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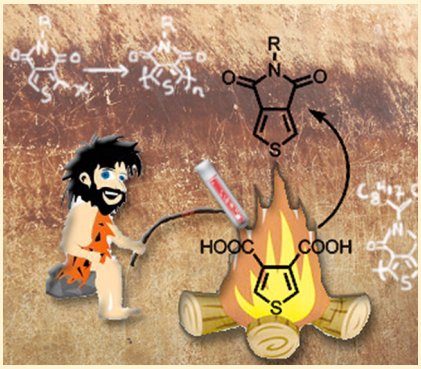
# Low-Cost Synthesis and Physical Characterization of Thieno[3,4-*c*]pyrrole-4,6-dione-Based Polymers

Philippe Berrouard, Stéphane Dufresne, Agnieszka Pron, Justine Veilleux, and Mario Leclerc*

Canada Research Chair on Electroactive and Photoactive Polymers, Département de Chimie, Université Laval, Québec City, Québec, Canada G1V 0A6

Supporting Information

**ABSTRACT:** The improved synthesis of thieno[3,4-*c*]pyrrole-4,6-dione (TPD) monomers, including Gewald thiophene ring formation, a Sandmeyer-type reaction, and neat condensation with an amine, is presented. This protocol enables faster, cheaper, and more efficient preparation of TPD units in comparison to traditional methods. Furthermore, a series of TPD homo- and pseudohomopolymers bearing various alkyl chains was synthesized via a direct heteroarylation polymerization (DHAP) procedure. UV−visible absorption and powder X-ray diffraction measurements revealed the relationship between the ratio of branched to linear alkyl chains and the optoelectronic properties of the polymers as well as their packing in the solid state.




## INTRODUCTION

Polymer-based organic photovoltaics (OPV) have received enormous attention over the past decade as an alternative source of energy.[1−6] In particular, thieno[3,4-*c*]pyrrole-4,6-dione (TPD) emerged as a very promising unit.[7−10] This building block combines rigidity and good solubility as well as a favorable 3D arrangement in the solid state. TPD-based materials have a relatively low energy band gap which is caused by the stabilization energy via formation of a quinoidal thiophene-maleimide structure in their excited state.[11]

Up to now, most of the research on TPD-based materials have concentrated on push−pull type copolymers.[12−15] Indeed, TPD homopolymers are very rare in the literature.[16−19] The first example was reported by Pomerantz et al.[17] in 2003. Another example of a TPD homopolymer with a molecular weight of 2−3 kDa prepared by Ullmann coupling was reported by Bjørnholm et al.[18] Recently, Facchetti et al.[16] synthesized a homopolymer with an *n*-dodecyl alkyl chain by Yamamoto polymerization. Although this approach is known to result in higher molecular weight polymers in comparison to Ullmann coupling, a $M_n$ value of only 4.7 kDa was reported, which is in good agreement with values reported by Bjørnholm. One can notice that all of the previously synthesized TPD homopolymers contained linear alkyl chains (*n*-$C_6H_{13}$, *n*-$C_8H_{17}$, *n*-$C_{12}H_{25}$), which most likely limit the solubility of the materials in comparison to branched chains. Recently, we prepared a TPD homopolymer bearing 2-octyldodecyl and 2-hexyldecyl side chains by the direct heteroarylation polymerization (DHAP) method.[19] These large and branched alkyl chains allowed a better solubility of the material during polymerization reactions. As a result, higher $M_n$ values were achieved (23 kDa) in comparison to previous data. Additionally, we noticed a great difference in the optical properties as well as solid-state packing between homopolymers bearing straight and branched alkyl substituents.

In order to shed more light on the optical and electrochemical properties of TPD polymers, we synthesized a series of homopolymers and pseudohomopolymers using the DHAP approach. This method proved to be very effective for the synthesis of TPD-based conjugated polymers.[20,21] It allowed the preparation of pseudohomopolymers consisting of a TPD backbone, with alternating linear and branched alkyl chains, which would be extremely difficult to synthesize using conventional synthetic methods. Furthermore, the synthesis of TPD monomers was redesigned to yield these units in a cheaper and more efficient way. It is important to remember here that, in principle, one of the major advantages of semiconductor plastic materials over standard inorganic materials is their potentially lower production cost. From this perspective, it is important to prepare low-cost monomers and polymers.

## RESULTS AND DISCUSSION

**Monomer Synthesis.** The most common pathway toward TPD units, shown in Scheme 1a, involves formation of thiophene anhydride from the corresponding 3,4-thiophenedicarboxylic acid (**1**) followed by a condensation with an amine.[22] This methodology possesses two drawbacks: (i) although 3,4-thiophenedicarboxylic acid is commercially available, it is a relatively expensive starting material[23] and (ii) the condensation reaction proceeds with moderate yield. The lower than

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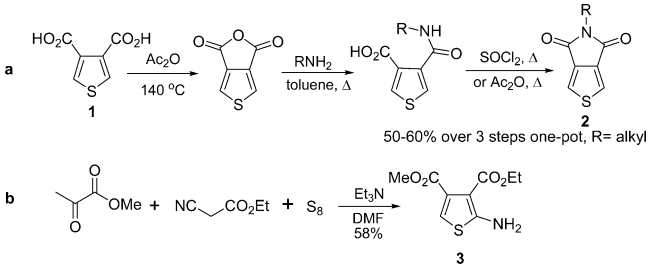
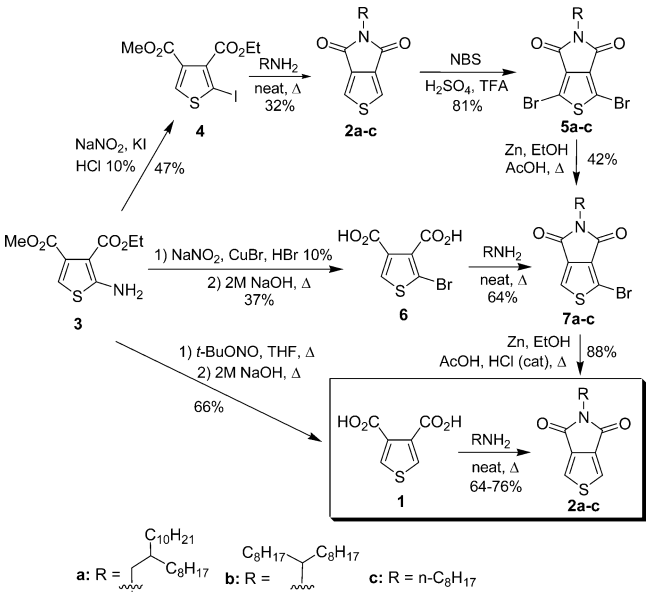
**Scheme 1. (a) Published Procedure for TPD and (b) Example of Gewald Reaction**




