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Highlights

π-Conjugated Polymers

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Semiconducting Polymers Prepared by Direct Arylation Polycondensation

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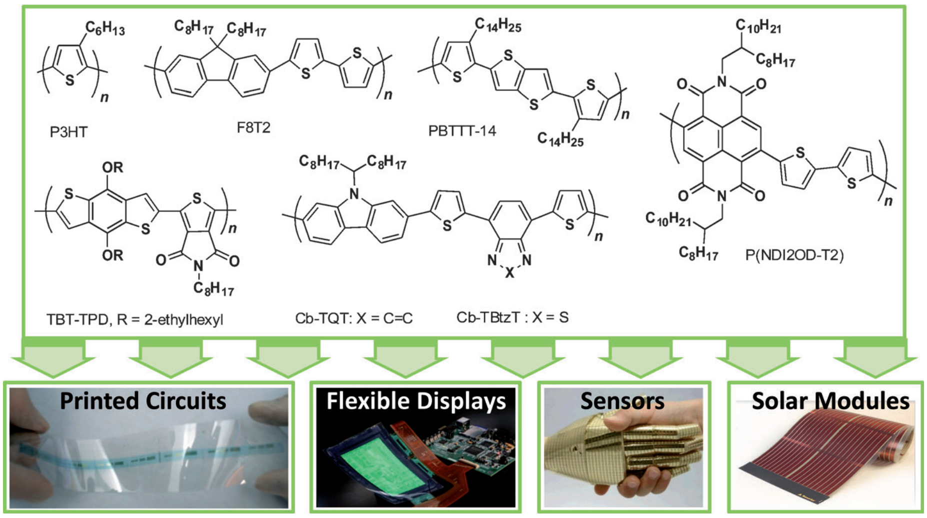
π-Conjugated polymers can be utilized for the fabrication of a variety of optoelectronic devices such as unipolar/complementary circuits, solar cells, light-emitting diodes and transistors, sensors, and displays.[1,2] These polymers are not expected to attain or exceed the performance level of established materials, but it may be possible to fabricate certain optoelectronic devices at lower cost (e.g., fewer processing steps, less waste, lower temperatures) and/or design completely new device functionalities (e.g., mechanical flexibility, impact resistance, optical transparency) which is challenging to achieve with (crystalline) silicon.[3] Organic semiconductors may also lead to a much better understanding of the nature of the electronic structure and charge-transport properties, as well as light–matter and charge–charge interactions in these materials.[4] Among the most important families of conjugated polymers in opto-electronics are those based on homo- and co-polymers of five-membered heterocycles such as poly(thiophene)s; fused (hetero)arenes such as poly(carbazole)s, poly(thienethiophene)s), poly(benzodithiophene)s, and poly(benzothiadiazole)s; and rylenes such as poly[naphthalenebis(dicarboxiimide)]s (Scheme 1). These materials have been synthesized mainly by metal-catalyzed step-growth polycondensation[5] and chain-growth polymerization.[6] Despite the great versatility and choices, these reactions have drawbacks such as numerous steps to monomer synthesis, instability of the organometallic reagents, and formation of stoichiometric amounts of toxic by-products.



Scheme 1. Examples of π-conjugated polymers and possible applications.

Direct arylation represents an economically attractive and ecologically benign alternative to the traditional cross-coupling methodologies[7] (Scheme 2). In these reactions, unfunctionalized (hetero)arenes are employed directly and coupled through C−H bond cleavage. However, since several C−H bonds exhibit comparable dissociation energies, the major challenge is enabling highly regioselective direct arylations for synthetically useful transformations. The re-

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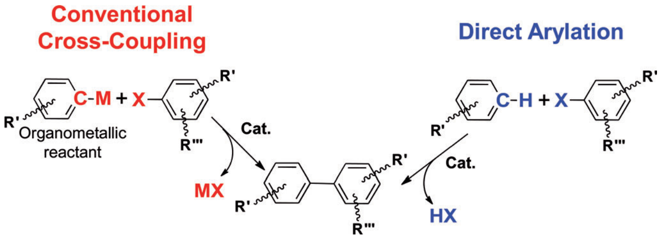


