Supporting Information of

Hybrid polymers bearing oligo-L-lysine(carboxybenzyl)s: investigations of secondary structure formation in 2,2,2-trifluoroethanol

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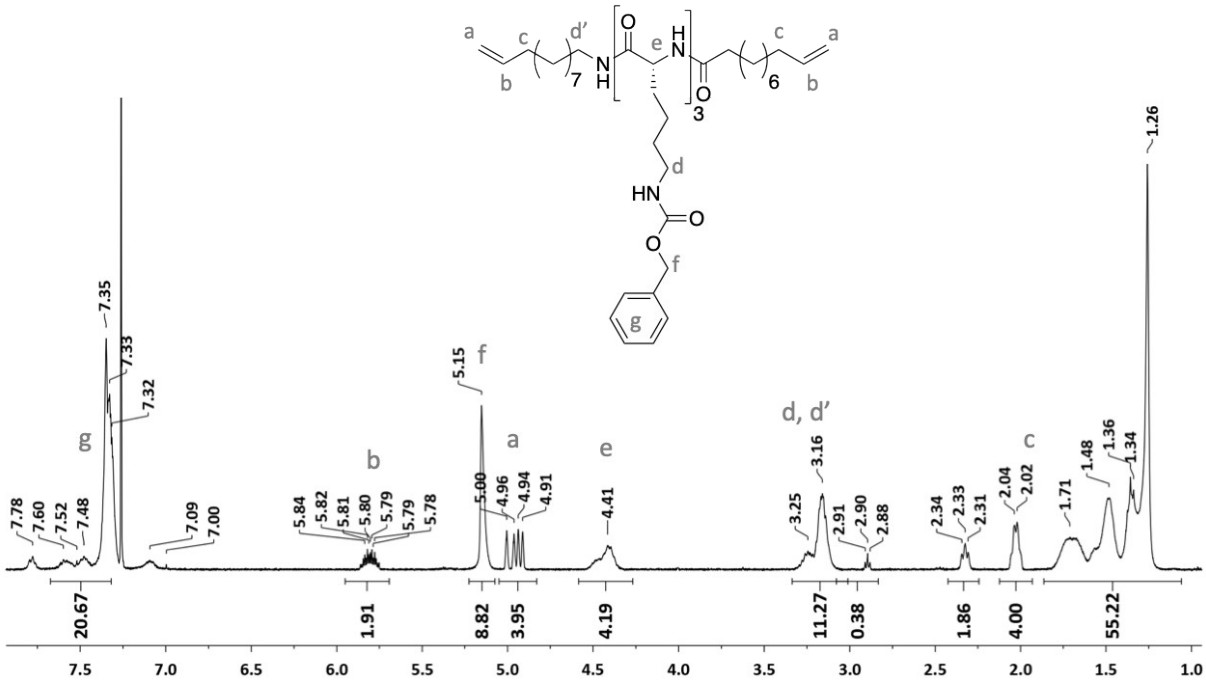

Figure 1S. ^{1}H-NMR of **Lys$_{n=3}$** (in $CDCl_3$ and 15 vol.% TFA).

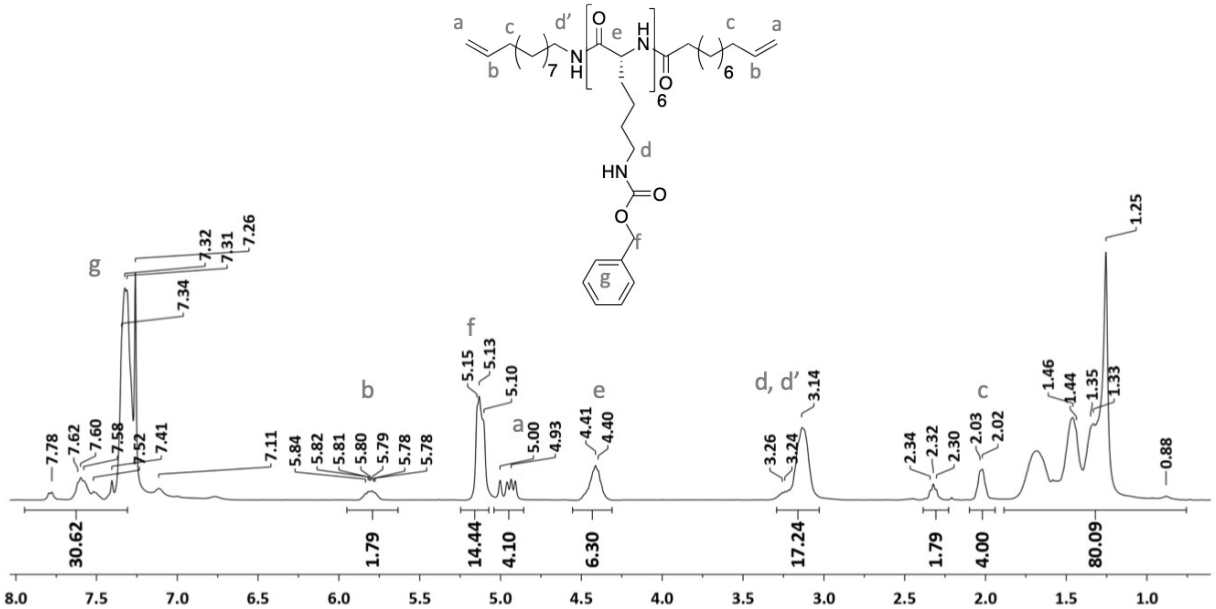

Figure 2S. ^{1}H-NMR of **Lys$_{n=6}$** (in $CDCl_3$ and 15 vol.% TFA).

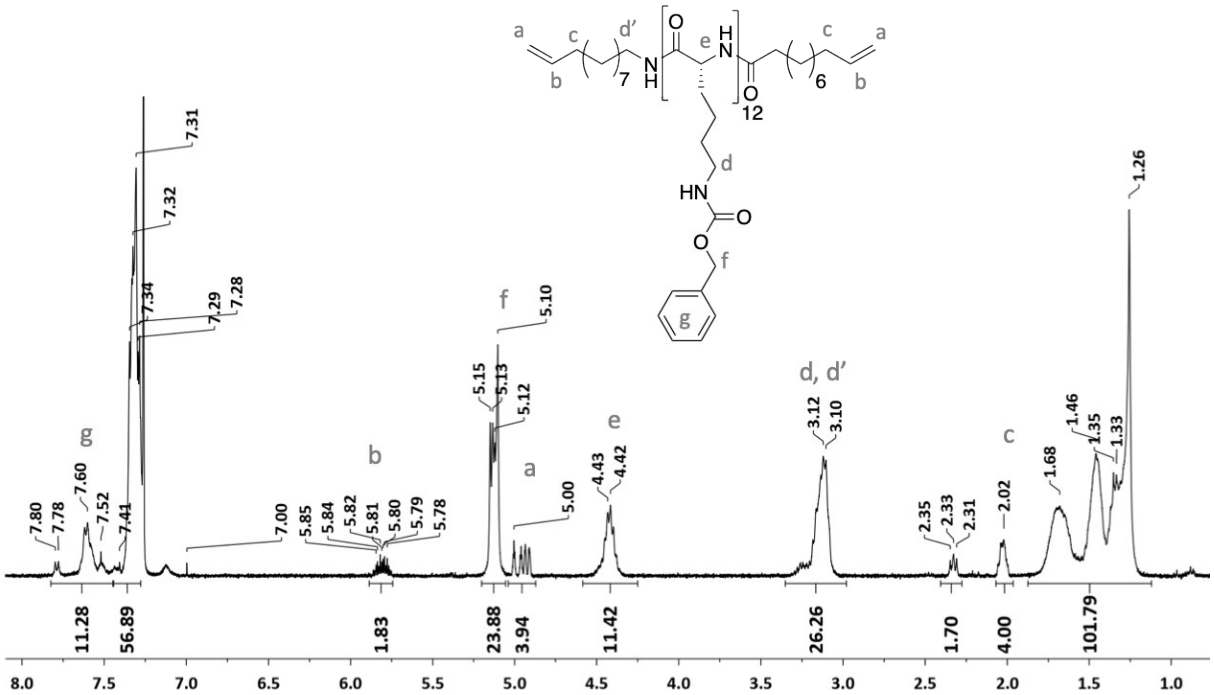

Figure 3S. ^{1}H-NMR of **Lys$_{n=12}$** (in $CDCl_3$ and 15 vol.% TFA).

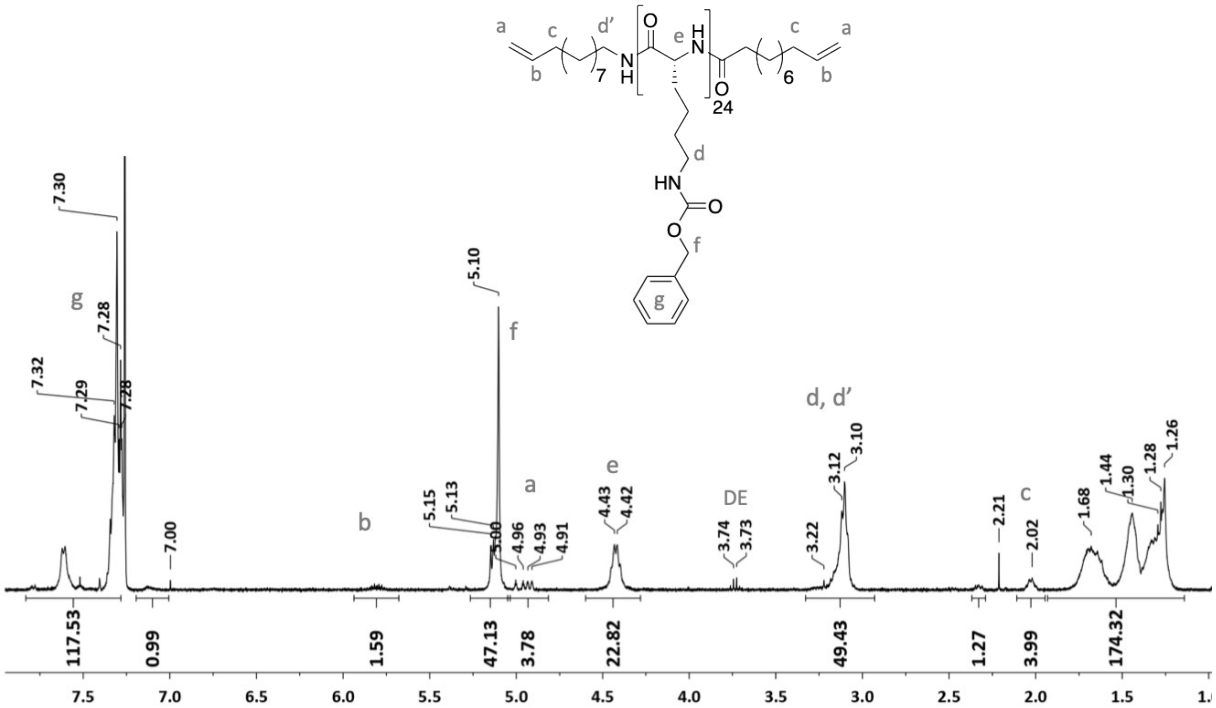

Figure 4S. ^{1}H-NMR of **Lys$_{n=24}$** (in $CDCl_3$ and 15 vol.% TFA).

