Supporting Information

to

Various Polystyrene Topologies Built from Tailored Cyclic Polystyrene via CuAAC Reactions.

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Materials

Styrene (STY: Aldrich, >99 %) was de-inhibited before use by passing through a basic alumina column.

The following chemicals were used as received: alumina, activated basic alumina (Aldrich: Brockmann I, standard grade, ~ 150 mesh, 58 Å), diethanolamine (Aldrich, 98 %), anhydrous magnesium sulfate ($MgSO_4$: Scharlau, extra pure), potassium carbonate (K_2CO_3: AnalaR, 99.9 %), silica gel 60 (230 – 400 mesh ATM (SDS)), triethylamine (TEA: Fluka, 98 %), 2-bromoisobutyryl bromide (BIB: Aldrich, 98 %), 2-bromopropionyl bromide (BPB: Aldrich, 98 %), propargyl bromide solution (80 wt % in xylene, Aldrich), propargyl ether (Aldrich, 99 %), sodium azide (NaN_3: Aldrich, ≥ 99.5 %) and tripropargylamine (TPA: Aldrich, 98 %).

The following solvents were used as received: acetone (ChemSupply, AR), chloroform ($CHCl_3$: Univar, AR grade), dichloromethane (DCM: Labscan, AR grade), diethyl ether (Univar, AR grade), ethanol (EtOH: ChemSupply, AR), ethyl acetate (EtOAc: Univar, AR grade), hexane (Wacol, technical grade, distilled), hydrochloric acid (HCl, Univar, 32 %), anhydrous methanol (MeOH: Mallinckrodt, 99.9 %, HPLC grade), Milli-Q water (Biolab, 18.2 MΩm), N,N-dimethylformamide (DMF: Labscan, AR grade), tetrahydrofuran (THF: Labscan, HPLC grade), toluene (HPLC, LABSCAN, 99.8%).

The following initiators, ligands and metals for the various polymerizations are given below and used as received unless otherwise stated. N,N,N’,N’,N’’-pentamethyldiethylenetriamine (PMDETA: Aldrich, 99 %), copper (I) bromide (CuBr: MV Laboratories, INC., 99.999 %), copper (II) bromide ($CuBr_2$: Aldrich, 99 %), ethyl 2-bromoisobutyrate (EBiB: Aldrich, 98 %).

Instruments and Measurements

Size Exclusion Chromatography (SEC)

All polymer samples were dried prior to analysis in a vacuum oven for two days at 25 ^{o}C. The dried polymer was dissolved in tetrahydrofuran (THF) to a concentration of 1 mg/mL and then filtered through a 0.45 μm PTFE syringe filter. Analysis of the molecular weight distributions of the polymers was accomplished using a Waters 2695 separations module, fitted with a Waters 410 refractive index detector maintained at 35 ^{o}C, a Waters 996 photodiode array detector, and two Ultrastyragel linear columns (7.8 x 300 mm) arranged in series. These columns were maintained at 40 ^{o}C for all analyses and are capable of separating polymers in the molecular weight range of 500 – 4 million g/mol with high resolution. All samples were eluted at a flow rate of 1.0 mL/min. Calibration was performed using narrow molecular weight PSTY standards (PDI $\leq$ 1.1) ranging from 500 to 2 million g/mol. Data acquisition was performed using Empower software, and molecular weights were calculated relative to polystyrene standards.

Absolute Molecular Weight Determination by Triple Detection-SEC

Absolute molecular weights of polymers were determined using a Polymer Labs GPC50 Plus equipped with dual angle laser light scattering detector, viscometer and differential refractive index detector. HPLC grade tetrahydrofuran was used as eluent at flow rate 1 mL/min. Separations were achieved using two PLGel Mixed C (7.8 x 300 mm) SEC columns connected in series and held at a constant temperature of 40 ^{o}C. The triple detection system was calibrated using a 2 mg/mL PSTY Standard (Polymer Laboratories: M_{wt} =110 K, *dn/dc* = 0.185 and IV = 0.4872 mL/g). Polymer samples of known concentration were freshly prepared in THF and passed through a

0.45 μm PTFE syringe filter just prior to injection. The absolute molecular weights and dn/dc values were determined using Polymer Labs Multi-Cirrus software. The dn/dc values determined by the quantitative mass recovery technique using the Cirrus software were in good agreement with the theoretical value.

Preparative Size Exclusion Chromatography (Prep-SEC)

Linear PSTY was purified using a Varian ProStar preparative SEC system equipped with a manual injector, differential refractive index detector and single wavelength ultraviolet-visible detector. HPLC grade tetrahydrofuran was used as eluent at flow rate of 10 mL/min. Separations were achieved using a PLgel 10 µm 10E3Å, 300 x 25 mm preparative SEC column held at 25 ^{o}C. The dried impure polymer was dissolved in THF to give a concentration of 100 mg/mL. This solution was filtered through a 0.45 um PTFE syringe filter prior to injection. Fractions were collected manually and the composition of each was determined using the Polymer Labs GPC50 Plus equipped with triple detection as described above.

^{1}H Nuclear Magnetic Resonance (NMR)

All NMR spectra were recorded on a Bruker DRX 500 MHz spectrometer at 25 ^{o}C firstly using an external lock ($CDCl_3$) and referenced to the residual non-deuterated solvent ($CHCl_3$). Then a DOSY experiment was run to acquire spectra presented herein by increasing the pulse gradient from 2 to 95 % of the maximum gradient strength and increasing d (***p30***) from 1 ms to 2 ms, using 256 scans.

Attenuated Total Reflectance Fourier Transform Spectroscopy (ATR-FTIR)

ATR-FTIR spectra were obtained using a horizontal, single bounce, diamond ATR accessory on a Nicolet Nexus 870 FT-IR. Spectra were recorded between 4000 and 500 cm^{-1} for 64 scans at 4 cm^{-1} resolution with an OPD velocity of 0.6289 cm/s. Solids were pressed directly onto the diamond internal reflection element of the ATR without further sample preparation.

Matrix-Assisted Laser Desorption Ionization – Time-of-Flight (MALDI-ToF) Mass Spectrometry

MALDI-ToF MS spectra were obtained using a Bruker MALDI-ToF autoflex III smartbeam equipped with a nitrogen laser (337 nm, 200 Hz maximum firing rate) with a mass range of 600 - 400,000 Da. All spectra were recorded in reflectron mode (1500 – 4500 Da). Trans-2-[3-(4-tert-butylphenyl)-2-methyl-propenylidene] malononitrile (DCTB; 20 mg/mL in THF) was used as the matrix and Ag(CF_3COO) (2 mg/mL in THF) as the cation source. Samples were prepared by co-spotting the matrix (20 μL), Ag(CF_3COO) (2 μL) and polymer (20 μL, 1 mg/mL in THF) solutions on the target plate.

Low Resolution-Electrospray Ionization-Mass Spectrometry (LR-ESI-MS). All mass spectra were recorded on a Bruker Esquire HCT (High Capacity 3D ion trap) instrument with a Bruker ESI source and positive ion model.

Synthesis of ATRP initiator 2. This compound was prepared by slight modification to the literature procedure.[1]

Preparation of 2,2'-(prop-2-ynylazanediyl)diethanol

To a mixture of diethanolamine (10.5 g, 0.100 mol) and anhydrous K_2CO_3 (14 g, 0.10 mol) in acetone (200 mL) under N_2 was charged propargyl bromide (10 mL, 0.09 mol). The reaction mixture was refluxed at 80 °C for 24 h with stirring. The reaction mixture was then cooled to RT, the potassium salts filtered off and the mixture was concentrated to give crude, viscous oil. This crude product was then purified by vacuum distillation (114 °C, 0.04 mmHg) to give a yellow viscous oil which became even more viscous (solid-like) on cooling (5.77 g, 86.8 %). ^1H NMR (δ, ppm, $CDCl_3$): 3.66 (m, 4H, $N(CH_2C\boldsymbol{H_2}OH)_2$), 3.49 (m, 2H, $NC\boldsymbol{H_2}C{\equiv}CH$), 2.77 (m, 4H, $N(C\boldsymbol{H_2}CH_2OH)_2$), 2.35 (s, broad, 2H, $(CH_2O\boldsymbol{H})_2$); 2.21 (m, 1H, $NCH_2C{\equiv}C\boldsymbol{H}$); LR-ESI-MS ($M-H^+$) Calc. *m/z* 144.10 Found *m/z* 144.07.

Preparation of 2-((2-hydroxyethyl)(prop-2-yn-1-yl)amino)ethyl 2-bromo-2-methylpropanoate 1

2-Bromoisobutyryl bromide (4.65 g, 2.02 x 10^{-2} mol) was added dropwise to a solution of 2,2'-(prop-2-ynylazanediyl)diethanol (2.88 g, 2.01 x 10^{-2} mol) and triethylamine (2.03 g, 2.00 x 10^{-2} mol) in dry THF (180 mL) at 0 °C. The solution was stirred at this temperature for 30 min then RT for 3 h. The mixture was then reduced in volume to dryness, transferred to a separation funnel with ethyl acetate (100 mL) and rinsed with deionized water (3 x 100ml) and brine (100 mL). The organic phase was then dried over $MgSO_4$, and the solvent was removed by rotary evaporation. The crude extract was further purified on a silica column (EtOAc/PET ether) and the second fraction was collected to give the pure viscous oil product (3.55 g, 60.5 %). R_f (1/1 EtOAc/PET ether) 0.25; ^{1}H NMR (δ, ppm, $CDCl_3$): 4.28 (m, 2H, $NCH_2C\boldsymbol{H_2}OCO$), 3.59 (m, 2H, $NCH_2C\boldsymbol{H_2}OH$), 3.50 (m, 2H, $NC\boldsymbol{H_2}C{\equiv}CH$), 2.91 (m, 2H, $NC\boldsymbol{H_2}CH_2OCO$); 2.77 (m, 2H, $NC\boldsymbol{H_2}CH_2OH$); 2.22 (m, 1H, $NCH_2C{\equiv}C\boldsymbol{H}$), 1.94 (m, 6H, $OCOC(C\boldsymbol{H_3})_2Br$). Microanalysis: Calculated for $C_{11}H_{18}BrNO_3$: C, 45.22; H, 6.21; N, 4.79 Found: C, 45.22; H, 6.40; N, 4.77.

Synthesis of $CuBr_2$/PMDETA complex

Cu(II)Br_2 (2.05 g, 9.18 x 10^{-3} mol) was stirred in MeOH (200 mL) until complete dissolution was achieved. To this stirred solution PMDETA (1.55 g, 8.94 x 10^{-3} mol) was added dropwise and stirred for a further 30 min at RT. The solution was then gravity filtered, the MeOH was removed by rotary evaporator and the complex was dried *in vacuo* for 17 h at 25 °C.

