Electronic Supporting Information for

Facile synthesis of well-defined ABC miktoarm star terpolymers bearing poly(*ε*-caprolactone), polystyrene and stereoregular helical poly(phenyl isocyanide) blocks

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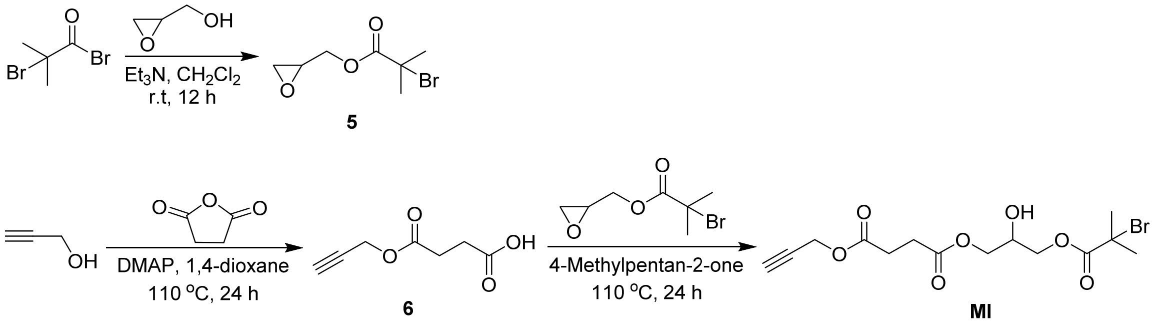
Instruments.

The ^{1}H, ^{13}C NMR spectra were recorded using a Bruker 600 or 400 MHz spectrometer {H}. Size exclusion chromatography (SEC) was performed on Waters 515 pump and Waters 2414 differential refractive index (RI) detector (set at 40 °C) using a series of linear Styragel HR1, HR2 and HR4 columns. Molecular weight (M_n) and its distribution (M_w/M_n) are reported relative to polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 0.3 mL/min. FT-IR spectra were recorded on Perkin-Elmer Spectrum BX FT-IR system using KBr pellets. UV-vis spectra were performed on a UNIC 4802 UV/VIS double beam spectrophotometer in 1.0 cm length quartz cell. Circular dichroism (CD) spectra were obtained in a 1.0 mm quartz cell at 25 °C using a JASCO J1500 spectropolarimeter. Samples for atomic force microscopy (AFM) measurements were prepared by drop casting solutions of the corresponding miktoarm star terpolymers onto mica wafer, placed in covered Petri dishes to slow the evaporation process. AFM images were acquired in tapping mode with a Digital Instruments Dimension 3100 Scanning Probe Microscope, performed at room temperature in air using standard silicon cantilevers with a nominal spring constant of 50 N/m and resonance frequency of ~300 kHz. The images were acquired at a scan frequency of 1 Hz in 1×1 μm^2 scan areas.

Materials

All solvents were purchased from Sinopharm Chem. Reagent Co., Ltd, and were purified by standard procedures before use. *ε*-Caprolactone (*ε*-CL) (Acros Organics, 99%) were dried over calcium hydride for 48 h at room temperature, followed by distillation under reduced pressure just before use. Styrene (St, 99.5%, Beijing Chemical Factory) was successively washed with aqueous NaOH (5.0 wt%) and water, then distilled over CaH_2 under reduced pressure. Pentamethyldiethylenetriamine (PMDETA), 4-dimethylaminopyridine (DMAP), copper(I) bromide (98%), propargyl alcohol (99%), tin(II) 2-ethylhexanoate ($Sn(Oct)_2$, 95%), 2,3-epoxy-1-propanol, and 2-bromoisobutyryl bromide were purchased from Sinopharm, and Aldrich Co. Ltd., and were used as received otherwise denoted. Phenyl isocyanide monomer **3**, and **4** were prepared according to the literatures reported by our group previously, the structures were confirmed by ^{1}H NMR.[1]

Scheme S1. Synthesis of the multifunctional initiator.



Synthesis of 5. A stirring solution of 2,3-epoxy-1-propanol (7.40 g, 0.10 mol,) and triethylamine (10.10 g, 0.10 mol) in CH_2Cl_2 (20 mL) was cooled to 0 °C, and then 2-bromoisobutyryl bromide (23.0 g, 0.10 mol) was added slowly within 1 h. After stirred at 0 °C for 2 h, the solution was warmed to room temperature and stirred overnight. The mixture was washed with water and the organic phases were dried over Na_2SO_4. After filtration, the solvent was removed by evaporation under reduced pressure. The crude product was purified by distillation under vacuum to afford **5** as yellowish oil (15.0 g, 67% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 4.47 (d, $J = 12$ Hz, 2H, CO_2CH_2), 4.08 (dd,

J_1 = 12 Hz, J_2 = 6 Hz, 2H, CO_2CH_2), 3.24 (s, 1H, CH), 2.84 (t, J = 6 Hz, 2H, CH_2), 2.69 (s, 2H, CH_2), 1.95 (s, 6H, CH_3).

Synthesis of 6. This compound was prepared according to the reported literature with slight modifications.[2] Propargyl alcohol (6.72 g, 0.12 mol), succinic anhydride (10.0 g, 0.10 mol), and DMAP (6.50 g, 52.9 mmol) were dissolved in dry 1,4-dioxane (50 mL). The mixture was refluxed for 24 h and then cooled to room temperature. The solvent was removed by evaporation under reduced pressure. The residue was dissolved in CH_2Cl_2 and washed with aqueous solution of 1 M HCl. The organic phase was further washed with deionized water until the pH = 7 and then dried over Na_2SO_4. After filtration, the solvent was removed by evaporation under reduced pressure. The product was isolated as a brown solid (8.30 g, 53% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 4.69 (d, J = 6 Hz, 2H, OCH_2), 2.69 (dd, J_1 = 18 Hz, J_2 = 6 Hz, 4H, CH_2), 2.50 (s, 1H, CH).

