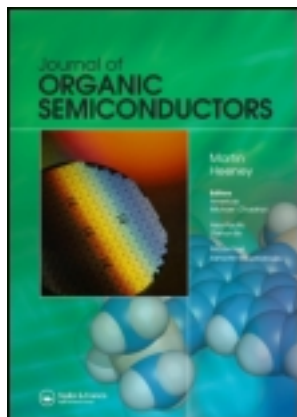


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Alkyl side-chain branching point effects in thieno[3,4-c]pyrrole-4,6-dione copolymers

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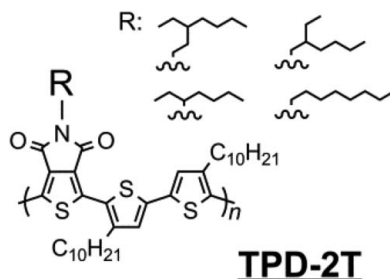
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A novel and efficient route to thieno[3,4-*c*]pyrrole-4,6-dione (TPD) facilitating late-stage alkylation is presented. Four copolymers with alkylated bithiophene (2T) are synthesised, with different TPD *N*-alkyl side-chain branching points. The effect of steric bulk on solid-state properties is investigated (UV–VIS, differential scanning calorimetry, X-ray diffraction) and C1-branching found to increase crystallinity and solid-state packing in TPD-2T.

Keywords: organic electronics; conjugated polymer; donor–acceptor copolymer; thieno[3,4-*c*]pyrrole-4,6-dione; alkyl side-chain; branching point



1. Introduction

Organic semiconducting materials have potential as large-scale, thin, flexible, lightweight and crucially low-cost electronic devices, fabricated by printing techniques. Currently organic field-effect transistors and bulk heterojunction (BHJ) solar cells routinely utilise π -conjugated polymers with donor–acceptor (D–A) hybridisation due to their readily tunable optical and electronic properties, with alkyl side-chains to afford the required solubility and processability.[1–6]

However, the exact structure of the solubilising chain is often overshadowed by energetic contributions that influence the frontier orbital band gap, despite evidence that considerations such as side-chain spacing, branching and length can prove vital.[7–12] The size of the solubilising chain is a key factor to consider during polymer synthesis: with a longer alkyl chain, solubility is generally gained.[13] However, this can come at the detriment of other factors such as packing, blend morphology and fullerene miscibility.[14,15] To improve device microstructure attention has also been paid to the

comparison of branched and linear alkyl chains, evaluating their effect on device performance, with the former preferred for organic photovoltaic applications and the latter for transistors.[16,17] More recently, a number of studies have begun to elucidate the effect of precision alkyl-chain engineering by shifting the branching point position, which has resulted in both improved photovoltaic efficiency and charge carrier mobility in field-effect transistors.[18–20] However, the preferred side-chain is largely dependent on the exact polymer system. Our approach herein is to conduct a systematic study of the alkyl side-chain branching point position, investigating the effects of overall steric bulk on solid-state properties in a promising class of semiconducting polymers.

The thieno[3,4-*c*]pyrrole-4,6-dione (TPD) unit is a commonly used *N*-alkylated acceptor. The electron-deficient nature of the TPD unit lowers the HOMO levels of D–A copolymers and promotes intramolecular charge transfer, while the thiophene–maleimide structure takes a quinoidal form in the excited state, lowering the bandgap. In addition, the planarity and ability to hydrogen-bond

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encourages intermolecular interactions such as π - π stacking. The relatively low cost of **TPD** further increases its potential for commercial use.

