

Supplemental Material

EXPERIMENTAL

General Details. Unless otherwise specified, ACS reagent grade starting materials were used as received from commercial suppliers. Tetrahydrofuran (THF) was dried by distillation from calcium hydride and then from sodium benzophenone ketyl under nitrogen. Proton nuclear magnetic resonance (^1H NMR) analyses were carried out at room temperature in CDCl_3 at 300 MHz on a Varian Gemini-300 spectrometer. The chemical shifts were calibrated using the residual CHCl_3 in the solvent and are reported relative to tetramethylsilane. Crystallinity and melting points were measured using a Perkin-Elmer DSC7 and a Nikon Optiphot2-POL polarizing microscope equipped with a Mettler FP82HT hot stage. The reported melting point range from microscopy corresponds to the onset temperature for the loss of birefringence, and the temperature where the sample becomes isotropic. The heating rates were $10\text{ }^\circ\text{C}/\text{min}$. The DSC7 experiments were run under a helium atmosphere and were calibrated with indium and hexyl bromide standards. The heating and cooling rates were $10\text{ }^\circ\text{C}/\text{min}$. The reported DSC melting points are the onset of the melting peak. (The melting point defined this way shows consistency with the optical microscopy results.) The heats of fusion were calculated from the endothermic peak of sample melting using the accompanied functions of the DSC7 software. X-ray diffraction (XRD) patterns were recorded on a Rigaku rotaflex 200B diffractometer equipped with a rotating anode, $\text{Cu K}\alpha$ x-ray radiation ($\lambda = 1.541838\text{ \AA}$) and a curved crystal graphite monochromator. Diffraction patterns were collected at $0.02^\circ 2\theta$ intervals using a scanning rate of $1^\circ \theta$ per minute.

Tri(ethylene glycol) ditosylate [$\text{Ts}(\text{OCH}_2\text{CH}_2)_3\text{OTs}$]: A solution of tri(ethylene glycol) (0.170 mol) and *p*-toluenesulfonyl chloride (0.360 mol) in THF (200 mL) was placed in a 500 mL flask. To this magnetically stirred mixture, cooled with an ice/water bath, a solution of KOH (0.509 mol) in water (120 mL) was added slowly over a period of 1 h. The ice-water bath was removed and the system was stirred for additional 3 h. The resulting suspension was poured into a mixture of 200 mL CH_2Cl_2 and 100 mL ice water and the aqueous layer was extracted with 2 150 mL portions of CH_2Cl_2 . The combined organic solutions were washed three times with distilled water, and dried over MgSO_4 over night. After removal of MgSO_4 and solvent, the solid was recrystallized twice from methanol to give a white crystalline product. Yield 87%. ^1H NMR (CDCl_3) δ (ppm): 7.77 (d, 4H), 7.32 (d, 4H), 4.12 (t, 4H), 3.63 (t, 4H), 3.51 (s, 4H), 2.43 (s, 6H). mp $80\text{--}81\text{ }^\circ\text{C}$ (lit.¹⁶ $80\text{--}81\text{ }^\circ\text{C}$).

Di(ethylene glycol) monotritylate [$\text{Tr}(\text{OCH}_2\text{CH}_2)_2\text{OH}$]: A 500 mL three neck round bottom flask equipped with a mechanical stirrer, thermometer, and nitrogen inlet was charged with di(ethylene glycol) (106 g, 1.00 mol) and pyridine (11.9 g, 0.150 mol). The mixture was heated and maintained at $45\text{ }^\circ\text{C}$ and trityl chloride (27.9 g, 0.100 mol) powder was added to the reaction mixture under vigorous stirring. After stirring at $45\text{ }^\circ\text{C}$ for 16 h, the suspension was filtered and the white solid was washed with distilled water 5 times. The crude product was recrystallized from isopropanol and twice from 2/1 EtOAc/hexanes to give a white crystalline solid. Yield 71%. ^1H NMR (CDCl_3) δ (ppm):

7.46 (d, 6H), 7.25 (m, 9H), 3.58-3.77 (m, 6H), 3.24 (t, 2H), 2.06 (t, 1H). mp 113.0-114.5 °C (lit.¹⁶ 112.7-114.5°C).

