

Polycondensation of thiophene-flanked cyanopyridine and carbazole via direct arylation polymerization for solar cell application

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ABSTRACT

In this work, we report the synthesis of new π -conjugated polymer designs through the polycondensation of 2-(octyloxy)-4,6-di(thiophen-2-yl)nicotinonitrile (**M1**) and 3,6-dibromo-9-octyl-9H-carbazole (**2a**) or 3,6-dibromo-9-hexadecyl-9H-carbazole (**2b**) via palladium-catalysed direct arylation polymerization (DARp) reaction for solar cell application. The DARp reactions were carried out in three major solvents (i.e. toluene, dimethylformamide (DMF), and dimethylacetamide (DMA) with triphenylphosphine (as ligand), and K_2CO_3 (as base), respectively. Polymerization reaction conditions were carefully optimized with and without the addition of pivalic acid (PivOH) as additive. Interestingly, the polymer synthesized in PivOH and DMA solvent under the aforementioned reaction conditions yielded the considerably high molecular weight (M_n) of 21.1 kDa and PDI of 1.14 than the rest of polymeric reactions conditions. Thus, DARp reaction under $Pd(OAc)_2$, PPh_3 , K_2CO_3 , PivOH and DMA conditions were found to be the ideal reaction conditions for the current monomeric systems. The synthesized polymer was used for photovoltaic studies and with the minimum optimization the obtained power conversion efficiency is reported.

1. Introduction

New π -conjugated polymers possessing enhanced solubility in common organic solvents with wide range of light harvesting properties are of high demand for the organic field effect transistors (OFETs) [1], organic light emitting diodes (OLEDs) [2,3], and organic photovoltaic (OPVs) [4]. In fact, the polymers as semiconductors have advantages like ease of processability, high thermal/photo-stability, and good charge transport properties. Conventionally, the conjugated polymers were synthesized via Suzuki–Miyaura and Migita–Kosugi–Stille cross coupling reactions wherein, the reaction requires the use of expensive organoboron or organotin compounds as monomers [5,6]. On the other hand, direct arylation polymerization (DARp) is a more facile and environmentally friendly method for the cross coupling of aryl-aryl C–C bond formation. Additionally, DARp has an advantage over other conventional synthetic methods like Stille and Suzuki reactions: neither, it requires the use of unstable organometallic intermediates nor it requires the secondary processes to remove the formed toxic by-products that can ultimately affect the device performance. Further, DARp is an

atom economical method of synthesis which precludes the use of toxic intermediates and affords high molecular weight polymers [7–9]. Furthermore, polymers synthesized in this method rivals material synthesized through traditional methods due to rampant mechanism caused because of unselective C–H bond cleavage [10,11]. Success of DARp synthesis mainly depends on designing the monomers for C–H bond selectivity for the polymerization and to preclude the insoluble branched polymers which is ubiquitous in DARp method.

In the literature, polycondensation of 2,7-dibromo-N-octadecylcarbazole with 1,2,4,5-tetrafluorobenzene produced an insoluble and cross linked polymeric products [12]. The formation of the cross-linking structures is due to the high reactivity of the C–H bonds at the 3- and 6-positions in the carbazole derivatives and direct arylation reaction likely occurred at these C–H bonds as well as at the C–H bonds of 1,2,4,5-tetrafluorobenzene. In contrast, the polycondensation reaction of 3,6-dibromo-N-octadecylcarbazole with 1,2,4,5-tetrafluorobenzene resulted in poly[(N-octadecylcarbazole-3,6-diyl)-(2,3,5,6-tetrafluoro-1,4-phenylene)], which was soluble in organic solvent. The improved solubility of polymer is due to the formation of relatively low cross-

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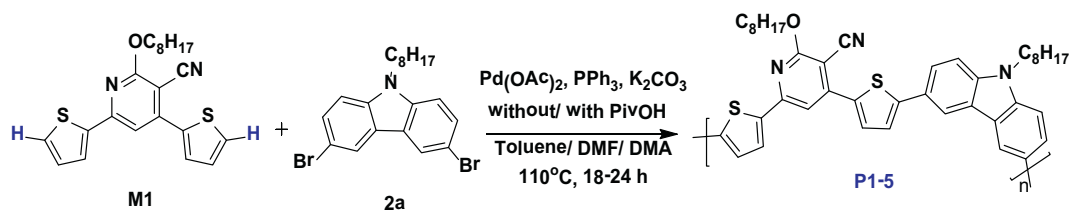
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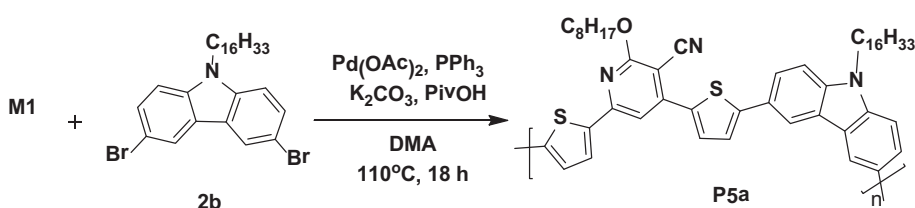


Scheme 1. Preparation of polymers (P1–5) from M1 and 2a via DARp reaction.

