Supplemental Material

Initiators for End-Group Functionalized Polypeptides via Tandem Addition Reactions

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Experimental

General Infrared spectra were recorded on a Perkin Elmer 1605 FTIR Spectrophotometer calibrated using polystyrene film. Tandem gel permeation chromatography/light scattering (GPC/LS) was performed on an SSI Accuflow Series III liquid chromatograph pump equipped with a Wyatt DAWN DSP light scattering detector and Wyatt Optilab DSP. Separations were effected by 10^5Å, 10^3Å, and 500Å Phenomenex 5μ columns using 0.1M LiBr in DMF eluent at 60 °C. NMR spectra were measured on Bruker AVANCE 200MHz spectrometer. FAB Mass Spectrometry was performed at the facility in the Chemistry Department at the University of California, Santa Barbara. MALDI mass spectra were collected using a Thermo BioAnalysis DYNAMO mass spectrometer running in positive ion mode with samples prepared by mixing solutions of analyte in TFA with solutions of 2,5-dihydroxybenzoic acid in TFA and allowing the mixtures to air dry. Fluorescence measurements were conducted on a SPEX FluoroMax-2. Chemicals were obtained from commercial suppliers and used without purification unless otherwise stated. Alloc-L-amino amides,[1] ε-CBZ-L-lysine

NCA,[2] (S)-phenylglycine NCA,[2] and γ-benzyl-L-glutamate NCA[2] were prepared according to literature procedures. Hexanes, THF, and THF-d_8 were purified by first purging with dry nitrogen, followed by passage through columns of activated alumina.[3] DMF and DMF-d_7 were purified by drying over 4Å molecular sieves followed by vacuum distillation.

Sample Procedure for Synthesis of Alloc-L-Amino Acid Amides: Alloc-L-Leucine-Isoamylamide Isoamylamine (1.4 mL, 12 mmol) was added to a solution of Alloc-L-leucine-N-hydroxysuccinimidyl ester (2.5 g, 8.0 mmol) in THF (5 mL). The reaction was stirred for 1 hr after which the resulting precipitate was removed by filtration and the solution was diluted with ethyl acetate (100 mL). This solution was sequentially washed with dilute aqueous HCl (2 x 30 mL), saturated aqueous $NaHCO_3$ (2 x 30 mL), and then saturated aqueous NaCl (2 x 30 mL) followed by drying over $MgSO_4$. The solvent was then evaporated *in vacuo* to leave the product (1.7 g, 77 %). IR(THF): 1724 cm^{-1} (νCO, Alloc, s), 1674 cm^{-1} (νCO, amide, s). ^1H NMR($CDCl_3$): δ 6.00 (br s, $(CH_3)_2CHCH_2CH(N\underline{H}C(O)OCH_2CH=CH_2)C(O)N\underline{H}CH_2CH_2CH(CH_3)_2$, 2H), 5.85 (m, $(CH_3)_2CHCH_2CH(NHC(O)OCH_2C\underline{H}=CH_2)C(O)NHCH_2CH_2CH(CH_3)_2$, 1H), 5.25 (t, $(CH_3)_2CHCH_2CH(NHC(O)OCH_2CH=C\underline{H}_2)C(O)NHCH_2CH_2CH(CH_3)_2$, 2H), 4.57 (d, $CH_3CHCH_2CH(NHC(O)OC\underline{H}_2CH=CH_2)C(O)NHCH_2CH_2CH(CH_3)_2$, 2H), 4.12 (m, $(CH_3)_2CHCH_2C\underline{H}(NHC(O)OCH_2CH=CH_2)C(O)NHCH_2CH_2CH(CH_3)_2$, 1H), 3.24 (q, $(CH_3)_2CHCH_2CH(NHC(O)OCH_2CH=CH_2)C(O)NHC\underline{H}_2CH_2CH(CH_3)_2$, 2H), 1.57 (m, $(CH_3)_2CHCH_2C\underline{H}(NHC(O)OCH_2CH=CH_2)C(O)NHCH_2CH_2C\underline{H}(CH_3)_2$, 2H), 1.40 (m, $(CH_3)_2CHC\underline{H}_2CH(NHC(O)OCH_2CHC=H_2)C(O)NHCH_2C\underline{H}_2CH(CH_3)_2$, 4H), 0.92 (d, $(C\underline{H}_3)_2CHCH_2CH(NHC(O)OCH_2CH=CH_2)C(O)NHCH_2CH_2CH(C\underline{H}_3)_2$, 12H).

