Supplementary Data

Organocatalytic Chiral Polymeric Nanoparticles for Asymmetric Aldol Reaction

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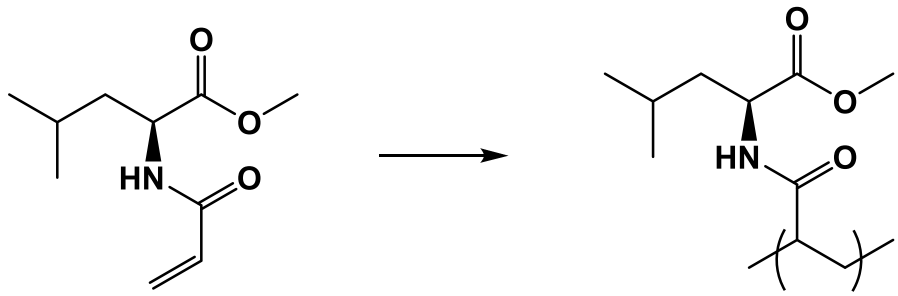
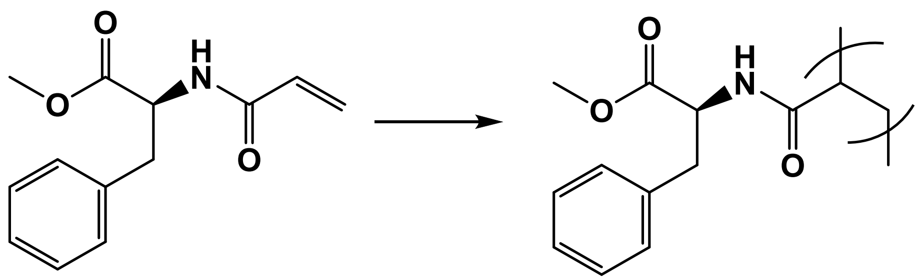
1. Structure of the monomers and polymers



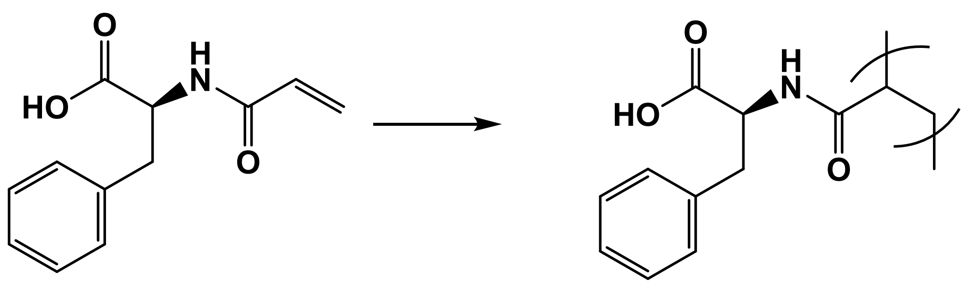
N-Acryloyl-L-Leucine Methyl Ester

Poly(L- Leu-OMe)



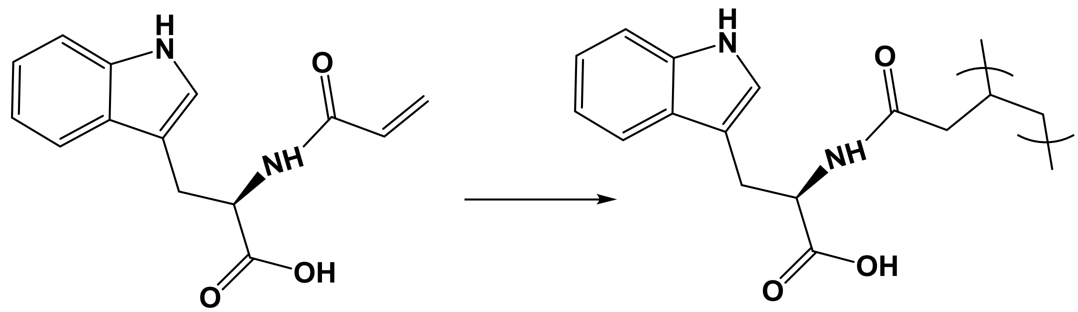
N-Acryloyl-L-Phenylalanine Methyl Ester

Poly(L- Phe-OMe)

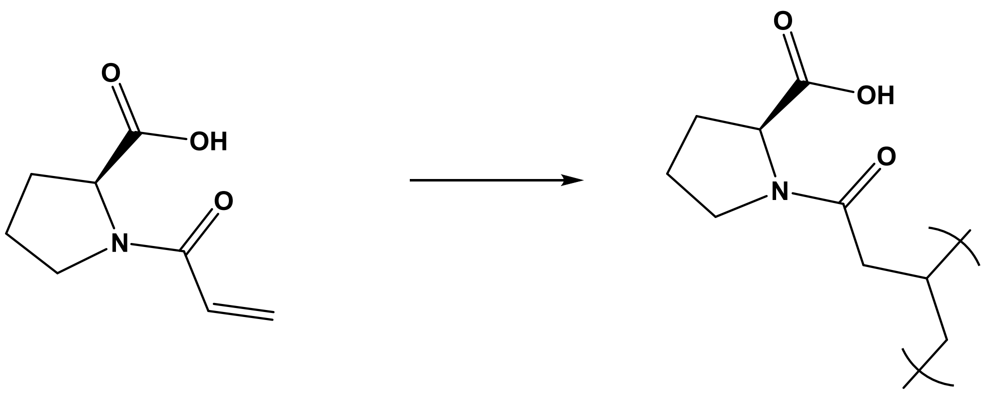


N-Acryloyl-L-Phenylalanine

Poly(L- Phe)



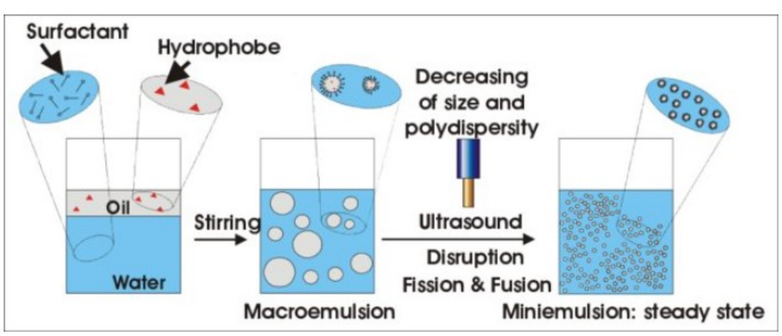
N-Acryloyl-L-Tryptophan Poly(L- Trp)



N-Acryloyl-L-Proline Poly(L- Proline)

