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Polymerization of Furylthiazoles with Palladium-Catalyzed Direct Arylation Polycondensation

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Polymerization of furylthiazoles with palladium-catalyzed direct arylation polycondensation

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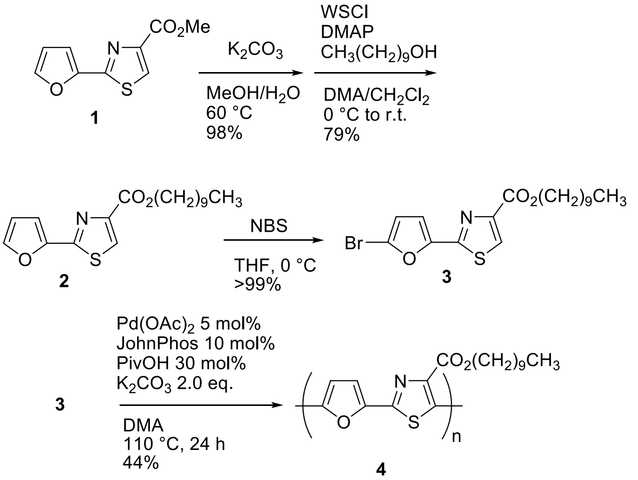
Effective transformation of a biomass-derived heteroaromatic compound furfural into conjugated polymer is described. Furylthiazole composed of furan and thiazole rings is employed as a monomer and palladium-catalyzed C-H coupling polycondensation furnishes the corresponding formal alternating copolymer. The coupling reaction in the presence of $Pd(OAc)_2$ (20 mol%) as a catalyst undergoes polymerization in >99% yield with M_n = 10.2 x 10^3.

Effective transformation of biomass-derived simple organic compounds into molecules of complex structures recently attracts considerable attention directed to achieve sustainable society.[1-4] It is particularly important to replace non-food feedstock biomass with chemicals of petrochemically-derived organic compounds. Cellulose has been shown to be subjected to degradation into glucose and several sugar derivatives through a biological process and the thus obtained sugars are transformed into various C1-C6 small organic molecules through a biological or chemical pathway. Furfural, which is an oxygen-containing five-membered-ring heteroaromatic compounds, is obtained by acid treatment of the resulting degradate monosaccharide from celluloses such as glucose and xylose and therefore serves as an organic building block as an important intermediate for pharmaceutical, agrochemical, and optoelectronic materials. We have recently shown that furfural undergoes oxidative condensation at the aldehyde moiety to form another heteroaromatic skeleton such as oxazoles, thiazoles, imidazoles, etc. and the obtained furyl azoles are transformed into a variety of π-conjugation-extended organic molecules via transition metal-catalyzed coupling reactions. In particular, furfural was shown to be efficiently transformed into furylazoles when natural α-amino acids such as L-cysteine and L-serine bearing an SH or OH group is subjected to the reaction of furfural under oxidative conditions.[5,6] The obtained furylazoles allowed further coupling reactions with several haloarenes and these coupling products showed photoluminescent characteristics based on the extended π-conjugation. It is also intriguing to prepare conjugated polymers by cross-coupling polycondensation since a wide variety of such polymers are utilized as materials for electronic devices.[7-12] We herein describe that a conjugated heteroaromatic compound composed of furan and thiazole rings is available as a monomer for direct C-H arylation polymerization with a palladium catalyst.

Preparation of furyl thiazoles was carried out as described in our recent report by oxidative condensation with L-cysteine leading to the corresponding thiazoline, which was transformed into the corresponding methyl ester. Treatment of the thiazoline ester with activated carbon under aerobic conditions led to furylthiazole **1**.[5,6]

Although attempted palladium-catalyzed polymerization of **1** was carried out after bromination at the furan ring with *N*-bromosuccinimide (NBS), the reaction only afforded insoluble materials. Accordingly, furylthiazole **1** was transformed into the ester bearing a longer alkyl chain. Hydrolysis of **1** under basic conditions afforded carboxylic acid, which was treated with 1-decanol in the presence of water soluble carbodiimide (WSCI: 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride) and 4-*N*,*N*-dimethylaminopyridine (DMAP) to afford the corresponding ester **2**. Bromination of the furan ring was carried out with *N*-bromosuccinimide (NBS) to furnish monomer **3**.

