Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPORTING INFORMATION

Amphiphilic and double hydrophilic block copolymers containing a polydehydroalanine block

Mark Billing,[1,2] Grit Festag,[1] Peter Bellstedt,[1] Felix H. Schacher[1,2]*

Laboratory of Organic Chemistry and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Humboldtstraße 10, D-07743 Jena, Germany

Email: *felix.schacher@uni-jena.de*

Jena Center for Soft Matter (JCSM), Friedrich-Schiller-University Jena, Philosophenweg 7, D-07743 Jena, Germany

Cleavage of the boc-group at RT / Cleavage of the methyl ester at 100 °C:

Starting from P*n*BA$_{25}$-*b*-P*t*BAMA$_{50}$, cleavage of the boc protective group was carried out by adding TFA (10 eq. per monomer unit) in DCM at RT for 44 h. After purification (see deprotection at RT for 44 h), 20% remaining methyl ester was observed (**Figure S1**). The cleavage of the methyl ester at 100 °C for 22 h with 21 eq. LiOH·H$_2$O (c = 60 g L^{-1}, 1,4-dioxane/water 2/5 v/v) led to complete cleavage of the methyl ester and approximately 90 % of the butyl ester in P*n*BA, as observed by the remaining small signal at 0.95 ppm. Besides, the intensity of the *boc* protective group at 1.4 ppm strongly decreased as well, hinting toward a cleavage of 85%.