Scheme S1. Structure of the synthesized monomers and polymers.

a. Scheme for the polymerization method



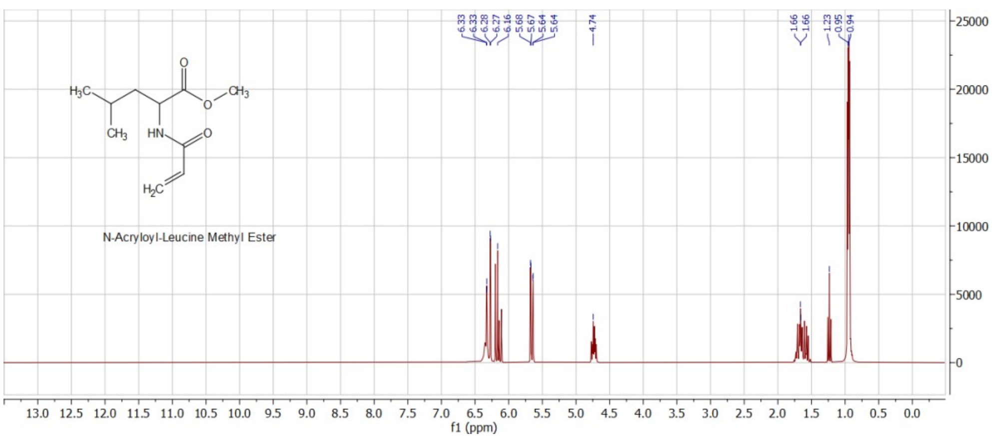
Scheme S2. Demonstration of miniemulsion polymerization[1].

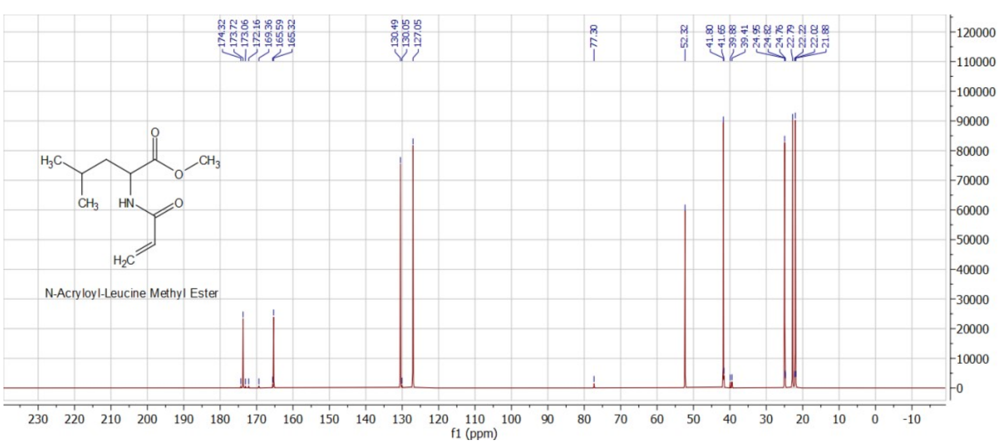
2. Characterization of the monomers

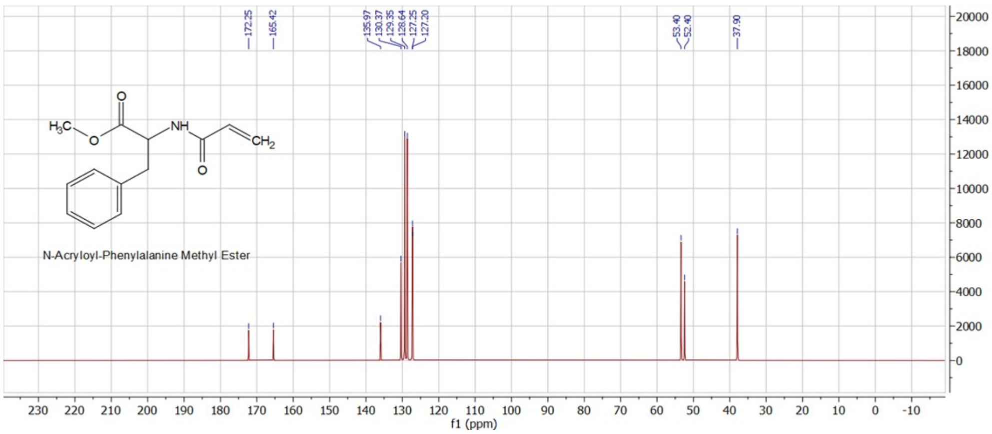
Monomer	^{1}H NMR	^{13}C NMR	Mass Spectroscopy
N-Acryloyl-L-Leucine Methyl Ester	($CDCl_3$, 400 MHz) δ: 6.30 (dd, *J* = 17, 2 Hz, 1H), 6.13 (dd, *J* = 17, 10 Hz, 1H), 6.08 (brd, 8 Hz, 1H), 5.67 (dd, *J* = 10, 2 Hz, 1H), 4.73 (dd, *J* = 8, 5 Hz, 1H), 1.72-1.52 (m, 3H), 0.94 (t, *J* = 6 Hz, 6H).	($CDCl_3$, 100 MHz) δ: 173.59 (C), 165.12 (C), 130.31 (CH), 127.16 (CH_2), 52.32 (CH), 42.82 (CH_2), 24.86 (CH), 22.74 (CH_3), 21.97 (CH_3).	m/z (ES^+): 222 ($[M+Na]^+$, 40), 200 (MH^+, 40), 168 ($[M-OMe]^+$, 40), 140 ($[M-CO_2Me]^+$, 100).
N-Acryloyl-L-Phenylalanine Methyl Ester	(300 MHz, $CDCl_3$) δ: 7.33-7.19 (m, 3H), 7.14-7.03 (m, 2H), 6.29 (dd, *J* = 18, 2 Hz, 1H), 6.09 (dd, *J* = 18, 10 Hz, 1H), 6.02 (brd, *J* = 8 Hz, 1H), 5.71 (dd, *J* = 10, 2 Hz, 1H), 4.97 (dt, *J* = 8, 6 Hz, 1H), 3.74 (s, 3H), abx system δ_A=3.20, δ_B=3.16 (dd, J_{AB}=13 Hz, J_{AX}= J_{BX}=6 Hz, 2H).	(100 MHz, $CDCl_3$) δ: 171.95 (C), 164.90 (C), 135.77 (C), 130.36 (CH), 129.32 (2xCH), 128.61 (2xCH), 127.20 (CH+CH_2), 53.18 (CH), 52.38 (CH_3), 37.88 (CH_2).	m/z (ES^+): ~~256~~ 234 ($[M+Na]^+$, 100), ~~234~~ 256 (MH^+, 4), 202 ($[M-OMe]^+$, 3), 174 ($[M-CO_2Me]^+$, 9).
N-Acryloyl-L-Phenylalanine	(300 MHz, DMSO-d_6) δ: 8.43 (d, 8Hz, 1H), 7.24 (m, 5H), 6.27 (q, 17, 10 Hz, 1H), 6.07 (dd, 17, 2 Hz, 1H), 5.57 (dd, 10, 2 Hz, 1H), 4.51 (ddd, 10, 8, 5 Hz, 1H), 3.09 (dd, 14, 5 Hz, 1H), 2.89 (dd, 14, 10 Hz, 1H)	(100 MHz, DMSO-d_6) δ: 172.92 (C), 164.43 (C),137.59 (C), 131.24 (CH), 129.01 (2xCH), 128.17 (2xCH), 126.40 (CH_2), 125.69 (CH), 53.52(CH), 36.73 (CH_2)	m/z (ES^+): 242 ($[M+Na]^+$, 100), 220 (MH^+, 15), 202 ($[M-OH]^+$, 3), 174 ($[M-CO_2H]^+$, 19).
N-Acryloyl-L-Tryptophan	(400 MHz, DMSO-d_6) δ: 10.8 (s, 1H), 8.4 (d, *J* = 8 Hz, 1H), 7.5 (d, *J* = 0.8 Hz, 1H) 7.3 (d, *J* = 0.8 Hz, 1H) 7.1 (d, *J* = 2.4 Hz, 1H) 6.9-7.0 (dt, 1 Hz, 2H), 6.3 (dd, *J* = 6.8 Hz, 1H), 6.0 (dd, *J* = 2 Hz, 1H) 5.5- (dd, *J* = 10.4 Hz, 1H), 4.5 (m, *J* = 4.8 Hz 1H), 3.1 (dd, *J* = 5.8 Hz, 1H), 3.0 (dd, *J* = 8.5 Hz, 1H).	(100 MHz, DMSO-d_6) δ: 173.59 (C), 165.12 (C), ~~174~~ 136 (C~~H~~), ~~165.0~~ 131 (CH_2), 118.0-127.0 (CH), 110.0-112.0 (CH_2), ~~24.86 (CH)~~, 54.0 (CH_3), 28.0 (CH_3).	m/z (ES^+): 259 (MH^+, 100), 281 ($[M+Na]^+$, 60),

