

Supporting Information

Chain-End Functionalization of Living Helical Polyisocyanides Through Pd(II)-Mediated Sonogashira Coupling Reaction

Xun-Hui Xu, Wen-Bin Liu, Xue Song, Li Zhou, Na Liu, Yuan-Yuan Zhu and Zong-Quan Wu*

Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, and Anhui Key Laboratory of Advanced Catalytic Materials and Reaction Engineering, Hefei University of Technology, Hefei 230009, Anhui Province, China.

Table of Contents

General considerations	S3
Synthetic procedure	S4
Synthesis of alkyne-R_{2a}, poly-$3a_{45}$, poly-$3b_{400}$, poly-$3c_{400}$ and poly-$3d_{75}$	S4-S13
Figure S1. 1H NMR spectrum of poly- $1a_{150}$	S14
Figure S2. 1H NMR spectrum of poly- $1b_{150}$	S14
Figure S3-S4. SEC curves and FT-IR spectra of poly- $1a_{20}$ and poly- $1a_{20}(L_n)-R_{2a}$	S14
Figure S5-S7. SEC curves, ^{19}F NMR spectra and of FT-IR spectra poly- $1a_{20}$ and poly- $1a_{20}(L_1)-R_{2b}$	S15
Figure S8-S9. SEC curves of and FT-IR spectra of poly- $1a_{20}$ and poly- $1a_{20}(L_1)-R_{2c}$	S16
Figure S10. FT-IR spectra of poly- $1a_{150}$, poly- $3a_{45}$ and poly($1a_{150}-b-3a_{45}$)	S16
Figure S11-S19. SEC, 1H NMR, FT-IR spectra of homopolymers and block copolymers	S17-S21
Figure S20. UV-vis absorption spectra of homopolymers and block copolymers	S21
Figure S21. DSC and TGA curves of the homopolymers and block copolymers	S22
Figure S22. SEC curves of M -poly- $1b_{150}$, M -poly($1b_{150}-b-3c_{60}$), poly- $1b_{150}$ and poly($1b_{150}-b-3c_{60}$)	S22
Figure S23-S24. 1H NMR and FT-IR spectra of M -poly- $1b_{150}$, poly- $3c_{60}$, and M -poly($1a_{150}-b-3c_{60}$)	S23
Figure S25. CD curves of M -poly- $1b_{150}$, M -poly($1b_{150}-b-3c_{60}$), poly- $1b_{150}$ and poly($1b_{150}-b-3c_{60}$)	S24
Figure S26. DSC and TGA curves of poly- $1b_{150}$, poly- $3c_{60}$, and poly($1b_{150}-b-3c_{60}$)	S24
Figure S27. AFM height images of poly($1a_{150}-b-3a_{45}$)	S24
Figure S28. SEC curves of poly- $1a_{150+150}$ is synthesized by one-pot method	S25
Figure S29. 1H NMR spectrum of poly- $1b_{20}-(TPY)$	S25
Figure S30. AFM phase image and of fluorescence spectra M -poly- $1b_{150+150}$	S25
Figure S31, S32. 1H NMR spectra of monomer $1a$ and monomer $1b$	S26
Figure S33, S34. 1H NMR spectra of Pd(II) initiator and L_1^s ligand	S27
Figure S35, S36. 1H NMR spectra of alkynyl- R_{2a} and alkynyl-ATRP initiator	S28
Figure S37, S38. 1H NMR spectra of product 4 and alkynyl-TPY	S29
References	S30

Experimental Procedures

General considerations. The nuclear magnetic resonance (NMR) spectra were recorded using a Bruker 600 MHz $\{^1\text{H}\}$ spectrometer operated in the Fourier Transform mode. Chemical shifts are reported in delta (δ) units and expressed in parts per million (ppm) downfield from tetramethylsilane using the residual proton solvent as an internal standard. Size exclusion chromatography (SEC) was performed on Waters 1515 pump and Waters 2414 differential refractive index (RI) detector. The eluent was tetrahydrofuran (THF) containing 0.1 wt% tetra-*n*-butylammonium bromide (TBAB) 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. Circular dichroism (CD) spectra were performed on JASCO J1500 using 10.0 mm quartz cells. Absorption spectra were recorded on UNIC 4802 UV/vis double beam spectrophotometer in a 1.0 cm quartz cell at 25 °C. The optical rotations were measured in CHCl_3 at room temperature using a 10.0 cm quartz cell on a WZZ-2S polarimeter. Atomic force microscope (AFM) was performed on a Cypher S microscope (Oxford Instruments, Asylum Research). Differential scanning calorimetric (DSC) measurements were carried on a Mettler-Toledo DSC821e instrument. Samples were first heated from 0 °C to 140 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere at a heating rate of 10 °C/min from 30 °C to 800 °C using a Netzsch TG 209 F3 instrument. All solvents and chemicals were purchased from Sinopharm, and Aladdin Co. Ltd., and were purified by the standard procedures before used. Tetrahydrofuran (THF) for polymerizations was further dried over sodium benzophenone ketyl, distilled onto lithium aluminum hydride under nitrogen, and distilled under high vacuum just before use. Monomer **1a**, **1b**, Pd(II)-catalyst and Wei-Phos (**L1**) were prepared according to the literatures and the structures were confirmed by ^1H NMR.¹⁻³

AFM Measurements.⁴ Both topographic and phase images of assemblies of different nanostructures were obtained in Tapping Mode using rectangular silicon cantilever with a spring constant of 26 N m⁻¹, a

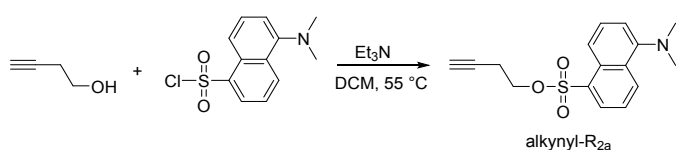
resonance frequency lying in the 62-120 kHz range and a radius of curvature of less than 10 nm. Samples were prepared by solvent casting at ambient temperature from 0.2 mg/mL with mixed solvents in different proportions. A drop (20 μ L) of suspension was deposited onto clean silicon wafer and after 2 minutes the excess of solution was removed with blotting paper. Subsequently, the substrate was dried under nitrogen flow during several minutes. Measurements of length and width were taken using the section Particle Analysis tool provided with the AFM software (Asylum Research).

Stock solutions of *M*-poly-**1b**₁₅₀ and *M*-poly-**1b**₁₅₀₊₁₅₀ in dry THF (0.02 mg/mL) were prepared. Samples for AFM measurements were prepared by casting 20 μ L aliquots of the stock solutions of the S6 polymers on freshly cleaved highly oriented pyrolytic graphite (HOPG) substrate. The samples on HOPG were annealed under THF vapor atmospheres at room temperature for 12 h, and then dried under vacuum for 2 h. The organic solvent vapor was prepared by putting 1 mL of THF into a 2 mL flask that was inside a 50 mL flask, and the HOPG substrates were then placed in the 50 mL flask.

Emission analyses:⁵ These experiments were carried out followed the reported literatures with modifications. Taking the photoluminescence (PL) spectrum in solution states for the poly-**1a**₂₀(**L**_n)-**R**_{2a} as an example. Put the polymer poly-**1a**₂₀(**L**_n)-**R**_{2a} solution (*c* = 0.005 mg/mL) into a fluorescent cuvette (optical path length = 1.0 cm) with a volume of about 3 mL at 25 °C, and the cuvette was installed into Hitachi F-4600 fluorescence. The fluorescence spectrum of the solution was monitored at 25 °C in the range of emission wavelength between 400 and 650 nm, excited by UV light at 369 nm.

Synthesis of alkynyl-**R**_{2a}, poly-**3a**₄₅, poly-**3b**₄₀₀, poly-**3c**₄₀₀ and poly-**3d**₇₅.

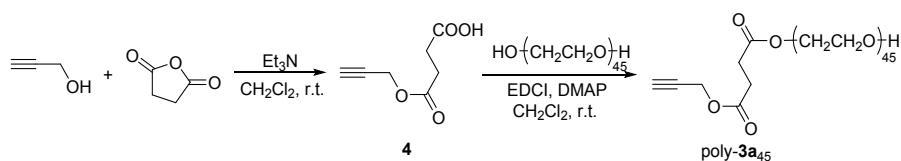
Scheme S1. Synthesis of alkynyl-**R**_{2a}



Alkynyl-R_{2a} was synthesized according the literature with slight modification.⁶ Butynol (31.0 mg, 0.44 mmol) and dansyl chloride (100 mg, 0.37 mmol) were added in a dried 10 mL oven-dried flask. Et₃N (2.0 mL) was added under a nitrogen atmosphere and 5.0 mL of THF was added to dissolve the raw materials. Then the reaction flask was heated to 60 °C for overnight. After the dansyl chloride was consumed completely, the solvent was removed in vacuo. The residue was purified by silica gel chromatography using petroleum ether/EtOAc (v/v = 8: 1) as eluent to afford the desired product as yellow oil (100.8 mg, 90% yield). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 8.52–8.51 (d, *J* = 6 Hz, H, aromatic), 8.26–8.25 (d, *J* = 6 Hz, H, aromatic), 8.19–8.18 (d, *J* = 6 Hz, H, aromatic), 7.59–7.56 (t, H, aromatic), 7.46– 7.44 (t, H, aromatic), 7.18–7.17 (d, *J* = 6 Hz, H, aromatic), 4.07 (t, 2H, CH₂), 2.86 (t, 6H, N(CH₃)₂), 2.52 (t, 2H, CH₂), 1.82 (t, H, alkyne).

Typical polymerization procedure of polyisocyanide.¹ All polyisocyanide polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under nitrogen atmosphere. Taking the polymerization of poly-**1a**₁₅₀ as an example. A 10 mL oven-dried flask was then evacuated on a vacuum line and flushed with dry nitrogen. After the evacuation-flush procedure had been repeated three times, a solution of the Pd(II) initiator (0.013 M in dry THF, 89 μL), a solution of the monomer **1a** (50.0 mg in 0.67 mL dry THF) was added via a syringe at room temperature. The concentrations of monomer **1a** and the Pd(II) initiator were 0.20 and 0.0013 M, respectively ($[\mathbf{1a}]_0/[\text{Pd}]_0 = 150$). The reaction flask was then immersed into a pre-heated oil bath at 55 °C and stirred for 12 h. After cooling to room temperature, the polymerization solution was precipitated into a large amount of methanol, the precipitated solid was isolated via centrifugation and dried under vacuum to afford poly-**1a**₁₅₀ as a yellow solid (45.1 mg, 91% yield). SEC (with reference to polystyrene standards): $M_n = 14.8$ kDa, $M_w/M_n = 1.21$. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 8.60–7.64 (brs, H, NH), 7.22–5.40 (brs, 4H, ArH), 4.86–3.64 (brs, 2H, CO₂CH₂), 1.86–1.20 (brs, 22H, CH₂ and CH₃), 0.83 (br, 3H, CH₃). ³¹P NMR (121.5 MHz, CDCl₃, 25 °C): δ (ppm) 13.56. FT-IR (KBr, cm⁻¹): 2960 ($\nu_{\text{C-H}}$), 2930 ($\nu_{\text{C-H}}$), 2854 ($\nu_{\text{C-H}}$), 1743 ($\nu_{\text{C=O}}$), 1635 ($\nu_{\text{C=O}}$), 1602 ($\nu_{\text{C=N}}$).