Polymerization of the obtained bromide **3** was carried out by palladium catalyzed C-H functionalization polymerization.[5,11-12] The reaction of **3** using 5 mol% $Pd(OAc)_2$ and JohnPhos[5,13] (2-(di-*tert*-butylphosphino)biphenyl 10 mol%) was examined with potassium carbonate (2.0 equiv) and 30 mol% pivalic acid at 110 ºC in DMA. The polymer **4** was afforded in 44% yield after stirring for 24 h. The obtained polymer was found to be dissolved in chloroform accompanied by small amount of unidentified insoluble materials. SEC analysis of the soluble part revealed to show M_n = 2.7 x 10^3 (M_w/M_n = 1.21). Measurement of ^{1}H NMR was also carried out with $CDCl_3$ as a solvent to result in showing signals of 0.7-2.0 ppm assigned as alkyl chains, while no signals corresponding to the aromatic regions was observed by broadening. Attempted measurement of ^{13}C NMR spectrum was also found to be unsuccessful due to the insufficient solubility.



Scheme 1. Preparation of monomer **3** and C-H arylation polymerization

Polymerization of **3** under several conditions was then studied with $Pd(OAc)_2$ as a catalyst. Use of tricyclohexylphosphine as a ligand of palladium resulted in slight progress in the yield of polymer **4** whereas remarkable progress of the molecular weight was not observed. (entry 2)

The reduced amount of catalyst loading showed little effect in the polymerization. (entry 3) The polymerization of **3** with $Pd(OAc)_2$ without ligand allowed the reaction at lower temperature. (entry 4) A longer reaction period resulted in giving higher molecular weight. (entry 5, 6) The M_n value of 7.2 x 10^3 (M_w/M_n = 1.48) was achieved when the reaction was performed at 60 ºC for 5 days (entry 7) affording **4** in quantitative yield. (Table 1)

Figure 1 shows MALDI-TOF mass spectrum of **4** indicating peaks with repeating unit of 333 Da, which reasonably corresponds to the unit structure of furylthiazole, whose *m*/*z* is calculated as 333.14.[14]

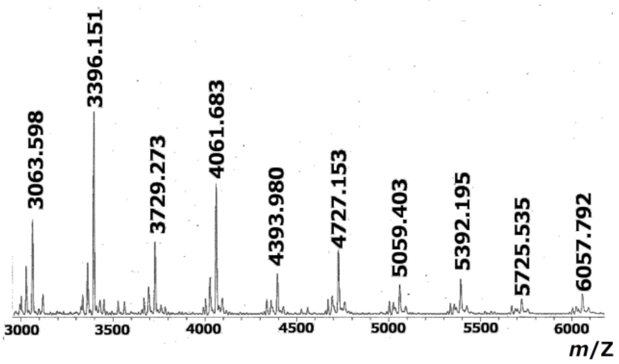


Figure 1. MALDI-TOF mass spectrum of furylthiazole polymer **4**.

Table 1. Polymerization of furylthiazole **3** with a palladium catalyst[a]

entry	Pd(OAc) (mol %)	temp (ºC)	time (h)	$M_n/10^3$ M_w/M_n[b]	yield (%)
1	5[c]	110	24	2.7[d] 1.21	44
2	5[e]	110	24	3.9[d] 1.30	78
3	2[e]	110	24	2.4[d] 1.11	94
4	2	60	24	4.0 1.19	80
5	2	60	48	6.3 1.55	>99
6	2	60	72	6.2 1.31	>99
7	2	60	120	7.2 1.48	>99

a. Unless noted, the reaction was carried out with **3** (0.3 mmol), palladium acetate, pivalic acid (30 mol %), and K_2CO_3 (0.6 mmol) in 1.0 mL of DMA under nitrogen atmosphere. b. M_n and M_w/M_n were estimated by SEC analysis using standard polystyrenes. c. Johnphos (2 eq. to Pd cat) was employed as a ligand. d. Measurement was carried out using a soluble part in chloroform. e. Tricyclohexylphophine (2 eq. to Pd cat) was employed as a ligand.

We further studied the detailed reaction conditions of the polymerization of **3**. Table 2 summarizes the results. It was found that use of sodium pivalate (30 mol%) instead of pivalic acid similarly effected the polymerization to afford **4**.[11] (entry 1-3) Addition of quaternary ammonium salt Bu_4NBr showed little effect to improve the M_n value whereas slight broadening of the molecular weight distribution was observed. (entry 4,5) Polymerization under diluted concentration (0.01 M) did not influence the molecular weight and the yield (entry 6), while higher concentration (0.4 M) resulted in giving highest molecular weight >10.0 x 10^3. (entry 7) The results suggest that polymerization with C-H arylation polycondensation with a palladium catalyst proceeds in a step-growth manner.