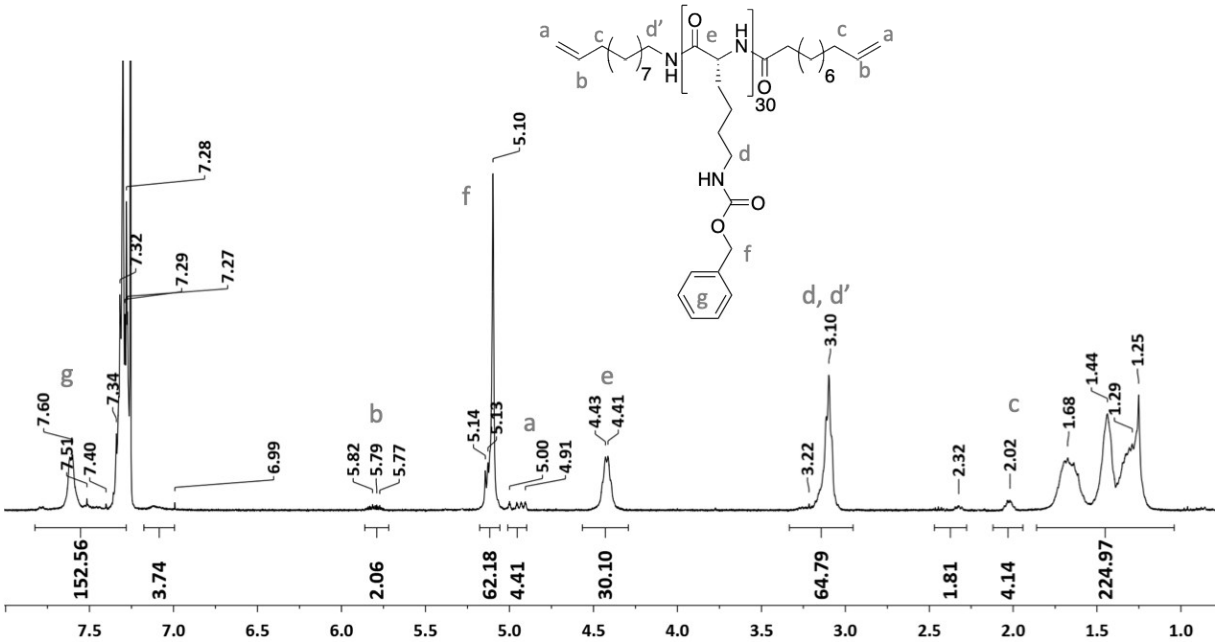

Figure 5S. ^{1}H-NMR of **Lys$_{n=30}$** (in $CDCl_3$ and 15 vol.% TFA).

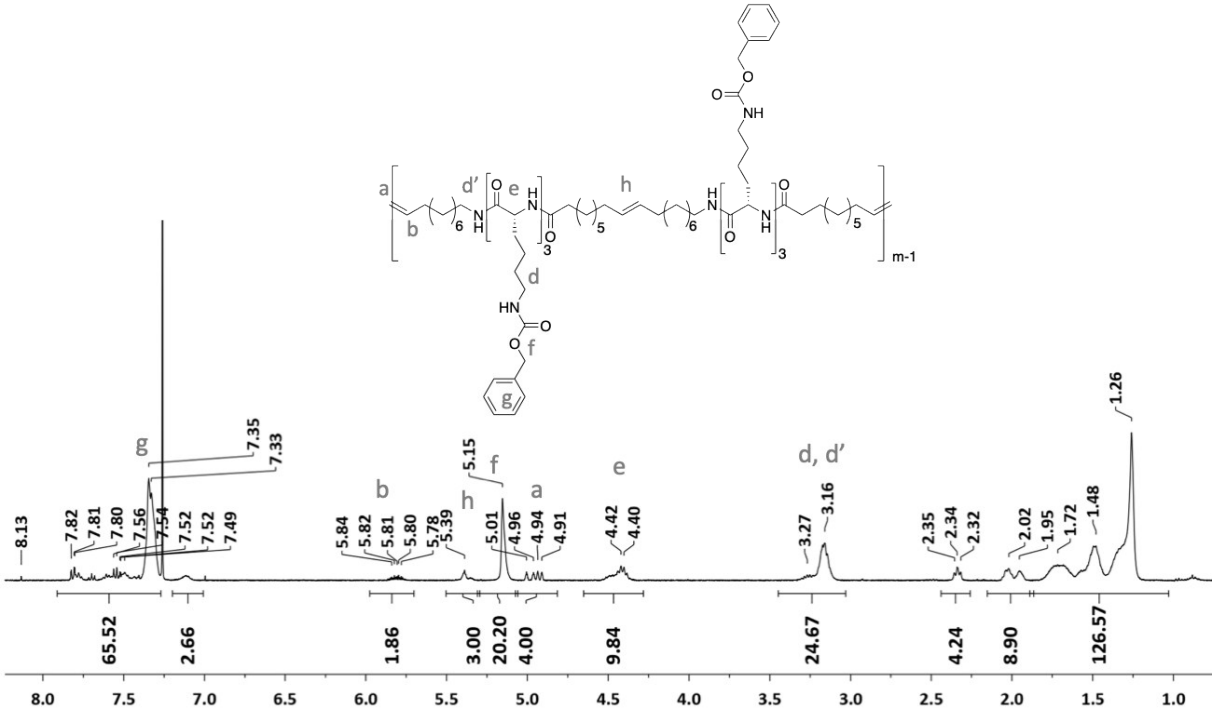

Figure 6S. ^{1}H-NMR of **A-[Lys$_{n=3}$]$_{m=3}$** (in $CDCl_3$ and 15 vol.% TFA).

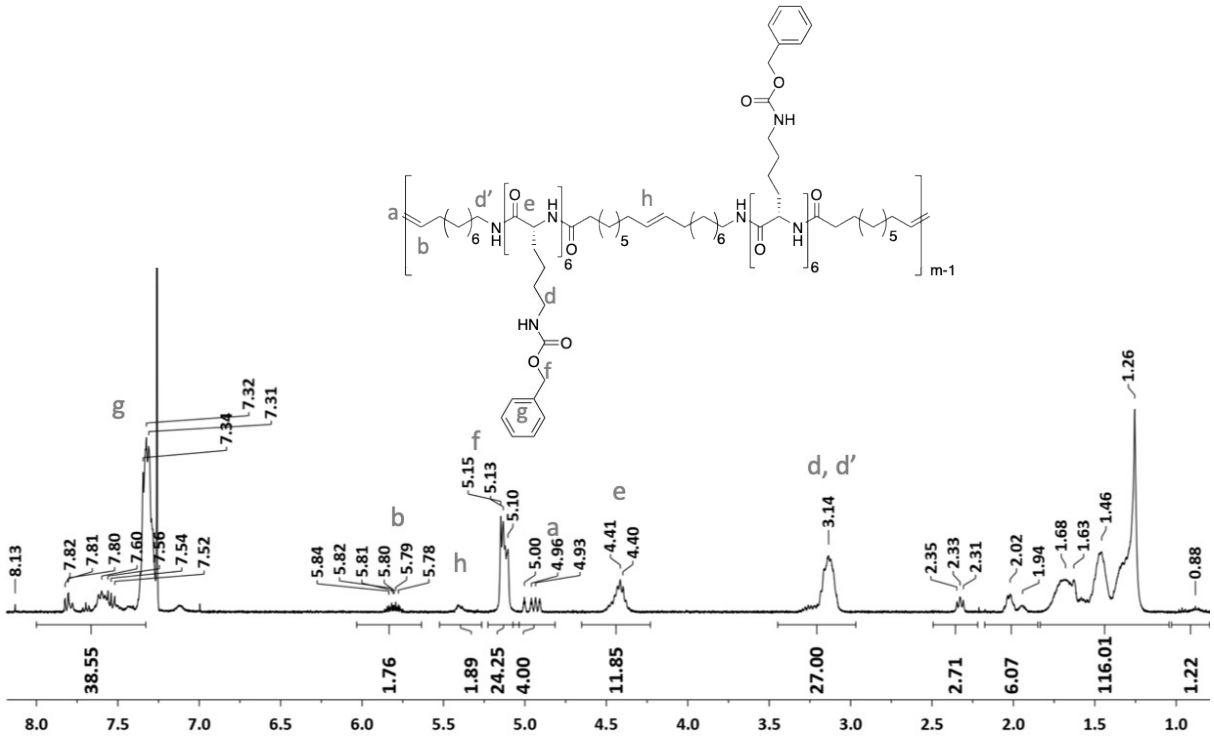

Figure 7S. ^{1}H-NMR of A-[**Lys**$_{n=6}$]$_{m=2}$ (in $CDCl_3$ and 15 vol.% TFA).