Alloc-L-Leucine Allyl Ester Allyl alcohol (5.0 mL, 74 mmol) and triethylamine(1.1 mL, 8.0 mmol) were added to a solution of Alloc-L-leucine N-hydroxysuccinimidyl ester (2.5 g, 8.0 mmol) in THF (5 mL). The reaction was stirred and refluxed for 1 d whereupon ethyl acetate (100 mL) was added. This solution was sequentially washed with dilute aqueous HCl (2 x 30 mL), saturated aqueous $NaHCO_3$ (2 x 30 mL), and then saturated aqueous NaCl (2 x 30 mL) followed by drying over $MgSO_4$. The solvent was then evaporated *in vacuo* to leave an oil. The product was purified by bulb to bulb distillation (1.4 g, 68 %). IR(THF): 1726 cm^{-1} (νCO, Alloc + ester, s). ^1H NMR($CDCl_3$): δ 5.90 (m, $(CH_3)_2CHCH_2CH(NHC(O)OCH_2C\underline{H}=CH_2)$-$C(O)OCH_2C\underline{H}=CH_2$, 2H), 5.24 (dt, $(CH_3)_2CHCH_2CH(NHC(O)OCH_2CH=C\underline{H}_2)$-$C(O)OCH_2CH=C\underline{H}_2$, 4H), 4.59 (dd, $(CH_3)_2CHCH_2CH(NHC(O)OC\underline{H}_2CH=CH_2)$-$C(O)OC\underline{H}_2CH=CH_2$, 4H), 4.39 (m, $(CH_3)_2CHCH_2C\underline{H}(NHC(O)OCH_2CH=CH_2)$-$C(O)OCH_2CH=CH_2$, 1H), 1.58 (m, $(CH_3)_2C\underline{H}C\underline{H}_2CH(NHC(O)OCH_2CH=CH_2)$-$C(O)OCH_2CH=CH_2$, 3H), 0.94 (dd, $(C\underline{H}_3)_2CHCH_2CH(NHC(O)OCH_2CH=C\underline{H}_2)$-$C(O)OCH_2CH=C\underline{H}_2$, 6H).

π-$C_3H_5(PEt_3)NiOC(O)NHC(CH_3)_3$ In the dry box, triethylphosphine (5.4 μL, 0.036 mmol) was added to yellow solution of bis(1,5-cyclooctadiene)nickel, $Ni(COD)_2$ (10 mg, 0.036 mmol) in toluene (0.5 mL) yielding a orange-yellow solution. A solution of N-Alloc *tert*-butyl amine (5.6 mg, 0.036 mmol) in toluene (0.5 mL) was added to the orange-yellow solution which was then stirred for 30 min. The volatiles were then removed *in vacuo* to leave the product as a brown oil (11 mg, 85%). IR(THF): 1616 cm^{-1} (νCO, carbamate, vs). ^1H NMR(C_6D_6): δ 5.15 (m, π-$CH_2C\underline{H}CH_2(P(CH_2CH_3)_3)NiOC(O)NHC(CH_3)_3$, 1H), 2.61 (d, π-$C\underline{H}_2CHCH_2$-$(P(CH_2CH_3)_3)NiOC(O)NHC(CH_3)_3$, 2H), 1.40 (s, π-$CH_2CHCH_2(P(CH_2CH_3)_3)Ni$-

OC(O)NHC(C$\underline{H}_3$)$_3$, 9H), 1.26 (br s, π-CH_2CHCH_2(P(C$\underline{H}_2$$CH_3$)$_3$)NiOC(O)NHC($CH_3$)$_3$, 6H), 0.93 (br s, π-$CH_2CHCH_2$(P($CH_2C\underline{H}_3$)$_3$)NiOC(O)NHC($CH_3$)$_3$, 9H).

