Electronic Supplementary Information

Effect of Residue Structure on the Thermal and Thermoresponsive Properties of γ-Substituted Poly(N-acryloyl-2-pyrrolidone)s

R. Bhat, H. Patel, P. Tsai, X. Sun, D. Daoud, R. A. Lalancette, B. Michniak-Kohn, Agostino Pietrangelo*

a Department of Chemistry, Rutgers University-Newark, 73 Warren Street, Newark, New Jersey 07102, United States
b Department of Pharmaceutics, Ernest Mario School of Pharmacy, Rutgers University, 160 Frelinghuysen Road, Piscataway, New Jersey 08854-8022, USA

Email: a.pietrangelo@rutgers.edu
### Table of Contents

Figure S 1. $^1$H NMR spectrum of 5-ethylthio-2-pyrrrolidone (500 MHz, CDCl$_3$). .................8  
Figure S 2. $^{13}$C NMR spectrum of 5-ethylthio-2-pyrrrolidone (126 MHz, CDCl$_3$). .................9  
Figure S 3. $^1$H NMR spectrum of EthSNP (500 MHz, CDCl$_3$). .............................................10  
Figure S 4. $^{13}$C NMR spectrum of EthSNP (126 MHz, CDCl$_3$). .............................................11  
Figure S 5. $^1$H NMR spectrum of 5-butythio-2-pyrrrolidone (500 MHz, CDCl$_3$). .................12  
Figure S 6. $^{13}$C NMR spectrum of 5-butythio-2-pyrrrolidone (126 MHz, CDCl$_3$) ..................13  
Figure S 7. 2D COSY NMR spectrum of EthONP (500 MHz, CDCl$_3$). .......................................14  
Figure S 8. 2D COSY NMR spectrum of EthSNP (500 MHz, CDCl$_3$). .......................................15  
Figure S 9. $^1$H NMR spectrum of BuSNP (500 MHz, CDCl$_3$). .............................................16  
Figure S 10. $^{13}$C NMR spectrum of BuSNP (126 MHz, CDCl$_3$). ...........................................17  
Figure S 11. $^1$H NMR spectrum of 5-cyclohexyloxy-2-pyrrrolidone (500 MHz, CDCl$_3$). ...........18  
Figure S 12. $^{13}$C NMR spectrum of 5-cyclohexyloxy-2-pyrrrolidone (126 MHz, CDCl$_3$). .........19  
Figure S 13. $^1$H NMR spectrum of CyONP (126 MHz, CDCl$_3$). .............................................20  
Figure S 14. $^{13}$C NMR spectrum of CyONP (126 MHz, CDCl$_3$). .............................................21  
Figure S 15. $^1$H NMR spectrum of 5-cyclohexylthio-2-pyrrrolidone (500 MHz, CDCl$_3$) ..........22  
Figure S 16. $^{13}$C NMR spectrum of 5-cyclohexylthio-2-pyrrrolidone (126 MHz, CDCl$_3$). ........23  
Figure S 17. $^1$H NMR spectrum of CySNP (500 MHz, CDCl$_3$). .............................................24  
Figure S 18. $^{13}$C NMR spectrum of CySNP (126 MHz, CDCl$_3$). .............................................25  
Figure S 19. $^1$H NMR spectrum of 5-phenylthio-2-pyrrrolidone (500 MHz, CDCl$_3$) ...............26  
Figure S 20. $^{13}$C NMR spectrum of 5-phenylthio-2-pyrrrolidone (126 MHz, CDCl$_3$). ..........27  
Figure S 21. $^1$H NMR spectrum of PhSNP (500 MHz, CDCl$_3$). .............................................28  
Figure S 22. $^{13}$C NMR spectrum of CySNP (126 MHz, CDCl$_3$). .............................................29  
Figure S 23. $^1$H NMR spectrum of 5-methoxyethylthio-2-pyrrrolidone (500 MHz, CDCl$_3$). ....30  
Figure S 24. $^{13}$C NMR spectrum of 5-methoxyethylthio-2-pyrrrolidone (126 MHz, CDCl$_3$). .......31  
Figure S 25. $^1$H NMR spectrum of MeOEthSNP (500 MHz, CDCl$_3$). .......................................32  
Figure S 26. $^{13}$C NMR spectrum of MeOEthSNP (126 MHz, CDCl$_3$). .......................................33  
Figure S 27. $^1$H NMR spectrum of 5-tetrahydofurfuryloxy-2-pyrrrolidone (500 MHz, CDCl$_3$). ..34  
Note: ........................................................................................................................................34  
Figure S 28. $^{13}$C NMR spectrum of 5-tetrahydofurfuryloxy-2-pyrrrolidone (126 MHz, CDCl$_3$). ..35  
Figure S 29. $^1$H NMR spectrum of FurONP (500 MHz, CDCl$_3$). .............................................36  
Figure S 30. $^{13}$C NMR spectrum of FurONP (126 MHz, CDCl$_3$). .............................................37  
Figure S 31. $^1$H NMR spectrum of 5-stearythio-2-pyrrrolidone (500 MHz, CDCl$_3$) ...............38  
Figure S 32. $^{13}$C NMR spectrum of 5-stearythio-2-pyrrrolidone (126 MHz, CDCl$_3$) ..........39  
Figure S 33. $^1$H NMR spectrum of StSNP (500 MHz, CDCl$_3$). ...............................................40  
Figure S 34. $^{13}$C NMR spectrum of StSNP (126 MHz, CDCl$_3$). ...............................................41  