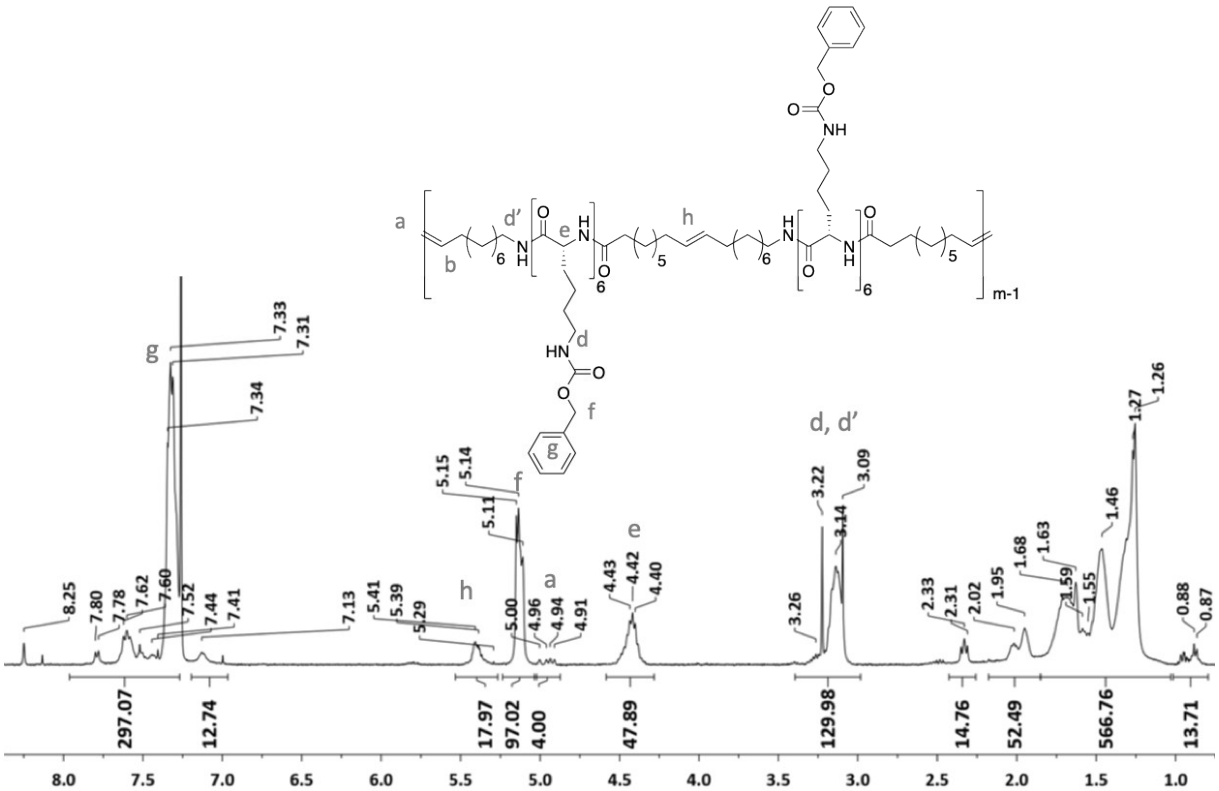

Figure 8S. ^{1}H-NMR of **A-[Lys$_{n=6}$]$_{m=12}$** (in $CDCl_3$ and 15 vol.% TFA).

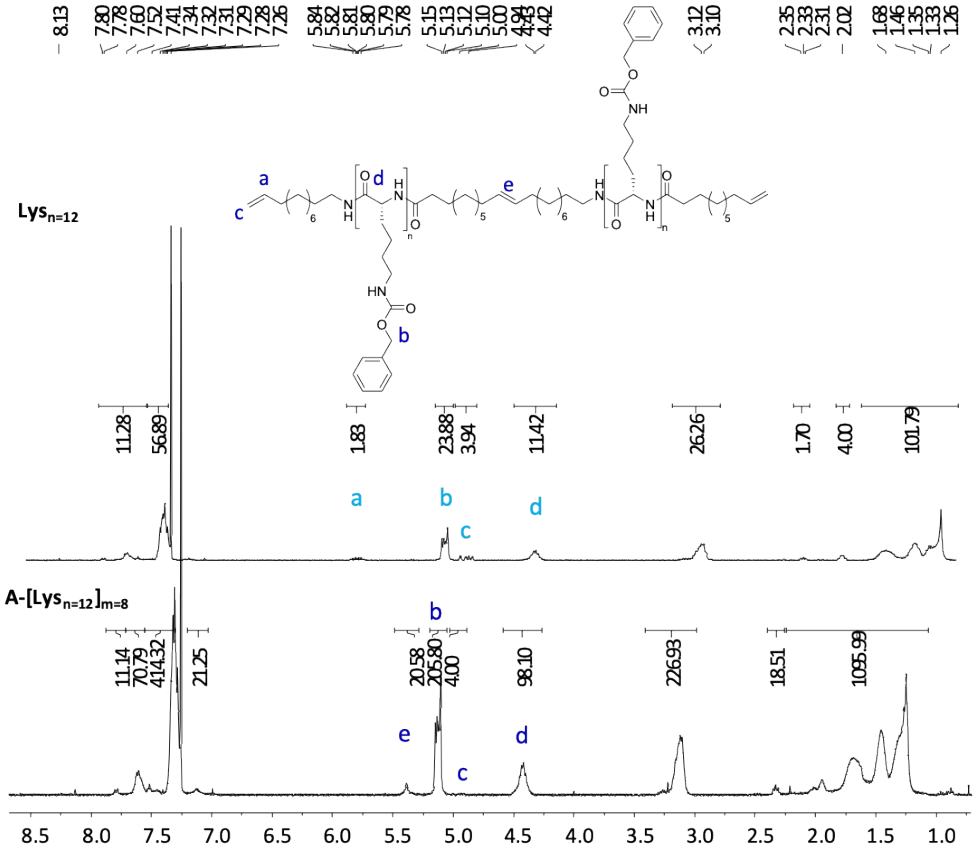

Figure 9S. ^{1}H-NMR of **Lys$_{n=12}$** and **A-[Lys$_{n=12}$]$_{m=8}$** (in $CDCl_3$ and 15 vol.% TFA).

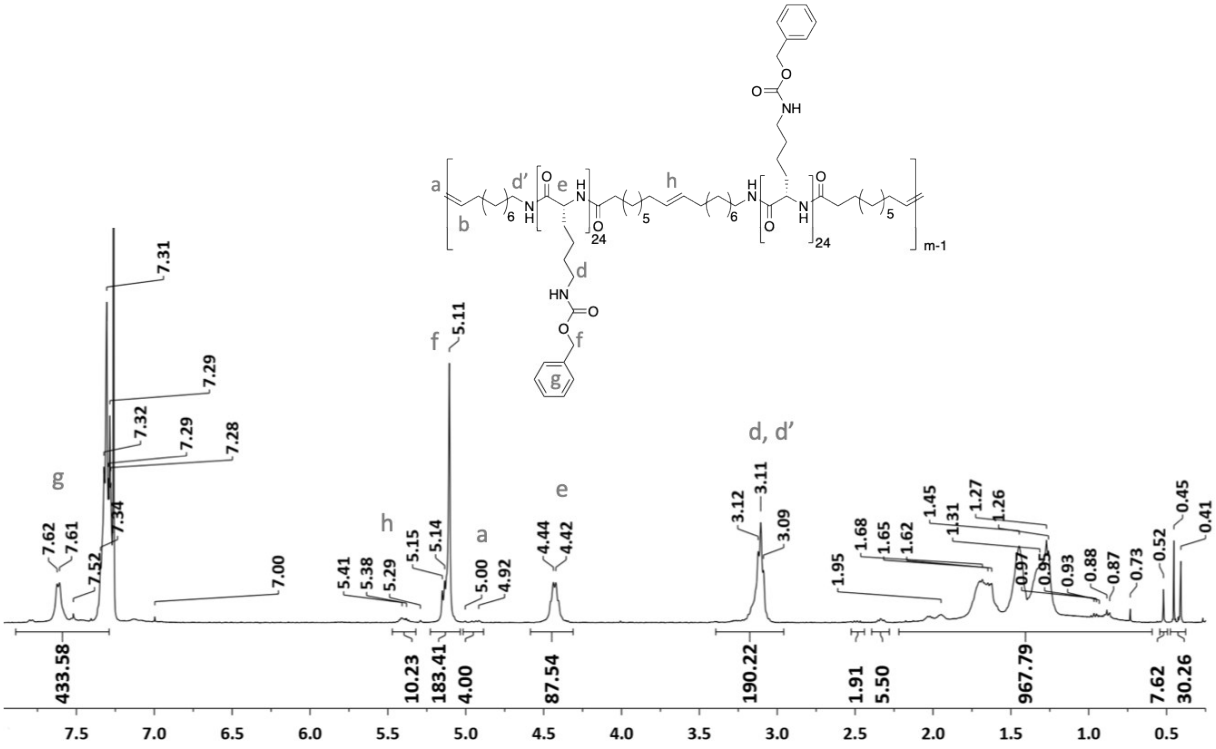

Figure 10S. ^{1}H-NMR of **A-[Lys$_{n=24}$]$_{m=4}$** (in $CDCl_3$ and 15 vol.% TFA).