Synthesis of Polymers by Atom Transfer Radical Polymerization (ATRP)

Synthesis of l-≡(HO)-$PSTY_{44}$-Br ***2****:* Styrene (6.00 g, 6.00 x 10^{-2} mol), PMDETA (4.00 x 10^{-2} mL, 1.80 x 10^{-4} mol), $CuBr_2$/PMDETA (1.43 x 10^{-2} g, 3.60 x 10^{-5} mol) and initiator **2** (0.11 g, 3.60 x 10^{-4} mol) were added to a 25 mL Schlenk flask equipped with a magnetic stirrer and sparged with argon for 25 min to remove oxygen. Cu(I)Br (2.58 x 10^{-2} g, 1.80 x 10^{-4} mol) was then carefully added to the solution under an argon blanket. The reaction mixture was further degassed for 5 min and then placed into a temperature controlled oil bath at 80 °C for 4 h. The reaction was quenched by cooling the reaction mixture to 0 °C, exposure to air, and dilution with DCM (*ca.* 3 fold to the reaction mixture volume). The copper salts were removed by passage through an activated basic alumina column. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into large volume of MeOH (20 fold excess to polymer solution) and vacuum filtration. The polymer was dried *in vacuo* for 24 h at 25 °C and characterized by SEC (M_n = 4500, PDI = 1.11) and Triple Detection SEC (M_n = 4600, PDI = 1.10).

Synthesis of l-PSTY$_{48}$-Br: Styrene (15 g, 0.15 mol), PMDETA (0.19 mL, 9.1 x 10^{-4} mol), EBiB (0.15 g, 7.4 x 10^{-4} mol) and $CuBr_2$/PMDETA (4.0 x 10^{-2} g, 1.6 x 10^{-4} mol) were added to a 50 mL Schlenk flask and sparged with N_2 for 25 min to remove oxygen. CuBr (0.11 g, 7.6 x 10^{-4} mol) was then carefully added to the solution under a nitrogen blanket. The reaction mixture was further degassed for 5 min and then placed into a temperature controlled oil bath at 80 °C for 200 min. The reaction was quenched by cooling the reaction mixture to 0 °C, exposure to air, and dilution with DCM (*ca.* 3 fold to the reaction mixture volume). The copper salts were removed by passage through an activated basic alumina column. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into large volume of MeOH (20 fold excess to polymer solution) and vacuum filtration. The polymer was dried *in vacuo* for 24 h at 25 °C and characterized by SEC (M_n = 4900, PDI = 1.10) and Triple Detection SEC (M_n = 5000, PDI = 1.11).

Azidation of Polymers

Synthesis of l-≡(HO)-PSTY$_{44}$-N_3 ***3****:* Polyner l-≡(HO)-PSTY$_{44}$-Br **2** (1.0 g, 2.2 x 10^{-4} mol) was dissolved in 10 mL of DMF in a 25 mL reaction vessel equipped with magnetic stirrer. To this solution NaN_3 (0.14 g, 2.2 x 10^{-3} mol) was added and the mixture stirred for 17 h at 25 °C. The polymer was precipitated into MeOH from

DMF, recovered by vacuum filtration and washed exhaustively with water and MeOH. The polymer was dried *in vacuo* for 24 h at 25 ^{o}C.

Synthesis of l-PSTY$_{48}$-N$_3$: Polymer PSTY-Br (4.0 g, 8.1 x 10^{-4} mol) was dissolved in 30 mL of DMF in a 50 mL reaction vessel equipped with magnetic stirrer. To this solution NaN$_3$ (0.53 g, 8.1 x 10^{-3} mol) was added and the mixture stirred for 17 h at 25 ^{o}C. The polymer was precipitated into MeOH, recovered by vacuum filtration and washed exhaustively with water and MeOH. The polymer was dried *in vacuo* for 24 h at 25 ^{o}C.

Cyclization reaction of 3 by CuAAc chemistry

*Synthesis of c-PSTY$_{44}$-OH **4**:* A solution of l-≡(HO)-PSTY$_{44}$-N$_3$ **3** (0.25 g, 5.6 x 10^{-5} mol) in toluene (10 mL) was sparged with argon for 25 min to remove oxygen. This polymer solution was added via syringe pump, at a flow rate of 1.240 mL/min, to a deoxygenated solution of Cu(I)Br (0.40 g, 2.8 x 10^{-3} mol) and PMDETA (0.59 mL, 2.8 x 10^{-3} mol) in toluene (10 mL) at 25 ^{o}C. After the addition of the polymer solution the reaction mixture was stirred up to 4 h. At the end of this period toluene was evaporated and the copper salts were removed through CHCl$_3$/water extraction. The residual copper salts were removed by passage through activated basic alumina column. The polymer was recovered by precipitation into MeOH (10 fold excess to polymer solution) and then by filtration. The polymer was dried *in vacuo* for 24 h at 25 ^{o}C. (Purity by SEC = 92 %). The procedure was then repeated.

The crude products were fractionated by preparative SEC and fractions combined and characterized by SEC (M_n = 3400, PDI = 1.07) and Triple Detection SEC (M_n = 4600, PDI = 1.09).

Chain-end modification of functional polymers

*Synthesis of c-PSTY$_{44}$-Br **5**: c-PSTY$_{44}$-OH **4*** (0.40 g, 8.7 x 10^{-5} mol), TEA (61 µL, 4.3 x 10^{-4} mol) and 30 mL of dry THF were added under an argon blanket to a dry 50 mL Shlenk flask that has been flushed with argon. The reaction was then cooled on ice. To this stirred mixture, a solution of BPB (46 µL, 4.3 x 10^{-4} mol) in dry THF (2.5 mL) was added drop-wise under argon via an air-tight syringe over 15 min. After stirring the reaction mixture for 56 h at RT, the polymer was precipitated into MeOH, filtered and washed three times with both MeOH and water. The polymer was dried for 48 h *in vacuo* at 25 ^{o}C.

*Synthesis of c-PSTY$_{44}$-N$_3$ **6**:* Polymer c-PSTY$_{44}$-Br **5** (0.36 g, 7.5 x 10^{-4} mol) was dissolved in 20 mL of DMF in a 50 mL reaction vessel equipped with magnetic stirrer. To this solution NaN_3 (5.0 x 10^{-2} g, 7.5 x 10^{-3} mol) was added and the mixture stirred for 17 h at 25 ^{o}C. The polymer was precipitated into MeOH, recovered by vacuum filtration and washed exhaustively with water and MeOH. The polymer was dried *in vacuo* for 24 h at 25 ^{o}C.

*Synthesis of c-PSTY$_{44}$-≡ **7**:* Polymer c-PSTY$_{44}$-N$_3$ **6** (7.0 x 10^{-2} g, 1.5 x 10^{-5} mol), PMDETA (3.1 µL, 1.5 x 10^{-5} mol), propargyl ether (4.4 x 10^{-2} mL, 4.4 x 10^{-4} mol) and toluene (0.5 mL) were added to a 10 mL Schlenk flask equipped with magnetic stirrer and the solution sparged with argon for 15 min. CuBr (2.1 x 10^{-3} g, 1.5 x 10^{-5} mol) was then carefully added under an argon blanket. The reaction mixture was purged with argon for a further 5 min and the flask was placed in a temperature controlled oil bath at 25 ^{o}C for 1.5 h. The reaction was then diluted with DCM (*ca*. 3 fold to the reaction mixture volume), and passed through activated basic alumina to remove the copper salts. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into a large amount of MeOH (20 fold excess to polymer solution) and filtration. The polymer was re-precipitated twice to ensure complete purity of the final product from propargyl ether. The polymer was dried *in vacuo* for 24 h at 25 ^{o}C

Synthesis of c-PSTY$_{44}$-(≡)$_2$ ***8***: Polymer c-PSTY$_{44}$-N$_3$ **6** (0.124 g, 2.62 x 10^{-5} mol), PMDETA (5.48 µL, 2.62 x 10^{-5} mol), TPA (0.110 mL, 7.86 x 10^{-4} mol) and toluene (0.5 mL) were added to a 10 mL Schlenk flask equipped with magnetic stirrer and the solution sparged with argon for 15 min. CuBr (3.76 x 10^{-3} g, 2.62 x 10^{-5} mol) was then carefully added under an argon blanket. The reaction mixture was purged with argon for a further 5 min and the flask was placed in a temperature controlled oil bath at 25 ^{o}C for 1.5 h. The reaction was then diluted with DCM (*ca*. 3 fold to the reaction mixture volume), and passed through activated basic alumina to remove the copper salts. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into a large amount of MeOH (20 fold excess to polymer solution) and filtration. The polymer was re-precipitated twice to ensure complete purity of the final product from TPA. The polymer was dried *in vacuo* for 24 h at 25 ^{o}C

Synthesis of l-PSTY$_{48}$-≡ ***9***: Polymer l-PSTY$_{48}$-N$_3$ (0.58 g, 1.2 x 10^{-4} mol), PMDETA (25 µL, 1.2 x 10^{-4} mol), propargyl ether (0.23 mL, 2.4 x 10^{-3} mol) and toluene (8 mL) were added to a 25 mL Schlenk flask equipped with magnetic stirrer and the solution sparged with argon for 25 min. CuBr (1.7 x 10^{-2} g, 1.2 x 10^{-4} mol) was then carefully added under an argon blanket. The reaction mixture was purged with argon for a further 5 min and the flask was placed in a temperature controlled oil bath at 25 °C for 1.5 h. The reaction was then diluted with DCM (*ca*. 3 fold to the reaction mixture volume), and passed through activated basic alumina to remove the copper salts. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into a large amount of MeOH (20 fold excess to polymer solution) and filtration. The polymer was re-precipitated twice to ensure complete purity of the final product from propargyl ether. The polymer was dried *in vacuo* for 24 h at 25 °C

Synthesis of l-PSTY$_{48}$*-(≡)*$_2$ ***10***: Polymer l-PSTY$_{48}$-N$_3$ (0.95 g, 1.9 x 10^{-4} mol), PMDETA (40 µL, 1.9 x 10^{-4} mol), TPA (0.54 mL, 3.8 x 10^{-3} mol) and toluene (8 mL) were added to a 25 mL Schlenk flask equipped with magnetic stirrer and the solution sparged with argon for 25 min. CuBr (2.8 x 10^{-2} g, 1.9 x 10^{-4} mol) was then carefully added under an argon blanket. The reaction mixture was purged with argon for a further 5 min and the flask was placed in a temperature controlled oil bath at 25 °C for 1.5 h. The reaction was then diluted with DCM (*ca*. 3 fold to the reaction mixture volume), and passed through activated basic alumina to remove the copper salts. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into a large amount of MeOH (20 fold excess to polymer solution) and filtration. The polymer was re-precipitated twice to ensure complete purity of the final product from TPA. The polymer was dried *in vacuo* for 24 h at 25 °C

