Supporting Information:

to

One Pot Synthesis of Mikto 3-arm AB_2 Stars Constructed from Linear and Macrocyclic Polymer Chains.

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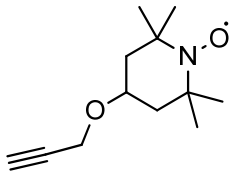
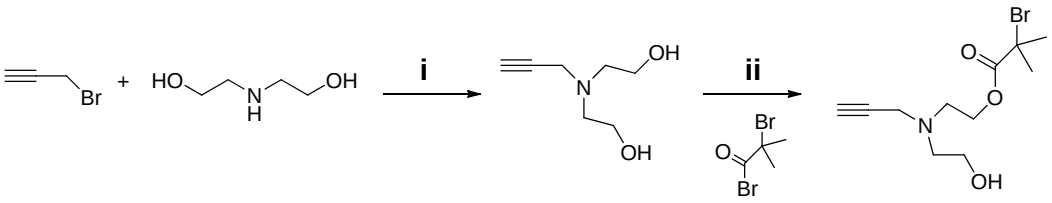
Synthesis of 4-propargyloxy-2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO-≡)



This compound was synthesized according to the method of Ciampolini *et al*. and is well documented.[1]

1.1 Synthesis of Alkyne(Hydroxyl) ATRP Initiator



Scheme S1: Synthesis of alkyne(hydroxyl) ATRP initiator. (i) K_2CO_3, acetone, reflux for 24 h; (ii) TEA, THF at 0 ºC.

Synthesis of Alkyne(hydroxyl) ATRP initiator. This compound was prepared by slight modification to the literature procedure.[2]

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 argon was charged propargyl bromide (10 mL, 0.09 mol). The reaction mixture was refluxed at 80 ºC 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 ºC, 0.04 mmHg) to give a yellow viscous oil which became even more viscous (solid-like) on cooling (5.77 g, 86.8 %). ^{1}H NMR (δ, ppm, $CDCl_3$): 3.66 (m, 4H, N(CH2C***H2***OH)2), 3.49 (m, 2H, NC***H2***C≡CH), 2.77 (m, 4H,

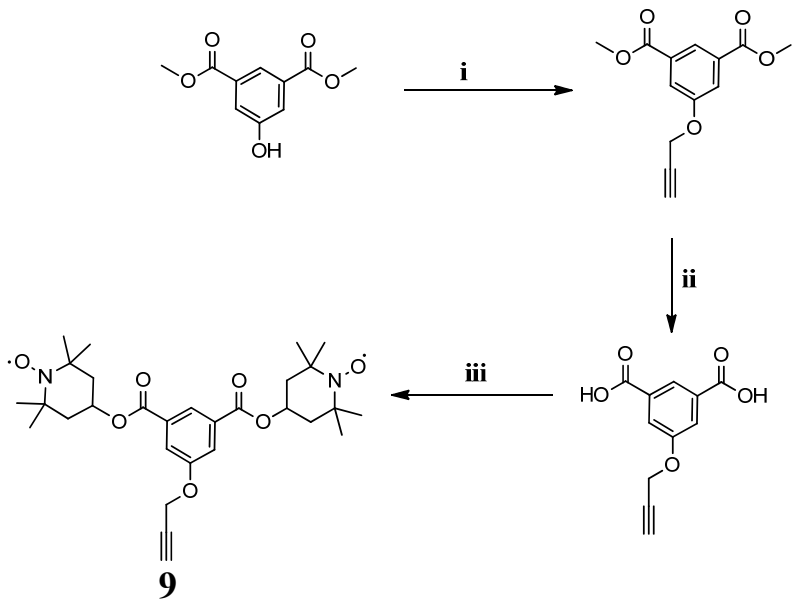
N(C***H2***CH2OH)2), 2.35 (s, broad, 2H, (CH2O***H***)2); 2.21 (m, 1H, NCH2C≡C***H***); LR-ESI-MS (M-H+) Calc. *m/z* 144.10 Found *m/z* 144.07.

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

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 ºC. 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 de-ionized water (3 x 100 mL) 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, NCH2C***H2***OCO), 3.59 (m, 2H, NCH2C***H2***OH), 3.50 (m, 2H, NC***H2***C≡CH), 2.91 (m, 2H, NC***H2***CH2OCO); 2.77 (m, 2H, NC***H2***CH2OH); 2.22 (m, 1H, NCH2C≡C***H***), 1.94 (m, 6H, OCOC(C***H3***)2Br). Microanalysis: Calculated for C11H18BrNO3: C, 45.22; H, 6.21; N, 4.79 Found: C, 45.22; H, 6.40; N, 4.77.

1.2 Synthesis of Tri-functional Core (1)

This compound was synthesized according to previously described procedure[3]



(i) K_2CO_3, propargyl bromide, 18-c-6, acetone, reflux 24 h; (ii) 2M NaOH, MeOH/acetone (60:40 v/v), RT, 24 h; (iii) TEMPO-≡, EDC.HCl, DMAP, DMF, 0 °C – RT, 48 h.

Scheme S2: Scheme for the synthesis of tri-functional core **1**

The trifunctional core **1** was synthesized according to previously described literature.[3]

Synthesis of dimethyl 5-(prop-2-yn-1-yloxy)isophthalate

This compound was synthesized according to the literature procedure of Joralemon *et al.* [4]

Synthesis of 5-(prop-2-yn-1-yloxy)isophthalic acid

Dimethyl 5-(prop-2-yn-1-yloxy)isophthalate (10.04 g, 0.040 mol) was stirred in 400 mL MeOH at RT. To this suspension was added 2M NaOH solution (160 mL) and acetone (250 mL). The solution became clear and was then allowed to stir for 24 hr at room temperature before concentrated by rotary evaporation to remove the volatile organics. The aqueous solution was then

cooled to 0 °C and acidified with 2M HCl solution (200 mL) where a white precipitate formed. This suspension was then stirred for 30 min, vacuum filtered and washed with Milli-Q water (3 x 100 mL). The white solid was then dried for 30 min then solubilized in acetone, dried with anhydrous magnesium sulfate, filtered and taken to complete dryness *in vacuo*. The product was obtained as a white powder (7.72 g, 86.7 %) and was used without further purification.

Synthesis of Bis(2,2,6,6-tetramethylpiperidin-4-yloxyl) 5-(prop-2-yn-1-yloxy)isophthalate (BTMPPI) ***1***

5-(Prop-2-yn-1-yloxy)isophthalic acid (6.99 g, 0.032 mol) and EDC.HCl (14.86 g, 0.078 mol) were stirred in 200 mL DMF at 0 °C. 4-(dimethylamino)pyridine (DMAP, 0.95 g, 0.008 mol) was added and the solution was then allowed to stir for 1 hr before 4-hydroxy TEMPO (13.23 g, 0.077 mol) was added. The solution was further stirred at 0 ºC for 30 min then warmed to RT and stirred for 2 days, after which it was poured into diethyl ether (100 mL) and extracted with Milli-Q water (3 x 100 mL), saturated $NaHCO_3$ (100 mL), Milli-Q water (100 mL) and finally brine (100 mL). The organic phase was collected and dried over anhydrous magnesium sulphate, filtered and concentrated by rotary evaporation to dryness. The crude product was purified by column chromatography with ethyl acetate/petroleum spirit (1/4, v/v) as the eluent. The product was obtained as a peach colored solid (9.54 g, 56.8 %). Rf (1:1 EtOAc/petroleum spirit) 0.58; ESI-MS *m/z* Theory: 529.64 (M-H+); Found: 530.14; IR (ATR) υ(max) 3258 (br), 2977 (br), 1711, 1595, 1463, 1451; Microanalysis: Calculated for $C_{29}H_{40}N_2O_7$: C, 65.89; H, 7.63; N, 5.30; Found: C, 65.38; H, 7.68; N, 5.31 %. The presence of paramagnetic nitroxide moieties precluded direct analysis by NMR. Consequently, **5** was reduced to the corresponding hydroxylamine with phenylhydrazine. ^{1}H NMR (CDCl3): δ 1.26 (s, 24H, C*H3*CNO), 1.75 (t, 4H, CH*CH2*C), 2.04 (dd, 4H, CH*CH2*C), 2.56 (t, *J*=2.3 Hz, 1H, OCH2C*CH*), 4.78 (d, *J*=2.3 Hz, 2H, O*CH2*CCH), 5.21 (b, 2H, COO*CH*CH2), 7.81 (s, 2H, Ar*H*), 8.26 (s, 1H, Ar*H*); ^{13}C NMR (CDCl3):165.00, 157.48, 151.21, 132.24, 123.63, 77.54, 76.33, 68.11, 56.25, 43.80, 31.72, 20.74

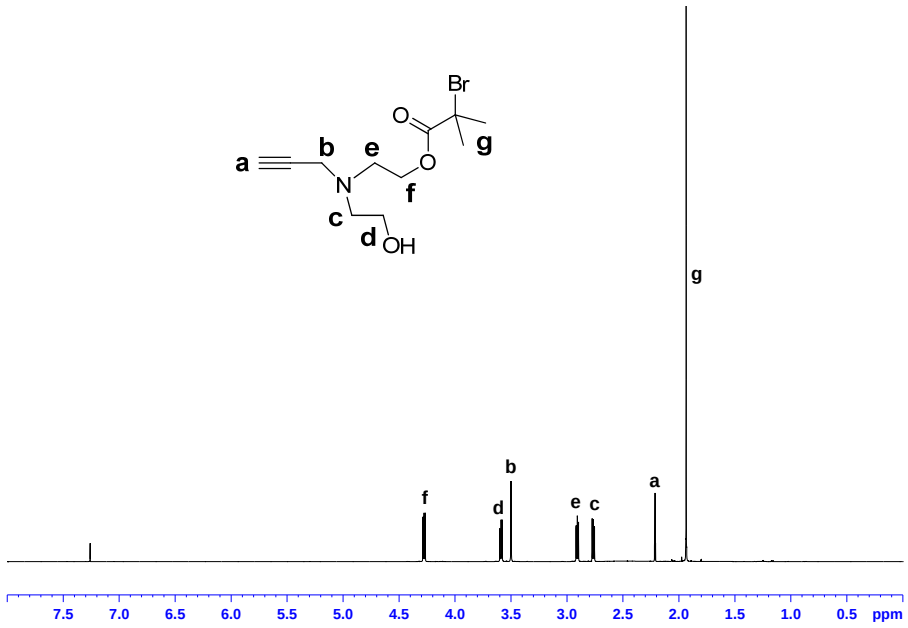


Figure S1: ^{1}H NMR spectra of ATRP initiator (**1**).

1.3 Synthesis of l-PSTY$_{24}$-Br (2)

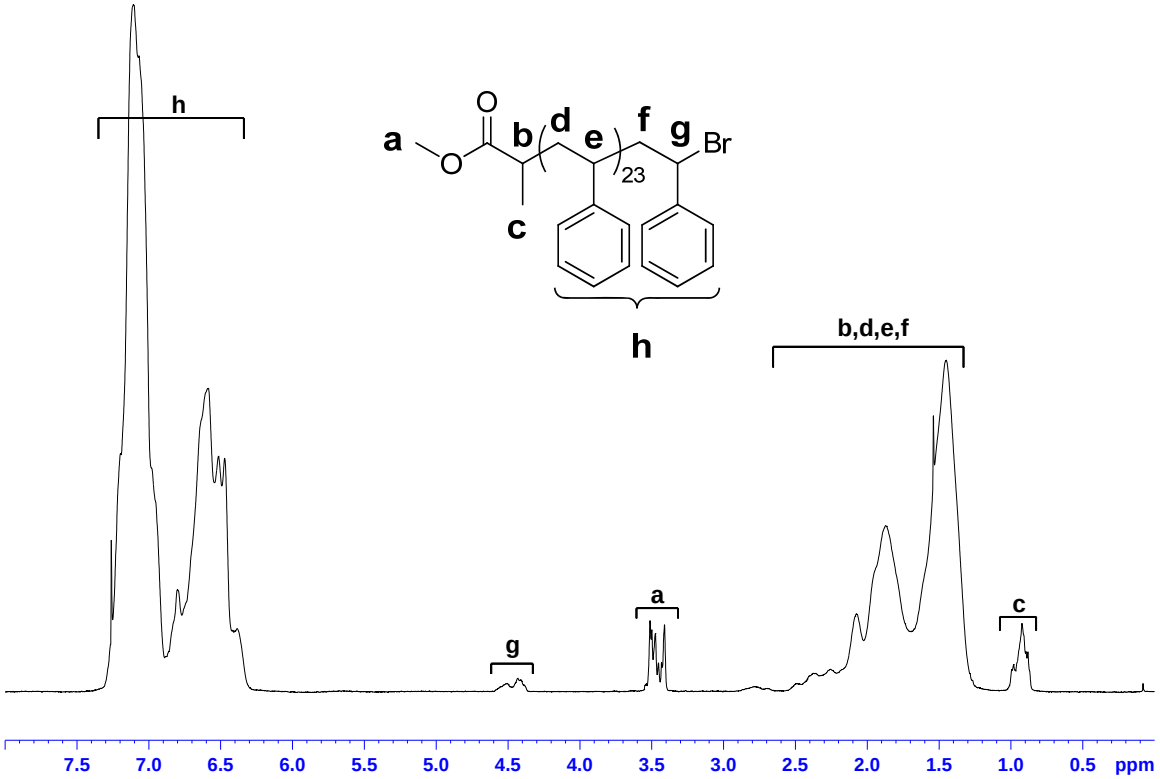


Figure S2: ^{1}H 1D DOSY NMR analysis of PSTY$_{24}$-Br (**2**).

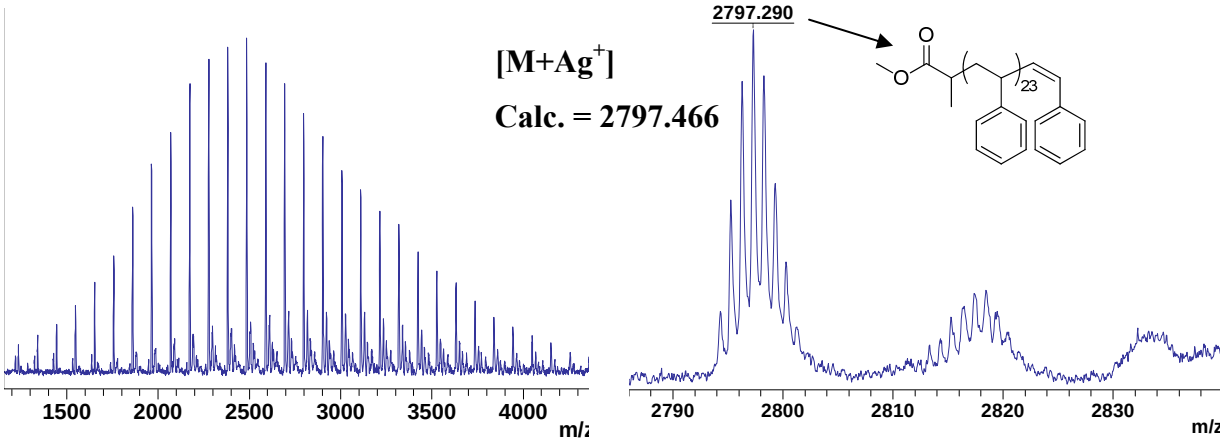


Figure S3: MALDI-ToF mass spectrum of PSTY$_{24}$-Br (**2**) with Ag salt as cationization agent from a DCTB matrix in reflectron mode: (left) full molecular weight distribution, (right) isotopic resolution of peaks.