Synthesis of MI. A mixed solution of **5** (2.23 g, 10.0 mmol,) and **6** (2.34 g, 15.0 mmol) in iso-butyl methyl ketone (3 mL) was refluxed for 24 h. After cooled to room temperature, the solvent was removed by evaporation under reduced pressure. The crude product was dissolved in CH_2Cl_2 and washed with aqueous solution of NaOH (wt 10%) and deionized water until the pH = 7. The organic phase was dried over Na_2SO_4, filtered, and evaporated to dryness. The crude product was purified by silica gel chromatography (eluent: *n*-hexane/ethyl acetate = 3/2, v/v). The product was isolated as a viscous and brown liquid (2.20 g, 58% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 4.69 (d, J = 6 Hz, 2H, $C{\equiv}CCH_2$), 4.15–4.27 (m, 4H, $C\underline{H_2}CHC\underline{H_2}$), 3.80 (m, 1H, CH), 2.72–2.66 (m, 4H, CH_2), 2.48 (s, 1H, $C{\equiv}CH$), 1.90 (s, 6H, CH_3). FT-IR (KBr, 25 °C, cm^{-1}): 3187 (ν_{C-H}), 2969 (ν_{C-H}), 2128 ($\nu_{C\equiv C}$), 1736 ($\nu_{C=O}$). MS m/z calcd for $C_{14}H_{18}O_7Br$ $(M-H)^-$: 377.0300; Found: 377.0274. Anal. Calcd (%) for $C_{14}H_{19}O_7Br$: C, 44.34; H, 5.05. Found: C, 44.08; H, 5.27.

Typical procedure for synthesis of poly-1$_{20}$. The polymerization was performed in a glovebox with a water content of less than 0.1 ppm. Into a 10 mL of Schlenk tube, **MI** (0.20 g, 0.53 mmol) and ε-CL monomer **1** (1.20 g, 10.56 mmol) were added ($[\mathbf{1}]_0 = 10.0$ mM, $[\mathbf{1}]_0/[\mathrm{MI}]_0 = 20$), and then Sn(Oct)$_2$ (0.21 g, 0.53 mmol) was added and the solution was stirred at 90 °C for 10 h. After the reaction, the polymerization mixture was diluted with CH_2Cl_2 and precipitated into excess of *n*-hexane. The isolated poly-**1**$_{20}$ was dried in vacuum at room temperature for 24 h (1.20 g, 86% yield). SEC: $M_n = 8.5 \times 10^3$, $M_w/M_n = 1.15$. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 4.67 (d, $J = 6$ Hz, 2H, $C{\equiv}CCH_2$), 4.36–4.14 (m, 4H, $C\underline{H_2}CHC\underline{H_2}$), 4.02 (t, $J = 12$ Hz, 28H, CH_2O), 3.61 (t, $J = 6$ Hz, 2H, $C\underline{H_2}OH$), 2.67–2.58 (m, 4H, CH_2), 2.47 (s, 1H, $HC{\equiv}C$), 2.27 (t, $J = 12$ Hz, 30H, CO_2CH_2), 1.90 (s, 6H, CH_3), 1.64–1.58 (m, 60H, $CO_2CH_2C\underline{H_2}CH_2C\underline{H_2}CH_2O$), 1.39–1.32 (m, 30H, $CO_2CH_2CH_2C\underline{H_2}CH_2CH_2O$). FT-IR (KBr, 25 °C, cm^{-1}): 2950 ($\nu_{C\text{-}H}$), 2860 ($\nu_{C\text{-}H}$), 2098 ($\nu_{C{\equiv}C}$), 1730 ($\nu_{C=O}$).

Synthesis of alkyne mid-functionalized poly(1$_{20}$-b-2$_{20}$). To a Schlenk tube equipped with a magnetic stirring bar, poly-**1**$_{20}$ (0.60 g, $M_n = 8.5 \times 10^3$, $M_w/M_n = 1.15$), monomer **2** (0.55 g, 5.28 mmol), PMDETA (0.05 g, 0.26 mmol), CuBr (0.04 g, 0.26 mmol) and toluene (1.0 mL) were sequentially added. After three times of vacuum-filling nitrogen cycle, the reaction mixture was stirred at 90 °C for 10 h. The polymerization mixture was diluted with CH_2Cl_2 and passed through a basic alumina column to remove the copper catalyst, and then precipitated into excess of methanol. The resulting poly(**1**$_{20}$-*b*-**2**$_{20}$) was dried in vacuum at room temperature for 24 h (0.94 g, 82% yield). SEC: $M_n = 1.1 \times 10^4$, $M_w/M_n = 1.18$. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 7.20–6.95 (br, 51H, ArH, *ortho* and *para* protons of the benzene ring, PS), 6.80–6.46 (br, 34H, ArH, *meta* proton of the benzene ring, PS), 4.69 (d, J = 6 Hz, 2H, $\mathrm{CH{\equiv}CC\underline{H_2}}$), 4.22–4.14 (m, 4H, $\mathrm{C\underline{H_2}CHC\underline{H_2}}$), 4.05 (t, J = 12 Hz, 28H, $\mathrm{OC\underline{H_2}}$, PCL), 3.64 (t, J = 6 Hz, 2H, $\mathrm{C\underline{H_2}OH}$), 2.67–2.59 (m, 4H, $\mathrm{CH_2}$), 2.30 (t, J = 6 Hz, 30H, $\mathrm{CO_2C\underline{H_2}}$, PCL), 1.88 (s, 6H, $\mathrm{C\underline{H_3}}$), 1.67–1.61 (m, 60H, $\mathrm{CO_2CH_2C\underline{H_2}CH_2C\underline{H_2}CH_2O}$, PCL), 1.42–1.35 (m, 30H, $\mathrm{CO_2CH_2CH_2C\underline{H_2}}$, PCL). FT-IR (KBr, 25 °C, $\mathrm{cm^{-1}}$): 2950 ($\nu_{\mathrm{C-H}}$), 2861 ($\nu_{\mathrm{C-H}}$), 2090 ($\nu_{\mathrm{C\equiv C}}$), 1730 ($\nu_{\mathrm{C=O}}$).

