Ru-catalyzed site-selective direct arylation polycondensation via ortho-metallation of pyrrole derivative

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Abstract. A π-conjugated polymer consisting of pyrrole and fluorene units was synthesized via Ru-catalyzed direct arylation polycondensation. The introduction of a 2-pyrimidinyl substituent into the N-position of the pyrrole monomer as a directing group induced ortho-metallation, with effective site-selective polycondensation at the α-position of the pyrrole monomer, without the need for protection of the β-position. Subsequent removal of the 2-pyrimidinyl substituent led to the elongation of π-conjugation along the main chain of the polymer via elimination of the steric hindrance due to the bulky substituent.

1. Introduction

π-Conjugated polymers have been extensively investigated for utilization in the fabrication of a variety of optoelectronic devices such as organic photovoltaic cells, field effect transistors, and light emitting diodes [1–5]. These polymers have been predominantly synthesized by polycondensation using transition metal-catalyzed cross-coupling reactions such as the Suzuki–Miyaura and Migita–Kosugi–Stille cross-coupling reactions [6–12]. Alternatively, syntheses of π-conjugated polymers via a dehydrohalogenative cross-coupling reaction (scheme 1), so-called direct arylation, have recently been actively investigated as this protocol should provide significant benefits by decreasing the number of reaction steps and reducing undesired waste from the organometallic reagents [13–39].

\[
\begin{align*}
\text{Cat.} & \quad \text{n} \cdot \text{X} \cdot \text{Ar}_1 \cdot \text{X} \quad + \quad \text{n} \cdot \text{H} \cdot \text{Ar}_2 \cdot \text{H} \\
\text{Scheme 1.} & \quad \rightarrow \quad \left( \text{Ar}_1 \cdot \text{Ar}_2 \right) \text{n} \quad + \quad 2n \text{HX}
\end{align*}
\]

Direct arylation polycondensation, however, has some limitations: C–H activation at undesired positions of the aromatic monomers provides branched and cross-linked structures in the polymer chains [20–22,26–28,29–33], which affects the solubility and optical properties of the polymers [21,28]. We previously reported that Pd-catalyzed direct arylation polycondensation of 3,3′,4,4′-tetramethylbithiophene with dibromoarylenes gave the corresponding polymers with high molecular weights and good solubility. In contrast, the use of 2,2′-bithiophene as a monomer gave insoluble products due to the occurrence of direct arylation at the β-position of the thiophene unit [32]. The β-position side reaction was also confirmed by carrying out a model reaction of bithiophene with p-
bromotoluene (scheme 2), where a trace amount of trisubstituted bithiophene was observed. Consequently, this minor side reaction induced the formation of cross-linked structures during the polycondensation reaction.

These observations initiated our interest in achieving direct arylation polycondensation with site selectivity in order to suppress the undesired side reaction. We thus focused on Ru-catalyzed direct arylation of pyrrole derivatives bearing a directing group [40,41]. In this reaction, the presence of the directing group on the aromatic substrates induced ortho-selective C–H bond functionalization via ortho-metalation [42–46]. As ortho-selective direct arylation promotes a cross-coupling reaction at the α-position of the pyrrole unit, even in the absence of protection of the β-position, the reaction is expected to be useful for the synthesis of π-conjugated polymers with well-defined linkages [47]. Pyrrole is consistently one of the most popular choices of monomer units for preparing π-conjugated polymers [48–51]. Therefore, the synthesis of pyrrole-based π-conjugated polymers via direct arylation would be an extremely useful step forward in the development of improved organic semiconducting materials. We here report the site-selective polycondensation of 1-(2-pyrimidinyl)pyrrole with 2,7-dibromo-9,9-dioctylfluorene via Ru-catalyzed direct arylation (scheme 3). The reaction for the subsequent removal of the directing group from the pyrrole unit of the polymer is also described (scheme 4).
2. Experimental

2.1. Typical polycondensation of 1-(2-pyrimidinyl)pyrrole with 2,7-dibromo-9,9-dioctylfluorene via Ru-catalyzed direct arylation: A mixture of [RuCl$_2$(p-cymene)]$_2$ (15.3 mg, 0.025 mmol), carboxylic acid (0.30 mmol, 60 mol%), K$_2$CO$_3$ (415 mg, 3.0 mmol), 2,7-dibromo-9,9-dioctylfluorene (274 mg, 0.50 mmol) and 1-(2-pyrimidinyl)pyrrole (72.6 mg, 0.50 mmol) was stirred in anhydrous m-xylene (2.00 mL) for 6-48 h at the indicated temperature under a nitrogen atmosphere. After cooling to room temperature, the solvent was removed by evaporation under vacuum. The residue was poured into an aqueous solution of ethylenediaminetetraacetic acid disodium salt (pH = 8). The suspension was stirred for 1 h at room temperature. The precipitates were separated by filtration and washed with 1 M (mol dm$^{-3}$) HCl solution, distilled water and MeOH. The filtered residue was poured into hexane and low-molecular-weight fraction was extracted by ultrasonic treatment for 1 h. The precipitates were separated by filtration. If the filtered residue was completely soluble in CHCl$_3$, the residue was dissolved in CHCl$_3$; otherwise, the residue was dissolved in DMF. The solution was filtered through a plug of Celite to remove insoluble materials. The filtrate was concentrated and the polymer (P-1) was precipitated by slowly adding the concentrated solution into MeOH.

