C-Terminal Functionalization of Nylon-3 Polymers: Effects of C-Terminal Groups on Antibacterial and Hemolytic Activities

Supporting Information Part 2

MALDI-TOF, GPC, $^1$H NMR, Bioassay and CAC data

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MALDI-TOF data samples generated during efforts to achieve C-terminal functionalization of poly(CO)

MALDI-TOF spectrum of the product from Table S1, entry 1. M refers to poly(CO) containing 15 units with an acetyl N-terminus and an imide C-terminus.
MALDI-TOF spectrum of the product from Table S1, entry 2. M refers to poly(CO) containing 10 subunits with an acetyl N-terminus and an imide C-terminus. Nu = benzylamine.
MALDI-TOF spectrum of the product from Table S1, entry 3. M refers to poly(CO) containing 12 subunits with an acetyl N-terminus and an imide C-terminus. Nu = benzylamine.
MALDI-TOF spectrum of the product from Table S1, entry 4. M refers to poly(CO) containing 19 subunits with an acetyl N-terminus and an imide C-terminus. Nu = benzylamine, Nu' = benzyl mercaptan.
MALDI-TOF spectrum of the product from Table S1, entry 5. M refers to poly(CO) containing 9 subunits with an acetyl N-terminus and an imide C-terminus. Nu = benzylamine.
MALDI-TOF spectrum of the product from Table S1, entry 6. The labels 1, 2 and 3 indicate [M+Nu+Li]$^+$ (2165), [M+Nu+Na]$^+$ (2181) and [M+Nu+K]$^+$ (2197) peaks, respectively, where M refers to poly(\text{CO}) containing 13 subunits with an acetyl N-terminus and an imide C-terminus. Nu = benzyl mercaptan.
MALDI-TOF spectrum of the product from Table S1, entry 7. M refers to poly(CO) containing 23 subunits with an acetyl $N$-terminus and an imide $C$-terminus.
MALDI-TOF spectrum of the product from Table S1, entry 8. M refers to poly(CO) containing 19 subunits with an acetyl N-terminus and an imide C-terminus.
MALDI-TOF spectrum of the product from Table S1, entry 10. M refers to poly(CO) containing 19 subunits with an acetyl N-terminus and an imide C-terminus. Nu = MeOH.
MALDI-TOF spectrum of the product from Table S1, entry 11. M refers to poly(CO) containing 8 subunits with an acetyl N-terminus and an imide C-terminus. Nu = EtOH.
MALDI-TOF spectrum of the product from Table S1, entry 12. M refers to poly(CO) containing 9 subunits with an acetyl N-terminus and an imide C-terminus. Nu = BnOH.
MALDI-TOF spectrum of the product from Table S1, entry 13. M refers to poly(CO) containing 8 subunits with an acetyl N-terminus and an imide C-terminus. Nu = HOCH₂CH₂NH₂.
MALDI-TOF spectrum of the product from Table S1, entry 14. M refers to poly(CO) containing 31 subunits with an acetyl N-terminus and an imide C-terminus.
MALDI-TOF spectrum of the product from Table S1, entry 15. M refers to poly(CO) containing 10 subunits with an acetyl N-terminus and an imide C-terminus.
MALDI-TOF spectrum of the product from Table S1, entry 16. M refers to poly(CO) containing 29 subunits with an acetyl N-terminus and an imide C-terminus.
GPC, $^1$H NMR and MALDI-TOF characterization data for C-terminal imide and C-terminal functionalized 37:63 CH:MM nylon-3 random copolymers (R’ = side chain of either CH or MM)

GPC trace (RI detection) of Boc-protected 1 in THF. $M_n = 4627$, PDI = 1.10, $dn/dc = 0.1$.

$^1$H NMR of 1 in D$_2$O at 10 mg/mL.
MALDI-TOF spectrum of 1.
GPC trace (RI detection) of Boc-protected 2 in THF. $M_n = 4749$, PDI = 1.13, $dn/dc = 0.1$.

