Dialkyl- and Dialkoxy-functionalized Poly(thieno[3,4-b]pyrazine)s via GRIM Polymerization: Side Chain Tuning of Electronic and Optical Properties

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Abstract

Thieno[3,4-b]pyrazine homopolymers were prepared via GRIM polymerization methods and characterized to illustrate the ability to tune these materials by selection of the solubilizing side chains. All of the generated poly(thieno[3,4-b]pyrazine)s exhibited low band gaps (0.95-1.13 eV), with both the band gap and frontier orbitals dependent on the choice of side chain. The effect of side chain length on polymer molecular weight was also investigated. Analysis of the resulting polymer properties reveal clear trends in which the material’s band gap increased with the use of either longer alkyl or more electron-donating alkoxy side chains.

Keywords: Poly(thieno[3,4-b]pyrazine)s; Conjugated polymers; GRIM polymerization; Low band gap; Side chain tuning

1. Introduction

Conjugated organic polymers date back to at least the beginning of the 20th century, yet it was the discovery of their conductive nature in the early 1960s that led to more focused efforts on the synthesis and applications of these semiconducting materials (Rasmussen 2011; Rasmussen 2014). Since that time, these polymers have continued to be of significant interest due to their combination of the optical and electronic characteristics of inorganic semiconducting materials with the mechanical flexibility and processability of traditional plastics. These combined properties have made this class of materials very attractive candidates for various electronic device applications, including organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic photovoltaics (OPVs) (Roncali 1997; Rasmussen and Pomerantz, 2007; Roncali, 2007; Skotheim and Reynolds, 2007; Rasmussen et al., 2008; Perepichka and Perepichka, 2009; Rasmussen et al., 2011; Rasmussen, 2015).

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One of the most useful qualities of conjugated materials is the ability to tune their optical, electronic, and mechanical properties on a molecular level (Roncali 1997; Rasmussen et al., 2008; Rasmussen, 2015). This has been accomplished by several methods, however, one of the most readily available methods stems from the side chains used to solubilize the material. As these side chains are a near requisite part of these polymers in order to afford solution processability, it makes sense to also utilize these to alter the electronic nature of the polymer and bulk mechanical properties.

Of the various properties of conjugated organic materials that are desirable to control, the band gap \((E_g)\) is perhaps one of the most critical parameters. The band gap is defined as the energetic separation between the filled valence and empty conduction bands, and thus corresponds to the HOMO–LUMO gap of the solid state material (Roncali 1997; Rasmussen and Pomerantz, 2007; Rasmussen et al., 2008; Rasmussen et al., 2011; Rasmussen, 2015). Thus, the band gap determines various material properties such as the as lowest energy absorption or the energy of any emitted light. A lower \(E_g\) can also be beneficial for some applications as it results in enhanced thermal population of the conduction band, thus increasing the number of intrinsic charge carriers. At the same time, the lower potential of oxidation often associated with a low \(E_g\) can result in the stabilization of the corresponding oxidized or p-doped state (Roncali 1997). As a result, significant effort has been applied to developing methods for controlling the \(E_g\) of these materials with the goal of producing technologically useful low band gap \((E_g < 1.5 \text{ eV})\) and reduced band gap \((E_g = 1.5–2.0 \text{ eV})\) polymers (Rasmussen et al., 2011; Mulholland et al., 2012; Rasmussen, 2015).

A class of polymers that have shown significant promise in the development of very low \(E_g\) materials are thieno[3,4-\(b\)]pyrazine-based materials (Rasmussen et al., 2011). As illustrated in Figure 1, these materials owe their low band gap to a combination of the quinoidal character of the thieno[3,4-\(b\)]pyrazine (TP) unit, as well as its strong ambipolar nature which results in an internal intramolecular charge transfer (ICT) transition from a thiophene-localized HOMO to a more pyrazine-localized LUMO (Wen et al., 2014). As such, even pure TP homopolymeric materials exhibit properties of donor-acceptor frameworks. Although traditional TP-based materials are typically limited to TP units functionalized with alkyl or aryl side chains, recent development of new synthetic methods has allowed the production of a wide variety of TP units featuring both electron-donating and electron-withdrawing side chains (Wen et al., 2008b; Schwiderski and Rasmussen, 2013). As a result, this now provides an avenue for much more significant tuning of the resulting conjugated materials based on these important building blocks and multiple examples have now been reported illustrating the extent in which the band gap can be tuned by simple changes in the TP side chains (Wen et al., 2009; Mulholland et al., 2012; Schwiderski and Rasmussen, 2014).

