

Electronic Supplementary Material (ESI) for Chemical Science.
This journal is © The Royal Society of Chemistry 2021

Electronic Supplementary Information

One-Pot Asymmetric Living Copolymerization-induced Chiral Self-assemblies and Circularly Polarized Luminescence

Run-Tan Gao,^a Shi-Yi Li,^a Bing-Hao Liu,^a Zheng Chen,^a Na Liu,^{*,b} Li Zhou,^c and Zong-Quan Wu^{*,a}

^aState Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, China.

^bThe School of Pharmaceutical Sciences, Jilin University, 1266 Fujin Road, Changchun, Jilin 130021, P.R. China.

^cDepartment of Polymer Science and Engineering, Hefei University of Technology, Hefei 230009, China.

Table of Contents

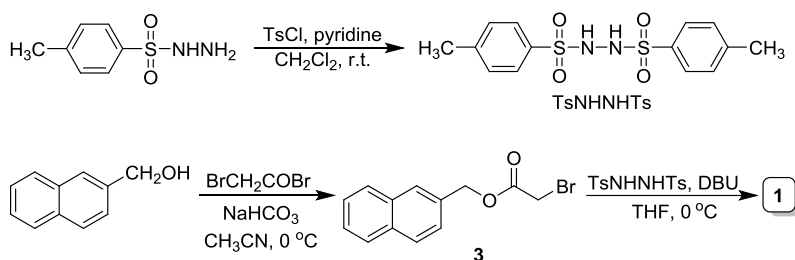
General considerations	S3-S4
Synthetic procedure	S4
Synthesis of monomer 1	S5-S6
Typical polymerization procedure	S7
Kinetic study for the block copolymerization	S8
High solid content polymerization induced self-assembly process	S9
AFM and TEM measurements	S9-S10
Emission and CPL measurements	S10
Fig. S1. SEC curves for the copolymerization of 2 initiated by <i>R</i> -poly- 1 ₁₀₅	S11
Fig. S2. FT-IR spectra of poly- 2 ₃₀ , <i>R</i> -poly(1 ₁₀₅ - <i>b</i> - 2 ₉₈), and <i>R</i> -poly- 1 ₁₀₅	S11
Fig. S3. TGA curves of <i>R</i> -poly- 1 ₁₀₅ , <i>R</i> -poly(1 ₁₀₅ - <i>b</i> - 2 ₉₈) and poly- 2 ₃₀	S12
Fig. S4. DSC curves of <i>R</i> -poly- 1 ₁₀₅ , <i>R</i> -poly(1 ₁₀₅ - <i>b</i> - 2 ₉₈) and poly- 2 ₃₀	S12
Fig. S5. CD and UV-vis spectra of <i>R</i> -poly- 1 ₁₀₅ and <i>S</i> -poly- 1 ₁₀₅	S13
Fig. S6. CD and UV-vis of <i>R</i> -poly- 1 ₁₀₅ in THF at different concentrations	S13
Fig. S7. CD and UV-vis of <i>R</i> -poly- 1 ₁₀₅ in THF at different temperatures	S14
Fig. S8. UV-vis spectra and <i>g</i> (CD) value at 460 nm of <i>R</i> -poly(1 ₁₀₅ - <i>b</i> - 2 _{<i>n</i>})	S14
Fig. S9. AFM images of the <i>S</i> -poly(1 ₁₀₅ - <i>b</i> - 2 _{<i>n</i>}) <i>s</i>	S15
Fig. S10. TEM images of <i>S</i> -poly(1 ₁₀₅ - <i>b</i> - 2 _{<i>n</i>}) <i>s</i>	S15
Fig. S11. AFM images of the <i>R</i> - and <i>S</i> - copolymer mixtures	S16
Fig. S12. TEM images of the <i>R</i> - and <i>S</i> - copolymer mixtures	S16
Fig. S13. Photographs of copolymerization of 2 by Pd(II)-terminated <i>R</i> -poly- 1 ₁₀₅	S16
Fig. S14. Emission and CPL spectra of <i>R</i> - and <i>S</i> -poly(1 ₁₀₅ - <i>b</i> - 2 _{<i>n</i>}) copolymers	S17
Fig. S15. Plot of <i>g</i> _{lum} against the DP of PPE blocks of <i>R</i> -poly(1 ₁₀₅ - <i>b</i> - 2 _{<i>n</i>})	S17
Fig. S16-S18. ¹ H NMR and ¹³ C NMR spectra of monomer 1 and 2	S18-S19
Fig. S19-S30. ¹ H NMR spectra of poly(1 ₁₀₅ - <i>b</i> - 2 _{<i>n</i>})	S19-S25
References	S26-S27

General considerations. The nuclear magnetic resonance (NMR) spectra were recorded using a Bruker 600 MHz or 400 MHz spectrometer {H}. 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 (set at 40 °C). A series of two linear TSK gel GMHHR-H columns were used. Molecular weight (M_n) and its polydispersity (M_w/M_n) values were reported with reference to the polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 0.8 mL/min. FT-IR spectra were recorded on Perkin-Elmer Spectrum BX FT-IR system using KBr pellets at 25 °C. Circular dichroism (CD) spectra were obtained in a 1.0 cm or 1.0 mm quartz cell using a JASCO J1500 spectropolarimeter. Absorption spectra were recorded on UNIC 4802 UV/vis double beam spectrophotometer in a 1.0 mm quartz cell at 25 °C. Emission spectra were recorded on Hitachi F-4600 fluorescence spectrophotometer. The circularly polarized luminescence (CPL) spectra using a JASCO CPL-300 spectrometer at room temperature. Atomic force microscope (AFM) was performed on a Cypher S microscope (Oxford Instruments, Asylum Research). Transmission electron microscopy (TEM) was performed on a JEM-2100F operating at 200 kV accelerating voltage. Dynamic light scattering (DLS) was recorded using a Nano-ZS 90 Zetasizer of Malvern (UK) instrument. Differential scanning calorimetric (DSC) measurements were carried on a Mettler-Toledo DSC821e instrument. Samples were first heated from 30 °C to 250 °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 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) and diisopropylamine (*i*Pr₂NH) for polymerizations were further dried over sodium benzophenone ketyl, distilled onto lithium aluminum hydride under nitrogen, and distilled under high vacuum just before use. Monomer **1**, **2**, and Wei-phos ligands (L^S and L^R) were prepared according to the literatures with modifications and the structures were confirmed by ¹H NMR.¹⁻⁵

Synthetic procedure:

Scheme S1. Synthesis of monomer **1**



Synthesis of N,N'-ditosylhydrazine (TsNHNHTs). This compound was prepared following the reported literatures with slight modifications.¹ A flame-dried 500 mL round-bottomed flask fitted with a magnetic stir bar was charged with *p*-toluenesulfonyl hydrazide (18.2 g, 0.1 mol) and *p*-toluenesulfonyl chloride (28.4 g, 0.2 mol) in anhydrous CH_2Cl_2 (200 mL). The mixed suspension was stirred at room temperature while pyridine (10.0 mL, 150.0 mmol) was added dropwise over 1.5 min. During the addition of pyridine, the reaction mixture became homogenous and turned yellow. White precipitate was observed

within 3 min and the reaction mixture was stirred for further 1.5 h. Diethyl ether (400 mL) and H₂O (200 mL) were added and the resulting mixture was stirred at 0 °C for 15 min. The white solid which precipitated was collected in a Büchner funnel using suction filtration and washed with diethyl ether (100 mL). The solid thus obtained was dissolved in boiling methanol (400 mL). After cooling to room temperature, precipitate appeared. About 200 mL of methanol was removed by rotary evaporation and cooled to 0 °C. The precipitate was collected in a Büchner funnel using suction filtration and washed with cold methanol (20 mL) and diethyl ether (100 mL) to give *N,N'*-ditosylhydrazine (TsNHNHTs) as a white solid (20.1 g, 83%).

Synthesis of 1. The monomer **1** was prepared following the reported literatures with slight modifications.¹⁻² Under N₂ atmosphere, bromoacetyl bromide (3.5 mL, 38.0 mmol) was added dropwise to a stirred suspension of benzyl alcohol (5.0 g, 32.0 mmol) and NaHCO₃ (8.1 g, 96.0 mmol) in acetonitrile (100 mL) at 0 °C. The resulting mixture was stirred for 10 min at this temperature. After the addition of H₂O, the mixture was extracted with CH₂Cl₂, and the organic phase was dried over anhydrous Na₂SO₄. After the removal of the solvent by evaporation under reduced pressure, the residue was used in the next step without further purification. The obtained residue (8.9 g, 32.0 mmol) and TsNHNHTs (15.3 g, 44.8 mmol) was dissolved in THF (100 mL) and cooled to 0 °C. After 1, 8-diazabicyclo [5.4.0] undec-7-ene (DBU, 14.0 mL, 96.0 mmol) was added dropwise, the mixture was stirred for 10 min at this temperature. The reaction was quenched by adding saturated aqueous NaHCO₃, then extracted with diethyl ether. The combined organic phase was

washed with brine, dried over anhydrous Na₂SO₄, and evaporated to dryness to give a crude product as a yellowish oil. This material was further purified by silica gel column chromatography using ethyl acetate/*n*-hexane (v/v = 8:1) as eluent, afforded monomer **1** as a yellowish oil (6.5 g, 90 % yield). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 7.86–7.83 (m, 4H, ArH), 7.51–7.26 (m, 3H, ArH), 5.36 (s, 2H, CH₂), 4.87 (s, 1H, N₂CH).

Preparation of the R- and S-Pd(II) catalysts. These catalyst solutions were prepared following the reported literature.³ A solution of commercial available π -allyl PdCl (10.5 mg, 0.03 mmol) in THF (1.0 mL) was treated with Wei-Phos (16.5 mg, 0.03 mmol) at room temperature. After the resulting mixture was stirred at room temperature for 0.5 h, it was directly used in the polymerization without further purification.

