBr pellets.

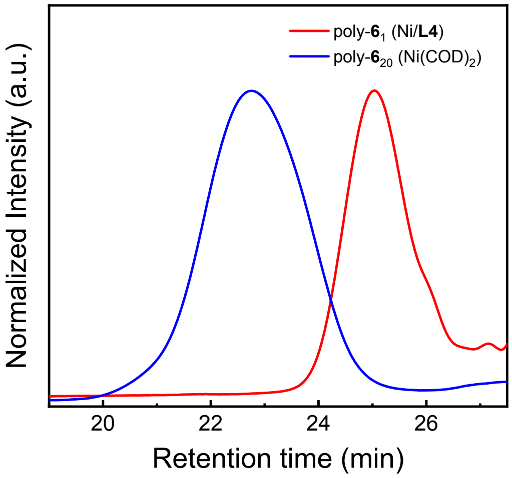


Fig. S27 SEC of poly-$\mathbf{6}_1$ and poly-$\mathbf{6}_{20}$ prepared in toluene at room temperature using Ni(II)/**L4** and Ni(COD)$_2$ in CH_2Cl_2 at room temperature respectively.

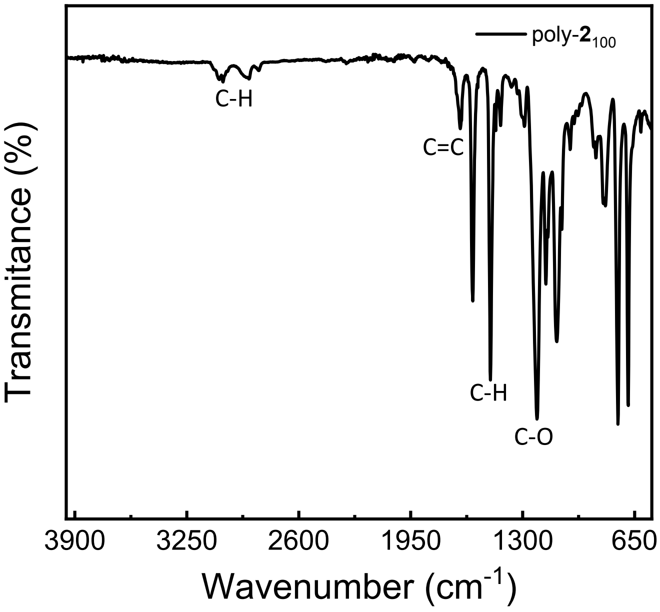


Fig. S28 FT-IR spectrum of poly-$\mathbf{2}_{100}$ measured at 25 °C using KBr pellets.

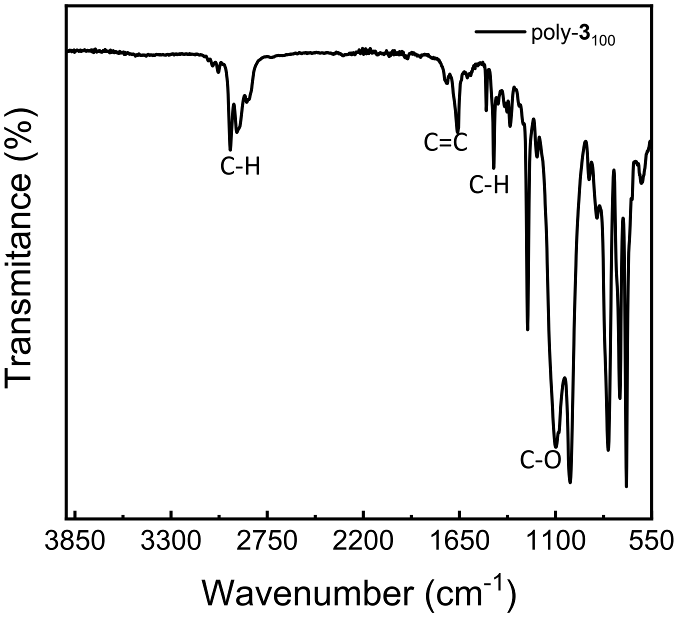


Fig. S29 FT-IR spectrum of poly-$\mathbf{3}_{100}$ measured at 25 °C using KBr pellets.

