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A novel class of *ortho*, *para*-alternating linked polyarenes is synthesized via catalyst-transfer Suzuki coupling polymerization with $Pd_2(dba)_3$/*t*-Bu_3P/*p*-BrC_6H_4COPh as initiator. Through a series of kinetic studies and MALDI-TOF analysis, the polymerization is shown to proceed in a chain-growth manner. The optical and thermal properties for the *ortho*, *para*-alternating linked polyarenes exhibit unusual molecular weight dependence. Thus, the polymer with lower molecular weight (*M*n = 6300 g/mol) emits green fluorescence whereas the one with higher molecular weight (*M*n = 13800 g/mol) emits blue fluorescence under UV (λ = 360 nm) irradiation. Furthermore, an all-conjugated block copolymer containing a polyfluorene block and the *ortho*, *para*-alternating linked block is also successfully prepared, in a one-pot procedure. These results can provide a pathway to obtain polyarenes with precisely controlled structures, hence, desirable properties.

Introduction

Polyarenes have been well investigated over the past decade because of their potential applications in optical sensors, electrochromic devices, organic solar cells and field effect transistors.[1-2] Although the study of polyarenes has long been focused on *para*-linked polyarenes, *ortho*-linked polyarenes have recently attracted more and more attention.[3-5] Unlike the rigid-rod conformation of *para*-linked polyarenes, *ortho*-linked polyarenes can twist to form numerous orientations along the backbone and even adopt a stable helical conformation.[6-10] Due to the unique twisted structure, *ortho*-linked polyarenes show distinctively different optoelectronic properties, and accordingly constitute a different class of functional polymers from *para*-linked polyarenes. For example, *ortho*-linked polyarenes can act as surface modifiers for homeotropic columnar ordering of discotic liquid crystals[11] and exhibit selective reflection of right-handed circular polarized light (CPL) in the visible region after annealing.[12] Furthermore, the *ortho*-linked polyarenes are also considered as good precursors for soluble, structurally precise graphene nanoribbons.[13-14]

The highly angled *ortho* connections in these *ortho*-linked polyarenes lead to strong repulsive forces that make production of these polymers difficult, limiting their availability for applications. Accordingly, a significant amount of attention has been given to the exploration of synthetic routes such as multiple successive insertion reactions of 1,2-diiso-cyanoarenes,[15] polymerization of aryne or aryne equivalent[16-17] and benzannulation of poly(phenylene ethynylene)s.[18-19] Despite successful syntheses of some *ortho*-linked polyarenes, these pioneering works often suffer from shortcomings, including limited monomer selection, low molecular weight and broad polydispersity index (PDI). Thus, a robust synthetic method for *ortho*-linked polyarenes is still highly desired. Palladium- or nickel-catalyzed coupling polymerization has been widely employed for the synthesis of *para*-linked polyarenes using a variety of aromatic monomers.[20] In contrast, this method has rarely been applied to the synthesis of *ortho*-linked polyarenes due to the poor cross-coupling efficiency during the polymerization.[21-22] We reasoned that cross-coupling polymerization through an intramolecular catalyst transfer mechanism, which turns a sterically-hindered intermolecular oxidative addition step to a more favorable intramolecular one, may improve the cross-coupling efficiency.[23-24] Based on this hypothesis, we reported the first example for the synthesis of *ortho*-linked poly(5-alkyl-2,3-thiophene)s through a catalyst transfer Suzuki coupling polymerization.[25] The *ortho*-linked poly(5-alkyl-2,3-thiophene)s could be obtained in up to 60 repeat units. Furthermore, the polymerization was found to proceed in a chain-growth manner, affording the polymer with tunable molecular weight, narrow PDI, and well-defined end groups. In the present work, we describe the application of this catalyst transfer Suzuki coupling polymerization to a strategically designed aromatic monomer for the controlled synthesis of *ortho*, *para*-alternating linked polyarenes. We also investigated the molecular weight related photochemical properties of the resulting *ortho*, *para*-alternating linked polyarenes. In addition, an all-conjugated block copolymer containing a polyfluorene block and the *ortho*, *para*-alternating linked block was successfully prepared in a one-pot procedure.