Synthesis of R- and S-poly-1_m. Taking poly-**1**₁₀₅ as an example. A solution of the as-prepared π -allyl PdCl/L^R catalyst in THF (0.03 mol/L, 0.3 mL, 0.009 mmol) was added to a solution of monomer **1** (100.0 mg, 0.9 mmol) in THF (0.7 mL) at room temperature. The concentrations of the monomer and the catalyst were 0.9 mol/L and 0.009 mol/L, respectively, corresponding to the feed ratio of monomer to catalyst was 100/1. The reaction mixture was stirred at room temperature and a large amount of bubble was released upon the addition of the Pd(II) catalyst. After the polymerization solution was stirred for 30 min, it was precipitated into a large amount of *n*-hexane. The precipitated solid was collected by centrifugation and dried in vacuum at room temperature overnight, afforded *R*-poly-**1**₁₀₅ as a white solid (83.0 mg, 83% yield). SEC: $M_n = 4.7$ kDa, $M_w/M_n = 1.15$. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 7.26–7.04 (br, 753H, ArH), 4.76 (br, 214H, OCH₂),

3.77 (br, 105H, CH of main chain), 3.02-3.05 (br, 2H, CH₂ of allyl). FT-IR (KBr, 25 °C): 3049 ($\nu_{\text{Ar-H}}$), 2919 ($\nu_{\text{C-H}}$), 2845 ($\nu_{\text{C-H}}$), 1720 ($\nu_{\text{C=O}}$) cm^{-1} .

S-poly-**1**₁₀₅ was prepared following the same procedure using π -allyl PdCl/L^S catalyst in 85% yield. SEC: $M_n = 5.9$ kDa, $M_w/M_n = 1.16$. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 7.26–7.04 (br, 760H, ArH), 4.76 (br, 215H, OCH₂), 3.77 (br, 105H, CH of main chain), 3.02-3.05 (br, 2H, CH₂ of allyl). FT-IR (KBr, 25 °C): 3105 ($\nu_{\text{Ar-H}}$), 2930 ($\nu_{\text{C-H}}$), 2855 ($\nu_{\text{C-H}}$), 1705 ($\nu_{\text{C=O}}$) cm^{-1} .

Typical block copolymerization procedure. The block copolymerization was carried out following Scheme 1 in the main text. A solution of the Pd(II)-terminate *R*-poly-**1**₁₀₅ macroinitiator (45.4 mg) in THF (0.5 mL) was added to the mixture of monomer **2** (40.8 mg, 0.09 mmol), CuI (1.7 mg, 0.01 mmol), and ⁱPr₂NH (0.5 mL) ($[\mathbf{2}]_0/[\text{Pd}]_0 = 100$). The solution was stirred at 55 °C for 12 h. The solution was poured in a large amount of *n*-hexane, the precipitated light yellowish solid was collected by centrifugation and washed with acetone three times. The collected solid was dried in vacuum at room temperature overnight afforded the expected block copolymer *R*-poly(**1**₁₀₅-*b*-**2**₉₈) (63.7 mg, 74% yield). SEC: $M_n = 12.1$ kDa, $M_w/M_n = 1.18$. ¹H NMR (600MHz, CDCl₃, 25 °C): δ 7.26–6.59 (br, 984H, ArH of poly-**1**₁₀₅ segment and ArH of poly-**2**₉₈ segment), 4.76 (br, 210H, OCH₂ of poly-**1**₁₀₅ segment), 4.03-3.34 (br, 298H, OCH₂ of poly-**2**₉₈ segment and CH of poly-**1**₁₀₅ main chain), 1.88–1.79 (br, 410H, OCH₂CH₂ of poly-**2**₉₈ segment), 1.60–1.46 (br, 392H, CH₂ of poly-**2**₉₈ segment), 1.40–1.21 (br, 1590H, CH₂ of poly-**2**₉₈ segment), 0.91–0.82 (br, 605H, CH₃ of poly-**2**₉₈ segment). FT-IR (KBr, 25 °C): 3054 ($\nu_{\text{C-H}}$), 2922 ($\nu_{\text{Ar-H}}$), 2856 ($\nu_{\text{Ar-}}$

H), 2196 ($\nu_{\text{C}=\text{C}}$), 1718 ($\nu_{\text{C}=\text{O}}$), 1140 ($\nu_{\text{C}-\text{O}-\text{C}}$), 1016 ($\nu_{\text{C}-\text{O}-\text{C}}$) cm^{-1} .

Synthesis of poly-2₉₈. This polymer was prepared according to the reported literature.⁴ Under N₂ atmosphere, monomer **2** (100.0 mg, 0.2 mmol), the ethynyl Pd(II) complex⁴ (1.1 mg, 0.002 mmol) and triphenylphosphine (2.1 mg, 0.008 mmol) and CuI (1.5 mg, 0.008 mmol) were dissolved in THF (0.5 mL) and triethylamine (0.5 mL). After the resulting mixture was stirred at 55 °C for 8 h, the solution was precipitated into a large amount of methanol. The precipitated solid was collected by filtration, and washed with acetone to precipitate and purify poly-**2**₉₈, which was collected by centrifugation and dried under vacuum at room temperature overnight to obtain a yellow solid. (91.0 mg, 90 % yield). SEC: $M_n = 22.1$ kDa, $M_w/M_n = 1.12$. ¹H NMR (600MHz, CDCl₃, 25 °C): δ 7.02 (s, 212H, ArH), 4.03 (br, 410H, OCH₂), 3.81 (s, 3H, OCH₃), 1.88–1.79 (br, 412H, OCH₂CH₂), 1.60–1.46 (br, 513H, CH₂), 1.40–1.21 (br, 1589H, CH₂), 0.91–0.82 (br, 589H, CH₃). ¹³C NMR (150 MHz, CDCl₃, 25 °C): δ 153.47, 117.24, 114.29, 91.58, 69.67, 31.86, 29.42, 29.33, 26.10, 26.01, 22.67, 14.09. FT-IR (KBr, 25 °C): 2952 ($\nu_{\text{C}-\text{H}}$), 2925 ($\nu_{\text{C}-\text{H}}$), 2853 ($\nu_{\text{C}-\text{H}}$), 2200 ($\nu_{\text{C}=\text{C}}$) cm^{-1} .

Kinetic study for the block copolymerization: A solution of the macroinitiator R-poly-**1**₁₀₅ (30.2 mg) in THF (0.5 mL) and ⁱPr₂NH (0.5 mL) was added to the mixture of monomer **2** (27.2 mg, 0.06 mmol), CuI (1.1 mg, 0.006 mmol), and internal standard polystyrene (PSt, $M_n = 44.2$ kDa, $D = 1.02$; 5.0 mg) in THF (1.0 mL) via a syringe ($[\mathbf{2}]_0 = 0.03$ M, $[\mathbf{2}]_0/[\text{Pd}]_0 = 100$). The solution was stirred at 55 °C and was followed by measuring SEC of the aliquots taking out from the reaction solution at appropriate time intervals. The conversion

of monomer **2** was calculated based on the peak area of unreacted **2** relative to that of the internal PSt standard on the basis of the linear calibration curve.

High solid content polymerization induced self-assembly process: Under N₂ atmosphere, *R*-poly-**1**₁₀₅ (231.0 mg, 0.05 mmol), monomer **2** (230.0 mg, 0.5 mmol), CuI (6.0 mg, 0.03 mmol) were dissolved in THF (0.3 mL) and ⁱPr₂NH (0.3 mL). After the resulting mixture was stirred at 55 °C for 12 h, the solution was precipitated into a large amount of *n*-hexane. The precipitated solid was collected by filtration, and washed with acetone to afford the desired chain-extended block copolymer *R*-poly(**1**₁₀₅-*b*-**2**₉₈) as a yellow solid (389.2 mg, 84 % yield). SEC: $M_n = 13.5$ kDa, $M_w/M_n = 1.16$.

AFM and TEM observations. AFM were performed at room temperature in a dry state using Cypher S microscope (Oxford Instruments), according to the reported literature.⁵ 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 a polymerization solution diluted to about 100-folds with THF. A drop (20 μL) 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 for several minutes. Measurements of length and width of the nanofibers were taken using the section Particle Analysis tool provided with the AFM software (Asylum Research).

The samples for TEM investigations were prepared under a way similar to AFM. The

obtained polymerization solutions were diluted 100-fold with THF. And a drop of the solution (20 μL) was placed on a copper grid for 1 min and then blotted with filter paper to remove excess solution. TEM observations were carried out on a JEM-2100F operating at 200 kV accelerating voltage.

Emission and CPL analyses. These experiments were conducted followed the reported literatures with slight modification.⁶ Taking the emission and circularly polarized luminescence (CPL) spectra of *R*-poly(**1**₁₀₅-*b*-**2**₉₈) as an example. Put the THF solution of *R*-poly(**1**₁₀₅-*b*-**2**₉₈) ($c = 0.2 \text{ mg/mL}$) 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 spectrophotometer or JASCO CPL-300 spectrometer. The fluorescence and CPL spectrum of the solution was monitored at 25 °C in the range of emission wavelength between 400 and 750 nm, excited by UV light at 364 nm. A drop-coated films prepared on a quartz substrate (Daico MFG, USQ-grade) from a THF solution of the polymers (ca. 40 mg mL^{-1}) was used for solid-state spectral measurements. A scanning rate of 100 nm/min, an excitation slit width of 3000 μm , a monitoring slit width of 3000 μm .