N-Acryloyl-L-Proline	(400 MHz, CD_3OD) δ: 6.7 (dd, *J* = 10 Hz, 1H), 6.3 (dd, *J*= 2 Hz, 1H), 5.78 (dd, *J*= 2 Hz, 1H), 4.5 (dd, 1H), 3.6-3.8 (m, 2H), 1.9-2.4 (m, 4H)	(100 MHz, CD_3OD) δ: 175.0-175.4 (–COOH), 167.1-167.4 (–CONH–), 129.9 (–CH=CH_2), 128.9 (–CH=CH_2), 60.2 (>CHCOOH), 30.2-32.2 (>NCH_2), 25.6 (–CH_2–CHCOOH), 23.8 (>NCH_2–CH_2)	m/z (ES^+): 170 (MH^+, 100)

Table S1. Characterization of the monomers by ^1H and ^{13}C NMR and MS instruments.



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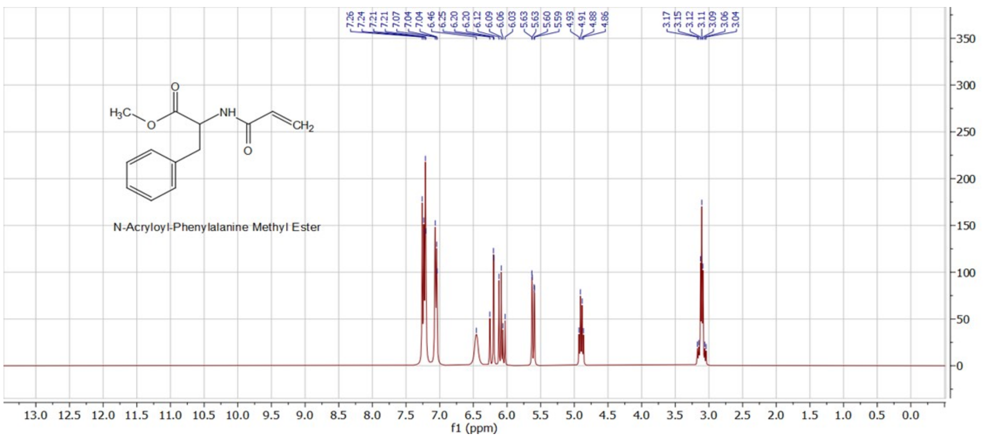
165.42
135.97
130.37
129.35
128.64
127.25
127.20
53.40
52.40
37.90
N-Acryloyl-Phenylalanine Methyl Ester
f1 (ppm)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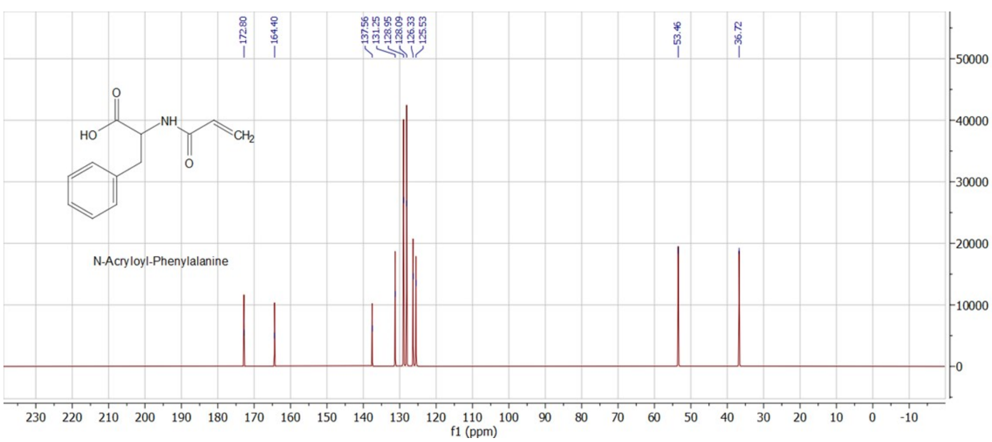