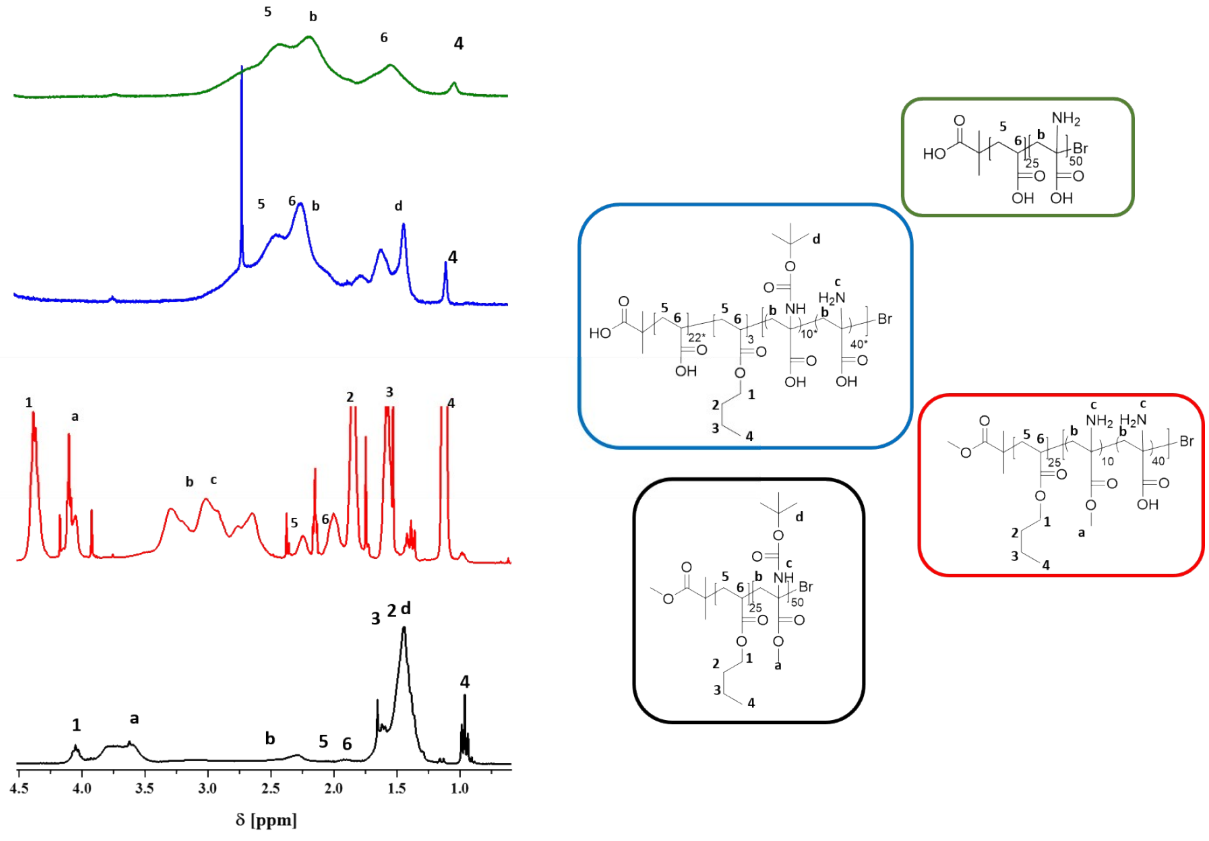

Figure S1: ^{1}H-NMR of P*n*BA$_{25}$-*b*-P*t*BAMA$_{50}$ (black line, CDCl$_3$), P*n*BA$_{25}$-*b*-(PAMA$_{10}$-*co*-PDha$_{35}$) (red line, *d*-TFA), PAA$_{25}$-*b*-(P*t*BAA$_{20}$-*co*-PDha$_{30}$) (blue line, D$_2$O, subscripts are marked with * to indicate estimated degrees of polymerizations due to an overlay of the signals), PAA$_{25}$-*b*-PDha$_{50}$ (green line, D$_2$O), numbers indicate signals of P*n*BA/PAA, letters indicate signals of P*t*BAMA, PAMA, P*t*BAA and PDha.

^{13}C-NMR spectroscopy results confirmed the results from ^{1}H-NMR data (**Figure S2**). After cleavage of the boc group, signals of the methyl ester can be still detected (59 ppm). Due to

aggregation of PAA_{25}-*b*-P*t*BAA_{50} in diverse NMR solvents at higher concentrations, ^{13}C-NMR was conducted in the solid state. In this case, both the signals of the carbonyl groups and the methyl groups of the boc group can be detected. Signals for the methyl ester of P*t*BAMA as well as for the butyl ester of P*n*BA are missing.

