A General Room Temperature Suzuki−Miyaura Polymerization Process for Organic Electronics

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Abstract

π-conjugated polymers (CPs) have broad applications in high-performance optoelectronics, energy storage, sensors, and biomedicine. However, developing green and efficient methods to precisely synthesize well-defined CP structures on a large scale remains challenging and critical for their industrialization. Here, a room-temperature, scalable, homogeneous Suzuki – Miyaura-type polymerization methodology is reported with broad generality validated for 24 CPs including donor – donor, donor – acceptor, and acceptor – acceptor connectivity classes, and consistently yielding device-quality polymers with molecular masses greater than 100.0 kDa. Furthermore, the present polymerization protocol significantly reduces homocoupling structural defects, yielding more structurally regular and higher performance electronic materials and opto-electronic devices than in conventional thermally-activated polymerizations. Experimental and theoretical studies reveal that a borate-transmetalation process plays a key role in suppressing protodeboronation, which is critical for large scale structural regularity. Thus, these results provide a general polymerization tool for mass producing device-quality CPs with well-defined structural regularity.

Introduction

π-Conjugated polymers (CPs) have achieved great technological importance as a consequence of their mechanical flexibility, solution processability, biocompatibility, and widely tunable optoelectronic properties, offering a pivotal role in opto-electronic devices, energy storage, sensors, and biomedicine. To efficiently manufacture and industrialize CPs, several key metrics must be realized. First, structural defects such as homocoupling defects must be minimized since they can be detrimental to carrier mobility, fill factor, short circuit current, on/off current, and magnetic properties, etc. Second, synthetic batch-to-batch variations in purity, molecular mass ($M_w$), and polydispersity index ($D$) must be minimized to ensure consistent process-dependent nano/microscopic and bulk properties, hence consequent uniform and predictable device performance. Finally, large-scale synthetic methodologies (e.g., kilogram scale) must be developed to reduce the materials cost for manufacture/commercialization.

In light of the aforementioned challenges, various thermally-activated transition-metal-catalyzed cross-coupling polymerization processes such as Suzuki – Miyaura, Stille, Negishi, and direct arylation polymerization (DArP), have been actively investigated with the goal of optimizing specifically for the challenge of CP synthesis. In comparison with the high toxicity of organostannanes (Stille), unstable zinc monomers (Negishi), and the low regioselectivity of DArP for aryls, the Suzuki – Miyaura polymerization is an ideal choice owing to its low toxicity, ease of handling, and high organoborane regioselectivity. Nevertheless, it suffers from several key limitations (Fig. 1a): 1) The typical high temperatures of these polymerizations are likely to compromise chemoselectivity, generating inseparable structural polymer backbone defects. 2) Traditional Suzuki – Miyaura reactions usually require exogenous bases to convert aryl boronates to boronic acids for efficient cross-coupling with aryl halides in two-phase (water-organic solvent) systems, resulting in a competing protodeboronation, especially for
heteroaryl boronates\textsuperscript{28,29}. This may depress polymer yields and lower the molecular masses, producing significant batch-to-batch nonuniformity\textsuperscript{30–33}. 3) Moreover, the two-phase reaction system complicates scalability due to the inhomogeneous reaction conditions\textsuperscript{14–16}. Thus, a general and scalable polymerization method for developing well defined conjugated polymers is highly demanding.

Here we report a general homogeneous Suzuki – Miyaura-type polymerization methodology at room temperature using a Buchwald-type precatalyst + potassium trimethylsilanolate\textsuperscript{34,35} (Fig. 1b). The broad generality of this polymerization protocol is exemplified by the synthesis of 24 CPs, including donor – donor, donor – acceptor, and acceptor – acceptor connectivity classes. Moreover, this polymerization can be operated with high batch-to-batch uniformity, yields > 100.0 kDa molecular masses, and significantly suppresses structural defects at room temperature. Importantly, this polymerization is scalable to greater than 100 grams, exhibiting excellent manufacturing/industrialization potential. Experimental and theoretical analyses reveal the key role of the borate direct-transmetalation process is to suppress defect-generating protodeboronation.

