

TOWARD POLY(3- AND 3,4-ALKOXYTHIOPHENES)

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Introduction

The discovery of electrical conductivity in conjugated polymers provoked tremendous amount of effort aimed at the development of practical conducting plastics.¹ Those efforts have been coming to realization with the development of polymer-based light emitting diodes², field-effect transistors³, elements for active matrix displays⁴, and all-polymer integrated circuits⁵. Properties of conjugated polymers are well exemplified by synthesis of regioregular poly(3-alkylthiophenes) (PATs) that are exceptionally stable, processable and can self-assemble into a well-defined superstructures.⁶ Formation of ordered super-molecular structures in these regioregular materials correlates strongly with their excellent electrical conductivities (thousands or hundreds of S cm⁻¹ in comparison with few S cm⁻¹ for regiorandom polymers).

Poly(3-alkoxy-substituted thiophenes), in comparison with their alkyl analogs, exhibit a variety of favorable properties which include a reduced band gap, low oxidation potential for the conversion to the highly stable conducting state.⁷ Grignard Metathesis Method⁸ (GRIM) was utilized to synthesize poly(3-hexyloxythiophene), poly(3-(2-(2-methoxyethoxy)ethoxy)thiophene) [or poly(3-MEethiophene)], poly(2,5-(3-dodecyl-3,4-ethylenedioxy)bithiophene) [or poly(2,5-(3-DD-3,4-EDO)bithiophene)], and poly(2,5-(3-MEE-3,4-EDO)bithiophene). This method afforded high molecular weight regioregular polymers in good yield. UV-vis-NIR spectroscopic studies and conductivity measurements revealed that these polymers due to the reduced band gap possess higher conductivities in the solid state, and are readily oxidized in an oxygen atmosphere

Experimental

Materials. All reactions were performed under prepurified nitrogen or argon, using either flame-dried or oven-dried glassware. All solvents were distilled prior to use and all reagents were used as received. In some cases, titration of the Grignard reagents was performed following the procedure described by Love.

Instrumentation. ¹H spectra were recorded on an IBM Bruker FT300 MHz spectrometer. All NMR spectra were recorded in CDCl₃ containing 0.003% TMS as an internal reference. MALDI-TOF MS was performed using a Voyager-DE STR BioSpectrometry Workstation by PerSeptive Biosystems. All GPC spectra were recorded using a Waters 6000A apparatus and a Waters R410 differential refractometer. The eluent was THF, which was kept at 25°C. Flow rate was 1.0 ml/min. The system was calibrated using polystyrene standards obtained from Polymer Standards Service. GC/MS was performed on a Hewlett-Packard 59970 GC/MS workstation. The GC column was a Hewlett-Packard fused silica capillary column cross-linked with 5% phenylmethyl silicone. Elemental analysis was performed by Midwest Microlab, Indianapolis, IN.

Synthesis of 3-hexyloxythiophene. In a dry 3-neck, 500-mL round bottom flask, sodium hydride powder (3.57 g, 149 mmol) was dissolved in DMF (23 mL). The DMF had been distilled over calcium oxide the day before and stored under dry nitrogen with activated molecular sieves. The solution was cooled to 0 °C under dry nitrogen. 1-Hexanol (70 mL, 559 mmol), which had been distilled over magnesium hexoxide, was then added slowly via syringe. After the effervescence ceased (1hr), 3-bromothiophene (12 mL, 128 mmol), which had been distilled over calcium hydride, was added via syringe, followed by addition of copper (I) bromide (1.96 g, 13.7 mmol). The mixture was then heated at 110 °C for 40 min. The reaction flask was removed from the temperature bath and poured into a 1 M aqueous ammonium chloride solution (300mL). This mixture was stirred overnight, followed by extraction with pentane (3x40 mL). The solution was dried over MgSO₄ and the solvent was removed under reduced pressure. The remaining starting materials were distilled over calcium hydride, leaving mostly product and hydride in the distillation flask. The suspension was diluted with methylene chloride (10 mL) and filtered through Celite 545 to remove the

solids. The solvent was removed under reduced pressure (ca. 35 torr) to give an oil that was flash chromatographed (silica, methylene chloride) to afford 10.39 g of 3-hexyloxythiophene (44% yield). ¹H NMR δ 0.91 (t, 3H, J = 7.2 Hz), 1.2-1.5 (m, 6H), 1.76 (m, 2H), 3.93 (t, 2H, J = 6.0 Hz), 6.23 (s, 1H), 6.74 (d, 1H, J = 4.8 Hz), 7.14 (t, 1H, J = 3 Hz). MS *m/z* (relative intensity): 184 (24), 100 (100), 85 (7), 55 (6). GC R_t = 10.9 min; purity = >99%.