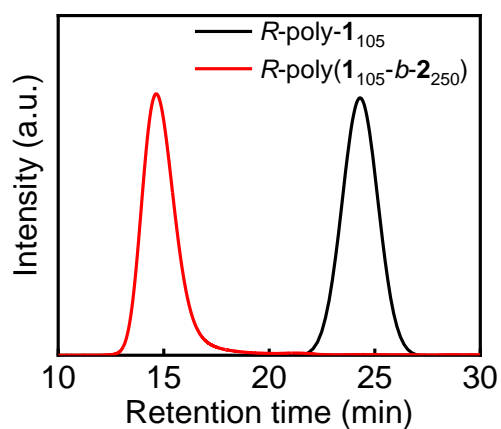


Fig. S1. SEC curves of *R*-poly-**1**₁₀₅ ($M_n = 4.7$ kg/mol, $M_w/M_n = 1.15$) and *R*-poly(**1**₁₀₅-*b*-**2**₂₅₀) ($M_n = 30.5$ kg/mol, $M_w/M_n = 1.10$).

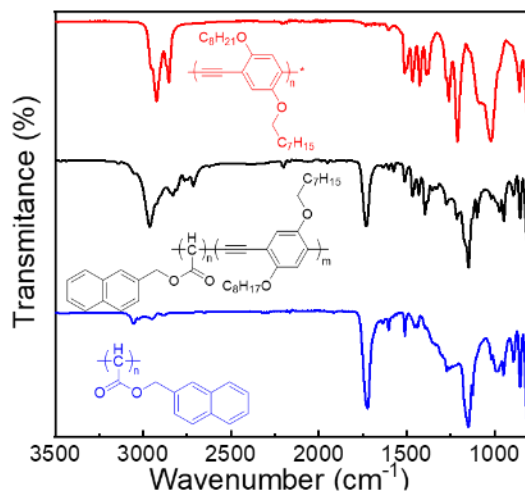


Fig. S2. FT-IR spectra of poly-**2**₃₀, *R*-poly(**1**₁₀₅-*b*-**2**₉₈), and *R*-poly-**1**₁₀₅ measured at 25 °C using KBr pellets.

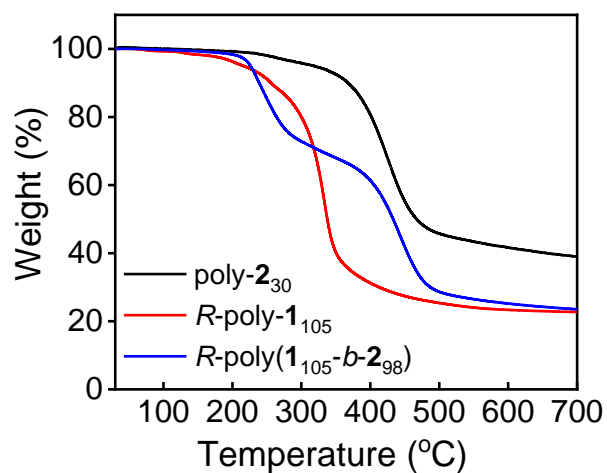


Fig. S3. TGA curves of R-poly-1₁₀₅, R-poly(1₁₀₅-b-2₉₈) and poly-2₃₀ (recorded at a heating rate of 10 °C/min under nitrogen atmosphere).

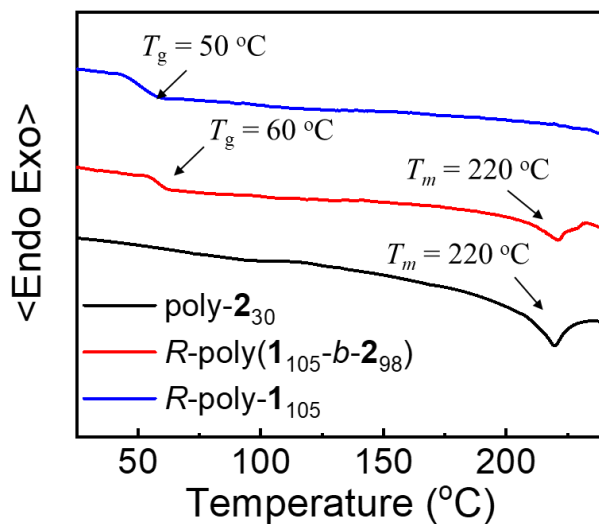


Fig. S4. DSC curves of poly-2₃₀, R-poly(1₁₀₅-b-2₉₈) and R-poly-1₁₀₅ (recorded from 30 °C to 250 °C at a heating rate of 10 °C/min under nitrogen atmosphere).

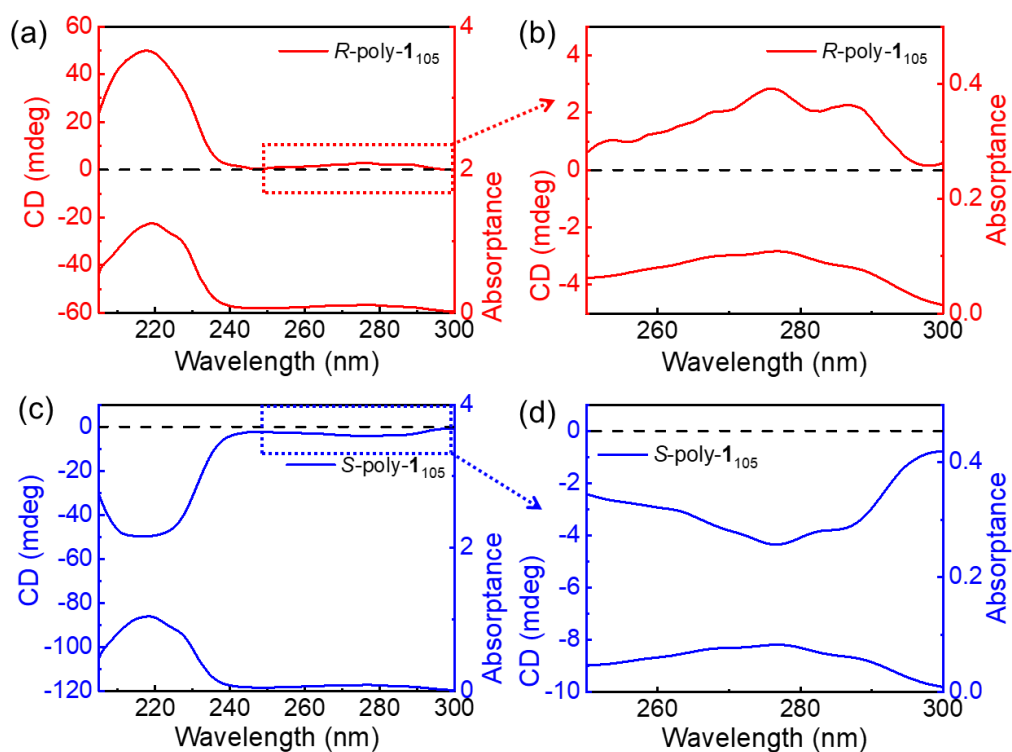


Fig S5. CD and UV-vis spectra of *R*-poly-**1**₁₀₅ (a) and amplification 250-300 nm (b), *S*-poly-**1**₁₀₅ (c) and amplification 250-300 nm (d) recorded in THF at 25 °C (0.2 mg/mL).

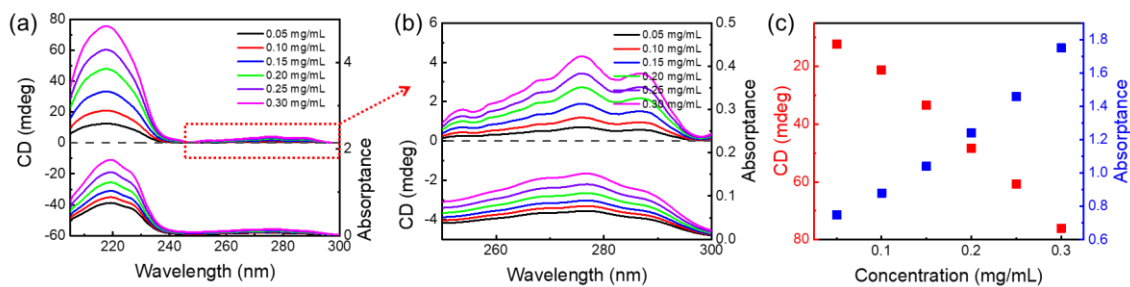


Fig S6. (a) CD and UV-vis spectra of *R*-poly-**1**₁₀₅ (a) and amplification 250-300 nm (b) measured in THF at different concentrations. (c) Plots of CD and UV-vis intensities at 220 nm with the concentration of *R*-poly-**1**₁₀₅ measured in THF at 25 °C.

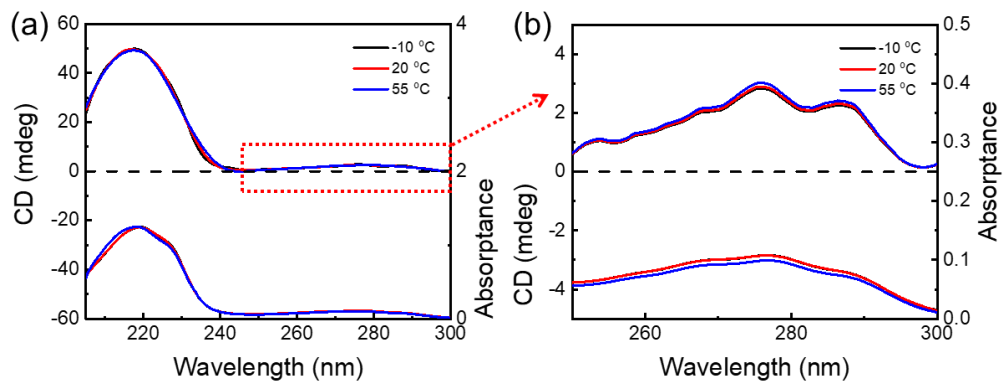


Fig. S7. CD and UV-vis spectra of R -poly- 1_{105} (a) and amplification 250-300 nm (b) measured in THF at different temperatures.