**Results**

**Polymerization strategy.** In order to address the protodeboronation side reaction arising from a two-phase reaction system, a homogeneous Suzuki – Miyaura polymerization was investigated under varying anhydrous conditions. We initiated the study with a focus on heteroaryl-based CPs by the polymerization of 2,7-dibromo-9,9-didodecyl-9\textsubscript{H}-fluorene (E1) and 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (N1). Based on previously reported catalysts for anhydrous Suzuki – Miyaura reactions\textsuperscript{36–40}, Pd-P(t-Bu)\textsubscript{3}-G3 was optimized to deliver copolymer P1 with a $M_n$ of 22.8 kDa but a low yield of 23\% (Table 1, entries 1 – 4). Surprisingly, replacing Pd-P(t-Bu)\textsubscript{3}-G3 (Buchwald G3) with Pd-P(t-Bu)\textsubscript{3}-G4 (Buchwald G4) afforded copolymer P1 with a significantly higher molecular mass ($M_n = 72.3$ kDa, $D = 1.81$) in 88\% yield (Table 1, entry 5), which is ascribed to the carbazole moiety in Pd-P(t-Bu)\textsubscript{3}-G3 that likely hinders chain growth during polymerization by a Buchwald – Hartwig amination reaction\textsuperscript{34}. Furthermore, various bases were screened (Table 1, entries 6 – 8), and potassium trimethylsilanolate (TMSOK) was found to be optimal for this polymerization and affords copolymer P1 with a high $M_n$ of 102.8 kDa in 91\% yield. Since the solvent is critical for polymerization to achieve high molecular masses\textsuperscript{16}, various solvents were also screened (Table 1, entries 9 and 10). The results argue that nonpolar toluene is a very effective solvent for the chain growth. After further tuning of reaction parameters, the optimal polymerization condition affords copolymer P1 with a $M_n$ of 114.2 kDa and a $D$ of 1.97 in 95\% yield when using Pd-P(t-Bu)\textsubscript{3}-G4 as the catalyst, TMSOK as the base, and toluene as the solvent (Table 1, entry 11; see Supplementary Table 1 for the optimization details). In sharp contrast, copolymer P1 was obtained with a low $M_n$ of 8.1 kDa in 68\% yield through the traditional Suzuki – Miyaura polymerization (Table 1, entry 12), indicating that the present homogeneous Suzuki – Miyaura methodology is a promising strategy to access diverse high-molecular-mass heteroaryl-based CPs.
Mechanistic studies. Experimental and theoretical analyses were conducted to probe the mechanism of this room-temperature polymerization (Fig. 2). First, heteroaryl-based boronate ester $S_{n1}$ was treated with TMSOK to study the protodeboronation under anhydrous conditions. No protodeboronation is observed, while a boronate-base complex (borate) $S_{n2}$ was isolated quantitatively, as determined by the $^1$H nuclear magnetic resonance (NMR) spectrum ($\delta$ 4.80 ppm), high-resolution mass spectrometry (HRMS), and density functional theory (DFT) calculations$^{41}$ (Fig. 2a, Supplementary Fig. 1). Next, a stoichiometric reaction between $S_{n2}$ and bromobenzene $S_{e1}$ was conducted, affording the cross-coupling product $S_{p1}$ in 98% yield in the absence of base, which indicates that the borate $S_{n2}$ can be transmetalated directly (Fig. 2a).

To further probe the pathway of this reaction, DFT calculations were performed at B3LYP level with a 6-31G(d, p) basis set (Fig. 2b). The reaction begins with the monophosphine-based catalyst Pd[P(t-Bu)$_3$]$_2$, which coordinates with $S_{e1}$ to form intermediate IM1 (-12.4 kcal mol$^{-1}$). Next, IM1 undergoes oxidative
addition (via $\text{TS1}$) to generate $\text{IM2}$. With the assistance of $\text{Sn2}$, $\text{IM2}$ is converted to $\text{IM3}$ with a small energy barrier of 16.2 kcal mol$^{-1}$, followed by an exergonic process to form $\text{IM4}$ by elimination of KBr. We also calculated the transmetalation process between $\text{IM2}$ and boronate ester $\text{Sn1}$ via $\text{TS2'}$, which indicates an energy barrier was as high as 57.3 kcal mol$^{-1}$. Subsequently, $\text{IM5}$ is formed from $\text{IM4}$ via $\text{TS2}$ with an energy barrier of only 6.4 kcal mol$^{-1}$, which indicates that the direct transmetalation of borate is a facile process with the assistance of the base. Finally, the reductive elimination of $\text{IM5}$ yields the final product $\text{Sp1}$ and regenerates the catalyst with an energy barrier of only 2.9 kcal mol$^{-1}$. These experimental results and theoretical analysis demonstrate that the combination of a stable borate without protodeboronation and borate direct-transmetalation process is the key to preparing minimum-defect (see more below) and high-molecular-mass device-quality CPs via the present variation of the Suzuki – Miyaura polymerization.

