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VIP **Polymerization**

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Synthesis of 5-Alkyl[3,4-*c*]thienopyrrole-4,6-dione-Based Polymers by Direct Heteroarylation**

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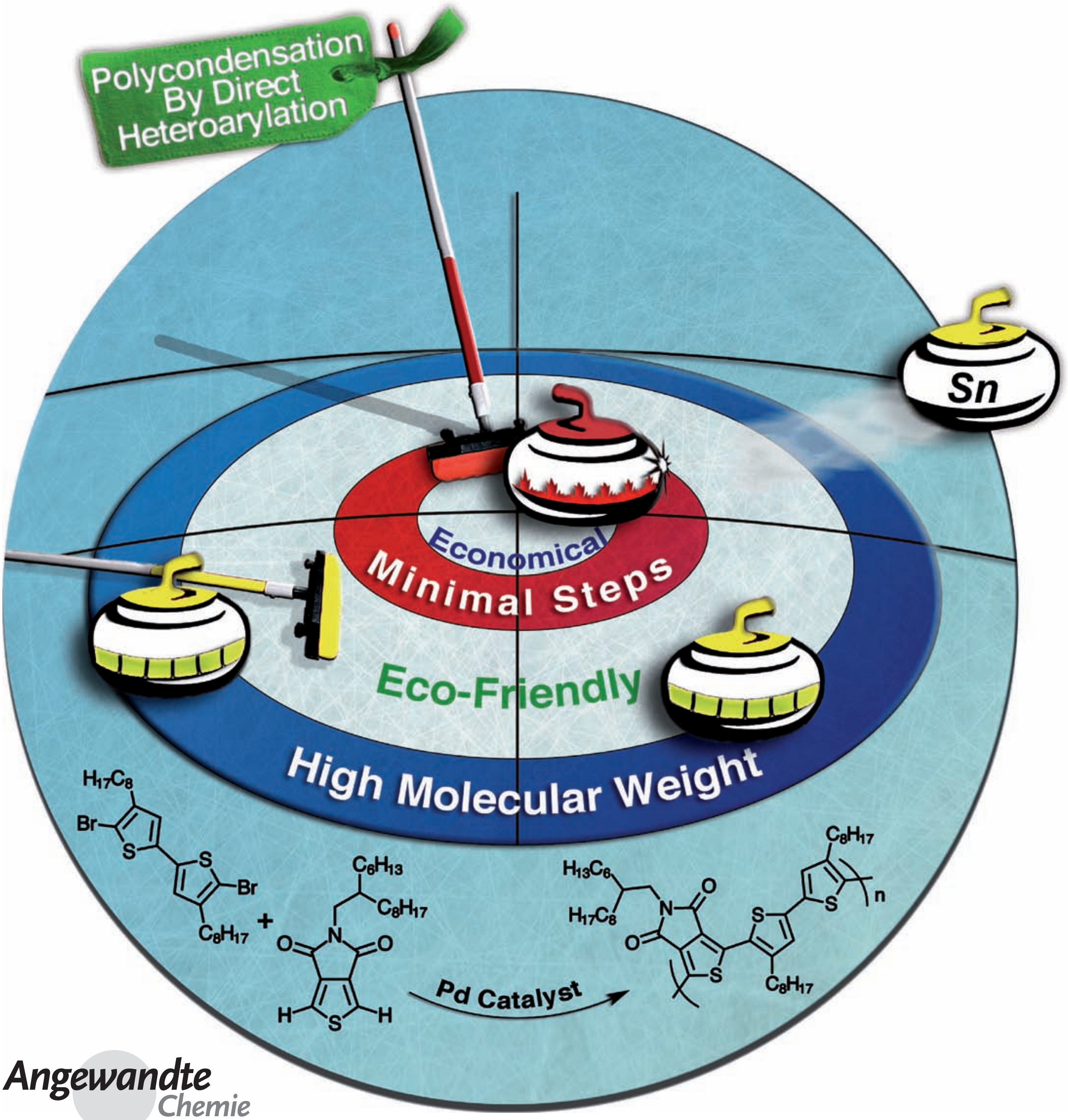

