## Supplementary Materials:

# Polymer Networks Synthesized from Poly(sorbitol adipate) and Functionalized Poly(ethylene glycol)

**Haroon Rashid[1,2], Yury Golitsyn[3], Muhammad Humayun Bilal[1], Karsten Mäder[2], Detlef Reichert[3], Jörg Kressler[1,*]**

[1] Department of Chemistry, Martin Luther University Halle-Wittenberg, D-06120 Halle (Saale), Germany; haroon.rashid@student.uni-halle.de (H.R.); muhammad.bilal@chemie.uni-halle.de (M.H.B.)

[2] Institute of Pharmacy, Martin Luther University Halle-Wittenberg, D-06120 Halle (Saale), Germany; karsten.maeder@pharmazie.uni-halle.de (K.M.)

[3] Department of Physics, Martin Luther University Halle-Wittenberg, D-06120 Halle (Saale), Germany; yury.golitsyn@physik.uni-halle.de (Y.G.); detlef.reichert@physik.uni-halle.de (D.R.)

* Correspondence: joerg.kressler@chemie.uni-halle.de (J.K.); Tel.: +49-345-552-5800

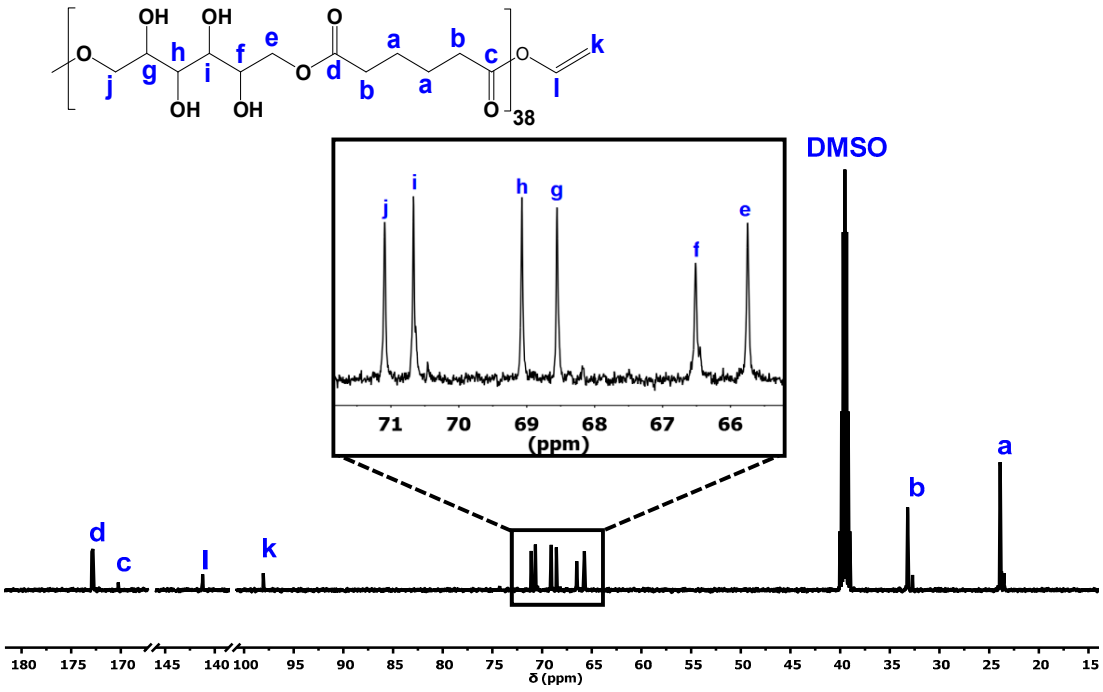



**Figure S1.** $^{13}C$ NMR spectrum of poly(sorbitol adipate) measured at 27°C using DMSO-$d_6$ as solvent.

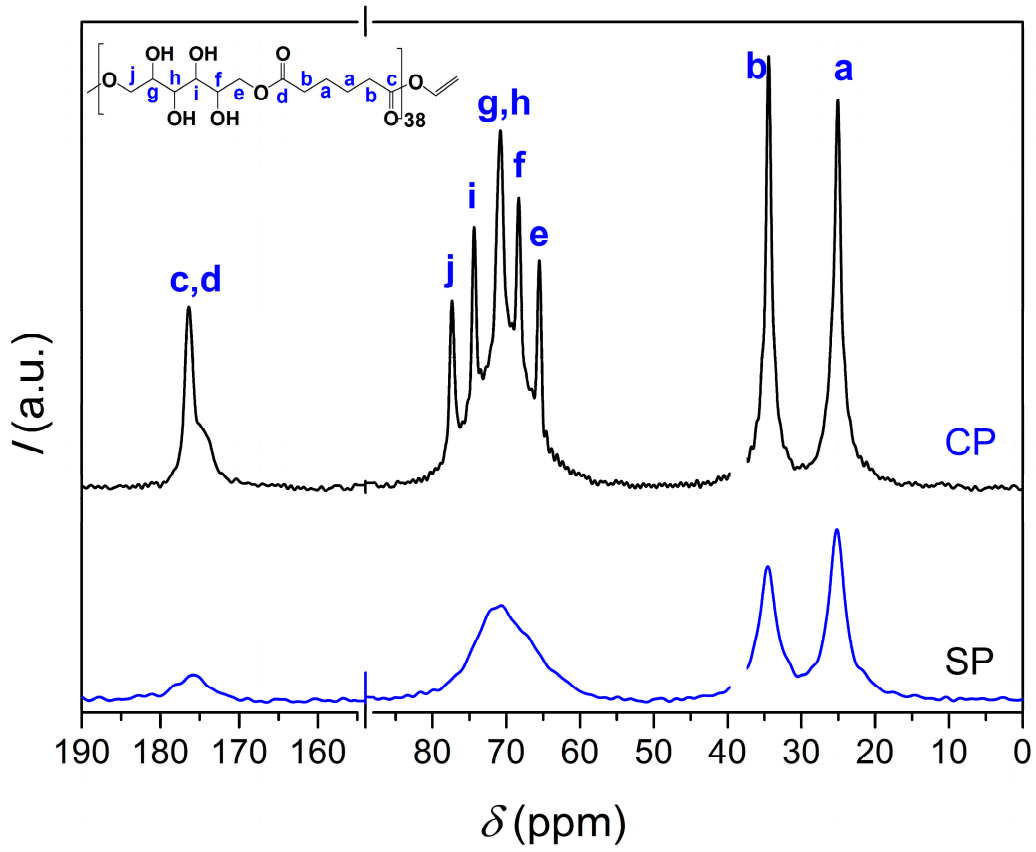
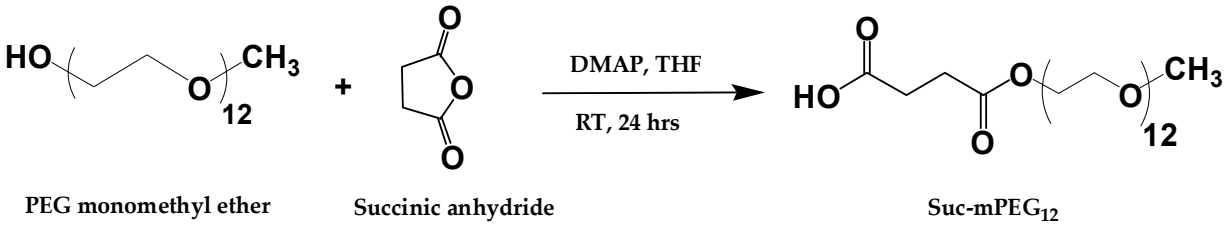



