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Supporting Information

Controlled Polymerization of β-Lactams Using Metal-Amido Complexes. Synthesis of Block Copoly(β-Peptides)

Jianjun Cheng and Timothy J. Deming*
Departments of Materials and Chemistry
University of California, Santa Barbara
Santa Barbara, CA 93106

Experimental Details:

General. Tetrahydrofuran, hexane, dichloromethane, dimethylformamide, and diethyl ether were dried by passage through alumina under nitrogen prior to use.[1] Chemicals were purchased from commercial supplies and used without purification. NMR spectra were recorded on a Bruker AVANCE 200 and 500 MHz spectrometer. Tandem gel permeation chromatography/light scattering (GPC/LS) was performed on a 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 and 10^3Å Phenomenex 5μm columns using 0.1M LiBr in DMF eluent at 60 °C. Viscosity measurements of poly(**1**) were made in dichloroacetic acid (DCA) solution using an Ubbelohde type capillary viscometer at 25 ± 0.1 °C. Circular Dichroism measurements were carried out on an Olis Rapid Scanning Monochromator running in conventional scanning mode at room temperature. The path length of the quartz cell was 1.0 mm and the concentration of polypeptide was 0.2 - 1.0 mg/mL. Optical rotations were measured on a Jasco Model P1020 Polarimeter using a 1 mL volume cell (1 dm length). Infrared spectra were recorded on a Perkin Elmer RX1 FTIR Spectrophotometer calibrated using polystyrene film. Deionized water (18 MΩ-cm) was obtained by passing in-house deionized water through a Barnstead E-pure purification system. (1,2-Bis(diethylphosphino)ethane)-$Ni(NHCH(CH(CH_3)_2)C(O)NC(CH_3)_3)$ (DepeNiAA) was prepared as previously described.[2] $Zn(N(TMS)_2)_2$ was purchased from Aldrich and used without further purification. 2-((2,6-diisopropylphenyl)amino)-4-((2,6-diisopropylphenyl)imino)-2-pentene (BDI-H),[3] monomer **5**,[13] $Co(N(TMS)_2)_2$,[4] $Sc(N(TMS)_2)_3$ (**2**),[4,5] $Cu(N(TMS)_2)_2$,[6] $Fe(N(TMS)_2)_3$,[4,5] $Cr(N(TMS)_2)_3$,[4,5] $Mg(N(TMS)_2)_3$,[7] $BDIZnN(TMS)_2$,[8] and $BDIMgN(TMS)_2$[9] were synthesized according to the literature procedures.

(S)-4-(Benzyloxycarbonyl)-2-azetidinone (1) **1** was synthesized according to a procedure similar to that reported by Salzmann.[10] A modified procedure[11] was adopted to achieve higher yields of **1**. Commercially available L-aspartic acid dibenzyl ester *p*-toluenesulfonate salt (25 g 0.052 mol) was charged to a dry schlenk flask. The substrate in the flask was dried under high vacuum for 2 h. Dry CH_2Cl_2 (450 mL) was transferred to the flask under N_2 and then the solution was cooled to 0 °C using an ice bath. Triethyl amine (15.8 mL, 0.1133 mol, 2.2 eq) was added and followed by addition of TMSCl (6.588 mL, 0.052 mol). The solution was slowly warmed to room temperature and stirred for an additional 12 h. The solution was then cooled again to 0 °C and *tert*-BuMgCl (77 mL of a 2.0 M solution in diethyl ether, 3.0 eq) was slowly added to the mixture. The solution was kept at 0 °C for 2 h and then slowly warmed to room temperature. The reaction was stopped 10 h later by addition of 200 mL wet CH_2Cl_2. The organic phase was washed with 1N HCl (2 × 400 mL), saturated $NaHCO_3$ (2 × 400 mL) and brine (2 × 400 mL). The organic phase was dried over $MgSO_4$. After the solvent was removed, a yellow solid was obtained. The solid was purified by crystallization from CH_3OH and then sublimation at 110 °C under high vacuum to give **1** as white crystals (6.1 g, 55 %). FTIR (THF): 1779 cm^{-1}(νCO, lactam, s), 1747 cm^{-1} (νCO, ester, s). ^{1}H NMR ($CDCl_3$, 500MHz) δ 7.25 (s, 5H, $CH_2C(O)NHCH(CO_2CH_2C_6\underline{H}_5)$), 6.0 (br, 1H, $CH_2C(O)N\underline{H}CH(CO_2CH_2C_6H_5)$), 5.15 (s, 2H, $CH_2C(O)NHCH(CO_2C\underline{H}_2C_6H_5)$), 4.24 (dd, 1H, $CH_2C(O)NHC\underline{H}(CO_2CH_2C_6H_5)$), 3.36 (ddd, 1H, $C\underline{H}_2C(O)NHCH(CO_2CH_2C_6H_5)$, 3.15 (ddd, 1H, $C\underline{H}_2C(O)NHCH(CO_2CH_2C_6H_5)$).

