

Supporting Information

Synthesis, morphology and properties of segmented poly(ether amide)s with uniform oxalamide based hard segments

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MATERIALS

Diethyl oxalate, bis(3-aminopropyl) polytetrahydrofuran ($M_n = 1.1 \times 10^3 \text{ g.mol}^{-1}$), 1,2-diaminoethane, 1,4-diaminobutane, 1,6-diaminohexane, 1,8-diaminooctane, 1,10-diaminodecane, 3-methoxypropylamine, triethylamine 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), deuterated chloroform ($\text{CDCl}_3\text{-d}_1$) and deuterated trifluoroacetic acid (TFA-d_1) were purchased from Aldrich (Zwijndrecht, The Netherlands). Irganox1330 was kindly provided by Ciba (Geigi, Switzerland). HPLC-quality chloroform was purchased from Lab-Scan (Gliwice, Poland). Diethyl ether, tetrahydrofuran, dichloromethane and toluene were obtained from Biosolve (Valkenswaard, The Netherlands) and chloroform and tetrabutylorthotitanoate ($\text{Ti}(\text{OBu})_4$) were purchased from Merck (Darmstadt, Germany). All materials were used as received.

METHODS

NMR. ^1H (300 MHz) and ^{13}C NMR (75.26 MHz) spectra were recorded on a Varian Inova Nuclear Magnetic Resonance Spectrometer using $\text{CDCl}_3\text{-d}_1$ and TFA-d_1 as solvents.

GPC. The GPC setup consisted of a Perkin Elmer series 200 binary pump, a Perkin Elmer series 200 autosampler, a Shimadzu CTO-AVP column oven, and a Shimadzu RID-10A refractive index detector. The eluent was $\text{CHCl}_3/\text{HFIP}$ (95/5 v/v). The flow was set at 1 ml.min^{-1} . The injection volume was 200 μL . The separation was performed on two PL Mixed-D columns ($300 \times 7.5 \text{ mm}$) from Polymer Laboratories Ltd., packed with 5 μm particles. The temperature of the columns was set at 30 $^\circ\text{C}$. Approximately 120 mg of sample is weighed in a 50 ml vial. To this vial 2 ml of HFIP is added and the solution is allowed to stand for 2 h. Next, 38 ml of warm ($\sim 35 \text{ }^\circ\text{C}$) HPLC-quality chloroform is added and mixed thoroughly. Prior to injection the sample solution is filtered through a Millex-LCR 0.45 μm filter (Millipore). The system was calibrated with 14 narrow polystyrene standards (Polymer Laboratories) with MW ranging from 5.8×10^2 to $1.0 \times 10^6 \text{ g.mol}^{-1}$. The standards were dissolved in $\text{CHCl}_3/\text{HFIP}$ (95/5 v/v). Because the K and α values of the samples are not known and a viscometer was

not available, no universal calibration could be performed. The reported molecular weights should, therefore, be regarded as PS-equivalent molecular weights. A calibration curve that is virtually linear over a broad molecular weight range was obtained. However, the three highest molecular weights tested ($6.75 \times 10^5 \text{ g.mol}^{-1}$, $8.41 \times 10^5 \text{ g.mol}^{-1}$, and $1.0 \times 10^6 \text{ g.mol}^{-1}$) elute near or in the exclusion limit of the column, causing an upward curvature at the high MW end.

TGA. Thermal gravimetric analysis was carried out with 5-10 mg samples under a nitrogen atmosphere in the 50-700 °C range at a heating rate of $10 \text{ }^\circ\text{C.min}^{-1}$, using a Perkin-Elmer Thermal Gravimetric Analyser TGA 7.

SYNTHESIS

PTHF-OXA (2). Diethyl oxalate (5.21 g, 0.036 mol) and bis(3-aminopropyl) polytetrahydrofuran (1) (39.25 g, 0.036 mol) were placed in a polymerization tube. Irganox1330 (1 wt% of the total mass) was added and the mixture was heated to 190 °C under a nitrogen flow. After 1 h, the pressure was slowly reduced to ~20 mbar. The ethanol distilling off during this period was collected in a trap cooled with liquid nitrogen. Subsequently, the pressure was further reduced to ~0.08 mbar over the following 3 h. The reaction mixture was cooled to room temperature under vacuum and the polymer was collected and dissolved in 200 ml of chloroform. The solution was casted in a petridish and after evaporation of the solvent the polymer was dried at room temperature in vacuo. The product was obtained as a yellow transparent sticky solid in a yield of 95 %.