expected yield can be attributed to the harsh conditions required ($SOCl_2$ and/or high temperature),[24] which cause decomposition of the product during the reaction. To overcome these problems, our research focused on developing a new synthetic pathway for TPD monomers, which would enable us to prepare the desired compounds in a simpler, less expensive, and more efficient way.

In this regard, the Gewald reaction (Scheme 1b) has recently gained a great deal of attention as a cheap and efficient method for the preparation of the functionalized aminothiophenes **3**.[25−27] In our previous studies, we showed that it is possible to convert aminothiophene into the iodothiophene derivative via a standard Sandmeyer reaction.[28] As shown in Scheme 2, by

**Scheme 2. Synthesis of TPD Units**




modifying the Sandmeyer protocol, we were able to achieve monoiodo (**4**), monobromo (**6**), and unsubstituted (**1**) thiophene-3,4-dicarboxylic acids/esters in moderate to good yields. It is worth mentioning that deamination of **3** required the utilization of *t*-BuONO in refluxing THF to achieve, after hydrolysis, **1** in 66% yield.[29,30] All attempts to carry out this transformation in aqueous media failed. Additionally, we discovered that neat condensation between alkylamine and thiophenedicarboxylic acids/esters (**4**, **6**, **1**) at temperatures above 200 °C results in the formation of TPD derivatives **2** and **7** as major products. Only 1 equiv of alkylamine was necessary to perform this reaction. Simple filtration through a pad of silica gave the desired products. Interestingly, in contrast to the bromo derivative **6**, during the condensation of **4**, iodine elimination occurred, leading directly to **2**. The mechanism of this reaction is under investigation. By using our protocol (Scheme 2), we were able to synthesize TPD units bearing various alkyl chains, both linear and branched ones. Yields of 64−76% were achieved for condensation of linear (*n*-octyl) and C2-branched (2-octyl-1-dodecyl) alkylamines with **1**. When C1-branched alkyl amines (heptadecan-9-amine) were used, slightly lower yields were obtained, most probably due to steric hindrance. Our new methodology, which involves (i) the Gewald formation of thiophene, (ii) the Sandmeyer-type reaction, and (iii) condensation with neat amine, enabled us to prepare TPD units in a much faster, cheaper, and more efficient way. The need for harsh conditions and toxic reagents such as thionyl chloride was eliminated. Our new methodology is a substantial improvement of the synthesis of TPD. We believe that it will ensure wide use of TPD monomers.

**Polymer Synthesis.** Taking advantage of the recent expertise in DHAP,[31,32] which allowed synthesis of well-defined conjugated polymers without the need for organometallic reagents, we prepared a series of homo and pseudohomo TPD-based polymers. As described in our previous work, polymer **P1** can be prepared from the iodo-TPD derivative **8**. As shown in Scheme 3, we were able to prepare the same polymer from the bromo derivative **7a**. Reactions with aryl bromides are more versatile than those with aryl iodides. Literature results show that iodine can potentially poison the catalyst.[33,34] Thus, by using bromine instead of iodide derivatives, we eliminated the need to use stoichiometric amounts of silver acetate. The polymerization of **7a** resulted in polymer **P1*** with similar $M_n$ values and comparable yield to the previously prepared polymer **P1**.

As shown in Scheme 3, we prepared various TPD homopolymers bearing long and branched alkyl chains to ensure good solubility. All polymers were synthesized using Herrmann's palladium[35] and tris(*o*-methoxyphenyl)phosphine as a catalytic system and potassium acetate as a base. The polymerization reaction was carried out in THF at 120 °C. Purification involved Soxhlet extractions with acetone, hexane, and chloroform, followed by precipitation from methanol. Alkyl chains branched both on C2 (**P1** and **P1***) and C1 (**P2** and **P2***) were incorporated into polymers for comparison studies. Polymers **P1** and **P2** are readily soluble in common organic solvents: i.e., chloroform and toluene. Much higher molecular weights (21−25 kDa) were obtained for **P1** and **P2** in comparison to polymers with straight-chain alkyl substituents ($M_n$ up to 4.7 kDa).[16−19] Our results clearly indicate that branched alkyl chains are necessary to obtain high-molecular-weight and processable polymers.