Table 2. Effect of catalyst loading and the amount of additive in the polymerization of furylthiazole **3**[a]

entry	Pd cat. (mol %)	conc. (M)	additive (mol %)	$M_n/10^3$ M_w/M_n[b]	yield
1	10	0.2	PivONa	5.9 1.32	82
2	20	0.2	PivONa	4.9 1.28	72
3	30	0.2	PivONa	7.4 1.81	>99
4	20	0.2	PivONa Bu_4NBr (100)	8.1 2.35	>99
5	20	0.2	PivONa[c] Bu_4NBr (100)	8.0 2.39	>99
6	20	0.01	PivONa	6.8 1.40	>99
7	20	0.4	PivONa	10.2 4.76	>99

a. Unless noted, The reaction was carried out with **3** (0.3 mmol), PivONa (^{t}BuCOONa, 30 mol %) and K_2CO_3 (0.6 mmol) in DMA at 60 ºC for 48 h under nitrogen atmosphere. b. M_n and M_w/M_n were estimated by SEC analysis using standard polystyrenes. c. Increased amount of PivONa (80 mol %) was employed.

Figure 2 shows UV-vis absorption spectrum of monomer **3** and polymer **4**. The λ_{max} of furylthiazole **3** and the polymer **4** was observed at 314 and 388 nm, respectively. It was found that shift to higher wavelength was observed by polymerization suggesting extended π-conjugation through the carbon-carbon bond formation between the 5, 5'-positions of furan and thiazole. Comparing with absorption wavelength of poly-3-alkylthiophenes, which showed λ_{max} value of ca. 450 nm in chloroform solution,[10] λ_{max} of the polymer composed of furylthiazole **4** indicated shorter wavelength. The result suggests insufficient extension of π-conjugation probably because of steric congestion of the ester substituent to inhibit the planer structure whereas the presence of longer alkyl chain improved solubilities in organic solvents.

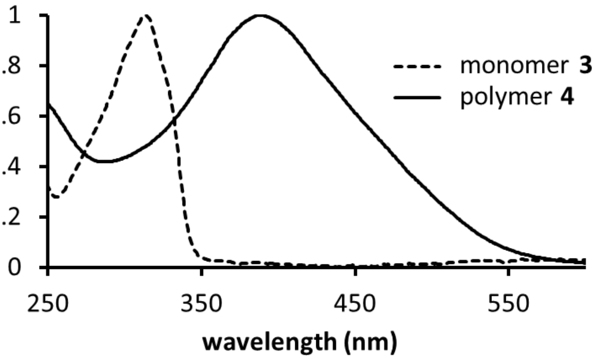


Figure 2. UV-vis absorption spectrum of furylthiazole monomer **3** (dotted) and the corresponding polymer **4** (solid) as 10^{-5} M (**3**) and 0.01 g/L (**4**) chloroform solutions, respectively. (normalized)

Experimental

Polymerization of furylthiazole **3** with a palladium catalyst: To a 20 mL Schlenk tube equipped with a magnetic stirring bar were added **3** (82.9 mg, 0.2 mmol), potassium carbonate (55.3 mg, 0.4 mmol), sodium pivalate (7.4 mg, 0.06 mmol), palladium(II) acetate (9.0 mg, 0.4 mmol) and *N*,*N*-dimethylacetamide (0.5 mL) under nitrogen atmosphere. The mixture was heated with stirring at 60 ºC for 48 h. After cooling to room temperature, the resulting mixture was poured into methanol to form precipitates, which was filtered and washed with methanol and acetone repeatedly to afford 77.2 mg of polymer **4** (>99%). Molecular weight and molecular weight distribution were estimated by SEC analysis (eluent: $CHCl_3$) to show $M_n = 10.2 \times 10^3$, $M_w / M_n = 4.76$.

In summary, furylazole composed of furan and thiazole rings was prepared and the brominated furylazole **3** was successfully transformed into the corresponding polymer **4** by C-H functionalization polycondensation in the presence of a palladium catalyst. The extended π-conjugation was observed by polymerization to reveal the λ_{max} value of ca. 400. Since furylazole can be prepared with furfural, which is a biomass-derived molecule easily transformed from sugar derivatives such as glucose, and natural amino acid cysteine, the component of the obtained polymer **4** is naturally derived and the thus afforded **4** can be recognized as conjugated bioplastic of extended π-conjugation.

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Supporting Information

Experimental details and spectroscopic data. This materials available on http://dx.doi.org/XXX/bcsj.XXX.

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14 An equation, *m*/Z = 332.7n + 69.3, is derived from the peaks of MALDI-TOF MS shown in Figure 1, suggesting the presence of hydrogen and bromine atoms at the termini of the polymer.

Short Articles

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C-H coupling polymerization of furylthiazole in the presence of a palladium catalyst gives the corresponding polymer with M_n of up to ca. 10 x 10^3.