^1H NMR (300 MHz, $\text{CDCl}_3\text{-d}_1$) δ = 7.73 (bt, 2H, NHCO), 3.49 (t, 4H, $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.30-3.50 (m, 54H, OCH_2CH_2), 3.30-3.50 (m, 4H, $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{O}$), 1.81 (m, 4H, $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{O}$), 1.55-1.70 (m, 54 H, OCH_2CH_2).

Bis(ethyl 2-(aminopropyl)-oxo acetate) polytetrahydrofuran (3). Diethyl oxalate (53.10 g, 0.36 mol) was added to a solution of bis(3-aminopropyl) polytetrahydrofuran (1) (100.00 g, 0.09 mol) in 500 ml of THF at room temperature. Subsequently, the mixture was stirred at room temperature for 16

h. The solvent was removed at reduced pressure. The excess of diethyl oxalate was removed by vacuum distillation (~ 0.1 mbar) at $70\text{ }^{\circ}\text{C}$ for 16 h. The product was obtained as a viscous yellow/orange liquid in a yield of 98 %.

^1H NMR (300 MHz, $\text{CDCl}_3\text{-d}_1$) δ = 7.73 (bt, 2H, OCOCONH), 4.32 (q, 4H, $\text{CH}_3\text{CH}_2\text{O}$), 3.54 (t, 4H, $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.30-3.40 (m, 54H, OCH_2CH_2), 3.30-3.40 (m, 4H, $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{O}$), 1.81 (m, 4H, $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{O}$), 1.50-1.70 (m, 54 H, OCH_2CH_2), 1.31 (t, 6H, $\text{CH}_3\text{CH}_2\text{O}$); ^{13}C NMR (75.26 MHz, $\text{CDCl}_3\text{-d}_1$) δ = 160.9 (OCOCONH), 156.7 (OCOCONH), 70.8 (OCH_2CH_2), 70.0 ($\text{NHCH}_2\text{CH}_2\text{CH}_2\text{O}$), 63.1 ($\text{CH}_3\text{CH}_2\text{O}$), 39.0 ($\text{NHCH}_2\text{CH}_2\text{CH}_2\text{O}$), 28.8 ($\text{NHCH}_2\text{CH}_2\text{CH}_2\text{O}$), 26.7 (OCH_2CH_2), 14.1 ($\text{CH}_3\text{CH}_2\text{O}$).

PTHF-OXA₂X (4a-e). Bis(ethyl 2-(aminopropyl)-oxo acetate) polytetrahydrofuran (3) was polymerized with different α,ω -diamines. In a typical example, bis(ethyl 2-(aminopropyl)-oxo acetate) polytetrahydrofuran (3) (30.00 g, 0.023 mol) and 1,6-diaminohexane (2.68 g, 0.023 mol) were placed in a polymerization tube. To this mixture were added $\text{Ti}(\text{OBu})_4$ (0.2 wt% relative to the total mass and dissolved in 1 ml of toluene) and Irganox1330 (1 wt% of the total mass). The mixture was heated to $190\text{ }^{\circ}\text{C}$ under a nitrogen flow. After 1 h, the pressure was slowly reduced to ~ 20 mbar to distill off the ethanol. Subsequently, the pressure was reduced to ~ 0.08 mbar in the following 4 h. The reaction mixture was then cooled to room temperature under vacuum. The polymer was collected and dissolved in 200 ml of chloroform at $50\text{ }^{\circ}\text{C}$ and subsequently precipitated in 2 L of diethyl ether. The polymer was filtered and dried at $60\text{ }^{\circ}\text{C}$ at reduced pressure. The product was obtained as a yellow transparent elastic solid in a yield of 95 %.

