Supporting Information

Living polymerization of arylisocyanide initiated by phenylethynyl palladium(II) complex

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**Instruments.**

The $^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded using a Bruker 400 and 600 MHz {H} spectrometer. Size exclusion chromatography (SEC) was performed on Waters 1515 pump and 2414 differential refractive index (RI) detector (set at 40 °C) using a series of linear Styrargel HR1, HR2 and HR4 columns. Molecular weight and polydispersity 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. UV-vis spectra were performed on a UNIC 4802 UV/VIS double beam spectrophotometer in 1.0 cm length quartz cell. Melting points were obtained with a Mel-Temp apparatus and are uncorrected. X-ray diffraction data of single crystals were collected on a Siemens Smart 1000 CCD diffractometer. The determination of unit cell parameters and data collections were performed with Mo-Kα radiation (λ = 0.71073 Å). Unit cell dimensions were obtained with least-squares refinements and all structures were solved by direct methods using SHELXS-97. The other nonhydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed using full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F2. The hydrogen atoms were added theoretically and riding on the concerned atoms.

**Materials**

All solvents were purified by the standard procedures before use. THF was further dried over sodium
benzophenone ketyl, distilled onto LiAlH₄ under nitrogen, and distilled under high vacuum just before use. 4-Ethynyltoluene, 4-ethynylanisole, 1-ethynylbenzene, 4-(methoxycarbonyl)phenylacetylene, ethynyltrimethylsilane, *trans*-dichlorobis(triethylphosphine)palladium(II) and copper(I) chloride were purchased from Aladdin and Sigma-Aldrich, and were used as received without further purification. Isocyanide monomer 2a, 2b, 2c, 2d, 2e, and 2f were prepared according to the literatures and the structures were confirmed by ¹H NMR.¹

**Synthetic procedure for 1a-d**

\[ \text{Pd}^\text{Cl}_3 \text{P} \text{Et}_3 \]

**Synthesis of 1a.** This Pd complex was prepared according to the reported procedure.² 4-Ethynyltoluene (50.0 mg, 0.43 mmol) was treated with *trans*-dichlorobis(triethylphosphine)palladium (178.0 mg, 0.43 mmol) in the presence of copper(I) chloride (2.5 mg, 0.025 mmol) as catalyst in 30 mL of diethylamine and dichloromethane (v/v = 1/1). The mixture was stirred at room temperature for 1 h. After the solvent was removed by evaporation under reduced pressure, the residue was purified by chromatography with petrol ether-ethyl acetate (10/1, v/v) as eluent. The crude product was recrystallized from petrol ether and methanol to afford 1a as a white solid (127 mg, 60% yield). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 7.16 (d, *J* = 8.8 Hz, 2H, aromatic), 7.03 (d, *J* = 8.8 Hz, 2H, aromatic), 2.31 (s, 3H, CH₃–Ph), 2.00–1.95 (m, 12H, PCH₂CH₃), 1.24–1.16 (m, 18H, PCH₂CH₃). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 135.45, 130.58, 128.86, 124.89, 106.42, 93.59, 21.35, 15.46, 8.40. ³¹P NMR (121.5 MHz, CDCl₃, 25 °C): δ 17.85. FT-IR (KBr, cm⁻¹): 2959 (νC–H, aromatic), 2932 (νC–H, aromatic), 2872 (νC–H, aromatic), 2112 (νC≡C), 1746 (νC=C, aromatic), 1693 (νC=C, aromatic).
Compounds 1b, 1c, and 1d were synthesized according to the similar procedure from the reaction of 4-ethynylanisole, 1-ethynylbenzene, and 4-(methoxycarbonyl)phenylacetylene with trans-dichlorobis(triethylphosphine)palladium in dichloromethane and diethylamine, respectively.

\[
\begin{align*}
\text{H}_3\text{CO} & \quad \equiv 
\text{Pd-Cl} \\
\text{PEt}_3 & \quad \text{PEt}_3
\end{align*}
\]