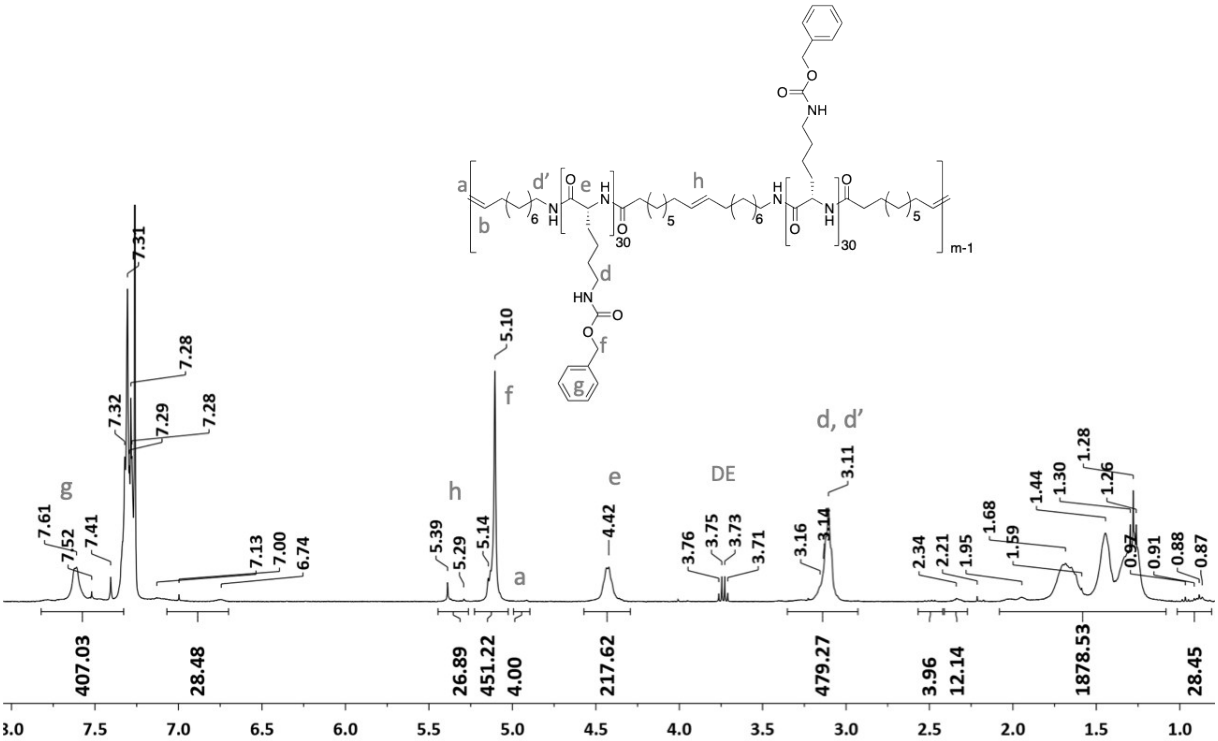

Figure 11S. ^{1}H-NMR of **A-[Lys$_{n=30}$]$_{m=7}$** (in $CDCl_3$ and 15 vol.% TFA).

II. MALDI-ToF MS analyses of oligo-L-Lysine(Z)s and ADMET polymers

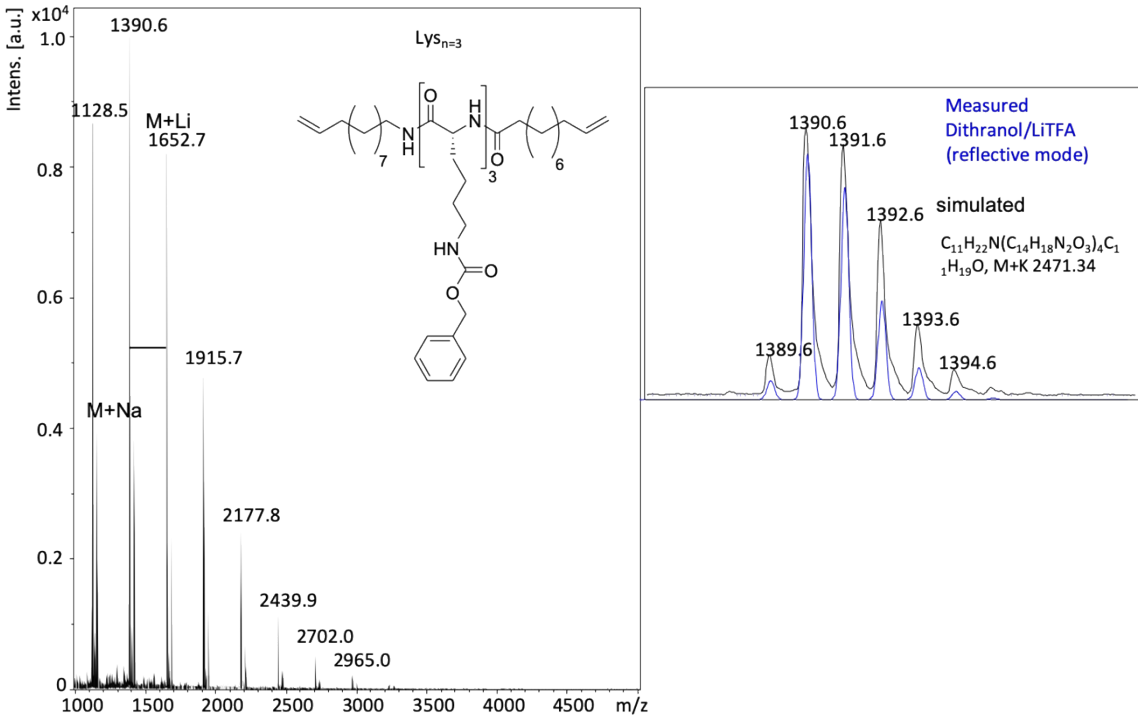

Figure 12S. MALDI-ToF MS spectra of **Lys$_{n=3}$** along with simulated isotopic pattern.

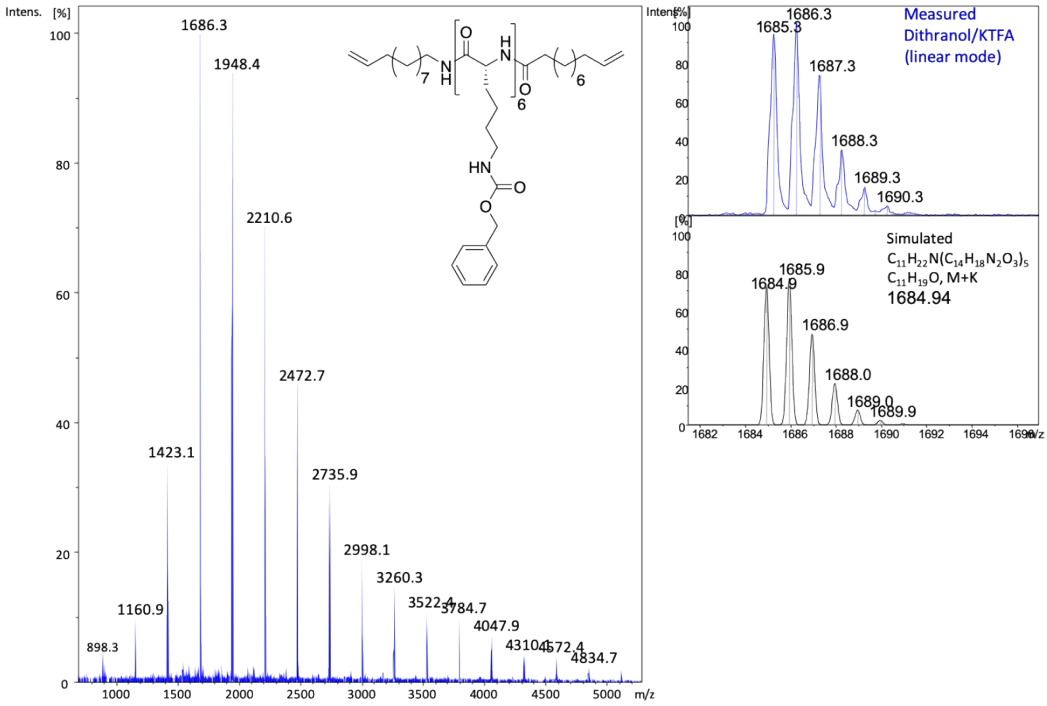

Figure 13S. MALDI-ToF MS spectra of **Lys$_{n=6}$** along with simulated isotopic pattern.

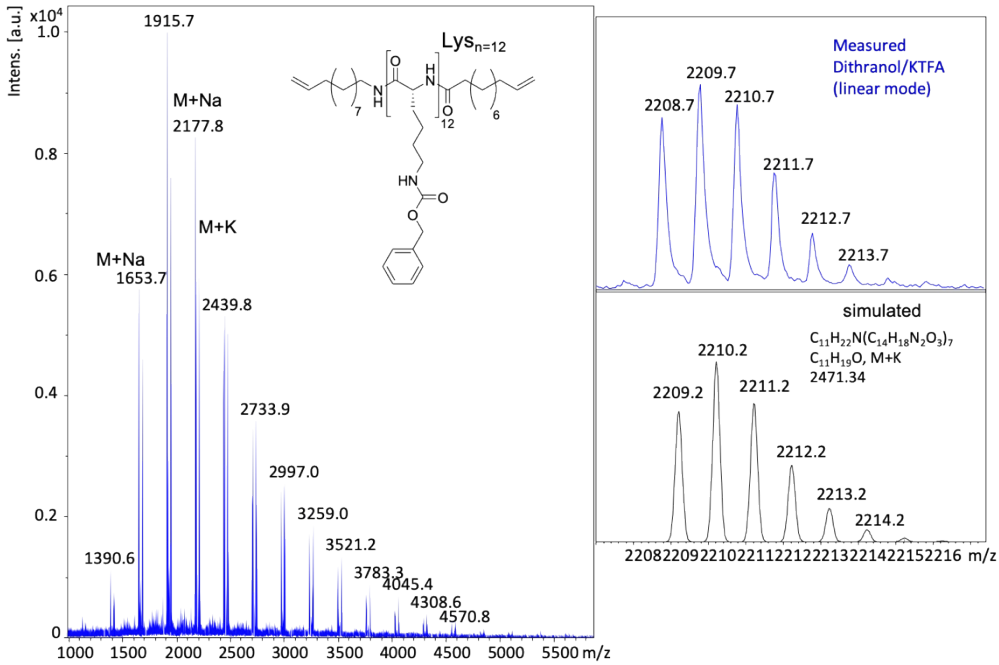

Figure 14S. MALDI-ToF MS spectra of **Lys$_{n=12}$** along with simulated isotopic pattern.