^{13}C NMR ($\mathrm{CDCl_3}$, 200 MHz) δ 171.0, 166.5, 135.1, 128.9, 128.7, 67.7, 47.5, 43.8. FTIR, ^{1}H NMR and ^{13}C NMR spectra of this compound were identical to literature data for **1**.[12]

(S)-4-(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)carbonyl-2-azetidinone (3) **3** was prepared by transesterification of **1** with triethyleneglycol monomethyl ether following the procedure reported by Muñoz-Guerra et al.[13] A vigorously stirred solution of **1** (2.05 g, 10 mmol) and titanium(IV) tetrabutoxide (0.1 g, 0.3 mmol) in dry tri(ethylene glycol) monomethyl ether (20 mL) was heated at 90 °C for 12 h. The course of transesterification was followed by TLC. The reaction was assumed to be complete when no trace of UV absorption indicative of **1** was detectable. The unreacted tri(ethylene glycol) monomethyl ether was distilled off under vacuum and can be reused. The remaining brown residue was purified by passage through a silica gel column (ethyl acetate and hexane, 1:1). The eluent fractions containing product were combined and the solvent was evaporated under vacuum to afford a light yellow oil. Pure compound **3** was obtained by vacuum distillation of this oil (1.21 g, 46%). FTIR (THF): 1779 cm^{-1}(νCO, lactam, s), 1745 cm^{-1} (νCO, ester, s). ^{1}H NMR ($\mathrm{CDCl_3}$, 500 MHz) δ 6.73 (br, 1H, $\mathrm{CH_2C(O)N\underline{H}CH(CO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)}$), 4.36 (m, 2H, $\mathrm{CH_2C(O)NHCH(CO_2C\underline{H}_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)}$), 4.19 (dd, 1H, $\mathrm{CH_2C(O)NHC\underline{H}(CO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)}$), 3.71 (m, 2H, $\mathrm{CH_2C(O)NHCH(CO_2CH_2C\underline{H}_2OCH_2CH_2OCH_2CH_2OCH_3)}$), 3.63 (m, 6H, $\mathrm{CH_2C(O)NHCH(CO_2CH_2CH_2OC\underline{H}_2C\underline{H}_2OC\underline{H}_2CH_2OCH_3)}$), 3.54 (m, 2H, $\mathrm{CH_2C(O)NHCH(CO_2CH_2CH_2OCH_2CH_2OCH_2C\underline{H}_2OCH_3)}$), 3.37 (s, 3H, $\mathrm{CH_2C(O)NHCH(CO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OC\underline{H}_3)}$), 3.26 (ddd, 1H, $\mathrm{C\underline{H}_2C(O)NHCH(CO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)}$), 3.08 (ddd, 1H, $\mathrm{C\underline{H}_2C(O)NHCH(CO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)}$). ^{13}C NMR ($\mathrm{CDCl_3}$, 200 MHz) δ 171.4, 166.4, 72.2, 71.0, 70.9, 70.8, 69.1, 64.9, 59.3, 47.6, 43.9. $[\alpha]^{25}_{D}$: -15.1 (C 0.52 in THF) MS calcd: 261.28; found: 262.33 ($\mathrm{MH^+}$).

