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Synthesis of pyrrole-based poly(arylenevinylene)s via Rh-catalyzed dehydrogenative direct alkenylation

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Polycondensation via Rh-catalyzed dehydrogenative direct alkenylation was conducted. The introduction of a directing group, such as a 2-pyrimidinyl substituent, to the pyrrole monomer promoted a polycondensation reaction, giving rise to corresponding poly(arylenevinylene)s with a *trans*-configuration in good yields. The absorption and electronic properties of the polymers were examined.

π -Conjugated polymers have been studied extensively for utilization in the fabrication of a variety of optoelectronic devices such as organic photovoltaic cells, field effect transistors (FETs), and light emitting diodes (LEDs).¹⁻² These polymers have been synthesized predominantly by polycondensation using transition metal-catalyzed cross-coupling reactions, such as the Suzuki-Miyaura and Migita-Kosugi-Stillé cross-coupling reactions.³ Alternatively, the synthesis of π -conjugated polymers via a dehydrohalogenative cross-coupling reaction, also termed as direct arylation, has been studied actively because the sp^2 C-H functionalization of aromatic monomers via a direct arylation reaction does not require organometallic monomers, thereby decreasing the number of synthetic steps for generating organometallic monomers and reducing the undesired waste originating from the organometallic reagents.⁴ As part of an ongoing study of the direct sp^2 C-H functionalization strategies towards the synthesis of π -conjugated polymers, we envisioned development of a new polycondensation reaction via catalytic dehydrogenative alkenylation of arenes, also termed as direct alkenylation (i.e., the oxidative Mizoroki-Heck reaction or Fujiwara-Moritani reaction):⁵ The reaction is the direct oxidative C-H/C-H cross-

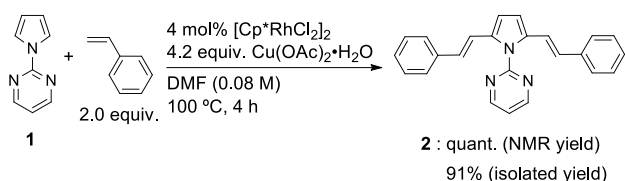
coupling reaction of arenes with alkenes, allowing straightforward access to alkenylated arenes.

Poly(arylenevinylene)s are an attractive family of π -conjugated polymers, and a large number of applications especially in the area of LEDs and FETs have been reported.² A variety of poly(arylenevinylene)s have been prepared via the polycondensation of *p*-quinodimethane intermediates (Gilch polymerization),^{7,8} olefin metathesis polymerization,^{7,9} Wittig reaction (Wittig-Horner polycondensation),^{7,10} Knoevenagel polycondensation,^{7,10c,11} Mizoroki-Heck reaction,^{7,12} Suzuki-Miyaura cross-coupling,^{7,13} and Migita-Kosugi-Stillé cross-coupling.^{7,14} Accordingly, this study is first example of the synthesis of poly(arylenevinylene)s via direct alkenylation. However, the utilization of a direct alkenylation reaction in polycondensation has been considered a challenge compared to direct arylation polycondensation, because the substrate scope of direct alkenylation is often restricted to alkenes bearing electron-deficient substituents, such as acrylates,⁵ whereas the coupling reaction should proceed efficiently to give high molecular weight polymers without regio-irregular structures. Alternatively, the introduction of a directing group to the aromatic substrate induces *ortho*-metalation and accelerates sp^2 C-H functionalization.^{5e,6} The regio-selective direct alkenylation of 1-(2-pyrimidinyl)pyrrole (**1**) with alkenes has also been examined.⁵ⁱ Pyrrole derivative **1** was also reported to be an efficient monomer for regio-selective direct arylation polycondensation.¹⁵ After polymerization, the directing group could be removed from the polymer. Pyrrole is an appropriate choice as an aromatic monomer for the synthesis of π -conjugated poly(arylenevinylene)s; a poly(arylenevinylene) containing pyrrole units was used to construct efficient supramolecular light-harvesting antennae with color-tunable emission.¹⁶ Herein, this paper reports polycondensation via the Rh-catalyzed direct alkenylation of **1** with diethenyl aromatic compounds to produce the corresponding poly(arylenevinylene)s with high regio-selectivity and a *trans*-configuration. Polycondensation of the related aromatic monomers was also conducted to highlight the usability of the

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Scheme 1 Model reaction of **1** with styrene.