1.4 Synthesis of l-PSTY$_{24}$-N$_3$ (3)

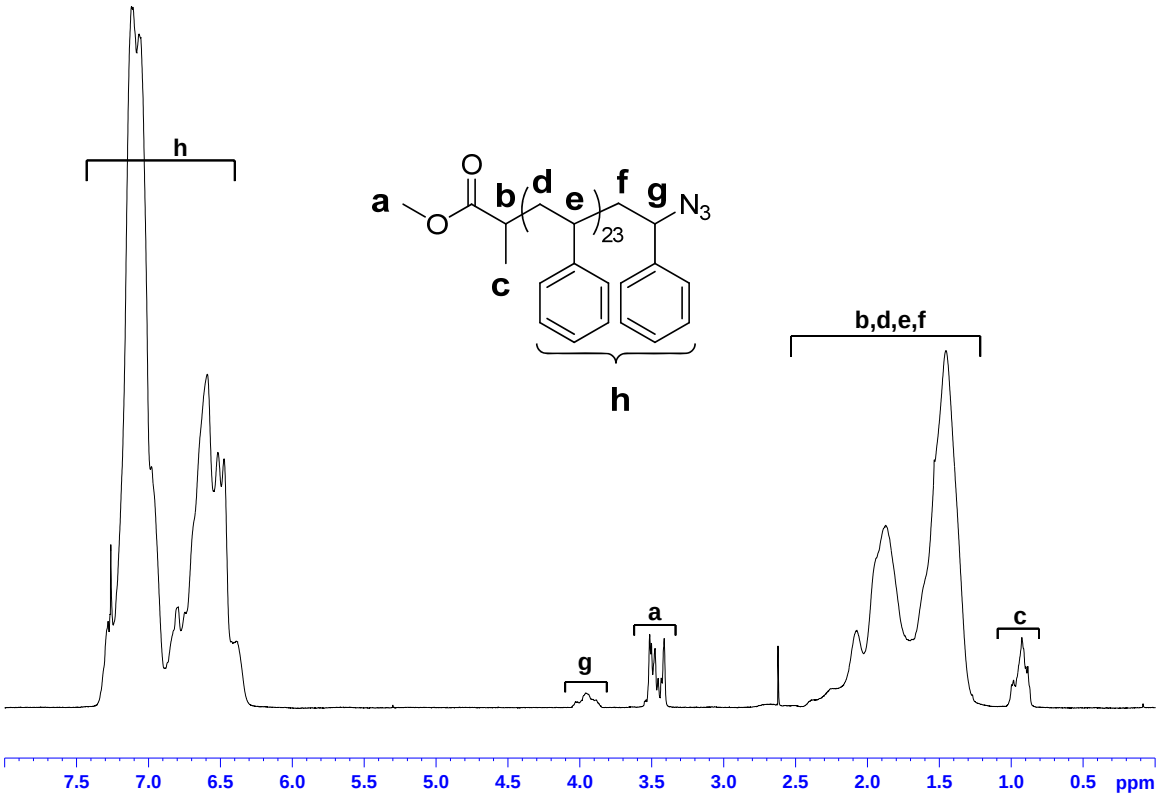


Figure S4: ^{1}H 1D DOSY NMR analysis of PSTY$_{24}$-N$_3$ (**3**).

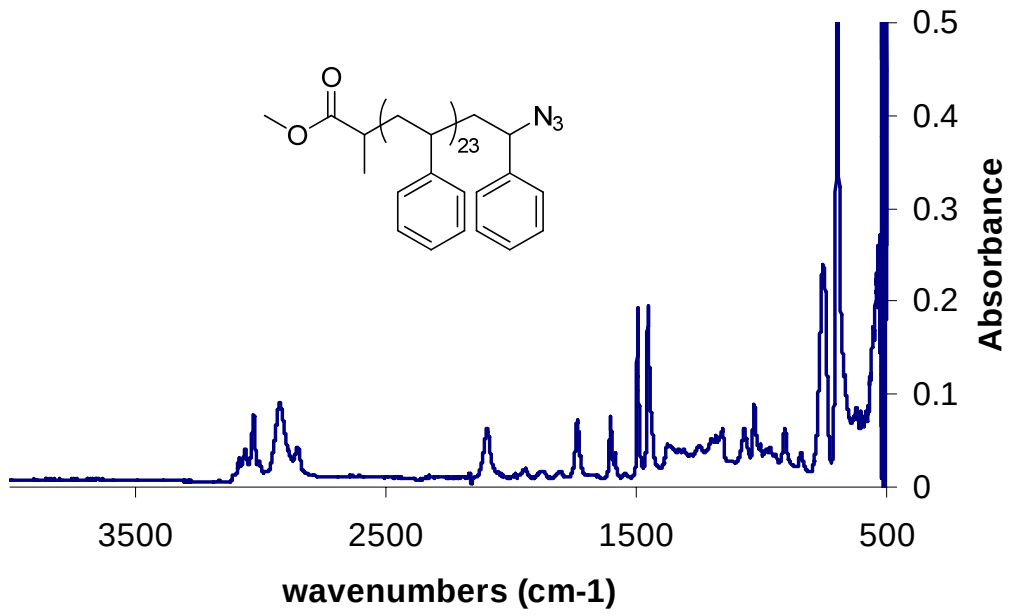


Figure S5: ATR-FTIR spectra of PSTY$_{24}$-N$_3$ (**3**)

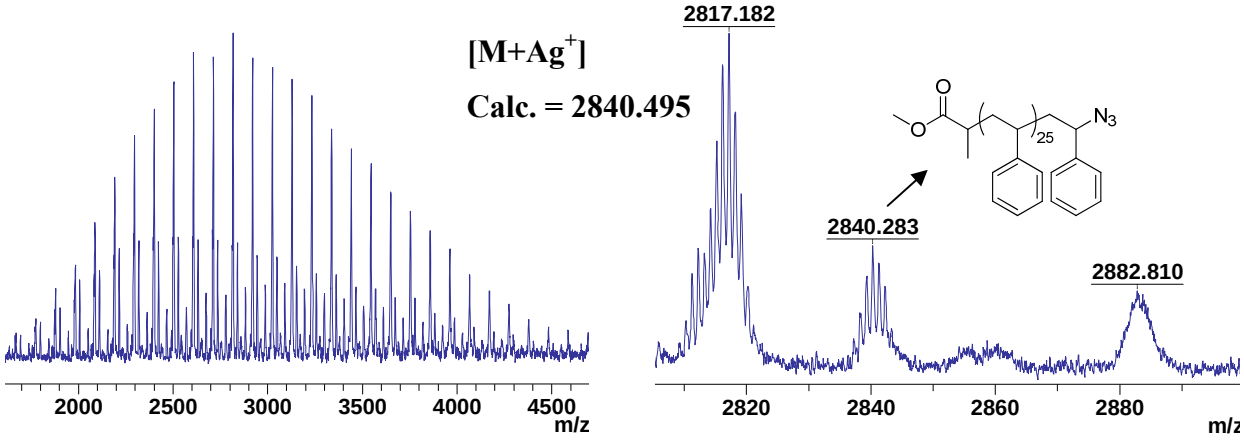


Figure S6: MALDI-ToF mass spectrum of $PSTY_{24}$-N_3 (**3**) with Ag salt as cationization agent from a DCTB matrix in reflectron mode: (left) full molecular weight distribution, (right) isotopic resolution of peaks.

1.5 Synthesis of l-PSTY precursors and c-PSTY-OH

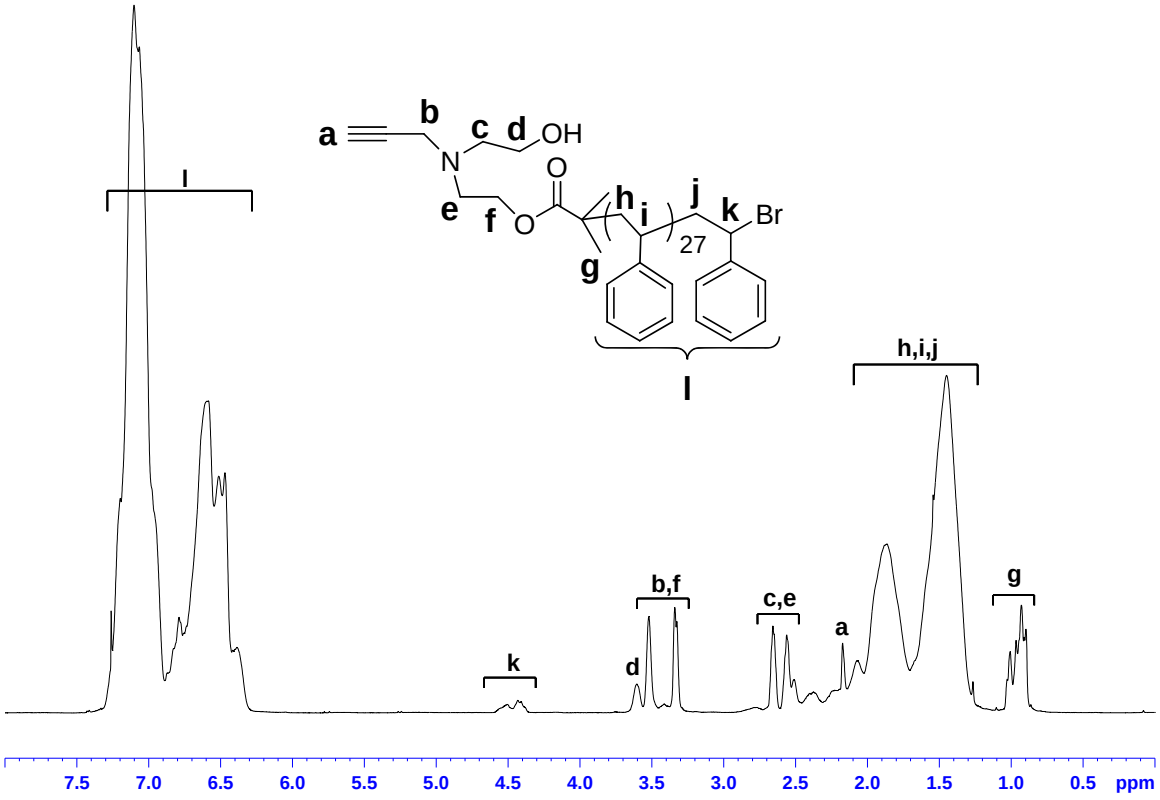


Figure S7: ^{1}H 1D DOSY NMR analysis of ≡(OH)-PSTY$_{28}$-Br.

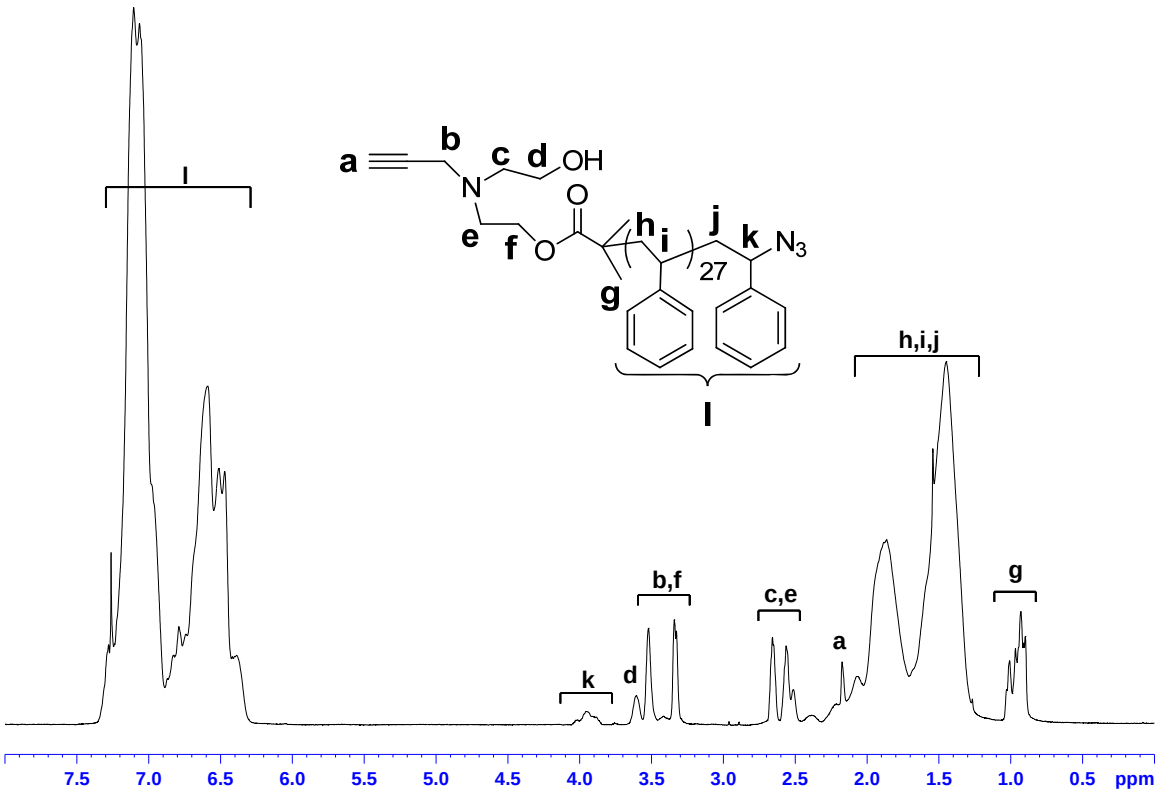


Figure S8: ^{1}H 1D DOSY NMR analysis of ≡(OH)-PSTY$_{28}$-N$_3$.