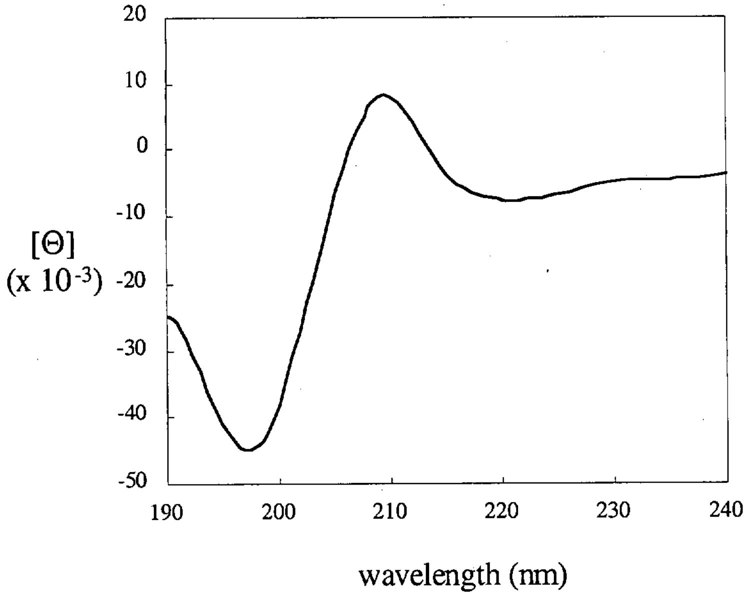
(S)-4-(2-(2-(2(2-Methoxyethoxy)ethoxy)ethoxy)ethoxy)carbonyl-2-azetidinone (4) **4** was prepared by transesterification of **1** with tetraethyleneglycol monomethyl ether following a procedure similar to the synthesis of **3**. A vigorously stirred solution of **1** (2.05 g, 10 mmol) and titanium(IV) tetrabutoxide (0.1 g, 0.3 mmol) in dry tetra(ethylene glycol) monomethyl ether (25 mL) was heated at 85 °C for 8-10 h. The course of transesterification was followed by TLC. The reaction was assumed to be complete when no trace of UV absorption indicative of **1** was detectable. The unreacted tetra(ethylene glycol) monomethyl ether was distilled off under vacuum and can be reused. The light brown residue was then passed through a silica gel column (MeOH /ethyl acetate, 1:20). The eluent fractions containing product were combined and the solvent was evaporated under vacuum to afford the product as a colorless oil. (1.21 g, 42 %). FTIR (THF): 1779 cm^{-1}(νCO, lactam, s), 1745 cm^{-1} (ν CO, ester, s). ^{1}H NMR ($\mathrm{CDCl_3}$, 500 MHz) δ 6.63 (br, 1H, $\mathrm{CH_2C(O)N\underline{H}CH(CO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)}$), 4.34 (m, 2H $\mathrm{CH_2C(O)NHCH(CO_2C\underline{H}_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)}$), 4.19 (dd, 1H $\mathrm{CH_2C(O)NHC\underline{H}(CO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)}$), 3.71-3.63 (m, 12H $\mathrm{CH_2C(O)NHCH(CO_2CH_2C\underline{H}_2OC\underline{H}_2C\underline{H}_2OC\underline{H}_2C\underline{H}_2OC\underline{H}_2CH_2OCH_3)}$), 3.55 (m, 2H, $\mathrm{CH_2C(O)NHCH(CO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2C\underline{H}_2OCH_3)}$), 3.35 (s, 3H, $\mathrm{CH_2C(O)NHCH(CO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OC\underline{H}_3)}$), 3.25 (ddd, 1H, $\mathrm{C\underline{H}_2C(O)NHCH(CO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)}$), 3.09 (ddd, 1H, $\mathrm{C\underline{H}_2C(O)NHCH(CO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)}$). ^{13}C NMR ($\mathrm{CDCl_3}$, 200 MHz) δ 171.5, 166.3, 72.9, 71.0, 70.9, 69.1, 65.0, 59.4, 47.6, 43.9. $[\alpha]^{25}_{D}$: -10.9 (C = 0.26 in THF). MS calcd: 305.33; found: 328.43 ($\mathrm{MNa^+}$).

