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Secondary structures of PEG-functionalized random copolymers derived from (*R*)- and (*S*)- families of alkyne polycarbodiimides

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Supplementary Data, vol. 1:

General Methods: all starting materials used were obtained from Sigma-Aldrich, Fluka or TCI America and were used without further purification unless otherwise noted. Thin layer chromatography (TLC) was performed on Sigma-Aldrich TLC Plates (silica gel on aluminum, 200 mm layer thickness, 2-25 mm particle size, 60 Å pore size). Column chromatography was performed using silica gel (230-400 mesh) from Merck. ^{1}H nuclear magnetic resonance spectra were recorded at 500 MHz on Bruker Avance III^{TM} 500 instrument at room temperature; ^{13}C NMR spectra were recorded on the same instrument at 125 MHz. ^{1}H and ^{13}C chemical shifts are reported in parts per million (ppm) relative to the corresponding residual solvent peak. Specific optical rotation data were recorded on JASCO P-1010 polarimeter at λ = 435 nm and at a sample concentration 2.0 mg/mL by using 100 mm path length cell. GPC polymer mass determination was done on Shimadzu Prominence instrument using HPLC grade $CHCl_3$, DMF or THF as mobile phase and polystyrene as a standard. Powder X-ray diffraction (pXRD) data profiles were recorded on Rigaku Ultima III XRD diffractometer (Nano Characterization Facility at UTD).

Synthesis and characterization of PEG-triazole polycarbodiimides

Synthesis of (*R*)- and (*S*)-families of PEG-triazole polycarbodiimides from their respective alkyne precursor polymers was performed according to the previously reported procedures[15a] with minor modifications.

PEG-triazole polycarbodiimides (general procedure for CuAAC click on alkyne polycarbodiimides)

To the stirring solution of alkyne polymer (1.0 eq.) in tetrahydrofuran, corresponding (1.2 eq.) PEG-N_3 and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 4.0 eq.) were placed at once followed by the addition of copper (I) iodide (0.1 eq.). The reaction mixture was allowed to stir overnight inside the glove box filled with nitrogen gas. Upon completion, reaction mixture was removed from glove box and precipitated from hexanes containing several drops of DBU. White solid was separated by filtration, washed with an excess of hexanes, filtered, and dried under high vacuum overnight.

(*R*)-15-TRZ-PEG2K-85-Ph, yield 87 %.^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 7.28, 7.02 (br), 6.78 (br), 3.77, 3.69, 3.68, 3.67, 3.66, 3.40, 1.83, 1.29, 0.92 (br), 0.76 (br). FTIR (neat, cm^{-1}): 2883 (C-H), 1623 (C=N), 1590, 1466, 1359, 1341, 1279, 1240, 1146, 1099, 1060, 961, 841, 717, 695.

(*R*)-15-TRZ-PEG20K-85-Ph, yield 87 %.^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 7.28, 7.03 (br), 6.78 (br), 3.67, 0.76 (br), 0.09. FTIR (neat, cm^{-1}): 2952, 2923, 2897 (C-H), 1617 (C=N), 1592, 1464, 1379, 1347, 1296, 1242, 1182, 1153, 1026, 997, 959, 905, 851, 797, 753, 715, 696, 622, 508.

(*S*)-15-TRZ-PEG2K-85-Ph, yield 92 %. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 7.28, 7.02 (br), 6.78 (br), 3.81, 3.71, 3.69, 3.68, 3.67, 3.66, 3.57, 3.56, 3.51, 3.40, 1.83, 1.27, 0.91 (br), 0.74 (br). FTIR (neat, cm^{-1}): 2883 (C-H), 1623 (C=N), 1589, 1466, 1359, 1341, 1279, 1240, 1145, 1100, 1060, 961, 841, 695, 510.

(*S*)-15-TRZ-PEG10K-85-Ph. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 7.28, 7.07 (br), 6.76 (br), 3.79, 3.66, 3.50, 2.04, 1.81, 1.74, 1.26, 0.90 (br), 0.74 (br). FTIR (neat, cm^{-1}): 2880 (C-H), 1626 (C=N), 1591, 1466, 1359, 1341, 1279, 1241, 1146, 1100, 1060, 961, 841, 695, 528.

(*R*)-30-TRZ-PEG2K-70-Ph, yield 97 %. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 7.28, 7.01 (br), 6.77 (br), 3.71, 3.68, 3.66, 3.60, 3.40, 3.04, 1.84, 1.27, 0.89 (br), 0.75 (br). FTIR (neat, cm^{-1}): 2869 (C-H), 1625 (C=N), 1590, 1466, 1341, 1359, 1279, 1240, 1150, 1096, 1061, 961, 841, 696.

(*R*)-30-TRZ-PEG20K-70-Ph, yield 61 %. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 7.29, 3.81, 3.67, 3.54, 3.46, 3.41, 1.77, 1.28, 0.90 (br). FTIR (neat, cm^{-1}): 2878 (C-H), 1630 (C=N), 1466, 1455, 1359, 1342, 1279, 1241, 1146, 1099, 1060, 961, 947, 841, 695.

(*S*)-30-TRZ-PEG2K-70-Ph, yield 96 %. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 7.28, 7.00 (br), 6.78 (br), 3.69, 3.68, 3.67, 3.40, 1.84, 1.27, 0.89 (br), 0.73 (br). FTIR (neat, cm^{-1}): 2861 (C-H), 1626 (C=N), 1590, 1466, 1359, 1342, 1279, 1241, 1145, 1099, 1060, 961, 841, 716, 695.

(*R*)-50-TRZ-PEG2K-50-Ph, yield 88 %. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 7.28, 3.67, 3.55, 3.41, 1.55, 1.32, 1.28, 0.90. FTIR (neat, cm^{-1}): 2922, 2857 (C-H), 1612 (C=N), 1487, 1466, 1454, 1444, 1359, 1342, 1314, 1240, 1185, 1144, 1102, 1061, 992, 958, 841, 694, 637, 528.

(*S*)-50-TRZ-PEG2K-50-Ph, yield 49 %. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 7.28, 7.07, 6.78, 3.68, 3.67, 3.66, 3.40, 3.39, 2.55, 1.27, 0.91 (br), 0.67 (br). ^{13}C NMR (126 MHz, $CDCl_3$), δ: 71.9, 70.6, 70.0, 59.0, 54.1, 50.7, 48.7, 29.2, 27.2, 24.4. FTIR (neat, cm^{-1}): 2878 (C-H), 1627 (C=N), 1591, 1466, 1359, 1341, 1279, 1241, 1146, 1098, 1060, 961, 841, 696, 529.

(*S*)-50-TRZ-PEG1K-50-Ph, yield 62 %. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 7.28, 7.02 (br), 6.74 (br), 3.80, 3.66, 3.60, 3.57, 3.40, 1.96, 1.66, 1.27, 0.90 (br), 0.72 (br), 0.60 (br). FTIR (neat, cm^{-1}): 2866 (C-H), 1625 (C=N), 1591, 1454, 1345, 1298, 1242, 1096, 947, 842, 696.

(*R*)-70-TRZ-PEG2K-30-Ph, yield 94 %. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 7.28, 3.80, 3.69, 3.68, 3.66, 3.52, 3.40, 1.75, 1.27, 0.90. FTIR (neat, cm^{-1}): 2880 (C-H), 1627 (C=N), 1466, 1359, 1341, 1279, 1240, 1146, 1097, 1060, 960, 841, 695, 529.

(*S*)-70-TRZ-PEG2K-30-Ph, yield 75 %. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 7.28, 3.81, 3.68, 3.67, 3.58, 3.57, 3.53, 3.52, 3.42, 3.40, 2.08, 1.90, 1.84, 1.33, 1.27, 0.57 (br). FTIR (neat, cm^{-1}): 2882 (C-H), 1631 (C=N), 1466, 1359, 1341, 1279, 1240, 1146, 1098, 1059, 959, 841, 696, 529.

(*R*)-85-TRZ-PEG2K-15-Ph, yield 90 %. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 7.28, 3.81, 3.80, 3.79, 3.74, 3.68, 3.67, 3.66, 3.58, 3.57, 3.56, 3.53, 3.52, 3.51, 3.42, 3.41, 3.40, 3.03, 2.07, 1.33, 1.28, 0.91. FTIR (neat, cm^{-1}): 2880 (C-H), 1628 (C=N), 1466, 1359, 1341, 1279, 1240, 1146, 1096, 1060, 960, 841, 696, 529.

(*S*)-85-TRZ-PEG2K-15-Ph, yield 86 %. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 7.28, 3.71, 3.68, 3.66, 3.60, 3.40, 3.08, 2.09, 1.68, 1.27, 0.91, 0.88. FTIR (neat, cm^{-1}): 2879 (C-H), 1629 (C=N), 1466, 1359, 1341, 1279, 1240, 1146, 1097, 1060, 960, 841, 696, 529.

(*R*)-100-TRZ-PEG2K, yield 76 %. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 7.28, 4.03, 3.85, 3.78, 3.71, 3.68, 3.66, 3.62, 3.41, 3.40, 2.98, 1.90, 1.82, 1.27, 0.88. FTIR (neat, cm^{-1}): 2879 (C-H), 1630 (C=N), 1466, 1359, 1341, 1279, 1240, 1146, 1097, 1060, 960, 841, 695, 529.

(*S*)-100-TRZ-PEG2K, yield 78 %. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 7.29, 3.82, 3.69, 3.68, 3.67, 3.57, 3.51, 3.41, 1.28, 0.89. FTIR (neat, cm^{-1}): 2878 (C-H), 1626 (C=N), 1466, 1359, 1341, 1279, 1241, 1145, 1098, 1060, 960, 841, 693, 529.

(*S*)-50-C=N-C_6-TRZ-PEG2K-50-Ph, yield 90 %. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 7.28, 3.79, 3.69, 3.68, 3.66, 3.52, 3.40, 2.06, 1.82, 1.73, 1.27, 0.91. FTIR (neat, cm^{-1}): 2882 (C-H), 1629 (C=N), 1589, 1466, 1359, 1342, 1279, 1241, 1146, 1100, 1060, 961, 841, 697, 529.

(*S*)-100-C=N-C_6-TRZ-PEG2K, yield 88 %. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 7.28, 3.70, 3.68, 3.66, 3.65, 3.40, 1.27, 0.91. FTIR (neat, cm^{-1}): 2878 (C-H), 1625 (C=N), 1466, 1359, 1342, 1279, 1241, 1147, 1102, 1060, 962, 842, 529.

(*S*)-100-C_6-TRZ-PEG2K, yield 93 %. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 7.28, 4.52, 3.88, 3.80, 3.66, 3.57, 3.39, 2.74, 2.04, 1.89, 1.84, 1.47, 1.30, 0.91, 0.89. FTIR (neat, cm^{-1}): 2881 (C-H), 1627 (C=N), 1466, 1359, 1342, 1279, 1241, 1147, 1100, 1060, 962, 842, 529.

Table S1. GPC analysis representative data: number average molecular weight (*M*n), weight average molecular weight (M_w), and PDI (M_w/M_n) values found for exemplary compositions of (*R*)- and (*S*)-PEG-PCDs in **$CHCl_3$** (0.45 μm filter was used to prepare solutions for GPC)

PEG-PCD`s acronym	M_n, Da	M_w, Da	PDI
(*R*)-15-TRZ-PEG2K-85-Ph	39629	55989	1.41
(*S*)-15-TRZ-PEG2K-85-Ph	54245	82254	1.51
(*R*)-30-TRZ-PEG2K-70-Ph	56137	87812	1.56
(*R*)-30-TRZ-PEG20K-70-Ph	37079	40381	1.08
(*S*)-30-TRZ-PEG2K-70-Ph	75913	118988	1.56
(*R*)-50-TRZ-PEG2K-50-Ph	45162	53701	1.18
(*R*)-50-TRZ-PEG1K-50-Ph	32282	47872	1.48
(*S*)-50-TRZ-PEG2K-50-Ph	37233	46214	1.24
(*S*)-50-TRZ-PEG1K-50-Ph	22217	29514	1.32
(*R*)-70-TRZ-PEG2K-30-Ph	43621	51496	1.18
(*S*)-70-TRZ-PEG2K-30-Ph	41742	47383	1.13
(*R*)-85-TRZ-PEG2K-15-Ph	50857	65192	1.28
(*S*)-85-TRZ-PEG2K-15-Ph	34895	40052	1.14

Table S2. GPC analysis representative data: number average molecular weight (M_n), weight average molecular weight (M_w), and PDI (M_w/M_n) values found for exemplary compositions of (*R*)- and (*S*)-PEG-PCDs in **DMF** (0.45 μm filter was used to prepare solutions for GPC)

PEG-PCD`s acronym	M_n, Da	M_w, Da	PDI
(*R*)-15-TRZ-PEG2K-85-Ph	81443	111103	1.36
(*S*)-15-TRZ-PEG2K-85-Ph	102064	137639	1.35
(*R*)-30-TRZ-PEG2K-70-Ph	94819	141783	1.50
(*S*)-30-TRZ-PEG2K-70-Ph	117380	161735	1.38
(*R*)-50-TRZ-PEG2K-50-Ph	100900	134832	1.34
(*R*)-50-TRZ-PEG1K-50-Ph	99977	149882	1.49
(*S*)-50-TRZ-PEG2K-50-Ph	131732	194264	1.48
(*R*)-70-TRZ-PEG2K-30-Ph	140979	217396	1.54
(*S*)-70-TRZ-PEG2K-30-Ph	97469	142329	1.46
(*R*)-85-TRZ-PEG2K-15-Ph	159364	192637	1.21
(*S*)-85-TRZ-PEG2K-15-Ph	135580	148919	1.09
(*R*)-100-TRZ-PEG2K	140640	155024	1.10

Table S3. Specific optical rotation [α] of representative PEGylated PCDs (***R***)- and (***S***)-families at 25^{o}C (C = 2.0 mg/mL, $CHCl_3$; λ = 365 nm)

PCD`s acronym	$[\alpha]^{25}_{365}$, deg.
(***R***)-15-TRZ-PEG2K-85-Ph	+38.9
(***S***)-15-TRZ-PEG2K-85-Ph	-35.1
(***R***)-50-TRZ-PEG2K-50-Ph	+67.9
(***S***)-50-TRZ-PEG2K-50-Ph	-138.5
(***R***)-85-TRZ-PEG2K-15-Ph	+10.0
(***S***)-85-TRZ-PEG2K-15-Ph	-13.3
(***R***)-100-TRZ-PEG2K	+15.4
(***S***)-100-TRZ-PEG2K	-20.8