π-C_3H_5(PEt_3)NiOC(O)N(CH_3)$_2$ In the dry box, triethylphosphine (5.4 μL, 0.036 mmol) was added to yellow solution of Ni(COD)$_2$ (10 mg, 0.036 mmol) in toluene (0.5 mL) yielding a orange-yellow solution. A solution of N-Alloc dimethyl amine (6.3 mg, 0.036 mmol) in toluene (0.5 mL) was added to the orange-yellow solution which was then stirred for 30 min. The volatiles were then removed *in vacuo* to leave the product as a brown oil (11 mg, 83%). IR(THF): 1582 cm^{-1} (νCO, carbamate, vs). ^{1}H NMR(C_6D_6): δ 5.16 (m, π-CH_2C$\underline{H}$$CH_2$(P($CH_2CH_3$)$_3$)NiOC(O)N($CH_3$)$_2$, 2H), 3.06 (s, π-$CH_2CHCH_2$-(P($CH_2CH_3$)$_3$)NiOC(O)N(C$\underline{H}_3$)$_2$, 6H), 2.60 (d, π-C$\underline{H}_2$$CHCH_2$(P($CH_2CH_3$)$_3$)Ni-OC(O)N($CH_3$)$_2$, 2H), 1.90 (t, π-$CH_2CHCH_2$(P(C$\underline{H}_2$$CH_3$)$_3$)NiOC(O)N($CH_3$)$_2$, 6H), 0.88 (q, π-$CH_2CHCH_2$(P($CH_2C\underline{H}_3$)$_3$)NiOC(O)N($CH_3$)$_2$, 9H).

(S)-phenNiNHC(H)RC(O)O, R = -$CH_2CH(CH_3)_2$ 1,10-Phenanthroline (phen) (13 mg, 0.073 mmol) was added to a suspension of Ni(COD)$_2$ (20 mg, 0.073 mmol) in DMF (2 mL) and let stand at room temperature for 30 min after which a solution of PhenNi(COD) had formed. Alloc-L-leucine allyl ester (20 mg, 0.073 mmol) was added to the purple solution, which subsequently became brown in color. After standing at room temperature for 5 h the solution was green, indicative of formation of the single oxidative-addition product. The green solution was heated at 80 °C for 20 h to yield a purple solution. The product was isolated from this solution by precipitation into diethyl ether (10 mL) followed by washing with THF (2 x 10 mL) and drying *in vacuo* to give a purple powder (16 mg, 68%). IR(THF): 1620 cm^{-1} (νCO, carboxylate, s br). An ^{1}H NMR spectrum could not be obtained in DMF-d_7, most likely because of paramagnetism of the complex (only broad lines for the methyl groups were observed). μ_{eff}(296K) = 2.05 μ_B.

(S)-phenNiNHC(H)RC(O)NCH$_2$R, R = -CH$_2$CH(CH$_3$)$_2$, 2 Phen (13 mg, 0.073 mmol) was added to a suspension of Ni(COD)$_2$ (20 mg, 0.073 mmol) in DMF (2 mL) and let stand at room temperature for 30 min after which a solution of phenNi(COD) had formed. Alloc-L-leucine isoamyl amide (20 mg, 0.073 mmol) was then added to the purple solution, which subsequently became brown in color. After standing at room temperature for 5 h the solution was green, indicative of formation of the single oxidative-addition product. The green solution was heated at 80 °C for 20 h to yield a purple solution. The product was isolated from this solution by precipitation into diethyl ether (10 mL) followed by washing with THF (2 x 10 mL) and drying *in vacuo* to give a purple powder (23 mg, 75%). IR(THF): 1578 cm^{-1} (νCO, amidate, s br). An ^{1}H NMR spectrum could not be obtained in DMF-d_7, most likely because of paramagnetism of the complex (only broad lines for the methyl groups were observed). μ_{eff}(296K) = 2.34 μ_B.

(S)-phenNiNHC(H)R^{13}C(O)NCH$_2$R, R = -CH$_2$CH(CH$_3$)$_2$, 2-^{13}C Phen (13 mg, 0.073 mmol) was added to a suspension of Ni(COD)$_2$ (20 mg, 0.073 mmol) in DMF (2 mL) and let stand at room temperature for 30 min after which a solution of phenNi(COD) had formed. ^{13}C(amide)-alloc-L-leucine isoamyl amide (20 mg, 0.073 mmol) was then added to the purple solution, which subsequently became brown in color. After standing at room temperature for 5 h the solution was green, indicative of formation of the single oxidative-addition product. The green solution was heated at 80 °C for 20 h to yield a purple solution. The product was isolated from this solution by precipitation into diethyl ether (10 mL) followed by washing with THF (2 x 10 mL) and drying *in vacuo* to give a purple powder (22 mg, 70%) IR(THF): 1541 cm^{-1} (ν^{13}CO, amidate, s br).

