Electronic Supplementary Information

Side Chain Modification of π-Stacked Helical Poly(quinoline-2,3-diylmethylene) via Thiol-Ene Reaction

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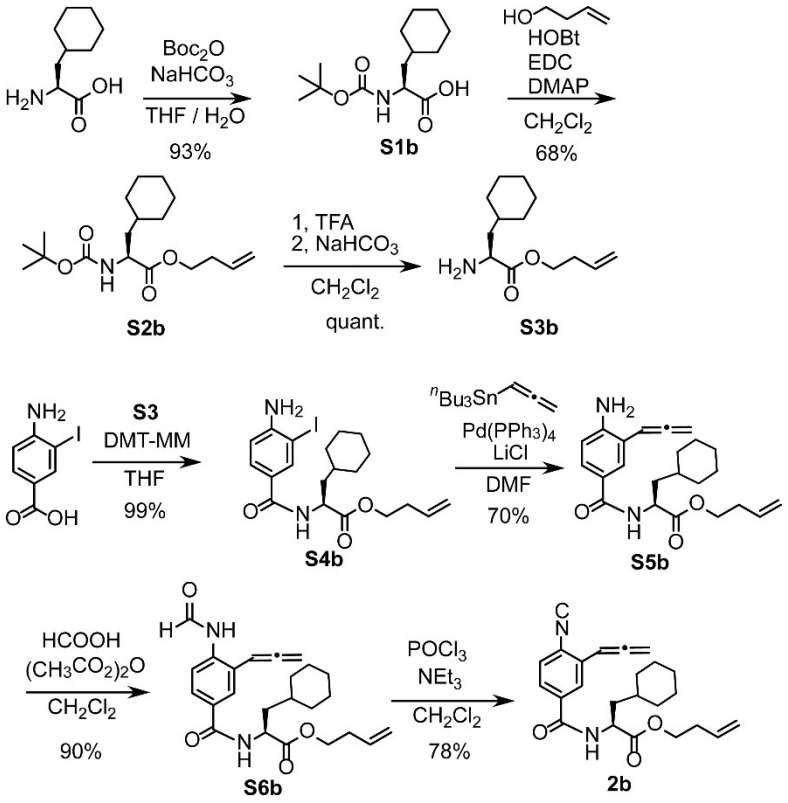
1. Experimental Section

General procedure

All reactions were carried out under an Ar atmosphere using the Schlenk technique, whereas the work-up was performed in air. ^{1}H and ^{13}C NMR spectra were recorded on, JEOL JNM-ECS400 and JNM-ECA500 spectrometers using $SiMe_4$ as an internal standard. The number-average molar mass (M_n) and and the molar mass dispersity (M_w/M_n) of the polymers were determined at 40 °C by size exclusion chromatography (SEC) using a SHIMADZU LC-10AS, SPD-10A UV-vis detector, and CTO-10A column oven equipped with two SEC columns SHODEX GPC KF-805L using THF as an eluent, and calibrated against standard PS samples. CD spectra were obtained by JASCO J-720WO. UV-vis spectra were obtained by SHIMADZU UV 3100PC.

Synthesis procedure 2b



Synthesis of S1b. To a solution of L-cyclohexylalanine (4.90 g, 28.6 mmol) in a mixture of water and THF (140 mL, 1:1 ratio), sodium bicarbonate ($NaHCO_3$) (7.26 g, 86.4 mmol) and di-tert-butyl dicarbonate (7.51 g, 34.0 mmol) were added at 0 °C. After stirring for 30 minutes, the reaction mixture was allowed to warm to room temperature and was stirred overnight. Water (100 mL) was then added to dissolve any precipitates. Unreacted di-tert-butyl dicarbonate was extracted three times with petroleum ether. The aqueous phase containing the *N*-Boc-protected amino acid was acidified with 1 M potassium hydrogen sulfate until pH 3 was reached and then extracted three times with ethyl acetate. The organic layers were combined and dried over sodium sulfate. After removal of the solvent under reduced pressure, a transparent oil was obtained (7.19 g, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 6.18-5.00 (m, 1H, -CO-N*H*-), 4.30 (q, *J* = 5.9Hz, 1H, C*H*CH_2CH_2) 1.85–1.60 (m, 6H, CHCH_2-Cy-*H*), 1.55–1.35 (m, 10H, Cy-*H*), 1.31–1.10 (m, 4H, Cy-*H*), 1.05–0.86 (m, 2H, Cy-*H*).

Synthesis of S2b. To a solution of **S1b** (7.19 g, 26.5 mmol) cooled to 0 °C in dichloromethane (40 mL), 1-hydroxybenzotriazole (HOBt) (3.93 g, 29.1 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (7.62 g, 40.1 mmol), and 4-dimethylaminopyridine (205 mg, 2.25 mmol) were added. After stirring for 5 minutes, 3-buten-1-ol (2.95 g, 41.0 mmol) was slowly added. The mixture was then allowed to warm to room temperature and stirred overnight. The reaction was quenched with saturated aqueous sodium bicarbonate and extracted with dichloromethane. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, then dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified using silica gel column chromatography, eluting with a mixture of *n*-hexane and ethyl acetate, to yield a transparent oil (5.83 g, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 5.76 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H, C*H*=CH_2), 5.15–5.02 (m, 2H, CH=CH_2), 4.84 (br, 1H, CON*H*), 4.31 (q, *J* = 6.7 Hz, 1H, C*H*CH_2CH_2), 4.24–4.06 (m, 2H, OCH_2), 2.44–2.32 (m, 2H, OCH_2CH_2), 1.78 (d, *J* = 13.0 Hz, 1H, Cy-*H*), 1.73–1.55 (m, 6H), 1.43 (s, 9H), 1.31–1.05 (m, 4H), 0.99–0.81 (m, 2H).

Synthesis of S3b. To a solution of **S2b** (5.83 g, 17.9 mmol) in dichloromethane (100 mL) cooled to 0 °C, trifluoroacetic acid (24 mL, 317 mmol) was added. The reaction mixture was stirred at room temperature for 1.5 hours, after which the mixture was co-distilled with dichloromethane 4-5 times under reduced pressure. The residue was extracted with saturated aqueous sodium bicarbonate and dichloromethane. The organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure to yield a yellow oil (6.00 g, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 5.73 (ddt, *J* = 17.1, 10.3, 6.7 Hz, 1H, C*H*═CH_2), 5.19–5.09 (m, 1H, CH═CH_2), 5.09 (t, *J* = 1.5 Hz, 1H, CH═CH_2), 4.34–4.17 (m, 2H, OCH_2), 4.06 (t, *J* = 6.7 Hz, 1H, C*H*CH_2CH_2), 2.42 (qt, *J* = 6.7, 1.4 Hz, 2H, OCH_2CH_2), 1.85–1.64 (m, 7H, Cy-*H*) , 1.43–1.35 (m, 1H, Cy-*H*), 1.31–1.09 (m, 3H, Cy-H), 0.97–0.87 (m, 2H, Cy-*H*).

Synthesis of S4b. To a solution of **S3b** (0.96 g, 3.76 mmol) and 4-amino-3-iodobenzoic acid (1.09 g, 4.14 mmol) in tetrahydrofuran (15 mL), 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (2.08 g, 7.52 mmol) was added. The mixture was stirred at room temperature for 18 hours. Afterward, the mixture was extracted with brine and ethyl acetate. The organic layer was washed with saturated aqueous sodium bicarbonate and brine, then dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was redissolved in diethyl ether and filtered to remove any white precipitate. The filtrate was then concentrated under reduced pressure to yield a red-brown oil (1.77 g, 99% yield).

Synthesis of S5b. To a solution of **S4b** (6.00 g, 12.8 mmol) and lithium chloride (1.00 g, 24.0 mmol) in *N*,*N*-dimethylformamide (30 mL), bis(triphenylphosphine)palladium dichloride (268 mg, 0.38 mmol) and allenyltributyltin (4.95 g, 15.0 mmol) were added. The mixture was stirred at 50 °C for 18 hours. Afterward, the reaction mixture was diluted with ethyl acetate (30 mL) and quenched with aqueous potassium fluoride (KF aq.) (5 g in 180 mL water). The precipitate was removed by filtration through a Celite pad, and the aqueous layer was extracted with ethyl acetate. The organic extracts were washed with brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography, eluting with a mixture of *n*-hexane and ethyl acetate (5:1 ratio), to yield a yellow oil (3.42 g, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 2.2 Hz, 1H, Ar-*H*), 7.47 (dd, *J* = 8.4 Hz, 2.2 Hz, 1H, Ar-*H*), 6.62 (dd, *J* = 8.4, 1.2 Hz, 1H, Ar-*H*), 6.36–6.26 (d, *J* = 8.1 Hz, 1H, N*H* and –C*H*═C═CH_2), 5.77 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H, C*H*=CH_2), 5.20 (d, *J* = 6.7 Hz, 2H, –CH═C═CH_2), 5.16–5.02 (m, 2H, CH=CH_2), 4.82 (td, *J* = 8.4, 5.7Hz, 1H, C*H*CH_2CH_2), 4.59 (s, 2H, NH_2), 4.27–4.10 (m, 2H, OCH_2), 2.40 (dtt, *J* = 8.4, 5.7, 1.2, Hz, 2H, OCH_2CH_2), 1.82 (d, *J* = 12.9 Hz, 1H, Cy-*H*), 1.79–1.54 (m, 5H, Cy-*H*), 1.45–1.32 (m, 1H, Cy-*H*), 1.29–1.16 (m, 4H, Cy-*H*), 1.14–0.97 (m, 2H, Cy-*H*).

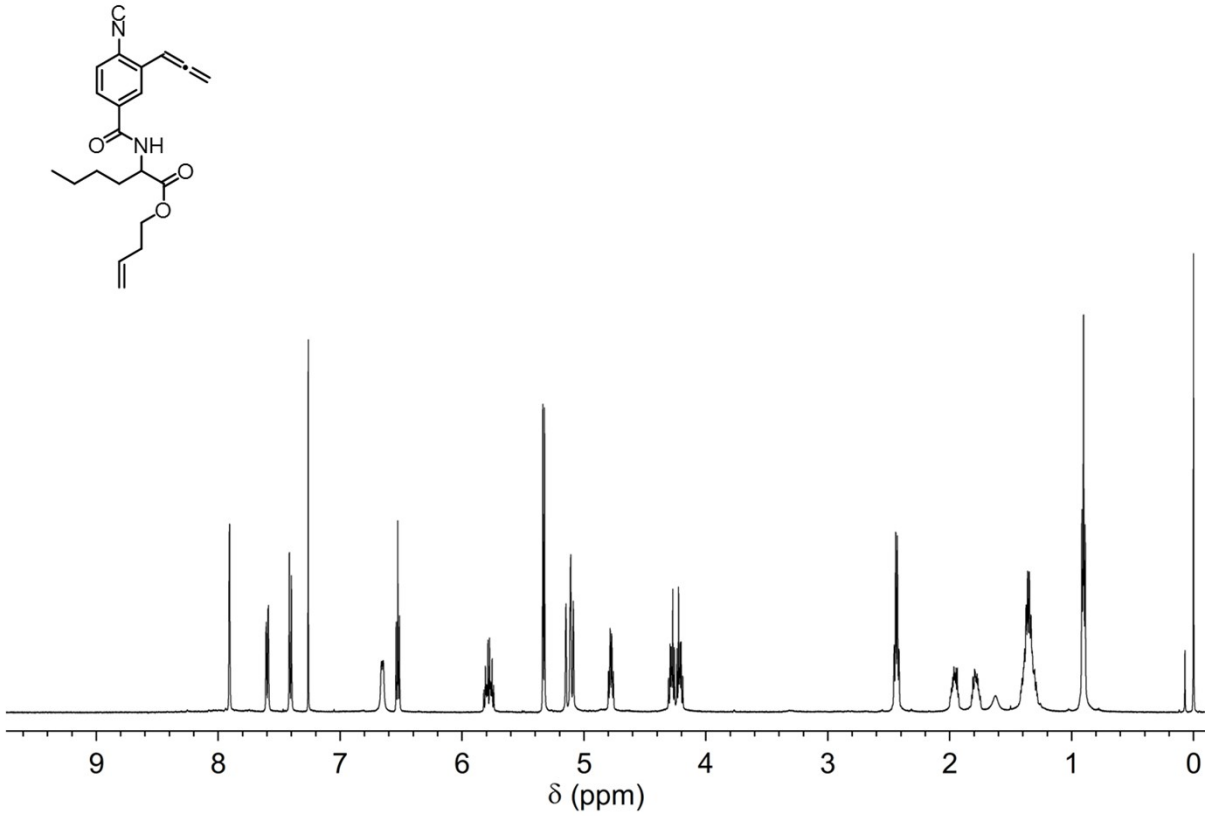
Synthesis of S6. A mixture of formic acid (6.07 mL, 161 mmol) and acetic anhydride (7.61 mL, 80.5 mmol) was heated to 50 °C for 1 hour and then cooled to 0 °C. This mixture was then added to a solution of **S5b** (3.42 g, 8.95 mmol) in dichloromethane (100 mL), which was also maintained at 0 °C. After stirring for 1 hour, the reaction mixture was quenched with saturated aqueous sodium bicarbonate and the aqueous phase was extracted with dichloromethane. The organic extract was washed with saturated aqueous sodium bicarbonate and brine, then dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using a *n*-hexane/ethyl acetate (1:1 ratio) eluent to yield a yellow solid (3.30 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, *J* = 10.9 Hz, 0.5H, NHC*H*O), 8.42 (s, 0.5H, NHC*H*O), 8.26–8.08 (m, 1.0 H, Ar-*H* and N*H*CHO), 7.76–7.67 (m, 1H, Ar-*H*) , 7.65–7.54 (m, 1H, Ar-*H*), 7.22 (d, *J* = 8.4 Hz, 0.5H, Ar-*H*), 6.63 (s, 1H, N*H*), 6.34–6024 (m, 1H, –C*H*═C═CH_2), 5.76 (ddt, *J* = 17.0, 10.2, 6.7, 1H, C*H*=CH_2), 5.30–5.20 (m, 2H, – CH═C═CH_2), 5.15–5.03 (m, 2H, CH=CH_2), 4.81 (q, *J* = 8.5 Hz, 1H, C*H*CH_2CH_2), 4.19 (qt, *J* = 10.2, 5.2 Hz, 2H, OCH_2), 2.40 (q, *J* = 6.7 Hz, 2H, OCH_2CH_2), 2.02–1.57 (m, 7H, Cy-*H*), 1.42–1.33 (m, 1H, Cy-*H*), 1.25–1.10 (m, 3H, Cy-*H*), 1.01–0.87 (t, *J* = 6.8Hz, 2H, Cy-*H*).