The main difficulties in the preparation of polymers suitable for organic electronics lie in balancing solubility in common organic solvents and good packing in the solid state. Thus, in order to better understand the structure−property and structure−packing relationships of the TPD homopolymer series, we designed and synthesized pseudohomo polymers **P3**−**P6**. Our approach was based on the idea of using branched chains to ensure processability and straight chains to sustain good packing in the solid state. As shown in Scheme 3, we synthesized a series of pseudohomopolymers with various ratios of branched vs linear chains. Polymers **P3** and **P4**, with a 1/1 ratio, were prepared by copolymerization of dibromo and unsubstituted TPDs **2b**/**2a** and **5c**, respectively. This approach ensured an alternating structure of the polymers. It should be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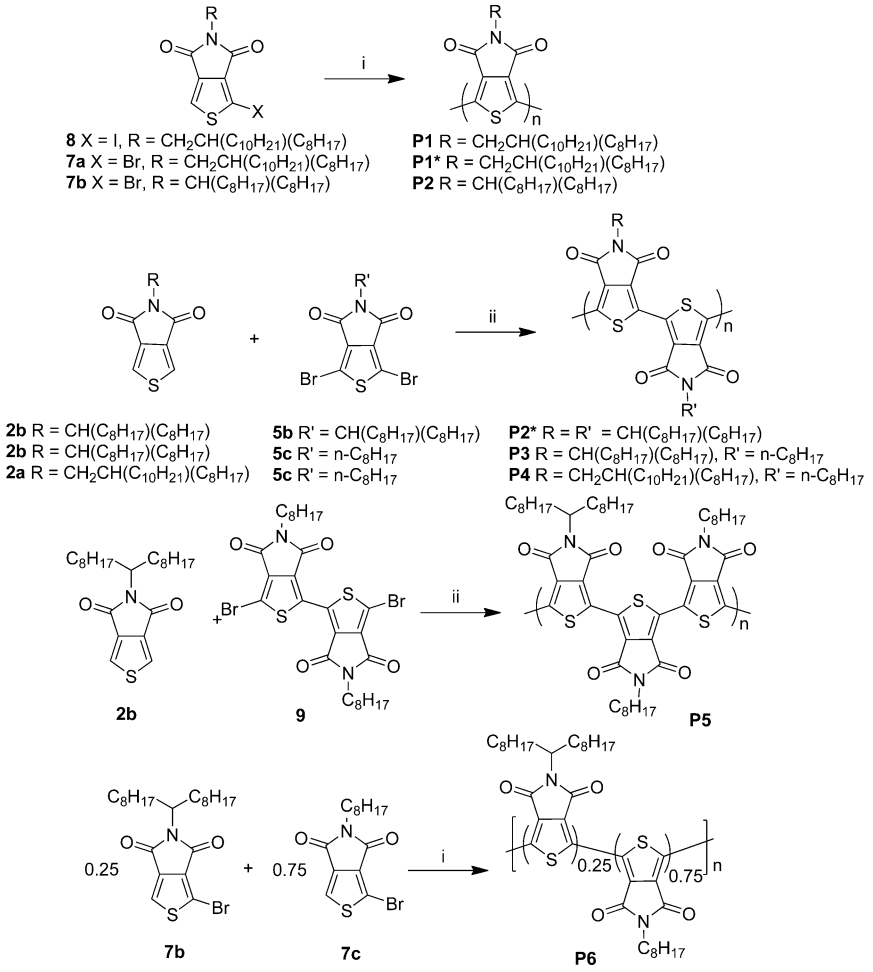
**Scheme 3. Polymer Synthesis**[a]




[a]Conditions: (i) 2% Herrmann's Pd, 8% tris(*o*-methoxyphenyl)phosphine, 1 equiv of KOAc, THF [0.25 M]; (ii) the same as for (i) except 2 equiv of KOAc.

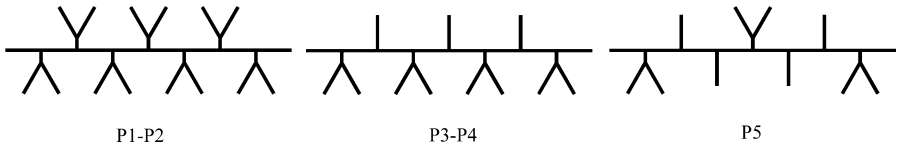



**Figure 1.** Schematic representation of chains orientation in TPD homopolymers.

noted that the crystal structure of TPD dimers indicated interactions between the carbonyl of the pyrroledione moiety and the sulfur of the thiophene unit.[28] As a result, two neighboring TPD units adopt an anticoplanar conformation (Figure 1). Reaction of dibromo-TPD dimer **9** bearing straight octyl chains and **2b** resulted in polymer **P5** with a 2/1 ratio of straight to branched alkyl chains. As shown in Figure 1, in the case of **P3** and **P4**, branched alkyl chains are on the same side of the polymer backbone, whereas in the case of **P5** they are oriented in opposite directions. Additionally, the reaction of monobrominated **7c** and **7b** resulted in the random polymer **P6** with a 3/1 ratio. The design limited the number of branched alkyl chains which can potentially induce twisting of the backbone. Regioregular polymers **P3**–**P5** demonstrate well the advantages of the DHAP method. Due to the difficulties in preparation of organometallic derivatives of TPD, it was not possible for us to synthesize these polymers via classical cross-coupling polymerization procedures.

**Properties of the Synthesized Polymers.** Polymers **P1**–**P6** exhibit very good thermal stability. TGA analysis revealed $T_{dec}$ > 380 °C (Table 1). DSC analysis showed no glass transitions between 50 and 350 °C. These results can be explained by the rigid-rod nature of the conjugated backbones.

In order to gain information about the solid-state organization of polymers, powder X-ray diffraction analyses were performed (Figure 2). Bjørnholm et al. reported that TPD homopolymers do not spontaneously crystallize and are mostly amorphous.[18] Peaks at low angle (27.8 Å) as well as at $2\theta$ = 19.4° (4.6 Å) were recorded for their polymers. The earlier peak corresponds to the lamellar repeating distance between the polymer chains, whereas the later peak can be attributed to the distance between alkyl chains and/or $\pi$-stacking. Polymers **P1**, **P2**, and **P6** show no peaks corresponding to $\pi$-stacking.


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**Table 1. Physical and Thermal Properties**

| polymer | $M_n$ (kDa) | PDI | $n^a$ (DP) | $T_{dec}{}^b$ (°C) |
|---|---|---|---|---|
| **P1** | 23 | 1.5 | 53 (53) | 420 |
| **P1*** | 22 | 1.4 | 51 (51) | 420 |
| **P2** | 21 | 1.5 | 54 (54) | 420 |
| **P2*** | 25 | 1.3 | 64 (32) | 420 |
| **P3** | 10 | 1.7 | 32 (16) | 410 |
| **P4** | 8 | 1.8 | 23 (11) | 420 |
| **P5** | 5 | 1.6 | 11 (5) | 440 |
| **P6** | 7 | 1.6 | 24 (24) | 380 |

[a]Number of TPD units. [b]Determined by TGA at 5% mass loss under nitrogen.