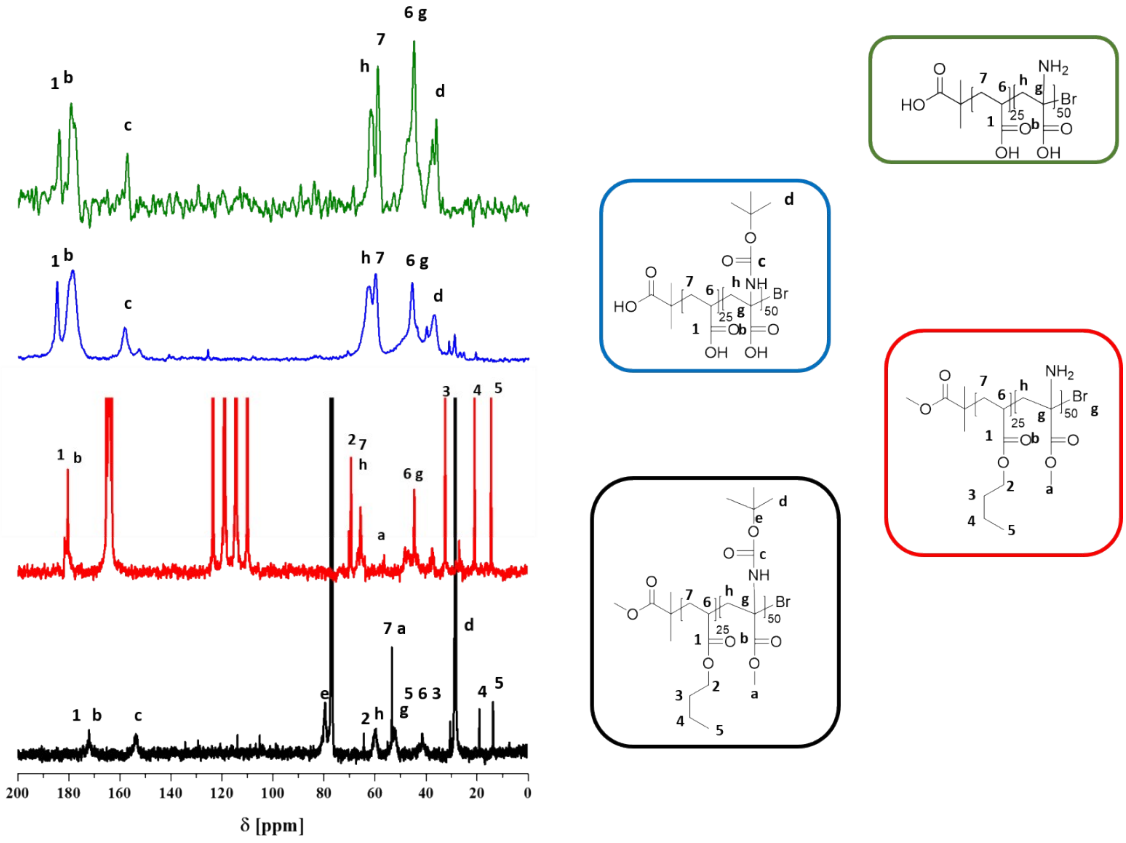

Figure S2: ^{13}C-NMR of P*n*BA_{25}-*b*-P*t*$BAMA_{50}$ (black line, $CDCl_3$), P*n*BA_{25}-*b*-($PAMA_{10}$-*co*-$PDha_{35}$) (red line, *d*-TFA), PAA_{25}-*b*-(P*t*BAA_{20}-*co*-$PDha_{30}$) (blue line, D_2O, subscripts are marked with * to indicate estimated degrees of polymerizations due to an overlay of the signals), PAA_{25}-*b*-$PDha_{50}$ (green line, D_2O), numbers indicate signals of P*n*BA/PAA, letters indicate signals of P*t*BAMA, PAMA, P*t*BAA and PDha.

Cleavage of the boc-group at 50 °C:

If carried out at 50 °C, the cleavage of the *boc* group shows a slightly higher selectivity, leading to P*n*BA$_{25}$-*b*-(PAMA$_{15}$-*co*-PDha$_{35}$) as observed by ^{1}H-NMR in deuterated TFA (dissolving in DCM led to a turbid suspension). In DCM, only signals for the P*n*BA block (4.2, 2.3, 1.98, 1.6, 1.4 and 0.98 ppm) were detected (**Figure S3**) and confirmed by ^{13} C-NMR (174, 64, 41, 35, 19 and 13 ppm, **Figure S4**). Upon dissolving the material in deuterated TFA, additional signals of the PAMA block (4.0 and 3 ppm) were detected.