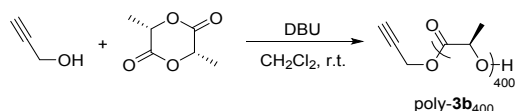
Scheme S2. Synthesis of poly-**3a**₄₅



Poly-**3a**₄₅ was synthesized according to the literature with slight modification.⁷ A mixture of succinic anhydride (6.2 g, 62 mmol, 1.2 eq), propargyl alcohol (3.0 mL, 51 mmol, 1.0 eq) and triethylamine (8.1 mL, 56 mmol, 1.1 eq) were stirred overnight in anhydrous CH₂Cl₂ (100 mL). The reaction solution was stirred at room temperature until the propargyl alcohol was completely consumed. The reaction mixture was quenched with 2 M HCl (50 mL). The aqueous layer was separated and extracted with CH₂Cl₂ (30 mL × 3). The organic phases were combined and washed with DI water (50 mL × 3) and brine (50 mL × 3) before drying with MgSO₄ and concentrated with reduced pressure. The crude was purified by silica gel chromatography with EtOAc and hexane (v/v = 1: 1) to yield the product 4-oxo-4-(prop-2-yn-1-yloxy)butanoic acid (**4**)(6.0 g, 75 % yield).

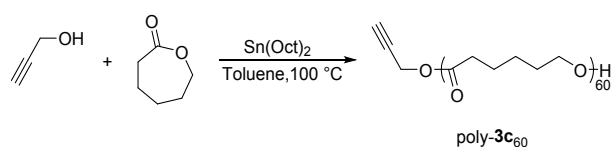
4-Dimethylaminopyridine (DMAP) (25.4 mg, 0.2 mmol, 0.8 eq) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) (60.1 mg, 0.3 mmol, 1.2 mmol) were added to a solution of **4** (54.6 mg, 0.35 mmol, 1.4 eq) in dry CH₂Cl₂ (150 mL). After the reaction mixture was stirred at 0 °C for 30 min under an atmosphere of argon, hydroxyl-PEG₂₀₀₀ (5.00 g, 0.25 mmol, 1 eq) was added to the mixture. The dispersion was stirred at room temperature for 12 h. After the reaction was completed, the residual solvent was removed by evaporation. After washing by ether, the product was recrystallized from frozen isopropanol as white crystals (3.61 g, 70% yield). SEC (with reference to polystyrene standards): $M_n = 2.0$ kDa, $M_w/M_n = 1.05$. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 3.63 (m, CH₂CH₂O), 3.12 (s, 2H, CH₂). 2.67(t, H, alkyne). FT-IR (KBr, cm⁻¹): 2878 (ν_{CH2}-), 1062 (ν_{C-O-C}-).

Scheme S3. Synthesis of poly-**3b**₄₀₀



Poly-**3b**₄₀₀ was synthesized according to the literature with slight modification.⁸ A 10 mL oven-dried flask was charged with monomer **3b** (1.26 g, 8.8 mmol, 250 eq), propargyl alcohol (2.0 mg, 0.035 mmol, 1.0 eq), anhydrous CH₂Cl₂ (2.0 mL) and a stir bar. A solution of 1,8-diazabicycloundec-7-ene (DBU) in CH₂Cl₂ (0.035 M, 1.0 mL) was added via a microsyringe to this stirring solution at ambient temperature. ([**3b**]₀/[OH]₀ = 200). After stirring at room temperature for 12 h, the polymerization solution was precipitated into a large amount of methanol, the precipitated solid was isolated via centrifugation and dried under vacuum to afford poly-**3b**₄₀₀ as white solid (1.1 g, 87% yield). SEC (with reference to polystyrene standards): $M_n = 13.3$ kDa, $M_w/M_n = 1.20$. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 5.16 (m, CH), 1.58 (m, CH₃). FT-IR (KBr, cm⁻¹): 2991 (ν_{C-H}), 2940 (ν_{C-H}), 2877 (ν_{C-H}), 1760 ($\nu_{C=O}$).

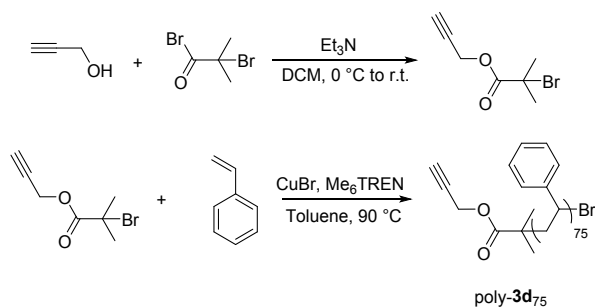
Scheme S4. Synthesis of poly-**3c**₆₀



Poly-**3c**₆₀ was synthesized according to the literature with slight modification.⁹ A 10 mL oven-dried flask was charged with monomer **4** (689.5 mg, 5.39 mmol, 70 eq), propargyl alcohol (4.3 mg, 0.077 mmol, 1 eq), anhydrous toluene (2.0 mL) and a stir bar. To this stirring solution was added a solution of Sn(Oct)₂ in toluene (0.035 M, 2.2 mL) via a microsyringe at ambient temperature, respectively ([**3c**]₀/[OH]₀ = 60). After stirred at 100 °C for 12 h, the polymerization solution was precipitated into a large amount of methanol, collected by centrifugation, and dried in vacuum at room temperature overnight (517.4 mg, 75% yield). SEC: $M_n = 7.2$ kDa, $M_w/M_n = 1.20$. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 4.05 (t, 2H, -CH₂O-

), 2.30 (t, 2H, CH₂), 1.65 (m, 4H, CH₂), 1.37 (m, 2H, CH₂). FT-IR (KBr, cm⁻¹): 2940 (ν_{CH₂-}), 1723 (ν_{C=O}), 1175 (ν_{C-O-C}).

Scheme S5. Synthesis of poly-**3d**₇₅



Poly-**3d**₇₅ was synthesized according the literature with slight modification.^[10] The propynol (1.0 g, 14.3 mmol), CH₂Cl₂ (50 mL) and Et₃N (6.3 mL) were added in a 100 mL reaction flask and the mixture stirred at 0 °C. 2-bromo-2-methylpropanoyl bromide (3.1 g, 13.5 mmol) was added to the solution gradually. Then, the reaction solution was warmed to room temperature and reacted for another 2 h. After the complete consuming of 2-bromo-2-methylpropanoyl bromide, the residual solvent was removed by evaporation. The crude product was purified by silica gel chromatography using petroleum ether/EtOAc (v/v = 4: 1) as eluent to afford the desired product as yellow oil (2.7 g, 90% yield). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 4.73 (d, 2H, CH₂), 2.50 (t, 1H, alkyne), 1.92 (m, 6H, CH₃).

A 10.0 mL oven-dried flask was then evacuated on a vacuum line and flushed with dry nitrogen. After the evacuation-flush procedure had been repeated three times, CuBr (10.2 mg, 0.071 mmol) was added. Then, a solution of ATRP initiator (18.5 mg, 0.09 mmol in dry toluene, 0.50 mL), a solution of styrene (711 mg in dry toluene, 6.0 mL) and ligand Me₆TREN (20.7 mg, 0.09 mmol in dry toluene, 0.50 mL) was added via a syringe at room temperature. The reaction flask was then immersed into a pre-heated oil bath at 90 °C and stirred for 5 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-**3d**₇₅ as a white solid (570 mg, 80% yield). SEC: $M_n = 7.8$ kDa, M_w/M_n

= 1.22. $^1\text{H NMR}$ (600 MHz, CDCl_3 , 25 °C): δ 7.23–6.26 (brs, 5H, aromatic), 2.48–0.68 (brs, 3H, CHCH_2). FT-IR (KBr, cm^{-1}): 3000 ($\nu_{\text{C-H}}$), 2923 ($\nu_{\text{C-H}_2}$), 1580 ($\nu_{\text{C=C}}$), 1372 ($\nu_{\text{C-H}}$).

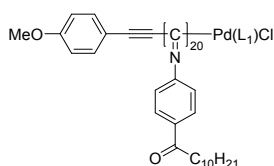
Small molecule for end-functionalization of polyisocyanide. Taking poly-**1a**₂₀-R_{2a} as an example. Poly-**1a**₂₀ was synthesized follow steps above mentioned, then the ligand exchange reaction was carried out according the literature.² Poly-**1a**₂₀ (50.2 mg, 0.017 mmol, 1.0 eq) and **L**₁ (49.1 mg, 0.085 mmol, 5.0 eq) were added to a 10 mL oven-dried flask, then aykne-R_{2a} (7.8 mg, 0.026 mmol, 1.5 eq), CuI (4.3 mg, 0.023 mmol, 0.87 eq.), THF (4.0 mL) and Et₃N (4.0 mL) under N₂ atmosphere. The reaction solution was stirred at 55 °C overnight. After the solution was cooled to room temperature, the solvent was removed under reduced pressure. The crude product was redissolved in a small amount of CH₂Cl₂, the solution was precipitated into a large amount of methanol and collected via filtration to obtain poly-**1a**₂₀-R_{2a} as light yellow solid (46.8 mg, 85% yield). SEC: $M_n = 2.4$ kDa, $M_w/M_n = 1.05$. $^1\text{H NMR}$ (600 MHz, CDCl_3 , 25 °C): δ 8.60–7.64 (brs, 1.6H, NH of poly-**1a**₂₀ segment, and Ar of R_{2a}), 7.22–5.40 (brs, 4.2H, Ar of poly-**1a**₂₀ segment, and Ar of R_{2a}), 4.86–3.64 (brs, 2.1H, CO₂CH₂ of poly-**1a**₂₀ segment, and CH₂ of R_{2a}), 2.90 (s, 0.6H, -N(CH₃)₂ of R_{2a}), 2.52 (t, 0.2H, CH₂ of R_{2a}), 1.86–0.63 (brs, 25H, CH₂ and CH₃ of poly-**1a**₂₀ segment). FT-IR (KBr, cm^{-1}): 2960 ($\nu_{\text{C-H}}$), 2930 ($\nu_{\text{C-H}}$), 2854 ($\nu_{\text{C-H}}$), 1743 ($\nu_{\text{C=O}}$), 1635 ($\nu_{\text{C=O}}$), 1602 ($\nu_{\text{C=N}}$) of poly-**1a**₂₀ segment. 1534 ($\nu_{\text{Ar-H}}$), 1148 ($\nu_{\text{O=S=O}}$) of R_{2a}.

Typical polymerization procedure of block copolymers. Taking poly-(**1a**₁₅₀-*b*-**3b**₄₀₀) as an example. Poly-**1a**₁₅₀ was synthesized follow steps above mentioned. Poly-**1a**₁₅₀ (230 mg, 1.0 eq) was added to a 10 mL oven-dried flask, then **L**₁ (14.5 mg, 0.025 mmol) and THF (2.0 mL) was added with a Pd (II) content of poly-**1a**₁₅₀. The solution was stirred 3 h at room temperature. After the ligand exchange was completed, poly-**3b**₄₀₀ (236 mg, 0.008 mmol, 1.5 eq) dissolved in THF (2.0 mL), Et₃N (4.0 mL) and CuI (4.3 mg, 0.023 mmol) were added under N₂ atmosphere, then the flask was immersed in an oil bath heated at 55 °C overnight. The solution was precipitated with a large amount of methanol, the yellow solid collected via filtration and washed with acetone three times repeatedly to remove the unreacted homopolymer poly-**1a**₁₅₀. Poly-(**1a**₁₅₀-*b*-**3b**₄₀₀) was obtained (320.5 mg, 83% yield). SEC: $M_n = 25.8$ kDa, $M_w/M_n = 1.15$. ^1H

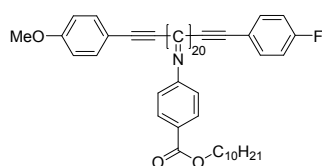
NMR (600MHz, CDCl₃, 25 °C): δ 7.69–6.86 (brs, 2H, Ar-*H* of poly-**1a**₁₅₀ segment), 6.04–5.36 (brs, 2H, Ar-*H* of poly-**1a**₁₅₀ segment), 5.16 (m, 2.8H, *CH* of poly-**3b**₄₀₀ segment), 4.57–3.44 (brs, 2H, CO₂CH₂ of poly-**1a**₁₅₀ segment), 1.83–0.69 (brs, 27.5H, CH₂ and CH₃ of poly-**1a**₁₅₀ segment, and CH₃ of poly-**3b**₄₀₀ segment). FT-IR (KBr, cm⁻¹): 2960 (ν_{C-H}), 2924 (ν_{C-H}), 2847 (ν_{C-H}), 1715 ($\nu_{C=O}$), 1602 ($\nu_{C=N}$) of poly-**1a**₁₅₀ segment. 2991 (ν_{C-H}), 1759 ($\nu_{C=O}$), 1099 (ν_{C-O-C}) of poly-**3b**₄₀₀ segment.