Figure S 35. GPC trace of poly(EthONP). ...................................................................................42  
Figure S 36. GPC trace of poly(EthSNP). ...................................................................................42  
Figure S 37. GPC trace of poly(BuONP). ...................................................................................43  
Figure S 38. GPC trace of poly(BuSNP). ...................................................................................43
Figure S 39. GPC trace of poly(CyONP). ................................................................. 44
Figure S 40. GPC trace of poly(CySNP). ................................................................. 44
Figure S 41. GPC trace of poly(PhSNP). ................................................................. 45
Figure S 42. GPC trace of poly(MeOEthONP). ....................................................... 45
Figure S 43. GPC trace of poly(MeOEthSNP). ....................................................... 46
Figure S 44. GPC trace of poly(FurONP). ............................................................... 46
Figure S 45. GPC trace of poly(StSNP). ................................................................. 47
Figure S 46. $^1$H NMR spectrum of poly(NP) (500 MHz, CDCl$_3$)......................... 48
Figure S 47. $^1$H NMR spectrum of poly(EthSNP) (500 MHz, CDCl$_3$). ................. 49
Figure S 48. $^1$H NMR spectrum of poly(BuSNP) (500 MHz, CDCl$_3$). ................. 50
Figure S 49. $^1$H NMR spectrum of poly(CyONP) (500 MHz, CDCl$_3$)............... 51
Figure S 50. $^1$H NMR spectrum of poly(CySNP) (500 MHz, CDCl$_3$). ................. 52
Figure S 51. $^1$H NMR spectrum of poly(PhSNP) (500 MHz, CDCl$_3$). ................. 53
Figure S 52. $^1$H NMR spectrum of poly(MeOEthSNP) (500 MHz, CDCl$_3$)........ 54
Figure S 53. $^1$H NMR spectrum of poly(FurONP) (500 MHz, CDCl$_3$). ................. 55
Figure S 54. $^1$H NMR spectrum of poly(StSNP) (500 MHz, CDCl$_3$). ................. 56
Figure S 55. $^1$H NMR spectrum of 3 (500 MHz, CDCl$_3$). ..................................... 57
Figure S 56. $^{13}$C NMR spectrum of 3 (500 MHz, CDCl$_3$). ..................................... 58
Figure S 57. 2D COSY NMR spectrum of 3 (500 MHz, CDCl$_3$). ......................... 59
Figure S 58. DSC traces of poly(EthONP) (red, solid), poly(EthSNP) (red, dash),
poly(BuONP) (black, solid), poly(BuSNP) (black, dash). Second scan, ramp rate: 10
$^\circ$C/min.................................................................................................................. 60
Figure S 59. DSC traces of poly(CyONP) (black, solid), poly(CySNP) (black, dash),
poly(PhSNP) (red, solid). Second scan, ramp rate: 10 $^\circ$C/min.............................. 60
Figure S 60. DSC traces of poly(FurONP) (black, solid), poly(NP) (black, dash),
poly(MeOEthONP) (red, solid) and poly(MeOEthSNP) (red, dash). Second scan,
ramp rate: 10 $^\circ$C/min ......................................................................................... 61
Figure S 61. DSC traces of poly(StSNP). Second scan, ramp rate: 10 $^\circ$C/min........ 61
Figure S 62. TGA thermograms of poly(NP). ......................................................... 62
Figure S 63. TGA thermograms of poly(EthONP) and poly(EthSNP). ................. 62
Figure S 64. TGA thermograms of poly(BuONP) and poly(BuSNP).................... 63
Figure S 65. TGA thermograms of poly(CyONP) and poly(CySNP). ................. 63
Figure S 66. TGA thermograms of poly(MeOEthONP) and poly(MeOEthSNP). .... 64
Figure S 67. TGA thermograms of poly(PhSNP) and poly(StSNP). .................... 64
**Experimental Section**

**Single Crystal X-Ray Analysis.** A suitable crystal of StSNP was selected and mounted on a Bruker-AXS SMART APEX II CCD diffractometer at 100(1)K. The cell dimensions and the intensities were collected with Cu-Kα radiation (l = 1.54178 Å). Data processing, Lorentz-polarization, and face-indexed numerical absorption corrections were performed using SAINT, APEX, and SADABS computer programs. The structure was solved by direct methods and refined by full-matrix least-squares methods on F², using the SHELXTL V 6.14 program package. All non-hydrogen atoms were refined anisotropically. All the H atoms in all of the structures were found in electron-density difference maps.