**Substrate scope.** Inspired by the above success, we next examined the generality of the present homogeneous Suzuki – Miyaura polymerization methodology. A series of electron-rich and electron-deficient electrophiles ($\text{E1–E16}$) and nucleophiles ($\text{N1–N16}$) was investigated and afforded more than 20 CPs ($\text{P1–P24}$, Table 2), including donor–acceptor (D–A), donor–donor (D–D), and acceptor–acceptor (A–A) types. First, the suitability of electron-rich electrophiles (aryl halides) and electron-rich nucleophiles (aryl boronate esters) in this polymerization process was investigated. Various thienyl-based boronate esters were examined to afford the corresponding D–D-type CPs ($\text{P1–P5}$) with high $M_n$ values (up to 168.4 kDa) in excellent yields (up to 99%). In addition to thienyl-based boronate esters, other heteroaryl-based boronate esters, e.g., furan-based and selenophene-based boronated esters, were also investigated, and these substrates were found to be compatible with the present polymerization protocol as well, affording $\text{P6}$ and $\text{P7}$ with $M_n$ values exceeding 42.4 kDa. As expected, phenyl-based boronate esters, which are widely used in traditional Suzuki – Miyaura polymerizations, were also effective in this polymerization protocol ($\text{P8}$). Subsequently, electron-rich electrophiles and electron-deficient nucleophiles were copolymerized, and D–A-type CPs were efficiently produced ($\text{P9–P12}$). Again, the copolymerization of electron-deficient thienyl-based boronate esters afforded $\text{P9–P11}$ with high $M_n$ values (24.1–88.5 kDa) in high yields (92–99%). Additionally, the isoindigo boronate ester produced $\text{P12}$ with a high $M_n$ (53.2 kDa) in excellent yield (98%). Furthermore, the copolymerization of electron-deficient electrophiles and electron-rich nucleophiles afforded eight A–D-type CPs ($\text{P13–P20}$). Specifically, the copolymerization of electron-deficient electrophiles with thienyl-based nucleophiles proceeded smoothly, affording $\text{P13–P17}$ with high $M_n$ values (22.2–37.8 kDa) in excellent yields (85–97%). Additionally, phenyl-based nucleophiles efficiently afforded $\text{P18–P20}$ with $M_n$ ranging from 16.4 to 28.5 kDa. Finally, the copolymerization of electron-deficient electrophiles and electron-deficient nucleophiles was investigated to afford A–A-type CPs ($\text{P21–P24}$); Note that the synthesis of A–A-type CPs is typically challenging owing to the low reactivities of electron-deficient arenes$^{32,42}$. Impressively, all these polymers exhibit high $M_n$ values (22.8–61.5 kDa) and are prepared in high yields (96–98%), effectively demonstrating the generality of this protocol.
Uniformity and scalability assessment. To further demonstrate the synthetic utility of this polymerization, the batch-to-batch variation was first assessed by performing four repeated experiments, affording copolymer P1 with nearly identical molecular masses \(M_n\), 114.2–123.4 kDa; \(D\), 1.97–2.11) in comparable yields (95–97%) (Fig. 3a), suggesting the excellent uniformity of this method. In addition, a 100 g-scale polymerization was performed to investigate the scalability of this polymerization, and copolymer P1 with a high \(M_n\) of 107.6 kDa was obtained in 95% yield even when the catalyst loading was
reduced from 5.0 mol% to 2.5 mol% (Fig. 3b and 3c). Therefore, this polymerization process demonstrates excellent reproducibility and scalability without obvious fluctuation in $M_n$ and yields.

**Defect analysis.** To investigate whether room temperature operation can suppress the homocoupling defects during this polymerization protocol, small-molecule model reactions were performed between electrophile $S_{e1}$ and nucleophile $S_{n1}$. Impressively, neither the homocoupling product of the electrophiles nor that of the nucleophiles was observed by gas chromatography-mass spectrometry (GC-MS) in this room-temperature catalytic system (Supplementary Fig. 5), indicating that this room-temperature homogeneous Suzuki–Miyaura polymerization protocol is a promising strategy for suppressing homocoupling defects in CPs.