Polyisocyanides chain extension through end-functionalization: After the ligand exchange of poly-**1a**₁₅₀ (110.0 mg) according to the above steps, then 1,4-diethynyl-benzene (1.2 mg, 0.01 mmol), Et₃N (4 mL) and CuI (4.3 mg, 0.023 mmol) were added to a 10 mL oven-dried flask. After reacting at 55 °C overnight, it was precipitated in a large amount of methanol and washed with acetone three times. Follow the above steps to end-functionalize with alkynyl- polyisocyanide and poly-**1a**₁₅₀(**L**₁). After the reaction is complete, the molecular mass of poly-**1a**₁₅₀₊₁₅₀ was approximately twice than poly-**1a**₁₅₀ measured by SEC analysis. (182.7 mg, 83% yield). SEC: $M_n = 31.3$ kDa, $M_w/M_n = 1.22$.

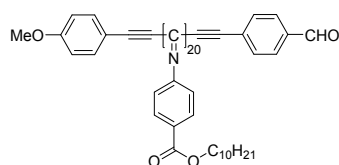
Use the method of end group functionalization to connect the polymer end with terpyridine (TPY) group *M*-poly-**1b**₁₅₀-TPY (410 mg). *M*-poly-**1b**₁₅₀-TPY, ZnClO₄·6H₂O (1.5 mg, 0.004 mmol) were added to a 10 mL oven-dried flask. Add 4 mL THF and 2 mL MeCN to the reaction flask under N₂ atmosphere, After reacting at 80 °C for 24h, samples were taken and analyzed by SEC to monitor the progress of the reaction. After adding 60.2 mg of *M*-poly-**1b**₁₅₀-TPY to the reaction flask, SEC analysis showed that almost all *M*-poly-**1b**₁₅₀-TPY was converted to *M*-poly-**1b**₁₅₀₊₁₅₀. The reaction solution was precipitated with methanol to obtain a polymer, and then washed with acetone three times repeatedly, and finally a yellow solid was obtained (372.8 mg, 79% yield). SEC: $M_n = 31.6$ kDa, $M_w/M_n = 1.23$.



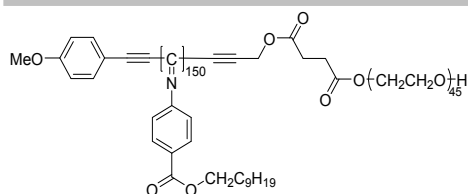
poly-1a₂₀(L₁): SEC: $M_n = 2.3$ kDa, $M_w/M_n = 1.08$. ¹H NMR (600MHz, CDCl₃, 25 °C): δ 8.26–7.21 (brs, 3.3H, Ar-*H* of poly-1a₂₀ segment and L₁), 6.14–5.45 (brs, 2H, Ar-*H* of poly-1a₂₀ segment and CH of L₁), 4.57–3.50 (brs, 2H, CO₂CH₂ of poly-1a₂₀ segment and -NH- of L₁), 2.53 (m, 0.04H, CH₂ of L₁), 2.05–0.73 (brs, 19.5H, CH₂ and CH₃ of poly-1a₂₀ segment and L₁). ³¹P NMR (121.5 MHz, CDCl₃, 25 °C): δ (ppm) 13.92, 13.91. FT-IR (KBr, cm⁻¹): 2961 (ν_{C-H}), 2933 (ν_{C-H}), 2852 (ν_{C-H}), 1741 ($\nu_{C=O}$), 1633 ($\nu_{C=O}$), 1608 ($\nu_{C=N}$) of poly-1a₂₀ segment.



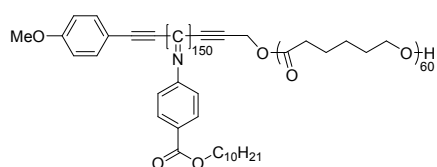
poly-1a₂₀-R_{2b}: SEC: $M_n = 2.4$ kDa, $M_w/M_n = 1.07$. ¹H NMR (600MHz, CDCl₃, 25 °C): δ 8.25–7.18 (brs, 2.2H, Ar-*H* of poly-1a₂₀ segment and Ar-*H* of R_{2b}), 7.00 (m, 0.2H, Ar-*H* of R_{2b}), 6.14–5.45 (brs, 2H, Ar-*H* of poly-1a₂₀ segment), 4.57–3.50 (brs, 2H, CO₂CH₂ of poly-1a₂₀ segment), 2.05–0.73 (brs, 19H, CH₂ and CH₃ of poly-1a₂₀ segment). FT-IR (KBr, cm⁻¹): 2960 (ν_{C-H}), 2930 (ν_{C-H}), 2854 (ν_{C-H}), 1743 ($\nu_{C=O}$), 1635 ($\nu_{C=O}$), 1602 ($\nu_{C=N}$) of poly-1a₂₀ segment. 2934(ν_{Ar-H}), 1050 (ν_{C-F}) of R_{2b}.



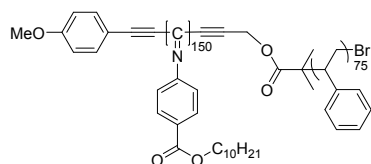
poly-1a₂₀-R_{2c}: SEC: $M_n = 2.5$ kDa, $M_w/M_n = 1.04$. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 9.76 (s, H, CHO of R_{2c}) 8.09–6.99 ((brs, 2.4H, Ar-*H* of poly-1a₂₀ segment and Ar-*H* of R_{2c}), 6.20–5.37 (brs, 2H, Ar-*H* of poly-1a₂₀ segment), 4.58–3.43 (brs, 2H, CO₂CH₂ of poly-1a₂₀ segment), 2.09–0.65 (brs, 19H, CH₂ and CH₃ of poly-1a₂₀ segment). FT-IR (KBr, cm⁻¹): 2960 (ν_{C-H}), 2930 (ν_{C-H}), 2854 (ν_{C-H}), 1743 ($\nu_{C=O}$), 1635 ($\nu_{C=O}$), 1602 ($\nu_{C=N}$) of poly-1a₂₀ segment. 2968(ν_{Ar-H}), 1693 (ν_{-CHO}) of R_{2c}.



poly(1a₁₅₀-b-3a₄₅): SEC: $M_n = 15.9$ kDa, $M_w/M_n = 1.18$. ^1H NMR (600MHz, CDCl_3 , 25 °C): δ 8.36–7.00 (brs, 2H, Ar-*H* of poly-1a₁₅₀ segment), 6.12–5.36 (brs, 2H, Ar-*H* of poly-1a₁₅₀ segment), 4.68 (d, 0.013H, CH_2 of poly-3a₄₅ segment), 4.58–3.67 (brs, 3.2H, CO_2CH_2 of poly-1a₁₅₀ segment, and $\text{CH}_2\text{CH}_2\text{O}$ of poly-3a₄₅ segment), 2.67 (s, 0.027H, CH_2 of poly-3a₄₅ segment), 2.08–0.57 (brs, 19H, CH_2 and CH_3 of poly-1a₁₅₀ segment). FT-IR (KBr, cm^{-1}): 2960 ($\nu_{\text{C-H}}$), 2930 ($\nu_{\text{C-H}}$), 1714 ($\nu_{\text{C=O}}$), 1602 ($\nu_{\text{C=N}}$) of poly-1a₁₅₀ segment. 2858 (ν_{CH_2}), 1087 ($\nu_{\text{C-O-C}}$) of poly-3a₄₅ segment.

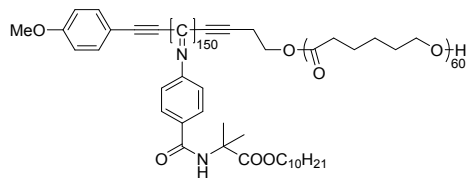


poly(1a₁₅₀-b-3c₆₀): SEC: $M_n = 19.3$ kDa, $M_w/M_n = 1.20$. ^1H NMR (600MHz, CDCl_3 , 25 °C): δ 8.30–6.98 (brs, 2H, Ar-*H* of poly-1a₁₅₀ segment), 6.15–5.24 (brs, 2H, Ar-*H* of poly-1a₁₅₀ segment), 4.62–3.43 (brs, 2.8H, CO_2CH_2 of poly-1a₁₅₀ segment and CH_2 of poly-3c₆₀ segment), 2.46–2.22 (t, 0.8H, CH_2 of poly-2c₆₀ segment), 2.06–0.56 (brs, 21.4H, CH_2CH_3 of poly-1a₁₅₀ segment and CH_2 of poly-3c₆₀ segment). FT-IR (KBr, cm^{-1}): 2917 ($\nu_{\text{C-H}}$), 2847 ($\nu_{\text{C-H}}$), 1718 ($\nu_{\text{C=O}}$), 1597 ($\nu_{\text{C=N}}$) of poly-1a₁₅₀ segment. 2961 (ν_{CH_2}), 1723 ($\nu_{\text{C=O}}$), 1154 ($\nu_{\text{C-O-C}}$) of poly-3c₆₀ segment.



poly(1a₁₅₀-b-3d₇₅): SEC: $M_n = 20.8$ kDa, $M_w/M_n = 1.18$. ^1H NMR (600MHz, CDCl_3 , 25 °C): δ 8.14–6.17 (brs, 4.5H, Ar-*H* of poly-1a₁₅₀ segment and Ar-*H* of poly-3d₇₅ segment), 6.11–5.20 (brs, 2H, Ar-*H* of poly-1a₁₅₀ segment), 4.71–3.36 (brs, 2H, CO_2CH_2 of poly-1a₁₅₀ segment), 2.30–0.48 (brs, 20.5H, CH_2 and CH_3 of poly-1a₁₅₀ segment, and CHCH_2 of poly-3d₇₅ segment). FT-IR (KBr, cm^{-1}): 2925 ($\nu_{\text{C-H}}$),

2854 ($\nu_{\text{C-H}}$), 1743 ($\nu_{\text{C=O}}$), 1602 ($\nu_{\text{C=N}}$) of poly-**1a**₁₅₀ segment. 1580 ($\nu_{\text{C=C}}$), 1372 ($\nu_{\text{C-H}}$), 1007 ($\nu_{\text{=CH}}$) of poly-**3d**₇₅ segment



poly(1b₁₅₀-b-3c₆₀): SEC: $M_n = 23.3$ kDa, $M_w/M_n = 1.45$. ^1H NMR (600MHz, CDCl_3 , 25 °C): δ 8.60–7.64 (brs, H, NH of poly-**1b**₁₅₀ segment), 7.22–5.40 (brs, 4H, Ar of poly-**1b**₁₅₀ segment), 4.86–3.30 (brs, 2.5H, CO_2CH_2 of poly-**1b**₁₅₀ segment, and CH_2 of poly-**3c**₆₀ segment), 2.43–2.19 (t, 0.5H, CH_2 of poly-**3c**₆₀ segment), 1.95–0.5 (brs, 26.5H, CH_2CH_3 of poly-**1b**₁₅₀ segment, and CH_2 of poly-**2c**₆₀ segment). FT-IR (KBr, cm^{-1}): 2960 ($\nu_{\text{C-H}}$), 2930 ($\nu_{\text{C-H}}$), 2854 ($\nu_{\text{C-H}}$), 1743 ($\nu_{\text{C=O}}$), 1635 ($\nu_{\text{C=O}}$), 1602 ($\nu_{\text{C=N}}$) of poly-**1b**₁₅₀ segment. 2940 (ν_{CH_2}), 1723 ($\nu_{\text{C=O}}$), 1175 ($\nu_{\text{C-O-C}}$) of poly-**3c**₆₀ segment.