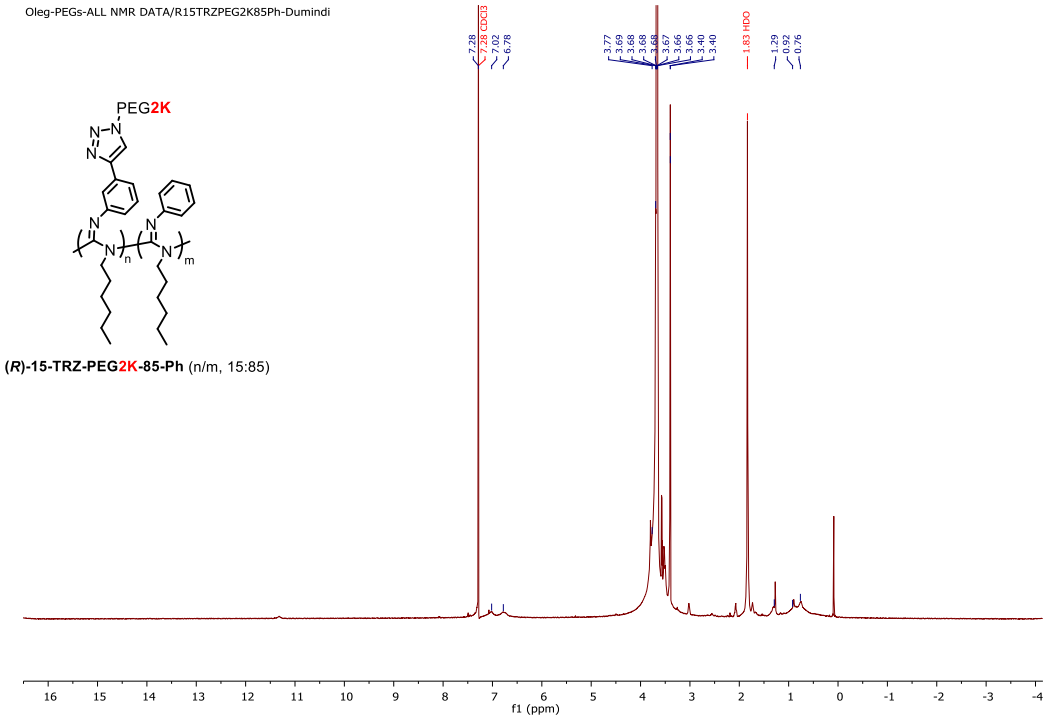

Figure S1. ^{1}H NMR spectrum of **(*R*)-15-TRZ-PEG2K-85-Ph** in $CDCl_3$

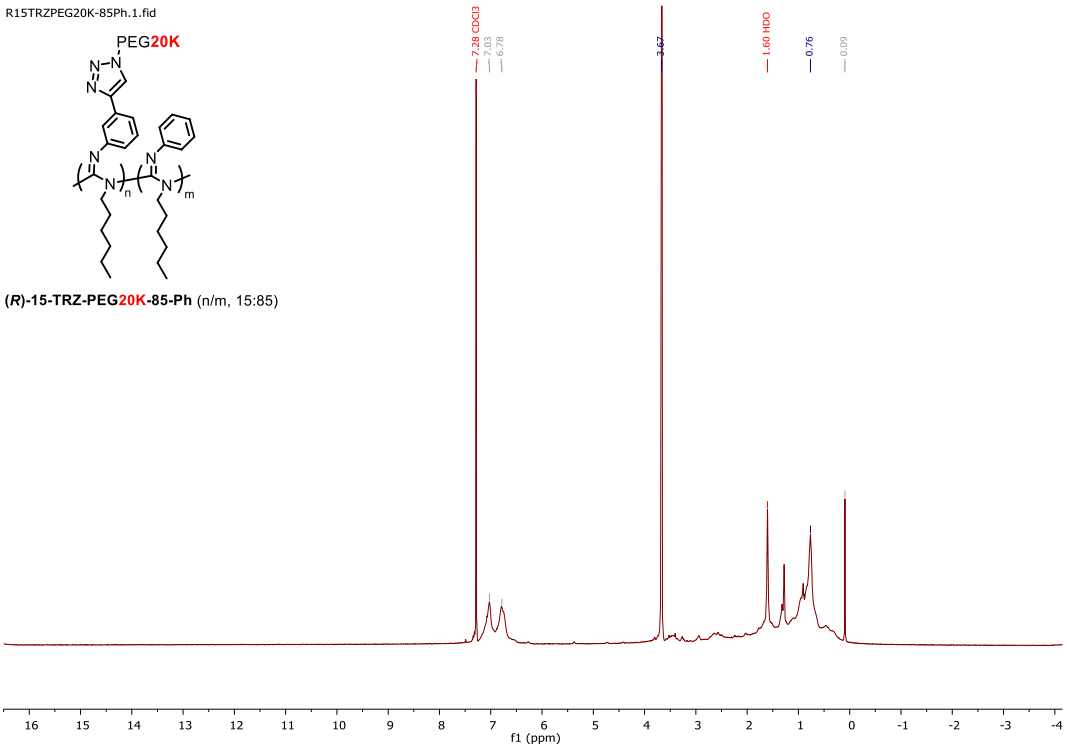

Figure S2. ^{1}H NMR spectrum of **(*R*)-15-TRZ-PEG20K-85-Ph** in $CDCl_3$

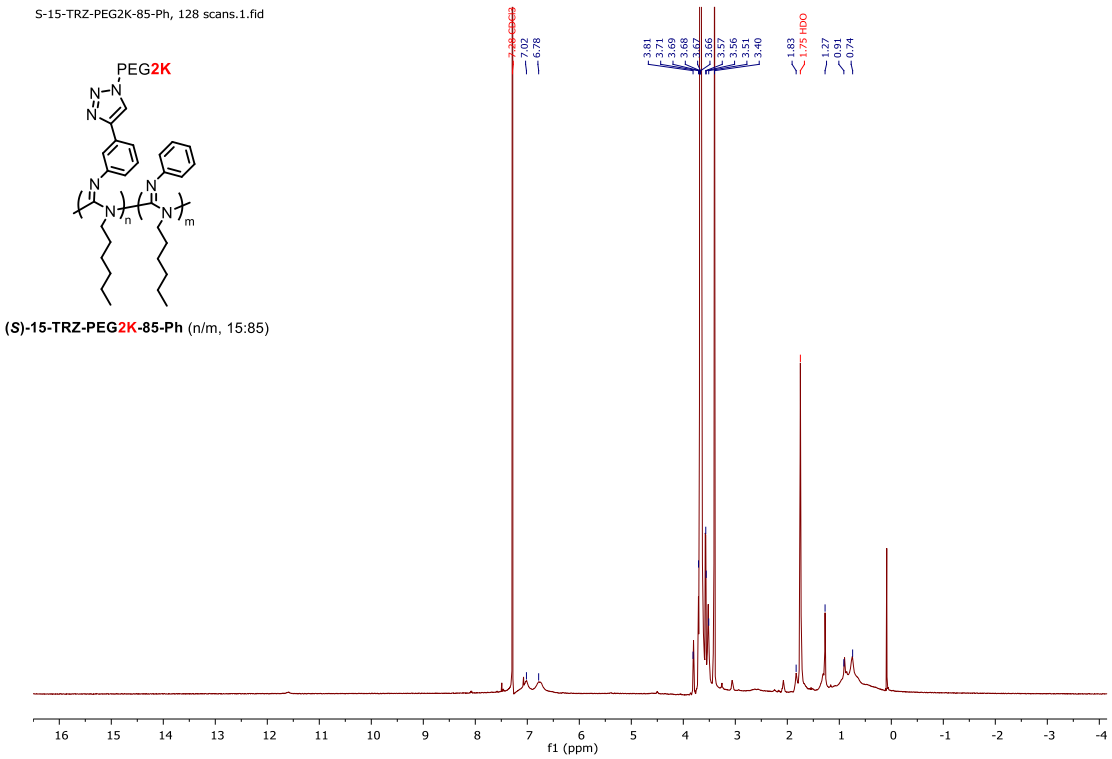

Figure S3. ^{1}H NMR spectrum of **(*S*)-15-TRZ-PEG2K-85-Ph** in $CDCl_3$

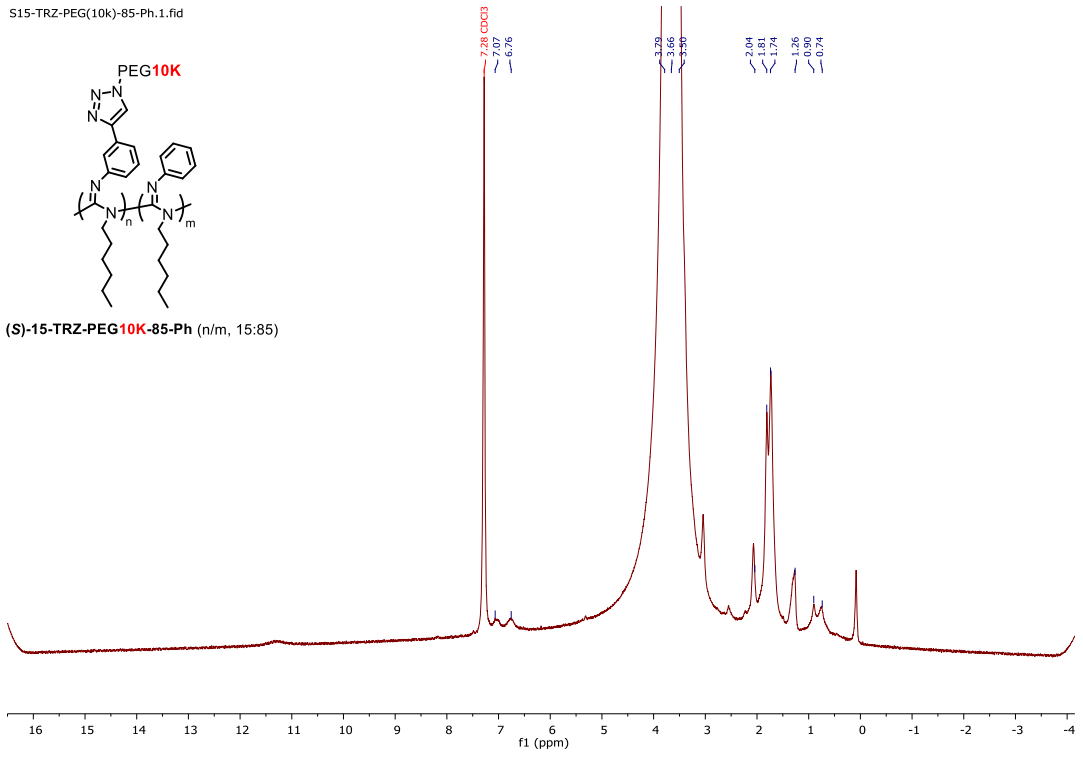

Figure S4. ^{1}H NMR spectrum of **(*S*)-15-TRZ-PEG10K-85-Ph** in $CDCl_3$

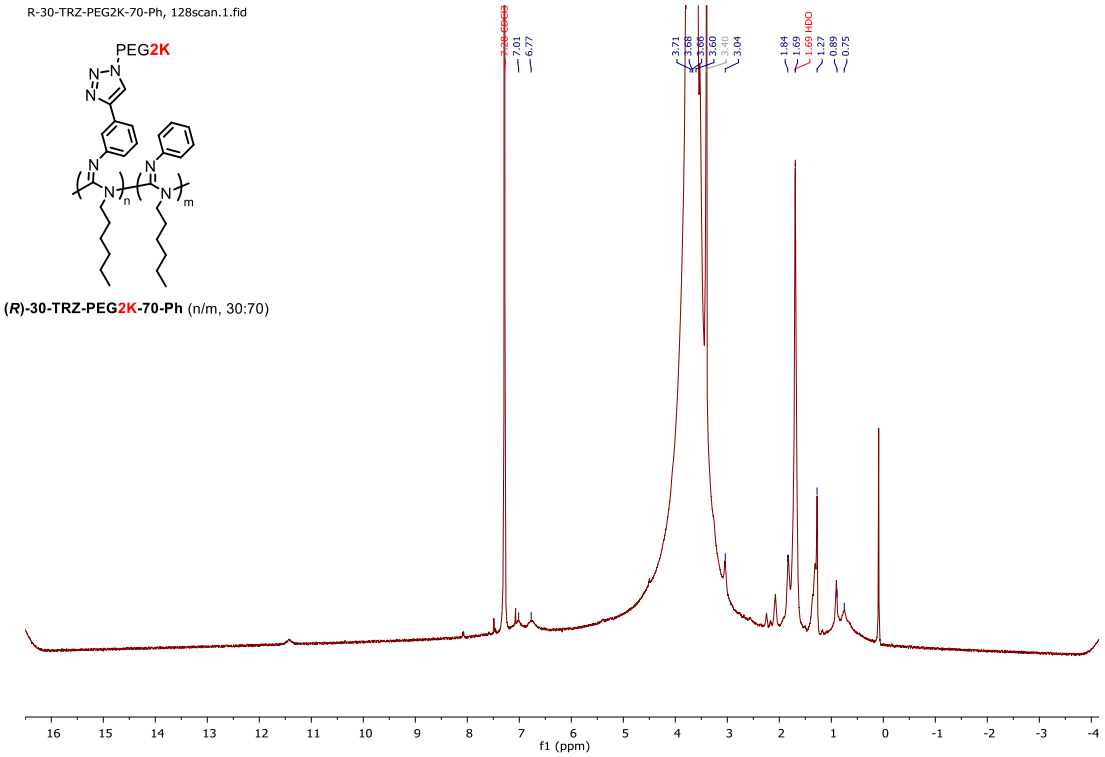

Figure S5. ^{1}H NMR spectrum of **(*R*)-30-TRZ-PEG2K-70-Ph** in $CDCl_3$