**Figure S2.** $^{13}C$ CP (top) and SP (bottom) MAS spectra of poly(sorbitol adipate). PSA is a highly viscous substance with low mobility. The SP experiment, therefore, does not provide spectral resolution. The CP experiment shows a well resolved spectrum.




**Scheme S1.** Synthesis scheme of mPEG12-Suc

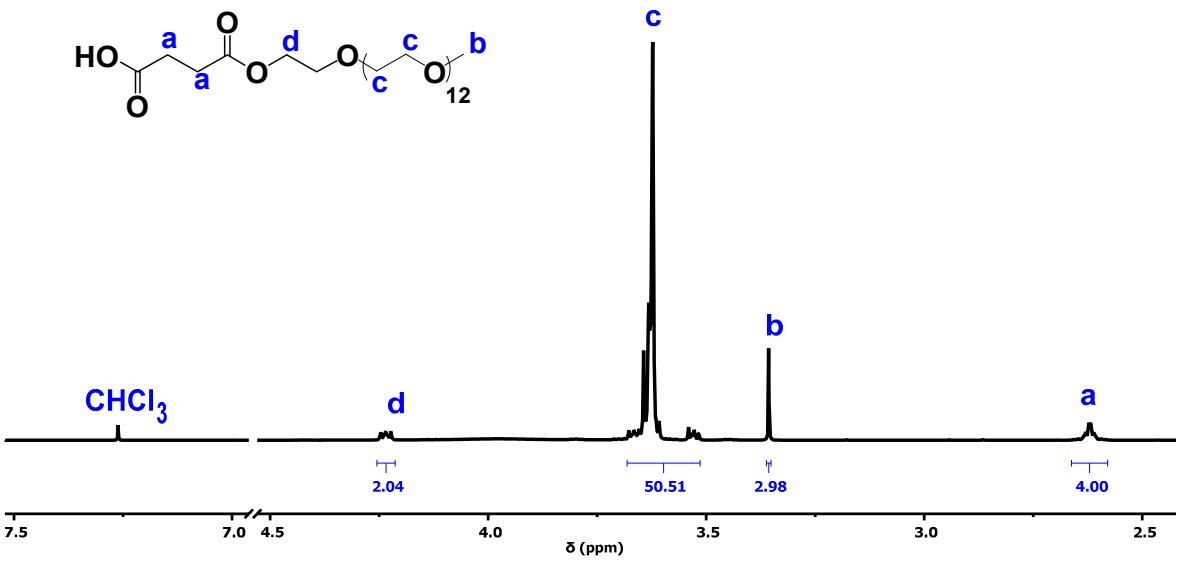



**Figure S3.** $^{1}$H NMR spectrum of mPEG12-Suc measured at 27°C using $CDCl_3$ as solvent.

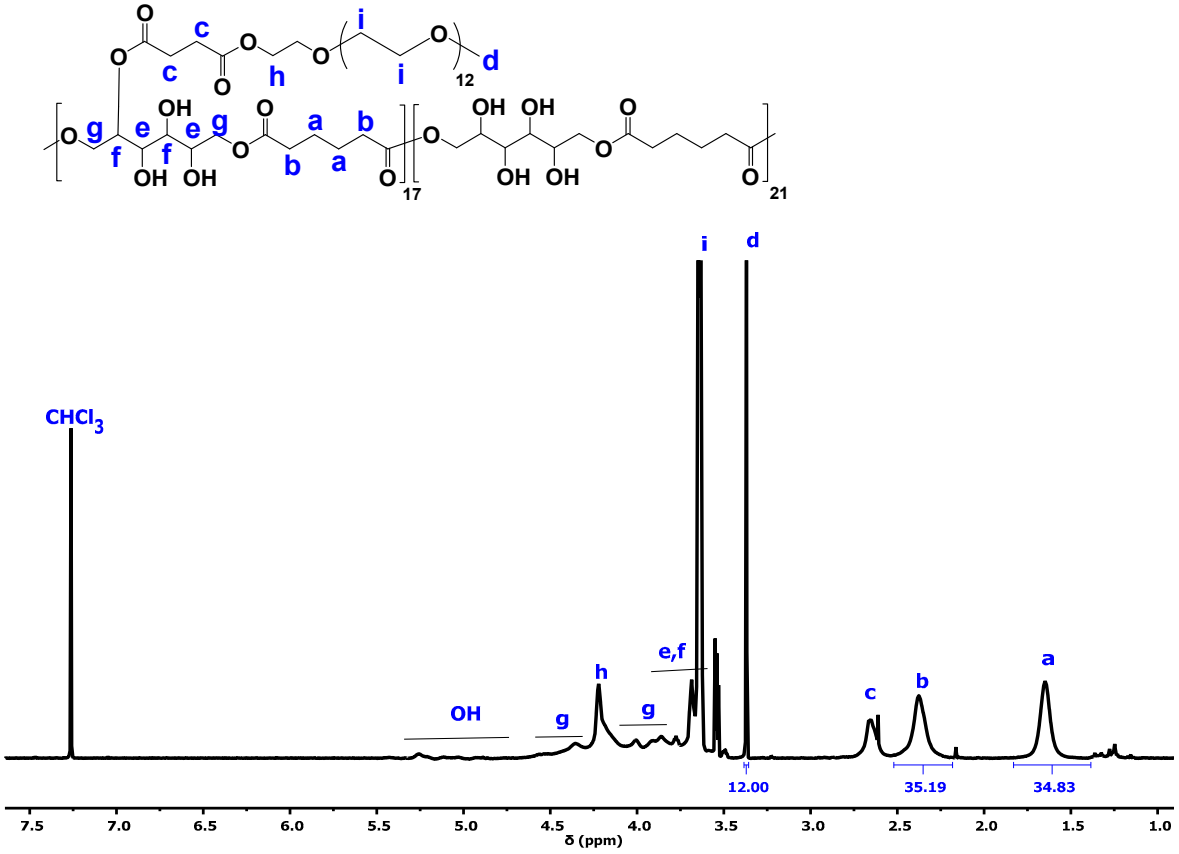



**Figure S4.** $^{1}$H NMR spectrum of PSA-*g*-mPEG$_{12}$ measured at 27°C using $CDCl_3$ as solvent.

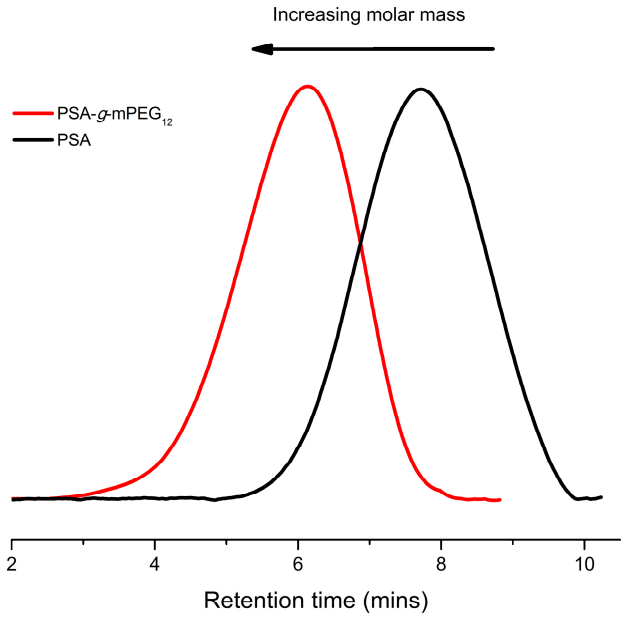