Next, copolymers $P5b$ and $P9b$ were prepared via traditional Stille polymerization for a direct comparison with $P5$ and $P9$ (also referred to as $P5a$ and $P9a$, respectively) since they exhibit sharp peaks in the $^1H$ NMR aromatic region, allowing accurate detection and quantitation of potential homocoupling structural defects (Fig. 4a and Supplementary Figs. 6–8). First, copolymers $P5n$ and $P5e$, which contain homocouplings of nucleophiles and electrophiles, respectively, were synthesized to serve as references to identify homocoupling defects in the product $^1H$ NMR spectra. The homocoupling defects in $P5n$ and $P5e$ are identified by the presence of peaks "n" ($\delta$ 7.77, 7.40, and 6.99 ppm) and "e" ($\delta$ 7.85 and 7.71 ppm) in the $^1H$ NMR spectra, respectively. The spectrum of copolymer $P5a$ shows minimal homocoupling defect peaks, whereas that of $P5b$ contains obvious homocoupling defect peaks at $\delta$ 7.85, 7.73, 7.40 and 6.99 ppm. Similarly, copolymer $P9a$ exhibits fewer homocoupling defects than $P9b$. To further investigate the homocoupling defects in the CPs, the composition of $P23$ was investigated by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI–TOF–MS), and the expected repeat units corresponding to C-Br/C-B cross-coupling products ($m/z$ = 993) are observed (Supplementary Fig. 9). Every peak in the MALDI–TOF–MS spectra was fully analyzed, and the peaks corresponding to the aryl and aryl bromide end groups identified. These results validate the well-defined alternating structure from the Suzuki–Miyaura room temperature polymerization protocol without detectable homocoupling defects in the polymer backbone.

To investigate the effects of structural defects on the photophysical properties of these materials, the $P9$-series copolymers$^{43,44}$ were further investigated. The ultraviolet–visible (UV–Vis) spectra of $P9a$ and $P9b$ in solution exhibit broad absorption peaks in the range of 550–900 nm (Fig. 4b, Supplementary Fig. 10). Notably, the absorption peak of $P9a$ (814 nm) reveals a significant redshift relative to that of $P9b$ (788 nm), which is mainly ascribed to the greater degree of polymer chain order$^{45}$. Moreover, the trap densities of the $P9a$ and $P9b$ films were measured using thermal admittance spectroscopy (TAS). The total trap density of the $P9a$ film was determined to be $2.6 \times 10^{16}$–$3.8 \times 10^{17} \text{ cm}^{-3}$ within an energy depth range of 0.20–0.36 eV, which was ~ 50% of that of the $P9b$ film ($5.9 \times 10^{16}$–$7.6 \times 10^{17} \text{ cm}^{-3}$) under the same conditions, consistent with greater charge delocalization (Fig. 4c, Supplementary Fig. 11). The charge transport properties of $P9a$ and $P9b$ films were next evaluated using field-effect transistors with a bottom-gate/bottom-contact configuration, revealing that the hole mobility of $P9a$-based organic field-effect
transistors (OFETs) (12.2 cm$^2$V$^{-1}$s$^{-1}$) is far greater than the P9b-based OFETs (4.4 cm$^2$V$^{-1}$s$^{-1}$) (Figs. 4d and 4e, Supplementary Table 5). These results underscore that this polymerization method can suppress the homocoupling defects and enhance device-relevant opto-electronic properties.

To further illustrate the effects of homocoupling defects on the solid state structures of P9a and P9b, 2D grazing incidence wide-angle X-ray scattering (2D–GIWAXS) measurements were employed to investigate the thin films of P9a and P9b (Figs. 4f–4h). Both P9a and P9b exhibit clear (h00) reflections in the out-of-plane direction and (010) peak reflections in the in-plane direction, indicative of the preferred edge-on orientations for the two polymers. However, P9a exhibits shorter lamellar packing and π–π stacking distances ($d_{100} = 20.1$ Å, $d_{010} = 3.74$ Å) and larger crystal coherence lengths (36.5 and 131.2 Å) than P9b, demonstrating more condensed and well-ordered packing (see Supplementary Tables 6 and 7 for a detailed analysis of the 2D–GIWAXS results). The above results confirm that the present variant of the homogeneous room temperature Suzuki – Miyaura polymerization affords device-quality CPs with significantly fewer homocoupling defects and thus enhanced charge transport properties of the resulting CPs.

**Conclusions**

Here a general, room-temperature, scalable Suzuki – Miyaura polymerization process was developed to access a diverse family of device-quality CPs with high molecular masses (up to 168.4 kDa) in high yields. Various aryl boronates, especially readily protodeboronated heteroaryl boronates, undergo selective direct transmetalation through a boronate-base intermediate at room temperature, generating more than 20 diverse types of CPs. Systematic studies reveal that these room-temperature synthesized CPs do not possess detectable homocoupling structural defects, essential for high-performance opto-electronics. Therefore, the present room temperature Suzuki – Miyaura polymerization process represents an energy-efficient, scalable, and general method for precisely synthesizing device-quality opto-electronic CPs for applications.