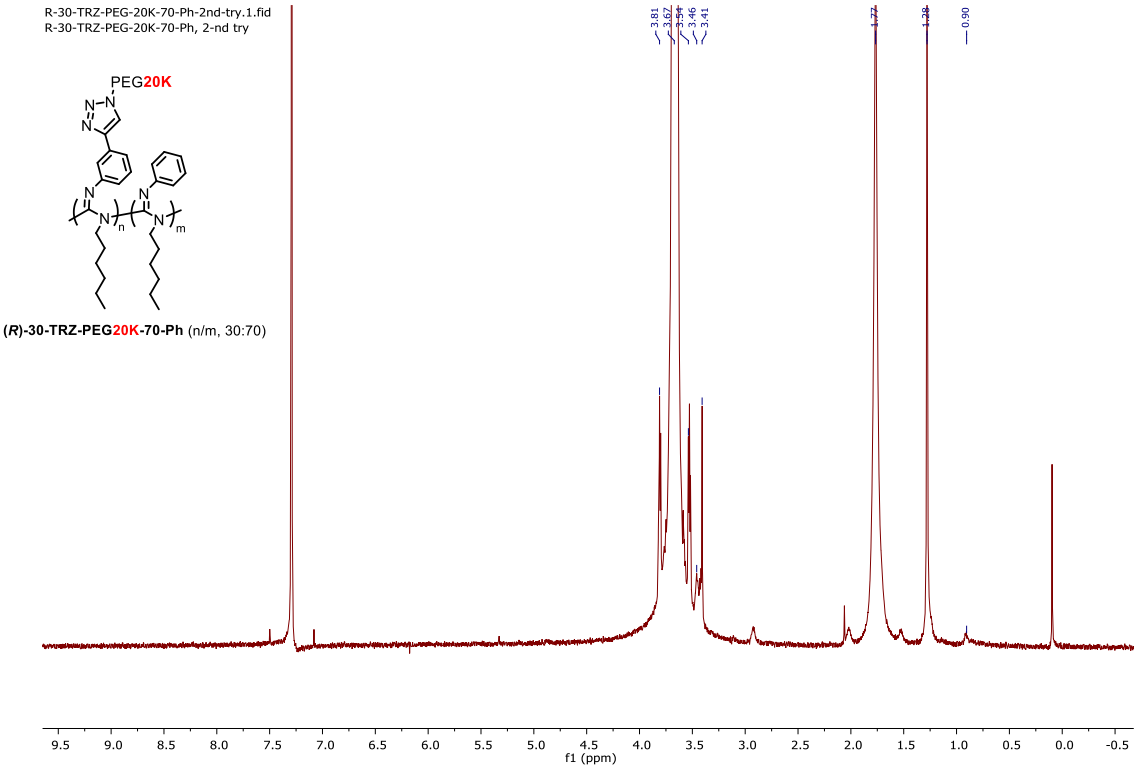

Figure S6. ^{1}H NMR spectrum of **(*R*)-30-TRZ-PEG20K-70-Ph** in $CDCl_3$

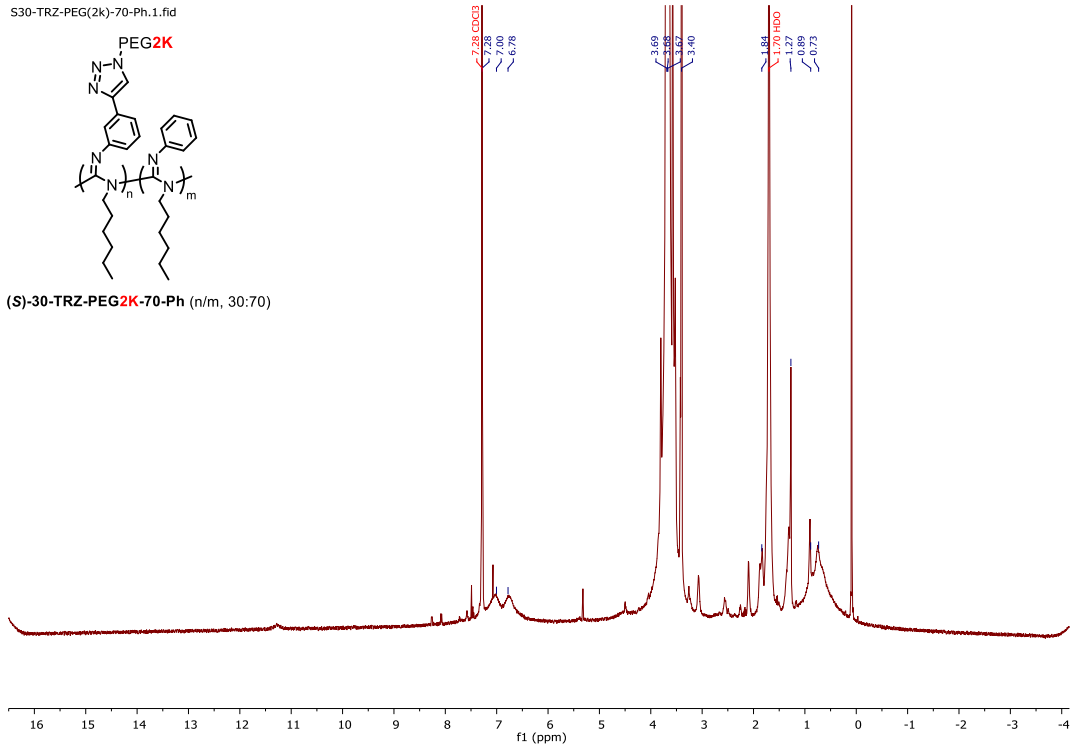

Figure S7. ^{1}H NMR spectrum of **(*S*)-30-TRZ-PEG2K-70-Ph** in $CDCl_3$

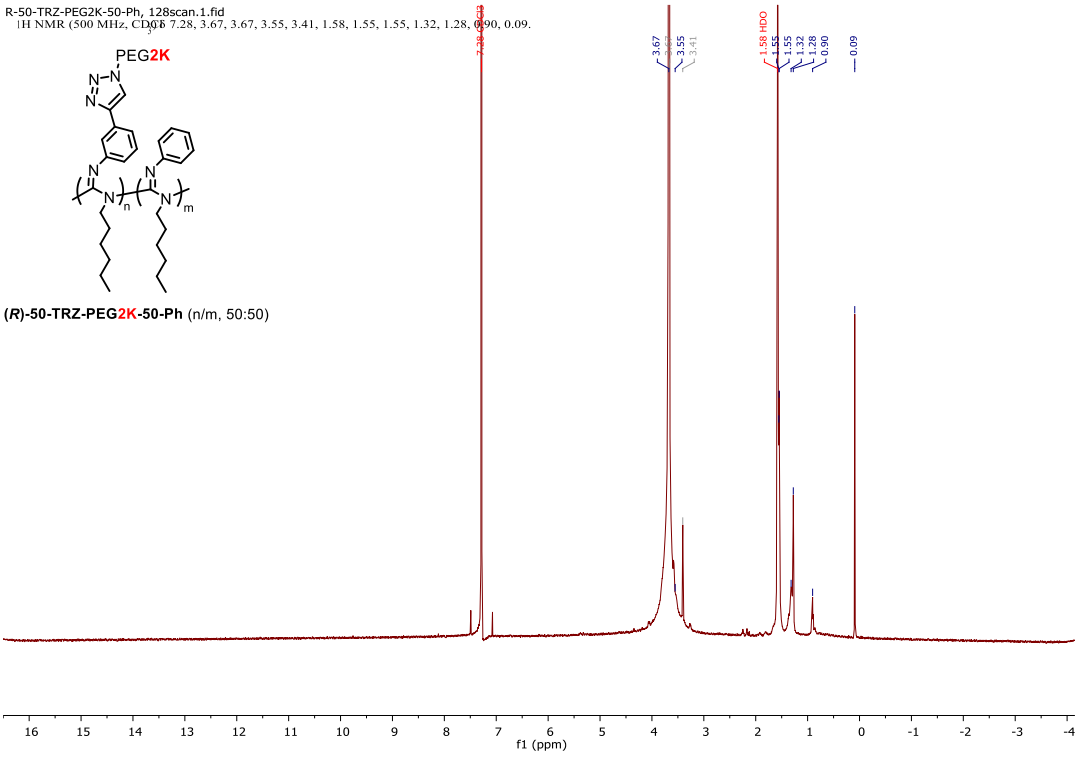

Figure S8. ^{1}H NMR spectrum of **(*R*)-50-TRZ-PEG2K-50-Ph** in $CDCl_3$

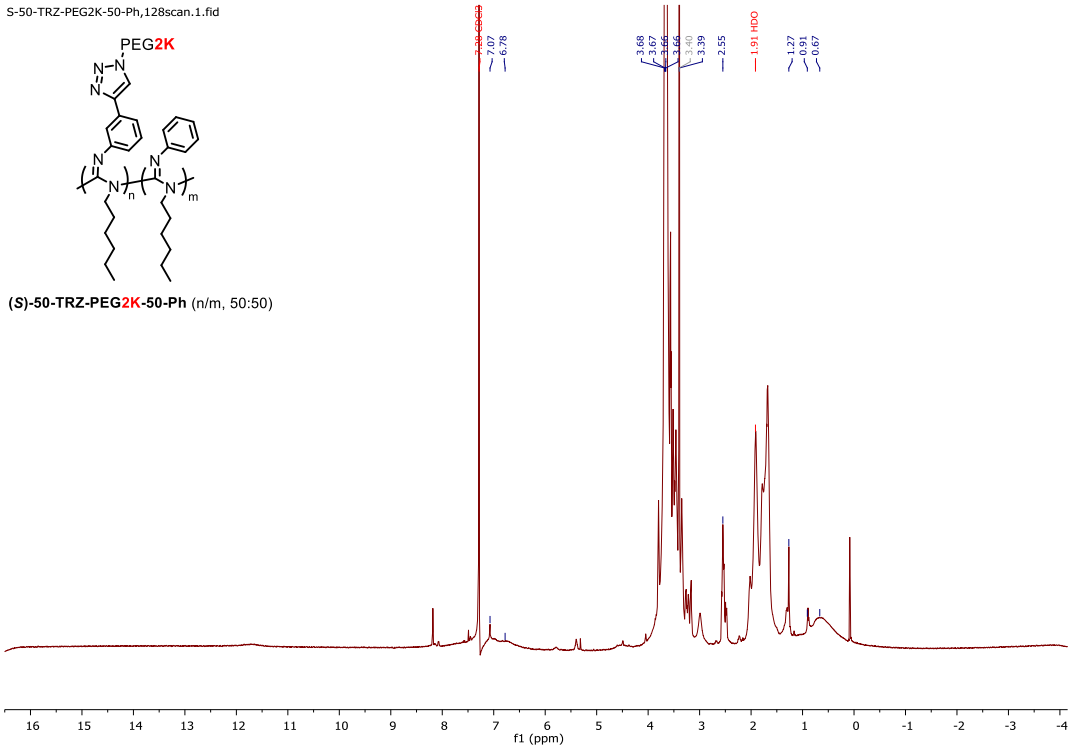

Figure S9. ^{1}H NMR spectrum of **(*S*)-50-TRZ-PEG2K-50-Ph** in $CDCl_3$

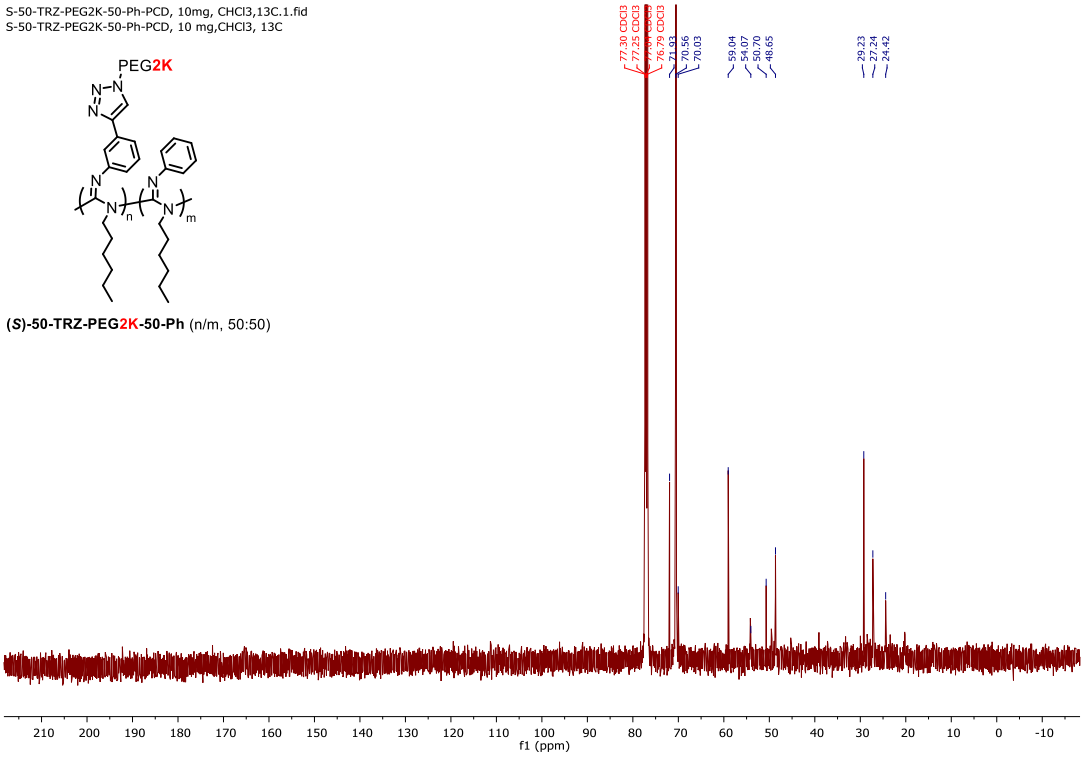

Figure S10. ^{13}C NMR spectrum of **(*S*)-50-TRZ-PEG2K-50-Ph** in $CDCl_3$