Synthesis of 2,5-dibromo-3-hexyloxythiophene. 3-hexyloxythiophene (1.22 g, 6.6 mmol) was added to a dry, 3-neck, 250-mL round bottom flask via syringe and followed by freshly distilled THF (100 mL). This solution was cooled to -78 °C under dry nitrogen. N-Bromosuccinimide (2.48 g, 13.9 mmol) was added followed by purging the flask with dry nitrogen for 2 minutes. The solution was stirred at -78 °C for 15 minutes and then allowed to come to room temperature overnight (20.5 h). The mixture was taken up in diethyl ether (30 mL) and was washed with DI H₂O (5 x 40 mL). The organic portion was then dried over MgSO₄ and the solvent was removed under reduced pressure. Column chromatography (silica, petroleum ether) was used for further purification to afford 1.18 g of 2,5-dibromo-3-hexyloxythiophene (52% yield). The product was stored cold as a dilute solution in ether under dry nitrogen. ¹H NMR δ 0.89 (t, 3H, J = 6.6 Hz), 1.21-1.49 (m, 6H), 1.72 (m, 2H), 3.97 (t, 2H, J = 6.6 Hz), 6.73 (s, 1H). MS *m/z* (relative intensity): 342 (7), 258 (100), 229 (14), 151 (16), 125 (28), 69 (64). GC R_t = 15.9 min; purity = >99%.

Synthesis of poly(3-hexyloxythiophene). 2,5-dibromo-3-hexyloxythiophene (3.75 g, 10.9 mmol) was added via syringe to a dry, 3-neck, 250-mL round bottom flask fitted for reflux. This was dissolved in freshly distilled THF (55 mL) and stirred under dry nitrogen. Methylmagnesium bromide solution in hexanes (3.6 mL, 10.9 mmol) was added slowly via syringe and then heated at reflux for 1 h. After removing the flask from the temperature bath, the solution was allowed to cool toward room temperature for 30 minutes. Ni(dppp)Cl₂ (0.059 g, 0.11 mmol) was then added and stirred at reflux for 1hour. After appreciable darkening of the solution occurred, the solution was allowed to cool toward room temperature and poured into methanol (200 mL). This led to precipitation. The solid was collected in a cellulose extraction thimble and air-dried overnight. The solid was then washed with methanol and hexanes in a Soxhlet apparatus. The polymer was dried in vacuum overnight and was afforded as a dark blue material (62% yield). ¹H NMR δ 0.89 (t, 3H), 1.39-1.56 (m, 6H), 1.86 (m, 2H), 4.14 (t, 2H), 6.90 (s, 1H). The solid was mostly intractable in common solvents (THF, chloroform) indicating that the polymer was doped. MALDI-MS: *m/z*: 33005.97[M⁺] (corresponds to a degree of polymerization of 18 of the soluble amount).

Synthesis of poly(3-MEethiophene). 2,5-dibromo-3-MEethiophene (2 g, 5.56 mmol) was added to a dry, 3-neck, 100-mL round bottom flask fitted for reflux and purged with dry nitrogen for 15 minutes. Freshly distilled THF (50 mL) was inserted via syringe and the solution was stirred under dry nitrogen. *t*-Butylmagnesium chloride solution in diethyl ether (2.78 mL, 5.56 mmol) was added slowly via syringe and then heated at reflux for 1 h. After removing the flask from the temperature bath, the solution was allowed to cool toward room temperature for 30 minutes. Ni(dppp)Cl₂ (30.1 mg, 0.0556 mmol) was then added and stirred at reflux for 1hour. After appreciable darkening of the solution occurred, the solution was allowed to cool toward room temperature and poured into methanol (200 mL). This led to precipitation. The solid was collected in a cellulose extraction thimble and air-dried overnight. The solid was then washed with methanol, hexanes, and acetone in a Soxhlet apparatus. The polymer was dried in vacuum overnight and was afforded as a dark blue material (34% yield). ¹H NMR δ 3.37 (s, 3H), 3.57 (t, 2H), 3.76 (t, 2H), 3.93 (t, 2H), 4.33 (t, 2H), 6.95 (s, 1H). MALDI-MS: *m/z*: 2806.53[M⁺] (corresponds to a degree of polymerization of 14 of the soluble amount).