7.21
7.21
7.07
7.04
7.04
6.46
6.25
6.20
6.20
6.12
6.09
6.06
6.03
5.63
5.63
5.60
5.59
4.93
4.91
4.88
4.86
3.17
3.15
3.12
3.11
3.09
3.06
3.04
N-Acryloyl-Phenylalanine Methyl Ester
f1 (ppm)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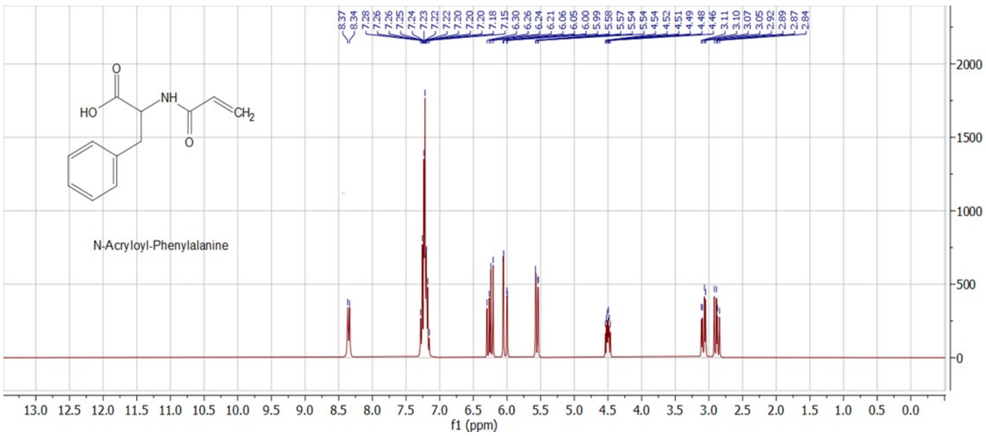
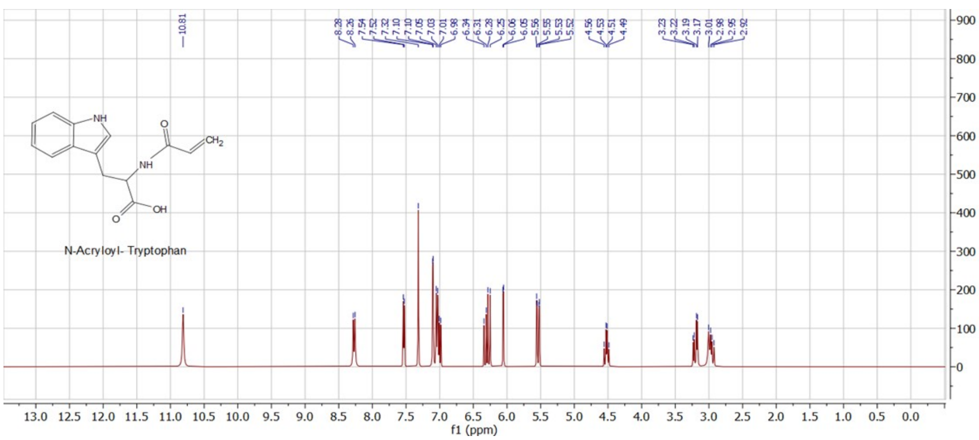
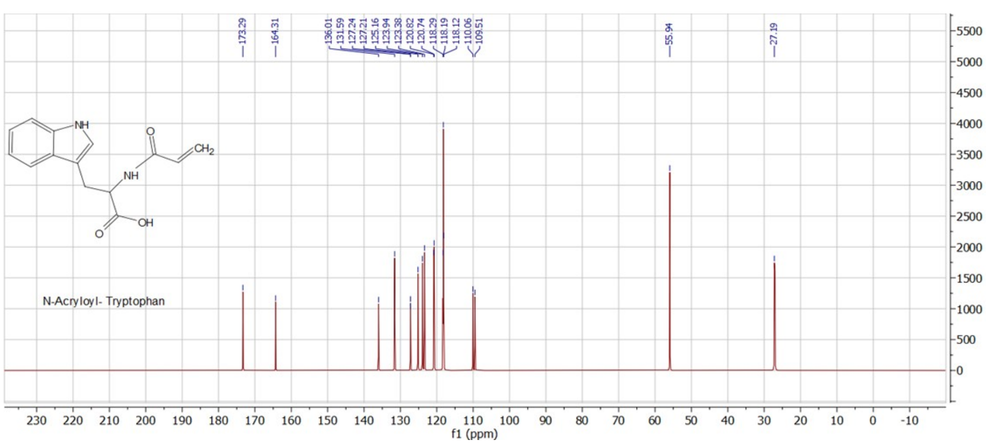
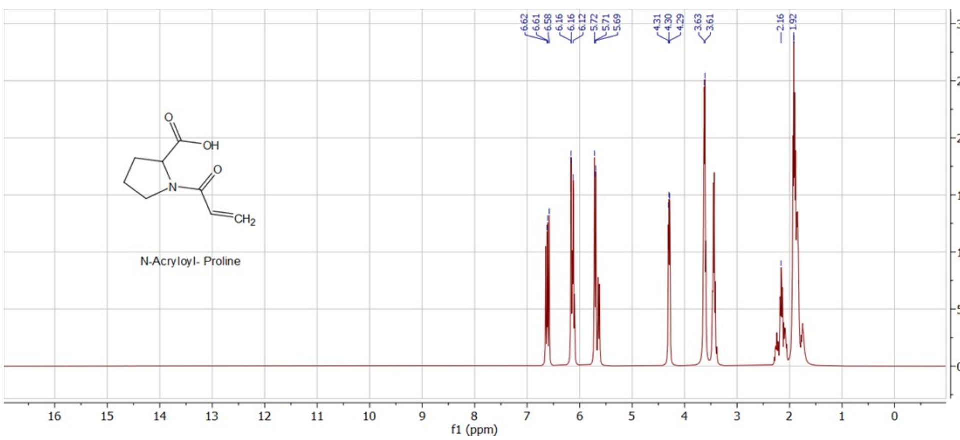
128.95
128.09
126.33
125.53
53.46
36.72
N-Acryloyl-Phenylalanine
f1 (ppm)


N-Acryloyl-Phenylalanine
f1 (ppm)


N-Acryloyl- Tryptophan
f1 (ppm)


N-Acryloyl- Tryptophan
f1 (ppm)


6.62
6.61
6.58
6.16
6.16
6.12
5.72
5.71
5.69
4.31
4.30
4.29
3.63
3.61
2.16
1.92
OH
O
O
N
CH2
N-Acryloyl- Proline
f1 (ppm)