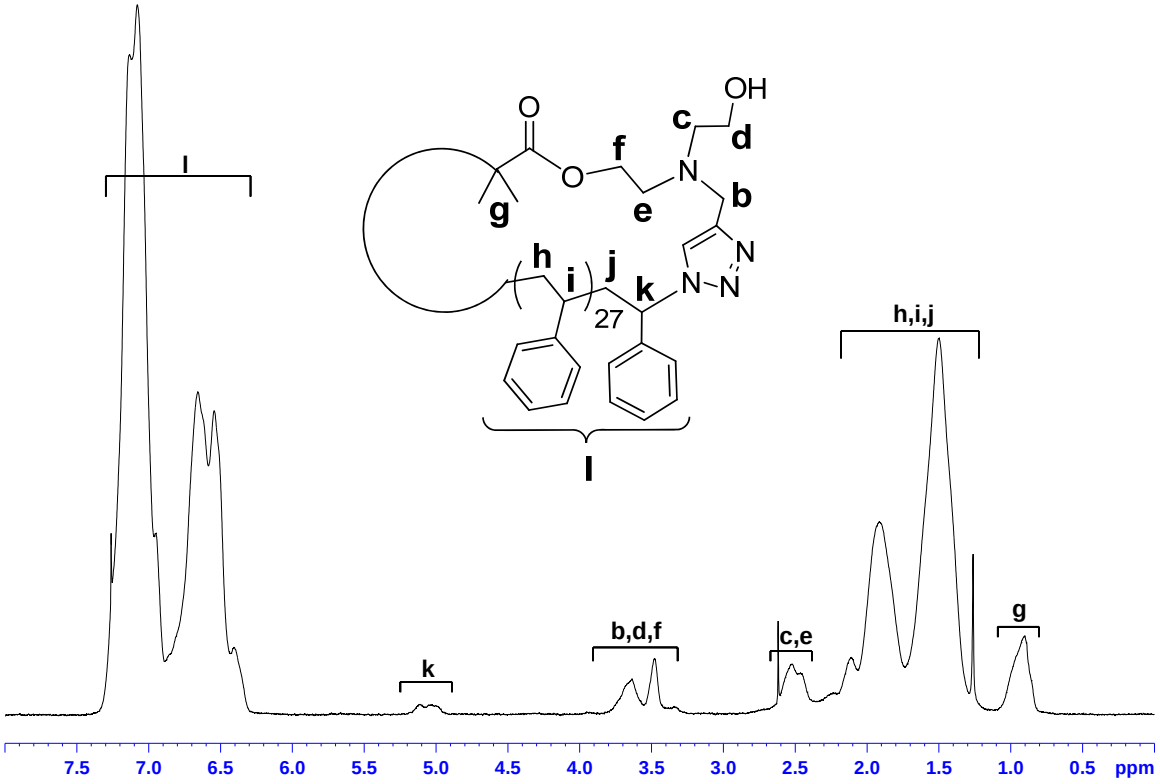


Figure S9: ^{1}H 1D DOSY NMR analysis of c-PSTY$_{28}$-OH.

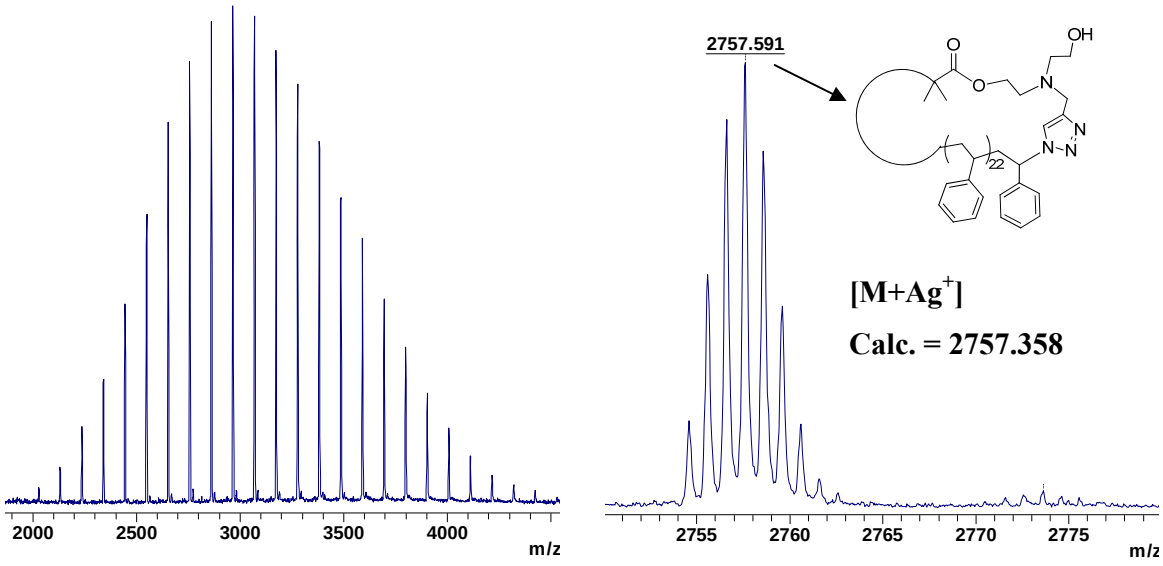


Figure S10: MALDI-ToF mass spectrum of c-PSTY$_{28}$-OH with Ag salt as cationization agent from a DCTB matrix in reflectron mode: (left) full molecular weight distribution, (right) isotopic resolution of peaks.

1.6 Synthesis of c-PSTY$_{28}$-Br (4)

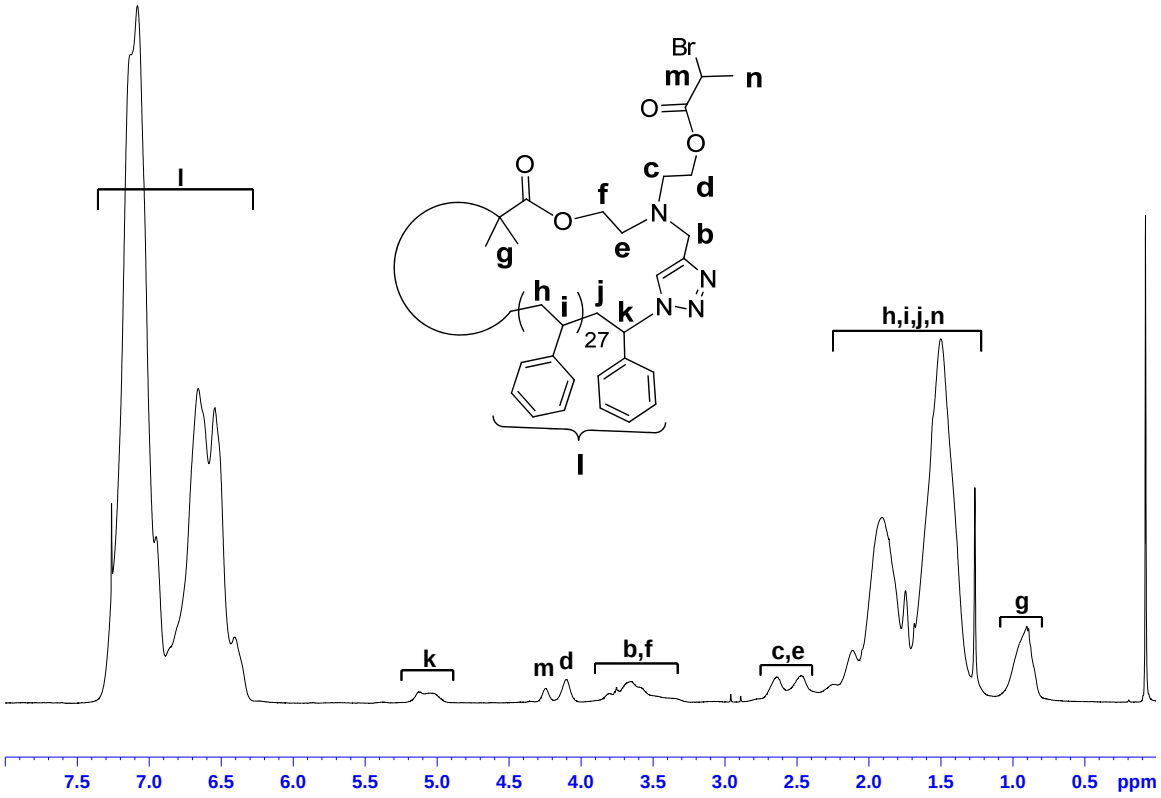


Figure S11: ^{1}H 1D DOSY NMR analysis of c-PSTY$_{28}$-Br (**4**).

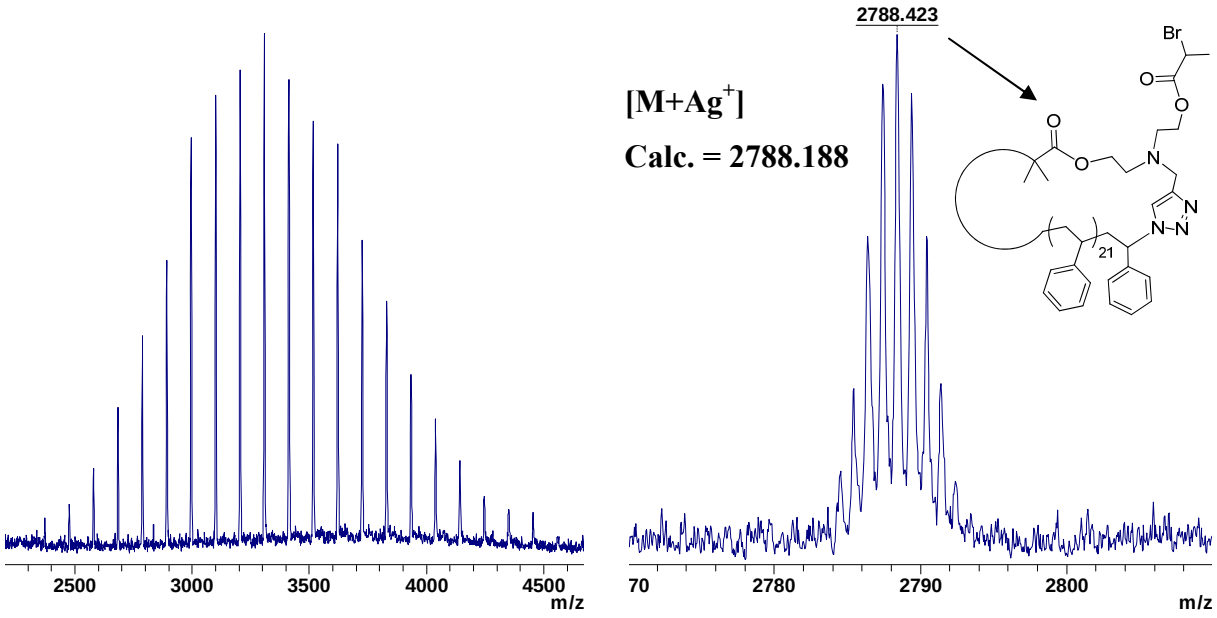


Figure S12: MALDI-ToF mass spectrum of c-PSTY$_{28}$-Br with Ag salt as cationization agent from a DCTB matrix in reflectron mode: (left) full molecular weight distribution, (right) isotopic resolution of peaks.

1.7 Synthesis of c-PSTY$_{28}$-N$_3$ (5)

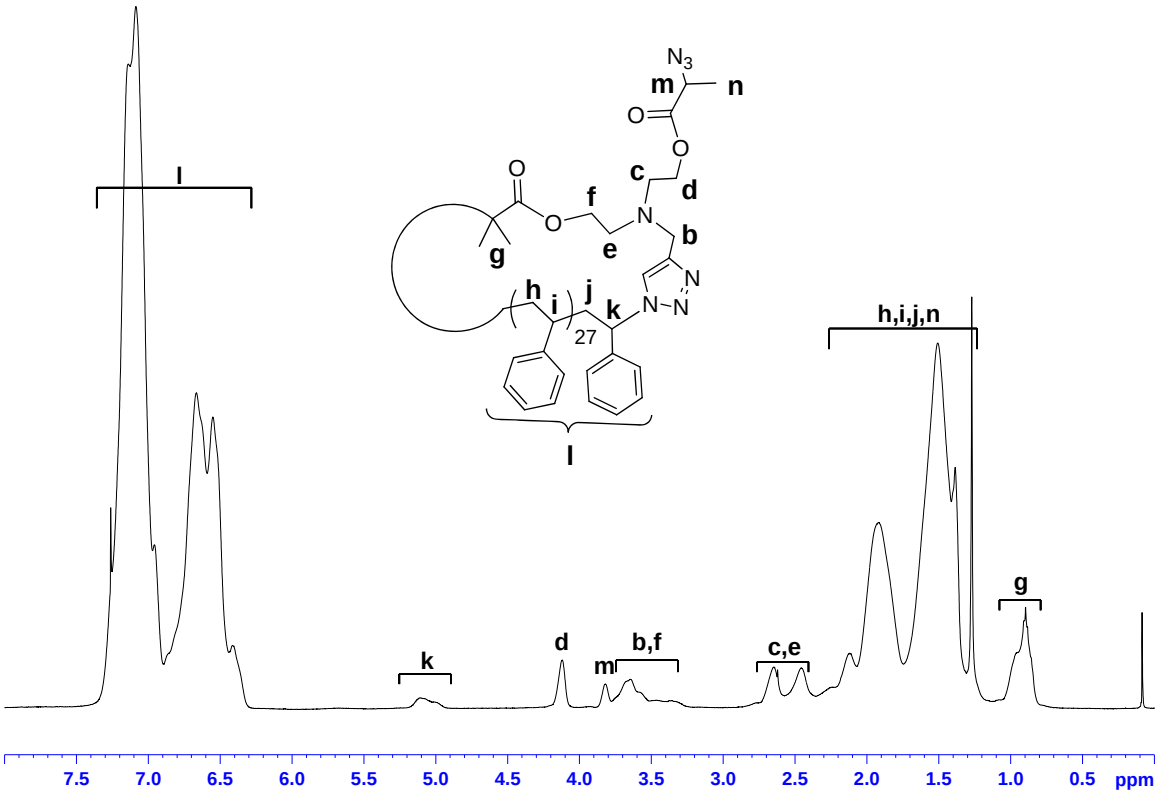


Figure S13: ^{1}H 1D DOSY NMR analysis of c-PSTY$_{28}$-N$_3$ (**5**).