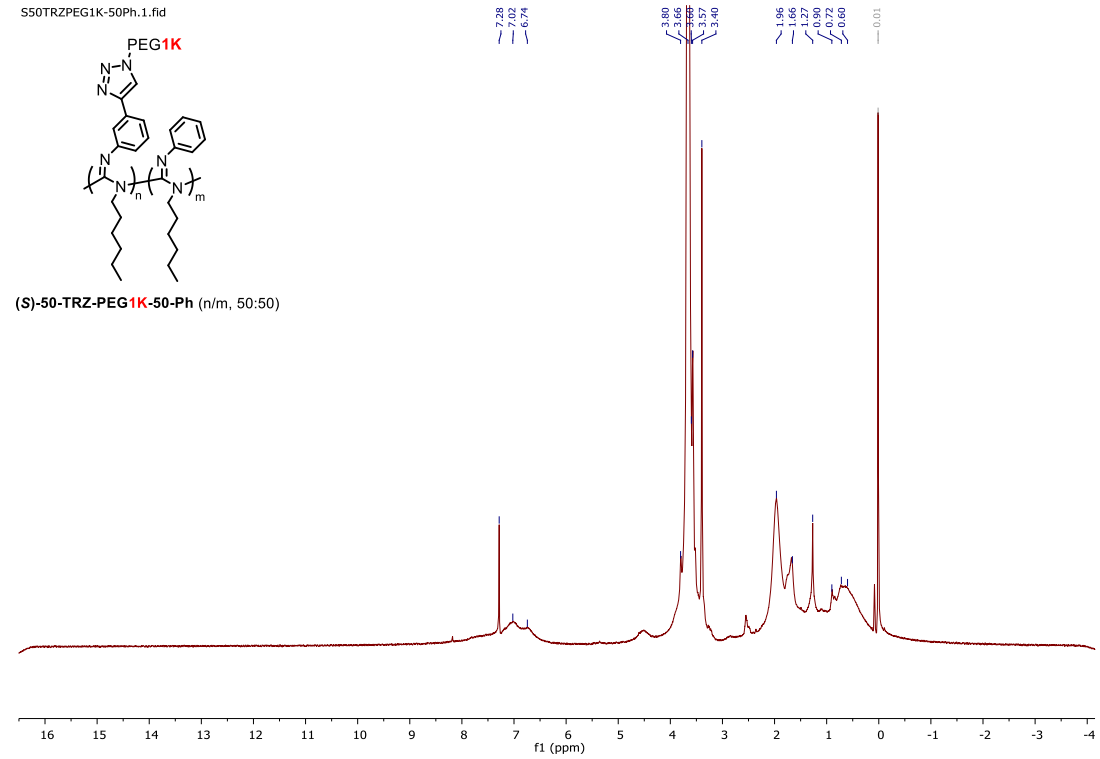

Figure S11. ^{1}H NMR spectrum of **(*S*)-50-TRZ-PEG1K-50-Ph** in $CDCl_3$

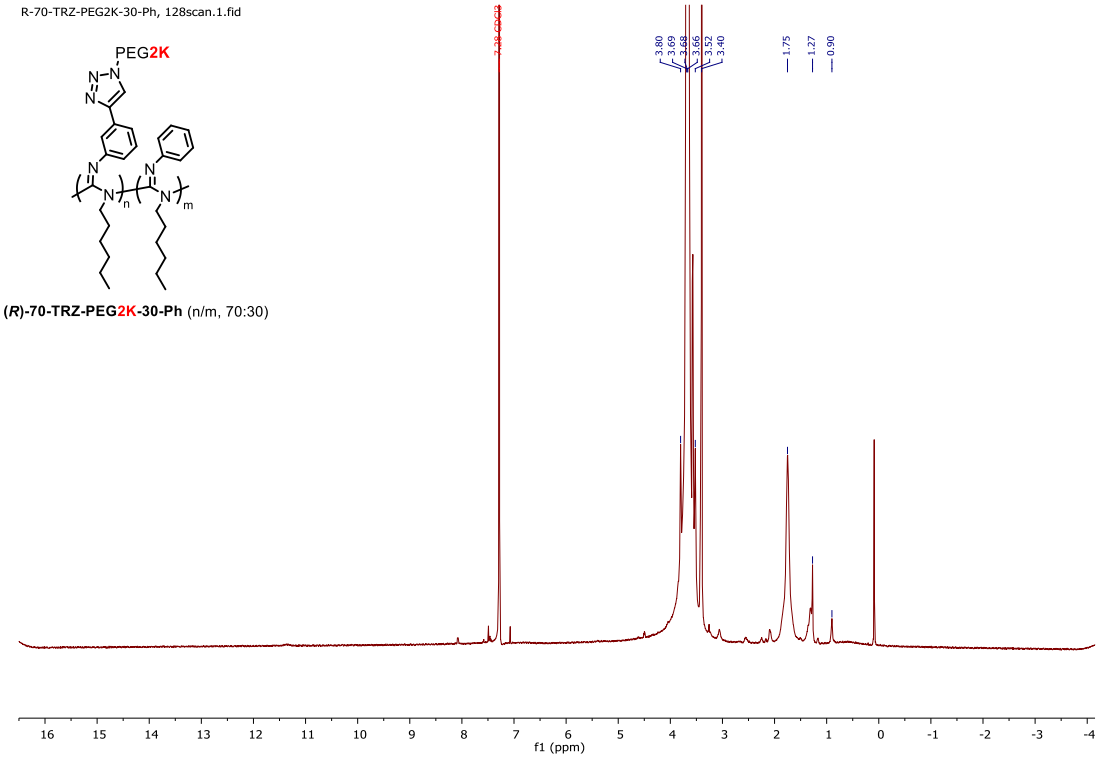

Figure S12. ^{1}H NMR spectrum of **(*R*)-70-TRZ-PEG2K-30-Ph** in $CDCl_3$

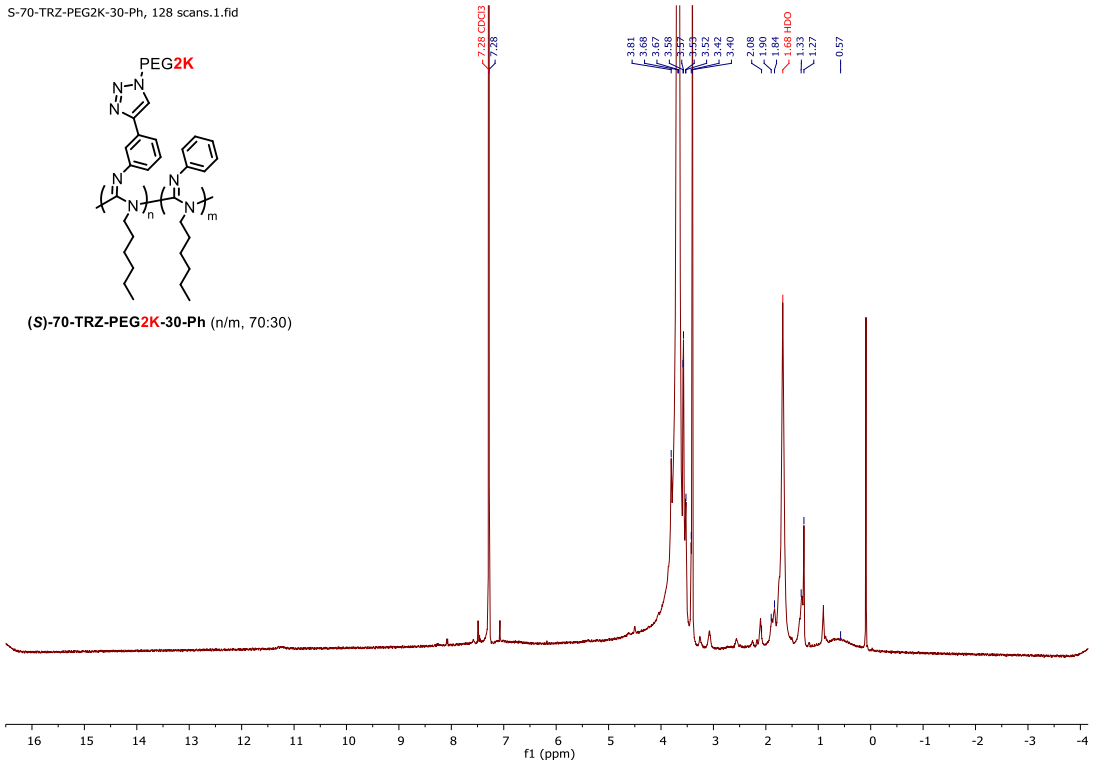

Figure S13. ^{1}H NMR spectrum of **(*S*)-70-TRZ-PEG2K-30-Ph** in $CDCl_3$

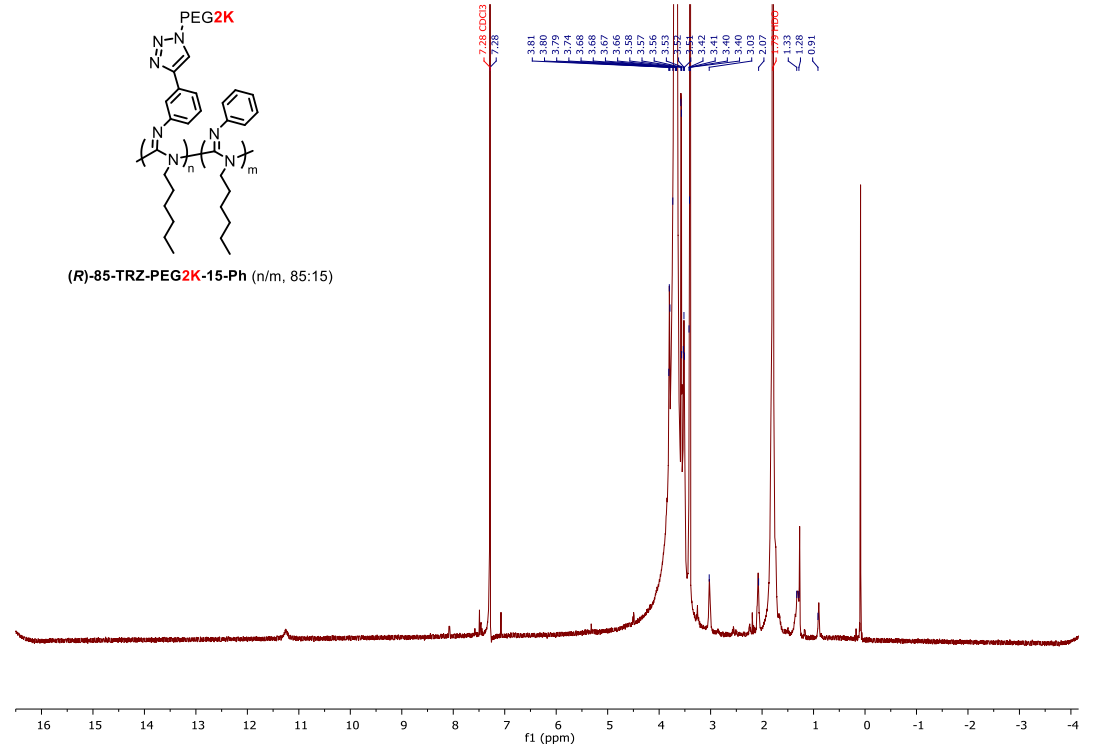

Figure S14. ^{1}H NMR spectrum of **(*R*)-85-TRZ-PEG2K-15-Ph** in $CDCl_3$

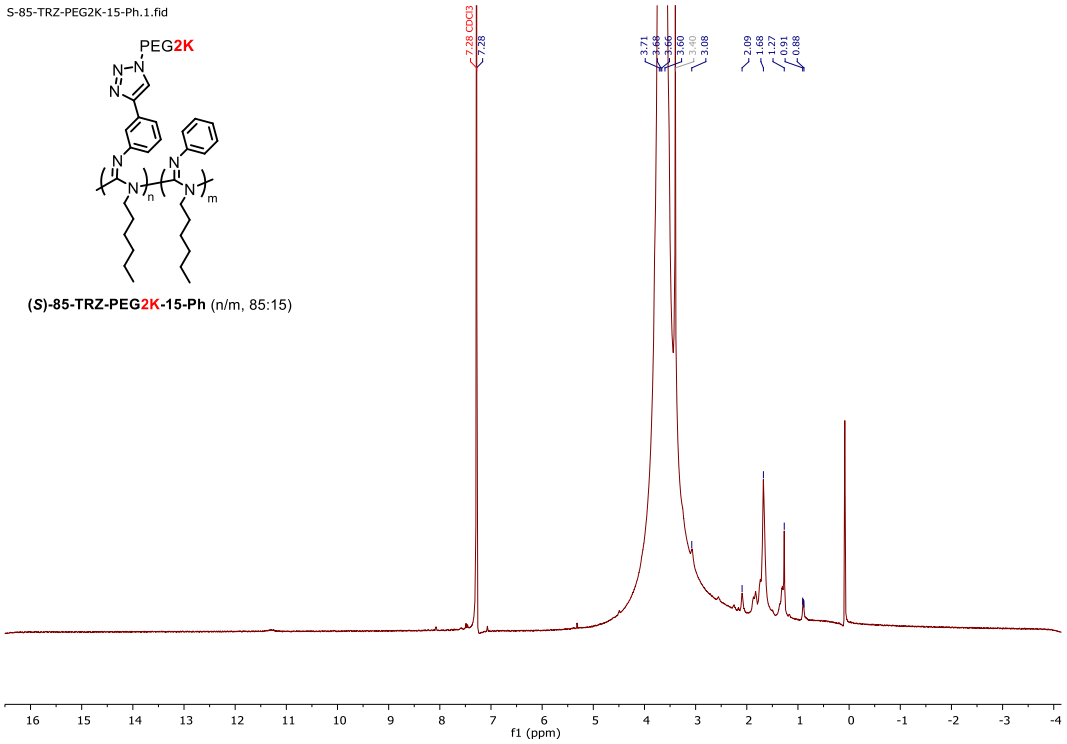

Figure S15. ^{1}H NMR spectrum of **(*S*)-85-TRZ-PEG2K-15-Ph** in $CDCl_3$

