Electronic Supplementary Material (ESI) for Polymer Chemistry.


# Electronic supporting information

## Simultaneous Synthesis and Chemical Functionalization of Emulsion-Templated Porous Polymers using Nitroxide-Terminated Macromolecular Surfactants.

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**Table S1.** NMP of PEO-*b*-PS-SG1 in 1,4-dioxane.

| Copolymers | $[S]_0$/ $[PEO\text{-}SG1]_0$ | Diox. (mL) | Time (h) | Conv. (%)[a] | $M_{n\ th\ PS}$[b] (g/mol) | $M_{n\ PS}$[c] (g/mol) |
|---|---|---|---|---|---|---|
| $PEO_{2K}$-*b*-$PS_{2.2K}$-SG1 | 58 | 7 | 3 | 40 | 2400 | 2200 |
| $PEO_{2K}$-*b*-$PS_{4.7K}$-SG1 | 116 | 4 | 2 | 50 | 6000 | 4700 |
| $PEO_{1K}$-*b*-$PS_{2.2K}$-SG1 | 44 | 5 | 4 | 55 | 2500 | 2200 |
| Alkyne-$PEO_{2.6K}$-*b*-$PS_{2.7K}$-SG1 | 75 | 2 | 6 | 46 | 3600 | 2700 |

[a] Determined by $^1H$ NMR in $CD_2Cl_2$. [b] $M_{n\ th} = ([S]_0/[PEO\text{-}CTA]_0) \times M_{n\ styrene} \times$ Conversion. [c] Determined by $^1H$ NMR in $CD_2Cl_2$.