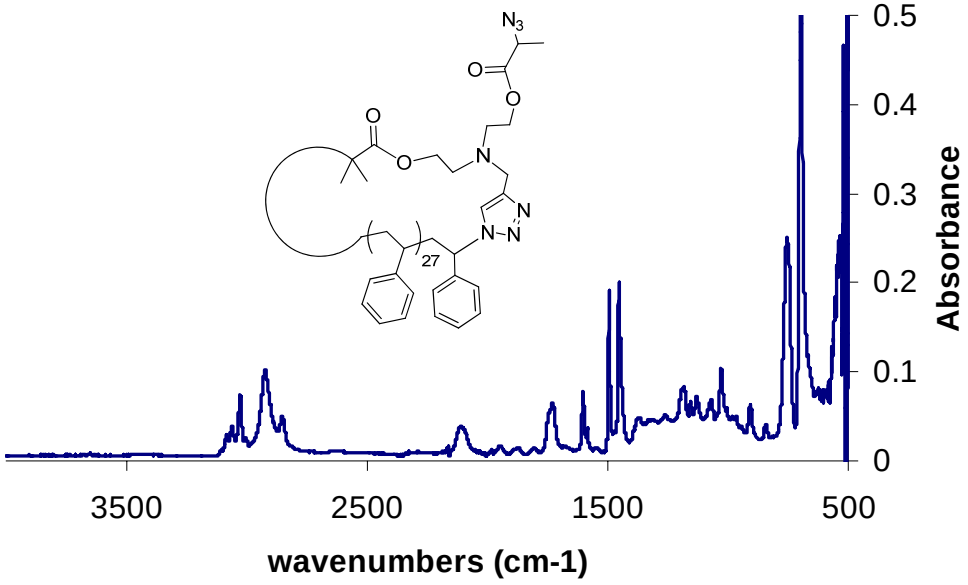


Figure S14: ATR-FTIR spectra of c-PSTY$_{28}$-N$_3$ (**5**)

1.8 Synthesis of P^{t}BA$_{25}$-Br (6)

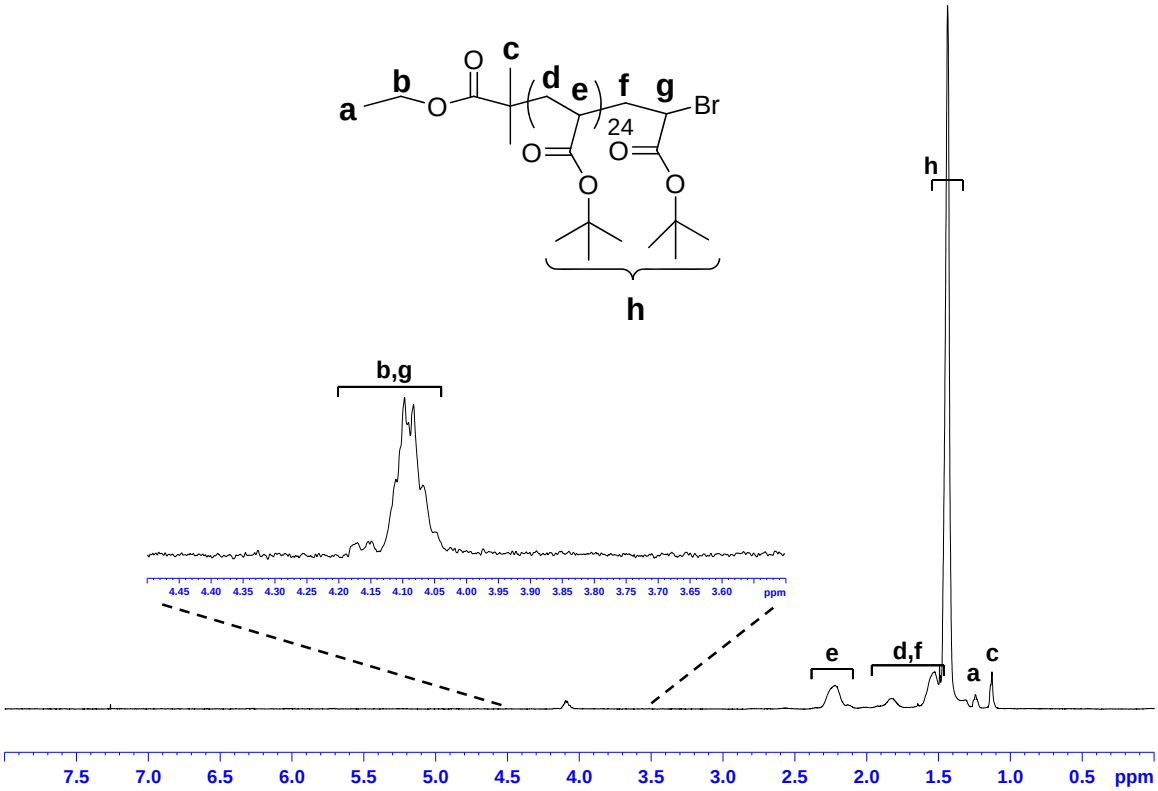


Figure S15: ^{1}H 1D DOSY NMR analysis of P^{t}BA$_{25}$-Br (**6**).

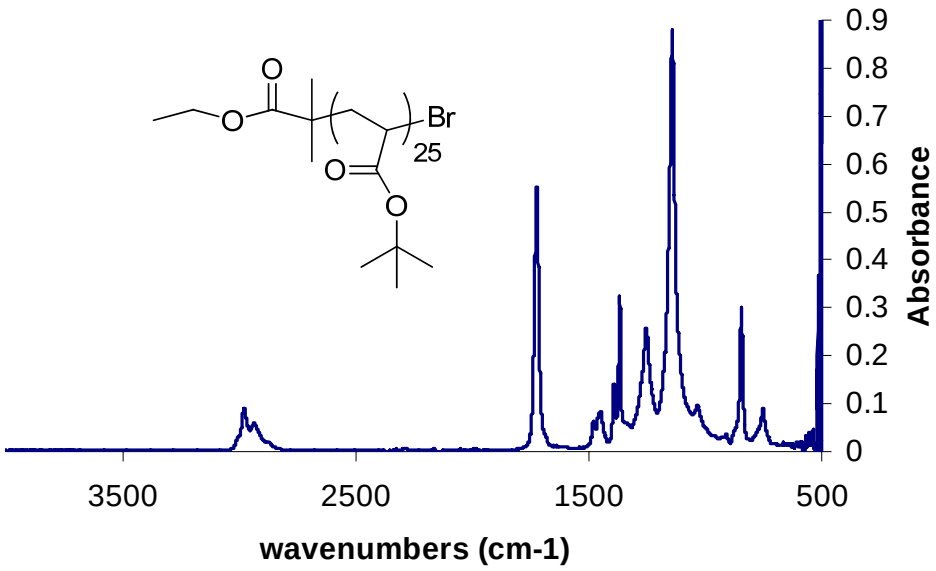


Figure S16: ATR-FTIR spectra of P^{t}BA$_{25}$-Br (**6**)

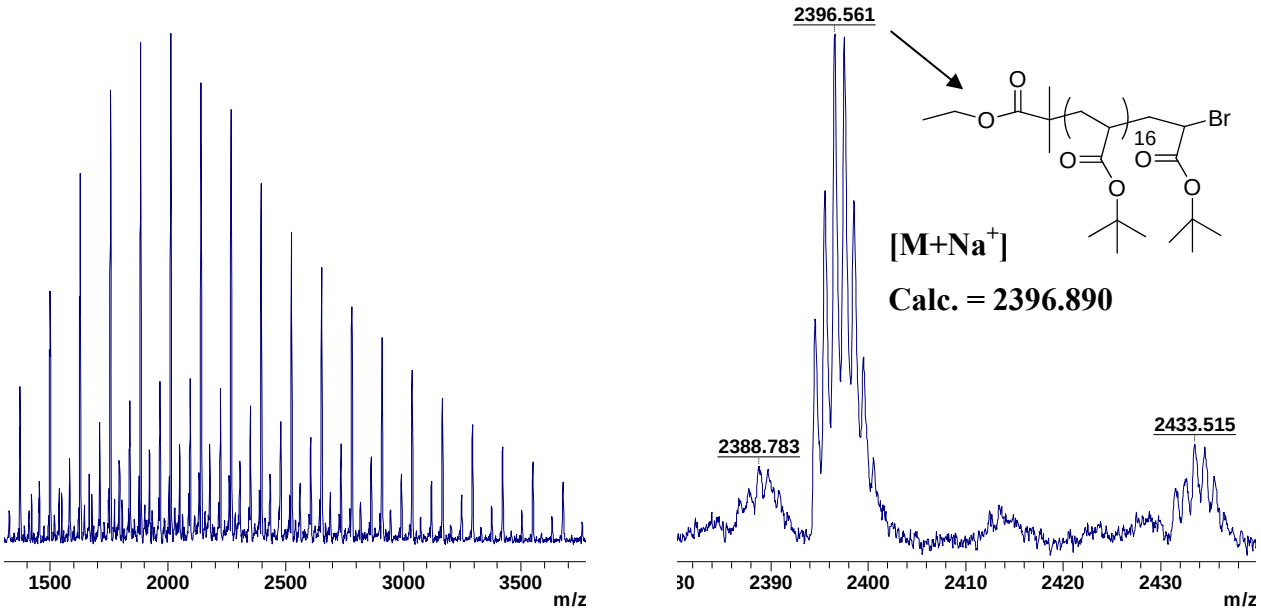


Figure S17: MALDI-ToF mass spectrum of P^{t}BA$_{25}$-Br **6** with Na salt as cationization agent from a DCTB matrix in reflectron mode: (left) full molecular weight distribution, (right) isotopic resolution of peaks.

1.9 Synthesis of P^tBA_{25}-N_3 (7)

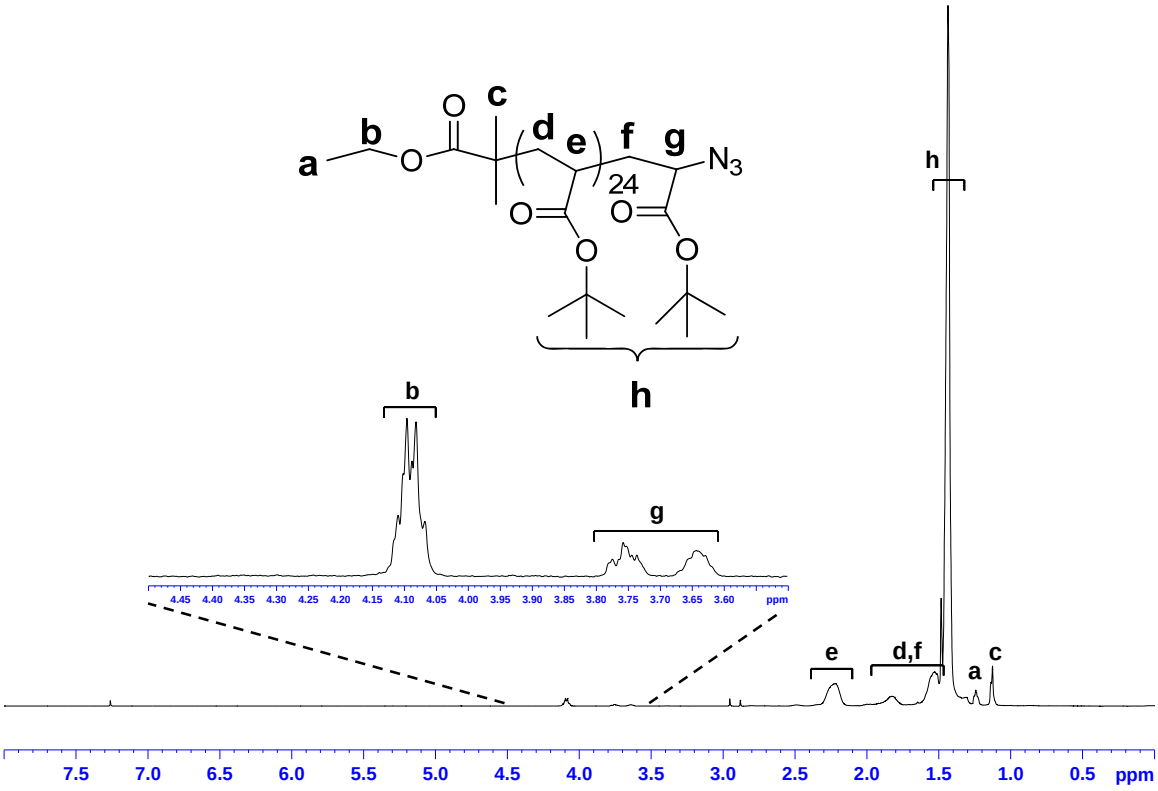


Figure S18: ^{1}H 1D DOSY NMR analysis of P^tBA_{25}-N_3 (**7**).

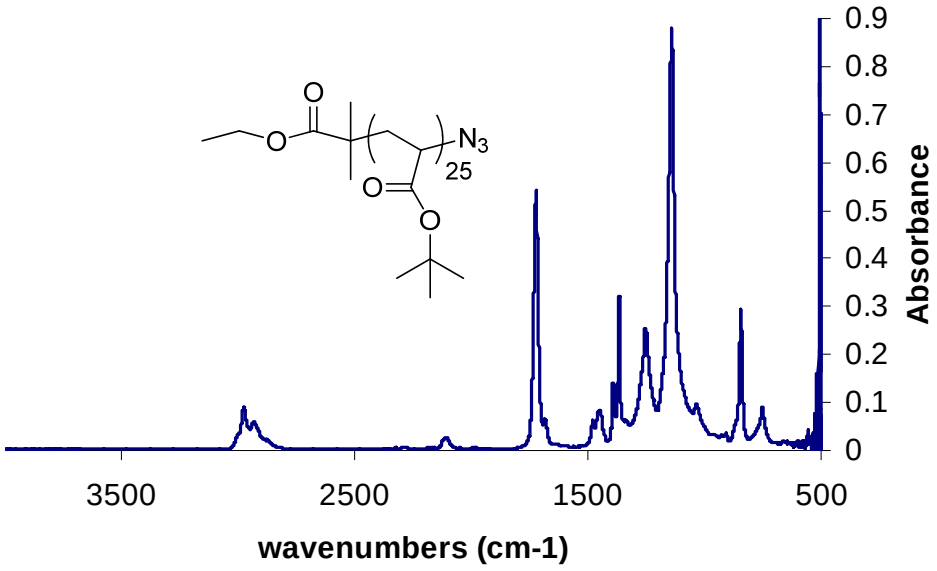


Figure S19: ATR-FTIR spectra of P^tBA_{25}-N_3 (**7**)

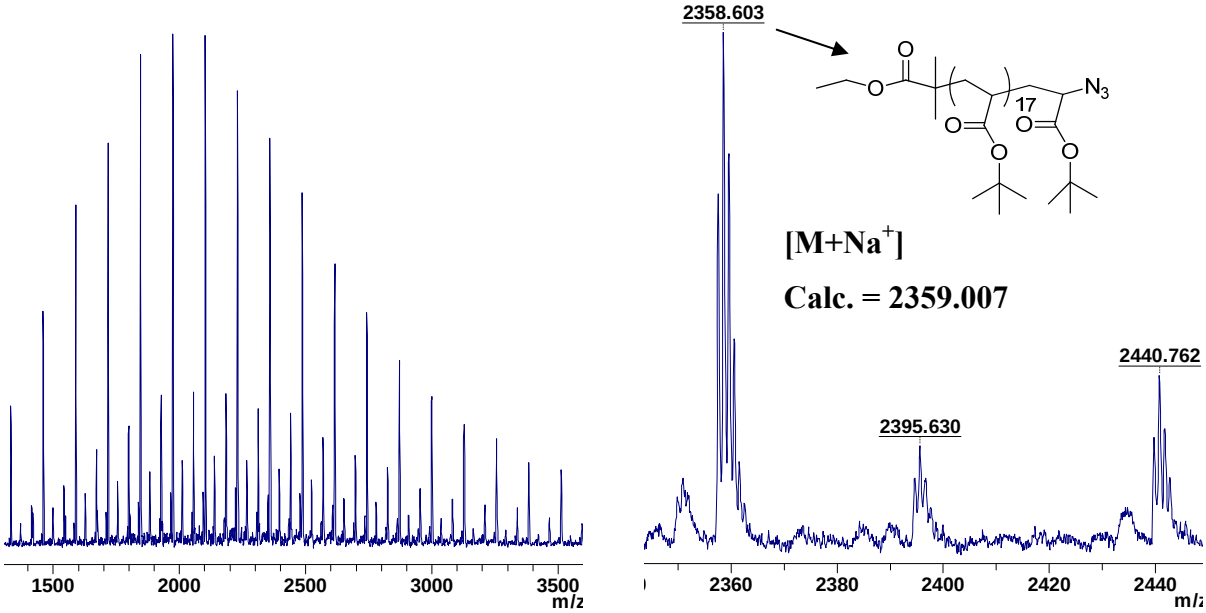


Figure S20: MALDI-ToF mass spectrum of P^tBA_{25}-N_3 (**7**) with Na salt as cationization agent from a DCTB matrix in reflectron mode: (left) full molecular weight distribution, (right) isotopic resolution of peaks.

