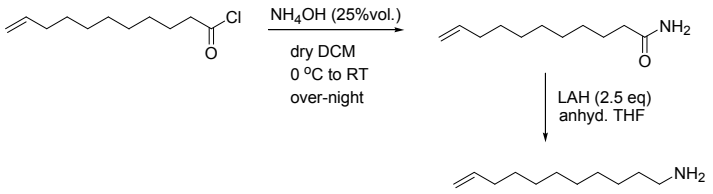
Electronic Supplementary Information (ESI) for:

Secondary structure of end group functionalized oligomeric-L-lysines: investigations of solvent and structure dependent helicity

Merve Basak Canalp, [a] Annette Meister [b] and Wolfgang H. Binder[c*]

1. Synthesis of 11-Amino-Undecene



Scheme 1S. Synthesis of 11-amino undecene.

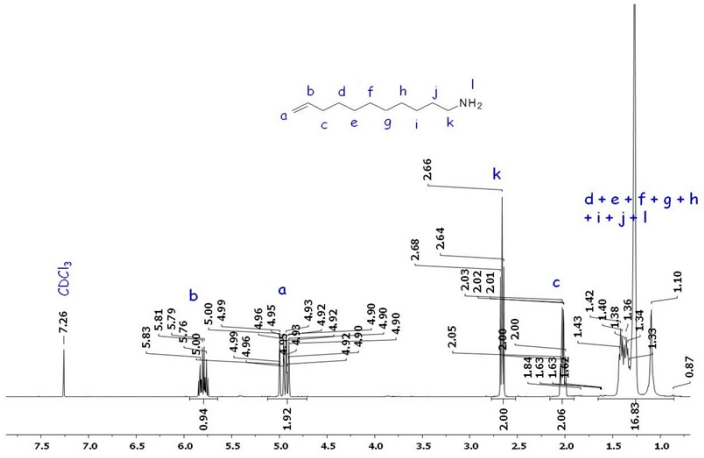


Figure 1S. ^{1}H-NMR of 11-undecene in $CDCl_3$.

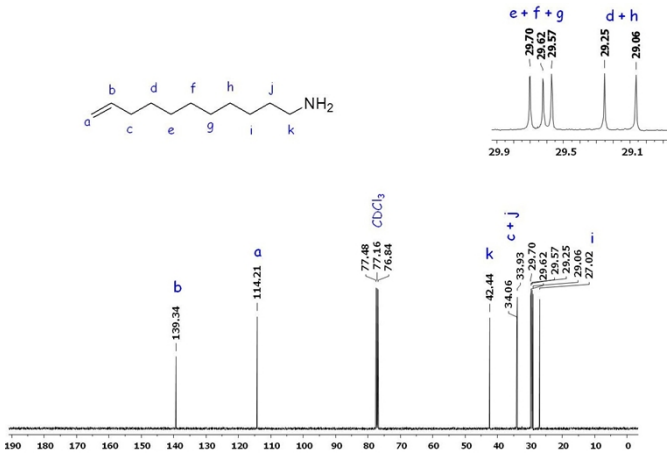
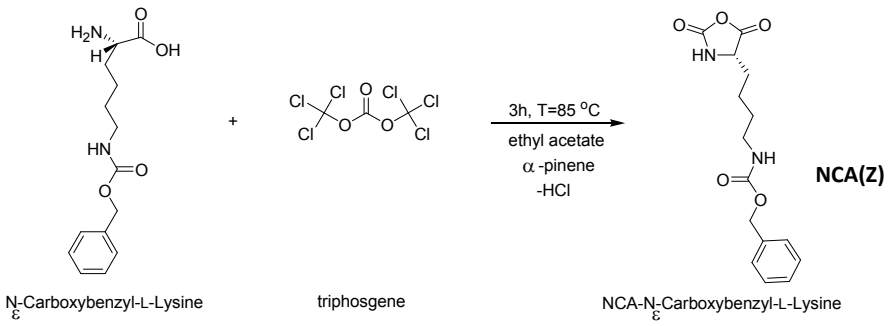


Figure 2S. ^{13}C-NMR of 11-undecene in $CDCl_3$.

2. N-carboxyanhydride of N-carboxybenzyl-L-Lysine, NCA(Z)

In a three-necked round bottom flask equipped with a magnetic stir bar and a reflux condenser, N_{ε}-carboxybenzyl-L-lysine (11.50 g, 41.03 mmol) and α-pinene (11.74 g, 86.15 mmol) were dissolved in 90 mL of dry ethyl acetate and stirred for around 30 minutes at room temperature. During that time, triphosgene (5.41 g, 18.23 mmol) which was dissolved in 25 mL of ethyl acetate and added slowly into the reaction mixture with the help of a syringe. The reaction mixture was refluxed at 85°C for around 3 hours. After removing 2/3 of the ethyl acetate by distillation, recrystallization was done in n-heptane for couple of time. The obtained pure NCA product was dried under vacuum and stored in a refrigerator. ^{1}H-NMR (DMSO-d_6, 400 MHz) δ (ppm): 9.06 (*s*, 1H, -N*H*), 7.39 – 7.28 (*m*, 5H, *ø-H*), 7.24 (*t*, 1H, -N*H*, $^{3}J_{H,H}$ = 5.5 Hz), 5.00 (*s*, 2H, -O-C*H2*-), 4.46 – 4.39 (*m*, 1H, -C*H*), 2.99 (*q*, 2H, -CH_2, $^{3}J_{H,H}$= 6.4 Hz), 1.80 – 1.21 (*m*, 6H, -CH_2). ^{13}C-NMR (DMSO-d_6, 125 MHz) δ (ppm): 171.6 (*C*=O), 156.1 (*C*=O), 151.9 (*C*=O), 137.2 (*ø*), 128.31 - 27. 7 (*ø*), 65.1 (O-*C*H_2-), 57.0 (*C*H), 40.1 (*C*H_2), 30.6 (*C*H_2), 28.7 (*C*H_2), 21.6 (*C*H_2). MS (ESI-ToF, MeOH): *m/z calc.* = 341.122 [M + Cl]$^-$, 305.150 [M - H]$^-$, *m/z exp.* = 341.101 [M + Cl]$^-$, 305.125 [M - H]$^-$.



Scheme 2S. Synthesis of N-carboxyanhydride of N-carboxybenzyl-L-Lysine, **NCA(Z)**.

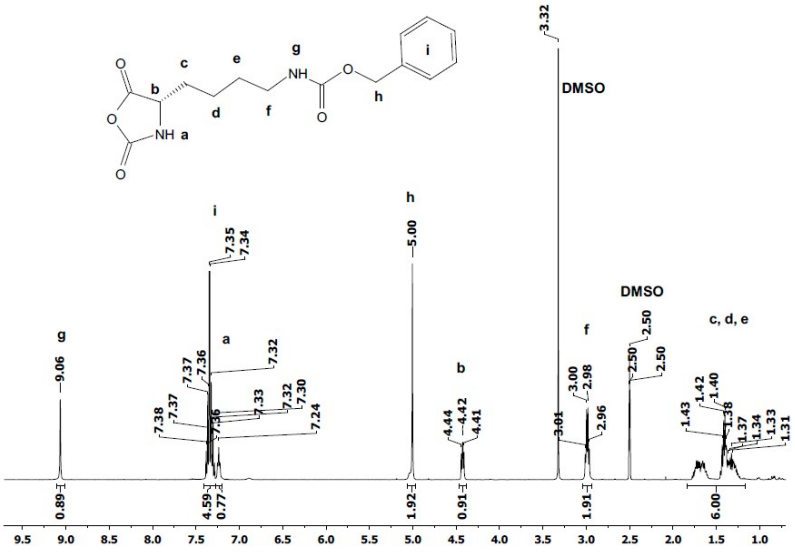


Figure 3S. ^{1}H-NMR of **NCA(Z)** in DMSO-d_6.

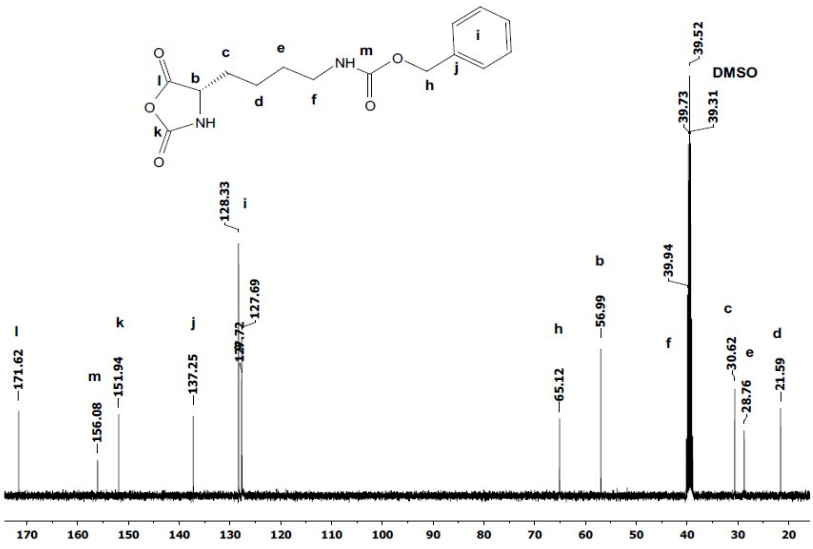


Figure 4S. ^{13}C-NMR of **NCA(Z)** in DMSO-d_6.

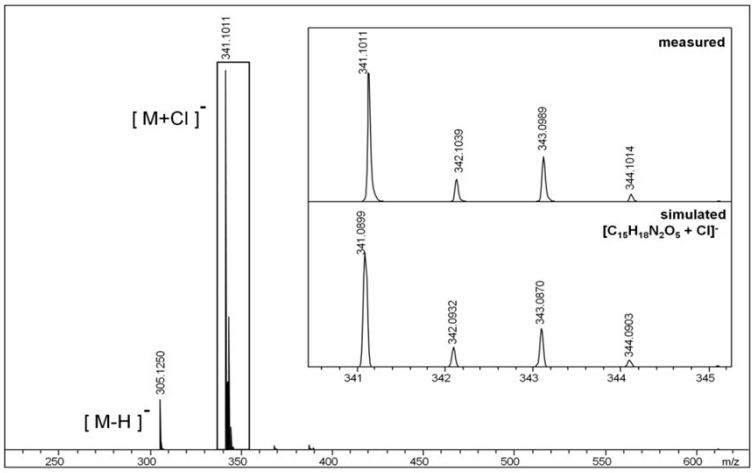


Figure 5S. ESI-ToF MS of **NCA(Z)**.

