

## Supporting Information

### Langmuir Film Polymerization of 1,22-Bis(2-aminophenyl)docosane: A Two-Dimensional Crosslinked Polyalkylaniline

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**11-Bromo-1-undecene.** 11-Bromo-1-undecene is commercially available; however, the purity was inadequate for this application. 10-Undecen-1-ol (82.5 g, 0.484 mol) and 500 mL chloroform were placed in a 1000 mL three neck round bottom flask, chilled to 0 °C, placed under argon atmosphere, and stirred. Then 78.3 mL pyridine (dried over CaH<sub>2</sub>) was added to the solution. While stirring, 15 g increments of solid 4-toluenesulfonyl chloride was added to the solution over a one hour period until a total of 138.4 g (1.5 eq) was added. The solution was allow to warm to room temperature and stir for an additional 12 h. The mixture was then washed with 3.0 M HCl (3 x 300 mL), saturated sodium bicarbonate (4 x 300 mL), and water (2 x 300 mL). The solution was dried over magnesium sulfate and the solvent was removed under reduced pressure. The 10-undecenyl-4-toluenesulfonate was dried in a vacuum oven (40 °C) for 12 h.

The 10-undecenyl-4-toluenesulfonate was transferred to a 2000 mL flask equipped with a condenser. Then 900 mL of freshly distilled acetone (CaSO<sub>4</sub>) was added to the flask and stirred under argon. One eq of lithium bromide was added to the reaction mixture and the solution was refluxed for 20 h. The mixture was cooled to room temperature and the precipitate was filtered, washed with pentane, and discarded. The acetone and pentane washings were combined and concentrated under reduced pressure. 300 mL of fresh pentane was added to the residue and

washed with water (3 x 250 mL), saturated sodium bicarbonate (2 x 250 mL), and 250 mL saturated sodium chloride. The organic layer was then dried over sodium sulfate and solvent was removed under reduced pressure. The product was dried under vacuum for 1.5 h, leaving 101 g of a very pale yellow liquid. This liquid was stirred over  $\text{CaH}_2$  for 24 h then vacuum transferred to a clean, dry vacuum flask. The yield was 89 % (100 g).  $^1\text{H NMR}(\text{CDCl}_3)$   $\delta$  = 1.27 (bs, 10H), 1.38 (m, 2H), 1.83 (m, 2H), 2.01 (m, 2H), 3.38 (t, 2H), 4.93 (m, 2H), 5.79 (m, 1H).  $^{13}\text{C NMR}(\text{CDCl}_3)$   $\delta$  = 28.14, 28.71, 28.87, 29.05, 29.34, 32.80, 33.75, 33.91, 114.10, 139.08.

**10-Undecenyltriphenylphosphonium bromide.** 11-Bromo-1-undecene (5.760 g, 24.70 mmol) was placed in a 100 mL round bottom flask with triphenylphosphine (6.802 g, 25.94 mmol) and 20 mL methylene chloride. The mixture was refluxed for 12 h and then allowed to cool to room temperature. The solvent was removed under reduced pressure, leaving a thick oil. The product was purified by column chromatography (silica) by first using methylene chloride as the mobile phase and eluting all of the mobile impurities, then the silica was removed from the column and mixed with methanol for 8 h. The silica was filtered and the methanol was removed under reduced pressure leaving a thick oil. The yield was 90 % (10.97 g).  $^1\text{H NMR}(\text{CDCl}_3)$   $\delta$  = 1.15 (bs, 10H), 1.57 (bs, 4H), 1.95 (m, 2H), 3.66 (bs, 2H), 4.87 (m, 2H), 5.71 (m, 1H), 7.66 - 7.78 (m, 15H).  $^{13}\text{C NMR}(\text{CDCl}_3)$   $\delta$  = 22.33, 22.44, 22.99, 28.66, 28.83, 28.95, 29.00, 29.15, 30.16, 30.36, 33.58, 113.96, 117.58, 118.72, 130.29, 130.46, 133.42, 133.55, 134.89, 134.93, 138.99. Anal. Calcd. for  $\text{C}_{29}\text{H}_{36}\text{PBr}$ : C, 70.30; H, 7.32; Br, 16.13. Found: C, 68.81; H, 7.45; Br, 18.58.