Synthesis of monomer 2b. To a solution of **S6b** (473 mg, 1.1 mmol) in dichloromethane (10 mL), trimethylamine (0.5 mL, 3.7 mmol) and phosphoryl chloride (0.21 mL, 2.2 mmol) were added at 0 °C. After stirring for 15 minutes, the reaction mixture was quenched with saturated aqueous sodium bicarbonate. The organic layer was then washed twice with brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using a *n*-hexane/ethyl acetate (4:1 ratio) eluent to yield a yellow solid (336.8 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 1.9 Hz, 1H, Ar-*H*), 7.58 (dd, *J* = 8.3 Hz, 2.0

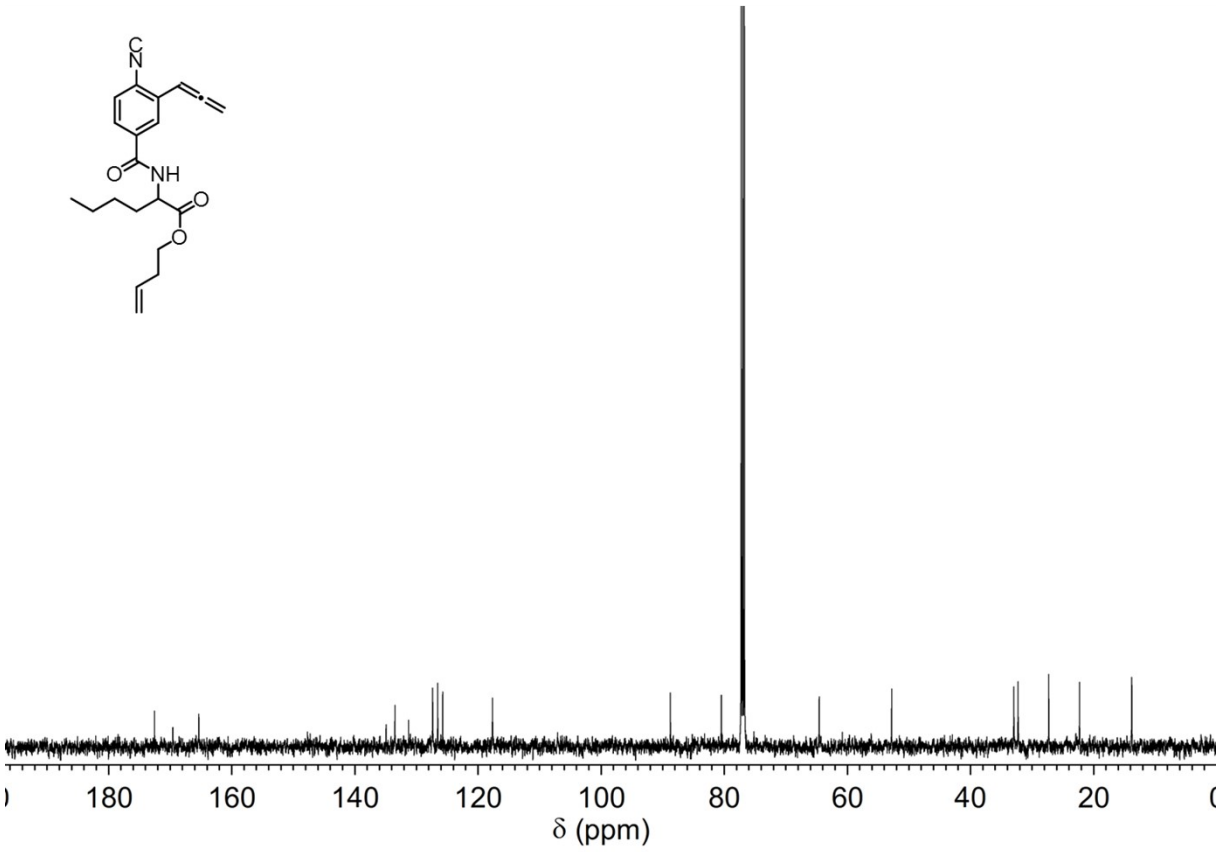
Hz, 1H, Ar-*H*), 7.40 (d, *J* = 8.3 Hz, 1H, Ar-*H*), 6.56–6.46 (m, 2H, N*H* and –C*H*═C═CH_2), 5.77 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H, C*H*=CH_2), 5.35–5.26 (m, 2H, – CH═C═CH_2), 5.17–5.04 (m, 2H, CH=CH_2), 4.81 (td, *J* = 8.3, 5.7 Hz, 1H, C*H*CH_2CH_2), 4.30–4.11 (m, 2H, OCH_2), 2.42 (qt, *J* = 6.7, 1.4 Hz, 2H, OCH_2CH_2), 1.86–1.59 (m, 7H, Cy-*H*), 1.41–1.59 (m, 1H, Cy-*H*), 1.29–1.09 (m, 3H, Cy-*H*), 1.02–0.88 (m, 2H, Cy-*H*).