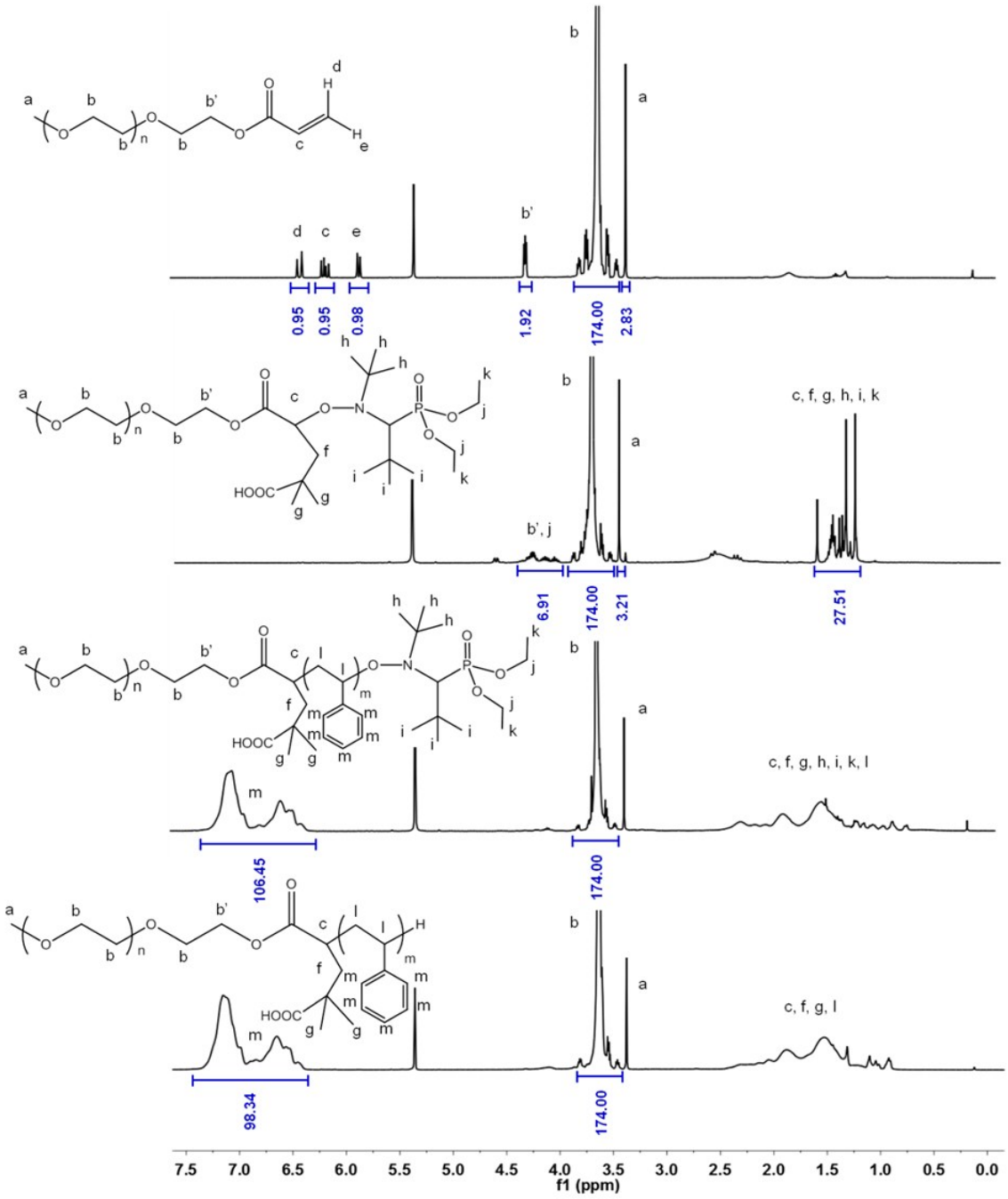


**Figure S1.** Overlay of $^{1}$H NMR spectra of $PEO_{2K}$-acrylate, $PEO_{2K}$-SG1, $PEO_{2K}$-*b*-$PS_{2.2K}$-SG1 and $PEO_{2K}$-*b*-$PS_{2.2K}$-H in $CD_2Cl_2$. Values of integrals are indicated in blue.

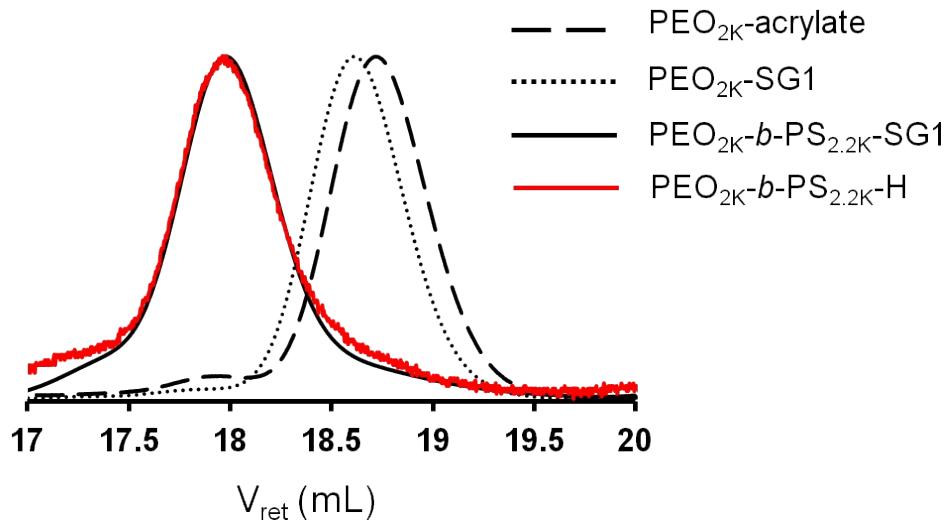


**Figure S2.** SEC chromatograms in THF of $PEO_{2K}$-acrylate (dotted line), $PEO_{2K}$-SG1 (small dotted line), $PEO_{2k}$-*b*-$PS_{2.2k}$-SG1 (black full line) and $PEO_{2k}$-*b*-$PS_{2.2k}$-H (red full line).