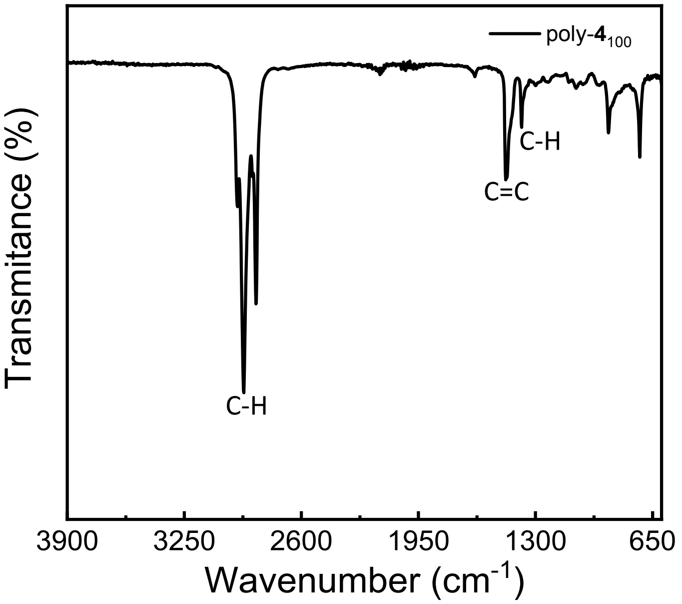


Fig. S30 FT-IR spectrum of poly-$\mathbf{4}_{100}$ measured at 25 °C using KBr pellets.

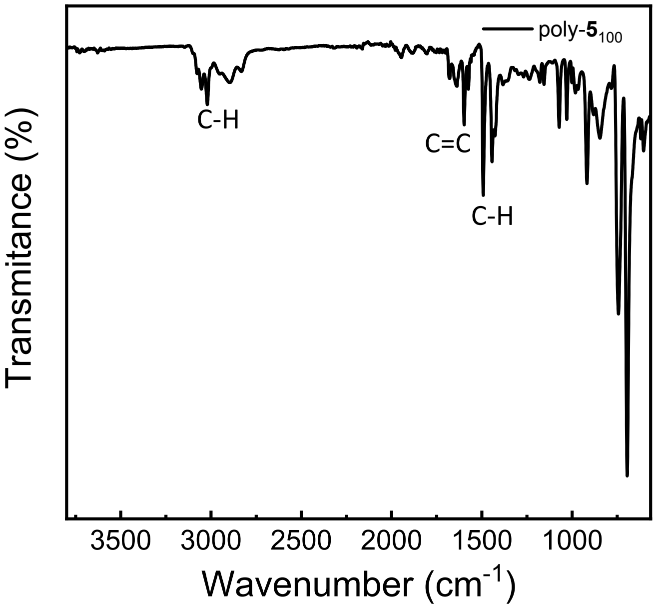


Fig. S31 FT-IR spectrum of poly-$\mathbf{5}_{100}$ measured at 25 °C using KBr pellets.

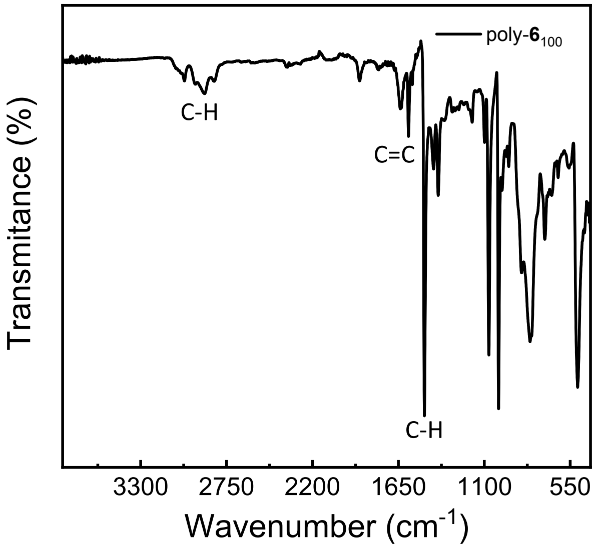


Fig. S32 FT-IR spectrum of poly-$\mathbf{6}_{100}$ measured at 25 °C using KBr pellets.