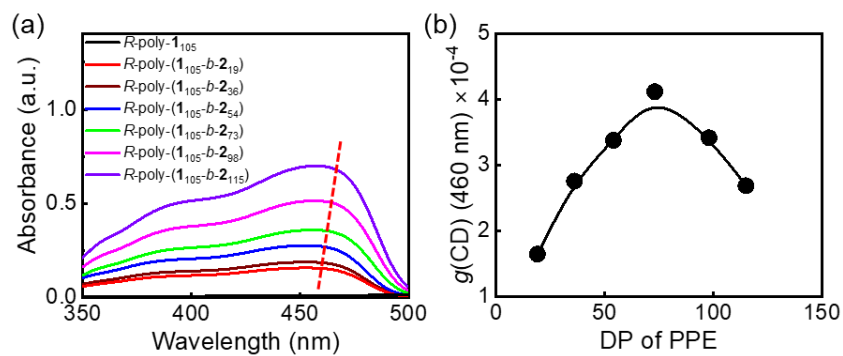


Fig. S8. (a) UV-vis spectra of R -poly(1_{105} - b - 2_n) measured in THF. (b) $g(\text{CD})$ value at 460 nm of different block copolymers.

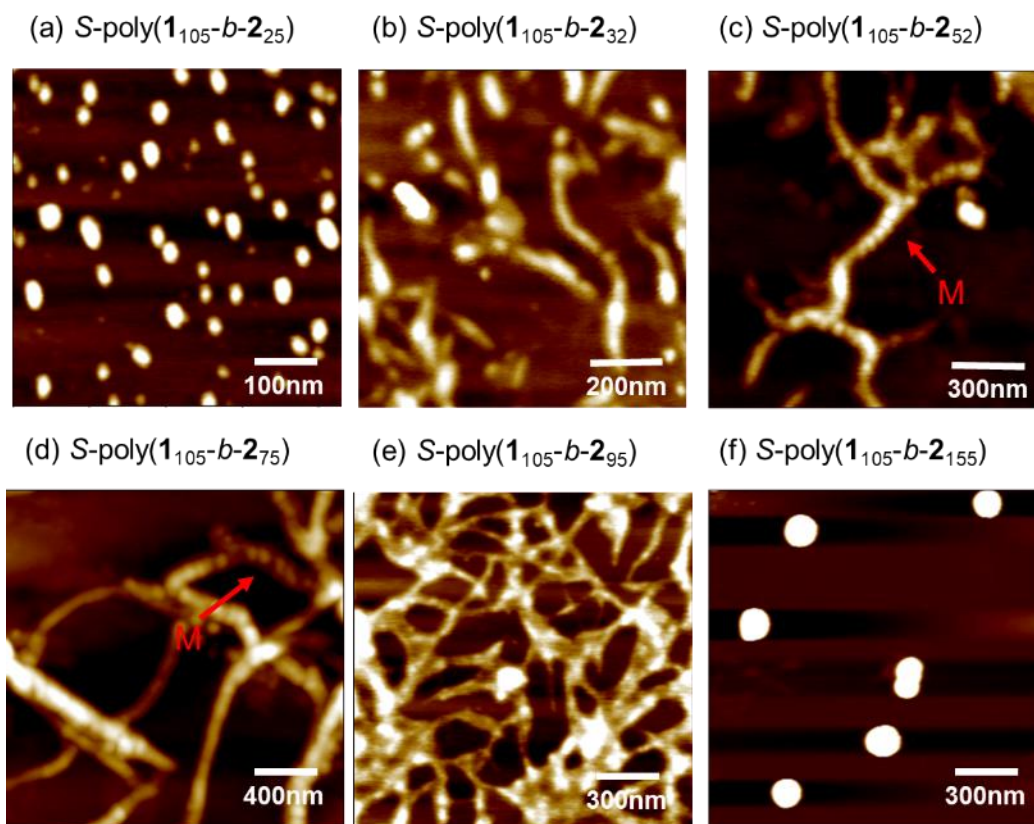


Fig. S9. AFM images of the *S*-poly(**1**₁₀₅-*b*-**2**₂₅) (a), *S*-poly(**1**₁₀₅-*b*-**2**₃₂) (b), *S*-poly(**1**₁₀₅-*b*-**2**₅₂) (c), *S*-poly(**1**₁₀₅-*b*-**2**₇₅) (d), *S*-poly(**1**₁₀₅-*b*-**2**₉₅) (e) and *S*-poly(**1**₁₀₅-*b*-**2**₁₅₅) (f) casted from THF solution (0.2 mg/mL).

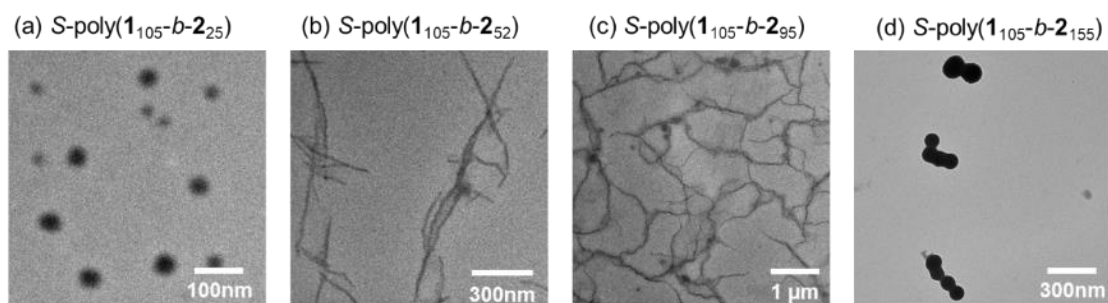


Fig. S10. TEM images of the *S*-poly(**1**₁₀₅-*b*-**2**₂₅) (a), *S*-poly(**1**₁₀₅-*b*-**2**₅₂) (b), *S*-poly(**1**₁₀₅-*b*-**2**₉₅) (c), and *S*-poly(**1**₁₀₅-*b*-**2**₁₅₅) (d) casted from THF solution (0.2 mg/mL).

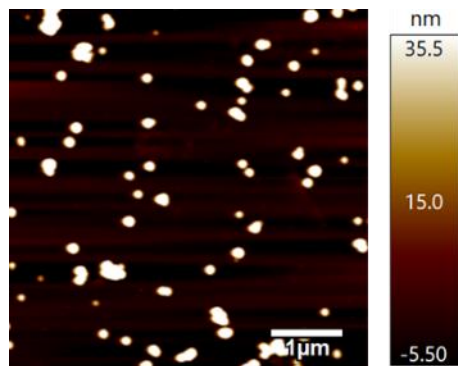


Fig. S11. AFM images of the assemblies formed from the equivalent mixtures of *R*-poly(**1**₁₀₅-*b*-**2**₅₄) and *S*-poly(**1**₁₀₅-*b*-**2**₅₂) in THF (0.2 mg/mL).

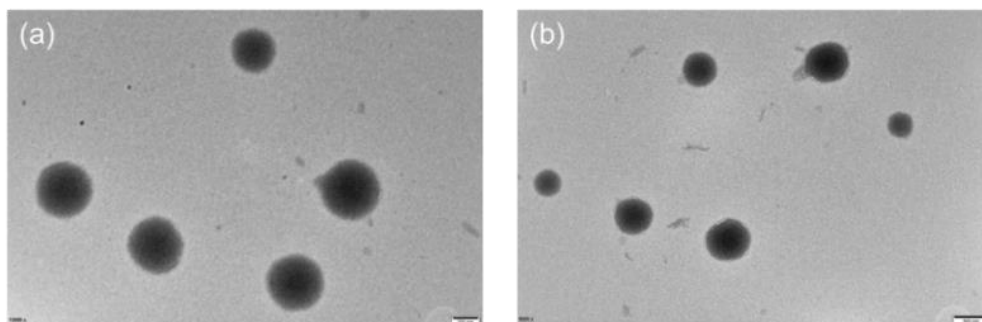


Fig. S12. TEM images of the assemblies formed from the equivalent mixtures of *R*-poly(**1**₁₀₅-*b*-**2**₅₄) and *S*-poly(**1**₁₀₅-*b*-**2**₅₂) in THF (0.2 mg/mL).

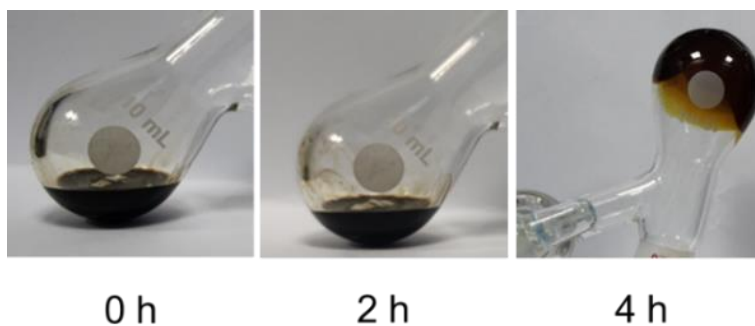


Fig. S13. Photographs of the copolymerization solution of monomer **2** initiated by Pd(II)-terminated *R*-poly-**1**₁₀₅ in THF at 55 °C ($[2]_0/[Pd]_0 = 100$, solids content 53% w/w).

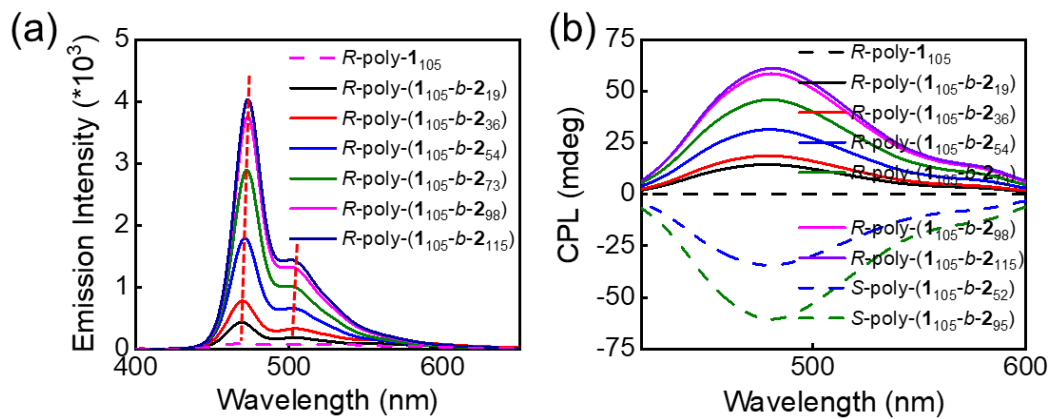


Fig. S14. (a) Emission spectra of R -poly(1_{105} - b - 2_n) copolymers irradiated at 365 nm. (B) CPL spectra of R - and S -poly(1_{105} - b - 2_n) irradiated at 380 nm.