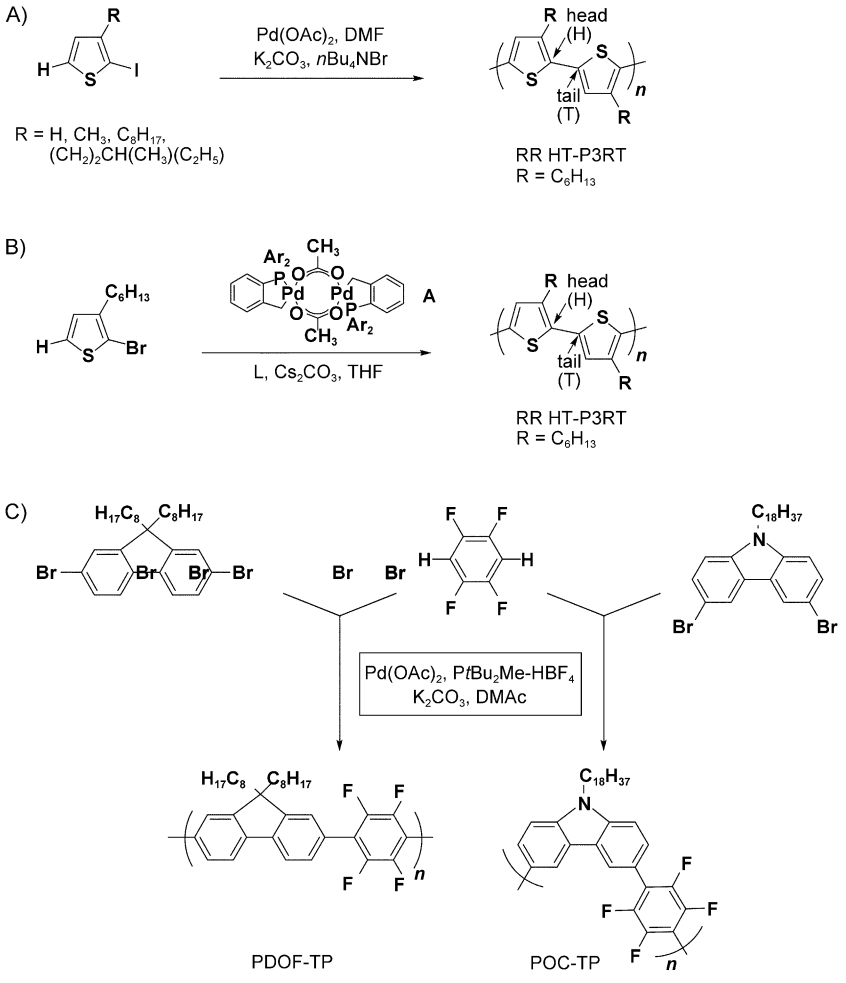
Scheme 2. Conventional cross-coupling versus direct arylation for the synthesis of π-conjugated polymers. M = SnR$_3$, B(OR)$_2$, MgX, ZnX, Cu, etc.; X = Cl, Br, I, OSO$_2$R.

gioselectivity of direct arylation can be controlled when the electronic structure of a given arene substrate dictates its reactivity. Several (hetero)arenes exhibit preferential reactive positions, and this was exploited in the highly regioselective metal-catalyzed direct functionalization of both electron-rich and electron-poor arenes. However, reactions of electronically unbiased arenes are often nonselective, yielding undesired mixtures of regioisomers, which are often difficult to purify. This is particularly critical for polycondensations aiming at the synthesis of regioregular π-conjugated polymers (see below) since just a few backbone defects can greatly compromise their electronic structure and solid-state properties.