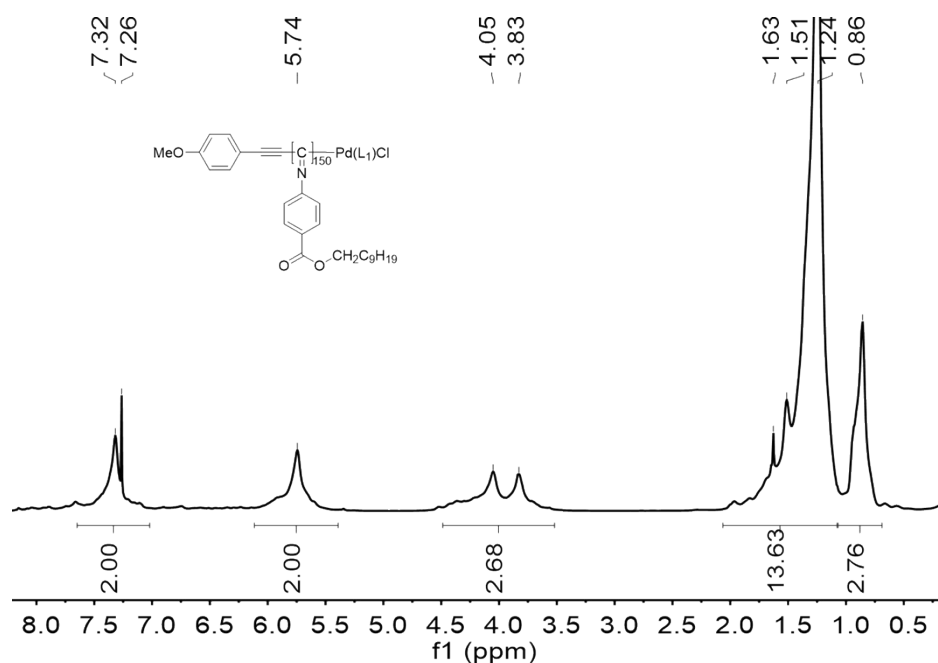


Figure S1. ^1H NMR (600 MHz) spectrum of poly-**1a**₁₅₀ measured in CDCl_3 at 25 °C.

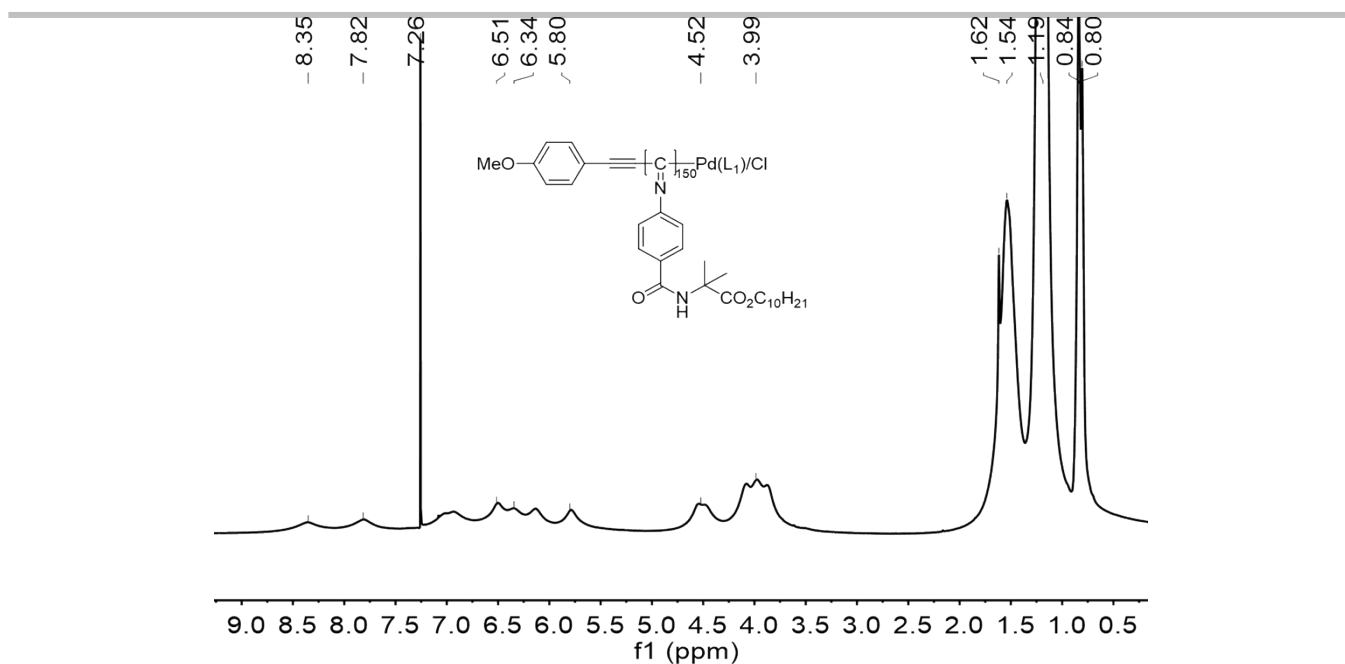


Figure S2. ^1H NMR (600 MHz) spectrum of poly-**1b**₁₅₀ measured in CDCl_3 at 25 °C.

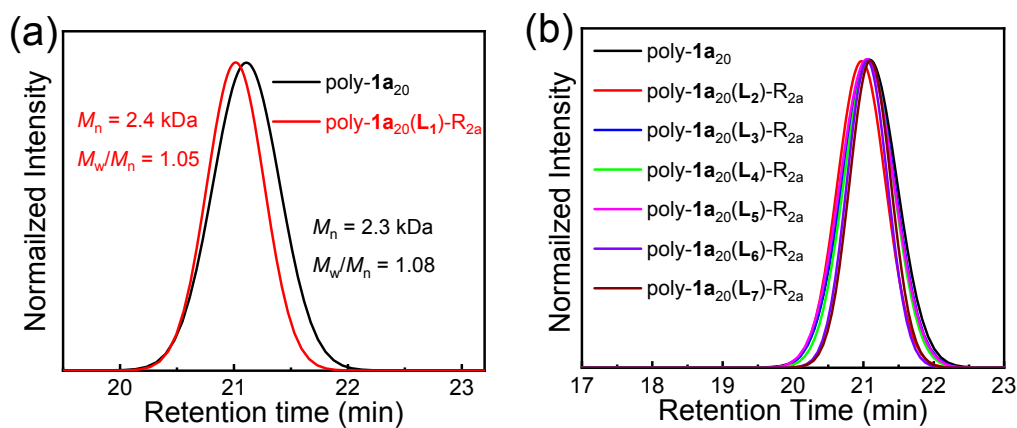


Figure S3. SEC curves of poly-**1a**₂₀ and poly-**1a**₂₀(**L**₁)-**R**_{2a} (a), poly-**1a**₂₀ and poly-**1a**₂₀(**L**_{*n*})-**R**_{2a} (b).

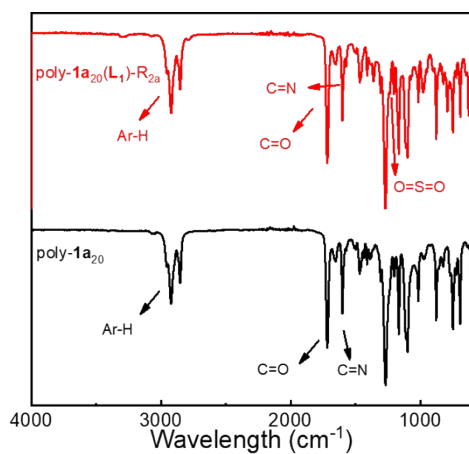


Figure S4. FT-IR spectra of poly-**1a**₂₀ and poly-**1a**₂₀(**L**₁)-**R**_{2a} measured at 25 °C using KBr pellets.

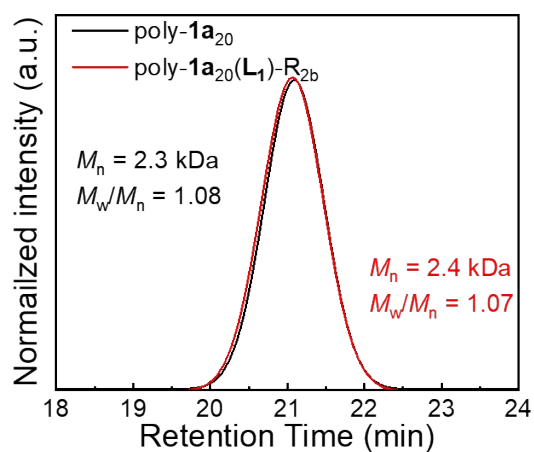


Figure S5. SEC curves of poly-**1a**₂₀ and poly-**1a**₂₀(**L**₁)-**R**_{2b}.

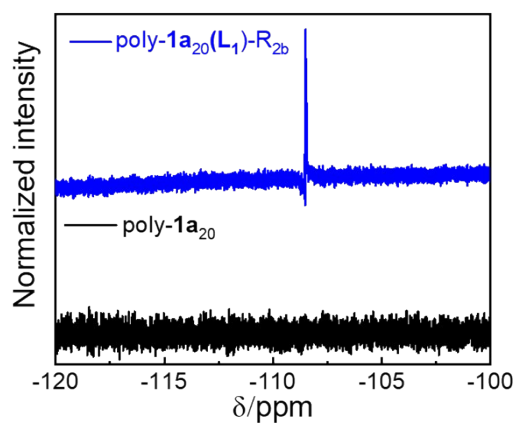


Figure S6. ¹⁹F NMR (564 MHz) spectra of poly-**1a**₂₀ and poly-**1a**₂₀(**L**₁)-**R**_{2b} measured in CDCl₃ at 25 °C.

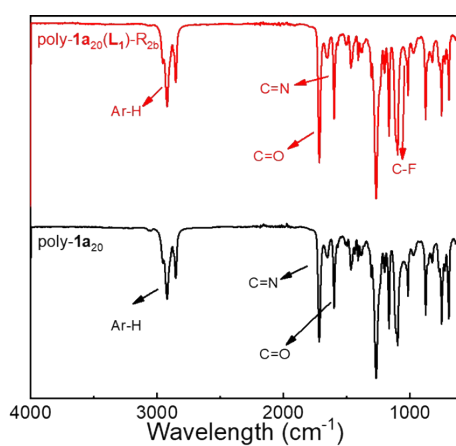


Figure S7. FT-IR spectra of poly-**1a**₂₀ and poly-**1a**₂₀(**L**₁)-**R**_{2b} measured at 25 °C using KBr pellets.

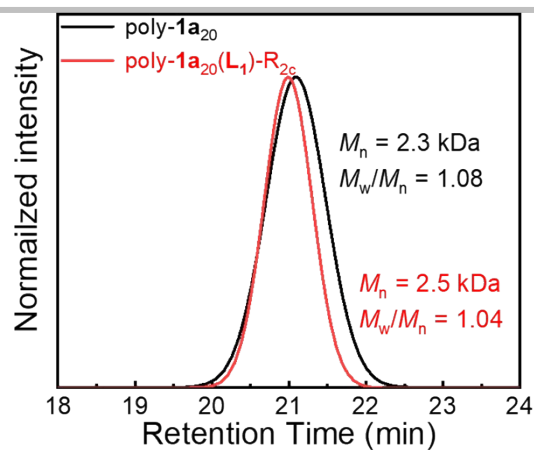


Figure S8. SEC curves of poly-**1a**₂₀ and poly-**1a**₂₀(L₁)-R_{2c}.