Synthesis of complex architectures

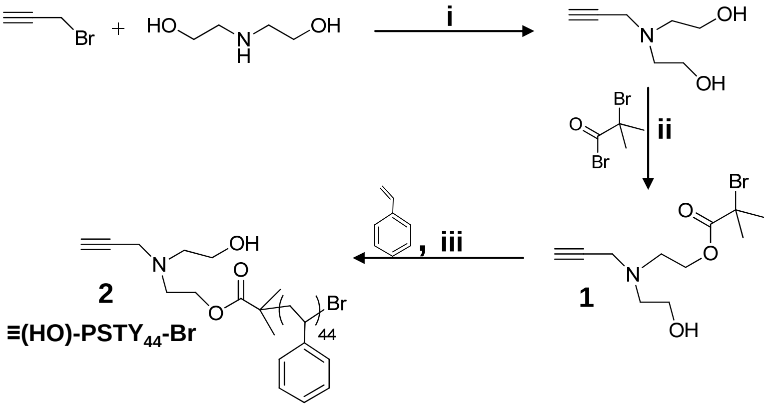
Synthesis of ***11****:* Polymer c-PSTY$_{44}$-N$_3$ **6** (2.1 x 10^{-2} g, 4.9 x 10^{-6} mol), polymer l-PSTY$_{48}$-≡ **9** (2.0 x 10^{-2} g, 4.0 x 10^{-6} mol), PMDETA (0.84 µL, 4.0 x 10^{-6} mol) and toluene (0.3 mL) were added to a 5 mL Schlenk flask equipped with magnetic stirrer and the solution sparged with argon for 15 min. CuBr (5.8×10^{-4} g, 4.0×10^{-6} mol) was then carefully added under argon . The reaction mixture was purged with argon for a further 2 min and the flask was placed in a temperature controlled oil bath at 25 °C for 1.5 h. The reaction was then diluted with DCM (*ca*. 3 fold to the reaction mixture volume), and passed through activated basic alumina to remove the copper salts. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into MeOH (10 fold excess to polymer solution) and filtration. The polymer was dried *in vacuo* for 24 h at 25 °C. The crude product was then fractionated by preparative SEC.

*Synthesis of **12**:* Polymer c-PSTY$_{44}$-N$_3$ **6** (3.8×10^{-2} g, 8.0×10^{-6} mol), polymer *PSTY$_{48}$-(≡)$_2$* **10** (2.0×10^{-2} g, 3.7×10^{-6} mol), PMDETA (1.6 µL, 7.5×10^{-6} mol) and toluene (0.3 mL) were added to a 5 mL Schlenk flask equipped with magnetic stirrer and the solution sparged with argon for 15 min. CuBr (1.1×10^{-3} g, 7.5×10^{-6} mol) was then carefully added under argon. The reaction mixture was purged with argon for a further 2 min and the flask was placed in a temperature controlled oil bath at 25 °C for 1.5 h. The reaction was then diluted with DCM (*ca*. 3 fold to the reaction mixture volume), and passed through activated basic alumina to remove the copper salts. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into MeOH (10 fold excess to polymer solution) and filtration. The polymer was dried *in vacuo* for 24 h at 25 °C. The crude product was then fractionated by preparative SEC.

*Synthesis of **13**:* Polymer c-PSTY$_{44}$-N$_3$ **6** (2.4×10^{-2} g, 5.2×10^{-6} mol), polymer c-PSTY$_{44}$-≡ **7** (2.0×10^{-2} g, 4.3×10^{-6} mol), PMDETA (0.90 µL, 4.3×10^{-6} mol) and toluene (0.3 mL) were added to a 5 mL Schlenk flask equipped with magnetic stirrer and the solution sparged with argon for 15 min. CuBr (6.5×10^{-4} g, 4.5×10^{-6} mol) was then carefully added under argon. The reaction mixture was purged with argon for a further 2 min and the flask was placed in a temperature controlled oil bath at 25 °C for 1.5 h. The reaction was then diluted with DCM (*ca*. 3 fold to the reaction mixture volume), and passed through activated basic alumina to remove the copper salts. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into MeOH (10 fold excess to polymer solution) and filtration. The polymer was dried *in vacuo* for 24 h at 25 °C. The crude product was then fractionated by preparative SEC.

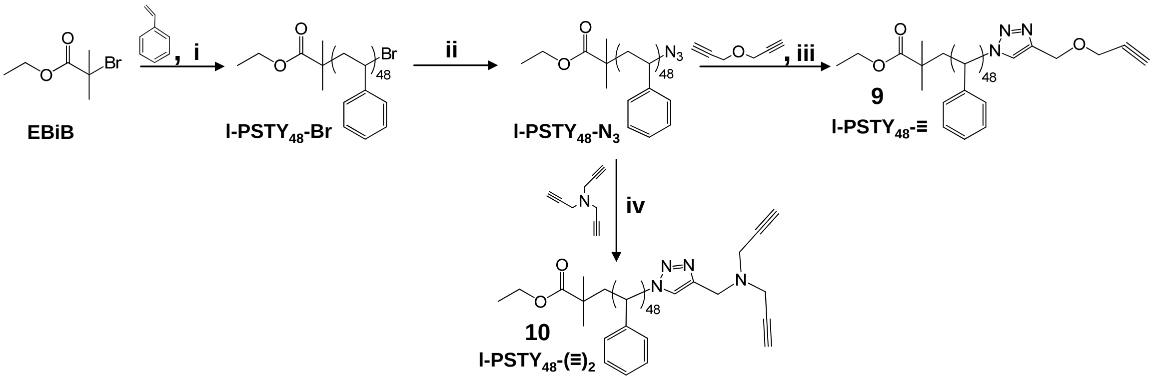
Synthesis of ***14****:* Polymer c-PSTY$_{44}$-N$_3$ **6** (4.2×10^{-2} g, 8.9×10^{-6} mol), polymer c-PSTY$_{44}$-($\equiv$)$_2$ **8** (2.0×10^{-2} g, 4.1×10^{-6} mol), PMDETA (1.7 µL, 8.1×10^{-6} mol) and toluene (0.3 mL) were added to a 5 mL Schlenk flask equipped with magnetic stirrer and the solution sparged with argon for 15 min. CuBr (1.2×10^{-3} g, 8.1×10^{-6} mol) was then carefully added under argon. The reaction mixture was purged with argon for a further 2 min and the flask was placed in a temperature controlled oil bath at 25 °C for 1.5 h. The reaction was then diluted with DCM (*ca*. 3 fold to the reaction mixture volume), and passed through activated basic alumina to remove the copper salts. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into MeOH (10 fold excess to polymer solution) and filtration. The polymer was dried *in vacuo* for 24 h at 25 °C. The crude product was then fractionated by preparative SEC.

Scheme S1: Synthetic Route for the Preparation of Functional Initiator **1** and its Utilization in ATRP to Produce ≡(HO)-PSTY$_{44}$-Br (**2**).



[a] Reactants and conditions: (i) K_2CO_3, acetone, reflux for 24 h; (ii) TEA, THF at 0 °C; (iii) CuBr, PMDETA, $CuBr_2$/PMDETA in bulk at 80 °C for 4 h.

Scheme S2: Synthetic Route for the Preparation of l-PSTY$_{48}$-Br and its Subsequent Chain-End Modification Reactions.



[a] Reactants and conditions: (i) CuBr, PMDETA, $CuBr_2$/PMDETA in bulk at 80 °C for 200 min; (ii) NaN_3 in DMF at 25 °C for 17 h; (iii) CuBr, PMDETA in toluene at 25 °C for 1.5 h; (iv) CuBr, PMDETA in toluene at 25 °C for 1.5 h.

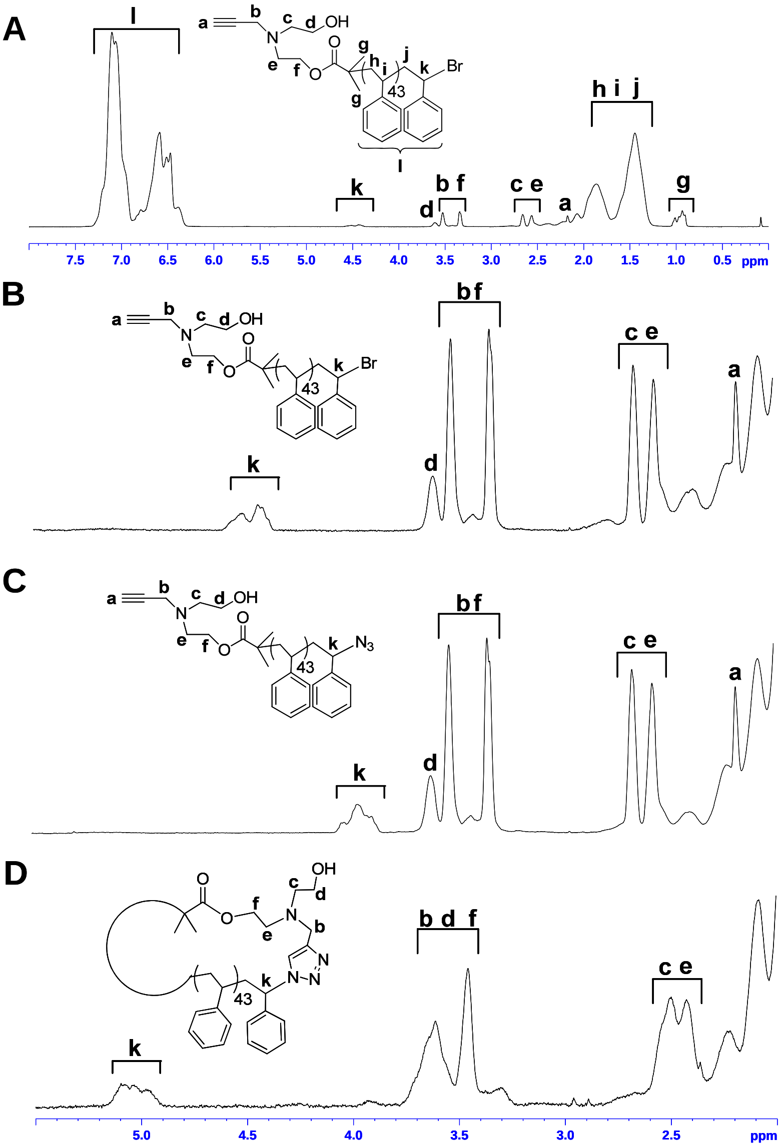


Figure S1: 500 MHz ^{1}H 1D DOSY NMR analysis of ≡(HO)-PSTY$_{44}$-Br **2** chain-end modification to ≡(HO)-PSTY$_{44}$-N$_3$ **3** and cyclization to form c-PSTY$_{44}$-OH **4**. **(A)** Full spectrum of ≡(HO)-PSTY$_{44}$-Br **2; (B)** Expanded spectrum of ≡(HO)-PSTY$_{44}$-Br **2; (C)** Expanded spectrum of ≡(HO)-PSTY$_{44}$-N$_3$ **3; (D)** Expanded spectrum of c-PSTY$_{44}$-OH **4**.

