

Supporting Information for

**Functional polydiynes prepared by metathesis
cyclopolymerization of 1,7-dihalogen-1,6-heptadiyne
derivatives**

Fulin Yang,^{†a} Zhiming Zhang,^{†a} Jie Zhang,^a Manyu Chen,^a Haoke Zhang,^{a,b} and
Jing Zhi Sun^{*a,b}

- a. MOE Key Laboratory of Macromolecules Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China. E-mail: sunjz@zju.edu.cn
- b. Center for Healthcare Materials, Shaoxing Institute, Zhejiang University, Shaoxing 312000, China

[†] These authors contributed equally.

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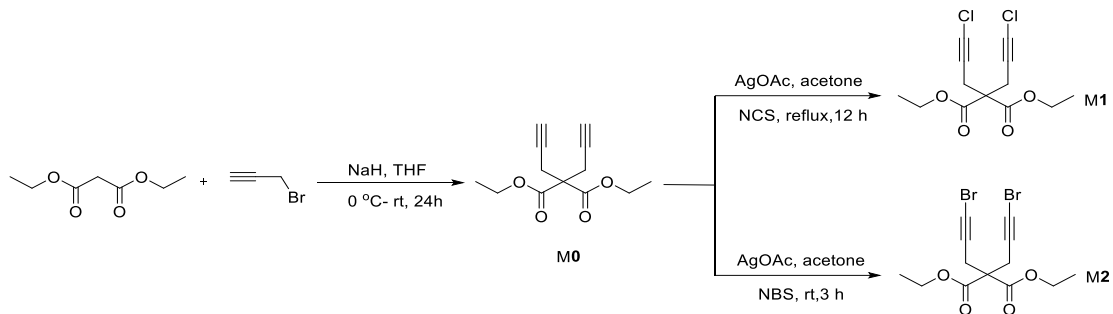
Materials

Unless otherwise noted, all the chemicals and solvents were used directly from commercial without further purification. Silver acetate (AgOAc), N-chlorosuccinimide (NCS), 1,2-dichloroethane (super-dry), palladium chloride, diethyl malonate, diisopropyl malonate, propargyl bromide, sodium hydride, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC.HCl), Dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene] (benzylidene) bis(3-bromopyridine)ruthenium(II) (The 3rd-generation-type Grubbs-catalyst $\text{RuCl}_2(\text{pyridine})_2(\text{IMesH}_2)(\text{CHC}_6\text{H}_5)$) and 4-dimethylaminopyridine (DMAP) were purchased from J&K. Dimethyl dipropargylmalonate and 4-(1,2,2-Triphenylvinyl)phenol were purchased from bidepharmatech. Molybdenum chloride and tungsten chloride were purchased from Aldrich and Tetra-n-butyltin was purchased from Alfa Aesar. Potassium hydroxide and Benzyl alcohol were purchased from Aladdin. Tetrahydrofuran (THF) and toluene were freshly distilled from sodium, benzophenone under nitrogen before use.

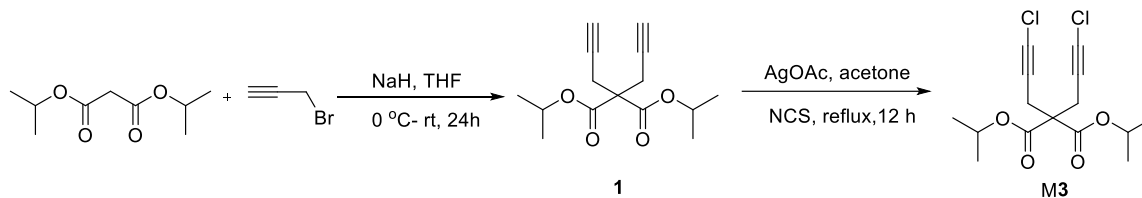
Instrument. Thin-layer chromatography (TLC) analysis was performed by illumination with a UV lamp (254 nm). The molecular weight (M_w and M_n) and polydispersity (M_w/M_n) of the polymers were estimated in THF by a Waters gel permeation chromatography (GPC) system by using a set of monodisperse polystyrene standards covering the molecular weight varying from 10^3 to 10^7 as calibration. FTIR spectra were recorded on a Bruker VECTOR 22 spectrometer. ^1H and ^{13}C NMR spectra were recorded on Bruker AVANCE III 400 spectrometers using CDCl_3 , $\text{DMSO}-d_6$ or CD_2Cl_2 as solvent. High-resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer in MALDI-TOF mode. Thermogravimetric analysis (TGA) was operated on a PerkinElmer TGA7 under nitrogen at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. DSC: Netzsch DSC 200 F3 under nitrogen atmosphere at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. UV-visible absorption spectra were measured with a Shimadzu UV-1800 Spectrophotometer and the transmittance of the samples was detected on a UV-visible spectrophotometer Shimadzu UV-1800 Spectrophotometer equipped with a

temperature controller. PL spectra were measured with an RF-5301 PC spectrofluorometer.

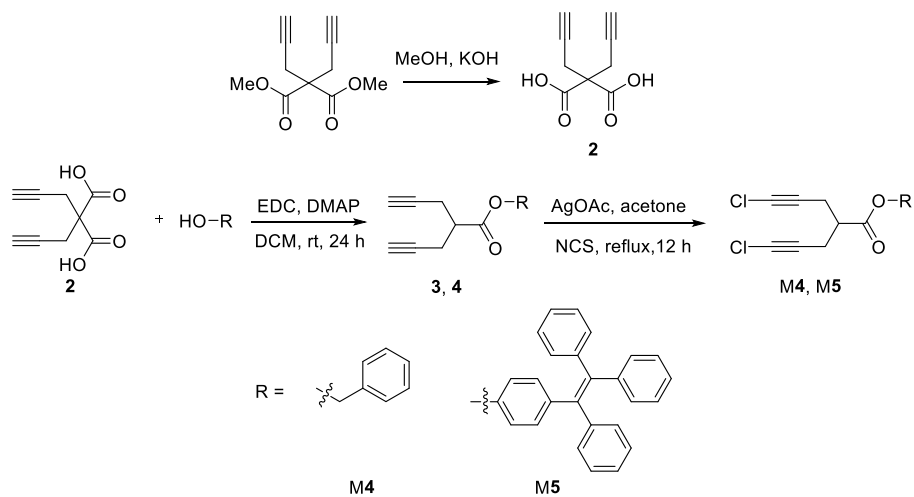
Monomer Preparation



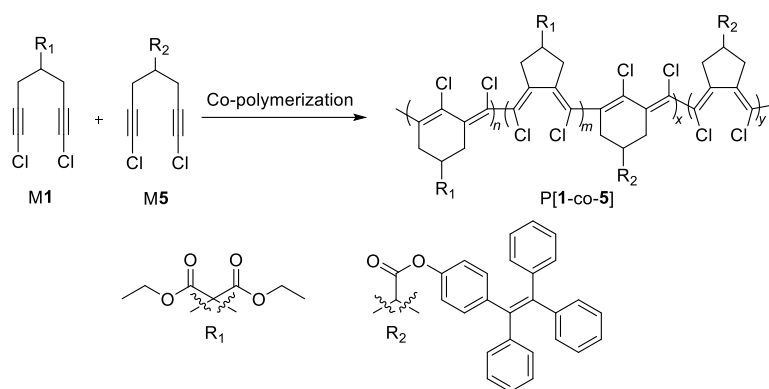
Scheme S1 Synthetic routes to M0-M2.



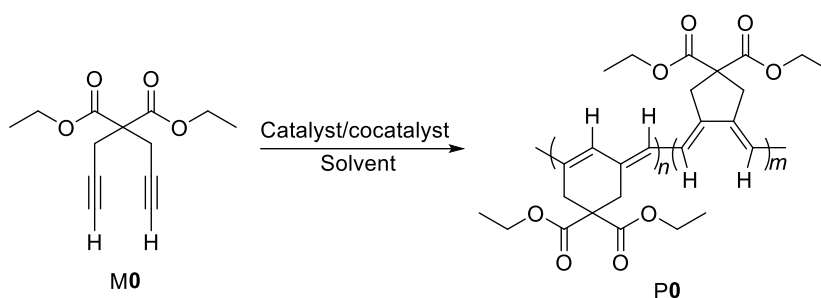
Scheme S2 Synthetic route to M3.



Scheme S3 Synthetic routes to M4 and M5.