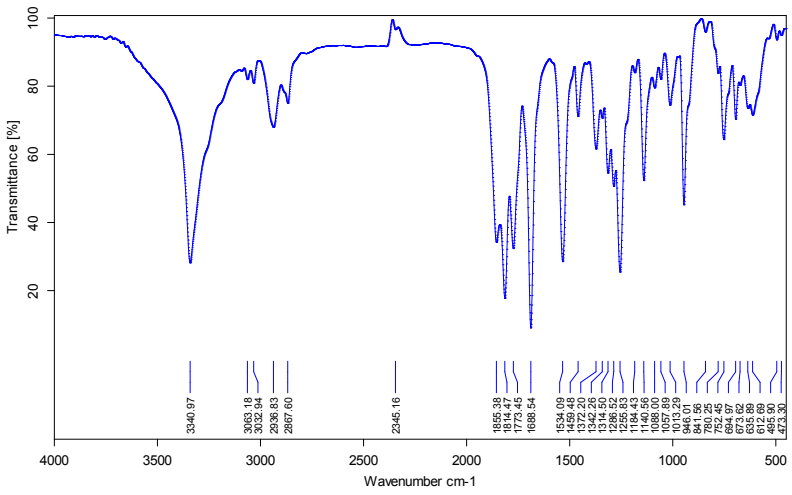
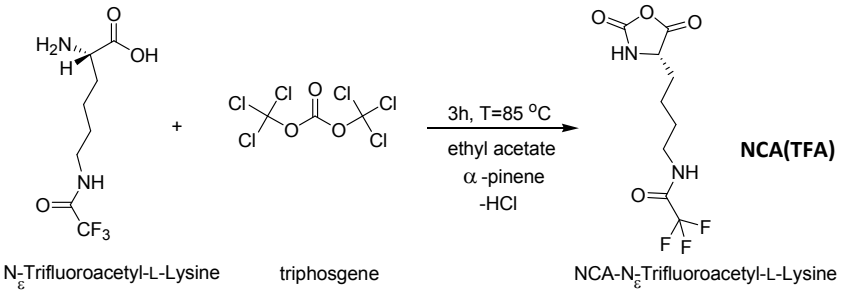


Figure 6S. AT-IR spectra of **NCA(Z)**.

3. N-carboxyanhydride of N-trifluoroaceticacid-L-Lysine, NCA(TFA)

N_ε- trifluoroacetyl-L-lysine (10.00 g, 41.29 mmol) and α-pinene (11.81 g, 86.71 mmol) were dissolved in 78 mL of dry ethyl acetate. Triphosgene (5.51 g, 18.58 mmol) was dissolved in 25 mL of ethyl acetate. ^{1}H-NMR (DMSO-d_6, 400 MHz,) δ (ppm): 9.46 – 9.09 (*m*, 2H, -N*H*), 4.45 (*dd*, 1H, C*H*, $^{3,3}J_{H,H}$= 7.3, 5.1 Hz), 3.19 (*dd*, 2H, CH_2, $^{3,3}J_{H,H}$ = 13.0, 6.7 Hz), 1.85 – 1.17 (*m*, 6H, CH_2). ^{13}C-NMR (DMSO-d_6, 125 MHz) δ (ppm): 171.6 (*C*=O), 156.3 (*C*=O), 151.9 (*C*=O), 124.2 (*C*F_3), 56.9 (*C*H), 40.0 (*C*H_2), 30.5 (*C*H_2), 27.6 (*C*H2), 21.6 (*C*H_2). MS (ESI-ToF, MeOH): *m/z calc.* = 303.035 $[M + Cl]^-$, 267.059 $[M - H]^-$, *m/z exp.* = 303.054 $[M + Cl]^-$, 267.078 $[M - H]^-$.



Scheme 3S. Synthesis of N-Carboxyanhydride of N-Trifluoroaceticacid-L-Lysine, **NCA(TFA)**.

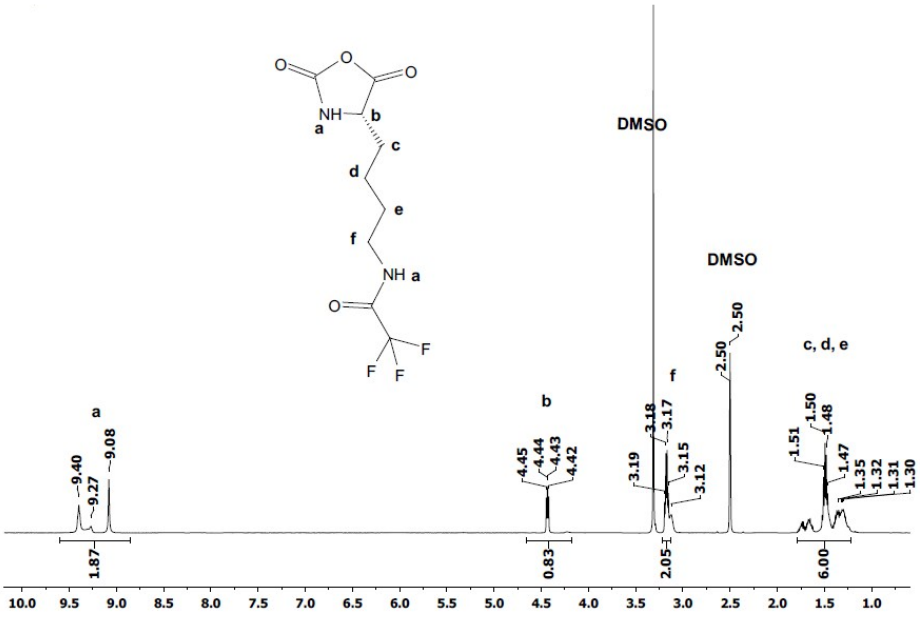


Figure 7S. ^{1}H-NMR of **NCA(TFA)** in DMSO-d_6.

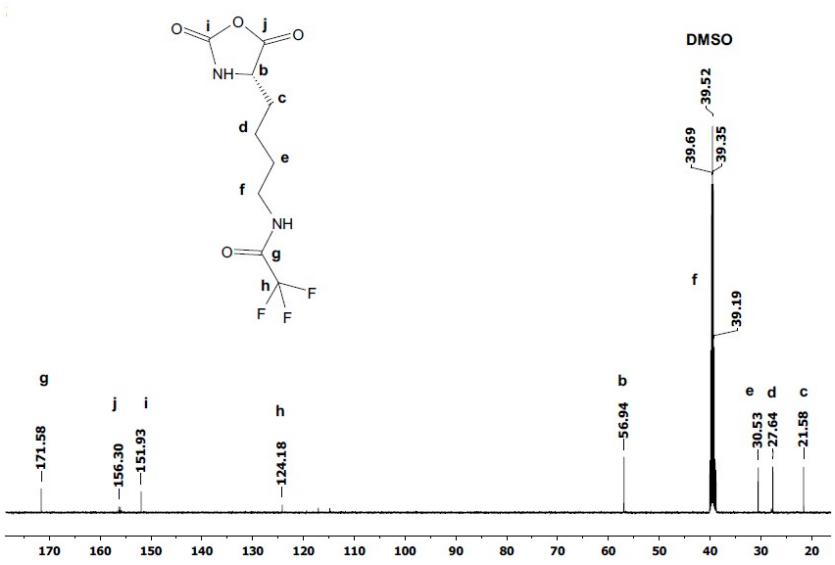


Figure 8S. ^{13}C-NMR of **NCA(TFA)** in DMSO-d_6.

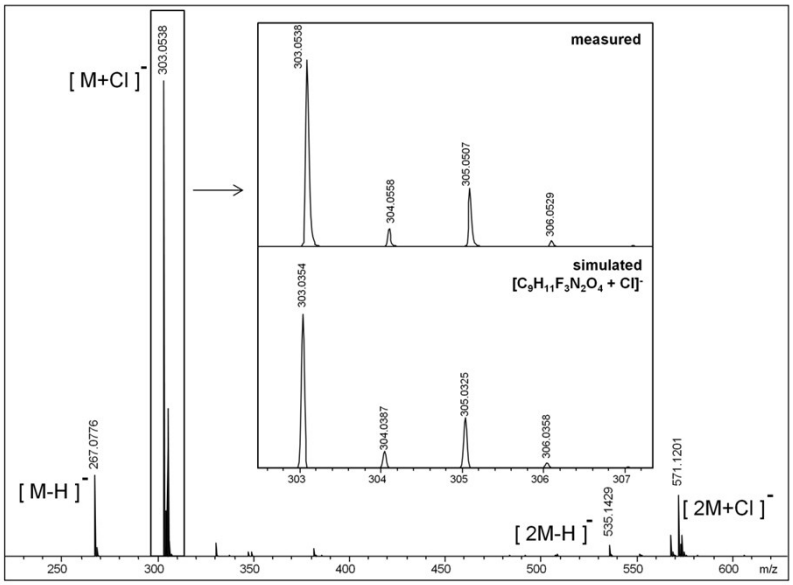
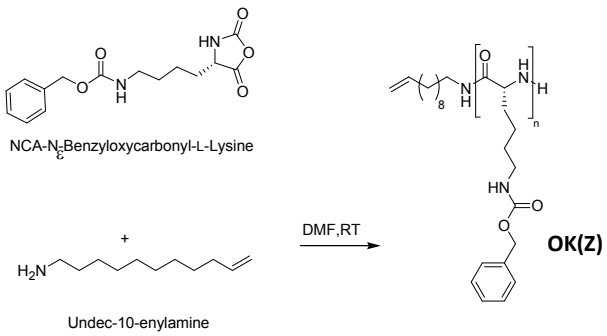


Figure 9S. ESI-ToF MS of **NCA(TFA)**.

4. N-Carboxyanhydride Ring Opening Polymerization of NCA(Z) with 11-Amino-Undecene, OK(Z)



Scheme 4S. Synthesis of **OK(Z)**.

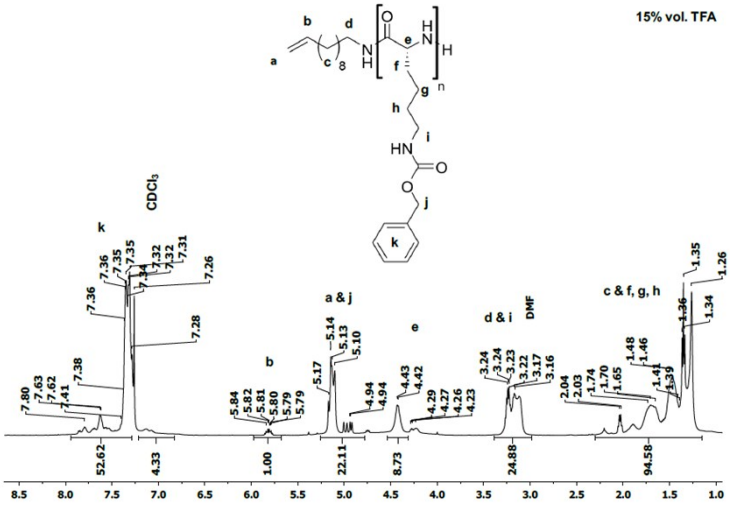


Figure 10S. ^{1}H-NMR **of OK(Z)** in $CDCl_3$ (15% vol. TFA added).