Polymerization of 1 using 2 In the dry box, compound **1** (41 mg, 0.2 mmol) was dissolved in $\mathrm{CH_2Cl_2}$ (10 mL) and placed in a 25 mL reaction tube which could be sealed with a Teflon stopcock. An aliquot of **2** (40 μL of a 0.05 M solution in THF) was then added *via* syringe to the flask. A stirbar was added and the flask was sealed, removed from the dry box, and stirred at room temperature for 24 h. Polymer was isolated by addition of the reaction mixture to methanol causing precipitation of the polymer. The polymer was then washed with methanol for several times and dried under vacuum to give poly(**1**) as a fibrous solid (40 mg, 98%). FTIR ($CHCl_3$): 1745 cm^{-1}(νCO, ester, s), 1652 cm^{-1} (νCO, amide I, br vs), 1552 cm^{-1} (νCO, amide II, br s). ^{1}H NMR (500 MHz, TFA-d): δ 7.61 (s, 5H, $-(NHCH(CO_2CH_2C_6\underline{H}_5)CH_2C(O))-$), 5.60 (d, 1H, $-(NHCH(CO_2C\underline{H}_2C_6H_5)CH_2C(O))-$, J = 11.8 Hz), 5.43 (d, 1H, $-(NHCH(CO_2C\underline{H}_2C_6H_5)CH_2C(O))-$, J = 11.8 Hz)), 5.17 (br, 1H, $-(NHC\underline{H}(CO_2CH_2C_6H_5)CH_2C(O))-$), 3.46 (d, 1H, $-(NHCH(CO_2CH_2C_6H_5)C\underline{H}_2C(O))-$, J = 12.7 Hz), 3.17 (d, 1H, $-(NHCH(CO_2CH_2C_6H_5)C\underline{H}_2C(O))-$, J = 12.7 Hz). ^{13}C NMR (500 MHz, TFA-d): δ 175.0, 174.7, 136.3, 131.4, 131.0, 130.8, 72.0, 52.0, 38.6. DEPT 135 NMR (500 MHz, TFA-d): 131.4 (+), 131.0 (+), 130.8 (+), 72.0 (-), 52.0 (+), 38.6 (-). $[\alpha]^{25}_D$: +5.5 (C = 0.31 in TFA).

Polymerization of 4 using 2 In the dry box, **4** (61 mg, 0.2 mmol) was dissolved in CH_2Cl_2 (10 mL) and placed in a 25 mL reaction tube which could be sealed with a Teflon stopcock. An aliquot of **2** (80 μL of a 0.05 M solution in THF) was then added *via* syringe to the flask. A stirbar was added and the flask was sealed, removed from the dry box, and stirred at room temperature for 24 h. Polymer was isolated by addition of the reaction mixture to ethyl ether causing precipitation of the polymer. The polymer was then dissolved in methanol and reprecipitated by addition to ethyl ether. Further purification of polymer was achieved by dialysis in water. The polymer was freeze dried to give poly(**4**) as a fibrous solid (59 mg, 96 %). FTIR (THF): 1745 cm^{-1}(νCO, ester, s), 1652 cm^{-1} (νCO, amide I, br vs), 1552 cm^{-1} (νCO, amide II, br s). ^{1}H NMR (TFA-d, 500 MHz) δ 5.07 (br, 1H, $-NHC\underline{H}(CO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)CH_2C(O)-$), 4.60 (br, 1H, $-NHCH(CO_2C\underline{H}_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)CH_2C(O)-$), 4.45 (br, 1H, $-NHCH(CO_2C\underline{H}_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)CH_2C(O)-$), 3.94 (br, 14H, $-NHCH(CO_2CH_2C\underline{H}_2OC\underline{H}_2C\underline{H}_2OC\underline{H}_2C\underline{H}_2OC\underline{H}_2C\underline{H}_2OCH_3)CH_2C(O)-$), 3.61 (br, 3H, $-NHCH(CO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OC\underline{H}_3)CH_2C(O)-$), 3.33 (br dd, 1H, $-NHCH(CO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)C\underline{H}_2C(O)-$), 3.15 (br dd, 1H, $-NHCH(CO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)C\underline{H}_2C(O)-$). ^{13}C NMR (TFA-d, 200 MHz) δ 175.0, 174.6, 112.1, 76.5, 73.3, 72.1, 71.7, 71.0, 67.7, 60.0, 58.6, 54.1, 40.9. GPC of the polymer in 0.1 M LiBr in DMF at 60 °C (d*n*/dc = 0.105 mL/g): M_n = 49 980; M_w/M_n = 1.23. $[\alpha]^{25}_D$: +41.7 (C = 0.07 in TFA).