(S)-depeNiNHC(H)R^{1}C(O)NCH$_2$R^2, R^1 = -CH(CH$_3$)$_2$, R^2 = -CH$_2$CH$_3$ 4 1,2-Bis(diethylphosphino)ethane, depe (17 μL, 0.073 mmol) was added to a solution of

$Ni(COD)_2$ (20 mg, 0.073 mmol) in THF (1 mL) and let stand at room temperature for 5 min after which a solution of depeNi(COD) had formed. Alloc-L-valine *n*-propyl amide (18.5 mg, 0.073 mmol) in DMF (1 mL) was then added to the yellow solution, which subsequently became orange-yellow in color. The solution was heated at 80 °C for 20 h to yield an orange solution. The solvent was removed in vacuo and the residue was redissolved in THF and isolated from this solution by precipitation into hexanes (10 mL). Drying of the solid *in vacuo* gave **4** as a yellow powder (16 mg, 53%). IR(THF): 1578 cm^{-1} (νCO, amidate, s br). An ^1H NMR spectrum could not be obtained in DMF-d_7, most likely because of paramagnetism of the complex (only broad lines for the alkyl groups were observed). $\mu_{eff}(296K) = 2.08\ \mu_B$.

Isolation of L-Leucine•HCl from (S)-phen$\overbrace{NiNHC(H)RC(O)O}$, R = -$CH_2CH(CH_3)_2$ Anhydrous 4M HCl in dioxane solution (1.0 mL) was added to a solution of (S)-Phen$\overbrace{NiNHC(H)RC(O)O}$, R = -$CH_2CH(CH_3)_2$ (10 mg, 0.027 mmol) in CH_2Cl_2. The solution immediately changed color from purple to orange. It was stirred for 2 hours and then the solvents were removed *in vacuo*. The remaining solid was extracted with water and the insoluble nickel-containing residue was removed by filtration. The water was then removed by freeze-drying to yield the desired product. FAB-MS: M-Cl: 132.19 calcd, 132 found.

Isolation of L-Leucine Allylamide•HCl from (S)-bpy$\overbrace{NiNHC(H)R^1C(O)NR^2}$, R^1 = -$CH_2CH(CH_3)_2$, R^2 = -$CH_2CH{=}CH_2$, 1 Anhydrous 4M HCl in dioxane solution (1.0 mL) was added to a solution of **1** (10 mg, 0.025 mmol) in CH_2Cl_2. The solution immediately changed color from purple to orange. It was stirred for 2 hours and then the solvents were removed *in vacuo*. The remaining solid was extracted with water and the insoluble nickel-containing residue was removed by filtration. The water was then

removed by freeze-drying to yield the desired product. ^{1}H NMR (D_2O): δ 5.91 (m, $(CH_3)_2CHCH_2CH(NH_2)C(O)NHCH_2C\underline{H}=CH_2$, 1H), 5.73 (t, $(CH_3)_2CHCH_2CH(NH_2)C(O)$-$NHCH_2CH=C\underline{H}_2$, 2H), 3.95 (m, $(CH_3)_2CHCH_2C\underline{H}(NH_2)C(O)NHCH_2CH=CH_2$, 1H), 3.81 (br s, $(CH_3)_2CHCH_2CH(NH_2)C(O)NHC\underline{H}_2CH=CH_2$, 2H), 1.74 (d, $(CH_3)_2C\underline{H}C\underline{H}_2CH$-$(NH_2)C(O)NHCH_2CH=CH_2$, 3H), 0.96 (d, $(C\underline{H}_3)_2CHCH_2CH(NH_2)C(O)NHCH_2CH=CH_2$, 6H). FAB-MS: M-Cl$^-$: 171.28 calcd, 171 found.