Synthesis of Pd(II) mid-functionalized poly(1$_{20}$-b-2$_{40}$). Poly($\mathbf{1}_{20}$-*b*-$\mathbf{2}_{40}$) (72.0 mg, 0.13 mmol) was treated with $\mathrm{Pd(PEt_3)_2Cl_2}$ (82.0 mg, 0.20 mmol) in the present of copper(I) chloride (13.0 mg, 0.13 mmol) as catalyst in diethylamine (3.0 mL) and dichloromethane (1.0 mL). The reaction mixture was stirred at room temperature for 5 h. After the reaction, the mixture passed through a basic alumina column to remove the copper catalyst, and then precipitated into a large amount of *n*-hexane. The product was dried for 24 h in a vacuum oven at room temperature to afford the Pd(II) mid-functionalized poly($\mathbf{1}_{20}$-*b*-$\mathbf{2}_{40}$) (80.0 mg, 66% yield). ^{1}H NMR (600 MHz, $\mathrm{CDCl_3}$, 25°C): δ 7.10–6.85 (br, 120H, ArH, *ortho* and *para* protons of the benzene ring, PS), 6.58–6.38 (br, 80H, ArH, *meta* proton of the benzene ring, PS), 4.71 (d, J = 6 Hz, 2H, $\mathrm{OC\underline{H_2}}$), 4.07 (t, J = 6Hz, 34H, $\mathrm{OC\underline{H_2}}$, PCL), 3.65 (t, J = 6 Hz, 2H, $\mathrm{HOC\underline{H_2}}$, PCL), 2.64–2.58 (m, 4H, $\mathrm{CH_2}$), 2.32 (t, J = 6 Hz, 36H, $\mathrm{CO_2CH_2}$, PCL), 1.92–1.86 (m, 12H, $\mathrm{PC\underline{H_2}CH_3}$), 1.69–1.63 (m, 72H, $\mathrm{CO_2CH_2C\underline{H_2}CH_2C\underline{H_2}CH_2O}$, PCL), 1.42–1.37 (m, 36H, $\mathrm{CO_2CH_2CH_2C\underline{H_2}CH_2CH_2O}$, PCL), 1.23–1.15 (m, 18H, $\mathrm{PCH_2C\underline{H_3}}$). ^{31}P (300Hz, $\mathrm{CDCl_3}$, 25 °C): δ 14.75. FT-IR (KBr, 25 °C, $\mathrm{cm^{-1}}$): 3030 ($\nu_{\mathrm{Ar-H}}$), 2939 ($\nu_{\mathrm{C-H}}$), 2863 ($\nu_{\mathrm{C-H}}$), 1727 ($\nu_{\mathrm{C=O}}$), 1606 ($\nu_{\mathrm{Ar-H}}$).

Synthesis of ABC miktoarm star terpolymer poly((1$_{20}$-b-2$_{20}$)-b-3$_{25}$). Into a 10 mL Schlenk tube, Pd(II) mid-functionalized poly($\mathbf{1}_{20}$-*b*-$\mathbf{2}_{20}$) block copolymer (42 mg, M_{n} =

1.1×10^4, $M_w/M_n = 1.18$), phenyl isocyanide monomer **3** (60.0 mg, 0.21 mmol) and THF (1.0 mL) were added ($[\mathbf{3}]_0 = 2.0$ mM, $[\mathbf{3}]_0/[\mathrm{Pd}]_0 = 25$). Under nitrogen protection, the mixture was stirred at 55 °C for 10 h. The mixture was diluted with THF and precipitated into a large amount of methanol. The resulting polymer was dried in vacuum at room temperature for 24 h to afford the desired ABC miktoarm star terpolymer poly(($\mathbf{1}_{20}$-*b*-$\mathbf{2}_{20}$)-*b*-$\mathbf{3}_{25}$) (80.0 mg, 78% yield). SEC: $M_n = 1.7 \times 10^4$, $M_w/M_n = 1.34$. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.31 (br, 32H, ArH, PPI), 7.16–6.90 (br, 51H, ArH, *ortho* and *para* protons of the benzene ring, PS), 6.59–6.35 (br, 34H, ArH, *meta* proton of the benzene ring, PS), 5.72 (br, 30H, ArH, PPI), 4.06 (t, $J = 6$ Hz, 28H, OCH_2, PCL), 3.83 (br, 32H, CO_2CH_2, PPI), 3.65 (t, $J = 6$ Hz, 2H, $HOC\underline{H_2}$, PCL), 2.30 (t, $J = 12$ Hz, 30H, CO_2CH_2, PCL), 1.87 (s, 6H, CH_3), 1.67–1.62 (m, 60H, $CO_2CH_2C\underline{H_2}CH_2C\underline{H_2}CH_2O$, PCL), 1.40–1.35 (m, 30H, $CO_2CH_2CH_2C\underline{H_2}CH_2CH_2O$, PCL), 1.25–0.84 (br, 304H, alkyl chain of PPI). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 173.43, 164.79, 162.67, 150.37, 129.38, 127.76, 125.72, 117.08, 64.97, 63.82, 34.10, 31.89, 29.59, 28.62, 25.52, 24.69, 22.38, 14.05. FT-IR (KBr, 25 °C, cm^{-1}): 2950 ($\nu_{C\text{-}H}$), 2860 ($\nu_{C\text{-}H}$), 1730 ($\nu_{C=O}$).

The ABC miktoarm star terpolymer *poly((1$_{20}$-b-2$_{40}$)-b-4$_{10}$)*. This terpolymer was synthesized followed the procedure similar to that of ***poly((1$_{20}$-b-2$_{20}$)-b-4$_{25}$)*** using the enantiomer pure phenyl isocyanide monomer **4** instead of achiral monomer **3** using the Pd(II) mid-functionalized poly($\mathbf{1}_{20}$-*b*-$\mathbf{2}_{40}$) ($M_n = 1.4 \times 10^4$, $M_w/M_n = 1.20$) as a macroinitiator initiator. The characteristic data for the ABC miktoarm star terpolymer poly(($\mathbf{1}_{20}$-*b*-$\mathbf{2}_{40}$)-*b*-$\mathbf{4}_{10}$) were showed below.

SEC: $M_n = 1.9 \times 10^4$, $M_w/M_n = 1.32$. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.47 (br, 16H, ArH, PPI), 7.08–6.96 (br, 120H, ArH, *ortho* and *para* protons of the benzene ring, PS), 6,75–6.37 (br, 80H, ArH, *meta* proton of the benzene ring, PS), 4.77 (m, 16H, PPI), 4.06 (t, J = 6 Hz, 34H, OCH_2, PCL), 3.65 (t, J = 6 Hz, 2H, $HOC\underline{H_2}$, PCL), 2.64 (m, 4H, CH_2), 2.30 (t, J = 12 Hz, 36H, CO_2CH_2, PCL), 1.88–1.83 (m, 12H, $PC\underline{H_2}CH_3$), 1.67–1.63 (m, 72H, $CO_2CH_2C\underline{H_2}CH_2C\underline{H_2}CH_2O$, PCL), 1.41–1.36 (m, 36H, $CO_2CH_2CH_2C\underline{H_2}CH_2CH_2O$, PCL), 1.25–0.87 (br, 152H, alkyl chain of PPI), 1.22–1.14 (m, 18H, $PCH_2C\underline{H_3}$). FT-IR (KBr, 25 °C, cm^{-1}): 2961($\nu_{C\text{-}H}$), 2923($\nu_{C\text{-}H}$), 2855($\nu_{C\text{-}H}$), 1734($\nu_{C=O}$).