The chain conformation of poly(**4**) was analyzed in water using CD. The CD spectrum of poly(**4**) at 20 °C showed a maximum at 209 nm and a minimum at 198 nm with molar ellipticities of 8.3×10^3 and $- 44.8 \times 10^3$ deg cm^2mol^{-1}, respectively (**Figure A**). The spectral features of this D-configuration polymer are the near-mirror image of those described by Seebach for the heptamer of L-configuration β-homolysine, which was reported to adopt a 3_1 helical conformation.[14]

Figure A. CD Spectrum of poly(4) in H_2O

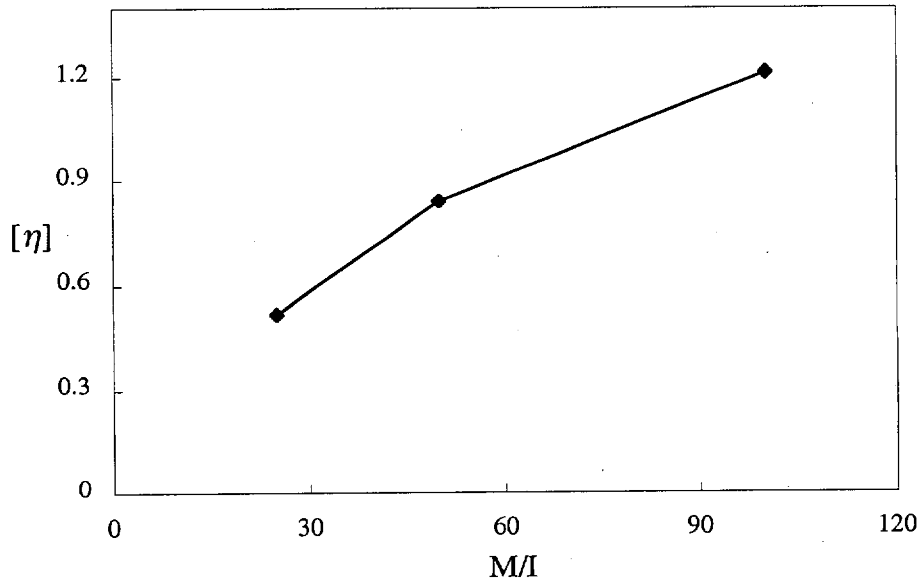


Block Copolymerization of 4 and 1 using 2 In the dry box, **4** (61 mg, 0.2 mmol) was dissolved in CH_2Cl_2 (10 mL) and placed in a 25 mL reaction tube which could be sealed with a Teflon stopcock. An aliquot of **2** (80 μL of a 0.05 M solution in THF) was then added *via* syringe to the flask. A stirbar was added and the flask was sealed. After stirring in dry box for 12 h, a CH_2Cl_2 (0.5 mL) solution of **1** (4.1 mg, 0.02 mmol) was added into the reaction tube, and the contents were stirred at room temperature for an additional 12 h. The block copolymer was isolated by addition of the reaction mixture to ethyl ether causing precipitation of the polymer. The polymer was then dialyzed in water for two days and then freeze dried to give the copolymer as a fibrous solid (62 mg, 95%). FT-IR ($CHCl_3$): 1745 cm^{-1}(νCO, ester, s), 1652 cm^{-1} (νCO, amide I, br vs), 1552 cm^{-1} (νCO, amide II, br s). ^1H NMR (TFA-d) δ 7.35 (br s, $-(NHCH(CO_2CH_2C_6\underline{H}_5)CH_2C(O))_n-(NHCH(CO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)-CH_2C(O))_m-$), 5.30 (dd, $-(NHCH(CO_2C\underline{H}_2C_6H_5)CH_2C(O))_n-(NHCH(CO_2CH_2CH_2O-CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)CH_2C(O))_m-$), 5.07 (br m, $-(NHCH(CO_2CH_2C_6H_5)CH_2C(O))_n-(NHC\underline{H}(CO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)-CH_2C(O))_m-$), 4.90 (br m, $-(NHC\underline{H}(CO_2CH_2C_6H_5)CH_2C(O))_n-(NHCH(CO_2CH_2CH_2O-CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)CH_2C(O))_m-$), 4.62 (br d, $-(NHCH(CO_2CH_2C_6H_5)CH_2C(O))_n-(NHCH(CO_2C\underline{H}_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)-CH_2C(O))_m-$), 4.45 (br d, $-(NHCH(CO_2CH_2C_6H_5)CH_2C(O))_n-(NHCH(CO_2C\underline{H}_2CH_2O-CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)-CH_2C(O))_m-$), 3.98 (m, $-(NHCH(CO_2CH_2C_6H_5)CH_2C(O))_n-(NHCH(CO_2CH_2C\underline{H}_2OC\underline{H}_2C\underline{H}_2OC\underline{H}_2C\underline{H}_2OC\underline{H}_2C\underline{H}_2OCH_3)CH_2C(O))_m-$), 3.64 (s, $-(NHCH(CO_2CH_2C_6H_5)CH_2C(O))_n-(NHCH(CO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OC\underline{H}_3)-CH_2C(O))_m-$), 3.33 (d, $-(NHCH(CO_2CH_2C_6H_5)CH_2C(O))_n-(NHCH(CO_2CH_2CH_2O-CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)C\underline{H}_2C(O))_m-$), 3.21 (d, $-(NHCH(CO_2CH_2C_6H_5)CH_2C(O))_n-(NHCH(CO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)C\underline{H}_2C(O))_m-$), 3.14 (d, $-(NHCH(CO_2CH_2C_6H_5)C\underline{H}_2C(O))_n-(NHCH(CO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)-CH_2C(O))_m-$), 2.90 (d, $-(NHCH(CO_2CH_2C_6H_5)C\underline{H}_2C(O))_n-(NHCH(CO_2CH_2CH_2O-CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)CH_2C(O))_m-$). GPC of the polymer in 0.1 M LiBr in DMF at 60 °C: $M_n = 54790$; $M_w/M_n = 1.26$.