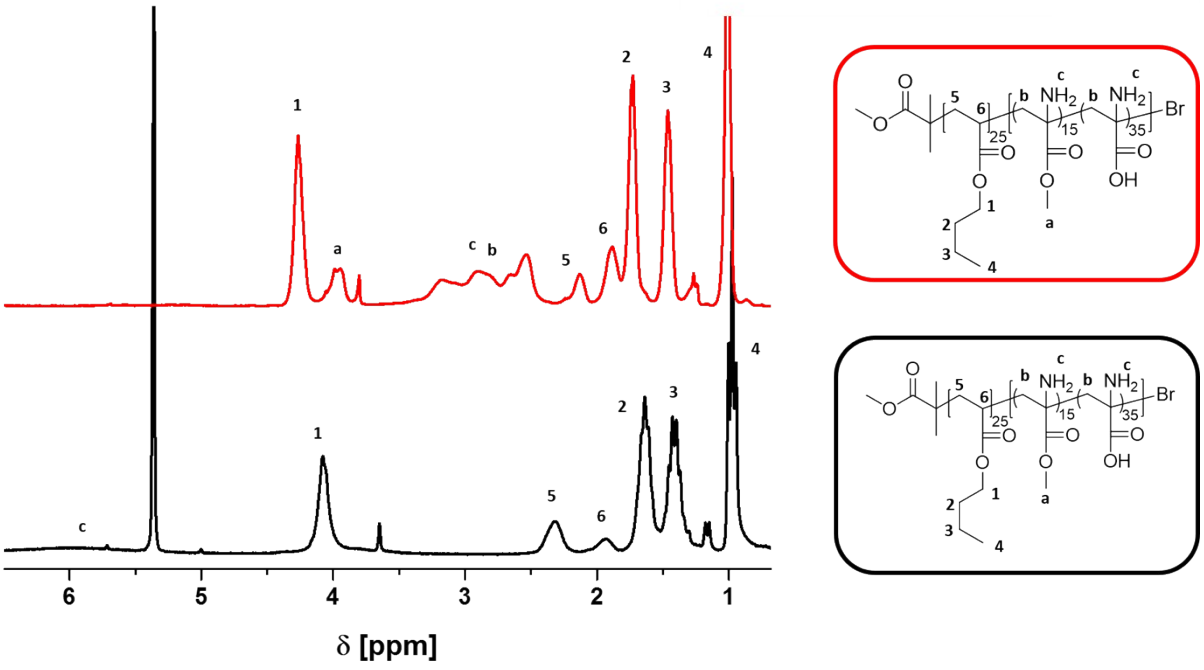

Figure S3: ^{1}H-NMR of P*n*BA$_{25}$-*b*-(PAMA$_{15}$-*co*-PDha$_{35}$) in TFA (red line) and dichloromethane (black line).

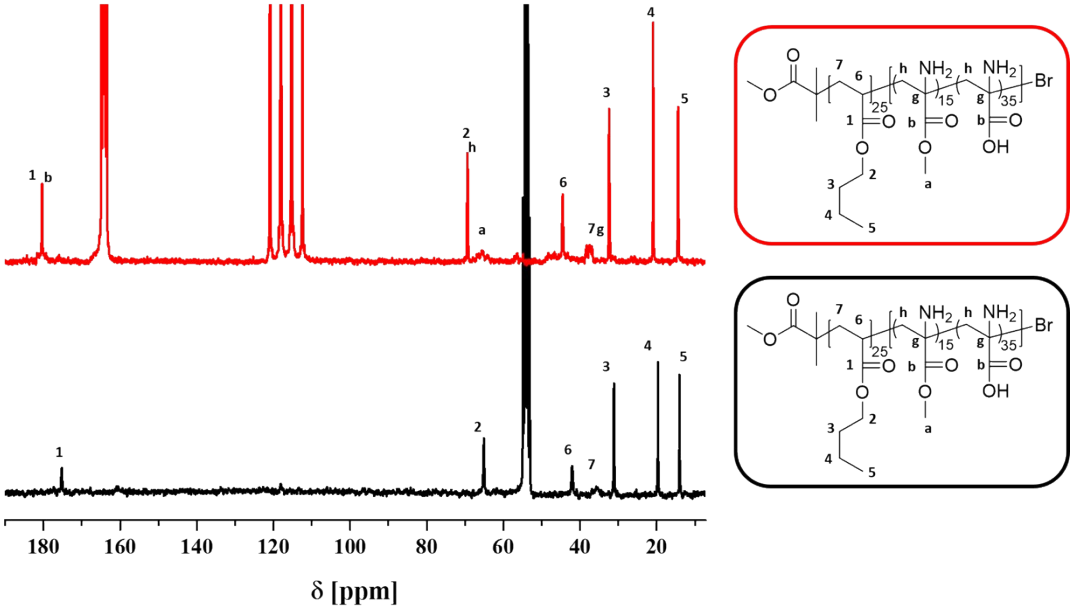

Figure S4: ^{13}C-NMR of P*n*BA$_{25}$-*b*-(PAMA$_{15}$-*co*-PDha$_{35}$)A in TFA (red line) and dichloromethane (black line).

Cleavage of the methyl ester at 80 °C:

Also, a slightly higher selectivity was found if the cleavage of the methyl ester was carried out at 80 °C and with a lower amount of LiOH (21 eq) for 3 h. Also here, the obtained NMR spectra differed if being taken in deuterated TFA or D_2O (**Figure S5**). Clearly, in D_2O the boc group (1.4 ppm) can be detected, but also additional signals for P*n*BA at 4 ppm and 0.98 ppm, hinting to an incomplete deprotection. These results were confirmed in ^{13}C-NMR showing the methyl carbons of the boc group at 27 ppm and at 65, 30, 18 and 13 ppm carbon atoms of P*n*BA (**Figure S6**).