When copolymerised with electronically coupled electron-rich bithiophene (**2T**) – which also features rigid, aromatic rings with a coplanar structure – crystalline morphologies and enhanced charge transport are achieved. Use of a bi(alkyl)thiophene aids solubility, though the tail-to-tail configuration of the alkyl chains is vital in preserving crystallinity.[21] Such alkylated **TPD-2T** polymers have achieved efficiencies as high as 7.3% in BHJ photovoltaic cells and field-effect transistors exhibit hole mobilities as high as $0.6 \text{ cm}^2/\text{Vs}$. [22–27] In addition, these polymers have recently been reported with both economic and green syntheses.[28,29]

Here, we report a novel and efficient synthesis of the **TPD** unit facilitating late-stage alkylation by haloalkanes and direct C-H activation polymerisation. Four novel **TPD-2T** polymers with different branching points in the *N*-alkyl side-chain are prepared (Chart 1) and their optical (UV–VIS) and thermal (differential scanning calorimetry (DSC)) properties, molecular models and X-ray diffraction (XRD) data presented. The impact on solid-state (thin-film) morphology is then analysed to derive a structure–property relationship.

2. Results and discussion

Synthesis. The dibromo-**TPD** monomers were prepared in four simple steps from 3,4-thiophene dicarboxylic acid with

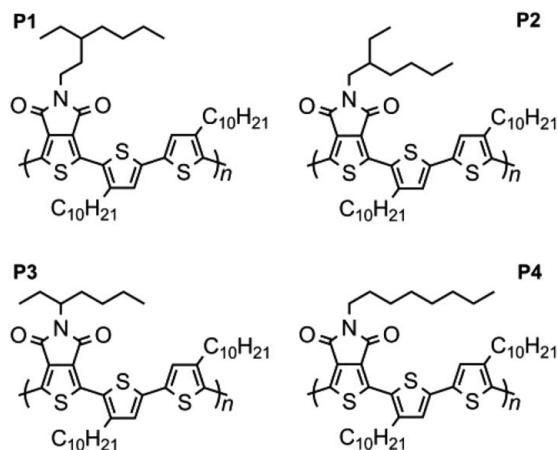
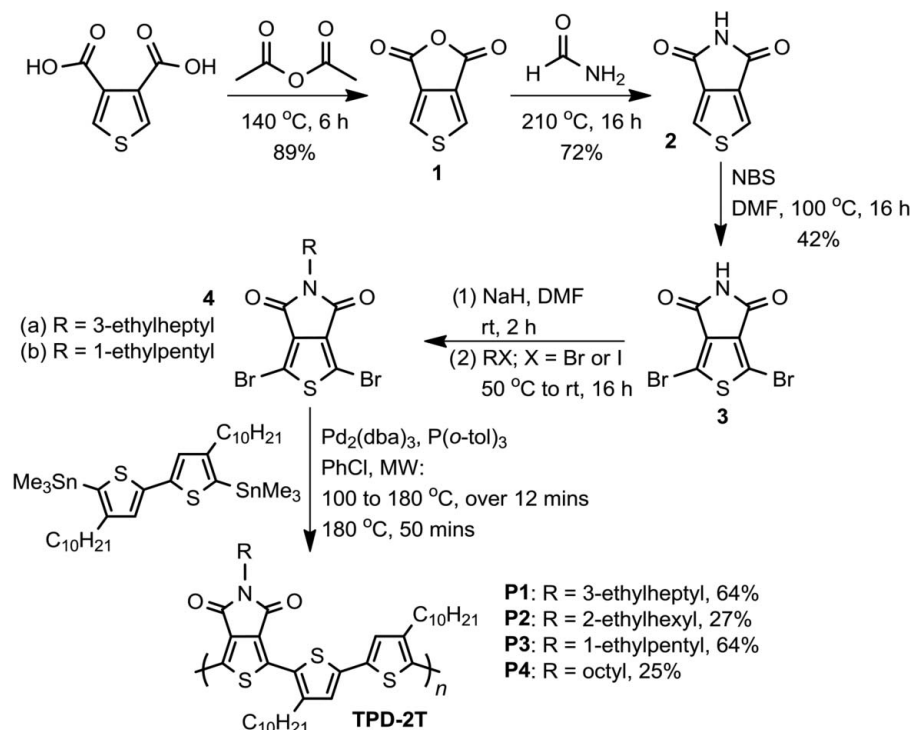
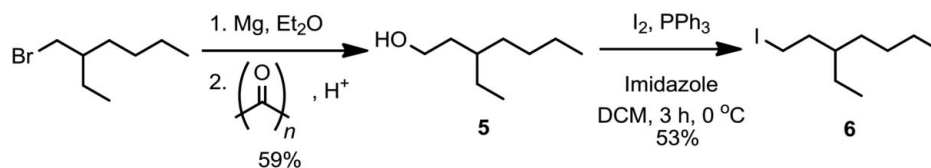


