## Synthesis and Study of Head-to-Tail Regioregular Poly(alkyl thiophene-3carboxylates)

Ananda S. Amarasekara, Martin Pomerantz\*

Center for Advanced Polymer Research, Department of Chemistry and Biochemistry, Box 19065, The University of Texas at Arlington, Arlington, Texas 76019-0065, USA Fax +1(817)2723811; E-mail: pomerantz@uta.edu

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**Abstract:** Regioregular head-to-tail poly(alkyl thiophene-3-carboxylates) have been prepared by very careful formation of the mono-Grignard reagent from alkyl 2,5-dibromothiophene-3-carboxylates (-40 °C, 1 h) followed by nickel-catalyzed polymerization. The spectral properties are reported along with the molecular weights.

**Key words:** Grignard reactions, cross-coupling, regioselectivity, polymers, thiophenes, esters

For a number of years we have been interested in the synthesis and study of polythiophenes containing electronwithdrawing carbonyl groups directly attached to the ring.<sup>1-6</sup> These polythiophenes are an important class of materials which we have shown have electroluminescence properties. In particular, we have reported on poly(hexyl thiophene-3-carboxylate) (1) and poly(octyl thiophene-3-carboxylate) (2) prepared from the corresponding hexyl 2,5-dibromothiophene-3-carboxylate (3) and octyl 2,5-dibromothiophene-3-carboxylate (4). It is well known that the optical properties of these materials are affected by the degree of planarity of the polymer backbone. As a result of the long alkyl ester chain ester groups, head-to-head (H–H) linkages in the backbone of the polymer will cause twisting and decrease the conjugation and, depending on the amount of H-H linkages, the UV/Vis absorption maximum will vary. The large torsional effect on the thiophene-thiophene linkage by ester groups in an H-H arrangement has recently been demonstrated by ab initio quantum mechanical calculations<sup>3</sup> and by X-ray crystallography on model bithiophene esters.<sup>5</sup> In this regard, poly(octyl thiophene-3-carboxylate) (2) prepared by the Ullmann reaction (Scheme 1) with a H-H/H-T (head-to-tail) ratio of 0.31:1 shows  $\lambda_{max}$  (THF) = 426 nm while that prepared by Ni(0) catalyzed coupling with a H–H/H–T ratio of 2.16:1 shows  $\lambda_{max}$  (THF) = 419 nm.<sup>4</sup> In addition, we have prepared the regioregular H-H/T-T version of these polymeric esters, 5 and 6, by coupling of the bithiophenes, dihexyl 5,5'-dibromo-2,2'-bithiophene-4,4'-dicarboxylate and dioctyl 5,5'-dibromo-2,2'bithiophene-4,4'-dicarboxylate again employing the Ullmann coupling as shown in Scheme 2. In this case  $\lambda_{max}$ (THF) = 389 nm and here the H–H/H–T ratio is >20:1.<sup>4</sup>

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We have also previously looked into the preparation the H-T regioregular polymer.<sup>4</sup> Prior to attempting coupling reactions to produce the polymer model reactions were examined. As Rieke had done to prepare regioregular, head-to-tail poly(3-alkylthiophenes)<sup>7-9</sup> an appropriate 2,5-dibromothiophene was reacted with Rieke zinc in an attempt to obtain the organozinc derivative with high regioselectivity. Thus, methyl 2,5-dibromothiophene-3-carboxylate was reacted with Rieke zinc at -78 °C and the product was quenched with water. <sup>1</sup>H NMR spectroscopy was used to examine the ratio of the methyl 2- bromothiophene-3-carboxylate to methyl 5-bromothiophene-3-carboxylate as shown in Scheme 3. The observed ratio was 14:86 indicating that the reaction was only moderately regioselective. In this paper we now report on a method for preparing these polythiophene esters with very high head-to-tail regioregularity. Since we have recently demonstrated using X-ray crystallography, that dimethyl 2,2'bithiophene-3,4'-dicarboxylate (7), a model for the H-T linkage, is planar in the solid state,<sup>5</sup> we assume that the regioregular polymers will be planar, at least in the solid state (film) and probably also in solution.