1.10 Synthesis of PEG_{47}-Br (8)

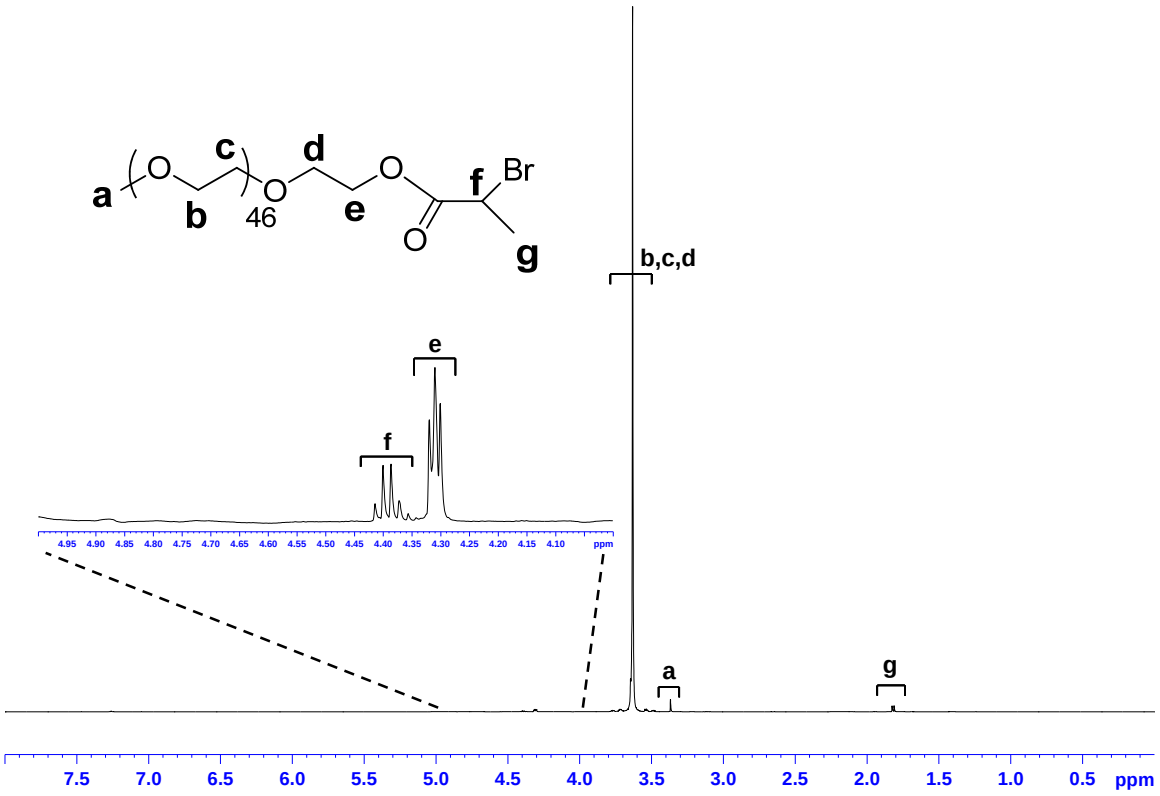


Figure S21: ^{1}H 1D DOSY NMR analysis of PEG_{47}-Br (**8**).

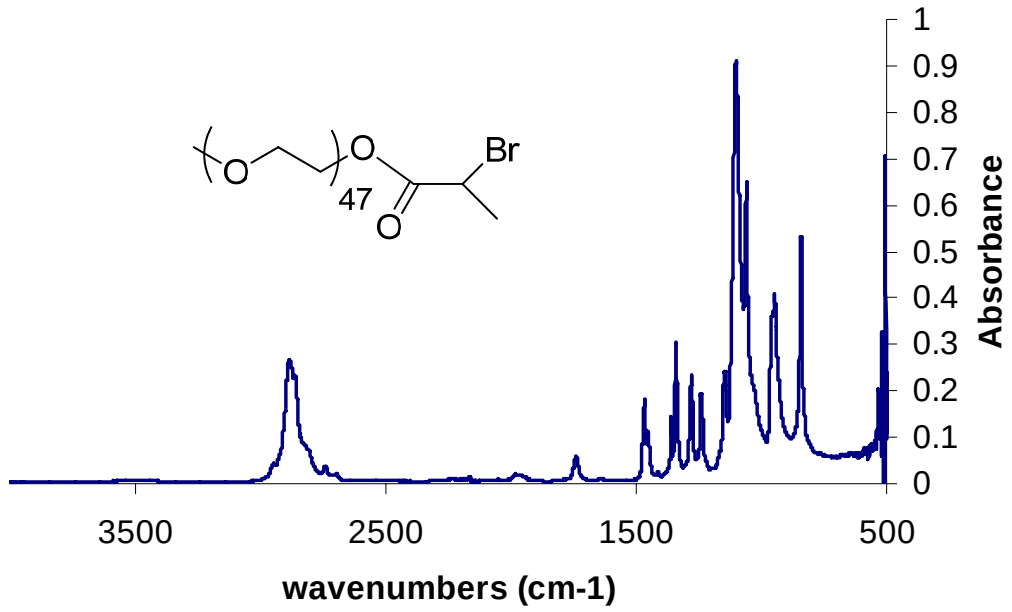


Figure S22: ATR-FTIR spectra of PEG_{47}-Br (**8**).

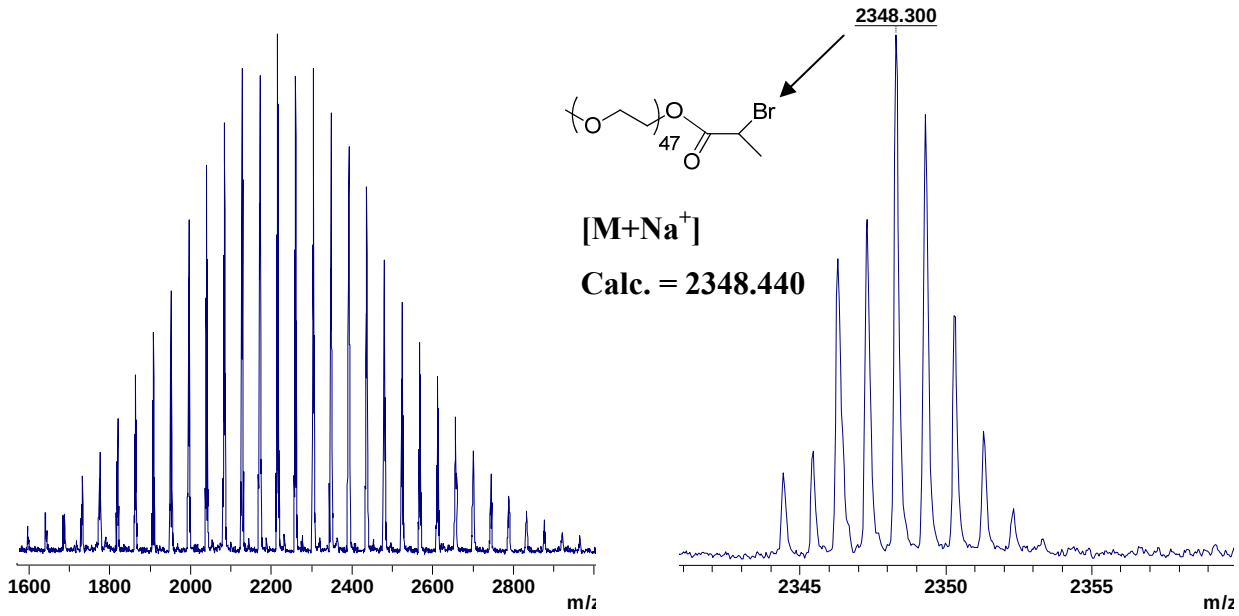


Figure S23: MALDI-ToF mass spectrum of PEG_{47}-Br (**8**) with Na salt as cationization agent from a 2-(4'-Hydroxybenzeneazo)benzoic acid (HABA) matrix in reflectron mode: (left) full molecular weight distribution, (right) isotopic resolution of peaks.

1.11 Synthesis of PEG_{47}-N_3 (9)

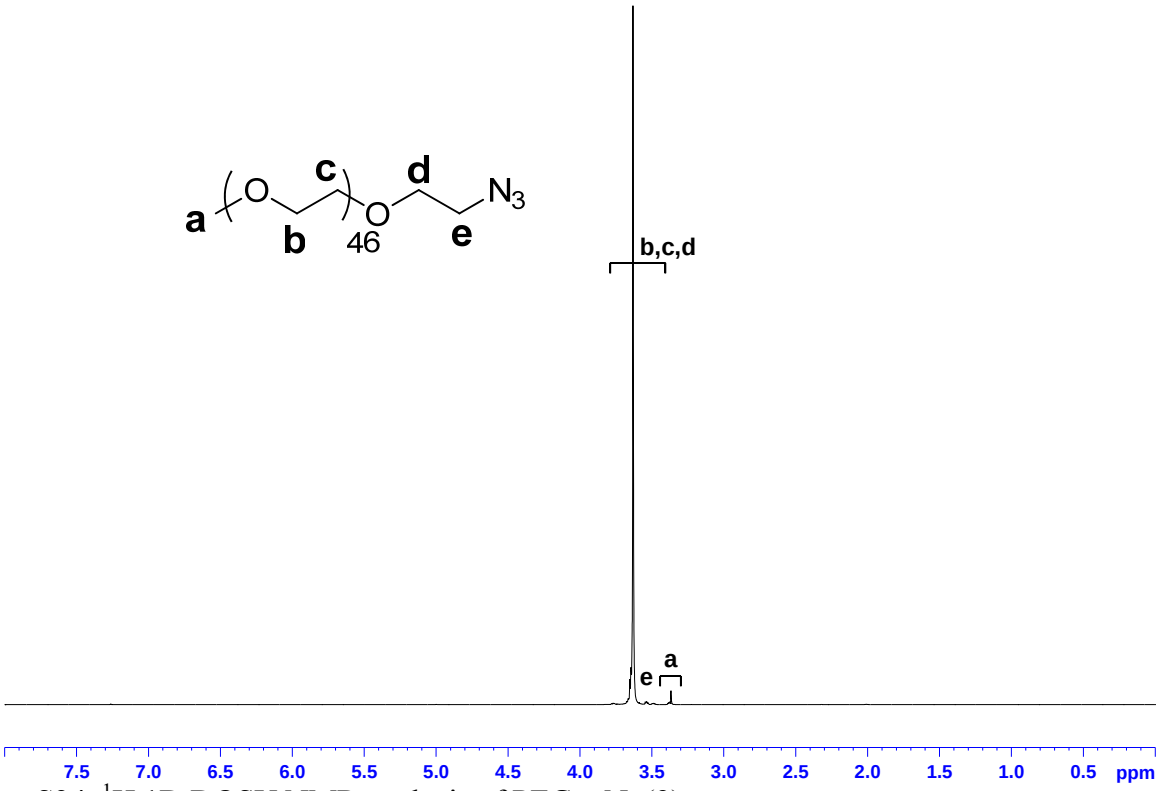


Figure S24: ^{1}H 1D DOSY NMR analysis of PEG_{47}-N_3 (**9**).

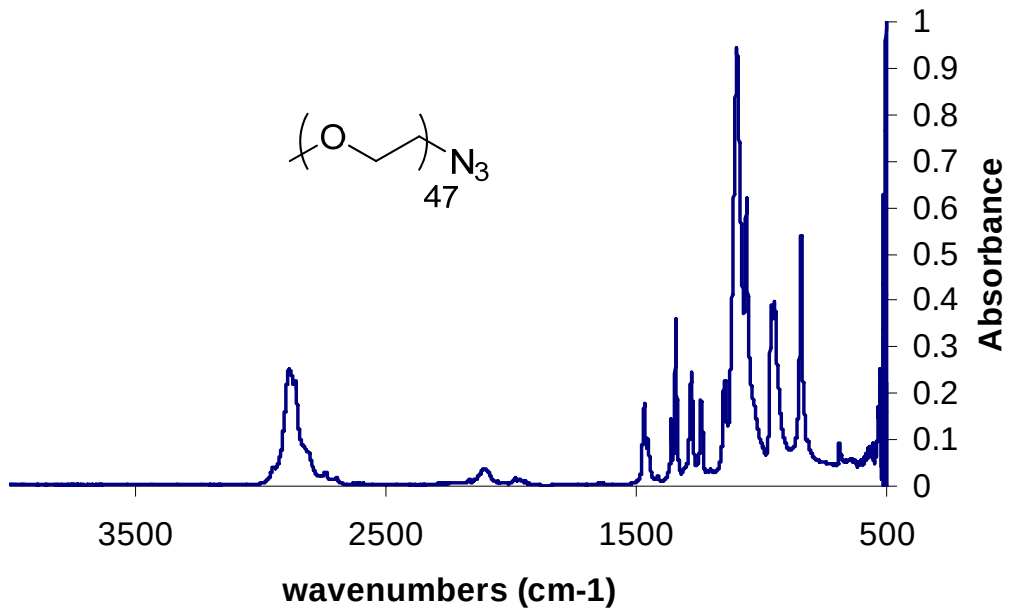


Figure S25: ATR-FTIR spectra of PEG_{47}-N_3 (**9**)