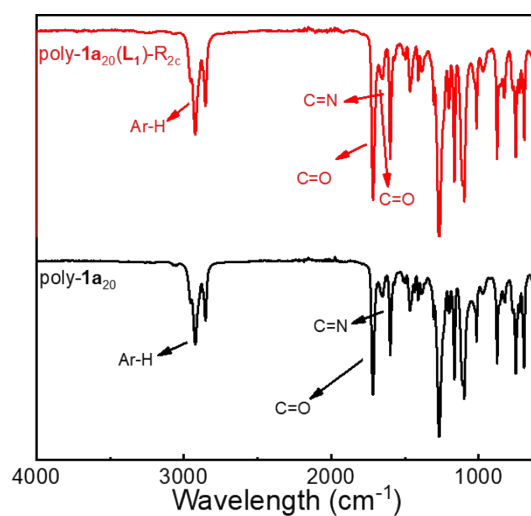


Figure S9. FT-IR spectra of poly-**1a**₂₀(L₁) and poly-**1a**₂₀(L₁)-R_{2c} measured at 25 °C using KBr pellets.

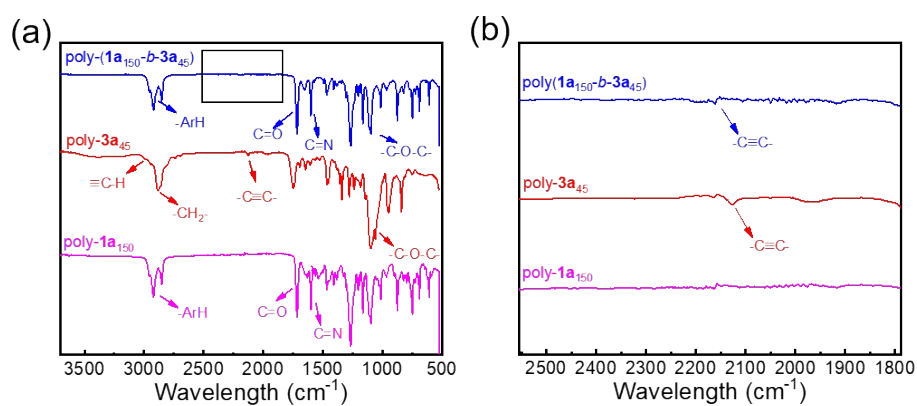


Figure S10 FT-IR spectrum of poly-**1a**₁₅₀, poly-**3a**₄₅ and poly(**1a**₁₅₀-*b*-**3a**₄₅) measured at 25 °C using KBr pellets.

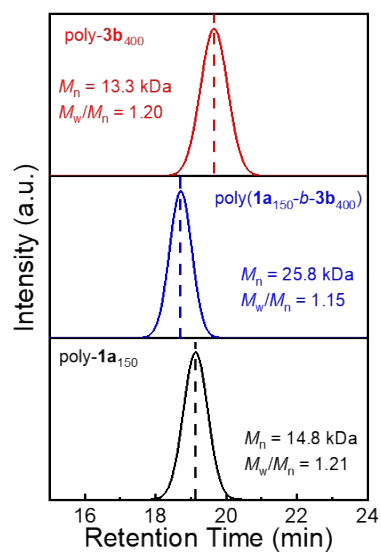


Figure S11. SEC curves of poly-1a₁₅₀, poly-3b₄₀₀ and poly(1a₁₅₀-b-3b₄₀₀).

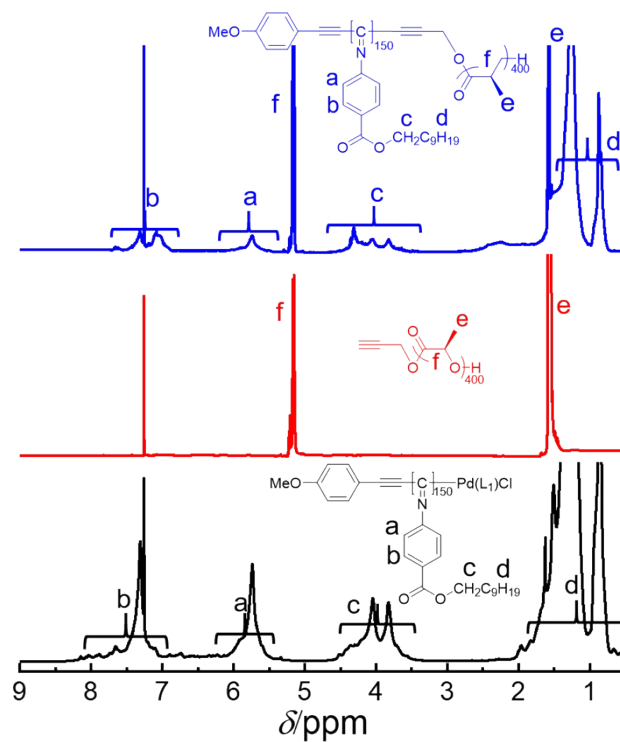


Figure S12. ¹H NMR spectra (600 MHz) of poly-1a₁₅₀, poly-3b₄₀₀, and poly(1a₁₅₀-b-3b₄₀₀) in CDCl₃ at 25 °C.

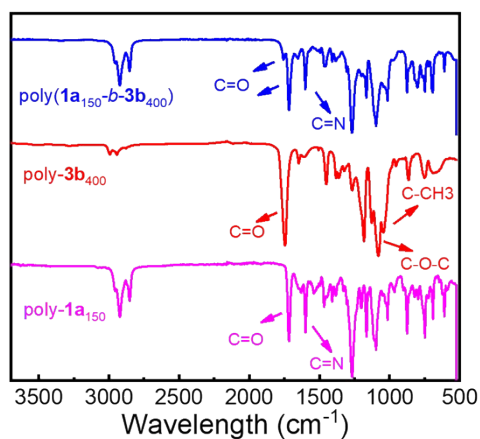


Figure S13. FT-IR spectra of poly-**1a**₁₅₀, poly-**3b**₄₀₀, and poly(**1a**₁₅₀-*b*-**3b**₄₀₀) measured at 25 °C using KBr pellets.

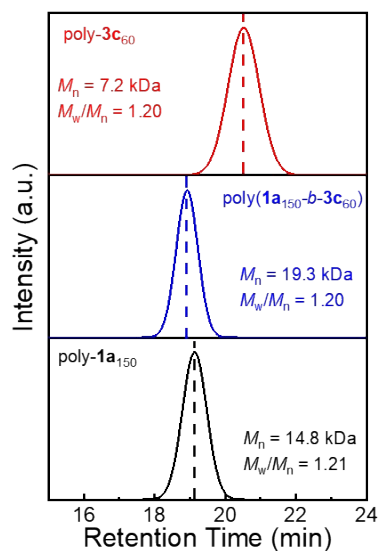


Figure S14. SEC curves of poly-**1a**₁₅₀, poly-**3c**₆₀, and poly(**1a**₁₅₀-*b*-**3c**₆₀).

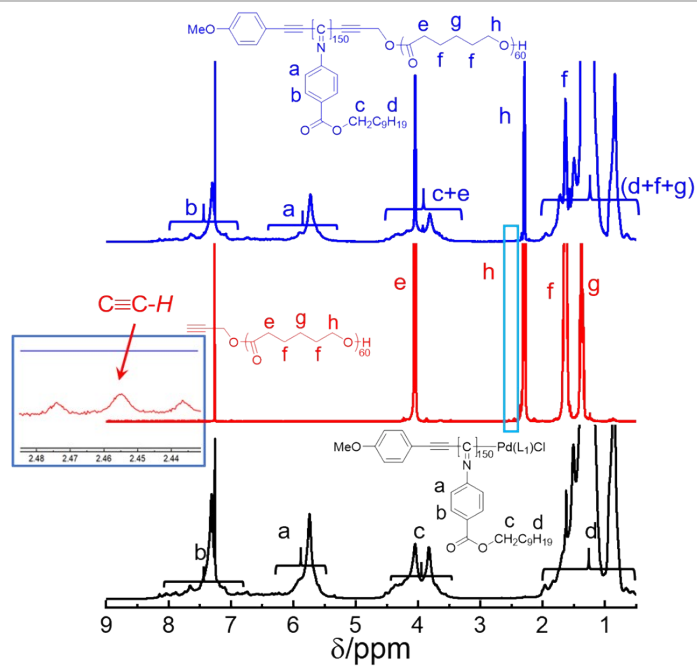


Figure S15. ^1H NMR spectra (600 MHz) of poly-**1a**₁₅₀, poly-**3c**₆₀, and poly(**1a**₁₅₀-**b-3c**₆₀) in CDCl_3 at 25 °C.

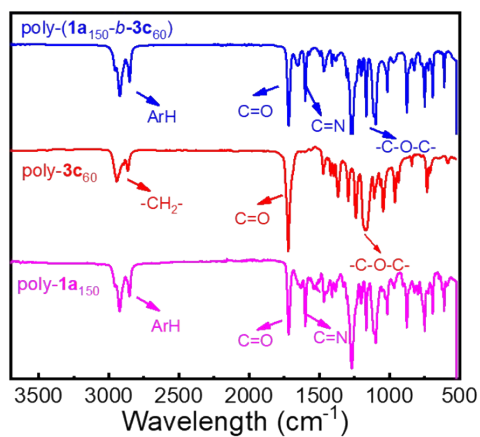


Figure S16. FT-IR spectra of poly-**1a**₁₅₀, poly-**3c**₆₀, and poly(**1a**₁₅₀-**b-3c**₆₀) measured at 25 °C using KBr pellets.

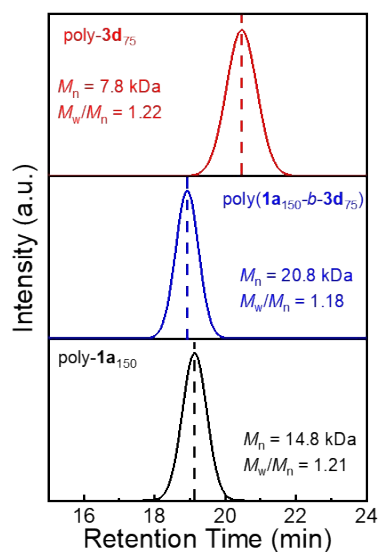


Figure S17. SEC curves of poly-**1a**₁₅₀, poly-**3d**₇₅, and poly(**1a**₁₅₀-**b-3d**₇₅).

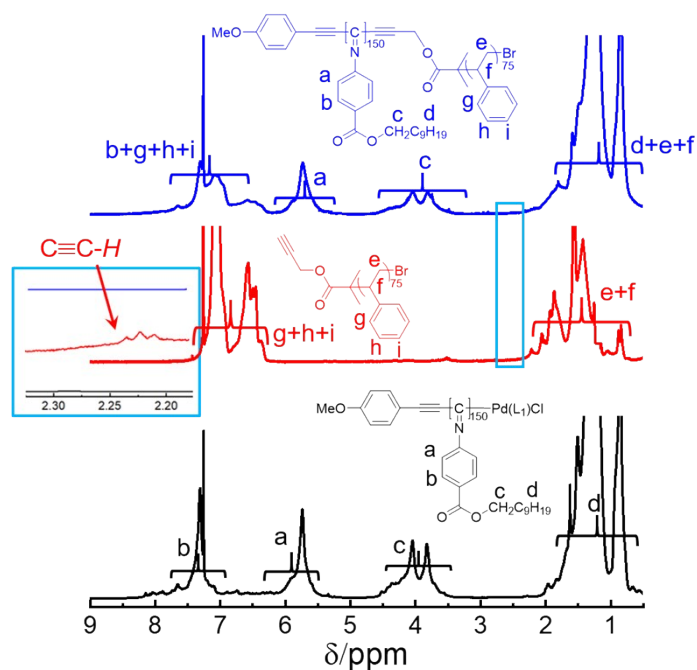


Figure S18. ¹H NMR spectra (600 MHz) of poly-**1a**₁₅₀, poly-**3d**₇₅, and poly(**1a**₁₅₀-**b-3d**₇₅) in CDCl₃ at 25 °C.

