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Supporting Information

A Facile Synthetic Route to Stereoregular Helical Poly(phenyl isocyanide)s with Defined Pendants and Controlled Helicity

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General consideration.

The ¹H, and ¹⁹F NMR spectra were recorded using a Bruker 600 or 400 MHz spectrometer {H}. Size exclusion chromatography (SEC) was performed on Waters 1515 pump and Waters 2414 differential refractive index (RI) detector (set at 40 °C) using a series of linear Styragel HR1, HR2 and HR4 columns. Molecular weight (M_n) and its polydispersity (M_w/M_n) data are reported relative to polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 0.3 mL/min. FT-IR spectra were recorded on Perkin-Elmer Spectrum BX FT-IR system using KBr pellets. Circular dichroism (CD) spectra were obtained in a 1.0 mm quartz cell at 25 °C using a JASCO J1500 spectropolarimeter. UV-vis spectra were performed on a UNIC 4802 UV/VIS double beam spectrophotometer in 1.0 cm length quartz cell. The polymer concentration was calculated on the basis of the monomer units and was 0.2 mg/mL. The optical rotations were measured in CHCl₃ at 25 °C using a 10.0 cm quartz cell on a WZZ-2B polarimeter. The water contact angles were measured at room temperature using a drop of water on an OCA15EC optical contact angle measuring device.

All solvents were obtained from Sinopharm. Co. Ltd., and were purified by the standard procedures before use. All chemicals were purchased from Aladdin, Sinopharm, and Sigma-Aldrich Chemical Co. Ltd., and were used as received without further purification otherwise denoted. Phenyl isocyanide monomers **1**, **5a-m**, and the Pd(II) initiator were prepared according to literatures reported by us.¹ The poly-**5**_ms were prepared via the polymerization of respective **5** monomers according the literatures reported by the same

group previously.² All the structures were confirmed by ¹H NMR spectra.

Polymerization procedures.

*Typical polymerization procedure for poly-I*_m: The polymerization procedure is given below taking poly-1₆₀ as an example. A 10 mL oven-dried flask was charged with monomer **1** (0.20 g, 0.639 mmol), alkyne-Pd(II) initiator (5.4 mg 0.011 mmol), dry THF (3.2 mL) and a stir bar. The concentrations of monomer **1** and Pd(II) initiator were 0.2 and 0.003 M respectively ([**1**]₀/[Pd]₀ = 60). The reaction flask was then immersed into an oil bath at 55 °C and stirred for 18 h. After cooled to room temperature, the polymerization solution was precipitated into a large amount of methanol, collected by centrifugation, and dried in vacuum at room temperature overnight, afford poly-**1**₆₀ as a yellow solid (0.18 g, 90% yield). SEC: $M_n = 17.5$ kDa, $M_w/M_n = 1.19$. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 7.59 (br, 2H, aromatic), 5.92 (br, 2H, aromatic). ¹⁹F NMR (564 MHz, CDCl₃, 25 °C): δ -153.51, – 157.38, –162.71. FT-IR (KBr, 25 °C, cm⁻¹): 1757 (vc=o), 1605 (vc=N), 1048 (vc=F), 1013 (vc=F).

Typical procedure for the post-polymerization modification: Typical procedure for the post-polymerization modification is given below taking poly-**3a**₆₀ as an example. Into a 10 mL reaction tube with magnetic stirring bar was added poly-**1**₆₀ (25.0 mg, 0.080 mmol), *n*-decyl alcohol **2a** (19.0 mg, 0.120 mmol, 1.5 eq. with respect to monomer **1**), DMAP (4.9 mg, 0.040 mmol) and dry THF (0.4 mL) under nitrogen. The reaction solution was kept stirring for 12 h at 55 °C. After that, the mixture was precipitated into a large amount of methanol, and the precipitated solid was collected by centrifugation. The isolated poly-**3a**₆₀

was washed with methanol several times, and then washed with 1.0 N HCl to remove traces of DMAP. After dried in vacuum at room temperature overnight, poly-**3a**₆₀ was obtained as a yellow solid (20.0 mg, 87% yield). SEC: $M_n = 17.0$ kDa, $M_w/M_n = 1.21$. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 7.31 (br, 2H, aromatic), 5.74 (br, 2H, aromatic), 4.06–3.79 (br, 2H, OCH₂), 1.25–0.86 (br, 19H, CH₂ and CH₃). ¹⁹F NMR (564 MHz, CDCl₃, 25 °C): δ nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2922 (v_{C-H}), 2852 (v_{C-H}), 1719 ($v_{C=0}$), 1605 ($v_{C=N}$).

The post-polymerization modifications of poly- $\mathbf{1}_{m}$ using amines were carried out under the same procedure described above. The characterization data of poly- $\mathbf{3b}_{60}$, poly- $\mathbf{3c}_{60}$, poly- $\mathbf{3d}_{60}$, poly- $\mathbf{3e}_{60}$, poly- $\mathbf{3f}_{60}$, poly- $\mathbf{3g}_{60}$, poly- $\mathbf{3h}_{60}$, poly- $\mathbf{3i}_{60}$, poly- $\mathbf{3j}_{60}$, poly- $\mathbf{3k}_{60}$, poly- $\mathbf{3l}_{30}$, and poly- $\mathbf{3m}_{30}$ were showed below.