Chart 1. Structures of the four thieno[3,4-*c*]pyrrole-4,6-dione copolymers with alkylated bithiophene (**TPD-2T**) showing the different *N*-alkyl side-chains.

late-stage alkylation and bromination (Scheme 1). Initially thiophene anhydride **1** is prepared from the dicarboxylic acid according to the literature procedure.[30] Typically a ring-opening condensation with an alkyl-amine and subsequent ring-closure then furnishes the *N*-alkylated **TPD** heterocycle. Whilst Leclerc et al. have recently reported an efficient one-step synthesis of **TPD** this requires the use of alkyl-amines (RNH_2), which are not always readily available.[31] We were interested in removing the necessity of alkyl amines from the synthesis of **TPD**. This would allow access to a greater number of alkyl chains which have



Scheme 1. Synthesis of the **TPD-2T** copolymers.



Scheme 2. Synthesis of 3-ethyl-iodoheptane.

Table 1. Properties of the **TPD-2T** copolymers.

TPD-2T polymer	<i>N</i> -alkyl side-chain	M_n (kDa) ^a	M_w (kDa) ^a	PDI ^a	$\lambda_{\max}^{\text{abs}}$ (nm)		E_g^{opt} (eV)	Energy levels (eV) ^d	
					Solution ^b	Film ^c		E_{HOMO}	E_{LUMO}
P1	3-Ethylheptyl	7	9	1.3	471	543	1.77	-5.2	-3.4
P2	2-Ethylhexyl	6	9	1.4	469	541	1.81	-5.2	-3.4
P3	1-Ethylpentyl	8	11	1.4	470	563	1.72	-5.2	-3.5
P4	Octyl	5	7	1.4	472	535	1.77	-5.2	-3.4

^aDetermined by gel permeation chromatography using polystyrene standards and PhCl as the eluent at 80°C.

^bSolutions in dilute PhCl.

^cThin-films spin-coated from ~5 mg/mL PhCl solutions on glass substrates.

^d E_{HOMO} found by AC2 (PESA) measurement; $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g^{\text{opt}}$.

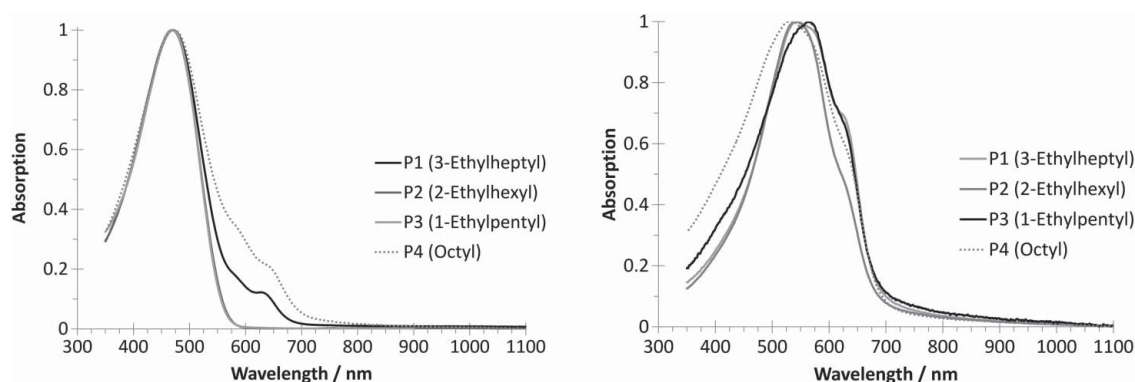


Figure 1. Normalised UV-VIS absorption spectra of the four thieno[3,4-*c*]pyrrole-4,6-dione-based (**TPD-2T**) copolymers as (left) solutions in dilute chlorobenzene and (right) thin-films spin-coated on glass substrates from 5 mg/mL hot chlorobenzene solutions.