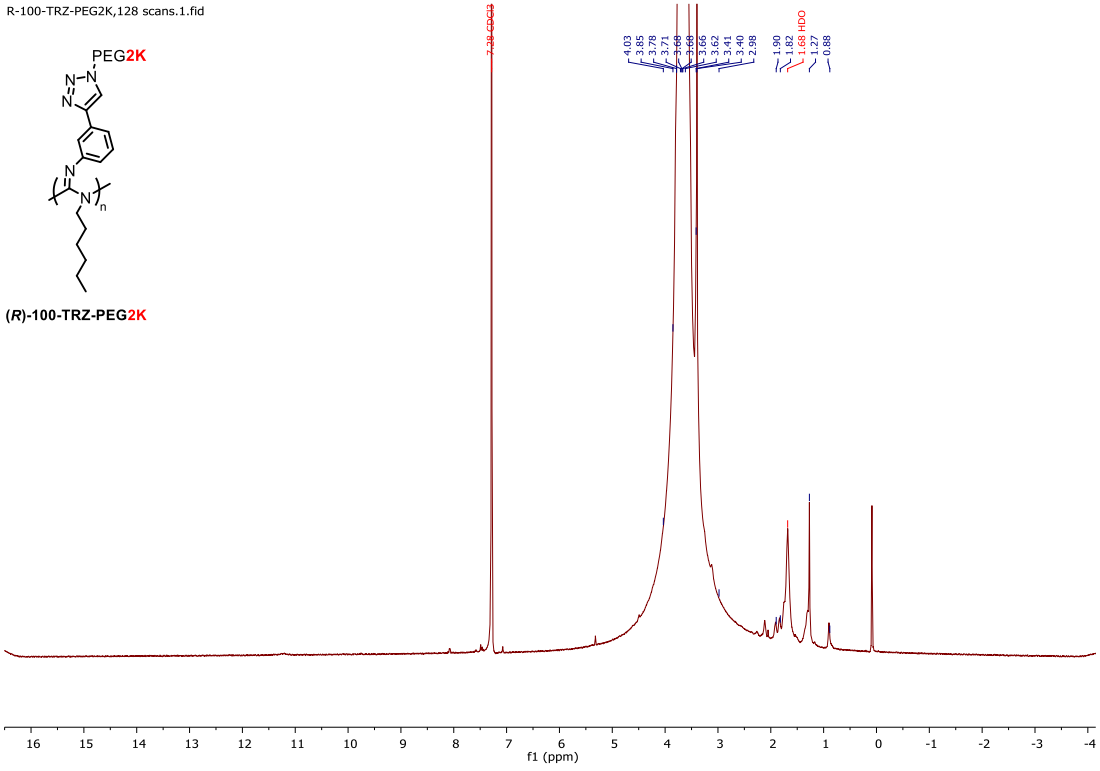

Figure S16. ^{1}H NMR spectrum of **(*R*)-100-TRZ-PEG2K** in $CDCl_3$

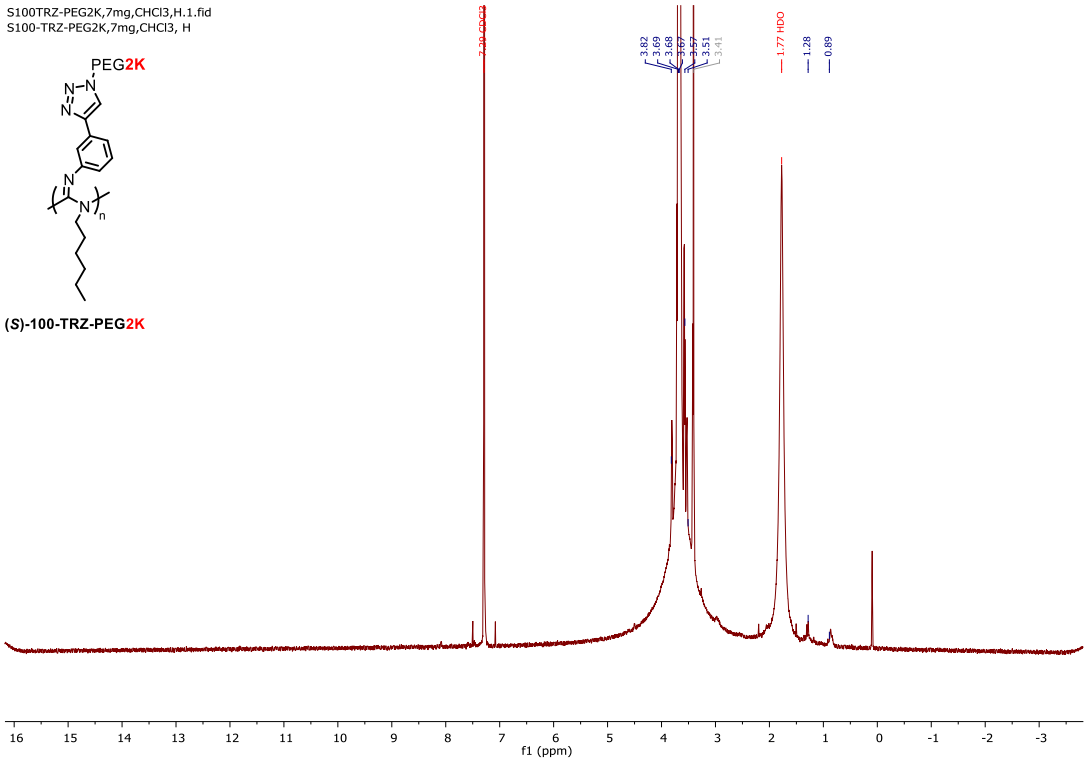

Figure S17. ^{1}H NMR spectrum of **(*S*)-100-TRZ-PEG2K** in $CDCl_3$

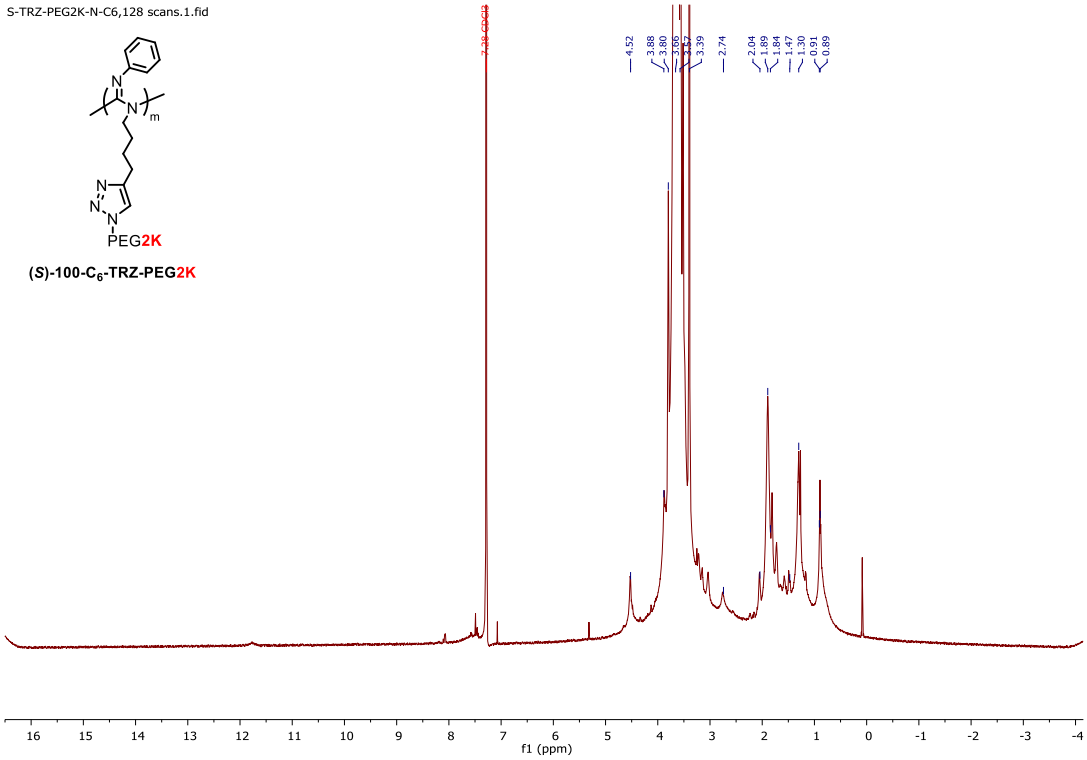

Figure S18. ^{1}H NMR spectrum of **(*S*)-100-C_6-TRZ-PEG2K** in $CDCl_3$

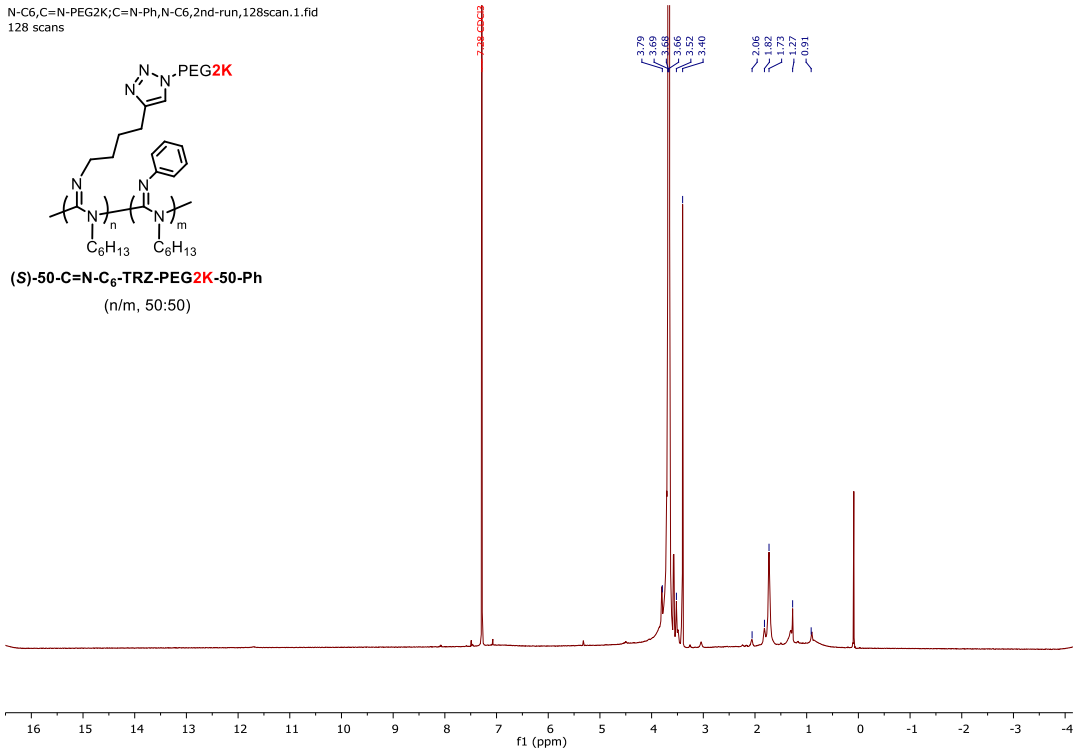

Figure S19. ^{1}H NMR spectrum of (***S***)-**50-C=N-C$_6$-TRZ-PEG2K-50-Ph** in $CDCl_3$

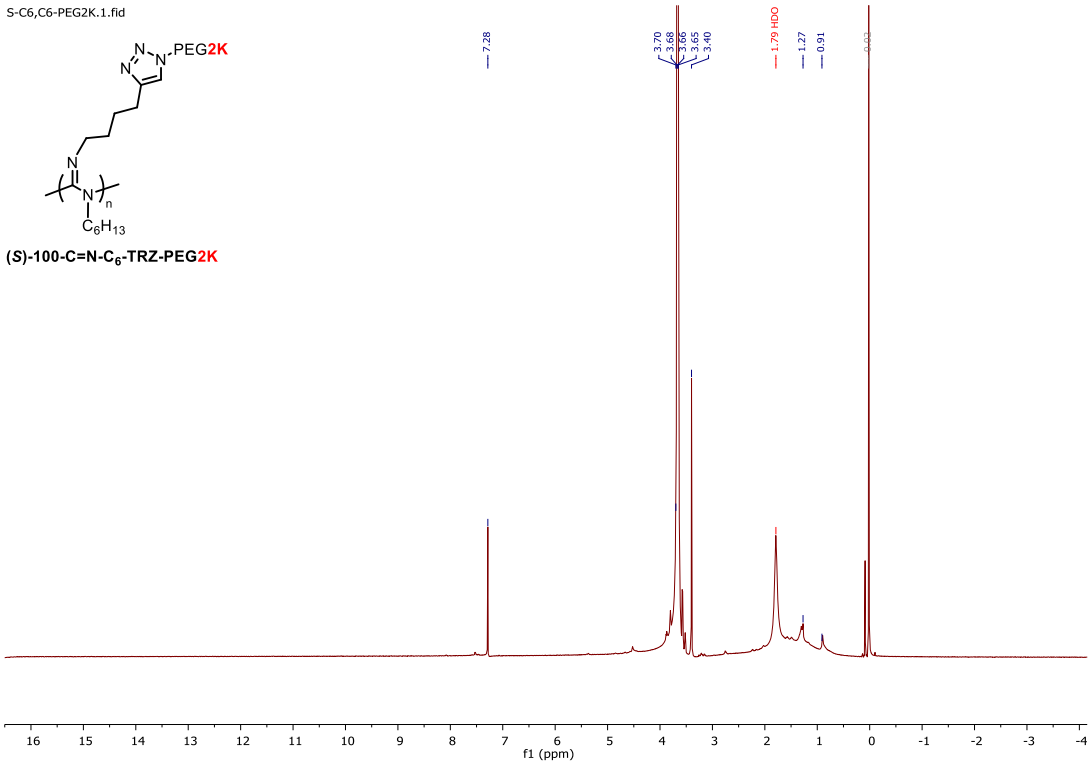

Figure S20. ^{1}H NMR spectrum of (***S***)-**100-C=N-C$_6$-TRZ-PEG2K** in $CDCl_3$