$^1$H NMR of 2 in D$_2$O at 10 mg/mL.
MALDI-TOF spectrum of 2.
GPC trace (RI detection) of Boc-protected 3 in THF. $M_n = 5845$, PDI = 1.15, $dn/dc = 0.1$.

$^1$H NMR of 3 in D$_2$O at 10 mg/mL.
MALDI-TOF spectrum of 3.
GPC trace (RI detection) of Boc-protected 4 (with trityl-protected thiol) in THF. $M_n = 5337$, PDI = 1.07, $dn/dc = 0.1$.

$^1$H NMR of 4 in D$_2$O at 10 mg/mL.
MALDI-TOF spectrum of 4.
GPC trace (RI detection) of Boc-protected 1B-a in THF. $M_n = 4890$, PDI = 1.13, $dn/dc = 0.1$.

$^1$H NMR of 1B-a in D$_2$O at 10 mg/mL.
MALDI-TOF spectrum of 1B-a.
GPC trace (RI detection) of Boc-protected 1B-b in THF. $M_n = 5975$, PDI = 1.07, $dn/dc = 0.1$.

$^1$H NMR of 1B-b in D$_2$O at 10 mg/mL.
MALDI-TOF spectrum of 1B-b.
GPC trace (RI detection) of Boc-protected 2B-a in THF. $M_n = 3948$, PDI = 1.13, $dn/dc = 0.1$.

$^1$H NMR of 2B-a in D$_2$O at 10 mg/mL.
MALDI-TOF spectrum of 2B-a.
GPC trace (RI detection) of Boc-protected 2B-b in THF. $M_n = 4837$, PDI = 1.12, dn/dc = 0.1.

$^1$H NMR of 2B-b in D$_2$O at 10 mg/mL.

Polymer 2B-b does not produce a MALDI-TOF spectrum.
GPC trace (RI detection) of Boc-protected 3B in THF. $M_n = 4112$, PDI = 1.12, $dn/dc = 0.1$.

$^1$H NMR of 3B in D$_2$O at 10 mg/mL.
MALDI-TOF spectrum of 3B.
GPC trace (RI detection) of Boc-protected 1C-a in THF. $M_n = 5072$, PDI = 1.09, $dn/dc = 0.1$.

$^1$H NMR of 1C-a in D$_2$O at 10 mg/mL.
MALDI-TOF spectrum of 1C-a.
GPC trace (RI detection) of Boc-protected 1C-b in THF. $M_n = 6135$, PDI = 1.12, dn/dc = 0.1.

$^1$H NMR of 1C-b in D$_2$O at 10 mg/mL.
MALDI-TOF spectrum of 1C-b.
GPC trace (RI detection) of Boc-protected 2D in THF. $M_n = 5753$, PDI = 1.11, dn/dc = 0.1.

$^1$H NMR of 1E in D$_2$O at 10 mg/mL.
MALDI-TOF spectrum of 1E.
GPC trace (RI detection) of Boc-protected 1D-a in THF. $M_n = 5676$, PDI = 1.06, $dn/dc = 0.1$.

$^1$H NMR of 1D-a in D$_2$O at 10 mg/mL.
MALDI-TOF spectrum of 1D-a.
GPC trace (RI detection) of Boc-protected 1D-b in THF. $M_n = 5544$, PDI = 1.09, $dn/dc = 0.1$.

$^1$H NMR of 1D-b in D$_2$O at 10 mg/mL.
MALDI-TOF spectrum of 1D-b.
GPC trace (RI detection) of Boc-protected 1F (with trityl-protected thiol) in THF. $M_n = 5449$, PDI = 1.11, $dn/dc = 0.1$.

$^1$H NMR of Boc-protected 1F (with trityl-protected thiol) in CDCl$_3$ at 10 mg/mL.
GPC trace (RI detection) of Boc-protected 2F (with trityl-protected thiol) in THF. $M_n = 4917$, PDI = 1.12, dn/dc = 0.1.