Isolation of L-Leucine Isoamylamide•HCl from (S)-phen$\overline{\text{NiNHC(H)RC(O)N}}CH_2$R, R = -CH$_2$CH(CH$_3$)$_2$, 2 Anhydrous 4M HCl in dioxane solution (1.0 mL) was added to a solution of **2** (10 mg, 0.024 mmol) in CH_2Cl_2. The solution immediately changed color from purple to orange. It was stirred for 2 hours and then the solvents were removed *in vacuo*. The remaining solid was extracted with water and the insoluble nickel-containing residue was removed by filtration. The water was then removed by freeze-drying to yield the desired product. ^{1}H NMR (D_2O): δ 3.94 (t, $NH_3C\underline{H}(CH_2CH(CH_3)_2)C(O)$-, 1H, J = 7.5 Hz), 3.33, 3.14 (dm, -$C(O)NHC\underline{H}_2CH_2CH(CH_3)_2$, 2H, J_{gem} = 10.7 Hz, J_{mult} = 6 Hz, 13 Hz), 1.72 (dd, $NH_3CH(C\underline{H}_2CH(CH_3)_2)C(O)$-, 2H, J = 6 Hz, 7 Hz), 1.68 (m, $NH_3CH(CH_2C\underline{H}(CH_3)_2)C(O)$-, 1H, J = 7 Hz), 1.63 (m, -$C(O)NHCH_2CH_2C\underline{H}(CH_3)_2$, 1H, J = 7 Hz), 1.43 (ddd, -$C(O)NHCH_2C\underline{H}_2CH(CH_3)_2$, 2H, J = 7 Hz), 0.98 (d, $NH_3CH(CH_2CH(C\underline{H}_3)_2)C(O)$-, 3H, J = 6 Hz), 0.96 (d, $NH_3CH(CH_2CH(C\underline{H}_3)_2)C(O)$-, 3H, J = 6 Hz), 0.92 (d, -$C(O)NHCH_2CH_2CH(C\underline{H}_3)_2$, 3H, J = 6 Hz), 0.90 (d, -$C(O)NHCH_2CH_2CH(C\underline{H}_3)_2$, 3H, J = 6 Hz). FAB-MS: M-Cl$^-$: 201.36 calcd, 201 found.

Isolation of 1,5 Hexadiene From Oxidative Addition of an N$_\alpha$-Alloc Amino Acid Allyl Ester to Nickel A solution of Alloc-L-leucine allyl ester (4.3 mg, 0.015 mmol) in benzene-d_6 (0.25 mL) was added to a solution of $(PPh_3)_4Ni$ (17 mg, 0.015

mmol) in benzene-d_6 (0.25 mL) resulting in a yellow-orange solution. This mixture was heated at 80 °C for 2 days during which the color changed to dark brown. The volatiles of the reaction were then vacuum distilled into an NMR tube to remove the paramagnetic nickel products. The presence of 1,5 hexadiene in the distillate was verified by ^{1}H NMR. ^{1}H NMR(C_6D_6): δ 5.71 (m, CH_2=C<u>H</u>CH_2CH_2C<u>H</u>=CH_2, 2H), 5.02 (t, C<u>H$_2$</u>=CHCH_2CH_2CH=C<u>H$_2$</u>, 4H), 2.05 (d, CH_2=CHC<u>H$_2$</u>C<u>H$_2$</u>CH=CH_2, 4H). Addition of authentic 1,5-hexadiene to this sample resulted in an increase in the intensities of these peaks and no new peaks were observed.

Polymerization of Glu NCA Using (S)-depeNiNHC(H)R^{1}C(O)NR^2, R^1 = -CH$_2$CH(CH$_3$)$_2$, R^2 = -1-Naphthyl, 3 In the dry box, γ-benzyl-L-glutamate-N-carboxyanhydride, Glu NCA (50 mg, 0.2 mmol) was dissolved in DMF (1.0 mL) and placed in a 25 mL reaction tube which could be sealed with a Teflon stopcock. An aliquot of **3** (140 μL of a 14 mM solution in DMF) was added via syringe to the flask. A stir bar was added and the flask was sealed, removed from the dry box and stirred at 25 °C in a thermostated bath for 24 h. Polymer was isolated by addition of the reaction mixture to methanol containing HCl (1 mM) causing precipitation of the polymer. The polymer was dried *in vacuo* to give a white solid, PBLG (19 mg, 90% yield) ^{13}C{^{1}H} NMR, ^{1}H NMR, and FTIR spectra of this material were identical to data found for authentic samples of PBLG.[4] GPC of the polymer in 0.1 M LiBr in DMF at 60 °C: M_n= 26,100 ;M_w/M_n= 1.15.