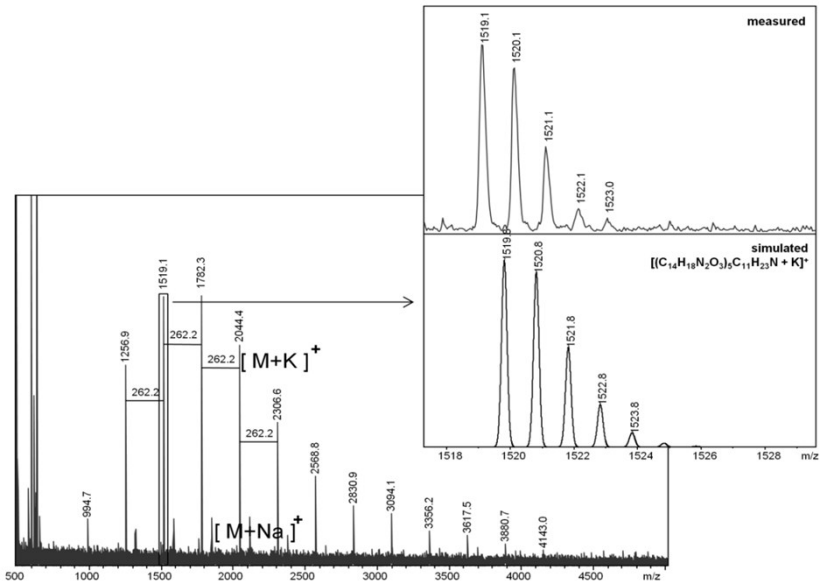
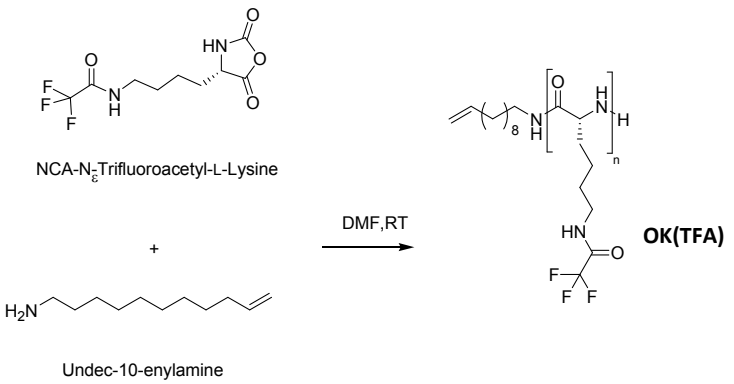


Figure 11S. MALDI-ToF MS of **OK(Z)**.

5. N-carboxyanhydride ring opening polymerization of NCA(TFA) with 11-amino-undecene, OK(TFA)



Scheme 5S. Synthesis of **OK(TFA)**.

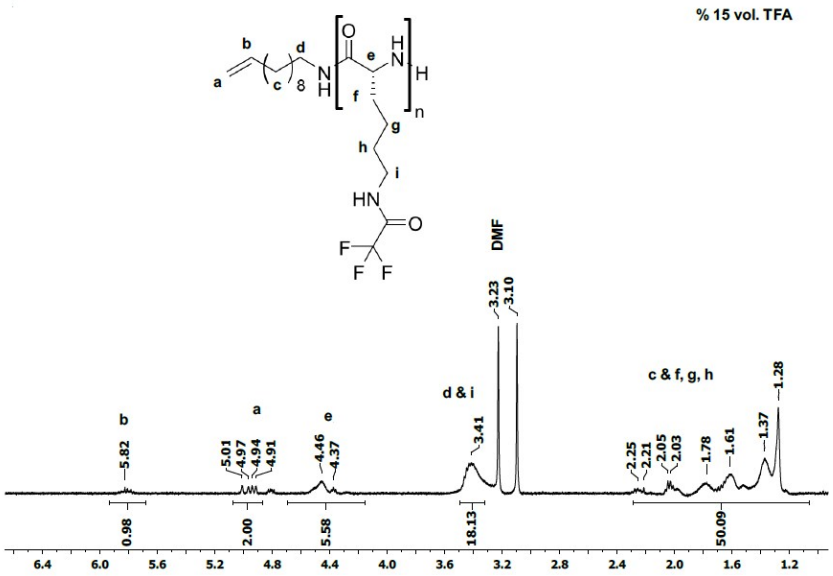


Figure 12S. ^{1}H-NMR of **OK(TFA)** in $CDCl_3$ (15% vol. TFA added).

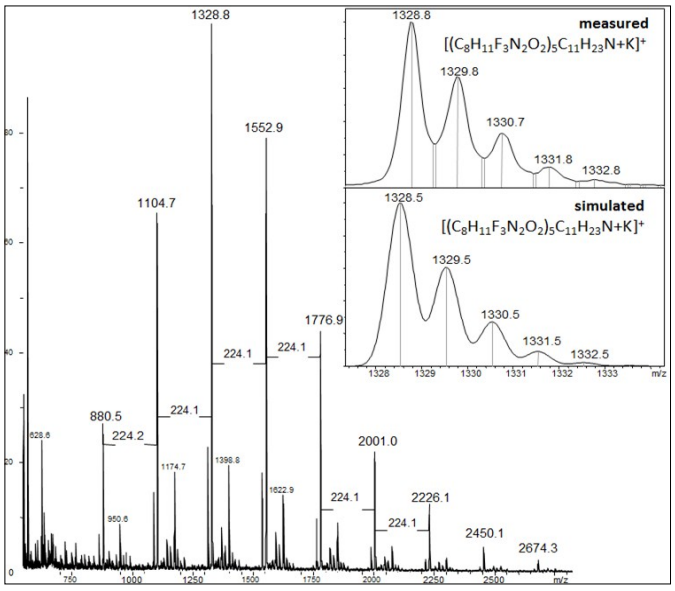
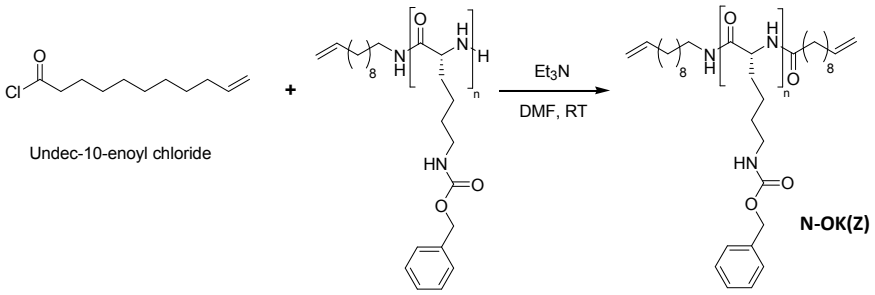


Figure 13S. MALDI-ToF MS of **OK(TFA)**.

6. *N*-terminus functionalization of oligo-carboxybenzyl-L-lysine, N-OK(Z)



Scheme 6S. Synthesis of **N-OK(Z)**.

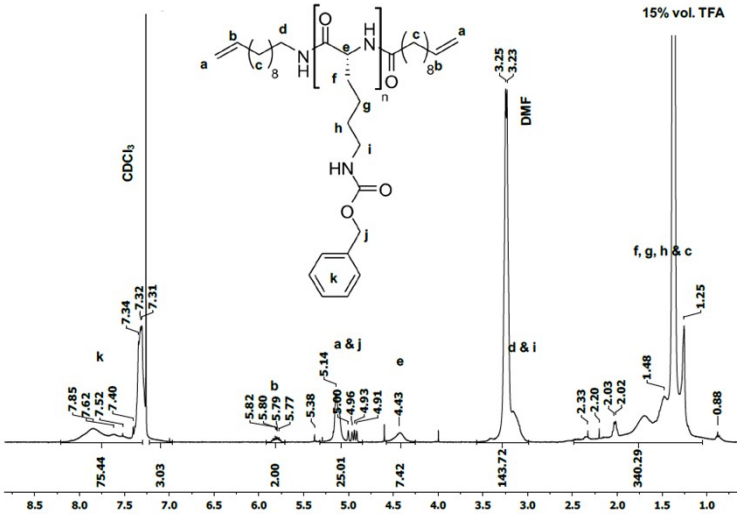


Figure 14S. ^{1}H-NMR of **N-OK(Z)** in $CDCl_3$ (15% vol. TFA added).

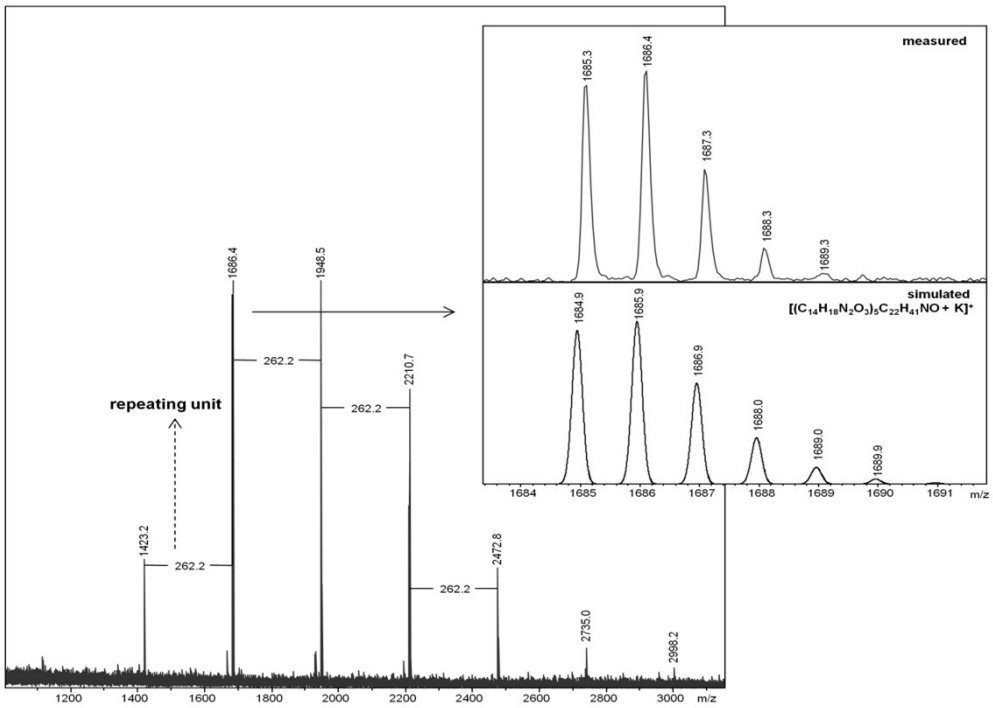
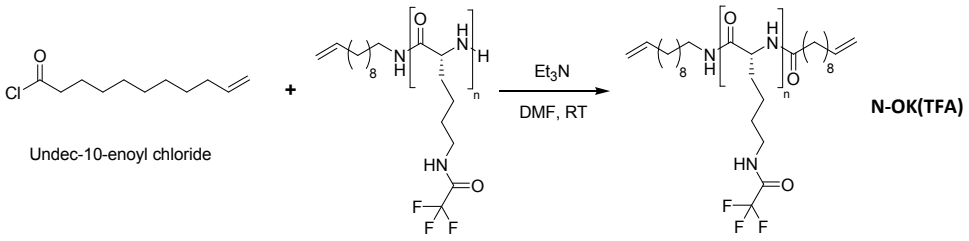


Figure 15S. MALDI-ToF MS of **N-OK(Z)**.

7. *N*-Terminus Functionalization of oligo-trifluoroacetyl-L-lysine, N-OK(TFA)



Scheme 7S. Synthesis of **N-OK(TFA)**.