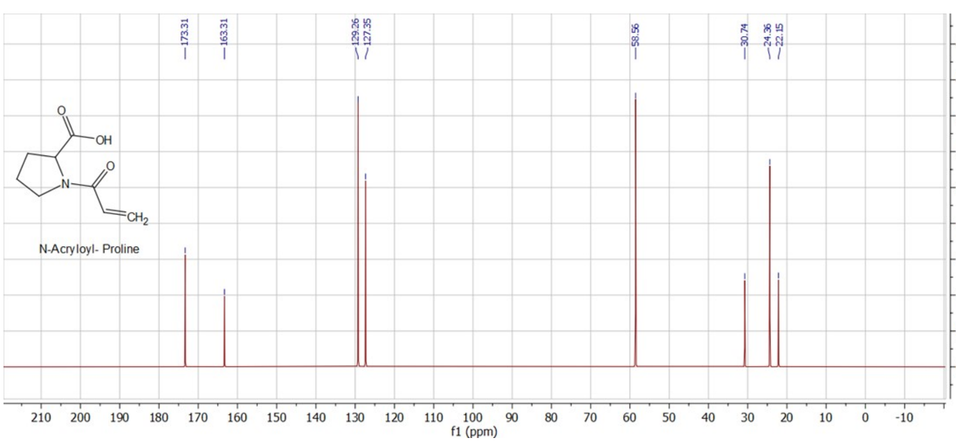
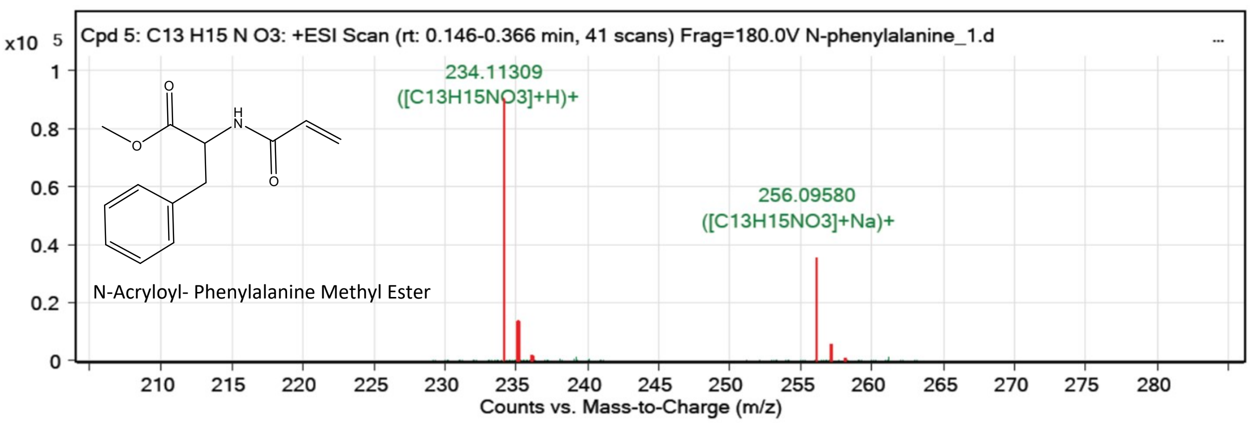
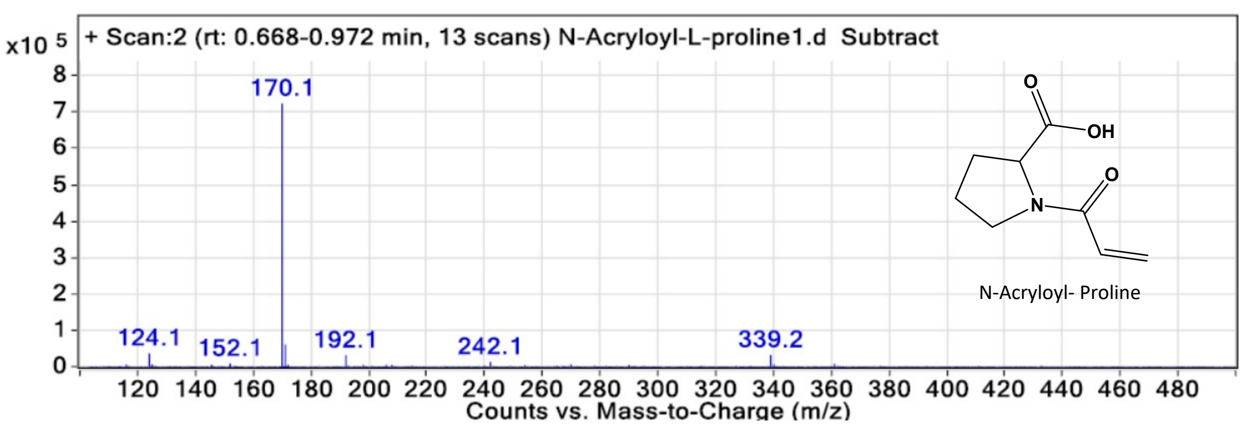

173.31
163.31
129.26
127.35
58.56
30.74
24.36
22.15
OH
O
O
N
CH2
N-Acryloyl- Proline
f1 (ppm)

Figure S1. ^{13}C and ^{1}H NMR diagram of the monomers.





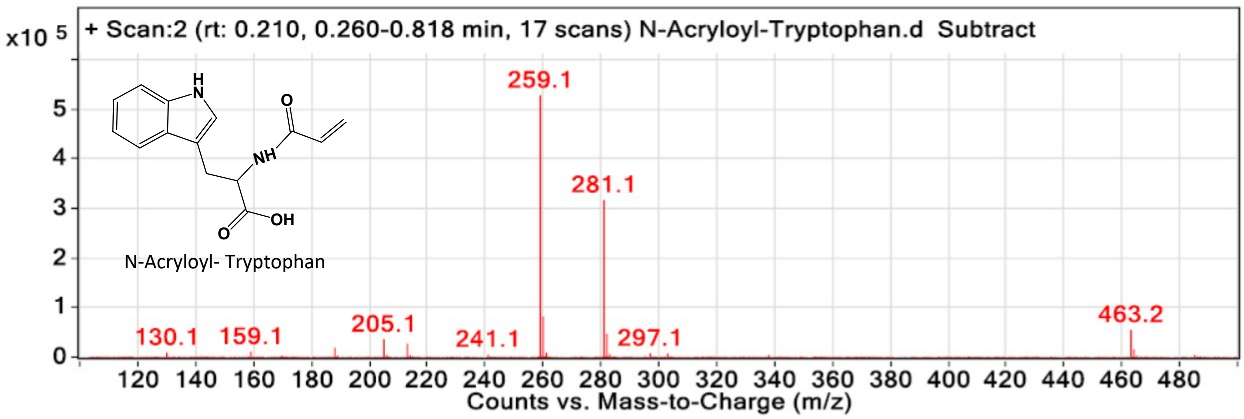


Figure S2. Mass diagram of the monomers.