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.

(2) O. Altintas, G. Hizal, U. Tunca, *J. Polym. Sci. Part A: Polym. Chem.,* 2006, **44**, 5699.

Table S1. Selected results for the polymerizations ABC miktoarm star copolymers containing PCL, PS, and helical PPI blocks[a]

run	poly-**1**$_{m}$				poly(**1**$_{m}$-*b*-**2**$_{n}$)[b]				poly((**1**$_{m}$-*b*-**2**$_{n}$)-*b*-**3**$_{o}$)				block ratio[c]
	M_n[d]	M_w/M_n[d]	$M_{n\,(NMR)}$[e]	yield[f]	M_n[d]	M_w/M_n[d]	$M_{n\,(NMR)}$[e]	yield[f]	M_n[d]	M_w/M_n[d]	$M_{n\,(NMR)}$[e]	yield[f]	PCL/PS/PPI
1	6.6×10^{3}	1.17	1.5×10^{3}	64%	2.5×10^{4}	1.25	1.9×10^{4}	83%	2.9×10^{4}	1.34	2.1×10^{4}	75%	15/180/10
2	6.6×10^{3}	1.17	1.5×10^{3}	64%	7.7×10^{3}	1.21	2.9×10^{3}	82%	2.3×10^{4}	1.35	1.3×10^{4}	80%	15/15/40
3	6.6×10^{3}	1.20	1.5×10^{3}	86%	9.3×10^{3}	1.18	3.3×10^{3}	82%	2.1×10^{4}	1.30	1.1×10^{4}	75%	15/20/30
4	8.5×10^{3}	1.15	2.1×10^{3}	84%	1.1×10^{4}	1.18	3.9×10^{3}	86%	1.7×10^{4}	1.34	1.0×10^{4}	78%	20/20/25
5	9.8×10^{3}	1.15	3.0×10^{3}	79%	1.3×10^{4}	1.13	6.7×10^{3}	75%	1.6×10^{4}	1.35	8.9×10^{3}	72%	30/40/10
6	9.8×10^{3}	1.15	3.1×10^{3}	79%	1.5×10^{4}	1.18	8.8×10^{3}	79%	3.1×10^{4}	1.34	2.0×10^{4}	85%	30/60/40

[a] The miktoarm star terpolymers were synthesized according to Scheme 1 in the main text. [b] The alkyne mid-functionalized PCL-*b*-PS block copolymer. [c] The block ratios were determined by integral analysis of ^{1}H NMR of the corresponding miktoarm star terpolymer. [d] The M_n and M_w/M_n values were determined by SEC analyses and reported as equivalent to their polystyrene standard. [e] The molecular weights were determined by ^{1}H NMR. [f] Isolated yield.

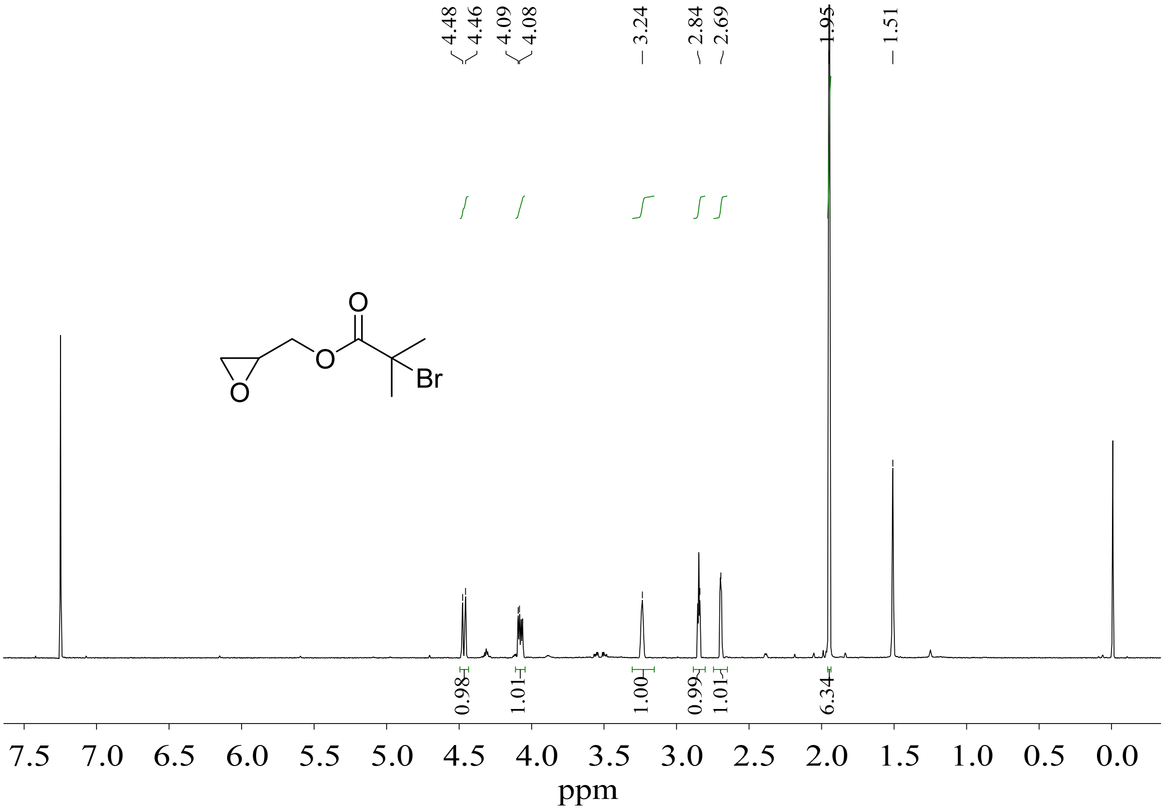


Fig. S1 ^{1}H NMR (600 MHz) spectrum of **5** measured in $CDCl_3$ at 25 °C.