Scheme S4 Synthetic route to P[1-co-5].



Scheme S5 Synthetic route to P0.

Table S1 Copolymerization of M1 and M5^a.

Entry	[M1]/[M5]	Yield ^b (%)	M_w^c	PDI ^c
1	1/9	95	98400	1.95

^a The reaction was carried out at 60 °C in 2 mL of DCE for 12 h by MoCl₅/*n*-Bu₄Sn catalyst system, [MoCl₅] = 0.005 mol/L, [*n*-Bu₄Sn] = 0.01 mol/L, [Monomer] = 0.25 mol/L. ^b The product was precipitated from Hexane/DCM (v/v, 120/2); ^c Estimated by GPC in THF against polystyrene (PS) calibration.

Synthetic procedure of M0 and compound 1-5:

Monomer M0 and intermediate reagent 1-4 were obtained by the early reported procedure.^[1-3] The synthetic routes are shown in Schemes S1-S3 and characterization data are shown below.

Diethyl 2,2-di(prop-2-yn-1-yl)malonate (M0): M0 was obtained in the yield of 70% with a colorless solid. ¹H NMR (500 MHz, CDCl₃, δ, ppm): 4.23 (q, 4H, *J* = 7.1 Hz), 2.99 (d, 4H, *J* = 2.6 Hz), 2.03 (t, 2H, *J* = 2.6 Hz), 1.27 (t, 6H, *J* = 7.1 Hz). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 168.60, 78.45, 71.67, 62.09, 56.27, 22.52, 14.02.

Diisopropyl 2,2-di(prop-2-yn-1-yl)malonate (1): The intermediate reagent 2 was

obtained in the yield of 85% with a colorless solid. ¹H NMR (500 MHz, CDCl₃, δ, ppm): 5.09 (hept, *J* = 6.3 Hz, 2H), 2.97 (d, *J* = 2.6 Hz, 4H), 2.02 (t, *J* = 2.6 Hz, 2H), 1.24 (d, *J* = 6.3 Hz, 12H).

2,2-Di(prop-2-yn-1-yl)malonic acid (2) The intermediate reagent **3** was obtained in the yield of 73% with a colorless solid. ¹H NMR (500 MHz, CDCl₃) δ (TMS, ppm): 13.28 (s, 2H), 2.96~2.95 (t, *J* = 2.6 Hz, 4H), 2.76 (d, *J* = 2.7 Hz, 6H).

Benzyl 2-(prop-2-yn-1-yl)pent-4-ynoate (3): The intermediate reagent **4** was obtained in the yield of 80% with a colorless solid. ¹H NMR (500 MHz, CDCl₃) δ (TMS, ppm): 7.38~7.31 (m, 5H), 5.17 (s, 2H), 2.85~2.79 (p, 1H), 2.67~2.64 (m, 4H), 2.00 (t, 2H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 172.17, 135.64, 128.55, 128.32, 128.23, 80.39, 77.34, 77.09, 76.83, 79.69, 66.87, 43.06, 19.92.

4-(1,2,2-Triphenylvinyl)phenyl 2-(prop-2-yn-1-yl)pent-4-ynoate (4): The intermediate reagent **5** was obtained in the yield of 75% with a white solid. ¹H NMR (500 MHz, CDCl₃) δ (TMS, ppm): 7.13-7.08 (m, 9H), 7.04-7.00 (m, 8H), 6.86-6.84 (m, 2H), 3.00-2.95 (p, 1H), 2.75-2.73 (m, 4H), 2.06-2.05 (t, 2H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 170.82, 148.91, 143.55, 143.44, 143.42, 141.50, 141.32, 139.86, 132.31, 131.33, 131.27, 131.26, 127.78, 127.68, 127.63, 126.57, 126.52, 126.47, 120.65, 80.07, 76.75, 70.91, 43.09, 19.95.

Synthetic procedure of M1-M6: monomers M1-M6 were prepared by optimizing synthetic routes of literatures. ^[4,5] The synthetic routes to monomers are shown in Schemes 1-3 and the detailed synthetic procedures are shown below.

Diethyl 2,2-bis(3-chloroprop-2-yn-1-yl)malonate (M1): The compound M1 was chlorinated following a slightly modified version of the reported procedure. Compound **1** (4.72 g, 20 mmol, 1 equiv), NCS (10.68 g, 80 mmol, 4 equiv) and AgOAc (166.91 mg, 8 mmol, 0.4 equiv) were dissolved in 100 mL of acetone under nitrogen atmosphere, and the mixture was heated to reflux overnight. The salts formed during the reaction were removed by filtration and washed several times with dichloromethane (DCM). The mixture was extracted with DCM, washed with brine and water, dried over MgSO₄, and evaporated. The residue was purified by column chromatography (SiO₂, PE/EA = 4:1, v/v) to give a colorless liquid in 67% yield. ¹H NMR (500 MHz, CDCl₃, δ, ppm):

4.26~4.21 (q, $J = 7.1$ Hz, 4H), 2.95 (s, 4H), 1.28~1.25 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3 , δ , ppm): 168.45, 63.89, 62.17, 60.93, 56.39, 23.11, 14.02. HRMS (TOF-MS): calcd. for $[\text{C}_{13}\text{H}_{15}\text{Cl}_2\text{O}_4]^+$ m/z 305.0342, found 305.0346.

Dimethyl 2,2-bis(3-chloroprop-2-yn-1-yl)malonate (M2): The synthetic procedures of M2 are similar with that of M1 and got in the yield of 76% with white solid. ^1H NMR (500 MHz, CDCl_3 , δ , ppm): 4.25~4.21 (q, $J = 7.1$ Hz, 4H), 2.98 (s, 4H), 1.28~1.25 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3 , δ , ppm): 168.38, 74.48, 62.18, 56.30, 41.93, 23.96, 14.04.

Diisopropyl 2,2-bis(3-chloroprop-2-yn-1-yl)malonate (M3): The synthetic procedures of M4 are similar with that of M1 and got in the yield of 95% with white solid. ^1H NMR (500 MHz, CDCl_3 , δ , ppm): 5.08 (hept, $J = 6.3$ Hz, 2H), 2.92 (s, 4H), 1.24 (d, $J = 6.2$ Hz, 12H). ^{13}C NMR (125 MHz, CDCl_3 , δ , ppm): 167.98, 69.72, 64.03, 60.71, 56.31, 23.02, 21.47. HRMS (TOF-MS): calcd. for $[\text{C}_{15}\text{H}_{19}\text{Cl}_2\text{O}_4]^+$ m/z 333.0655, found 333.0657.

Benzyl 5-chloro-2-(3-chloroprop-2-yn-1-yl)pent-4-ynoate (M4): The synthetic procedures of M5 are similar with that of M1 and got in the yield of 76% with white solid. ^1H NMR (500 MHz, CD_2Cl_2) δ (TMS, ppm): 7.37~7.36 (m, 5H), 5.18 (s, 2H), 2.80~2.75 (p, 1H), 2.67~2.57 (m, 4H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ (ppm): 171.97, 135.53, 128.60, 128.33, 128.15, 66.93, 65.69, 59.88, 43.02, 20.42. HRMS (TOF-MS): calcd. for $[\text{C}_{15}\text{H}_{12}\text{Cl}_2\text{O}_2]^+$ m/z 295.0288, found 295.0283.

4-(1,2,2-Triphenylvinyl)phenyl 5-chloro-2-(3-chloroprop-2-yn-1-yl)pent-4-ynoate (M5): The synthetic procedures of M6 are similar with that of M1 and got in the yield of 76% with white solid. ^1H NMR (500 MHz, CDCl_3) δ (TMS, ppm): 7.13~7.08 (m, 9H), 7.05~7.00 (m, 8H), 6.84~6.82 (m, 2H), 2.95~2.92 (p, 1H), 2.71~2.69 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 170.64, 148.82, 143.53, 143.43, 143.39, 141.58, 141.39, 139.84, 132.37, 131.33, 131.28, 131.25, 127.79, 127.70, 127.64, 126.59, 126.54, 126.48, 120.57, 65.42, 60.20, 43.12, 20.47. HRMS (TOF-MS): calcd. for $[\text{C}_{34}\text{H}_{25}\text{Cl}_2\text{O}_2]^+$ m/z 535.1227, found 535.1245.