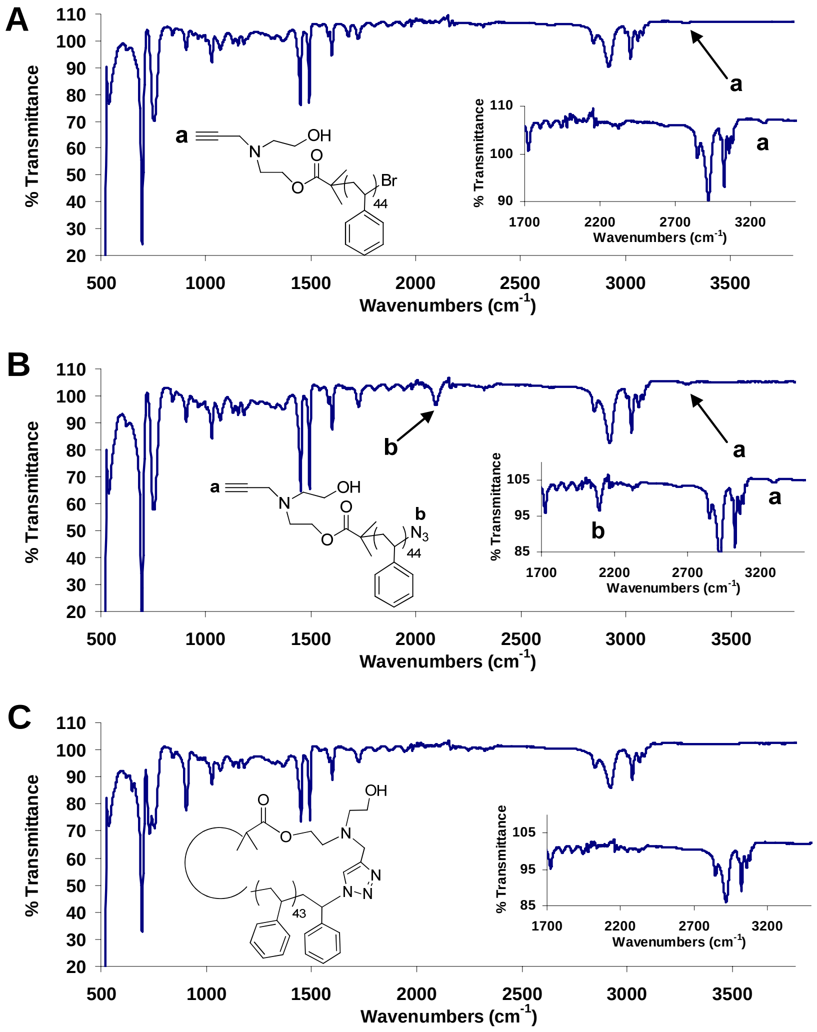


Figure S2: ATR-FTIR analysis of **(A)** ≡(HO)-PSTY$_{44}$-Br **2; (B)** ≡(HO)-PSTY$_{44}$-N$_3$ **3** and **(C)** c-PSTY$_{44}$-OH **4**. **(a)** alkyne stretch at 3295 cm^{-1}, **(b)** azide stretch at 2094 cm^{-1}.

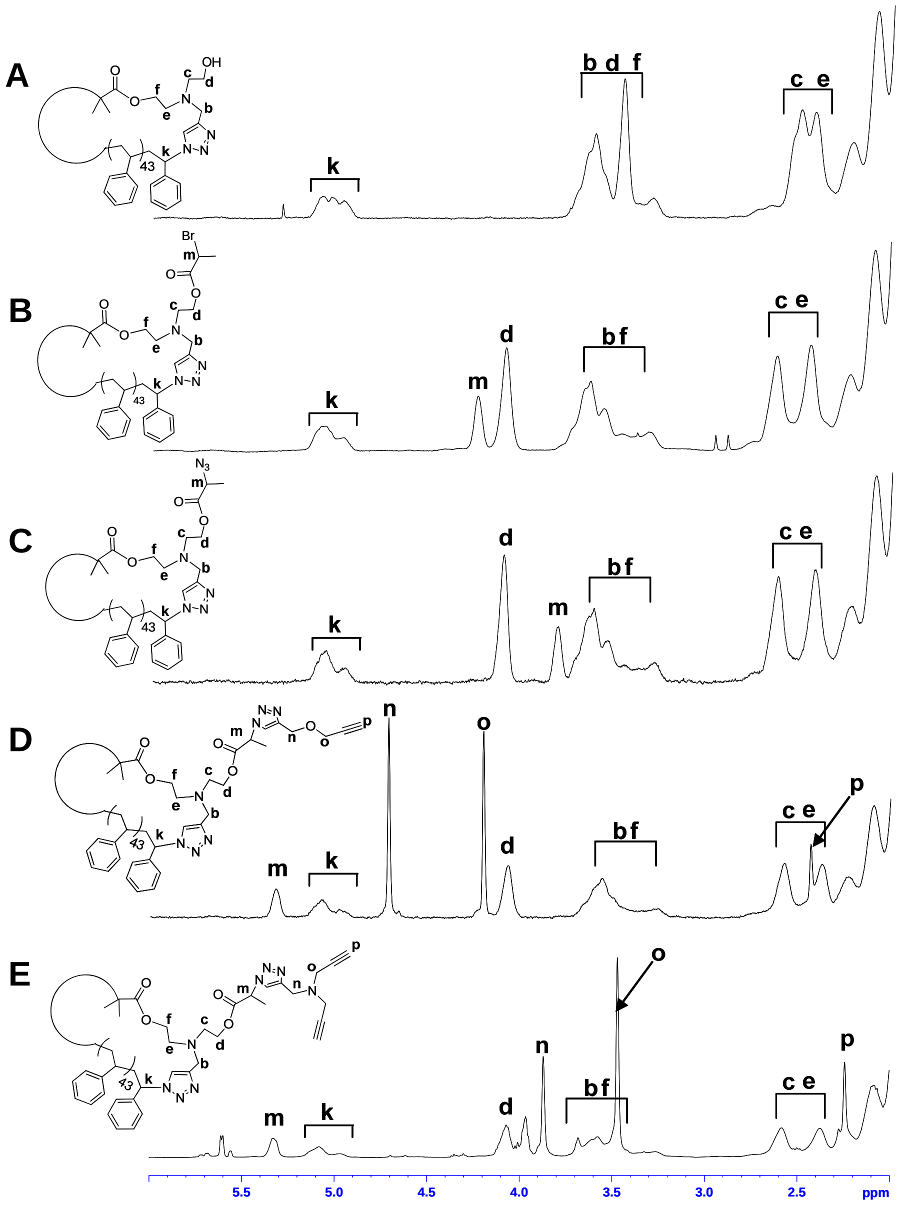


Figure S3: 500 MHz ^{1}H 1D DOSY NMR analysis of c-PSTY$_{44}$-OH functional chain-end modification. Refer to Scheme 1 compounds **4-8**. The following are the expanded spectra of **(A)** c-PSTY$_{44}$-OH; **(B)** c-PSTY$_{44}$-Br; **(C)** c-PSTY$_{44}$-N$_3$; **(D)** c-PSTY$_{44}$-≡; **(E)** c-PSTY$_{44}$-(≡)$_2$.

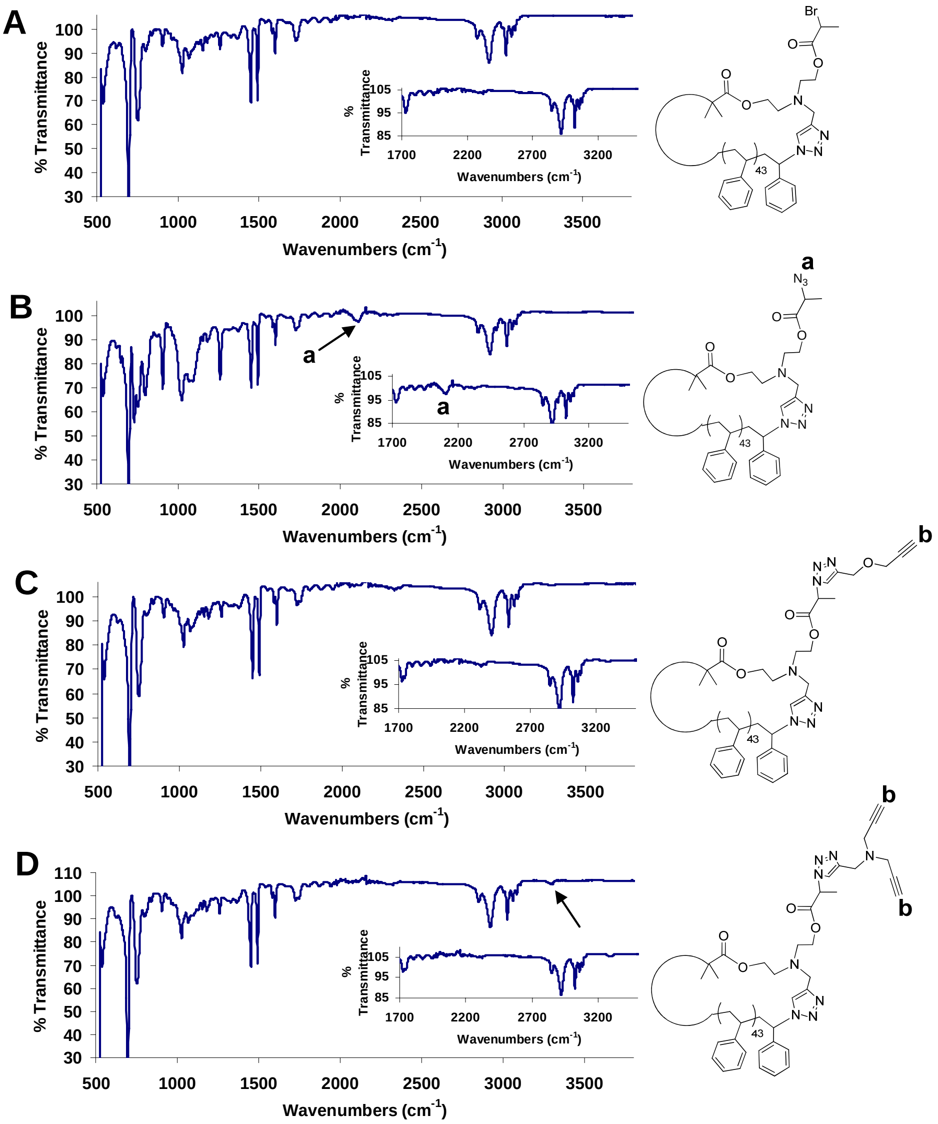


Figure S4: ATR-FTIR analysis of the c-PSTY$_{44}$-Br and its chain end modifications. Refer to Scheme 1, compounds **5-8**. Spectra of **(A)** c-PSTY$_{44}$-Br; **(B)** c-PSTY$_{44}$-N$_3$; **(C)** c-PSTY$_{44}$-≡; **(D)** c-PSTY$_{44}$-(≡)$_2$. **(a)** azide stretch at 2094 cm^{-1}; **(b)** alkyne stretch at 3295 cm^{-1}.