Viscosity Measurements Polymer solution viscosities were measured by comparing the time (t) required for a specific volume of polymer solution to flow through a capillary tube compared to the time (t_o) for pure solvent. Specific viscosity (η_{sp}) and intrinsic viscosity ($[\eta]$) are given by $\eta_{sp} = (t - t_o) / t_o$ and $[\eta] = [(\ln(t/t_o) / C]_{c=0}$. $[\eta]$ was obtained by plotting η_{sp}/C against C (C = concentration of polymer solution in g/dL) according to the equation: $\eta_{sp}/C = [\eta] + k'C$.[15]

Poly(**1**) (21.4 mg) was dissolved in DCA to give 13 mL of solution. The solution was then maintained in an Ubbelohde type capillary viscometer for 30 minutes at 25 ± 0.1 °C using a water bath. The time (*t*) was then measured three times at this temperature and the average of the data was calculated. The intrinsic viscosities of poly(**1**) prepared using **2** at different [M]/[I] ratios is plotted in **Figure B-1**.

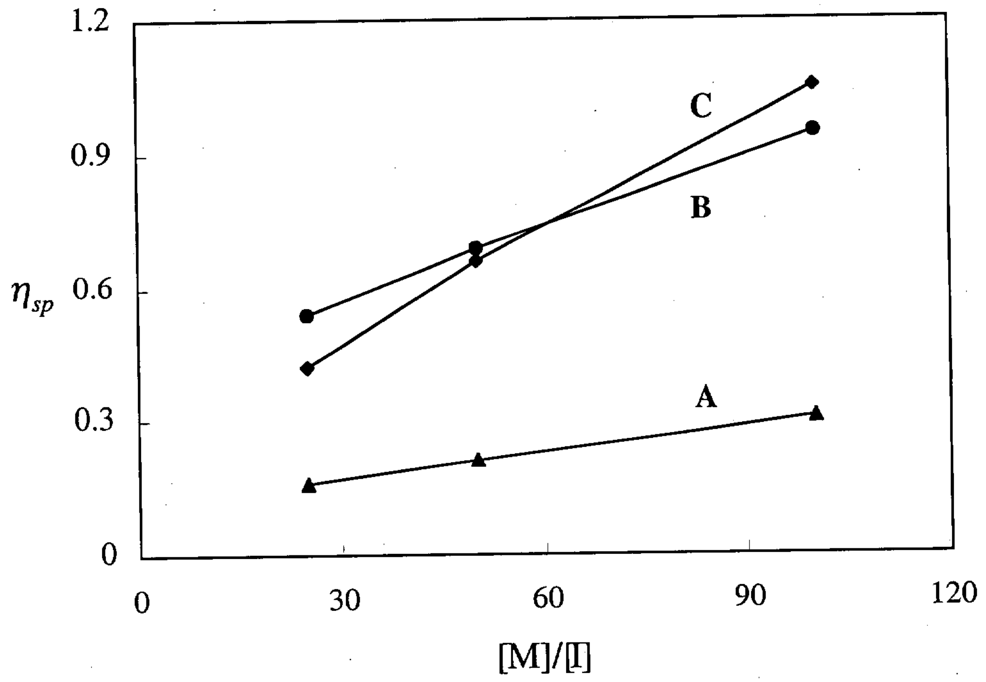
Figure B-1. Intrisic viscosity of poly(1) prepared using 2



According to the Mark-Houwink-Sakurada equation, $[\eta] = KM_v^a$, $[\eta]$ is proportional to polymer molecular weight. **Figure B-1** shows that the molecular weight of poly(**1**) increased with the monomer to initiator ratio.