Polymer Preparation

General Procedure for Polymerization. The polymerization reaction was carried out under dry nitrogen by using the standard glovebox or Schlenk technique except for polymer purification. The catalysts and co-catalysts were stirred in the desired solvent at a pre-set temperature for 20 min, and then a certain amount of monomers solution were added. The mixture was stirred at a pre-set temperature for desired time and the reaction was quenched with nearly 2~4 mL methanol. The resulting polymer was precipitated in nearly 100 mL hexane and wash three times by hexane before filtered and dried under vacuum. A typical procedure for the polymerization of **M1** (Table 1, entry 7) is given below as an example.

M1 (1.53 mg, 0.05 mmol) was placed into a 10 mL Schlenk tube 1. After being evacuated and refilled with nitrogen (99.999%) three times, 1 mL of 1, 2-dichloroethane (DCE) was injected into tube 1 to prepare the solution of **M1**. MoCl₅ (2.8 mg, 0.01 mmol) and *n*-Bu₄Sn (3.5 mg, 0.02 mmol) were weighed in the glove box and placed into a 10 mL Schlenk tube 2. Then removed tube 2 from the glove box and injected DCE (1mL) into this tube under a nitrogen atmosphere to prepare the solution of catalyst system. The solution of catalyst system was stirred at 60 °C for 20 min, then the solution of **M1** was added. The mixture was stirred at 60 °C for 24 h. After cooling down to room temperature, the resultant solution was precipitated in 202 mL of hexane/DCE (100/1, v/v) under stirring. The precipitate was filtrated and washed with hexane (50 mL) three times. The resultant product was dried to a constant weight, affording a fluffy and white solid.

The characterization data of resultant polymers **P1-P5** are shown below.

Characterization Data of P0: The molecular weight (M_w) is 137000 and the polydispersion index (PDI) is 1.36. IR (KBr), ν (cm⁻¹): 2957, 2925, 2855, 1738, 1462, 1440, 1368, 1301, 1255, 1186, 1160, 1096, 1072, 1050, 1018, 950, 891, 861, 825, 797. ¹H NMR (600 MHz, CDCl₃) δ (TMS, ppm): 6.94~6.17, 4.56~3.97, 3.73~2.82, 1.55~0.99. ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 171.92, 170.82, 136.94, 123.14, 61.89, 58.18, 57.26, 54.34, 41.45, 40.11, 32.24, 30.17, 14.12, 14.09, 14.06, 14.01.

Characterization Data of P1: IR (KBr), ν (cm⁻¹): 2986, 2923, 2850, 1740, 1445, 1299, 1254, 1189, 1162, 1114, 1071, 1056, 1010, 861, 809. ¹H NMR (600 MHz, CDCl₃) δ

(TMS, ppm): 4.45~3.93, 3.92~2.50, 1.35~1.09. ^{13}C NMR (150 MHz, CDCl_3) δ (ppm): 170.41, 169.36, 135.66, 127.19, 124.65, 61.94, 58.00, 53.70, 52.80, 42.56, 35.28, 33.79, 14.04.

Characterization Data of P2: IR (KBr), ν (cm^{-1}): 2928, 2853, 1740, 1464, 1444, 1367, 1298, 1255, 1188, 1163, 1097, 1072, 1055, 1014, 946, 861, 790, 713. ^1H NMR (600 MHz, CDCl_3) δ (TMS, ppm): 4.42~3.97, 3.68~2.71, 1.52~1.01. ^{13}C NMR (150 MHz, CDCl_3) δ (ppm): 170.47, 169.61, 137.98, 132.04, 123.37, 118.89, 114.35, 61.95, 57.69, 53.89, 43.62, 42.39, 38.96, 34.43, 14.12.

Characterization Data of P3: IR (KBr), ν (cm^{-1}): 2979, 2933, 2869, 1732, 1466, 1376, 1261, 1194, 1147, 1105, 1069, 1051, 914, 825, 812. ^1H NMR (500 MHz, CDCl_3) δ (TMS, ppm): 5.11~4.91, 3.85~2.65, 1.36~1.07. ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 169.90, 135.98, 127.20, 124.43, 69.29, 58.01, 42.59, 21.53.

Characterization Data of P4: IR (KBr), ν (cm^{-1}): 3034, 2958, 2921, 2856, 1737, 1497, 1455, 1380, 1344, 1275, 1256, 1197, 1166, 1084, 1040, 1018, 907, 808, 750, 698. ^1H NMR (500 MHz, CD_2Cl_2) δ (TMS, ppm): 7.61~7.11, 5.30~4.95, 3.60~2.44. ^{13}C NMR (125 MHz, CD_2Cl_2) δ (ppm): 174.17, 172.85, 137.66, 136.53, 128.91, 128.53, 125.13, 66.95, 41.23, 39.10, 32.93.

Characterization Data of P5: IR (KBr), ν (cm^{-1}): 3078, 3060, 3030, 2958, 2928, 2856, 1758, 1599, 1575, 1502, 1443, 1358, 1277, 1197, 1166, 1144, 1104, 1076, 1033, 1017, 999, 977, 916, 880, 876, 809, 764, 745, 699. ^1H NMR (500 MHz, CDCl_3) δ (TMS, ppm): 7.17~6.84, 6.84~6.50, 3.72~2.22. ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 172.36, 172.19, 149.03, 143.58, 141.34, 139.90, 136.72, 136.19, 132.34, 131.30, 127.67, 126.59, 124.62, 120.61, 41.08, 38.58, 31.06.

Characterization Data of P[1-co-5]: IR (KBr), ν (cm^{-1}): 2985, 2932, 2861, 1740, 1600, 1502, 1466, 1446, 1392, 1367, 1296, 1256, 1187, 1166, 1114, 1097, 1076, 1056, 1016, 861, 813, 764, 750, 702. ^1H NMR (500 MHz, CDCl_3) δ (TMS, ppm): 7.16~6.68, 4.34~4.19, 3.74~2.63, 1.92~1.44, 1.34~1.04. ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 170.52, 170.20, 143.58, 143.45, 141.31, 139.89, 135.65, 132.25, 131.26, 128.06, 127.77, 127.67, 127.63, 126.52, 124.63, 120.67, 61.94, 57.88, 43.25, 42.63, 14.03.

Structural Characterization

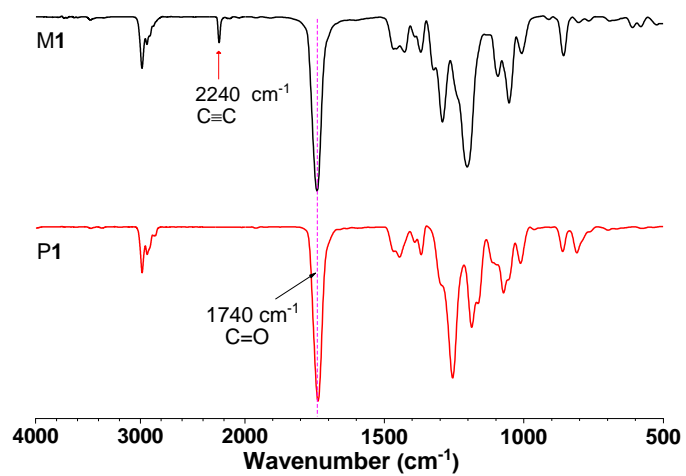


Figure S1 FT-IR spectra of M1 and P1.

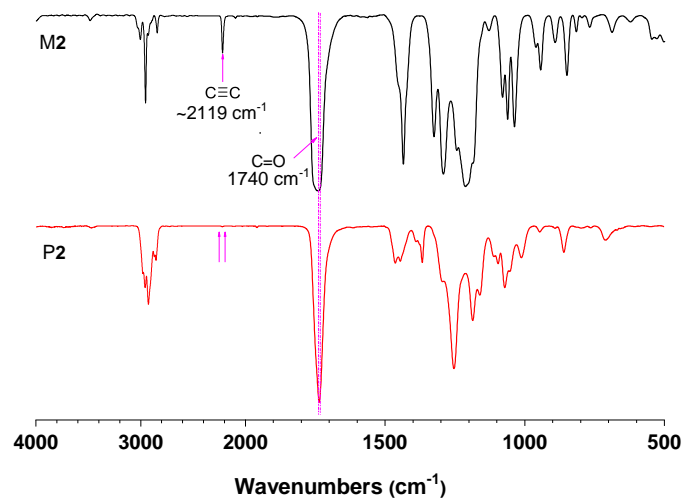


Figure S2 FT-IR spectra of M2 and P2.