Their absence can be explained by (i) the chirality of the side chain in the case of **P1**, (ii) the bulkiness of the side chains in the case of **P2**, and (iii) the statistical distribution of the monomer with branched side chains in the structure of **P6**. On the other hand, polymers **P3**−**P5** exhibit a small peak at $2\theta$ = 24.5° (3.6 Å) corresponding to $\pi$-stacking of the polymer backbone. The additional organization was introduced by the increased percentage of the linear side chain, which allowed a better stacking of the polymer chains. Comparison of polymers **P3**−**P5** and a Bjørnholm homopolymer bearing a straight *n*-dodecyl chain revealed that the distance attributed to $\pi$-stacking is greater for **P3**−**P5** and the intensity of the peak is weaker as a result of the incorporation of the branched alkyl chains. Similar results were observed in the case of regioregular polythiophenes bearing linear and branched alkyl chains by Thompson et al.[36] These results show that it is important to balance the percentage of bulky substituents, which ensure solubility, and straight chains, which provide organization within the material.

UV−vis absorption spectra of polymers **P1**−**P6** in solution and in thin films are shown in Figures 3 and 4, respectively. One can easily notice (Table 2) a strong blue shift (42 nm) of the absorption maximum of **P2** (481 nm) in comparison to **P1** (523 nm). This could be explained by the fact that, in order to accommodate bulky 9-heptadecyl chains branched on C1 in **P2**, it may be necessary to distort bonds of the pyrrolidone moiety. As a result, the distance between the oxygen atom of pyrrolidone unit and the sulfur atom of the next TPD unit may decrease, causing twisting of adjacent TPD units. In the case of **P1**, branching on C2, further from the backbone, allows much more flexibility. A 16 nm bathochromic shift is observed for **P1**, on comparison of absorption in solution and in the solid state, indicating additional interchain interactions and further planarization in the bulk. Additionally, the well-defined and probably coplanar backbone of **P1** results in pronounced vibronic bands. Bulkiness of the chains in **P2** prevents any interactions in the solid state; thus, no shift was observed when UV−vis absorption spectra were compared in solution and in films. Substitution of each second branched chain by a linear chain (**P3**) allows much more flexibility of the TPD unit; thus, planarization of the backbone is possible. As a result, a pronounced red shift (36 nm) of the absorption maximum is observed in comparison to **P2**. When the ratio of the linear vs branched chains increases, i.e. 2/1 and 3/1 for **P5** and **P6**, respectively, a further red shift of the absorption maxima is observed.

In order to investigate the electrochemical properties of the synthesized polymers, cyclic voltammetry measurements of polymer films were performed. Oxidation at 1.5 V and reduction at −0.4 V were estimated for polymer **P1**, which corresponded to a HOMO energy level at −6.1 eV and a LUMO energy level at −4.3 eV, respectively. The electrochemical band gap (1.8 eV) is in good agreement with the optical band gap (1.9 eV) calculated from the onset of the absorption spectra. It is interesting to note that TPD-based homopolymers have almost the same band gap as regioregular poly(3-alkylthiophenes), but with HOMO and LUMO energy levels lower by about 1.0 eV. Incorporation of some of these polymers into OFET devices did reveal electron mobility of about $10^{-3}$ $cm^2$ $V^{-1}$ $s^{-1}$ that could lead to interesting electron acceptors in all-polymer solar cells.