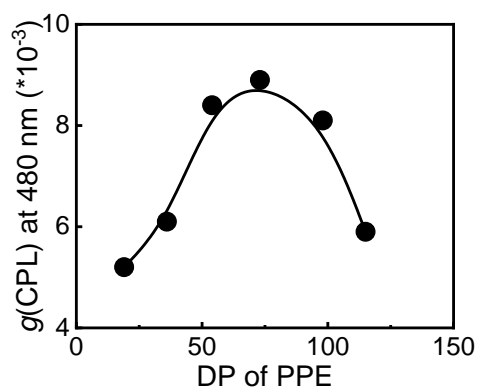


Fig. S15. Plot of $|g_{\text{lum}}|$ against the DP of PPE block of R -poly(1_{105} - b - 2_n) copolymers.

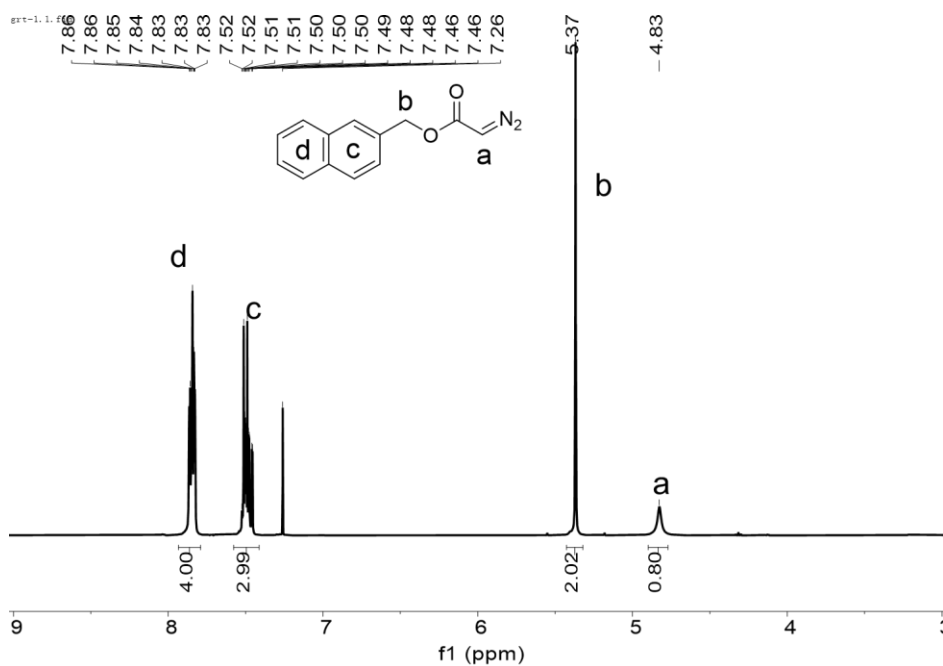


Fig. S16. ¹H NMR (600 MHz) spectra of **1** recorded in CDCl₃ at room temperature.

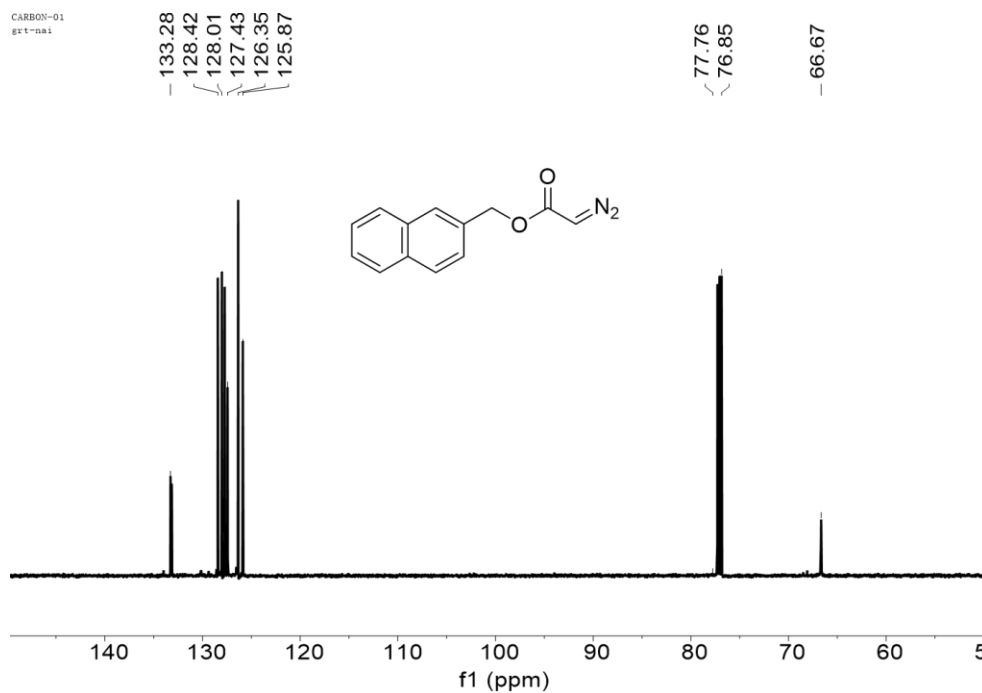


Fig. S17. ¹³C NMR (150 MHz) spectrum of **1** measured in CDCl₃ at room temperature.

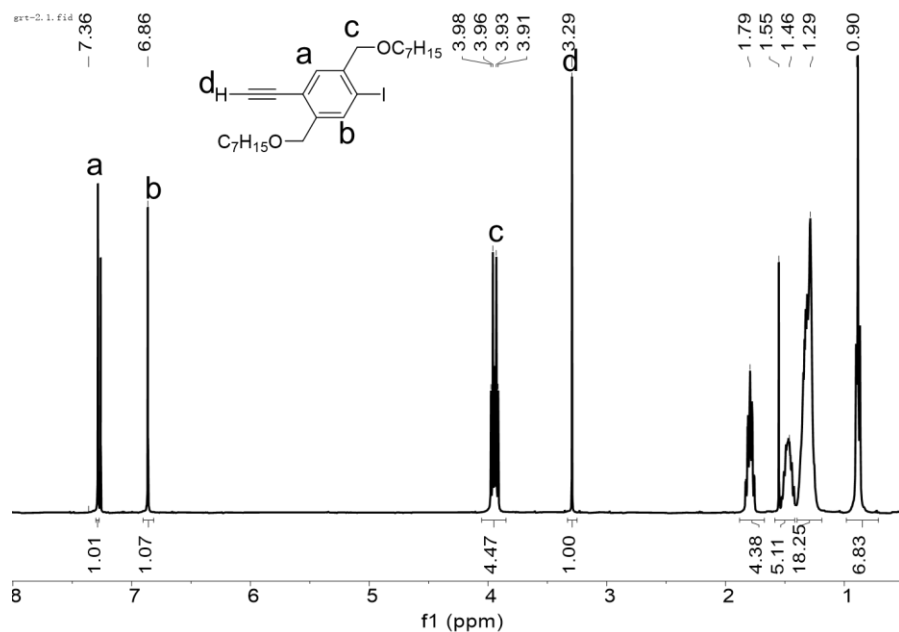


Fig. S18. ^1H NMR (600 MHz) spectra of **2** recorded in CDCl_3 at room temperature.

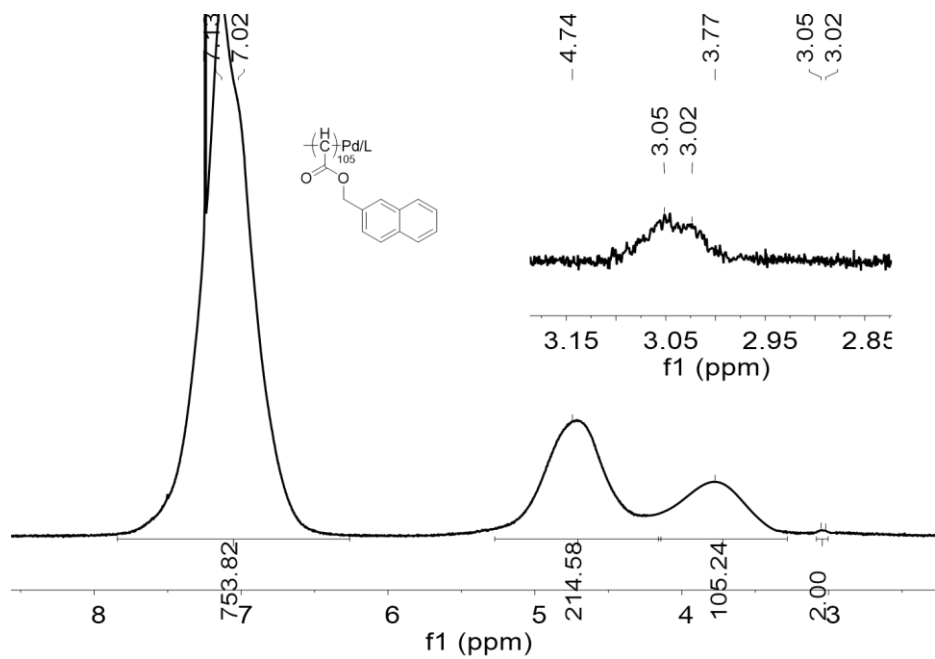


Fig. S19. ^1H NMR (400 MHz) spectra of *R*-poly-**1**₁₀₅ recorded in CDCl_3 at room temperature.