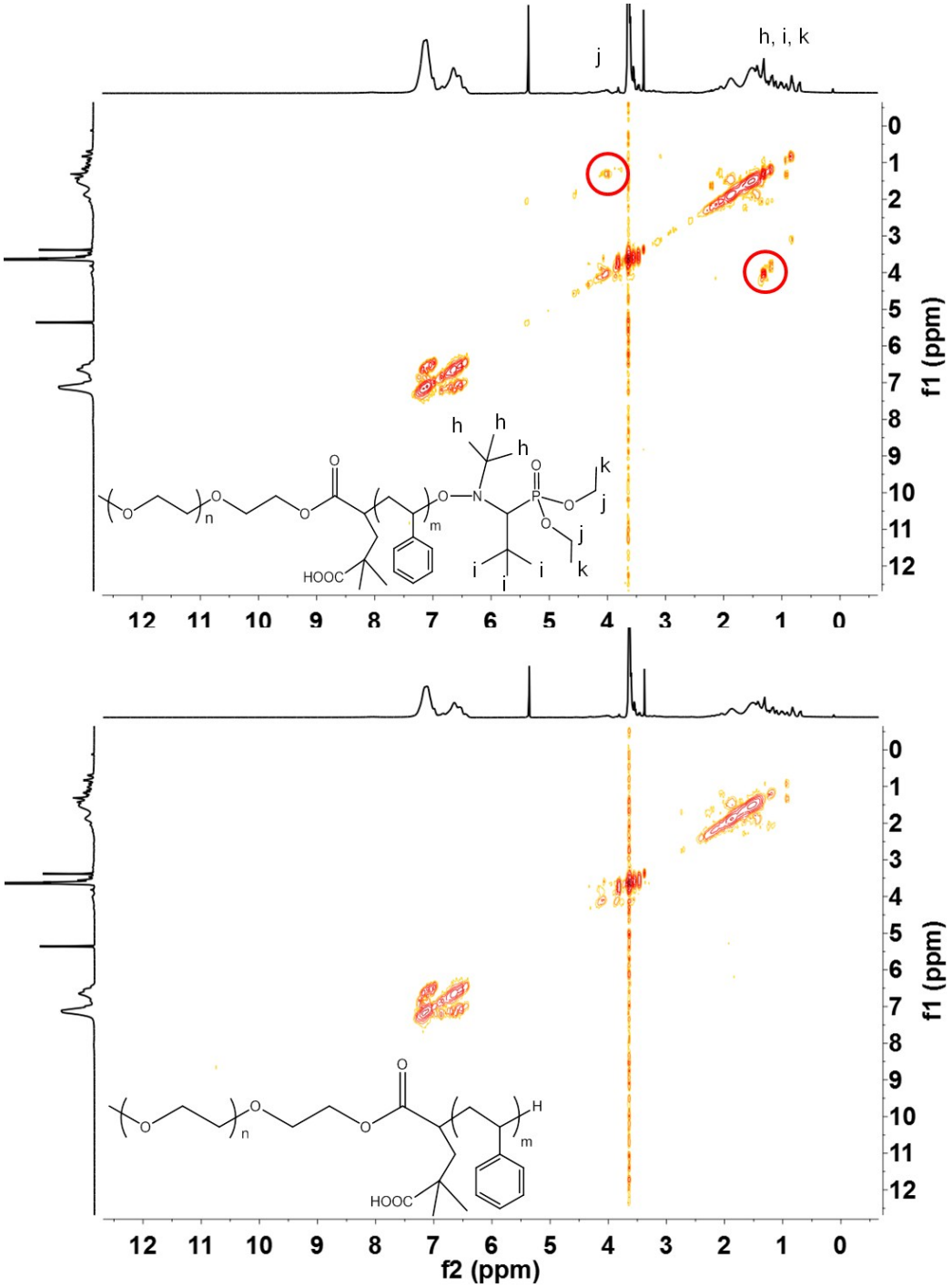


**Figure S3**. $^{1}H$-$^{1}H$ COSY NMR of $PEO_{2K}$-*b*-$PS_{2.2K}$-SG1 (top spectrum) and $PEO_{2K}$-*b*-$PS_{2K}$-H (bottom spectrum) in $CD_2Cl_2$

**Figure S4**. Illustration of a water-in-S/DVB HIPE emulsion stabilized by a PEO-*b*-PS-SG1 surfactant after 4 h at 30 °C.