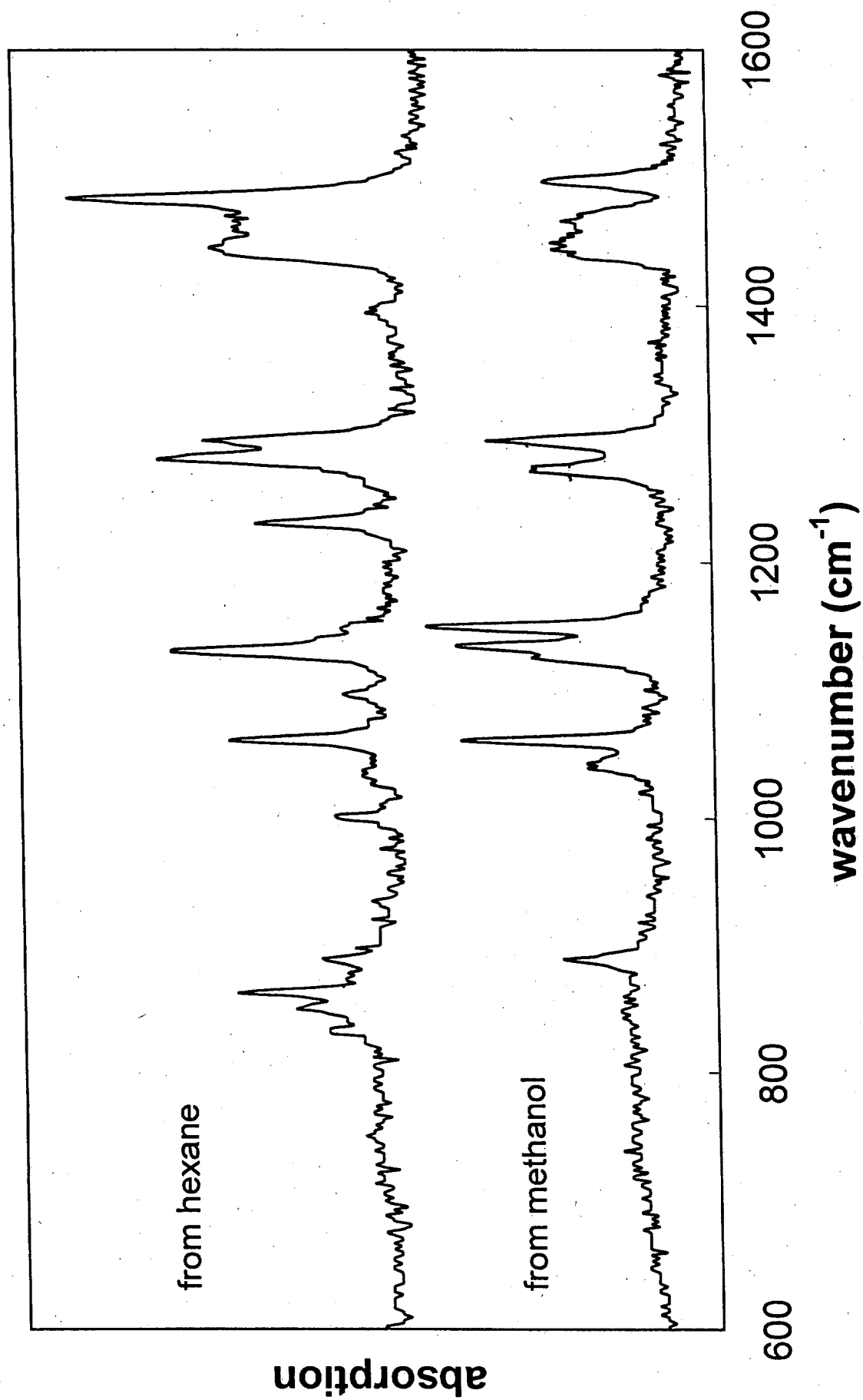
Heptaethylene glycol ditritylate [Tr(OCH₂CH₂)₇OTr]: A 500 mL Schlenk flask with an argon inlet was charged with NaH (3.00 g, 0.125 mol). Di(ethylene glycol) monotritylate (34.8 g, 0.100 mol) dissolved in 200 mL THF was added dropwise and the mixture was stirred for 24 h. A solution of Ts(OCH₂CH₂)₃OTs (23.0 g, 0.050 mol) in 150 mL THF was added dropwise, and the mixture was stirred for 96 h at room temperature. The solid was removed by filtration, and the organic filtrate was washed with saturated aqueous NaCl 3 times, dried over MgSO₄, and concentrated to give a quantitative yield of the ditritylate as a yellow oil. ¹H NMR (CDCl₃) δ (ppm): 7.45 (d, 12H), 7.18-7.28 (m, 18H), 3.62 (m, 24H), 3.20 (t, 4H).