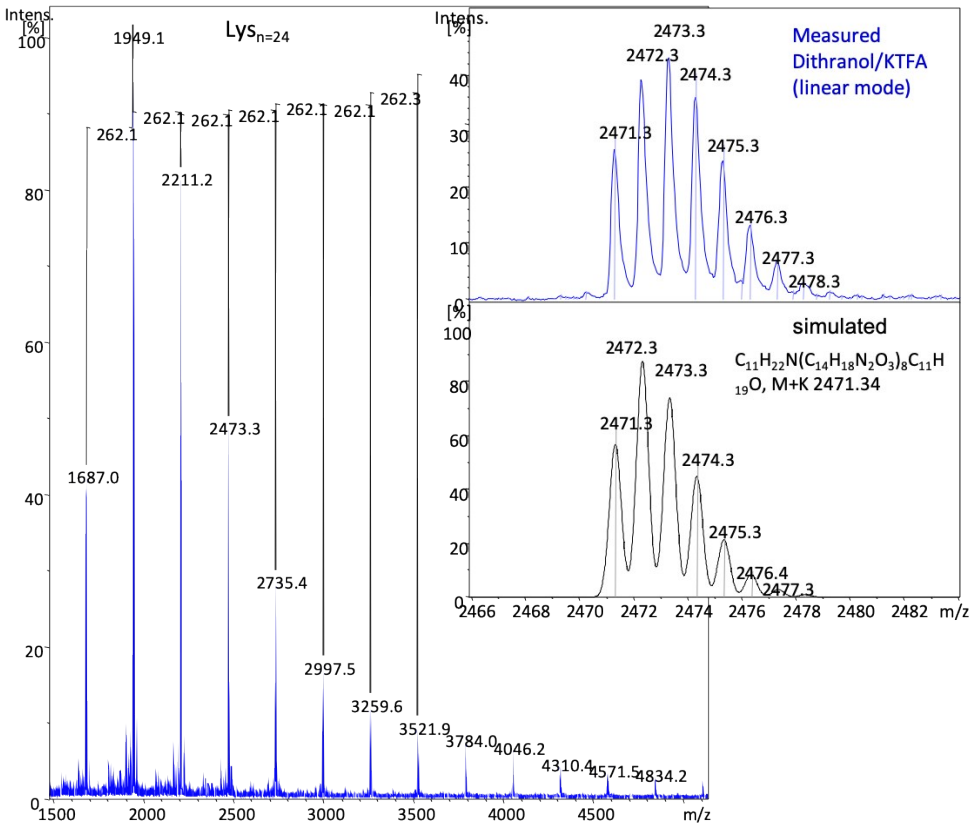

Figure 15S. MALDI-ToF MS spectra of **Lys$_{n=24}$** along with simulated isotopic pattern.

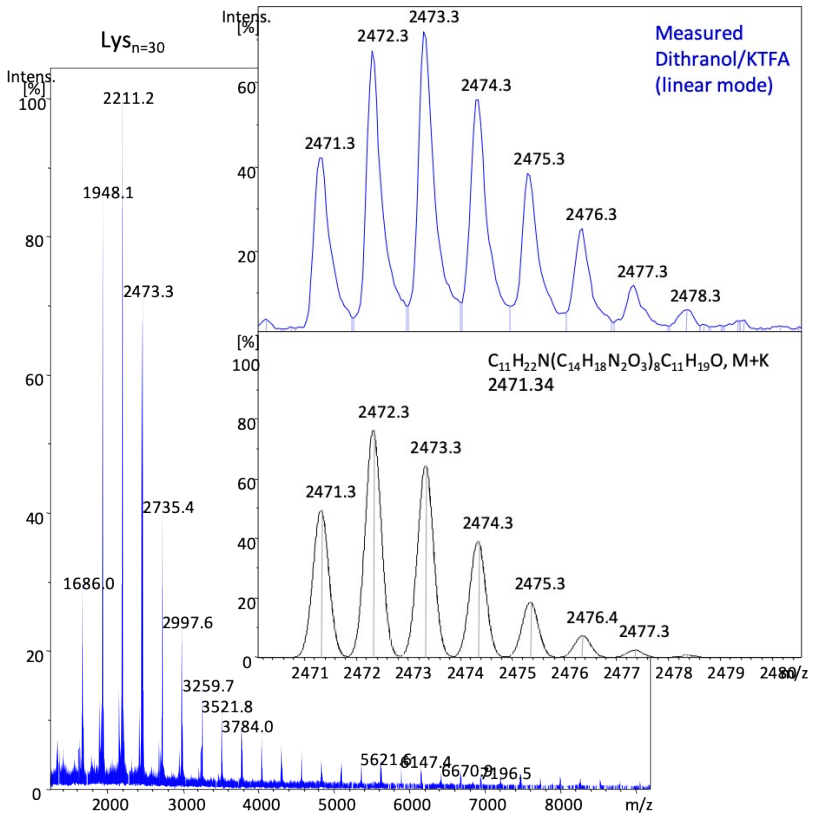

Figure 16S. MALDI-ToF MS spectra **of Lys$_{n=30}$** along with simulated isotopic pattern.

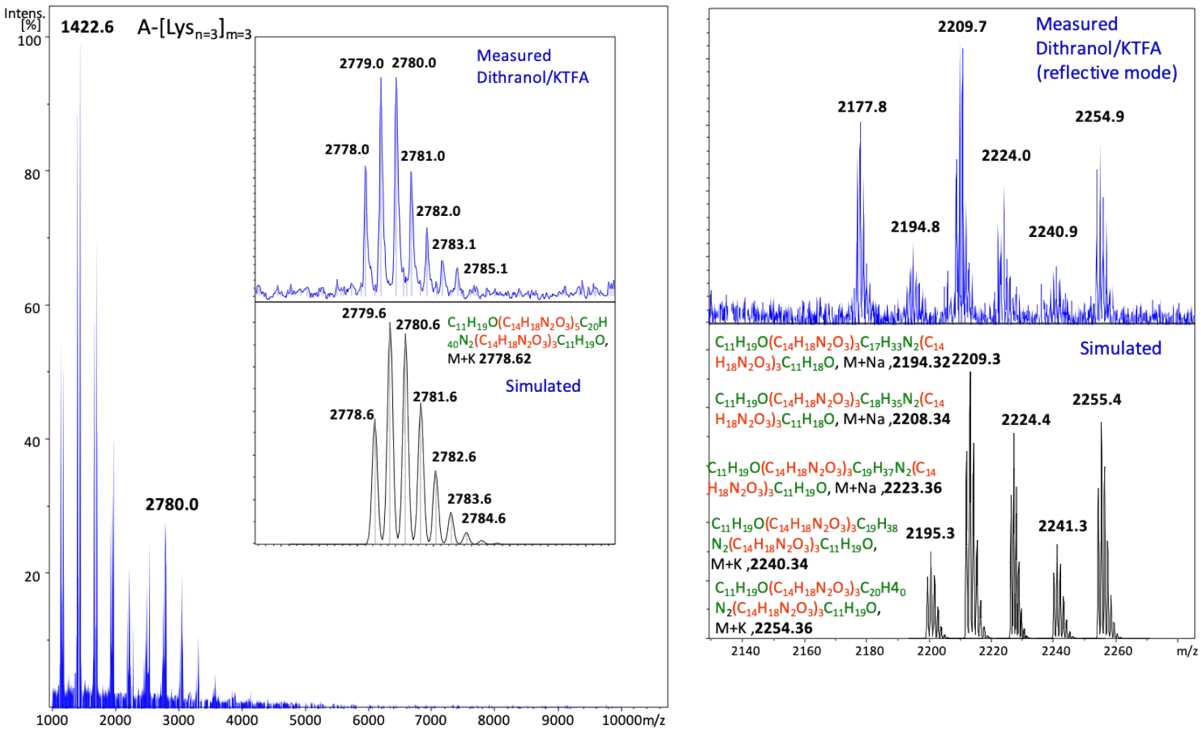

Figure 17S. MALDI-ToF MS spectra of **A-[Lys$_{n=3}$]$_{m=3}$** along with simulated isotopic pattern.

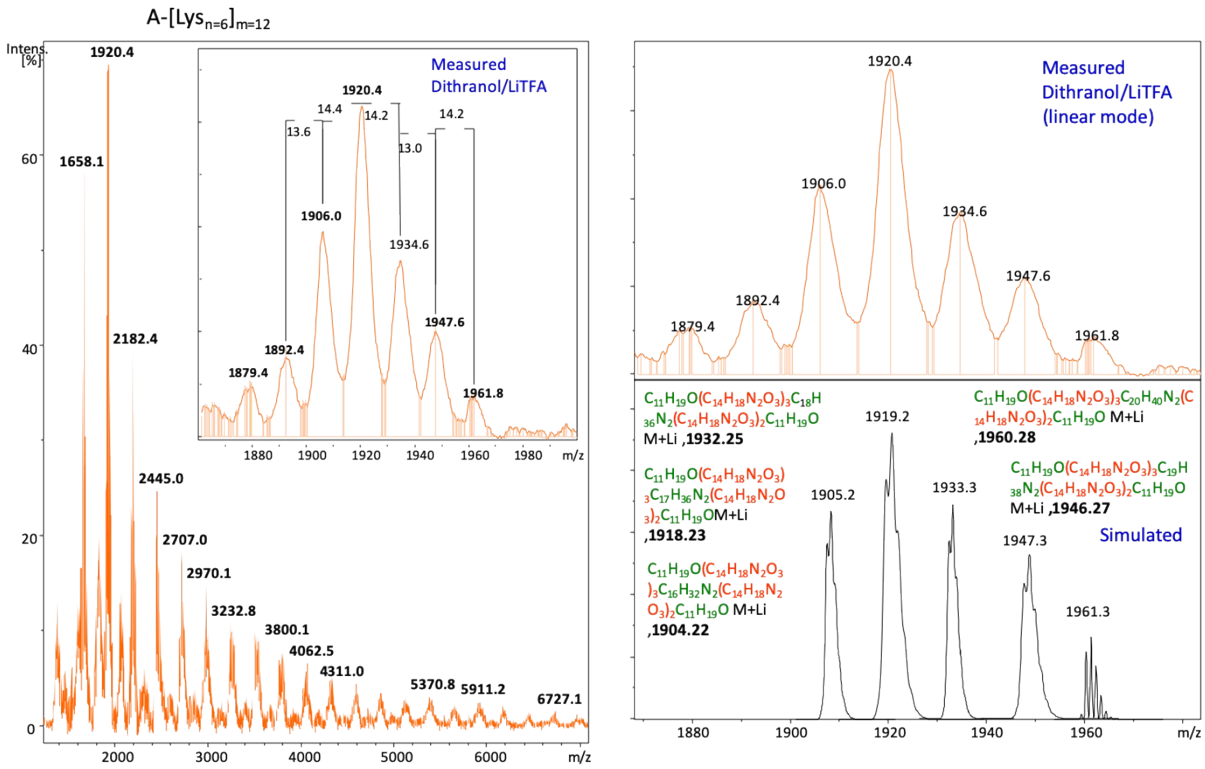

Figure 18S. MALDI-ToF MS spectra of **A-[Lys$_{n=6}$]$_{m=12}$** along with simulated isotopic pattern.