Poly-**3b**₆₀: yellow solid obtained in yield 82% by precipitation from diethyl ether. SEC: $M_n = 17.8 \text{ kDa}, M_w/M_n = 1.23. {}^{1}\text{H} \text{ NMR} (400 \text{ MHz}, \text{ CDCl}_3, 25 {}^{\circ}\text{C}): \delta 7.32 \text{ (br, 2H, aromatic)}, 5.77 \text{ (br, 2H, aromatic)}, 3.62 \text{ (br, 20H, CH}_2 \text{ and OCH}_2), 3.37 \text{ (br, 3H, CH}_3). {}^{19}\text{F}$ NMR (376 MHz, CDCl₃, 25 {}^{\circ}\text{C}): δ nothing. FT-IR (KBr, 25 {}^{\circ}\text{C}, \text{cm}^{-1}): 2926 ($v_{\text{C-H}}$), 2864 ($v_{\text{C-H}}$), 1724 ($v_{\text{C=O}}$), 1600 ($v_{\text{C=N}}$).

Poly-**3c**₆₀: yellow solid obtained in yield 82% by precipitation from MeOH. SEC: M_n = 16.8 kDa, M_w/M_n = 1.20. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 7.15 (br, 2H, aromatic), 5.74 (br, 2H, aromatic), 4.26 (br, 2H, OCH₂), 2.56 (br, 6H, CH₂), 0.99 (br, 6H, CH₃). ¹⁹F NMR (376 MHz, CDCl₃, 25 °C): δ nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2922 (v_{C-H}), 2851 (v_{C-H}), 1720 ($v_{C=0}$), 1600 ($v_{C=N}$).

Poly-**3d**₆₀: yellow solid obtained in yield 83% by precipitation from MeOH. $[\alpha]^{25}D = 0$

(*c* = 0.1, CHCl₃, 25 °C). SEC: *M*_n = 17.3 kDa, *M*_w/*M*_n = 1.22. ¹H NMR (400 MHz, CDCl₃, 25 °C): *δ* 7.68–7.06 (br, 2H, aromatic), 5.96–5.58 (br, 2H, aromatic), 4.95–4.36 (br, 1H, OCH), 2.17–0.42 (br, 18H, CH, CH₂ and CH₃). ¹⁹F NMR (376 MHz, CDCl₃, 25 °C): *δ* nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2952 (*v*_{C-H}), 2914 (*v*_{C-H}), 2864 (*v*_{C-H}), 1716 (*v*_{C=0}), 1600 (*v*_{C=N}).

Poly-**3e**₆₀: yellow solid obtained in 86% yield by precipitation from MeOH. [α]²⁵_D = 0 (c = 0.1, CHCl₃, 25 °C). SEC: $M_n = 17.0$ kDa, $M_w/M_n = 1.22$. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 7.68–7.06 (br, 2H, aromatic), 5.96–5.58 (br, 2H, aromatic), 4.95–4.36 (br, 1H, OCH), 2.17–0.42 (br, 18H, CH, CH₂ and CH₃). ¹⁹F NMR (376 MHz, CDCl₃, 25 °C): δ nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2956 (vC–H), 2914 (vC–H), 2872 (vC–H), 1716 (vC=O), 1600 (vC=N).

Poly-**3f**₃₀: yellow solid obtained in 82% yield by precipitation from MeOH. $[\alpha]^{25}_{D} = 0$ (*c* = 0.1, CHCl₃, 25 °C). SEC: $M_n = 7.3$ kDa, $M_w/M_n = 1.25$. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 7.52–7.19 (br, 7H, aromatic), 5.83–5.39 (br, 3H, aromatic and CH), 2.04–0.83 (br, 3H, CH₃). ¹⁹F NMR (376 MHz, CDCl₃, 25 °C): δ nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2973 (ν C-H), 2926 (ν C-H), 1720 (ν C=O), 1598 (ν C=N).

Poly-**3g**₃₀: yellow solid obtained in 85% yield by precipitation from MeOH. [α]²⁵_D = 0 (c = 0.1, CHCl₃, 25 °C). SEC: $M_n = 7.8$ kDa, $M_w/M_n = 1.20$. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 7.51–7.05 (br, 7H, aromatic), 5.78–5.37 (br, 3H, aromatic and CH), 1.82–0.83 (br, 3H, CH₃). ¹⁹F NMR (376 MHz, CDCl₃, 25 °C): δ nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2973 (v_{C-H}), 2926 (v_{C-H}), 1720 ($v_{C=O}$), 1598 ($v_{C=N}$).