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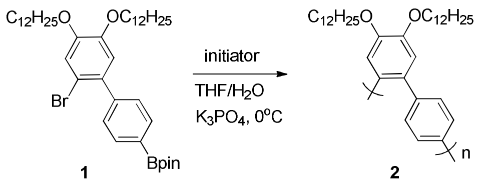
Results and discussion

Our study began with the synthesis of the desired monomer. To prepare the target *ortho*, *para*-linked aromatic polymers, monomer **1,** containing a biphenyl core, has been designed and prepared through four steps from commercially-available starting materials in gram scale quantities (See SI for details). The bromide was designed to be connected to the more electron rich phenylene and the boronic acid pinacol ester at the adjacent phenylene, since the intramolecular catalyst transfer is more favorable when proceeding from relatively electron poor to relatively electron rich arylenes.[26] The structure of monomer **1** was determined by NMR and high resolution mass spectrometry (HRMS). With the monomer **1** in hand, we then shifted our attention toward polymerization. Although catalyst-transfer coupling polymerization has been reported for the preparation of many homo-aromatic polymers including polythiophenes,[27] polyphenylenes[28] and polyfluorenes,[29-30] preparation of alternating copolymers via controlled manner is still challenging due to the longer intramolecular catalyst transfer distance.[31-35] After conducting a brief survey, the polymerization was found to proceed smoothly using several initiator systems, with the combination of $Pd_2(dba)_3$/*t*-Bu_3P/*p*-BrC_6H_4COPh providing the best result.[36] Thus, the polymerization was performed with potassium phosphate as base, a mixture of THF and water as solvent, and the combination of $Pd_2(dba)_3$/*t*-Bu_3P/*p*-BrC_6H_4COPh as initiator, affording polymer **2** with a molecular weight of 7000 and a PDI of 1.16 (see Table 1, entry 4). For application purposes, the polymerization was next performed at gram scale and afforded polymer **2** with molecular weight of 6600 and a PDI of 1.15 (Table 1, entry 6). The obtained *ortho*, *para*-linked polyarene **2** is soluble in common organic solvents such as chloroform, dichloromethane, tetrahydrofuran, and toluene.

Table 1 Suzuki cross-coupling polymerization of monomer **1**



Entry[a]	initiator	Yield (%)[b]	M_n[c]	PDI[c]
1	PEPPSI-IPr	77	12 000	1.27
2	$Pd_2(dba)_3$/t-Bu_3P/p-BrC_6H_4OTf	70	18 000	1.42
3	$Pd_2(dba)_3$/t-Bu_3P/p-$BrC_6H_4CH_2OH$	70	14 000	1.30
4	$Pd_2(dba)_3$/t-Bu_3P/p-BrC_6H_4COPh	83	7 000	1.16
5[d]	$Pd_2(dba)_3$/t-Bu_3P/p-BrC_6H_4COPh	80	13 500	1.22
6[e]	$Pd_2(dba)_3$/t-Bu_3P/p-BrC_6H_4COPh	83	6 600	1.15

a. Polymerization condition: monomer (0.1 mmol), initiator (6%), K_3PO_4 (1 mmol, solid), H_2O (0.3 mL), THF (6 mL), 0°C, 40 min. b. Isolated yield. c. GPC analysis (polystyrene as standard, THF, 40 °C). d. 3% initiator was used. e. 2 mmol of monomer **1** (1.45 g) was used for polymerization

Intrigued by the narrow PDI and similarity to the predicted theoretical molecular weight, we then performed kinetic studies of the polymerization process to determine if the polymerization of monomer **1** was controlled. Using the combination of $Pd_2(dba)_3$/*t*-Bu_3P/*p*-BrC_6H_4COPh as the initiator, the relationship between the monomer conversion and the molecular weight of the generated polymer was investigated. A linear relationship between them with slightly increased PDIs for polymers of different conversions, a characteristic of chain-growth polymerization, was then observed (see Fig. S1 in SI).

After successful synthesis of *ortho*, *para*-linked polyarene **2**, we next turned our attention to the chain end functionality issue. Thus, we prepared polymer with the combination of $Pd_2(dba)_3$/*t*-Bu_3P/*p*-BrC_6H_4COPh as initiator and then performed *in situ* capping with phenylboronic acid post polymerization. The obtained polymer was analyzed by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry (Fig. 1). Only one series of peaks (>99%) was observed with the quenching of phenylboronic acid, which corresponded to the polymer with *para*-benzoylphenyl group at one end and a phenyl group at the other end (designated as $PhCOC_6H_4$/Ph). Since the *para*-benzoylphenyl group and phenyl group are considered to be derived from the initiator and cross-coupling between a bromide end group and/or the palladium complex end group with a phenyl boronic acid, polymerization seems to proceed in a chain-growth manner. Thus, the *ortho*, *para*-linked polyarene **2** with tunable molecular weight, narrow PDI and well-defined functional end groups could be prepared through this catalyst transfer Suzuki coupling polymerization.