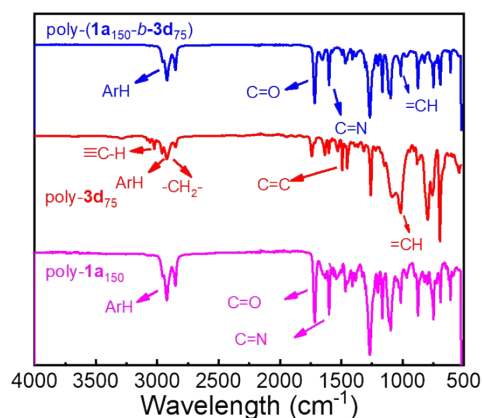


Figure S19. FT-IR spectra of poly-**1a**₁₅₀, poly-**3d**₇₅, and poly(**1a**₁₅₀-*b*-**3d**₇₅) measured at 25 °C using KBr pellets.

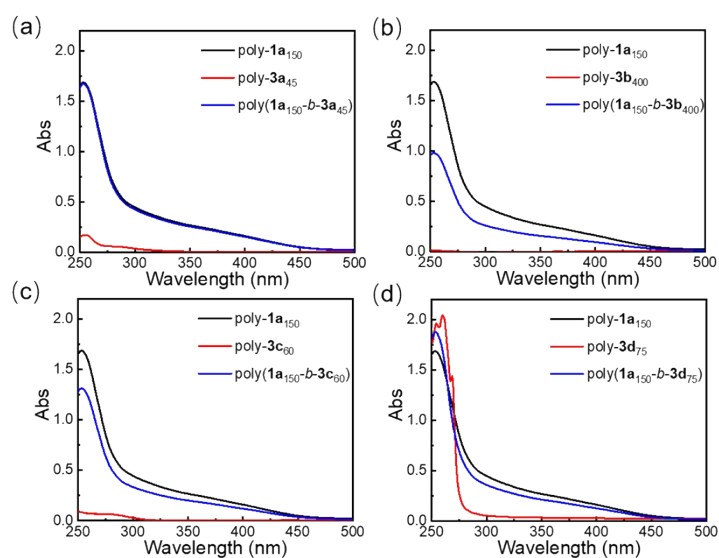


Figure S20. UV-vis absorption spectra of homopolymers and block copolymers measured in THF at 25 °C ($c = 0.01$ mg/mL).

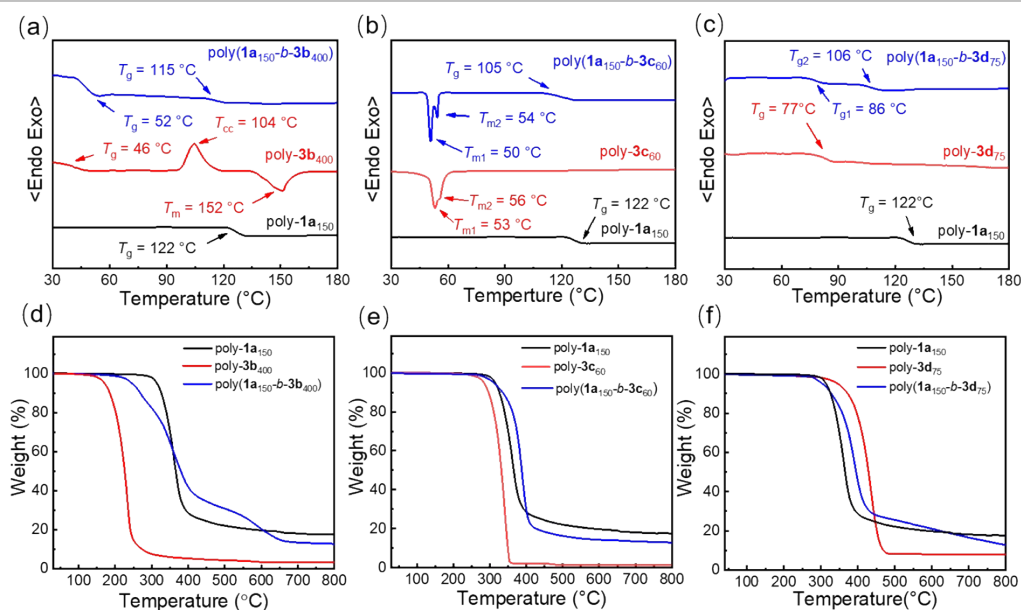


Figure S21. (a-c) DSC curves of the homopolymers and block copolymers. (d-f) TGA curves of the homopolymers and block copolymers.

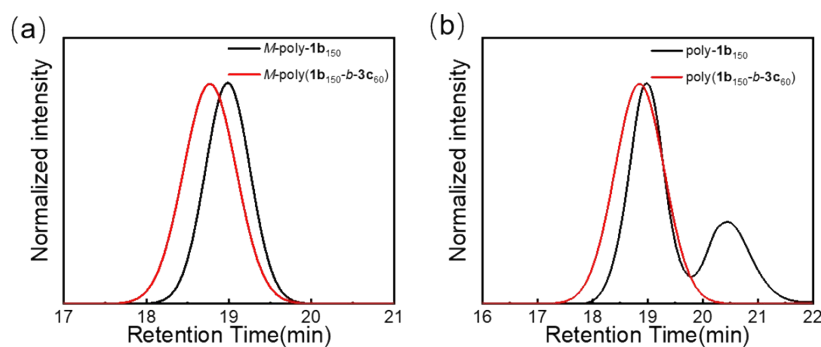


Figure S22. (a) SEC curves of *M*-poly-1b₁₅₀ and *M*-poly(1b₁₅₀-b-3c₆₀). (b) SEC curves of poly-1b₁₅₀ and poly(1b₁₅₀-b-3c₆₀).

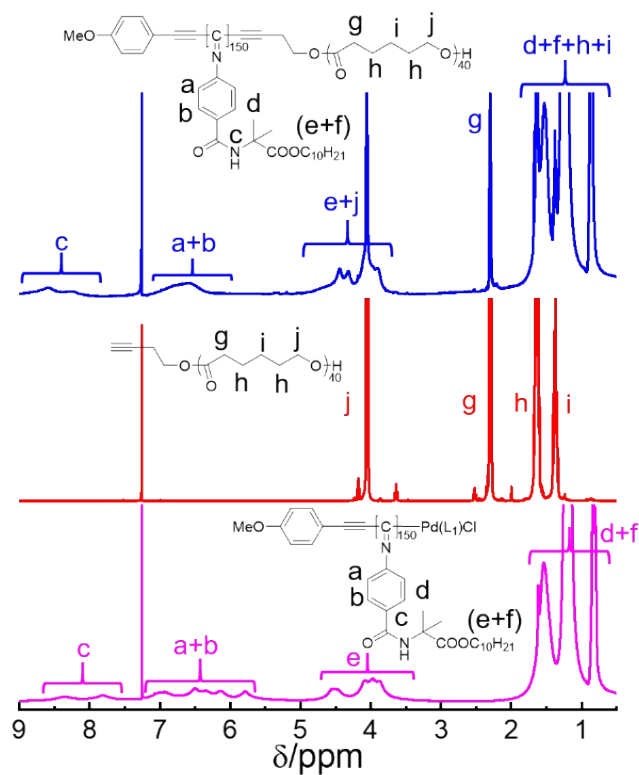


Figure S23. ^1H NMR spectra (600 MHz) of *M*-poly-**1b**₁₅₀, poly-**3c**₆₀, and *M*-poly(**1a**₁₅₀-*b*-**3c**₆₀) in CDCl_3 at 25 °C.

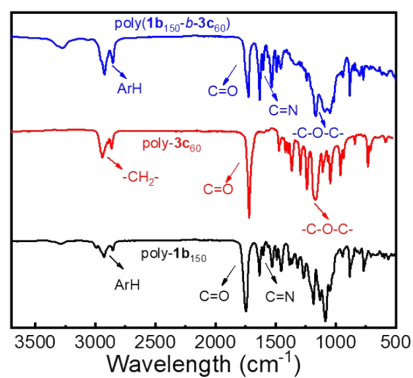


Figure S24. FT-IR spectra of poly-**1b**₁₅₀, poly-**3c**₆₀, and poly(**1b**₁₅₀-*b*-**3c**₆₀) measured at 25 °C using KBr pellets.

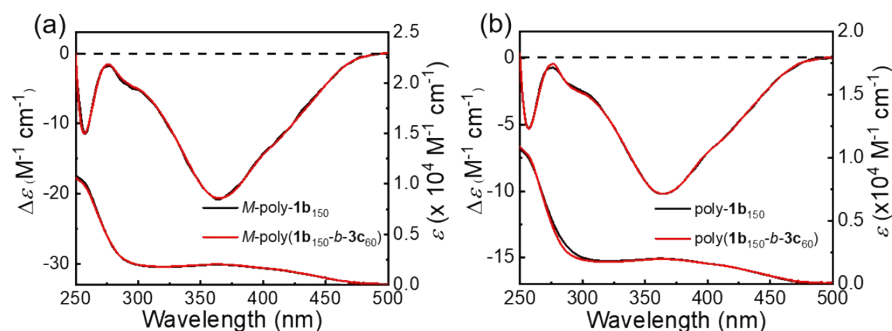


Figure S25. (a) CD and UV-vis curves of M -poly- $1b_{150}$ and M -poly($1b_{150}$ - b - $3c_{60}$). (b) CD and UV-vis spectra of poly- $1b_{150}$ and poly($1b_{150}$ - b - $3c_{60}$).

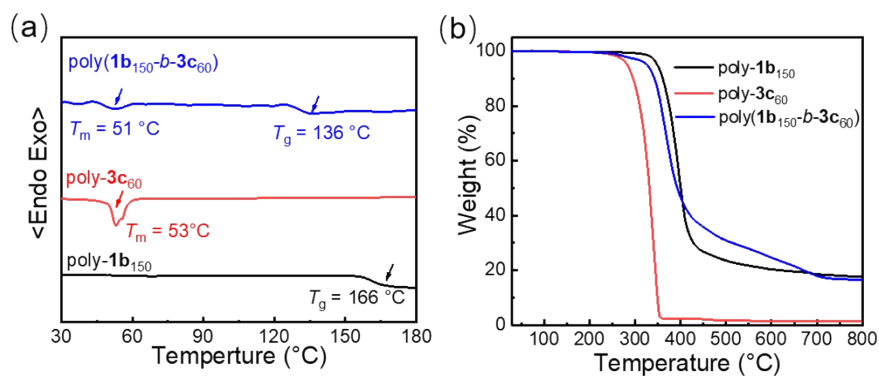


Figure S26. (a) DSC curves of the poly- $1b_{150}$, poly- $3c_{60}$, and poly($1b_{150}$ - b - $3c_{60}$). (b) TGA curves of the poly- $1b_{150}$, poly- $3c_{60}$, and poly($1b_{150}$ - b - $3c_{60}$).

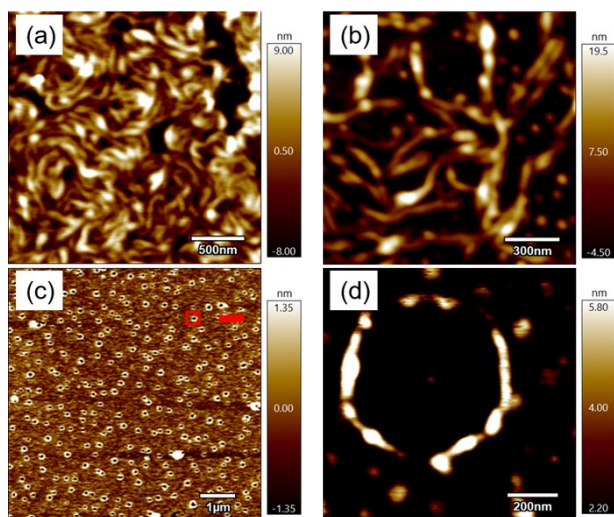


Figure S27. AFM height images of poly($1a_{150}$ - b - $3a_{45}$) measured in the mixture of THF and n -hexane ($v/v = 10:0$) (a); THF: n -hexane ($v/v = 8:2$) (b); THF: n -hexane ($v/v = 6:4$) (c). (d) The zoomed image of the red area in Figure c ($c = 0.05$ mg/mL).