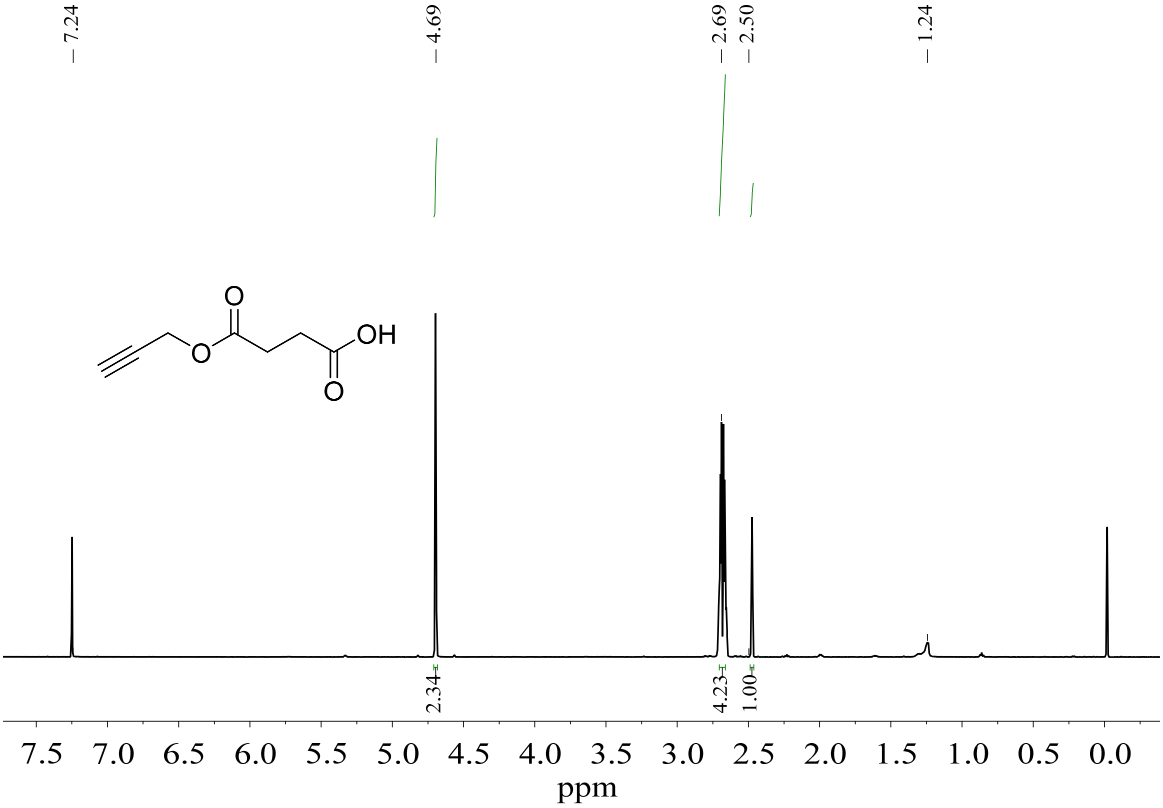


Fig. S2 ^{1}H NMR (600 MHz) spectrum of **6** measured in $CDCl_3$ at 25 °C.

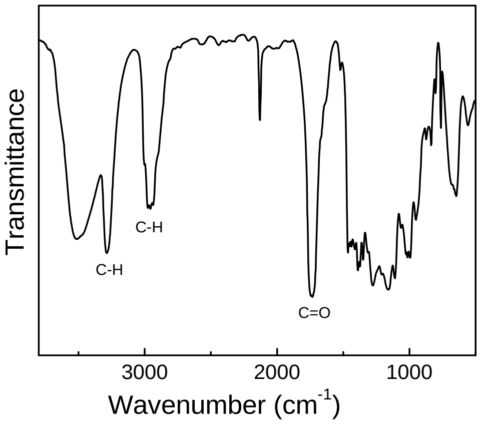


Fig. S3 FT-IR spectrum of the multifunctional initiator measured at 25 °C using KBr pellets.

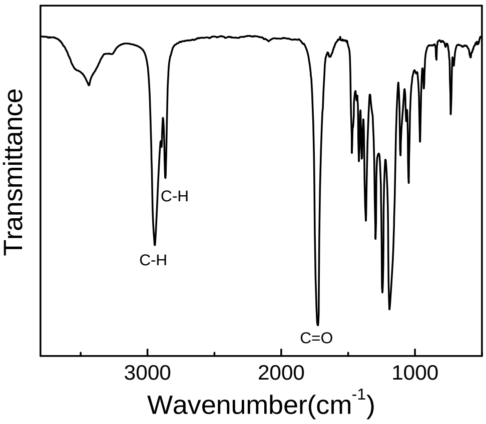


Fig. S4 FT-IR spectrum of PCL homopolymer poly-$\mathbf{1}_{20}$ (M_n = 8.5 × 10^3, M_w/M_n = 1.15) measured at 25 °C using KBr pellets.

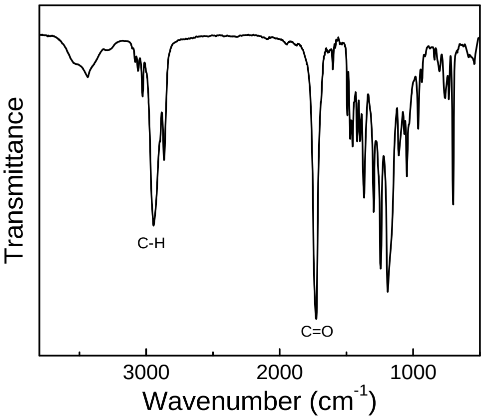


Fig. S5 FT-IR spectrum of alkynyl mid-functionalized PCL-*b*-PS block copolymer poly($\mathbf{1}_{20}$-*b*-$\mathbf{2}_{20}$) measured at 25 °C using KBr pellets.