**1-(2-Nitrophenyl)-1,11-dodecadiene.** 10-Undecenyltriphenylphosphonium bromide (10.44 g, 21.06 mmol) was placed in a 250 mL round bottom flask with 2-nitrobenzaldehyde

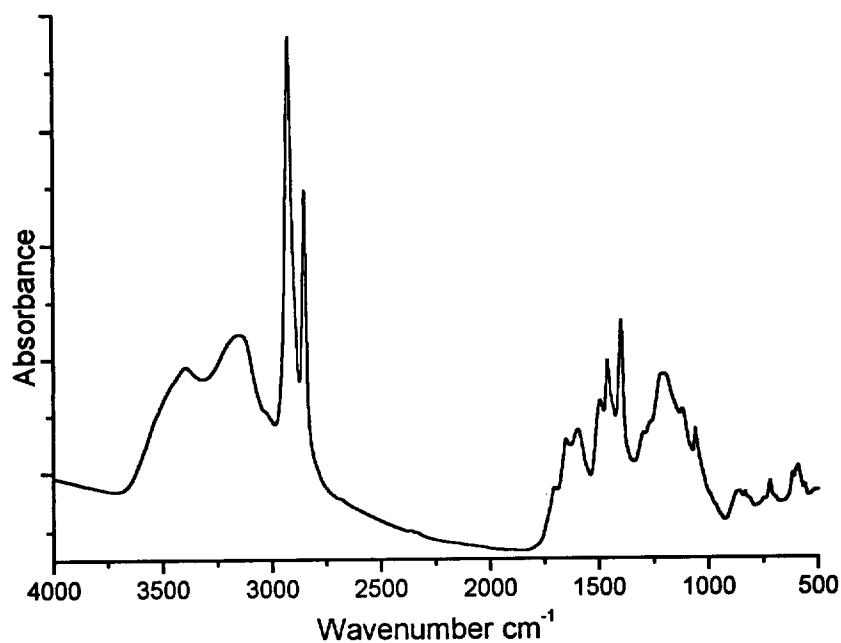
(3.183 g, 21.06 mmol) and 70 mL dry THF. The solution was mixed under argon at  $-78\text{ }^{\circ}\text{C}$ , then potassium *tert*-butoxide (2.363 g, 21.06 mmol) was added in one portion to the solution. The mixture was stirred for 3 h at  $-78\text{ }^{\circ}\text{C}$ , then mixed for 8 h at room temperature. The mixture was poured into a 100 mL solution of ice and water, then extracted with methylene chloride (3 x 50 mL). The combined extracts were washed with deionized water and then dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the product was purified by column chromatography (silica/1:1 hexanes and methylene chloride) to give 3.41 g of a light yellow oil. The yield was 56 %. The product was a mixture of *cis* and *trans* isomers.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.22 - 1.62$  (m, 12H); 1.99-2.29 (m, 4H); 4.94 (m, 2H); 5.73-6.28 (m, 2H); 6.67-6.86 (m, 1H); 7.26-7.58 (m, 3H); 7.85-8.00 (m, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 28.35, 28.84, 28.92, 29.04, 29.27, 29.30, 29.36, 29.41, 33.13, 33.73, 114.05, 124.26, 124.35, 124.80, 124.91, 127.24, 127.54, 128.31, 131.81, 132.47, 132.70, 132.88, 133.32, 134.75, 136.86, 139.11, 147.63, 148.30$ . Anal. Calcd. for  $\text{C}_{18}\text{H}_{25}\text{NO}_2$ : C, 75.22; H, 8.77; N, 4.87. Found: C, 74.61; H, 8.76; N, 4.87.

**1,22-Bis(2-nitrophenyl)-1,11,21-docostriene.** 1-(2-Nitrophenyl)-1,11-dodecadiene (1.00 g, 3.32 mmol) was combined with 14.0 mg of the ruthenium metathesis catalyst,  $\text{Ru}(\text{Cl})_2(\text{P}(\text{C}_6\text{H}_{11})_3)_2(\text{CHC}_6\text{H}_5)$ , in a dry box. Regular bubbling began to occur within five minutes, which indicated the evolution of ethylene from the mixture. The reaction flask was then attached to a vacuum line and a vacuum was pulled on the solution while it was stirred at room temperature. After 72 h, the flask was opened to the atmosphere and toluene (5 mL) and silica (ca.0.5 g) were added to the flask. The solution was filtered and the silica was washed with toluene (3 x 5 mL). The toluene was removed under reduced pressure leaving 0.867 g of a light