Based on a recent report that that halogen atoms in substituted aromatic molecules could be efficiently exchanged with isopropylmagnesium bromide and in particular that ethyl 2,5-dibromothiophene-3-carboxylate provided the 2-bromomagnesium derivative **7** as a result of chelation with the ester group,<sup>10</sup> we examined this reaction as a route to the H–T-regioregular polymers. Interestingly, it was reported that, at –40 °C in THF solvent, in addition to the major regioisomeric magnesium reagent there was

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Scheme 3



Scheme 4

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also 10% of the minor regioisomeric magnesium reagent, namely ethyl 2-bromo-5-(bromomagnesio)thiophene-3-carboxylate (8) (Scheme 4).<sup>10</sup>

When hexyl 2,5-dibromothiophene-3-carboxylate (3) and octyl 2,5-dibromothiophene-3-carboxylate (4) were allowed to react with one equivalent of isopropylmagnesium bromide in THF the corresponding thiophene Grignard reagents were formed. In order to determine the regioselectivity of the reaction, the extent of formation of the two Grignard reagents formed upon reaction of octyl 2,5-dibromothiophene-3-carboxylate (4) with isopropylmagnesium bromide in THF was studied as a function of temperature. The ratio of the products, octyl 5-bromothiophene-3-carboxylate (9) and octyl 2- bromothiophene-3-carboxylate (10) formed after aqueous hydrolysis, was obtained by <sup>1</sup>H NMR spectroscopy (Scheme 5). Table 1 shows the 9:10 ratio as a function of the temperature of the bromine-magnesium exchange reaction, all reactions being carried out for 1 h. Clearly, in agreement with the observations of Abarbri et al., the temperature which provides the best regioselectivity is -40 °C. Our observation of a 93:7 ratio of 9:10 is similar to their observed ratio of 90:10 for the ethyl ester.<sup>10</sup> In addition, when the Grignard reagents are formed at -40 °C (1 h) and then allowed to warm to room temperature over an additional hour there is substantial equilibration that takes place.





When hexyl 2,5-dibromothiophene-3-carboxylate (3) was reacted with 1 equiv of *i*-PrMgBr in THF at -40 °C for 1 h and then 1.0 mol% of Ni(dppp)Cl<sub>2</sub> [dppp = 1,3bis(diphenylphosphino)propane] was added to couple the Grignard carbon atom with the bromine containing carbon,<sup>11</sup> followed by warming to room temperature and refluxing for 2 h, poly(hexyl thiophene-3-carboxylate) (11) (Scheme 6) was produced as a red powder after precipitation with methanol. The <sup>1</sup>H NMR spectrum showed a singlet at  $\delta = 7.86$  ppm for the single hydrogen on the thiophene ring. This compares quite favorably with the value of  $\delta = 7.85$  ppm reported for one of the four triads in the 'regiorandom' version of 3.4 In addition, the chemical shift of the methylene hydrogens adjacent to the ester oxygen was at  $\delta = 4.30$  ppm in agreement with the previous assignment that the H–T dyad appeared at  $\delta = 4.30$ ppm in the 'regiorandom' polymer.<sup>4</sup>

Table 1Effect of Temperature on Selectivity of Mg–Br Exchangein 4

Reaction temp (°C), time (h)	9:10		
-78, 1	No reaction		
-40, 1	93:7		
25, 1	72:28		
-40, 1; then -40 to 25, 1	79:21		



#### Scheme 6

The <sup>13</sup>C NMR spectrum also showed the regioregularity of the polymer. Unlike the 'regiorandom' material, which showed 4 carbonyl and multiple thiophene ring carbon atoms due to the 4 triads and 16 pentads,<sup>4</sup> H–T regioregular **11** showed a single carbonyl absorption at  $\delta = 162.8$  ppm along with 4 singlets for the thiophene carbons at  $\delta =$ 128.2, 132.3, 132.4 and 143.0 ppm. What was most interesting was that, although the quenching experiments showed that the Grignard reagent was prepared with 93% regioregularity, the polymer **11** was >97% regioregular as determined by NMR spectroscopy.

Head-to-tail regioregular poly(octyl thiophene-3-carboxylate) (12) (Scheme 6) was prepared similarly by using octyl 2,5-dibromothiophene-3-carboxylate (4). <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy likewise confirmed the >97% regioregularity. Table 2 shows the UV/Vis spectra of 11 and 12 taken both in THF solution and as cast films. Interestingly, while most substituted polythiophenes, such as poly(3alkylthiophenes), show a fairly substantial red shift in going from solution to solid (film) phase due to intermolecular interactions,<sup>12</sup> these polymers show a small shift of the absorption maximum in the opposite direction. However, upon closer inspection it is seen that there is a shoulder in the spectra on the long wavelength side in both the solution and film spectra. The band edge in these cases, shown in Table 2, does show a bathochromic shift of about 50-60 nm for both polymers 11 and 12. In the poly(3-alkylthiophenes) both the  $\lambda_{max}$  and the band edge of the H-T regioregular polymers show a large bathochromic shift in going from solution to solid. The reason the H–T regioregular ester polymers 11 and 12 do not show this shift in  $\lambda_{max}$  is not apparent at the present time.