Poly-**3h**₆₀: yellow solid obtained in yield 87% by precipitation from MeOH. [α]²⁵_D = 0 (c = 0.1, CHCl₃, 25 °C). SEC: $M_n = 20.5$ kDa, $M_w/M_n = 1.21$. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 8.74 (br, 1H, CONH), 6.94 (br, 2H, aromatic), 5.68 (br, 2H, aromatic), 4.56 (br, 1H, CH), 4.09 (br, 2H, OCH₂), 1.58–1.26 (br, 19H, CH₂ and CH₃), 0.87 (br, 3H, CH₃). ¹⁹F NMR (564 MHz, CDCl₃, 25 °C): δ nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2914 (v_{C-H}), 2855 (v_{C-H}), 1730 ($v_{NHC=0}$), 1635($v_{OC=0}$), 1503 ($v_{C=N}$).

Poly-**3i**₆₀: yellow solid obtained in 85% yield by precipitation from MeOH. $[\alpha]^{25}_{D} = 0$ (*c* = 0.1, CHCl₃, 25 °C). SEC: $M_n = 21.2$ kDa, $M_w/M_n = 1.23$. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 8.74 (br, 1H, CONH), 6.94 (br, 2H, aromatic), 5.68 (br, 2H, aromatic), 4.56 (br, 1H, CH), 4.09 (br, 2H, OCH₂), 1.58–0.87 (br, 22H, CH₂ and CH₃). ¹⁹F NMR (564 MHz, CDCl₃, 25 °C): δ nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2914 (*v*_{C-H}), 2855 (*v*_{C-H}), 1730 (*v*_{C=0}), 1598 (*v*_{C=N}).

Poly-**3j**₆₀: yellow solid obtained in 84% yield by precipitation from MeOH. SEC: $M_n = 20.8 \text{ kDa}, M_w/M_n = 1.20. {}^{1}\text{H} \text{ NMR} (400 \text{ MHz}, \text{CDCl}_3, 25 {}^{\circ}\text{C}): \delta 8.37-7.83 (br, 1H, COHN),$ 7.01–5.82 (br, 4H, aromatic), 4.57–3.99 (br, 2H, OCH₂), 1.55–0.84 (br, 25H, CH₂ and CH₃). ¹⁹F NMR (376 MHz, CDCl₃, 25 {}^{\circ}\text{C}): δ nothing. FT-IR (KBr, 25 {}^{\circ}\text{C}, cm⁻¹): 2964 (*v*_{C-H}), 2922 (*v*_{C-H}), 2855 (*v*_{C-H}), 1745 (*v*_{C=0}), 1598 (*v*_{C=N}).

Poly-**3k**₆₀: yellow solid obtained in 83% yield by precipitation from MeOH. SEC: $M_n = 16.0 \text{ kDa}$, $M_w/M_n = 1.21$. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 8.43 (br, 1H, CONH), 6.86 (br, 2H, aromatic), 5.69 (br, 2H, aromatic), 3.98–3.71 (br, 1H, CH), 2.22–0.85 (br, 10H, CH₂). ¹⁹F NMR (564 MHz, CDCl₃, 25 °C): δ nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2964 (v_{C-1})

н), 2931 (vc-н), 2855 (vc-н), 1636 (vnнс=0), 1598 (vc=n).

Poly-**31**₃₀: yellow solid obtained in yield 85% by precipitation from MeOH. $[\alpha]^{25}_{D} = 0$ (*c* = 0.1, CHCl₃, 25 °C). SEC: $M_n = 6.5$ kDa, $M_w/M_n = 1.18$. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 9.33–8.97 (br, 1H, CONH), 7.58–7.31 (br, 7H, aromatic), 6.66 (br, 1H, CH), 5.35 (br, 2H, aromatic), 2.00–0.85 (br, 3H, CH₃). ¹⁹F NMR (376 MHz, CDCl₃, 25 °C): δ nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2956 (*v*_{C-H}), 2922 (*v*_{C-H}), 2855 (*v*_{C-H}), 1636 (*v*_{NHC=O}), 1598 (*v*_{C=N}).

Poly-**3m**₃₀: yellow solid obtained in 87% yield by precipitation from MeOH. [α]²⁵_D = 0 (c = 0.1, CHCl₃, 25 °C). SEC: $M_n = 6.0$ kDa, $M_w/M_n = 1.20$. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 9.27–8.94 (br, 1H, CONH), 7.58–7.24 (br, 7H, aromatic), 6.68–6.64 (br, 1H, CH), 5.36 (br, CH₂, aromatic), 1.64–0.81 (br, 3H, CH₃). ¹⁹F NMR (564 MHz, CDCl₃, 25 °C): δ nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2947 (v_{C-H}), 2926 (v_{C-H}), 2855 (v_{C-H}), 1636 ($v_{NHC=0}$), 1598 ($v_{C=N}$).