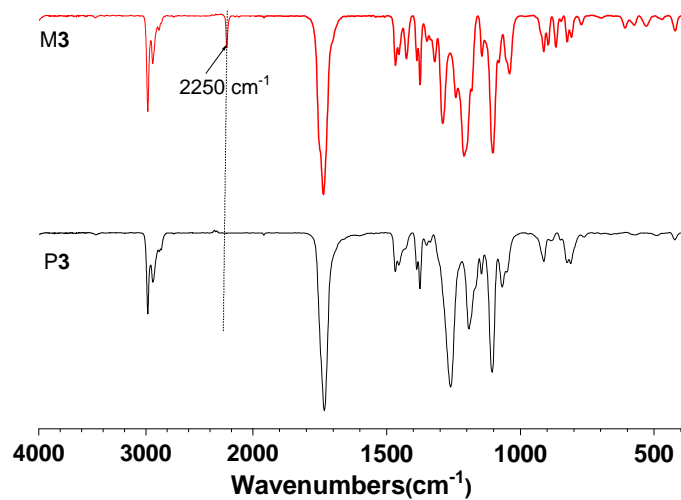


Figure S3 FT-IR spectra of M3 and P3.

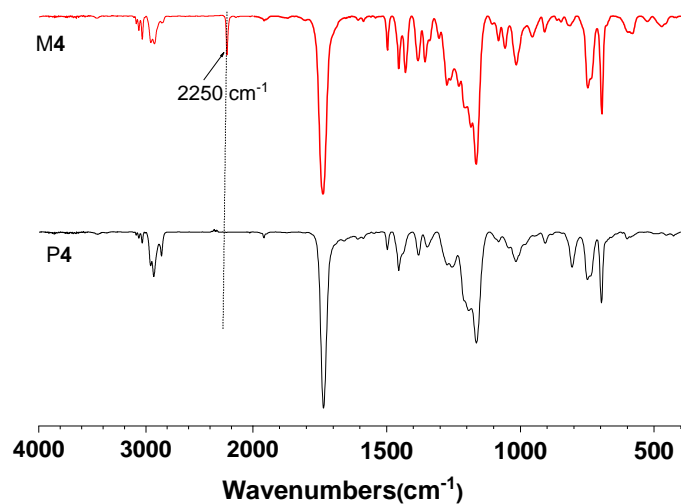


Figure S4 FT-IR spectra of M4 and P4.

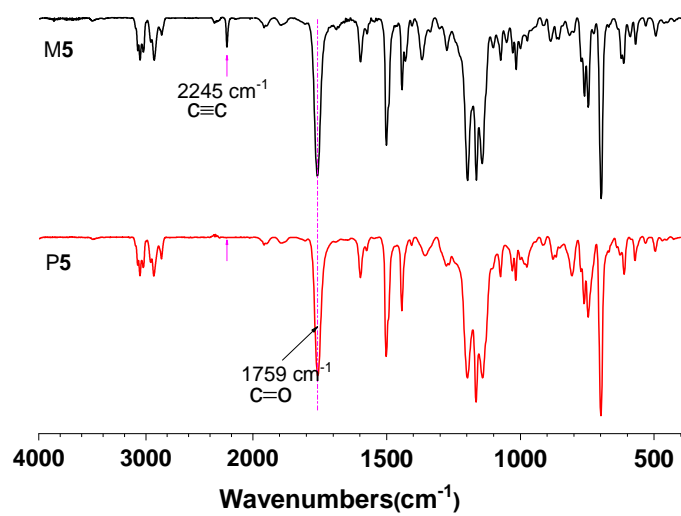


Figure S5 FT-IR spectra of M5 and P5.

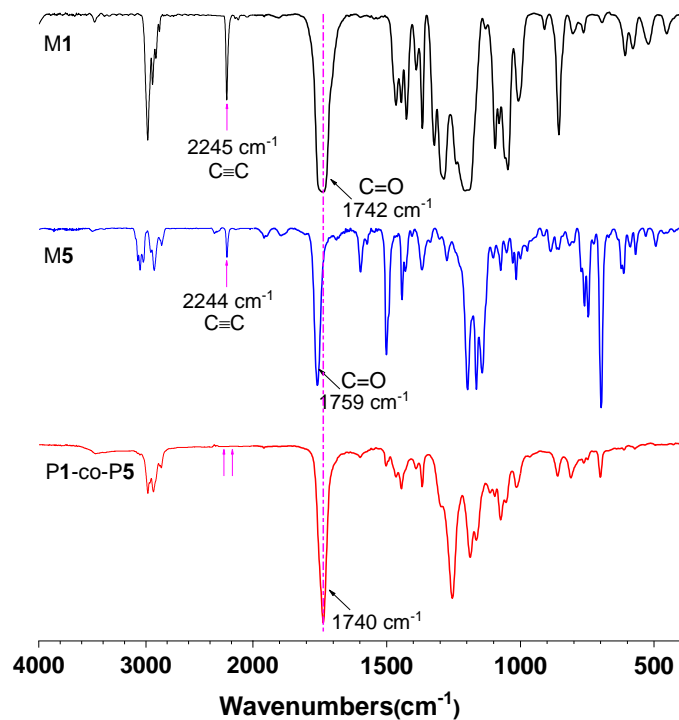


Figure S6 FT-IR spectra of M1, M5 and P[1-co-5].

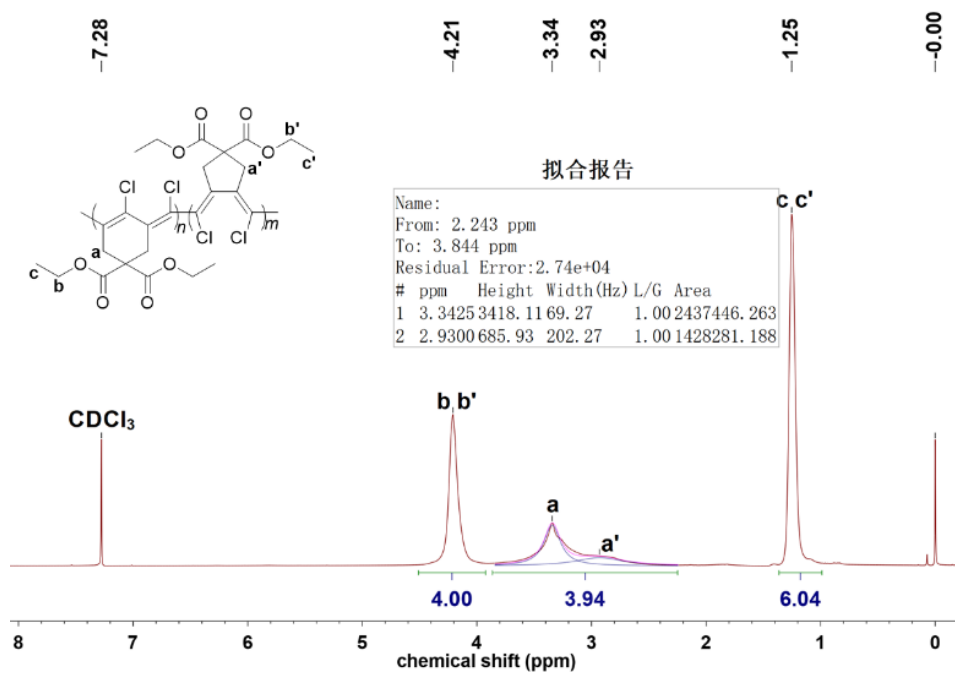


Figure S7 ¹H NMR spectrum of P1 in CDCl₃ with NMR signal integration.

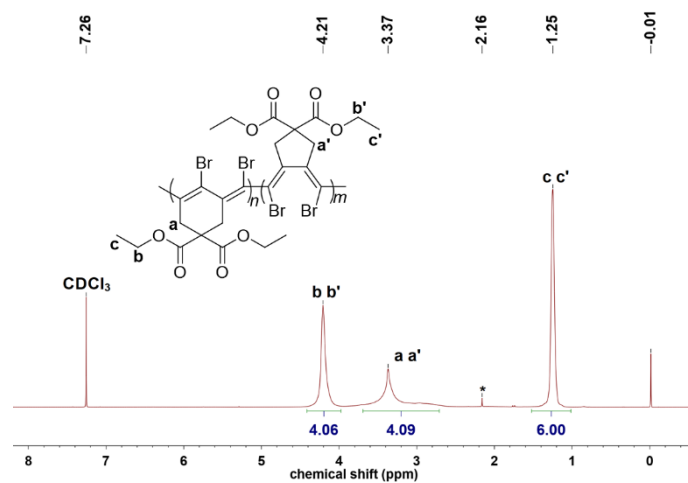


Figure S8 ^1H NMR spectrum of P2 in CDCl_3 .