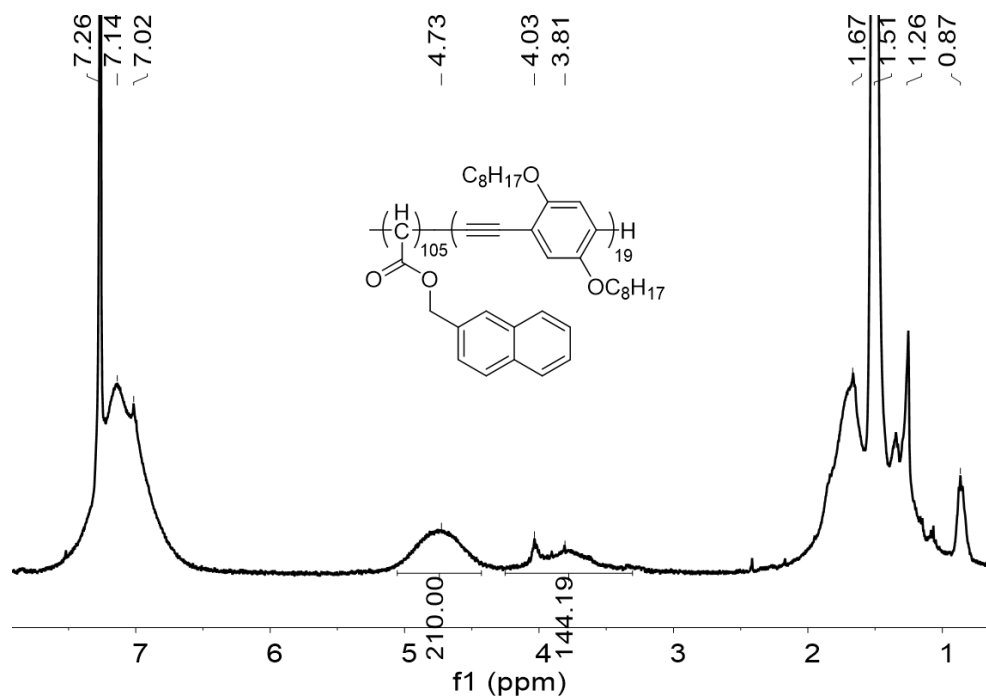


Fig. S20. ^1H NMR (400 MHz) spectra of R -poly($\mathbf{1}_{105}$ - b - $\mathbf{2}_{19}$) recorded in CDCl_3 at room temperature.

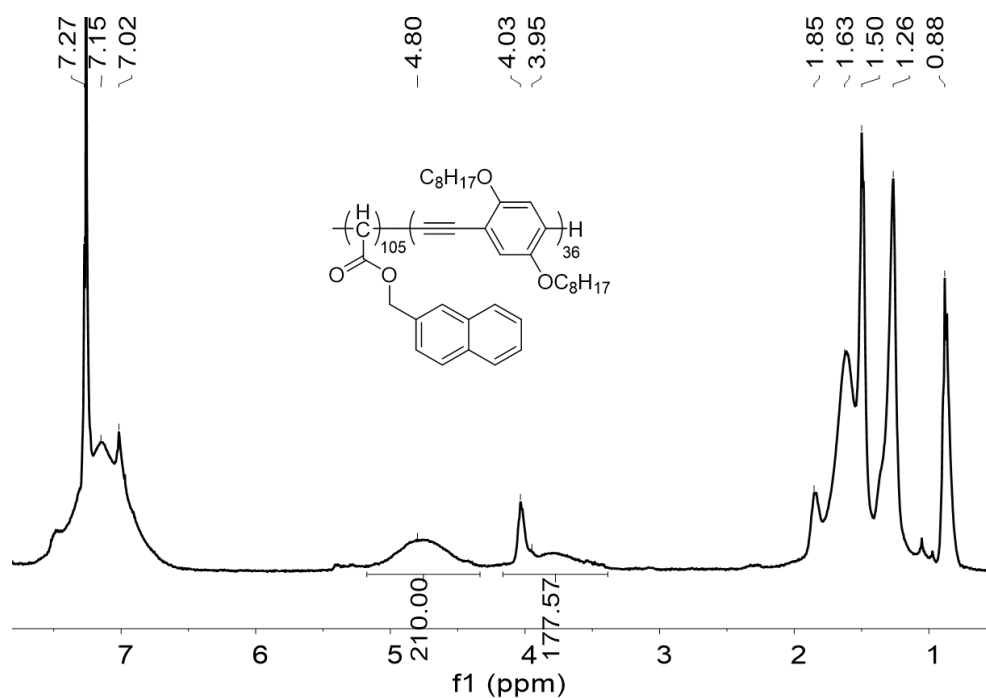


Fig. S21. ^1H NMR (400 MHz) spectra of R -poly($\mathbf{1}_{105}$ - b - $\mathbf{2}_{36}$) recorded in CDCl_3 at room temperature.

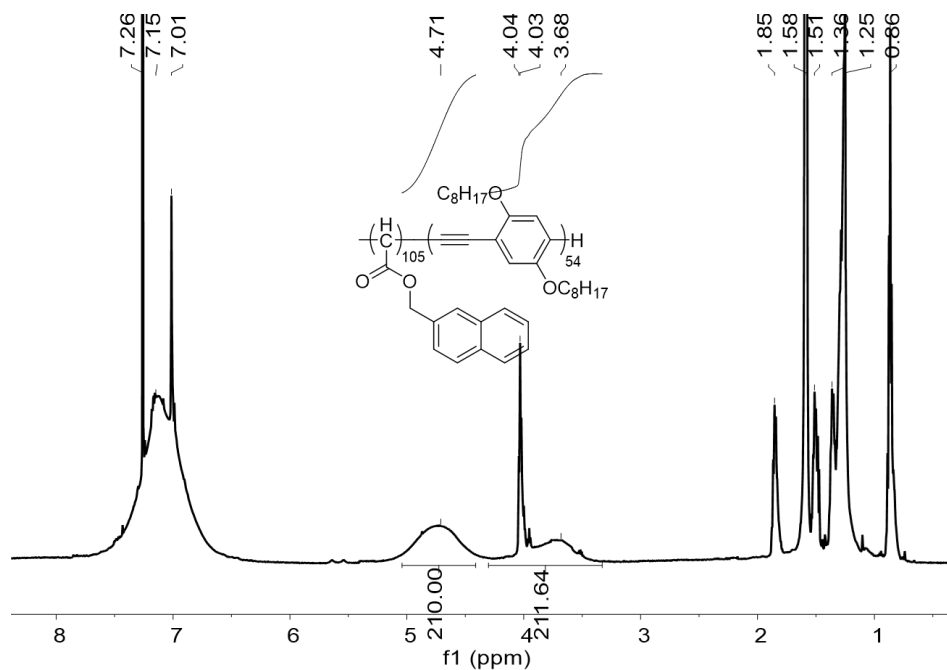


Fig. S22. ^1H NMR (400 MHz) spectra of R -poly($\mathbf{1}_{105}$ - b - $\mathbf{2}_{54}$) recorded in CDCl_3 at room temperature.

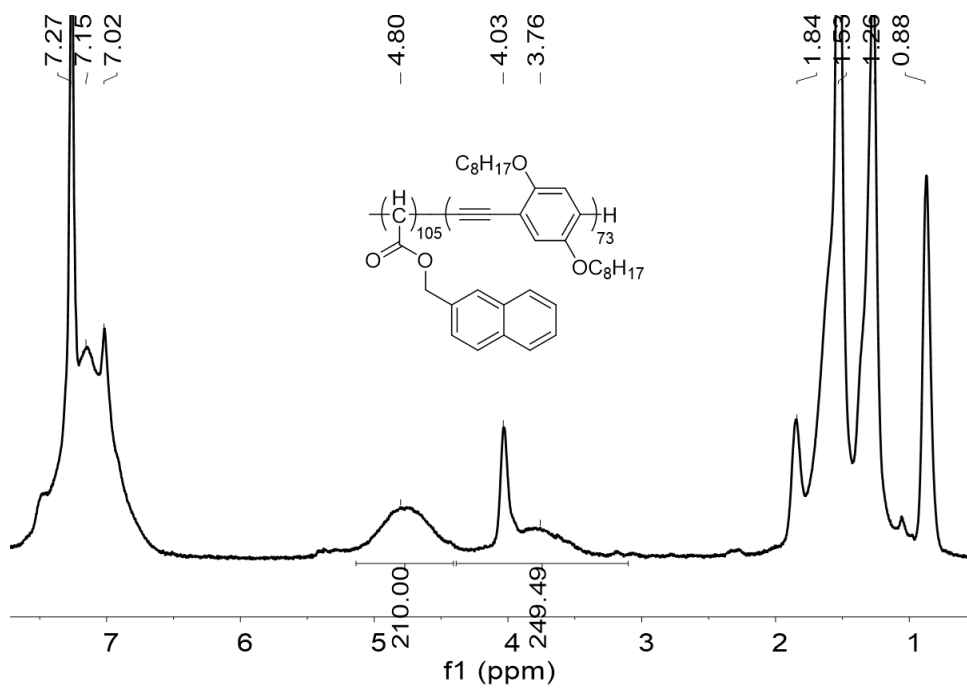


Fig. S23. ^1H NMR (400 MHz) spectra of R -poly($\mathbf{1}_{105}$ - b - $\mathbf{2}_{73}$) recorded in CDCl_3 at room temperature.