The methyl H atoms were put in ideally staggered positions with C---H distances of 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C). The methine, methylene, and pyrrolidone Hs were all placed in geometrically idealized positions and constrained to ride on their parent C atoms with C---H distances of 0.93, 0.97, and 0.98 Å, respectively, and U_{iso}(H) = 1.2U_{eq}(C).

**5-Ethylthio-2-pyrrolidone.** Method A. Yield, 70%. Analytical data consistent with reported data. ¹H NMR (500 MHz, CDCl₃): δ 7.13 (br, s, 1H), 4.83 (m, 1H), 2.64 (q, 3J_{HH} = 7.40 Hz, 2H), 2.52 (m, 2H), 2.33 (m, 1H), 2.09 (m, 1H), 1.30 (t, 3J_{HH} = 7.40 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃): δ 178.24, 58.89, 29.75, 28.58, 24.35, 14.79.

**EthSNP.** Yield, 25%. R_f = 0.54. ¹H NMR (500 MHz, CDCl₃): δ 7.44 (dd, 3J_{HH} = 16.95 Hz, 3J_{HH} = 10.47 Hz, 1H), 6.52 (d, 3J_{HH} = 16.91 Hz, 1H), 5.87 (d, 3J_{HH} = 10.27 Hz, 1H), 5.67 (d, 3J_{HH} = 7.38 Hz, 1H), 2.88 (m, 2H), 2.73 (m, 1H), 2.55 (m, 1H), 2.45 (m, 1H), 2.14 (m, 1H), 1.30 (t, 3J_{HH} = 7.31 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃): δ 174.79, 165.28, 131.33, 129.13, 61.34, 32.53, 27.54, 26.38, 14.88. GC/MS: m/z (%): 199 (6%) [M⁺], 138 (90%), 84 (23%), 55 (100%), 28 (12%).

**poly(EthSNP).** Yield, 76%. ¹H NMR (500 MHz, CDCl₃): δ 5.66 (br, s, 1H), 3.69 (br, s, 1H), 2.83–2.52 (br, m, 4H), 2.01 – 1.51 (br, m, 4H), 1.27(s, 3H).

**5-Butylthio-2-pyrrolidone.** Method A. Yield, 40%. Analytical data consistent with reported data. ¹H NMR (500 MHz, CDCl₃): δ 6.51 (s, 1H), 4.78 (dd, 3J_{HH} = 7.16 Hz, 3J_{HH} = 3.52 Hz, 1H), 2.52 (m, 4H), 2.30 (m, 1H), 2.09 (m, 1H), 1.57 (m, 2H), 1.39 (m, 2H), 0.90 (t, 3J_{HH} = 7.32 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃): δ 178.24, 59.17, 31.69, 29.93, 29.75, 28.64, 22.02, 13.63. GC/MS: m/z (%): 128 (100%), 98 (49%), 90 (3%), 83 (9%), 68 (5%), 55 (9%), 45 (33%), 28 (24%).

**BuSNP.** Yield, 53%. R_f = 0.61. ¹H NMR (500 MHz, CDCl₃): δ 7.43 (dd, 3J_{HH} = 16.96 Hz, 3J_{HH} = 10.46 Hz, 1H), 6.55 – 6.48 (m, 1H), 5.90 – 5.83 (m, 1H), 5.63 (d, 3J_{HH} = 7.46 Hz, 1H), 2.92 (m, 1H), 2.81 (m, 1H), 2.70 (m, 1H), 2.55 (m, 1H), 2.44 (m, 1H), 2.15 (m, 1H), 1.60 (m, 2H), 1.41 (m, 2H), 0.92 (t, 3J_{HH} = 7.25 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃): δ 174.82, 165.25, 131.31, 129.15, 61.67, 32.52, 31.98, 31.94, 27.59, 21.99, 13.65.
poly(BuSNP). Yield, 25%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 5.49 (s, 1H), 3.63-3.47 (m, 1H), 3.01-2.60 (m, 4H), 1.97 (s, 3H), 1.56 (s, 3H), 1.38 (s, 2H), 0.89 (s, 3H).

5-Phenylthio-2-pyrrolidone. Method A. Yield, 86%. Analytical data consistent with reported data. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.58 – 7.39 (m, 2H), 7.42 – 7.28 (m, 3H), 6.14 (s, 1H), 5.03 (d, $^3$J$_{HH}$ = 7.3 Hz, 1H), 2.56 (m, 1H), 2.31 – 2.04 (m, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 177.71, 134.54, 131.53, 129.39, 128.78, 62.27, 29.11, 28.22.

PhSNP. Yield, 21%. R$_f$ = 0.38. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.58 – 7.39 (m, 2H), 7.42 – 7.28 (m, 3H), 6.14 (s, 1H), 5.03 (d, $^3$J$_{HH}$ = 7.3 Hz, 1H), 2.56 (m, 1H), 2.31 – 2.04 (m, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 177.71, 134.54, 131.53, 129.39, 128.78, 62.27, 29.11, 28.22.

poly(PhSNP). Yield, 35% $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.51 (s, 2H), 7.27 (s, 3H), 5.67 (s, 1H), 3.66 (s, 1H), 2.38 – 1.32 (br m, 6H).