Table 2UV/Vis Spectra and Band Edges for Polymers 11 and 12 inTHF Solution of as Films

THF Solution				Cast Film			
$\lambda_{max}$ (nm)		Band (nm)	Edge	$\lambda_{max}\left( nm\right)$		Band Edge (nm)	
11	12	11	12	11	12	11	12
410	406	518	518	395, 475 (sh)	410, 469 (sh)	572	576

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a JEOL Eclipse 500 spectrometer at 500.16 and 125.78 MHz, respectively. CDCl<sub>3</sub> was used as the solvent with TMS ( $\delta = 0.00$  ppm) used as internal reference. FT-IR spectra were obtained on a Digilab FTS-40 instrument using powdered samples (approximately 1-2 weight%) in a KBr disc. Gel permeation chromatography (GPC) was carried out on a Waters GPC system, using a Waters Model 510 HPLC pump, a Model 490 multiwavelength detector ( $\lambda = 254$  nm), Millennium 2010 Software, a serial combination of 10<sup>3</sup>, 10<sup>4</sup>, and 10<sup>5</sup> Å Ultrastyragel columns and THF with a flow rate of 1.0 mL/min. The calibration curve was established by use of polystyrene standards with a molecular weight range of 800 to  $9 \times 10^5$  g/mol. UV/Vis-NIR spectra were recorded on a Cary 5E UV/Vis-NIR spectrophotometer using THF solutions and polymer thin films cast onto quartz cuvettes from CHCl<sub>3</sub> solutions. Fluorescence spectra were measured on a Perkin-Elmer Model 204 Fluorescence spectrophotometer using a Perkin-Elmer 150 Xenon power supply. Samples were either polymer-THF solutions or polymer thin films on glass substrates. Elemental analyses were obtained on a Perkin-Elmer 2400 CHN analyzer.

# H–T Regioregular Poly(alkyl thiophene-3-carboxylates); General Procedure

Alkyl 2,5-dibromothiophene-3-carboxylate<sup>1</sup> (4.0 mmol) was dissolved in anhyd THF (25 mL) and cooled to -40 C under an argon atmosphere. To this solution was added, via syringe, isopropylmagnesium bromide (4.4 mmol) in anhyd THF (10 mL) (freshly prepared from 4.4 mmol of isopropyl bromide and 4.5 mg-atom of Mg) over a period of 5 min. The mixture was stirred under argon for 1 h at -40 C and then Ni(dppp)Cl<sub>2</sub> (22 mg, 0.04 mmol, 1 mol%) was added, the cooling bath was removed and the mixture was allowed to warm to r.t. over about an hour. It was then refluxed for 2 h, allowed to cool and the solvent was removed under reduced pressure. The residue was dissolved in CHCl<sub>3</sub> (200 mL), washed with aq HCl (10%; 50 mL), H<sub>2</sub>O (2 × 50 mL), and dried (MgSO<sub>4</sub>) to yield an orange solution. MeOH was slowly added to this solution to precipitate the polymer as a red powder.

## H-T Regioregular Poly(hexyl thiophene-3-carboxylate) (11)

Starting with hexyl 2,5-dibromothiophene-3-carboxylate (1.480 g, 4.00 mmol) gave **11**.

Yield: 395 (47% yield).

IR (KBr): 771, 835, 990, 1151, 1230, 1432, 1467, 1718, 2855, 2925 cm<sup>-1</sup>.

 $^1H$  NMR (CDCl\_3):  $\delta$  = 0.88 (br s, 3 H), 1.28 (br s, 6 H), 1.74 (br s, 2 H), 4.29 (br s, 2 H), 7.86 (br s, H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 14.2, 22.7, 25.7, 28.6, 31.6, 65.5, 128.2, 132.3, 132.4, 143.0, 162.8.

UV (THF):  $\lambda_{max} = 410$  nm.

UV (film cast from CHCl<sub>3</sub>):  $\lambda_{max} = 395$ , 475 (sh) nm.

Anal. Calcd for  $C_{11}H_{14}O_2S$ : C, 62.83; H,, 6.71. Found: C, 62.75; H, 6.90.

GPC (THF; 1.0 mL/min): number average molecular weight  $(M_n) = 6200 \text{ gmol}^{-1}$ ; polydispersity  $(M_w/M_n) = 1.6$ .

#### H-T Regioregular Poly(octyl thiophene-3-carboxylate) (12)

Starting with octyl 2,5-dibromothiophene-3-carboxylate (1.592 g, 4.00 mmol) gave **12**.

Yield: 495 mg (52%).

IR (KBr): 774, 827, 991, 1157, 1233, 1436, 1457, 1716, 2854, 2925  $\rm cm^{-1}.$ 

 $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  = 0.87 (br s, 3 H), 1.28 (br s, 10 H), 1.74 (br s, 2 H), 4.29 (br s, 2 H), 7.86(br s, 1 H).