The simplest TP-based materials are the homopolymeric poly(thieno[3,4-\(b\)]pyrazine)s, which also exhibit the lowest band gaps of this class of materials, with \(E_g\) values as low as 0.7 eV (Rasmussen et al, 2011). To date, these homopolymers have been produced via chemical oxidative polymerization (Pomerantz et al., 1992; Pomerantz et al., 1993; Kenning and Rasmussen, 2003; Wen et al, 2008a), electropolymerization (Kenning and Rasmussen, 2003; Wen et al., 2009), and Grignard metathesis (GRIM) polymerization (Wen et al., 2008a; Willot et al., 2014). Of these methods, however, only GRIM polymerization results in materials which are both processible and free of significant defects. As GRIM polymerization has previously been applied to only two alkyl TP derivatives, this current study presents the expansion of these methods to the polymerization of a series of various alkyl and alkoxy side chains, with a focus on the side chain effects on the resulting polymer properties.
2. Experimental

2.1 General

Unless noted, all materials were reagent grade and used without further purification. Chromatographic separations were performed using standard column chromatography methods with silica gel (230-400 mesh). Dry DMF was obtained by mixing with MgSO₄, followed by flushing through silica gel, purging over nitrogen for 1 h, and storing under molecular sieves. Dry THF was obtained via distillation over sodium/benzophenone. All glassware was oven-dried, assembled hot, and cooled under a dry nitrogen stream before use. Transfer of liquids was carried out using standard syringe techniques and all reactions were performed under a dry nitrogen stream. The ¹H NMR and ¹³C NMR were completed on a 400 MHz spectrometer. All NMR data was referenced to the CHCl₃ signal and peak multiplicity was reported as follows: s = singlet d = double, t = triplet, q = quartet, p = pentet, m = multiplet, and br = broad. Melting points were determined using a digital thermal couple with a 0.1 °C resolution. Polymer molecular weights were determined by gel permeation chromatography in reference to polystyrene standards. Samples were prepared in THF (1 mg/mL) and passed through a 0.45 µm filter prior to injection. 2,3-Dibromothieno[3,4-b]pyrazine, 2,3-didecylthieno[3,4-b]pyrazine (1b) and 2,3-didodecylthieno[3,4-b]pyrazine (1c), were synthesized according to previously reported literature procedures (Kenning et al., 2002; Wen et al., 2008b). Samples of poly(2,3-dihexylthieno[3,4-b]pyrazine) (3a) were prepared via GRIM polymerization from 5,7-dibromo-2,3-dihexylthieno[3,4-b]pyrazine (2a) as previously reported (Wen et al., 2008a).

2.2 UV-vis-NIR Absorption Spectroscopy

All absorption spectroscopy was performed on a Carry 500 dual-beam UV-vis-NIR spectrophotometer. Solution-state spectra were measured from samples prepared as dilute CH₃Cl solutions in quartz cuvettes. Solid-state spectra were measured from non-annealed, spin-coated polymer thin films on glass slides. Optical band gaps (Eₚ) were determined from the onset of the lowest energy absorption by extrapolation of the steepest slope to the intersection with the absorption baseline.

2.3 Electrochemistry

All electrochemical methods were performed using a three-electrode cell consisting of a Pt disc working electrode, Pt coil auxiliary electrode, and a Ag/Ag⁺ reference electrode (0.1 M AgNO₃ and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in CH₃CN; 0.251 V vs. SCE). Supporting electrolyte consisted of 0.10 M TBAPF₆ in CH₃CN distilled over CaH₂ under dry nitrogen. Solutions
were deoxygenated with Ar prior to each scan and blanketed with Ar during the experiments. Solutions of polymers in CHCl₃ were drop cast on the working electrode and dried to form a solid film. Measurements were collected at a scan rate of 100 mV/s. E_HOMO values were estimated from the onset of oxidation in relation to ferrocene (50 mV vs. Ag/Ag⁺), using the value of 5.1 eV vs. vacuum (Cardona et al., 2011). E_LUMO was determined from the difference of E_HOMO and E_g.