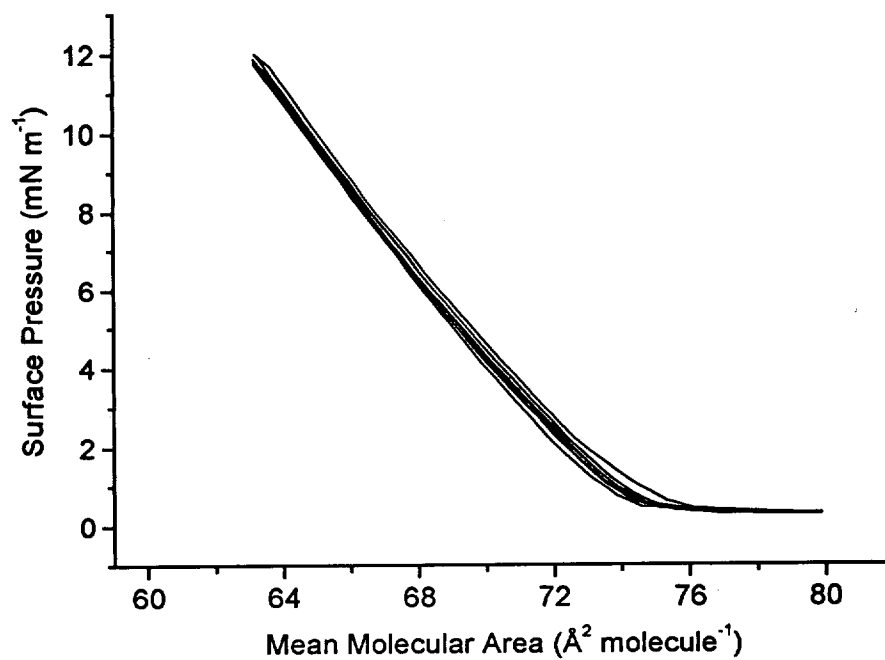
yellow oil. The yield was 95%.  $^1\text{H}$  NMR data clearly showed that the reaction was selective toward the terminal olefin, giving only 1,22-bis(2-nitrophenyl)-1,11,21-docosatriene as the product. The compatibility of an olefin with the ruthenium alkylidene catalyst can also be determined through *cis-trans* metathesis isomerization, as previous work has shown that the *trans* isomer is the favored product when isomerization occurs. (Hillmyer, M. A., Nguyen, S. T., Grubbs, R. H. *Macromolecules* 1997, 30, 718.)  $^1\text{H}$  NMR indicates that the percentage of *cis* olefin adjacent to the aromatic ring was unchanged by this self-metathesis reaction (ca. 72%), further indicating a lack of reactivity of the internal olefin.  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$  = 1.22 - 1.50 (m, 24H), 1.95 (bs, 4H), 2.04 - 2.29 (m, 4H), 5.37 (bs, 2H), 5.77 - 6.28 (m, 2H), 6.66 - 6.85 (m, 2H), 7.26 - 7.58 (m, 6H), 7.84 - 7.99 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 27.13, 28.34, 28.92, 29.05, 29.19, 29.29, 29.40, 29.54, 29.66, 32.51, 33.12, 124.25, 124.33, 124.76, 124.88, 127.22, 127.52, 128.30, 129.79, 130.25, 131.80, 132.46, 132.70, 132.86, 133.29, 134.74, 136.86, 147.60, 148.28. MS(FAB) exact mass calcd. ( $m+1$ ): 547.3536, Found: 547.3555. Anal. Calcd. for  $\text{C}_{34}\text{H}_{46}\text{N}_2\text{O}_4$ : C, 74.69; H, 8.48; N, 5.12. Found: C, 74.73; H, 8.37; N, 5.10.

**1,22-Bis(2-aminophenyl)docosane.** 1,22-Bis(2-nitrophenyl)-1,11,21-docostriene (0.817 g, 1.49 mmol) was placed in 15 mL of 95% ethanol with 0.20 grams of 10% palladium on carbon. The solution was stirred under a pure hydrogen gas atmosphere until no more hydrogen gas was consumed (4 days). The hydrogenation was carried out under normal atmospheric pressure and at room temperature. The mixture was filtered, the catalyst was washed with methylene chloride, the ethanol and methylene chloride solvents were combined, and the solvents were removed under reduced pressure yielding a white solid. Purification was carried out by column chromatography (silica/methylene chloride) and was verified by GC. The melting point was 64.0 - 66.0 °C. The

yield was 96% (0.703 g).  $^1\text{H NMR}(\text{CDCl}_3)$   $\delta$  = 1.25 (s, 36H), 1.60 (m, 4H), 2.47 (t, 4H), 3.56 (bs, 4H), 6.64 - 6.74 (m, 4H), 6.99 - 7.04 (m, 4H).  $^{13}\text{C NMR}(\text{CDCl}_3)$   $\delta$  = 28.71, 29.54, 29.60, 29.67, 31.27, 115.44, 118.65, 126.75, 126.90, 129.35, 143.97. MS(FAB) exact mass calcd. (m +1): 493.4522. Found: 493.4585. Anal. Calcd. for  $\text{C}_{34}\text{H}_{56}\text{N}_2$ : C, 82.86; H, 11.45; N, 5.68. Found: C, 82.99; H, 11.43; N, 5.58.



Infrared spectrum produced from ten combined samples of poly(BAD), which were polymerized on a 0.2 M HCl and 0.03 M  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  subphase and pressed into a KBr pellet. Measurement was done on a Mattson Instruments Research Series-1 FTIR spectrometer with a deuterated triglycine sulfate detector.



Hysteresis plot of poly(BAD) on a 0.1 M H<sub>2</sub>SO<sub>4</sub> and 0.03 M (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> subphase. The film was compressed and expanded four times at 10 Å<sup>2</sup> molecule<sup>-1</sup> min<sup>-1</sup>.