1.12 Synthesis of P(^{t}BA$_{25}$-b-(STY$_{24}$)$_2$) **10**

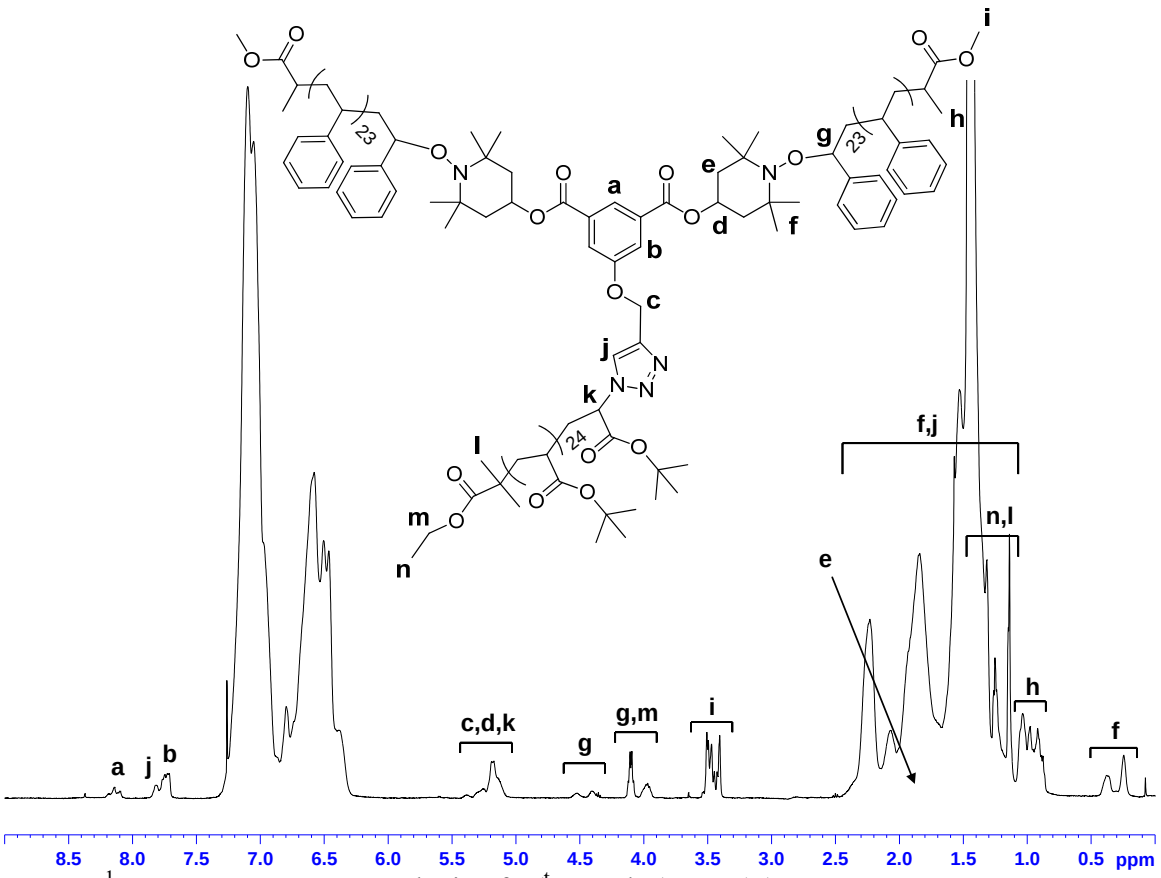


Figure S26: ^{1}H 1D DOSY NMR analysis of P(^{t}BA$_{25}$-b-(STY$_{24}$)$_2$) **10**

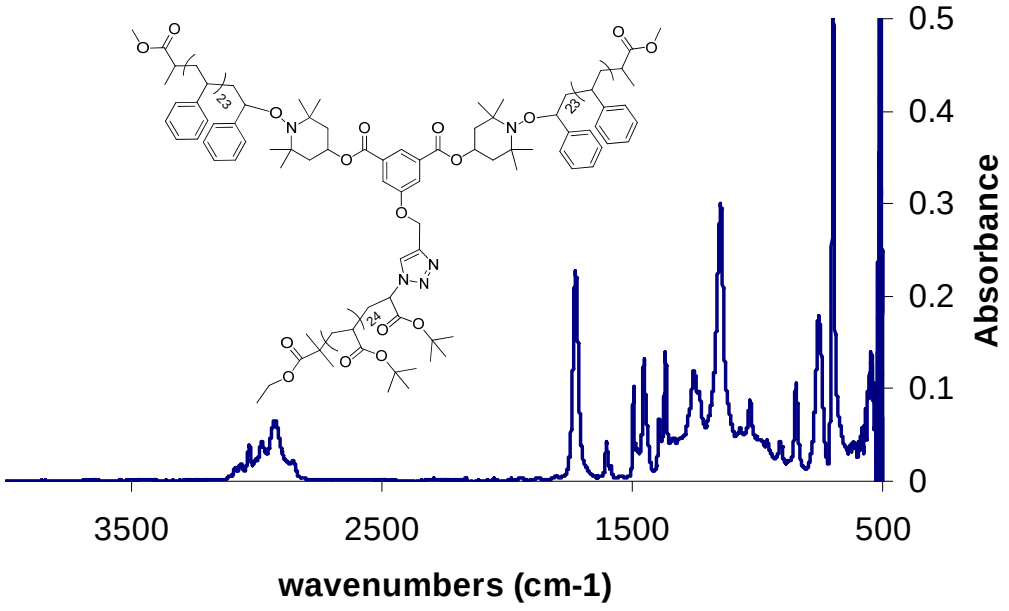


Figure S27: ATR-FTIR spectra of P(^{t}BA$_{25}$-b-(STY$_{24}$)$_2$) **10**

1.13 Synthesis of $P(EG_{47}\text{-b-}(STY_{24})_2)$ 11

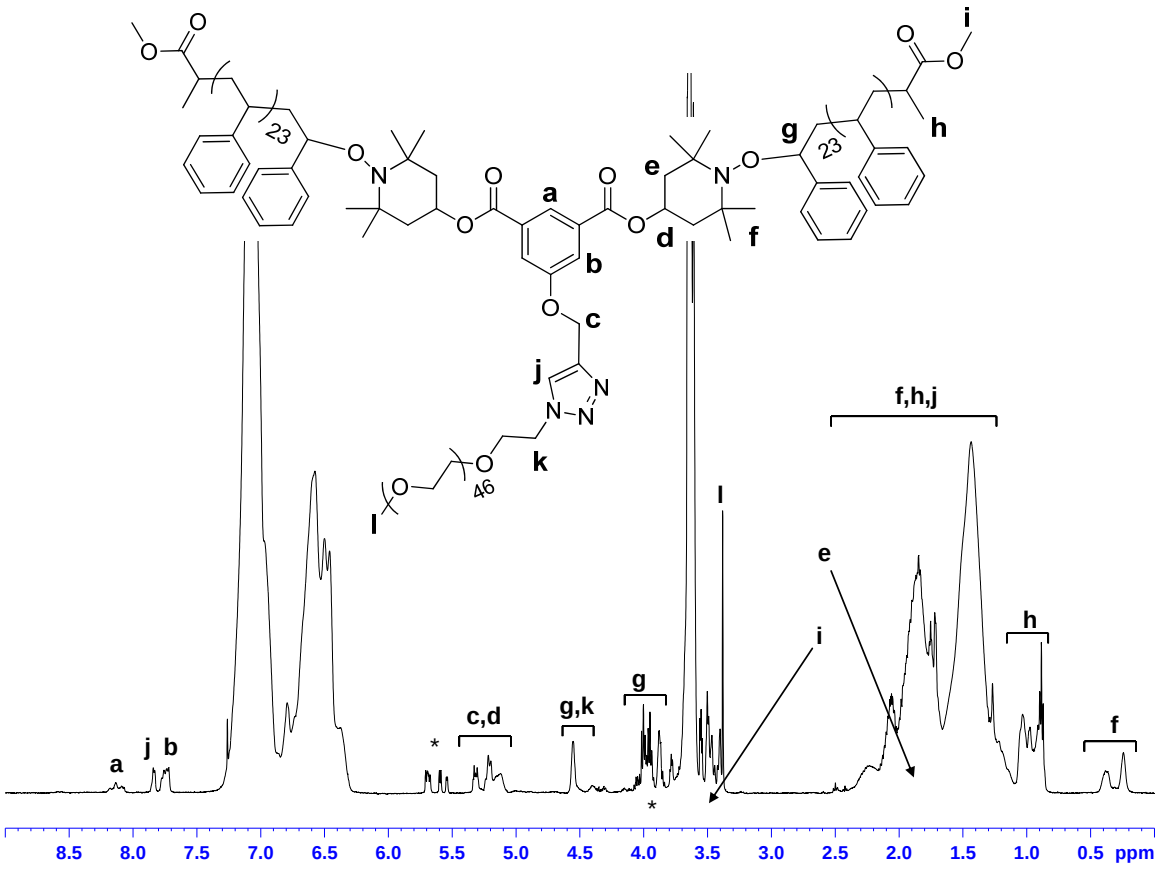


Figure S28: ^{1}H 1D DOSY NMR analysis of $P(EG_{47}\text{-b-}(STY_{24})_2)$ **11**
(* impurities from PREP-SEC)

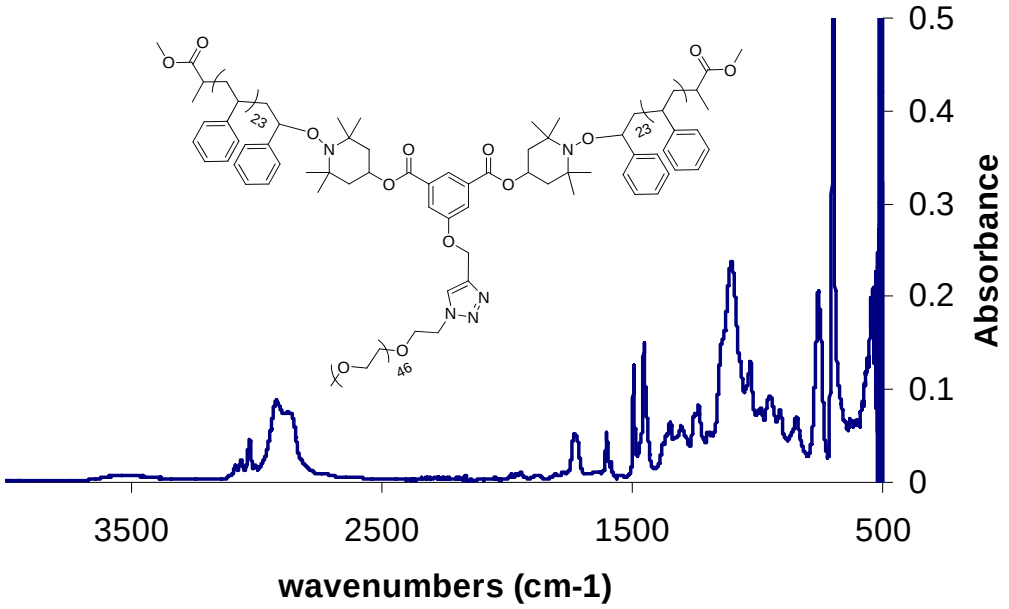


Figure S29: ATR-FTIR spectra of $P(EG_{47}\text{-b-}(STY_{24})_2)$ **11**

1.14 Synthesis of P(STY$_{24}$-b-(^{t}BA$_{25}$)$_2$) 12

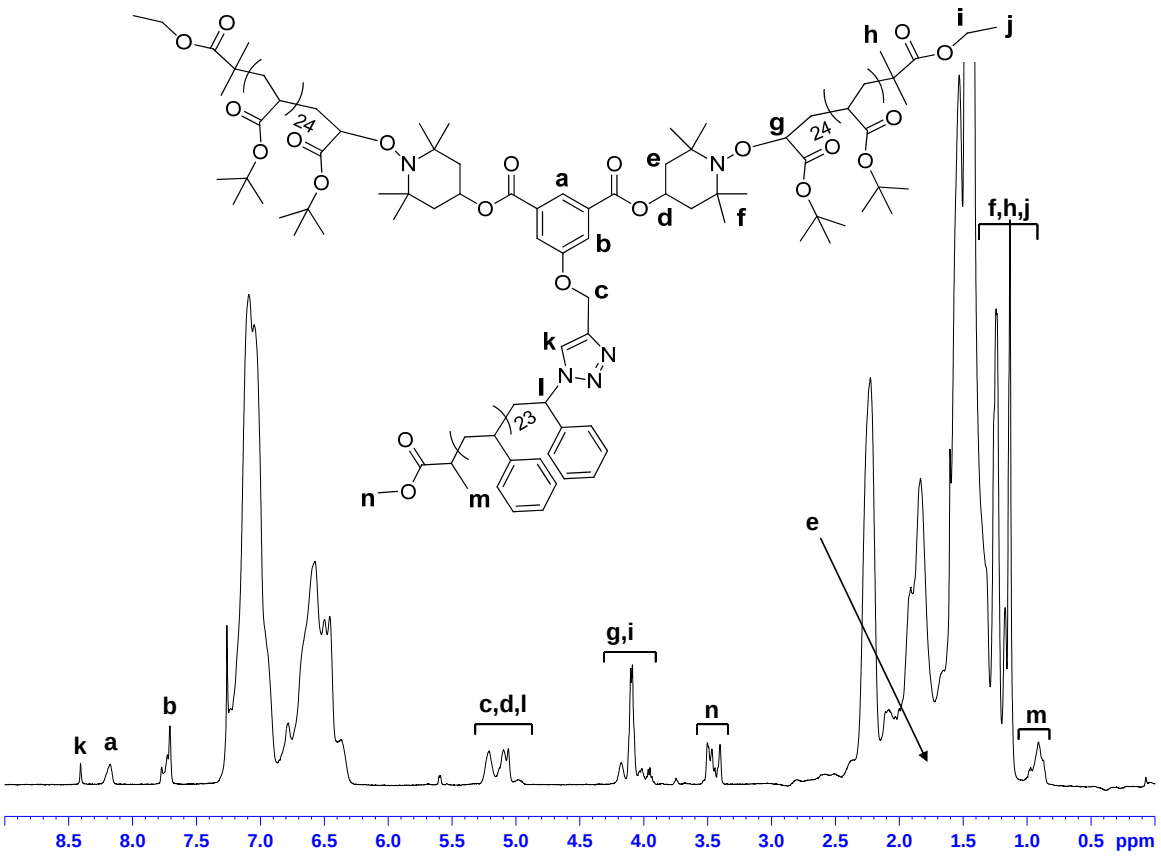


Figure S30: ^{1}H 1D DOSY NMR analysis of P(STY$_{24}$-b-(^{t}BA$_{25}$)$_2$) **12**