2.4 Synthesis of 2,3-bis(ethyloxy)thieno[3,4-b]pyrazine (1d).

Monomer 1d was synthesized via a modification of previously reported methods (Wen et al., 2008b). Hexanes (20 mL) was added to a flask containing 60% NaH dispersion in mineral oil (0.50 g, 12.5 mmol) and stirred for 20 min under nitrogen. The liquid was then removed via syringing and the NaH was dried via evacuation. The flask was again filled with nitrogen, followed by dry DMF (40 mL). Absolute ethanol (0.35 mL, 6.0 mmol) was then added via syringe and the solution stirred for 5 min. 2,3-Dibromothieno[3,4-b]pyrazine (0.60 g, 2.0 mmol) was added and the reaction stirred for 3 h. Aqueous NH₄Cl was then added and the mixture extracted with CH₂Cl₂. The combined organic layers were dried with MgSO₄ and solvent was removed via rotary evaporation. Further purification occurred via column chromatography using hexanes:ethyl acetate (95:5) to give a white powder (>95% yield), mp 123.1-124.4 °C. ¹H NMR: δ 7.31 (s, 2H), 4.45 (q, J = 7.2 Hz, 4H), 1.41 (t, J = 7.2 Hz, 6H); ¹³C NMR: δ 150.1, 140.1, 117.3, 65.3, 14.1.

2.5 Synthesis of 2,3-bis(hexyloxy)thieno[3,4-b]pyrazine (1e)

Monomer 1e was prepared as 1d above, substituting ethanol with 1-hexanol. The product was purified via column chromatography first using hexanes to remove excess 1-hexanol, followed by hexanes:ethyl acetate (95:5) to give a white powder (>95% yield), mp 69.9-71.1 °C. ¹H NMR: δ 7.33 (s, 2H), 4.38 (t, J = 6.8 Hz, 4H), 1.81 (p, J = 8.8 Hz, 4H), 1.45 (p, J = 7.2 Hz, 4H), 1.35-1.30 (m, 8H), 0.85 (t, J = 7.4 Hz, 6H); ¹³C NMR: δ 150.2, 138.3, 112.4, 67.2, 31.6, 28.6, 25.8, 22.7, 14.1.

2.6 Synthesis of 5,7-dibromo-2,3-didecylthieno[3,4-b]pyrazine (2b).

Monomer 1a (2.07 g, 5.0 mmol) was added to a 100 mL flask, which was then evacuated and placed under a dry nitrogen stream. Dry DMF (50 mL) was then added via syringe and the resulting solution cooled to -78 °C (dry ice/acetone). A solution of NBS (2.22 g, 12.5 mmol) in DMF (10 mL) was then added dropwise, after which the mixture was warmed to -15 °C (ice/salt bath) and stirred for 3 h. The mixture was then poured into 100 mL of ice, stirred for 10 min, and the resulting precipitate collected by filtration. The product was then dissolved in diethyl ether, and washed with NH₄Cl, H₂O, and brine. The organic layer was then dried with MgSO₄ and concentrated via rotary evaporation. Further purification was performed via silica gel chromatography in hexanes:Et₂O (97:3) to give a yellow solid (63% yield), mp 45.0-46.2 °C; ¹H NMR: δ 2.89 (t, J = 7.6 Hz, 4H), 1.79 (p, J = 8.0 Hz, 4H), 1.46-1.19 (m, 31H), 0.87 (q, J = 6.8 Hz, 6H). ¹³C NMR: δ 158.4, 139.9, 103.5, 35.6, 32.1, 29.8, 29.8, 29.7, 29.5, 29.3, 28.2, 22.9, 14.3.

2.7 Synthesis of 5,7-dibromo-2,3-didecylthieno[3,4-b]pyrazine (2c).

Monomer 2c was produced as a yellow solid in the same manner as 2b above, substituting 1b with 1c (67% yield), mp 45.2 - 46.4 °C; ¹H NMR: δ 2.29 (t, J = 7.6 Hz, 2H), 1.77 (p, J = 7.6 Hz, 2H), 1.34 (m,
18H), 0.87 (t, J = 6.8 Hz 6H). $^{13}$C NMR: δ 156.6, 141.9, 116.0, 35.9, 32.1, 31.1, 30.0, 29.8, 29.7, 21.6, 29.5, 29.2, 28.5, 22.9, 14.3.

2.8 Synthesis of 5,7-dibromo-2,3-bis(ethyloxy)thieno[3,4-b]pyrazine (2d).

Monomer 2d was produced as a yellow solid in the same manner as 2b above, substituting 1b with 1d (65% yield). mp 61.2-62.0 °C; $^1$H NMR: δ 4.64 (q, J = 6.8, 4H), 1.47 (t, J = 7.2, 6H). $^{13}$C NMR: δ 184.8, 153.9, 142.7, 65.6, 14.2.