**Figure S5.** GPC traces of PSA before and after modification with mPEG$_{12}$-Suc.

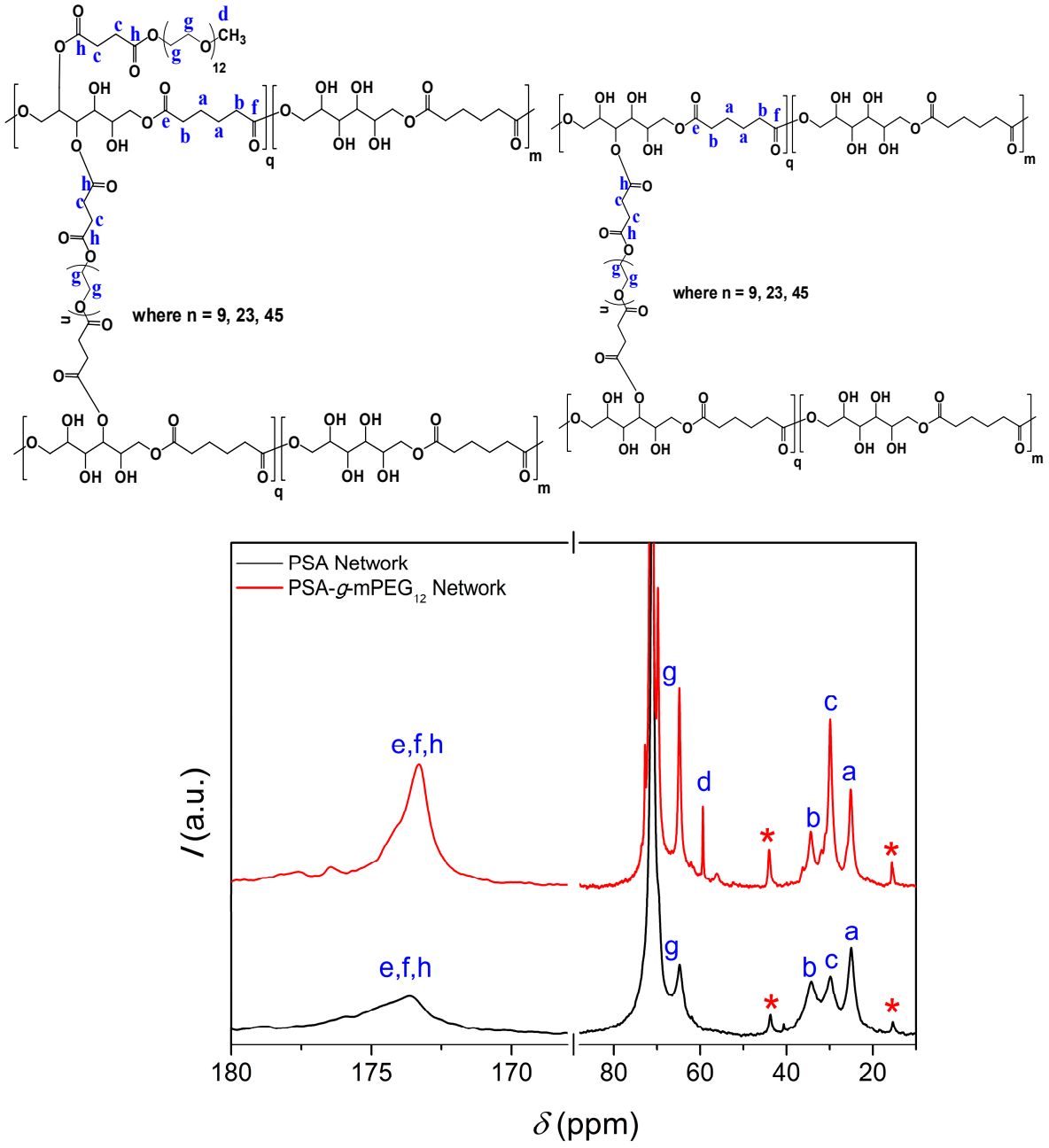



**Figure S6**. $^{13}C$ SP spectra of PSA and PSA-*g*-mPEG$_{12}$ networks with a Suc-PEG$_9$-Suc cross-linker. Both spectra show incorporation of identical cross-linker's succinyl peaks at 30 ppm while carbon peaks from ethylene glycol part are appearing around 70 ppm. Difference between both type of networks is that PSA-*g*-mPEG$_{12}$ network shows a carbon peak of methyl at 58 ppm from mPEG$_{12}$ which is absent in the PSA network. Furthermore, from PSA-*g*-mPEG$_{12}$ network spectra, carbon peaks at around 30 ppm and 173 ppm shows greater intensity due to the grafted chains of mPEG$_{12}$-Suc. There are two unknown extra carbon peaks appearing around 15 ppm and 45 ppm, marked by an asterisk. One possible reason can be peak splitting of PEG based cross-linker after formation of the network.

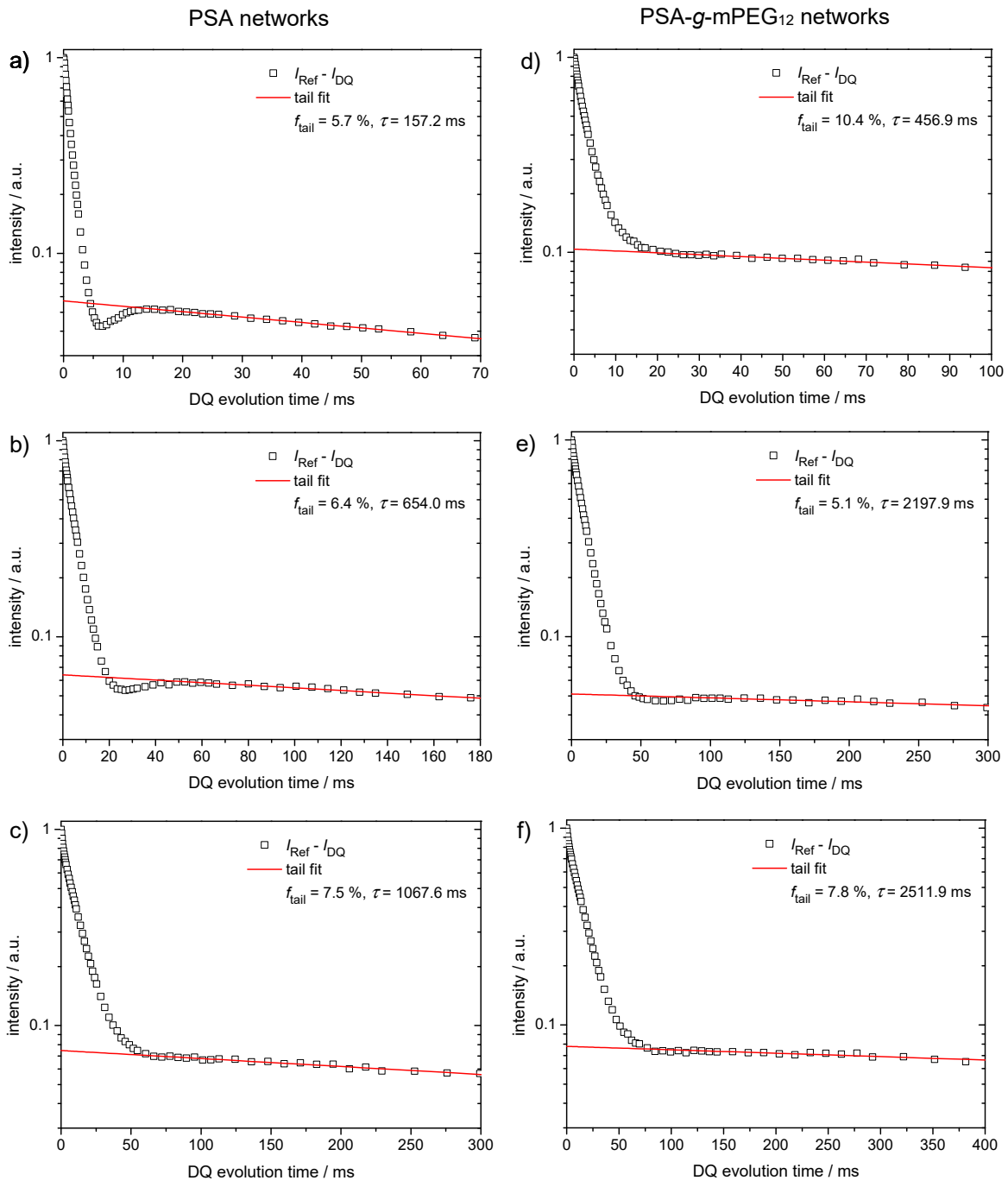



**Figure S7.** Determination of the tail fraction through $^{1}$H DQ NMR for (a-c) PSA networks cross-linked with the Suc-PEG$_n$-Suc (where n = 9, 23, 45) and (d-f) PSA-*g*-mPEG$_{12}$ networks cross-linked with the Suc-PEG$_n$-Suc (where n = 9, 23, 45).

