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Interdigited π-stacked low band gap polymers through Friedel Crafts post functionalization of Suzuki coupled phenylene-*alt*-thiophene copolymers

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ABSTRACT

Friedel Crafts post functionalization, a new molecular engineering approach, is experimented on structures of two semiconducting polymers (i.e., 1,4-dihexyloxy and dioctyloxy-phenylene-*alt*-thiophene copolymers) obtained through Suzuki cross coupling reaction to increase molecular weight and lowering of band gap. This unique post treatment demonstrates two and half fold increase of molecular weight and significant reduction of band gap (1.8–1.5 eV); the pre-functionalized value is above 2 eV. AFM and SEM micrograph before and after post functionalization show a clearer, smoother, more compact and interconnected biphasic nanostructure for post functionalized polymers in solid state. Significant red shifting of absorption onset ($\Delta\lambda_{absonset} \approx 85$–$210$ nm) and emission peak maxima ($\Delta\lambda_{em.max} \approx 175$ nm) at solid state is attributed to the formation of more rigid planar interdigited π-stack 3D structure. Exfoliation of polymers layers to single polymer wire in polar solvent is clearly demonstrated by comparing the photophysical properties in solid and solution.

1. Introduction

Molecular engineering on structures of π-conjugated semiconducting polymers is one of the interesting current research areas to produce soluble, processable materials possessing enhanced electrical conductivities and optical properties to be used as a potential alternative to inorganic semiconductor for low cost optoelectronic and photovoltaic devices [1–5]. Key issues associated with the development of organic semiconducting polymers are their poor air stability and high band gap compared to metals. Stability of organic semiconducting polymers towards oxidative doping is related to their ionization potential, i.e., their highest occupied molecular orbital (HOMO) levels in vacuum and lowering of HOMO energy level improves stability. Greater environmental stability can be achieved by a number of methods; reducing effective conjugation length to inhibits delocalization, copolymerizing thiophene with fluorenes [6] and incorporating thieno [2,3-bis] thiophene [3] or naphthalene unit [7] into polymer backbone. Very little information are available on polythiophene having electron withdrawing substituent (reduce HOMO energy level), presumably due to their difficulty in synthesis [8,9]. Polythiophenes with electron withdrawing ester group attached at the 3-position, namely poly (alkyl thiophene-3-carboxylates) have been synthesized by the Pomerantz group using Ullmann [10,11]/Kumada coupling reaction [12]. Introduction of electron donating groups, such as alkoxy or alkythio group, at β-position of thiophene unit also lowers the HOMO level [13].

The photoluminescence (PL) and PL quantum efficiency of the polymers can be improved by inserting suitably substituted phenylene rings into the backbone of polythiophene [14] and thus, introducing 2,5-dioctyl phenylene groups at 2- and 5-position of thiophene rings enhances PL efficiencies from 3 to 24% [15,16]. This large side chain in phenylene–thiophene oligomer form useful light emitting layer in OLEDs, organic laser diodes [17], and organic thin film transistors (OTFTs) [18]. Nature of the substituted group generally affects the electronic and optical properties of the conjugated polymers in two ways [19]; the electronic feature and steric hindrance arising from the substituted group. It has been demonstrated both experimentally and theoretically that alkyl side chains do not take part in the delocalization of π-bonds, but their steric hindrance could induce considerable inter-ring twisting, giving rise to a substantial reduction of the polymer conjugation length. The increase of torsional angles between aromatic rings results spectral blue shift in absorption [20]. Presence of two alkoxy chain at 2- and 5-positions of the phenylene ring, on the other hand, induces spectral red shift of the same polymers [21,22] owing to their strong electron-donating characteristic and less steric hindrance compared to alkyl substituents. Theoretical work suggest that the effective optical gap (π–π* transition) of the copolymer composed of alternative low (thiophene units) and high (phenylene units) band gap materials is the weight average band gap value of the contributing units [23]. Experimental observation records a

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shift towards higher energy by 20–40 nm of the absorption maxima in dilute chloroform solution on inserting a single phenylene unit in 5-ring copolymer compared to pristine thiophene analogs [24].