2.9 Synthesis of 5,7-dibromo-2,3-bis(hexyloxy)thieno[3,4-b]pyrazine (2e).

Monomer 2e was produced as a yellow solid in the same manner as 2b above, substituting 1b with 1e (67% yield). mp 45.2 - 46.4 °C; $^1$H NMR: δ 4.48 (t, J = 6.8 Hz, 4H), 1.86 (t, J = 6.8 Hz, 4H), 1.38 (m, 14H), 0.89 (t, J = 2.4 Hz, 6H); $^{13}$C NMR: δ 151.1, 136.3, 98.8, 67.9, 31.6, 28.5, 25.8, 22.7, 14.1.

2.10 Synthesis of poly(2,3-didecylthieno[3,4-b]pyrazine) (3b).

Polymer 3b was produced via GRIM polymerization through a modification of previously reported methods (Wen et al., 2008b). Dibromide 2b (0.54 g, 1.0 mmol) was added to a 25 mL flask, which was evacuated and placed under a dry nitrogen stream. THF (10 mL) was then added via syringe to produce a homogeneous solution. MeMgCl (0.34 mL, 3.0 M solution in THF, 1.0 mmol,) was then added via syringe and the mixture heated to reflux for 1 h, after which Ni(dppp)Cl$_2$ (0.003 g, 5.5 x 10$^{-3}$ mmol) was added. The reaction was then heated for another hour, poured into methanol (100 mL) and stirred for an additional 2 h. The resulting precipitate was collected and purified by Soxhlet extraction with methanol, acetone, and hexanes. The soluble fraction was then isolated by extraction with CHCl$_3$, which was then concentrated via rotary evaporation to give a purple-black solid (55% yield). $^1$H NMR: δ 2.90, 2.12, 1.26, 0.89; GPC: $M_w$ = 3500, $M_n$ = 2500, PDI = 1.4.

2.11 Poly(2,3-didodecylthieno[3,4-b]pyrazine) (3c).

Polymer 3c was produced in the same manner as 3b above, substituting 2b with 2c. The CHCl$_3$ soluble fraction of the polymer was concentrated via rotary evaporation to give a purple-black solid (56% yield). $^1$H NMR: δ 1.54, 1.41, 0.84; GPC: $M_w$ = 5300, $M_n$ = 3300, PDI = 1.6.

2.12 Poly(2,3-bis(ethyloxy)thieno[3,4-b]pyrazine) (3d).

Dibromide 2d (0.35 g, 1.0 mmol) was added to a 25 mL flask, which was evacuated and placed under a dry nitrogen stream. THF (10 mL) was then added via syringe to produce a homogeneous solution. MeMgCl (0.46 mL, 3.0 M solution in THF, 1.5 mmol,) was then added via syringe and the mixture heated to reflux for 1 h, after which Ni(dppp)Cl$_2$ (0.003 g, 5.5 x 10$^{-3}$ mmol) was added. The reaction was then heated for another hour, poured into methanol (100 mL) and stirred for an additional 2 h. The resulting precipitate was collected and purified by Soxhlet extraction with methanol, acetone, and hexanes. The soluble fraction was then isolated by extraction with CHCl$_3$, which was then concentrated via rotary evaporation to give a purple-black solid (61% yield). $^1$H NMR: δ 4.71, 1.48; GPC: $M_w$ = 1200, $M_n$ = 920, PDI = 1.3.
2.13 Poly(2,3-bis(hexyloxy)thieno[3,4-b]pyrazine) (3e).

Polymer 3e was produced in the same manner as 3d above, substituting 2d with 2e. The CHCl₃ soluble fraction of the polymer was concentrated via rotary evaporation to yield a blue-black solid (62% yield). ¹H NMR: δ 4.70, 1.89, 1.45, 0.89; GPC: Mₙ = 4900, Mₚ = 4100, PDI = 1.2.