PTHF-OXA₂2 (4a): ^1H NMR (300 MHz, TFA-d_1) δ = 3.78 (t, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 3.60-3.75 (m, 54H, OCH_2CH_2), 3.60-3.75 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 3.51 (t, 4H, CONHCH_2), 2.01 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 1.70-1.80 (m, 54 H, OCH_2CH_2);

PTHF-OXA₂4 (**4b**): ¹H NMR (300 MHz, CDCl₃-d₁) δ = 7.83 (bt, 2H, OCH₂CH₂CH₂NHCO), 7.54 (bt, 2H, CONHCH₂CH₂), 3.48 (t, 4H, OCH₂CH₂CH₂NH), 3.30-3.50 (m, 54H, OCH₂CH₂), 3.30-3.50 (m, 4H, OCH₂CH₂CH₂NH), 3.30 (q, 4H, CONHCH₂CH₂), 1.80 (m, 4H, OCH₂CH₂CH₂NH), 1.60-1.70 (m, 54 H, OCH₂CH₂), 1.50-1.60 (m, 4H, CONHCH₂CH₂);

PTHF-OXA₂6 (**4c**): ¹H NMR (300 MHz, CDCl₃-d₁) δ = 7.83 (bt, 2H, OCH₂CH₂CH₂NHCO), 7.48 (bt, 2H, CONHCH₂CH₂CH₂), 3.49 (t, 4H, OCH₂CH₂CH₂NH), 3.30-3.50 (m, 54H, OCH₂CH₂), 3.30-3.50 (m, 4H, OCH₂CH₂CH₂NH), 3.30 (t, 4H, CONHCH₂CH₂CH₂), 1.79 (m, 4H, OCH₂CH₂CH₂NH), 1.60-1.70 (m, 54 H, OCH₂CH₂), 1.50-1.60 (m, 4H, CONHCH₂CH₂CH₂), 1.35 (m, 4H, CONHCH₂CH₂CH₂);

PTHF-OXA₂8 (**4d**): ¹H NMR (300 MHz, CDCl₃-d₁) δ = 7.83 (bt, 2H, OCH₂CH₂CH₂NHCO), 7.47 (bt, 2H, CONHCH₂CH₂CH₂CH₂), 3.49 (t, 4H, OCH₂CH₂CH₂NH), 3.30-3.50 (m, 54H, OCH₂CH₂), 3.30-3.50 (m, 4H, OCH₂CH₂CH₂NH), 3.30 (q, 4H, CONHCH₂CH₂CH₂CH₂), 1.81 (m, 4H, OCH₂CH₂CH₂NH), 1.60-1.70 (m, 54 H, OCH₂CH₂), 1.50-1.60 (m, 4H, CONHCH₂CH₂CH₂CH₂), 1.36-1.27 (m, 4H, CONHCH₂CH₂CH₂CH₂), 1.36-1.27 (m, 4H, CONHCH₂CH₂CH₂CH₂);

PTHF-OXA₂10 (**4e**): ¹H NMR (300 MHz, CDCl₃-d₁) δ = 7.83 (bt, 2H, OCH₂CH₂CH₂NHCO), 7.47 (bt, 2H, CONHCH₂CH₂CH₂CH₂CH₂), 3.48 (t, 4H, OCH₂CH₂CH₂NH), 3.30-3.50 (m, 54H, OCH₂CH₂), 3.30-3.50 (m, 4H, OCH₂CH₂CH₂NH), 3.29 (q, 4H, CONHCH₂CH₂CH₂CH₂CH₂), 1.80 (m, 4H, OCH₂CH₂CH₂NH), 1.60-1.70 (m, 54 H, OCH₂CH₂), 1.50-1.60 (m, 4H, CONHCH₂CH₂CH₂CH₂CH₂), 1.21-1.36 (m, 4H, CONHCH₂CH₂CH₂CH₂CH₂), 1.21-1.36 (m, 4H, CONHCH₂CH₂CH₂CH₂CH₂), 1.21-1.36 (m, 4H, CONHCH₂CH₂CH₂CH₂CH₂);

N,N'-bis(6-aminohexyl)oxalamide (5). Diethyl oxalate (19.30 g, 0.13 mol) was slowly added to a solution of 1,6-diaminohexane (53.70 g, 1.32 mol) in 300 ml of chloroform at room temperature. Subsequently, the mixture was stirred at room temperature for 16 h. After filtration, the product was

washed twice with diethyl ether and dried under vacuum. The product was obtained as a white powder in a yield of 85 % (mp 120 °C).