Heptaethylene glycol [H(OCH₂CH₂)₇OH]: A high pressure monel bomb with a glass insert was charged with 36.6 g (45.0 mmol) heptaethylene glycol ditritylate, 150 mL CH₂Cl₂, and 0.677g 10% palladium on carbon. Hydrogenolysis was carried out at room temperature under 50 atm hydrogen pressure for 48 hours. Upon completion of the reaction, the catalyst (which can be reused) was filtered and washed with CH₂Cl₂. The combined filtrate was concentrated to give a mixture of white solid (triphenylmethane) and oil. The mixture was dissolved in 100 mL boiling methanol and the majority of the triphenylmethane crystallized when the solution was cooled to 0 °C. The mixture was filtered and the filtrate washed 6 times with hexanes to remove trace amount of triphenylmethane. Removal of solvent gave a 97% yield of the glycol as a clear colorless oil. ¹H NMR (CDCl₃) δ (ppm): 3.72-3.67 (t, 4H), 3.66-3.61 (s, 20H), 3.60-3.55 (t, 4H), 2.9 (s, 2H). bp 180-195 °C/50 mtorr.²¹

Heptaethylene glycol ditetradecyl ether H(CH₂)₁₄(OCH₂CH₂)₇O(CH₂)₁₄H: Heptaethylene glycol (1.00 g, 3.07 mmol) in 20 mL dry THF was added dropwise to 95% NaH (0.19 g, 7.67 mmol) in a 100 mL Schlenk flask with an Ar inlet. The reaction mixture was stirred overnight, and then tetradecyl bromide (1.74 g, 6.26 mmol) in 30 mL THF was added dropwise and stirring was continued for 72 h at room temperature. Upon completion of the reaction, 10 mL of water were added slowly and stirred for 10 min. The layers were separated and the water layer was extracted with ether (3 × 20 mL). The combined organic solutions were washed with saturated NaCl solution (2 × 80 mL), dried over MgSO₄, and concentrated. Crystallization from methanol gave white crystals. Yield 88%. ¹H NMR (CDCl₃) δ (ppm): 3.59-3.65 (m, 24H), 3.55 (m, 4H), 3.42 (t, 4H), 1.20-1.60 (m, 48H), 0.86 (t, 6H). mp 41 °C.

Sample preparation: To ensure complete dissolution of the 14-7-14 oligomer samples, they were dissolved in methanol or hexanes and heated to near the boiling point of the solvent. For XRD experiments, the white crystalline samples were obtained by slow removal of the solvents under vacuum. For Raman and IR experiments, thin film samples were deposited on substrates by evaporating several drops of the solutions to dryness.

Raman spectrum



IR spectrum