To date, there have been very few studies addressing the use of direct arylation for the synthesis of π-conjugated polymers (Scheme 3).[8] Lemaire and co-workers[8a] reported the direct arylation/polycondensation of four thiophene derivatives affording the corresponding poly(3-alkylthiophene)s (P3RTs; Scheme 3 A). The general procedure consisted of reacting the 2-iodothiophene derivative with catalytic amounts of Pd(OAc)$_2$ and equimolar amounts of tetrabutylammonium bromide and K$_2$CO$_3$ as base in DMF at 80 °C. In all cases, the polymers were obtained in good yields although the molecular weights were low ($M_w \approx 6000$ polydispersity index (PDI) ≈ 2, degree of polymerization (DP) ≈ 15). For the P3RTs, the ^{1}H NMR resonance at 6.98 ppm indicates the degree of head-to-tail regioregularity (RR HT), and although some additional signals were observed in the aromatic region, the authors claimed that they had achieved RR HT-P3ARTs.

Ozawa et al.[8b] successfully polymerized 2-bromo-3-hexylthiophene to P3HT (R = hexyl) using Herrmann's catalyst **A** and tris(2-dimethylaminophenyl)phosphine as catalyst precursors (Scheme 3 B); RR HT-P3HT was obtained with high molecular weight ($M_n = 30600$, $M_w/M_n = 1.60$) and high regioregularity (98 %) in quantitative yields (99 %).

Kanbara et al.[8c] focused on the Pd-catalyzed direct arylation in the polycondensation of 1,2,4,5-tetrafluorobenzene with 2,7-dibromo-9,9-dioctylfluorene (or 3,6-dibromo-*N*-octadecylcarbazole), which was carried out in the presence of Pd(OAc)$_2$ (5 mol %), a phosphine ligand (10 mol %), and K$_2$CO$_3$ (2 equiv) in DMA (Scheme 3 C). Under these conditions, high-molecular-weight PDOF-TP (or POC-TP) was obtained in a single step (M_n = 17600–31500 or 8300). The polycondensation providing PDOF-TP was carried out under various conditions. For the ligand of the catalytic system, P*t*Bu$_2$Me/HBF$_4$ was found effective, whereas the catalytic system without the added phosphine ligand or with P*t*Bu$_3$/HBF$_4$ and 2-dicyclohexylphosphino-20,60-dimethoxybiphenyl (S-Phos) did not promote the reaction. A decreased catalyst amount (2.5 mol %) gave a low yield. The solvent

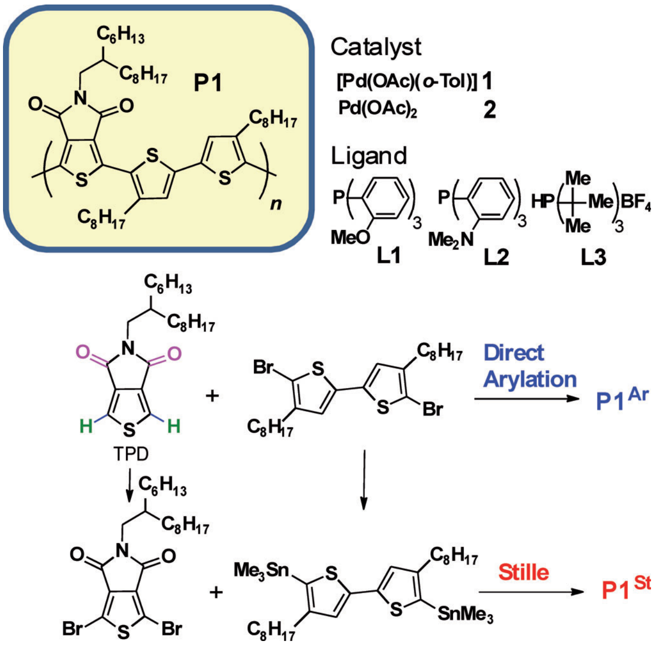


Scheme 3. Previous syntheses of π-conjugated polymers by direct arylation. L = various aryl phosphine ligands.

effect was also examined and no polymeric product was obtained in toluene or 1,2-dichlorobenzene. Considering yield and molecular weight of the polymer, DMA is the best solvent for this polymerization. The polycondensation time was tested from 6 h to 48 h, and 24 h was found to be the optimal.