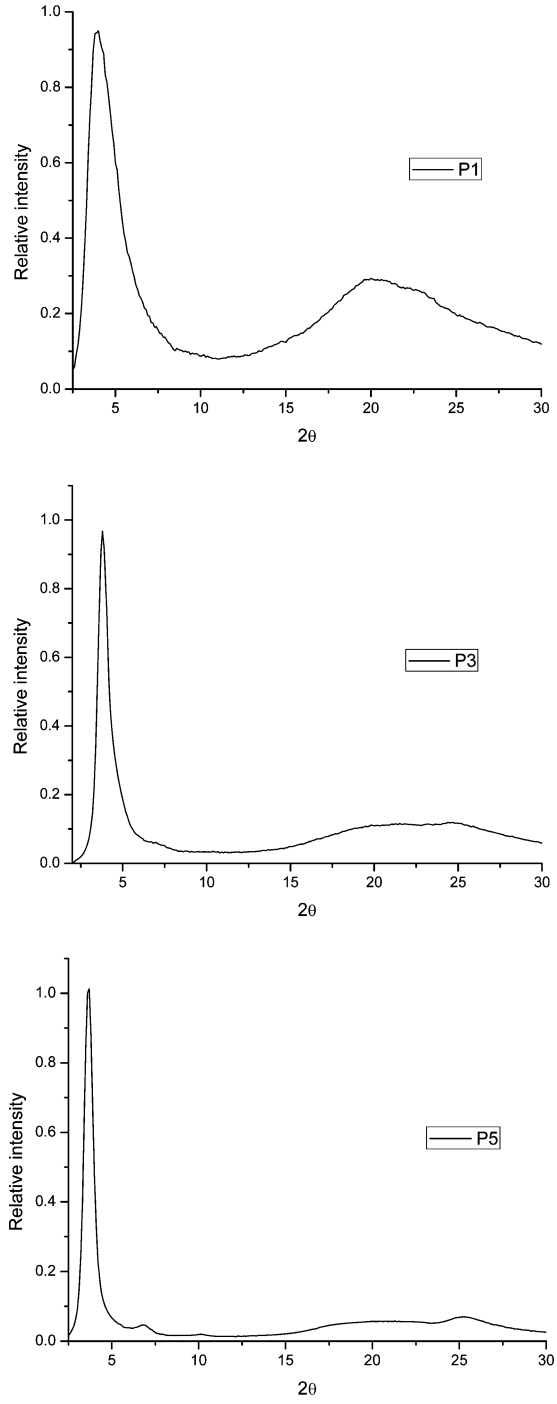


**Figure 2.** Powder XRD spectra of polymers **P1**, **P3**, and **P5**.


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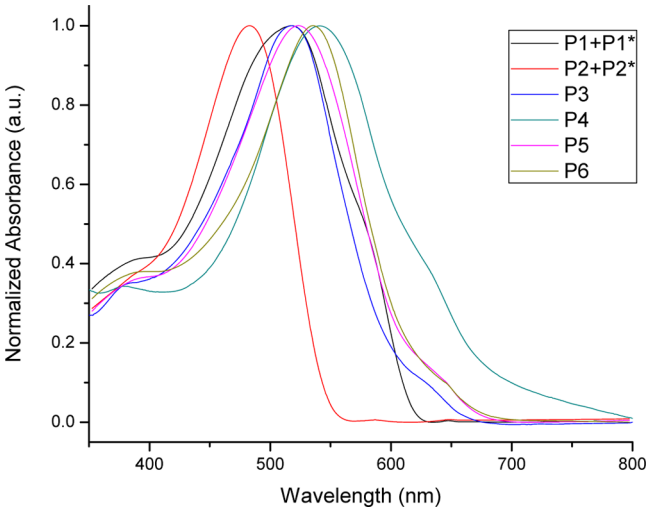


**Figure 3.** UV−visible absorption spectra in $CHCl_3$ solution of **P1**−**P6**.

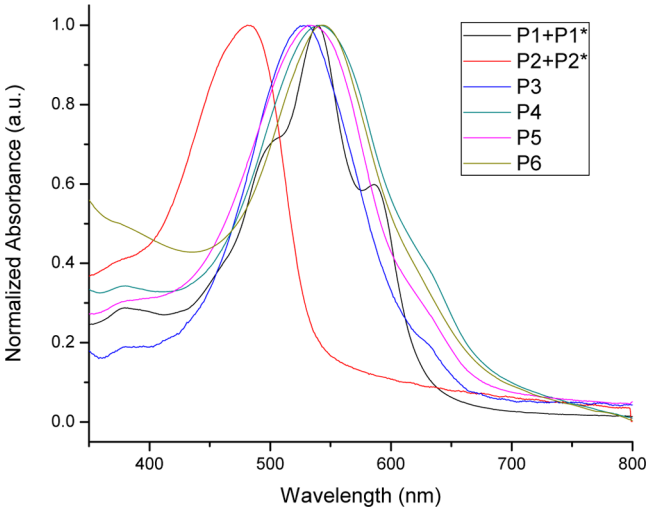


**Figure 4.** Solid-state UV−visible absorption spectra of **P1**−**P6**.

**Table 2. Optical Properties**

| polymer | $\lambda_{max}$ [a] (nm) | $\lambda_{max}$ (nm) | $E_{g\ opt}$ (eV) |
|---|---|---|---|
| **P1** | 523 | 539 | 1.9 |
| **P1*** | 523 | 539 | 1.9 |
| **P2** | 481 | 481 | 2.2 |
| **P2*** | 481 | 481 | 2.2 |
| **P3** | 518 | 527 | 1.9 |
| **P4** | 531 | 542 | 1.8 |
| **P5** | 523 | 533 | 1.8 |
| **P6** | 536 | 544 | 1.8 |

[a]Measured in $CHCl_3$ solution.

## CONCLUSION

In conclusion, we were able to improve the synthetic strategy toward TPD monomers. Our approach including Gewald thiophene ring formation and a Sandmeyer-type reaction followed by a neat condensation with an amine enabled us to prepare various TPD units in a cheaper and more efficient way in comparison to traditional methods. Taking advantage of the DHAP method, we synthesized various TPD-based homo- and pseudohomopolymers. Their investigation by means of UV−vis absorption and powder XRD measurements revealed that pseudohomopolymers with ratios of linear to branched alkyl chains 1/1 and 1/2, polymers **P3** and **P5**, respectively, combine good solubility and good packing in the solid state. Incorporation of the synthesized polymers into electrochemical and electronic devices is in progress.

## EXPERIMENTAL SECTION

**General Experimental Methods: Instrumentation.** $^1H$ and $^{13}C$ NMR spectra were recorded in deuterated chloroform or acetone solution at 298 K. Number-average ($M_n$) and weight-average ($M_w$) molecular weights were determined by size exclusion chromatography (SEC) using styrene-DVB gel columns in TCB at 110 °C. For the calibration curve, a series of monodisperse polystyrene standards was used. Differential scanning calorimetry (DSC) analyses were calibrated with ultrapure indium, at a scanning rate of 20 °C/min under a nitrogen flow. UV−vis−near-IR absorption spectra were recorded using a spectrophotometer and dropcast films on glass plates have been used for solid-state measurements. Optical band gaps were determined from the onset of the absorption band. Wide-angle X-ray diffraction (WAXD) spectra were obtained by a X-ray diffractometer using a graphite-monochromated copper radiation (K$\alpha$ = 1.5418 Å). The operation power was 40 kV, 20 mA, and the collimator is 0.8 mm in diameter. The samples were inserted in 0.01 mm thin-walled glass capillary tubes (1.0 mm diameter). Cyclic voltammograms (CV) were recorded on a Solartron 1287 potentiostat using platinum wires as working and counter electrodes at a scan rate of 50 mV/s. A thin polymeric film was coated on the working electrode. The reference electrode was $Ag/Ag^+$ (0.01 M of $AgNO_3$ in acetonitrile), and the electrolyte was a 0.1 M solution of tetrabutylammonium tetrafluoroborate in dry acetonitrile. Under these conditions, the oxidation potential of ferrocene was 0.09 V versus $Ag/Ag^+$, whereas the oxidation potential of ferrocene was 0.41 V versus SCE. The HOMO and LUMO energy levels were determined from the oxidation and reduction onsets (where the current differs from the baseline) assuming that the SCE electrode is −4.7 eV from vacuum.