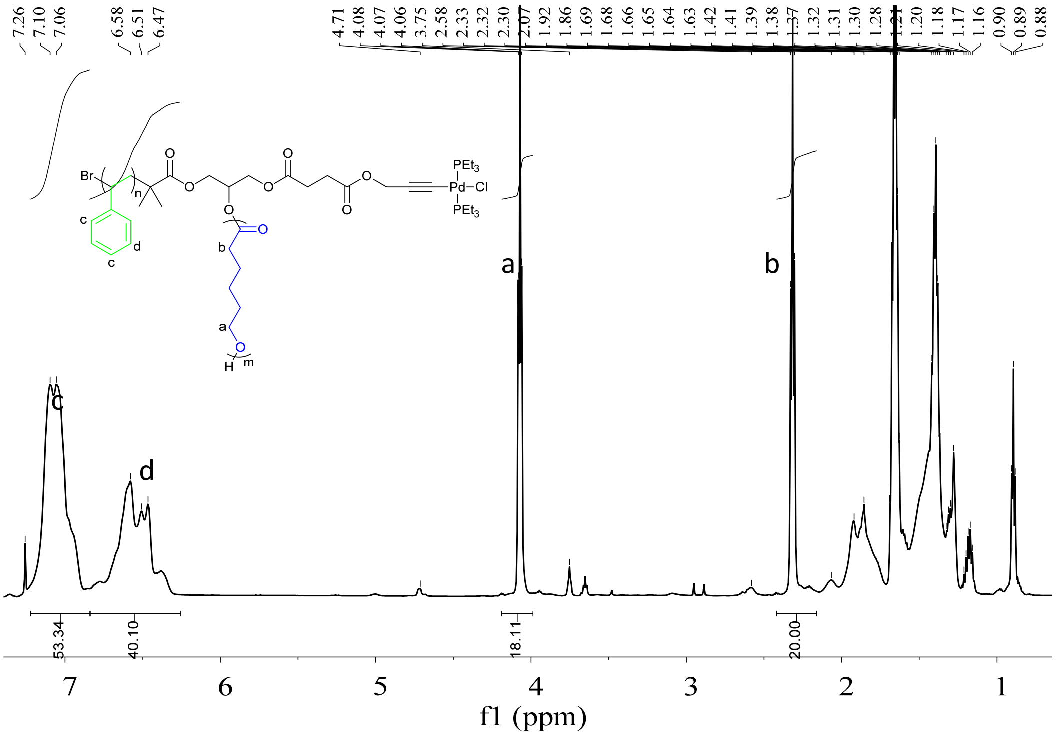


Fig. S6 ^{1}H NMR spectrum of Pd(II) mid-functionalized PCL-*b*-PS block copolymer poly($\mathbf{1}_{20}$-*b*-$\mathbf{2}_{40}$) measured in $CDCl_3$ at 25 °C.

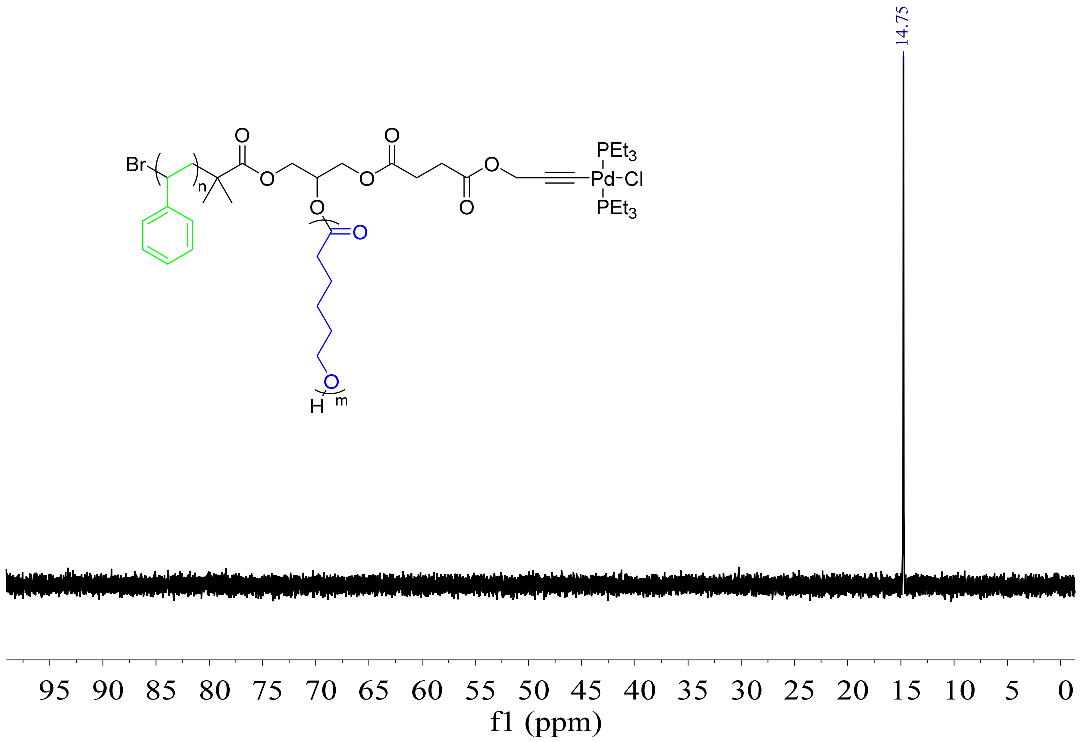


Fig. S7 ^{31}P NMR spectrum of Pd(II) mid-functionalized PCL-*b*-PS block copolymer poly(**1**$_{20}$-*b*-**2**$_{40}$) measured in CDCl$_3$ at 25 °C.

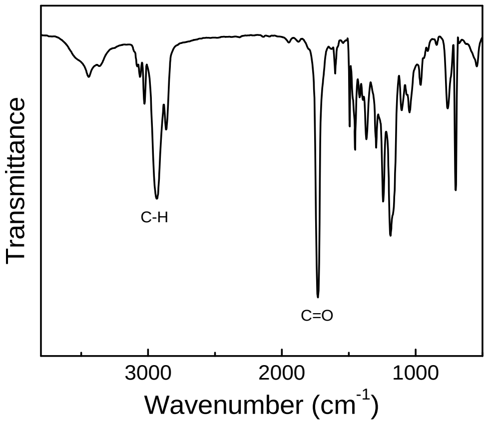


Fig. S8 FT-IR spectrum of the Pd(II) mid-functionalized PCL-*b*-PS block copolymer poly(**1**$_{20}$-*b*-**2**$_{40}$) measured at 25 °C using KBr pellets.