3. Results and Discussion

3.1 Synthesis.

The production of the poly(thieno[3,4-b]pyrazines) 3a-e via GRIM polymerization was performed as outlined in Figure 2. Monomeric TPs were first converted to the corresponding dibromides 2a-e in moderate to good yield by treatment with N-bromosuccinimide (NBS) in DMF. Compounds 2a-e were converted to the corresponding homopolymers via modifications of the GRIM polymerization methods established by McCullough and coworkers (Loewe et al., 1999; Loewe et al., 2001; Iovu et al., 2005; Sheina et al., 2005, Jeffries-El and McCullough, 2007). In the systems reported here, this entailed reacting 2a-e with methylmagnesium chloride (MeMgCl) to produce the corresponding TP Grignard intermediate via Grignard metathesis, followed by addition of a nickel catalyst to allow polymerization via Kumada cross-coupling. The final cross-coupling step was performed at high temperature, as previous studies in the production of 3a were found to give higher yields and a larger soluble fraction when the polymerization was carried out via reflux conditions, rather than alternate room temperature conditions (Wen et al., 2008a).

![Fig. 2. GRIM Polymerization of thieno[3,4-b]pyrazines.](image)

The initial focus of this study was to determine the effect of increasing the length of alkyl side chains on molecular weight, with the idea that increased side chain length might improve the solubility of the material formed during polymerization, thus allowing further chain growth. Higher molecular weights would improve the film forming properties of the materials, an important aspect for the application of these materials in technological devices. In addition, higher molecular weights would also correspond to higher degrees of polymerization (i.e. n), which can result in higher conjugation lengths, improved electronic properties, and lower band gaps (Rasmussen, 2015). While the yields of the decyl and dodecyl analogues (3b and 3c, respectively) were quite comparable to the previously reported values of the hexyl derivative 3a (Wen et al., 2008a), it was found that Mₚ was significantly reduced for both 3b and 3c (Table 1). In the case of 3a, it has been concluded that the molecular weight is a limit of solubility and is consistent with the Mₚ values of soluble fractions of 3a produced via other methods (Wen et al., 2008a). While the hope was that increasing the alkyl chain length would increase the polymer solubility, the results here point to the opposite effect, with the polymer precipitating out of solution at an earlier point of the polymerization process.
Due to the high density of side chains on the poly(thieno[3,4-b]pyrazine) backbone, it is believed that the reduced solubility with the longer side chains is the result of side chain crystallization (Ho et al., 1993; Zheng et al., 1994; Park and Levon, 1997). Thus, as the side chains become longer, the Van der Waals forces between side chains increase, leading to stronger alkyl-alkyl interactions between the closely packed side chains. Providing that these interactions are strong enough, the alkyl-alkyl interactions could be favored over the alkyl-solvent interactions that normally lead to solubility. Side chain crystallization has been previously observed in poly(3-alkylthiophene)s with decyl or larger side chains (Ho et al., 1993). As this is the same length of side chains in 3b and 3c, but with twice the side chain density, the likelihood of this competing factor here is quite reasonable. It should be pointed out, however, that a separate study concerning the production of 3c via GRIM methods has very recently been reported (Willot et al., 2014), in which it is claimed that the molecular weight is not governed by solubility, but via a termination step involving the dissociation of the catalyst from the growing polymer chain. Of course, this conclusion does not provide an adequate explanation for why such a proposed termination step would be a greater problem for the production of 3c over 3a, both of which should have nearly identical reactivity. The molecular weights given in this independent study are in close agreement with the values reported in Table 1.

### Table 1 Comparison of reaction yields and molecular weights.

<table>
<thead>
<tr>
<th>Material</th>
<th>R</th>
<th>Yield (%)</th>
<th>$M_n$</th>
<th>PDI</th>
<th>$n$ (average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>C$<em>6$H$</em>{13}$</td>
<td>55</td>
<td>4900</td>
<td>1.5</td>
<td>16</td>
</tr>
<tr>
<td>3b</td>
<td>C$<em>{10}$H$</em>{21}$</td>
<td>55</td>
<td>2500</td>
<td>1.4</td>
<td>6</td>
</tr>
<tr>
<td>3c</td>
<td>C$<em>{12}$H$</em>{25}$</td>
<td>56</td>
<td>3300</td>
<td>1.6</td>
<td>7</td>
</tr>
<tr>
<td>3d</td>
<td>OC$_2$H$_5$</td>
<td>61</td>
<td>920</td>
<td>1.3</td>
<td>4</td>
</tr>
<tr>
<td>3e</td>
<td>OC$<em>6$H$</em>{13}$</td>
<td>62</td>
<td>4100</td>
<td>1.2</td>
<td>12</td>
</tr>
</tbody>
</table>

- $a$ Reported yield of the soluble polymer fraction is based on the isolated mass in relation to the theoretical yield determined from the polymer repeat unit.
- $b$ Number average molecular weight ($M_n$) and polydispersity index (PDI) were determined by gel permeation chromatography in comparison to polystyrene standards.
- $c$ Average degree of polymerization ($n$) was determined by dividing the $M_n$ of the polymer by the molecular mass of its repeat unit.