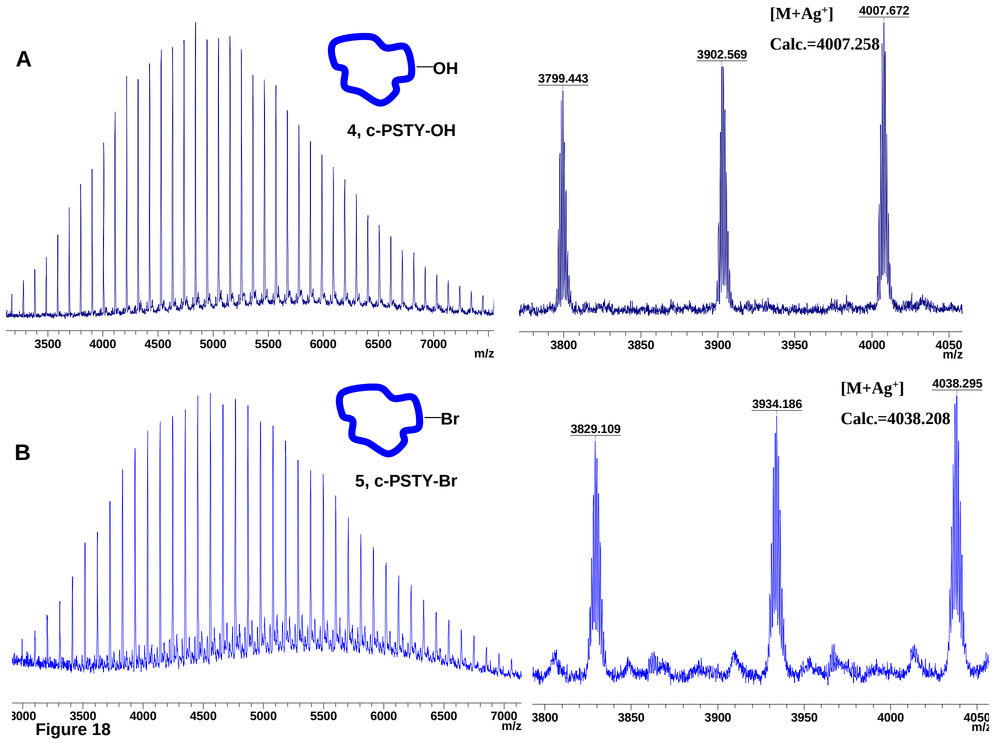


Figure S5: MALDI-ToF mass spectra acquired in reflectron mode with Ag salt as cationization agent and DCTB matrix. The full and expanded spectra correspond to structures: **(A)** **4**, c-PSTY-OH; calculated $[M+Ag^+]$ = 4007.26, DP_n = 35; **(B)** **5**, c-PSTY-Br; calculated $[M+Ag^+]$ = 4038.21, DP_n = 34.

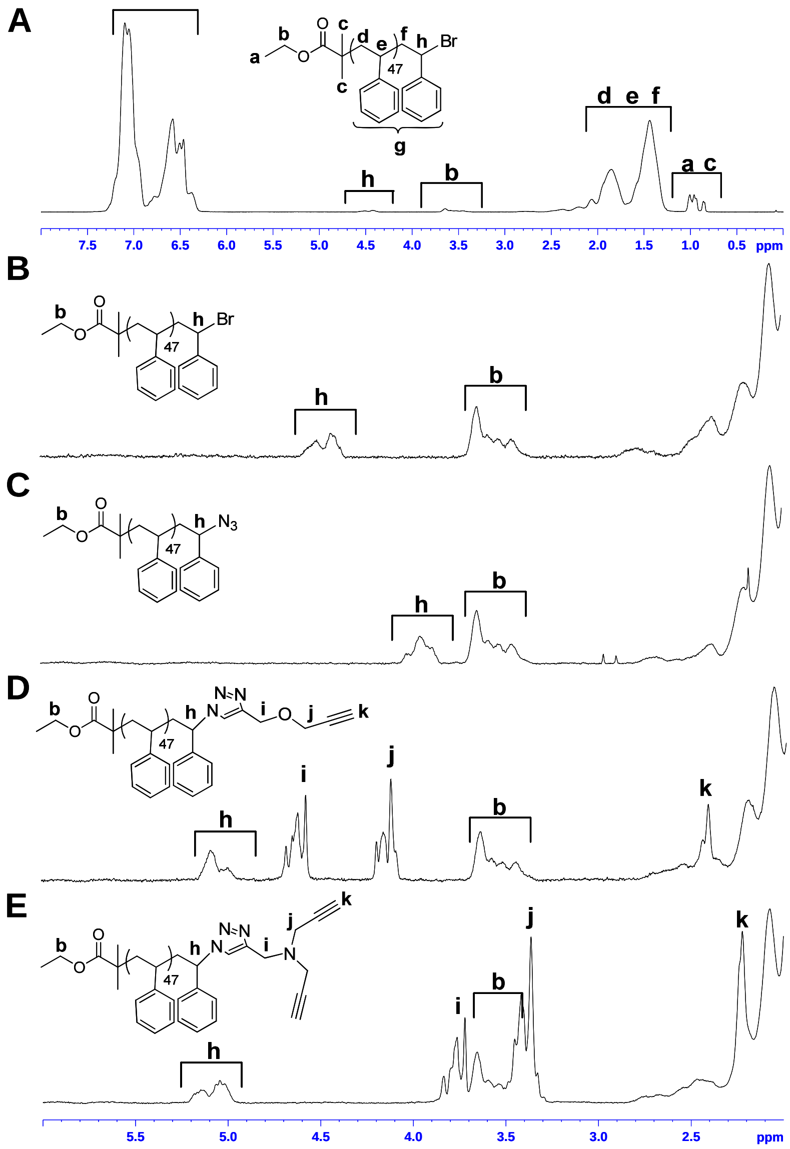


Figure S6: 500 MHz ^{1}H 1D DOSY NMR analysis of l-PSTY$_{48}$-Br chain-end modification. **(A)** Full spectra of l-PSTY$_{48}$-Br; **(B)** Expanded spectra of l-PSTY$_{48}$-Br; **(C)** Expanded spectra of l-PSTY$_{48}$-N$_3$; **(D)** Expanded spectra of l-PSTY$_{48}$-≡; **(E)** Expanded spectra of l-PSTY$_{48}$-(≡)$_2$.

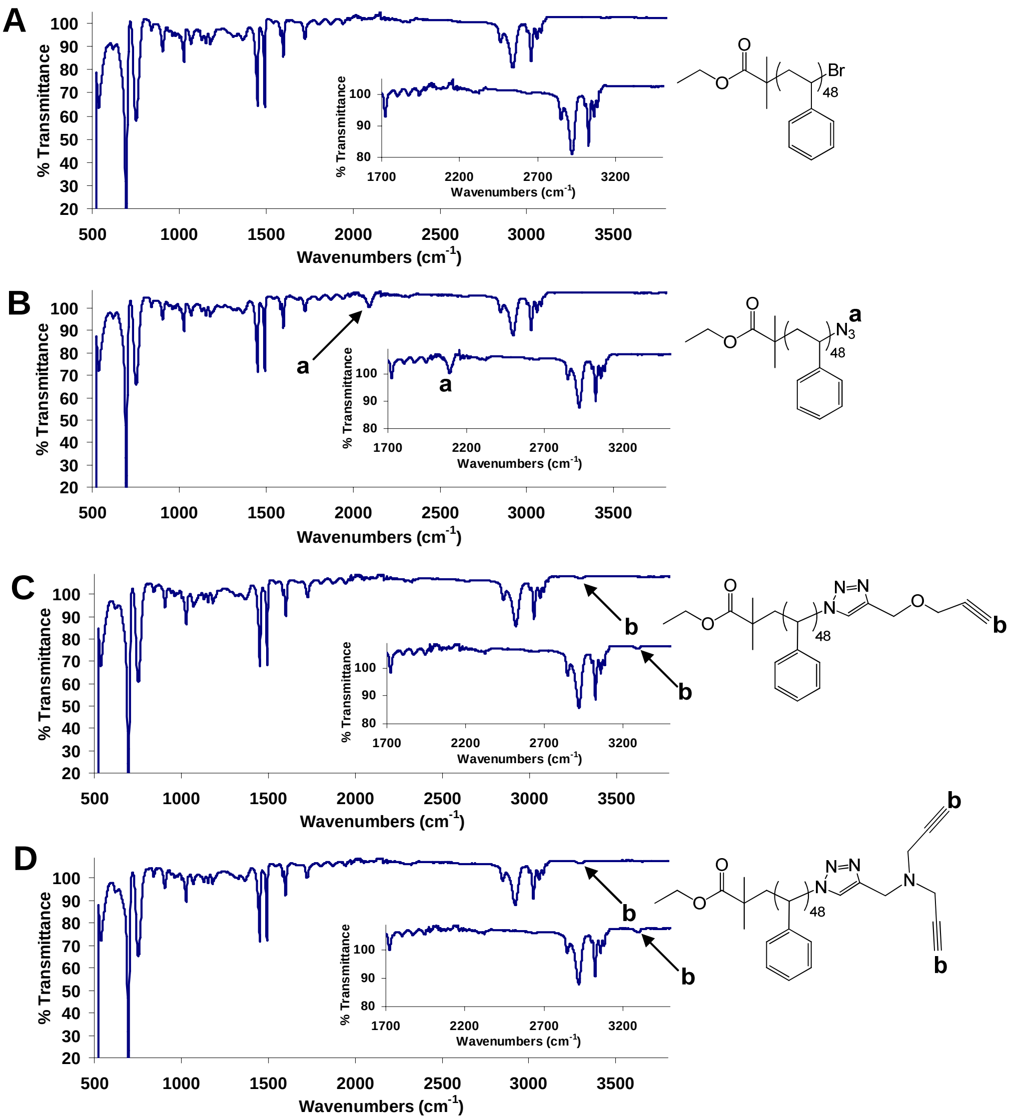


Figure S7: ATR-FTIR analysis of l-PSTY$_{48}$-Br and its chain-end modifications. Spectra of **(A)** l-PSTY$_{48}$-Br; **(B)** l-PSTY$_{48}$-N$_3$; **(C)** l-PSTY$_{48}$-≡; **(D)** l-PSTY$_{48}$-(≡)$_2$. **(a)** azide stretch at 2094 cm^{-1}; **(b)** alkyne stretch at 3295 cm^{-1}.