5-Stearylthio-2-pyrrolidone. Method A. Yield, 74%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.84 (br, s, 1H), 4.81 (dd, $^3$J$_{HH}$ = 7.37 Hz, $^3$J$_{HH}$ = 3.52 Hz, 1H), 2.59 (t, $^3$J$_{HH}$ = 7.42, 2H), 2.52 (m, 2H), 2.33 (m, 1H), 2.11 (m, 1H), 1.60 (m, 2H), 1.38 (m, 2H), 1.26 (s, 28H), 0.88 (t, $^3$J$_{HH}$ = 6.93Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 174.87, 165.28, 131.42, 129.12, 61.69, 32.55, 32.35, 31.93, 29.89, 29.71, 29.67, 29.60, 29.51, 29.38, 29.21, 28.92, 27.60, 22.71, 14.15.

poly(StSNP). Yield, 44%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 5.60 (s, 1H), 3.51 (s, 1H), 2.71 (br d, 4H), 1.99 (s, 1H), 1.59 (s, 2H), 1.29 (s, 32H), 0.91 (t, $^3$J$_{HH}$ = 6.73 Hz, 3H).

5-Cyclohexylthio-2-pyrrolidone. Method A. Yield, 77% $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.50 (br s, 1H), 4.90 (dd, $^3$J$_{HH}$ = 7.36, $^3$J$_{HH}$ = 4.09 Hz, 1H), 2.79 (m, 1H), 2.53 (m, 2H), 2.33 (m, 1H), 2.09 (m, 1H), 1.97 (m, 2H), 1.79 (m, 1H), 1.64 (m, 1H), 1.46 – 1.21 (m, 5H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 177.42, 157.81, 43.40, 34.30, 32.40, 29.50, 29.43, 26.03, 25.91, 25.59.

CySNP. Yield, 36%. R$_f$ = 0.38. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.45 (dd, $^3$J$_{HH}$ = 17.01, 10.45 Hz, 1H), 6.53 (d, $^3$J$_{HH}$ = 17.01 Hz, $^3$J$_{HH}$ = 1.76Hz, 1H), 5.88 (dd, $^3$J$_{HH}$ = 10.46 Hz, $^3$J$_{HH}$ = 1.76 Hz, 1H), 5.68 (d, $^3$J$_{HH}$ = 7.32 Hz, 1H), 2.80 (m, 1H), 2.63 – 2.46 (m, 2H), 2.33 (m, 1H), 2.22 – 2.08 (m, 1H), 1.96 (m, 2H), 1.78 (m, 2H), 1.69 – 1.59 (m, 1H), 1.37
\( ^{13}\text{C} \text{NMR} (126 \text{ MHz, CDCl}_3): \delta 174.87, 165.17, 131.21, 129.24, 60.50, 44.48, 34.68, 33.48, 32.49, 28.47, 25.70 \text{ ppm.} \text{GC/MS: m/z (\%)}: 253 (9\%) [M^+], 170 (4\%), 138 (100\%), 84 (18\%), 55 (78\%). \)

dybrid (FurONP). Yield, 74\%, \( ^1\text{H} \text{NMR (500 MHz, CDCl}_3): \delta 5.55 \text{ (s, 1H)}, 3.52 \text{ (s, 1H)}, 3.21 – 2.28 \text{ (m, 6H)}, 1.97 \text{ (m, 4H)}, 1.76 – 1.29 \text{ (m, 7H)}. \)

\textbf{5-Methoxyethanethio-2-pyrrolidone.} Method A. Yield, 70\%, \( ^1\text{H} \text{NMR (500 MHz, CDCl}_3): \delta 7.06 \text{ (br s, 1H)}, 4.85 \text{ (dd, } J_{HH} = 7.52 \text{ Hz, } J_{HH} = 4.50 \text{ Hz, 1H)}, 3.68 \text{ (m, 1H)}, 3.60 \text{ (m, 1H)}, 3.41 \text{ (s, 3H)}, 2.83 \text{ (m, 2H)}, 2.53 \text{ (m, 2H)}, 2.36 \text{ (m, 1H)}, 2.02 \text{ (m, 1H)}. \text{ } ^{13}\text{C} \text{NMR (126 MHz, CDCl}_3): \delta 176.79, 73.77, 60.69, 58.87, 32.50, 29.94, 28.48. \)