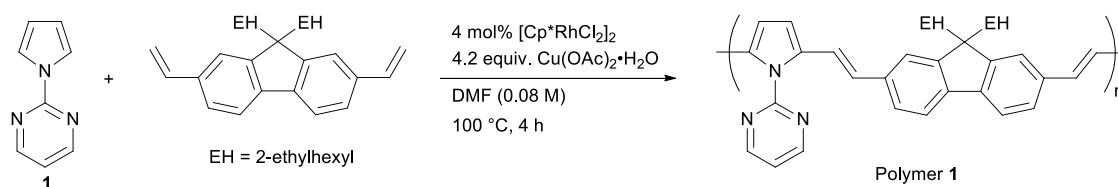
synthetic protocol. The optical and FET properties of the polymers were evaluated.

Miura *et al.* have reported 2,6-dialkenylation of 1-phenylpyrazoles with styrenes through Rh-catalyzed direct alkenylation.^{5h} Consequently, the investigation began with the model reaction of **1** with 2.0 equivalents of styrene in the presence of $[\text{Cp}^*\text{RhCl}_2]_2$ (4 mol%) and $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$ (4.2 equiv.) in DMF at 100 °C for 4 h. The reaction proceeded smoothly and gave the dialkenylated compound (**2**) in a good yield (Scheme 1). The product was isolated as a dialkenylated product with the *E,E*-isomer, and only a trace amount of mono-alkenylated product was observed. To demonstrate the effects of the 2-pyrimidinyl substituent on the reaction, 1-phenylpyrrole and 1-methylpyrrole were tested under the same reaction conditions: The control experiments did not give the corresponding dialkenylated compound (Scheme S1[†]). The reaction of **1** was also examined in the absence of styrene under the same reaction conditions shown in Scheme 1: The reaction did not give the corresponding dimer of **1** (Scheme S2[†]). These results show that the presence of the 2-pyrimidinyl substituent not only induces *ortho*-metalation at the α -position of the pyrrole

moiety and accelerates the direct alkenylation reaction smoothly, but also prevents homo-coupling of the pyrrole moiety, presumably due to steric hindrance of the bulky directing group.

Subsequently, to determine the appropriate polymerization conditions, the reaction of **1** with 2,7-diethenyl-9,9-bis(2-ethylhexyl)-9H-fluorene was carried out under a range of conditions (Scheme 2). Removal of copper salts and the rhodium catalyst was carried out with chelating agents (see supplemental information). Table 1 lists the results of polycondensation. The polycondensation reaction with $[\text{Cp}^*\text{RhCl}_2]_2$ (4 mol%) and $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$ (4.2 equiv.) in DMF at 100 °C for 4 h yielded the corresponding polymer (Polymer **1**) with a molecular weight of 22,400 in 81% yield (entry 2). The number average molecular weight of Polymer **1** did not increase with a prolonged reaction time, because the polymer was partly insolubilized in DMF (entry 3). The decrease in temperature (60 °C) somewhat reduced the catalytic activity, but increasing the reaction time to 24 h afforded the polymeric product (entry 4). The addition of large amounts of $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$ (6.0 equiv.) decreased reaction yield slightly, whereas AgOAc did not serve as an oxidant in the reaction (entries 5,6). Aprotic solvents, such as DMAc and NMP, were also available for the reaction (entries 7, 8). The increasing polydispersity in molecular weight could be attributed to precipitation of the polymer from the reaction mixture during the reaction.¹⁵ Other control experiments on the effects of the catalyst and additive are summarized in Table S1. [†]

The chemical structure of Polymer **1** was elucidated by nuclear magnetic resonance (NMR) spectroscopy and matrix-assisted laser desorption/ionisation-time of flight-mass spectrometry (MALDI-TOF-MS). Figure 1 shows the ¹H NMR



Scheme 2 Polycondensation of **1** with 2,7-diethenyl-9,9-bis(2-ethylhexyl)-9H-fluorene.