Table S1: Molecular weight distributions of starting and chain-end modified polymers used in the synthesis of complex architectures **11-14**.

	RI Detection[a]			**Absolute Detection**[b]		
Polymer	**M_n**	**M_p**	**PDI**	**M_n**	**M_p**	**PDI**
≡(HO)-PSTY$_{44}$-Br (2)	4600	4900	1.11	4600	5000	1.10
≡(HO)-PSTY$_{44}$-N$_3$ (3)	4700	5000	1.09	4500	4800	1.11
c-PSTY$_{44}$-OH (4)	3400	3700	1.07	4600	5100	1.09
c-PSTY$_{44}$-Br (5)	3600	3900	1.09	4800	5100	1.09
c-PSTY$_{44}$-N$_3$ (6)	3500	3800	1.09	4700	5200	1.10
c-PSTY$_{44}$-≡ (7)	3800	4000	1.09	4700	5000	1.10
c-PSTY$_{44}$-(≡)$_2$ (8)	3800	4000	1.09	4900	5300	1.10
l-PSTY$_{48}$-Br	5000	5400	1.10	5000	5500	1.11
l-PSTY$_{48}$-N$_3$	5000	5300	1.09	5200	5600	1.09
l-PSTY$_{48}$-≡ (9)	5400	5700	1.09	5000	5300	1.11
l-PSTY$_{48}$-(≡)$_2$ (10)	5300	5600	1.10	5300	5700	1.12

[a] The data was acquired using SEC (RI detector) and is based on PSTY calibration curve

[b] The data was acquired using Triple Detection SEC

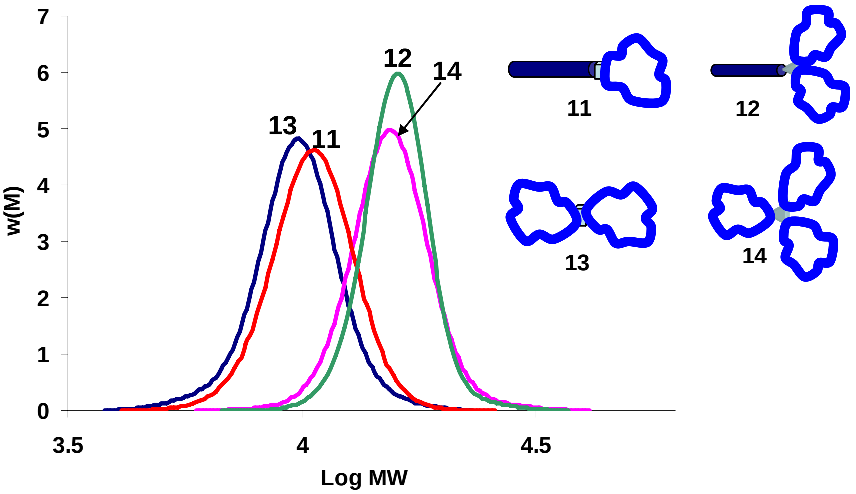


Figure S8: Triple Detection (absolute molecular weight) SEC chromatogram of complex architectures **11-14** after purification by Preparative SEC.

Table S2: Molecular weight distribution data for synthesised structures **11-14**

	RI Detection[a]		
Polymer	**M_n**	**M_p**	**PDI**
11	9700	10000	1.05
12	12300	12800	1.06
13	7500	7900	1.06
14	10500	10700	1.05

[a] The data was acquired using RI detector only and is based on PSTY calibration curve

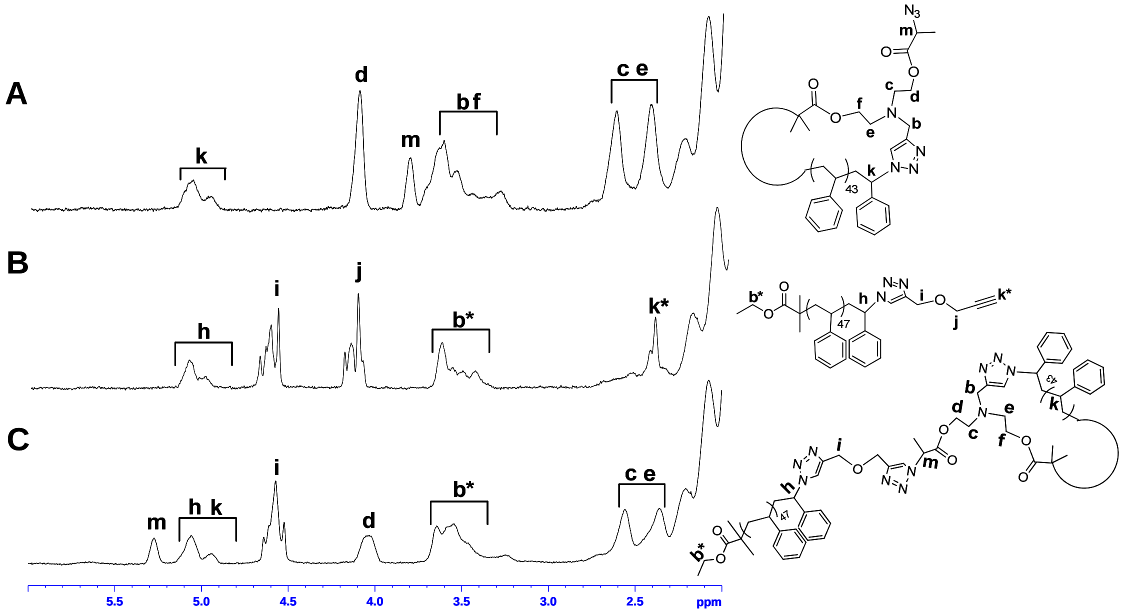


Figure S9: 500 MHz ^{1}H 1D DOSY NMR expanded spectra for **(A)** c-PSTY$_{44}$-N$_3$ **6; (B)** l-PSTY$_{48}$-≡ **9; (C)** CuAAC coupling of **6** and **9** to produce structure **11**.

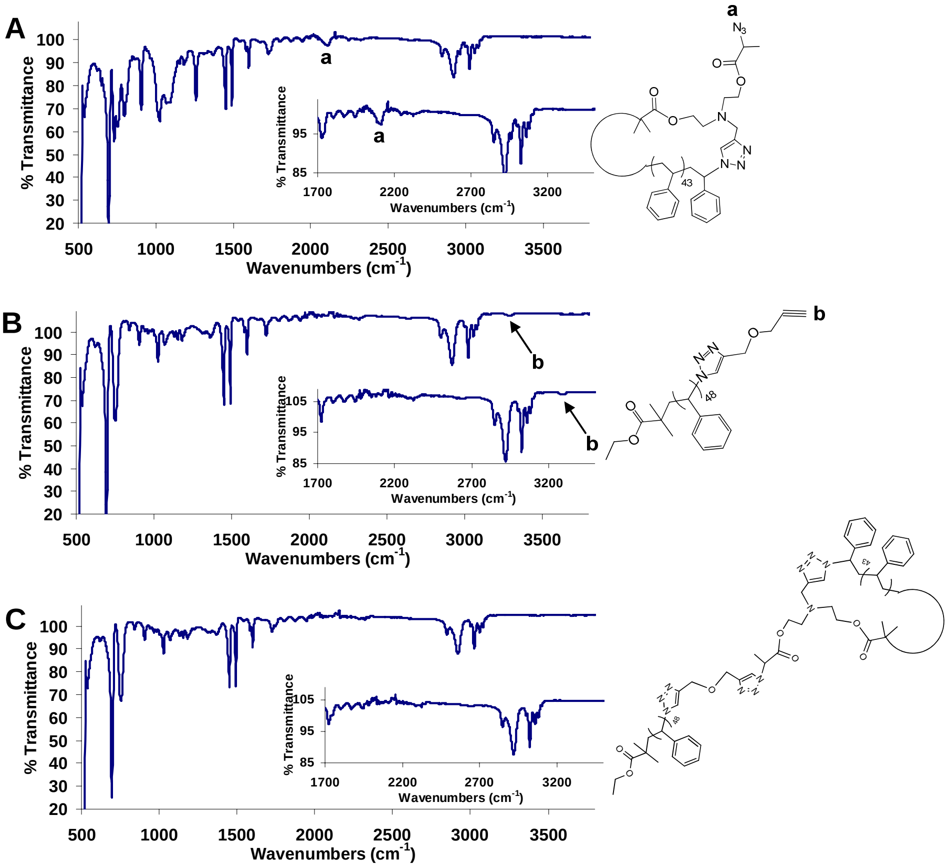


Figure S10: ATR-FTIR analysis of structure **11** formation. Spectra of **(A)** c-PSTY$_{44}$-N$_3$ **6**; **(B)** l-PSTY$_{48}$-≡; **(C)** Structure **11** **(a)** azide stretch at 2094 cm^{-1}; **(b)** alkyne stretch at 3295 cm^{-1}.