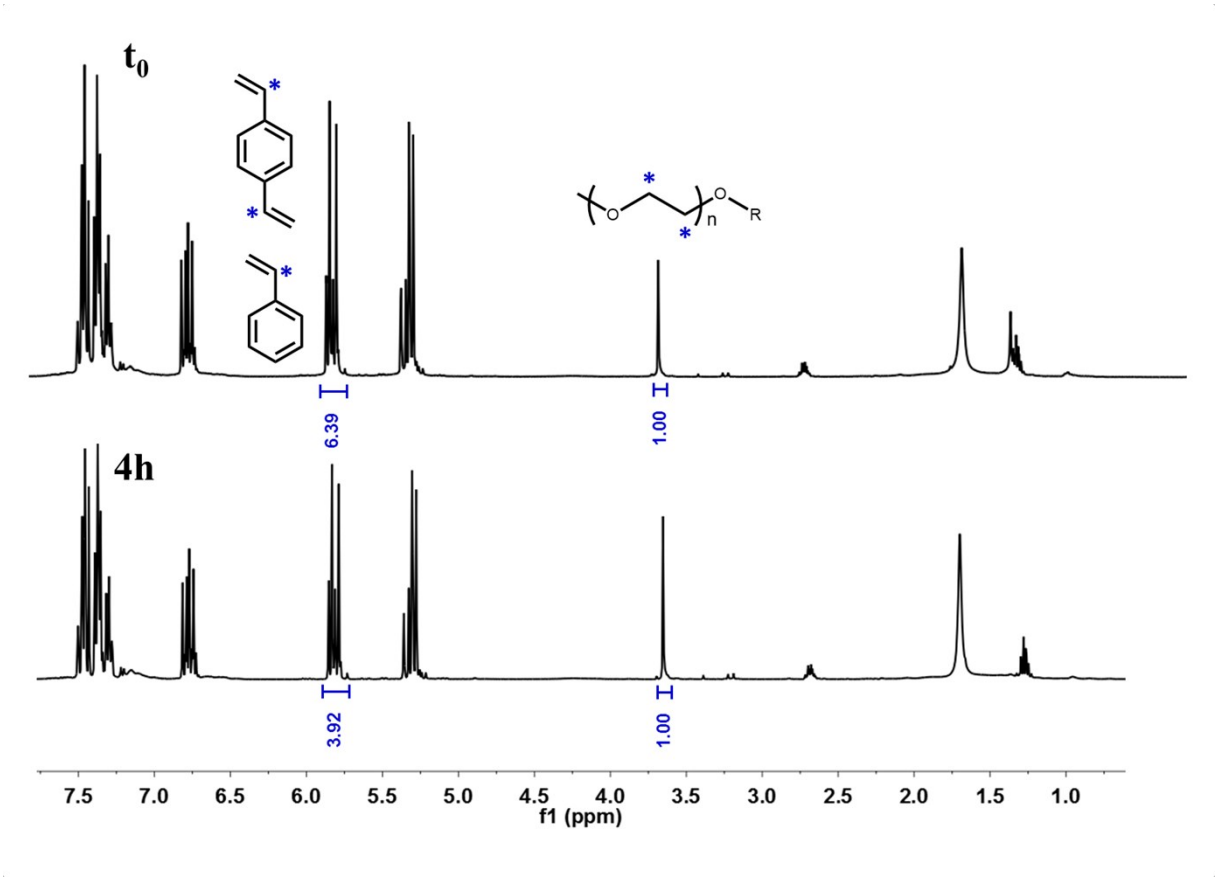


**Figure S5**. $^{1}H$ NMR in $CD_2Cl_2$ of the water-in-S/DVB HIPE emulsion stabilized by a PEO-b-PS-SG1 surfactant after 0 h (upper spectrum) and 4 h (bottom spectrum) at 30 °C. The styrene/DVB conversion was evaluated to 39 % after 4 h at 30°C based on the relative intensities of the olefinic signals of the monomers and the methylene signal of PEO used as an internal standard.