Angewandte
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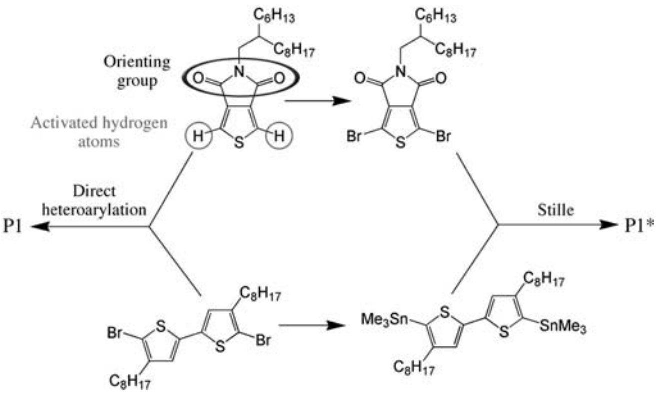
The Stille cross-coupling reaction has allowed significant advances in the synthesis of new organic molecules.[1] This reaction also had a huge impact in macromolecular chemistry, especially for the synthesis of conjugated polymers.[1,2] Despite its great versatility, the Stille reaction involves drawbacks such as the formation of a stoichiometric amount of toxic by-products and in some cases, some instability of the organometallic reagents.

Recently, the development of reactions called "direct arylations" has received much attention.[3] These reactions allow the formation of carbon–carbon bonds between aromatic units having activated hydrogen atoms without the use of organometallic intermediates. These reactions are mostly developed for the synthesis of small molecules.[4] Indeed, up until now, only a few publications have reported the use of direct arylation in polymerization reactions.[5] Moreover, there are very few examples showing the coupling between thiophenes or thiophene derivatives by direct heteroarylation despite the fact that these moieties are particularly important monomers for plastic electronics.

In parallel, the thieno[3,4-*c*]pyrrole-4,6-dione (TPD) unit has become a building block of choice for the development of new conjugated polymers for organic solar cells (power conversion efficiencies up to 7.3 %)[6] and more recently, for organic field-effect transistors (hole mobilities up to 0.6 $cm^2 V^{-1} s^{-1}$).[7] Interestingly, the imide group may act as an orienting and activating group[8] for the hydrogen atoms at the 2- and 2′-positions (Scheme 1), and on this basis, this monomer could be a good candidate for direct heteroarylation polycondensation reactions.

Ultimately, by merging the advantages of plastic solar cells with new ecofriendly synthetic procedures, new opportunities for the production of green energy from green materials may emerge. The use of more environmentally friendly materials, which produce no tin by-products, could also show improved performance and stability. In this regard, our present work was devoted to the development of a catalytic system for the synthesis of TPD-based polymers using direct heteroarylation polycondensation reactions instead of the standard Stille cross-coupling reactions.

As shown in Scheme 1, **P1** was synthesized by both Stille and direct heteroarylation polymerization reactions. This copolymer is an analogue of other TPD-based copolymers recently reported as being used in highly efficient plastic solar cells[6c,9] and field-effect transistors.[7] Stille polymerization was carried out essentially following methods from those previous studies[6c] (yield of 71 % for the soluble fraction in chloroform). In agreement with polystyrene-calibrated size-exclusion chromatography (SEC) data reported for similar copolymers,[6c,7,9] Stille-polymerized **P1*** shows an M_n of only 9 kDa. This relatively low molecular weight might be related to the loss of some functional groups during the Stille polymerization. In parallel, for the preparation of **P1** using direct heteroarylation polycondensation reactions, several reaction conditions were tested (Table 1). The optimal reaction conditions were obtained with ligand **L1** and catalyst **1**. For the synthesis of **P1**, palladium acetate (**2**) is not as efficient as catalyst **1** and this is probably due to the higher thermal stability of the Herrmann catalyst.[5a] The temperature, time, solvent, and concentration were kept constant for this work and were based on general procedures reported in the literature.[3a–h,5a–c] A high M_n of 56 kDa (PDI of 2.6) with a yield of 96 % (soluble fraction in chloroform) was obtained when using catalyst **1** and ligand **L1** (Table 1, entry 1). Other examples of polymerizations of TPD-based monomers using the same catalytic system are shown in the Supporting

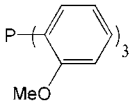


Scheme 1. Comparison of the Stille (**P1***) versus direct heteroarylation (**P1**) polymerization approach.