^1H NMR (300 MHz, TFA- d_1) δ = 6.83 (bt, 4H, NH_2), 3.56 (t, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}$), 3.37 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 1.95 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}$), 1.82 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 1.60-1.70 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}$), 1.60-1.70 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$); ^{13}C NMR (75.26 MHz, TFA- d_1) δ = 159.7 (NHCO), 40.7 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 39.7 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}$), 27.3 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 26.2 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}$), 25.0 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 24.6 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}$).

PTHF-OXA₃66 (6). N,N'-bis(6-aminohexyl)oxalamide (6) (7.69 g, 0.027 mol) and bis(ethyl 2-(aminopropyl)-oxo acetate) polytetrahydrofuran (3) (34.94 g, 0.027 mol) were placed in a polymerization tube. To this mixture was added Irganox1330 (1 wt% of the total mass). The mixture was heated to 270 °C under a nitrogen flow. After 1 h, the pressure was slowly reduced to ~20 mbar to distill off the ethanol. Subsequently, the pressure was reduced to ~0.08 mbar over the following 4 h. The reaction mixture was then cooled to room temperature under vacuum. The polymer was dried at 60 °C at reduced pressure. The product was obtained as a yellow transparent elastic solid in a yield of 95 %.

^1H NMR (300 MHz, TFA- d_1) δ = 3.80 (t, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 3.60-3.75 (m, 54H, OCH_2CH_2), 3.54 (t, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 3.41 (t, 4H, $\text{CONHCH}_2\text{CH}_2\text{CH}_2$), 2.03 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 1.70-1.80 (m, 54 H, OCH_2CH_2), 1.69 (m, 4H, $\text{CONHCH}_2\text{CH}_2\text{CH}_2$), 1.42 (m, 4H, $\text{CONHCH}_2\text{CH}_2\text{CH}_2$).

Diethyl 2,2'-(hexane-1,6-diylbis(azanediyl))bis(2-oxoacetate) (OXA₂6) (7). A solution of 1,6-diaminohexane (20.00 g, 0.17 mol) in 200 ml of tetrahydrofuran was slowly added to diethyl oxalate (252.00 g, 1.72 mol). Subsequently the mixture was stirred at room temperature for 16 h. The solvent and excess of diethyl oxalate were removed by filtration. The solids were dissolved in chloroform and filtered. The chloroform was removed under reduced pressure and the product was washed two times with diethyl ether and dried under vacuum. The product was obtained as a white powder in a yield of 85 % (mp 90 °C). ^1H NMR (300 MHz, $\text{CDCl}_3\text{-d}_1$) δ = 7.35 (bt, 2H, OCOCONH), 4.25 (q, 4H, $\text{CH}_3\text{CH}_2\text{O}$),

3.29 (m, 4H, $\text{NHCH}_2\text{CH}_2\text{CH}_2$), 1.59 (m, 4H, $\text{NHCH}_2\text{CH}_2\text{CH}_2$), 1.25 (m, 4H, $\text{NHCH}_2\text{CH}_2\text{CH}_2$), 1.25 (t, 6H, $\text{CH}_3\text{CH}_2\text{O}$); ^{13}C NMR (75.26 MHz, $\text{CDCl}_3\text{-d}_1$) δ = 160.9 (OCOCNH), 156.9 (OCOCNH), 63.4 ($\text{CH}_3\text{CH}_2\text{O}$), 40.0 ($\text{NHCH}_2\text{CH}_2\text{CH}_2$), 29.1 ($\text{NHCH}_2\text{CH}_2\text{CH}_2$), 26.3 ($\text{NHCH}_2\text{CH}_2\text{CH}_2$), 14.2 ($\text{CH}_3\text{CH}_2\text{O}$).