The polycondensation proceeding under the optimized conditions gave P-1 in 86% yield (table 1, run 8). GPC (DMF): $M_n = 19800$, $M_w/M_n = 3.82$; $^1$H NMR (600 MHz, DMF-$d_7$, 293 K): δ 8.91 (2H, d, $J = 4.8$ Hz, H$_i$), 7.75 (2H, d, $J = 7.8$ Hz, H$_j$), 7.62 (1H, br, H$_k$), 7.36 (2H, d, $J = 7.8$ Hz, H$_g$), 6.88 (2H, br, H$_e$), 6.61 (2H, br, H$_h$), 1.63 (4H, br, H$_d$), 1.30-0.87 (20H, m, H$_b$), 0.83 (6H, t, $J = 7.2$ Hz, H$_a$), 0.28 (4H, br, H$_c$); $^{13}$C{$_1$H} NMR (150 MHz, DMF-$d_7$, 293 K): δ 160.4, 160.0, 151.5, 140.3, 138.6, 133.3, 128.2, 123.1, 121.8, 120.8, 111.4, 55.8, 41.2 (CH$_2$), 32.7 (CH$_2$), 30.8 (CH$_2$), 30.3 (CH$_2$), 30.1 (CH$_2$), 24.8 (CH$_2$), 23.4 (CH$_3$), 14.6 (CH$_3$).

2.2 Polymer reaction for the removal of 2-pyrimidinyl substituent on the pyrrole unit of the polymer: A mixture of KOH (1.26 g, 22.5 mmol) and P-1 (79.8 mg, 0.15 mmol; table 1, run 8) was stirred in anhydrous N-methylpyrrolidone (30.0 mL) for 48 h at 200 °C under a nitrogen atmosphere. After cooling to room temperature, the mixture was poured into distilled water. The suspension was stirred for 1 h at room temperature. The precipitates were separated by filtration and washed with distilled water, MeOH and hexane. The filtered residue was dissolved in CHCl$_3$ and the solution was filtered through a plug of Celite to remove insoluble materials. The filtrate was concentrated and the polymer (P-1) was precipitated by slowly adding the concentrated solution into MeOH.

The polymer was stored under a nitrogen atmosphere. $^1$H NMR (400 MHz, CDCl$_3$, 293 K): δ 8.71 (1H, br, N-H), 7.73 (2H, d, $J = 7.6$ Hz, H$_j$), 7.57 (2H, d, $J = 7.6$ Hz, H$_h$), 7.52 (2H, br, H$_h$), 6.71 (2H, br, H$_h$), 2.07 (4H, br, H$_d$), 1.16 (20H, br, H$_b$), 0.67 (10H, br, H$_a$); $^{13}$C{$_1$H} NMR (100 MHz, CDCl$_3$, 293 K): δ 151.8, 139.6, 134.0, 131.3, 122.8, 120.2, 118.3, 108.3, 55.4, 40.8 (CH$_2$), 31.9 (CH$_2$), 30.2 (CH$_2$), 29.5 (CH$_2$), 29.4 (CH$_2$), 24.0 (CH$_2$), 22.7 (CH$_2$), 14.2 (CH$_3$).
3. Results and Discussion

3.1. Polycondensation

The investigation was conducted employing the polycondensation of 1-(2-pyrimidinyl)pyrrole with 2,7-dibromo-9,9-dioctylfluorene, as the latter possesses good reactivity toward direct arylation polycondensation, and high selectivity against side reactions [25,29–35]. The reaction was firstly examined in the presence of \([\text{RuCl}_2(p\text{-cymene})]_2\) (5 mol%), 1-adamantanecarboxylic acid (1-AdCOOH) (60 mol%), and \(\text{K}_2\text{CO}_3\) (6 equiv) in \(m\)-xylene according to the literature [40], giving the corresponding polymer (P-1) in good yield (table 1, run 6). In contrast, use of the related pyrrole derivatives, 1-methylpyrrole and 1-phenylpyrrole, as monomers did not give the corresponding polymeric products under the same reaction conditions (scheme 5). The control experiments revealed that the presence of the 2-pyrimidinyl substituent induced ortho-metalation at the \(\alpha\)-position of the pyrrole monomer and promoted the direct arylation.