**Methods**

**Representative polymerization procedure.** In a flame-dried Schlenk tube, E1–E16 (0.15 mmol, 1.0 equiv.), N1–N16 (0.15 mmol, 1.0 equiv.), Pd-P(t-Bu)$_3$G4 (0.0075 mmol, 5 mol%), TMSOK (0.33 mmol, 2.2 equiv.), and dry toluene (3.0 ml, 0.05 M) were added under a nitrogen atmosphere. The reaction mixture was then stirred at 25°C for 24 h. Afterwards, the reaction mixture was poured into methanol, collected by filtration, and purified by successive Soxhlet extractions with acetone, hexane, chloroform, and chlorobenzene. The chloroform or chlorobenzene solution was then concentrated, poured into methanol, and the corresponding copolymers collected by filtration.

**OFET fabrication and characterization.** Heavily p-doped Si wafers with a 300 nm thermally grown SiO$_2$ layer served as the gate electrode and the dielectric layer, respectively. Interdigital Cr/Au (3/20 nm) source and drain electrodes (channel width 1400 µm, channel length 40–50 µm) were patterned onto the
substrates using a conventional lift-off photolithography technique. Before the deposition of the polymers, the substrates were treated with octadecyltrichlorosilane (ODTS) vapor in a vacuum oven at 120°C, forming a self-assembled monolayer. After sequentially rinsing in chloroform, hexane, and isopropanol, 5 mg ml$^{-1}$ polymer solution in chloroform was spin-coated at a speed of 5000 rpm and subsequently annealed at 100°C for 30 min. The electrical characteristics of the completed devices were measured at ambient conditions using a Keysight B1500A source meter. Carrier mobilities ($\mu$) were calculated from the source-drain current ($I_{SD}$) versus gate voltage ($V_G$) characteristics measured in the saturated regime, following the formula:

$$I_{SD} = C_i\mu(W/2L)(V_G - V_{th})^2$$

where $C_i$ is the capacitance per unit area of the gate dielectric layer; $W$ and $L$ are the semiconductor channel width and length, respectively; and $V_{th}$ is the threshold voltage. Threshold voltages were obtained from the x-intercept of $V_G$ versus $I_{SD}^{1/2}$ plots. Thirty devices were measured for each polymer.

**Declarations**

**Data availability**

All relevant data supporting the findings of this study are available in this paper and its Supplementary Information. Synthetic procedures and characterization for all the new compounds, computational studies and all copies of NMR spectra and GPC traces are available in the Supplementary Information.

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**Author contributions**

H.H. directed the investigations and provided overall supervision. H.X. designed the experiments. H.X., W.X., X.Z. and Q.S. performed the synthetic experiments. Q.L. and D.Z. performed the device fabrications. Y. Lu., S.W. and Z.W. performed the DFT calculations. Y. Li and Y. Lin performed the trap density measurements. S.W., C.L. and X.Z. performed the AFM, GIWAXS measurements. H.X., Q.S., T. J. M. and H.H. prepared the manuscript.

**Competing interests**

The authors declare no competing interests.
References


**Figures**
Figure 1

Suzuki–Miyaura polymerization to access \( \pi \)-conjugated polymers. 

a, Previous work: Suzuki–Miyaura polymerization via boronic acids.

b, This work: general homogeneous Suzuki–Miyaura polymerization via borates to access well-defined copolymers with high molecular masses.
Figure 2

Mechanistic study results. **a**, Synthesis, characterization and conversion of borate $S_{n2}$. **b**, DFT-calculated free energy profile. The Gibbs free energy values (kcal/mol) are provided to facilitate a discussion of energy.
Figure 3

Investigation of the practical uniformity and scalability of the present polymerization protocol. a, Reproducibility of this polymerization. b and c, Scale-up of this polymerization.
Homocoupling defect analysis. a, $^1$H NMR spectra for the identification of homocoupling defects and comparison of P5-series copolymers. b, UV–Vis absorption spectra of P9a and P9b. c, Trap density of states (tDOS) determined by thermal admittance spectroscopy of P9a and P9b thin films. d and e, OFET transfer curves of P9a and P9b thin films. f and g, 2D–GIWAXS patterns of P9a and P9b thin films. h, Corresponding 2D–GIWAXS scattering profiles along the in-plane and out-of-plane directions of P9a and P9b thin films.

Supplementary Files

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