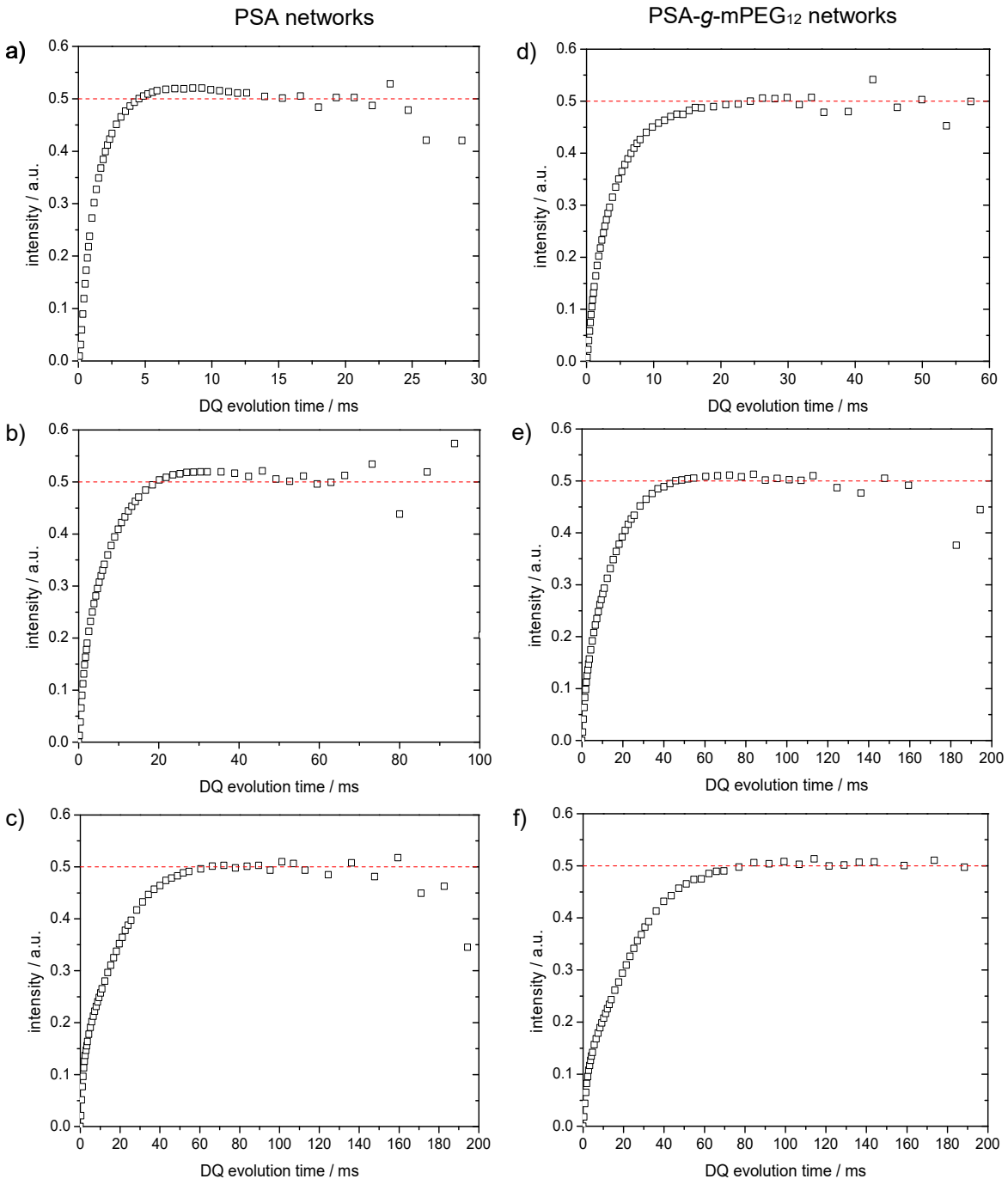



**Figure S8.** Normalized double quantum curves *nDQ* through $^{1}$H DQ NMR for (a-c) PSA networks cross-linked with the Suc-PEG$_n$-Suc (where n = 9, 23, 45) and (d-f) PSA-*g*-mPEG$_{12}$ networks cross-linked with the Suc-PEG$_n$-Suc (where n = 9, 23, 45).