$^1$H NMR of Boc-protected 2F (with trityl-protected thiol) in CDCl$_3$ at 10 mg/mL.
$^1$H NMR of 2F D$_2$O at 10 mg/mL.

MALDI-TOF spectrum of 2F.
GPC trace (RI detection) of Boc-protected 4C (with trityl-protected thiol) in THF. $M_n = 4573$, PDI = 1.13, $dn/dc = 0.1$.

$^1$H NMR of Boc-protected 4C (with trityl-protected thiol) in CDCl$_3$ at 10 mg/mL.
$^1$H NMR of 4C D$_2$O at 10 mg/mL.

MALDI-TOF spectrum of 4C.
3 Antibacterial and hemolytic assays

Dose-response curves of antibacterial activity of polymer 1. Numbers in the parentheses are the MIC values (µg/mL) deduced from the corresponding curves. The lines simply connect the data points.

Dose-response curves of antibacterial activity of polymer 2. Numbers in the parentheses are the MIC values (µg/mL) deduced from the corresponding curves. The lines simply connect the data points.
Dose-response curves of antibacterial activity of polymer 3. Numbers in the parentheses are the MIC values (µg/mL) deduced from the corresponding curves. The lines simply connect the data points.

Dose-response curves of antibacterial activity of polymer 1B-a. Numbers in the parentheses are the MIC values (µg/mL) deduced from the corresponding curves. The lines simply connect the data points.
Dose-response curves of antibacterial activity of polymer 1B-b. Numbers in the parentheses are the MIC values (µg/mL) deduced from the corresponding curves. The lines simply connect the data points.

Dose-response curves of antibacterial activity of polymer 2B-a. Numbers in the parentheses are the MIC values (µg/mL) deduced from the corresponding curves. The lines simply connect the data points.
Dose-response curves of antibacterial activity of polymer 2B-b. Numbers in the parentheses are the MIC values (µg/mL) deduced from the corresponding curves. The lines simply connect the data points.

Dose-response curves of antibacterial activity of polymer 3B. Numbers in the parentheses are the MIC values (µg/mL) deduced from the corresponding curves. The lines simply connect the data points.
Dose-response curves of antibacterial activity of 1C-a. Numbers in the parentheses are the MIC values (µg/mL) deduced from the corresponding curves. The lines simply connect the data points.

Dose-response curves of antibacterial activity of 1C-b. Numbers in the parentheses are the MIC values (µg/mL) deduced from the corresponding curves. The lines simply connect the data points. The polymer is not fully soluble in BHI > 100 µg/mL.
Dose-response curves of antibacterial activity of **1D-a**. Numbers in the parentheses are the MIC values (µg/mL) deduced from the corresponding curves. The lines simply connect the data points.

Dose-response curves of antibacterial activity of **1D-b**. Numbers in the parentheses are the MIC values (µg/mL) deduced from the corresponding curves. The lines simply connect the data points.
Dose-response curves of antibacterial activity of 1E. Numbers in the parentheses are the MIC values (µg/mL) deduced from the corresponding curves. The lines simply connect the data points. The polymer is not fully soluble in BHI > 200 µg/mL.
Dose-response curves of hemolytic activity. Numbers in the parentheses are the MHC values (µg/mL) deduced from the corresponding curves. The lines simply connect the data points.
Dose-response curves of hemolytic activity. Numbers in the parentheses are the MHC (µg/mL) values deduced from the corresponding curves. The lines simply connect the data points.
CAC measurements in Tris-buffered saline

DPH fluorescence plot for the non-aggregating polymers

\[ y = 2.40 \times 10^5 \ln(x) - 1.19 \times 10^6 \]
\[ R^2 = 0.989 \]

DPH fluorescence plot for \textbf{1C-a}. CAC = 220 µg/mL.
DPH fluorescence plot for 1C-b. CAC = 70 µg/mL.

DPH fluorescence plot for 1E. CAC = 360 µg/mL.
DPH fluorescence plot for DDM. CAC = 0.19 mM (lit. 0.17 mM).