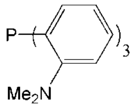
Table 1: Reaction conditions for the polymerization of **P1** by direct heteroarylation.

Entry	Cat (mol %)	**L** (mol %)	M_n [kDa]	PDI	DP
1[a] (**P1**)	**1** (4)	**L1** (8)	56	2.6	80
2[a] (**P1**)	**1** (4)	**L2** (8)	–[b]	–[b]	–[b]
3[a] (**P1**)	**1** (4)	**L3** (8)	–[c]	–[c]	–[c]
4[a] (**P1**)	**2** (4)	**L1** (8)	21	2.5	33
5[a] (**P1**)	**2** (5)	**L1** (15)	–[c]	–[c]	–[c]
6[a] (**P1**)	**2** (5)	**L1** (15)[d]	9	1.8	14
7 (**P1***)	[e]	[e]	9	1.5	14

[a] **P1** was synthesized by direct heteroarylation following the procedure described in the experimental section. [b] No polymerization reaction occurred. [c] All the reaction product was recovered with acetone Soxhlet extraction and no further characterization was made on these materials. [d] Reaction time was 44 h instead of 22 h. [e] **P1*** was synthesized by Stille cross-coupling following the procedure described in the experimental section. M_n = number-average molecular weight, PDI = polydispersity index, DP = degree of polymerization.



L1



L2

$PtBu_3HBF_4$ **L3**

Pd(OAc)(*o*-Tol) **1**

$Pd(OAc)_2$ **2**

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Information. To further characterize and compare these macromolecules, different analytical techniques were utilized. For instance, the UV/Vis absorption spectra of **P1** and **P1***
exhibit similar features (Figure 1 a) with an absorption maximum at 464 nm (**P1***) and 474 nm (**P1**) in a chloroform solution. This absorption maximum is in good agreement with previous data reported for similar alternating copolymers.[7,9]

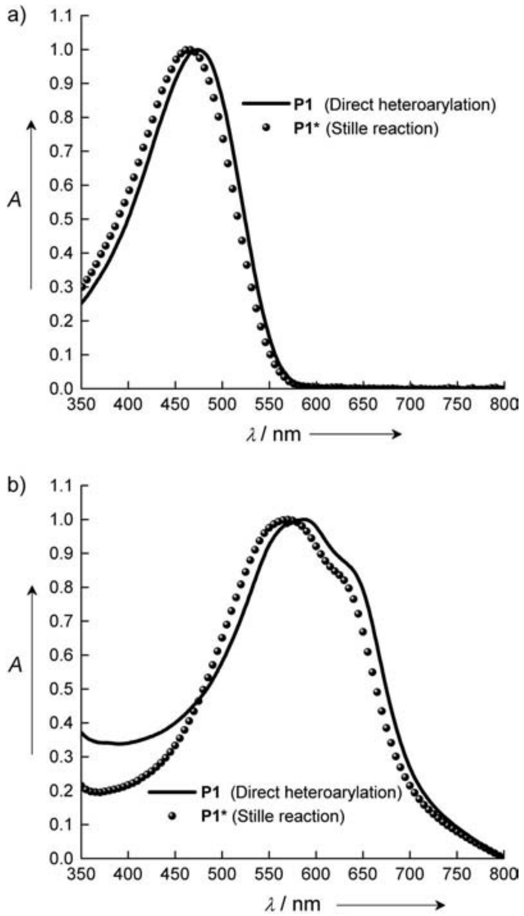

Figure 1. UV/Vis absorption spectra of **P1**(R1), and **P1***(R7) a) in a chloroform solution and b) in the solid state.