been shown to have a significant effect on device performance. To this end we subjected the thiophene anhydride to refluxing formamide, isolating the unalkylated **TPD** heterocycle **2** from a one-pot reaction in good yield.[32] This novel route does not require prior bromination, which means that alternative polymerisations conditions, such as direct heteroarylations can also be performed.[28,33] Here we proceeded with bromination, albeit non-facile, and subsequent alkylation of amide **3** with haloalkanes.[34] The use of a C1-branched alkyl chain (from 3-bromopentane) results in a lower yield, most likely as a result of increased steric hindrance on alkylation. The C3-branched alkyl chain was installed from 3-ethyl-iodoheptane (**6**) (Scheme 2), the key step in preparation of which was the one-pot formation of a Grignard reagent from 2-ethyl-bromohexane and subsequent addition to formaldehyde, the latter being prepared *in situ* by decomposition of paraformaldehyde.

The four **TPD-2T** polymers were synthesised under standard microwave Stille coupling conditions in chlorobenzene. The polymers were purified by precipitation from methanol followed by Soxhlet extraction using acetone, hexane and finally chloroform. The latter fraction was heated and stirred vigorously with aqueous sodium diethyldithiocarbamate to remove residual catalytic metal impurities. Stille polymerisation whilst versatile and reliable affords number-average molecular weights (M_n) below 10 kDa (Table 1), as has been observed with those reported for similar copolymers.[26,29] It may be possible to achieve higher molecular weights by direct heteroarylation polymerisations.[28]

Optical properties. UV-VIS absorption spectra of the **TPD-2T** polymers are shown in Figure 1 and key properties summarised in Table 1. Dilute solutions were in chlorobenzene and thin-films spin-coated from ~5 mg/mL

chlorobenzene solutions on glass substrates. The polymers all exhibited absorption maximum over 530 nm in thin-films, being assigned to internal charge transfer between the **TPD** and bithiophene units, while the vibronic shoulders at ~ 630 nm imply an ordered arrangement in the solid state. The thin-film maxima are red-shifted by ~ 70 nm in comparison with their solutions due to increased π orbital overlap in the planar, conjugated polymers, which reduces the bandgap. The small difference in each of the UV–VIS spectra could be explained by a different morphology in the solid state and/or the different molecular weights. However, the red-shift of the **P3** thin-film absorption maximum could be attributed to the reduction in steric bulk of the overall shorter alkyl chain, reducing any distortion of bonds in the pyrrolidone moiety and enhancing any planarising interaction between the carbonyls and neighbouring sulphur atoms of the bithiophene units.

Energy levels. Ionisation potentials are summarised in Table 1, having been measured by Photo Electron Spectroscopy in air using the same polymer thin-film samples as for optical analysis. The **TPD-2T** polymers all exhibited Highest Occupied Molecular Orbital (HOMO) energy levels of -5.2 eV, confirming the minimal impact of the alkyl side-chain on ionisation potential. In addition, these reasonably low HOMO energy levels (below -5 eV) could lead to a high open-circuit voltage (V_{oc}) in devices and indicate good stability towards unintentional doping by atmospheric oxidants. The **TPD-2T** polymers all exhibited optical bandgaps of 1.8 eV, with the exception of **P3** which was 0.1 eV lower (1.7 eV), attributable to the reduction in overall steric bulk aiding planarisation, as aforementioned, resulting in increased π orbital overlap and delocalisation of electrons stabilising the LUMO; the LUMO levels were found by adding the optical bandgap to the PESA-determined HOMO of the same sample. An optimised structure of the **TPD-2T** polymer backbone reveals this to be effectively fully planar, possibly as a result of planarising intra-molecular interactions between the carbonyl on the pyrrolidone and sulphur on the thiophene moieties[35] (Figure S1, Supplementary Information) (modelled at the B3LYP/6-31G* level, for an *N*-methyl substituted tetramer). Notably the HOMO and LUMO densities are extensively delocalised along the polymer chain, as opposed to being localised on the D–A parts, respectively, which could facilitate enhanced charge transport.