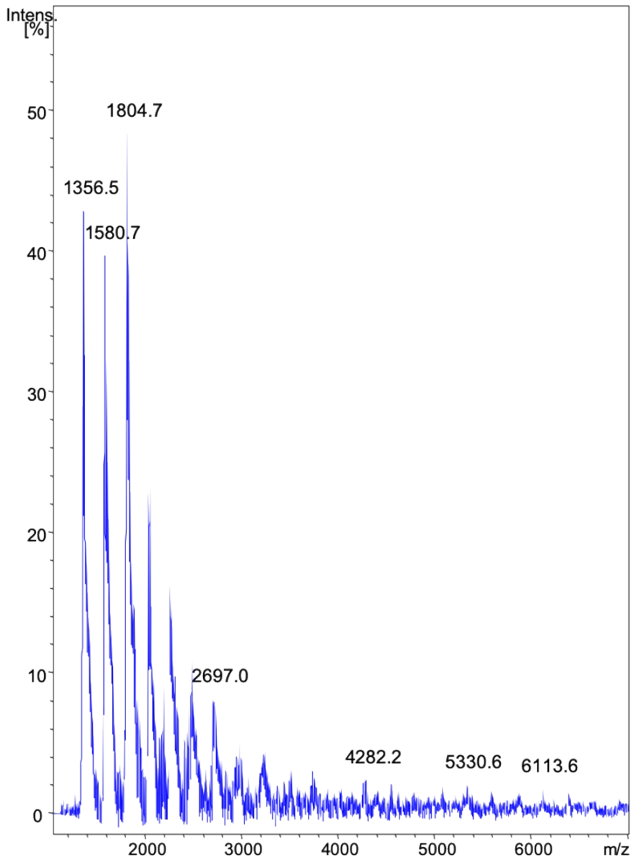

Figure 19S. MALDI-ToF MS spectra of **A-[Lys$_{n=30}$]$_{m=7}$**

III. CD spectroscopy investigations in TFE

The measured CD spectroscopy data were reported as ellipticity (θ) [mdeg]. The percentage values of α-helicity of the samples were calculated according to the Equation (1S), used for the estimation of the helicity of the peptide chains by Krannig and Sun et al.[1]:

Equation (1S) $$\alpha-\text{helix}(\%) = (-[\theta]_{222} + 3000)/39\,000) \times 100\%$$

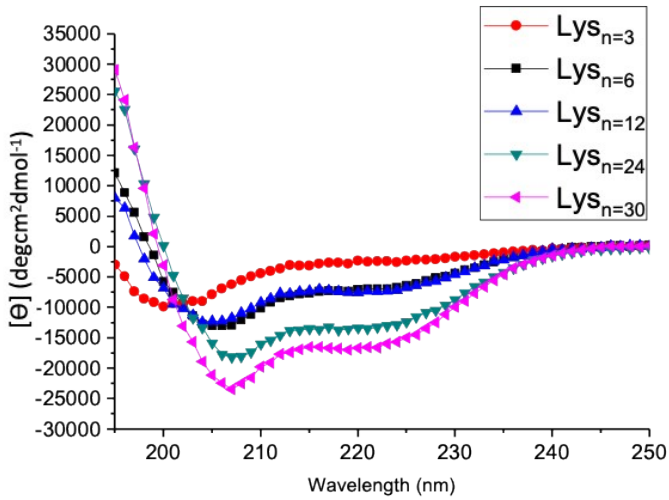

Figure 20S. CD spectra of **Lys$_n$**s in TFE (c= 0.2 mg/mL at 20 °C).

IV. IR spectroscopy investigations in TFE

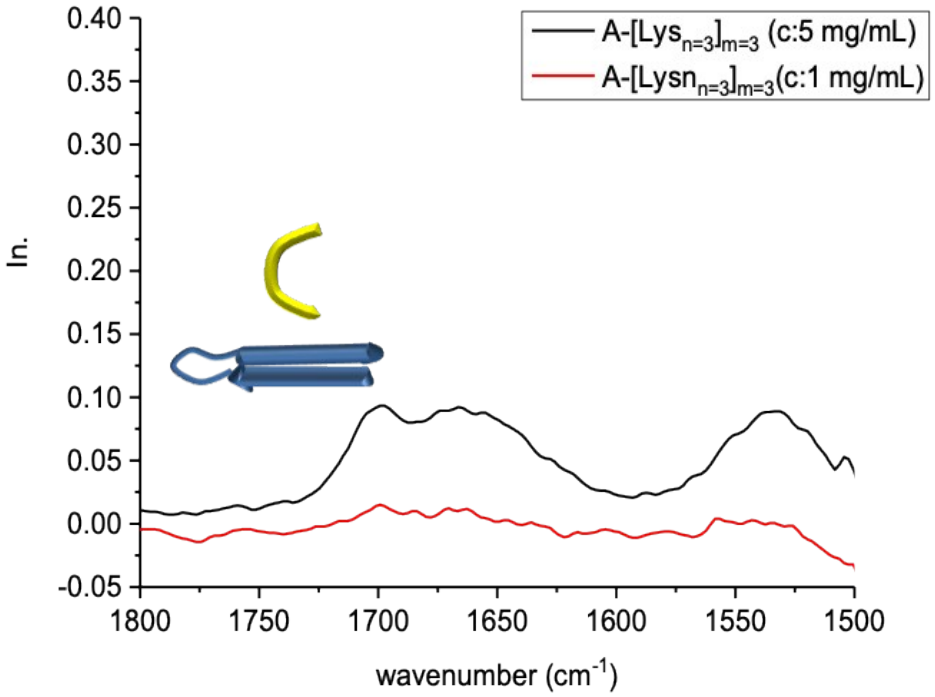

Figure 21S. IR spectra of **A-[Lys$_{n=3}$]$_{m=3}$** (c= 1 mg/mL and c= 5 mg/mL in TFE).

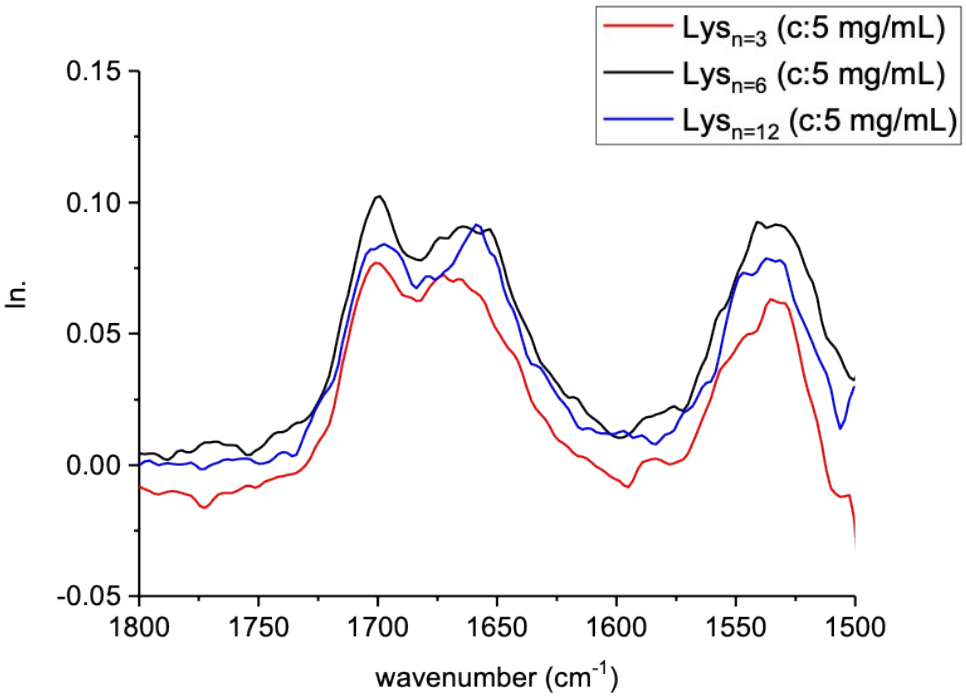

Figure 22S. IR spectra of **Lys$_{n=3}$**, **Lys$_{n=6}$** and **Lys$_{n=12}$** (c: 5 mg/mL in TFE).

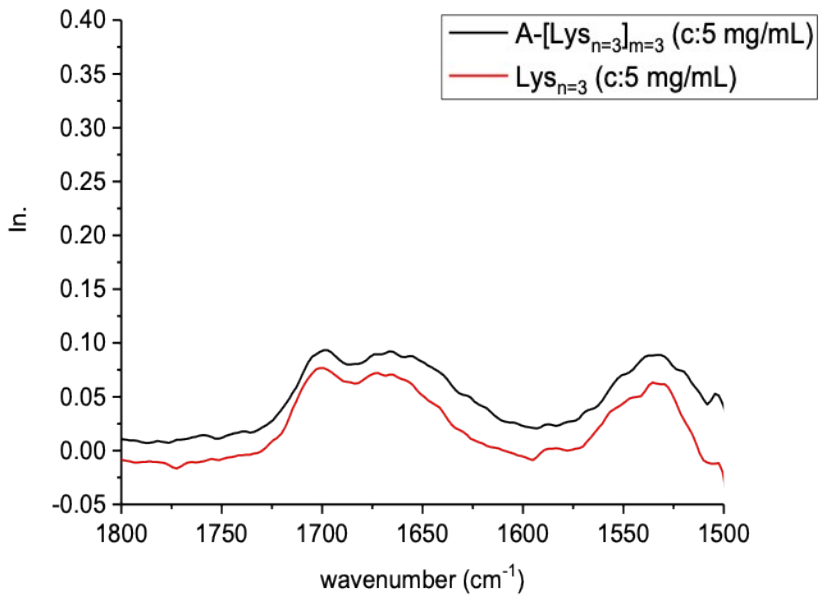

Figure 23S. IR spectra of **Lys$_{n=3}$** and **A-Lys$_{n=3}$** (c: 5 mg/mL in TFE).