2. NMR Analysis

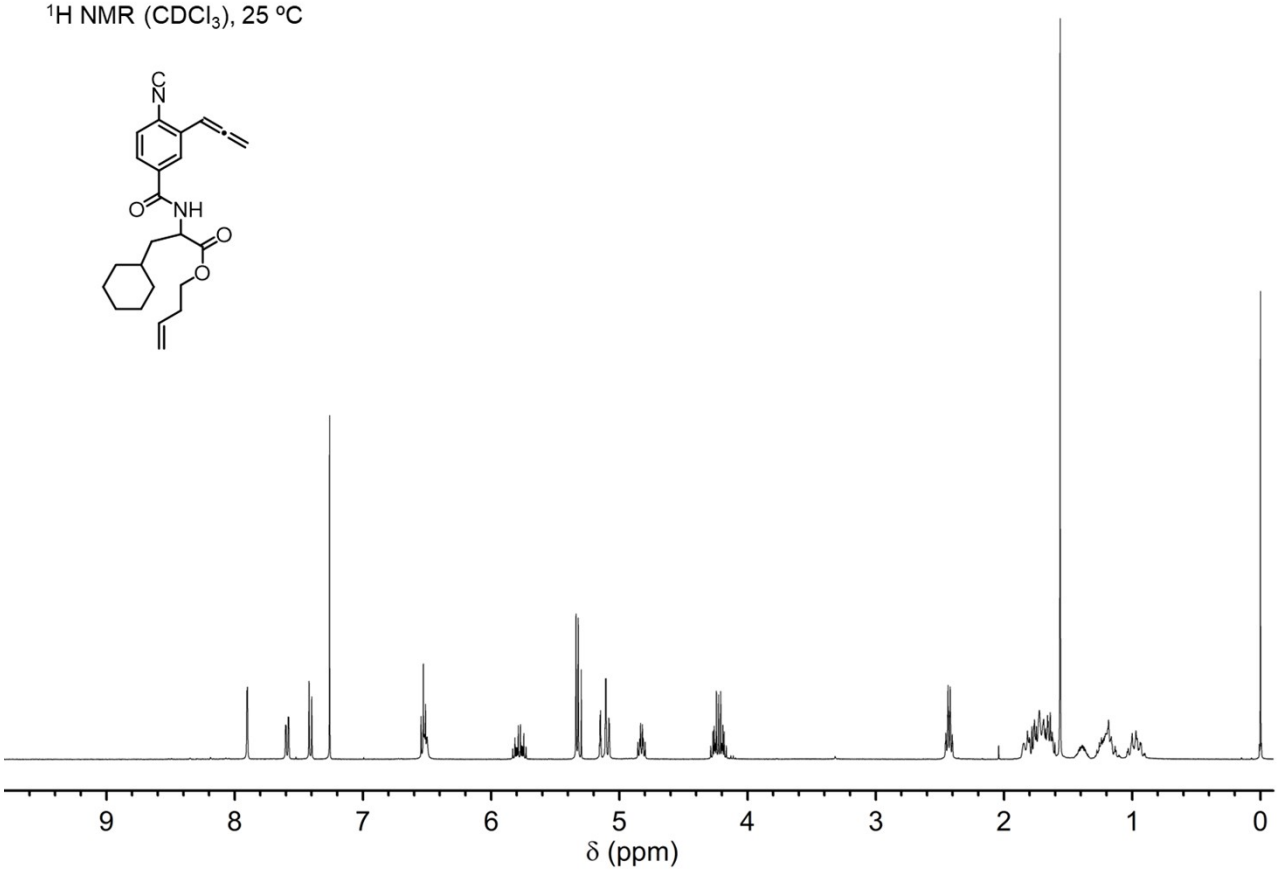
^{1}H NMR ($CDCl_3$), 25 ºC

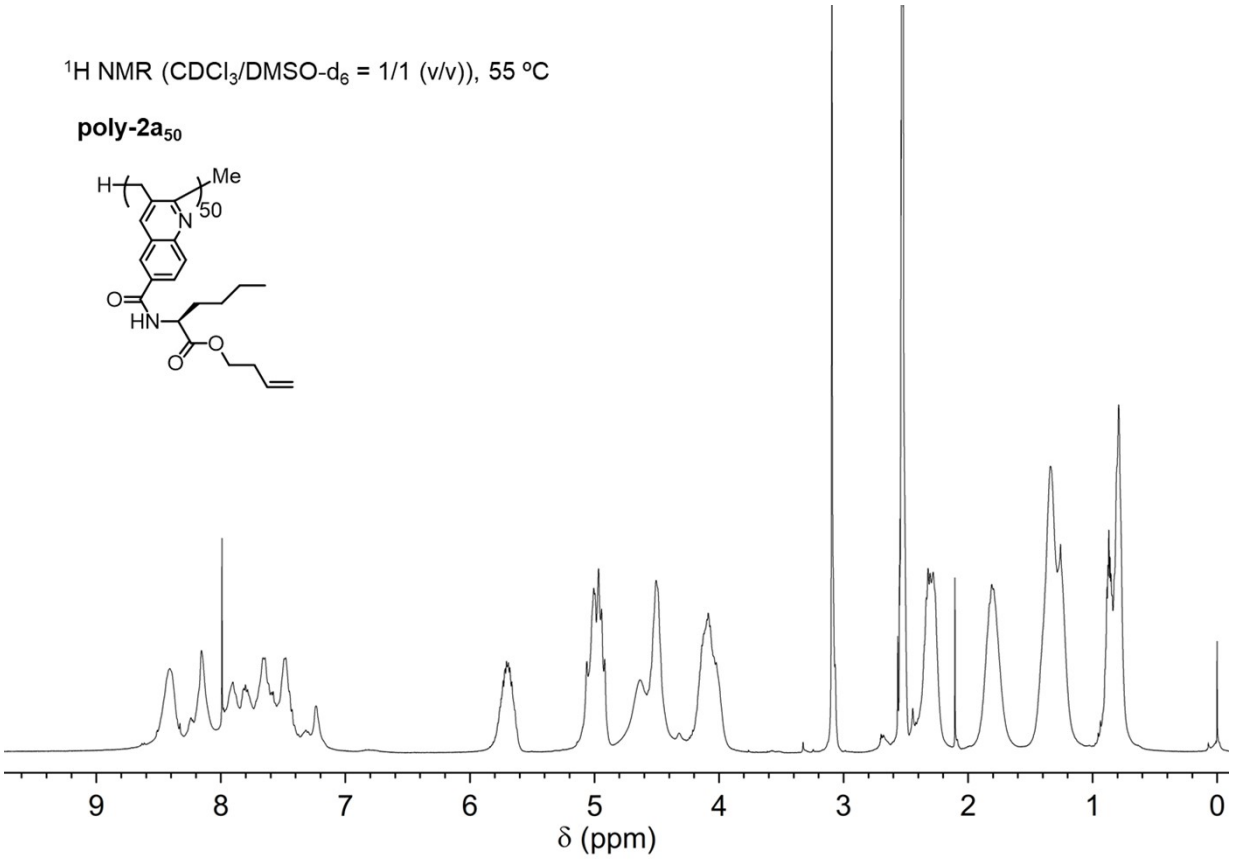


^{13}C NMR ($CDCl_3$), 25 ºC

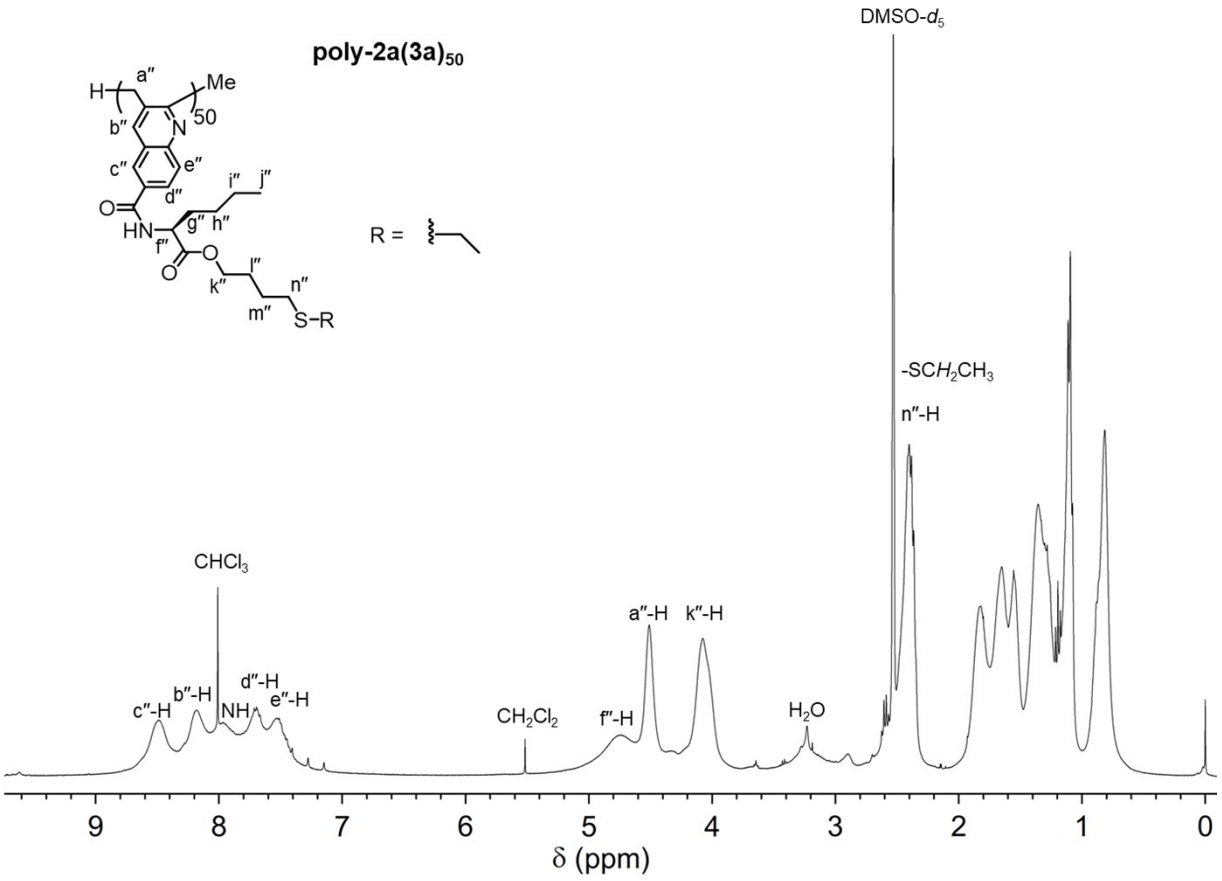


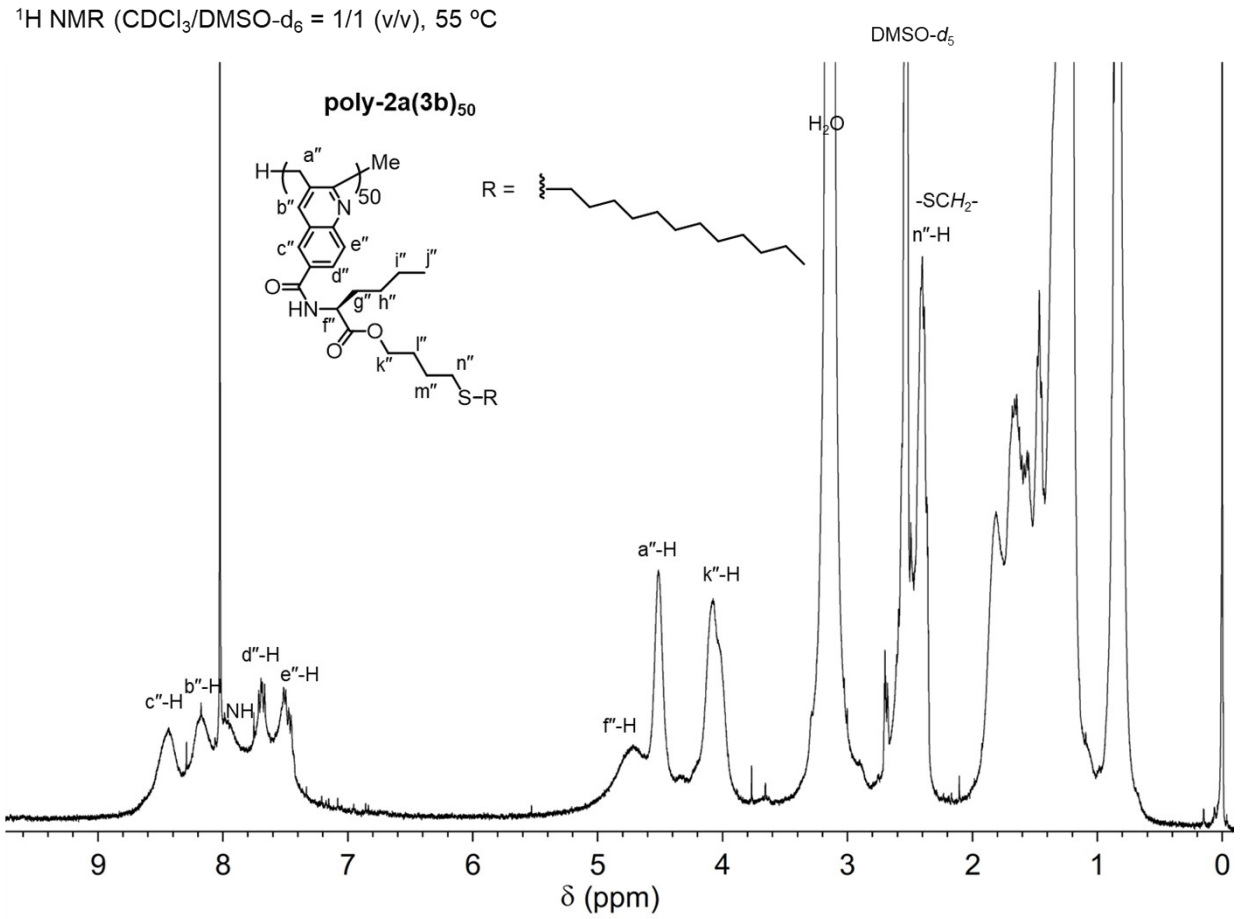
^{1}H NMR ($CDCl_3$), 25 ºC

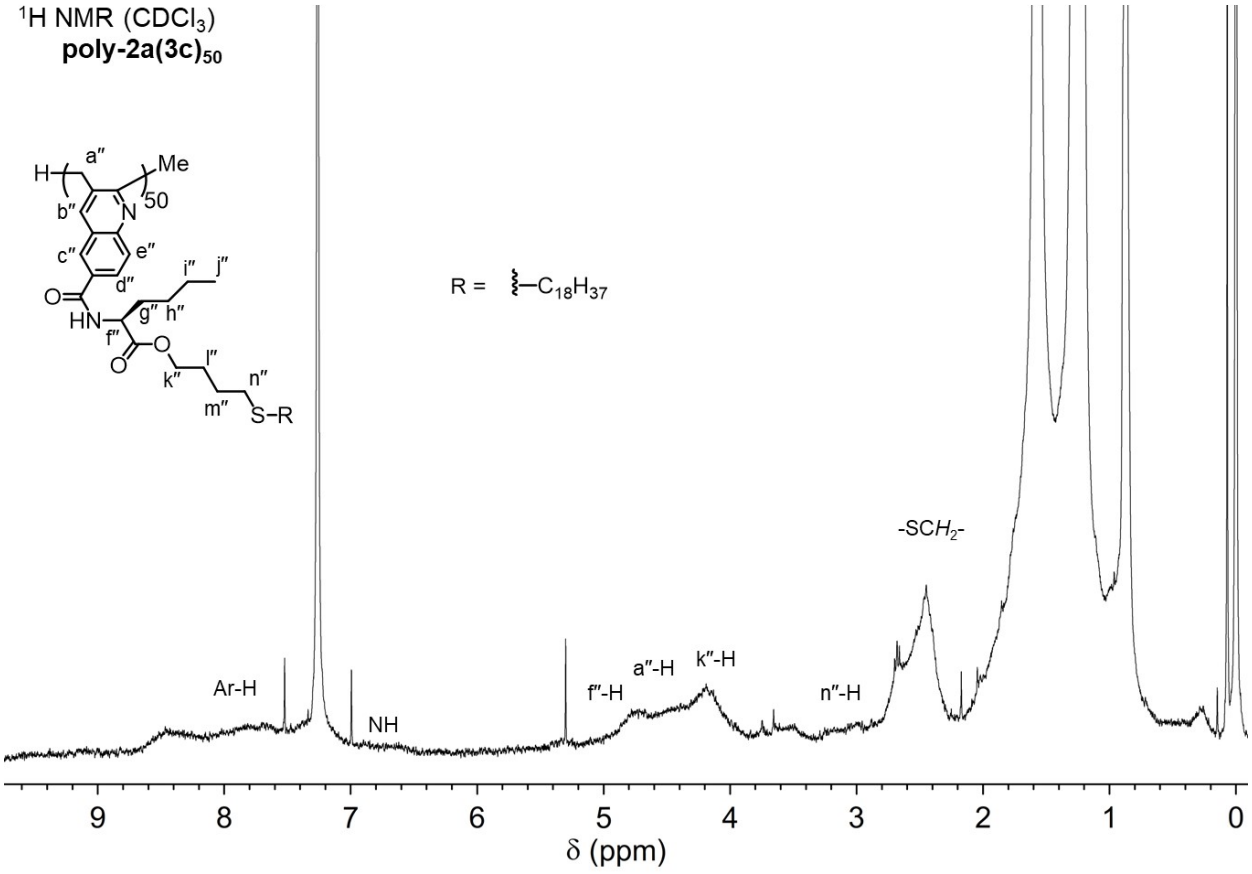



^{1}H NMR (CDCl$_3$/DMSO-d$_6$ = 1/1 (v/v)), 55 ºC
poly-2a$_{50}$
H
Me
N
50
O
HN
O
O
9
8
7
6
5
4
3
2
1
0
δ (ppm)

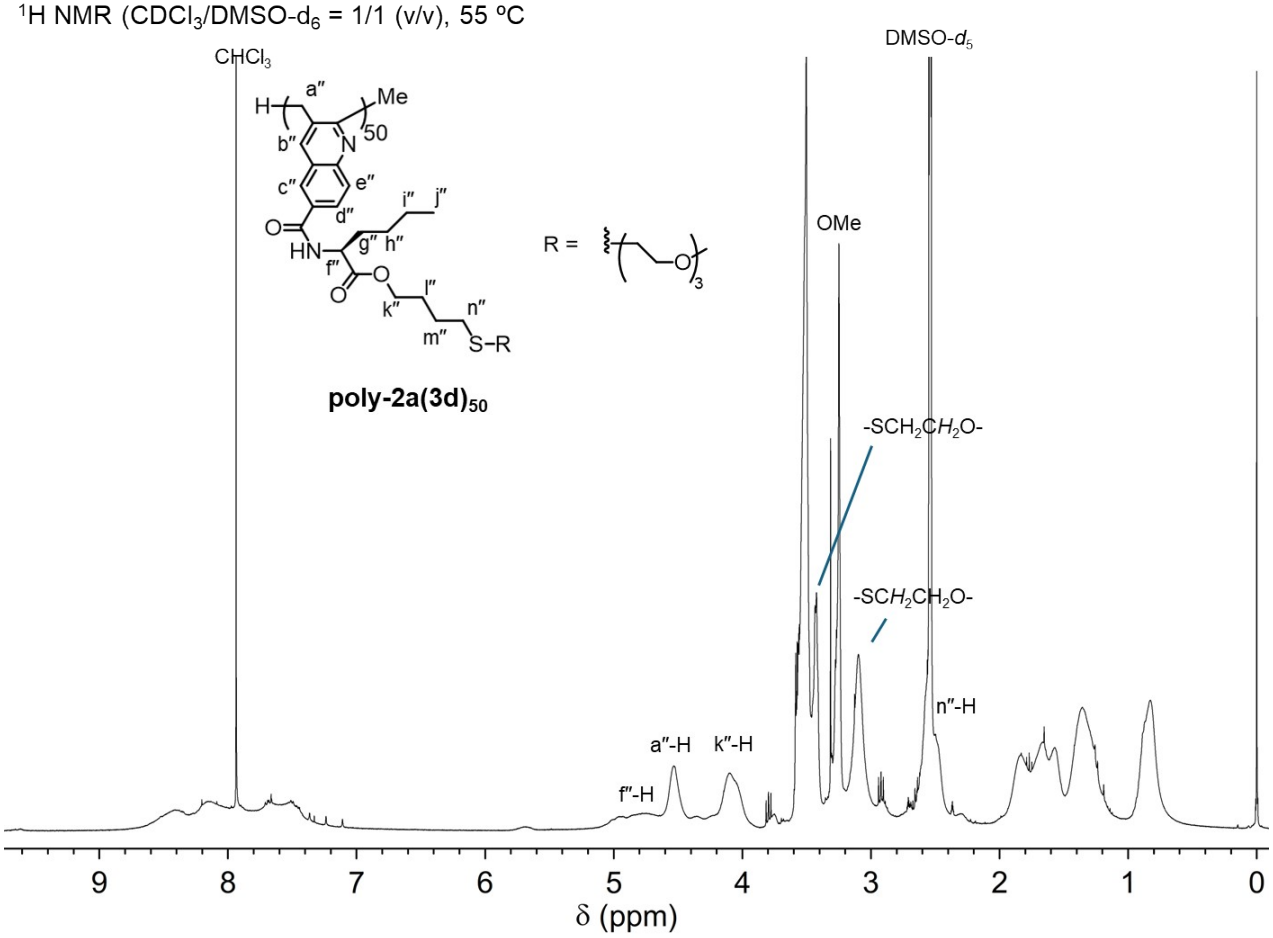
^{1}H NMR ($CDCl_3$/DMSO-d_6 = 1/1 (v/v), 55 ºC