Thermal properties. The DSC thermograms exhibit well-defined melt and crystallisation peaks (Figure 2) (under a nitrogen atmosphere with a heating rate of $10^\circ\text{C}/\text{min}$). There is a steady increase in melt and crystallisation temperatures as the branch-point of the alkyl side-chain is moved from C3 to C2 to C1. While this could be attributed in part to molecular weight effects, the higher melting points are more indicative of better stability in the crystals as alkyl side-chain bulk is reduced. As expected, **P4** which has a linear octyl side-chain – being isomeric with

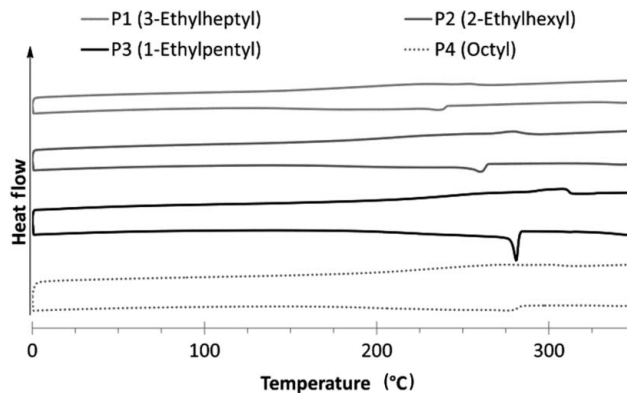


Figure 2. DSC scans of the **TPD-2T** copolymers exhibit an increase in crystallisation and melt temperatures with a reduction in steric bulk of the alkyl side-chain; (0 – 350°C temperature range; heating at $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere).

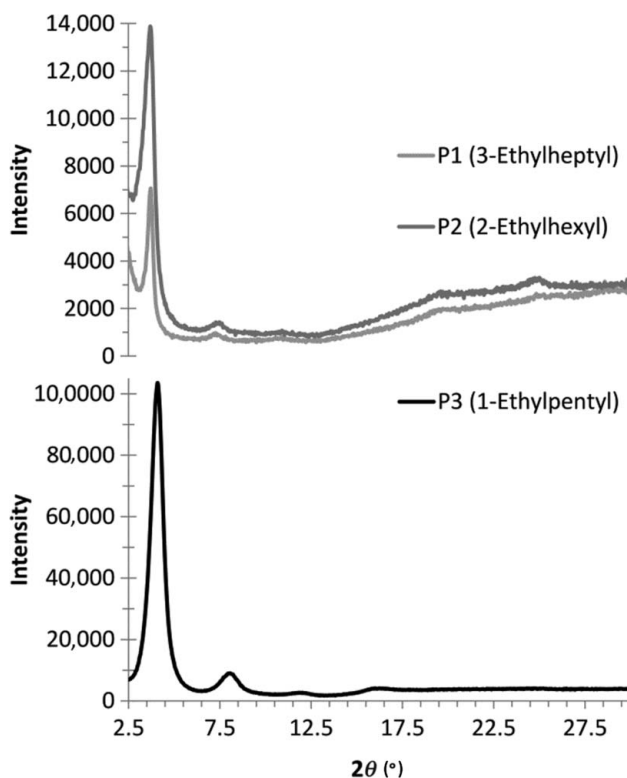


Figure 3. XRD diagrams of the **TPD-2T** copolymers exhibit a higher degree of crystallinity with a reduction in steric bulk of the alkyl side-chain; (polymers as drop cast thin-films on Si substrates from 10 mg/mL hot chlorobenzene solutions).

the branched side-chain of **P2**, and containing one more carbon than that of **P3** – sits between the two, demonstrating the presence of both side-chain size and shape effect on polymer properties.