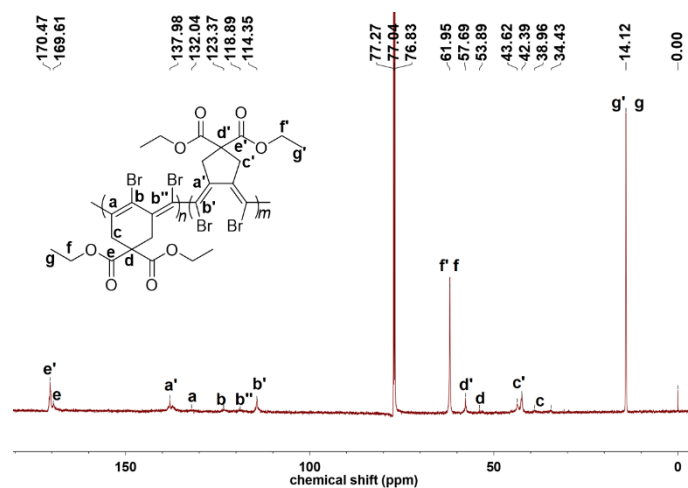


Figure S9 ^{13}C NMR spectrum of P2 in CDCl_3 .

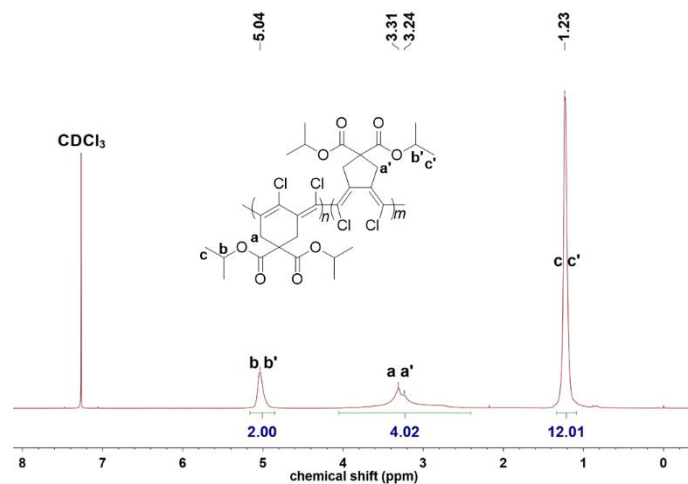


Figure S10 ^1H NMR spectrum of P3 in CDCl_3 .

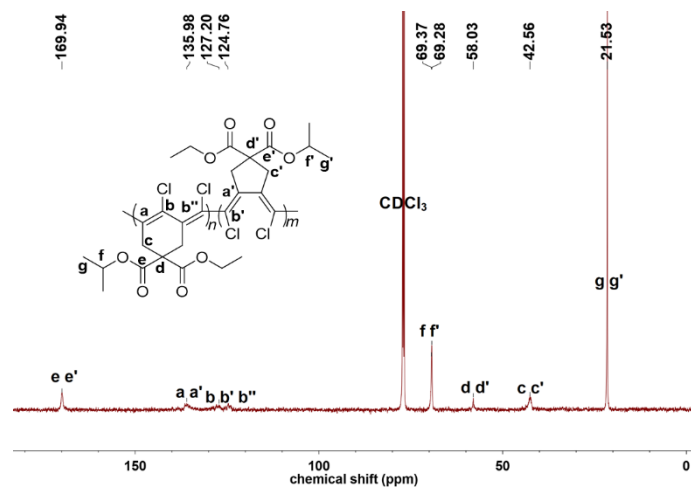


Figure S11 ^{13}C NMR spectrum of P3 in CDCl_3 .

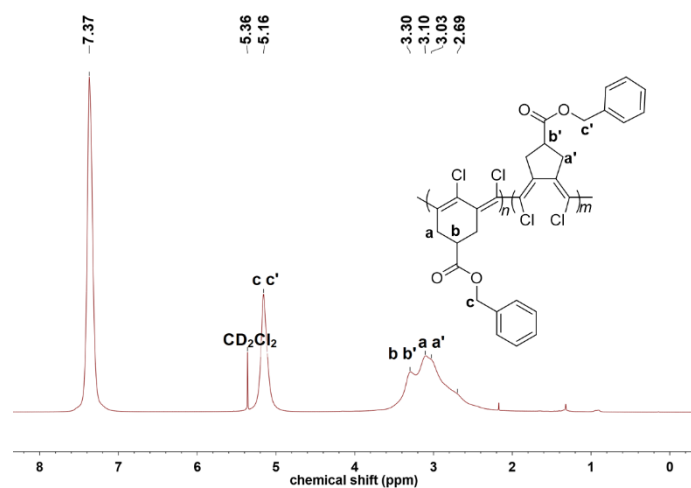


Figure S12 ^1H NMR spectrum of P4 in CD_2Cl_2 .

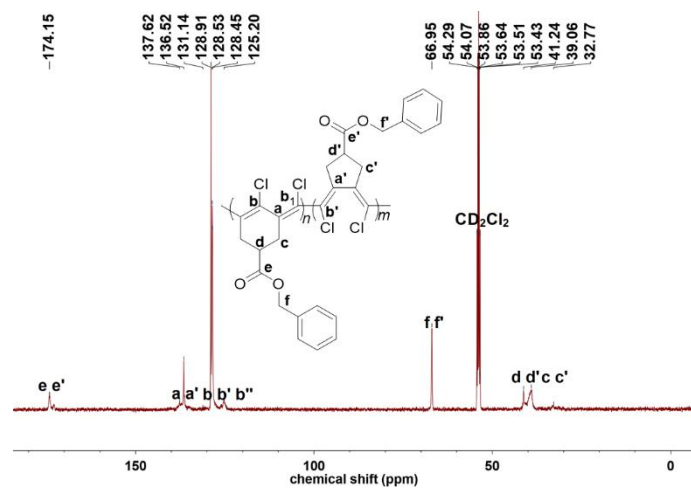


Figure S13 ^{13}C NMR spectrum of P4 in CD_2Cl_2 .

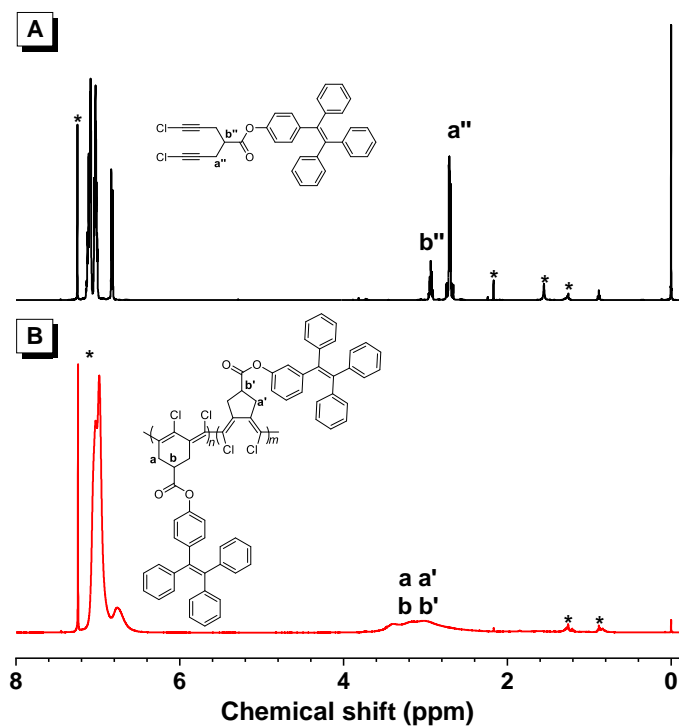


Figure S14 ^1H NMR spectra of M5 (A) and P5 (B) in CDCl_3 . The solvent peaks are marked with asterisks.