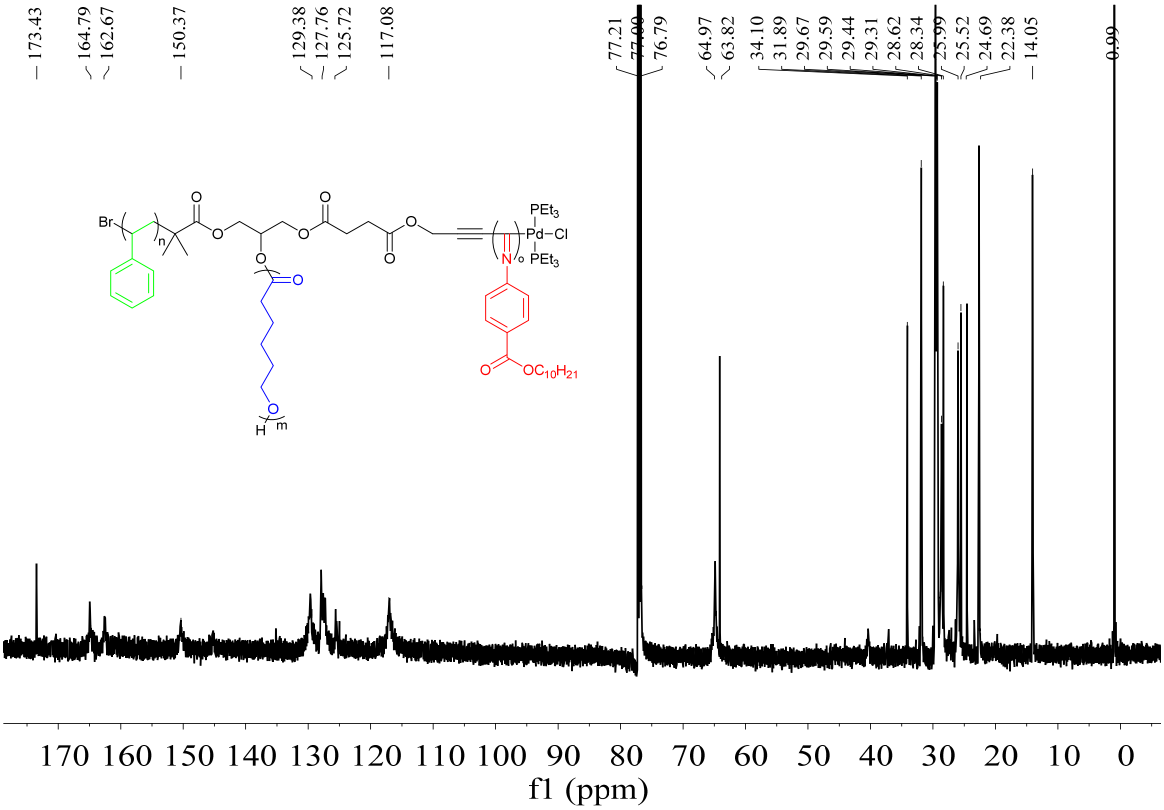


Fig. S9 ^{13}C NMR spectrum of the miktoarm star terpolymer poly(($\mathbf{1}_{20}$-*b*-$\mathbf{2}_{20}$)-*b*-$\mathbf{3}_{25}$) measured in CDCl$_3$ at at 25 °C.

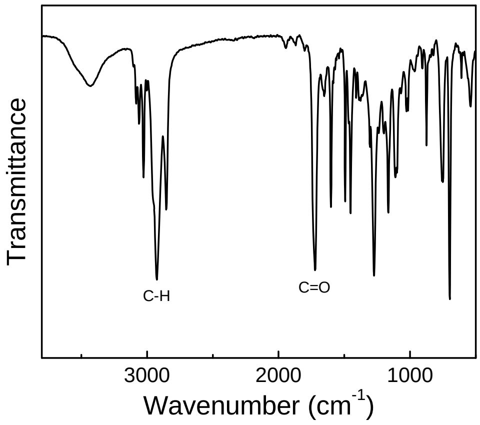


Fig. S10 FT-IR spectrum of the miktoarm star terpolymer poly(($\mathbf{1}_{20}$-*b*-$\mathbf{2}_{20}$)-*b*-$\mathbf{3}_{25}$) measured at 25 °C using KBr pellets.

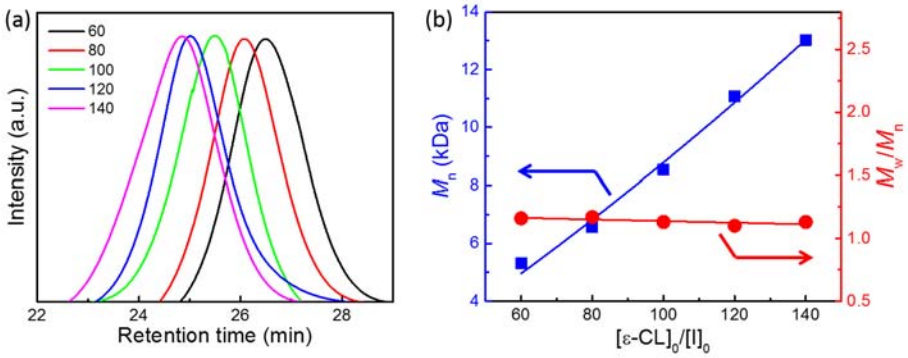


Fig. S11 (a) Size exclusion chromatograms of poly-$\mathbf{1}_m$s prepared in different initial feed ratios of monomer to initiator. (b) Plots of M_n and M_w/M_n values of poly-$\mathbf{1}_m$s as a function of the initial feed ratios of monomer to initiator. SEC conditions: eluent = THF, temperature = 40 °C.