Specific viscosities of poly(β-peptides) as functions of monomer to initiator ratio for different initiators were also measured (**Figure B-2**). All polymerizations were carried out at 20 °C in CH_2Cl_2 at initial [**1**] = 0.02 M. [M]/[I] = initial [**1**]/[initiator]. Specific viscosities were measured in dichloroacetic acid solution ([poly(**1**)] = 0.165 g/dL) at 25.0 ± 0.1 °C using an Ubbelohde type capillary viscometer. **A** = poly(**1**) prepared using $Sc(N(TMS)_2)_3$; **B** = poly(**1**) prepared using $BDIMgN(TMS)_2$; **C** = poly(**1**) prepared using DepeNiAA.

Figure B-2. Specific viscosities of poly(1) prepared using metal in



Specific viscosity of poly(1) at different monomer conversions In the dry box, **1** (1.03 g, 5 mmol) was dissolved in 200 mL CH_2Cl_2. A solution of **2** (0.67 mL 0.05 M in THF) was added. The mixture was stirred for 2 min and then separated into four flasks (50 mL aliquots each). Polymerization was terminated at different time intervals by adding methanol to the individual polymerization flasks. The resulting polymers were washed with methanol and dried *in vacuo*. Conversion of monomer was calculated based on the yield of poly(**1**). η_{sp} values for poly(**1**) were measured as described above. The plot of η_{sp} vs monomer conversion is shown in **Figure** C, and shows an increase in polymer chain length as the reaction proceeds, indicative of the lack of substantial chain transfer reactions.

Molecular weight analysis of poly(4) prepared using 2 as a function of monomer conversion In the dry box, **4** (305 mg, 1 mmol) was dissolved in CH_2Cl_2 (30.5 mL). A solution of **2** in THF (134 µL, 0.05 M) was added the mixture. The mixture was stirred for 2 min and then separated into four flasks (7.6 mL aliquots each). At different time intervals, monomer conversions were determined by measuring the intensity of the lactam IR stretch at 1779 cm^{-1} for residual monomer in the polymerization solution. Polymerizations were terminated immediately after IR analysis by precipitating the polymers into wet diethyl ether. The resulting polymers were washed with ether and dried *in vacuo*. Molecular weights of the Poly(**4**) samples were then analyzed by GPC in 0.1 M LiBr in DMF at 60 °C.

Kinetic analysis of polymerization of 4 using 2 **4** (100 mg, 0.325 mmol) was dissolved in CH_2Cl_2 (10.0 mL). A solution of **2** in THF (43 µL, 0.05M) was added to this mixture in the dry box ([**4**]/[**2**] =150). The resulting solution was stirred for 2 min, and then divided into 10 equal portions (1.0 mL) and each injected into an ampule. The ampules were sealed with grease and then placed in a thermostated bath (25 °C). The intensity of the lactam infrared stretching absorption at 1779 cm^{-1} was measured at various time intervals by injecting an aliquot of polymerization solution into a Wilmad 0.1 mm NaCl cell. The polymerization rate constant (k_{obs} = 1.53 × 10^{-3} s^{-1}) was obtained by plotting the log of the lactam concentration versus polymerization time and fitting the data using standard rate expressions (**Figure D**).