$\text{N}^1, \text{N}^{1'}$ -(hexane-1,6-diyl)bis(N2-(3-methoxypropyl)oxalamide) (8). 3-Methoxypropylamine (5.64 g, 63.3 mmol) and OXA₂6 (5) (10.0 g, 31.6 mol) were dissolved in 100 ml of chloroform. Subsequently, the solution was stirred at 70 °C for 16 h. The product was isolated by filtration and subsequently washed two times with chloroform and two times with diethyl ether and dried under vacuum. The product was obtained as a white powder in a yield of 95 % (mp 210 °C).

^1H NMR (300 MHz, TFA-d_1): δ = 8.43 (bt, 2H, $\text{NHCH}_2\text{CH}_2\text{CH}_2$), 8.29 (bt, 2H, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 3.58 (dt, 4H, $\text{NHCH}_2\text{CH}_2\text{CH}_2$), 3.39 (t, 4H, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 3.36 (s, 6H, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 1.85 (m, 4H, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 1.48 (m, 4H, $\text{NHCH}_2\text{CH}_2\text{CH}_2$), 1.24 (m, 4H, $\text{NHCH}_2\text{CH}_2\text{CH}_2$); ^{13}C NMR (75.26 MHz, TFA-d_1): δ = 160.1 ($\text{CONHCH}_2\text{CH}_2\text{CH}_2$), 159.8 ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{NHCO}$), 70.0 ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 57.0 ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 40.2 ($\text{NHCH}_2\text{CH}_2\text{CH}_2$), 37.2 ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 27.8 ($\text{NHCH}_2\text{CH}_2\text{CH}_2$), 26.8 ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 25.7 ($\text{NHCH}_2\text{CH}_2\text{CH}_2$).

GPC

A typical GPC profile of segmented poly(ether amide)s (**2**, **4a-e** and **6**).

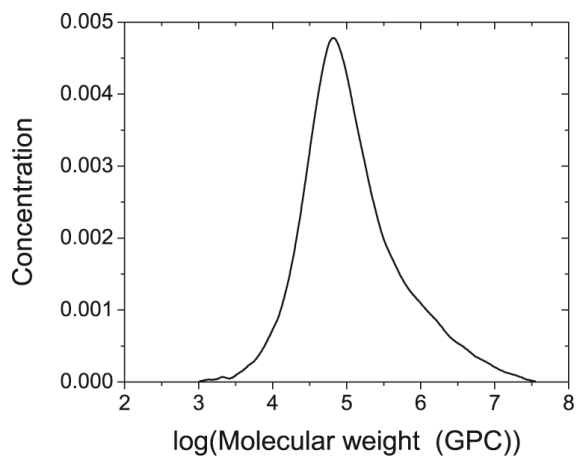


Figure S-2. GPC profile of segmented poly(ether amide) (**4c**).

TGA.