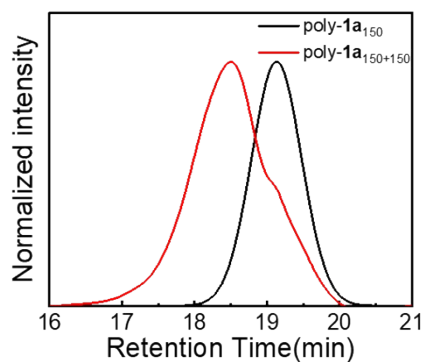


Figure S28. SEC curves of poly-**1a**₁₅₀₊₁₅₀ is synthesized by one-pot method.

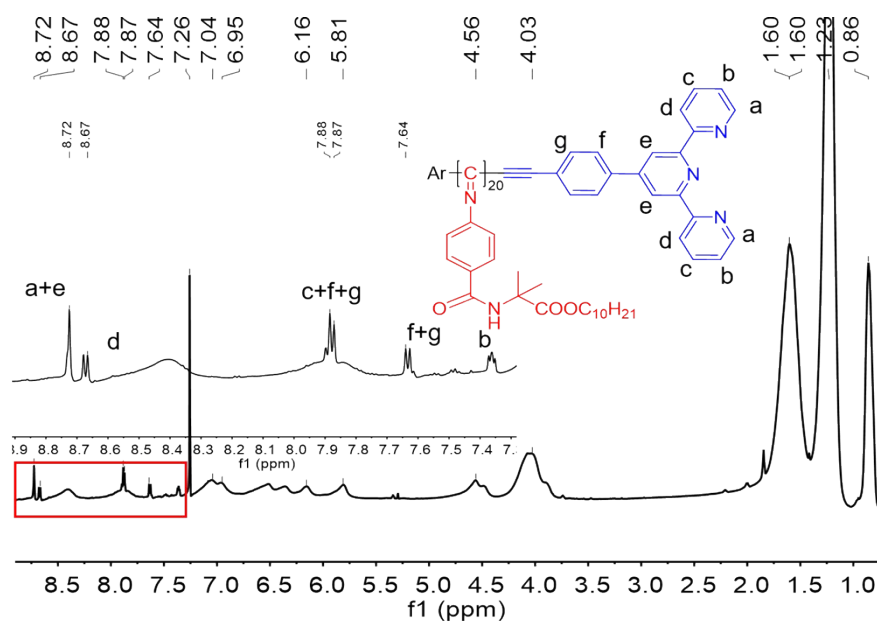


Figure S29. ¹H NMR (600 MHz) spectrum of poly-**1b**₂₀-(TPY) measured in CDCl₃ at 25 °C.

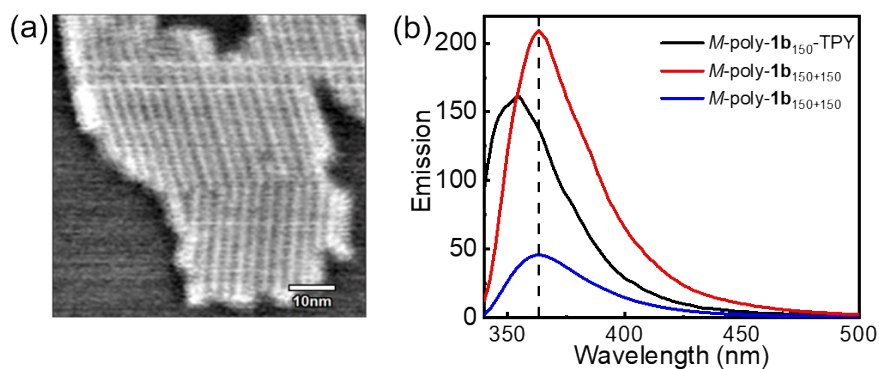


Figure S30. (a) AFM phase image of *M*-poly-**1b**₁₅₀₊₁₅₀. (b) Fluorescence spectra of poly-**1b**₁₅₀-TPY and poly-**1b**₁₅₀₊₁₅₀ in THF at 25 °C. (The red and black lines indicated a concentration of 0.005 mg/mL, the blue line indicated a concentration of 0.001 mg/mL)

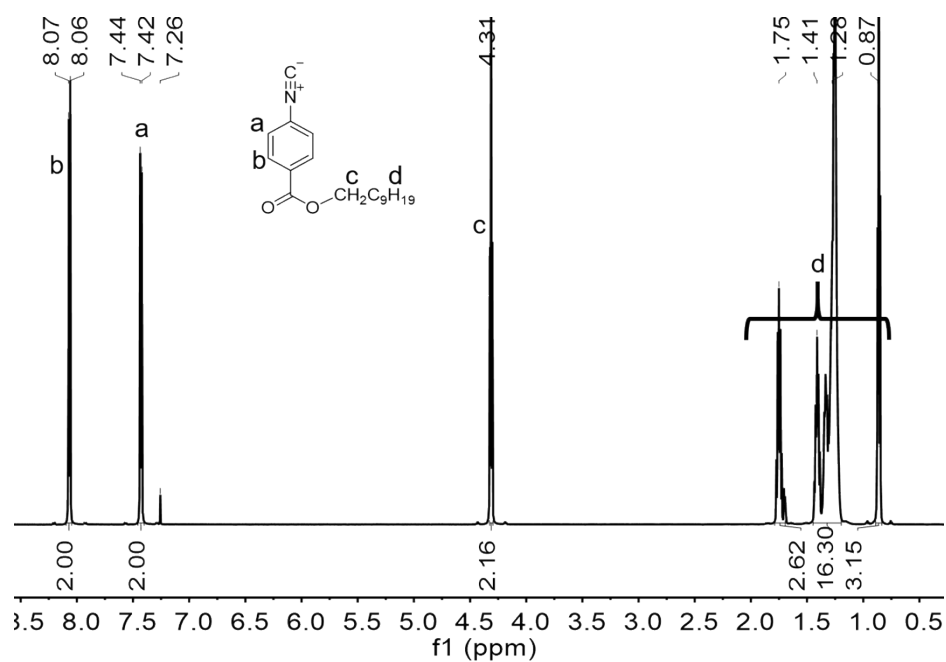


Figure S31. ^1H NMR (600 MHz) spectrum of monomer **1a** measured in CDCl_3 at $25\text{ }^\circ\text{C}$.

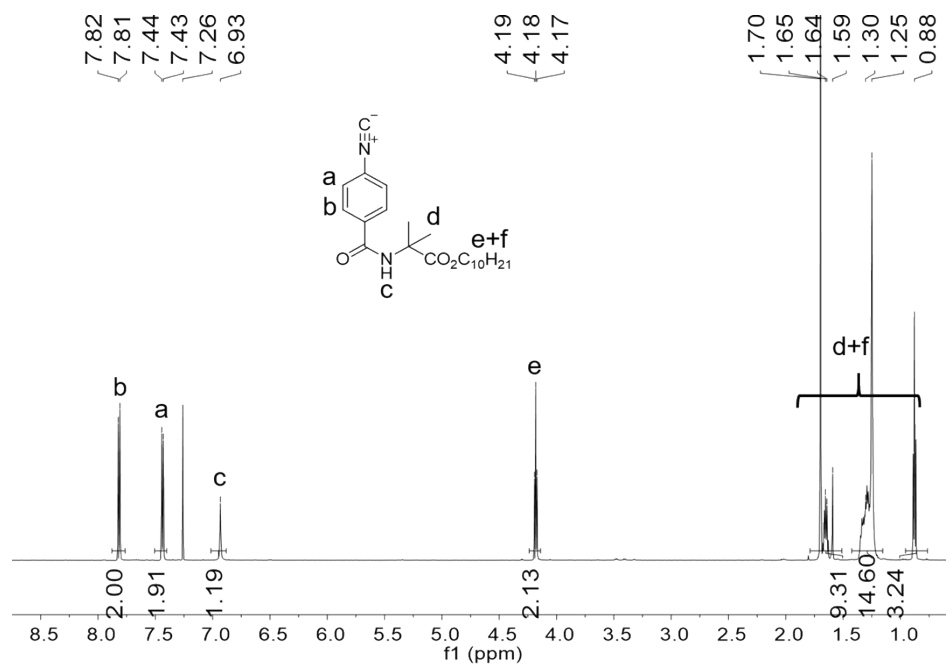


Figure S32. ^1H NMR (600 MHz) spectrum of monomer **1b** measured in CDCl_3 at $25\text{ }^\circ\text{C}$.

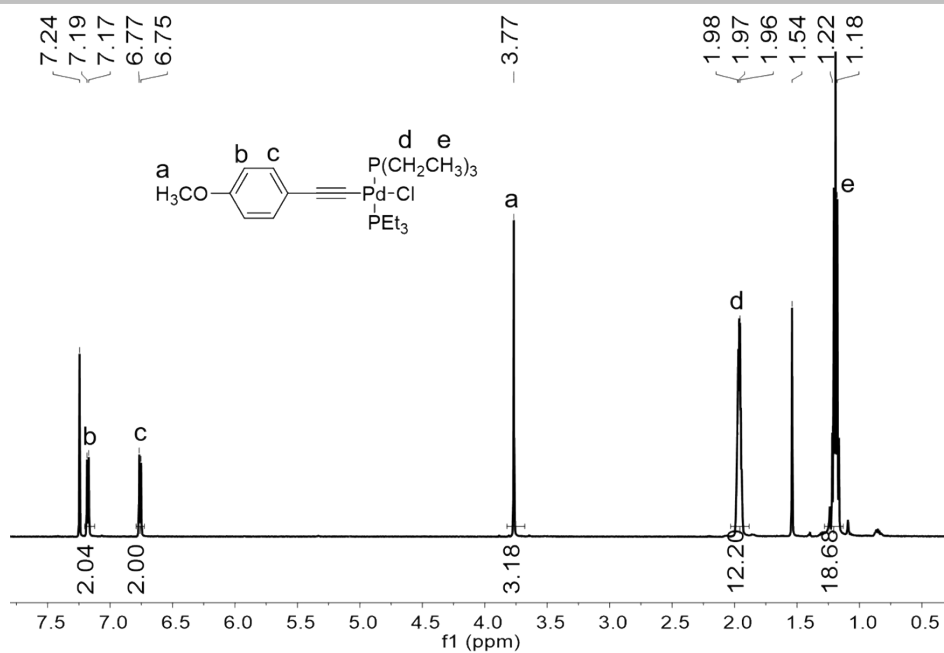


Figure S33. ^1H NMR (600 MHz) spectrum of Pd(II) initiator measured in CDCl_3 at 25°C .

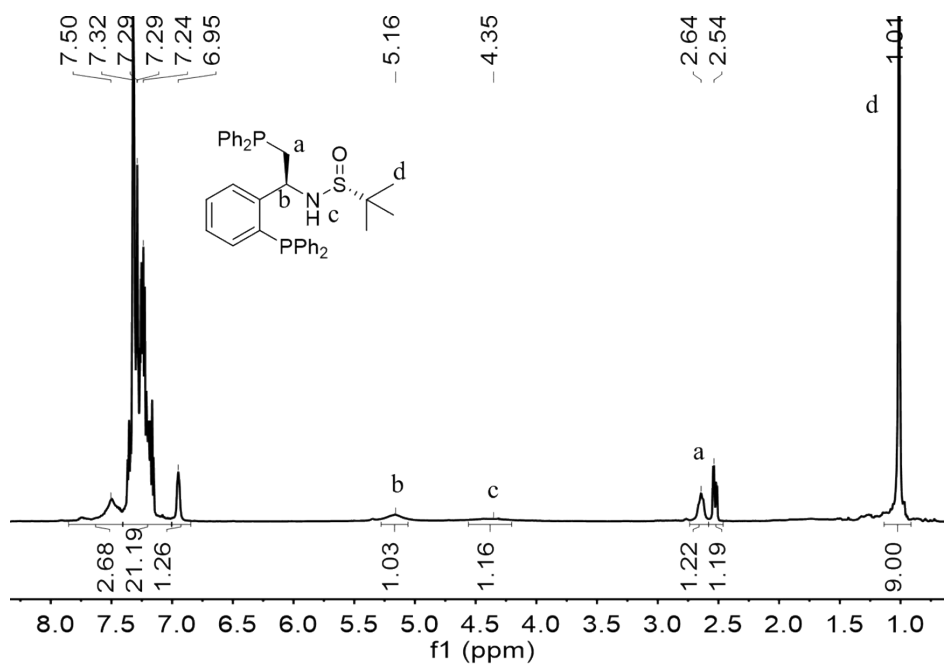


Figure S34. ^1H NMR (600 MHz) spectrum of L_1 measured in CDCl_3 at 25°C .