Table 1. Direct alkenylation polycondensation of **1** with 2,7-diethenyl-9,9-bis(2-ethylhexyl)-9H-fluorene ^a

Entry	Solvent	Temp. / °C	Reaction time / h	Yield ^b / %	$M_n \times 10^{-3}$ ^c	PDI ^c
1	DMF	100	2	65	8.3	2.4
2	DMF	100	4	81	22.4	5.6
3	DMF	100	6	71	22.6	7.9
4	DMF	60	24	79	14.8	2.3
5 ^d	DMF	100	4	64	16.7	6.8
6 ^e	DMF	100	4	No polymer	-	-
7	DMAc	100	4	71	17.8	4.7
8	NMP	100	4	70	20.2	5.4
9	Dioxane	100	4	No polymer	-	-

^a Reactions were conducted using $[\text{Cp}^*\text{RhCl}_2]_2$ (4 mol%) and $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$ (4.2 equiv.) in solvent (0.08 M).

^b The products were obtained by reprecipitation from $\text{CHCl}_3\text{-CH}_3\text{OH}$.

^c Estimated by GPC calibrated on polystyrene standards.

^d $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$ (6.0 equiv.) was used. ^e $\text{Ag}(\text{OAc})$ (4.2 equiv.) was used instead of $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$.

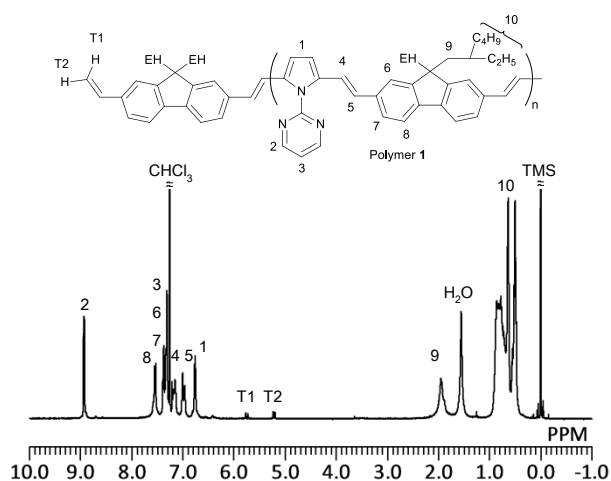


Fig. 1 ^1H NMR spectrum of Polymer 1 (400 MHz, CDCl_3).

spectrum of Polymer 1 (entry 2 in Table 1). Each signal was assigned to the repeating unit; the integral ratios of the signals agreed with the assignments and were consistent with the alternating structure with high regio-selectivity and *trans*-configuration. The minor signals at δ 5.22 and 5.75 ppm were assigned to the terminal ethenyl unit. All $^{13}\text{C}\{^1\text{H}\}$ NMR signals were also assigned to the carbons in the recurring unit (Fig. S3[†]). The MS spectrum exhibited peaks at regular intervals in the measurable molecular weight range, corresponding to the alternating structure (Fig. S4[†]).

The same reaction protocol made it possible to achieve the polycondensation of other targeting aromatic monomers bearing the directing groups and diethenyl monomer (Table 2): The reactions with the appropriate reaction time and temperature yielded the corresponding polymers (Polymers 2–5) in good yields. These results suggest that the 2-pyridinyl substituent also served as a directing group, and other aromatic moieties were available for the polycondensation reaction. Polymers 2–5 were also characterized by NMR spectroscopy and MALDI-TOF-MS (Figs. S5–16[†]). The results are consistent with the trend observed in the synthesis of Polymer 1.