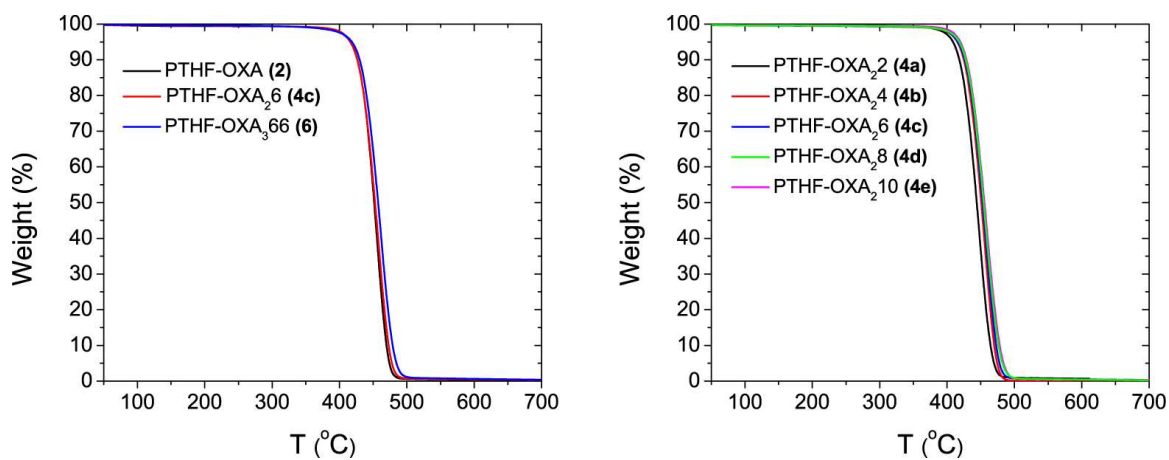


Figure S-2. TGA traces of segmented poly(ether amide)s (**2**, **4a-e** and **6**).

POLARIZED RAMAN SPECTROSCOPY

In Figure S-3, the N-H and C=O stretching bands at 3291 and 1675 cm^{-1} , respectively, show parallel polarization since the intensity of these bands is stronger in the spectra where the fiber axis is parallel to the direction of the polarizer and analyzer. On the other hand, the amide II band at 1547 cm^{-1} , which is attributed to C-N stretching and N-H in-plane bending, shows perpendicular polarization. These results clearly indicate that the beta-sheets are oriented parallel to the stretching direction, *i.e.* parallel to the ***a***-direction.

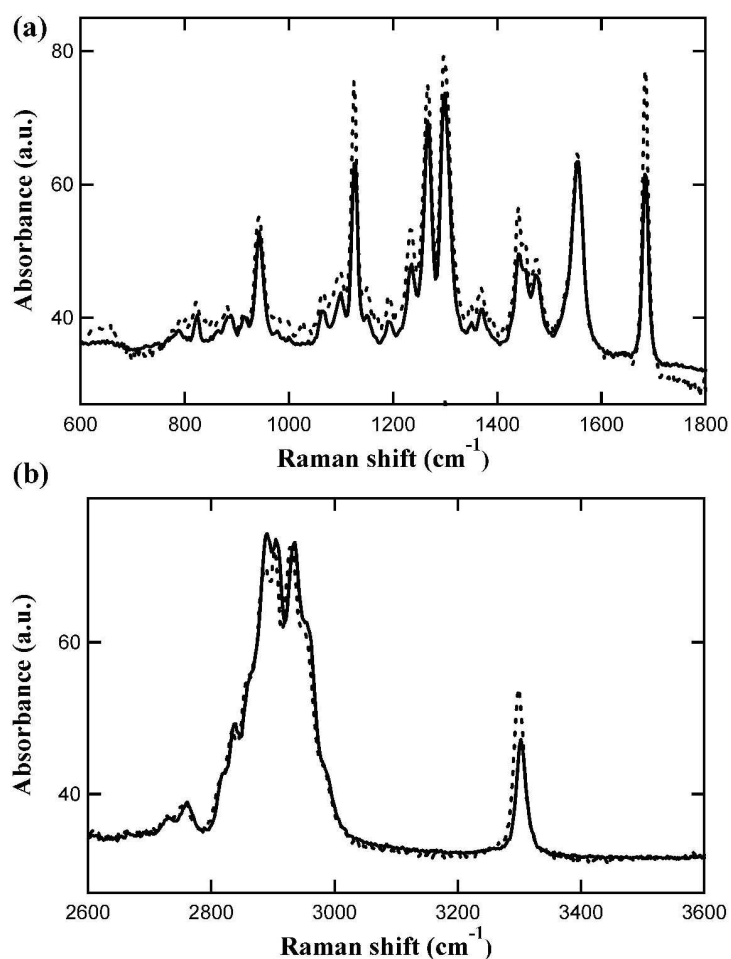


Figure S-3. Polarized Raman spectra of an oriented MeOProp-OXA26-PropOMe (**4**) fiber showing the regions from 600 to 1800 cm^{-1} (a) and from 2600 to 3600 cm^{-1} (b). The spectra corresponding to

situations where the fiber axis is parallel and perpendicular to the polarizer/analyzer plane are given in dotted and solid lines, respectively.