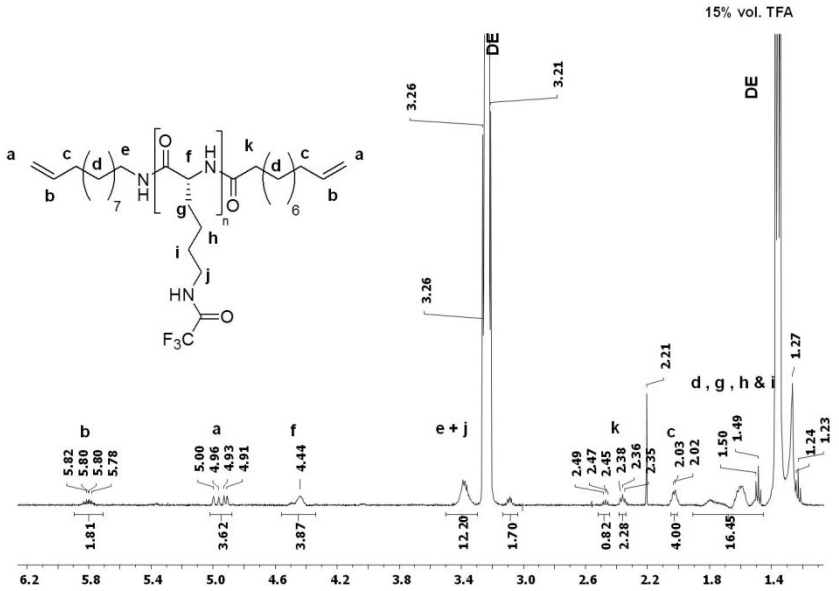


Figure 16S. ^{1}H-NMR of **N-OK(TFA)** in $CDCl_3$ (15% vol. TFA added).

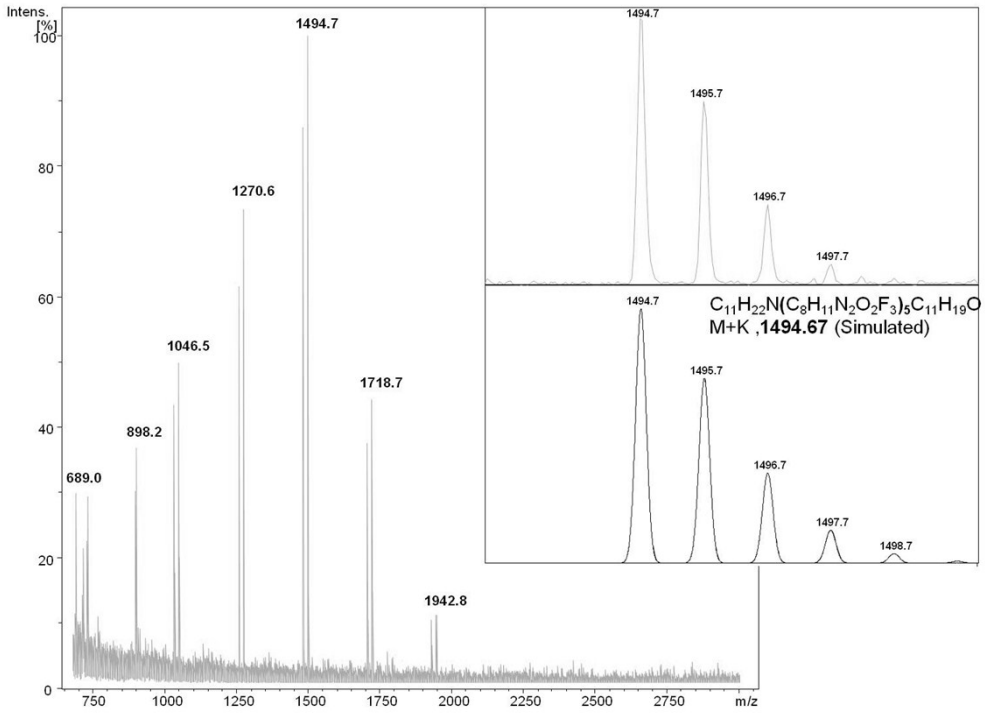


Figure 17S. MALDI-ToF MS of **N-OK(TFA)**.

8. Preparative GPC analyses of N-OK(Z)

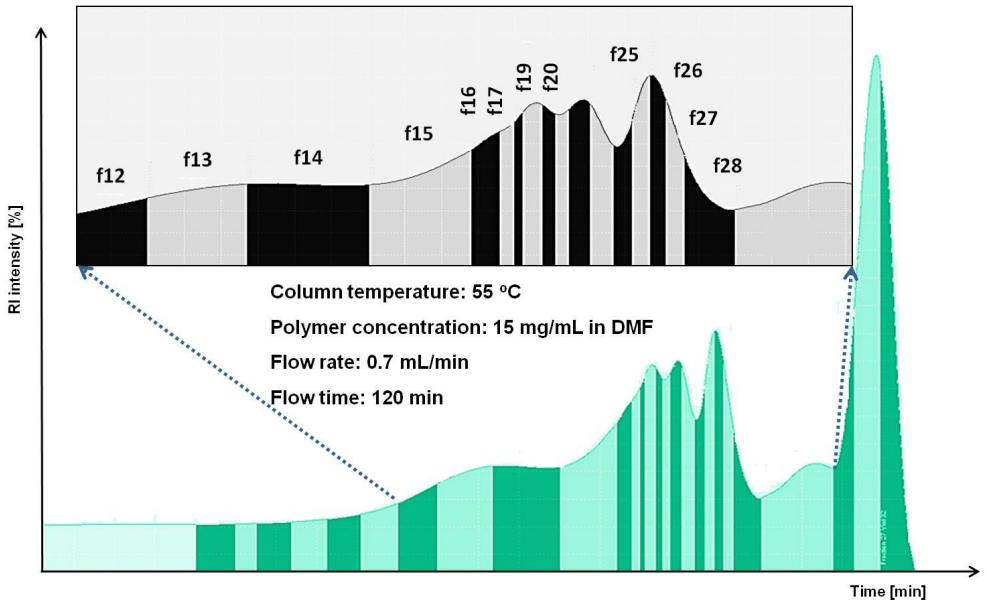


Figure 18S. Preparative GPC trace of **N-OK(Z)** along with the selected fractions.

9. MALDI-ToF analyses of fractions of N-OK(Z)

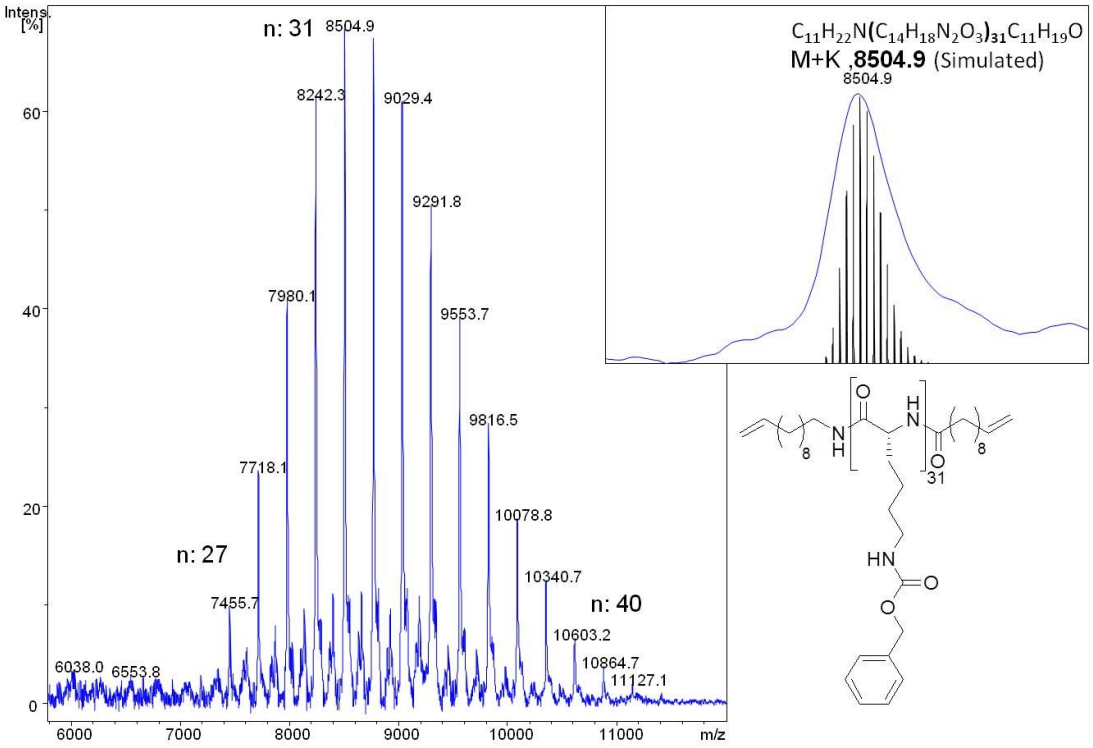


Figure 19S. MALDI-ToF MS of fraction of N-OK(Z), **f12**.

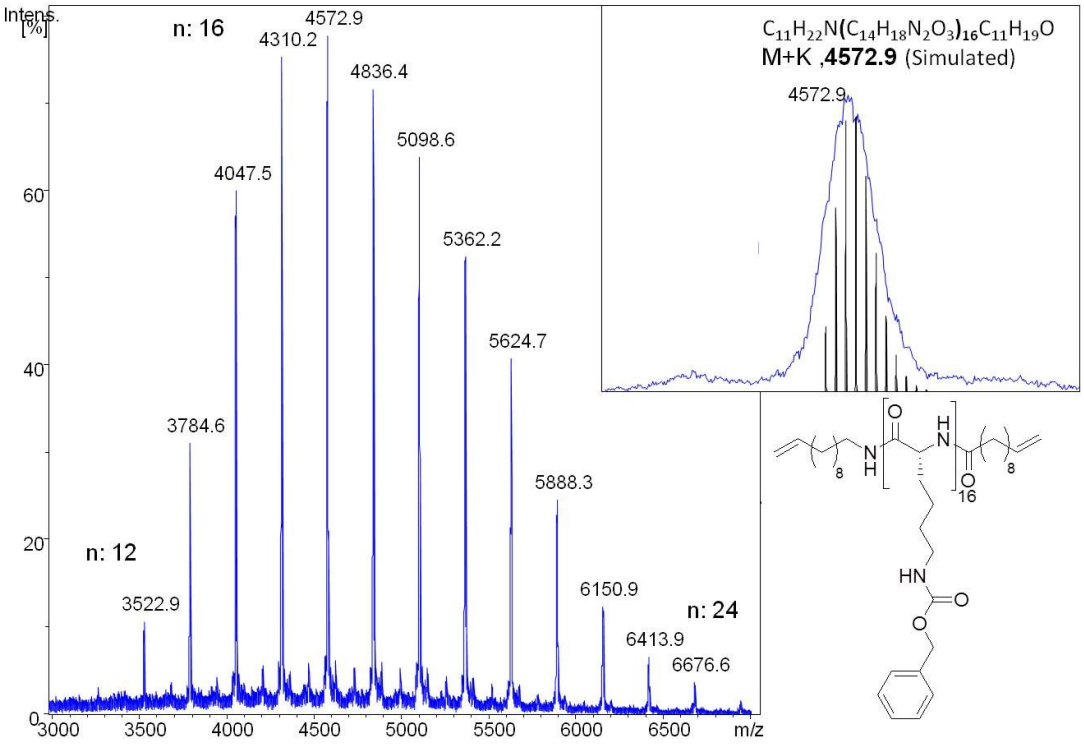


Figure 20S. MALDI-ToF MS of fraction of N-OK(Z), **f14**.