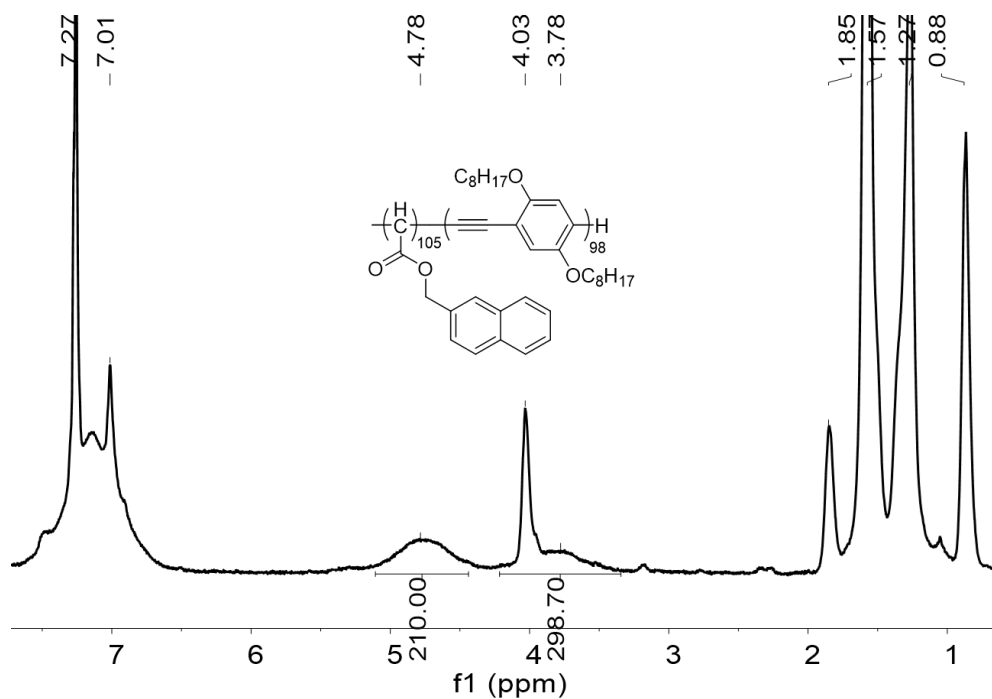


Fig. S24. ^1H NMR (400 MHz) spectra of R -poly($\mathbf{1}_{105}$ - b - $\mathbf{2}_{98}$) recorded in CDCl_3 at room temperature.

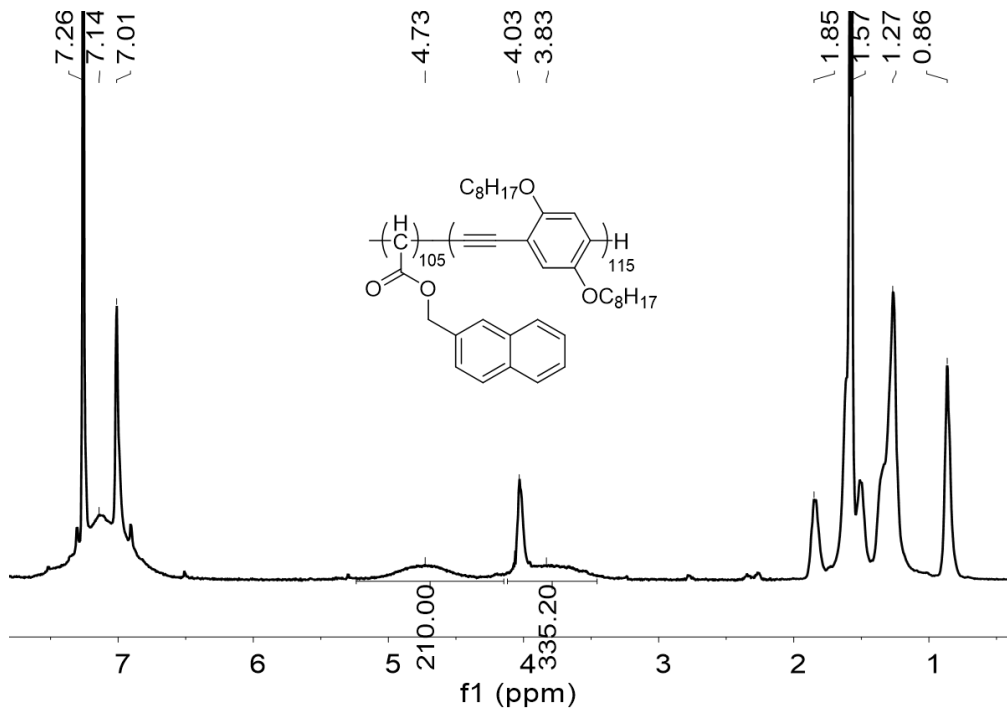


Fig. S25. ^1H NMR (400 MHz) spectra of R -poly($\mathbf{1}_{105}$ - b - $\mathbf{2}_{115}$) recorded in CDCl_3 at room temperature.

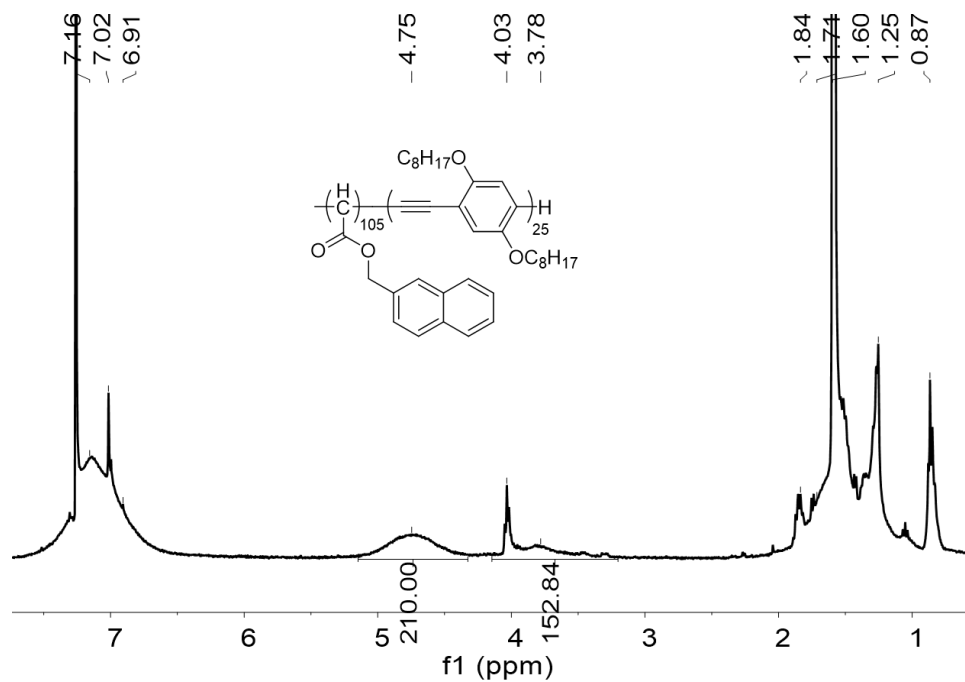


Fig. S26. ¹H NMR (400 MHz) spectra of *S*-poly(**1**₁₀₅-*b*-**2**₂₅) recorded in CDCl₃ at room temperature.

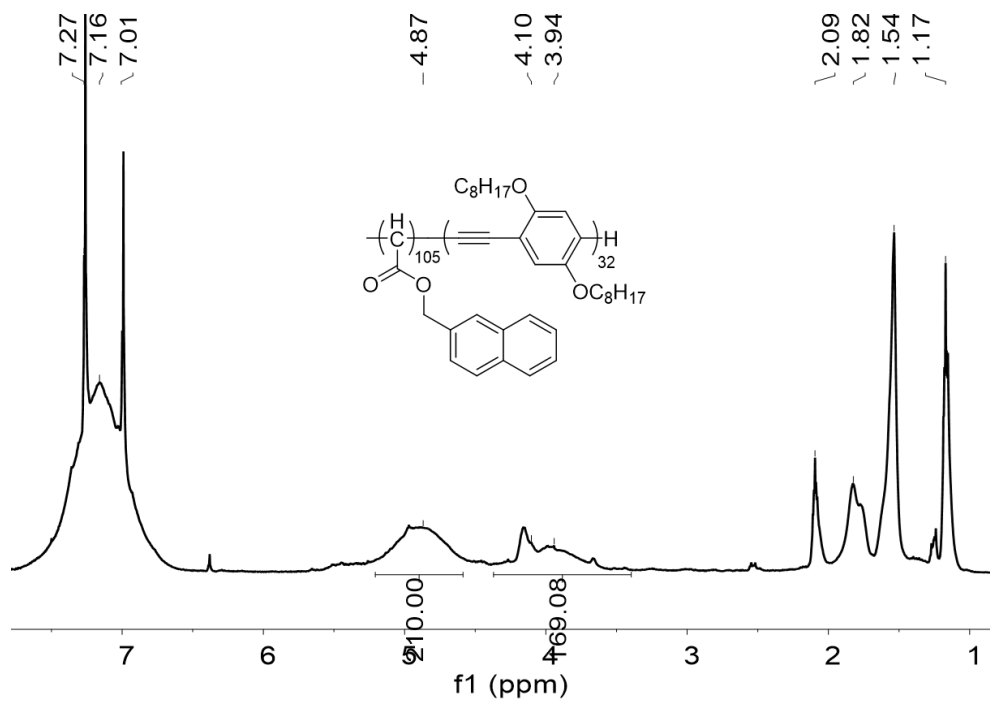


Fig. S27. ¹H NMR (400 MHz) spectra of *S*-poly(**1**₁₀₅-*b*-**2**₃₂) recorded in CDCl₃ at room temperature.