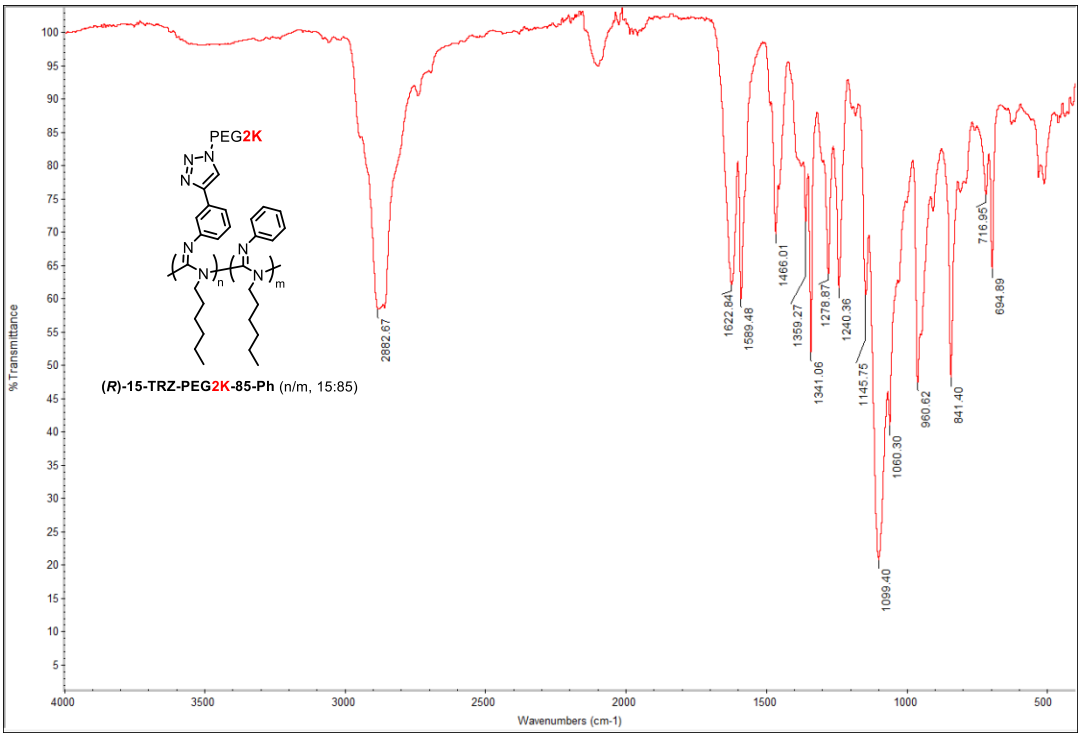

Figure S21. FTIR spectrum (neat) of **(*R*)-15-TRZ-PEG2K-85-Ph**

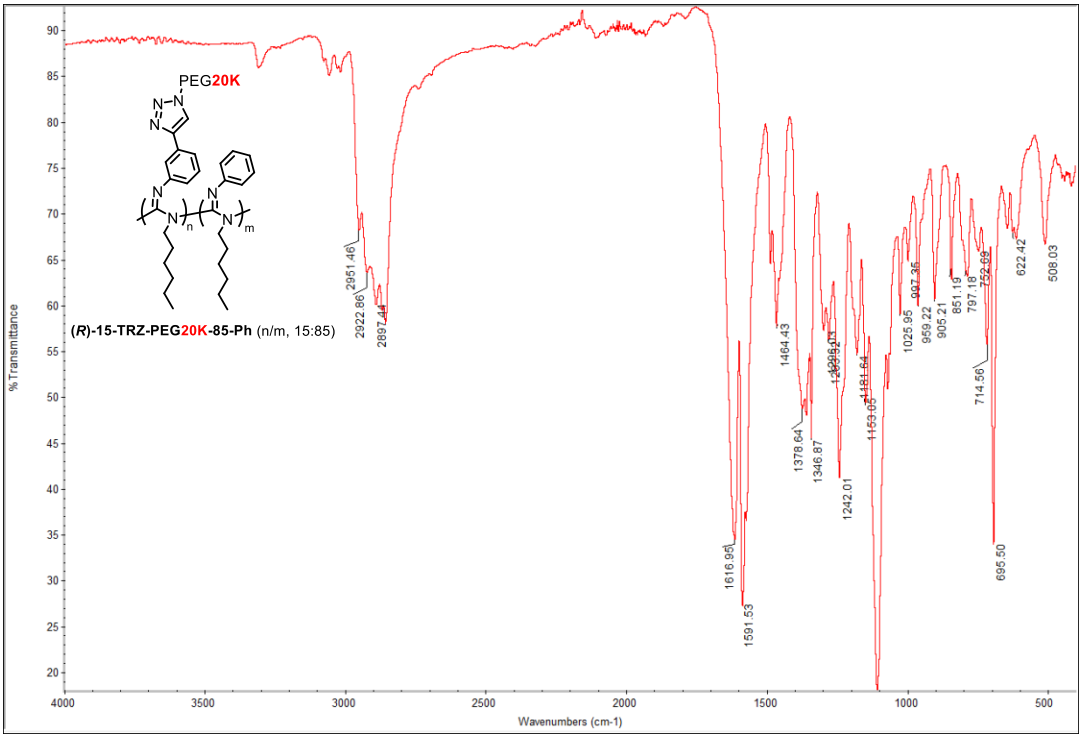

Figure S22. FTIR spectrum (neat) of **(*R*)-15-TRZ-PEG20K-85-Ph**

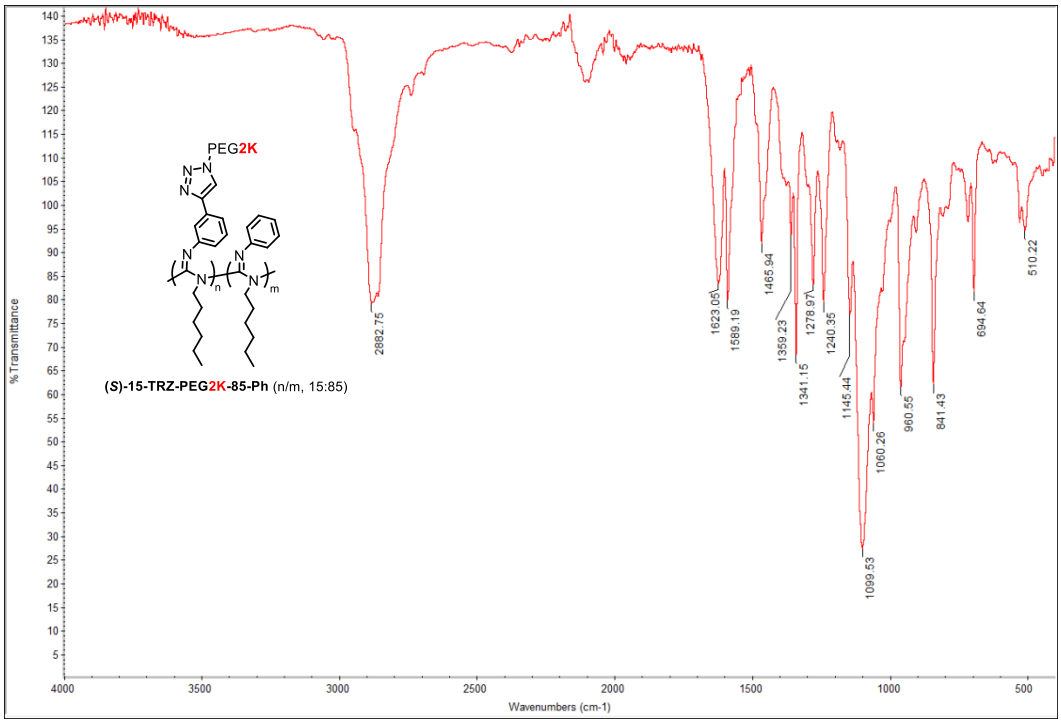

Figure S23. FTIR spectrum (neat) of **(*S*)-15-TRZ-PEG2K-85-Ph**

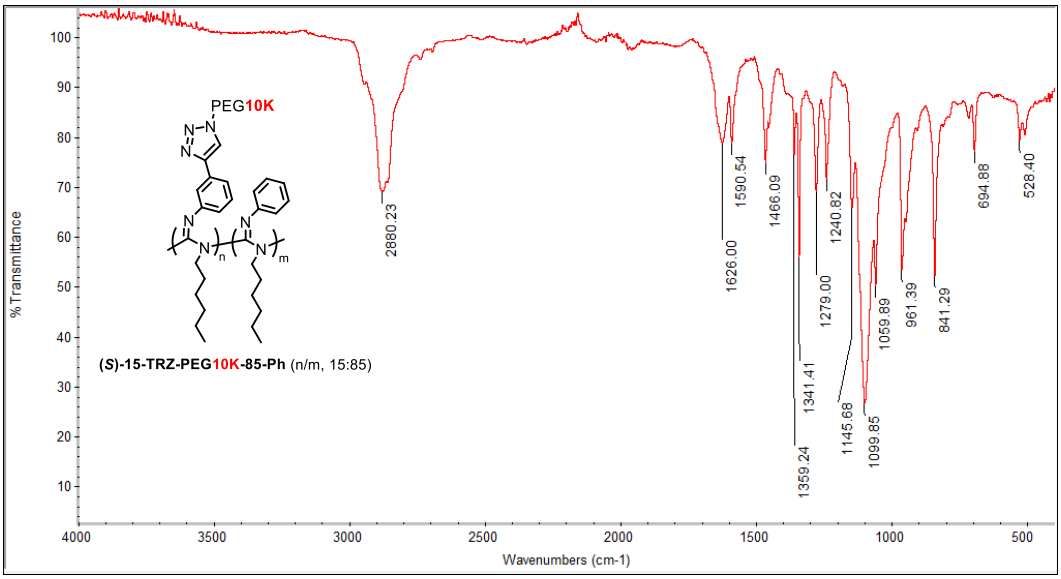

Figure S24. FTIR spectrum (neat) of **(*S*)-15-TRZ-PEG10K-85-Ph**

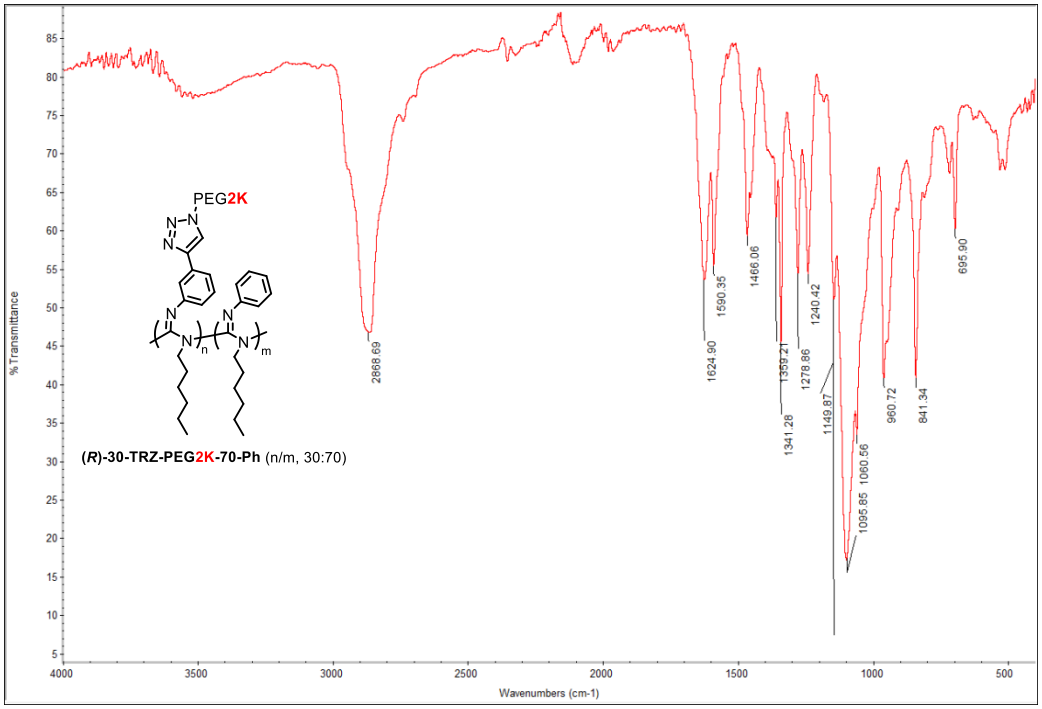

Figure S25. FTIR spectrum (neat) of **(*R*)-30-TRZ-PEG2K-70-Ph**

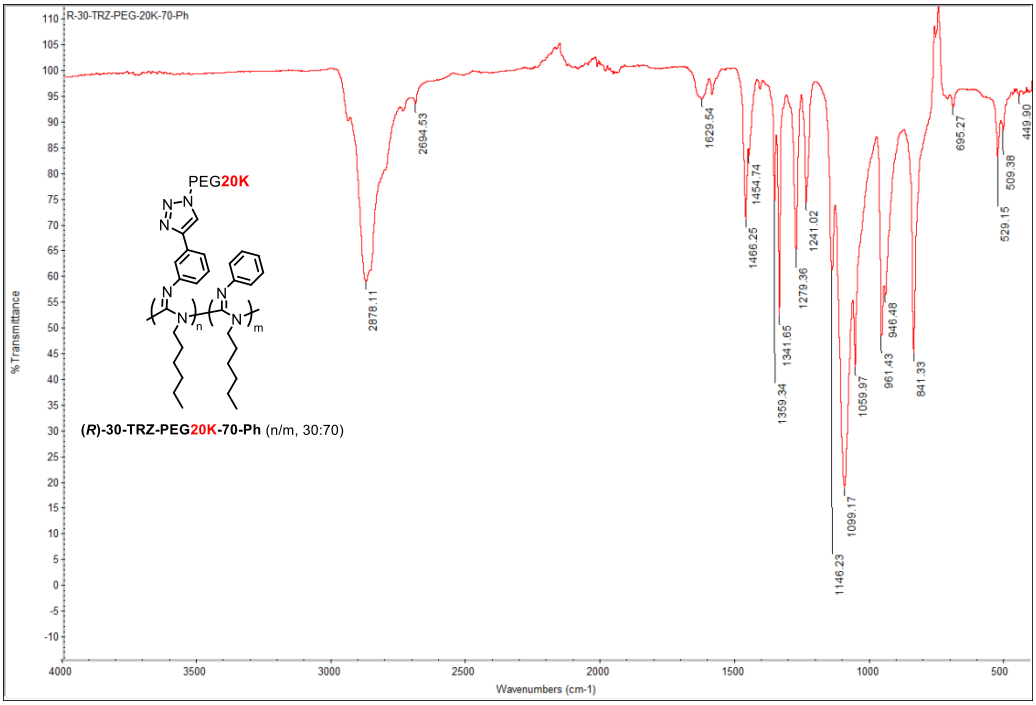

Figure S26. FTIR spectrum (neat) of **(*R*)-30-TRZ-PEG20K-70-Ph**

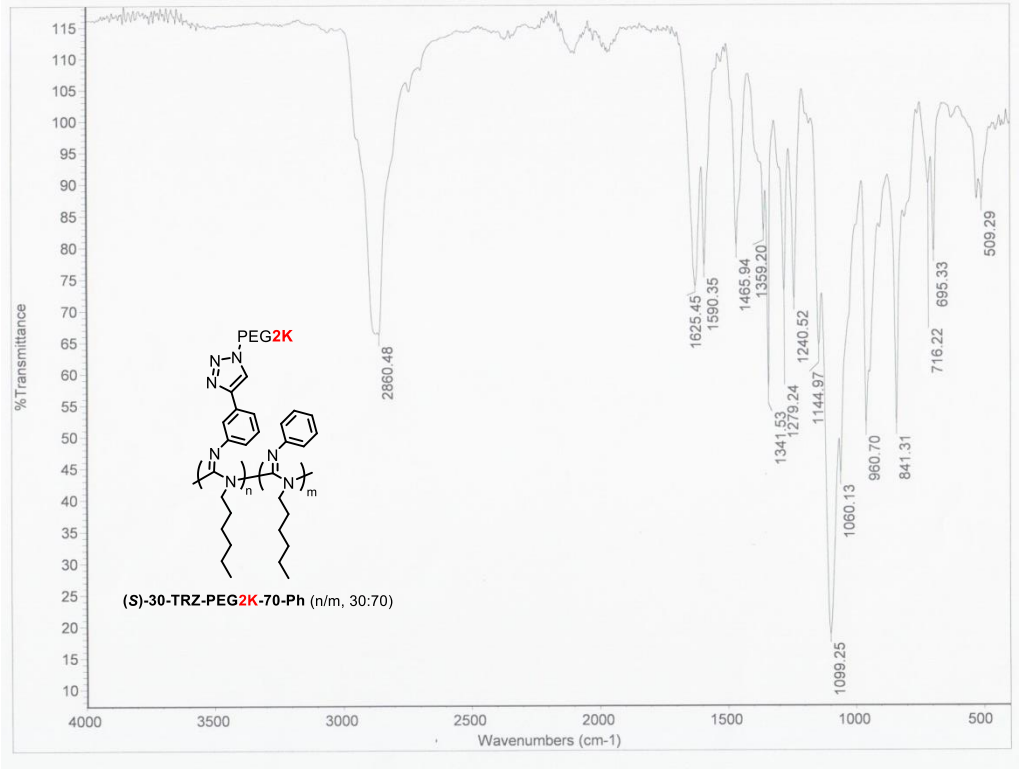

Figure S27. FTIR spectrum (neat) of **(*S*)-30-TRZ-PEG2K-70-Ph**

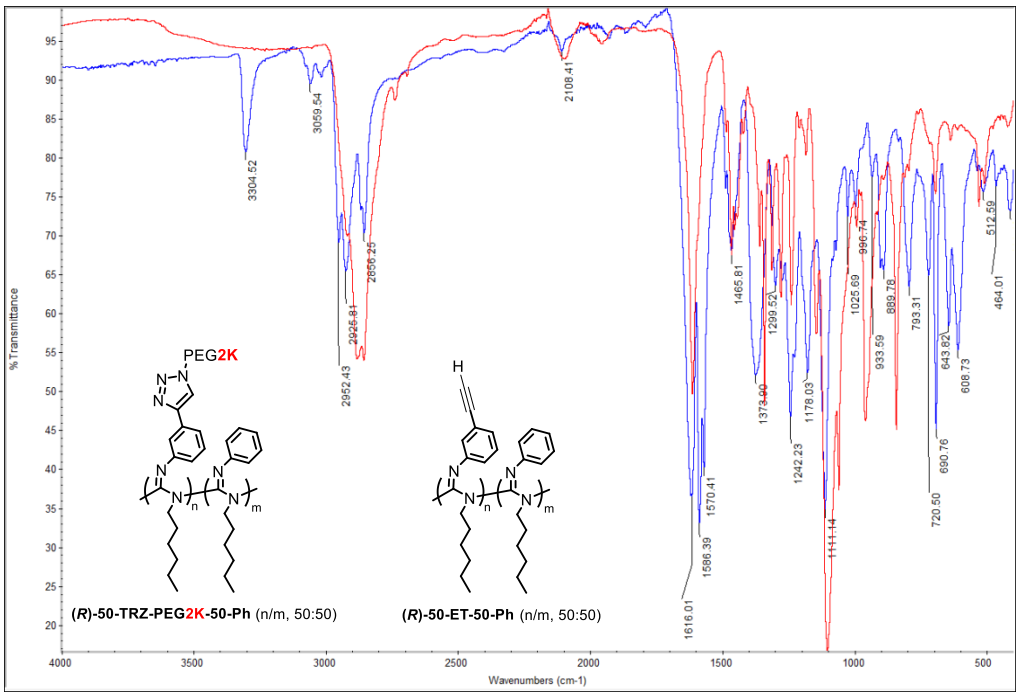

Figure S28. FTIR spectra overlay (neat) of **(*R*)-50-TRZ-PEG2K-50-Ph** (**red line**) and its respective alkyne precursor **(*R*)-50-ET-50-Ph** (**blue line**)