Moreover, the solid-state UV/Vis absorption spectra are also similar, showing a vibronic fine structure and a bandgap of about 1.75 eV (Figure 1 b). The absorption maximum of **P1** (586 nm) is red shifted by approximately 18 nm compared to **P1*** (568 nm). This small difference for the UV/Vis spectra could be explained by the different molecular weights and/or a slightly different morphology in the solid state.

The ^{1}H NMR spectra confirmed that both **P1** and **P1*** correspond to an alternating copolymer (Figure 2). These ^{1}H NMR spectra are similar to those reported by Marks and co-workers[7] for analogous polymers, which differed only by the alkyl side chains. As reported by these authors, different small peaks can be observed for **P1*** around 6.8–7.1, 3.5, and 2.7 ppm which might be due to end groups. Not surprisingly, such extra peaks are barely observed for the high molecular weight **P1** copolymer. Moreover, for both **P1** and **P1***, a small broad peak (with a relative integration of about 2 %) can be observed near 2.55 ppm, which may be tentatively related to some end groups and/or the presence of some bithiophene–bithiophene couplings (a side reaction), leading to so-called head-to-head couplings.[10] This extra and broad peak can also be observed in some ^{1}H NMR spectra reported by Marks and co-workers for similar copolymers.

To further validate the structural regularity of these alternating copolymers, thermal and X-ray analyses were also performed. The DSC thermograms of both **P1** and **P1*** present some well-defined crystallization and melting peaks (Figure 3). The enthalpies of crystallization (ΔH_c) and of melting (ΔH_m) are slightly higher for **P1** ($\Delta H_c = 16.4\ \mathrm{J\,g^{-1}}$ and $\Delta H_m = 15.4\ \mathrm{J\,g^{-1}}$) than for **P1*** ($\Delta H_c = 14.6\ \mathrm{J\,g^{-1}}$ and $\Delta H_m = 14.3\ \mathrm{J\,g^{-1}}$); this difference indicates a more important degree of crystallinity for **P1**. The higher melting point for **P1** also indicates a better stability of the crystal; this stability is probably related to the higher molecular weight. The X-ray diffraction patterns (see the Supporting Information) show the same features for both polymers, meaning that **P1** and **P1*** are similarly organized in the solid state. Consequently, the red-shifted solid-state optical spectrum of **P1** should be mainly related to a higher molecular weight. In conclusion, we showed that the direct heteroarylation polycondensation

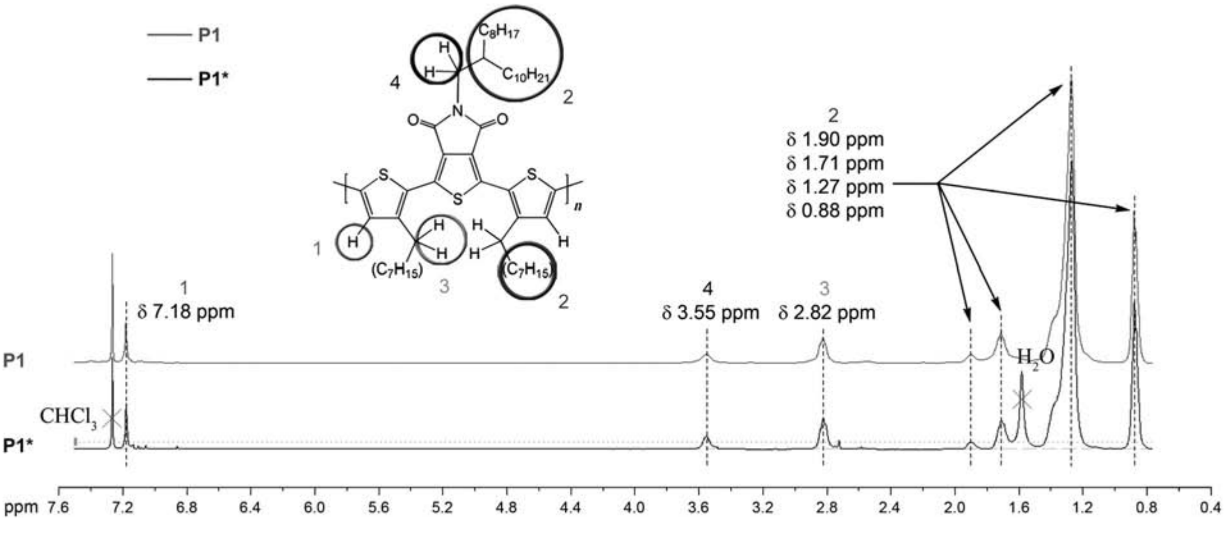

Figure 2. ^{1}H NMR spectra of **P1** and **P1*** in $CDCl_3$.