During the initial investigation of the alkoxy derivatives, it was noted that after the addition of one equivalent of MeMgCl, the reaction to produce the Grignard intermediate did not go to completion and some starting material remained. It was found, however, that the addition of another 0.5 equivalent of MeMgCl successfully converted the remaining starting material to the desired Grignard intermediate, which then underwent successful polymerization in a similar manner to the previous alkyl analogues. It is believed that the observed reactivity is due to the fact that the dialkoxy functionalization of 2d and 2e allows chelation of a portion of the added MeMgCl (Figure 3) which limits its use in producing the desired Grignard intermediate. The fact that full conversion to the Grignard intermediate only requires a total of 1.5 equivalents of MeMgCl, rather than a full two equivalents, suggests that any chelated magnesium is in equilibrium with free MeMgCl, as outlined in Figure 3.
Once the issue with successful formation of the Grignard intermediate was solved, polymerization proceeded smoothly and the resulting yields for polymers 3d and 3e were slightly higher than those of the previously discussed alkyl analogues (Table 1). In terms of molecular weights, polymer 3d is quite low and essentially corresponds to oligomeric species, rather than anything that can be considered polymeric. The low molecular weight here is not overly surprising considering the short length of the alkoxy side chain. It is well known that in order to provide sufficient solubility in conjugated polymers, side chains of butyl or longer are required. As the ethoxy side chain is equivalent in length to a propyl side chain, its inability to contribute sufficient solubility is consistent with previous reports. The hexyloxy derivative 3e, however, was much more successful and produced materials with $M_n$ values comparable to the hexyl derivative 3a, thus allowing the desired comparison of the side chain electronics on the resulting properties of the polymers.

### 3.2 UV-vis-NIR Absorbance Spectroscopy

The polymeric samples 3a-c and 3e were analyzed via UV-vis-NIR spectroscopy and the collected absorbance is given in Table 2. In all cases, a red shift in absorbance is observed from solution to the solid state, as typical of the majority of conjugated polymers. This red shift is typically attributed to an intrachain coil-to-rod conformational change, as well as increased π-stacking, both of which result in extended delocalization (Rasmussen et al., 1998). Comparing the thin film spectra of the three alkyl derivatives (3a-c, Figure 4), all three materials exhibit a low energy transition assigned to an ICT transition from a HOMO delocalized along the conjugated backbone to a pyrazine-localized LUMO (Wen et al., 2014). While the two lower molecular weight samples do exhibit some low-energy tailing, the majority of the low energy onset is slightly blue-shifted in comparison to 3a. In addition, both 3b and 3c exhibit reduced absorbance at higher energy, resulting in a more narrow spectral profile. Both characteristics would be consistent with reduced delocalization as a result of a molecular weight dependent conjugation limit. As the maximum effective conjugation length of typical polythiophenes is thought to be ~20-30 rings (Rasmussen 2015), size dependent properties would be expected for the current materials as the molecular weights determined above all suggest chain lengths below that limit. As a result of the blue shift in absorbance onset for 3b and 3c, these materials also exhibit a slightly higher band gap in comparison to 3a.
Table 2 Visible-NIR absorbance data.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>R</th>
<th>$\lambda_{max}$ (nm, CHCl$_3$)$^a$</th>
<th>$\lambda_{max}$ (nm, film)$^{ab}$</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>C$<em>6$H$</em>{13}$</td>
<td>(885), 970</td>
<td>890, (1050)</td>
<td>0.95</td>
</tr>
<tr>
<td>3b</td>
<td>C$<em>{10}$H$</em>{21}$</td>
<td>851, (972)</td>
<td>(926), 1027</td>
<td>1.03</td>
</tr>
<tr>
<td>3c</td>
<td>C$<em>{12}$H$</em>{25}$</td>
<td>850, (974)</td>
<td>(952), 1050</td>
<td>1.03</td>
</tr>
<tr>
<td>3e</td>
<td>O$<em>6$C$</em>{6}$H$_{13}$</td>
<td>899</td>
<td>925</td>
<td>1.13</td>
</tr>
</tbody>
</table>

$^a$ Values in parentheses denote prominent shoulders. $^b$ Unannealed films.