1b: \(^1H\) NMR (400 MHz, CDCl\(_3\), 25 °C): \(\delta\) 7.19 (d, \(J = 8.8\) Hz, 2H, aromatic), 6.78 (d, \(J = 8.8\) Hz, 2H, aromatic), 3.78 (s, 3H, OCH\(_3\)), 2.02–1.94 (m, 12H, PCH\(_2\)CH\(_3\)), 1.25–1.17 (m, 18H, PCH\(_2\)CH\(_3\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\), 25 °C): \(\delta\) 157.81, 131.93, 120.46, 113.79, 105.97, 92.21, 55.38, 15.52, 8.45. \(^{31}\)P NMR (121.5 MHz, CDCl\(_3\), 25 °C): \(\delta\) 17.80. FT-IR (KBr, cm\(^{-1}\)): 3060 (\(\nu_{\text{C-H}}\), aromatic), 2932 (\(\nu_{\text{C-H}}\), aromatic), 2873 (\(\nu_{\text{C-H}}\), aromatic), 2112 (\(\nu_{\text{C=C}}\)), 1600 (\(\nu_{\text{C=C}}\), aromatic), 1570 (\(\nu_{\text{C=C}}\), aromatic).

\[
\begin{align*}
\text{PEt}_3 & \quad \text{Pd-Cl} \\
\text{PEt}_3 & \quad \text{PEt}_3
\end{align*}
\]

1c: \(^1H\) NMR (600 MHz, CDCl\(_3\), 25 °C): \(\delta\) 7.27–7.25 (m, 2H, aromatic), 7.24–7.21 (m, 2H, aromatic), 7.16–7.14 (m, 1H, aromatic), 2.00–1.95 (m, 12H, PCH\(_2\)CH\(_3\)), 1.23–1.18 (m, 18H, PCH\(_2\)CH\(_3\)). \(^{13}\)C NMR (150 MHz, CDCl\(_3\), 25 °C): \(\delta\) 130.79, 128.18, 127.95, 125.73, 106.63, 95.16, 15.54, 8.47. \(^{31}\)P NMR (121.5 MHz, CDCl\(_3\), 25 °C): \(\delta\) 17.95. FT-IR (KBr, cm\(^{-1}\)): 2959 (\(\nu_{\text{C-H}}\), aromatic), 2933 (\(\nu_{\text{C-H}}\), aromatic), 2873 (\(\nu_{\text{C-H}}\), aromatic), 2113 (\(\nu_{\text{C=C}}\)), 1750 (\(\nu_{\text{C=C}}\), aromatic), 1650 (\(\nu_{\text{C=C}}\), aromatic).

\[
\begin{align*}
\text{H}_3\text{CO} & \quad \equiv 
\text{Pd-Cl} \\
\text{PEt}_3 & \quad \text{PEt}_3
\end{align*}
\]

1d: M.P.: 49.6–50.3 °C. \(^1H\) NMR (400 MHz, CDCl\(_3\), 25 °C): \(\delta\) 7.90 (d, \(J = 8.4\) Hz, 2H, aromatic), 7.28 (d, \(J = 8.4\) Hz, 2H, aromatic), 3.89 (s, 3H, COOCH\(_3\)), 1.99–1.96 (m, 12H, PCH\(_2\)CH\(_3\)), 1.25–1.17 (m,
18H, PCH₂CH₃). ¹³C NMR (150 MHz, CDCl₃, 25 °C): δ 166.97, 132.60, 130.49, 129.45, 126.83, 106.66, 101.73, 52.07, 15.40, 8.38. ³¹P NMR (121.5 MHz, CDCl₃, 25 °C): δ 18.30. FT-IR (KBr, cm⁻¹): 2970 (νᵥC−H, aromatic), 2930 (νᵥC−H, aromatic), 2870 (νᵥC−H, aromatic), 2110 (νᵥC≡C), 1720 (νᵥC=O). HRMS m/z calcd for C₂₂H₃₇ClO₂P₂Pd [M⁺]: 536.0992; Found: C₂₂H₃₇ClO₂P₂Pd, 536.0990. Anal. Calcd (%) for C₂₂H₃₇ClO₂P₂Pd (536.10): C, 49.17; H, 6.94; Found: C, 49.00; H, 7.19.