Typical procedure for the one-pot polymerization of **1** *with alcohol and amine.* Typical experimental procedure for the one-pot polymerization of **1** *with alcohol and amine is given* below taking poly-**4a**₆₀ as an example. Into a 10 mL reaction tube with magnetic stirring bar was added monomer **1** (25.0 mg, 0.080 mmol), *n*-decyl alcohol **2a** (19.0 mg, 0.120 mmol, 1.5 eq. with respect to monomer **1**), DMAP (4.9 mg, 0.04 mmol), alkyne-Pd(II) initiator (0.7 mg, 0.013 moml, 0.017 eq. to monomer **1**) and dry THF (0.4 mL) under nitrogen. The concentrations of monomer **1** and alkyne-Pd(II) complex were 0.2 and 0.003 M, respectively ([**1**]₀/[Pd]₀= 60). The reaction flask was then immersed into an oil bath at

55 °C and stirred for 18 h. After cooled to room temperature, the polymerization solution was precipitated into a large amount of methanol, and collected by centrifugation. The isolated poly-**4a**₆₀ was additionally washed with 1.0 N HCl to remove traces of DMAP. After dried in vacuum at room temperature overnight, poly-**4a**₆₀ was obtained as a yellow solid (21.0 mg, 85% yield). SEC: $M_n = 17.1$ kDa, $M_w/M_n = 1.20$. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 7.31 (br, 2H, aromatic), 5.75 (br, 2H, aromatic), 4.06–3.79 (br, 2H, OCH₂), 1.25–0.86 (br, 19H, CH₂ and CH₃). ¹⁹F NMR (564 MHz, CDCl₃, 25 °C): δ nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2922 (*v*_{C-H}), 2852 (*v*_{C-H}), 1719 (*v*_{C=0}), 1605 (*v*_{C=N}).

The one-pot polymerizations of **1** with the presence of amines using the Pd(II) initiator were followed the same procedure described above. The characterization data for poly-**4b**₆₀, poly-**4c**₆₀, poly-**4d**₆₀, poly-**4e**₆₀, poly-**4f**₃₀, poly-**4g**₃₀ poly-**4h**₆₀, poly-**4i**₆₀, poly-**4j**₆₀, poly-**4j**₆₀, poly-**4k**₆₀, poly-**4l**₃₀, and poly-**4m**₃₀ were showed below.

Poly-**4b**₆₀: yellow solid obtained in 83% yield by precipitation from diethyl ether. SEC: $M_n = 17.1 \text{ kDa}, M_w/M_n = 1.14. {}^{1}\text{H} \text{ NMR} (400 \text{ MHz}, \text{ CDCl}_3, 25 {}^{\circ}\text{C}): \delta 7.30 \text{ (br, 2H, aromatic)}, 5.70 \text{ (br, 2H, aromatic)}, 3.60–3.34 \text{ (br, 23H, CH}_2 \text{ and CH}_3). {}^{19}\text{F} \text{ NMR} (376 \text{ MHz}, \text{CDCl}_3): \delta \text{ nothing}. FT-IR (KBr, 25 {}^{\circ}\text{C}, \text{cm}^{-1}): 2946 (v_{C-H}), 2910 (v_{C-H}), 1702 (v_{C=0}), 1598 (v_{C=N}).$

Poly-**4c**₆₀: yellow solid obtained in 81% yield by precipitation from MeOH. SEC: $M_n =$ 16.6 kDa, $M_w/M_n = 1.18$. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 7.32 (br, 2H, aromatic), 5.74 (br, 2H, aromatic), 4.27 (br, 2H, OCH₂), 2.58 (br, 6H, CH₂), 1.00–0.83 (br, 6H, CH₃). ¹⁹F NMR (564 MHz, CDCl₃, 25 °C): δ nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2964 (v_{C-H}), 2910 (vс-н), 1716 (vс=о), 1598 (vс=л).

Poly-**4d**₆₀: yellow solid obtained in 85% yield by precipitation from MeOH. [α]²⁵_D = +1123 (c = 0.1, CHCl₃, 25 °C). SEC: $M_n = 17.5$ kDa, $M_w/M_n = 1.20$. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 7.65–6.95 (br, 2H, aromatic), 5.92–5.56 (br, 2H, aromatic), 4.93–4.36 (br, 1H, OCH), 2.18–0.44 (br, 18H, CH, CH₂ and CH₃). ¹⁹F NMR (564 MHz, CDCl₃, 25 °C): δ nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2956 (v_{C-H}), 2914 (v_{C-H}), 2872 (v_{C-H}), 1716 ($v_{C=O}$), 1600 ($v_{C=N}$).

Poly-**4e**₆₀: yellow solid obtained in 88% yield by precipitation from MeOH. [α]²⁵_D = – 1108 (c = 0.1, CHCl₃, 25 °C). SEC: $M_n = 17.2$ kDa, $M_w/M_n = 1.20$. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 7.65–6.95 (br, 2H, aromatic), 5.92–5.56 (br, 2H, aromatic), 4.93–4.36 (br, 1H, OCH), 2.18–0.44 (br, 18H, CH, CH₂ and CH₃). ¹⁹F NMR (376 MHz, CDCl₃, 25 °C): δ nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2956 (v_{C-H}), 2914 (v_{C-H}), 2872 (v_{C-H}), 1716 ($v_{C=0}$), 1600 ($v_{C=N}$).