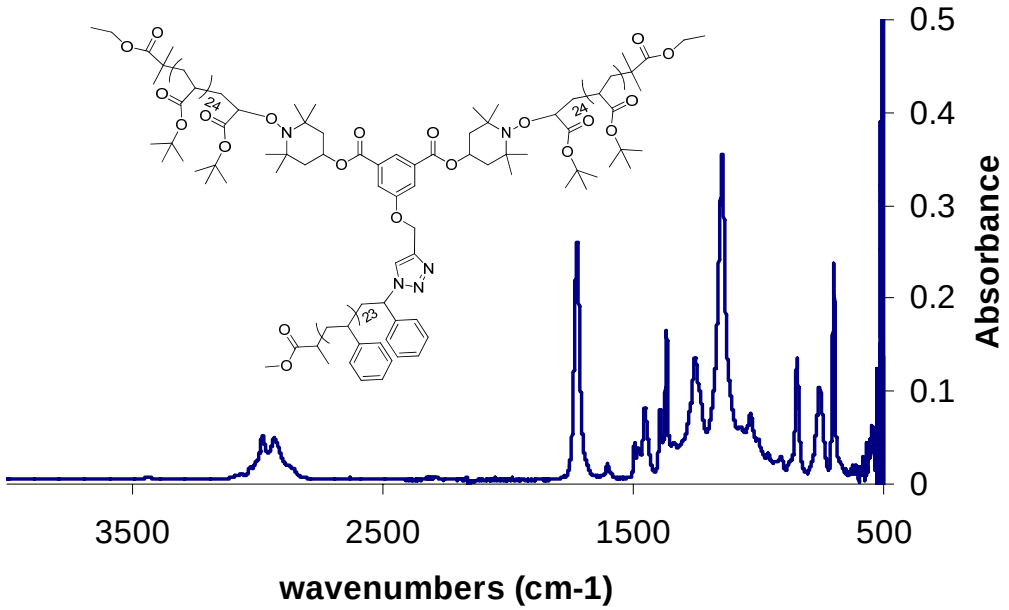


Figure S31: ATR-FTIR spectra of P(STY$_{24}$-b-(^{t}BA$_{25}$)$_2$) **12**

1.15 Synthesis of P(STY$_{24}$-b-(EG$_{47}$)$_2$) 13

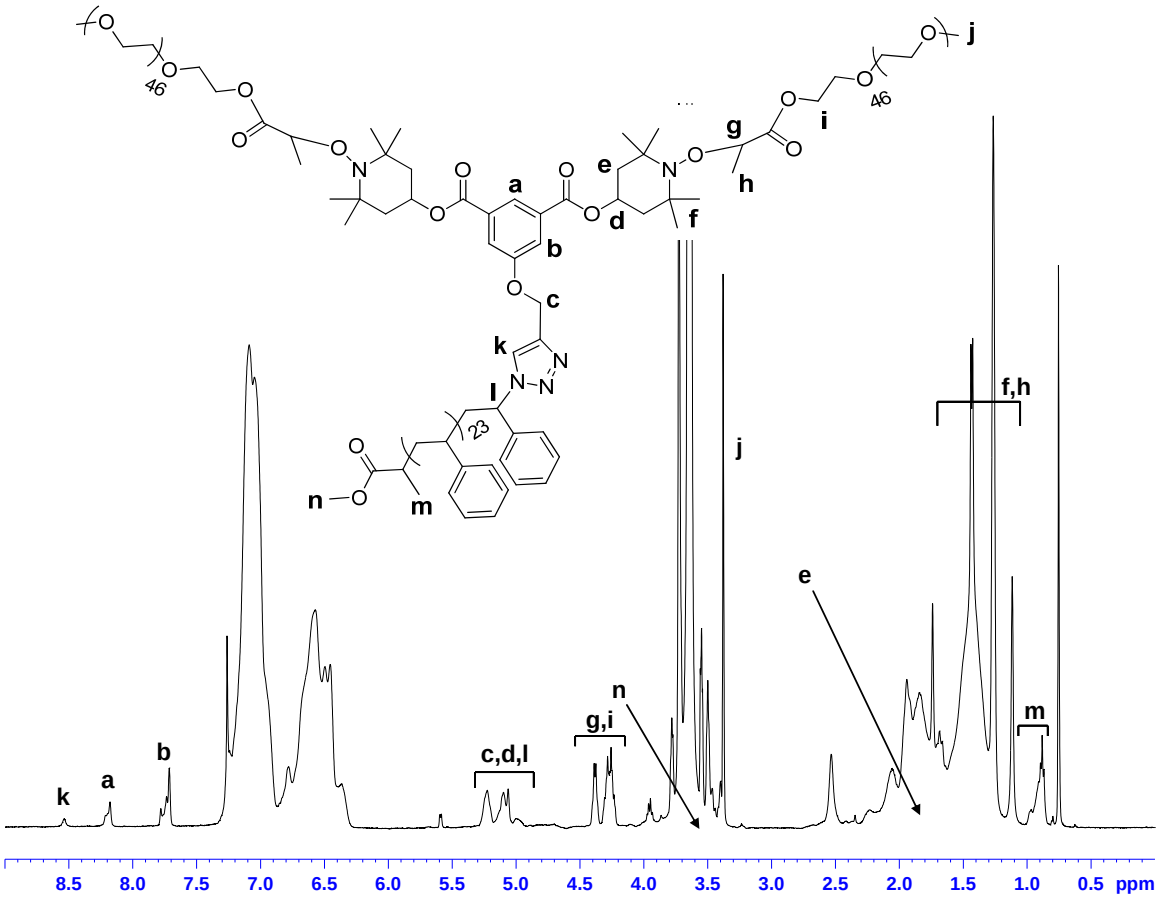


Figure S32: ^{1}H 1D DOSY NMR analysis of P(STY$_{24}$-b-(EG$_{47}$)$_2$) **13**

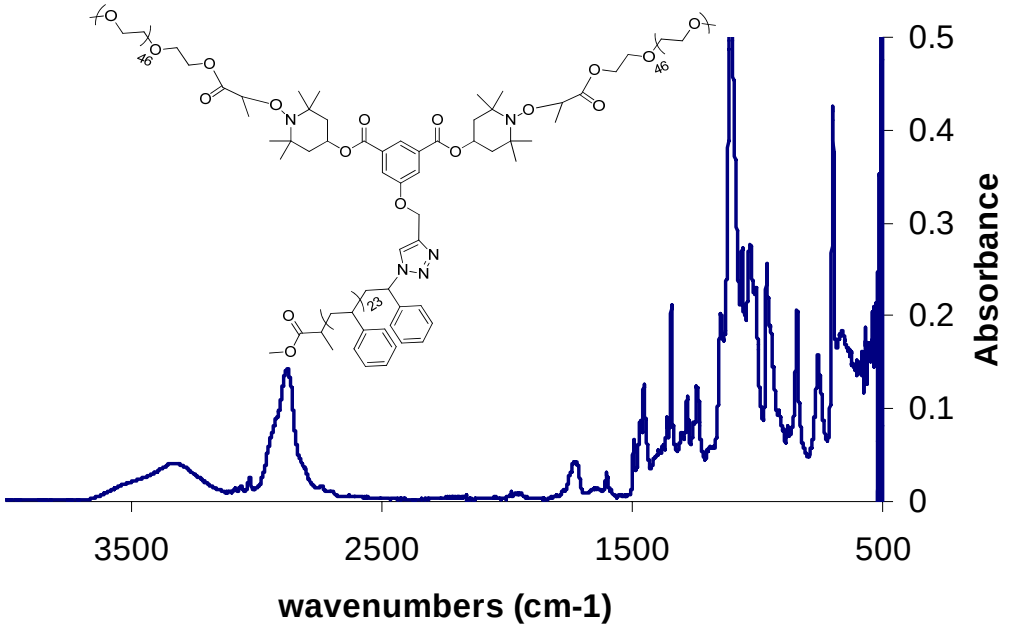


Figure S33: ATR-FTIR spectra of P(STY$_{24}$-b-(EG$_{47}$)$_2$) **13**

1.16 Synthesis of P(^{t}BA$_{25}$-b-(cSTY$_{28}$)$_2$) 14

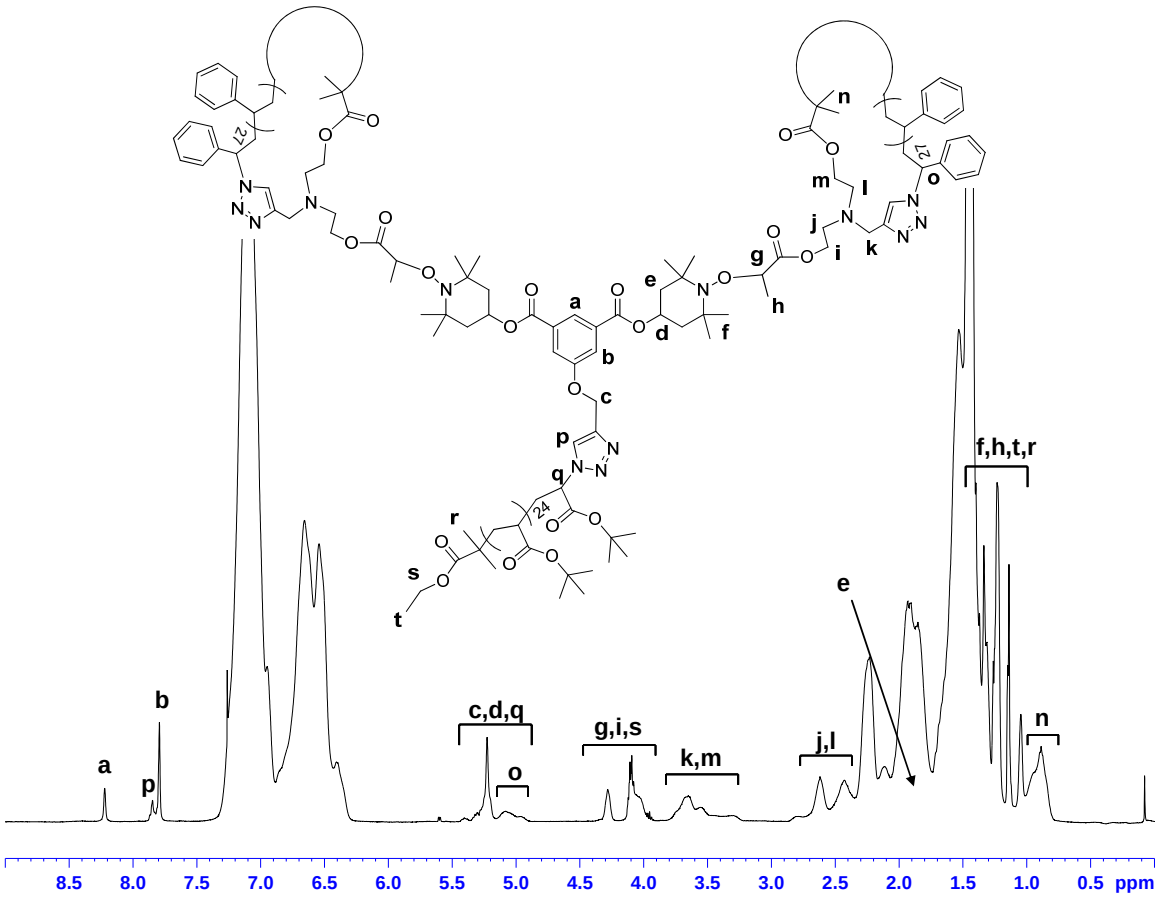


Figure S34: ^{1}H 1D DOSY NMR analysis of P(^{t}BA$_{25}$-b-(cSTY$_{28}$)$_2$) **14**