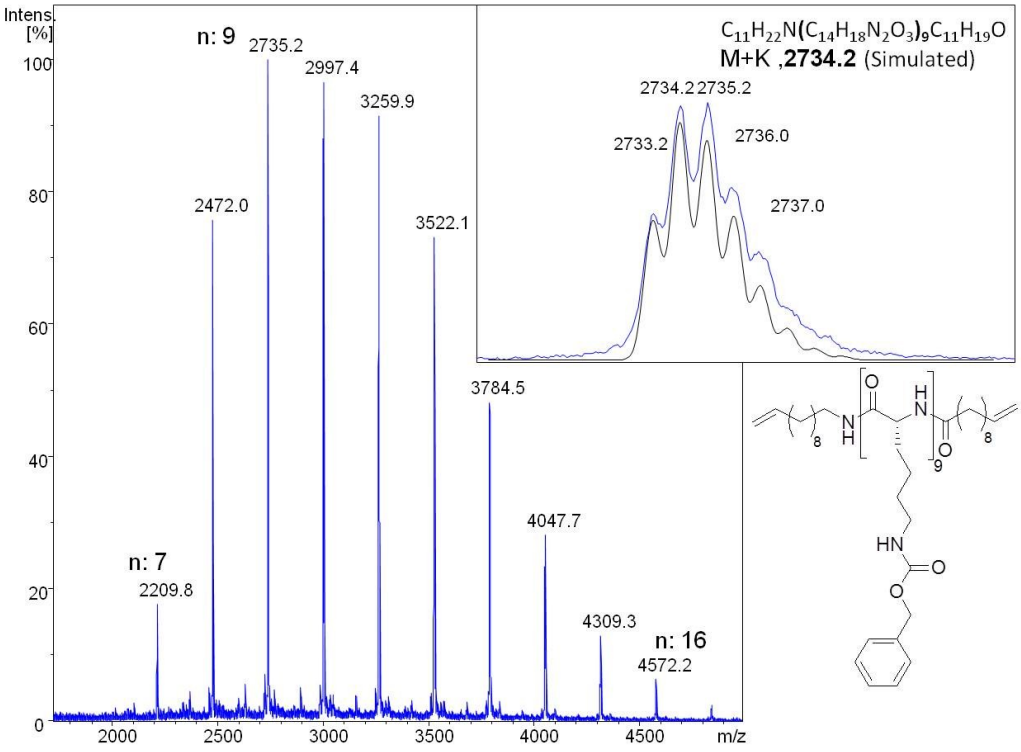


Figure 21S. MALDI-ToF MS of fraction of N-OK(Z), **f15**.

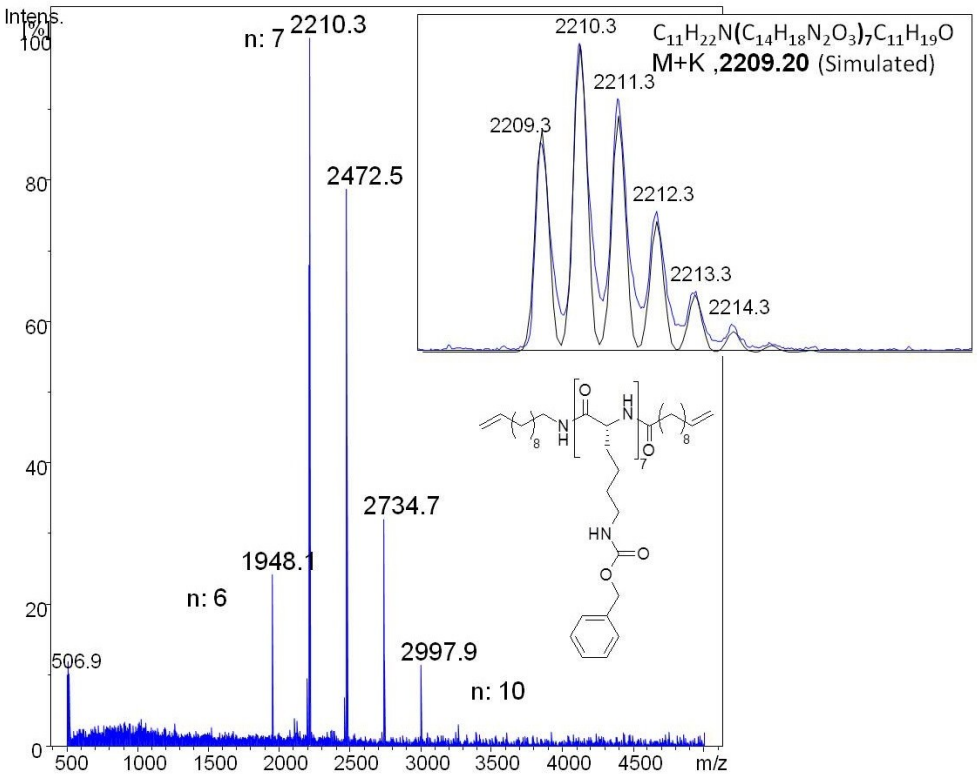


Figure 22S. MALDI-ToF MS of fraction of N-OK(Z), **f16**.

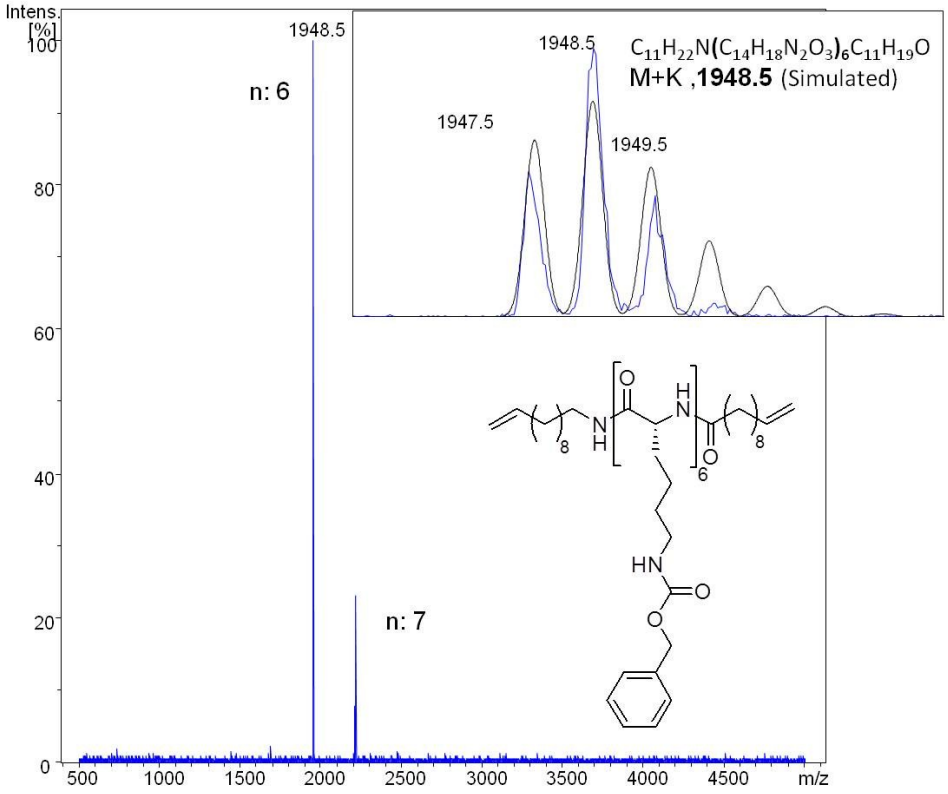


Figure 23S. MALDI-ToF MS of fraction of N-OK(Z), **f19**.

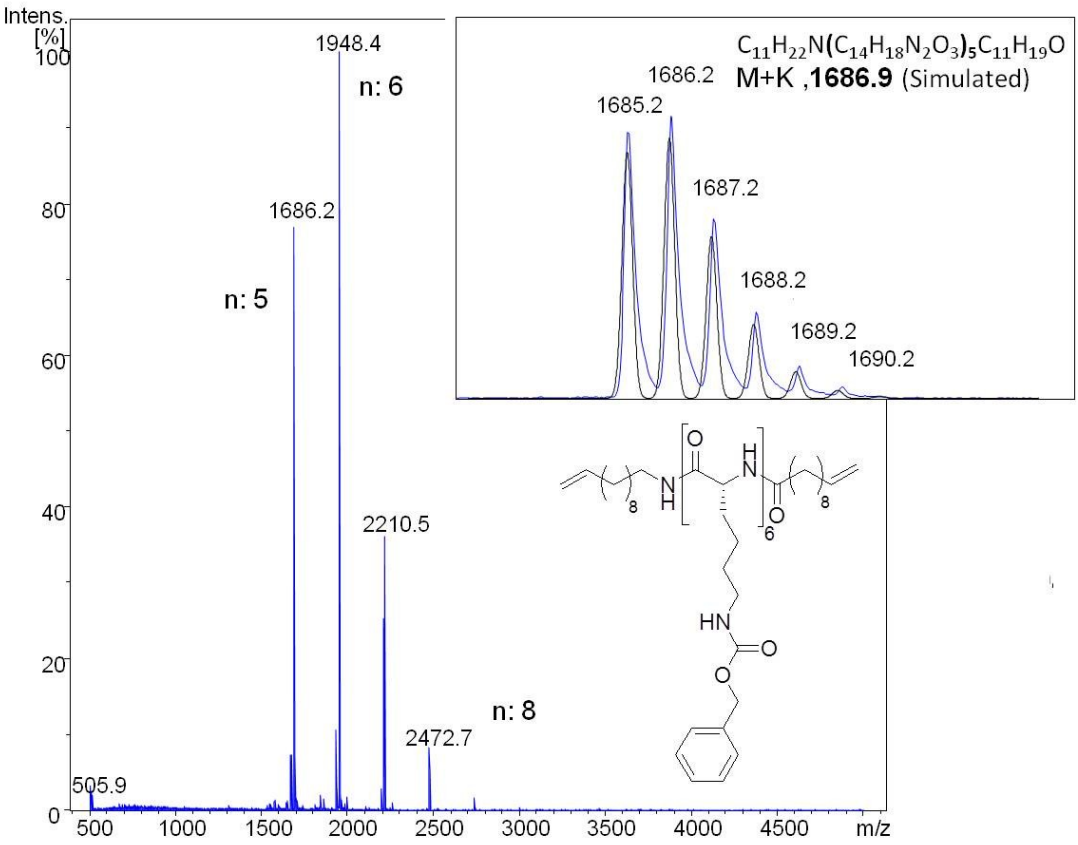


Figure 24S. MALDI-ToF MS of fraction of N-OK(Z), **f20**.