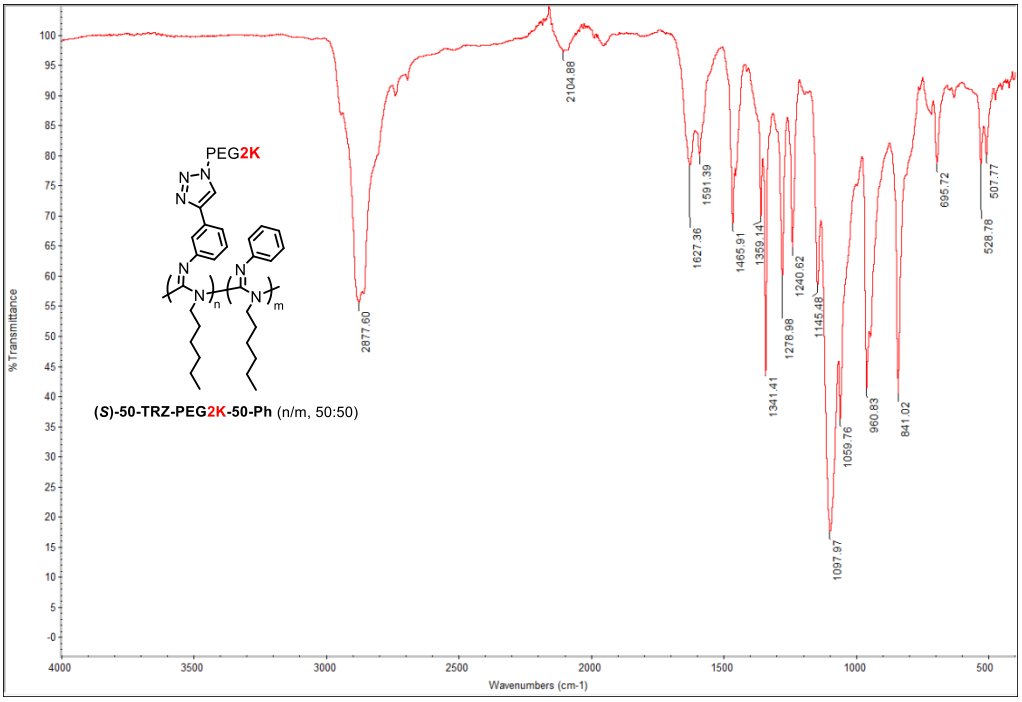

Figure S29. FTIR spectrum (neat) of **(*S*)-50-TRZ-PEG2K-50-Ph**

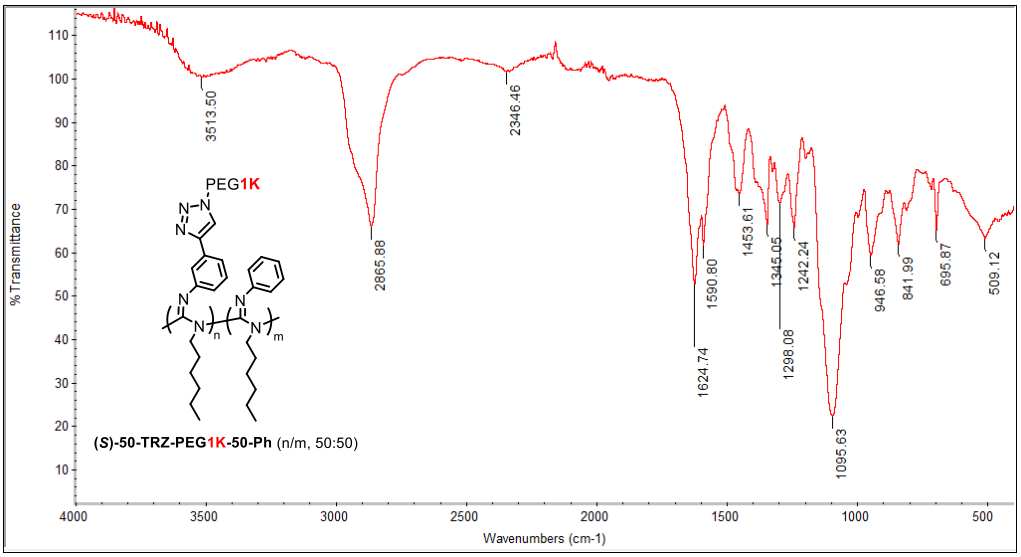

Figure S30. FTIR spectrum (neat) of **(*S*)-50-TRZ-PEG1K-50-Ph**

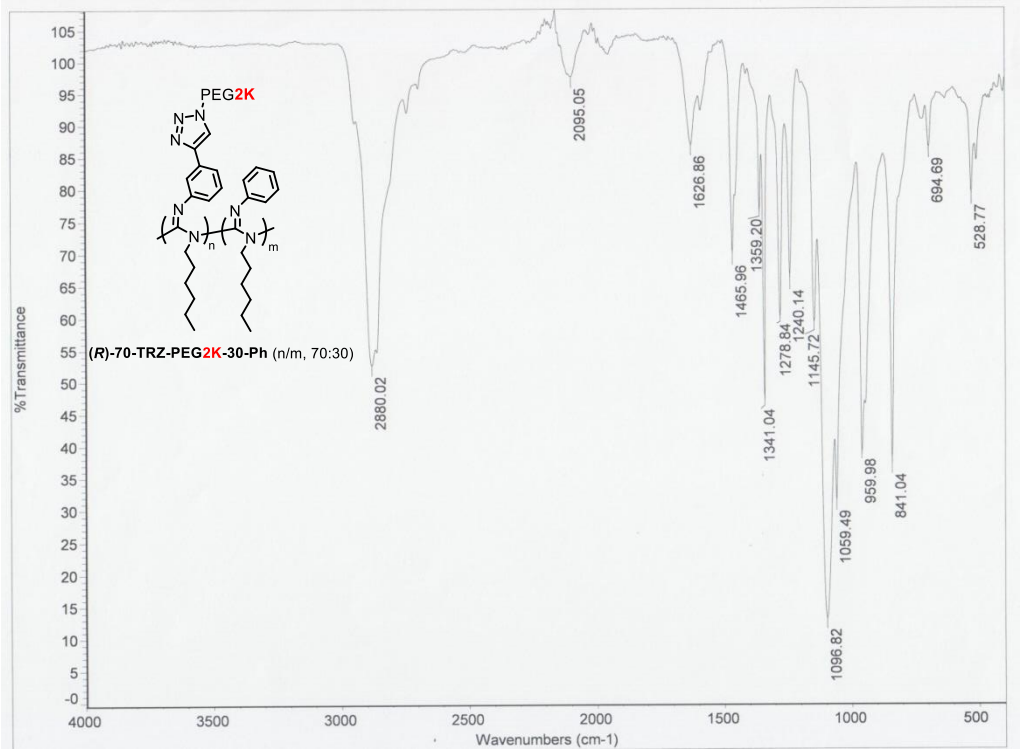

Figure S31. FTIR spectrum (neat) of **(*R*)-70-TRZ-PEG2K-30-Ph**

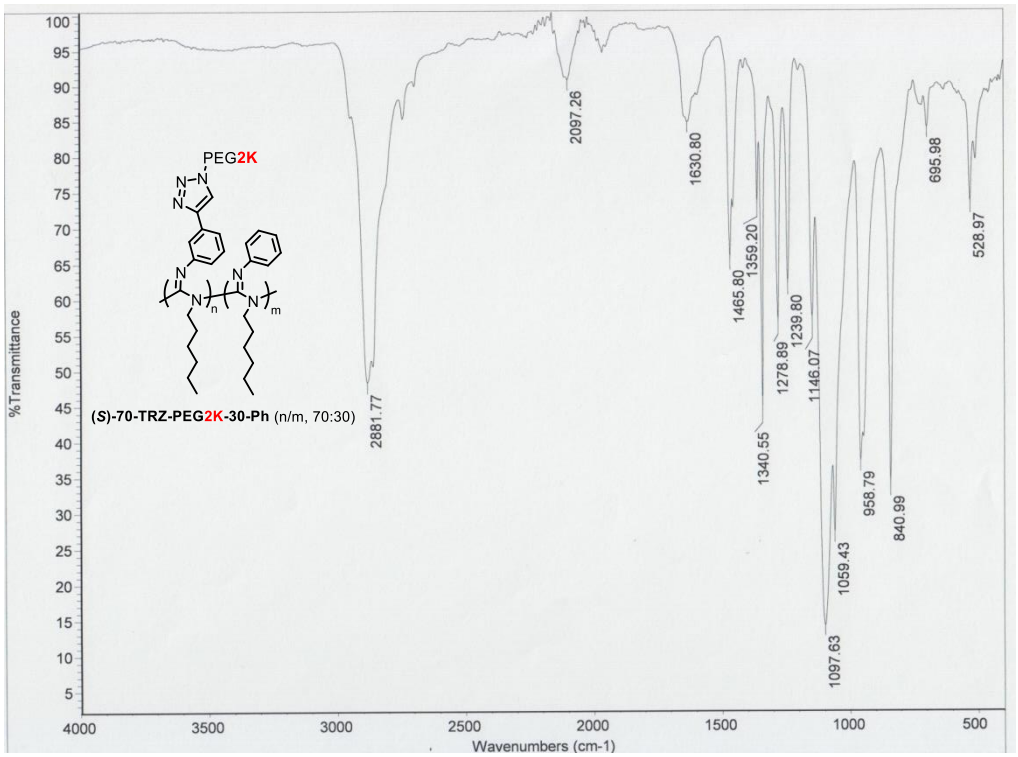

Figure S32. FTIR spectrum (neat) of **(*S*)-70-TRZ-PEG2K-30-Ph**

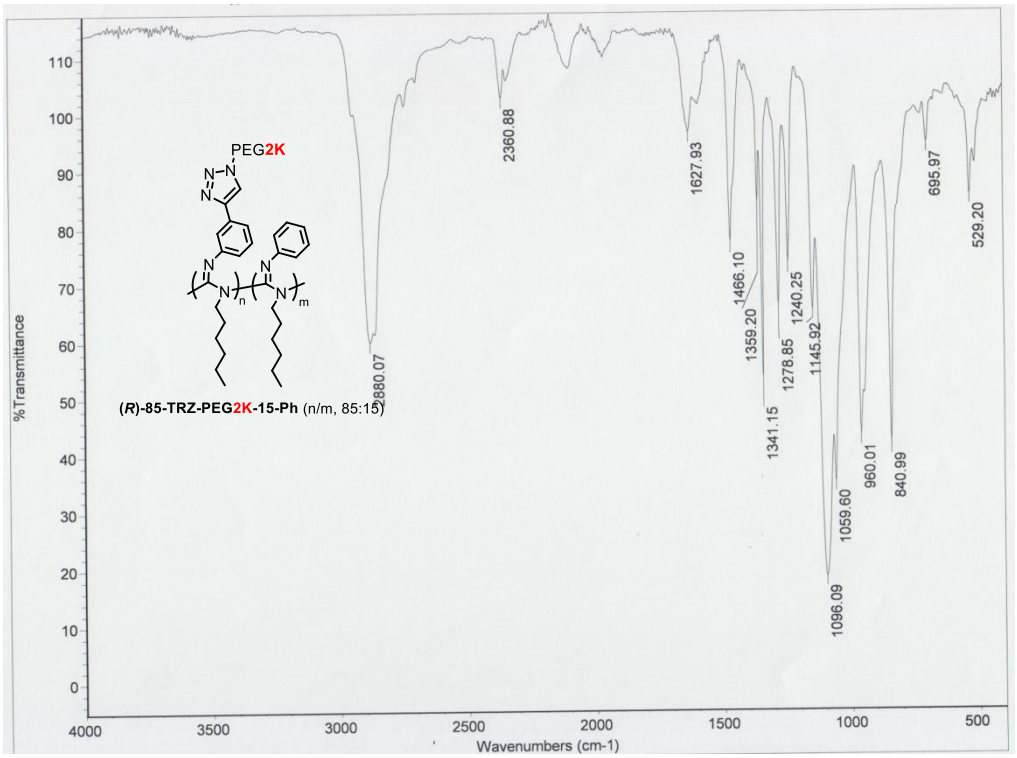

Figure S33. FTIR spectrum (neat) of **(*R*)-85-TRZ-PEG2K-15-Ph**

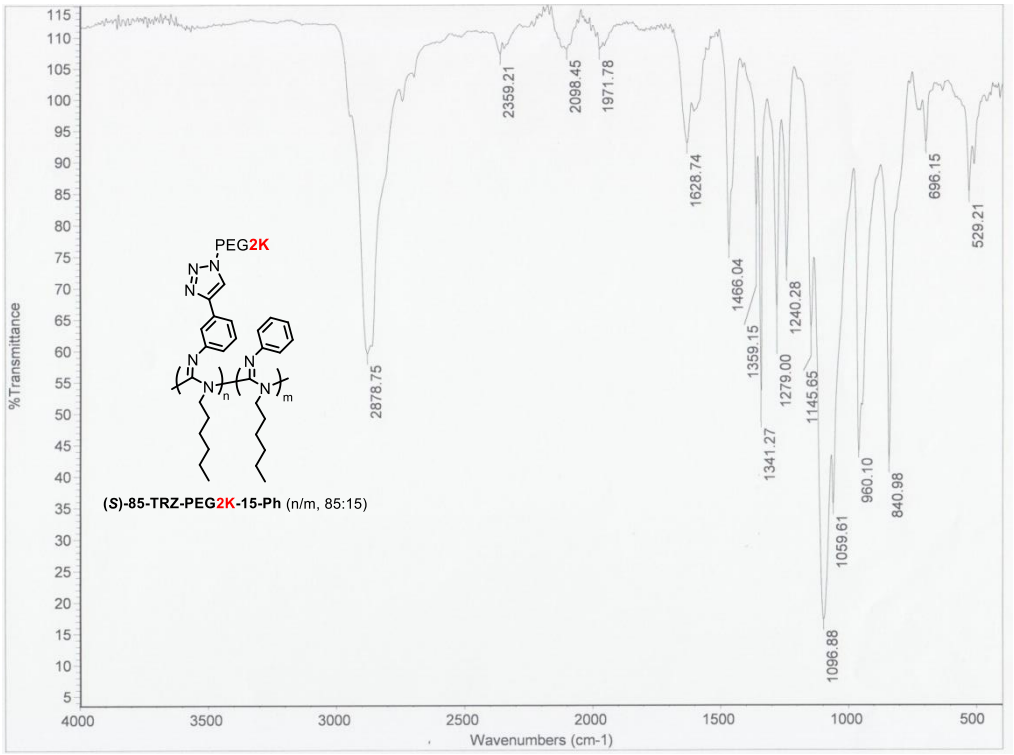

Figure S34. FTIR spectrum (neat) of **(*S*)-85-TRZ-PEG2K-15-Ph**

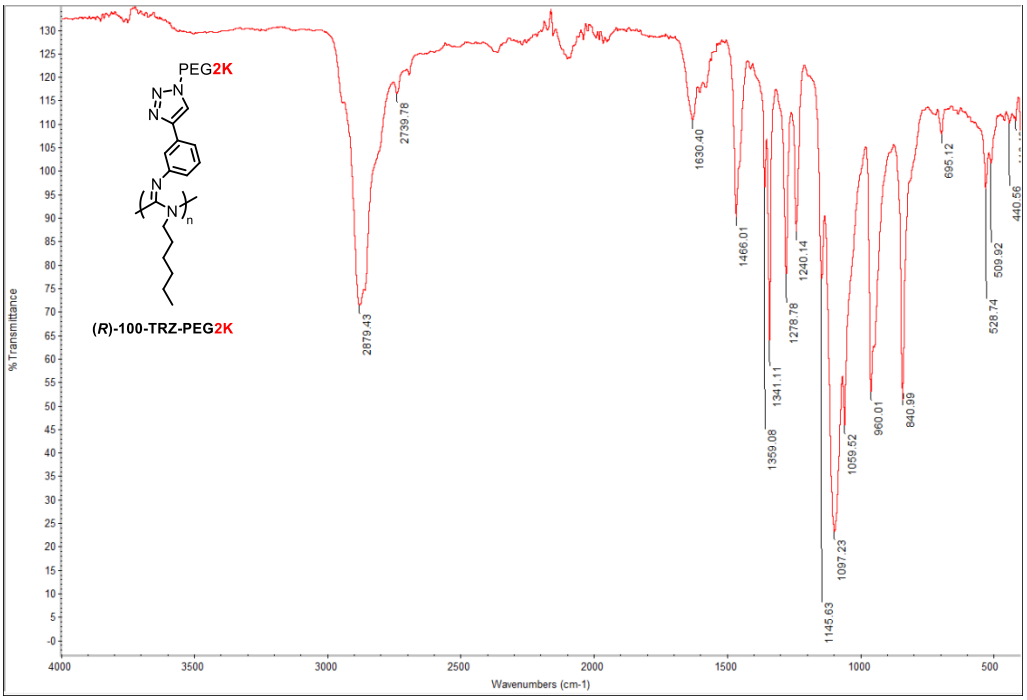

Figure S35. FTIR spectrum (neat) of **(*R*)-100-TRZ-PEG2K**

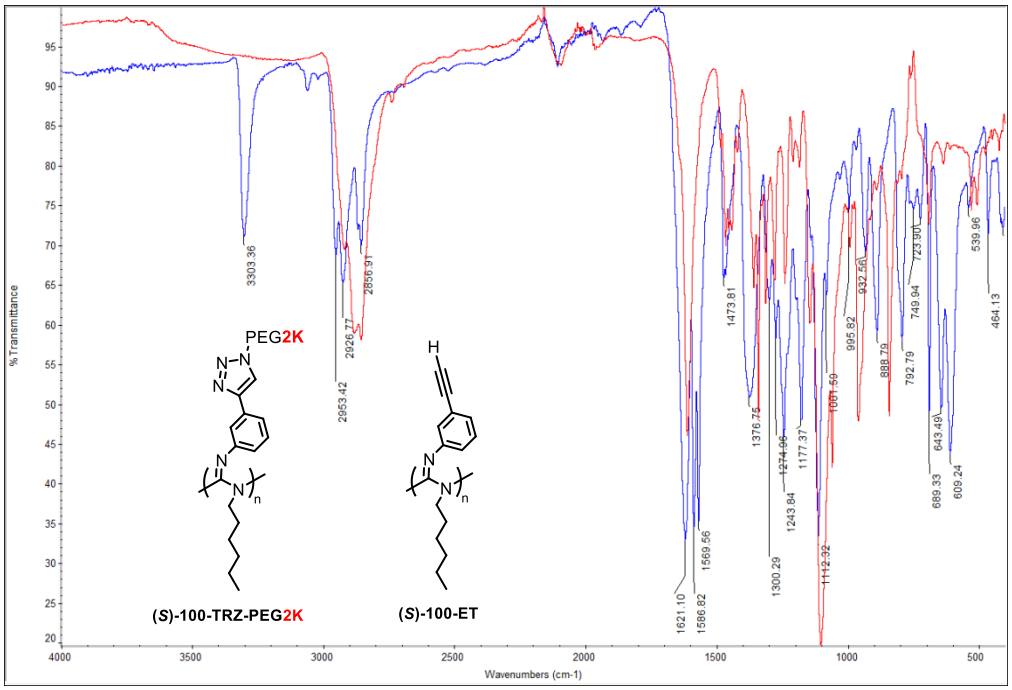

Figure S36. FTIR spectra overlay (neat) of **(*S*)-100-TRZ-PEG2K** (**red line**) and its respective alkyne precursor **(*S*)-100-ET** (**blue line**)