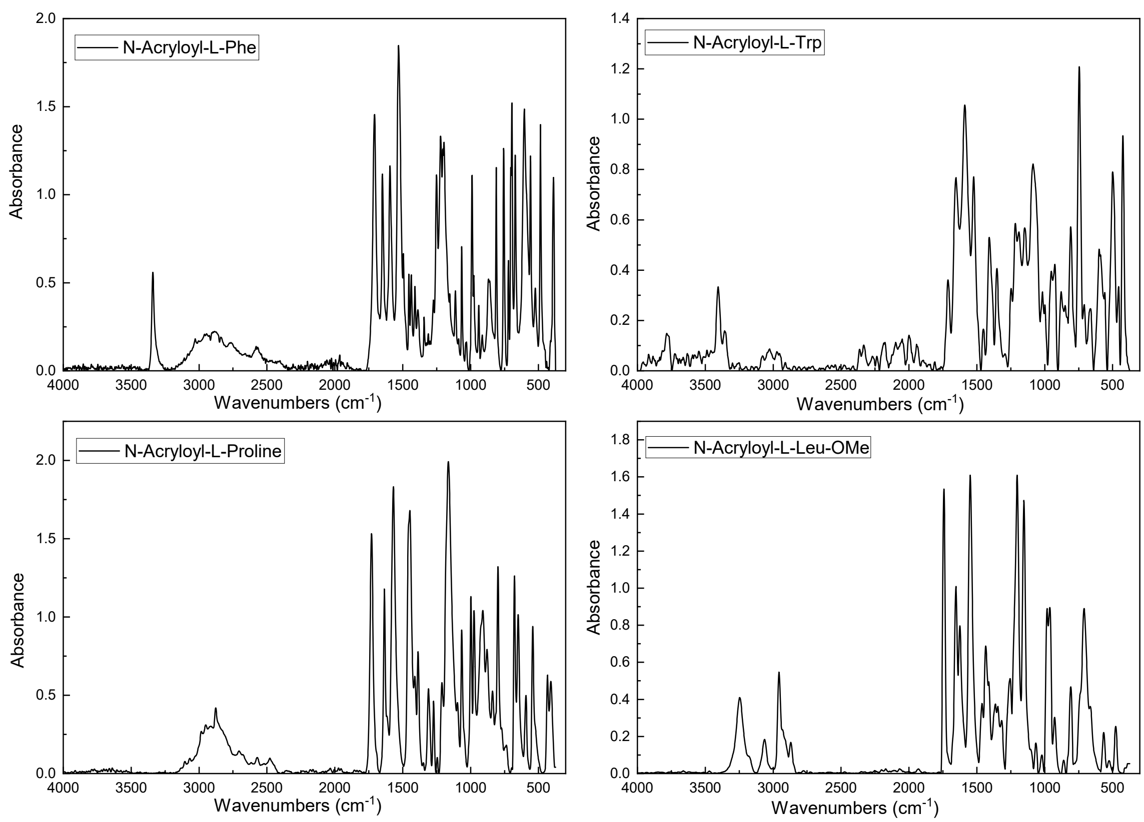
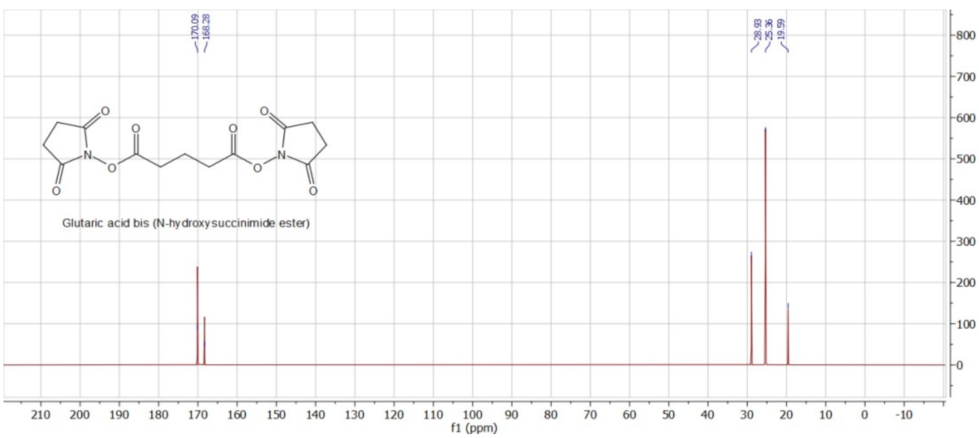


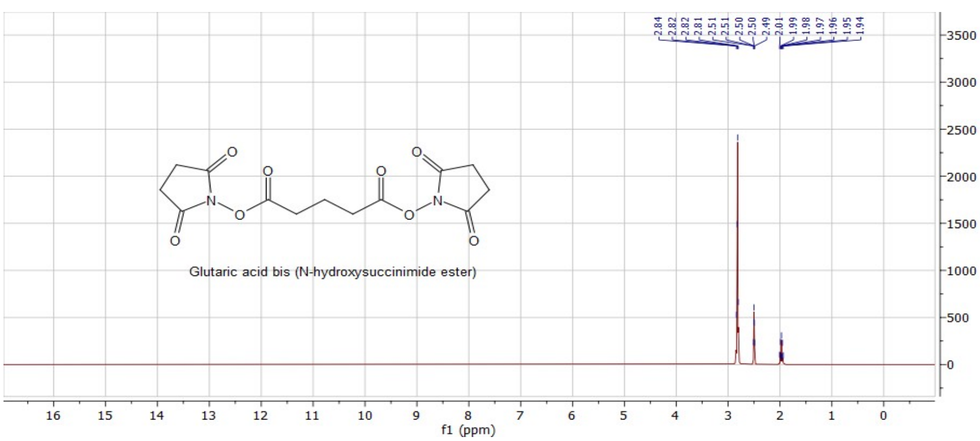
Figure S3. FTIR results of the monomers.

3. Characterization of the crosslinker

	^{1}H NMR	^{13}C NMR	Mass
Glutaric acid bis(N-hydroxysuccinimide ester)	(400 MHz, DMSO-d_6) δ: 10.8 (s, 1H), 8.4 (d, *J* = 8 Hz, 1H), 7.5 (d, *J* = 0.8 Hz, 1H) 7.3 (d, *J* = 0.	(100 MHz, DMSO-d_6) δ: 170.08 (N-C=O), 168.27 (C-C=O), 39.65 (CH_2- CH_2 aliphatic), 25.35 (CH_2- CH_2 aromatic), 19.59 (-CH_2 - aliphatic)	m/z (ES^+): 259 ($[M+Na]^+$, 100)

Table S2. Characterization of the crosslinker by ^{1}H NMR and ^{13}C NMR instruments.