Poly-**4f**₃₀: yellow solid obtained in 82% yield by precipitation from MeOH. [α]²⁵_D = +427 (c = 0.1, CHCl₃, 25 °C). SEC: $M_n = 7.5$ kDa, $M_w/M_n = 1.25$. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 7.51–7.17 (br, 7H, aromatic), 5.80–5.35 (br, 3H, aromatic and CH), 1.85–0.83 (br, 3H, CH₃). ¹⁹F NMR (376 MHz, CDCl₃, 25 °C): δ nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2973 (v_{C-H}), 2926 (v_{C-H}), 1720 ($v_{C=O}$), 1598 ($v_{C=N}$).

Poly-**4g**₃₀: yellow solid obtained in 85% yield by precipitation from MeOH. $[\alpha]^{25}_{D} = -510 \ (c = 0.1, \text{ CHCl}_3, 25 \text{ °C}).$ SEC: $M_n = 7.8 \text{ kDa}, M_w/M_n = 1.17.$ ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 7.12 (br, 7H, aromatic), 5.80 (br, 3H, aromatic and CH), 1.73–0.83 (br,

3H, CH₃). ¹⁹F NMR (376 MHz, CDCl₃, 25 °C): *δ* nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2973 (*v*_{C-H}), 2926 (*v*_{C-H}), 1720 (*v*_{C=0}), 1598 (*v*_{C=N}).

Poly-**4h**₆₀: yellow solid obtained in 88% yield by precipitation from MeOH. [α]²⁵_D = – 1227 (c = 0.1, CHCl₃, 25 °C). SEC: $M_n = 22.9$ kDa, $M_w/M_n = 1.15$. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 8.56–8.21 (br, 1H, CONH), 6.60–5.78 (br, 4H, aromatic), 4.43–4.31 (br, 1H, CH), 4.07–3.89 (br, 2H, OCH₂), 1.61–0.86 (br, 22H, CH₂ and CH₃). ¹⁹F NMR (564 MHz, CDCl₃, 25 °C): δ nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2960 (v_{C-H}), 2926 (v_{C-H}), 2848 (v_{C-H}), 1714 ($v_{OC=O}$), 1640 ($v_{NHC=O}$), 1598 ($v_{C=N}$).

Poly-**4i**₆₀: yellow solid obtained in 87% yield by precipitation from MeOH. $[α]^{25}_D =$ +1196 (*c* = 0.1, CHCl₃, 25 °C). SEC: *M*_n = 21.5 kDa, *M*_w/*M*_n = 1.20. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 8.57–8.27 (br, 1H, CONH), 6.84–5.85 (br, 4H, aromatic), 4.47 (br, 1H, CH), 4.08 (br, 2H, OCH₂), 1.64–0.88 (br, 22H, CH₂ and CH₃). ¹⁹F NMR (564 MHz, CDCl₃, 25 °C): δ nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2956 (*v*C-H), 2930 (*v*C-H), 2845 (*v*C-H), 1718 (*v*OC=O), 1635 (*v*NHC=O), 1600 (*v*C=N).

Poly-**4j**₆₀: yellow solid obtained in 89% yield by precipitation from MeOH. SEC: M_n = 21.5 kDa, M_w/M_n = 1.18. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 8.38–7.83 (br, 1H, CONH), 6.98–5.80 (br, 4H, aromatic), 4.57–4.00 (br, 2H, OCH₂), 1.56–0.84 (br, 25H, CH₂ and CH₃). ¹⁹F NMR (376 MHz, CDCl₃, 25 °C): δ nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2964 (ν_{C-H}), 2922 (ν_{C-H}), 2855 (ν_{C-H}), 1730 ($\nu_{OC=O}$), 1644 ($\nu_{NHC=O}$), 1598 ($\nu_{C=N}$).

Poly-**4k**₆₀: yellow solid obtained in 80% yield by precipitation from MeOH. SEC: $M_n = 16.4 \text{ kDa}$, $M_w/M_n = 1.20$. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 8.43 (br, 1H, CONH), 6.85

(br, 2H, aromatic), 5.69 (br, 2H, aromatic), 3.98–3.70 (br, 1H, CH), 2.21–0.84 (br, 10H, CH₂). ¹⁹F NMR (564 MHz, CDCl₃, 25 °C), *δ* nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2931 (*v*_{C-} H), 2851 (*v*_{C-H}), 1632 (*v*_{NHC=O}), 1598 (*v*_{C=N}).

Poly-**4I**₃₀: yellow solid obtained in 83% yield by precipitation from MeOH. $[\alpha]^{25}_{D} =$ +1128 (*c* = 0.1, CHCl₃, 25 °C). SEC: *M*_n = 6.5 kDa, *M*_w/*M*_n = 1.15. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 9.33–8.97 (br, 1H, CONH), 7.58–7.31 (br, 7H, aromatic), 6.66 (br, 1H, CH), 5.35 (br, 2H, aromatic), 2.00–0.85 (br, 3H, CH₃). ¹⁹F NMR (376 MHz, CDCl₃, 25 °C), δ nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2973 (*v*C-H), 2956 (*v*C-H), 2922 (*v*C-H), 1628 (*v*NHC=O), 1590 (*v*C=N).