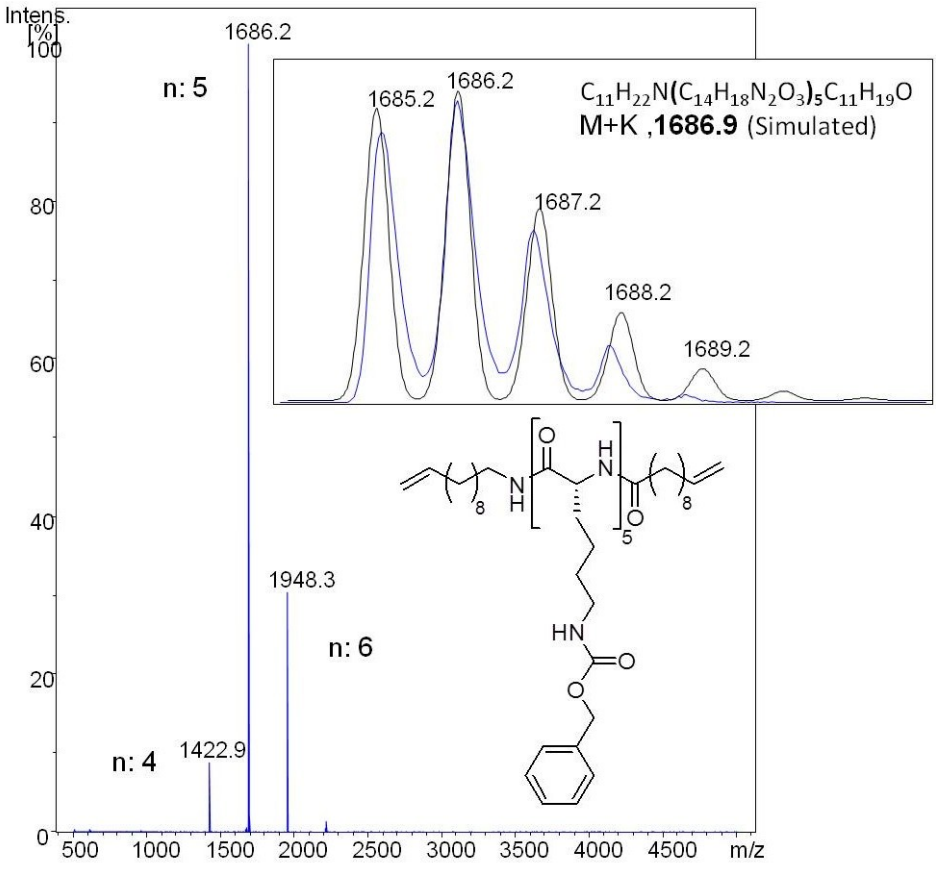


Figure 25S. MALDI-ToF MS of fraction of N-OK(Z), **f22**.

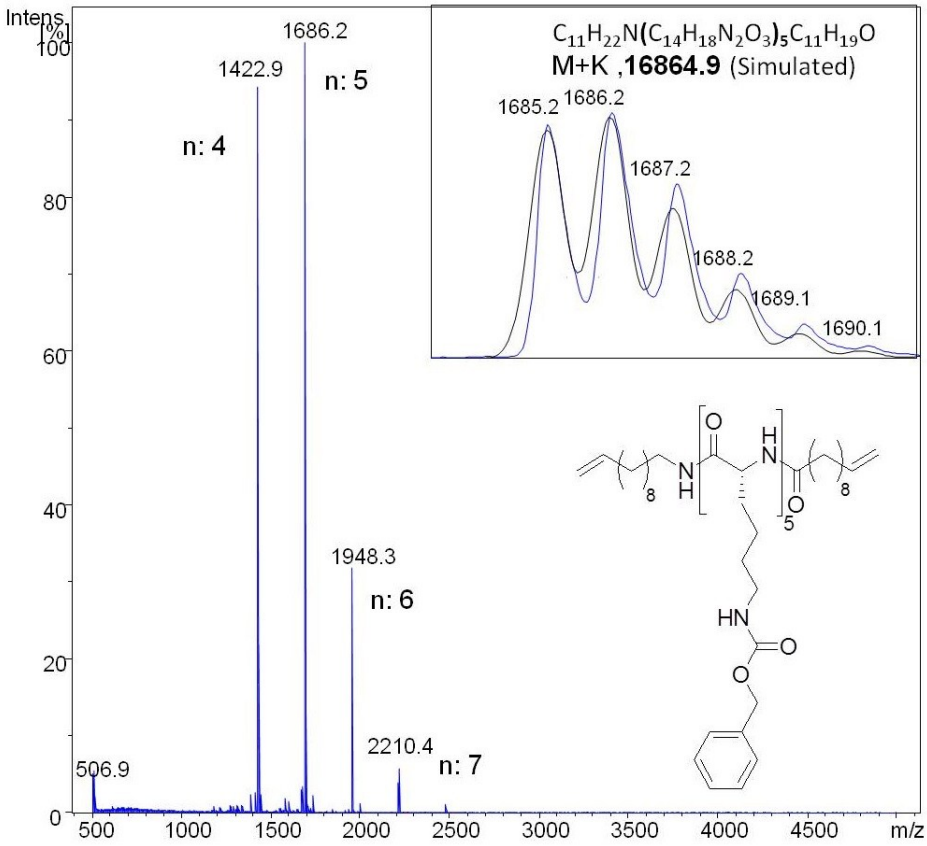


Figure 26S. MALDI-ToF MS of fraction of N-OK(Z), **f23**.

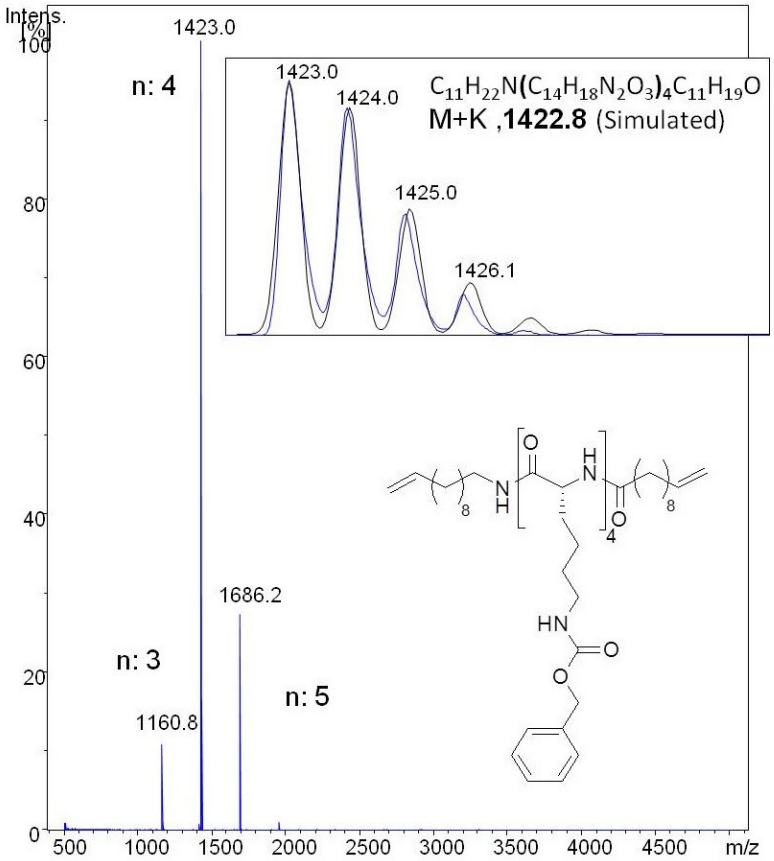


Figure 27S. MALDI-ToF MS of fraction of N-OK(Z), **f25**.

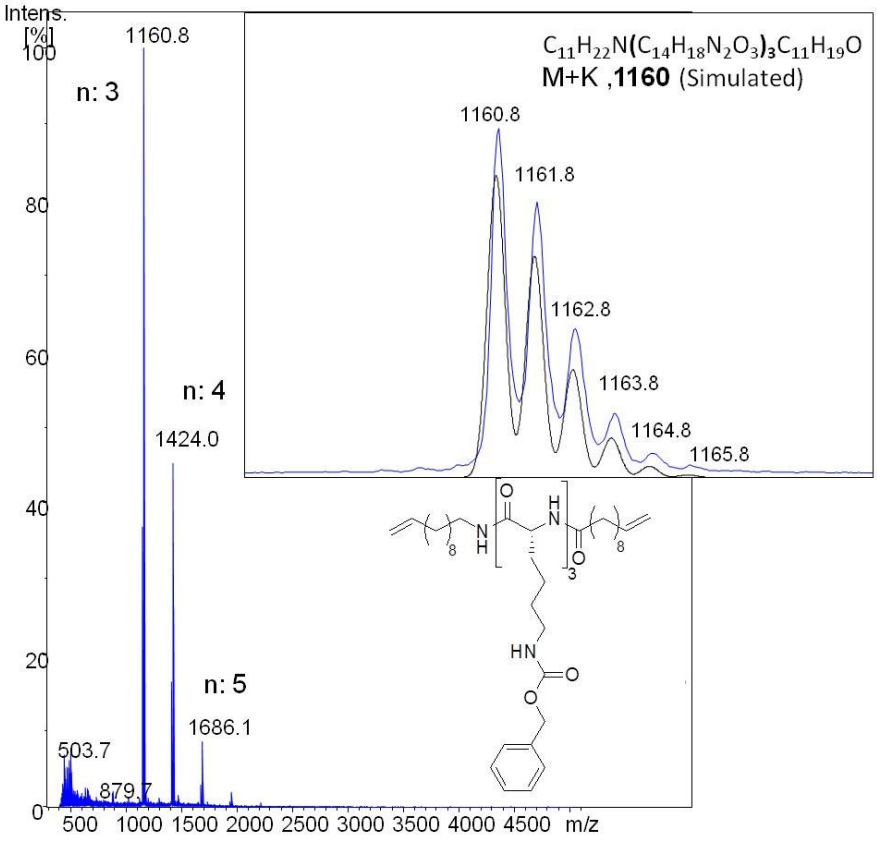


Figure 28S. MALDI-ToF MS of fraction of N-OK(Z), **f27**.