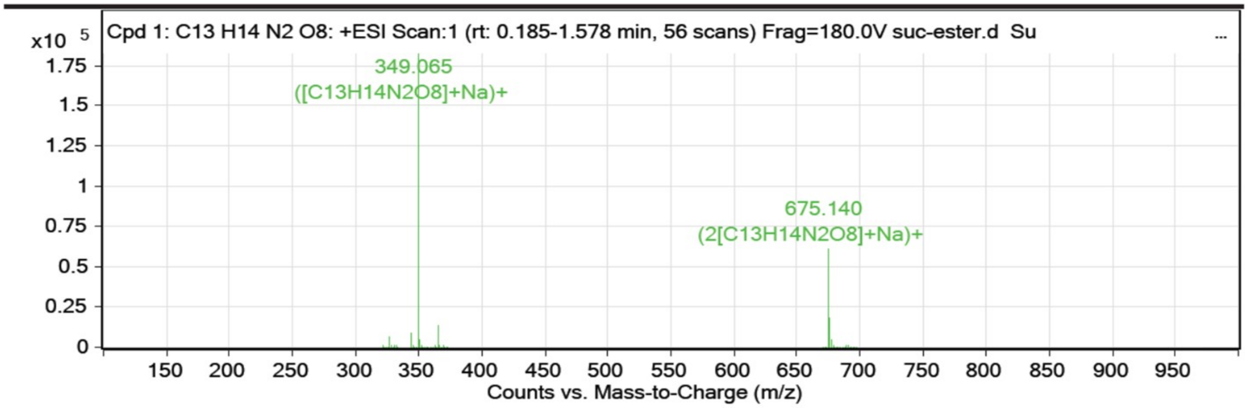


Figure S4. [13]C and [1]H NMR and Mass diagram of the crosslinker.

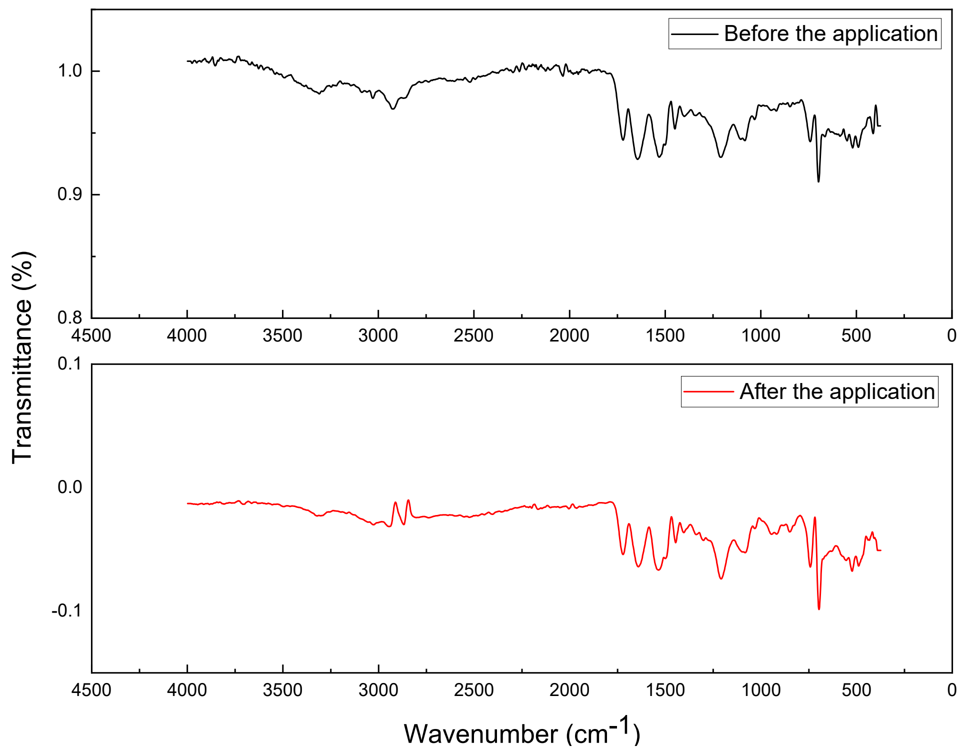


Figure S5. FTIR results of the crosslinker.

4. DLS results of nanoparticles

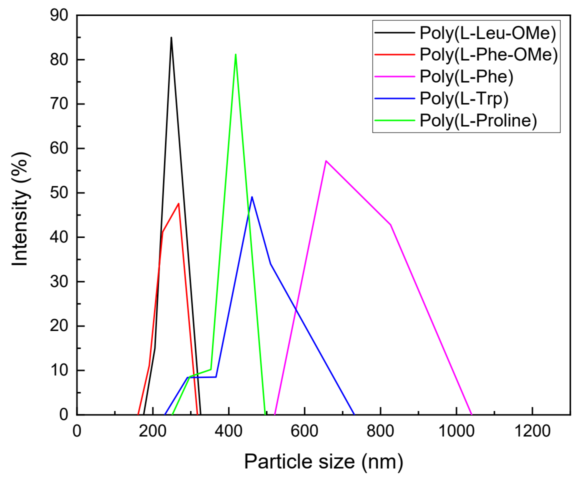


Figure S6. DLS results of nanoparticles; L- Leu-OMe, L- Phe-OMe, L- Phe, L-Trp and L-Proline

5. HPLC chromatograms of the catalysts

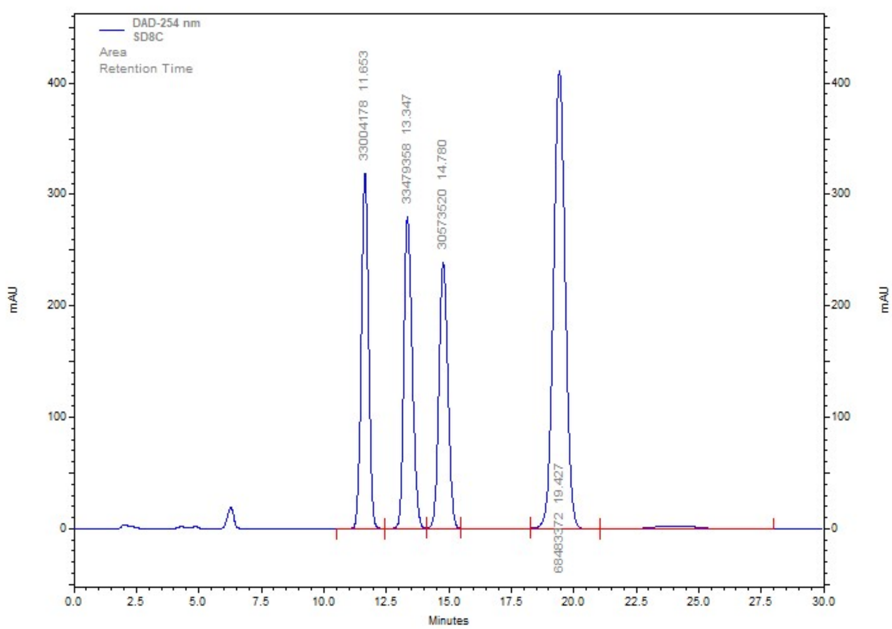


Figure S7. Non-crosslinked protected (L)-phenylalanine polymer, ee 39%.