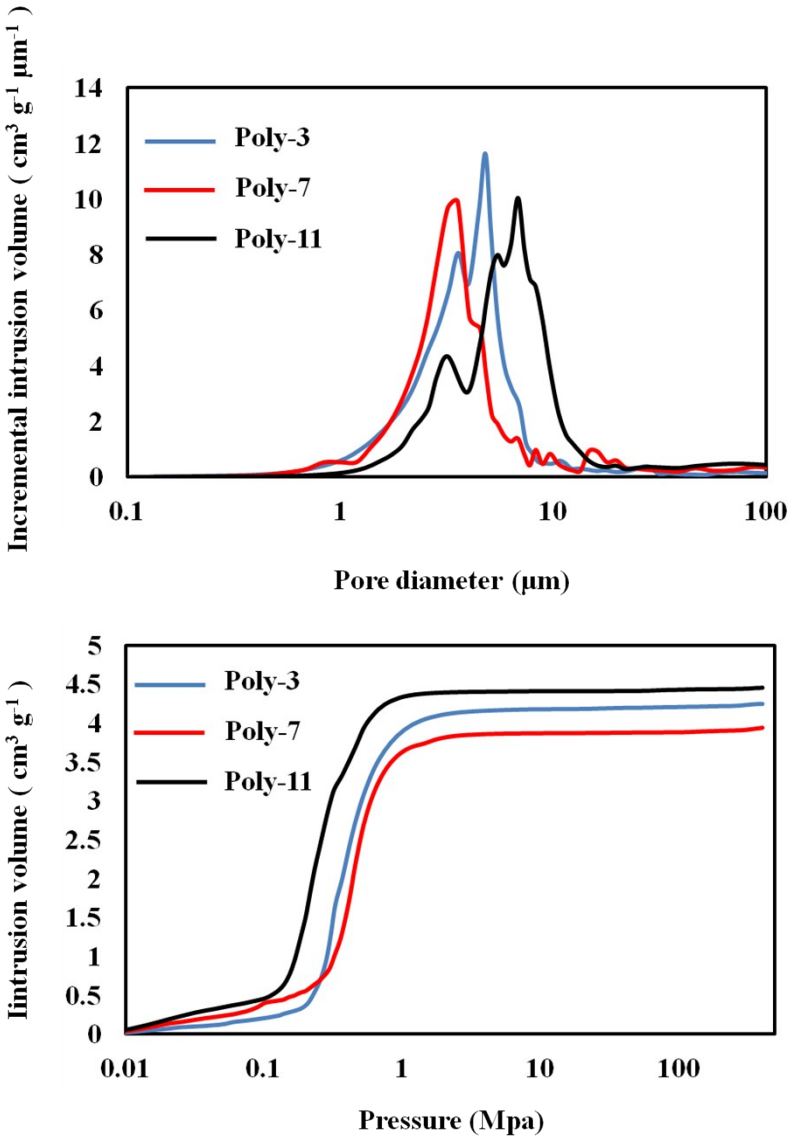


**Figure S6**. Pore throat diameter distributions (top) and mercury intrusion volume (bottom) determined by mercury porosimetry of Poly-3, Poly-7 and Poly-11.