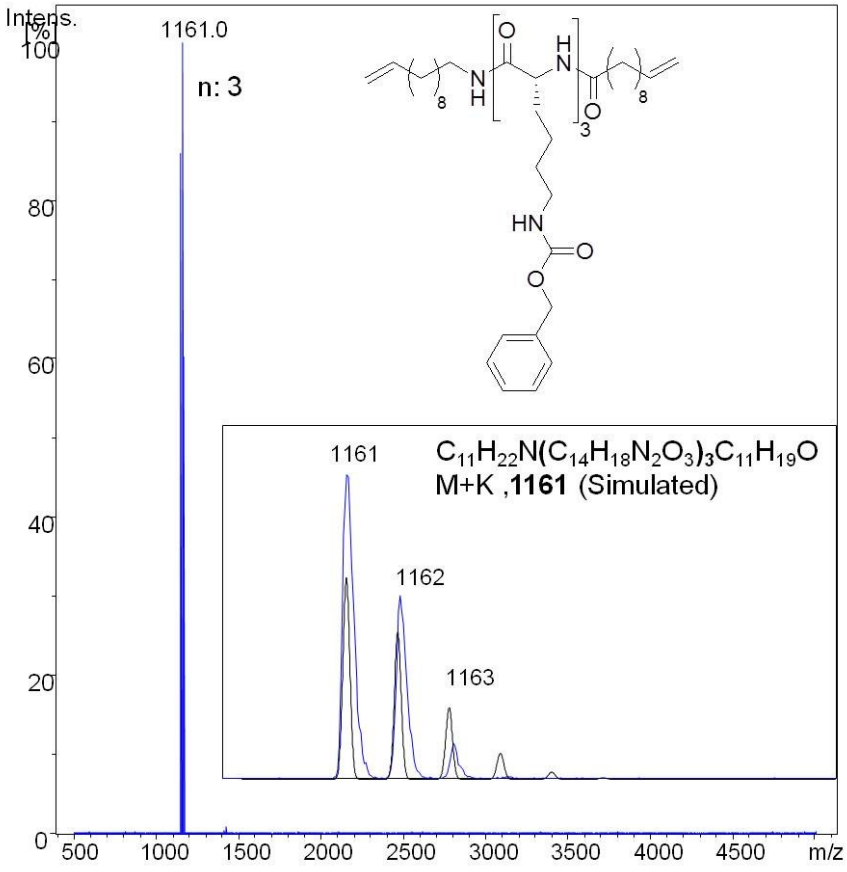


Figure 29S. MALDI-ToF MS of fraction of N-OK(Z), **f28**.

10. Preparative GPC analyses of N-OK(TFA)

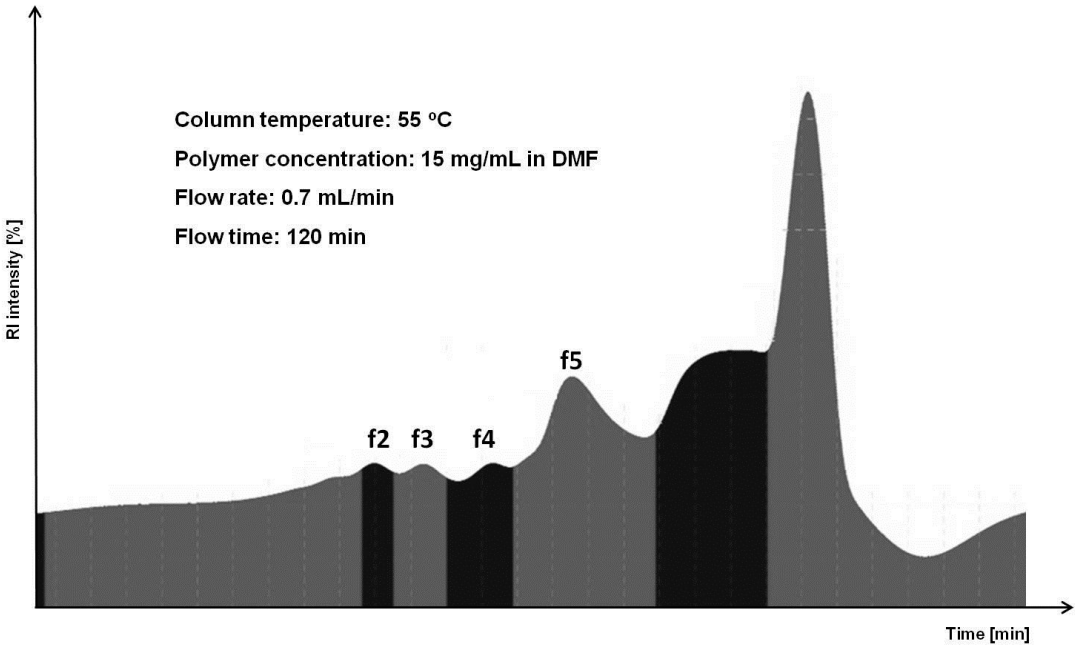


Figure 30S. Preparative GPC trace of **N-OK(TFA)** along with the selected fractions.

11. MALDI-ToF analyses of fractions of N-OK(TFA)

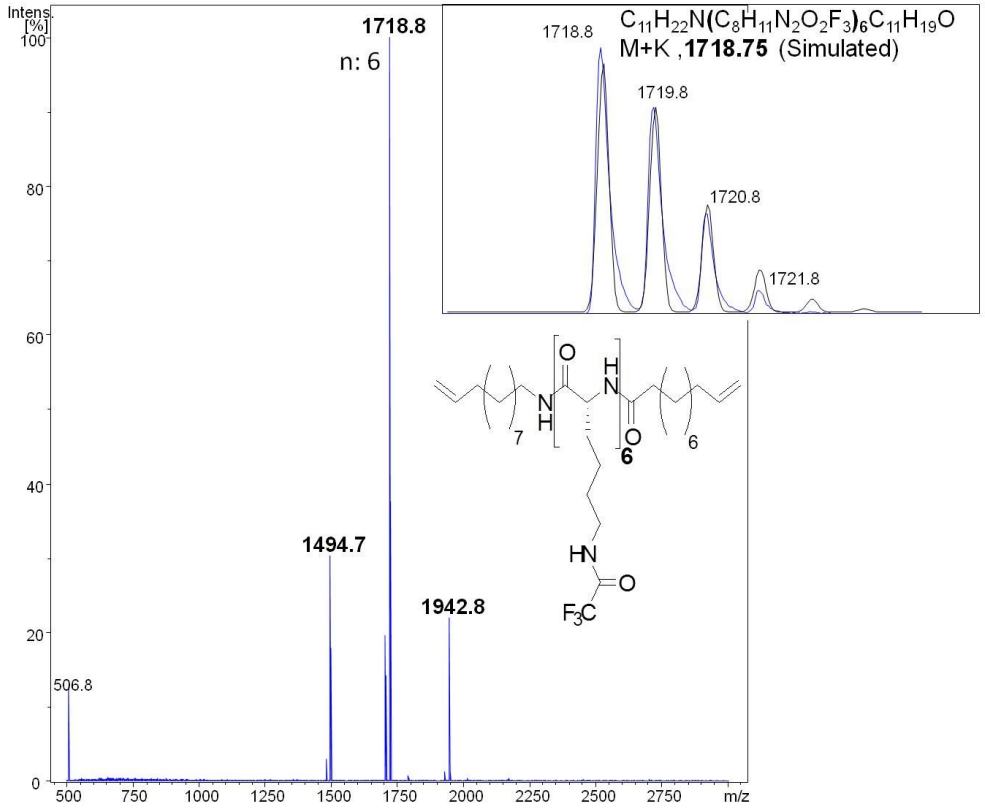


Figure 31S. MALDI-ToF MS of fraction of N-OK(TFA), **f2**.

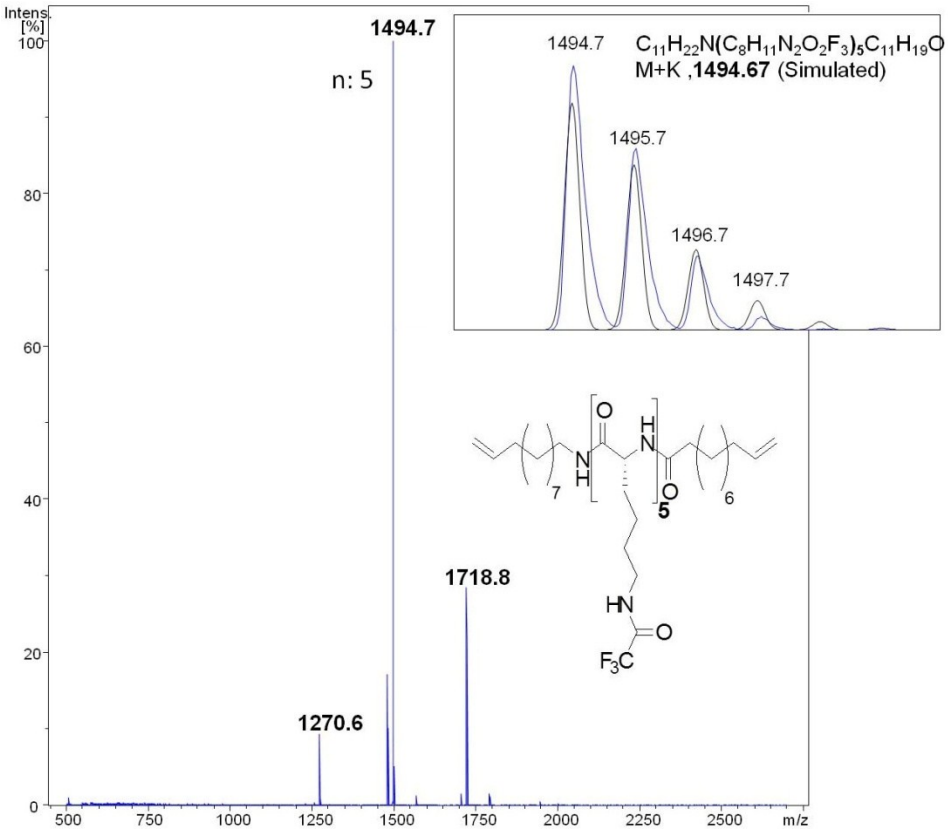


Figure 32S. MALDI-ToF MS of fraction of N-OK(TFA), **f3**.

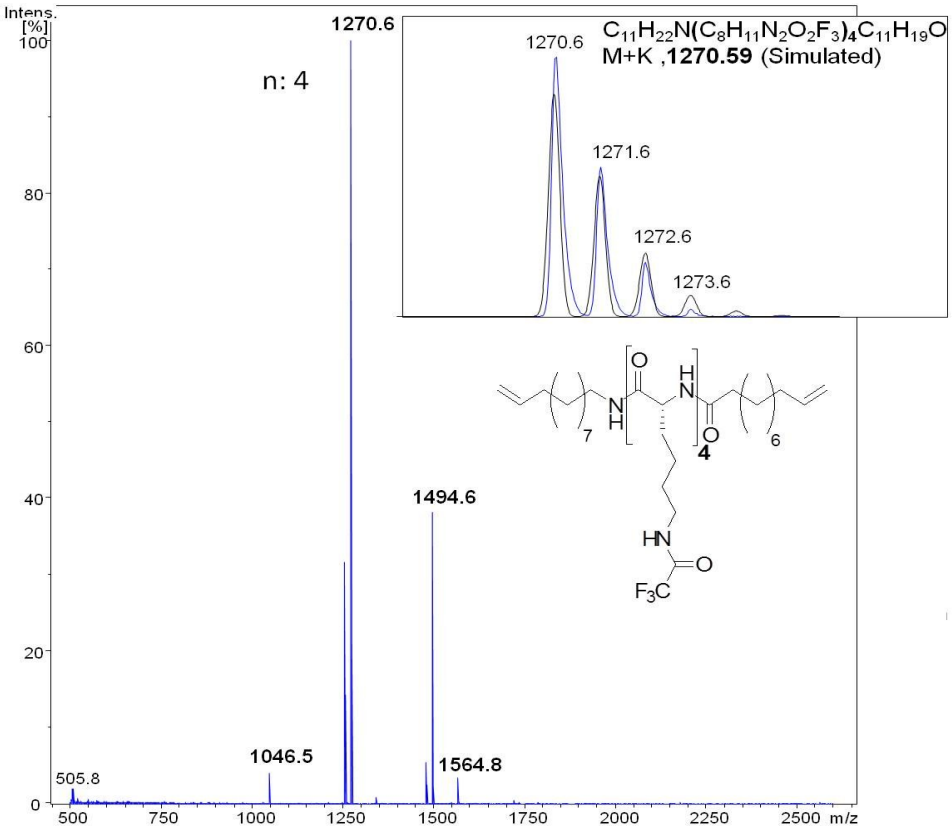


Figure 33S. MALDI-ToF MS of fraction of N-OK(TFA), **f4**.