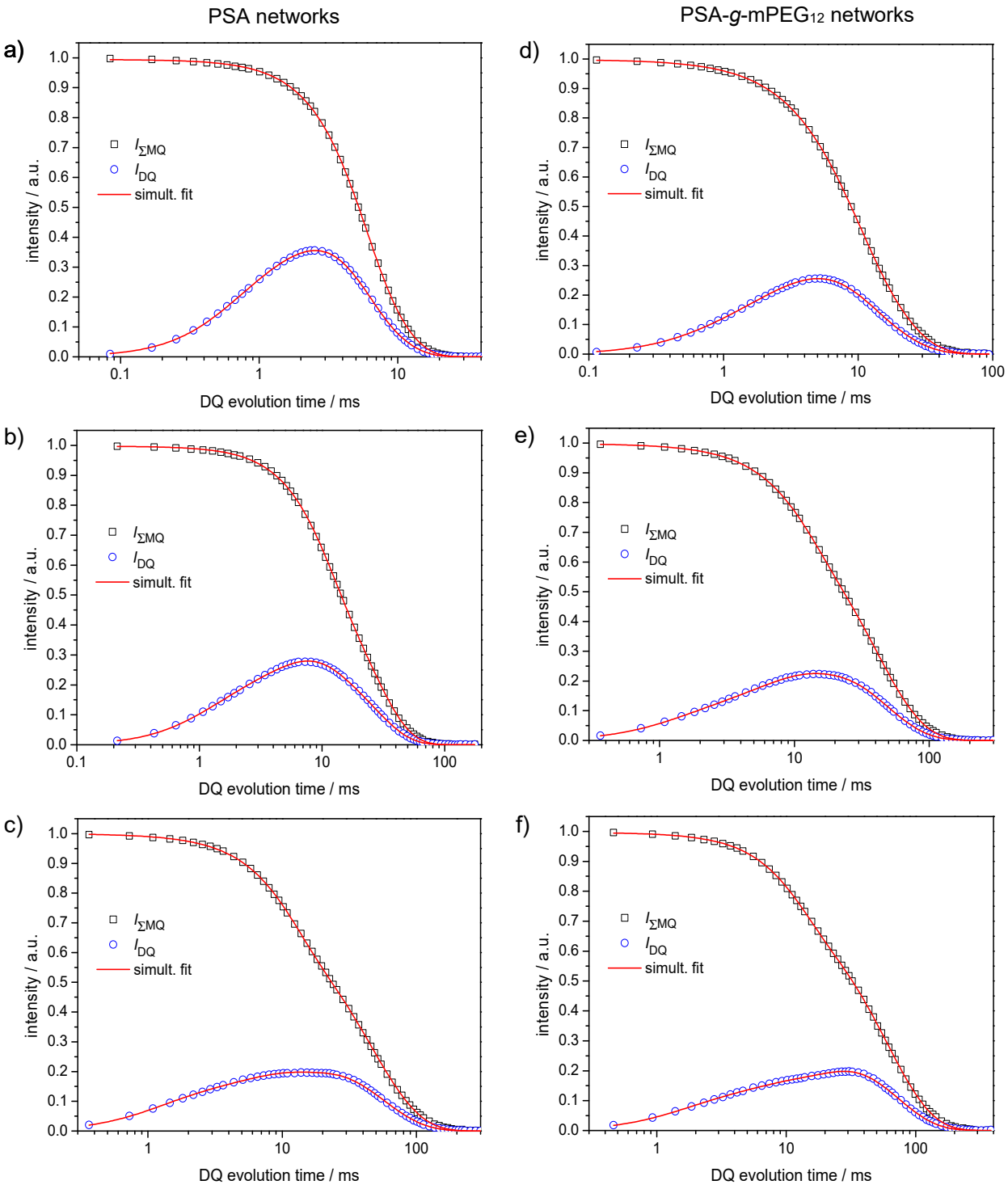



**Figure S9.** Simultaneous fitting to the sum intensity $I_{\Sigma}$ and DQ intensity $I_{DQ}$ through $^{1}$H DQ NMR after tail correction for (a-c) PSA networks cross-linked with the Suc-PEG$_n$-Suc (where n = 9, 23, 45) and (d-f) PSA-*g*-mPEG$_{12}$ networks cross-linked with the Suc-PEG$_n$-Suc (where n = 9, 23, 45).

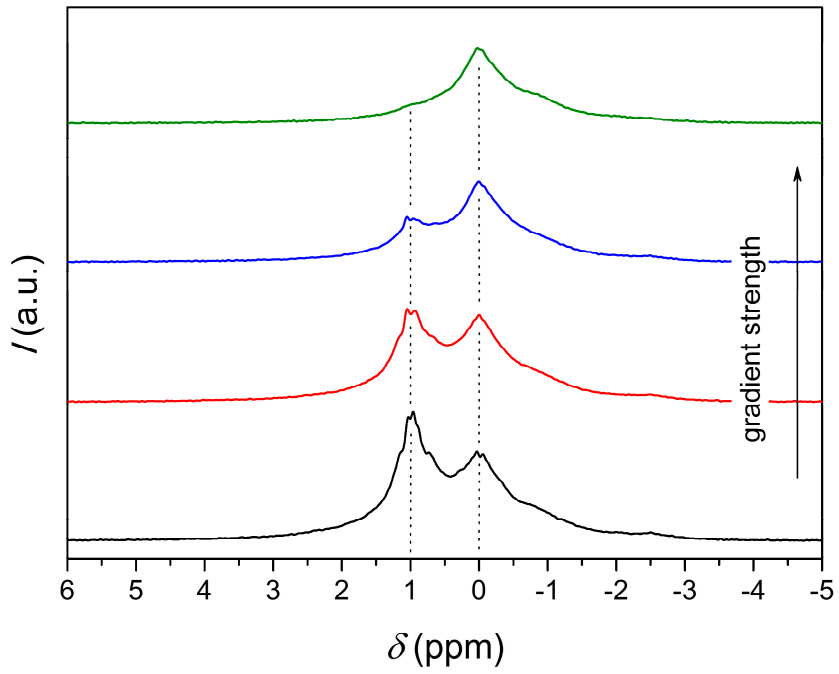



**Figure S10.** $^{1}$H NMR spectra measured with PFG NMR spectroscopy of PSA-*g*-mPEG$_{12}$ network (Suc-PEG$_{9}$-Suc) with $Q$ = 6.2 and $D_2O$ as solvent by varying field gradient strength at $T$ = 30°C. The spectrum was referenced to the center of the right peak.