Phenylene–thiophene oligomer was first introduced in 1999–2000 by Hotta and Lee [25]. Synthesis of phenylene–thiophene oligomer/polymers employing Suzuki coupling reaction are sensitive to several reaction parameters and generally yields low molecular weight (high band gap) materials [26]. Post polymerization functionalization of Suzuki polymers may be a useful approach to increase molecular weight. This also enables reduction of band gap and incorporation of newer properties in developed materials. In classical organic synthesis, Friedel Craft post functionalization employing oxalyl chloride and anhyd. $AlCl_3$ (cyclizing reagent) is extensively used to synthesize new cyclic hydrocarbon combining two aromatic rings [27–29]. Other lewis acid e.g., polyphosphoric acid [30], trichloroacetic anhydride [31], bismuth (III) [32] have also been used in several cases.

The present article reports the synthesis of 2,5-dialkoxy phenylene-*alt*-thiophene copolymers by Suzuki cross coupling reaction and their Friedel Craft post functionalization using oxalyl chloride and anhyd. $AlCl_3$. This unique and important post treatment has several interesting implications in developing properties which otherwise difficult to achieve in final products. Bulky alkoxy group and low reactivity of phenyl ring makes it difficult to yield high molecular weight polymers through simple Suzuki cross coupling reaction. Friedel Craft post functionalization can be a viable alternative to increase the molecular weight. Presence of electron withdrawing group (e.g., naphtho [1,2-b] thiophene-4,5-dione) substantially reduces the reactivity and the polymerization will be difficult in these monomers. Post functionalization provides a viable alternative to incorporate this electron withdrawing group in polymers. Stabilization of interdigited π-stacked layer structure through dipolar interaction enhances 3D planarity in solid state and significantly reduce band gap of post functionalized polymers.

2. Results and discussion

2.1. Synthesis

2,5-Dialkoxy phenylene-*alt*-thiophene copolymers synthesized by Suzuki cross coupling reaction [33,34] of 2,5-thiophene bis boronic acid and diiodo dialkoxy benzene are outlined in Scheme 1. In a typical synthesis, 1,4-dihydroxy benzene is reacted for 24 h with alkyl halides at refluxing condition in presence of base to form 1,4-dialkoxy benzene (**A**). Treatment with I_2/KIO_3 converts (**A**) into 2,5-diiodo 1,4-dialkoxy benzene (**B**). Suzuki cross coupling reaction of 2,5-thiophene bis (boronic acid) (**C**) and diiodo dialkoxy benzene (**B**) in the presence of $Pd(OAc)_2$ catalyst produces phenylene-*alt*-thiophene copolymers in good yield. Two different 2,5-dialkoxy, i.e., hexyloxy and octyloxy, phenylene-*alt*-thiophene polymers (now referred as Suzuki polymers **P-1** and **P-2**), are synthesized employing similar reaction conditions. The crude polymers dissolved in chloroform are re-precipitated from excess of methanol (non solvent, repeated three times) yielding colored powder materials.

Friedel Craft post functionalization is carried out using excess of oxalyl chloride and anhyd. $AlCl_3$ (Scheme 1). Use of excess oxalyl chloride and anhyd. $AlCl_3$ execute two typical events; intramolecular cyclization [29,35] of the thiophene-phenylene rings yielding naphtho [1,2-b] thiophene-4,5-dione and also combines two such repeat units through oxalyl spacer. In a typical synthesis, CS_2 solution of poly [2,5-bis (alkyloxy) phenyl-*alt*-thiophene] was added slowly in drop wise manner to the CS_2 solution of oxalyl chloride under nitrogen atmosphere. After complete addition of polymer, anhyd. $AlCl_3$ was then added to the stirring reaction mass. The reaction mixture was stirred at room temperature for 14 h to complete the reaction. The crude concentrated reaction mass (under reduced pressure on rotary evaporator) was then poured into cold methanol to obtain solid precipitate and washed several times with methanol to get the Friedel Craft post functionalized product (now referred as post functionalized polymers **PF-1** and **PF-2**).