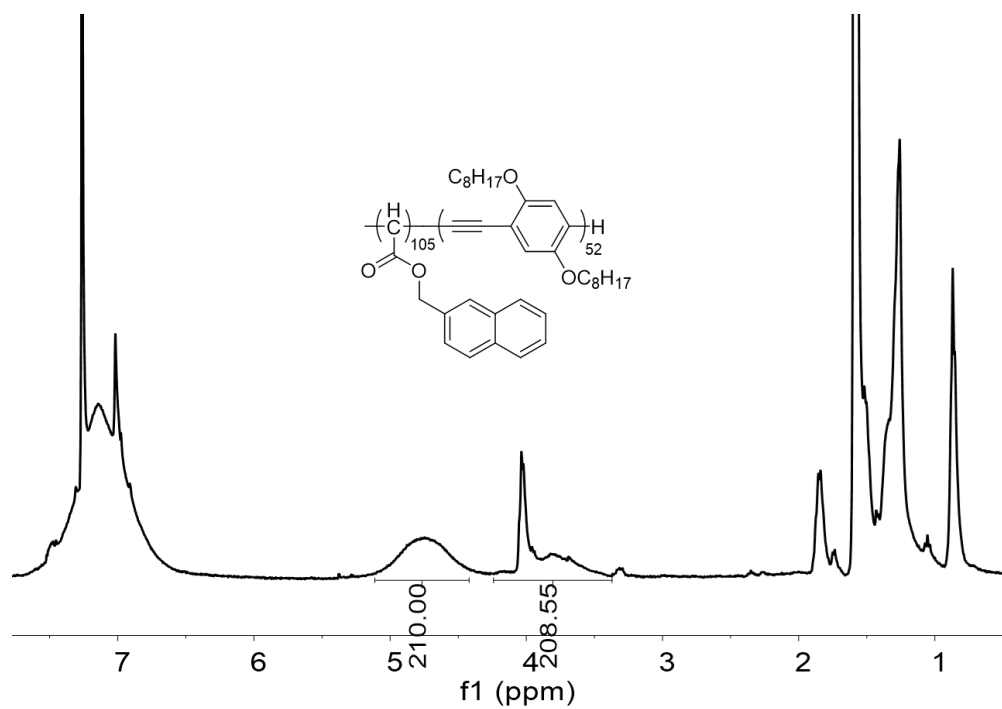


Fig. S28. ^1H NMR (400 MHz) spectra of *S*-poly(**1**₁₀₅-*b*-**2**₅₂) recorded in CDCl_3 at room temperature.

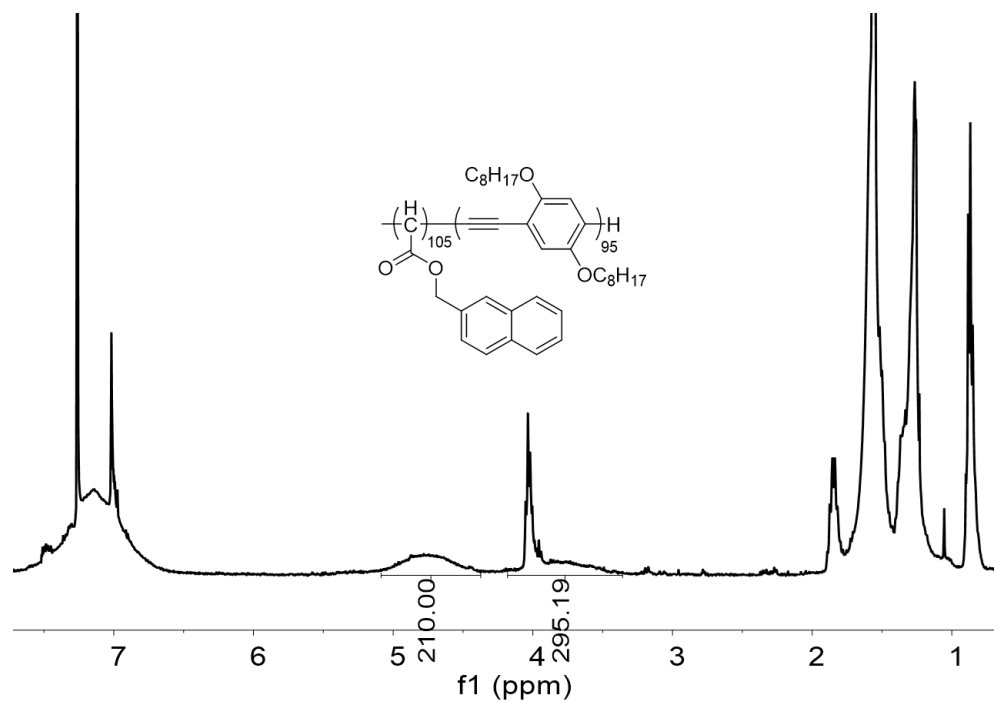


Fig. S29. ^1H NMR (400 MHz) spectra of *S*-poly(**1**₁₀₅-*b*-**2**₉₅) recorded in CDCl_3 at room temperature.

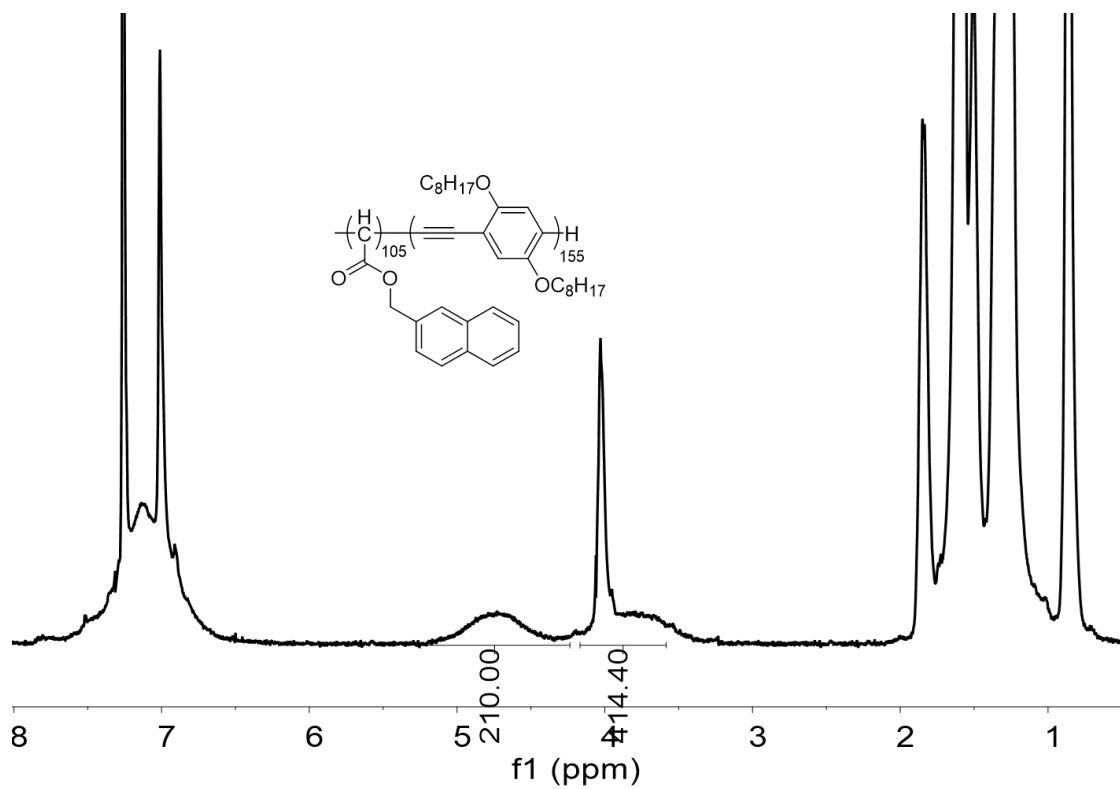


Fig. S30. ¹H NMR (400 MHz) spectra of *S*-poly(**1**₁₀₅-*b*-**2**₁₅₅) recorded in CDCl₃ at room temperature.

References

1. T. Toma, J. Shimokawa, T. Fukuyama, N, N'-Ditosylhydrazine: A Convenient Reagent for Facile Synthesis of Diazoacetates. *Org. Lett.* 2007, **9**, 3195–3197.
2. L. Zhou, X.-H. Xu, Z.-Q. Jiang, L. Xu, B.-F. Chu, N. Liu, Z.-Q. Wu, Selective Synthesis of Single-Handed Helical Polymers from Achiral Monomer and a Mechanism Study on Helix-Sense-Selective Polymerization. *Angew. Chem. Int. Ed.* 2021, **60**, 806–812.
3. M. Su, N. Liu, Q. Wang, H. Wang, J. Yin, Z.-Q. Wu, Facile Synthesis of Poly(phenyleneethynylene)-block-Polyisocyanide Copolymers via Two Mechanistically Distinct, Sequential Living Polymerizations Using a Single Catalyst. *Macromolecules* 2016, **49**, 110–119.
4. W. Zhou, X. Su, M. Tao, C. Zhu, Q. Zhao, J. Zhang, Chiral Sulfinamide Bisphosphine Catalysts: Design, Synthesis, and Application in Highly Enantioselective Intermolecular Cross-Rauhut–Currier Reactions. *Angew. Chem. Int. Ed.* 2015, **54**, 14853–14857.
5. C. Grazon, P. Salas-Ambrosio, E. Ibarboure, A. Buol, E. Garanger, M. W. Grinstaff, S. Lecommandoux, C. Bonduelle, Aqueous Ring-Opening Polymerization-Induced Self - Assembly (ROPISA) of N-Carboxyanhydrides. *Angew. Chem., Int. Ed.* 2020, **59**, 622–626.
6. T. Ikai, M. Okubo, Y. Wada, Helical Assemblies of One-Dimensional Supramolecular

Polymers Composed of Helical Macromolecules: Generation of Circularly Polarized Light Using an Infinitesimal Chiral Source. *J. Am. Chem. Soc.* 2020, **142**, 3254–3261.