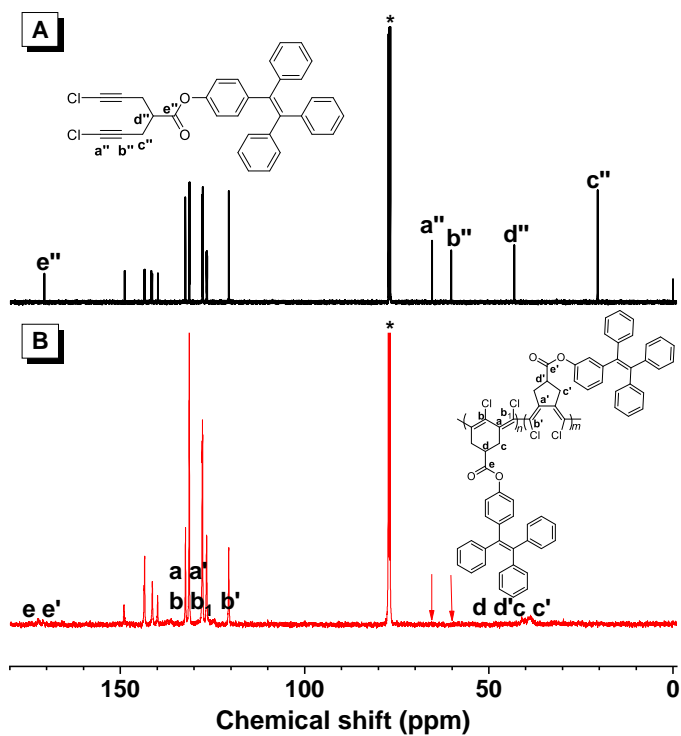


Figure S15 ^{13}C NMR spectra of M5 (A) and P5 (B) in CDCl_3 . The solvent peaks are marked with asterisks.

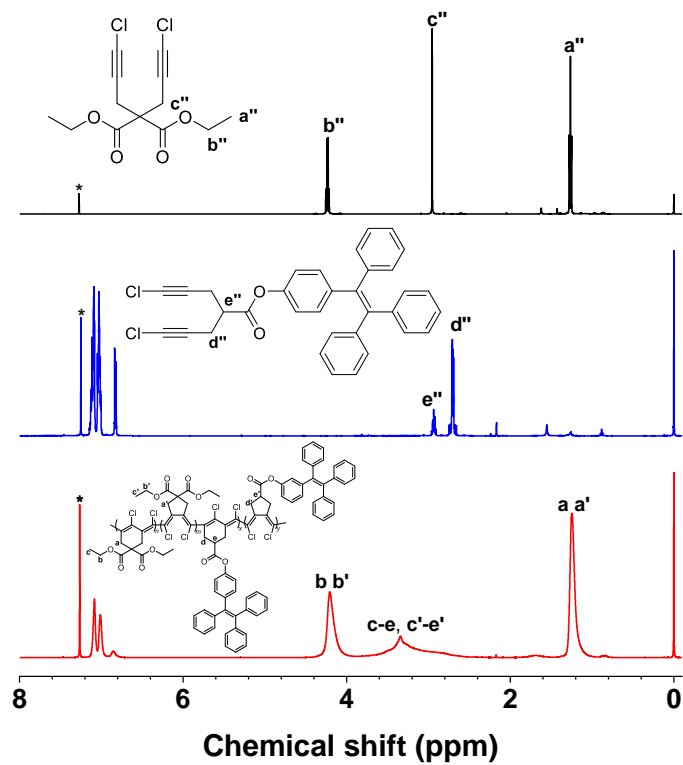


Figure S16 ^1H NMR spectra of M1, M5 and P(1-co-5) in CDCl_3 .

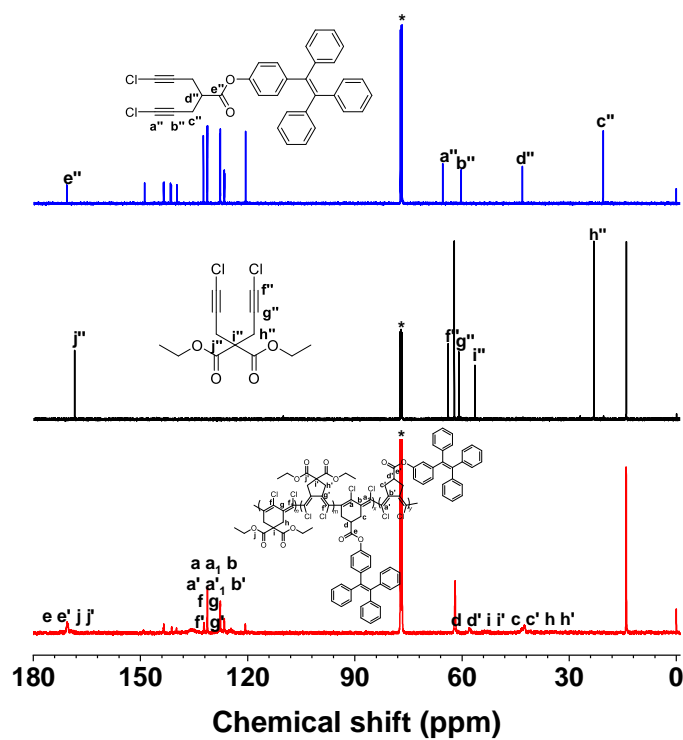


Figure S17 ^{13}C NMR spectra of M1, M5 and P(1-co-5) in CDCl_3 .

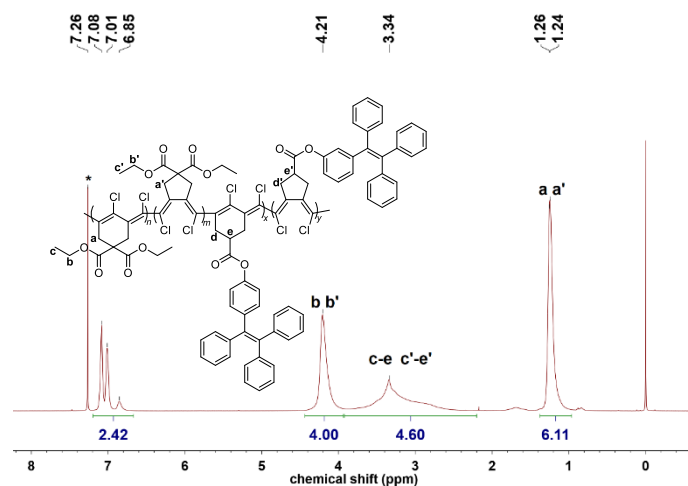


Figure S18 ¹H NMR spectra of P[1-co-5] in CDCl₃ with NMR signal integration of each monomer unit.

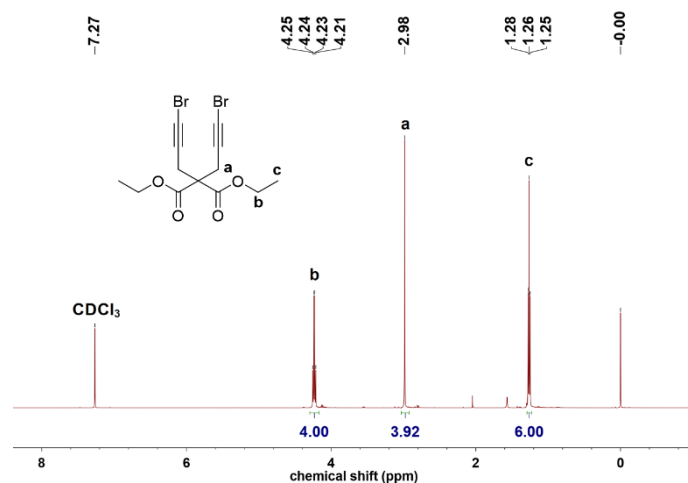


Figure S19 ¹H NMR spectra of M2 in CDCl₃.