**Typical Polymerization Procedure of 1a–d with 2a (poly-a2a₁₀₀):** A 10 mL oven-dried flask was charged with monomer 2a (50.0 mg, 0.17 mmol), THF (0.87 mL) and a stir bar. To this stirring solution was added a solution of 1a in THF (0.017 M, 0.10 mL) via a microsyringe at ambient temperature. The concentrations of monomer 2a and initiator 1a were 0.20 and 0.002 M, respectively ([2a]₀/[1a]₀ = 100). The reaction flask was then immersed into an oil bath at 55 °C and stirred for 10 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 to give poly-a2a₁₀₀ (45.0 mg, 91% yield). SEC: Mₙ = 3.1 × 10⁴, Mₘ₀/Mₙ = 1.10. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 7.48–7.24 (br, aromatic), 4.58–3.42 (br, OCH₂), 1.75–0.73 (br, CH₂ and CH₃). ¹³C NMR (150 MHz, CDCl₃, 25 °C): δ 165.11, 162.70, 150.50, 129.79, 127.38, 117.19, 65.03, 32.03, 29.74, 29.58, 29.46, 28.76, 26.13, 22.78, 14.19. FT-IR (KBr, cm⁻¹): 2952 (νᵥC−H, aromatic), 2919 (νᵥC−H, aromatic), 2852 (νᵥC−H, aromatic), 2190 (νᵥC≡C), 1720 (νᵥC=O), 1599 (νᵥC=N).

**Typical Procedure Used to Grow Poly(phenyl isocyanide)s of Various Molecular Weights from Palladium Complex 1a–d.** Various amounts of palladium complex 1a in THF ([1a]₀ = 0.002 M) were added via a microsyringe to a series solutions of isocyanide monomer 2a (50.0 mg, 0.17mmol) in THF. The concentration of 2a was 0.20 M. The initial feed ratios of 2a to 1a were 25, 40, 55, 70, 85, and 100,
respectively. Each of the reaction mixtures were then stirred for 10 h at 55 °C and quenched by the addition of a large amount of methanol, collected by centrifugation, washed with methanol, and dried under vacuum to afford the expected polymers. The $M_n$ and $M_w/M_n$ of these polymers were characterized by SEC (Fig. 1a in maintext).

**Typical Kinetic Study of the Polymerization of 2a with 1a-d.** A mixture of 2a (100.0 mg, 0.35 mmol) and a standard polystyrene ($M_n = 2630$, 50.0 mg for 1a, and 1c, 40.0 mg for 1b, and 1d) were placed in a dry ampule, and dry THF (1.36 mL) was added by a syringe. To this was added a solution of 1a in THF (15 $\mu$M, 0.39 mL) via a microsyringe at ambient temperature. The concentrations of 1a and 2a were 0.0033 and 0.2 M, respectively. The mixture was then heated to 55 °C ([2a]$_0$ = 0.2 M, [2a]$_0$/[1a]$_0$ = 60). The conversion of 2a was followed by measuring the SEC of the reaction mixture at appropriate time intervals. The peak area of the unreacted 2a relative to that of the internal standard (PSt) was used for the determination of the conversion of 2a on the basis of the linear calibration curve. The $M_n$ and $M_w/M_n$ were estimated by SEC and reported as equivalent to standard polystyrene.