 $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  = 14.2, 22.7, 26.1, 28.7, 29.3, 29.8, 31.9, 65.5, 128.2, 132.3, 132.4, 143.0, 162.8.

UV (THF):  $\lambda_{max} = 410$  nm.

UV (film cast from CHCl<sub>3</sub>):  $\lambda_{max} = 405$ , 485 (sh) nm.

Anal. Calcd for  $C_{13}H_{18}O_2S$ : C, 65.51; H, 7.61. Found: C, 65.38; H, 7.86.

GPC (THF; 1.0 mL/min): number average molecular weight  $(M_n) = 5200 \text{ gmol}^{-1}$ ; polydispersity  $(M_w/M_n) = 1.4$ .

#### **Octyl 2-Bromothiophene-4-carboxylate (9)**

This molecule was prepared as described previously.<sup>4,13</sup>

### Octyl 2-Bromothiophene-3-carboxylate (10)<sup>13</sup>

2-Bromothiophene-3-carboxylic acid<sup>5</sup> (1.035g, 5.00 mmol) was dissolved in thionyl chloride (1.0 mL; 1.63 g, 13.70 mmol) and the mixture was refluxed for 1 h. The excess thionyl chloride was removed under a stream of argon and the residue was treated with a solution of 1-octanol (715 mg, 5.50 mmol) in pyridine (1.00 mL). It was further refluxed for 2 h and allowed to cool. The resultant mixture was dissolved in  $CH_2Cl_2$  (50 mL) and washed with  $H_2O$  (2 × 20 mL), dried (MgSO<sub>4</sub>) and concentrated to yield the crude product, which was purified by column chromatography (silica gel; EtOAc–hexane, 10%).

Yield: 1.387g, 4.35 mmol (87%); colorless viscous oil.

IR (neat film): 708, 999, 1160, 1262, 1418, 1461, 1523, 1719, 2862, 2928 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 0.85 (t, *J* = 7.0 Hz, 3 H), 1.25 (m, 8 H), 1.27 (m, 2 H), 1.71 (m, 2 H), 4.24 (t, *J* = 6.8 Hz, 2 H), 7.17 (d, *J* = 5.8 Hz, 1 H), 7.33 (d, *J* = 5.8 Hz, 1 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 14.2, 22.7, 26.1, 28.7, 29.3 (2 C), 31.9, 65.2, 119.6, 125.9, 129.5, 131.4, 162.0.

Anal. Calcd for  $C_{13}H_{19}BrO_2S$ : C, 48.91; H, 6.00. Found: C, 49.16; H, 5.89.

## Temperature Effect on Selectivity of Br–Mg Exchange in Octyl 2,5-Dibromothiophene-3-carboxylate (4)

Octyl 2,5-dibromothiophene-3-carboxylate (4) (398 mg, 1.0 mmol) was dissolved in anhyd THF (10 mL) and cooled to -78 °C under

an argon atmosphere. Then isopropyl magnesium bromide (1.0 mmol) in anhyd THF (5 mL) (freshly prepared from 1.0 mmol of isopropyl bromide and 1.1 mg-atom of Mg) was added over a period of 5 min. The mixture was stirred at -78 °C for 1 h and quenched with H<sub>2</sub>O (1.0 mL). It was then diluted with CHCl<sub>3</sub> (30 mL), washed with aq HCl (10%; 20 mL), H<sub>2</sub>O ( $2 \times 20$  mL), dried (MgSO<sub>4</sub>) and concentrated in vacuo to give the product as a pale yellow oil. The composition of this mixture was analyzed by <sup>1</sup>H NMR spectroscopy [9 shows its thiophene hydrogens at  $\delta = 7.46$  (d, J = 1.5 Hz) and 7.97 (d,  $J = 1.5 \text{ Hz})^4$  while **10** shows its thiophene hydrogens at  $\delta =$ 7.21 (d, J = 5.5 Hz) and 7.36 (d, J = 5.5 Hz)]. This experiment was repeated at -40 and 25 C. In the fourth experiment the equivalent of isopropylmagnesium bromide was added at -40 C and allowed to stand at -40 C for 1 h, then the reaction mixture was slowly warmed to room temperature (25 C) over a period of 1 h before quenching with H<sub>2</sub>O. The 9:10 product ratios from four experiments are shown in Table 1.

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- (13) Although octyl 2-bromothiophene-3-carboxylate and hexyl 2-bromothiophene-3-carboxylate are said to be reported in a reference,<sup>4</sup> the compounds reported are actually octyl 2bromothiophene-4-carboxylate and hexyl 2-bromothiophene-4-carboxylate since there is a typographical error in the experimental section of the paper.