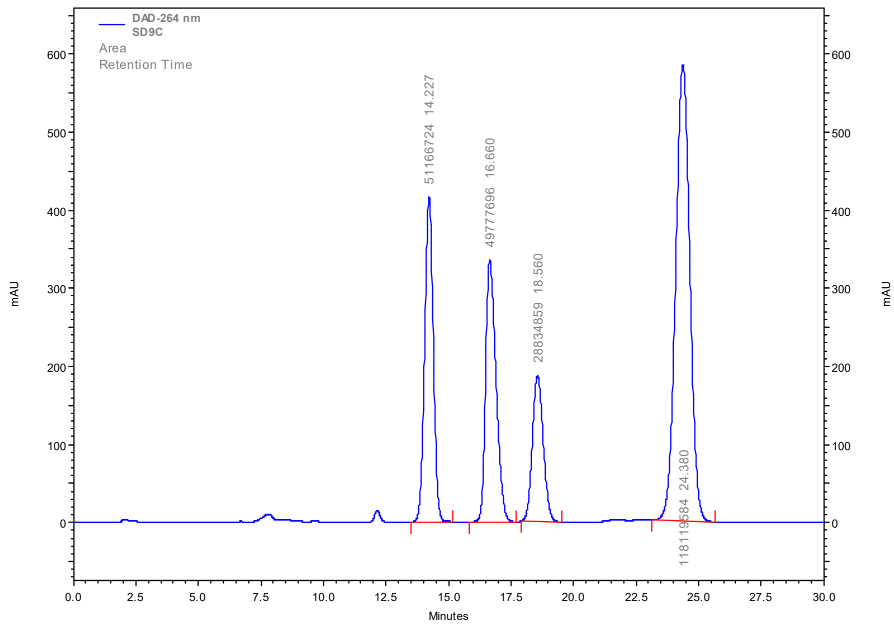


Figure S8. Non-crosslinked unprotected (L)-phenylalanine polymer, ee 61%

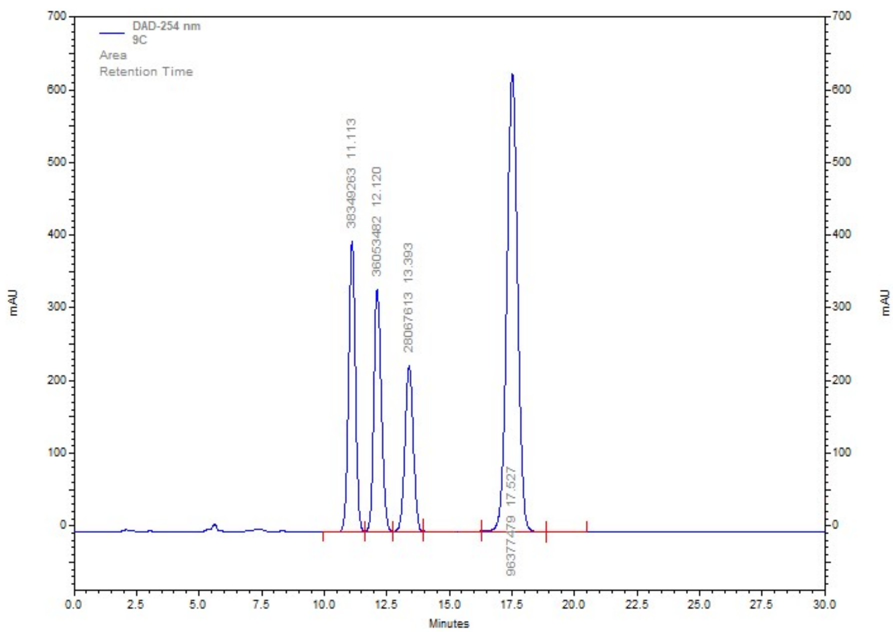


Figure S9. Non-crosslinked unprotected (L)-tyrosine polymer, ee 57%.

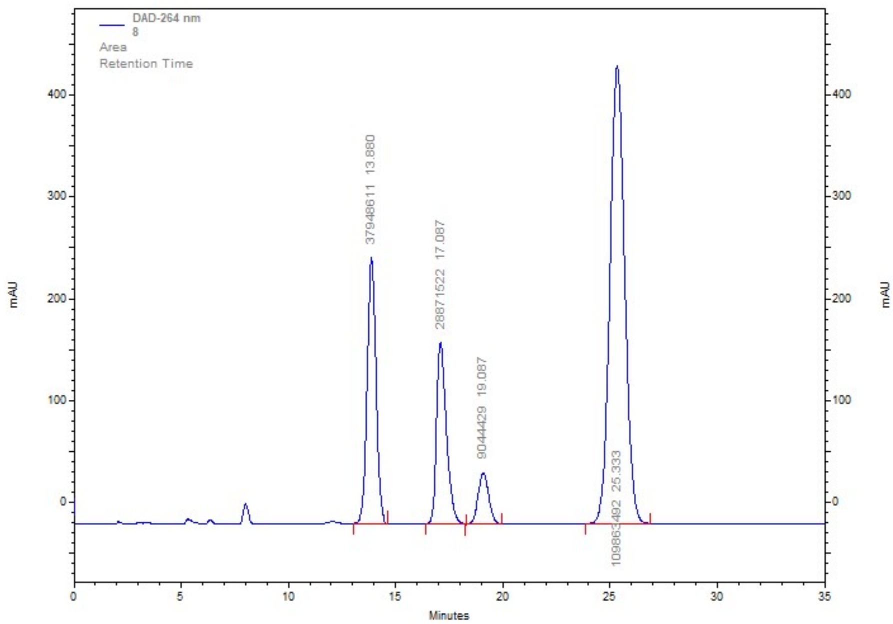


Figure S10. Non-crosslinked unprotected (L)-tryptophan polymer, ee 86%.

6. Reference

1. Montenegro RV. Crystallization, biomimetics and semiconducting polymers in confined systems.

Universität Potsdam; 2003.