Isolation of Mixed Hexenes From Oxidative Addition of N$_\alpha$-*trans* 2-Hexenyloxycarbonyl-L-Leucine Isoamyl Amide to Nickel. A solution of trans 2-hexenyloxycarbonyl-L-leucine isoamyl amide (231 mg, 0.015 mmol) in THF (0.5 mL)

was added to a solution of $(PPh_3)_4Ni$ (741 mg, 0.015 mmol) in THF (0.5 mL) resulting in a yellow-orange solution. This mixture was heated at 80 °C for 2 days during which the color changed to dark brown. The volatiles of the reaction were then vacuum distilled into an NMR tube to remove the paramagnetic nickel products. The presence of a mixture of 1-hexene, 2-hexenes and 3-hexenes in the distillate was verified by ^{13}C NMR. The mixture of hexenes was likely formed by facile isomerization of the intermediate η^3-hexenyl-nickel species formed in the reaction. ^{13}C NMR(THF): δ 139.05 ($CH_3CH_2CH_2CH_2\underline{C}H=\underline{C}H_2$), 132.15 (trans-$CH_3CH_2\underline{C}H=\underline{C}HCH_2CH_3$), 131.44 (cis-$CH_3CH_2CH_2\underline{C}H=\underline{C}HCH_3$), 130.53 (trans-$CH_3CH_2CH_2\underline{C}H=\underline{C}HCH_3$), 128.56 (cis-$CH_3CH_2\underline{C}H=\underline{C}HCH_2CH_3$), 125.92 (cis-$CH_3CH_2CH_2\underline{C}H=CHCH_3$), 124.79 (trans-$CH_3CH_2CH_2\underline{C}H=CHCH_3$), 114.10 ($CH_3CH_2CH_2CH_2\underline{C}H=CH_2$), 34.95 (trans-$CH_3CH_2\underline{C}H_2CH=CHCH_3$), 33.73 ($CH_3CH_2\underline{C}H_2CH_2CH=CH_2$), 31.44 ($CH_3CH_2CH_2\underline{C}H_2CH=CH_2$), 29.71 (cis-$CH_3CH_2\underline{C}H_2CH=CHCH_3$), 22.89 ($CH_3\underline{C}H_2CH_2CH_2CH=CH_2$), 22.38 (trans-$CH_3CH_2CH_2CH=CH\underline{C}H_3$), 18.05 (trans-$CH_3\underline{C}H_2CH_2CH=CHCH_3$) 15.04 (cis-$\underline{C}H_3CH_2CH=CHCH_2\underline{C}H_3$), 14.44 (trans-$CH_3CH_2\underline{C}H=\underline{C}HCH_2CH_3$), 13.79 (cis-$CH_3\underline{C}H_2CH_2CH=CHCH_3$), 13.60 ($\underline{C}H_3CH_2CH_2CH_2CH=CH_2$), 13.32 (trans-$\underline{C}H_3CH_2CH_2CH=CHCH_3$), 13.20 (cis-$\underline{C}H_3CH_2CH_2CH=CHCH_3$).

Polymerization of Glu NCA with (S)-phen$\overline{\text{NiNHC(H)RC(O)O}}$, R = -$CH_2CH(CH_3)_2$. In the dry box, Glu NCA (50 mg, 0.2 mmol) was dissolved in DMF (1.0 mL) and placed in a 25 mL reaction tube which could be sealed with a Teflon stopcock. An aliquot of the initiator (100 μL of a 36 mM solution in DMF) was added via syringe to the flask. A stir bar was added and the flask was sealed, removed from the dry box and stirred at 25 °C in a thermostated bath for 24 h. Polymer was isolated by addition of the

reaction mixture to methanol containing HCl (1 mM) causing precipitation of the polymer. The polymer was dried *in vacuo* to give a white solid, PBLG (18.1 mg, 87% yield) $^{13}C\{^1H\}$ NMR, ^1H NMR, and FTIR spectra of this material were identical to data found for authentic samples of PBLG.[4] GPC of the polymer in 0.1 M LiBr in DMF at 60 °C: M_n= 45,500; M_w/M_n= 1.24.