**General Procedure for the Synthesis of Monomers and Intermediates.** 3-Ethyl 4-methyl 2-aminothiophene-3,4-dicarboxylate (**3**), 3-ethyl 4-methyl 2-iodothiophene-3,4-dicarboxylate (**4**), 1,3-dibromo-5-(2-octyldodecyl)thieno[3,4-*c*]pyrrole-4,6-dione (**5a**), 1,3-dibromo-5-octylthieno[3,4-*c*]pyrrole-4,6-dione (**5c**), 1-iodo-5-(2-octyldodecyl)thieno[3,4]pyrrole-4,6-dione (**8**), and 3,3′-dibromo-5,5′-dioctyl 1,1′-bi(thieno[3,4-*c*]pyrrole)-4,4′,6,6′-tetrone (**9**) were prepared via procedures reported in previous work.[15,19,24,28]

*Preparation of 5-Alkylthieno[3,4-c]pyrrole-4,6-diones **2a**−**c** from **4**.* In a small vial was placed **2** (1 equiv) and the desired alkylamine (1 equiv). The neat reaction mixture was gradually warmed to 200−280 °C in a graphite bath over 10 min. The product was purified through a silica plug with dichloromethane. The resulting product was washed or recrystallized with acetone and a few drops of water to give **2a**−**c** (32%) as white solids.

*Preparation of 5-Alkylthieno[3,4-c]pyrrole-4,6-diones **2a**−**c** from **7**.* In a round-bottom flask was placed **7a**−**5c** (1 equiv) in 0.05 M EtOH/AcOH (3/1) solution. Zinc powder (2 equiv) was added, and the reaction mixture was refluxed for 3 h. Water was then added and the precipitate filtered. The resulting product was washed or recrystallized with a minimum amount of acetone and a small amount of water to give the title compound (88%) as a white solid.

*Preparation of 5-Alkylthieno[3,4-c]pyrrole-4,6-diones **2a**−**c** from **1**.* This synthesis was performed as described for the preparation of **2a**−**c** from **4**.

**2a**: $^1H$ NMR (400 MHz, $CDCl_3$, ppm) $\delta$ 7.79 (s, 2H), 3.47 (d, 2H, $J$ = 7.2 Hz), 1.83 (m, 1H), 1.22 (m, 32H), 0.85 (t, 6H, $J$ = 2.2 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm) $\delta$ 163.1, 136.8, 125.6, 42.9, 37.0, 32.1, 32.1, 31.6, 31.6, 30.2, 30.2, 29.9, 29.9, 29.8, 29.8, 29.6, 29.5, 26.5, 26.5, 22.9, 22.9, 14.4, 14.4; HRMS (ESI-TOF) $m/z$ $[M + H]^+$ calcd for $C_{26}H_{44}NO_2S$ 434.3093, found 434.3104; mp 35−37 °C (uncorrected).

**2b**: $^1H$ NMR (400 MHz, $CDCl_3$, ppm) $\delta$ 7.78 (s, 2H), 4.10 (hept, 1H), 2.10−1.95 (m, 2H), 1.71−1.60 (m, 2H), 1.33−1.18 (m, 24H), 0.85 (t, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm) $\delta$ 163.3, 136.7,


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125.5, 52.9, 32.0, 29.7, 29.5, 29.5, 26.9, 22.9, 14.3; HRMS (ESI-TOF) $m/z$ $[M + H]^+$ calcd for $C_{23}H_{38}NO_2S$ 392.2623, found 392.2618; mp 40−42 °C (uncorrected).

**2c**: $^1H$ NMR (400 MHz, $CDCl_3$, ppm) $\delta$ 7.81 (s, 2H), 3.61 (t, 2H, $J$ = 7.4 Hz), 1.63 (m, 2H), 1.24 (m, 10H), 0.86 (t, 3H, $J$ = 7.0 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm) $\delta$ 162.4, 136.7, 125.2, 37.9, 31.7, 29.2, 29.2, 28.4, 26.8, 22.4, 14.1; HRMS (ESI-TOF) $m/z$ $[M + H]^+$ calcd for $C_{14}H_{20}NO_2S$ 266.1215, found 266.1219; mp 120−122 °C (uncorrected).

*Preparation of 1,3-Dibromo-5-(1-octylnonyl)thieno[3,4-c]-pyrrole-4,6-dione (**5b**).* To a mixture of **2b** (0.7 g, 1.79 mmol) in trifluoroacetic acid and sulfuric acid (9 mL/3 mL) was added NBS (0.95 g, 5.36 mmol) in one portion. The resulting mixture was stirred in the dark overnight. The mixture was extracted with chloroform, and the organic phase was washed with an aqueous solution of KOH, dried over $MgSO_4$, and concentrated under vacuum. The product was purified by column chromatography (silica gel) using hexane/DCM (1/2) as an eluent. A pure sample was obtained as a low melting point beige solid in 81% yield (0.79 g): $^1H$ NMR (400 MHz, $CDCl_3$, ppm) $\delta$ 4.06 (hept, 1H), 2.05−1.93 (m, 2H), 1.69−1.57 (m, 2H), 1.31−1.14 (m, 24H), 0.86 (t, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm) $\delta$ 160.94, 134.70, 113.01, 53.58, 32.39, 32.06, 29.65, 29.50, 29.46, 26.90, 22.88, 14.13; HRMS (ESI-TOF) $m/z$ $[M + H]^+$ calcd for $C_{23}H_{36}Br_2NO_2S$ 548.0833, found 548.0838; mp 42−44 °C.

*Preparation of 1-Bromo-5-(alkyl)thieno[3,4-c]pyrrole-4,6-diones **7a−c** from **6**.* In a small vial was placed **6** (1 equiv) and the desired alkylamine (1 equiv). The neat mixture was then heated to 260 °C over 10 min. The product was purified through a silica plug with dichloromethane. The resulting product was washed or recrystallized with a minimum amount of acetone and a small amount of water to give the title compound (64−76%) as an off-white solid/oil.