**References**


Table S1. Polymerization Results of 2b–e with 1b as Initiator ([2]₀ = 0.2 M)ᵃ

<table>
<thead>
<tr>
<th>Run</th>
<th>Monomer</th>
<th>[2]₀/[1b]₀ᵇ</th>
<th>Solvent</th>
<th>T</th>
<th>Polymer</th>
<th>Mₙᶜ</th>
<th>Mₙ/Mₙᶜ</th>
<th>Yieldᵈ</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>2b</td>
<td>50</td>
<td>THF</td>
<td>55 °C</td>
<td>poly-b2b₅₀</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>2c</td>
<td>25</td>
<td>Toluene</td>
<td>90 °C</td>
<td>poly-b2c₂₅</td>
<td>5.6×10³</td>
<td>1.22</td>
<td>90%</td>
</tr>
<tr>
<td>3</td>
<td>2c</td>
<td>30</td>
<td>Toluene</td>
<td>90 °C</td>
<td>poly-b2c₃₀</td>
<td>6.8×10³</td>
<td>1.22</td>
<td>91%</td>
</tr>
<tr>
<td>4</td>
<td>2c</td>
<td>60</td>
<td>Toluene</td>
<td>90 °C</td>
<td>poly-b2c₆₀</td>
<td>1.4×10⁴</td>
<td>1.27</td>
<td>87%</td>
</tr>
<tr>
<td>5</td>
<td>2d</td>
<td>50</td>
<td>THF</td>
<td>55 °C</td>
<td>poly-b2d₅₀</td>
<td>1.7×10⁴</td>
<td>1.18</td>
<td>97%</td>
</tr>
<tr>
<td>6</td>
<td>2d</td>
<td>100</td>
<td>THF</td>
<td>55 °C</td>
<td>poly-b2d₁₀₀</td>
<td>3.4×10⁴</td>
<td>1.22</td>
<td>95%</td>
</tr>
<tr>
<td>7</td>
<td>2e</td>
<td>50</td>
<td>THF</td>
<td>55 °C</td>
<td>poly-b2e₅₀</td>
<td>1.3×10⁴</td>
<td>1.16</td>
<td>97%</td>
</tr>
<tr>
<td>8</td>
<td>2e</td>
<td>100</td>
<td>THF</td>
<td>55 °C</td>
<td>poly-b2e₁₀₀</td>
<td>2.7×10⁴</td>
<td>1.15</td>
<td>93%</td>
</tr>
</tbody>
</table>

ᵃThe polymers were synthesized according to Scheme 1 in main text.ᵇThe initial feed ratio of monomer to initiator. ᶜThe Mₙ and Mₙ/Mₙ were determined by SEC and reported as equivalent to standard polystyrene.ᵈIsolated yield.

Fig. S1 Single crystal structure of Pd(II) complex 1c. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1–C2, 1.210(5); C1–Pd, 1.947(4); Cl1–Pd, 2.3512(8); P1–Pd,
2.3136(10); P2–Pd, 2.3055(10); C1–Pd–P2, 90.58(12); C1–Pd–P2, 90.48(12); P2–Pd–P1, 176.92(5);
C1–Pd–Cl1, 177.71(17); P2–Pd–Cl1, 89.10(4); P1–Pd–Cl1, 89.95(4).

Fig. S2 FT-IR spectrum of poly-a2a_{100} measured at 25 °C using KBr pellets.
**Fig. S3** $^1$H NMR spectrum of poly-a2a$_{100}$ measured in CDCl$_3$ at 25 °C (400 MHz).

**Fig. S4** $^{13}$C NMR spectrum of poly-a2a$_{100}$ measured in CDCl$_3$ at 25 °C (150 MHz).
**Fig. S5** $^{31}$P NMR spectrum of poly-a2a$_{100}$ measured in CDCl$_3$ at 25 °C (121.5 MHz).

**Fig. S6** UV-vis spectrum of poly-a2a$_{100}$ measured in CHCl$_3$ at 25 °C.
**Fig. S7** SEC chromatograms of poly-\textbf{a2a}_{75}(t) and poly-\textbf{a2a}_{100}(t) prepared from 2a with 1a as initiator in toluene at 55°C.