Fig. 4. Solid-state absorption spectra of poly(2,3-dialkylthieno[3,4-b]pyrazine)s (3a-c) and poly(2,3-dihexyloxythieno[3,4-b]pyrazine) (3e).

As shown in Figure 4, the incorporation of alkoxy side chains resulted in a fairly significant blue shift in the thin film absorbance of 3e in comparison to the alkyl analogue 3a, resulting in an increase of the $E_g$ by nearly 0.2 eV. This shift in absorbance is in good agreement with the side chain effects observed in monomeric TPs (Wen et al., 2008b), as well as other TP-based conjugated polymers (Wen et al., 2009; Mulholland et al., 2012; Schwiderski and Rasmussen, 2014). In all cases, the basis of this tuning is due to a greater electronic effect on the material LUMO in comparison to the HOMO. In the case of the alkoxy functionalities of 3e, the electron-donating nature of the alkoxy groups destabilizes both the HOMO and LUMO, but affects the LUMO to a greater extent, thus resulting in an increase in the energetic separation.

3.3 Electrochemistry.

The polymeric samples 3a-c and 3e were also analyzed via cyclic voltammetry (CV) in order to determine the relative energies of the material's frontier orbitals. The collected electrochemical data is given in Table 3. For the three alkyl derivatives, both 3b and 3c undergo oxidation at higher potentials than 3a, with shifts of approximately 250-500 mV. As increasing conjugation lengths result in destabilization of the HOMO and thus lower potentials of oxidation, the shifts in the potentials of oxidation for 3b and 3c are consistent with the lower molecular weights determined above. Related influence on the LUMO energies are minimized, as this frontier orbital is more localized on the pyrazine rings and thus less affected by the extent of conjugation.
Table 3 Electrochemical data.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>R</th>
<th>Oxidation, E_{pa} (V)^a</th>
<th>E_{HOMO} (eV)^b</th>
<th>E_{LUMO} (eV)^c</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>C_6H_{13}</td>
<td>0.65</td>
<td>-5.1</td>
<td>-4.2</td>
</tr>
<tr>
<td>3b</td>
<td>C_{10}H_{21}</td>
<td>0.91</td>
<td>-5.3</td>
<td>-4.3</td>
</tr>
<tr>
<td>3c</td>
<td>C_{12}H_{25}</td>
<td>1.17</td>
<td>-5.4</td>
<td>-4.4</td>
</tr>
<tr>
<td>3e</td>
<td>OC_6H_{13}</td>
<td>0.61</td>
<td>-5.0</td>
<td>-3.9</td>
</tr>
</tbody>
</table>

^a Potentials vs Ag/Ag^+ in 0.1 M TBAPF_6 in MeCN. ^b E_{HOMO} = -(E_{onset,ox} \text{vs. Fc+/Fc}) + 5.1(eV). ^c E_{LUMO} = E_{HOMO} - E_g.

Comparing the dialkyl analogue 3a with the corresponding dialkoxy analogue 3e shows that the electron-donating nature of the alkoxy group contributes to further destabilization of the HOMO and thus undergoes oxidation at even lower potential. The effect on the pyrazine-localized LUMO, however, is significantly greater, as the functional groups are directly connected to the pyrazine ring of the TP monomer. Thus, the change from alkyl to alkoxy side chains results in a destabilization of the LUMO energy by 0.3 eV. This shift is again in good agreement with the side chain effects observed in monomeric TPs (Wen et al., 2008b), as well as other TP-based conjugated polymers (Wen et al., 2009; Mulholland et al., 2012; Schwiderski and Rasmussen, 2014).

4. Conclusions

The application of GRIM polymerization to a series of thieno[3,4-b]pyrazines successfully produced low band gap polymers with E_g values of 0.95-1.13 eV. Although attempts to increase solubility via longer alkyl side chains instead decreased solubility and thus the molecular weights of the resulting materials, it was found that GRIM polymerization could be successfully applied to the production of poly(2,3-dialkoxythieno[3,4-b]pyrazine)s with only slight modifications of the experimental conditions. Lastly, comparison of analogous poly(thieno[3,4-b]pyrazine)s containing alkyl vs. alkoxy side chains illustrated the ability to modulate the band gap and frontier orbitals of these low band gap materials via simple molecular tuning.

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