Fluorescence Measurements of 1-Naphthyl Functionalized PBLG. A solution of 1-naphthyl funtionalized PBLG (26.5 mg) in THF (2 ml) was placed into a cuvette. The sample was excited at a frequency of 324 nm which yielded an emission with maximum intensity at 390 nm. This emission was characteristic of the 1-naphthyl end-group. When the molecular weights of the polymers were varied, the corresponding emission intensities were found to vary inversely with chain length, indicating that the number of end-groups was proportional to the number of chains. Control experiments showed that the emission from labeled polymers was an order of magnitude greater than that from unlabeled PBLG.

Entry	Polymer	Mass(mg)	M_n	Intensity(cps)
1	PBLG-Nap	26.5	14400	7593550
2	PBLG-Nap	26.5	26100	4238040
3	PBLG	26.5	36100	800000

Isolation of *cis*-5-Norbornene-*endo*-2-Carboxylic acid-3-Carboxyl L-Valine n-Propyl Amide from Reaction of 4. A solution of *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (6.0 mg, 0.037 mmol) in THF (1 mL) was added to a solution of **4** (16 mg, 0.037 mmol) in THF (1 ml). The yellow solution was heated at 40 °C for 2 d until the anhydride stretch at 1780 cm^{-1} was no longer detectable by FTIR. A dilute solution of HCl in water (0.5 mL) was added to the reaction which then immediately changed color from yellow to orange. The mixture was stirred for 2 h and then the

volatiles were removed *in vacuo*. The remaining solid was extracted with THF, filtered, and then added to Et_2O to precipitate the nickel-containing byproducts. The solubles were then condensed *in vacuo* to yield the product (11 mg, 92 %). FAB-MS: MH^+: 323.8 calc, 323 found.

Polymerization of (S)-phenylglycine NCA Using (S)-depeNiNHC(H)R^{1}C(O)NR^2, R^1 = -CH$_2$CH(CH$_3$)$_2$, R^2 = -CH$_2$CH$_2$CH(CH$_3$)$_2$, 7. In the dry box, (S)-phenylglycine NCA (50 mg, 0.28 mmol) was dissolved in THF (1.0 mL) and placed in a 25 mL reaction tube which could be sealed with a Teflon stopcock. An aliquot of **7** (560 μL of a 50 mM solution in THF) was added via syringe to the flask. A stir bar was added and the flask was sealed, removed from the dry box and stirred at 25 °C in a thermostated bath for 24 h. Polymer was observed to precipitate from solution during this time period. Polymer was isolated by addition of the reaction mixture to methanol containing HCl (1 mM) followed by centrifugation. The polymer was washed with excess water, methanol, and then diethyl ether and then dried *in vacuo* to give the product as a white solid (35 mg, 93% yield) ^{1}H NMR(TFA-*d*) and FTIR spectra of this material were identical to data found for authentic samples of poly (S)-phenylglycine. MALDI mass spectroscopy of the polymer showed a distribution of masses ranging from *ca.* 1000 – 4500 Da, with the separation between the peaks equal to the mass of the phenylglycine repeats (133.15 Da). Below 1000 Da, the spectra were complicated by the presence of large amounts of matrix peaks. Analysis of the absolute masses of the peaks revealed that nearly all chains were end-functionalized with the leucine residue of the initiator (Figure 1). Some of the chains contained the intact leucine isoamylamide end-group (**b**-series), while the remainder contained a leucine end-group where the C-terminal amide had been cleaved by hydrolysis after dissolution in wet TFA (**a**-series). As an

example peak, **9a**: expected MH^+: 1331.44 Da; found MH^+: 1330.13 Da. Only very small peaks were observed where non-functionalized oligo(phenylglycines) should appear (**c**-series), and these peaks may also contain adducts formed with functionalized chains. For example, **10c** (1350.43 Da) has a mass nearly equal to **9a**+O (1347.44 Da) [peak observed at 1347.53 Da]. From comparison of the peak intensities for the **a**- and **b**-series of peaks (and adducts) to the **c**-series of peaks, it was determined that the degree of chain functionalization was greater than 98%.