*Preparation of 1-Bromo-5-(alkyl)thieno[3,4-c]pyrrole-4,6-diones **7a−c** from **5**.* **5a−c** (0.5 mmol) was placed in a 25 mL three-necked flask with a condenser. A solution of ethanol (3.25 mL), acetic acid (1 mL), and 1 drop of HCl was added and then heated until dissolution of the solid. Zinc powder (0.5 mmol) was then added, and the mixture was refluxed for 1 h. The mixture was then filtered through fritted glass, and the solvent was evaporated under vacuum. A silica column was made using a gradient of 100% hexane to 100% chloroform to give the pure products **7a−c** (42%).

**7a**: product obtained as a pale yellow oil; $^1H$ NMR (400 MHz, $CDCl_3$, ppm) $\delta$ 7.72 (s, 1H), 3.49 (d, 2H, $J$ = 7.2 Hz), 1.63 (m, 1H), 1.24 (m, 32H), 0.87 (t, 6H, $J$ = 12.3 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm) $\delta$ 161.8, 136.9, 134.4, 126.8, 113.6, 43.1, 37.1, 32.16, 32.14, 31.7, 30.2, 29.94 (two peaks overlap), 29.88 (two peaks overlap), 29.84 (two peaks overlap), 29.79 (two peaks overlap), 29.59 (two peaks overlap), 29.53, 26.50, 22.93, 14.38; HRMS (ESI-TOF) $m/z$ $[M + H]^+$ calcd for $C_{26}H_{43}BrNO_2S$ 512.2198, found 512.2220.

**7b**: product obtained as a pale yellow oil; $^1H$ NMR (400 MHz, $CDCl_3$, ppm) $\delta$ 7.70 (s, 1H), 4.09 (m, 1H), 1.65 (m, 2H), 2.00 (m, 2H), 1.23 (m, 24H), 0.87 (t, 6H, $J$ = 13.6 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm) $\delta$ 162.2, 161.8, 136.7, 134.1, 126.7, 126.6, 113.4, 32.16, 32.4, 32.0, 31.8, 31.1, 29.66 (two peaks overlap), 29.50 (two peaks overlap), 29.44 (two peaks overlap), 29.40 (two peaks overlap), 26.88, 22.8, 14.34; HRMS (ESI-TOF) $m/z$ $[M + H]^+$ calcd for $C_{23}H_{37}BrNO_2S$ 470.1728, found 434.1740.

**7c**: product obtained as a white solid; $^1H$ NMR (400 MHz, $CDCl_3$, ppm) $\delta$ 7.72 (s, 1H), 3.60 (t, 2H, $J$ = 7.3 Hz), 1.63 (m, 2H), 1.29 (m, 10H), 0.84 (t, 3H, $J$ = 7.2 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm) $\delta$ 161.9, 161.6, 137.0, 134.5, 126.8, 113.6, 38.9, 32.0, 29.4, 29.4, 28.6, 27.1, 22.9, 14.3; HRMS (ESI-TOF) $m/z$ $[M + H]^+$ calcd for $C_{14}H_{19}BrNO_2S$ 344.0320, found 344.0324; mp 86−88 °C (uncorrected).

*Preparation of 2-Bromothiophene-3,4-dicarboxylic Acid (**6**).* 3-Ethyl 4-methyl 2-aminothiophene-3,4-dicarboxylate (**3**; 15.00 g, 65 mmol) in HBr (10% aqueous, 300 mL) was stirred at room temperature for 20 min. The solution was cooled to 0 °C, and $NaNO_2$ (6.78 g, 130.88 mmol) was added to the solution. The mixture was allowed to react for 30 min. Then CuBr (28.12 g, 196 mmol) was added in small portions. The solution was heated at 80 °C for 1 h. The mixture was extracted with diethyl ether (10 × 75 mL) and washed with saturated sodium bisulfite solution (5 × 100 mL) and water (3 × 100 mL). The combined organic layer was dried with $Na_2SO_4$ and evaporated to dryness. The crude product was chromatographed over silica gel using methylene chloride as eluent to give a white solid (7.29 g, 25 mmol). This solid was diluted in 250 mL of NaOH (1 M), and the solution was stirred at 80 °C in a one-necked flask overnight. The solution was then acidified with HCl to pH 3 and extracted with diethyl ether (10 × 150 mL). The combined organic layers were dried with $Na_2SO_4$ and evaporated to dryness to give a white solid (6.12 g, 24 mmol, 37%): $^1H$ NMR (400 MHz, acetone-$d_6$, ppm) $\delta$ 8.28 (s, 1H); $^{13}C$ NMR (100 MHz, acetone-$d_6$, ppm) $\delta$ 164.0, 161.6, 136.3, 135.1, 132.8, 113.6; HRMS (ESI-TOF) $m/z$ $[M + H]^+$ calcd for $C_6H_4BrO_4S$ 250.9014, found 250.9013; mp 165−167 °C (uncorrected).

*Preparation of Thiophene-3,4-dicarboxylic Acid (**1**).* A solution of **3** (0.84 g, 3.7 mmol) in 75 mL of anhydrous THF was added dropwise to a boiling solution of *tert*-butyl nitrite (0.40 g, 3.9 mmol) in 100 mL of anhydrous THF under nitrogen. The mixture was refluxed for 3 h before it was evaporated under reduced pressure. The remaining dark brown oil was purified by chromatography on silica using 30% ethyl acetate/70% hexanes as the eluent to give the product as an oil (0.53 g). This oil was diluted in 25 mL of NaOH (1 M), and the solution was stirred at 80 °C in a one-necked flask overnight. The solution was then acidified with HCl to pH 3 and extracted with diethyl ether (10 × 150 mL). The combined organic layers were dried with $Na_2SO_4$ and evaporated to dryness to give a white solid (0.43 g, yield 66%): $^1H$ NMR (400 MHz, acetone-$d_6$) $\delta$ 12.44 (broad peak), 8.54 (s, 2H); $^{13}C$ NMR (100 MHz, acetone-$d_6$) $\delta$ 205.7, 164.5, 139.1 ppm; HRMS (ESI-TOF) $m/z$ $[M + H]^+$ calcd for $C_6H_5O_4S$ 172.9909, found 172.9908; mp 218−220 °C (uncorrected).