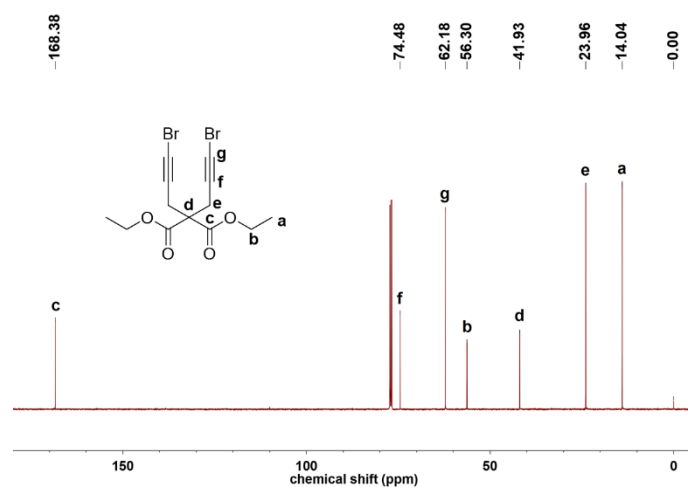


Figure S20 ¹³C NMR spectra of M2 in CDCl₃.

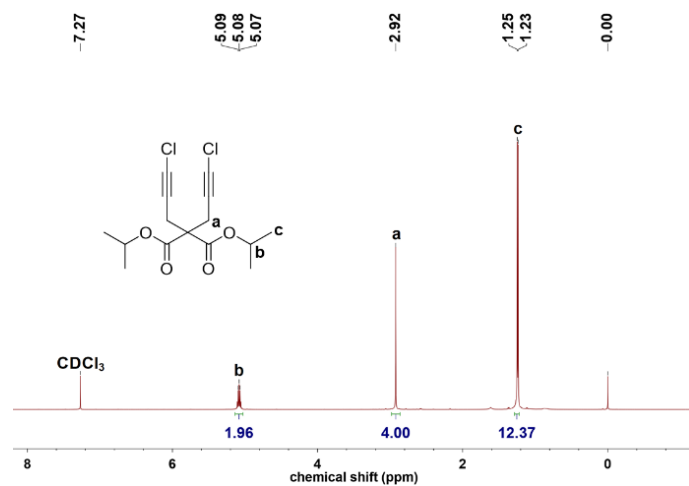


Figure S21 ^1H NMR spectrum of M3 in CDCl_3 .

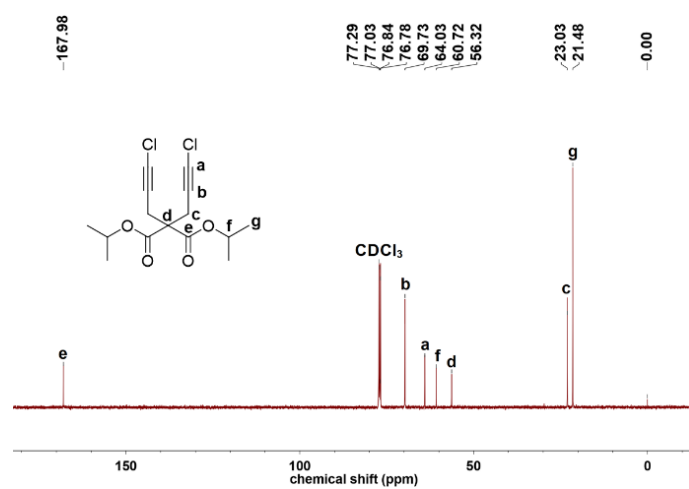


Figure S22 ^{13}C NMR spectrum of M3 in CDCl_3 .

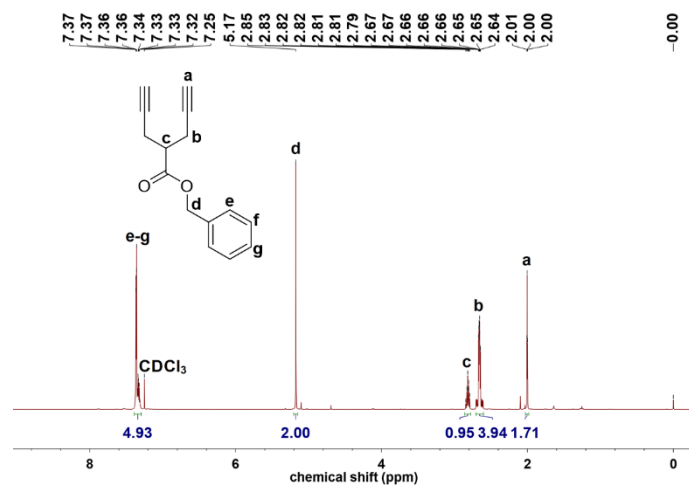


Figure S23 ^1H NMR spectrum of 3 in CDCl_3 .

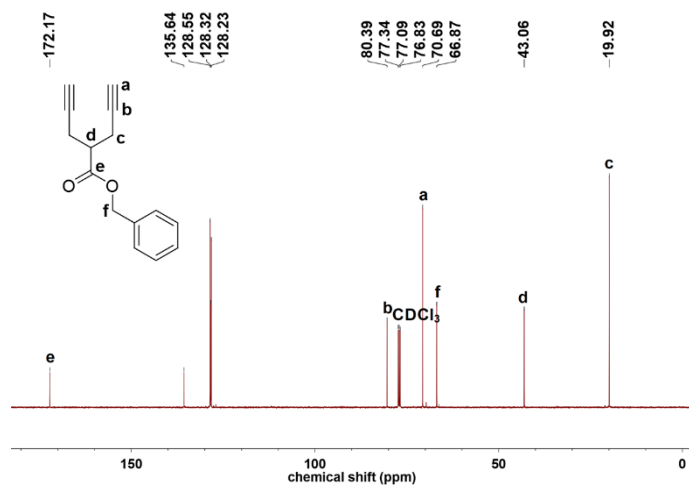


Figure S24 ¹³C NMR spectrum of **3** in CDCl₃.

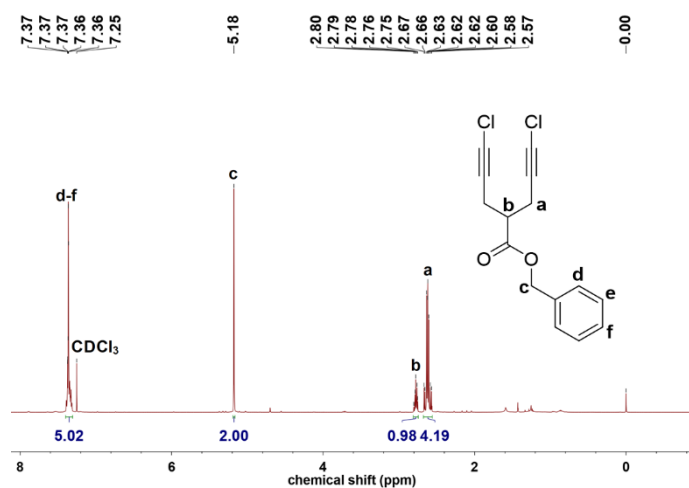


Figure S25 ¹H NMR spectrum of **M4** in CDCl₃.

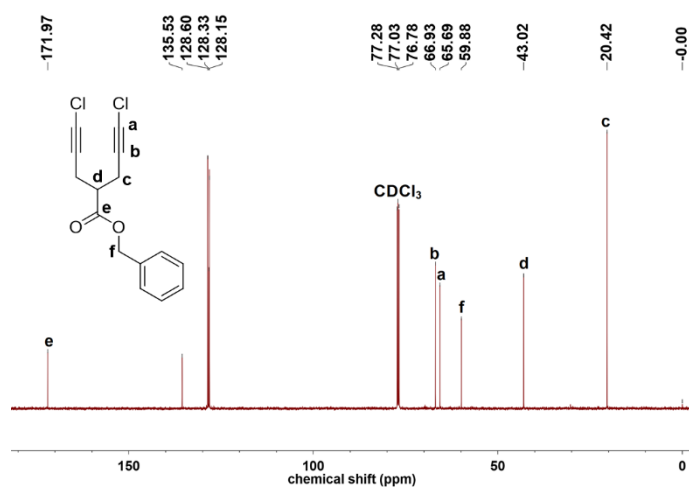


Figure S26 ¹³C NMR spectrum of **M4** in CDCl₃.