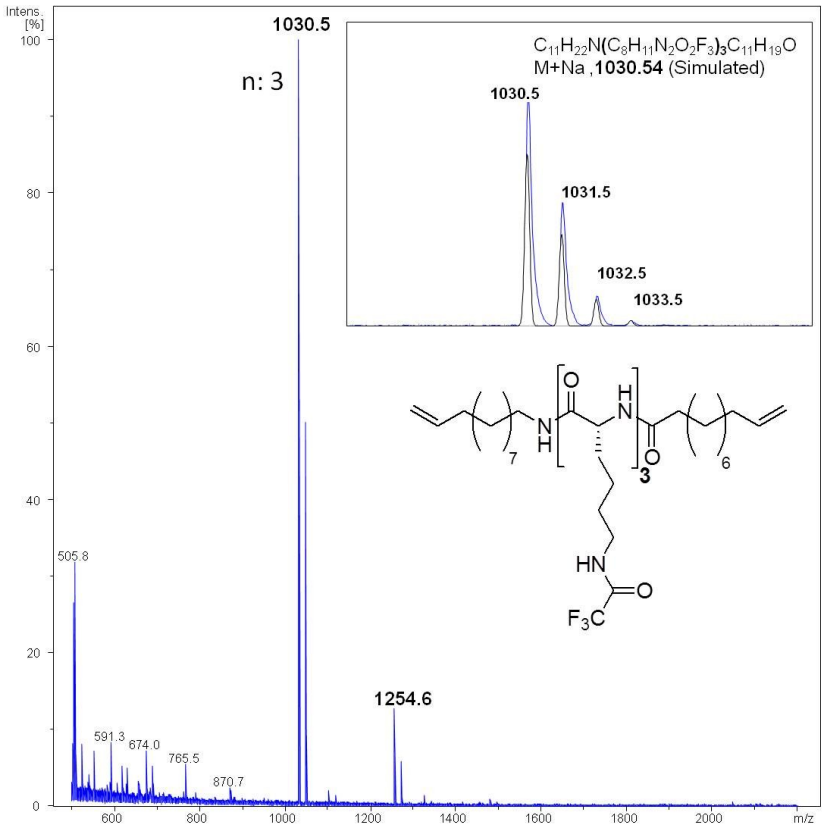


Figure 34S. MALDI-ToF MS of fraction of N-OK(TFA), **f5**.

12. ^{1}H-NMR analysis of fraction of N-OK(TFA)

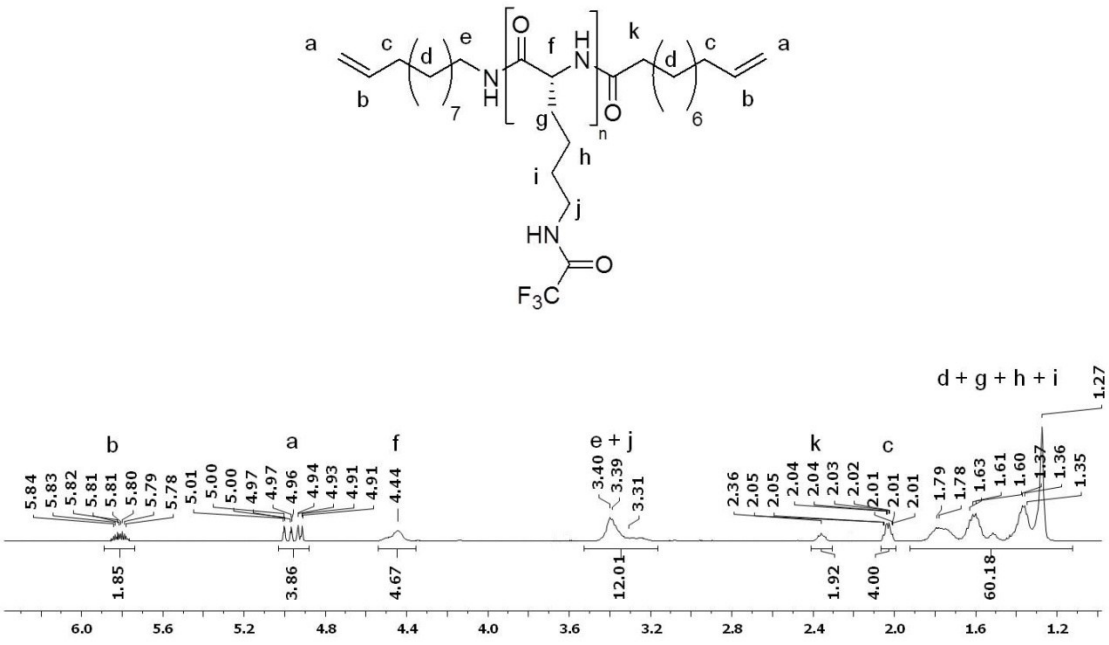


Figure 35S. ^{1}H-NMR of fraction of N-OK(TFA), **f3** in $CDCl_3$ (15% vol. TFA).

13. CD spectroscopy analyses of oligomers

The measured CD data were reported as ellipticity (ϑ) [mdeg]. The molar ellipticity ([ϑ]) [deg cm^2 dmol^{-1}], was obtained according to the Equation 1S stated below:

$$[\Theta] = \frac{\Theta \text{ x } M_{\text{repeating unit}}}{10 \text{ x } c \text{ x } l} \quad [\text{deg cm}^2\,\text{dmol}^{-1}] \qquad \textbf{(Equation 1S)}$$

where, c is the concentration of the sample polymer (mg/mL), l is the UV-cuvette cell diameter (0.1 cm) and $M_{\text{repeating unit}}$ is the molecular weight of the repeating unit of the polymer (g/mol).

The percentage values of the α-helicity of the samples were calculated with Equation 1.

14. TEM analyses of various samples

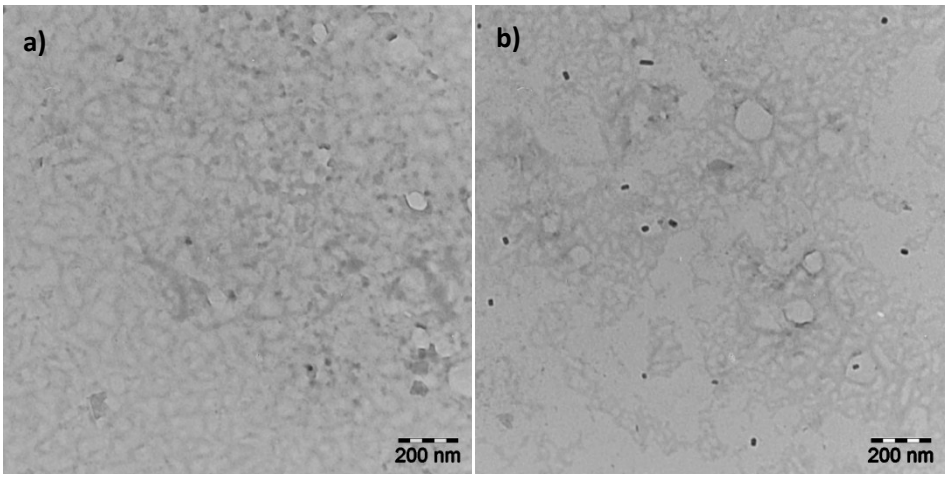


Figure 36S. TEM images of **N-OK(Z)-2** a) in TFE and b) in HFIP.

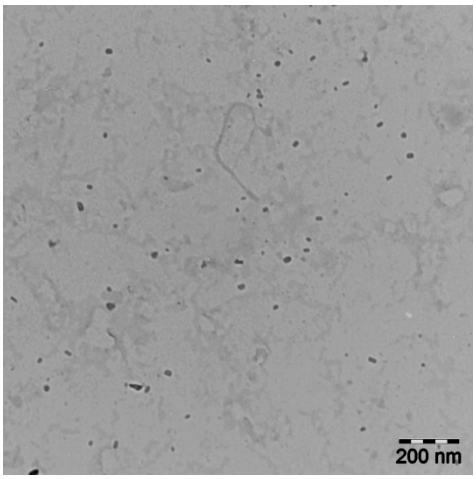


Figure 37S. TEM image of **f19** in HFIP.

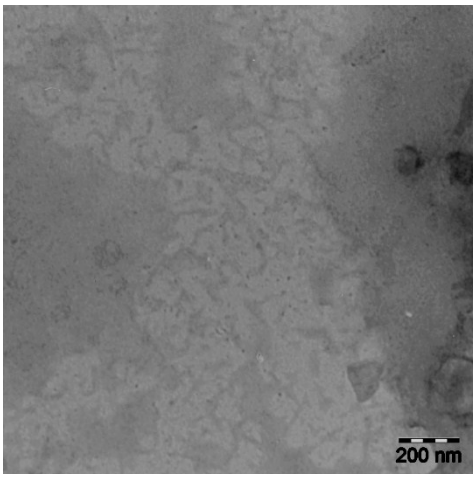


Figure 38S. TEM image of **f14** in TFE.

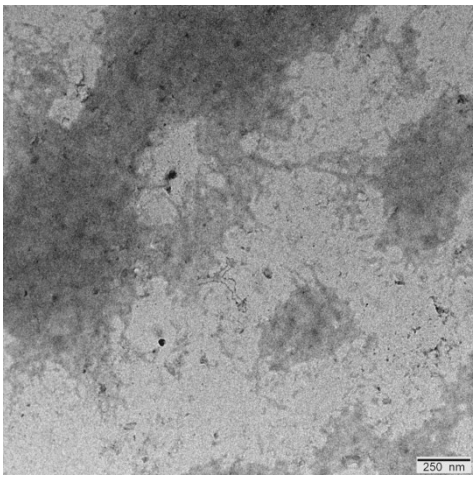


Figure 39S. TEM image of **f15** in TFE.

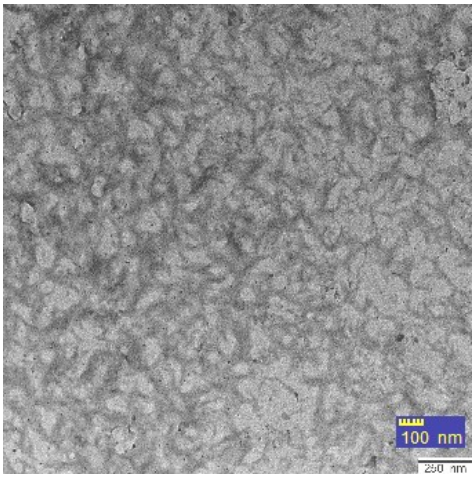


Figure 40S. TEM image of **f25** in TFE.