Table 1

Effect of ligand, additive, base and solvents on polycondensation reaction.^a

Entry	Polymer	Solvent/base	Ligand	Additive	Time	Yield ^c	M _n ^b (Da)	M _w /M _n
1	P1 ^d	Toluene/K ₂ CO ₃	PPh ₃	–	24 h	–	–	–
2	P2	DMF/K ₂ CO ₃	PPh ₃	–	24 h	72%	2073	1.74
3	P3	DMA/K ₂ CO ₃	PPh ₃	–	24 h	75%	5071	3.50
4	P4 ^e	DMA/K ₂ CO ₃	PPh ₃	PivOH	24 h	70%	2863	1.71
5	P5	DMA/K ₂ CO ₃	PPh ₃	PivOH	18 h	85%	21,095	1.14
6	P5a	DMA/K ₂ CO ₃	PPh ₃	PivOH	18 h	83%	14,224	1.93

^a Reactions were carried out at 110 °C by using Pd(OAc)₂ (5 mol%), ligand (10 mol%), PivOH (0.3 eqv) and base (2 eqv).^b Measured by GPC with polystyrene as standard.^c The yields after precipitation from CHCl₃-MeOH.^d No precipitate in MeOH.^e With 2.5 mol% Pd(OAc)₂.

Scheme 2. Polycondensation of polymer P5a.

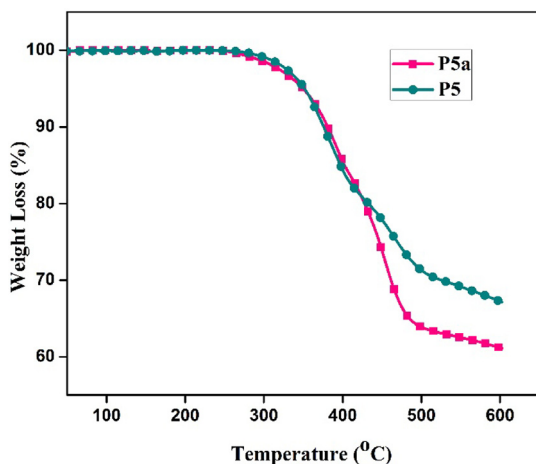


Fig. 1. Thermograms of P5 and P5a.

linked products. This is because of the unavailability of active C–H bonds at the 3- and 6-positions of 3,6-dibromo-N-octadecylcarbazole. Thus, the possibility of side reactions in the 3,6-dibromo-N-octadecylcarbazoles are considerably suppressed over the side reactions in the 2,7-dibromo-N-octadecylcarbazoles. In addition, certain 3,6-dibromocarbazole derivatives were reported to be more selective towards DARp reactions and produced the good organic solvent soluble polymers [9,13]. On the other hand, it is reported that some of the pyridine motifs reacts poorly towards DARp reaction due to its low reactivity and selectivity for the C–H arylation [14]. [15–17] In addition, substituting the pyridine with electron acceptor moieties enhances the reactivity of

Table 2

Optical properties of P5 and P5a.

Polymer	Solution state		Film state		
	λ _{max} (nm)	λ _{em} (nm)	λ _{max} (nm)	λ _{max} ^{onset} (nm)	E _g ^{opt} (eV) ^a
P5	275,430	520	470	613	2.02
P5a	275,425	515	440	564	2.19

^a Calculated with onset edge of absorption spectra of film.

the molecule and especially cyano (-CN) substitution at 3-position influences pyridine towards direct arylation reaction [14,18,19]. 3-cyanopyridine is an asymmetric moiety which induces a twisted nature to the target molecule and this leads to interesting photophysical behaviour such aggregation in the solid state [20,21].

Against this background, two thiophene units were attached at position –4 and –6 of 3-cyanopyridine during the design of 2-(octyloxy)-4,6-di(thiophen-2-yl)nicotinonitrile (M1) monomer to achieve better reactivity and selectivity for the C–H arylation. In this design, the proton at the C-5 position of thiophene rings are more acidic as these rings connected by the electron deficient 3-cyanopyridine [20] moiety, which makes the monomer more selective for DARp reaction.

In this work, we have investigated the DARp reaction of diligently designed 2-(octyloxy)-4,6-di(thiophen-2-yl)nicotinonitrile (M1) and 3,6-dibromo-9-octyl-9H-carbazole (2a) or 3,6-dibromo-9-hexadecyl-9H-carbazole (2b) monomers through varied reaction conditions like catalyst, additive, ligand, base and solvent to obtain donor-acceptor (D-A) copolymer. This systematic optimization of reaction conditions would assist in controlling the growth of polymerization reaction as well as to acquire least structural defects and good solubility in organic

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