\textbf{MeOEtSNP.} Yield, 16\%, \( R_f = 0.23. \) \( ^1\text{H} \text{NMR (500 MHz, CDCl}_3): \delta 7.45 \text{ (dd, } J_{HH} = 17.00, 10.45 \text{ Hz, 1H}), 6.53 \text{ (dd, } J_{HH} = 17.00, 1.71 \text{ Hz, 1H}), 5.89 \text{ (dd, } J_{HH} = 10.45, 1.70 \text{ Hz, 1H}), 5.71 \text{ (d, } J_{HH} = 7.51 \text{ Hz, 1H}), 3.62 \text{ (m, 2H)}, 3.39 \text{ (s, 3H)}, 3.08 \text{ (m, 1H)}, 2.93 \text{ (m, 2H)}, 2.63 – 2.40 \text{ (m, 2H)}, 2.20 \text{ (m, 1H)}. \text{ } ^{13}\text{C} \text{NMR (126 MHz, CDCl}_3): \delta 174.78, 165.42, 131.44, 129.12, 72.20, 62.16, 58.80, 32.46, 32.14, 27.64. \text{GC/MS: m/z (\%)}: 229 (2\%) [M^+], 197 (13\%), 170 (9\%), 138 (100\%), 84 (24\%), 55 (80\%). \)

dybrid (MeOEtSNP). Yield, 61\% \( ^1\text{H} \text{NMR (500 MHz, CDCl}_3): \delta 5.59 \text{ (br s, 1H)} 3.64 \text{ (br, m, 3H)}, 3.39 \text{ (s, 3H)}, 3.04 – 2.05 \text{ (br m, 5H)}, 2.04 – 1.25 \text{ (br m, 3H)}. \)

\textbf{5-Tetrahydrofurfuryloxy-2-pyrrolidone.} Method B. Yield, 22\%. \( ^1\text{H} \text{NMR (500 MHz, CDCl}_3): \delta 7.23 \text{ (br d, } d, \text{ 1H)}, 4.99 \text{ (m, 1H)}, 3.99 \text{ (m, 1H)}, 3.86 \text{ (m, 1H)}, 3.76 \text{ (m, 1H)}, 3.62 - 3.54 \text{ (m, 1H)}, 3.41 \text{ (m, 1H)}, 2.49 \text{ (m, 1H)}, 2.24 \text{ (m, 2H)}, 2.05 \text{ (m, 1H)}, 1.90 \text{ (m, 4H)}, 1.58 – 1.47 \text{ (m, 1H)}. \text{ } ^{13}\text{C} \text{NMR (126 MHz, Chloroform-d): } \delta 177.48, 176.98, 85.30, 84.54, 77.62, 76.33, 76.01, 69.34, 68.01, 66.44, 66.39, 66.19, 62.79, 26.58, 26.49, 26.36, 26.26, 25.95, 25.24, 23.97, 23.61, 23.58. \)

\textbf{FurONP:} Yield, 13% \( R_f = 0.12. \) \( ^1\text{H} \text{NMR (500 MHz, CDCl}_3): \delta 7.44 \text{ (dd, } J_{HH} = 17.00, 10.45 \text{ Hz, 1H}), 6.51 \text{ (d, } J_{HH} = 17.01 \text{ Hz, 1H}), 5.88 \text{ (m, 1H)}, 5.80 \text{ (d, } J_{HH} = 5.28 \text{ Hz, 1H}}, 4.00 \text{ (m, 1H)}, 3.86 \text{ (m, 1H)}, 3.80 \text{ (m, 1H)}, 3.66 \text{ (m, 2H)}, 2.91 \text{ (m, 1H)}, 2.48 \text{ (m, 1H)}, 2.11 \text{ (m, 2H)}, 1.99 – 1.78 \text{ (m, 3H)}, 1.56 \text{ (m, 1H)}. \text{ } ^{13}\text{C} \text{NMR (126 MHz, CDCl}_3): 175.78, 175.74, 166.04, 166.02, 131.37, 129.27, 87.63, 87.35, 78.06, 77.73, 76.82, 73.08, 72.53, 68.46, 68.32, 31.51, 27.94, 27.78, 26.47, 26.42, 25.72, 25.55. \text{GC/MS: m/z (\%)}: 169 (11\%), 138 (69\%), 111 (6\%), 84 (74\%), 71 (100\%), 55 (70\%), 43 (22\%), 27 (9\%). \)

dybrid (FurONP). Yield, 34\% \( ^1\text{H} \text{NMR (500 MHz, CDCl}_3): \delta 5.68 \text{ (s, 1H)}, 4.01 \text{ (s, 2H)}, 3.87-3.60 \text{ (m, 4H)}, 2.78-1.61 \text{ (br, m, 10H)}. \)

\textbf{5-Cyclohexanoxy-2-pyrrolidone.} Method B. Yield, 40\%, \( ^1\text{H} \text{NMR (500 MHz, CDCl}_3): 6.87 \text{ (br, m, 1H)}, 5.12 \text{ (d, } J_{HH} = 6.10 \text{ Hz, 1H}), 3.37 \text{ (m, 1H)}, 2.55 \text{ (m, 1H)}, 2.33 \text{ (m, 1H)}, 2.23 \text{ (m, 1H)}, 2.05 \text{ (m, 1H)}, 1.87 \text{ (m, 2H)}, 1.76 \text{ (m, 2H)}, 1.56 \text{ (m, 1H)}, 1.37-1.21 \text{ (m, 5H)}. \text{ } ^{13}\text{C} \text{NMR (126 MHz, CDCl}_3): \delta 178.88, 83.62, 75.44, 33.36, 32.36, 29.16, 28.35, 25.55, 24.15, 24.06. \)