Poly-**4m**₃₀: yellow solid obtained in 85% yield by precipitation from MeOH. [α]²⁵_D = – 1253 (c = 0.1, CHCl₃, 25 °C). SEC: $M_n = 7.3$ kDa, $M_w/M_n = 1.18$. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 9.32–8.94 (br, 1H, CONH), 7.55–7.26 (br, 7H, aromatic), 6.68 (br, 1H, CH), 5.37 (br, 2H, aromatic), 1.64–0.83 (br, 3H, CH₃). ¹⁹F NMR (376 MHz, CDCl₃, 25 °C), δ nothing. FT-IR (KBr, 25 °C, cm⁻¹): 2970 (v_{C-H}), 2958 (v_{C-H}), 2922 (v_{C-H}), 1625 ($v_{NHC=0}$), 1600 ($v_{C=N}$).

Kinetic studies: A mixture of monomer **1** (60.0 mg, 0.192 mmol), DMAP (11.7 mg, 0.096 mmol, 0.5 eq.) and the Pd(II) initiator (1.9 mg, 0.004 mmol, 0.005 eq) were placed in a dry ampule, which was then evacuated on a vacuum line and flushed with dry nitrogen. After the evacuation-flush procedure had been repeated three times, a three-way stopcock was attached to the ampule, and dry THF (0.9 mL) was added via a syringe. To this was added a solution of L-amine **2h** (43.9 mg, 0.19 mmol, 1.0 equiv. with respect to **1**) in THF *via* a

microsyringe at 25 °C. The concentrations of monomer **1** and the Pd(II) initiator were 0.2 and 0.003 M, respectively. The mixture was then stirred under a dry nitrogen atmosphere and heated to 55 °C ($[1]_0/[Pd]_0 = 60$). The reaction was followed by measuring ¹H NMR of the small aliquots taking out from the reaction mixture at appropriate time intervals.

References

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run	polymer ^a	M_{n}^{b} (Da)	$M_{ m W}/M_{ m n}{}^{b}$	yield ^c (%)	$\Delta arepsilon$ 364 d	$[\alpha]^{25} \mathrm{D}^{e}$
1	poly- 3h 60	2.05×10^4	1.21	87	0	0
2	poly- 3i 60	2.12×10^{4}	1.23	85	0	0
3	poly- 3j 60	2.08×10^{4}	1.20	84		
4	poly- 3k 60	1.60×10^4	1.21	83		
5	poly- 31 30	0.65×10^4	1.18	85	0	0
6	poly -3m 30	0.60×10^{4}	1.20	87	0	0

Table S1. Results for the Post-Polymerization Modification of Poly-160 with Amines

^{*a*}The polymers were prepared according to the Scheme 1 in main text via the postpolymerization modification of poly-1₆₀ with the presence of amines (1.0 equiv. with respect to the repeat unit of poly-1₆₀) in THF at 55 °C using the Pd(II) initiator. ^{*b*}M_n and M_w/M_n values were determined by SEC with equivalent to polystyrene standards. ^{*c*}The isolated yields. ^{*d*}The molar CD intensity at 364 nm measured in THF at 25 °C (c = 0.2 g/L). ^{*e*}The optical rotations were measured in CHCl₃ at 25 °C (c = 0.1).



Figure S1. Size exclusion chromatograms of poly- 1_{ms} prepared from the polymerization of monomer 1 using the Pd(II) initiator with different initial feed ratios of monomer to initiator. SEC condition: eluent = THF, temperature = 40 °C.



Figure S2. Plot of M_n and M_w/M_n values of poly-1_{ms} as a function of the initial feed ratios of monomer to initiator. M_n and M_w/M_n were determined by SEC with polystyrene standards (eluent = THF, temperature = 40 °C).



Figure S3. UV-vis absorption spectra of poly- 1_{60} in THF at 25 °C (c = 0.02 g/L).



Figure S4. ¹H NMR (400 MHz) spectrum of poly-5a₆₀ measured in CDCl₃ at 25 °C.



Figure S5. UV-vis absorption spectra of poly-**5a**₆₀ in THF at 25 °C (c = 0.02 g/L).



Figure S6. ¹H NMR (400 MHz) spectrum of poly-3b₆₀ measured in CDCl₃ at 25 °C.



Figure S7. FT-IR spectrum of poly-3b₆₀ measured at 25 °C using KBr pellets.



Figure S8. UV-vis absorption spectrum of poly-**3b**₆₀ in THF at 25 °C (c = 0.02 g/L).



Figure S9. ¹H NMR (400 MHz) spectrum of poly-3c₆₀ measured in CDCl₃ at 25 °C.



Figure S10. FT-IR spectrum of poly-3c₆₀ measured at 25 °C using KBr pellets.



Figure S11. UV-vis absorption spectra of poly- $3c_{60}$ in THF at 25 °C (c = 0.02 g/L).



Figure S12. ¹H NMR (400 MHz) spectrum of poly-**3d**₆₀ measured in CDCl₃ at 25 °C. The asterisk denotes a residual solvent peak.



Figure S13. ¹⁹F NMR (376 MHz) spectrum of poly-3d₆₀ measured in CDCl₃ at 25 °C.