Figure 2 presents the absorption spectra of the polymers in the thin-film state. The absorption of Polymers 1, 2, and 3

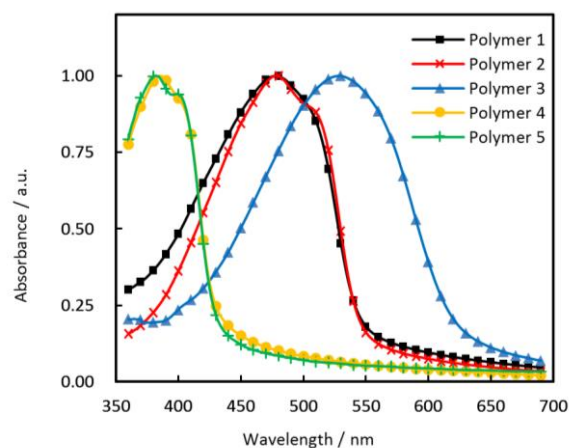


Fig. 2 Absorption spectra of Polymers 1–5 in the thin-film state.

appears in long-wavelength regions compared with those of Polymers 4 and 5. The wide band gap of Polymers 4 and 5 was associated with the limited effective conjugation owing to *meta* linkage. The optical bandgaps of Polymers 1, 2, and 3 were determined to be 2.3, 2.3, and 2.0 eV, respectively. The highest occupied molecular orbital (HOMO) levels of Polymers 1 and 2 were similar (\sim -5.4 eV), as determined by photoelectron yield spectroscopy (PSY) of the polymer films. To evaluate the carrier mobility of the polymers, top-contact FETs were fabricated using Polymers 1 and 2. Table 3 lists the results of the measurements. The FETs with Polymers 1 and 2 exhibited p-type semiconducting characteristics, showing a field-effect hole mobility (μ_{h}) of $7.5 \pm 0.7 \times 10^{-5}$ and $1.8 \pm 0.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. The μ_{h} values were comparable to those of poly(*p*-phenylenevinylene) type polymers, reported previously.¹⁷ Polymers 1 and 2 showed high thermal stability; The temperatures for 5% weight loss are higher than 370 °C (Table S3[†], Fig. S19[†]).

In summary, polycondensation via Rh-catalyzed direct alkenylation was demonstrated. The molecular design of the pyrrole monomer bearing the directing groups induced efficient *ortho*-metalation, and accelerated the direct alkenylation smoothly, giving rise to corresponding poly(arylenevinylene)s with regio-selectivity and *trans*-configuration in good yields.

Table 2. Synthesis of Polymers 1–5 via direct alkenylation polycondensation^a

Entry	Product	Temp. / °C	Reaction time / h	Yield ^b / %	$M_n \times 10^{-3}$ ^c	PDI ^c
1	Polymer 2	60	10	85	55.8	4.2
2	Polymer 3	60	10	78	23.8	2.9
3	Polymer 4	100	4	79	10.1	1.9
4	Polymer 5	100	4	82	21.3	2.5

^a Reactions were conducted using $[\text{Cp}^*\text{RhCl}_2]_2$ (4 mol%) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (4.2 eq.) in DMF (0.08 M).

^b The yields of CHCl_3 -soluble and CH_3OH -insoluble fraction.

^c Estimated by GPC calibrated on polystyrene standards

Table 3. OFET characteristics ^a

Polymer	$\mu_{\text{h}}^{\text{b}}$ [cm ² V ⁻¹ s ⁻¹]	on / off ratio	V_{th}^{c} [V]
Polymer 1 ^d	$7.5 \pm 0.7 \times 10^{-5}$	$1.6 \pm 0.3 \times 10^3$	-28 ± 2
Polymer 2	$1.8 \pm 0.4 \times 10^{-4}$	$3 \pm 1 \times 10^3$	-31 ± 3

^a The average value with standard error were calculated from the results of four OFET samples. OFET configuration; Glass / Au gate electrode / Parylene-C insulator / Polymer / Au source-drain electrodes.

^b Field-effect hole mobility.

^c Threshold voltage.

^d Entry 4 in Table 1

Recently, the Pd- and Cu-catalyzed oxidative C-H/C-H homocoupling polycondensation reactions of aromatic monomers, such as thiophene and thiazole derivatives, have been reported.¹⁸ On the other hand, the present work is the first access to the polycondensation reaction via the direct oxidative C-H/C-H cross-coupling of arene with alkenes.^{19,20} Therefore, this fundamental protocol provides new insights and expands the direct sp² C-H functionalization strategies for the synthesis of π -conjugated polymers. Further efforts to address the atom- and step-economical protocol, such as reducing the amount of Cu(OAc)₂ using O₂ as the terminal oxidant are currently underway.

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