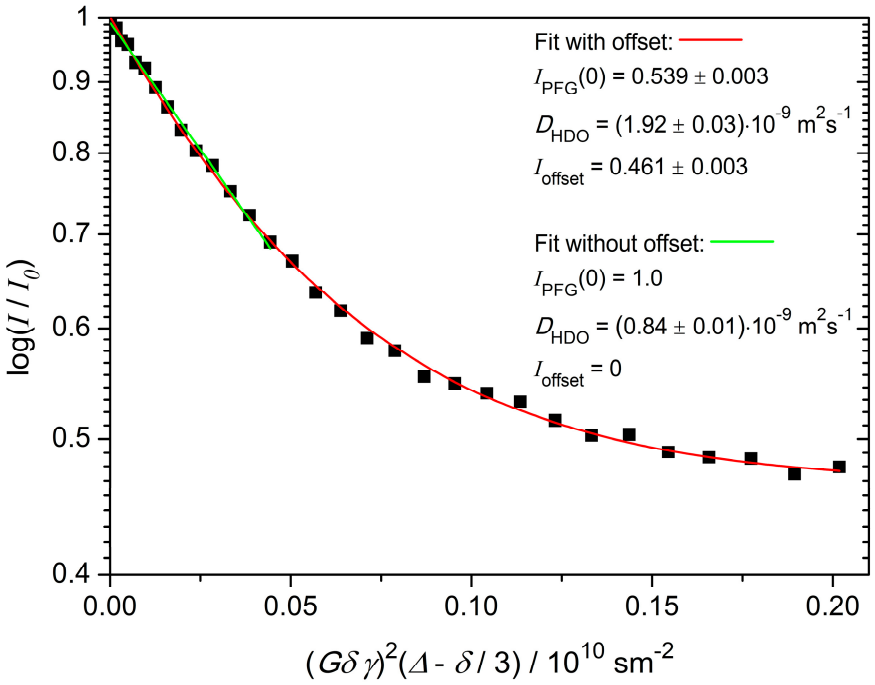
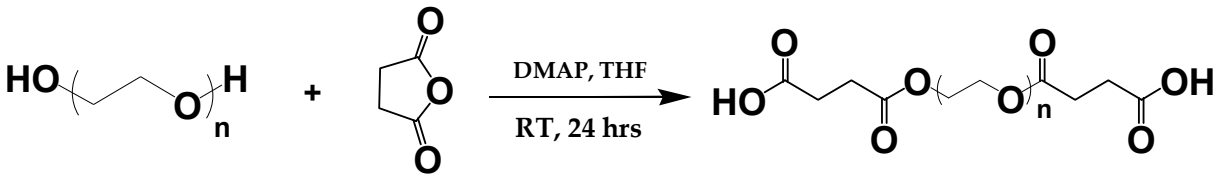



**Figure S11.** Fit example for the network sample cross-linked with Suc-PEG$_{45}$-Suc according to eq.2. Different fit strategies for estimation of the diffusion coefficient were tested. The red line: fit with constant offset of 46 % provides $D_{HDO}$ = (1.92 ± 0.03)·10$^{-9}$ m$^2$·s$^{-1}$. The green line: fit of the initial decay (linear part of the decay) without offset, which provides $D_{HDO}$ = (0.84 ± 0.01)·10$^{-9}$ m$^2$·s$^{-1}$. This value is about 50% lower and corresponds to the arithmetic average of the first value and the offset ($D_{offset}$ = 0).