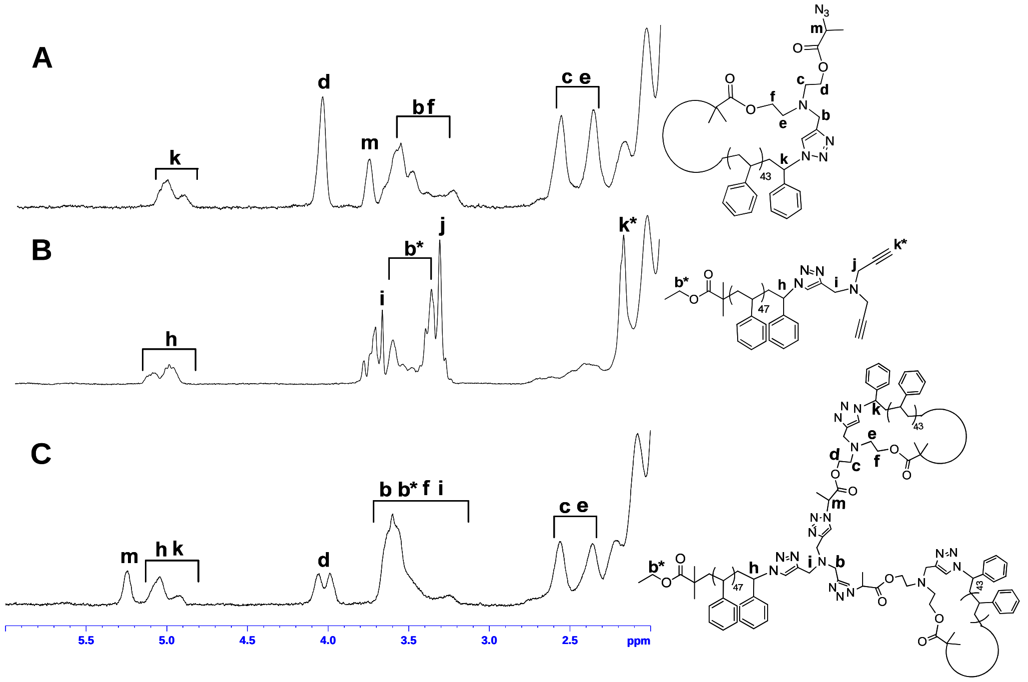


Figure S11: 500 MHz ^{1}H 1D DOSY NMR expanded spectra for **(A)** c-PSTY$_{44}$-N$_3$ **6; (B)** l-PSTY$_{48}$-(≡)$_2$ **10; (C)** CuAAC coupling of **6** and **10** to produce structure **12**.

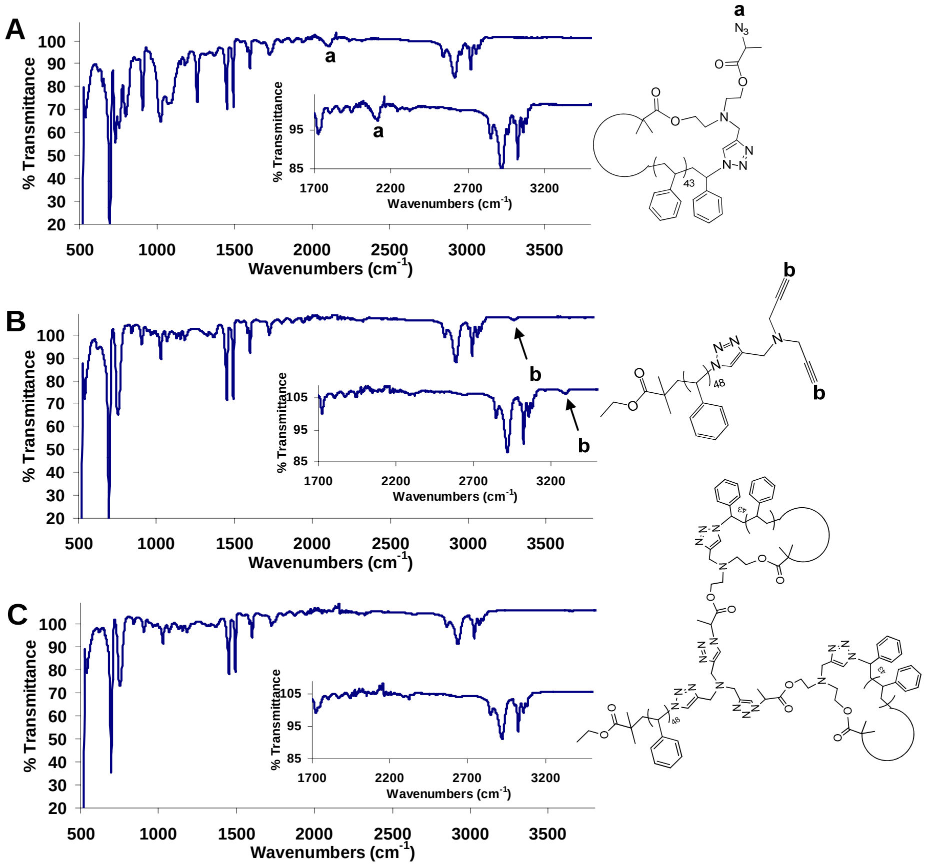


Figure S12: ATR-FTIR analysis of structure **12** formation. Spectra of **(A)** c-PSTY$_{44}$-N$_3$ **6**; **(B)** l-PSTY$_{48}$-(≡)$_2$; **(C)** Structure **12** **(a)** azide stretch at 2094 cm^{-1}; **(b)** alkyne stretch at 3295 cm^{-1}.

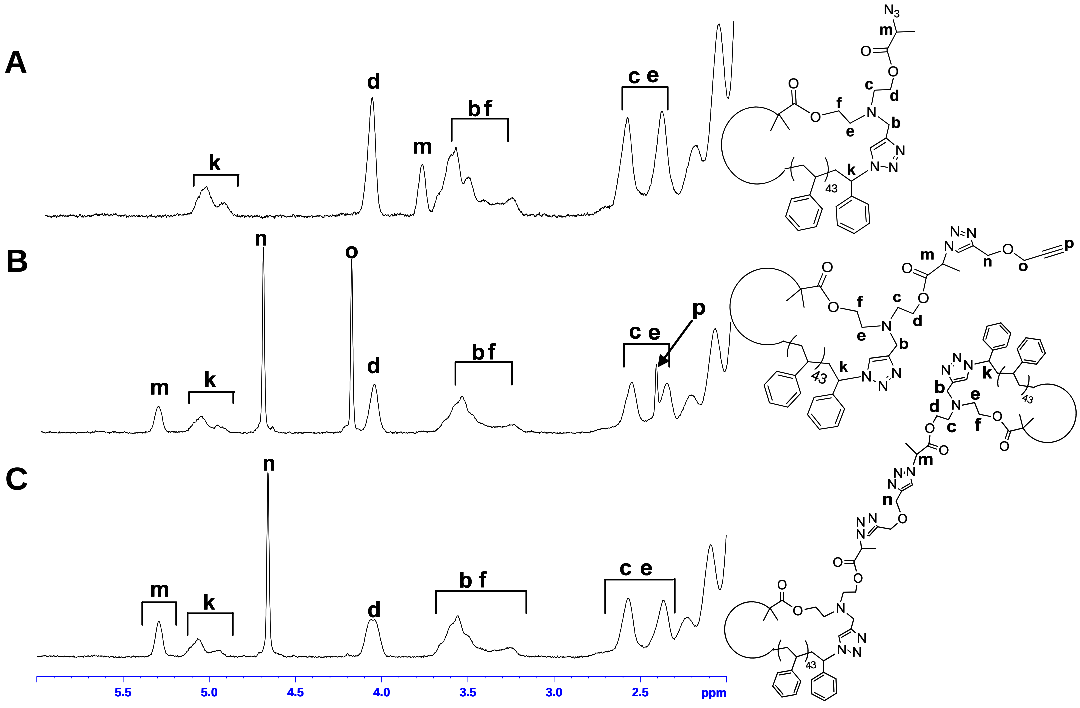


Figure S13: 500 MHz ^{1}H 1D DOSY NMR expanded spectra for **(A)** c-PSTY$_{44}$-N$_3$ **6; (B)** c-PSTY$_{44}$-≡ **7; (C)** CuAAC coupling of **6** and **7** to produce structure **13**.

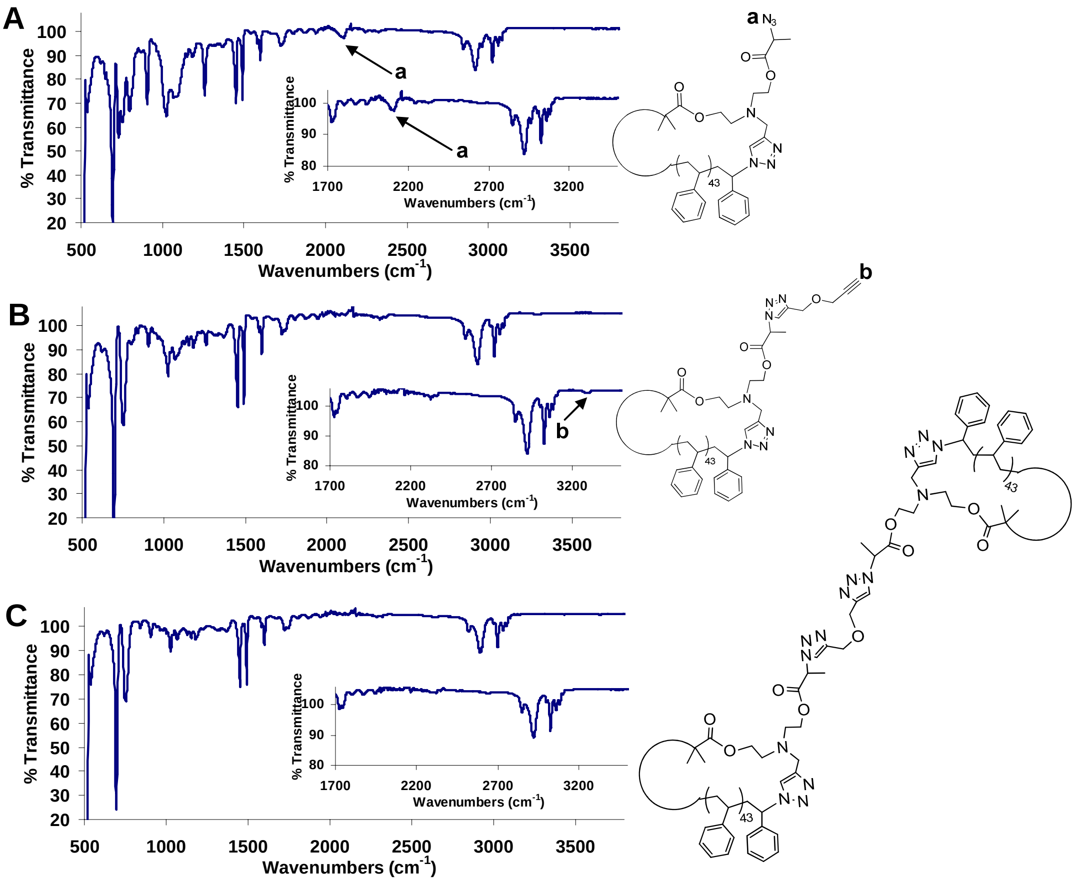


Figure S14: ATR-FTIR analysis of structure **13** formation. Spectra of **(A)** c-PSTY$_{44}$-N$_3$ **6**; **(B)** c-PSTY$_{44}$-≡ **7**; **(C)** Structure **13** **(a)** azide stretch at 2094 cm^{-1}; **(b)** alkyne stretch at 3295 cm^{-1}.