Figure S14. FT-IR spectrum of poly-3d₆₀ measured at 25 °C using KBr pellets.



Figure S15. ¹H NMR (400 MHz) spectrum of poly-**3e**₆₀ measured in CDCl₃ at 25 °C. The asterisk denotes a residual solvent peak.



Figure S16. FT-IR spectrum of poly-3e₆₀ measured at 25 °C using KBr pellets.



Figure S17. ¹H NMR (400 MHz) spectrum of poly-3f₃₀ measured in CDCl₃ at 25 °C.



Figure S18. FT-IR spectrum of poly-3f₃₀ measured at 25 °C using KBr pellets.



Figure S19. ¹H NMR (400 MHz) spectrum of poly-3g₃₀ measured in CDCl₃ at 25 °C.



Figure S20. FT-IR spectrum of poly-3g₃₀ measured at 25 °C using KBr pellets.



Figure S21. Size exclusion chromatograms of poly-**3b**₆₀, poly-**4b**₆₀, poly-**3c**₆₀, poly-**4c**₆₀, poly-**3e**₆₀, poly-**3f**₃₀, poly-**4f**₃₀, poly-**3g**₃₀ and poly-**4g**₃₀. SEC condition: eluent = THF, temperature = 40 °C.



Figure S22. The water contact angles of the films prepared from the THF solution of poly-

 $\mathbf{1}_{60}$ (a), poly- $\mathbf{3a}_{60}$ (b), poly- $\mathbf{3b}_{60}$ (c), and poly- $\mathbf{3c}_{60}$ (d) measured at room temperature.



Figure S23. Size exclusion chromatograms of poly-**3d**₆₀, poly-**4d**₆₀, poly-**5d**₆₀, poly-**4e**₆₀, and poly-**5e**₆₀. SEC condition: eluent = THF, temperature = 40 °C.



Figure S24. Size exclusion chromatograms for the polymerization of monomer **1** using the Pd(II) initiator with the presence of L-menthol (**2d**) and D-menthol (**2e**) in different molar ratios. SEC condition: eluent = THF, temperature = $40 \, ^{\circ}$ C.



Figure S25. CD and UV-vis spectra of the polymers prepared via the polymerization of monomer **1** using the Pd(II) initiator with the presence of L-menthol (**2d**) and D-menthol (**2e**) in different molar ratios in THF at 55 °C ($[1]_0/[2d+2e]_0/[Pd]_0 = 60/90/1$, $[1]_0 = 0.2$ M).



Figure S26. ¹H NMR (400 MHz) spectrum of poly-4b₆₀ measured in CDCl₃ at 25 °C.



Figure S27. FT-IR spectrum of poly-4b₆₀ measured at 25 °C using KBr pellets.



Figure S28. UV-vis absorption spectra of poly-4b₆₀ in THF at 25 °C (c = 0.02 g/L).



Figure S29. ¹H NMR (600 MHz) spectrum of poly-4c₆₀ measured in CDCl₃ at 25 °C.



Figure S30. FT-IR spectrum of poly-4c₆₀ measured at 25 °C using KBr pellets.



Figure S31. UV-vis absorption spectra of poly-4c₆₀ in THF at 25 °C (c = 0.02 g/L).



Figure S32. ¹H NMR (400 MHz) spectrum of poly-4e₆₀ measured in CDCl₃ at 25 °C.



Figure S33. FT-IR spectrum of poly-4e₆₀ measured at 25 °C using KBr pellets.



Figure S34. ¹H NMR (400 MHz) spectrum of poly-4f₃₀ measured in CDCl₃ at 25 °C.



Figure S35. FT-IR spectrum of poly-4f₃₀ measured at 25 °C using KBr pellets.



Figure S36. ¹H NMR (400 MHz) spectrum of poly-4g₃₀ measured in CDCl₃ at 25 °C.



Figure S37. FT-IR spectrum of poly-4g₃₀ measured at 25 °C using KBr pellets.



Figure S38. CD and UV-vis spectra of poly-4f₃₀ and poly-4g₃₀ measured in THF at 25 °C

with c = 0.2 mg/mL.



Figure S39. Size exclusion chromatograms for poly-**5h**₆₀, poly-**4h**₆₀, poly-**3h**₆₀, poly-**4i**₆₀, and poly-**5i**₆₀. SEC condition: eluent = THF, temperature = 40 °C.



Figure S40. ¹H NMR (600 MHz) spectrum of poly-3h₆₀ measured in CDCl₃ at 25 °C.



Figure S41. FT-IR spectrum of poly-3h₆₀ measured at 25 °C using KBr pellets.



Figure S42. Size exclusion chromatograms for poly- $3h_{60}$, poly- $3i_{60}$, poly- $3j_{60}$, poly- $3k_{60}$, poly- $3l_{30}$ and poly- $3m_{30}$. SEC condition: eluent = THF, temperature = 40 °C.



Figure S43. ¹H NMR (600 MHz) spectrum of poly-3i₆₀ measured in CDCl₃ at 25 °C.