References

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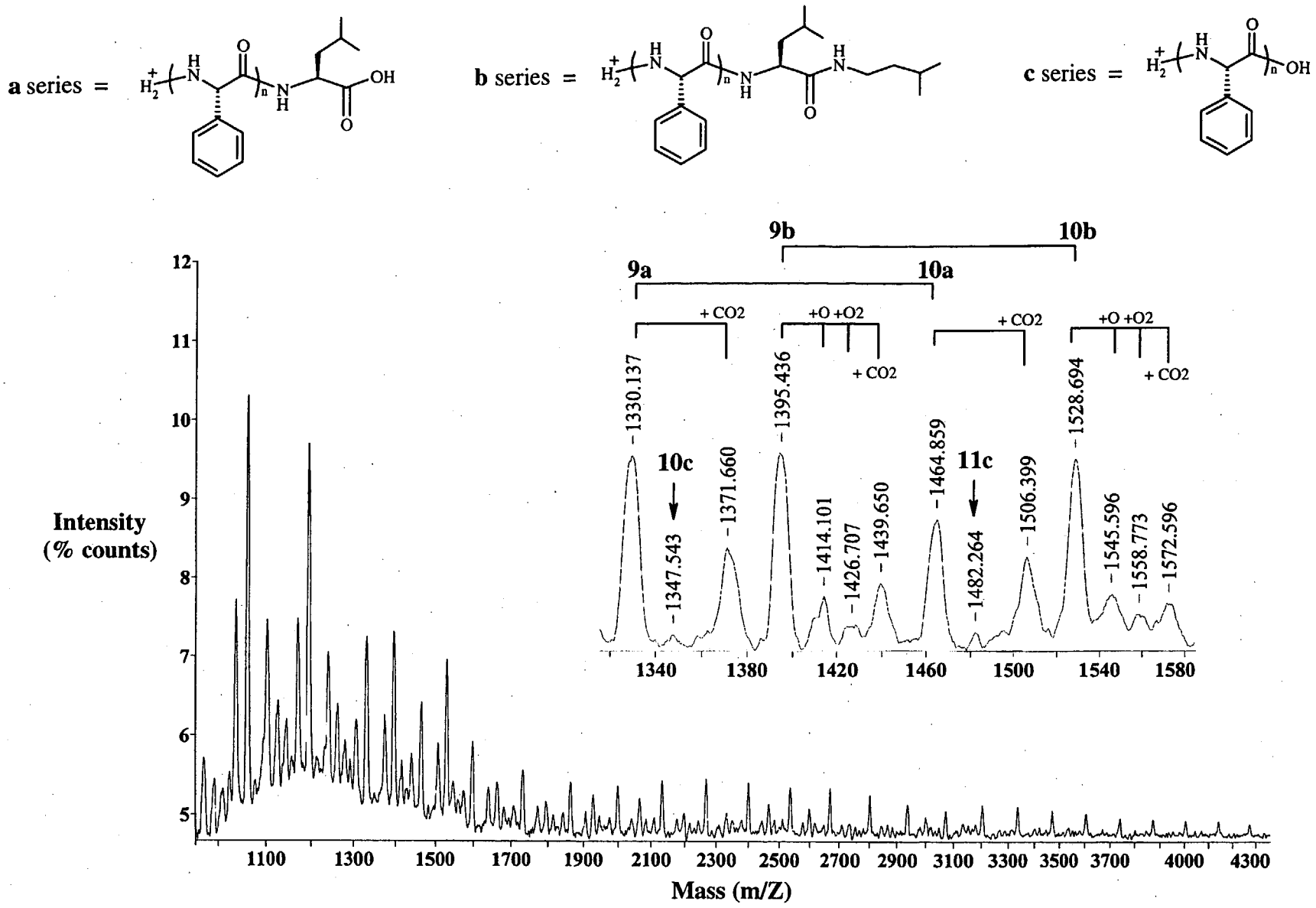

Figure 1. MALDI-MS of leucyl isoamylamide-C-terminated oligo(phenylglycine)s. A partial expansion of the spectrum is shown in the upper right. Mass series were observed for (**a**) leucine-OH terminated oligomers resulting from hydrolysis of the terminal amide in TFA, (**b**) Leucine isoamylamide terminated oligomers resulting from intact end-functionalized chains, and (**c**) non-functionalized chains. For example, **9a** indicates the MH+ ion of the nona(phenylglycine) of the **a** series, the **b** and **c** series are labeled similarly. The ions of the various series also formed adducts with O atoms and CO_2, and are labeled as such.