![Polymerization scheme](image)

**Table 1.** Results of polycondensation of 1-(2-pyrimidinyl)pyrrole with 2,7-dibromo-9,9-dioctylfluorene under various conditions.

| Run | Additive\(^b\) | Temp. / °C | Time / h | Yield\(^c\) / % | GPC (DMF)\(^d\) | \(M_n\) | \(M_w/M_n\) |
|-----|-----------------|------------|----------|----------------|-----------------|--------|-------------|
| 1   | 1-AdCOOH        | 120        | 24       | 63             | 9700            | 1.73   |
| 2   | PivOH           | 120        | 24       | 87             | 11100           | 1.84   |
| 3   | MesCOOH         | 120        | 24       | 7              | 7600            | 2.00   |
| 4   | AcOH            | 120        | 24       | 24             | 7400            | 1.53   |
| 5   | PCCA            | 120        | 24       | 53             | 8300            | 1.77   |
| 6   | 1-AdCOOH        | 120        | 48       | 87             | 13100           | 2.66   |
| 7   | PivOH           | 120        | 48       | 82\(^e\)      | 14700           | 2.35   |
| 8   | PivOH           | 140        | 48       | 86\(^f\)      | 19800           | 3.82   |
| 9\(^f\) | -               | 120        | 24       | 20             | 7600            | 1.84   |
| 10\(^g\) | -              | 120        | 24       | 39             | 7900            | 1.40   |
| 11\(^f\) | 1-AdCOOH\(^h\) | 120        | 24       | 31             | 8800            | 1.95   |
| 12\(^g\) | PivOH\(^i\)    | 120        | 24       | 43             | 11200           | 2.00   |

\(^a\) Reactions were conducted using \([\text{RuCl}_2(p\text{-cymene})]_2\) (5 mol%), additive (60 mol%), and \(\text{K}_2\text{CO}_3\) (6 equiv.) in \(m\)-xylene (2 mL).

\(^b\) MesCOOH : 2,4,6-trimethylbenzoic acid; PCCA: 1-phenyl-1-cyclopentanecarboxylic acid.

\(^c\) Re precipitation from CHCl\(_3\)/methanol.

\(^d\) Calibrated by GPC (a DMF solution of LiCl (0.01 M)), polystyrene standards.

\(^e\) Re precipitation from DMF/methanol.

\(^f\) \([\text{Ru}(1\text{-AdCOO})(p\text{-cymene})] (10 \text{ mol\%})\) was used instead of \([\text{RuCl}_2(p\text{-cymene})]_2 (5 \text{ mol\%}).

\(^g\) \([\text{Ru}(\text{PivO})(p\text{-cymene})] (10 \text{ mol\%})\) was used instead of \([\text{RuCl}_2(p\text{-cymene})]_2 (5 \text{ mol\%}).

\(^h\) 40 mol\%.
In order to determine the appropriate reaction conditions, the reaction was next conducted under a variety of conditions, as summarized in table 1. In terms of the additive in the catalytic system, pivalic acid (PivOH) was found to be superior to the other carboxylic acids tested (runs 1–5). The carboxylic acid serves as a carboxylate ligand under the basic conditions used, which assists the deprotonation of the pyrrole unit in the direct arylation [31–34,52]. As PivOH has the lowest acidity ($pK_a = 5.01$) [53], the high basicity of its conjugated carboxylate ligand is likely to promote a smooth reaction. Increases in reaction time and temperature improved the molecular weight of the products (runs 6–8). In addition, Ru complexes, [Ru(PivO)$_2$(p-cymene)] and [Ru(1-AdCOO)$_2$(p-cymene)] [54,55], were also prepared and examined as catalysts (runs 9–12), as the use of structurally well-defined Ru complexes was expected to reveal the scope of the direct arylation. Although the use of these complexes was less catalytically competent than that of the in situ prepared catalytic system used in the present study, a similar trend was observed with respect to the conjugated carboxylate ligand of the complexes.

As the polymeric products were soluble in DMF, the chemical structure of P-1 was elucidated using NMR and MALDI-TOF-MASS spectroscopy. The $^1$H NMR spectrum of P-1 (run 8) is shown in figure 1. All the signals were assignable to the protons in the recurring unit; the signal assignable to the protons at the β-position of the pyrrole unit was observed at $\delta$ 6.6 ppm, while that assigned to the