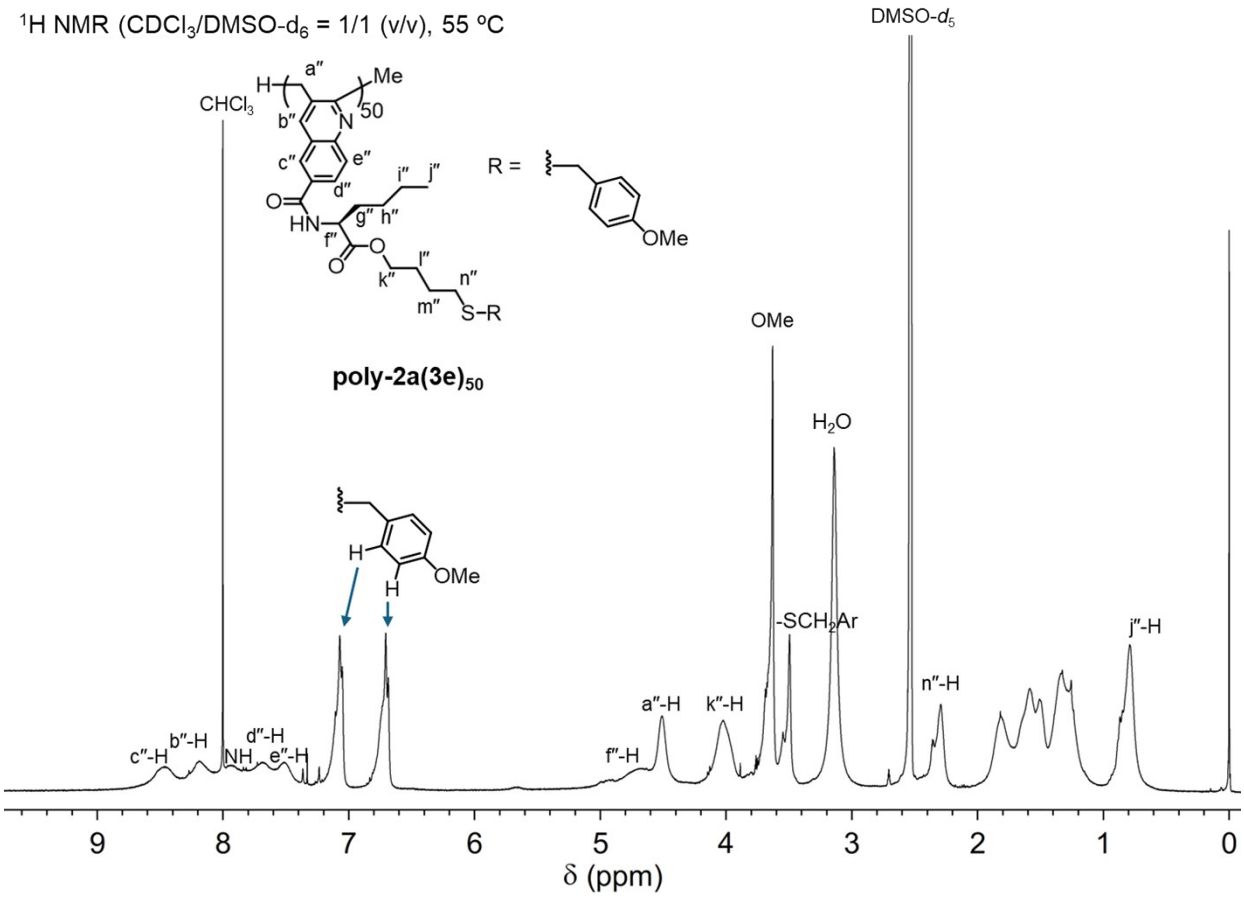


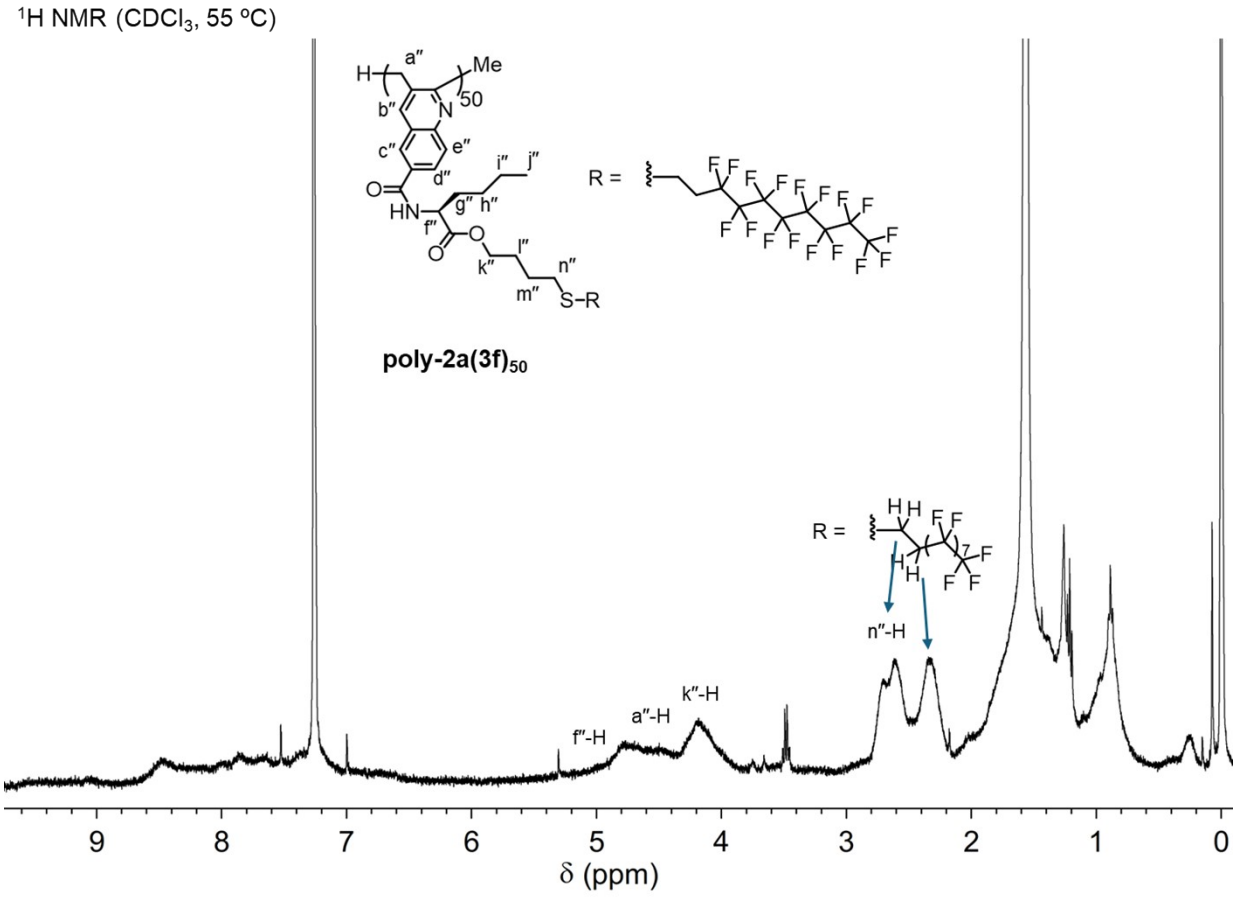

^{1}H NMR (CDCl$_3$/DMSO-d$_6$ = 1/1 (v/v), 55 ºC
poly-2a(3b)$_{50}$
DMSO-d_5
H$_2$O
-SCH_2-
n″-H
a″-H
k″-H
d″-H
e″-H
b″-H
c″-H
NH
f″-H
δ (ppm)


^{1}H NMR (CDCl$_3$)
poly-2a(3c)$_{50}$
R = –C$_{18}$H$_{37}$
-SCH_2-
Ar-H
NH
f″-H
a″-H
k″-H
n″-H
δ (ppm)

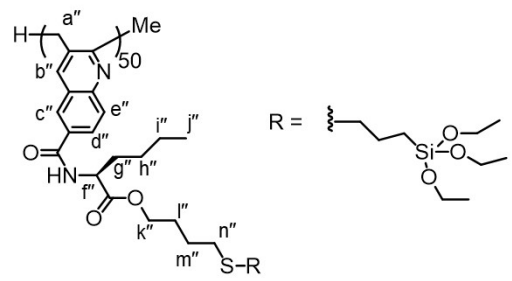
^{1}H NMR ($CDCl_3$/DMSO-d_6 = 1/1 (v/v), 55 ºC




^{1}H NMR (CDCl$_3$/DMSO-d$_6$ = 1/1 (v/v), 55 ºC
DMSO-d_5
CHCl$_3$
R =
OMe
poly-2a(3e)$_{50}$
OMe
H$_2$O
-SCH$_2$Ar
j″-H
n″-H
a″-H
k″-H
f″-H
c″-H
b″-H
d″-H
NH
e″-H
δ (ppm)

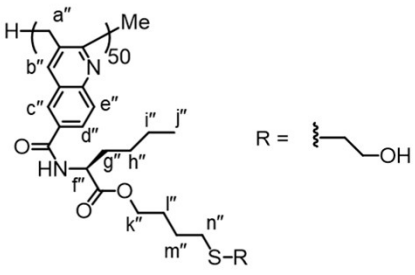

^{1}H NMR (CDCl$_3$, 55 ºC)
R =
poly-2a(3f)$_{50}$
n″-H
k″-H
a″-H
f″-H
δ (ppm)

^{1}H NMR ($CDCl_3$), 25 ºC



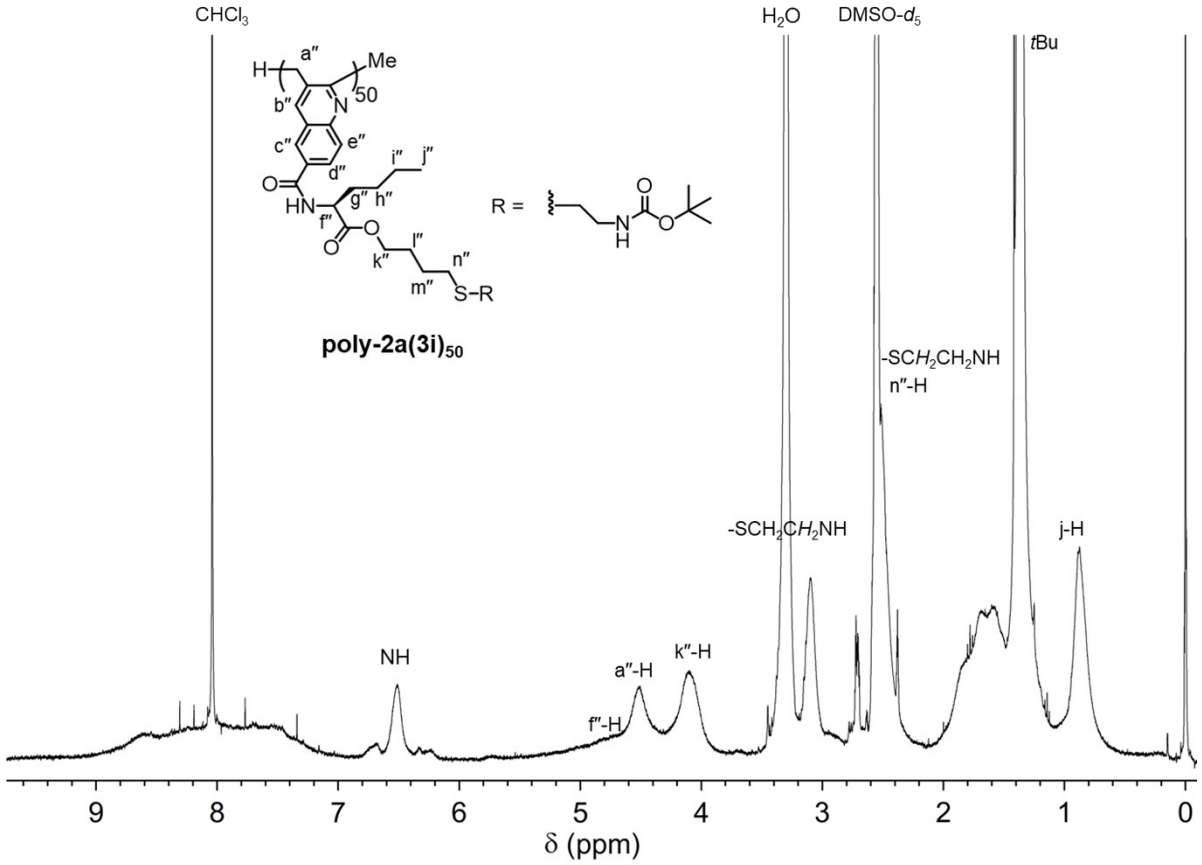
poly-2a(3g)$_{50}$

^{1}H NMR ($CDCl_3$/DMSO-d_6 = 1/1 (v/v), 55 ºC

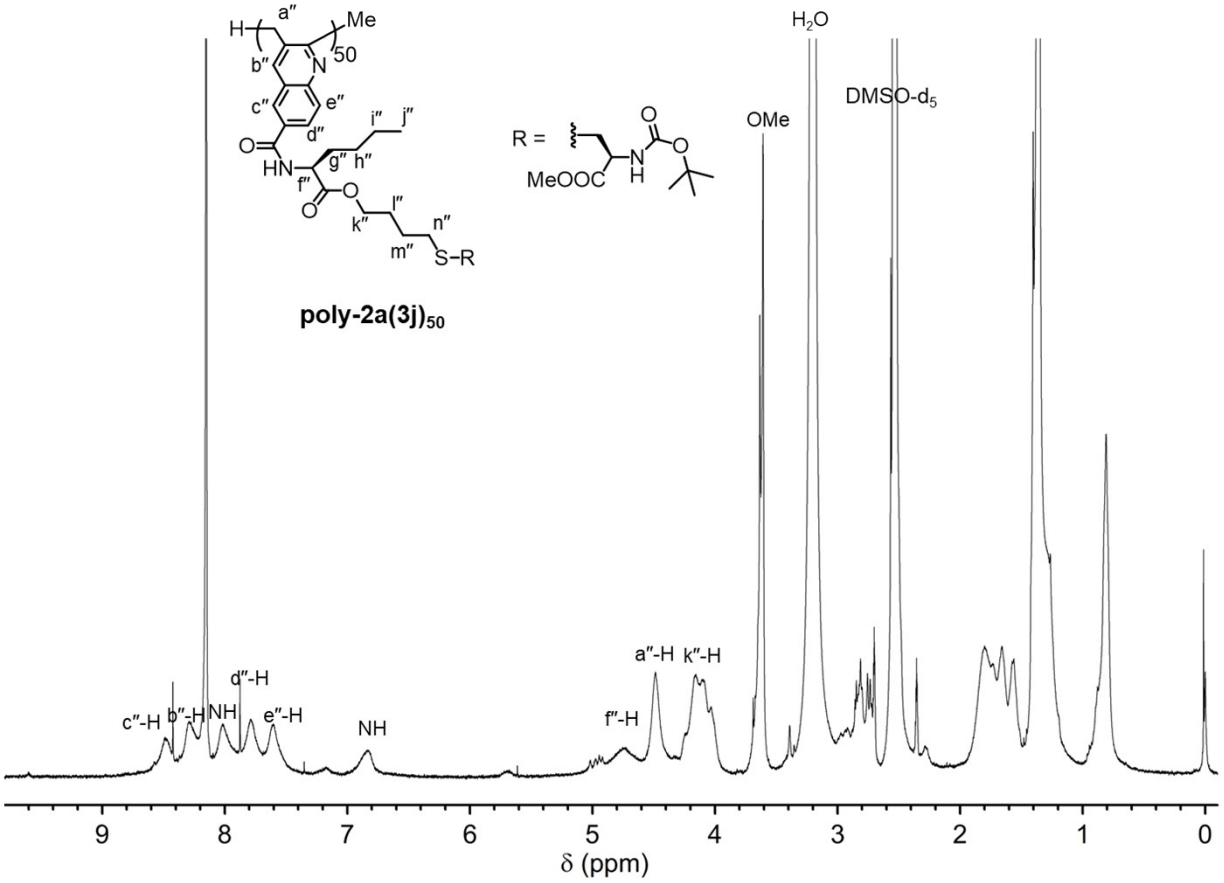


poly-2a(3h)$_{50}$

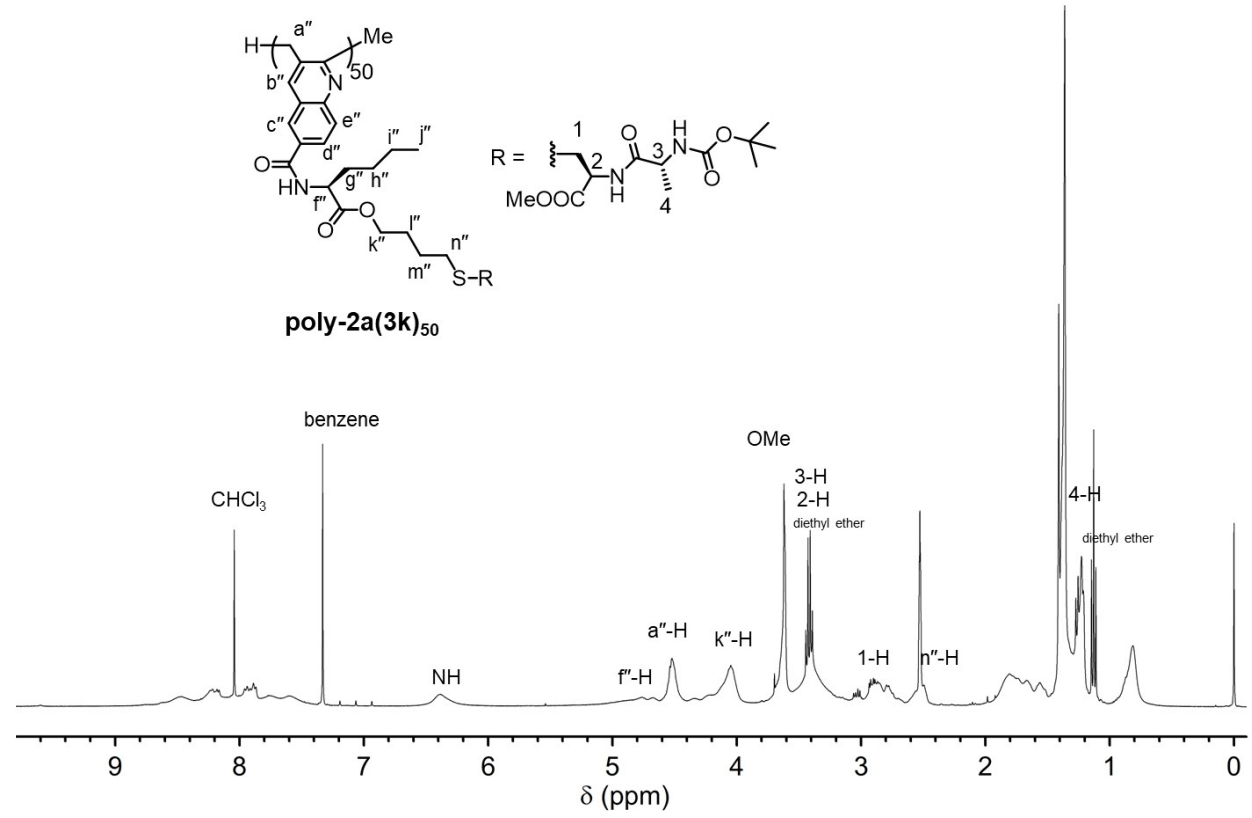
^{1}H NMR ($CDCl_3$/DMSO-d_6 = 1/1 (v/v), 55 ºC