Morphology. Thin-films of the **TPD-2T** copolymers were investigated by XRD (Figure 3 and Table 2). Thin-films were drop-cast from polymer solution (10 mg/mL hot chlorobenzene) onto Si substrates and allowed to dry in air. While the **P1** and **P2** films exhibited an out-of-plane

Table 2. XRD data for the **TPD-2T** copolymers.

TPD-2T polymer	<i>N</i> -alkyl side-chain	2θ (°)	<i>d</i> Spacing (Å)	2θ (°)	<i>d</i> Spacing (Å)	2θ (°)	<i>d</i> Spacing (Å)	2θ (°)	<i>d</i> Spacing (Å)
		<i>n</i> = 1		<i>n</i> = 2		<i>n</i> = 3		<i>n</i> = 4	
P1	3-Ethylheptyl	3.71	23.8	7.26	24.3	10.54	25.2	—	—
P2	2-Ethylhexyl	3.68	24.0	7.46	23.7	10.87	24.4	—	—
P3	1-Ethylpentyl	4.08	21.6	8.07	21.9	11.82	22.4	16.25	21.8

Note: Polymer thin-films were drop-cast on silicon substrates from 10 mg/mL hot chlorobenzene solutions and allowed to dry in air.

primary reflection peak at $2\theta \approx 3.7^\circ$, this was slightly larger for **P3** being $\sim 4.1^\circ$. The low angle diffraction peaks are characteristic of lamellar-type crystallinity in π stacked conjugated polymers, being associable with the interlayer *d*-spacing distance, calculated to be ~ 24 Å for **P1** and **P2** and ~ 22 Å for **P3**. The reduced lamellar spacing (~ 2 Å) for **P3** may be attributed to the reduction in steric bulk of the alky side-chains allowing the polymer chains to pack closer together. In addition, **P3** appears to exhibit increased crystallinity with higher intensities of the reflection peaks and a discernible quaternary reflection peak, while the tertiary is the highest order reflection peak readily observed for **P1** and **P2**. In common with previous studies, the (100), (200) and (300) diffraction peaks dominate the spectra making indefinite any (010) peak, associable with facial π - π stacking between polymeric backbones.[29] The difference in XRD patterns mean the polymers are organised differently in the solid state and as such the differences in optical absorption spectra and DSC thermograms are unlikely to be attributed to variations in molecular weight.

The increase in solid-state crystallinity for **P3** may be attributed to a reduction in side-chain steric bulk (as opposed to length), promoting crystallisation of the polymer. This has been shown to improve current in devices by strengthening polymer/PCBM interactions and as such the synthesis and device performance of high molecular weight *N*-1-ethylpentyl alkylated **TPD-2T** will be of interest.[14,16]

3. Conclusions

In summary, we have described a novel and efficient route to thieno[3,4-*c*]pyrrole-4,6-dione (**TPD**) allowing for late-stage alkylation and direct C-H polymerisation. A series of four copolymers with alkylated bithiophene are synthesised, in this case by Stille polymerisation, with different **TPD** *N*-alkyl side-chain branching points. The nature of an alkyl side-chain has a minimal effect on the energetics of the polymer, exhibiting greater influence over the morphology. The exact position of a side-chain branch-point (if any) and the length of the chain are two independent factors, with the overall steric bulk induced at the side-chain being responsible for changes in the properties of a polymer series. The use of a C1-branched side-chain

promotes increased crystallinity and solid-state packing effects in **TPD-2T** polymers. To conclude, high molecular weight *N*-1-ethylpentyl alkylated **TPD-2T** polymers may exhibit enhanced device performance in organic field-effect transistors and BHJ solar cells.

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