Figure S44. FI-IR spectrum of poly-3i₆₀ measured at 25 °C using KBr pellets.



Figure S45.¹H NMR (400 MHz) spectrum of poly-3j₆₀ measured in CDCl₃ at 25 °C.



Figure S46. FT-IR spectrum of poly-3j₆₀ measured at 25 °C using KBr pellets.



Figure S47. UV-vis absorption spectra of poly- $3j_{60}$ in THF at 25 °C (c = 0.02 g/L).



Figure S48. ¹H NMR (600 MHz) spectrum of poly-3k₆₀ measured in CDCl₃ at 25 °C.



Figure S49. FT-IR spectrum of poly-3k₆₀ measured at 25 °C using KBr pellets.



Figure S50. UV-vis absorption spectra of poly- $3\mathbf{k}_{60}$ in THF at 25 °C (c = 0.02 g/L).



Figure S51. ¹H NMR (400 MHz) spectrum of poly-**3**l₃₀ measured in CDCl₃ at 25 °C. The asterisk denotes a residual solvent peak.



Figure S52. FT-TR spectrum of poly-3l₃₀ measured at 25 °C using KBr pellets.



Figure S53. ¹H NMR (400 MHz) spectrum of poly-3m₃₀ measured in CDCl₃ at 25 °C.



Figure S54. FT-TR spectrum of poly-3m₃₀ measured at 25 °C using KBr pellets.



Figure S55. ¹H NMR (600 MHz) spectrum of poly-4h₆₀ measured in CDCl₃ at 25 °C.



Figure S56. ¹⁹F NMR (564 MHz) spectrum of poly-4h₆₀ measured in CDCl₃ at 25 °C.



Figure S57. FT-IR spectrum of poly-4h₆₀ measured at 25 °C using KBr pellets.



Figure S58. Size exclusion chromatograms of the polymerization of monomer **1** using the Pd(II) initiator with the presence of L-amine (**2h**) and achiral amine (**2j**) in different proportion.



Figure S59. CD and UV-vis spectra of the polymerization of monomer **1** using the Pd(II) initiator with the presence of L-amine (**2h**) and achiral amine (**2j**) in different proportion in THF at 55 °C ([**1**] $_0/[2\mathbf{h}+2\mathbf{j}]_0/[Pd]_0 = 60/60/1$, [**1**] $_0 = 0.2$ M). The spectra were measured in THF at 25 °C with c = 0.2 mg/mL.



Figure S60. Size exclusion chromatograms of poly- $4\mathbf{k}_{60}$, poly- $4\mathbf{l}_{30}$, and poly- $4\mathbf{m}_{30}$. SEC condition: eluent = THF, temperature = 40 °C.



Figure S61. ¹H NMR (600 MHz) spectrum of poly-4i₆₀ measured in CDCl₃ at 25 °C.



Figure S62. FT-IR spectrum of poly-4i₆₀ measured at 25 °C using KBr pellets.



Figure S63.¹H NMR (400 MHz) spectrum of poly-**4j**₆₀ measured in CDCl₃ at 25 °C. The asterisk denotes a residual solvent peak.



Figure S64. FT-IR spectrum of poly-4j₆₀ measured at 25 °C using KBr pellets.



Figure S65. UV-vis absorption spectra of poly-4j₆₀ in THF at 25 °C (c = 0.02 g/L).



Figure S66. ¹H NMR (600 MHz) spectrum of poly-4k₆₀ measured in CDCl₃ at 25 °C.



Figure S67. FT-IR spectrum of poly-4k₆₀ measured at 25 °C using KBr pellets.



Figure S68. UV-vis absorption spectra of poly- $4\mathbf{k}_{60}$ in THF at 25 °C (c = 0.02 g/L).



Figure S69. ¹H NMR (400 MHz) spectrum of poly-**4l**₃₀ measured in CDCl₃ at 25 °C. The asterisk denotes a residual solvent peak.



Figure S70. FT-IR spectrum of poly-4l₃₀ measured at 25 °C using KBr pellets.



Figure S71. ¹H NMR (400 MHz) spectrum of poly-4m₃₀ measured in CDCl₃ at 25 °C.



Figure S72. FT-IR spectrum of poly-4m₃₀ measured at 25 °C using KBr pellets.



Figure S73. CD and UV-vis spectra of poly-4l₃₀ and poly-4m₃₀ measured in THF at 25 °C

with c = 0.2 mg/mL.



Figure S74. ¹H NMR (600 MHz) spectra of the one-pot polymerization of monomer 1 using the Pd(II) initiator with the presence of chiral amine **2h** at different times, using the DMAP as the internal standard.



Figure S75. (a) Plots of the conversions with reaction time for the substitution reaction of PFP-ester of monomer 1 with 2d, and the polymerization of 5d using the Pd(II)-initiated in THF at 55 °C. (b) First-order kinetic plots for the reaction of monomer 1 with 2d using the Pd(II)-initiated polymerization of 5d in THF at 55 °C ($[1]_0 = 0.2$ M, $[2d]_0 = 0.3$ M, $[1]_0/[Pd]_0 = 60$).