**General Procedure for the Polymer Synthesis.** ***P1** (H-A-I).* 1-Iodo-5-(2-octyldodecyl)thieno[3,4-*c*]pyrrole-4,6-dione (**8**; 100.00 mg, 0.18 mmol), *trans*-bis(*μ*-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]-dipalladium(II) (3.34 mg, 2 mol %), tris(*o*-methoxyphenyl)phosphine (5.04 mg, 8 mol %), cesium carbonate (58.64 mg, 0.18 mmol), and silver acetate (29.97 mg, 0.18 mmol) were added in a Biotage microwave vial (size 2−5 mL) with a magnetic stirring bar. The vial was sealed with a cap and then purged with nitrogen to remove the oxygen. A 0.7 mL portion of THF was added, and the reaction mixture was heated with an oil bath at 120 °C (reaction under pressure). After 22 h, the reaction mixture was cooled and the corresponding 5-alkylthieno[3,4-*c*]pyrrole-4,6-dione was added as a capping agent (50 mg in 1 mL). The solution was heated again at 120 °C for 1 h to complete the end-capping procedure. After an additional 1 h of reaction, the whole mixture was cooled to room temperature and poured into 500 mL of cold methanol. The precipitate was filtered. Soxhlet extractions with acetone followed with chloroform were done. The solvent was reduced to about 10 mL, and the mixture was poured into cold methanol. The precipitate was filtered. **P1** was achieved in 79% yield of soluble fraction in $CHCl_3$ ($M_n$ of 23 kDa).

***P1*** and **P2** (H-A-Br).* Monomer (**7a** or **7b**; 0.18 mmol), *trans*-bis(*μ*-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (3.34 mg, 2 mol %), tris(*o*-methoxyphenyl)phosphine (5.04 mg, 8 mol %), and potassium acetate (17.67 mg, 0.18 mmol) were added in a Biotage microwave vial (size 2−5 mL) with a magnetic stirring bar. The vial was sealed with a cap and then purged with nitrogen to remove the oxygen. A 1 mL portion of THF was added, and the reaction mixture was heated with an oil bath at 120 °C (reaction under pressure). After 22 h, the reaction mixture was cooled and the corresponding 5-alkylthieno[3,4-*c*]pyrrole-4,6-dione was added as a capping agent (50 mg in 1 mL). The solution was heated again at 120 °C for 1 h to complete the end-capping procedure. After an additional 1 h of reaction, the whole mixture was cooled to room temperature and poured into 500 mL of cold methanol. The precipitate was filtered. Soxhlet extractions with acetone followed by chloroform were done. The solvent was reduced to about 10 mL, and the mixture was poured into cold methanol. The precipitate was filtered. **P1*** and **P2** were obtained in 75−85% yields of soluble fraction in $CHCl_3$ ($M_n$ of 22 for **P1*** and 22 kDa for **P2**).


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***P2*–P5*** *(H-A-H + Br-B-Br).* Monomer A (0.25 mmol), monomer B (0.25 mmol), *trans*-bis(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]-dipalladium(II) (2 mol %), tris(*o*-methoxyphenyl)phosphine (8 mol %), and potassium acetate (0.50 mmol) were added in a Biotage microwave vial (size 2–5 mL) with a magnetic stirring bar. The vial was sealed with a cap and then purged with nitrogen to remove the oxygen. A 1 mL portion of THF was added, and the reaction mixture was heated with an oil bath at 120 °C (reaction under pressure). After 22 h, the reaction mixture was cooled and the corresponding 5-alkylthieno[3,4-*c*]pyrrole-4,6-dione was added as a capping agent (50 mg in 1 mL). The solution was heated again at 120 °C for 1 h to complete the end-capping procedure. After an additional 1 h of reaction, the whole mixture was cooled to room temperature and poured into 500 mL of cold methanol. The precipitate was filtered. Soxhlet extractions with acetone followed by hexanes removed catalytic residues and low-molecular-weight materials. Polymers were then extracted with chloroform. The solvent was reduced to about 10 mL, and the mixture was poured into cold methanol. The precipitate was filtered. **P2*–P4** were obtained in 60–75% yields of soluble fraction in $CHCl_3$ and 55% for **P5** in $CHCl_3$ and *o*-DCB ($M_n$ of 25 for **P2***, 10 for **P3**, 8 for **P4**, and 5 kDa for **P5**).

***P6*** *(H-A-Br + H-B-Br).* **5c** (0.75 mmol), **5d** (0.25 mmol), *trans*-bis(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (0.02 mmol), tris(*o*-methoxyphenyl)phosphine (0.08 mmol), and potassium acetate (1.00 mmol) were added in a Biotage microwave vial (size 2–5 mL) with a magnetic stirring bar. The vial was sealed with a cap and then purged with nitrogen to remove the oxygen. A 2 mL portion of THF was added, and the reaction mixture was heated with an oil bath at 120 °C (reaction under pressure). After 22 h, the reaction mixture was cooled and the corresponding 5-alkylthieno[3,4-*c*]pyrrole-4,6-dione was added as a capping agent (50 mg in 1 mL). The solution was heated again at 120 °C for 1 h to complete the end-capping procedure. After an additional 1 h of reaction, the whole mixture was cooled to room temperature and poured into 500 mL of cold methanol. The precipitate was filtered. Soxhlet extractions with acetone followed by hexanes removed catalytic residues and low-molecular-weight materials. Polymers were then extracted with chloroform. The solvent was reduced to about 10 mL, and the mixture was poured into cold methanol. The precipitate was filtered. **P6** was obtained in 39% yield of soluble fraction in $CHCl_3$ and *o*-DCB ($M_n$ of 7 kDa).

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Figures giving NMR spectra of all compounds as well as UV–visible absorption spectra and powder XRD of all polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail: mario.leclerc@chm.ulaval.ca.

### Notes

The authors declare no competing financial interest.

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