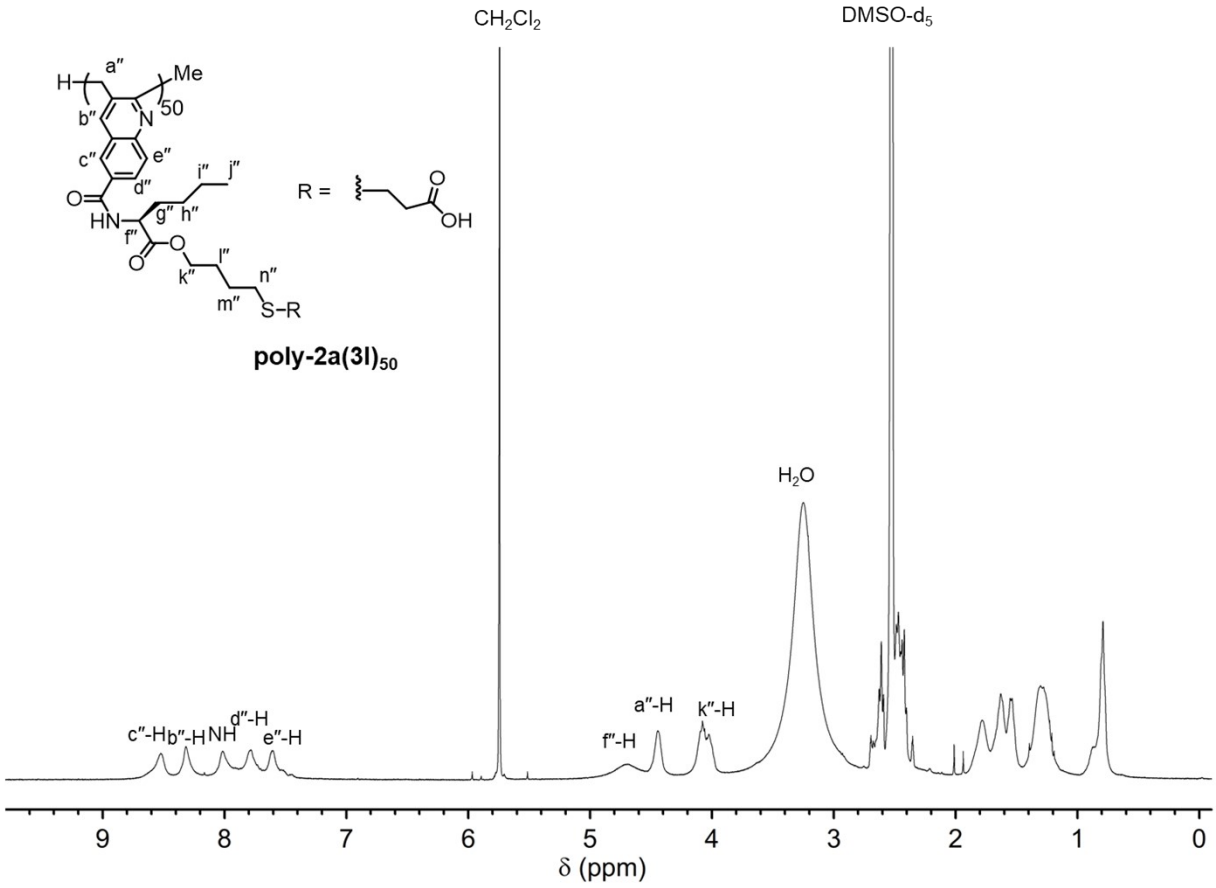
^{1}H NMR ($CDCl_3$/DMSO-d_6 = 1/1 (v/v), 55 ºC