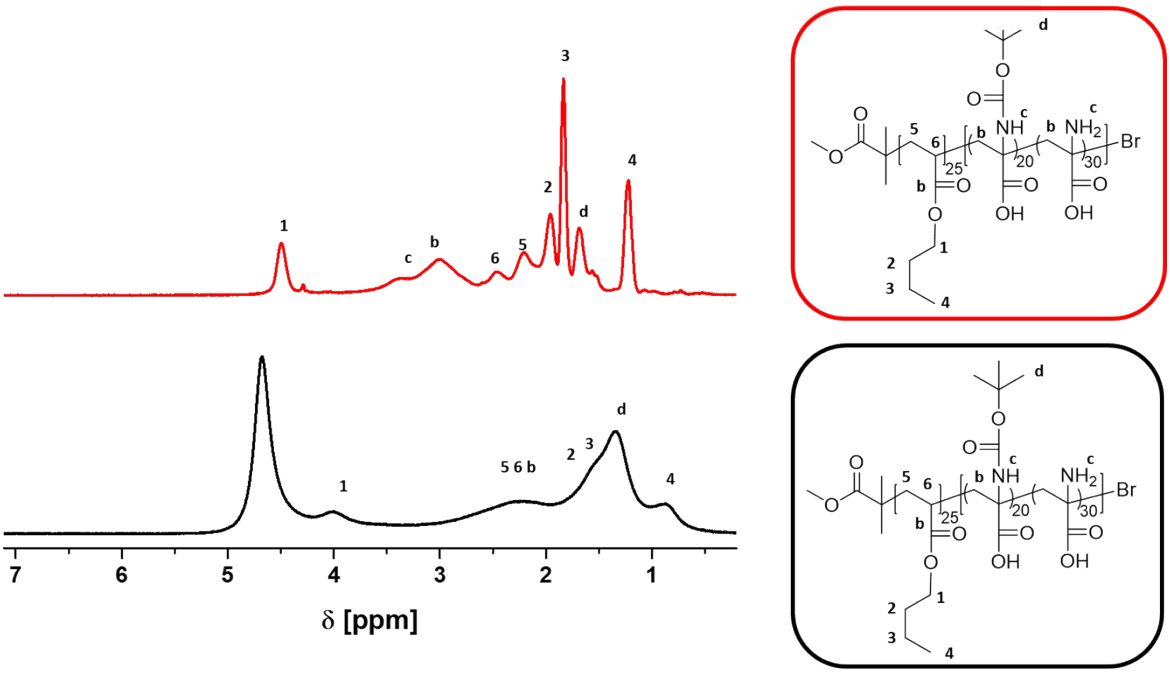

Figure S5: ^{1}H-NMR of P*n*BA$_{25}$-*b*-(P*t*BAA$_{20}$-*co*-PDha$_{30}$) in TFA (red line) and D_2O (black line).