The Leclerc group has been leading the research in π-conjugated polymers for applications in solar devices and transistors.[9] Among others, this team explored a thieno[3,4-*c*]pyrrole-4,6-dione (TPD)[10] in combination with an alkoxybenzodithiophene (TBT) to synthesize the very interesting copolymer TBT-TPD (Scheme 1) by Stille coupling.[11] TPD is a very simple, easy-to-synthesize compound with a planar core, and TBT-TPD can be used in solar cells with a power conversion efficiency (PCE, a metric for OPV performance) of roughly 5.5 %. Other interesting copolymers were obtained by polycondensation of 2,7-carbazole derivatives with quinoxaline (Cz-TQT) or benzothiadiazole (Cb-TBtzT; Scheme 1).[12]

Recent work from the Leclerc group has focused on the development of direct heteroarylation polycondensations for the synthesis of a TPD-based polymer (**P1**, Scheme 4).[13] The TPD monomer was selected because of the excellent performance of the corresponding polymers in both solar cells (PCEs up to 7.3 %)[1] and field-effect transistors (hole mobilities up to 0.6 $cm^2V^{-1}s$);[14] in addition the imide group may act as an orienting and activating group[15] for the C–H bonds. To prove their concept, the authors synthesized polymer **P1** by both Stille (**P1**St) and direct heteroarylation (**P1**^{Ar}) polymerizations (Scheme 4). The Stille reaction was carried out under previously described conditions (71 % yield)[13] and an M_n of approximately 9 kDa was determined by size-exclusion chromatography (polystyrene standard). **P1**^{Ar} was synthesized under several different sets of reaction conditions (Scheme 4) and the optimal results were obtained with ligand **L1** (8 mol %) and catalyst **1** (4 mol %). A high M_n of 56 kDa (PDI = 2.6) and a yield of 96 % were obtained.



Scheme 4. Chemical structure of **P1** and corresponding synthesis investigated by Leclerc et al. In the TPD structure the orienting groups are in pink and the activated hydrogen atoms are in green.

The two polymers were characterized by optical absorption, ^1H NMR spectroscopy, thermal analysis, and thin-film X-ray diffraction. Their UV/Vis absorption spectra exhibit similar features with an absorption maximum at 464 nm (**P1**St) and 474 nm (**P1**^{Ar}) in $CHCl_3$. Moreover, the solid-state UV/Vis absorption spectra are also similar, showing a vibronic fine structure and a bandgap of about 1.75 eV. The ^1H NMR spectra are similar to those reported previously,[13] only differing for the alkyl side chains. To further validate the structural regularity of these alternating copolymers, thermal and X-ray analyses were also performed. The differential scanning calorimetry (DSC) thermograms of both polymers exhibit well-defined exothermic (crystallization) and endothermic (melting) transitions. The enthalpies of crystallization (ΔH_c) and of melting (ΔH_m) are slightly higher for **P1**^{Ar} ($\Delta H_c = 16.4\ J\,g^{-1}$ and $\Delta H_m = 15.4\ J\,g^{-1}$) than for **P1**St ($\Delta H_c = 14.6\ J\,g^{-1}$ and $\Delta H_m = 14.3\ J\,g^{-1}$) indicating greater crystallinity for **P1**^{Ar}. The higher melting point for **P1**^{Ar} also indicates greater solid-state stability, probably a consequence of the higher molecular weight. The XRD diffraction patterns show the same features for both polymers, meaning that **P1**^{Ar} and **P1**St are similarly organized in the solid state. Consequently, the red-shifted UV/Vis spectrum of **P1**^{Ar} was related to a higher molecular weight, indicating that this synthetic method can also lead to an increase in polymer molecular weight.

In conclusion, the work of Leclerc et al. demonstrates that direct arylation polycondensations can be used to synthesize important π-conjugated homo- and copolymers. Fundamental questions remain on how to address selectivity and regioregularity in the reactions of a broader range of monomers lacking directing groups. However, this study opens new possibilities for the efficient, sustainable synthesis of semiconducting polymers which will facilitate the entrance of these materials into the optoelectronic market.

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