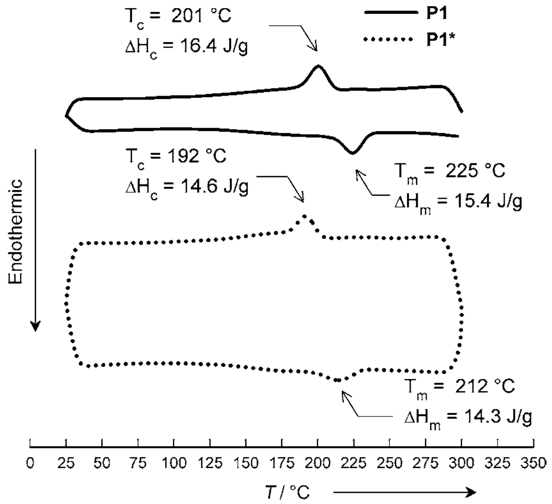

Figure 3. DSC curves of **P1** and **P1***.

reaction is a very promising method to synthesize high molecular weight conjugated polymers with high yields in a more environmentally friendly and faster way. Our future work will investigate the versatility of this polymerization reaction for the synthesis of other TPD-based polymers and their utilization in various electronic devices. Finally, the present results should stimulate the development of novel synthetic methods for electroactive and photoactive conjugated polymers.

Experimental Section

Polymerization procedure of **P1**: 5-(2-hexyldecyl)-5H-thieno[3,4-*c*]-pyrrole-4,6-dione (94.4 mg, 0.25 mmol), 5,5′-dibromo-4,4′-dioctyl-2,2′-bithiophene (128.1 mg, 0.25 mmol), catalyst (4% mol), ligand (8% mol) and Cs_2CO_3 (162.9 mg; 0.50 mmol) were put in a pristine Biotage microwave vial (vial size of 2 to 5 mL) with a magnetic stirring bar. The vial was sealed with a cap and then purged with nitrogen to remove the oxygen. Tetrahydrofuran (1 mL) was added and the reaction was heated with an oil bath at 120 °C (reaction under pressure). At the end of the reaction time, the reaction was cooled and the corresponding 5-alkyl[3,4-c]pyrrole-4,6-dione was added (50 mg dissolved in 1 mL of THF) as a capping agent. The solution was heated again at 120 °C for 1 hour to complete the end-capping procedure. After an additional hour of stirring, the whole mixture was cooled to room temperature and poured in 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 5 mL and the mixture was poured into cold methanol.

Polymerization procedure of **P1***: Experimental conditions were those reported by Wei et al. for similar copolymers.[9] 1,3-Dibromo-5-(2-hexyldecyl)-5H-thieno[3,4-*c*]pyrrole-4,6-dione (74.7 mg, 0.140 mmol), 4,4′-dioctyl-5,5′-bis(trimethylstannyl)-2,2′-bithiophene (100.0 mg, 0.140 mmol), $[Pd_2(dba)_3]$ (2.6 mg, 2% mol), and P(*o*-tolyl)$_3$ (6.8 mg, 16%) were put in a 15 mL round bottom flask then purged with N_2. Chlorobenzene (5 mL) was added and the mixture was stirred at 130 °C for 48 h. Then bromobenzene was added to the reaction and after 1 hour, trimethylphenyltin was also added as a capping agent. After an additional hour of reaction, the whole mixture was cooled to room temperature and poured in 500 mL of cold methanol. The precipitate was filtered, cleaned, and extracted as described above.

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