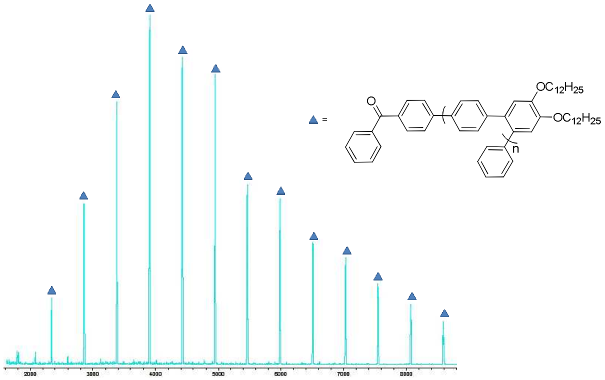


Fig. 1 MALDI-TOF-MS spectrum of $Pd_2(dba)_3$/*t*-Bu_3P/*p*-BrC_6H_4COPh initiated polymerization of monomer 1 capping with phenylboronic acid

By taking advantage of the chain-growth mechanism, we could easily prepare and characterize polymer **2** in different molecular weights with narrow PDI. As shown in Table 1 (entries 4 and 5), polymer **2a** with lower molecular weight (*M*n=6600 g/mol) was obtained using a larger amount of initiator, whereas polymer **2b** with higher molecular weight (*M*n=13500 g/mol) was obtained using a smaller amount of initiator. The photochemical properties of polymer **2a** and **2b** were then probed via UV-vis spectroscopy and fluorescence in solution. We found that the polymers afforded similar UV-vis spectra with λ_{max} at 304 nm in $CHCl_3$ (0.2 mg/mL) (see Fig. S4 in SI). However, polymers **2a** and **2b** in $CHCl_3$ (0.2 mg/mL) showed different emission peaks in the fluorescence spectra (Fig. 2(a)). Polymer **2a** displayed a λ_{max} at 520 nm with a shoulder at 460 nm. In contrast, polymer **2b** showed a λ_{max} at 460 nm. The distinctive blue-shift in fluorescence for polymer **2b** with higher molecular weight compared to polymer **2a** can be explained by the fact that chain configuration of the polymer dominated their aggregation behavior in solution. It is known that inter-segment interactions are primary factors in dictating the optoelectronic properties of a conjugated polymer. Most results have suggested that the intrachain exciton migration processes is much more efficient than the interchain migration in dilute solution, indicting more efficient intrachain interactions.[37] The fluorescence spectrum of polymer **2b** as a function of concentration was thus investigated. It was found that the peak at 460 nm decreased and the peak at

520 nm increased on changing from a relatively dilute solution (0.2 mg/mL in $CHCl_3$) to a concentrated solution (2 mg/mL in $CHCl_3$) (Fig. 2(b)). This result suggested that the fraction of polymer **2b** that is aggregated increases as a function of concentration, with the aggregation behavior at 2 mg/mL being similar to that observed for polymer **2a** at its lower (0.2 mg/mL) concentration. This is a distinctive difference from the traditional trend of *para*-linked polyarenes, wherein the polymers with longer chains display a red shift in UV-vis and fluorescence spectra, that can be attributed to the twisted configuration of the polymer chains.[38] A more detailed investigation of these aggregates, including the nature of the aggregation in various solvents and their photoluminescence lifetime, is in progress.