\textbf{CyONP.} Yield, 26\%. \( R_f = 0.62 \) \( ^1\text{H} \text{NMR (500 MHz, CDCl}_3): \delta 7.47 \text{ (dd, } J_{HH} = 17.00 \text{ Hz, } J_{HH} = 10.45 \text{ Hz, 1H)}, 6.55 \text{ (d, } J_{HH} = 17.02 \text{ Hz, 1H}), 5.88 \text{ (d, } J_{HH} = 10.47 \text{ Hz, 1H}), 5.85 \text{ ppm.} \)
(d, 3\textsubscript{J}HH 5.4 Hz, 1H), 3.70 (m, 1H), 2.93 (m, 1H), 2.48 (m, 1H) 2.15 (m, 1H); 2.03 (m, 1H); 1.96 (m, 1H) 1.88 (m, 1H) 1.74 (m, 2H); 1.55 (m, 1H); 1.3 (m, 5H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): \textdelta 175.75, 165.86, 131.14, 129.47, 85.13, 32.93, 32.72, 31.56, 27.20, 25.61, 24.14, 24.06 GC/MS: m/z (%): 207 (1%), 138 (100%), 111 (9%), 84 (32%), 55 (100%), 28 (20%).

\textbf{poly(CyONP).} Yield, 65\%. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \textdelta 5.70 (br, s, 1H), 3.65 (br, m, 2H), 2.77 (br, m, 3H), 2.17 (br m, 2H), 1.86 (br, m, 3H), 1.70 (br, s, 1H), 1.51 (br, s, 2H), 1.27 (br, m, 5H).

\textbf{poly(PNP).} Yield, 68\% \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \textdelta 3.74 (br, m, 3H), 2.48 (br, m, 2H), 1.97 (s, 2H), 1.71 - 1.38 (br, m, 2H).