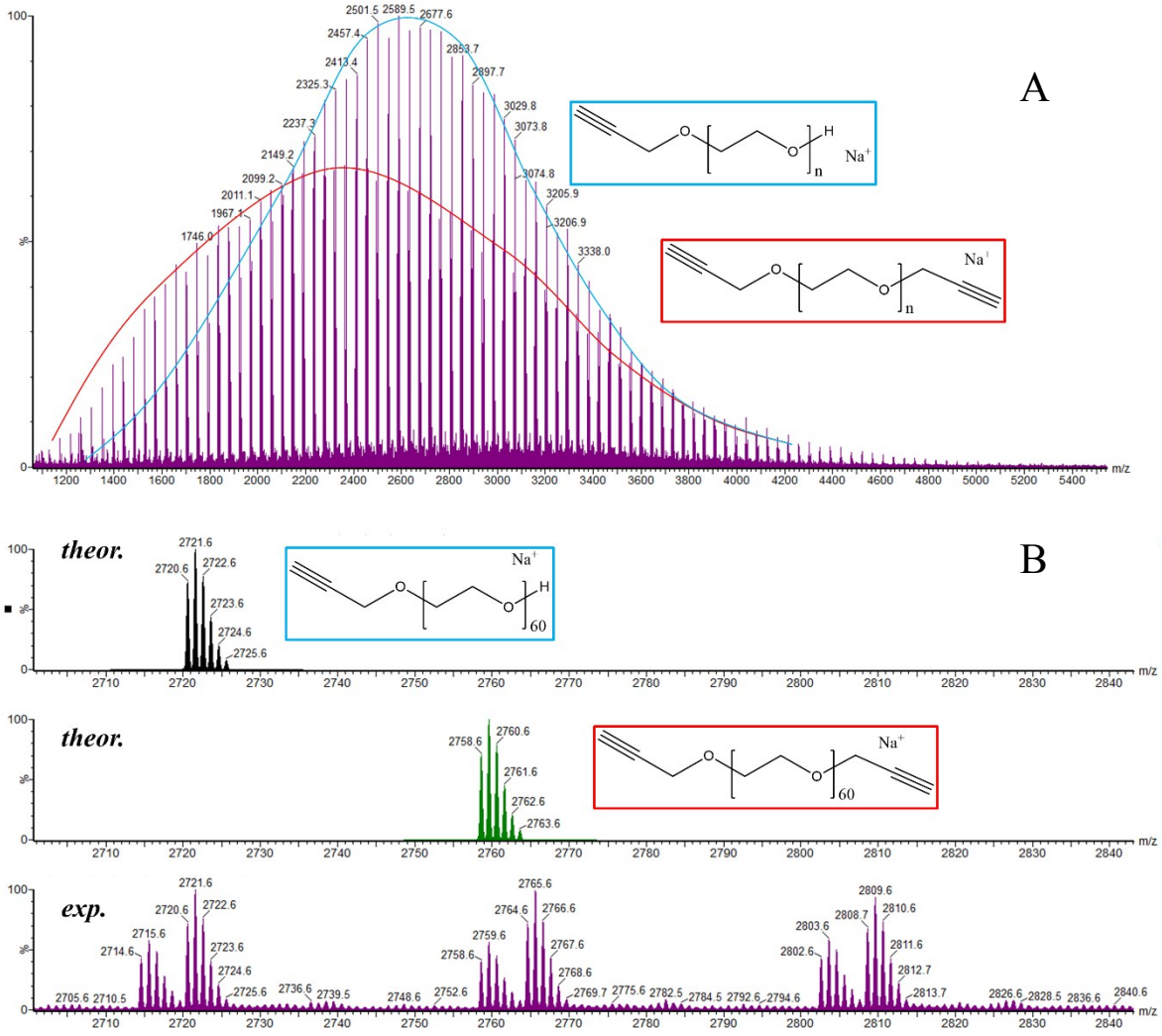


**Figure S7.** (A) full MALDI-ToF mass spectrum of the commercial alkyne-PEO-OH (cationization with NaI) and (B) magnification between *m/z* 2700 and *m/z* 2850 with comparison between the experimental mass spectrum (purple) and theoretical model for alkyne-PEO-OH (black) and alkyne-PEO-alkyne (green).