^{1}H NMR ($CDCl_3$/DMSO-d_6 = 1/1 (v/v), 55 ºC

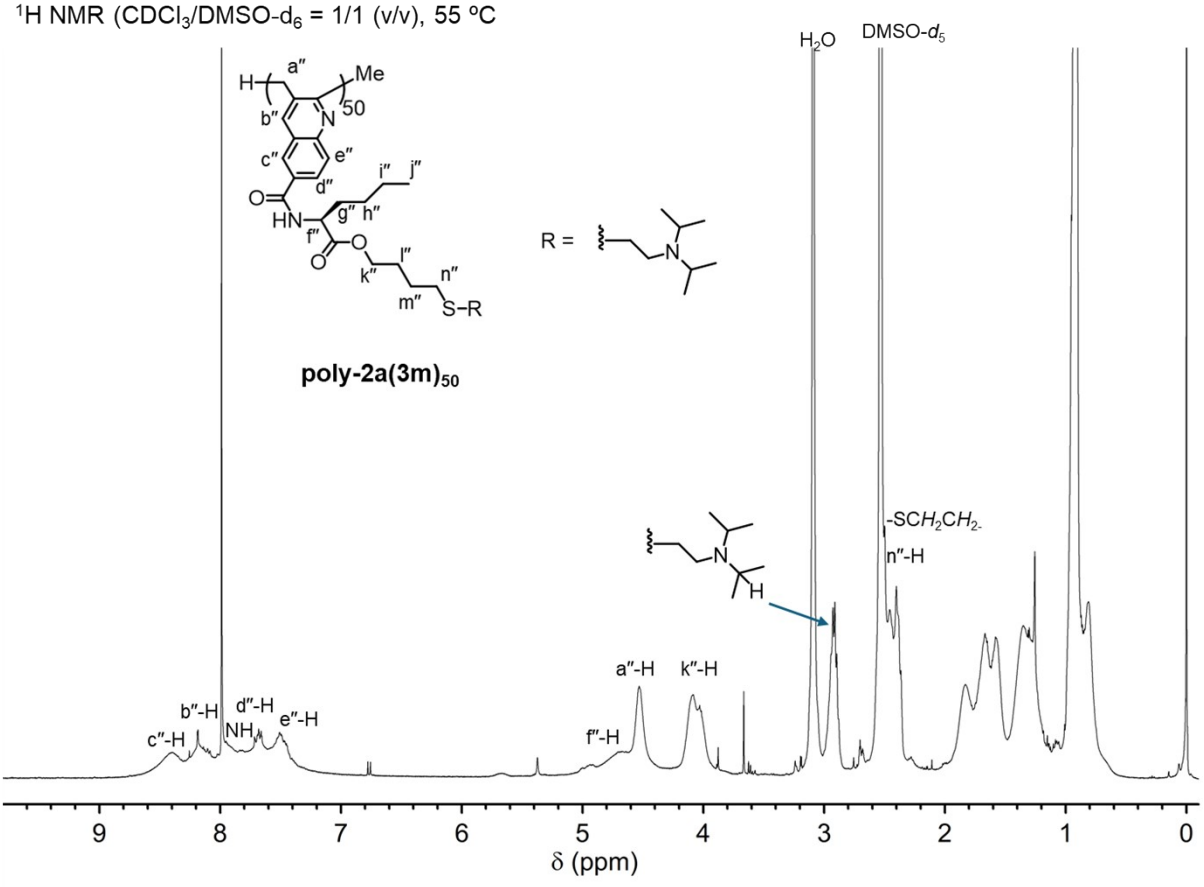


^{1}H NMR (DMSO-d_6 55 ºC

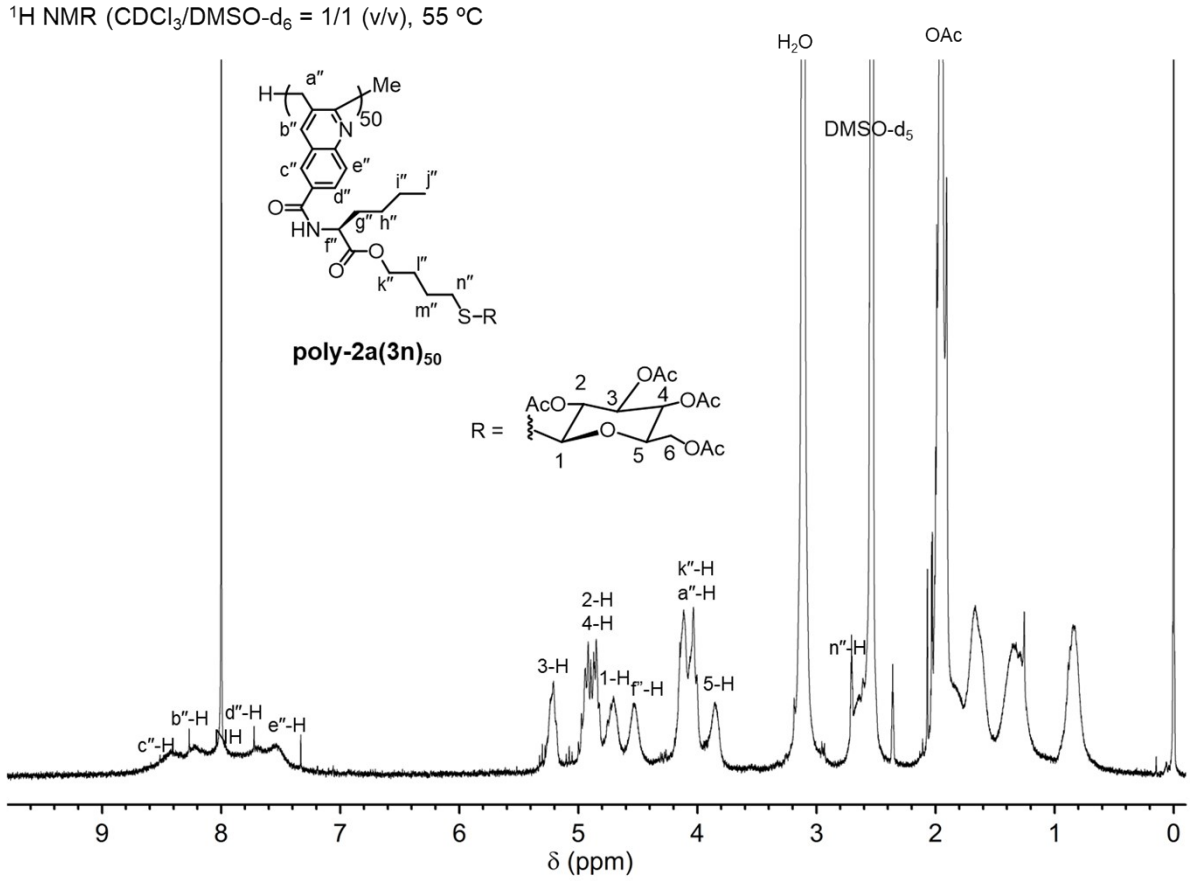


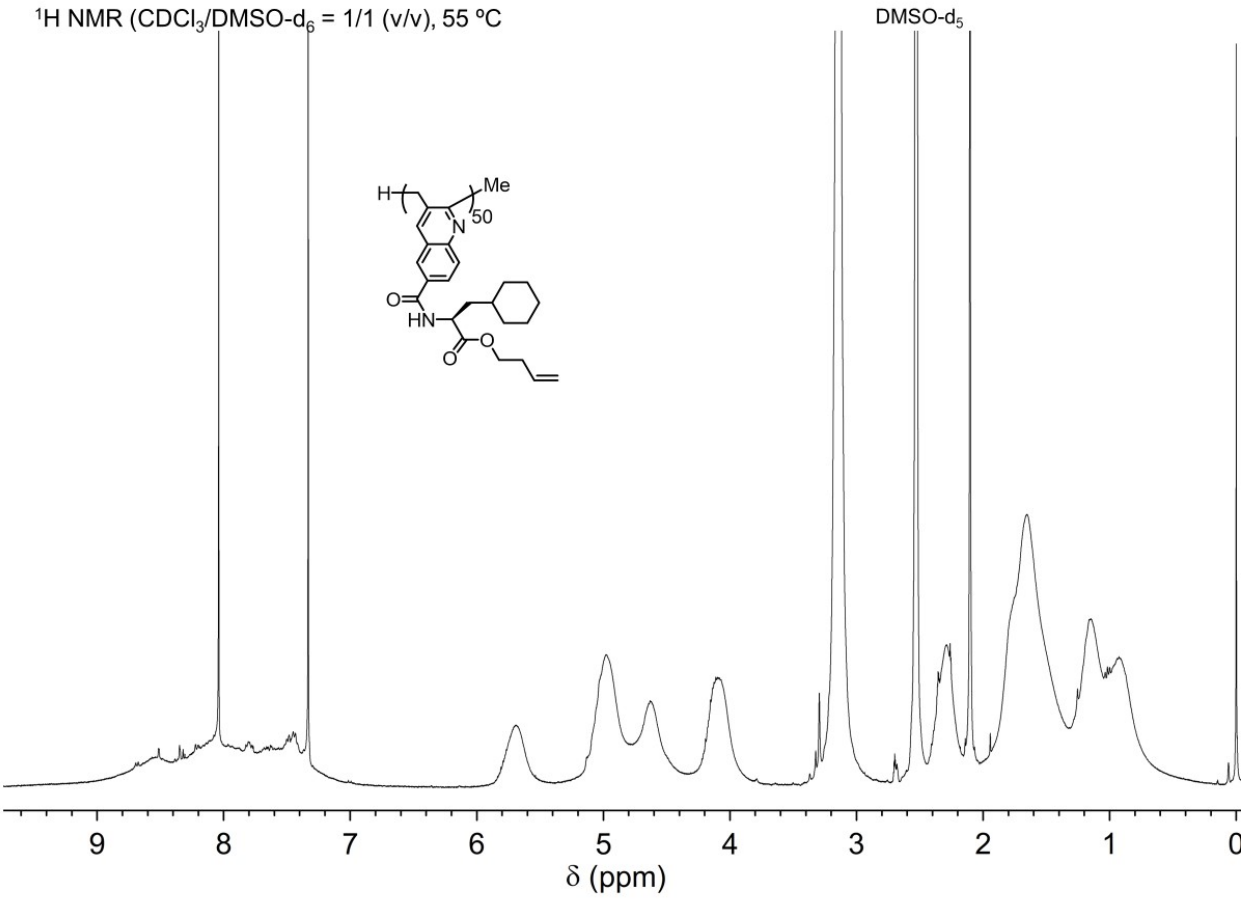
poly-2a(3l)$_{50}$

^{1}H NMR (CDCl$_3$/DMSO-d_6 = 1/1 (v/v), 55 ºC

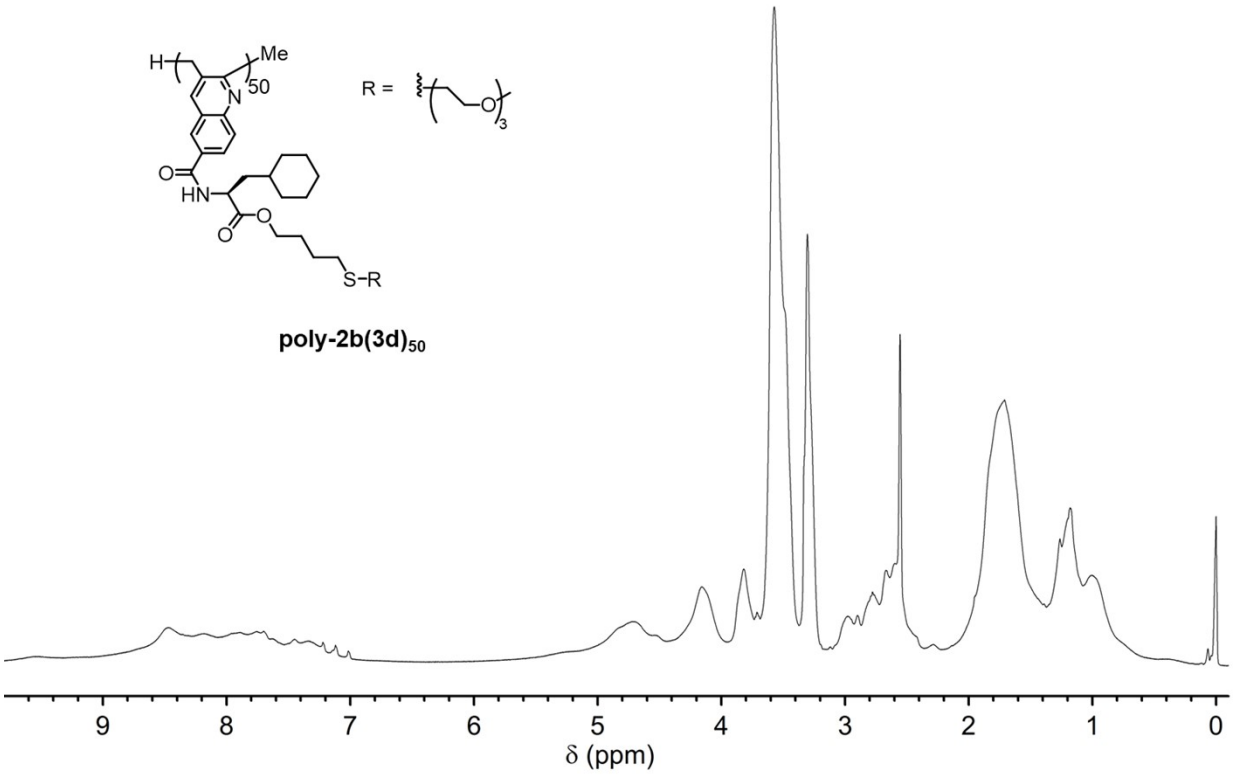


poly-2a(3m)$_{50}$

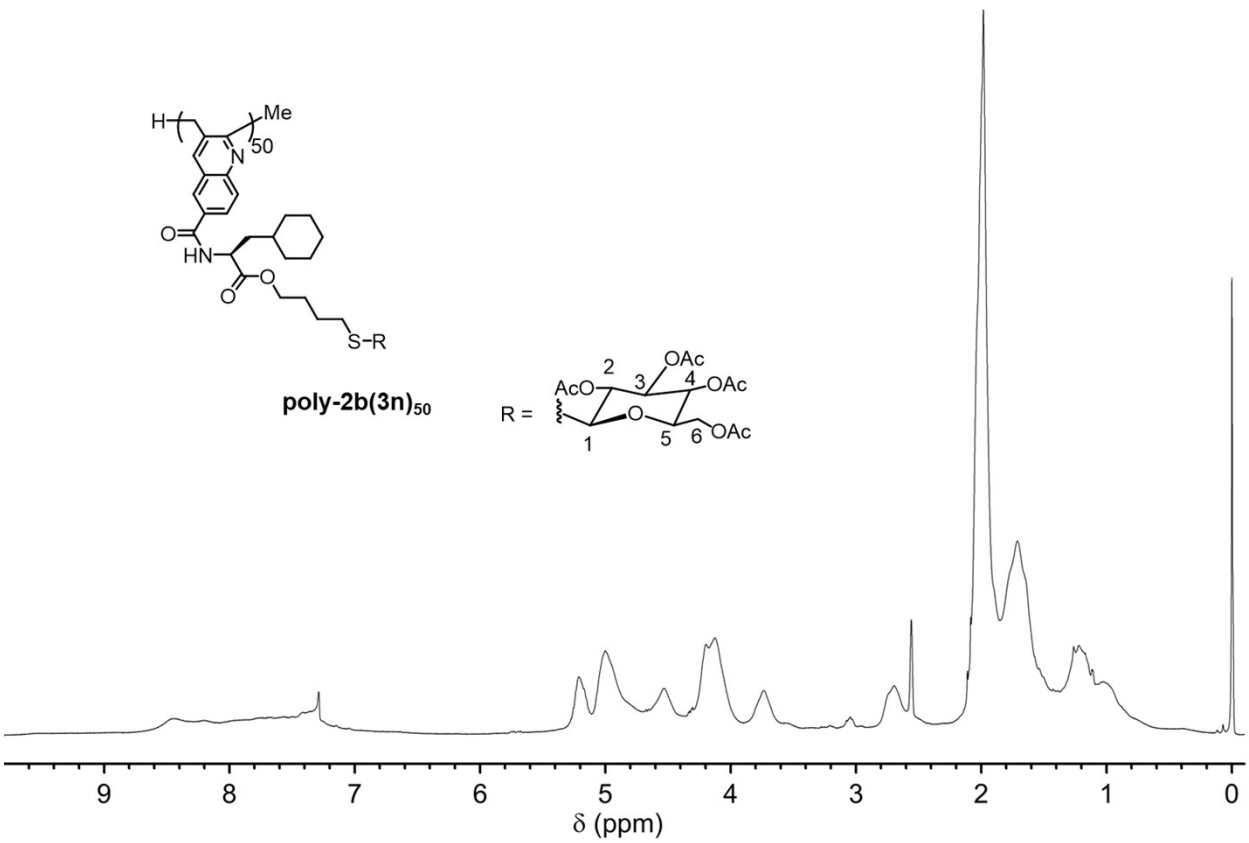

1H NMR (CDCl3/DMSO-d6 = 1/1 (v/v), 55 ºC
H2O
OAc
DMSO-d5
poly-2a(3n)50
R =
c″-H
b″-H
d″-H
NH
e″-H
3-H
2-H
4-H
1-H
f″-H
k″-H
a″-H
5-H
n″-H
δ (ppm)


1H NMR (CDCl3/DMSO-d6 = 1/1 (v/v), 55 ºC
DMSO-d5
δ (ppm)

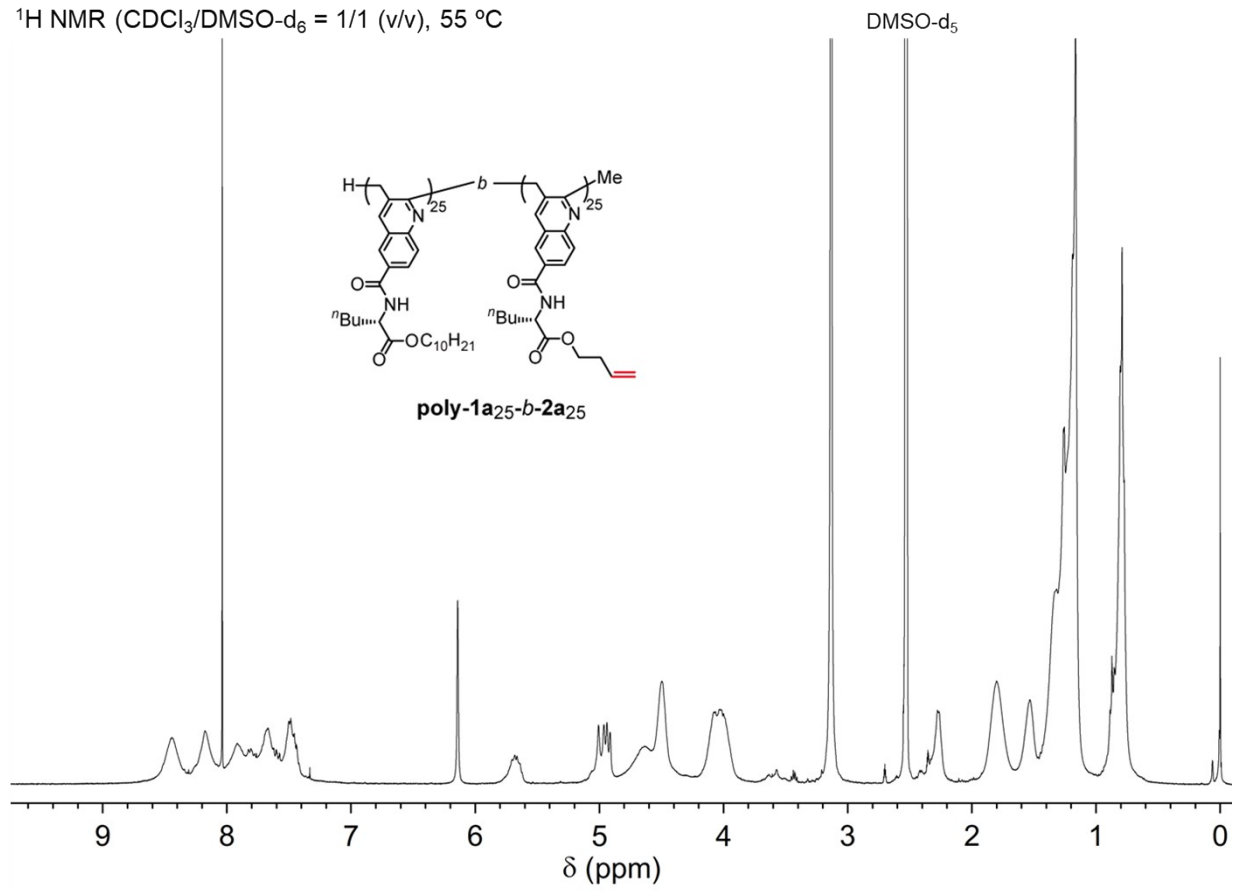
^{1}H NMR ($CDCl_3$/DMSO-d_6 = 1/1 (v/v), 55 ºC