**Figure 1.** $^1$H NMR spectrum of P-1 (table 1, run 8, 600 MHz, in DMF- $d_7$).

**Figure 2.** Positive ion MALDI-TOF-MASS spectrum of P-1 (table 1, run 8) using dithranol as a matrix and des-Arg$^1$-Bradykinin, Angiotensin I and Glu$^1$-Flibrinopeptide B as external standards.
proton at the \( \alpha \)-position of the pyrrole unit (\( \delta \) 7.8 ppm) [40] had a negligible intensity. These data indicate that the site-selective direct arylation smoothly proceeded at the \( \alpha \)-position of the pyrrole unit, affording well-defined \( \mathbf{P-1} \). The MALDI-TO-MASS indicates a structure of \( \mathbf{P-1} \) that is consistent with that obtained from the NMR spectrum (figure 2); the main peaks correspond to the recurring unit, and there are no peaks corresponding to the branched structures. In order to elucidate further details of the Ru catalytic system, control experiments were conducted using a Pd catalytic system. When Pd-catalyzed direct arylation of 1-(2-pyrimidinyl)pyrrole with 2,7-dibromo-9,9-dioctylfluorene was carried out under the same reaction conditions as in our previous reports [31,32], the reaction did not give a polymeric product. Alternatively, the reaction of 1-phenylpyrrole with 2,7-dibromo-9,9-dioctylfluorene gave a polymer containing a large insoluble fraction (scheme 6). The IR spectrum of the DMF-insoluble fraction was essentially identical to that of the DMF-soluble fraction, while the MALDI-TOF-MASS spectral analysis suggested the existence of irregular structures. These results indicate that the reaction afforded uncontrollable cross-linked structures at undesired C–H bonds of each aromatic unit [20–22,26–28,29–33,56]. These data also support the occurrence of site-selective polycondensation by Ru-catalyzed direct arylation via \textit{ortho}-metalation, giving the well-defined structure of \( \mathbf{P-1} \).

### Scheme 6.

3.2. Polymer reaction

In terms of \( \pi \)-conjugated polymers, steric hindrance due to bulky substituents on the aromatic recurring units sometimes leads to limited \( \pi \)-conjugation along the polymer main chain [33,57,58]. There are a number of reports concerning reactions used to remove directing groups [40,41,59]; therefore, we utilized this knowledge to remove the 2-pyrimidinyl substituent on the pyrrole unit of \( \mathbf{P-1} \) (scheme 7). The 2-pyrimidinyl group was efficiently cleaved from \( \mathbf{P-1} \) by treatment with KOH, giving the corresponding polymer (\( \mathbf{P-2} \)) with high recovery. The GPC data of \( \mathbf{P-2} \) indicate that decomposition of the polymer main chain is likely to be negligible owing to the thermal stability.

### Scheme 7.

The \( ^1\)H NMR spectrum of \( \mathbf{P-2} \) reveals efficient conversion of the pyrrole unit, as shown in figure 3. The signals assigned to the 2-pyrimidinyl substituent that are evident in the spectrum of \( \mathbf{P-1} \) (figure 1) are no longer visible, but a new signal assignable to the 1-H proton of the pyrrole unit can be observed at \( \delta \) 8.7 ppm, which was confirmed by the decrease in signal upon addition of \( \text{D}_2\text{O} \). The integral ratios of the signals are essentially identical to the corresponding recurring unit of \( \mathbf{P-2} \). The \( ^1\)C\{\( ^1\)H\} NMR and MALDI-TOFMASS spectra provide further evidence of efficient removal.
3.3. Optical properties

The optical properties of the polymers were compared using UV-vis absorption spectroscopy. Figure 4 shows the UV-vis absorption spectra of the polymers in thin film state. P-1 gave similar absorptions in the solution and thin-film states, which suggests weak interchain interactions such as π–π stacking in the film state. This is likely caused by the steric hindrance from the bulky 2-pyrimidinyl substituent. The spectrum of P-2 exhibits a red shift of the absorption by 26 and 41 nm in solution and thin film states, respectively, when compared with P-1. Removal of the 2-pyrimidinyl substituent led to the elongation of π-conjugation along the main chain of polymer, resulting in the red shift of absorption.

In terms of the emission properties, the solution and film of P-1 exhibited cyan (452 nm) and green (483 nm) emission, respectively; whereas, P-2 showed only weak emission (498 nm) in solution.

![Figure 3. 1H NMR spectrum of P-2 (400 MHz, in CDCl₃).](image)

![Figure 4. UV-vis absorption spectra of P-1 and P-2 in film.](image)

4. Conclusion

Site-selective polycondensation was demonstrated using Ru-catalyzed direct arylation via ortho-metalation. The molecular design of the aromatic monomer bearing the directing group efficiently suppressed the formation of branched and cross-linked structures during the direct arylation polycondensation. Subsequent removal of the 2-pyrimidinyl directing group enhanced the coplanarity of the π-conjugated polymer. Although this polycondensation reaction has limited scope at present, and the introduction and removal of the directing group is not ideal with respect to atom efficiency, this strategy should present new possibilities for direct arylation polycondensation in the synthesis of π-conjugated polymers with well-defined linkages between the recurring units.
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