**Fig. S8** SEC chromatograms of poly-\textbf{a2a}_{50}(c) and poly-\textbf{a2a}_{80}(c) prepared from 2a with 1a as initiator in CHCl$_3$ at 55 °C.
**Fig. S9** SEC chromatograms of poly-\( \text{a2a}_{50}(d) \) and poly-\( \text{a2a}_{80}(d) \) prepared from 2a with 1a as initiator in DMF at 55 °C.

**Fig. S10** SEC chromatograms of poly-\( \text{a2a}_{50}(a) \) and poly-\( \text{a2a}_{80}(h) \) prepared from 2a with 1a as initiator in acetone and hexane at 55 °C.
**Fig. S11** SEC chromatograms of poly-b2a<sub>m</sub> prepared from 2a with 1b as initiator in THF at 55 °C with different initial feed ratios.

**Fig. S12** Plot of $M_n$ and $M_w/M_n$ values of poly-b2a<sub>m</sub> as a function of the initial feed ratios of 2a to 1b. $M_n$ and $M_w/M_n$ were determined by SEC with polystyrene standard (SEC conditions: eluent = THF, temperature = 40 °C).
**Fig. S13** SEC chromatograms of poly-c2a_m prepared from 2a with 1c as initiator in THF at 55 °C with different initial feed ratios.

**Fig. S14** Plot of $M_n$ and $M_w/M_n$ values of poly-c2a_m as a function of the initial feed ratios of 2a to 1c. $M_n$ and $M_w/M_n$ were determined by SEC with polystyrene standard (SEC conditions: eluent = THF, temperature = 40 °C).
**Fig. S15** SEC chromatograms of poly-d2a\textsubscript{m} prepared from 2a with 1d as initiator in THF at 55 °C with different initial feed ratios.

**Fig. S16** Plot of $M_n$ and $M_w/M_n$ values of poly-d2a\textsubscript{m} as a function of the initial feed ratios of 2a to 1d. $M_n$ and $M_w/M_n$ were determined by SEC with polystyrene standard (SEC conditions: eluent = THF, temperature = 40 °C).
**Fig. S17** Time-dependent SEC chromatograms for 1b-initiated polymerization of 2a in THF at 55 °C with PST ($M_n = 2630, M_w/M_n = 1.06$) as internal standard ([2a]$_0$ = 0.2 M, [2a]$_0$/[1b]$_0$ = 60).

**Fig. S18** Plot of $M_n$ and $M_w/M_n$ values as a function of conversion of 2a with 1b as initiator in THF at 55 °C ([2a]$_0$ = 0.2 M, [2a]$_0$/[1b]$_0$ = 60).
**Fig. S19** Time-dependent SEC chromatograms for 1c-initiated polymerization of 2a in THF at 55 °C with PSt ($M_n = 2630$, $M_w/M_n = 1.06$) as internal standard ($[2a]_0 = 0.2$ M, $[2a]_0/[1c]_0 = 60$).

**Fig. S20** Plot of $M_n$ and $M_w/M_n$ values as a function of conversion of 2a with 1c as initiator in THF at 55 °C ($[2a]_0 = 0.2$ M, $[2a]_0/[1c]_0 = 60$).
Fig. S21 Time-dependent SEC chromatograms for 1d-initiated polymerization of 2a in THF at 55 °C with PSt ($M_n = 2630, \frac{M_w}{M_n} = 1.06$) as internal standard ([2a]₀ = 0.2 M, [2a]₀/[1d]₀ = 60).

Fig. S22 Plot of $M_n$ and $M_w/M_n$ values as a function of conversion of 2a with 1d as initiator in THF at 55 °C ([2a]₀ = 0.2 M, [2a]₀/[1d]₀ = 60).
Fig. S23 SEC chromatograms of poly-\(b_2c_{25}\), poly-\(b_2c_{30}\), and poly-\(b_2c_{60}\) prepared from \(2c\) with \(1b\) as initiator in toluene at 90 °C.

Fig. S24 SEC chromatograms of poly-\(b_2d_{50}\) and poly-\(b_2d_{100}\) prepared from \(2d\) with \(1b\) as initiator in THF at 55 °C.
Fig. S25 SEC chromatograms of poly-b2e$_{50}$ and poly-b2e$_{100}$ prepared from 2e with 1b as initiator in THF at 55 °C.