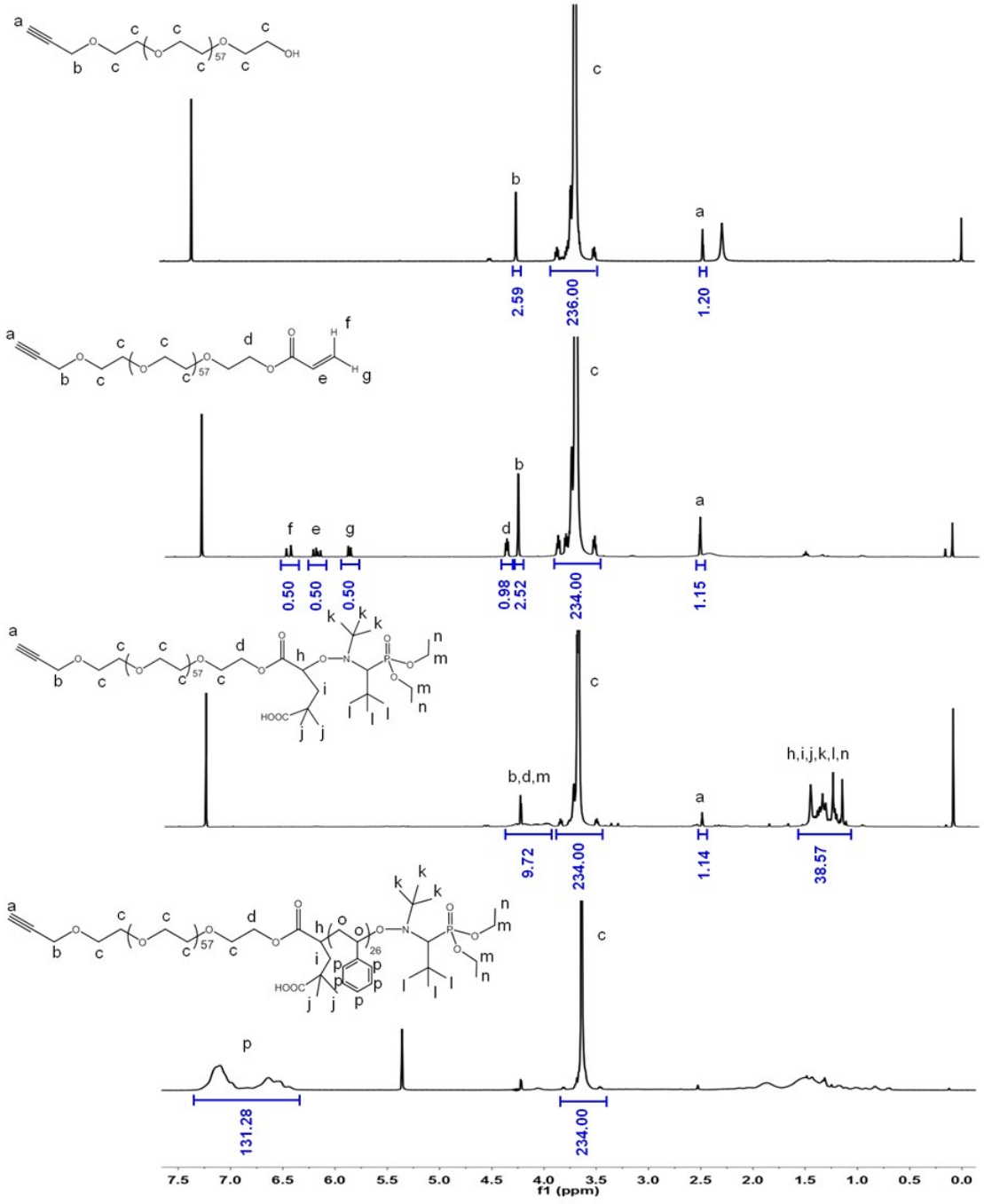


**Figure S8.** Overlay of $^{1}$H NMR spectra of alkyne-$PEO_{2.6K}$-OH, alkyne-$PEO_{2.6K}$-acrylate, alkyne-$PEO_{2.6K}$-SG1 and alkyne-$PEO_{2.6K}$-*b*-$PS_{2.7K}$-SG1 in $CD_2Cl_2$. Values of integrals are indicated in blue.

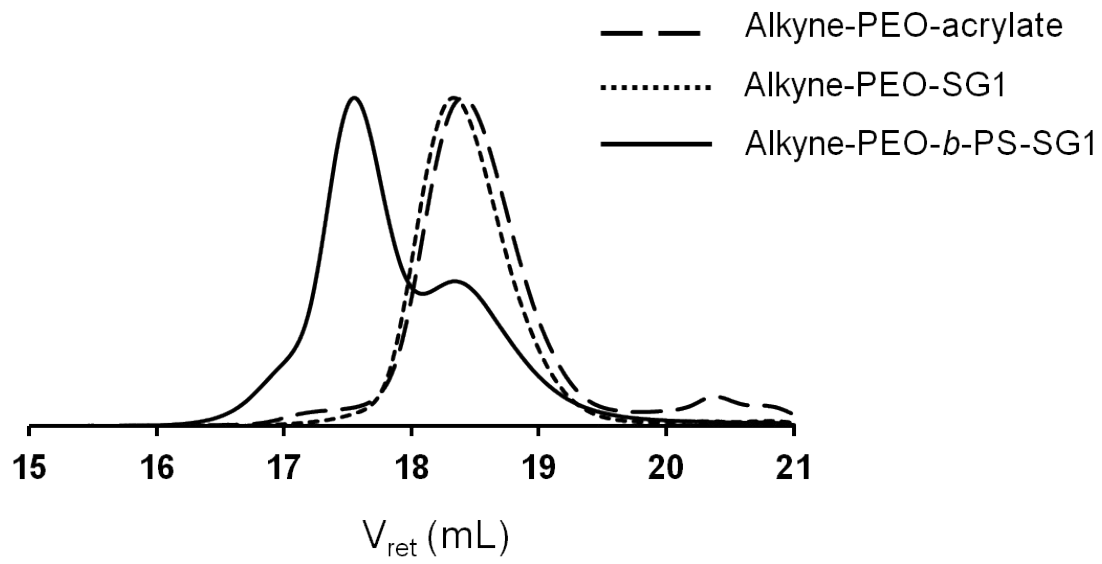


**Figure S9**. SEC chromatograms in THF of alkyne-$PEO_{2.6K}$-acrylate (dotted line), alkyne-$PEO_{2.6K}$-SG1 (small dotted line), alkyne-$PEO_{2.6k}$-b-$PS_{2.7k}$-SG1 (black full line).