\textbf{Compound 3.} Over a period of 30 min, \textit{n}-butyllithium (1.6 M in hexanes, 13.76 mmol) was added drop-wise to a solution of 5-methoxyethoxy-2-pyrrolidone (12.5 mmol) in anhydrous THF (\textit{ca.} 50 mL) at -78 °C. The reaction mixture was stirred at same temperature for 2.5 hr followed by the addition of acryloyl chloride (2.3mL, 16.5 mmol). The solution was allowed to warm up to room temperature overnight. The next morning the solution was quenched with saturated aqueous NH\textsubscript{4}Cl (\textit{ca.} 5 mL). The solvent was removed by reduced pressure and the residue extracted with ethyl acetate (3 x 50 mL). The organic phases were combined and washed with brine (\textit{ca.} 10mL) and dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}. After filtering the mixture, the solvent was removed under reduced pressure to afford a yellow opaque oil. The crude product was purified twice by column chromatography (silica followed by alumina, ethyl acetate/hexanes, 1:1) to afford the product. Yield, 70\%, \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \textdelta 5.78 (d, 3\textsubscript{J}HH = 4.78 Hz, 1H), 3.90 – 3.71 (m, 2H), 3.68 – 3.56 (m, 1H), 3.51 (t, 3\textsubscript{J}HH = 4.63 Hz, 2H), 3.37 (s, 3H), 2.91 (m, 1H), 2.47 (m, 1H), 2.09 (m, 2H), 1.71 (m, 2H), 1.62 – 1.39 (m, 2H), 0.92 (t, 3\textsubscript{J}HH = 7.43 Hz, 3H), 0.88 (t, 3\textsubscript{J}HH = 7.42 Hz, 3H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): \textdelta 177.82, 175.30, 87.49, 72.00, 69.37, 58.97, 46.78, 31.83, 26.23, 24.54, 24.05, 11.62, 11.36. GC/MS: m/z (%): 228 (1%), 198 (3%), 182 (45%), 174 (3%), 153 (8%), 126 (1%), 115 (1%), 98 (58%), 84 (100%), 71 (48%), 59 (16%), 43 (8%).
Figure S 1. $^1$H NMR spectrum of 5-ethylthio-2-pyrrolidone (500 MHz, CDCl$_3$).
Figure S 2. $^{13}$C NMR spectrum of 5-ethylthio-2-pyrrolidone (126 MHz, CDCl$_3$).
Figure S 3. $^1$H NMR spectrum of EthSNP (500 MHz, CDCl$_3$).
Figure S 4. $^{13}$C NMR spectrum of EthSNP (126 MHz, CDCl$_3$).
**Figure S 5.** $^1$H NMR spectrum of 5-butylthio-2-pyrrolidone (500 MHz, CDCl$_3$).
Figure S 6. $^{13}$C NMR spectrum of 5-butylthio-2-pyrrolidone (126 MHz, CDCl$_3$).
Figure S 7. 2D COSY NMR spectrum of EthONP (500 MHz, CDCl₃).
Figure S 8. 2D COSY NMR spectrum of EthSNP (500 MHz, CDCl₃).
Figure S 9. $^1$H NMR spectrum of BuSNP (500 MHz, CDCl$_3$).
**Figure S 10.** $^{13}$C NMR spectrum of BuSNP (126 MHz, CDCl$_3$).
Figure S 11. $^1$H NMR spectrum of 5-cyclohexyloxy-2-pyrrolidone (500 MHz, CDCl$_3$).
Figure S 12. $^{13}$C NMR spectrum of 5-cyclohexyloxy-2-pyrrolidone (126 MHz, CDCl$_3$).
Figure S 13. $^1$H NMR spectrum of CyONP (126 MHz, CDCl$_3$).
Figure S 14. $^{13}$C NMR spectrum of CyONP (126 MHz, CDCl$_3$).
Figure S 15. $^1$H NMR spectrum of 5-cyclohexylthio-2-pyrrolidone (500 MHz, CDCl$_3$).
Figure S 16. $^{13}$C NMR spectrum of 5-cyclohexylthio-2-pyrrolidone (126 MHz, CDCl$_3$).
Figure S 17. $^1$H NMR spectrum of CySNP (500 MHz, CDCl$_3$).
Figure S 18. $^{13}$C NMR spectrum of CySNP (126 MHz, CDCl$_3$).
Figure S 19. $^1$H NMR spectrum of 5-phenylthio-2-pyrrolidone (500 MHz, CDCl$_3$).
Figure S 20. $^{13}$C NMR spectrum of 5-phenylthio-2-pyrrolidone (126 MHz, CDCl$_3$).
Figure S 21. $^1$H NMR spectrum of PhSNP (500 MHz, CDCl$_3$).
Figure S 22. $^{13}$C NMR spectrum of CySNP (126 MHz, CDCl$_3$).
Figure S 23. $^1$H NMR spectrum of 5-methoxyethylthio-2-pyrrolidone (500 MHz, CDCl$_3$).
**Figure S 24.** $^{13}$C NMR spectrum of 5-methoxyethylthio-2-pyrrolidone (126 MHz, CDCl$_3$).
Figure S 25. $^1$H NMR spectrum of MeOEthSNP (500 MHz, CDCl$_3$).
Figure S 26. $^{13}$C NMR spectrum of MeOEthSNP (126 MHz, CDCl$_3$).
Figure S 27. $^1$H NMR spectrum of 5-tetrahydrofurfuryloxy-2-pyrrolidone (500 MHz, CDCl$_3$). Note:
Figure S 28. $^{13}$C NMR spectrum of 5-tetrahydrofurfuryloxy-2-pyrrolidone (126 MHz, CDCl$_3$).
Figure S 29. $^1$H NMR spectrum of FurONP (500 MHz, CDCl$_3$).
Figure S 30. $^{13}$C NMR spectrum of FurONP (126 MHz, CDCl$_3$).
Figure S 31. $^1$H NMR spectrum of 5-stearlthio-2-pyrrolidone (500 MHz, CDCl$_3$).
Figure S 32. $^{13}$C NMR spectrum of 5-stearylthio-2-pyrrolidone (126 MHz, CDCl$_3$).
Figure S 33. $^1$H NMR spectrum of StNP (500 MHz, CDCl$_3$).
Figure S 34. $^{13}$C NMR spectrum of StSNP (126 MHz, CDCl$_3$).
Figure S 35. GPC trace of poly(EthONP).

Figure S 36. GPC trace of poly(EthSNP).
Figure S 37. GPC trace of poly(BuONP).

Figure S 38. GPC trace of poly(BuSNP).
Figure S 39. GPC trace of poly(CyONP).

Figure S 40. GPC trace of poly(CySNP).
Figure S 41. GPC trace of poly(PhSNP).

Figure S 42. GPC trace of poly(MeOEthONP).
Figure S 43. GPC trace of poly(MeOEthSNP).

Figure S 44. GPC trace of poly(FurONP).
Figure S 45. GPC trace of poly(StSNP).
Figure S 46. $^1$H NMR spectrum of poly(NP) (500 MHz, CDCl$_3$).
Figure S 47. $^1$H NMR spectrum of poly(EthSNP) (500 MHz, CDCl$_3$).
Figure S 48. $^1$H NMR spectrum of poly(BuSNP) (500 MHz, CDCl$_3$).
Figure S 49. $^1$H NMR spectrum of poly(CyONP) (500 MHz, CDCl$_3$).
**Figure S 50.** $^1$H NMR spectrum of poly(CySNP) (500 MHz, CDCl$_3$).
Figure S 51. $^1$H NMR spectrum of poly(PhSNP) (500 MHz, CDCl$_3$).
Figure S 52. $^1$H NMR spectrum of poly(MeOEthSNP) (500 MHz, CDCl$_3$).
Figure S 53. $^1$H NMR spectrum of poly(FurONP) (500 MHz, CDCl$_3$).
Figure S 54. $^1$H NMR spectrum of poly(StSNP) (500 MHz, CDCl$_3$).
Figure S 55. $^1$H NMR spectrum of 3 (500 MHz, CDCl$_3$).
Figure S 56. $^1$C NMR spectrum of 3 (500 MHz, CDCl$_3$).
Figure S 57. 2D COSY NMR spectrum of 3 (500 MHz, CDCl$_3$).
Figure S 58. DSC traces of poly(EthONP) (red, solid), poly(EthSNP) (red, dash), poly(BuONP) (black, solid), poly(BuSNP) (black, dash). Second scan, ramp rate: 10 °C/min.