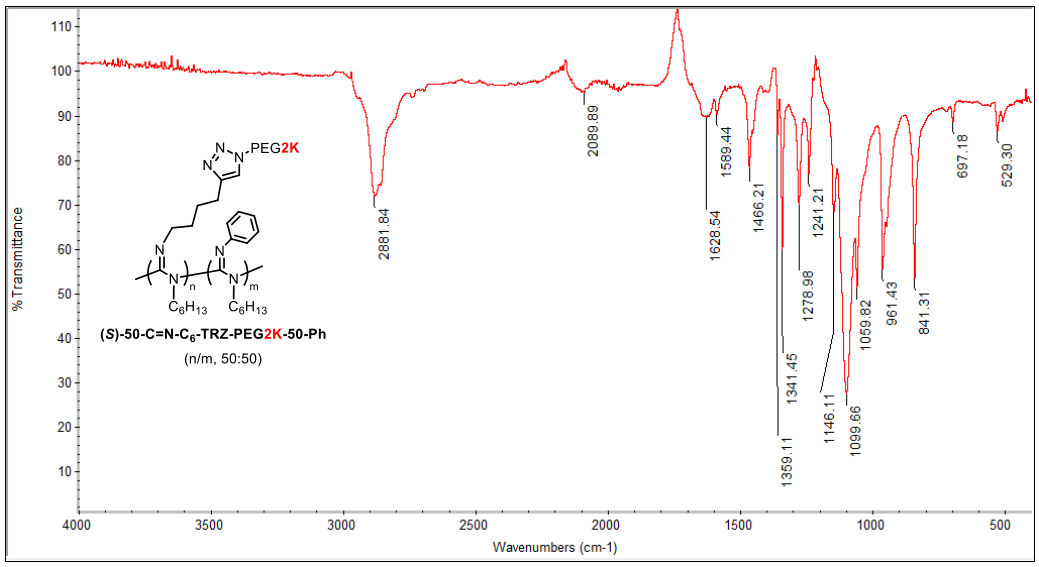

Figure S37. FTIR spectrum (neat) of (***S***)-**50-C=N-C$_6$-TRZ-PEG2K-50-Ph**

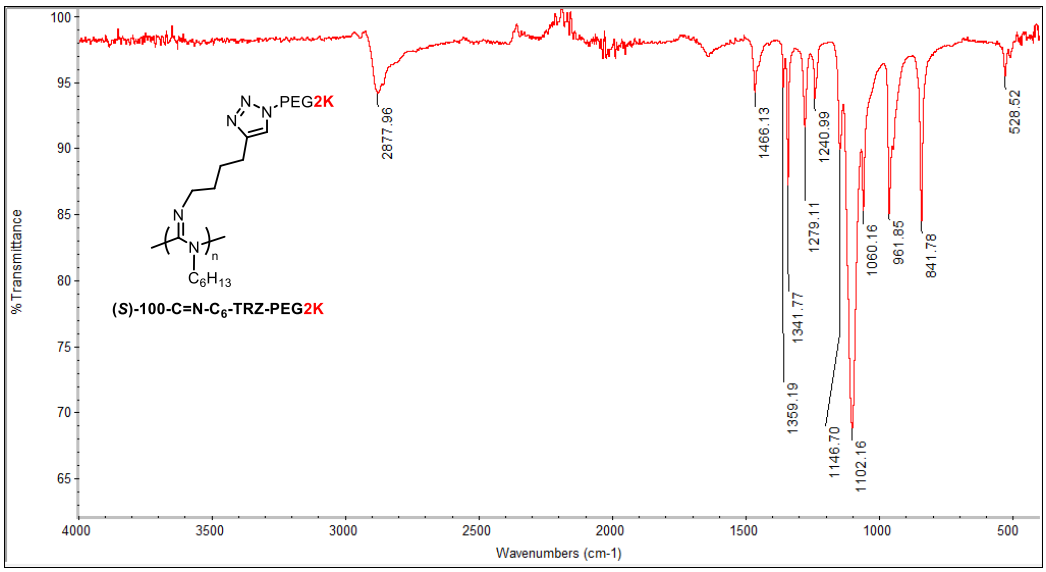

Figure S38. FTIR spectrum (neat) of (***S***)-**100-C=N-C$_6$-TRZ-PEG2K**

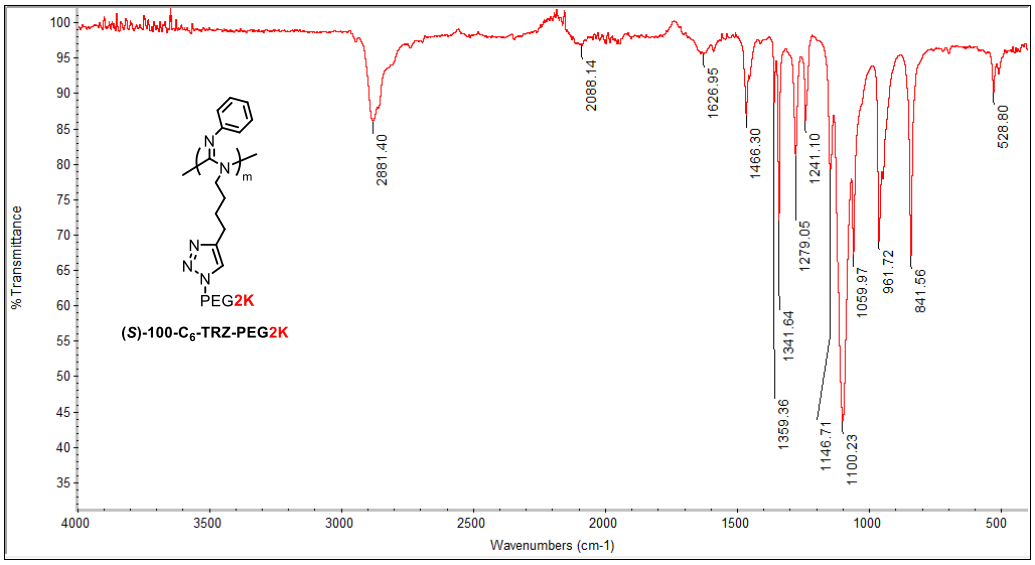

Figure S39. FTIR spectrum (neat) of **(*S*)-100-C_6-TRZ-PEG2K**

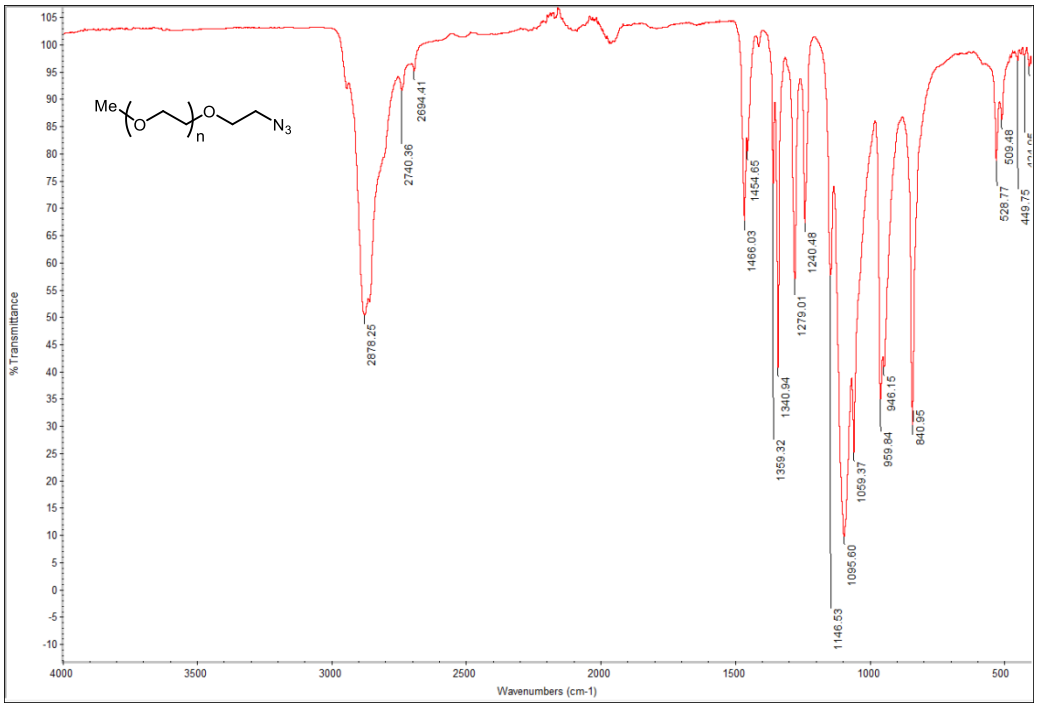

Figure S40. FTIR spectrum (neat) of **PEG20K-N_3**

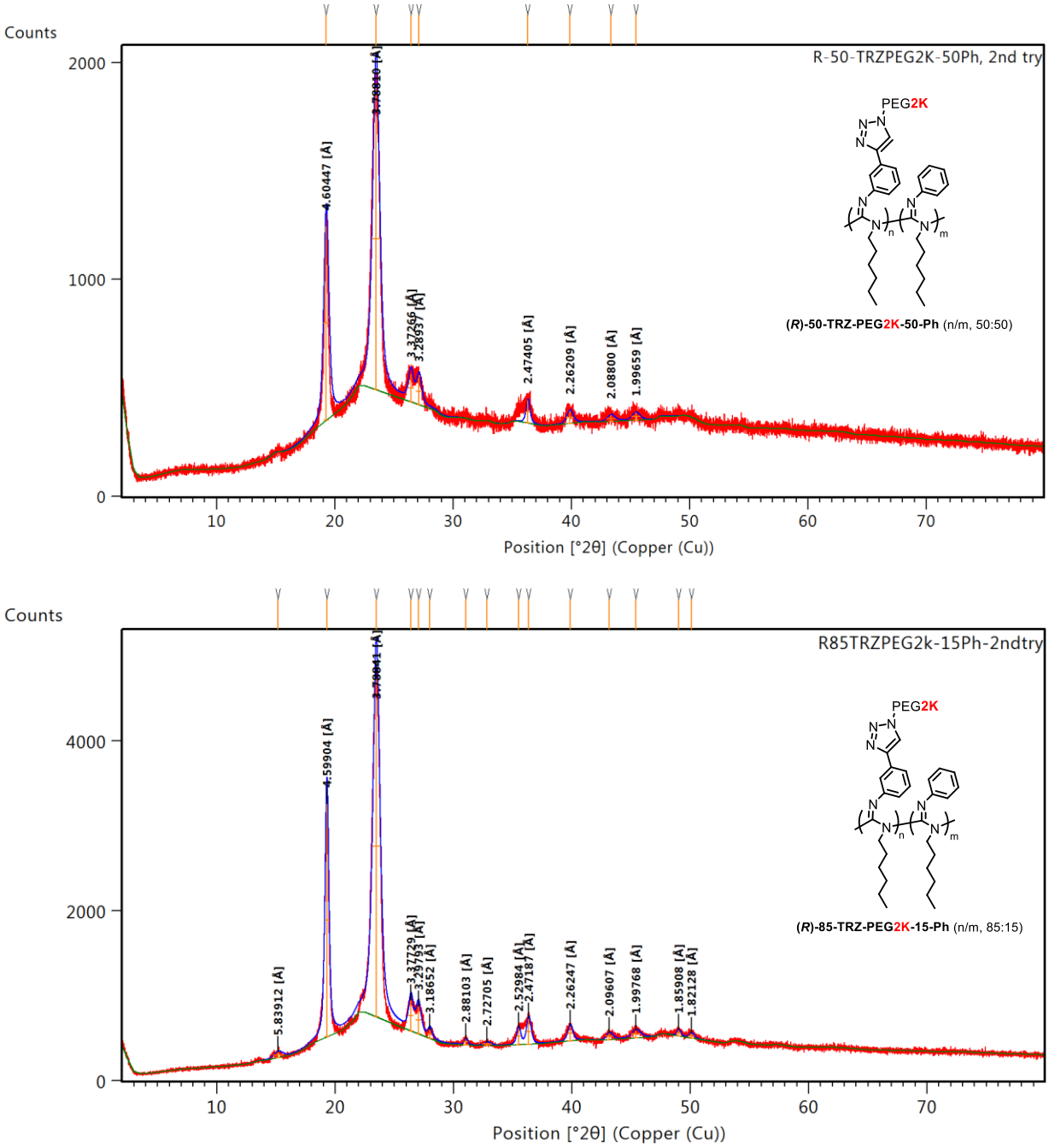

Figure S41. XRD profiles (powder) of **(*R*)-50-TRZ-PEG2K-50-Ph** (top) and **(*R*)-85-TRZ-PEG2K-15-Ph** (bottom)

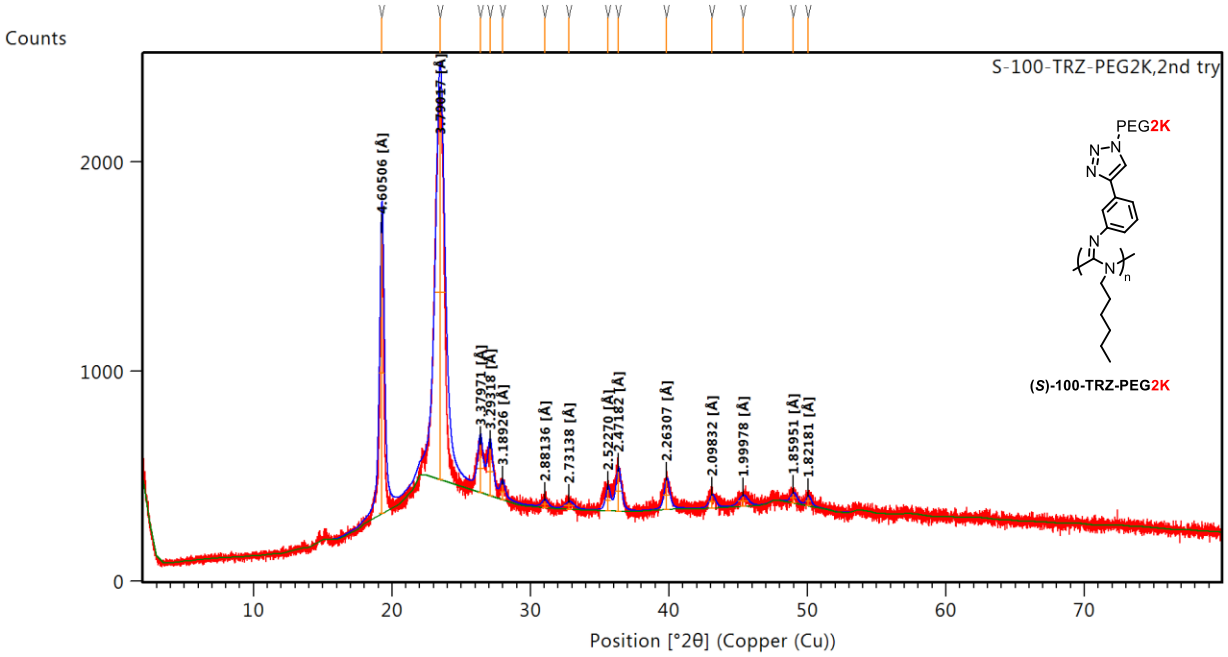

Figure S42. XRD profile (powder) of **(*S*)-100-TRZ-PEG2K**