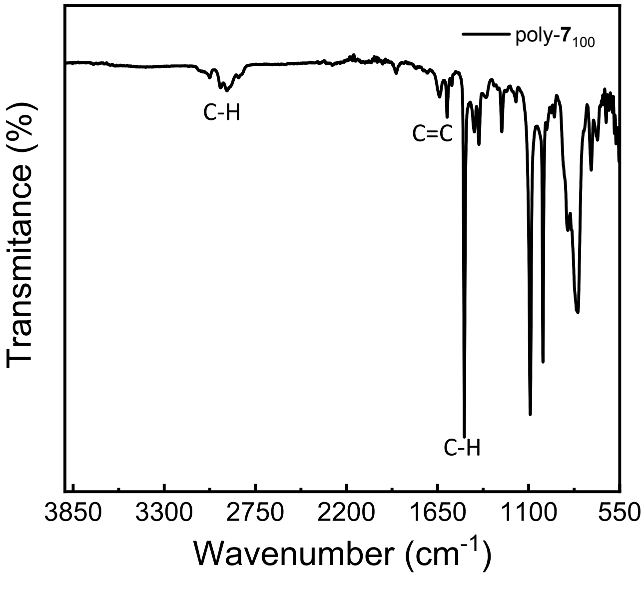


Fig. S33 FT-IR spectrum of poly-$\mathbf{7}_{100}$ measured at 25 °C using KBr pellets.

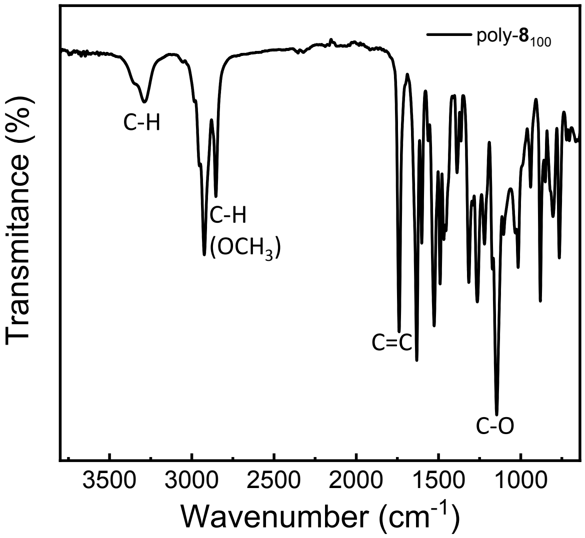


Fig. S34 FT-IR spectrum of poly-$\mathbf{8}_{100}$ measured at 25 °C using KBr pellets.

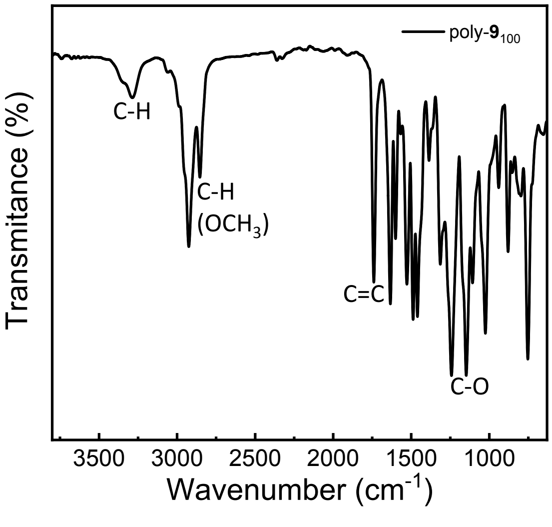


Fig. S35 FT-IR spectrum of poly-$\mathbf{9}_{100}$ measured at 25 °C using KBr pellets.