V. Preparative GPC analyses of ADMET polymer A-[Lys$_{n=3}$]$_{m=3}$

Table 1S. Fractions of **A-[Lysn$_{=3}$]$_{m=3}$** along with their M_w, M_n and PDI values.

Fractions (F)	A-[Lys$_{n=3}$]$_{m=3}$	M_n (g/mol)	M_w (g/mol)	PDI
	F1+F2	NA	NA	NA
	F3+F4+F5	NA	NA	NA
	F6-9	NA	NA	NA
	F10+F12	23 253	28 052	1.206
	F13+F14	12 773	14 310	1.12
	F15	9 192	9 892	1.076
	F16	7 230	7 689	1.063
	F17	5 780	6 087	1.053
	F18	4 692	4 933	1.051
	F19	3 950	4 118	1.043
	F20	3 418	3 571	1.045
	F21	2 841	2 969	1.045
	F22	2 680	2 829	1.056
	F23	2 383	2 487	1.043
	F24	2 157	2 228	1.033
	F25	1 933	1 985	1.027

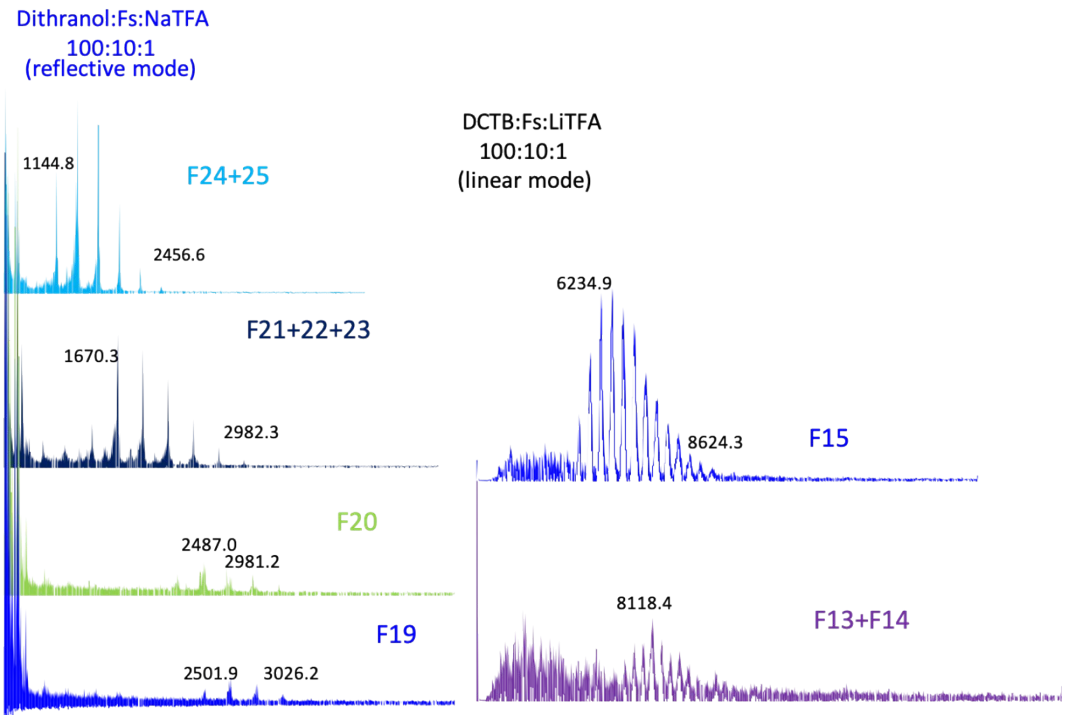

Figure 24S. MALDI spectra of A-[$Lys_{n=3}$]$_{m=3}$: **F24+F25**, **F21+F22+F23**, **F20**, **F19**, **F15**, **F13+F14**.

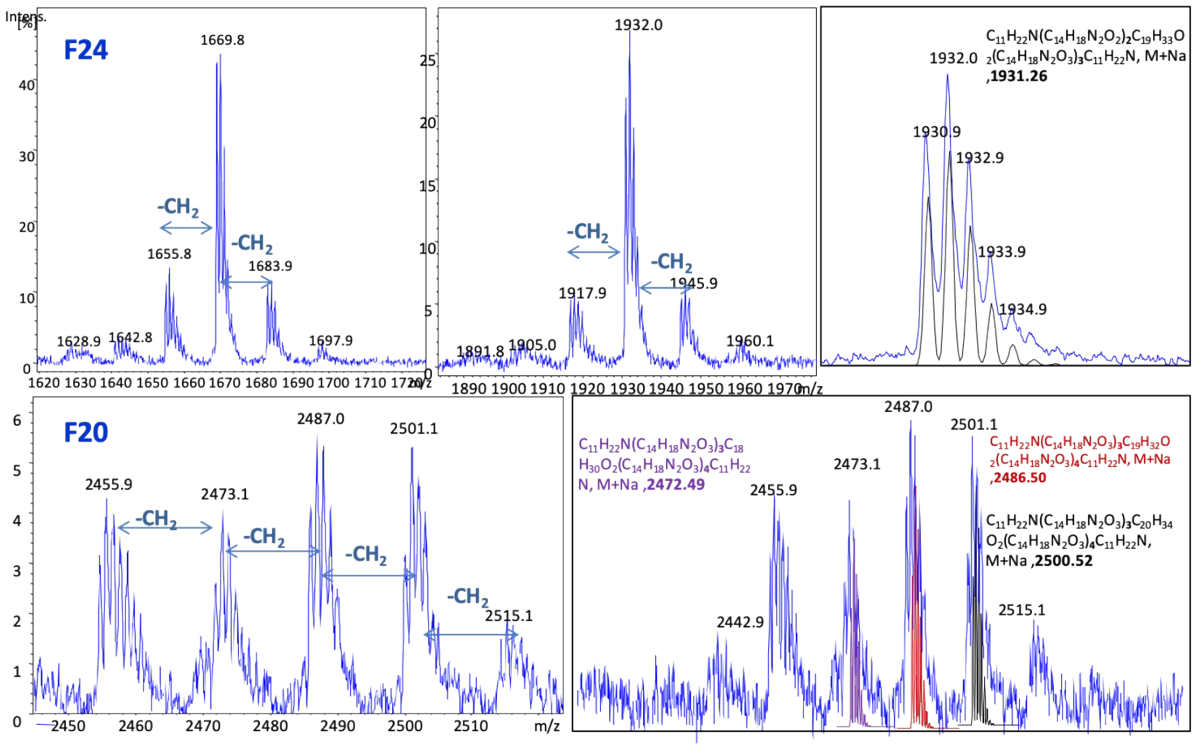

Figure 25S. MALDI-ToF MS spectra of **F24** and **F20** along with their simulated isotopic patterns.

VI. Preparative GPC analyses of ADMET polymer A-[Lys$_{n=24}$]$_{m=4}$

Table 2S. Fractions of **A-[Lysn$_{=24}$]$_{m=4}$** along with their M_w, M_n and PDI values.

	A-[Lys$_{n=24}$]$_{m=4}$	M_n (g/mol)	M_w(g/ mol)	PDI
Fractions (F)	**F1-7**	15 897	22 654	1.425
	F8	13 444	31 193	2.326
	F9	23 863	48 096	2.016
	F10	22 595	33 355	1.476
	F11	22 970	28 973	1.261
	F12	23 259	26 916	1.157
	F13	19 078	21 952	1.151
	F14	15 094	16 855	1.117
	F15	12 136	13 022	1.073
	F16	10 873	11 640	1.071
	F17	8 711	9 528	1.094
	F18	7 156	7 711	1.078

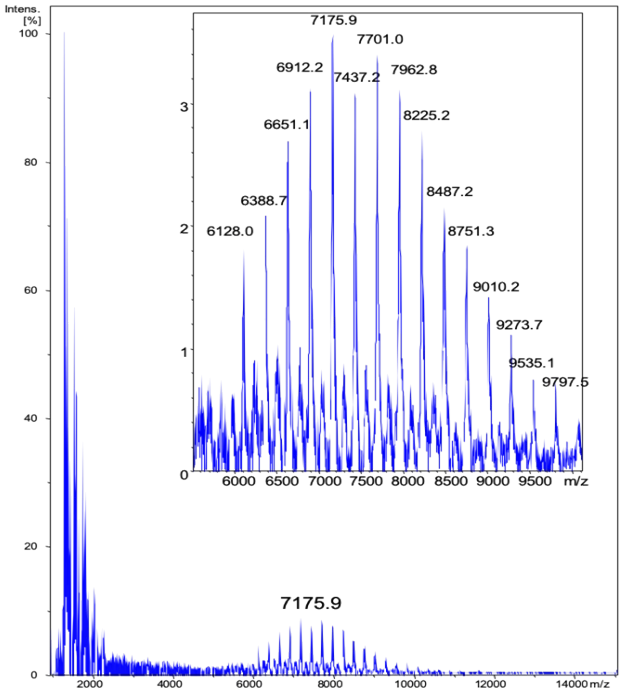

Figure 26S. MALDI-ToF MS spectra of **F18**.