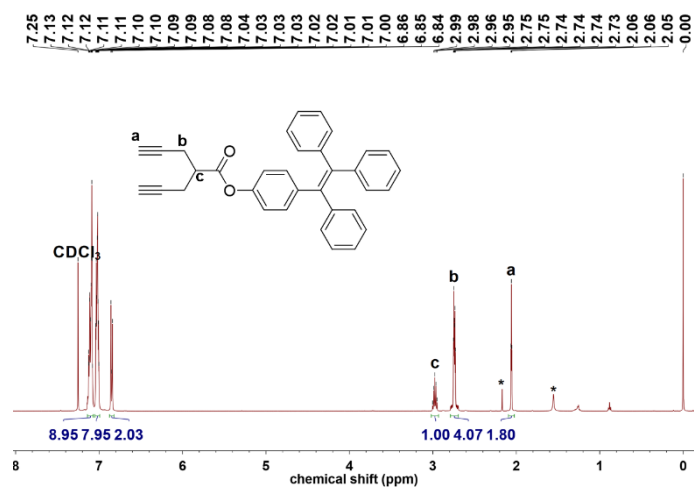


Figure S27 ^1H NMR spectrum of 4 in CDCl_3 .

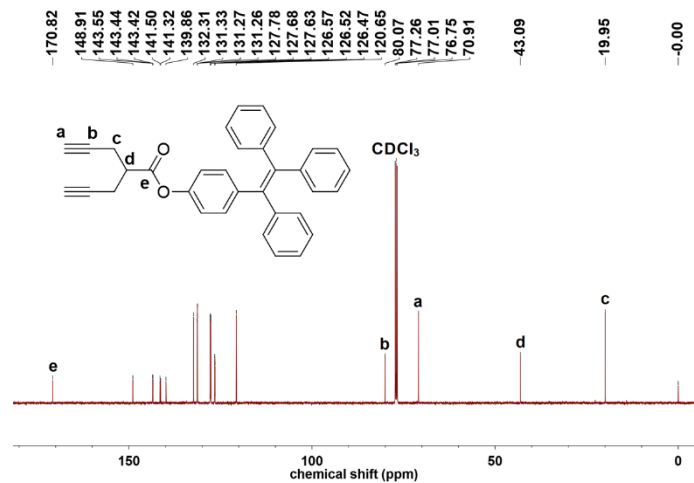


Figure S28 ^{13}C NMR spectrum of 4 in CDCl_3 .

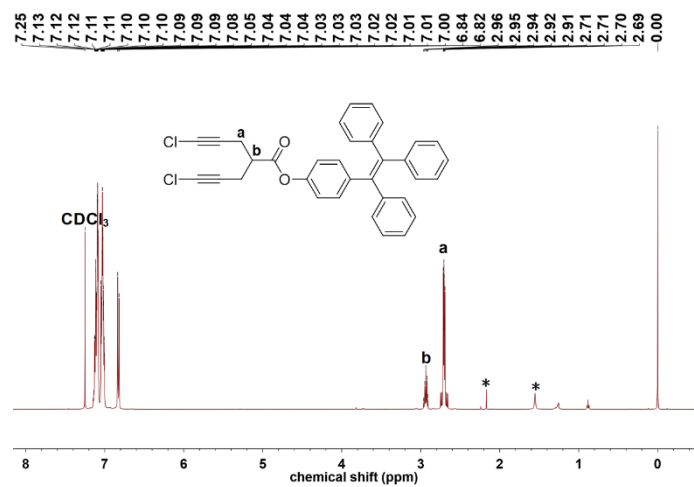


Figure S29 ^1H NMR spectrum of M5 in CDCl_3 .

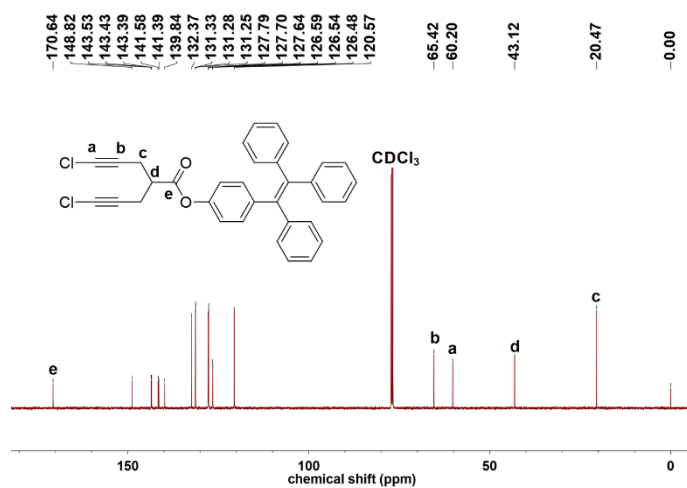


Figure S30 ¹³C NMR spectrum of M5 in CDCl₃.

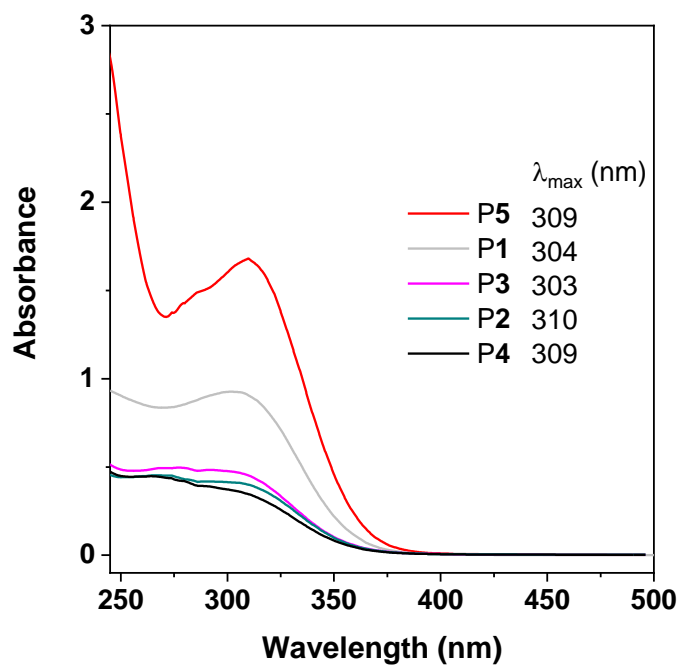


Figure S31 Absorption spectra of monomers P1-P5 (10^{-4} M) in DCM.

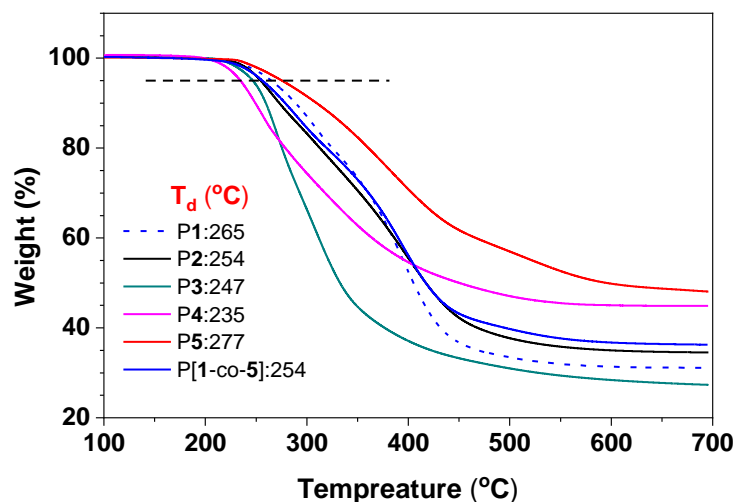


Figure S32 TGA thermograms of P1-P5 and P[1-co-5]. T_d represents the temperature of 5% weights loss.

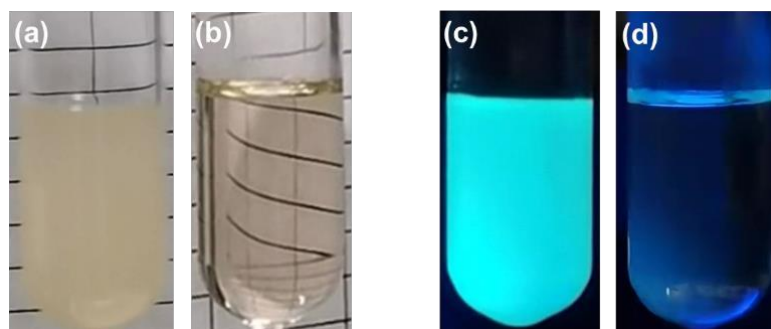


Figure S33 Photographs of P5 taken under daylight (a) 30 °C, (b) 120 °C and illumination by 365 nm UV light (c) 30 °C, (d) 120 °C.

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