Figure S 59. DSC traces of poly(CyONP) (black, solid), poly(CySNP) (black, dash), poly(PhSNP) (red, solid). Second scan, ramp rate: 10 °C/min.
Figure S 60. DSC traces of poly(FuONP) (black, solid), poly(NP) (black, dash), poly(MeOEthONP) (red, solid) and poly(MeOEthSNP) (red, dash). Second scan, ramp rate: 10 °C/min.

Figure S 61. DSC traces of poly(StSNP). Second scan, ramp rate: 10 °C/min.
Figure S 62. TGA thermograms of poly(NP).

Figure S 63. TGA thermograms of poly(EthONP) and poly(EthSNP).
Figure S 64. TGA thermograms of poly(BuONP) and poly(BuSNP).

Figure S 65. TGA thermograms of poly(CyONP) and poly(CySNP).
Figure S 66. TGA thermograms of poly(MeOEthONP) and poly(MeOEthSNP).

Figure S 67. TGA thermograms of poly(PhSNP) and poly(StSNP).
Table S 1. Cloud point temperatures of poly(MeOEthONP) and poly(FurONP).\(^a\)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Conc. (mg/mL)</th>
<th>Medium</th>
<th>CP (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(MeOEthONP)</td>
<td>0.2</td>
<td>DI-water</td>
<td>47</td>
</tr>
<tr>
<td>poly(MeOEthONP)</td>
<td>0.4</td>
<td>DI-water</td>
<td>44</td>
</tr>
<tr>
<td>poly(MeOEthONP)</td>
<td>0.6</td>
<td>DI-water</td>
<td>40</td>
</tr>
<tr>
<td>poly(MeOEthONP)</td>
<td>0.8</td>
<td>DI-water</td>
<td>40</td>
</tr>
<tr>
<td>poly(MeOEthONP)</td>
<td>1.0</td>
<td>DI-water</td>
<td>37</td>
</tr>
<tr>
<td>poly(MeOEthONP)</td>
<td>0.2</td>
<td>PBS</td>
<td>45</td>
</tr>
<tr>
<td>poly(MeOEthONP)</td>
<td>0.4</td>
<td>PBS</td>
<td>40</td>
</tr>
<tr>
<td>poly(MeOEthONP)</td>
<td>0.6</td>
<td>PBS</td>
<td>39</td>
</tr>
<tr>
<td>poly(MeOEthONP)</td>
<td>0.8</td>
<td>PBS</td>
<td>38</td>
</tr>
<tr>
<td>poly(MeOEthONP)</td>
<td>1.0</td>
<td>PBS</td>
<td>36</td>
</tr>
<tr>
<td>poly(FurONP)</td>
<td>0.2</td>
<td>DI-water</td>
<td>15</td>
</tr>
<tr>
<td>poly(FurONP)</td>
<td>0.4</td>
<td>DI-water</td>
<td>13</td>
</tr>
<tr>
<td>poly(FurONP)</td>
<td>0.6</td>
<td>DI-water</td>
<td>10</td>
</tr>
<tr>
<td>poly(FurONP)</td>
<td>0.8</td>
<td>DI-water</td>
<td>10</td>
</tr>
<tr>
<td>poly(FurONP)</td>
<td>1.0</td>
<td>DI-water</td>
<td>9</td>
</tr>
<tr>
<td>poly(FurONP)</td>
<td>0.2</td>
<td>PBS</td>
<td>16</td>
</tr>
<tr>
<td>poly(FurONP)</td>
<td>0.4</td>
<td>PBS</td>
<td>17</td>
</tr>
<tr>
<td>poly(FurONP)</td>
<td>0.6</td>
<td>PBS</td>
<td>9</td>
</tr>
<tr>
<td>poly(FurONP)</td>
<td>0.8</td>
<td>PBS</td>
<td>7</td>
</tr>
<tr>
<td>poly(FurONP)</td>
<td>1.0</td>
<td>PBS</td>
<td>6</td>
</tr>
</tbody>
</table>

\(^a\) Cloud points were measured by turbidimetry (\(\lambda = 500\) nm) and taken as the temperature at which the solution lost 50% of its original optical transmission during the heating scan.

---