**Poly(ethylene glycol) where n = 9, 23, 45** | **Succinic anhydride** | **Suc-PEG$_n$-Suc where n = 9, 23, 45**

**Scheme S2.** Synthesis scheme of Suc-PEG$_n$-Suc.

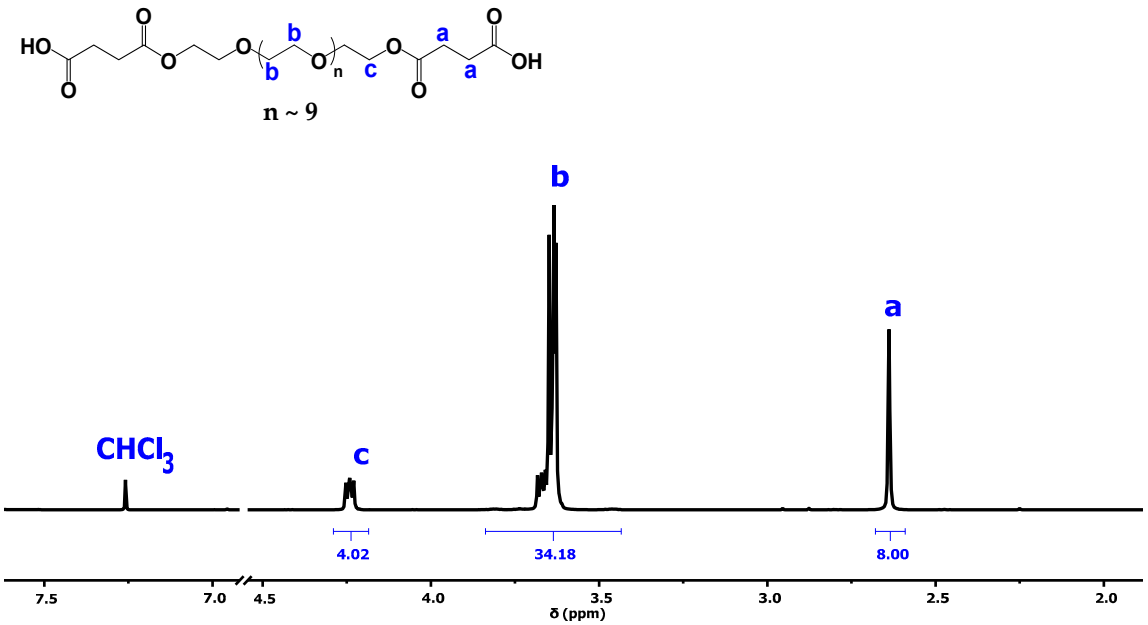



**Figure S12.** $^1$H NMR spectrum of Suc-PEG$_9$-Suc measured at 27°C using $CDCl_3$ as solvent.

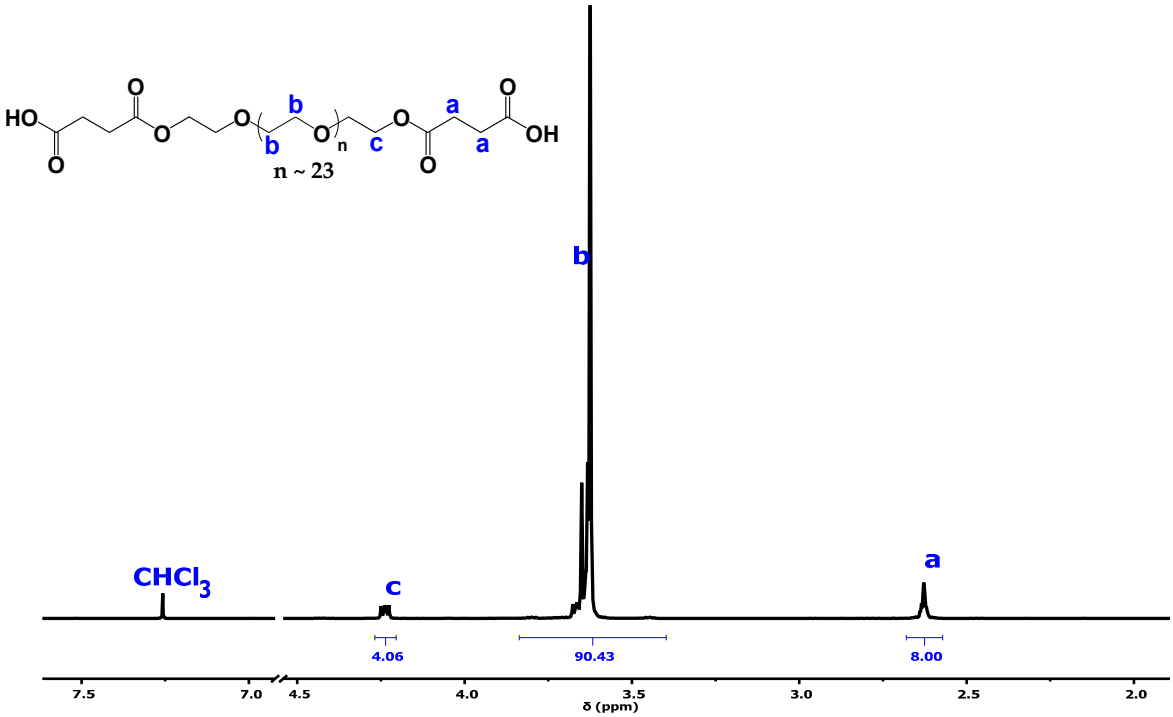



**Figure S13.** $^{1}$H NMR spectrum of Suc-PEG$_{23}$-Suc measured at 27°C using $CDCl_3$ as solvent.

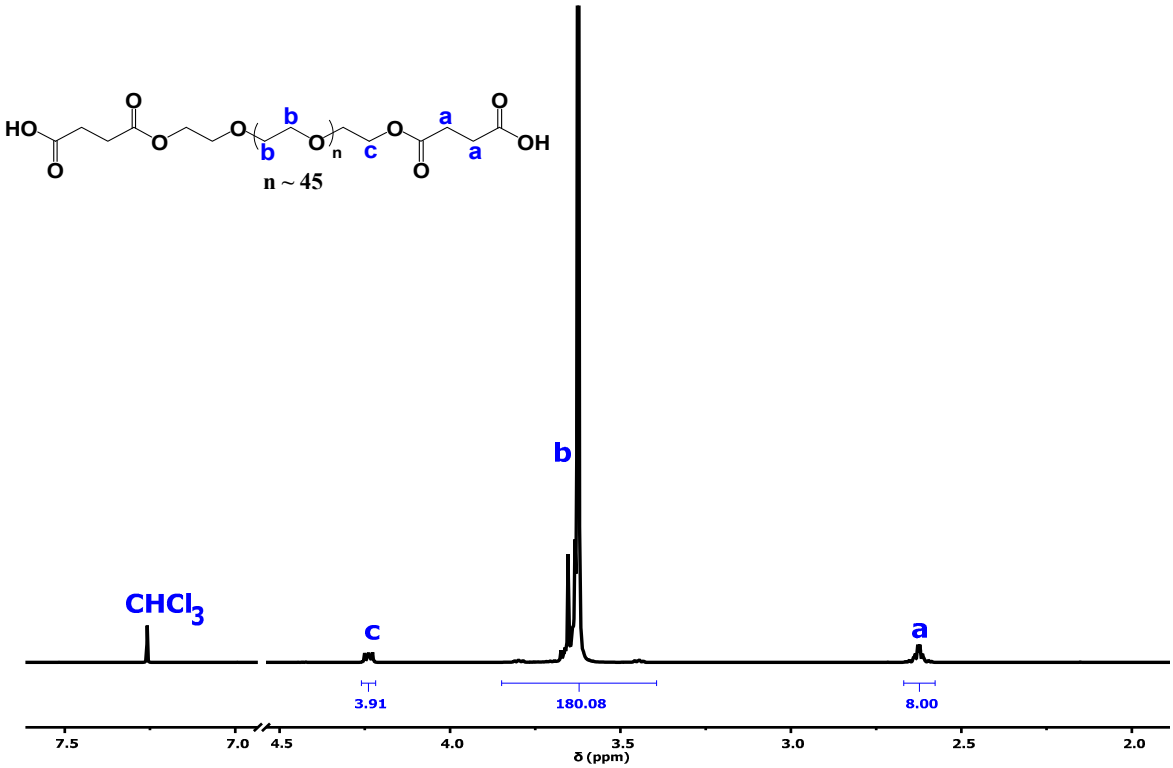



**Figure S14.** $^{1}$H NMR spectrum of Suc-PEG$_{45}$-Suc measured at 27°C using $CDCl_3$ as solvent.