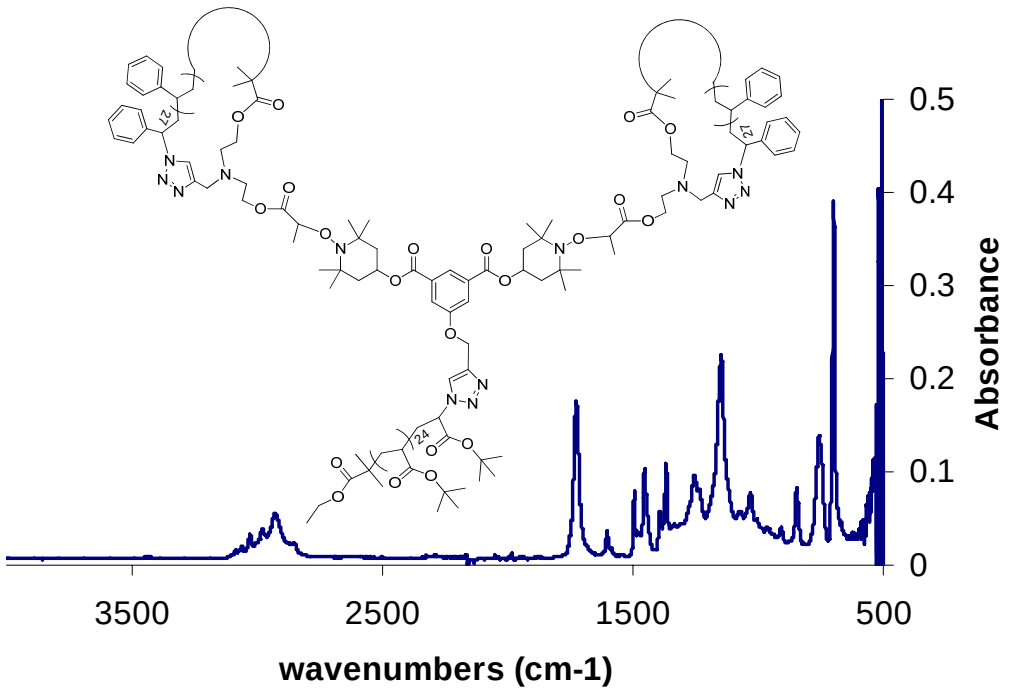


Figure S35: ATR-FTIR spectra of P(^{t}BA$_{25}$-b-(cSTY$_{28}$)$_2$) **14**

1.17 Synthesis of P(EG_{47}-b-($cSTY_{28}$)$_2$) 15

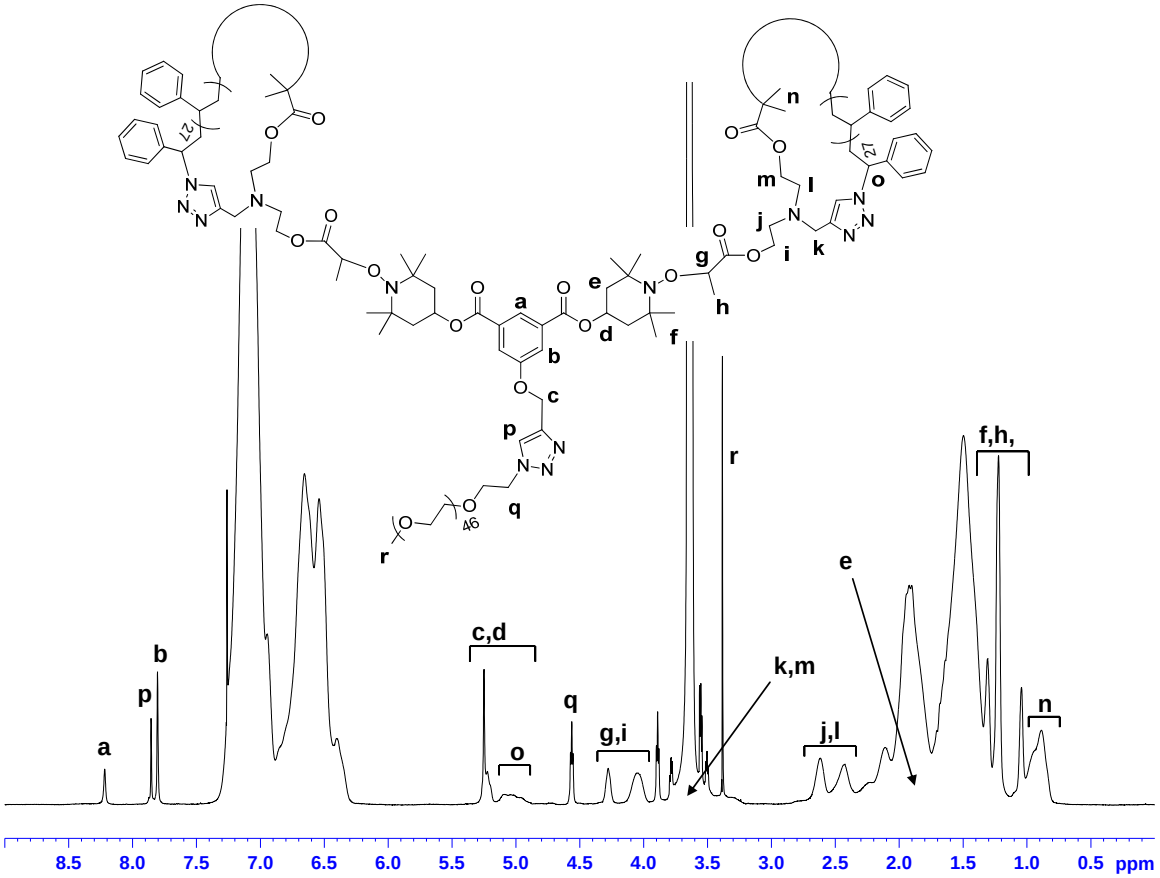


Figure S36: ^{1}H 1D DOSY NMR analysis of P(EG_{47}-b-($cSTY_{28}$)$_2$) **15**

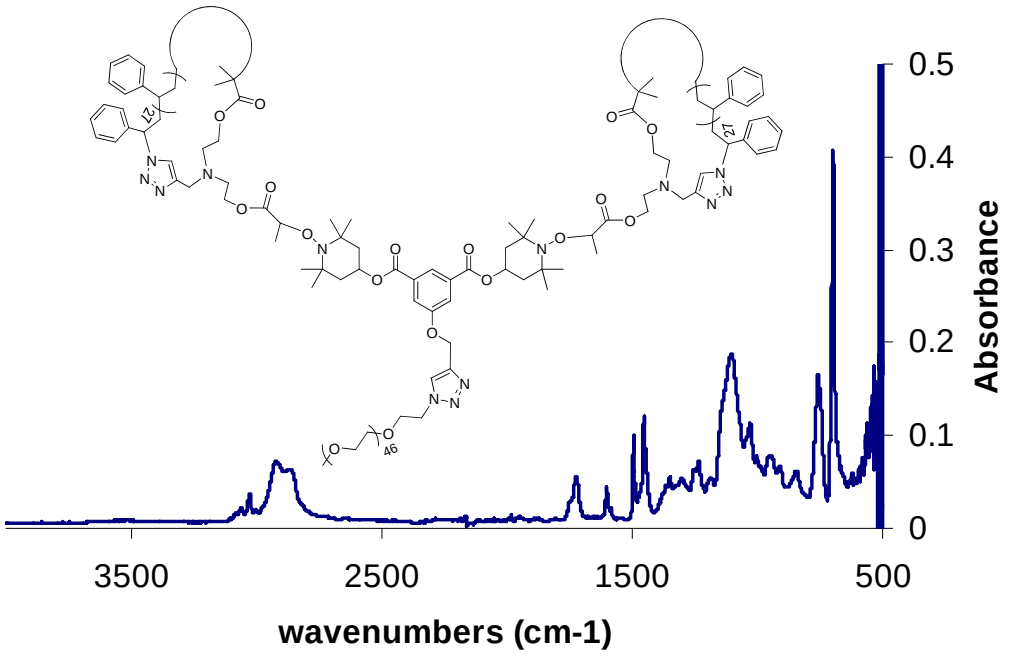


Figure S37: ATR-FTIR spectra of P(EG_{47}-b-($cSTY_{28}$)$_2$) **15**

1.18 Synthesis of P(cSTY$_{28}$-b-(^{t}BA$_{25}$)$_2$) 16

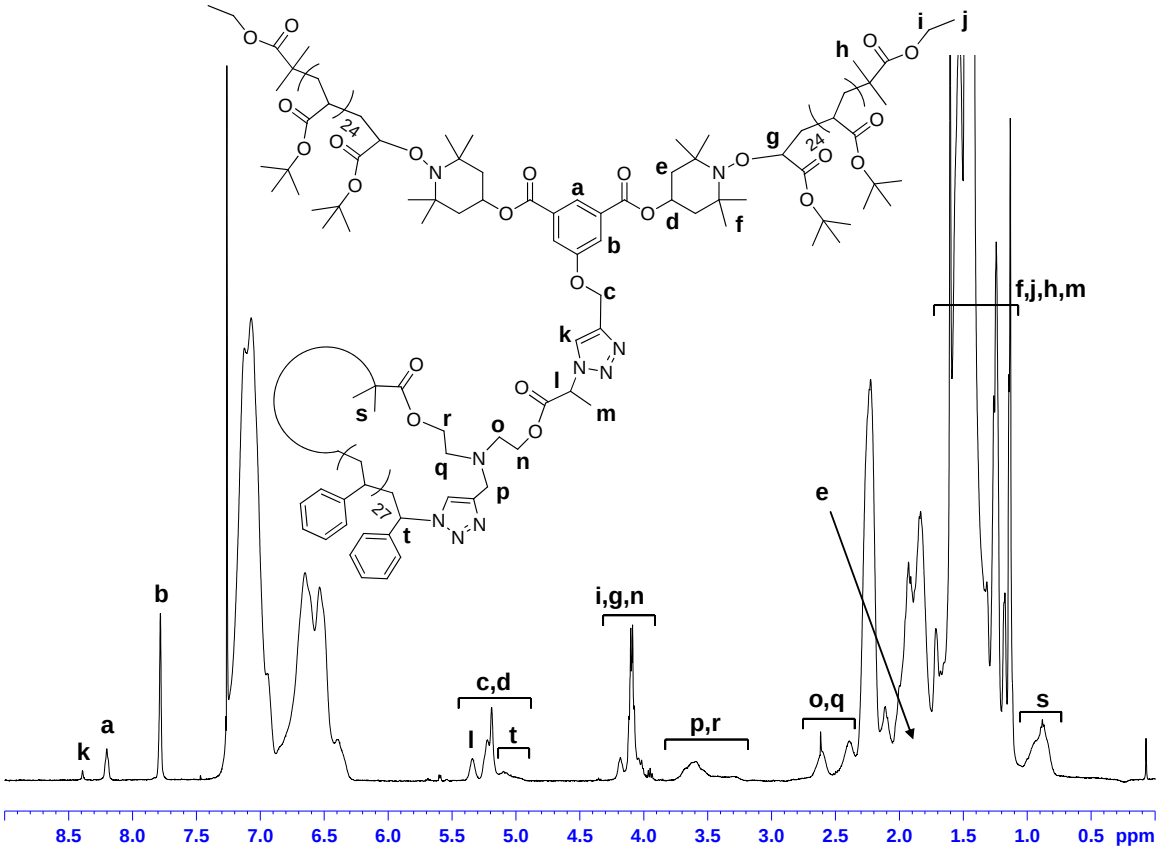


Figure S38: ^{1}H 1D DOSY NMR analysis of P(cSTY$_{28}$-b-(^{t}BA$_{25}$)$_2$) **16**

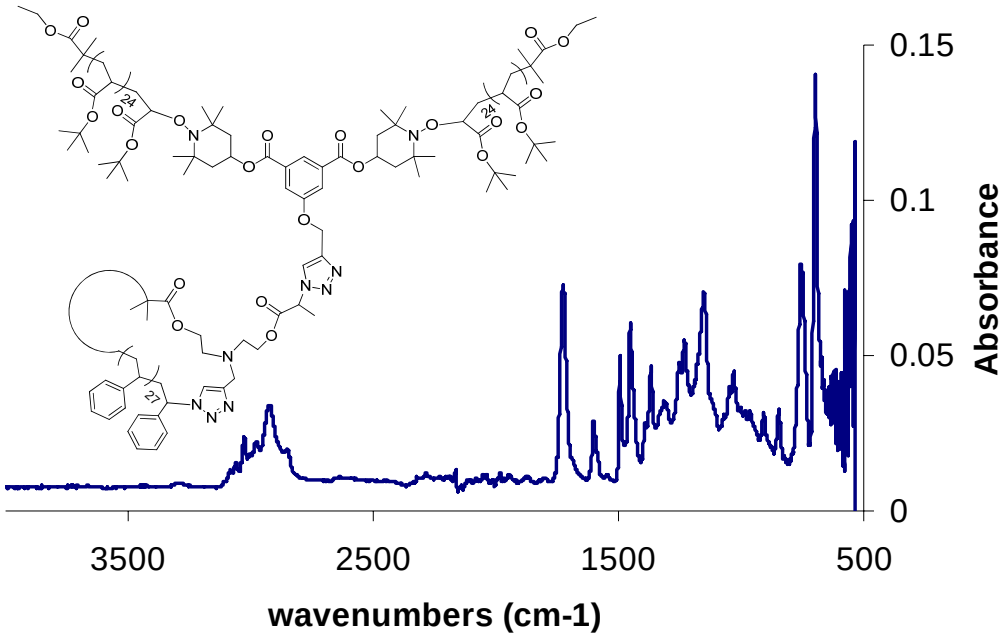


Figure S39: ATR-FTIR spectra of P(cSTY$_{28}$-b-(^{t}BA$_{25}$)$_2$) **16**

1.19 Synthesis of P(cSTY$_{28}$-b-(EG$_{47}$)$_2$) 17

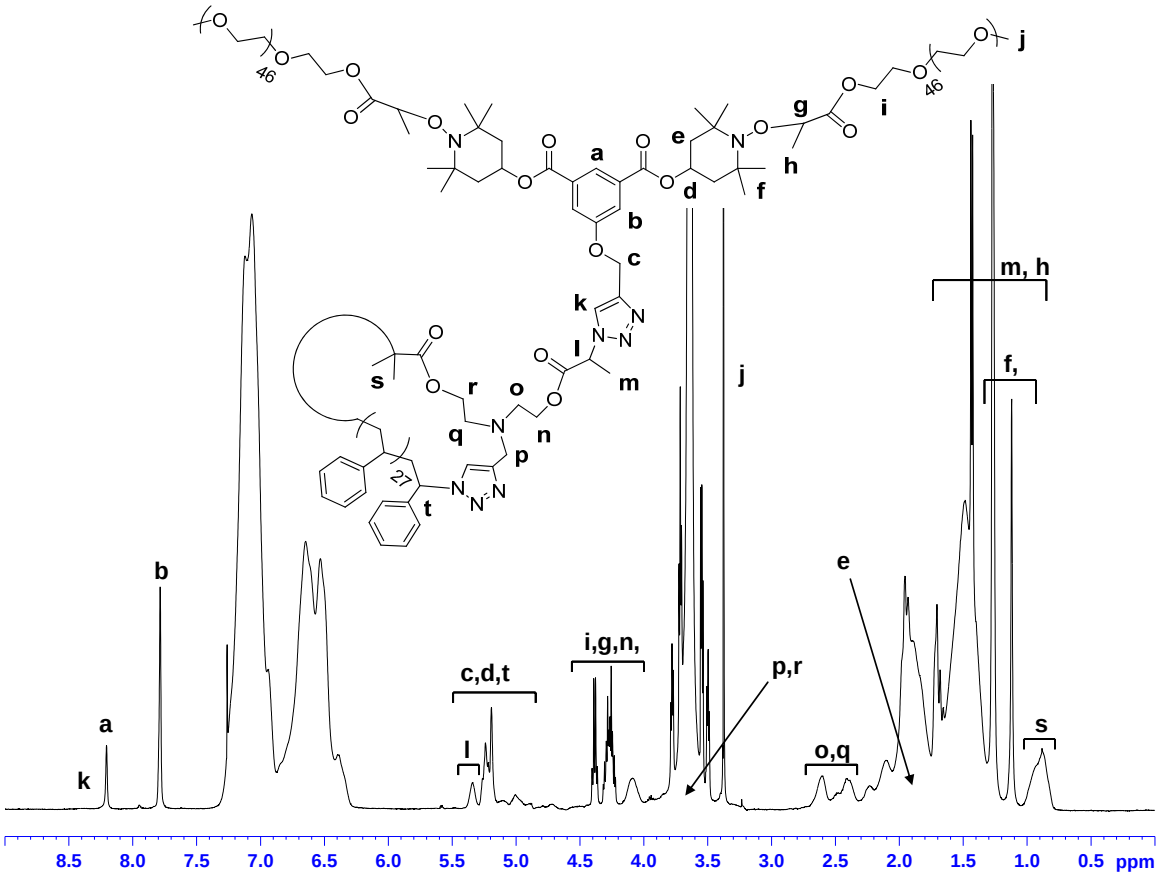


Figure S40: ^{1}H 1D DOSY NMR analysis of P(cSTY$_{28}$-b-(EG$_{47}$)$_2$) **17**

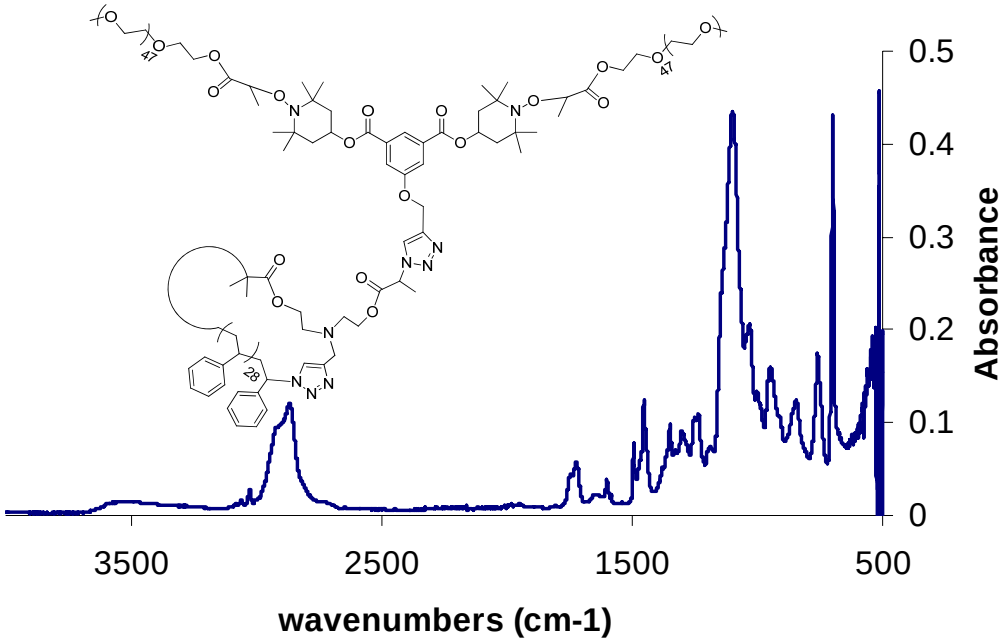


Figure S41: ATR-FTIR spectra of P(cSTY$_{28}$-b-(EG$_{47}$)$_2$) **17**

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