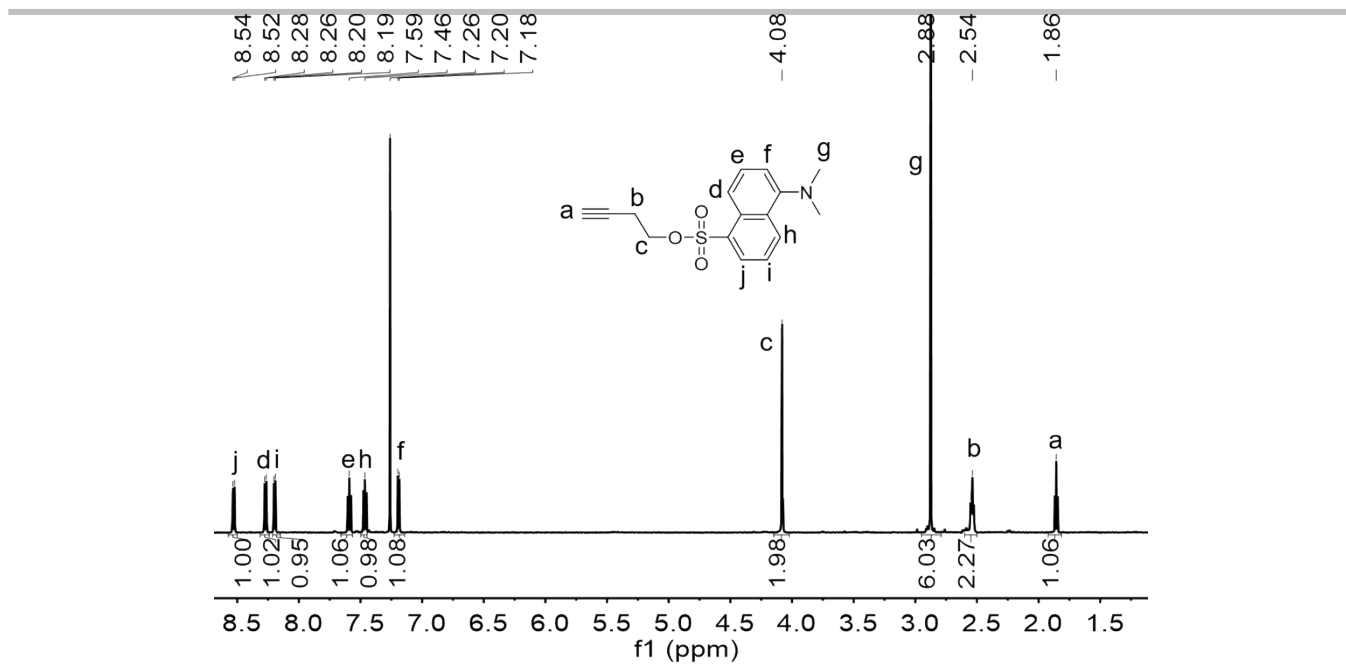


Figure S35. ^1H NMR (600 MHz) spectrum of alkyne- R_{2a} measured in CDCl_3 at 25°C .

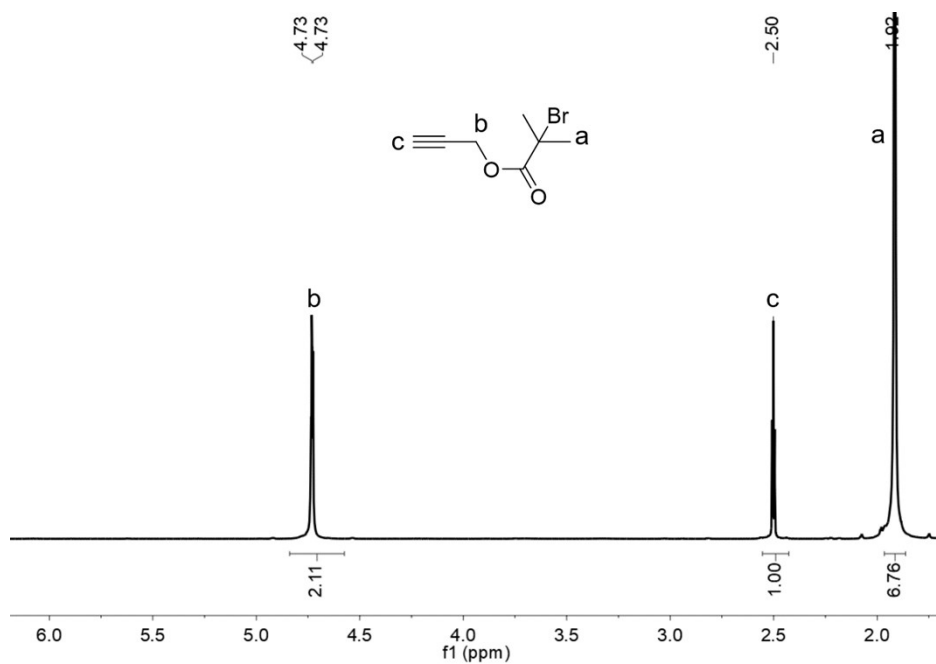


Figure S36. ^1H NMR (600 MHz) spectrum of alkyne-ATRP initiator measured in CDCl_3 at 25°C .

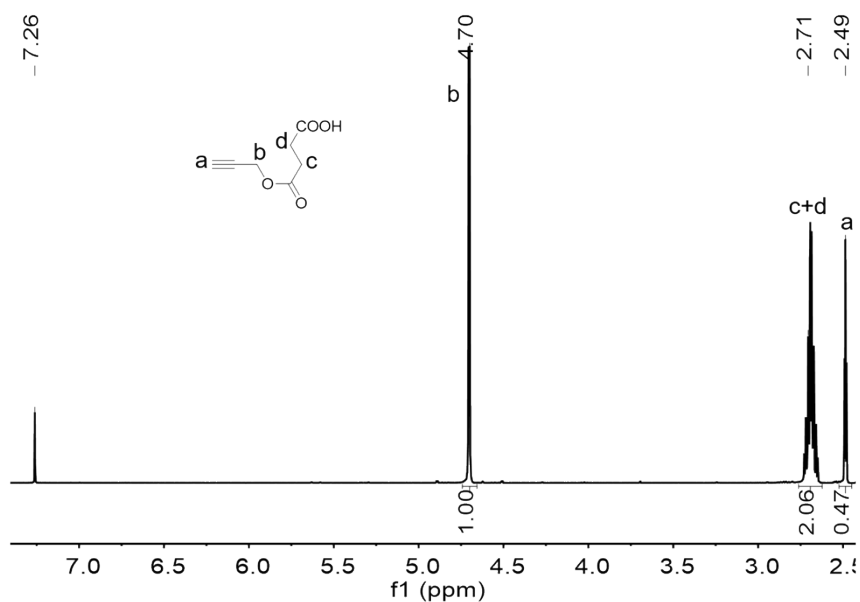


Figure S37. ¹H NMR (600 MHz) spectrum of 4-oxo-4-(prop-2-yn-1-yloxy)butanoic acid [4] measured in CDCl₃ at 25 °C.

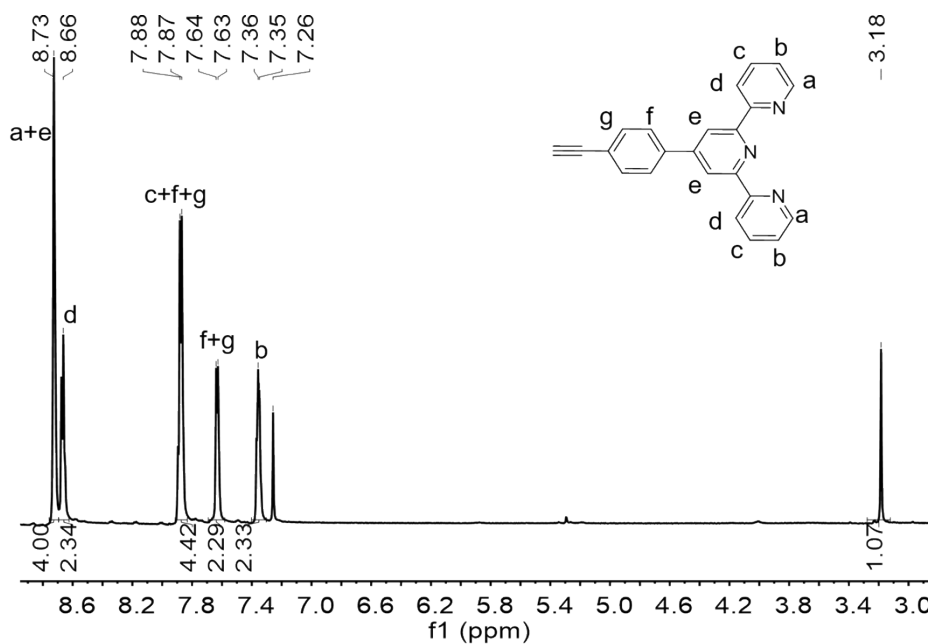


Figure S38. ¹H NMR (600 MHz) spectrum of alkylnyl-TPY measured in CDCl₃ at 25 °C.

References

- 1 Y.-X. Xue, Y.-Y. Zhu, L.-M. Gao, X.-Y. He, N. Liu, W.-Y. Zhang, J. Yin, Y. Ding, H. Zhou, Z.-Q. Wu, *J. Am. Chem. Soc.* **2014**, *136*, 4706–4713.
- 2 L.-Zhou, X.-H. Xu, Z.-Q. Jiang, L. Xu, B.-F. Chu, N. Liu, Z.-Q. Wu, *Angew. Chem. Int. Ed.* **2021**, *60*, 806–812.
- 3 W. Zhou, X. Su, M. Tao, C. Zhu, Q. Zhao, J. Zhang, *Angew. Chem.* **2015**, *127*, 15066–15070.
- 4 L. Xu, L. Yang, Z. Guo, N. Liu, Y.-Y. Zhu, Z. Li, Z.-Q. Wu, *Macromolecules* **2019**, *52*, 5698–5706.
- 5 Y.-X. Li, L. Xu, S.-M. Kang, L. Zhou, N. Liu, Z.-Q. Wu, *Angew. Chem. Int. Ed.* **2021**, *60*, 7174–7179.
- 6 T. Kaufmann, M. T. Gokmen, S. Rinnen, H. F. Arlinghaus, F. D. Prez, B. J. Ravoo, *J. Mater. Chem.* **2012**, *22*, 6190–6199.
- 7 G.-Y. Shi, L.-P. Yang, C.-Y. Pan, *Journal of Polymer Science: Part A: Polymer Chemistry.* **2008**, *46*, 6496–6508.
- 8 J.-L. Chen, M. Su, Z.-Q. Jiang, N. Liu, J. Yin, Y.-Y. Zhu, Z.-Q. Wu, *Polym. Chem.* **2015**, *6*, 4784–4793.
- 9 J. Huang, Y. Xu, H. Xiao, Z. Xiao, Y. Guo, D. Cheng, X. Shuai, *ACS Nano* **2019**, *13*, 7036–7049.
- 10 Q. Zhang, P. Wilson, Z. Li, R. McHale, J. Godfrey, A. Anastasaki, C. Waldron, D. M. Haddleton, *J. Am. Chem. Soc.* **2013**, *135*, 7355–7363.