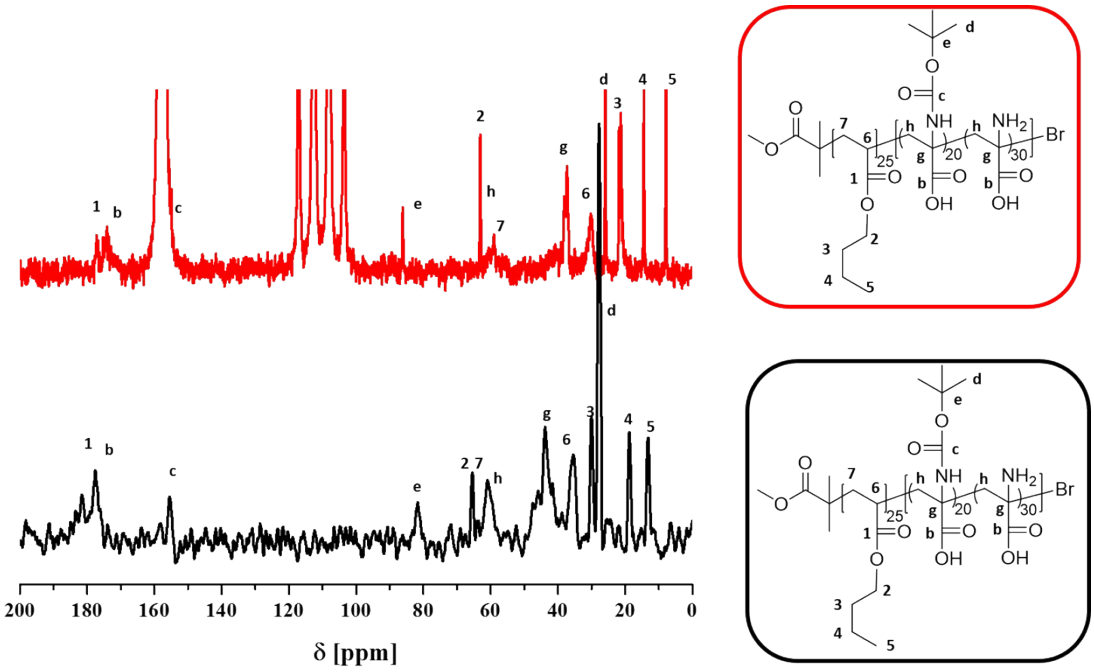

Figure S6: ^{13}C-NMR of P*n*BA$_{25}$-*b*-(P*t*BAA$_{20}$-*co*-PDha$_{30}$) in TFA (red line) and D$_2$O (black line).

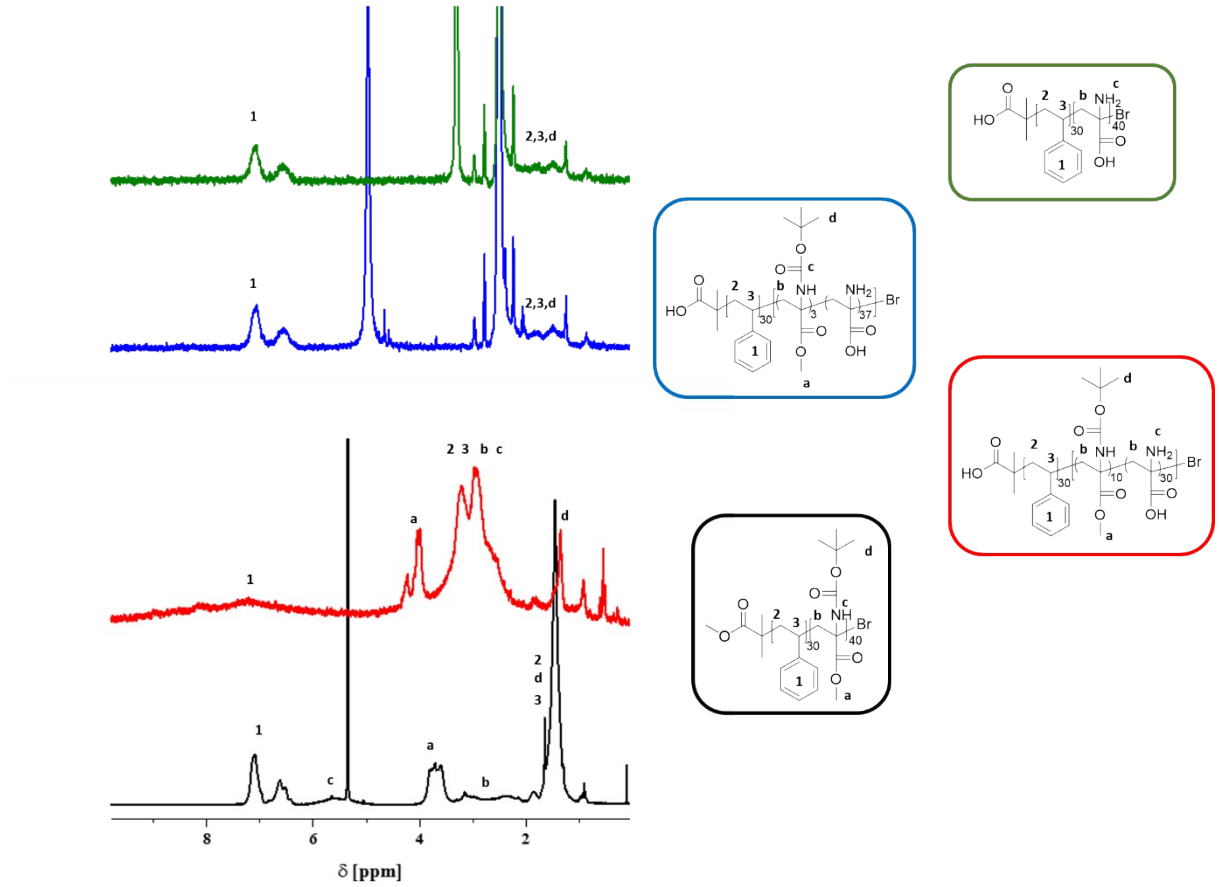

Figure S7: ^{1}H-NMR of PS_{30}-*b*-P*t*$BAMA_{40}$ (black line CD_2Cl_2), PS_{30}-*b*-($PAMA_{10}$-*co*-$PDha_{30}$) (red line *d*-TFA), PS_{30}-*b*-(P*t*$BAMA_3$-*co*-$PDha_{37}$) (blue line DMSO), PS_{30}-*b*-$PDha_{40}$ (green line DMSO).