Fig. S26 CD and UV-vis spectra of poly-b2e$_{50}$ measured in THF at room temperature.
**Fig. S27** $^1$H NMR spectrum of 1a measured in CDCl$_3$ at 25 °C (400 MHz).

**Fig. S28** $^{13}$C NMR spectrum of 1a measured in CDCl$_3$ at 25 °C (100 MHz).
Fig. S29 $^{31}$P NMR spectrum of 1a measured in CDCl$_3$ at 25 °C (121.5 MHz).

Fig. S30 FT-IR spectrum of 1a measured at 25 °C using KBr pellets.
Fig. S31 $^1$H NMR spectrum of 1b measured in CDCl$_3$ at 25 °C (400 MHz).

Fig. S32 $^{13}$C NMR spectrum of 1b measured in CDCl$_3$ at 25 °C (100 MHz).
**Fig. S33** $^{31}$P NMR spectrum of 1b measured in CDCl$_3$ at 25 °C (121.5 MHz).

**Fig. S34** FT-IR spectrum of 1b measured at 25 °C using KBr pellets.
Fig. S35 $^1$H NMR spectrum of 1c measured in CDCl$_3$ at 25 °C (600 MHz).

Fig. S36 $^{13}$C NMR spectrum of 1c measured in CDCl$_3$ at 25 °C (150 MHz).
**Fig. S37** $^{31}$P NMR spectrum of $\textbf{1c}$ measured in CDCl$_3$ at 25 °C (121.5 MHz).

**Fig. S38** FT-IR spectrum of $\textbf{1c}$ measured at 25 °C using KBr pellets.
Fig. S39 $^1$H NMR spectrum of 1d measured in CDCl$_3$ at 25 °C (400 MHz).

Fig. S40 $^{13}$C NMR spectrum of 1d measured in CDCl$_3$ at 25 °C (150 MHz).
**Fig. S41** $^{31}$P NMR spectrum of 1b measured in CDCl$_3$ at 25 °C (121.5 MHz).

**Fig. S42** FT-IR spectrum of 1d measured at 25 °C using KBr pellets.
Fig. S43 $^1$H NMR spectrum of 2c measured in CDCl$_3$ at 25 °C (400 MHz).

Fig. S44 $^1$H NMR spectrum of poly-b2c$_{60}$ measured in CDCl$_3$ at 25 °C (600 MHz).
Fig. S45 FT-IR spectrum of poly-b2c60 measured at 25 °C using KBr pellets.

Fig. S46 UV-vis spectrum of poly-b2c60 measured in CHCl3 at 25 °C.
Fig. S47 $^{31}$P NMR spectrum of poly-b2c$_{60}$ measured in CDCl$_3$ at 25 °C (121.5 MHz).

Fig. S48 $^1$H NMR spectrum of poly-b2d$_{50}$ measured in CDCl$_3$ at 25 °C (600 MHz).
**Fig. S49** FT-IR spectrum of poly-b2d_{50} measured at 25 °C using KBr pellets.

**Fig. S50** UV-vis spectrum of poly-b2d_{50} measured in CHCl₃ at 25 °C.
Fig. S51 $^{31}$P NMR spectrum of poly-$b2d_{50}$ measured in CDCl$_3$ at 25 °C (121.5 MHz).

Fig. S52 $^1$H NMR spectrum of poly-$b2e_{50}$ measured in CDCl$_3$ at 25 °C (600 MHz).
**Fig. S53** FT-IR spectrum of poly-b2e$_{50}$ measured at 25 °C using KBr pellets.

**Fig. S54** UV-vis spectrum of poly-b2e$_{50}$ measured in CHCl$_3$ at 25 °C.
**Fig. S55** $^{31}$P NMR spectrum of poly-b$_2$e$_{50}$ measured in CDCl$_3$ at 25 °C (121.5 MHz).