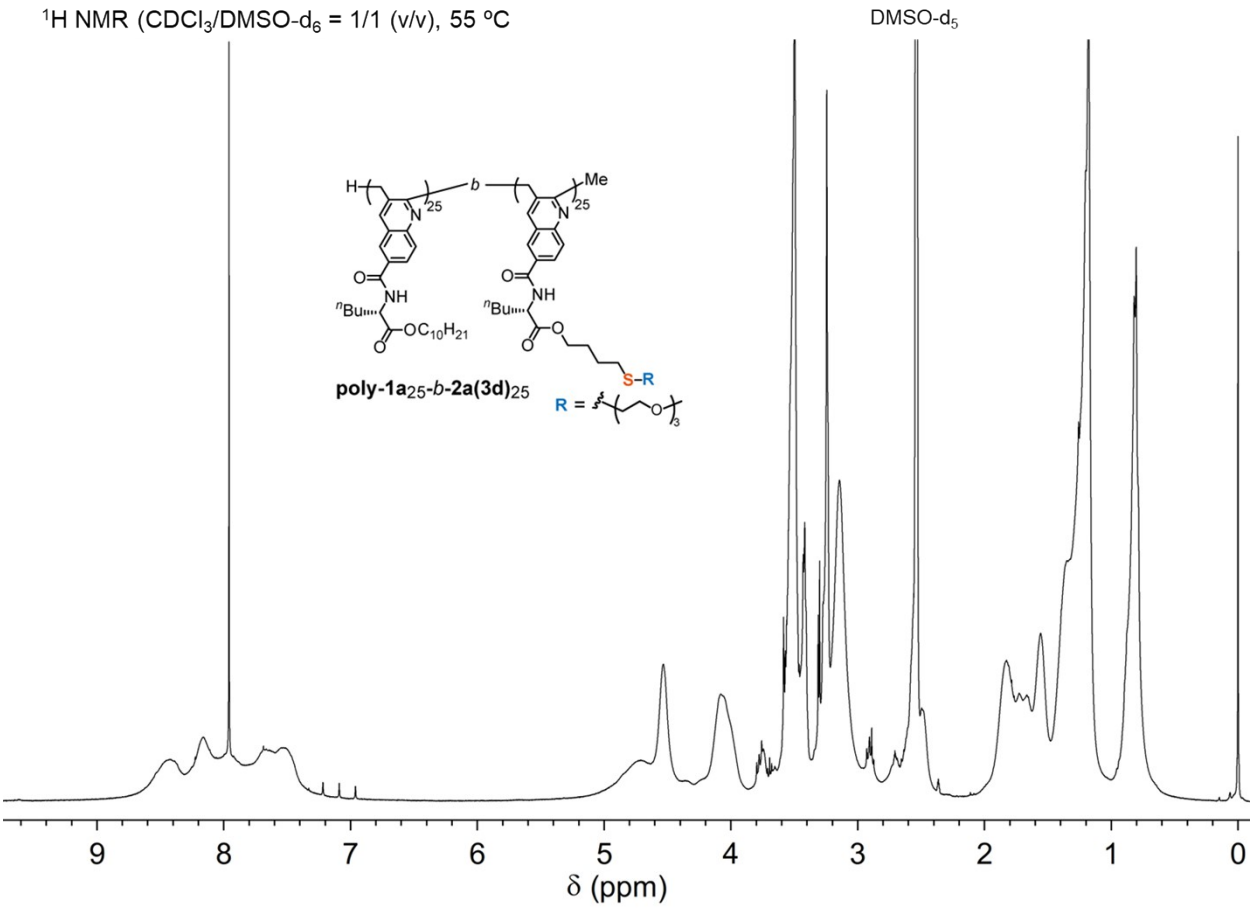


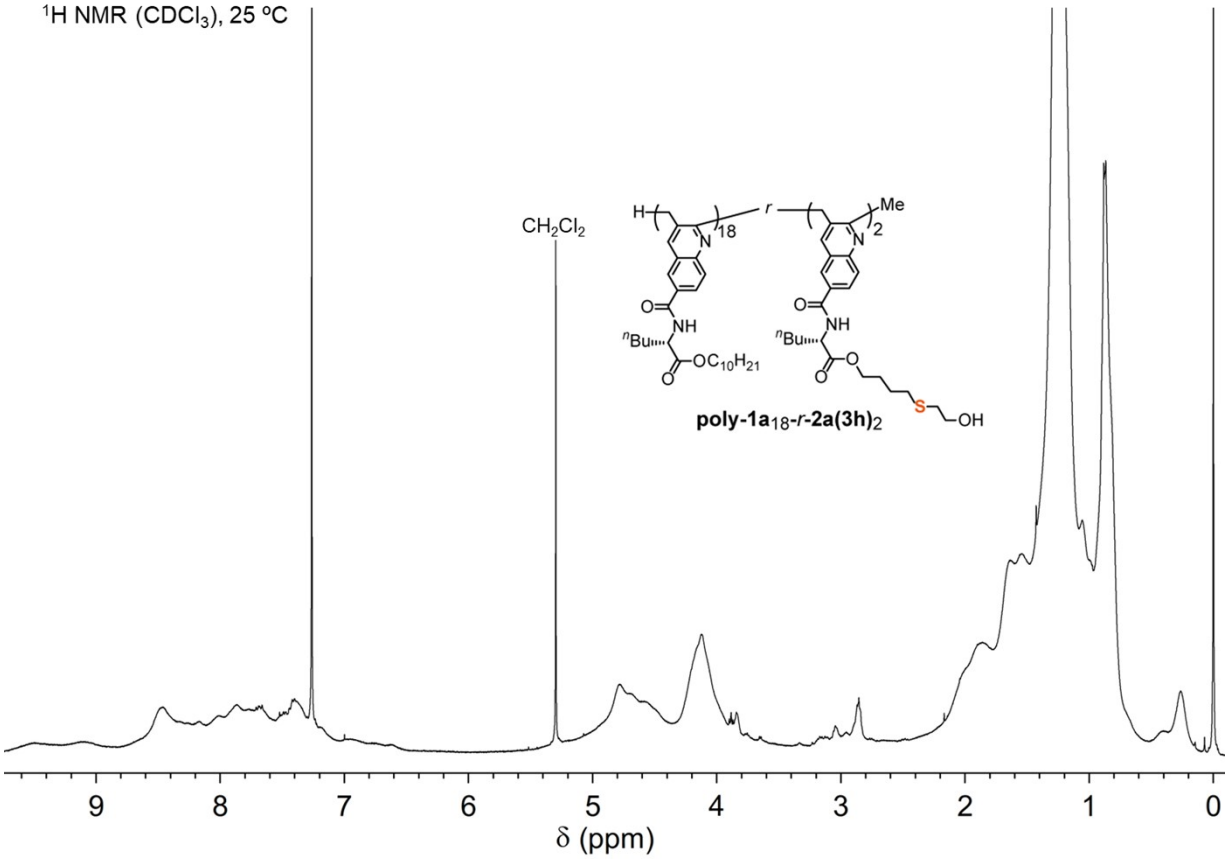
poly-2b(3d)$_{50}$

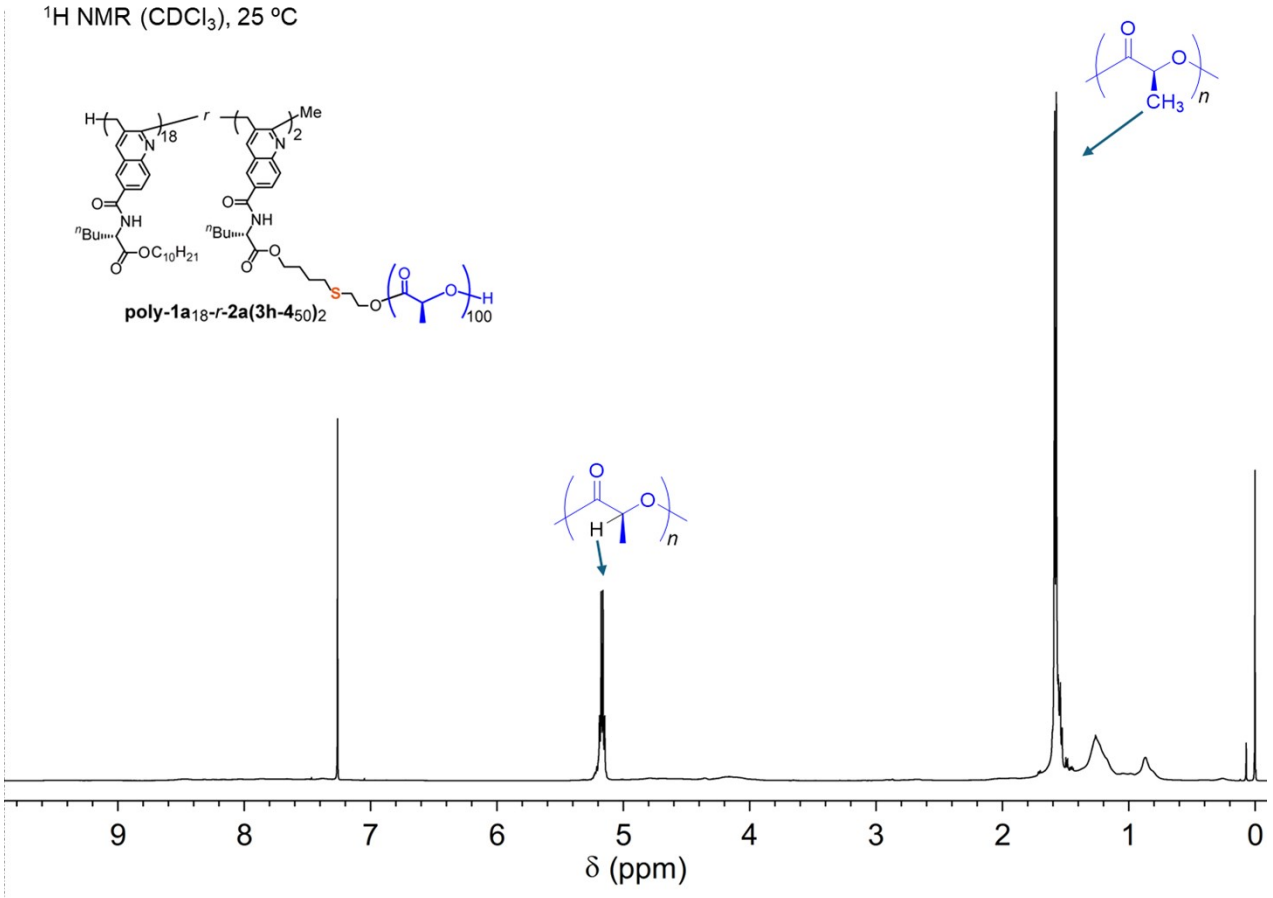


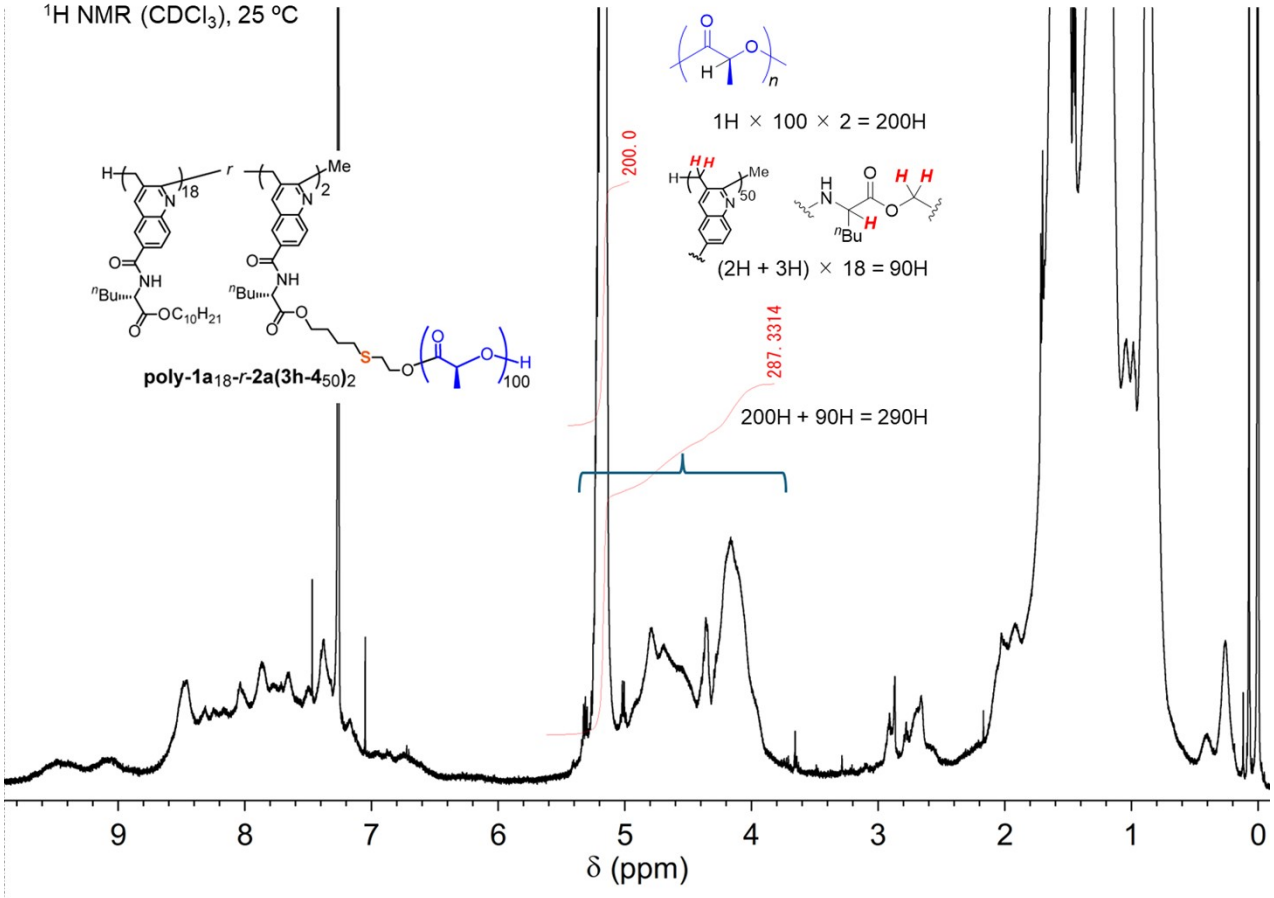
poly-2b(3n)$_{50}$


^{1}H NMR ($CDCl_3$/DMSO-d_6 = 1/1 (v/v), 55 ºC
DMSO-d_5
poly-1a$_{25}$-*b*-2a$_{25}$
9
8
7
6
5
4
3
2
1
0
δ (ppm)


^{1}H NMR ($CDCl_3$/DMSO-d_6 = 1/1 (v/v), 55 ºC
DMSO-d_5
poly-1a$_{25}$-*b*-2a(3d)$_{25}$
R =
9
8
7
6
5
4
3
2
1
0
δ (ppm)

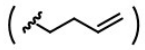
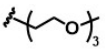
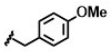
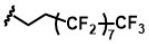
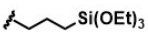
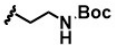
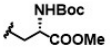
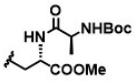
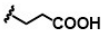
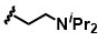
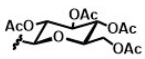

^{1}H NMR ($CDCl_3$), 25 ºC
CH_2Cl_2
poly-1a$_{18}$-*r*-2a(3h)$_2$
9
8
7
6
5
4
3
2
1
0
δ (ppm)


1H NMR (CDCl3), 25 ºC
poly-1a18-r-2a(3h-450)2
δ (ppm)


1H NMR (CDCl3), 25 ºC
1H × 100 × 2 = 200H
(2H + 3H) × 18 = 90H
200H + 90H = 290H
poly-1a18-r-2a(3h-450)2
δ (ppm)

3. Solubility of the Polymers

Table S1

	R	hexane	Et_2O	CH_2Cl_2	$CHCl_3$	THF	MeCN	MeOH	Water
poly-2		×	×	○	○	○	×	×	×
poly-2a(3a)		×	×	○	○	○	×	×	×
poly-2a(3b)		×	○	○	○	○	×	×	×
poly-2a(3c)		○	○	△	△	×	×	×	×
poly-2a(3d)		×	×	○	○	○	○	○	×
poly-2a(3e)		×	×	○	○	○	×	×	×
poly-2a(3f)		×	×	△	△	○	×	×	×
poly-2a(3g)		×	×	△	△	×	×	×	×
poly-2a(3h)		×	×	○	○	○	×	○	×
poly-2a(3i)		×	×	○	○	○	×	○	×
poly-2a(3j)		×	×	○	○	○	○	○	×
poly-2a(3k)		×	×	○	○	○	○	○	×
poly-2a(3l)		×	×	×	×	○	×	○	×
poly-2a(3m)		×	×	○	○	○	○	○	×
poly-2a(3n)		×	×	○	○	○	○	×	×

○ : soluble × : insolble △ : partly soluble — : not measured (1mg / 1 mL)

4. SEC Analysis

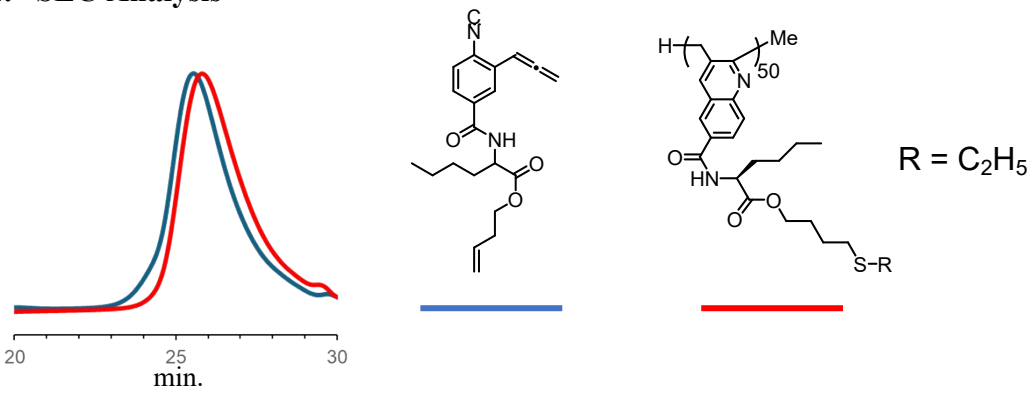


Figure S1. SEC curves of **poly-2a$_{50}$** and **poly-2a(3n)$_{50}$**.

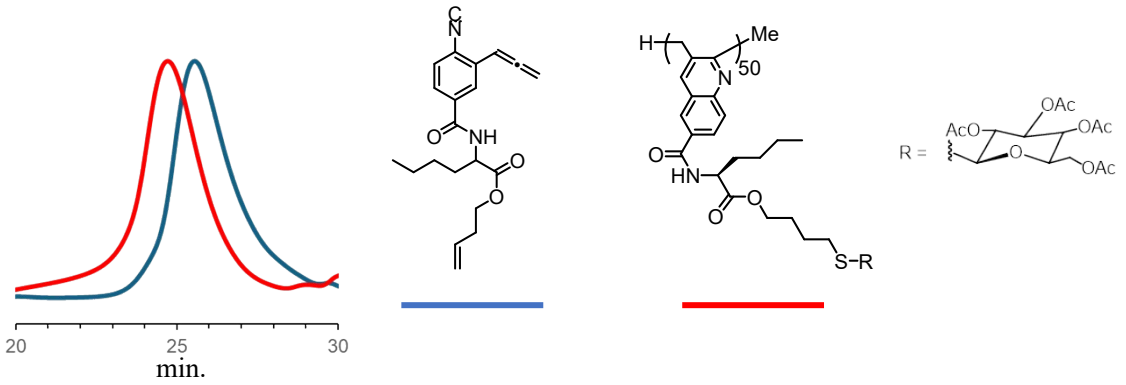


Figure S2. SEC curves of **poly-2a$_{50}$** and **poly-2a(3a)$_{50}$**.