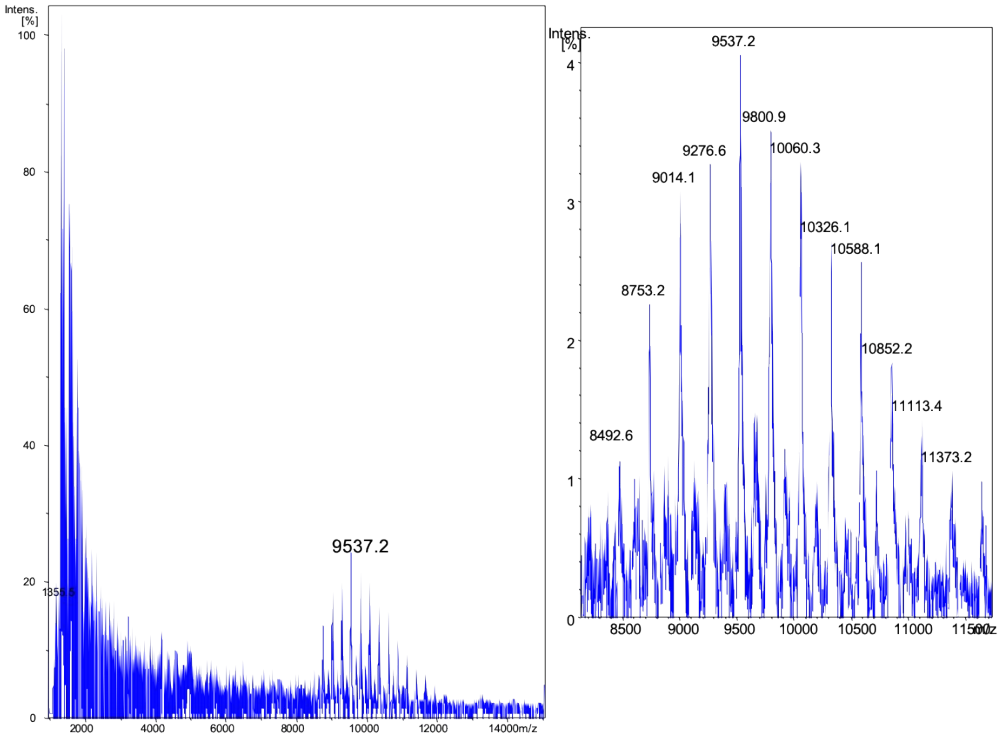

Figure 27S. MALDI-ToF MS spectra of **F17**.

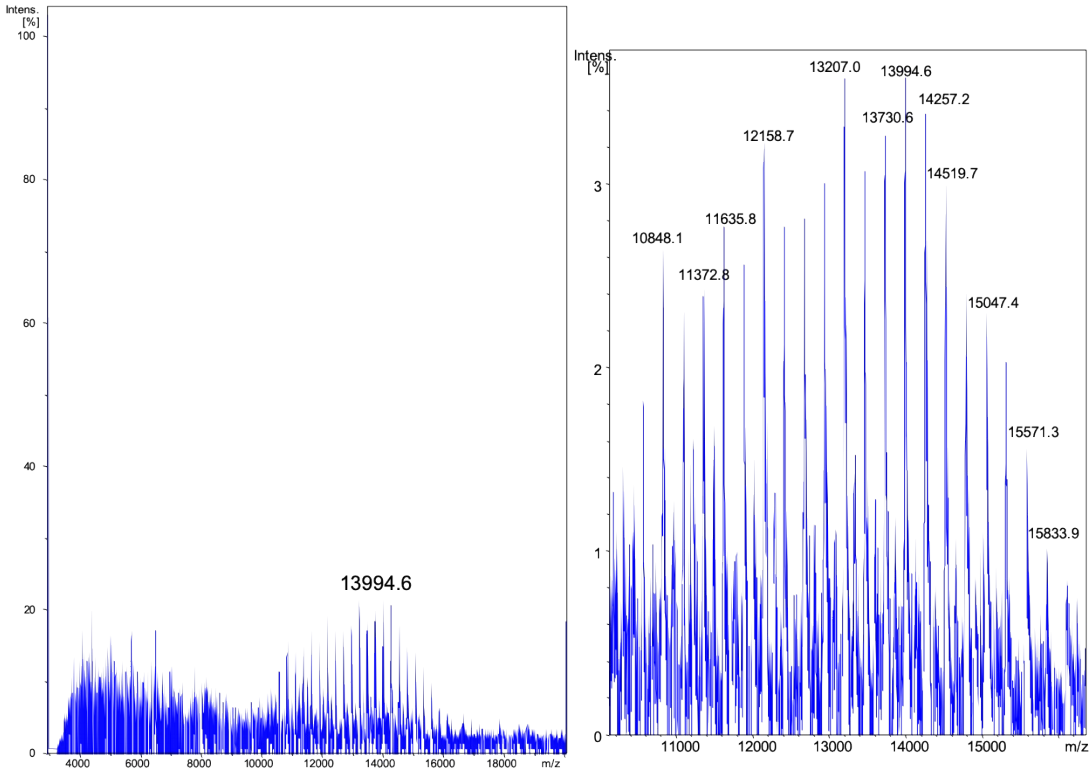

Figure 28S. MALDI-ToF MS spectra of **F16**.

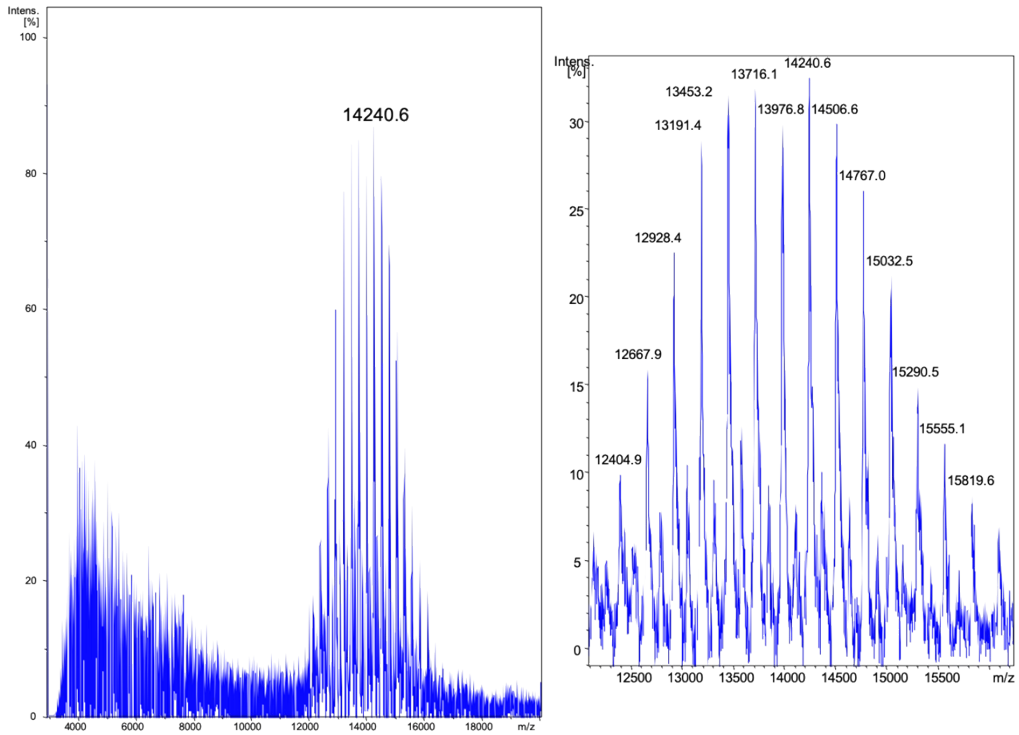

Figure 29S. MALDI-ToF MS spectra of **F15.**

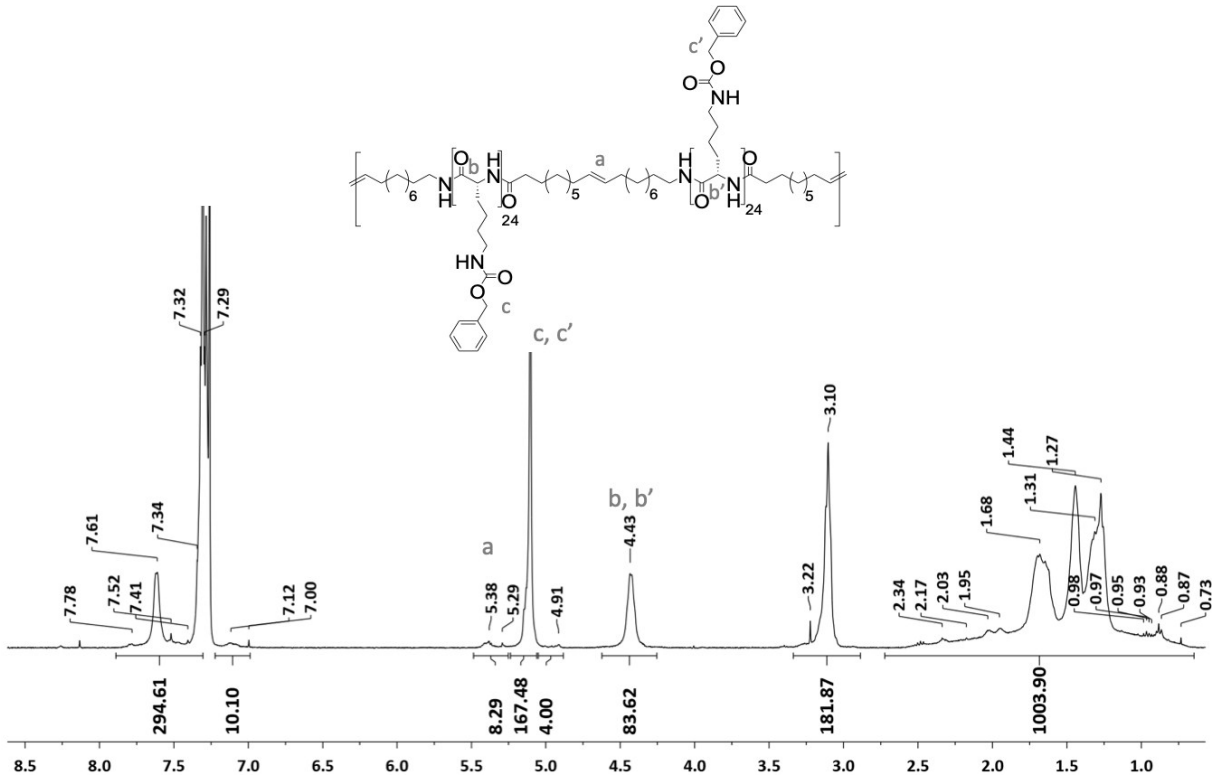

Figure 30S. ^{1}H-NMR of A-[Lys$_{n=24}$]$_{m=4}$ fraction, **F13**.

References

1. K.-S. Krannig, J. Sun and H. Schlaad, *Biomacromolecules*, 2014, **15**, 978-984.