2.2. Product integrity and structure identification

The poly-condensation via palladium cross-coupling is very sensitive to purity of the precursors [36] and any deviation may drop molecular weights of the polymers drastically. Lot of other parameters also influence the Suzuki cross-coupling reaction and polymers characteristics [37], such as, the choice of palladium source and its associated base, the solvent, the nature of boronic substituent, and the temperature used during the reaction. The Suzuki cross-coupling poly-condensation involving 1,4-dibromo 2,5-dialkoxyphenylene and thiophene 2,5-bis boronic acid monomer were carried out in $THF/H_2O/EtOH$ under nitrogen using $Pd(OAc)_2$ catalyst and a weak base (potassium carbonate). Attention was paid to maintain the absolute oxygen-free conditions and strict stoichiometry of the co-monomers, as the first one poisoning the Pd complex and the second one dramatically decreasing the molecular weight of the polymer. GPC analysis determines the average molecular weight (M_w and M_n) and poly-dispersity index (PDI) of as-obtained Suzuki copolymers and estimates more than two folds increase of molecular weight on Friedel Craft post functionalization reaction. Thus, the molecular weight of octyloxy copolymer (**P-2**, $M_w \approx 8063$) is increased to about 2.5 folds ($M_w \approx 18{,}544$) on Friedel Craft post treatment (Table 1). Suzuki copolymers (**P-1** and **2**) are reddish yellow crystalline solid soluble in organic solvents (like $CHCl_3$, THF, etc.), whereas post functionlalized polymers (**PF-1** and **2**) are brown color powder materials with sparing solubility in THF, DMSO.

The structures of Suzuki copolymers and post functionalized polymers are elucidated through spectroscopic techniques. FT-IR spectroscopy gives interesting information on the nature of the atoms and bonds present in molecule or in polymer. The IR spectrum of copolymer resulting from the coupling between two different precursors **B** and **C** should contain the information on each precursor. The characteristic vibration modes of the iodine in phenylene (**B**) and boronic acid substituent of thiophene precursors (**C**) are of interest, since their signature is expected to disappear in the spectra of the corresponding copolymers. The iodine substituent of phenylene unit gives a stretching vibration mode around 500 cm^{-1}. The diboronic acid of thiophene gives three significant vibrations at 750, 1497, and 3338 cm^{-1}, corresponding to the O–B–O scissoring, B–O asymmetrical stretching, and O–H stretching vibration modes, respectively [26]. All these characteristic vibrations are clearly absent in their corresponding copolymers. Importantly, the characteristic C–O–C stretching vibration peaks of alkoxy groups at around 1275 and 1081 cm^{-1} is still present in the Suzuki copolymers (**P-1** and **2**). To study the structural changes occurring during Friedel Craft post functionalization, the IR spectra of the Suzuki polymers before and after post function are recorded. The typical FTIR spectra of Suzuki copolymers (**P-1** and **2**) and post functionalized polymers (**PF-1** and **2**) are presented in Fig. 1. C–O–C stretching vibration peaks of alkoxy groups in copolymers (**P-1** and **2**) appeared at 1277 cm^{-1} and 1036 cm^{-1} are slightly shifted in post functionalized polymers (**PF-1** and **2**) to 1259 cm^{-1} and 1060 cm^{-1} respectively. The aliphatic C–H stretching peak of CH_2 alkyl group observed around 2922 cm^{-1} in Suzuki copolymers is also shifted in post functionalized product and appears at around 2962 cm^{-1}. Never the less, appearance of these peaks support the retention of