Synthesis of 2,5(2,5-dibromo-3-MEE-3,4-EDO)bithiophene oligomers. 2,5-(3-MEE-3,4-EDO)bithiophene (0.50 g, 1.46 mmol) dissolved in freshly distilled THF (2 mL) was added to a dry, 3-neck, 100-mL round bottom flask and purged with dry nitrogen for 15 minutes. Additional freshly distilled THF (25 mL) was added to the flask via syringe. The solution was cooled to -78 °C under dry nitrogen. 1,3-Dibromo-5,5-dimethylhydantoin (or bromantoin) (0.418 g, 1.46 mmol) was added followed by purging the flask with dry nitrogen for 2 minutes. The solution was stirred at -78 °C for 1 hour and then allowed to come to room temperature overnight (20.5 h). The

mixture was taken up in DI H₂O (100 mL) and stirred for 1 hour at oxygen atmosphere. Appreciable darkening of the solution occurred and it was poured into THF (500 mL). This led to precipitation. The solid was collected in a cellulose extraction thimble and air-dried overnight. The final product was isolated as a black powder (80% yield) which is soluble in DMF resulting in deep purple color. El. Anal. Found: C, 39.42; H, 3.63; Br, 22.78; S, 13.47. Calculated for C₁₅H₁₆Br₂O₅S₂: C, 36.03; H, 3.23; Br, 31.96; S, 12.82. MALDI-MS: *m/z*: 1173.97[M⁺] (corresponds to a degree of polymerization of 3). GPC (in DMF): Mn = 1494 g/mol (PDI= 1.1).

Results and Discussion

Polymer Synthesis. Polymer **2** was synthesized by Grignard Metathesis Method⁸ (GRIM) **Figure 1**. This method involves treatment of dibrominated species with a grignard reagent (methylmagnesium bromide or *t*-butylmagnesium chloride) in THF in order to generate a Grignard intermediate, followed by addition of nickel catalyst to produce HT-coupled regioregular polymer. Polymer **2(A)** initial ¹H NMR exhibited broad aromatic and α proton peak, which was assumed to be due to polymer being partially self-doped in oxygen atmosphere. This was confirmed by UV-vis-NIR spectra, where a polaron band was observed around 1200 nm. All polymers have higher absorption maximum (λ_{max}) compared to their alkyl analogs in both solution and solid state indicating that an introduction of an electron donating oxygen on the α position of the side chain renders the π system more electron rich thus lowering the energy band gap. Incorporation of an oxygen atom also leads to a lower solubility of polymers.⁹ All the polymers were exposed to I₂ and it was observed that the polymers not only remain in the doped state for prolonged periods of time but their conductivity measurements increase with time.

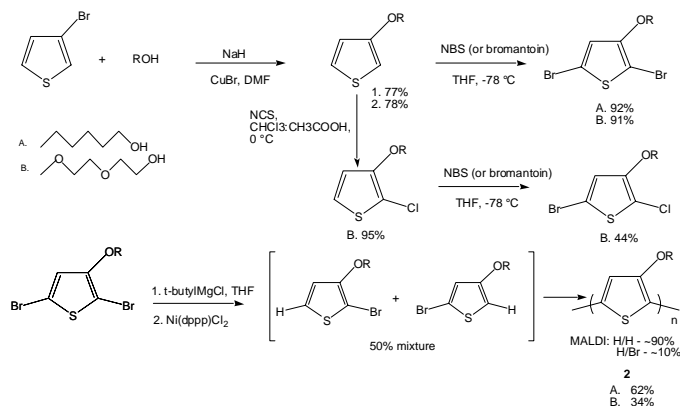


Figure 1. Polymer Synthesis.

Conclusions

GRIM Methodology affords a fast and efficient synthesis of 3-alkoxy substituted polythiophenes, which self-oxidize in oxygen atmosphere.

References

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