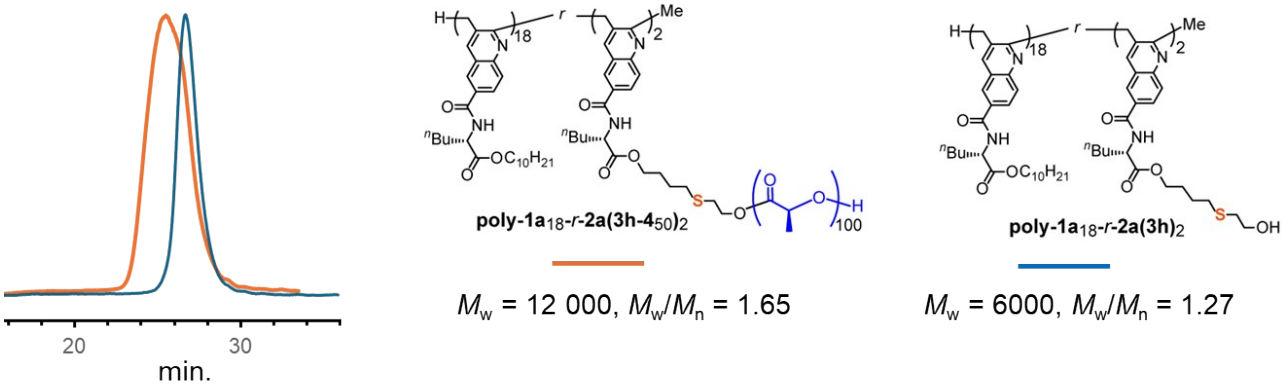
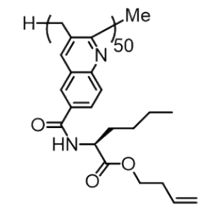
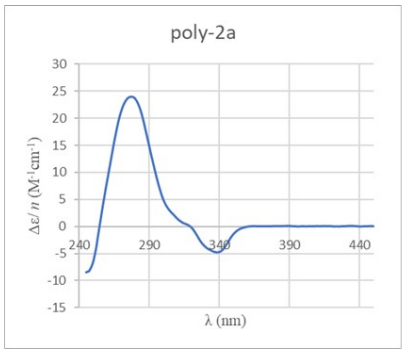


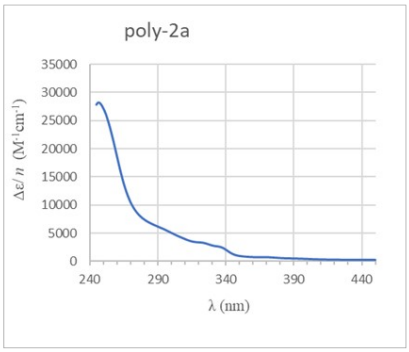
Figure S3. SEC curves of **poly-1a$_{18}$-*r*-1a(3h-4$_{50}$)$_2$** and **poly-1a$_{18}$-*r*-1a(3h-4$_{50}$)$_2$**.

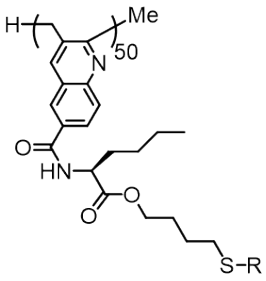
5. CD and UV Spectra

poly-2a$_{50}$

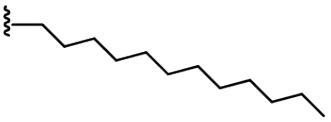




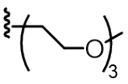


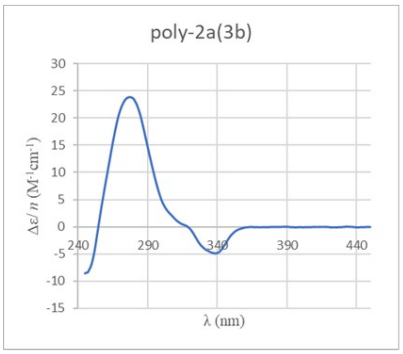


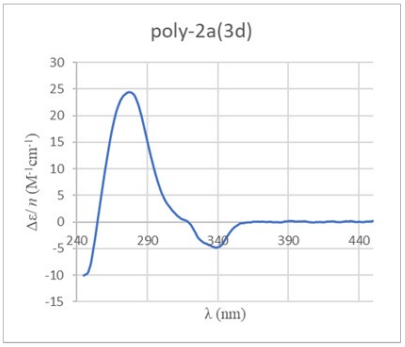
R =

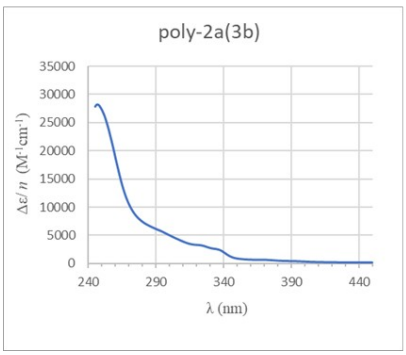


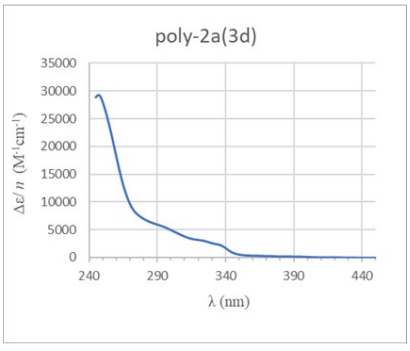
R =

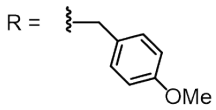


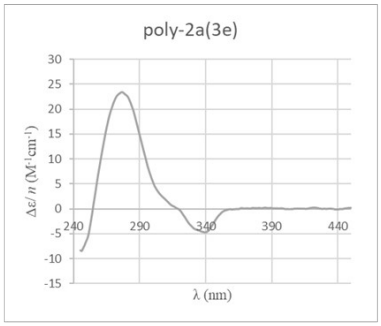


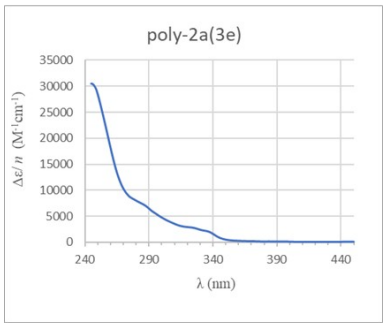


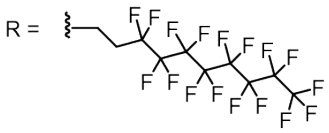


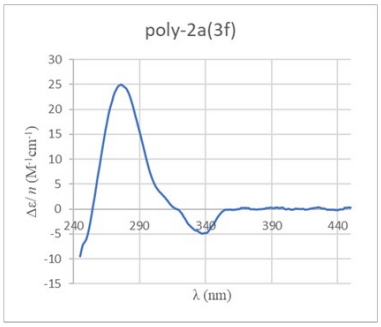


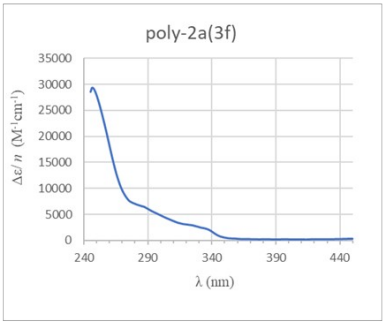
R = 

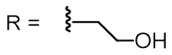

poly-2a(3e)
Δε/ n (M-1cm-1)
λ (nm)

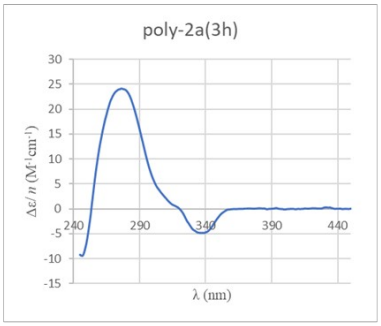

poly-2a(3e)
Δε/ n (M-1cm-1)
λ (nm)

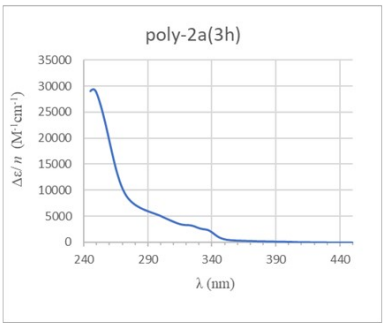
R = 

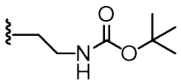

poly-2a(3f)
Δε/ n (M-1cm-1)
λ (nm)

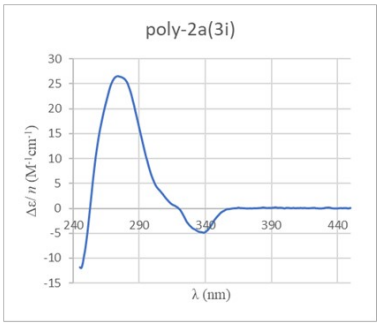

poly-2a(3f)
Δε/ n (M-1cm-1)
λ (nm)

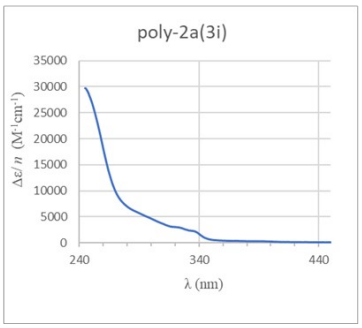
R = 

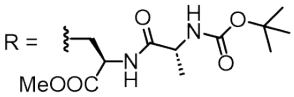

poly-2a(3h)
Δε/ n (M-1cm-1)
λ (nm)

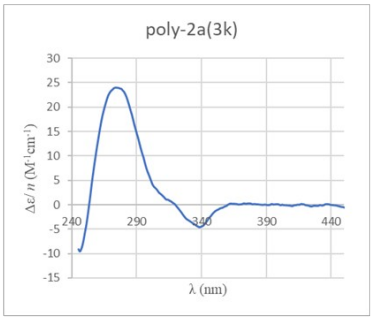

poly-2a(3h)
Δε/ n (M-1cm-1)
λ (nm)

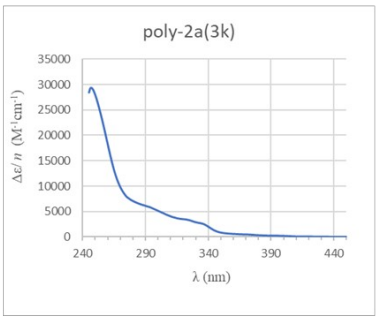
R = 

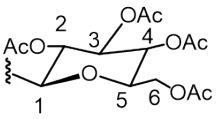

poly-2a(3i)
Δε/ n (M-1cm-1)
λ (nm)

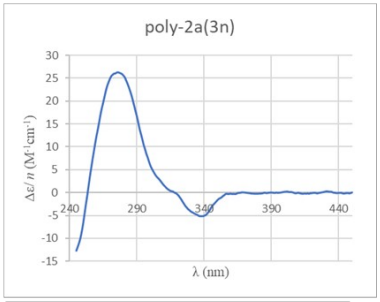

poly-2a(3i)
Δε/ n (M-1cm-1)
λ (nm)

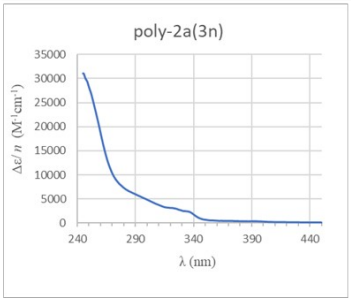
R = 

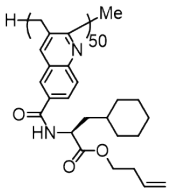

poly-2a(3k)
Δε/ n (M-1cm-1)
λ (nm)

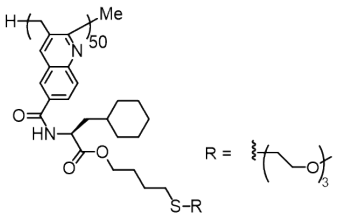

poly-2a(3k)
Δε/ n (M-1cm-1)
λ (nm)

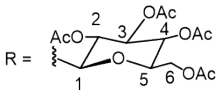
R = 

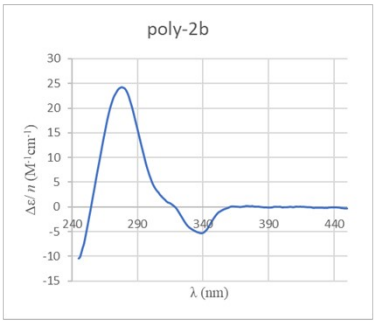

poly-2a(3n)
Δε/ n (M-1cm-1)
λ (nm)

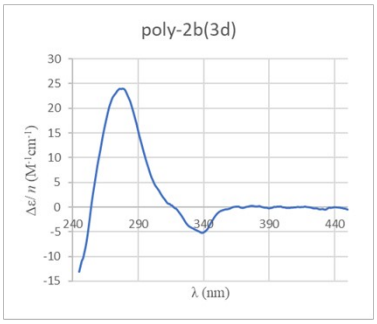

poly-2a(3n)
Δε/ n (M-1cm-1)
λ (nm)

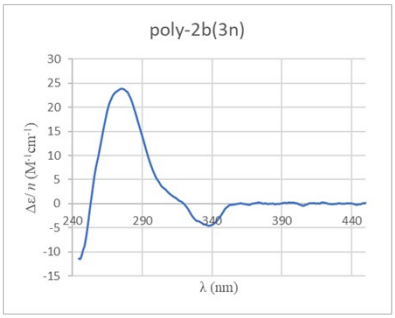

H
Me
N
50
O
HN
O
O

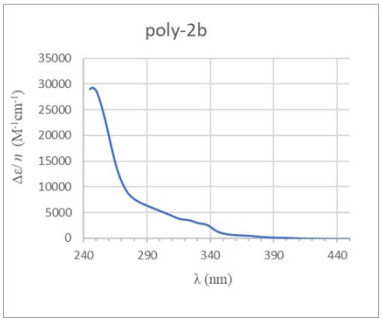

H
Me
N
50
O
HN
O
O
S–R
R =
O
3

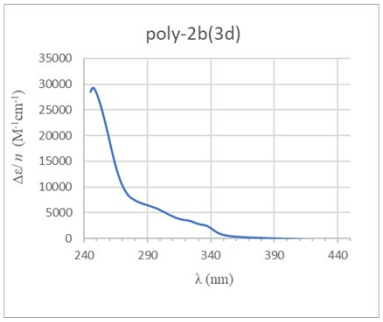

R =
AcO
2
3
OAc
4
OAc
O
1
5
6
OAc

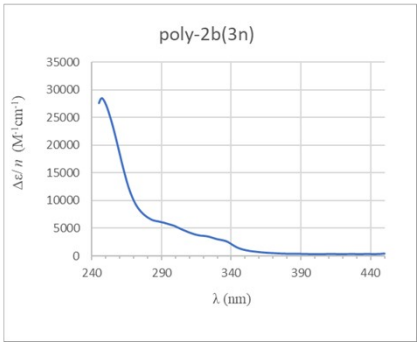

poly-2b
Δε / n (M⁻¹cm⁻¹)
λ (nm)


poly-2b(3d)
Δε / n (M⁻¹cm⁻¹)
λ (nm)


poly-2b(3n)
Δε / n (M⁻¹cm⁻¹)
λ (nm)


poly-2b
Δε / n (M⁻¹cm⁻¹)
λ (nm)


poly-2b(3d)
Δε / n (M⁻¹cm⁻¹)
λ (nm)


poly-2b(3n)
Δε / n (M⁻¹cm⁻¹)
λ (nm)