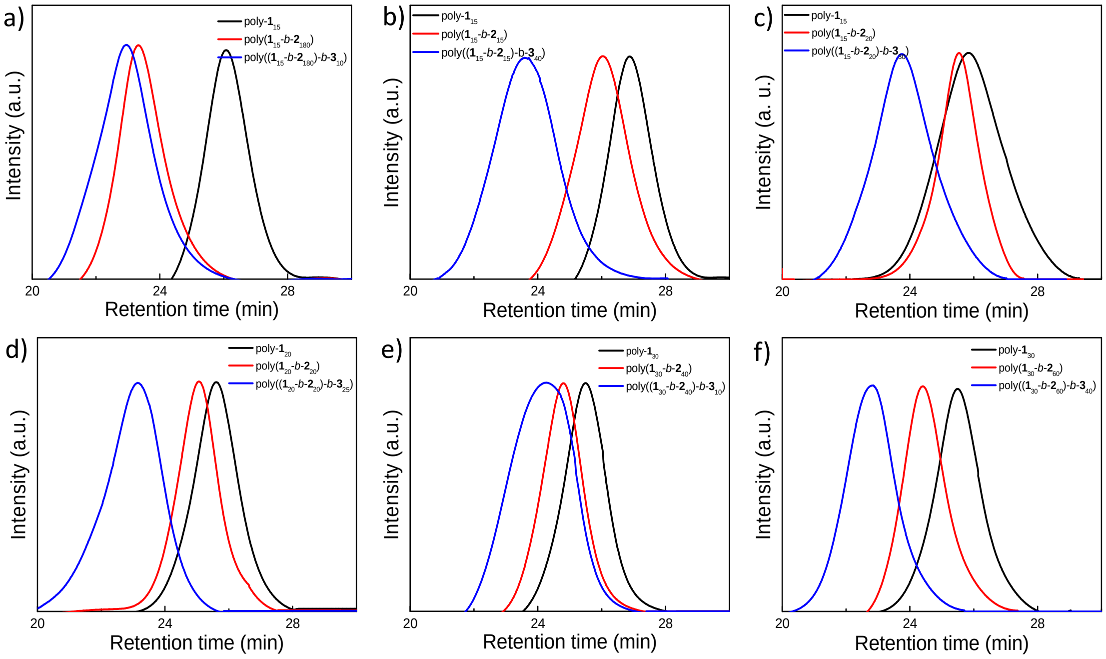


Fig. S12 Size exclusion chromatograms of PCL homopolymer poly-$\mathbf{1}_m$, alkynyl mid-functionalize PCL-*b*-PS block copolymer poly($\mathbf{1}_m$-*b*-$\mathbf{2}_n$), and the resulting miktoarm star terpolymer poly(($\mathbf{1}_m$-*b*-$\mathbf{2}_n$)-*b*-$\mathbf{3}_o$) (see Table S1 for the M_n and M_w/M_n data, a-f corresponding to run 1-6 in Table S1, respectively). SEC conditions: eluent = THF, temperature = 40 °C.

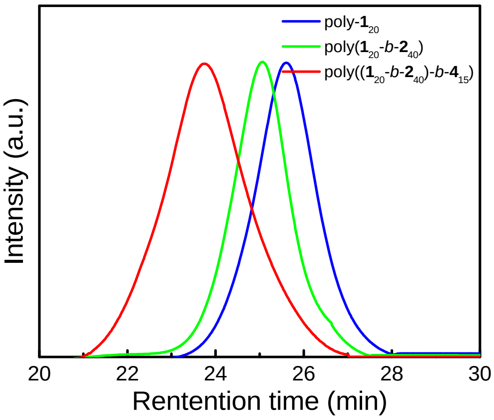


Fig. S13 Size exclusion chromatograms of PCL homopolymer poly-**1**$_{20}$, alkynyl mid-functionalized PCL-*b*-PS block copolymer poly(**1**$_{20}$-*b*-**2**$_{40}$), and the resulting ABC miktoarm star terpolymer poly(**1**$_{20}$-*b*-**2**$_{40}$)-*b*-**4**$_{10}$).

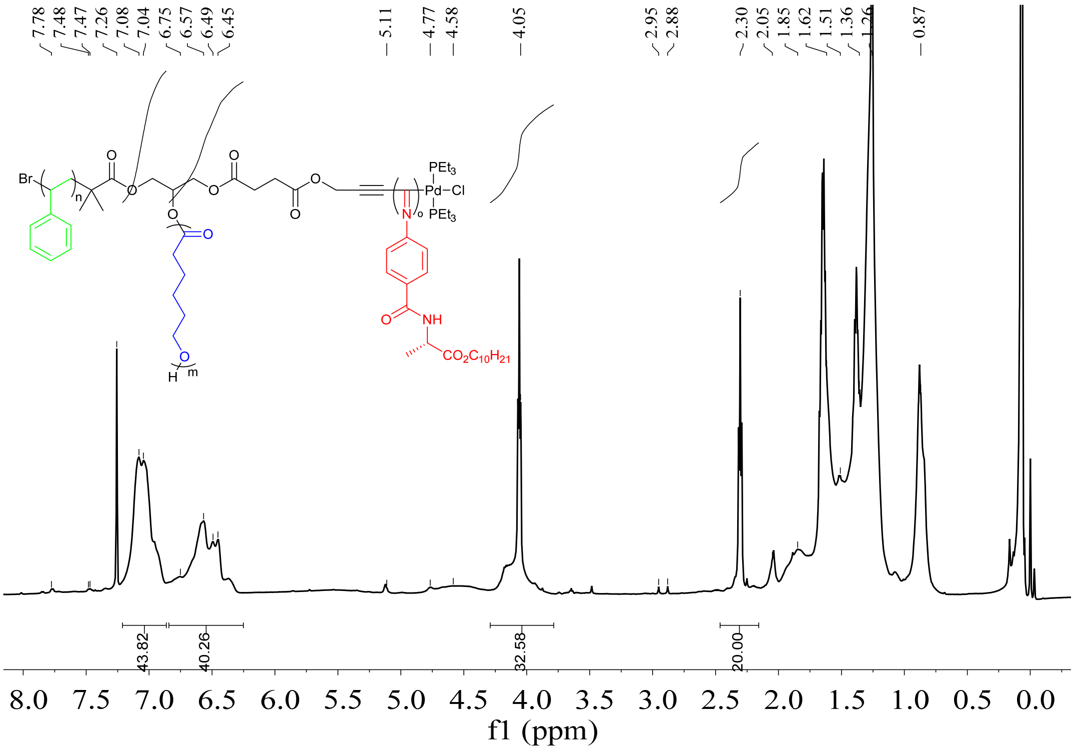


Fig. S14 ^{1}H NMR spectrum of ABC miktoarm star terpolymer poly((**1**$_{20}$-*b*-**2**$_{40}$)-*b*-**4**$_{10}$) measured in $CDCl_3$ at 25 °C.

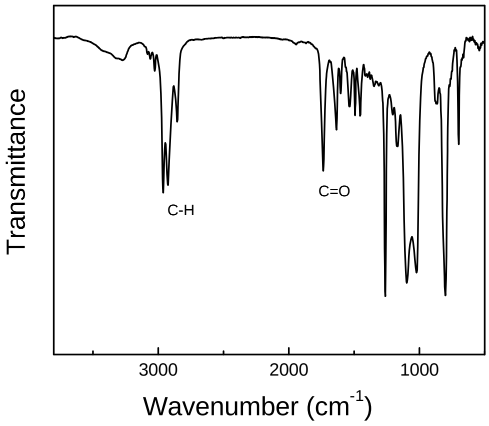


Fig. S15 FT-IR spectrum of the miktoarm star terpolymer poly((**1**$_{20}$-*b*-**2**$_{40}$)-*b*-**4**$_{10}$) measured at 25 °C using KBr pellets.