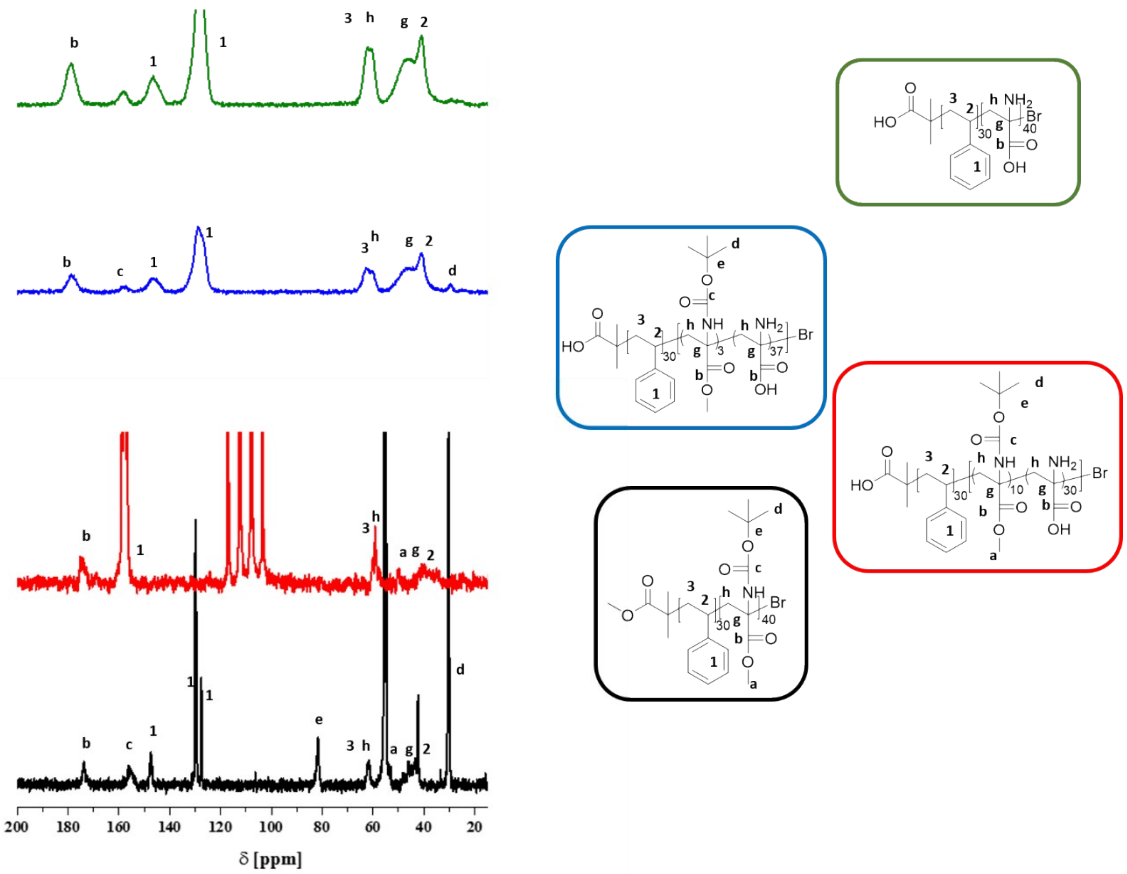

Figure S8: ^{13}C-NMR of PS_{30}-*b*-P*t*BAMA$_{40}$ (black line CD_2Cl_2), PS_{30}-*b*-(PAMA$_{10}$-*co*-PDha$_{30}$) (red line *d*-TFA), PS_{30}-*b*-(P*t*BAMA$_3$-*co*-PDha$_{37}$) (blue line solid state), PS_{30}-*b*-PDha$_{40}$ (green line solid state) with < 10% remaining *boc*-group (159 ppm).