Figure C. Polymerization of 1 using 2

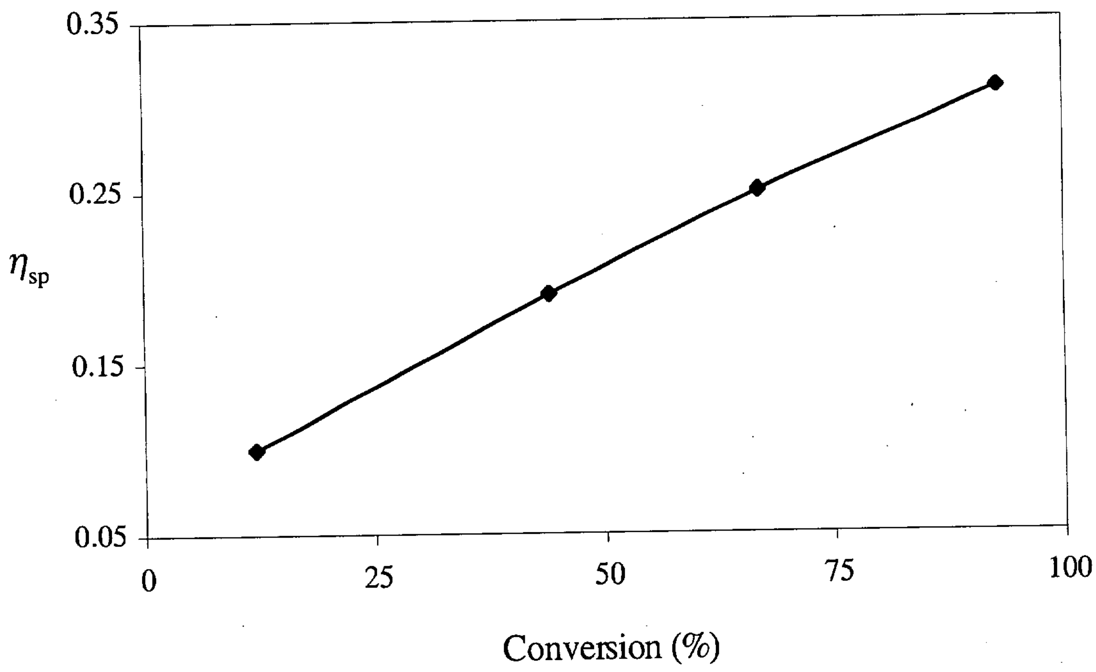
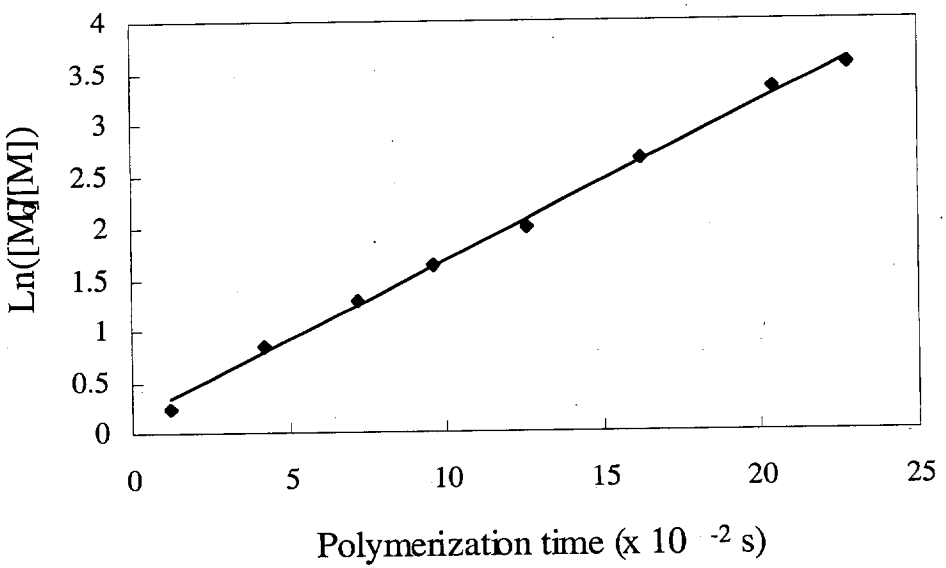


Figure D. Kinetic study of polymerization of 4 using



NMR analysis of polymerization initiation of 1 using 2 In the dry box, **1** (4.5 mg, 0.02 mmol) was dissolved in 1 mL dry $CDCl_3$, and to this a solution of **2** (24 mg in 0.5 mL dry $CDCl_3$, 2 eq) was added. The solution was stirred for 1 min and transferred to a 5 mm

NMR tube, which was sealed with a septum. A ^{1}H NMR spectrum was acquired for this sample at 25 °C. The $CHCl_3$ reasonance (chemical shift δ 7.27) was used as the internal reference. Two high field peaks were observed: δ 0.28 ($Sc(N(Si(C\underline{H}_3)_3)_2)_3$), 0.08 ($NH(Si(C\underline{H}_3)_3)_2$); Intensity ratio: 3:1. The resonances were assigned by addition of authentic samples to the reaction mixture.

References:

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