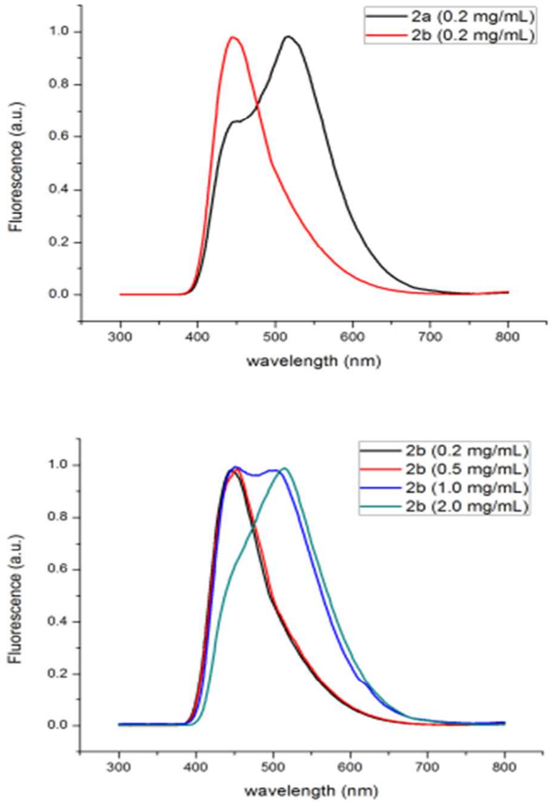
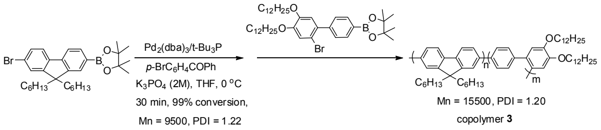


Fig. 2 (a) fluorescence spectra of **2a** and **2b** in $CHCl_3$. (b) fluorescence spectra of polymer **2b** in $CHCl_3$ at different concentrations.

The thermal properties of polymer **2a** and **2b** were next analyzed by differential scanning calorimetry (DSC). We recorded the second heating traces (10 ^oC/min rate) of polymer **2a** and **2b** (see Fig. S5 in SI). Polymer **2a** showed a melting peak around 118 ^oC, with a melting enthalpy of 12.42 J/g, whereas polymer **2b** showed the melting peak at a slightly lower temperature (116 ^oC), with a much lower melting enthalpy of 0.86 J/g. This result indicated that the crystal formed by polymer **2b** with higher molecular weight is much smaller than the one formed by polymer **2a**. In other words, longer polymer chains apparently impede efficient packing of the polymers in crystal lattice. This is also confirmed by the wide-angle X-Ray diffraction (see Fig. S6 in SI).

With the success of controlled polymerization of monomer **1**, subsequent efforts were directed toward synthesizing block copolymers containing polyfluorene and *ortho*, *para*-linked polymer **2**. It is well known that successive catalyst-transfer polymerizations should be conducted from a monomer with lower π–donor ability to a monomer with higher π–donor ability. Thus, we synthesized polyfluorene first, with $Pd_2(dba)_3$/*t*-Bu_3P/*p*-BrC_6H_4COPh as initiator, potassium phosphate as base, and a mixture of THF and water as solvent, for 30 min (conversion of monomers: 99%, polyfluorene: *M*n = 9500; PDI = 1.22). Then, monomer **1** was added to the reaction mixture, which was stirred for another 30 min, followed by quenching with 6N HCl. GPC analysis of the resulting polymer **3** showed an unimodal peak with *M*n = 15500 and PDI = 1.20, which was obviously shifted toward the higher-molecular-weight region as compared with polyfluorene (see Fig. S7 in SI). Furthermore, the ^1H NMR spectrum of polymer **3** clearly showed featured signals of polyfluorene and polymer **2** (see Fig. S8 in SI). These results indicated that an all-conjugated block copolymer containing a polyfluorene block and the *ortho*, *para*-alternating linked block could be directly prepared by a sequential polymerization procedure.



Scheme 1 Synthesis of copolymer **3** employing a sequential polymerization procedure

Conclusions

In summary, we report a general method for the synthesis of an *ortho*, *para*-linked aromatic polymer **2** via catalyst-transfer Suzuki coupling polymerization. The polymerization was shown to proceed in a chain-growth manner via kinetic study and MALDI-TOF analysis. Taking advantage of the chain-growth mechanism, polymer **2** with tunable molecular weight, narrow PDIs and well-defined functional end groups can be easily prepared. This work ultimately extended the scope of monomers for catalyst-transfer Suzuki coupling polymerization. Moreover, we found the optical and thermal properties of polymer **2** could be tuned by varying the molecular weight, due possibly to its twisted structure. As a consequence, polymer **2** of different molecular weights showed different colors of fluorescence under UV (λ = 360 nm) irradiation. We further synthesized an all-conjugated block copolymer containing a polyfluorene block and the *ortho*, *para*-alternating linked block in a one-pot procedure. These results can pave the way toward synthesizing polyarenes with precisely controlled structures, with interesting and desirable properties.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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