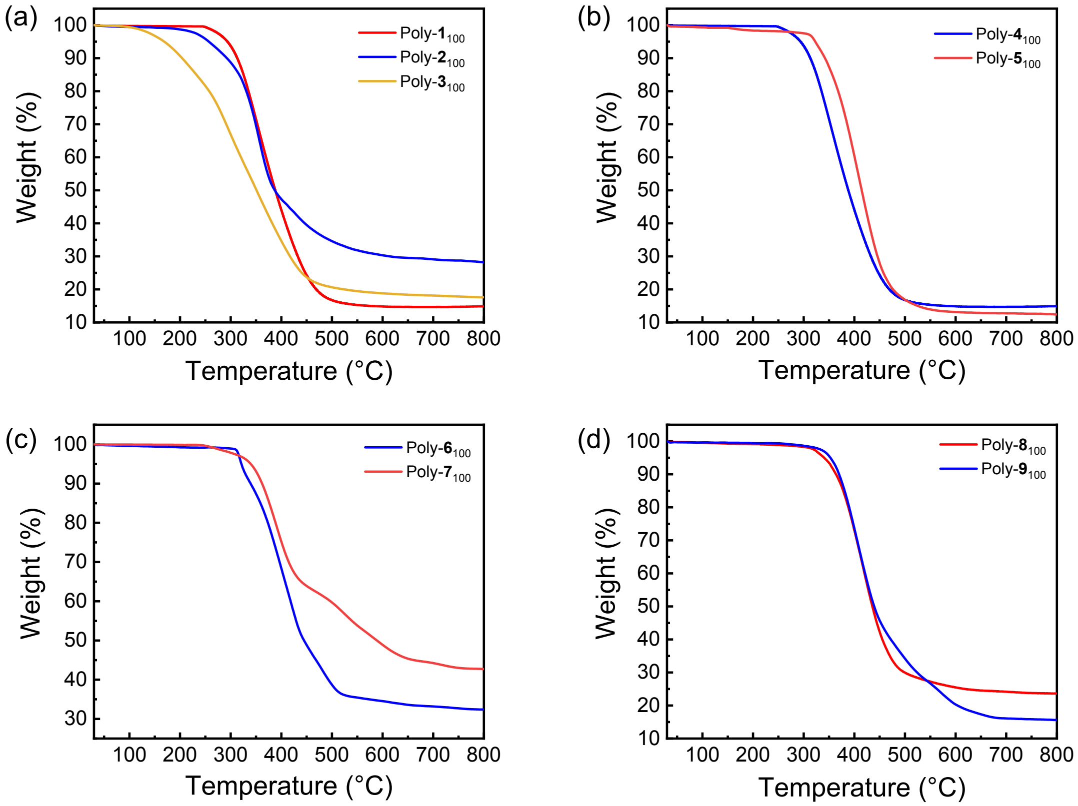


Fig. S36 TGA curves of poly-$\mathbf{1}_{100}$, poly-$\mathbf{2}_{100}$ and poly-$\mathbf{3}_{100}$ (a); poly-$\mathbf{4}_{100}$ and poly-$\mathbf{5}_{100}$ (b); poly-$\mathbf{6}_{100}$ and poly-$\mathbf{7}_{100}$ (c); poly-$\mathbf{8}_{100}$ and poly-$\mathbf{9}_{100}$ (d) in nitrogen at a heating rate of 10 ℃ min^{-1} respectively.

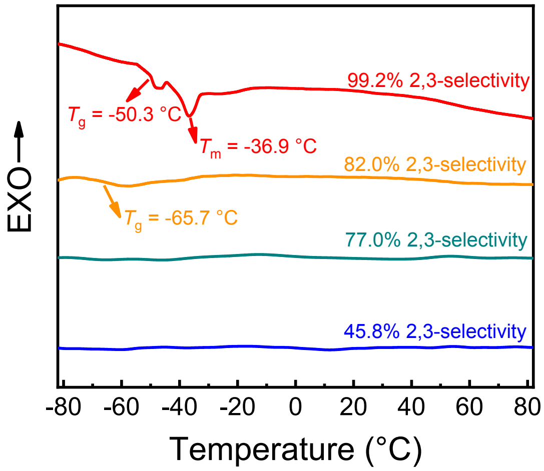


Fig. S37 DSC curves of poly-$\mathbf{1}_{100}$ with different 2,3-polymerization selectivity in nitrogen at a heating rate of 5 ℃ min^{-1} in the second heating run.

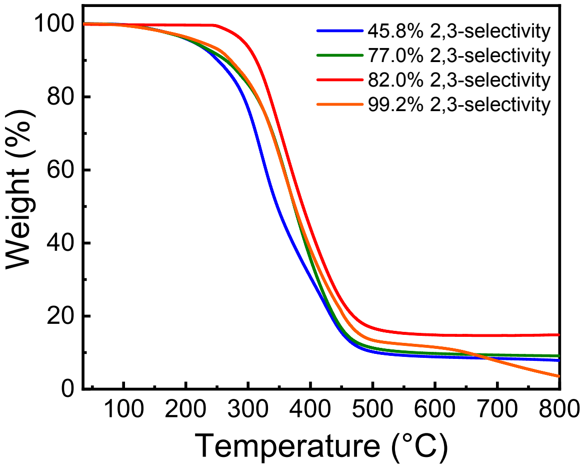


Fig. S38 TGA curves of poly-$\mathbf{1}_{100}$ with different 2,3-polymerization selectivity in nitrogen at a heating rate of 10 ℃ min^{-1}.

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