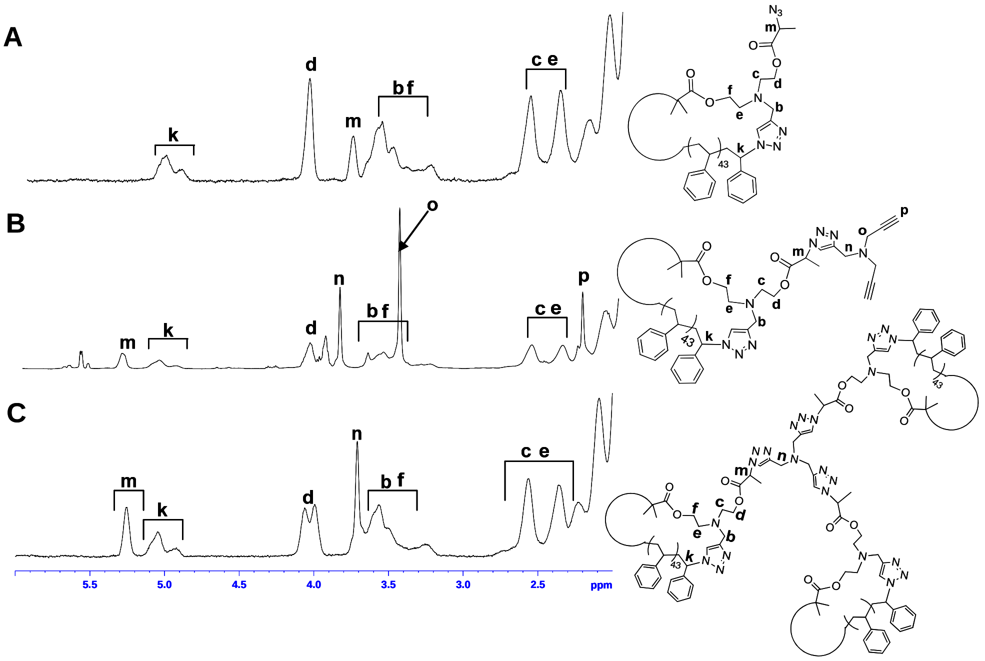


Figure S15: 500 MHz ^{1}H 1D DOSY NMR expanded spectra for **(A)** c-PSTY$_{44}$-N$_3$ **6;** **(B)** c-PSTY$_{44}$-(≡)$_2$ **8;** **(C)** CuAAC coupling of **6** and **8** to produce structure **14**.

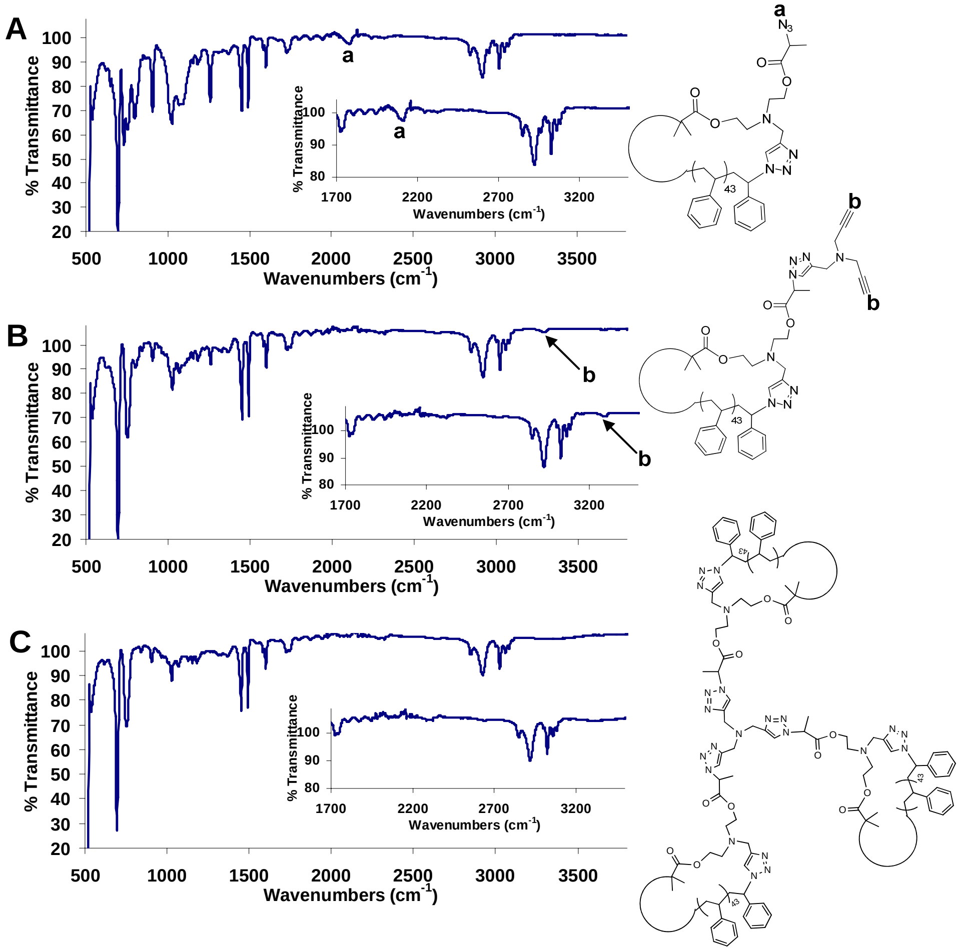


Figure S16: ATR-FTIR analysis of structure **14** formation. Spectra of **(A)** c-PSTY$_{44}$-N$_3$ **6**; **(B)** c-PSTY$_{44}$-(≡)$_2$ **8**; **(C)** Structure **14** **(a)** azide stretch at 2094 cm^{-1}; **(b)** alkyne stretch at 3295 cm^{-1}.

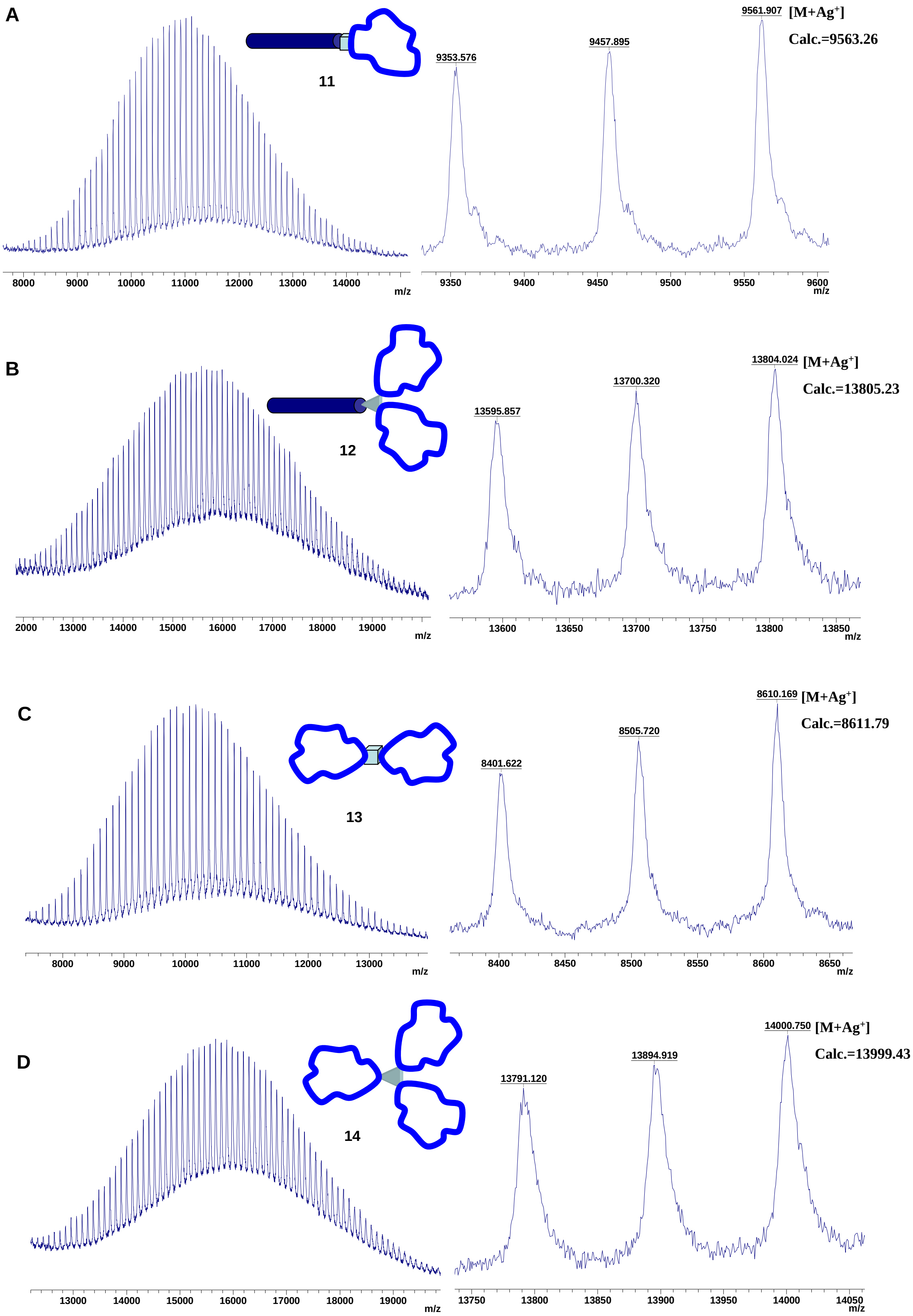


Figure S17: MALDI-ToF mass spectra acquired in linear mode with Ag salt as cationization agent and DCTB matrix. The full and expanded spectra correspond to structures: **(A) 11** calculated [M+Ag$^+$] = 9563.26, DP$_n$ = 85; **(B) 12** calculated [M+Ag$^+$] = 13805.23, DP$_n$ = 122; **(C) 13** calculated [M+Ag$^+$] = 8611.79, DP$_n$ = 74; **(D) 14** calculated [M+Ag$^+$] = 13999.43, DP$_n$ = 122. All products were analysed by MALDI-ToF after purification by preparative SEC.

References:

1. Peng, Y.; Liu, H.; Zhang, X.; Liu, S.; Li, Y. *Macromolecules* **2009**, 42 (17), 6457-6462